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SUPPLEMENTARY INFORMATION

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A general asymmetric copper-catalysed Sonogashira C(sp^3)–C(sp) coupling

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Supplementary Materials for

A general asymmetric copper-catalysed Sonogashira C(sp^3)–C(sp) coupling

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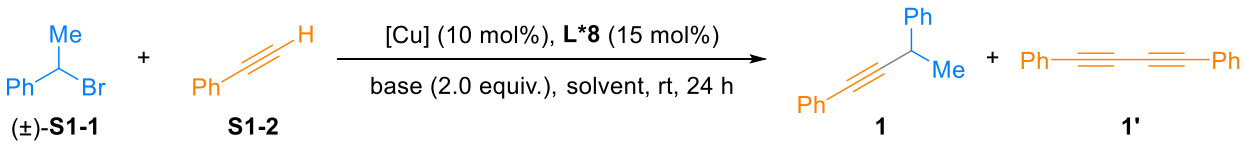
Table of contents

Supplementary Table 1.

Screening of reaction conditions[a]

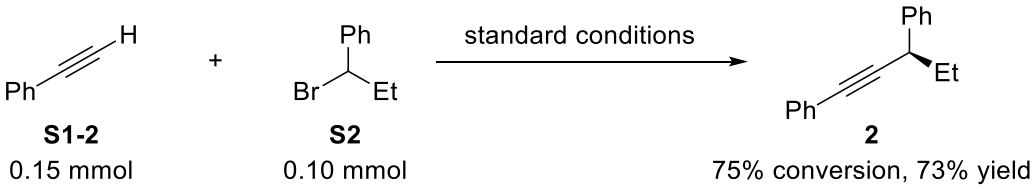


Entry	[Cu]	Base (x equiv.)	Solvent	Yield (%)[b]		ee (%)[c]
				1	**1′**	
1	CuI	Cs_2CO_3	CH_3CN	81	trace	50
2	CuI	Cs_2CO_3	EtOAc	85	trace	72
3	CuI	Cs_2CO_3	MTBE	83	trace	78
4	CuI	Cs_2CO_3	Toluene	65	trace	79
5	CuI	Cs_2CO_3	THF	79	trace	73
6	CuI	Cs_2CO_3	MeOH	81	trace	53
7	CuI	Cs_2CO_3	Et_2O	87	trace	81
8	CuI	Cs_2CO_3	CH_2Cl_2	65	trace	61
9	CuI	Cs_2CO_3	DCE	52	trace	54
10	CuCl	Cs_2CO_3	Et_2O	83	trace	82
11	CuBr	Cs_2CO_3	Et_2O	84	trace	82
12	CuTc	Cs_2CO_3	Et_2O	89	trace	82
13	$(CuOTf)_2{\cdot}PhCH_3$	Cs_2CO_3	Et_2O	88	trace	82
14	CuTc	Na_2CO_3	Et_2O	trace	trace	ND
15	CuTc	K_3PO_4	Et_2O	88	trace	81
16	CuTc	NaOH	Et_2O	87	trace	81

[a]Reaction conditions: (±)-**S1-1** (0.050 mmol), **S1-2** (1.5 equiv.), [Cu] (10 mol%), **L*8** (15 mol%), and base (2.0 equiv.) in solvent (0.50 mL) or Et_2O (1.0 mL) at room temperature for 24 h under argon.
[b]Yield of **1** was based on ^1H NMR analysis of the crude product using 4-bromo-*N*,*N*-dimethylaniline as an internal standard, and that of **1'** was based on GC analysis.
[c]Ee value was based on HPLC analysis.

Supplementary Table 2.

Contents of trace metal impurities in the crude reaction mixture



S1-2 0.15 mmol | **S2** 0.10 mmol | **2** 75% conversion, 73% yield

Element	Percentage (w/w_{Cu}%)
Fe	1
Co	0.03
Ni	0.08
Pd	0.005

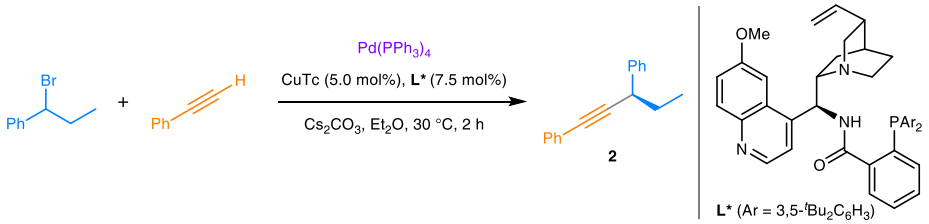
Supplementary Table 3.

Contents of trace metal impurities in the CuTc catalyst

Element	Percentage (w/w_{Cu}%)
Fe	0.1
Co	0.006
Ni	0.01
Pd	0.004

Supplementary Table 4.

Effects of Pd additive

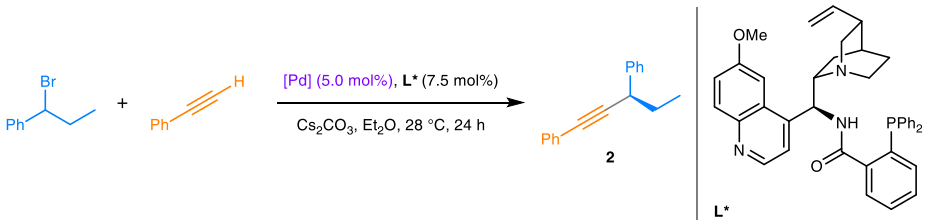


Entry	[Pd] (ppm)	Conversion (%)	Yield (%)	Ee (%)
1	0	45	43	97
2	100	42	41	97
3	1000	46	45	97
4	10000	48	41	97

Reaction conditions: Racemic (1-bromopropyl)benzene (0.10 mmol), phenylacetylene (1.5 equiv.), CuTc (5.0 mol%), **L*** (7.5 mol%), Cs_2CO_3 (2.0 equiv.), and appropriate amounts of $Pd(PPh_3)_4$ in Et_2O (2.0 mL) under argon at room temperature for 2 h; Yield was determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard; Ee was determined by HPLC.

Supplementary Table 5.

Catalytic performance of Pd catalysts

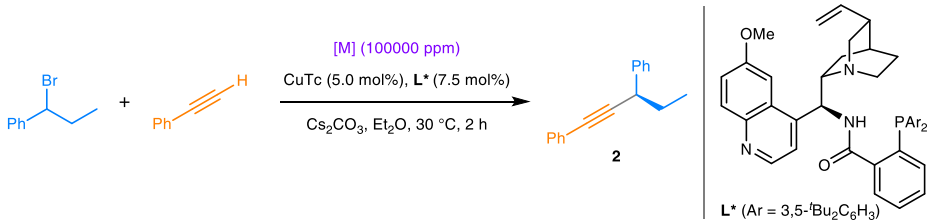


Entry	[Pd]	Conversion (%)	Ee (%)
1	$Pd(PPh_3)_4$	0	/
2	$Pd(PPh_3)_2Cl_2$	0	/
3	$Pd_2(dba)_3$	0	/
4	$Pd(OAc)_2$	0	/

Reaction conditions: Racemic (1-bromopropyl)benzene (0.10 mmol), phenylacetylene (1.5 equiv.), Pd (5.0 mol%), L* (7.5 mol%), and Cs_2CO_3 (2.0 equiv.) in Et_2O (2.0 mL) under argon at room temperature; Yield was determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard.

Supplementary Table 6.

Effects of other transition metal additives

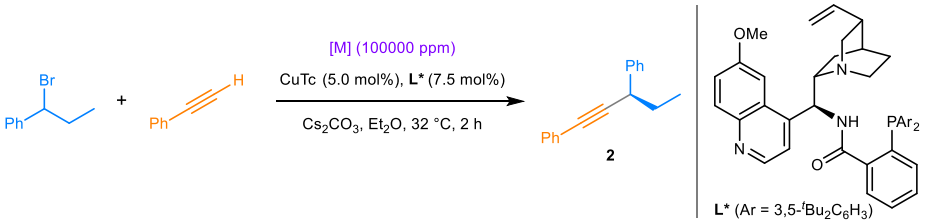


Entry	[M]	Conversion (%)	Yield (%)	Ee (%)
1	none	47	46	97
2	$FeCl_3$	50	46	97
3	$Ni(acac)_2$	58	47	97

Reaction conditions: Racemic (1-bromopropyl)benzene (0.10 mmol), phenylacetylene (1.5 equiv.), CuTc (5.0 mol%), L* (7.5 mol%), Cs_2CO_3 (2.0 equiv.), and metal additive (100000 ppm) in Et_2O (2.0 mL) under argon at room temperature for 2 h; Yield was determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard; Ee was determined by HPLC.

Supplementary Table 7.

Effects of other transition metal additives

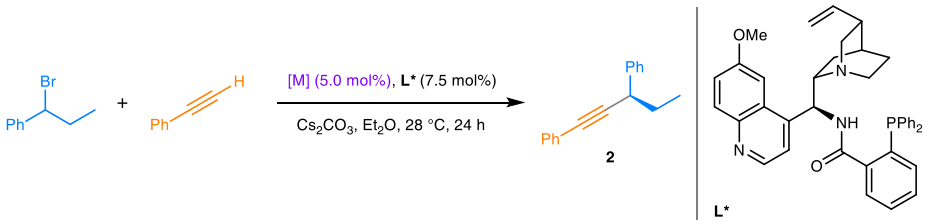


Entry	[M]	Conversion (%)	Yield (%)	Ee (%)
1	none	58	52	97
2	$Co(PPh_3)_3Cl$	60	54	97

Reaction conditions: Racemic (1-bromopropyl)benzene (0.10 mmol), phenylacetylene (1.5 equiv.), CuTc (5.0 mol%), L* (7.5 mol%), Cs_2CO_3 (2.0 equiv.), and metal additive (100000 ppm) in Et_2O (2.0 mL) under argon at room temperature for 2 h; Yield was determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard; Ee was determined by HPLC.

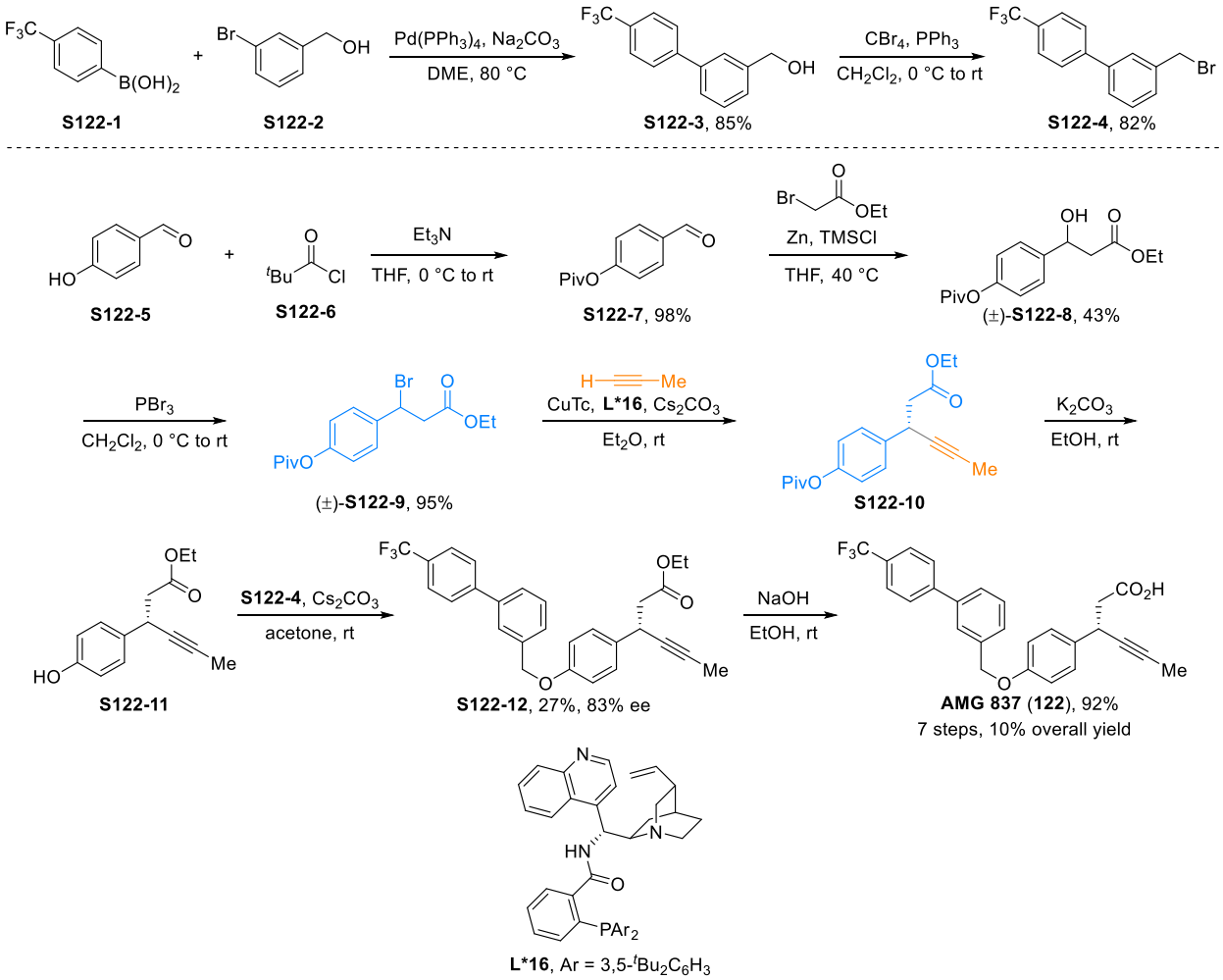
Supplementary Table 8.

Catalytic performance of other transition metal catalysts

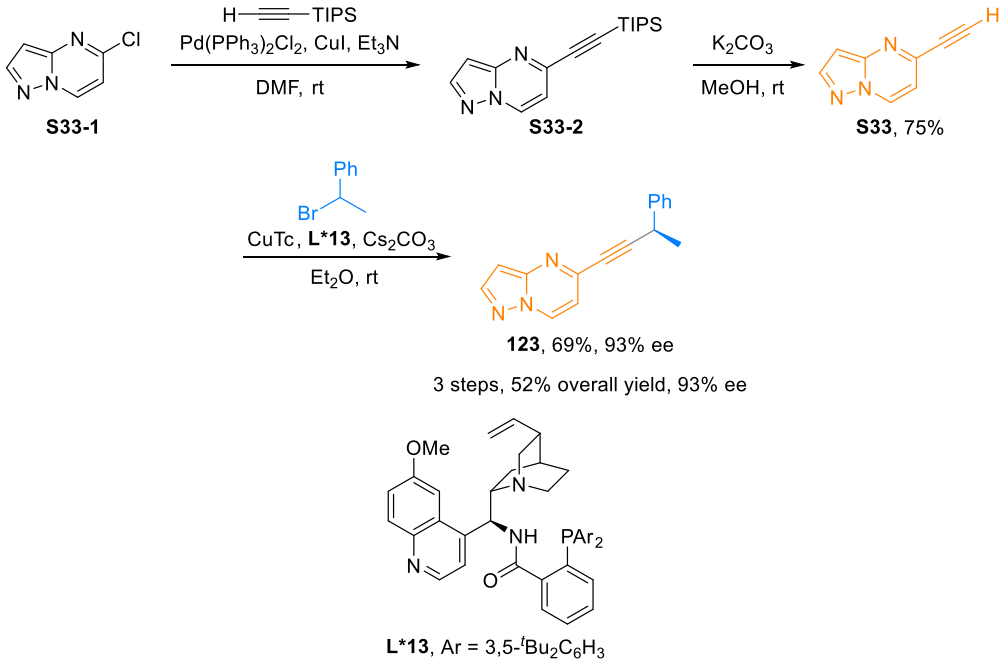


Entry	[M]	Conversion (%)	Ee (%)
1	$FeCl_3$	0	/
2	$Co(PPh_3)_3Cl$	0	/
3	$NiCl_2$	0	/
4	$NiBr_2$	0	/
5	$Ni(PCy_3)_2Cl_2$	0	/
6	$Ni(PPh_3)_2Cl_2$	0	/

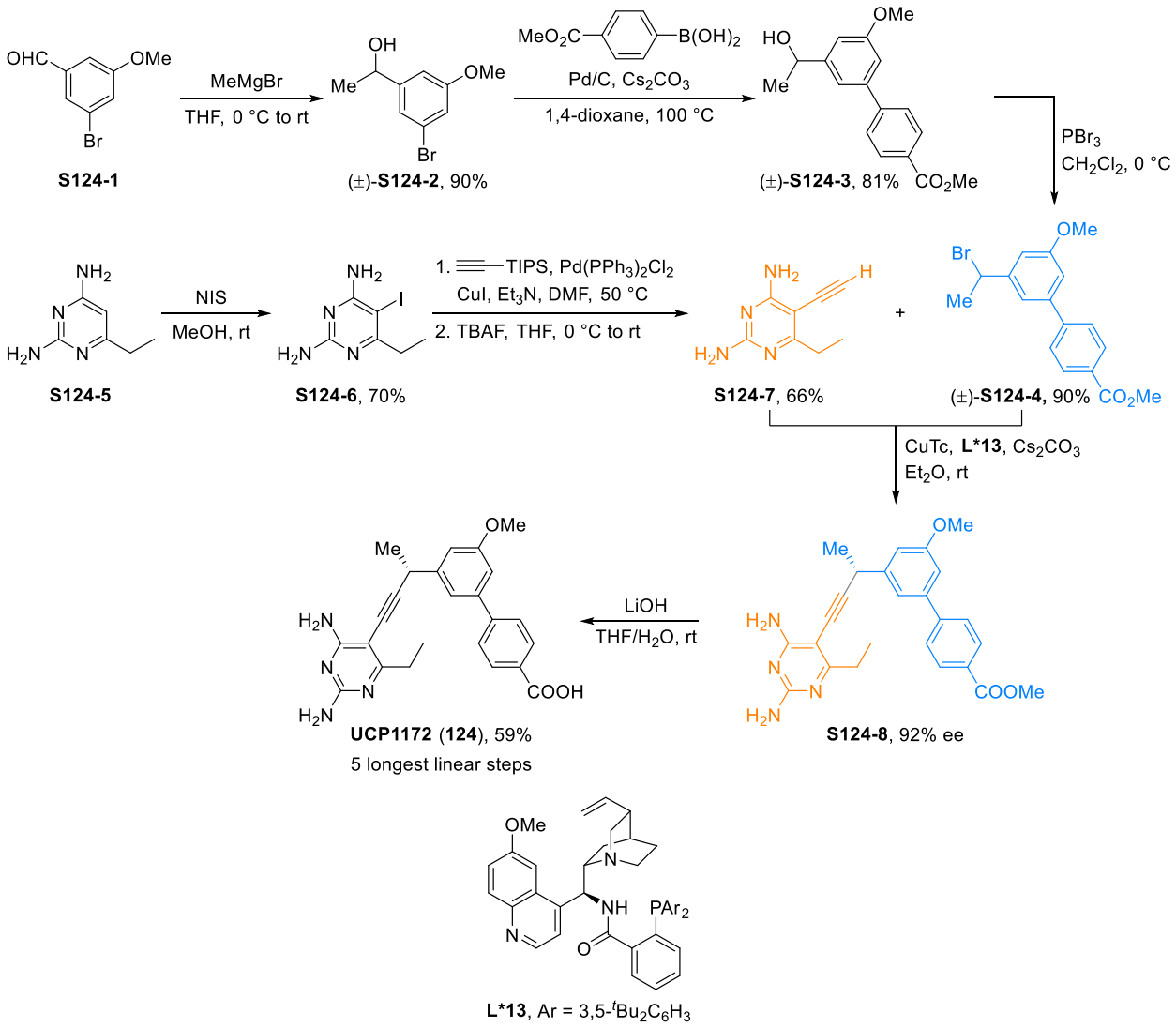
Reaction conditions: Racemic (1-bromopropyl)benzene (0.10 mmol), phenylacetylene (1.5 equiv.), [M] (5.0 mol%), L* (7.5 mol%), and Cs_2CO_3 (2.0 equiv.) in Et_2O (2.0 mL) under argon at room temperature; Yield was determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard.



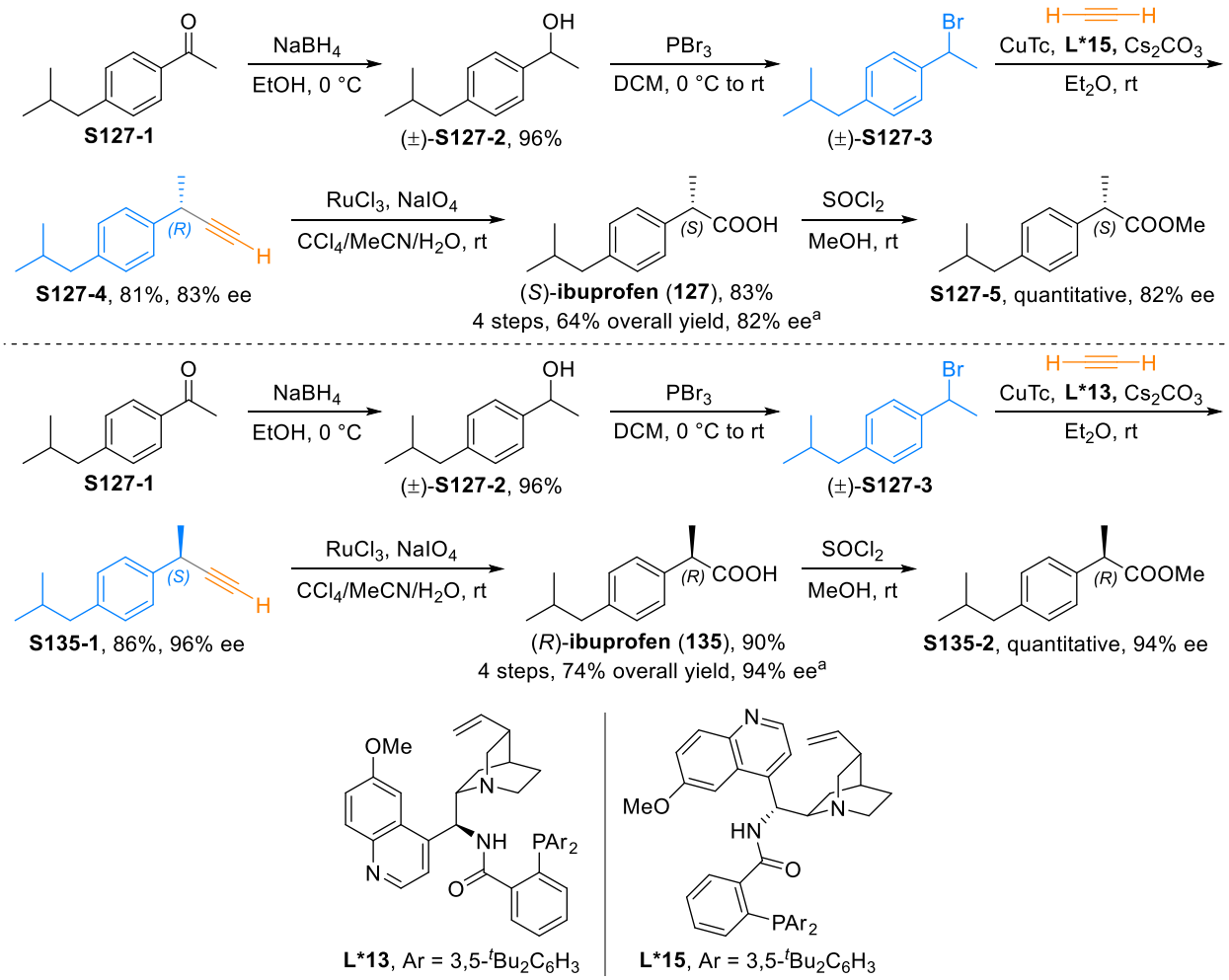
Supplementary Fig. 1.
Enantioselective synthesis of **AMG 837 (122)**



Supplementary Fig. 2.
Enantioselective synthesis of **123**

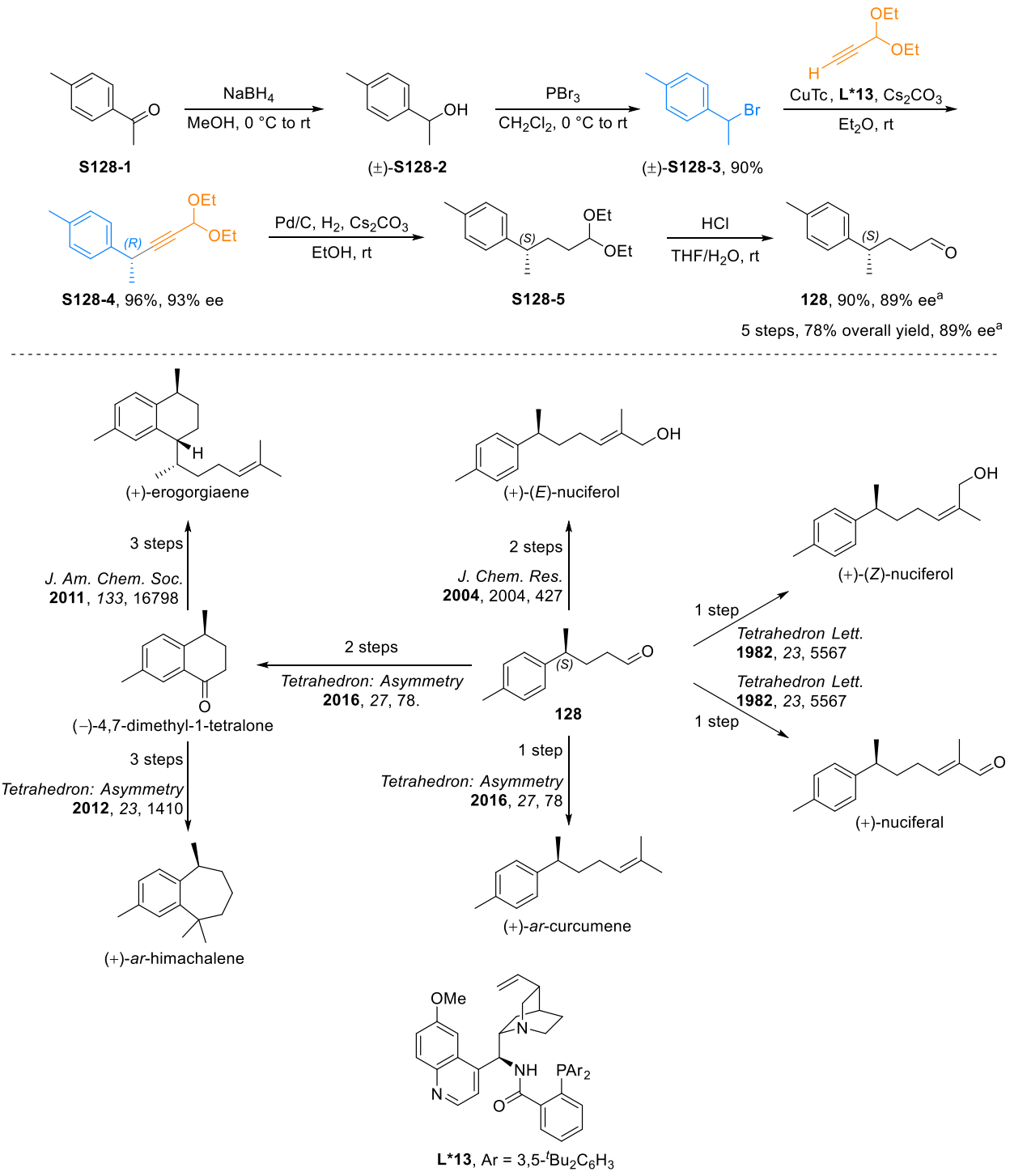


Supplementary Fig. 3.
Enantioselective synthesis of **UCP1172 (124)**



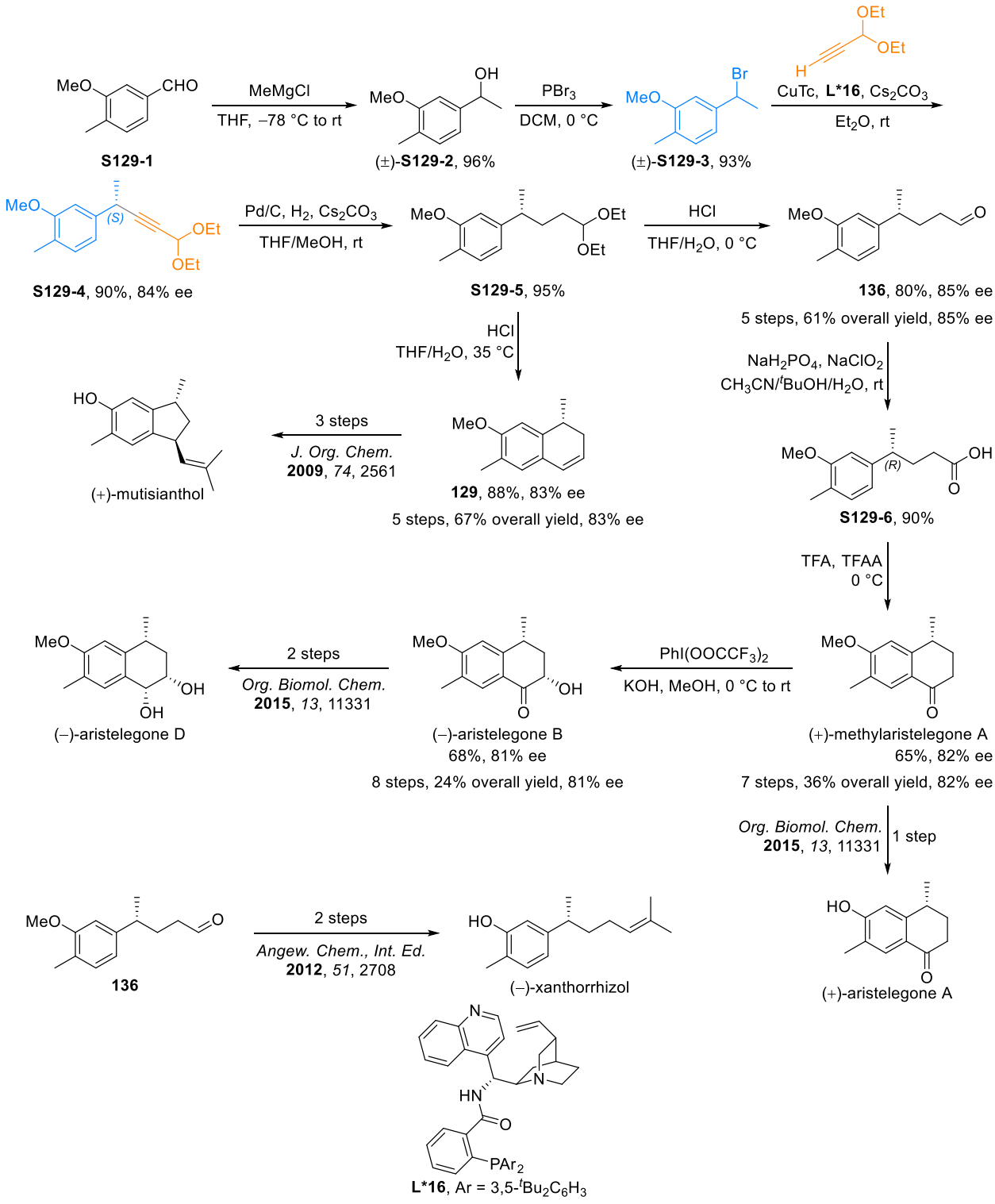
Supplementary Fig. 4.

Enantioselective synthesis of (*S*)-**ibuprofen** (**127**) and (*R*)-**ibuprofen** (**135**). [a]The ee value was determined on a derivative of the product.



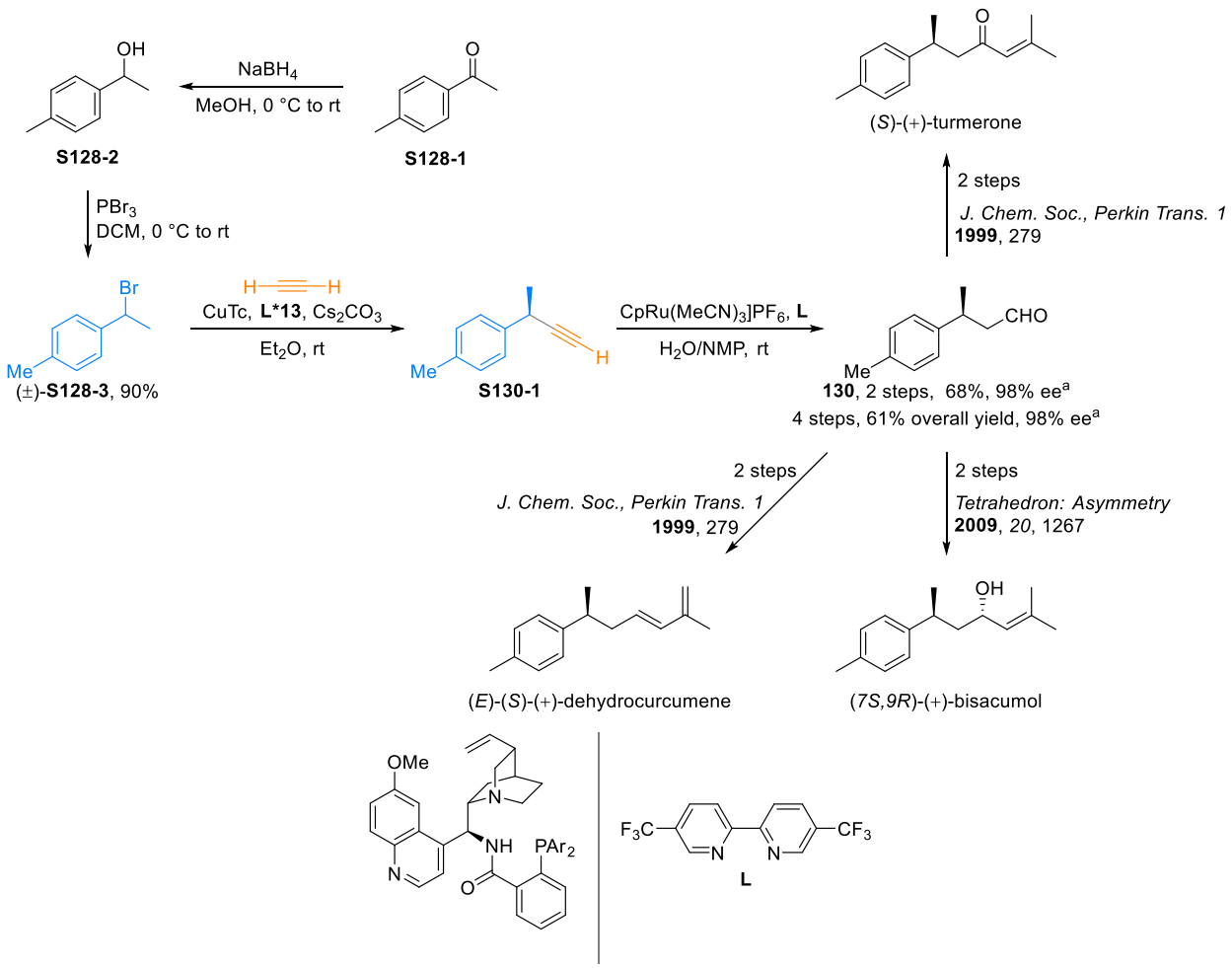
Supplementary Fig. 5.

Enantioselective synthesis of **128** and formal synthesis of (+)-(*Z*)-nuciferol, (+)-nuciferal, (+)-*ar*-curcumene, (+)-(*E*)-nuciferol, (–)-4,7-dimethyl-1-tetralone, (+)-erogorgiaene, and (+)-*ar*-himachalene. [a]The ee value was determined on a derivative of the product.



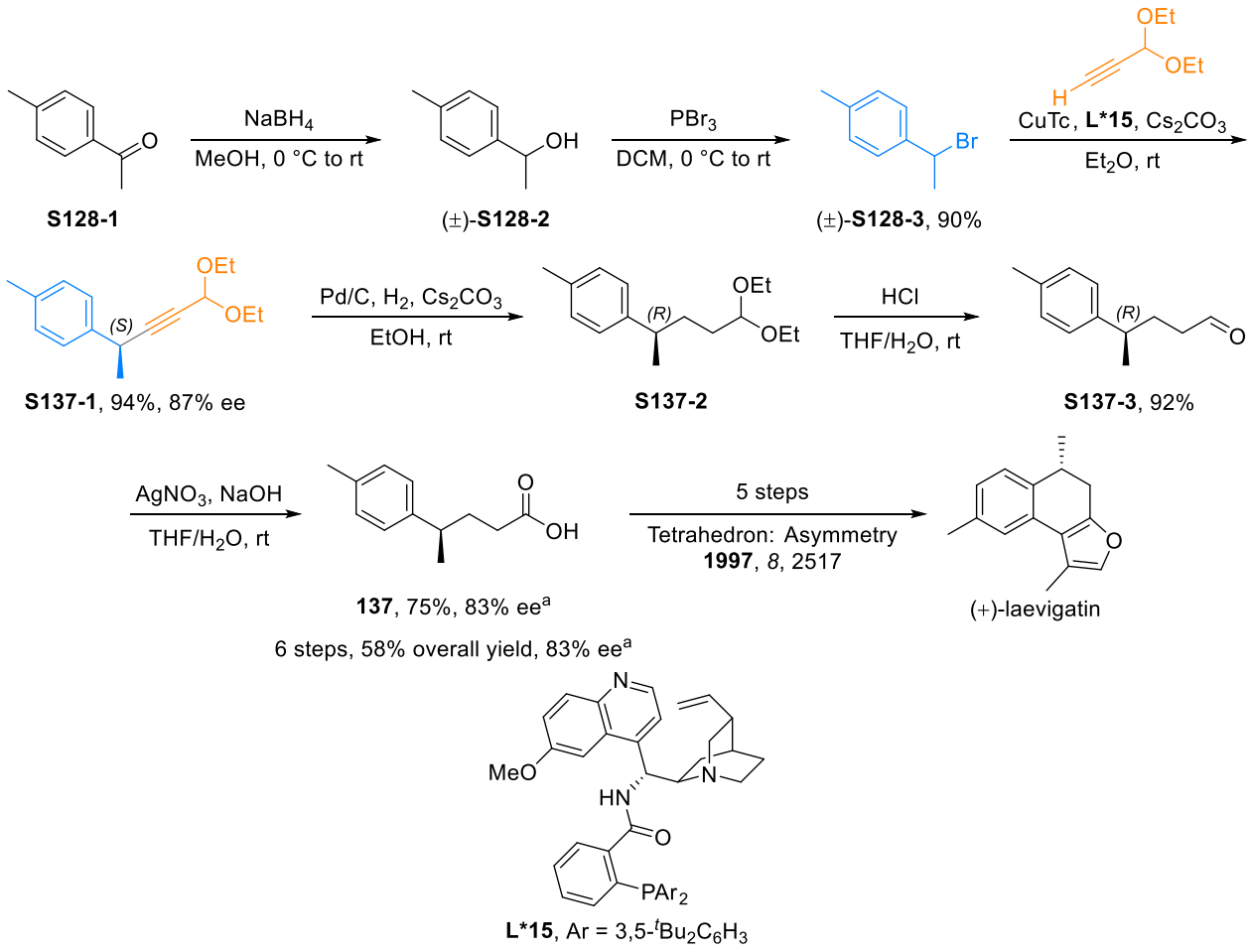
Supplementary Fig. 6.

Enantioselective synthesis of **129**, **136**, (+)-methylaristelegone A, and (–)-aristelegone B and formal synthesis of (+)-mutisianthol, (–)-aristelegone D, and (–)-xanthorrizol.



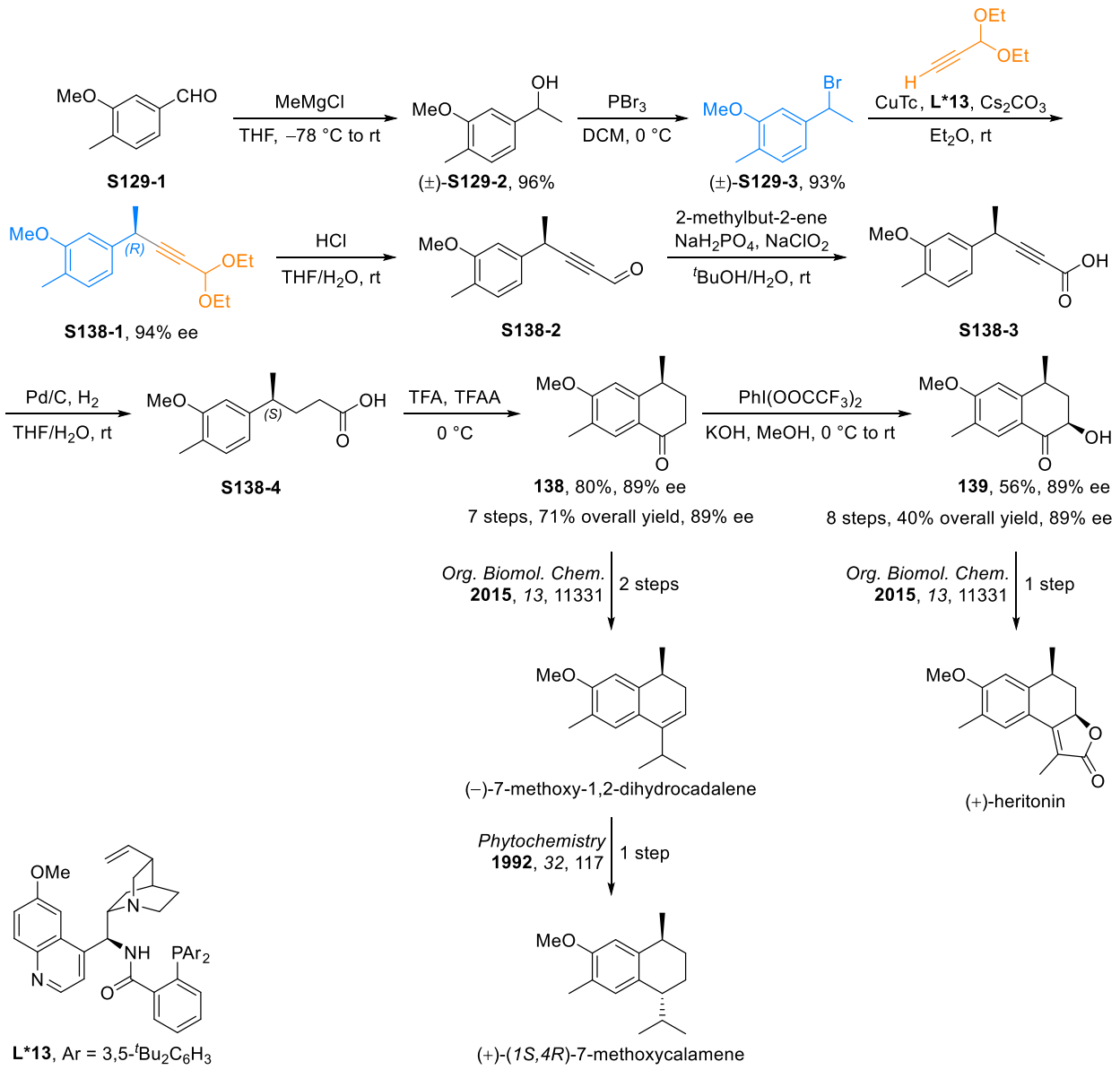
Supplementary Fig. 7.

Enantioselective synthesis of **130** and formal synthesis of (7*S*,9*R*)-(+)-bisacumol, (*E*)-(*S*)-(+)-dehydrocurcumene, and (*S*)-(+)-turmerone. [a]The ee value was determined on a derivative of the product.



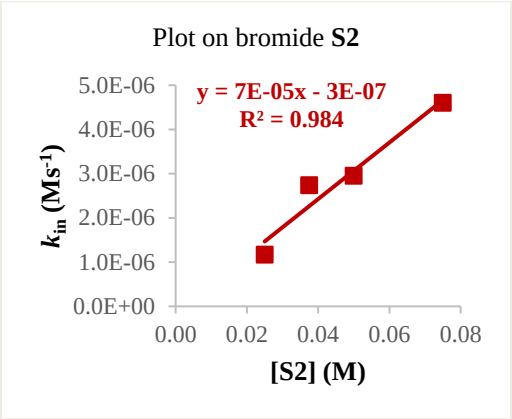
Supplementary Fig. 8.

Enantioselective synthesis of **137** and formal synthesis of (+)-laevigatin. [a]The ee value was determined on a derivative of the product.



Supplementary Fig. 9.

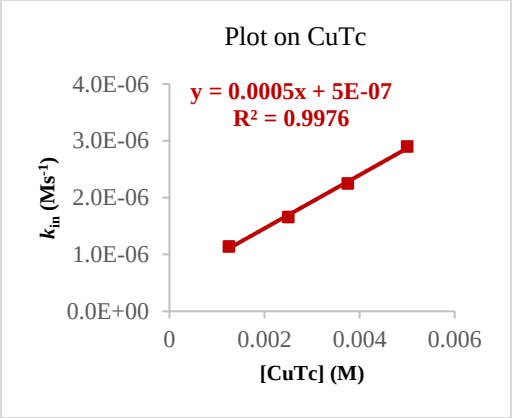
Enantioselective synthesis of **138** and **139** and formal synthesis of (–)-7-methoxy-1,2-dihydrocadalene, (+)-(1*S*,4*R*)-7-methoxycalamene, and (+)-heritonin.



Supplementary Fig. 10.

Kinetic study on concentrations of 1-phenylpropyl bromide **S2** in the reaction with phenylacetylene **S1-2**

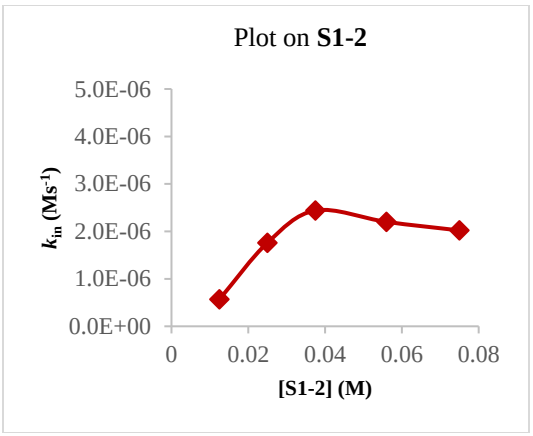
The results reveal a first-order dependence of the initial reaction rate on the initial concentration of **S2**.



Supplementary Fig. 11.

Kinetic study on concentrations of CuTc catalyst in the reaction of 1-phenylpropyl bromide **S2** with phenylacetylene **S1-2**

The results reveal a first-order dependence of the initial reaction rate on the initial concentration of CuTc.



Supplementary Fig. 12.

Kinetic study on concentrations of phenylacetylene **S1-2** in the reaction with 1-phenylpropyl bromide **S2**

The results reveal that the reaction was initially promoted and then inhibited along with the increasing concentration of **S1-2**.

General information

Most of reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. CuI was purchased from Sigma-Aldrich. CuTc was purchased from Alfa Aesar and Bide. Anhydrous diethyl ether (Et_2O) was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd, which was directly used without further treatment. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm), iodine or basic $KMnO_4$ indicator. NMR spectra were recorded on Bruker DRX-400 and DPX-500 spectrometers at 400 or 500 MHz for ^1H NMR, 100 or 125 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR, respectively, in $CDCl_3$, CD_3OD or DMSO-d_6 with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (ee) was determined using Agilent high-performance liquid chromatography (HPLC) with a Hatachi detector (at appropriate wavelength). Column conditions are reported in the experimental section below. Specific optical rotation was measured on a Rudolph-Autopol I. ICP-MS was tested with the instrument of iCAP RQ.

The synthesis of terminal alkyne substrates

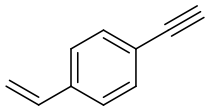
General procedure 1:

To a mixture of aryl bromide (1.0 mmol, 1.0 equiv.), bis(triphenylphosphine)palladium(II) chloride (35.1 mg, 0.050 mmol, 5.0 mol%), and trimethylsilylacetylene (196.0 mg, 2.0 mmol, 2.0 equiv.) in triethylamine (4.0 mL) was added copper(I) iodide (9.5 mg, 0.050 mmol, 5.0 mol%) under argon atmosphere. The resulting reaction mixture was stirred at 50 °C for 24 h. After completion of reaction (monitored by TLC), the reaction mixture was cooled to room temperature, filtered, and concentrated under reduced pressure. The residue was briefly purified by column chromatography on silica gel and the crude product thus obtained was dissolved in anhydrous THF (1.0 mL) under argon atmosphere. Tetra-*n*-butylammonium fluoride (1.5 mL, 1.0 M in THF, 1.5 equiv.) was added to the solution dropwise at 0 °C, and the reaction mixture was warmed up to room temperature and stirred for 0.5 h. After completion of reaction (monitored by TLC), the solvent was removed by evaporator and the residue was purified by column chromatography on silica gel to afford the corresponding terminal alkyne product.

General procedure 2:

To a mixture of aryl halide (bromide or chloride) (1.0 mmol, 1.0 equiv.), ethynyltriisopropylsilane (364.8 mg, 2.0 mmol, 2.0 equiv.), bis(triphenylphosphine)palladium(II) chloride (35.1 mg, 0.050 mmol, 5.0 mol%), and copper(I) iodide (9.5 mg, 0.050 mmol, 5.0 mol%) in *N*,*N*-dimethyl formamide (DMF, 10.0 mL) was added triethylamine (0.30 mL, 2.0 mmol, 2.0 equiv.) under argon atmosphere and the resulting reaction mixture was stirred at 40 °C for 24 h. After completion of reaction (monitored by TLC), the reaction was quenched by water. The mixture was poured into EtOAc and the aqueous layer was extracted with EtOAc three times. The combined organic layer was then washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was briefly purified by column chromatography on silica gel and the crude product thus obtained was dissolved in MeOH (2.0 mL), treated with K_2CO_3 (0.28 g, 2.0 mmol, 2.0 equiv.), and stirred at room temperature for 3 h. After completion of reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel to afford the corresponding terminal alkyne product.

1-Ethynyl-4-vinylbenzene (S22)



S22

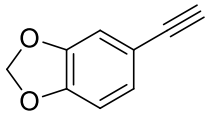
According to **General procedure 1** with 1-bromo-4-vinylbenzene (182.0 mg, 1.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **S22** as a colorless oil (84.5 mg, 66% yield over two steps). The product was unstable in air and turned red in a short time. Therefore, it was stored in CH_2Cl_2 at –20 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.83 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.36 (dd, *J* = 10.9, 0.9 Hz, 1H), 3.18 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 136.2, 132.4, 126.2, 121.4, 115.1, 83.7, 77.9.

HRMS (ESI) *m/z* calcd. for $C_{10}H_9$ $[M + H]^+$ 129.0699, found 129.0699.

5-Ethynylbenzo[*d*][1,3]dioxole (S25)



S25

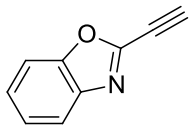
According to **General procedure 1** with 5-bromobenzo[*d*][1,3]dioxole (200.0 mg, 1.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **S25** as a brown amorphous powder (67.2 mg, 46% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 2H), 3.00 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 147.4, 126.9, 115.3, 112.0, 108.4, 101.4, 83.6, 75.6.

HRMS (ESI) *m/z* calcd. for $C_9H_7O_2$ $[M + H]^+$ 147.0441, found 147.0440.

2-Ethynylbenzo[*d*]oxazole (S28)



S28

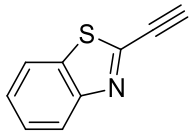
According to **General procedure 2** with 2-chlorobenzo[*d*]oxazole (153.0 mg, 1.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **S28** as a brown amorphous powder (108.7 mg, 76% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 1H), 7.58 – 7.53 (m, 1H), 7.50 – 7.35 (m, 2H), 3.41 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 146.4, 140.4, 126.8, 125.2, 120.7, 110.8, 81.8, 71.7.

HRMS (ESI) *m/z* calcd. for C_9H_6NO $[M + H]^+$ 144.0444, found 144.0443.

2-Ethynylbenzo[*d*]thiazole (S29)



S29

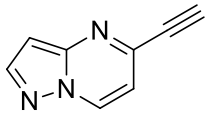
According to **General procedure 2** with 2-bromobenzo[*d*]thiazole (212.9 mg, 1.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **S29** as a yellow amorphous powder (130.4 mg, 82% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 1H), 7.91 – 7.85 (m, 1H), 7.59 – 7.43 (m, 2H), 3.62 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 147.5, 135.2, 126.8, 126.6, 123.9, 121.4, 84.0, 76.8.

HRMS (ESI) *m/z* calcd. for C_9H_6NS $[M + H]^+$ 160.0215, found 160.0214.

5-Ethynylpyrazolo[1,5-*a*]pyrimidine (S33)



S33

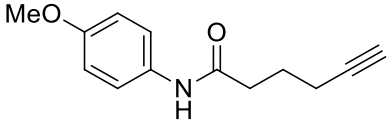
According to **General procedure 2** with 5-chloropyrazolo[1,5-*a*]pyrimidine (153.0 mg, 1.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **S33** as a white amorphous powder (107.3 mg, 75% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 7.1 Hz, 1H), 8.13 (d, *J* = 2.3 Hz, 1H), 6.93 – 6.86 (m, 1H), 6.71 – 6.69 (m, 1H), 3.00 – 2.83 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 145.7, 141.9, 134.4, 111.2, 104.4, 97.6, 96.5.

HRMS (ESI) *m/z* calcd. for $C_8H_6N_3$ $[M + H]^+$ 144.0556, found 144.0556.

***N*-(4-Methoxyphenyl)hex-5-ynamide (S40)**



S40

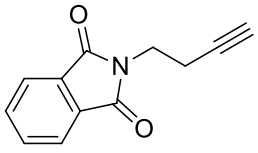
To a mixture of hex-5-ynoic acid (123.2 mg, 1.1 mmol, 1.1 equiv.), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (230.0 mg, 1.2 mmol, 1.2 equiv.), and 4-dimethylaminopyridine (DMAP) (12.2 mg, 0.10 mmol, 0.10 equiv.) in CH_2Cl_2 (2.0 mL) was added the 4-methoxyaniline (123.0 mg, 1.0 mmol, 1.0 equiv.) in one portion under argon atomsphere at 0 °C. The reaction mixture was naturally warmed up to room temperature and stirred overnight. After completion of reaction (monitored by TLC), the reaction was quenched by saturated $NaHCO_3$ and extracted with EtOAc three times. The combined organic phase was washed by brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to afford the alkynyl product **S40** as a white amorphous powder (173.6 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (br s, 1H), 7.39 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 3.77 (s, 3H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.29 (td, *J* = 7.2, 2.7 Hz, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.94 – 1.87 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 156.4, 131.0, 121.9, 114.1, 83.5, 69.4, 55.5, 35.8, 24.1, 17.9.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{16}NO_2$ $[M + H]^+$ 218.1176, found 218.1175.

2-(But-3-yn-1-yl)isoindoline-1,3-dione (S41)

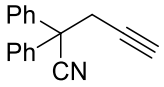


S41

To a mixture of isoindoline-1,3-dione (147.0 mg, 1.0 mmol, 1.0 equiv.) and K_2CO_3 (276.0 mg, 2.0 mmol, 2.0 equiv.) in DMF (5.0 mL) was added 4-bromobut-1-yne (158.4 mg, 1.2 mmol, 1.2 equiv.) under argon atmosphere and the resulting reaction mixture was stirred at room temperature overnight. Upon completion, the reaction was quenched by water and extracted with EtOAc three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtered, and

concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to afford the product **S41** as a white amorphous powder (161.1 mg, 81% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.78 – 7.68 (m, 2H), 3.97 – 3.79 (m, 2H), 2.69 – 2.55 (m, 2H), 1.97 (t, *J* = 2.6 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 134.0, 132.0, 123.4, 80.3, 70.3, 36.5, 18.3.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{10}NO_2$ $[M + H]^+$ 200.0706, found 200.0706.

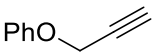
2,2-Diphenylpent-4-ynenitrile (S43)



S43

S43 was synthesized as a white solid (1.12 g, 97% yield) with 2,2-diphenylacetonitrile (0.97 g, 5.0 mmol) according to reported literature[1].
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 10H), 3.25 (s, 2H), 2.12 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 128.9, 128.4, 127.1, 121.6, 78.3, 73.3, 51.2, 30.9.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{14}N$ $[M + H]^+$ 232.1121, found 232.1119.

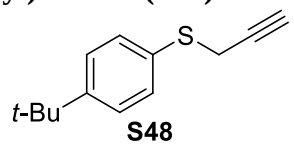
(Prop-2-yn-1-yloxy)benzene (S47)



S47

To a mixture of phenol (94.0 mg, 1.0 mmol, 1.0 equiv.) and K_2CO_3 (276.0 mg, 2.0 mmol, 2.0 equiv.) in DMF (5.0 mL) was added propargyl bromide (142.8 mg, 1.2 mmol, 1.2 equiv.) under argon atmosphere and the resulting reaction mixture was stirred at room temperature overnight. Upon completion, the reaction was quenched by water and extracted with EtOAc three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to afford the product **S47** as a yellow oil (120.1 mg, 91% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 2H), 7.11 – 6.95 (m, 3H), 4.73 (d, *J* = 2.4 Hz, 2H), 2.55 (t, *J* = 2.4 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 129.5, 121.6, 114.9, 78.7, 75.5, 55.8.
HRMS (ESI) *m/z* calcd. for C_9H_9O $[M + H]^+$ 133.0648, found 133.0649.

(4-(*tert*-Butyl)phenyl)(prop-2-yn-1-yl)sulfane (S48)

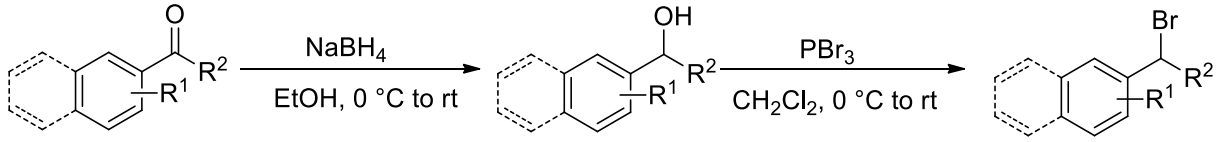


S48

To a mixture of 4-(*tert*-butyl)benzenethiol (166.0 mg, 1.0 mmol, 1.0 equiv.) and K_2CO_3 (276.0 mg, 2.0 mmol, 2.0 equiv.) in DMF (5.0 mL) was added propargyl bromide (142.8 mg, 1.2 mmol, 1.2 equiv.) under argon atmosphere and the resulting reaction mixture was stirred at room temperature overnight. Upon completion, the reaction was quenched by water and extracted with EtOAc three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to afford the product **S48** as a yellow oil (179.5 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 1H), 7.48 – 7.41 (m, 1H), 7.26 – 7.18 (m, 2H), 3.67 (d, *J* = 2.7 Hz, 2H), 2.27 (t, *J* = 2.7 Hz, 1H), 1.55 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 134.3, 133.2, 127.1, 126.64, 126.60, 79.8, 71.7, 36.6, 30.7, 24.5.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}S$ $[M + H]^+$ 205.1045, found 205.1045.

The synthesis of alkyl halide substrates

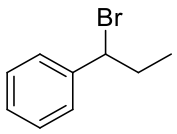


General procedure 3:

To a solution of ketone (3.0 mmol, 1.0 equiv.) in EtOH (9.0 mL) was added $NaBH_4$ (136.8 mg, 3.6 mmol, 1.2 equiv.) at 0 °C and the reaction mixture was stirred at room temperature for 0.5 – 2 h. After completion of reaction (monitored by TLC), the reaction was quenched by water, diluted with CH_2Cl_2, and extracted with CH_2Cl_2 three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the corresponding alcohol, which was directly used in the next step without further purfication.

To a solution of the residue obtained above in CH_2Cl_2 (9.0 mL) was added PBr_3 (0.20 mL, 2.1 mmol, 0.70 equiv.) under argon atmosphere at 0 °C and the resulting reaction mixture was stirred at room temperature. After completion of reaction (monitored by TLC), the mixture was quenched by water and extracted with CH_2Cl_2 three times. The combined organic phase was washed by brine, filtered by a pad of silica gel, and concentrated under reduced pressure to afford the corresponding crude alkyl bromide, which was directly used in the next step without further purification or stored in a refridgerator. (The product readily decomposed in air or on silica gel).

(1-Bromopropyl)benzene (S2)



S2

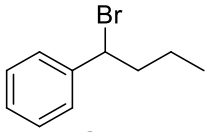
According to **General procedure 3** with propiophenone (0.40 g, 3.0 mmol, 1.0 equiv.), **S2** was obtained as a colorless oil (0.56 g, 94% crude yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.24 (m, 1H), 4.88 (t, *J* = 7.4 Hz, 1H), 2.36 – 2.23 (m, 1H), 2.22 – 2.10 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 128.8, 128.4, 127.4, 57.7, 33.4, 13.1.

HRMS (ESI) *m/z* calcd. for C_9H_{11} $[M - Br]^+$ 119.0855, found 119.0853.

(1-Bromobutyl)benzene (S57)



S57

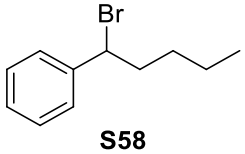
According to **General procedure 3** with 1-phenylbutan-1-one (0.44 g, 3.0 mmol, 1.0 equiv.), **S57** was obtained as a colorless oil (0.61 g, 95% crude yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.24 (m, 1H), 4.97 (t, *J* = 7.6 Hz, 1H), 2.34 – 2.21 (m, 1H), 2.17 – 2.04 (m, 1H), 1.58 – 1.42 (m, 1H), 1.41 – 1.24 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 128.8, 128.4, 127.4, 55.6, 42.1, 21.6, 13.5.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{13}$ $[M - Br]^+$ 133.1012, found 133.1009.

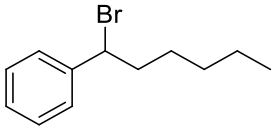
(1-Bromopentyl)benzene (S58)



S58

According to **General procedure 3** with 1-phenylpentan-1-one (0.49 g, 3.0 mmol, 1.0 equiv.), **S58** was obtained as a colorless oil (0.63 g, 93% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.22 (m, 1H), 4.94 (dd, *J* = 8.4, 7.2 Hz, 1H), 2.33 – 2.22 (m, 1H), 2.18 – 2.07 (m, 1H), 1.50 – 1.39 (m, 1H), 1.38 – 1.31 (m, 2H), 1.29 – 1.22 (m, 1H), 0.88 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 128.7, 128.3, 127.3, 55.9, 39.8, 30.5, 22.1, 14.0.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{15}$ $[M - Br]^+$ 147.1168, found 147.1167.

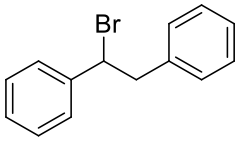
(1-Bromohexyl)benzene (S59)



S59

According to **General procedure 3** with 1-phenylhexan-1-one (0.53 g, 3.0 mmol, 1.0 equiv.), **S59** was obtained as a colorless oil (0.66 g, 92% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.41 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 5.00 (dd, *J* = 8.0, 6.8 Hz, 1H), 2.40 – 2.26 (m, 1H), 2.24 – 2.12 (m, 1H), 1.60 – 1.44 (m, 1H), 1.42 – 1.28 (m, 5H), 0.96 – 0.89 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 128.7, 128.3, 127.3, 55.9, 40.1, 31.2, 28.0, 22.5, 14.1.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{17}$ $[M - Br]^+$ 161.1325, found 161.1325.

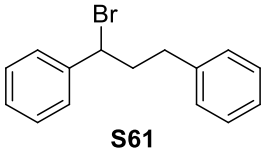
(1-Bromoethane-1,2-diyl)dibenzene (S60)



S60

According to **General procedure 3** with 1,2-diphenylethan-1-one (0.59 g, 3.0 mmol, 1.0 equiv.), **S60** was obtained as a colorless oil (0.64 g, 82% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.28 – 7.14 (m, 6H), 7.10 – 7.05 (m, 2H), 5.10 (t, *J* = 7.6 Hz, 1H), 3.52 (dd, *J* = 14.1, 7.8 Hz, 1H), 3.44 (dd, *J* = 14.1, 7.4 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 138.1, 129.3, 128.7, 128.4, 127.6, 126.9, 55.6, 46.5.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{13}$ $[M - Br]^+$ 181.1012, found 181.1011.

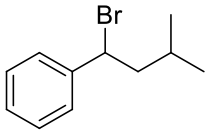
(1-Bromopropane-1,3-diyl)dibenzene (S61)



S61

According to **General procedure 3** with 1,3-diphenylpropan-1-one (0.63 g, 3.0 mmol, 1.0 equiv.), **S61** was obtained as a colorless oil (0.71 g, 86% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 6H), 7.19 – 7.11 (m, 4H), 4.87 (dd, *J* = 8.4, 6.4 Hz, 1H), 2.81 – 2.72 (m, 1H), 2.71 – 2.61 (m, 1H), 2.60 – 2.52 (m, 1H), 2.44 – 2.34 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 140.5, 128.8, 128.6, 128.5, 127.4, 126.3, 54.8, 41.4, 34.3.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{15}$ $[M - Br]^+$ 195.1168, found 195.1168.

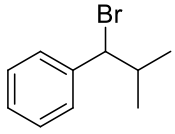
(1-Bromo-3-methylbutyl)benzene (S63)



S63

According to **General procedure 3** with 3-methyl-1-phenylbutan-1-one (0.49 g, 3.0 mmol, 1.0 equiv.), **S63** was obtained as a colorless oil (0.61 g, 90% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 5.03 (dd, *J* = 8.4, 7.2 Hz, 1H), 2.26 – 2.12 (m, 1H), 2.02 – 1.89 (m, 1H), 1.76 – 1.61 (m, 1H), 0.91 (d, *J* = 5.6 Hz, 3H), 0.90 (d, *J* = 5.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 128.7, 128.3, 127.3, 54.1, 48.8, 26.8, 22.3, 22.0.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{15}$ $[M - Br]^+$ 147.1168, found 147.1168.

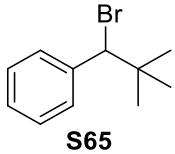
(1-Bromo-2-methylpropyl)benzene (S64)



S64

According to **General procedure 3** with 2-methyl-1-phenylpropan-1-one (0.44 g, 3.0 mmol, 1.0 equiv.), **S64** was obtained as a colorless oil (0.58 g, 91% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.27 – 7.24 (m, 1H), 4.71 (d, *J* = 8.4 Hz, 1H), 2.39 – 2.24 (m, 1H), 1.19 (d, *J* = 6.4 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 128.5, 128.1, 127.9, 64.4, 36.7, 21.7, 20.6.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{13}$ $[M - Br]^+$ 133.1012, found 133.1013.

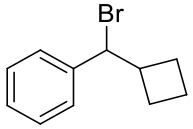
(1-Bromo-2,2-dimethylpropyl)benzene (S65)



S65

According to **General procedure 3** with 2,2-dimethyl-1-phenylpropan-1-one (0.49 g, 3.0 mmol, 1.0 equiv.), **S65** was obtained as a colorless oil (0.55 g, 81% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.29 – 7.27 (m, 1H), 7.25 – 7.21 (m, 2H), 4.84 (s, 1H), 1.06 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 129.2, 127.9, 127.7, 69.1, 37.1, 27.7.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{15}$ $[M - Br]^+$ 147.1168, found 147.1168.

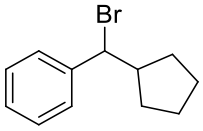
(Bromo(cyclobutyl)methyl)benzene (S66)



S66

According to **General procedure 3** with cyclobutyl(phenyl)methanone (0.48 g, 3.0 mmol, 1.0 equiv.), **S66** was obtained as a colorless oil (0.59 g, 88% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 4.96 (d, *J* = 10.8 Hz, 1H), 3.24 – 3.08 (m, 1H), 2.41 – 2.27 (m, 1H), 2.10 – 1.96 (m, 1H), 1.94 – 1.75 (m, 3H), 1.70 – 1.59 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 128.7, 128.4, 127.7, 61.8, 43.1, 28.7, 27.0, 16.2.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{13}$ $[M - Br]^+$ 145.1012, found 145.1012.

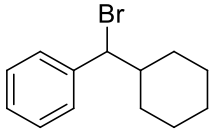
(Bromo(cyclopentyl)methyl)benzene (S67)



S67

According to **General procedure 3** with cyclopentyl(phenyl)methanone (0.52 g, 3.0 mmol, 1.0 equiv.), **S67** was obtained as a colorless oil (0.61 g, 85% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.32 – 7.26 (m, 2H), 7.26 – 7.20 (m, 1H), 4.76 (d, *J* = 10.0 Hz, 1H), 2.81 – 2.62 (m, 1H), 2.23 – 2.06 (m, 1H), 1.75 – 1.38 (m, 6H), 1.12 – 0.93 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 128.6, 128.1, 127.6, 61.9, 48.6, 33.5, 31.5, 26.1, 25.2.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{15}$ $[M - Br]^+$ 159.1168, found 159.1169.

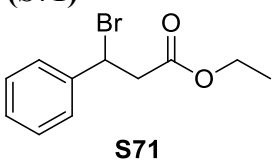
(Bromo(cyclohexyl)methyl)benzene (S68)



S68

According to **General procedure 3** with cyclohexyl(phenyl)methanone (0.56 g, 3.0 mmol, 1.0 equiv.), **S68** was obtained as a white solid (0.68 g, 90% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 7.35 – 7.30 (m, 1H), 4.80 (d, *J* = 8.8 Hz, 1H), 2.47 – 2.34 (m, 1H), 2.13 – 1.98 (m, 1H), 1.95 – 1.83 (m, 1H), 1.80 – 1.64 (m, 2H), 1.63 – 1.52 (m, 1H), 1.44 – 1.08 (m, 4H), 1.00 – 0.86 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 128.4, 128.0, 127.9, 63.3, 45.5, 32.2, 31.0, 26.2, 26.1, 26.0.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}$ $[M - Br]^+$ 173.1325, found 173.1325.

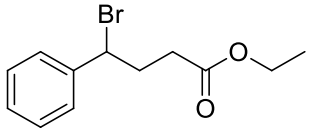
Ethyl 3-bromo-3-phenylpropanoate (S71)



S71

According to **General procedure 3** with ethyl 3-oxo-3-phenylpropanoate (0.58 g, 3.0 mmol, 1.0 equiv.), **S71** was obtained as a colorless oil (0.63 g, 82% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.37 – 7.24 (m, 3H), 5.40 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.20 – 4.05 (m, 2H), 3.33 (dd, *J* = 16.1, 9.0 Hz, 1H), 3.18 (dd, *J* = 16.1, 6.2 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 140.8, 128.83, 128.75, 127.2, 61.1, 48.1, 44.9, 14.2.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{14}BrO_2$ $[M + H]^+$ 257.0172, found 257.0170.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{13}O_2$ $[M - Br]^+$ 177.0910, found 177.0910.

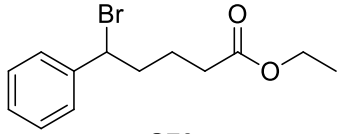
Ethyl 4-bromo-4-phenylbutanoate (S72)



S72

According to **General procedure 3** with ethyl 4-oxo-4-phenylbutanoate (0.62 g, 3.0 mmol, 1.0 equiv.), **S72** was obtained as a colorless oil (0.69 g, 85% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 1H), 5.07 – 5.00 (m, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.66 – 2.31 (m, 4H), 1.25 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 141.6, 128.9, 128.6, 127.4, 60.7, 54.4, 35.1, 32.9, 14.3.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{16}BrO_2$ $[M + H]^+$ 271.0328, found 271.0331.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{15}O_2$ $[M - Br]^+$ 191.1067, found 191.1065.

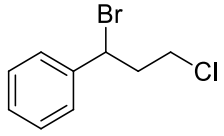
Ethyl 5-bromo-5-phenylpentanoate (S73)



S73

According to **General procedure 3** with ethyl 5-oxo-5-phenylpentanoate (0.66 g, 3.0 mmol, 1.0 equiv.), **S73** was obtained as a colorless oil (0.75 g, 88% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 4.95 (dd, *J* = 8.0, 6.8 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.37 – 2.25 (m, 3H), 2.24 – 2.13 (m, 1H), 1.91 – 1.77 (m, 1H), 1.71 – 1.58 (m, 1H), 1.25 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 142.0, 128.8, 128.5, 127.3, 60.5, 54.9, 39.4, 33.5, 23.8, 14.4.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}O_2$ $[M - Br]^+$ 205.1223, found 205.1222.

(1-Bromo-3-chloropropyl)benzene (S81)[2]

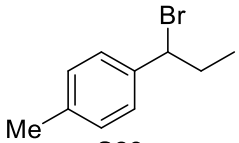


S81

According to **General procedure 3** with 3-chloro-1-phenyl-1-propanone (0.51 g, 3.0 mmol, 1.0 equiv.), **S81** was obtained as a colorless oil (0.64 g, 92% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.25 (m, 5H), 5.21 (dd, *J* = 9.0, 5.7 Hz, 1H), 3.82 – 3.65 (m, 1H), 3.63 – 3.39 (m, 1H), 2.85 – 2.60 (m, 1H), 2.56 – 2.38 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 129.0, 128.8, 127.5, 51.5, 42.9, 42.2.

HRMS (ESI) *m/z* calcd. for $C_9H_{10}Cl$ $[M - Br]^+$ 153.0466, found 153.0466.

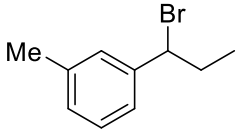
1-(1-Bromopropyl)-4-methylbenzene (S83)



S83

According to **General procedure 3** with 1-(*p*-tolyl)propan-1-one (0.44 g, 3.0 mmol, 1.0 equiv.), **S83** was obtained as a colorless (0.57 g, 89% crude yield oil over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.86 (t, *J* = 7.4 Hz, 1H), 2.32 (s, 3H), 2.30 – 2.21 (m, 1H), 2.19 – 2.08 (m, 1H), 0.98 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.2, 129.4, 127.3, 57.9, 33.3, 21.3, 13.2.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{13}$ $[M - Br]^+$ 133.1012, found 133.1012.

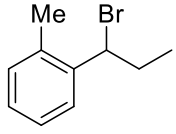
1-(1-Bromopropyl)-3-methylbenzene (S84)



S84

According to **General procedure 3** with 1-(*m*-tolyl)propan-1-one (0.44 g, 3.0 mmol, 1.0 equiv.), **S84** was obtained as a colorless oil (0.54 g, 85% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.12 (m, 3H), 7.07 – 7.02 (m, 1H), 4.82 (dd, *J* = 8.0, 6.8 Hz, 1H), 2.31 (s, 3H), 2.29 – 2.19 (m, 1H), 2.18 – 2.06 (m, 1H), 0.97 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 138.3, 129.1, 128.5, 128.0, 124.4, 57.8, 33.3, 21.4, 13.1.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{13}$ $[M - Br]^+$ 133.1012, found 133.1012.

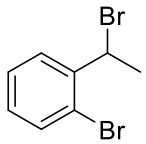
1-(1-Bromopropyl)-2-methylbenzene (S85)



S85

According to **General procedure 3** with 1-(*o*-tolyl)propan-1-one (0.44 g, 3.0 mmol, 1.0 equiv.), **S85** was obtained as a colorless oil (0.51 g, 80% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.24 – 7.10 (m, 3H), 5.12 (dd, *J* = 8.4, 6.8 Hz, 1H), 2.41 – 2.29 (m, 4H), 2.25 – 2.12 (m, 1H), 1.03 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 135.5, 130.7, 128.2, 126.72, 126.70, 54.0, 32.2, 19.2, 13.2.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{13}$ $[M - Br]^+$ 133.1012, found 133.1012.

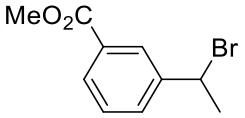
1-Bromo-2-(1-bromoethyl)benzene (S91)



S91

According to **General procedure 3** with 1-(2-bromophenyl)ethan-1-one (0.59 g, 3.0 mmol, 1.0 equiv.), **S91** was obtained as a colorless oil (0.70 g, 89% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.35 (td, *J* = 7.6, 1.3 Hz, 1H), 7.16 – 7.12 (m, 1H), 5.61 (q, *J* = 6.9 Hz, 1H), 2.04 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 133.2, 129. 8, 128.4, 128.2, 123.2, 47.6, 26.2.
HRMS (ESI) *m/z* calcd. for C_8H_8Br $[M - Br]^+$ 182.9804, found 182.9804.

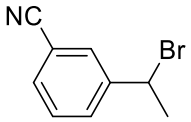
Methyl 3-(1-bromoethyl)benzoate (S94)[3]



S94

According to **General procedure 3** with methyl 3-acetylbenzoate (0.53 g, 3.0 mmol, 1.0 equiv.), **S94** was obtained as a colorless oil (0.68 g, 93% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 5.23 (q, *J* = 6.9 Hz, 1H), 3.93 (s, 3H), 2.06 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 143.8, 131.6, 130.7, 129.6, 129.0, 128.0, 52.4, 48.4, 26.8.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{11}O_2$ $[M - Br]^+$ 163.0754, found 163.0753.

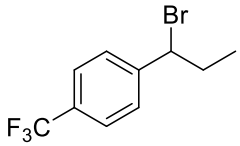
3-(1-Bromoethyl)benzonitrile (S95)



S95

According to **General procedure 3** with 3-acetylbenzonitrile (0.44 g, 3.0 mmol, 1.0 equiv.), **S95** was obtained as a colorless oil (0.55 g, 88% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.67 – 7.63 (m, 1H), 7.58 – 7.54 (m, 1H), 7.47 – 7.42 (m, 1H), 5.15 (q, *J* = 6.9 Hz, 1H), 2.03 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 131.9, 131.5, 130.5, 129.7, 118.4, 112.7, 46.9, 26.6.
HRMS (ESI) *m/z* calcd. for C_9H_8N $[M - Br]^+$ 130.0651, found 130.0652.

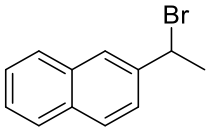
1-(1-Bromopropyl)-4-(trifluoromethyl)benzene (S96)



S96

According to **General procedure 3** with 1-(4-(trifluoromethyl)phenyl)propan-1-one (0.61 g, 3.0 mmol, 1.0 equiv.), **S96** was obtained as a colorless oil (0.75 g, 94% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 4.87 (dd, *J* = 8.4, 6.8 Hz, 1H), 2.34 – 2.22 (m, 1H), 2.20 – 2.07 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 130.4 (q, *J* = 32.5 Hz), 128.1, 125.8 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.1 Hz), 55.7, 33.2, 12.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7 (s, 3F).
HRMS (ESI) *m/z* calcd. for $C_{10}H_{10}F_3$ $[M - Br]^+$ 187.0729, found 187.0728.

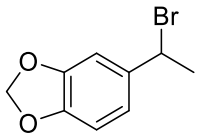
2-(1-Bromoethyl)naphthalene (S98)



S98

According to **General procedure 3** with 1-(naphthalen-2-yl)ethan-1-one (0.51 g, 3.0 mmol, 1.0 equiv.), **S98** was obtained as a white solid (0.59 g, 84% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.77 (m, 4H), 7.59 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.53 – 7.43 (m, 2H), 5.40 (q, *J* = 6.9 Hz, 1H), 2.14 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 133.3, 133.2, 128.8, 128.2, 127.8, 126.62, 126.60, 125.3, 125.2, 50.1, 26.9.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{11}$ $[M - Br]^+$ 155.0855, found 155.0855.

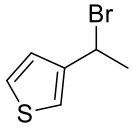
5-(1-Bromoethyl)benzo[*d*][1,3]dioxole (S99)



S99

According to **General procedure 3** with 1-(benzo[*d*][1,3]dioxol-5-yl)ethan-1-one (0.49 g, 3.0 mmol, 1.0 equiv.), **S99** was obtained as a slightly yellow oil (0.56 g, 82% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.86 – 6.73 (m, 2H), 5.95 (s, 2H), 4.81 (q, *J* = 6.4 Hz, 1H), 1.46 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 146.8, 140.0, 118.7, 108.1, 106.1, 101.0, 70.2, 25.1.
HRMS (ESI) *m/z* calcd. for $C_9H_9O_2$ $[M - Br]^+$ 119.0597, found 149.0597.

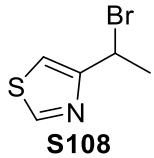
3-(1-Bromoethyl)thiophene (S105)



S105

According to **General procedure 3** with 1-(thiophen-3-yl)ethan-1-one (0.38 g, 3.0 mmol, 1.0 equiv.), **S105** was obtained as a brown oil (0.43 g, 76% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 5.2, 2.8 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.21 (dd, *J* = 5.2, 1.2 Hz, 1H), 5.35 (q, *J* = 6.9 Hz, 1H), 2.09 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 126.9, 126.4, 121.7, 44.4, 26.7.
HRMS (ESI) *m/z* calcd. for C_6H_7S $[M - Br]^+$ 111.0263, found 111.0266.

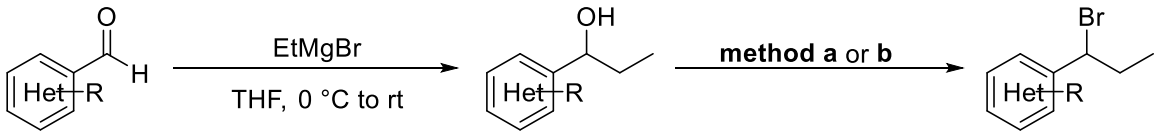
4-(1-Bromoethyl)thiazole (S108)



S108

According to **General procedure 3** with 1-(thiazol-4-yl)ethan-1-one (0.38 g, 3.0 mmol, 1.0 equiv.),

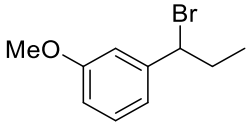
S108 was obtained as a yellow oil (0.39 g, 68% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 5.42 (q, *J* = 6.4 Hz, 1H), 2.14 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 153.3, 115.1, 42.9, 25.4.
HRMS (ESI) *m/z* calcd. for C_5H_7BrNS $[M + H]^+$ 191.9477, found 191.9476.
HRMS (ESI) *m/z* calcd. for C_5H_6NS $[M - Br]^+$ 112.0215, found 112.0218.



method a: PPh_3, CBr_4, THF, Ar, 0 °C to rt
method b: PBr_3, CH_2Cl_2, 0 °C to rt

General procedure 4:
To a solution of aldehyde in anhydrous THF (2.0 mL/mmol aldehyde) was slowly added ethylmagnesium bromide (1.0 M in THF, 1.2 equiv.) at 0 °C under argon atmosphere. Then, the reaction mixture was warmed up to room temperature and stirred until the aldehyde was completely consumed (monitored by TLC). The reaction was quenched by 3.0 M HCl and extracted with CH_2Cl_2 three times. The combined organic phase was dried over Na_2SO_4, filtered, concentrated under reduced pressure, and briefly purified by column chromatography on silica gel to afford the desired alcohol, which was directly used in the next step without further purification.
Method a: To a mixture of the crude alcohol obtained above and triphenylphosphine (1.8 equiv.) in THF (2.0 mL/mmol alcohol) was added carbon tetrabromide (1.5 equiv.) in one portion at 0 °C under argon atmosphere. After stirred at 0 °C for a while, the reaction mixture was allowed to warm to room temperature and stirred for another 25 min. The mixture was filtered through a pad of celite with THF as the eluent. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to provide the corresponding alkyl bromide product.
Method b: To a solution of the crude alcohol obtained above in CH_2Cl_2 (2.0 mL/mmol alcohol) was added PBr_3 (0.7 equiv.) with vigorous stirring at 0 °C and the resulting reaction mixture was stirred at room temperature. After completion of reaction (monitored by TLC), the mixture was quenched by water and extracted with CH_2Cl_2 three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered through a silica gel pad, and concentrated under reduced pressure to afford the corresponding crude alkyl bromide product, which was directly used in the next step without further purification or stored in a refrigerator unless otherwise noted. (The product usually readily decomposed in air and on silica gel.)

1-(1-Bromopropyl)-3-methoxybenzene (S86)

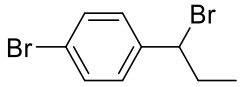


S86

According to **General procedure 4** with 3-methoxybenzaldehyde (0.41 g, 3.0 mmol, 1.0 equiv.) and ***Method b***, **S86** was obtained as a colorless oil (0.63 g, 92% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.0 Hz, 1H), 7.07 – 6.94 (m, 2H), 6.90 – 6.83 (m, 1H), 4.88 (t, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 2.40 – 2.11 (m, 2H), 1.04 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 143.6, 129.7, 119.6, 113.7, 113.0, 57.4, 55.3, 33.3, 13.0.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{13}O$ $[M - Br]^+$ 149.0961, found 149.0961.

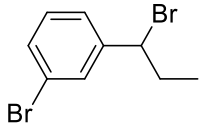
1-Bromo-4-(1-bromopropyl)benzene (S89)



S89

According to **General procedure 4** with 4-bromobenzaldehyde (0.93 g, 5.0 mmol, 1.0 equiv.) and ***Method b***, **S89** was obtained as a yellow oil (1.08 g, 78% crude yield over two steps).
The analytic data are consistent with the reported ones[4].

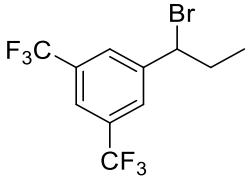
1-Bromo-3-(1-bromopropyl)benzene (S90)



S90

According to **General procedure 4** with 3-bromobenzaldehyde (0.93 g, 5.0 mmol, 1.0 equiv.) and ***Method b***, **S90** was obtained as a yellow oil (1.14 g, 82% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 1.8 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 4.82 (dd, *J* = 8.1, 6.7 Hz, 1H), 2.35 – 2.06 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 131.4, 130.4, 130.3, 126.1, 122.6, 55.9, 33.2, 13.0.
HRMS (ESI) *m/z* calcd. for $C_9H_{10}Br$ $[M - Br]^+$ 196.9960, found 196.9960.

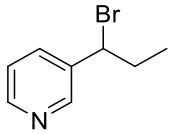
1-(1-Bromopropyl)-3,5-bis(trifluoromethyl)benzene (S97)



S97

According to **General procedure 4** with 3,5-bis(trifluoromethyl)benzaldehyde (0.73 g, 3.0 mmol, 1.0 equiv.) and ***Method b***, **S97** was obtained as a colorless oil (0.95 g, 95% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.83 (s, 1H), 4.92 (dd, *J* = 8.3, 6.4 Hz, 1H), 2.39 – 2.28 (m, 1H), 2.24 – 2.14 (m, 1H), 1.07 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 132.1 (q, *J* = 33.5 Hz), 127.5, 123.1 (q, *J* = 272.8 Hz), 122.2 – 122.0 (m), 54.0, 33.1, 12.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9 (s, 6F).
HRMS (ESI) *m/z* calcd. for $C_{11}H_9F_6$ $[M - Br]^+$ 255.0603, found 255.0603.

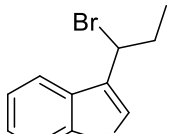
3-(1-Bromopropyl)pyridine (S101)



S101

According to **General procedure 4** with nicotinaldehyde (0.32 g, 3.0 mmol, 1.0 equiv.) and ***Method a***, **S101** was obtained as a slight yellow oil (0.48 g, 80% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 2.0 Hz, 1H), 8.53 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.75 (dt, *J* = 7.6, 1.8 Hz, 1H), 7.29 (dd, *J* = 7.6, 4.8 Hz, 1H), 4.87 (dd, *J* = 8.4, 6.8 Hz, 1H), 2.36 – 2.23 (m, 1H), 2.21 – 2.09 (m, 1H), 1.02 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 148.6, 137.9, 134.9, 123.7, 54.0, 33.1, 12.9.
HRMS (ESI) *m/z* calcd. for $C_8H_{11}BrN$ $[M + H]^+$ 200.0069, found 200.0066.
HRMS (ESI) *m/z* calcd. for $C_8H_{10}N$ $[M – Br]^+$ 120.0808, found 120.0808.

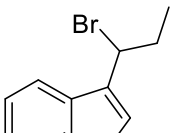
3-(1-Bromopropyl)benzo[*b*]thiophene (S104)



S104

According to **General procedure 4** with benzo[*b*]thiophene-3-carbaldehyde (0.49 g, 3.0 mmol, 1.0 equiv.) and ***Method b***, **S104** was obtained as a yellow oil (0.53 g, 70% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 7.44 – 7.39 (m, 1H), 7.38 – 7.33 (m, 1H), 5.26 (dd, *J* = 8.3, 6.2 Hz, 1H), 2.52 – 2.29 (m, 2H), 1.11 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 137.0, 136.6, 124.8, 124.2, 124.0, 123.0, 122.5, 50.4, 31.6, 13.3.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{11}S$ $[M – Br]^+$ 175.0576, found 175.0573.

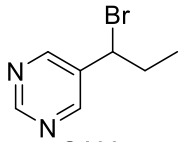
3-(1-Bromopropyl)benzofuran (S106)



S106

According to **General procedure 4** with benzofuran-3-carbaldehyde (0.44 g, 3.0 mmol, 1.0 equiv.) and ***Method b***, **S106** was obtained as a yellow oil (0.52 g, 72% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 1H), 7.67 (s, 1H), 7.54 – 7.50 (m, 1H), 7.40 – 7.29 (m, 2H), 5.23 – 5.09 (m, 1H), 2.54 – 2.30 (m, 2H), 1.14 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 141.8, 125.9, 125.0, 122.8, 122.4, 120.8, 111.8, 47.9, 31.9, 13.2.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{11}O$ $[M – Br]^+$ 159.0804, found 159.0802.

5-(1-Bromopropyl)pyrimidine (S109)



S109

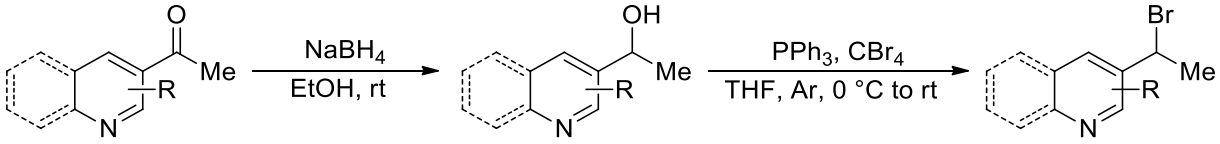
According to **General procedure 4** with pyrimidine-5-carbaldehyde (0.32 g, 3.0 mmol, 1.0 equiv.) and ***Method a***, **S109** was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) as a slight yellow oil (0.29 g, 48% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.75 (s, 2H), 4.79 (dd, *J* = 8.2, 6.6 Hz, 1H), 2.35 – 2.22 (m, 1H), 2.21 – 2.08 (m, 1H), 1.04 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 155.9, 136.0, 50.0, 32.8, 12.8.

HRMS (ESI) *m/z* calcd. for $C_7H_{10}BrN_2$ $[M + H]^+$ 201.0022, found 201.0022.

HRMS (ESI) *m/z* calcd. for $C_7H_9N_2$ $[M - Br]^+$ 121.0760, found 121.0762.

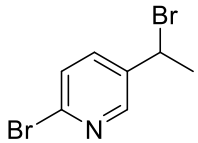


General procedure 5:

To a solution of ketone (5.0 mmol, 1.0 equiv.) in EtOH (20.0 mL) was added $NaBH_4$ (228.0 mg, 6.0 mmol, 1.2 equiv.) at room temperature for 0.5 – 2 h. After completion of reaction (monitored by TLC), the reaction was quenched by water, diluted with CH_2Cl_2, and extracted with CH_2Cl_2 three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the corresponding alcohol, which was directly used in the next step without further purification

To a solution of the crude alcohol obtained above and triphenylphosphine (1.8 equiv.) in THF (2.0 mL/mmol alcohol) was added carbon tetrabromide (1.5 equiv.) in one portion at 0 °C under argon atmosphere and the resulting reaction mixture was stirred at 0 °C for 5 min. Then, the mixture was allowed to warm up to room temperature and stirred for another 2 h. The precipitate was filtered off through a pad of celite and washed by cold THF. The solution was concentrated under reduced pressure and purified by column chromatography on silica gel to provide the corresponding bromo compound.

2-Bromo-5-(1-bromoethyl)pyridine (S102)



S102

According to **General procedure 5** with 1-(6-bromopyridin-3-yl)ethanone (1.0 g, 5.0 mmol, 1.0 equiv.), **S102** was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) as a colorless oil (1.1 g, 84% yield over two steps).

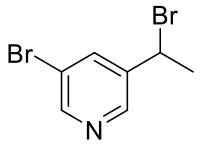
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.6 Hz, 1H), 7.65 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 5.13 (q, *J* = 7.0 Hz, 1H), 2.03 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 141.8, 138.5, 137.3, 128.4, 44.3, 26.6.

HRMS (ESI) *m/z* calcd. for $C_7H_8Br_2N$ $[M + H]^+$ 263.9018, found 263.9017.

HRMS (ESI) *m/z* calcd. for C_7H_7BrN $[M - Br]^+$ 183.9756, found 183.9756.

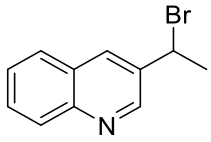
3-Bromo-5-(1-bromoethyl)pyridine (S103)



S103

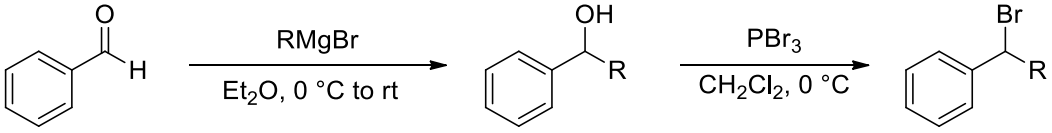
According to **General procedure 5** with 1-(5-bromopyridin-3-yl)ethanone (1.0 g, 5.0 mmol, 1.0 equiv.), **S103** was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) as a colorless oil (1.1 g, 82% yield over two steps).
1H NMR (400 MHz, CDCl3) δ 8.56 (dd, *J* = 12.2, 2.1 Hz, 2H), 7.91 (t, *J* = 2.0 Hz, 1H), 5.11 (q, *J* = 7.0 Hz, 1H), 2.03 (d, *J* = 7.0 Hz, 3H).
13C NMR (100 MHz, CDCl3) δ 150.7, 146.3, 140.6, 137.2, 120.9, 44.1, 26.6.
HRMS (ESI) *m/z* calcd. for $C_7H_8Br_2N$ $[M + H]^+$ 263.9018, found 263.9017.
HRMS (ESI) *m/z* calcd. for C_7H_7BrN $[M - Br]^+$ 183.9756, found 183.9756.

3-(1-Bromoethyl)quinolone (S107)



S107

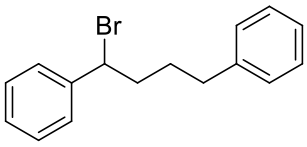
According to **General procedure 5** with 1-(quinolin-3-yl)ethanone (0.86 g, 5.0 mmol, 1.0 equiv.), **S107** was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) as a slight yellow oil (0.64 g, 54% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 2.3 Hz, 1H), 8.15 (d, *J* = 2.3 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.82 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.72 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.57 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 5.39 (q, *J* = 7.0 Hz, 1H), 2.17 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 147.8, 136.1, 133.1, 130.1, 129.4, 128.1, 127.6, 127.3, 46.0, 26.5.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{10}N$ $[M - Br]^+$ 156.0808, found 156.0807.



General procedure 6:
To a solution of benzaldehyde (0.32 g, 3.0 mmol, 1.0 equiv.) in dry Et_2O (9.0 mL) was added appropriate Grignard reagent RMgBr (3.6 mmol, 1.2 equiv.) dropwise at 0 °C under argon atomsphere. The reaction mixture was warmed to room temperature and stirred for another 1 h until the aldehyde was completely consumed (monitored by TLC). After that, the reaction was quenched by 3.0 M HCl and extracted with CH_2Cl_2 three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product thus obtained was directly used in the next step without further purification.
To a solution of the crude alcohol obtained above in CH_2Cl_2 was added PBr_3 (0.7 equiv.) dropwise at 0 °C with vigorous stirring. The resulting reaction mixture was then stirred at 0 °C for 3 h. After

completion of reaction (monitored by TLC), the reaction was quenched by water and extracted with CH_2Cl_2 three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered through a short silica gel pad, and concentrated under reduced pressure to afford the corresponding alkyl bromide, which was directly used in the next step without further purification.

(1-Bromobutane-1,4-diyl)dibenzene (S62)



S62

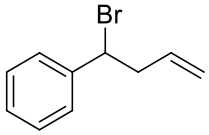
According to **General procedure 6** with (3-phenylpropyl)magnesium bromide (3.6 mL, 3.6 mmol, 1.0 M in THF, 1.2 equiv.), **S62** was obtained as a colorless oil (0.78 g, 90% crude yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 7H), 7.20 – 7.13 (m, 3H), 4.94 (dd, *J* = 8.0, 6.8 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.36 – 2.25 (m, 1H), 2.22 – 2.10 (m, 1H), 1.89 – 1.76 (m, 1H), 1.69 – 1.55 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 141.8, 128.8, 128.50, 128.49, 128.4, 127.4, 126.0, 55.5, 39.6, 35.2, 30.1.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{17}$ $[M - Br]^+$ 209.1325, found 209.1325.

(1-Bromobut-3-en-1-yl)benzene (S69)



S69

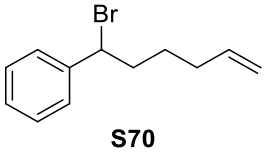
According to **General procedure 6** with allylmagnesium bromide (3.6 mL, 3.6 mmol, 1.0 M in THF, 1.2 equiv.), **S69** was obtained as a colorless oil (0.60 g, 95% crude yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.25 (m, 1H), 5.82 – 5.65 (m, 1H), 5.19 – 5.04 (m, 2H), 4.96 (dd, *J* = 8.0, 7.0 Hz, 1H), 3.12 – 2.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 134.8, 128.8, 128.5, 127.5, 118.3, 54.2, 44.2.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{11}$ $[M - Br]^+$ 131.0855, found 131.0856.

(1-Bromohex-5-en-1-yl)benzene (S70)



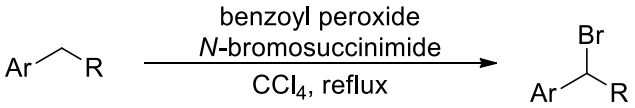
S70

According to **General procedure 6** with pent-4-en-1-ylmagnesium bromide (3.6 mL, 3.6 mmol, 1.0 M in THF, 1.2 equiv.), **S70** was obtained as a colorless oil (0.63 g, 88% crude yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 5.78 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.09 – 4.91 (m, 3H), 2.38 – 2.23 (m, 1H), 2.23 – 2.04 (m, 3H), 1.71 – 1.57 (m, 1H), 1.45 – 1.37 (m, 1H).

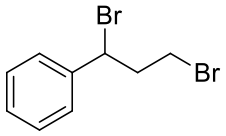
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 138.0, 128.7, 128.3, 127.3, 115.1, 55.5, 39.4, 33.0, 27.5.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{15}$ $[M - Br]^+$ 159.1168, found 159.1168.



General procedure 7:
To a solution of benzyl derivative (5.0 mmol, 1.0 equiv.) in CCl_4 (10.0 mL) were added *N*-bromosuccinimide (0.89 g, 5.5 mmol, 1.1 equiv.) and benzoyl peroxide (36.3 mg, 0.15 mmol, 3.0 mol%) and then the resulting mixture was refluxed overnight. After completion of reaction (monitored by TLC), the reaction mixture was cooled to room temperature. The precipitate was filtered off through a pad of celite and washed with CCl_4 (10.0 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the corresponding alkyl bromide product.

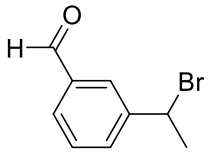
(1,3-Dibromopropyl)benzene (S80)



S80

According to **General procedure 7** with (3-bromopropyl)benzene (0.99 g, 5.0 mmol, 1.0 equiv.), **S80** was obtained by column chromatography on silica gel (petroleum ether) as a colorless oil (1.2 g, 88% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 5H), 5.33 – 5.03 (m, 1H), 3.62 – 3.50 (m, 1H), 3.49 – 3.39 (m, 1H), 2.85 – 2.73 (m, 1H), 2.63 – 2.48 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 129.0, 128.9, 127.5, 52.6, 42.2, 31.1.
HRMS (ESI) *m/z* calcd. for $C_9H_{10}Br$ $[M - Br]^+$ 196.9960, found 196.9962.

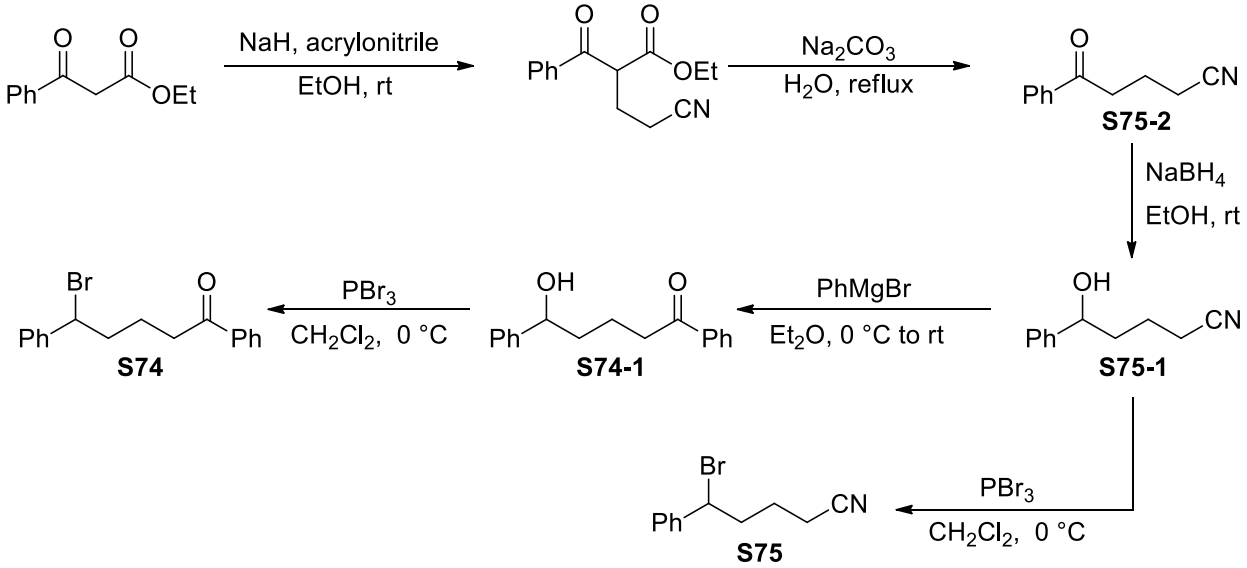
3-(1-Bromoethyl)benzaldehyde (S92)



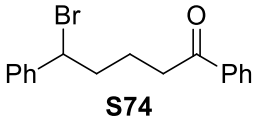
S92

According to **General procedure 7** with 3-ethylbenzaldehyde (0.67 g, 5.0 mmol, 1.0 equiv.), **S92** was obtained by column chromatography on silica gel (petroleum ether) as a colorless oil (0.93 g, 88% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.94 (t, *J* = 1.8 Hz, 1H), 7.80 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 5.24 (q, *J* = 6.9 Hz, 1H), 2.07 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 144.5, 136.9, 133.1, 129.9, 129.6, 127.7, 47.9, 26.8.
HRMS (ESI) *m/z* calcd. for $C_9H_{10}BrO$ $[M + H]^+$ 212.9910, found 212.9908.
HRMS (ESI) *m/z* calcd. for C_9H_9O $[M - Br]^+$ 133.0648, found 133.0648.

The synthesis of substrates S74 and S75



5-Bromo-1,5-diphenylpentan-1-one (S74)



To a stirred solution of **S75-1** (1.1 g, 6.3 mmol, 1.0 equiv.) in dry Et_2O (30.0 mL) was added dropwise phenylmagnesium bromide (6.3 mL, 2.5 M in THF, 15.8 mmol, 2.5 equiv.) at 0 °C under argon atmosphere and the resulting reaction mixture was stirred at room temperature for another 3 h. The reaction was quenched by 2.0 M HCl and extracted with Et_2O three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethhyl acetate = 10/1) to afford compound **S74-1** (1.2 g, 75% yield). The analytic data are consistent with the reported one[5].

According to ***Method b*** of **General procedure 4** with **S74-1** (0.76 g, 3.0 mmol, 1.0 equiv.), **S74** was obtained as a white solid (0.80 g, 84% yield).

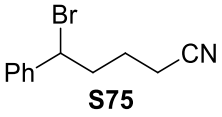
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 2H), 7.59 – 7.53 (m, 1H), 7.49 – 7.39 (m, 4H), 7.37 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 5.05 – 4.97 (m, 1H), 3.01 (t, *J* = 7.1 Hz, 2H), 2.46 – 2.17 (m, 2H), 2.01 – 1.90 (m, 1H), 1.85 – 1.71 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 142.0, 136.9, 133.2, 128.9, 128.8, 128.5, 128.1, 127.4, 55.2, 39.5, 37.7, 23.0.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}O$ $[M - Br]^+$ 237.1274, found 237.1272.

S75-2 was synthesized according to reported literature[6].

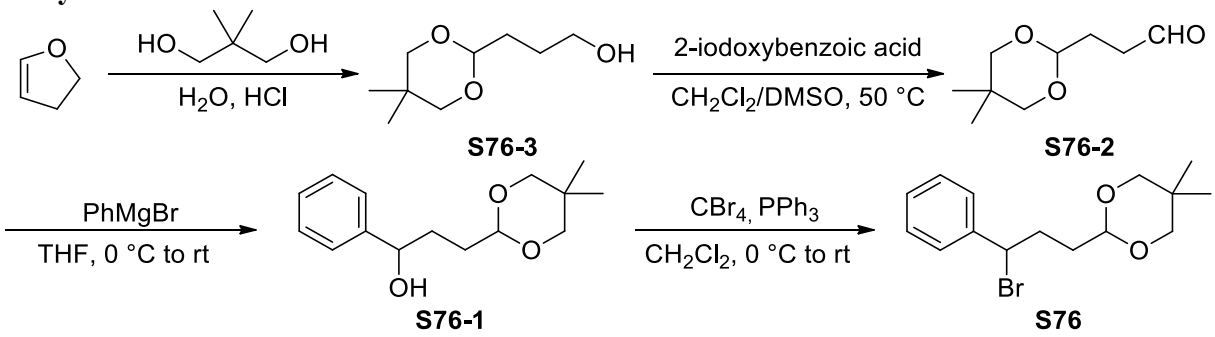
5-Bromo-5-phenylpentanenitrile (S75)



According to **General procedure 3** with **S75-2** (0.52 g, 3.0 mmol, 1.0 equiv.), **S75** was obtained as a colorless oil (0.63 g, 88% crude yield over two steps).

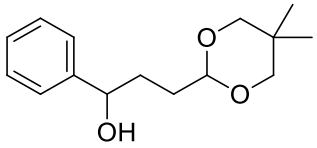
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 4.94 (dd, *J* = 8.4, 6.0 Hz, 1H), 2.46 – 2.35 (m, 3H), 2.33 – 2.22 (m, 1H), 1.98 – 1.84 (m, 1H), 1.76 – 1.62 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 128.9, 128.7, 127.2, 119.1, 53.8, 38.7, 24.2, 16.6.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{13}BrN$ $[M + H]^+$ 238.0226, found 238.0224.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}N$ $[M - Br]^+$ 158.0964, found 158.0964.

The synthesis of substrate S76



S76-3 was synthesized according to reported literature[7].
To a solution of alcohol **S76-3** (2.1 g, 12.0 mmol, 1.0 equiv.) in a mixture of CH_2Cl_2 (40.0 mL) and DMSO (8.0 mL) was added 2-iodoxybenzoic acid (4.0 g, 14.4 mmol, 1.0 equiv.) and the reaction mixture was stirred at 50 °C for 2 h. After completion of reaction (monitored by TLC), the reaction mixture was quenched with water, filtered on a pad of celite, and extracted with CH_2Cl_2 three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to afford aldehyde **S76-2** as a colorless liquid (1.4 g, 67% yield). The analytical data are consistent with the reported ones[8].

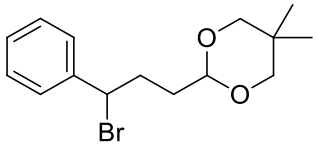
4-(5,5-Dimethyl-1,3-dioxan-2-yl)-1-phenylbutan-1-ol (S76-1)



S76-1

According to **General procedure 4** with phenylmagnesium bromide (3.0 M in THF, 2.4 mL, 1.2 equiv.), **S76-1** was obtained as a colorless oil (0.98 g, 62% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.27 – 7.21 (m, 1H), 4.69 (td, *J* = 6.4, 2.8 Hz, 1H), 4.45 (t, *J* = 4.6 Hz, 1H), 3.68 – 3.53 (m, 2H), 3.41 (d, *J* = 10.7 Hz, 2H), 2.88 (d, *J* = 3.2 Hz, 1H), 1.93 – 1.86 (m, 2H), 1.84 – 1.64 (m, 2H), 1.18 (s, 3H), 0.71 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 128.4, 127.4, 125.9, 101.9, 77.3, 74.2, 33.4, 31.2, 30.2, 23.1, 21.9.

2-(4-Bromo-4-phenylbutyl)-5,5-dimethyl-1,3-dioxane (S76)

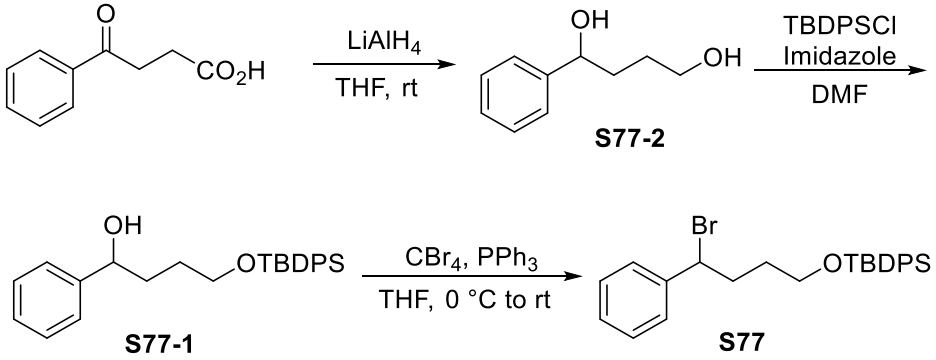


S76

According to ***Method a*** of **General procedure 4** with **S76-2** (0.79 g, 3.0 mmol, 1.0 equiv.),

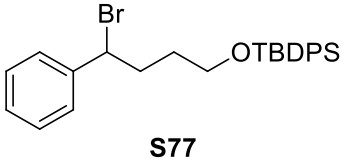
triphenylphosphine (0.94 g, 3.6 mmol, 1.2 equiv.), and carbon tetrabromide (1.19 g, 3.6 mmol, 1.2 equiv.) in CH_2Cl_2 (20.0 mL), **S76** was obtained as a coloreless oil (0.62 g, 64% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.24 (m, 5H), 5.03 – 4.96 (m, 1H), 4.45 (t, J = 4.7 Hz, 1H), 3.62 – 3.54 (m, 2H), 3.39 (d, J = 11.1 Hz, 2H), 2.49 – 2.25 (m, 2H), 1.90 – 1.79 (m, 1H), 1.71 – 1.63 (m, 1H), 1.17 (s, 3H), 0.71 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 128.8, 128.4, 127.4, 101.2, 77.3, 55.6, 34.4, 33.6, 30.2, 23.1, 21.9.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{21}O_2$ $[M - Br]^+$ 233.1536, found 233.1534.

The synthesis of substrate S77



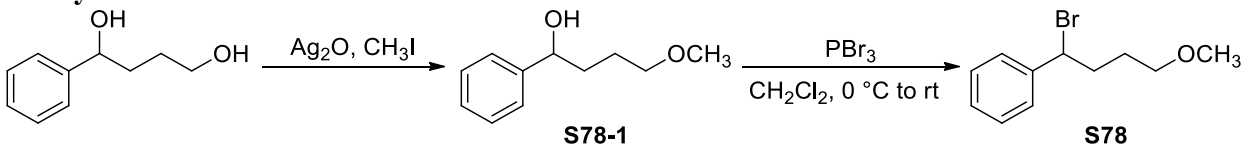
S77-2 was synthesized according to reported literature[9,10].
S77-1 was synthesized according to reported literature[11].

(4-Bromo-4-phenylbutoxy)(*tert*-butyl)diphenylsilane (S77)

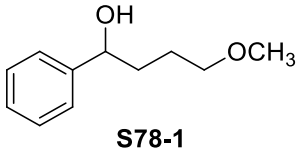


According to ***Method a*** of **General procedure 4** with **S77-1** (1.2 g, 3.0 mmol, 1.0 equiv.), triphenylphosphine (0.94 g, 3.6 mmol, 1.2 equiv.), and carbon tetrabromide (1.2 g, 3.6 mmol, 1.2 equiv.), **S77** was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) as a coloreless oil (0.84 g, 60% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 4H), 7.48 – 7.29 (m, 11H), 5.05 – 4.92 (m, 1H) 3.79 – 3.63 (m, 2H), 2.46 – 2.24 (m, 2H), 1.83 – 1.69 (m, 1H), 1.67 – 1.51 (m, 1H), 1.08 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 135.7, 133.9, 129.8, 128.8, 128.4, 127.8, 127.4, 63.1, 55.6, 36.6, 31.2, 27.0, 19.3.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{31}OSi$ $[M - Br]^+$ 387.2139, found 387.2137.

The synthesis of S78



4-Methoxy-1-phenylbutan-1-ol (S78-1)



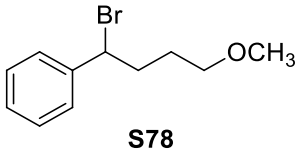
S78-1

To a mixture of diol (0.83 g, 5.0 mmol, 1.0 equiv.) in iodomethane (15.0 mL) was added Ag_2O (3.5 g, 15.0 mmol, 3.0 equiv.) in one portion and the resulting reaction mixture was stirred at room temperature overnight. After completion of reaction (monitored by TLC), the reaction mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 6/1) to afford **S78-1** as a colorless liquid (0.45 g, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 4.64 (td, *J* = 6.4, 3.1 Hz, 1H), 3.38 (t, *J* = 6.1 Hz, 2H), 3.30 (s, 3H), 3.18 (d, *J* = 3.3 Hz, 1H), 1.82 – 1.76 (m, 2H), 1.74 – 1.53 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 128.4, 127.3, 125.9, 74.1, 72.8, 58.6, 36.5, 26.2.

(1-Bromo-4-methoxybutyl)benzene (S78)



S78

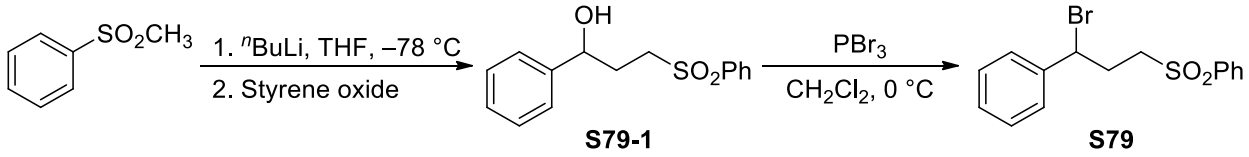
According to ***Method b*** of **General procedure 4** with **S78-1** (0.36 g, 2.0 mmol, 1.0 equiv.), **S78** was obtained as a colorless oil (0.48 g, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 1H), 4.98 (dd, *J* = 8.4, 6.7 Hz, 1H), 3.44 – 3.36 (m, 2H), 3.31 (s, 3H), 2.42 – 2.18 (m, 2H), 1.84 – 1.71 (m, 1H), 1.66 – 1.52 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 128.8, 128.5, 127.4, 71.9, 58.7, 55.6, 36.9, 28.5.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{15}O$ $[M - Br]^+$ 163.1117, found 163.1110.

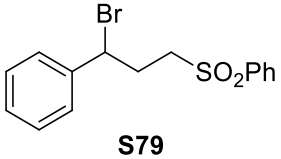
The synthesis of S79



S79-1 **S79**

S79-1 was synthesized according to reported literature[12].

(1-Bromo-3-(phenylsulfonyl)propyl)benzene (S79)



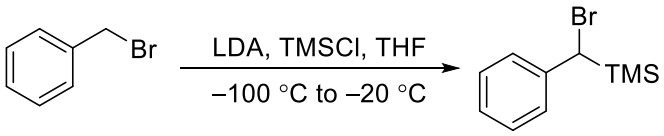
S79

According to ***Method b*** of **General procedure 4** with **S79-1** (0.83 g, 3.0 mmol, 1.0 equiv.), **S79** was obtained as a colorless oil (0.96 g, 95% crude yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.71 – 7.64 (m, 1H), 7.61 – 7.55 (m, 2H), 7.36 – 7.27 (m, 5H), 5.00 (dd, *J* = 8.7, 6.3 Hz, 1H), 3.41 – 3.26 (m, 1H), 3.25 – 3.07 (m, 1H), 2.75 –

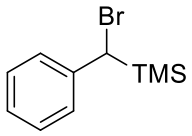
2.45 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 139.0, 134.1, 129.6, 129.1, 129.0, 128.1, 127.3, 54.8, 52.1, 33.1.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{15}O_2S$ $[M - Br]^+$ 259.0787, found 259.0785.

The synthesis of substrate(S82)



S82

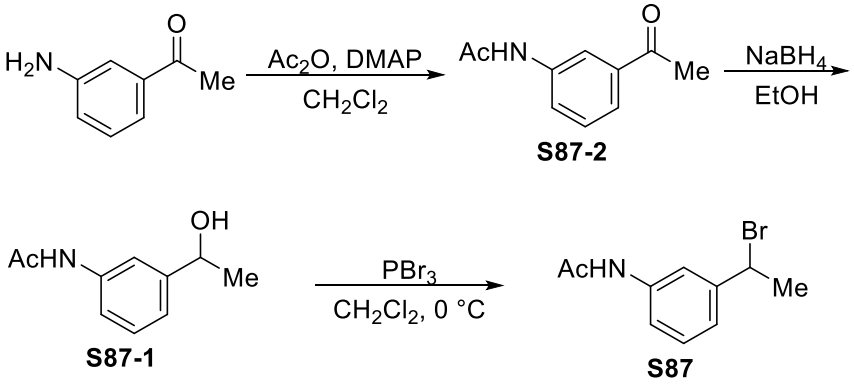
(Bromo(phenyl)methyl)trimethylsilane (S82)



S82

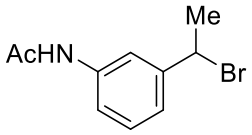
To a solution of commercially available lithium diisopropylamide (LDA) (4.0 mL, 8.0 mmol, 1.0 equiv., 2.0 M in THF/heptane/ethylbenzene) in anhydrous THF (4.0 mL) and hexane (4.0 mL) was added a solution of benzyl bromide (1.37 g, 8.0 mmol, 1.0 equiv.) and chlorotrimethylsilane (TMSCl) (1.04 g, 9.6 mmol, 1.2 equiv.) in anhydrous THF (4.0 mL) at –100 °C. The resulting mixture was stirred under the same conditions for another 1 h before warmed up to –20 °C. Then, the reaction was quenched by water and the organic phase was separated. The aqueous phase was extracted with Et_2O three times. The combined organic phase was washed with 2.0 M HCl and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by distillation under reduced pressure to afford **S82** as a colorless oil (1.05 g, 54% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.06 (m, 5H), 4.17 (s, 1H), 0.00 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 128.4, 128.0, 126.8, 43.8, –2.8.

The synthesis of substrate (S87)



S87-2 was synthesized according to reported literature[13].

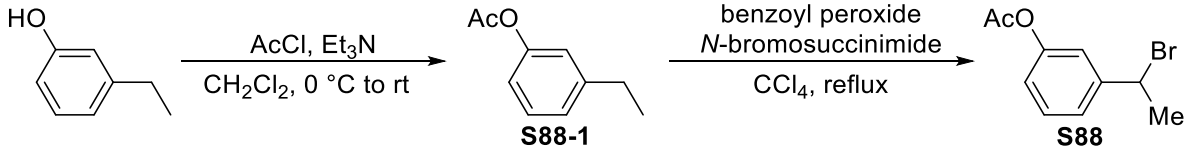
***N*-(3-(1-Bromoethyl)phenyl)acetamide (S87)**



S87

According to **General procedure 3** with *N*-(3-acetylphenyl)acetamide **S87-2** (0.53 g, 3.0 mmol, 1.0 equiv.), **S87** was obtained as a colorless oil (0.42 g, 58% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.52 (s, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.24 (m, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 5.16 (q, *J* = 6.9 Hz, 1H), 2.18 (s, 3H), 2.02 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 144.1, 138.2, 129.3, 122.8, 120.2, 118.7, 49.3, 26. 8, 24.4.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{12}NO$ $[M - Br]^+$ 162.0913, found 162.0912.

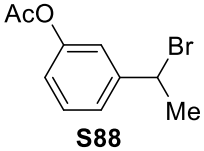
The synthesis of S88



S88-1 **S88**

S88-1 was synthesized according to reported literature[14].

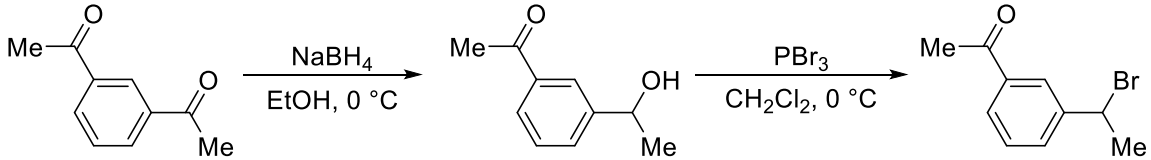
3-(1-Bromoethyl)phenyl acetate (S88)



S88

According to **General procedure 7** with **S88-1** (0.82 g, 5.0 mmol, 1.0 equiv.), **S88** was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) as a colorless oil (1.0 g, 86% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 2H), 7.18 (t, *J* = 2.0 Hz, 1H), 7.05 – 7.00 (m, 1H), 5.18 (q, *J* = 6.9 Hz, 1H), 2.30 (s, 3H), 2.03 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 150.8, 144.9, 129.7, 124.4, 121.7, 120.2, 48.4, 26.8, 21.2.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{11}O_2$ $[M - Br]^+$ 163.0754, found 163.0753.

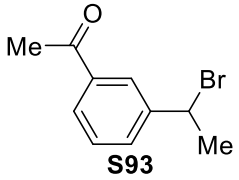
The synthesis of S93



S93-1 **S93**

S93-1 was synthesized according to reported literature[15].

1-(3-(1-Bromoethyl)phenyl)ethan-1-one (S93)



S93

According to **General procedure 3** with 1,1'-(1,3-phenylene)diethanone **S93-1** (0.82 g, 5.0 mmol, 1.0 equiv.), **S93** was obtained as a colorless oil (1.0 g, 89% crude yield).

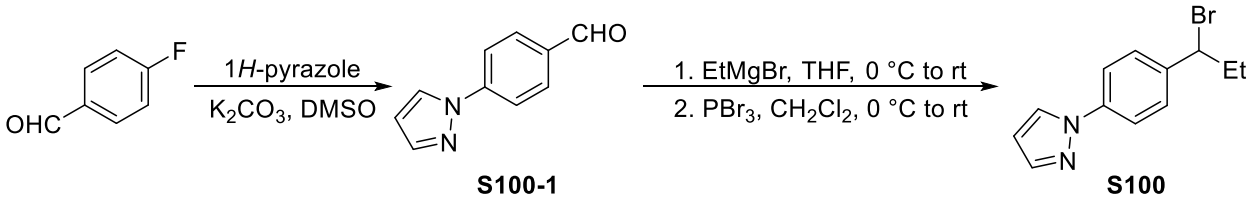
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (t, *J* = 1.8 Hz, 1H), 7.86 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.65 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 5.23 (q, *J* = 6.9 Hz, 1H), 2.61 (s, 3H), 2.06 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 144.0, 137.6, 131.7, 129.2, 128.4, 126.5, 48.5, 26.84, 26.82.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{12}BrO$ $[M + H]^+$ 227.0066, found 227.0066.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{11}O$ $[M - Br]^+$ 147.0804, found 147.0804.

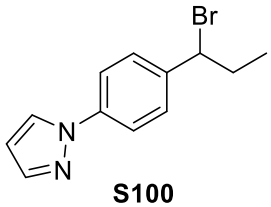
The synthesis of S100



S100-1 **S100**

S100-1 (4.8 g, 56% yield) was synthesized according to reported literature[16].

1-(4-(1-Bromopropyl)phenyl)-1*H*-pyrazole (S100)



S100

According to ***Method b*** of **General procedure 4** with 4-(1*H*-pyrazol-1-yl)benzaldehyde **S100-1** (0.86 g, 5.0 mmol, 1.0 equiv.), **S100** was obtained as a slight yellow oil (1.1 g, 86% crude yield over two steps).

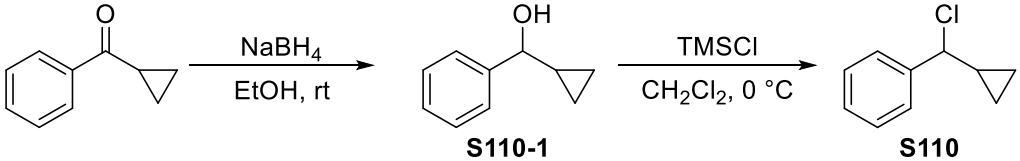
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.4 Hz, 1H), 7.75 (d, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 6.49 (t, *J* = 2.4 Hz, 1H), 4.93 (t, *J* = 7.2 Hz, 1H), 2.40 – 2.27 (m, 1H), 2.27 – 2.14 (m, 1H), 1.04 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 140.3, 139.8, 128.5, 126.7, 119.3, 107.8, 56.6, 33.3, 13.0.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{14}BrN_2$ $[M + H]^+$ 265.0335, found 265.0332.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{13}N_2$ $[M - Br]^+$ 185.1073, found 185.1072.

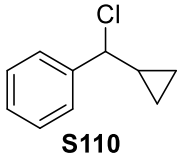
The synthesis of S110



S110-1 **S110**

To a solution of cyclopropylphenylmethanone (1.5 g, 10.0 mmol, 1.0 equiv.) in EtOH (40.0 mL) was added $NaBH_4$ (0.46 g, 12.0 mmol, 1.2 equiv.) and the mixture was stirred at room temperature for 3 h before cooled in an ice bath. The reaction was quenched by water, then most of the solvent was removed under reduced pressure, and the aqueous layer was extracted with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford **S110-1** as a colorless oil (1.4 g, 94% crude yield). The analytical data are consistent with the reported ones[17].

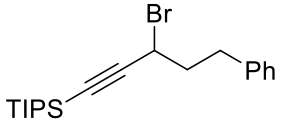
(Chloro(cyclopropyl)methyl)benzene (S110)



S110

To a solution of cyclopropyl(phenyl)methanol (0.89 g, 6.0 mmol, 1.0 equiv.) in CH_2Cl_2 (6.0 mL) was added dropwise chlorotrimethylsilane (2.60 mL, 30.0 mmol, 5.0 equiv.) at 0 °C under argon atmosphere. The reaction mixture was stirred at 0 °C for 1 h, quenched by water, and extracted with CH_2Cl_2 three times. The combined organic layer was washed by brine, dried over Na_2SO_4, and concentrated under reduced pressure to yield **S110** as a colorless oil (0.90 g, 90% crude yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.29 (m, 5H), 4.32 (d, *J* = 9.2 Hz, 1H), 1.66 – 1.51 (m, 1H), 0.90 – 0.80 (m, 1H), 0.76 – 0.66 (m, 1H), 0.65 – 0.56 (m, 1H), 0.50 – 0.39 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 128.7, 128.3, 127.2, 69.1, 20.0, 6.6, 6.4.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{11}$ $[M - Cl]^+$ 131.0855, found 131.0856.

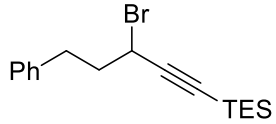
(3-Bromo-5-phenylpent-1-yn-1-yl)triisopropylsilane (S111)



S111

S111 was synthesized according to reported literature[18].
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 4.49 (t, *J* = 6.7 Hz, 1H), 3.08 – 2.66 (m, 2H), 2.47 – 2.15 (m, 2H), 1.09 (s, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 128.7, 126.4, 105.7, 89.4, 41.6, 36.7, 33.6, 18.7, 11.3.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{31}Si$ $[M - Br]^+$ 299.2190, found 299.2189.

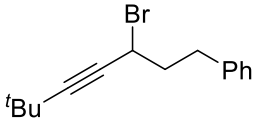
(3-Bromo-5-phenylpent-1-yn-1-yl)triethylsilane (S112)



S112

S112 was synthesized according to reported literature[18].
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.30 – 7.22 (m, 3H), 4.52 (t, *J* = 6.8 Hz, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.46 – 2.26 (m, 2H), 1.07 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 128.7, 126.4, 105.0, 90.2, 41.4, 36.6, 33.6, 7.6, 4.4.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{25}Si$ $[M - Br]^+$ 257.1720, found 257.1719.

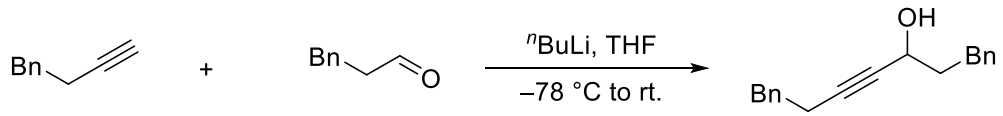
(3-Bromo-6,6-dimethylhept-4-yn-1-yl)benzene (S113)



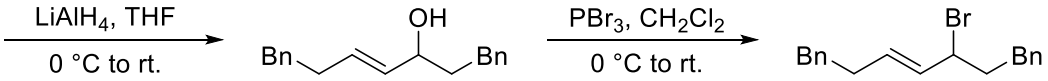
S113

S113 was synthesized according to reported literature[18].
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.23 – 7.16 (m, 3H), 4.48 (t, *J* = 6.7 Hz, 1H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.44 – 2.04 (m, 2H), 1.23 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 128.7, 128.6, 126.3, 96.8, 77.8, 41.9, 37.9, 33.6, 30.9, 27.7.
HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{19}$ $[M - Br]^+$ 199.1481, found 199.1480.

The synthesis of S114



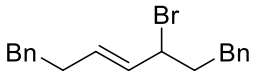
S114-1



S114-2 **S114**

To a solution of 4-phenyl-1-butyne (0.80 mL, 7.7 mmol, 1.0 equiv.) in THF (20 mL) was added ^{n}BuLi (3.9 mL, 9.3 mmol, 1.2 equiv., 2.4 M in hexane) at −78 °C over 5 min. One hour later, 3-phenylpropanal (0.82 mL, 7.7mmol, 1.0 equiv.) was added dropwise to the mixture. Upon complete consumption of 4-phenyl-1-butyne as monitored by TLC, the reaction was quenched by the addition of a saturated ammonium chloride aqueous solution. The aqueous phase was extracted with EtOAc three times. Then the combined organic phase was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue thus obtained was purified by column chromatography on silica gel to afford **S114-1** as a colorless oil (1.9 g, 94% yield).
To a suspension of **S114-1** (1.1 g, 4.1 mmol, 1.0 equiv.) in THF (10 mL) was added $LiAlH_4$ (312 mg, 8.2 mmol, 2.0 equiv.) slowly at 0 °C. The reaction mixture was stirred at room temperature for 24 h and the reaction was quenched with $Na_2SO_4 \cdot 10H_2O$. The residue was then filtered and the organic solvent was removed under reduced pressure to afford **S114-2** as a colorless oil (1.02 g, 94% yield).
To a suspension of **S114-2** (1.02 g, 3.8 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was added PBr_3 (513 mg, 1.9 mmol, 0.5 equiv.) at 0 °C. The reaction mixture was stirred at room temperature for 2 h and then, quenched with water. The aqueous phase was extracted with CH_2Cl_2 three times. Then the combined organic layers was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Thus, crude **S114** was afforded as a colorless oil (1.06 g, 85% yield), which could be used in the next step without further purification.

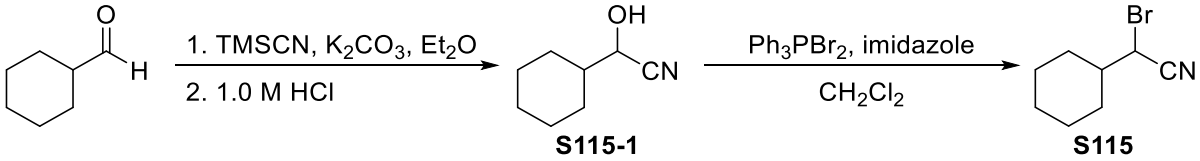
(*E*)-(5-Bromohept-3-ene-1,7-diyl)dibenzene



S114

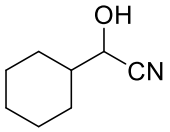
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.11 (m, 10H), 5.88 – 5.57 (m, 2H), 4.55 – 4.37 (m, 1H), 2.84 – 2.54 (m, 4H), 2.43 – 2.33 (m, 2H), 2.30 – 2.17 (m, 1H), 2.15 – 1.99 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 140.7, 132.7, 132.2, 128.6, 128.5, 128.4, 126.2, 126.0, 55.4, 40.8, 35.3, 33.9, 33.7.
HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{21}$ $[M - Br]^+$ 249.1638, found 249.1634.

The synthesis of S115



S115-1 **S115**

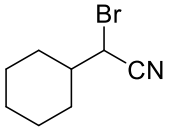
2-Cyclohexyl-2-hydroxyacetonitrile (S115-1)



S115-1

To a mixture of cyclohexanecarbaldehyde (1.68 g, 15.0 mmol, 1.0 equiv.) and K_2CO_3 (0.41 g, 3.0 mmol, 0.2 equiv.) in Et_2O (30 ml) was added trimethylsilyl cyanide (1.63 g, 16.5 mmol, 1.1 equiv.) and the mixture was stirred at room temperature overnight. After completion (monitored by TLC), the reaction was quenched with saturated $NaHCO_3$ and extracted with Et_2O three times. The combined organic phase was washed with brine and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to yield the product **S115-1** as a colorless oil (1.90 g, 91% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (d, *J* = 6.4 Hz, 1H), 3.95 (br s, 1H), 1.96 – 1.63 (m, 6H), 1.34 – 1.02 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 119.5, 66.1, 42.1, 28.2, 27.9, 25.9, 25.4(3), 25.4(1).

2-Bromo-2-cyclohexylacetonitrile (S115)



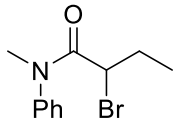
S115

To a solution of **S115-1** (0.70 g, 5.0 mmol, 1.0 equiv.) in CH_2Cl_2 (25 mL) were added triphenylphosphine dibromide (2.53 g, 6.0 mmol, 1.2 equiv.) and imidazole (0.41 g, 6.0 mmol, 1.2 equiv.) with vigorous stirring at 0 °C under argon,. Then the reaction was allowed to warm to room temperature and stirred overnight. After completion (monitored by TLC), the reaction was quenched with saturated NH_4Cl and extracted with CH_2Cl_2 three times. The organic phase was washed with brine and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **S115** as a yellow oil (0.55 g, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (d, *J* = 5.7 Hz, 1H), 2.10 – 1.93 (m, 2H), 1.92 – 1.87 (m, 3H), 1.77 – 1.68 (m, 1H), 1.41 – 1.12 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 116.6, 42.7, 34.3, 30.4, 29.5, 25.6, 25.5.

The synthesis of S116

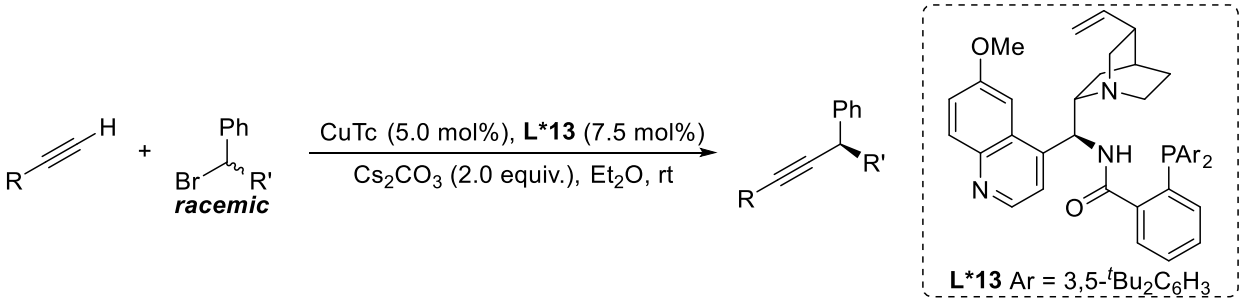
2-Bromo-*N*-methyl-*N*-phenylbutanamide (S116)



S116

A 100-mL flask was charged with *N*-methylaniline (2.17 mL, 20.0 mmol), evacuated, and back-filled with argon. The flask was cooled to 0 °C in an ice bath and then, Et_3N (3.06 mL, 22.0 mmol) and THF (40 mL) were added. The orange solution was stirred for 5 min and then, 2-bromobutyryl bromide (2.66 mL, 22.0 mmol) was added slowly via syringe, leading to the formation of a precipitate. The resulting suspension was stirred for 10 min at 0 °C, and then the reaction was quenched by the addition of ice/water. The mixture was extracted three times with Et_2O (40 mL), and the combined extracts were washed with brine, dried over sodium sulfate, and concentrated. The resulting oil was purified by column chromatography on silica gel (petroleum ether/ethyl acetate= 15/1) to afford the titled product **S116** as a colorless oil (4.61 g, 90% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.36 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 2H), 4.02 (t, *J* = 7.4 Hz, 1H), 3.31 (s, 3H), 2.25 – 2.05 (m, 1H), 2.02 – 1.85 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 143.0, 130.1, 128.5, 127.3, 45.9, 38.1, 28.7, 12.2.
HRMS (ESI) *m*/*z* calcd. for $C_{11}H_{15}BrNO$ $[M + H]^+$ 256.0332, found 256.0328.

Asymmetric Sonogashira C(sp)−C(sp^3) cross-coupling: Scope of alkynes



General procedure A:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (1.9 mg, 0.010 mmol, 5.0 mol%), **L*13** (12.5 mg, 0.015 mmol, 7.5 mol%), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous Et_2O (4.0 mL). Then, alkyl halide (0.30 mmol, 1.5 equiv.) and alkyne (0.20 mmol, 1.0 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 24 to 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by Et_2O or petroleum ether. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

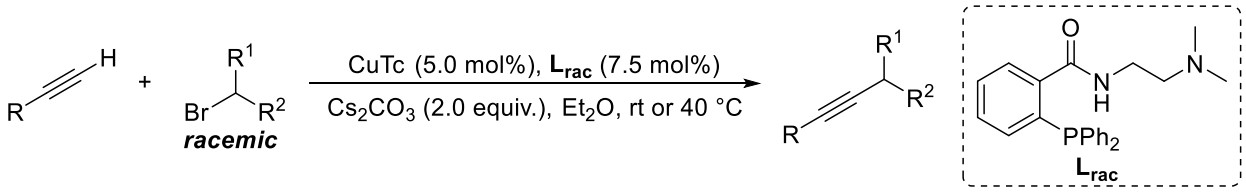
General procedure B:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (1.9 mg, 0.010 mmol, 5.0 mol%), **L*13** (12.5 mg, 0.015 mmol, 7.5 mol%), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous Et_2O (4.0 mL). Then, alkyl halide (0.20 mmol, 1.0 equiv.) and alkyne (0.30 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 16 to 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by Et_2O or petroleum ether. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure C:

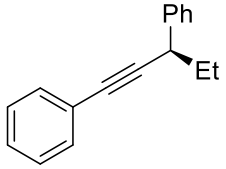
An oven-dried 25 mL Schlenk flask equipped with a magnetic stir bar was charged with CuTc (1.91 mg, 0.010 mmol, 5.0 mol%), **L*13** (12.5 mg, 0.015 mmol, 7.5 mol%), and Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.). The flask was evacuated with oil pump followed by the addition of a solution of alkyl bromide (0.20 mmol, 1.0 equiv.) in diethyl ether (4.0 mL) via syringe. Then, acetylene gas in a balloon was introduced into the flask via the side arm with a stopcock. Upon completion, the reaction mixture was stirred at room temperature for 18 h. After completion of reaction (monitored by TLC), the reaction mixture was diluted with petroleum ether, filtered on silica gel, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the corresponding product.

Note: Most of the products were unstable in neat state in air after purification, and should be stored in solvent (CH_2Cl_2 or Et_2O) at –10 °C. Their characterization by NMR, HPLC or HRMS should be done as soon as possible. Meanwhile, the reaction is sensitive to water and air, and thus, Schlenk tubes and the reagents must be dried prior to use.



The racemates of products were prepared following the same procedure described above using CuTc (1.9 mg, 0.010 mmol, 5.0 mol%) and $\mathbf{L_{rac}}$ (5.6 mg, 0.015 mmol, 7.5 mol%) as catalyst and ligand, respectively, at room temperature or 40 °C in anhydrous Et_2O (4.0 mL) for 24 to 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed with Et_2O, the filtrate was concentrated, and the residue was purified by column chromatography on silica gel to afford the desired product.

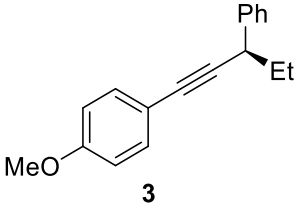
(*R*)-Pent-1-yne-1,3-diyldibenzene (2)



2

According to **General procedure B** with (1-bromopropyl)benzene **S2** (39.8 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **2** as a colorless oil (36.1 mg, 82% yield, 97% ee).
$\mathbf{[\alpha]_D^{27}}$ = –14 (*c* 1.5, CH_2Cl_2).
HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.57 min, t_R (major) = 15.33 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 3H), 7.43 (s, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.29 (m, 3H), 7.28 – 7.24 (m, 1H), 3.81 (t, *J* = 6.8 Hz, 1H), 2.00 – 1.79 (m, 2H), 1.07 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 131.7, 128.4, 128.2, 127.7, 127.6, 126.7, 123.9, 91.5, 83.4, 40.0, 31.7, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}$ $[M + H]^+$ 221.1325, found 221.1323.

(*R*)-1-Methoxy-4-(3-phenylpent-1-yn-1-yl)benzene (3)

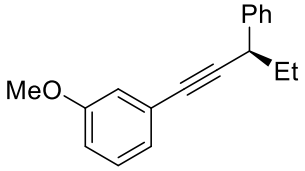


3

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-ethynyl-4-methoxybenzene **S3** (26.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **3** as a colorless oil (33.0 mg, 66% yield, 95% ee).
$\mathbf{[\alpha]_D^{25}}$ = –5.0 (*c* 1.4, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 18.67

min, t_R (major) = 19.31min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 4H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.20 (m, 1H), 6.87 – 6.77 (m, 2H), 3.80 (s, 3H), 3.79 – 3.74 (m, 1H), 1.93 – 1.77 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 142.3, 133.0, 128.4, 127.6, 126.6, 116.0, 113.8, 89.9, 83.1, 55.3, 40.0, 31.8, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}O$ $[M + H]^+$ 251.1430, found 251.1429.

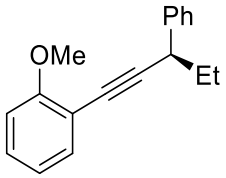
(*R*)-1-Methoxy-3-(3-phenylpent-1-yn-1-yl)benzene (4)



4

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-ethynyl-3-methoxybenzene **S4** (26.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **4** as a colorless oil (47.0 mg, 94% yield, 96% ee).
$[\alpha]_D^{27}$ = –6.5 (*c* 2.9, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.78 min, t_R (major) = 10.58 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.43 – 7.35 (m, 2H), 7.32 – 7.22 (m, 2H), 7.10– 7.07 (m, 1H), 7.07 – 7.00 (m, 1H), 6.93 – 6.86 (m, 1H), 3.91 – 3.76 (m, 1H), 3.84 (s, 3H), 2.06 – 1.77 (m, 2H), 1.11 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 141.9, 129.2, 128.4, 127.5, 126.6, 124.8, 124.2, 116.5, 114.3, 91.3, 83.2, 55.2, 39.9, 31.6, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}O$ $[M + H]^+$ 251.1430, found 251.1434.

(*R*)-1-Methoxy-2-(3-phenylpent-1-yn-1-yl)benzene (5)

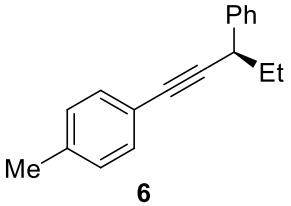


5

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-ethynyl-2-methoxybenzene **S5** (26.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **5** as a colorless oil (42.0 mg, 84% yield, 97% ee).
$[\alpha]_D^{27}$ = –2.8 (*c* 3.9, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 254 nm), t_R (minor) = 22.55 min, t_R (major) = 33.92 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.42 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.28 – 7.20 (m, 2H), 6.94 – 6.82 (m, 2H), 3.91 – 3.82 (m, 1H), 3.87 (s, 3H), 1.98 – 1.79 (m, 2H), 1.07 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 142.1, 133.5, 129.0, 128.3, 127.6, 126.5, 120.3, 113.0, 110.6, 95.6, 79.6, 55.8, 40.2, 31.8, 11.7.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}O$ $[M + H]^+$ 251.1430, found 251.1433.

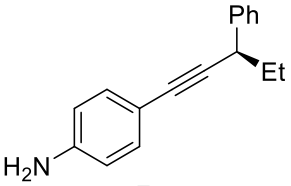
(*R*)-1-Methyl-4-(3-phenylpent-1-yn-1-yl)benzene (6)



6

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-ethynyl-4-methylbenzene **S6** (23.2 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **6** as a colorless oil (36.6 mg, 78% yield, 97% ee).
[α]$_D^{27}$ = –11 (*c* 1.7, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 26.02 min, t_R (major) = 30.94 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.43 – 7.34 (m, 4H), 7.31 – 7.25 (m, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 3.83 (t, *J* = 7.0 Hz, 1H), 2.38 (s, 3H), 1.97 – 1.82 (m, 2H), 1.10 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 137.7, 131.5, 128.9, 128.4, 127.5, 126.6, 120.7, 90.6, 83.4, 40.0, 31.7, 21.4, 11.8.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}$ $[M + H]^+$ 235.1481, found 235.1481.

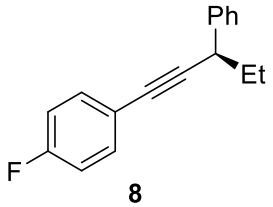
(*R*)-4-(3-Phenylpent-1-yn-1-yl)aniline (7)



7

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 4-ethynylaniline **S7** (23.4 mg, 0.20 mmol, 1.0 equiv.) and after completion of reaction (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **7** as a colorless oil (41.0 mg, 87% yield, 97% ee).
[α]$_D^{27}$ = –18 (*c* 4.1, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 35.08 min, t_R (major) = 37.23 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 2H), 7.41 – 7.32 (m, 2H), 7.32 – 7.24 (m, 3H), 6.67 – 6.57 (m, 2H), 3.85 – 3.66 (m, 3H), 1.93 – 1.81 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 142.4, 132.8, 128.3, 127.6, 126.5, 114.7, 113.4, 88.9, 83.6, 40.0, 31.8, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{18}N$ $[M + H]^+$ 236.1434, found 236.1432.

(*R*)-1-Fluoro-4-(3-phenylpent-1-yn-1-yl)benzene (8)



8

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-ethynyl-4-fluorobenzene **S8** (24.0 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **8** as a colorless oil (39.6 mg, 83% yield, 96% ee).

[α]$_D^{27}$ = –19 (*c* 0.40, CH_2Cl_2).

HPLC analysis: Chiralcel OJH (hexane, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 16.85 min, t_R (major) = 18.97 min.

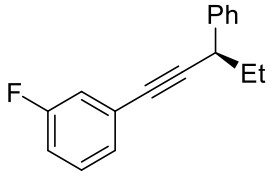
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 7.37 – 7.29 (m, 2H), 7.28 – 7.21 (m, 1H), 7.04 – 6.94 (m, 2H), 3.83 – 3.71 (m, 1H), 1.94 – 1.77 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 248.4 Hz), 141.9, 133.4 (d, *J* = 8.4 Hz), 128.4, 127.5, 126.7, 119.9 (d, *J* = 3.4 Hz), 115.4 (d, *J* = 22.1 Hz), 91.1 (d, *J* = 1.5 Hz), 82.2, 39.9, 31.6, 11.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ –112.02 – –112.12 (m, 1F).

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}F$ $[M + H]^+$ 239.1231, found 239.1229.

(*R*)-1-Fluoro-3-(3-phenylpent-1-yn-1-yl)benzene (9)



9

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-ethynyl-3-fluorobenzene **S9** (24.0 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **9** as a colorless oil (46.5 mg, 98% yield, 96% ee).

[α]$_D^{27}$ = –13 (*c* 1.5, CH_2Cl_2).

HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 99.8/0.2, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 8.53 min, t_R (major) = 9.20 min.

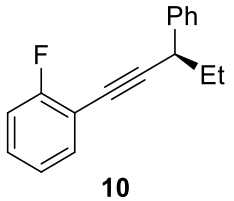
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.37 – 7.30 (m, 2H), 7.28 – 7.19 (m, 3H), 7.17 – 7.11 (m, 1H), 7.02 – 6.94 (m, 1H), 3.78 (t, *J* = 7.2 Hz, 1H), 1.94 – 1.79 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.1 Hz), 141.7, 129.7 (d, *J* = 8.7 Hz), 128.5, 127.5, 126.8, 125.7 (d, *J* = 9.5 Hz), 118.4 (d, *J* = 22.5 Hz), 115.0 (d, *J* = 21.2 Hz), 92.6, 82.2 (d, *J* = 3.4 Hz), 39.9, 31.5, 11.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ –113.3 (td, *J* = 9.0, 5.3 Hz, 1F).

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}F$ $[M + H]^+$ 239.1231, found 239.1230.

(*R*)-1-Fluoro-2-(3-phenylpent-1-yn-1-yl)benzene (10)



10

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-ethynyl-2-fluorobenzene **S10** (24.0 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **10** as a colorless oil (44.6 mg, 94% yield, 97% ee).

[α]$_D^{27}$ = –11 (*c* 2.6, CH_2Cl_2).

HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 99.8/0.2, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 10.49 min, t_R (major) = 11.32 min.

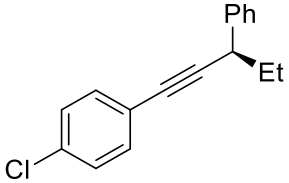
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 3H), 7.38 – 7.30 (m, 2H), 7.29 – 7.21 (m, 2H), 7.09 – 7.02 (m, 2H), 3.83 (t, *J* = 7.0 Hz, 1H), 1.93 – 1.81 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 250.6 Hz), 141.6, 133.5 (d, *J* = 1.4 Hz), 129.3 (d, *J* = 7.9 Hz), 128.4, 127.5, 126.7, 123.8 (d, *J* = 3.7 Hz), 115.4 (d, *J* = 21.1 Hz), 112.3 (d, *J* = 15.8 Hz), 96.9 (d, *J* = 3.3 Hz), 76.7, 40.1, 31.6, 11.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ –110.46 – –110.55 (m, 1F).

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}F$ $[M + H]^+$ 239.1231, found 239.1225.

(*R*)-1-Chloro-4-(3-phenylpent-1-yn-1-yl)benzene (11)



11

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv..) and 1-chloro-4-ethynylbenzene **S11** (27.3 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **11** as a colorless oil (41.0 mg, 81% yield, 97% ee).

[α]$_D^{27}$ = –5.4 (*c* 3.3, CH_2Cl_2).

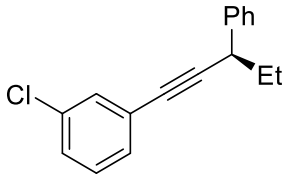
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 13.57 min, t_R (major) = 15.78 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 6H), 7.29 – 7.22 (m, 3H), 3.77 (t, *J* = 7.0 Hz, 1H), 1.94 – 1.78 (m, 2H), 1.04 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 133.6, 132.9, 128.51, 128.50, 127.5, 126.7, 122.3, 92.5, 82.2, 40.0, 31.5, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}Cl$ $[M + H]^+$ 255.0935, found 255.0937.

(*R*)-1-Chloro-3-(3-phenylpent-1-yn-1-yl)benzene (12)



12

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-chloro-3-ethynylbenzene **S12** (27.3 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **12** as a colorless oil (50.0 mg, 98% yield, 94% ee).

[α]$_D^{27}$ = –10 (*c* 2.8, CH_2Cl_2).

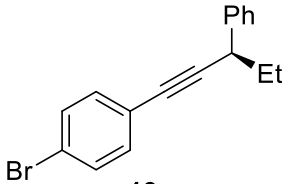
HPLC analysis: Chiralcel ODH (hexane, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.43 min, t_R (major) = 11.49 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.28 (m, 6H), 7.28 – 7.17 (m, 3H), 3.77 (t, *J* = 6.8 Hz, 1H), 1.94 – 1.77 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 134.0, 131.5, 129.8, 129.4, 128.5, 128.0, 127.5, 126.8, 125.5, 92.9, 82.0, 39.9, 31.5, 11.8.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}Cl$ $[M + H]^+$ 255.0935, found 255.0933.

(*R*)-1-Bromo-4-(3-phenylpent-1-yn-1-yl)benzene (13)



13

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-bromo-4-ethynylbenzene **S13** (36.2 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **13** as a colorless oil (57.0 mg, 96% yield, 97% ee).

[α]$_D^{27}$ = –8.2 (*c* 4.4, CH_2Cl_2).

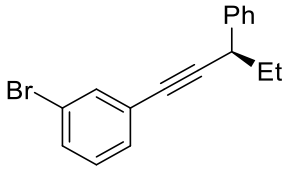
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 14.73 min, t_R (major) = 17.19 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 4H), 7.37 – 7.27 (m, 4H), 7.27 – 7.22 (m, 1H), 3.76 (t, *J* = 7.0 Hz, 1H), 1.92 – 1.77 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 133.1, 131.4, 128.5, 127.5, 126.7, 122.8, 121.8, 92.8, 82.3, 40.0, 31.5, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}Br$ $[M + H]^+$ 299.0435 and 301.0415, found 299.0428 and 301.0408.

(*R*)-1-Bromo-3-(3-phenylpent-1-yn-1-yl)benzene (14)



14

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-bromo-3-ethynylbenzene **S14** (36.2 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **14** as a colorless oil (57.0 mg, 96% yield, 94% ee).

[α]$_D^{27}$ = –8.2 (*c* 4.4, CH_2Cl_2).

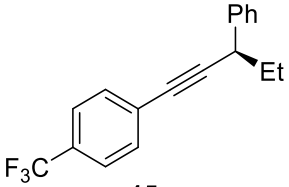
HPLC analysis: Chiralcel ODH (hexane, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.43 min, t_R (major) = 11.49 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 1H), 7.46 – 7.29 (m, 6H), 7.29 – 7.21 (m, 1H), 7.18 – 7.10 (m, 1H), 3.77 (t, *J* = 7.0 Hz, 1H), 1.93 – 1.78 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 134.4, 130.9, 130.2, 129.6, 128.5, 127.5, 126.7, 125.8, 122.0, 93.0, 81.9, 39.9, 31.5, 11.8.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}Br$ $[M + H]^+$ 299.0435, found 299.0430.

(*R*)-1-(3-Phenylpent-1-yn-1-yl)-4-(trifluoromethyl)benzene (15)



15

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-ethynyl-4-(trifluoromethyl)benzene **S15** (34.0 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **15** as a colorless oil (48.1 mg, 84% yield, 97% ee).

[α]$_D^{27}$ = –2.4 (*c* 4.0, CH_2Cl_2).

HPLC analysis: Chiralcel IG (hexane, flow rate 0.3 mL/min, λ = 254 nm), t_R (minor) = 15.70 min, t_R (major) = 17.38 min.

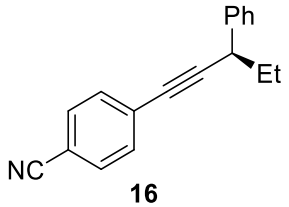
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 4H), 7.44 – 7.38 (m, 2H), 7.38 – 7.31 (m, 2H), 7.29 – 7.23 (m, 1H), 3.80 (t, *J* = 7.0 Hz, 1H), 1.95 – 1.80 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 131.9, 129.5 (q, *J* = 32.5 Hz), 128.6, 127.7 (d, *J* = 1.4 Hz), 127.5, 126.9, 125.2 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.1 Hz), 94.3, 82.2, 40.0, 31.5, 11.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{18}H_{16}F_3$ $[M + H]^+$ 289.1199, found 289.1192.

(*R*)-4-(3-Phenylpent-1-yn-1-yl)benzonitrile (16)



16

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 4-ethynylbenzonitrile **S16** (25.4 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **16** as a colorless oil (47.7 mg, 97% yield, 96% ee).

[α]$_D^{27}$ = –19 (*c* 3.0, CH_2Cl_2).

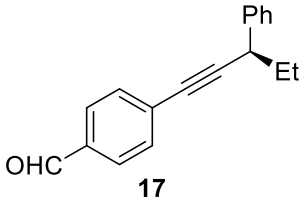
HPLC analysis: Chiralcel AS3 (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 15.37 min, t_R (major) = 20.43 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.36 (m, 4H), 7.33 – 7.27 (m, 1H), 3.84 (t, *J* = 7.1 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.09 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 132.1, 131.9, 128.7, 128.5, 127.4, 126.9, 118.5, 111.0, 96.6, 81.9, 40.0, 31.3, 11.8.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{16}N$ $[M + H]^+$ 246.1277, found 246.1274.

(*R*)-4-(3-Phenylpent-1-yn-1-yl)benzaldehyde (17)



17

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 4-ethynylbenzaldehyde (26.0 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **17** as a colorless oil (48.0 mg, 97% yield, 96% ee).

[α]$_D^{27}$ = –22 (*c* 4.0, CH_2Cl_2).

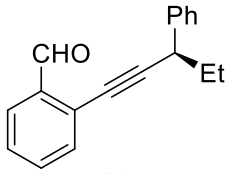
HPLC analysis: Chiralcel IE (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 254 nm), t_R (minor) = 40.38 min, t_R (major) = 44.14 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.90 – 7.80 (m, 2H), 7.66 – 7.58 (m, 2H), 7.49 – 7.34 (m, 4H), 7.34 – 7.27 (m, 1H), 3.85 (t, *J* = 7.0 Hz, 1H), 2.03 – 1.82 (m, 2H), 1.10 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 141.4, 135.1, 132.2, 130.3, 129.5, 128.6, 127.5, 126.9, 96.2, 82.7, 40.1, 31.5, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}O$ $[M + H]^+$ 249.1274, found 249.1273.

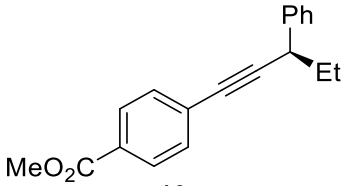
(*R*)-2-(3-Phenylpent-1-yn-1-yl)benzaldehyde (18)



18

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 2-ethynylbenzaldehyde **S18** (26.0 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **18** as a colorless oil (39.0 mg, 79% yield, 91% ee).
[α]$_D^{27}$ = –23 (*c* 1.5, CH_2Cl_2).
HPLC analysis: Chiralcel IE (hexane/*i*-PrOH = 99/1, flow rate 0.4 mL/min, λ = 254 nm), t_R (minor) = 19.32 min, t_R (major) = 20.77 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (d, *J* = 0.7 Hz, 1H), 7.97 – 7.85 (m, 1H), 7.60 – 7.45 (m, 2H), 7.44 – 7.31 (m, 5H), 7.29 – 7.23 (m, 1H), 3.85 (t, *J* = 7.1 Hz, 1H), 1.99 – 1.85 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 141.2, 136.0, 133.7, 133.4, 128.6, 128.1, 127.5, 127.4, 127.0, 126.9, 99.2, 78.9, 40.2, 31.4, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}O$ $[M + H]^+$ 249.1274, found 249.1279.

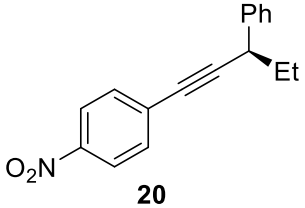
Methyl (*R*)-4-(3-phenylpent-1-yn-1-yl)benzoate (19)



19

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and methyl 4-ethynylbenzoate **S19** (32.0 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **19** as a colorless oil (51.2 mg, 92% yield, 96% ee).
[α]$_D^{27}$ = –26 (*c* 1.6, CH_2Cl_2).
HPLC analysis: Chiralcel IF (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 254 nm), t_R (minor) = 29.10 min, t_R (major) = 32.49 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.54 – 7.47 (m, 2H), 7.45 – 7.38 (m, 2H), 7.37 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 3.90 (s, 3H), 3.80 (t, *J* = 7.0 Hz, 1H), 1.94 – 1.82 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 141.6, 131.6, 129.4, 129.1, 128.7, 128.5, 127.5, 126.8, 95.0, 82.8, 52.2, 40.1, 31.5, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{19}O_2$ $[M + H]^+$ 279.1380, found 279.1378.

(*R*)-1-Nitro-4-(3-phenylpent-1-yn-1-yl)benzene (20)



20

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-ethynyl-4-nitrobenzene **S20** (29.4 mg, 0.20 mmol, 1.0 equiv.) at −10 °C for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **20** as a colorless oil (50.0 mg, 94% yield, 98% ee).

[α]$_D^{27}$ = –20 (*c* 3.3, CH_2Cl_2).

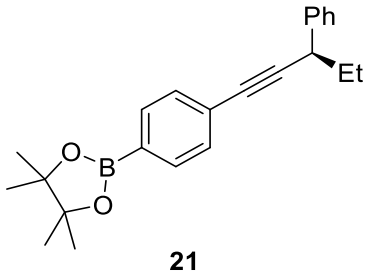
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 230 nm), t_R (minor) = 29.20 min, t_R (major) = 31.13 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.11 (m, 2H), 7.60 – 7.54 (m, 2H), 7.47 – 7.36 (m, 4H), 7.35 – 7.26 (m, 1H), 3.86 (t, *J* = 7.1 Hz, 1H), 2.02 – 1.86 (m, 2H), 1.10 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 141.1, 132.4, 130.9, 128.6, 127.5, 127.0, 123.5, 97.7, 81.8, 40.2, 31.4, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}NO_2$ $[M + H]^+$ 266.1176, found 266.1176.

(*R*)-4,4,5,5-Tetramethyl-2-(4-(3-phenylpent-1-yn-1-yl)phenyl)-1,3,2-dioxaborolane (21)



21

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 2-(4-ethynylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **S21** (45.6 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **21** as a colorless oil (65.0 mg, 94% yield, 96% ee).

[α]$_D^{27}$ = –29 (*c* 1.5, CH_2Cl_2).

HPLC analysis: Chiralcel OD3 (hexane, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 18.44 min, t_R (minor) = 22.31 min.

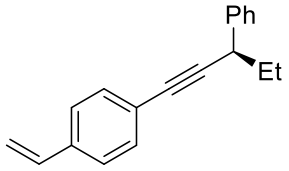
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.48 – 7.38 (m, 4H), 7.37 – 7.30 (m, 2H), 7.27 – 7.20 (m, 1H), 3.79 (t, *J* = 7.0 Hz, 1H), 1.92 – 1.81 (m, 2H), 1.34 (s, 12H), 1.05 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 134.5, 130.8, 128.4, 127.5, 126.7, 126.6, 92.9, 83.9, 83.5, 40.0, 31.6, 24.9, 11.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.5.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}BO_2$ $[M + H]^+$ 347.2177, found 347.2175.

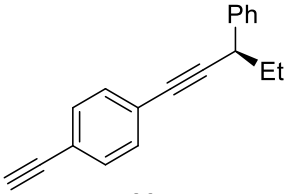
(*R*)-1-(3-Phenylpent-1-yn-1-yl)-4-vinylbenzene (22)



22

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-ethynyl-4-vinylbenzene **S22** (25.6 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **22** as a colorless oil (38.0 mg, 77% yield, 96% ee).
[α]$_D^{27}$ = +0.61 (*c* 1.8, CH_2Cl_2).
HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 7.88 min, t_R (minor) = 8.50 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 4H), 7.40 – 7.33 (m, 4H), 7.32 – 7.24 (m, 1H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.78 (d, *J* = 17.6 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 3.82 (t, *J* = 7.0 Hz, 1H), 1.97 – 1.80 (m, 2H), 1.09 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 136.9, 136.3, 131.8, 128.4, 127.6, 126.7, 126.0, 123.2, 114.4, 92.2, 83.4, 40.1, 31.7, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{19}$ $[M + H]^+$ 247.1481, found 247.1481.

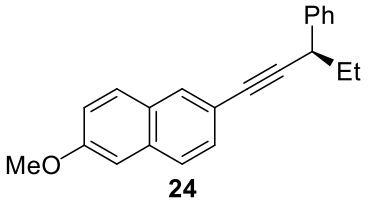
(*R*)-1-Ethynyl-4-(3-phenylpent-1-yn-1-yl)benzene (23)



23

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1,4-diethynylbenzene **S23** (25.2 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 99/1) to yield the product **23** as a colorless oil (31.7 mg, 65% yield, 96% ee).
[α]$_D^{27}$ = –0.90 (*c* 4.0, CH_2Cl_2).
HPLC analysis: Chiralcel AY3 (hexane, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 13.38 min, t_R (major) = 15.93 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 6H), 7.41 – 7.35 (m, 2H), 7.32 – 7.26 (m, 1H), 3.83 (t, *J* = 7.6 Hz, 1H), 3.18 (s, 1H), 1.96 – 1.85 (m, 2H), 1.09 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 132.0, 131.6, 128.5, 127.5, 126.8, 124.4, 121.3, 93.8, 83.4, 82.9, 78.5, 40.1, 31.6, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{17}$ $[M+H]^+$ 245.1325, found 245.1321.

(*R*)-2-Methoxy-6-(3-phenylpent-1-yn-1-yl)naphthalene (24)



24

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 2-ethynyl-6-methoxynaphthalene **S24** (36.4 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **24** as an amorphous powder (56.0 mg, 93% yield, 97% ee).

$[\alpha]_D^{27}$ = –17 (*c* 0.67, CH_2Cl_2).

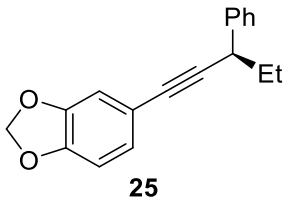
HPLC analysis: Chiralcel OJ3 (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 31.22 min, t_R (minor) = 44.53 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.66 (t, *J* = 8.6 Hz, 2H), 7.51 – 7.42 (m, 3H), 7.39 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 7.13 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 3.90 (s, 3H), 3.83 (t, *J* = 7.0 Hz, 1H), 1.97 – 1.83 (m, 2H), 1.09 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 142.1, 133.8, 131.0, 129.3, 129.1, 128.5, 128.4, 127.6, 126.6, 119.2, 118.8, 105.7, 91.0, 83.8, 55.3, 40.1, 31.7, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{21}O$ $[M + H]^+$ 301.1587, found 301.1584.

(*R*)-5-(3-Phenylpent-1-yn-1-yl)benzo[*d*][1,3]dioxole (25)



25

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 5-ethynylbenzo[*d*][1,3]dioxole **S25** (29.2 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **25** as a colorless oil (39.7 mg, 75% yield, 98% ee).

$[\alpha]_D^{27}$ = –6.2 (*c* 1.4, CH_2Cl_2).

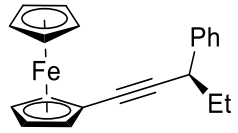
HPLC analysis: Chiralcel OJ3 (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 19.52 min, t_R (major) = 27.61 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.36 – 7.29 (m, 2H), 7.27 – 7.20 (m, 1H), 6.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.90 (d, *J* = 1.6 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.94 (s, 2H), 3.75 (dd, *J* = 7.7, 6.3 Hz, 1H), 1.93 – 1.75 (m, 2H), 1.04 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 147.3, 142.1, 128.4, 127.6, 126.6, 126.0, 117.1, 111.8, 108.3, 101.2, 89.7, 83.1, 40.0, 31.7, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}O_2$ $[M + H]^+$ 265.1223, found 265.1222.

(*R*)-1-(3-Phenylpent-1-yn-1-yl)ferrocene (26)



26

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 1-ethynylferrocene **S26** (42.0 mg, 0.20 mmol, 1.0 equiv.) for 28 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **26** as a colorless oil (58.0 mg, 88% yield, 98% ee).

[α]$_D^{27}$ = –0.25 (*c* 4.0, CH_2Cl_2).

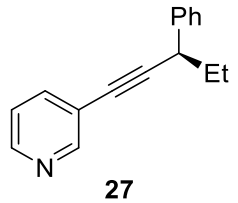
HPLC analysis: Chiralcel OJ3 (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 254 nm), t_R (major) = 36.68 min, t_R (minor) = 43.21 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.42 – 7.35 (m, 2H), 7.32 – 7.25 (m, 1H), 4.48 – 4.41 (m, 2H), 4.24 (s, 5H), 4.21 – 4.19 (m, 2H), 3.73 (dd, *J* = 8.0, 6.0 Hz, 1H), 1.96 – 1.78 (m, 2H), 1.10 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 128.4, 127.6, 126.6, 87.5, 81.3, 71.3, 69.8, 68.3, 66.3, 40.1, 31.8, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{20}Fe$ $[M]^+$ 328.0909, found 328.0906.

(*R*)-3-(3-Phenylpent-1-yn-1-yl)pyridine (27)



27

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 3-ethynylpyridine **S27** (20.6 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **27** as a colorless oil (38.0 mg, 86% yield, 95% ee).

[α]$_D^{27}$ = –15.6 (*c* 0.66, CH_2Cl_2).

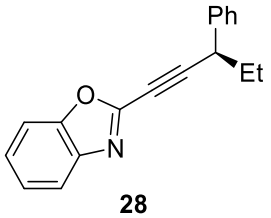
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 12.39 min, t_R (minor) = 13.45 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.51 (s, 1H), 7.72 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.31 (m, 2H), 7.29 – 7.20 (m, 2H), 3.80 (t, *J* = 7.1 Hz, 1H), 1.94 – 1.82 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 148.1, 141.4, 138.5, 128.5, 127.5, 126.8, 122.9, 95.2, 80.0, 40.0, 31.5, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}N$ $[M + H]^+$ 222.1277, found 222.1277.

(*R*)-2-(3-Phenylpent-1-yn-1-yl)benzo[*d*]oxazole (28)



28

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 2-ethynylbenzo[*d*]oxazole **S28** (28.6 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **28** as a colorless oil (45.9 mg, 88% yield, 97% ee).

[α]$_D^{27}$ = –1.2 (*c* 1.9, CH_2Cl_2).

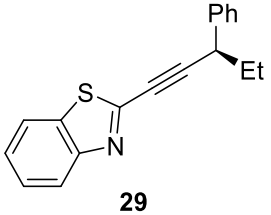
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 19.70 min, t_R (major) = 29.06 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 1H), 7.53 – 7.49 (m, 1H), 7.43 – 7.32 (m, 6H), 7.31 – 7.27 (m, 1H), 3.87 (t, *J* = 7.1 Hz, 1H), 2.03 – 1.90 (m, 2H), 1.09 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.7, 140.9, 139.7, 128.7, 127.6, 127.2, 126.1, 124.9, 120.3, 110.5, 97.1, 71.9, 39.9, 30.9, 11.8.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{16}NO$ $[M + H]^+$ 262.1226, found 262.1226.

(*R*)-2-(3-Phenylpent-1-yn-1-yl)benzo[*d*]thiazole (29)



29

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 2-ethynylbenzo[*d*]thiazole **S29** (31.8 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **29** as a colorless oil (55.0 mg, 99% yield, 96% ee).

[α]$_D^{27}$ = –12 (*c* 3.1, CH_2Cl_2).

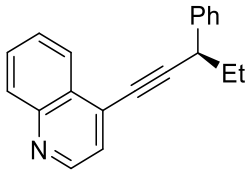
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 98/2, flow rate 0.3 mL/min, λ = 254 nm), t_R (major) = 32.68 min, t_R (minor) = 35.49 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 1H), 7.89 – 7.82 (m, 1H), 7.56 – 7.50 (m, 1H), 7.48 – 7.42 (m, 3H), 7.42 – 7.35 (m, 2H), 7.34 – 7.27 (m, 1H), 3.91 (t, *J* = 7.1 Hz, 1H), 2.07 – 1.90 (m, 2H), 1.11 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 149.0, 140.2, 135.2, 128.7, 127.6, 127.1, 126.6, 126.0, 123.5, 121.3, 99.6, 77.1, 40.2, 31.1, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{16}NS$ $[M + H]^+$ 278.0998, found 278.0998.

(*R*)-4-(3-Phenylpent-1-yn-1-yl)quinoline (30)



30

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 4-ethynylquinoline **S30** (30.6 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **30** as a colorless oil (54.0 mg, 99% yield, 94% ee).

[α]$_D^{27}$ = –10 (*c* 2.5, CH_2Cl_2).

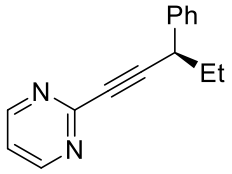
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 98/2, flow rate 0.3 mL/min, λ = 254 nm), t_R (major) = 29.85 min, t_R (minor) = 32.12 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.5 Hz, 1H), 8.33 – 8.23 (m, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.72 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.58 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.41 – 7.34 (m, 2H), 7.32 – 7.23 (m, 1H), 3.96 (t, *J* = 7.0 Hz, 1H), 1.98 (p, *J* = 7.3 Hz, 2H), 1.13 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 148.1, 141.2, 130.4, 129.82, 129.76, 128.7, 128.2, 127.6, 127.1, 127.0, 126.1, 123.8, 101.8, 79.4, 40.4, 31.6, 12.0.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{18}N$ $[M + H]^+$ 272.1434, found 272.1433.

(*R*)-2-(3-Phenylpent-1-yn-1-yl)pyrimidine (31)



31

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 2-ethynylpyrimidine **S31** (20.8 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product **31** as a colorless oil (43.0 mg, 97% yield, 97% ee).

[α]$_D^{27}$ = –3.8 (*c* 2.1, CH_2Cl_2).

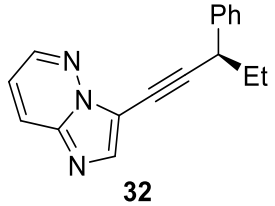
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.09 min, t_R (minor) = 10.38 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.0 Hz, 2H), 7.44 – 7.42 (m, 2H), 7.36 – 7.31 (m, 2H), 7.27 – 7.19 (m, 2H), 3.84 (t, *J* = 7.2 Hz, 1H), 2.01 – 1.87 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 153.3, 140.5, 128.6, 127.6, 126.9, 119.6, 91.4, 82.4, 39.8, 31.1, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{15}N_2$ $[M + H]^+$ 223.1230, found 223.1229.

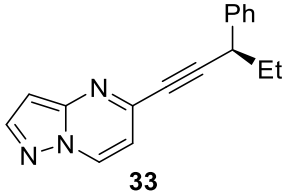
(*R*)-3-(3-Phenylpent-1-yn-1-yl)imidazo[1,2-*b*]pyridazine (32)



32

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 3-ethynylimidazo[1,2-*b*]pyridazine **S32** (28.6 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **32** as a colorless oil (47.5 mg, 91% yield, 96% ee).
[α]$_D^{27}$ = +7.8 (*c* 2.5, CH_2Cl_2).
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 33.91 min, t_R (major) = 40.60 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 4.4, 1.6 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.49 – 7.45 (m, 2H), 7.38 – 7.33 (m, 2H), 7.28 – 7.23 (m, 1H), 7.04 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.97 (t, *J* = 7.0 Hz, 1H), 1.96 (p, *J* = 7.3 Hz, 2H), 1.10 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 141.2, 139.1, 137.8, 128.5, 127.6, 126.8, 125.7, 117.1, 113.6, 101.5, 70.0, 40.4, 31.5, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}N_3$ $[M + H]^+$ 262.1339, found 262.1337.

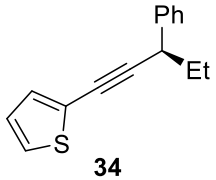
(*R*)-5-(3-Phenylpent-1-yn-1-yl)pyrazolo[1,5-*a*]pyrimidine (33)



33

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 5-ethynylpyrazolo[1,5-*a*]pyrimidine **S33** (28.6 mg, 0.20 mmol, 1.0 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **33** as a colorless oil (51.7 mg, 99% yield, 96% ee).
[α]$_D^{27}$ = –28 (*c* 2.3, CH_2Cl_2).
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 29.14 min, t_R (major) = 32.46 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 7.2, 1.0 Hz, 1H), 8.11 (d, *J* = 2.3 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 7.28 – 7.23 (m, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.67 (dd, *J* = 2.3, 0.9 Hz, 1H), 3.84 (t, *J* = 7.1 Hz, 1H), 2.02 – 1.87 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 145.6, 142.6, 140.5, 134.5, 128.6, 127.6, 127.0, 110.9, 97.3, 96.1, 82.0, 40.0, 31.1, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}N_3$ $[M + H]^+$ 262.1339, found 262.1337.

(*R*)-2-(3-Phenylpent-1-yn-1-yl)thiophene (34)



34

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 2-ethynylthiophene **S34** (21.2 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **34** as a colorless oil (41.0 mg, 91% yield, 97% ee).

[α]$_D^{27}$ = –13 (*c* 1.1, CH_2Cl_2).

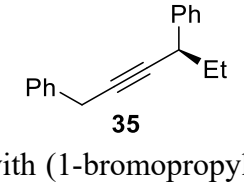
HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.86 min, t_R (major) = 12.84 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.29 (m, 2H), 7.27 – 7.22 (m, 1H), 7.22 – 7.13 (m, 2H), 6.95 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.79 (t, *J* = 7.0 Hz, 1H), 1.93 – 1.78 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 131.2, 128.4, 127.5, 126.8, 126.7, 126.2, 123.9, 95.4, 76.4, 40.2, 31.5, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{15}S$ $[M + H]^+$ 227.0889, found 227.0889.

(*R*)-Hex-2-yne-1,4-diyldibenzene (35)



35

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and prop-2-yn-1-ylbenzene **S35** (23.2 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **35** as a colorless oil (43.0 mg, 92% yield, 96% ee).

[α]$_D^{27}$ = –2.3 (*c* 3.3, CH_2Cl_2).

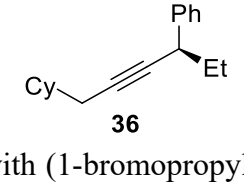
HPLC analysis: Chiralcel OJ3 (hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, λ = 214 nm), t_R (major) = 15.50 min, t_R (minor) = 17.04 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 4H), 7.35 – 7.28 (m, 4H), 7.25 – 7.19 (m, 2H), 3.68 (d, *J* = 1.8 Hz, 2H), 3.65 – 3.58 (m, 1H), 1.84 – 1.73 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 137.4, 128.4, 128.3, 127.8, 127.5, 126.5, 126.4, 84.0, 80.5, 39.6, 31.8, 25.3, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}$ $[M + H]^+$ 235.1481, found 235.1481.

(*R*)-(6-Cyclohexylhex-4-yn-3-yl)benzene (36)

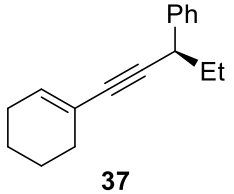


36

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.), prop-2-yn-1-ylcyclohexane **S36** (24.4 mg, 0.20 mmol, 1.0 equiv.), and KO^{t}Bu (44.8 mg, 0.40 mmol, 2.0 equiv.) instead of Cs_2CO_3 for 36 h, the reaction mixture was purified by column

chromatography on silica gel (cyclohexane) to yield the product **36** as a colorless oil (42.2 mg, 88% yield, 98% ee).
[α]$_D^{27}$ = +0.50 (*c* 0.40, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane, flow rate 0.3 mL/min, λ = 214 nm), t_R (minor) = 19.98 min, t_R (major) = 26.49 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 4H), 7.27 – 7.21 (m, 1H), 3.64 – 3.56 (m, 1H), 2.17 (dd, *J* = 6.6, 2.3 Hz, 2H), 1.92 – 1.64 (m, 7H), 1.58 – 1.45 (m, 1H), 1.36 – 1.06 (m, 5H), 1.02 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 128.3, 127.5, 126.4, 82.4, 82.1, 39.5, 37.7, 32.8, 32.0, 26.7, 26.4, 26.2, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{25}$ $[M + H]^+$ 241.1951, found 241.1950.

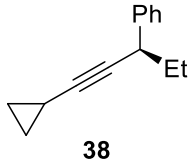
(*R*)-(1-(Cyclohex-1-en-1-yl)pent-1-yn-3-yl)benzene (37)



37

According to **General procedure B** with (1-bromopropyl)benzene **S2** (39.6 mg, 0.20 mmol, 1.0 equiv.) and 1-ethynylcyclohex-1-ene **S37** (31.8 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **37** as a colorless oil (33.1 mg, 74% yield, 97% ee).
[α]$_D^{27}$ = –4.0 (*c* 2.4, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane, flow rate 0.2 mL/min, λ = 230 nm), t_R (minor) = 23.22 min, t_R (major) = 24.85 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 4H), 7.28 – 7.22 (m, 1H), 6.15 – 6.09 (m, 1H), 3.75 – 3.67 (m, 1H), 2.23 – 2.16 (m, 2H), 2.16 – 2.08 (m, 2H), 1.86 – 1.75 (m, 2H), 1.70 – 1.59 (m, 4H), 1.03 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 133.5, 128.3, 127.5, 126.4, 120.9, 88.5, 85.2, 39.8, 31.8, 29. 6, 25.6, 22.4, 21.6, 11.8.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{21}$ $[M + H]^+$ 225.1638, found 225.1638.

(*R*)-(1-Cyclopropylpent-1-yn-3-yl)benzene (38)

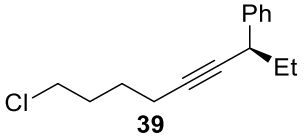


38

According to **General procedure B** with (1-bromopropyl)benzene **S2** (39.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylcyclopropane **S38** (19.8 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **38** as a colorless oil (29.8 mg, 81% yield, 97% ee).
[α]$_D^{27}$ = +1.3 (*c* 2.3, CH_2Cl_2).
HPLC analysis: Chiralcel IG (hexane, flow rate 0.3 mL/min, λ = 214 nm), t_R (minor) = 17.83 min, t_R (major) = 22.16 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.26 – 7.20 (m, 1H), 3.53 (ddd, *J* = 7.9, 6.0,

1.8 Hz, 1H), 1.83 – 1.65 (m, 2H), 1.36– 1.26 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.81 – 0.74 (m, 2H), 0.72 – 0.64 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 128.3, 127.5, 126.4, 86.3, 76.9, 39.4, 31.8, 11.8, 8.24, 8.17, –0.3.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{17}$ $[M + H]^+$ 185.1325, found 185.1325.

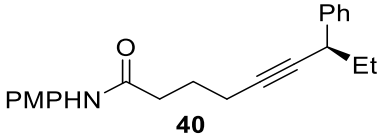
(*R*)-(9-Chloronon-4-yn-3-yl)benzene (39)



39

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 6-chlorohex-1-yne **S39** (23.3 mg, 0.20 mmol, 1.0 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **39** as a colorless oil (41.0 mg, 88% yield, 97% ee).
$[\alpha]_D^{27}$ = +1.3 (*c* 2.3, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane, flow rate 0.5 mL/min, λ = 214 nm), t_R (minor) = 22.13 min, t_R (major) = 29.06 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 4H), 7.28 – 7.21 (m, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 3.59 – 3.52 (m, 1H), 2.32 (td, *J* = 7.0, 2.2 Hz, 2H), 2.00 – 1.89 (m, 2H), 1.83 – 1.67 (m, 4H), 1.00 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 128.3, 127.4, 126.5, 82.4, 82.2, 44.7, 39.5, 31.8, 31.6, 26.2, 18.2, 11.8.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{20}Cl$ $[M + H]^+$ 235.1248, found 235.1247.

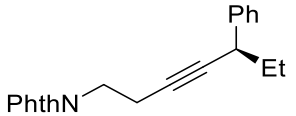
(*R*)-*N*-(4-Methoxyphenyl)-7-phenylnon-5-ynamide (40)



40

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and *N*-(4-methoxyphenyl)hex-5-ynamide **S40** (43.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product **40** as a colorless oil (52.0 mg, 78% yield, 97% ee).
$[\alpha]_D^{27}$ = +4.1 (*c* 1.0, CH_2Cl_2).
HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 32.97 min, t_R (major) = 44.03 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 6H), 7.28 – 7.22 (m, 1H), 7.13 (br s, 1H), 6.89 – 6.83 (m, 2H), 3.81 (s, 3H), 3.61 – 3.53 (m, 1H), 2.49 (t, *J* = 7.3 Hz, 2H), 2.39 (td, *J* = 6.8, 2.2 Hz, 2H), 1.97 (p, *J* = 7.0 Hz, 2H), 1.83 – 1.72 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 156.3, 142.6, 130.9, 128.4, 127.4, 126.6, 121.7, 114.1, 83.2, 81.9, 55.5, 39.5, 36.1, 31.7, 24.7, 18.2, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{26}NO_2$ $[M + H]^+$ 336.1958, found 336.1957.

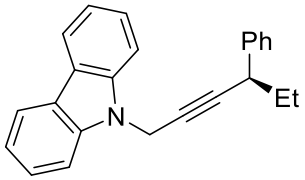
(*R*)-2-(5-Phenylhept-3-yn-1-yl)isoindoline-1,3-dione (41)



41

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 2-(but-3-yn-1-yl)isoindoline-1,3-dione **S41** (39.8 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **41** as a colorless oil (61.0 mg, 96% yield, 97% ee).
[α]$_D^{27}$ = –1.2 (*c* 4.4, CH_2Cl_2).
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 15.77 min, t_R (major) = 17.71 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 2H), 7.78 – 7.69 (m, 2H), 7.31 – 7.14 (m, 5H), 3.91 (t, *J* = 7.1 Hz, 2H), 3.52 – 3.44 (m, 1H), 2.69 (td, *J* = 7.1, 2.2 Hz, 2H), 1.77 – 1.59 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 142.2, 133.9, 132.1, 128.2, 127.4, 126.4, 123.3, 83.9, 78.7, 39.3, 37.1, 31.5, 18.7, 11.7.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{20}NO_2$ $[M + H]^+$ 318.1489, found 318.1487.

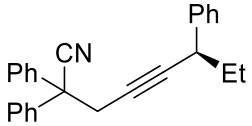
(*R*)-9-(4-Phenylhex-2-yn-1-yl)-9*H*-carbazole (42)



42

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 9-(prop-2-yn-1-yl)-9*H*-carbazole **S42** (41.0 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **42** as a colorless oil (63.0 mg, 98% yield, 98% ee).
[α]$_D^{27}$ = +28 (*c* 3.1, CH_2Cl_2).
HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 254 nm), t_R (minor) = 26.12 min, t_R (major) = 34.75 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.65 – 7.49 (m, 4H), 7.41 – 7.21 (m, 7H), 5.15 (d, *J* = 2.1 Hz, 2H), 3.62 – 3.51 (m, 1H), 1.85 – 1.63 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 140.1, 128.4, 127.5, 126.7, 125.8, 123.2, 120.4, 119.3, 109.0, 86.1, 77.0, 39.3, 33.0, 31.3, 11.7.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{22}N$ $[M + H]^+$ 324.1747, found 324.1745.

(*R*)-2,2,6-Triphenyloct-4-ynenitrile (43)

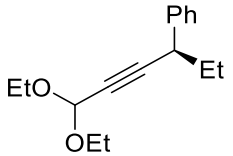


43

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 2,2-diphenylpent-4-ynenitrile **S43** (46.2 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the

reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **43** as a colorless oil (69.0 mg, 99% yield, 96% ee).
[α]$_D^{27}$ = –8.0 (*c* 1.9, CH_2Cl_2).
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 12.24 min, t_R (minor) = 15.72 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.33 (m, 10H), 7.31 – 7.19 (m, 3H), 7.19 – 7.13 (m, 2H), 3.55 – 3.47 (m, 1H), 3.36 (d, *J* = 2.1 Hz, 2H), 1.78 – 1.57 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 139.3, 139.2, 128.8, 128.3, 128.18, 128.16, 127.5, 127.3, 127.2, 126.5, 122.0, 86.9, 77.3, 51.8, 39.4, 31.6, 31.5, 11.6.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{24}N$ $[M + H]^+$ 350.1903, found 350.1902.

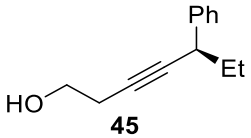
(*R*)-(6,6-Diethoxyhex-4-yn-3-yl)benzene (44)



44

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and 3,3-diethoxyprop-1-yne **S44** (25.6 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **44** as a colorless oil (45.0 mg, 91% yield, 96% ee).
[α]$_D^{27}$ = –2.0 (*c* 2.8, CH_2Cl_2).
HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 214 nm), t_R (major) = 16.70 min, t_R (minor) = 22.81 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.30 – 7.22 (m, 1H), 5.37 (d, *J* = 1.4 Hz, 1H), 3.87 – 3.73 (m, 2H), 3.71 – 3.56 (m, 3H), 1.83 (p, *J* = 7.3 Hz, 2H), 1.26 (td, *J* = 7.1, 3.3 Hz, 6H), 1.01 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 128.4, 127.5, 126.7, 91.6, 87.5, 78.6, 60.73, 60.66, 39.3, 31.3, 15.15, 15.13, 11.8.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{23}O_2$ $[M + H]^+$ 247.1693, found 247.1693.

(*R*)-5-Phenylhept-3-yn-1-ol (45)

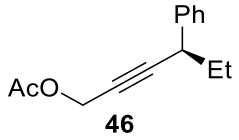


45

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and but-3-yn-1-ol **S45** (14 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product **45** as a colorless oil (34.0 mg, 90% yield, 98% ee).
[α]$_D^{27}$ = +1.6 (*c* 2.1, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 34.03 min, t_R (minor) = 44.67 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 4H), 7.26 – 7.18 (m, 1H), 3.79 – 3.66 (m, 2H), 3.60 – 3.50 (m, 1H), 2.52 (td, *J* = 6.2, 2.2 Hz, 2H), 1.85 – 1.65 (m, 3H), 0.97 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 128.4, 127.4, 126.6, 84.2, 79.2, 61.4, 39.4, 31.7, 23.3, 11.8.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}O$ $[M + H]^+$ 189.1274, found 189.1274.

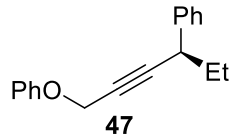
(*R*)-4-Phenylhex-2-yn-1-yl acetate (46)



46

According to **General procedure B** with (1-bromopropyl)benzene **S2** (39.6 mg, 0.20 mmol, 1.0 equiv.) and prop-2-yn-1-yl acetate **S46** (29.4 mg, 0.30 mmol, 1.5 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **46** as a colorless oil (42.3 mg, 98% yield, 97% ee).
$[\alpha]_D^{27}$ = +3.9 (*c* 2.9, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 214 nm), t_R (major) = 26.51min, t_R (minor) = 30.44 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.27 – 7.20 (m, 1H), 4.74 (d, *J* = 2.1 Hz, 2H), 3.64 – 3.56 (m, 1H), 2.09 (s, 3H), 1.78 (p, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 141.4, 128.5, 127.5, 126.7, 88.8, 76.8, 52.8, 39.4, 31.3, 20.8, 11.8.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{17}O_2$ $[M + H]^+$ 217.1223, found 217.1225.

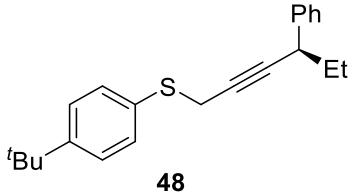
(*R*)-(6-Phenoxyhex-4-yn-3-yl)benzene (47)



47

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and (prop-2-yn-1-yloxy)benzene **S47** (26.4 mg, 0.20 mmol, 1.0 equiv.) for 18 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **47** as a colorless oil (49.5 mg, 98% yield, 96% ee).
$[\alpha]_D^{27}$ = +0.50 (*c* 4.5, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 214 nm), t_R (minor) = 15.24 min, t_R (major) = 17.36 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 6H), 7.30 – 7.22 (m, 1H), 7.09 – 6.99 (m, 3H), 4.81 (d, *J* = 1.9 Hz, 2H), 3.70 – 3.59 (m, 1H), 1.89 – 1.72 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 141.5, 129.4, 128.4, 127.5, 126.7, 121.3, 115.2, 89.5, 77.9, 56.5, 39.5, 31.4, 11.7.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}O$ $[M + H]^+$ 251.1430, found 251.1431.

(*R*)-(4-(*tert*-Butyl)phenyl)(4-phenylhex-2-yn-1-yl)sulfane (48)

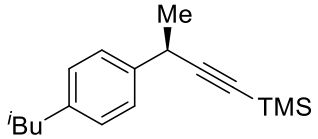


48

According to **General procedure A** with (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) and (4-(*tert*-butyl)phenyl)(prop-2-yn-1-yl)sulfane **S48** (40.8 mg, 0.20 mmol, 1.0 equiv.) for

18 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **48** as a colorless oil (61.0 mg, 95% yield, 97% ee).
[α]$_D^{27}$ = –3.9 (*c* 2.3, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 26.53 min, t_R (major) = 30.94 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 1H), 7.48 – 7.44 (m, 1H), 7.35 – 7.17 (m, 7H), 3.78 (d, *J* = 2.2 Hz, 2H), 3.58 (ddt, *J* = 8.2, 6.0, 2.2 Hz, 1H), 1.84 – 1.69 (m, 2H), 1.56 (s, 9H), 0.96 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 141.9, 134.6, 133.2, 128.3, 127.5, 126.8, 126.6, 126.5, 126.4, 85.3, 78.6, 39.5, 36.6, 31.5, 30.7, 25.0, 11.8.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{27}S$ $[M + H]^+$ 323.1828, found 323.1825.

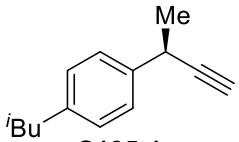
(*R*)-(3-(4-Isobutylphenyl)but-1-yn-1-yl)trimethylsilane (49)



49

According to **General procedure B** with 1-(1-bromoethyl)-4-isobutylbenzene **S127-3** (48.0 mg, 0.20 mmol, 1.0 equiv.) and ethynyltrimethylsilane **S49** (29.4 mg, 0.30 mmol, 1.5 equiv.) for 18 h, the reaction mixture was filtered and washed by petroleum ether. The filtrate was concentrated under reduced pressure and the crude product **49** was obtained as a colorless oil (51.0 mg, 99% crude yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 3.84 (q, *J* = 7.1 Hz, 1H), 2.53 (d, *J* = 7.2 Hz, 2H), 1.93 (dp, *J* = 13.5, 6.8 Hz, 1H), 1.54 (d, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 7H), 0.26 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 139.9, 129.2, 126.6, 109.8, 86.0, 45.1, 32.5, 30.3, 24.7, 22.48, 22.46, 0.3.

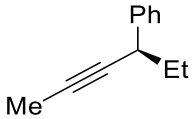
(*S*)-1-(But-3-yn-2-yl)-4-isobutylbenzene (S135-1)



S135-1

The crude product **49** obtained above was dissolved in MeOH (1.0 mL), treated with K_2CO_3 (55.2 mg, 0.40 mmol, 2.0 equiv.), and stirred at room temperature for 3 h. After completion of reaction (monitored by TLC), the mixture was concentrated under reduced pressure and purified by column chromatography to yield **S135-1** as a colorless oil (33.9 mg, 91% yield, 95% ee).
[α]$_D^{27}$ = –5.2 (*c* 6.9, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane, flow rate 0.3 mL/min, λ = 214 nm), t_R (major) = 18.13 min, t_R (minor) = 23.43 min.

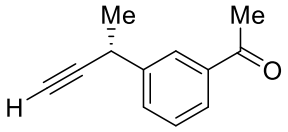
(*R*)-Hex-4-yn-3-ylbenzene (50)



50

According to **General procedure B** with (1-bromopropyl)benzene **S2** (39.6 mg, 0.20 mmol, 1.0 equiv.) and propyne (0.5 mL, 1.0 M in THF, 0.50 mmol, 2.5 equiv.) for 16 h, the reaction mixture was purified by column chromatography on silica gel (cyclohexane) to yield the product **50** as a colorless oil (27.8 mg, 88% yield, 97% ee).
[α]$_D^{27}$ = +19 (*c* 0.80, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane, flow rate 0.3 mL/min, λ = 214 nm), t_R (minor) = 24.67 min, t_R (major) = 26.48 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 4H), 7.27 – 7.21 (m, 1H), 3.60 – 3.47 (m, 1H), 1.90 (d, *J* = 2.4 Hz, 3H), 1.84 – 1.68 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 128.3, 127.5, 126.4, 80.8, 78.3, 39.5, 31.7, 11.9, 3.7.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{15}$ $[M + H]^+$ 159.1168, found 159.1169.

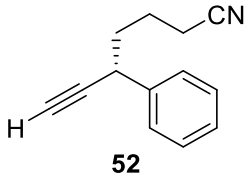
(*S*)-1-(3-(but-3-yn-2-yl)phenyl)ethan-1-one (51)



51

According to **General procedure C** with 1-(3-(1-bromoethyl)phenyl)ethan-1-one **S93** (45.2 mg, 0.20 mmol, 1.0 equiv.) and acetylene (1 atm) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **51** as a colorless oil (33.0 mg, 96% yield, 96% ee).
[α]$_D^{27}$ = +15 (*c* 1.0, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.3/0.7, flow rate 0.3 mL/min, λ = 254 nm), t_R (minor) = 38.82 min, t_R (major) = 43.46 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (t, *J* = 1.8 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.68 – 7.61 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 3.86 (qd, *J* = 7.2, 2.5 Hz, 1H), 2.64 (s, 3H), 2.33 (d, *J* = 2.5 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 143.3, 137.5, 131.6, 128.9, 127.0, 126.7, 86.4, 70.8, 31.6, 26.7, 24.2.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{13}O$ $[M + H]^+$ 173.0961, found 173.0961.

(*S*)-5-Phenylhept-6-ynenitrile (52)

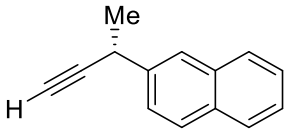


52

According to **General procedure C** with 5-bromo-5-phenylpentanenitrile **S75** (47.4 mg, 0.20 mmol, 1.0 equiv.) and acetylene (1 atm) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **52** as a

colorless oil (28.2 mg, 77% yield, 95% ee).
[α]D^{27} = +8.6 (*c* 1.2, CH_2Cl_2).
HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 85/15, flow rate 0.5 mL/min, λ = 214 nm), t_R (minor) = 11.88 min, t_R (major) = 12.52 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 5H), 3.73 (ddd, *J* = 8.3, 5.8, 2.5 Hz, 1H), 2.39 (t, *J* = 6.9 Hz, 2H), 2.34 (d, *J* = 2.5 Hz, 1H), 2.01 – 1.75 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 128.7, 127.3, 127.2, 119.3, 84.6, 72.0, 36.9, 36.8, 23.0, 16.9.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{14}N$ $[M + H]^+$ 184.1121, found 184.1120.

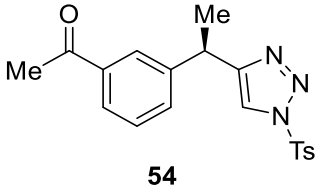
(*S*)-2-(but-3-yn-2-yl)naphthalene (53)



53

According to **General procedure C** with 2-(1-bromoethyl)naphthalene **S98** (46.8 mg, 0.20 mmol, 1.0 equiv.) and acetylene (1 atm) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **53** as a colorless oil (25.6 mg, 71% yield, 93% ee).
[α]D^{27} = +1.2 (*c* 2.2, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 254 nm), t_R (minor) = 18.49 min, t_R (major) = 21.05 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.78 (m, 4H), 7.60 – 7.41 (m, 3H), 3.97 (qd, *J* = 7.1, 2.5 Hz, 1H), 2.36 (d, *J* = 2.5 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 133.5, 132.4, 128.3, 127.8, 127.6, 126.1, 125.7, 125.4, 125.1, 87.1, 70.4, 31.8, 24.1.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{13}$ $[M + H]^+$ 181.1012, found 181.1011.

(*R*)-1-(3-(1-(1-Tosyl-1*H*-1,2,3-triazol-4-yl)ethyl)phenyl)ethan-1-one (54)

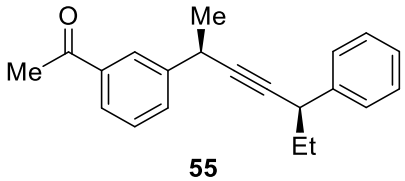


54

According to **General procedure C** with 1-(3-(1-bromoethyl)phenyl)ethan-1-one **S93** (47.4 mg, 0.20 mmol, 1.0 equiv.) and acetylene (1 atm) for 18 h, the reaction mixture was filtered and concentrated. Without further purification, the residue was dissolved in toluene (2.0 mL) under argon atmosphere, and then, 4-methylbenzenesulfonyl azide (39.4 mg, 0.20 mmol, 1.0 equiv.) and copper thiophene-2-carboxylate (1.91 mg, 0.010 mmol, 5.0 mol%) were added. The reaction mixture was stirred under the same conditions for 3 h, and then, was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product **54** as a yellow amorphous powder (59.8 mg, 81% yield over two steps, 95% ee).
[α]D^{27} = +8.2 (*c* 0.60, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 90/10, flow rate 0.4 mL/min, λ = 240 nm), t_R (minor) = 63.56 min, t_R (major) = 67.30 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.88 – 7.82 (m, 2H), 7.77 (s, 1H), 7.49 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 4.34 (q, *J* = 7.2 Hz, 1H), 2.60 (s, 3H), 2.46 (s, 3H), 1.72 (d, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 151.7, 147.3, 144.1, 137.6, 133.0, 132.3, 130.4, 129.1, 128.7, 127.2, 127.0, 120.3, 37.0, 26.7, 21.9, 21.1.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{20}N_3O_3S$ $[M + H]^+$ 370.1220, found 370.1217.

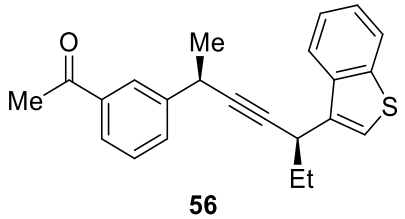
1-(3-((2*R*,5*R*)-5-Phenylhept-3-yn-2-yl)phenyl)ethan-1-one (55)



55

According to **General procedure C** with 1-(3-(1-bromoethyl)phenyl)ethan-1-one **S93** (47.4 mg, 0.20 mmol, 1.0 equiv.) and acetylene (1 atm) for 18 h, the reaction mixture was filtered and concentrated. Without further purification, the residue was directly used in the next step. To a mixture of **L*13** (12.5 mg, 0.015 mmol, 7.5 mol%), copper thiophene-2-carboxylate (1.91 mg, 0.010 mmol, 5.0 mol%), and anhydrous cesium carbonate (130.4 mg, 0.40 mmol, 2.0 equiv.) in diethyl ether (4.0 mL) were added the residue obtained above and (1-bromopropyl)benzene **S2** (59.4 mg, 0.30 mmol, 1.5 equiv.) sequentially under argon atmosphere, and the reaction mixture was stirred at room temperature for 72 h. After completion of reaction, the reaction was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **55** as a colorless oil (39.4 mg, 68% yield over two steps, 95% ee). The diastereomeric ratio was roughly estimated by HPLC to be larger than 20:1.
$[\alpha]_D^{27}$ = +2.8 (*c* 1.8, CH_2Cl_2).
HPLC analysis: Chiralcel AZ3 (hexane/*i*-PrOH = 98/2, flow rate 0.4 mL/min, λ = 240 nm), t_R (major) = 18.96 min, t_R (minor) = 24.70 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 7.28 – 7.22 (m, 1H), 3.92 (q, *J* = 7.0 Hz, 1H), 3.66 (t, *J* = 6.9 Hz, 1H), 2.61 (s, 3H), 1.89 – 1.75 (m, 2H), 1.56 (d, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 144.6, 142.4, 137.4, 131.7, 128.7, 128.4, 127.5, 126.9, 126.58, 126.55, 85.2, 84.5, 39.5, 32.0, 31.8, 26.7, 24.9, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{23}O$ $[M + H]^+$ 291.1743, found 291.1740.

1-(3-((2*R*,5*S*)-5-(Benzo[*b*]thiophen-3-yl)hept-3-yn-2-yl)phenyl)ethan-1-one (56)



56

According to **General procedure C** with 1-(3-(1-bromoethyl)phenyl)ethan-1-one **S93** (47.4 mg, 0.20 mmol, 1.0 equiv.) and acetylene (1 atm) for 18 h, the reaction mixture was filtered and concentrated. Without further purification, the residue was directly used in the next step. To a

mixture of **L*13** (12.5 mg, 0.015 mmol, 7.5 mol%), copper thiophene-2-carboxylate (1.91 mg, 0.01 mmol, 5.0 mol%), and anhydrous cesium carbonate (130.4 mg, 0.4 mmol, 2.0 equiv.) in diethyl ether (4.0 mL) were added the residue obtained above and 3-(1-bromopropyl)benzo[*b*]thiophene **S104** (76.2 mg, 0.30 mmol, 1.5 equiv.) sequentially under argon atmosphere, and the reaction mixture was stirred at room temperature for 72 h. After completion of reaction, the reaction was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **56** as a yellow oil (33.9 mg, 49% yield over two steps, 95% ee). The diastereomeric ratio was roughly estimated by HPLC to be larger than 20:1.

$[\alpha]_D^{27}$ = +6.4 (*c* 0.50, CH_2Cl_2).

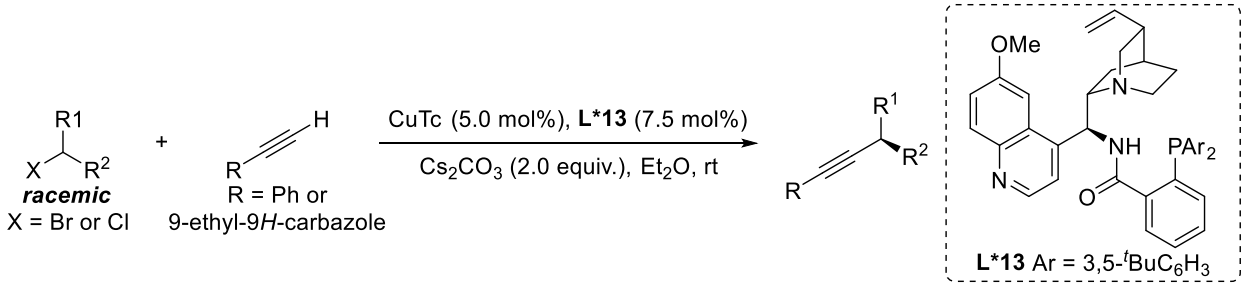
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 29.15 min, t_R (major) = 46.89 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, *J* = 1.9 Hz, 1H), 7.92 – 7.82 (m, 3H), 7.67 – 7.61 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.41 – 7.35 (m, 3H), 4.10 – 4.03 (m, 1H), 3.92 (qd, *J* = 7.2, 2.1 Hz, 1H), 2.56 (s, 3H), 2.10 – 1.84 (m, 2H), 1.56 (d, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 144.4, 140.9, 137.5, 137.4, 136.5, 131.7, 128.8, 126.8, 126.6, 124.2, 123.8, 123.0, 122.5, 122.0, 85.0, 83.7, 33.7, 32.0, 29.0, 26.7, 24.8, 11.9.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}OS$ $[M + H]^+$ 347.1464, found 347.1463.

Asymmetric Sonogashira C(sp)−C(sp^3) cross-coupling: Scope of secondary alkyl halides



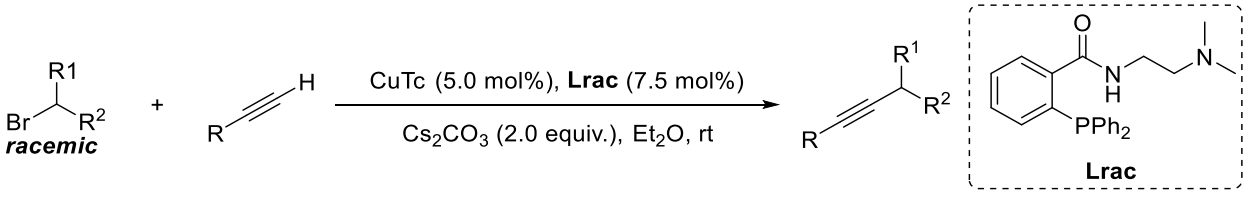
General procedure B:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (1.9 mg, 0.010 mmol, 5.0 mol%), **L*13** (12.5 mg, 0.015 mmol, 7.5 mol%), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous Et_2O (4.0 mL). Then, alkyl halide (0.20 mmol, 1.0 equiv.) and alkyne (0.30 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 24 to 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed by Et_2O or petroleum ether. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure D:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (3.8 mg, 0.020 mmol, 10.0 mol%), **L*13** (25.1 mg, 0.03 mmol, 15.0 mol%), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous Et_2O (4.0 mL). Then, alkyl halide (0.20 mmol, 1.0 equiv.) and alkyne (0.30 mmol, 1.5 equiv.) were sequentially added into the mixture, which was stirred at room temperature for 24 to 72 h afterwards. Upon completion (monitored by TLC), the precipitate was filtered off and washed by Et_2O or petroleum ether. The filtrate was concentrated and the residues was purified by column chromatography on silica gel to afford the desired product.

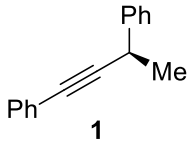
Note: Most of the products were unstable in neat state in air after purification, and should be stored in solvent (CH_2Cl_2 or Et_2O) at –10 °C. Their characterization by NMR, HPLC or HRMS should be done as soon as possible. Meanwhile, the reaction is sensitive to water and air, and thus, Schlenk tubes and the reagents must be dried prior to use.



The racemates of products were prepared following the same procedure described above using CuTc (1.9 mg, 0.010 mmol, 5.0 mol%) and $\mathbf{L_{rac}}$ (5.6 mg, 0.015 mmol, 7.5 mol%) as catalyst and ligand, respectively, at room temperature in anhydrous Et_2O (4.0 mL) for 24 to 72 h. Upon completion (monitored by TLC), the precipitate was filtered off and washed with Et_2O, the filtrate was concentrated, and the residue was purified by column chromatography on silica gel to afford the desired product.

Note: Since the reaction is sensitive to water and air, Schlenk tubes and the reagents must be dried prior to use.

(*R*)-But-1-yne-1,3-diyldibenzene (1)

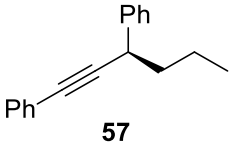


1

According to **General procedure B** with (1-bromoethyl)benzene **S1-1** (37.0 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **1** as a colorless oil (30.9 mg, 75% yield, 94% ee).
[α]$_D^{27}$ = –29 (*c* 1.4, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.30 min, t_R (major) = 17.52 min.

According to **General procedure D** with (1-chloroethyl)benzene **S1-3** (28.1 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **1** as a colorless oil (28.9 mg, 70% yield, 94% ee).
[α]$_D^{27}$ = –30 (*c* 1.2, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.99 min, t_R (major) = 16.61 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.26 – 7.24 (m, 1H), 4.00 (q, *J* = 7.1 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 131.6, 128.6, 128.2, 127.8, 127.0 126.7, 123.7, 92.6, 82.4, 32.5, 24.6.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}$ $[M + H]^+$ 207.1168, found 207.1161.

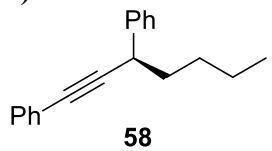
(*R*)-Hex-1-yne-1,3-diyldibenzene (57)



57

According to **General procedure B** with (1-bromobutyl)benzene **S57** (42.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **57** as a colorless oil (36.0 mg, 77% yield, 96% ee).
[α]$_D^{27}$ = –10 (*c* 2.1, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.04 min, t_R (major) = 13.82 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.20 (m, 4H), 3.84 (dd, *J* = 8.2, 6.3 Hz, 1H), 1.89 – 1.71 (m, 2H), 1.63 – 1.42 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 131.7, 128.5, 128.2, 127.7, 127.5, 126.7, 123.9, 91.7, 83.2, 40.9, 38.2, 20.7, 13.9.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}$ $[M + H]^+$ 235.1481, found 235.1479.

(*R*)-Hept-1-yne-1,3-diyldibenzene (58)



58

According to **General procedure B** with (1-bromopentyl)benzene **S58** (45.4 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **58** as a colorless oil (34.7 mg, 70% yield, 96% ee).

[α]$_D^{27}$ = –9.4 (*c* 2.1, CH_2Cl_2).

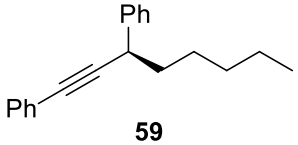
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.83 min, t_R (major) = 14.51 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 3H), 7.41 (d, *J* = 0.5 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.26 – 7.20 (m, 1H), 3.83 (t, *J* = 7.2 Hz, 1H), 1.91 – 1.75 (m, 2H), 1.58 – 1.40 (m, 2H), 1.40 – 1.28 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 131.7, 128.5, 128.2, 127.7, 127.5, 126.7, 123.9, 91.8, 83.2, 38.48, 38.47, 29.7, 22.5, 14.1.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}$ $[M + H]^+$ 249.1638, found 249.1632.

(*R*)-Oct-1-yne-1,3-diyldibenzene (59)



59

According to **General procedure B** with (1-bromohexyl)benzene **S59** (48.2 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **59** as a colorless oil (34.1 mg, 65% yield, 96% ee).

[α]$_D^{27}$ = –7.5 (*c* 2.3, CH_2Cl_2).

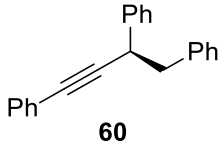
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.91 min, t_R (major) = 15.15 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 3H), 7.40 (d, *J* = 0.7 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.25 – 7.20 (m, 1H), 3.83 (dd, *J* = 7.9, 6.5 Hz, 1H), 1.88 – 1.71 (m, 2H), 1.61 – 1.39 (m, 2H), 1.35 – 1.23 (m, 4H), 0.93 – 0.80 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 131.7, 128.5, 128.2, 127.7, 127.5, 126.7, 123.9, 91.8, 83.2, 38.7, 38.5, 31.6, 27.2, 22.6, 14.1.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}$ $[M + H]^+$ 263.1794, found 263.1794.

(*R*)-But-3-yne-1,2,4-triyltribenzene (60)

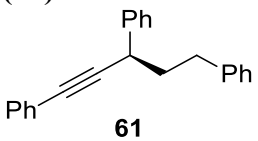


60

According to **General procedure B** with (1-bromoethane-1,2-diyl)dibenzene **S60** (52.2 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the

product **60** as a colorless oil (35.0 mg, 62% yield, 92% ee).
[α]$_D^{27}$ = +35 (*c* 1.5, CH_2Cl_2).
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.76 min, t_R (minor) = 14.37 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 3H), 7.34 (d, *J* = 0.9 Hz, 1H), 7.31 (dd, *J* = 6.9, 1.8 Hz, 2H), 7.29 – 7.23 (m, 6H), 7.23 – 7.20 (m, 1H), 7.20 – 7.15 (m, 2H), 4.07 (t, *J* = 7.3 Hz, 1H), 3.10 (d, *J* = 7.3 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 139.0, 131.6, 129.6, 128.5, 128.3, 128.1, 127.9, 127.8, 127.0, 126.5, 123.7, 91.1, 84.4, 45.2, 40.9.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{19}$ $[M + H]^+$ 283.1481, found 283.1477.

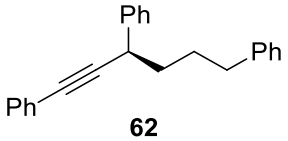
(*R*)-Pent-1-yne-1,3,5-triyltribenzene (61)



61

According to **General procedure B** with (1-bromopropane-1,3-diyl)dibenzene **S61** (55.0 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **61** as a colorless oil (42.0 mg, 71% yield, 94% ee).
[α]$_D^{27}$ = +31 (*c* 2.4, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 26.12 min, t_R (major) = 27.24 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.38 – 7.27 (m, 6H), 7.26 (d, *J* = 1.6 Hz, 1H), 7.24 – 7.15 (m, 4H), 3.84 (t, *J* = 7.2 Hz, 1H), 2.93 – 2.74 (m, 2H), 2.27 – 1.99 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 141.7, 131.7, 128.6, 128.5, 128.3, 127.9, 127.6, 126.9, 126.0, 123.8, 91.2, 83.9, 40.2, 37.8, 33.7.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{21}$ $[M + H]^+$ 283.1638, found 283.1633.

(*R*)-Hex-1-yne-1,3,6-triyltribenzene (62)

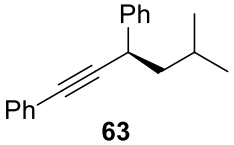


62

According to **General procedure B** with (1-bromobutane-1,4-diyl)dibenzene **S62** (57.8 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **62** as a colorless oil (32.2 mg, 52% yield, 95% ee).
[α]$_D^{27}$ = +1.0 (*c* 1.8, CH_2Cl_2).
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 4.65 min, t_R (major) = 6.81 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.40 (d, *J* = 1.4 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.20 (m, 6H), 7.19 – 7.13 (m, 3H), 3.86 (t, *J* = 6.7 Hz, 1H), 2.74 – 2.55 (m, 2H), 1.97 – 1.72 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 142.1, 131.7, 128.6, 128.5, 128.4, 128.3, 127.8, 127.5, 126.8, 125.8, 123.8, 91.5, 83.4, 38.4, 38.2, 35.6, 29.2.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{23}$ $[M + H]^+$ 311.1794, found 311.1793.

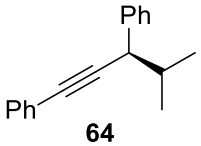
(*R*)-(5-Methylhex-1-yne-1,3-diyl)dibenzene (63)



63

According to **General procedure B** with (1-bromo-3-methylbutyl)benzene **S63** (45.4 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **63** as a colorless oil (34.7 mg, 70% yield, 96% ee).
$[\alpha]_D^{27}$ = –11 (*c* 2.3, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.18 min, t_R (major) = 11.86 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 4H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.21 (m, 4H), 3.88 (dd, *J* = 9.7, 6.1 Hz, 1H), 1.99 – 1.85 (m, 1H), 1.80 (ddd, *J* = 13.2, 9.7, 5.4 Hz, 1H), 1.57 (ddd, *J* = 13.2, 8.5, 6.1 Hz, 1H), 0.98 (dd, *J* = 8.4, 6.6 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 131.7, 128.6, 128.2, 127.7, 127.5, 126.7, 123.9, 91.7, 83.0, 48.1, 36.6, 26.2, 23.1, 21.9.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}$ $[M + H]^+$ 249.1638, found 249.1634.

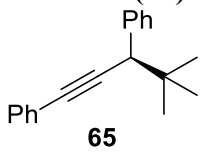
(*R*)-(4-Methylpent-1-yne-1,3-diyl)dibenzene (64)



64

According to **General procedure B** with (1-bromo-2-methylpropyl)benzene **S64** (42.6 mg, 0.20 mmol, 1.0 equiv.), ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.), and **L*8** (9.2 mg, 0.015 mmol, 7.5 mol%) instead of **L*13** for 24 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **64** as a colorless oil (37.9 mg, 81% yield, 98% ee).
$[\alpha]_D^{27}$ = –34 (*c* 1.0, CH_2Cl_2).
HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.14 min, t_R (major) = 10.67 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.27 (m, 5H), 7.24 (t, *J* = 7.2 Hz, 1H), 3.73 (d, *J* = 5.9 Hz, 1H), 2.05 (dq, *J* = 13.1, 6.5 Hz, 1H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 131.7, 128.25, 128.22, 127.7, 126.6, 124.0, 90.2, 84.3, 45.8, 35.2, 21.3, 18.7.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}$ $[M + H]^+$ 235.1481, found 235.1478.

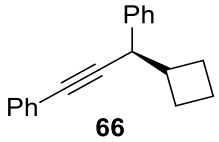
(*R*)-(4,4-Dimethylpent-1-yne-1,3-diyl)dibenzene (65)



65

According to **General procedure B** with (1-bromo-2,2-dimethylpropyl)benzene **S65** (45.4 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **65** as a colorless oil (14.9 mg, 30% yield, 96% ee).
[α]$_D^{27}$ = −15 (*c* 1.1, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 15.55 min, t_R (major) = 16.04 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.39 – 7.34 (m, 2H), 7.34 – 7.26 (m, 5H), 7.26 – 7.22 (m, 1H), 3.62 (s, 1H), 1.04 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 131.6, 129.7, 128.2, 127.6, 126.7, 124.0, 91.4, 83.7, 50.3, 35.5, 27.8.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}$ $[M + H]^+$ 249.1638, found 249.1632.

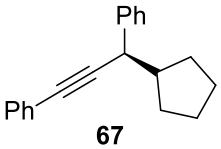
(*R*)-(3-Cyclobutylprop-1-yne-1,3-diyl)dibenzene (66)



66

According to **General procedure B** with (bromo(cyclobutyl)methyl)benzene **S66** (45.0 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **66** as a colorless oil (35.9 mg, 73% yield, 96% ee).
[α]$_D^{27}$ = +19 (*c* 2.1, CH_2Cl_2).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 99.8/0.2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.15 min, t_R (minor) = 5.62 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.34 – 7.26 (m, 5H), 7.25 – 7.19 (m, 1H), 3.80 (d, *J* = 7.7 Hz, 1H), 2.67 (h, *J* = 8.1 Hz, 1H), 2.13 – 2.00 (m, 2H), 1.99 – 1.88 (m, 2H), 1.86 – 1.75 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 131.8, 128.4, 128.2, 127.8, 127.6, 126.7, 123.9, 90.2, 83.7, 44.1, 42.2, 26.7, 26.0, 17.6.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{19}$ $[M + H]^+$ 247.1481, found 247.1486.

(*R*)-(3-Cyclopentylprop-1-yne-1,3-diyl)dibenzene (67)

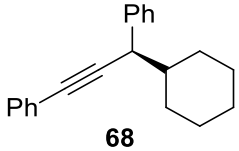


67

According to **General procedure B** with (bromo(cyclopentyl)methyl)benzene **S67** (47.8 mg, 0.20 mmol, 1.0 equiv.), ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.), and **L*8** (9.2 mg, 0.015 mmol, 7.5 mol%) instead of **L*13** for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **67** as a colorless oil (41.1 mg,

79% yield, 96% ee).
[α]$_D^{27}$ = –1.1 (*c* 2.9, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.22 min, t_R (major) = 10.57 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 3H), 7.39 (s, 1H), 7.35 – 7.25 (m, 5H), 7.25 – 7.21 (m, 1H), 3.78 (d, *J* = 7.3 Hz, 1H), 2.32 – 2.17 (m, 1H), 2.33 – 2.18 (m, 1H), 1.85 – 1.72 (m, 1H), 1.72 – 1.54 (m, 5H), 1.47 – 1.38 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 131.7, 128.3, 128.2, 127.9, 127.7, 126.6, 124.0, 91.2, 83.3, 47.3, 43.3, 31.2, 30.0, 25.4, 25.2.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}$ $[M + H]^+$ 261.1638, found 261.1636.

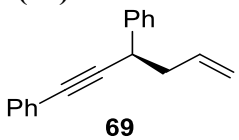
(*R*)-(3-Cyclohexylprop-1-yne-1,3-diyl)dibenzene (68)



68

According to **General procedure B** with (bromo(cyclohexyl)methyl)benzene **S68** (50.6 mg, 0.20 mmol, 1.0 equiv.), ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.), and **L*8** (9.2 mg, 0.015 mmol, 7.5 mol%) instead of **L*13** for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **68** as a colorless oil (44.9 mg, 82% yield, 98% ee).
[α]$_D^{27}$ = –10 (*c* 1.6, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.62 min, t_R (major) = 11.41 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.26 (m, 5H), 7.26 – 7.21 (m, 1H), 3.68 (d, *J* = 6.2 Hz, 1H), 1.86 (s, 1H), 1.80 – 1.75 (m, 2H), 1.70 – 1.55 (m, 3H), 1.27 – 1.09 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 131.7, 128.4, 128.25, 128.22, 127.7, 126.6, 124.0, 90.8, 84.1, 45.2, 44.7, 31.7, 29.6, 26.5, 26.4, 26.3.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{23}$ $[M + H]^+$ 275.1794, found 275.1793.

(*R*)-Hex-5-en-1-yne-1,3-diyldibenzene (69)

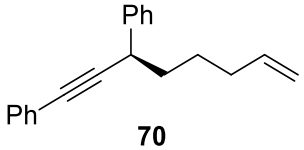


69

According to **General procedure B** with (1-bromobut-3-en-1-yl)benzene **S69** (42.2 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **69** as a colorless oil (29.7 mg, 64% yield, 96% ee).
[α]$_D^{27}$ = –2.2 (*c* 1.1, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.62 min, t_R (major) = 13.43 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.26 – 7.23 (m, 1H), 5.92 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.15 – 5.02 (m, 2H), 3.92 (t, *J* = 7.1 Hz, 1H), 2.59 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 135.5, 131.7, 128.5, 128.2, 127.8, 127.6, 126.9, 123.7, 117.1, 91.0, 83.8, 42.8, 38.6.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}$ $[M + H]^+$ 233.1325, found 233.1321.

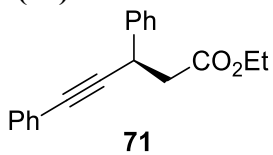
(*R*)-Oct-7-en-1-yne-1,3-diyldibenzene (70)



70

According to **General procedure B** with (1-bromohex-5-en-1-yl)benzene **S70** (47.8 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **70** as a colorless oil (39.1 mg, 75% yield, 96% ee).
$[\alpha]_D^{27}$ = –6.0 (*c* 2.3, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.61 min, t_R (major) = 21.67 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 3H), 7.40 (s, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.26 – 7.17 (m, 1H), 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.01 (ddd, *J* = 17.1, 3.4, 1.6 Hz, 1H), 4.97 – 4.92 (m, 1H), 3.84 (t, *J* = 7.2 Hz, 1H), 2.18 – 2.04 (m, 2H), 1.90 – 1.77 (m, 2H), 1.73 – 1.43 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 138.6, 131.7, 128.5, 128.2, 127.8, 127.5, 126.7, 123.8, 114.7, 91.5, 83.3, 38.3, 38.1, 33.5, 26.7.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}$ $[M + H]^+$ 261.1638, found 261.1638.

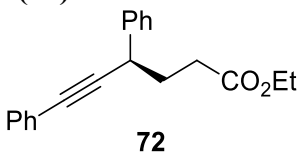
Ethyl (*R*)-3,5-diphenylpent-4-ynoate (71)



71

According to **General procedure B** with ethyl 3-bromo-3-phenylpropanoate **S71** (51.4 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 20/1) to yield the product **71** as a colorless oil (18.9 mg, 34% yield, 92% ee).
$[\alpha]_D^{27}$ = –12 (*c* 0.80, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.17 min, t_R (minor) = 7.75 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.25 (m, 4H), 4.38 (t, *J* = 7.6 Hz, 1H), 4.19 – 4.10 (m, 2H), 2.90 (dd, *J* = 15.1, 8.4 Hz, 1H), 2.79 (dd, *J* = 15.1, 6.9 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 140.5, 131.7, 128.7, 128.2, 128.0, 127.5, 127.3, 123.3, 89.9, 83.6, 60.7, 43.4, 34.9, 14.2.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{19}O_2$ $[M + H]^+$ 279.1380, found 279.1377.

Ethyl (*R*)-4,6-diphenylhex-5-ynoate (72)



72

According to **General procedure B** with ethyl 4-bromo-4-phenylbutanoate **S72** (54.2 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 20/1) to yield the product **72** as a colorless oil (50.2 mg, 86% yield, 86% ee).

[α]$_D^{27}$ = –1.7 (*c* 4.5, CH_2Cl_2).

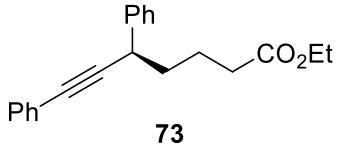
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.56 min, t_R (major) = 10.32 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 4H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.24 (m, 4H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.98 (dd, *J* = 8.4, 5.9 Hz, 1H), 2.66 – 2.45 (m, 2H), 2.28 – 2.08 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 141.2, 131.7, 128.6, 128.3, 128.0, 127.6, 127.0, 123.5, 90.3, 84.1, 60.5, 37.6, 33.4, 32.0, 14.3.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}O_2$ $[M + H]^+$ 293.1536, found 293.1533.

Ethyl (*R*)-5,7-diphenylhept-6-ynoate (73)



73

According to **General procedure B** with ethyl 5-bromo-5-phenylpentanoate **S73** (57.1 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 20/1) to yield the product **73** as a colorless oil (45.9 mg, 75% yield, 92% ee).

[α]$_D^{27}$ = –7.0 (*c* 3.8, CH_2Cl_2).

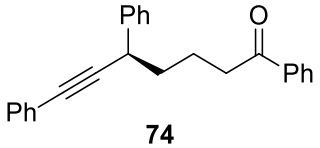
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.93 min, t_R (major) = 11.48 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 4.1 Hz, 1H), 7.44 – 7.42 (m, 2H), 7.41 (s, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.27 (m, 3H), 7.26 – 7.21 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.86 (t, *J* = 6.5 Hz, 1H), 2.35 (t, *J* = 6.9 Hz, 2H), 1.95 – 1.78 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 141.8, 131.7, 128.6, 128.2, 127.8, 127.5, 126.8, 123.7, 91.0, 83.6, 60.3, 38.2, 37.9, 34.0, 22.9, 14.3.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{23}O_2$ $[M + H]^+$ 307.1693, found 307.1687.

(*R*)-1,5,7-Triphenylhept-6-yn-1-one (74)

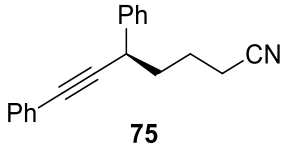


74

According to **General procedure B** with 5-bromo-1,5-diphenylpentan-1-one **S74** (63.4 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction

mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 15/1) to yield the product **74** as a colorless oil (56.8 mg, 84% yield, 92% ee).
[α]$_D^{27}$ = –3.6 (*c* 3.6, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.16 min, t_R (major) = 18.19 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.55 (ddd, *J* = 6.8, 4.0, 1.2 Hz, 1H), 7.50 – 7.42 (m, 6H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.27 – 7.24 (m, 1H), 3.94 (t, *J* = 6.7 Hz, 1H), 3.11 – 2.93 (m, 2H), 2.10 – 1.87 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 141.9, 137.0, 133.0, 131.7, 128.61, 128.60, 128.2, 128.1, 127.8, 127.5, 126.8, 123.7, 91.2, 83.7, 38.3, 38.2, 38.1, 22.3.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{23}O$ $[M + H]^+$ 339.1743, found 339.1743.

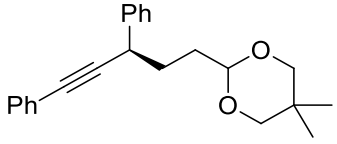
(*R*)-5,7-Diphenylhept-6-ynenitrile (75)



75

According to **General procedure B** with 5-bromo-5-phenylpentanenitrile **S75** (47.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 8/1) to yield the product **75** as a colorless oil (43.0 mg, 83% yield, 94% ee).
[α]$_D^{27}$ = –7.6 (*c* 3.1, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.97 min, t_R (major) = 14.98 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.28 (m, 3H), 7.27 – 7.23 (m, 1H), 3.90 (dd, *J* = 7.8, 6.0 Hz, 1H), 2.36 (t, *J* = 7.0 Hz, 2H), 2.02 – 1.92 (m, 2H), 1.91 – 1.78 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 131.7, 128.7, 128.3, 128.1, 127.4, 127.1, 123.3, 119.5, 90.1, 84.2, 37.7, 37.2, 23.2, 17.0.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{18}N$ $[M + H]^+$ 260.1434, found 260.1437.

(*R*)-2-(3,5-Diphenylpent-4-yn-1-yl)-5,5-dimethyl-1,3-dioxane (76)

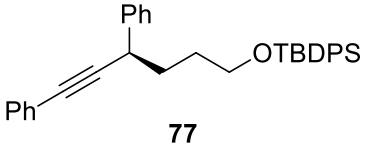


76

According to **General procedure B** with 2-(3-bromo-3-phenylpropyl)-5,5-dimethyl-1,3-dioxane **S76** (62.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **76** as a colorless oil (49.4 mg, 74% yield, 94% ee).
[α]$_D^{27}$ = –2.1 (*c* 3.5, CH_2Cl_2).
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 17.29 min, t_R (major) = 18.52 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.21 (m, 4H), 4.45 (t, *J* = 4.6 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.60 (d, *J* = 3.1 Hz, 1H), 3.58 (d, *J* = 2.9 Hz, 1H),

3.41 (d, J = 3.0 Hz, 1H), 3.38 (d, J = 3.0 Hz, 1H), 2.04 – 1.88 (m, 3H), 1.88 – 1.75 (m, 1H), 1.18 (s, 3H), 0.70 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 131.7, 128.5, 128.2, 127.7, 127.6, 126.8, 123.7, 101.9, 91.1, 83.6, 77.2, 38.2, 32.9, 32.7, 30.2, 23.0, 21.9.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{27}O_2$ $[M + H]^+$ 335.2006, found 335.1998.

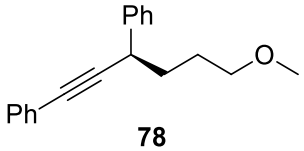
(*R*)-*tert*-Butyl((4,6-diphenylhex-5-yn-1-yl)oxy)diphenylsilane (77)



77

According to **General procedure B** with (4-bromo-4-phenylbutoxy)(*tert*-butyl)diphenylsilane **S77** (93.4 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **77** as a colorless oil (81.1 mg, 83% yield, 95% ee).
[α]$_D^{27}$ = –2.2 (*c* 2.2, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.3/0.7, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 7.80 min, t_R (major) = 9.81 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 4H), 7.43 – 7.41 (m, 3H), 7.39 (d, J = 5.3 Hz, 3H), 7.36 – 7.31 (m, 6H), 7.30 – 7.21 (m, 4H), 3.87 (t, J = 7.6 Hz, 1H), 3.79 – 3.63 (m, 2H), 2.01 – 1.85 (m, 2H), 1.85 – 1.68 (m, 2H), 1.04 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 135.6, 134.01, 134.00, 131.7, 129.6, 128.5, 128.2, 127.7, 127.6, 127.5, 126.7, 123.8, 91.5, 83.4, 63.6, 38.0, 34.9, 30.3, 26.9, 19.3.
HRMS (ESI) *m/z* calcd. for $C_{34}H_{37}OSi$ $[M + H]^+$ 489.2608, found 489.2600.

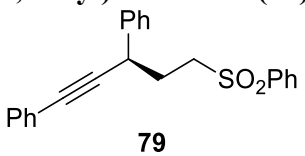
(*R*)-(6-Methoxyhex-1-yne-1,3-diyl)dibenzene (78)



78

According to **General procedure B** with (1-bromo-4-methoxybutyl)benzene **S78** (48.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 50/1) to yield the product **78** as a colorless oil (43.8 mg, 83% yield, 95% ee).
[α]$_D^{27}$ = –11 (*c* 3.1, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 97/3, flow rate 0.3 mL/min, λ = 254 nm), t_R (minor) = 14.89 min, t_R (major) = 16.42 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 4H), 7.33 (t, J = 7.5 Hz, 2H), 7.30 – 7.20 (m, 4H), 3.87 (dd, J = 7.8, 6.2 Hz, 1H), 3.46 – 3.35 (m, 2H), 3.31 (s, 3H), 1.98 – 1.69 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 131.7, 128.5, 128.2, 127.8, 127.5, 126.8, 123.8, 91.3, 83.5, 72.5, 58.6, 38.2, 35.3, 27.6.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}O$ $[M + H]^+$ 265.1587, found 265.1585.

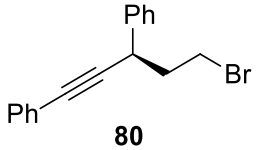
(*R*)-(5-(Phenylsulfonyl)pent-1-yne-1,3-diyl)dibenzene (79)



79

According to **General procedure B** with (1-bromo-3-(phenylsulfonyl)propyl)benzene **S79** (67.8 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 8/1) to yield the product **79** as a colorless oil (66.2 mg, 92% yield, 80% ee).
[α]$_D^{27}$ = –0.60 (*c* 5.5, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.02 min, t_R (major) = 10.32 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.88 (t, *J* = 1.6 Hz, 1H), 7.69 – 7.59 (m, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 4H), 7.31 – 7.29 (m, 3H), 7.29 – 7.23 (m, 1H), 4.00 (dd, *J* = 8.2, 5.8 Hz, 1H), 3.36 – 3.21 (m, 2H), 2.33 – 2.08 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 139.0, 133.8, 131.7, 129.4, 128.8, 128.33, 128.28, 128.0, 127.44, 127.38, 122.9, 88.8, 84.9, 54.0, 36.9, 31.1.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{21}O_2S$ $[M + H]^+$ 361.1257, found 361.1255.

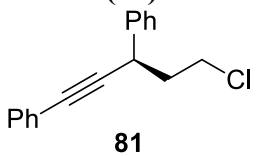
(*R*)-(5-Bromopent-1-yne-1,3-diyl)dibenzene (80)



80

According to **General procedure B** with (1,3-dibromopropyl)benzene **S80** (55.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **80** as a colorless oil (45.9 mg, 77% yield, 96% ee).
[α]$_D^{27}$ = +8.8 (*c* 3.3, CH_2Cl_2).
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.15 min, t_R (minor) = 10.66 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.44 (d, *J* = 2.6 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.25 (m, 4H), 4.13 (dd, *J* = 8.5, 6.2 Hz, 1H), 3.64 (ddd, *J* = 10.0, 7.7, 6.6 Hz, 1H), 3.48 (dt, *J* = 10.1, 6.2 Hz, 1H), 2.44 – 2.21 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 131.7, 128.8, 128.3, 128.1, 127.6, 127.2, 123.3, 89.7, 84.1, 41.2, 36.9, 31.3.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}Br$ $[M + H]^+$ 299.0430, found 299.0426.

(*R*)-(5-Chloropent-1-yne-1,3-diyl)dibenzene (81)

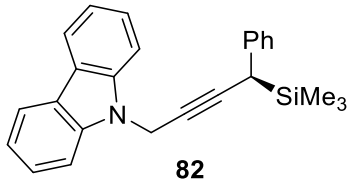


81

According to **General procedure B** with (1-bromo-3-chloropropyl)benzene **S81** (54.9 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction

mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **81** as a colorless oil (39.6 mg, 78% yield, 97% ee).
[α]$_D^{27}$ = +6.2 (*c* 3.5, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 16.07 min, t_R (major) = 16.95 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.24 (m, 4H), 4.14 (dd, *J* = 8.5, 6.3 Hz, 1H), 3.78 (ddd, *J* = 10.9, 7.6, 6.3 Hz, 1H), 3.64 – 3.55 (m, 1H), 2.35 – 2.16 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 131.7, 128.8, 128.3, 128.1, 127.6, 127.2, 123.3, 89.8, 84.0, 42.7, 41.1, 35.7.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}Cl$ $[M + H]^+$ 255.0935, found 255.0933.

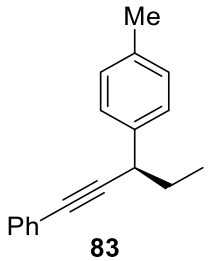
(*R*)-9-(4-phenyl-4-(trimethylsilyl)but-2-yn-1-yl)-9*H*-carbazole (82)



82

According to **General procedure A** with (bromo(phenyl)methyl)trimethylsilane **S82** (72.6 mg, 0.30 mmol, 1.5 equiv.) and 9-(prop-2-yn-1-yl)-9*H*-carbazole **S42** (41.0 mg, 0.20 mmol, 1.0 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **82** as a colorless oil (63.1 mg, 86% yield, 97% ee).
[α]$_D^{27}$ = –3.7 (*c* 1.1, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 18.73 min, t_R (minor) = 20.47 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 2H), 7.62 – 7.50 (m, 4H), 7.34 – 7.29 (m, 2H), 7.28 – 7.22 (m, 2H), 7.17 – 7.08 (m, 3H), 5.18 (d, *J* = 2.2 Hz, 2H), 3.09 (t, *J* = 2.4 Hz, 1H), –0.11 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 138.9, 128.1, 126.9, 125.8, 125.1, 123.3, 120.4, 119.3, 109.1, 84.6, 76.8, 33.1, 29.3, –3.4.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{26}NSi$ $[M + H]^+$ 368.1829, found 368.1827.

(*R*)-1-Methyl-4-(1-phenylpent-1-yn-3-yl)benzene (83)

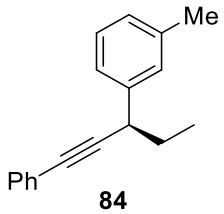


83

According to **General procedure B** with 1-(1-bromopropyl)-4-methylbenzene **S83** (42.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **83** as a colorless oil (39.8 mg, 85% yield, 96% ee).
[α]$_D^{27}$ = –2.6 (*c* 2.6, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R

(minor) = 9.24 min, t_R (major) = 15.76 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 4.5 Hz, 1H), 7.43 (d, *J* = 1.9 Hz, 1H), 7.34 – 7.26 (m, 5H), 7.15 (d, *J* = 7.9 Hz, 2H), 3.75 (t, *J* = 7.0 Hz, 1H), 2.34 (s, 3H), 1.90 – 1.79 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 136.2, 131.7, 129.1, 128.2, 127.7, 127.4, 123.9, 91.7, 83.2, 39.6, 31.7, 21.1, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}$ $[M + H]^+$ 235.1481, found 235.1480.

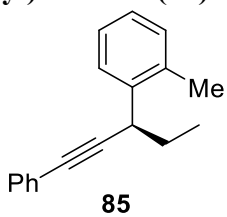
(*R*)-1-Methyl-3-(1-phenylpent-1-yn-3-yl)benzene (84)



84

According to **General procedure B** with 1-(1-bromopropyl)-3-methylbenzene **S84** (42.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **84** as a colorless oil (37.0 mg, 79% yield, 93% ee).
$[\alpha]_D^{27}$ = −10 (*c* 2.8, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.82 min, t_R (major) = 13.69 min.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.33 – 7.28 (m, 3H), 7.26 – 7.21 (m, 3H), 7.10 – 7.04 (m, 1H), 3.76 (dd, *J* = 7.6, 6.4 Hz, 1H), 2.38 (s, 3H), 1.93 – 1.81 (m, 2H), 1.07 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 138.0, 131.7, 128.34, 128.31, 128.2, 127.7, 127.4, 124.6, 123.9, 91.7, 83.3, 39.9, 31.7, 21.5, 12.0.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}$ $[M + H]^+$ 235.1481, found 235.1481.

(*S*)-1-Methyl-2-(1-phenylpent-1-yn-3-yl)benzene (85)

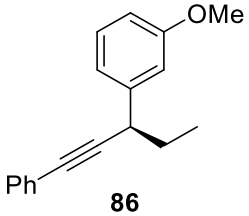


85

According to **General procedure B** with 1-(1-bromopropyl)-2-methylbenzene **S85** (42.6 mg, 0.20 mmol, 1.0 equiv.), ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.), and **L*8** (9.2 mg, 0.015 mmol, 7.5 mol%) instead of **L*13** for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **85** as a colorless oil (20.1 mg, 43% yield, 95% ee).
$[\alpha]_D^{27}$ = −11 (*c* 0.80, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.66 min, t_R (minor) = 10.85 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.34 – 7.27 (m, 3H), 7.25 – 7.18 (m, 1H), 7.18 – 7.13 (m, 2H), 3.97 (dd, *J* = 8.3, 5.8 Hz, 1H), 2.39 (s, 3H), 1.91 – 1.74 (m, 2H), 1.12 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 134.9, 131.6, 130.4, 128.2, 127.7, 126.6, 126.2, 123.9, 91.9, 82.7, 36.5, 30.1, 19.3, 12.2.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}$ $[M + H]^+$ 235.1481, found 235.1480.

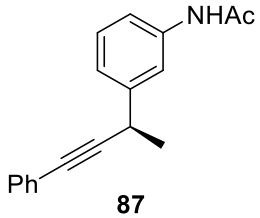
(*R*)-1-Methoxy-3-(1-phenylpent-1-yn-3-yl)benzene (86)



86

According to **General procedure B** with 1-(1-bromopropyl)-3-methoxybenzene **S86** (45.8 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 100/1) to yield the product **86** as a colorless oil (35.0 mg, 70% yield, 96% ee).
$[\alpha]_D^{27}$ = –6.8 (*c* 1.4, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 4.89 min, t_R (major) = 5.55 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.40 (m, 2H), 7.39 – 7.27 (m, 4H), 7.03 (d, *J* = 6.1 Hz, 2H), 6.85 – 6.77 (m, 1H), 3.84 (s, 3H), 3.79 (t, *J* = 7.0 Hz, 1H), 1.97 – 1.83 (m, 2H), 1.09 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 143.7, 131.7, 129.4, 128.2, 127.7, 123.9, 120.0, 113.5, 111.9, 91.4, 83.5, 55.2, 40.0, 31.6, 11.9.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}O$ $[M + H]^+$ 251.1430, found 251.1425.

(*R*)-*N*-(3-(4-Phenylbut-3-yn-2-yl)phenyl)acetamide (87)

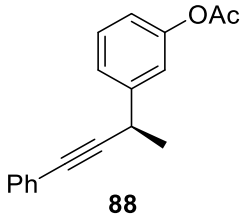


87

According to **General procedure B** with *N*-(3-(1-bromoethyl)phenyl)acetamide **S87** (48.4 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 10/1) to yield the product **87** as a colorless oil (47.3 mg, 90% yield, 90% ee).
$[\alpha]_D^{27}$ = –4.4 (*c* 3.9, CH_2Cl_2).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.96 min, t_R (major) = 14.66 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.49 – 7.43 (m, 3H), 7.40 (s, 1H), 7.33 – 7.26 (m, 4H), 7.19 (d, *J* = 7.7 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 1H), 2.16 (s, 3H), 1.57 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 144.3, 138.1, 131.7, 129.2, 128.2, 127.8, 123.6, 122.9, 118.4, 118.3, 92.3, 82.6, 32.4, 24.6, 24.4.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{18}NO$ $[M + H]^+$ 264.1383, found 264.1382.

(*R*)-3-(4-Phenylbut-3-yn-2-yl)phenyl acetate (88)



88

According to **General procedure B** with 3-(1-bromoethyl)phenyl acetate **S88** (48.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 20/1) to yield the product **88** as a colorless oil (50.1 mg, 95% yield, 92% ee).

$[\alpha]_D^{27}$ = –10 (*c* 4.5, CH_2Cl_2).

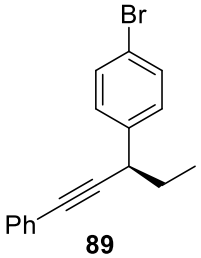
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.84 min, t_R (major) = 8.48 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 4.3 Hz, 1H), 7.45 (t, *J* = 2.7 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.33 – 7.29 (m, 3H), 7.21 (d, *J* = 1.8 Hz, 1H), 7.03 – 6.99 (m, 1H), 4.01 (q, *J* = 7.1 Hz, 1H), 2.31 (s, 3H), 1.60 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 150.9, 145.0, 131.7, 129.5, 128.3, 127.9, 124.5, 123.6, 120.2, 119.9, 92.0, 82.8, 32.3, 24.3, 21.2.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}O_2$ $[M + H]^+$ 265.1223, found 265.1221.

(*R*)-1-Bromo-4-(1-phenylpent-1-yn-3-yl)benzene (89)



89

According to **General procedure B** with 1-bromo-4-(1-bromopropyl)benzene **S89** (55.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **89** as a colorless oil (50.0 mg, 84% yield, 96% ee).

$[\alpha]_D^{27}$ = –6.5 (*c* 4.5, CH_2Cl_2).

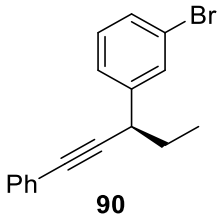
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.93 min, t_R (major) = 23.05 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 1H), 7.46 (d, *J* = 2.1 Hz, 2H), 7.44 (t, *J* = 2.8 Hz, 1H), 7.31 (t, *J* = 3.7 Hz, 3H), 7.29 (d, *J* = 2.4 Hz, 2H), 3.76 (t, *J* = 7.2 Hz,, 1H), 1.91 – 1.75 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 131.7, 131.5, 129.3, 128.3, 127.9, 123.6, 120.5, 90.7, 83.7, 39.4, 31.5, 11.7.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}Br$ $[M + H]^+$ 299.0430, found 299.0430.

(*R*)-1-Bromo-3-(1-phenylpent-1-yn-3-yl)benzene (90)



90

According to **General procedure B** with 1-bromo-3-(1-bromopropyl)benzene **S90** (55.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **90** as a colorless oil (36.9 mg, 62% yield, 95% ee).

[α]$_D^{27}$ = –3.0 (*c* 2.5, CH_2Cl_2).

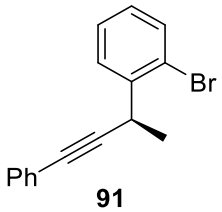
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 12.81 min, t_R (major) = 16.94 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 1.7 Hz, 1H), 7.48 – 7.46 (m, 1H), 7.45 (t, *J* = 2.8 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.21 (t, *J* = 7.8 Hz, 1H), 3.76 (t, *J* = 7.6 Hz, 1H), 1.97 – 1.72 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 131.7, 130.7, 130.0, 129.8, 128.3, 127.9, 126.3, 123.5, 122.5, 90.5, 83.9, 39.6, 31.6, 11.8.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}Br$ $[M + H]^+$ 299.0430, found 299.0425.

(*S*)-1-Bromo-2-(4-phenylbut-3-yn-2-yl)benzene (91)



91

According to **General procedure B** with 1-bromo-2-(1-bromoethyl)benzene **S91** (52.8 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **91** as a colorless oil (21.6 mg, 38% yield, 95% ee).

[α]$_D^{27}$ = –19 (*c* 1.3, CH_2Cl_2).

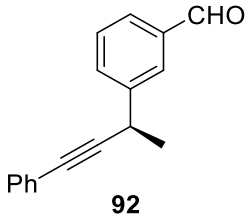
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.23 min, t_R (minor) = 9.18 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.56 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.48 (d, *J* = 4.1 Hz, 1H), 7.46 (t, *J* = 2.8 Hz, 1H), 7.38 – 7.29 (m, 4H), 7.13 (td, *J* = 7.8, 1.6 Hz, 1H), 4.45 (q, *J* = 7.0 Hz, 1H), 1.57 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 132.9, 131.7, 128.8, 128.4, 128.3, 127.9, 123.6, 123.1, 92.0, 82.6, 32.4, 23.1.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{14}Br$ $[M + H]^+$ 285.0273, found 285.0277.

(*R*)-3-(4-Phenylbut-3-yn-2-yl)benzaldehyde (92)



92

According to **General procedure B** with 3-(1-bromoethyl)benzaldehyde **S92** (42.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 20/1) to yield the product **92** as a colorless oil (31.8 mg, 68% yield, 90% ee).

[α]$_D^{27}$ = –5.5 (*c* 2.7, CH_2Cl_2).

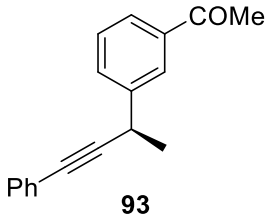
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 8.80 min, t_R (minor) = 9.63 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.97 (s, 1H), 7.85 – 7.71 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.46 (m, 1H), 7.45 (t, *J* = 2.7 Hz, 1H), 7.35 – 7.26 (m, 3H), 4.08 (q, *J* = 7.1 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 144.5, 136.8, 133.2, 131.7, 129.3, 128.4, 128.3, 128.1, 128.0, 123.4, 91.6, 83.1, 32.3, 24.3.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{15}O$ $[M + H]^+$ 235.1117, found 235.1115.

(*R*)-1-(3-(4-Phenylbut-3-yn-2-yl)phenyl)ethan-1-one (93)



93

According to **General procedure B** with 1-(3-(1-bromoethyl)phenyl)ethan-1-one **S93** (45.4 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 20/1) to yield the product **93** as a colorless oil (47.1 mg, 95% yield, 93% ee).

[α]$_D^{27}$ = –13 (*c* 4.4, CH_2Cl_2).

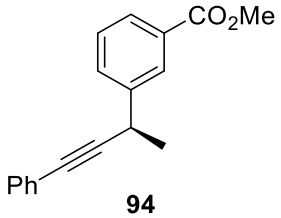
HPLC analysis: Chiralcel OJ3 (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 17.45 min, t_R (major) = 20.28 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (t, *J* = 1.7 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.39 – 7.27 (m, 3H), 4.06 (q, *J* = 7.1 Hz, 1H), 2.63 (s, 3H), 1.61 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 144.0, 137.5, 131.8, 131.6, 128.9, 128.3, 128.0, 126.9, 126.8, 123.5, 91.9, 83.0, 32.4, 26.8, 24.4.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}O$ $[M + H]^+$ 249.1274, found 249.1272.

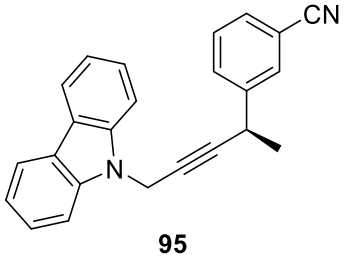
Methyl (*R*)-3-(4-phenylbut-3-yn-2-yl)benzoate (94)



94

According to **General procedure B** with methyl-3-(1-bromoethyl)benzoate **S94** (48.6 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 20/1) to yield the product **94** as a colorless oil (48.0 mg, 91% yield, 89% ee).
[α]$_D^{27}$ = –9.3 (*c* 3.7, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.82 min, t_R (major) = 9.38 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H). 7.47 – 7.41 (m, 3H), 7.38 – 7.28 (m, 3H), 4.05 (q, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 1.61 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 143.7, 131.7, 131.6, 130.5, 128.7, 128.3, 128.2, 128.0, 127.9, 123.5, 91.9, 82.9, 52.2, 32.4, 24.4.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}O_2$ $[M + H]^+$ 265.1223, found 265.1221.

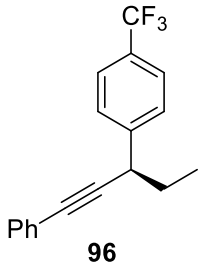
(*R*)-3-(5-(9*H*-Carbazol-9-yl)pent-3-yn-2-yl)benzonitrile (95)



95

According to **General procedure B** with 3-(1-bromoethyl)benzonitrile **S95** (42.0 mg, 0.20 mmol, 1.0 equiv.) and 9-(prop-2-yn-1-yl)-9*H*-carbazole **S42** (61.5 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 20/1) to yield the product **95** as a colorless oil (58.8 mg, 88% yield, 84% ee).
[α]$_D^{27}$ = +15 (*c* 3.9, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 16.97 min, t_R (major) = 18.84 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, *J* = 0.9 Hz, 1H), 8.11 (t, *J* = 0.9 Hz, 1H), 7.60 (t, *J* = 1.7 Hz, 1H), 7.55 – 7.44 (m, 6H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.26 (m, 2H), 5.11 (d, *J* = 2.0 Hz, 2H), 3.72 (qt, *J* = 7.0, 1.7 Hz, 1H), 1.40 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 139.9, 131.5, 130.5, 129.3, 125.9, 123.3, 120.5, 119.5, 118.8, 112.6, 108.8, 85.6, 77.4, 32.8, 31.5, 23.9.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{19}N_2$ $[M + H]^+$ 335.1543, found 335.1542.

(*R*)-1-(1-Phenylpent-1-yn-3-yl)-4-(trifluoromethyl)benzene (96)



96

According to **General procedure B** with 1-(1-bromopropyl)-4-(trifluoromethyl)benzene **S96** (53.4 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **96** as a colorless oil (39.7 mg, 69% yield, 96% ee).

[α]$_D^{27}$ = −11 (*c* 2.8, CH_2Cl_2).

HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.52 min, t_R (major) = 19.36 min.

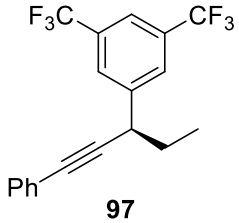
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 3.7 Hz, 1H), 7.45 (t, *J* = 2.9 Hz, 1H), 7.36 – 7.29 (m, 3H), 3.86 (t, *J* = 5.6 Hz, 1H), 1.96 – 1.82 (m, 2H), 1.07 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 131.7, 129.0 (q, *J* = 32.5 Hz), 128.3, 128.0, 127.9, 125.4 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 274.6 Hz), 123.4, 90.3, 84.0, 39.8, 31.5, 11.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.3 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{18}H_{16}F_3$ $[M + H]^+$ 289.1199, found 289.1201.

(*R*)-1-(1-Phenylpent-1-yn-3-yl)-3,5-bis(trifluoromethyl)benzene (97)



97

According to **General procedure B** with 1-(1-bromopropyl)-3,5-bis(trifluoromethyl)benzene **S97** (67.0 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **97** as a colorless oil (52.7 mg, 74% yield, 94% ee).

[α]$_D^{27}$ = −1.2 (*c* 2.3, CH_2Cl_2).

HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.36 min, t_R (minor) = 17.39 min.

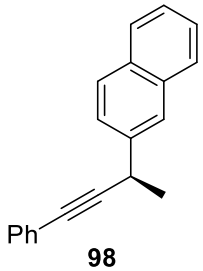
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.79 (s, 1H), 7.54 – 7.43 (m, 2H), 7.36 – 7.30 (m, 3H), 3.95 (dd, *J* = 8.0, 6.0 Hz, 1H), 2.04 – 1.75 (m, 2H), 1.10 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 131.74 (q, *J* = 32.5 Hz), 131.68, 128.4, 128.3, 127.8, 123.4 (q, *J* = 274.6 Hz), 123.0, 121.0 – 120.8 (m), 89.0, 84.9, 39.8, 31.5, 11.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8 (s, 6F).

HRMS (ESI) *m/z* calcd. for $C_{19}H_{15}F_6$ $[M + H]^+$ 357.1072, found 357.1065.

(*R*)-2-(4-Phenylbut-3-yn-2-yl)naphthalene (98)



98

According to **General procedure B** with 2-(1-bromoethyl)naphthalene **S98** (47.0 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **98** as a colorless oil (43.0 mg, 84% yield, 90% ee).

[α]$_D^{27}$ = –16 (*c* 3.3, CH_2Cl_2).

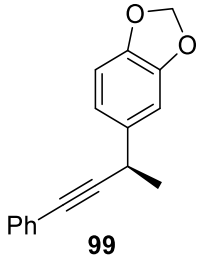
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 4.82 min, t_R (major) = 5.08 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.88 – 7.83 (m, 3H), 7.61 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.56 – 7.43 (m, 4H), 7.40 – 7.28 (m, 3H), 4.18 (q, *J* = 7.1 Hz, 1H), 1.70 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 133.6, 132.5, 131.7, 128.34, 128.29, 127.9, 127.8, 127.7, 126.1, 125.6, 125.2, 123.8, 92.6, 82.7, 32.7, 24.4.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{17}$ $[M + H]^+$ 257.1325, found 257.1322.

(*R*)- 5-(4-Phenylbut-3-yn-2-yl)benzo[*d*][1,3]dioxole (99)



99

According to **General procedure B** with 5-(1-bromoethyl)benzo[*d*][1,3]dioxole **S99** (45.8 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **99** as a colorless oil (25.0 mg, 50% yield, 91% ee).

[α]$_D^{27}$ = –0.77 (*c* 1.8, CH_2Cl_2).

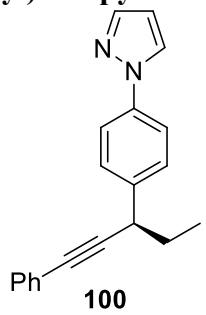
HPLC analysis: Chiralcel IA (hexane, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 20.33 min, t_R (minor) = 23.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.35 – 7.29 (m, 3H), 7.00 (d, *J* = 1.6 Hz, 1H), 6.92 (dd, *J* = 8.0, 1.6Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.98 (s, 2H), 3.94 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 146.3, 137.4, 131.6, 128.2, 127.8, 123.7, 119.9, 108.2, 107.6, 101.0, 92.6, 82.4, 32.2, 24.7.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{15}O_2$ $[M + H]^+$ 251.1067, found 251.1065

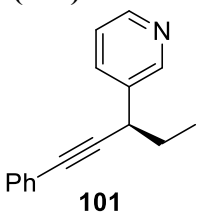
(*R*)-1-(4-(1-Phenylpent-1-yn-3-yl)phenyl)-1*H*-pyrazole (100)



100

According to **General procedure B** with 1-(4-(1-bromopropyl)phenyl)-1*H*-pyrazole **S100** (52.8 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 10/1) to yield the product **100** as a colorless oil (45.8 mg, 80% yield, 96% ee).
[α]$_D^{27}$ = –1.6 (*c* 4.3, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 17.73 min, t_R (major) = 19.99 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.3 Hz, 1H), 7.72 (d, *J* = 1.2 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 4.2 Hz, 1H), 7.46 (d, *J* = 1.9 Hz, 1H), 7.36 – 7.27 (m, 3H), 6.46 (t, *J* = 2.0 Hz, 1H), 3.84 (t, *J* = 6.9 Hz, 1H), 1.95 – 1.78 (m, 2H), 1.07 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.4, 138.9, 131.7, 128.6, 128.2, 127.8, 126.7, 123.7, 119.3, 107.5, 91.0, 83.7, 39.4, 31.6, 11.7.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}N_2$ $[M + H]^+$ 287.1543, found 287.1541.

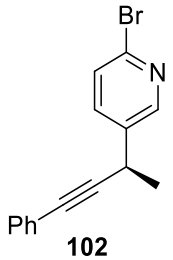
(*S*)-3-(1-Phenylpent-1-yn-3-yl)pyridine (101)



101

According to **General procedure B** with 3-(1-bromopropyl)pyridine **S101** (40.0 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 15/1) to yield the product **101** as a colorless oil (34.0 mg, 77% yield, 97% ee).
[α]$_D^{27}$ = –1.6 (*c* 1.9, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.01 min, t_R (major) = 9.10min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 1.9 Hz, 1H), 8.50 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.76 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.34 – 7.25 (m, 4H), 3.82 (t, *J* = 7.2 Hz, 1H), 1.95 – 1.76 (m, 2H), 1.07 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 148.2, 137.5, 135.1, 131.7, 128.3, 128.0, 123.4, 123.3, 89.9, 84.0, 37.5, 31.4, 11.7.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}N$ $[M + H]^+$ 222.1277, found 222.1276.

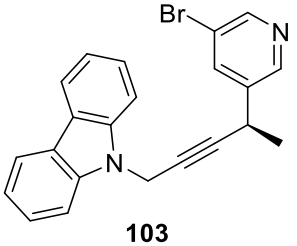
(*S*)-2-Bromo-5-(4-phenylbut-3-yn-2-yl)pyridine (102)



102

According to **General procedure B** with 2-bromo-5-(1-bromoethyl)pyridine **S102** (53.0 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 20/1) to yield the product **102** as a colorless oil (37.6 mg, 66% yield, 93% ee).
[α]$_D^{27}$ = –0.96 (*c* 2.6, CH_2Cl_2).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.41 min, t_R (major) = 9.24 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 2.6 Hz, 1H), 7.67 (dd, *J* = 8.2, 2.6 Hz, 1H), 7.50 – 7.39 (m, 3H), 7.35 – 7.27 (m, 3H), 3.98 (q, *J* = 7.1 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 140.3, 138.2, 137.4, 131.6, 128.3, 128.2, 128.0, 123.0, 90.4, 83.4, 29.6, 24.1.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{13}BrN$ $[M + H]^+$ 286.0226, found 286.0224.

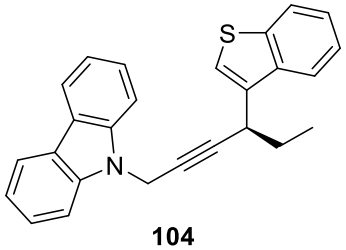
(*S*)-9-(4-(5-Bromopyridin-3-yl)pent-2-yn-1-yl)-9*H*-carbazole (103)



103

According to **General procedure B** with 3-bromo-5-(1-bromoethyl)pyridine **S103** (53.0 mg, 0.20 mmol, 1.0 equiv.) and 9-(prop-2-yn-1-yl)-9*H*-carbazole **S42** (61.5 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **103** as a colorless oil (59.9 mg, 77% yield, 87% ee).
[α]$_D^{27}$ = +31 (*c* 2.6, CH_2Cl_2).
HPLC analysis: Chiralcel ID (hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 26.47 min, t_R (minor) = 31.05 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.2 Hz, 1H), 8.43 (d, *J* = 1.9 Hz, 1H), 8.12 (dt, *J* = 7.8, 0.9 Hz, 2H), 7.75 (td, *J* = 2.1, 0.6 Hz, 1H), 7.56 – 7.46 (m, 4H), 7.32 – 7.27 (m, 2H), 5.09 (d, *J* = 2.1 Hz, 2H), 3.78 – 3.64 (m, 1H), 1.41 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 146.8, 140.1, 140.0, 137.1, 126.0, 123.3, 120.8, 120.5, 119.6, 108.8, 85.0, 77.6, 32.8, 29.3, 23.8.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{18}BrN_2$ $[M + H]^+$ 389.0648, found 389.0641.

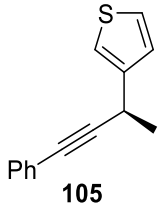
(*S*)-9-(4-(Benzo[*b*]thiophen-3-yl)hex-2-yn-1-yl)-9*H*-carbazole (104)



104

According to **General procedure B** with 3-(1-bromopropyl)benzo[*b*]thiophene **S104** (51.0 mg, 0.20 mmol, 1.0 equiv.) and 9-(prop-2-yn-1-yl)-9*H*-carbazole **S42** (61.5 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **104** as a colorless oil (59.1 mg, 78% yield, 99% ee).
[α]$_D^{27}$ = +19 (*c* 3.0, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 17.41 min, t_R (minor) = 20.76 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.88 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.49 (m, 4H), 7.40 – 7.29 (m, 4H), 7.24 (s, 1H), 5.13 (d, *J* = 2.0 Hz, 2H), 3.95 (td, *J* = 5.6, 2.4 Hz, 1H), 2.00 – 1.77 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.1, 137.4, 135.6, 125.8, 124.3, 123.9, 123.3, 123.0, 122.7, 121.9, 120.4, 119.4, 108.9, 85.2, 76.8, 33.5, 32.9, 28.6, 11.8.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{22}NS$ $[M + H]^+$ 380.1467, found 380.1461.

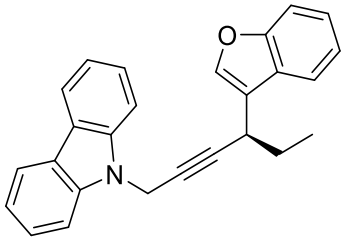
(*S*)-3-(4-Phenylbut-3-yn-2-yl)thiophene (105)



105

According to **General procedure B** with 3-(1-bromoethyl)thiophene **S105** (38.2 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **105** as a colorless oil (36.9 mg, 87% yield, 92% ee).
[α]$_D^{27}$ = –9.3 (*c* 1.4, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane, flow rate 0.4 mL/min, λ = 254 nm), t_R (minor) = 11.03 min, t_R (major) = 11.95 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.35 – 7.31 (m, 4H), 7.28 – 7.25 (m, 1H), 7.17 (dd, *J* = 4.9 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 131.6, 128.2, 127.8, 126.9, 125.9, 123.6, 120.3, 92.4, 81.8, 27.9, 23.2.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{13}S$ $[M + H]^+$ 213.0732, found 213.0729.

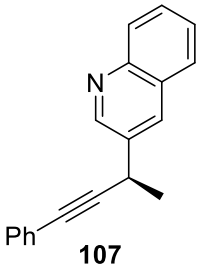
(*S*)-9-(4-(Benzofuran-3-yl)hex-2-yn-1-yl)-9*H*-carbazole (106)



106

According to **General procedure B** with 3-(1-bromopropyl)benzofuran **S106** (47.8 mg, 0.20 mmol, 1.0 equiv.) and 9-(prop-2-yn-1-yl)-9*H*-carbazole **S42** (61.5 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **106** as a colorless oil (55.2 mg, 76% yield, 98% ee).
[α]$_D^{27}$ = +28 (*c* 1.5, CH_2Cl_2).
HPLC analysis: Chiralcel AS3 (hexane/*i*-PrOH = 97/3, flow rate 0.7 mL/min, λ = 254 nm), t_R (minor) = 9.36 min, t_R (major) = 10.04 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.09 (m, 2H), 7.59 – 7.48 (m, 6H), 7.44 (s, 1H), 7.36 – 7.29 (m, 3H), 7.23 – 7.15 (m, 1H), 5.13 (d, *J* = 2.0 Hz, 2H), 3.83 – 3.69 (m, 1H), 1.99 – 1.76 (m, 2H), 0.99 (td, *J* = 7.2, 1.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 141.7, 140.0, 126.6, 125.8, 124.3, 123.3, 122.4, 120.44, 120.40, 120.1, 119.4, 111.6, 108.9, 84.7, 76.4, 32.8, 29.4, 28.3, 11.6.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{22}NO$ $[M + H]^+$ 364.1696, found 364.1688.

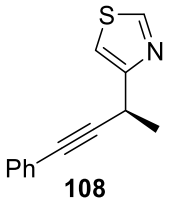
(*S*)-3-(4-Phenylbut-3-yn-2-yl)quinoline (107)



107

According to **General procedure D** with 3-(1-bromoethyl)quinoline **S107** (47.2 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 10/1) to yield the product **107** as a colorless oil (32.9 mg, 64% yield, 90% ee).
[α]$_D^{27}$ = +6.7 (*c* 2.1, CH_2Cl_2).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 14.05 min, t_R (major) = 18.30 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, *J* = 2.1 Hz, 1H), 8.21 (d, *J* = 2.1 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.52 – 7.44 (m, 2H), 7.39 – 7.27 (m, 3H), 4.21 (q, *J* = 7.1 Hz, 1H), 1.70 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 147.2, 135.9, 133.1, 131.7 129.2, 129.1, 128.3, 128.1, 128.0, 127.7, 126.8, 123.3, 91.1, 83.4, 30.4, 24.1.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{16}N$ $[M + H]^+$ 258.1277, found 258.1276.

(*S*)-4-(4-Phenylbut-3-yn-2-yl)thiazole (108)



108

According to **General procedure B** with 4-(1-bromoethyl)thiazole **S108** (38.4 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 20/1) to yield the product **108** as a colorless oil (26.0 mg, 61% yield, 82% ee).

[α]$_D^{27}$ = –6.1 (*c* 2.4, CH_2Cl_2).

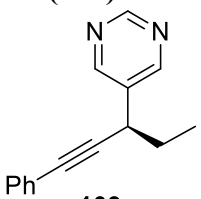
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.00 min, t_R (major) = 7.02 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 3.7 Hz, 1H), 7.45 (t, *J* = 2.9 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.33 – 7.27 (m, 3H), 4.25 (q, *J* = 7.1 Hz, 1H), 1.69 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 153.1, 131.7, 128.2, 128.0, 123.4, 113.6, 91.2, 82.4, 29.3, 22.1.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{12}NS$ $[M + H]^+$ 214.0685, found 214.0684.

(*S*)-5-(1-Phenylpent-1-yn-3-yl)pyrimidine (109)



109

According to **General procedure B** with 5-(1-bromopropyl)pyrimidine **S109** (40.2 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc= 10/1) to yield the product **109** as a colorless oil (31.1 mg, 70% yield, 97% ee).

[α]$_D^{27}$ = –1.1 (*c* 2.8, CH_2Cl_2).

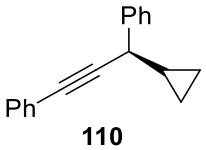
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 11.17 min, t_R (major) = 13.73 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.80 (s, 2H), 7.51 – 7.38 (m, 2H), 7.34 – 7.27 (m, 3H), 3.84 (dd, *J* = 7.6, 6.4 Hz, 1H), 1.96 – 1.79 (m, 2H), 1.09 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 156.1, 135.2, 131.7, 128.4, 128.3, 122.8, 88.2, 84.8, 35.4, 31.1, 11.6.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{15}N_2$ $[M + H]^+$ 223.1230, found 223.1230.

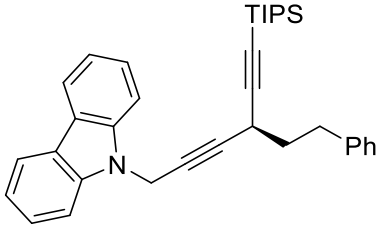
(*R*)-3-Cyclopropylprop-1-yne-1,3-diyl)dibenzene (110)



110

According to **General procedure D** with (chloro(cyclopropyl)methyl)benzene **S110** (33.3 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) to yield the product **110** as a colorless oil (24.1 mg, 52% yield, 92% ee).
$[\alpha]_D^{27}$ = +21 (*c* 0.63, CH_2Cl_2).
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 7.57 min, t_R (major) = 8.65 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.46 – 7.41 (m, 2H), 7.38 – 7.33 (m, 2H), 7.31 – 7.26 (m, 4H), 3.69 (d, *J* = 6.6 Hz, 1H), 1.24 – 1.19 (m, 1H), 0.71 – 0.42 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 131.8, 128.6, 128.3, 127.9, 127.7, 127.0, 123.8, 89.7, 83.4, 41.5, 17.6, 4.2, 3.3.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}$ $[M + H]^+$ 233.1325, found 233.1320.

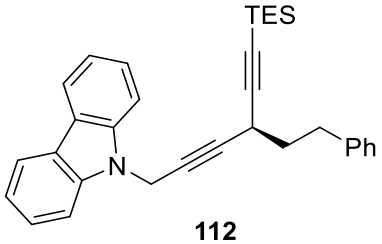
(*S*)-9-(4-Phenethyl-6-(triisopropylsilyl)hexa-2,5-diyn-1-yl)-9*H*-carbazole (111)



111

According to **General Procedure A** with (3-bromo-5-phenylpent-1-yn-1-yl)triisopropylsilane **S111** (83.8 mg, 0.30 mmol, 1.5 equiv), 9-(prop-2-yn-1-yl)-9*H*-carbazole **S42** (41.1 mg, 0.20 mmol, 1.0 equiv.), CuTc (3.0 mg, 0.016 mmol, 8.0 mol%), and **L*13** (20.1 mg, 0.024 mmol, 12 mol%) in CH_2Cl_2 (4 mL) for 40 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **111** as a slight yellow oil (93.7 mg, 93% yield, 96% ee).
$[\alpha]_D^{27}$ = –6.4 (*c* 3.0, CH_2Cl_2).
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 254 nm), t_R (minor) = 16.73 min, t_R (major) = 17.38 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.73 – 7.39 (m, 4H), 7.31 – 7.09 (m, 5H), 7.09 – 6.83 (m, 2H), 5.05 (d, *J* = 2.1 Hz, 2H), 3.59 – 3.13 (m, 1H), 2.84 – 2.54 (m, 2H), 1.91 (q, *J* = 7.5 Hz, 2H), 1.05 (s, 21H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 140.1, 128.7, 128.5, 126.1, 125.9, 123.3, 120.5, 119.5, 109.0, 105.5, 82.5, 82.3, 75.4, 37.6, 33.0, 32.9, 23.9, 18.8, 11.3.
HRMS (ESI) *m/z* calcd. for $C_{35}H_{42}NSi$ $[M + H]^+$ 504.3081, found 504.3079.

(*S*)-9-(4-Phenethyl-6-(triethylsilyl)hexa-2,5-diyn-1-yl)-9*H*-carbazole (112)



112

According to **General Procedure A** with (3-bromo-5-phenylpent-1-yn-1-yl)triethylsilane **S112**

(101.2 mg, 0.30 mmol, 1.5 equiv), 9-(prop-2-yn-1-yl)-9*H*-carbazole **S42** (41.1 mg, 0.20 mmol, 1.0 equiv.), CuTc (3.0 mg, 0.016 mmol, 8.0 mol%), and **L*13** (20.1 mg, 0.024 mmol, 12 mol%) in CH_2Cl_2 (4 mL) for 40 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **112** as a slight yellow oil (76.6 mg, 83% yield, 92% ee).

$[\alpha]_D^{27}$ = –5.7 (*c* 2.7, CH_2Cl_2).

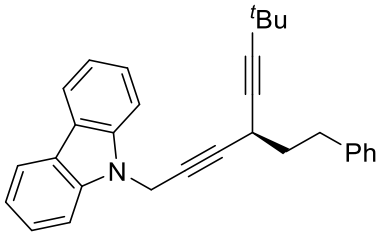
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 214 nm), t_R (minor) = 18.78 min, t_R (major) = 21.28 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dt, *J* = 7.8, 0.9 Hz, 2H), 7.54 – 7.43 (m, 4H), 7.29 – 7.17 (m, 4H), 7.17 – 7.11 (m, 1H), 7.04 – 6.99 (m, 2H), 5.06 (d, *J* = 2.1 Hz, 2H), 3.37 – 3.23 (m, 1H), 2.77 – 2.60 (m, 2H), 1.91 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 8.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.1, 128. 7, 128.5, 126.1, 125.9, 123.3, 120.5, 119.5, 109.0, 104.9, 83.5, 82.4, 75.6, 37.5, 32.9, 23.8, 7.6, 4.5.

HRMS (ESI) *m*/*z* calcd. for $C_{32}H_{36}NSi$ $[M + H]^+$ 462.2612, found 462.2608.

(*R*)-9-(7,7-Dimethyl-4-phenethylocta-2,5-diyn-1-yl)-9*H*-carbazole (113)



113

According to **General Procedure A** with (3-bromo-6,6-dimethylhept-4-yn-1-yl)benzene **S113** (83.8 mg, 0.30 mmol, 1.5 equiv), 9-(prop-2-yn-1-yl)-9*H*-carbazole **S42** (41.1 mg, 0.20 mmol, 1.0 equiv.), CuTc (3.0 mg, 0.016 mmol, 8.0 mol%), and **L*13** (20.1 mg, 0.024 mmol, 12 mol%) in CH_2Cl_2 for 40 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to yield the product **113** as a slight yellow oil (67.8 mg, 84% yield, 91% ee).

$[\alpha]_D^{27}$ = –5.8 (*c* 2.3, CH_2Cl_2).

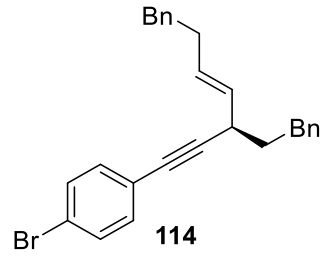
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 97/3, flow rate 0.4 mL/min, λ = 254 nm), t_R (minor) = 11.79 min, t_R (major) = 14.11 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.53 – 7.42 (m, 4H), 7.27 – 7.16 (m, 4H), 7.16 – 7.10 (m, 1H), 7.04 – 6.96 (m, 2H), 5.02 (d, *J* = 2.1 Hz, 2H), 3.27 – 3.16 (m, 1H), 2.72 – 2.57 (m, 2H), 1.86 (q, *J* = 7.5 Hz, 2H), 1.19 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.1, 128.7, 128.4, 126.0, 125.9, 123.3, 120.5, 119.5, 109.1, 90.4, 83.5, 76.2, 75.0, 37.8, 33.0, 31.2, 27.5, 22.7.

HRMS (ESI) m/z calcd. for $C_{30}H_{30}N$ $[M + H]^+$ 404.2373, found 404.2370.

(*R*,*E*)- (5-((4-Bromophenyl)ethynyl)hept-3-ene-1,7-diyl)dibenzene (114)



114

According to **General Procedure B** with (*E*)-(5-bromohept-3-ene-1,7-diyl)dibenzene **S114** (65.8 mg, 0.20 mmol, 1.0 equiv), 1-bromo-4-ethynylbenzene **S13** (72.4 mg, 0.40 mmol, 2.0 equiv.), and $Cu(PPh_3)_3Br$ (9.3 mg, 0.010 mmol, 5.0 mol%) in dioxane (4.0 mL) for 24 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether = 100) to yield the product **114** as a colorless oil (83 mg, 97% yield, *E*:*Z* = 4:1, 76% ee of the major product).

[α]$_D^{27}$ = –8.2 (*c* 1.2, CH_2Cl_2).

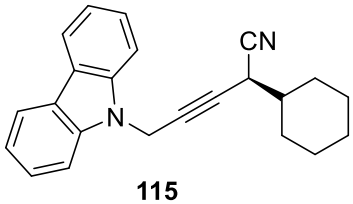
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.16 min, t_R (minor) = 20.55 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.23 (m, 6H), 7.21 – 7.16 (m, 6H), 5.77 (dtd, *J* = 15.0, 6.7, 1.3 Hz, 1H), 5.55 – 5.23 (m, 1H), 3.20 (q, *J* = 6.8 Hz, 1H), 2.89 – 2.61 (m, 4H), 2.53 – 2.24 (m, 2H), 2.01 – 1.73 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7(9), 141.7(5), 133.1, 131.4, 130.9, 129.8, 128.5(3), 128.5(0), 128.4, 128.3, 125.9, 125.8, 122.8, 121.8, 92.3, 82.5, 77.3, 37.3, 35.8, 34.5, 34.1, 33.2.

HRMS (ESI) m/z calcd. for $C_{27}H_{26}Br$ $[M + H]^+$ 429.1212, found 429.1208.

(*S*)-5-(9*H*-Carbazol-9-yl)-2-cyclohexylpent-3-ynenitrile (115)



115

According to **General procedure A** with 2-bromo-2-cyclohexylacetonitrile **S115** (60.3 mg, 0.30 mmol, 1.5 equiv.) and 9-(prop-2-yn-1-yl)-9*H*-carbazole **S42** (41.0 mg, 0.20 mmol, 1.0 equiv.) at –40 °C for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **115** as a colorless oil (39.8 mg, 61% yield, 77% ee).

[α]$_D^{27}$ = –2.8 (*c* 1.1, CH_2Cl_2).

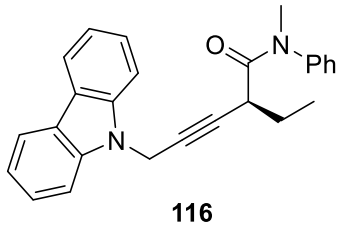
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 24.98 min, t_R (minor) = 34.36 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 2H), 7.57 – 7.45 (m, 4H), 7.34 – 7.28 (m, 2H), 5.11 – 5.07 (m, 2H), 3.37 – 7.27 (m, 1H), 1.84 – 1.62 (m, 6H), 1.25 – 1.04 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 125.9, 123.3, 120.5, 119.7, 116.6, 108.8, 79.1, 75.6, 40.7, 32.5, 30.0, 29.9, 29.8, 25.6, 25.5.

HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}N_2$ $[M + H]^+$ 327.1856, found 327.1850.

(*S*)-5-(9*H*-Carbazol-9-yl)-2-ethyl-*N*-methyl-*N*-phenylpent-3-ynamide (116)



116

According to **General Procedure B** with 2-bromo-*N*-methyl-*N*-phenylbutanamide **S116** (51.2 mg, 0.20 mmol, 1.0 equiv) and and 9-(prop-2-yn-1-yl)-9*H*-carbazole **S42** (61.5 mg, 0.30 mmol, 1.5 equiv.) for 40 h except that CuTc (3.0 mg, 0.016 mmol, 8.0 mol%), **L*13** (20.1 mg, 0.024 mmol, 12.0 mol%) were used, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate= 5/1) to yield the product **116** as a colorless oil (70.2 mg, 92% yield, 86% ee).

$[\alpha]_D^{27}$ = –143.4 (*c* 2.2, CH_2Cl_2).

HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 20.76 min, t_R (minor) = 23.44 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.52 – 7.44 (m, 4H), 7.29 – 7.23 (m, 2H), 7.14 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.94 – 6.87 (m, 2H), 5.00 (t, *J* = 2.0 Hz, 2H), 3.19 (s, 3H), 3.00 – 2.89 (m, 1H), 1.84 – 1.72 (m, 1H), 1.68 – 1.59 (m, 1H), 0.77 (t, *J* = 7.4 Hz, 3H).

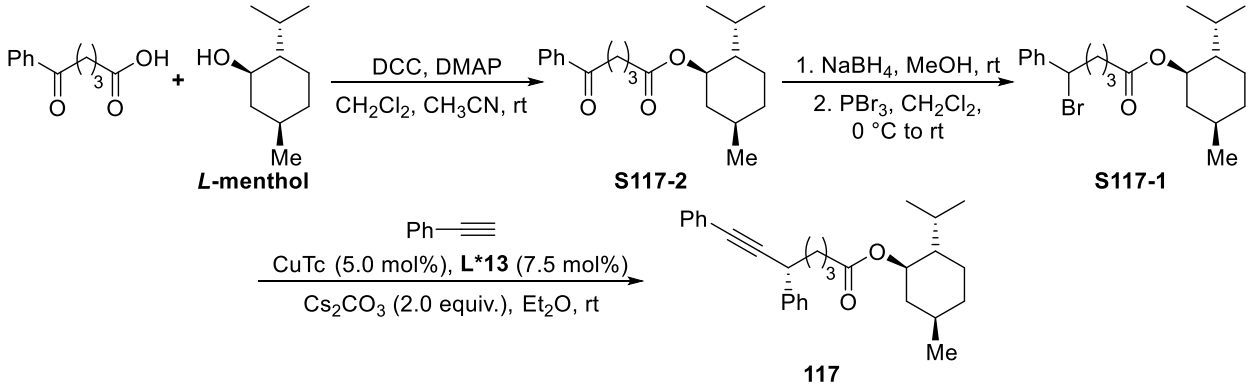
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 143.1, 140.0, 129.7, 127.9, 127.2, 125.8, 123.2, 120.4, 119.4, 109.0, 82. 6, 76.4, 37.8, 37.1, 32.8, 25.8, 11.8.

HRMS (ESI) m/z calcd. for $C_{26}H_{25}N_2O$ $[M + H]^+$ 381.1961, found 381.1957.

Procedure for synthetic applications

Synthesis of derivatives of bioactive or functional molecules

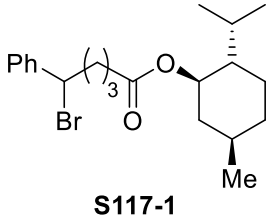
The synthesis of 117



To a solution of 5-oxo-5-phenylpentanoic acid (1.92 g, 10.0 mmol, 1.0 equiv.) in a mixture of CH_2Cl_2 (8.0 mL) and CH_3CN (8.0 mL) were added *L*-menthol (1.56 g, 10.0 mmol, 1.0 equiv.), dicyclohexylcarbodiimide (2.20 g, 11.0 mmol, 1.1 equiv.), and DMAP (122.0 mg, 1.0 mmol, 0.1 equiv.) sequentially at room temperature. The reaction mixture was stirred overnight. Water was added and the mixture was extracted with EtOAc three times. The combined organic layer was filtered through a short pad of silica gel and rinsed with elution (petroleum ether/EtOAc = 2/1). The filtrate was evaporated under reduced pressure to afford the crude product **S117-2** (2.10 g) as a colorless oil, which was directly used without further purification.

To a cooled solution of **S117-2** (1.00 g, crude product) in MeOH (15.0 mL) was added $NaBH_4$ (240.0 mg, 6.4 mmol) at 0 °C. The reaction mixture was stirred for 30 min, and then was quenched by saturated NH_4Cl. CH_2Cl_2 was used to extract the product from the aqueous layer three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was dissolved in anhydrous CH_2Cl_2 and cooled down to 0 °C. To this cooled solution was added PBr_3 (0.58 g, 2.1 mmol, 0.7 equiv.). The reaction mixture was stirred for 30 min and quenched by water. CH_2Cl_2 was used to extract the product from the aqueous layer three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by flash column chromatography to afford **S117-1** as a sticky oil (0.80 g, a mixture of diastereomers, 40% overall yield).

(1*R*,2*R*,5*R*)-2-Isopropyl-5-methylcyclohexyl 5-bromo-5-phenylpentanoat (S117-1)



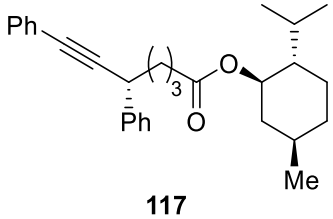
S117-1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 4.98 – 4.94 (m, 1H), 4.76 – 4.65 (m, 1H), 2.36 – 2.29 (m, 3H), 2.24 – 2.15 (m, 1H), 2.00 – 1.94 (m, 2H), 1.90 – 1.81 (m, 2H), 1.72 – 1.61 (m, 3H), 1.55 – 1.33 (m, 2H), 1.14 – 0.86 (m, 8H), 0.75 (t, *J* = 5.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 141.9, 141.8, 128.7, 128.4, 127.2, 74.2, 60.4, 54.8, 54.7, 46.9, 40.9, 39.2(5), 39.2(2), 34.2, 33.7, 33.7, 31.3, 26.2, 26.2, 23.8, 23.7, 23.3, 22.0, 20.7, 16.2.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{31}O_2$ $[M - Br]^+$ 315.2319, found 315.2313.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (*R*)-5,7-diphenylhept-6-ynoate (117)



117

According to **General procedure B** with **S117-1** (80.0 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (31.0 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 9/1) to yield the product **117** as a colorless oil (62.0 mg, 75% yield, dr > 20:1). The diastereomeric ratio was determined by crude ^{1}H NMR spectroscopy.

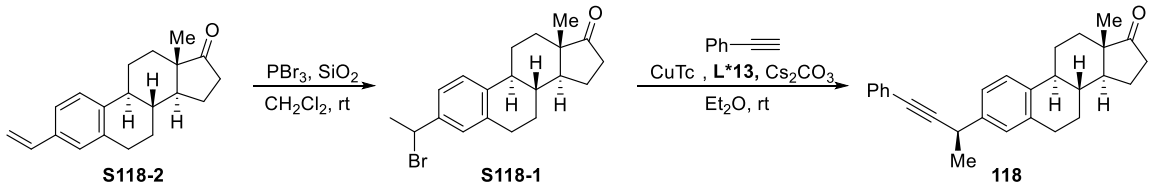
[α]$_D^{27}$ = −15 (*c* 4.6, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 4H), 7.40 – 7.27 (m, 6H), 4.71 (td, *J* = 10.9, 4.4 Hz, 1H), 3.97 – 3.85 (m, 1H), 2.42 – 2.33 (m, 2H), 2.04 – 1.98 (m, 1H), 1.98 – 1.82 (m, 5H), 1.74 – 1.66 (m, 2H), 1.57 – 1.46 (m, 1H), 1.44 – 1.35 (m, 1H), 1.14 – 0.96 (m, 2H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.87 – 0.82 (m, 1H), 0.77 (d, *J* = 7.0 Hz, 3H).

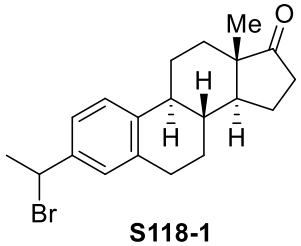
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 141.8, 131.6, 128.5, 128.2, 127.8, 127.4, 126.8, 123.6, 90.9, 83.6, 74.1, 47.0, 40.9, 38.1, 37.9, 34.3, 34.2, 31.4, 26.2, 23.4, 23.0, 22.0, 20.7, 16.2.

HRMS (ESI) *m/z* calcd. for $C_{29}H_{37}O_2$ $[M + H]^+$ 417.2788, found 417.2778.

The synthesis of 118



(8*R*,9*S*,13*S*,14*S*)-3-(1-Bromoethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (S118-1)



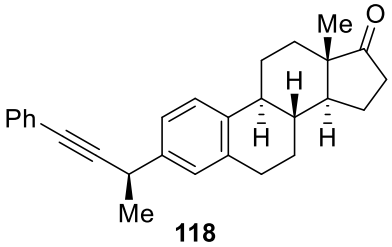
S118-1

To a stirred solution of **S118-2**[19] (0.56 g, 2.0 mmol, 1.0 equiv.) and silica gel (1.0 g) in CH_2Cl_2 (5.0 mL) was added a solution of PBr_3 (0.54 g, 2.0 mmol, 1.0 equiv.) in CH_2Cl_2 (2.0 mL) at room temperature. The reaction mixture was stirred for 20 min, filtered, and rinsed with CH_2Cl_2. The filtrate was washed with saturated $NaHCO_3$ and brine sequentially. The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to afford the product **S118-1** as a sticky solid

(0.71 g, 95% yield, dr = 1:1). The diastereomeric ratio was determined by crude ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.20 (s, 1H), 5.24 – 5.20 (m, 1H), 2.96 – 2.93 (m, 2H), 2.57 – 1.95 (m, 10H), 1.71 – 1.43 (m, 6H), 0.93 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 220.9, 140.7, 140.1, 136.9, 136.8, 127.3, 125.7, 124.2, 124.1, 50.4, 49.8, 49.7, 47.9, 44.4, 38.0, 35.8, 31.5, 29.4, 26.7, 26.7, 26.4, 25.6, 21.6, 13.8.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{25}O$ $[M - Br]^+$ 281.1900, found 281.1893.

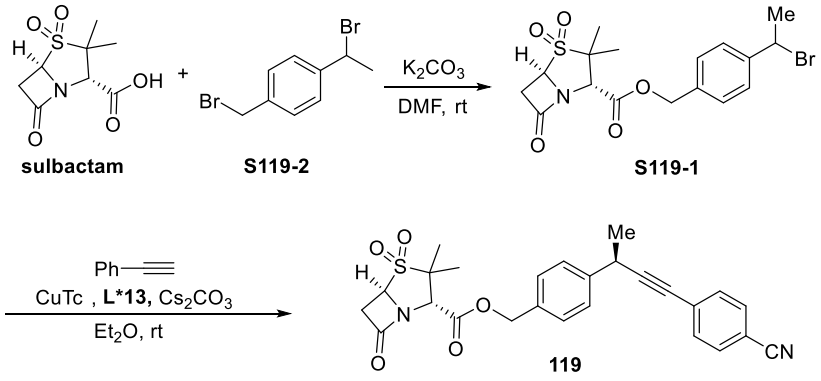
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-((*R*)-4-phenylbut-3-yn-2-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (118)



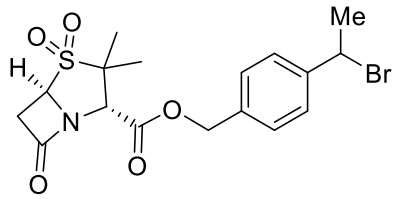
118

According to **General procedure B** with **S118-1** (72.0 mg, 0.20 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (31.0 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 9/1) to yield the product **118** as a colorless oil (66.0 mg, 87% yield, dr > 20:1). The diastereomeric ratio was determined by crude ^{1}H NMR spectroscopy.
[α]$_D^{27}$ = +46 (*c* 3.2, CH_2Cl_2).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.42 (m, 2H), 7.36 – 7.26 (m, 5H), 7.22 (s, 1H), 3.96 (q, *J* = 7.1 Hz, 1H), 2.98 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.63 – 2.44 (m, 2H), 2.34 (td, *J* = 10.9, 4.3 Hz, 1H), 2.23 – 2.15 (m, 1H), 2.13 – 1.98 (m, 3H), 1.72 – 1.44 (m, 9H), 0.95 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 220.9, 140.8, 138.1, 136.6, 131.6, 128.2, 127.7, 127.5, 125.6, 124.4, 123.8, 92.8, 82.2, 50.5, 48.0, 44.3, 38.2, 35.9, 32.0, 31.6, 29.5, 26.5, 25.7, 24.4, 21.6, 13.8.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{31}O$ $[M + H]^+$ 383.2369, found 383.2364.

The synthesis of 119



4-(1-Bromoethyl)benzyl(2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0] heptane-2-carboxylate 4,4-dioxide (S119-1)

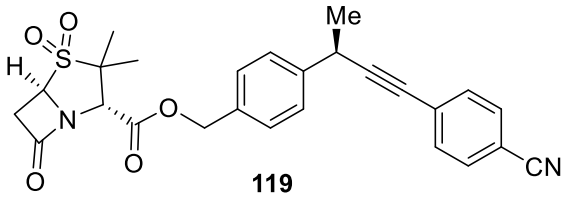


S119-1

To a solution of sulbactam (70.0 mg, 0.30 mmol, 1.0 equiv.) in DMF (2.0 mL) was added K_2CO_3 (42.0 mg, 0.30 mmol, 1.0 equiv.) and **S119-2** (83.0 mg, 0.30 mmol, 1.0 equiv.). The reaction mixture was stirred for 3 h and quenched with water. Et_2O was added and the organic layer was washed with water two times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **S119-1** as a sticky oil (88.0 mg, a mixture of diastereomers, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 5.29 – 5.14 (m, 3H), 4.62 (dd, *J* = 4.3, 2.1 Hz, 1H), 4.43 (s, 1H), 3.59 – 3.36 (m, 2H), 2.05 (d, *J* = 6.9 Hz, 3H), 1.58 (s, 3H), 1.31 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 166.8, 144.1, 134.4, 129.1, 127.3, 67.6, 63.2, 62.8, 61.1, 48.6, 38.3, 26.7, 20.2, 18.6.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{21}BrNO_5S$ $[M + H]^+$ 430.0318, found 430.0308.

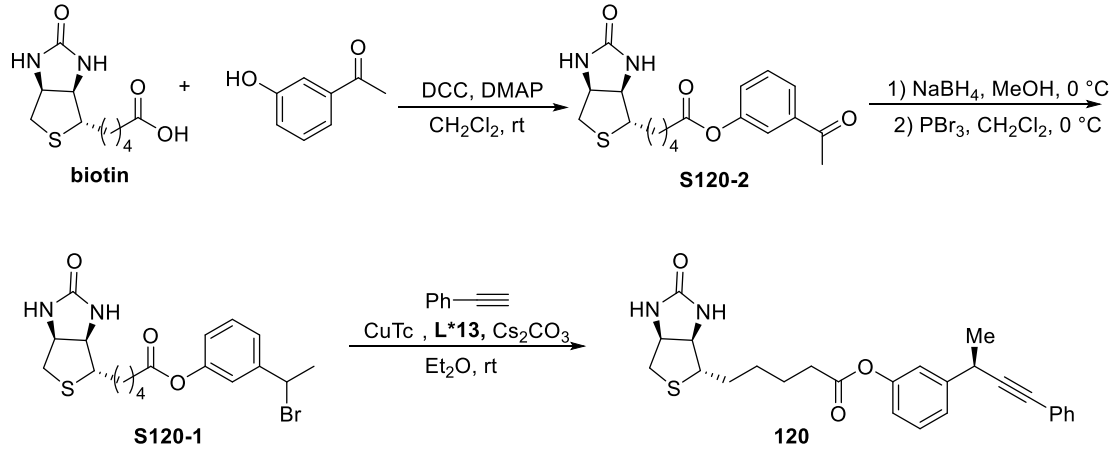
4-((*R*)-4-(4-Cyanophenyl)but-3-yn-2-yl)benzyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (119)



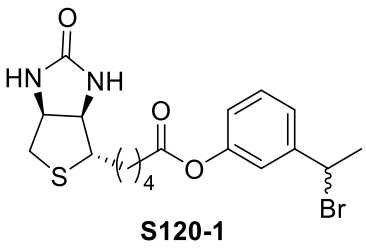
119

According to **General procedure B** with **S119-1** (43.0 mg, 0.10 mmol, 1.0 equiv.) and 1-ethynyl-4-cyanobenzene **S16** (16.0 mg, 0.15 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the product **119** as a colorless oil (24.0 mg, 50% yield, dr > 20:1). The diastereomeric ratio was determined by crude ^{1}H NMR spectroscopy.
$[\alpha]_D^{27}$ = +132 (*c* 1.1, CH_2Cl_2).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 2H), 7.57 – 7.50 (m, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 5.34 – 5.15 (m, 2H), 4.62 (dd, *J* = 4.1, 2.2 Hz, 1H), 4.43 (s, 1H), 4.04 (q, *J* = 7.1 Hz, 1H), 3.58 – 3.38 (m, 2H), 1.66 – 1.57 (m, 6H), 1.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 166.8, 143.5, 133.0, 132.1, 131.9, 129.2, 128.4, 127.3, 118.5, 111.2, 96.9, 81.3, 67.8, 63.2, 62.7, 61.10, 38.35, 32.3, 24.0, 20.1, 18.6.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{25}N_2O_5S$ $[M + H]^+$ 477.1479, found 477.1464.

The synthesis of 120



3-(1-Bromoethyl)phenyl5-((3*aR*,4*S*,6*aS*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)pentanoate (S120-1)



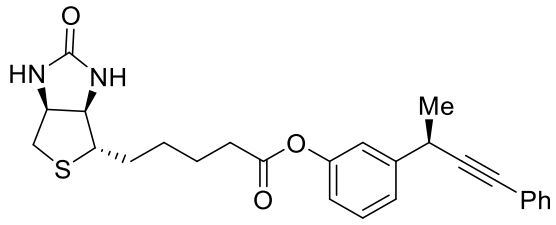
To a solution of biotin (0.97 g, 4.0 mmol, 1.0 equiv.) and 1-(3-hydroxyphenyl)ethan-1-one (0.60 g, 4.4 mmol, 1.1 equiv.) in CH_2Cl_2 (20.0 mL) were added sequentially DCC (0.90 g, 4.4 mmol, 1.1 equiv.) and DMAP (50.0 mg, 0.40 mmol, 0.1 equiv.) at room temperature. The reaction mixture was stirred for 12 h, then quenched by water, and extracted with EtOAc three times. The combined organic layer was washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford a residue, which was filtered through a short pad of silica gel and rinsed with EtOAc. The filtrate was concentrated to afford the crude product **S120-2** (0.80 g), which was directly used without further purification.

To a cooled solution of **S120-2** (0.80 g, crude product) in MeOH (15.0 mL) was added $NaBH_4$ (80.0 mg, 2.1 mmol) at 0 °C. The reaction mixture was stirred for 30 min, then quenched by saturated NH_4Cl, and extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was dissolved in anhydrous CH_2Cl_2 (15.0 mL) and cooled down to 0 °C. To this cooled solution was added PBr_3 (0.19 g, 0.7 mmol) and the reaction mixture was stirred for 30 min. After completion of reaction, the reaction was quenched by water and extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was purified by flash column chromatography to afford **S120-1** as a sticky oil (0.20 g, 10% overall yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 2H), 7.19 (s, *J* = 1.9 Hz, 1H), 7.05 – 7.02 (m, 1H), 6.06 (s, 0.75H), 5.89 (s, 0.25H), 5.48 (s, 1H), 5.20 (q, *J* = 6.9 Hz, 0.75H), 5.09 (q, *J* = 6.9 Hz, 0.25H), 4.53 – 4.50 (m, 1H), 4.35 – 4.30 (m, 1H), 3.24 – 3.14 (m, 1H), 2.94 – 2.89 (m, 1H), 2.76

– 2.72 (m, 1H), 2.61 (t, *J* = 7.5 Hz, 1.5H), 2.35 (t, *J* = 7.5 Hz, 0.5H), 2.05 (d, *J* = 6.9 Hz, 2H), 1.85 (d, *J* = 6.9 Hz, 1H), 1.83 – 1.65 (m, 4H), 1.60 – 1.46 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 163.8, 150.7, 144.8, 129.6, 124.2, 121.6, 120.1, 62.0, 60.1, 55.5, 48.4, 40.6, 34.0, 28.4, 28.3, 26.7, 24.7.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{24}BrN_2O_3S$ $[M + H]^+$ 427.0686, found 427.0679.

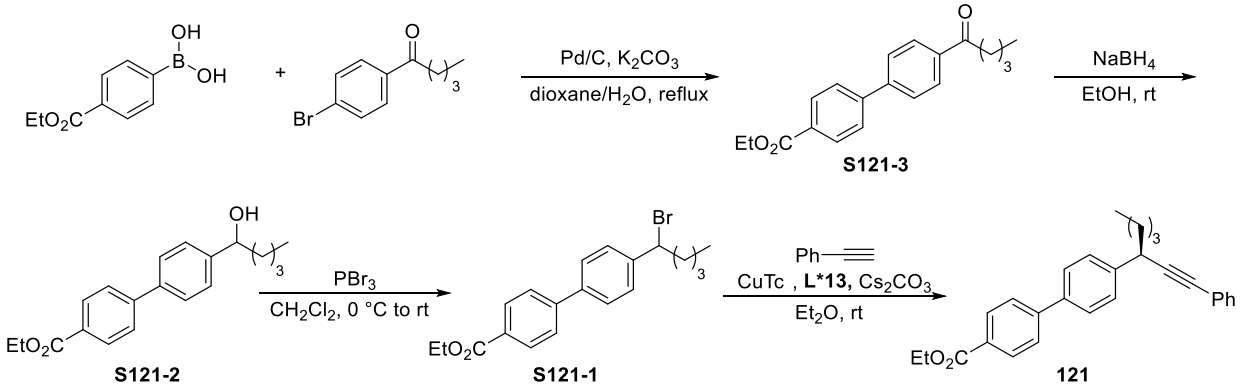
3-((*R*)-4-Phenylbut-3-yn-2-yl)phenyl-5-((3*aR*,4*S*,6*aS*)-2-oxohexahydro-1*H*-thieno[3,4 -*d*]imidazol-4-yl)pentanoate (120)



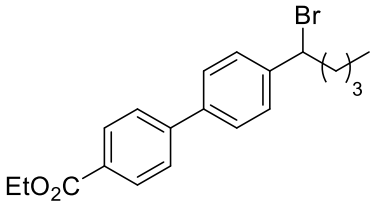
120

According to **General procedure B** with **S120-1** (43.0 mg, 0.10 mmol, 1.0 equiv.) and ethynylbenzene **S1-2** (15.3 mg, 0.15 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 98/2) to yield the product **120** as a colorless oil (11.0 mg, 25% yield, dr > 20:1). The diastereomeric ratio was determined by crude ^{1}H NMR spectroscopy.
[α]$_D^{27}$ = +12 (*c* 0.90, CH_2Cl_2).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.39 – 7.30 (m, 5H), 7.18 (s, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 5.65 (s, 1H), 5.13 (s, 1H), 4.51 (d, *J* = 12.7 Hz, 1H), 4.33 (d, *J* = 12.5 Hz, 1H), 4.01 (q, *J* = 7.1 Hz, 1H), 3.20 (t, *J* = 6.7 Hz, 1H), 2.92 (dd, *J* = 12.9, 5.2 Hz, 1H), 2.75 (d, *J* = 12.8 Hz, 1H), 2.62 (t, *J* = 7.4 Hz, 2H), 1.87 – 1.76 (m, 4H), 1.62 – 1.53 (m, 5H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 163.4, 150.8, 145.0, 131.7, 129.5, 128.2, 127.9, 124.5, 123.5, 120.1, 119.9, 92.0, 82.7, 62.0, 60.1, 55.4, 40.6, 34.0, 32.3, 28.4, 28.3, 24.7, 24.3.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{29}N_2O_3S$ $[M + H]^+$ 449.1893, found 449.1884.

The synthesis of 121



Ethyl 4'-(1-bromopentyl)-[1,1'-biphenyl]-4-carboxylate (S121-1)



S121-1

To a mixture of (4-(ethoxycarbonyl)phenyl)boronic acid (2.3 g, 12.0 mmol, 1.2 equiv.), 1-(4-bromophenyl)pentan-1-one (2.41 g, 10.0 mmol, 1.0 equiv.), and K_2CO_3 (4.14 g, 30.0 mmol, 3.0 equiv.) in a mixed solvent of H_2O (15.0 mL) and dioxane (15.0 mL) was added Pd/C (100.0 mg, 10% *w*/*w* Pd on carbon,0.094 mmol, 1 mol%) under argon atmosphere and the mixture was refluxed for 4 h. After completion of reaction, the mixture was cooled to room temperature, diluted with EtOAc and water, and then, extracted with EtOAc three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the coupling product **S121-3** as a white solid (2.5 g, 81%).

According to ***Method b*** of **General procedure 4** with **S121-3** (1.6 g, 5.0 mmol, 1.0 equiv.), **S121-1** was obtained as a white solid (1.7 g, 92% crude yield over two steps).

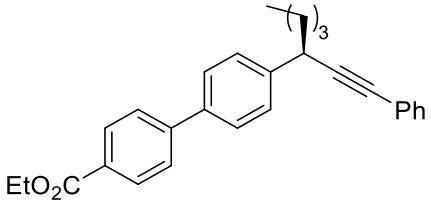
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 5.03 (t, *J* = 7.6 Hz, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 2.41 – 2.28 (m, 1H), 2.26 – 2.15 (m, 1H), 1.61 – 1.26 (m, 7H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.8, 142.3, 139.9, 130.1, 129.5, 127.9, 127.6, 126.9, 61.0, 55.2, 39.6, 30.4, 22.1, 14.4, 13.9.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}BrO_2$ $[M + H]^+$ 375.0954, found 375.0954.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}O_2$ $[M - Br]^+$ 295.1693, found 295.1693.

Ethyl (*R*)-4'-(1-phenylhept-1-yn-3-yl)-[1,1'-biphenyl]-4-carboxylate (121)



121

According to **General procedure B** with ethynylbenzene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) and ethyl 4'-(1-bromopentyl)-[1,1'-biphenyl]-4-carboxylate **S121-1** (75.0 mg, 0.20 mmol, 1.0 equiv.) for 48 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **121** as a colorless oil (65.7 mg, 83% yield, 96% ee).

$[\alpha]_D^{27}$ = –3.5 (*c* 3.4, CH_2Cl_2).

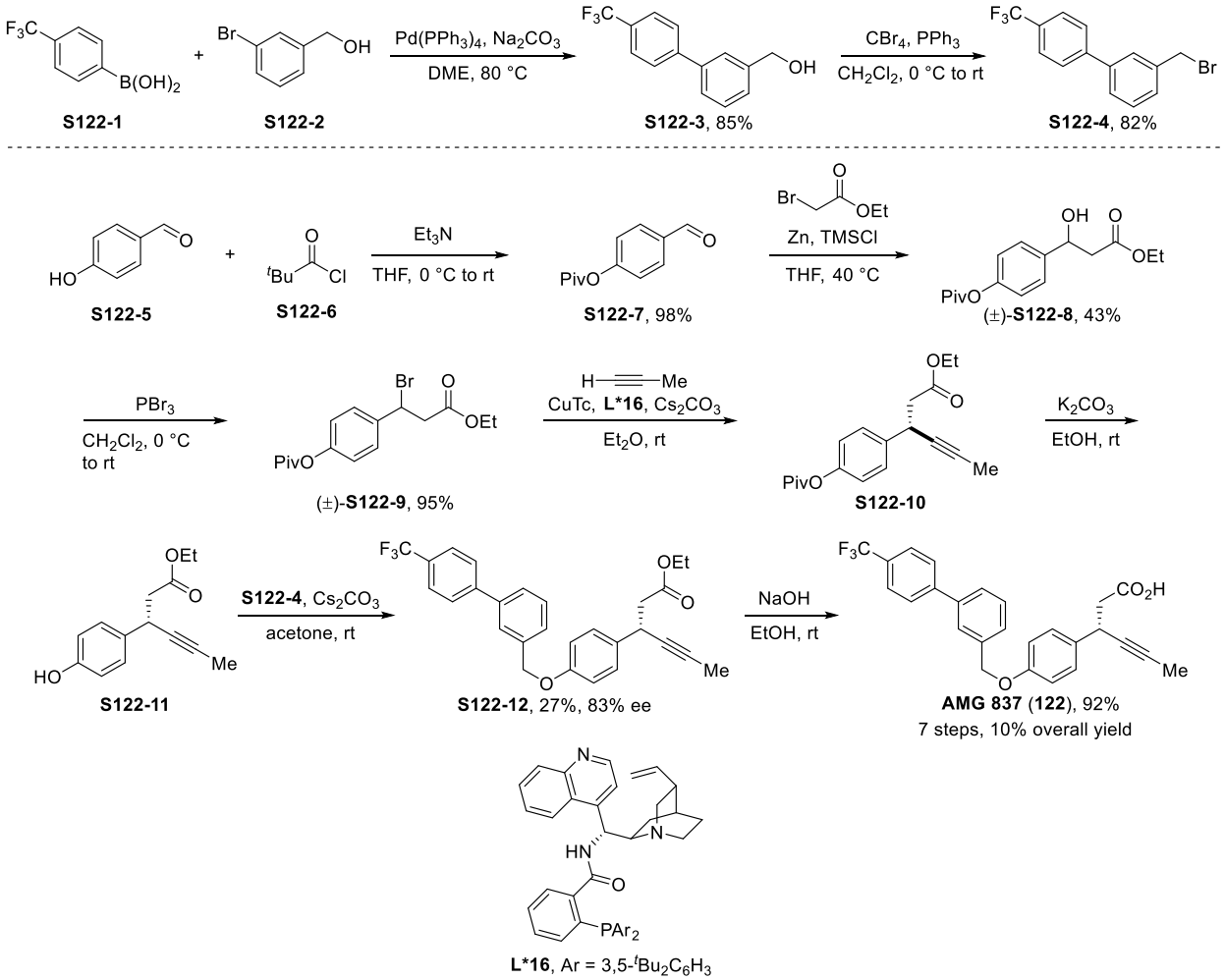
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.76 min, t_R (major) = 10.88 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.45 (m, 2H), 7.33 – 7.24 (m, 3H), 4.39 (q, *J* = 7.1 Hz,

2H), 3.88 (t, *J* = 7.2 Hz, 1H), 1.94 – 1.79 (m, 2H), 1.59 – 1.44 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 4H), 1.38 – 1.32 (m, 1H), 0.92 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 145.3, 142.5, 138.4, 131.7, 130.1, 129.2, 128.3, 128.1, 127.8, 127.4, 126.9, 123.8, 91.5, 83.4, 61.0, 38.4, 38.2, 29.7, 22.5, 14.4, 14.1.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{29}O_2$ $[M + H]^+$ 397.2162, found 397.2162.

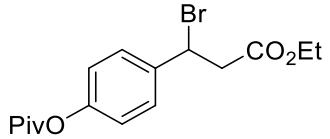
The synthesis of C(sp^3)-C(sp) drug and drug leads

The synthesis of AMG 837(122)



S122-4 was synthesized according to literature procedures[20].

4-(1-Bromo-3-ethoxy-3-oxopropyl)phenyl pivalate (S122-9)



(±)–**S122-9**

To a solution of 4-hydroxybenzaldehyde **S122-5** (3.7 g, 30 mmol, 1.0 equiv.) in THF (30.0 mL) were added sequentially Et_3N (6.2 mL, 45 mmol, 1.5 equiv.) and pivaloyl chloride **S122-6** (5.5 mL, 45 mmol, 1.5 equiv.) at 0 °C. Then, the reaction mixture was warmed up to room temperature and

stirred for 2 h. After completion of reaction, the reaction was quenched by saturated NH_4Cl and extracted with EtOAc three times. The organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure, and purified by column chromatography on silica gel (petroleum ether/EtOAc = 8/1) to yield the desired product **S122-7** (6.1 g, 98% yield).

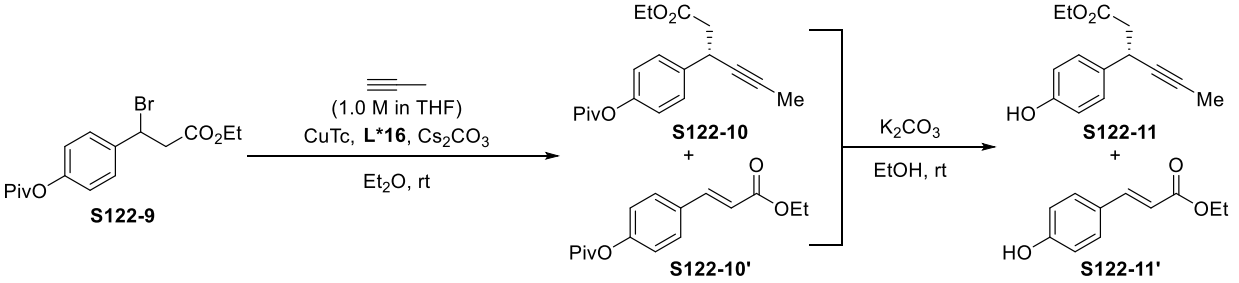
To a suspension of activated Zn power (1.10 g, 17.0 mmol, 1.7 equiv.) in dry THF (20.0 mL) was added TMSCl (70 μL, 0.50 mmol) and the reaction mixture was refluxed for 30 min. After that, ethyl 2-bromoacetate (1.30 mL, 12.0 mmol, 1.2 equiv.) was added dropwise to the suspension at 40 °C and the stirring was continued for another 30 min under the same conditions. Then, 4-formylphenyl pivalate **S122-7** (2.10 g, 10.0 mmol, 1.0 equiv.) was slowly added to the suspension and the reaction mixture was stirred at room temperature for 8 h. After completion of reaction, the reaction mixture was quenched by saturated NH_4Cl and extracted with EtOAc three times. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated, and the residue was purified by column chromatography (petroleum ether/EtOAc = 5/1) to yield the desired product **S122-8** (1.30 g, 43% yield). The analytic data were consistent with those in literature[21].

To a solution of 4-(3-ethoxy-1-hydroxy-3-oxopropyl)phenyl pivalate **S122-8** (588.0 mg, 2.0 mmol, 1.0 equiv.) in CH_2Cl_2 (6.0 mL) was slowly added PBr_3 (0.13 mL, 1.4 mmol) at 0 °C. Then, the reaction mixture was warmed up to room temperature and stirred for another 3 h. After completion of reaction, the reaction was quenched by saturated Na_2CO_3 and extracted with CH_2Cl_2 three times. The organic layer was washed by brine, dried over anhydrous Na_2SO_4, filtered through a pad of silica gel, and concentrated under reduced pressure to afford the crude product **S122-9** (678.3 mg, 95% yield), which was directly used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 5.40 (dd, J = 8.8, 6.4 Hz, 1H), 4.20 – 4.06 (m, 2H), 3.32 (dd, J = 16.2, 8.9 Hz, 1H), 3.18 (dd, J = 16.1, 6.3 Hz, 1H), 1.35 (s, 9H), 1.23 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 169.5, 151.1, 138.1, 128.3, 121.9, 61.1, 47.2, 45.0, 39.1, 27.1, 14.1.

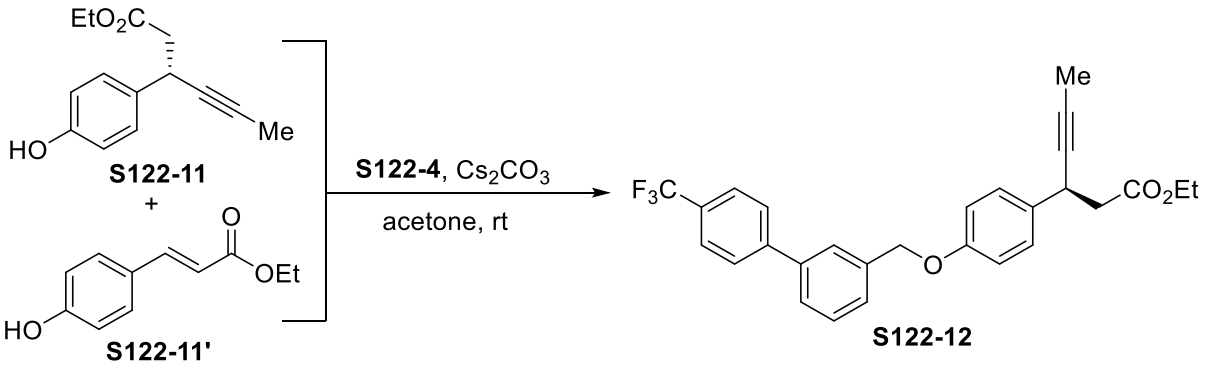
HRMS (ESI) *m/z* calcd. for $C_{16}H_{21}O_4$ $[M - Br]^+$ 277.1434, found 277.1429.



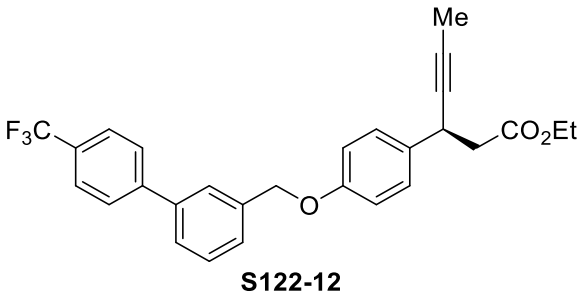
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (15.2 mg, 0.080 mmol, 20.0 mol%), **L*16** (97.0 mg, 0.12 mmol, 30.0 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 2.0 equiv.), and anhydrous Et_2O (8.0 mL). Then, 4-(1-bromo-3-ethoxy-3-oxopropyl)phenyl pivalate **S122-9** (143.0 mg, 0.40 mmol, 1.0 equiv.) and propyne (1.0 M in THF, 2.0 mL, 2.0 mmol, 5.0 equiv.) were added sequentially and the reaction mixture was stirred at room temperature for 72 h. Upon completion, the precipitate was filtered off and washed by Et_2O. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to afford an inseparable mixture of products **S122-10** and **S122-10'**.

To a solution of the mixture of **S122-10** and **S122-10'** in EtOH (4.0 mL) was added K_2CO_3 powder (165.6 mg, 1.2 mmol, 3.0 equiv.) in one portion and the reaction mixture was stirred at room

temperature for 4 h. Upon completion, the reaction mixture was diluted with EtOAc and washed by 1.0 M HCl followed by brine. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated to afford an inseparable mixture of products **S122-11** and **S122-11'**.

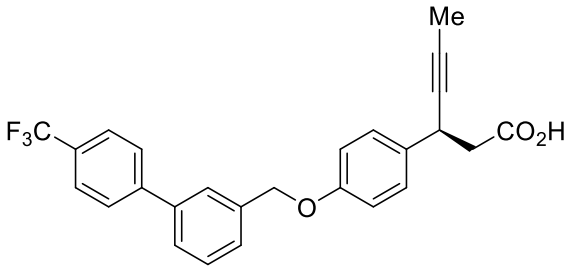


(*S*)-Ethyl-3-(4-((4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)methoxy)phenyl)hex-4-ynoate (S122-12)



To a solution of the mixture of **S122-11** and **S122-11'** in acetone (4.0 mL) were added 3-(bromomethyl)-4'-(trifluoromethyl)-1,1'-biphenyl **S122-4** (138.6 mg, 0.44 mmol, 1.1 equiv.) and Cs_2CO_3 powder (143.4 mg, 0.44 mmol, 1.1 equiv.) and the reaction mixture was stirred at room temperature for 24 h. After completion of reaction, the solvent was removed under reduced pressure. The residue was diluted with water and EtOAc and the aqueous layer was extracted with EtOAc three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield product **S122-12** (50.3 mg, 27% yield over three steps, 83% ee).
$[\alpha]_D^{27}$ = +4.5 (*c* 0.71, CH_2Cl_2).
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.77 min, t_R (major) = 11.98 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 4H), 7.66 (s, 1H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.12 (s, 2H), 4.19 – 4.01 (m, 3H), 2.75 (dd, *J* = 15.1, 8.4 Hz, 1H), 2.65 (dd, *J* = 15.1, 7.0 Hz, 1H), 1.83 (d, *J* = 2.2 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 157.7, 144.4, 140.2, 137.9, 133.8, 129.5 (q, *J* = 32.4 Hz), 129.3, 128.5, 127.5, 127.3, 126.9, 126.3, 125.8 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 271.9 Hz), 114.9, 79.6, 78.8, 69.9, 60.6, 43.6, 33.5, 14.2, 3.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ –62.4 (s, 3F).
HRMS (ESI) *m/z* calcd. for $C_{28}H_{26}F_3O_3$ $[M + H]^+$ 467.1829, found 467.1820.

(*S*)-3-(4-((4'-(Trifluoromethyl)-[1,1'-biphenyl]-3-yl)methoxy)phenyl)hex-4-ynoic acid (122 (AMG 837))



122 (**AMG 837**)

A mixture of **S122-12** (30.0 mg, 0.064 mmol) and NaOH (10% in water, 0.070 mL, 0.19 mmol, 3.0 equiv.) in EtOH (1.0 mL) was stirred at room temperature for 5 h. After completion of reaction, the pH of the reaction mixture was adjusted to 1~2 with 3.0 M HCl. The aqueous phase was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to afford the desired product **122 (AMG 837)** (25.9 mg, 92% yield).

[α]$_D^{27}$ = +4.3 (*c* 0.75, CH_2Cl_2).

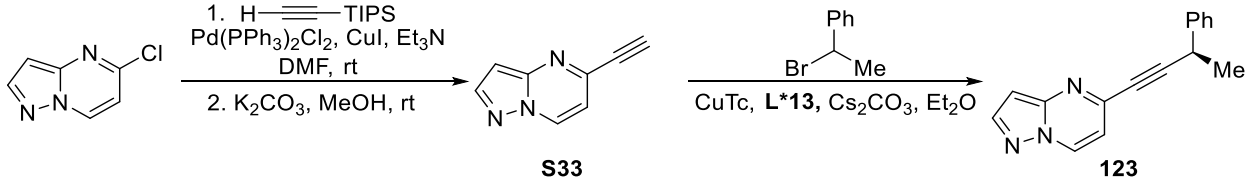
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 4H), 7.67 (s, 1H), 7.57 (d, *J* = 6.8 Hz, 1H), 7.55 – 7.44 (., 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 5.13 (s, 2H), 4.08 (s, 1H), 2.83 (dd, *J* = 15.6, 8.4 Hz, 1H), 2.73 (dd, *J* = 15.7, 6.6 Hz, 1H), 1.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 157.8, 144.4, 140.2, 137.9, 133.4, 129.5 (q, *J* = 32.0 Hz), 129.3, 128.5, 127.5, 127.3, 126.9, 126.4, 125.8 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 270.3 Hz), 115.0, 79.4, 79.2, 69.9, 43.3, 33.2, 3.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.3 (s, 3F).

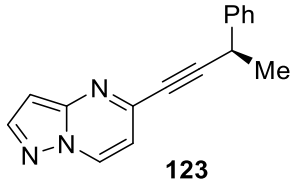
HRMS (ESI) *m/z* calcd. for $C_{26}H_{22}F_3O_3$ $[M + H]^+$ 439.1516, found 439.1506.

The synthesis of 123



S33 **123**

(*R*)-5-(3-Phenylbut-1-yn-1-yl)pyrazolo[1,5-*a*]pyrimidine (123)



123

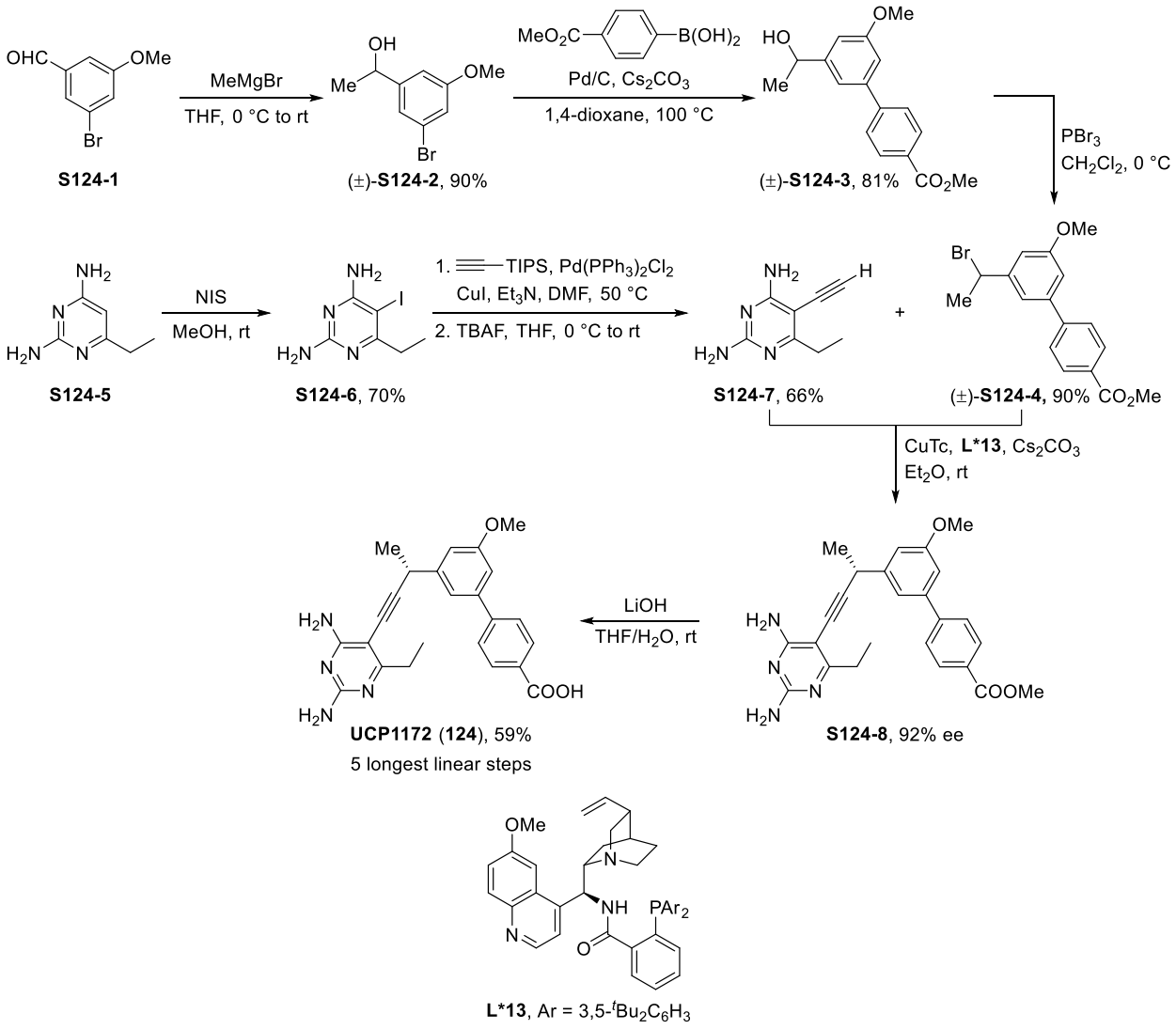
According to **General procedure A** with (1-bromoethyl)benzene **S1-1** (55.2 mg, 0.30 mmol, 1.5 equiv.) and 5-ethynylpyrazolo[1,5-*a*]pyrimidine **S33** (28.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product **123** as a colorless oil (34.1 mg, 69% yield, 93% ee).

[α]$_D^{27}$ = –8.1 (*c* 0.70, CH_2Cl_2).

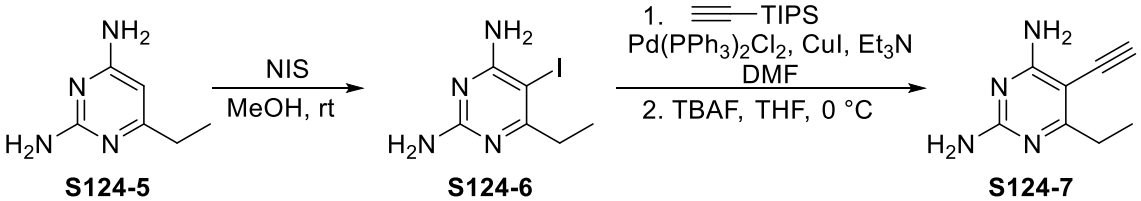
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 95/5, flow rate 0.3 mL/min, λ = 254 nm), t_R (minor) = 52.07 min, t_R (major) = 54.80 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.2 Hz, 1H), 8.18 – 8.07 (m, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.25 (m, 1H), 6.86 (d, *J* = 7.0 Hz, 1H), 6.68 (s, 1H), 4.05 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 145.7, 142.5, 141.8, 134.5, 128.8, 127.1, 127.0, 110.8, 97.3, 97.0, 81.0, 32.5, 23.8.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{13}N_3$ $[M + H]^+$ 248.1182, found 248.1180.

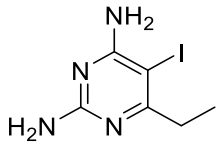
The synthesis of 124 (UCP1172)



The synthesis of S124-7



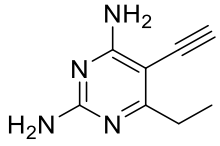
6-Ethyl-5-iodopyrimidine-2,4-diamine (S124-6)[22]



S124-6

A mixture of 2,4-diamino-6-ethylpyrimidine **S124-5** (0.54 g, 3.9 mmol, 1.0 equiv.) and *N*-iodosuccinimide (884.0 mg, 3.9 mmol, 1.0 equiv.) in MeOH (10.0 mL) was stirred at room temperature for 30 min. After completion of reaction, the reaction mixture was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to afford the product **S124-6** as a white solid (0.73 g, 70% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (br s, 2H), 5.12 (br s, 2H), 2.72 (q, *J* = 7.5 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 172.8, 162.7, 162.1, 34.4, 12.4.

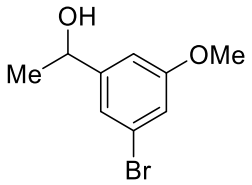
6-Ethyl-5-ethynylpyrimidine-2,4-diamine (S124-7)



S124-7

Followed the **General procedure 2** with **S124-6** (0.66 g, 2.5 mmol, 1.0 equiv.), **S124-7** was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 1/4) as a brown powder (0.27 g, 66% yield).
^{1}H NMR (400 MHz, CD_3OD) δ 3.84 (s, 1H), 2.54 (q, *J* = 7.7 Hz, 2H), 1.10 (t, *J* = 7.7 Hz, 3H).
^{13}C NMR (100 MHz, CD_3OD) δ 173.1, 165.1, 161.2, 88.2, 86.4, 76.2, 28.7, 11.7.
HRMS (ESI) *m/z* calcd. for $C_8H_{14}N_4$ $[M + H]^+$ 163.0978, found 163.0977.

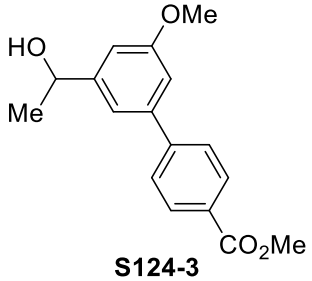
1-(3-Bromo-5-methoxyphenyl)ethanol (S124-2)



S124-2

To a solution of 3-bromo-5-methoxybenzaldehyde **S124-1** (0.68 g, 3.0 mmol, 1.0 equiv.) in dry THF (5.0 mL) was slowly added methylmagnesium bromide (3.6 mL, 1.0 M in THF, 3.6 mmol, 1.2 equiv.) at 0 °C under argon atmosphere. The reaction mixture was warmed up to room temperature and stirred for 1 h until the aldehyde was completely consumed (monitored by TLC). The reaction mixture was quenched by 3.0 M HCl and extracted with CH_2Cl_2 three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford the **S124-2** as a colorless oil (0.63 g, 90% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 1H), 6.98 – 6.93 (m, 1H), 6.87 – 6.83 (m, 1H), 4.82 (q, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 1.46 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 149.1, 122.8, 120.9, 115.9, 110.2, 69.8, 55.5, 25.2.

Methyl 3'-(1-hydroxyethyl)-5'-methoxy-[1,1'-biphenyl]-4-carboxylate (S124-3)



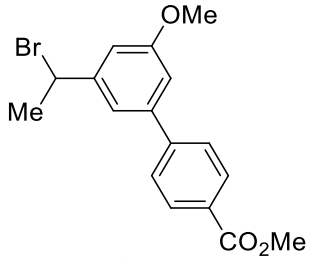
S124-3

To a mixture of (4-(methoxycarbonyl)phenyl)boronic acid (0.43 g, 2.4 mmol, 1.2 equiv.), 1-(3-bromo-5-methoxyphenyl)ethan-1-ol **S124-2** (0.46 g, 2.0 mmol, 1.0 equiv.), and Cs_2CO_3 (1.3 g, 4.0 mmol, 2.0 equiv.) in dioxane (10.0 mL) was added Pd/C (100 mg, 10% *w*/*w* Pd on carbon, 0.09 mmol, 5 mol%) under argon atmosphere. Then, the reaction mixture was stirred at 100 °C for 4 h. After completion of reaction, the reaction mixture was cooled to room temperature, diluted with EtOAc and water, and extracted with EtOAc three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product **S124-3** was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) as a white solid (0.46 g, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 2H), 7.70 – 7.56 (m, 2H), 7.20 (s, 1H), 7.04 (s, 1H), 6.97 (s, 1H), 4.98 – 4.91 (m, 1H), 3.98 – 3.92 (m, 3H), 3.90 – 3.85 (m, 3H), 1.57 – 1.55 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 160.3, 148.3, 145.4, 141.6, 130.1, 129.0, 127.1, 116.8, 112.0, 110.6, 70.3, 55.4, 52.2, 25.4.

Methyl 3'-(1-bromoethyl)-5'-methoxy-[1,1'-biphenyl]-4-carboxylate (S124-4)



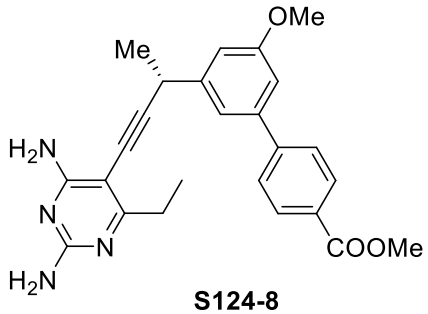
S124-4

To a solution of methyl 3'-(1-hydroxyethyl)-5'-methoxy-[1,1'-biphenyl]-4-carboxylate **S124-3** (0.46 g, 1.6 mmol, 1.0 equiv.) in CH_2Cl_2 (9.0 mL) was added PBr_3 (0.30 g, 1.1 mmol, 0.7 equiv.) at 0 °C. The reaction mixture was stirred at room temperature. After completion of reaction (monitored by TLC), the reaction mixture was quenched by water and extracted with CH_2Cl_2 three times. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the corresponding crude product **S124-4** (0.50 g, 90% crude yield), which was directly used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.9 Hz, 2H), 7.70 – 7.58 (m, 2H), 7.26 (d, J = 1.5 Hz, 1H), 7.10 – 7.05 (m, 2H), 5.21 (q, J = 6.2 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 2.06 (d, J = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 160.2, 145.3, 144.9, 141.7, 130.1, 129.2, 127.1, 118.2, 112.9, 112.2, 55.4, 52.1, 49.2, 26.9.

(*R*)-Methyl-3'-(4-(2,4-diamino-6-ethylpyrimidin-5-yl)but-3-yn-2-yl)-5'-methoxy-[1,1'-biphenyl]-4-carboxylate (S124-8)



S124-8

According to **General procedure B** with **S124-4** (34.8 mg, 0.10 mmol, 1.0 equiv.) and **S124-7** (24.3 mg, 0.15 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (EtOAc) to yield a mixture of product **S124-8** (92% ee) and **S124-7**. An analytically pure sample of **S124-8** was obtained by preparative TLC for NMR and HPLC analysis.

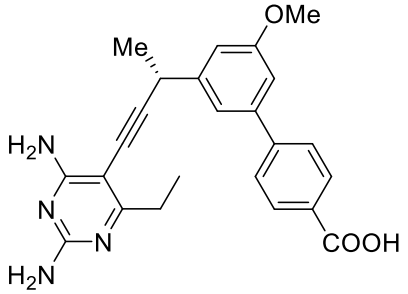
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 60/40, flow rate 0.7 mL/min, λ = 270 nm), t_R (minor) = 31.69 min, t_R (major) = 45.12 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.25 (s, 1H), 7.03 (d, *J* = 5.3 Hz, 2H), 5.40 – 5.30 (m, 4H), 4.09 (q, *J* = 7.1 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.64 (d, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 166.9, 164.2, 160.4, 160.0, 145.5, 145.4, 141.9, 130.1, 129.2, 127.1, 118.4, 112.3, 111.3, 101.6, 90.6, 75.0, 55.5, 52.2, 33.2, 29.1, 24.7, 12.6.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{27}N_4O_3$ $[M + H]^+$ 431.2078, found 431.2078.

(*R*)-3'-(4-(2,4-Diamino-6-ethylpyrimidin-5-yl)but-3-yn-2-yl)-5'-methoxy-[1,1'-biphenyl]-4-carboxylic acid (124 (UCP1172))



124 (UCP1172)

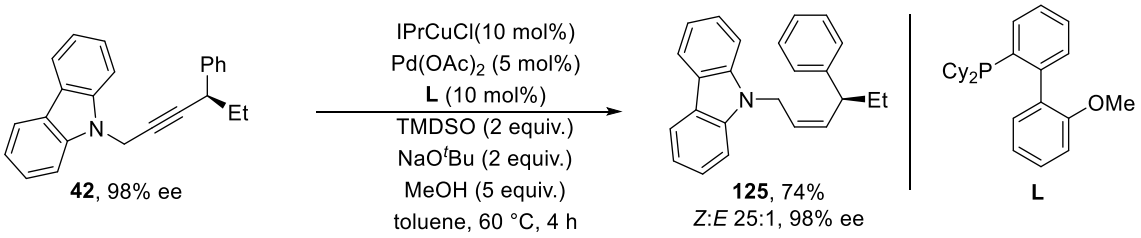
To a solution of the mixture of **S124-8** (ca. 0.050 mmol) and **S124-7** obtained above in a mixed solvent of THF (0.5 mL) and water (0.5 mL) was added $LiOH·H_2O$ (10.5 mg, 0.25 mmol, 5.0 equiv.) with vigorous stirring. The resulting reaction mixture was stirred at room temperature for 5 h. After completion of reaction (monitored by TLC), the mixture was diluted with EtOAc and water and extracted with EtOAc three times. The combined organic layer was washed by brine and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (MeOH/EtOAc = 1/50) to afford the product **124 (UCP1172)** as a white powder (12.3 mg, 59% yield over two steps).

$[\alpha]_D^{27}$ = –2.2 (*c* 0.090, CH_2Cl_2).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.36 (s, 1H),

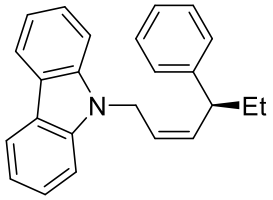
7.11 (s, 1H), 7.06 (s, 1H), 6.27 (br s, 2H), 6.17 (br s, 2H), 4.15 (q, J = 6.9 Hz, 1H), 3.84 (s, 3H), 2.56 (q, J = 7.6 Hz, 2H), 1.56 (d, J = 7.1 Hz, 3H), 1.11 (t, J = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 172.1, 164.7, 161.7, 160.4, 146.4, 141.6, 130.3, 126.8, 118.3, 112.6, 110.9, 100.9, 88.2, 76.6, 55.7, 32.8, 29.4, 25.1, 12.9.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{25}N_4O_3$ $[M + H]^+$ 417.1921, found 417.1922.

The synthesis of chiral C(sp^3)–C(sp^2) and C(sp^3)–C(sp^3) bonds in drugs and natural products
The synthesis of *Z*-alkene (125)



To a flamed Schlenk tube charged with a stir bar were added NaO^{t}Bu (19.2 mg, 0.20 mmol, 2.0 equiv.), **42** (98% ee, 32.3 mg, 0.10 mmol, 1.0 equiv.), $Pd(OAc)_2$ (1.12 mg, 0.005 mmol, 5 mol%), **L** (3.8 mg, 0.010 mmol, 10 mol%), IPrCuCl (4.88 mg, 0.010 mmol, 10 mol%), TMDSO (1,1,3,3-tetramethyldisiloxane) (26.8 mg, 0.20 mmol, 2.0 equiv.), MeOH (16.0 mg, 0.50 mmol, 5.0 equiv.), and toluene (1.0 mL). The reaction mixture was stirred at 60 °C for 4 h. Upon completion, the reaction mixture was filtered through a short plug of silica gel eluted with EtOAc (1.5 mL) and purified by column chromatography (petroleum ether) to afford **125** as a slight yellow oil (*Z*:*E* = 25:1, 24.1 mg, 74% yield, 98% ee).

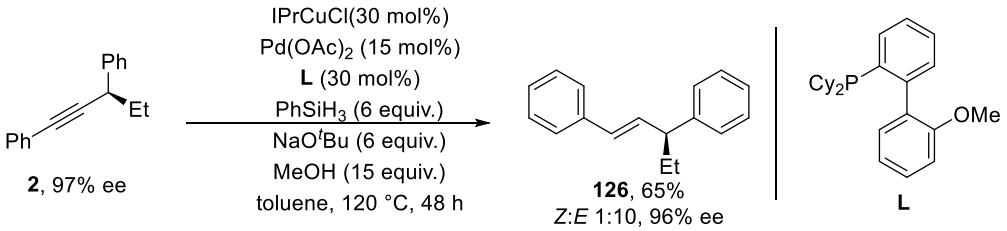
(*S,Z*)-9-(4-Phenylhex-2-en-1-yl)-9*H*-carbazole (125)



125

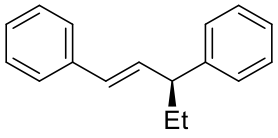
[α]$_D^{27}$ = +15 (*c* 1.9, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 16.60 min, t_R (minor) = 22.36 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.7 Hz, 2H), 7.48 – 7.39 (m, 4H), 7.36 – 7.23 (m, 7H), 5.89 – 5.80 (m, 1H), 5.63 – 5.53 (m, 1H), 5.05 (ddd, J = 16.8, 5.9, 2.0 Hz, 1H), 4.95 (ddd, J = 16.8, 6.3, 1.9 Hz, 1H), 3.74 (dd, J = 16.9, 7.5 Hz, 1H), 1.94-1.78 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144. 7, 140.2, 136.4, 128.8, 127.6, 126.4, 125.6, 125.5, 123.0, 120.4, 119.0, 108.8, 46.0, 40.6, 30.5, 12.3.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}N$ $[M + H]^+$ 326.1903, found 326.1896.

The synthesis of *E*-alkene (126)



To a flamed Schlenk tube charged with a stir bar were added NaO^{t}Bu (57.6 mg, 0.60 mmol, 6.0 equiv.), **2** (22.0 mg, 0.10 mmol, 1.0 equiv.), $Pd(OAc)_2$ (3.36 mg, 0.015 mmol, 15 mol%), **L** (11.4 mg, 0.030 mmol, 30 mol%), IPrCuCl (14.6 mg, 0.03 mmol, 30 mol%), $PhSiH_3$ (64.9 mg, 0.60 mmol, 6.0 equiv.), MeOH (48.0 mg, 1.5 mmol, 15 equiv.), and toluene (1.0 mL). The reaction mixture was stirred at 120 °C for 48 h. Upon completion, the reaction mixture was filtered through a short plug of silica gel eluted with EtOAc (1.5 mL) and purified by column chromatography (petroleum ether) to afford **126** as a slight yellow oil (*Z*:*E* = 1:10, 14.4 mg, 65% yield, 96% ee).

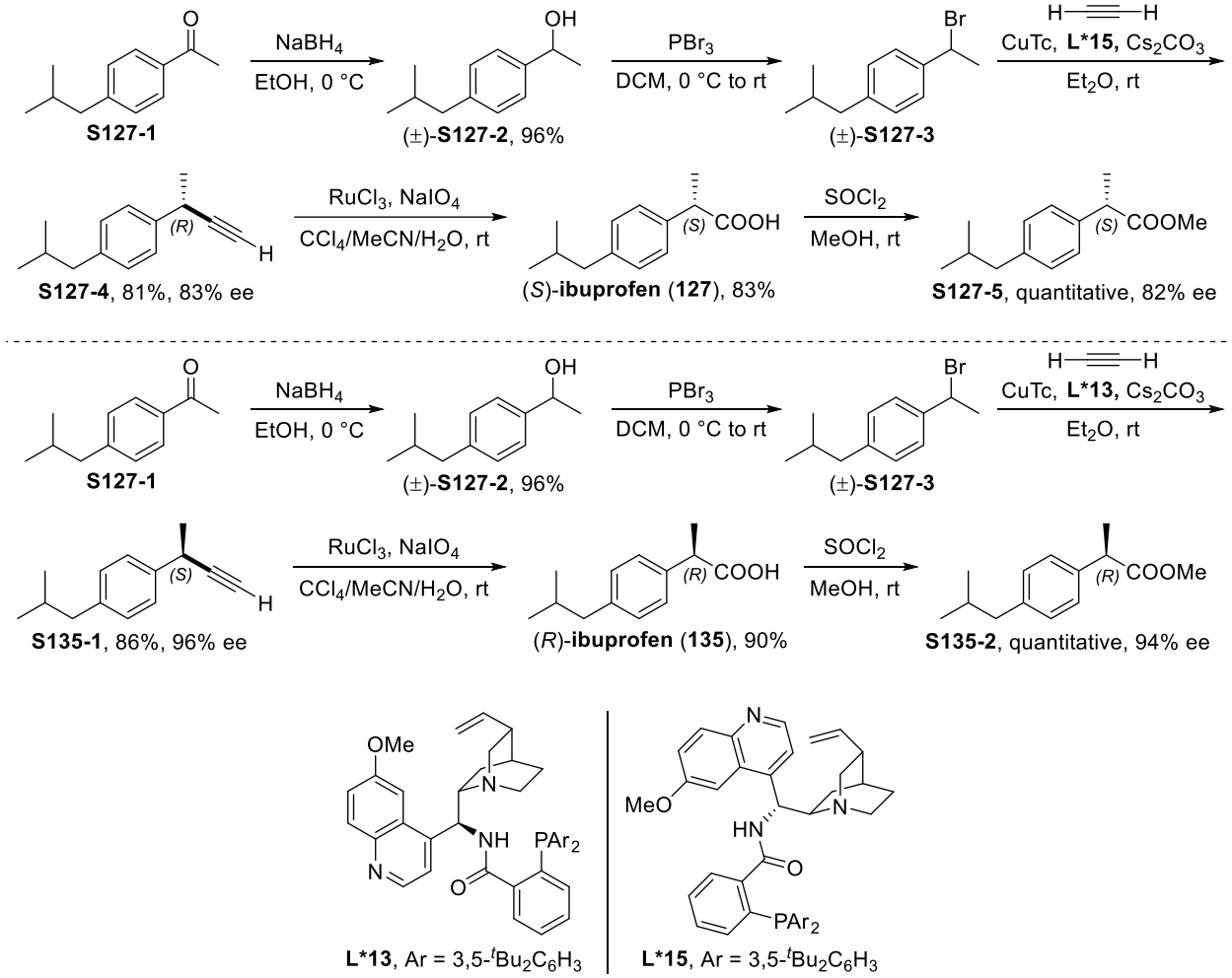
(*S*,*E*)-Pent-1-ene-1,3-diyldibenzene (126)



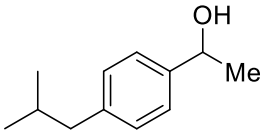
126

[α]$_D^{27}$ = –24 (*c* 0.71, CH_2Cl_2).
HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.85 min, t_R (minor) = 16.63 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.08 (m, 10H), 6.42 – 6.29 (m, 2H), 3.31 (q, *J* = 7.3 Hz, 1H), 1.89 – 1.72 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 137.7, 134.3, 129.5, 128.5, 127.7, 127.0, 126.20, 126.15, 51.0, 28.8, 12.3.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}$ $[M + H]^+$ 223.1481, found 223.1478.

The synthesis of (*S*)-ibuprofen (127) and (*R*)-ibuprofen (135)



1-(4-Isobutylphenyl)ethanol (S127-2)



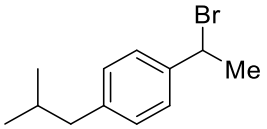
(±)-**S127-2**

To a stirred solution of 1-(4-isobutylphenyl)ethanone **S127-1** (176.1 mg, 1.0 mmol, 1.0 equiv.) in ethanol (5.0 mL) was carefully added $NaBH_4$ (76.0 mg, 2.0 mmol, 2.0 equiv.) at 0 °C. The reaction mixture was stirred under the same conditions. After completion of reaction (monitored by TLC), the reaction mixture was quenched by saturated NH_4Cl, extracted with EtOAc three times, and the organic layer was dried over Na_2SO_4. The residue was filtered through a pad of silica gel and the filtrate was concentrated to afford the crude product **S127-2** as a colorless oil (171.0 mg, 96% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 4.96 – 4.82 (m, 1H), 2.50 (d, *J* = 7.1 Hz, 2H), 1.98 – 1.81 (m, 1H), 1.52 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 141.0, 129.2, 125.2, 70.3, 45.1, 30.3, 25.0, 22.4.

1-(1-Bromoethyl)-4-isobutylbenzene (S127-3)



(±)-**S127-3**

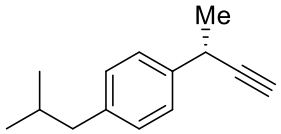
To a solution of 1-(4-isobutylphenyl)ethanol **S127-2** (178.0 mg, 1.0 mmol, 1.0 equiv.) in CH_2Cl_2 (5.0 mL) was added dropwise phosphorus tribromide (189.7 mg, 0.70 mmol, 0.7 equiv.) at 0 °C under argon atmosphere with vigorous stirring. Then, the mixture was naturally warmed up to room temperature and stirred overnight. The reaction was quenched by water and extracted with petroleum ether three times. The organic layer was washed by brine and filtered through a pad of silica gel. The filtrate was concentrated to afford the crude product **S127-3** as a colorless liquid (220.8 mg, 92% yield), which was directly used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.26 (q, *J* = 6.9 Hz, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 2.08 (d, *J* = 6.9 Hz, 3H), 1.89 (dp, *J* = 13.6, 6.7 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 140.5, 129.4, 126.6, 50.0, 45.1, 30.2, 26.8, 22.4.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{17}$ $[M - Br]^+$ 161.1325, found 161.1324.

(*R*)-1-(But-3-yn-2-yl)-4-isobutylbenzene (S127-4)



S127-4

According to the **General procedure C** with 1-(1-bromoethyl)-4-isobutylbenzene **S127-3** (48.0 mg, 0.20 mmol, 1.0 equiv.) and **L*15** (12.5 mg, 0.015 mmol, 7.5 mol%) instead of **L*13**, **S127-4** was obtained by column chromatography on silica gel (cyclohexane) as a colorless oil (30.0 mg, 81% yield over two steps, 83% ee).

$[\alpha]_D^{25}$ = –5.2 (*c* 6.9, CH_2Cl_2).

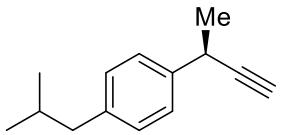
HPLC analysis: Chiralcel OD3 (hexane, flow rate 0.3 mL/min, λ = 214 nm), t_R (minor) = 15.81 min, t_R (major) = 21.57 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 3.78 (qd, *J* = 7.2, 2.5 Hz, 1H), 2.49 (d, *J* = 7.1 Hz, 2H), 2.28 (d, *J* = 2.5 Hz, 1H), 1.87 (tp, *J* = 12.9, 6.6 Hz, 1H), 1.53 (d, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 139.9, 129.3, 126.5, 87.4, 69.9, 45.0, 31.2, 30.2, 24.2, 22.40, 22.39.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{19}$ $[M + H]^+$ 187.1481, found 187.1482.

(*S*)-1-(But-3-yn-2-yl)-4-isobutylbenzene (S135-1)



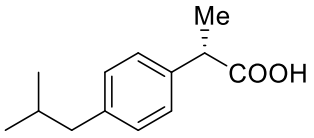
S135-1

According to the **General procedure C** with 1-(1-bromoethyl)-4-isobutylbenzene **S127-3** (48.0 mg, 0.20 mmol, 1.0 equiv.), **135-1** was obtained by column chromatography on silica gel

(cyclohexane) as a colorless oil (32.0 mg, 86% yield over two steps, 96% ee).
[α]$_D^{25}$ = +2.3 (*c* 0.90, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane, flow rate 0.3 mL/min, λ = 214 nm), t_R (major) = 15.56 min, t_R (minor) = 21.37 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 3.78 (qd, *J* = 7.2, 2.5 Hz, 1H), 2.49 (d, *J* = 7.1 Hz, 2H), 2.28 (d, *J* = 2.5 Hz, 1H), 1.87 (tp, *J* = 12.9, 6.6 Hz, 1H), 1.53 (d, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 139.9, 129.3, 126.5, 87.4, 69.9, 45.0, 31.2, 30.2, 24.2, 22.40, 22.39.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{19}$ $[M + H]^+$ 187.1481, found 187.1482.

General procedure for the oxidation of S127-4 or 135-1:
To a mixture of $RuCl_3$ (1.5 mg, 0.010 mmol, 5.0 mol%) and sodium periodate (171.0 mg, 0.80 mmol, 4.0 equiv.) in a mixed solvent of CCl_4 (0.4 mL) and water (0.6 mL) was added a solution of 1-(but-3-yn-2-yl)-4-isobutylbenzene **S127-4** or **135-1** (37.2 mg, 0.20 mmol, 1.0 equiv.) in MeCN (0.4 mL) in one portion. The reaction mixture was stirred at room temperature for 2 h, and then, was concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) to afford the product.

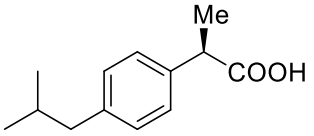
(*S*)-2-(4-Isobutylphenyl)propanoic acid (127 ((*S*)-ibuprofen))



127 ((***S***)**-ibuprofen**)

According to the procedure described above with **S127-4**, **127** ((*S*)-**ibuprofen**) was obtained as a white solid (34.2 mg, 83% yield).
[α]$_D^{25}$ = +40 (*c* 1.1, CH_2Cl_2).

(*R*)-2-(4-Isobutylphenyl)propanoic acid (135 ((*R*)-ibuprofen))



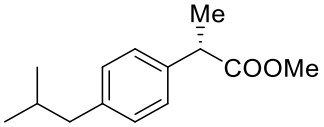
135 ((***R***)**-ibuprofen**)

According to the procedure described above with **135-1**, **135 ((***R***)-ibuprofen)** was obtained as a white solid (37.1 mg, 90% yield).
[α]$_D^{25}$ = –40 (*c* 4.1, CH_2Cl_2).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 3.74 (q, *J* = 7.1 Hz, 1H), 2.49 (d, *J* = 7.1 Hz, 2H), 1.96 – 1.80 (m, 1H), 1.54 (d, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 140.9, 137.0, 129.4, 127.3, 45.1, 45.0, 30.2, 22.4, 18.1.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{19}O_2$ $[M + H]^+$ 207.1380, found 207.1379.

General procedure for esterification:
To a solution of ibuprofen (41.2 mg, 0.20 mmol, 1.0 equiv.) in MeOH (1.0 mL) was added $SOCl_2$ (119.0 mg, 1.0 mmol, 5.0 equiv.) dropwise at 0 °C. Then, the reaction mixture was warmed up to

room temperature and stirred for another 3 h. After completion of reaction, the reaction mixture was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the product.

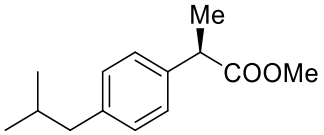
(*S*)-Methyl 2-(4-isobutylphenyl)propanoate ((*S*)-S127-5)



(*S*)-**S127-5**

According to the procedure described above with **127** ((*S*)-**ibuprofen**), **S127-5** was obtained as a colorless oil (44.0 mg, quantitative yield, 82% ee).
[α]$_D^{25}$ = +53 (*c* 7.1, CH_2Cl_2).
HPLC analysis: Chiralcel OJ3 (hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 12.97 min, t_R (minor) = 14.34 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 3.75 (q, *J* = 7.2 Hz, 1H), 3.69 (s, 2H), 2.50 (d, *J* = 7.2 Hz, 1H), 1.54 (d, *J* = 7.2 Hz, 2H), 0.95 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 140.5, 137.8, 129.4, 127.2, 51.9, 45.09, 45.05, 30.2, 22.4, 18.7.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{21}O_2$ $[M + H]^+$ 221.1536, found 221.1535.

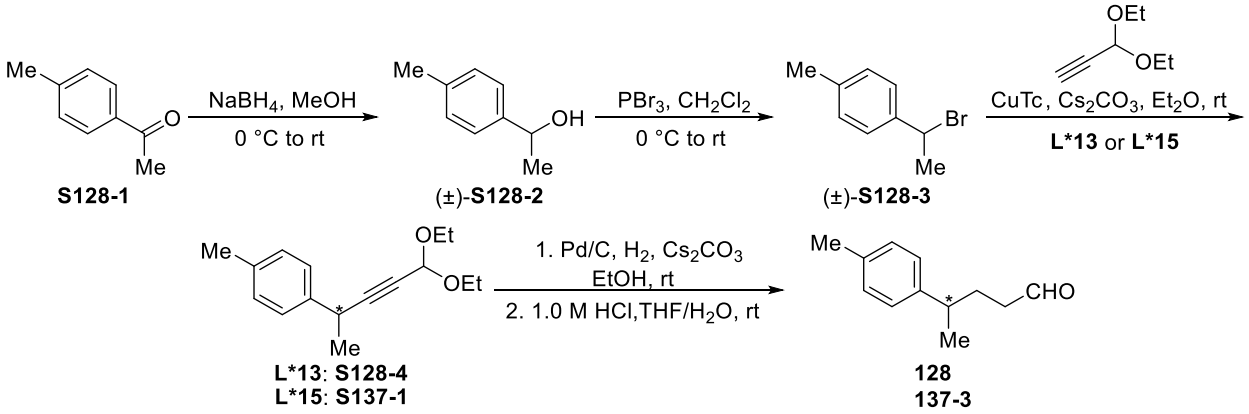
(*R*)-Methyl 2-(4-isobutylphenyl)propanoate (S135-2)



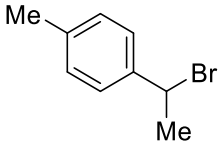
S135-2

According to the procedure described above with **135 (**(*R*)-**ibuprofen**), **S135-2** was obtained as a colorless oil (44.0 mg, quantitative yield, 94% ee).
[α]$_D^{25}$ = –91 (*c* 6.9, CH_2Cl_2).
HPLC analysis: Chiralcel OJ3 (hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 214 nm), t_R (minor) = 16.04 min, t_R (major) = 20.30 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 3.75 (q, *J* = 7.2 Hz, 1H), 3.69 (s, 2H), 2.50 (d, *J* = 7.2 Hz, 1H), 1.54 (d, *J* = 7.2 Hz, 2H), 0.95 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 140.5, 137.8, 129.4, 127.2, 51.9, 45.09, 45.05, 30.2, 22.4, 18.7.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{21}O_2$ $[M + H]^+$ 221.1536, found 221.1535.

The synthesis of 128 and 137



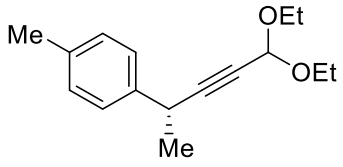
1-(1-Bromoethyl)-4-methylbenzene (S128-3)



S128-3

According to **General Procedure 3** with 1-(*p*-tolyl)ethan-1-one **S128-1** (1.34 g, 10.0 mmol, 1.0 equiv.) and MeOH (30 mL) instead of ethanol as the solvent for the first reduction step, the crude product **S128-3** was obtained as a colorless oil (1.78 g, 90% crude yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 5.29 (q, *J* = 6.9 Hz, 1H), 2.42 (s, 3H), 2.12 (dd, *J* = 7.0, 0.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 138.3, 129.4, 126.8, 49.9, 26.9, 21.3.
HRMS (ESI) m/z calcd. for C_9H_{11} $[M - Br]^+$ 119.0855, found 119.0853.

(*R*)-1-(5,5-Diethoxypent-3-yn-2-yl)-4-methylbenzene (S128-4)

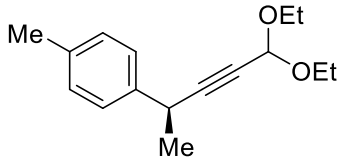


S128-4

According to **General procedure B** with 1-(1-bromoethyl)-4-methylbenzene **S128-3** (39.6 mg, 0.20 mmol, 1.0 equiv.) and 3,3-diethoxyprop-1-yne **S44** (38.4 mg, 0.30 mmol, 1.5 equiv.) for 36 h, the crude product **S128-4** was obtained without column purification as a colorless oil (47.2 mg, 96% crude yield, 93% ee).
[α]$_D^{27}$ = –2.6 (*c* 1.8, CH_2Cl_2).
HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 210 nm), t_R (major) = 4.82 min, t_R (minor) = 5.86 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 5.34 (s, 1H), 3.84 – 3.74 (m, 3H), 3.66 – 3.58 (m, 2H), 2.35 (s, 3H), 1.51 (d, *J* = 7.2 Hz, 3H), 1.31 – 1.23 (m, 6H).
^{13}C NMR (100 MHz, CDCl3) δ 139.6, 136.3, 129.2, 126.8, 91.6, 88.8, 77.5, 60.7, 31.4, 24.2, 21.0, 15.2.

HRMS (ESI) m/z calcd. for $C_{16}H_{22}NaO_2$ $[M + Na]^+$ 269.1512, found 269.1510.

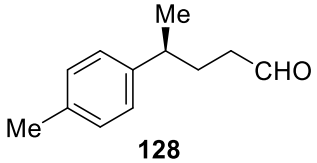
(*S*)-1-(5,5-Diethoxypent-3-yn-2-yl)-4-methylbenzene (S137-1)



S137-1

According to **General Procedure B** with 1-(1-bromoethyl)-4-methylbenzene **S128-3** (39.6 mg, 0.20 mmol, 1.0 equiv.), 3,3-diethoxyprop-1-yne **S44** (38.4 mg, 0.30 mmol, 1.5 equiv.), and **L*15** (12.5 mg, 0.015 mmol, 7.5 mol%) instead of **L*15** for 36 h, the crude **S137-1** was obtained without column purification as a colorless oil (47.2 mg, 94% yield, 87% ee).
$[\alpha]_D^{27}$ = +16 (*c* 2.7, CH_2Cl_2).
HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 210 nm), t_R (minor) = 4.74 min, t_R (major) = 5.71 min.

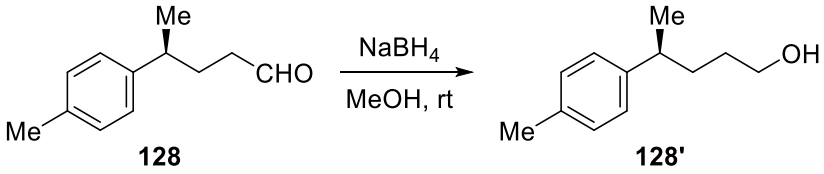
(*S*)-4-(*p*-Tolyl)pentanal (128)



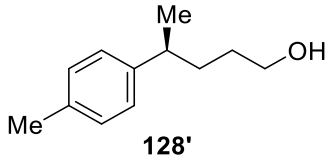
128

To a mixture of Pd/C (50.0 mg, 10% *w*/*w* Pd on carbon, 0.047 mmol, 23 mol%) and Cs_2CO_3 (130.0 mg, 0.40 mmol, 2.0 equiv.) in EtOH (2.0 mL) was added **S128-4**(49.2 mg, 0.20 mmol, 1.0 equiv.) under argon atmosphere. Then, the reaction flask was evacuated and refilled with hydrogen through a balloon. The resulting reaction mixture was stirred under the hydrogen atmosphere at room temperature for 12 h. After completion, the reaction mixture was filtered and rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was dissolved in a mixture of THF (1.0 mL) and H_2O (1.0 mL) followed by the addition of two drops of 1.0 M HCl. Then, the reaction mixture was stirred until the acetal intermediate was completely consumed (monitored by TLC). The reaction mixture was diluted with EtOAc, washed by water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford **128** as a colorless oil (31.7 mg, 90% yield). Due to the instability of **128**, its enantiomeric excess was determined by HPLC to be 89% after reduction with $NaBH_4$, as described below.
$[\alpha]_D^{27}$ = +34 (*c* 1.8, CH_2Cl_2).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (t, *J* = 1.6 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.76 – 2.66 (m, 1H), 2.40 – 2.29 (m, 2H), 2.34 (s, 3H), 2.03 – 1.81 (m, 2H), 1.29 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 143.0, 135.8, 129.2, 126.9, 42.2, 38.9, 30.4, 22.4, 21.0.
HRMS (ESI) m/z calcd. for $C_{12}H_{16}NaO$ $[M + Na]^+$ 199.1093, found 199.1094.

Reduction of 128

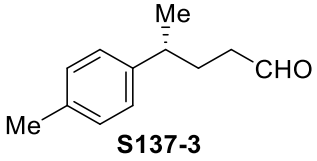


(*S*)-4-(*p*-Tolyl)pentan-1-ol (128')



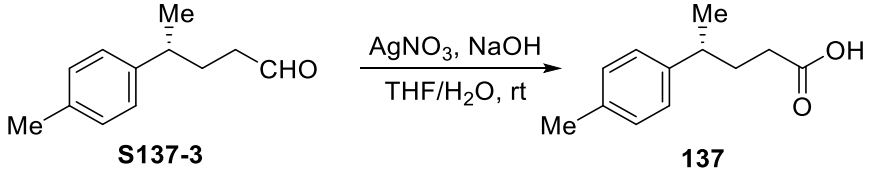
To a solution of **128** (17.6 mg, 0.1 mmol, 1.0 equiv.) in MeOH (1.0 mL) was added $NaBH_4$ (4.6 mg, 0.12 mmol, 1.2 equiv.) and the mixture was stirred at room temperature for 2 h. After completion of reaction (monitored by TLC), the reaction mixture was quenched by water, diluted with CH_2Cl_2, and extracted with CH_2Cl_2 three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford **128'** (17.0 mg, 96% crude yield, 89% ee).
[α]$_D^{27}$ = +17 (*c* 1.2, CH_2Cl_2).
HPLC analysis: Chiralcel OD-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), t_R (minor) = 5.42 min, t_R (major) = 6.68 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.02 (m, 4H), 3.57 (t, *J* = 6.5 Hz, 2H), 2.72 – 2.60 (m, 1H), 2.31 (s, 3H), 1.68 – 1.58 (m, 2H), 1.56 – 1.37 (m, 3H), 1.24 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 135.4, 129.1, 126.9, 63.1, 39.4, 34.4, 31.0, 22.6, 21.0.

(*R*)-4-(*p*-Tolyl)pentanal (S137-3)

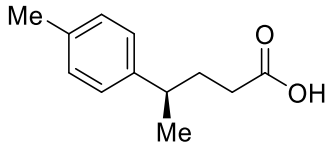


According to the same procedure as that described for **128** with **S137-1** (49.2 mg, 0.20 mmol, 1.0 equiv.) instead of **S128-4**, **S137-3** was obtained as a colorless oil (32.4 mg, 92% yield).
[α]$_D^{27}$ = –11 (*c* 1.2, CH_2Cl_2).

The synthesis of 137



(*R*)-4-(*p*-Tolyl)pentanoic acid (137)



137

To a solution of aldehyde **S137-3** (26.4 mg, 0.15 mmol. 1.0 equiv.) in a mixed solvent of THF and H_2O (THF/H_2O = 3/1, *v*/*v*, 8.0 mL) was sequentially added a solution of $AgNO_3$ (63.8 mg, 0.38 mmol, 2.5 equiv.) in H_2O (1.0 mL) and aqueous NaOH (2.5 mL, 10% *m*/*v*) with vigorously stirring. Then, the reaction mixture was stirred at room temperature for 2 h. After completion, the reaction mixture was filtered and washed by water. The filtrate was washed with Et_2O three times, acidified to pH = 1 with conc. hydrochloric acid at 0 °C, and extracted with CH_2Cl_2 four times. The combined organic layer was washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 10/1) to give **137** (21.6 mg, 75% yield) as a yellow oil. For convenience, the enantiomeric excess of **137** was determined to be –83% after reduction with lithium aluminum hydride.

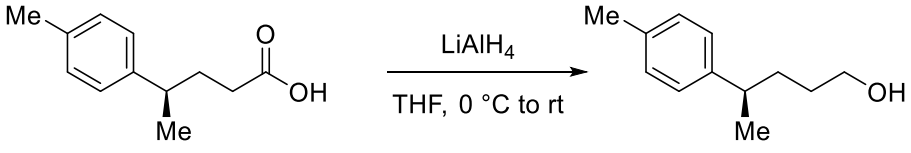
$[\alpha]_D^{27}$ = –14 (*c* 1.8, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 – 7.01 (m, 2H), 7.01 – 6.96 (m, 2H), 2.67 – 2.56 (m, 1H), 2.24 (s, 3H), 2.18 – 2.11 (m, 2H), 1.90 – 1.72 (m, 2H), 1.18 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 143.0, 135.8, 129.2, 126.9, 38.9, 33.0, 32.3, 22.3, 21.0.

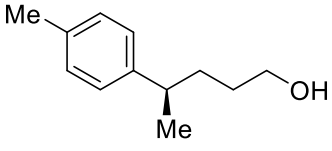
HRMS (ESI) m/z calcd. for $C_{12}H_{16}NaO$ $[M + Na]^+$ 215.1043, found 215.1044.

The reduction of 137



137 **137'**

(*R*)-4-(*p*-Tolyl)pentan-1-ol (137')



137'

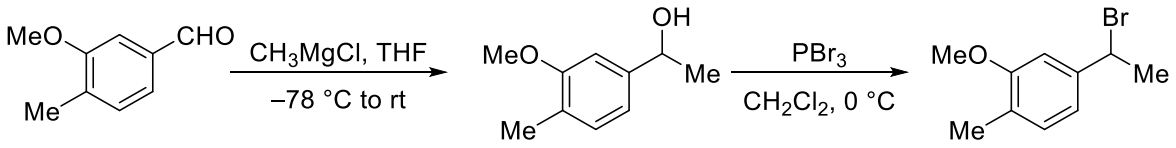
To a solution of **137** (38.4 mg, 0.2 mmol, 1.0 equiv.) in THF (2.0 mL) was added $LiAlH_4$ (15.2 mg, 0.4 mmol, 2.0 equiv.) at 0 ℃ and the resulting reaction mixture was stirred at rt for 2 h. After completion of reaction (monitored by TLC), the reaction mixture was quenched with $Na_2SO_4 \cdot xH_2O$ and filtered. The filtrate was concentrated under reduced pressure to afford the corresponding alcohol **137'** (35.0 mg, 90% crude yield, 83% ee).

HPLC analysis: Chiralcel OD-H (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), t_R (major) = 5.42 min, t_R (minor) = 6.68 min.

$[\alpha]_D^{27}$ = –6.8 (*c* 0.19, CH_2Cl_2).

The synthesis of 129, 136, 138, 139, (+)-methylaristelegone A, and (–)-aristelegone B

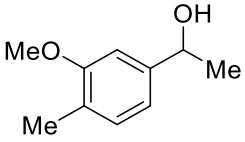
The synthesis of substrate S129-3



S129-1 **S129-2** **S129-3**

To a solution of 3-methoxy-4-methylbenzaldehyde **S129-1** (0.75 g, 5.0 mmol, 1.0 equiv.) in THF (10 mL) was slowly added methylmagnesium chloride (2.0 mL, 3.0 M in THF, 6.0 mmol, 1.2 equiv.) at −78 °C under argon atmosphere. The reaction mixture was then warmed up to room temperature and stirred for 1 h until the aldehyde was completely consumed (monitored by TLC). The reaction mixture was quenched by 3.0 M HCl and extracted with CH_2Cl_2 three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford **S129-2** as a colorless oil (0.80 g, 96% yield).

1-(3-Methoxy-4-methylphenyl)ethan-1-ol (S129-2)

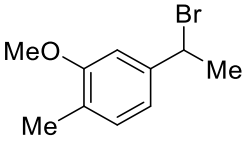


S129-2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 1.6 Hz, 1H), 6.83 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.85 (q, *J* = 6.4 Hz, 1H), 3.84 (s, 3H), 2.21 (d, *J* = 0.8 Hz, 3H), 1.49 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 145.0, 130.6, 125.9, 117.2, 107.1, 70.5, 55.4, 25.3, 16.1.

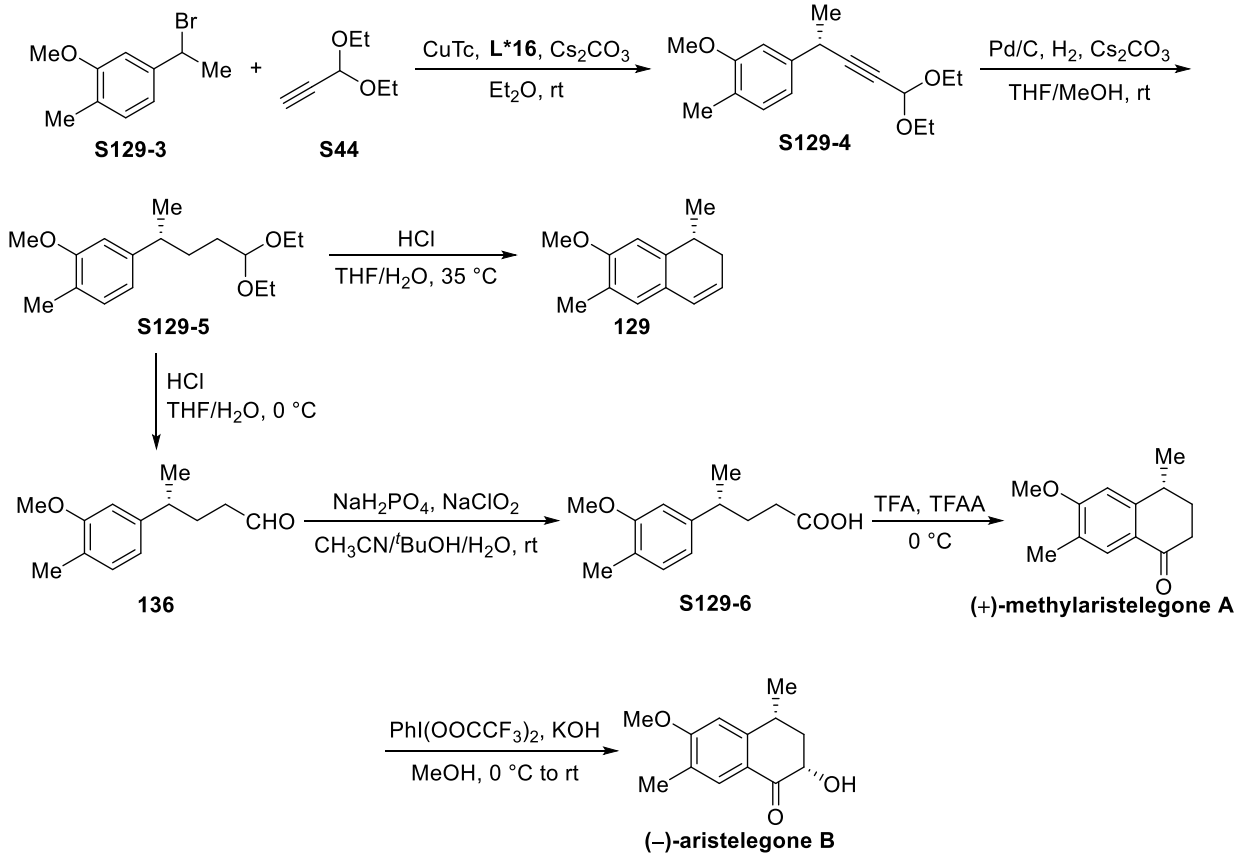
To a solution of 1-(3-methoxy-4-methylphenyl)ethan-1-ol **S129-2** (0.50 g, 3.0 mmol, 1.0 equiv.) in CH_2Cl_2 (10.0 mL) was added dropwise PBr_3 (0.20 mL, 2.1 mmol, 0.70 equiv.) at 0 °C. The reaction mixture was stirred at this temperature for 2 h, then quenched by water, and extracted with CH_2Cl_2 three times. The combined organic phase was dried over Na_2SO_4, filtered through a pad of silica gel, and concentrated under reduced pressure to afford the crude product **S129-3** (0.64 g, 93% yield) as a white solid, which was directly used in the next step without further purification.

4-(1-Bromoethyl)-2-methoxy-1-methylbenzene (S129-3)

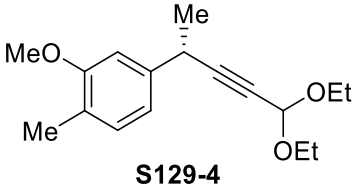


S129-3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.5 Hz, 1H), 6.94 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.91 (d, *J* = 1.7 Hz, 1H), 5.22 (q, *J* = 6.9 Hz, 1H), 3.86 (s, 3H), 2.21 (s, 3H), 2.06 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 142.2, 130.7, 127.3, 118.5, 108.6, 55.4, 50.4, 27.0, 16.2.
HRMS (ESI) *m/z* calcd. for $C_{10}H_{13}O$ $[M - Br]^+$ 149.0961, found 149.0966.



(*S*)-4-(5,5-Diethoxypent-3-yn-2-yl)-2-methoxy-1-methylbenzene (S129-4)



S129-4

A 10 mL Schlenk tube was sequentially charged with CuTc (3.82 mg, 0.020 mmol, 5.0 mol%), **L*16** (24.2 mg, 0.030 mmol, 7.5 mol%), and Cs_2CO_3 (260.8 mg, 0.80 mmol, 2.0 equiv.). Then, the tube was evacuated and refilled with argon three times. Next, anhydrous Et_2O (8.0 mL), 4-(1-bromoethyl)-2-methoxy-1-methylbenzene **S129-3** (91.2 mg, 0.40 mmol, 1.0 equiv.), and 3,3-diethoxyprop-1-yne **S44** (76.8 mg, 0.60 mmol, 1.5 equiv.) were sequentially added under an argon flow. Upon completion, the reaction mixture was stirred at room temperature for 18 h. After completion of reaction (monitored by TLC), the reaction mixture was filtered through a silica gel pad to remove insoluble solid and rinsed by CH_2Cl_2. The filtrate was concentrated under reduced pressure then purified by column chromatography on silica gel (petroleum ether) to afford **S129-4** as a colorless oil (99.5 mg, 90% yield, 84% ee)

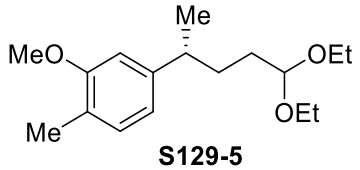
$[\alpha]_D^{27}$ = –4.9 (*c* 1.6, CH_2Cl_2).

HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.4 mL/min, λ = 214 nm), t_R (minor) = 13.79 min, t_R (major) = 15.32 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.5 Hz, 1H), 6.86 (s, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 5.32 (s, 1H), 3.83 (s, 3H), 3.81 – 3.70 (m, 3H), 3.66 – 3.53 (m, 2H), 2.18 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H), 1.23 (td, *J* = 7.1, 3.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 141.6, 130.7, 125.1, 118.7, 108.9, 91.7, 89.0, 77.7, 60.84, 60.81, 55.4, 31.9, 24.3, 16.0, 15.3.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{25}O_3$ $[M + H]^+$ 277.1798, found 277.1796.

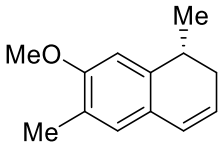
(*R*)-4-(5,5-Diethoxypentan-2-yl)-2-methoxy-1-methylbenzene (S129-5)



S129-5

A mixture of **S129-4** (83.0 mg, 0.30 mmol, 1.0 equiv.), Cs_2CO_3 (48.9 mg, 0.15 mmol, 0.50 equiv.), and Pd/C (20.0 mg, 10% *w*/*w* Pd on carbon, 0.019 mmol, 6 mol%) in a mixture of THF and MeOH (1/3 *v*/*v*, 10.0 mL) was hydrogenated with a hydrogen balloon for 24 h. Then, the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc. After concentration, the crude **S129-5** was obtained as a colorless oil (80.0 mg, 95% yield), which was directly used in the next step without further purification.

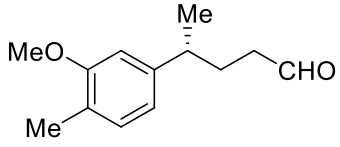
(*R*)-7-Methoxy-1,6-dimethyl-1,2-dihydronaphthalene (129)



129

To a stirred solution of **S129-5** (56.0 mg, 0.20 mmol, 1.0 equiv.) in THF (6.0 mL) was dropwise added HCl (2.0 mL, 2.0 M, 4.0 mmol, 20 equiv.) at room temperature and the reaction mixture was stirred at 35 °C for 1 h. Upon completion, the reaction mixture was quenched by saturated $NaHCO_3$ at 0 °C and extracted with EtOAc three times. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15/1) to afford **129** (33.0 mg, 88% yield, 83% ee) as a colorless oil.
$[\alpha]_D^{27}$ = +29 (*c* 0.42, CH_2Cl_2).
HPLC analysis: Chiralcel OJ3 (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 270 nm), t_R (minor) = 26.19 min, t_R (major) = 35.32 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.67 (s, 1H), 6.37 (d, *J* = 9.5 Hz, 1H), 5.85 – 5.75 (m, 1H), 3.84 (s, 3H), 2.95 – 2.82 (m, 1H), 2.50 – 2.40 (m, 1H), 2.18 (s, 3H), 2.15 – 2.03 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 139.5, 128.8, 126.9, 126.0, 124.3, 124.1, 108.7, 55.6, 32.2, 31.3, 20.5, 15.9.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}O$ $[M + H]^+$ 189.1274, found 189.1274.

(*R*)-4-(3-Methoxy-4-methylphenyl)pentanal (136)



136

To a stirred solution of **S129-5** (78.0 mg, 0.28 mmol, 1.0 equiv.) in THF (10.0 mL) were dropwise added HCl (3.0 mL, 0.50 M, 1.5 mmol, 5 equiv.) at 0 °C and the reaction mixture was stirred under the same conditions for 4 h. Upon completion, the reaction mixture was quenched by saturated $NaHCO_3$ at 0 °C and extracted with EtOAc. The combined organic phase was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford the **136** (46.2 mg, 80%, 85% ee) as a colorless oil.

$[\alpha]_D^{27}$ = –12 (*c* 2.8, CH_2Cl_2).

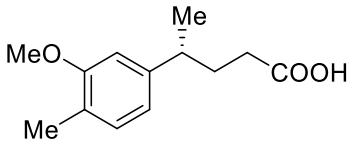
HPLC analysis: Chiralcel OJ3 (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, λ = 280 nm), t_R (major) = 42.70 min, t_R (minor) = 47.03 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.63 (s, 1H), 3.83 (s, 3H), 2.73 – 2.64 (m, 1H), 2.41 – 2.26 (m, 2H), 2.19 (s, 3H), 2.00 – 1.79 (m, 2H), 1.28 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 157.9, 145.1, 130.7, 124.6, 118.7, 108.9, 55.4, 42.4, 39.5, 30.5, 22.6, 16.0.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{19}O_2$ $[M + H]^+$ 207.1380, found 207.1381.

(*R*)-4-(3-Methoxy-4-methylphenyl)pentanoic acid (S129-6)



S129-6

To a solution of **136** (41.0 mg, 0.20 mmol, 1.0 equiv.) in a mixture of CH_3CN, ^{t}BuOH, and H_2O (2/2/1 *v*/*v*/*v*, 10.0 mL) were sequentially added NaH_2PO_4 (72.0 mg, 0.60 mmol, 3.0 equiv.) and $NaClO_2$ (89.5 mg, 1.2 mmol, 6.0 equiv.). The resulting reaction mixture was stirred at room temperature for 2 h. Upon completion, the reaction mixture was diluted with EtOAc, washed with saturated $Na_2S_2O_3$ and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2/MeOH = 10/1) to afford **S129-6** (40.0 mg, 90% yield) as a colorless oil. The analytic data were consistent with those reported[23,24].

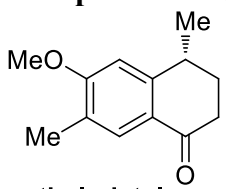
$[\alpha]_D^{27}$ = –19 (*c* 1.8, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.64 (s, 1H), 3.82 (s, 3H), 2.76 – 2.64 (m, 1H), 2.25 (t, *J* = 7.6 Hz, 2H), 2.18 (s, 3H), 2.00 – 1.83 (m, 2H), 1.27 (d, *J* = 7.4 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 157.9, 145.1, 130.7, 124.6, 118.8, 109.0, 55.4, 39.5, 33.1, 32.4, 22.4, 16.0.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{19}O_3$ $[M + H]^+$ 223.1329, found 223.1327.

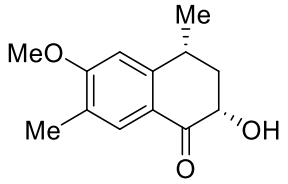
(*R*)-6-Methoxy-4,7-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one ((+)-methylaristelegone A)



(+)-methylaristelegone A

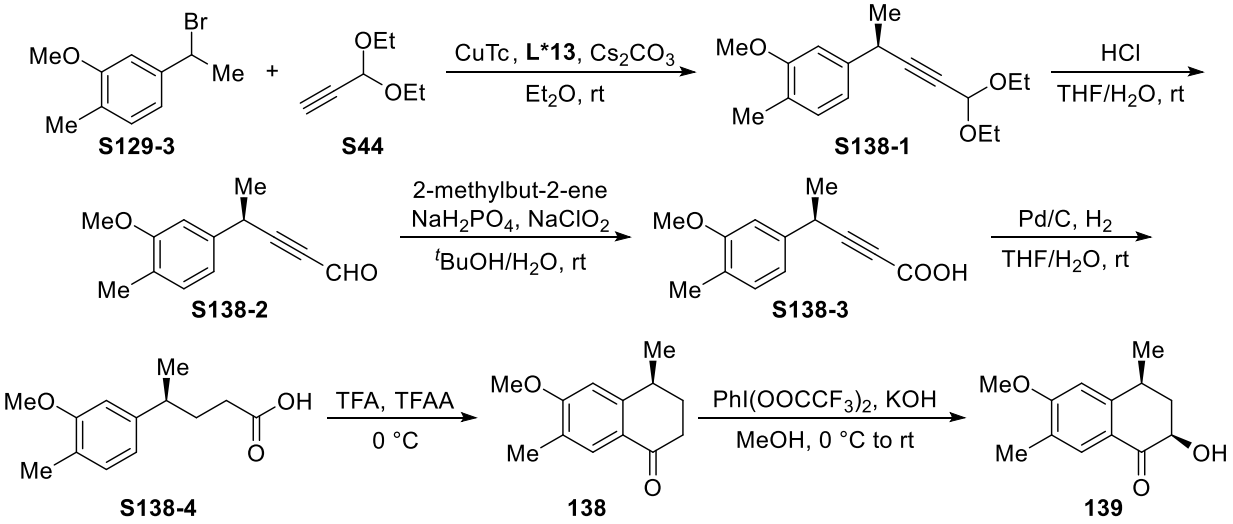
To a flask containing the (*R*)-**S129-6** (44.4 mg, 0.20 mmol, 1.0 equiv.) were added a mixture of trifluoroacetic acid (22.8 mg, 0.20 mmol, 1.0 equiv.) and trifluoroacetic anhydride (168.0 mg, 0.80 mmol, 4.0 equiv.) at 0 °C under argon atmosphere. The resulting reaction mixture was stirred under the same conditions until completion of reaction (monitored by TLC). Then, the reaction mixture was quenched by saturated $NaHCO_3$ at 0 °C and extracted with Et_2O three times. The combined organic layer was washed by brine, dried over the Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford **(+)-methylaristelegone A** (32.6 mg, 65% yield, 82% ee) was obtained as a white solid. The analytic data were consistent with those reported[24].
[α]$_D^{27}$ = +14 (*c* 0.50, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 98/2, flow rate 0.4 mL/min, λ = 254 nm), t_R (minor) = 19.97 min, t_R (major) = 21.44 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.67 (s, 1H), 6.37 (d, *J* = 9.5 Hz, 1H), 5.85 – 5.75 (m, 1H), 3.84 (s, 3H), 2.95 – 2.82 (m, 1H), 2.50 – 2.40 (m, 1H), 2.18 (s, 3H), 2.15 – 2.03 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 139.5, 128.8, 126.9, 126.0, 124.3, 124.1, 108.7, 55.6, 32.2, 31 .3, 20.5, 15.9.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}O_2$ $[M + H]^+$ 205.1223, found 205.1222.

(2*S*,4*R*)-2-Hydroxy-6-methoxy-4,7-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one ((–)-aristelegone B)

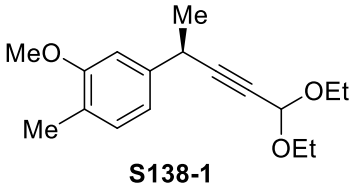


(–)-aristelegone B

To a mixture of **(+)-methylaristelegone A** (36.8 mg, 0.18 mmol, 1.0 equiv.) and KOH (56.0 mg, 1.0 mmol, 10.0 equiv.) in MeOH (0.5 mL) was added $PhI(OCOCF_3)_2$ (51.6 mg, 0.12 mmol, 1.2 equiv.) under argon atmosphere at 0 °C. The resulting reaction mixture was then naturally warmed up to the room temperature and stirred for 3 h. After completion of reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure and the residue was purified by semi-preparative HPLC purification to afford **(–)-aristelegone B** as a white solid (27.0 mg, 68%, 81% ee).
[α]$_D^{27}$ = –0.50 (*c* 1.0, CH_2Cl_2).
HPLC analysis: Chiralcel OJ3 (hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 270 nm), t_R (major) = 12.27 min, t_R (minor) = 14.60 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 6.77 (s, 1H), 4.33 (dd, *J* = 13.5, 5.3 Hz, 1H), 3.96 – 3.88 (m, 4H), 3.25 – 3.06 (m, 1H), 2.54 – 2.43 (m, 1H), 2.21 (s, 3H), 1.76 (q, *J* = 12.6 Hz, 1H), 1.45 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 163.1, 149.2, 129.9, 126.2, 122.9, 107.1, 73.1, 55.6, 41.0, 31.8, 20.7, 15.9.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}O_3$ $[M + H]^+$ 221.1172, found 221.1170.



(*R*)-4-(5,5-Diethoxypent-3-yn-2-yl)-2-methoxy-1-methylbenzene (S138-1)



S138-1

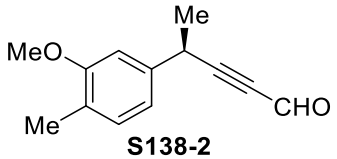
A 10 mL Schlenk tube was sequentially charged with CuTc (1.91 mg, 0.010 mmol, 5.0 mol%), **L*13** (12.5 mg, 0.015 mmol, 7.5 mol%), and Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.). Then, the tube was evacuated and refilled with argon three times. Next, anhydrous Et_2O (4.0 mL), 4-(1-bromoethyl)-2-methoxy-1-methylbenzene **S129-3** (45.6 mg, 0.20 mmol, 1.0 equiv.), and 3,3-diethoxyprop-1-yne **S44** (38.4 mg, 0.30 mmol, 1.5 equiv.) were sequentially added under an argon flow. Upon completion, the reaction mixture was stirred at room temperature for 18 h. After completion of reaction (monitored by TLC), the reaction mixture was filtered through a silica gel pad to remove insoluble solid and rinsed by CH_2Cl_2. The filtrate was concentrated under reduced pressure to afford the crude **S138-1** (94% ee), which was directly used in the next without further purification.

HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.4 mL/min, λ = 254 nm), t_R (major) = 13.59 min, t_R (minor) = 14.94 min.

Crude ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.5 Hz, 1H), 6.92 – 6.85 (m, 2H), 5.36 (s, 1H), 3.87 (s, 3H), 3.85 – 3.74 (m, 3H), 3.71 – 3.56 (m, 2H), 2.23 (s, 3H), 1.54 (d, *J* = 7.2 Hz, 3H), 1.27 (td, *J* = 7.1, 3.0 Hz, 8H).

Crude ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 141.5, 130.6, 125.0, 118.6, 108.7, 91.6, 88.9, 60.7, 60.7, 55.2, 31.8, 24.2, 15.9, 15.2.

(*R*)-4-(3-Methoxy-4-methylphenyl)pent-2-ynal (S138-2)

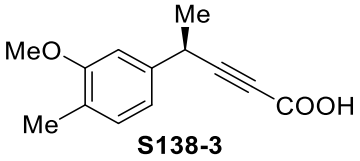


S138-2

To a solution of the crude (*R*)-**S138-1** obtained above (ca. 0.20 mmol) in THF (2.0 mL) was added dropwise HCl (1.0 M, 0.10 mL, 0.10 mmol, 0.50 equiv.) at 0 °C and the resulting reaction mixture

was stirred at 0 °C for 6 h. After completion of reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure to afford the crude product **S138-2**, which was directly used in the next step without further purification.

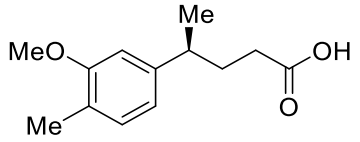
(*R*)-4-(3-Methoxy-4-methylphenyl)pent-2-ynoic acid (S138-3)



S138-3

To a solution of the crude **S138-2** obtained above in a mixture of H_2O (2.0 mL) and ^{t}BuOH (2.0 mL) were sequentially added 2-methylbut-2-ene (0.28 g, 4.0 mmol, 20.0 equiv.), NaH_2PO_4 (0.12 g, 1.0 mmol, 5.0 equiv.), and $NaClO_2$ (68.0 mg, 80% purity, 0.60 mmol, 3.0 equiv.). Upon completion, the reaction mixture was stirred at room temperature until the starting material was completely consumed (monitored by TLC). Then, the reaction mixture was diluted with EtOAc and extracted with EtOAc three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude product **S138-3**, which was directly used in the next step without further purification.

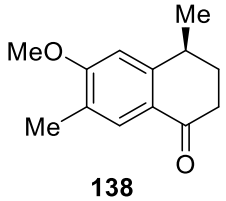
(*S*)-4-(3-Methoxy-4-methylphenyl)pentanoic acid (S138-4)



S138-4

To a two-neck flask containing Pd/C (50 mg, 10% *w*/*w* Pd on carbon, 0.047 mmol, 23 mol%) was added a solution of the crude **S138-3** obtained above (ca. 0.20 mmol) in a mixture of THF (1.0 mL) and water (1.0 mL) via syringe and the resulting mixture was stirred under an atmosphere of hydrogen gas provided by a hydrogen balloon at room temperature overnight. After completion of reaction (monitored by TLC), the reaction mixture was filtered and concentrated under reduced pressure to afford the crude product **S138-4**, which was directly used in the next step without further purification.

(*S*)-6-Methoxy-4,7-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (138)

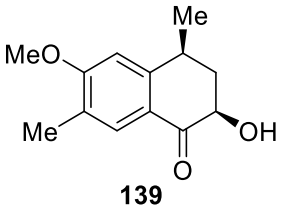


138

To a flask containing the crude **S138-4** obtained above (ca. 0.20 mmol) were added a mixture of trifluoroacetic acid (22.8 mg, 0.20 mmol, 1.0 equiv.) and trifluoroacetic anhydride (168.0 mg, 0.80 mmol, 4.0 equiv.) at 0 °C under argon atmosphere. The resulting reaction mixture was stirred under the same conditions until completion of reaction (monitored by TLC). Then, the reaction mixture was quenched by saturated $NaHCO_3$ at 0 °C and extracted with Et_2O three times. The combined organic layer was washed by brine, dried over the Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum

ether/EtOAc = 5/1) to afford **138** as a white powder (16.3 mg, 80% yield over five steps, 89% ee).
[α]$_D^{25}$ = –22 (*c* 0.40, CH_2Cl_2).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 98/2, flow rate 0.3 mL/min, λ = 270 nm), t_R (major) = 29.56 min, t_R (minor) = 32.48 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 6.70 (s, 1H), 3.92 (s, 3H), 3.14 – 3.00 (m, 1H), 2.66 (dddd, *J* = 78.8, 17.3, 8.6, 4.9 Hz, 2H), 2.30 – 2.23 (m, 1H), 2.22 (s, 3H), 1.98 – 1.84 (m, 1H), 1.41 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 162.2, 149.5, 129.6, 125.5, 124.8, 107.6, 55.5, 35.9, 33.1, 30.8, 20.8, 15.8.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}O_2$ $[M + H]^+$ 205.1223, found 205.1222.

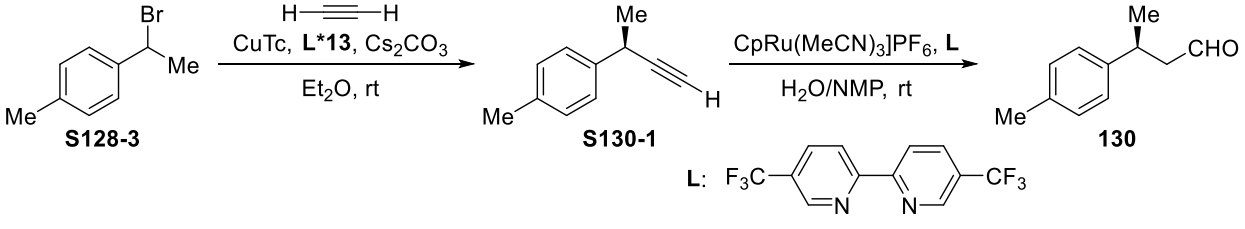
(2*R*,4*S*)-2-Hydroxy-6-methoxy-4,7-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one (139)



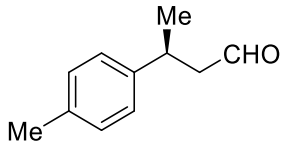
139

To a mixture of **138** (21.0 mg, 0.10 mol, 1.0 equiv.) and KOH (56.0 mg, 1.0 mmol, 10.0 equiv.) in MeOH (0.5 mL) was added $PhI(OCOCF_3)_2$ (51.6 mg, 0.12 mmol, 1.2 equiv.) under argon atmosphere at 0 °C. The resulting reaction mixture was then naturally warmed up to the room temperature and stirred for 3 h. After completion of reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford **139** as a white solid (56% yield, 6.7:1.0 dr, 89% ee).
[α]$_D^{25}$ = +21 (*c* 0.20, CH_2Cl_2).
HPLC analysis: Chiralcel OZ3 (hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 37.34 min, t_R (minor) = 42.80 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 6.80 (s, 1H), 4.36 (dd, *J* = 13.4, 5.3 Hz, 1H), 3.94 (s, 3H), 3.24 – 3.13 (m, 1H), 2.51 (dt, *J* = 12.5, 4.7 Hz, 1H), 2.24 (s, 3H), 1.78 (q, *J* = 12.6 Hz, 1H), 1.48 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 162.9, 149.1, 129.7, 126.1, 107.0, 73.0, 55.5, 40.8, 31.6, 20.5, 15.8.
HRMS (ESI) *m/z* calcd. for $C_{13}H_{17}O_3$ $[M + H]^+$ 221.1172, found 221.1170.

The synthesis of 130



(*S*)-3-(*p*-Tolyl)butanal (130)



130

According to **General procedure C** with 1-(1-bromoethyl)-4-methylbenzene **S128-3** (39.6 mg, 0.20 mmol, 1.0 equiv.), the crude product **S130-1** was obtained as a colorless oil, which was directly used in the next step without further purification.

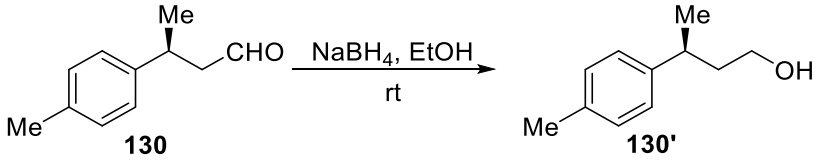
To a Schlenk tube containing $[CpRu(MeCN)_3]PF_6$ (1.7 mg, 0.0040 mmol, 2.0 mol%) and 5,5'-bis(trifluoromethyl)-2,2'-bipyridine **L** (1.2 mg, 0.0040 mmol, 2.0 mol%) was added a solution of the crude **S130-1** (ca. 0.20 mmol) in a mixture of NMP (0.8 mL) and water (0.2 mL) under argon atmosphere and the reaction mixture was stirred at 25 °C overnight. After completion of reaction (monitored by TLC), the reaction mixture was diluted by EtOAc, washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to afford **130** as a colorless oil (22.0 mg, 68% over two steps). Due to the instability of aldehyde **130**, its enantiomeric excess was determined to be 98% ee after reduction with $NaBH_4$.

$[\alpha]_D^{27}$ = +40 (*c* 0.4, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (t, *J* = 2.1 Hz, 1H), 7.14 (s, 4H), 3.39 – 3.23 (m, 1H), 2.79 – 2.60 (m, 2H), 2.34 (s, 3H), 1.32 (d, *J* = 6.8 Hz, 3H).

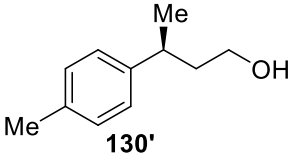
^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 142.4, 136.1, 129.3, 126.6, 51.8, 33.9, 22.3, 21.0.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{14}NaO$ $[M + Na]^+$ 185.0937, found 185.0938.



130 **130'**

(*S*)-3-(*p*-Tolyl)butan-1-ol (130')



130'

To a solution of aldehyde **130** (16.2 mg, 0.10 mmol, 1.0 equiv.) in EtOH (1.0 mL) was added $NaBH_4$ (7.6 mg, 0.20 mmol, 2.0 equiv.) and the resulting reaction mixture was stirred at room temperature for 3 h. After completion of reaction (monitored by TLC), the reaction mixture was quenched by water and extracted with EtOAc three times. The combined organic layer was washed by brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford **130'** as a colorless oil (14.9 mg, 91% yield, 98% ee).

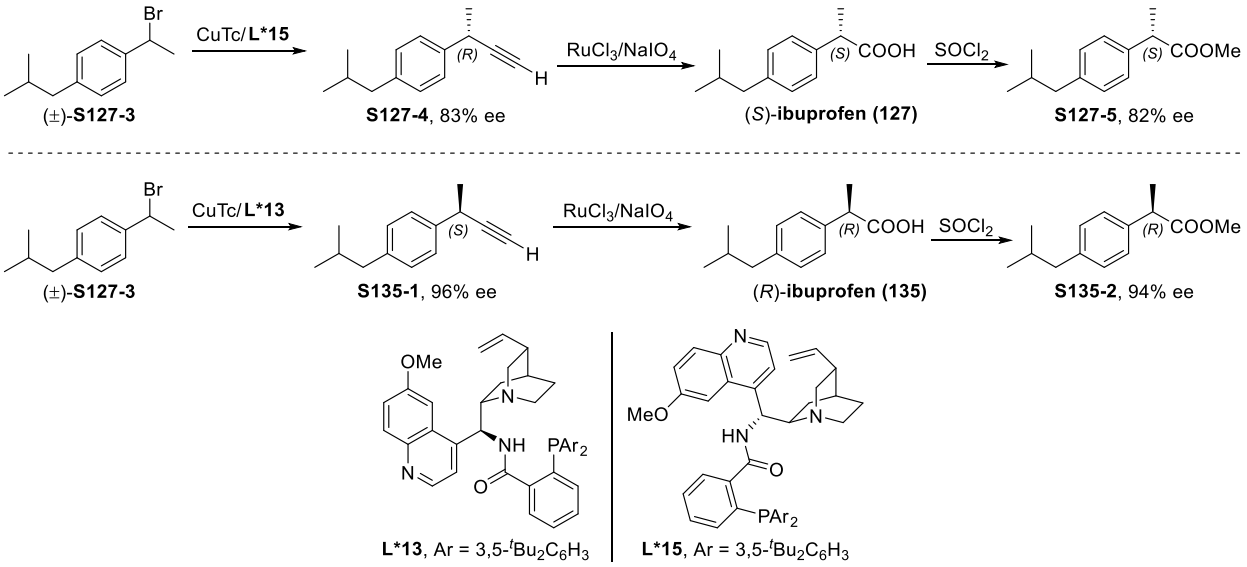
$[\alpha]_D^{27}$ = +13 (*c* 0.31, CH_2Cl_2).

HPLC analysis: Chiralcel AY3 (hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 214 nm), t_R (minor) = 20.81 min, t_R (major) = 22.80 min.

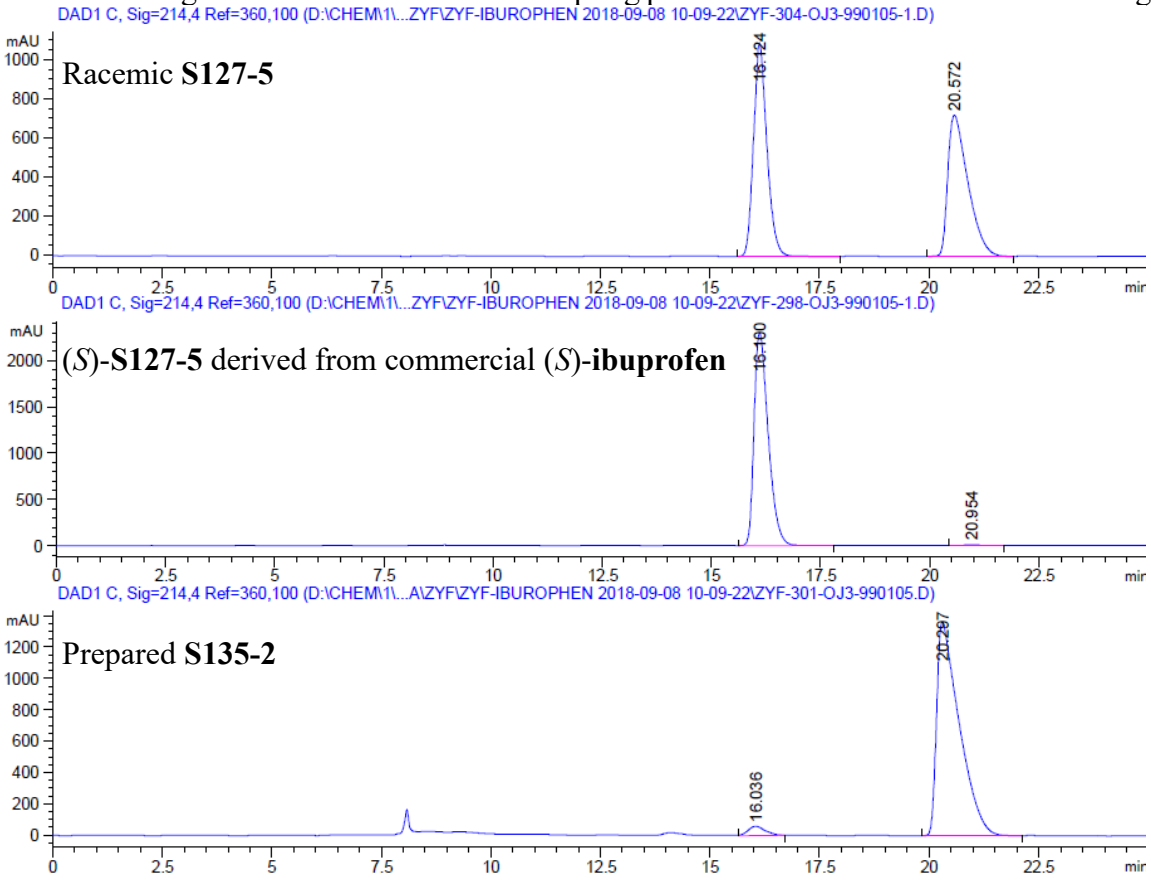
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 4H), 3.62 – 3.49 (m, 2H), 2.91 – 2.80 (m, 1H), 2.32 (s, 3H), 1.91 – 1.77 (m, 2H), 1.26 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 135.6, 129.2, 126.8, 61.3, 41.0, 36.1, 22.6, 21.0.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{16}NaO$ $[M + Na]^+$ 187.1093, found 187.1093.

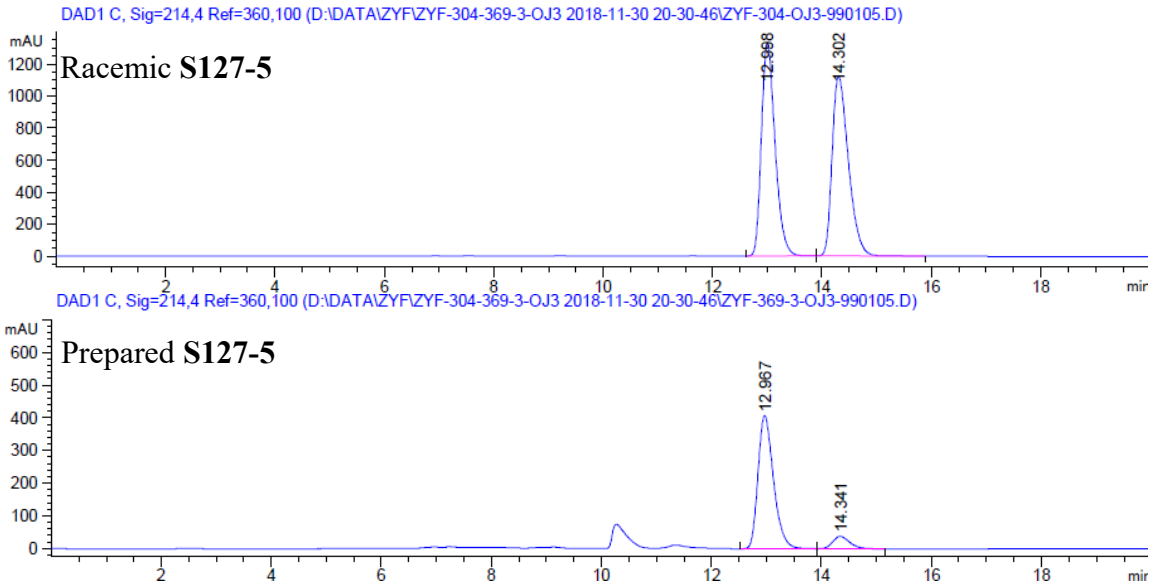
Assignment of absolute stereochemistry

Method I: The synthesis of ibuprofen derivatives



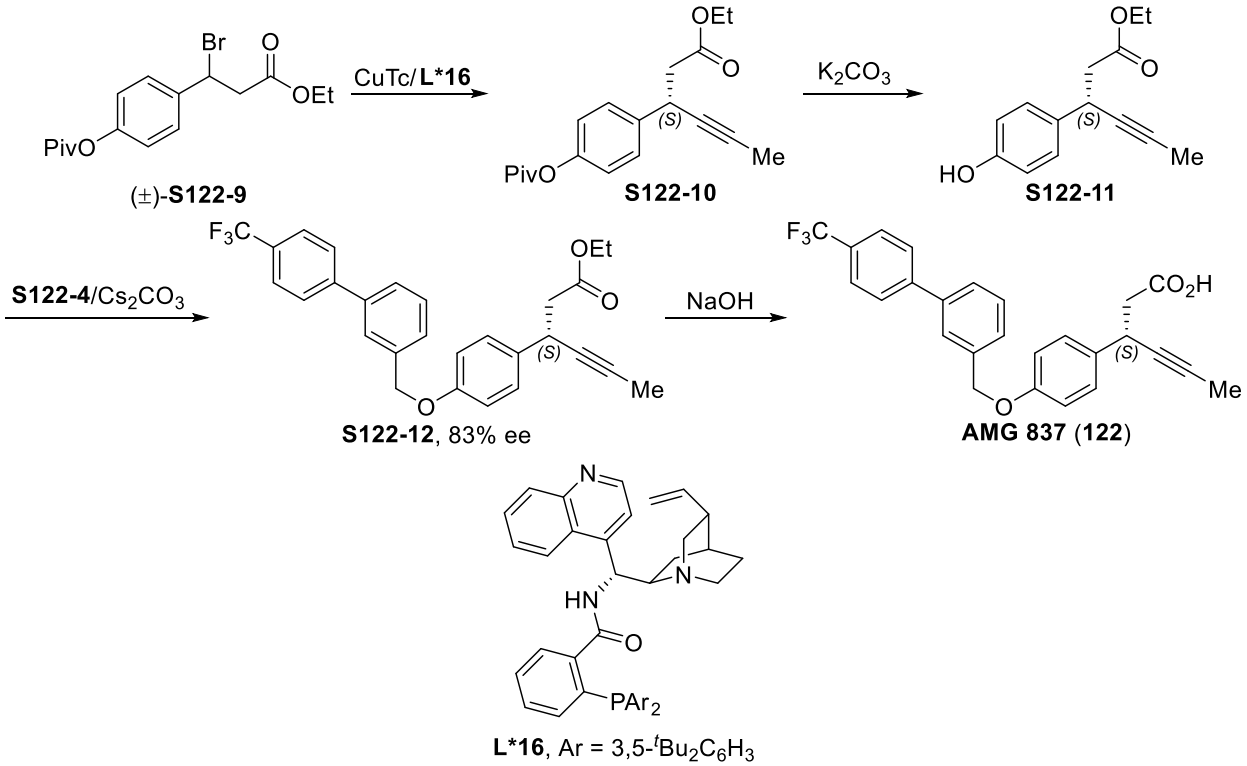
The absolute configuration was determined by comparing HPLC traces of prepared **S127-5** and the one derived from commercial (*S*)-**ibuprofen**(**127**) (*purchased from Shanghai Bidepharm technology Ltd.*), as shown below. Accordingly, **L*13** leads to coupling product **S135-1** of the *S* absolute configuration and **L*15** leads to coupling product **S127-4** of the *R* absolute configuration.





Entry	Sample	Absolute configuration	Ee/%
1	(*S*)-**S127-5** derived from commercial (*S*)-**ibuprofen**	*S*	–99
2	Prepared **S135-2**	*R*	94
3	Prepared **S127-5**	*S*	–82

Method II: The synthesis of AMG 837

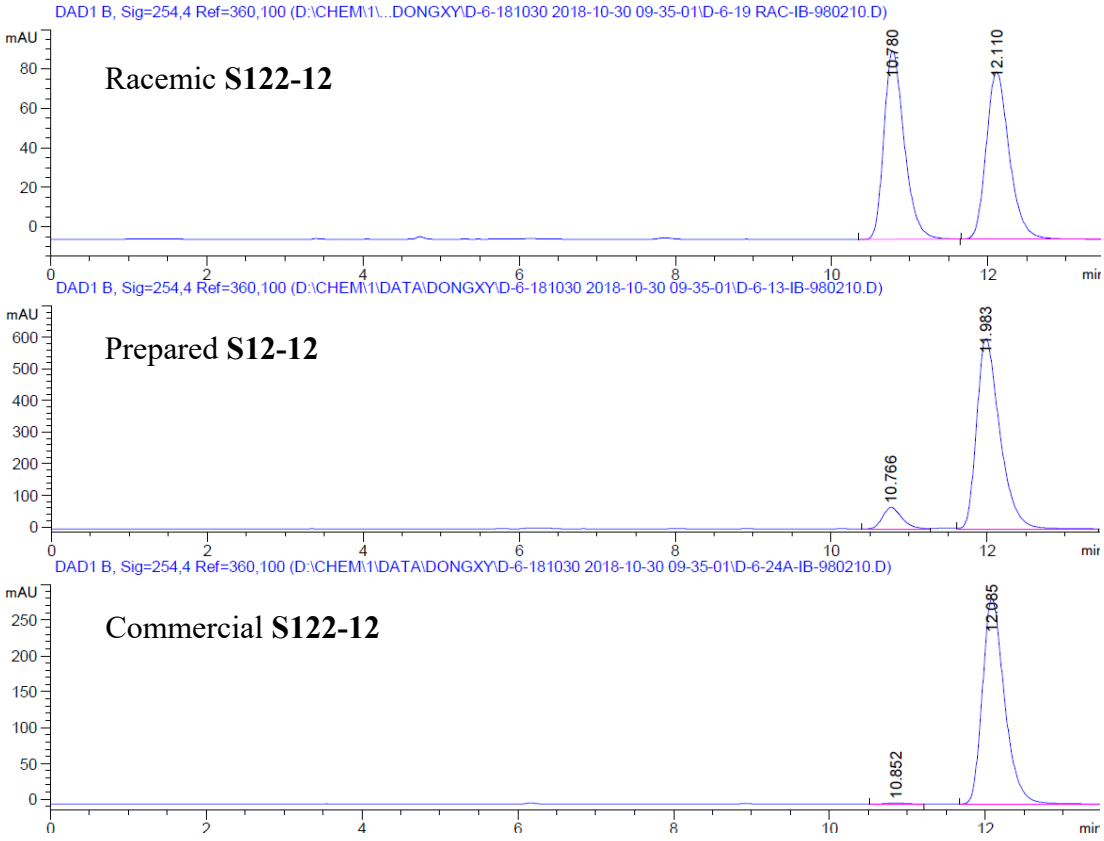


The absolute configuration could also be determined by comparing HPLC traces or specific optical rotations of prepared **S122-12** and **AMG 837** (**122**) with the commercial ones (*purchased from*

WuXi AppTec with >99% purity), respectively, as shown below. Accordingly, **L*16** leads to coupling product **S122-12** of the *S* absolute configuration.

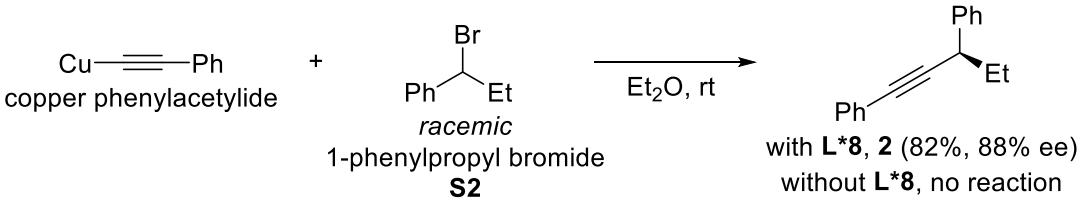
Entry	Sample	Ee/%	Configuration	$[\alpha]_D^{27}$
1	Prepared **S122-12**	–83	*S*	+4.5 (*c* 0.71, CH_2Cl_2)
2	Commercial **S1229-12**	–99	*S*	+5.5 (*c* 2.8, CH_2Cl_2)
3	Prepared **AMG 837 (122)**		*S*	+4.3 (*c* 0.75, CH_2Cl_2)
4	Commercial **AMG 837 (122)**		*S*	+7.5 (*c* 0.91, CH_2Cl_2)*

Reported specific optical rotation of* **AMG 837 of the *S* absolution configuration: $[\alpha]_D^{22}$= +10.9 (*c* 0.44, $CHCl_3$, >99% ee)[25].



Mechanistic study

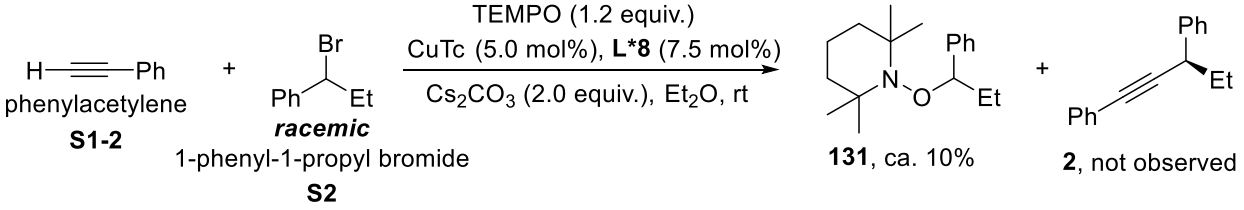
Control experiment with copper phenylacetylide



Copper phenylacetylide was synthesized according to literature[26].
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with copper phenylacetylide (16.5 mg, 0.10 mmol, 1.0 equiv.), (1-bromopropyl)benzene **S2** (19.9 mg, 0.10 mmol, 1.0 equiv.), **L*8** (61.1 mg, 0.10 mmol, 1.0 equiv.), and anhydrous Et_2O (2.0 mL). The resulting reaction mixture was stirred at room temperature for 12 h. Upon completion of reaction (monitored by TLC), the reaction mixture was filtered and washed by Et_2O. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether) to afford **2** (18.0 mg, 82% yield, 88% ee).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 4.84 min, t_R (major) = 5.63 min.

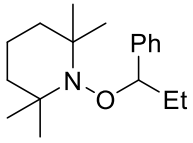
The procedure for the reaction without **L*8** was the same with that described above except that **L*8** was not added. No desired product **2** was observed.

Control experiment with TEMPO



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with (1-bromopropyl)benzene **S2** (39.8 mg, 0.20 mmol, 1.0 equiv.), phenylacetylene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.), CuTc (1.9 mg, 0.010 mmol, 5.0 mol%), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (37.4 mg, 0.24 mmol, 1.2 equiv.), **L*8** (9.2 mg, 0.015 mmol, 7.5 mol%), Cs_2CO_3 (130.4 mg, 0.40 mmol, 2.0 equiv.), and anhydrous Et_2O (4.0 mL). The resulting reaction mixture was stirred at room temperature for 72 h. Upon completion, the reaction was filtered and washed by Et_2O. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford **131** (ca. 5.5 mg, ca. 10% yield)[27] with a trace amount of impurities. No product **2** was observed.

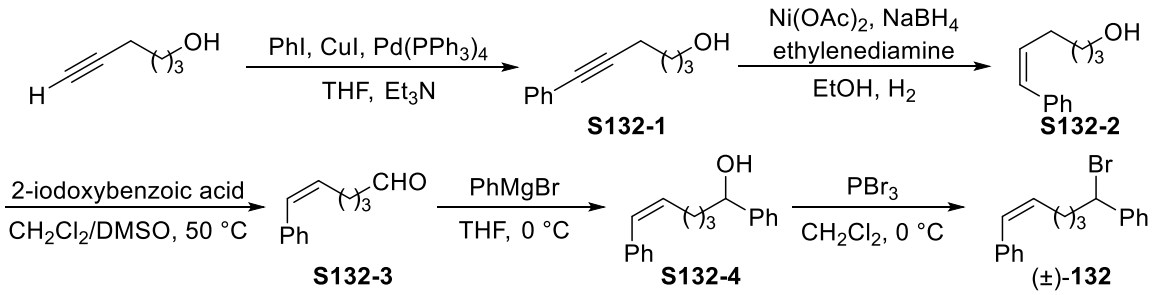
2,2,6,6-Tetramethyl-1-(1-phenylpropoxy)piperidine (131)



131

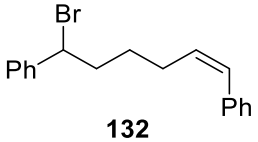
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 1H), 7.31 – 7.27 (m, 3H), 7.25 – 7.19 (m, 1H), 4.53 (dd, *J* = 9.5, 3.9 Hz, 1H), 2.15 – 2.05 (m, 1H), 1.84 – 1.75 (m, 1H), 1.49 (br s, 3H), 1.36 – 1.23 (m, 6H), 1.17 (br s, 3H), 1.01 (br s, 3H), 0.89 – 0.84 (m, 1H), 0.66 (t, *J* = 7.5 Hz, 3H), 0.58 (br s, 2H).
HRMS (ESI) *m/z* calcd. for $C_{18}H_{30}NO$ $[M + H]^+$ 276.2321, found 276.2313.

The synthesis of 132



S132-3 was prepared according to a reported procedure from 5-hexyn-1-ol[28,29].

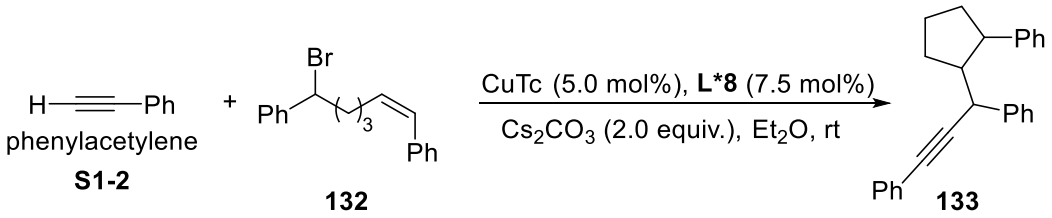
(*Z*)-(6-Bromohex-1-ene-1,6-diyl)dibenzene (132)



132

According to ***Method b*** of **General procedure 4** with **S132-3** (0.52 g, 3.0 mmol, 1.0 equiv.) and phenylmagnesium bromide (3.6 mL, 1.0 M in Et_2O, 3.6 mmol, 1.2 equiv.), **132** was obtained as a colorless oil (0.69 g, 73% crude yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.26 (m, 10H), 6.52 (d, *J* = 11.5 Hz, 1H), 5.75 – 5.62 (m, 1H), 4.98 (t, *J* = 7.6 Hz, 1H), 2.49 – 2.40 (m, 2H), 2.40 – 2.32 (m, 1H), 2.30 – 2.18 (m, 1H), 1.78 – 1.65 (m, 1H), 1.62 – 1.48 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 137.6, 132.0, 129.7, 128.82, 128.77, 128.4, 128.3, 127.3, 126.7, 55.4, 39.5, 28.5, 27.8.
HRMS (ESI) *m/z* calcd. For $C_{18}H_{19}$ $[M – Br]^+$ 235.1481, found 235.1479.

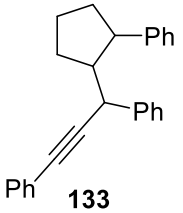
Radical clock experiment



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (1.9 mg, 0.01 mmol, 5.0 mol%), **L*8** (9.2 mg, 0.015 mmol, 7.5 mol%), Cs_2CO_3 (130.4 mg, 0.4 mmol, 2.0 equiv.), and anhydrous Et_2O (4.0 mL). Then, (*Z*)-(6-bromohex-1-ene-1,6-diyl)dibenzene **132** (63.0 mg, 0.20 mmol, 1.0 equiv.) and phenylacetylene **S1-2** (30.6 mg, 0.30 mmol, 1.5 equiv.) were sequentially added and the resulting reaction mixture was stirred at room temperature for 72 h. Upon completion of reaction (monitored by TLC), the reaction

mixture was filtered and washed with petroleum ether. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford **133** as a colorless oil (51.0 mg, 76% yield).

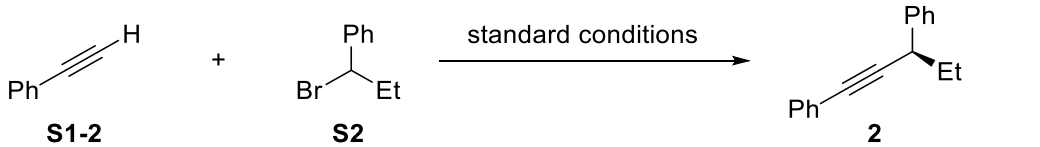
(3-(2-Phenylcyclopentyl)prop-1-yne-1,3-diyl)dibenzene (133)



133

^{1}H NMR (400 MHz, $CDCl_3$) (a mixture of diastereomers) δ 7.56 – 7.53 (m, 1H), 7.44 – 7.38 (m, 1H), 7.37 – 7.34 (m, 5H), 7.33 (d, *J* = 4.2 Hz, 2H), 7.31 (d, *J* = 2.3 Hz, 1H), 7.30 (d, *J* = 2.2 Hz, 1H), 7.27 (s, 1H), 7.26 – 7.22 (m, 2H), 7.22 – 7.18 (m, 1H), 3.93 (d, *J* = 3.9 Hz, 0.73H), 3.53 (d, *J* = 6.3 Hz, 0.27H), 3.21 – 3.11 (m, 1H), 2.36 – 2.23 (m, 1H), 2.21 – 2.15 (m, 1H), 2.13 – 1.99 (m, 1H), 1.97 – 1.84 (m, 1H), 1.84 – 1.75 (m, 2H), 1.71 – 1.58 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) (a mixture of diastereomers) δ 144.6, 142.8, 142.0, 141.6, 131.8, 131.5, 129.0, 128.6, 128.33, 128.29, 128.24, 128.22, 128.1, 128.0, 127.9, 127.7, 127.6, 126.51, 126.46, 126.3, 126.1, 124.0, 123.9, 91.7, 89.0, 84.9, 83.6, 55.1, 50.9, 50.6, 48.8, 39.9, 39.3, 34.9, 31.8, 28.7, 27.2, 24.2, 23.8.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{25}$ $[M + H]^+$ 337.1951, found 337.1946.

ICP-MS analysis
Analysis of the crude reaction mixture



S1-2 0.15 mmol | **S2** 0.10 mmol | **2** 75% conversion, 73% yield

The reaction was run on a 0.10 mmol scale under the standard conditions for 12 h. Upon completion, the reaction mixture was evaporated under reduced pressure. The residue thus obtained was mixed with concentrated HNO_3 (4 mL) and heated at 90 °C for 2 h until a clear solution was obtained. Next, the solution was diluted with HNO_3 (2%) to a total volume of 50 mL. The resulting solution was subjected to ICP-MS analysis.

Contents of trace metal impurities in the crude reaction mixture

Element	Percentage (w/w_{Cu}%)
Fe	1
Co	0.03
Ni	0.08
Pd	0.005

Analysis of CuTc catalyst

A mixture of CuTc (25 mg) and concentrated HNO_3 (1 mL) was heated at 50 °C for 0.5 h until a clear solution was obtained. The solution was next diluted with HNO_3 (2%) to a total volume of 50 mL. The resulting solution was subjected to ICP-MS analysis.

Contents of trace metal impurities in the CuTc catalyst

Element	Percentage (w/w_{Cu}%)
Fe	0.1
Co	0.006
Ni	0.01
Pd	0.004

Trace metal control experiments

Reaction note:

All the equipments used (Schlenk tube, magnetic stir bar, *etc.*) were new in order to reduce the background contents of trace metals as much as possible.

Preparation of metal stock solutions:

$Pd(PPh_3)_4$ (3.5 mg) was dissolved in 10.0 mL of toluene. For reactions containing 100, 1000, and 10000 ppm of Pd, 1, 10, and 100 μL of the Pd stock solutions were added with Hamilton syringes to the reaction mixture, respectively

$FeCl_3$ (9.0 mg) was weighed in a glovebox, and then dissolved in 10.0 mL of toluene. The mixture was ultrasonicated for 0.5 h. For the reaction containing 100000 ppm of Fe, 100 μL of the Fe stock solution was added with a Hamilton syringe to the reaction mixture.

$Ni(acac)_2$ (1.4 mg) was dissolved in 1.0 mL of toluene and the mixture was ultrasonicated for 0.5 h. For the reaction containing 100000 ppm of Ni, 100 μL of the Ni stock solution was added with a Hamilton syringe to the reaction mixture.

General procedure E with metal additives

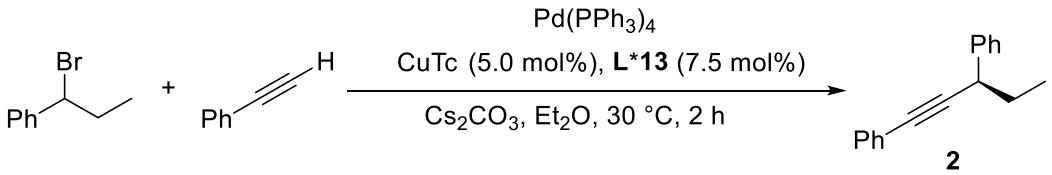
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (0.95 mg, 0.0050 mmol, 5.0 mol%), **L*13** (6.3 mg, 0.0075 mmol, 7.5 mol%), Cs_2CO_3 (65.2 mg, 0.20 mmol, 2.0 equiv.), and anhydrous Et_2O (2.0 mL). Then, 1-phenylpropyl bromide (19.9 mg, 0.10 mmol, 1.0 equiv.), phenylacetylene (15.3 mg, 0.15 mmol, 1.5 equiv.), and a metal solution mentioned above were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 2 h. Upon completion, the reaction mixture was concentrated, and then 1,3,5-trimethoxybenzene (5.6 mg, 0.033 mmol, 0.033 equiv.) was added as an internal standard to obtain conversion and yield with ^{1}H-NMR analysis. Then the residue was purified by column chromatography on silica gel to afford the desired product for determination of ee with HPLC analysis.

General procedure F with other metal catalysts

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with the corresponding metal catalyst [M] (0.0050 mmol, 5.0 mol%), **L*8** (4.6 mg, 0.0075 mmol, 7.5 mol%), Cs_2CO_3 (65.2 mg, 0.20 mmol, 2.0 equiv.), and anhydrous Et_2O (2.0 mL). Then, 1-phenylpropyl bromide (19.9 mg, 0.10 mmol, 1.0 equiv.) and phenylacetylene (15.3 mg,

0.15 mmol, 1.5 equiv.) were added sequentially and the reaction mixture was stirred at room temperature for 24 h. Upon completion, the reaction mixture was concentrated and then, 1,3,5-trimethoxybenzene (5.6 mg, 0.033 mmol, 0.033 equiv.) was added as an internal standard to obtain conversion and yield with ^{1}H NMR. Then, the residue was purified by column chromatography on silica gel to afford the desired product for determination of ee with HPLC analysis.

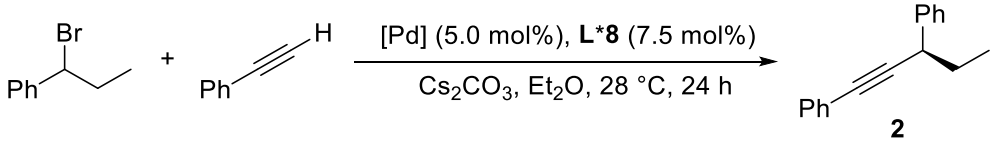
Effects of Pd additive



According to **General procedure E**, 100, 1000, and 10000 ppm of $Pd(PPh_3)_4$ were added to the reaction mixture, respectively. After 2 h, the reaction results were as follows.

Entry	[Pd] (ppm)	Conversion (%)	Yield (%)	Ee (%)
1	0	45	43	97
2	100	42	41	97
3	1000	46	45	97
4	10000	48	41	97

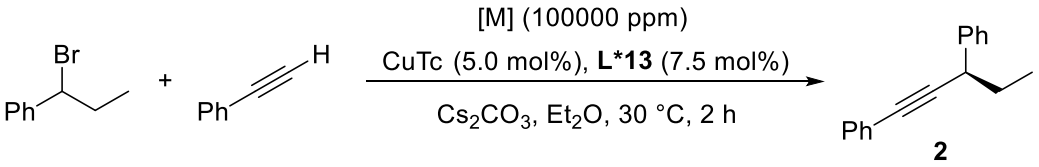
Catalytic performance of Pd catalysts



According to **General procedure F**, $Pd(PPh_3)_4$ (5.8 mg), $Pd(PPh_3)_2Cl_2$ (3.5 mg), $Pd_2(dba)_3$ (2.3 mg), and $Pd(OAc)_2$ (1.1 mg) were used as metal catalysts instead of CuTc. The reaction results were as follows.

Entry	[Pd]	Conversion (%)	Ee (%)
1	$Pd(PPh_3)_4$	0	/
2	$Pd(PPh_3)_2Cl_2$	0	/
3	$Pd_2(dba)_3$	0	/
4	$Pd(OAc)_2$	0	/

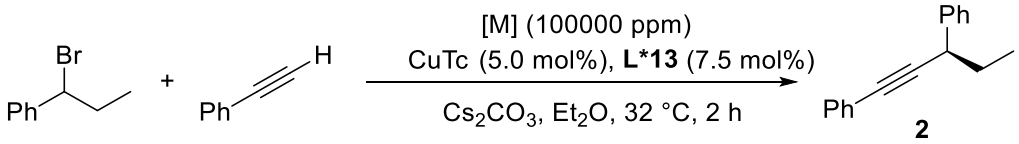
Effects of [Fe] and [Ni] additives



According to **General procedure E**, 100000 ppm of $FeCl_3$ and 100000 ppm of $Ni(acac)_2$ were added to the reaction mixtures, respectively. After 2 h, the reaction results were as follows.

Entry	[M]	Conversion (%)	Yield (%)	Ee (%)
1	none	47	46	97
2	$FeCl_3$	50	46	97
3	$Ni(acac)_2$	58	47	97

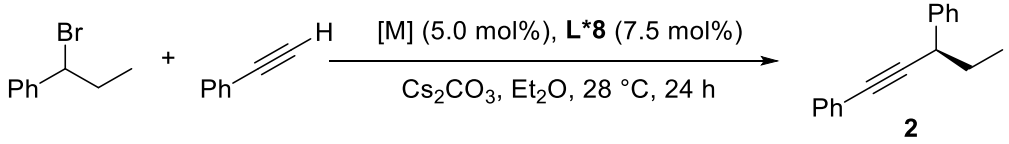
Effects of [Co] additive



According to **General procedure E**, 100000 ppm of $Co(PPh_3)_3Cl$ (0.48 mg) was added to the reaction mixture. After 2 h, the reaction results were as follows.

Entry	[M]	Conversion (%)	Yield (%)	Ee (%)
1	none	58	52	97
2	$Co(PPh_3)_3Cl$	60	54	97

Catalytic performance of other transition metal catalysts

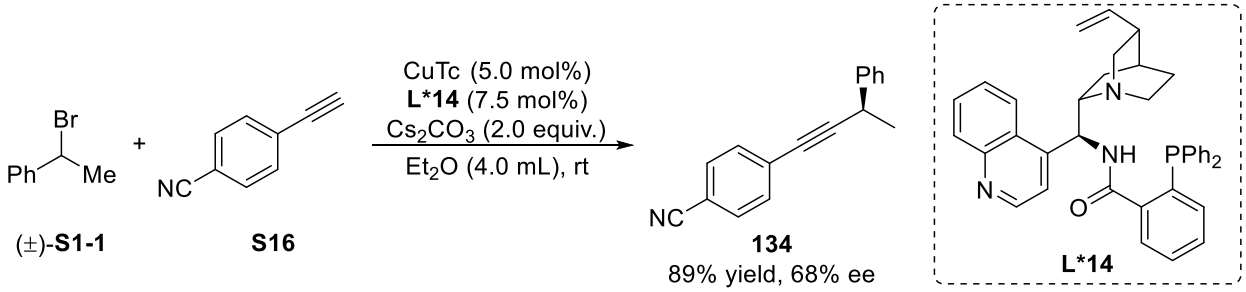


According to **General procedure F**, $FeCl_3$ (0.81 mg), $Co(PPh_3)_3Cl$ (4.4 mg), $NiCl_2$ (0.65 mg), $NiBr_2$ (1.1 mg), $Ni(PCy_3)_2Cl_2$ (3.4 mg), and $Ni(PPh_3)_2Cl_2$ (3.3 mg) were used as metal catalysts, respectively, instead of CuTc. The reaction results were as follows.

Entry	[M]	Conversion (%)	Ee (%)
1	$FeCl_3$	0	/
2	$Co(PPh_3)_3Cl$	0	/

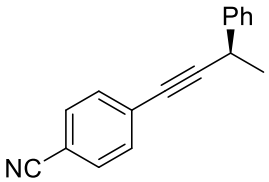
3	$NiCl_2$	0	/
4	$NiBr_2$	0	/
5	$Ni(PCy_3)_2Cl_2$	0	/
6	$Ni(PPh_3)_2Cl_2$	0	/

Experiments with racemic and enantioenriched alkyl bromide S1-1



According to **General procedure A** with (1-bromoethyl)benzene (±)-**S1-1** (57.0 mg, 0.30 mmol, 1.5 equiv.), 4-ethynylbenzonitrile **S16** (25.0 mg, 0.20 mmol, 1.0 equiv.), and **L*14** (9.0 mg, 0.015 mmol, 7.5 mol%) instead of **L*13** for facile determination of yield by ^{1}H NMR, **134** (44.0 mg, 89% yield, 68% ee) was obtained.

(*R*)-4-(3-phenylbut-1-yn-1-yl)benzonitrile (134)



134

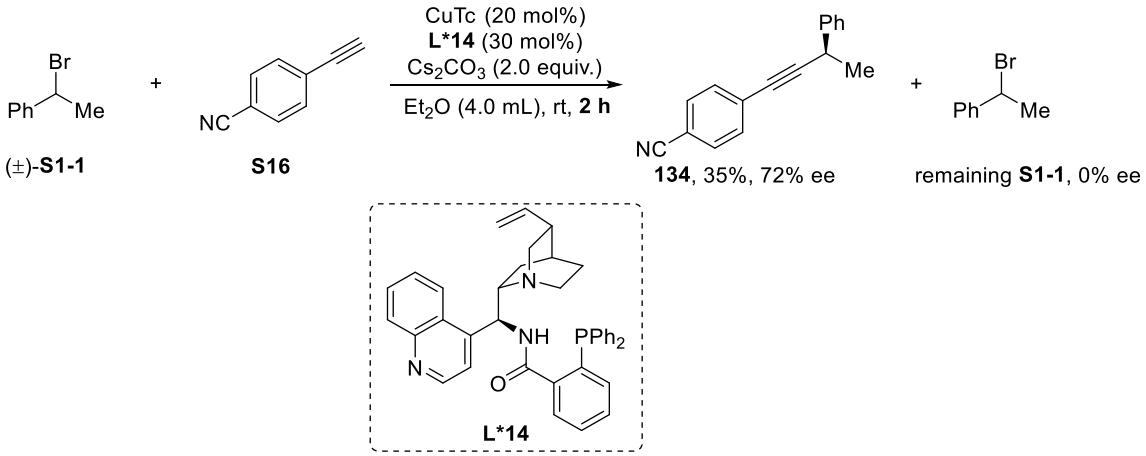
[α]$_D^{27}$ = –3.3 (*c* 4.4, CH_2Cl_2).

HPLC analysis: Chiralcel ASH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.02 min, t_R (major) = 13.70 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.56 – 7.50 (m, 2H), 7.48 – 7.42 (m, 2H), 7.40 – 7.36 (m, 2H), 7.33 – 7.27 (m, 1H), 4.03 (q, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 7.1 Hz, 3H).

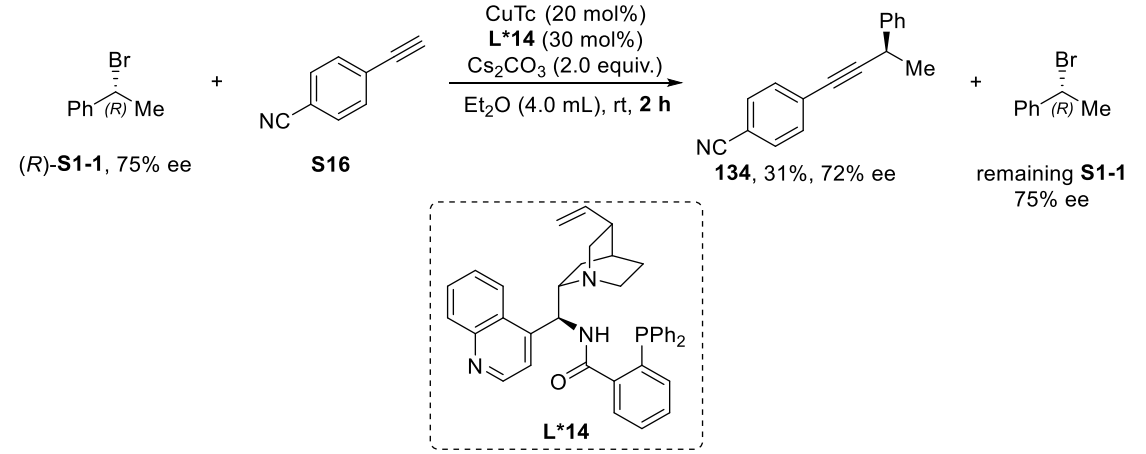
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 132.2, 131.9, 128.7, 127.0, 126.9, 118.6, 111.1, 97.6, 81.1, 32.6, 24.1.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{14}N$ $[M + H]^+$ 232.1121, found 232.1117.



An oven-dried Schlenk tube was sequentially charged with CuTc (3.8 mg, 0.02 mmol, 20 mol%), **L*14** (18.0 mg, 0.030 mmol, 30 mol%), and Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv.). The tube was evacuated and back-filled with argon three times. Then, Et_2O (4.0 mL), **S16** (13.0 mg, 0.10 mmol, 1.0 equiv.), and 1-phenylethyl bromide (±)-**S1-1** (18.0 mg, 0.10 mmol, 1.0 equiv.) were added under argon atmosphere. The resulting mixture was stirred at room temperature for 2 h. Upon completion, two aliquots of the reaction mixture (0.2 mL) were taken out. One aliquot was quenched with H_2O and extracted with Et_2O. The combined organic layer was concentrated to afford crude product **134** together with remaining **S1-1** for the determination of ee values. Meanwhile, the other aliquot was concentrated and the residue was analyzed by ^1H NMR with 4-bromo-*N*,*N*-dimethylaniline as an internal standard.

Reaction time	Yield of **134**	ee of remaining **S1-1**	ee of **134**
2 h	35%	0%	72%

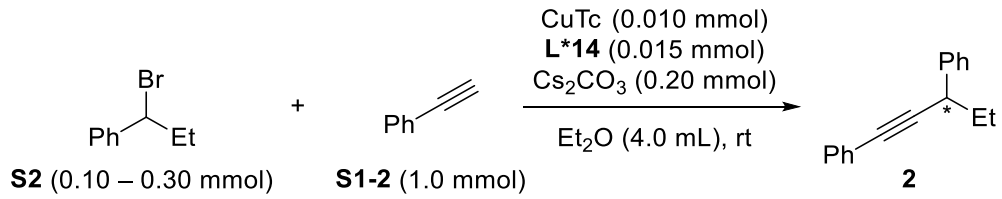


The procedure for the reaction with (*R*)-1-phenylethyl bromide[30] (*R*)-**S1-1** was the same with that for (±)-**S1-1** described above except that (*R*)-**S1-1** (18.0 mg, 75% ee, 0.10 mmol, 1.0 equiv.) was used instead of (±)-**S1-1**.

Reaction time	Yield of **134**	ee of remaining **S1-1**	ee of **134**
2 h	31%	75%	72%

Kinetic Studies

Experiment for determining the dependence of reaction rate on the concentration of alkyl bromide



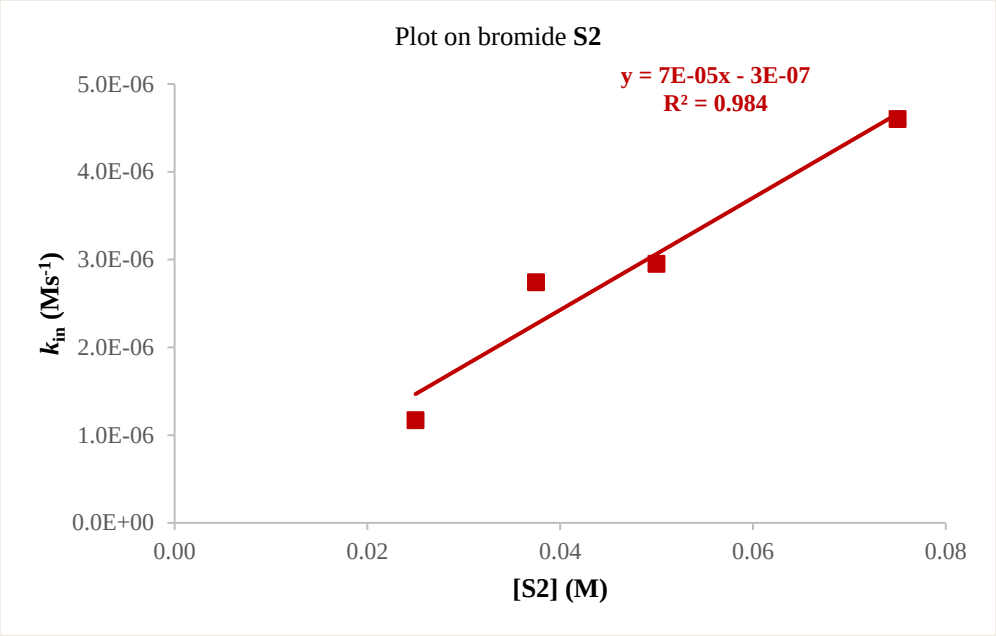
An oven-dried Schlenk tube was sequentially charged with CuTc (1.9 mg, 0.010 mmol), **L*14** (9.0 mg, 0.015 mmol), Cs_2CO_3 (65 mg, 0.20 mmol), and 4-bromo-*N*,*N*-dimethylaniline (20 mg, 0.10 mmol, as an internal standard). The tube was evacuated and back-filled with argon three times. Then, Et_2O (4.0 mL), phenylacetylene **S1-2** (0.11 mL, 0.10 g, 1.0 mmol), and 1-phenylpropyl bromide **S2** (19.9 – 59.7 mg, 0.10 – 0.30 mmol) were added under argon atmosphere. The resulting reaction mixture was stirred at room temperature. An aliquot of the reaction mixture (0.2 mL) was taken out at 6, 12, 18, 24, 30, and 36 min, respectively, and quenched with H_2O immediately. The reaction mixture was next extracted with Et_2O and the combined organic layer was concentrated. The residue was analyzed by ^1H NMR spectroscopy.

Supplementary Table 9. The molar concentrations of product **2** ([**2**]/M) with different initial concentrations of 1-phenylpropyl bromide (**S2**) at different time intervals

Times (s)	0.025 M [S2]	0.0375 M [S2]	0.050 M [S2]	0.075 M [S2]
360	0.00042	0.00056	0.00052	0.00088
720	0.00098	0.00110	0.00103	0.00140
1080	0.00142	0.00230	0.00230	0.00290
1440	0.00158	0.00310	0.00350	0.00360
1800	0.00223	0.00450	0.00460	0.00680
2160				0.00910

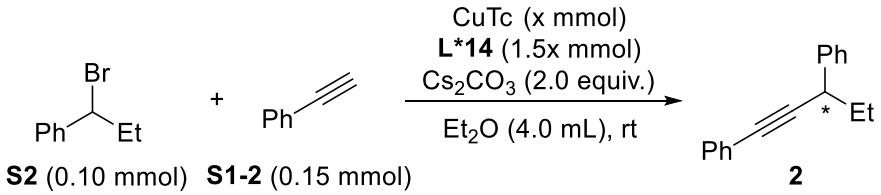
Supplementary Table 10. The k_{in} values at different initial concentrations of 1-phenylpropyl bromide (**S2**)

[S2] (M)	k_{in} (Ms^{-1})
0.0250	1.17×10^{-6}
0.0375	2.74×10^{-6}
0.0500	2.95×10^{-6}
0.0750	4.60×10^{-6}



Supplementary Fig. 10. Plot of k_{in} versus [**S2**] from the reactions with 0.025 M, 0.0375 M, 0.050 M, and 0.075 M of 1-phenylpropyl bromide **S2**.

Experiment for determining the dependence of reaction rate on the concentration of CuTc



S2 (0.10 mmol) **S1-2** (0.15 mmol) **2**

An oven-dried Schlenk tube was sequentially charged with CuTc (x mmol, x = 0.0050 – 0.020, 5.0 – 20 mol%) and **L*14** (1.5x mmol, 7.5 – 30 mol%), Cs_2CO_3 (65.0 mg, 0.20 mmol, 2.0 equiv.), and 4-bromo-*N*,*N*-dimethylaniline (20 mg, 0.10 mmol, as an internal standard). The tube was evacuated and back-filled with argon three times. Then, Et_2O (4.0 mL), phenylacetylene **S1-2** (16 µL, 15 mg, 0.15 mmol, 1.5 equiv.), and 1-phenylpropyl bromide **S2** (20 mg, 0.10 mmol, 1.0 equiv.) were added under argon atmosphere. The resulting reaction mixture was stirred at room temperature. An aliquot of the reaction mixture (0.2 mL) was taken out at 12, 18, 24, 30, and 36 min, respectively, and quenched with H_2O immediately. The reaction mixture was extracted with Et_2O and the combined organic layer was concentrated. The residue was analyzed by ^1H NMR spectroscopy. (For the reaction with 0.0050 mmol CuTc, the reaction times were 20, 40, 60, and 80 min, respectively)

Supplementary Table 11. The molar concentrations of product **2** ([**2**]/**M**) in with difference 0.00125 M initial concentration of CuTc/ligand at different time intervals

Reaction time (s)	**0.00125 M [CuTc]**
1200	0.00034

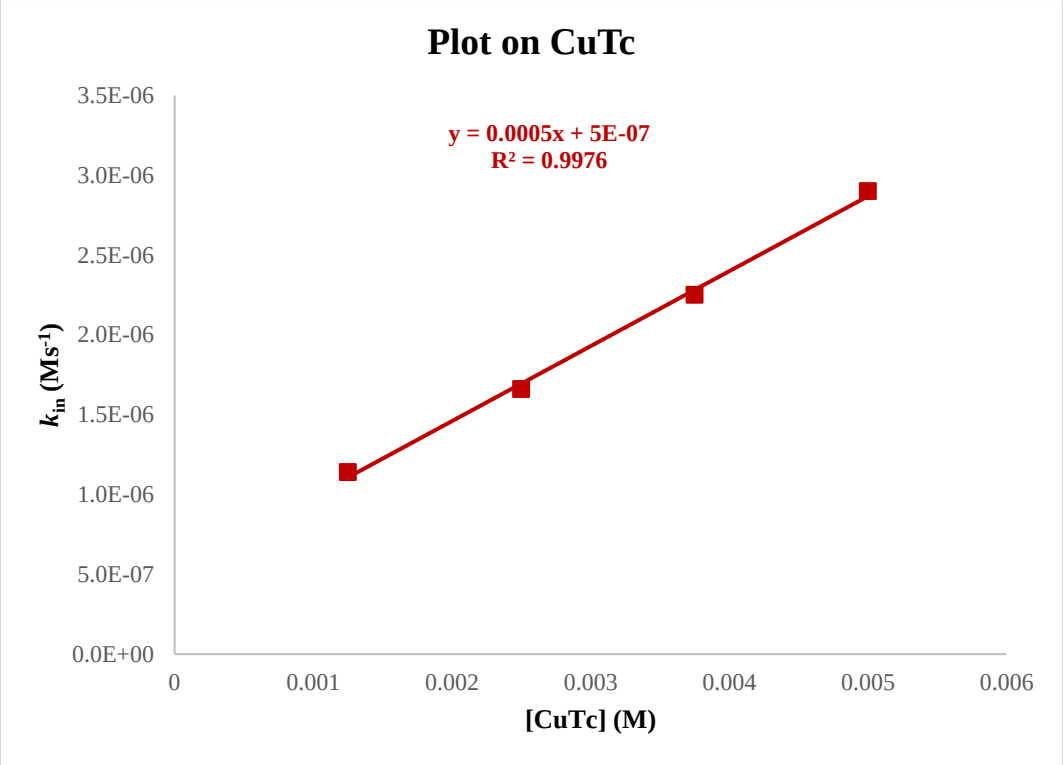
2400	0.00130
3600	0.00370
4800	0.00410

Supplementary Table 12. The molar concentrations of product **2** ([**2**]/M) with different initial concentrations of CuTc at different time intervals

Reaction time (s)	0.0025 M [CuTc]	0.00375 M [CuTc]	0.0050 M [CuTc]
720	0.00054	0.00105	0.00105
1080	0.00093	0.00190	0.00210
1440	0.00165	0.00300	0.00310
1800	0.00220	0.00350	0.00420
2160	0.00290	0.00430	

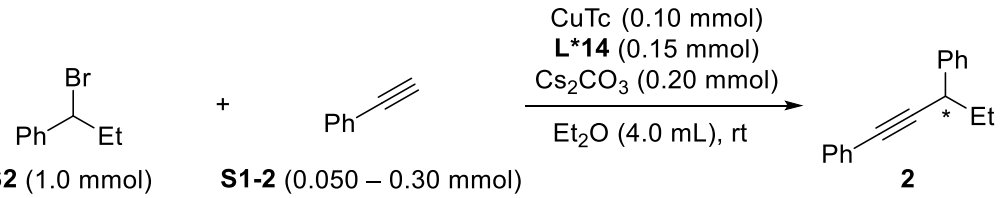
Supplementary Table 13. The k_{in} values at different initial concentrations of CuTc

[CuTc] (M)	k_{in} (Ms^{-1})
0.00125	1.14×10^{-6}
0.00250	1.66×10^{-6}
0.00375	2.25×10^{-6}
0.00500	2.90×10^{-6}



Supplementary Fig. 11. Plot of k_{in} versus [CuTc] from the reactions with 0.00125 M, 0.00250 M, 0.00375 M, and 0.00500 M of CuTc.

Experiment for determining the dependence of reaction rate on the concentration of alkyne



An oven-dried Schlenk tube was sequentially charged with CuTc (1.9 mg, 0.010 mmol, 0.10 equiv.), **L*14** (9.0 mg, 0.015 mmol, 0.15 equiv.), Cs_2CO_3 (65 mg, 0.20 mmol, 2.0 equiv.), and 4-bromo-*N*,*N*-dimethylaniline (20 mg, 0.10 mmol, as an internal standard). The tube was evacuated and back-filled with argon three times. Then, Et_2O (4.0 mL), phenylacetylene **S1-2** (0.050 mmol to 0.30 mmol), and 1-phenylpropyl bromide **S2** (0.20 g, 1.0 mmol, 1.0 equiv.) were added under argon atmosphere. An aliquot of the reaction mixture (0.2 mL) was taken out at 12, 18, 24, 30, and 36 min, respectively, and quenched with H_2O immediately. The reaction mixture was extracted with Et_2O and the combined organic layer was concentrated. The residue was analyzed by ^1H NMR spectroscopy. (For the reaction with 0.050 mmol phenylacetylene **S1-2**, the reaction times were 10, 20, 30, 40, 50, and 60 min, respectively)

Supplementary Table 14. The molar concentrations of product **2** ([**2**]/M) with 0.0125 M initial concentration of phenylacetylene **S1-2** at different time intervals

Reaction times (s)	**0.0125 M [S1-2]**
600	0.00078
1200	0.00104
1800	0.00160
2400	0.00200
3000	0.00220
3600	0.00240

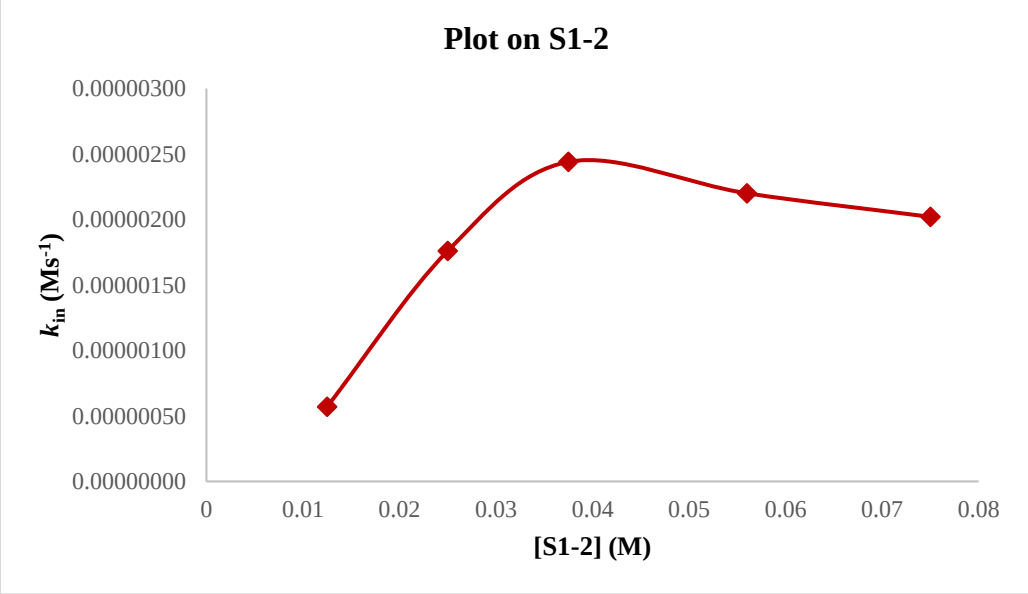
Supplementary Table 15. The molar concentrations of product **2** ([**2**]/M) with different initial concentrations of phenylacetylene **S1-2** at different time intervals

Reaction time (s)	**0.0250 M [S1-2]**	**0.0375 M [S1-2]**	**0.00561 M [S1-2]**	**0.0750 M [S1-2]**
720	0.00047	0.00105	0.00084	0.00087
1080	0.00101	0.00180	0.00130	0.00150
1440	0.00170	0.00250	0.00170	0.00230
1800	0.00230	0.00370	0.00270	0.00310
2160	0.00300	0.00450	0.00410	0.00370

Supplementary Table 16. The k_{in} value of product in different concentration of CuTc

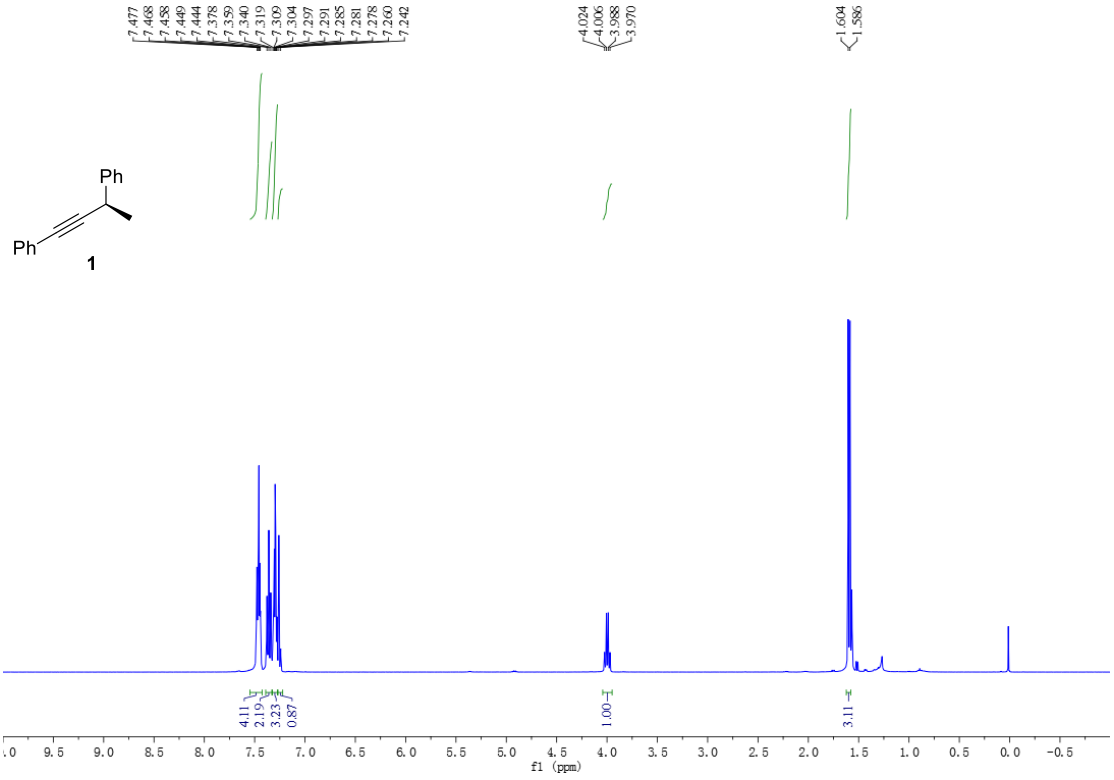
[S1-2] (M)	**k_{in} (Ms^{-1})**
0.0125	0.57×10^{-6}
0.0250	1.76×10^{-6}
0.0375	2.44×10^{-6}

0.0561	2.20×10^{-6}
0.0750	2.02×10^{-6}



Supplementary Fig. 12. Plot of k_{in} versus [**S1-2**] from the reactions with 0.125 M, 0.025 M, 0.0375 M, 0.056 M, and 0.075 M of phenylacetylene **S1-2**.

NMR spectra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7.278
7.260
7.242
4.024
4.006
3.988
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Ph
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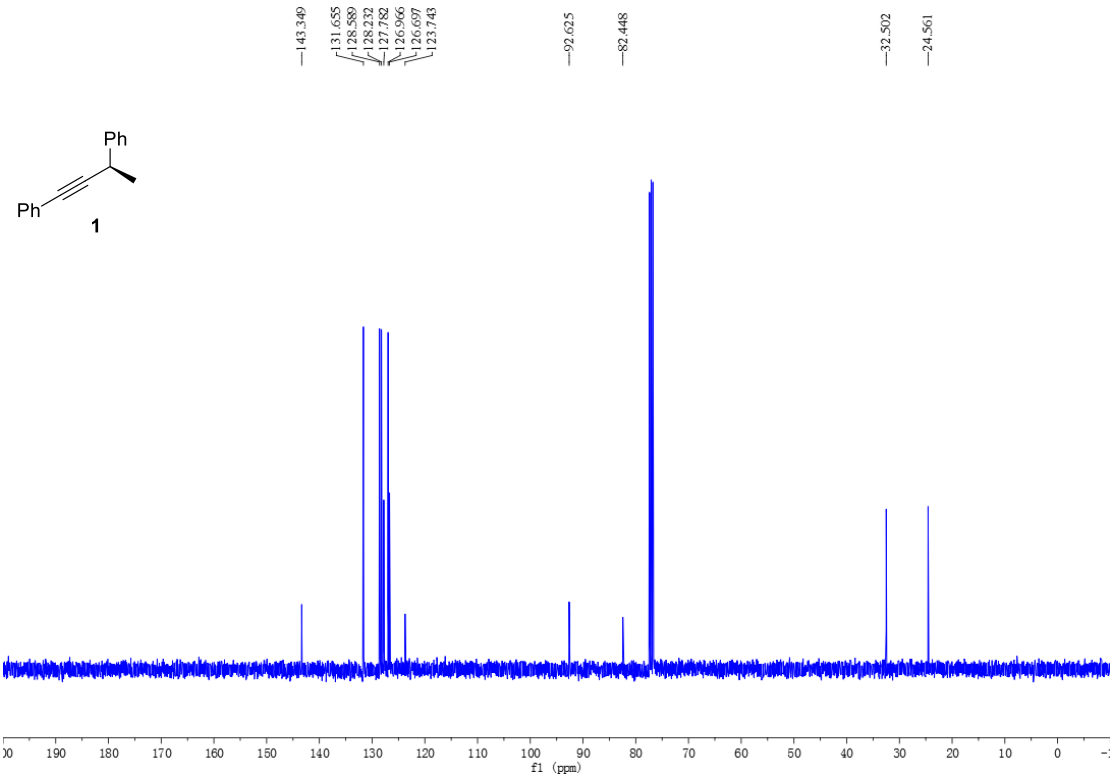
f1 (ppm)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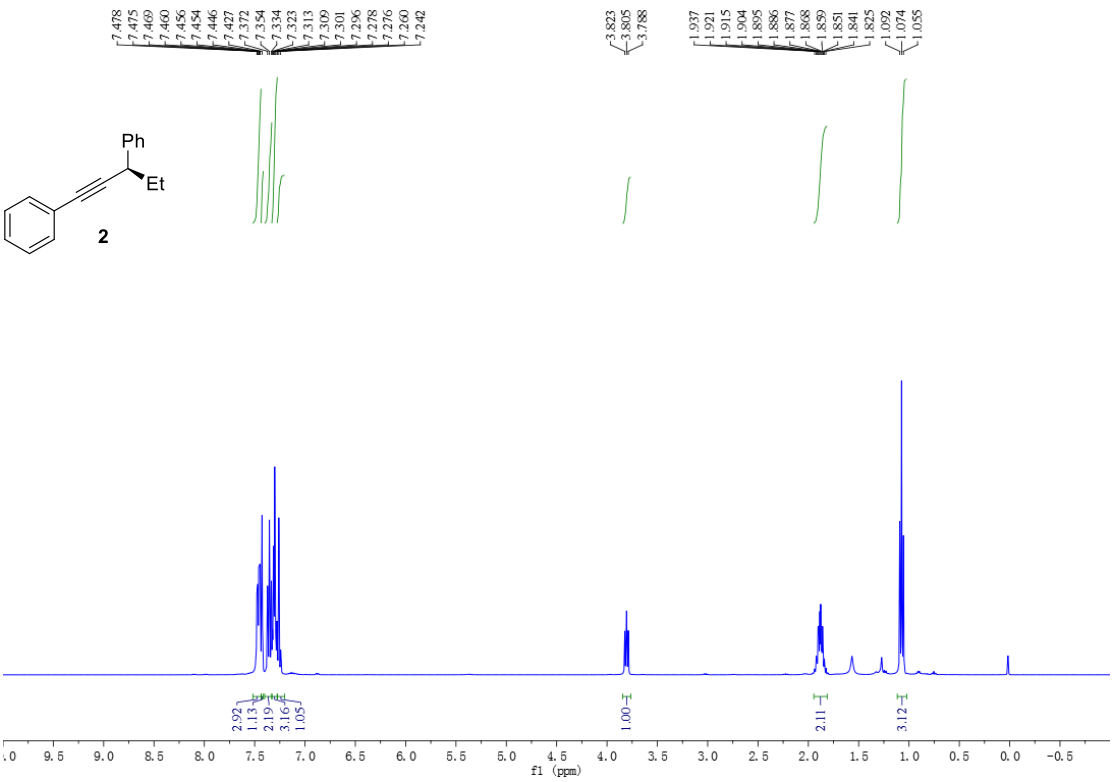
f1 (ppm)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7.276
7.260
7.242
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3.788
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1.921
1.915
1.904
1.895
1.886
1.877
1.868
1.859
1.851
1.841
1.825
1.092
1.074
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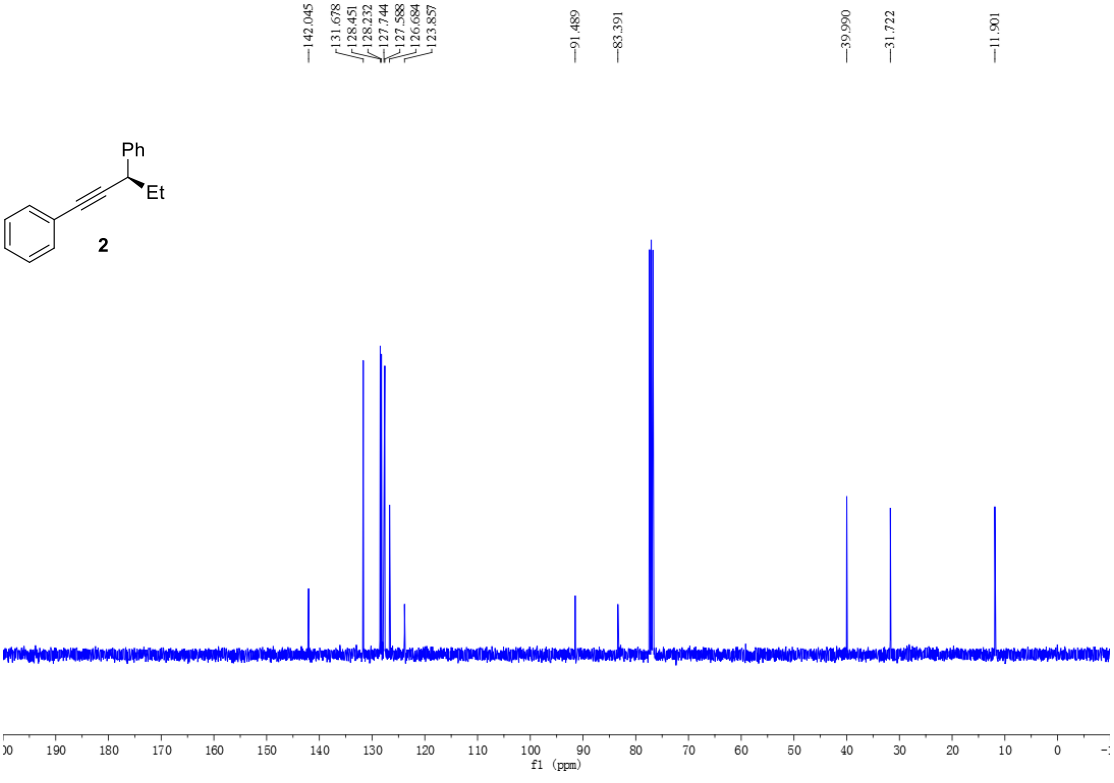
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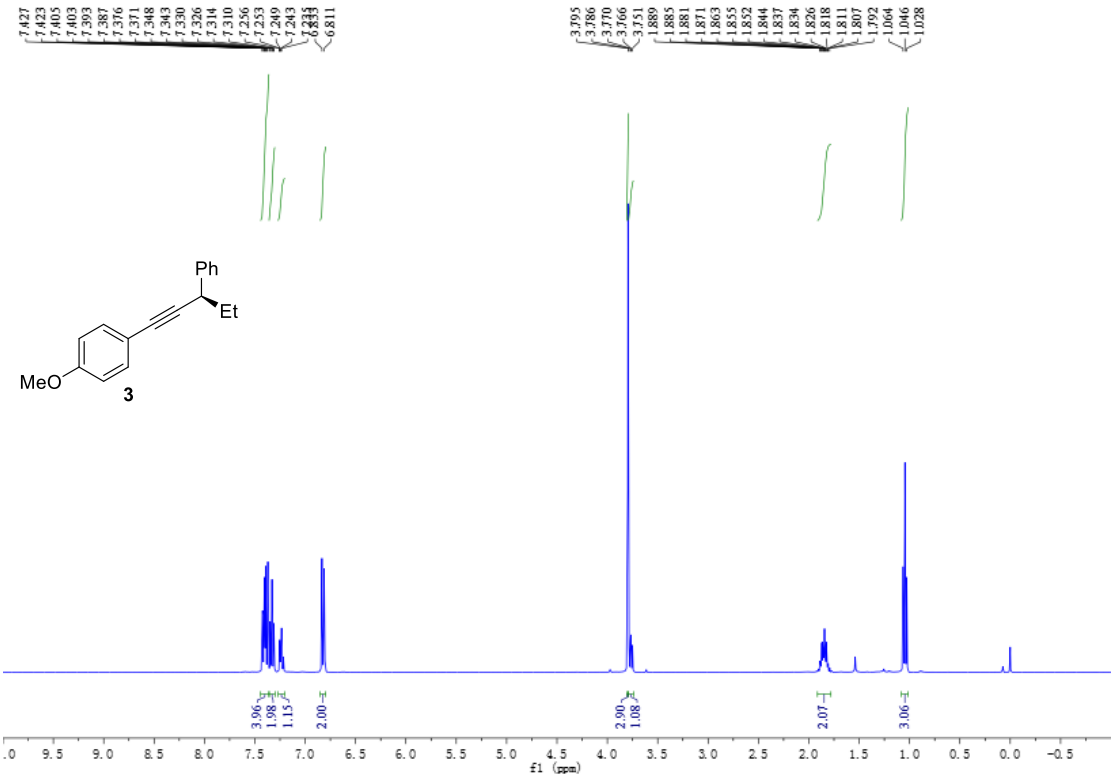
Ph
Et
2
f1 (ppm)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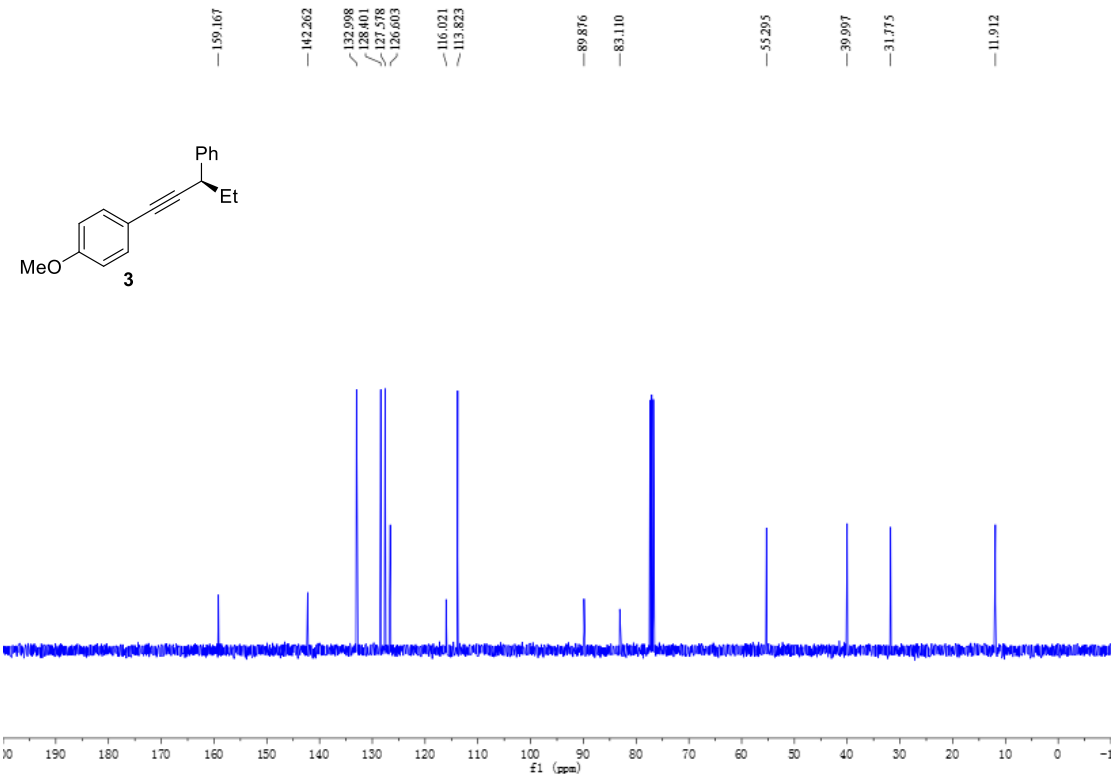
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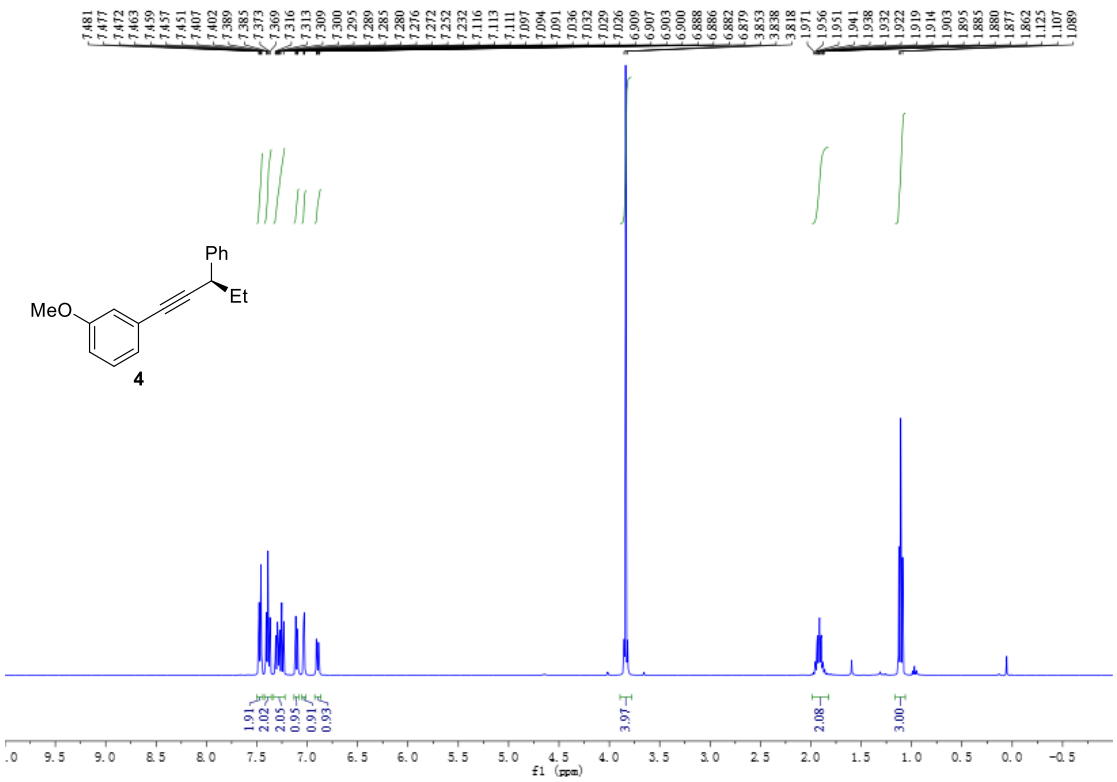
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1.932
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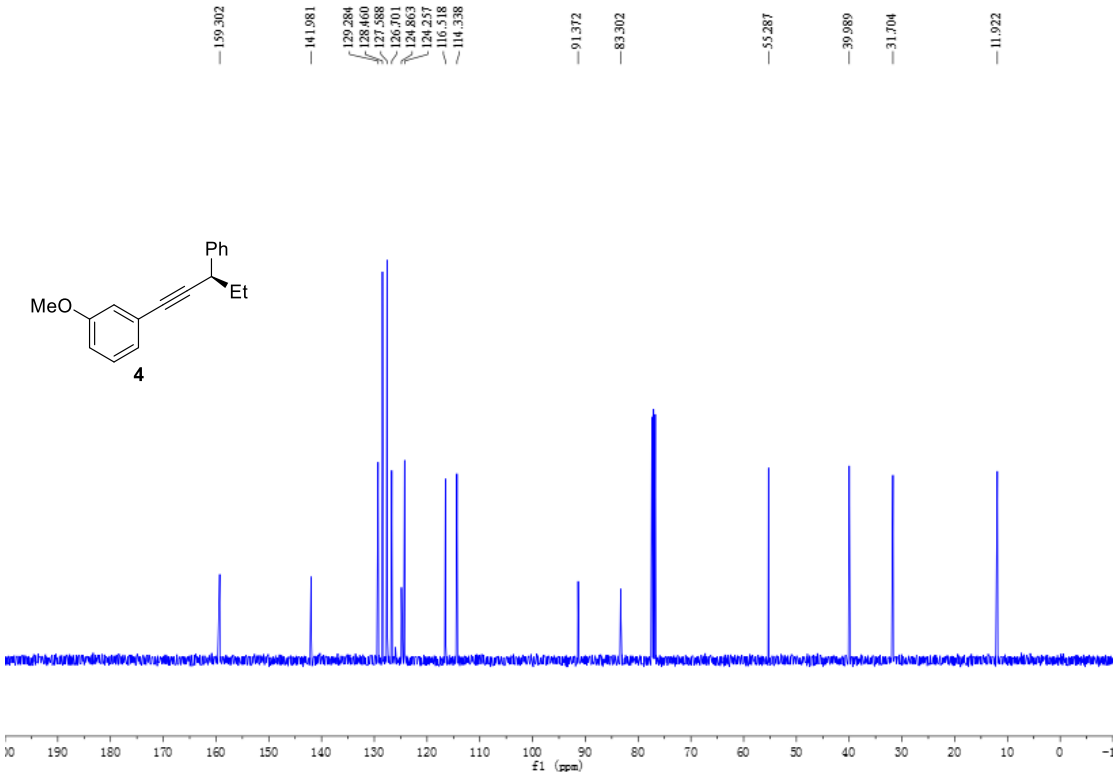
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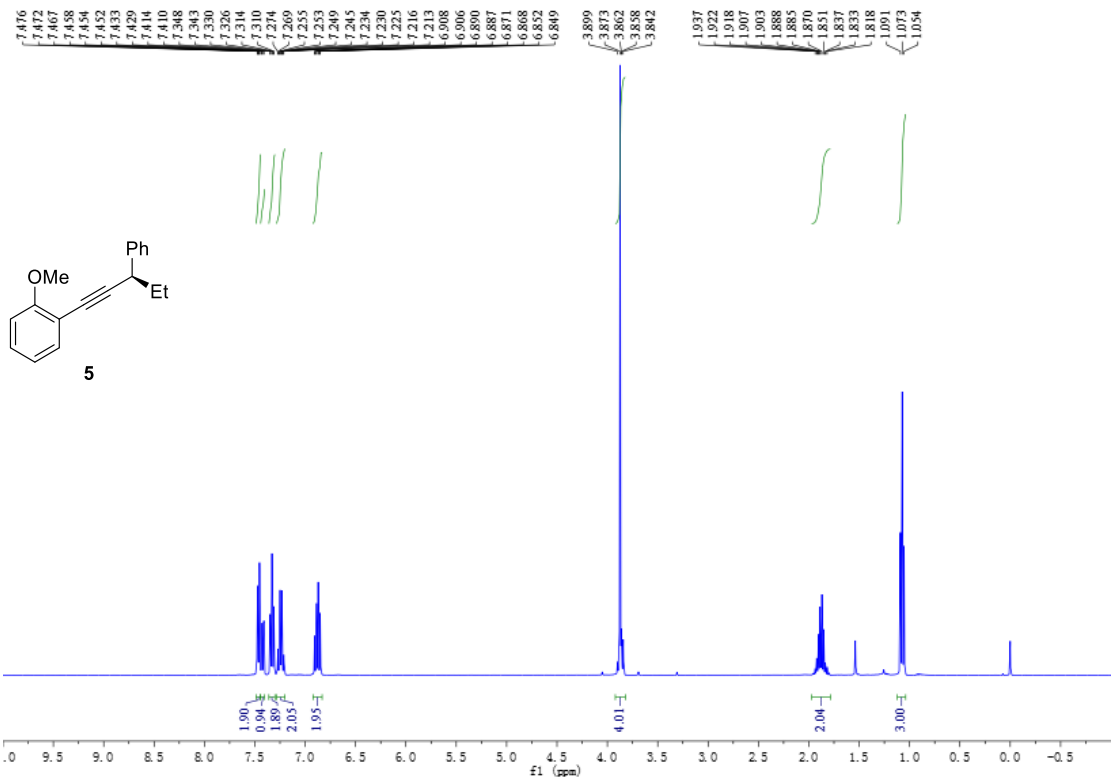
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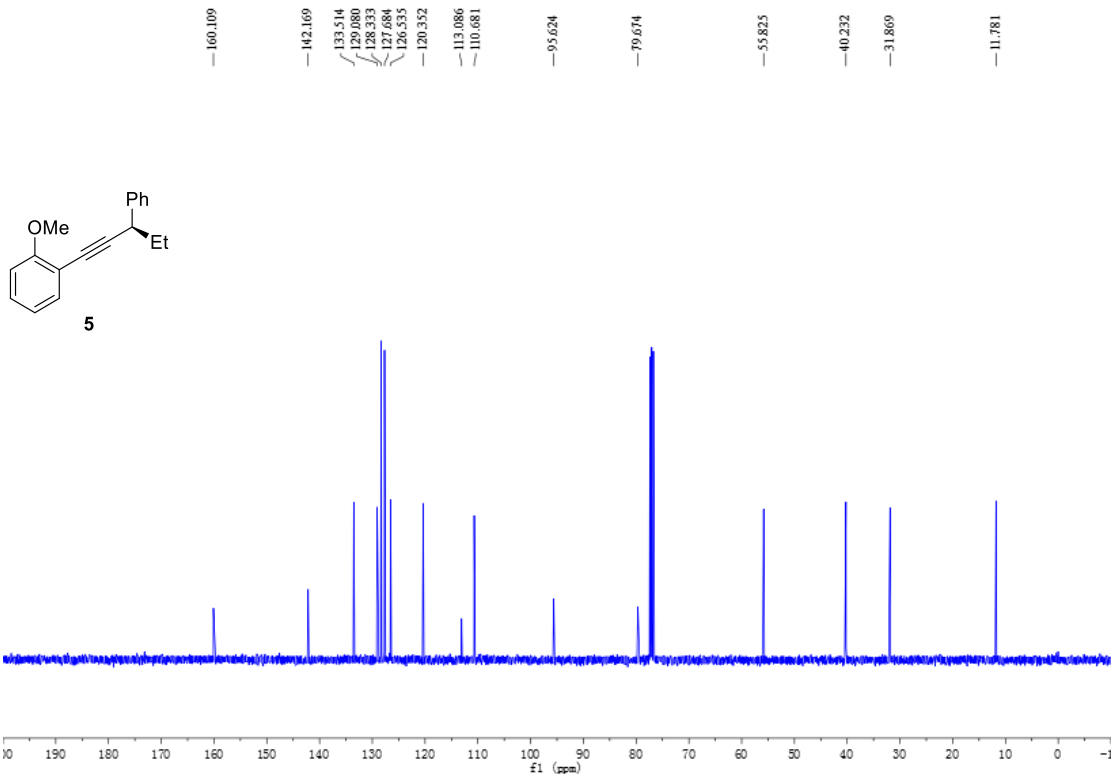
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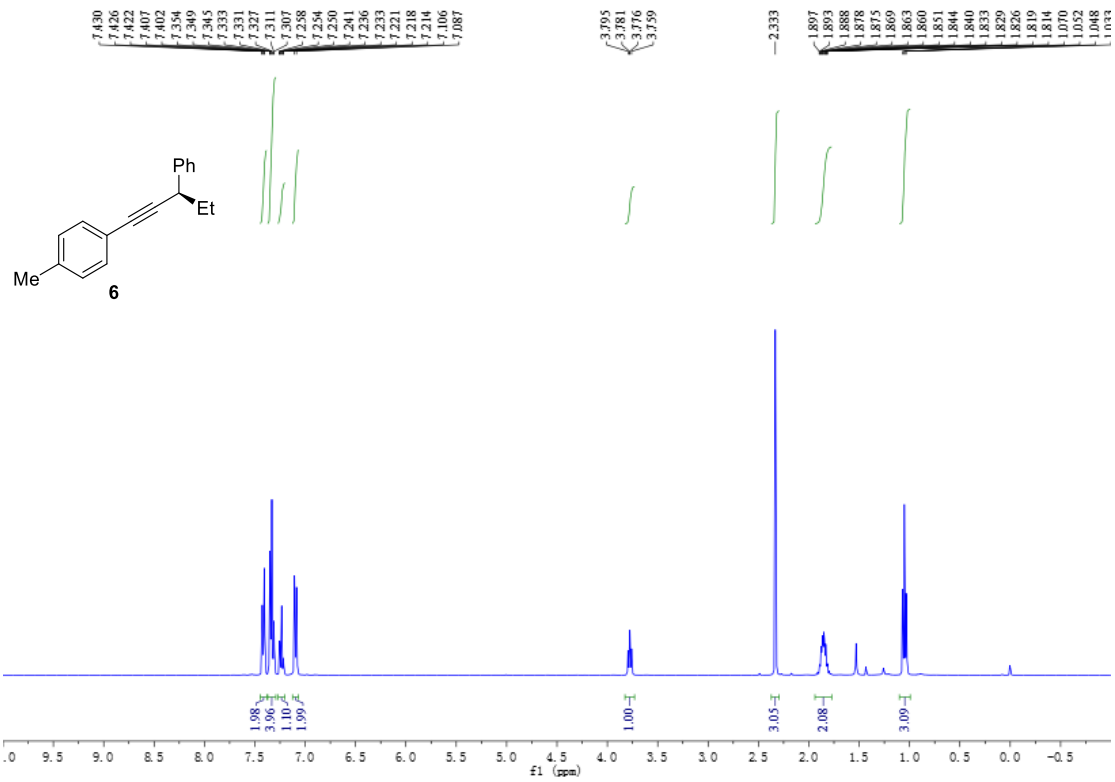
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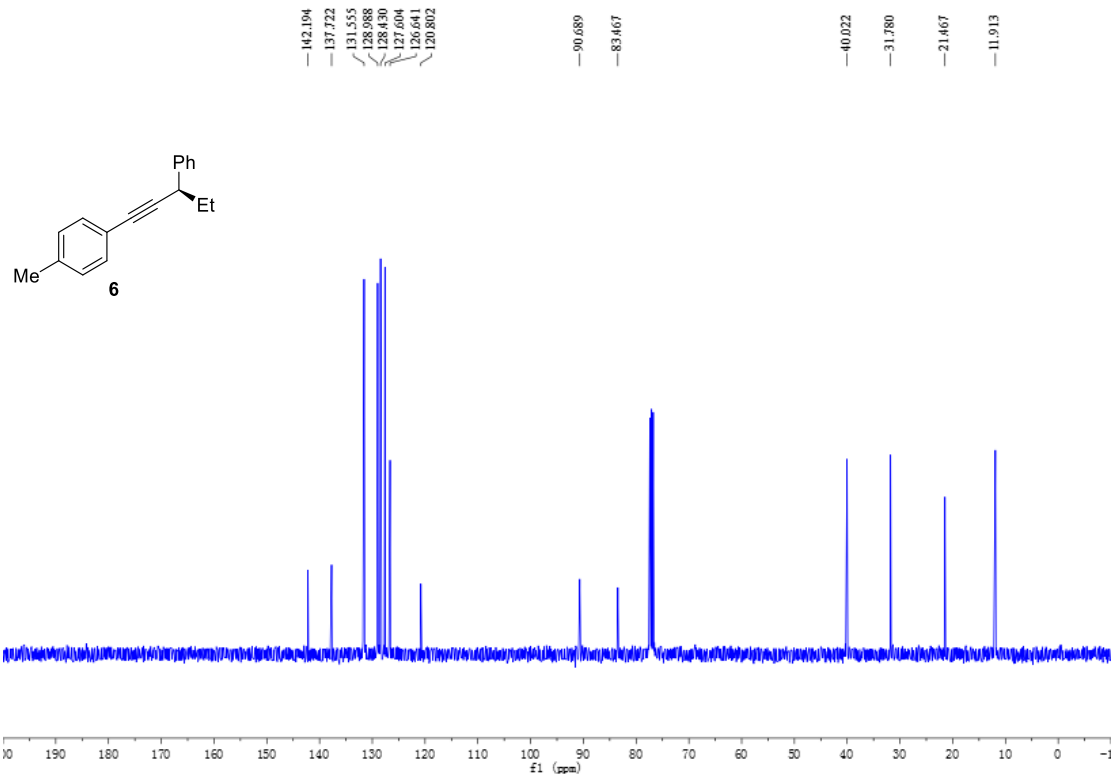
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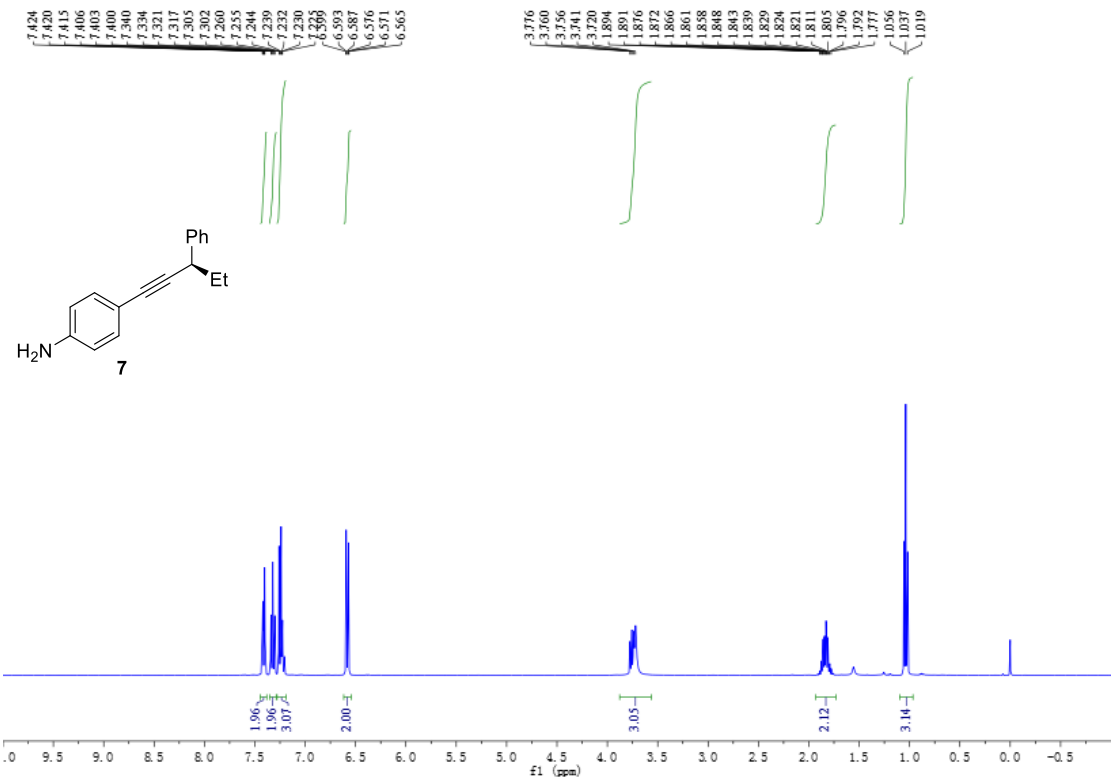
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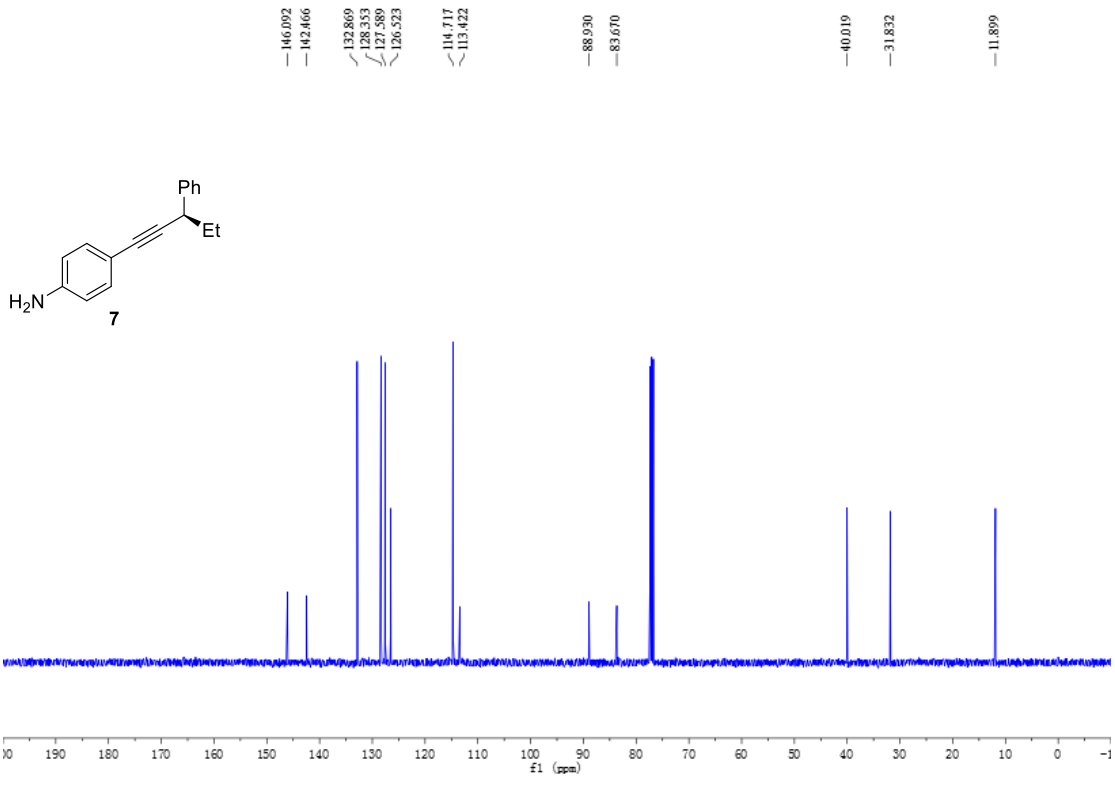
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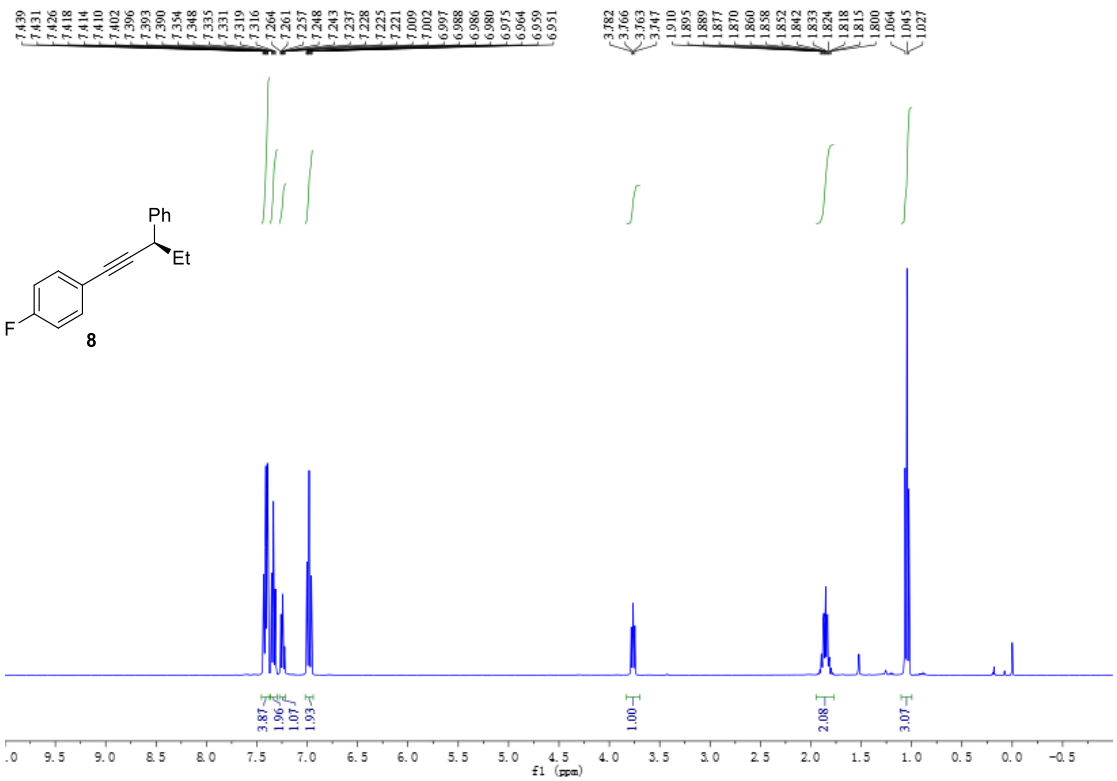
f1 (ppm)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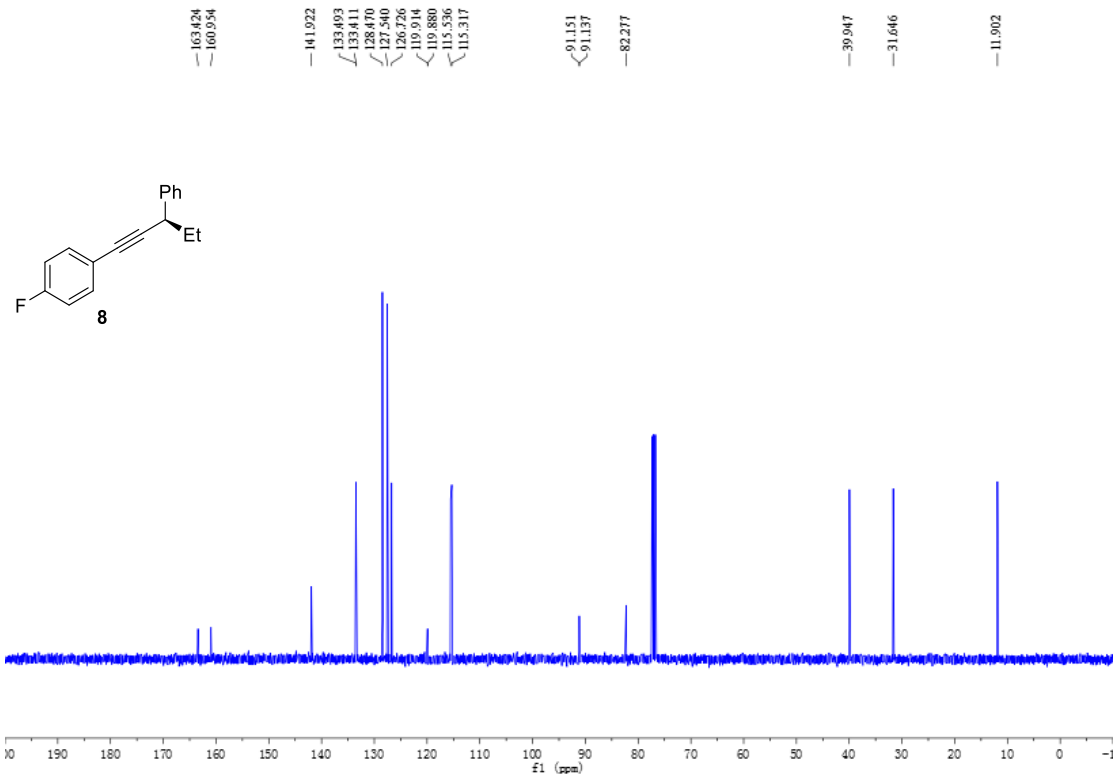
f1 (ppm)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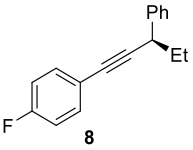
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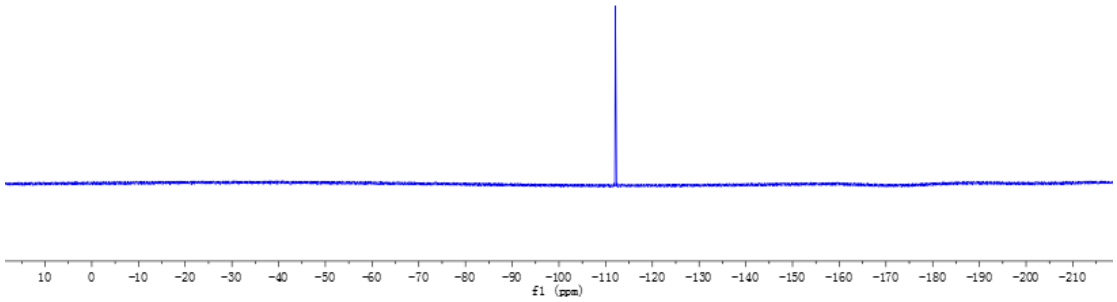
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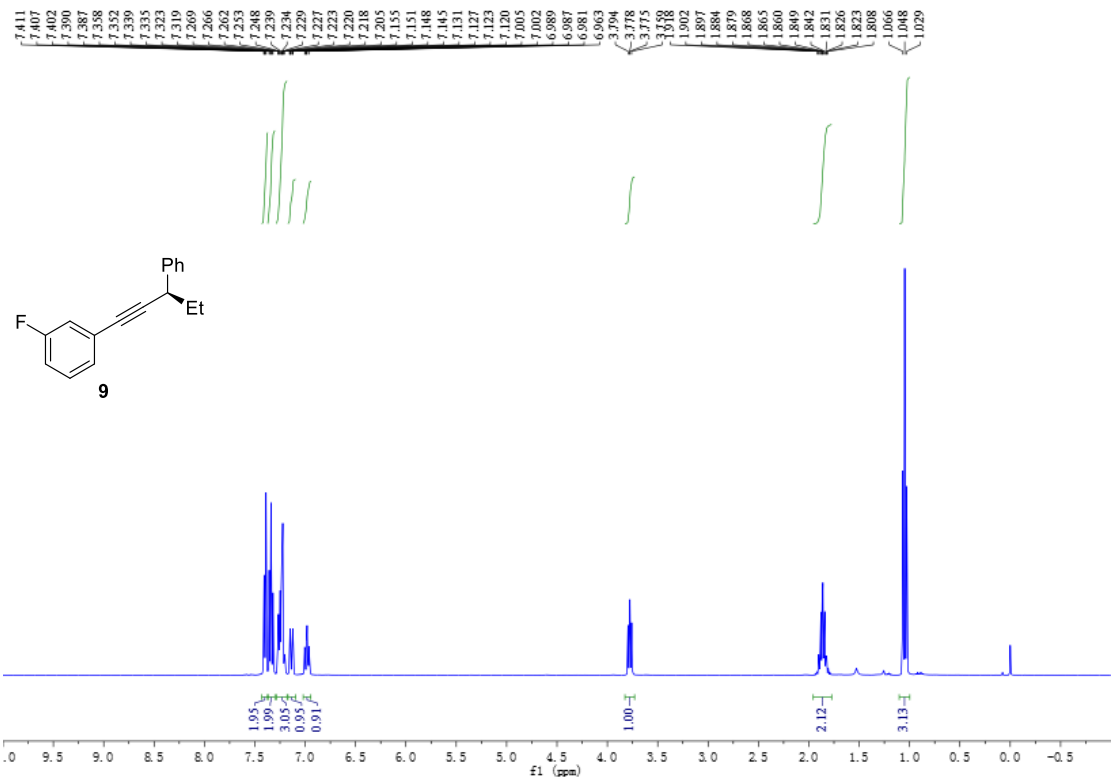
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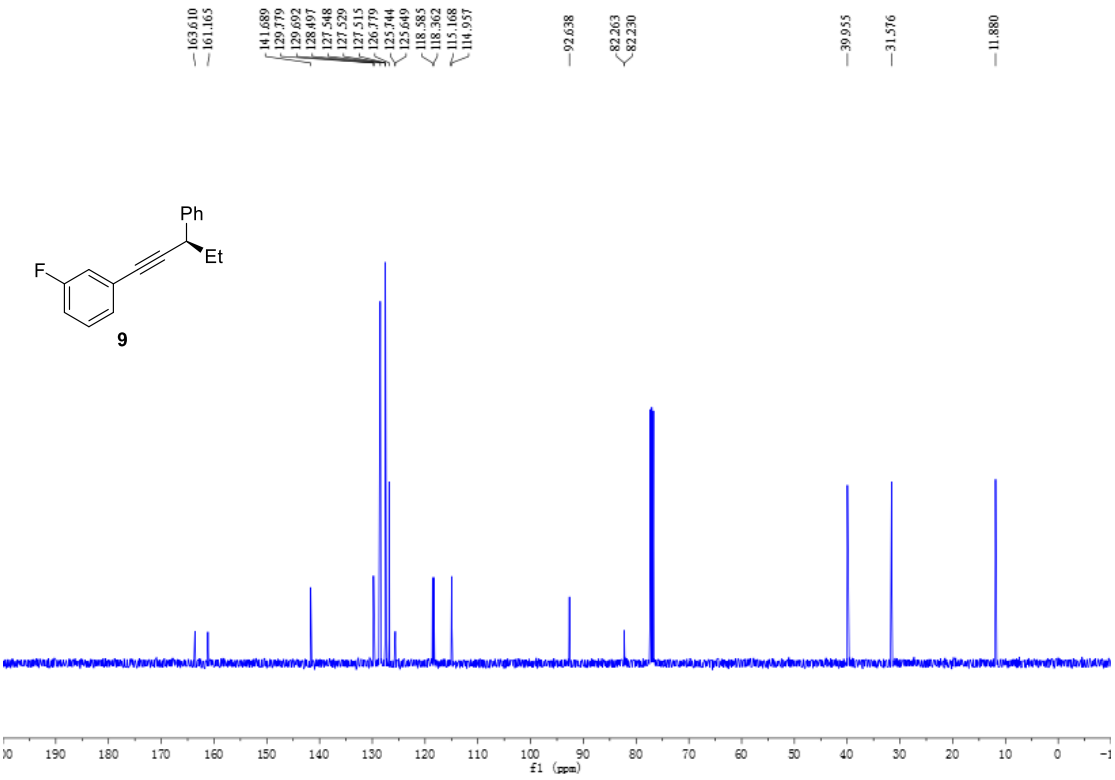
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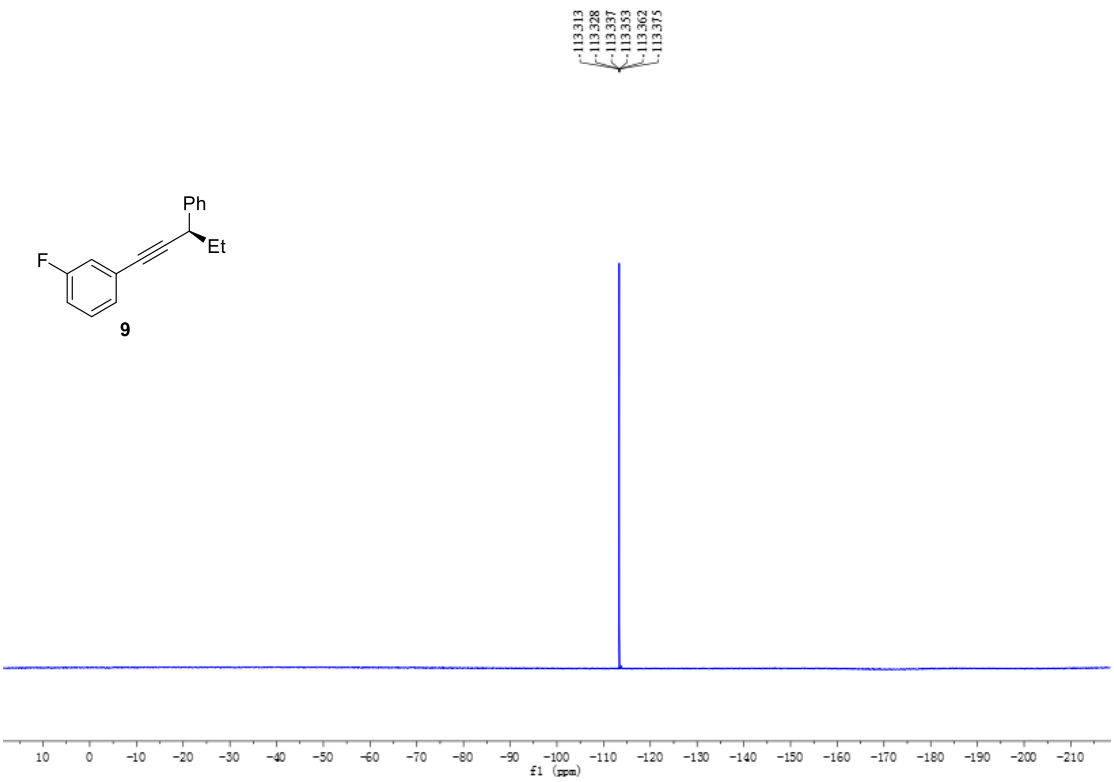
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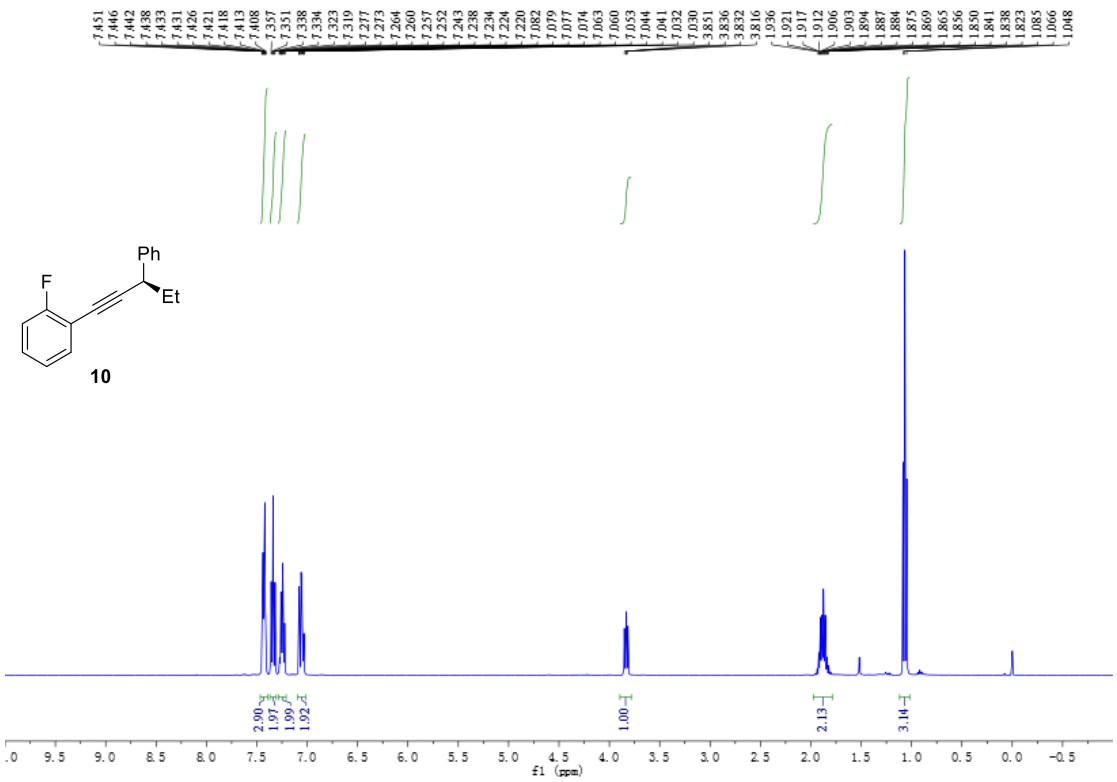
f1 (ppm)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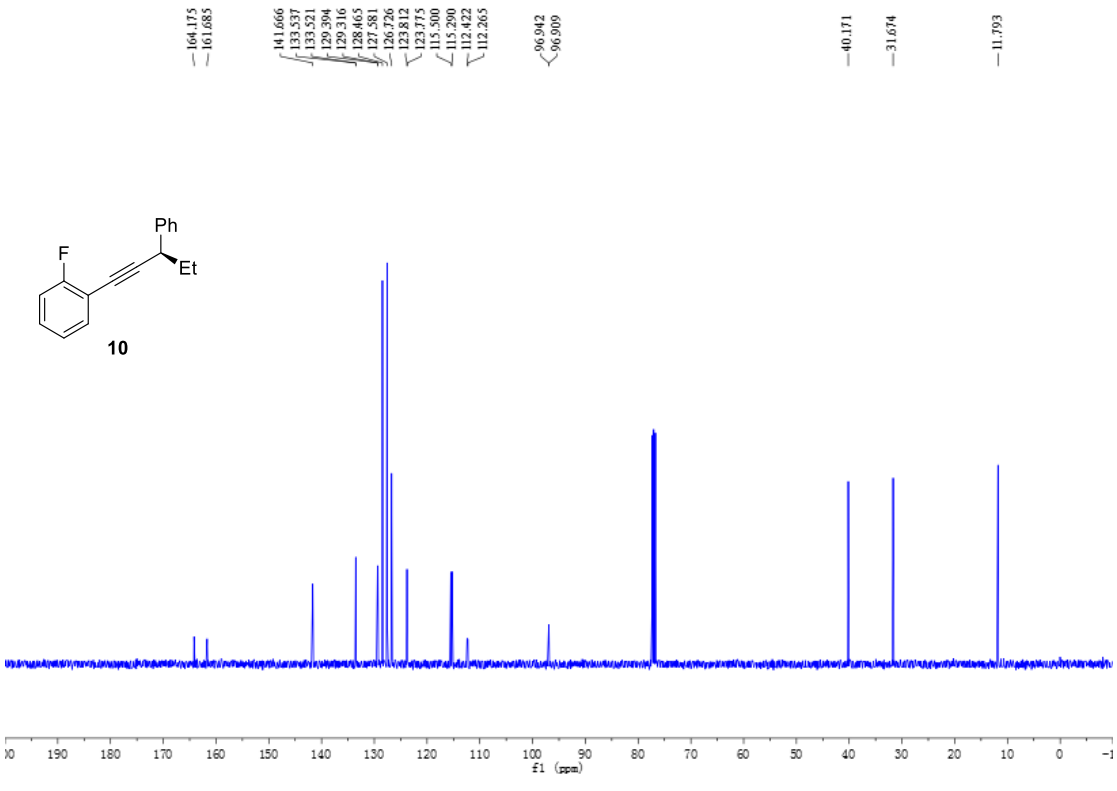
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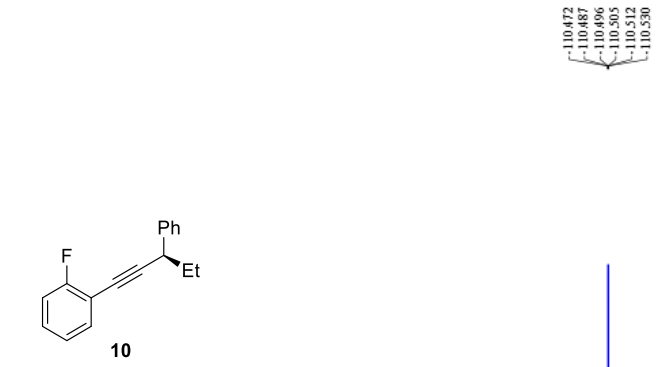
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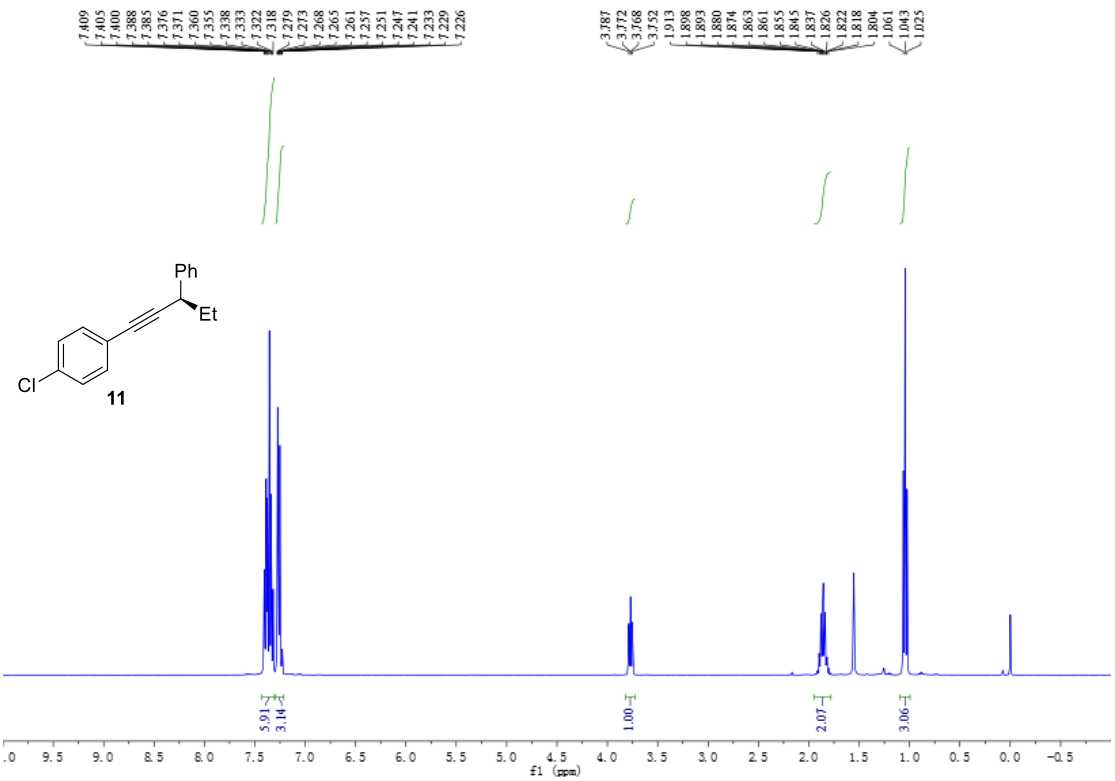
f1 (ppm)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1.880
1.874
1.863
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1.855
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1.837
1.826
1.822
1.818
1.804
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Ph
Et
Cl
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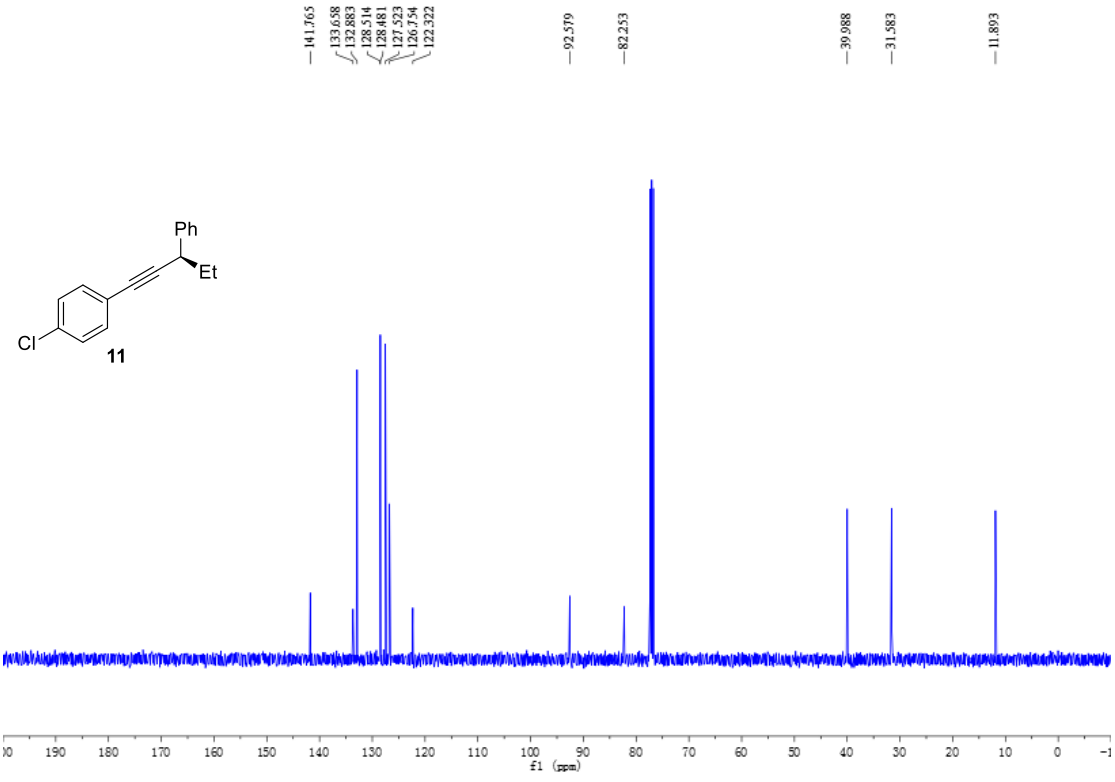
3.06
f1 (ppm)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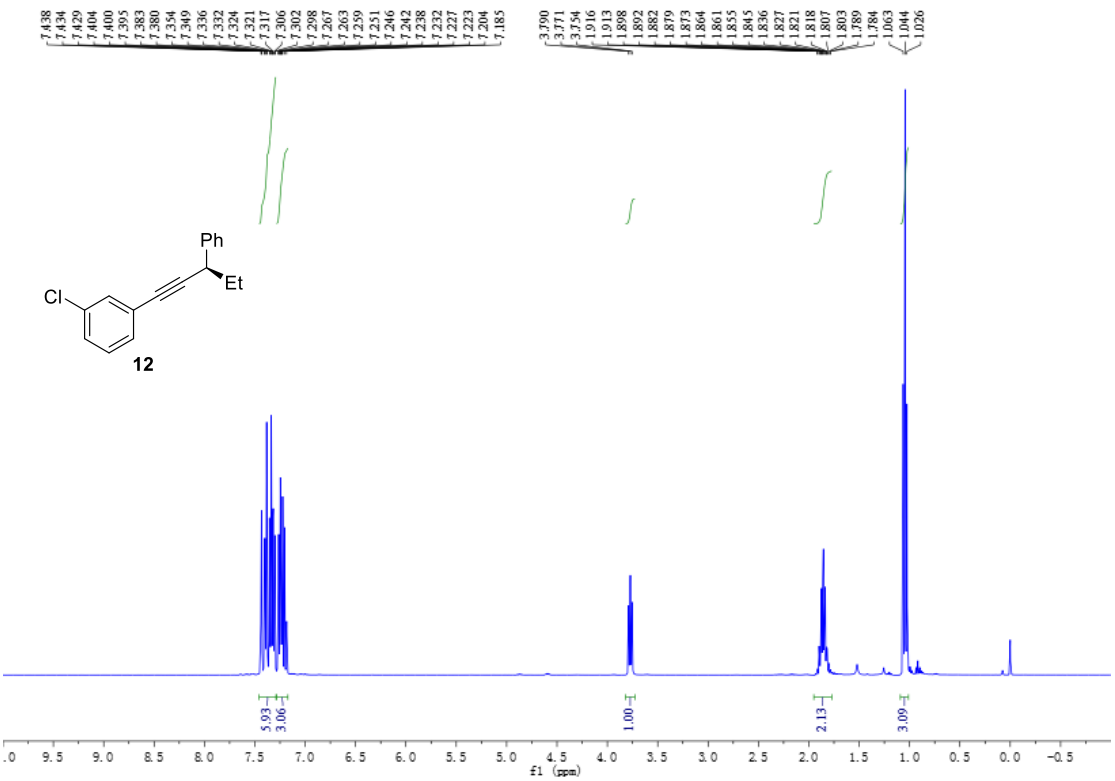
Et
Cl
11
f1 (ppm)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Et
Cl
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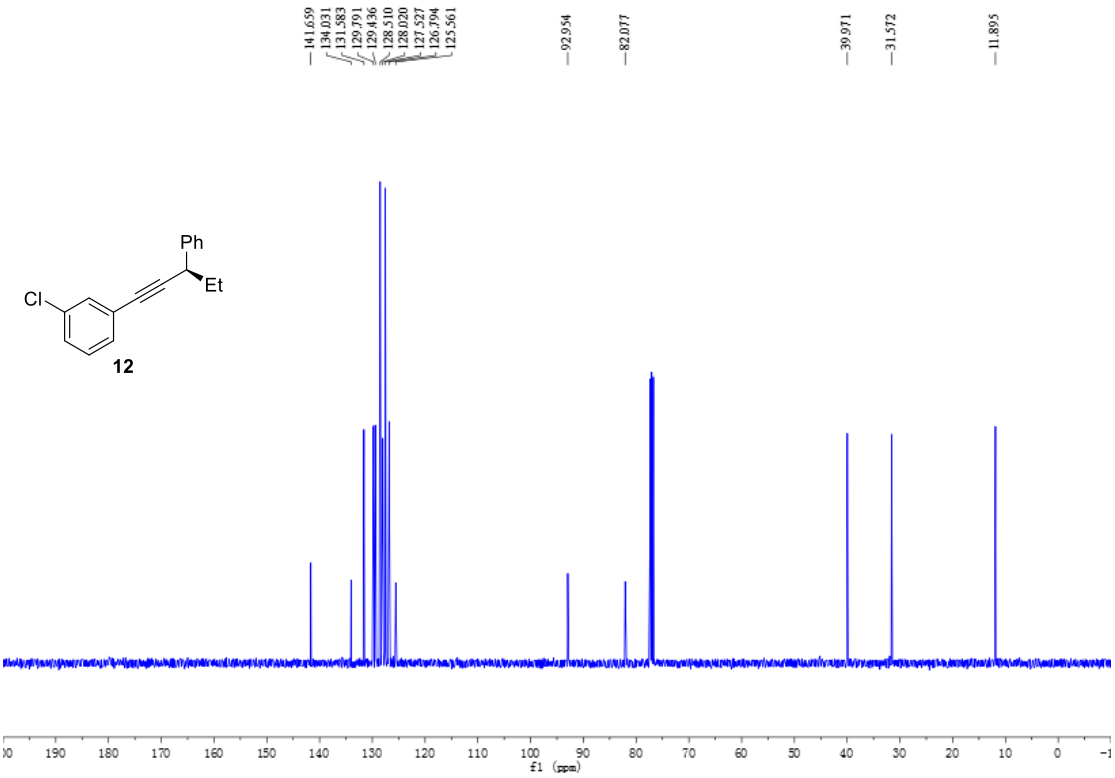
f1 (ppm)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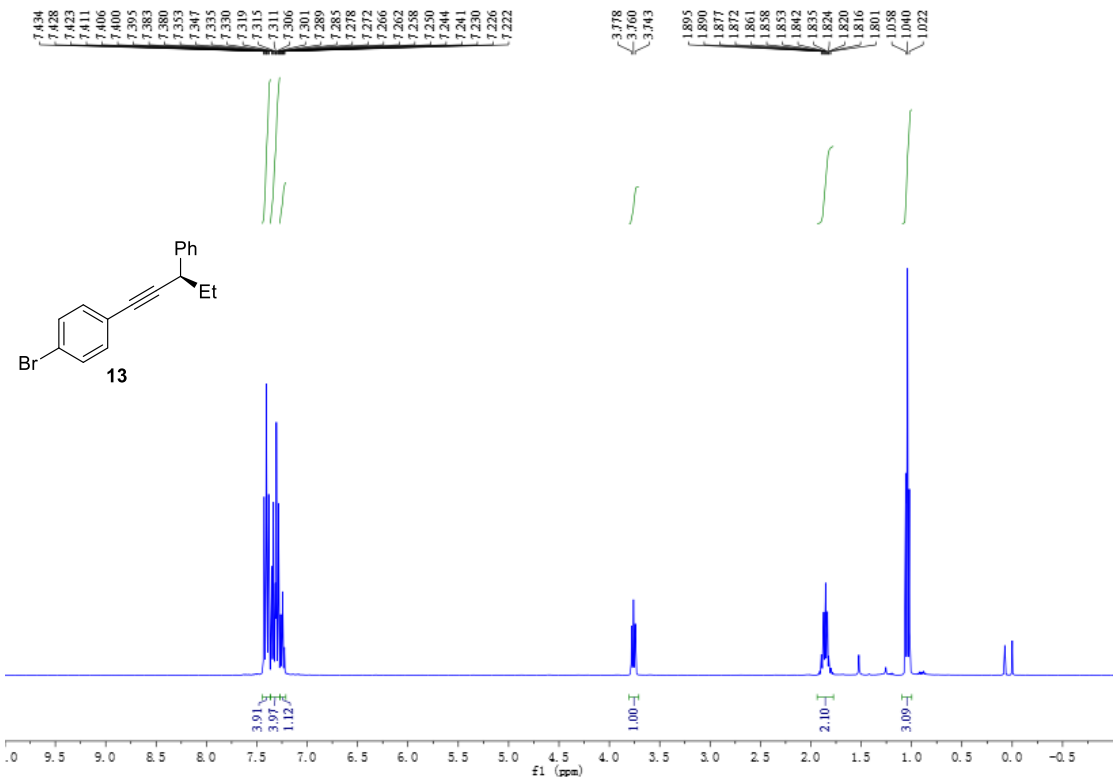
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7.311
7.306
7.301
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7.278
7.272
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7.262
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7.222
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1.820
1.816
1.801
1.058
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Ph
Et
Br
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1.00
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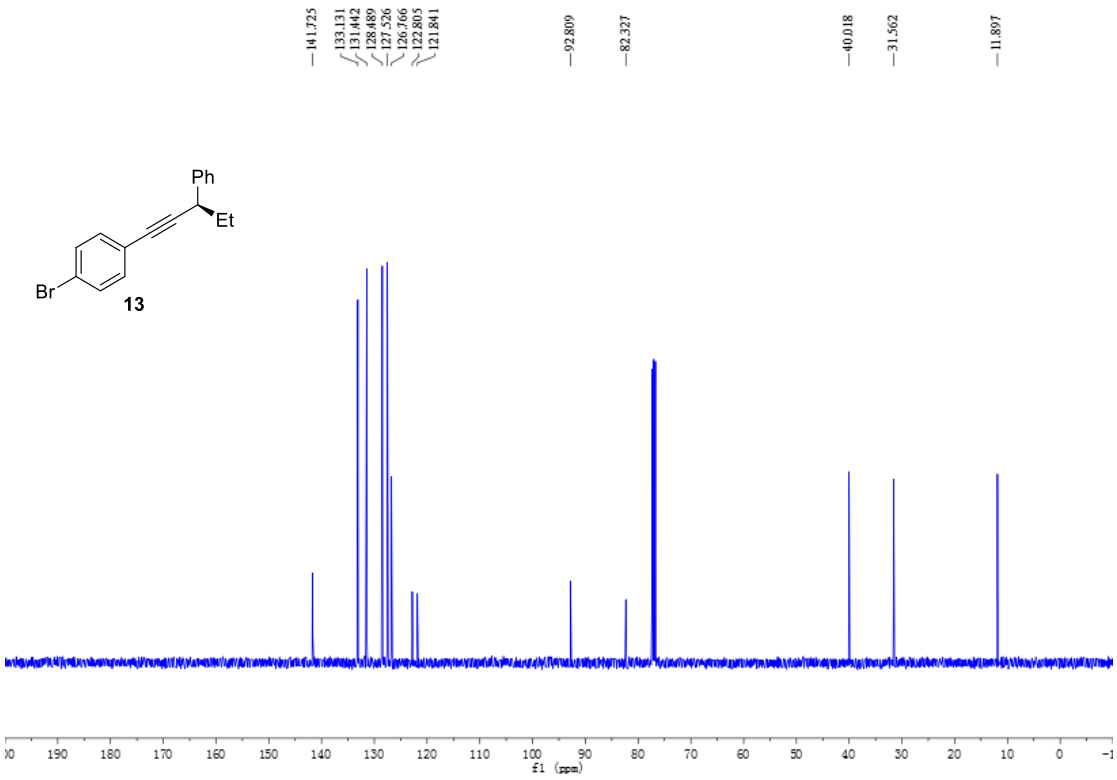
3.09
f1 (ppm)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121.841
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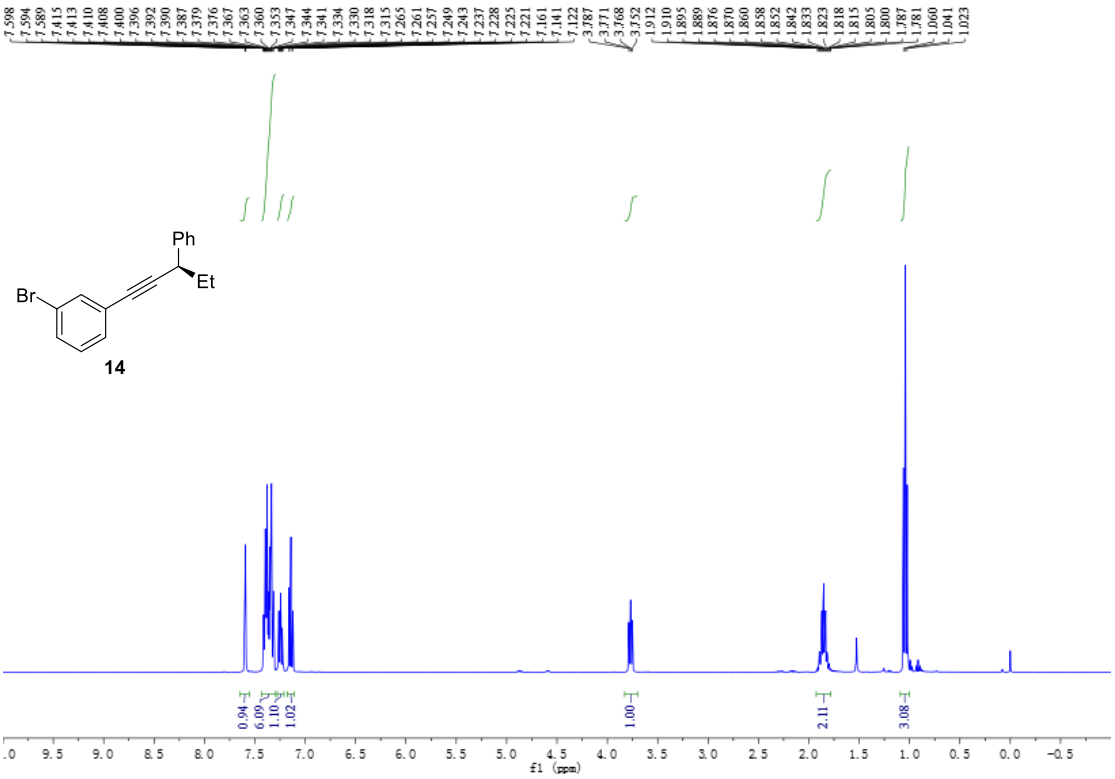
11.897
Ph
Et
Br
13
f1 (ppm)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Et
Br
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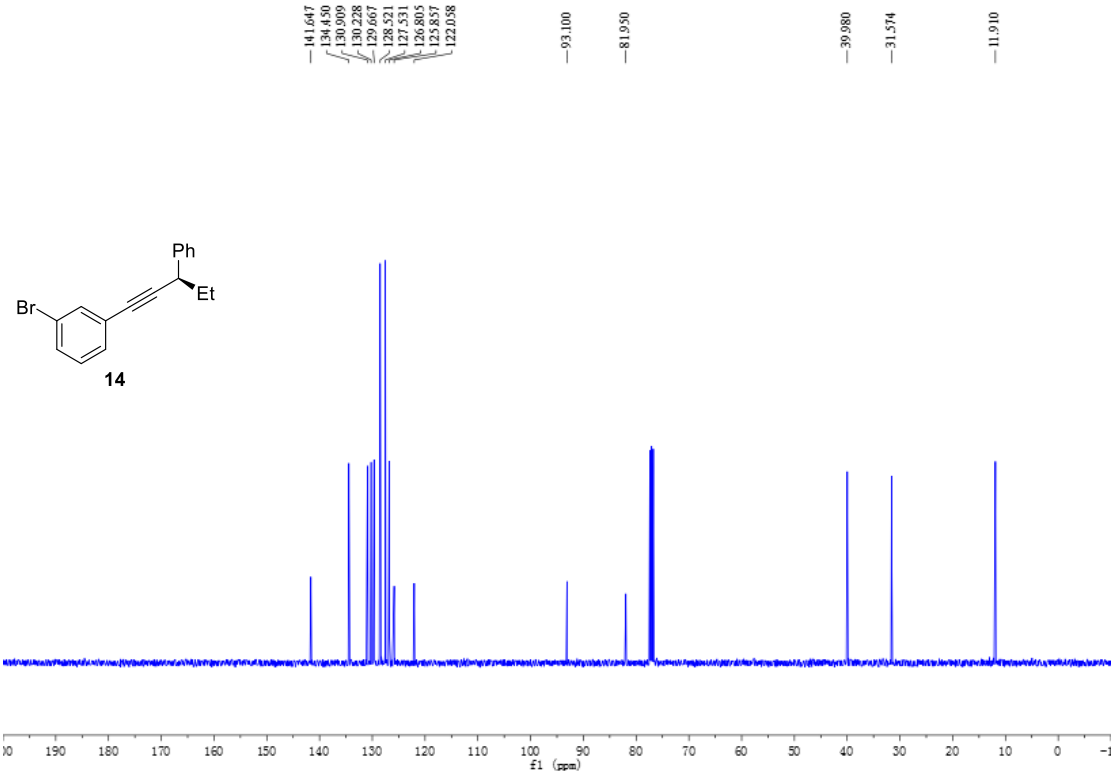
3.08
f1 (ppm)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Br
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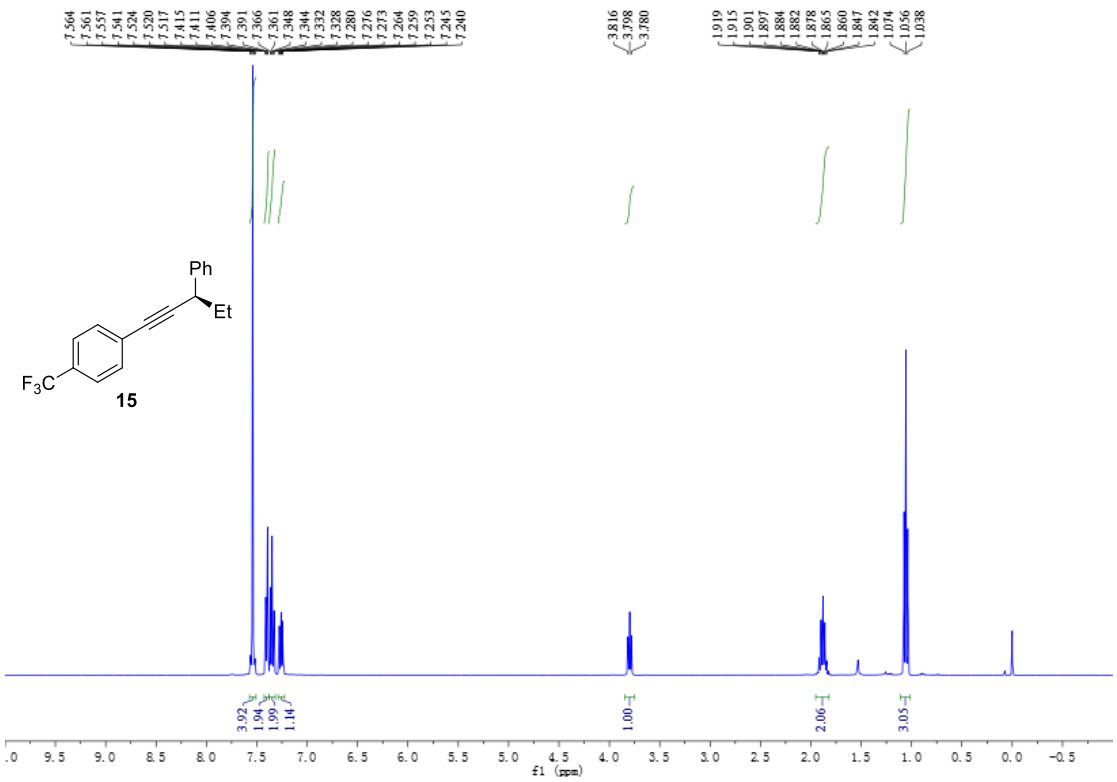
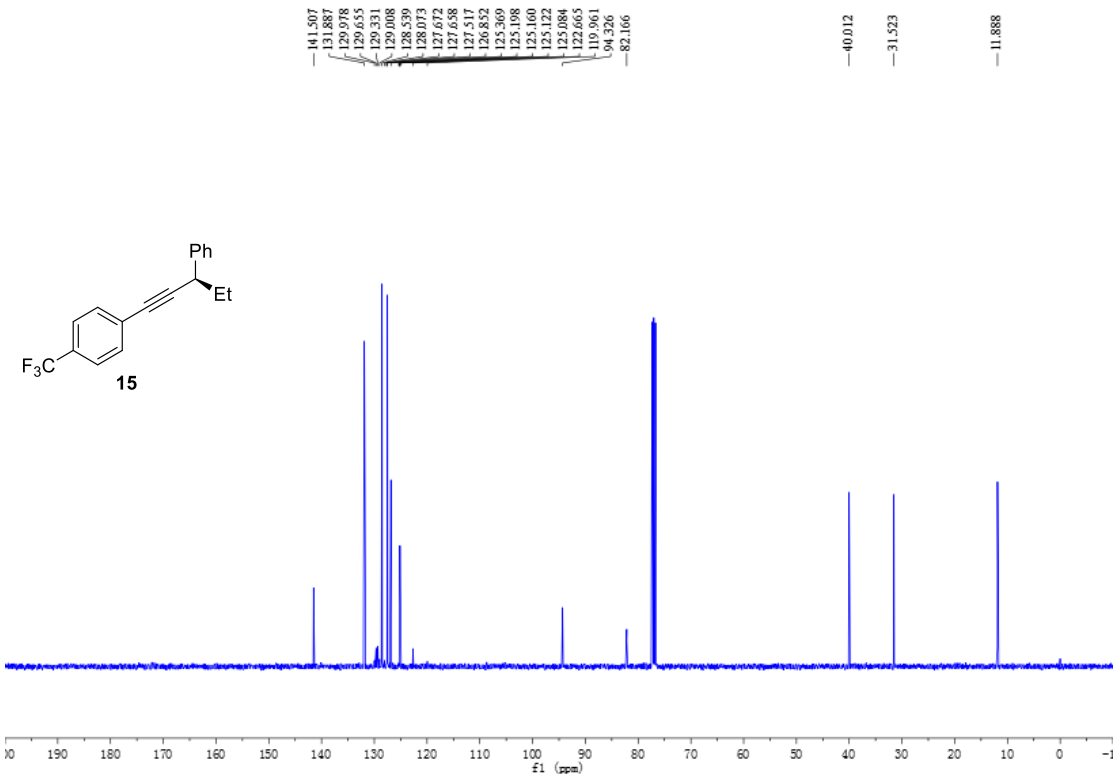
f1 (ppm)


Ph
Et
F3C
15
f1 (ppm)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Et
F3C
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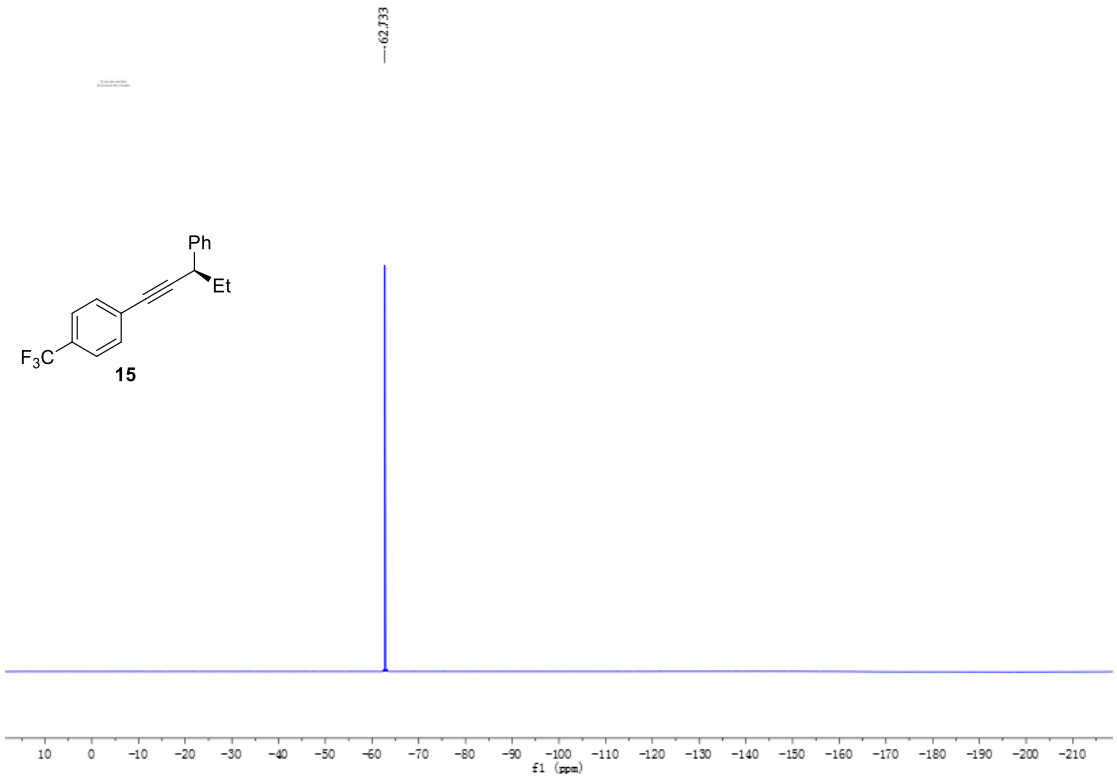
f1 (ppm)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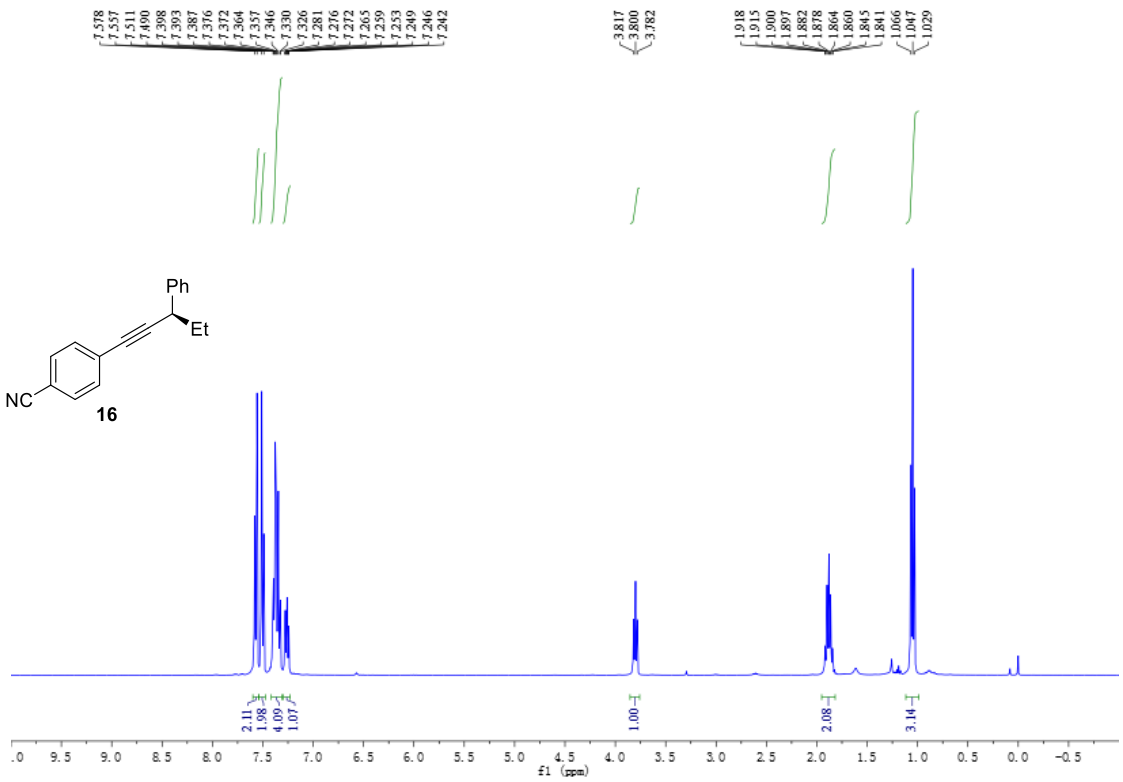
Ph
Et
F3C
15
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.330
7.326
7.281
7.276
7.272
7.265
7.259
7.253
7.249
7.246
7.242
3.817
3.800
3.782
1.918
1.915
1.900
1.897
1.882
1.878
1.864
1.860
1.845
1.841
1.066
1.047
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NC
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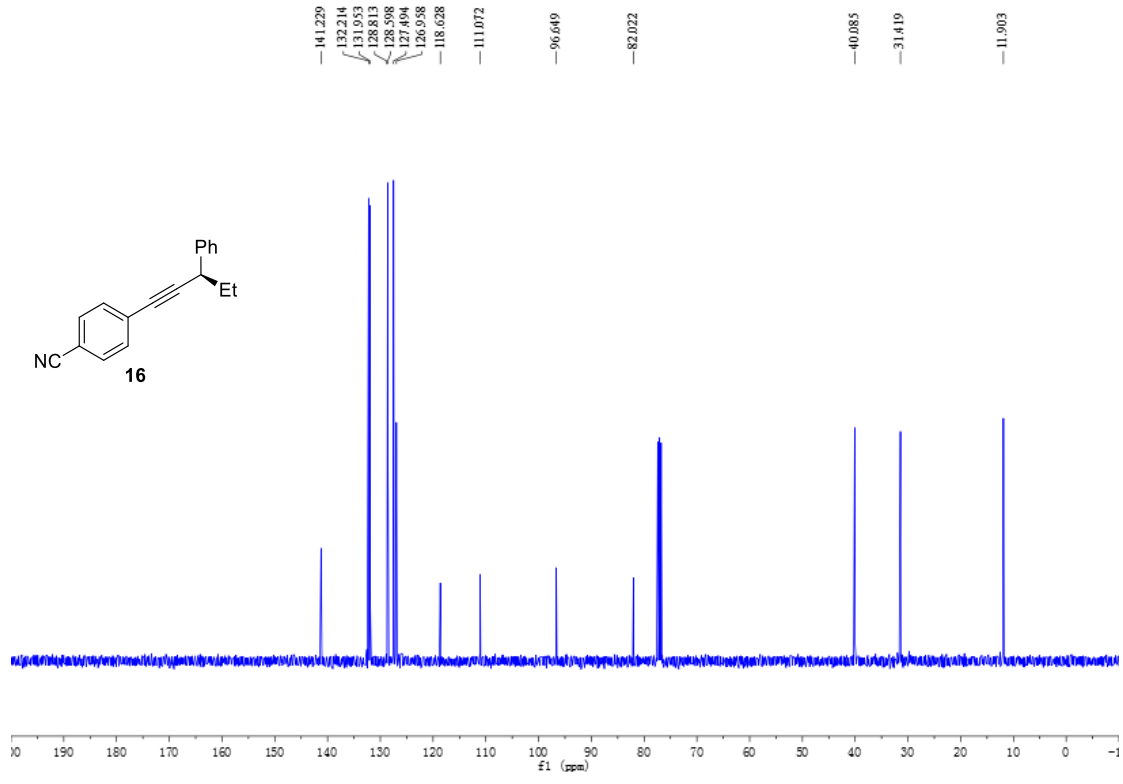
1.98
4.09
1.07
1.00
2.08
3.14
f1 (ppm)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127.494
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82.022
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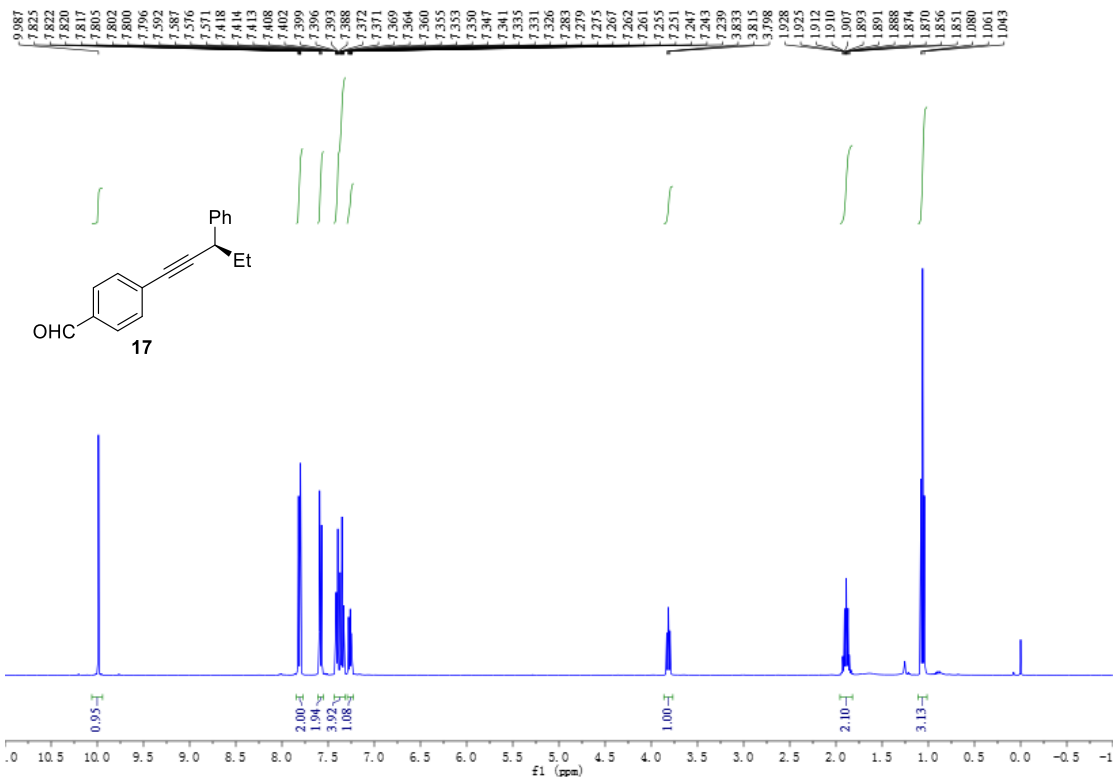
11.903
Ph
Et
NC
16
f1 (ppm)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Et
OHC
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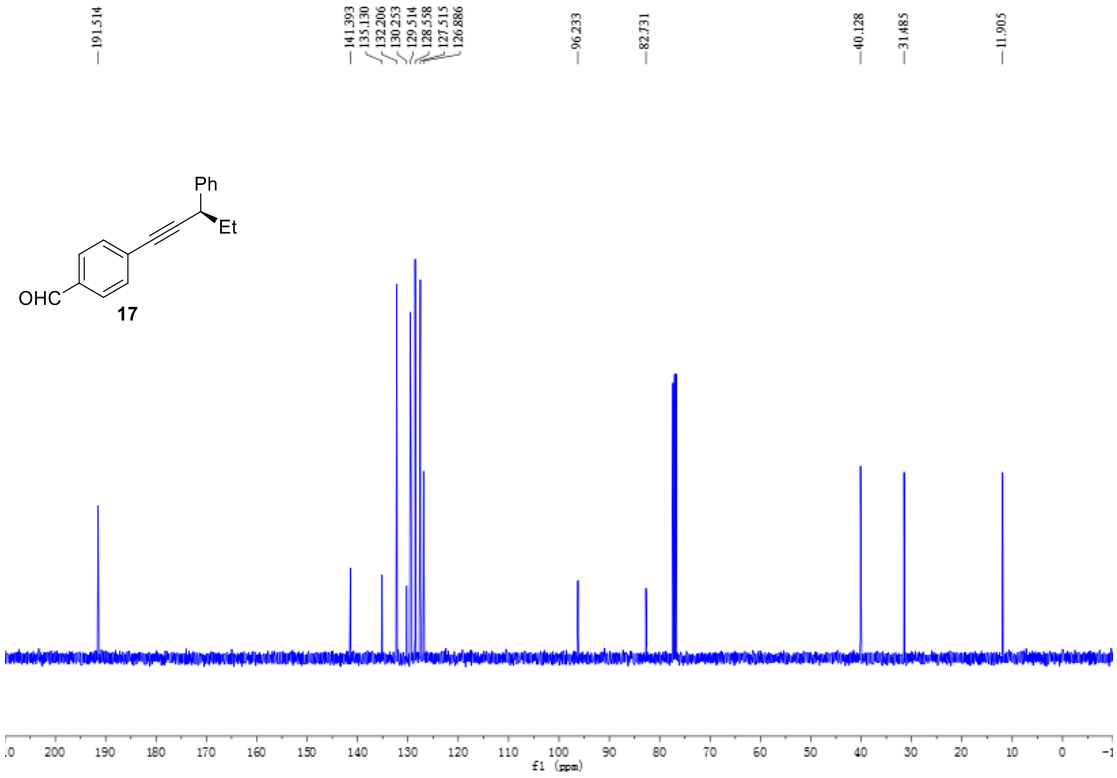
f1 (ppm)


Ph
Et
OHC
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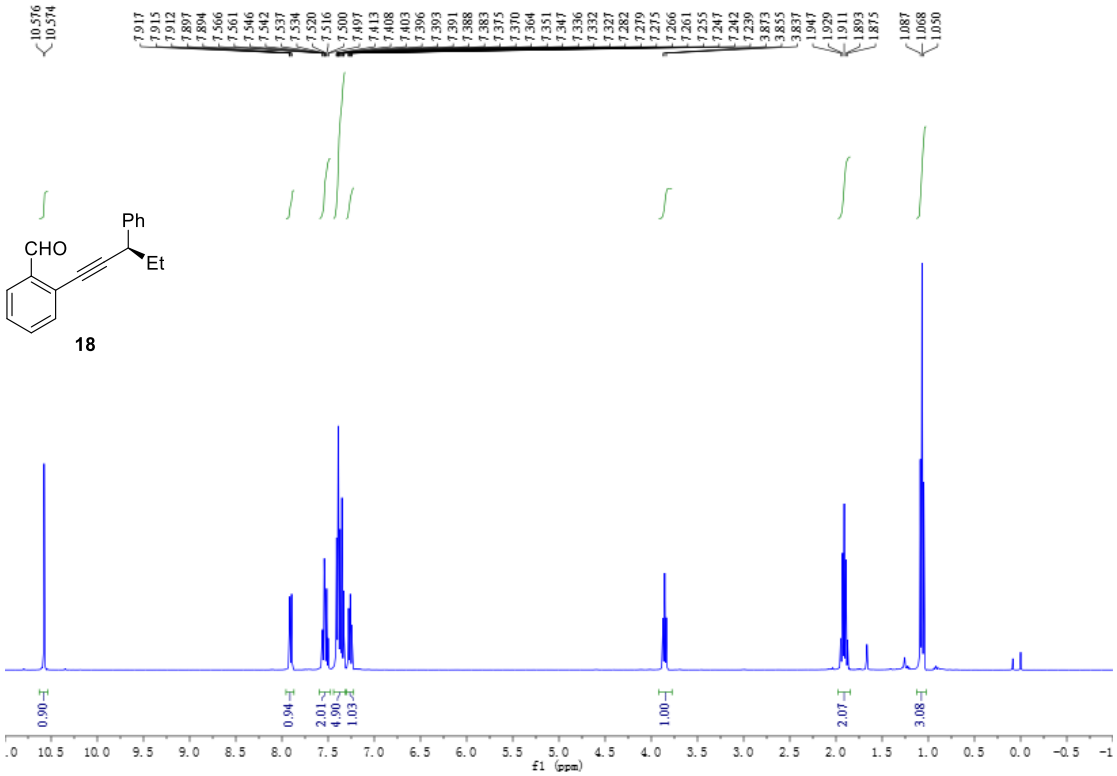
f1 (ppm)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7.537
7.534
7.520
7.516
7.500
7.497
7.413
7.408
7.403
7.396
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7.388
7.383
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7.336
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7.239
3.873
3.855
3.837
1.947
1.929
1.911
1.893
1.875
1.087
1.068
1.050
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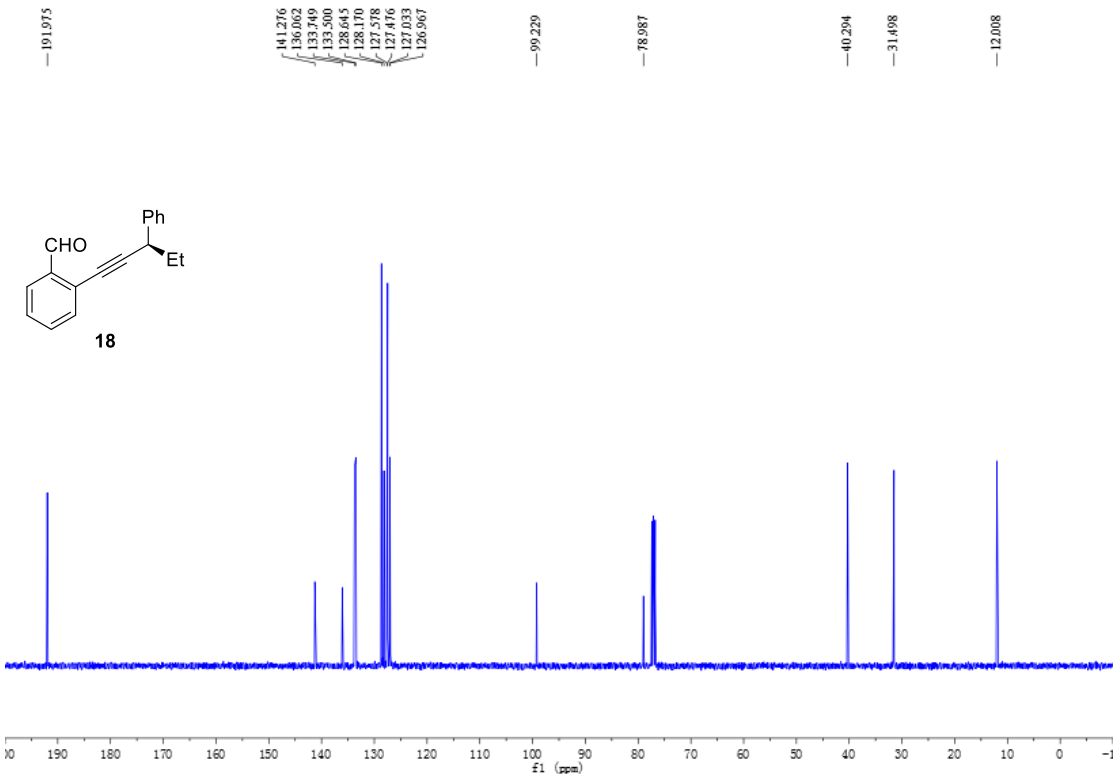
1.00
2.07
3.08
f1 (ppm)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78.987
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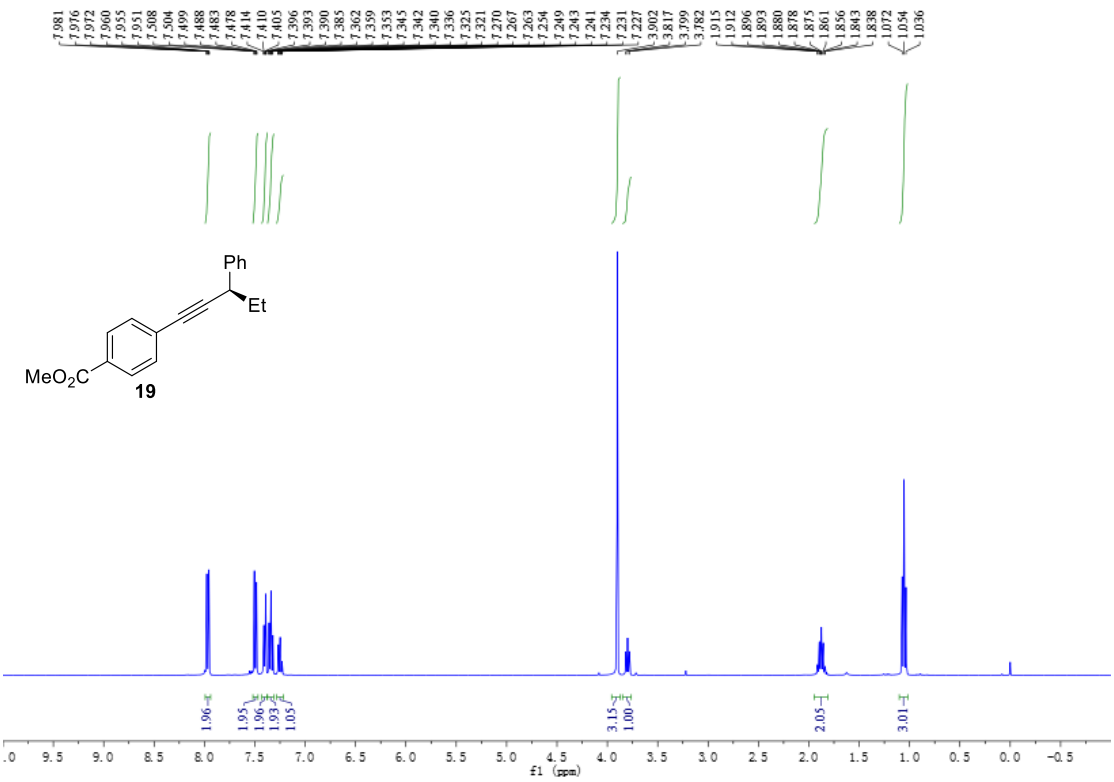
Ph
CHO
Et
18
f1 (ppm)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7.340
7.336
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7.263
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7.241
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7.231
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3.782
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1.912
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1.893
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1.875
1.861
1.856
1.843
1.838
1.072
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1.036
Ph
Et
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1.00
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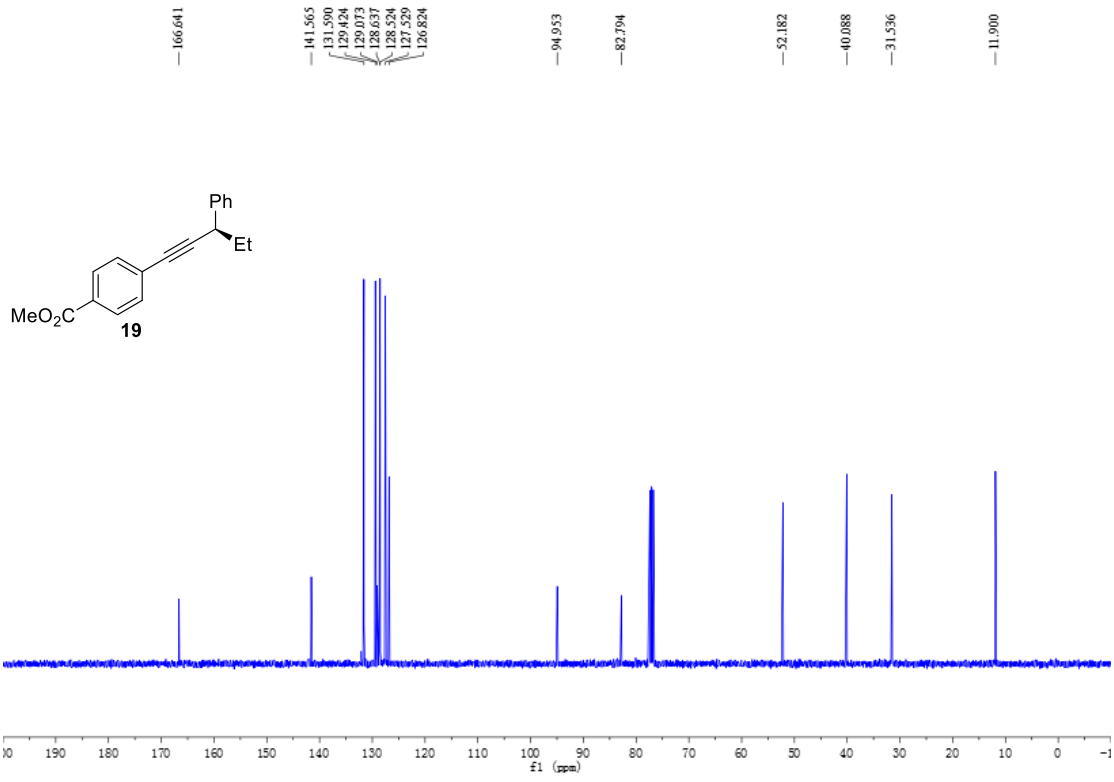
3.01
f1 (ppm)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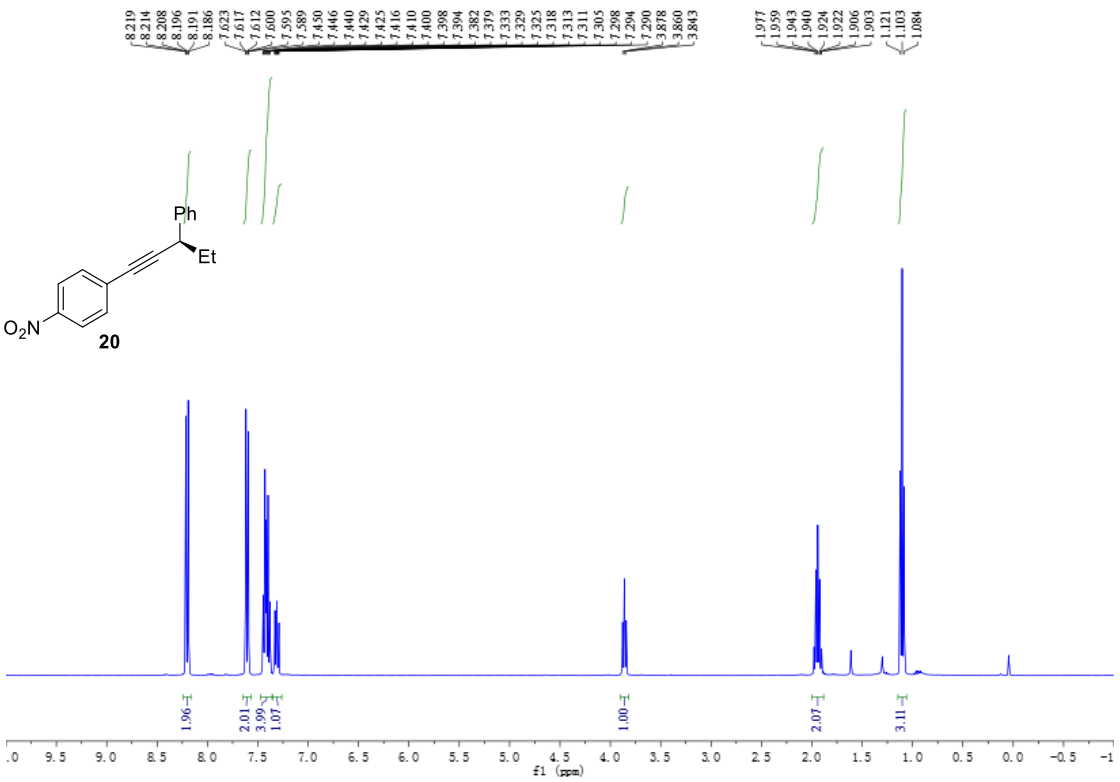
Et
MeO2C
19
f1 (ppm)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7.429
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7.398
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7.325
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7.311
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3.843
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1.959
1.943
1.940
1.924
1.922
1.906
1.903
1.121
1.103
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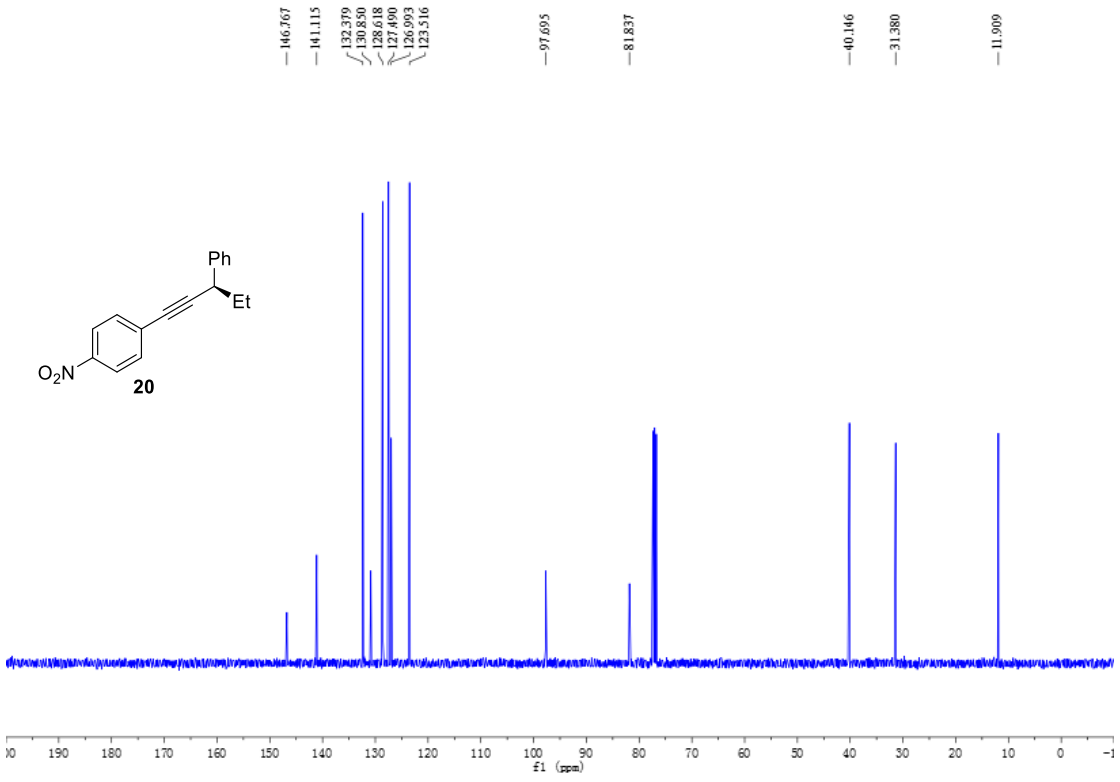
f1 (ppm)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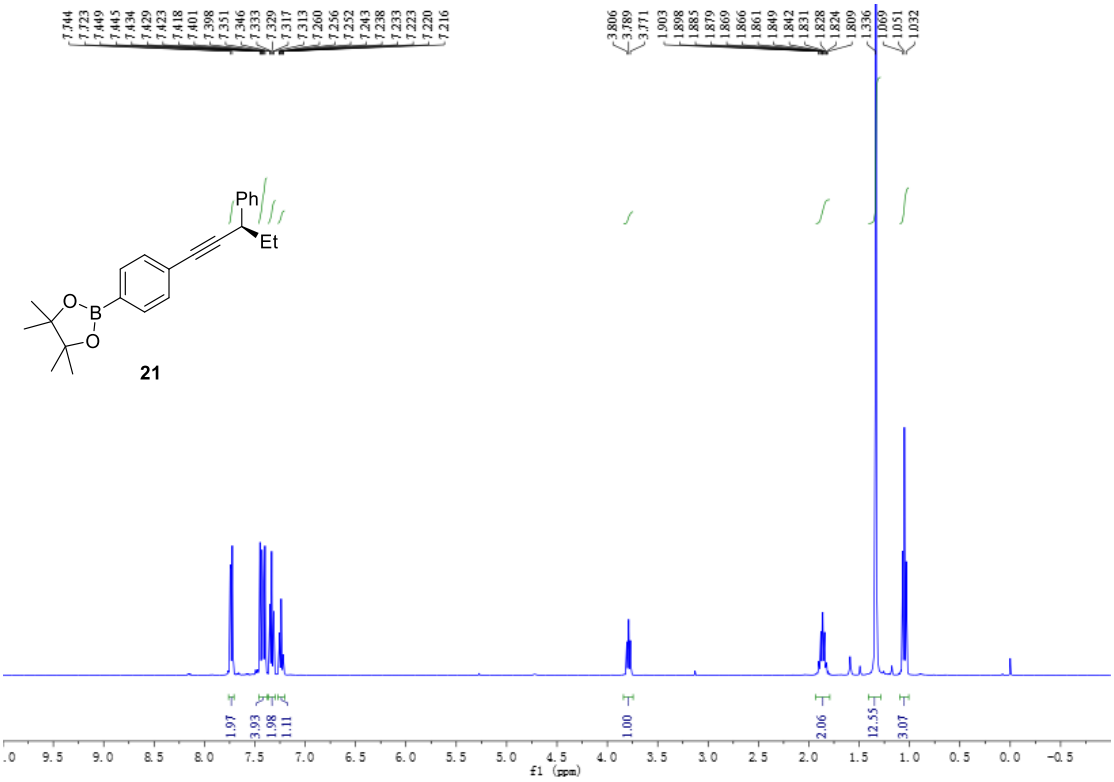
40.146
31.380
11.909
Ph
Et
O2N
20
f1 (ppm)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7.223
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1.824
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1.032
Ph
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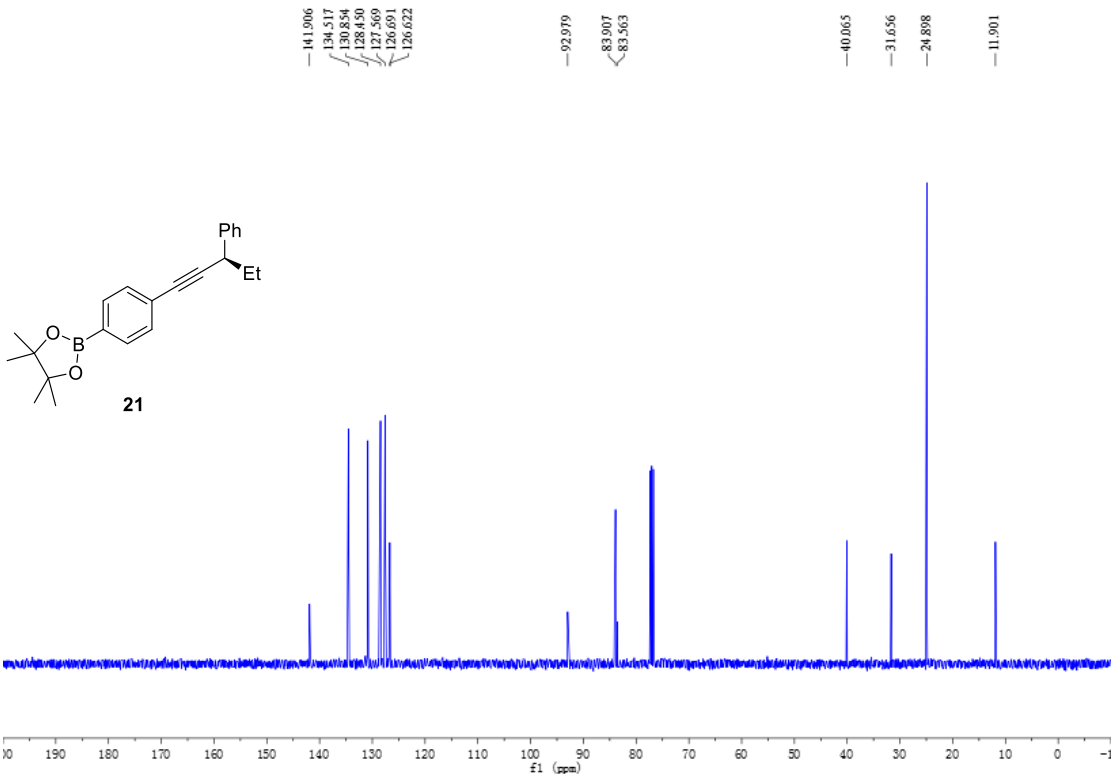
12.55
3.07
f1 (ppm)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128.430
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126.691
126.622
92.979
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83.563
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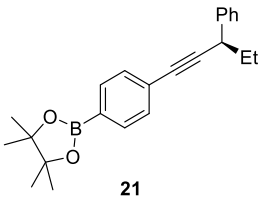
24.898
11.901
Ph
Et
O
B
O
21
f1 (ppm)


Ph
Et
O
B
O

21

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-60
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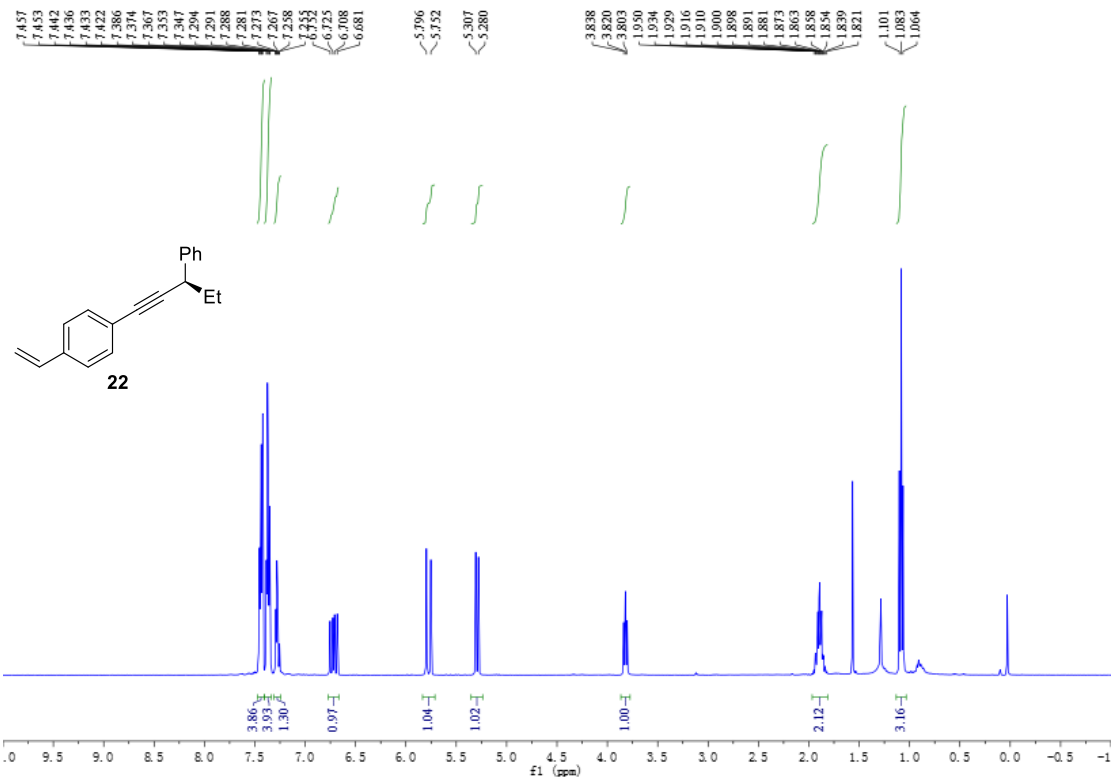
-90
f1 (ppm)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1.839
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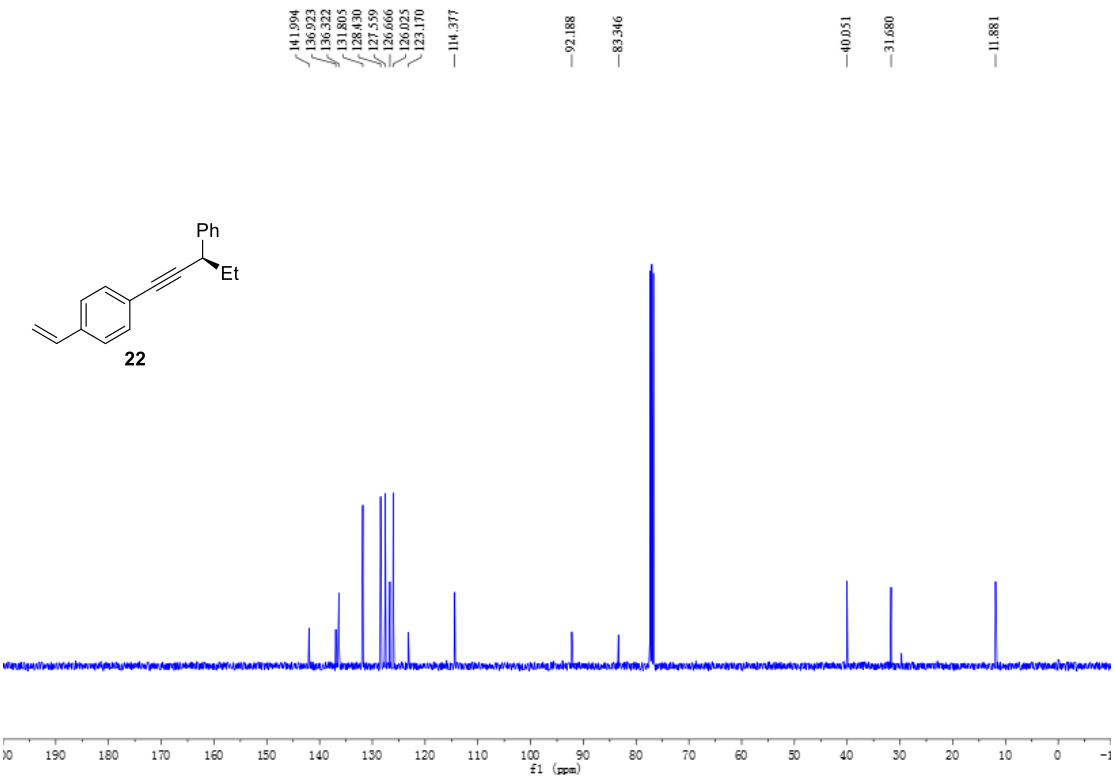
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136.923
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127.559
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92.188
83.346
40.051
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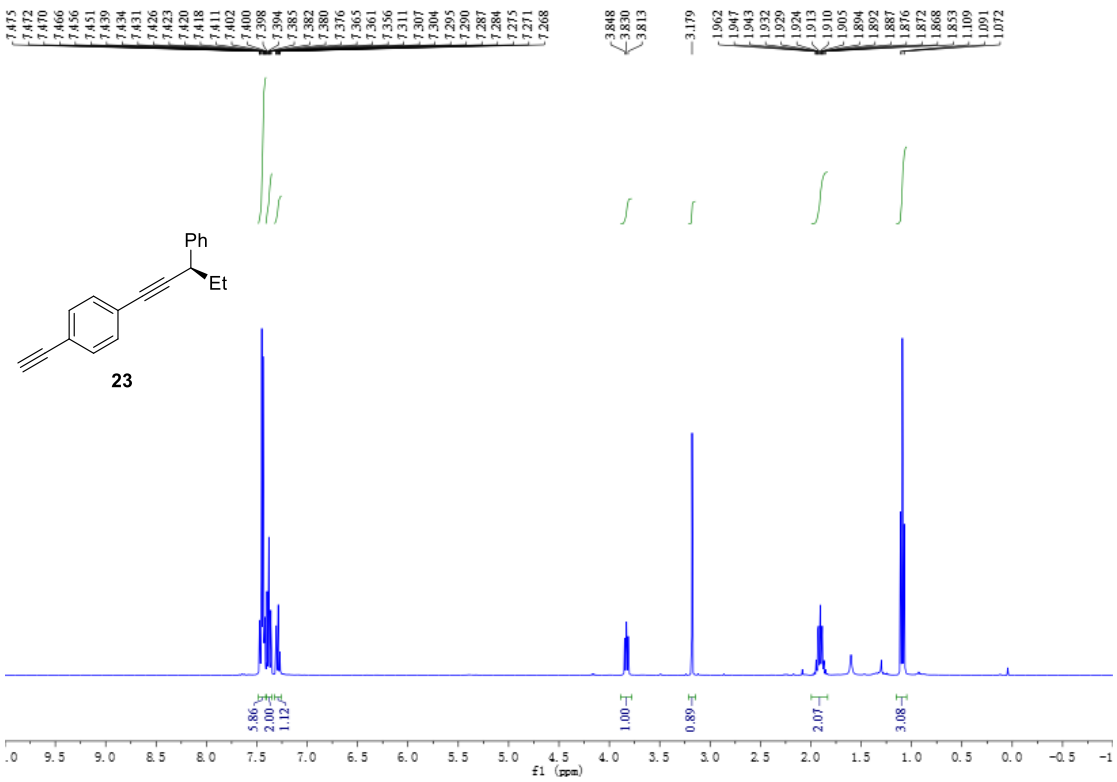
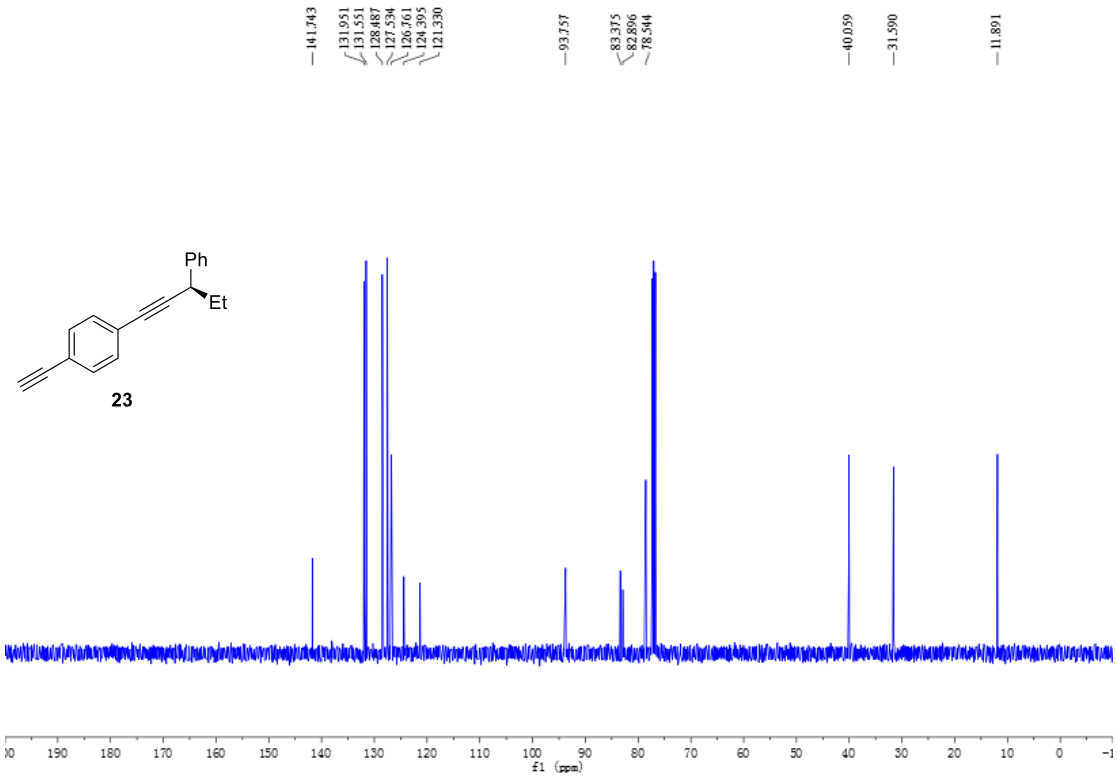
Ph
Et
22
f1 (ppm)


Ph
Et
23
f1 (ppm)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Et
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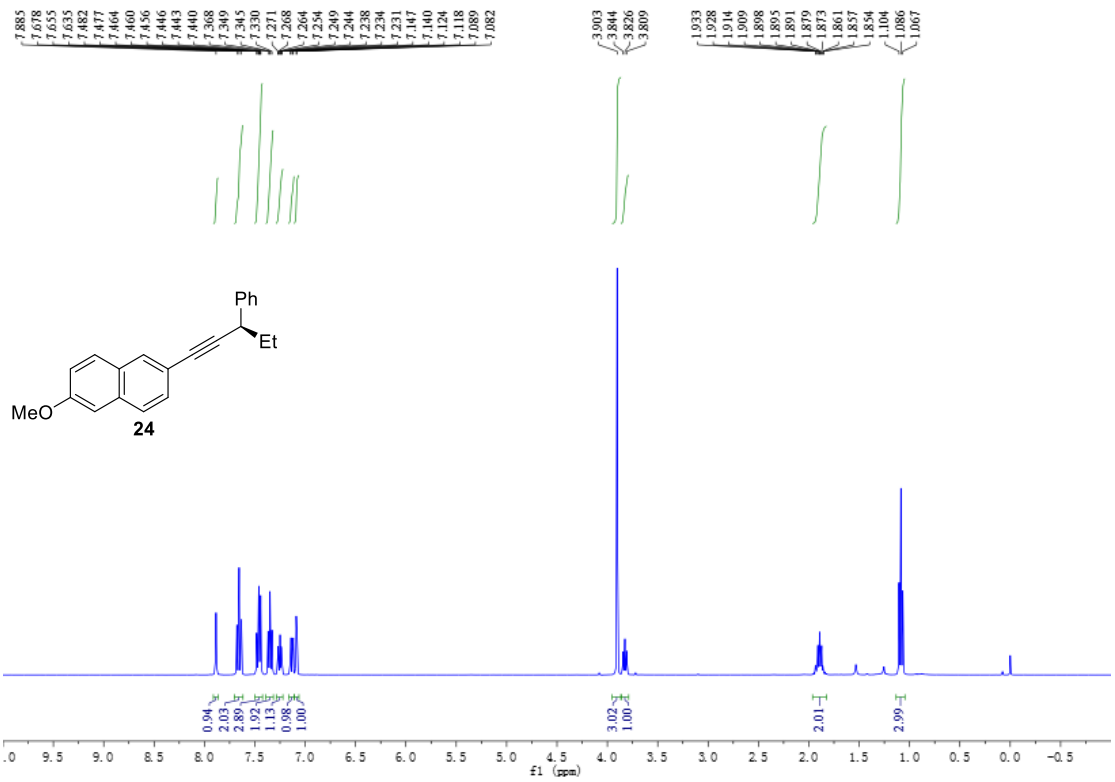
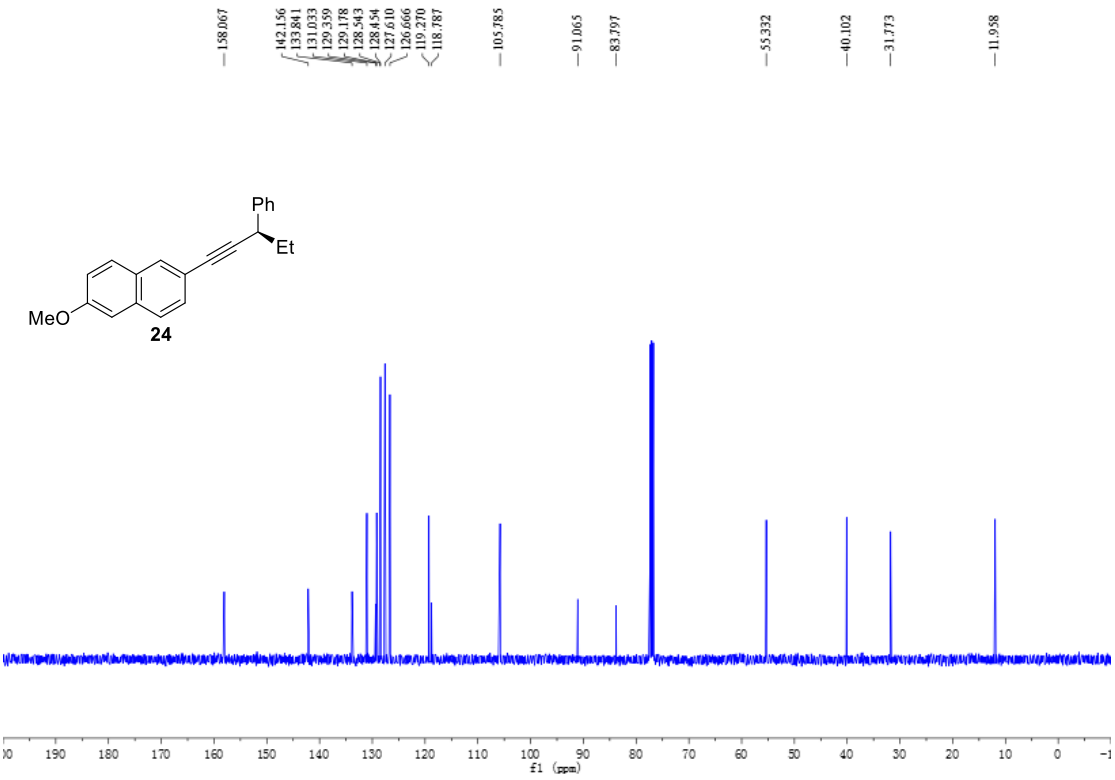
f1 (ppm)


Ph
Et
MeO
24
f1 (ppm)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Et
MeO
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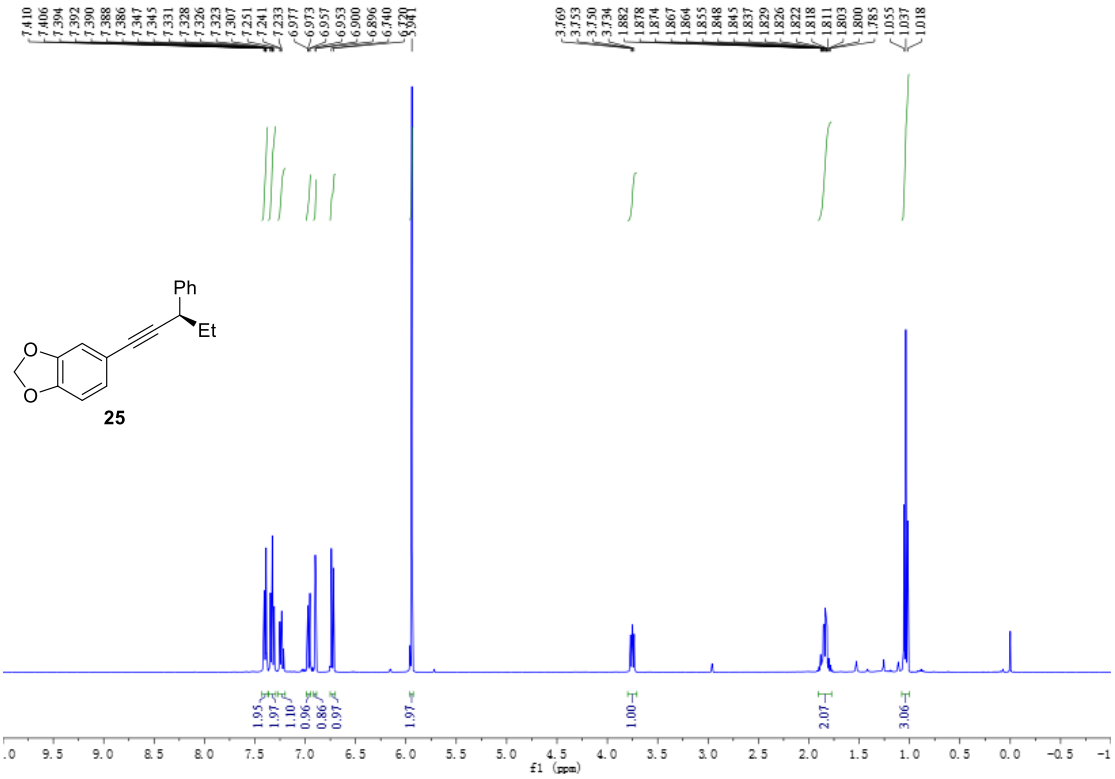
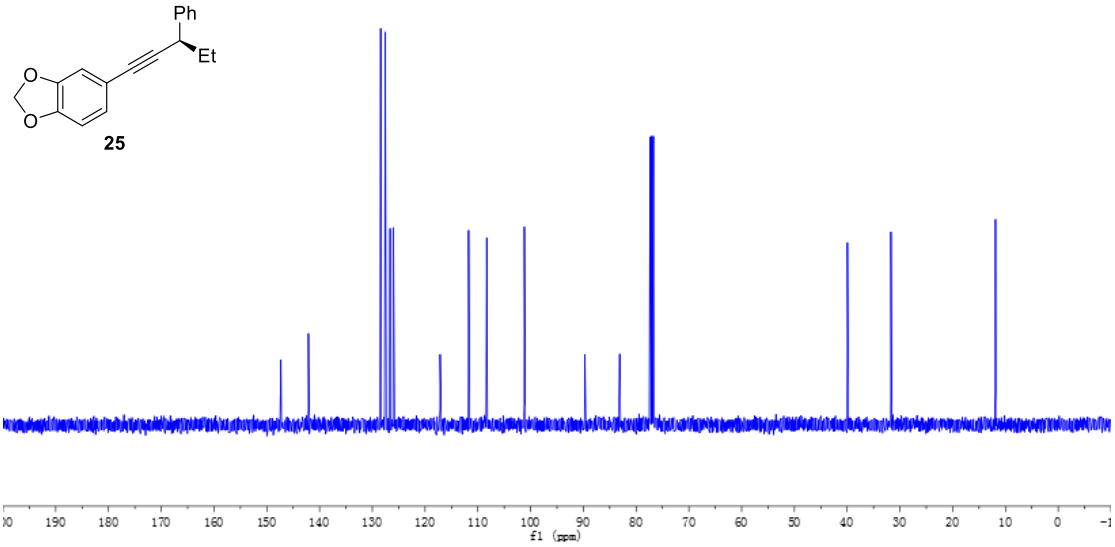
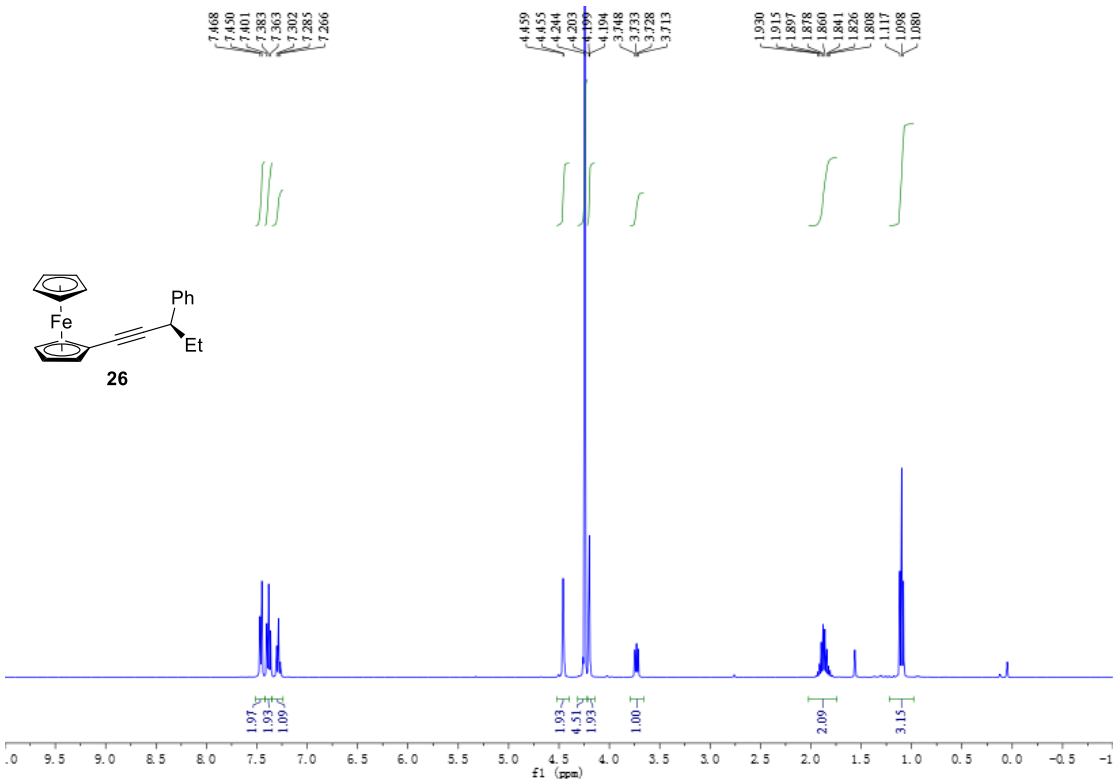
f1 (ppm)


Ph
Et
O
O
25
f1 (ppm)


Ph
Et
O
O
25
f1 (ppm)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7.266
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4.455
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4.203
4.199
4.194
3.748
3.733
3.728
3.713
1.930
1.915
1.897
1.878
1.860
1.841
1.826
1.808
1.117
1.098
1.080
Fe
Ph
Et
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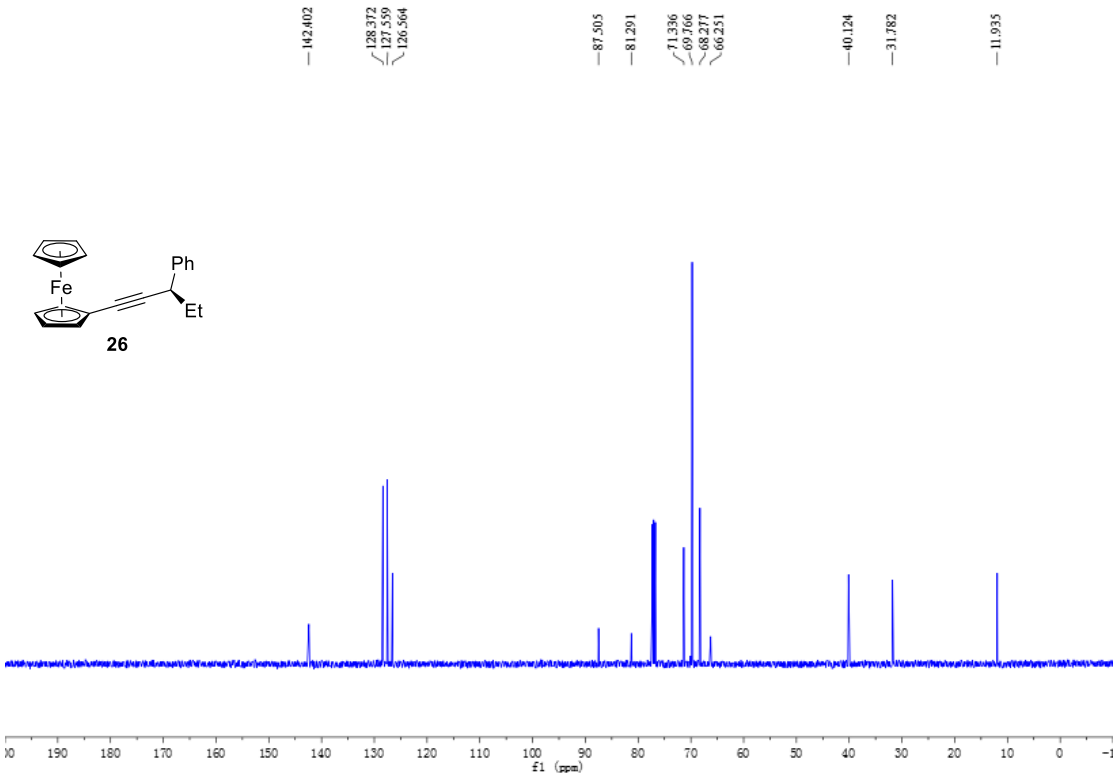
1.93
1.09
1.93
4.51
1.93
1.00
2.09
3.15
f1 (ppm)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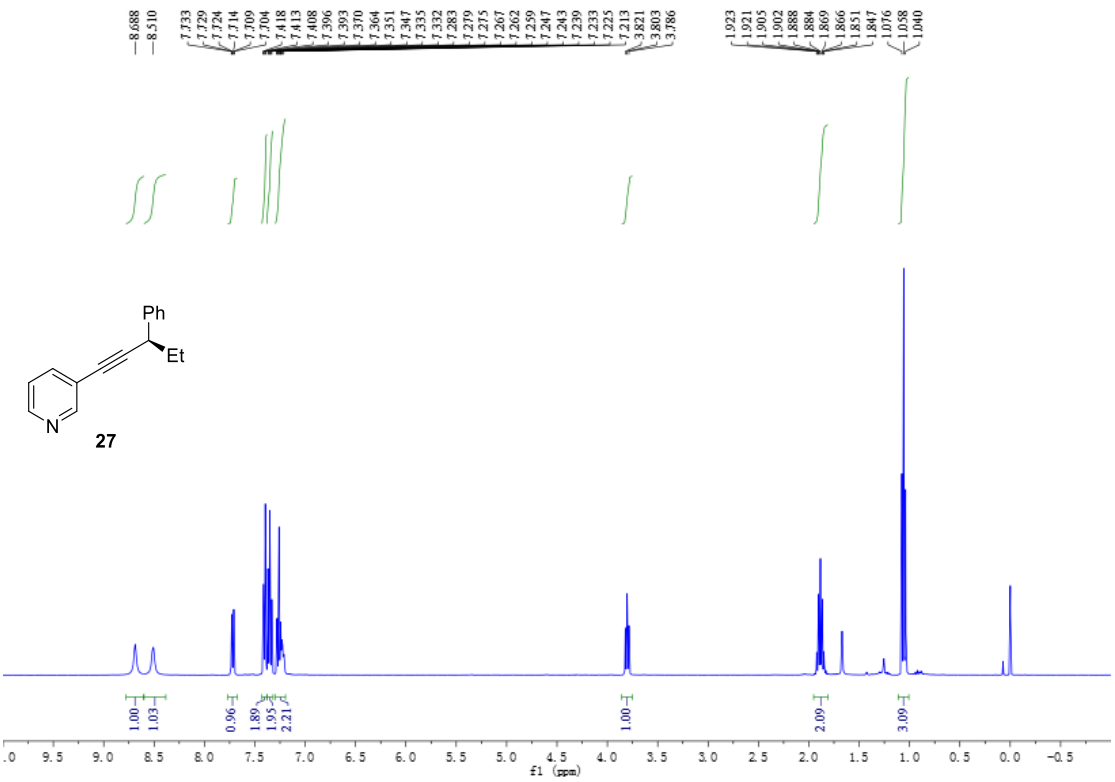
31.782
11.935
Fe
Ph
Et
26
f1 (ppm)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7.393
7.370
7.364
7.351
7.347
7.335
7.332
7.283
7.279
7.275
7.267
7.262
7.259
7.247
7.243
7.239
7.233
7.225
7.213
3.821
3.803
3.786
1.923
1.921
1.905
1.902
1.888
1.884
1.869
1.866
1.851
1.847
1.076
1.058
1.040
Ph
Et
N
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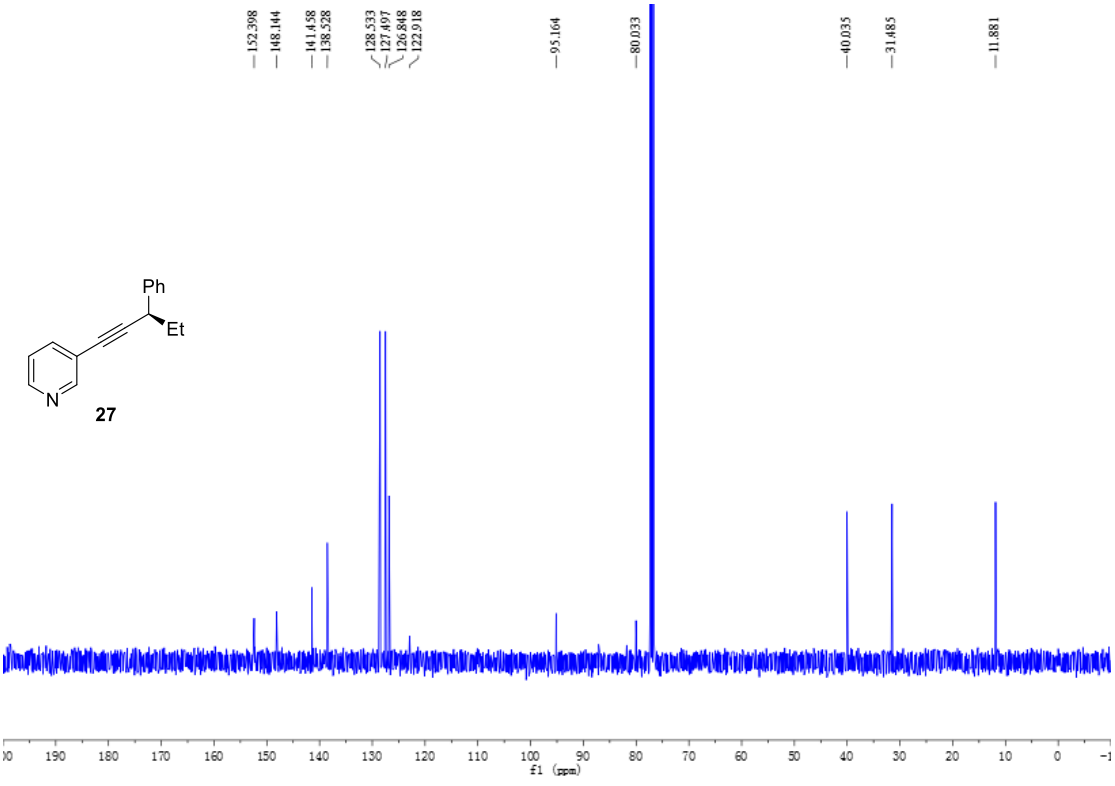
1.03
0.96
1.89
1.95
2.21
1.00
2.09
3.09
f1 (ppm)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141.458
138.528
128.533
127.497
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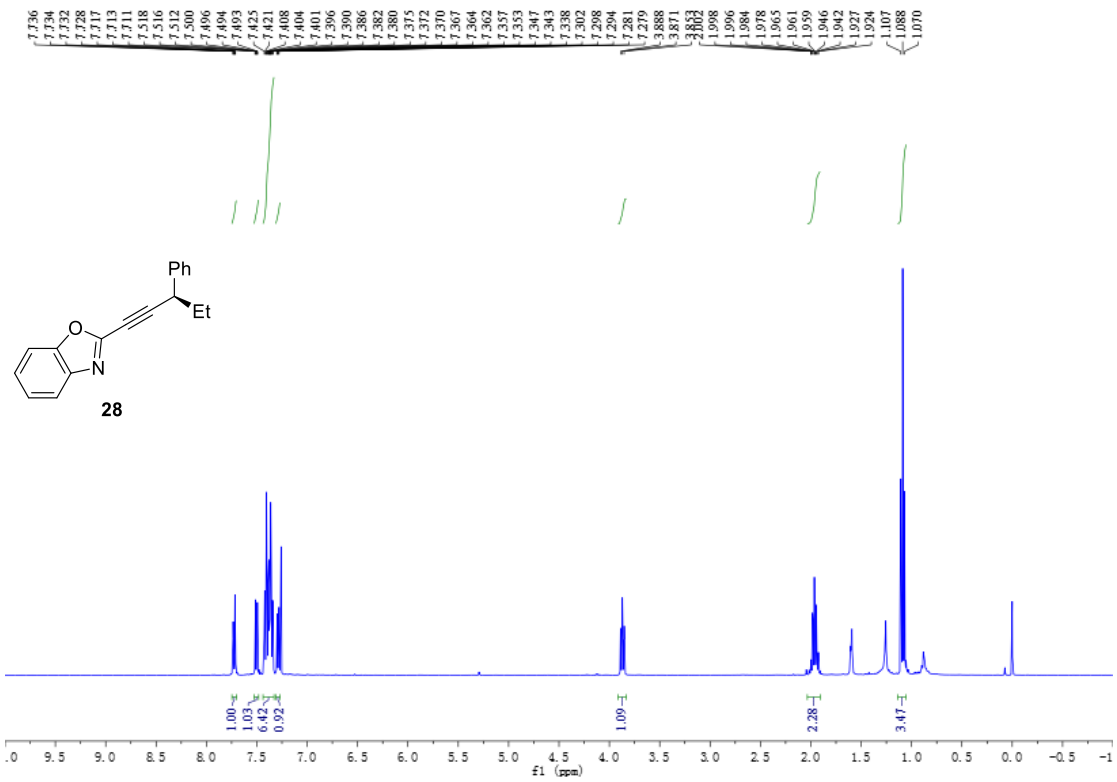
122.918
95.164
80.033
40.035
31.485
11.881
Ph
Et
N
27
f1 (ppm)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O
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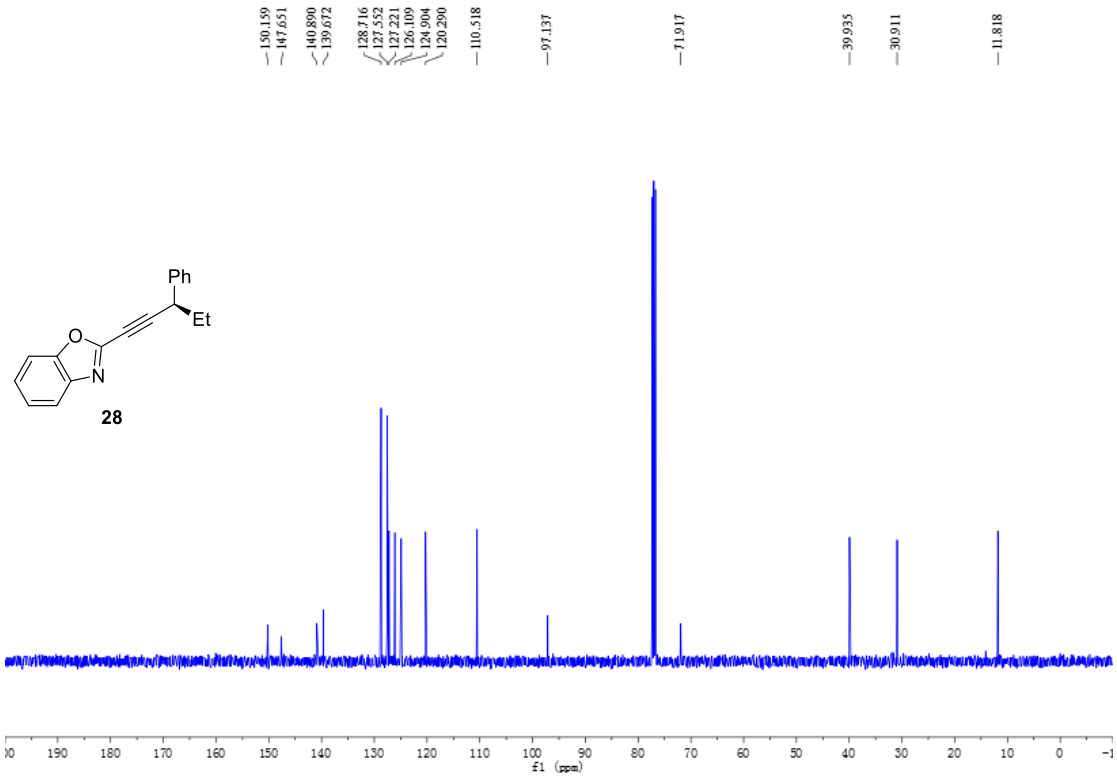
0.92
1.09
2.28
3.47
f1 (ppm)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126.109
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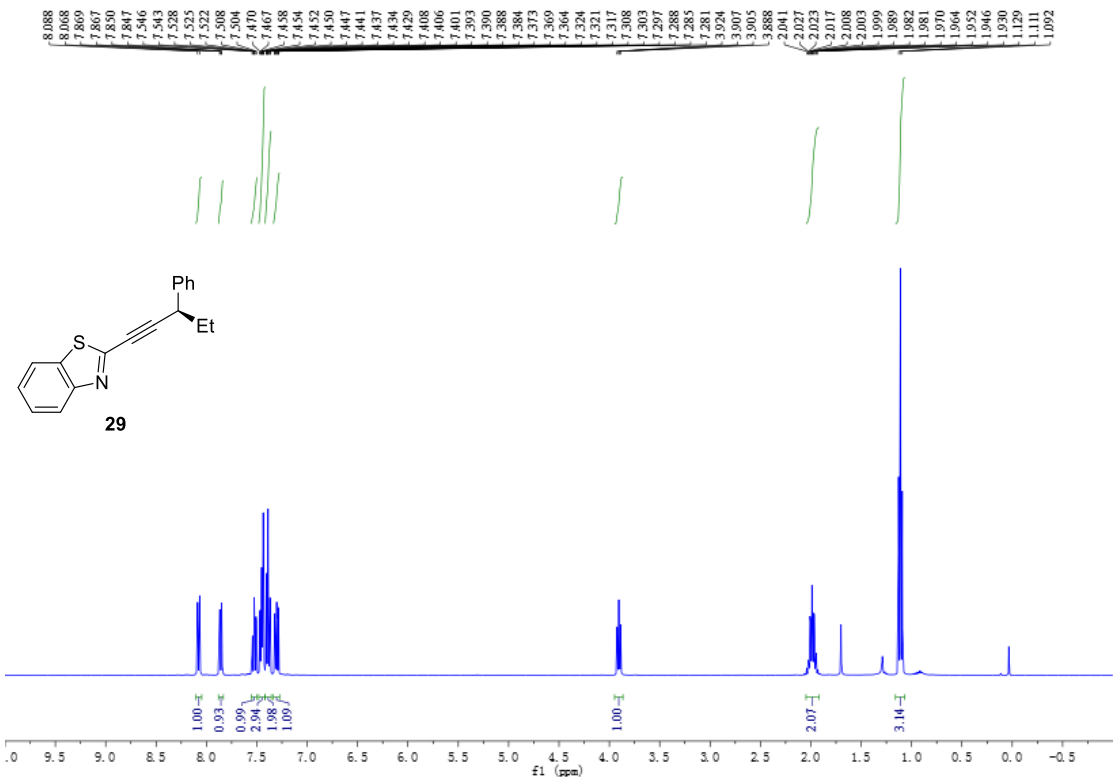
Ph
Et
O
N
28
f1 (ppm)


Ph
Et
S
N
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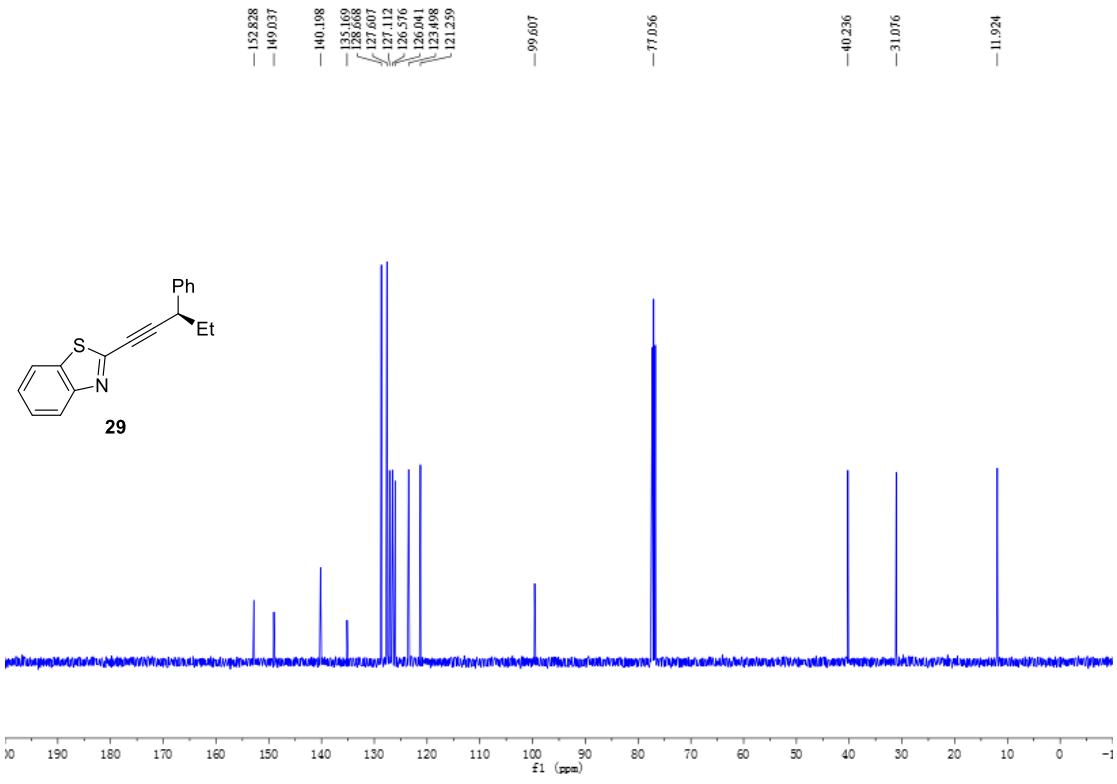
0.99
2.94
1.98
1.09
1.00
2.07
3.14
f1 (ppm)


Ph
Et
S
N
29
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149.037
140.198
135.169
128.668
127.607
127.112
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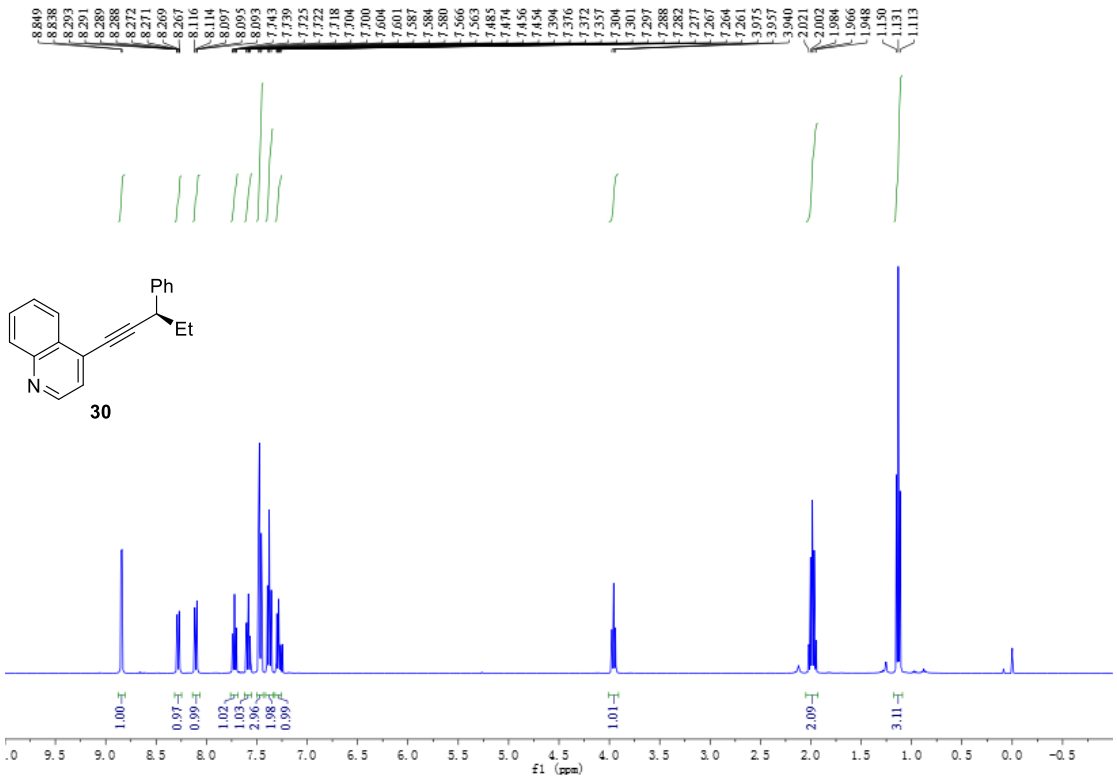
126.041
123.498
121.259
99.607
77.056
40.236
31.076
11.924
f1 (ppm)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8.289
8.288
8.272
8.271
8.269
8.267
8.116
8.114
8.097
8.095
8.093
7.743
7.739
7.725
7.722
7.718
7.704
7.700
7.604
7.601
7.587
7.584
7.580
7.566
7.563
7.485
7.474
7.456
7.454
7.394
7.376
7.372
7.357
7.304
7.301
7.297
7.288
7.282
7.277
7.267
7.264
7.261
3.975
3.957
3.940
2.021
2.002
1.984
1.966
1.948
1.150
1.131
1.113
Ph
Et
N
30
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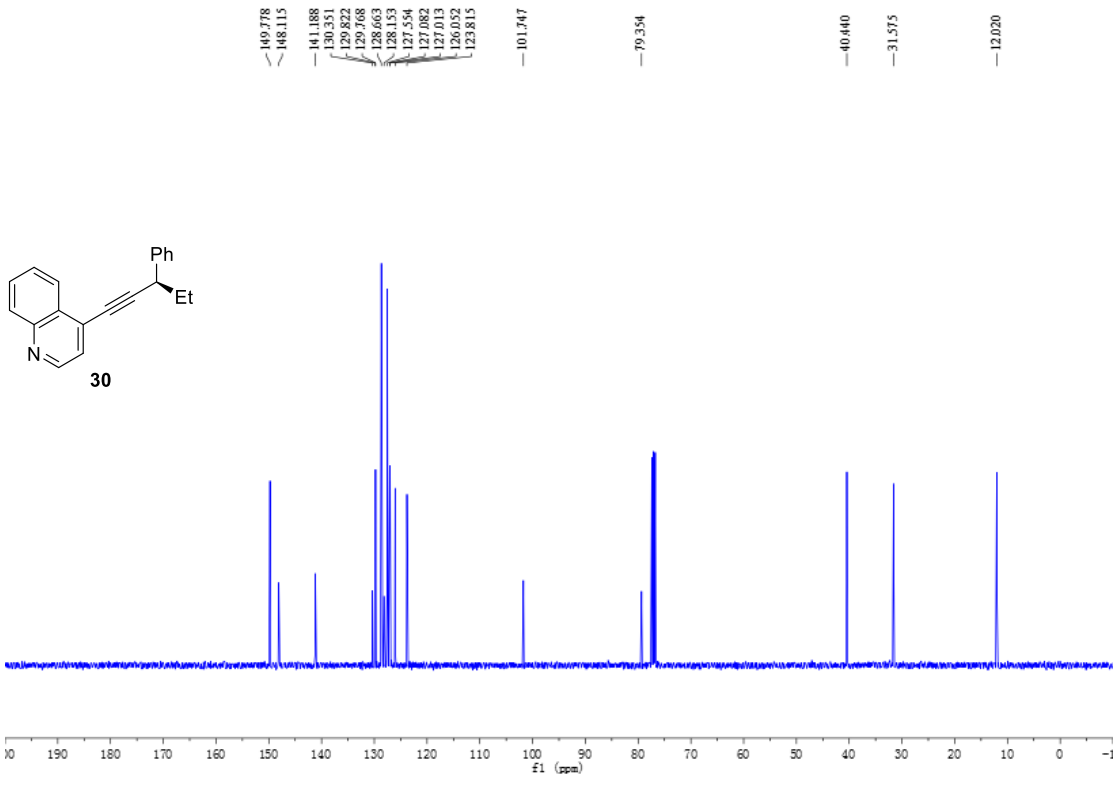
0.97
0.99
1.02
1.03
2.96
1.98
0.99
1.01
2.09
3.11
f1 (ppm)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141.188
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129.768
128.663
128.153
127.554
127.082
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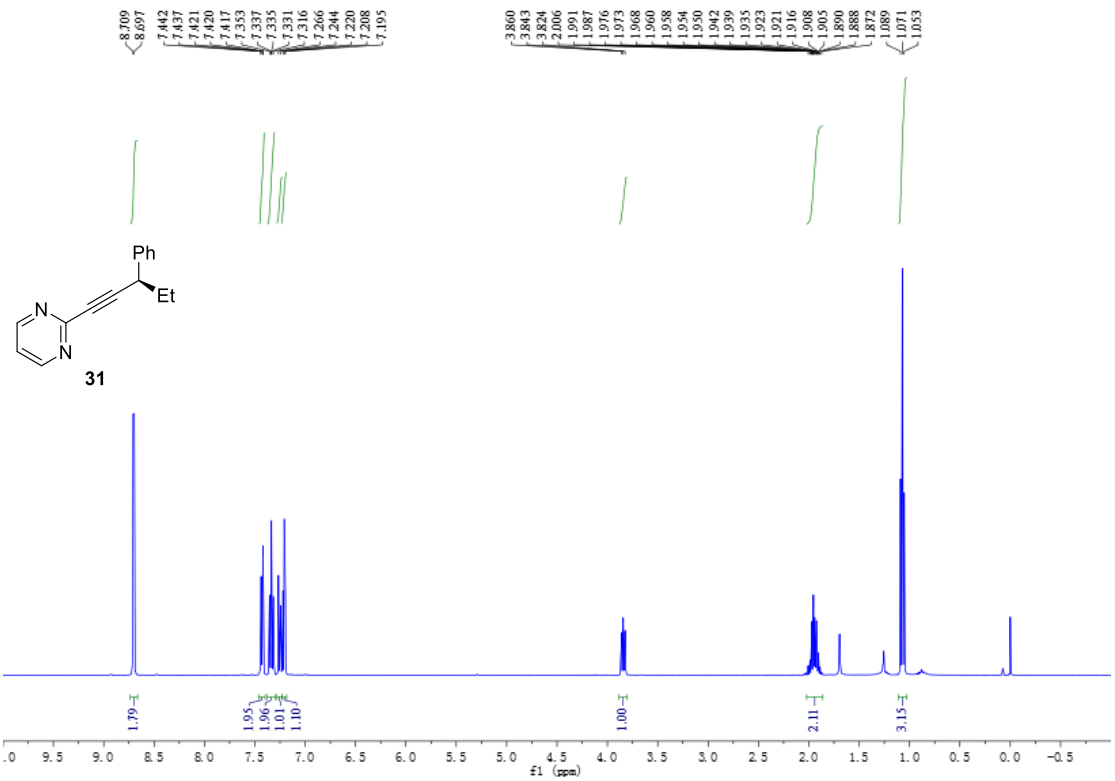
123.815
101.747
79.354
40.440
31.575
12.020
Ph
Et
N
30
f1 (ppm)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7.421
7.420
7.417
7.353
7.337
7.335
7.331
7.316
7.266
7.244
7.220
7.208
7.195
3.860
3.843
3.824
2.006
1.991
1.987
1.976
1.973
1.968
1.960
1.958
1.954
1.950
1.942
1.939
1.935
1.923
1.921
1.916
1.908
1.905
1.890
1.888
1.872
1.089
1.071
1.053
Ph
Et
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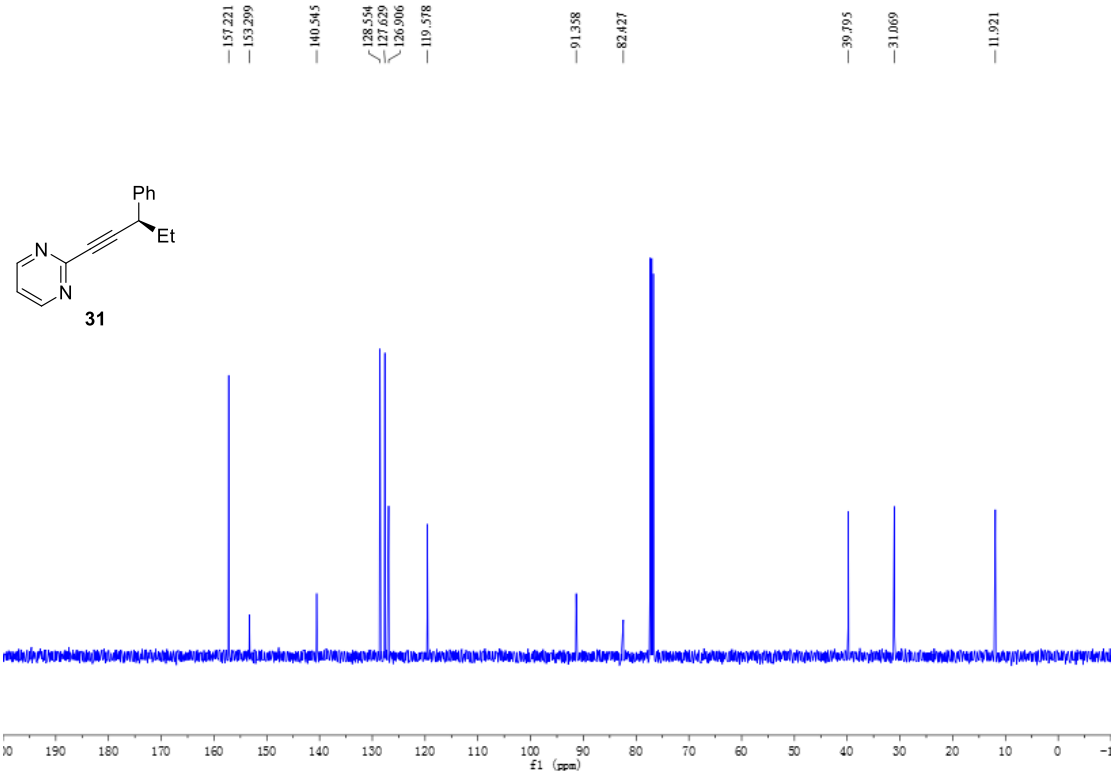
1.79
1.95
1.96
1.01
1.10
1.00
2.11
3.15
f1 (ppm)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153.299
140.545
128.554
127.629
126.906
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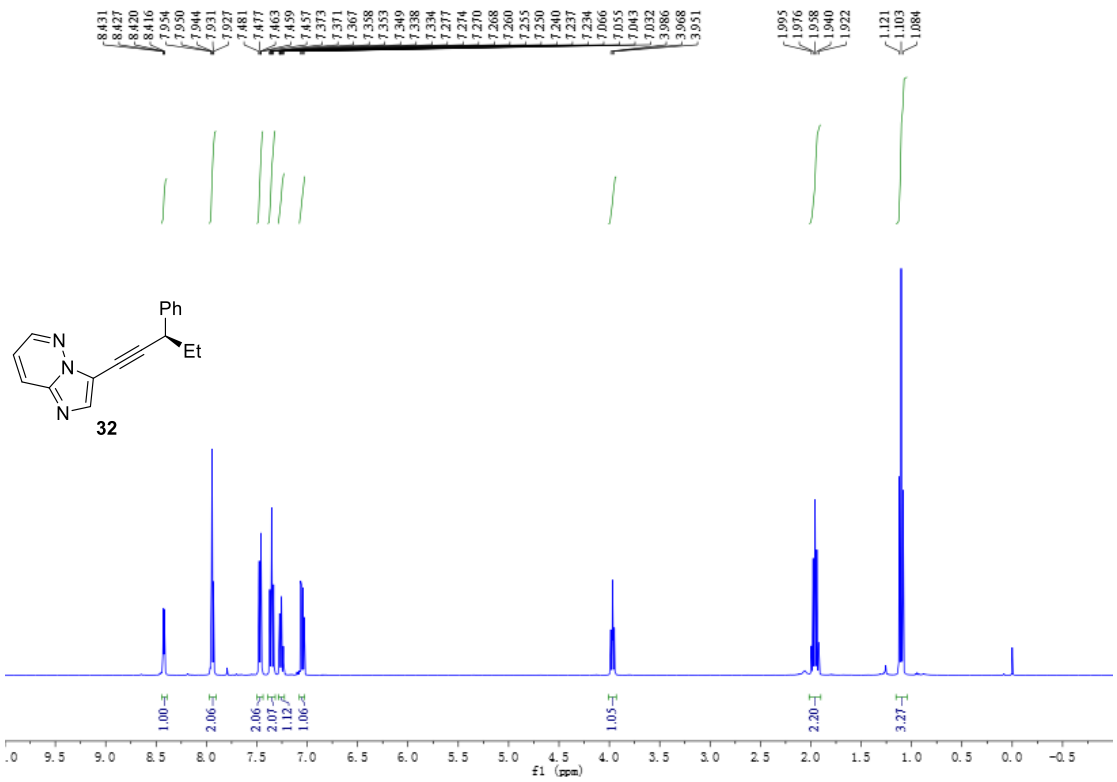
91.358
82.427
39.795
31.069
11.921
Ph
Et
N
N
31
f1 (ppm)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7.950
7.944
7.931
7.927
7.481
7.477
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7.459
7.457
7.373
7.371
7.367
7.358
7.353
7.349
7.338
7.334
7.277
7.274
7.270
7.268
7.260
7.255
7.250
7.240
7.237
7.234
7.066
7.055
7.043
7.032
3.986
3.968
3.951
1.995
1.976
1.958
1.940
1.922
1.121
1.103
1.084
Ph
Et
N
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2.06
2.07
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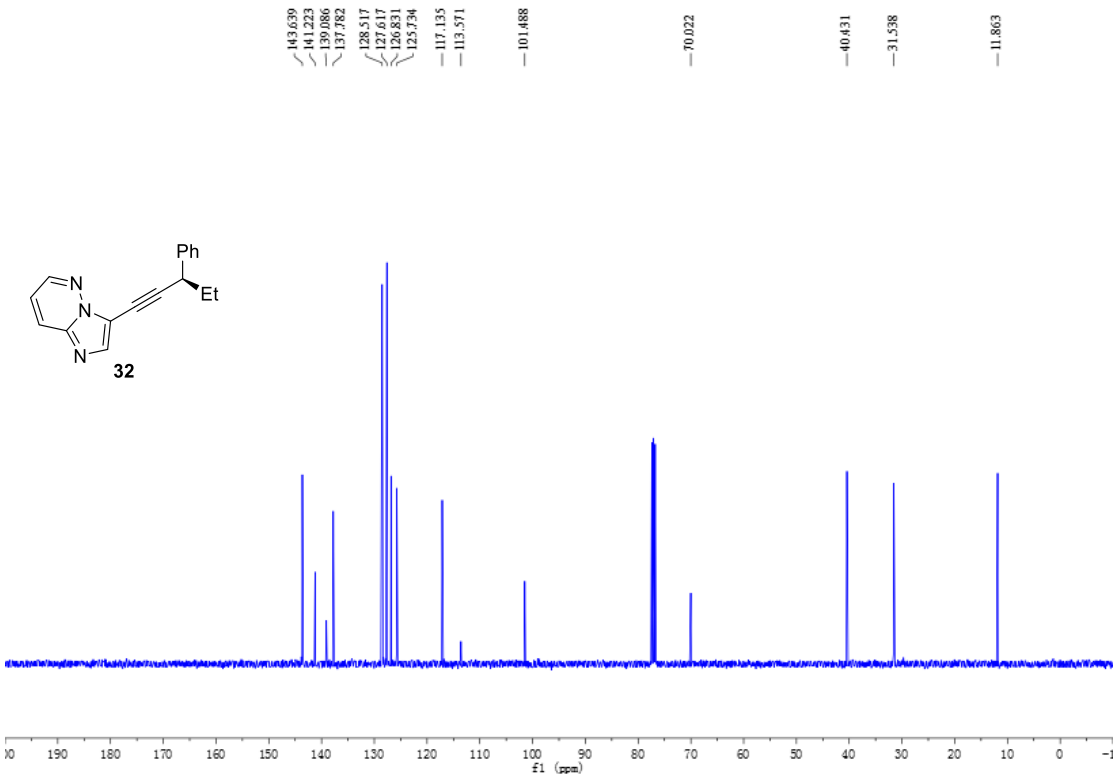
1.06
1.05
2.20
3.27
f1 (ppm)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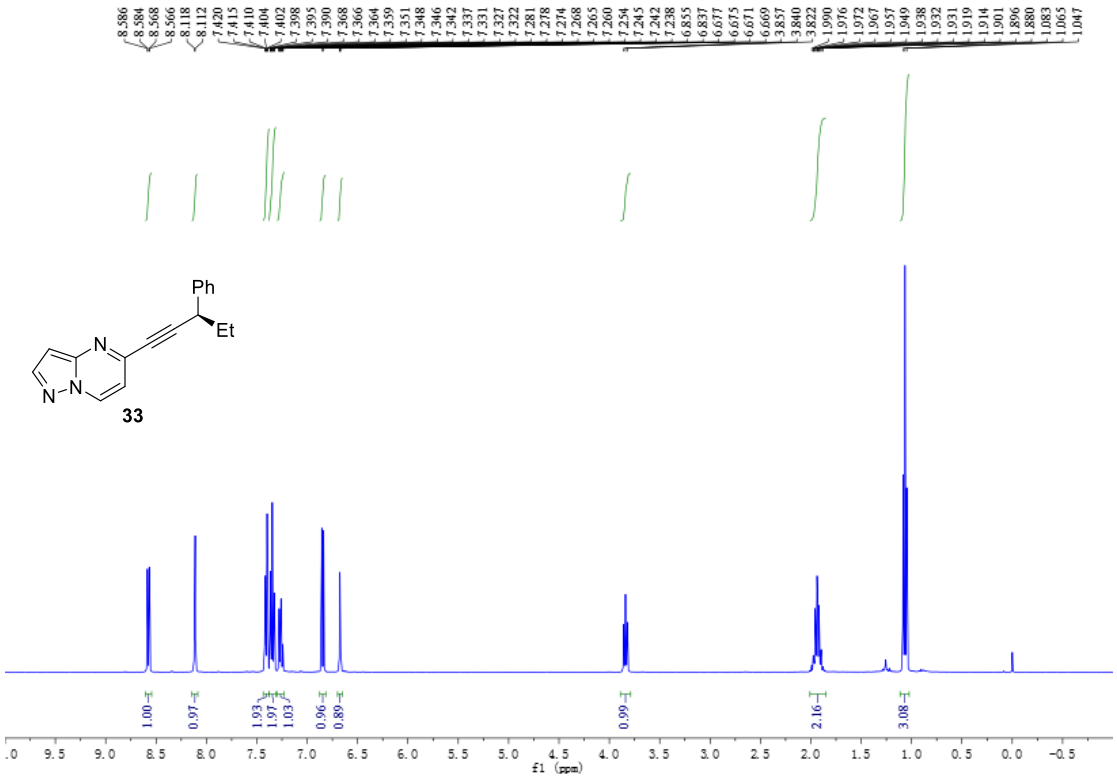
141.223
139.086
137.782
128.517
127.617
126.831
125.734
117.135
113.571
101.488
70.022
40.431
31.538
11.863
Ph
Et
N
N
N
32
f1 (ppm)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Et
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N
N
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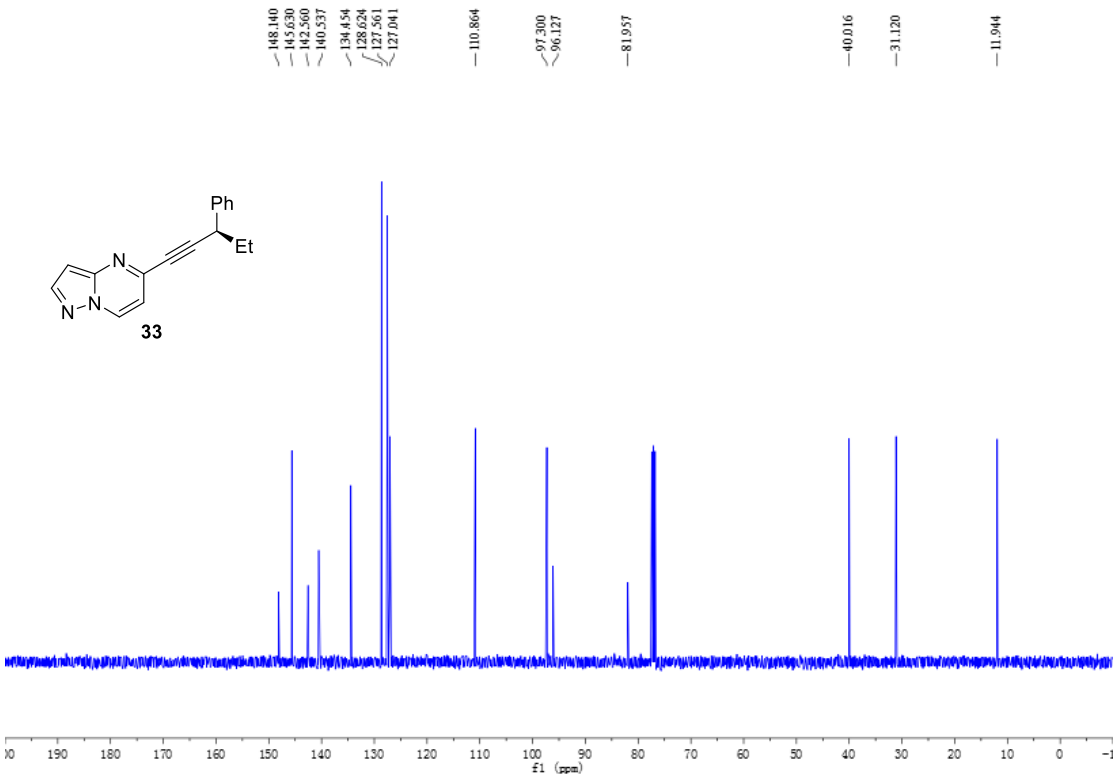
1.03
0.96
0.89
0.99
2.16
3.08
f1 (ppm)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127.561
127.041
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81.957
40.016
31.120
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Et
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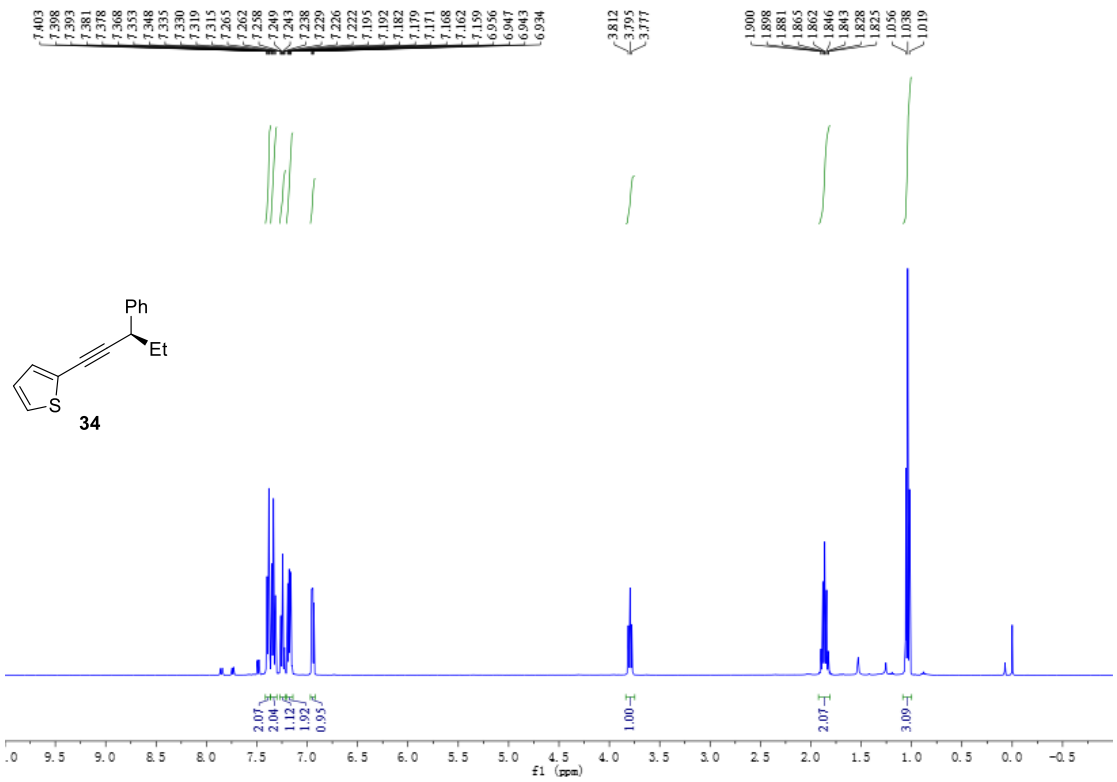
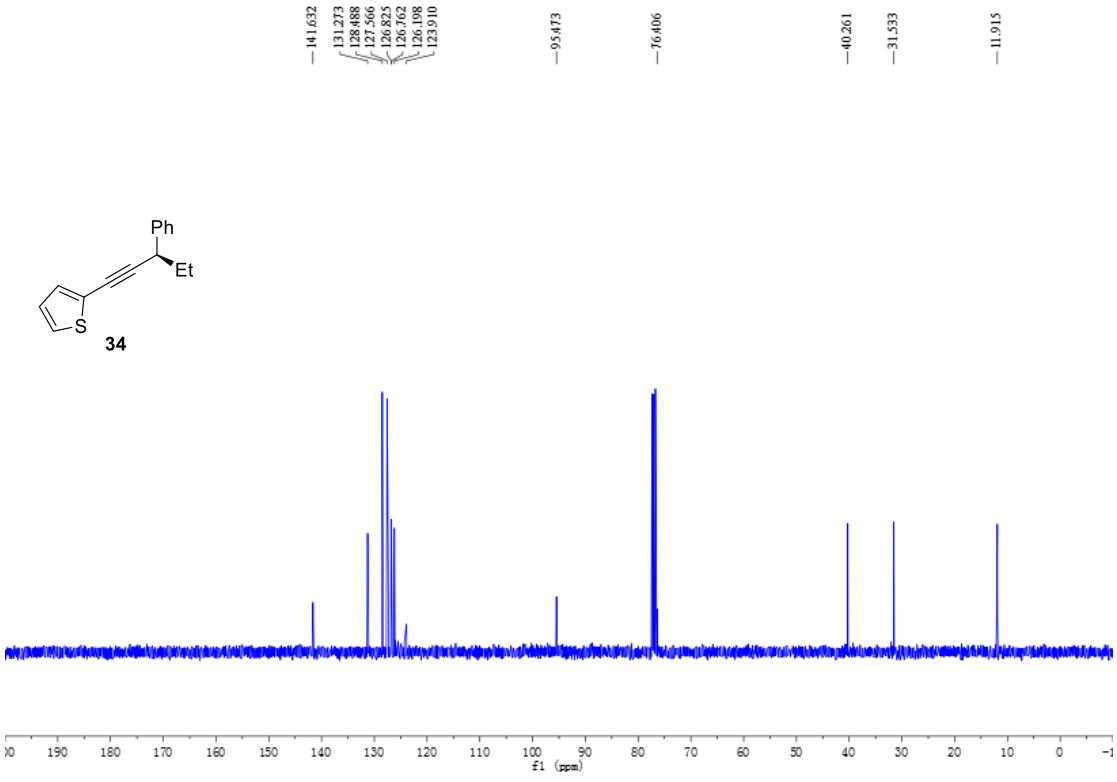
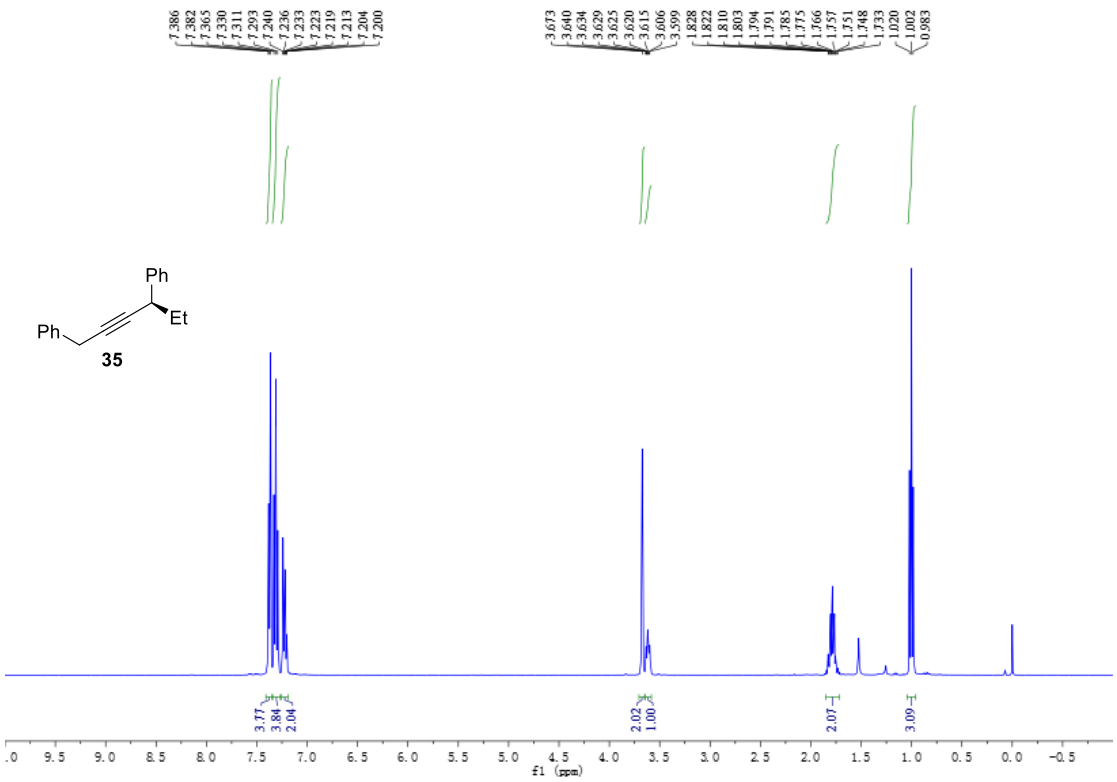
33
f1 (ppm)


Ph
Et
S
34
f1 (ppm)


Ph
Et
S
34
f1 (ppm)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7.200
3.673
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1.794
1.791
1.785
1.775
1.766
1.757
1.751
1.748
1.733
1.020
1.002
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Et
Ph
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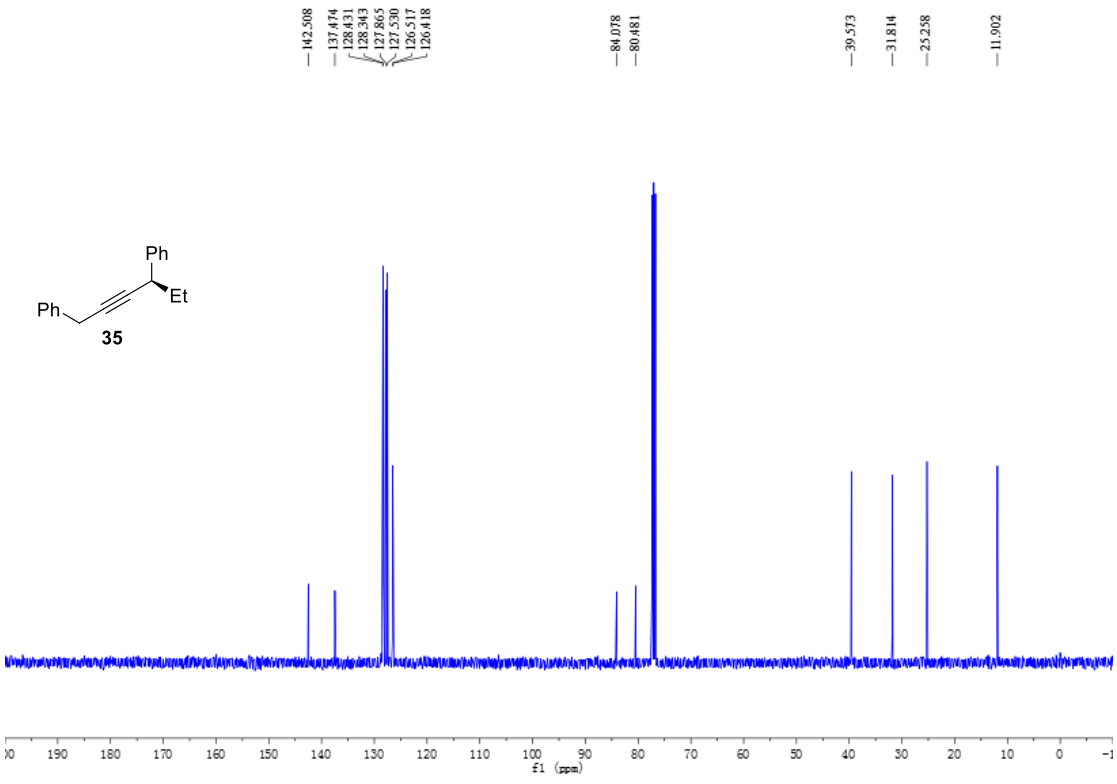
3.84
2.04
2.02
1.00
2.07
3.09
f1 (ppm)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137.474
128.431
128.343
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127.530
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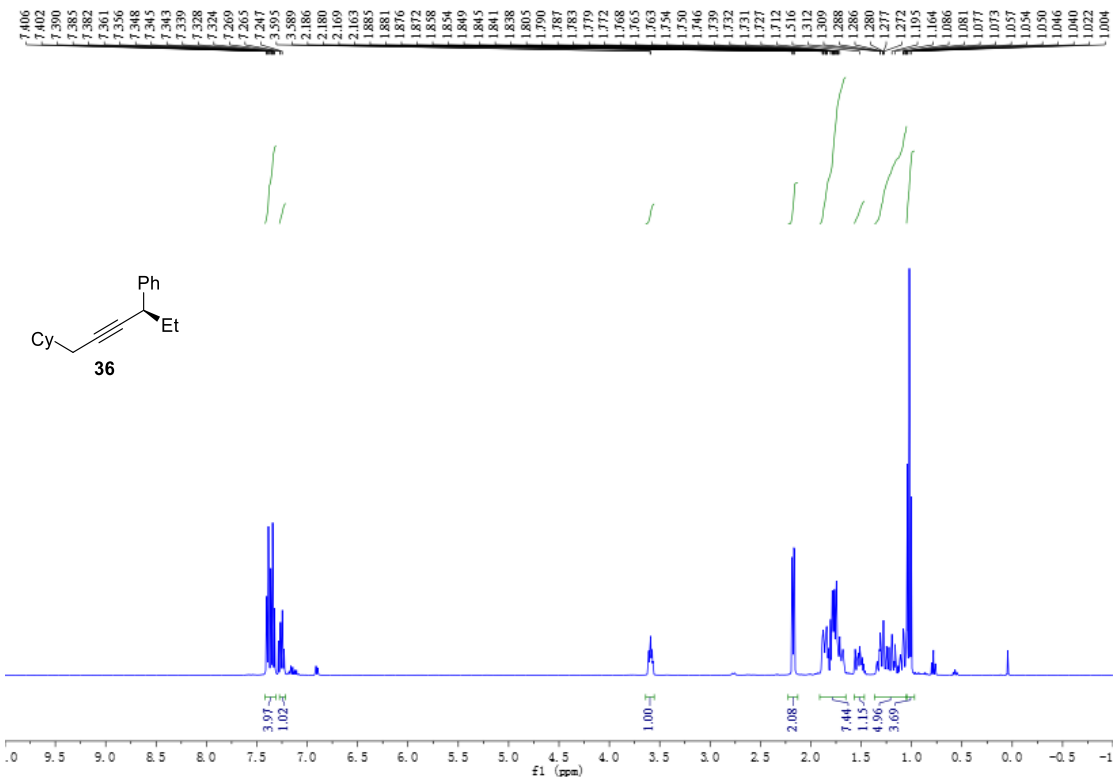
80.481
39.573
31.814
25.258
11.902
Ph
Et
Ph
35
f1 (ppm)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Et
Cy
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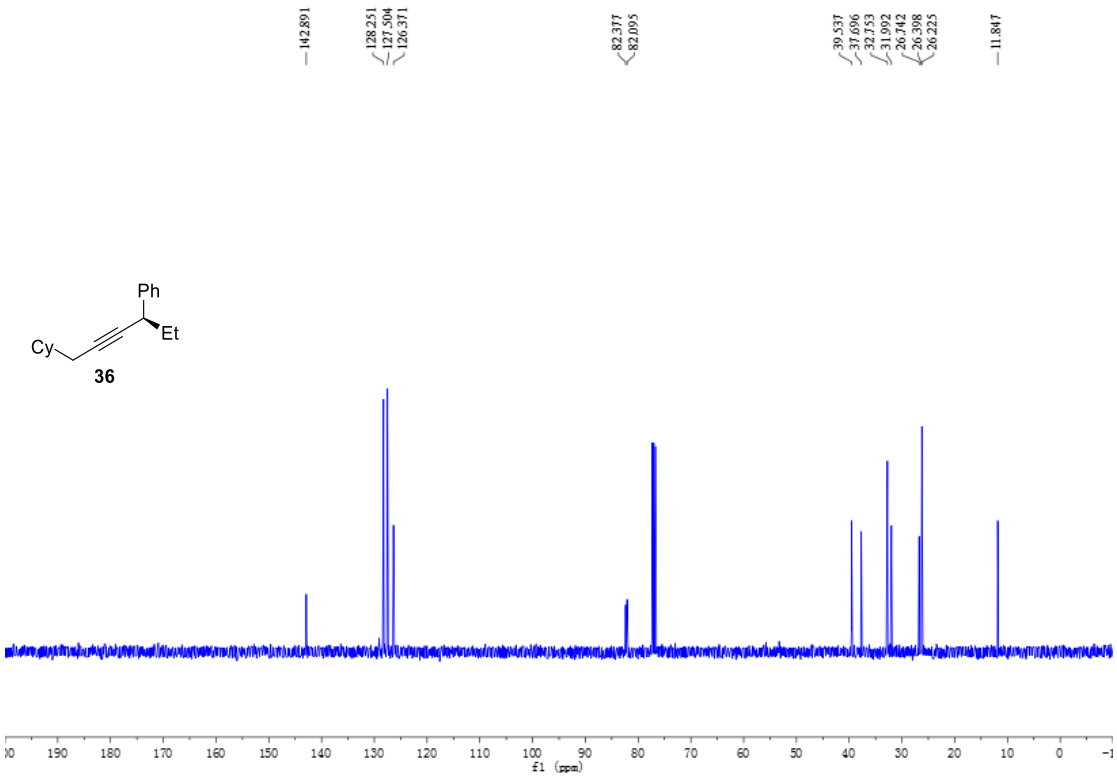
f1 (ppm)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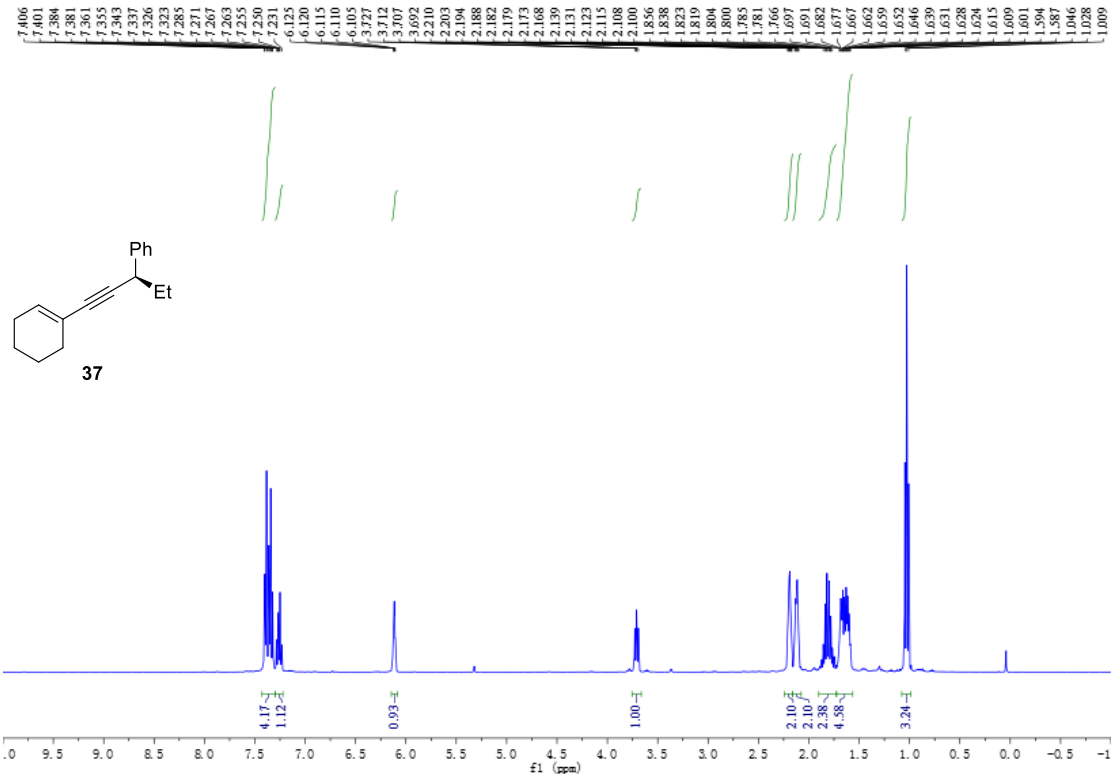
f1 (ppm)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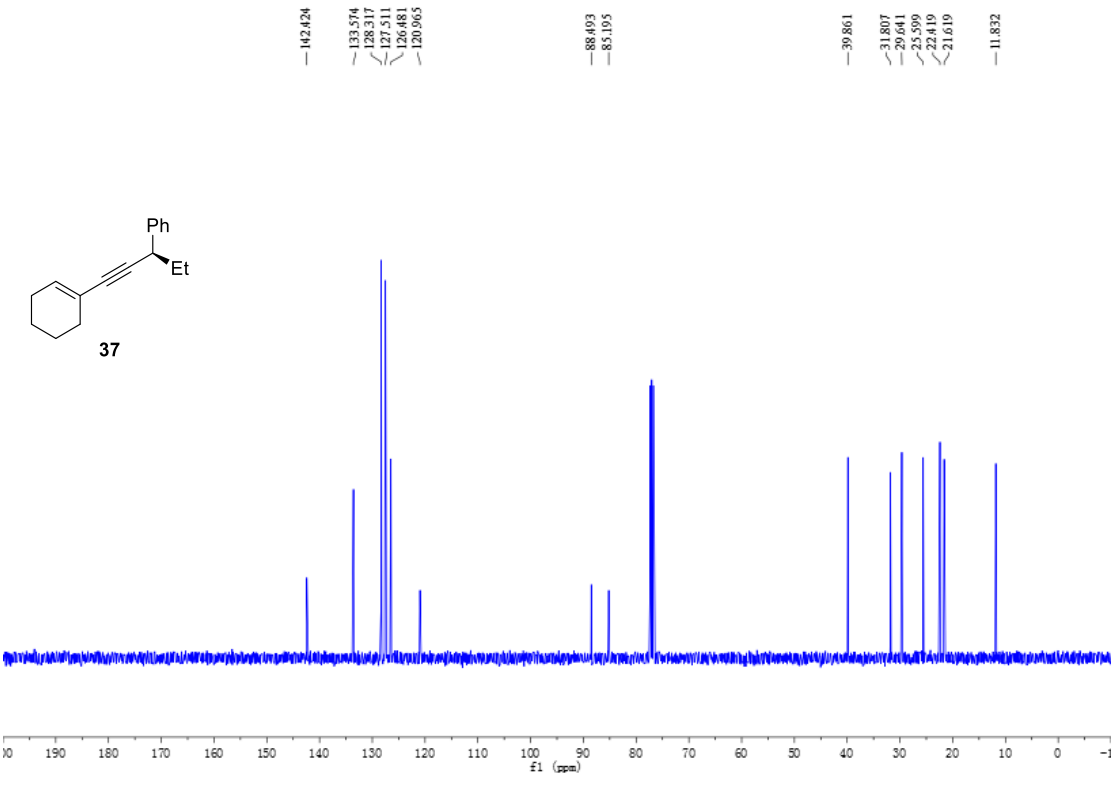
Et
37
f1 (ppm)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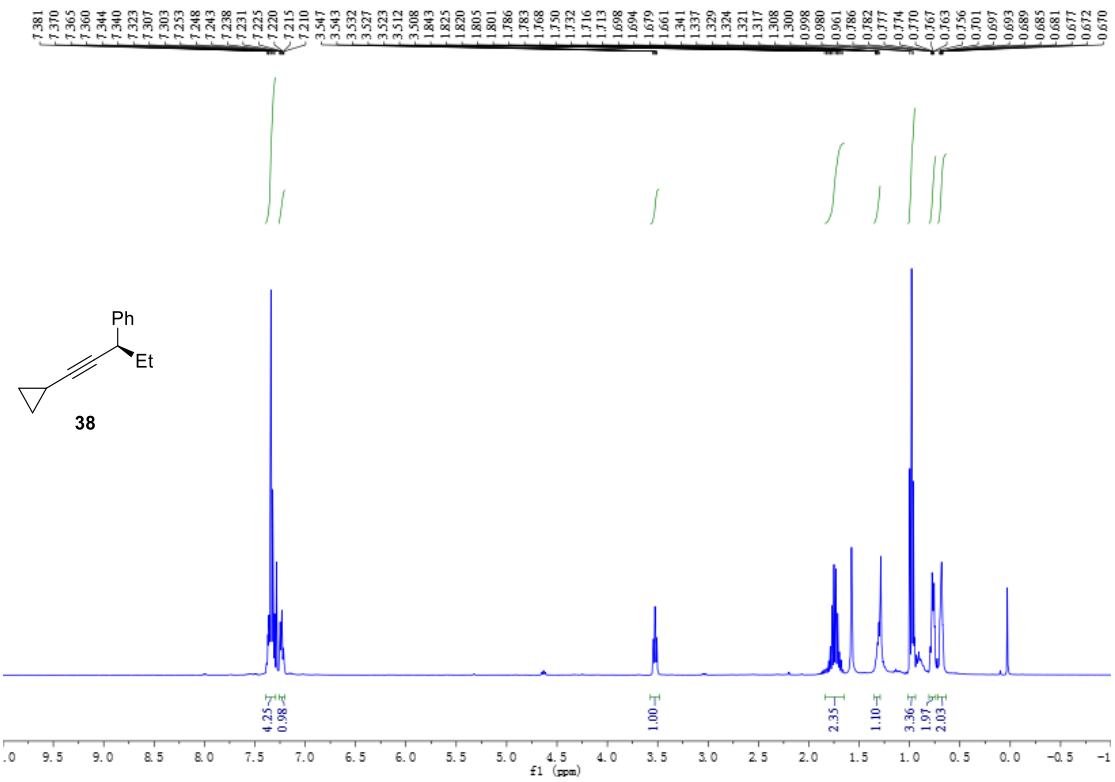
Et
37
f1 (ppm)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Et
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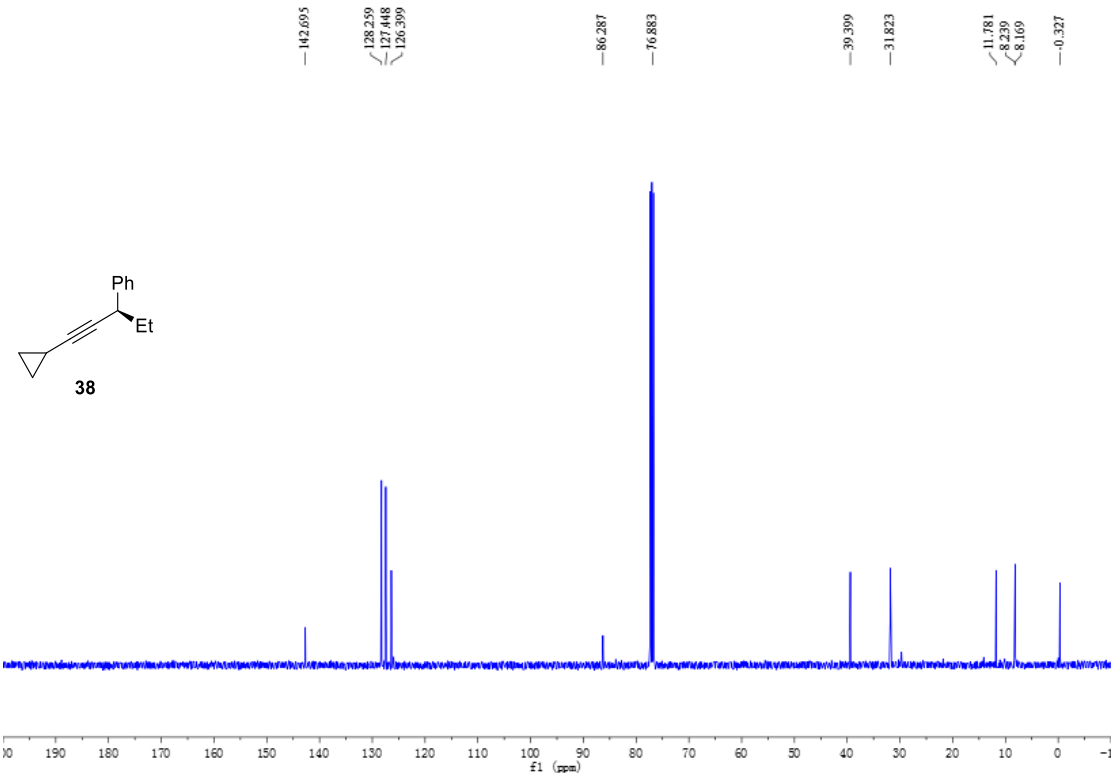
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Et
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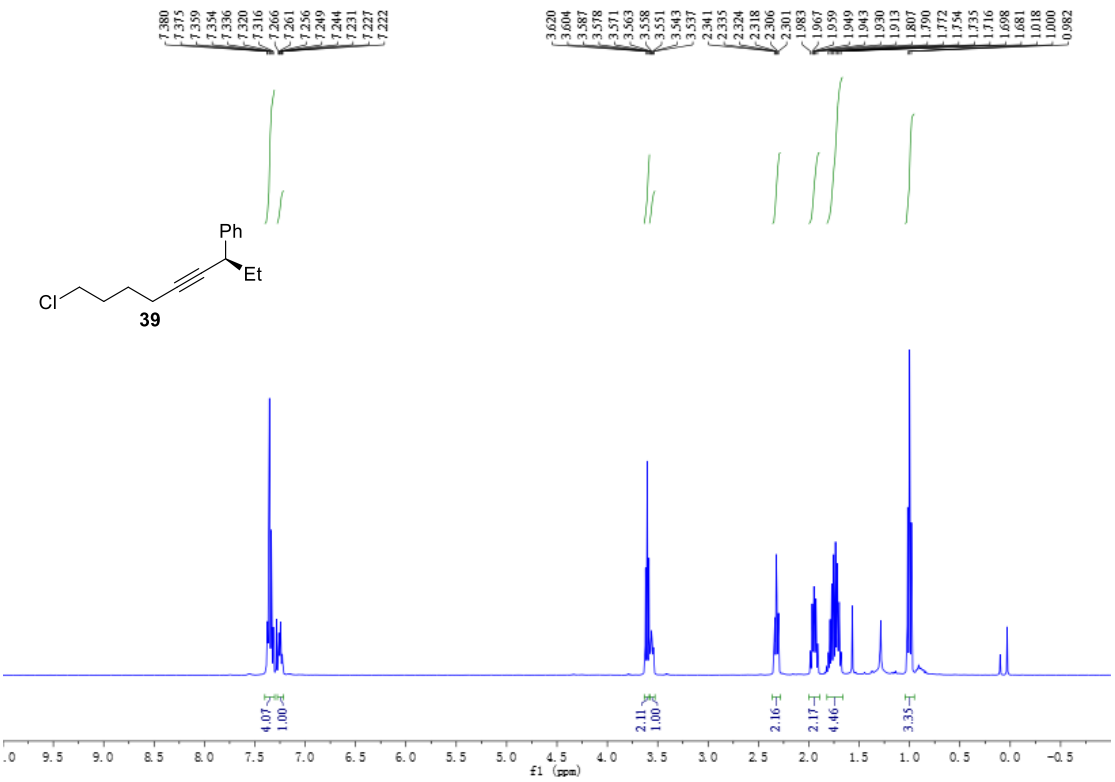
f1 (ppm)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Et
Cl
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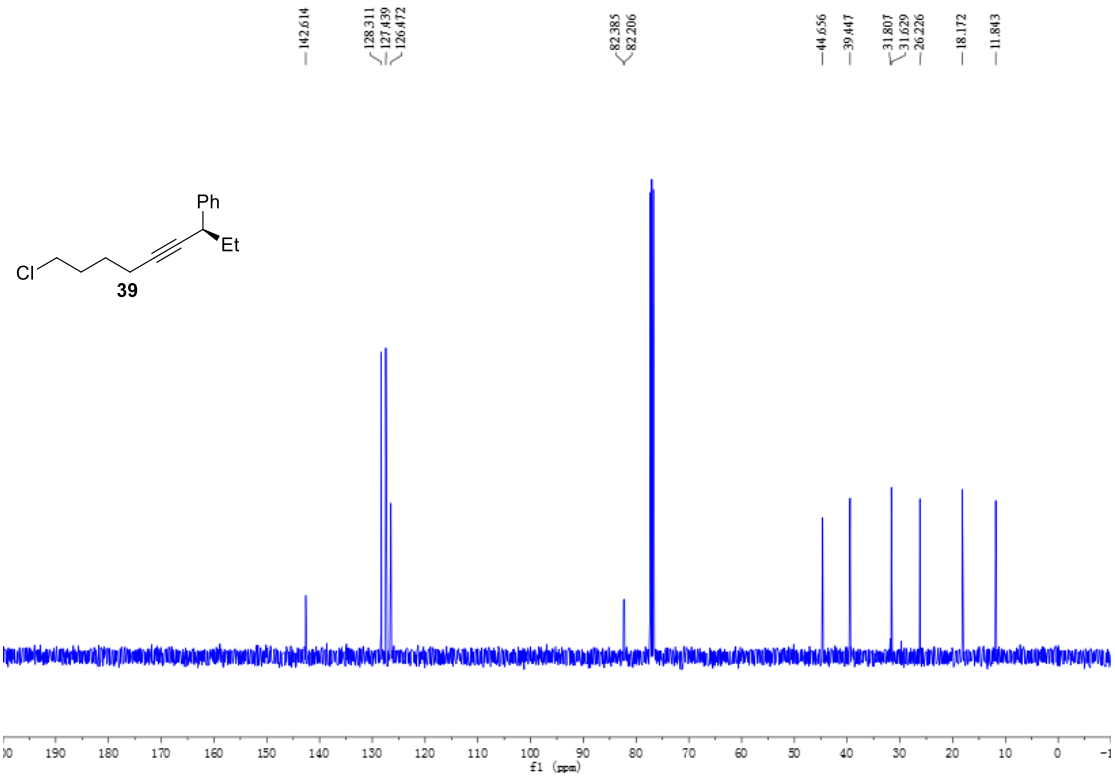
f1 (ppm)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Cl
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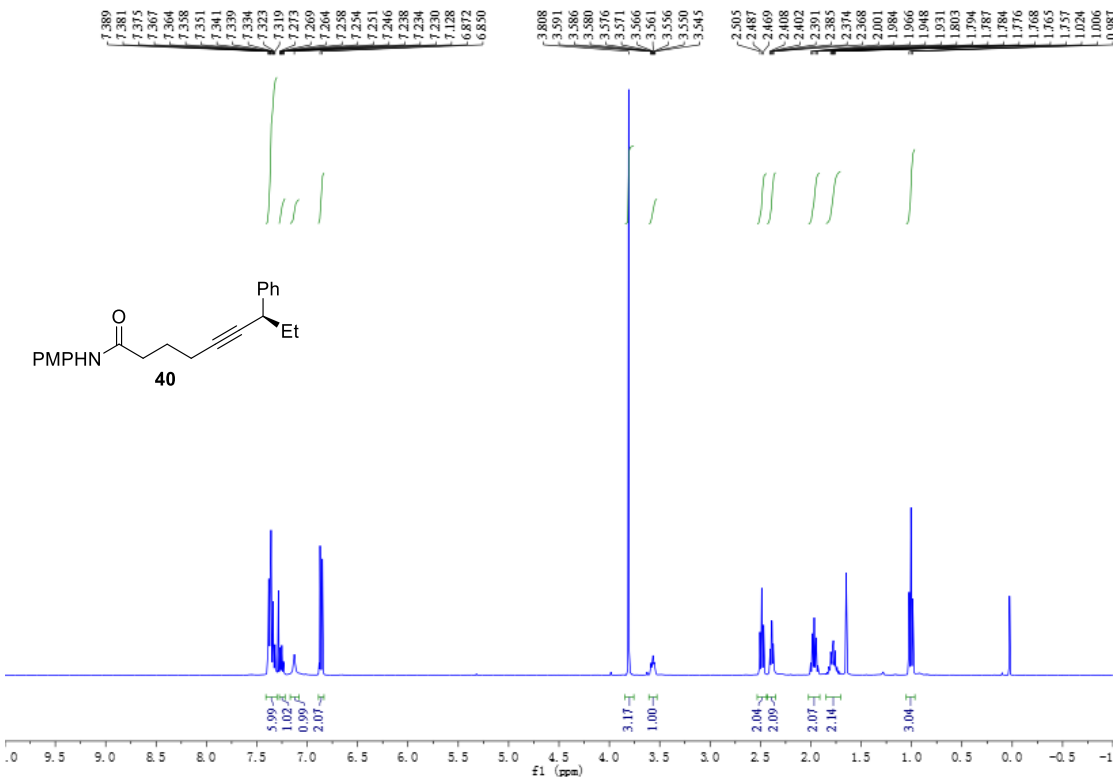
f1 (ppm)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O
PMPHN
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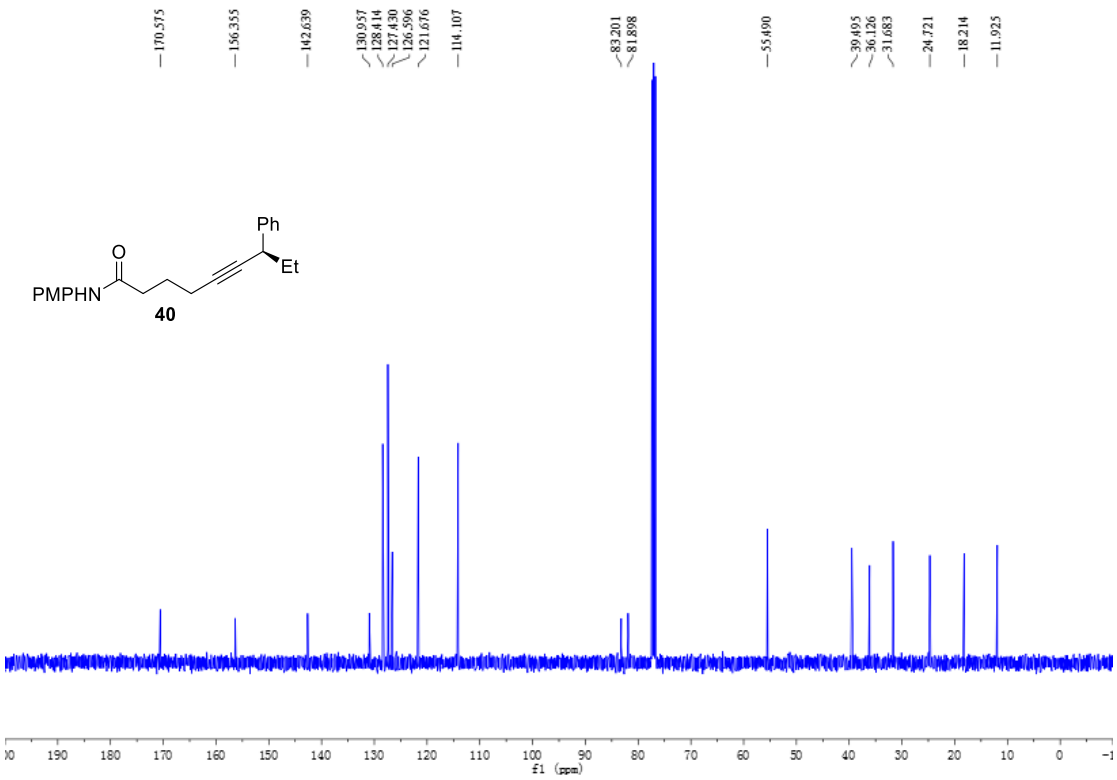
f1 (ppm)


Ph
Et
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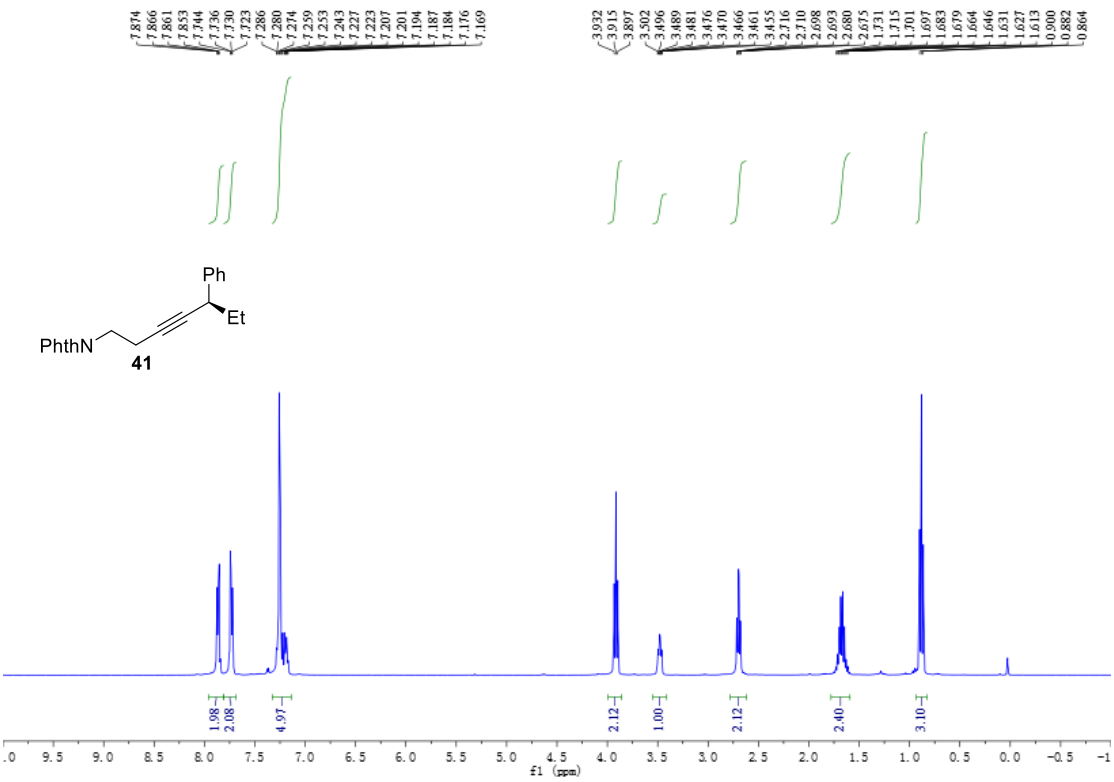
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7.253
7.243
7.227
7.223
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7.201
7.194
7.187
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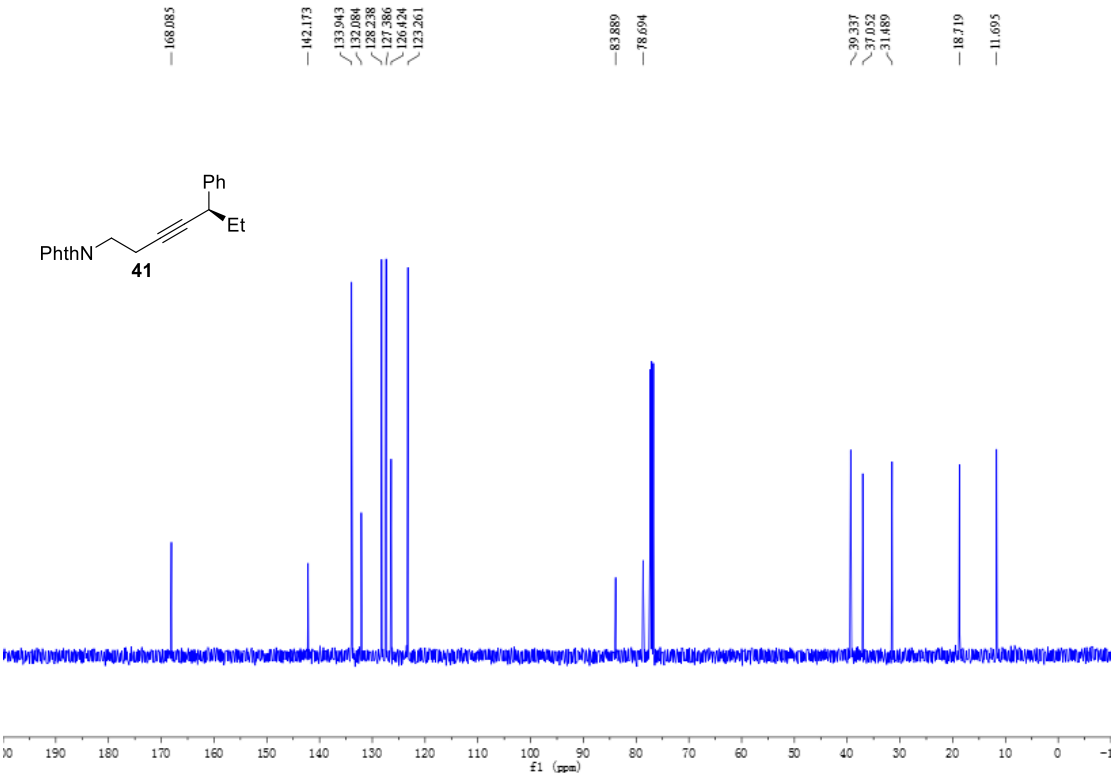
7.176
7.169
3.932
3.915
3.897
3.502
3.496
3.489
3.481
3.476
3.470
3.466
3.461
3.455
2.716
2.710
2.698
2.693
2.680
2.675
1.731
1.715
1.701
1.697
1.683
1.679
1.664
1.646
1.631
1.627
1.613
0.900
0.882
0.864
Ph
Et
PhthN
41
1.98
2.08
4.97
2.12
1.00
2.12
2.40
3.10
f1 (ppm)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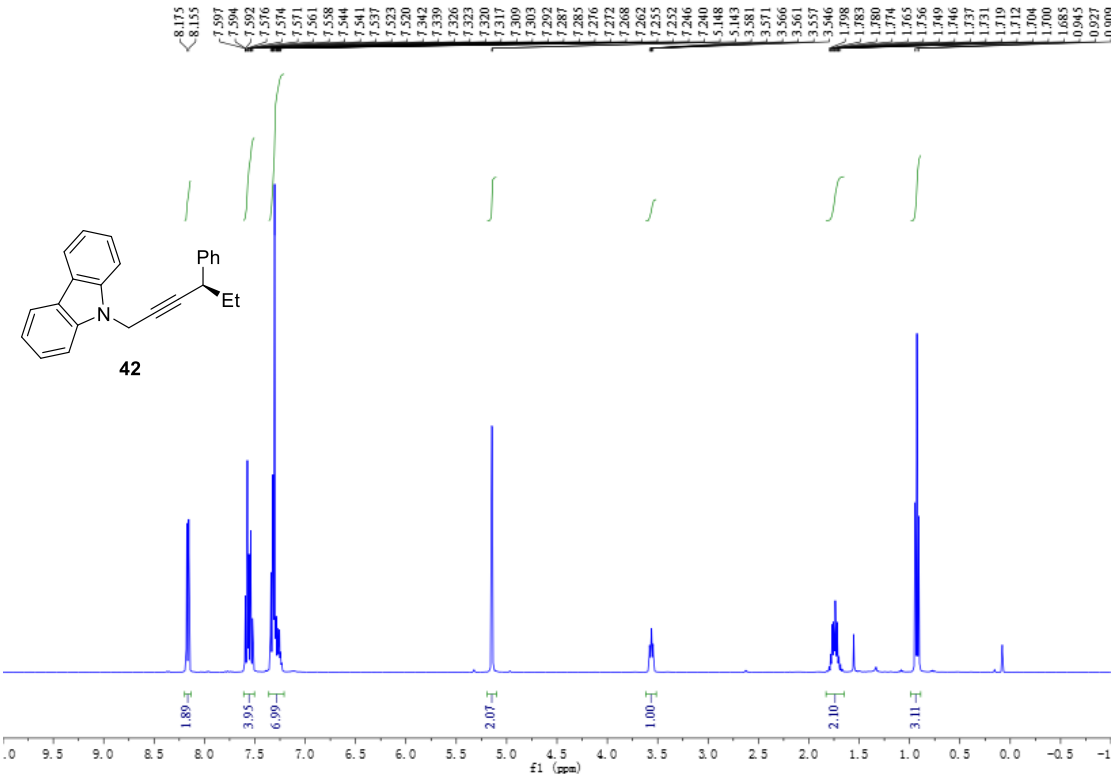
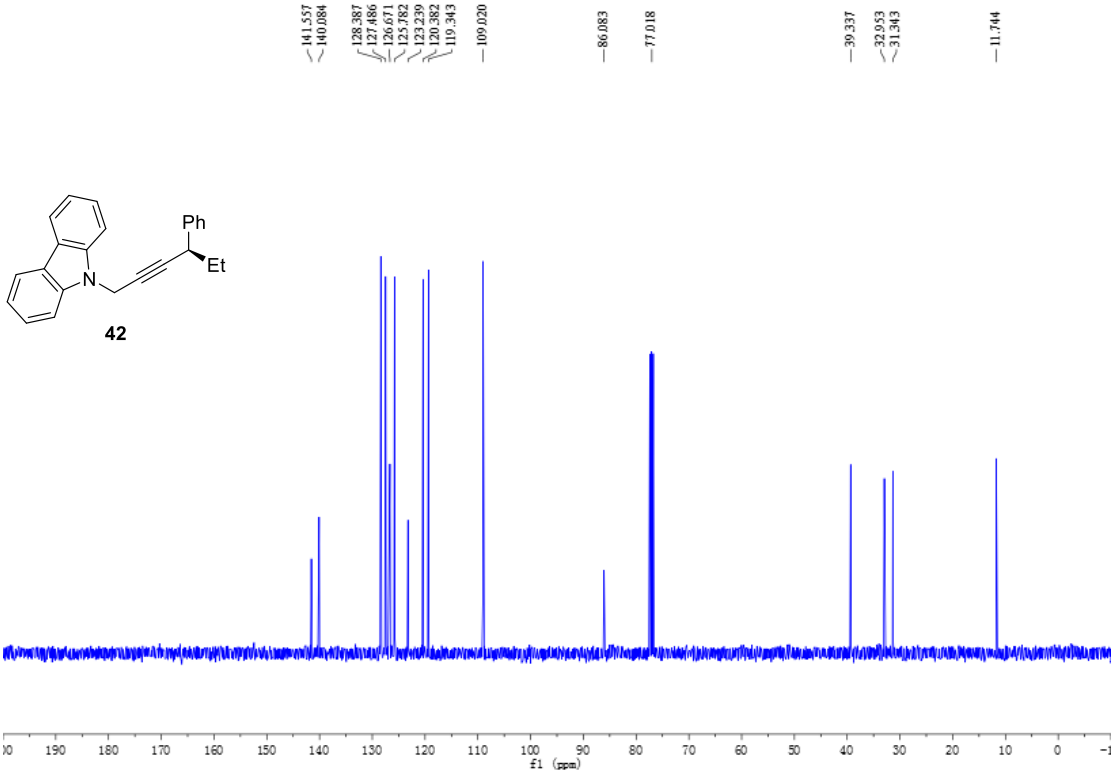
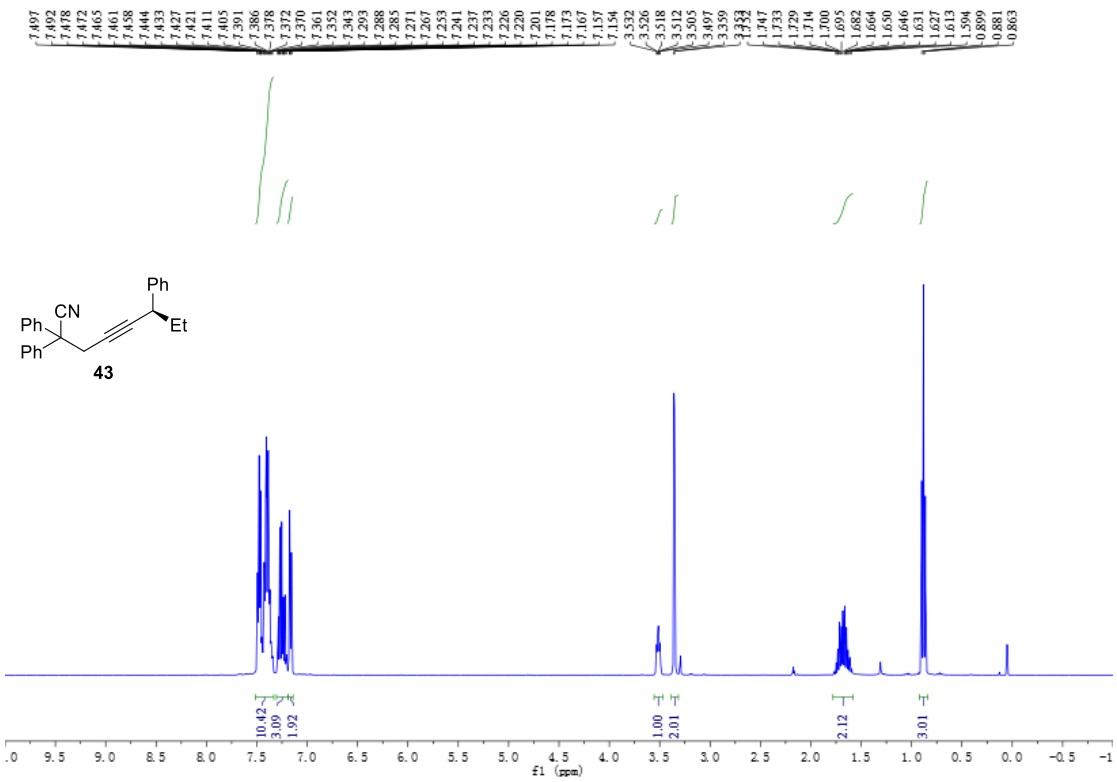
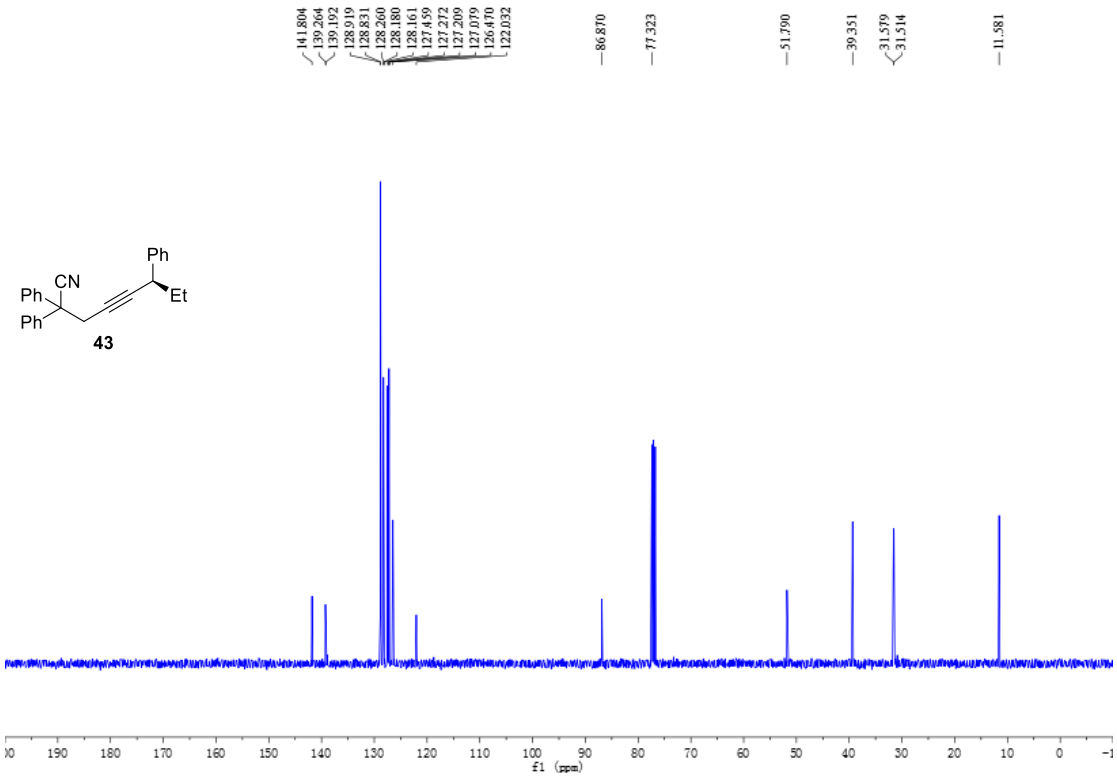
142.173
133.943
132.084
128.238
127.386
126.424
123.261
83.889
78.694
39.337
37.052
31.489
18.719
11.695
Ph
Et
PhthN
41
f1 (ppm)


Ph
Et
N
42
f1 (ppm)


Ph
Et
N
42
f1 (ppm)


Ph
CN
Ph
Ph
Et
43
10.42
3.09
1.92
1.00
2.01
2.12
3.01
f1 (ppm)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139.264
139.192
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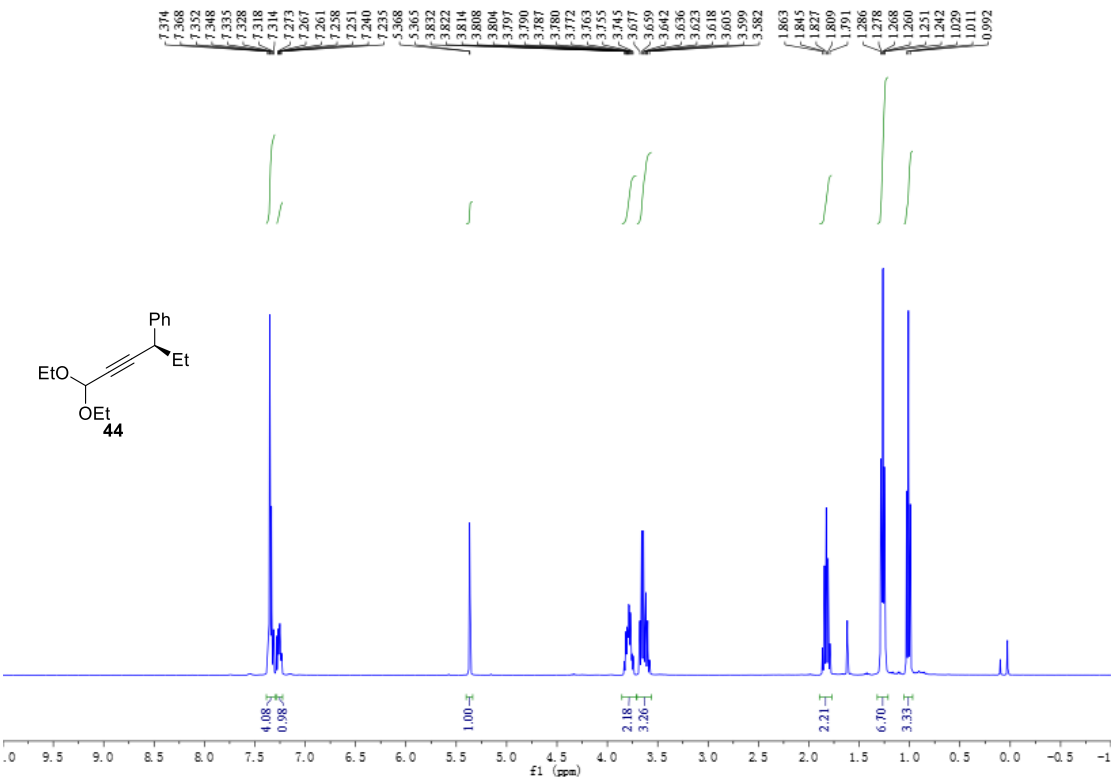
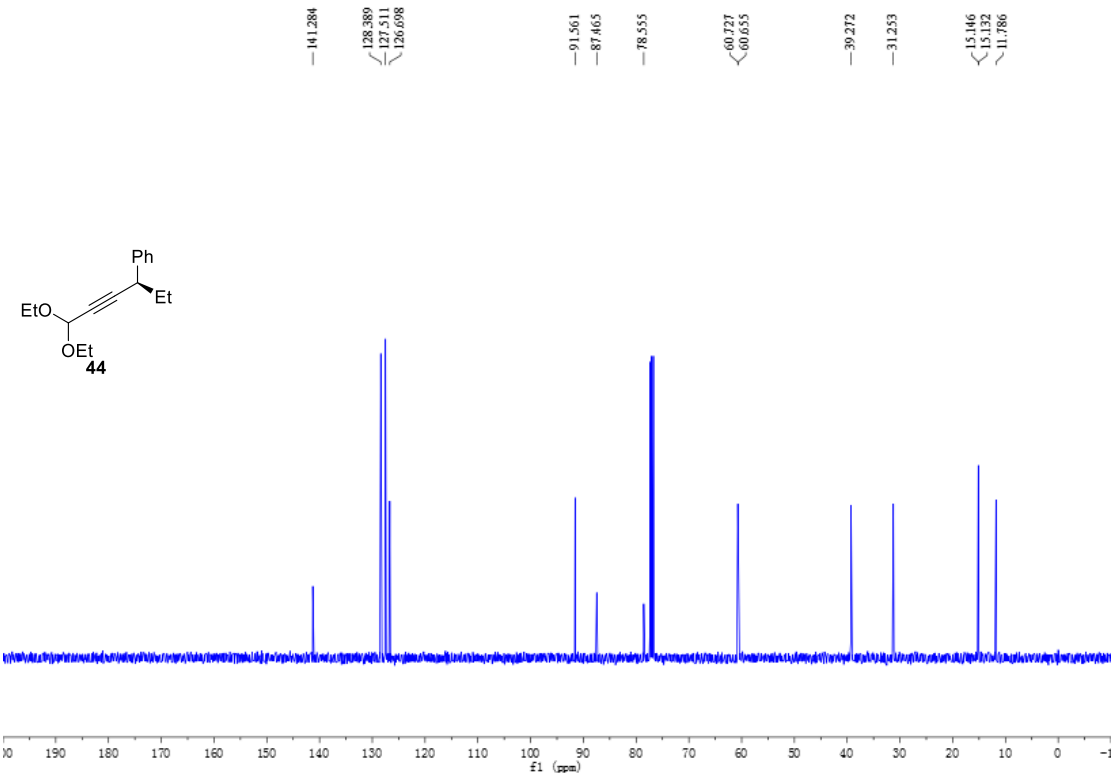
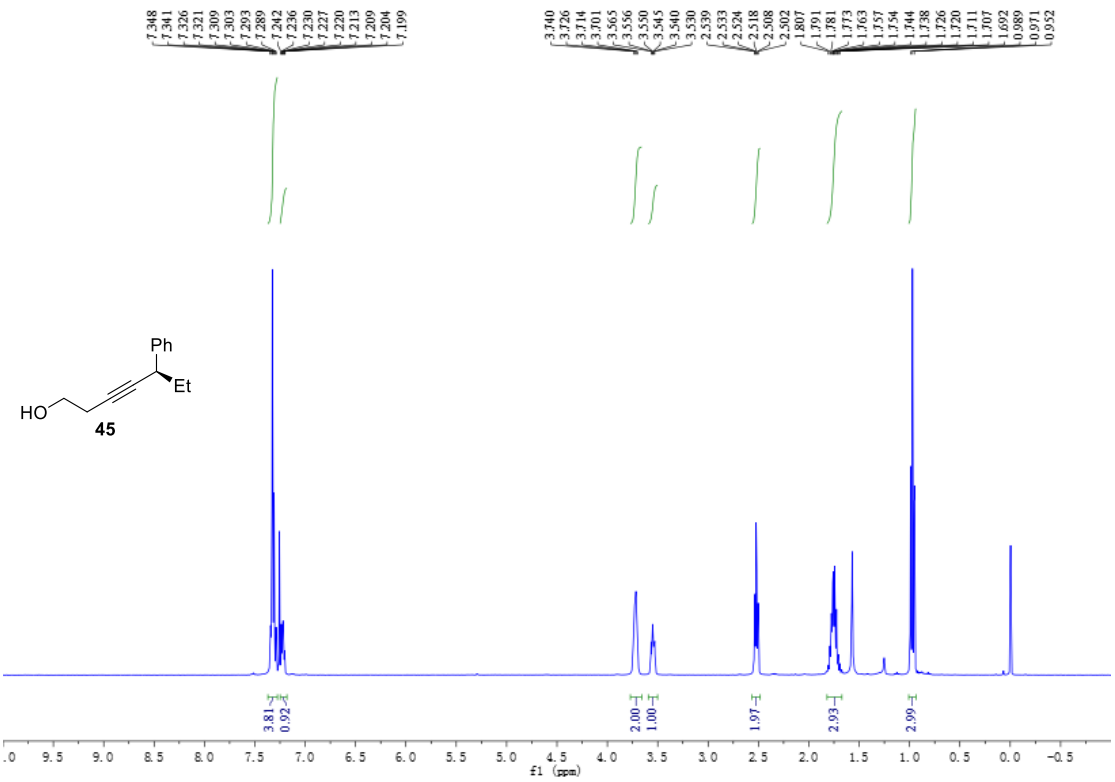
128.260
128.180
128.161
127.459
127.272
127.209
127.079
126.470
122.032
86.870
77.323
51.790
39.351
31.579
31.514
11.581
Ph
CN
Ph
Ph
Et
43
f1 (ppm)


Ph
Et
EtO
OEt
44
f1 (ppm)


Ph
Et
EtO
OEt
44
f1 (ppm)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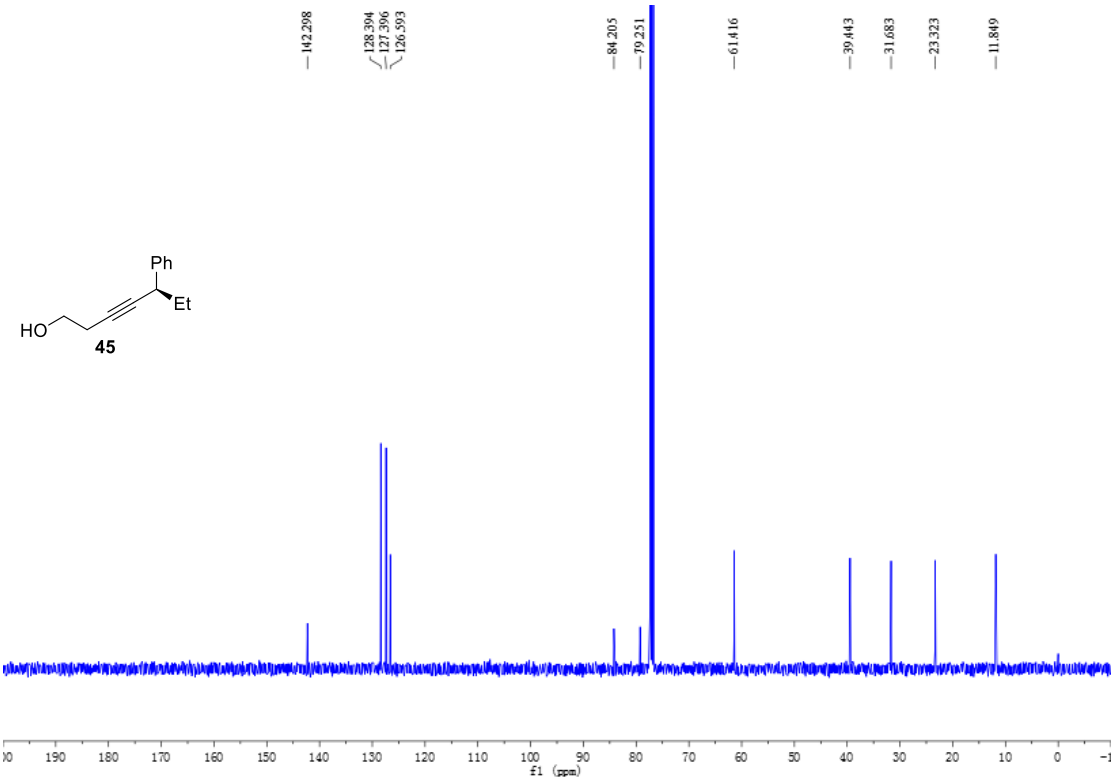
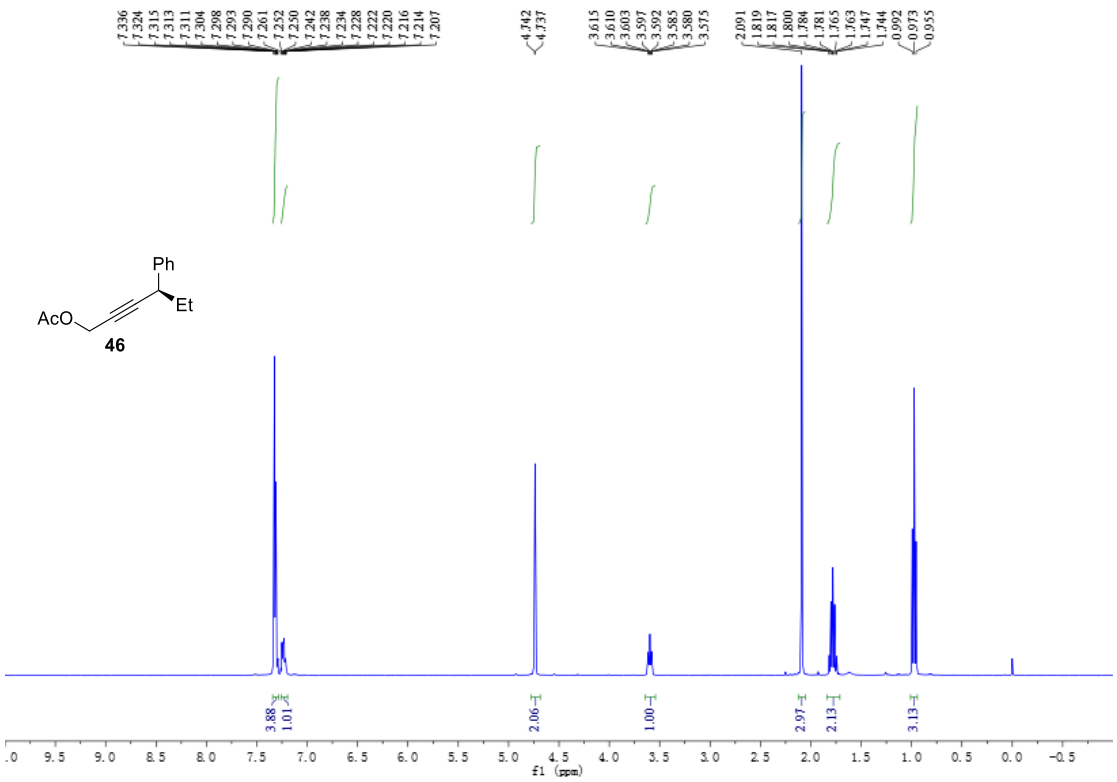
7.341
7.326
7.321
7.309
7.303
7.293
7.289
7.242
7.236
7.230
7.227
7.220
7.213
7.209
7.204
7.199
3.740
3.726
3.714
3.701
3.565
3.556
3.550
3.545
3.540
3.530
2.539
2.533
2.524
2.518
2.508
2.502
1.807
1.791
1.781
1.773
1.763
1.757
1.754
1.744
1.738
1.726
1.720
1.711
1.707
1.692
0.989
0.971
0.952
Ph
Et
HO
45
3.81
0.92
2.00
1.00
1.97
2.93
2.99
f1 (ppm)


142.298
128.394
127.396
126.593
84.205
79.251
61.416
39.443
31.683
23.323
11.849
Ph
Et
HO
45
f1 (ppm)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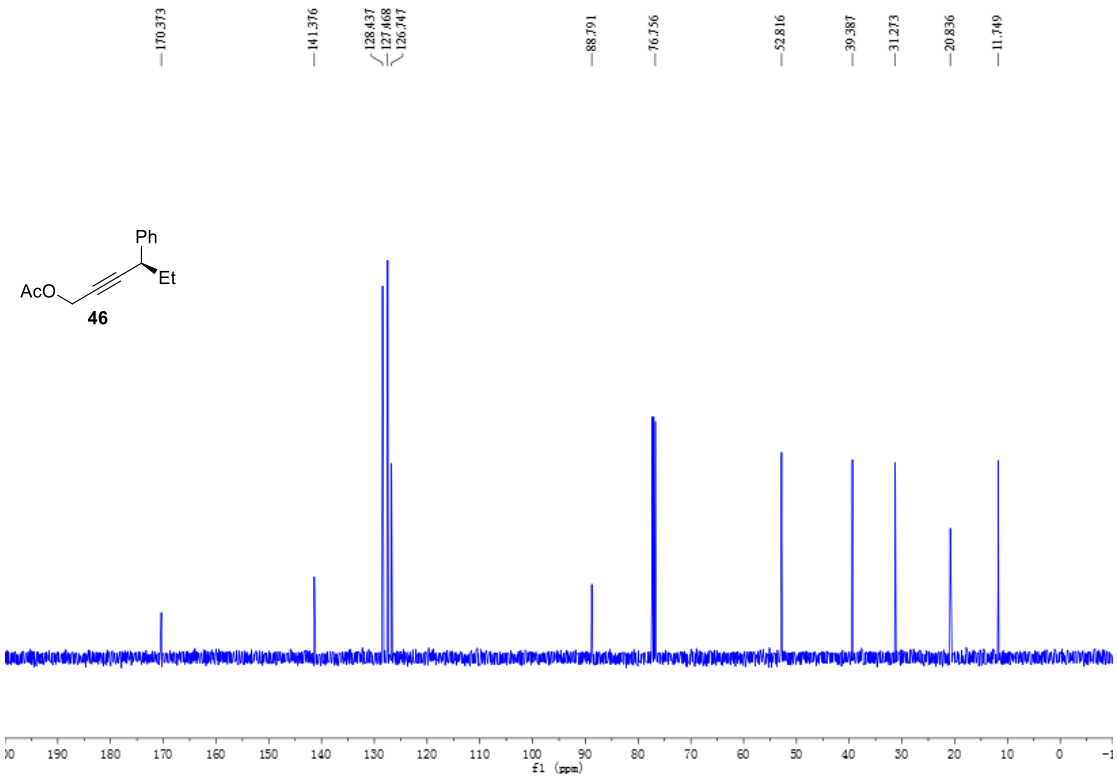
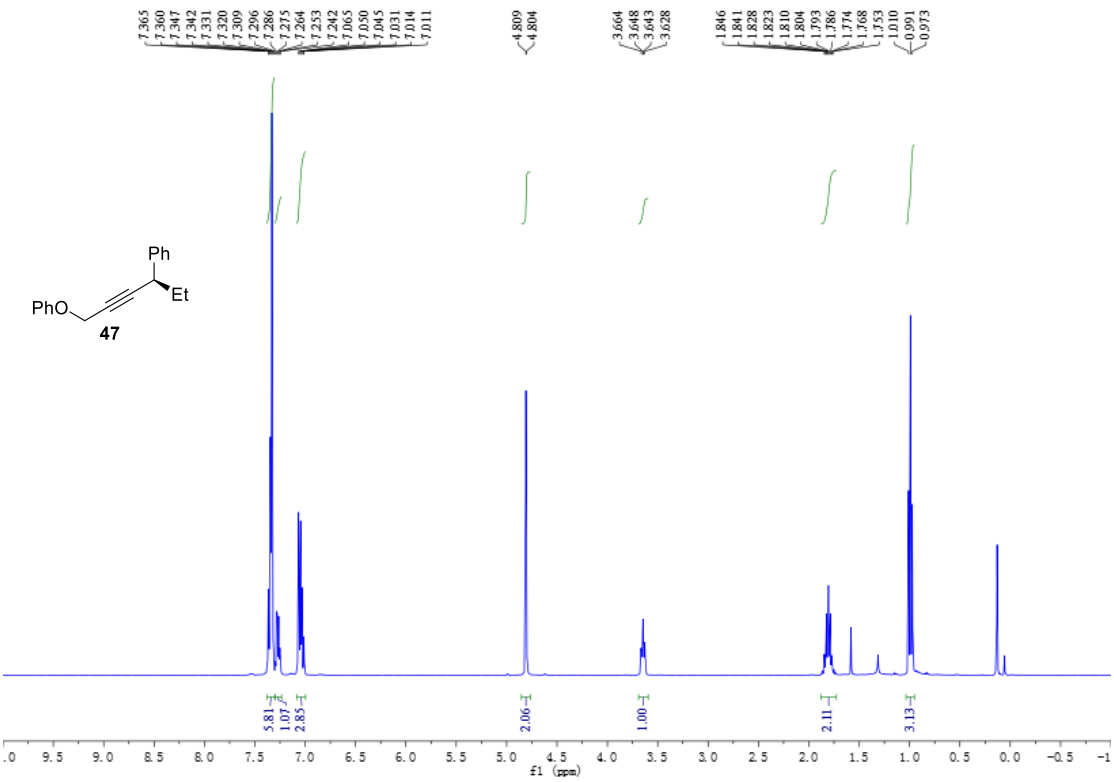
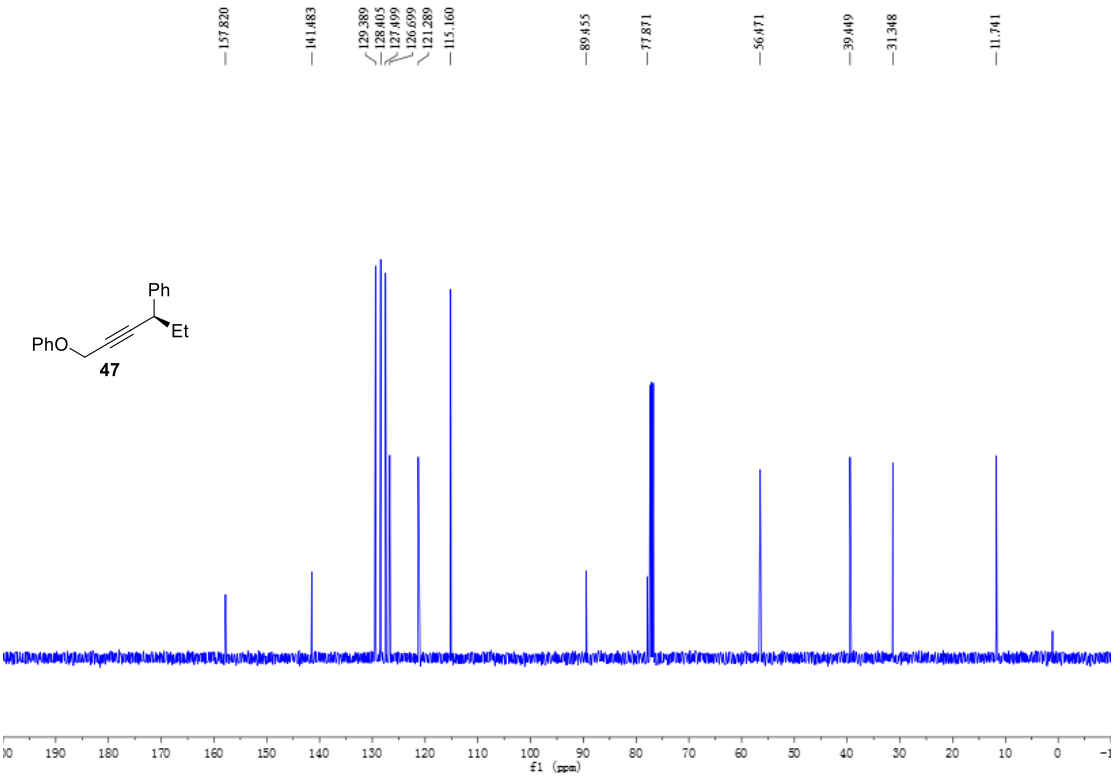
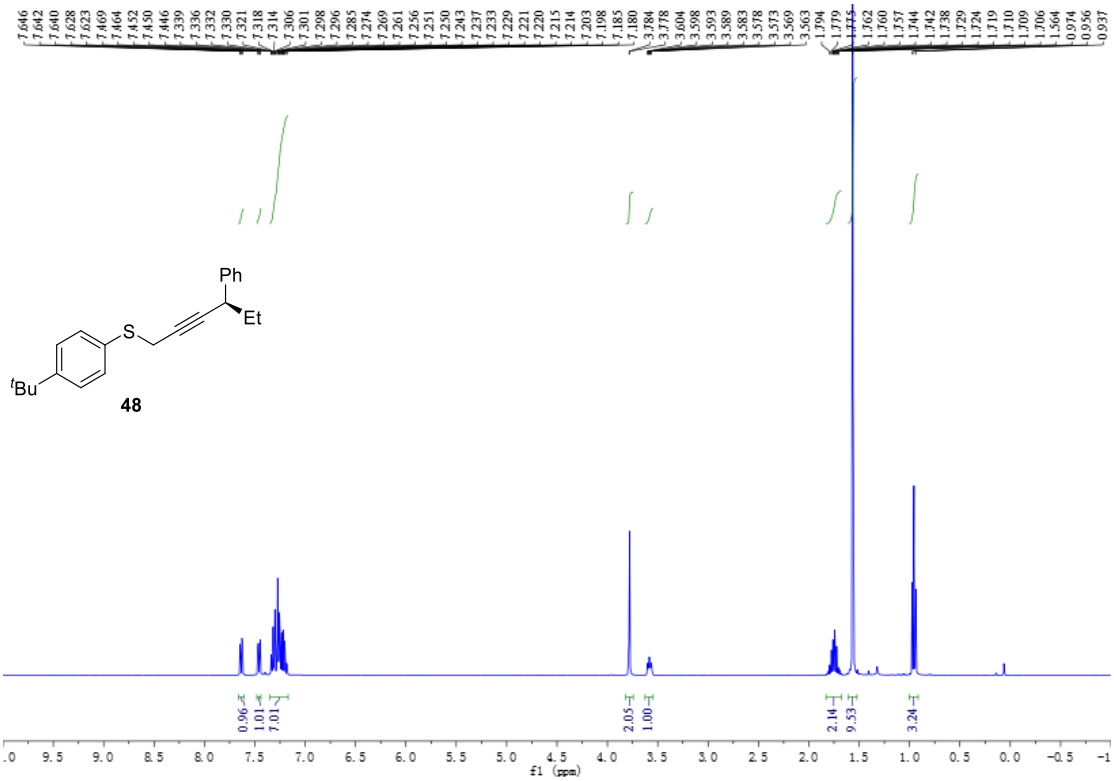
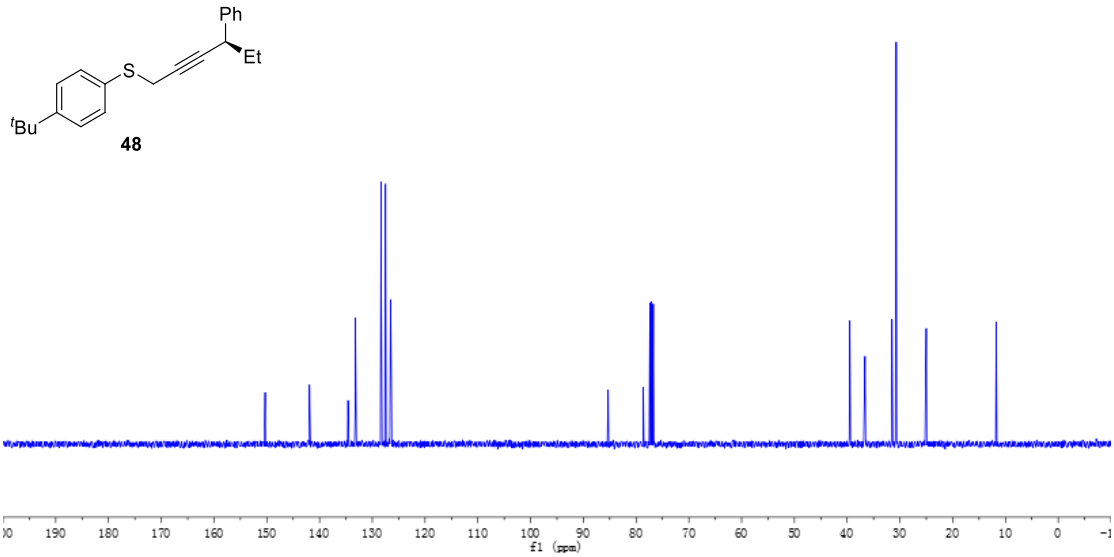
7.324
7.315
7.313
7.311
7.304
7.298
7.293
7.290
7.261
7.252
7.250
7.242
7.238
7.234
7.228
7.222
7.220
7.216
7.214
7.207
4.742
4.737
3.615
3.610
3.603
3.597
3.592
3.585
3.580
3.575
2.091
1.819
1.817
1.800
1.784
1.781
1.765
1.763
1.747
1.744
0.992
0.973
0.955
Ph
Et
AcO
46
3.88
1.01
2.06
1.00
2.97
2.13
3.13
f1 (ppm)

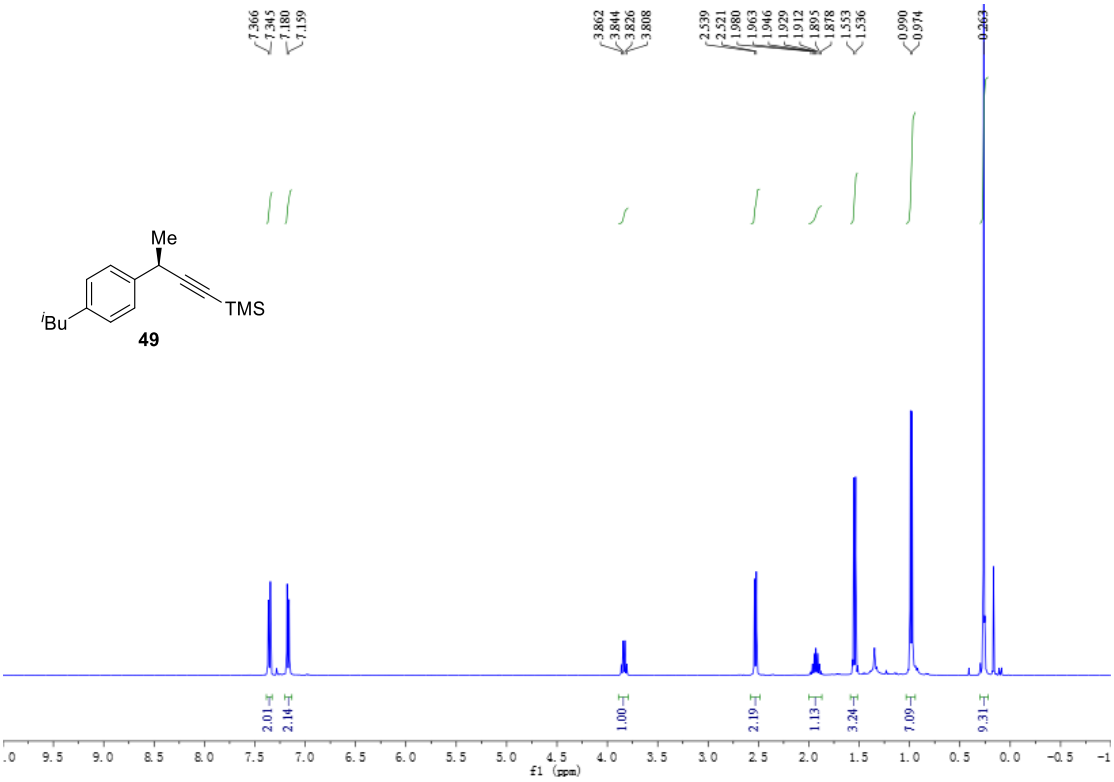

170.373
141.376
128.437
127.468
126.747
88.791
76.756
52.816
39.387
31.273
20.836
11.749
Ph
Et
AcO
46
f1 (ppm)


7.365
7.360
7.347
7.342
7.331
7.320
7.309
7.296
7.286
7.275
7.264
7.253
7.242
7.065
7.050
7.045
7.031
7.014
7.011
4.809
4.804
3.664
3.648
3.643
3.628
1.846
1.841
1.828
1.823
1.810
1.804
1.793
1.786
1.774
1.768
1.753
1.010
0.991
0.973
Ph
Et
PhO
47
5.81
1.07
2.85
2.06
1.00
2.11
3.13
f1 (ppm)


157.820
141.483
129.389
128.405
127.499
126.699
121.289
115.160
89.455
77.871
56.471
39.449
31.348
11.741
Ph
Et
PhO
47
f1 (ppm)


Ph
Et
S
tBu
48
f1 (ppm)


Ph
Et
S
tBu
48
f1 (ppm)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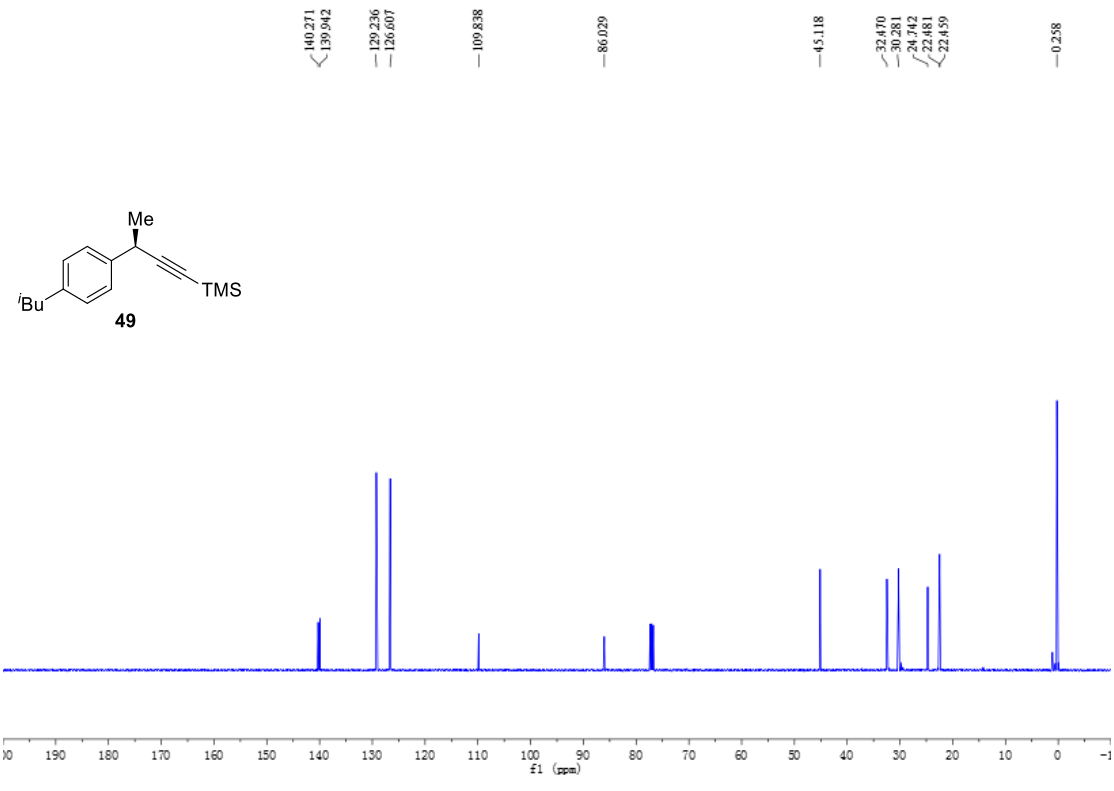
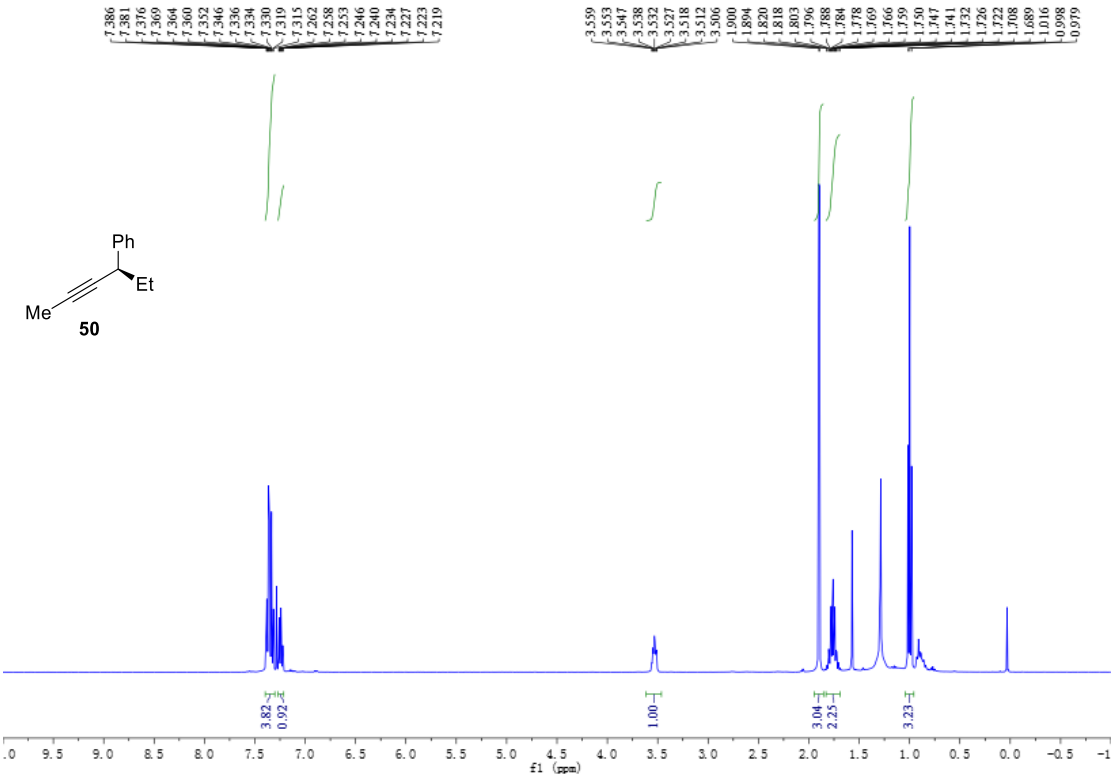
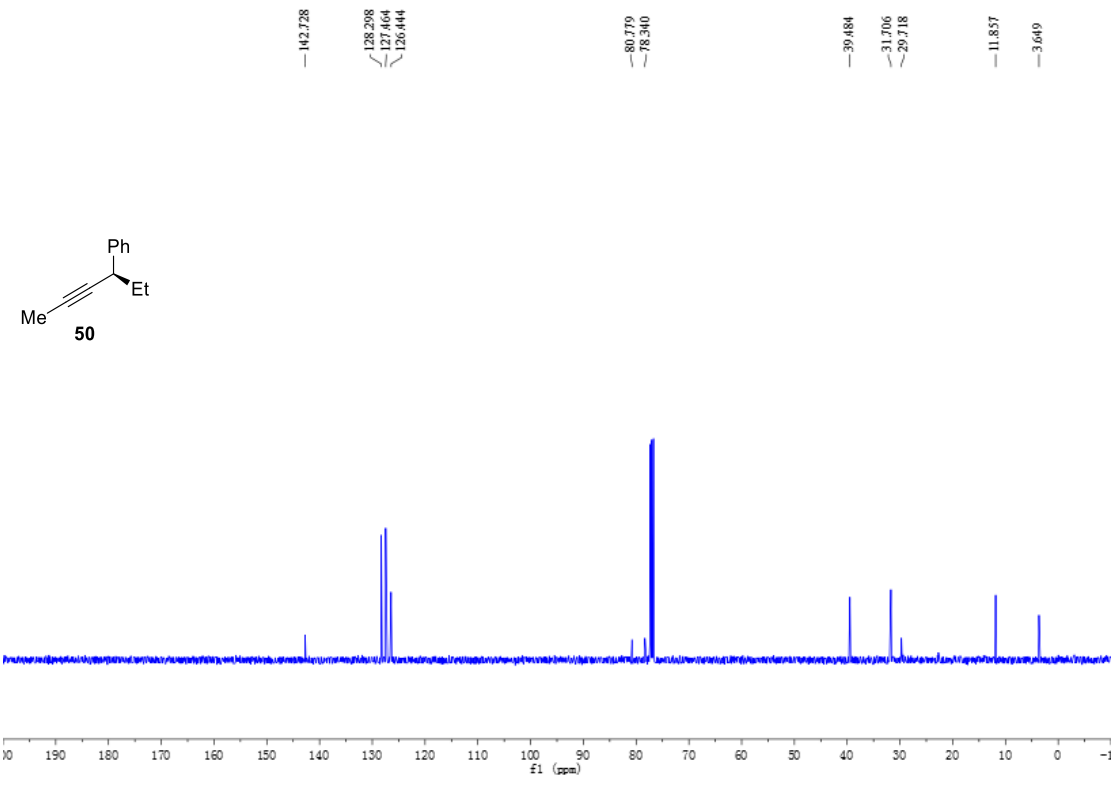
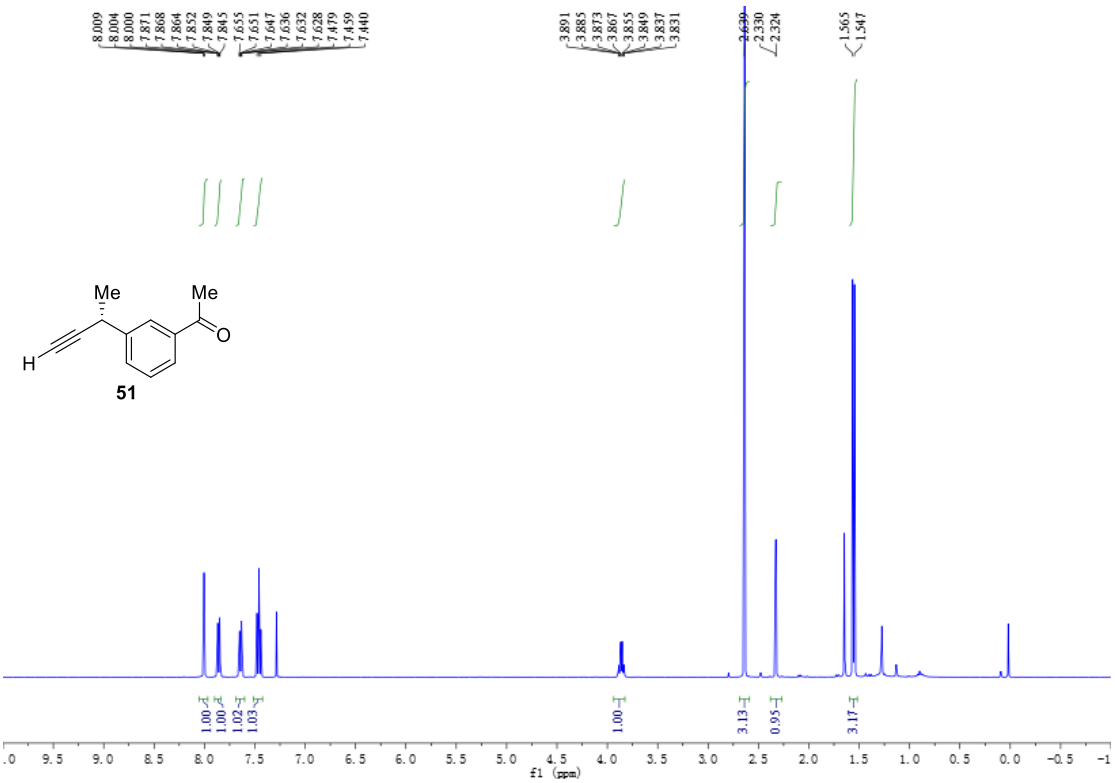
7.180
7.159
3.862
3.844
3.826
3.808
2.539
2.521
1.980
1.963
1.946
1.929
1.912
1.895
1.878
1.553
1.536
0.990
0.974
0.263
Me
TMS
iBu
49
2.01
2.14
1.00
2.19
1.13
3.24
7.09
9.31
f1 (ppm)


140.271
139.942
129.236
126.607
109.838
86.029
45.118
32.470
30.281
24.742
22.481
22.459
0.258
Me
TMS
iBu
49
f1 (ppm)


Ph
Et
Me
50
f1 (ppm)


Ph
Et
Me
50
f1 (ppm)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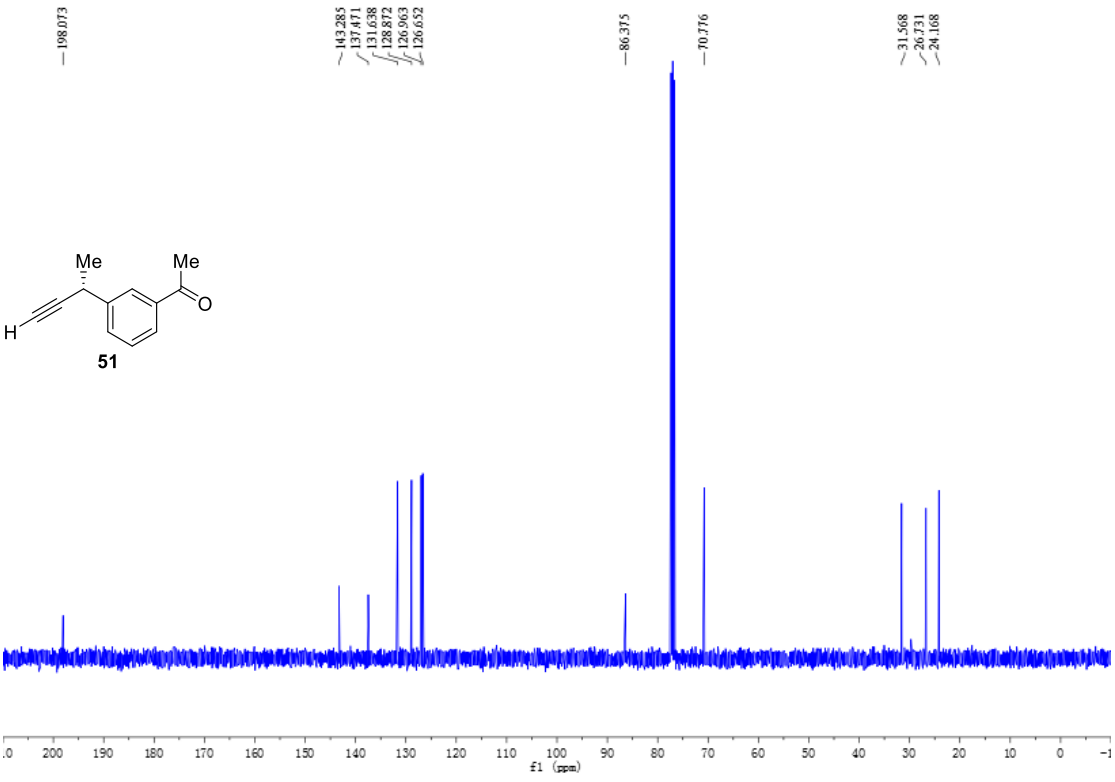
8.004
8.000
7.871
7.868
7.864
7.852
7.849
7.845
7.655
7.651
7.647
7.636
7.632
7.628
7.479
7.459
7.440
3.891
3.885
3.873
3.867
3.855
3.849
3.837
3.831
2.639
2.330
2.324
1.565
1.547
Me
Me
O
H
51
1.00
1.00
1.02
1.03
1.00
3.13
0.95
3.17
f1 (ppm)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137.471
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128.872
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86.375
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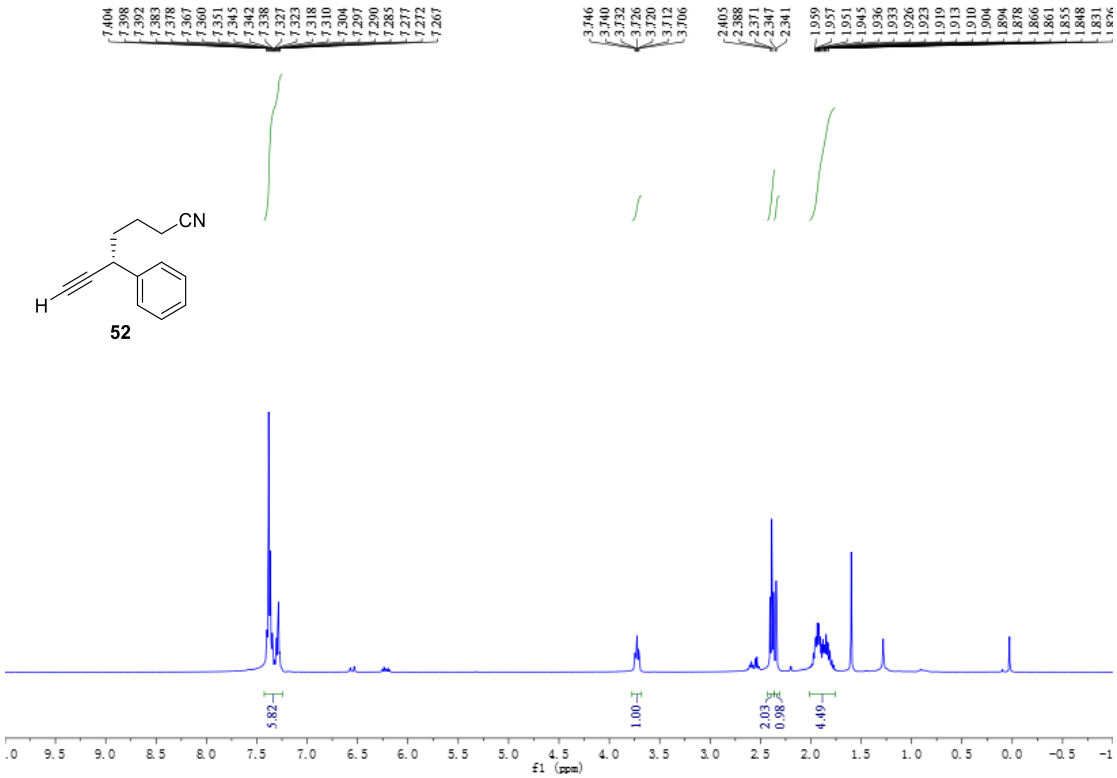
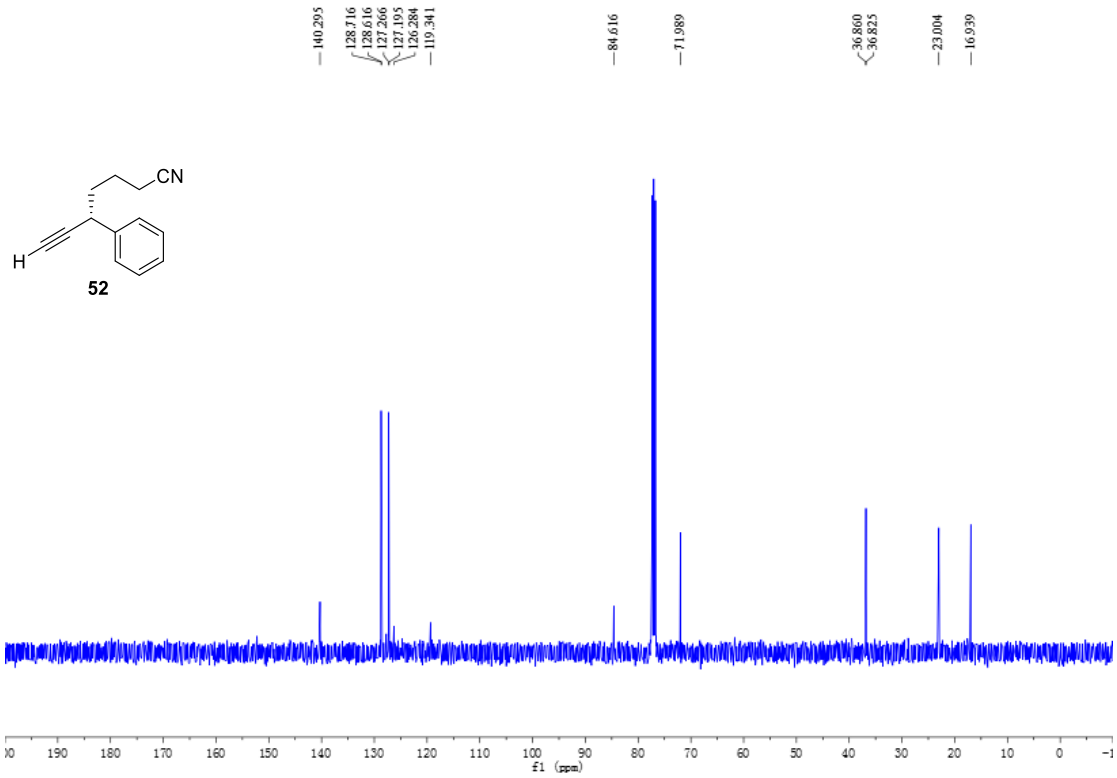
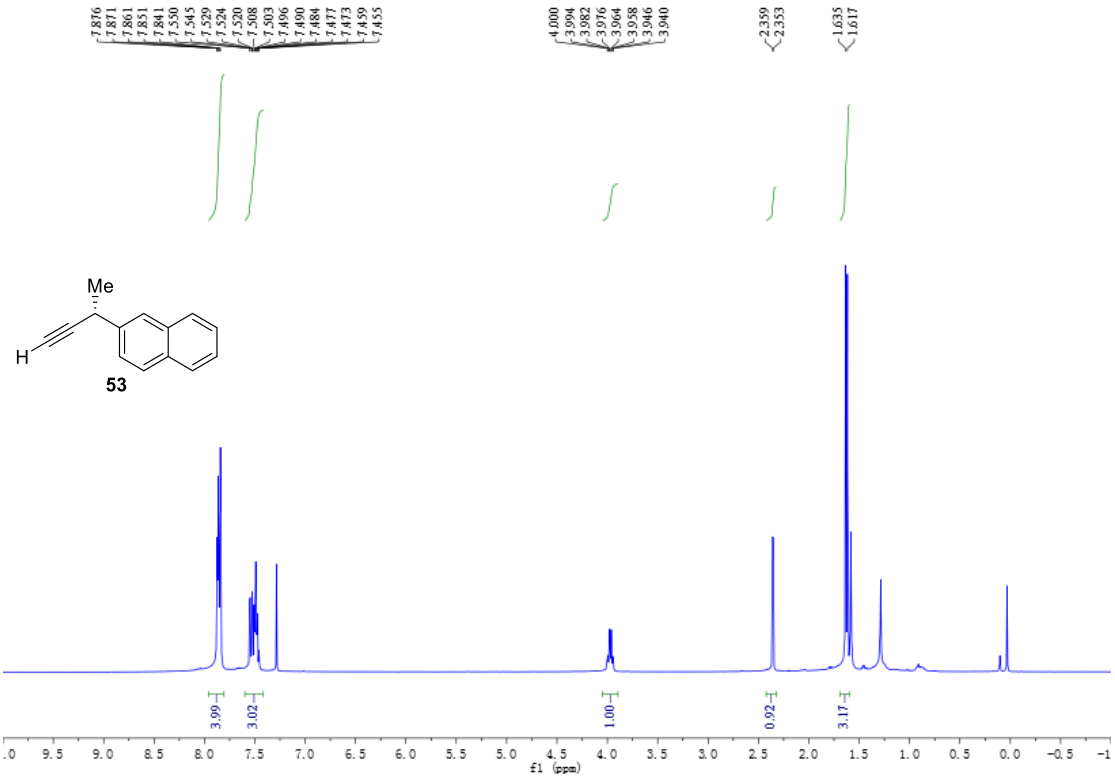
31.568
26.731
24.168
Me
Me
O
H
51
f1 (ppm)


CN
H
52
f1 (ppm)


CN
H
52
f1 (ppm)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7.529
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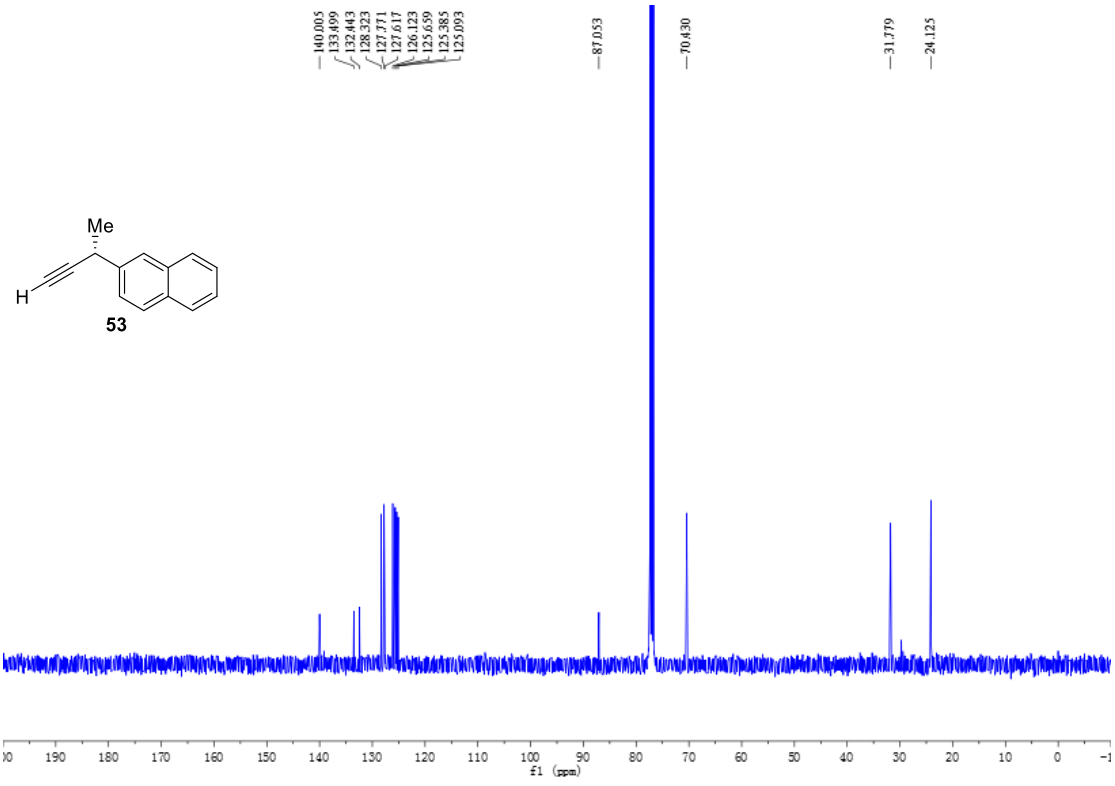
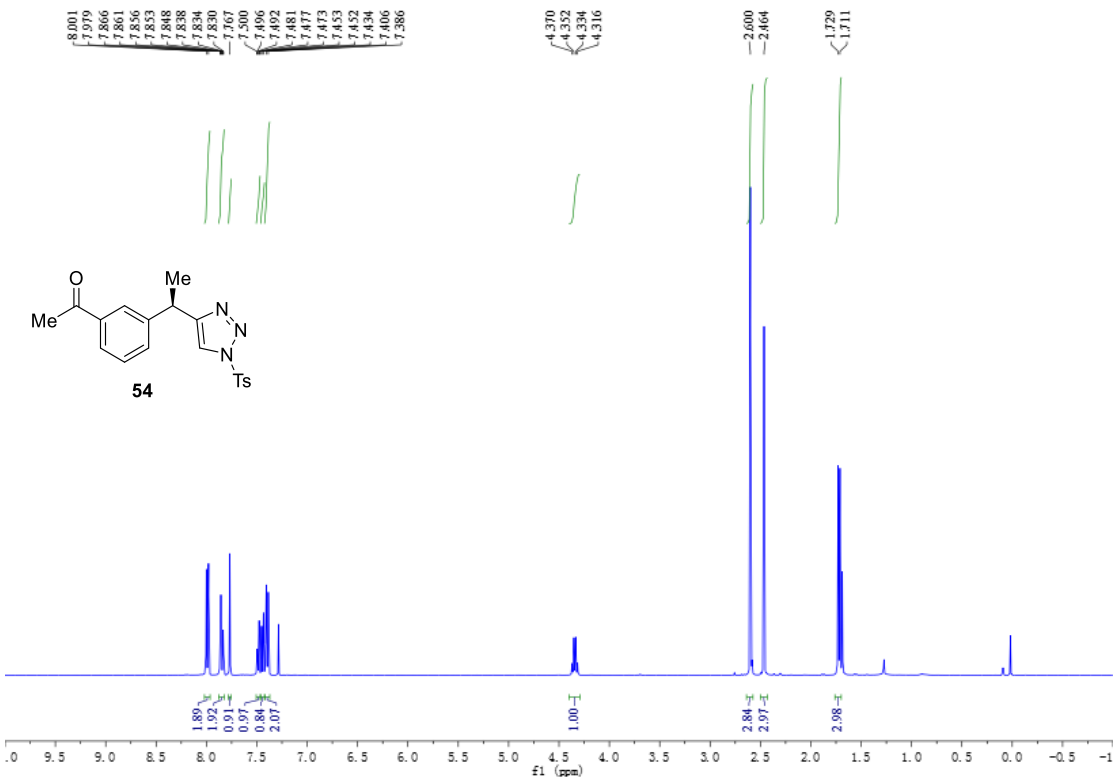
7.520
7.508
7.503
7.496
7.490
7.484
7.477
7.473
7.459
7.455
4.000
3.994
3.982
3.976
3.964
3.958
3.946
3.940
2.359
2.353
1.635
1.617
Me
H
53
3.99
3.02
1.00
0.92
3.17
f1 (ppm)


140.005
133.499
132.443
128.323
127.771
127.617
126.123
125.639
125.385
125.093
87.053
70.430
31.779
24.125
Me
H
53
f1 (ppm)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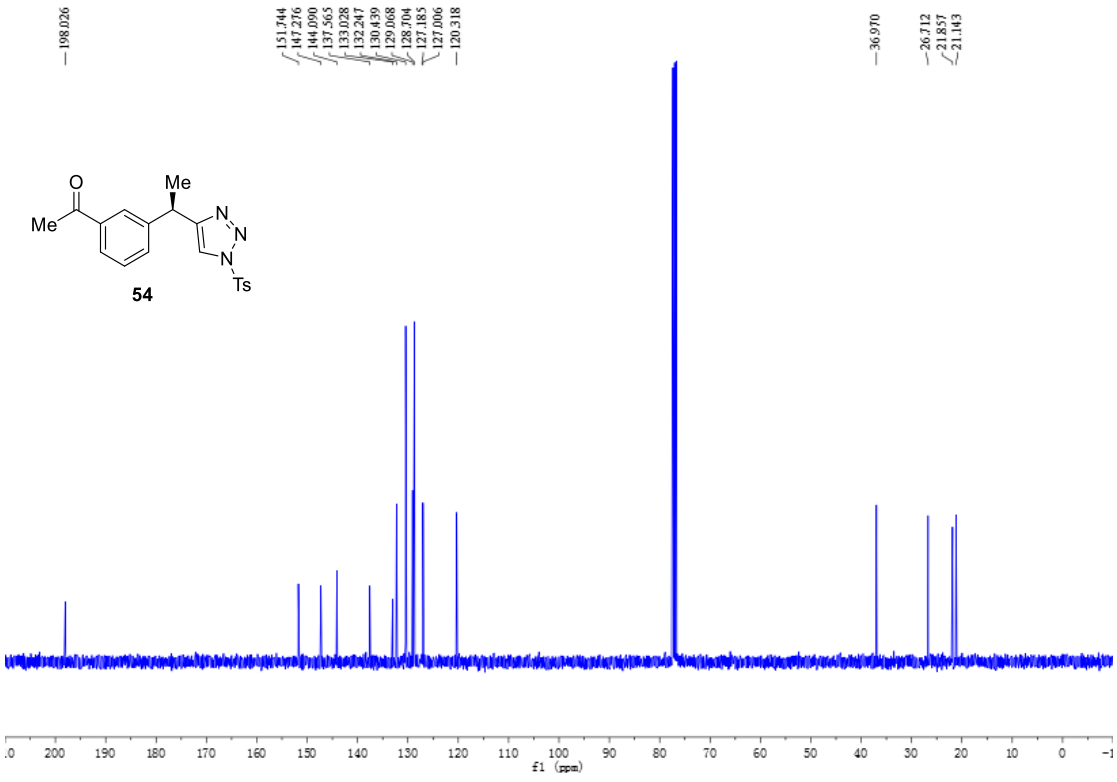
7.856
7.853
7.848
7.838
7.834
7.830
7.767
7.500
7.496
7.492
7.481
7.477
7.473
7.453
7.452
7.434
7.406
7.386
4.370
4.352
4.334
4.316
2.600
2.464
1.729
1.711
O
Me
Me
N
N
N
Ts
54
1.89
1.92
0.91
0.97
0.84
2.07
1.00
2.84
2.97
2.98
f1 (ppm)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132.247
130.439
129.068
128.704
127.185
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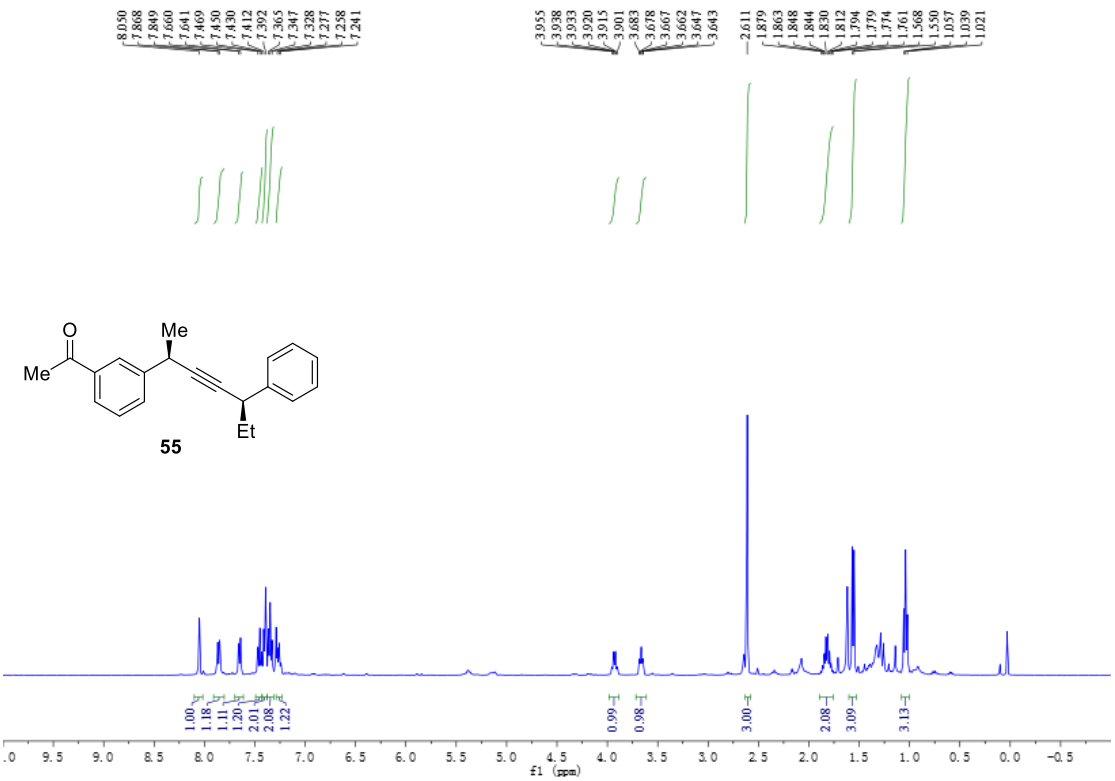
36.970
26.712
21.857
21.143
O
Me
Me
N
N
N
Ts
54
f1 (ppm)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7.660
7.641
7.469
7.450
7.430
7.412
7.392
7.365
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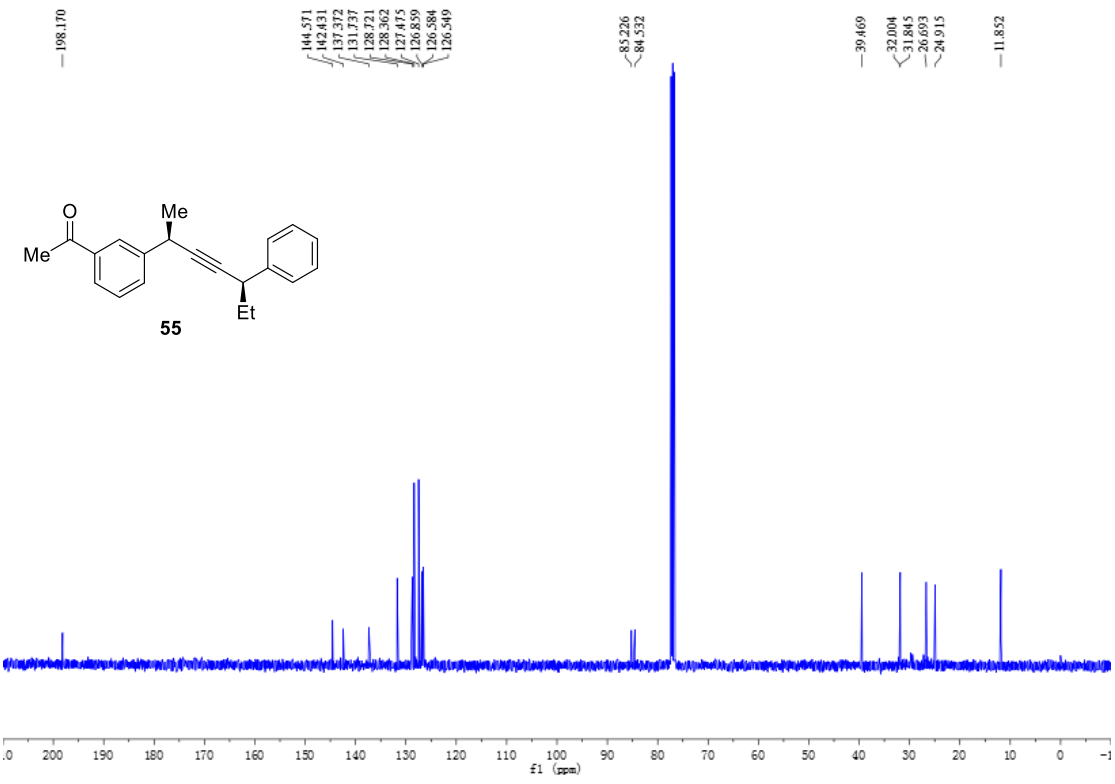
7.328
7.277
7.258
7.241
3.955
3.938
3.933
3.920
3.915
3.901
3.683
3.678
3.667
3.662
3.647
3.643
2.611
1.879
1.863
1.848
1.844
1.830
1.812
1.794
1.779
1.774
1.761
1.568
1.550
1.057
1.039
1.021
O
Me
Me
Et
55
1.00
1.18
1.11
1.20
2.01
2.08
1.22
0.99
0.98
3.00
2.08
3.09
3.13
f1 (ppm)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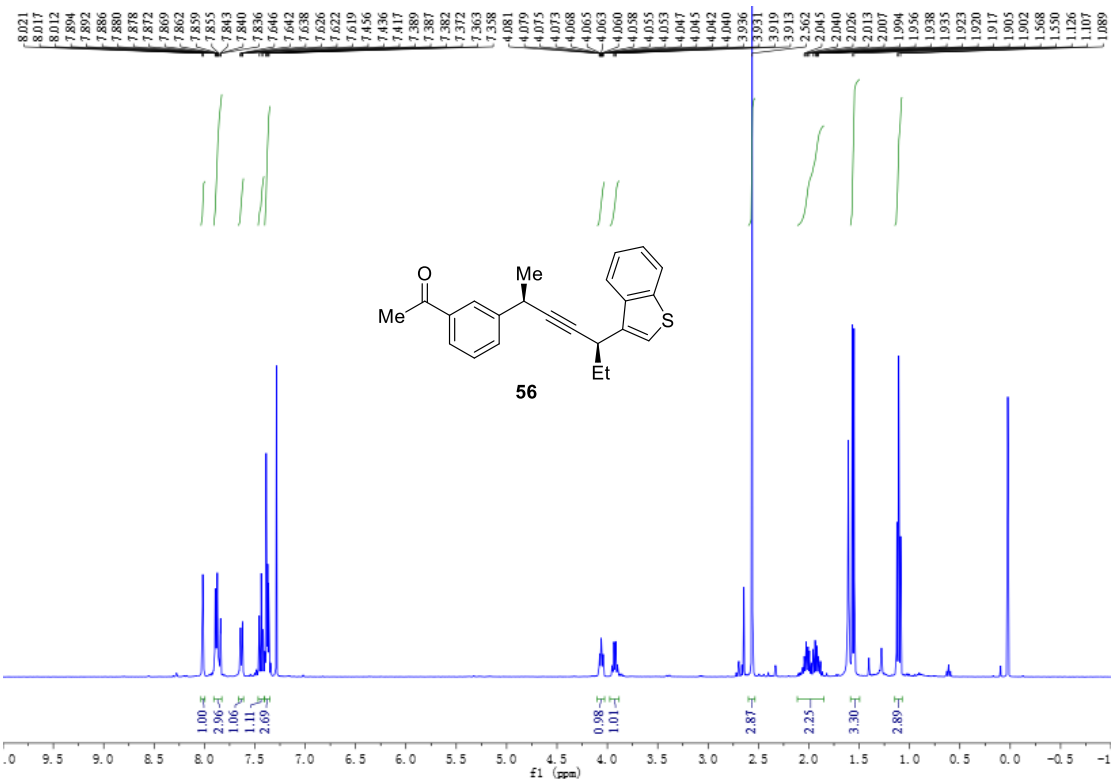
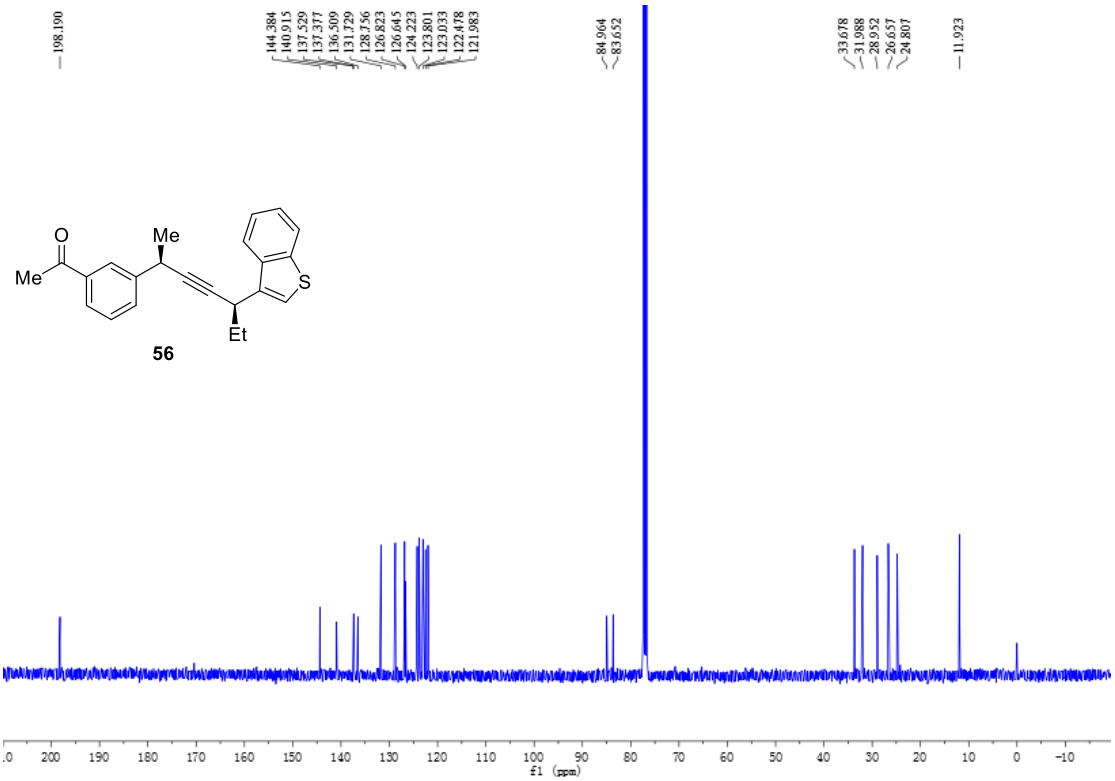
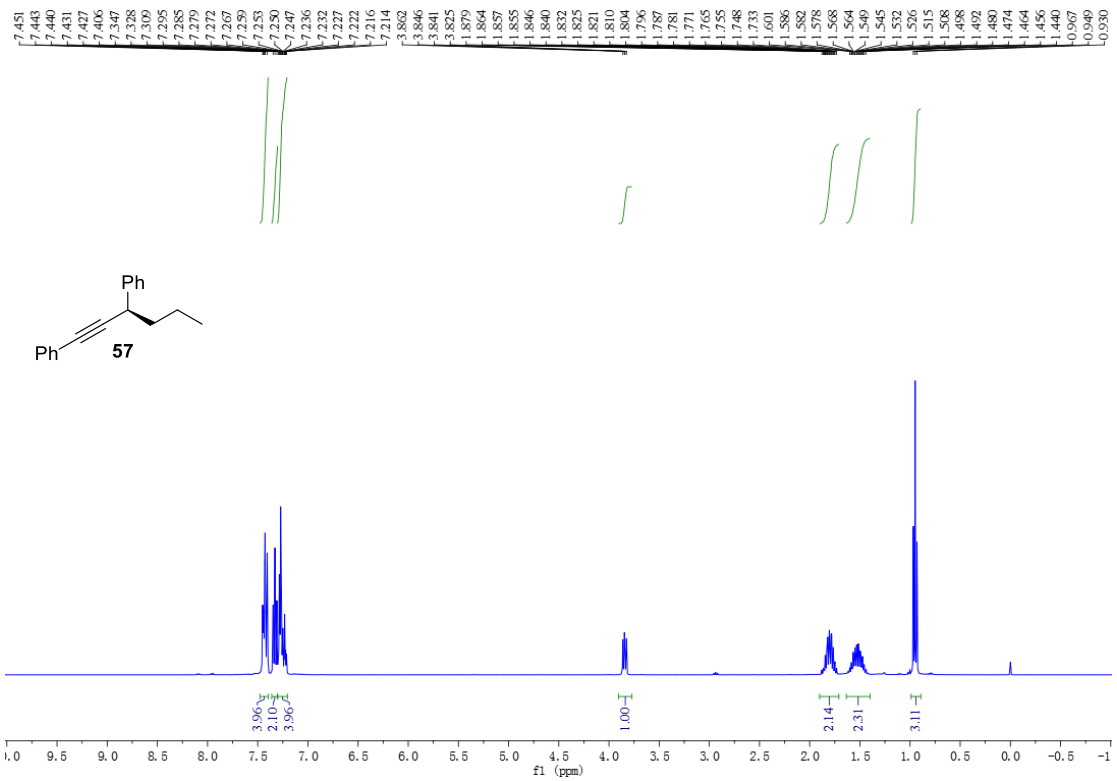
142.431
137.372
131.737
128.721
128.362
127.475
126.859
126.584
126.549
85.226
84.532
39.469
32.004
31.845
26.693
24.915
11.852
O
Me
Me
Et
55
f1 (ppm)


O
Me
Me
S
Et
56
f1 (ppm)


O
Me
Me
S
Et
56
f1 (ppm)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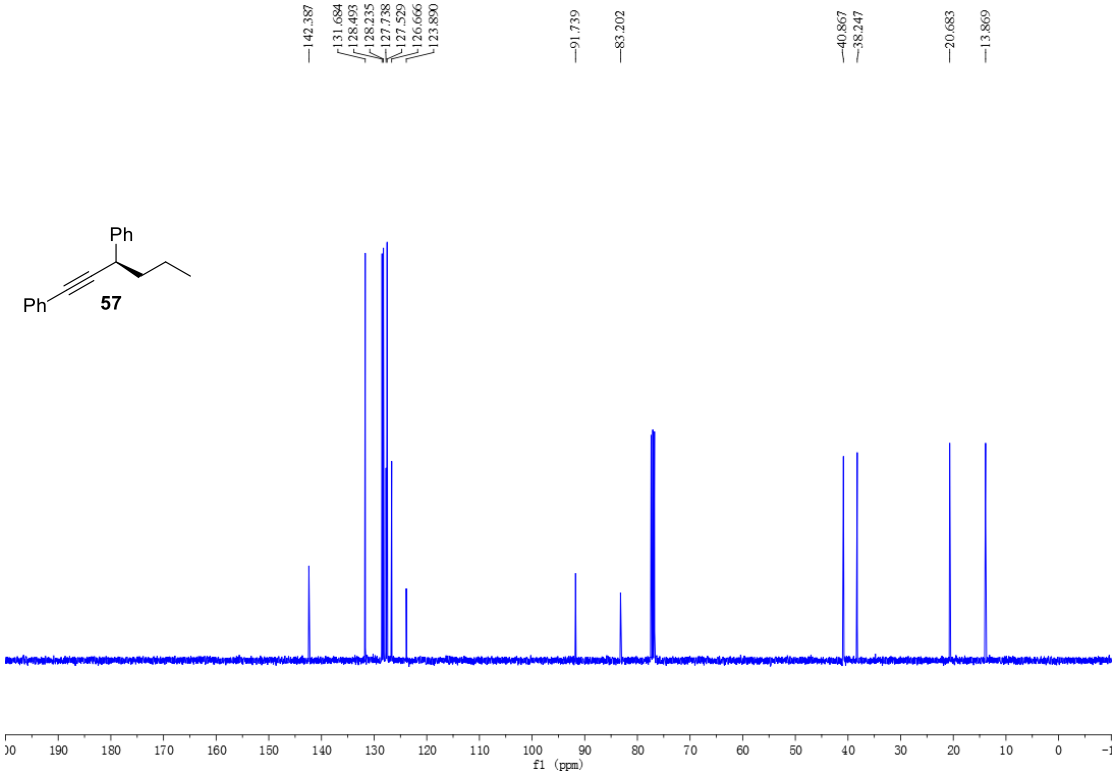
Ph
57
f1 (ppm)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Ph
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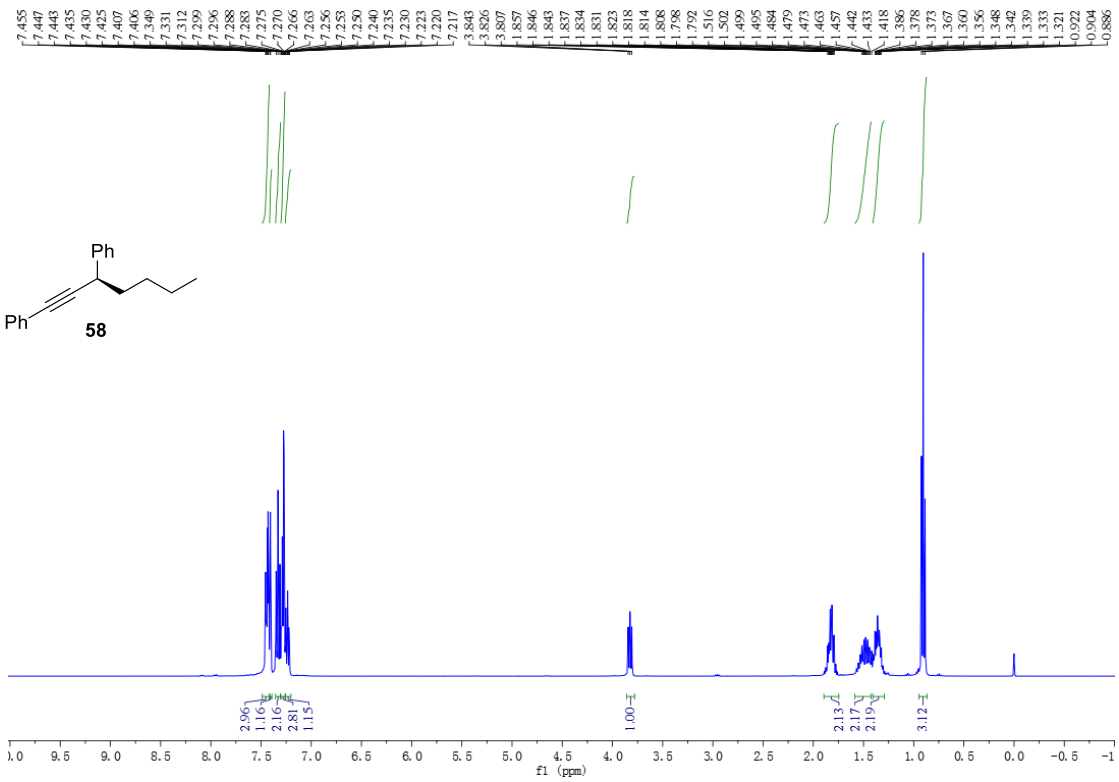
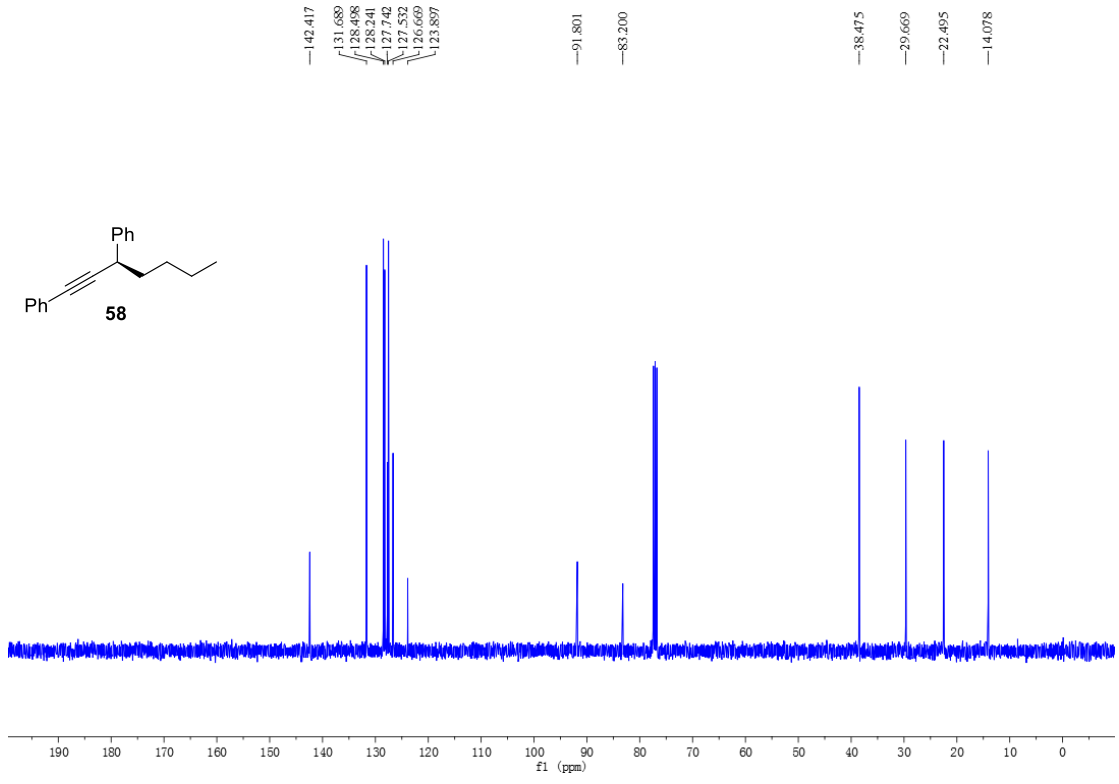
f1 (ppm)


Ph
Ph
58
f1 (ppm)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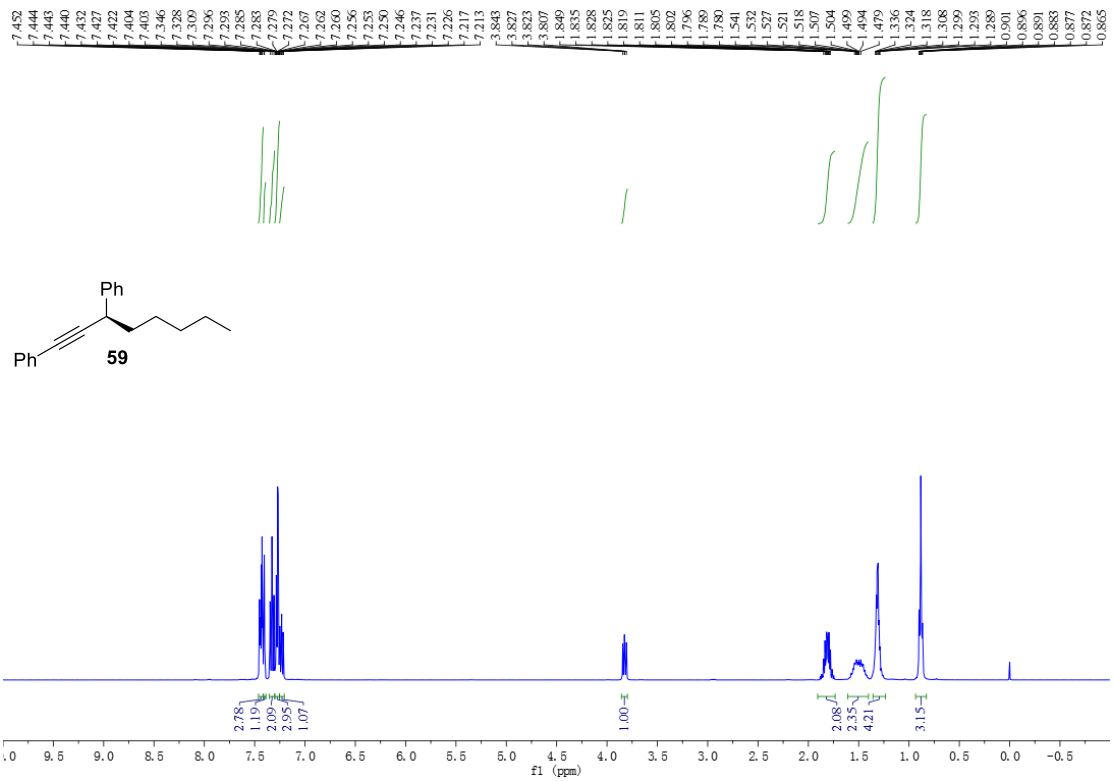
f1 (ppm)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7.422
7.404
7.403
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7.309
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7.293
7.285
7.283
7.279
7.272
7.267
7.262
7.260
7.256
7.253
7.250
7.246
7.237
7.231
7.226
7.217
7.213
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3.827
3.823
3.807
1.849
1.835
1.828
1.825
1.819
1.811
1.805
1.802
1.796
1.789
1.780
1.541
1.532
1.527
1.521
1.518
1.507
1.504
1.499
1.494
1.479
1.336
1.324
1.318
1.308
1.299
1.293
1.289
0.901
0.896
0.891
0.883
0.877
0.872
0.865
Ph
Ph
59
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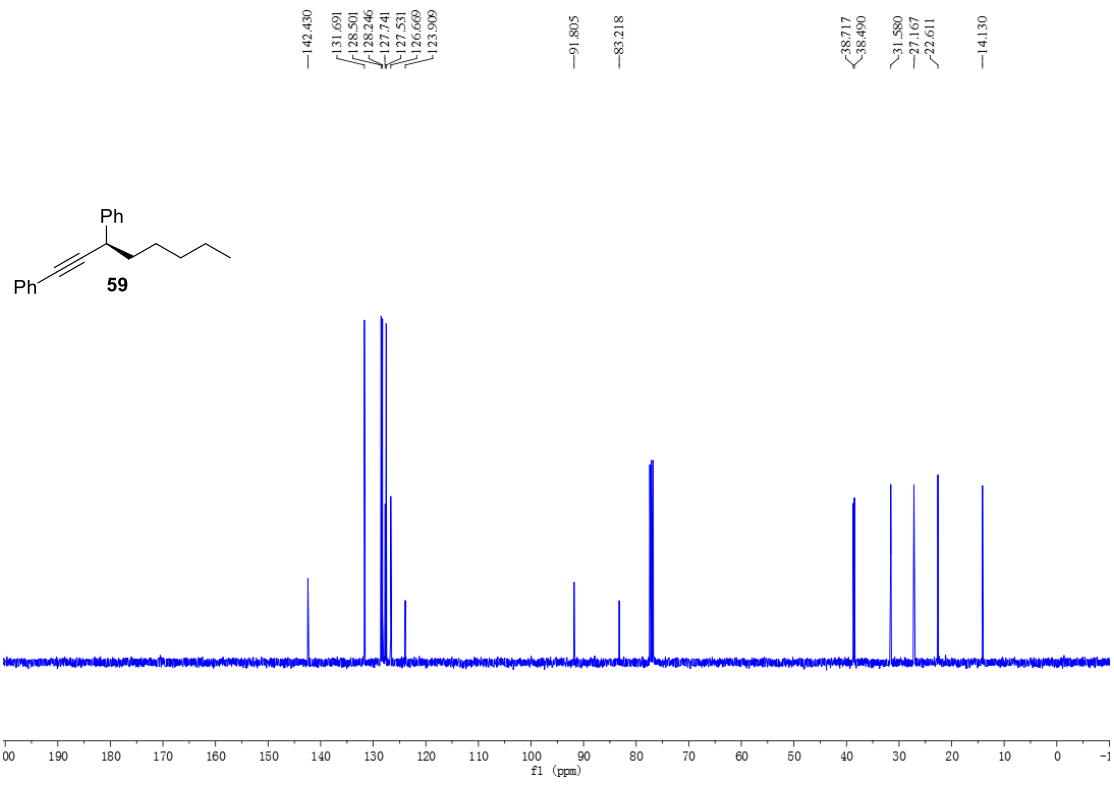
2.09
2.55
1.07
1.00
2.08
2.35
4.21
3.15
f1 (ppm)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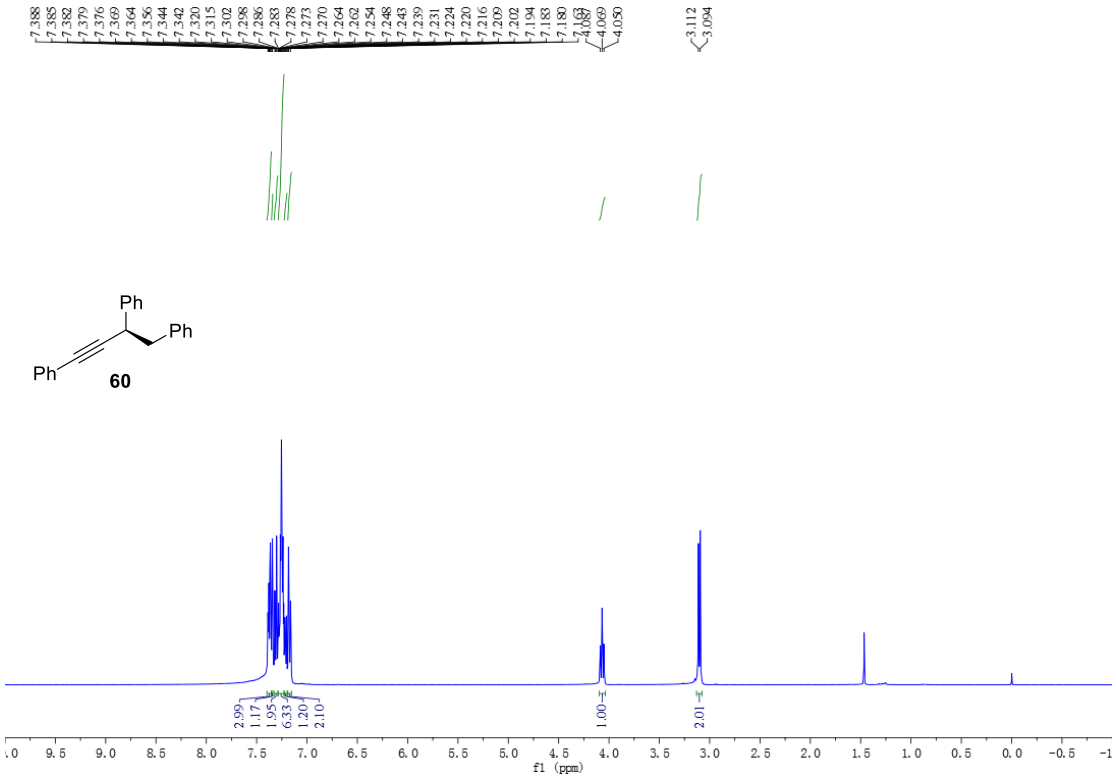
128.501
128.246
127.741
127.531
126.669
123.909
91.805
83.218
38.717
38.490
31.580
27.167
22.611
14.130
Ph
Ph
59
f1 (ppm)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7.356
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7.302
7.298
7.286
7.283
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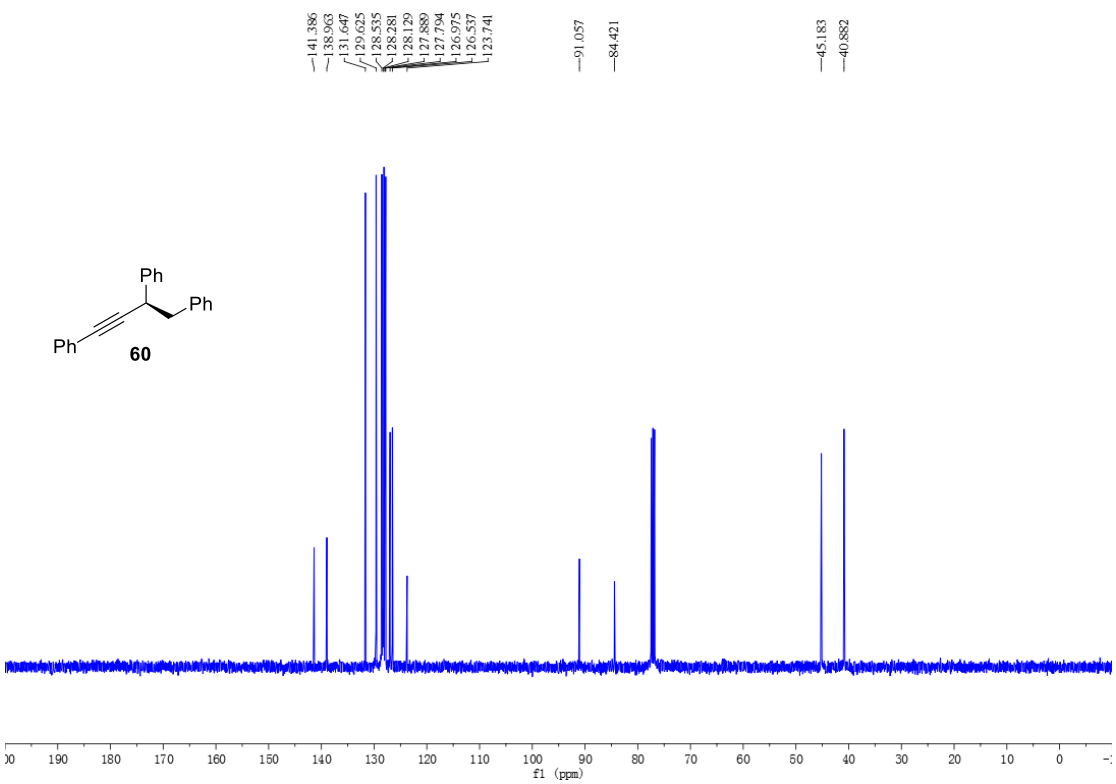
7.270
7.264
7.262
7.254
7.248
7.243
7.239
7.231
7.224
7.220
7.216
7.209
7.202
7.194
7.183
7.180
7.163
4.087
4.069
4.050
3.112
3.094
Ph
Ph
Ph
60
2.99
1.17
1.95
6.33
1.20
2.10
1.00
2.01
f1 (ppm)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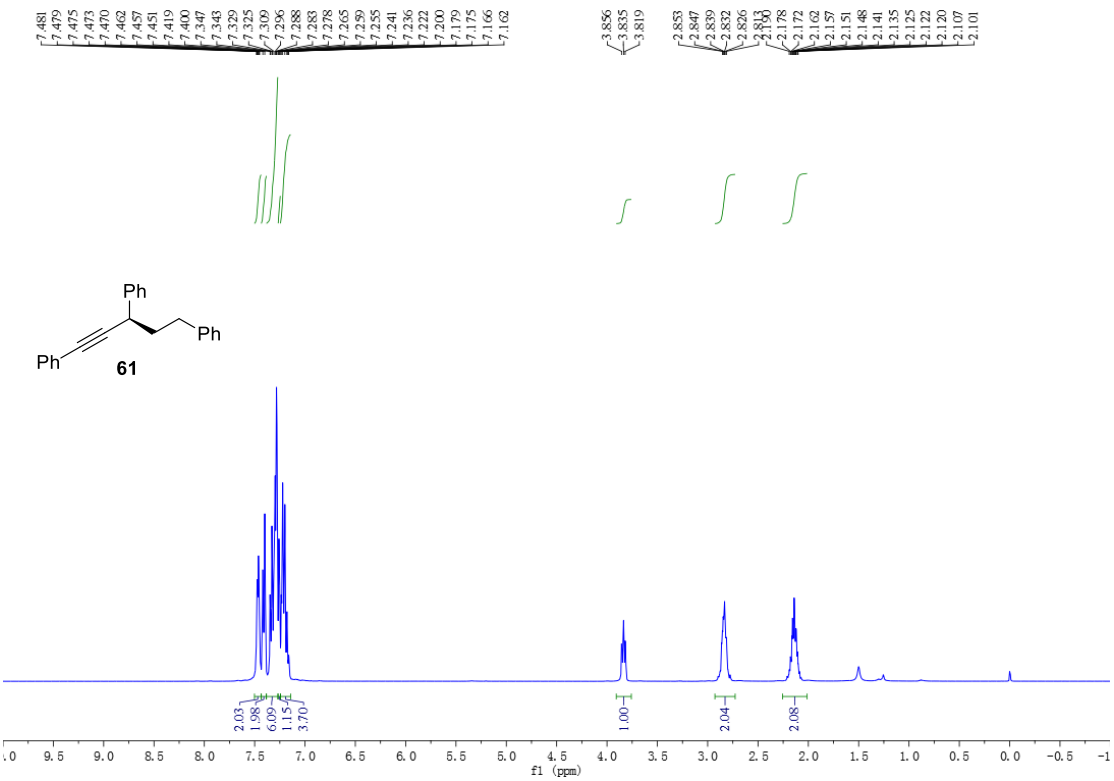
131.647
129.625
128.535
128.281
128.129
127.889
127.794
126.975
126.537
123.741
91.057
84.421
45.183
40.882
Ph
Ph
Ph
60
f1 (ppm)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7.475
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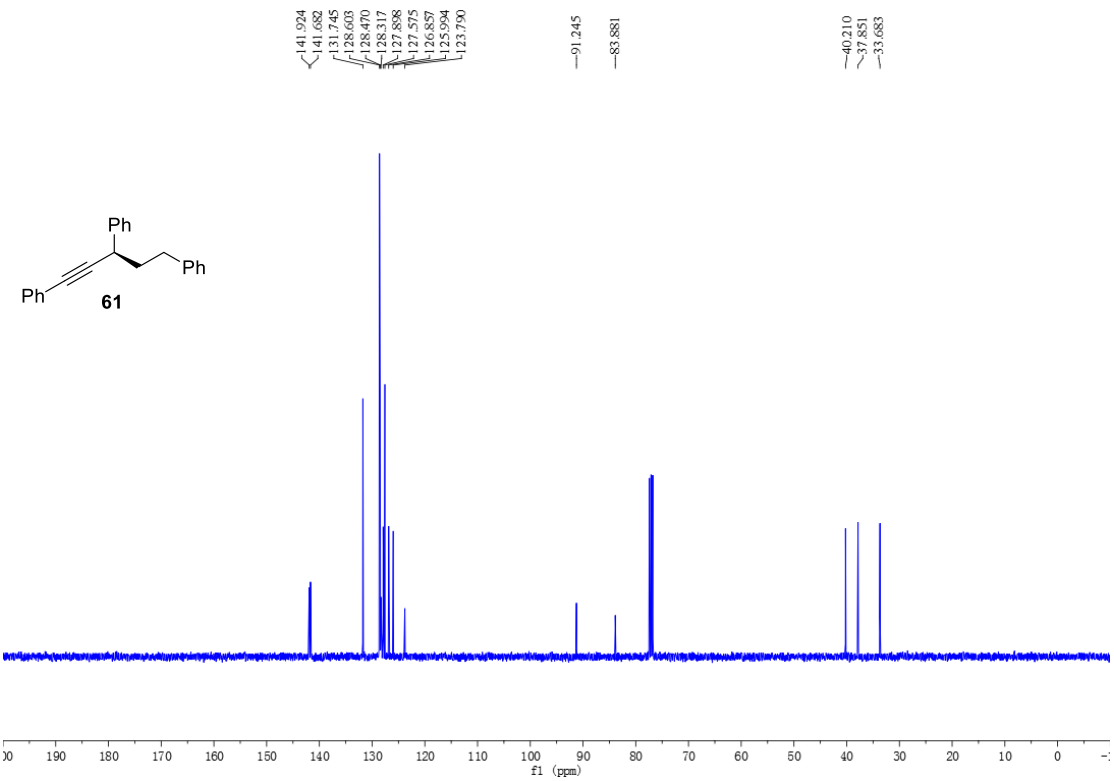
7.470
7.462
7.457
7.451
7.419
7.400
7.347
7.343
7.329
7.325
7.309
7.296
7.288
7.283
7.278
7.265
7.259
7.255
7.241
7.236
7.222
7.200
7.179
7.175
7.166
7.162
3.856
3.835
3.819
2.853
2.847
2.839
2.832
2.826
2.813
2.190
2.178
2.172
2.162
2.157
2.151
2.148
2.141
2.135
2.125
2.122
2.120
2.107
2.101
Ph
Ph
Ph
61
2.03
1.98
6.09
1.15
3.70
1.00
2.04
2.08
f1 (ppm)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128.470
128.317
127.898
127.575
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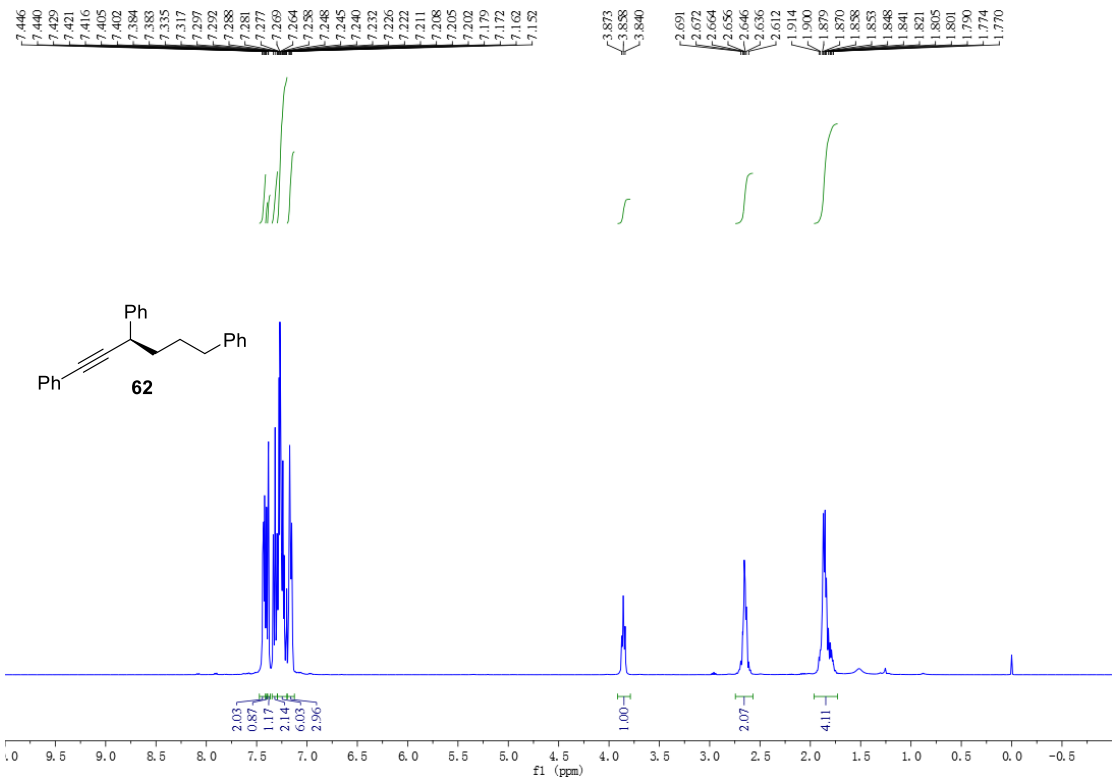
123.790
91.245
83.881
40.210
37.851
33.683
Ph
Ph
Ph
61
f1 (ppm)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7.421
7.416
7.405
7.402
7.394
7.383
7.335
7.317
7.297
7.292
7.288
7.281
7.277
7.269
7.264
7.258
7.248
7.245
7.240
7.232
7.226
7.222
7.211
7.208
7.205
7.202
7.179
7.172
7.162
7.152
3.873
3.858
3.840
2.691
2.672
2.664
2.656
2.646
2.636
2.612
1.914
1.900
1.879
1.870
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1.853
1.848
1.841
1.821
1.805
1.801
1.790
1.774
1.770
Ph
Ph
Ph
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0.87
1.17
2.14
6.03
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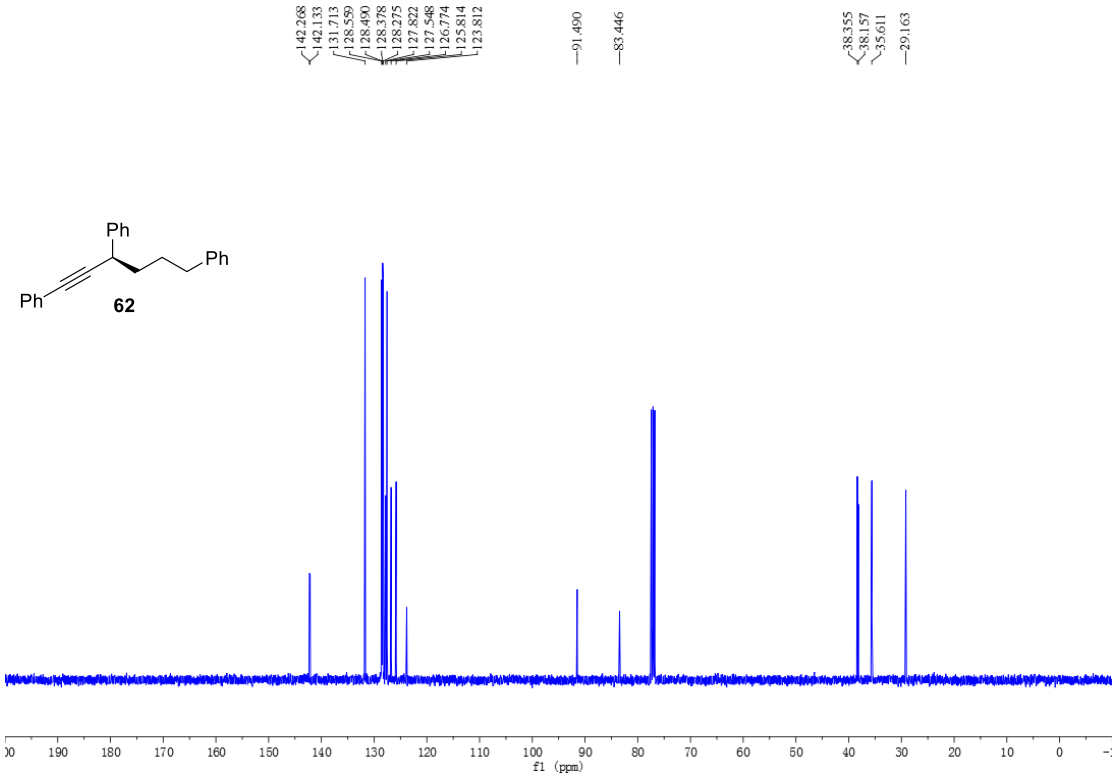
4.11
f1 (ppm)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128.490
128.378
128.275
127.822
127.548
126.774
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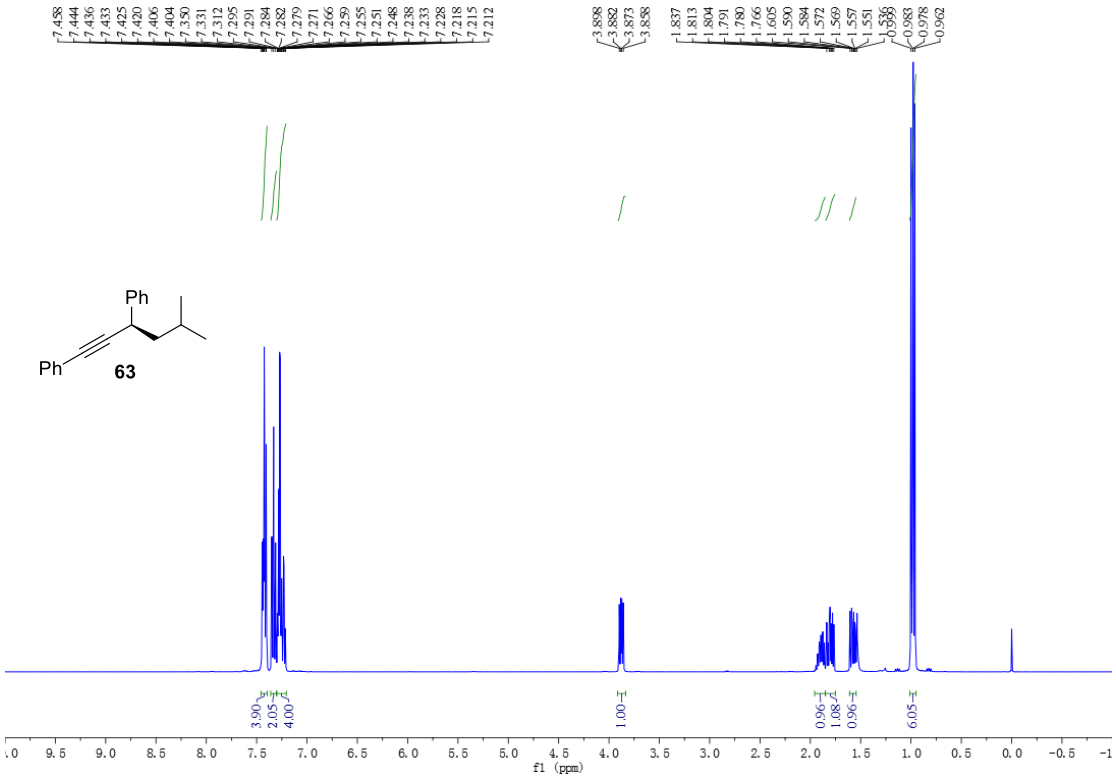
91.490
83.446
38.355
38.157
35.611
29.163
Ph
Ph
Ph
62
f1 (ppm)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7.433
7.425
7.420
7.406
7.404
7.350
7.331
7.312
7.295
7.291
7.284
7.282
7.279
7.271
7.266
7.259
7.255
7.251
7.248
7.238
7.233
7.228
7.218
7.215
7.212
3.898
3.882
3.873
3.858
1.837
1.813
1.804
1.791
1.780
1.766
1.605
1.590
1.584
1.572
1.569
1.557
1.551
1.538
0.999
0.983
0.978
0.962
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Ph
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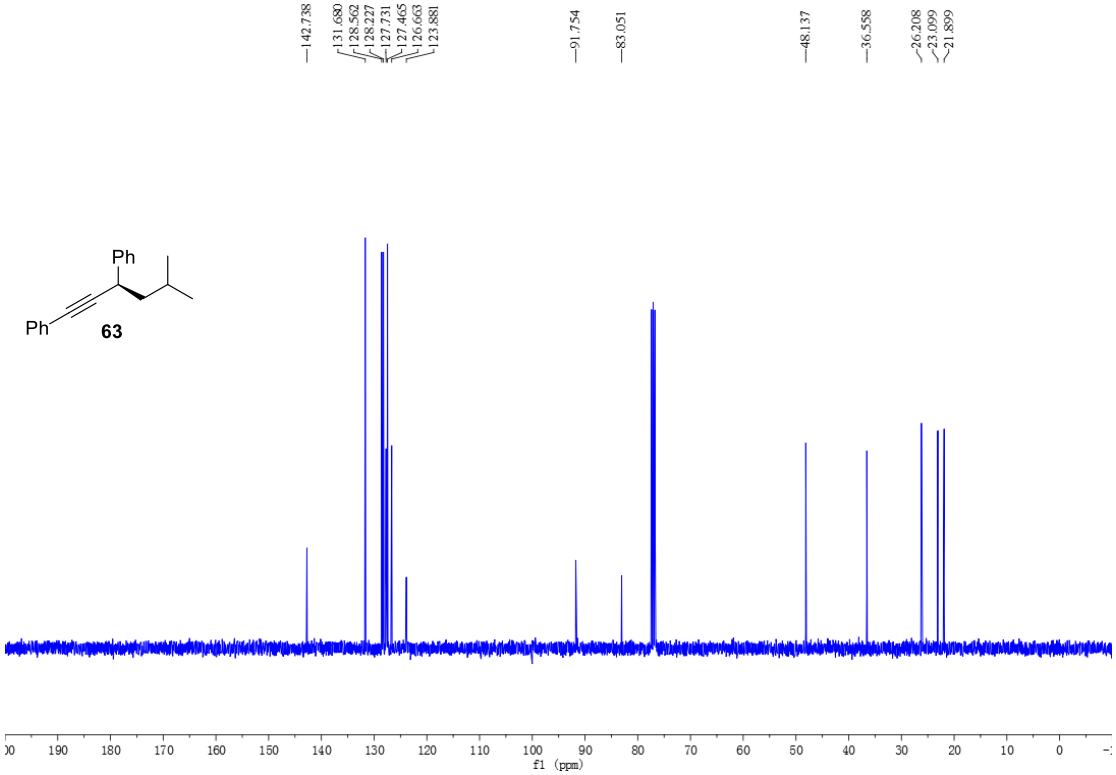
2.05
4.00
1.00
0.96
1.08
0.96
6.05
f1 (ppm)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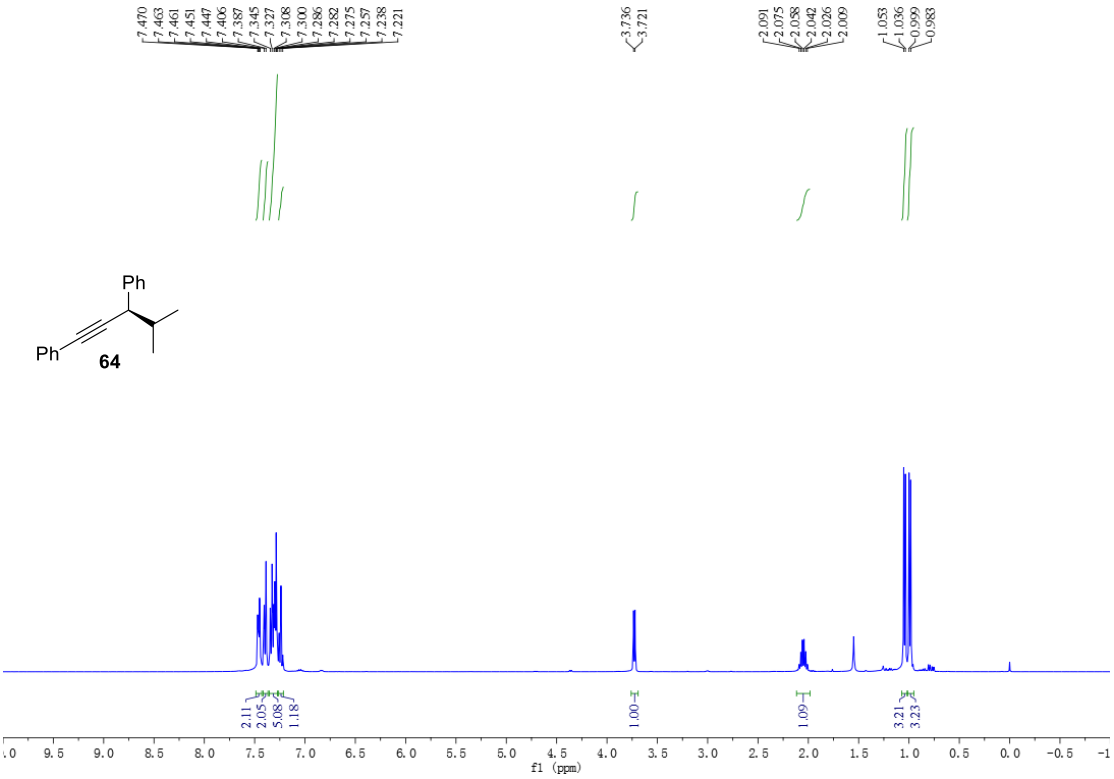
36.558
26.208
23.099
21.899
Ph
Ph
63
f1 (ppm)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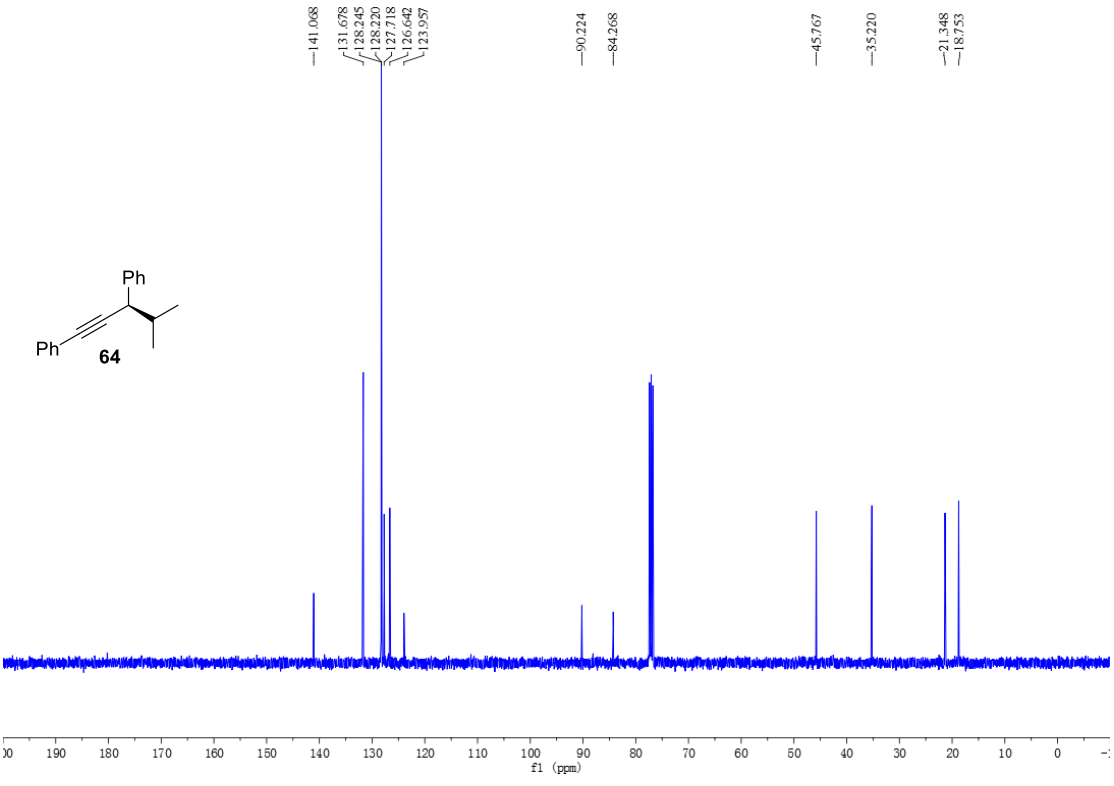
7.447
7.406
7.387
7.345
7.327
7.308
7.300
7.286
7.282
7.275
7.257
7.238
7.221
3.736
3.721
2.091
2.075
2.058
2.042
2.026
2.009
1.053
1.036
0.999
0.983
Ph
Ph
64
2.11
2.05
5.08
1.18
1.00
1.09
3.21
3.23
f1 (ppm)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Ph
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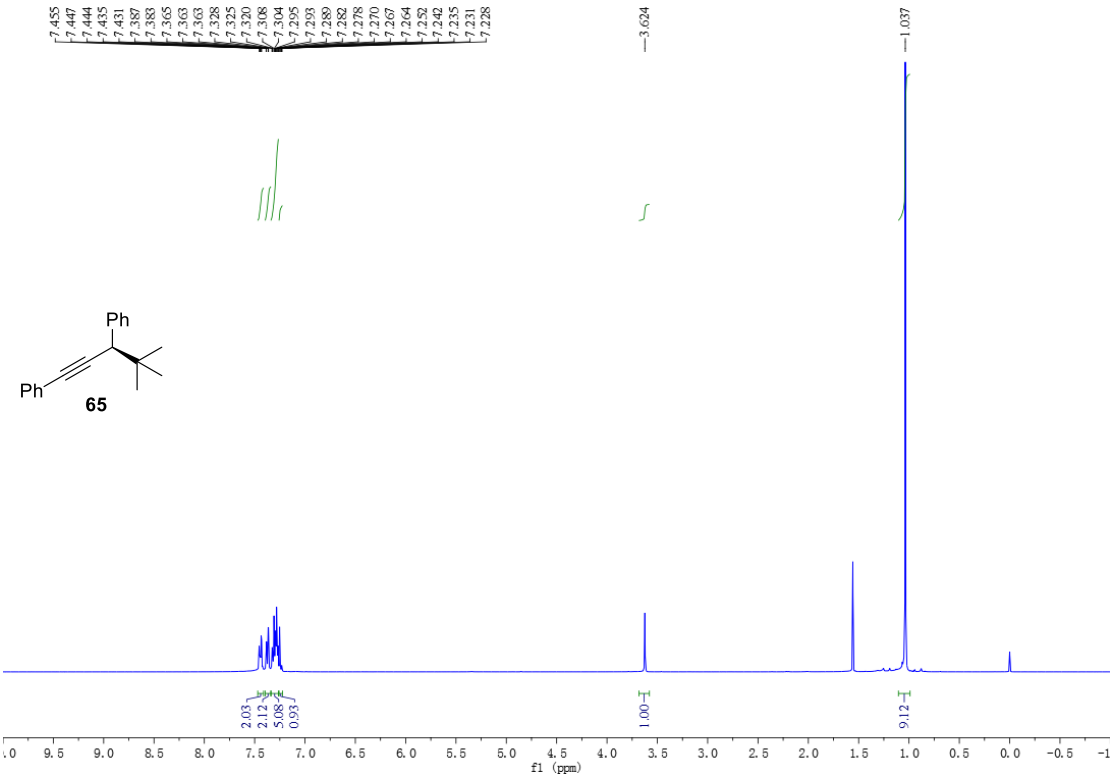
f1 (ppm)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7.320
7.308
7.304
7.295
7.293
7.289
7.282
7.278
7.270
7.267
7.264
7.252
7.242
7.235
7.231
7.228
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Ph
Ph
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5.08
0.93
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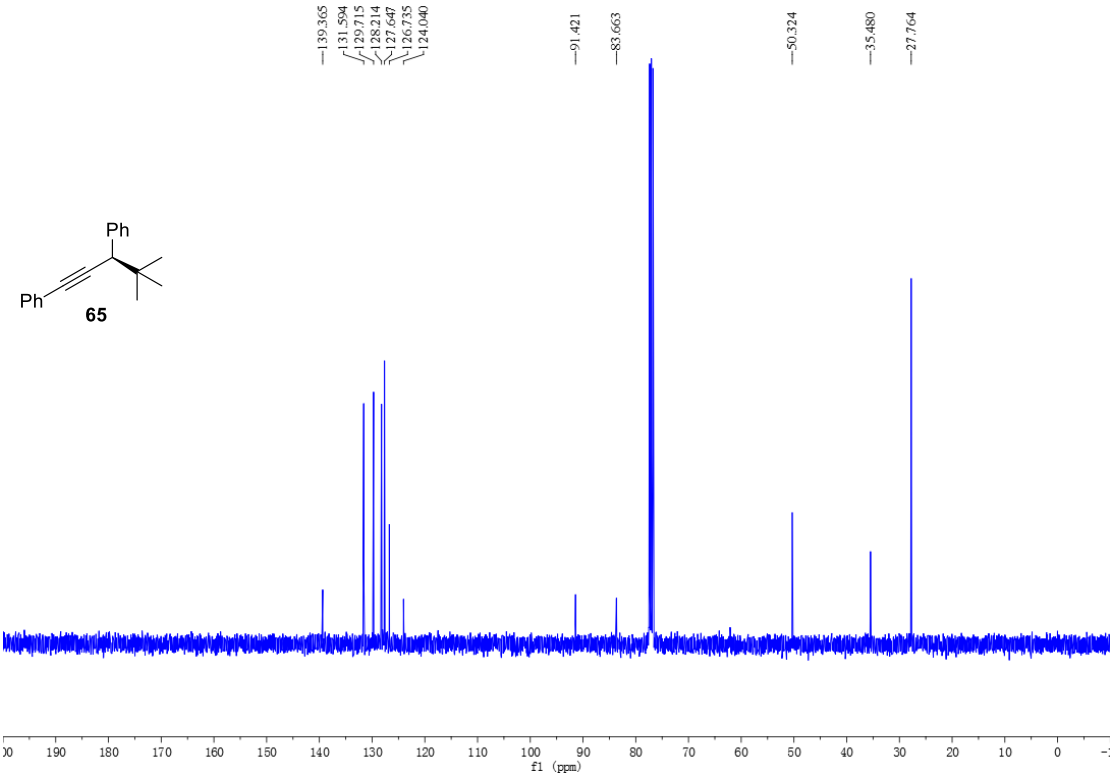
9.12
f1 (ppm)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50.324
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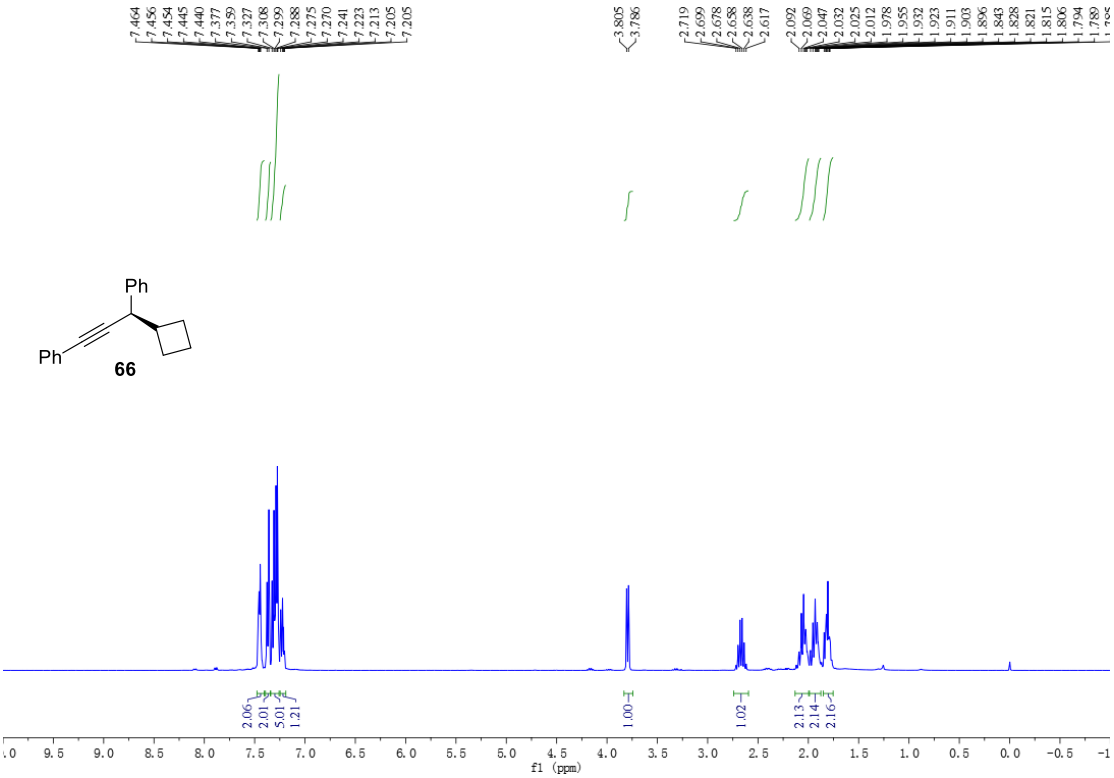
Ph
Ph
65
f1 (ppm)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7.241
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3.805
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1.932
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1.903
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1.843
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1.821
1.815
1.806
1.794
1.789
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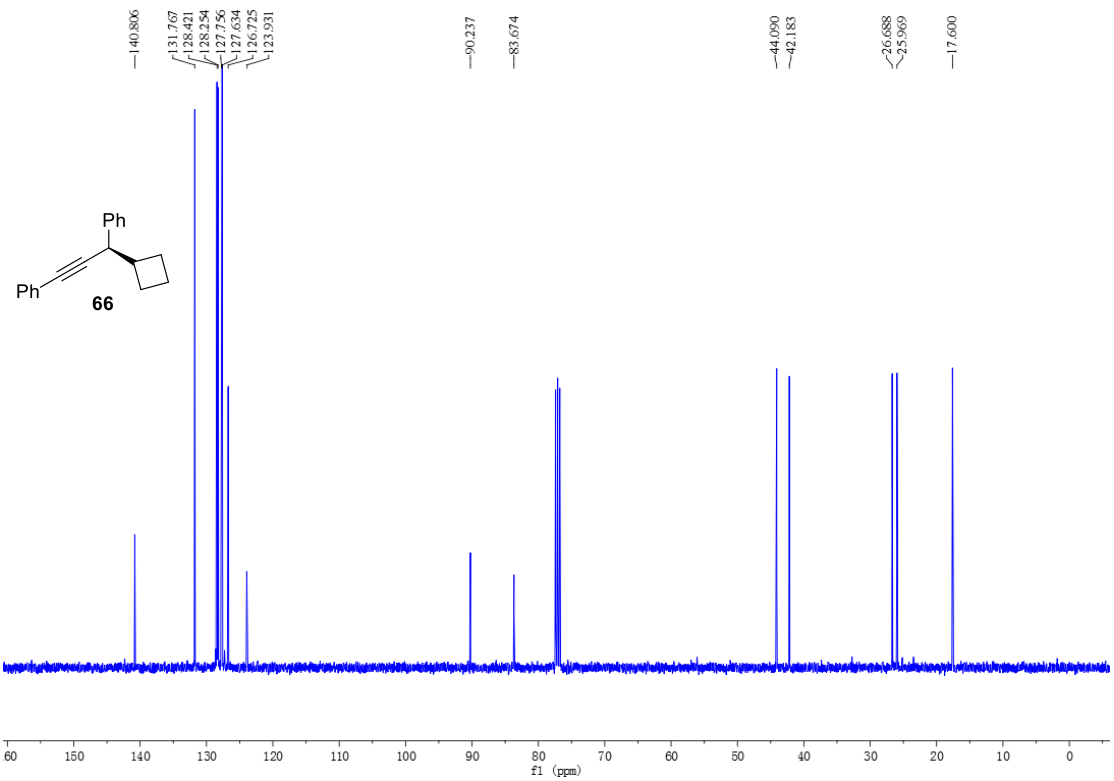
f1 (ppm)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127.634
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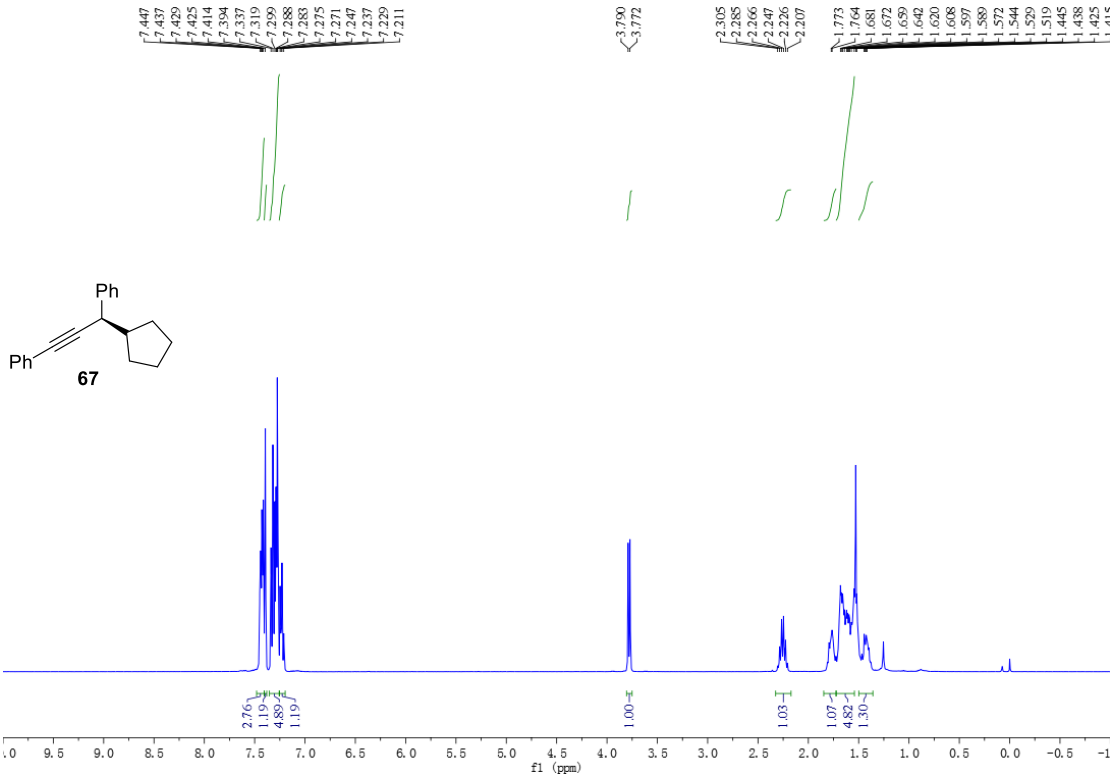
44.090
42.183
26.688
25.969
17.600
Ph
Ph
66
f1 (ppm)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Ph
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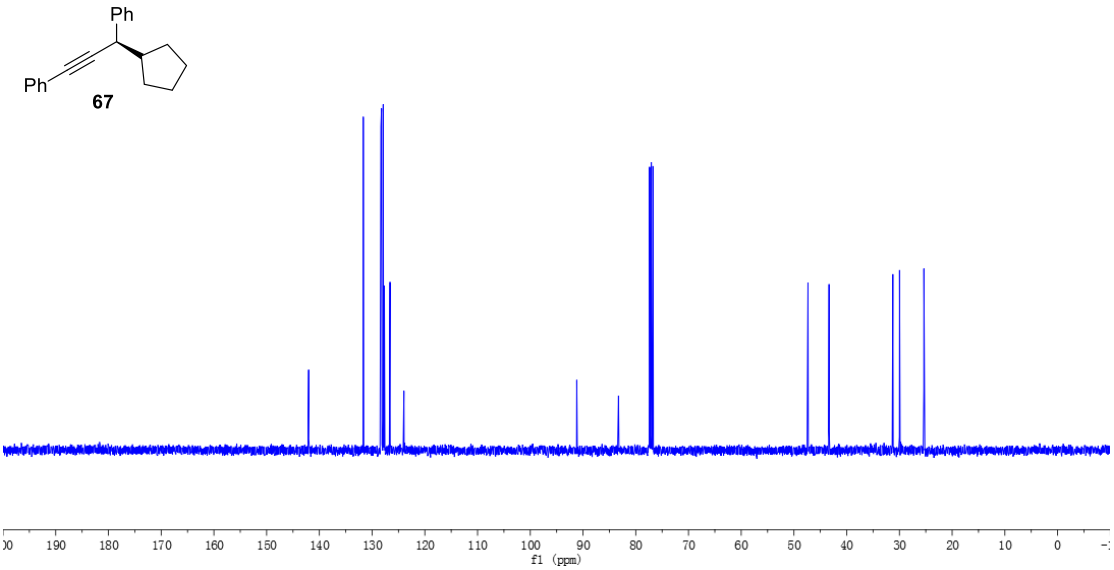
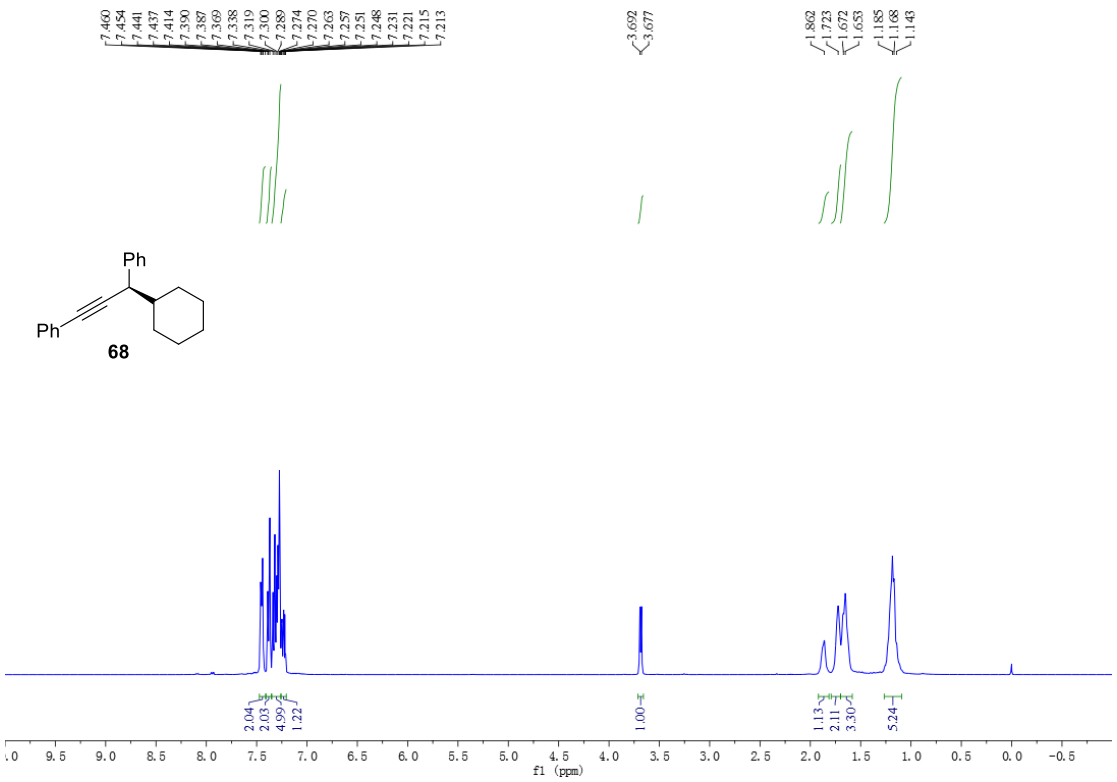
f1 (ppm)


Ph
Ph
67
f1 (ppm)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7.300
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7.274
7.270
7.263
7.257
7.251
7.248
7.231
7.221
7.215
7.213
3.692
3.677
1.862
1.723
1.672
1.653
1.185
1.168
1.143
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2.03
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1.00
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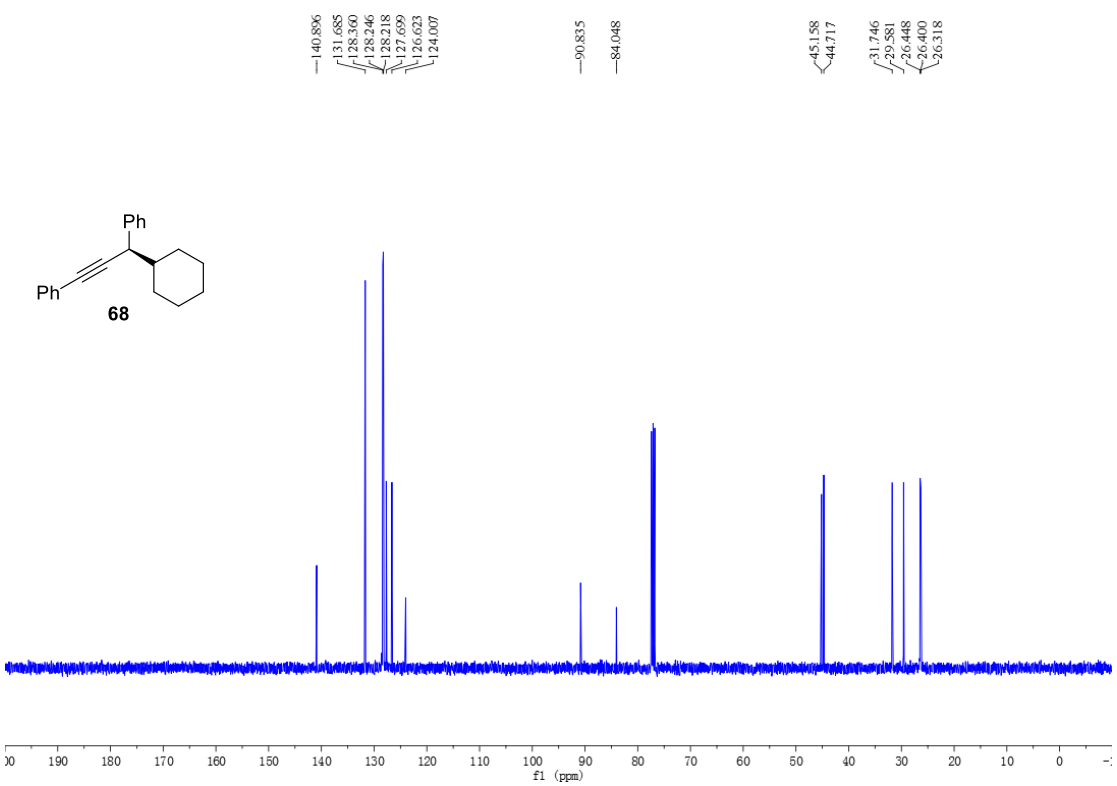
2.11
3.30
5.24
f1 (ppm)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128.218
127.699
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124.007
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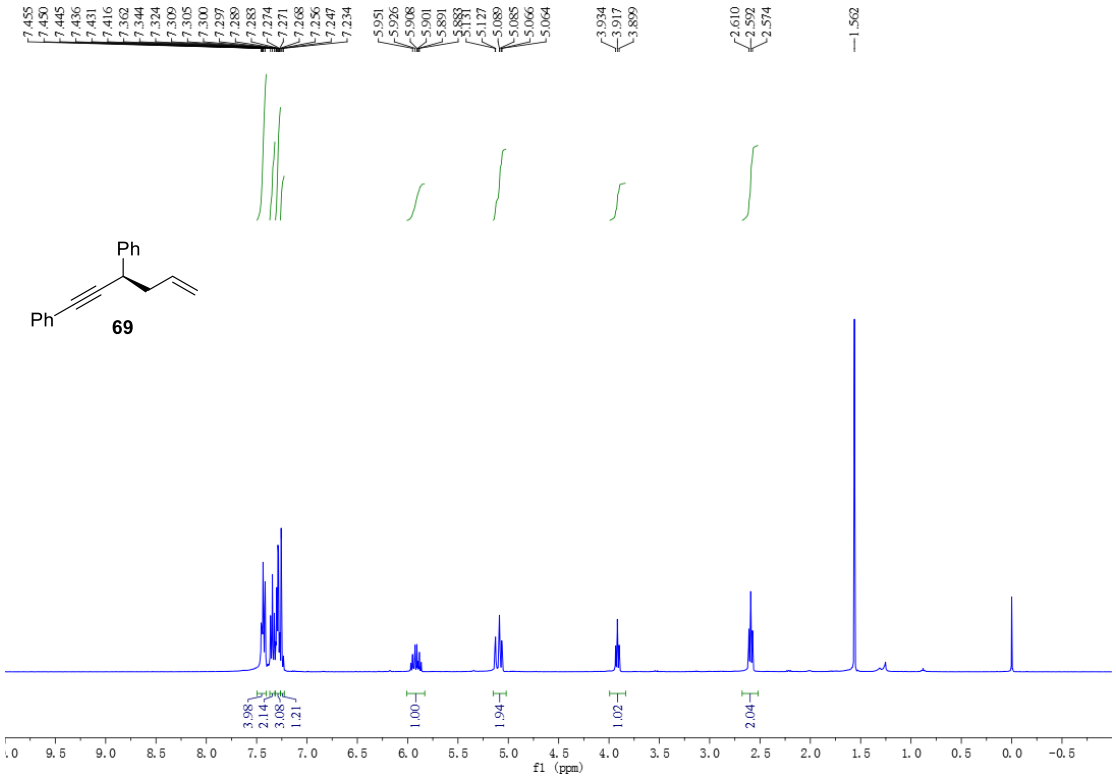
44.717
31.746
29.581
26.448
26.400
26.318
Ph
Ph
68
f1 (ppm)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7.445
7.436
7.431
7.416
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7.305
7.300
7.297
7.289
7.283
7.274
7.271
7.268
7.256
7.247
7.234
5.951
5.926
5.908
5.901
5.891
5.883
5.881
5.127
5.089
5.085
5.066
5.064
3.934
3.917
3.899
2.610
2.592
2.574
1.562
Ph
Ph
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3.08
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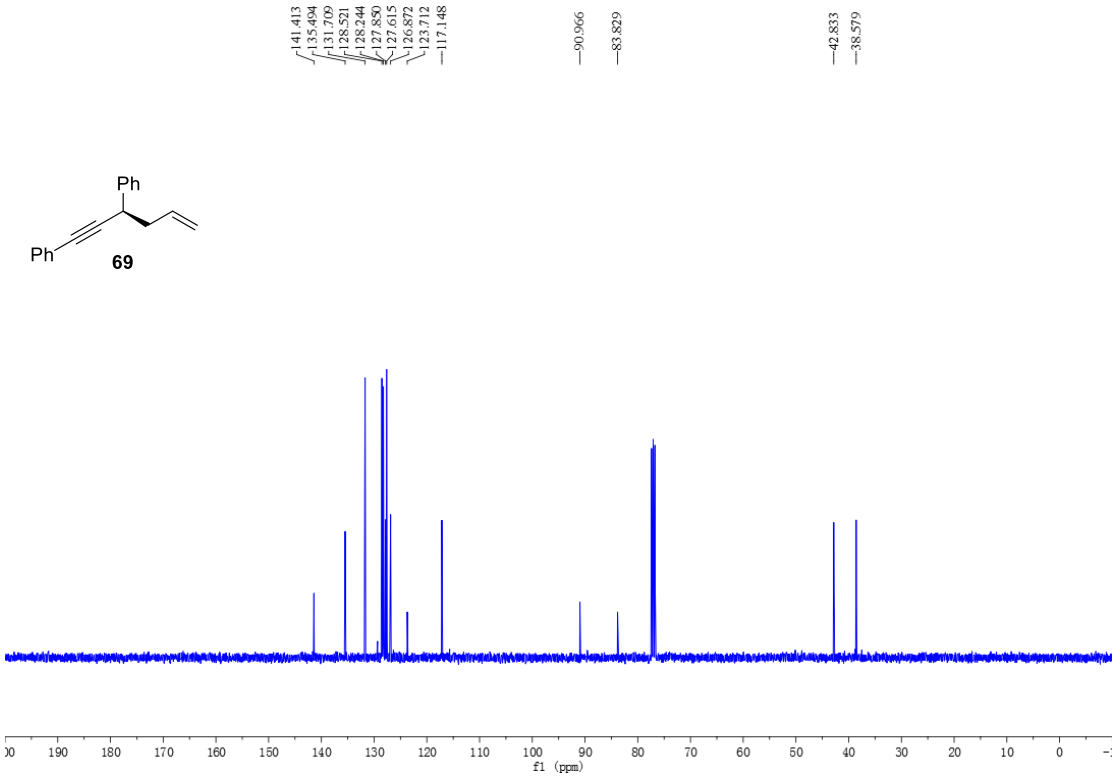
1.00
1.94
1.02
2.04
f1 (ppm)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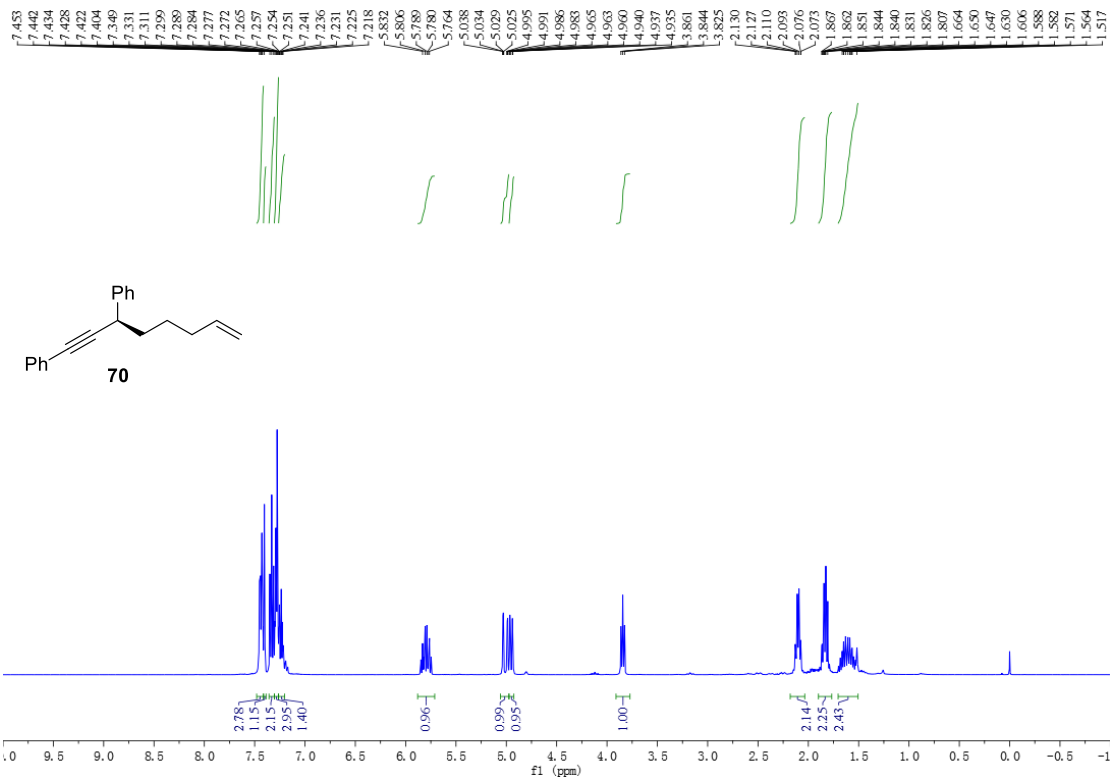
128.521
128.244
127.850
127.615
126.872
123.712
117.148
90.966
83.829
42.833
38.579
Ph
Ph
69
f1 (ppm)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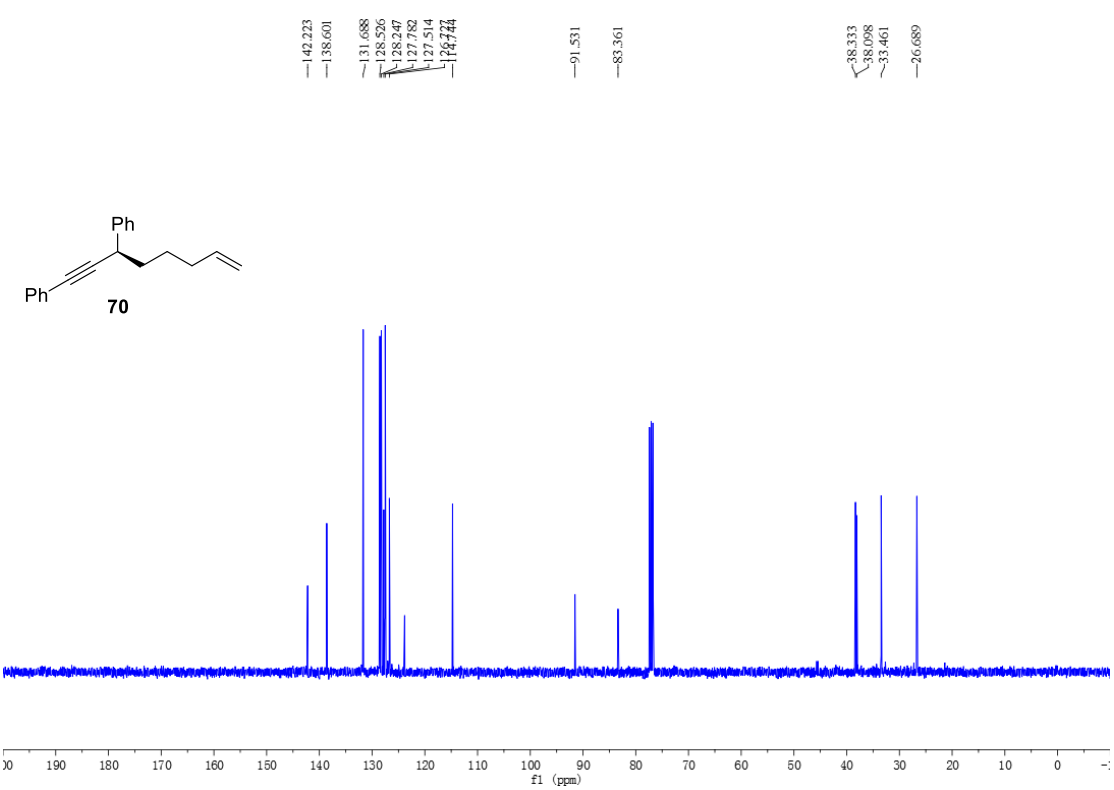
7.284
7.277
7.272
7.265
7.257
7.254
7.251
7.241
7.236
7.231
7.225
7.218
5.832
5.806
5.789
5.780
5.764
5.038
5.034
5.029
5.025
4.995
4.991
4.986
4.983
4.965
4.963
4.960
4.940
4.937
4.935
3.861
3.844
3.825
2.130
2.127
2.110
2.093
2.076
2.073
1.867
1.862
1.851
1.844
1.840
1.831
1.826
1.807
1.664
1.650
1.647
1.630
1.606
1.588
1.582
1.571
1.564
1.517
Ph
Ph
70
2.78
1.15
2.15
2.95
1.40
0.96
0.99
0.95
1.00
2.14
2.25
2.43
f1 (ppm)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138.601
131.688
128.526
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91.531
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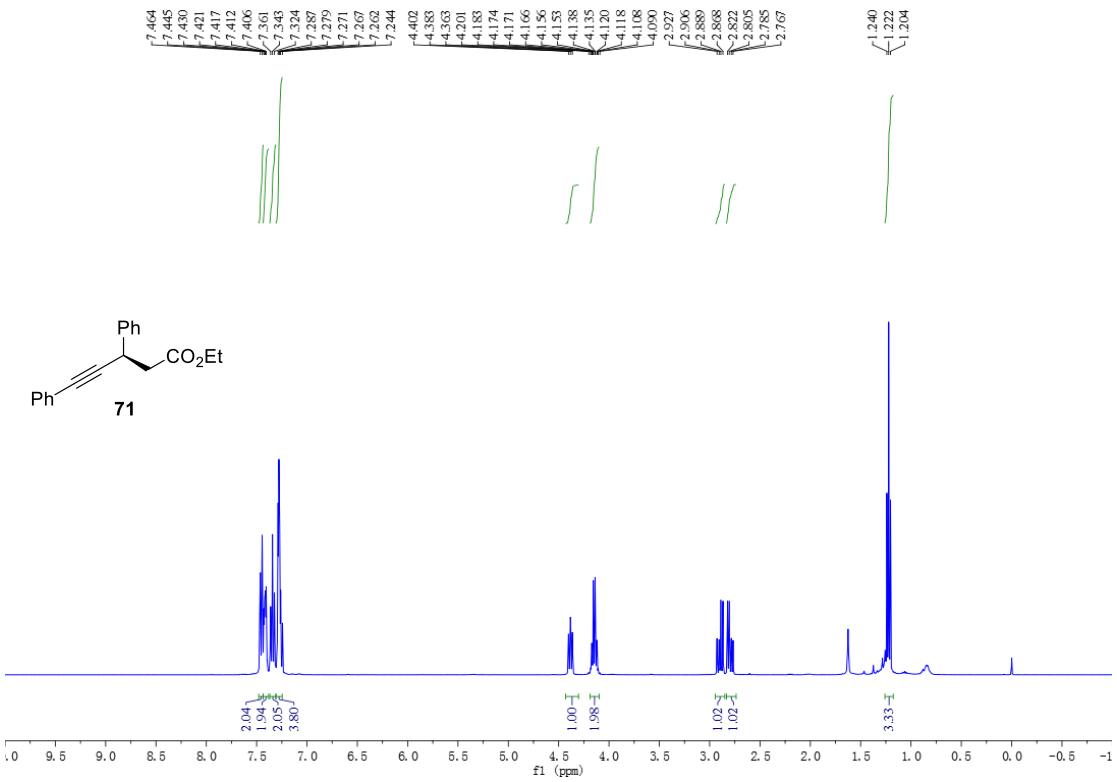
38.333
38.098
33.461
26.689
Ph
Ph
70
f1 (ppm)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7.430
7.421
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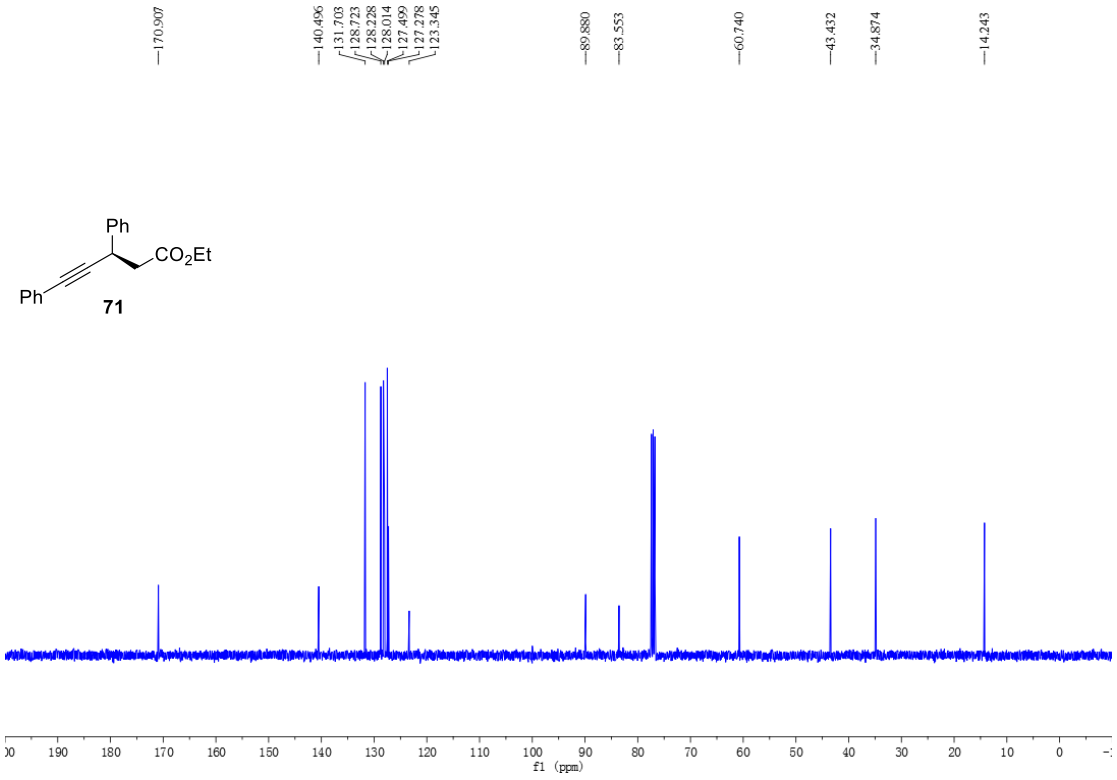
7.361
7.343
7.324
7.287
7.279
7.271
7.267
7.262
7.244
4.402
4.383
4.363
4.201
4.183
4.174
4.171
4.166
4.156
4.153
4.138
4.135
4.120
4.118
4.108
4.090
2.927
2.906
2.889
2.868
2.822
2.805
2.785
2.767
1.240
1.222
1.204
Ph
CO2Et
Ph
71
2.04
1.04
2.05
3.80
1.00
1.98
1.02
1.02
3.33
f1 (ppm)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140.496
131.703
128.723
128.228
128.014
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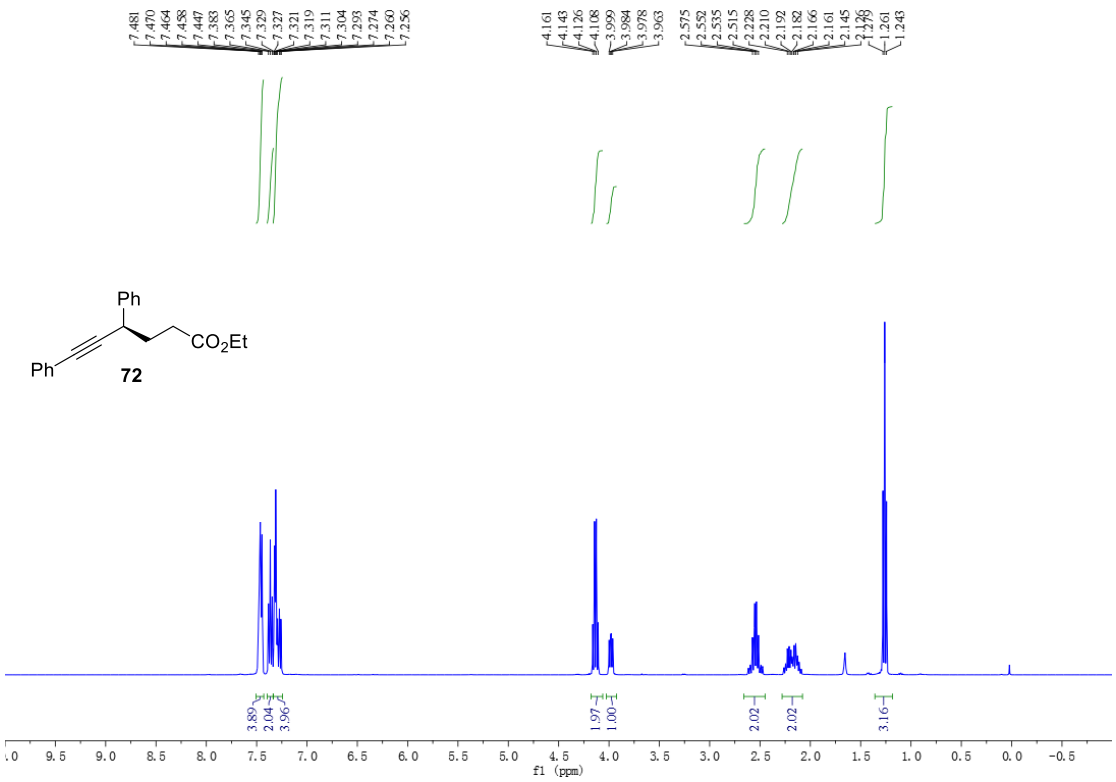
43.432
34.874
14.243
Ph
CO2Et
Ph
71
f1 (ppm)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7.447
7.383
7.365
7.345
7.329
7.327
7.321
7.319
7.311
7.304
7.293
7.274
7.260
7.256
4.161
4.143
4.126
4.108
3.999
3.984
3.978
3.963
2.575
2.552
2.535
2.515
2.228
2.210
2.192
2.182
2.166
2.161
2.145
2.126
1.261
1.243
Ph
CO2Et
Ph
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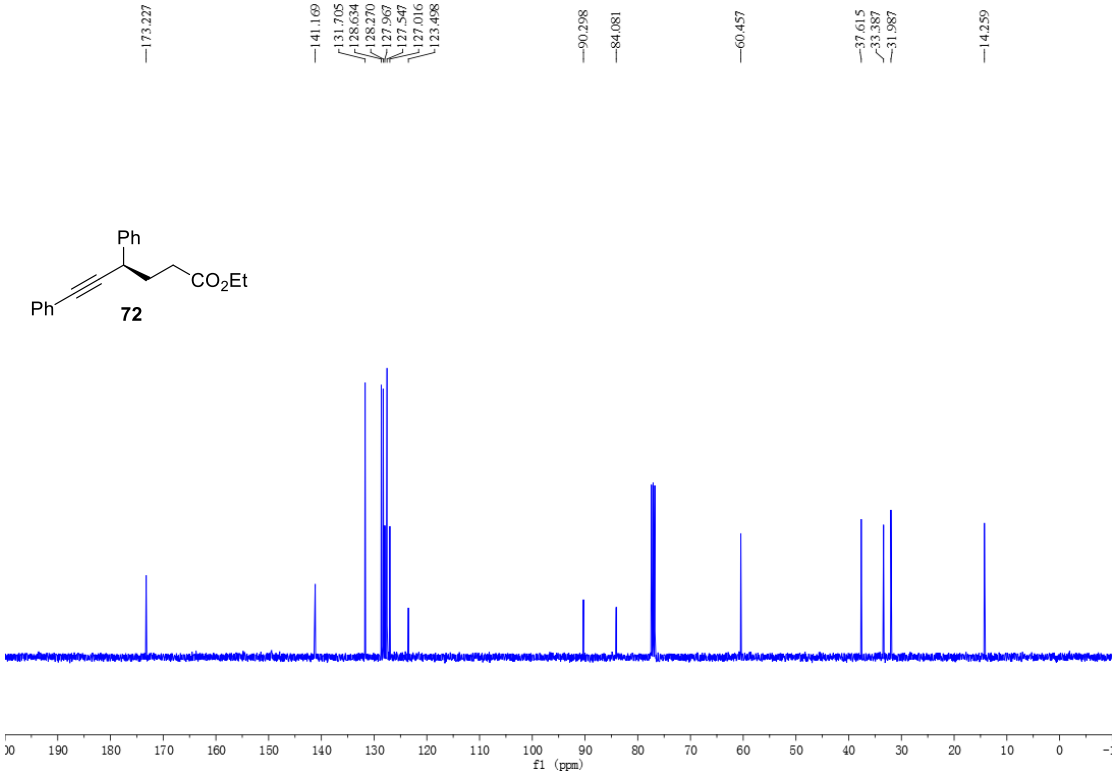
2.04
3.96
1.97
1.00
2.02
2.02
3.16
f1 (ppm)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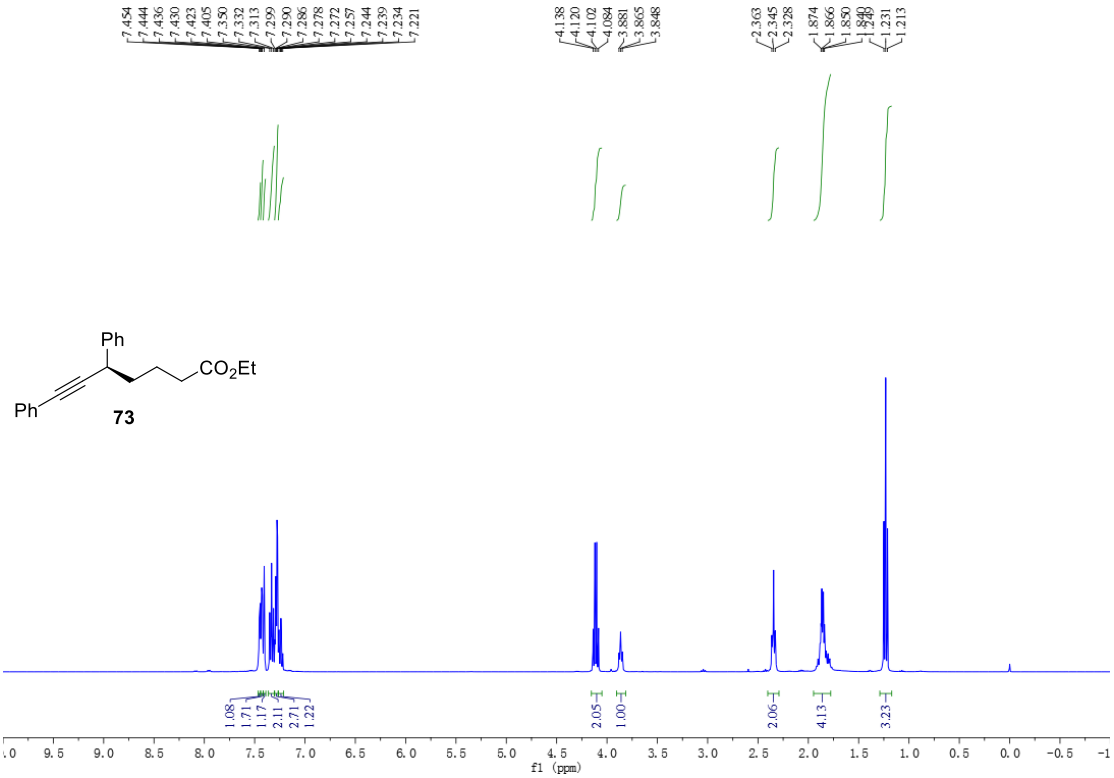
141.169
131.705
128.634
128.270
127.967
127.547
127.016
123.498
90.298
84.081
60.457
37.615
33.387
31.987
14.259
Ph
CO2Et
Ph
72
f1 (ppm)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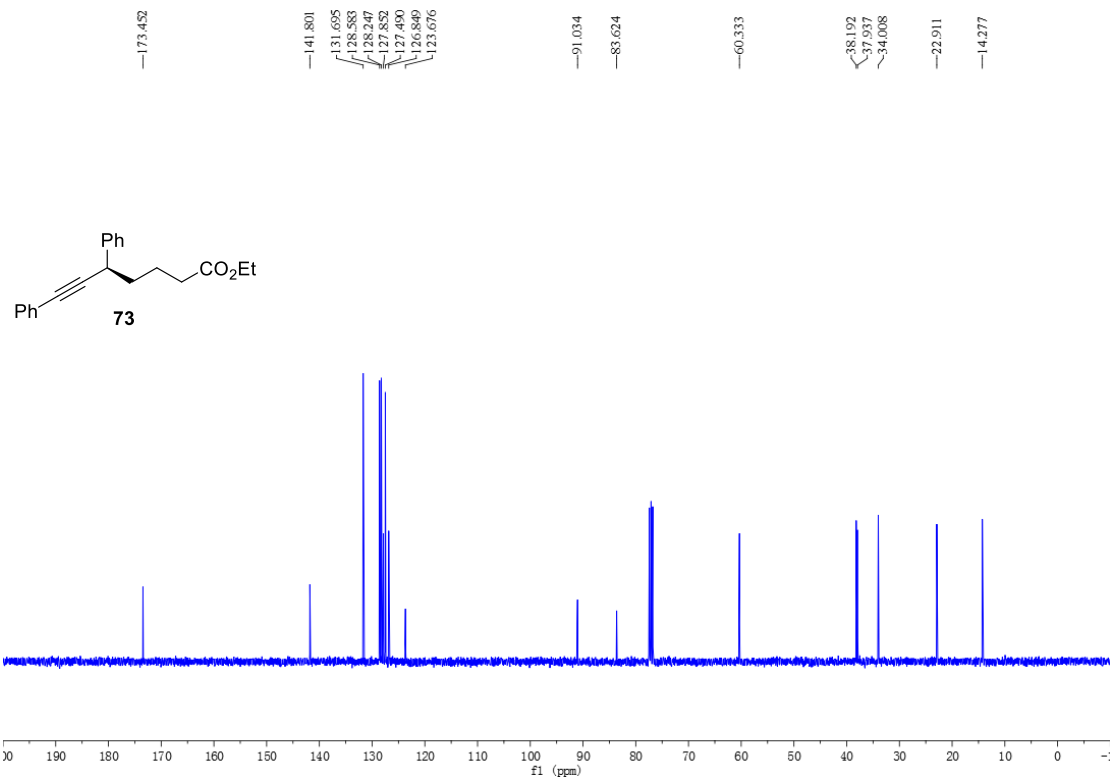
7.430
7.423
7.405
7.350
7.332
7.313
7.299
7.290
7.286
7.278
7.272
7.257
7.244
7.239
7.234
7.221
4.138
4.120
4.102
4.084
3.881
3.865
3.848
2.363
2.345
2.328
1.874
1.866
1.850
1.840
1.231
1.213
Ph
CO2Et
Ph
73
1.08
1.71
1.17
2.11
2.71
1.22
2.05
1.00
2.06
4.13
3.23
f1 (ppm)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127.852
127.490
126.849
123.676
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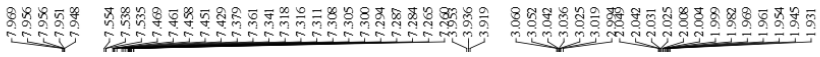
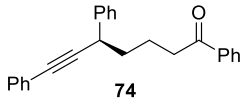
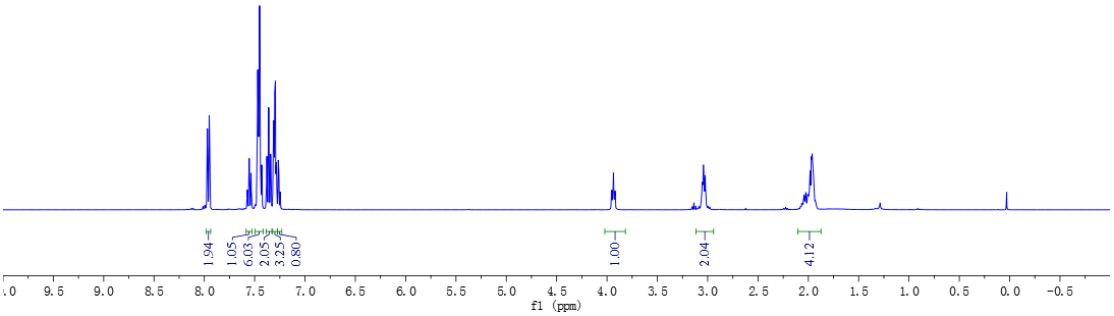
83.624
60.333
38.192
37.937
34.008
22.911
14.277
Ph
CO2Et
Ph
73
f1 (ppm)




Ph
O
Ph
Ph

74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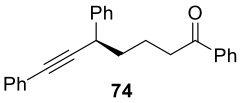
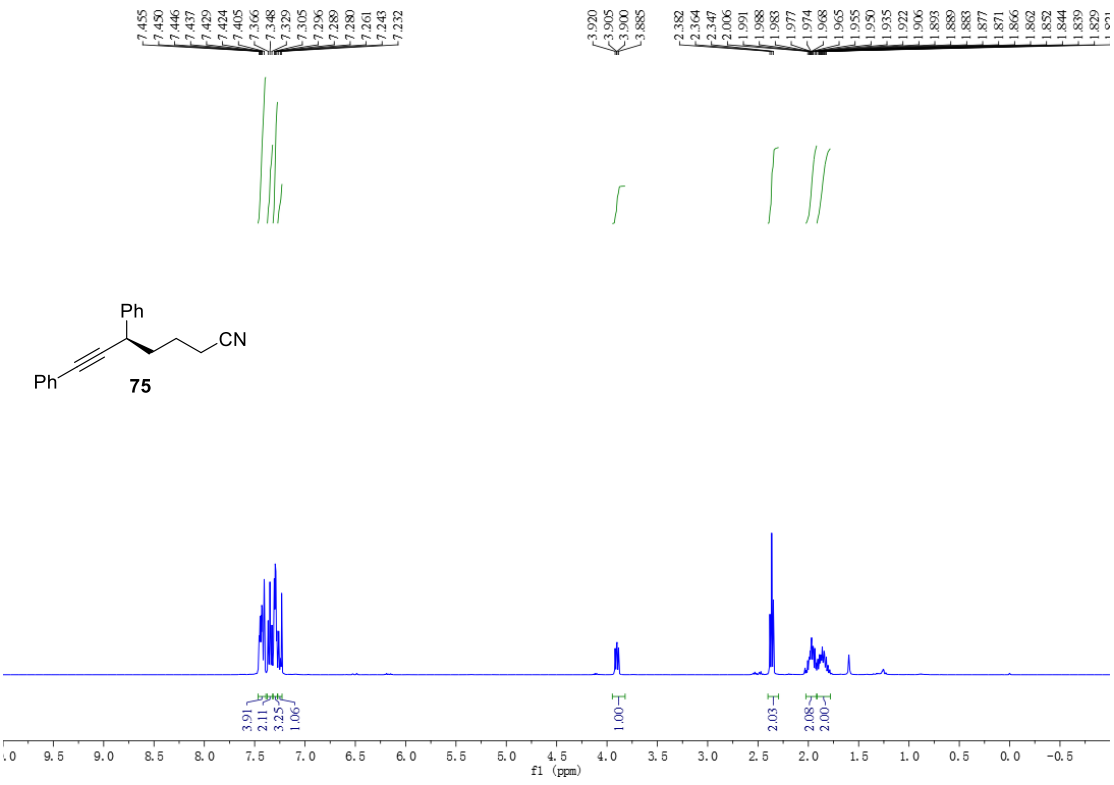
1.05
6.03
2.05
3.25
0.80
1.00
2.04
4.12
f1 (ppm)


Ph
O
Ph
Ph

74

f1 (ppm)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7.424
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7.366
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7.329
7.305
7.296
7.289
7.280
7.261
7.243
7.232
3.920
3.905
3.900
3.885
2.382
2.364
2.347
2.006
1.991
1.988
1.983
1.977
1.974
1.968
1.965
1.955
1.950
1.935
1.922
1.906
1.893
1.889
1.883
1.877
1.871
1.866
1.862
1.852
1.844
1.839
1.829
Ph
CN
Ph
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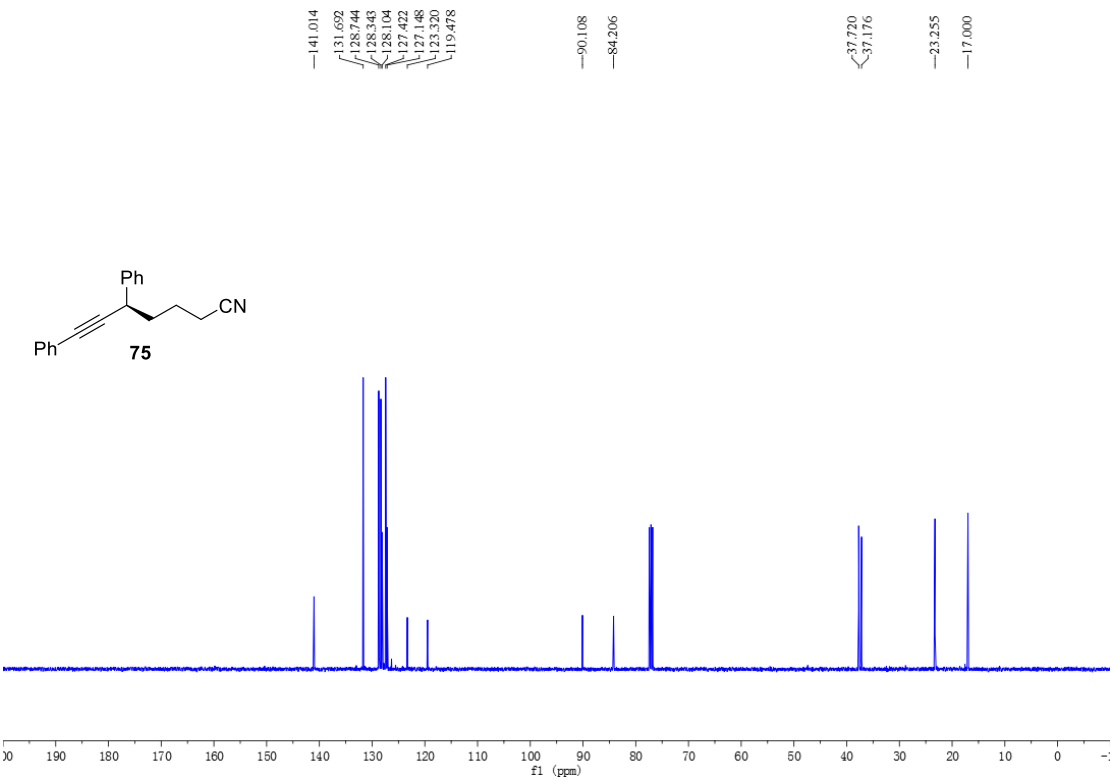
3.91
2.11
3.25
1.06
1.00
2.03
2.08
2.00
f1 (ppm)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128.744
128.343
128.104
127.422
127.148
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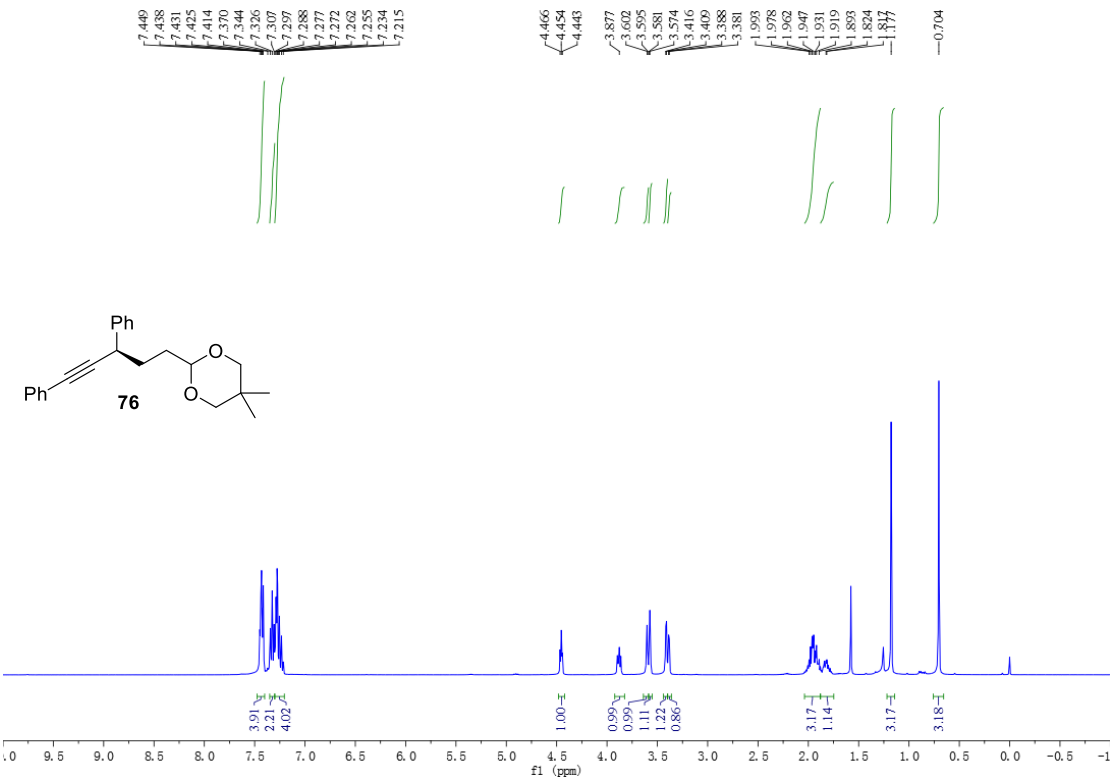
119.478
90.108
84.206
37.720
37.176
23.255
17.000
Ph
CN
Ph
75
f1 (ppm)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7.431
7.425
7.414
7.370
7.344
7.326
7.307
7.297
7.288
7.277
7.272
7.262
7.255
7.234
7.215
4.466
4.454
4.443
3.877
3.602
3.595
3.581
3.574
3.416
3.409
3.388
3.381
1.993
1.978
1.962
1.947
1.931
1.919
1.893
1.824
1.817
1.177
0.704
Ph
Ph
O
O
76
3.91
2.21
4.02
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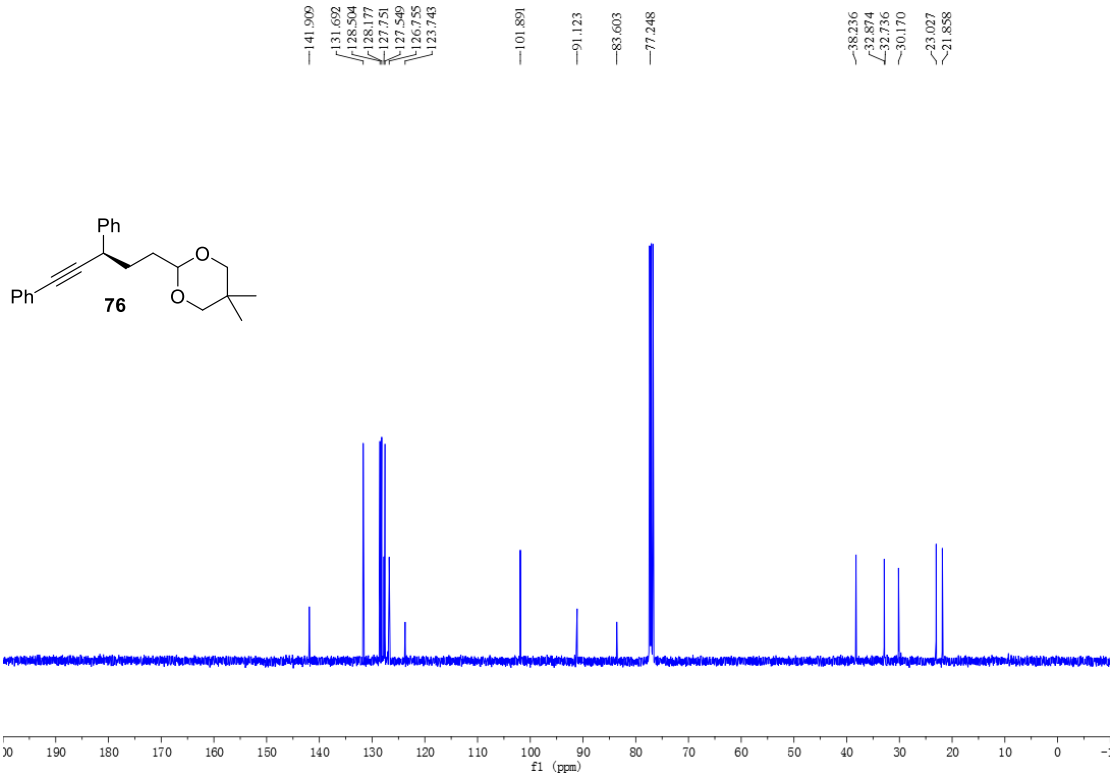
0.99
0.99
1.11
1.22
0.86
3.17
1.14
3.17
3.18
f1 (ppm)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128.504
128.177
127.751
127.549
126.755
123.743
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91.123
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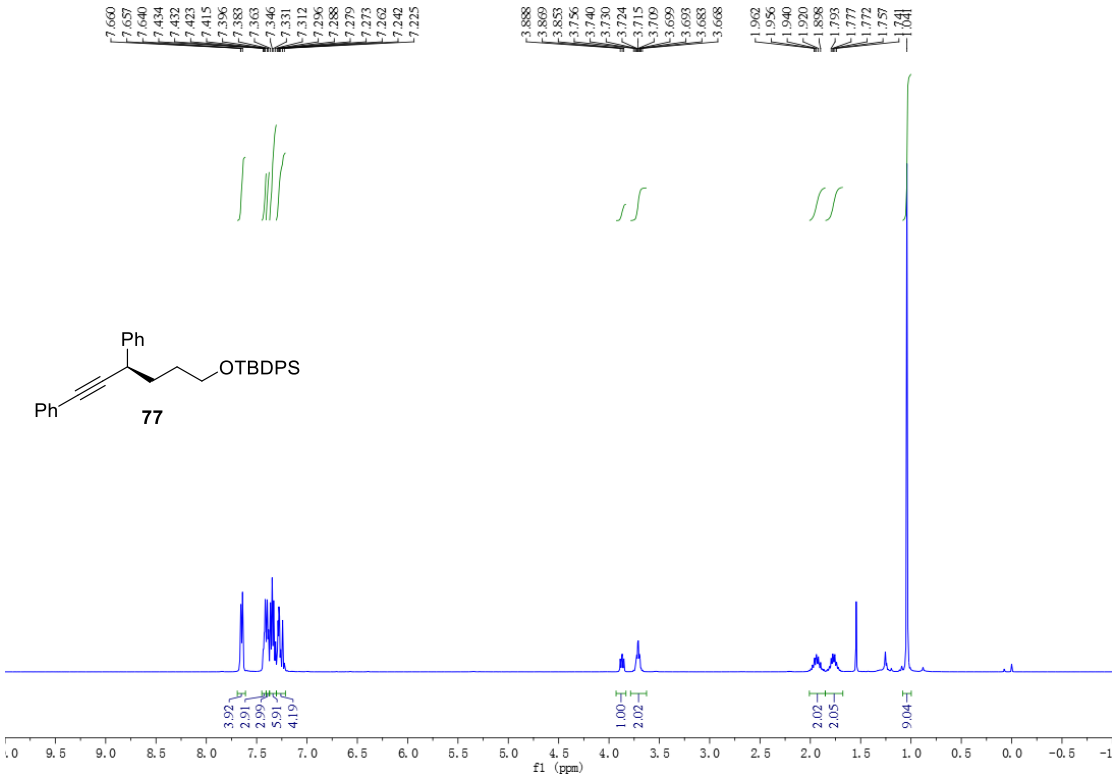
32.874
32.736
30.170
23.027
21.858
Ph
Ph
O
O
76
f1 (ppm)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7.312
7.296
7.288
7.279
7.273
7.262
7.242
7.225
3.888
3.869
3.853
3.756
3.740
3.730
3.724
3.715
3.709
3.699
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1.962
1.956
1.940
1.920
1.898
1.793
1.777
1.772
1.757
1.741
1.041
Ph
OTBDPS
Ph
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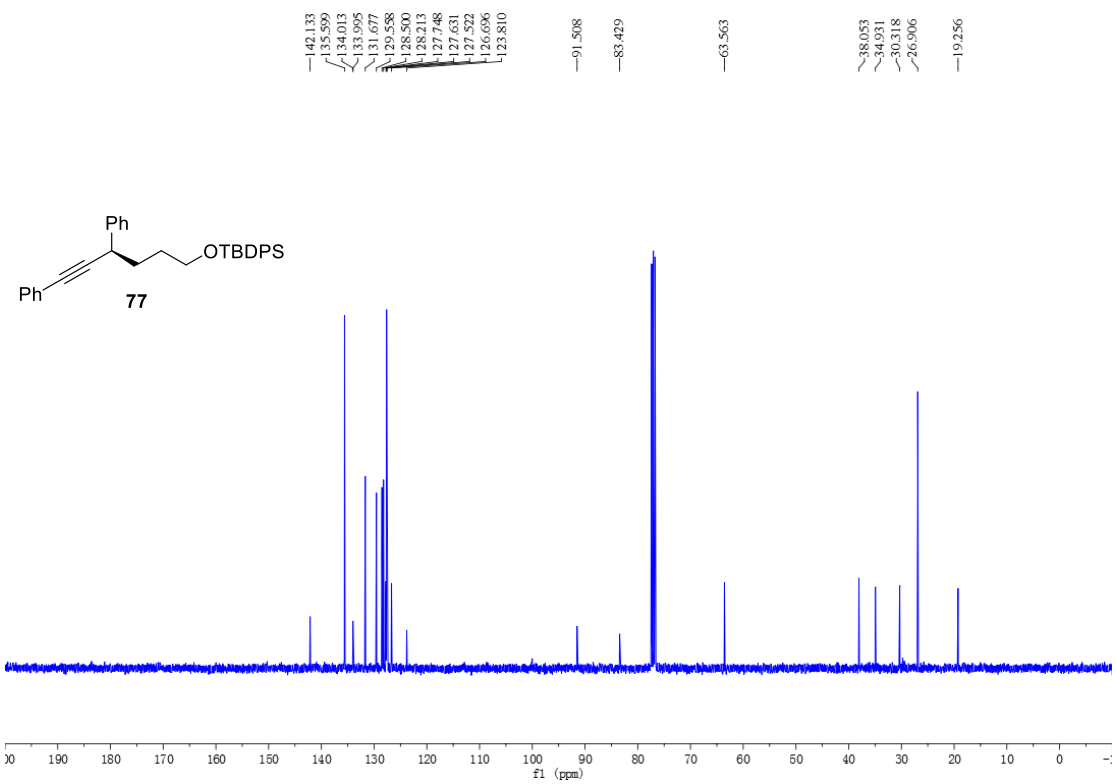
2.99
5.91
4.19
1.00
2.02
2.02
2.05
9.04
f1 (ppm)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133.995
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128.213
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127.522
126.696
123.810
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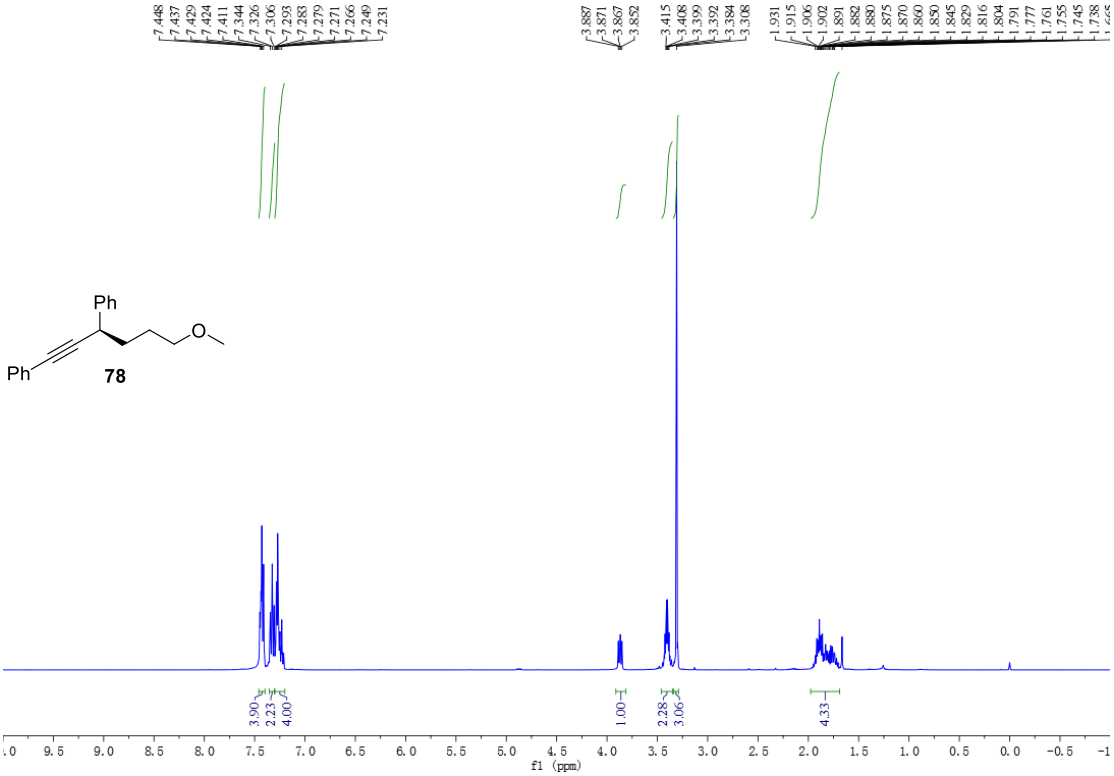
19.256
Ph
OTBDPS
Ph
77
f1 (ppm)


Ph
O
Ph
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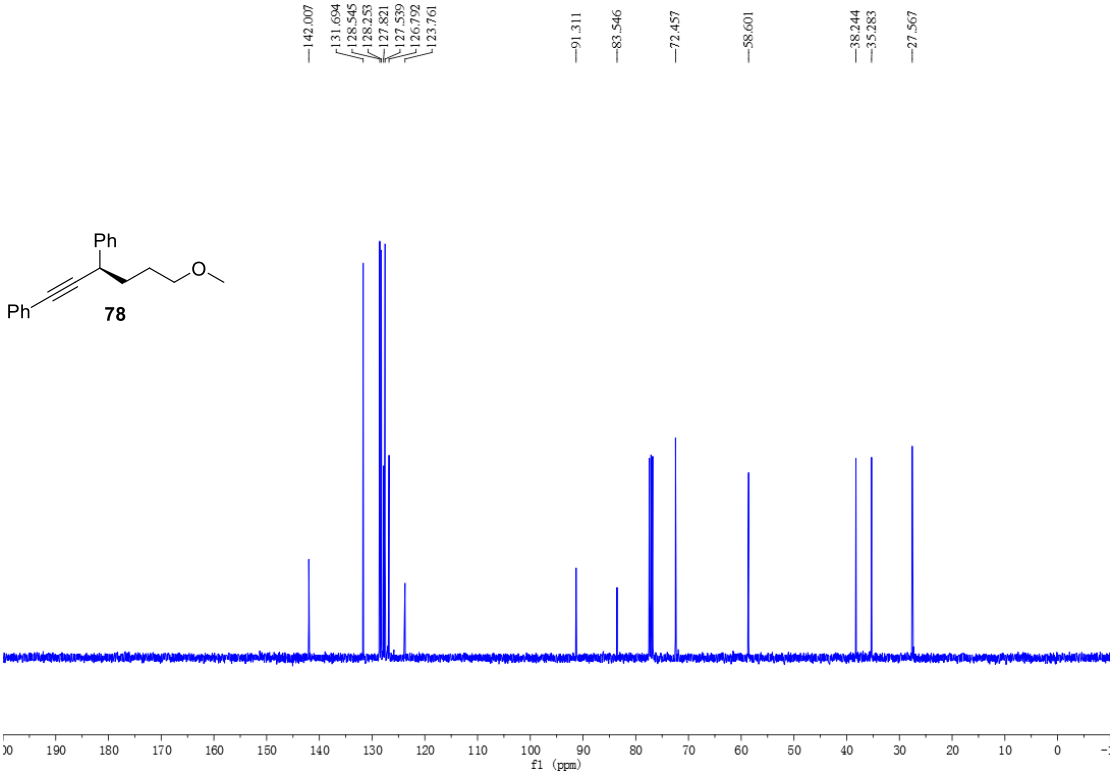
f1 (ppm)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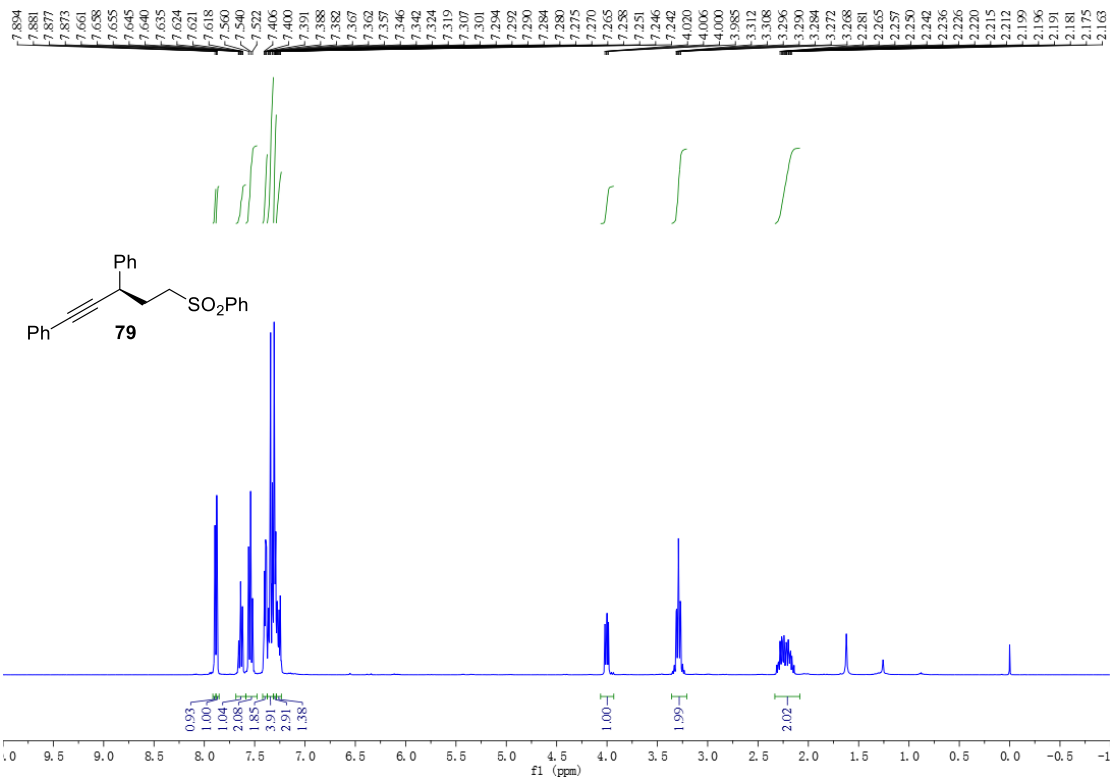
O
Ph
78
f1 (ppm)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SO2Ph
Ph
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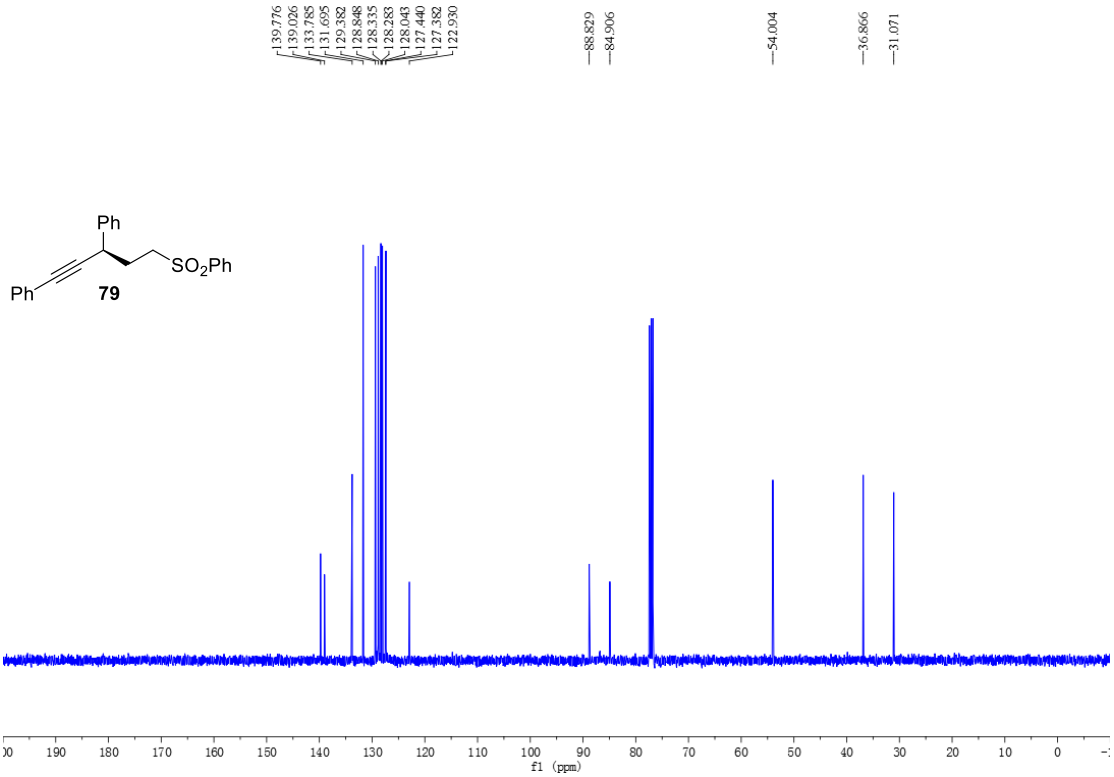
f1 (ppm)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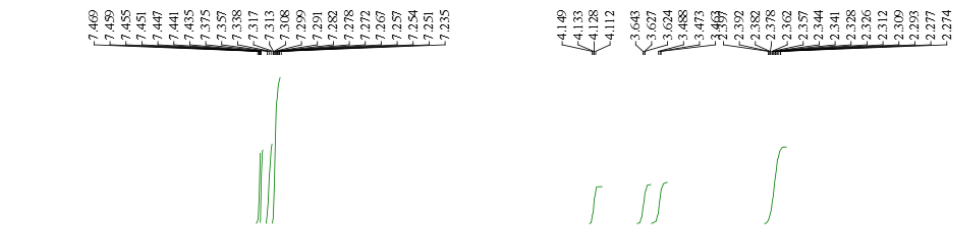
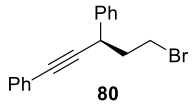
SO2Ph
Ph
79
f1 (ppm)





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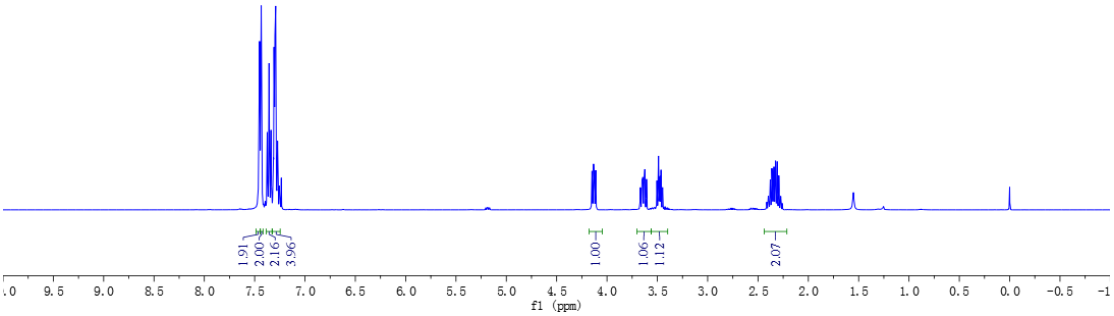

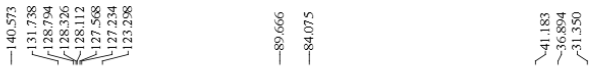

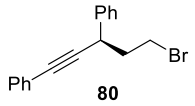

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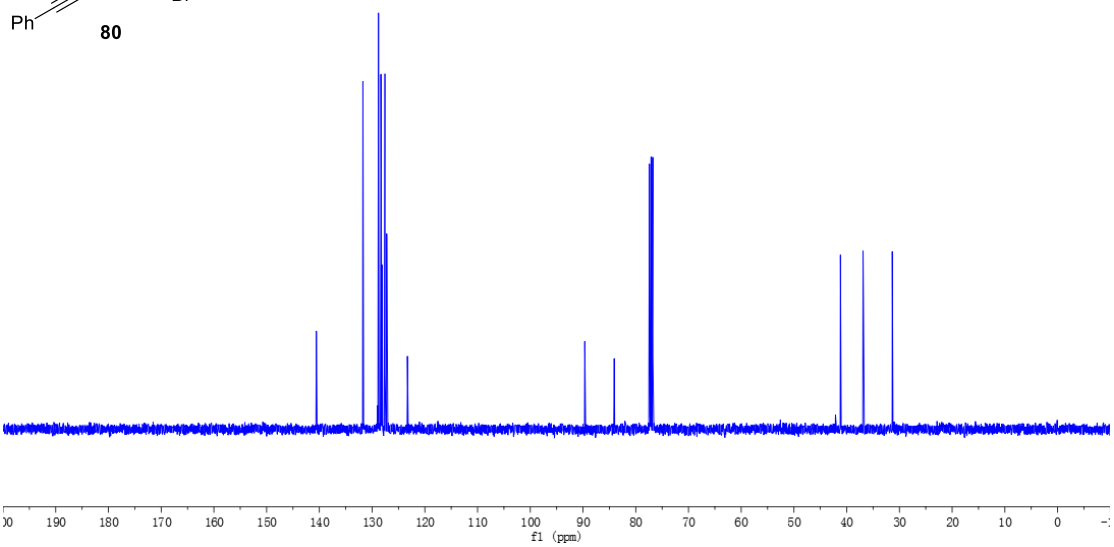

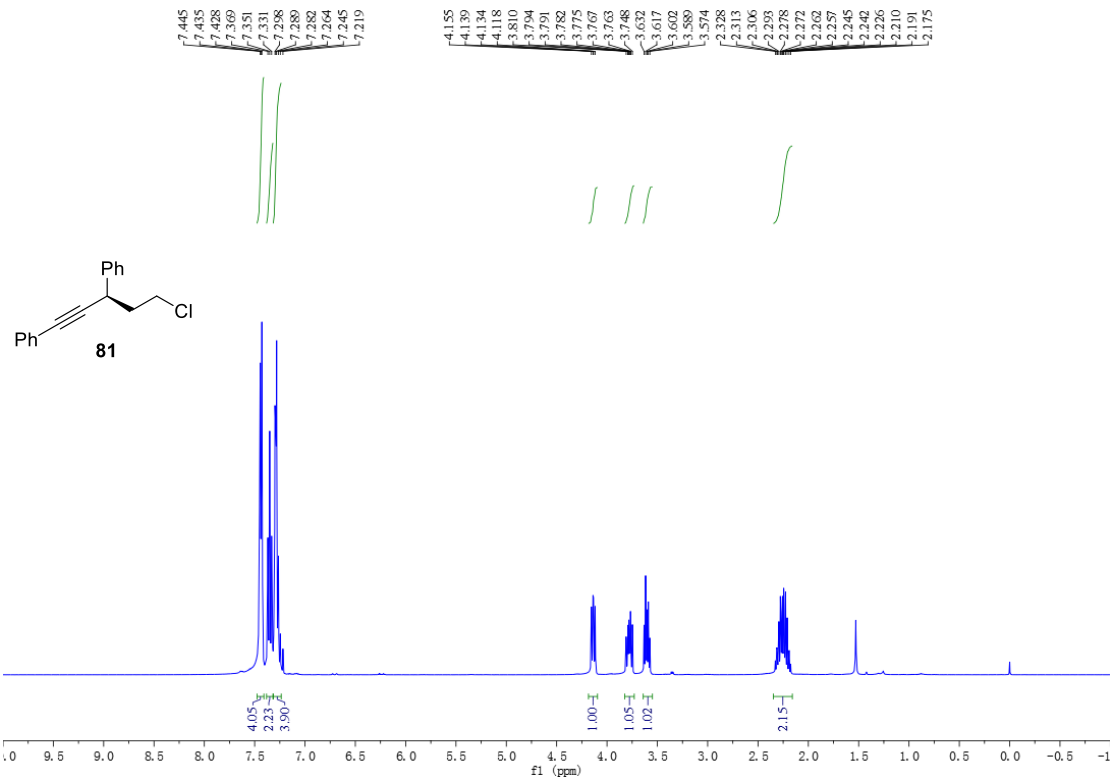
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7.219
4.155
4.139
4.134
4.118
3.810
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3.791
3.782
3.775
3.767
3.763
3.748
3.632
3.617
3.602
3.589
3.574
2.328
2.313
2.306
2.293
2.278
2.272
2.262
2.257
2.245
2.242
2.226
2.210
2.191
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Cl
Ph
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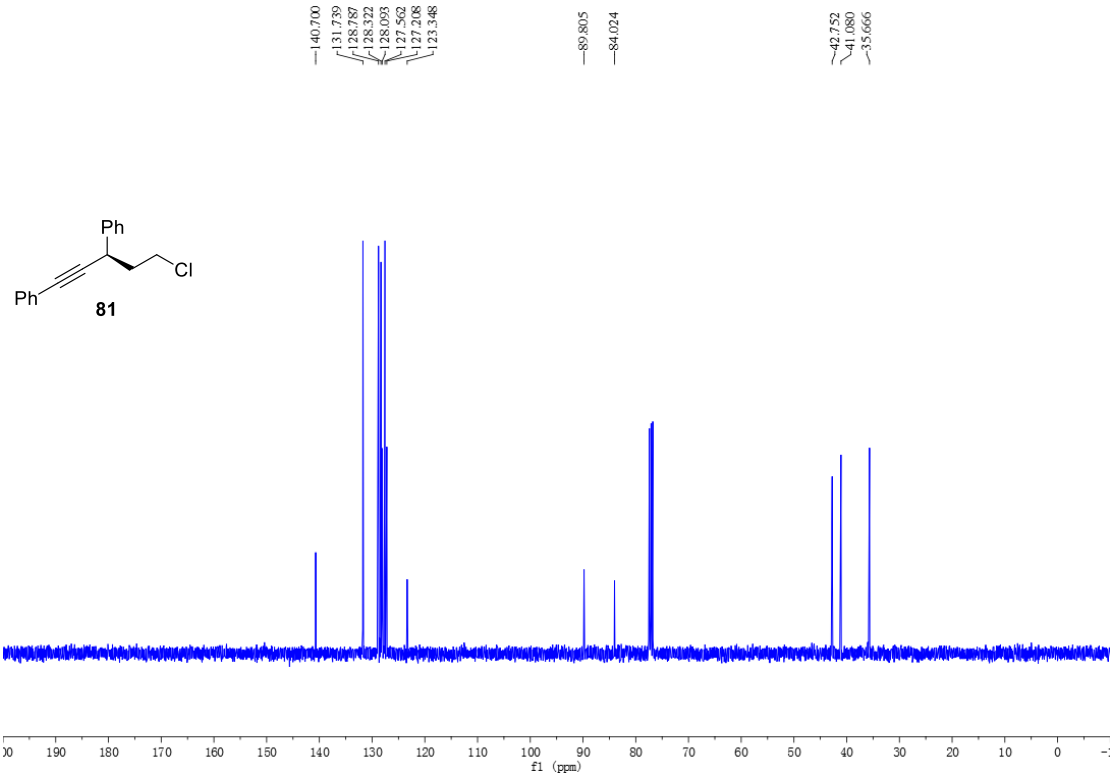
2.15
f1 (ppm)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127.208
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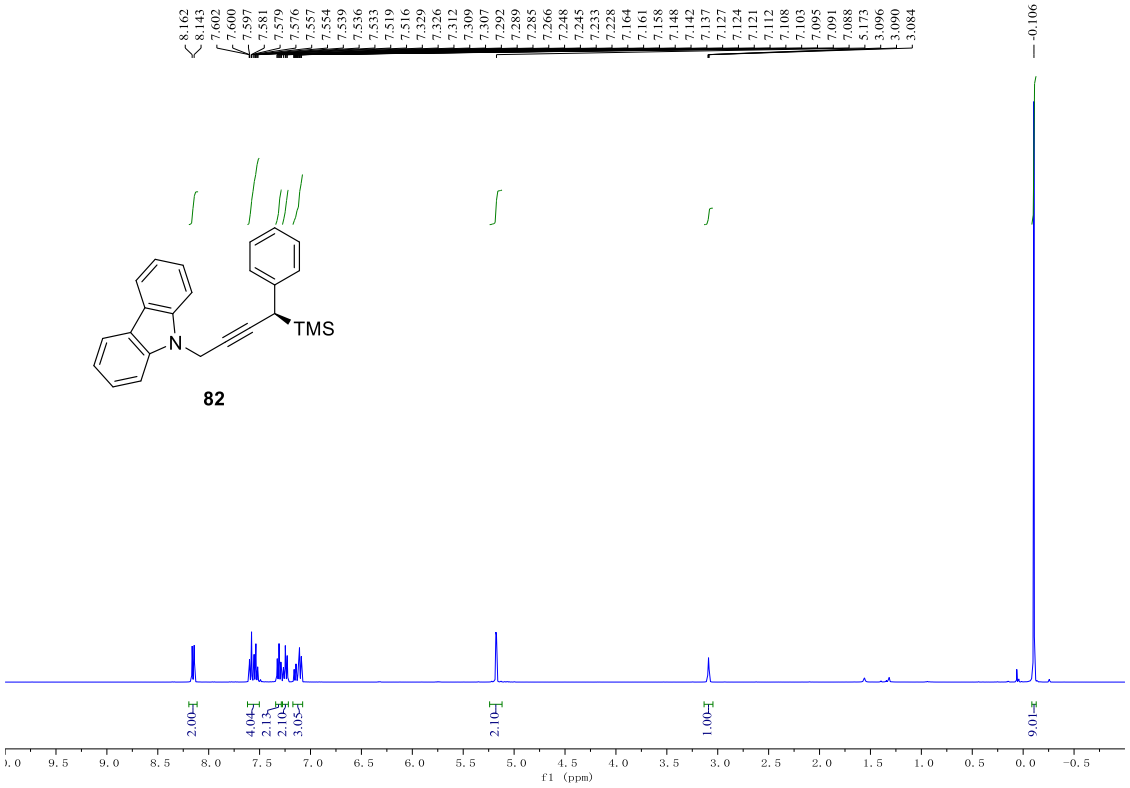
35.666
Ph
Cl
Ph
81
f1 (ppm)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8.143
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7.581
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7.576
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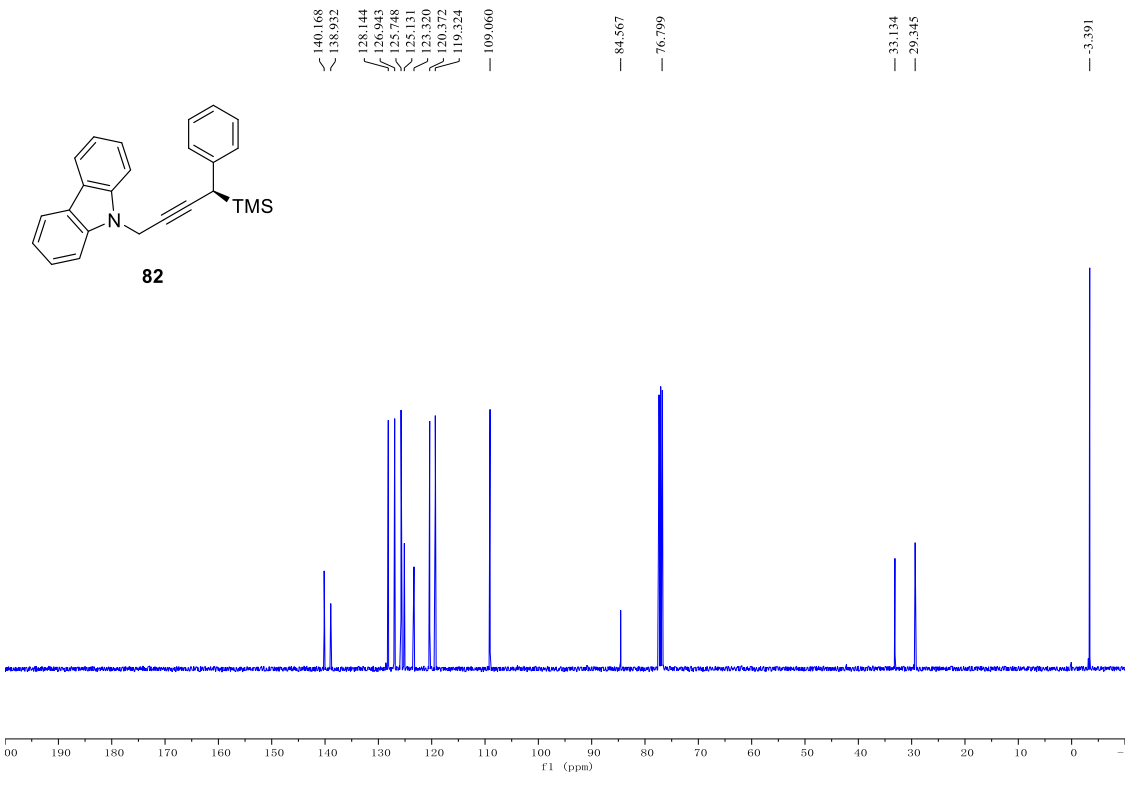
7.536
7.533
7.519
7.516
7.329
7.326
7.312
7.309
7.307
7.292
7.289
7.285
7.266
7.248
7.245
7.233
7.228
7.164
7.161
7.158
7.148
7.142
7.137
7.127
7.124
7.121
7.112
7.108
7.103
7.095
7.091
7.088
5.173
3.096
3.090
3.084
-0.106
TMS
N
82
2.00
4.04
2.13
2.10
3.05
2.10
1.00
9.01
f1 (ppm)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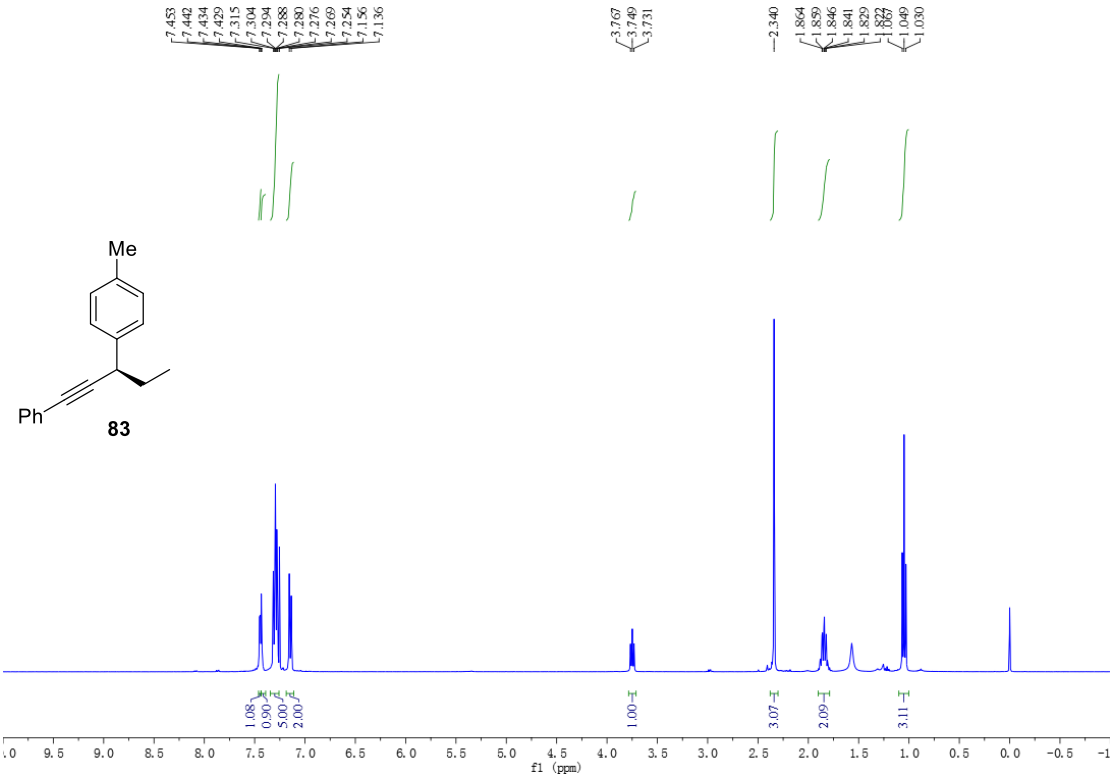
138.932
128.144
126.943
125.748
125.131
123.320
120.372
119.324
109.060
84.567
76.799
33.134
29.345
-3.391
TMS
N
82
f1 (ppm)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7.294
7.288
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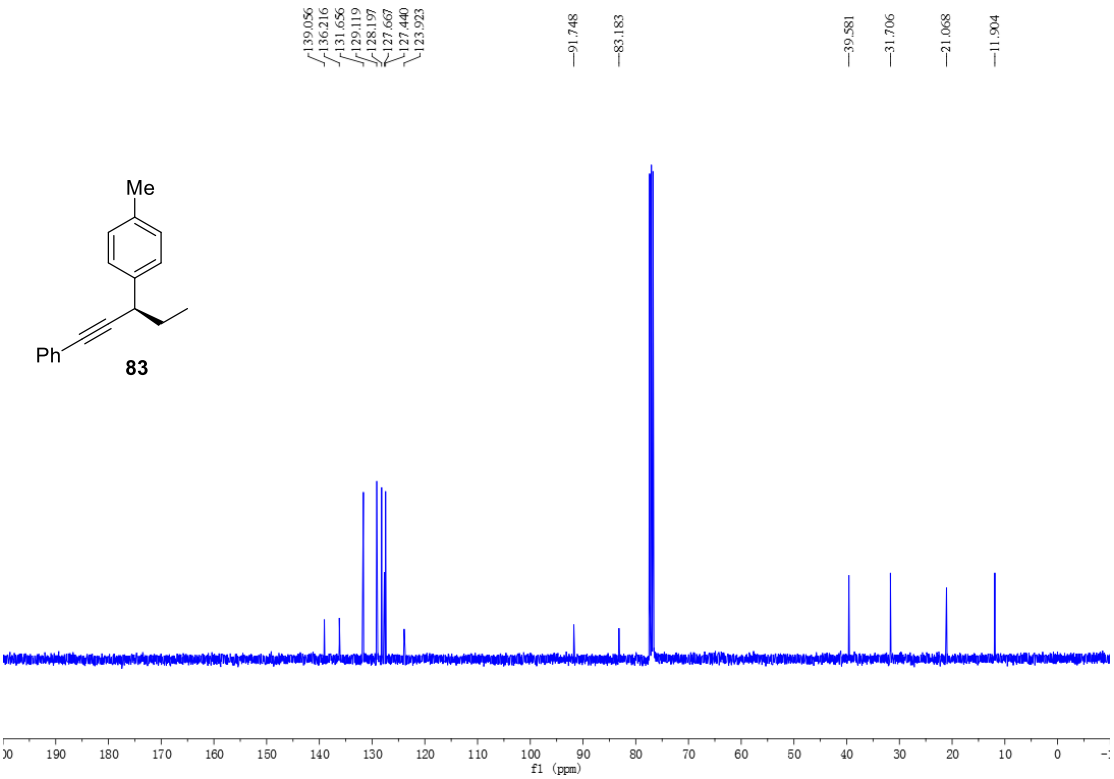
7.276
7.269
7.254
7.156
7.136
3.767
3.749
3.731
2.340
1.864
1.859
1.846
1.841
1.829
1.049
1.030
Me
Ph
83
1.08
0.90
5.00
2.00
1.00
3.07
2.09
3.11
f1 (ppm)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136.216
131.656
129.119
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127.667
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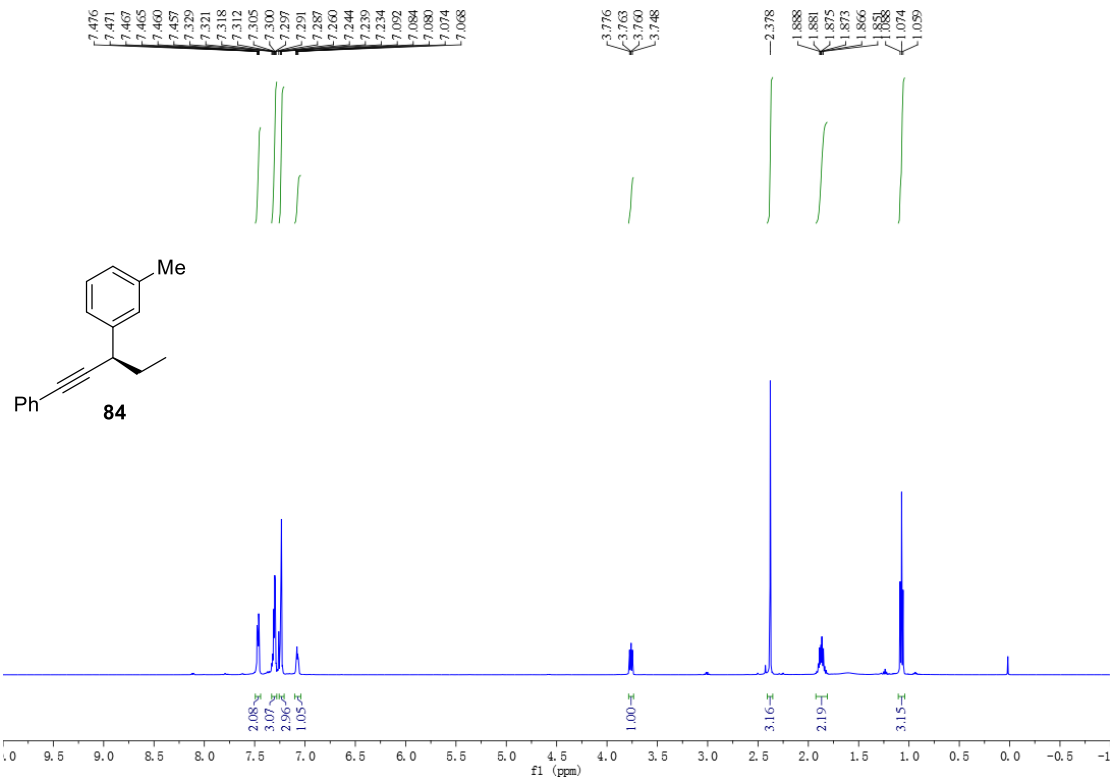
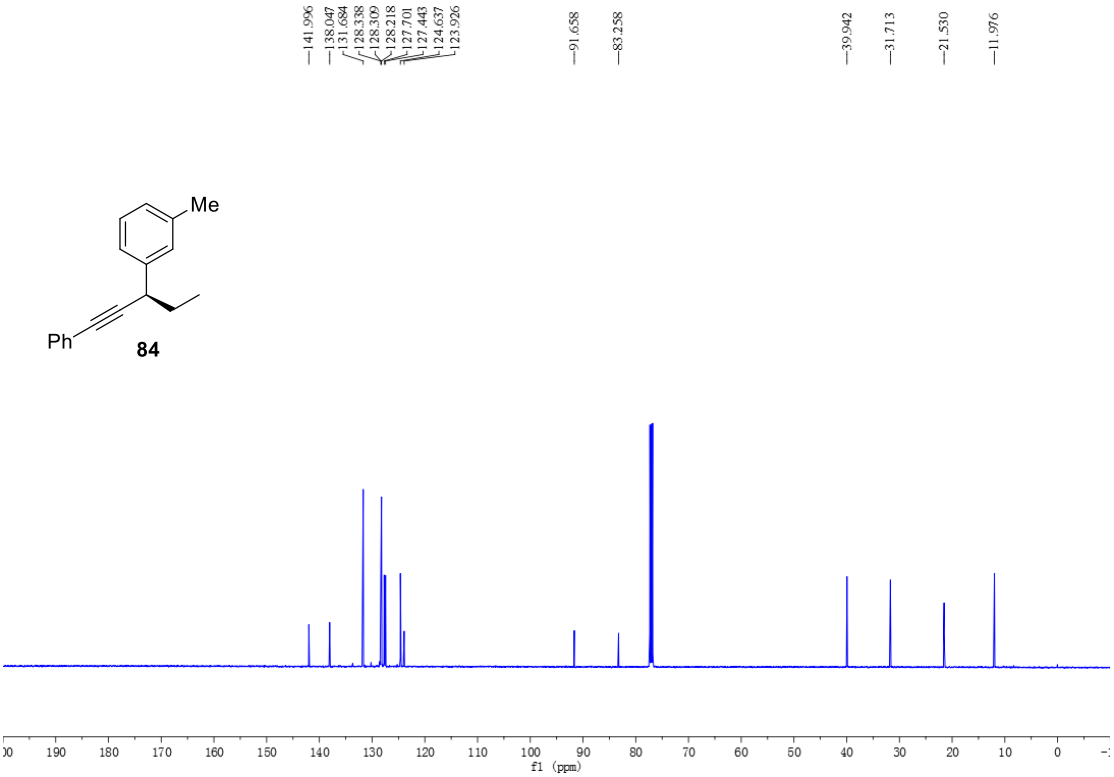
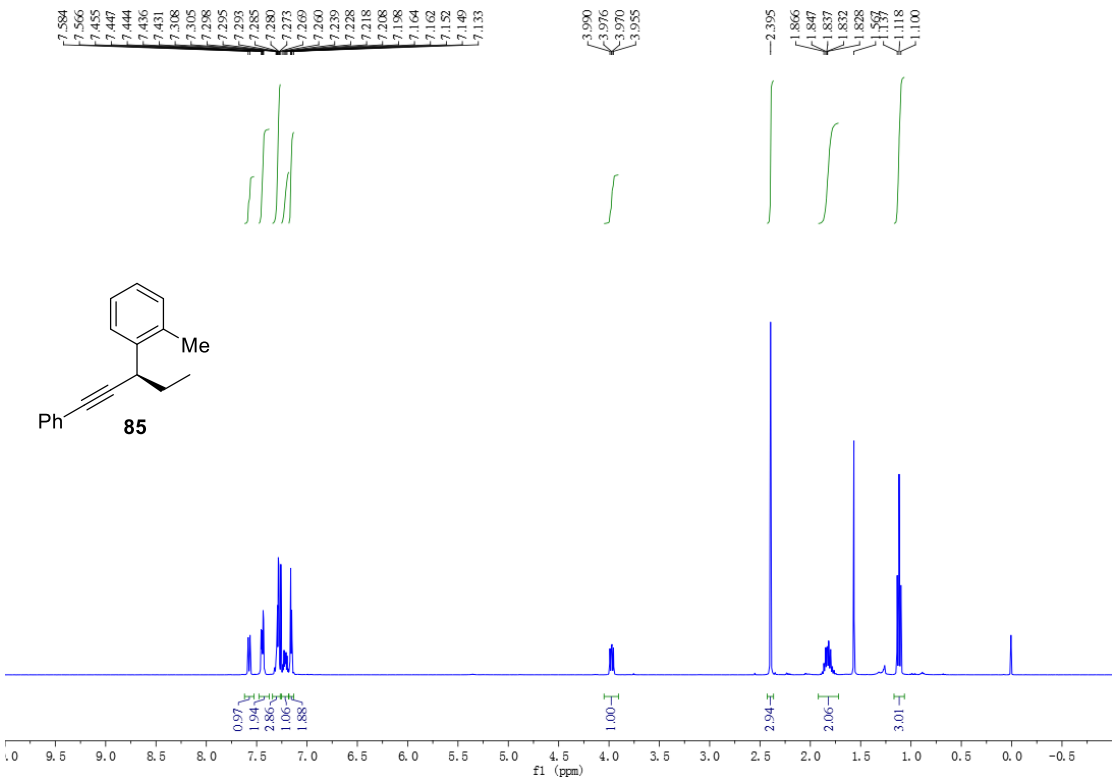
123.923
91.748
83.183
39.581
31.706
21.068
11.904
Me
Ph
83
f1 (ppm)


Me
Ph
84
f1 (ppm)


Me
Ph
84
f1 (ppm)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7.455
7.447
7.444
7.436
7.431
7.308
7.305
7.298
7.295
7.293
7.285
7.280
7.273
7.269
7.260
7.239
7.228
7.218
7.208
7.198
7.164
7.162
7.152
7.149
7.133
3.990
3.976
3.970
3.955
2.395
1.866
1.847
1.837
1.832
1.828
1.567
1.137
1.118
1.100
Me
Ph
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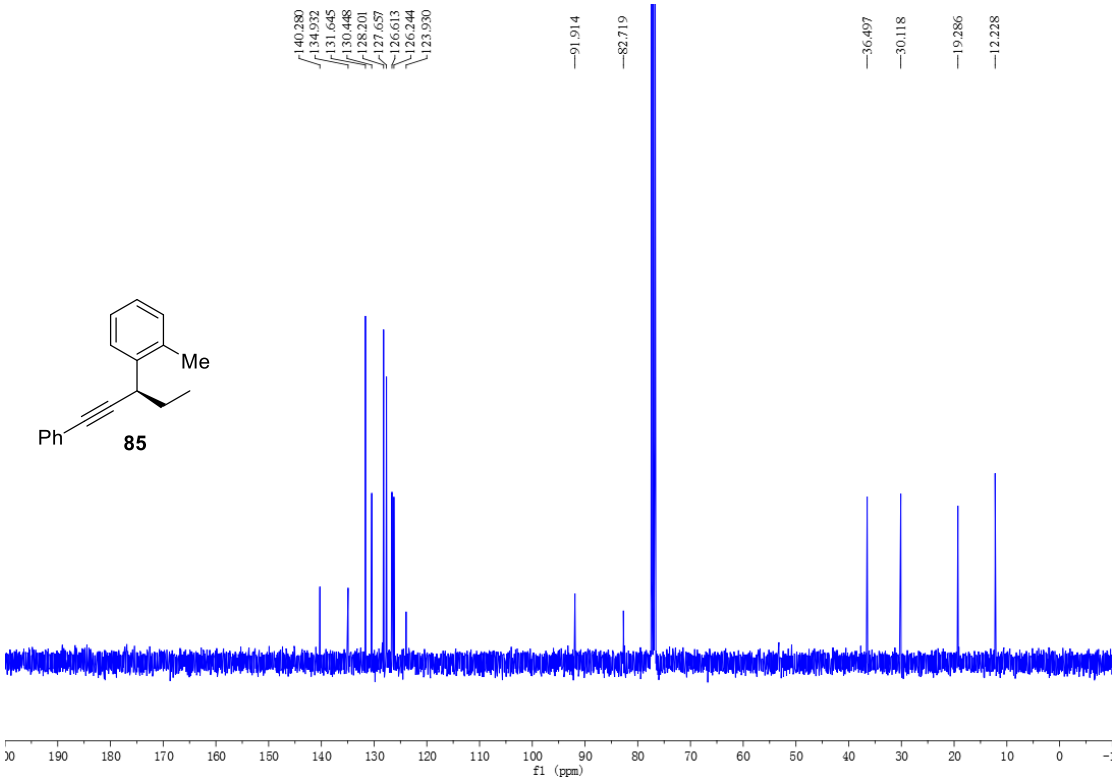
0.97
1.94
2.86
1.06
1.88
1.00
2.94
2.06
3.01
f1 (ppm)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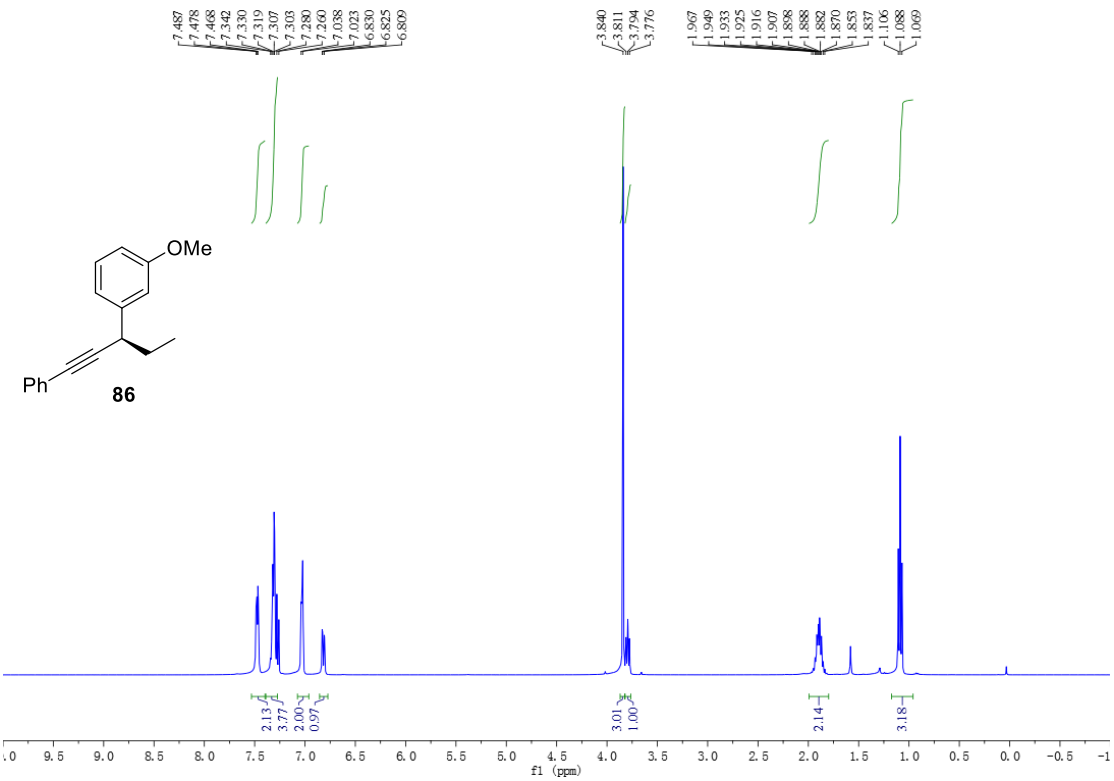
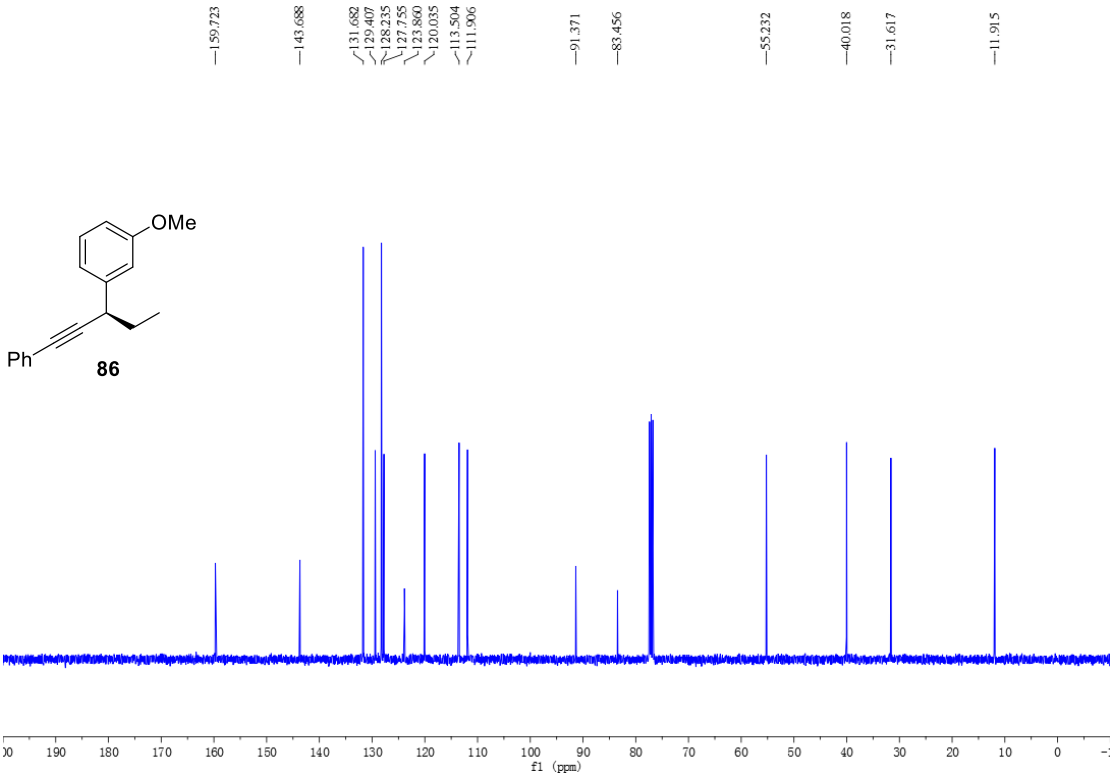
134.932
131.645
130.448
128.201
127.657
126.613
126.244
123.930
91.914
82.719
36.497
30.118
19.286
12.228
Me
Ph
85
f1 (ppm)


7.487
7.478
7.468
7.342
7.330
7.319
7.307
7.303
7.280
7.260
7.038
7.023
6.830
6.825
6.809
3.840
3.811
3.794
3.776
1.967
1.949
1.933
1.925
1.916
1.907
1.898
1.888
1.882
1.870
1.853
1.837
1.106
1.088
1.069
OMe
Ph
86
2.13
3.77
2.00
0.97
3.01
1.00
2.14
3.18
f1 (ppm)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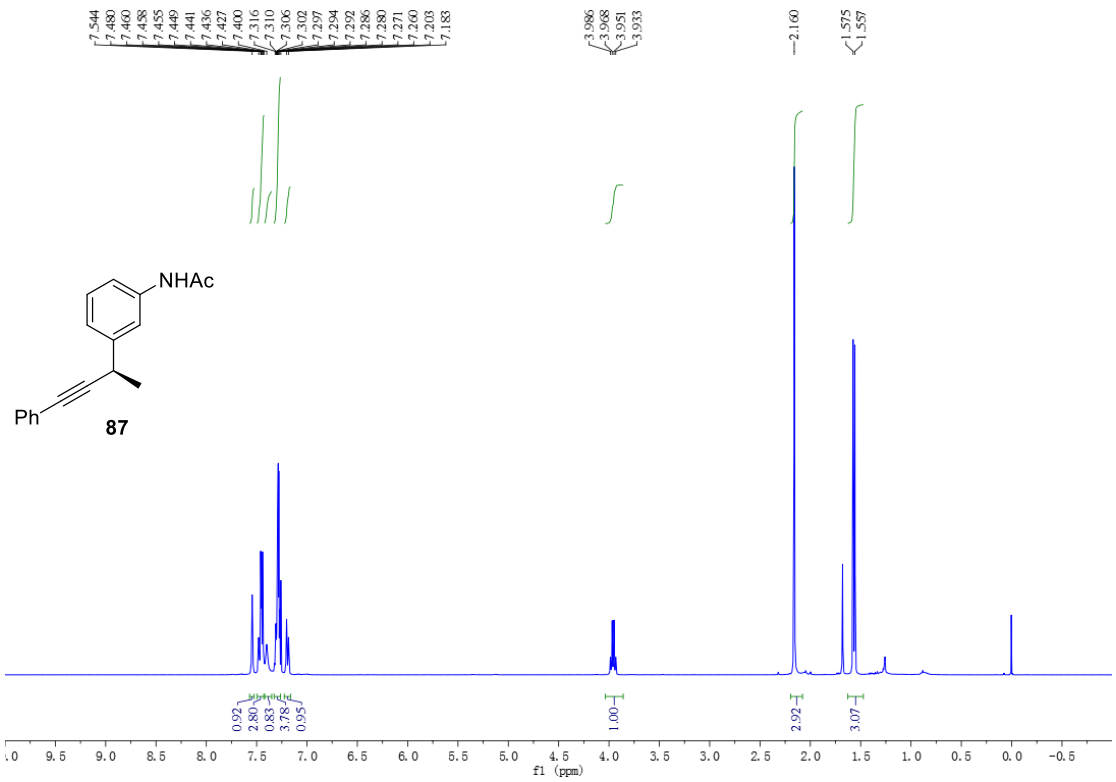
143.688
131.682
129.407
128.235
127.755
123.860
120.035
113.504
111.906
91.371
83.456
55.232
40.018
31.617
11.915
OMe
Ph
86
f1 (ppm)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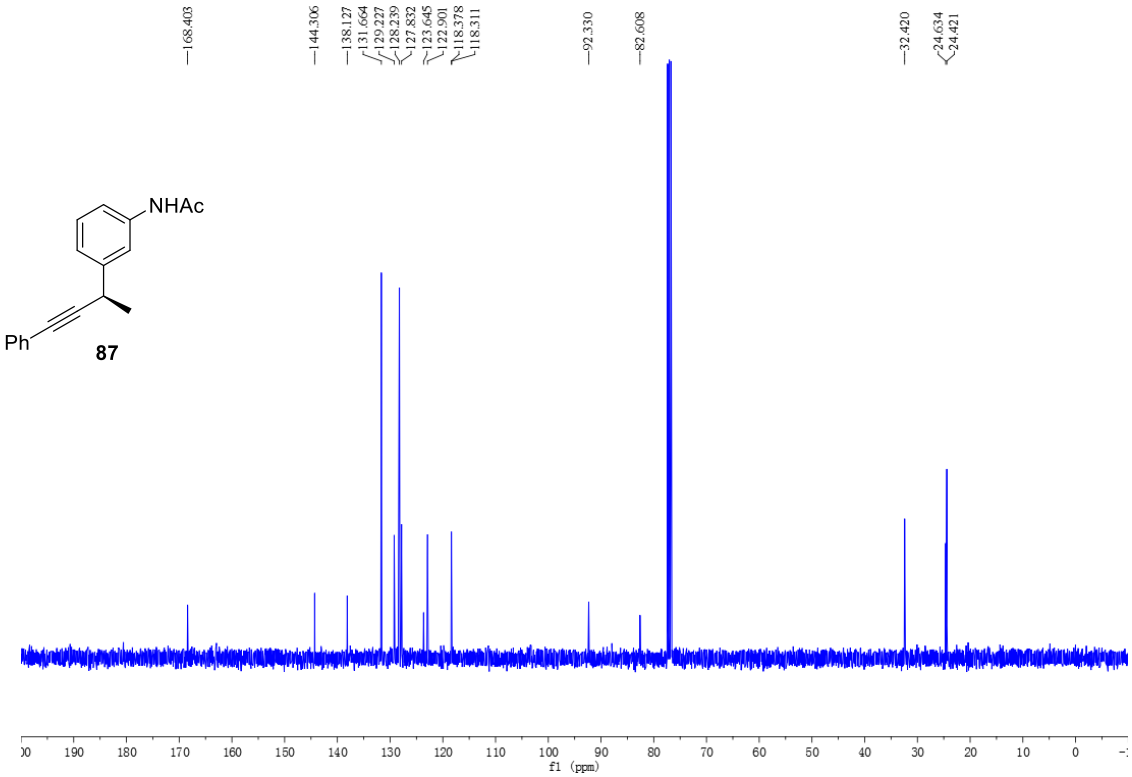
7.480
7.460
7.458
7.455
7.449
7.441
7.436
7.427
7.400
7.316
7.310
7.306
7.302
7.297
7.294
7.292
7.286
7.280
7.271
7.260
7.203
7.183
3.986
3.968
3.951
3.933
2.160
1.575
1.557
NHAc
Ph
87
0.92
2.80
0.83
3.78
0.95
1.00
2.92
3.07
f1 (ppm)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144.306
138.127
131.664
129.227
128.239
127.832
123.645
122.901
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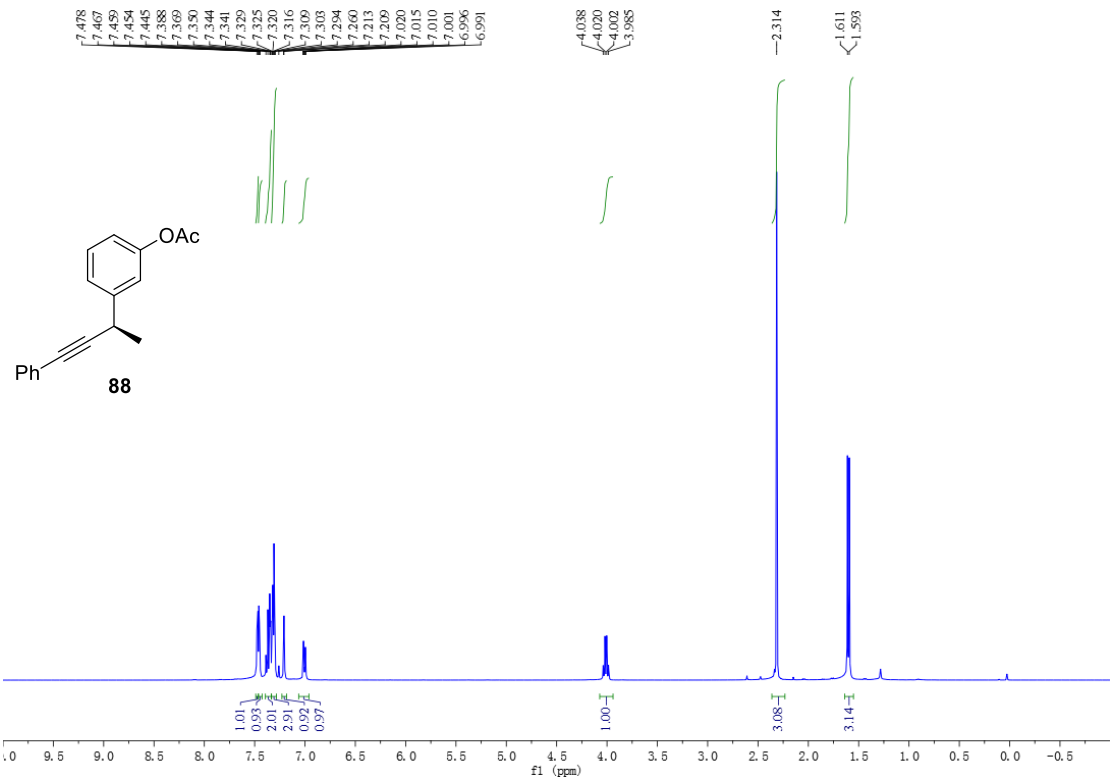
118.311
92.330
82.608
32.420
24.634
24.421
NHAc
Ph
87
f1 (ppm)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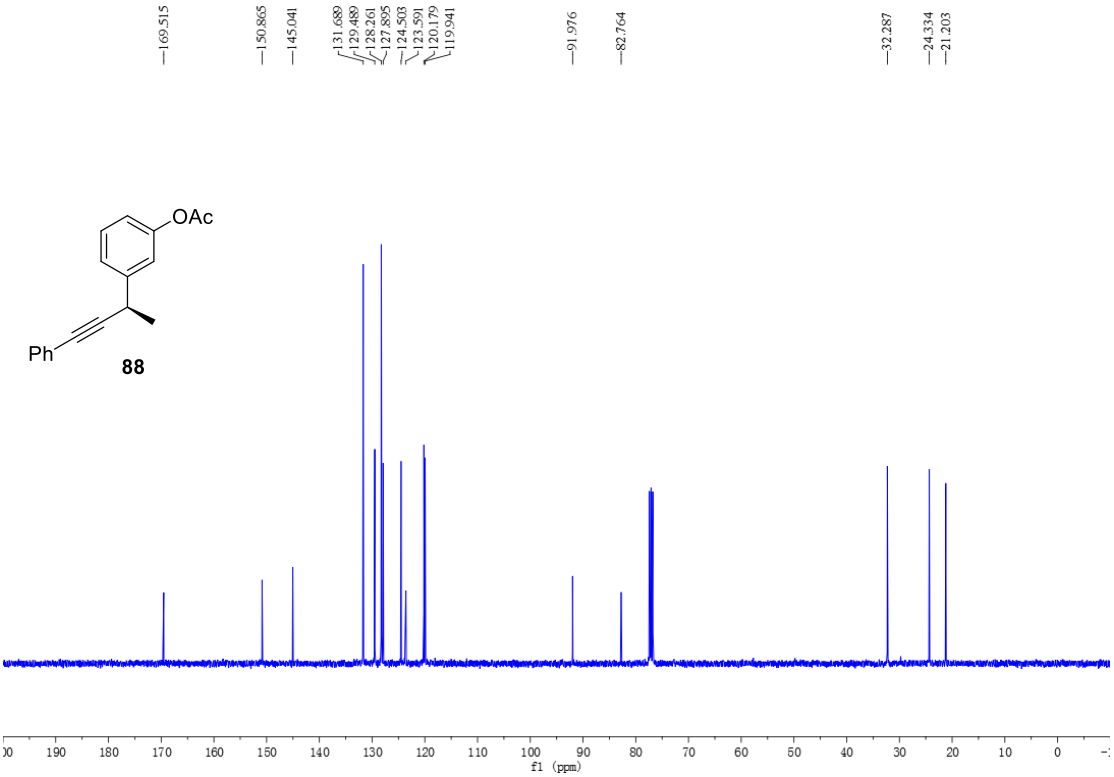
7.467
7.459
7.454
7.445
7.388
7.369
7.350
7.344
7.341
7.329
7.325
7.320
7.316
7.309
7.303
7.294
7.260
7.213
7.209
7.020
7.015
7.010
7.001
6.996
6.991
4.038
4.020
4.002
3.985
2.314
1.611
1.593
OAc
Ph
88
1.01
0.93
2.01
2.91
0.92
0.97
1.00
3.08
3.14
f1 (ppm)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150.865
145.041
131.689
129.489
128.261
127.895
124.503
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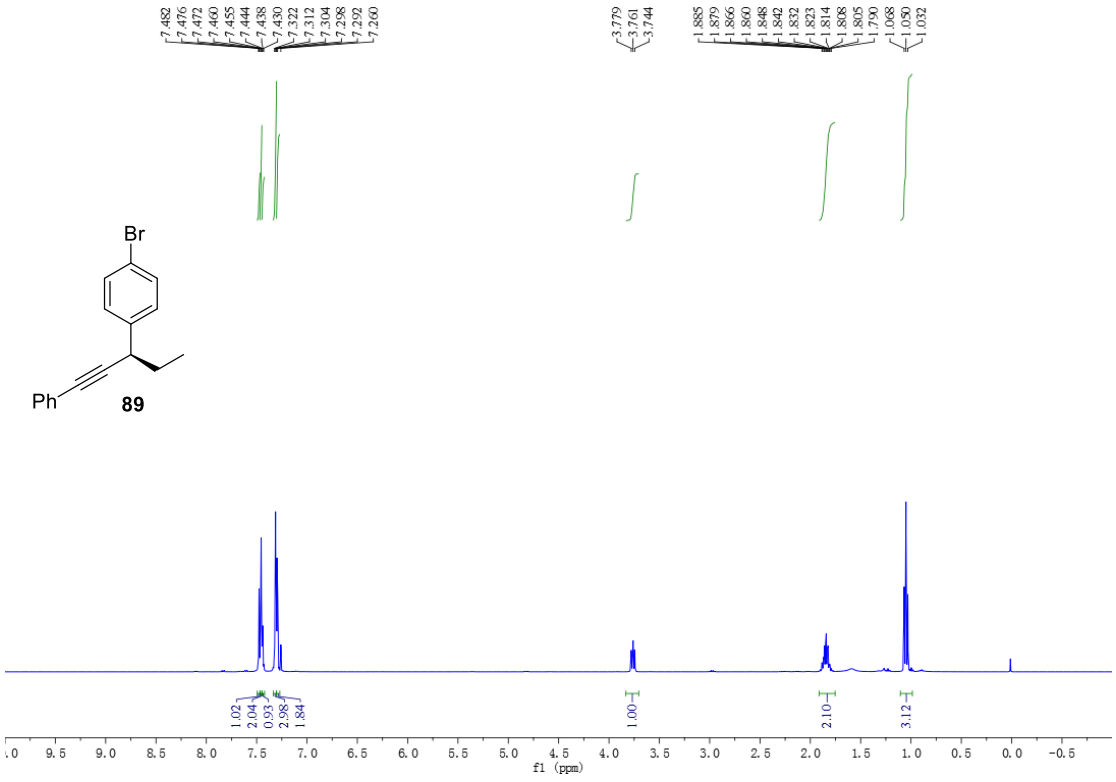
119.941
91.976
82.764
32.287
24.334
21.203
OAc
Ph
88
f1 (ppm)


7.482
7.476
7.472
7.460
7.455
7.444
7.438
7.430
7.322
7.312
7.304
7.298
7.292
7.260
3.779
3.761
3.744
1.885
1.879
1.866
1.860
1.848
1.842
1.832
1.823
1.814
1.808
1.805
1.790
1.068
1.050
1.032
Br
Ph
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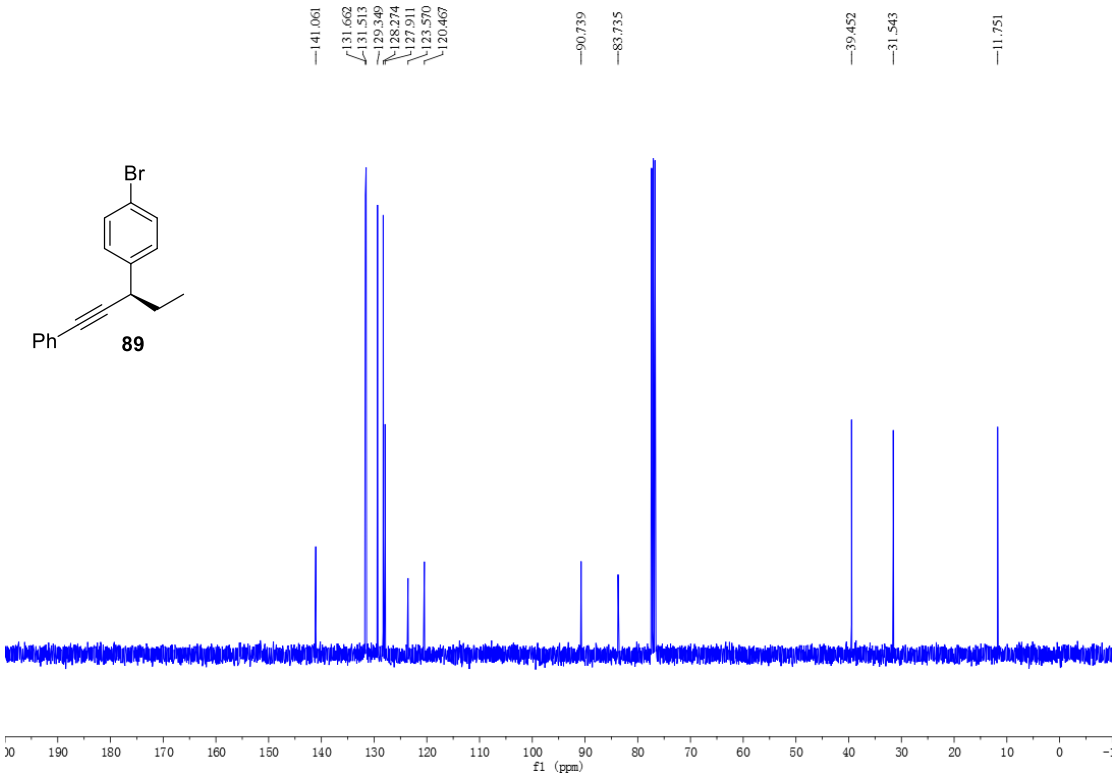
1.02
2.04
0.93
2.98
1.84
1.00
2.10
3.12
f1 (ppm)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129.349
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120.467
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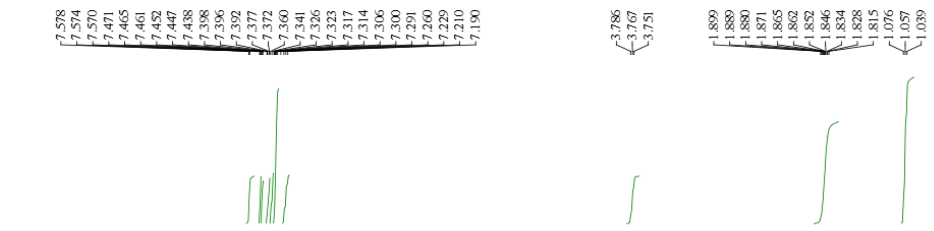
83.735
39.452
31.543
11.751
Br
Ph
89
f1 (ppm)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7.377
7.372
7.360
7.341
7.326
7.323
7.317
7.314
7.306
7.300
7.291
7.260
7.229
7.210
7.190
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1.815
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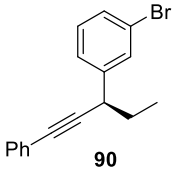
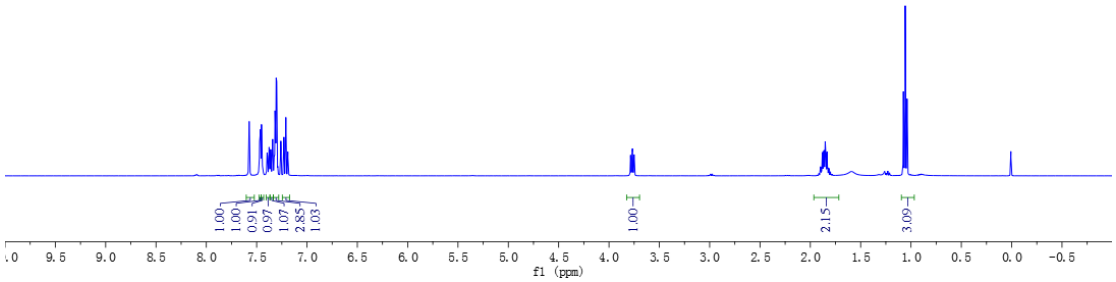
1.057
1.039


Br
Ph

90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1.00
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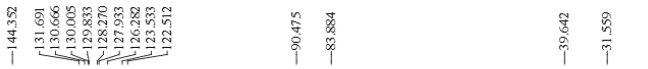
0.97
1.07
2.85
1.03
1.00
2.15
3.09
f1 (ppm)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127.933
126.282
123.533
122.512
90.475
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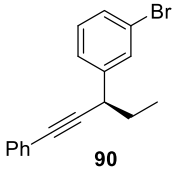
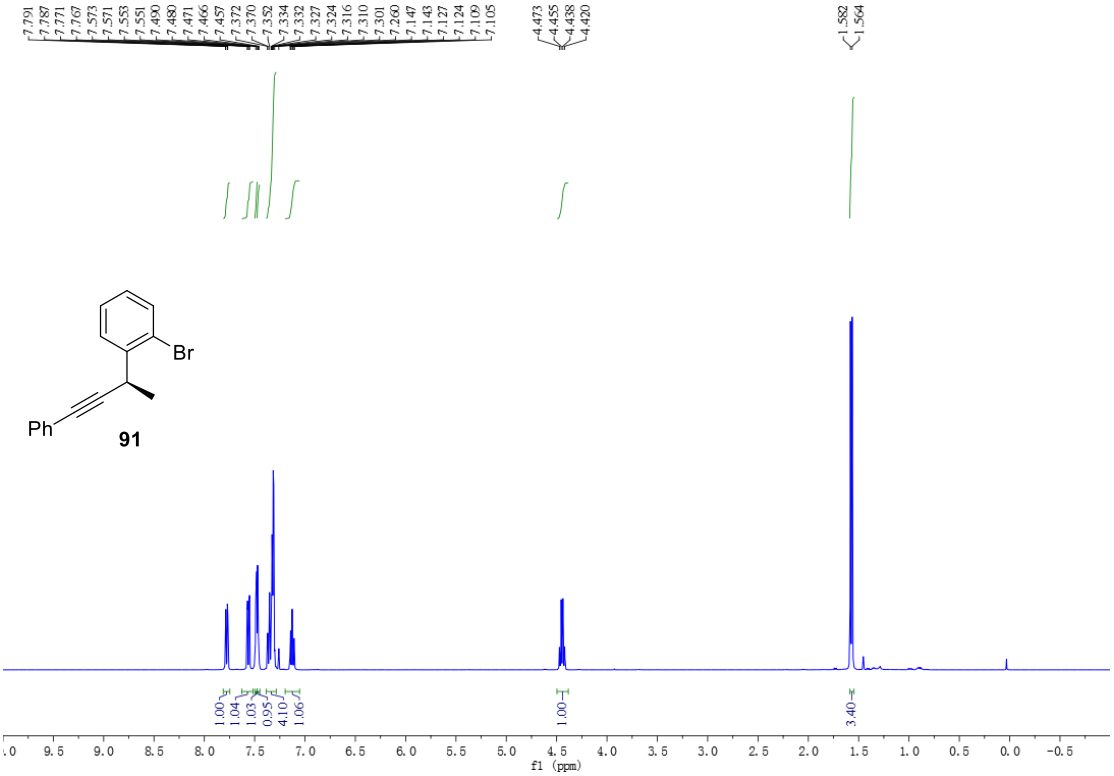
39.642
31.559
11.783


Br
Ph

90

f1 (ppm)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7.551
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7.480
7.471
7.466
7.457
7.372
7.370
7.352
7.334
7.332
7.327
7.324
7.316
7.310
7.301
7.260
7.147
7.143
7.127
7.124
7.109
7.105
4.473
4.455
4.438
4.420
1.582
1.564
Br
Ph
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1.03
0.95
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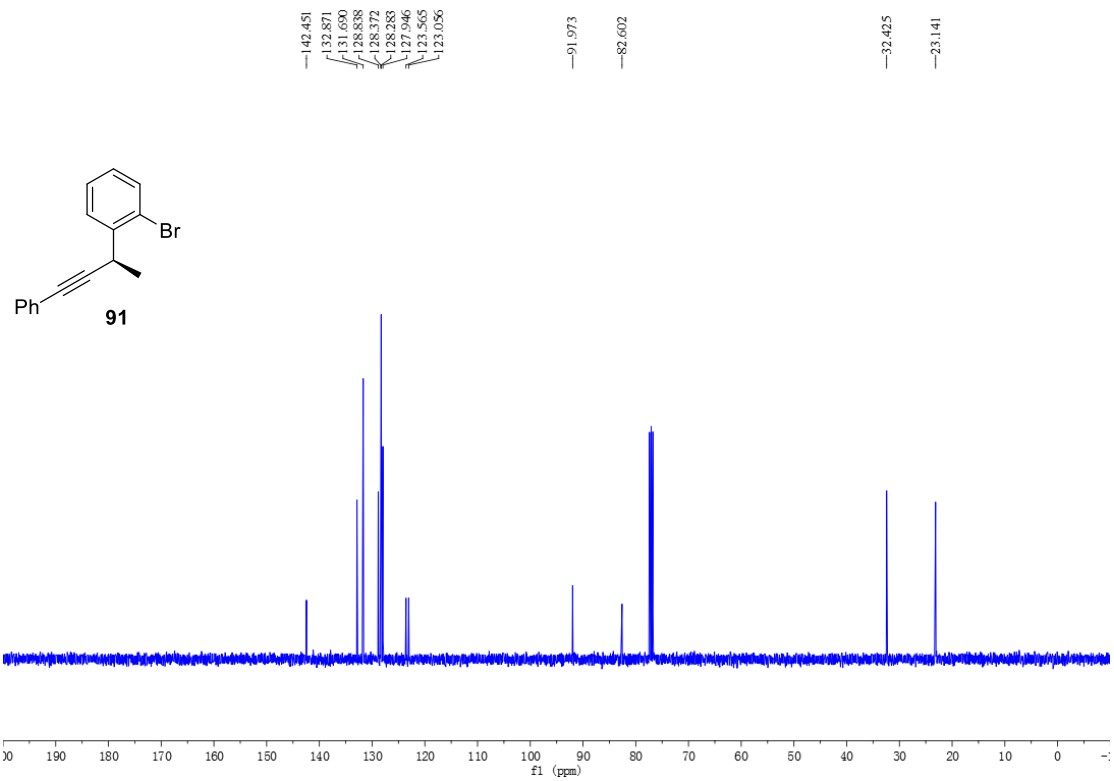
1.06
1.00
3.40
f1 (ppm)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128.372
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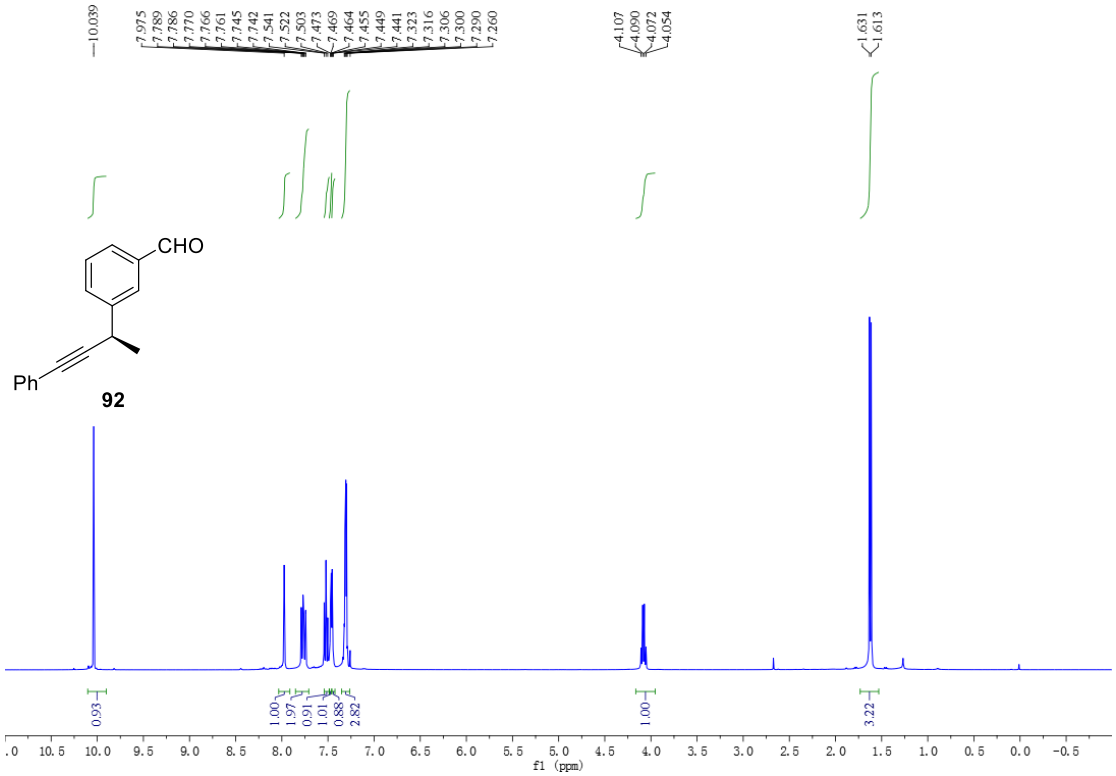
Br
Ph
91
f1 (ppm)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7.745
7.742
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7.522
7.503
7.473
7.469
7.464
7.455
7.449
7.441
7.323
7.316
7.306
7.300
7.290
7.260
4.107
4.090
4.072
4.054
1.631
1.613
CHO
Ph
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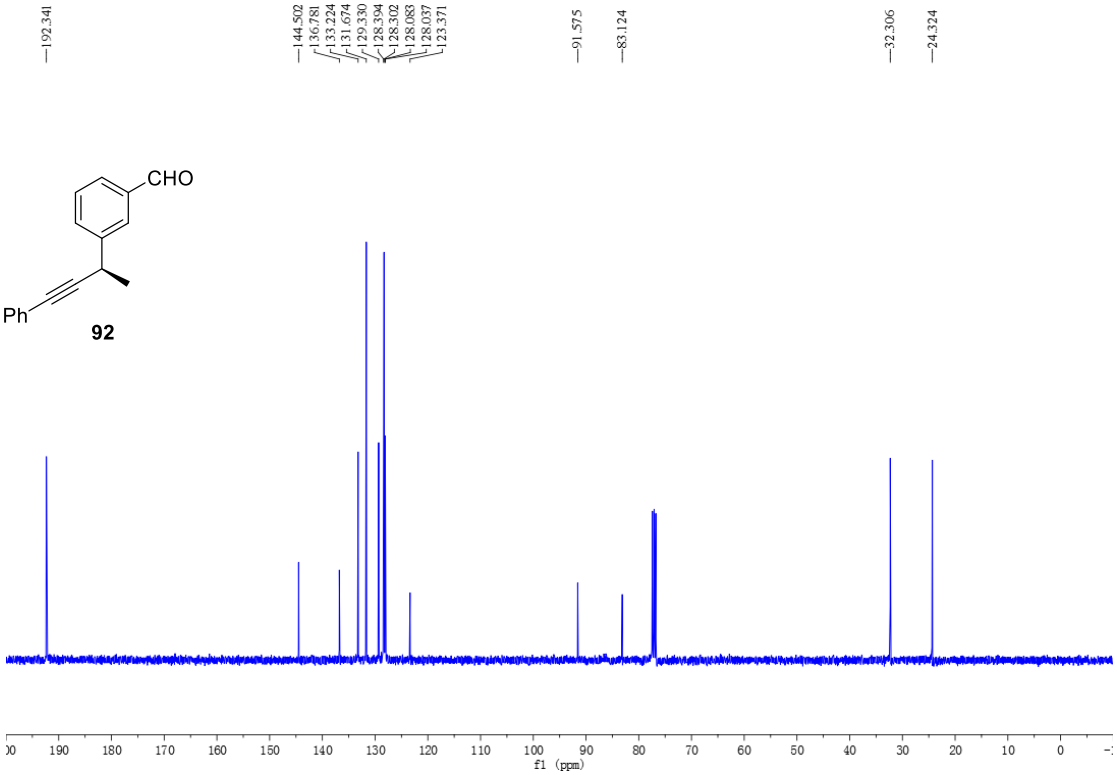
2.82
1.00
3.22
f1 (ppm)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129.330
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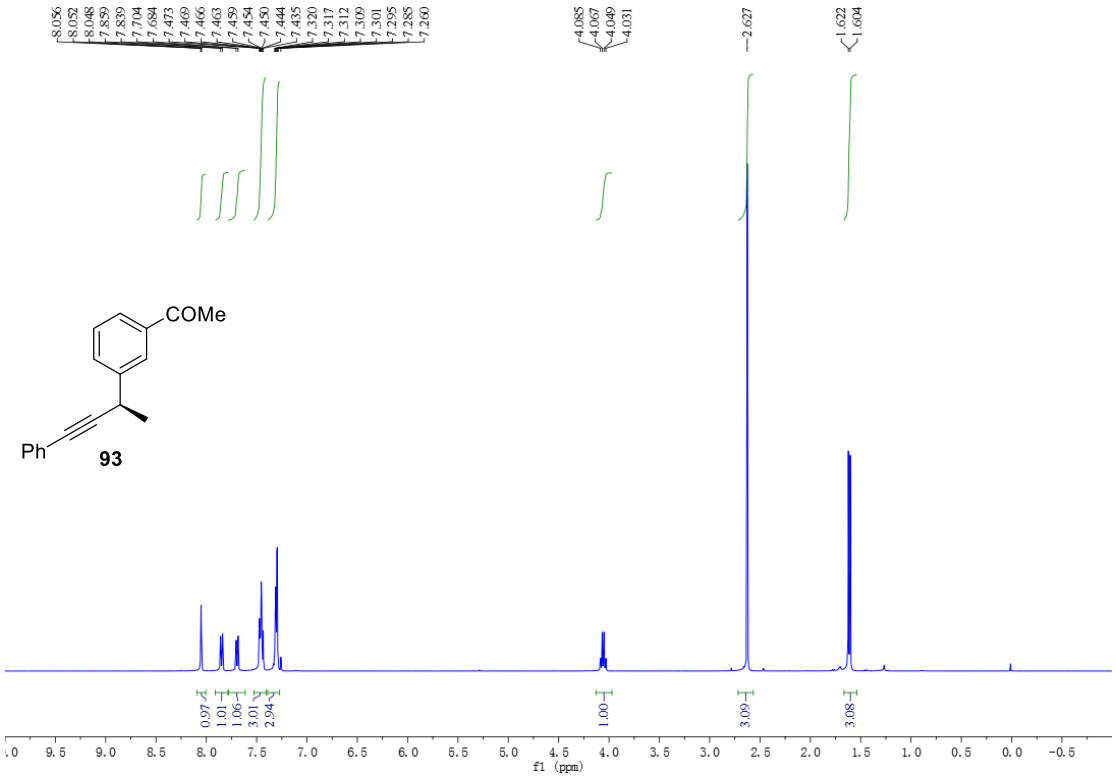
128.083
128.037
123.371
91.575
83.124
32.306
24.324
CHO
Ph
92
f1 (ppm)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8.052
8.048
7.859
7.839
7.704
7.684
7.473
7.469
7.466
7.463
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7.450
7.444
7.435
7.320
7.317
7.312
7.309
7.301
7.295
7.285
7.260
4.085
4.067
4.049
4.031
2.627
1.622
1.604
COMe
Ph
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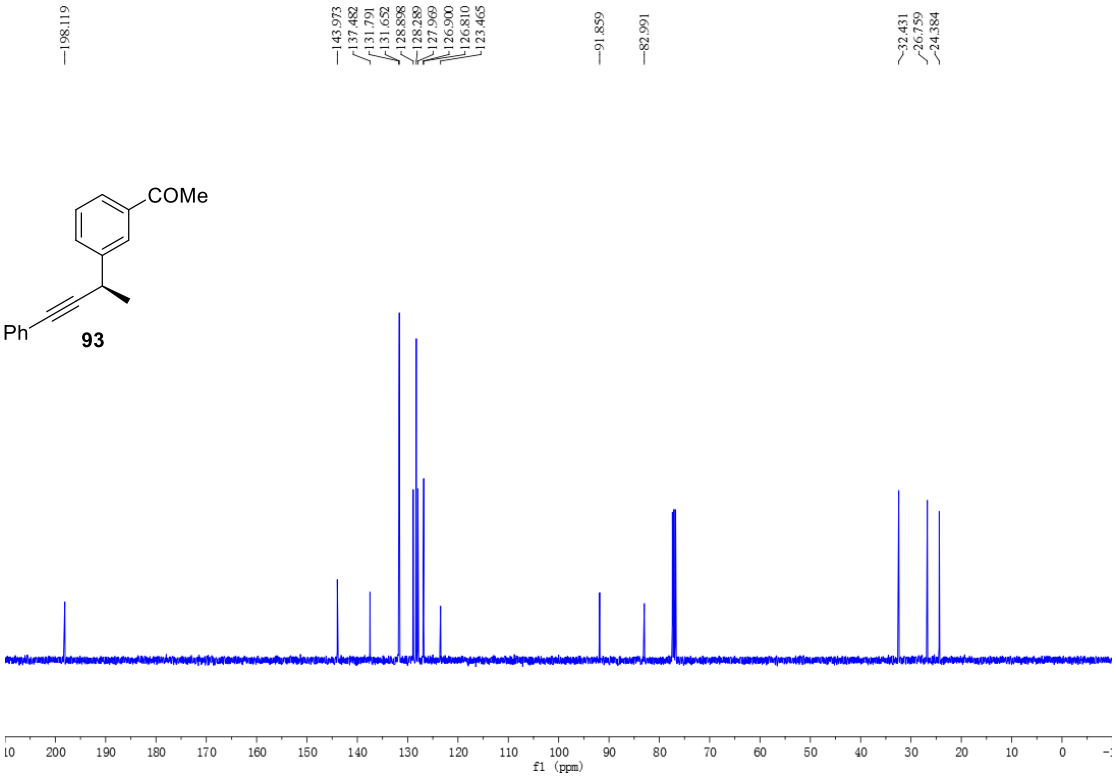
0.97
1.01
1.06
3.01
2.94
1.00
3.09
3.08
f1 (ppm)


198.119
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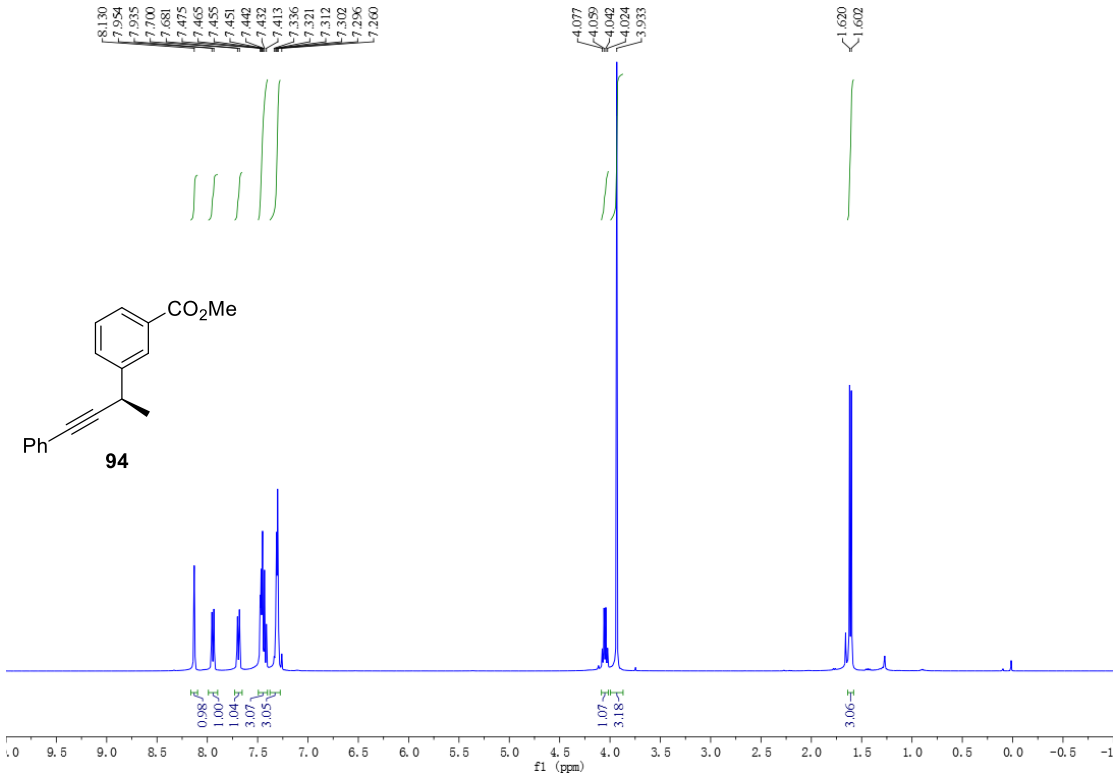
137.482
131.791
131.652
128.898
128.289
127.969
126.900
126.810
123.465
91.859
82.991
32.431
26.759
24.584
COMe
Ph
93
f1 (ppm)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7.475
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7.455
7.451
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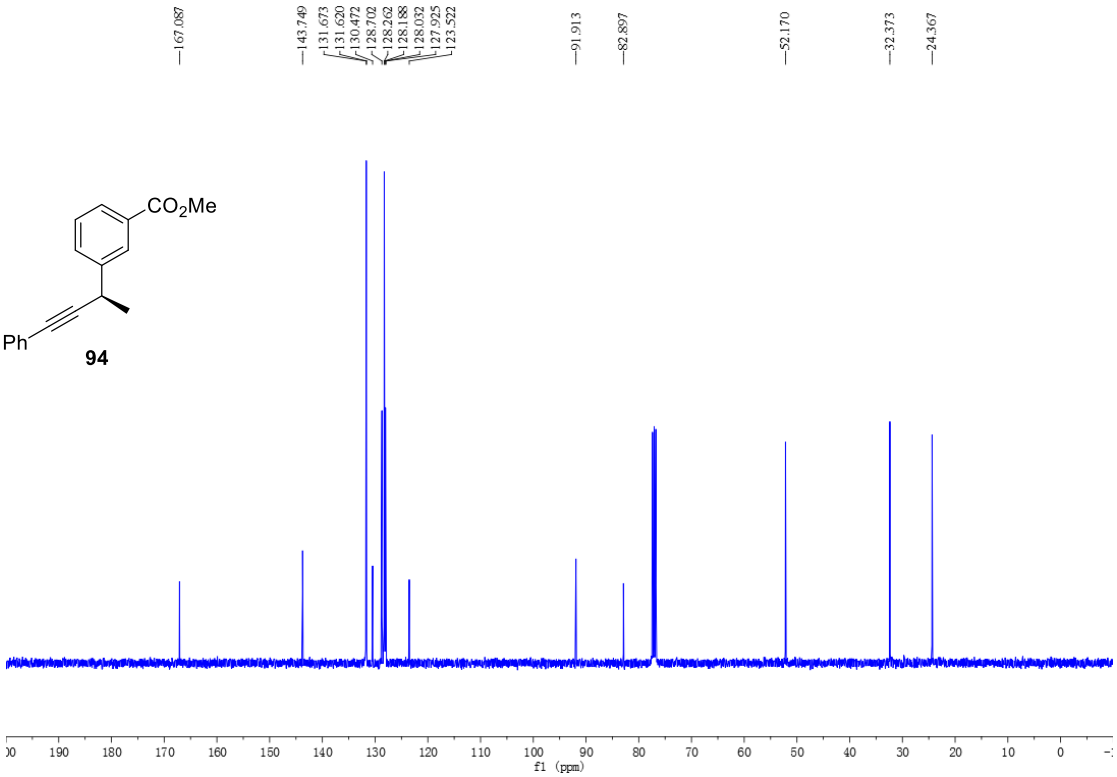
7.432
7.413
7.336
7.321
7.312
7.302
7.296
7.260
4.077
4.059
4.042
4.024
3.933
1.620
1.602
CO2Me
Ph
94
0.98
1.00
1.04
3.07
3.05
1.07
3.18
3.06
f1 (ppm)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128.262
128.188
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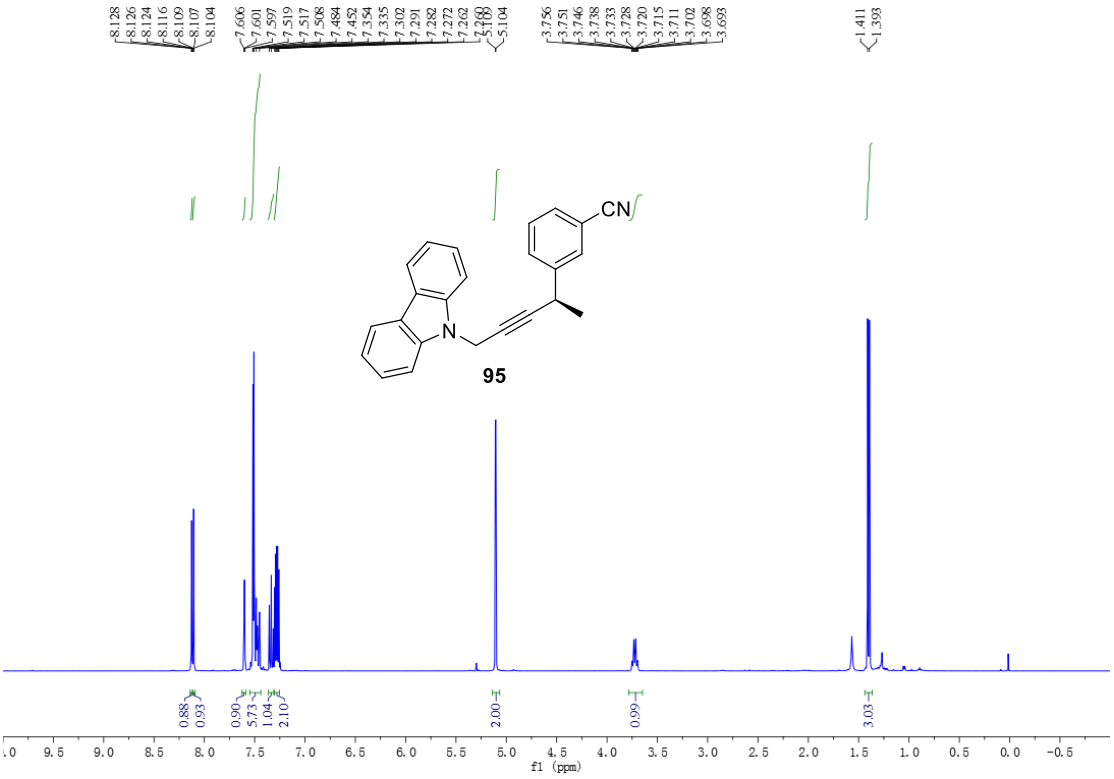
123.522
91.913
82.897
52.170
32.373
24.367
CO2Me
Ph
94
f1 (ppm)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8.124
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8.107
8.104
7.606
7.601
7.597
7.519
7.517
7.508
7.484
7.452
7.354
7.335
7.302
7.291
7.282
7.272
7.262
7.260
5.108
5.104
3.756
3.751
3.746
3.738
3.733
3.728
3.720
3.715
3.711
3.702
3.698
3.693
1.411
1.393
CN
N
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0.93
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2.00
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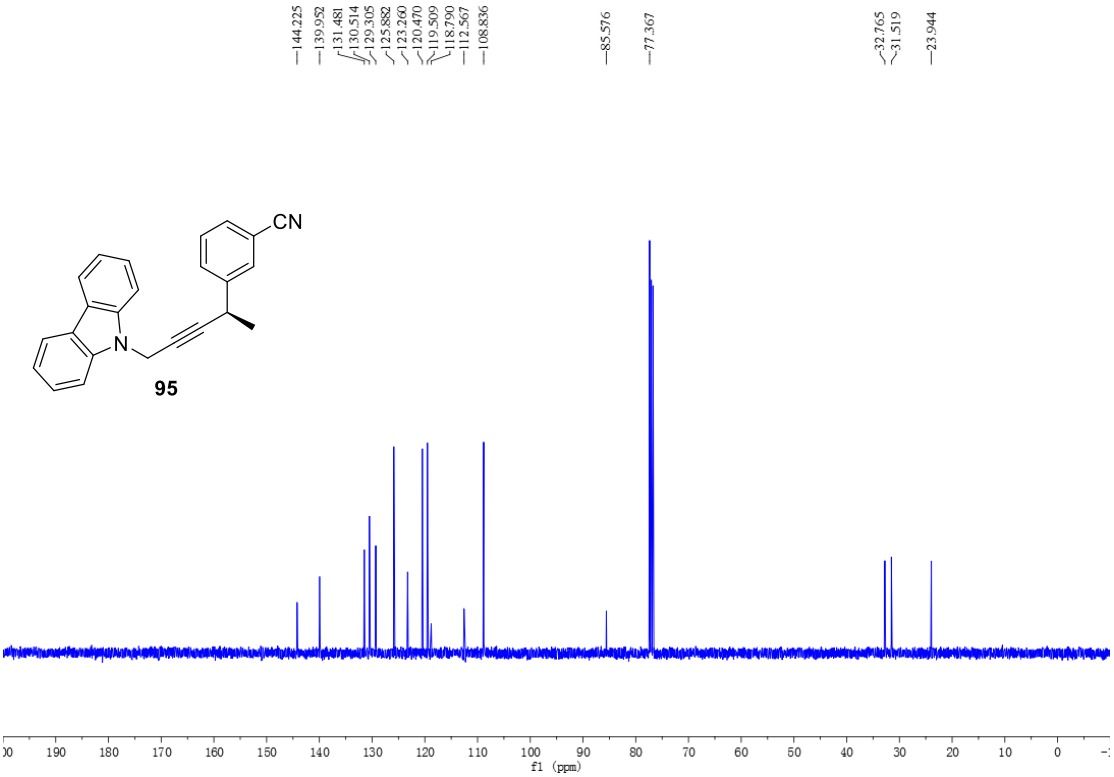
f1 (ppm)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131.481
130.514
129.305
125.882
123.260
120.470
119.509
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108.836
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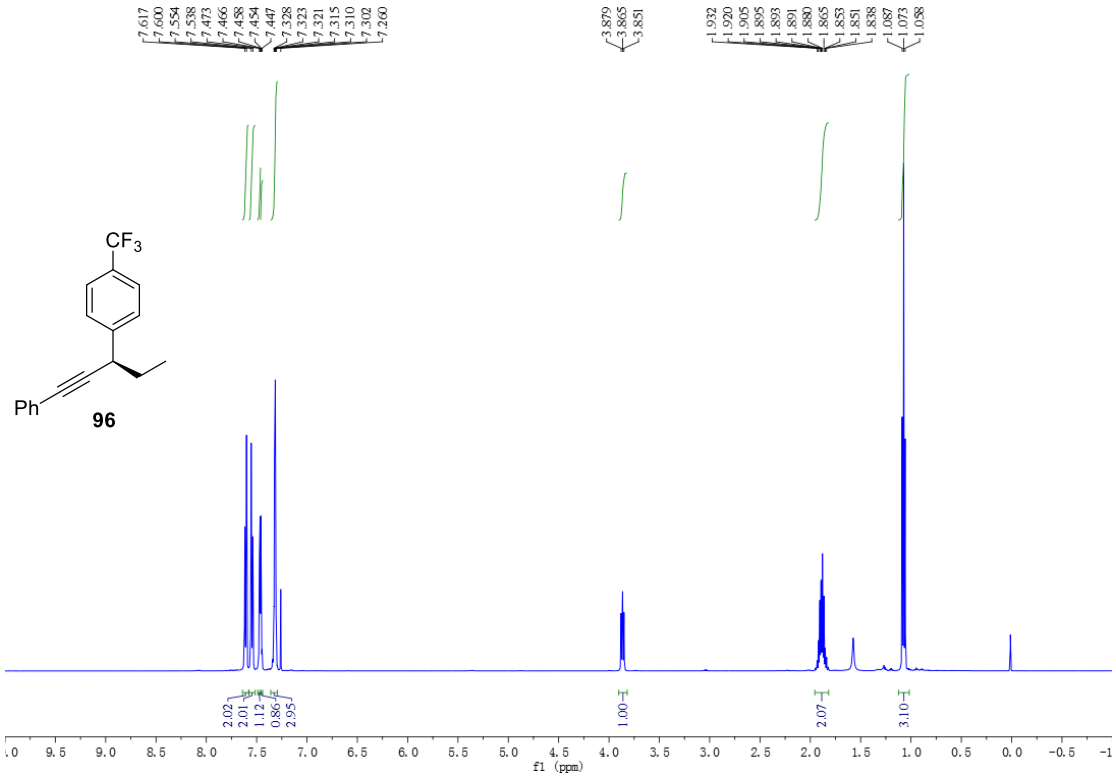
77.367
32.765
31.519
23.944
CN
N
95
f1 (ppm)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7.454
7.447
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7.323
7.321
7.315
7.310
7.302
7.260
3.879
3.865
3.851
1.932
1.920
1.905
1.895
1.893
1.891
1.880
1.865
1.853
1.851
1.838
1.087
1.073
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CF3
Ph
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2.01
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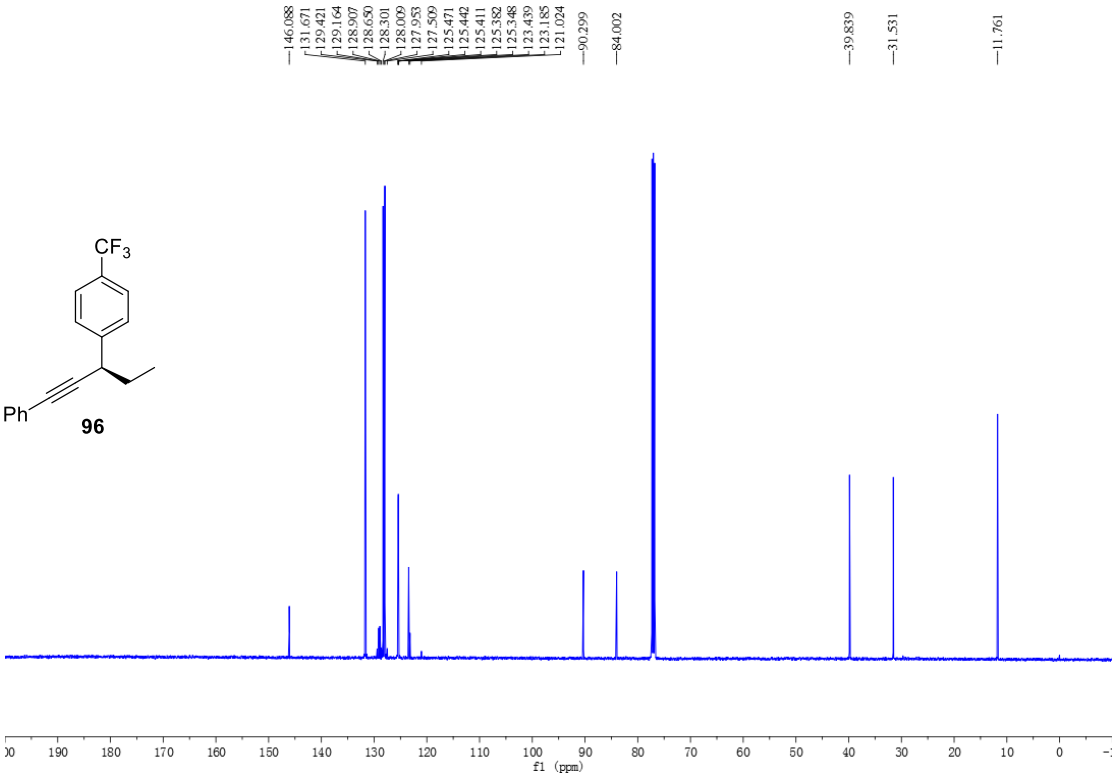
1.00
2.07
3.10
f1 (ppm)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129.421
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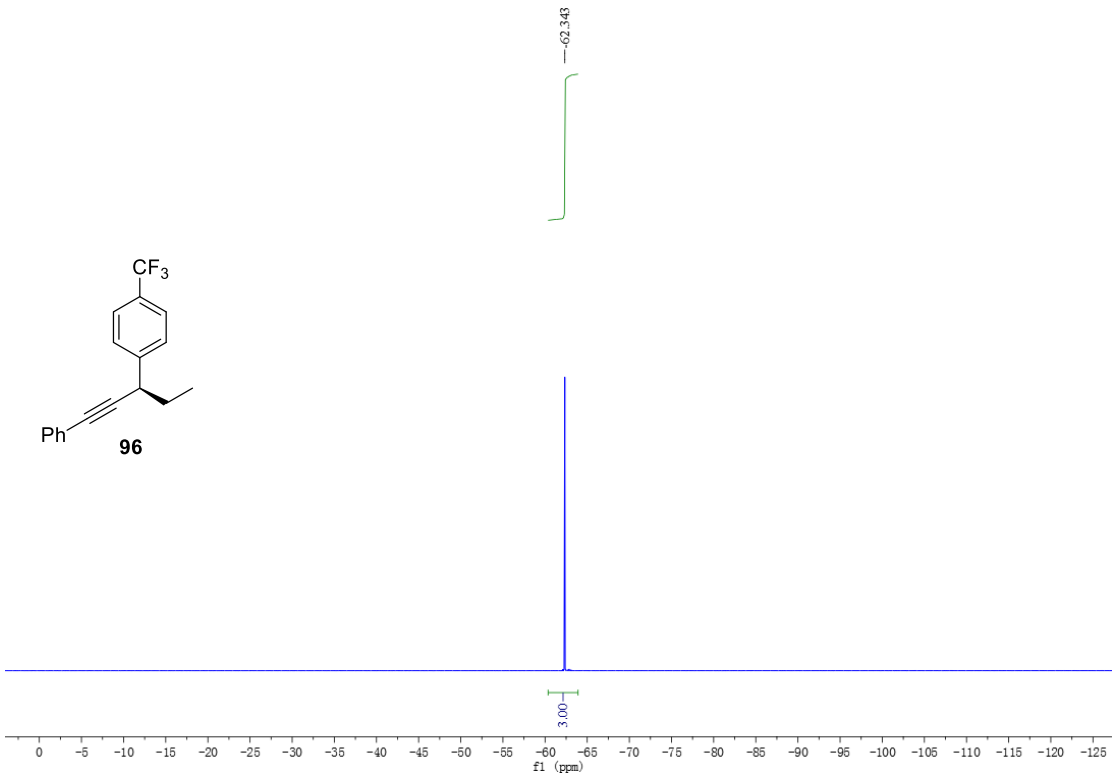
125.471
125.442
125.411
125.382
125.348
123.439
123.185
121.024
90.299
84.002
39.839
31.531
11.761
CF3
Ph
96
f1 (ppm)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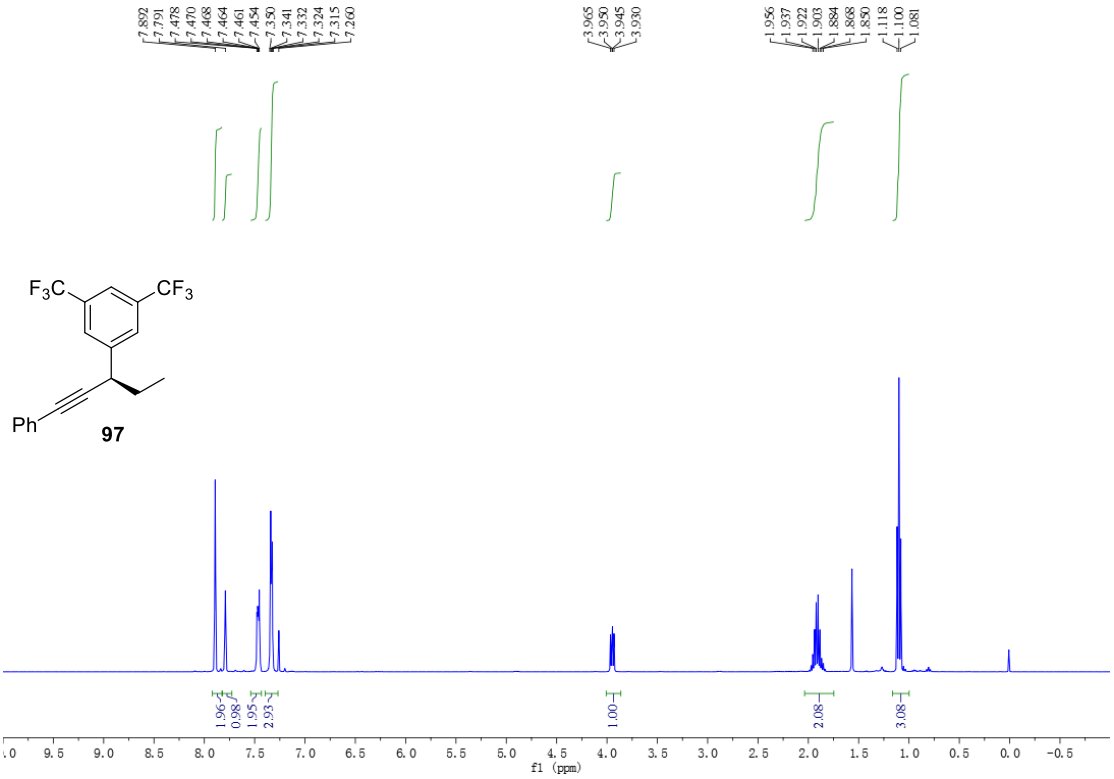
CF3
Ph
96
3.00
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125
f1 (ppm)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7.464
7.461
7.454
7.350
7.341
7.332
7.324
7.315
7.260
3.965
3.950
3.945
3.930
1.956
1.937
1.922
1.903
1.884
1.868
1.850
1.118
1.100
1.081
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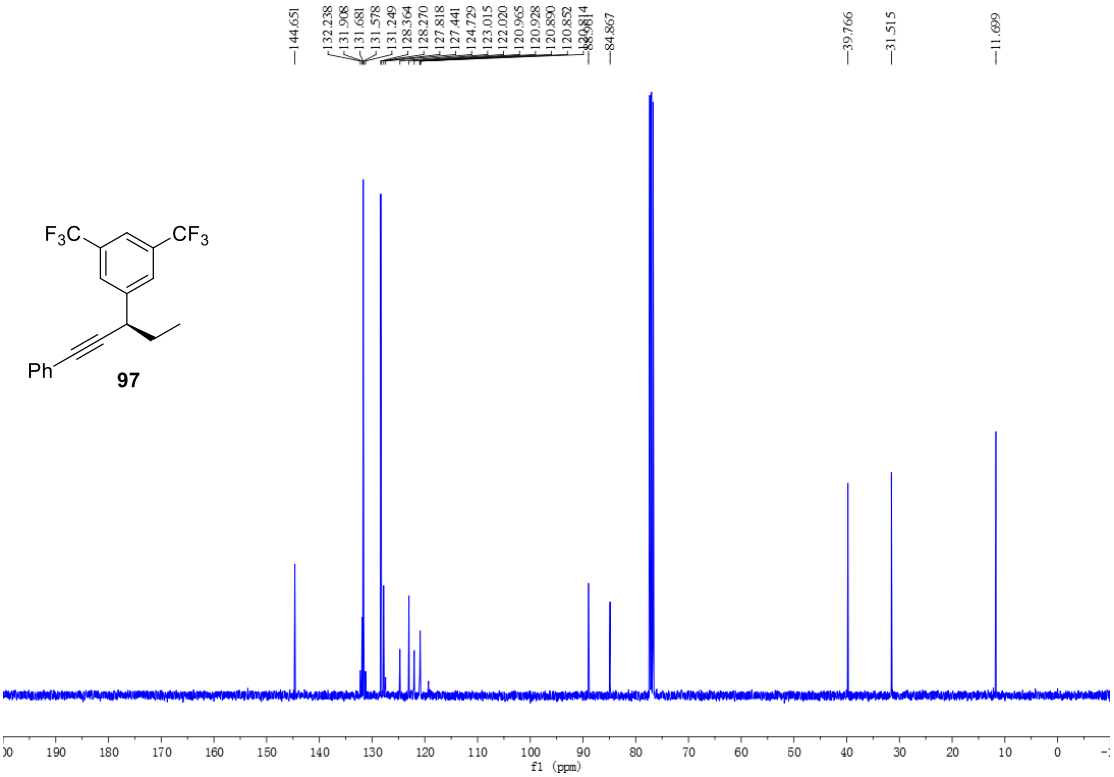
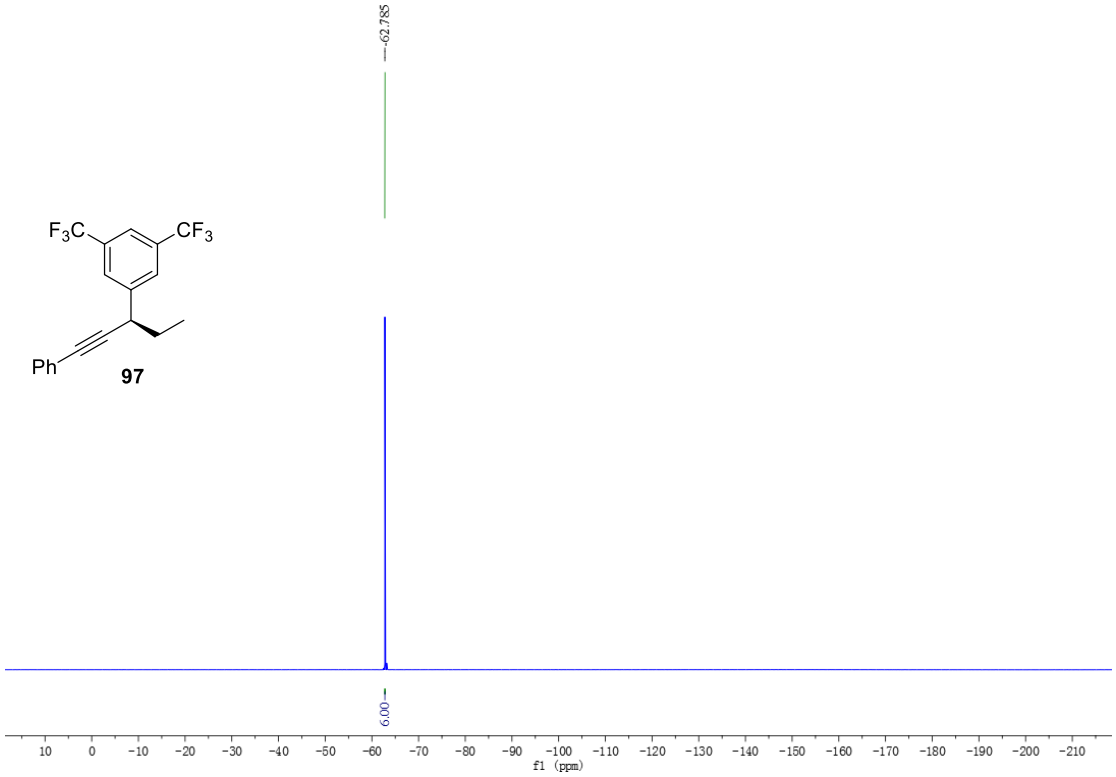
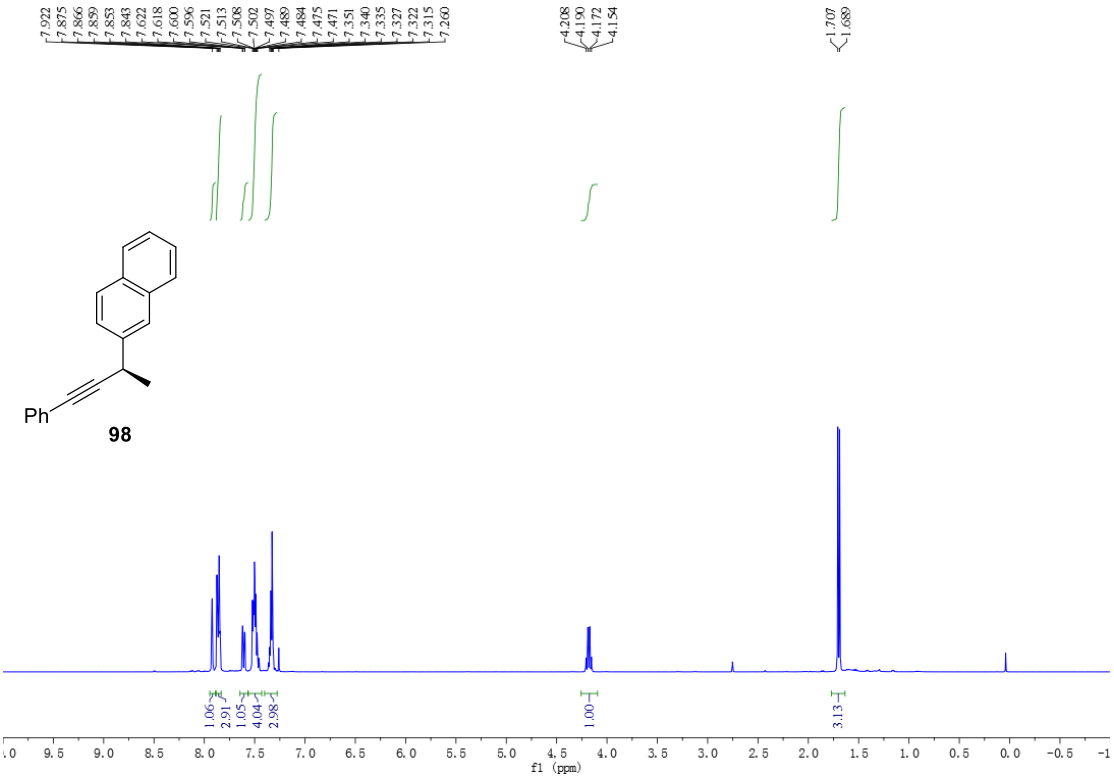
CF3
Ph
97
1.96
0.98
1.95
2.93
1.00
2.08
3.08
f1 (ppm)


144.651
132.238
131.908
131.681
131.578
131.249
128.364
128.270
127.818
127.441
124.729
123.015
122.020
120.965
120.928
120.890
120.852
84.867
39.766
31.515
11.699
F3C
CF3
Ph
97
f1 (ppm)


-62.785
F3C
CF3
Ph
97
6.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.859
7.853
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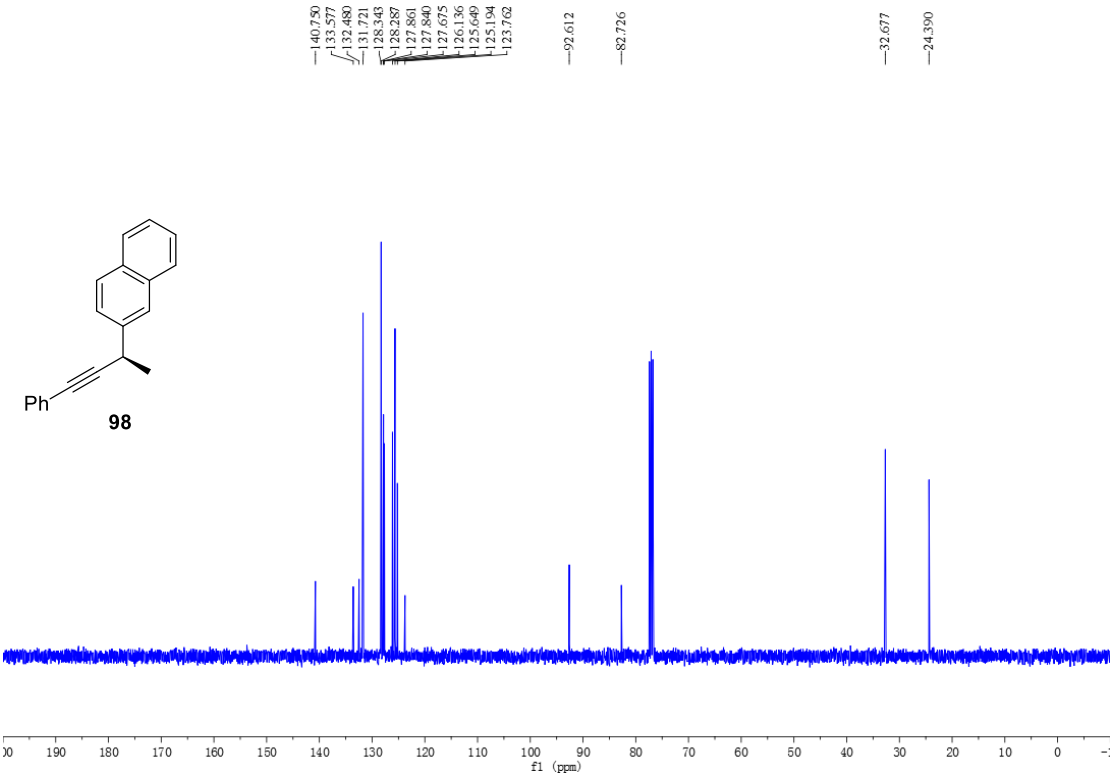
7.618
7.600
7.596
7.521
7.513
7.508
7.502
7.497
7.489
7.484
7.475
7.471
7.351
7.340
7.335
7.327
7.322
7.315
7.260
4.208
4.190
4.172
4.154
1.707
1.689
Ph
98
1.06
2.91
1.05
4.04
2.98
1.00
3.13
f1 (ppm)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132.480
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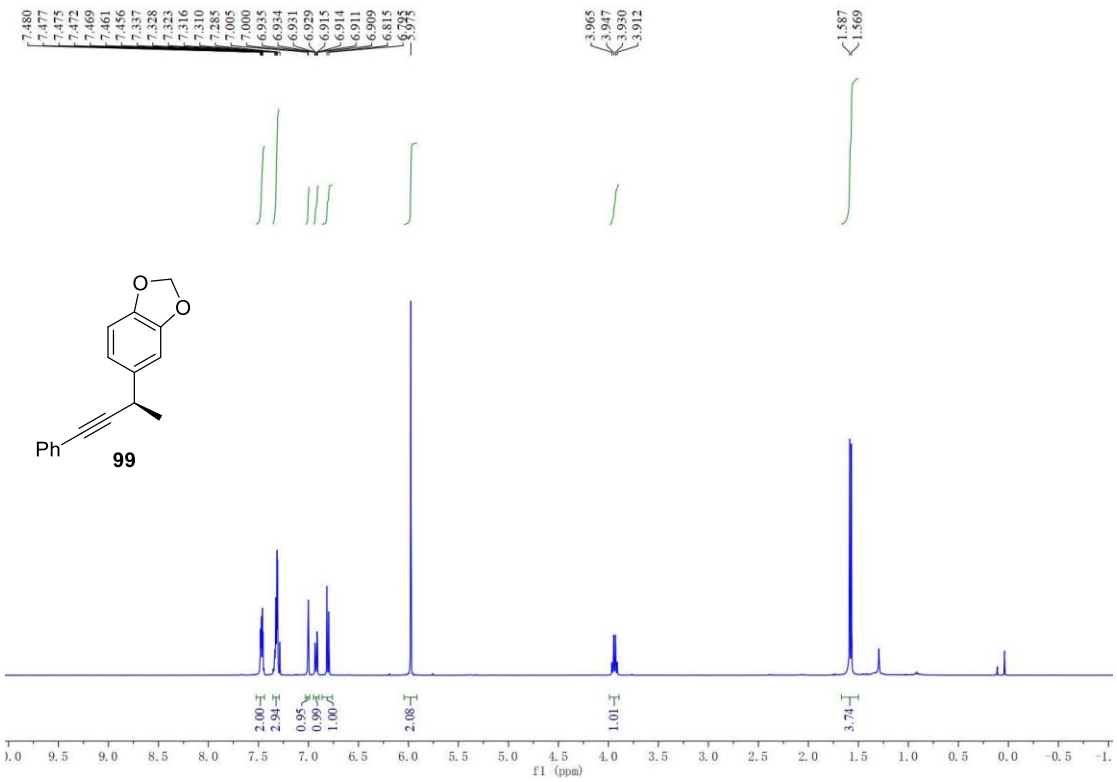
125.649
125.194
123.762
92.612
82.726
32.677
24.390
Ph
98
f1 (ppm)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7.477
7.475
7.472
7.469
7.461
7.456
7.337
7.328
7.323
7.316
7.310
7.285
7.005
7.000
6.935
6.934
6.931
6.929
6.915
6.914
6.911
6.909
6.815
6.795
3.965
3.947
3.930
3.912
1.587
1.569
O
O
Ph
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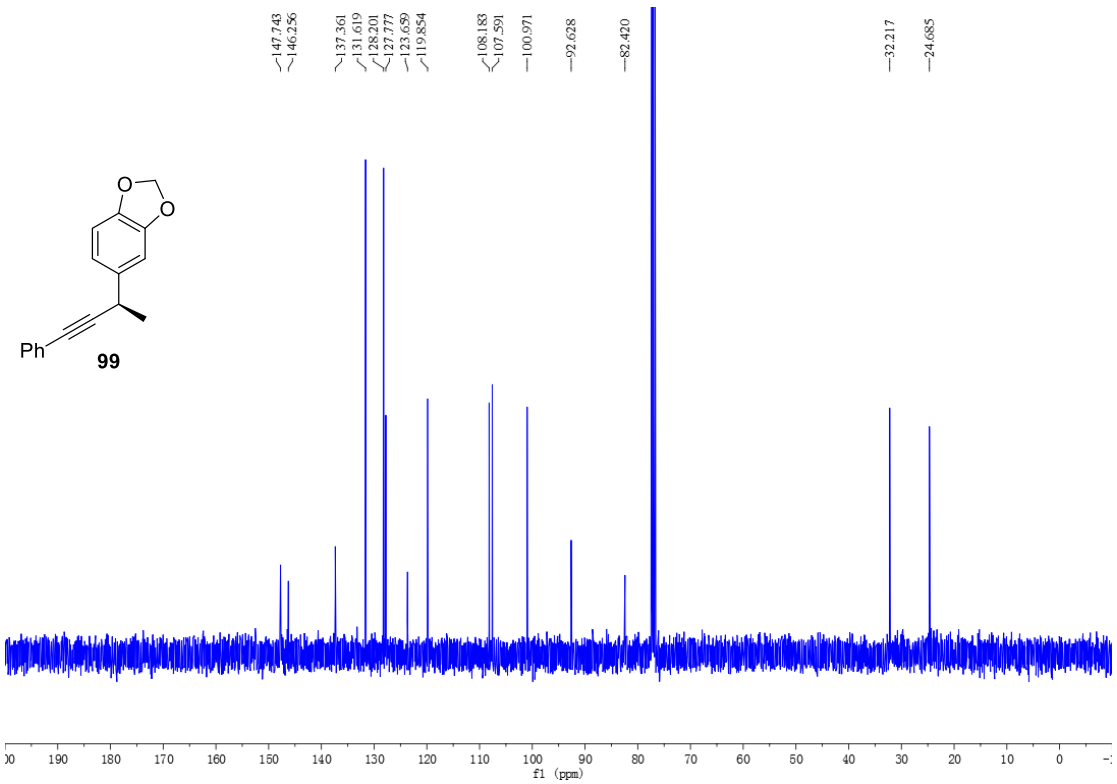
2.00
2.94
0.95
0.99
1.00
2.08
1.01
3.74
f1 (ppm)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131.619
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100.971
92.628
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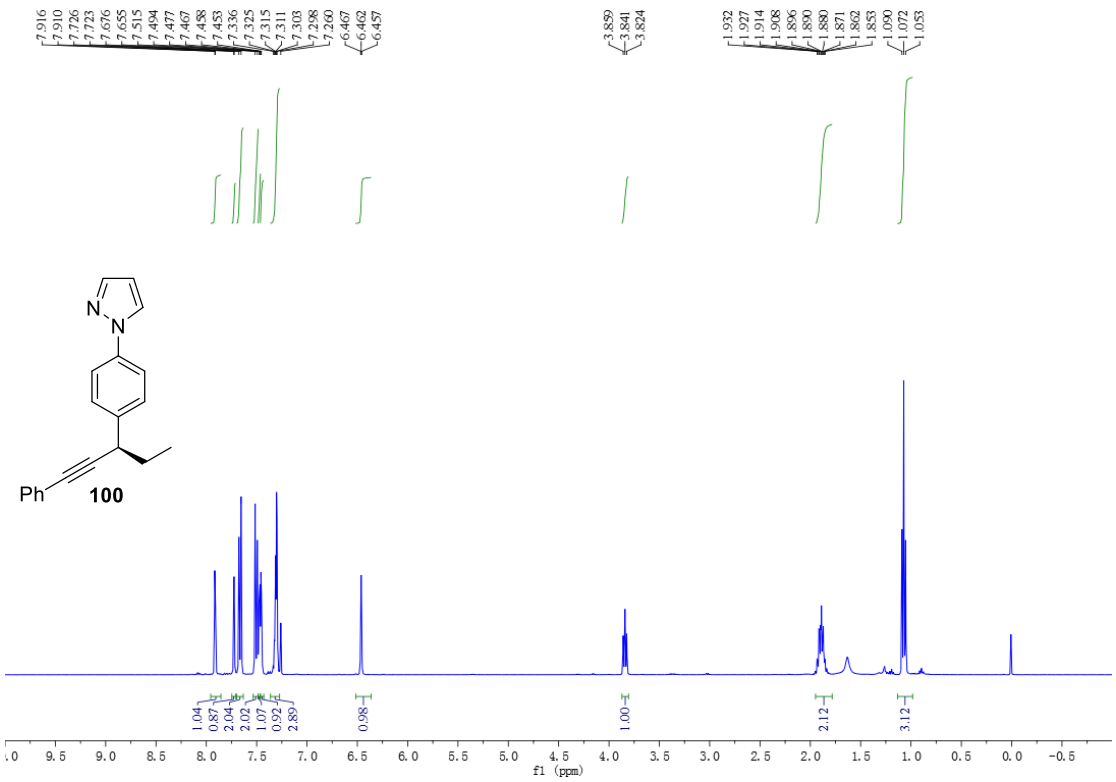
32.217
24.685
O
O
Ph
99
f1 (ppm)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7.726
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7.676
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7.515
7.494
7.477
7.467
7.458
7.453
7.336
7.325
7.315
7.311
7.303
7.298
7.260
6.467
6.462
6.457
3.859
3.841
3.824
1.932
1.927
1.914
1.908
1.896
1.890
1.880
1.871
1.862
1.853
1.090
1.072
1.053
Ph
100
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1.07
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2.89
0.98
1.00
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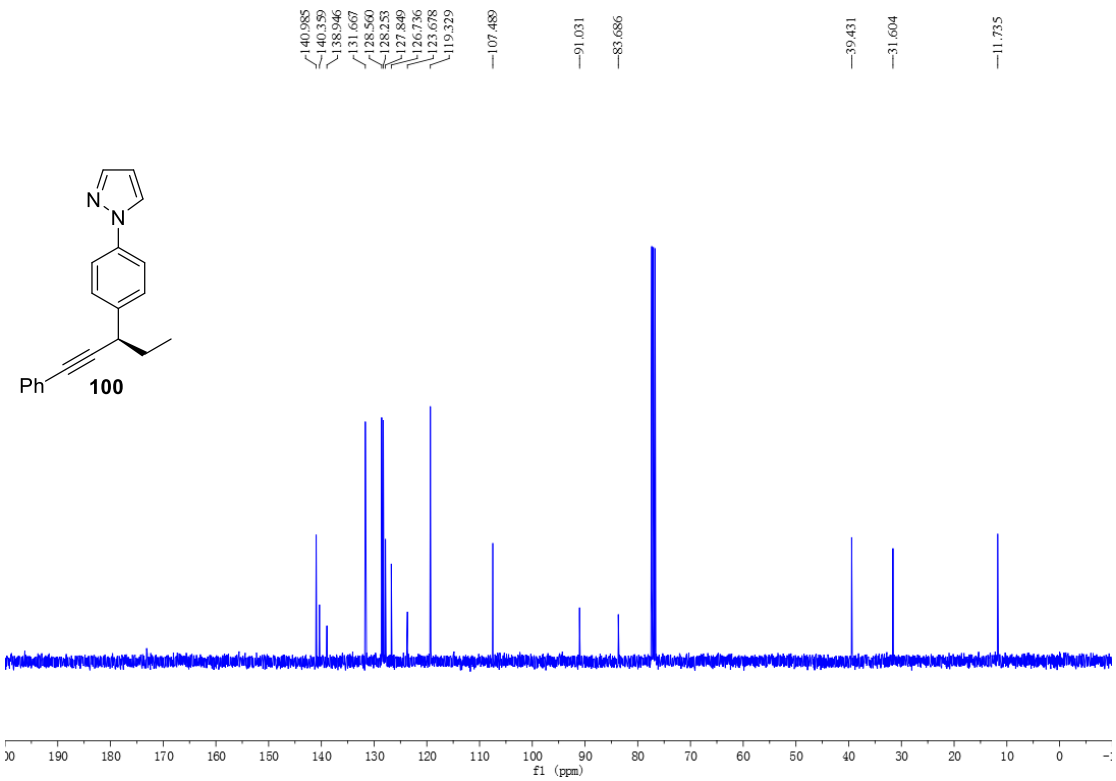
3.12
f1 (ppm)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91.031
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31.604
11.735
Ph
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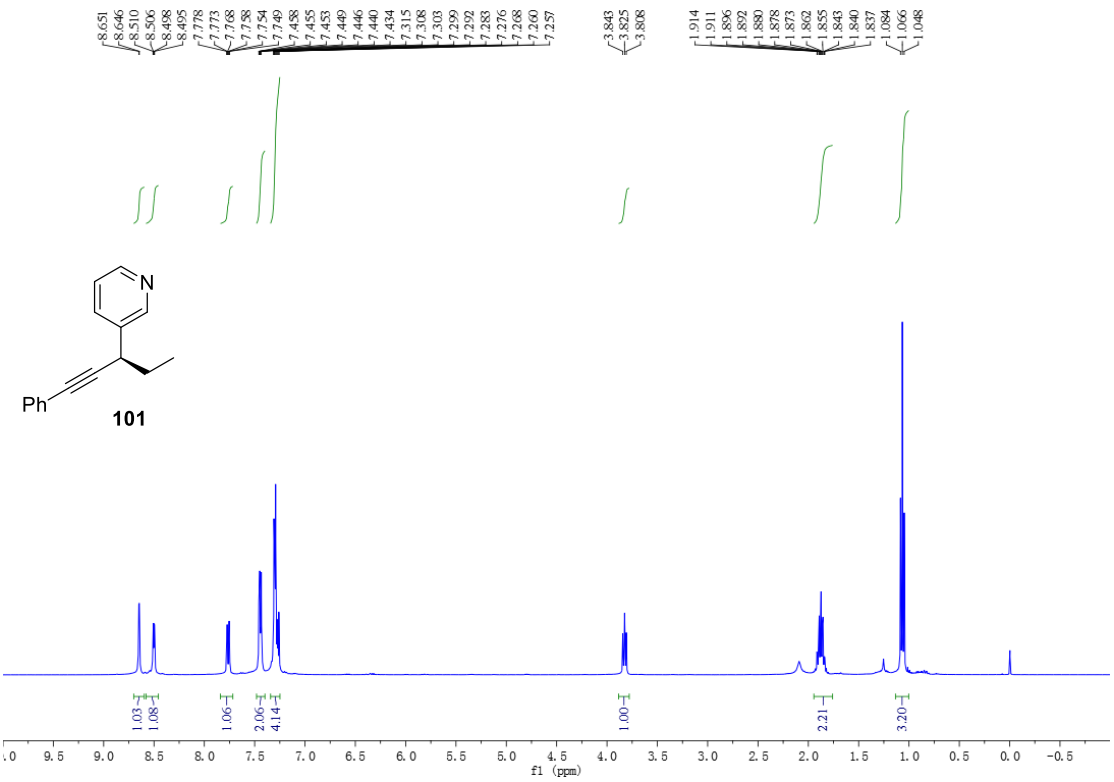
f1 (ppm)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8.506
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7.773
7.768
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7.754
7.749
7.458
7.455
7.453
7.449
7.446
7.440
7.434
7.315
7.308
7.303
7.299
7.292
7.283
7.276
7.268
7.260
7.257
3.843
3.825
3.808
1.914
1.911
1.896
1.892
1.880
1.878
1.873
1.862
1.855
1.843
1.840
1.837
1.084
1.066
1.048
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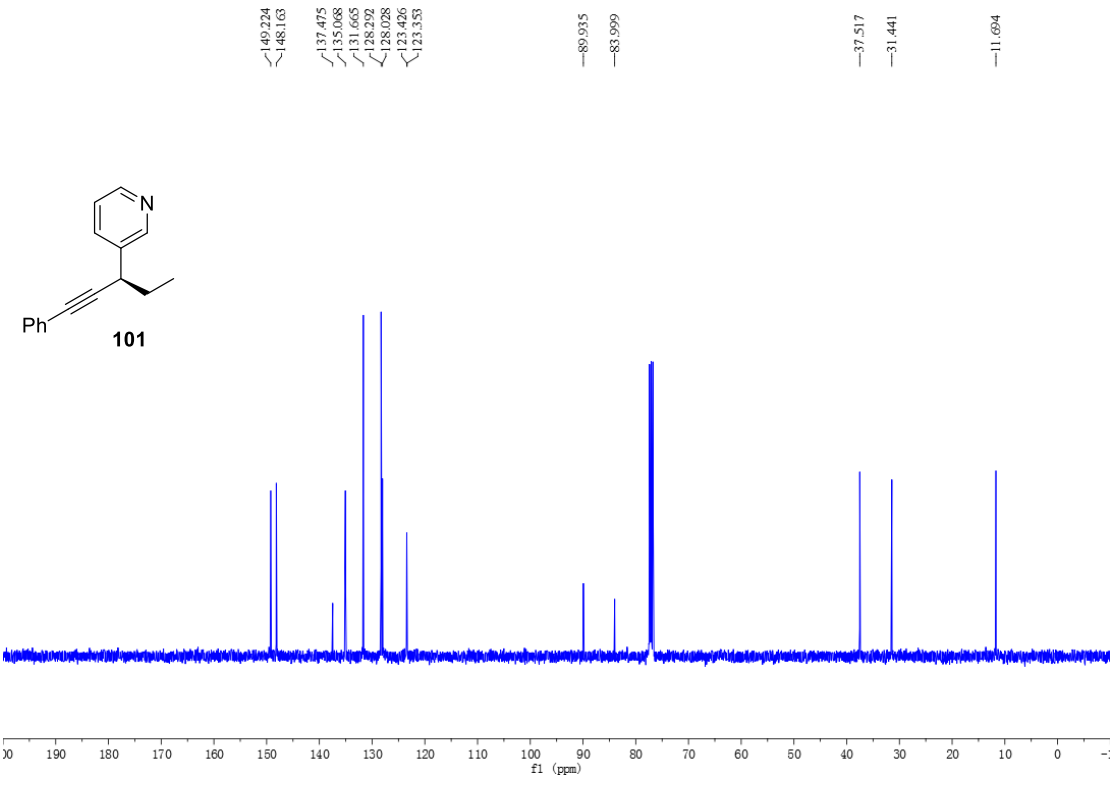
1.08
1.06
2.06
4.14
1.00
2.21
3.20
f1 (ppm)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148.163
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31.441
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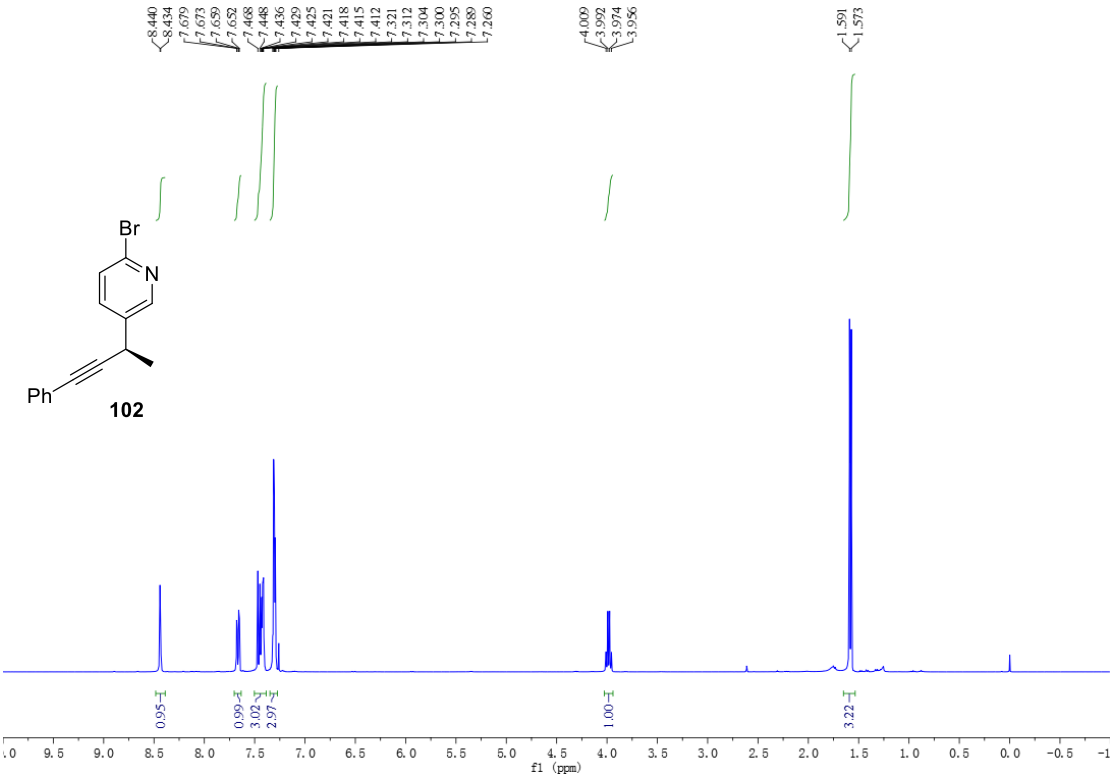
Ph
101
f1 (ppm)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7.418
7.415
7.412
7.321
7.312
7.304
7.300
7.295
7.289
7.260
4.009
3.992
3.974
3.956
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Br
N
Ph
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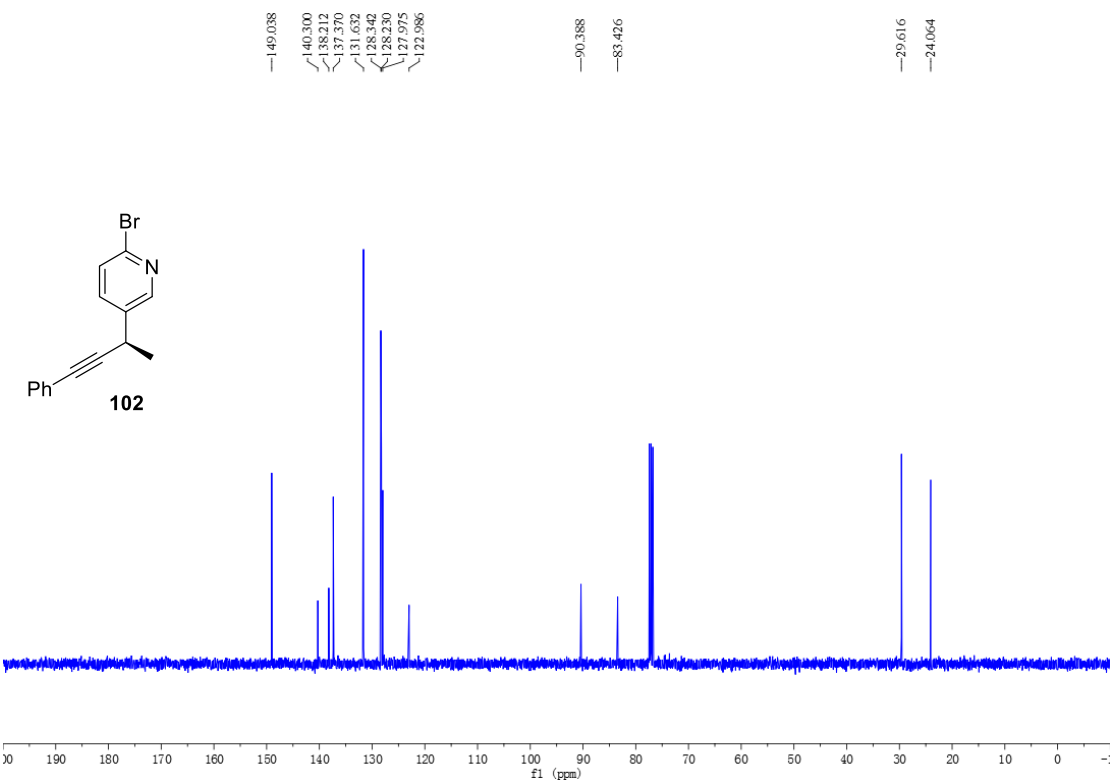
3.22
f1 (ppm)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137.370
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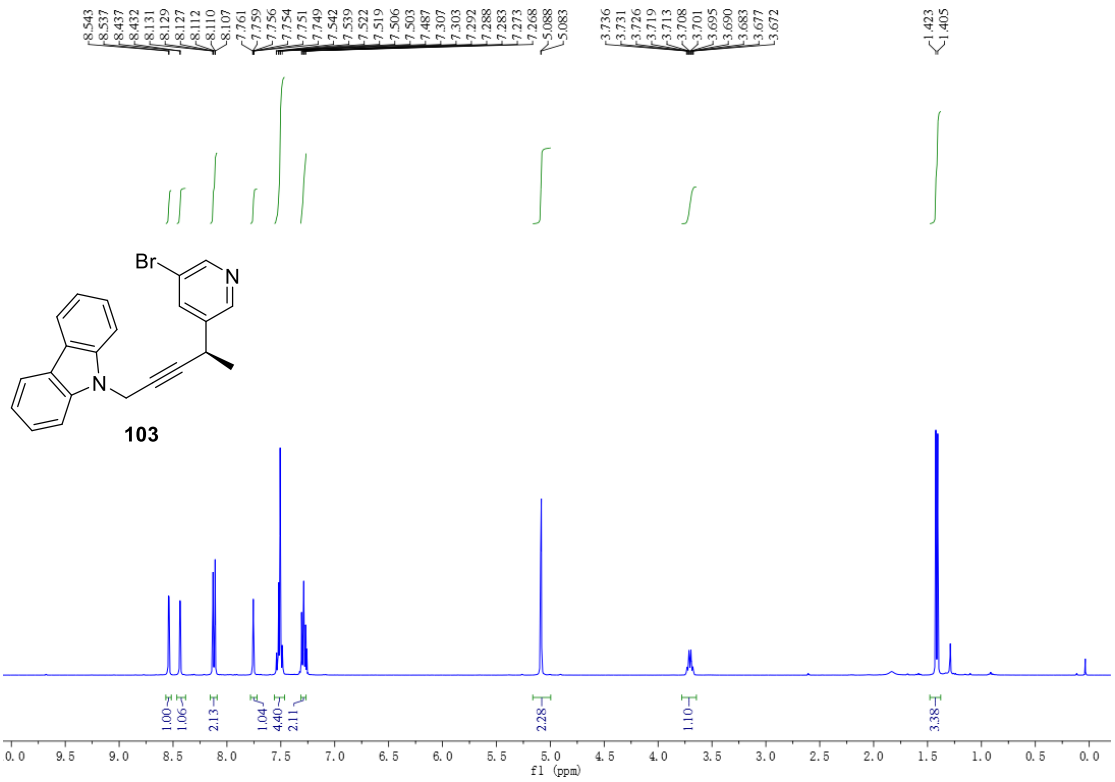
29.616
24.064
Br
N
Ph
102
f1 (ppm)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8.112
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7.754
7.751
7.749
7.542
7.539
7.522
7.519
7.506
7.503
7.487
7.307
7.303
7.292
7.288
7.283
7.273
7.268
5.088
5.083
3.736
3.731
3.726
3.719
3.713
3.708
3.701
3.695
3.690
3.683
3.677
3.672
1.423
1.405
Br
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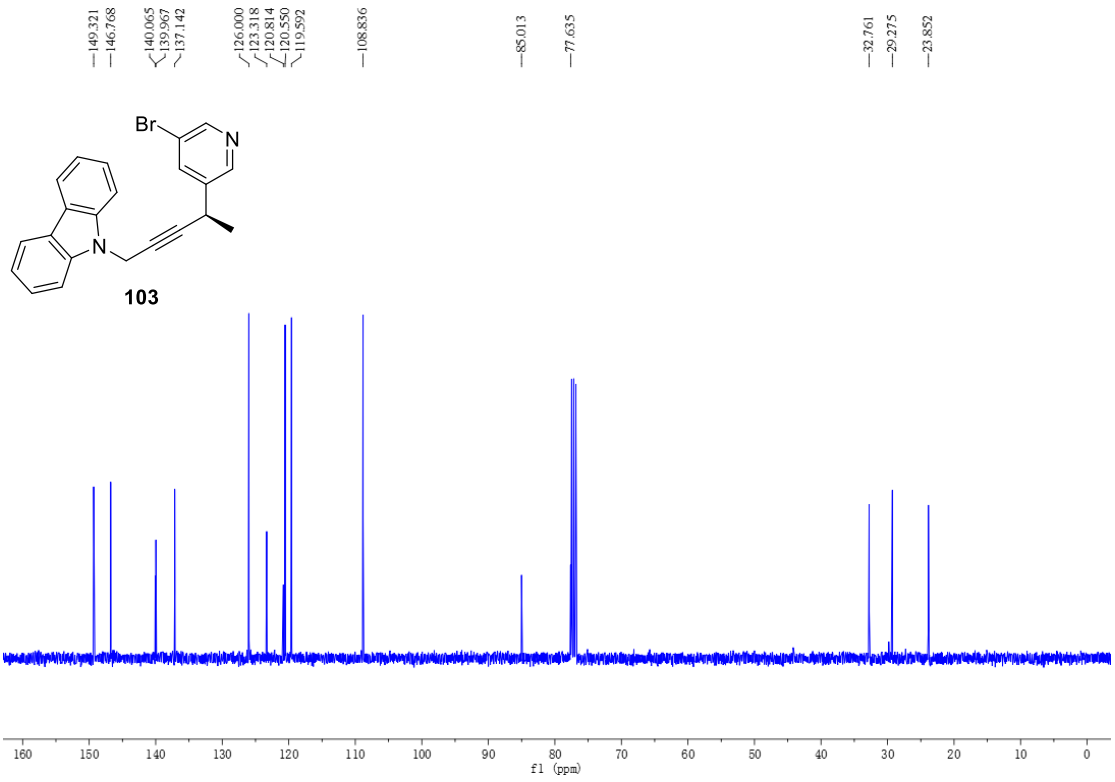
3.38
f1 (ppm)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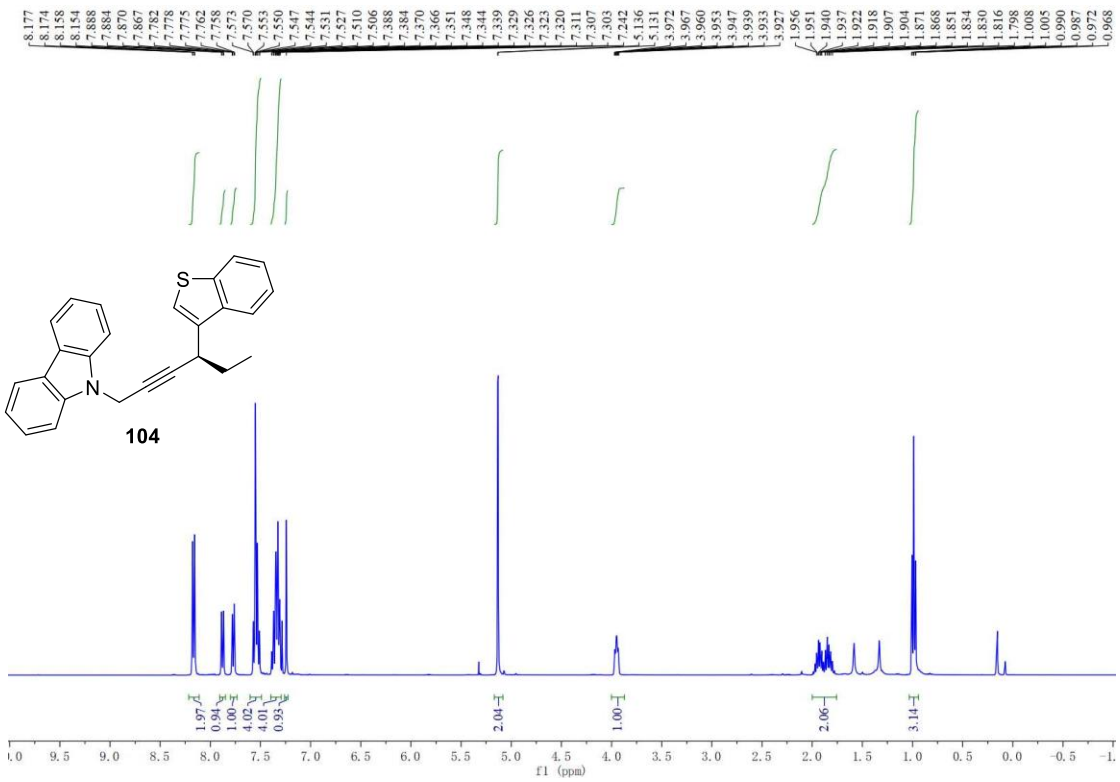
139.967
137.142
126.000
123.318
120.814
120.550
119.592
108.836
85.013
77.635
32.761
29.275
23.852
Br
N
N
103
f1 (ppm)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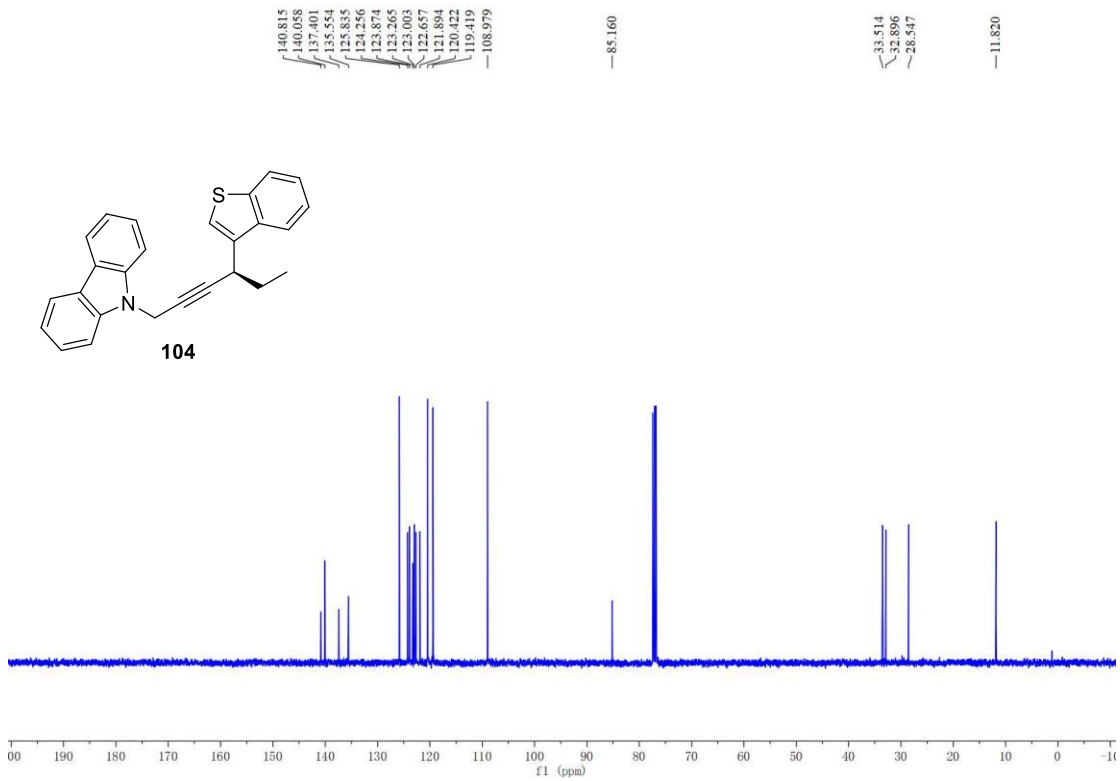
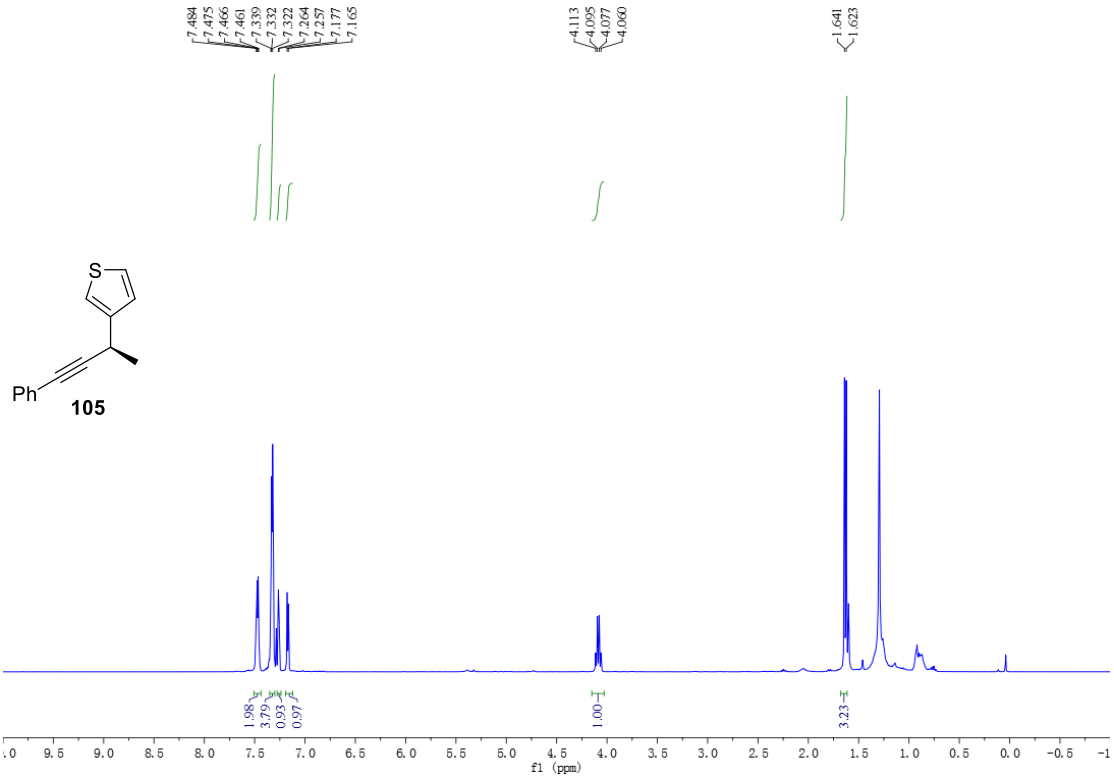
f1 (ppm)


104
f1 (ppm)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7.461
7.339
7.332
7.322
7.264
7.257
7.177
7.165
4.113
4.095
4.077
4.060
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S
Ph
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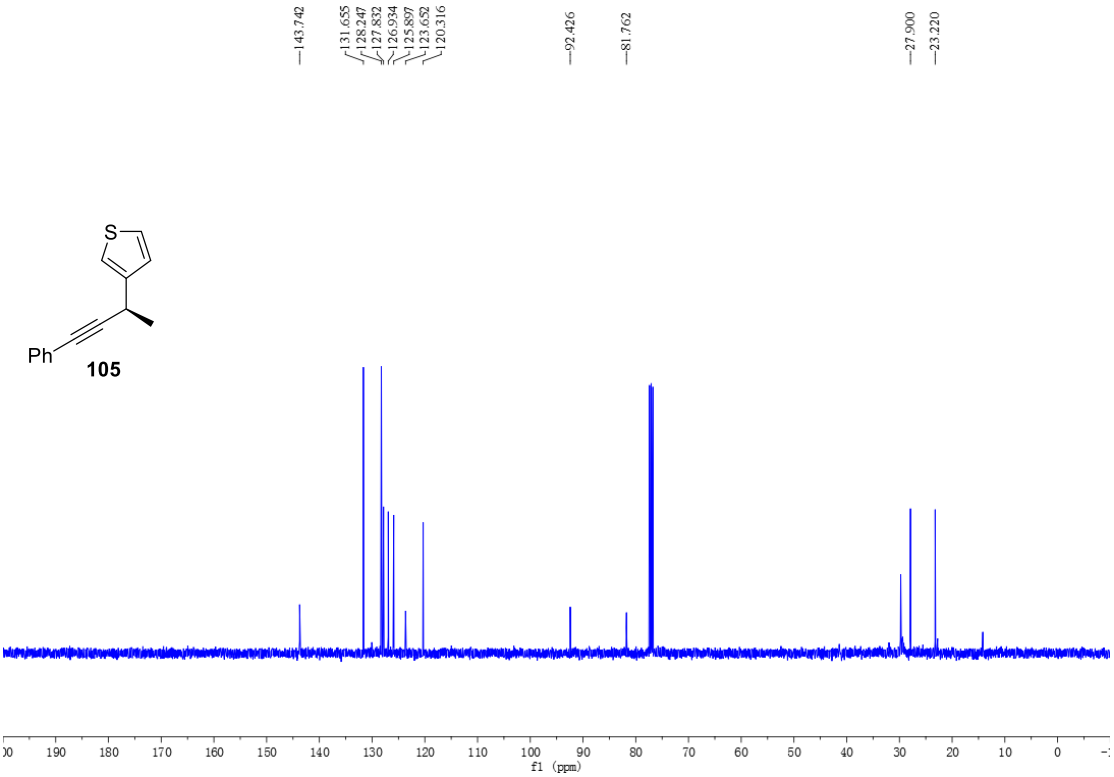
1.00
3.23
f1 (ppm)


143.742
131.655
128.247
127.832
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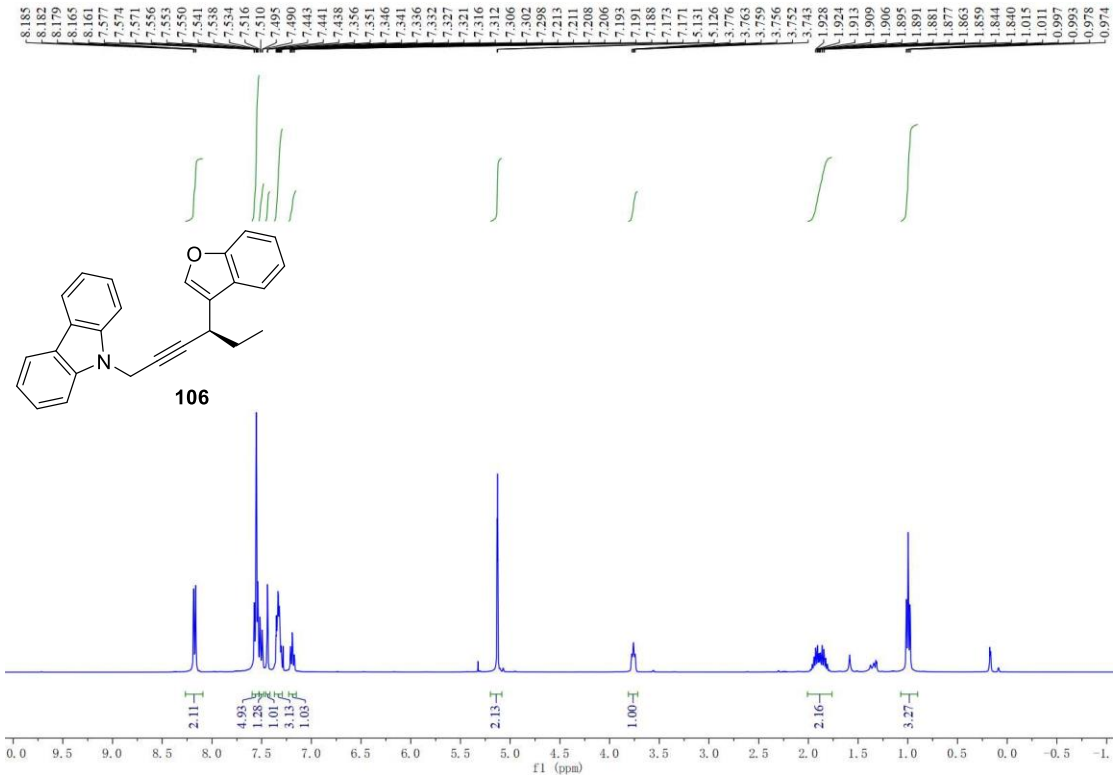
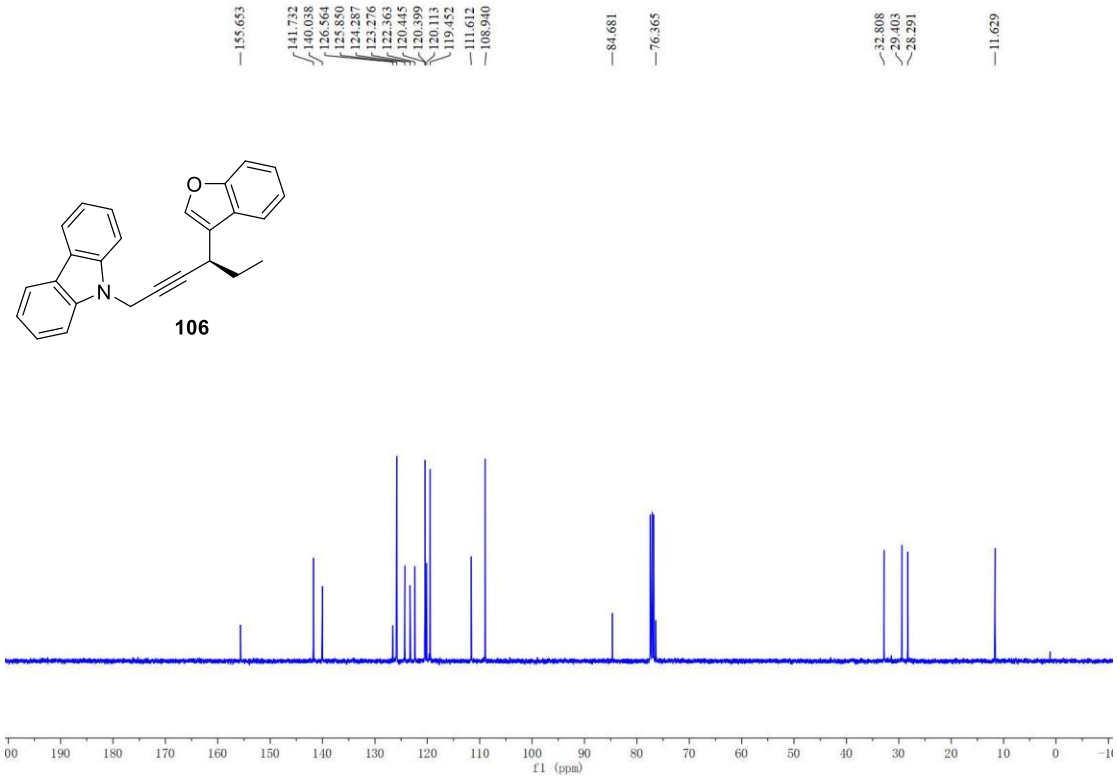
123.652
120.316
92.426
81.762
27.900
23.220
S
Ph
105
f1 (ppm)


106
f1 (ppm)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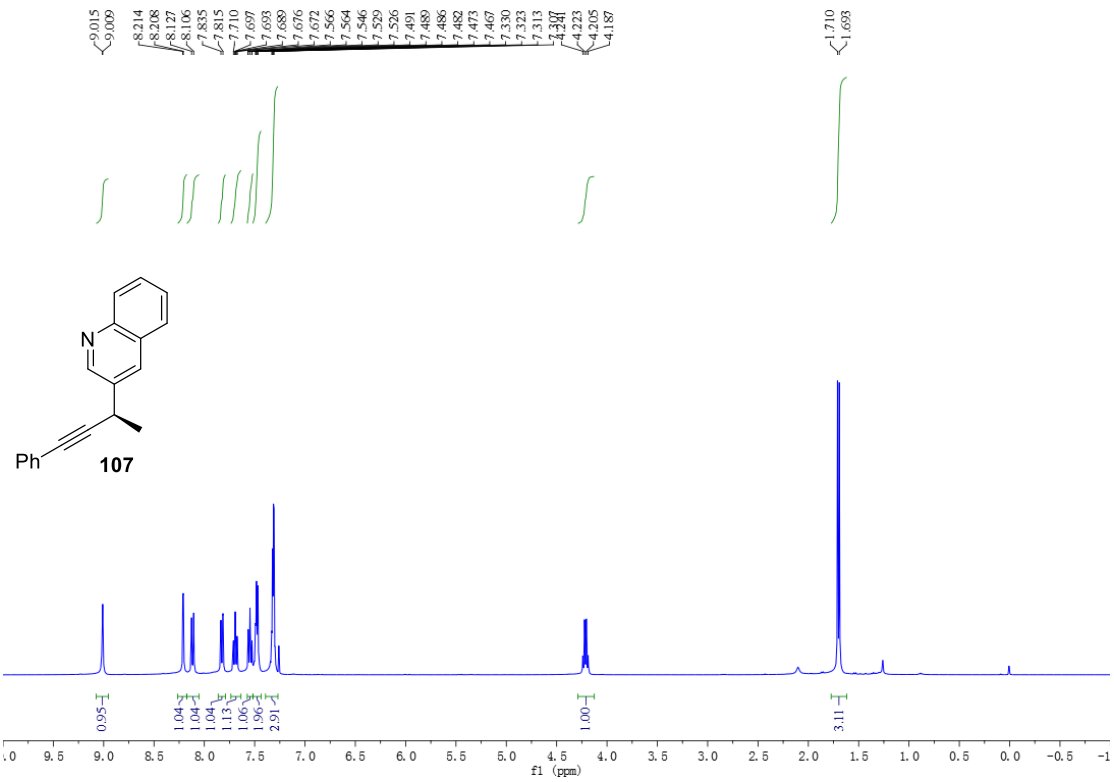
f1 (ppm)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7.467
7.330
7.323
7.313
4.241
4.223
4.205
4.187
1.710
1.693
N
Ph
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1.04
1.13
1.06
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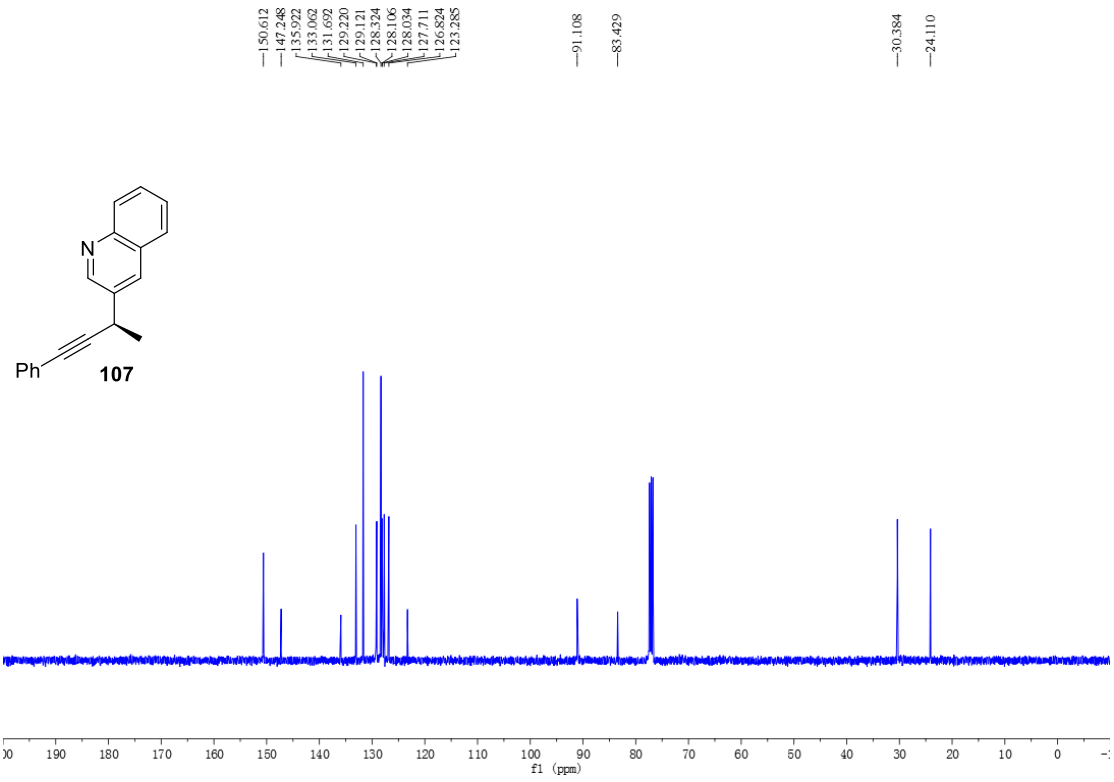
3.11
f1 (ppm)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128.324
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91.108
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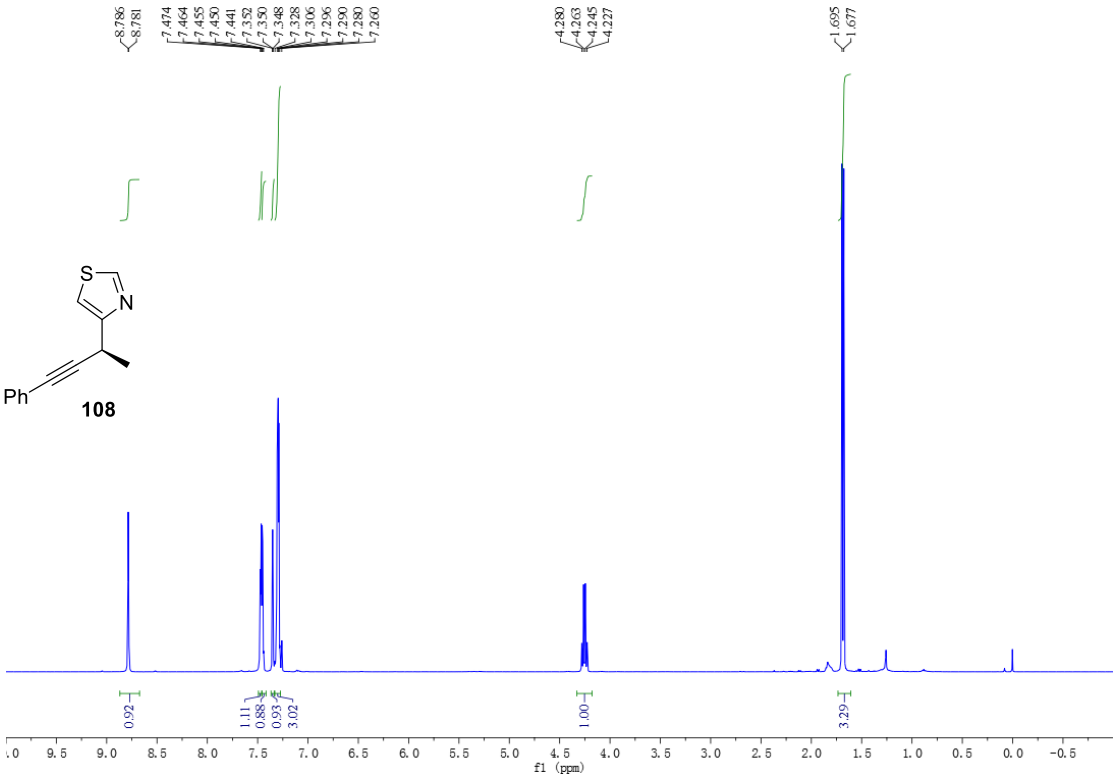
Ph
107
f1 (ppm)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7.352
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7.328
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7.290
7.280
7.260
4.280
4.263
4.245
4.227
1.695
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N
Ph
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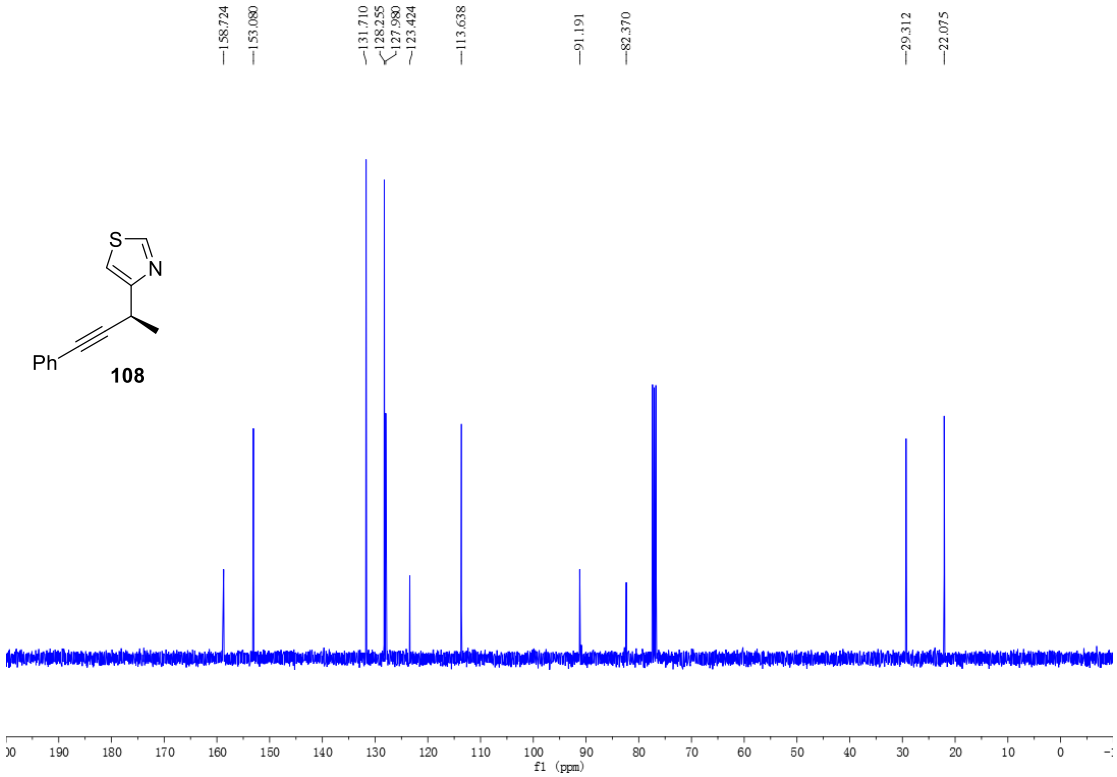
3.02
1.00
3.29
f1 (ppm)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153.080
131.710
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91.191
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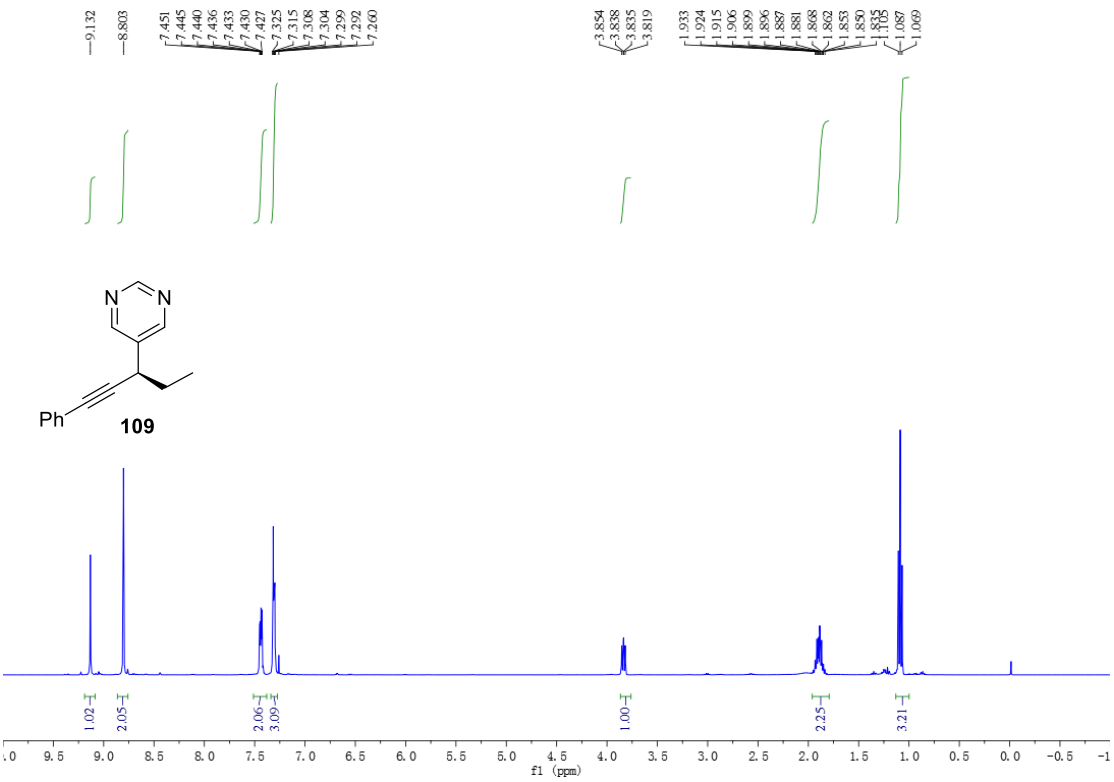
22.075
S
N
Ph
108
f1 (ppm)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7.430
7.427
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7.315
7.308
7.304
7.299
7.292
7.260
3.854
3.838
3.835
3.819
1.933
1.924
1.915
1.906
1.899
1.896
1.887
1.881
1.868
1.862
1.853
1.850
1.835
1.105
1.087
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Ph
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2.05
2.06
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1.00
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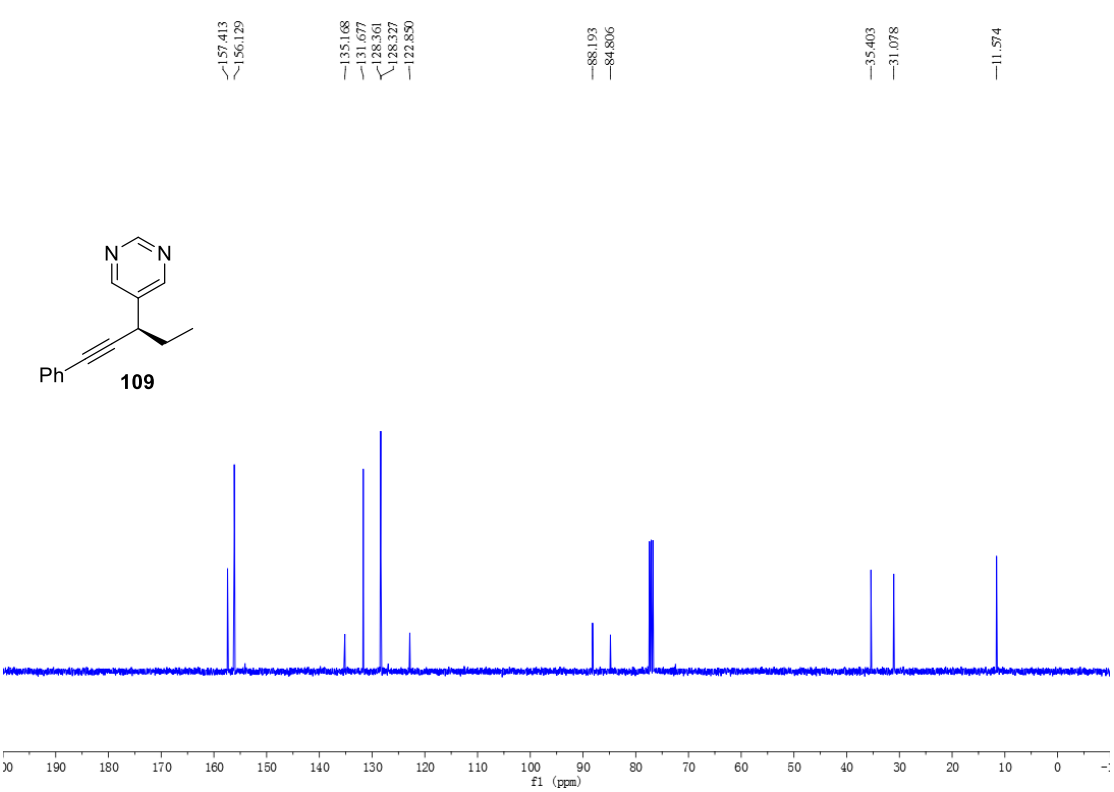
f1 (ppm)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156.129
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88.193
84.806
35.403
31.078
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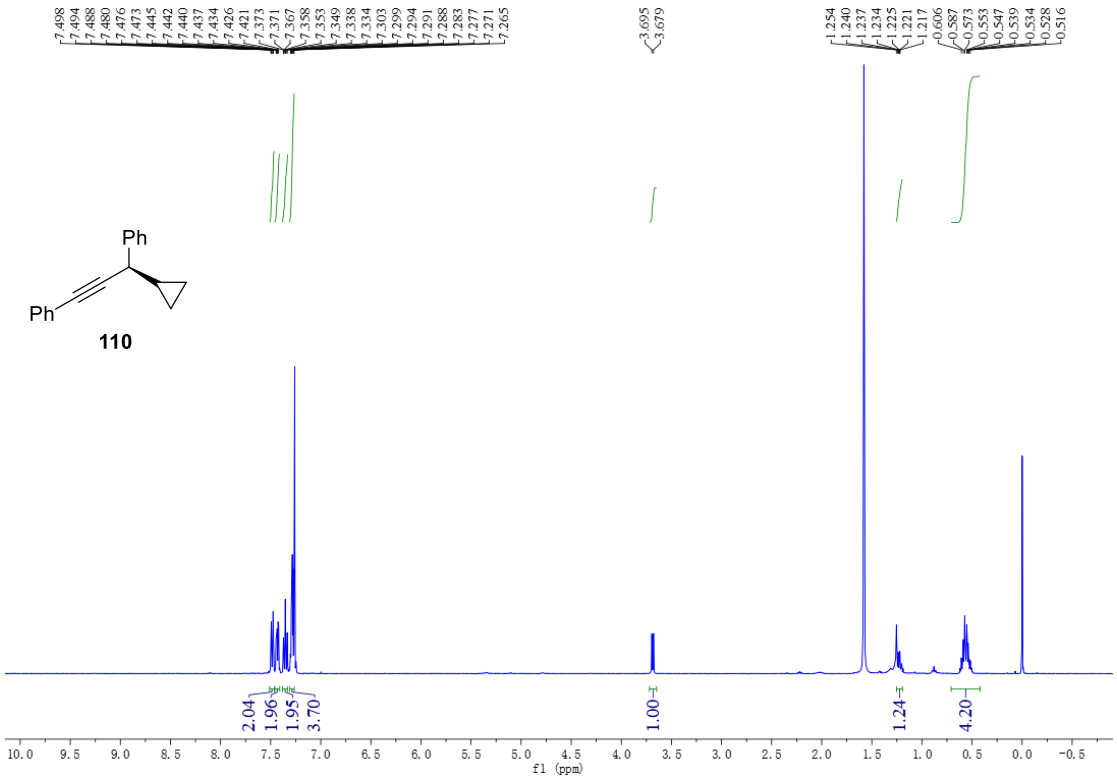
N
N
Ph
109
f1 (ppm)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7.442
7.440
7.437
7.434
7.426
7.421
7.373
7.371
7.367
7.358
7.353
7.349
7.338
7.334
7.303
7.299
7.294
7.291
7.288
7.283
7.277
7.271
7.265
3.695
3.679
1.254
1.240
1.237
1.234
1.225
1.221
1.217
0.606
0.587
0.573
0.553
0.547
0.539
0.534
0.528
0.516
Ph
Ph
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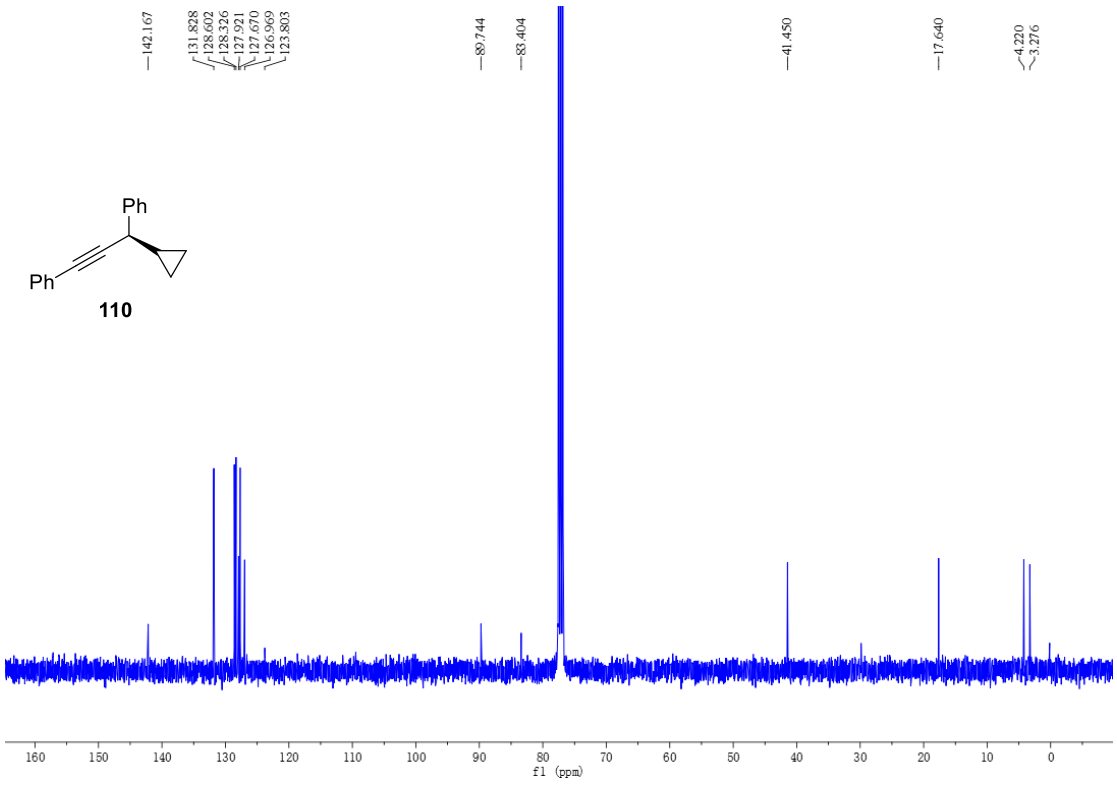
1.95
3.70
1.00
1.24
4.20
f1 (ppm)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128.326
127.921
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83.404
41.450
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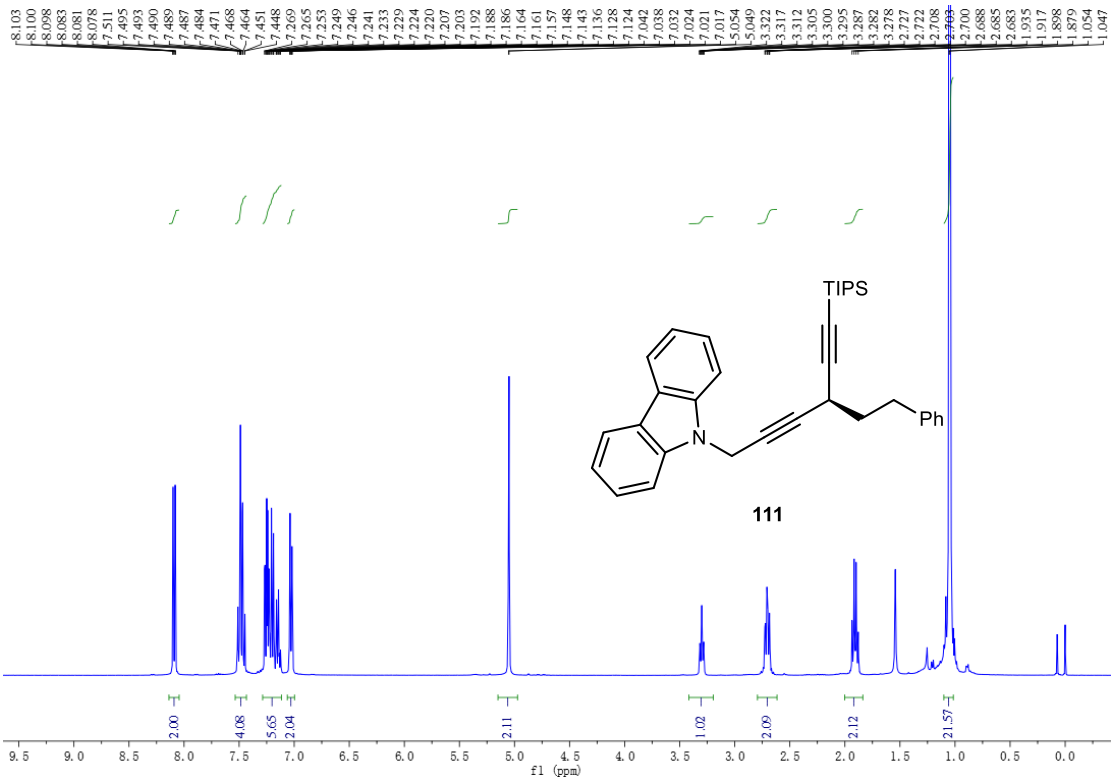
4.220
3.276
Ph
Ph
110
f1 (ppm)


TIPS
Ph
N
111
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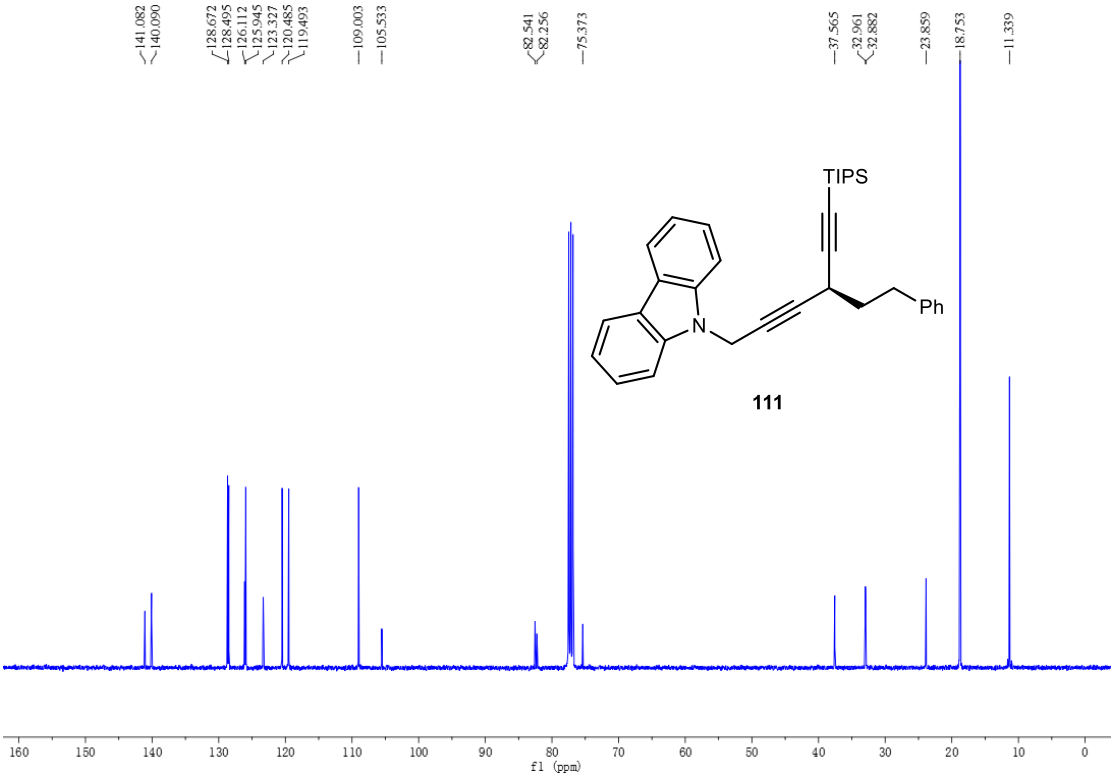
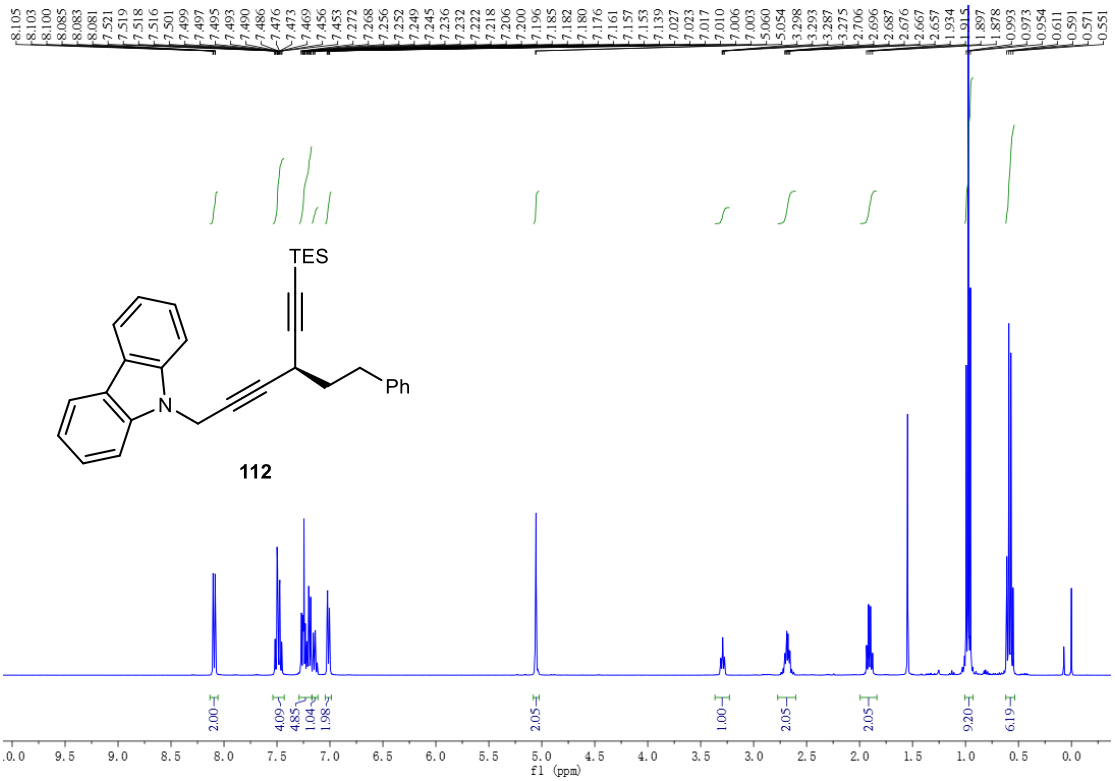
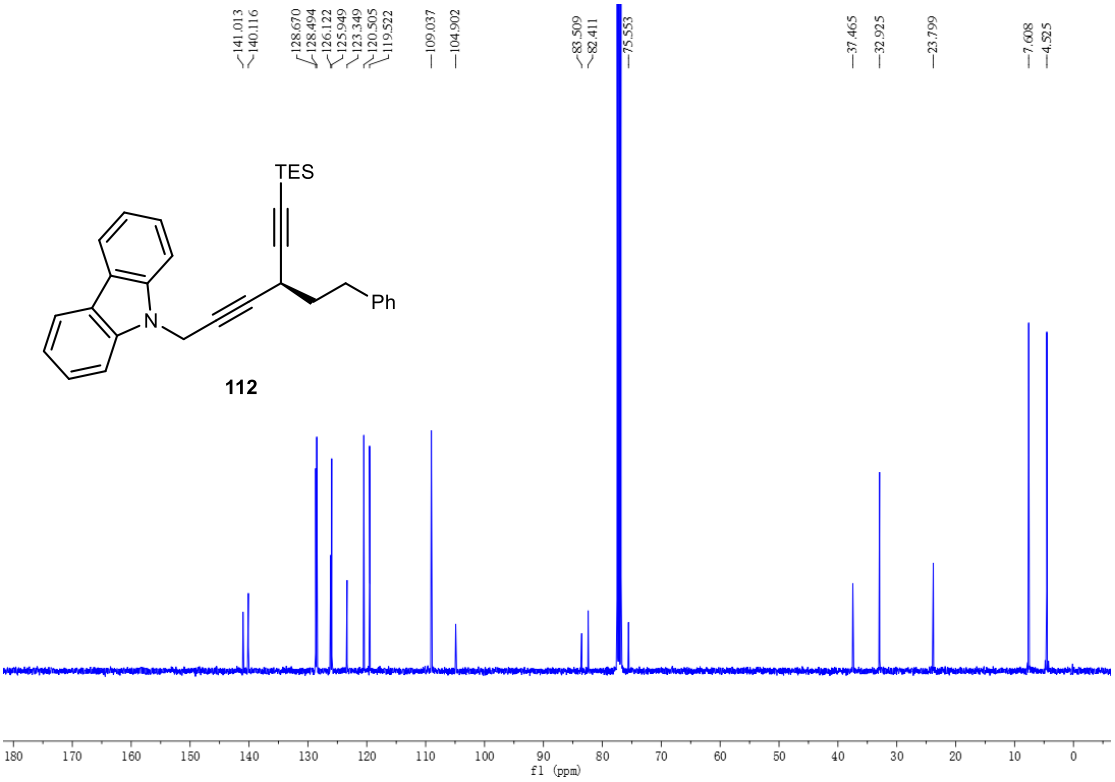
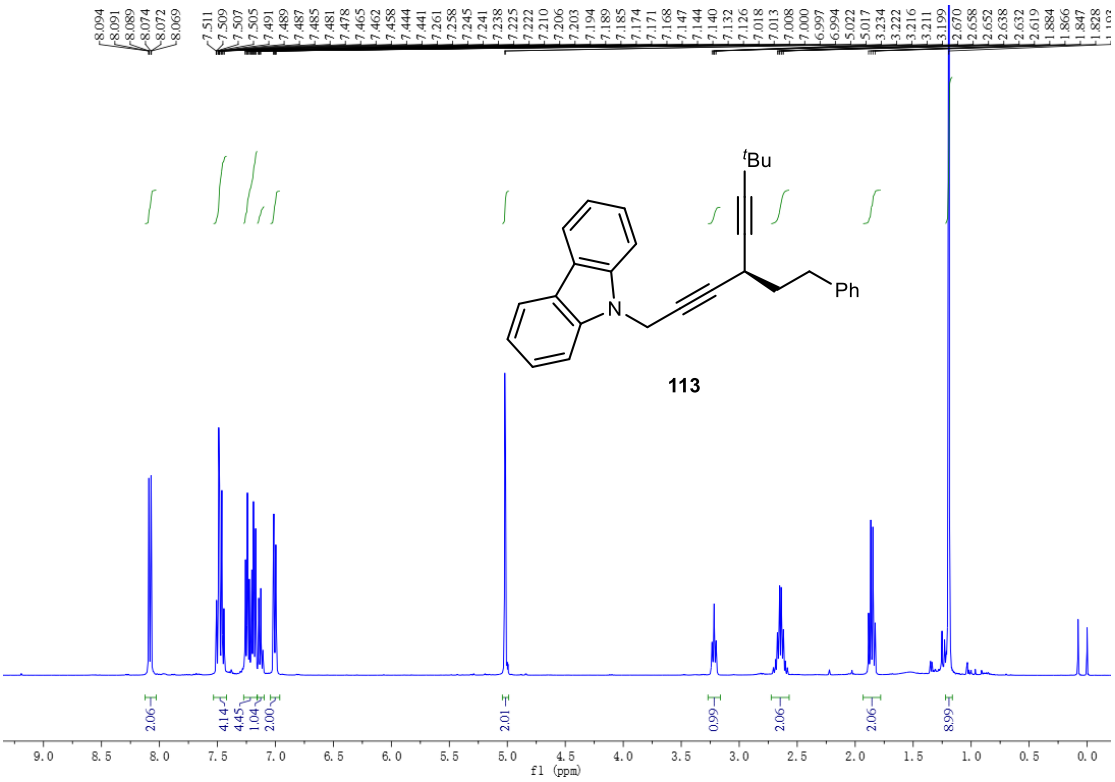
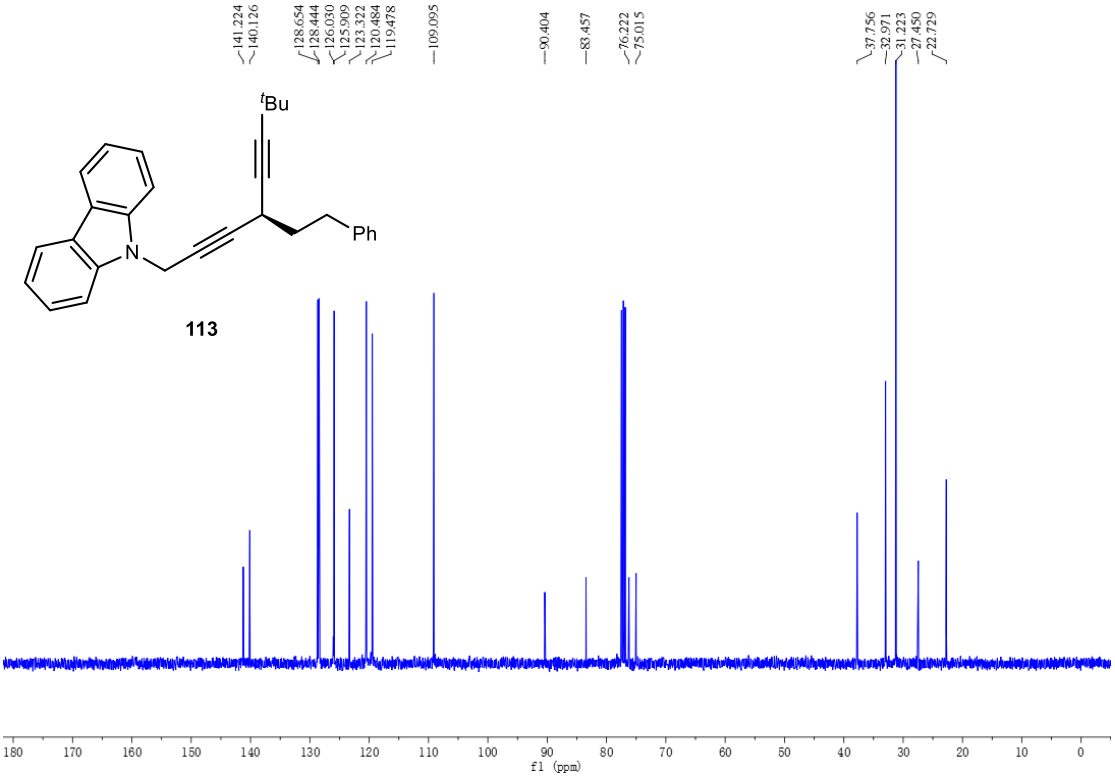
4.08
5.65
2.04
2.11
1.02
2.09
2.12
21.57
f1 (ppm)

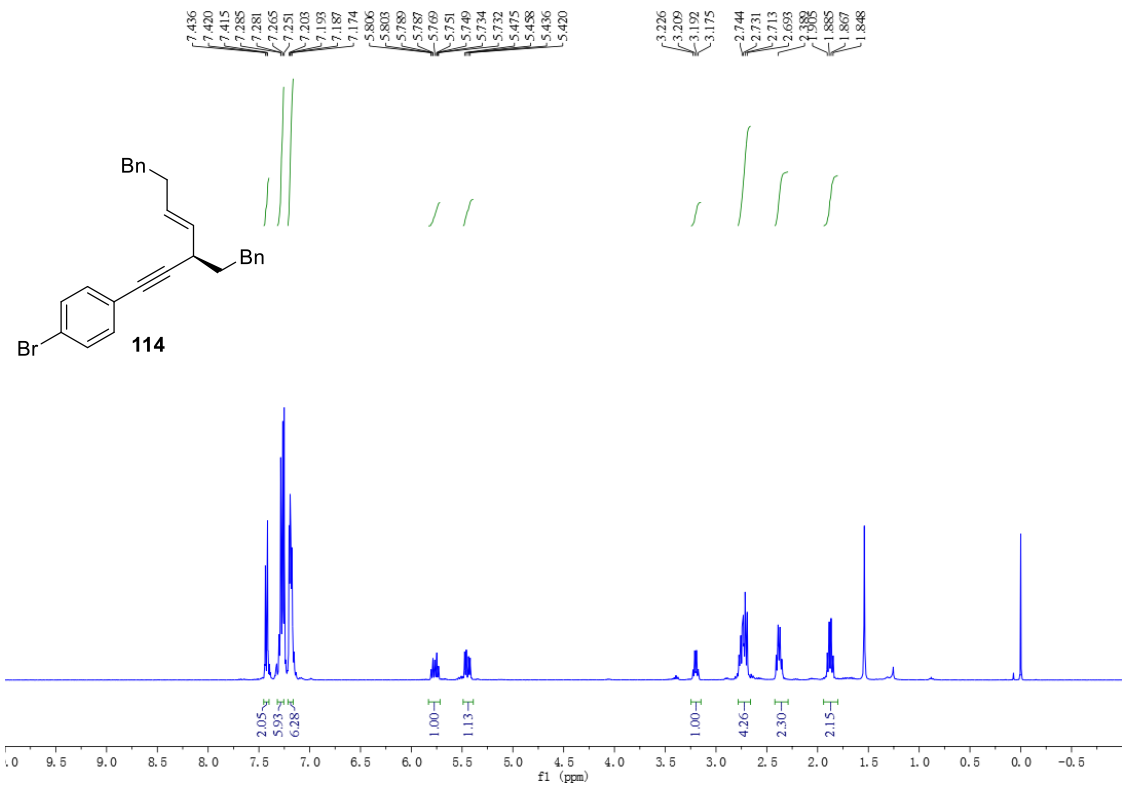

TIPS
Ph
N
111
f1 (ppm)

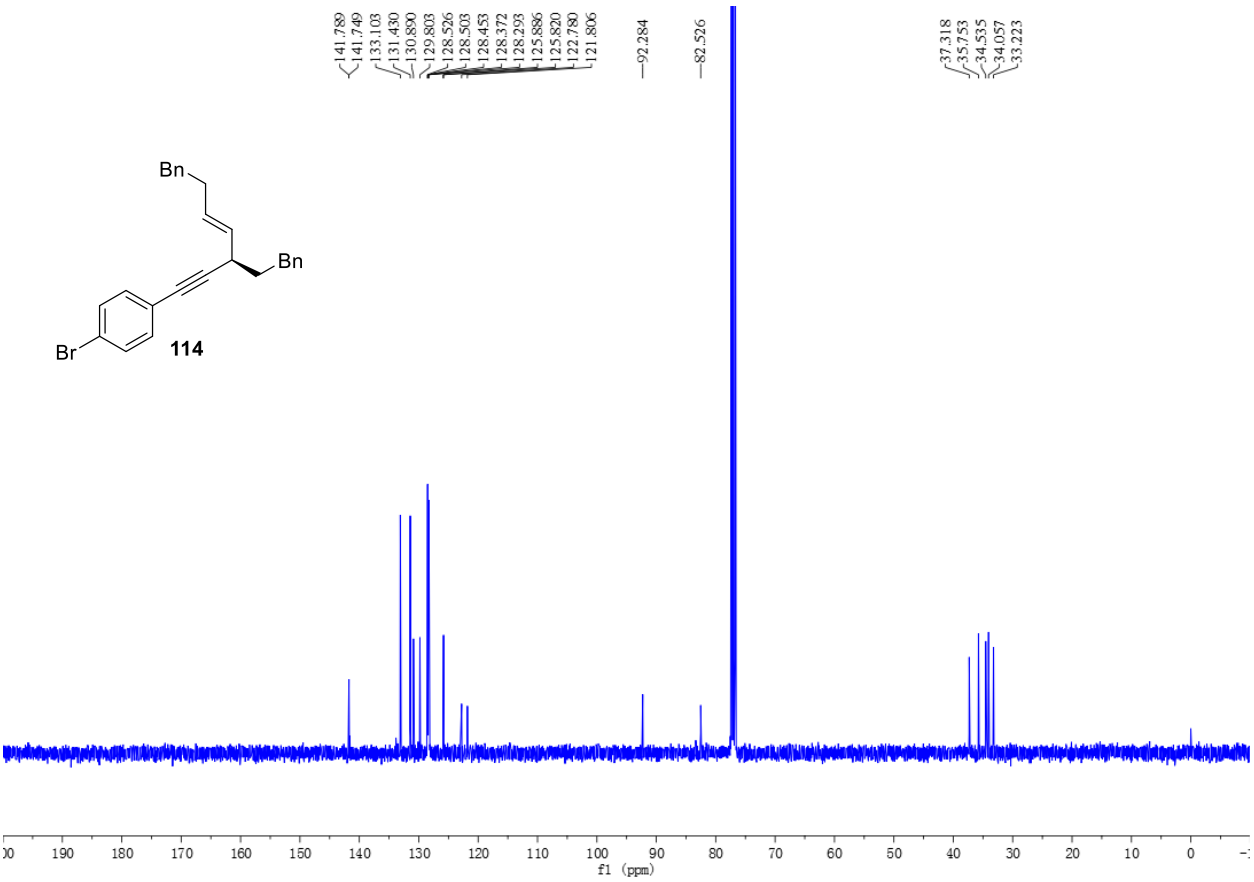

TES
Ph
N
112
f1 (ppm)

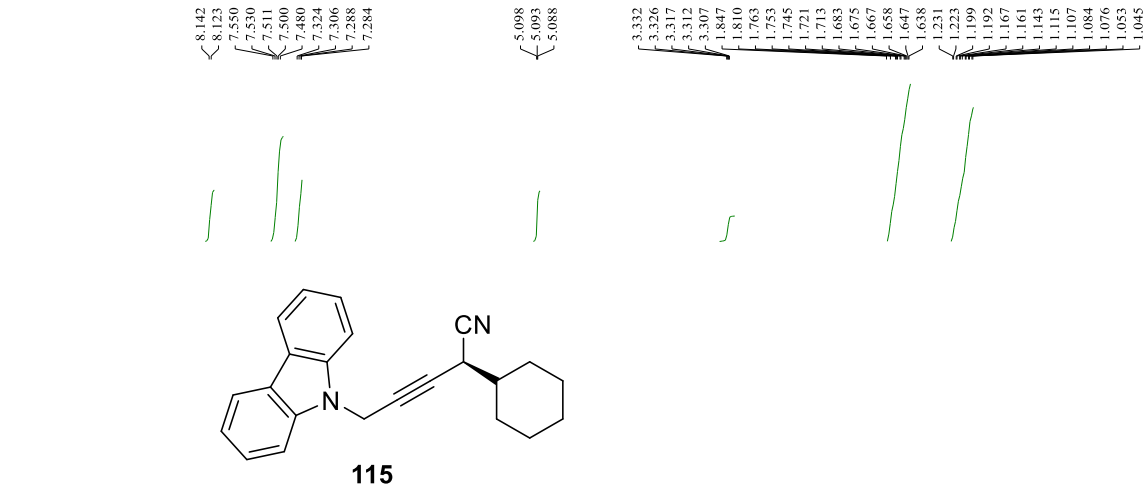

TES
Ph
N
112
f1 (ppm)


tBu
Ph
N
113
f1 (ppm)


tBu
Ph
N
113
f1 (ppm)


Bn
Bn
Br
114
f1 (ppm)


Bn
Bn
Br
114
f1 (ppm)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7.500
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7.324
7.306
7.288
7.284
5.098
5.093
5.088
3.332
3.326
3.317
3.312
3.307
1.847
1.810
1.763
1.753
1.745
1.721
1.713
1.683
1.675
1.667
1.658
1.647
1.638
1.231
1.223
1.199
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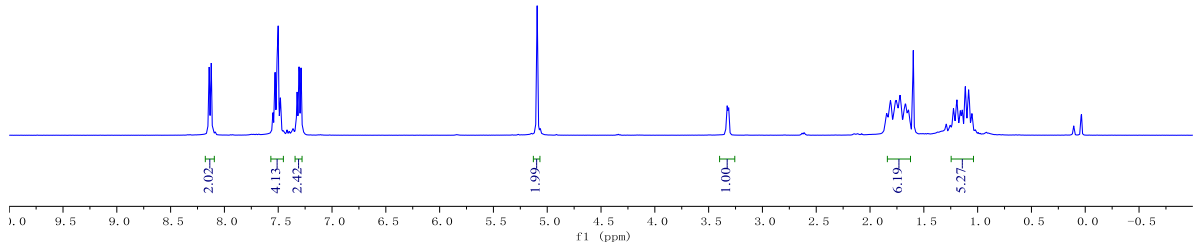
CN
N
115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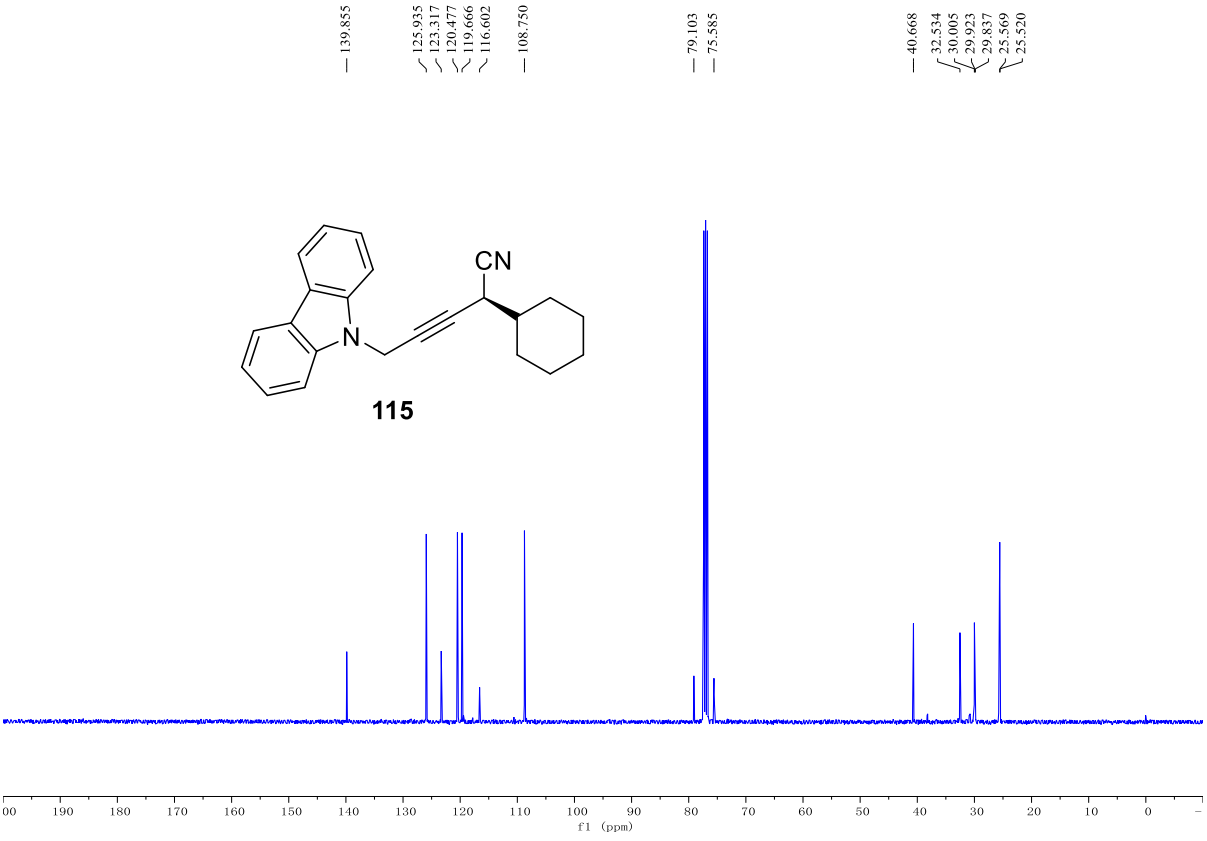
4.13
2.42
1.99
1.00
6.19
5.27
f1 (ppm)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123.317
120.477
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108.750
79.103
75.585
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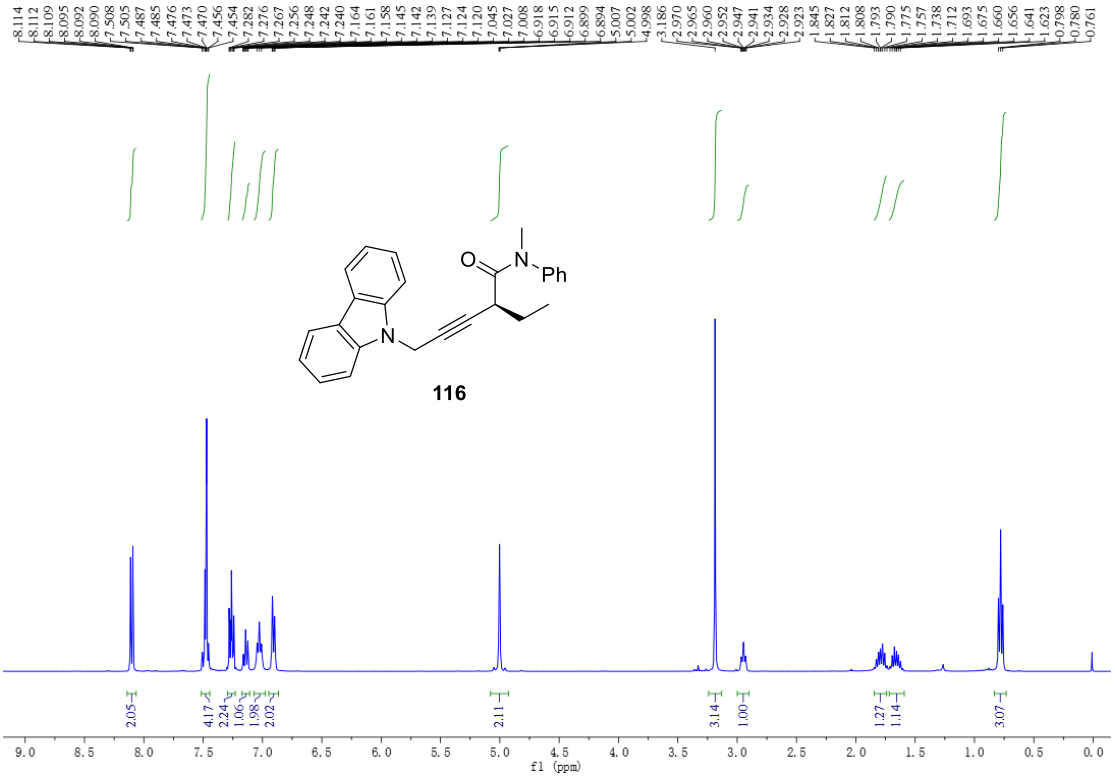
32.534
30.005
29.923
29.837
25.569
25.520
CN
N
115
f1 (ppm)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8.090
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7.473
7.470
7.456
7.454
7.282
7.276
7.267
7.256
7.248
7.242
7.240
7.164
7.161
7.158
7.145
7.142
7.139
7.127
7.124
7.120
7.045
7.027
7.008
6.918
6.915
6.912
6.899
6.894
5.007
5.002
4.998
3.186
2.970
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2.960
2.952
2.947
2.941
2.934
2.928
2.923
1.845
1.827
1.812
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1.793
1.790
1.775
1.757
1.738
1.712
1.693
1.675
1.660
1.656
1.641
1.623
0.798
0.780
0.761
O
N
Ph
N
116
2.05
4.17
2.24
1.06
1.98
2.02
2.11
3.14
1.00
1.27
1.14
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
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1.0
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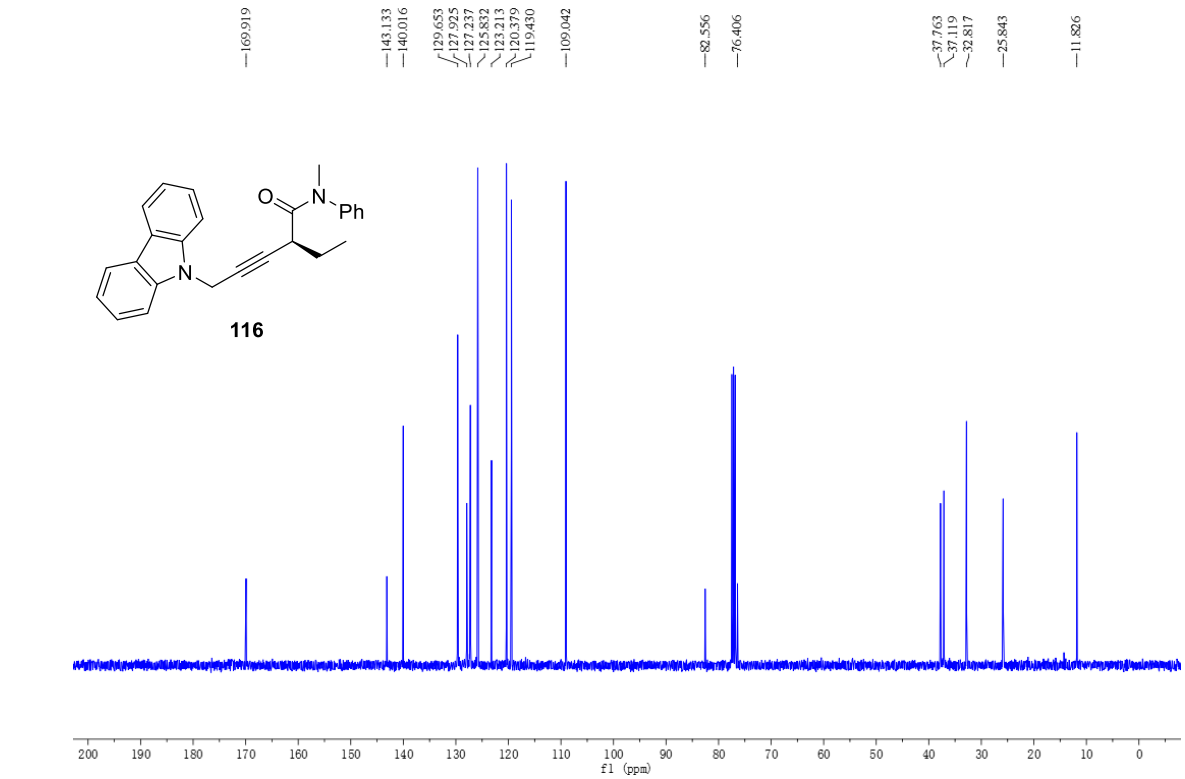
f1 (ppm)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123.213
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109.042
82.556
76.406
37.763
37.119
32.817
25.843
11.826
O
N
Ph
N
116
200
190
180
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110
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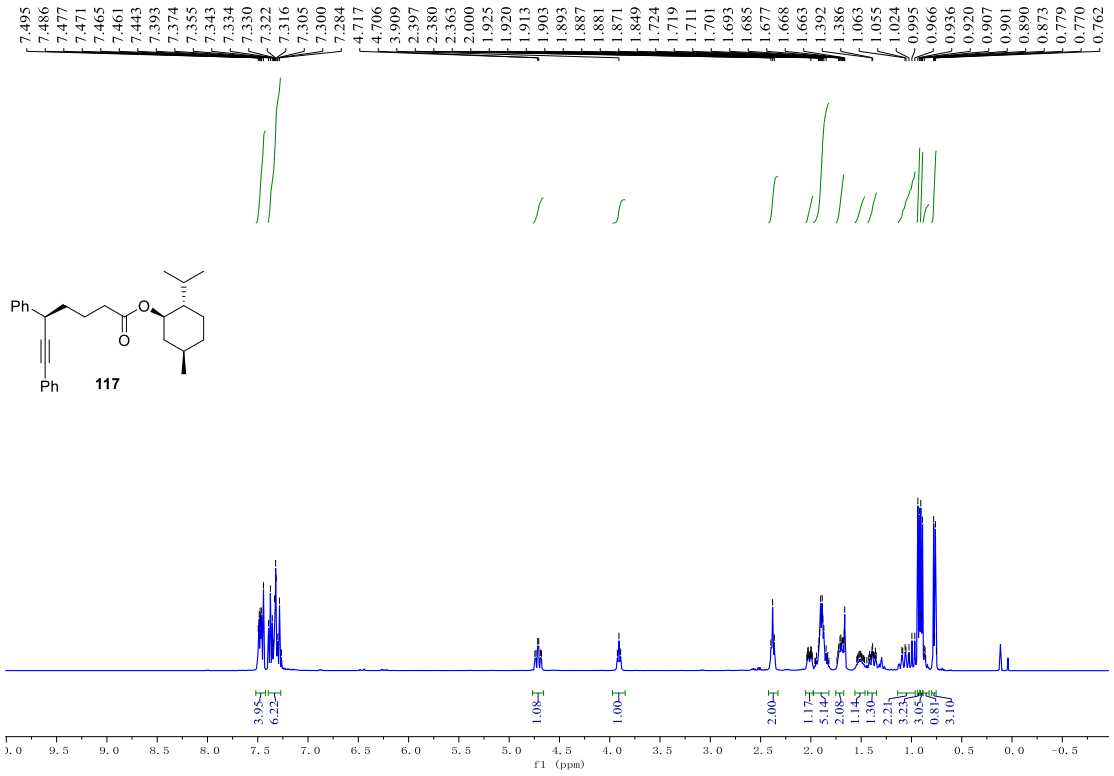
70
60
50
40
30
20
10
0
f1 (ppm)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7.316
7.305
7.300
7.284
4.717
4.706
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2.363
2.000
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1.920
1.913
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1.887
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1.849
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1.719
1.711
1.701
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1.677
1.668
1.663
1.392
1.386
1.063
1.055
1.024
0.995
0.966
0.936
0.920
0.907
0.901
0.890
0.873
0.779
0.770
0.762
Ph
O
O
Ph
117
3.95
6.22
1.08
1.00
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2.21
3.23
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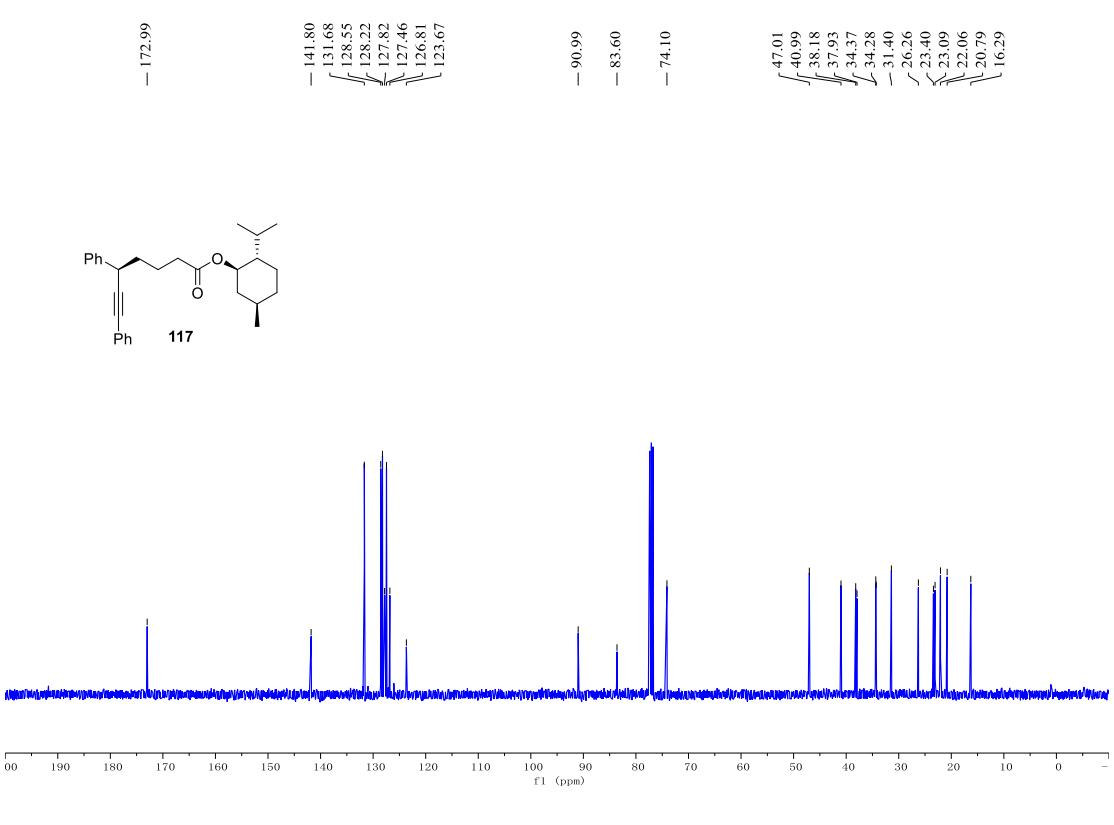
3.10
f1 (ppm)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126.81
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90.99
83.60
74.10
47.01
40.99
38.18
37.93
34.37
34.28
31.40
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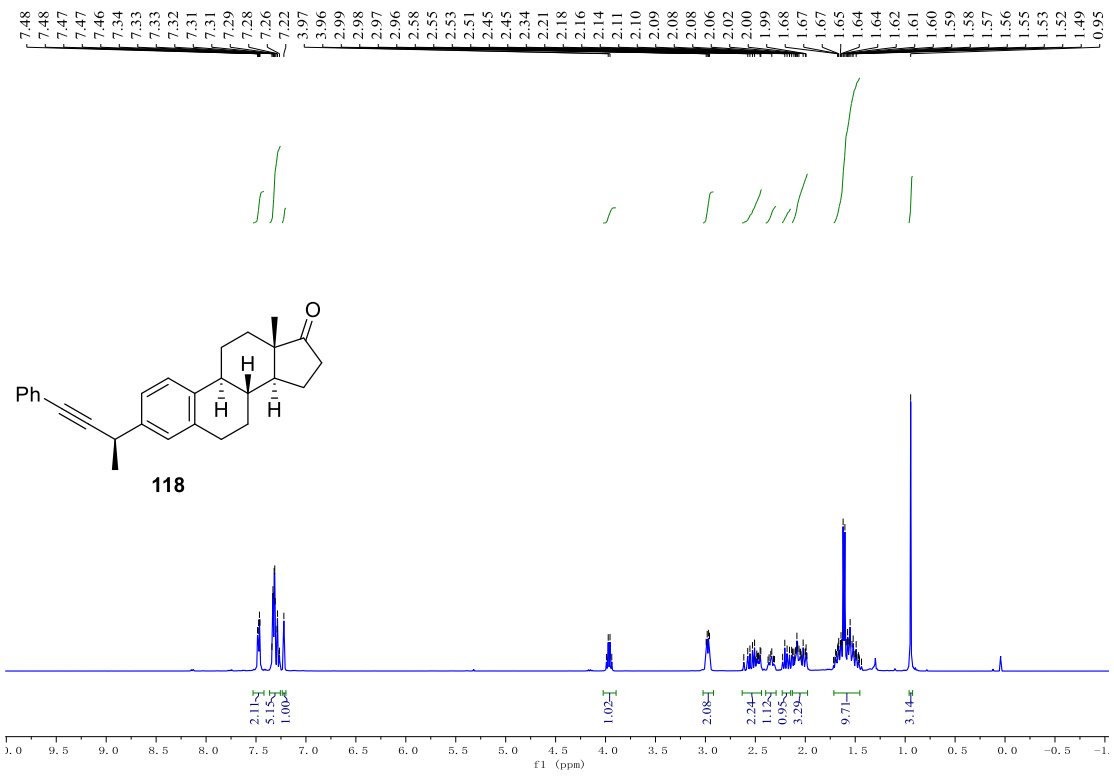
23.40
23.09
22.06
20.79
16.29
Ph
O
O
Ph
117
f1 (ppm)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O
H
H
H
Ph
118
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2.08
2.24
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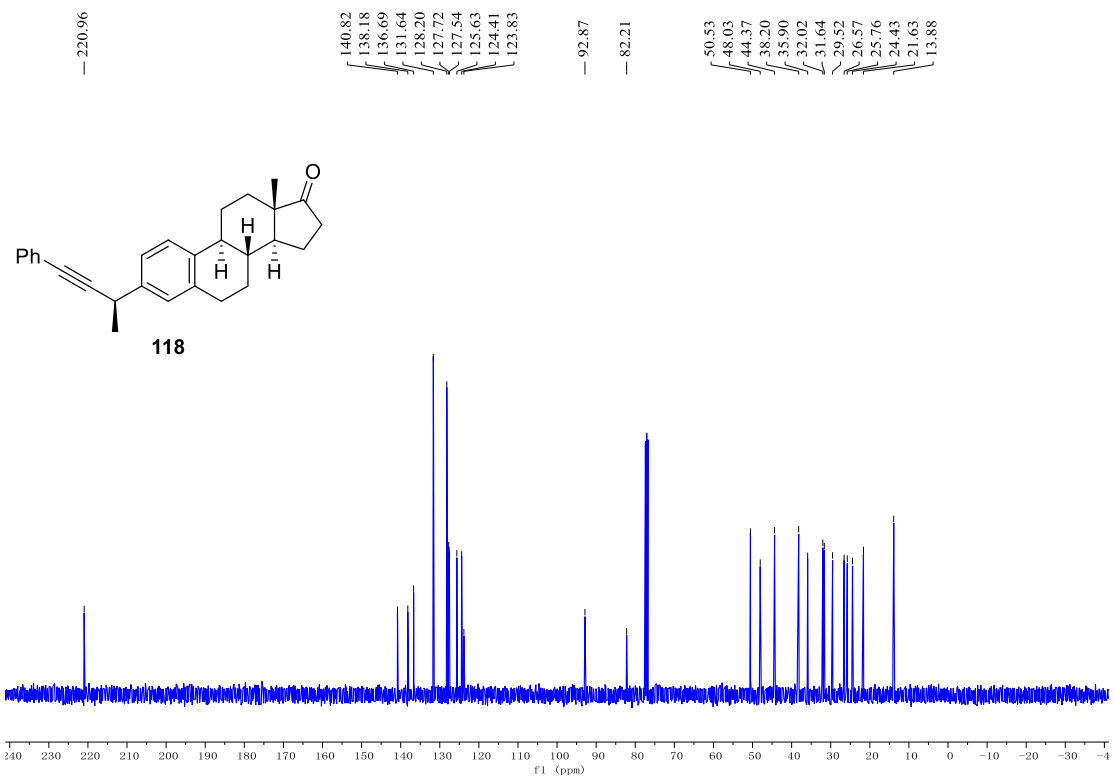
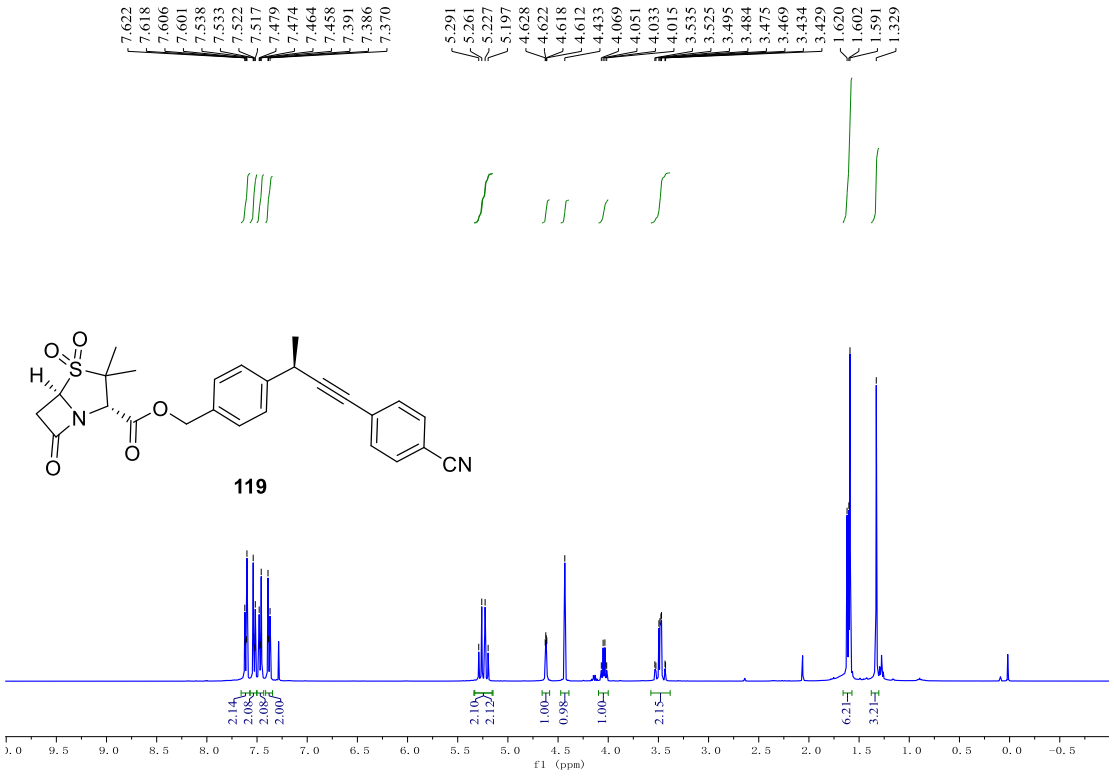
f1 (ppm)


220.96
140.82 138.18 136.69 131.64 128.20 127.72 127.54 125.63 124.41 123.83
92.87
82.21
50.53 48.03 44.37 38.20 35.90 32.02 31.64 29.52 26.57 25.76 24.43 21.63 13.88
O
H
H
H
Ph
118
f1 (ppm)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7.386
7.370
5.291
5.261
5.227
5.197
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4.622
4.618
4.612
4.433
4.069
4.051
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3.525
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3.484
3.475
3.469
3.434
3.429
1.620
1.602
1.591
1.329
119
CN
2.14
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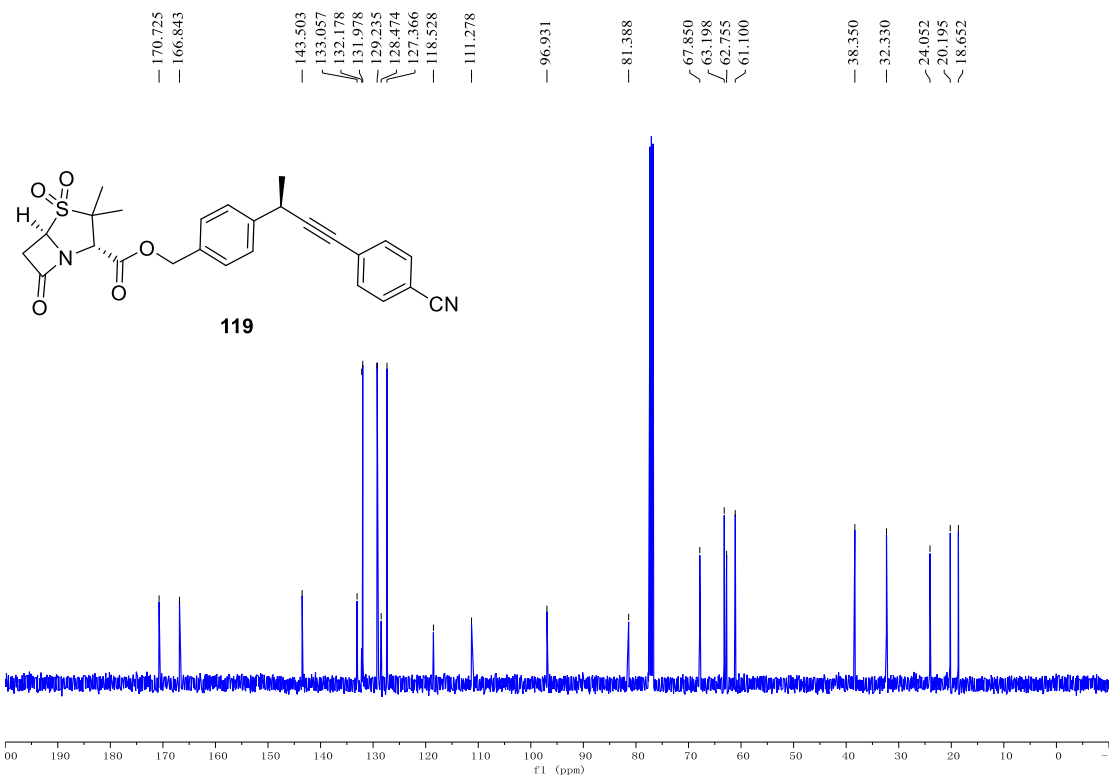
f1 (ppm)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111.278
96.931
81.388
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62.755
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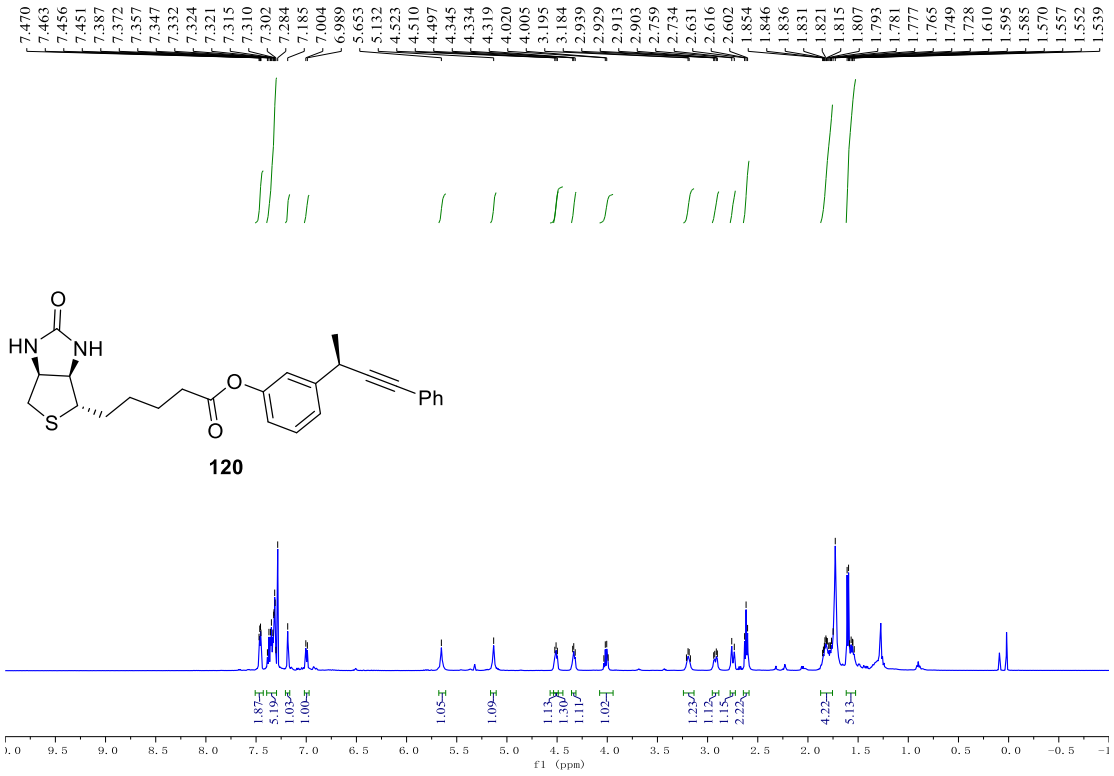
32.330
24.052
20.195
18.652
119
CN
f1 (ppm)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7.451
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7.372
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7.302
7.284
7.185
7.004
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5.653
5.132
4.523
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4.334
4.319
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4.005
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3.184
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2.913
2.903
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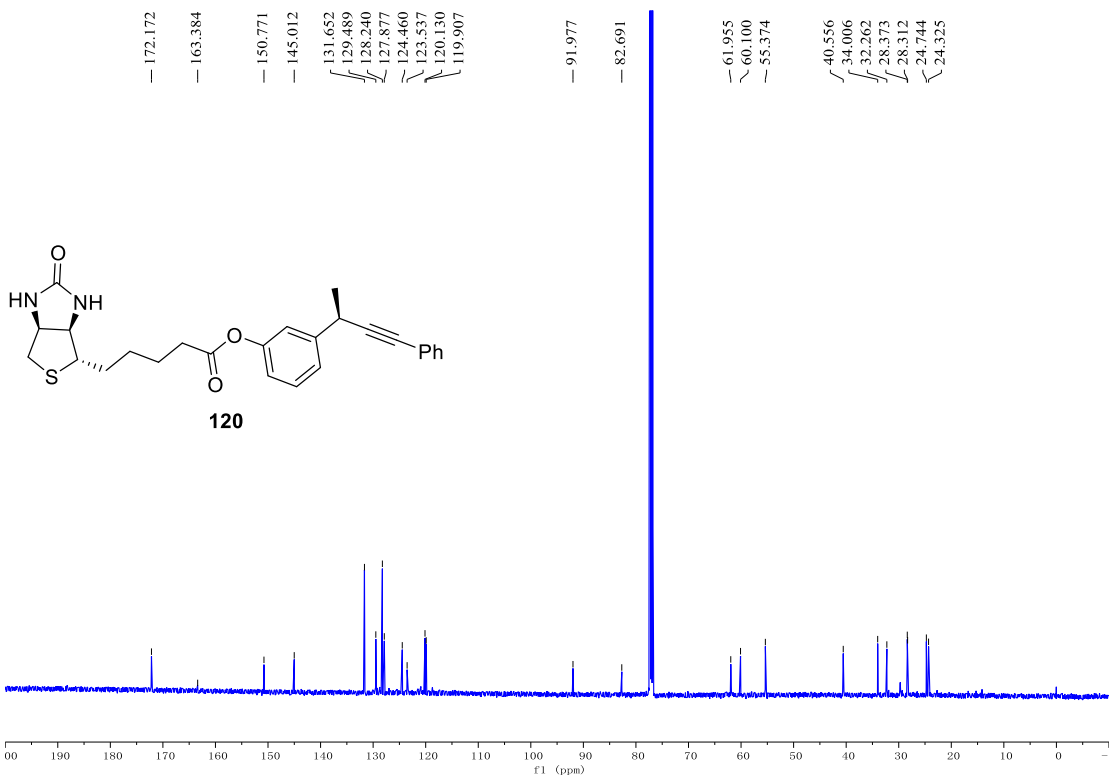
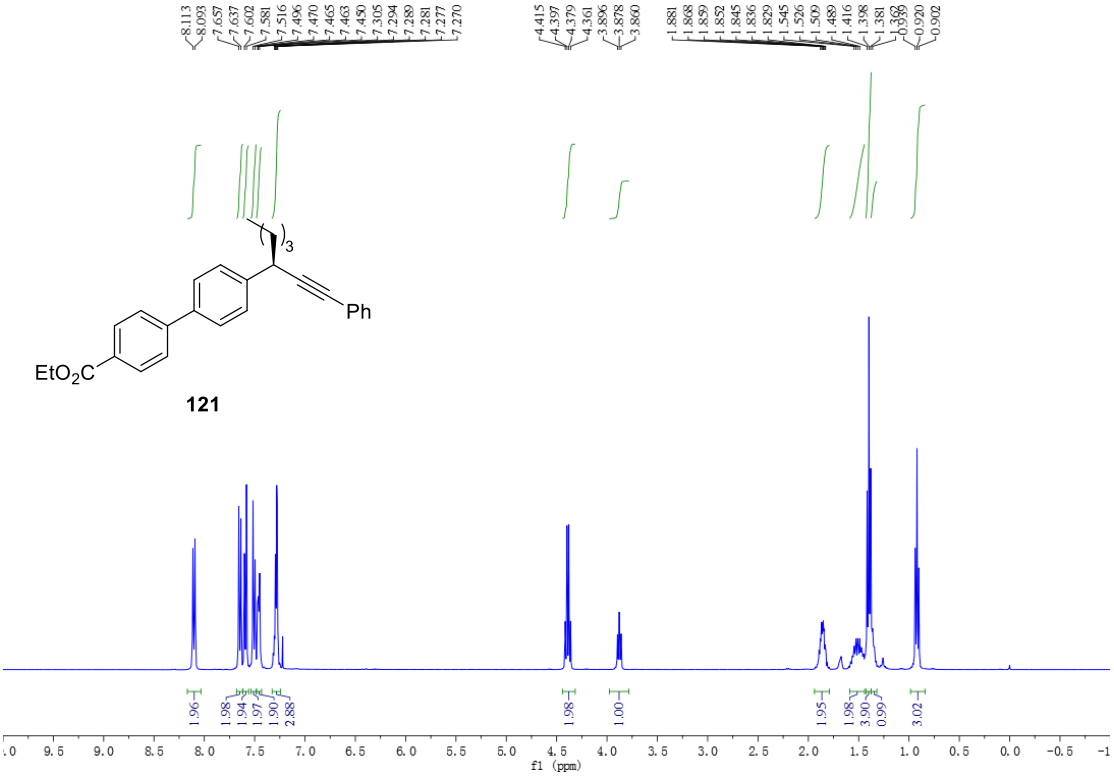
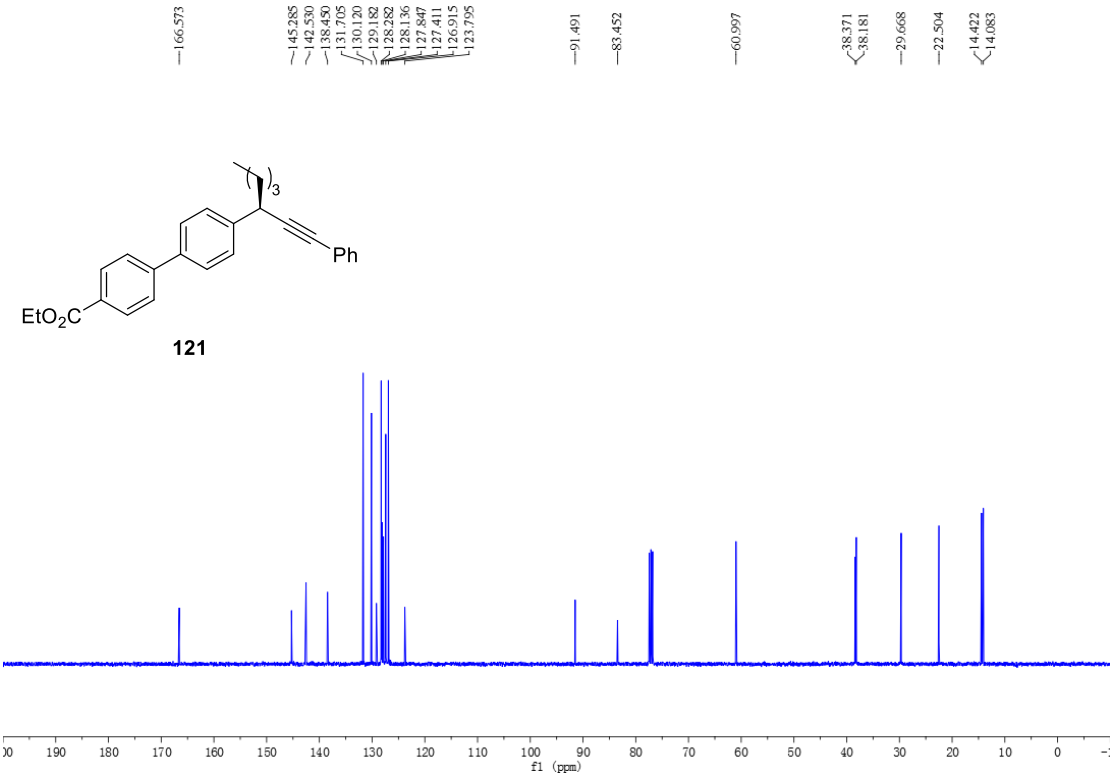
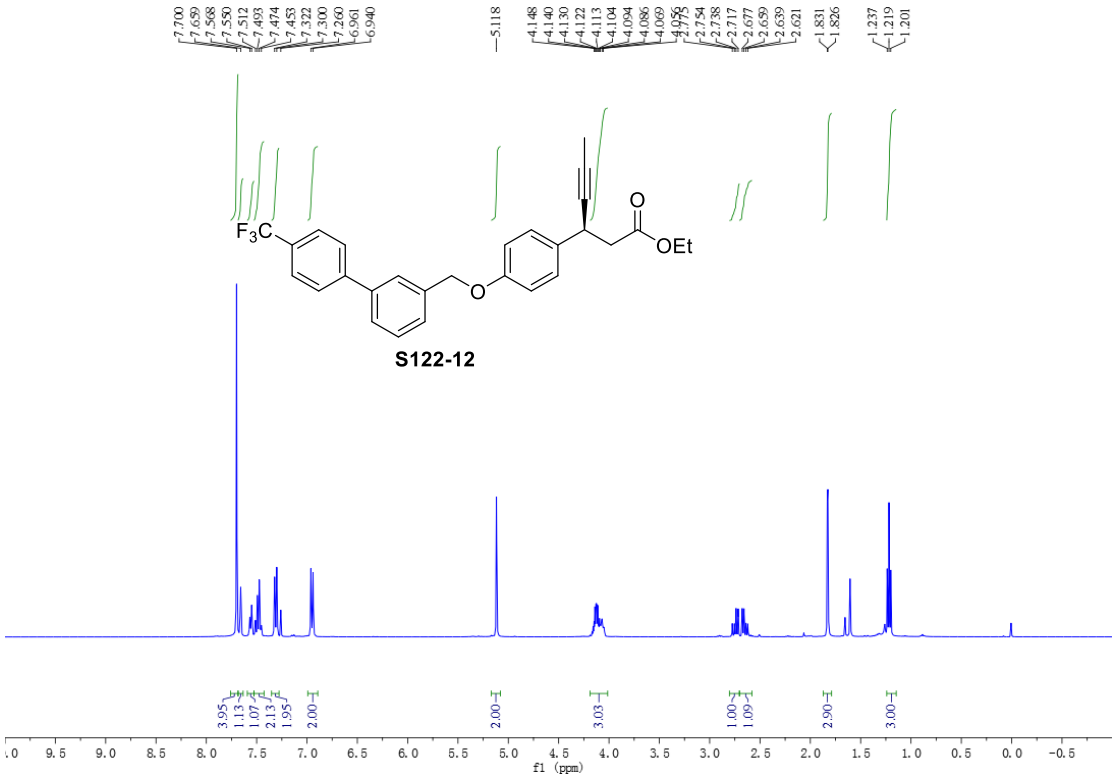
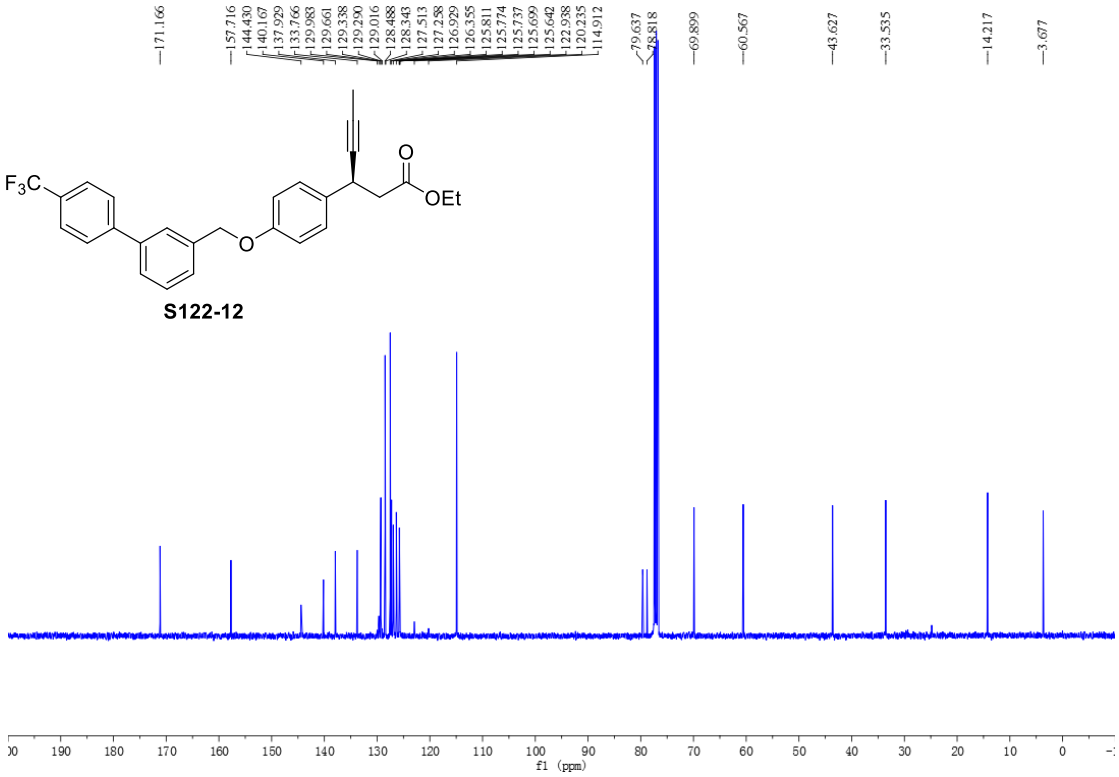
1.836
1.831
1.821
1.815
1.807
1.793
1.781
1.777
1.765
1.749
1.728
1.610
1.595
1.585
1.570
1.557
1.552
1.539
HN
NH
O
S
O
O
Ph
120
1.87
5.19
1.03
1.00
1.05
1.09
1.13
1.30
1.11
1.02
1.23
1.12
1.15
2.22
4.22
5.13
f1 (ppm)

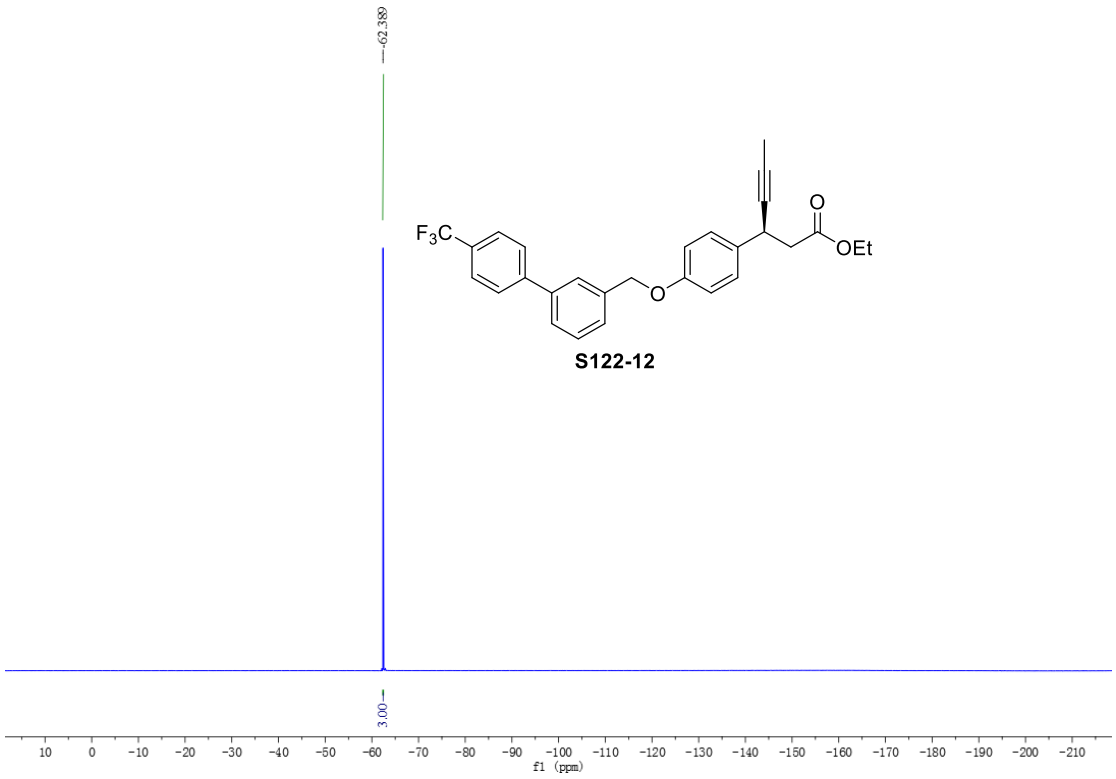

172.172
163.384
150.771
145.012
131.652
129.489
128.240
127.877
124.460
123.537
120.130
119.907
91.977
82.691
61.955
60.100
55.374
40.556
34.006
32.262
28.373
28.312
24.744
24.325
HN
NH
O
S
O
O
Ph
120
f1 (ppm)

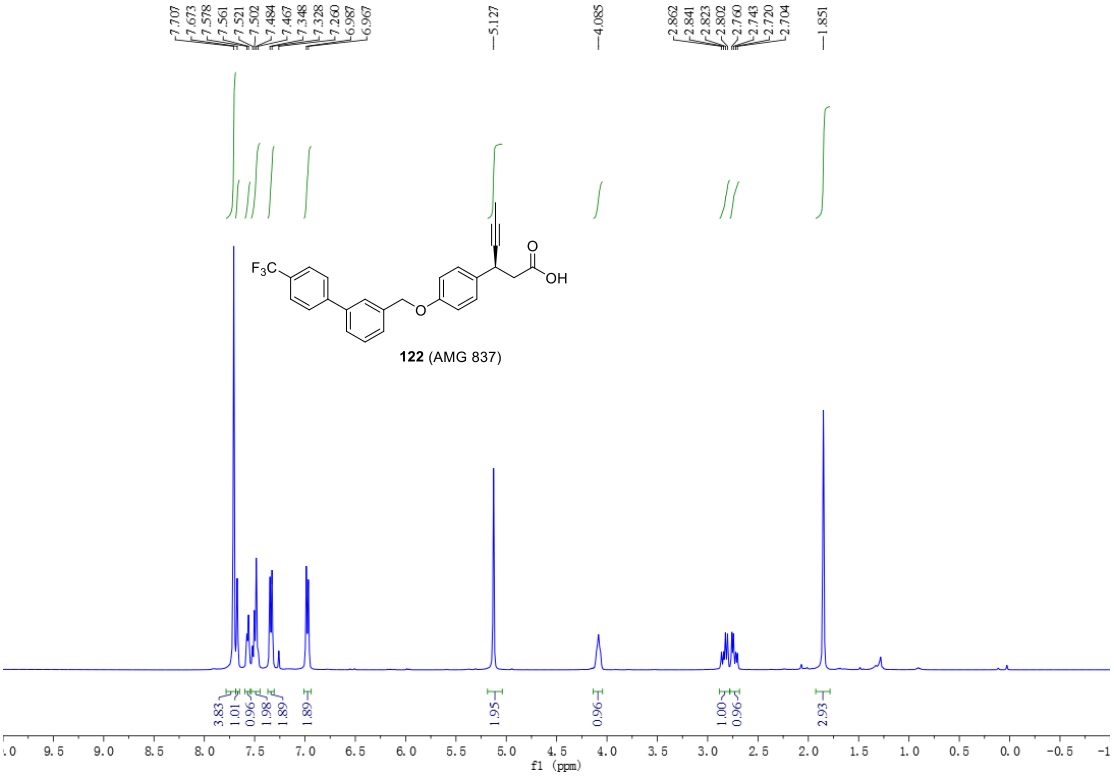

8.113
8.093
7.657
7.637
7.602
7.581
7.516
7.496
7.470
7.465
7.463
7.450
7.305
7.294
7.289
7.281
7.277
7.270
4.415
4.397
4.379
4.361
3.896
3.878
3.860
1.881
1.868
1.859
1.852
1.845
1.836
1.829
1.545
1.526
1.509
1.489
1.416
1.398
1.381
0.939
0.920
0.902
Ph
EtO2C
121
1.96
1.98
1.94
1.97
1.90
2.88
1.98
1.00
1.95
1.98
3.90
0.99
3.02
f1 (ppm)

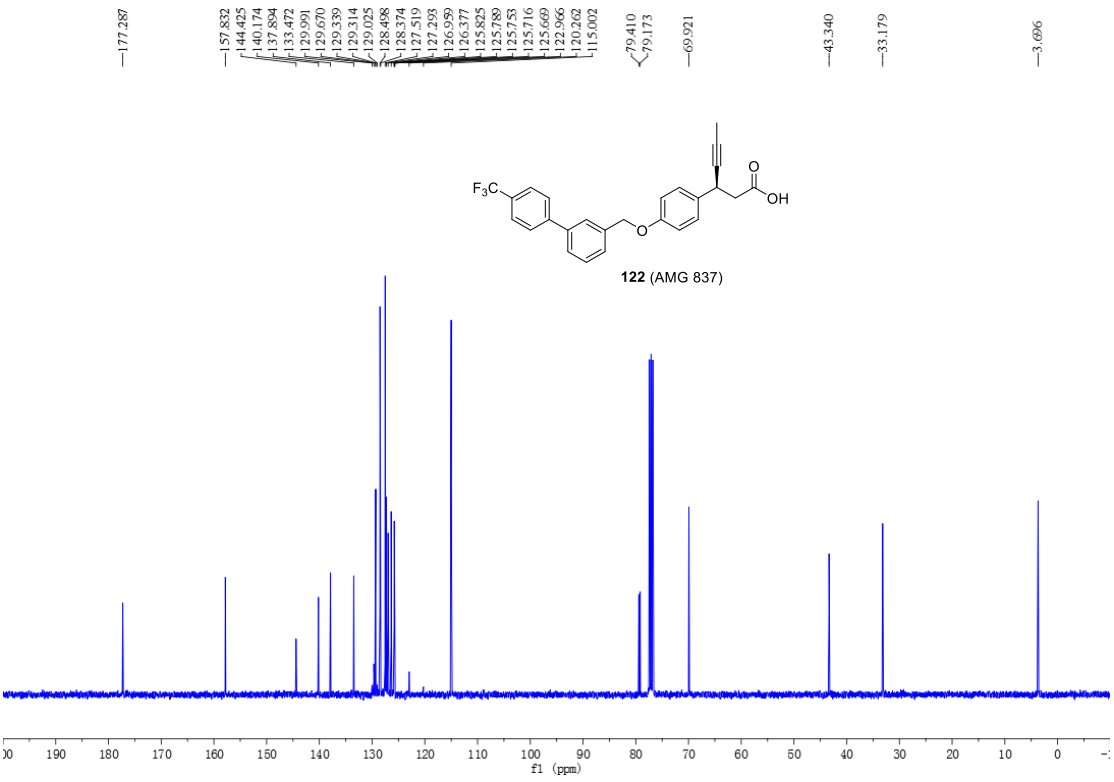

166.573
145.285
142.530
138.450
131.705
130.120
129.182
128.282
128.136
127.847
127.411
126.915
123.795
91.491
83.452
60.997
38.371
38.181
29.668
22.504
14.422
14.083
Ph
EtO2C
121
f1 (ppm)

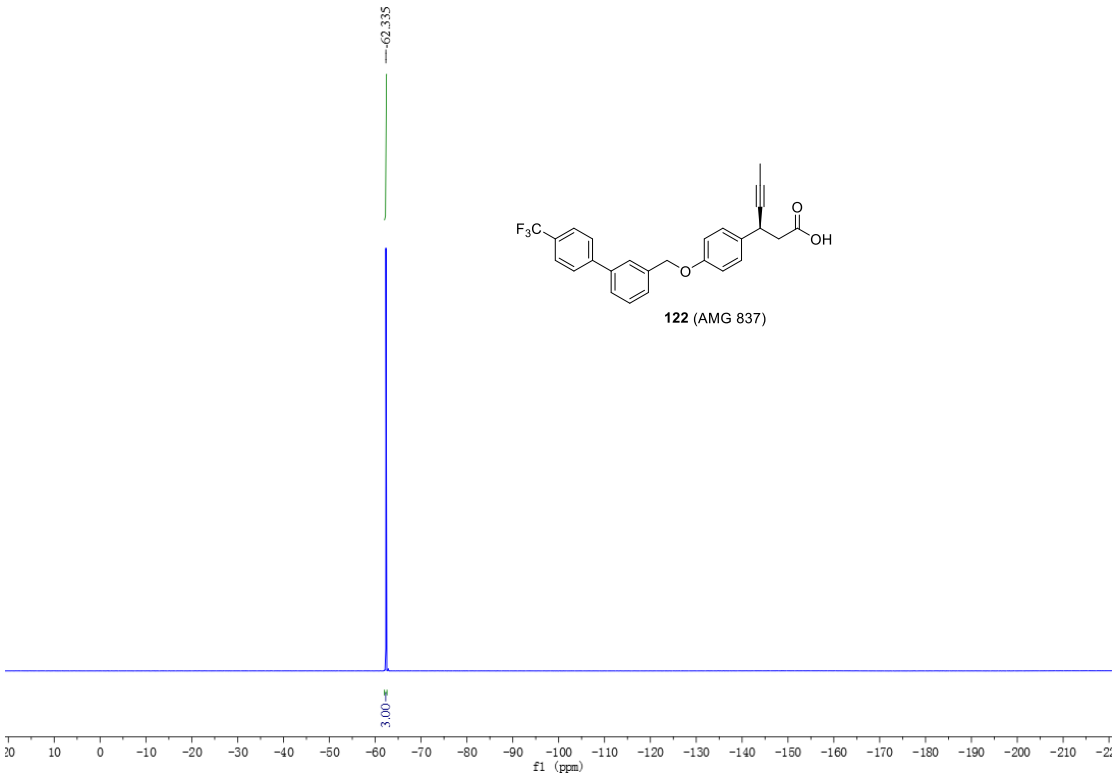

7.700
7.659
7.568
7.550
7.512
7.493
7.474
7.453
7.322
7.300
7.260
6.961
6.940
5.118
4.148
4.140
4.130
4.122
4.113
4.104
4.094
4.086
4.069
4.055
2.775
2.754
2.738
2.717
2.677
2.659
2.639
2.621
1.831
1.826
1.237
1.219
1.201
F3C
O
OEt
O
S122-12
3.95
1.13
1.07
2.13
1.95
2.00
2.00
3.03
1.00
1.09
2.90
3.00
f1 (ppm)


171.166
157.716
144.430
140.167
137.929
133.766
129.983
129.661
129.338
129.290
129.016
128.488
128.343
127.513
127.258
126.929
126.355
125.811
125.774
125.737
125.699
125.642
122.938
120.235
114.912
79.637
78.818
69.899
60.567
43.627
33.535
14.217
3.677
F3C
O
OEt
O
S122-12
f1 (ppm)

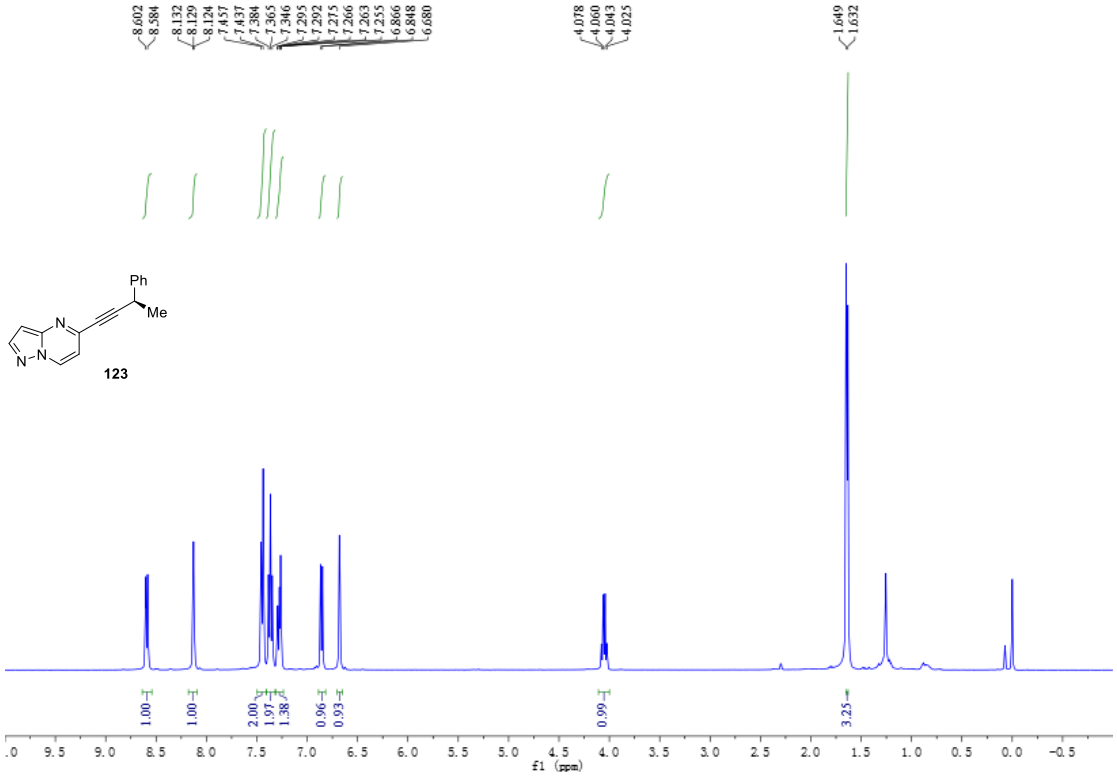

-62.389
F3C
O
OEt
O
S122-12
3.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

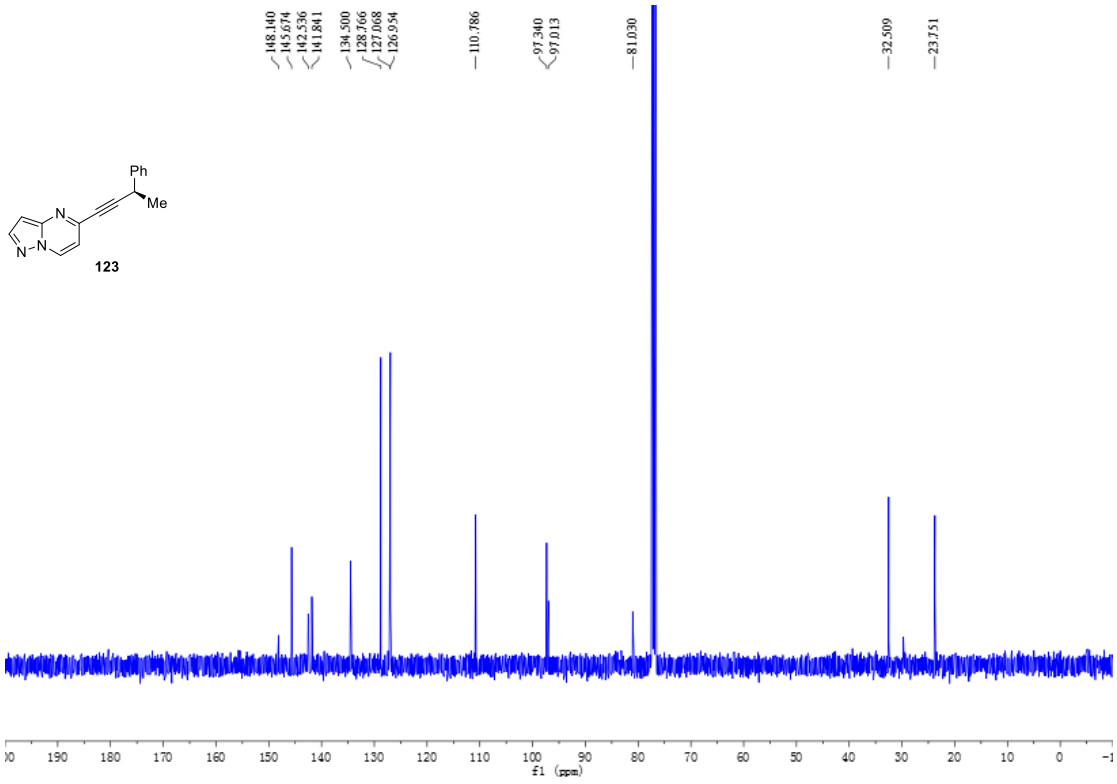

7.707
7.673
7.578
7.561
7.521
7.502
7.484
7.467
7.348
7.328
7.260
6.987
6.967
5.127
4.085
2.862
2.841
2.823
2.802
2.760
2.743
2.720
2.704
1.851
F3C
O
OH
O
122 (AMG 837)
3.83
1.01
0.96
1.98
1.89
1.89
1.95
0.96
1.00
0.96
2.93
f1 (ppm)

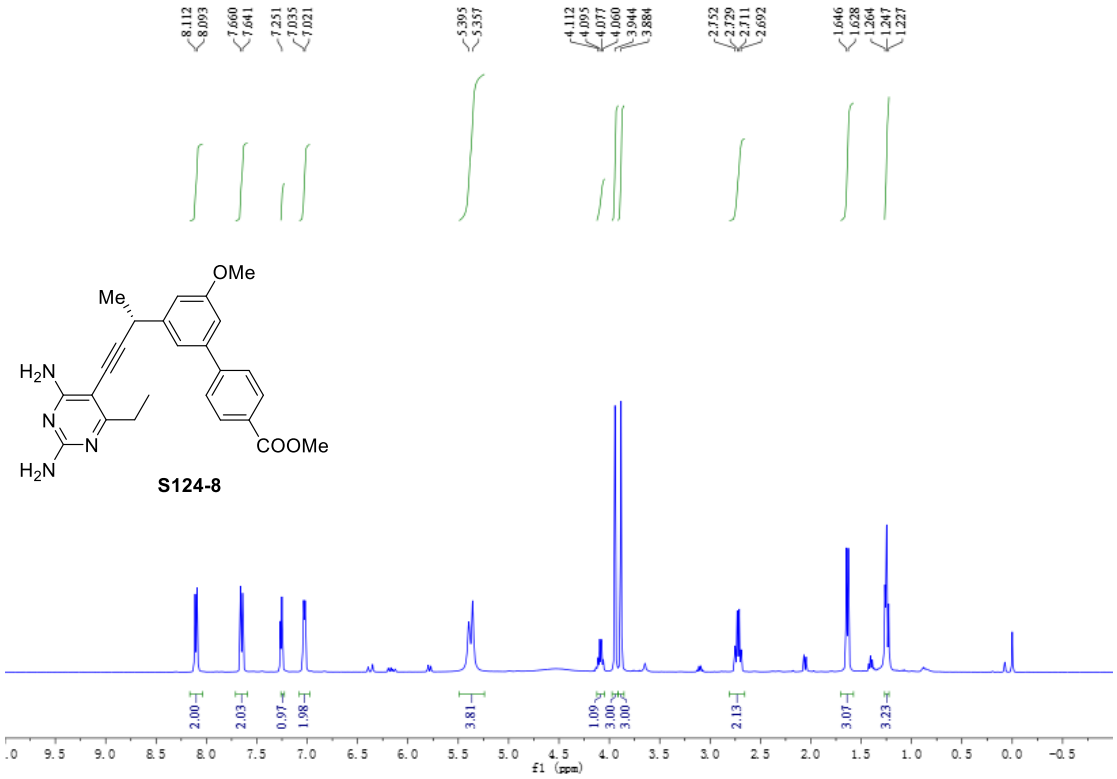

177.287
157.832
144.425
140.174
137.894
133.472
129.991
129.670
129.339
129.314
129.025
128.498
128.374
127.519
127.293
126.959
126.377
125.825
125.789
125.753
125.716
125.669
122.966
120.262
115.002
79.410
79.173
69.921
43.340
33.179
3.696
F3C
O
OH
O
122 (AMG 837)
f1 (ppm)

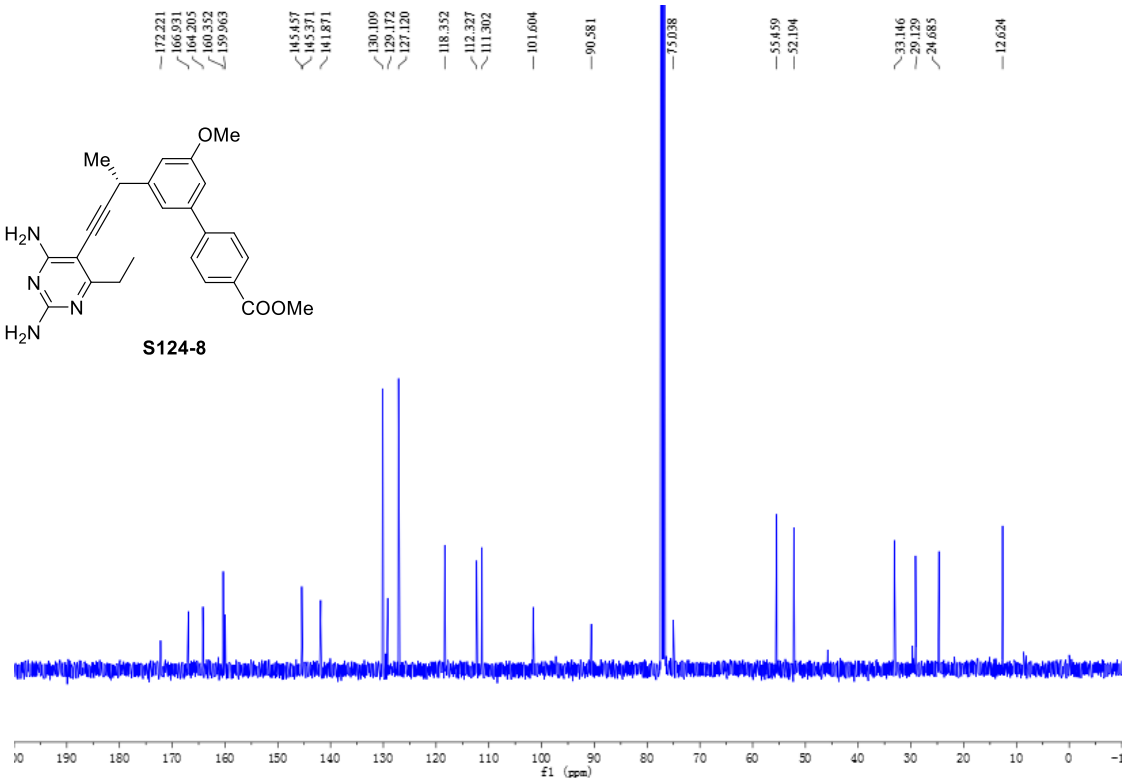


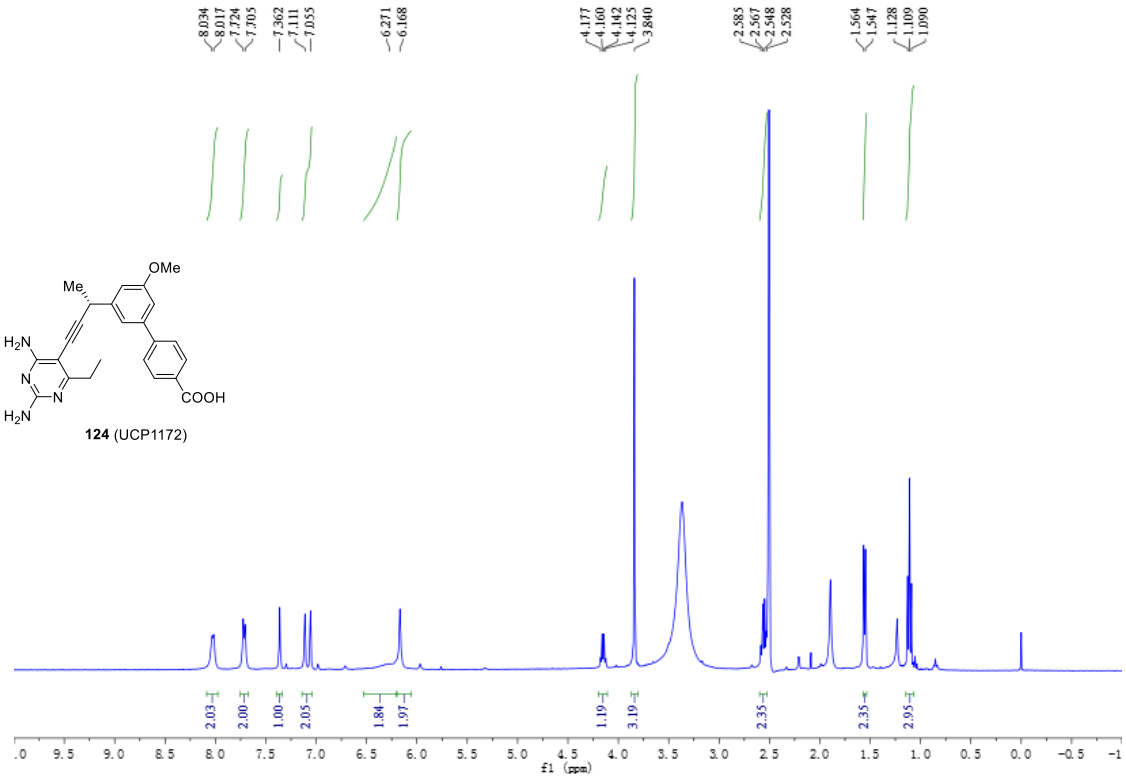
122 (AMG 837)


8.602
8.584
8.132
8.129
8.124
7.457
7.437
7.384
7.365
7.346
7.295
7.292
7.275
7.266
7.263
7.255
6.866
6.848
6.680
4.078
4.060
4.043
4.025
1.649
1.632
Ph
Me
N
N
N
123
1.00
1.00
2.00
1.97
1.38
0.96
0.93
0.99
3.25
f1 (ppm)

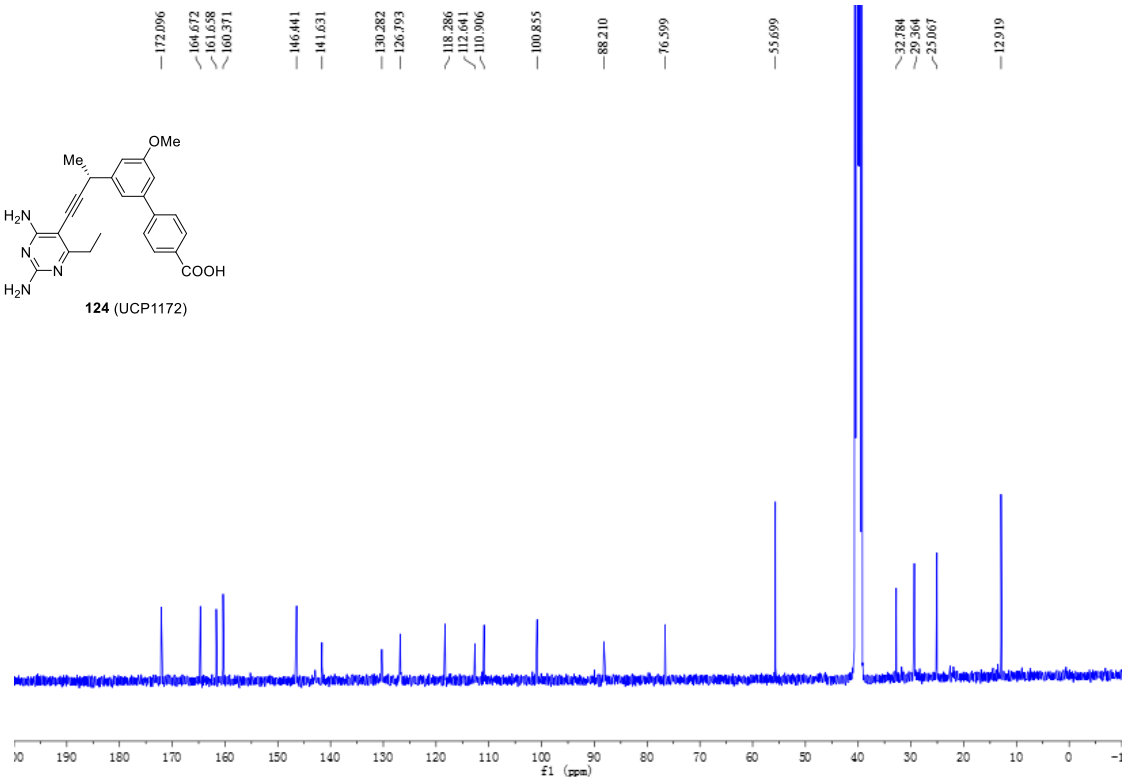

148.140
145.674
142.536
141.841
134.500
128.766
127.068
126.954
110.786
97.340
97.013
81.030
32.509
23.751
Ph
Me
N
N
N
123
f1 (ppm)


8.112
8.093
7.660
7.641
7.251
7.035
7.021
5.395
5.357
4.112
4.095
4.077
4.060
3.944
3.884
2.752
2.729
2.711
2.692
1.646
1.628
1.264
1.247
1.227
OMe
Me
H2N
N
N
H2N
COOMe
S124-8
2.00
2.03
0.97
1.98
3.81
1.09
3.00
3.00
2.13
3.07
3.23
f1 (ppm)

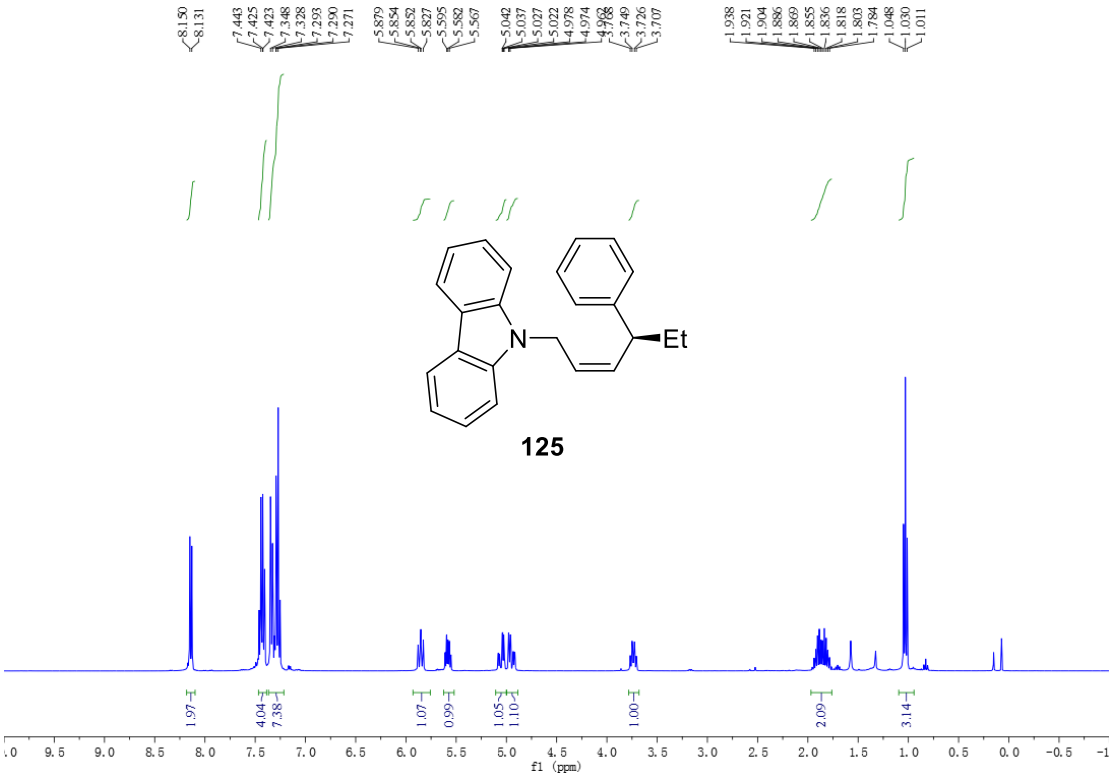

172.221
166.931
164.205
160.352
159.963
145.457
145.371
141.871
130.109
129.172
127.120
118.352
112.327
111.302
101.604
90.581
75.038
55.459
52.194
33.146
29.129
24.685
12.624
OMe
Me
H2N
N
N
H2N
COOMe
S124-8
f1 (ppm)

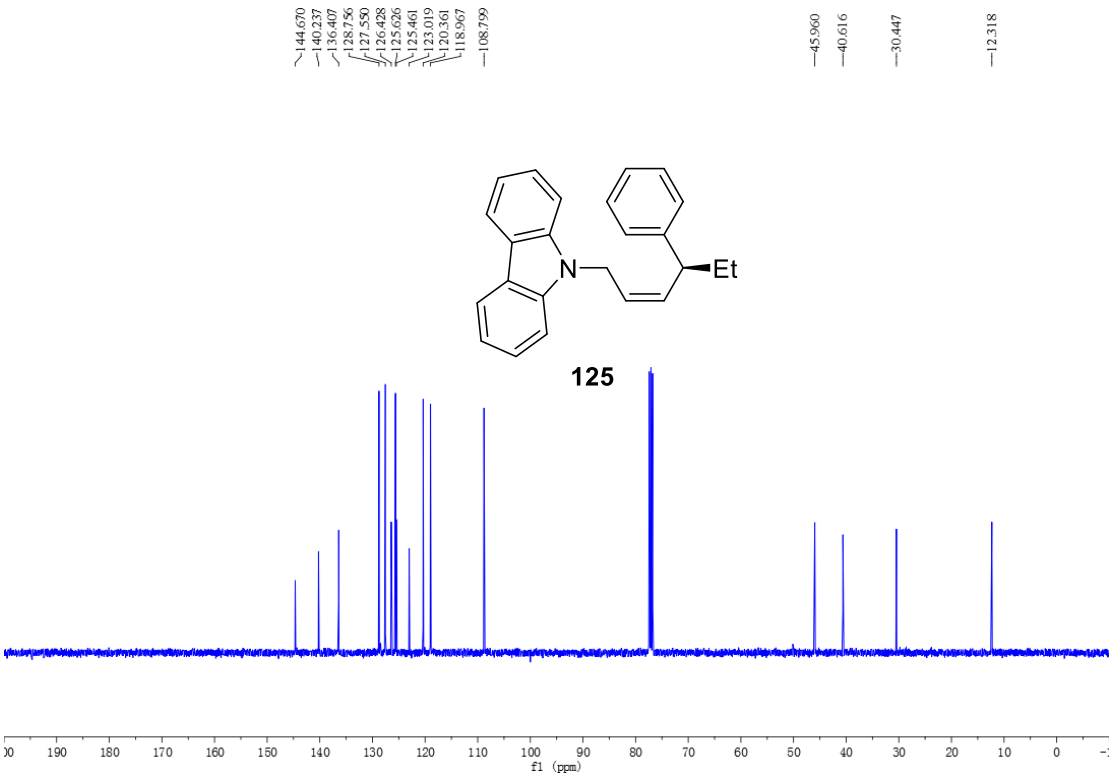


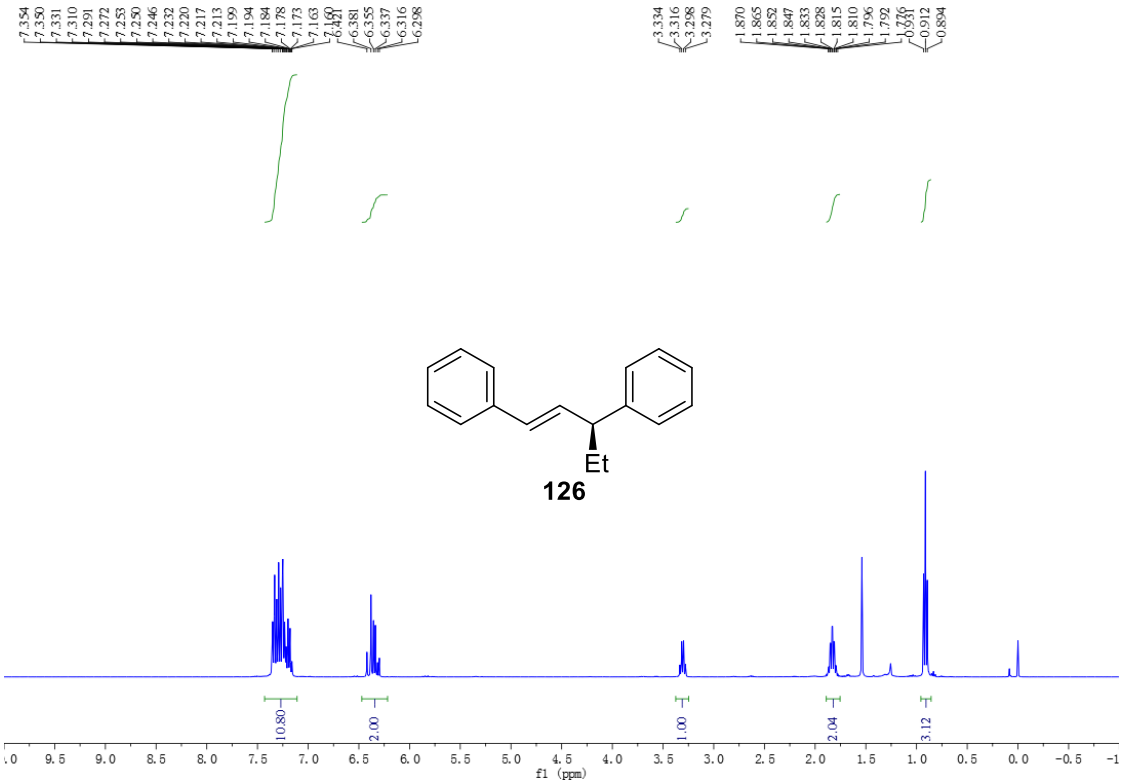
124 (UCP1172)

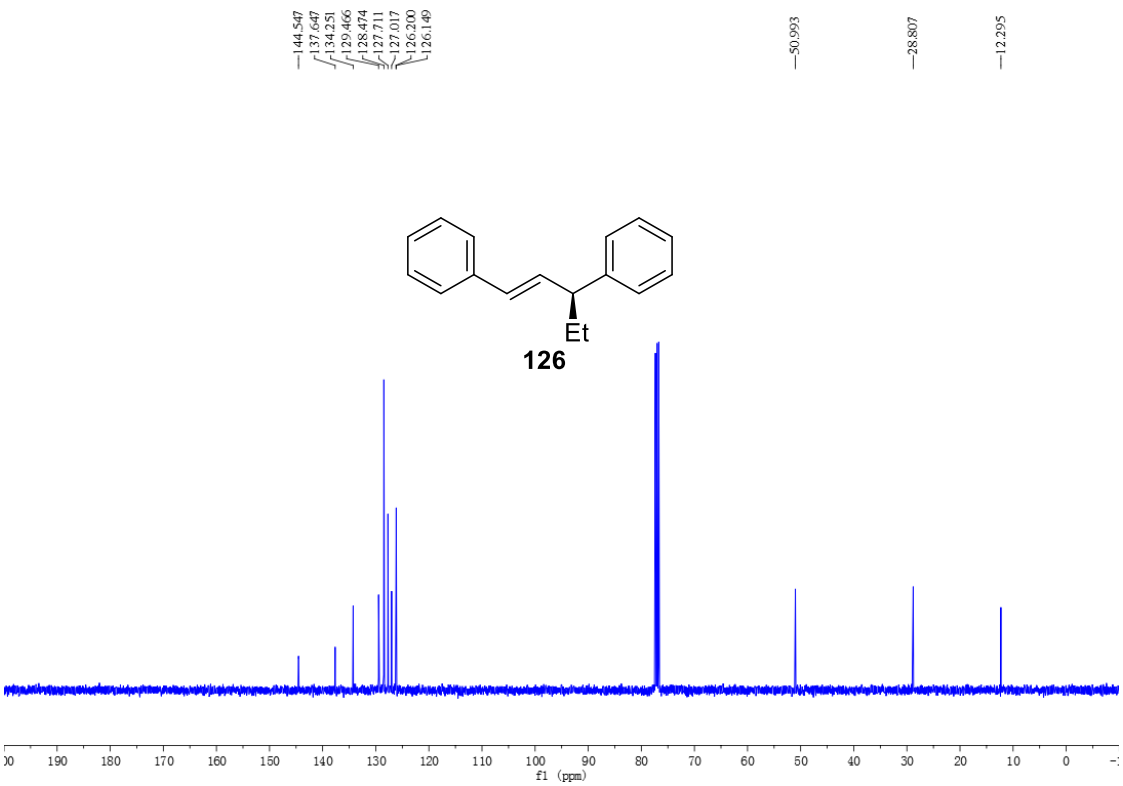


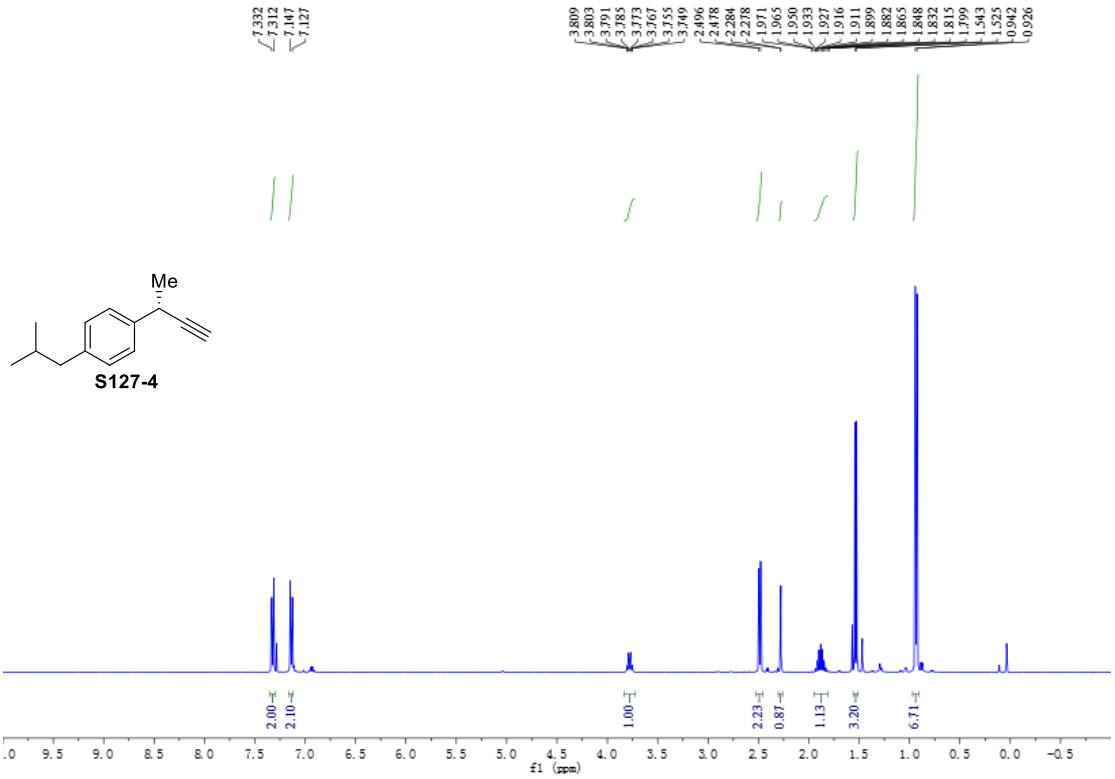
124 (UCP1172)

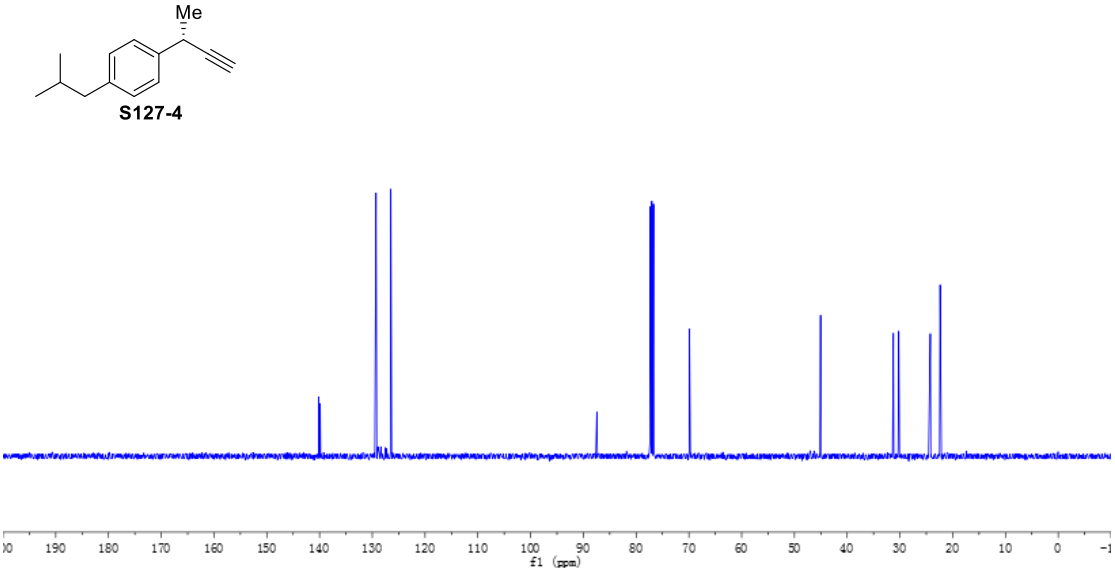

8.150
8.131
7.443
7.425
7.423
7.348
7.328
7.293
7.290
7.271
5.879
5.854
5.852
5.827
5.595
5.582
5.567
5.042
5.037
5.027
5.022
4.978
4.974
4.968
4.908
3.749
3.726
3.707
1.938
1.921
1.904
1.886
1.869
1.855
1.836
1.818
1.803
1.784
1.048
1.030
1.011
N
Et
125
1.97
4.04
7.38
1.07
0.99
1.05
1.10
1.00
2.09
3.14
f1 (ppm)

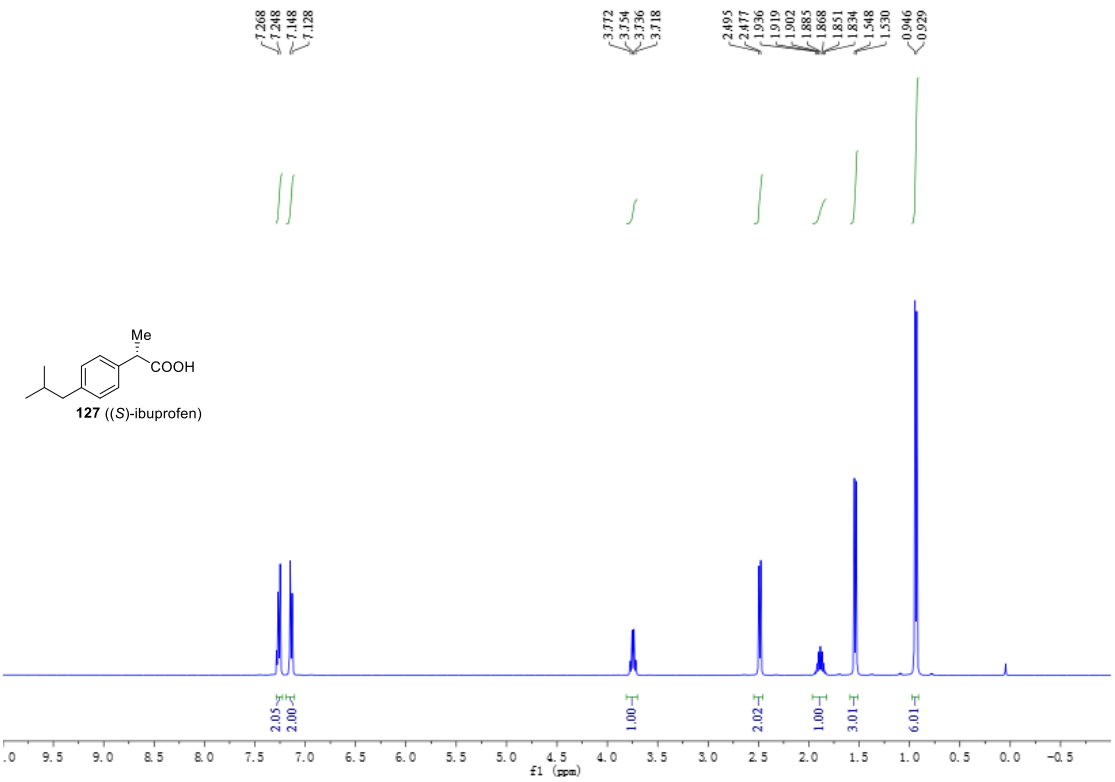

144.670
140.237
136.407
128.756
127.550
126.428
125.626
125.461
123.019
120.361
118.967
108.799
45.960
40.616
30.447
12.318
N
Et
125
f1 (ppm)

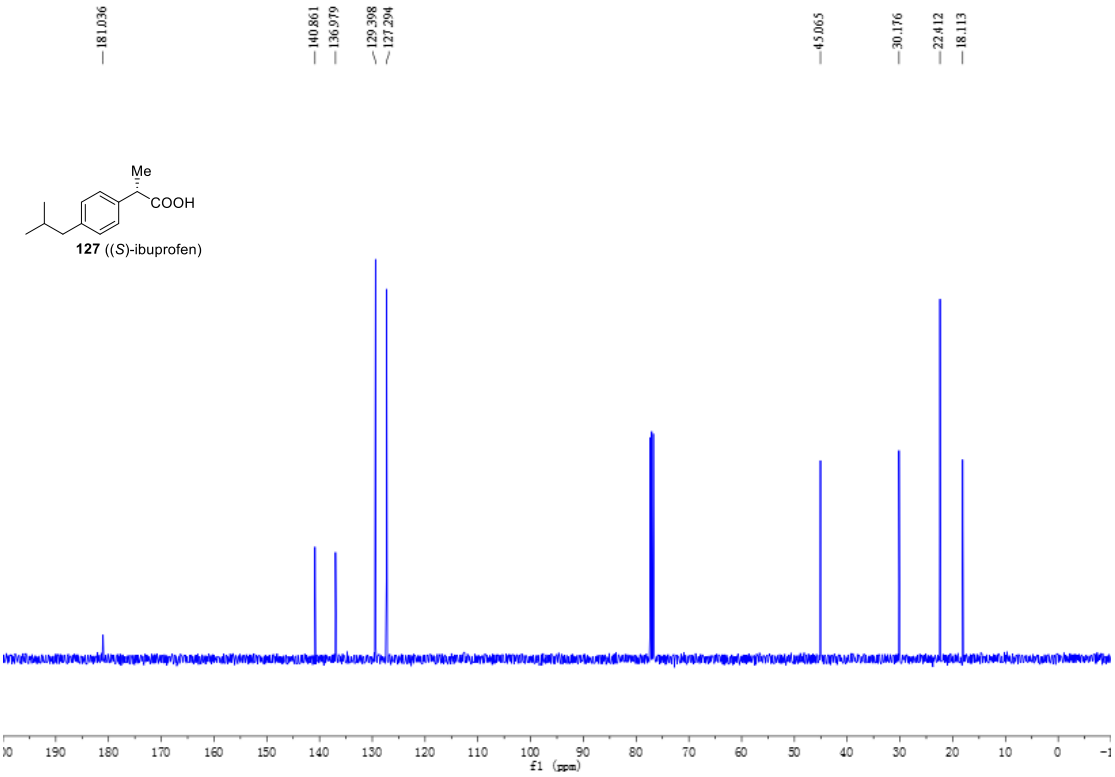

Et
126
10.80
2.00
1.00
2.04
3.12
f1 (ppm)

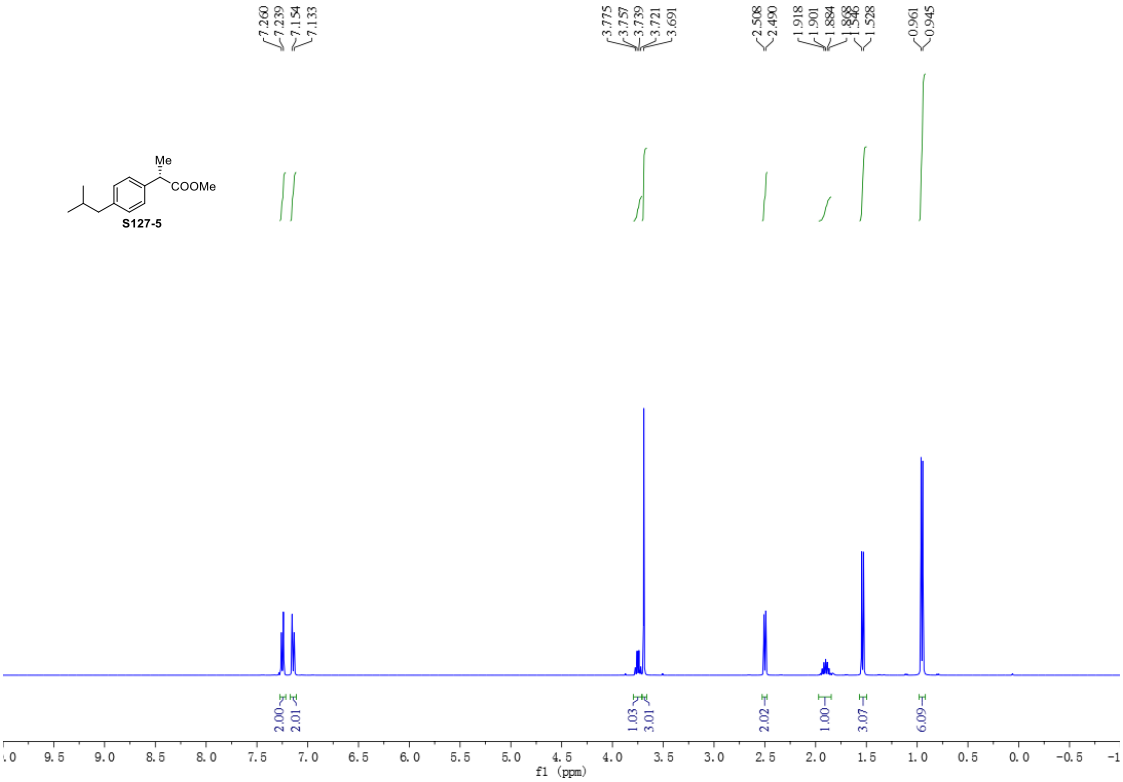

Et
126
f1 (ppm)

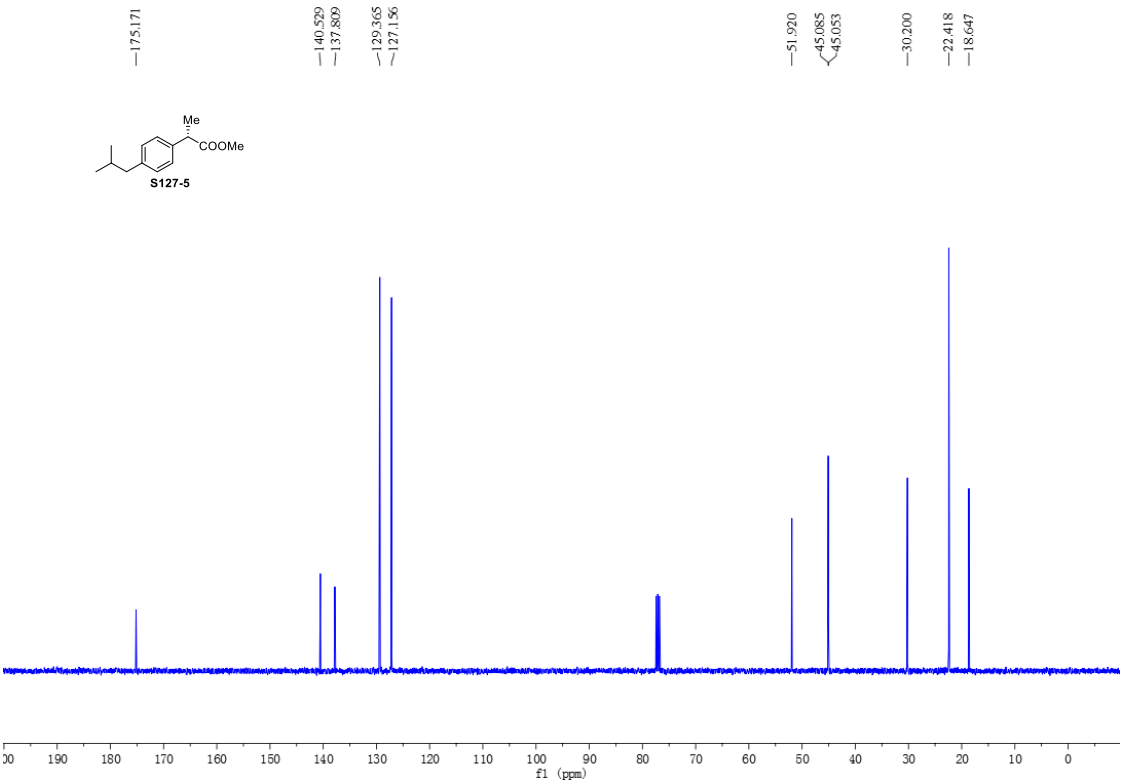

Me
S127-4
f1 (ppm)

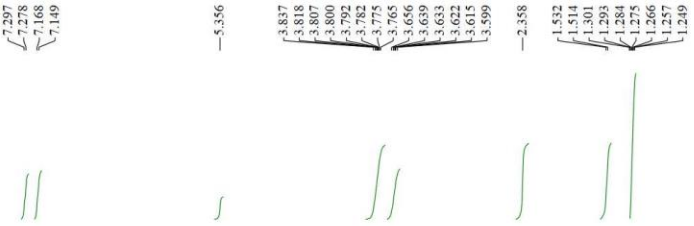

Me
S127-4
f1 (ppm)


7.268
7.248
7.148
7.128
3.772
3.754
3.736
3.718
2.495
2.477
1.936
1.919
1.902
1.885
1.868
1.851
1.834
1.548
1.530
0.946
0.929
Me
COOH
127 ((S)-ibuprofen)
2.05
2.00
1.00
2.02
1.00
3.01
6.01
f1 (ppm)


181.036
140.861
136.979
129.398
127.294
45.065
30.176
22.412
18.113
Me
COOH
127 ((S)-ibuprofen)
f1 (ppm)


7.260
7.239
7.154
7.133
3.775
3.757
3.739
3.721
3.691
2.508
2.490
1.918
1.901
1.884
1.868
1.546
1.528
0.961
0.945
Me
COOMe
S127-5
2.00
2.01
1.03
3.01
2.02
1.00
3.07
6.09
f1 (ppm)


175.171
140.529
137.809
129.365
127.156
51.920
45.085
45.053
30.200
22.418
18.647
Me
COOMe
S127-5
f1 (ppm)


7.297
7.278
7.168
7.149
5.356
3.837
3.818
3.807
3.800
3.792
3.782
3.775
3.765
3.656
3.639
3.633
3.622
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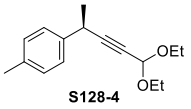
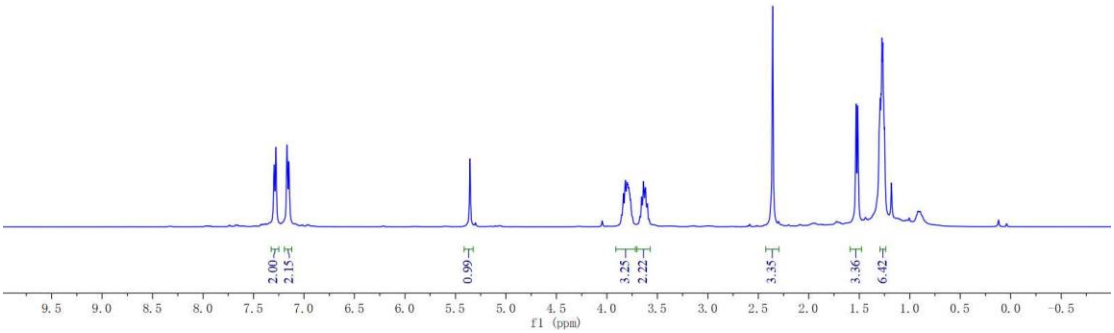
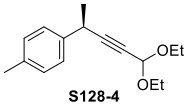
1.293
1.284
1.275
1.266
1.257
1.249


OEt
OEt

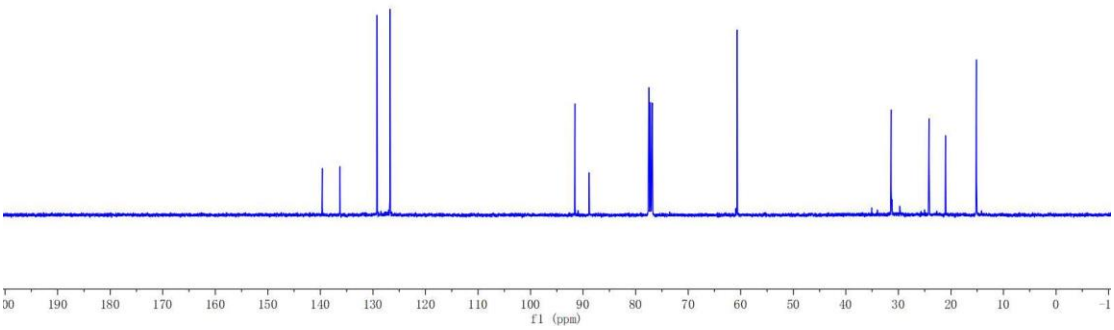
S128-4

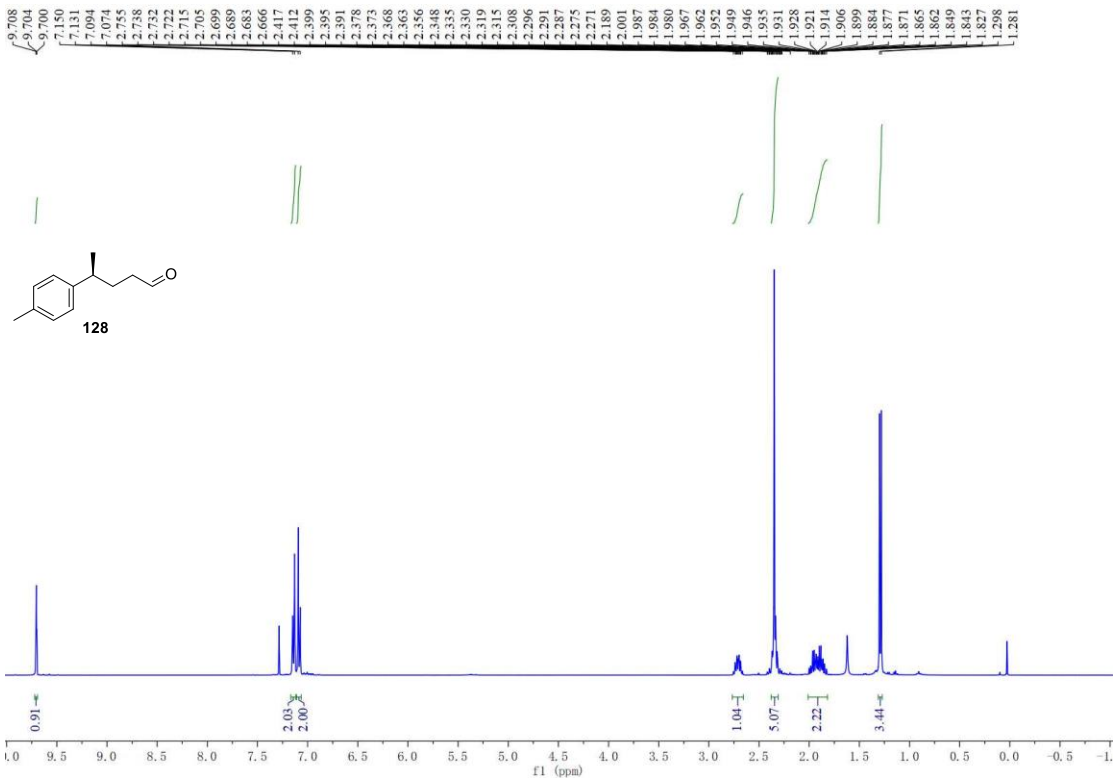

2.00
2.15
0.99
3.25
2.22
3.35
3.36
6.42
f1 (ppm)

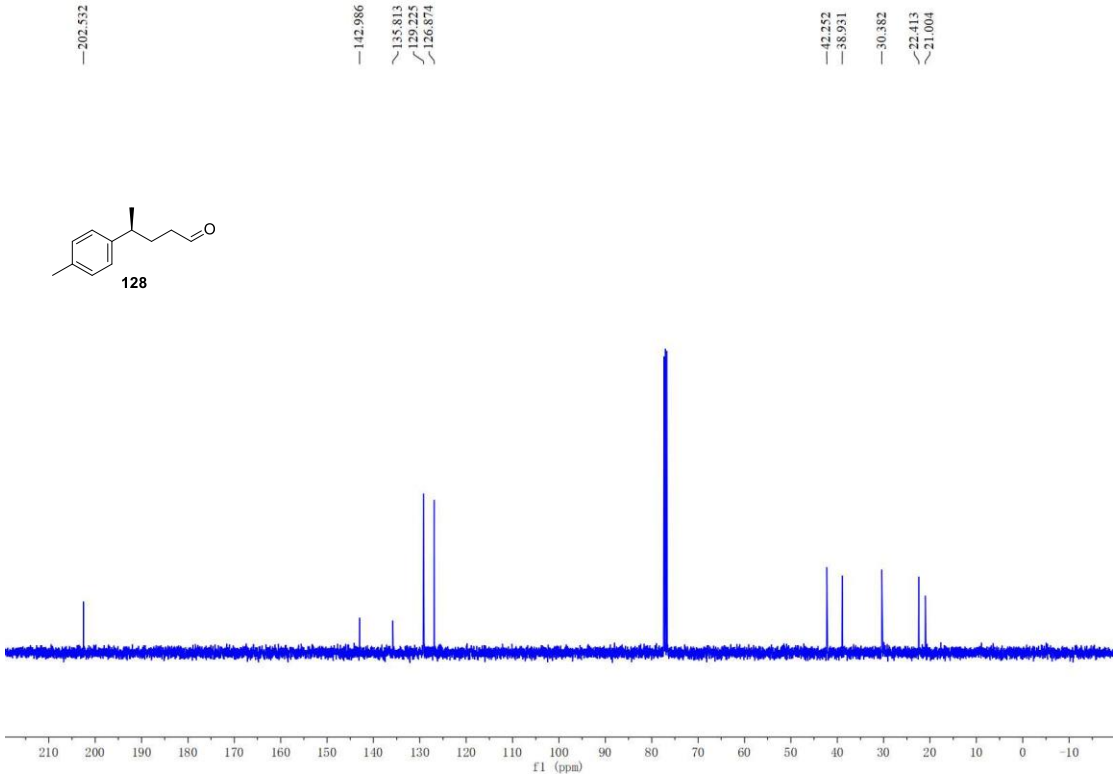

139.640
136.264
129.209
126.746
91.555
88.845
77.469
60.676
31.391
24.174
21.025
15.150

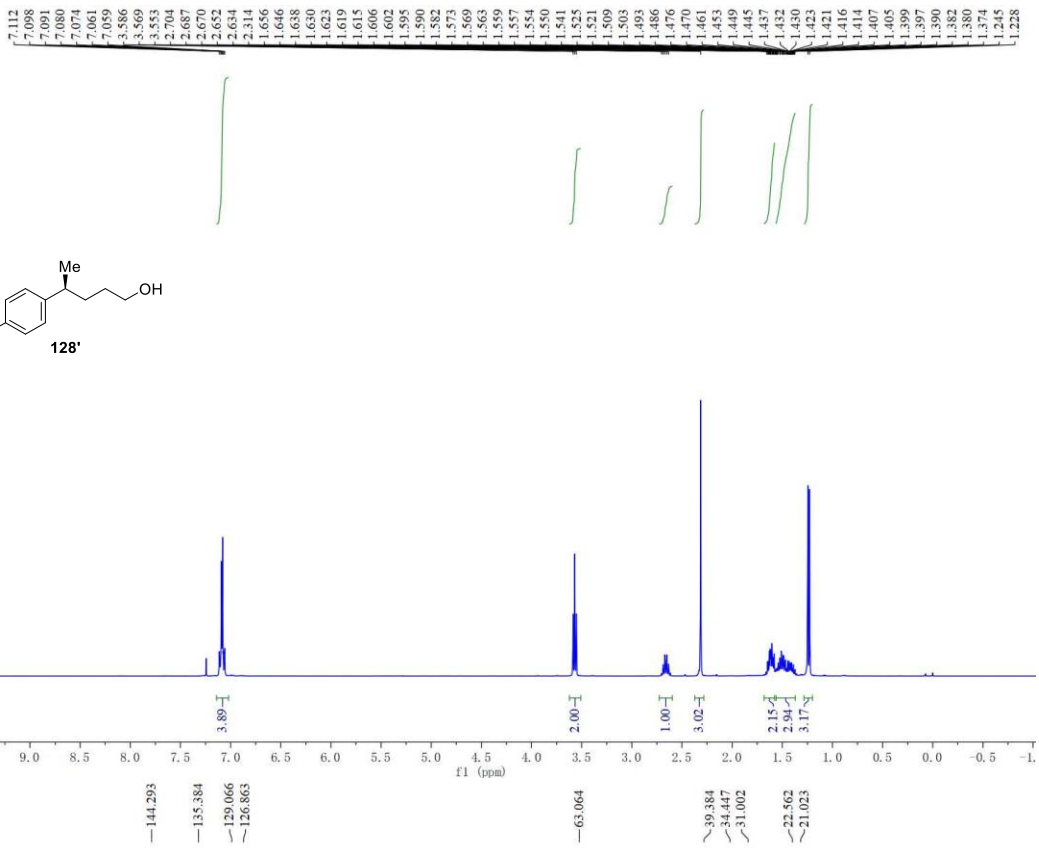

OEt
OEt

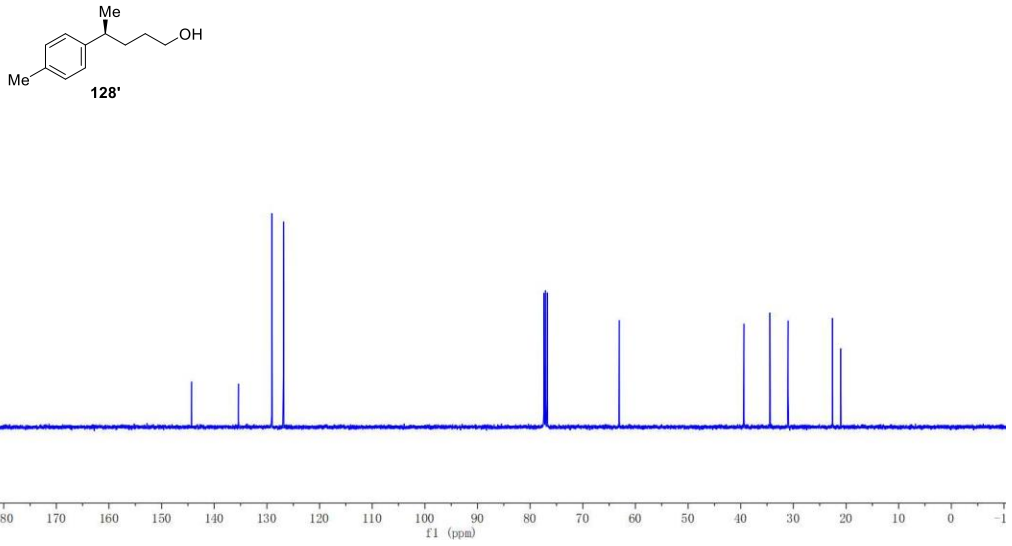
S128-4

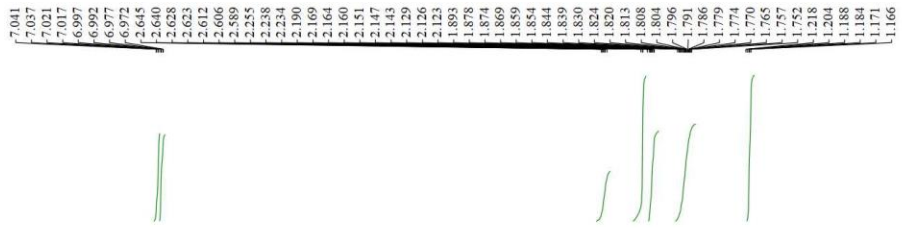

f1 (ppm)


9.708
9.704
9.700
7.150
7.131
7.094
7.074
2.755
2.738
2.732
2.722
2.715
2.705
2.699
2.689
2.683
2.666
2.417
2.412
2.399
2.395
2.391
2.378
2.373
2.368
2.363
2.356
2.348
2.335
2.330
2.319
2.315
2.308
2.296
2.291
2.287
2.275
2.271
2.189
2.001
1.987
1.984
1.980
1.967
1.962
1.952
1.949
1.946
1.935
1.931
1.928
1.921
1.914
1.906
1.899
1.884
1.877
1.871
1.865
1.862
1.849
1.843
1.827
1.298
1.281
O
128
0.91
2.03
2.00
1.04
5.07
2.22
3.44
f1 (ppm)


202.532
142.986
135.813
129.225
126.874
42.252
38.931
30.382
22.413
21.004
O
128
f1 (ppm)


7.112
7.098
7.091
7.080
7.074
7.061
7.059
3.586
3.569
3.553
2.704
2.687
2.670
2.652
2.634
2.314
1.656
1.646
1.638
1.630
1.623
1.619
1.615
1.606
1.602
1.595
1.590
1.582
1.573
1.569
1.563
1.559
1.557
1.554
1.550
1.541
1.525
1.521
1.509
1.503
1.493
1.486
1.476
1.470
1.461
1.453
1.449
1.445
1.437
1.432
1.430
1.423
1.421
1.416
1.414
1.407
1.405
1.399
1.397
1.390
1.382
1.380
1.374
1.245
1.228
Me
OH
Me
128'
3.89
2.00
1.00
3.02
2.15
2.94
3.17
f1 (ppm)
144.293
135.384
129.066
126.863
63.064
39.384
34.447
31.002
22.562
21.023


Me
OH
Me
128'
f1 (ppm)


7.041
7.037
7.021
7.017
6.997
6.992
6.977
6.972
2.645
2.640
2.628
2.623
2.612
2.606
2.589
2.255
2.238
2.234
2.190
2.169
2.164
2.160
2.151
2.147
2.143
2.129
2.126
2.123
1.893
1.878
1.874
1.869
1.859
1.854
1.844
1.839
1.830
1.824
1.820
1.813
1.808
1.804
1.796
1.791
1.786
1.779
1.774
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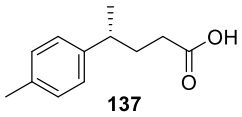
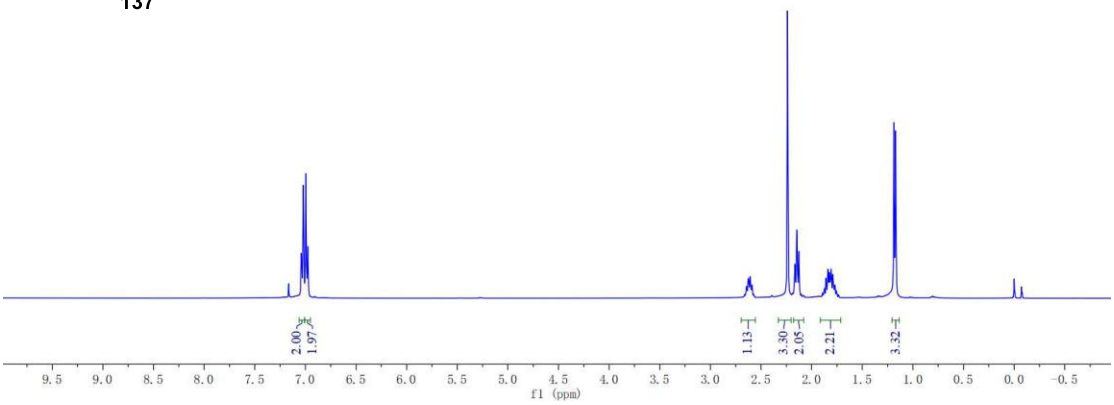
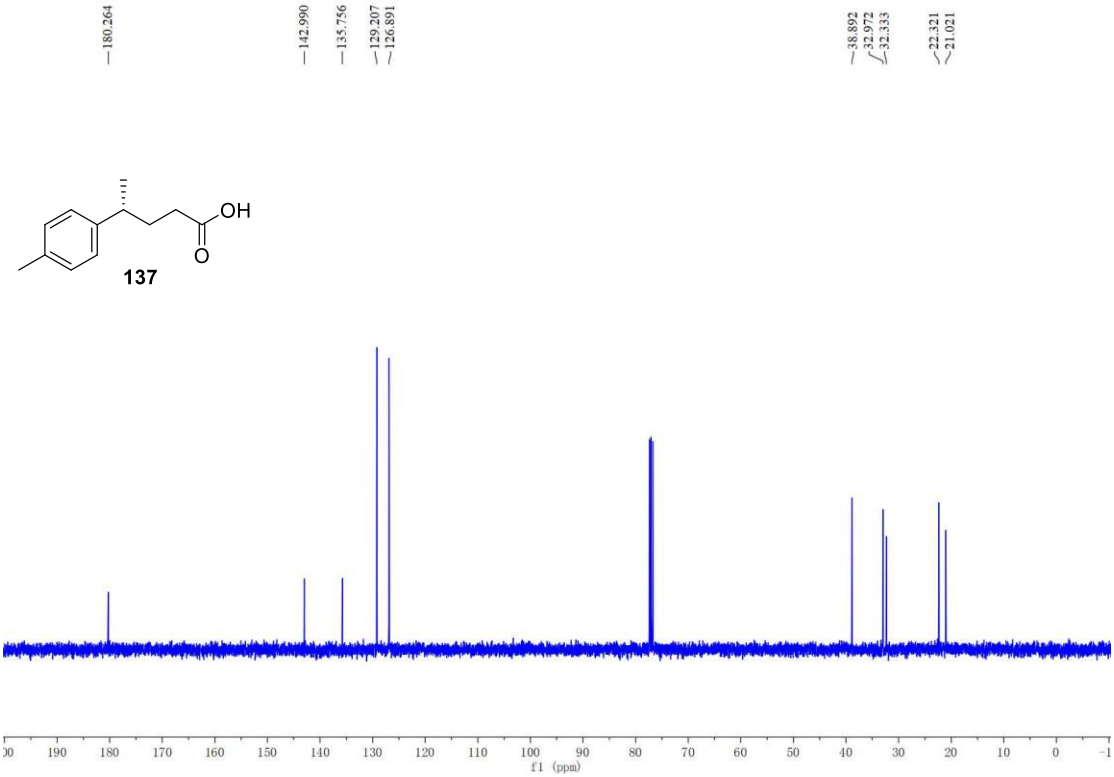
1.765
1.757
1.752
1.218
1.204
1.188
1.184
1.171
1.166


OH
O

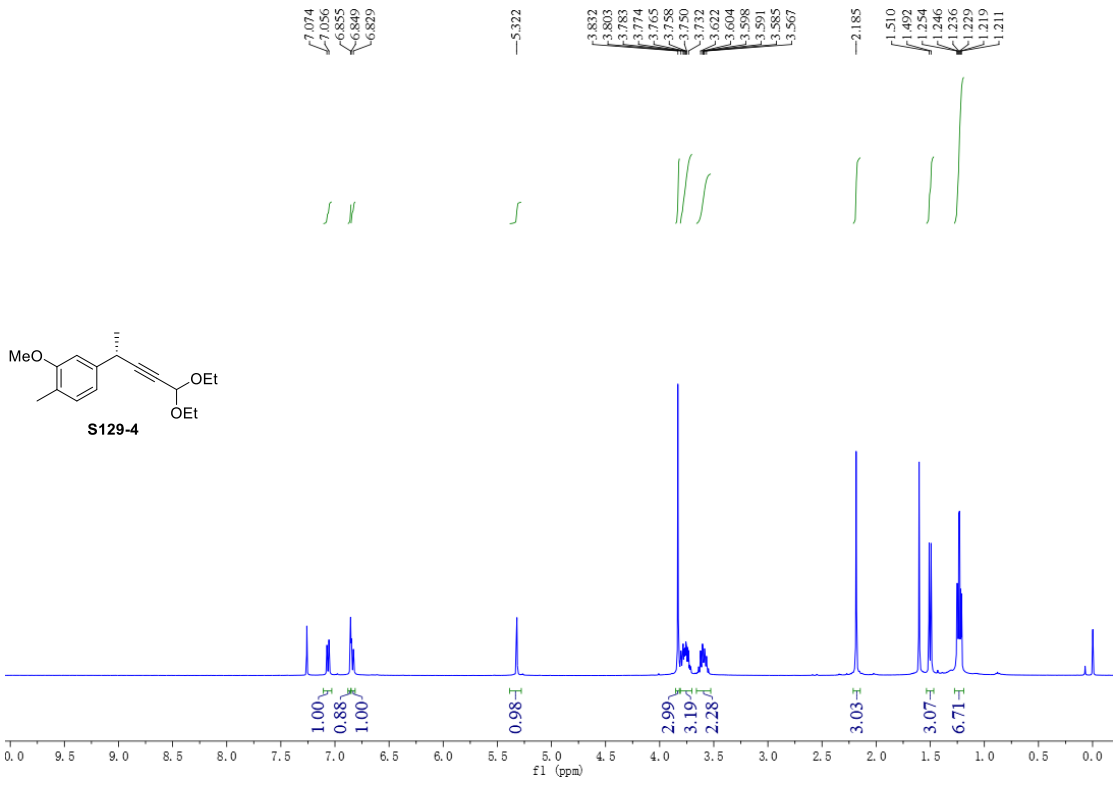
137

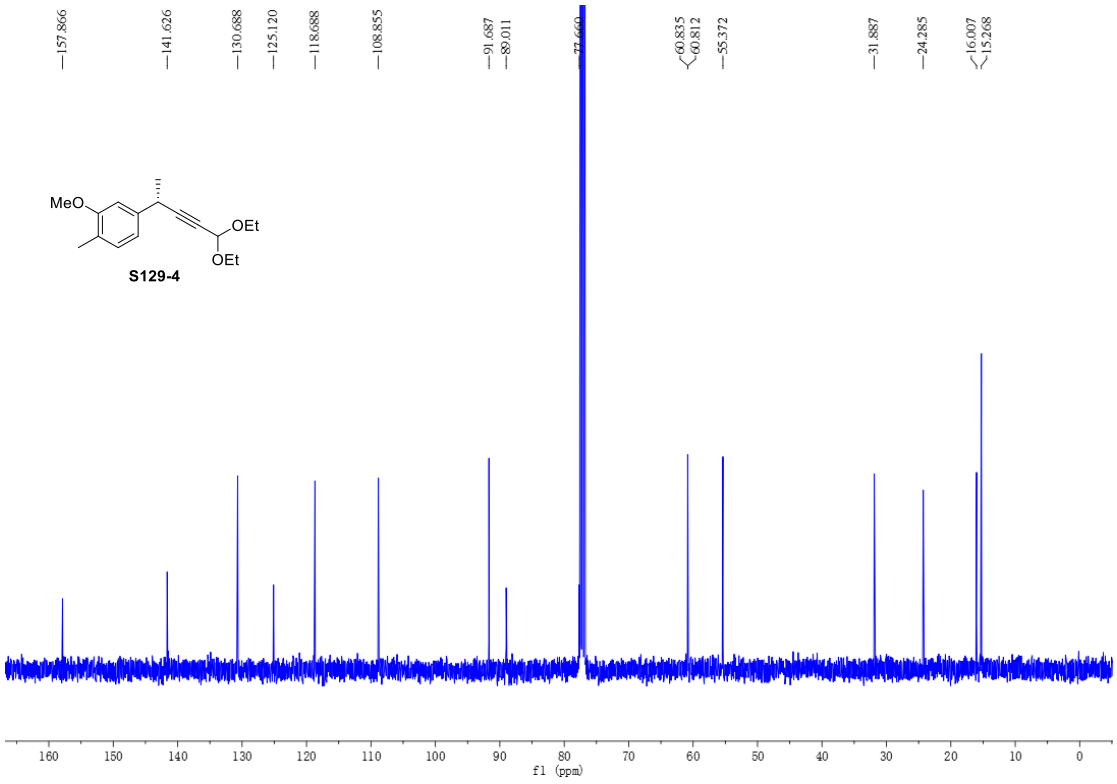

2.00
1.97
1.13
3.30
2.05
2.21
3.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

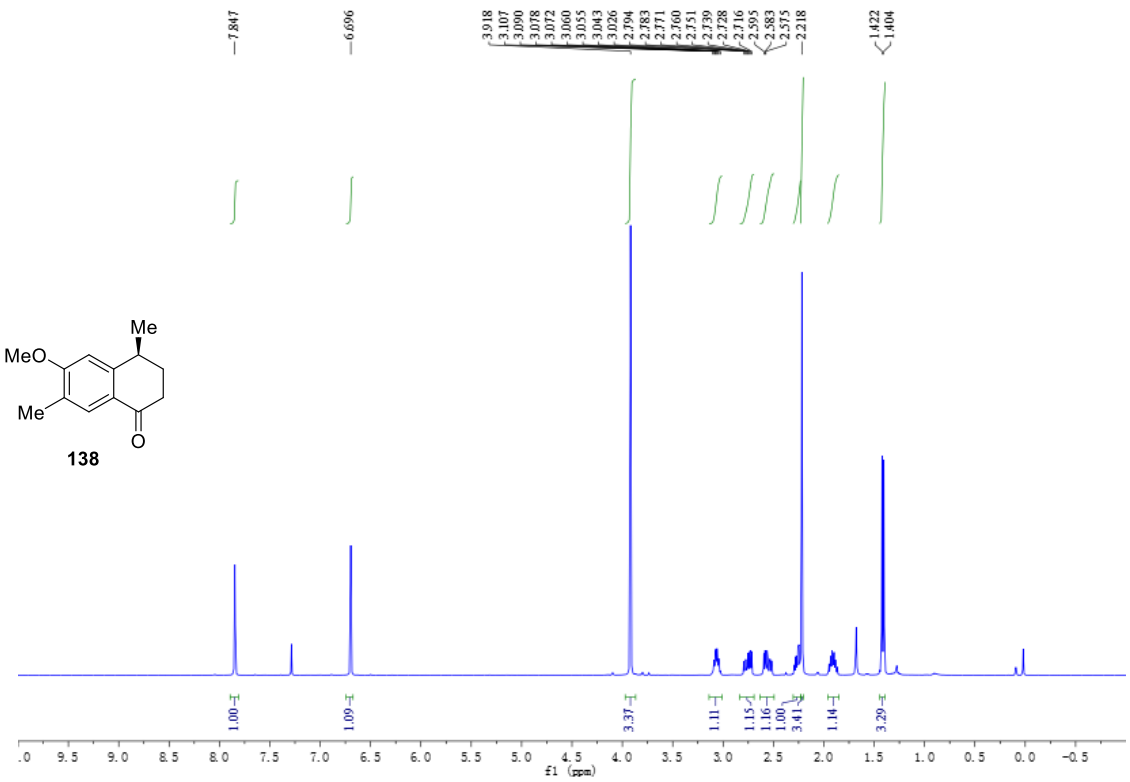

180.264
142.990
135.756
129.207
126.891
38.892
32.972
32.333
22.321
21.021
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

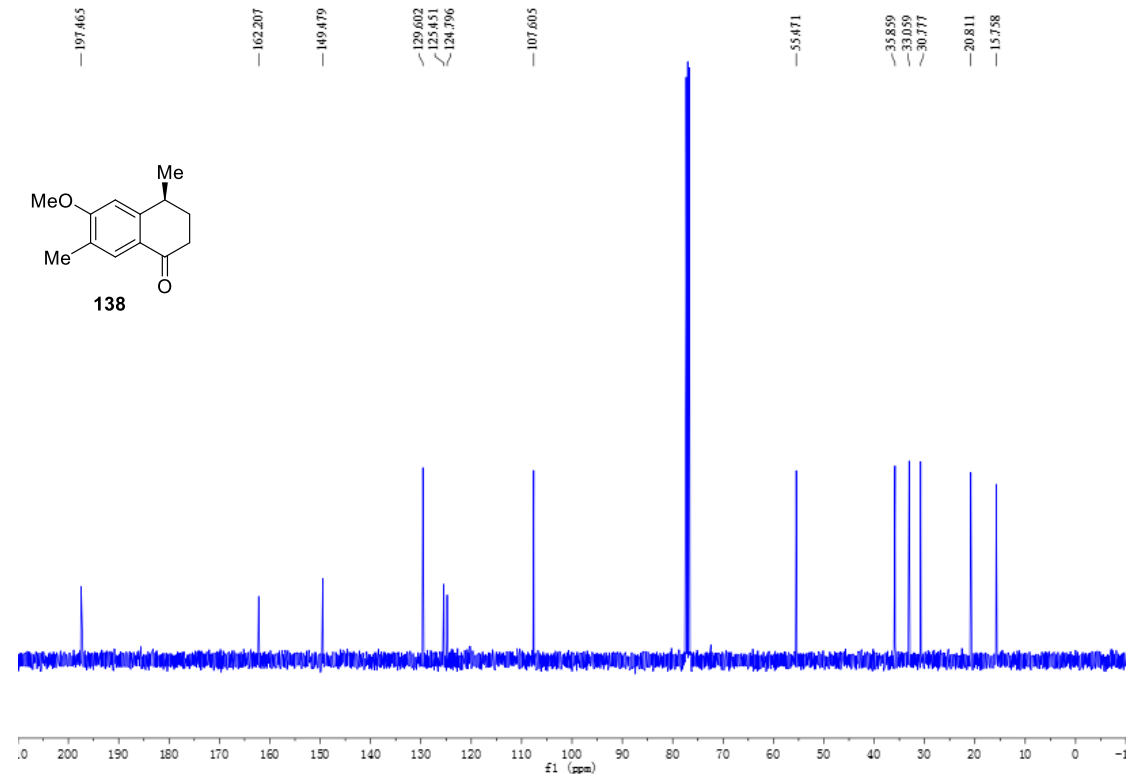
OH
O

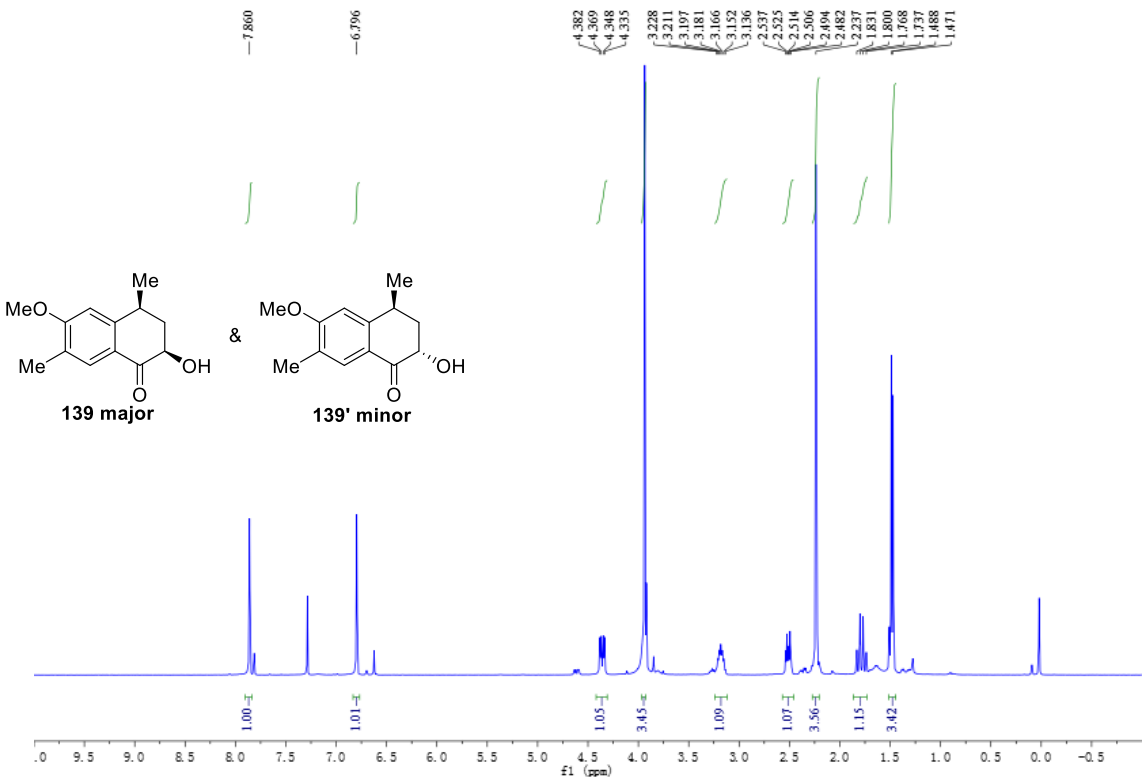
137

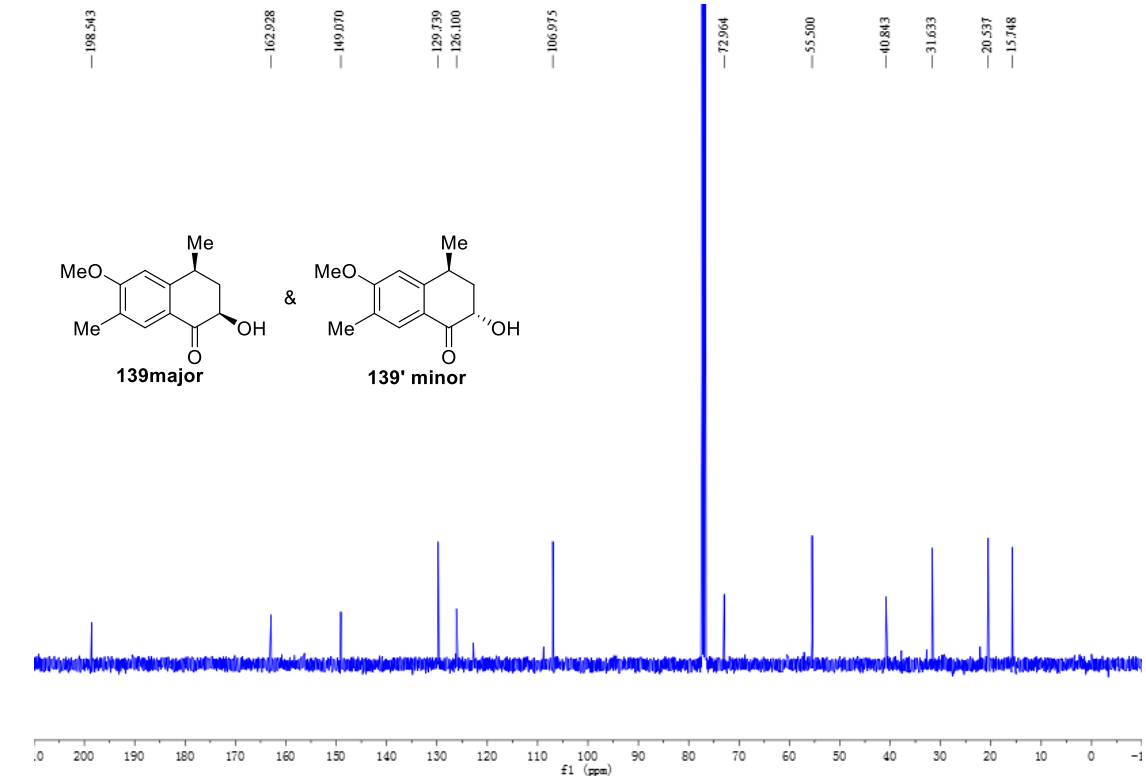

7.074
7.056
6.855
6.849
6.829
5.322
3.832
3.803
3.783
3.774
3.765
3.758
3.750
3.732
3.622
3.604
3.598
3.591
3.585
3.567
2.185
1.510
1.492
1.254
1.246
1.236
1.229
1.219
1.211
MeO
OEt
OEt
S129-4
1.00
0.88
1.00
0.98
2.99
3.19
2.28
3.03
3.07
6.71
f1 (ppm)

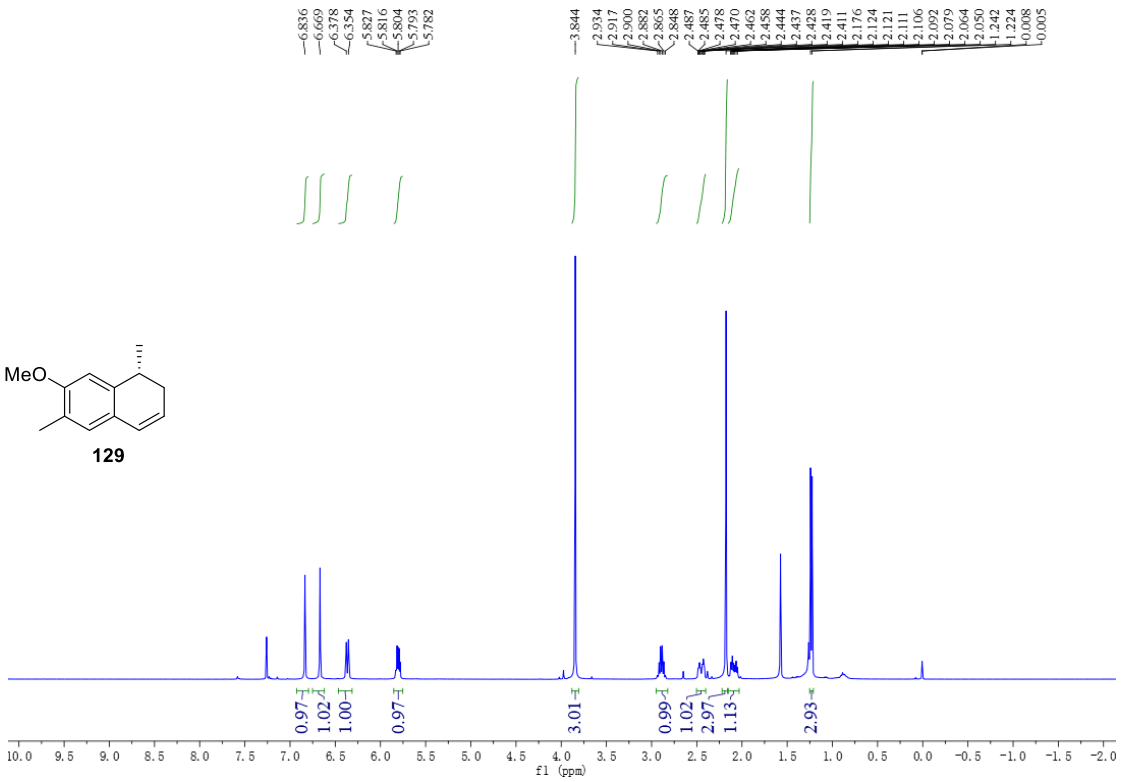

157.866
141.626
130.688
125.120
118.688
108.855
91.687
89.011
77.660
60.835
60.812
55.372
31.887
24.285
16.007
15.268
MeO
OEt
OEt
S129-4
f1 (ppm)

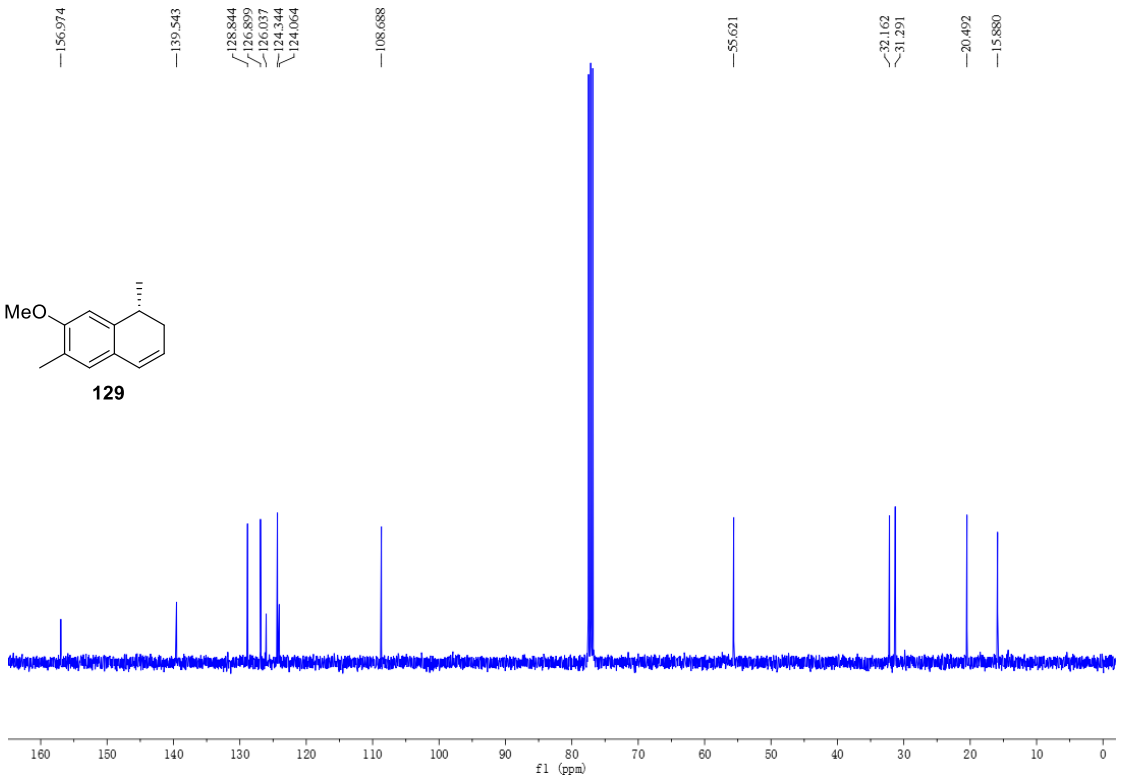

7.847
6.696
3.918
3.107
3.090
3.078
3.072
3.060
3.055
3.043
3.026
2.794
2.783
2.771
2.760
2.751
2.739
2.728
2.716
2.595
2.583
2.575
2.218
1.422
1.404
Me
MeO
Me
O
138
1.00
1.09
3.37
1.11
1.15
1.16
1.00
3.41
1.14
3.29
f1 (ppm)

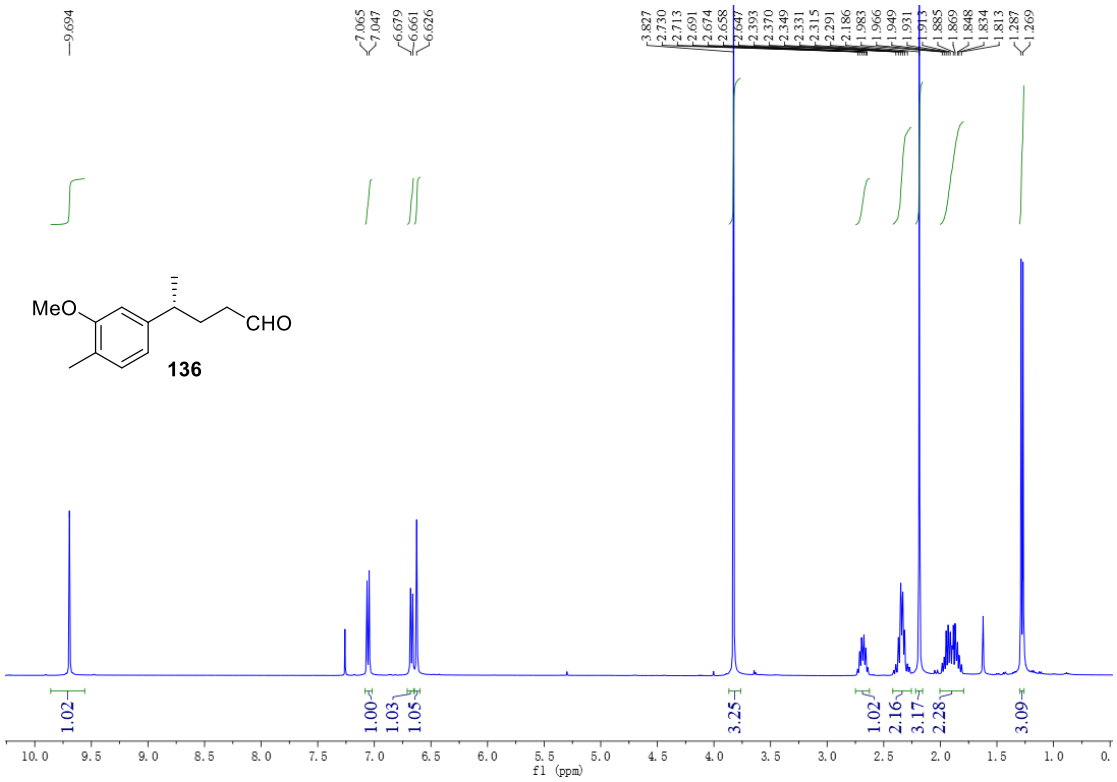

197.465
162.207
149.479
129.602
125.451
124.796
107.605
55.471
35.859
33.059
30.777
20.811
15.758
Me
MeO
Me
O
138
f1 (ppm)

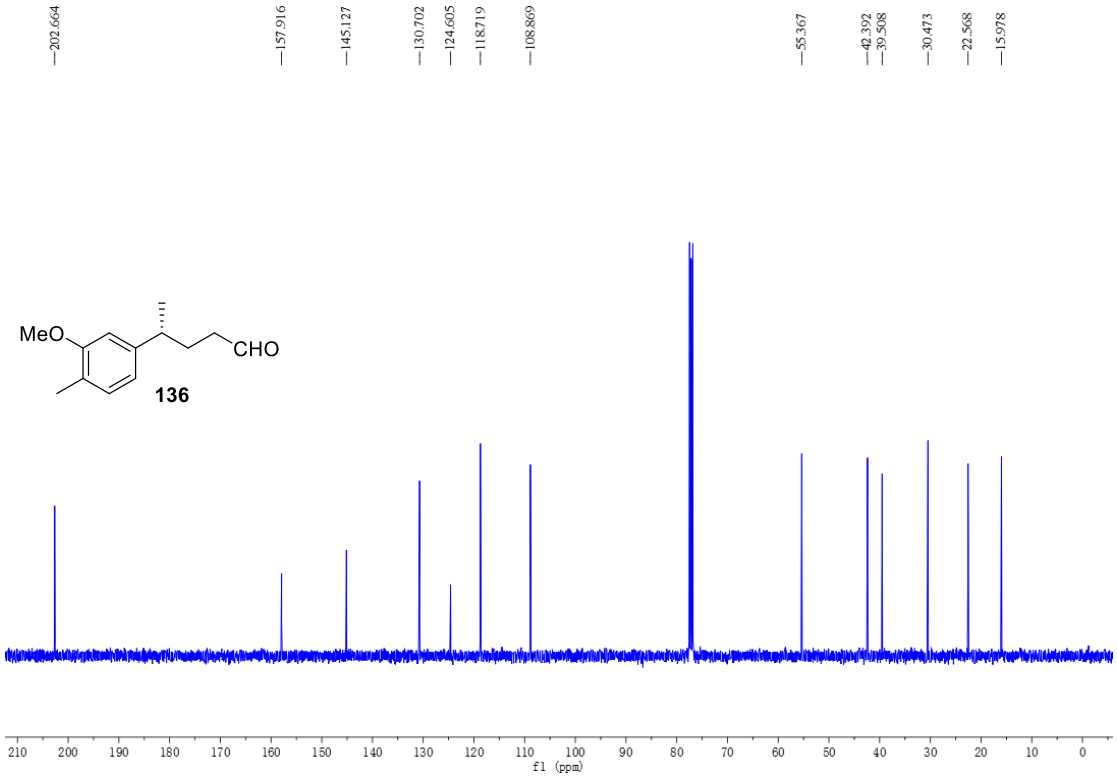

7.860
6.796
4.382
4.369
4.348
4.335
3.228
3.211
3.197
3.181
3.166
3.152
3.136
2.537
2.525
2.514
2.506
2.494
2.482
2.237
1.831
1.800
1.768
1.737
1.488
1.471
Me
MeO
Me
OH
O
&
139 major
139' minor
1.00
1.01
1.05
3.45
1.09
1.07
3.56
1.15
3.42
f1 (ppm)

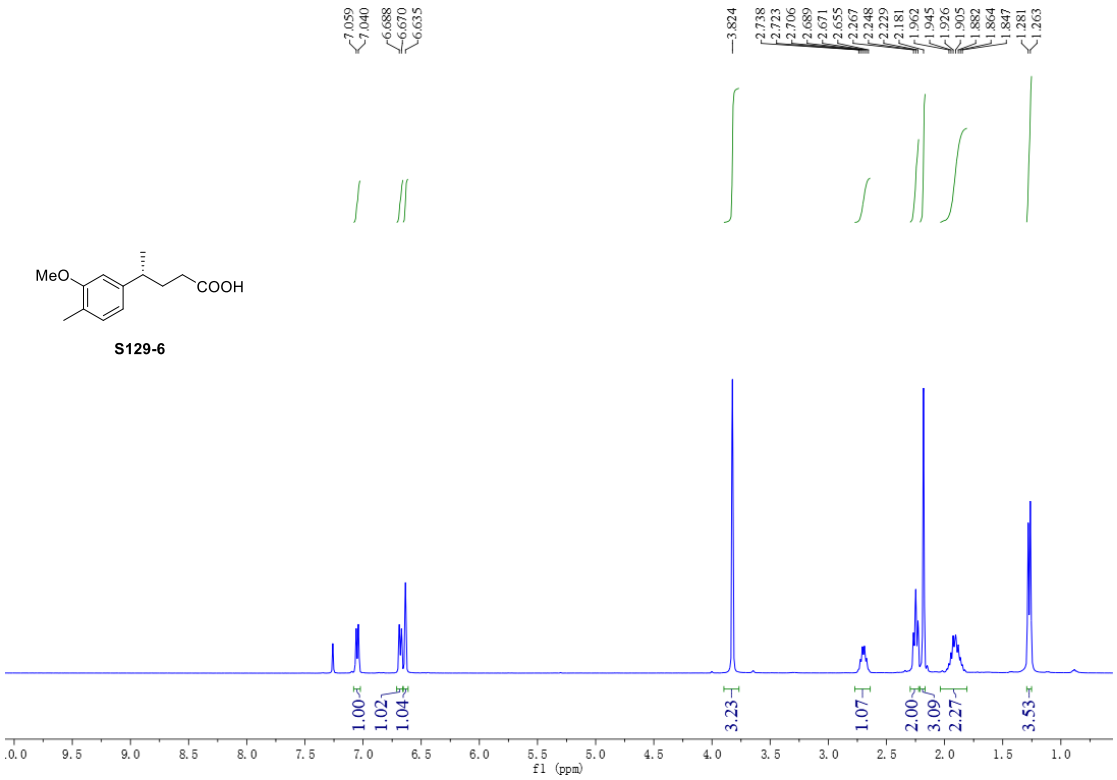

198.543
162.928
149.070
129.739
126.100
106.975
72.964
55.500
40.843
31.633
20.537
15.748
Me
MeO
Me
OH
O
&
139major
139' minor
f1 (ppm)

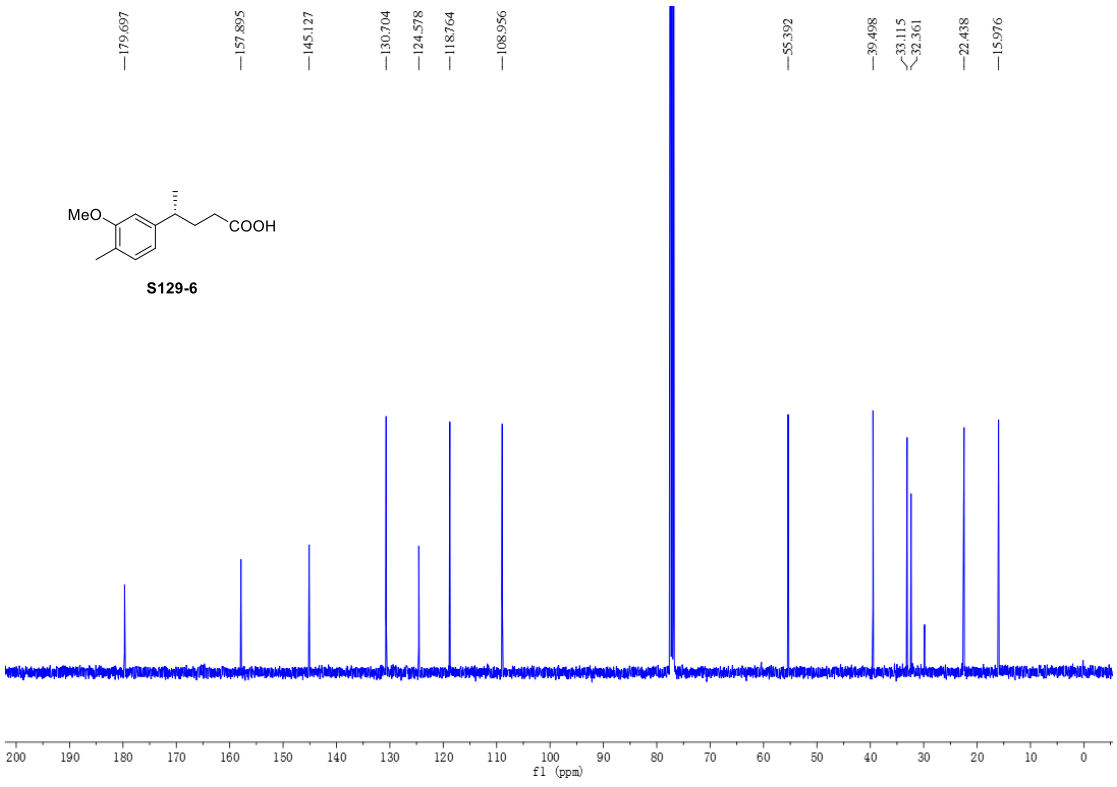

6.836
6.669
6.378
6.354
5.827
5.816
5.804
5.793
5.782
3.844
2.934
2.917
2.900
2.882
2.865
2.848
2.487
2.485
2.478
2.470
2.462
2.458
2.444
2.437
2.428
2.419
2.411
2.176
2.124
2.121
2.111
2.106
2.092
2.079
2.064
2.050
1.242
1.224
0.008
0.005
MeO
129
0.97
1.02
1.00
0.97
3.01
0.99
1.02
2.97
1.13
2.93
f1 (ppm)

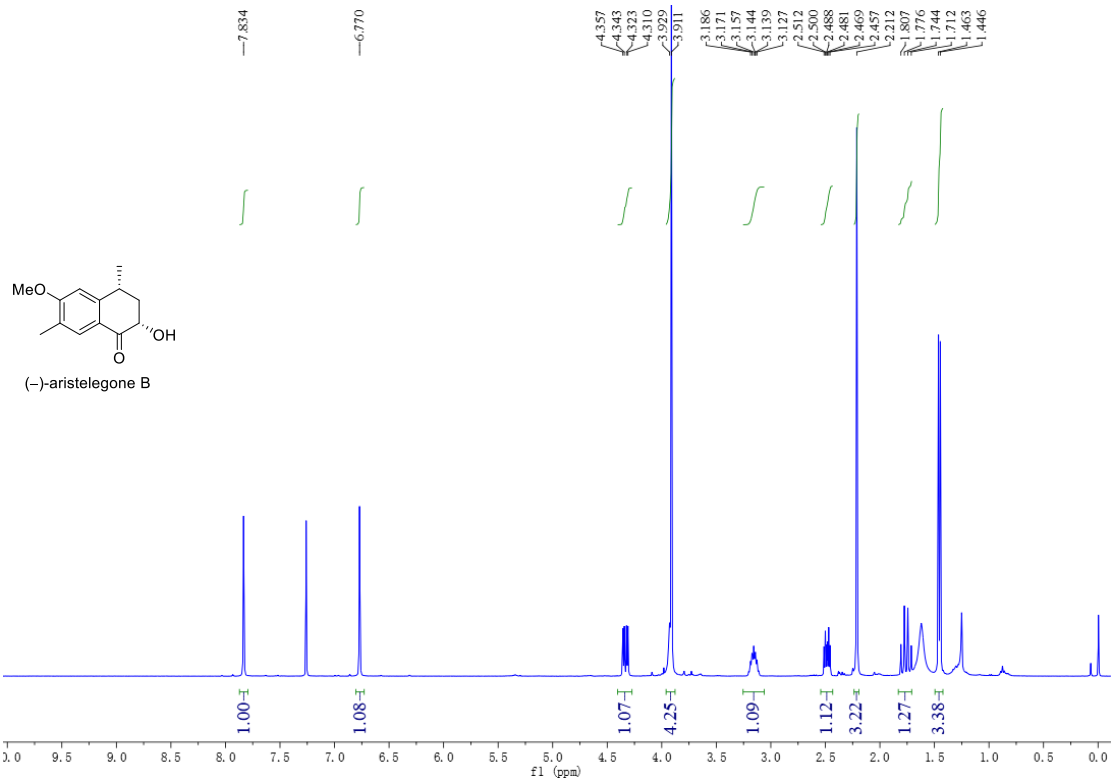

156.974
139.543
128.844
126.899
126.037
124.344
124.064
108.688
55.621
32.162
31.291
20.492
15.880
MeO
129
f1 (ppm)

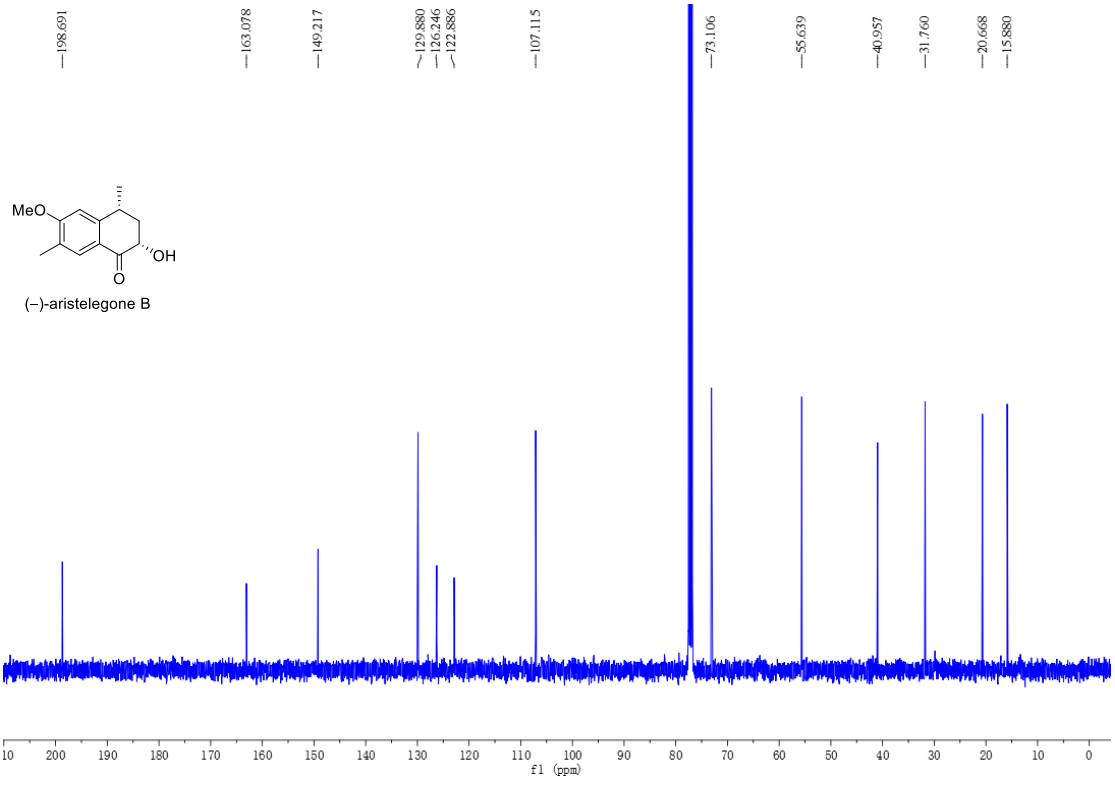

9.694
7.065
7.047
6.679
6.661
6.626
3.827
2.730
2.713
2.691
2.674
2.658
2.647
2.393
2.370
2.349
2.331
2.315
2.291
2.186
1.983
1.966
1.949
1.931
1.913
1.885
1.869
1.848
1.834
1.813
1.287
1.269
MeO
CHO
136
1.02
1.00
1.03
1.05
3.25
1.02
2.16
3.17
2.28
3.09
f1 (ppm)

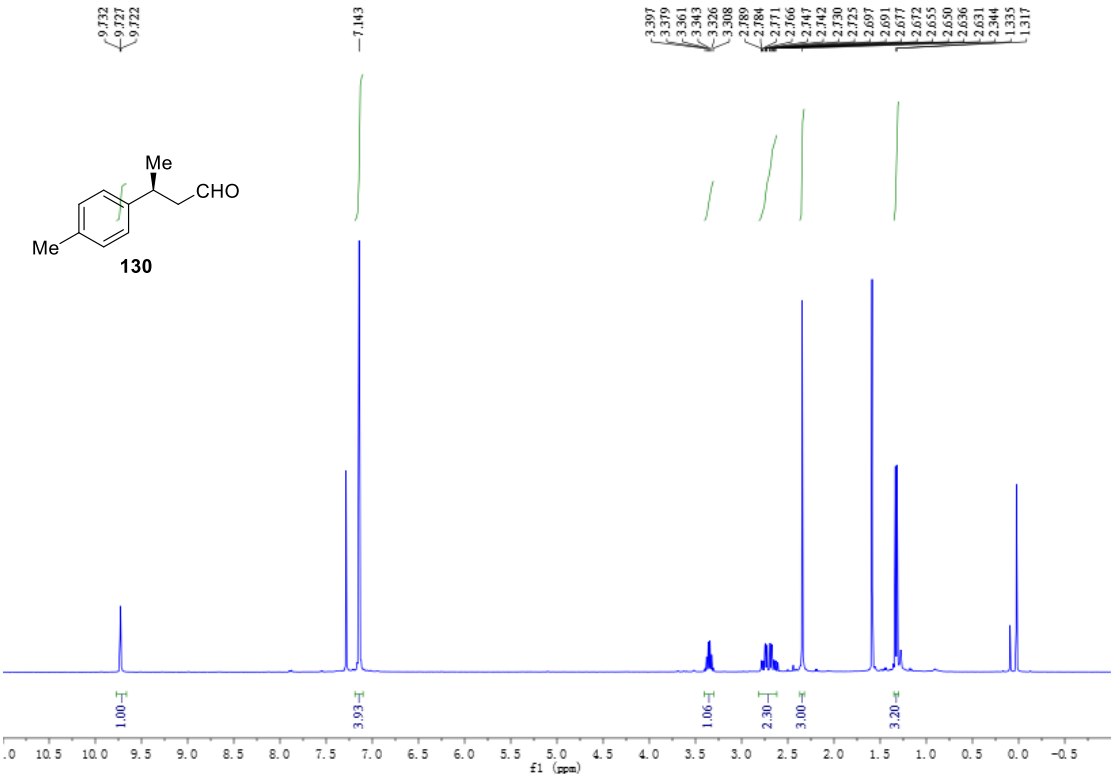

202.664
157.916
145.127
130.702
124.605
118.719
108.869
55.367
42.392
39.508
30.473
22.568
15.978
MeO
CHO
136
f1 (ppm)

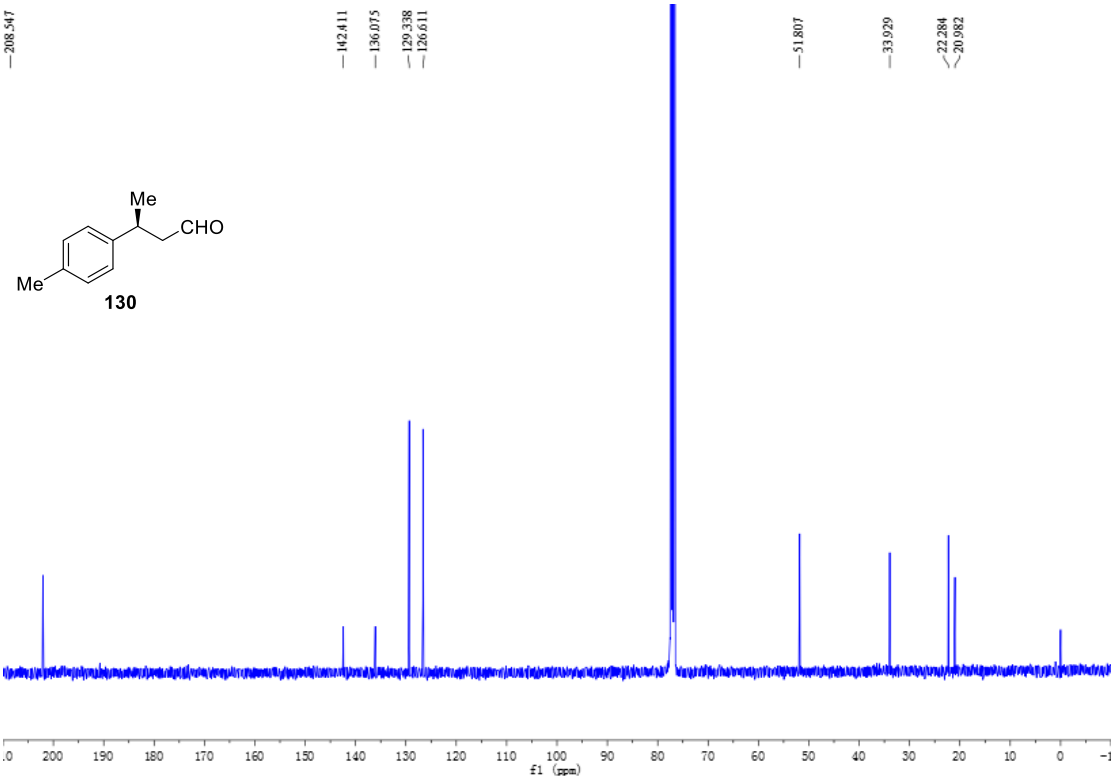

7.059
7.040
6.688
6.670
6.635
3.824
2.738
2.723
2.706
2.689
2.671
2.655
2.267
2.248
2.229
2.181
1.962
1.945
1.926
1.905
1.882
1.864
1.847
1.281
1.263
MeO
COOH
S129-6
1.00
1.02
1.04
3.23
1.07
2.00
3.09
2.27
3.53
f1 (ppm)

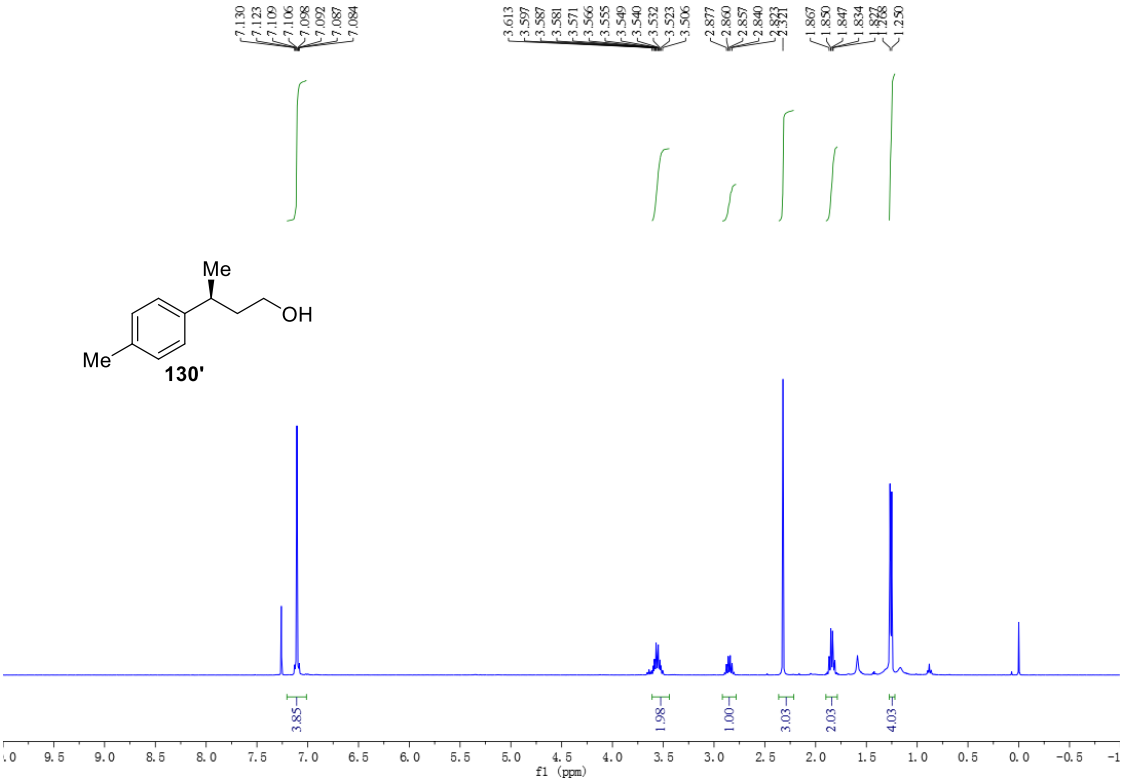

179.697
157.895
145.127
130.704
124.578
118.764
108.956
55.392
39.498
33.115
32.361
22.438
15.976
MeO
COOH
S129-6
f1 (ppm)

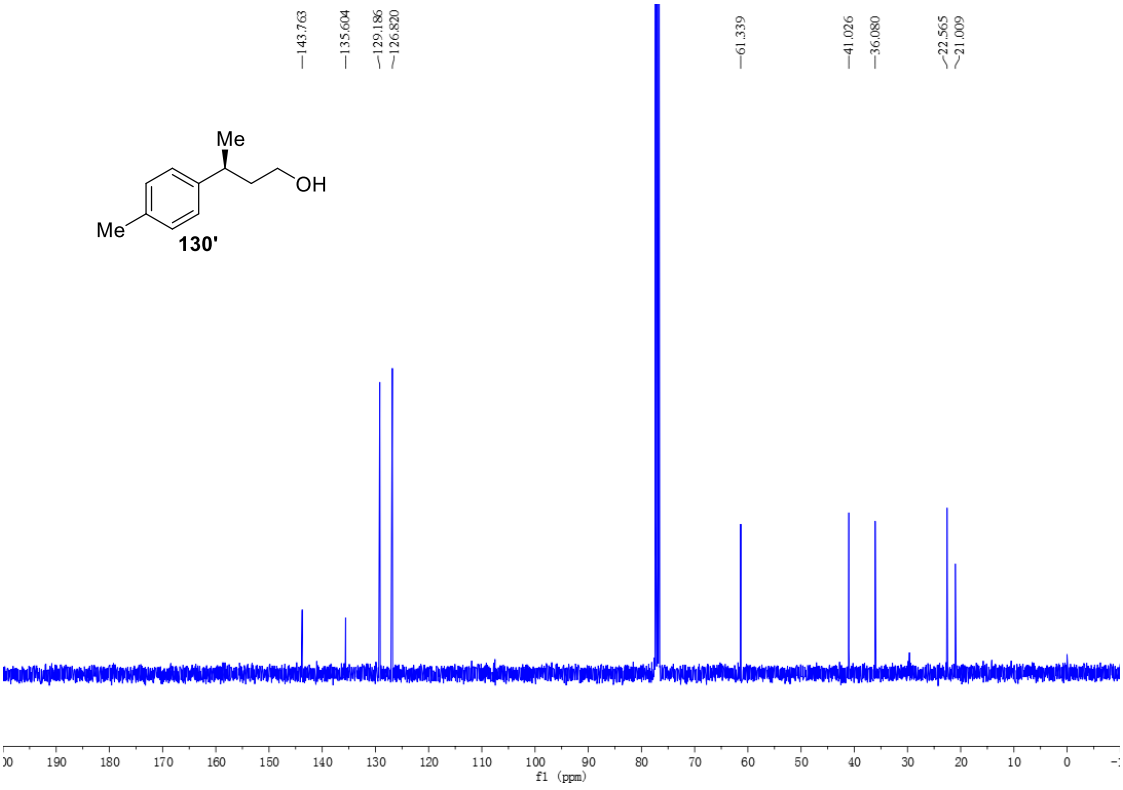

7.834
6.770
4.357
4.343
4.323
4.310
3.929
3.911
3.186
3.171
3.157
3.144
3.139
3.127
2.512
2.500
2.488
2.481
2.469
2.457
2.212
1.807
1.776
1.744
1.712
1.463
1.446
MeO
OH
O
(–)-aristelegone B
1.00
1.08
1.07
4.25
1.09
1.12
3.22
1.27
3.38
f1 (ppm)

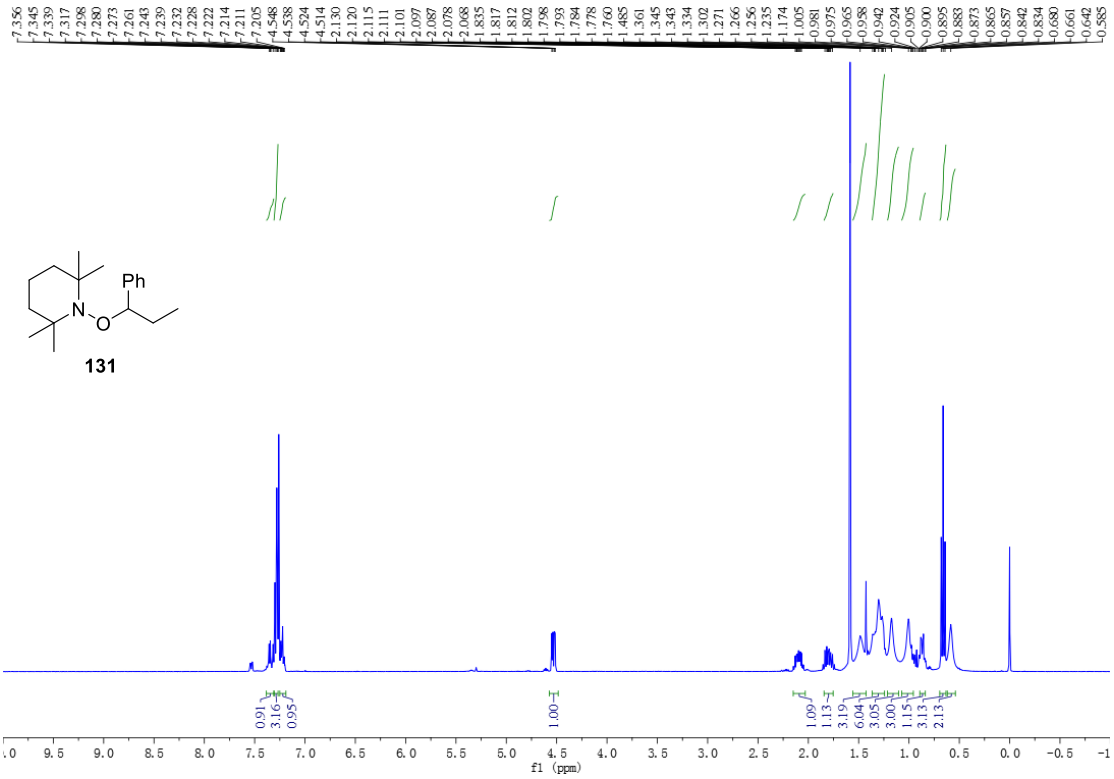

198.691
163.078
149.217
129.880
126.246
122.886
107.115
73.106
55.639
40.957
31.760
20.668
15.880
MeO
OH
O
(–)-aristelegone B
f1 (ppm)

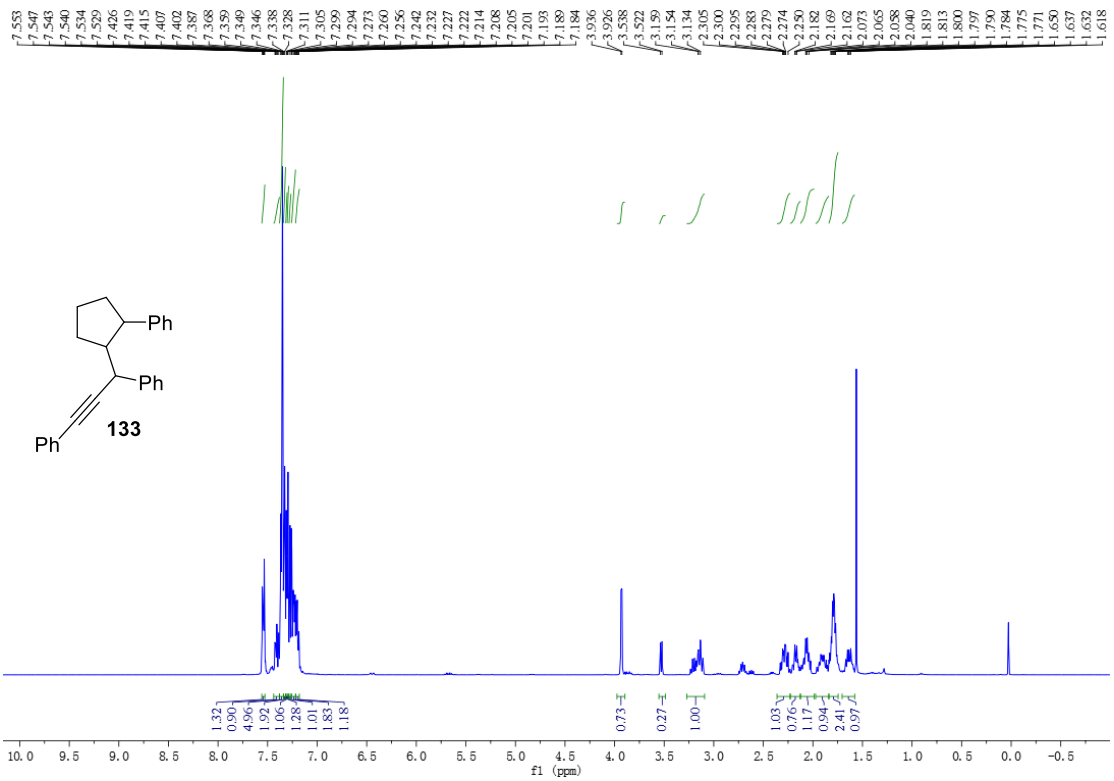

9.732
9.727
9.722
7.143
3.397
3.379
3.361
3.343
3.326
3.308
2.789
2.784
2.771
2.766
2.747
2.742
2.730
2.725
2.697
2.691
2.677
2.672
2.655
2.650
2.636
2.631
2.344
1.335
1.317
Me
CHO
Me
130
1.00
3.93
1.06
2.30
3.00
3.20
f1 (ppm)

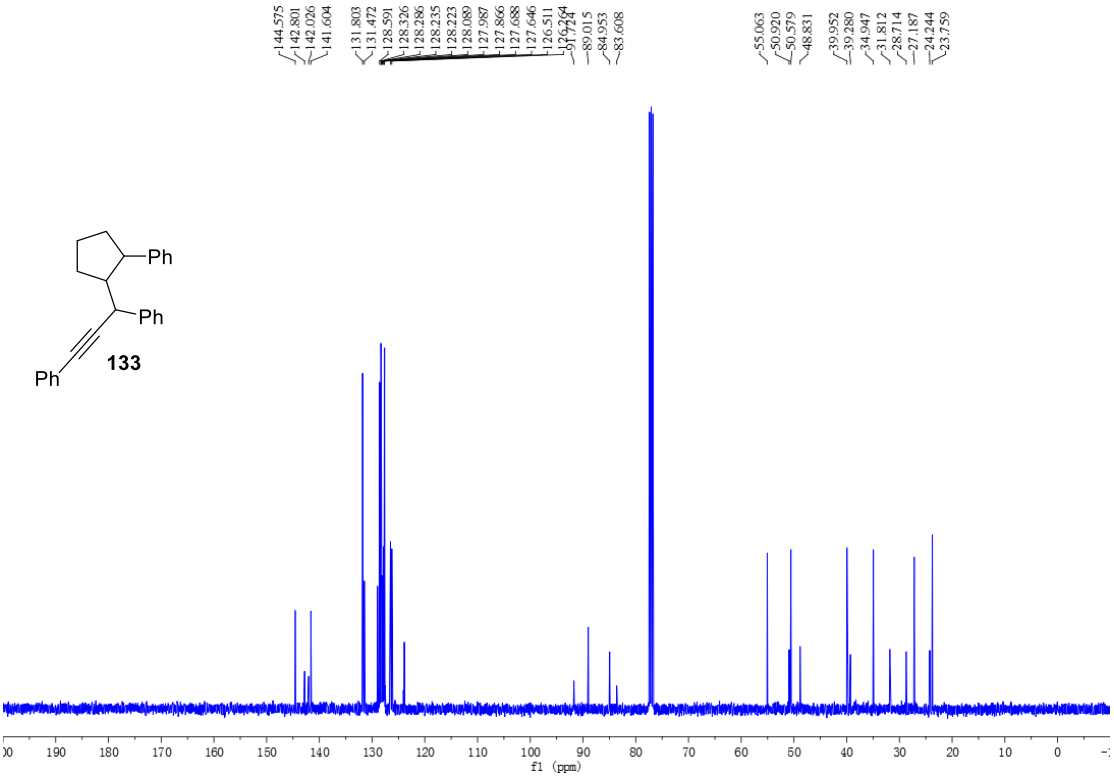

208.547
142.411
136.075
129.338
126.611
51.807
33.929
22.284
20.982
Me
CHO
Me
130
f1 (ppm)

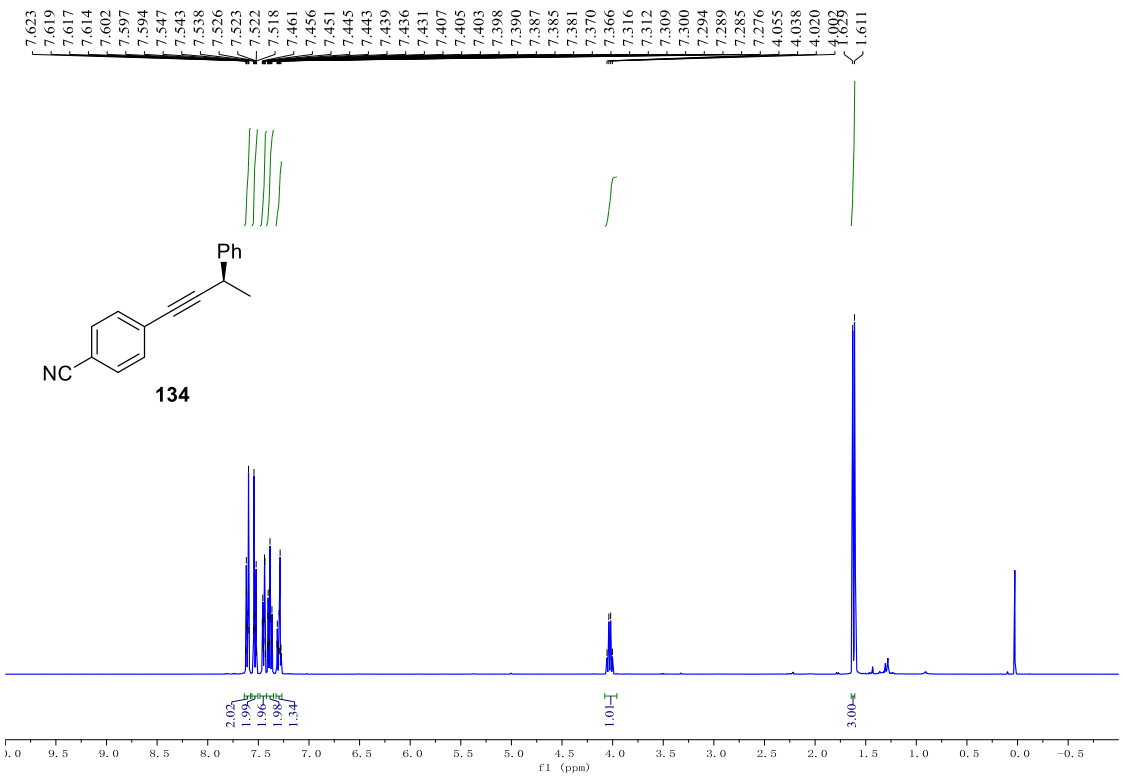

7.130
7.123
7.109
7.106
7.098
7.092
7.087
7.084
3.613
3.597
3.587
3.581
3.571
3.566
3.555
3.549
3.540
3.532
3.523
3.506
2.877
2.860
2.857
2.840
2.823
2.321
1.867
1.850
1.847
1.834
1.827
1.268
1.250
Me
OH
Me
130'
3.85
1.98
1.00
3.03
2.03
4.03
f1 (ppm)


143.763
135.604
129.186
126.820
61.339
41.026
36.080
22.565
21.009
Me
OH
Me
130'
f1 (ppm)


Ph
N
O
131
f1 (ppm)


Ph
Ph
Ph
133
f1 (ppm)


Ph
Ph
Ph
133
f1 (ppm)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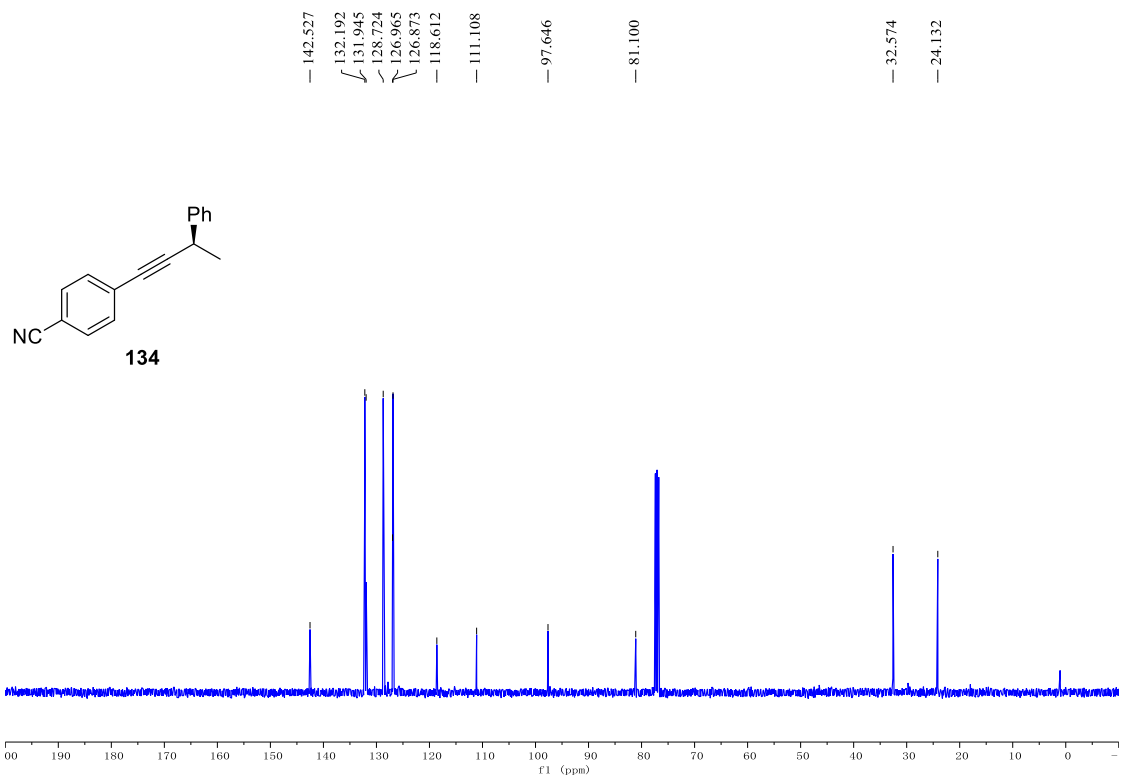
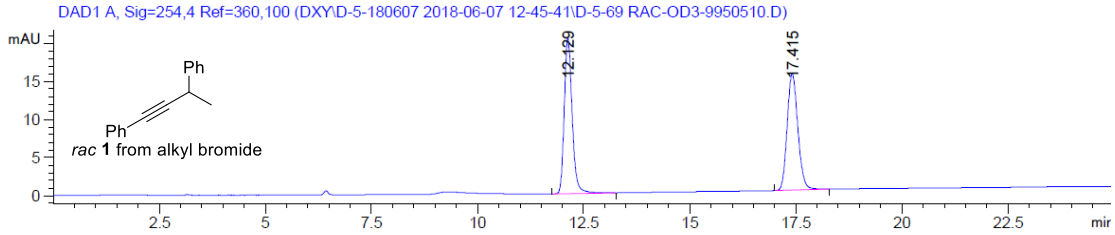
7.619
7.617
7.614
7.602
7.597
7.594
7.547
7.543
7.538
7.526
7.523
7.522
7.518
7.461
7.456
7.451
7.445
7.443
7.439
7.436
7.431
7.407
7.405
7.403
7.398
7.390
7.387
7.385
7.381
7.370
7.366
7.316
7.312
7.309
7.300
7.294
7.289
7.285
7.276
4.055
4.038
4.020
4.002
1.629
1.611
Ph
NC
134
2.02
1.94
1.96
1.98
1.34
1.01
3.00
f1 (ppm)

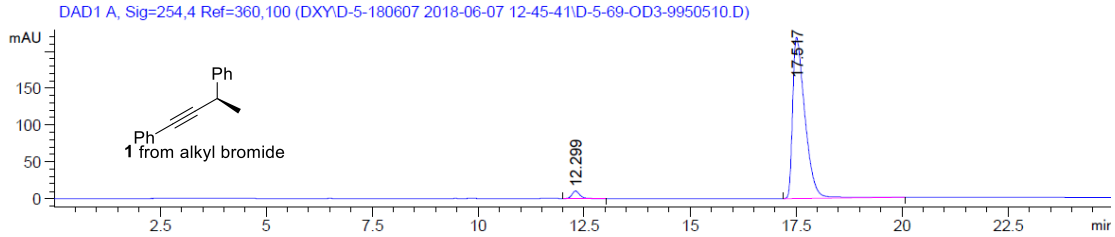

142.527
132.192
131.945
128.724
126.965
126.873
118.612
111.108
97.646
81.100
32.574
24.132
Ph
NC
134
f1 (ppm)

HPLC spectra



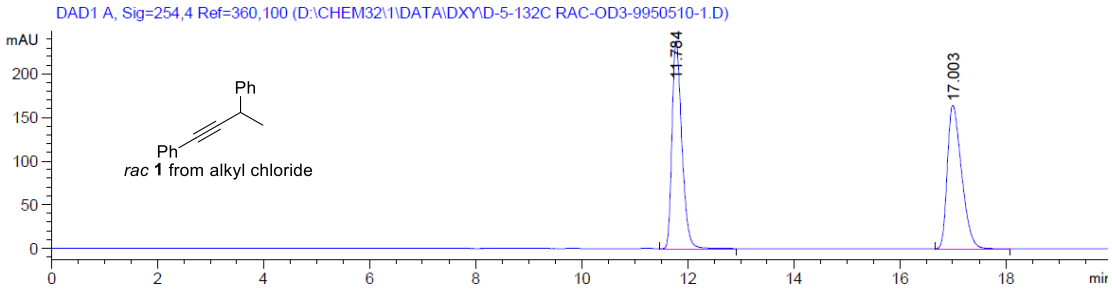
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.129	BB	0.1995	264.39798	20.36222	49.6549
2	17.415	BB	0.2685	268.07257	15.29708	50.3451
Totals :				532.47055	35.65929	



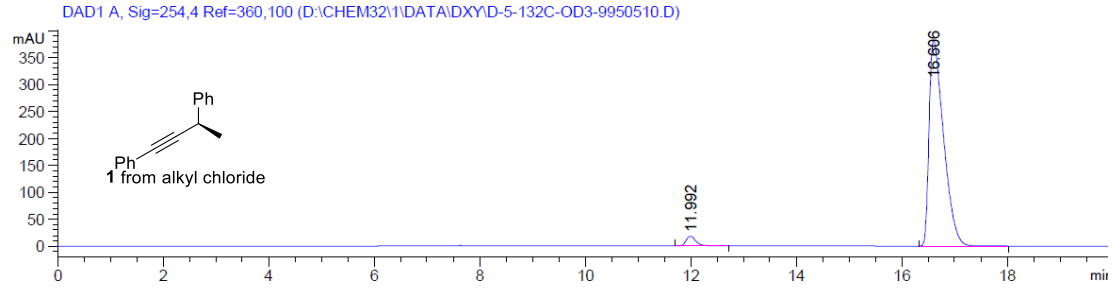
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.299	VV	0.2033	135.53612	10.17958	2.9601
2	17.517	BB	0.3088	4443.17236	218.92792	97.0399
Totals :				4578.70848	229.10750	



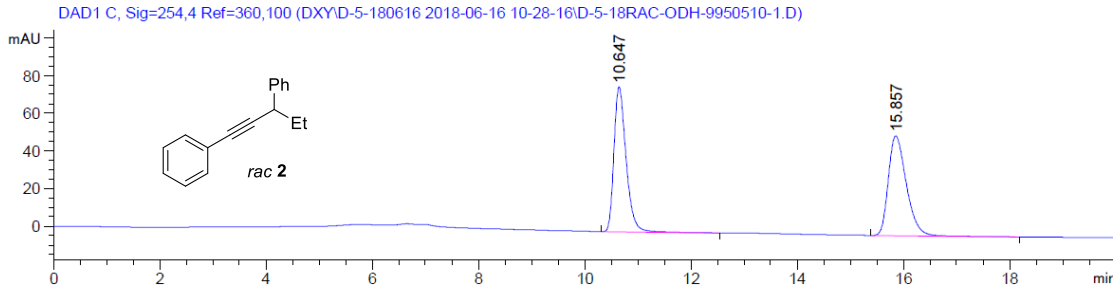
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.784	VB	0.1978	3060.64697	238.29568	49.8762
2	17.003	BB	0.2900	3075.84229	164.62596	50.1238
Totals :				6136.48926	402.92165	



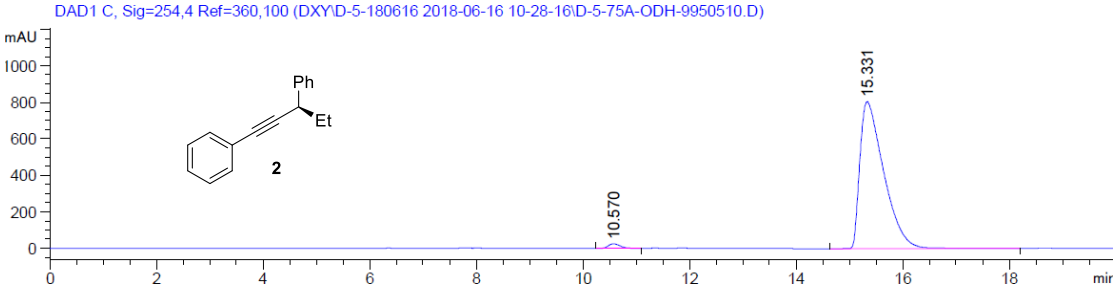
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.992	VB	0.2023	245.09161	18.53197	3.2485
2	16.606	BB	0.2912	7299.59521	381.52097	96.7515
Totals :				7544.68683	400.05294	



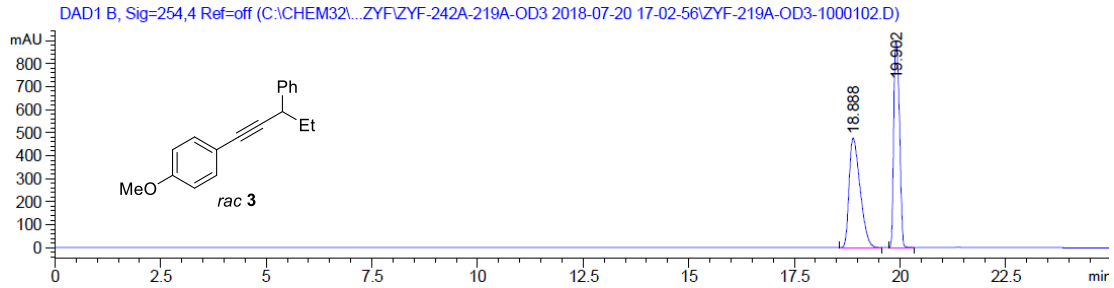
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.647	BB	0.2434	1224.23206	77.01841	49.5488
2	15.857	BBA	0.3628	1246.52661	52.91837	50.4512
Totals :				2470.75867	129.93678	



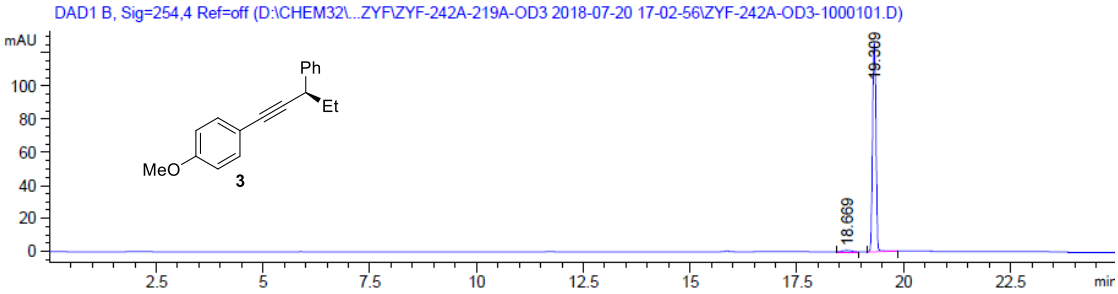
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.570	BV	0.2467	402.50595	25.14823	1.5798
2	15.331	BV	0.4757	2.50764e4	804.44165	98.4202
Totals :				2.54789e4	829.58988	



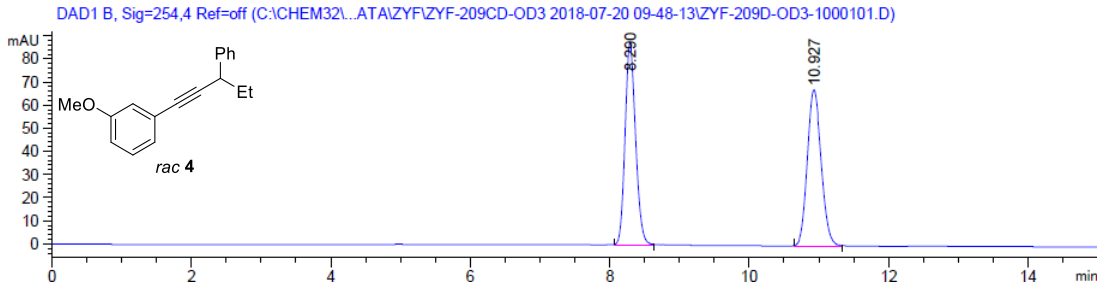
Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.888	BB	0.2787	8593.72168	475.91660	50.3738
2	19.902	BB	0.1562	8466.16895	896.19354	49.6262
Totals :				1.70599e4	1372.11014	



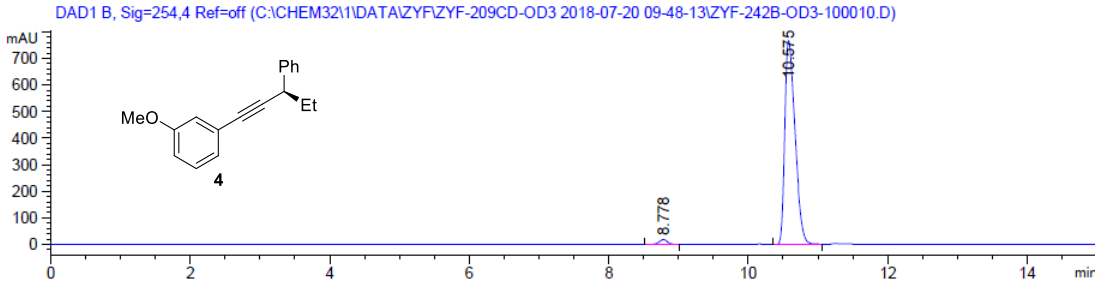
Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.669	MM R	0.2662	17.26094	1.08052	2.3802
2	19.309	BB	0.0912	707.91315	126.76484	97.6198
Totals :				725.17408	127.84535	



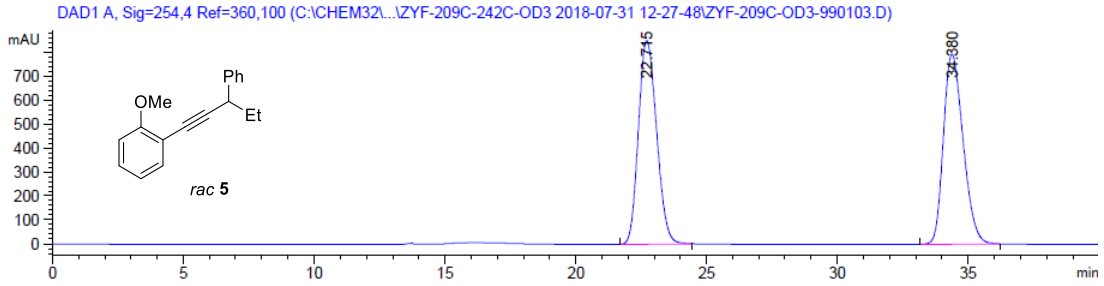
Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.290	BB	0.1628	922.52661	87.63383	49.7885
2	10.927	BB	0.2149	930.36481	67.46291	50.2115
Totals :				1852.89142	155.09673	



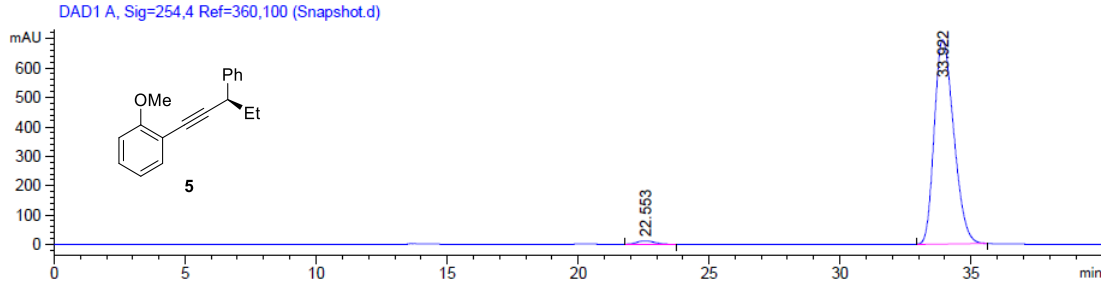
Signal 2: DAD1 B, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.778	BB	0.1276	151.30748	18.09315	1.9187
2	10.575	VB	0.1555	7734.43506	768.07104	98.0813
Totals :				7885.74254	786.16420	



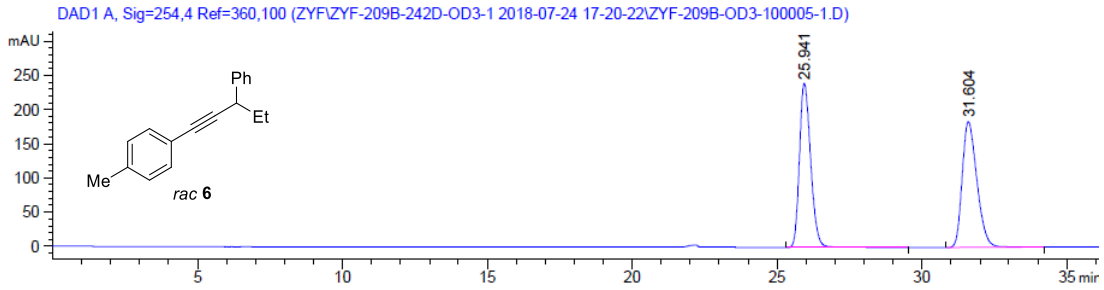
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.715	BB	0.7679	4.11060e4	850.49390	49.7388
2	34.380	BB	0.8143	4.15377e4	793.98975	50.2612
Totals :				8.26437e4	1644.48364	



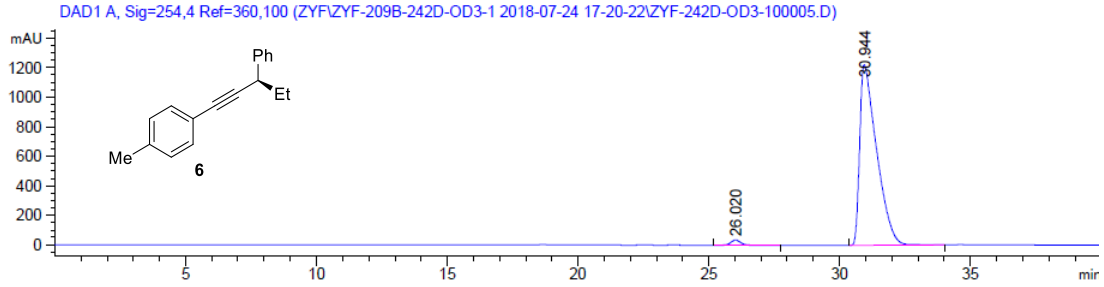
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.553	BB	0.7284	557.75629	11.77877	1.5274
2	33.922	BB	0.8115	3.59579e4	695.11975	98.4726
Totals :				3.65156e4	706.89852	



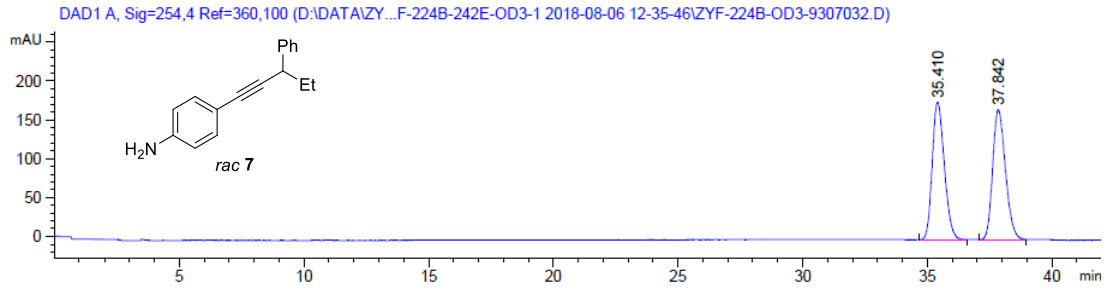
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.941	BB	0.4187	6493.12158	240.71945	49.9693
2	31.604	BB	0.5459	6501.08838	184.13448	50.0307
Totals :				1.29942e4	424.85393	



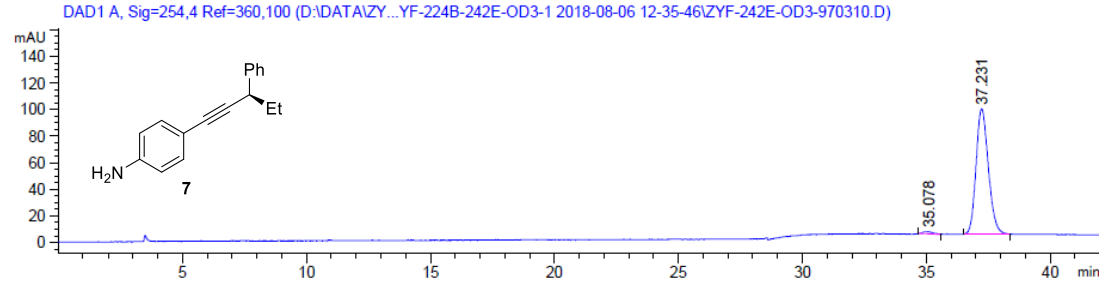
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.020	BB	0.4095	933.37164	35.18318	1.6755
2	30.944	BB	0.6492	5.47731e4	1221.27087	98.3245
Totals :				5.57064e4	1256.45406	



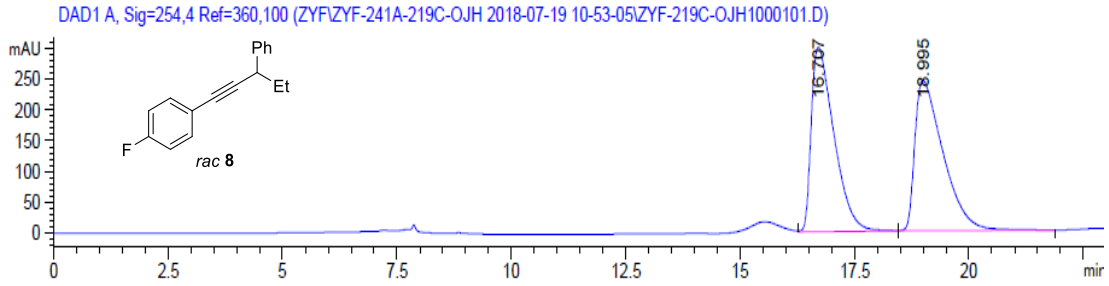
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.410	BB	0.5249	5960.94629	177.01788	50.0406
2	37.842	BB	0.5389	5951.26904	167.34419	49.9594
Totals :				1.19122e4	344.36208	



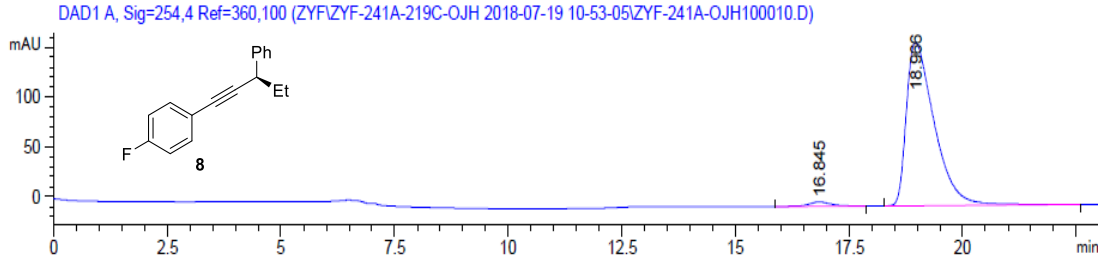
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.078	BB	0.3249	44.51665	1.67032	1.3474
2	37.231	BB	0.5234	3259.37622	94.26747	98.6526
Totals :				3303.89287	95.93779	



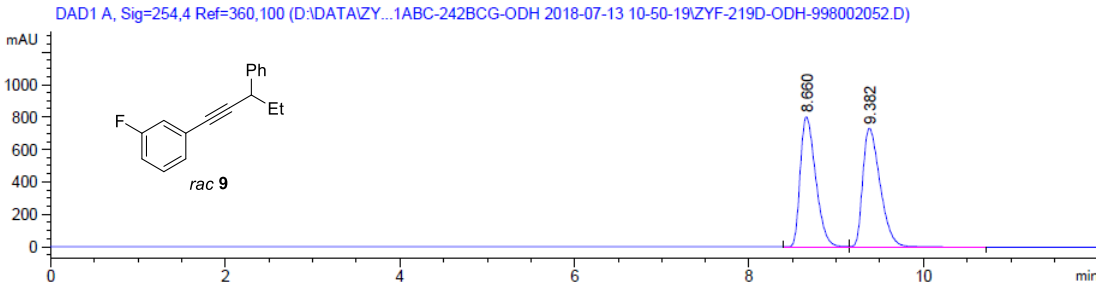
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.707	VB	0.5267	1.03530e4	299.92587	49.8251
2	18.995	BB	0.6445	1.04257e4	244.01630	50.1749
Totals :				**2.07786e4**	**543.94217**	



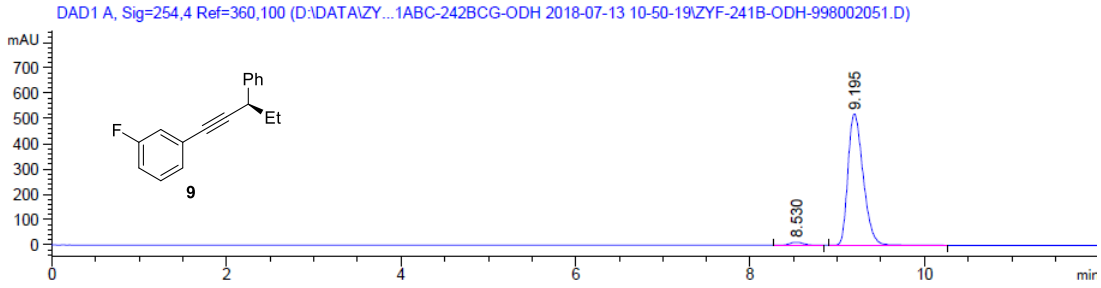
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.845	BB	0.5055	138.54382	4.21442	1.9388
2	18.966	BB	0.6443	7007.41699	164.05574	98.0612
Totals :				7145.96082	168.27016	



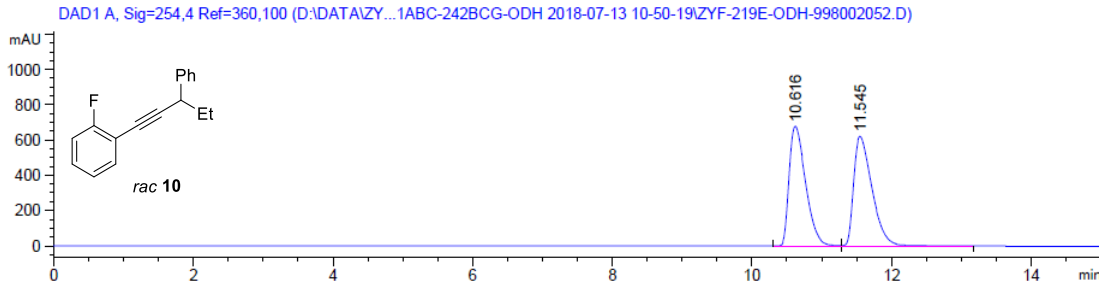
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.660	BV	0.1917	9875.91406	801.61652	49.4401
2	9.382	VB	0.2131	1.00996e4	731.20892	50.5599
Totals :				1.99755e4	1532.82544	



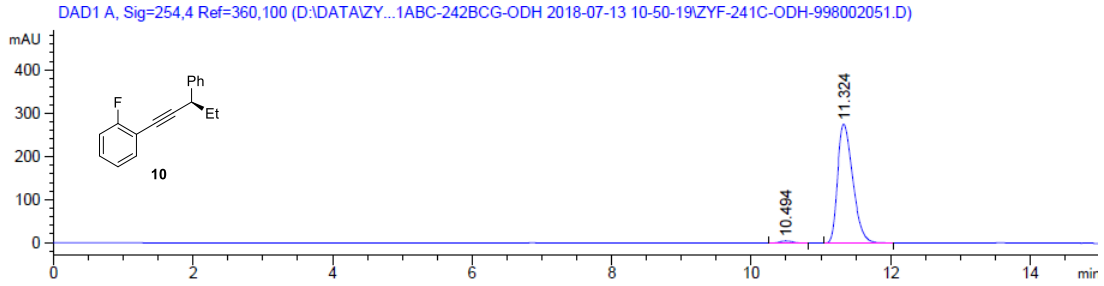
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.530	BB	0.1641	128.66992	12.29945	2.0138
2	9.195	BB	0.1886	6260.73535	519.36041	97.9862
Totals :				6389.40527	531.65986	



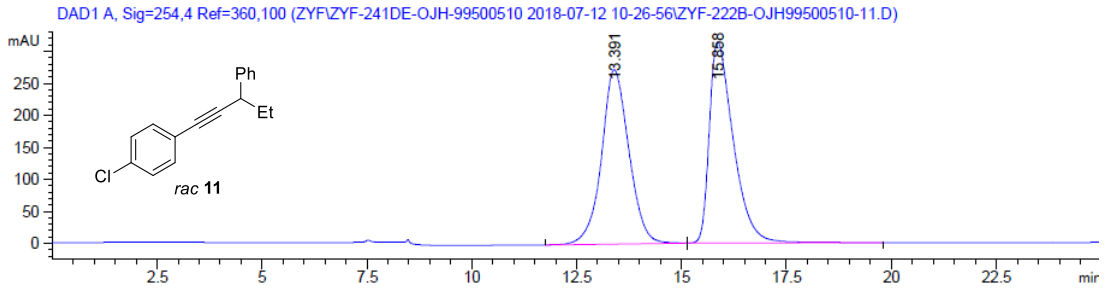
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.616	BV	0.2541	1.10557e4	678.34991	49.3877
2	11.545	VB	0.2829	1.13298e4	620.94147	50.6123
Totals :				2.23855e4	1299.29138	



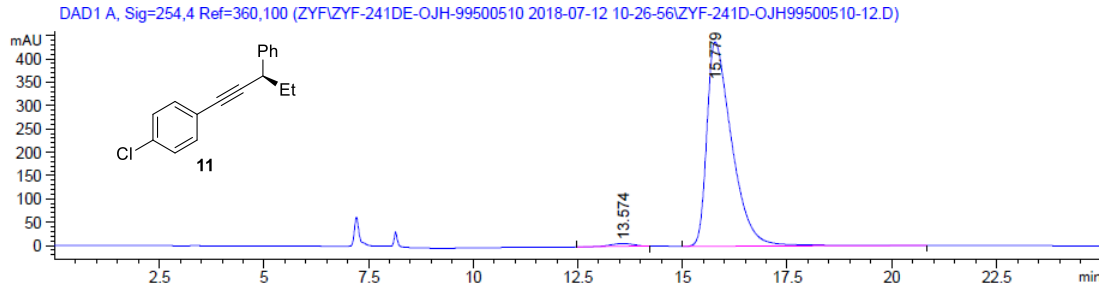
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.494	BB	0.1990	70.79667	5.39749	1.6716
2	11.324	BB	0.2362	4164.48486	275.74173	98.3284
Totals :				4235.28153	281.13922	



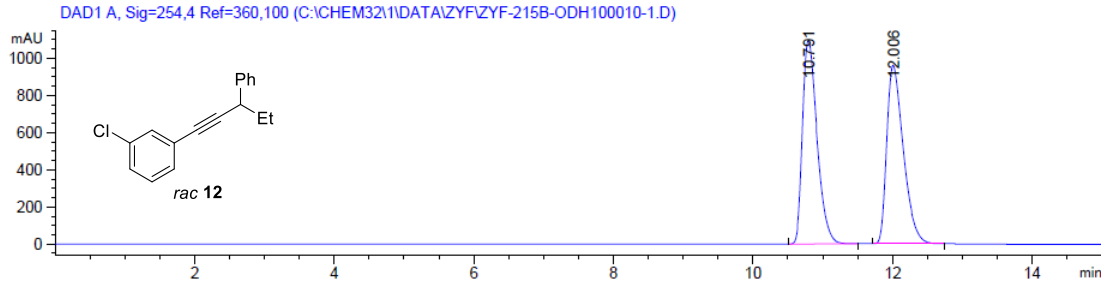
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.391	BB	0.6864	1.24058e4	272.87119	49.7185
2	15.858	BB	0.6009	1.25463e4	314.83203	50.2815
Totals :				2.49522e4	587.70322	



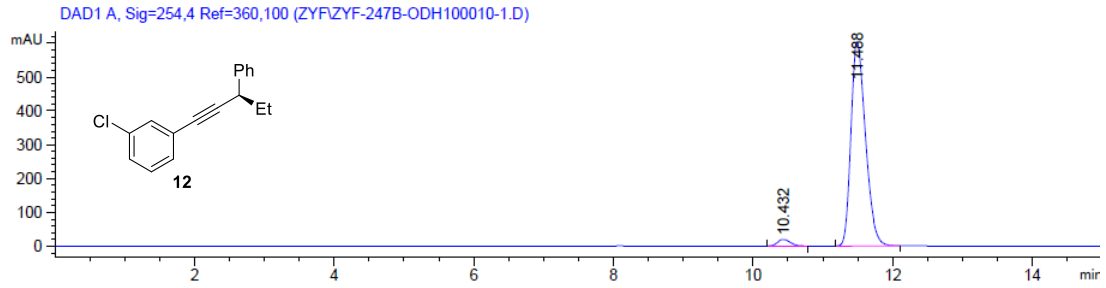
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.574	BB	0.5746	248.60632	6.49450	1.3432
2	15.779	BB	0.6264	1.82604e4	438.00558	98.6568
Totals :				1.85090e4	444.50009	



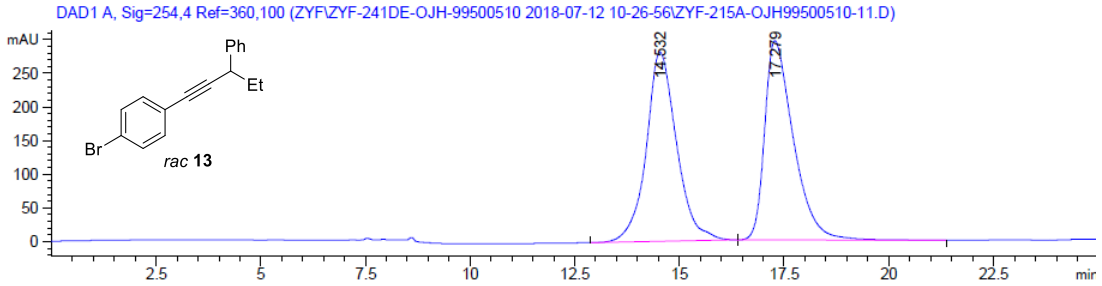
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.791	BB	0.2249	1.58623e4	1095.58386	49.9184
2	12.006	BB	0.2550	1.59142e4	961.77240	50.0816
Totals :				3.17764e4	2057.35626	



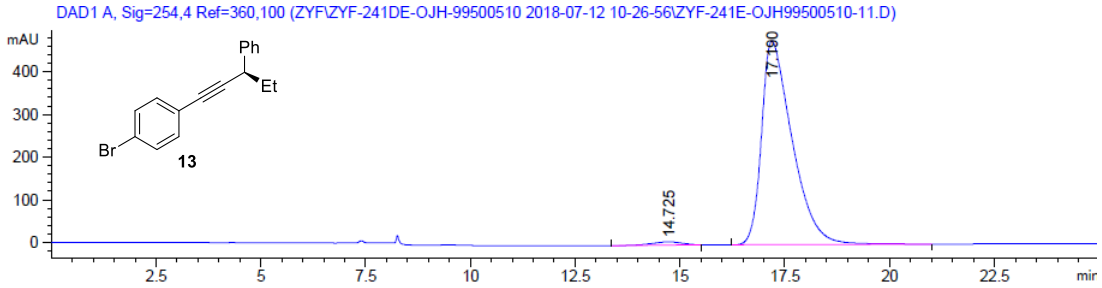
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.432	BB	0.1957	255.07809	20.15316	2.8271
2	11.488	BB	0.2255	8767.37891	603.60968	97.1729
Totals :				9022.45700	623.76284	



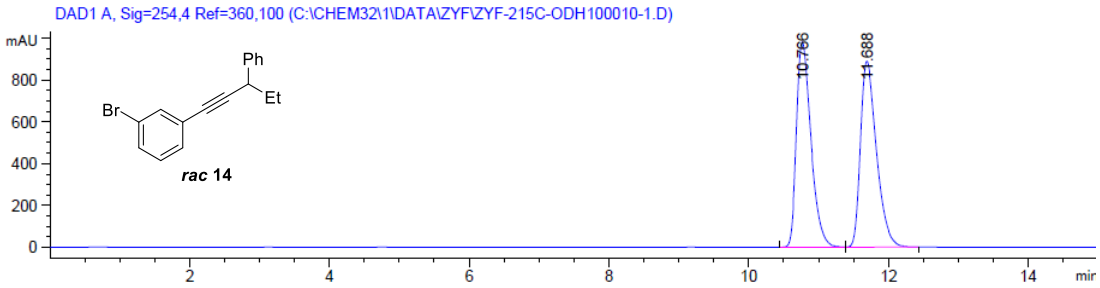
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.532	BB	0.7503	1.42013e4	281.61133	50.0256
2	17.279	BB	0.7165	1.41868e4	296.32831	49.9744
Totals :				2.83881e4	577.93964	



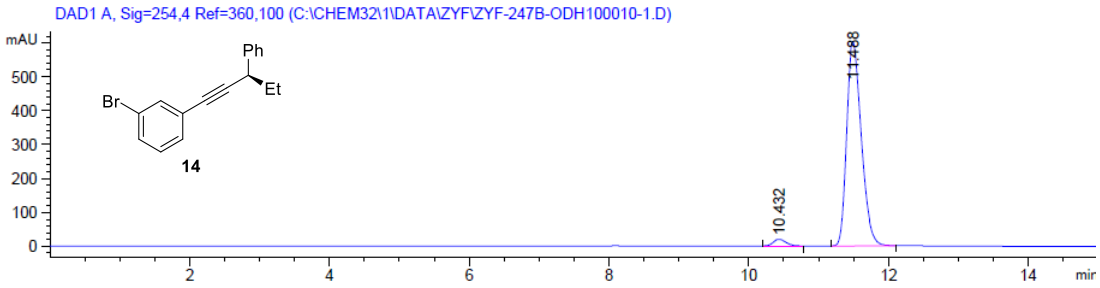
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.725	BB	0.7411	386.64621	7.81661	1.5678
2	17.190	BB	0.7567	2.42747e4	477.81192	98.4322
Totals :				2.46613e4	485.62853	



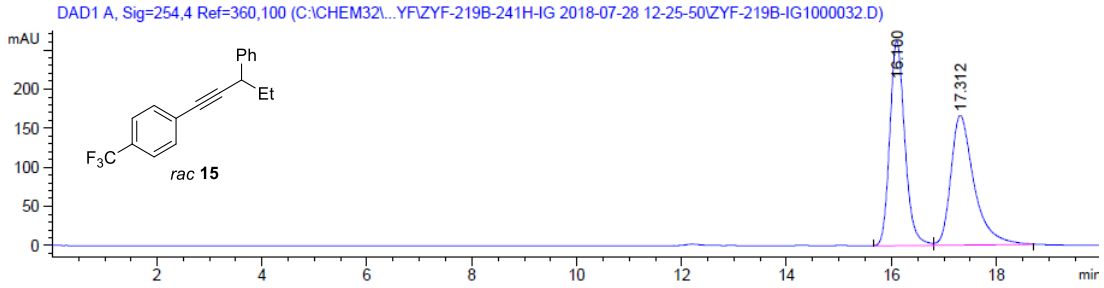
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.766	BV	0.2198	1.41134e4	981.53076	49.9526
2	11.688	VB	0.2435	1.41402e4	889.38660	50.0474
Totals :				2.82536e4	1870.91736	



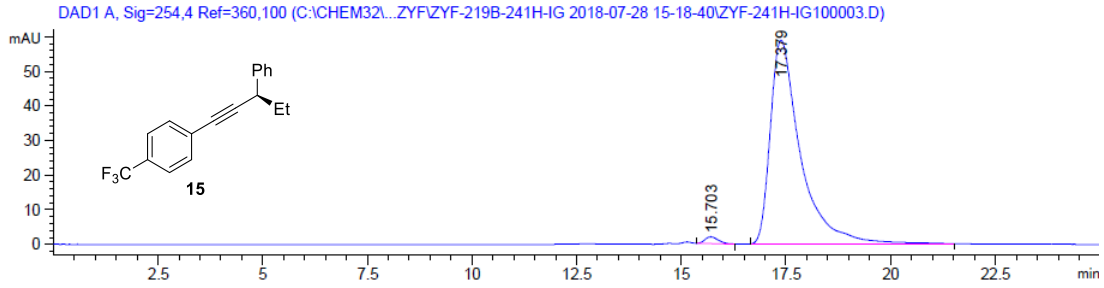
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.432	BB	0.1957	255.07809	20.15316	2.8271
2	11.488	BB	0.2255	8767.37891	603.60968	97.1729
Totals :				9022.45700	623.76284	



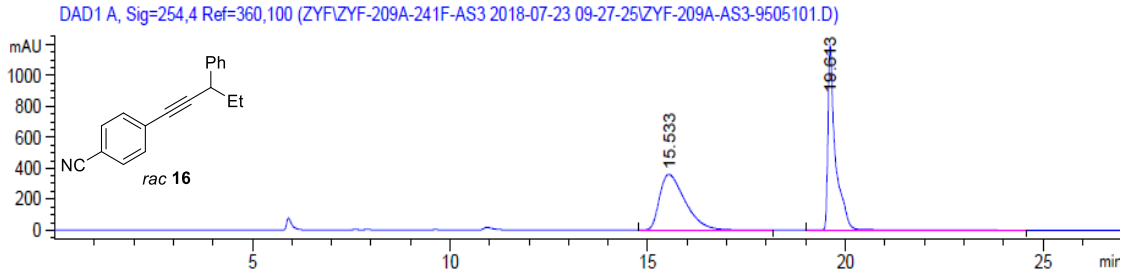
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.100	BV	0.3058	5201.87012	261.75916	50.5184
2	17.312	VB	0.4606	5095.11914	165.78093	49.4816
Totals :				1.02970e4	427.54008	



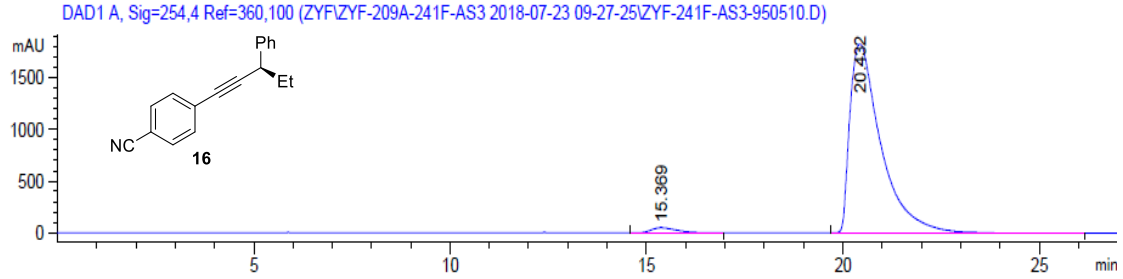
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.703	BB	0.3317	44.80248	2.01245	1.4837
2	17.379	MM R	0.8416	2974.74976	58.91287	98.5163
Totals :				3019.55223	60.92532	



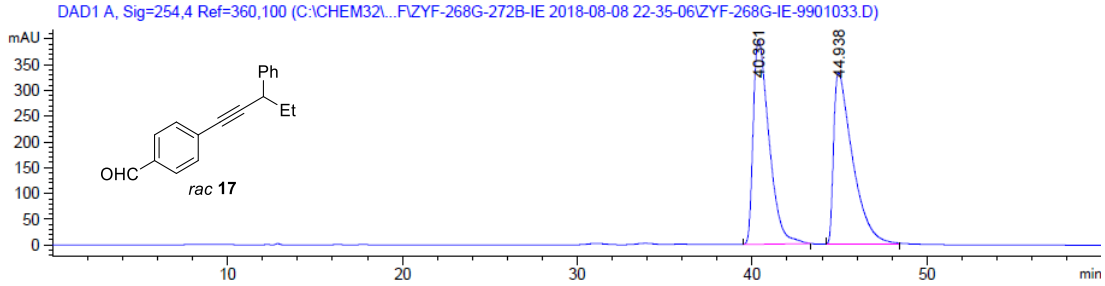
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.533	BB	0.6888	1.60558e4	358.30255	50.3634
2	19.613	BB	0.1823	1.58241e4	1196.18945	49.6366
Totals :				3.18798e4	1554.49200	



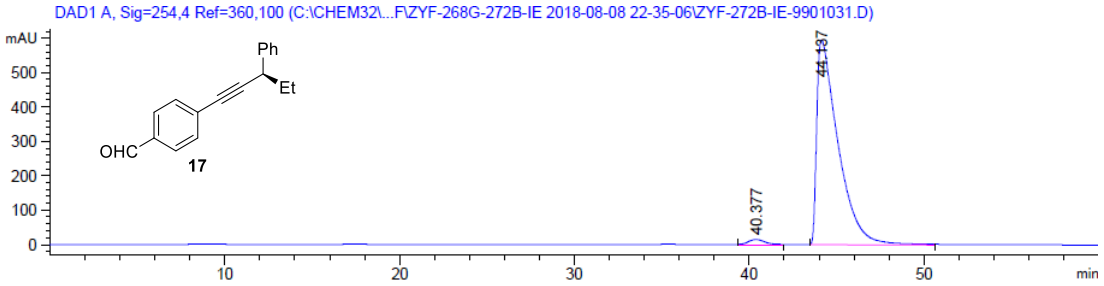
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.369	BB	0.6798	2195.66357	49.46752	2.1473
2	20.432	BB	0.8196	1.00057e5	1825.01074	97.8527
Totals :				1.02252e5	1874.47826	



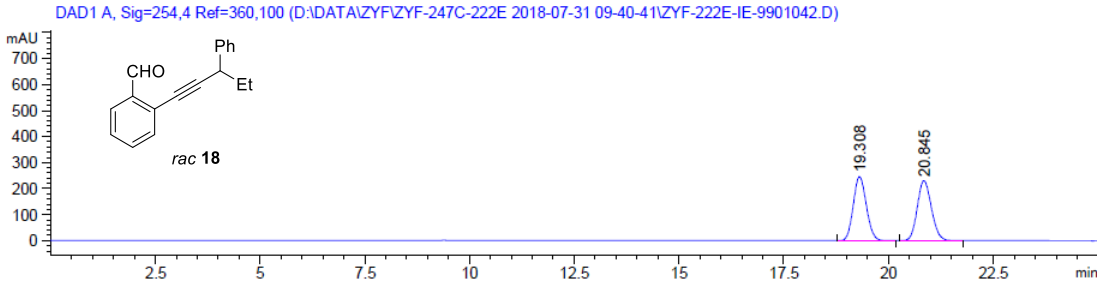
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.361	BB	0.9562	2.49682e4	396.73505	50.0192
2	44.938	MM R	1.2491	2.49491e4	332.89548	49.9808
Totals :				4.99173e4	729.63052	



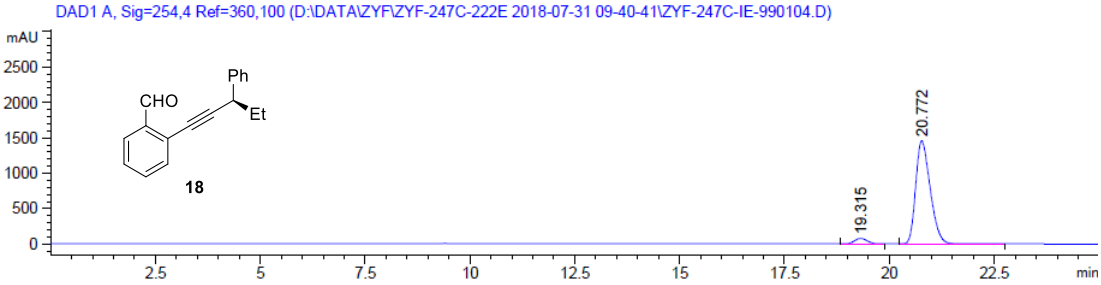
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.377	BB	0.9014	901.57147	14.57962	1.7510
2	44.137	MM R	1.4176	5.05867e4	594.73804	98.2490
Totals :				5.14882e4	609.31766	



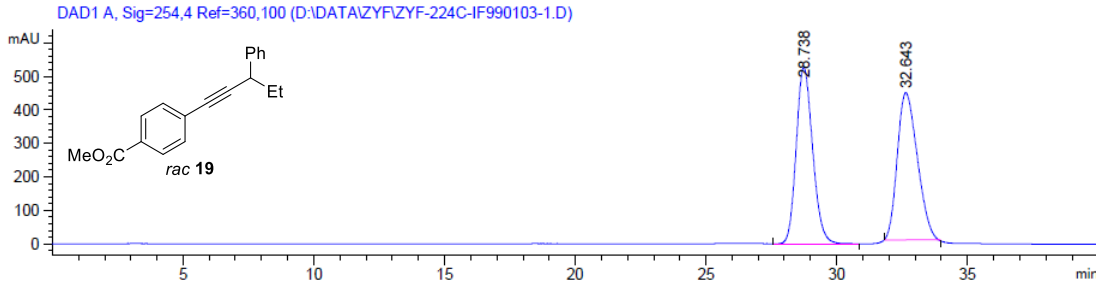
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.308	BB	0.3399	5357.65869	246.15463	49.8181
2	20.845	BB	0.3616	5396.77490	230.12372	50.1819
Totals :				1.07544e4	476.27835	



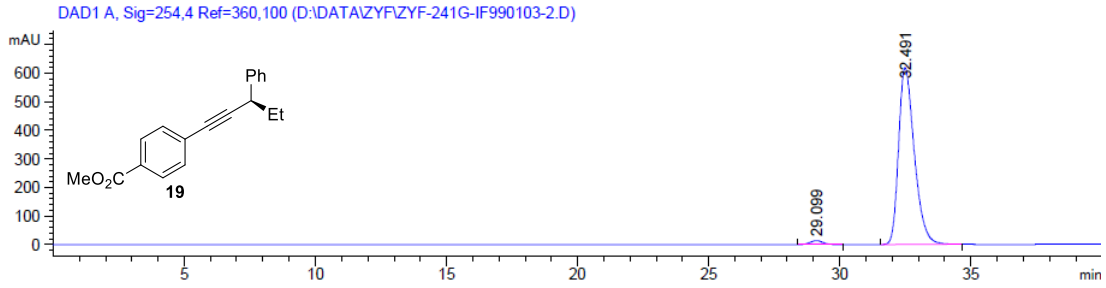
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.315	BB	0.3324	1677.26501	78.79146	4.5529
2	20.772	BB	0.3716	3.51618e4	1456.74829	95.4471
Totals :				3.68391e4	1535.53975	



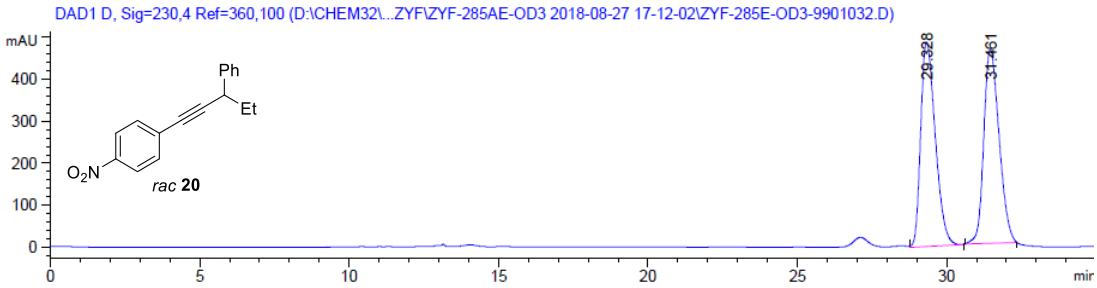
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.738	MM R	0.7342	2.32970e4	528.85754	49.8738
2	32.643	MM R	0.8873	2.34149e4	439.81506	50.1262
Totals :				4.67118e4	968.67261	



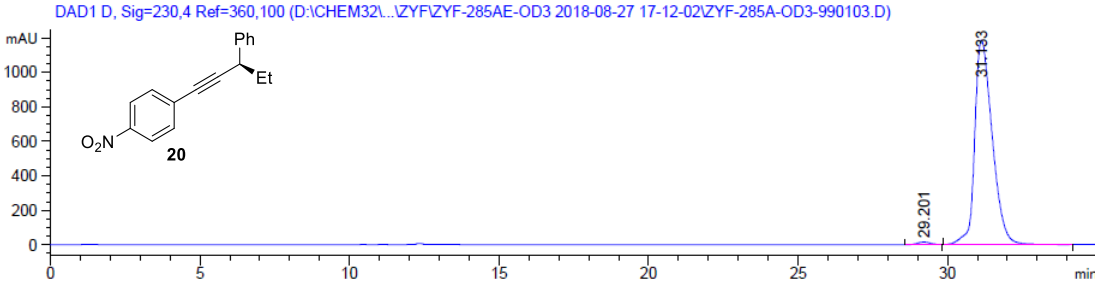
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.099	BB	0.4415	462.92401	13.86570	1.7602
2	32.491	BB	0.6409	2.58367e4	619.04327	98.2398
Totals :				2.62996e4	632.90898	



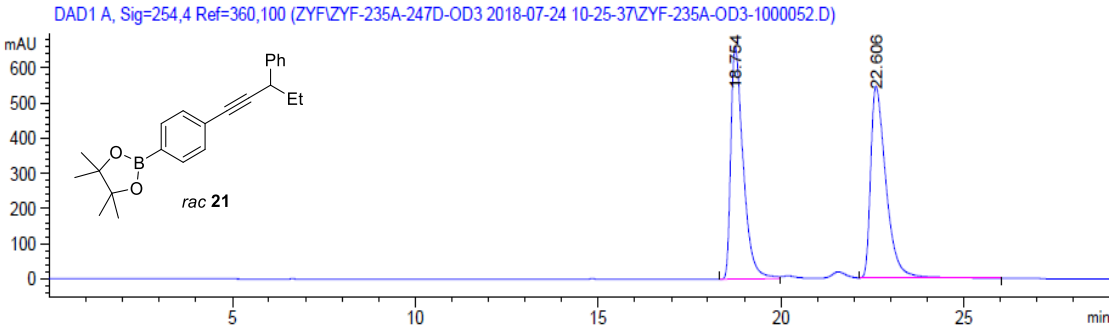
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.328	MM R	0.5631	1.64566e4	487.05371	50.0507
2	31.461	MM R	0.5928	1.64233e4	461.71606	49.9493
Totals :				3.28799e4	948.76978	



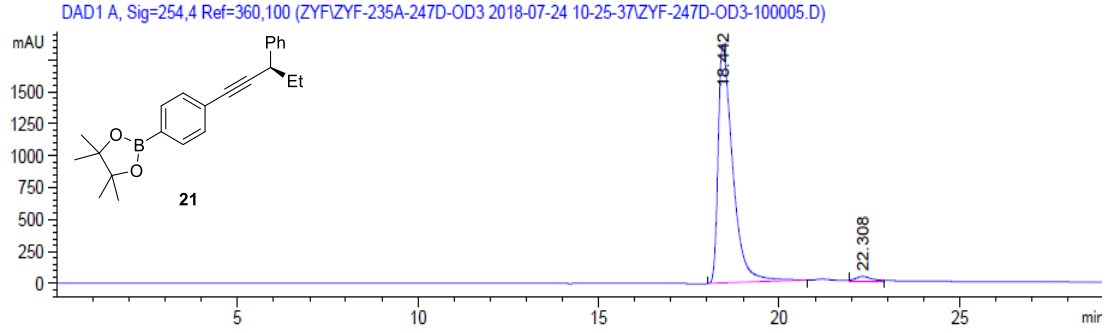
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.201	BV	0.4991	488.16226	15.26644	0.9912
2	31.133	MM R	0.6846	4.87633e4	1187.12793	99.0088
Totals :				4.92514e4	1202.39437	



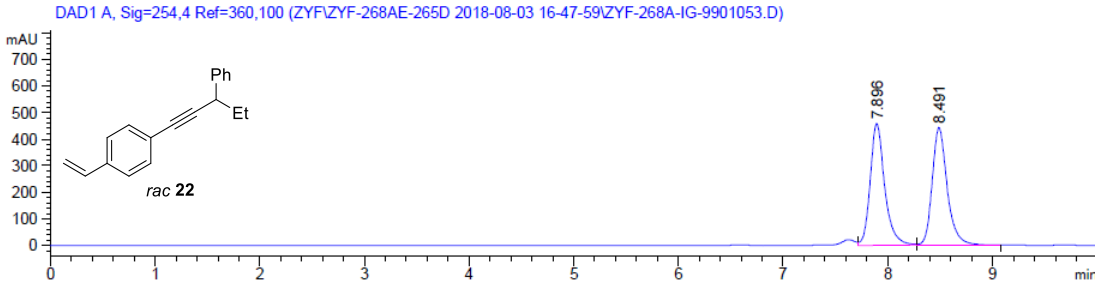
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.754	BV	0.3538	1.55617e4	662.97375	49.4436
2	22.606	VB	0.4353	1.59120e4	547.14362	50.5564
Totals :				3.14737e4	1210.11737	



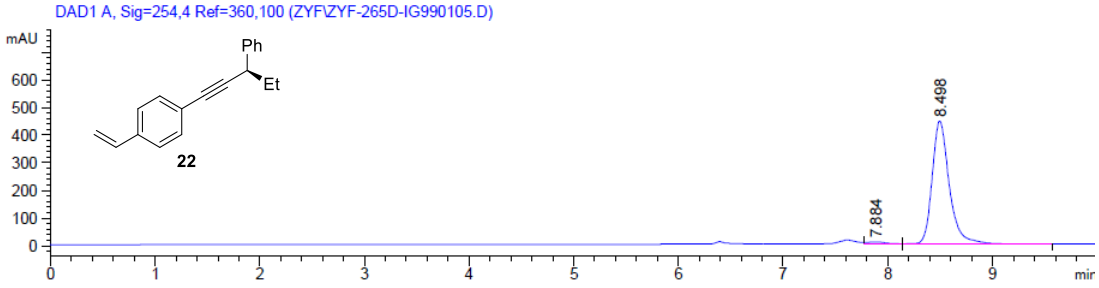
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.442	BB	0.4168	5.23371e4	1868.56177	97.8485
2	22.308	MM R	0.5131	1150.80811	37.38110	2.1515
Totals :				5.34879e4	1905.94287	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.896	VV	0.1448	4418.32617	457.16644	49.9387
2	8.491	VB	0.1507	4429.17041	442.85693	50.0613
Totals :				8847.49658	900.02338	

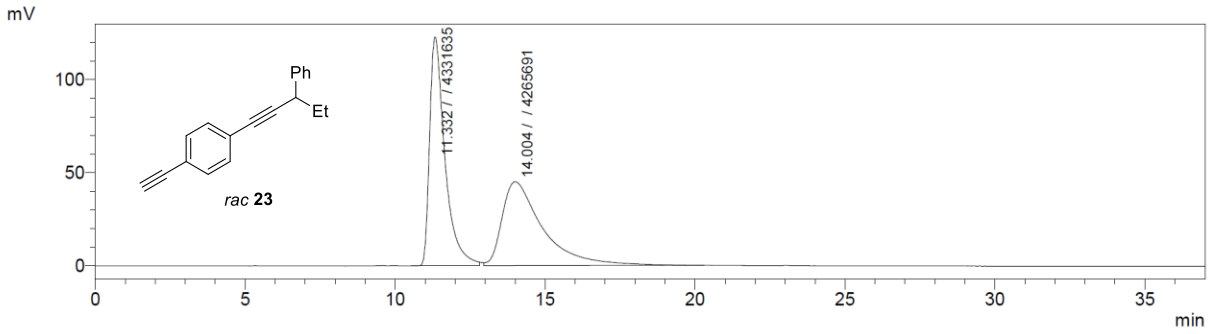


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.884	VV	0.1785	93.61378	7.77233	1.8127
2	8.498	VB	0.1709	5070.62842	445.25797	98.1873
Totals :				5164.24220	453.03029	

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	: lzl-7-89-racemic AY3 100-0 06ml 50 min		Sample ID
Vial#	: 1-40	Injection Volume	: 3 uL
Date Acquired	: 2018/8/14 12:50:34	Acquired by	: System Administrator
Date Processed	: 2018/11/22 16:22:05	Modified by	: System Administrator
Data Filename	: D:\LZL\lzl-7-89-racemic AY3 100-0 06ml 50 min.lcd		
Method Filename	: D:\LZL\AY3 100-0 06ml 50 min.lcm		
Batch Filename	:		

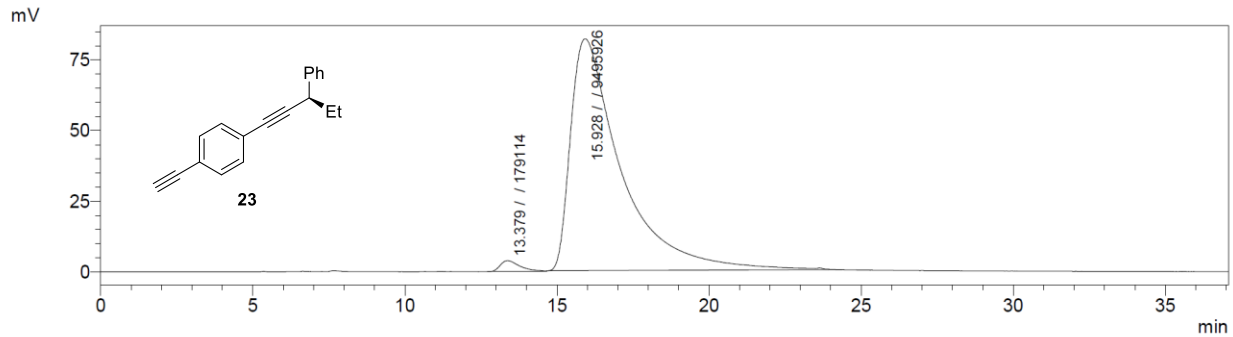


检测器A Ch1 254nm

Peak#	Ret. Time	Area%
1	11.332	50.384
2	14.004	49.616
总计		100.000

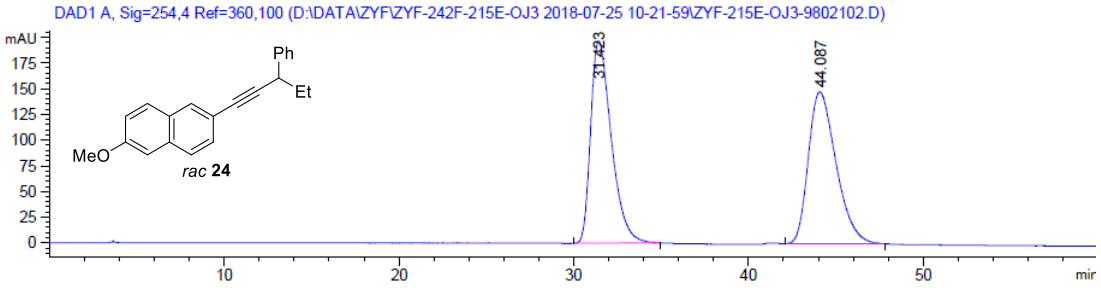
==== Shimadzu LabSolutions Analysis Report ====

Sample Name	: lzl-7-89-p AY3 100-0 06ml 50 min		Sample ID : lzl-7-89-p A
Vial#	: 1-41	Injection Volume	: 3 uL
Date Acquired	: 2018/8/14 13:58:33	Acquired by	: System Administrator
Date Processed	: 2018/11/22 16:14:54	Modified by	: System Administrator
Data Filename	: D:\LZL\lzl-7-89-pAY3 100-0 06ml 50 min.lcd		
Method Filename	: D:\LZL\AY3 100-0 06ml 50 min.lcm		
Batch Filename	:		



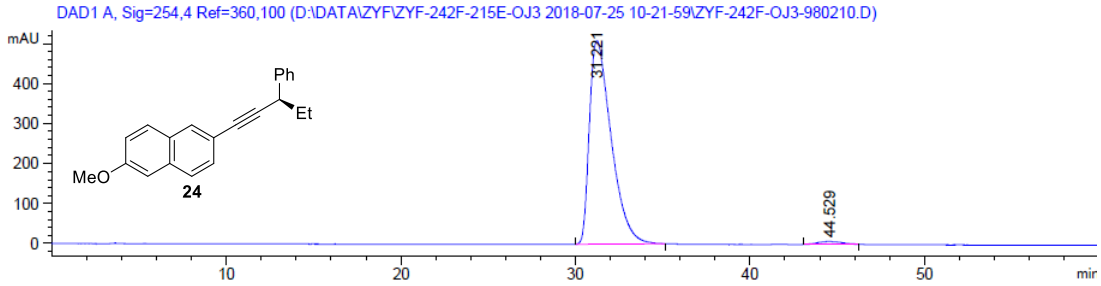
检测器A Ch1 254nm

Peak#	Ret. Time	Area%
1	13.379	1.851
2	15.928	98.149
总计		100.000



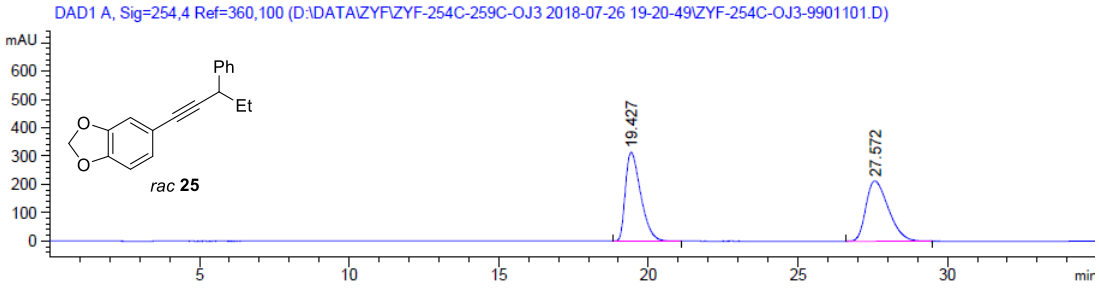
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.423	BB	1.1557	1.61906e4	196.83044	49.8795
2	44.087	BB	1.3113	1.62688e4	147.67677	50.1205
Totals :				3.24593e4	344.50722	



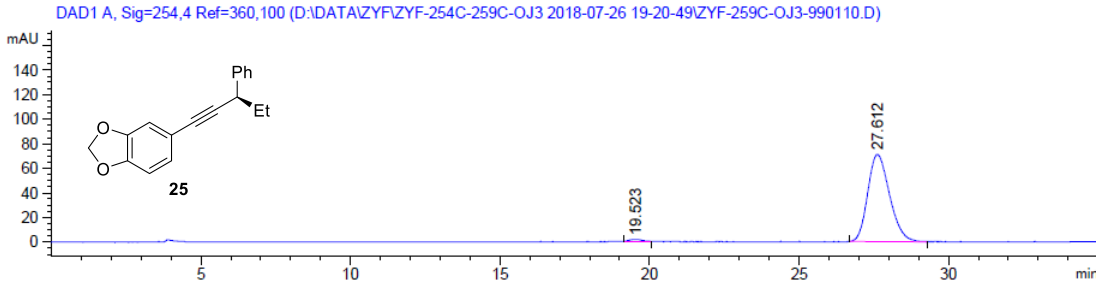
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.221	BB	1.1887	4.41599e4	508.72049	98.4446
2	44.529	BB	1.1343	697.72070	7.24030	1.5554
Totals :				4.48576e4	515.96079	



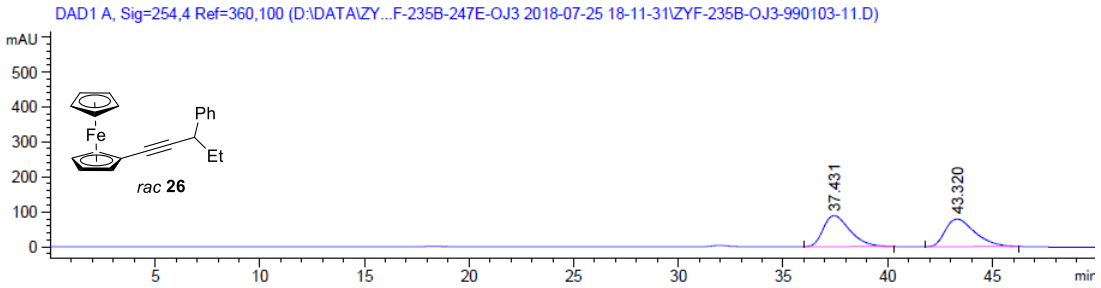
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.427	BB	0.5476	1.11598e4	313.23969	50.0848
2	27.572	BB	0.7945	1.11220e4	213.24927	49.9152
Totals :				2.22818e4	526.48895	



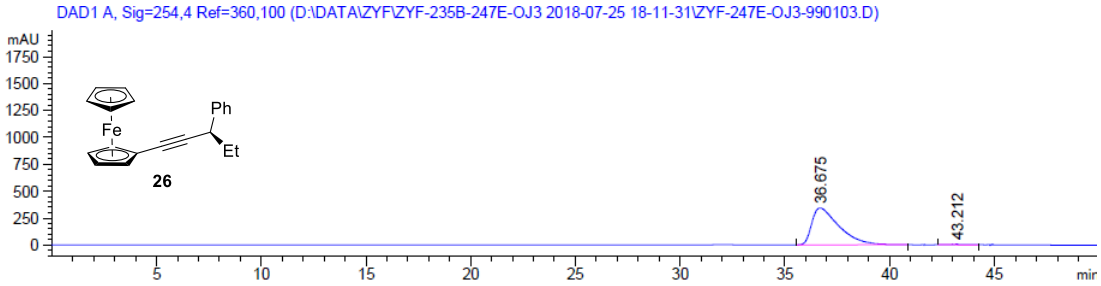
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.523	BB	0.3328	44.99253	1.63610	1.2364
2	27.612	BB	0.7352	3593.90259	70.92384	98.7636
Totals :				3638.89512	72.55993	



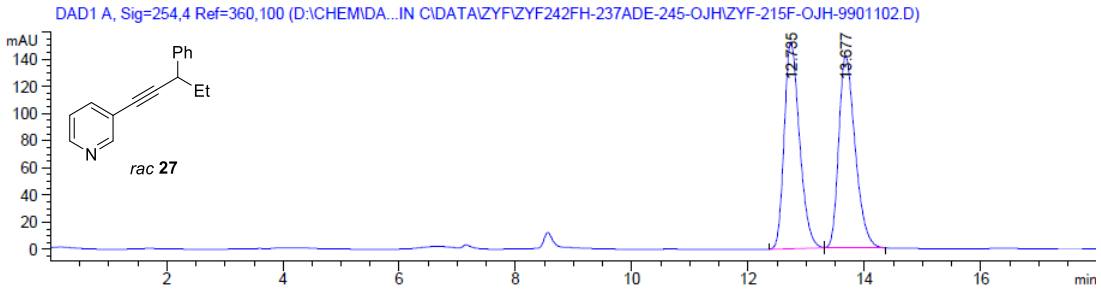
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.431	BB	1.0686	7913.17285	89.05843	50.4011
2	43.320	BB	1.1777	7787.23535	79.02314	49.5989
Totals :				1.57004e4	168.08157	



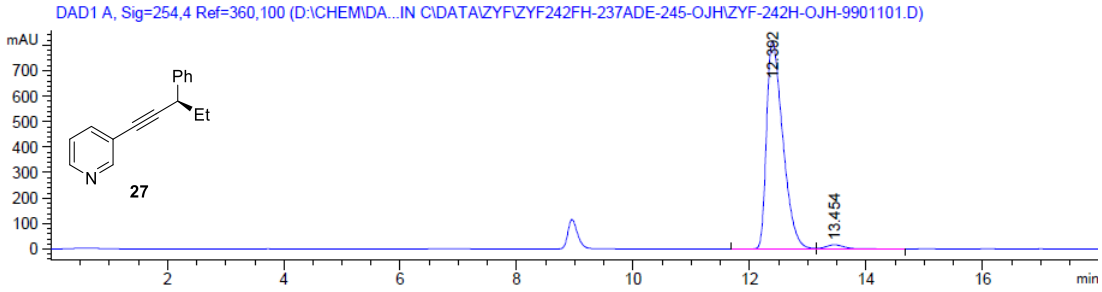
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.675	MM R	1.5154	3.13142e4	344.39029	98.7594
2	43.212	MM R	1.2402	393.35709	5.28621	1.2406
Totals :				3.17076e4	349.67650	



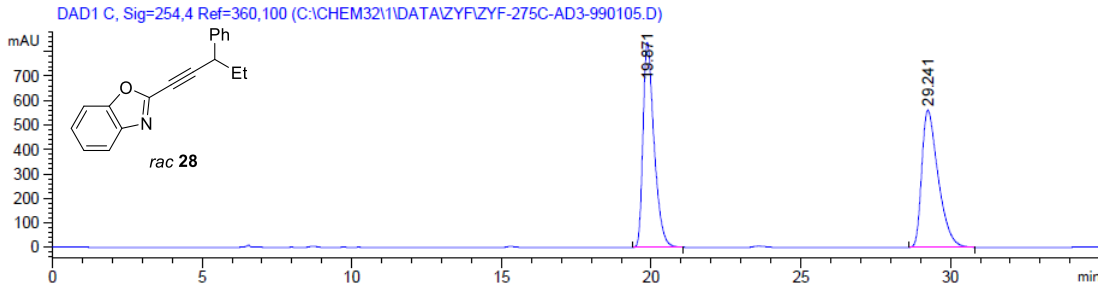
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.735	MM R	0.3041	2778.11670	152.26492	50.0591
2	13.677	MM R	0.3271	2771.55420	141.19966	49.9409
Totals :				5549.67090	293.46458	



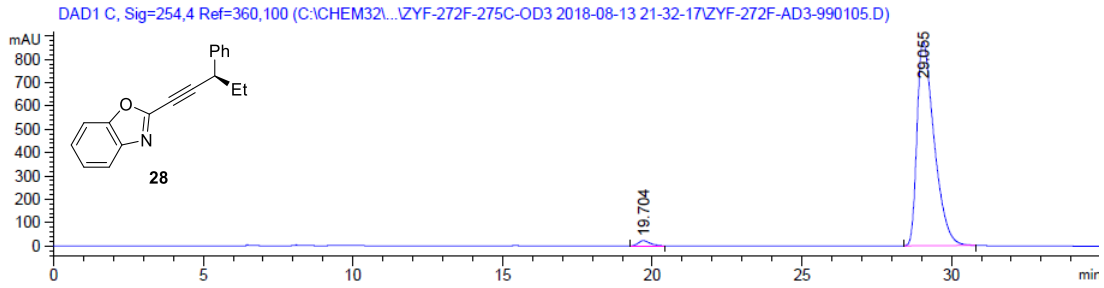
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.392	BV	0.3014	1.58896e4	815.07422	97.7355
2	13.454	VB	0.3341	368.15637	16.51166	2.2645
Totals :				1.62578e4	831.58588	



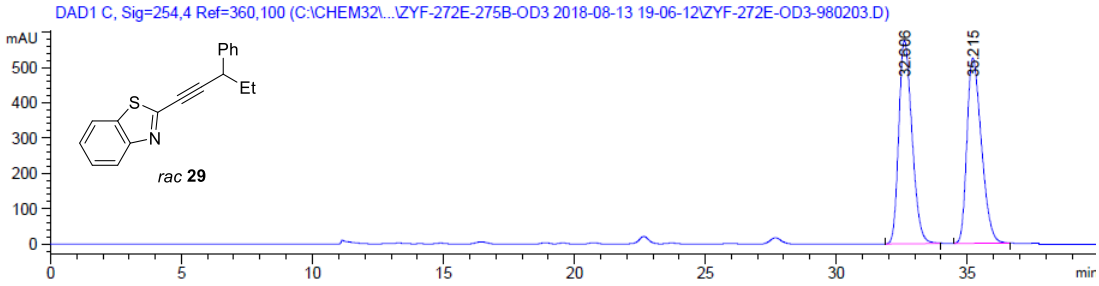
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.871	BB	0.3835	2.15508e4	839.45325	50.1782
2	29.241	BB	0.5765	2.13978e4	561.61377	49.8218
Totals :				4.29486e4	1401.06702	



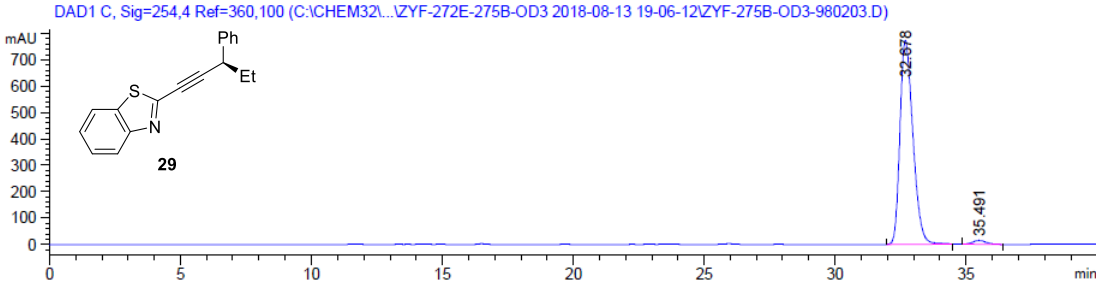
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.704	BB	0.4147	608.64178	22.28293	1.7184
2	29.055	BB	0.6019	3.48101e4	875.39990	98.2816
Totals :				3.54188e4	897.68284	



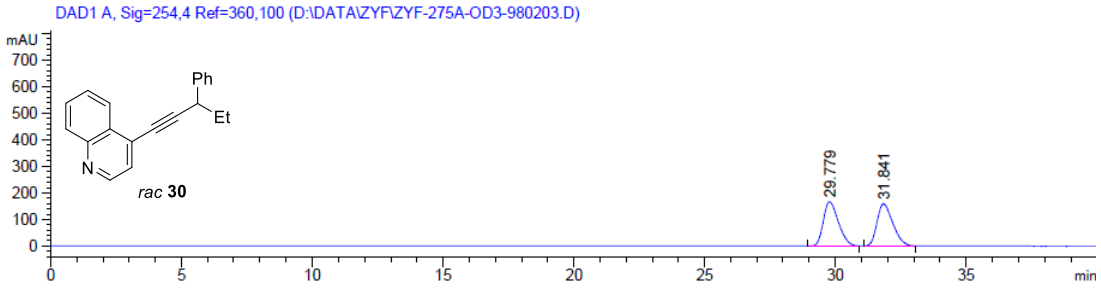
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.606	BB	0.5466	2.01726e4	575.92828	50.0468
2	35.215	BB	0.5957	2.01348e4	524.71289	49.9532
Totals :				4.03074e4	1100.64117	



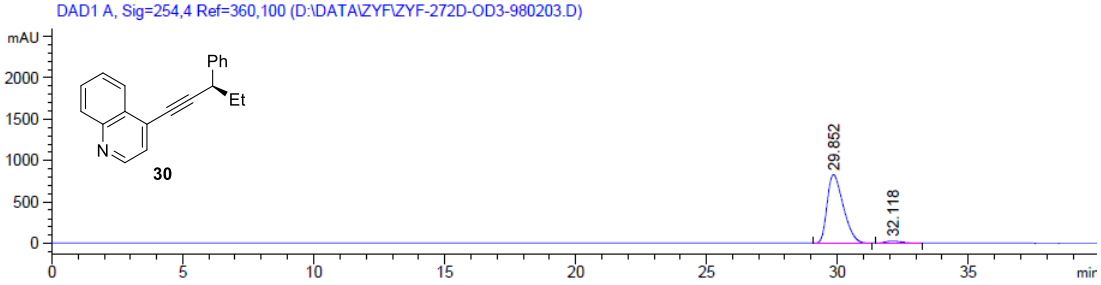
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.678	BB	0.5311	2.66145e4	774.03754	98.1579
2	35.491	BB	0.5445	499.46088	14.40484	1.8421
Totals :				2.71140e4	788.44238	



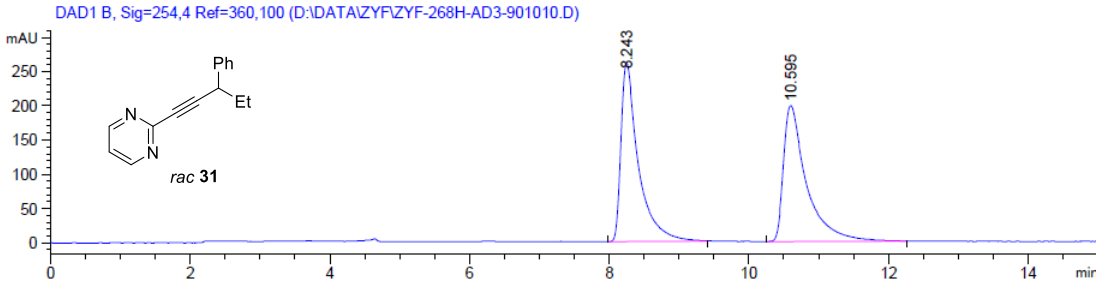
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.779	BB	0.5944	6689.38721	167.34102	50.1421
2	31.841	BB	0.6395	6651.47559	158.54236	49.8579
Totals :				1.33409e4	325.88338	



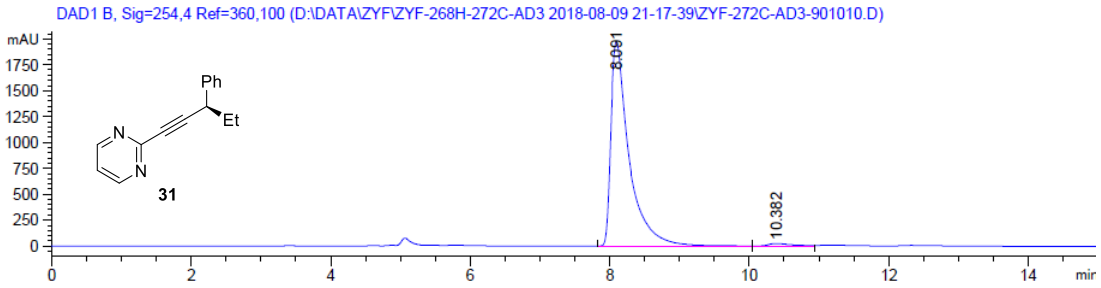
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.852	BB	0.6415	3.56214e4	828.75372	96.8548
2	32.118	BV	0.5275	1156.73889	27.12849	3.1452
Totals :				3.67781e4	855.88221	



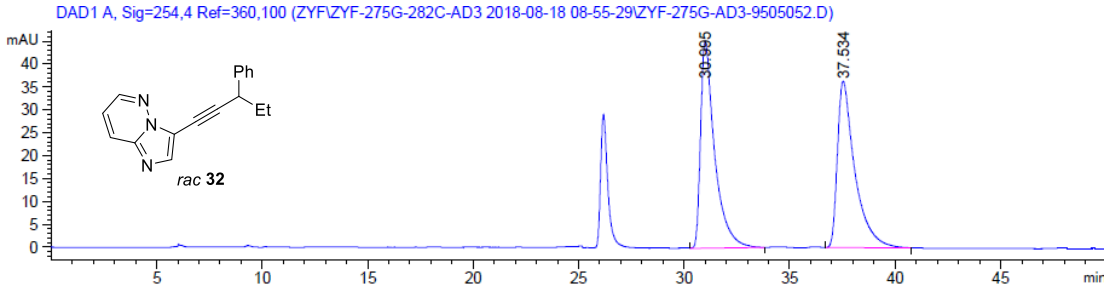
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.243	BV	0.2504	4515.66309	260.29944	50.0169
2	10.595	BB	0.3272	4512.60303	198.51224	49.9831
Totals :				9028.26611	458.81168	



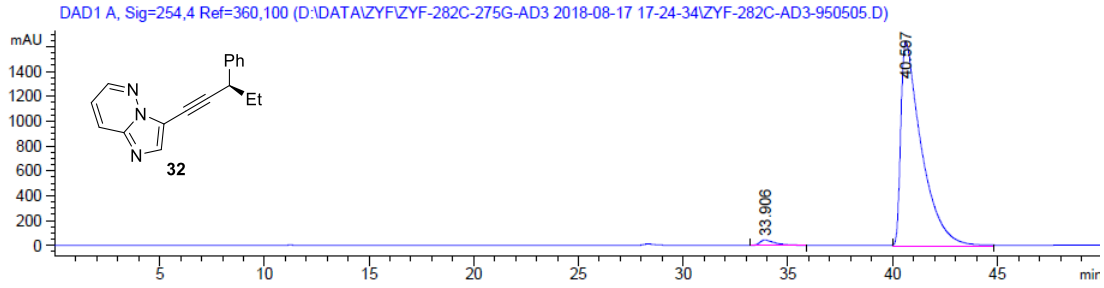
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.091	BV	0.2587	3.56787e4	1975.26855	98.5700
2	10.382	VV	0.3114	517.60181	23.45664	1.4300
Totals :				3.61963e4	1998.72519	



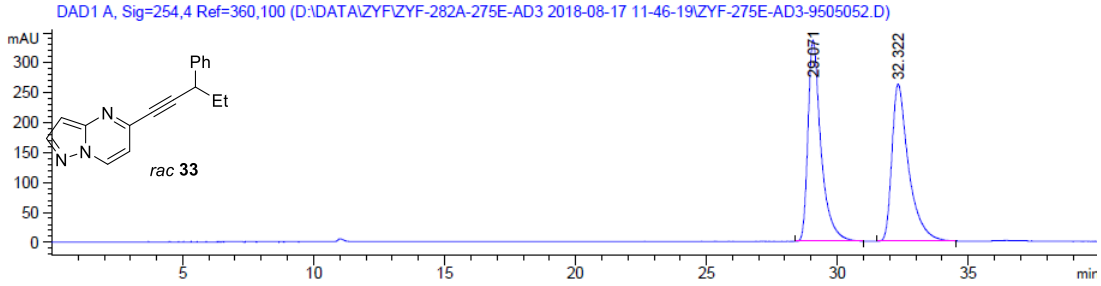
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.995	BB	0.6663	2090.99023	45.14823	50.1121
2	37.534	BB	0.8265	2081.63281	36.32701	49.8879
Totals :				4172.62305	81.47523	



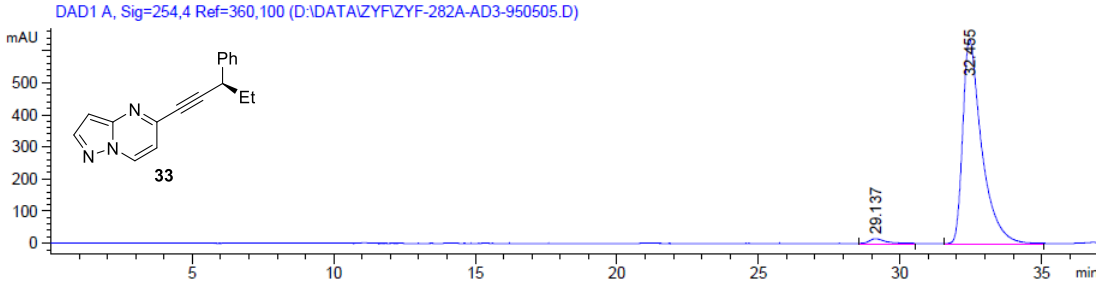
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.906	BB	0.6798	2180.35547	42.69677	1.8941
2	40.597	MM R	1.1406	1.12932e5	1650.13416	98.1059
Totals :				1.15112e5	1692.83093	



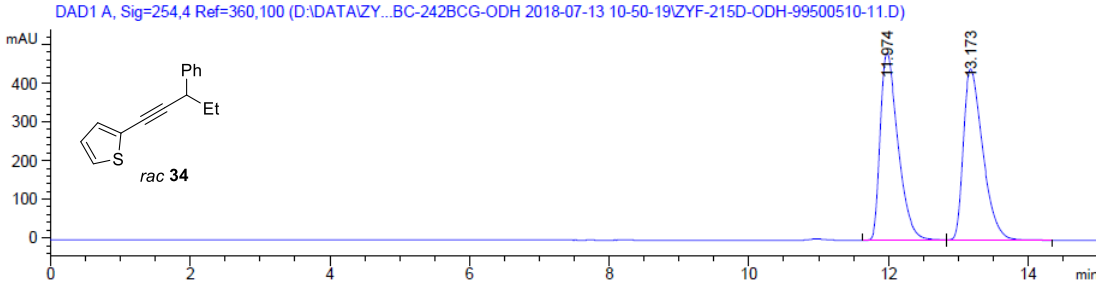
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.071	BB	0.5068	1.16266e4	336.71359	49.9456
2	32.322	BV	0.6515	1.16520e4	262.66809	50.0544
Totals :				2.32786e4	599.38168	



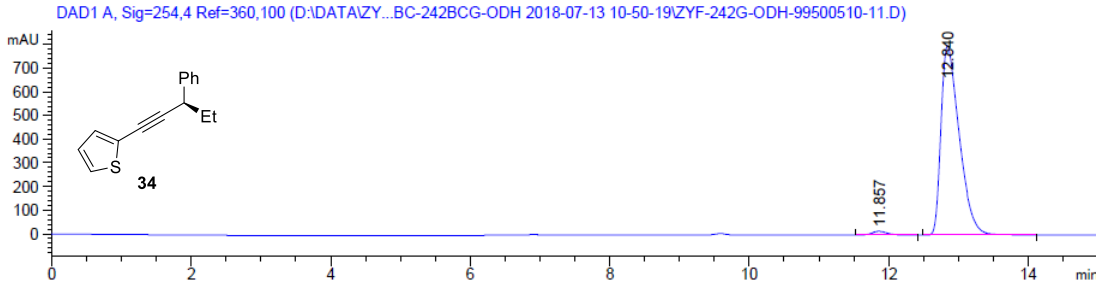
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.137	BB	0.4667	568.98859	14.99488	1.8931
2	32.455	VB	0.6689	2.94863e4	635.95776	98.1069
Totals :				3.00553e4	650.95265	



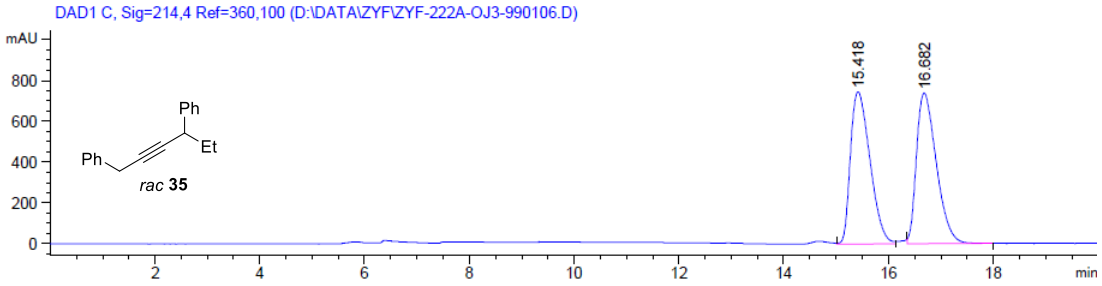
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.974	BV	0.2704	8578.38379	484.86606	49.9233
2	13.173	VB	0.2964	8604.74805	443.42398	50.0767
Totals :				1.71831e4	928.29004	



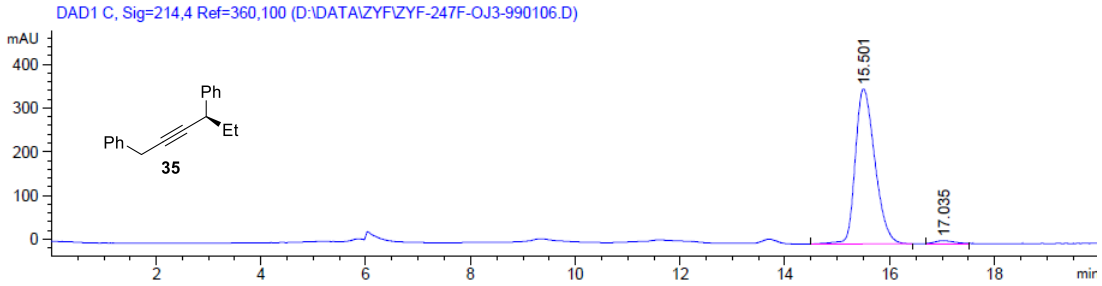
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.857	BB	0.2353	243.06520	15.81790	1.6421
2	12.840	BB	0.2802	1.45587e4	800.34314	98.3579
Totals :				1.48017e4	816.16104	



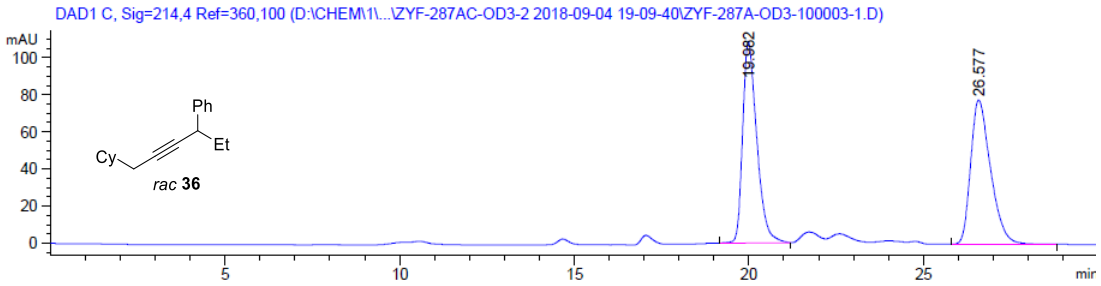
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.418	VV	0.3918	1.92898e4	745.61151	49.7638
2	16.682	FM R	0.4395	1.94729e4	738.36646	50.2362
Totals :				3.87627e4	1483.97797	



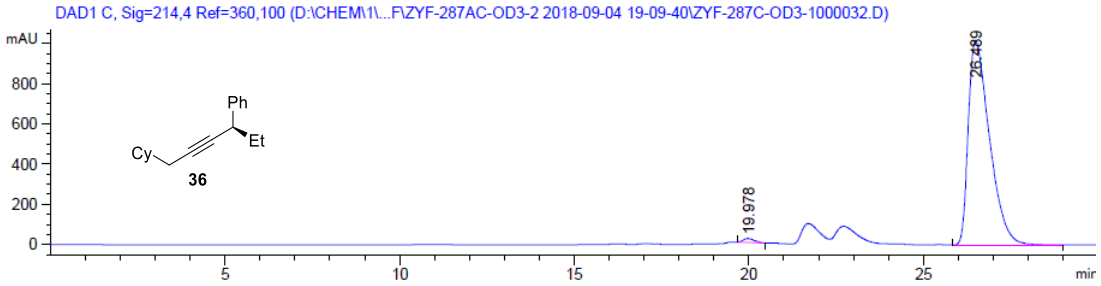
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.501	BB	0.4038	9210.27051	353.68369	97.9846
2	17.035	MM R	0.4483	189.44368	7.04302	2.0154
Totals :				9399.71419	360.72670	



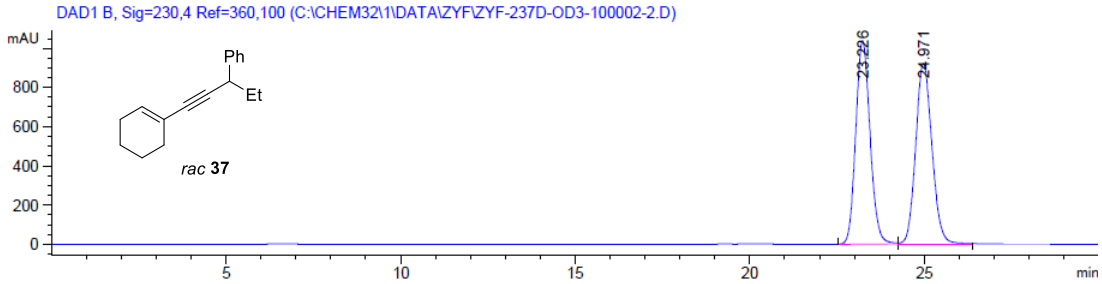
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.982	BB	0.4219	3054.34082	108.67959	49.7819
2	26.577	BB	0.5961	3081.09985	77.79543	50.2181
Totals :				6135.44067	186.47502	



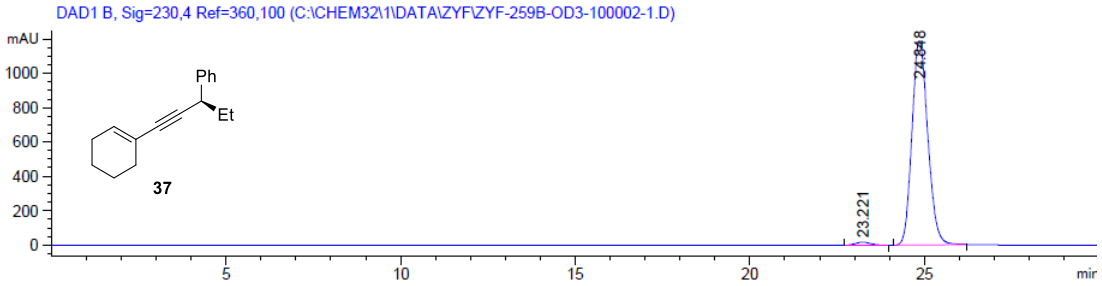
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.978	MM R	0.3700	446.15106	20.09427	1.0309
2	26.489	BB	0.6375	4.28300e4	1016.56030	98.9691
Totals :				4.32761e4	1036.65457	



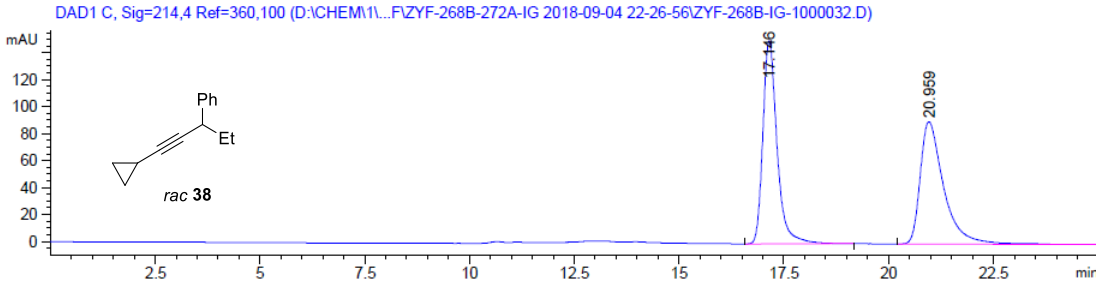
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.226	BV	0.4403	2.95642e4	1037.87671	49.8504
2	24.971	VB	0.5057	2.97416e4	918.63763	50.1496
Totals :				5.93058e4	1956.51434	



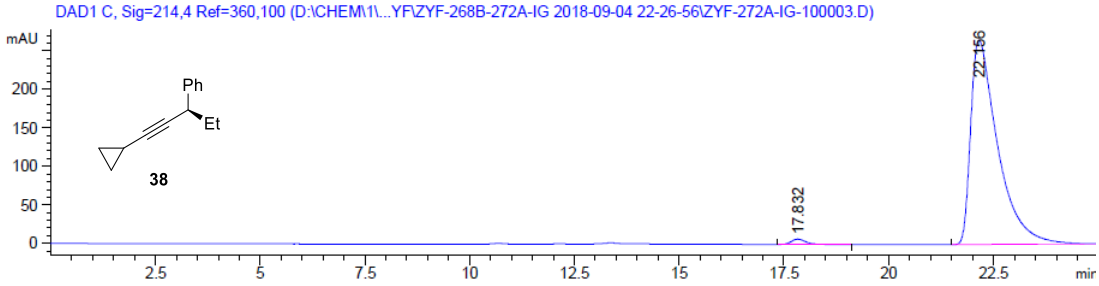
Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.221	BB	0.4468	512.88031	17.87194	1.3513
2	24.848	BB	0.4919	3.74429e4	1187.43506	98.6487
Totals :				3.79558e4	1205.30700	



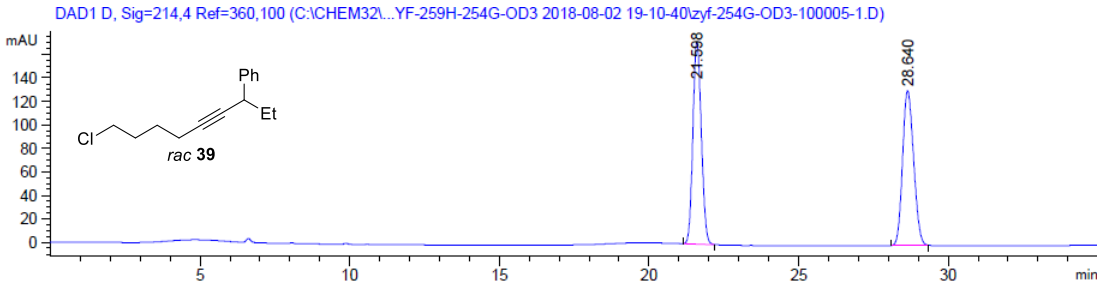
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.146	BB	0.3567	3547.48193	150.65921	50.0770
2	20.959	BBA	0.5768	3536.57666	90.71382	49.9230
Totals :				7084.05859	241.37303	



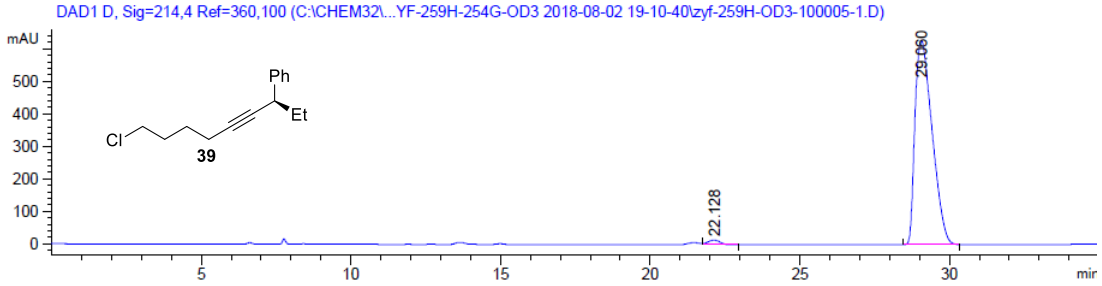
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.832	BB	0.3681	169.98508	6.97980	1.4048
2	22.156	BBA	0.6585	1.19301e4	265.38165	98.5952
Totals :				1.21000e4	272.36146	



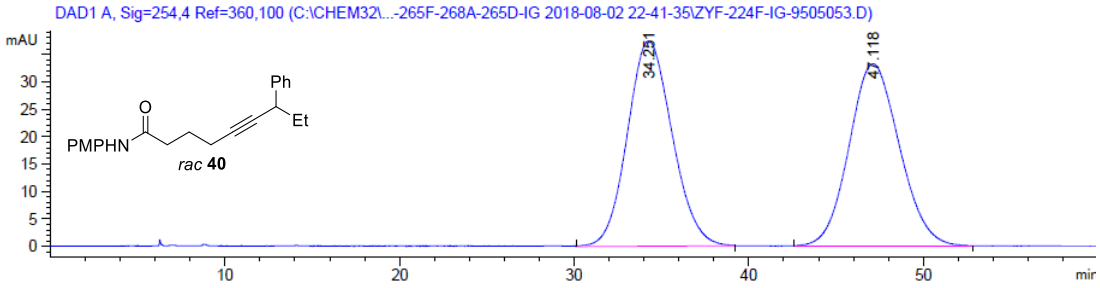
Signal 3: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.598	BB	0.3061	3367.44287	172.20221	49.8659
2	28.640	BB	0.4014	3385.55469	131.91463	50.1341
Totals :				6752.99756	304.11684	



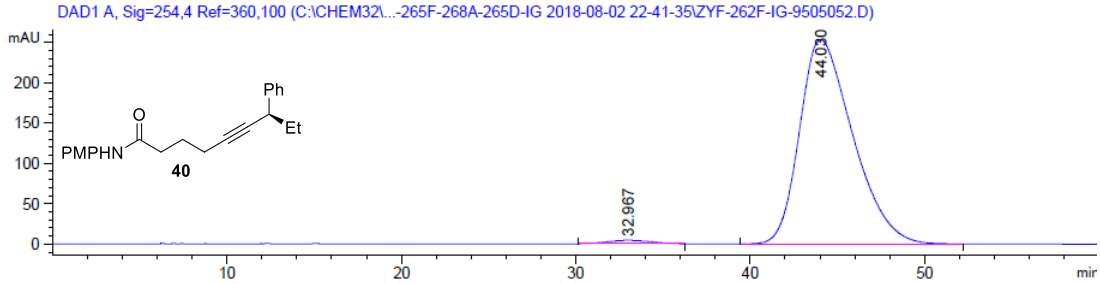
Signal 3: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.128	VB	0.4530	373.95935	13.26077	1.4734
2	29.060	BB	0.6296	2.50061e4	629.31921	98.5266
Totals :				2.53800e4	642.57998	



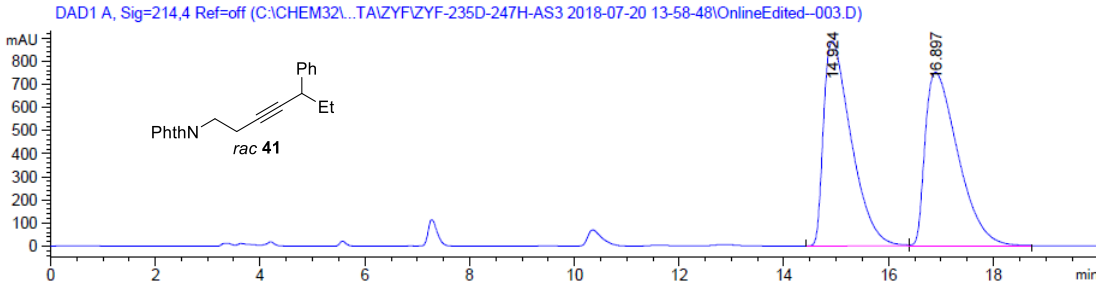
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.251	MM R	2.9729	6672.92529	37.40999	49.7914
2	47.118	MM R	3.3674	6728.82813	33.30407	50.2086
Totals :				1.34018e4	70.71405	



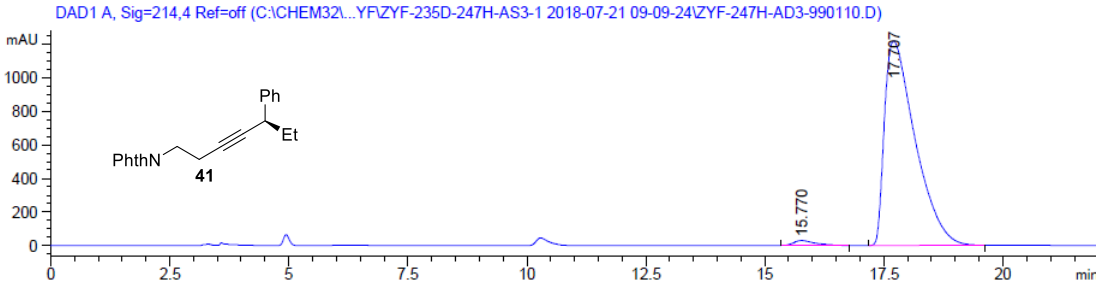
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.967	MM R	2.7888	696.95215	4.16515	1.2720
2	44.030	MM R	3.5534	5.40954e4	253.72458	98.7280
Totals :				5.47923e4	257.88973	



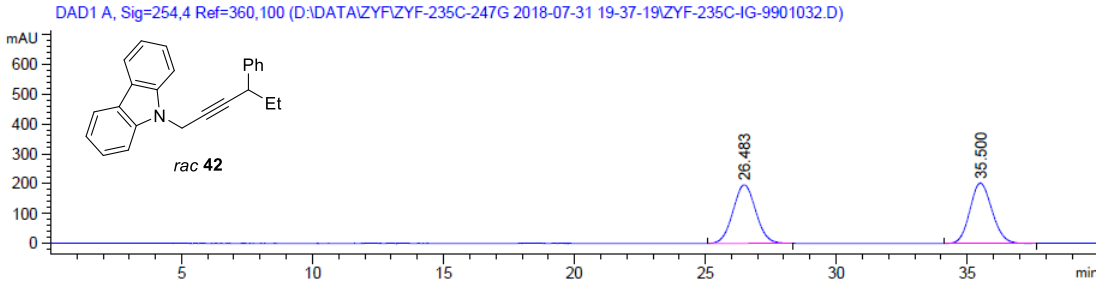
Signal 1: DAD1 A, Sig=214,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.924	BV	0.5589	3.24391e4	886.42572	49.8960
2	16.897	VB	0.6741	3.25744e4	750.87933	50.1040
Totals :				6.50135e4	1637.30505	



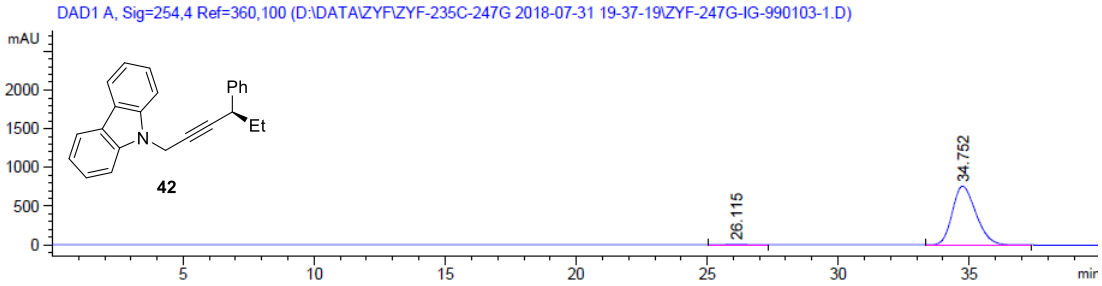
Signal 1: DAD1 A, Sig=214,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.770	BB	0.4580	926.71851	29.53647	1.6700
2	17.707	BB	0.6775	5.45639e4	1220.71472	98.3300
Totals :				5.54907e4	1250.25119	



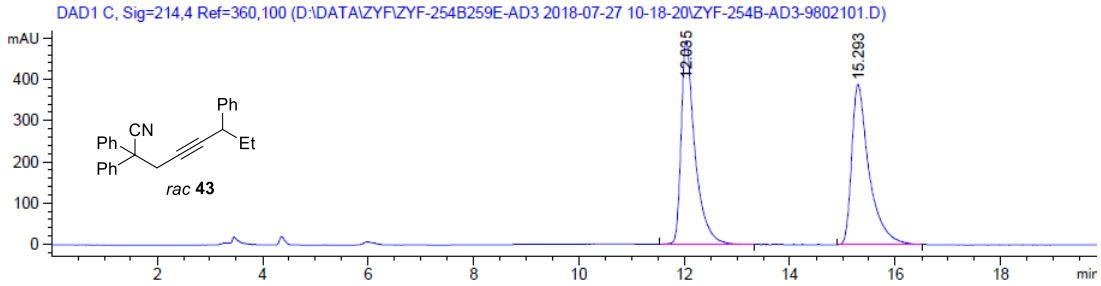
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.483	BB	0.8992	1.18750e4	196.46379	49.8476
2	35.500	BB	0.8719	1.19476e4	202.62947	50.1524
Totals :				2.38226e4	399.09326	



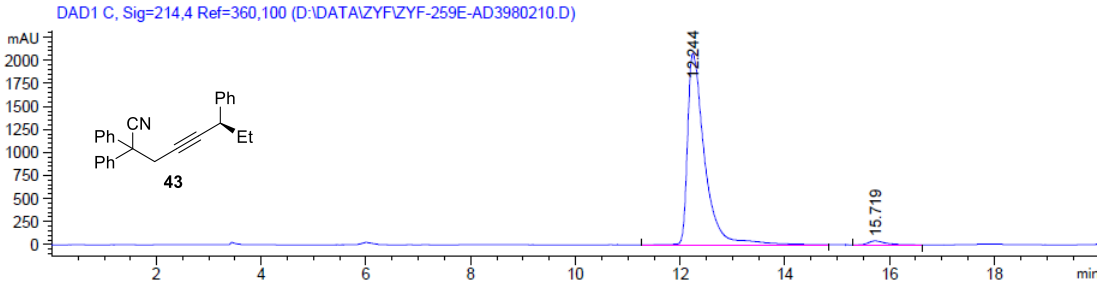
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.115	BB	0.7071	492.66336	8.29301	1.0248
2	34.752	BB	0.9350	4.75801e4	759.34204	98.9752
Totals :				4.80728e4	767.63505	



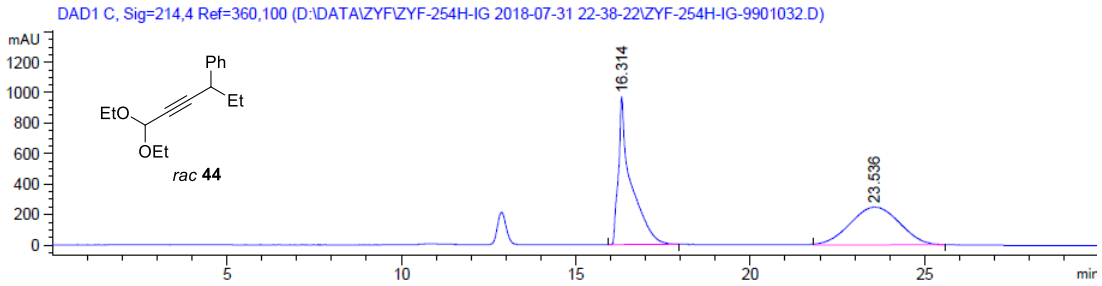
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.035	BB	0.2658	8966.57813	493.94589	50.0661
2	15.293	BV	0.3378	8942.89648	389.58029	49.9339
Totals :				1.79095e4	883.52618	



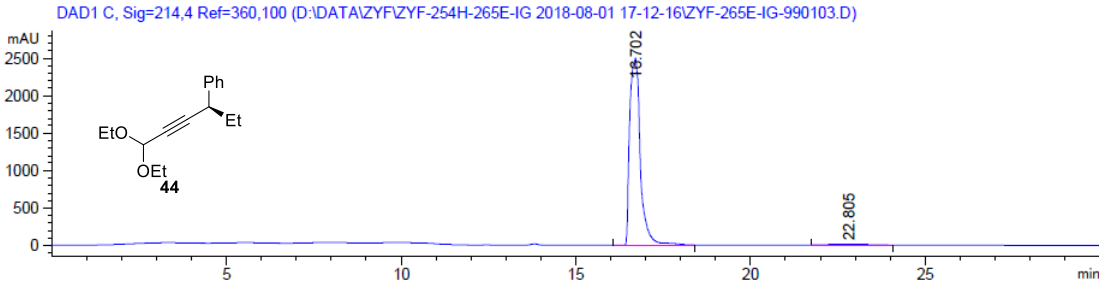
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.244	VV	0.3077	4.73083e4	2077.49316	97.8243
2	15.719	VV	0.3494	1052.15979	43.94050	2.1757
Totals :				4.83604e4	2121.43367	



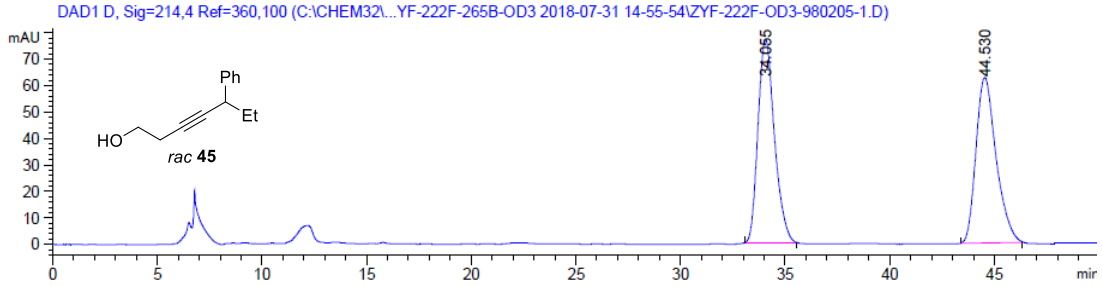
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.314	BV	0.3167	2.45554e4	972.11029	49.9843
2	23.536	MM R	1.6456	2.45708e4	248.84756	50.0157
Totals :				4.91262e4	1220.95786	



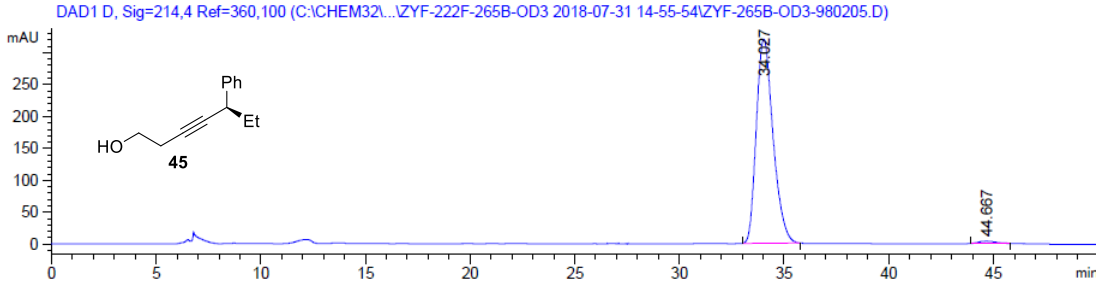
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.702	BB	0.2596	5.32252e4	2507.62939	98.0054
2	22.805	MM R	1.4143	1083.23572	12.76550	1.9946
Totals :				5.43084e4	2520.39490	



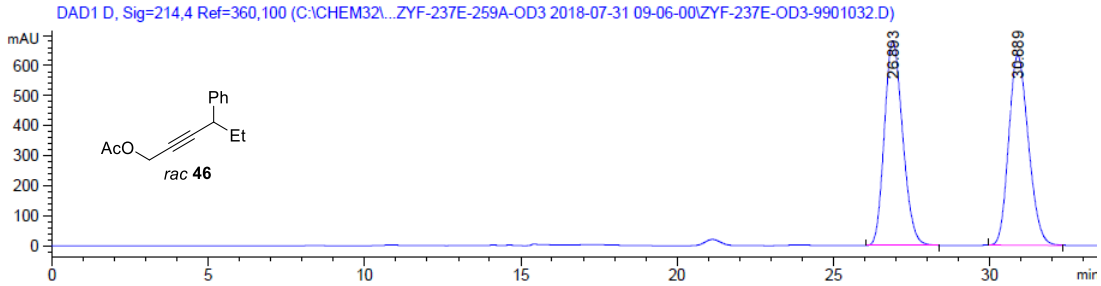
Signal 4: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.055	BB	0.8362	4217.30127	76.85201	50.1884
2	44.530	BB	1.0097	4185.63330	62.47102	49.8116
Totals :				8402.93457	139.32303	



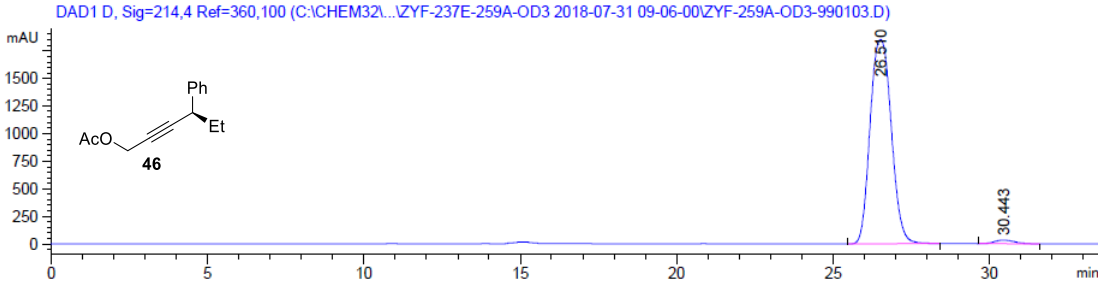
Signal 4: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.027	BB	0.8641	1.78390e4	320.13788	98.8404
2	44.667	BB	0.7036	209.29718	3.54072	1.1596
Totals :				1.80483e4	323.67860	



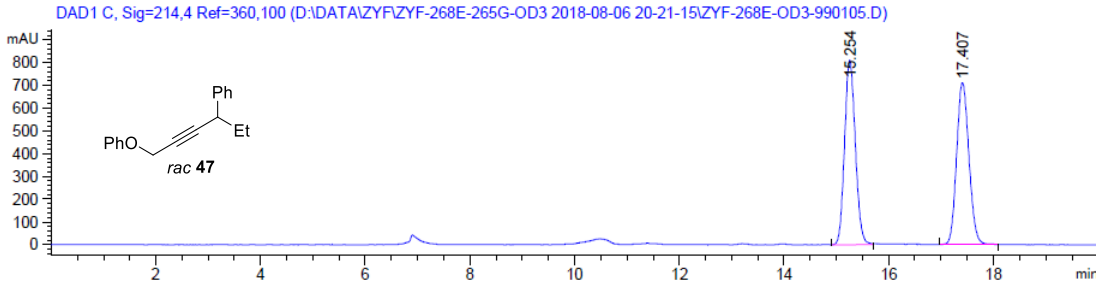
Signal 4: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.893	BB	0.6337	2.77644e4	680.97668	50.0291
2	30.889	BB	0.6817	2.77320e4	632.25671	49.9709
Totals :				5.54964e4	1313.23340	



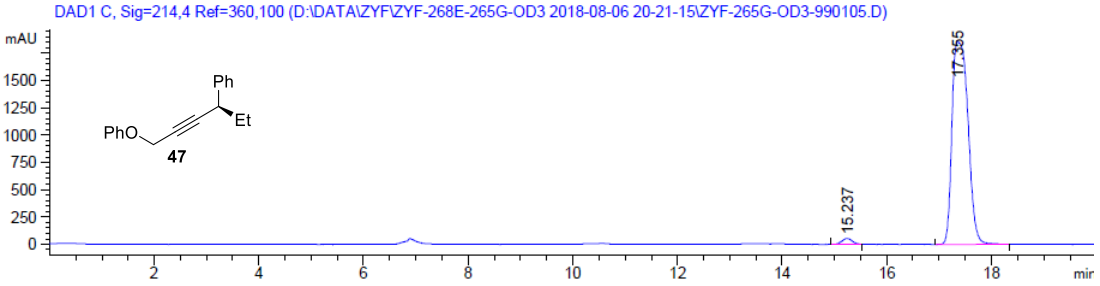
Signal 4: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.510	BB	0.7480	8.70670e4	1853.46350	98.3176
2	30.443	BB	0.6882	1489.87512	33.54101	1.6824
Totals :				8.85569e4	1887.00451	



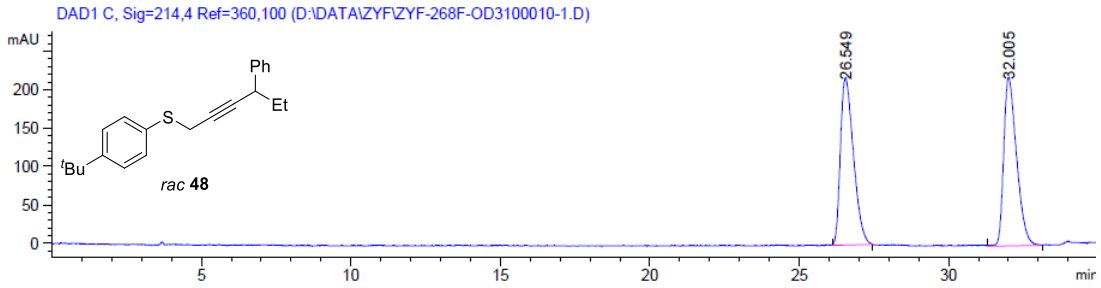
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.254	BV	0.2244	1.15893e4	812.61871	49.8796
2	17.407	VV	0.2507	1.16453e4	712.29321	50.1204
Totals :				2.32346e4	1524.91193	



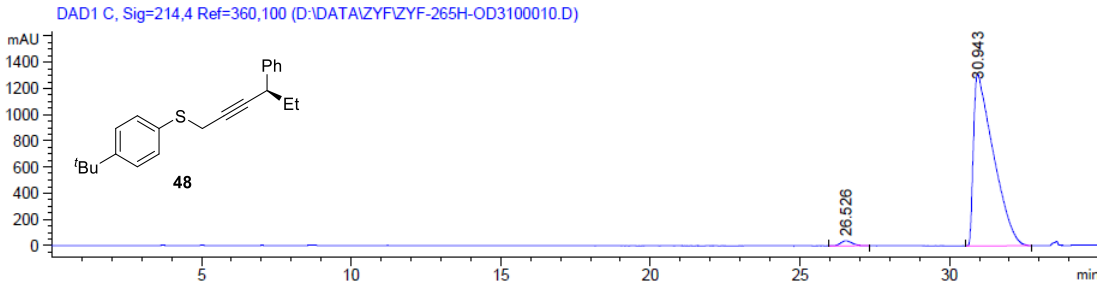
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.237	VV	0.2105	773.69470	54.88098	1.9216
2	17.355	BV	0.2860	3.94884e4	1872.67419	98.0784
Totals :				4.02621e4	1927.55518	



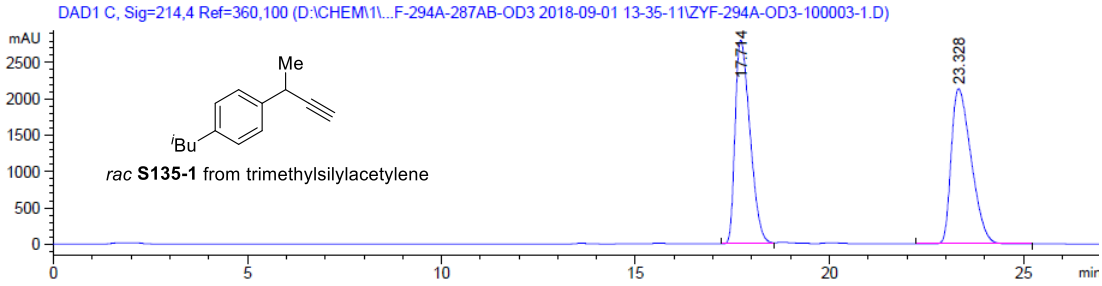
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.549	MM R	0.5038	6576.79785	217.57635	50.1743
2	32.005	MM R	0.4955	6531.11377	219.66495	49.8257
Totals :				1.31079e4	437.24130	



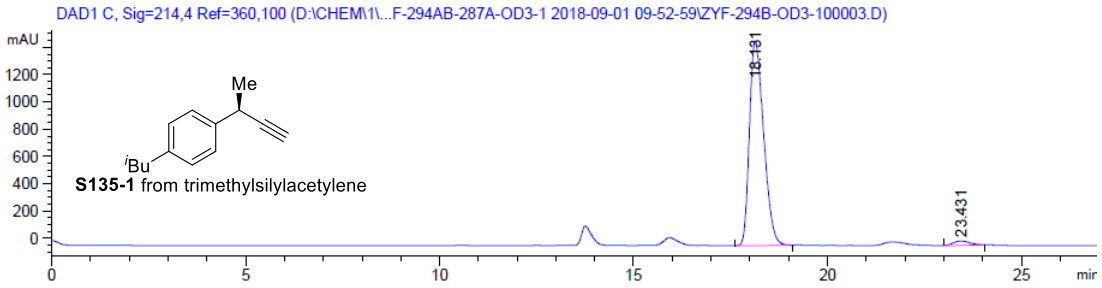
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.526	BB	0.3374	1079.75671	38.95827	1.7462
2	30.943	VV	0.6010	6.07539e4	1310.22034	98.2538
Totals :				6.18336e4	1349.17860	



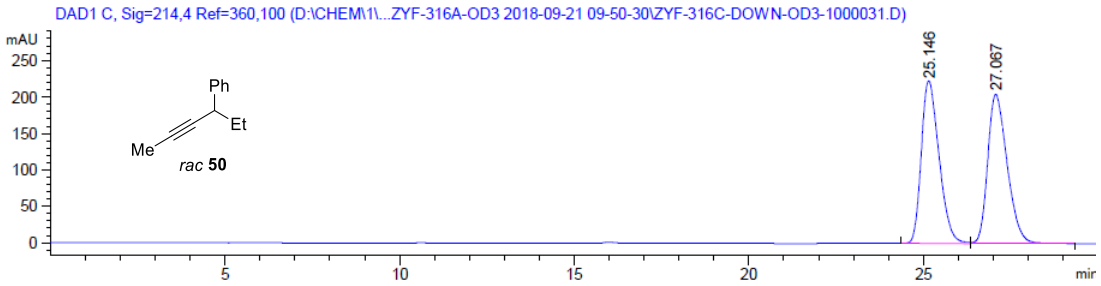
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.714	BV	0.4184	7.49801e4	2799.94263	49.5595
2	23.328	BB	0.5570	7.63130e4	2135.12793	50.4405
Totals :				1.51293e5	4935.07056	



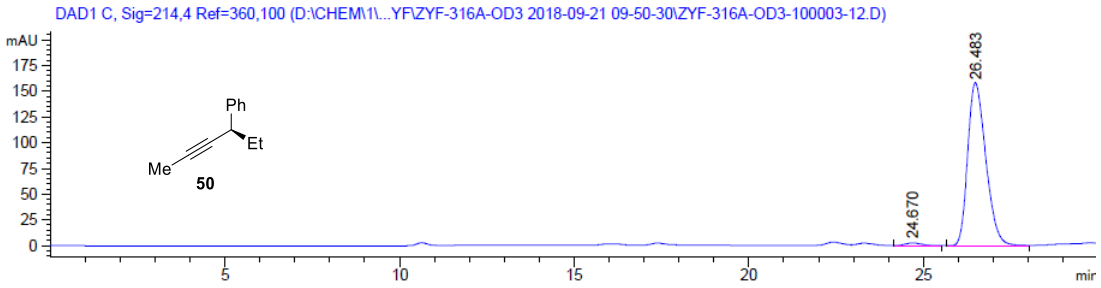
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.131	BB	0.3964	3.80441e4	1497.36194	97.4156
2	23.431	MM R	0.5122	1009.30011	32.84372	2.5844
Totals :				3.90534e4	1530.20565	



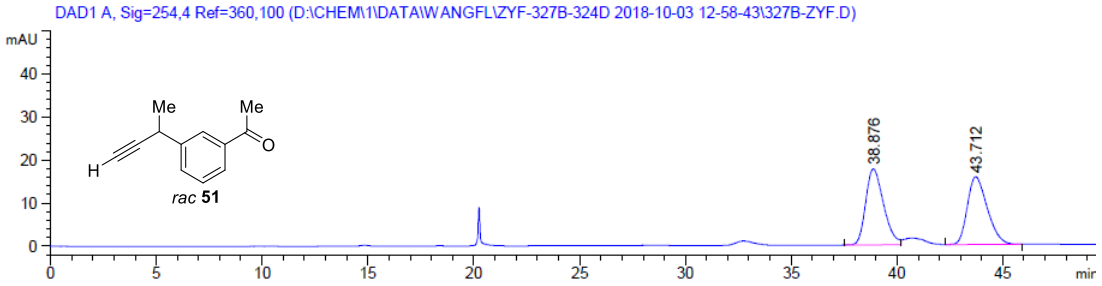
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.146	BV	0.5422	7884.64355	223.16814	49.9327
2	27.067	VB	0.5966	7905.88721	204.71608	50.0673
Totals :				1.57905e4	427.88422	



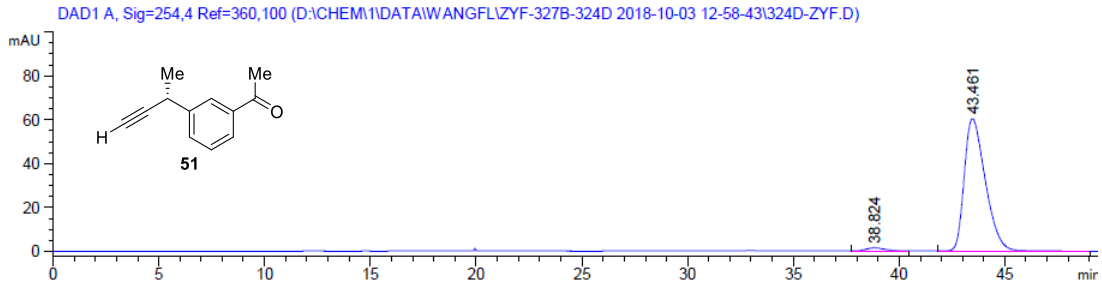
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.670	BB	0.4709	80.24489	2.52385	1.3903
2	26.483	BB	0.5550	5691.55957	158.49454	98.6097
Totals :				5771.80446	161.01839	



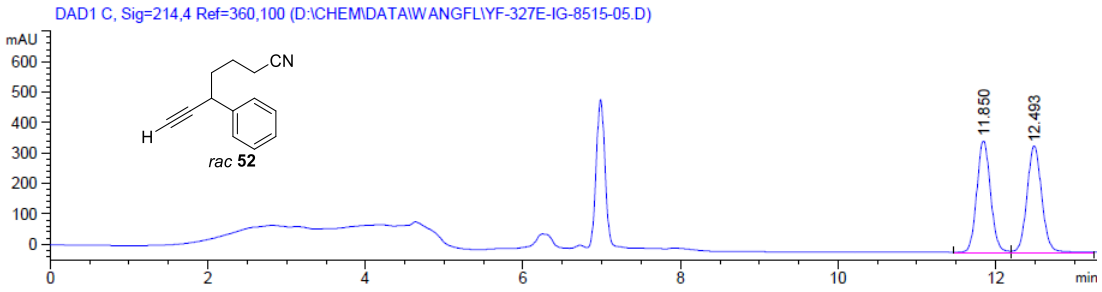
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.876	BV	0.9034	1031.06531	17.60242	50.0711
2	43.712	VB	1.0167	1028.13843	15.68589	49.9289
Totals :				2059.20374	33.28831	



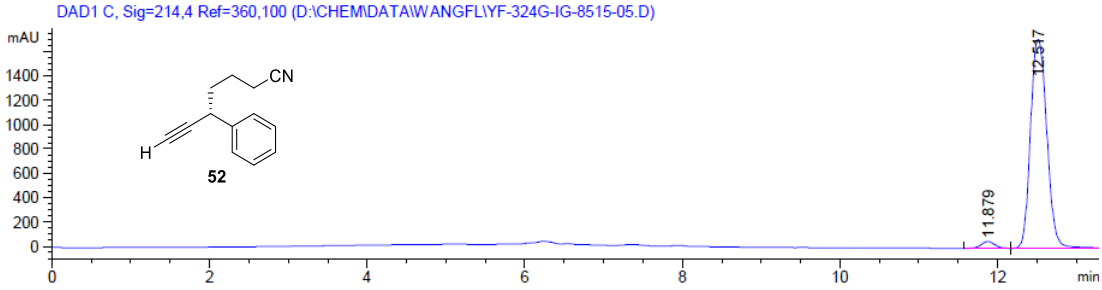
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.824	BB	0.8935	84.85453	1.44420	2.0043
2	43.461	BB	1.0603	4148.79688	60.17645	97.9957
Totals :				4233.65141	61.62065	



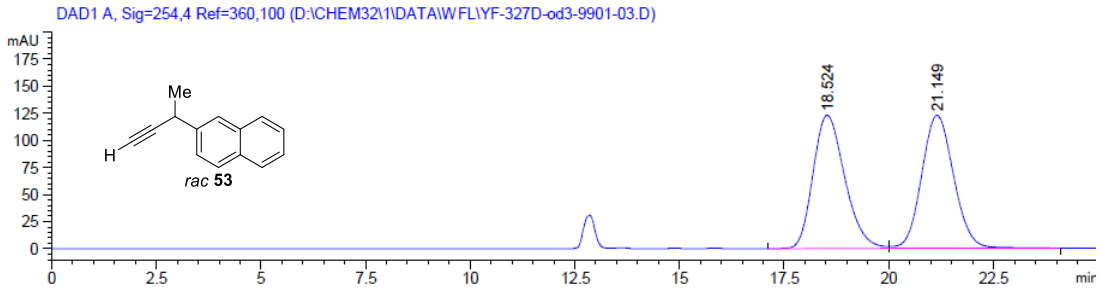
Signal 2: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.850	BV	0.1865	4421.74561	367.10599	49.3257
2	12.493	VV	0.1997	4542.64746	349.33694	50.6743
Totals :				8964.39307	716.44293	



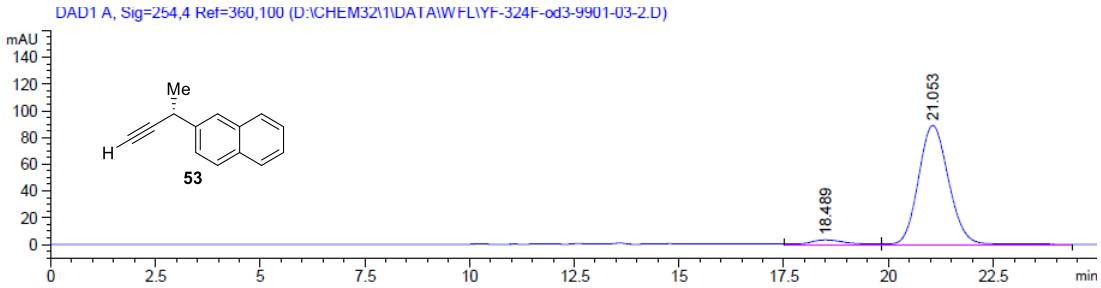
Signal 2: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.879	BV	0.1801	651.14355	55.81726	2.5655
2	12.517	VV	0.2302	2.47293e4	1714.79480	97.4345
Totals :				2.53805e4	1770.61206	



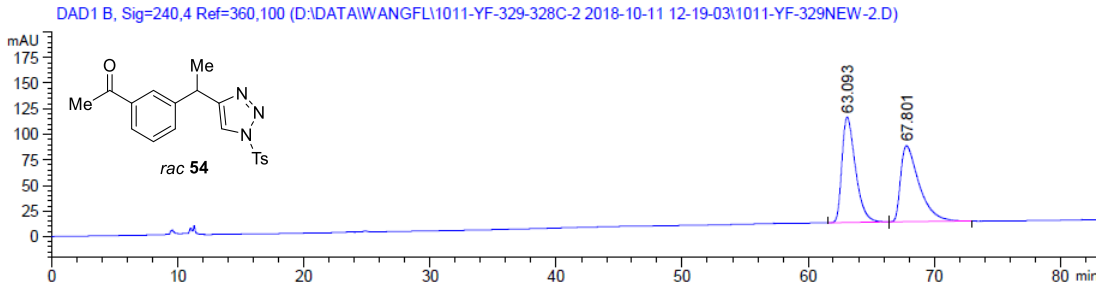
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.524	BV	0.8232	6487.49854	123.03183	49.7340
2	21.149	VB	0.8227	6556.90332	122.83845	50.2660
Totals :				1.30444e4	245.87028	



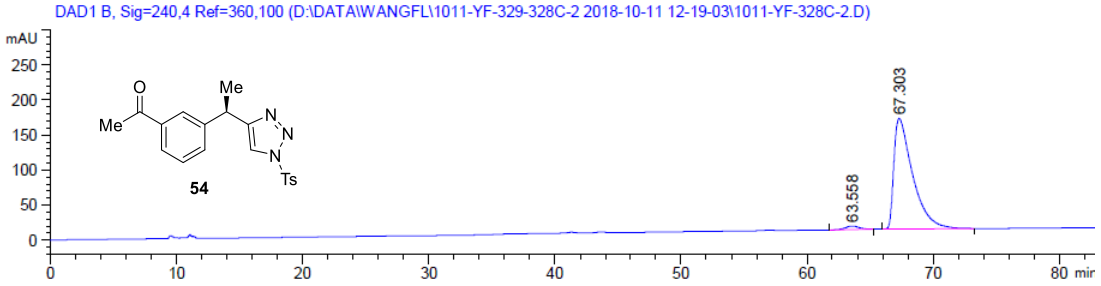
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.489	BV	0.7350	165.46567	3.26630	3.6071
2	21.053	VB	0.7714	4421.75586	89.03152	96.3929
Totals :				4587.22153	92.29782	



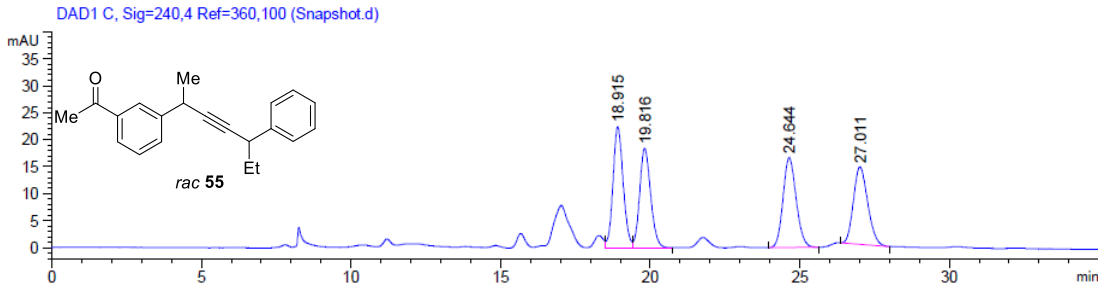
Signal 2: DAD1 B, Sig=240,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	63.093	BB	1.1233	7697.03076	103.05814	50.3305
2	67.801	BB	1.4719	7595.93750	74.35125	49.6695
Totals :				1.52930e4	177.40939	



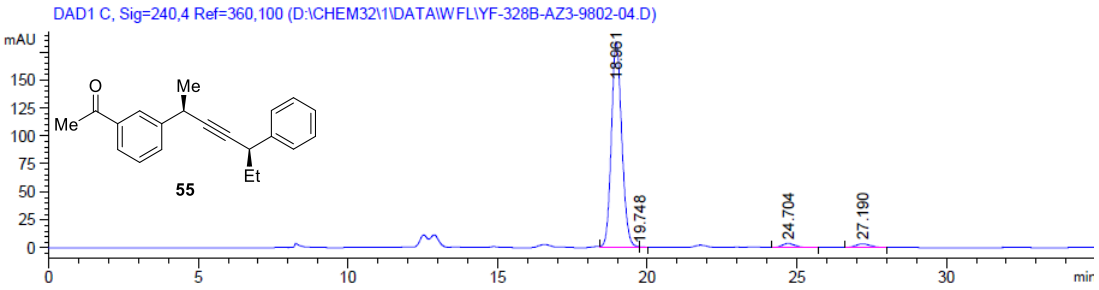
Signal 2: DAD1 B, Sig=240,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	63.558	BB	0.9025	379.83737	5.04419	2.2728
2	67.303	BB	1.4738	1.63328e4	157.75995	97.7272
Totals :				1.67126e4	162.80414	



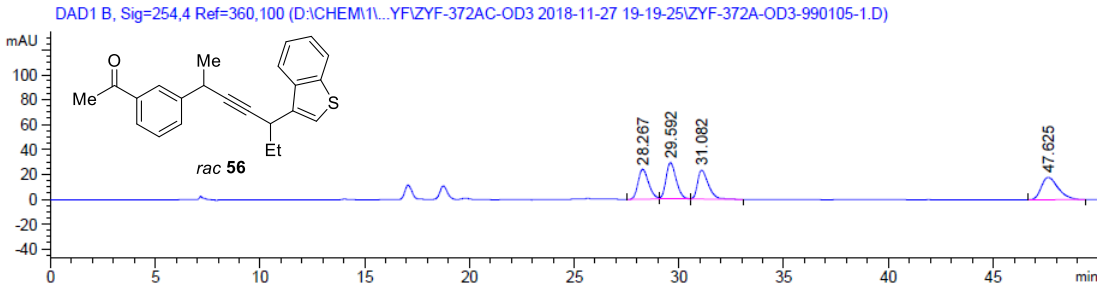
Signal 3: DAD1 C, Sig=240,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.915	VV	0.3614	529.38959	22.43040	26.6730
2	19.816	VB	0.3901	471.39404	18.44934	23.7510
3	24.644	BB	0.4656	507.72324	16.65811	25.5814
4	27.011	BB	0.4987	476.23013	14.36609	23.9946
Totals :				1984.73700	71.90393	



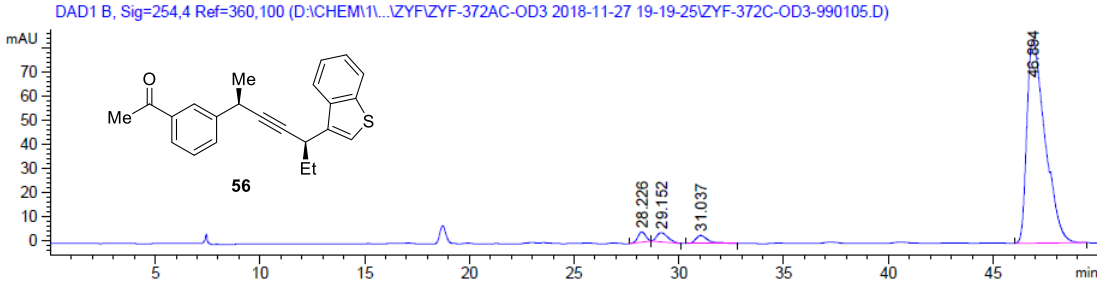
Signal 3: DAD1 C, Sig=240,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.961	MM R	0.4005	4415.10303	183.72699	95.0861
2	19.748	MM R	0.1342	8.07137	7.39303e-1	0.1738
3	24.704	BB	0.4383	109.25283	3.59805	2.3529
4	27.190	BB	0.4711	110.84118	3.34058	2.3871
Totals :				4643.26840	191.40492	



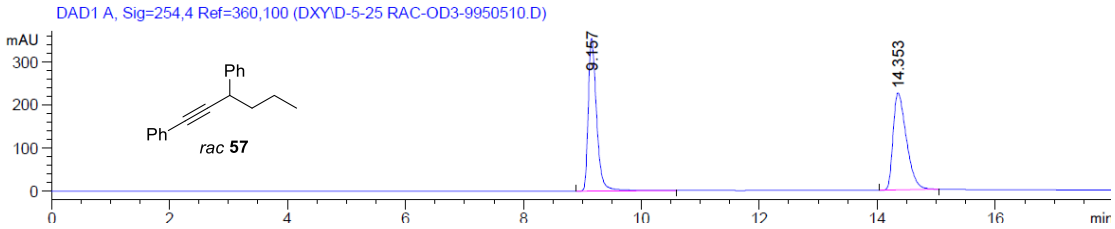
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.267	BV	0.5480	849.17456	24.04538	23.1842
2	29.592	VB	0.5206	983.61786	29.23291	26.8548
3	31.082	BB	0.5536	838.41919	23.20208	22.8905
4	47.625	BB	0.8495	991.52002	17.91926	27.0705
Totals :				3662.73163	94.39963	



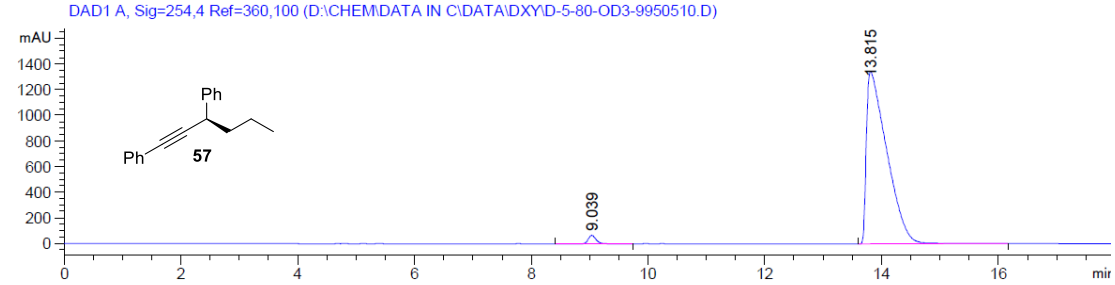
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.226	BB	0.4288	109.24695	4.18188	1.9969
2	29.152	BB	0.5614	135.96524	3.72877	2.4853
3	31.037	BB	0.6233	139.98323	3.33750	2.5587
4	46.894	MM R	1.0052	5085.59180	84.32143	92.9590
Totals :				5470.78722	95.56959	



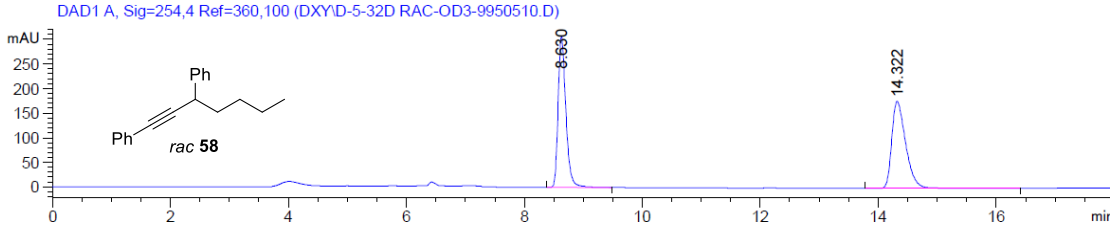
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.157	MM R	0.1651	3509.30347	354.17551	49.9244
2	14.353	MM R	0.2605	3519.92896	225.17508	50.0756
Totals :				7029.23242	579.35059	



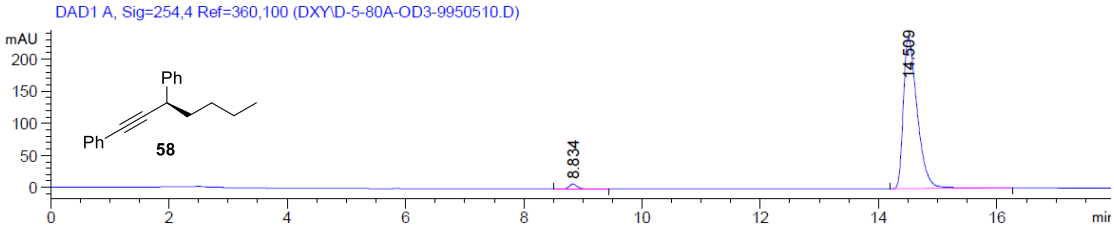
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.039	VB R	0.1448	642.49323	65.93994	1.9333
2	13.815	BB	0.3682	3.25905e4	1347.44873	98.0667
Totals :				3.32329e4	1413.38867	



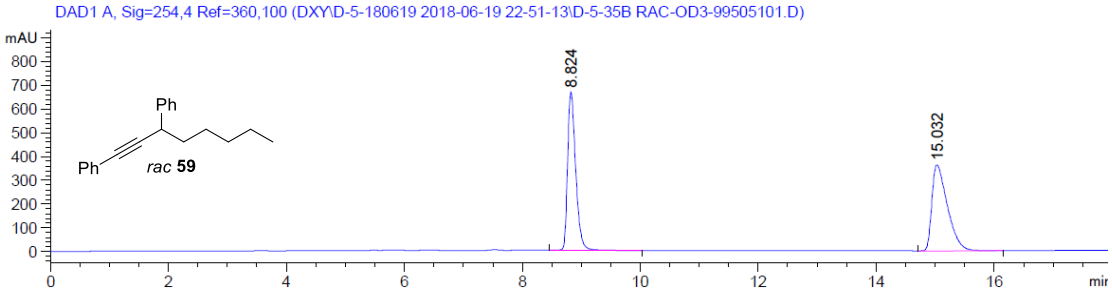
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.630	BV	0.1405	2800.01538	306.65811	49.2534
2	14.322	BB	0.2508	2884.90625	176.43123	50.7466
Totals :				5684.92163	483.08934	



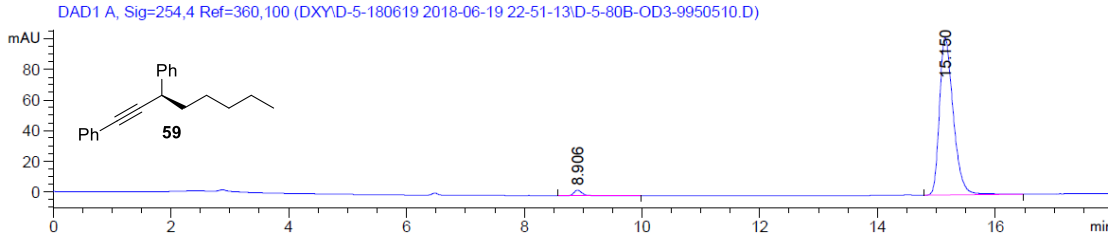
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.834	BV	0.1421	71.05782	7.67225	1.8168
2	14.509	BB	0.2480	3840.02075	235.75974	98.1832
Totals :				3911.07857	243.43198	



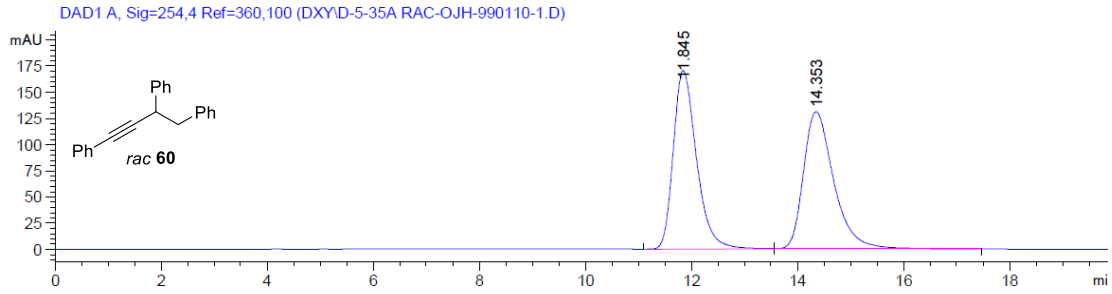
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.824	VV	0.1480	6407.71045	667.49701	49.0971
2	15.032	BV	0.2782	6643.39746	361.78152	50.9029
Totals :				1.30511e4	1029.27853	



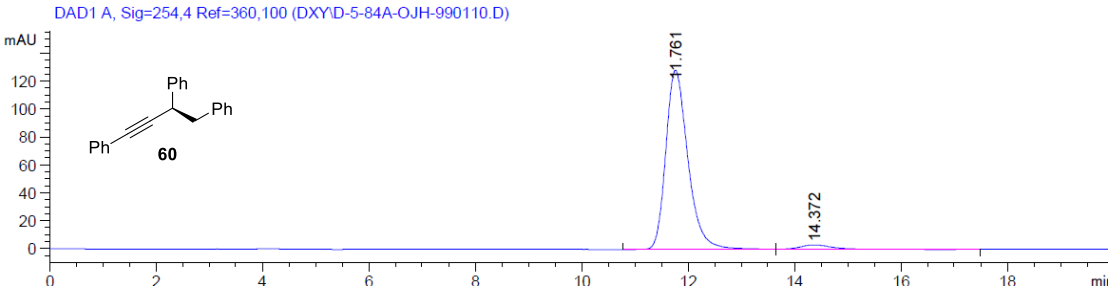
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.906	BB	0.1460	34.94700	3.63885	2.0489
2	15.150	BB	0.2491	1670.71729	103.07497	97.9511
Totals :				1705.66428	106.71382	



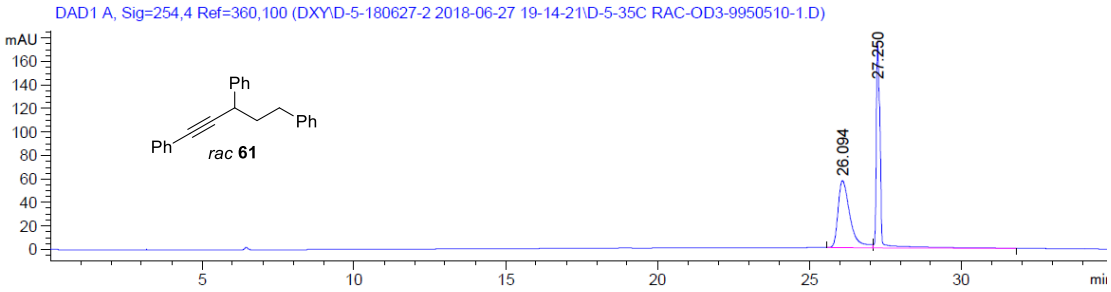
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.845	BV	0.4654	5199.83887	170.69756	49.8204
2	14.353	VB	0.6053	5237.32715	131.31052	50.1796
Totals :				1.04372e4	302.00807	



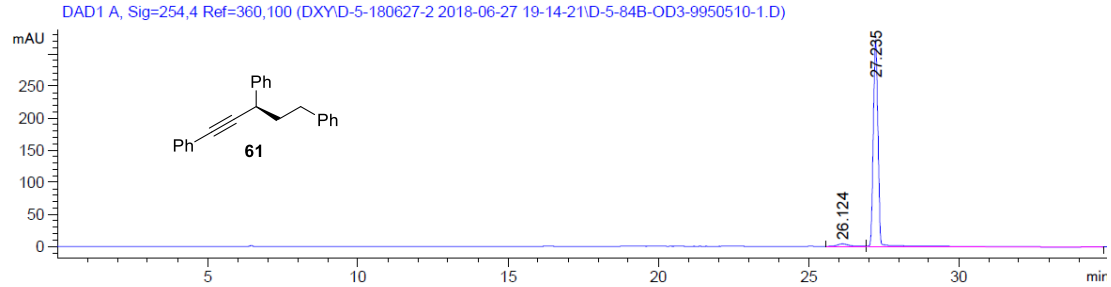
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.761	BV	0.4419	3719.47998	128.41241	96.1026
2	14.372	VB	0.7014	150.84100	3.16855	3.8974
Totals :				3870.32098	131.58096	



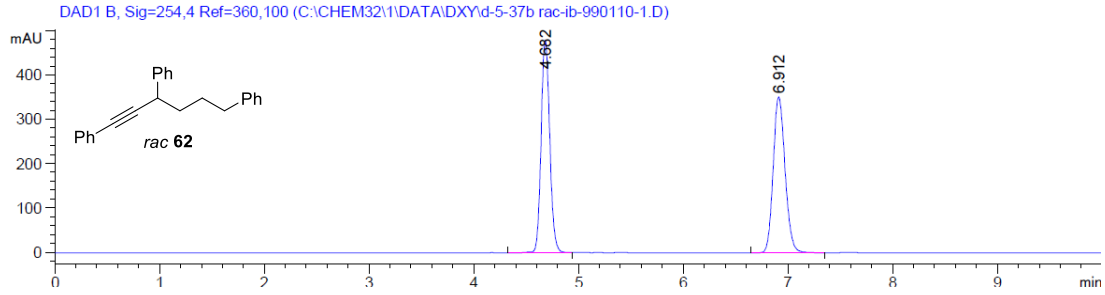
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.094	BV	0.4107	1549.11328	57.07290	49.8971
2	27.250	VBA	0.1273	1555.50476	175.67784	50.1029
Totals :				3104.61804	232.75074	



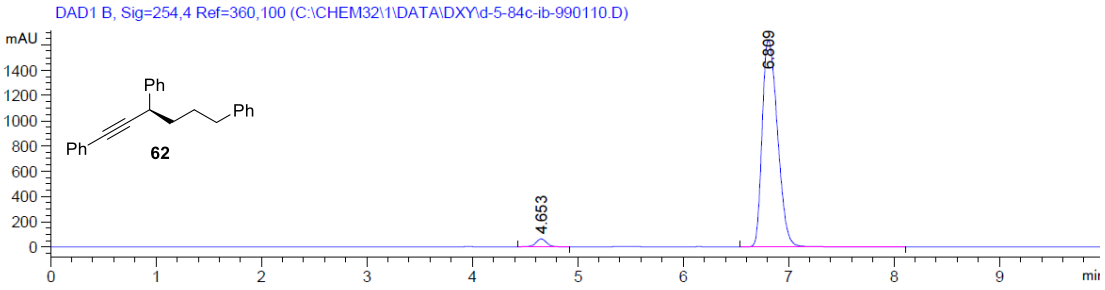
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.124	BV	0.4026	103.57114	3.89071	2.7995
2	27.235	VBA	0.1764	3596.06128	321.63211	97.2005
Totals :				3699.63242	325.52282	



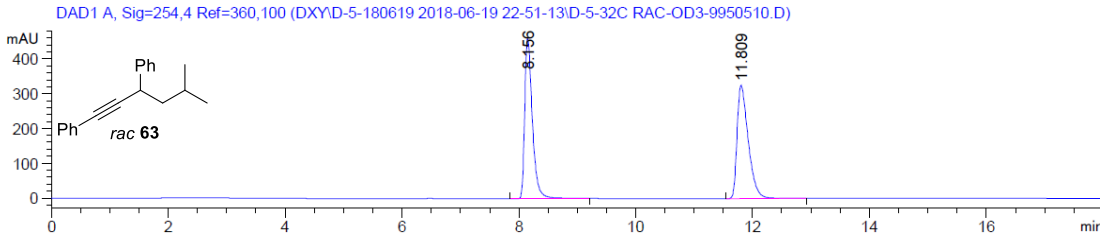
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.682	BV	0.0910	2748.42749	478.47278	49.6870
2	6.912	VV	0.1246	2783.05933	350.52350	50.3130
Totals :				5531.48682	828.99628	



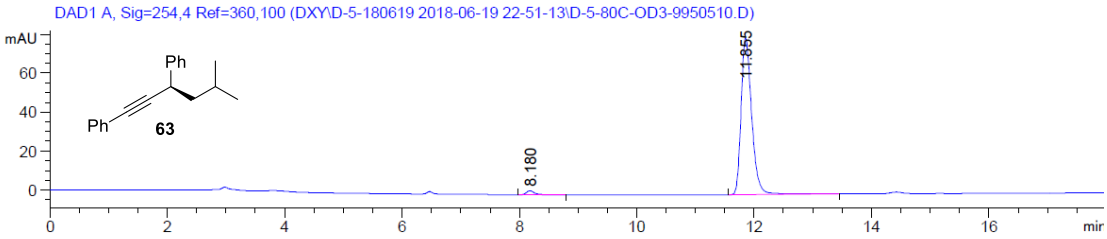
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.653	VB	0.1123	453.27383	62.70433	2.6662
2	6.809	BB	0.1621	1.65474e4	1634.02283	97.3338
Totals :				1.70007e4	1696.72715	



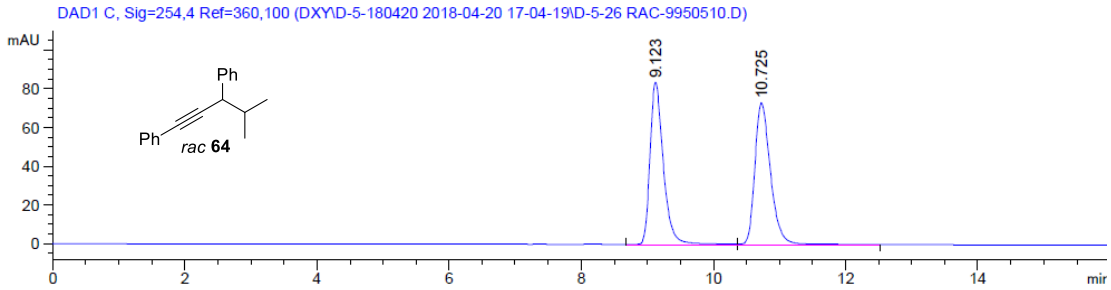
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.156	BV	0.1390	4228.69922	460.92819	49.3894
2	11.809	BV	0.2013	4333.25830	325.59735	50.6106
Totals :				8561.95752	786.52554	



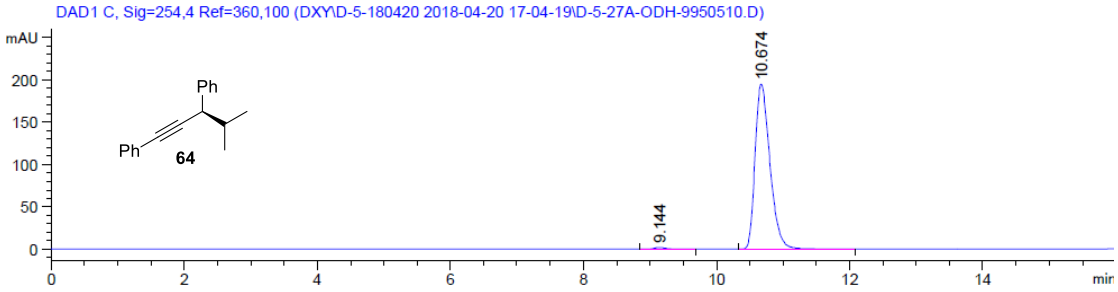
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.180	BV	0.1464	20.03817	2.08067	1.9417
2	11.855	BB	0.1929	1011.95392	80.34559	98.0583
Totals :				1031.99209	82.42625	



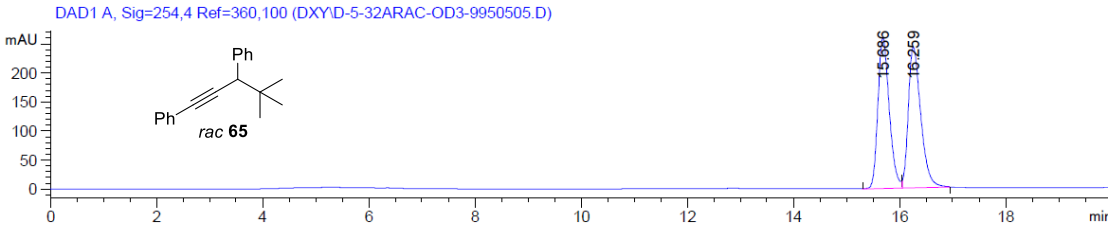
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.123	BV	0.2116	1172.66895	83.61730	49.4600
2	10.725	VB	0.2492	1198.27429	73.10712	50.5400
Totals :				2370.94324	156.72442	



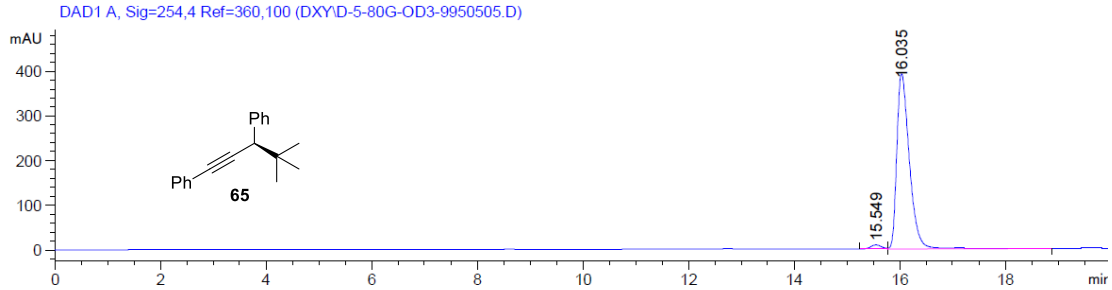
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.144	BB	0.2064	26.47406	1.97528	0.8670
2	10.674	BB	0.2392	3027.19824	194.92703	99.1330
Totals :				3053.67230	196.90231	



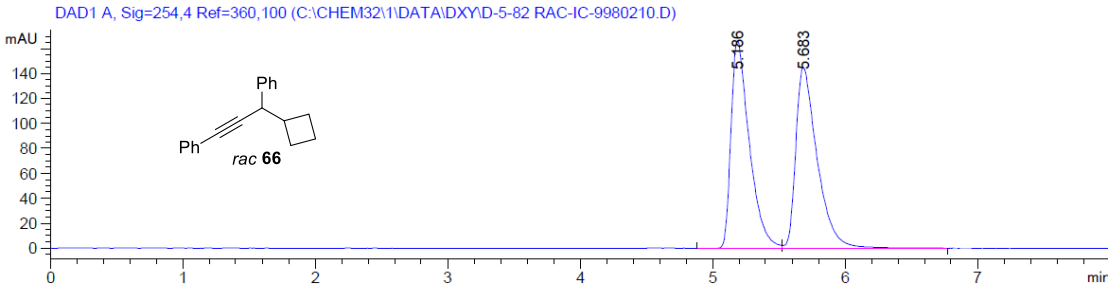
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.686	MF R	0.2487	3874.16528	259.59927	49.3543
2	16.259	FM R	0.2724	3975.53979	243.22359	50.6457
Totals :				7849.70508	502.82286	



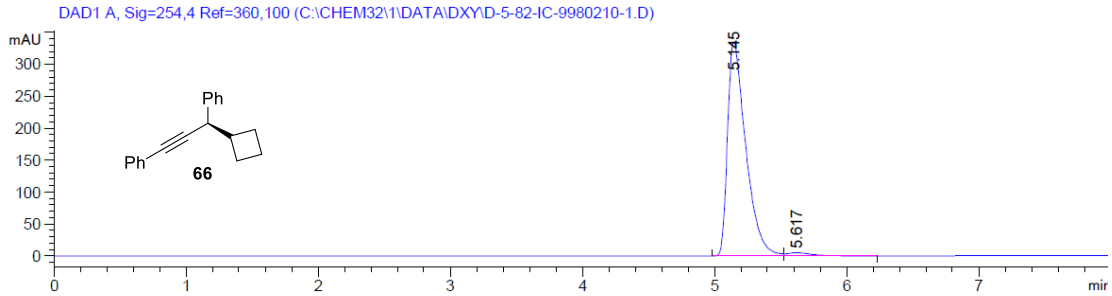
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.549	BV	0.2203	132.32033	9.39441	2.0006
2	16.035	VB	0.2506	6481.84570	392.64679	97.9994
Totals :				6614.16603	402.04120	



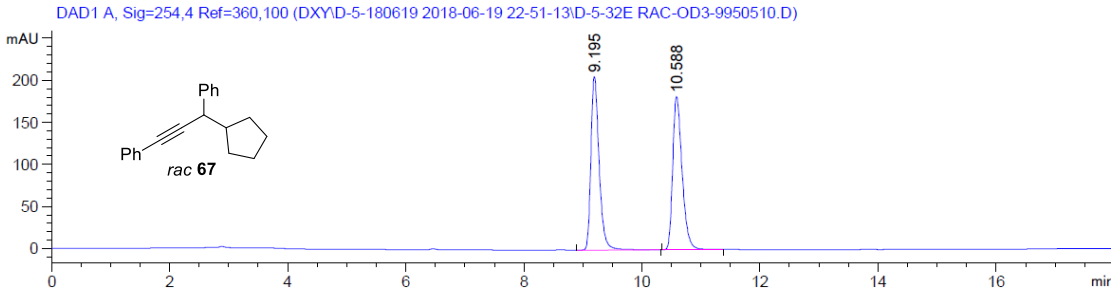
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.186	BV	0.1437	1597.34106	166.84236	49.4560
2	5.683	VB	0.1693	1632.48413	145.08865	50.5440
Totals :				3229.82520	311.93102	



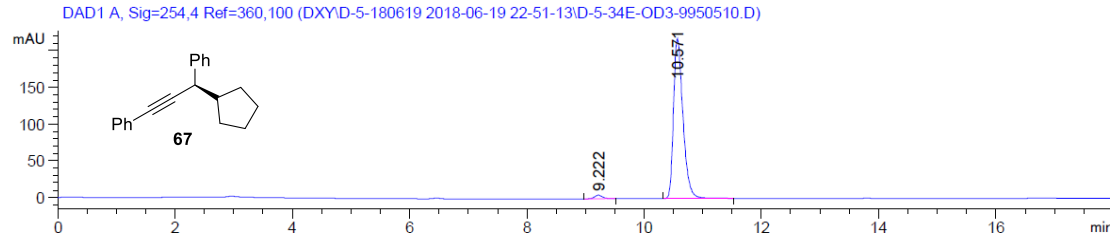
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.145	BV	0.1437	3211.51978	335.30856	97.8519
2	5.617	VB	0.1825	70.49967	5.39355	2.1481



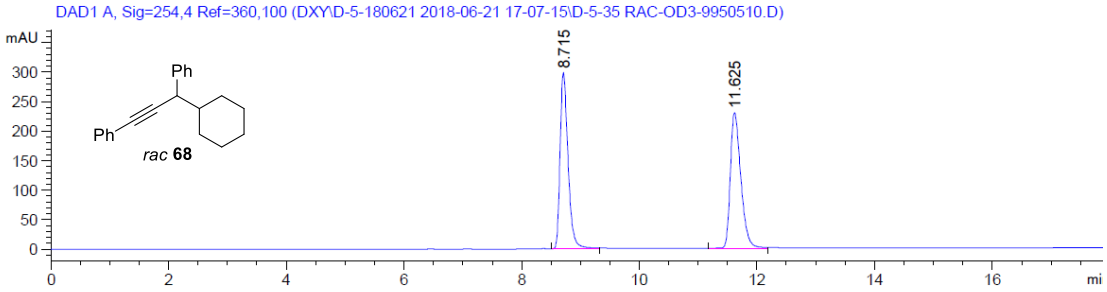
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.195	VB	0.1489	1996.21326	206.22379	49.5912
2	10.588	BV	0.1700	2029.12329	182.10483	50.4088
Totals :				4025.33655	388.32861	



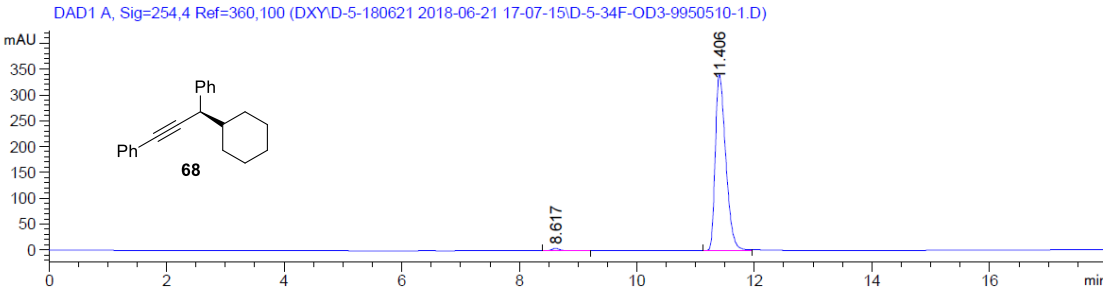
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.222	MM R	0.1590	45.31701	4.75155	1.8313
2	10.571	MM R	0.1855	2429.30908	218.25255	98.1687
Totals :				2474.62609	223.00410	



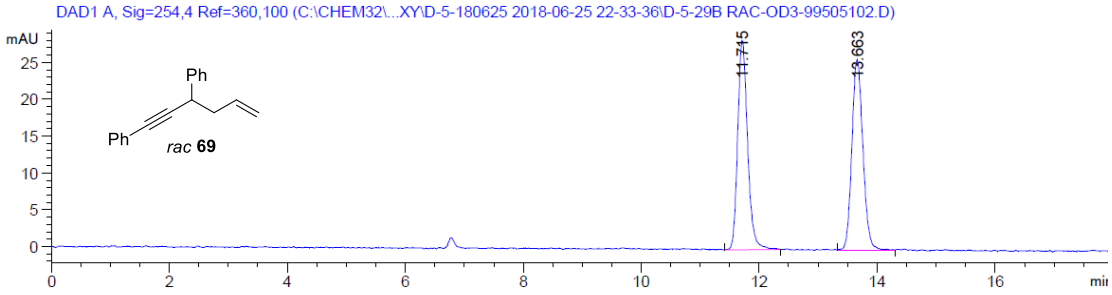
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.715	BV	0.1438	2810.19873	298.69604	49.5390
2	11.625	BV	0.1914	2862.50659	229.60918	50.4610
Totals :				5672.70532	528.30522	



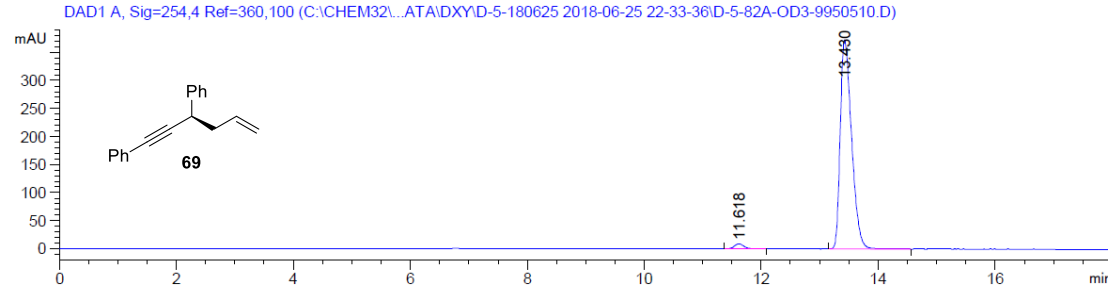
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.617	BB	0.1471	43.20060	4.53612	1.0121
2	11.406	BV	0.1908	4225.07422	340.38824	98.9879
Totals :				4268.27482	344.92436	



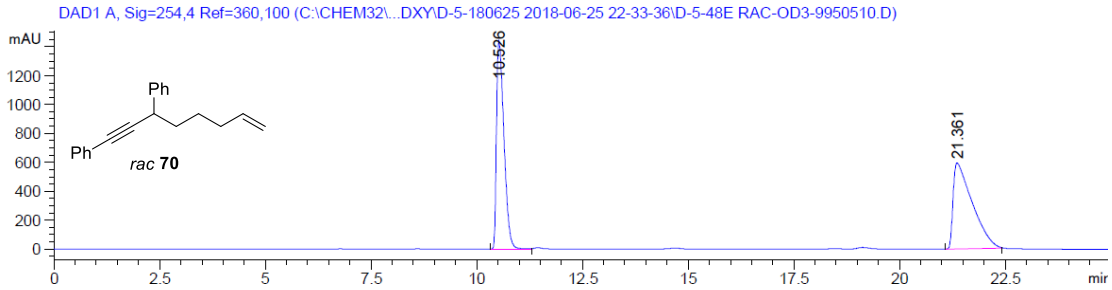
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.715	BB	0.1782	332.11545	28.44024	49.7807
2	13.663	BB	0.2013	335.04193	25.82912	50.2193
Totals :				667.15738	54.26936	



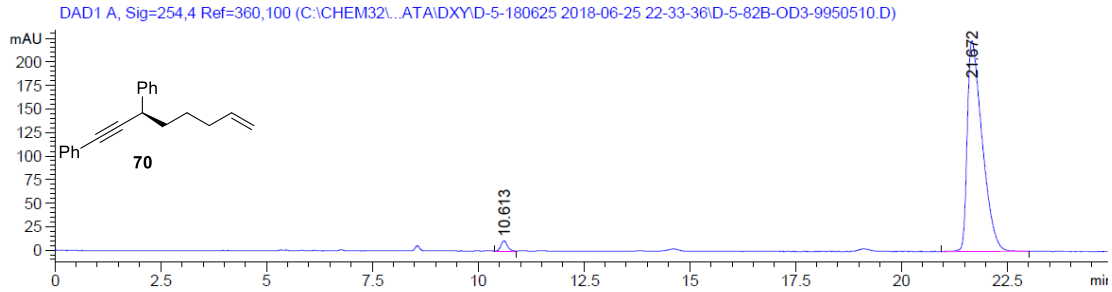
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.618	BB	0.1762	103.25012	9.11395	2.0168
2	13.430	BB	0.2068	5016.31787	373.16656	97.9832
Totals :				5119.56799	382.28052	



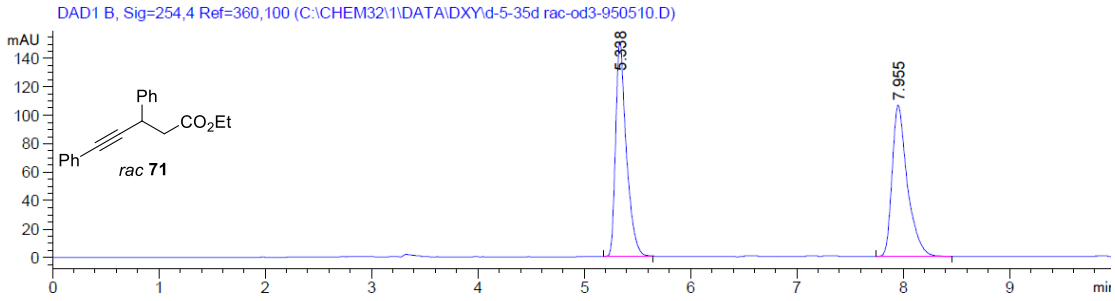
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.526	MM R	0.2040	1.76476e4	1441.89697	48.5799
2	21.361	MM R	0.5239	1.86793e4	594.21759	51.4201
Totals :				3.63269e4	2036.11456	



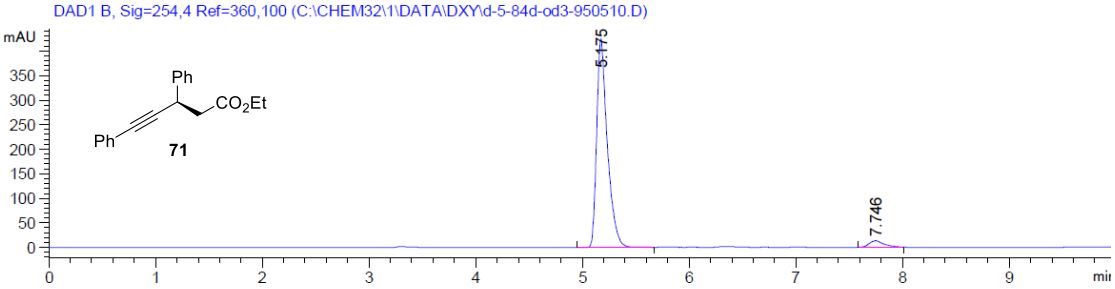
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.613	BV	0.1621	111.89137	10.68883	1.9971
2	21.672	BB	0.3687	5490.84375	223.45345	98.0029
Totals :				5602.73512	234.14227	



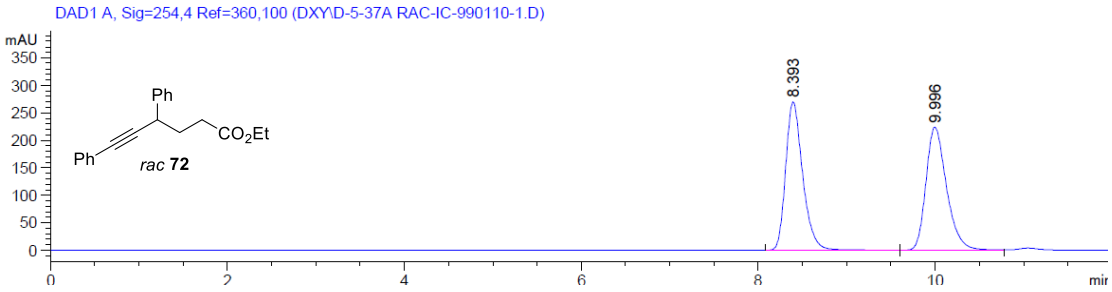
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.338	MM R	0.1158	1055.06970	151.88887	49.9253
2	7.955	BV	0.1481	1058.22754	106.38145	50.0747
Totals :				2113.29724	258.27032	



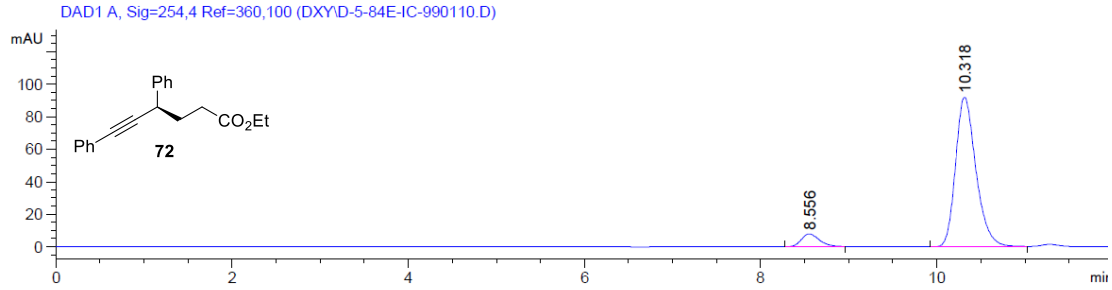
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.175	BV	0.1055	2944.85498	421.80933	95.9238
2	7.746	MM R	0.1609	125.13839	12.96452	4.0762
Totals :				3069.99337	434.77385	



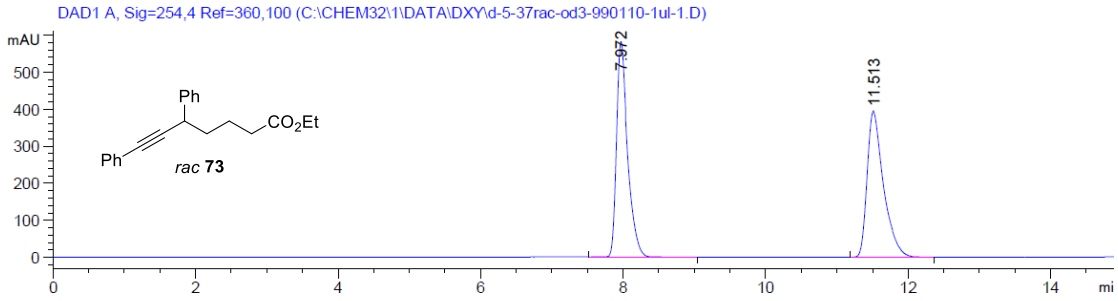
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.393	VB	0.2042	3606.80981	269.40469	49.9173
2	9.996	BV	0.2466	3618.76685	223.82932	50.0827
Totals :				7225.57666	493.23401	



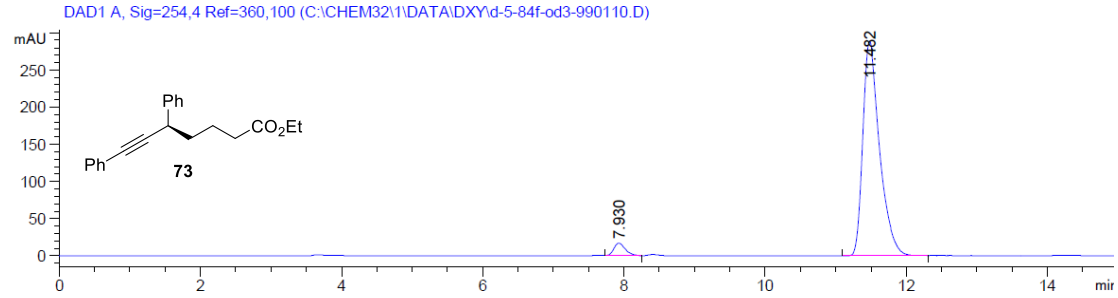
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.556	MM R	0.2325	109.63827	7.85782	6.9051
2	10.318	MM R	0.2677	1478.14124	92.04308	93.0949
Totals :				1587.77950	99.90089	



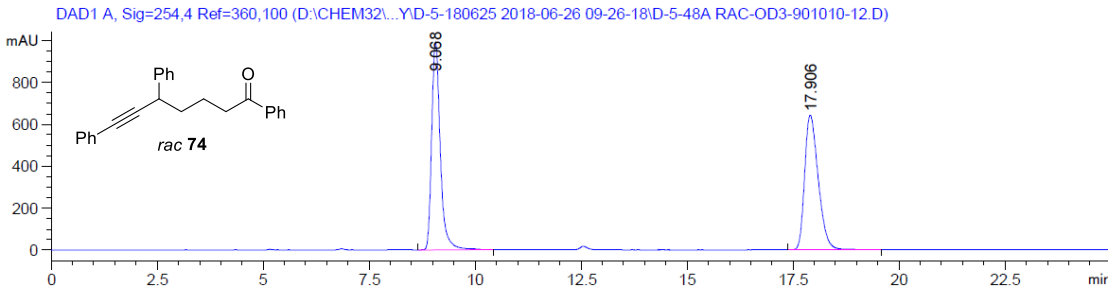
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.972	BB	0.1615	6263.23730	582.44818	49.7253
2	11.513	VV	0.2389	6332.43457	395.29041	50.2747
Totals :				1.25957e4	977.73859	



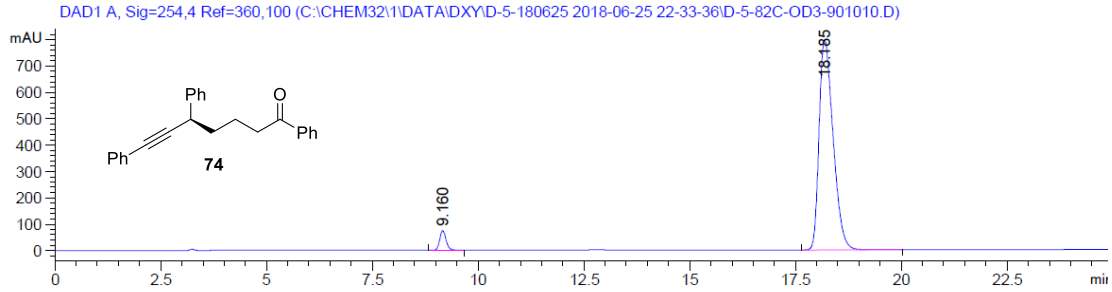
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.930	VV	0.1707	196.86623	17.30227	3.9851
2	11.482	BB	0.2474	4743.17627	289.06384	96.0149
Totals :				4940.04250	306.36611	



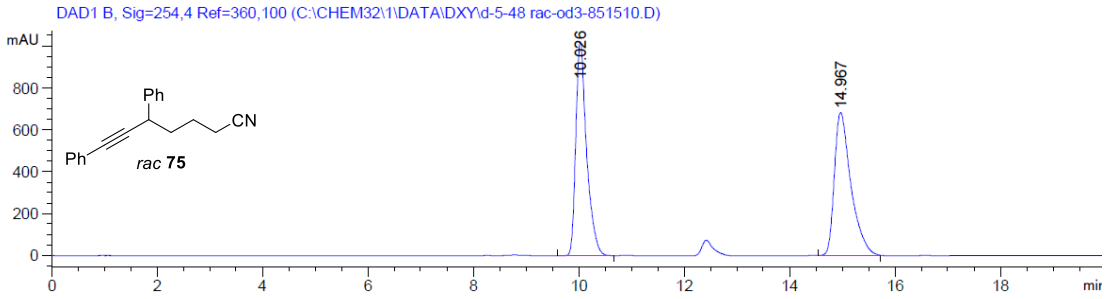
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.068	BV	0.2181	1.41108e4	991.26245	49.5502
2	17.906	BV	0.3450	1.43670e4	642.23199	50.4498
Totals :				2.84777e4	1633.49445	



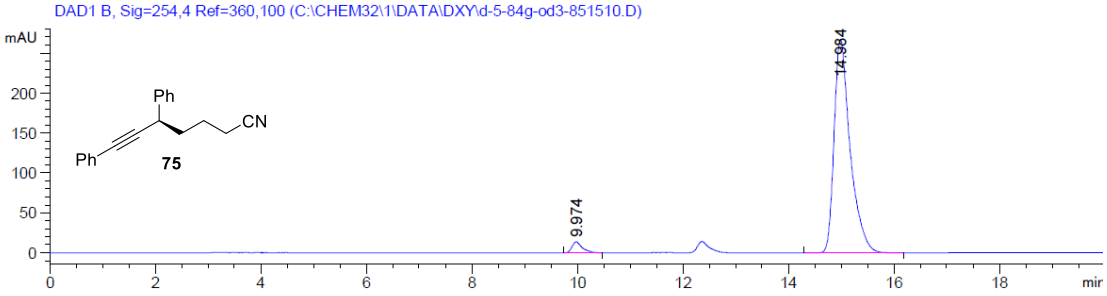
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.160	BB	0.1613	762.71191	73.34933	3.9893
2	18.185	BB	0.3547	1.83560e4	797.00592	96.0107
Totals :				1.91187e4	870.35526	



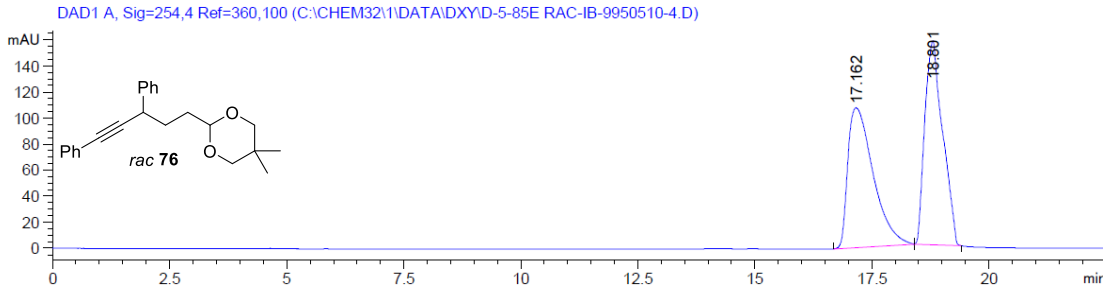
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.026	BV	0.2099	1.45434e4	1022.50031	49.5945
2	14.967	MM R	0.3623	1.47812e4	679.99146	50.4055
Totals :				2.93247e4	1702.49176	



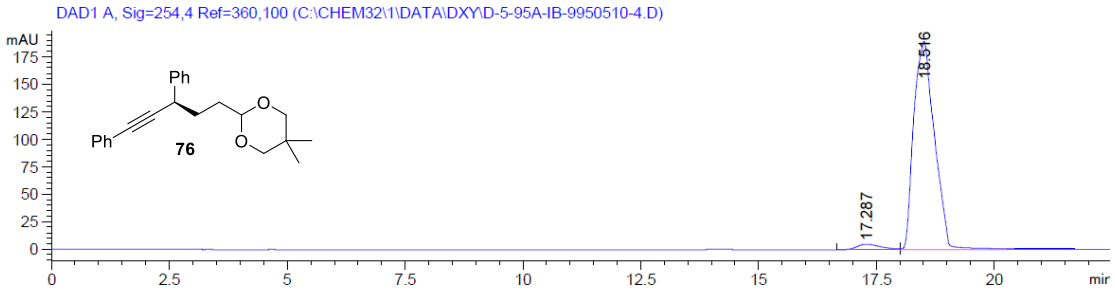
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.974	BB	0.1996	189.63519	13.86204	3.2472
2	14.984	BV	0.3145	5650.36328	267.48099	96.7528
Totals :				5839.99847	281.34303	



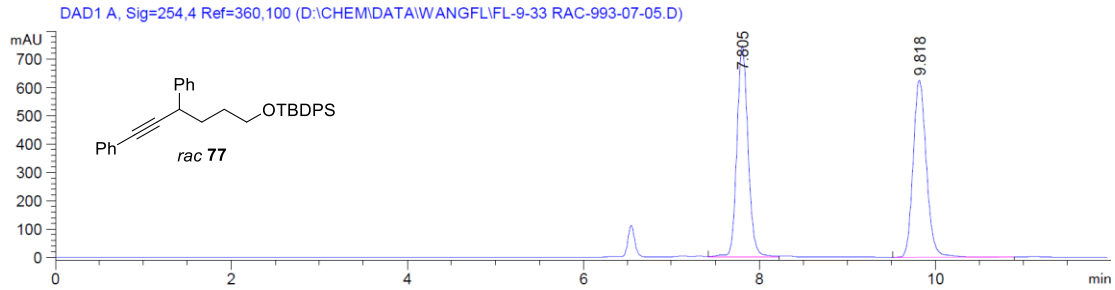
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.162	MM R	0.6265	4036.53271	107.38785	49.3428
2	18.801	MM R	0.4414	4144.05762	156.46883	50.6572
Totals :				8180.59033	263.85667	



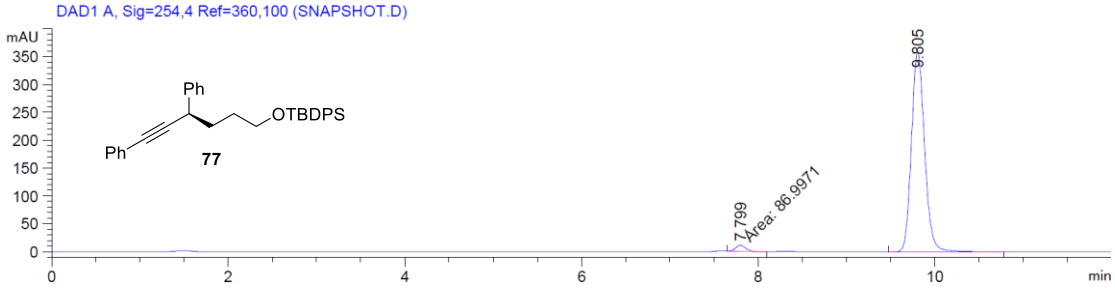
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.287	BV	0.4931	169.26418	4.92276	2.8272
2	18.516	VB	0.4645	5817.77100	189.33855	97.1728
Totals :				5987.03517	194.26130	



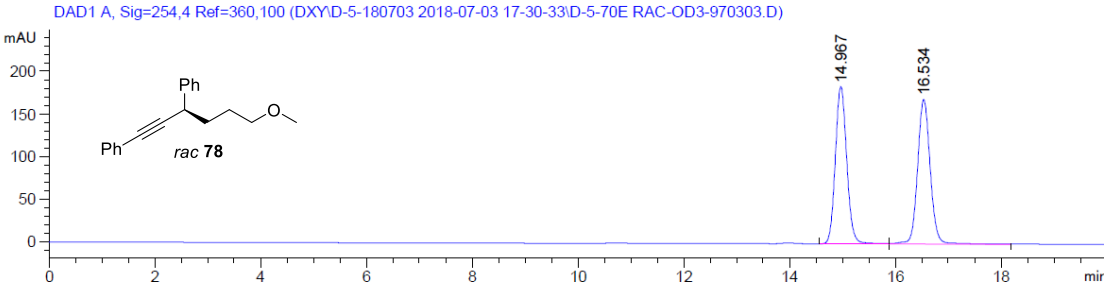
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.805	VV	0.1371	6595.20313	746.07758	50.1534
2	9.818	BB	0.1622	6554.85986	625.85046	49.8466
Totals :				1.31501e4	1371.92804	



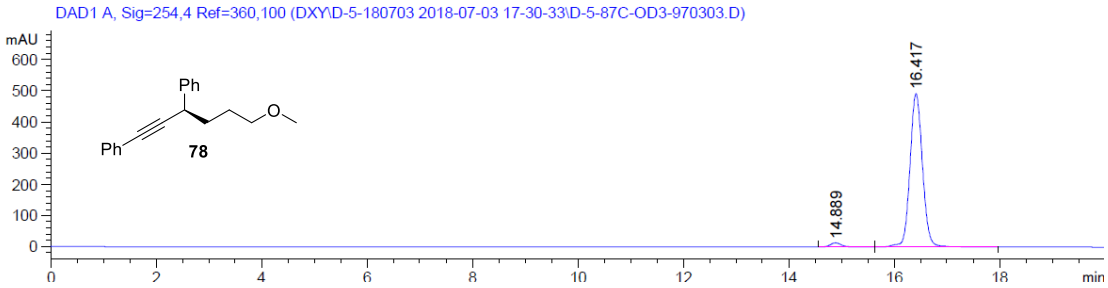
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.799	MF	0.1363	86.99709	10.63763	2.2940
2	9.805	BB	0.1587	3705.33228	358.25650	97.7060
Totals :				3792.32937	368.89413	



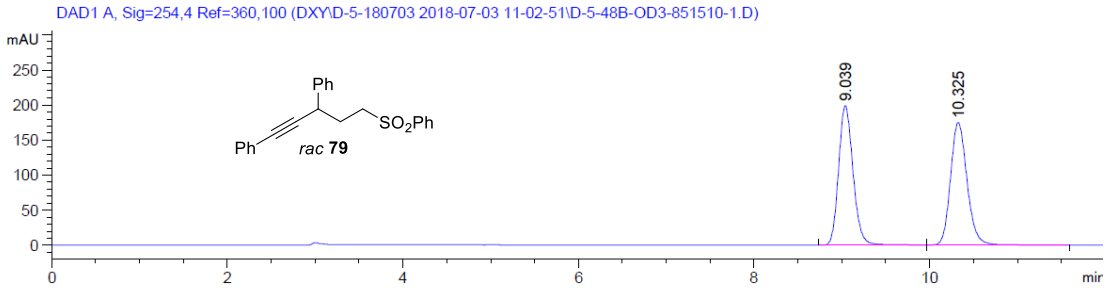
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.967	BV	0.2327	2763.48169	184.58707	49.5310
2	16.534	VV	0.2556	2815.81128	169.69910	50.4690
Totals :				5579.29297	354.28616	



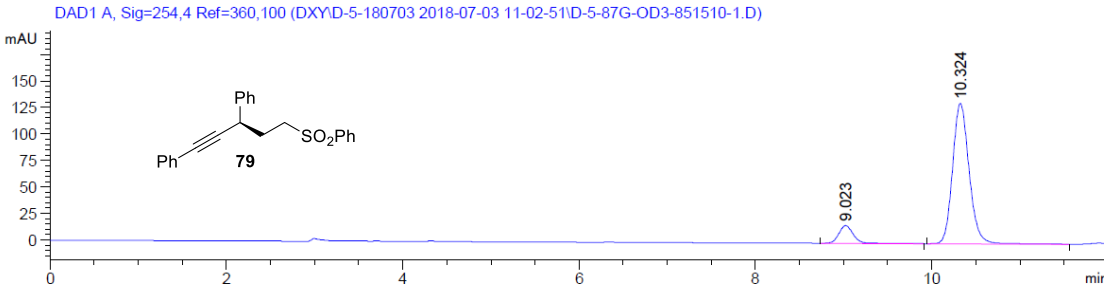
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.889	BV	0.2349	210.04489	13.69742	2.5125
2	16.417	VV	0.2573	8149.89844	491.97894	97.4875
Totals :				8359.94333	505.67636	



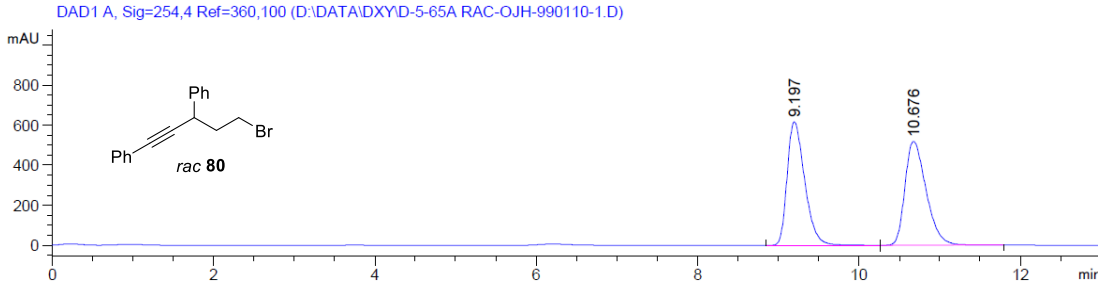
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.039	BV	0.1784	2291.22583	198.92213	49.6302
2	10.325	VV	0.2047	2325.37402	175.32954	50.3698
Totals :				4616.59985	374.25168	



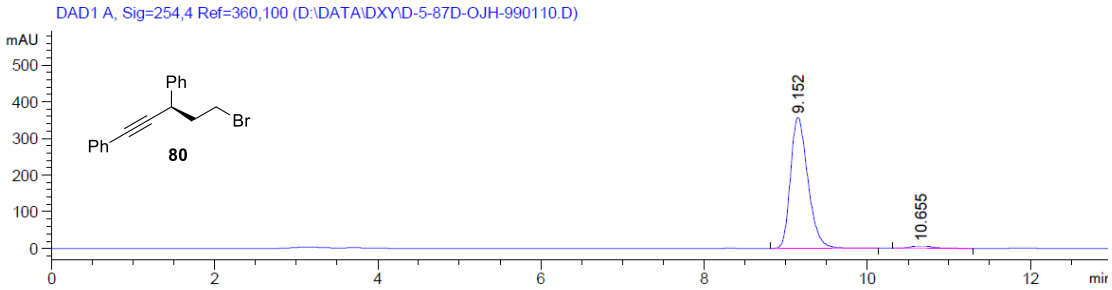
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.023	VB	0.1764	189.19994	16.66546	9.9106
2	10.324	BB	0.2017	1719.86365	132.28712	90.0894
Totals :				1909.06358	148.95259	



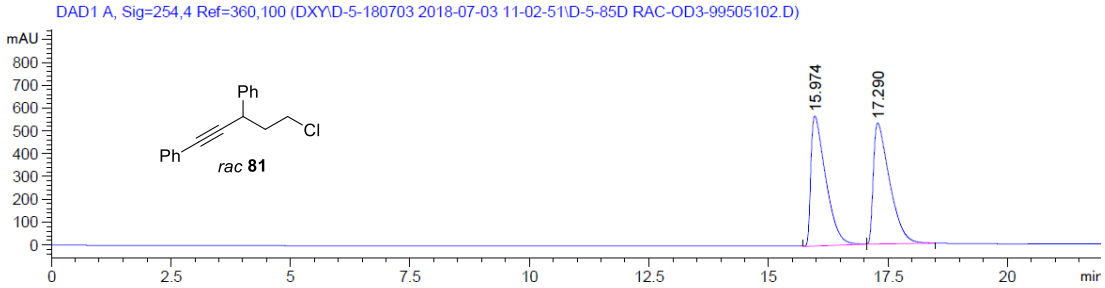
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.197	BB	0.2324	9327.83398	617.03815	49.6820
2	10.676	BB	0.2802	9447.23145	519.44867	50.3180
Totals :				1.87751e4	1136.48682	



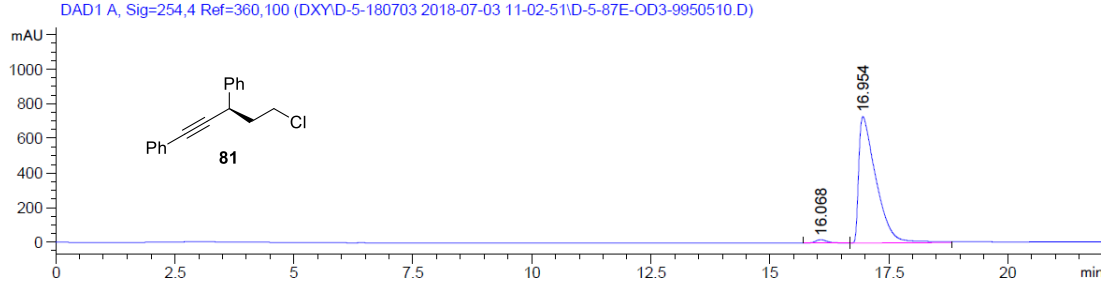
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.152	BB	0.2288	5283.96582	356.81369	97.8010
2	10.655	BB	0.2741	118.80792	6.59794	2.1990
Totals :				5402.77374	363.41163	



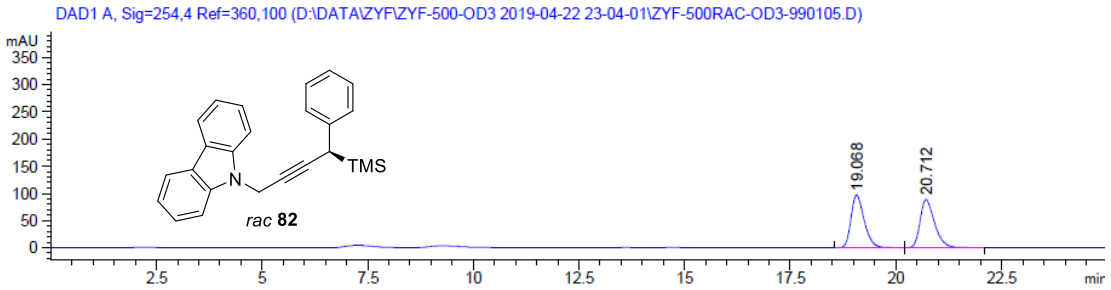
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.974	MM R	0.3610	1.23580e4	570.50580	49.6302
2	17.290	MM R	0.3928	1.25421e4	532.14966	50.3698
Totals :				2.49001e4	1102.65546	



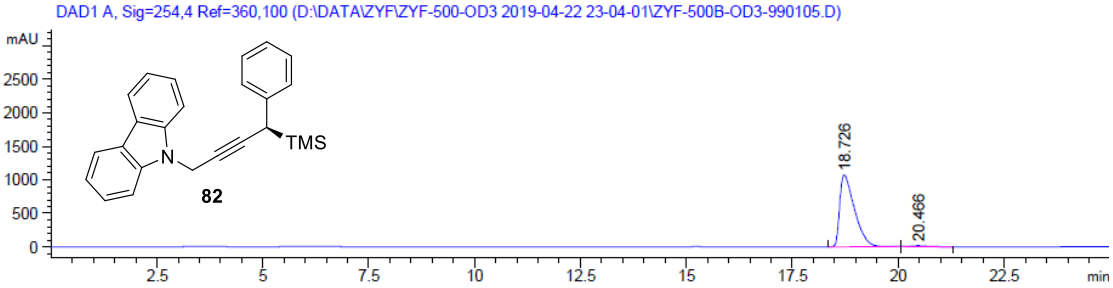
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.068	BB	0.2569	328.00027	19.43730	1.7370
2	16.954	BV	0.3750	1.85555e4	728.83557	98.2630
Totals :				1.88835e4	748.27287	



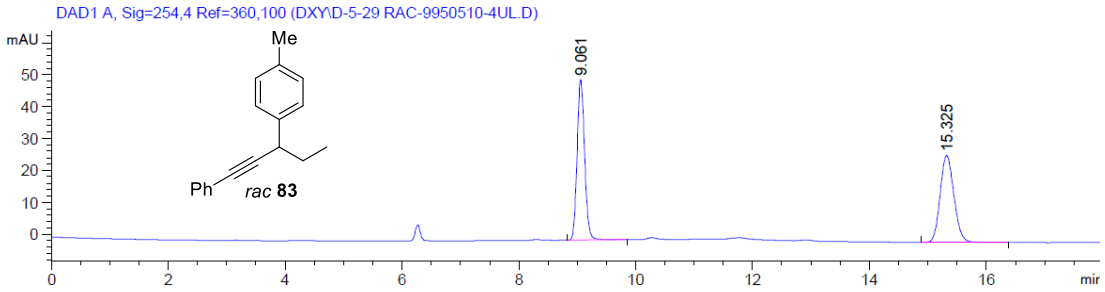
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.068	BB	0.3303	2092.41455	96.76926	50.0383
2	20.712	BB	0.3619	2089.20923	88.35926	49.9617
Totals :				4181.62378	185.12852	



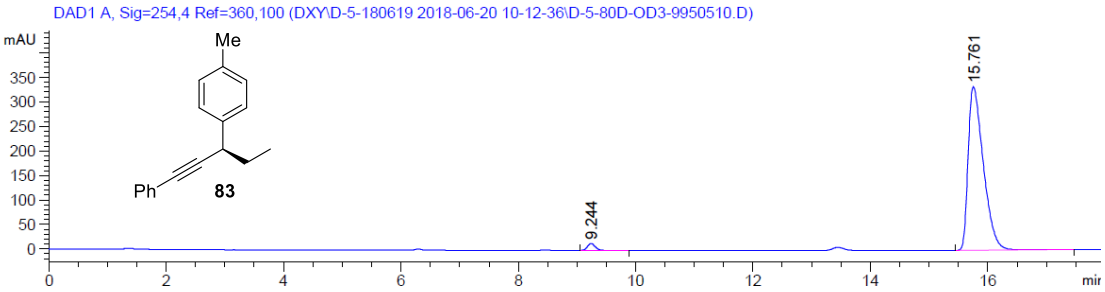
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.726	BB	0.3659	2.58934e4	1071.63269	98.7026
2	20.466	BB	0.3590	340.34872	14.54276	1.2974
Totals :				2.62338e4	1086.17545	



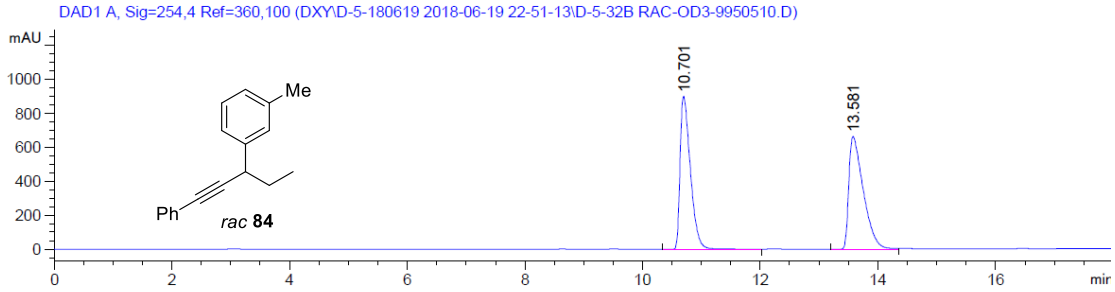
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.061	BB	0.1385	450.21799	50.25706	50.1925
2	15.325	BB	0.2553	446.76471	27.24672	49.8075
Totals :				896.98270	77.50378	



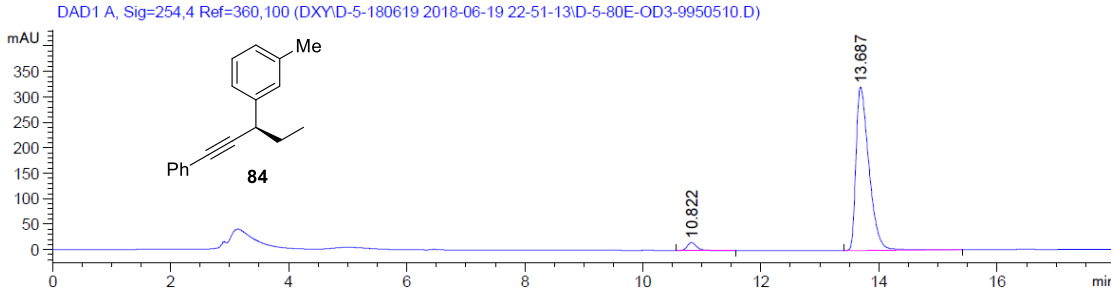
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.244	VB	0.1472	134.76401	14.14410	2.1948
2	15.761	BB	0.2744	6005.36963	332.95587	97.8052
Totals :				6140.13364	347.09998	



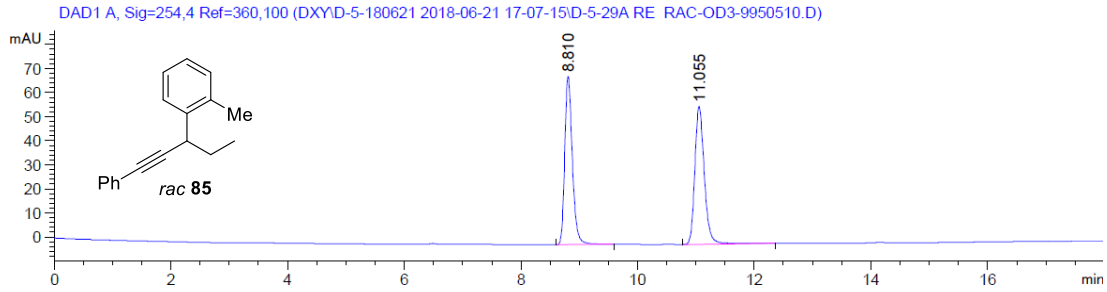
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.701	BV	0.1862	1.09750e4	900.47235	49.1974
2	13.581	BV	0.2556	1.13331e4	662.50806	50.8026
Totals :				2.23081e4	1562.98041	



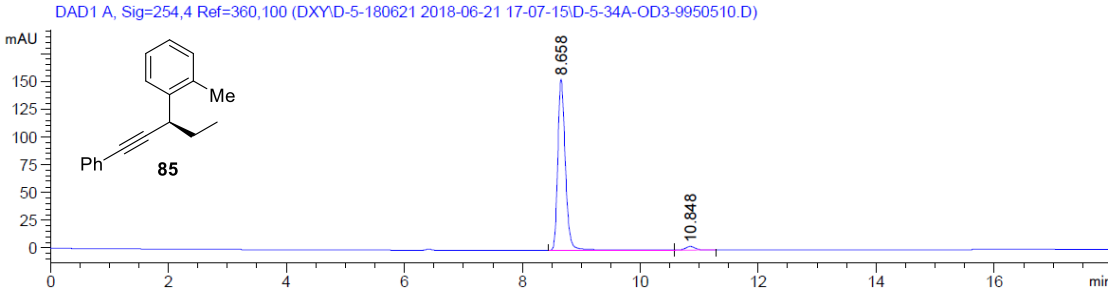
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.822	BV	0.1683	175.41963	15.95358	3.4599
2	13.687	BB	0.2319	4894.71094	320.93167	96.5401
Totals :				5070.13057	336.88525	



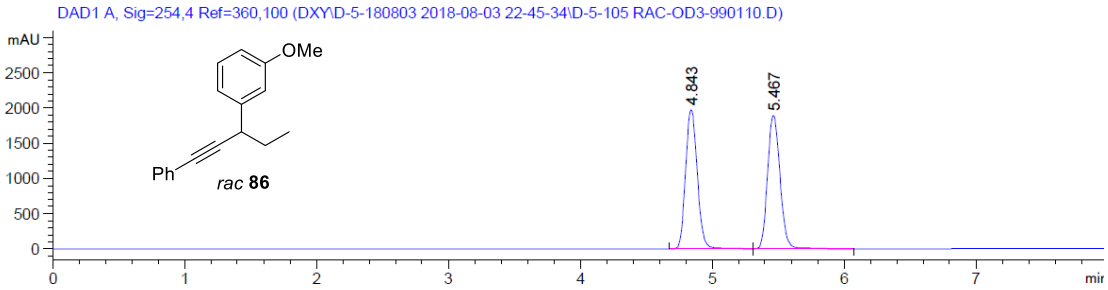
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.810	BB	0.1399	634.85712	69.97263	49.4331
2	11.055	BB	0.1719	649.41779	57.42860	50.5669
Totals :				1284.27490	127.40123	



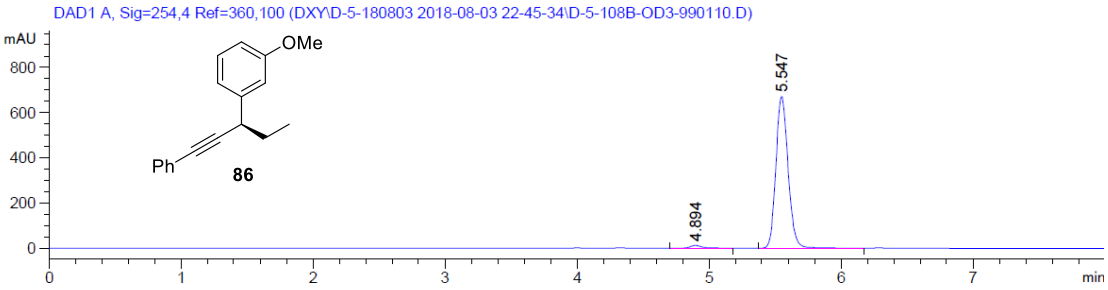
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.658	BV	0.1390	1385.34070	153.88037	97.5293
2	10.848	VB	0.1710	35.09517	3.17505	2.4707
Totals :				1420.43587	157.05542	



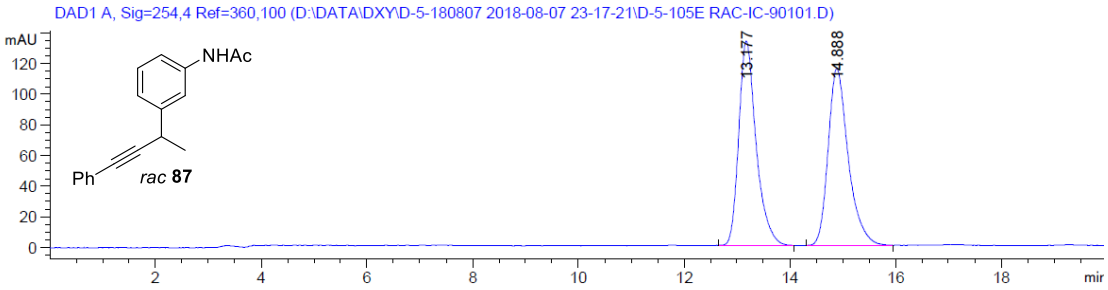
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.843	BB	0.0976	1.21210e4	1975.27771	49.3886
2	5.467	BV	0.1046	1.24211e4	1893.02734	50.6114
Totals :				2.45421e4	3868.30505	



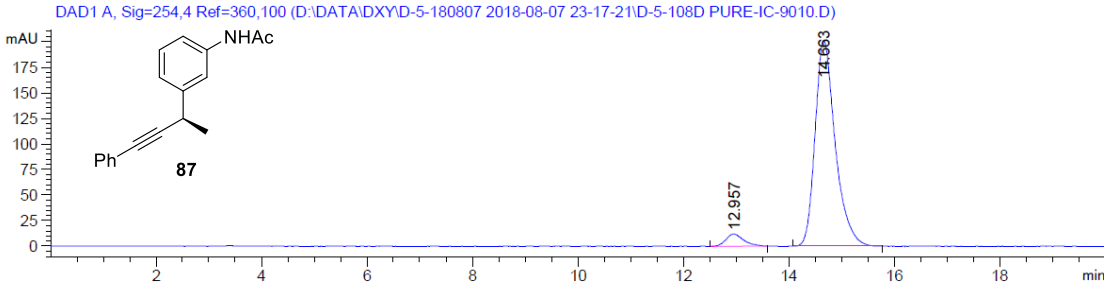
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.894	BB	0.0957	80.47669	12.41076	1.8394
2	5.547	BV	0.0986	4294.78223	671.68512	98.1606
Totals :				4375.25892	684.09588	



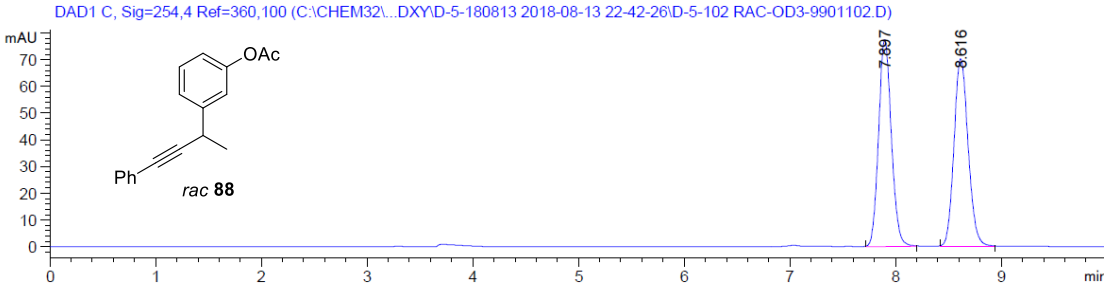
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.177	BB	0.3426	3046.11914	133.29784	49.9921
2	14.888	BB	0.4003	3047.08716	115.32556	50.0079
Totals :				6093.20630	248.62340	



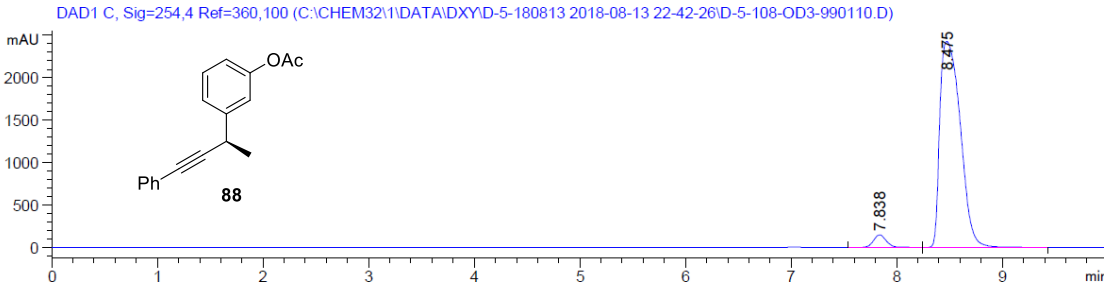
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.957	BB	0.3268	277.64099	11.96029	4.9473
2	14.663	BB	0.4011	5334.34863	201.35074	95.0527
Totals :				5611.98962	213.31103	



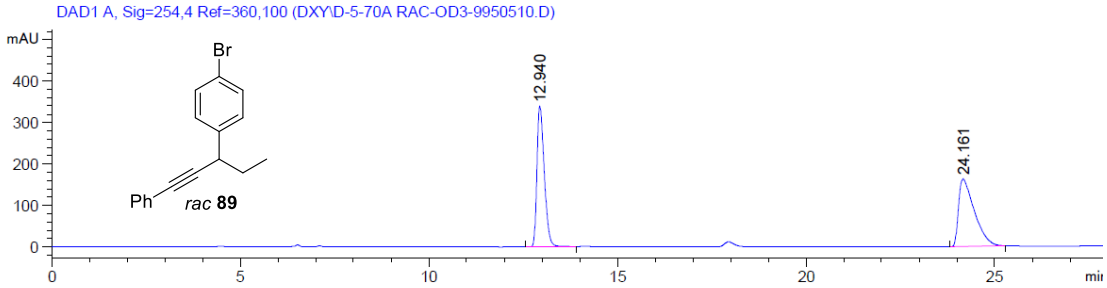
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.897	BB	0.1302	652.20728	77.49670	50.0211
2	8.616	BB	0.1442	651.65643	70.25856	49.9789
Totals :				1303.86371	147.75526	



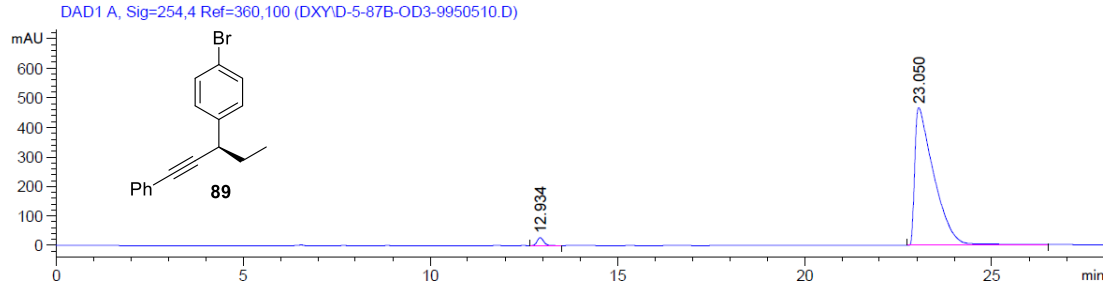
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.838	VV	0.1336	1285.73230	147.62207	3.7954
2	8.475	VB	0.2226	3.25906e4	2427.29565	96.2046
Totals :				3.38763e4	2574.91772	



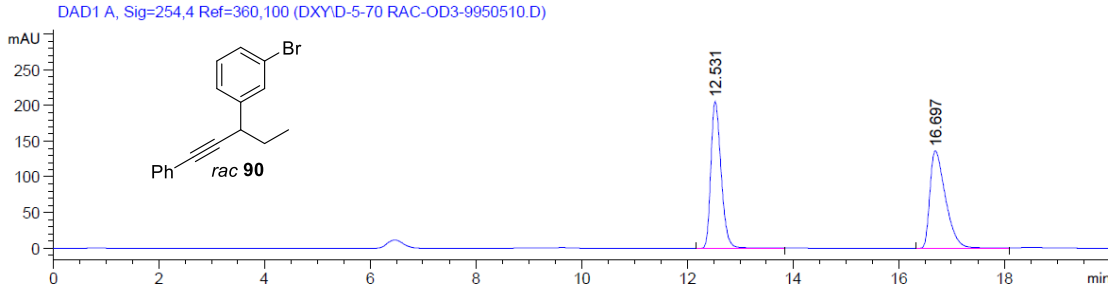
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.940	BV	0.2088	4625.80273	339.76202	49.3917
2	24.161	MM R	0.4852	4739.73682	162.79475	50.6083
Totals :				9365.53955	502.55678	



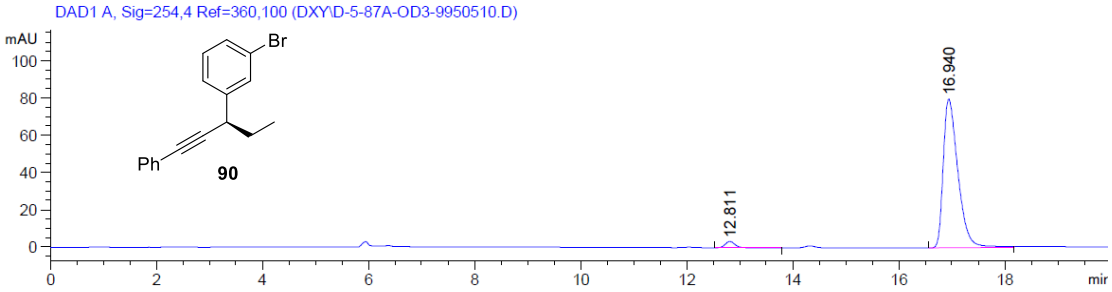
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.934	VB	0.1921	328.11060	26.56098	1.9128
2	23.050	BV	0.5129	1.68253e4	466.42291	98.0872
Totals :				1.71534e4	492.98389	



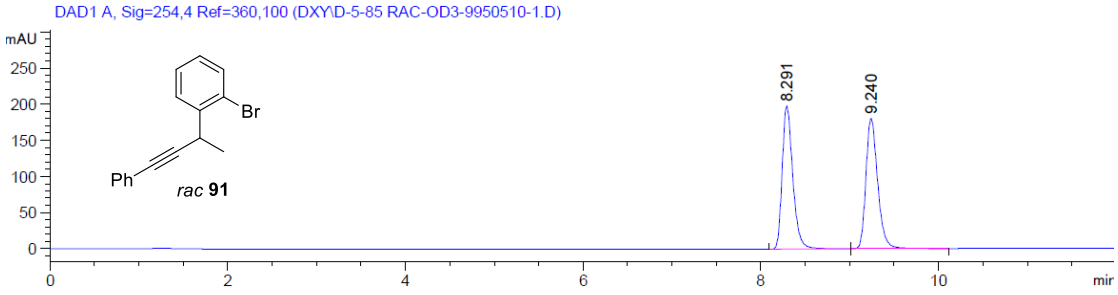
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.531	BV	0.2087	2796.47754	205.63589	49.7589
2	16.697	BV	0.3149	2823.57275	136.74744	50.2411
Totals :				5620.05029	342.38333	



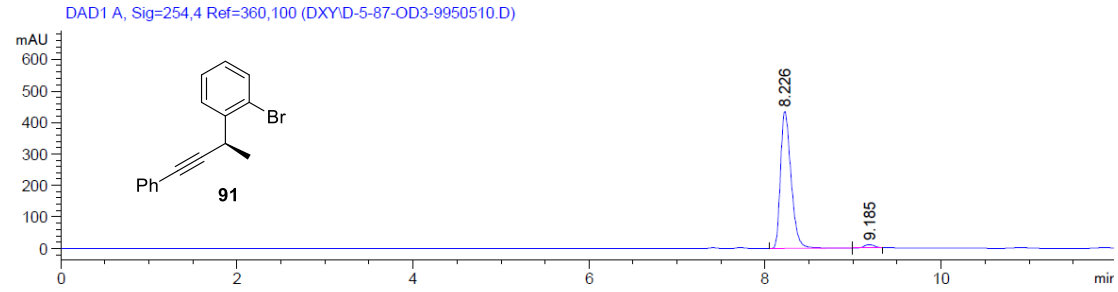
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.811	BB	0.2042	43.58640	3.29702	2.7493
2	16.940	BV	0.2954	1541.77209	79.78614	97.2507
Totals :				1585.35849	83.08316	



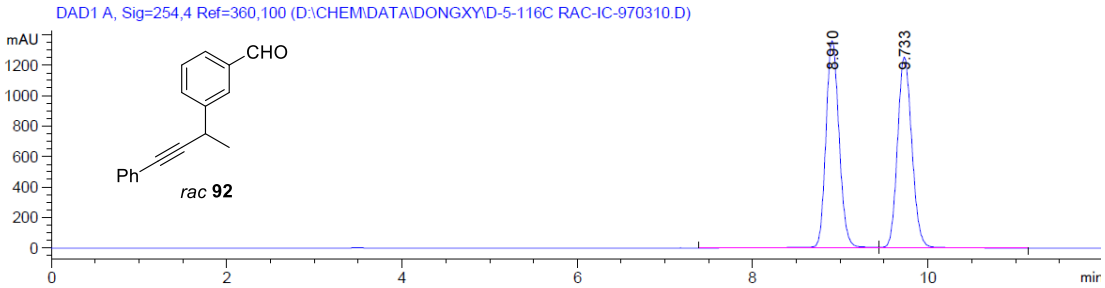
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.291	BB	0.1275	1650.12219	197.51003	49.7205
2	9.240	BV	0.1417	1668.67407	180.69342	50.2795
Totals :				3318.79626	378.20345	



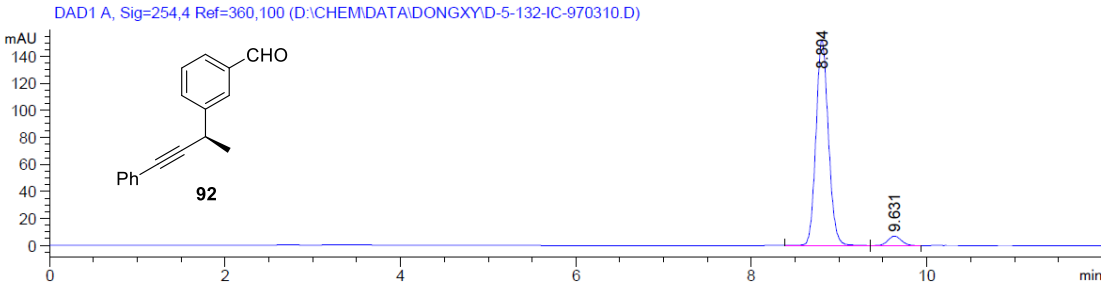
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.226	BB	0.1296	3635.26807	434.59790	97.3157
2	9.185	BV	0.1354	100.27347	11.54084	2.6843
Totals :				3735.54153	446.13874	



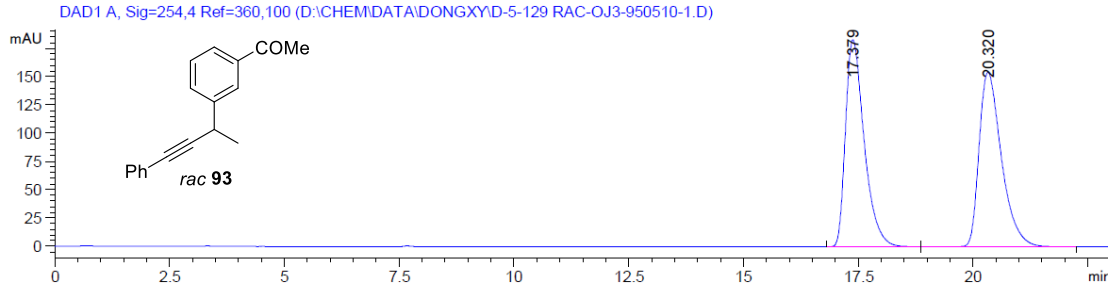
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.910	BV	0.1630	1.43477e4	1361.10132	50.0713
2	9.733	VV	0.1792	1.43068e4	1253.41797	49.9287
Totals :				2.86545e4	2614.51929	



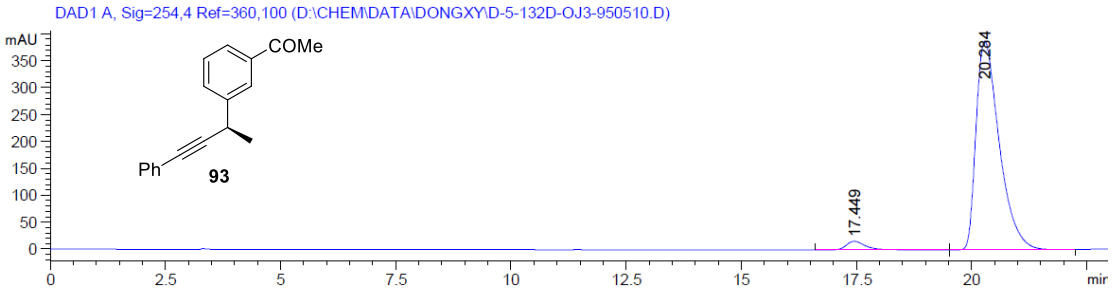
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.804	VB	0.1536	1503.58728	151.75322	95.1781
2	9.631	BB	0.1669	76.17422	7.11587	4.8219
Totals :				1579.76150	158.86909	



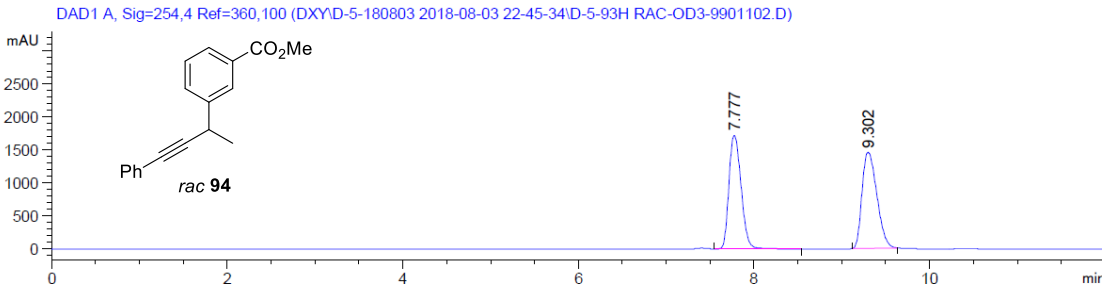
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.379	BB	0.4329	5190.33008	183.00511	49.8764
2	20.320	BV	0.5185	5216.05176	154.25903	50.1236
Totals :				1.04064e4	337.26414	



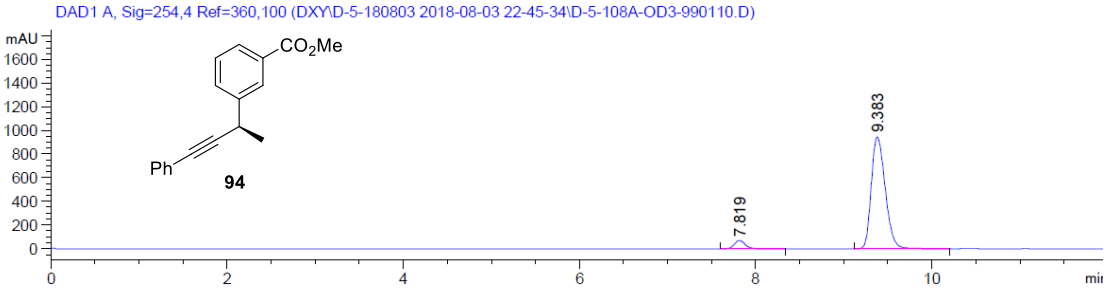
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.449	BB	0.4418	458.36240	15.73718	3.2650
2	20.284	BV	0.5362	1.35805e4	388.11813	96.7350
Totals :				1.40388e4	403.85532	



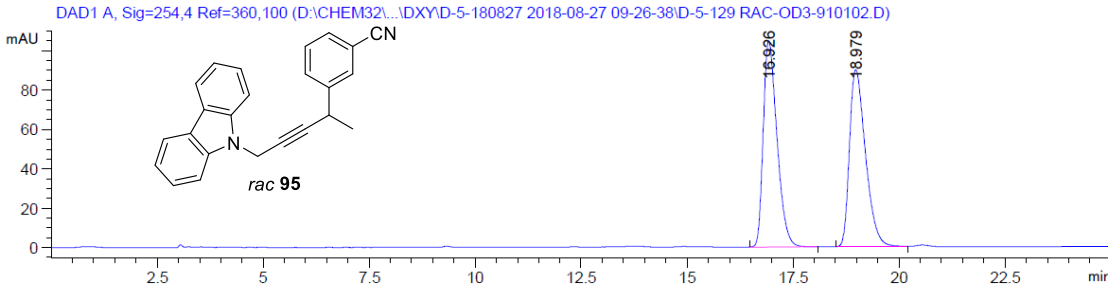
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.777	MM R	0.1601	1.65449e4	1722.80652	49.2560
2	9.302	MM R	0.1949	1.70447e4	1457.61633	50.7440
Totals :				3.35896e4	3180.42285	



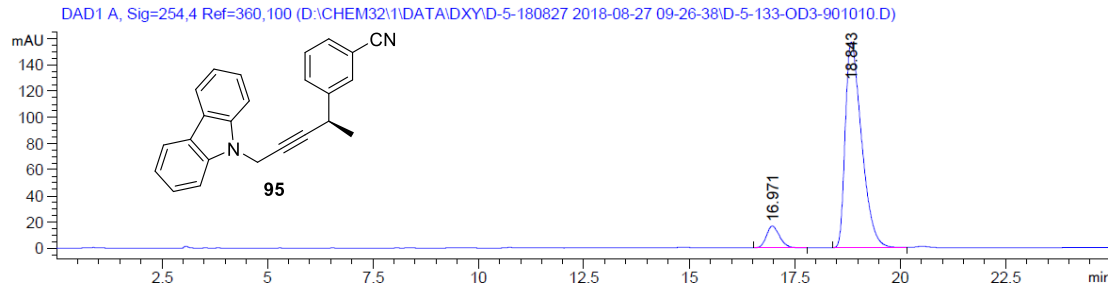
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.819	BB	0.1305	596.22595	70.63197	5.4423
2	9.383	BB	0.1720	1.03592e4	944.25189	94.5577
Totals :				1.09554e4	1014.88386	



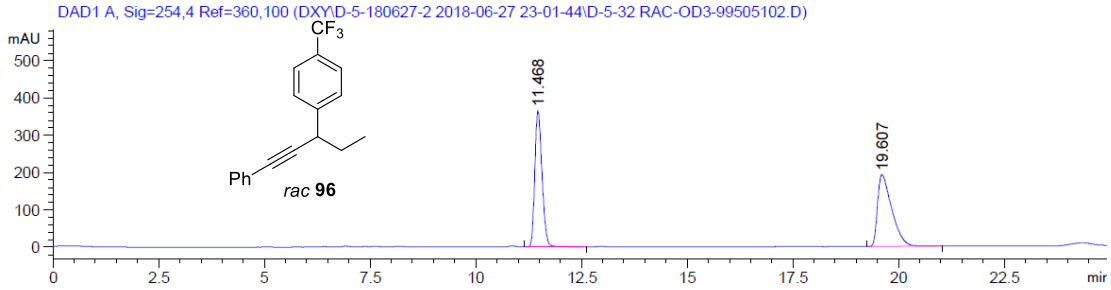
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.926	BB	0.3470	2360.33618	104.70464	49.8958
2	18.979	BV	0.4075	2370.19336	89.93477	50.1042
Totals :				4730.52954	194.63940	



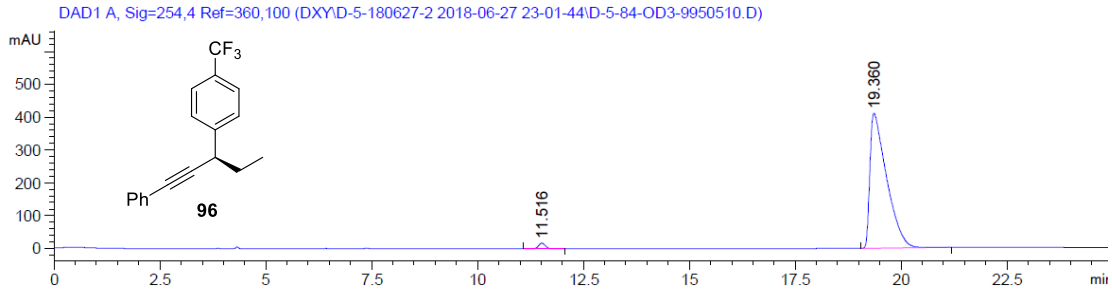
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.971	BB	0.3367	359.10321	16.58188	7.8249
2	18.843	BV	0.4105	4230.14307	156.94539	92.1751
Totals :				4589.24628	173.52727	



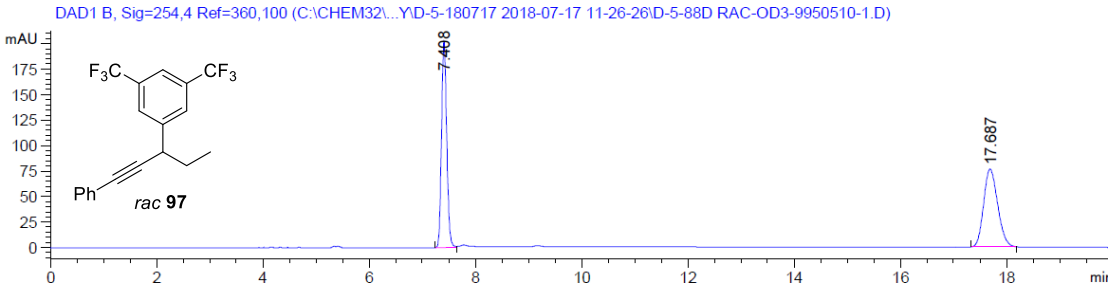
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.468	VV	0.1848	4341.11328	364.85193	49.0781
2	19.607	BB	0.3487	4504.19482	192.67992	50.9219
Totals :				8845.30811	557.53185	



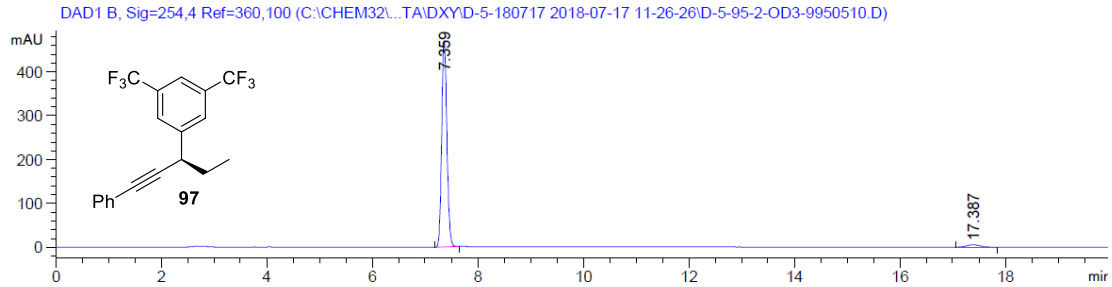
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.516	VB	0.1798	207.21509	17.79824	1.7977
2	19.360	BB	0.3985	1.13193e4	412.07855	98.2023
Totals :				1.15265e4	429.87680	



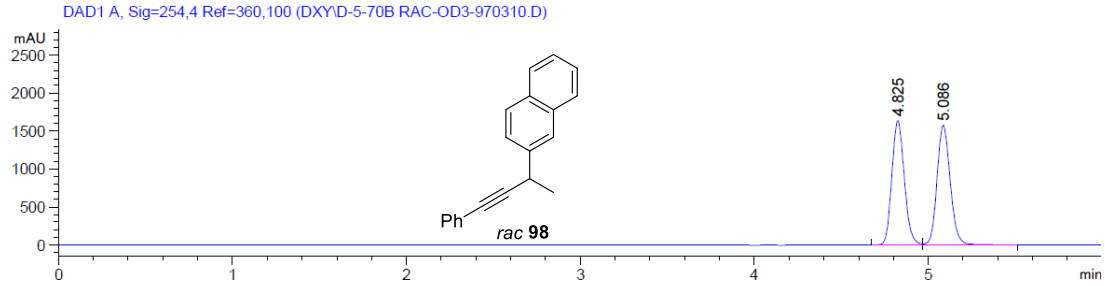
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.408	BV	0.1055	1380.25549	202.63139	49.6513
2	17.687	MM R	0.3054	1399.64307	76.38766	50.3487
Totals :				2779.89856	279.01906	



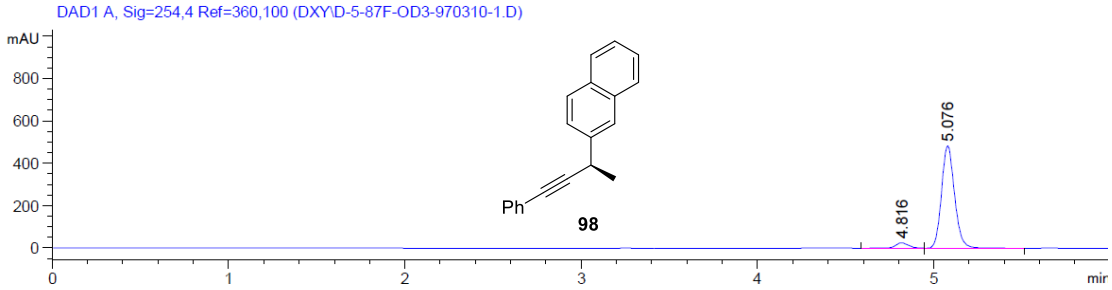
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.359	BB	0.1063	3227.74927	469.01553	97.2253
2	17.387	BB	0.2707	92.11673	5.30189	2.7747
Totals :				3319.86600	474.31743	



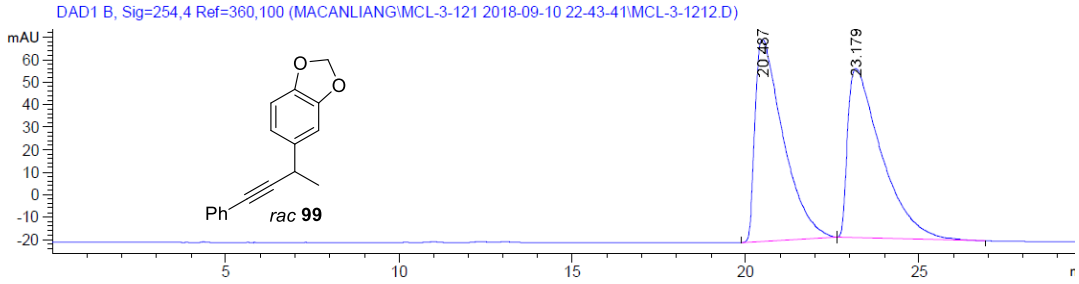
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.825	BV	0.0782	8157.84814	1635.51770	49.4101
2	5.086	VB	0.0837	8352.65039	1580.15552	50.5899
Totals :				1.65105e4	3215.67322	



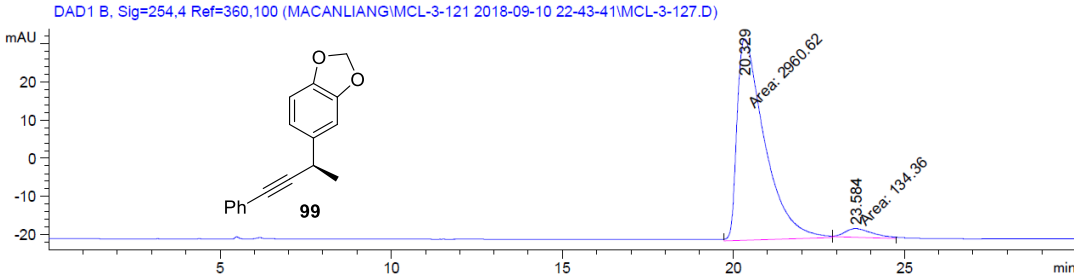
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.816	BV	0.0821	136.40704	25.61650	5.1663
2	5.076	VV	0.0804	2503.90503	483.93454	94.8337
Totals :				2640.31207	509.55104	



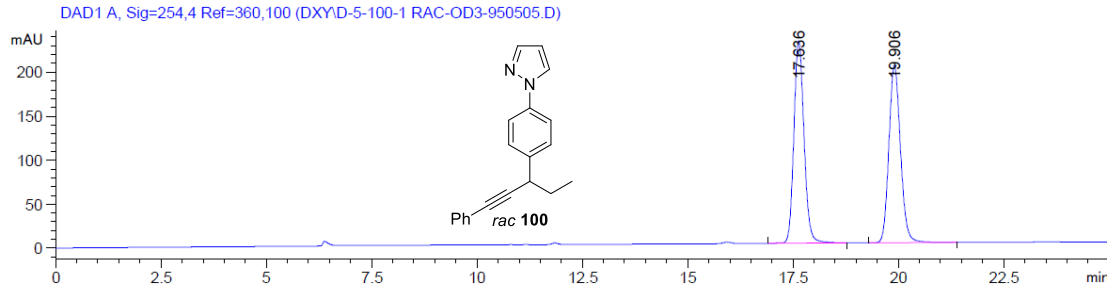
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.488	BV	0.8596	5265.90967	90.39780	48.9067
2	23.179	VBA	1.0297	5501.34521	77.35395	51.0933
Totals :				1.07673e4	167.75175	



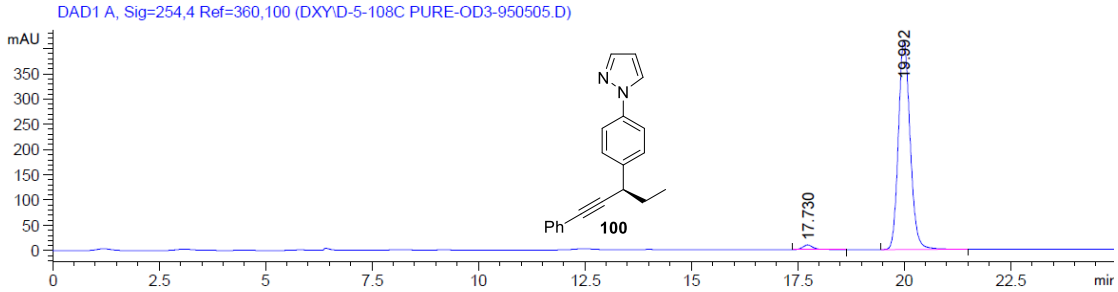
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.329	MM	0.9338	2960.61768	52.84401	95.6588
2	23.584	MM	0.9753	134.36031	2.29604	4.3412
Totals :				3094.97798	55.14005	



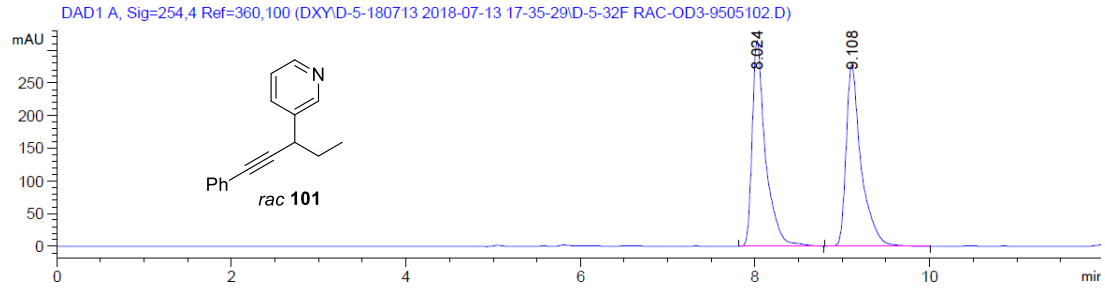
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.636	BB	0.2594	3851.31396	229.92250	49.9683
2	19.906	BB	0.2952	3856.20557	201.54102	50.0317
Totals :				7707.51953	431.46352	



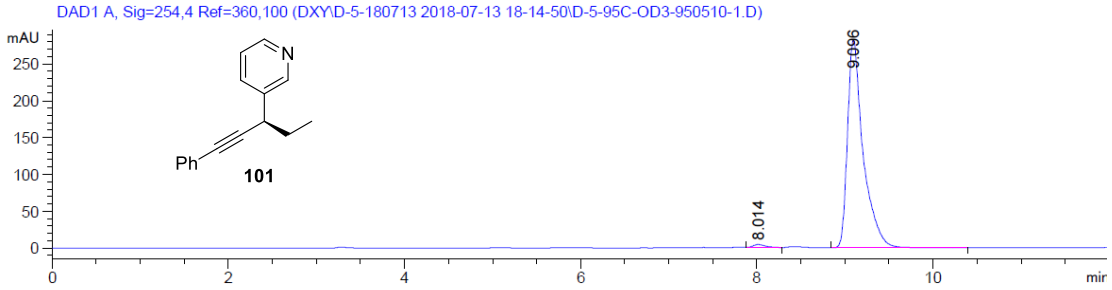
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.730	BB	0.2610	151.05272	8.94683	1.8717
2	19.992	BB	0.2972	7919.12012	413.98062	98.1283
Totals :				8070.17284	422.92745	



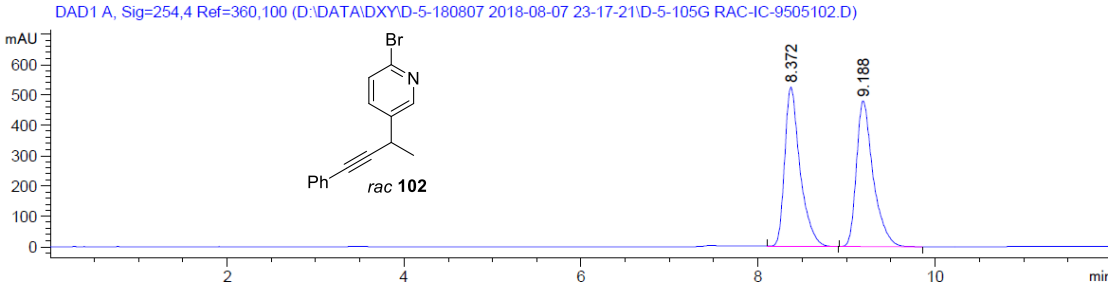
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.024	BB	0.1538	3339.50024	314.63614	50.2950
2	9.108	BB	0.1728	3300.32324	277.31552	49.7050
Totals :				6639.82349	591.95166	



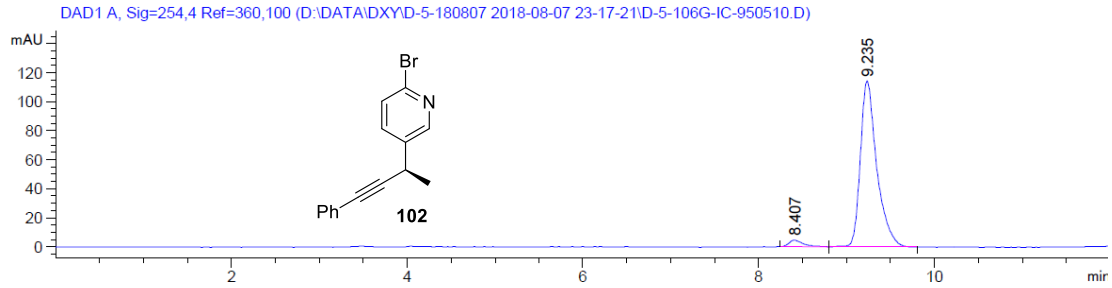
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.014	VV	0.1600	51.00438	4.64731	1.4455
2	9.096	BB	0.1775	3477.59863	282.75851	98.5545
Totals :				3528.60301	287.40582	



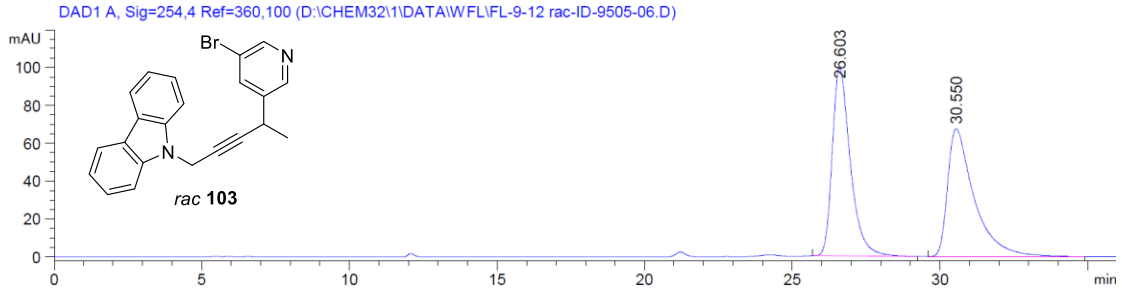
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.372	VB	0.1788	6325.94141	524.04596	50.0854
2	9.188	BB	0.1955	6304.37988	479.23672	49.9146
Totals :				1.26303e4	1003.28268	



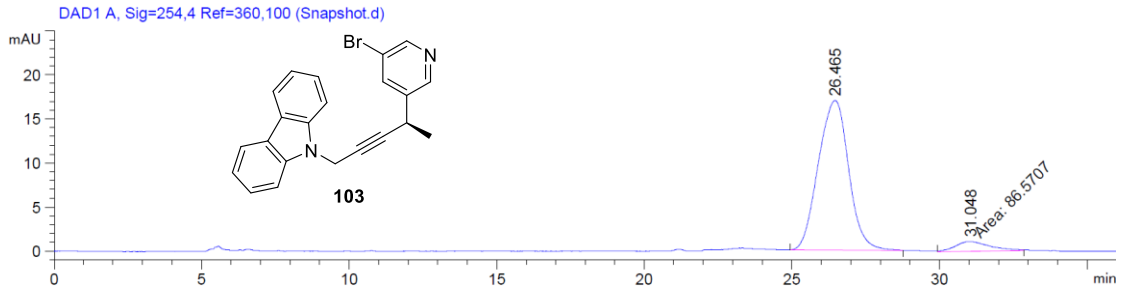
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.407	BV	0.1617	50.17692	4.44553	3.2750
2	9.235	VB	0.1914	1481.93958	114.17977	96.7250
Totals :				1532.11650	118.62530	



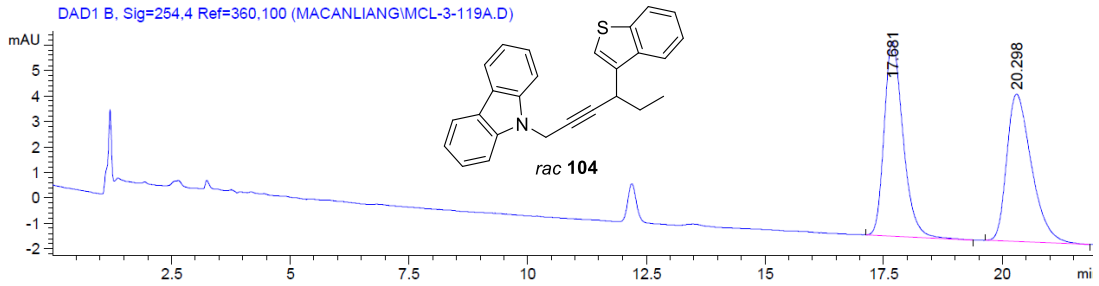
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.603	BB	0.6468	4247.18408	99.33396	50.0965
2	30.550	BB	0.9090	4230.81787	67.52043	49.9035
Totals :				8478.00195	166.85439	



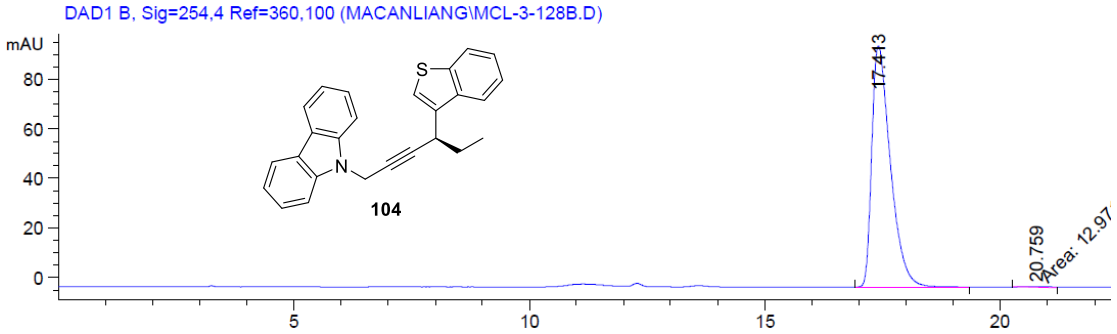
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.465	BB	0.9670	1215.83826	16.98841	93.3530
2	31.048	MM	1.3253	86.57066	1.08871	6.6470
Totals :				1302.40892	18.07712	



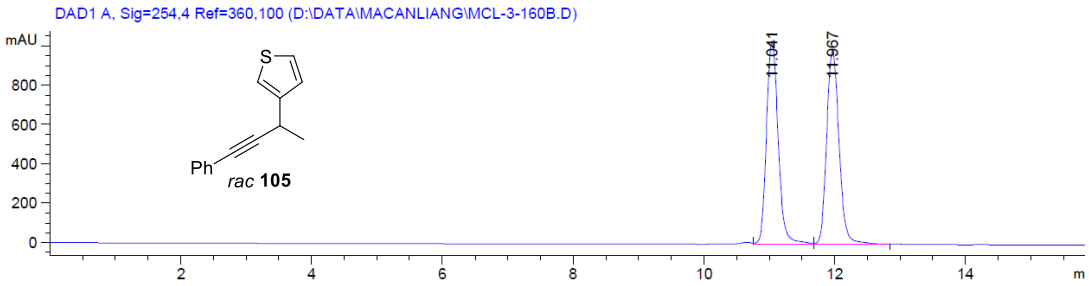
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.681	BB	0.4205	210.27303	7.65445	50.0104
2	20.298	BB	0.5410	210.18591	5.79745	49.9896
Totals :				420.45894	13.45190	



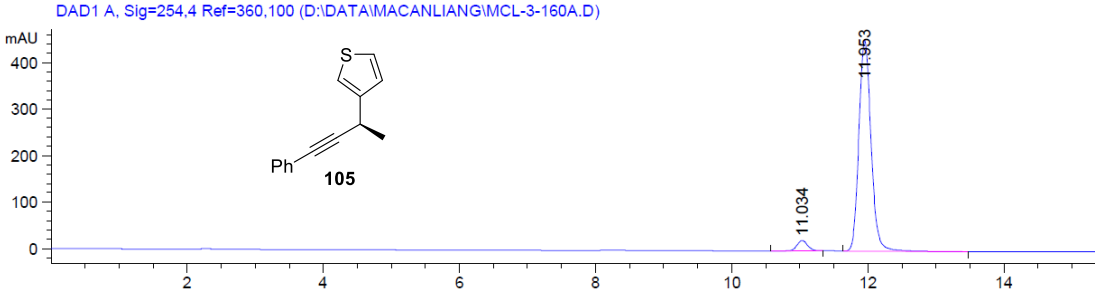
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.413	BB	0.4159	2665.91284	97.22016	99.5158
2	20.759	MM	0.6417	12.97126	3.36893e-1	0.4842
Totals :				2678.88410	97.55705	



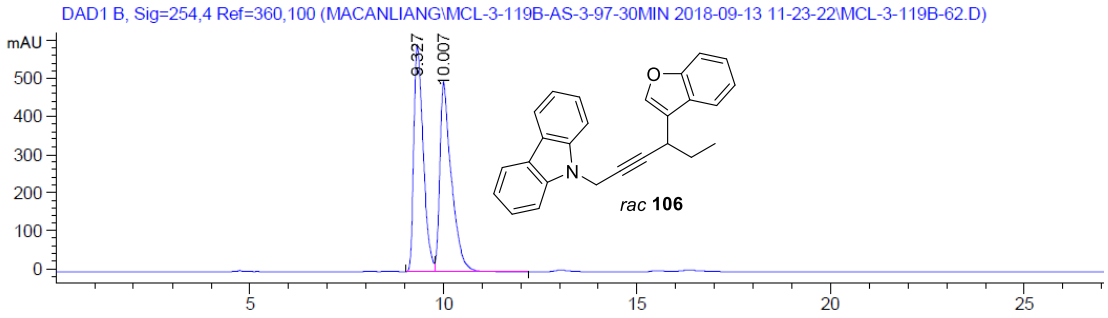
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.041	VV	0.1960	1.29174e4	1032.18884	49.8887
2	11.967	VB	0.2080	1.29750e4	982.76196	50.1113
Totals :				2.58924e4	2014.95081	



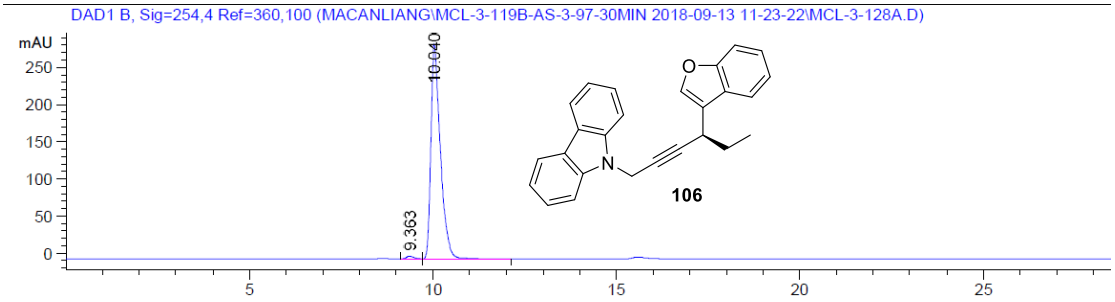
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.034	BB	0.1690	244.14145	22.42584	4.1524
2	11.953	BB	0.1906	5635.44629	454.75473	95.8476
Totals :				5879.58774	477.18057	



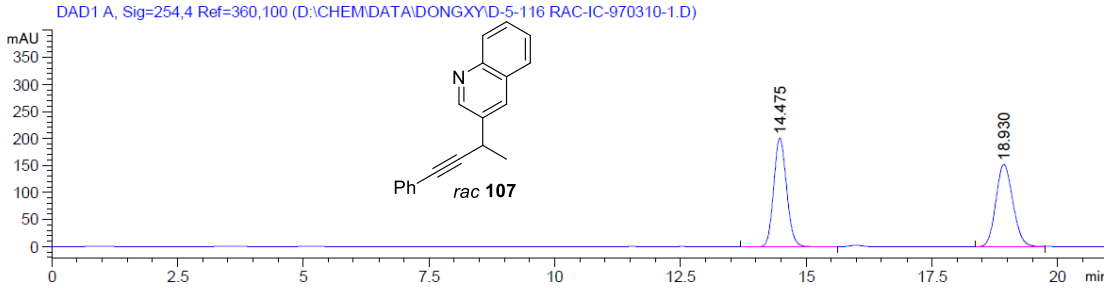
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.328	BV	0.2608	1.00467e4	595.65686	49.2666
2	10.008	VB	0.2967	1.03458e4	501.56064	50.7334
Totals :				2.03925e4	1097.21750	



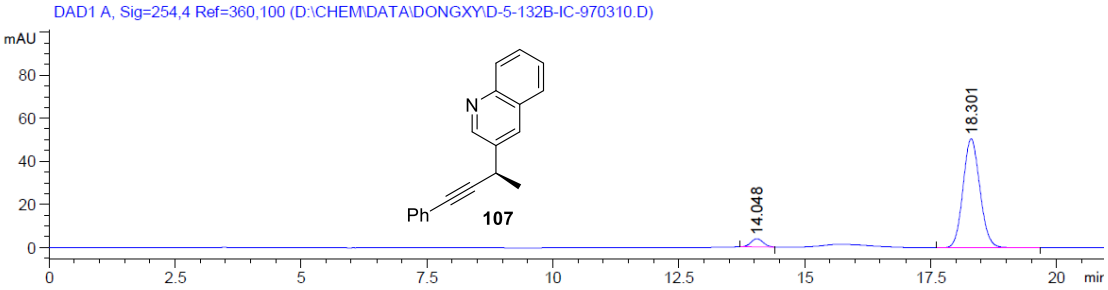
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.364	VV	0.2256	52.20297	3.42965	0.9928
2	10.040	VV	0.2659	5205.96045	289.39093	99.0072
Totals :				5258.16342	292.82058	



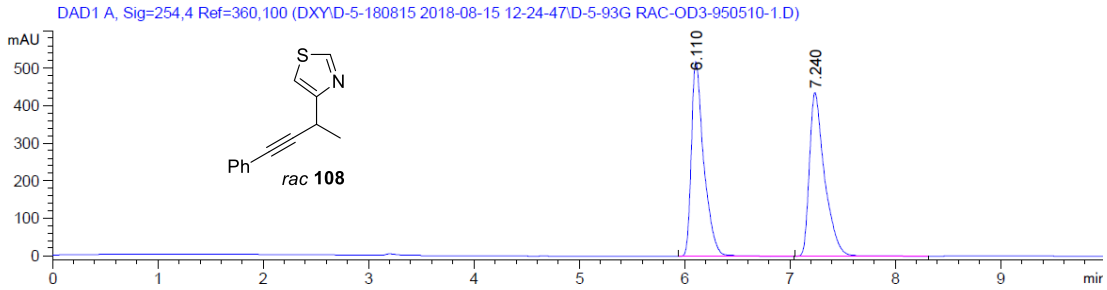
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.475	VV	0.2759	3583.96753	201.12248	49.9480
2	18.930	MM R	0.3926	3591.43408	152.47926	50.0520
Totals :				7175.40161	353.60175	



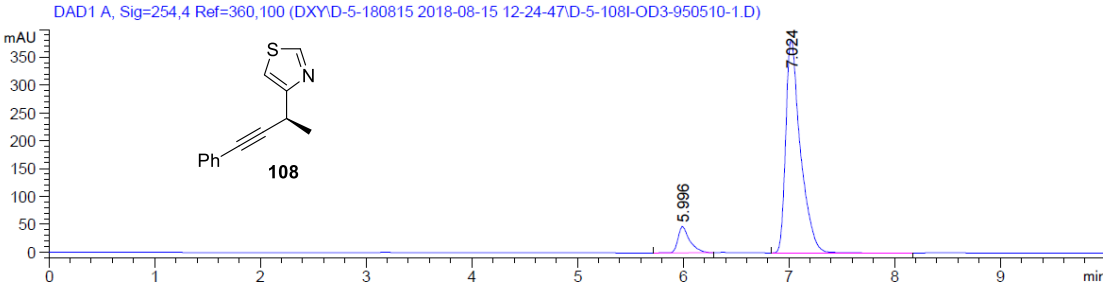
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.048	MM R	0.2786	62.86724	3.76037	5.0686
2	18.301	BB	0.3614	1177.45117	50.62039	94.9314
Totals :				1240.31842	54.38076	



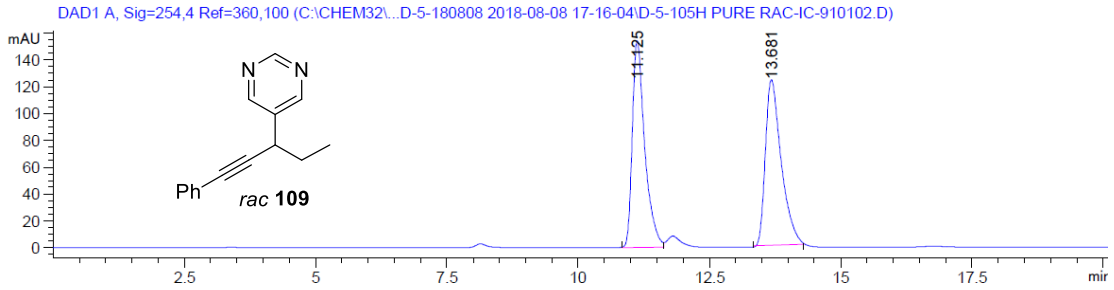
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.110	BB	0.1197	4252.19824	518.57141	49.4286
2	7.240	BB	0.1463	4350.50635	436.45572	50.5714



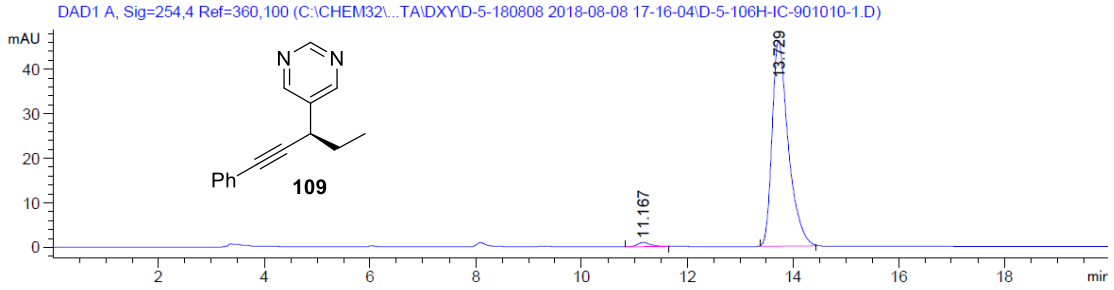
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.996	BV	0.1134	363.38046	47.41119	8.9630
2	7.024	BB	0.1404	3690.82544	383.03204	91.0370
Totals :				4054.20590	430.44324	



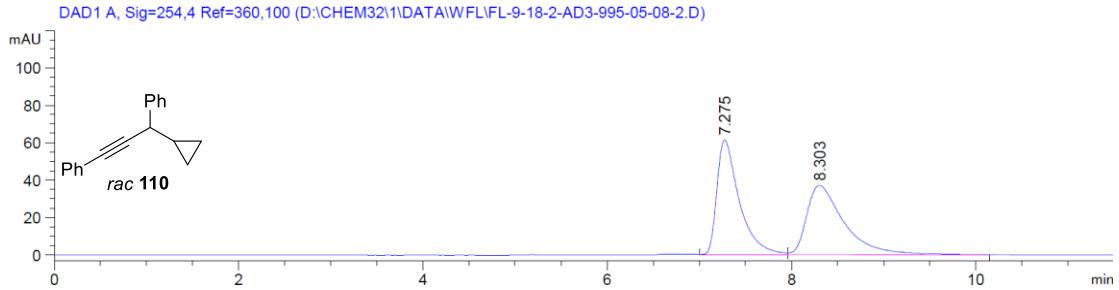
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.125	BV	0.2460	2534.44775	154.03815	49.5753
2	13.681	MM R	0.3476	2577.87183	123.61256	50.4247
Totals :				5112.31958	277.65070	



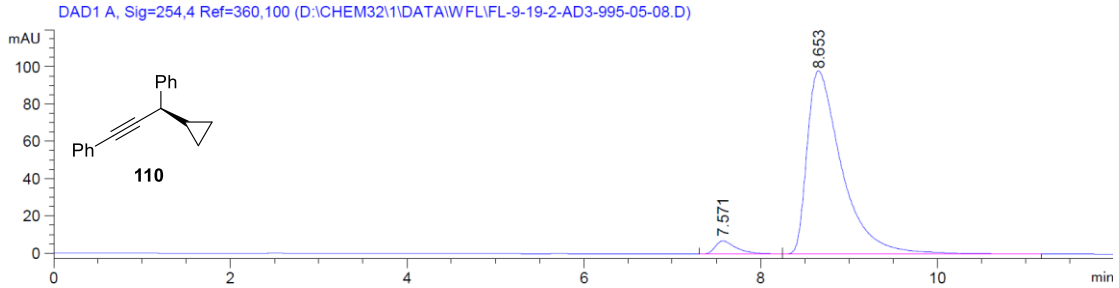
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.167	MM R	0.2757	15.74029	9.51566e-1	1.5755
2	13.729	BB	0.3180	983.30457	46.26448	98.4245
Totals :				999.04486	47.21604	



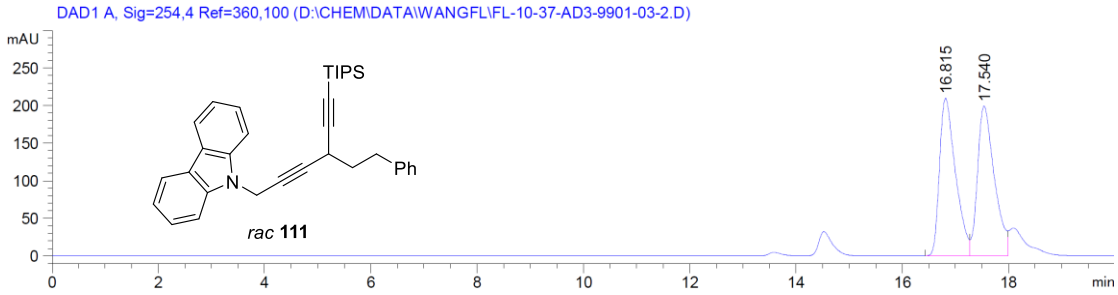
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.275	BV	0.2485	1029.10706	61.10640	49.5568
2	8.303	MF R	0.4722	1047.51550	36.97319	50.4432



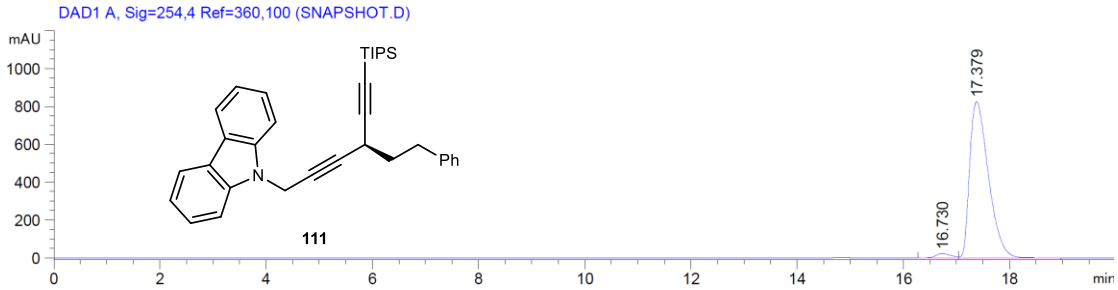
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.571	BB	0.2430	114.50272	6.99561	4.0979
2	8.653	BB	0.4099	2679.67871	98.35485	95.9021
Totals :				2794.18143	105.35046	



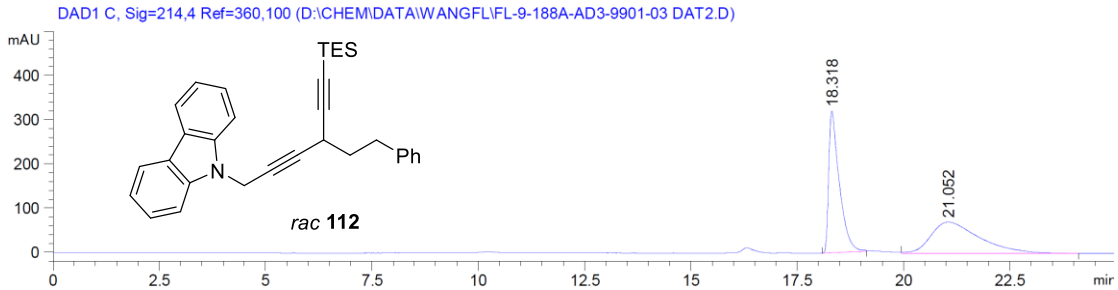
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.815	FM R	0.3491	4400.22559	210.10132	49.9717
2	17.540	VV	0.3256	4405.21094	199.49884	50.0283
Totals :				8805.43652	409.60016	



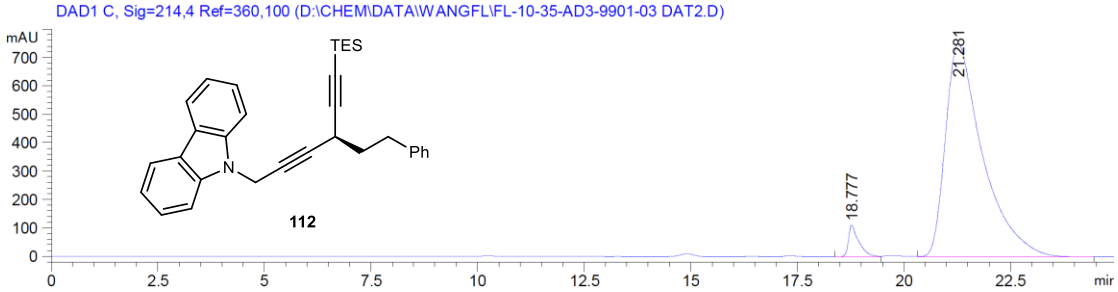
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.730	BV	0.2964	446.41916	22.80643	2.1613
2	17.379	VB	0.3820	2.02083e4	824.34442	97.8387
Totals :				2.06547e4	847.15085	



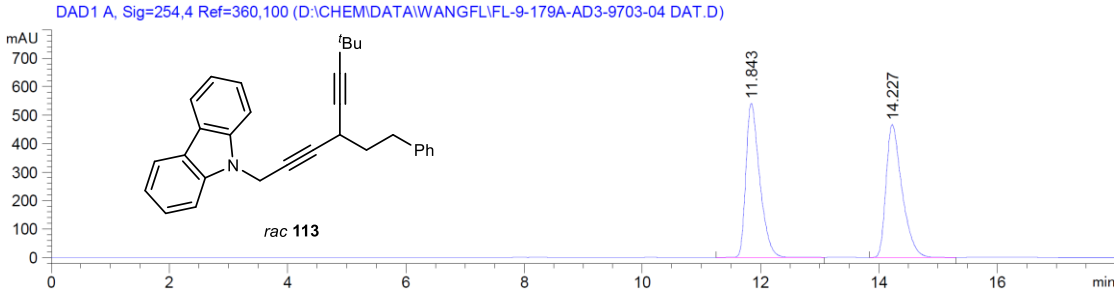
Signal 2: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.318	MM R	0.2889	5556.76270	320.52151	50.2187
2	21.052	VB	1.1245	5508.36865	70.12117	49.7813
Totals :				1.10651e4	390.64268	



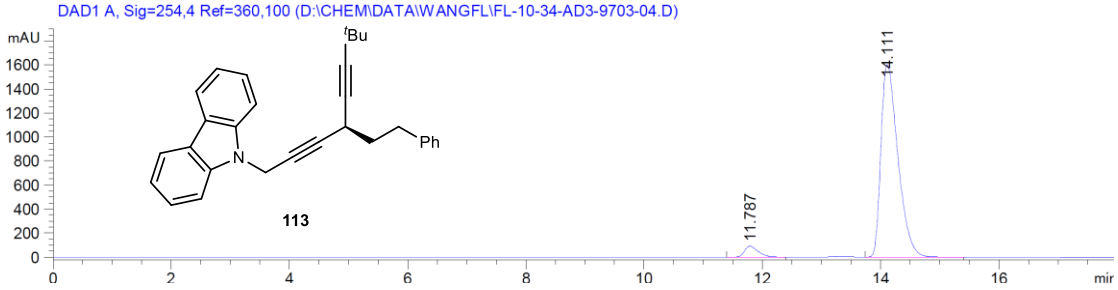
Signal 2: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.777	BV	0.2370	1886.52405	111.70656	3.9817
2	21.281	VB	0.8778	4.54928e4	749.83270	96.0183
Totals :				4.73794e4	861.53926	



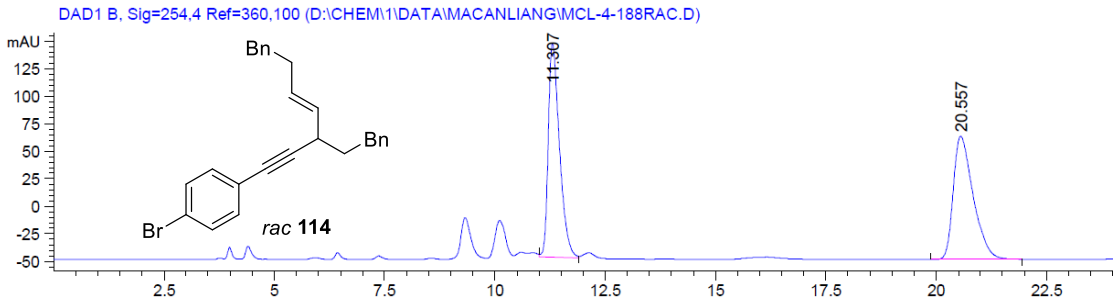
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.843	BV	0.2454	8780.37598	540.96216	50.0544
2	14.227	BB	0.2794	8761.29297	465.97086	49.9456
Totals :				1.75417e4	1006.93301	



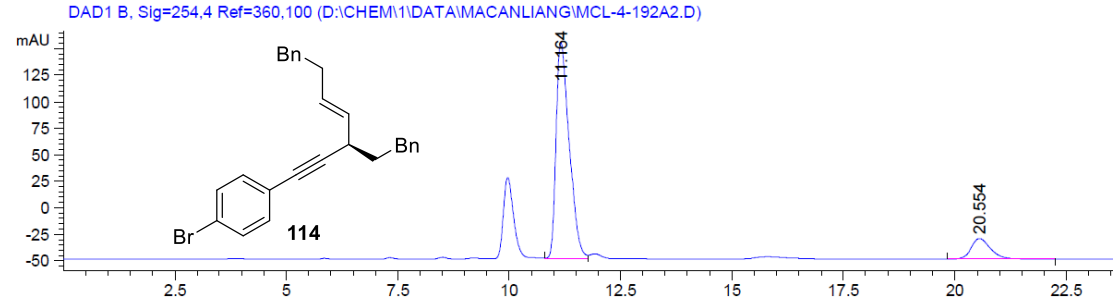
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.787	BV	0.2447	1479.19055	91.46500	4.4295
2	14.111	BV	0.3044	3.19148e4	1602.15845	95.5705
Totals :				3.33940e4	1693.62345	



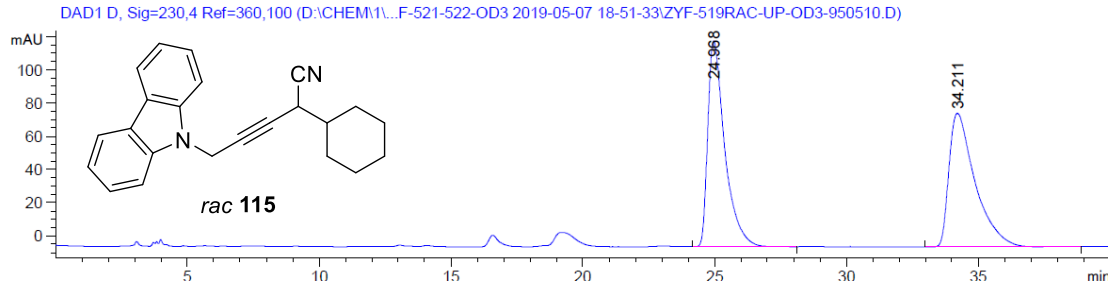
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.307	VV	0.2703	3427.28540	193.85973	49.3595
2	20.557	BV	0.4749	3516.22485	111.82334	50.6405
Totals :				6943.51025	305.68307	



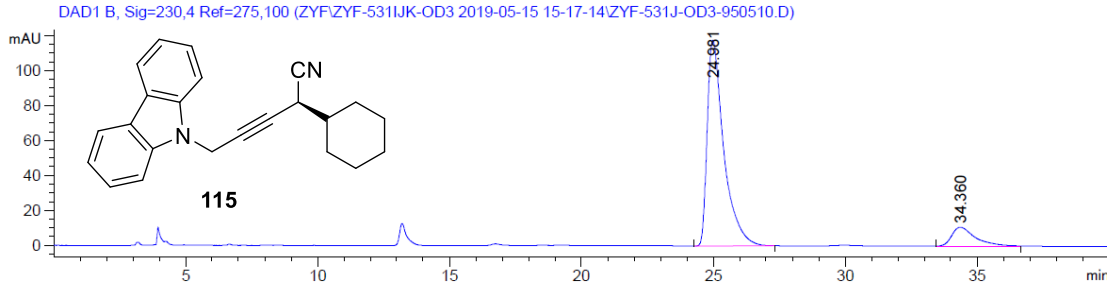
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.164	VV	0.3118	4199.09766	204.27986	87.7384
2	20.554	VV	0.4650	586.83386	19.39582	12.2616
Totals :				4785.93152	223.67568	



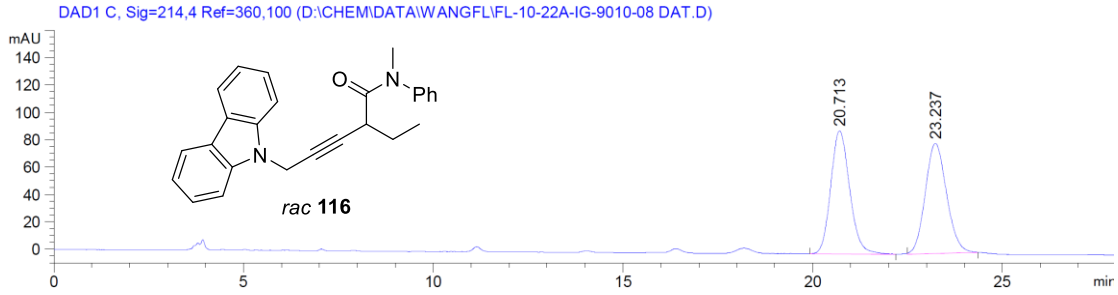
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.968	VV	0.6702	5545.03955	123.88957	50.0653
2	34.211	BB	1.0192	5530.56885	80.32954	49.9347
Totals :				1.10756e4	204.21911	



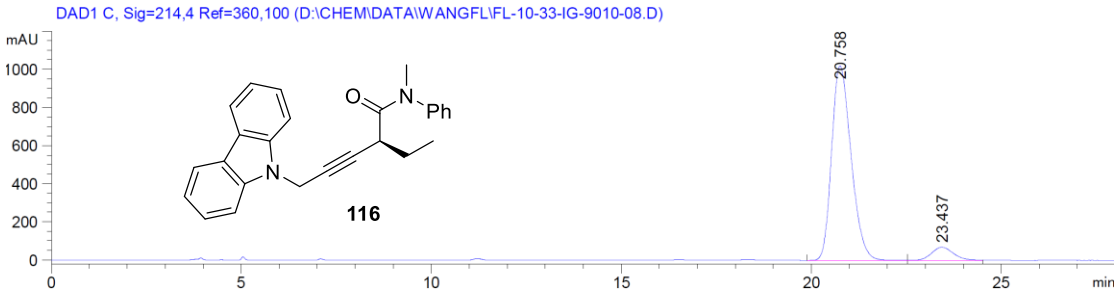
Signal 2: DAD1 B, Sig=230,4 Ref=275,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.981	BB	0.6529	5117.39648	117.77612	88.4608
2	34.360	BB	0.8152	667.53156	10.85860	11.5392
Totals :				5784.92804	128.63471	



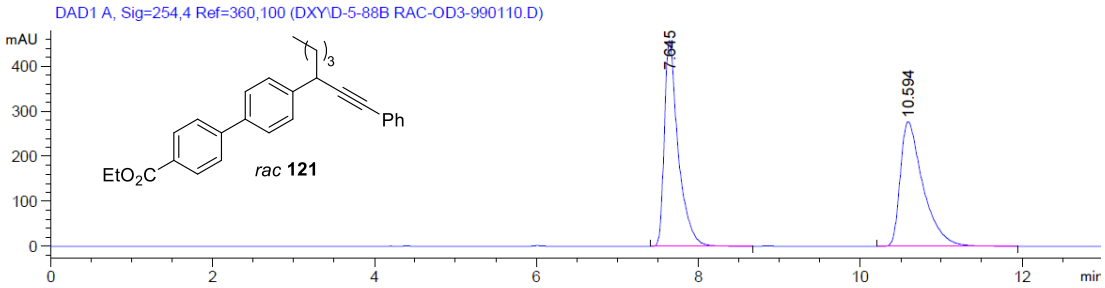
Signal 2: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.713	BB	0.5408	3119.88599	89.92107	49.7442
2	23.237	MM R	0.6521	3151.97656	80.56358	50.2558
Totals :				6271.86255	170.48465	



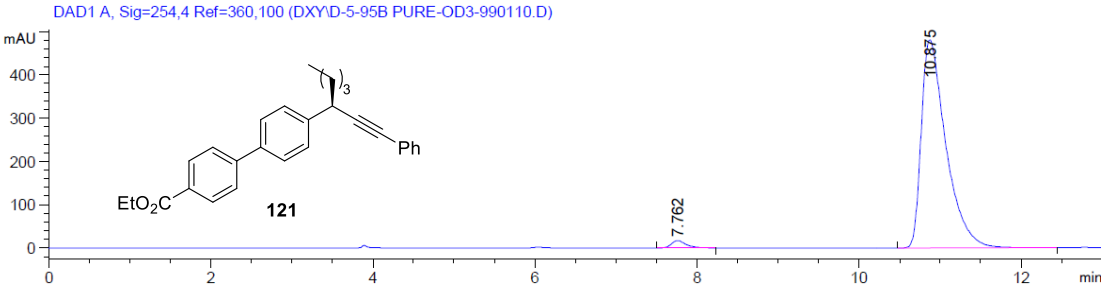
Signal 2: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.758	BV	0.5540	3.63495e4	1019.43213	92.8633
2	23.437	MF R	0.6735	2793.50098	69.12454	7.1367
Totals :				3.91430e4	1088.55667	



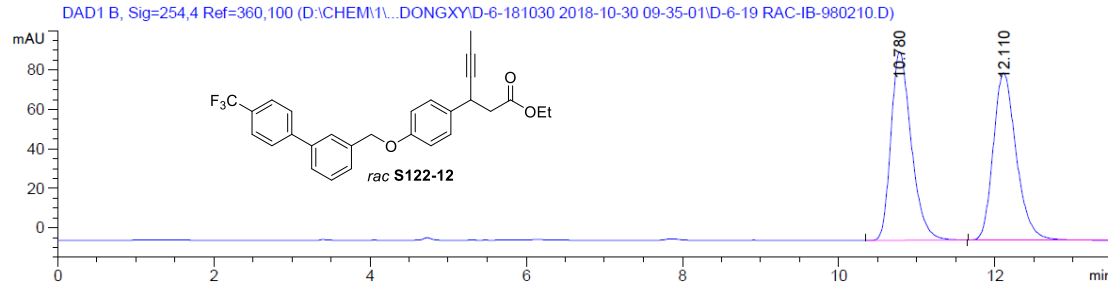
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.645	BB	0.1744	5424.28223	457.11203	49.9918
2	10.594	BB	0.2909	5426.07178	276.57697	50.0082
Totals :				1.08504e4	733.68900	



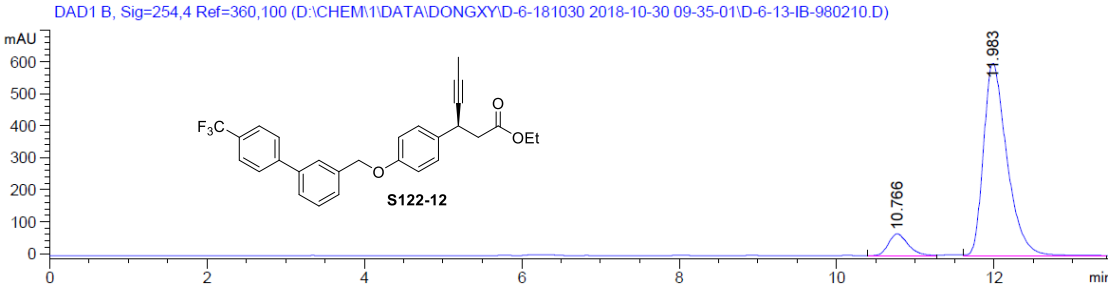
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.762	BB	0.1893	211.64348	16.75782	2.0454
2	10.875	BB	0.3160	1.01358e4	480.69107	97.9546
Totals :				1.03475e4	497.44889	



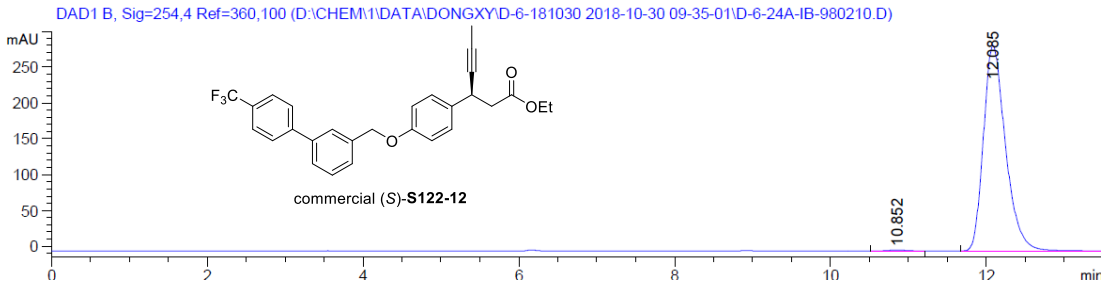
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.780	BB	0.2755	1732.62378	95.55478	49.8964
2	12.110	BB	0.3152	1739.81921	84.84905	50.1036



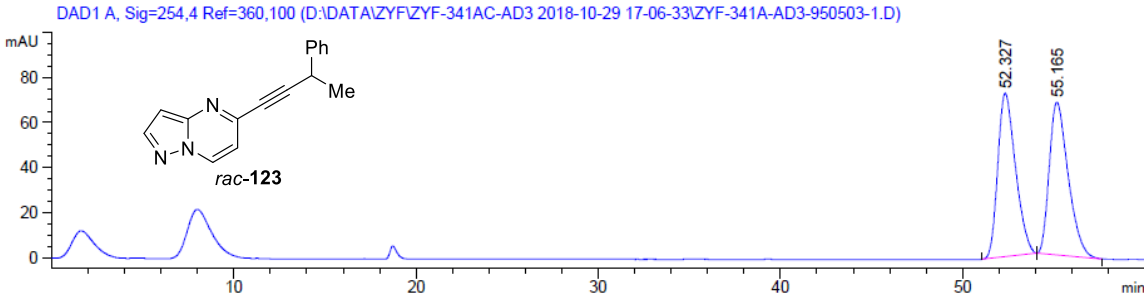
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.766	BV	0.2644	1174.35913	67.68858	8.6326
2	11.983	VB	0.3107	1.24295e4	602.48096	91.3674
Totals :				1.36038e4	670.16953	



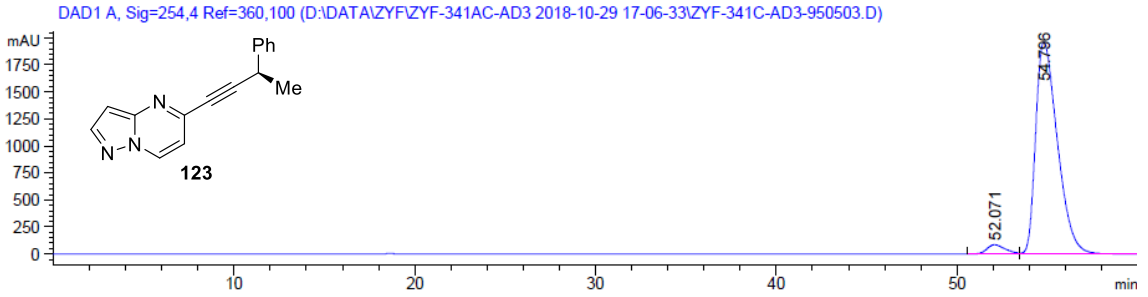
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.852	MM R	0.2807	24.54374	1.45736	0.4327
2	12.085	MM R	0.3282	5647.03662	286.77472	99.5673



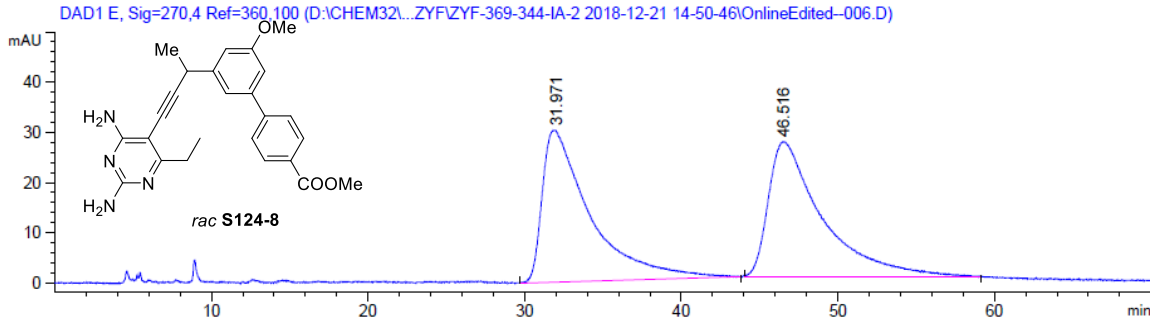
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.327	BB	1.0174	4901.61475	72.44415	50.0276
2	55.165	BB	1.0676	4896.20459	67.87166	49.9724
Totals :				9797.81934	140.31581	



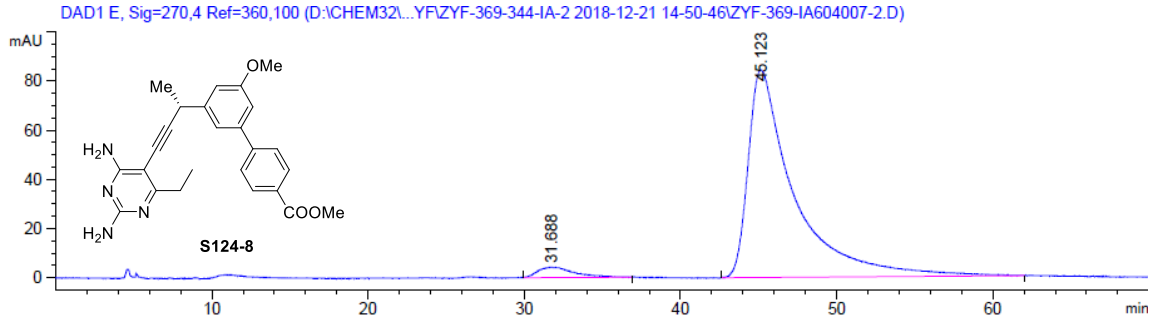
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.071	BV	1.0748	6052.77002	85.61668	3.5671
2	54.796	VBA	1.2369	1.63630e5	1958.19946	96.4329
Totals :				1.69682e5	2043.81615	



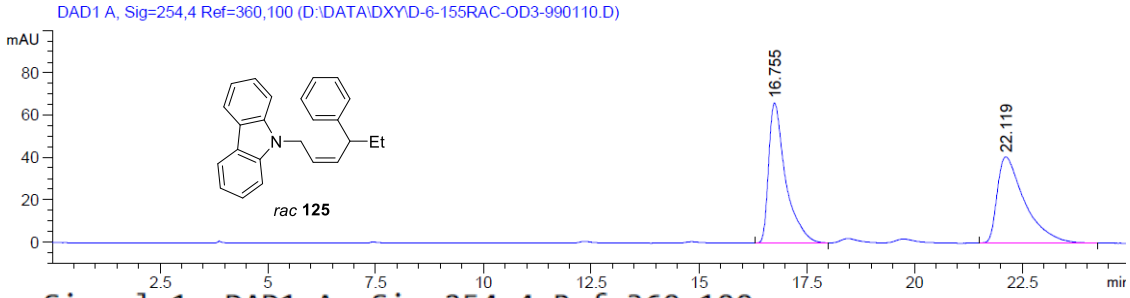
Signal 5: DAD1 E, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.971	MM R	3.5332	6422.60840	30.29618	50.0799
2	46.516	MM R	3.9681	6402.11914	26.89009	49.9201
Totals :				1.28247e4	57.18626	



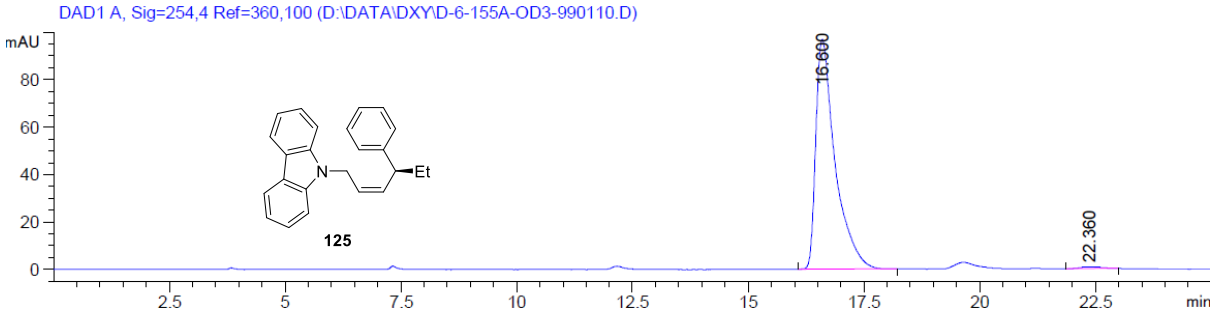
Signal 5: DAD1 E, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.688	MM R	2.7067	684.36041	4.21393	3.8116
2	45.123	MM R	3.4092	1.72702e4	84.42842	96.1884
Totals :				1.79545e4	88.64235	



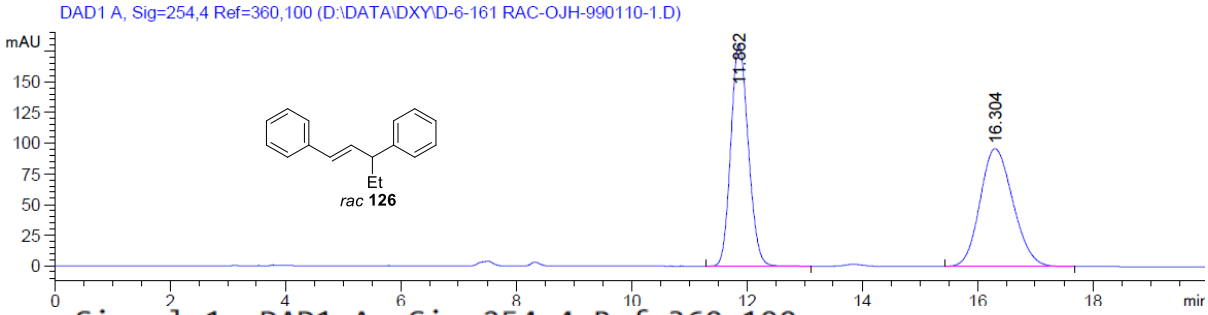
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.755	BB	0.4048	1808.71960	66.20146	50.1330
2	22.119	BB	0.6372	1799.12537	40.74022	49.8670
Totals :				3607.84497	106.94168	



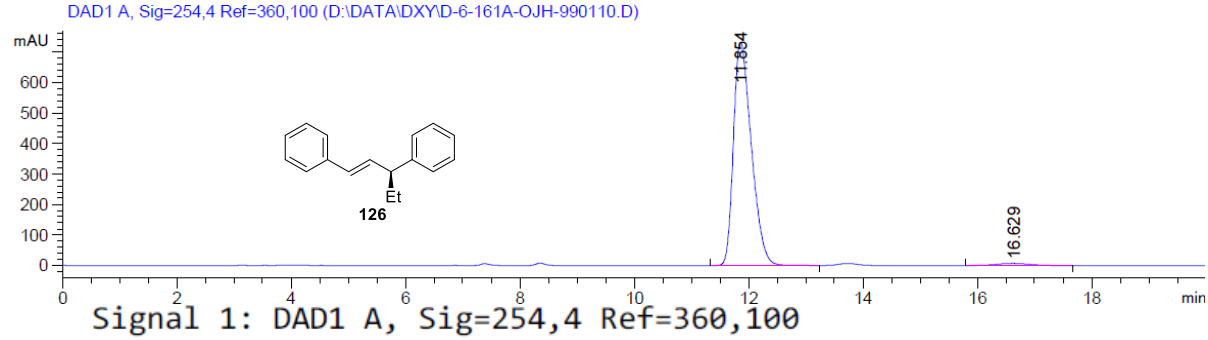
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.600	BB	0.4261	2808.86255	96.92719	99.1433
2	22.360	MM R	0.5560	24.27226	7.27569e-1	0.8567
Totals :				2833.13481	97.65475	



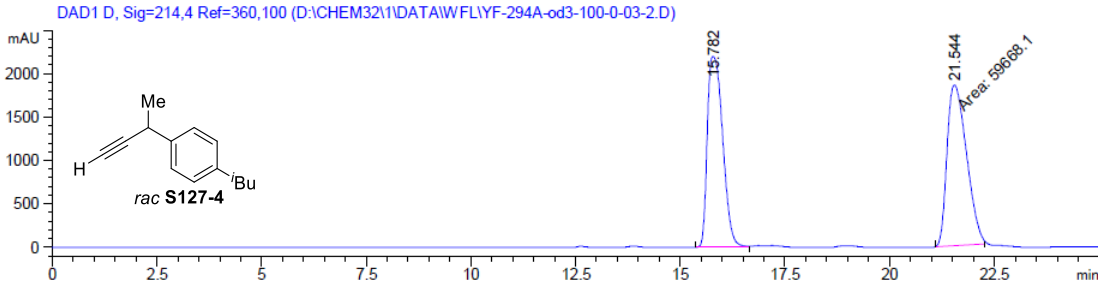
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.862	BB	0.3270	3815.18091	181.67833	50.0337
2	16.304	BB	0.6183	3810.04590	96.14732	49.9663
Totals :				7625.22681	277.82565	



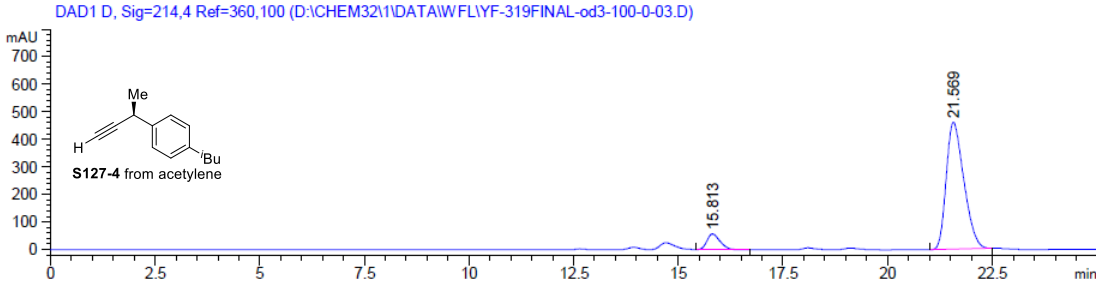
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.854	BB	0.3353	1.58935e4	732.05829	98.1452
2	16.629	BB	0.5571	300.36978	7.31411	1.8548
Totals :				1.61938e4	739.37240	



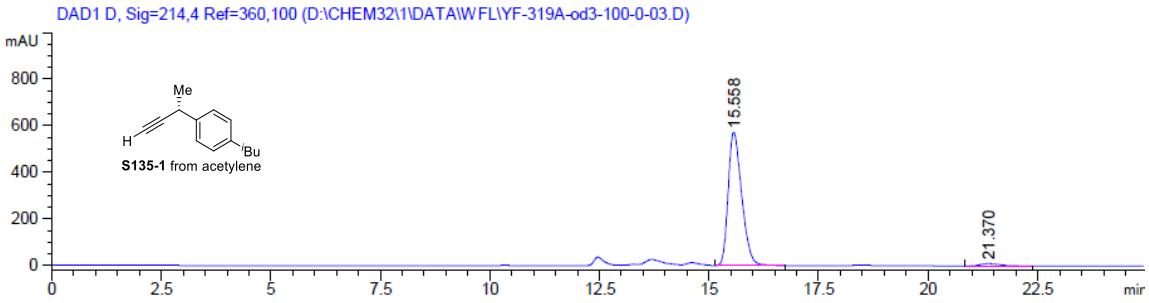
Signal 4: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.782	BV	0.4103	5.61162e4	2195.06421	48.4662
2	21.544	MM	0.5385	5.96681e4	1846.71960	51.5338
Totals :				1.15784e5	4041.78381	



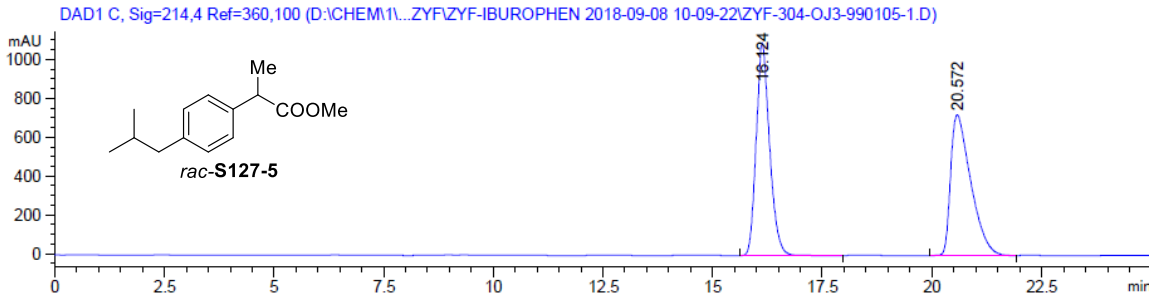
Signal 4: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.813	VB	0.3306	1258.59875	57.23086	8.5591
2	21.569	BB	0.4451	1.34463e4	459.89804	91.4409
Totals :				1.47049e4	517.12890	



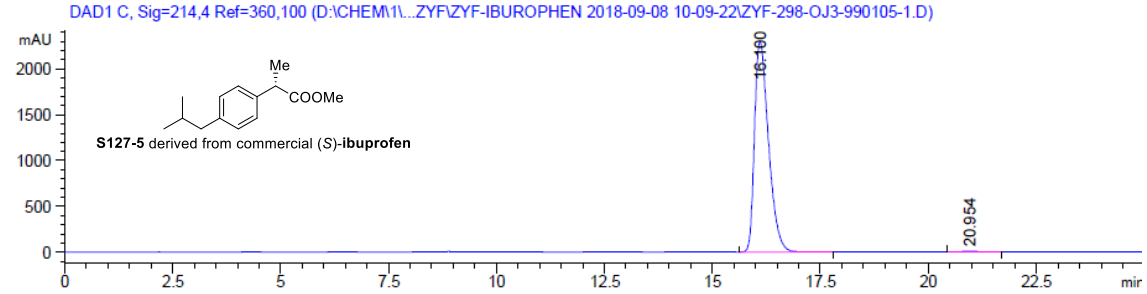
Signal 4: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.558	BB	0.3258	1.22469e4	572.04364	97.7744
2	21.370	BB	0.4269	278.77255	9.32173	2.2256
Totals :				1.25257e4	581.36537	



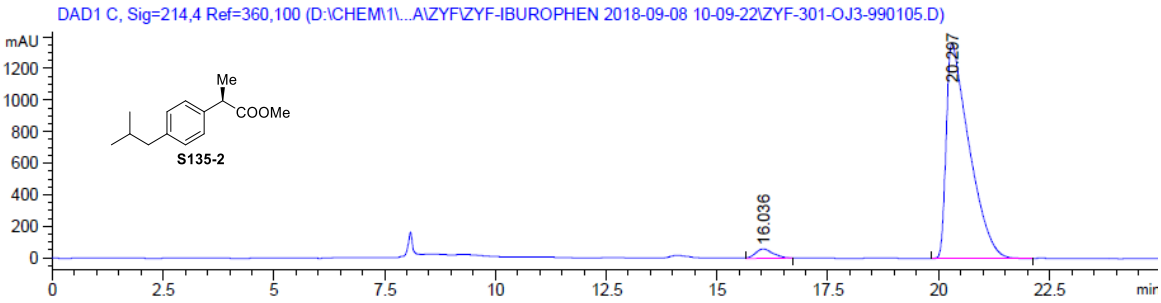
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.124	BB	0.3052	2.32092e4	1095.39001	49.9638
2	20.572	BB	0.4834	2.32429e4	726.20929	50.0362
Totals :				4.64520e4	1821.59930	



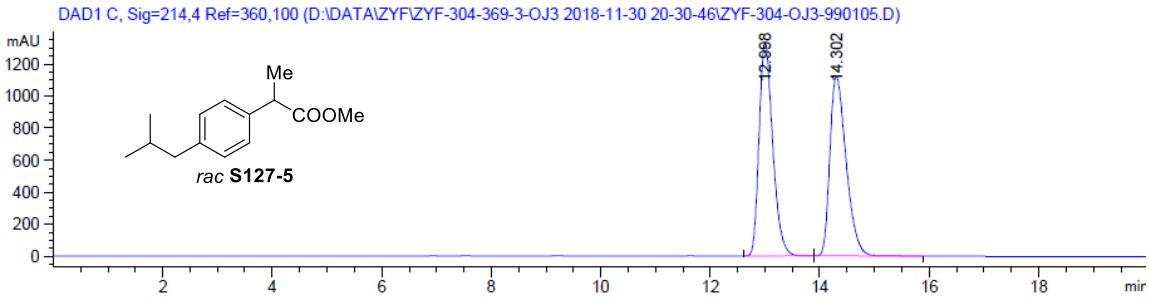
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.100	BB	0.3460	5.16688e4	2300.85547	99.6764
2	20.954	BB	0.4904	167.73508	5.28337	0.3236
Totals :				5.18366e4	2306.13884	



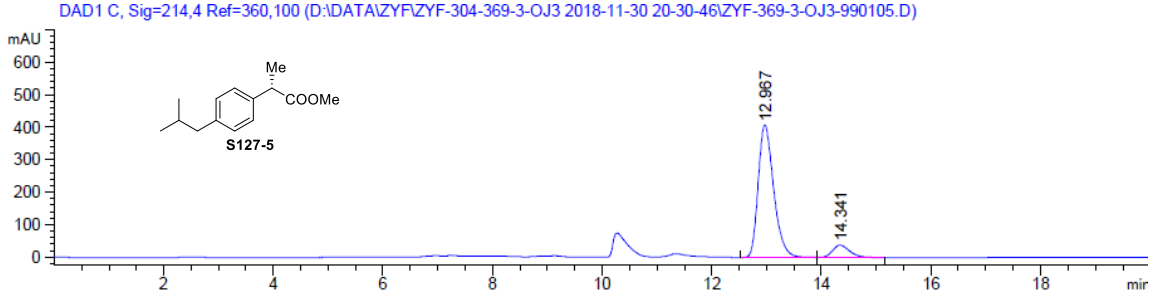
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.036	MM R	0.4527	1628.96680	59.97729	3.2245
2	20.297	BB	0.5090	4.88902e4	1361.31201	96.7755
Totals :				5.05192e4	1421.28930	



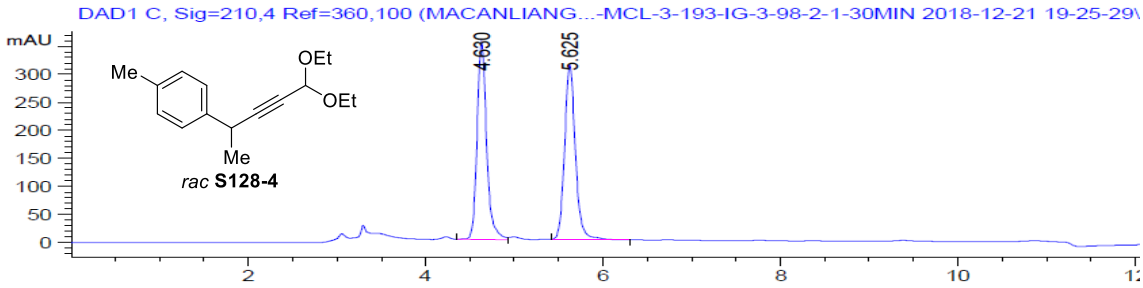
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.998	BB	0.2686	2.31393e4	1332.23669	50.0044
2	14.302	BB	0.3180	2.31352e4	1124.75562	49.9956
Totals :				4.62744e4	2456.99231	



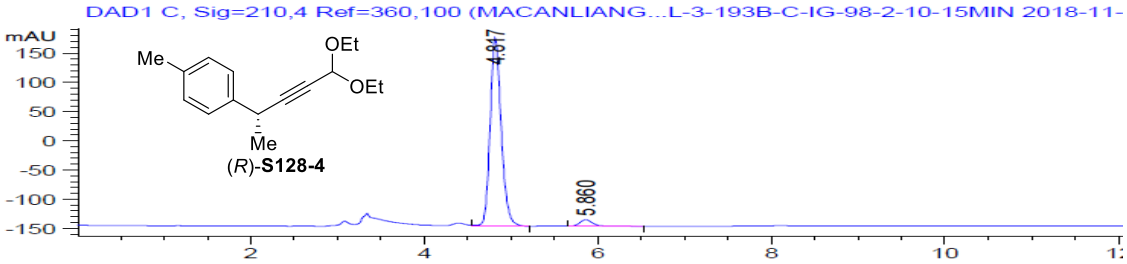
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.967	BB	0.3001	7968.88916	407.65662	90.8971
2	14.341	BB	0.3267	798.04718	37.73350	9.1029
Totals :				8766.93634	445.39011	



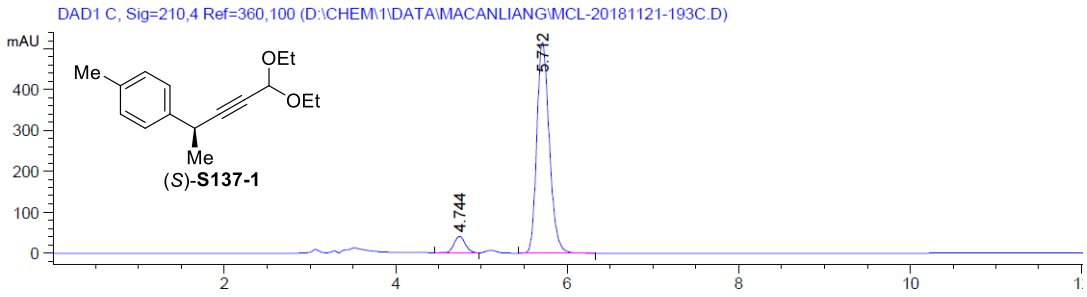
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.630	BV	0.1124	2622.88086	354.14059	49.6588
2	5.625	VB	0.1312	2658.92896	312.58624	50.3412
Totals :				5281.80981	666.72684	



Signal 3: DAD1 C, Sig=210,4 Ref=360,100

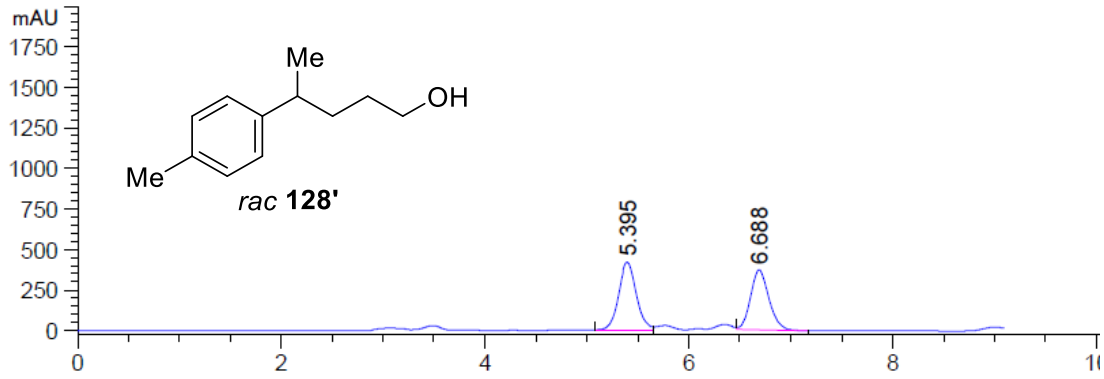
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.817	VB	0.1383	2886.07617	322.93533	96.3024
2	5.860	BB	0.1554	110.81418	10.82364	3.6976
Totals :				2996.89035	333.75897	



Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.744	BV	0.1428	370.42572	40.45568	6.6493
2	5.712	BB	0.1577	5200.47949	515.53857	93.3507
Totals :				5570.90521	555.99425	

DAD1 C, Sig=210,4 Ref=360,100 (D:\CHEM\1\DATA\MACANLIANG\190104-4-61-2.D)

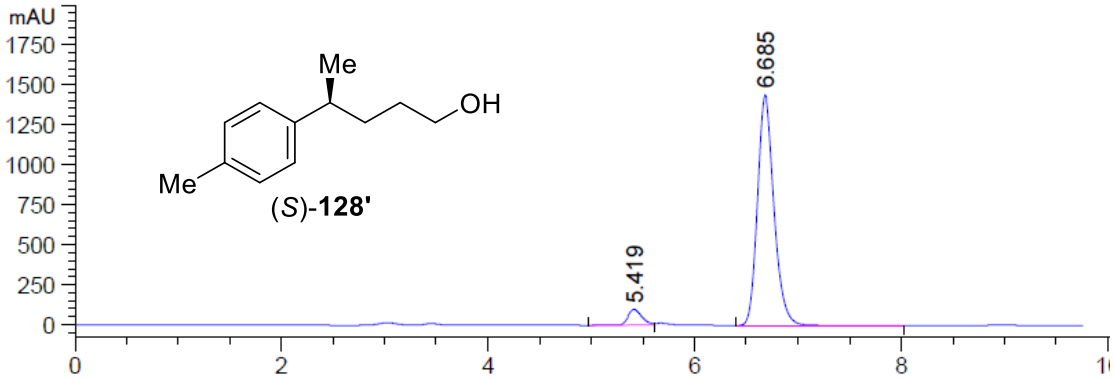


rac **128'**

Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.395	VV	0.1850	5064.30518	418.99078	51.9161
2	6.688	VB	0.1951	4690.48145	371.94617	48.0839
Totals :				9754.78662	790.93695	

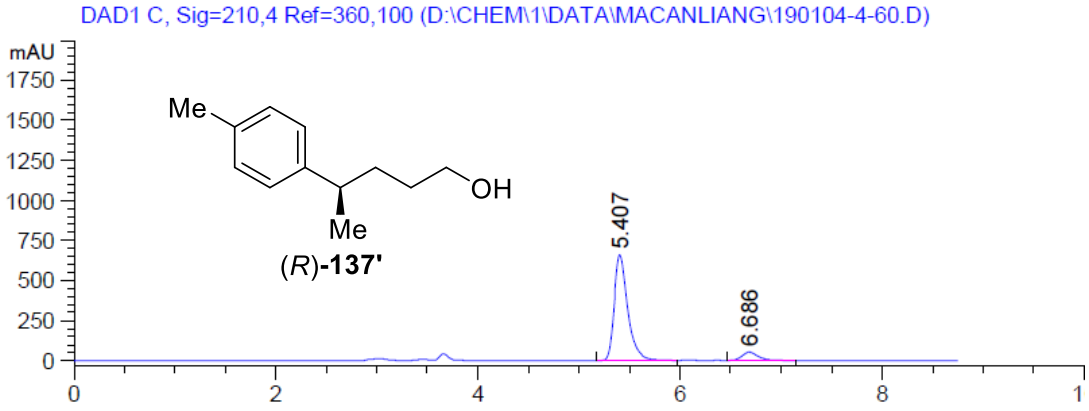
DAD1 C, Sig=210,4 Ref=360,100 (D:\CHEM\1\DATA\MACANLIANG\190104-4-58-2.D)



(*S*)-**128'**

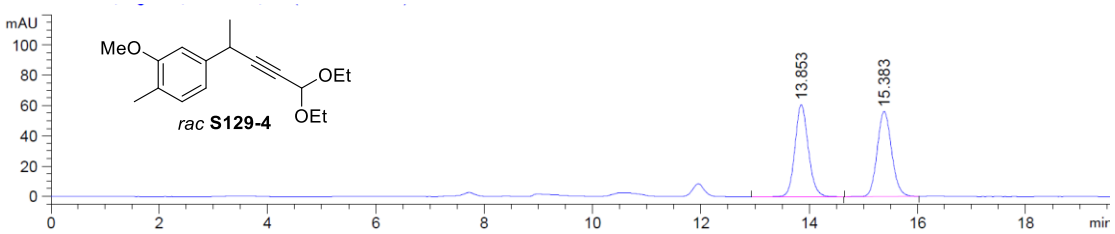
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.419	BV	0.1429	924.92639	99.05288	5.4365
2	6.685	BB	0.1723	1.60884e4	1440.01318	94.5635
Totals :				1.70133e4	1539.06606	



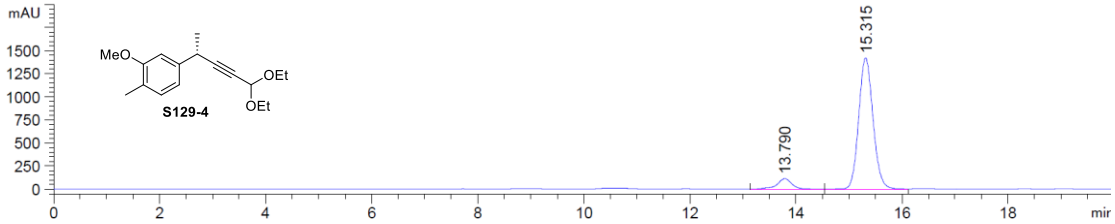
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.407	BV	0.1410	6158.89355	659.19073	91.4108
2	6.686	BB	0.1673	578.70392	53.04985	8.5892
Totals :				6737.59747	712.24059	



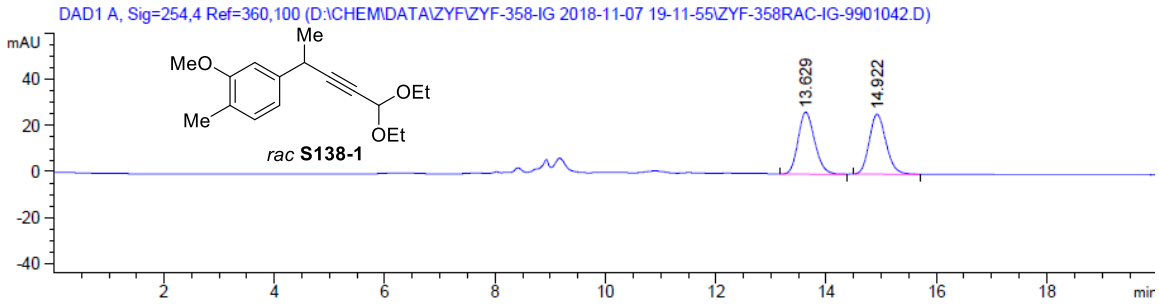
Signal 2: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.853	BB	0.2652	1047.07214	60.70442	50.3369
2	15.383	BB	0.2826	1033.05701	56.16744	49.6631
Totals :				2080.12915	116.87186	



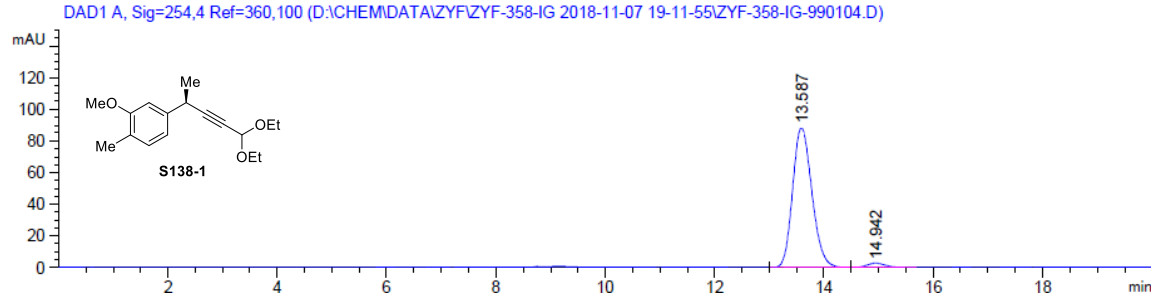
Signal 2: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.790	FM R	0.3285	2259.82813	114.65798	7.8044
2	15.315	BV	0.2953	2.66958e4	1419.98499	92.1956
Totals :				2.89557e4	1534.64297	



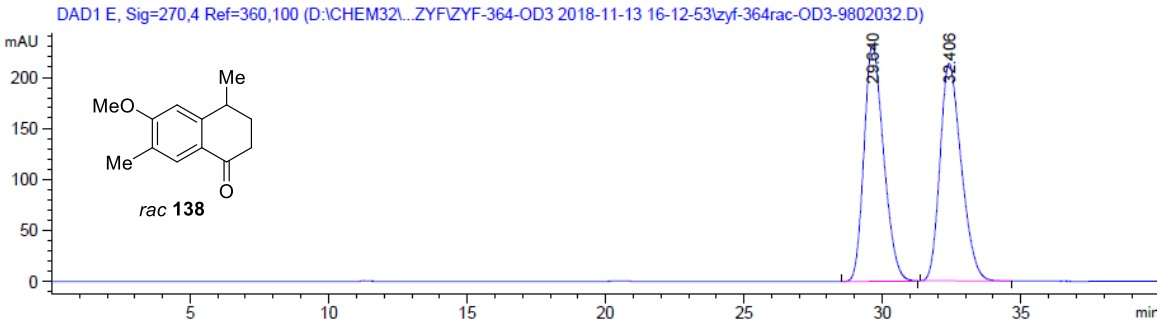
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.629	BB	0.3255	559.35809	26.79470	50.2263
2	14.922	MM R	0.3554	554.31683	25.99382	49.7737
Totals :				1113.67493	52.78853	



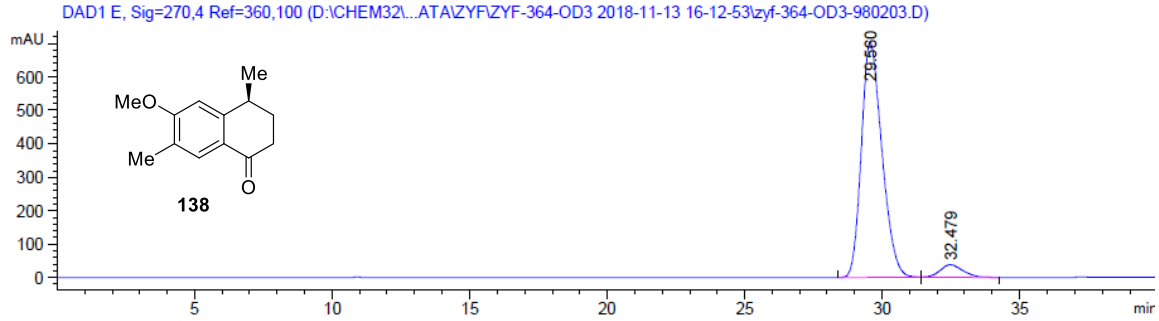
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.587	BB	0.3810	2161.59302	88.48470	97.1823
2	14.942	BB	0.3605	62.67313	2.66418	2.8177
Totals :				2224.26614	91.14888	



Signal 5: DAD1 E, Sig=270,4 Ref=360,100

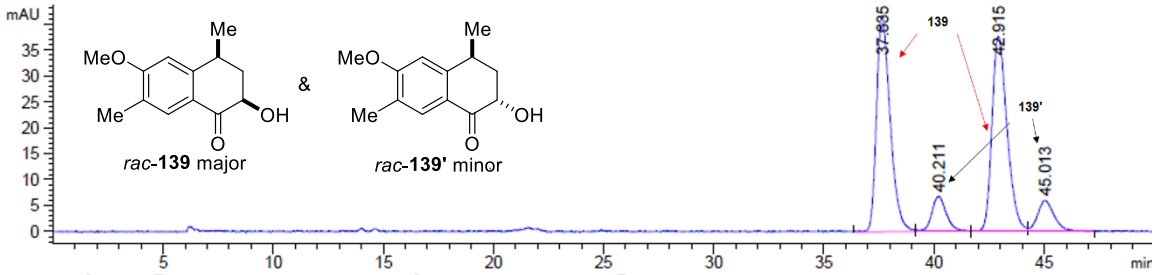
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.640	BB	0.7394	1.13860e4	231.65884	49.9846
2	32.406	BB	0.8116	1.13930e4	213.13380	50.0154
Totals :				2.27790e4	444.79265	



Signal 5: DAD1 E, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.560	BB	0.7883	3.65100e4	702.49487	94.5256
2	32.479	BB	0.7989	2114.44141	37.09962	5.4744
Totals :				3.86245e4	739.59449	

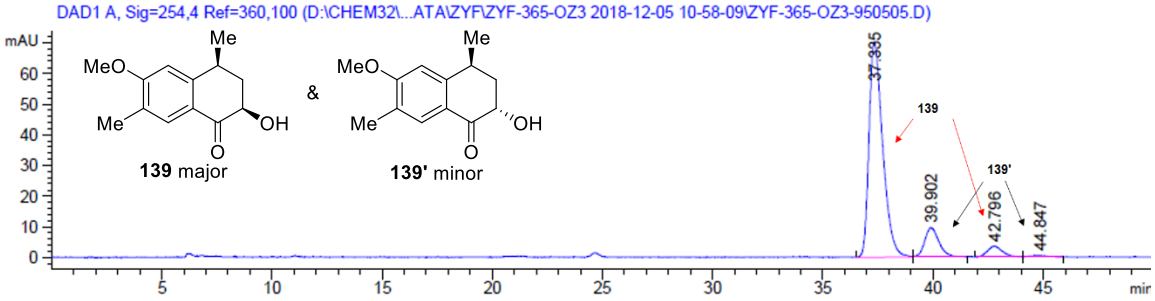
DAD1 A, Sig=254,4 Ref=360,100 (D:\CHEM32\...ZYF\ZYF-365-OZ3 2018-12-05 10-58-09\ZYF-365RAC-OZ3-9505052.D)



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

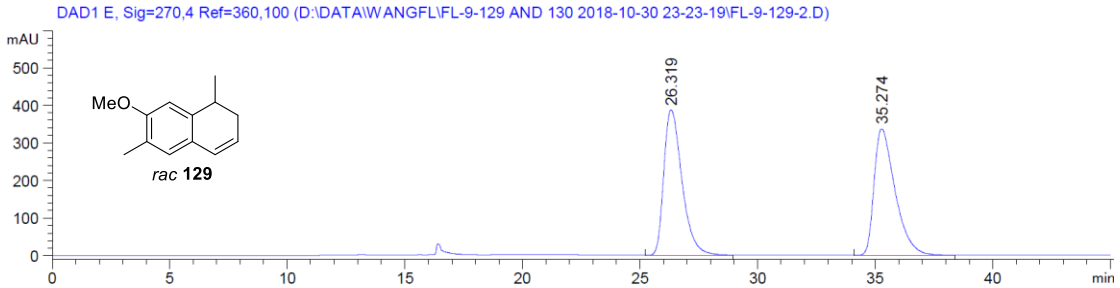
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.635	BV	0.6444	1799.26563	41.61333	42.6211
2	40.211	VB	0.6589	313.35535	6.73366	7.4228
3	42.915	BV	0.7167	1791.30078	37.53936	42.4324
4	45.013	VB	0.7039	317.62006	5.90146	7.5238
Totals :				4221.54181	91.78781	

DAD1 A, Sig=254,4 Ref=360,100 (D:\CHEM32\...ATA\ZYF\ZYF-365-OZ3 2018-12-05 10-58-09\ZYF-365-OZ3-950505.D)



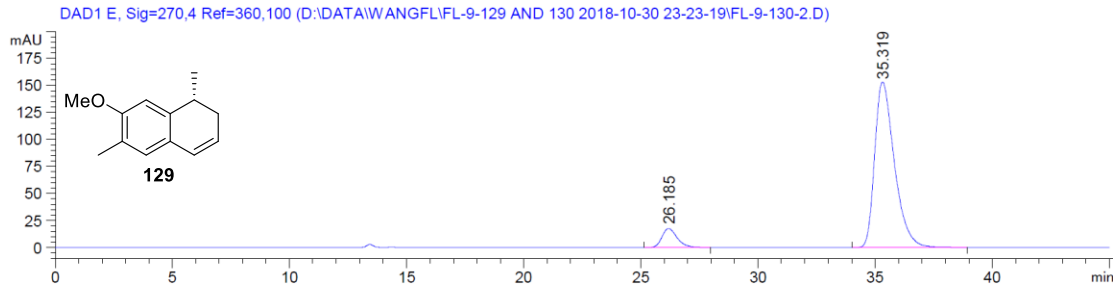
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.335	VV	0.6500	3023.52832	70.27174	82.4961
2	39.902	VB	0.6812	438.57040	9.52470	11.9663
3	42.796	BV	0.5886	172.92241	3.65070	4.7181
4	44.847	VB	0.6480	30.03448	5.57949e-1	0.8195
Totals :				3665.05561	84.00509	



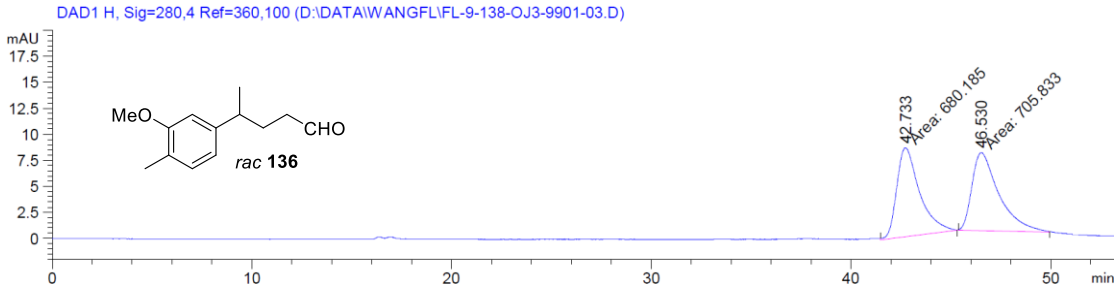
Signal 5: DAD1 E, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.319	MF R	0.8984	2.08918e4	387.58243	49.9463
2	35.274	MF R	1.0348	2.09367e4	337.22458	50.0537
Totals :				4.18285e4	724.80701	



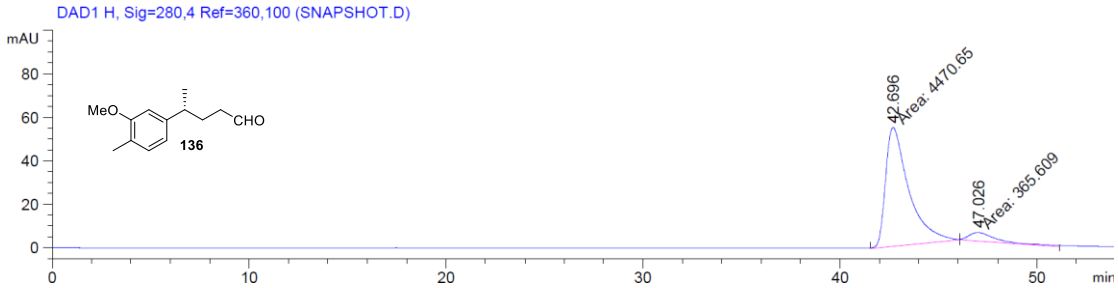
Signal 5: DAD1 E, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.185	MF R	0.7615	807.29089	17.66849	8.2508
2	35.319	MF R	0.9770	8977.05664	153.13568	91.7492
Totals :				9784.34753	170.80417	



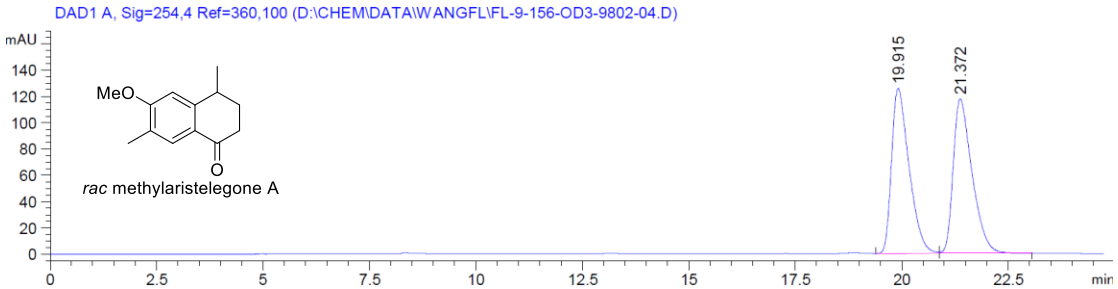
Signal 8: DAD1 H, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.733	MM	1.3271	680.18494	8.54247	49.0747
2	46.530	MM	1.5662	705.83331	7.51125	50.9253
Totals :				1386.01825	16.05372	



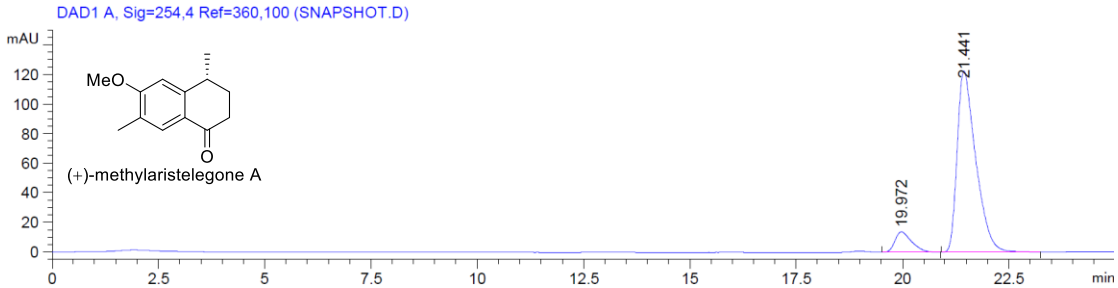
Signal 8: DAD1 H, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.696	MM	1.3630	4470.64648	54.66646	92.4403
2	47.026	MM	1.5909	365.60876	3.83033	7.5597
Totals :				4836.25525	58.49678	



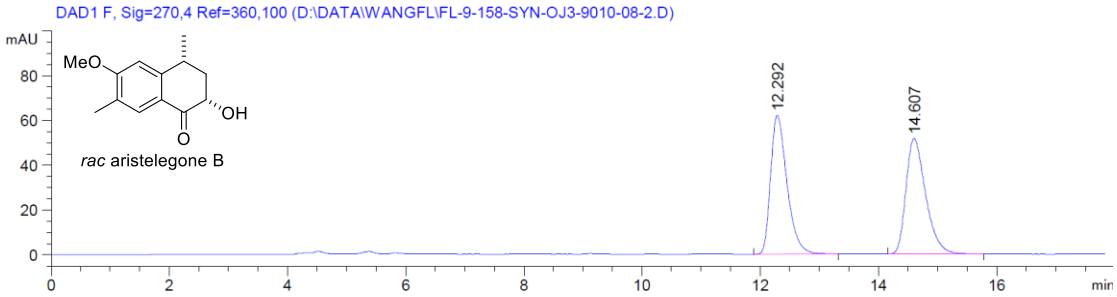
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.915	BV	0.4280	3594.52490	125.57507	49.7701
2	21.372	VB	0.4579	3627.73047	117.60072	50.2299
Totals :				7222.25537	243.17579	



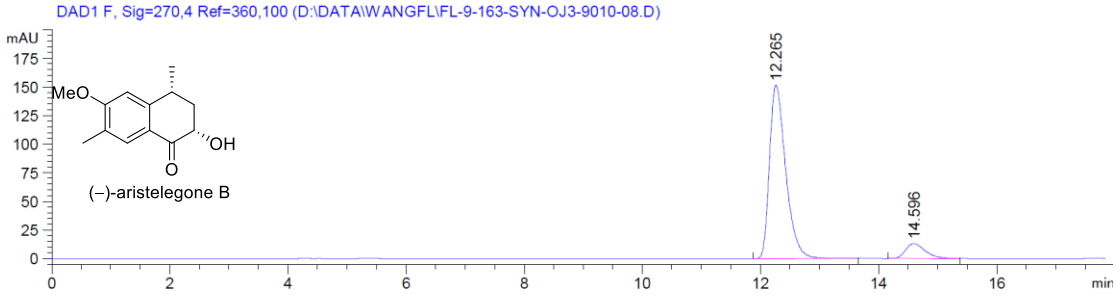
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.972	BB	0.4055	379.89069	13.87387	9.2462
2	21.441	BB	0.4504	3728.70532	122.73405	90.7538
Totals :				4108.59601	136.60791	



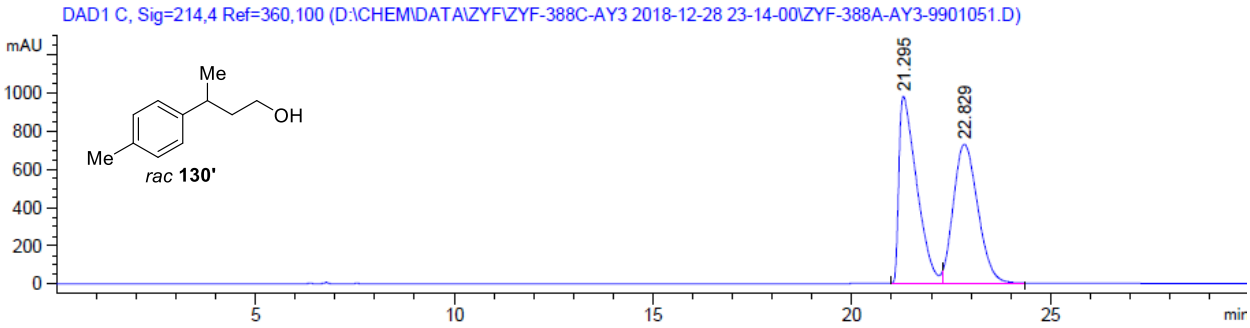
Signal 6: DAD1 F, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.292	MF R	0.3219	1194.94751	61.87358	50.1761
2	14.607	MF R	0.3850	1186.56152	51.36784	49.8239
Totals :				2381.50903	113.24142	



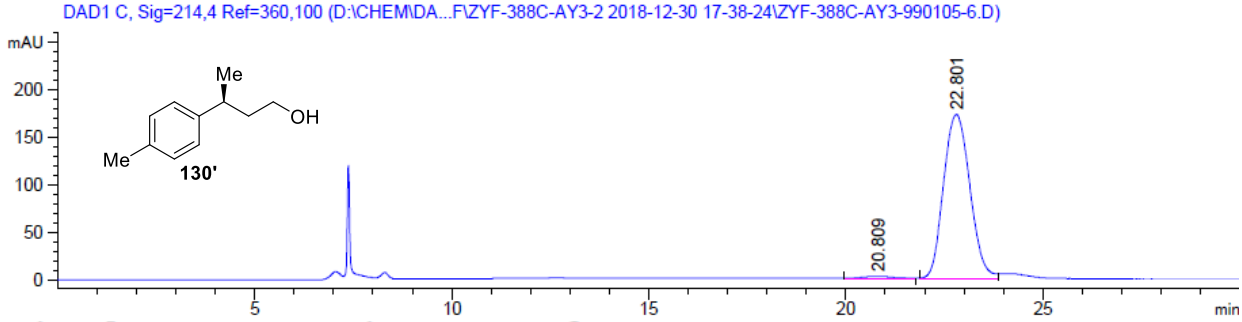
Signal 6: DAD1 F, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.265	BB	0.2924	2886.53394	151.44171	90.6051
2	14.596	MF R	0.3822	299.30759	13.05281	9.3949
Totals :				3185.84152	164.49452	



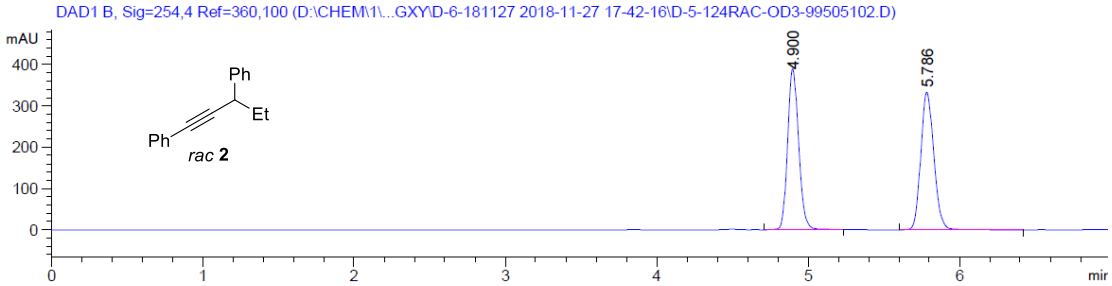
Signal 2: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.295	MF R	0.5162	3.03759e4	980.84656	49.5674
2	22.829	FM R	0.7099	3.09061e4	725.62122	50.4326
Totals :				6.12819e4	1706.46777	



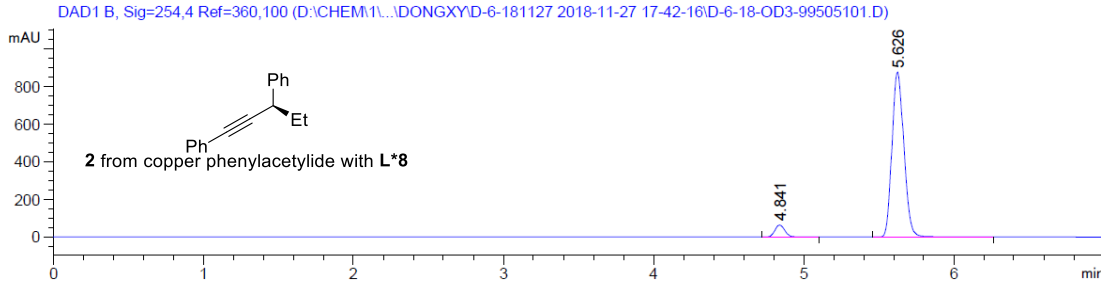
Signal 2: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.809	BB	0.5776	85.75143	1.83379	1.0504
2	22.801	MF R	0.7793	8077.85498	172.75610	98.9496
Totals :				8163.60641	174.58990	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.900	BV	0.0793	1985.84436	390.98450	49.7979
2	5.786	BB	0.0940	2001.96509	333.73199	50.2021
Totals :				3987.80945	724.71649	



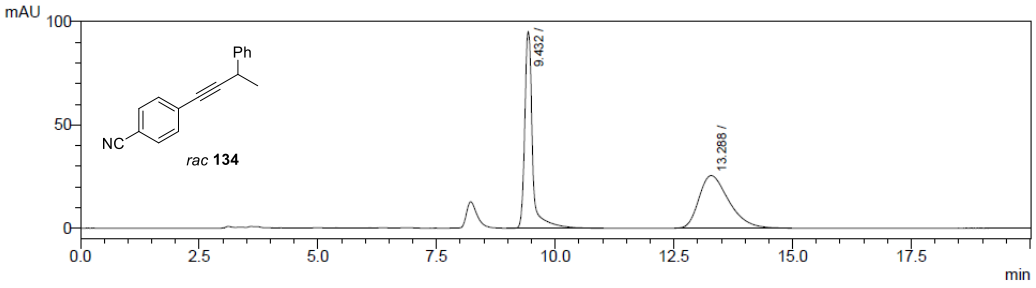
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.841	BB	0.0731	300.78320	63.71975	5.8303
2	5.626	BV	0.0866	4858.16064	877.14264	94.1697
Totals :				5158.94385	940.86239	

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	: lzl-7-137-1re ASH 90-10 1ml		Sample ID : lzl-7-137-1
Vial#	: 1-4	Injection Volume	: 5 uL
Date Acquired	: 2018/12/6 14:28:09	Acquired by	: System Administrator
Date Processed	: 2018/12/6 14:55:46	Modified by	: System Administrator

Data Filename : D:\LI ZHONGLIANG\lzl-7-137-1re ASH 90-10 1ml.lcd
Method Filename : D:\LI ZHONGLIANG\ASH 90-10 1ml 20 min.lcm
Batch Filename : D:\LSY\20181206\F41-s-IB-8020-1.0.lcb



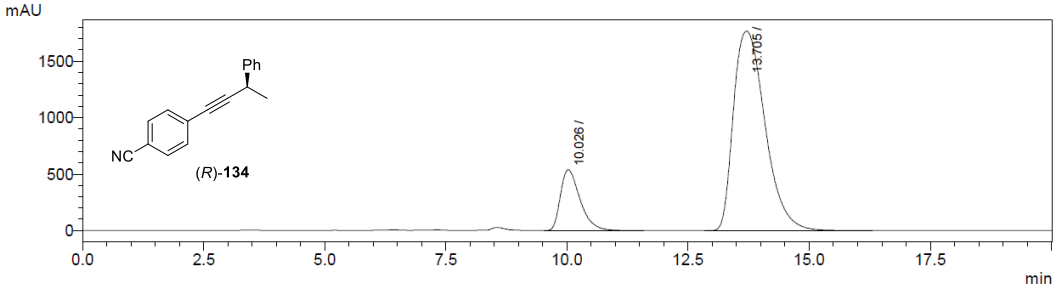
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.432	1082210	49.344
2	13.288	1110976	50.656
总计		2193186	100.000

==== Shimadzu LabSolutions Analysis Report ====

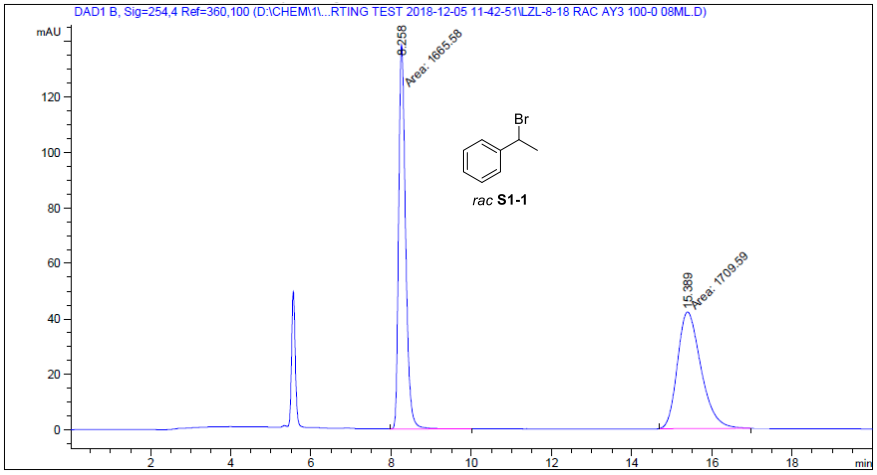
Sample Name	: lzl-7-137-2 ASH 90-10 1ml 20min		Sample ID : lzl-7-137
Vial#	: 1-2	Injection Volume	: 10 uL
Date Acquired	: 2018/9/20 20:08:56	Acquired by	: System Administrator
Date Processed	: 2018/12/5 15:13:57	Modified by	: System Administrator

Data Filename : D:\LI ZHONGLIANG\lzl-7-137-2 ASH 90-10 1ml 20min.lcd
Method Filename : D:\LI ZHONGLIANG\ASH 90-10 1ml 20 min.lcm
Batch Filename :



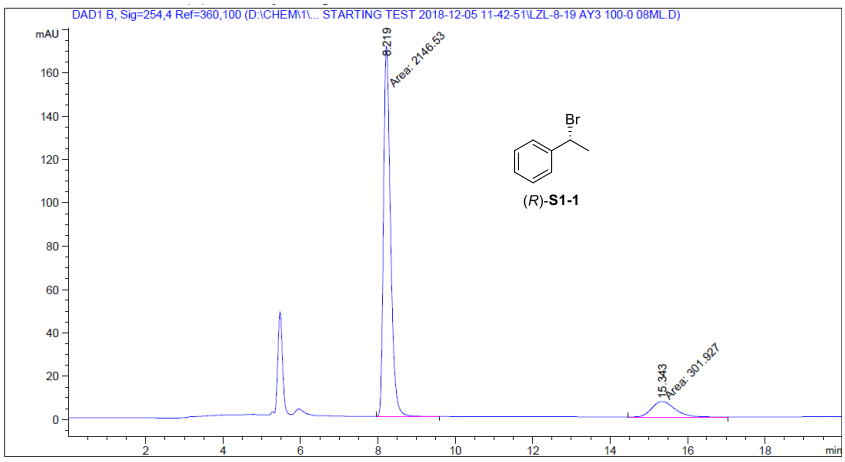
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.026	15172653	15.910
2	13.705	80192534	84.090
总计		95365188	100.000



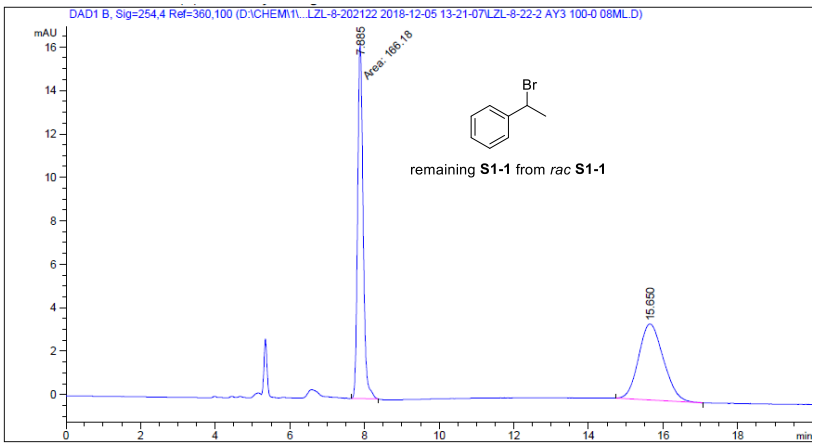
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	8.258	1	MM	1665.57874	138.41049	49.3480
2	15.389	1	MM	1709.59375	41.99697	50.6520



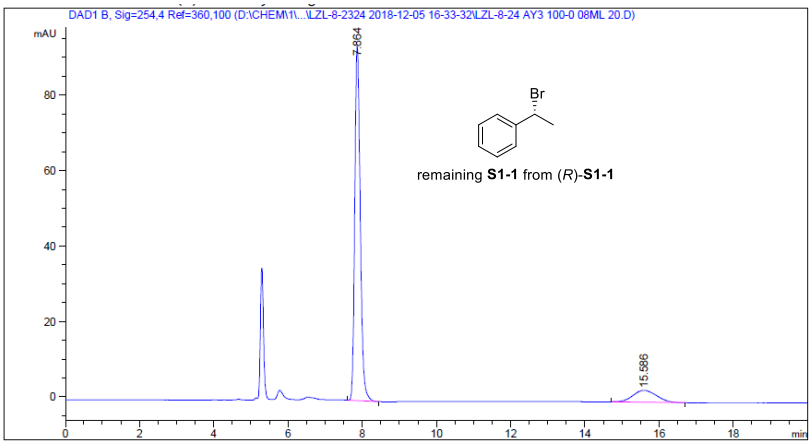
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	8.219	1	MM	2146.52734	170.89351	87.6687
2	15.343	1	MM	301.92722	7.21739	12.3313



Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.885	1	MM	166.17976	16.28563	50.7657
2	15.650	1	BB	161.16673	3.49884	49.2343

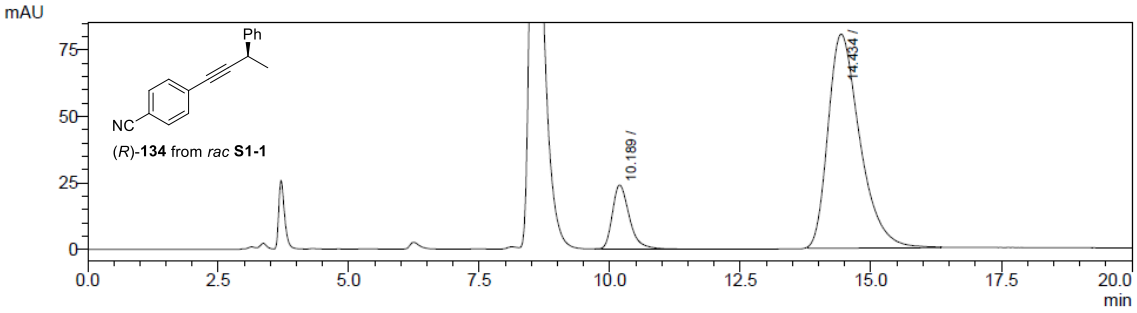


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.864	1	BB	968.83099	94.12112	87.5570
2	15.586	1	BB	137.68405	3.13706	12.4430

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	: lzl-8-22-2 ASH 90-10 1 ml 20min	Sample ID	: lzl-8-22-2 A
Vial#	: 1-5	Injection Volume	: 2 uL
Date Acquired	: 2018/12/5 16:19:16	Acquired by	: System Administrator
Date Processed	: 2018/12/5 18:47:02	Modified by	: System Administrator
Data Filename	: D:\LI ZHONGLIANG\lzl-8-22-2 ASH 90-10 1 ml 20min.lcd		
Method Filename	: D:\LI ZHONGLIANG\ASH 90-10 1ml 20min.lcm		
Batch Filename	:		

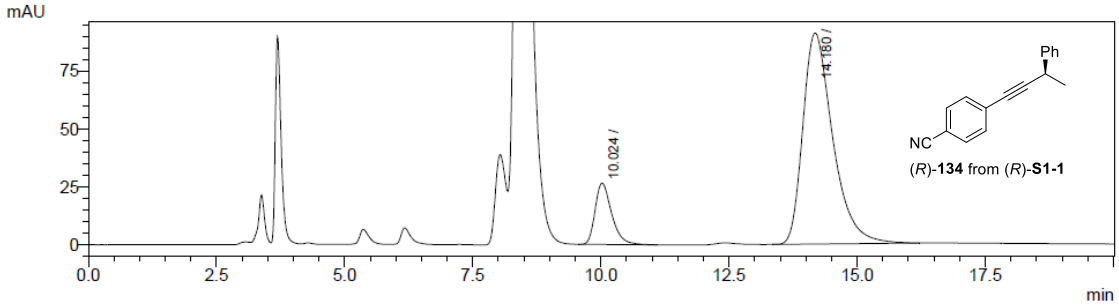


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.189	543169	13.716
2	14.434	3416965	86.284

==== Shimadzu LabSolutions Analysis Report ====

Sample Name	: lzl-8-24 ASH 90-10 1	Sample ID	: lzl-8-24 AS
Vial#	: 1-4	Injection Volume	: 2 uL
Date Acquired	: 2018/12/5 19:14:53	Acquired by	: System Administrator
Date Processed	: 2018/12/5 20:00:06	Modified by	: System Administrator
Data Filename	: D:\LI ZHONGLIANG\lzl-8-24 ASH 90-10 1.lcd		
Method Filename	: D:\LI ZHONGLIANG\ASH 90-10 1ml 20min.lcm		
Batch Filename	: D:\WYB\WYB07-073BOZ3950505-1.lcb		



PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.024	593285	13.806
2	14.180	3704054	86.194

Supplementary references

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