Supporting Information

Copper-Catalyzed Intermolecular Enantioselective Radical Oxidative C(sp^3)–H/C(sp)–H Cross-Coupling with Rationally Designed Oxazoline-Derived N,N,P(O)-Ligand

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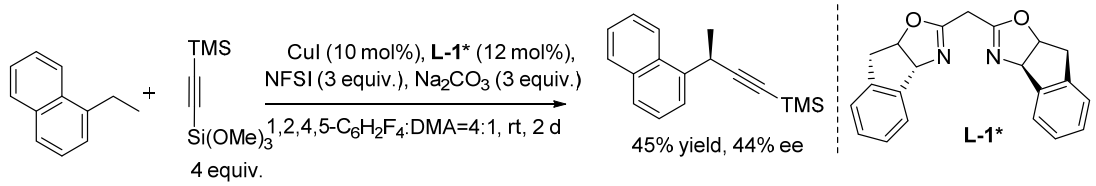
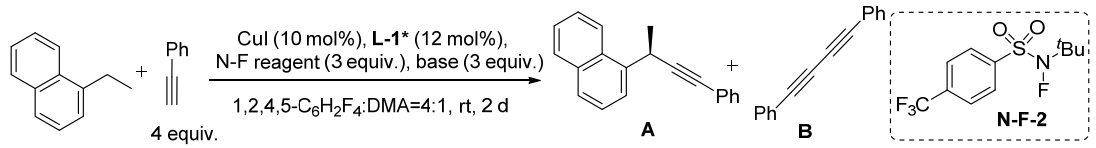
(a) Repeat experiment with $(MeO)_3Si$-prefunctionalized alkyne as nucleophile (ref 6d in the manuscript. *J. Am. Chem. Soc.* **2020**, *142*, 12493).



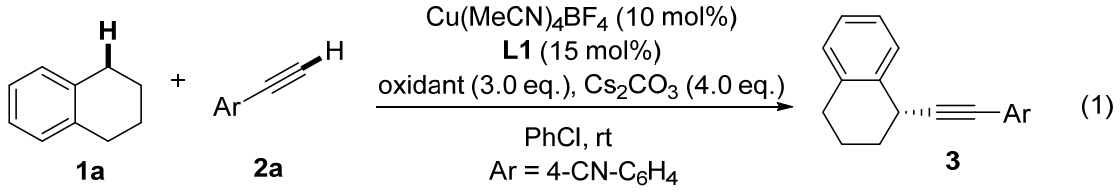
(b) Test of terminal alkyne as nucleophile using chiral bisoxazoline ligand



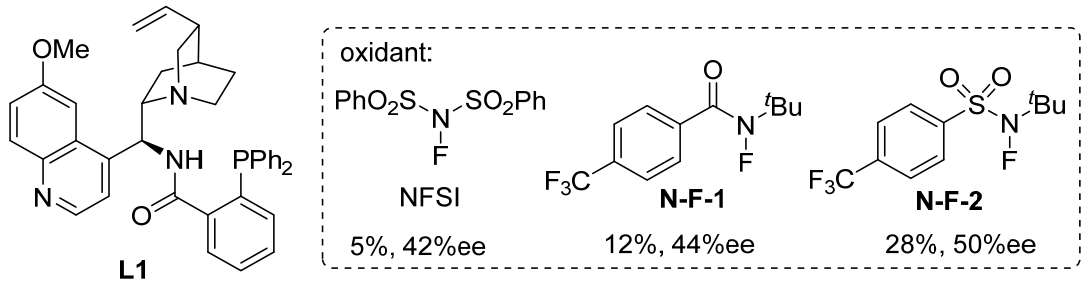
Entry	N-F reagent	Base	Yield of **A** (%)	Yield of **B** (%)
1	NFSI	Na_2CO_3	0	0
2	**N-F-2**	Na_2CO_3	0	0
3	NFSI	Cs_2CO_3	0	5%
4	**N-F-2**	Cs_2CO_3	0	17%

When Na_2CO_3 was used as base, both alkynylated product **A** and homo-coupling product **B** were not detected in the reaction mixture (entries **1** and **2**). When Cs_2CO_3 was used as base, only **B** was detected in 5% and 17% yield, respectively, while **A** was not detected in the reaction mixture (entries **3** and **4**).

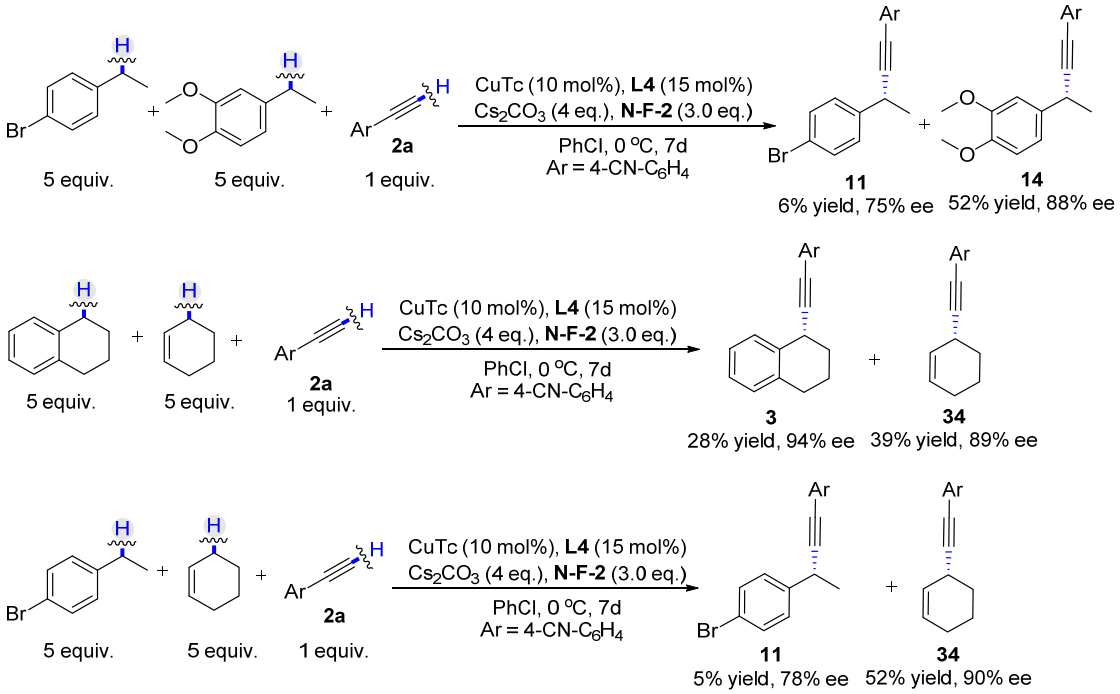
Scheme S1 Result of benzylic C(sp^3)-H alkynylation using terminal alkyne with Cu/chiral Box ligand catalytic system.



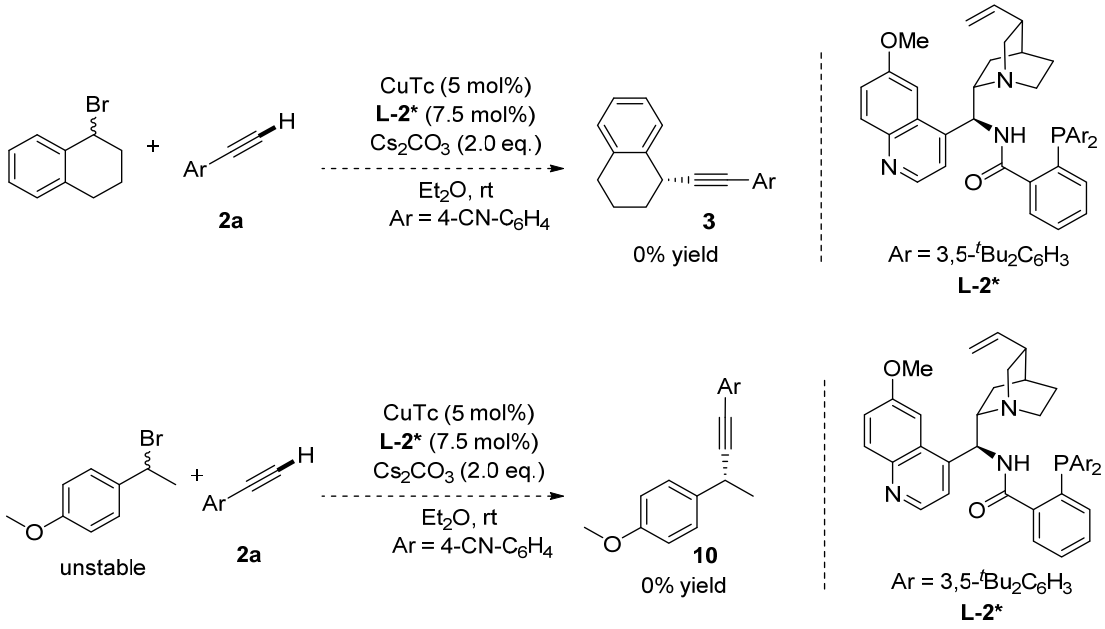
(1)



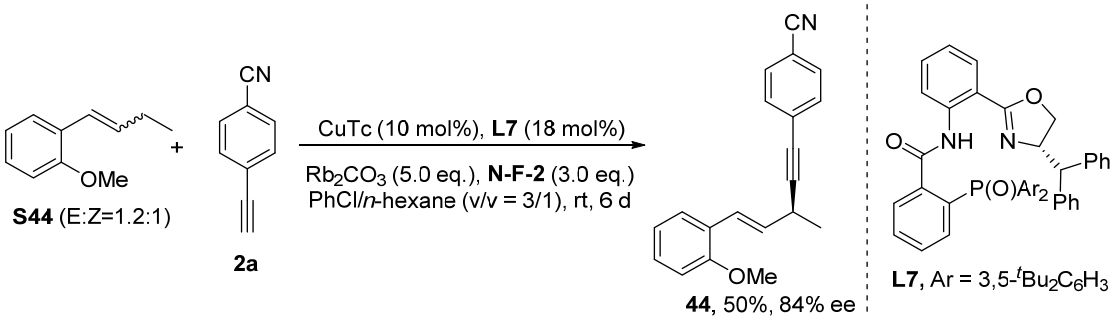
Scheme S2. An initial attempt with Cu^I/N,N,P-ligand in intermolecular asymmetric oxidative C(sp^3)–H/C(sp)–H cross-coupling



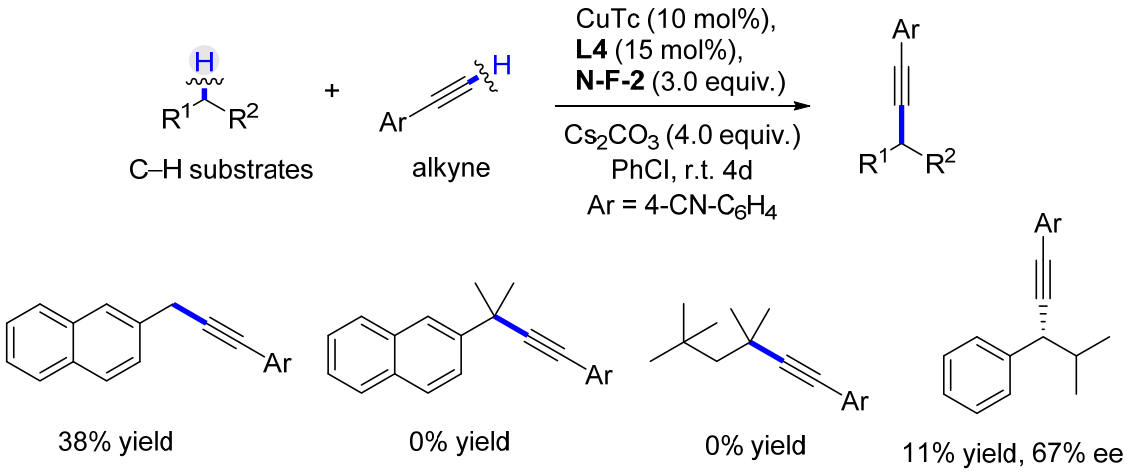
Scheme S3 Competition experiments between different types of C–H substrates



Scheme S4 Sonogashira C(sp^3)–C(sp) coupling reaction of cyclic benzylic halide and benzyl halide with *p*-OMe substituent with terminal alkyne under our previous Cu/chiral N.N.P-ligand catalytic system (refer 9c in the manuscript: *Nat. Chem.* **2019**, *11*,1158)

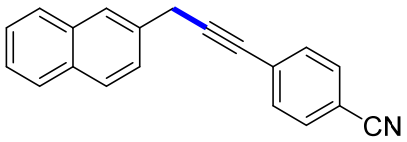


Scheme S5 Asymmetric alkynylation of **S44** with phosphine oxide ligand **L7**



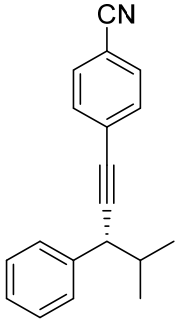
Scheme S6 Result of asymmetric alkynylation of substrates with other potentially reactive C–H bonds.

4-(3-(naphthalen-2-yl)prop-1-yn-1-yl)benzonitrile

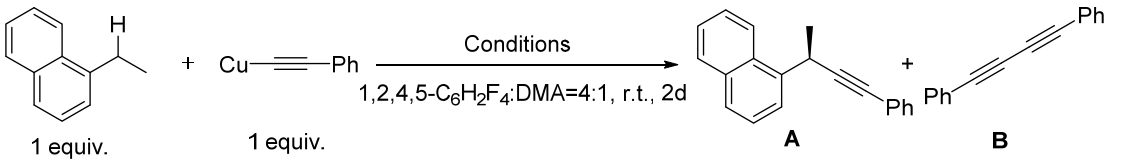


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.75 (m, 4H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.51-7.43 (m, 3H), 4.01 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 133.5, 133.4, 132.4, 132.2, 132.0, 128.6, 128.4, 127.7, 127.6, 126.31, 126.30, 125.8, 118.6, 111.2, 92.6, 81.5, 26.1.

***(R)*-4-(4-methyl-3-phenylpent-1-yn-1-yl)benzonitrile**

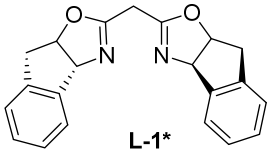


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.53 (m, 2H), 7.52-7.45 (m, 2H), 7.42-7.31 (m, 4H), 7.30-7.21 (m, 1H), 3.90 (dd, *J* = 9.2, 6.2 Hz, 1H), 1.90-1.70 (m, 2H), 1.69-1.49 (m, 1H), 0.98 (dd, *J* = 6.5, 5.2 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 132.2, 131.9, 128.8, 128.6, 127.3, 126.9, 118.6, 111.0, 96.9, 81.6, 47.6, 36.6, 26.1, 22.9, 21.8.
HPLC condition: Chiralcel AD-3, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min. λ = 254 nm, t(minor) = 8.2 min, t(major) = 12.4 min, 67% ee.



Conditions:
entry 1: **L-1*** (100 mol%). NFSI (3 equiv.), Cs_2CO_3 (3 equiv.)
entry 2: **L-1*** (100 mol%). NFSI (3 equiv.), Na_2CO_3 (3 equiv.)
entry 3: NFSI (3 equiv.), Na_2CO_3 (3 equiv.)

Results
A (0%), **B** (60.4%)
A (0%), **B** (70.3%)
A (0%), **B** (61.4%)



L-1*

Scheme S7 Results of benzylic C(sp^3)-H alkynylation using copper-phenylacetylide and chiral Box ligand system.

Test of stability of ligand L1 and L4 under different N-F reagents

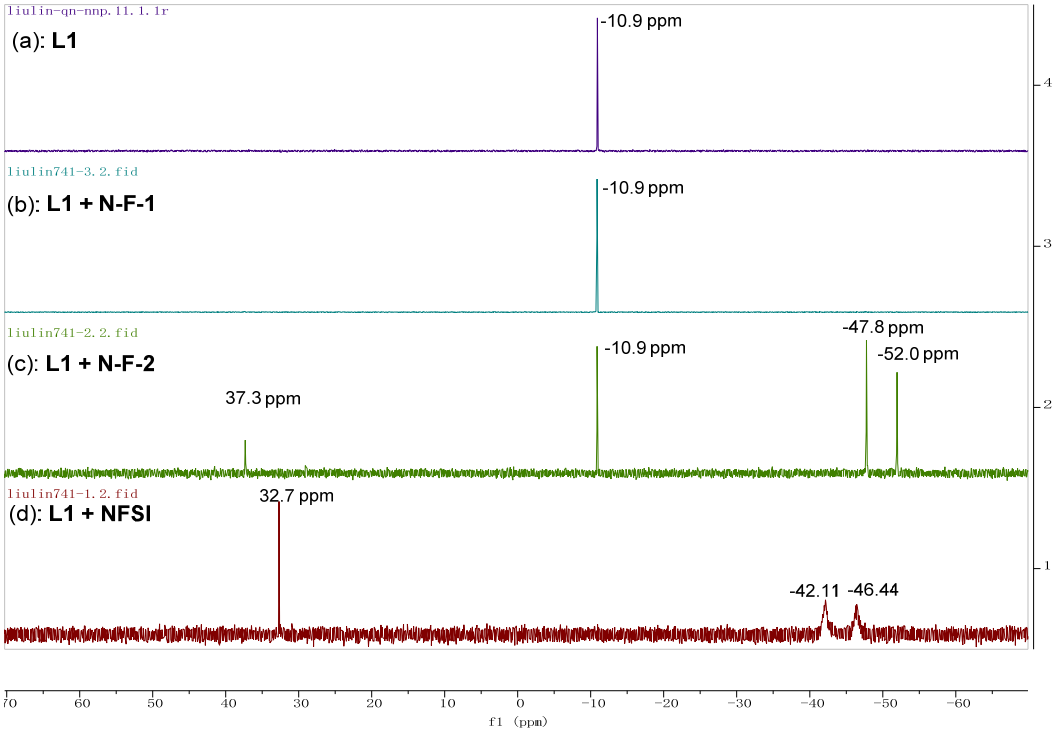


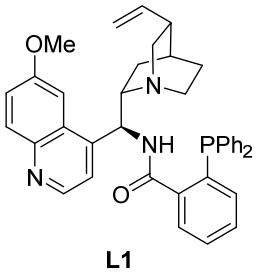
Figure S1: Test of stability of ligand **L1** under different N-F reagents. ^{31}P NMR spectrum of reaction system resulting from ligand **L1** (1 equiv.) and different N-F reagents (1.2 equiv.) under the ultrasonic conditions in $CDCl_3$ for 1h at rt. (a) ^{31}P NMR of ligand **L1**; (b) ^{31}P NMR of ligand **L1** and **N-F-1**; (c) ^{31}P NMR of ligand **L1** and N-F-2; (d) ^{31}P NMR of ligand **L1** and NFSI.

In **Figure S1b**: No change in phosphine spectrum indicates **L1** is stable under mild oxidant N-fluoroalkylamide (N-F-1)

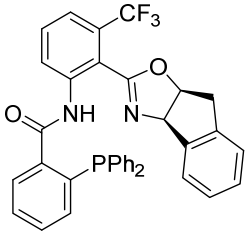
In **Figure S1c**: Partial changes in phosphine spectrum indicates **L1** proceeds slow decomposition under relatively strong oxidant N-fluoroalkylsulfonamide (**N-F-2**).

In **Figure S1d**: Complete change of phosphine spectrum indicates **L1** is incompatible with strong oxidant NFSI.

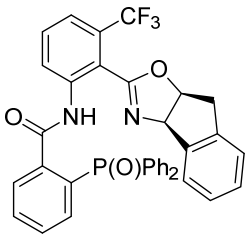
Conclusion: Order of ligand **L1** tolerance to oxidants: **N-F-1** > **N-F-2** > NFSI



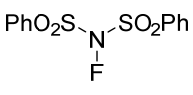
L1



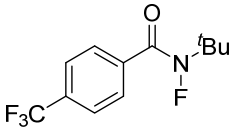
L4



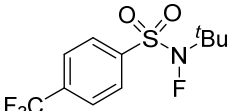
L5



NFSI



N-F-1



N-F-2

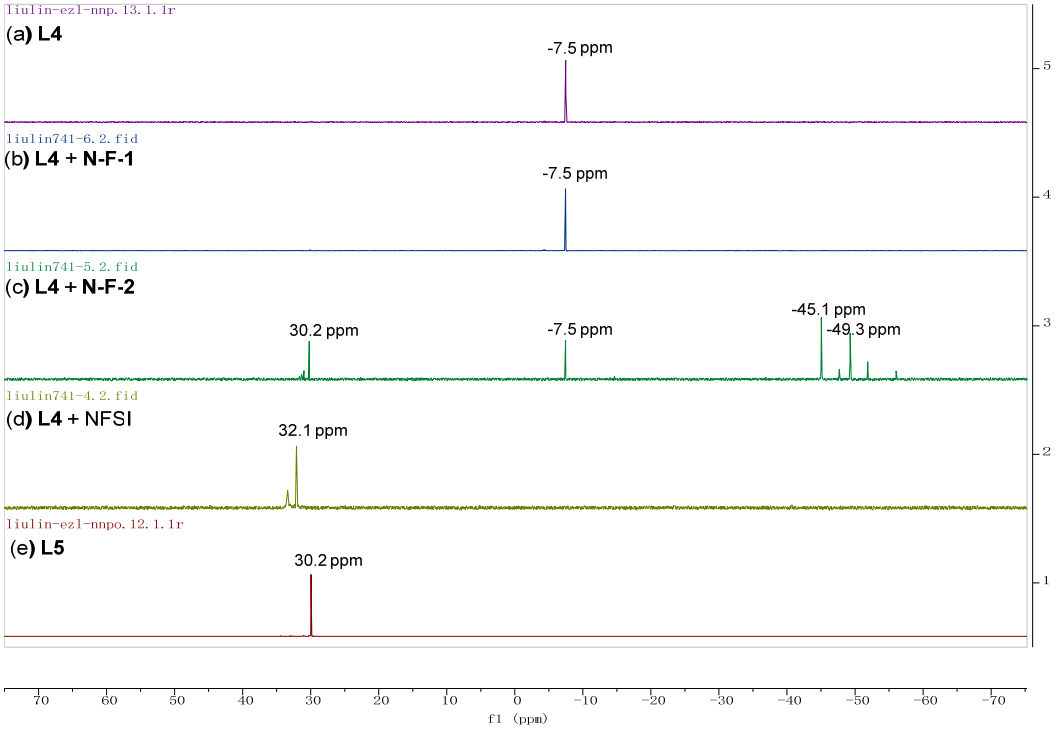


Figure S2: Test of stability of ligand **L4** under different N-F reagents. ^{31}P NMR spectrum of reaction system resulting from ligand **L4** (1 equiv.) and different N-F reagents (1.2 equiv.) under the ultrasonic conditions in $CDCl_3$ for 1h at rt. (a) ^{31}P NMR of ligand **L4**; (b) ^{31}P NMR of ligand **L4** and N-F-1; (c) ^{31}P NMR of ligand **L4** and N-F-2; (d) ^{31}P NMR of ligand **L4** and NFSI. (e) ^{31}P NMR of ligand **L5**.

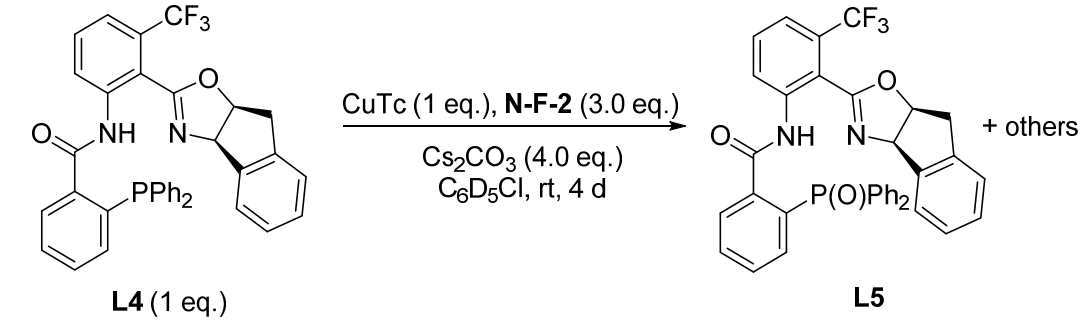
In **Figure S2b**: No change in phosphine spectrum indicates **L1** is stable under mild oxidant N-fluoroalkylamide (N-F-1).

In **Figure S2c**: Partial changes in phosphine spectrum **L4** proceeds slow decomposition under relatively strong oxidant N-fluoroalkylsulfonamide (**N-F-2**). Interestingly, new signals might be assigned to phosphine oxide **L5** (30.2 ppm) and possible phosphine-fluorine ligands[1-3] (-45.1 and -49.3).

In **Figure S2d**: Complete change of phosphine spectrum indicates **L4** is incompatible with strong oxidant NFSI.

Conclusion: Order of ligand **L4** tolerance to oxidants: **N-F-1** > **N-F-2** > NFSI.

Quantitative Analysis of Ligand L4 with N-F-2



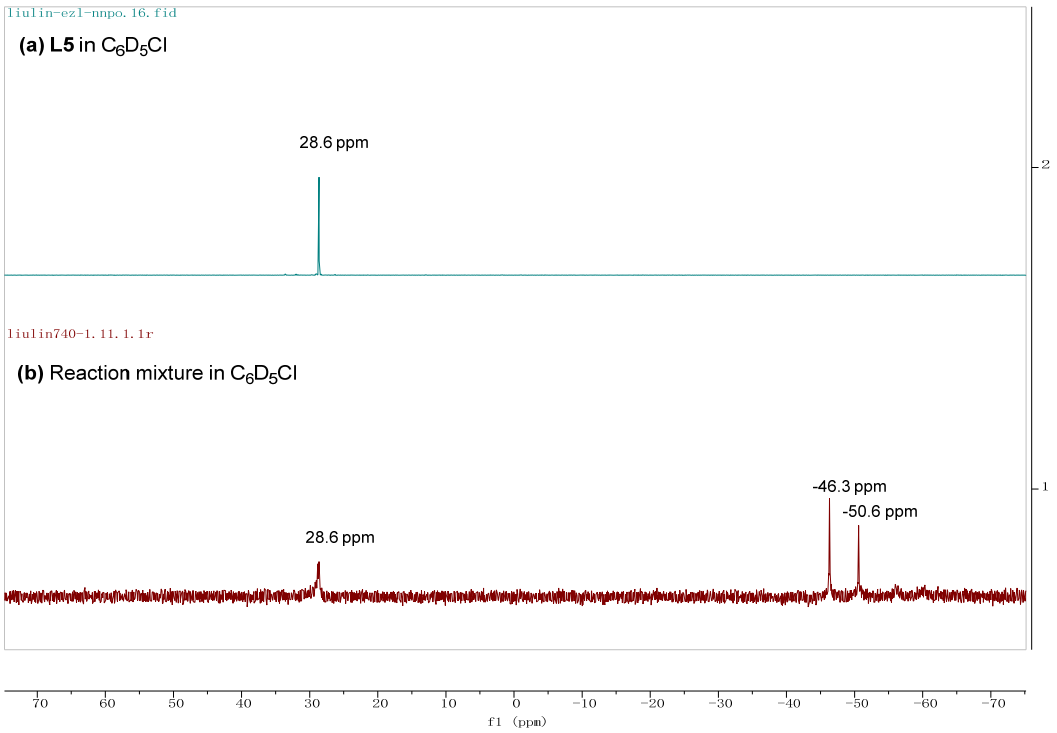


Figure S3-1. (a) ^{31}P NMR of ligand L5; (b) ^{31}P NMR of reaction mixture.

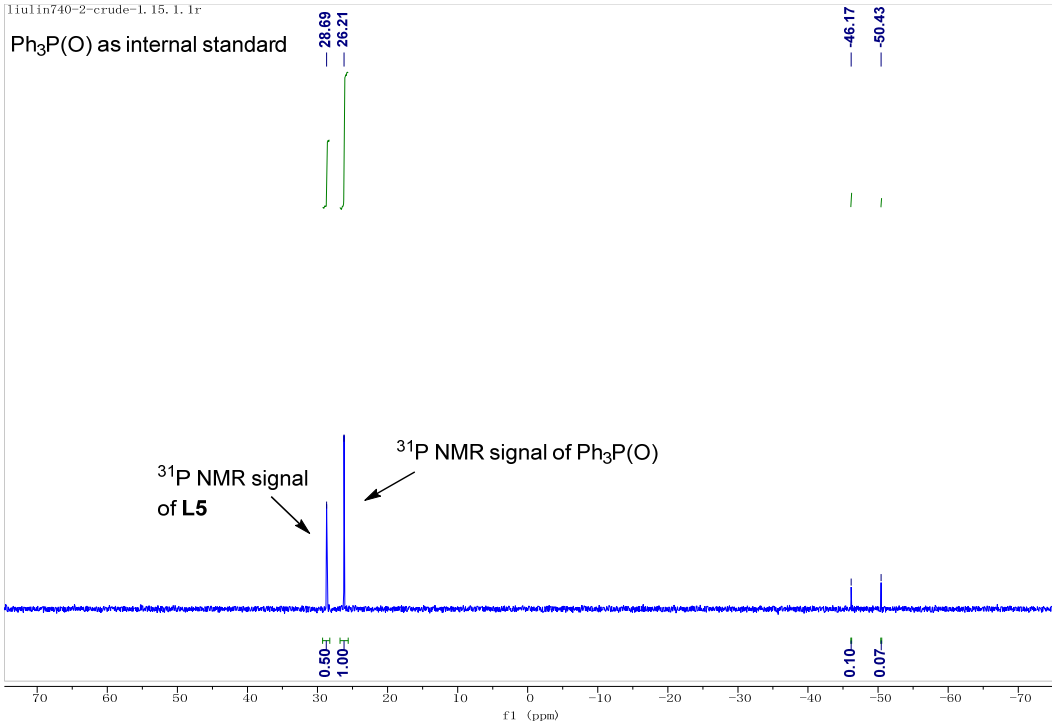


Figure S3-2. ^{31}P NMR of reaction mixture shown in **S3-1** after further reaction for 4 h under ultrasonic conditions under air using $Ph_3P(O)$ as internal standard.

Conclusion: In the reaction system, complete conversion of phosphine ligand **L4** into the possible phosphine-fluorine ligands[1-3] and ligand **L5** was observed. Moreover, the possible phosphine-fluorine ligand could be finally converted to **L5** under air conditions. Actually, the pentavalent phosphine oxide **L5** is also active for catalyzing this transformation.

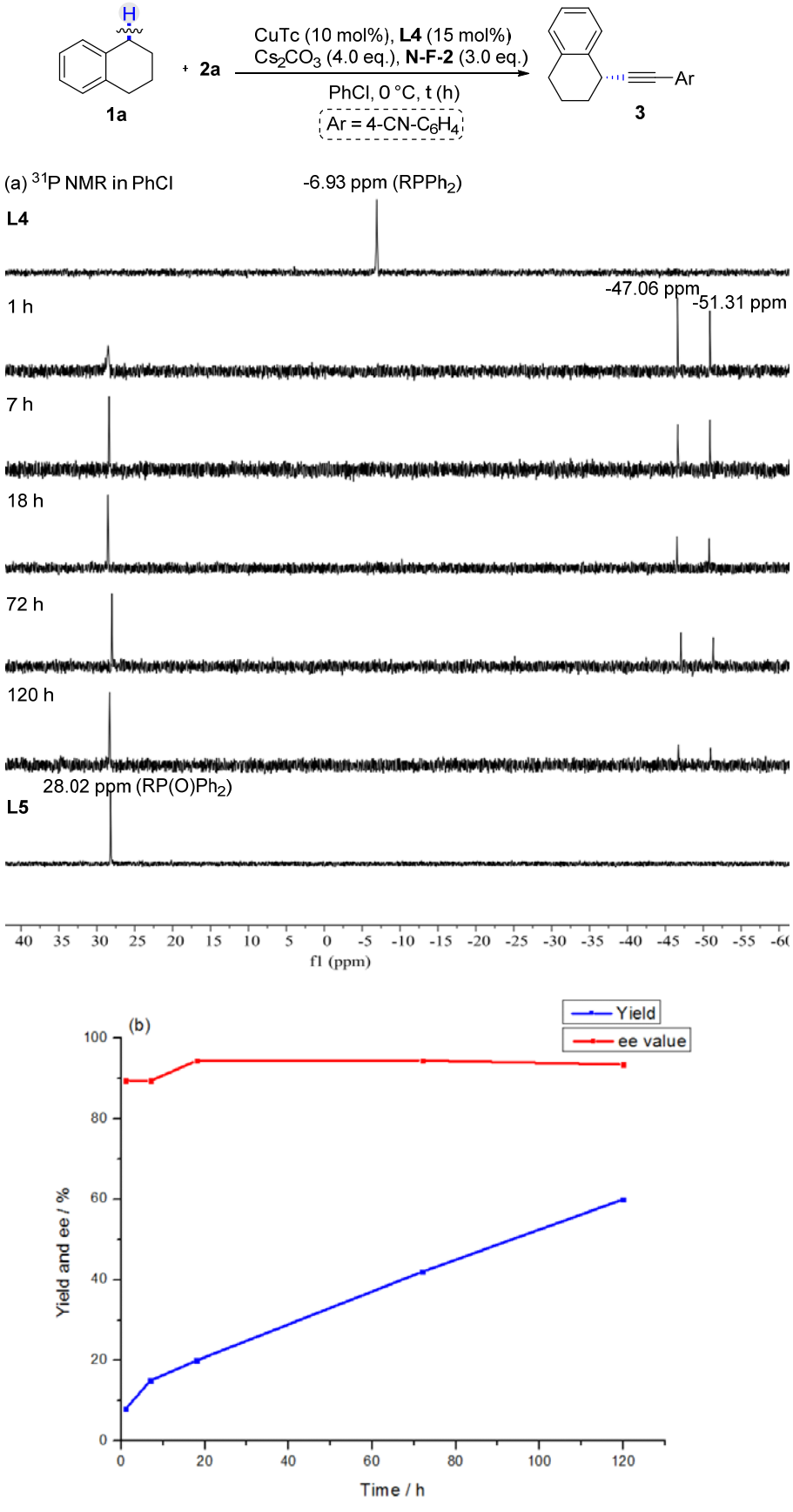
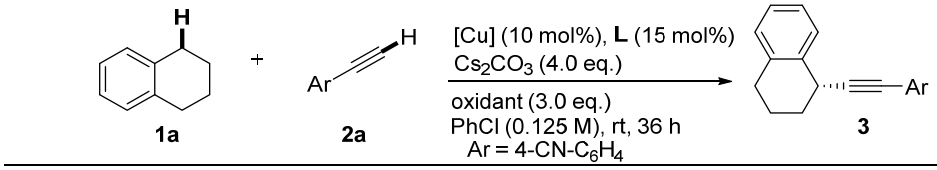
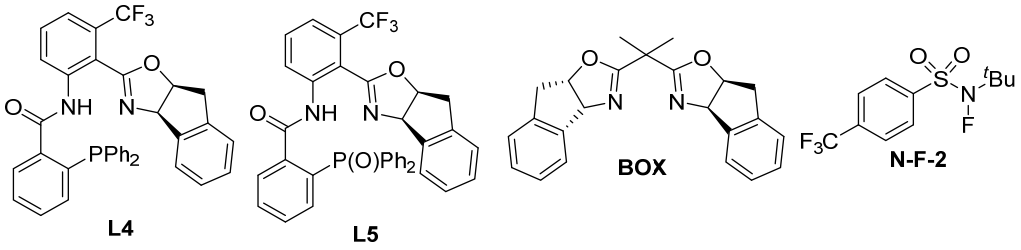


Figure S4. (a) ^{31}P NMR of reaction mixture at different time. (b) Yield and ee of **3** at different time.

Table S1 Screening of reaction conditions for benzylic alkynylation[a]



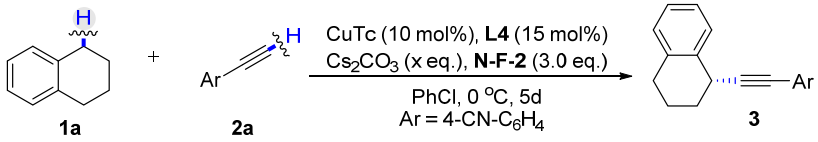


entry	[Cu]	L	oxidant	solvent	yield(%)[b](conv.)	ee(%)[c]
1	CuTc	**L4**	$(^tBuO)_2$	PhCl	0	ND
2	CuTc	**L4**	$^tBuO_2H$	PhCl	0	ND
3	CuTc	**L4**	$PhCO_3{}^tBu$	PhCl	0	ND
4	CuTc	**L4**	BPO	PhCl	0	ND
5	CuTc	**L4**	$Na_2S_2O_8$	PhCl	0	ND
6	CuTc	**L4**	$PhI(OAc)_2$	PhCl	0	ND
7	CuTc	**L4**	DDQ	PhCl	0	ND
8	CuTc	**L4**	Selectfluor	PhCl	0	ND
9	CuTc	**L4**	**N-F-2**	PhCl	43	85
10	CuI	**L4**	**N-F-2**	PhCl	51	87
11	$Cu(MeCN)_4PF_6$	**L4**	**N-F-2**	PhCl	45	88
12	$Cu(MeCN)_4BF_4$	**L4**	**N-F-2**	Benzene	24(68)	86
13	$Cu(MeCN)_4BF_4$	**L4**	**N-F-2**	$PhCF_3$	27(81)	87
14	$Cu(MeCN)_4BF_4$	**L4**	**N-F-2**	PhF	17(60)	86
15	$Cu(MeCN)_4BF_4$	BOX	**NFSI**	PhCl	trace(82)	ND
16	$Cu(MeCN)_4BF_4$	BOX	**N-F-2**	PhCl	trace	ND
17	–	**L4**	**N-F-2**	PhCl	trace	ND
18	$Cu(MeCN)_4BF_4$	–	**N-F-2**	PhCl	trace	ND
19[d]	$Cu(MeCN)_4BF_4$	**L4**	**N-F-4**	PhCl	trace	ND

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.05 mmol), [Cu] (10 mol%), **L** (15 mol%), Cs_2CO_3 (0.2 mmol) and oxidant (0.15 mmol) in dry PhCl (0.4 mL) at rt for 36 h. [b] Yield based on ^1H NMR analysis of the crude product using $Cl_2CHCHCl_2$ as an internal standard. [c] Ee values based on HPLC analysis. [d] Without base.

Note: In case that Selectfluor, $(^tBuO)_2$, $PhCO_3{}^tBu$, and $Na_2S_2O_8$ are used as the oxidant, the Glaser homocoupling product (5–20%) was observed.

Table S2 Screening of the effect of the amount of base for benzylic alkynylation[a]

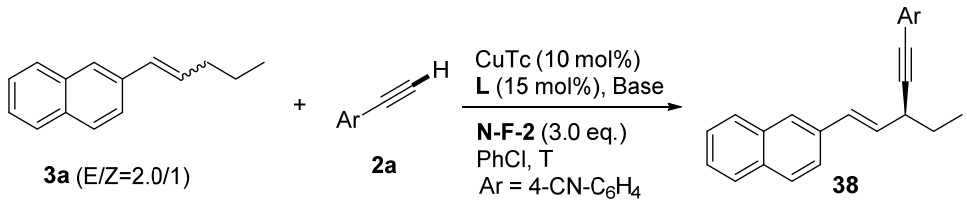


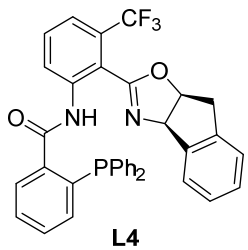
1a 2a 3

entry	X (eq.)	conv. of **2a** (%)	yield of **3** (%)	ee (%)
1	1.0	52	28	94
2	2.0	71	42	93
3	3.0	90	52	93
4	4.0	98	68	93
5	5.0	98	57	93

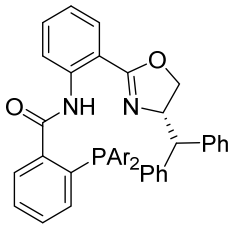
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.05 mmol), CuTc (10 mol%), **L4** (15 mol%), Cs_2CO_3 (x eq.) and **N-F-2** (0.30 mmol) in dry PhCl (0.8 mL) at 0 °C for 5 d.

Table S3 Screening of reaction conditions for allylic alkynylation[a]

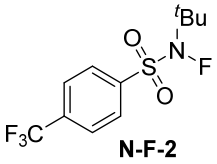




L4



L6, Ar = 3,5-(^{t}Bu)$_2$-C$_6$H$_3$
L8, Ar = Ph



N-F-2

entry	L	base (equiv.)	T (°C)	t	Yield (%)[b](conv.)	ee (%)[c]
1	**L4**	Cs_2CO_3 (4.0)	0	5 d	3(70)	ND
2	**L4**	Cs_2CO_3 (4.0)	rt	5 d	10	-17
3	**L8**	Cs_2CO_3 (4.0)	rt	5 d	16(80)	65
4	**L6**	Cs_2CO_3 (4.0)	rt	5 d	15(85)	77
5	**L6**	Rb_2CO_3 (5.0)	rt	5 d	51(95)	85
6[d]	**L6**	Rb_2CO_3 (5.0)	rt	5 d	40(95)	84
7[e]	**L6**	Rb_2CO_3 (5.0)	rt	5 d	38(98)	86
8[f]	**L6**	Rb_2CO_3 (5.0)	rt	5 d	32	87
9[g]	**L6**	Rb_2CO_3 (5.0)	rt	5 d	50(98)	88

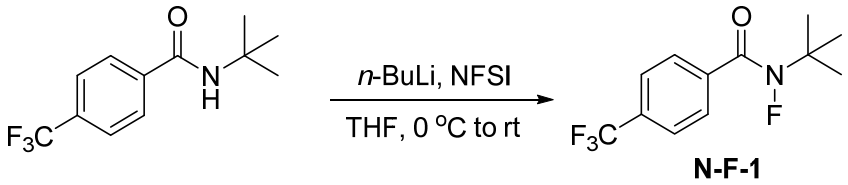
[a] Reaction conditions: **3a** (0.5 mmol), **2a** (0.05 mmol), CuTc (10 mol%), **L** (15 mol%), base (x eq.) and **N-F-2** (0.15 mmol) in dry solvent. [b] Yield based on ^{1}H NMR analysis of the crude product using $Cl_2CHCHCl_2$ as an internal standard. [c] Ee values based on HPLC analysis. [d] **3a** (5 eq.). [e] PhCl/n-hex (v/v=2/1) as solvent. [f] CuTc (15 mol%) and **L6** (20 mol%). [g] CuTc (10 mol%), **L6** (18 mol%) and PhCl/n-hex (v/v=3/1) as solvent, **2a** (0.1 mmol).

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. CuTc and $Cu(MeCN)_4BF_4$ were purchased from TCI. Anhydrous chlorobenzene (PhCl) was purchased from Shanghai Energy-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 at 400 MHz for **^{1}H NMR**, 101 MHz for **^{13}C NMR** 376 MHz for **^{19}F NMR** and 162 MHz for **^{31}P NMR** respectively, in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for **^{1}H 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).

The synthesis of N-F reagents and ligands

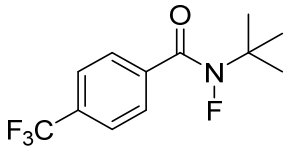
General Procedure for Synthesis of N-F reagents



N-F-1

In a 250 mL round-bottomed flask, to a solution of N-(tert-butyl)-4-(trifluoromethyl)benzamide[4] (7.35 g, 30 mmol, 1 equiv.) in anhydrous THF (60 mL) was slowly added *n*-BuLi (15 mL, 2.4 M in hexane, 36 mmol, 1.2 equiv.) at 0 °C under argon atmosphere. After stirring for 30 min, N-fluoro-benzenesulfonimide (NFSI, 18.6 g, 60 mmol, 2 equiv.) was added. The reaction mixture was stirred for another 12 h, then quenched with 1 M HCl. The reaction mixture was extracted with CH_2Cl_2. The organic layers were combined and dried over anhydrous Na_2SO_4, and filtered through a pad of Celite. The organic solvent was removed under vaccum, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) to afford the product **N-F-1** (4.02 g, 51% yield) as a white solid.

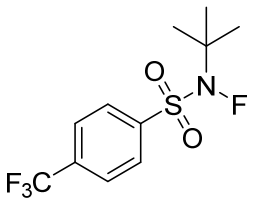
N-(tert-butyl)-N-fluoro-4-(trifluoromethyl)benzamide



N-F-1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 1.55 (d, *J* = 2.0 Hz, 9H); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.11, -65.08.
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1 (d, J_{C-F} = 8.3 Hz), 137.4, 133.3 (q, J_{C-F} = 32.6 Hz), 129.22, 129.16, 125.0 (q, J_{C-F} = 3.6 Hz), 123.5 (q, J_{C-F} = 273.71 Hz), 64.4 (d, J_{C-F} = 10.5 Hz), 26.8 (d, J_{C-F} = 5.9 Hz).
HRMS (ESI) *m*/*z* calcd. for $C_{12}H_{14}F_4NO$ $[M + H]^+$ 264.1006, found 264.1003.

N-(tert-butyl)-N-fluoro-4-(trifluoromethyl)benzenesulfonamide

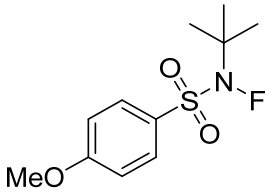


N-F-2

According to the general procedure with N-(tert-butyl)-4-(trifluoromethyl) benzene-sulfonamide[5] (8.43 g, 30 mmol, 1.0 equiv) and N-fluoro-benzenesulfonimide (NFSI, 18.6 g, 60 mmol, 2 equiv.) for 12 h, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **N-F-2** (4.31 g) in 48% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 1.50 (d, *J* = 2.1 Hz, 9H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.78, -63.38.
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 135.7 (q, J_{C-F} = 33.1 Hz), 132.9, 129.6, 126.1 (q, J_{C-F} = 3.7 Hz), 123.1 (q, J_{C-F} = 273.7 Hz), 67.1 (d, J_{C-F} = 12.3 Hz), 27.2 (d, J_{C-F} = 6.0 Hz).
HRMS (ESI) *m*/*z* calcd. for $C_{11}H_{13}F_4NNaO_2S$ $[M + Na]^+$ 322.0495, found 322.0493.

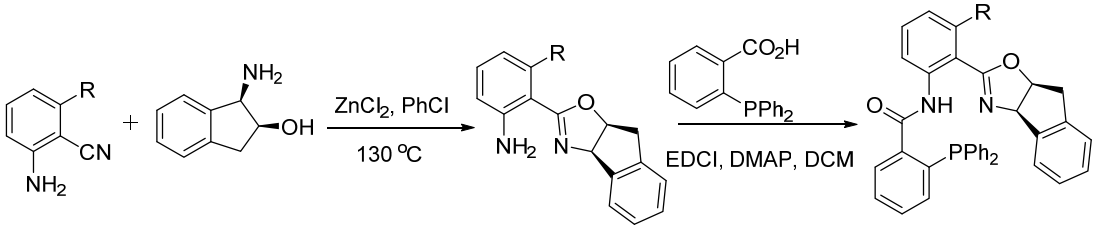
N-(tert-butyl)-N-fluoro-4-methoxybenzenesulfonamide



N-F-4

According to general procedure with N-(tert-butyl)-4-methoxybenzenesulfonamide[6] (7.29 g, 30 mmol, 1.0 equiv) and N-fluoro-benzenesulfonimide (NFSI, 18.6 g, 60 mmol, 2 equiv.) for 12 h, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **N-F-4** (2.90 g) in 37% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H), 1.45 (d, *J* = 1.8 Hz, 9H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.33.
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 131.4 (d, J_{C-F} = 1.3 Hz), 128.7, 114.2, 66.3 (d, J_{C-F} = 12.1 Hz), 55.7, 27.1 (d, J_{C-F} = 6.1 Hz).
HRMS (ESI) *m*/*z* calcd. for $C_{11}H_{16}FNNaO_3S$ $[M + Na]^+$ 284.0727, found 284.0724.

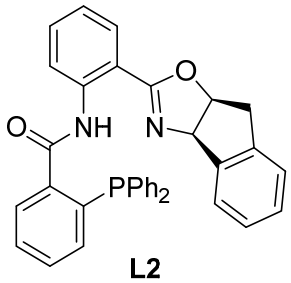
General Procedure for Synthesis of chiral ligand (L2-L4)



Under argon atmosphere, a dry 100mL Schlenk flask equipped with a magnetic stir bar was charged with substituted-2-aminobenzonitrile (10 mmol, 1 equiv.), (*1R,2S*)-1-amino-2-indanol (1.79 g, 12 mmol, 1.2 equiv), dry $ZnCl_2$ (2.05 g, 15 mmol, 1.5 equiv.), and 40 mL of chlorobenzene, then reflux the reaction mixture for 3-5 d, Upon completion (monitored by TLC), Dissolve the residue in H_2O, EA and 2 mL ethylenediamine. Extract the mixture with EA. Remove the solvent under vacuum to obtain the crude red oil. Purify the crude red oil by silica gel. to obtain substituted-2-(*(3aR,8aS)*-3a,8a-dihydro-8H-indeno[1,2-d]oxazol-2-yl)aniline as a white solid.
Under argon atmosphere, to a solution of substituted-2-(*(3aR,8aS)*-3a,8a-dihydro-8H-indeno[1,2-d]oxazol-2-yl)aniline (10 mmol, 1 equiv.) in anhydrous DCM (30 mL) was added 2-(diphenylphosphino)benzoic acid (6.12 g, 20 mmol, 2 equiv.), 4-dimethylaminopyridine (2.44 g, 20 mmol, 2 equiv.) and 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (3.84 g, 20 mmol, 2 equiv.). The reaction mixture was

stirred at ambient temperature for 24 h, concentrated and purified by flash chromatography (PE/ EA = 4/1) to provide the chiral ligand as a white solid.

N-(2-((*3aR,8aS*)-3a,8a-dihydro-8H-indeno[1,2-d]oxazol-2-yl)phenyl)-2-(diphenylphosphanyl)benzamide (L2)



L2

According to the general procedure with 2-aminobenzonitrile (1.18 g, 10 mmol, 1.0 equiv), *(1R,2S)*-1-amino-2-indanol (1.79 g, 12 mmol, 1.2 equiv) and 2-(diphenylphosphino)benzoic acid (6.12 g, 20 mmol, 2 equiv.), the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **L2** (2.72 g, 5.1 mmol) in 51% isolated yield.

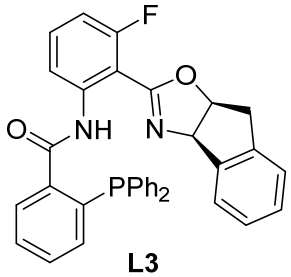
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.75 (s, 1H), 8.70 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.87 (ddd, *J* = 7.8, 3.9, 1.3 Hz, 1H), 7.82 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.54 (td, *J* = 7.5, 1.3 Hz, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.40-7.18 (m, 15H), 7.10 (ddd, *J* = 7.8, 3.9, 1.2 Hz, 1H), 7.02 (td, *J* = 7.7, 1.2 Hz, 1H), 5.75 (d, *J* = 7.9 Hz, 1H), 5.42 (ddd, *J* = 8.2, 6.9, 1.7 Hz, 1H), 3.52 (dd, *J* = 18.1, 6.9 Hz, 1H), 3.37 (dd, *J* = 17.9, 1.6 Hz, 1H).

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.84.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 163.9, 141.7, 141.5, 141.3, 139.9, 139.7, 139.1, 138.8, 138.6, 138.5, 138.1, 138.0, 134.8, 134.1, 133.9, 133.8, 133.6, 132.5, 129.0, 128.7, 128.4, 128.31, 128.27, 128.25, 128.22, 128.15, 127.49, 127.45, 127.41, 125.5, 125.0, 122.3, 120.0, 113.3, 81.7, 76.6, 39.8.

HRMS (ESI) m/z calcd. for $C_{35}H_{28}N_2O_2P$ $[M+H]^+$ 539.1883, found 539.1884.

N-(2-((*3aR,8aS*)-3a,8a-dihydro-8H-indeno[1,2-d]oxazol-2-yl)-3-fluorophenyl)-2-(diphenylphosphanyl)benzamide (L3)



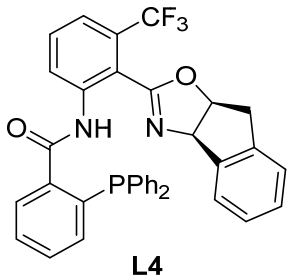
L3

According to the general procedure with 2-amino-6-fluorobenzonitrile (1.36 g, 10 mmol, 1.0 equiv), *(1R,2S)*-1-amino-2-indanol (1.79 g, 12 mmol, 1.2 equiv), and 2-(diphenylphosphino)benzoic acid (6.12 g, 20 mmol, 2 equiv.), the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **L3** (2.50 g, 4.5 mmol) in 45% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.53 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.74 (ddd, *J* = 7.7, 3.7, 1.3 Hz, 1H), 7.52 (td, *J* = 7.5, 1.3 Hz, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.37-

7.12 (m, 13H), 7.08 (ddd, *J* = 7.8, 4.0, 1.2 Hz, 1H), 7.07-6.94 (m, 2H), 6.75 (ddd, *J* = 11.5, 8.3, 1.1 Hz, 1H), 5.65 (d, *J* = 8.0 Hz, 1H), 5.47 (ddd, *J* = 8.2, 6.7, 1.8 Hz, 1H), 3.49 (dd, *J* = 18.1, 6.7 Hz, 1H), 3.39 (dd, *J* = 18.2, 1.7 Hz, 1H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -106.56; **^{31}P NMR (162 MHz, $CDCl_3$)** δ -7.61.
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 162.8, 162.3, 162.2, 160.2, 141.3, 141.2, 140.9, 140.7, 140.6, 139.6, 138.8, 138.6, 137.9, 137.8, 137.7, 137.6, 134.6, 134.1, 133.88, 133.85, 133.7, 133.0, 132.9, 130.3, 128.6, 128.5, 128.33, 128.31, 128.28, 128.2, 128.12, 128.05, 127.4, 127.3, 127.20, 127.16, 125.5, 125.3, 125.2, 124.9, 115.99, 115.96, 110.6, 110.3, 103.3, 103.2, 82.4, 75.0, 39.7.
HRMS (ESI) m/z calcd. for $C_{35}H_{27}FN_2O_2P$ $[M+H]^+$ 557.1789, found 557.1788.

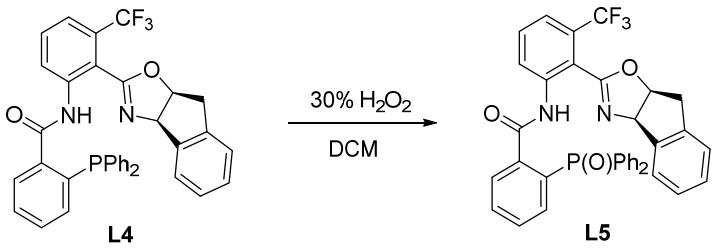
N-(2-((*3aR,8aS*)-3a,8a-dihydro-8H-indeno[1,2-d]oxazol-2-yl)-3-(trifluoromethyl)phenyl)-2-(diphenylphosphanyl)benzamide (L4)



L4

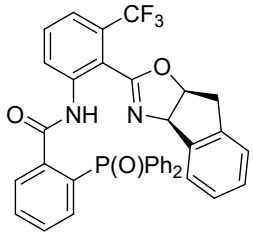
According to the general procedure with 2-amino-6-trifluoromethylbenzonitrile (1.86 g, 20 mmol, 1.0 equiv), (*1R,2S*)-1-amino-2-indanol (1.79 g, 12 mmol, 1.2 equiv) and 2-(diphenylphosphino)benzoic acid (6.12 g, 20 mmol, 2 equiv.), the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **L4** (2.55 g, 4.2 mmol) in 42% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 8.44-8.40 (m, 1H), 7.58 (ddd, *J* = 7.5, 3.6, 1.6 Hz, 1H), 7.50-7.32 (m, 4H), 7.34-7.28 (m, 5H), 7.25-7.16 (m, 4H), 7.13-7.09 (m, 2H), 7.06-7.01 (m, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.77 (td, *J* = 7.6, 1.2 Hz, 1H), 5.72 (d, *J* = 7.8 Hz, 1H), 5.48 (ddd, *J* = 7.7, 5.6, 2.2 Hz, 1H), 3.49-3.39 (m, 2H).
^{19}F NMR (376 MHz, $CDCl_3$): δ -58.86; **^{31}P NMR (162MHz, $CDCl_3$)**: δ -7.52.
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 162.3, 141.0, 140.5, 140.3, 139.5, 138.7, 138.6, 138.4, 137.6, 137.5, 137.4, 134.53, 134.51, 134.2, 134.1, 134.0, 133.9, 131.1, 130.6, 130.0 (q, J_{C-F} = 31.8 Hz), 128.8, 128.7, 128.6, 128.5, 128.5, 128.3, 128.2, 127.5, 127.3, 127.2, 125.5, 124.7, 124.6, 123.6 (q, J_{C-F} = 272.1 Hz), 121.7 (q, J_{C-F} = 5.5 Hz), 114.3-114.2 (m, 1C), 83.8, 76.4, 39.0.
HRMS (ESI) m/z calcd. for $C_{36}H_{27}F_3N_2O_2P$ $[M+H]^+$ 607.1757, found 607.1759.

N-(2-((*3aR,8aS*)-3a,8a-dihydro-8H-indeno[1,2-d]oxazol-2-yl)-3-(trifluoromethyl)phenyl)-2-(diphenylphosphoryl)benzamide (L5)



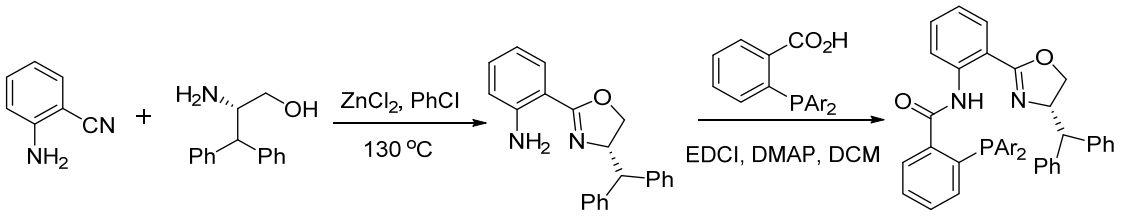
L4 **L5**

To a solution of **L4** (303 mg, 0.5 mmol) in CH_2Cl_2 (2 mL) was added H_2O_2 (30 wt%, 95 μL, 2.0 mmol). The reaction was kept at room temperature with stirring overnight. Water (20 mL) was added to the reaction mixture. The mixture was extracted with CH_2Cl_2 (20 × 5 mL). The organic layer was dried over Na_2SO_4 and filtered. The organic solvent was removed under vaccum, and the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (1:1) to afford the product **L5** (283 mg, 91% yield) as a white solid.



L5

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.99-7.86 (m, 2H), 7.78-7.60 (m, 4H), 7.52 (ddd, *J* = 7.3, 4.0, 1.5 Hz, 1H), 7.44-7.25 (m, 5H), 7.24-7.12 (m, 5H), 7.08 (td, *J* = 7.4, 3.1 Hz, 2H), 6.87 (dt, *J* = 8.2, 4.1 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.68 (d, *J* = 7.6 Hz, 1H), 5.48 (ddd, *J* = 7.5, 5.0, 2.3 Hz, 1H), 3.46 (t, *J* = 3.3 Hz, 2H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -58.92; **^{31}P NMR (162 MHz, $CDCl_3$)** δ 29.95.
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 166.2, 161.6, 141.0, 140.5, 140.4, 139.3, 137.9, 134.5, 134.4, 132.5, 132.4, 132.14, 132.11, 132.0, 131.9, 131.8, 131.6, 131.5, 131.39, 131.37, 131.2, 131,1, 130.9, 130.5, 130.0, 129.90, 129.85, 129.5, 128.8, 128.2, 128.1, 127.90, 127.86, 127.8, 127.6, 125.3, 124.6, 124.4, 122.0, 121.9-121.6 (m, 1C), 115.0, 83.9, 76.2, 38.8.
HRMS (ESI) *m/z* calcd. for $C_{36}H_{27}F_3N_2O_3P$ $[M + H]^+$ 623.1708, found 623.1706.

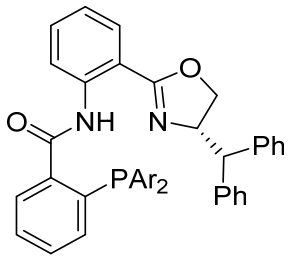


L6, Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$

Under argon atmosphere, a dry 100mL Schlenk flask equipped with a magnetic stir bar was charged with 2-aminobenzonitrile (0.71 g, 6 mmol, 1 equiv.), *(S)*-2-amino-3,3-diphenylpropan-1-ol (2.05 g, 9 mmol, 1.5 equiv), dry $ZnCl_2$ (1.64 g, 12 mmol, 2 equiv.), and 20 mL of chlorobenzene, then reflux the reaction mixture for 3 d, Upon completion (monitored by TLC), Dissolve the residue in H_2O, EA and 2 mL ethylenediamine. Extract the mixture with EA. Remove the solvent under vacuum to obtain the crude red

oil. Purify the crude red oil by silica gel. to obtain *(S)*-2-(4-benzhydryl-4,5-dihydrooxazol-2-yl)aniline (1.41 g, 4.3 mmol) in 72% isolated yield.
Under argon atmosphere, to a solution of *(S)*-2-(4-benzhydryl-4,5-dihydrooxazol-2-yl) aniline (0.492 g, 1.5 mmol, 1 equiv.) in anhydrous DCM (10 mL) was added 2-(bis(3,5-di-tert-butylphenyl)phosphanyl) benzoic acid (0.83 g, 1.6 mmol, 1.1 equiv.), 4-dimethylaminopyridine (0.55 g, 4.5 mmol, 3 equiv.) and 1-(3-dimethylaminopropyl) -3-ethylcarbodiimide hydrochloride (0.89 g, 4.5 mmol, 3 equiv.). The reaction mixture was stirred at ambient temperature for 24 h, concentrated and purified by flash chromatography (PE/ EA 8/1) to provide the chiral ligand **L6** (0.64 g, 0.77 mmol) as a white solid in 51% isolated yield.

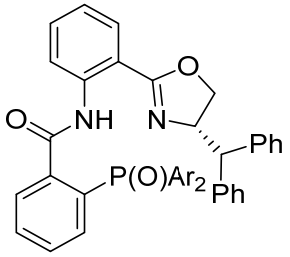
***(S)*-N-(2-(4-benzhydryl-4,5-dihydrooxazol-2-yl)phenyl)-2-(bis(3,5-di-tert-butylphenyl)phosphanyl)benzamide (L6)**



L6, Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.21 (s, 1H), 8.50 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.39 (ddd, *J* = 7.8, 3.7, 1.3 Hz, 1H), 7.33 (tq, *J* = 4.3, 1.8 Hz, 3H), 7.28-7.11 (m, 12H), 7.05-6.91 (m, 6H), 5.14 (td, *J* = 9.3, 7.5 Hz, 1H), 4.30 (t, *J* = 9.1 Hz, 1H), 4.05 (dd, *J* = 8.7, 7.5 Hz, 1H), 3.98 (d, *J* = 9.2 Hz, 1H), 1.20 (d, *J* = 8.4 Hz, 36H). **^{31}P NMR (162 MHz, $CDCl_3$)** δ -4.35.
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 164.2, 150.08, 150.05, 150.02, 149.98, 141.8, 141.5, 139.9, 134.2, 132.4, 129.6, 128.8, 128.7, 128.4, 128.31, 128.29, 128.2, 128.1, 127.0, 126.7 126.4, 122.3, 122.2, 122.1, 120.3, 113.3, 70.1, 70.1, 56.7, 34.8, 34.7, 31.33, 31.31.
HRMS (ESI) m/z calcd. for $C_{57}H_{66}N_2O_2P$ $[M+H]^+$ 841.4856, found 841.4849.

***(S)*-N-(2-(4-benzhydryl-4,5-dihydrooxazol-2-yl)phenyl)-2-(bis(3,5-di-tert-butylphenyl)phosphoryl)benzamide (L7)**



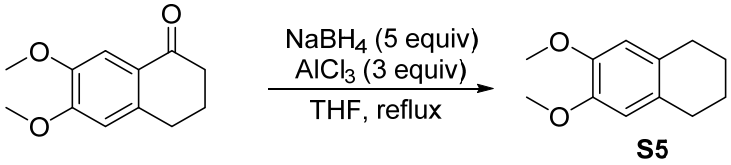
L7, Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$

The ligand **L7** (77.1 mg, 0.09 mmol) from **L6** (85.0 mg, 0.1 mmol) was obtained in 90% isolated yield following the same procedure as the preparation of **L5**

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95 (s, 1H), 8.04-7.93 (m, 1H), 7.77-7.69 (m, 2H), 7.61 (dd, *J* = 19.6, 13.1Hz, 4H), 7.46 (dd, *J* = 11.7, 8.5 Hz, 3H), 7.37-7.31 (m, 1H), 7.30-7.26 (m, 1H), 7.25-7.13 (m, 9.6 H), 7.07-6.99 (m, 3H), 6.96 (t, *J* = 7.6 Hz, 1H), 5.18 (q, *J* = 8.0 Hz, 1H), 4.31 (t, *J* = 9.1 Hz, 1H), 4.03 (t, *J* = 8.4 Hz, 1H), 3.96 (d, *J* = 9.7 Hz, 1H), 1.20 (d, *J* = 2.1 Hz, 36H). **^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.34.
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 166.28, 164.1, 150.3, 150.1, 142.0, 141.7, 140.5, 140.4, 139.3, 135.1, 135.0, 133.3, 132.7, 132.5, 132.4, 132.1, 131.8, 131.8, 131.7, 131.5, 129.7, 129.6, 128.8, 128.8, 128.4, 128.3, 128.2, 127.1, 127.0, 126.8, 126.6, 126.3, 126.3, 126.2, 126.2, 125.5, 122.4, 120.4, 113.7, 70.3, 70.2, 56.8, 34.9, 31.3.
HRMS (ESI) m/z calcd. for $C_{57}H_{66}N_2O_3P$ $[M+H]^+$ 857.4806, found 857.4795.

The synthesis of C(sp^3)−H substrates

6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (S5)



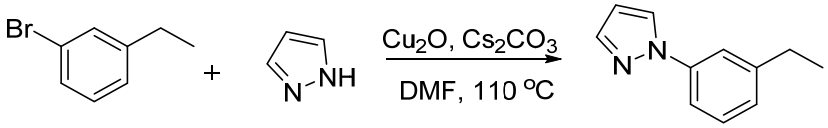
S5

In a 100 mL round-bottomed flask, to a solution of 6,7-dimethoxy-3,4-dihydronaphthalen-1(2H)-one (1.03 g, 5 mmol) and aluminium trichloride (2.0 g, 15 mmol) in THF (30 mL), sodium borohydride (0.95 g, 25 mmol) was added at 0 °C under Ar atmosphere. The resulting solution was heated to reflux overnight. The reaction was slowly quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted with ethyl acetate, then the combined organic layer was dried over $MgSO_4$ and then concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel (PE:EA=20:1) to afford the target compound **S5** (0.53 g, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (s, 2H), 3.84 (s, 6H), 2.67-2.70 (m, 4H), 1.87-1.70 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 128.8, 112.0, 55.9, 29.0, 23.4.

1-(3-ethylphenyl)-1*H*-pyrazole (S13)



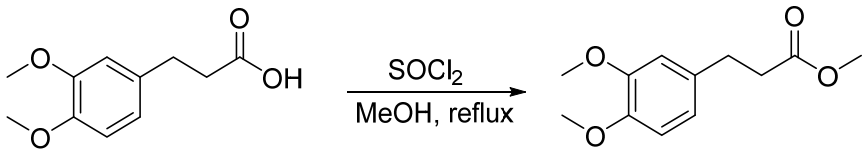
S13

To an oven-dried flask were added Cu_2O (143 mg, 1 mmol), Cs_2CO_3 (6.52 g, 20 mmol) and pyrazole (0.68 g, 10 mmol). Under argon atmosphere, 1-bromo-3-ethylbenzene (2.76 g, 15 mmol) was added followed by anhydrous DMF (20 mL). The flask was sealed and heated up to 110 °C with stirring. After 20 h, the reaction mixture was cooled to room temperature and diluted with dichloromethane. The resulting solution was filtered through a pad of silica gel and the solvent was removed under reduced pressure. The residue was then diluted with EtOAc and washed with water, and the organic phase was dried over $MgSO_4$, filtered and concentrated in vaccum. The crude residue was purified by silica column chromatography to afford the target compound **S13** (0.95 g, 5.5 mmol, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.4 Hz, 1H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.46 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.17-7.05 (m, 1H), 6.52-6.31 (m, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 140.8, 140.2, 129.2, 126.7, 126.0, 118.9, 116.4, 107.4, 28.8, 15.4.

Methyl 3-(3,4-dimethoxyphenyl)propanoate (S15)



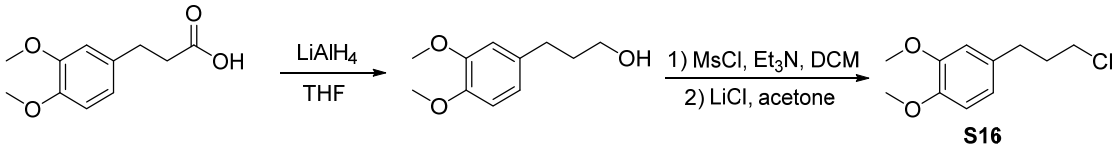
S15

To a solution of substituted 3-(3,4-dimethoxyphenyl)propanoic acid (2.10 g, 10 mmol) in methanol (30 mL) was added thionyl chloride (3.6 mL, 50 mmol) dropwise. After completion of addition, the reaction mixture was stirred for another 2 h under reflux condition. After completion of reaction, the reaction mixture was poured into water, extracted with ethyl acetate. The extract was washed with water, brine solution, dried over $MgSO_4$ and concentrated. The crude compound was subjected to column chromatography on silica gel to afford methyl 3-(3,4-dimethoxyphenyl)propanoate (**S15**) with 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (m, 1H), 6.74 (m, 2H), 3.86 (d, *J* = 6.2 Hz, 6H), 3.67 (s, 3H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.61 (t, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 148.7, 147.4, 133.0, 120.0, 111.5, 111.2, 55.8, 55.7, 51.5, 35.9, 30.5.

4-(3-chloropropyl)-1,2-dimethoxybenzene (S16)



S16

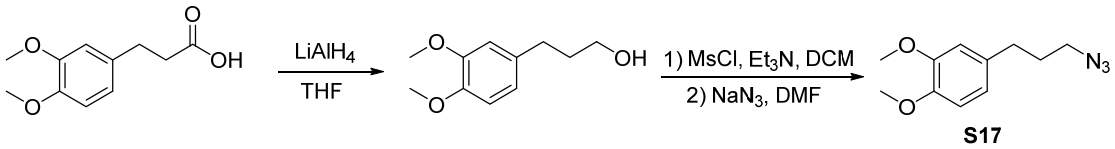
$LiAlH_4$ (3.0 g, 80 mmol) was added slowly to the THF (80 ml) solution of 3-(3,4-dimethoxyphenyl)propanoic acid (8.4 g, 40 mmol) at 0 ºC and then the solution was stirred for 2 h at room temperature. After that, a solution of NaOH (10% in water) was added carefully until a white solid precipitated. After filtration over $MgSO_4$ and evaporation of the solvent the crude 3-(3,4-dimethoxyphenyl)propan-1-ol was obtained in quantitative yields.

To a stirred solution of 3-(3,4-dimethoxyphenyl)propan-1-ol (3.92 g, 10 mmol) in dry CH_2Cl_2 (20 mL) was added Et_3N (2.76 ml, 20 mmol). The mixture was cooled to 0 ºC, and mesyl chloride (0.98 ml, 12 mmol) was slowly added. The mixture was stirred overnight at rt. The reaction mixture was then concentrated to remove MsCl, and then LiCl (2.1 g, 50 mmol) and acetone (30 ml) were added. The resulting mixture was stirred at 50 ºC for 4 h. The residue was purified by flash column chromatography on silica gel to afford **S16** (52% yield for two steps, 1.11 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85-6.75 (m, 1H), 6.75-6.65 (m, 2H), 3.85 (d, *J* = 8.6 Hz, 6H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.64 (dd, *J* = 8.2, 6.8 Hz, 2H), 1.93-1.82 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 147.1, 133.1, 120.0, 111.2, 111.0, 55.6, 55.5, 50.3, 32.0, 30.3.

4-(3-azidopropyl)-1,2-dimethoxybenzene (S17)



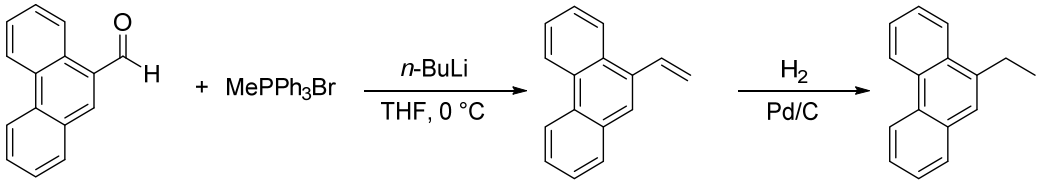
S17

The product **S16** (48% yield two steps) was obtained following the same procedure as **S15**. The reaction mixture was then concentrated to remove MsCl, and then NaN_3 (3.2 g, 50 mmol) and DMF (30 ml) were added. The resulting mixture was stirred at rt for 4 h. The residue was purified by flash column chromatography on silica gel to afford **S17** (48% yield two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85-6.78 (m, 1H), 6.74 (d, *J* = 7.2 Hz, 2H), 3.87 (d, *J* = 7.5 Hz, 6H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.79-2.67 (m, 2H), 2.13-2.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 147.2, 133.1, 120.2, 111.7, 111.2, 55.8, 55.7, 44.1, 34.0, 32.2.

9-ethylphenanthrene (**S22**)



S22

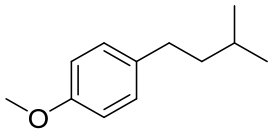
In a 100 mL round-bottomed flask, to a suspension of methyltriphenylphosphonium bromide (4.29 g, 12 mmol) in THF (20 mL) were added *n*-BuLi (2.4 M in *n*-hexane) (5 mL, 12 mmol) at 0 °C, and the resulting mixture was stirred at ambient temperature for 1 h. Then 9-phenanthrenecarbaldehyde (2.06 g, 10 mmol) was added and stirred for 5 h at rt. The mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford olefin (82% yield, 1.38 g).

The olefin (1.38 g, 8.2 mmol) and 10 % Pd/C (138 mg, 10 wt % of the substrate) in MeOH (20 mL) in a 100 mL flask was stirred under atmospheric (balloon) H_2 pressure at 25 °C for 6 h. Filter the catalyst on filter paper and wash the catalyst with ethanol. The residue was purified by flash column chromatography on silica gel to afford **S22** (99% yield, 1.38 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78-8.70 (m, 1H), 8.65 (dd, *J* = 7.4, 1.9 Hz, 1H), 8.17-8.08 (m, 1H), 7.87-7.80 (m, 1H), 7.69-7.53 (m, 5H), 3.16 (q, *J* = 7.5 Hz, 2H), 1.45 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 132.0, 131.3, 130.6, 129.6, 128.0, 126.5, 126.5, 126.1, 125.8, 124.9, 124.3, 123.2, 122.4, 26.1, 14.5.

1-isopentyl-4-methoxybenzene (S52)



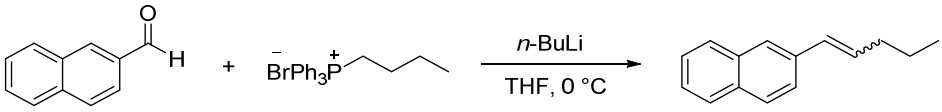
S52

The substrate **S52** (64% yield two steps) was obtained following the same procedure as **S22**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.61-2.50 (m, 2H), 1.57 (dp, *J* = 13.1, 6.6 Hz, 1H), 1.52-1.43 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 135.2, 129.2, 113.7, 55.2, 41.1, 32.8, 27.6, 22.5.

2-(pent-1-en-1-yl)naphthalene (S38) (E:Z = 2:1)



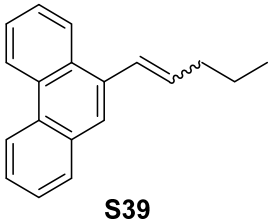
S38

In a 250 mL round-bottomed flask, to a suspension of butyltriphenylphosphonium bromide (9.65 g, 24 mmol) in THF (40 mL) were added *n*-BuLi (2.4 M in *n*-hexane) (10 mL, 24 mmol) at 0 °C, and the resulting mixture was stirred at ambient temperature for 1 h. Then, 2-naphthaldehyde (3.12 g, 20 mmol) was added and stirred for 5 h in room temperature. The mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **S38** (68% yield, 2.66 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.72 (m, 3.36H), 7.69 (s, 1H), 7.57 (dd, *J* = 8.5, 1.8 Hz, 0.67H), 7.48-7.36 (m, 2.33H), 6.63-6.46 (m, 1H), 6.41 (dt, *J* = 15.8, 6.9 Hz, 0.66H), 5.81 (dt, *J* = 11.6, 7.2 Hz, 0.33H)., 2.39 (qd, *J* = 7.3, 1.9 Hz, 0.69H), 2.24 (qd, *J* = 7.1, 1.4 Hz, 1.31H), 1.52 (m, 2H), 0.96 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 33.7, 133.5, 132.6, 131.5, 123.0, 128.9, 128.0, 127.9, 127.8, 127.59, 127.55, 127.50, 127.4, 127.3, 126.1, 126.0, 125.6, 125.4, 125.2, 123.6, 35.3, 30.8, 23.2, 22.6, 13.9, 13.8.

9-(pent-1-en-1-yl)phenanthrene (S39) (E:Z = 1:3)



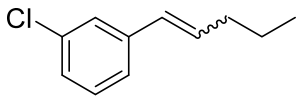
S39

The product **S39** (71% yield) was obtained following the same procedure as **S38**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82-8.65 (m, 2H), 8.25-8.22 (m, 0.25H), 8.15-8.13 (m, 0.75H), 7.93-7.90 (m, 1H), 7.83 (s, 0.25H), 7.74-7.60 (m, 4.75H), 7.16 (dq, J = 11.6, 1.6 Hz, 0.25H), 6.94 (dq, *J* = 11.6, 1.6 Hz, 0.75H), 6.37 (dt, *J* = 15.6, 6.8 Hz, 0.25H),

6.05 (dt, *J* = 15.6, 6.8 Hz, 0.75H), 2.40 (qd, *J* = 7.4, 1.6 Hz, 0.5H), 2.26 (qd, *J* = 7.4, 1.6 Hz, 1.5H), 1.72-1.62 (m, 0.5H), 1.60-1.43 (m, 1.5H), 1.10 (t, *J* = 7.4 Hz, 0.75H), 0.92 (t, *J* = 7.4 Hz, 2.25H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.8(1), 134.8(0), 134.7, 133.5, 132.1, 131.7, 131.5, 130.9, 130.4, 129.9(9), 129.9, 128.52, 128.50, 127.7, 127.3, 126.9, 126.7, 126.6(6), 126.5, 126.5, 126.4, 126.3(6), 126.3(1), 126.2, 125.8, 124.9, 124.3, 123.0, 122.9, 122.5(4), 122.5(1), 35.5, 30.8, 23.0, 22.6, 13.8(8), 13.8(6).

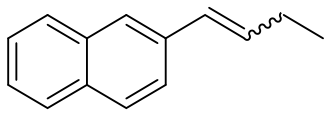
1-chloro-3-(pent-1-en-1-yl)benzene (S41) (E/Z = 1/1.3)



S41

The product **S41**(71% yield) was obtained following the same procedure as **S38**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.21 (m, 1.6H), 7.21-7.11 (m, 2.4H), 6.39-6.28 (m, 1H), 6.23 (dt, *J* = 15.8, 6.5 Hz, 0.41H), 5.70 (dt, *J* = 11.7, 7.3 Hz, 0.52H), 2.28 (qd, *J* = 7.3, 1.9 Hz, 1.12H), 2.18 (q, *J* = 7.1 Hz, 0.86H), 1.53-1.44 (m, 2H), 0.96-0.91 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 139.6, 134.4, 133.9, 132.6, 129.6, 129.3, 128.7, 128.6, 127.6, 126.9, 126.7, 126.4, 125.8, 124.1, 30.6, 23.0, 22.4, 13.8, 13.7.

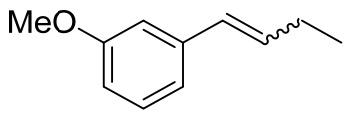
2-(but-1-en-1-yl)naphthalene (S42) (E:Z = 2:1)



S42

The product **S42** (77% yield) was obtained following the same procedure as **S38**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 3H), 7.69 (d, *J* = 14.9 Hz, 1H), 7.62-7.53 (m, 1H), 7.49-7.37 (m, 2H), 6.54 (d, *J* = 16.2 Hz, 1H), 6.40 (dt, *J* = 16.0, 6.4 Hz, 0.68H), 5.74 (dt, *J* = 11.7, 7.2 Hz, 0.32H), 2.43 (tt, *J* = 9.4, 6.7 Hz, 0.67H), 2.29 (tt, *J* = 7.4, 1.4 Hz, 1.33H), 1.12 (dt, *J* = 14.1, 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4, 135.2, 133.7, 133.1, 132.6, 128.9, 128.3, 128.0, 127.9, 127.8, 127.6, 127.54, 127.52, 127.3, 127.2, 126.1, 126.0, 125.6, 125.4, 125.3, 123.6, 26.2, 22.1, 14.5, 13.7.

1-(but-1-en-1-yl)-3-methoxybenzene (S43) (E:Z = 1:1)

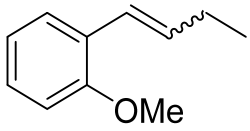


S43

The product **S43** (83% yield) was obtained following the same procedure as **S38**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 15.3, 7.7 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 0.5H), 6.94-6.88 (m, 1H), 6.84 (s, 0.5H), 6.83-6.74 (m, 1H), 6.36 (m, 1H), 6.29 (dt, *J* =

15.8, 6.1 Hz, 0.5H), 5.68 (dt, *J* = 11.6, 7.3 Hz, 0.5H), 3.84 (s, 3H), 2.38 (pd, *J* = 7.5, 1.8 Hz, 1H), 2.26 (qd, *J* = 7.4, 6.0 Hz, 1H), 1.10 (dt, *J* = 12.0, 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 159.4, 139.4, 139.1, 135.0, 133.0, 129.4, 129.1, 128.7, 128.1, 121.3, 118.6, 114.3, 112.4, 112.0, 111.2, 55.2, 26.0, 22.0, 14.5, 13.6.

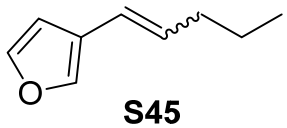
1-(but-1-en-1-yl)-3-methoxybenzene (S44) (E:Z = 1.2:1)



S44

The product **S44** (86% yield) was obtained following the same procedure as **S38**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.7 Hz, 1H), 7.28-7.16 (m, 1H), 6.99-6.85 (m, 2H), 6.77-6.68 (d, *J* = 15.9 Hz, 0.55H), 6.52 (d, *J* = 11.6 Hz, 0.45H), 6.28 (dt, *J* = 15.9, 6.6 Hz, 0.55H), 5.74 (dt, *J* = 11.5, 7.3 Hz, 0.45H), 3.87 (d, *J* = 3.4 Hz, 3H), 2.36-2.23 (m, 2H), 1.10 (dt, *J* = 22.0, 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 156.3, 134.6, 133.4, 130.0, 128.0, 127.8, 127.0, 126.5, 126.4, 123.6, 123.3, 120.6, 120.0, 110.8, 110.4, 55.44, 55.42, 26.5, 22.0, 14.4, 13.8.

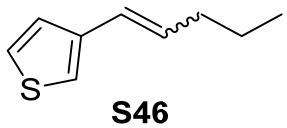
3-(pent-1-en-1-yl)furan (S45) (E:Z = 1:1.5)



S45

The product **S45** (58% yield) was obtained following the same procedure as **S38**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.28 (m, 2H), 6.48 (d, *J* = 18.8, Hz, 1H), 6.28-6.08 (m, 1H), 5.94 (dt, *J* = 15.7, 6.9 Hz, 0.38H), 5.57 (dt, *J* = 11.4, 7.1 Hz, 0.62H), 2.25 (qd, *J* = 7.2, 1.8 Hz, 1.27H), 2.13 (qd, *J* = 7.2, 1.5 Hz, 0.73H), 1.48 (m, 2H), 0.95 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 142.6, 140.8, 139.3, 132.0, 130.6, 119.3, 118.7, 111.0, 107.6, 35.0, 31.3, 22.7, 22.5, 13.9, 13.7.

2-(pent-1-en-1-yl)thiophene (S46) (E:Z = 1:2)

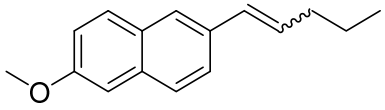


S46

The product **S46** (61% yield) was obtained following the same procedure as **S38**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 4.9, 2.9 Hz, 0.57H), 7.24 (dd, *J* = 5.0, 2.9 Hz, 0.37H), 7.18 (dd, *J* = 5.0, 1.3 Hz, 0.33H), 7.15 (m 0.60H), 7.10 (dd, *J* = 4.9, 1.3 Hz, 0.62H), 7.04 (dd, *J* = 3.0, 1.2 Hz, 0.33H), 6.43–6.28 (m, 1H), 6.08 (dt, *J* = 15.9, 7.0 Hz, 0.33H), 5.61 (dt, *J* = 11.5, 7.1 Hz, 0.68H), 2.33 (qd, *J* = 7.2, 1.9 Hz, 1.27H), 2.15 (qd, *J* = 7.2, 1.5 Hz, 0.73H), 1.48 (m, 2H), 0.95 (q, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.2, 131.0, 128.6, 125.7, 125.0, 124.8, 124.2, 123.0, 122.5, 120.3, 35.0, 31.2, 22.9, 22.5, 13.9, 13.7.

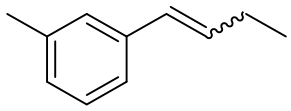
2-methoxy-6-(pent-1-en-1-yl)naphthalene (S48) (E:Z = 1.5:1)



S48

The product **S48** (91% yield) was obtained following the same procedure as **S38**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.65 (m, 3H), 7.61 (dd, *J* = 8.6, 1.7 Hz, 0.6H), 7.47 (dd, *J* = 8.6, 1.7 Hz, 0.33H), 7.23-7.12 (m, 2H), 6.65-6.52 (m, 1H), 6.36 (dt, *J* = 15.4, 6.9Hz, 0.62H), 5.77 (dt, *J* = 11.7, 7.3Hz, 0.38H), 3.96 (d, *J* = 4.0 Hz, 3H), 2.46 (qd, *J* = 7.3, 1.8 Hz, 1H), 2.30 (qd, *J* = 7.3, 1.4 Hz, 1H), 1.59 (m, 2H), 1.04 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 157.4, 133.7, 133.3, 133.2, 132.8, 130.3, 123.0, 129.4, 129.3, 129.1, 128.9, 128.8, 127.8, 127.2, 126.9, 126.4, 125.1, 124.1, 118.80, 118.76, 105.8, 105.6, 55.24, 55.21, 35.2, 30.8, 23.2, 22.6, 13.9, 13.8.

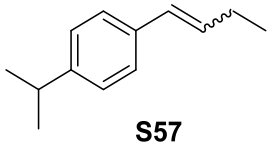
1-(but-1-en-1-yl)-3-methylbenzene (S56) (E:Z = 2:1)



S56

The product **S56** (71% yield) was obtained following the same procedure as **S38**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.12 (m, 2.33H), 7.10-7.05 (m, 0.67H), 7.05-6.97 (m, 1H), 6.38-6.30 (m, 1H), 6.25 (dt, *J* = 15.8, 6.2 Hz, 0.67H), 5.63 (dt, *J* = 11.6, 7.3 Hz, 0.33H), 2.34 (d, *J* = 6.8 Hz, 3.5H), 2.26-2.18 (m, 1.5H), 1.07 (dt, *J* = 11.6, 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 137.9, 137.7, 137.6, 134.6, 132.4, 129.5, 128.8, 128.4, 128.3, 128.0, 127.5, 127.2, 126.6, 125.8, 123.1, 26.1, 22.0, 21.4, 21.4, 14.5, 13.7.

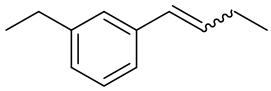
1-(but-1-en-1-yl)-4-isopropylbenzene (S57) (E:Z = 1.5:1)



S57

The product **S57** (73% yield) was obtained following the same procedure as **S38.**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 1H), 7.32-7.24 (m, 2H), 7.24-7.20 (m, 1H), 6.43 (d, *J* = 14.2 Hz, 1H), 6.29 (dt, *J* = 15.8, 6.4 Hz, 0.6H), 5.68 (dt, *J* = 11.6, 7.2 Hz, 0.4H), 2.95 (dq, *J* = 14.1, 6.9 Hz, 1H), 2.43 (pd, *J* = 7.4, 1.8 Hz, 1H), 2.35-2.23 (m, 1H), 1.32 (dd, *J* = 6.9, 6.2 Hz, 6H), 1.14 (q, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 147.1, 135.6, 135.3, 134.0, 131.7, 128.7, 128.6, 128.1, 126.5, 126.1, 125.8, 33.8, 33.8, 26.1, 24.0, 22.0, 14.5, 13.7.

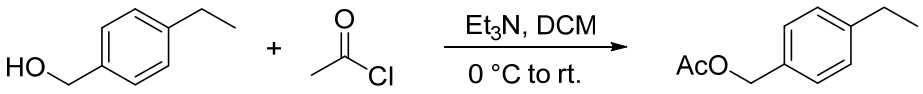
1-(but-1-en-1-yl)-4-ethylbenzene (S58) (E:Z = 1.5:1)



S58

The product **S58** (62% yield) was obtained following the same procedure as **S38**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21 (m, 2.2H), 7.17 (dt, *J* = 3.8, 1.7 Hz, 0.8H), 7.11 (m, 1H), 6.48-6.39 (m, 1H), 6.32 (dt, *J* = 15.8, 6.3 Hz, 0.6H), 5.70 (dt, *J* = 11.6, 7.3 Hz, 0.4H), 2.70 (p, *J* = 7.4 Hz, 2H), 2.42 (pd, *J* = 7.5, 1.8 Hz, 1.2H), 2.29 (m, 0.8H), 1.30 (dt, *J* = 7.6, 3.0 Hz, 3H), 1.14 (dt, *J* = 11.3, 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 144.0, 137.9, 137.7, 134.5, 132.4, 128.9, 128.42, 128.38, 128.32, 128.0, 126.4, 126.02, 126.01, 125.5, 123.3, 28.9, 26.1, 22.0, 15.7, 15.6, 14.5, 13.7.

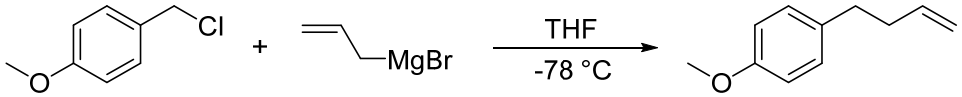
4-ethylbenzyl acetate (S54)



S54

A mixture of substituted (4-ethylphenyl)methanol (1.0 g, 7.34 mmol) and trimethylamine (3.18 mL, 23 mmol) in dichloromethane (20 mL) was treated slowly with acetyl chloride (0.57 mL, 8 mmol) drop wise at 0 ºC. After completion of addition, the reaction mixture was stirred for another 2 h at rt. After completion of reaction, the reaction mixture was poured into water (50 mL), extract with DCM. The extract was washed with water, brine solution, dried over $MgSO_4$ and concentrated. The crude compound was subjected to column chromatography on silica gel to obtained 4-ethylbenzyl acetate **S54** with 74% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.09 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 144.5, 133.1, 128.5, 128.1, 66.3, 28.6, 21.0, 15.5.

1-(but-3-en-1-yl)-4-methoxybenzene (S55)



S55

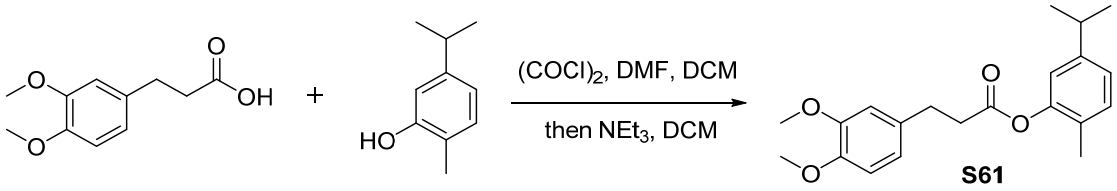
In a 50 mL round-bottomed flask, to a suspension of 1-(chloromethyl)-4-methoxybenzene (1.57 g, 10 mmol, 1.0 equiv.) in THF (10 mL) were added allylmagnesium bromide (1.0 M in Et_2O) (20 mL, 2.0 equiv.) at -78 °C, and the resulting mixture was stirred at low temperature for 1 h. Then, stir overnight at room temperature. The mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$ and

concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **S55** (61% yield, 1.0 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.06 (m, 2H), 6.89-6.77 (m, 2H), 5.85 (m, 1H), 5.10-4.91 (m, 2H), 3.78 (s, 3H), 2.65 (t, *J* = 8.9 Hz, 2H), 2.34 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 138.2, 134.0, 129.3, 114.8, 113.7, 55.2, 35.8, 34.5.

5-isopropyl-2-methylphenyl-3-(3,4-dimethoxyphenyl)propanoate (S61)



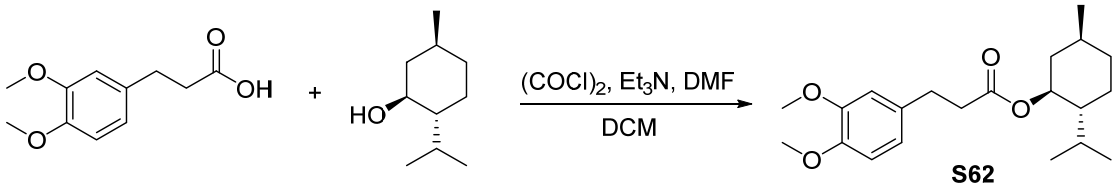
A 100 mL round-bottom flask was charged with 3-(3,4-dimethoxyphenyl)propanoic acid (1.05 g, 5 mmol), dry DCM (30 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. And then $(COCl)_2$ (0.85 mL, 10 mmol) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. then concentrated to obtain the acyl chloride crude product.

A mixture of carvacrol (0.75 g, 5 mmol) and trimethylamine (1.4 mL, 10 mmol) in DCM (20 mL) was treated slowly with the acyl chloride crude product at 0 °C. After completion of addition, the reaction mixture was stirred for another 2 h at rt. After completion of reaction, the reaction mixture was poured into water, extract with DCM. The extract was washed with water, brine solution, dried over $MgSO_4$ and concentrated. The crude compound was subjected to column chromatography on silica gel to obtained **S61** (1.40 g, 4.1 mmol) in 82% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.8 Hz, 1H), 6.92 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.75 (d, *J* = 1.0 Hz, 2H), 6.73 (d, *J* = 1.2 Hz, 1H), 6.69 (d, *J* = 1.8 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 2.97 (t, *J* = 7.4 Hz, 2H), 2.88-2.67 (m, 3H), 1.97 (s, 3H), 1.14 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 149.1, 148.9, 148.0, 147.6, 132.8, 130.8, 127.1, 124.1, 120.2, 119.6, 111.7, 111.3, 55.9, 55.8, 36.0, 33.5, 30.6, 23.8, 15.6.

(*1R,2R,5S*)-2-isopropyl-5-methylcyclohexyl 3-(3,4-dimethoxyphenyl) propanoate (S62)

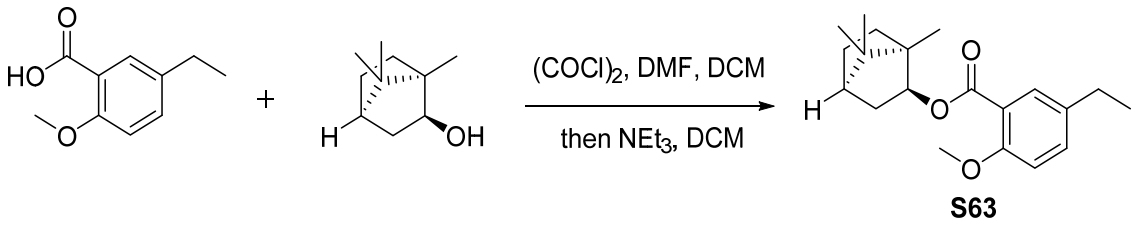


The product **S62** (2.85 g, 8.2 mmol, 82% yield) was obtained from 3-(3,4-dim ethoxyphenyl)propanoic acid (2.10 g, 10 mmol) and L-menthol (1.56 g, 10 mm ol) following the same procedure as **S61**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82-6.70 (m, 3H), 4.67 (td, *J* = 10.9, 4.4 Hz, 1H), 3.86 (d, *J* = 6.0 Hz, 6H), 2.90 (t, *J* = 7.7 Hz, 2H), 2.59 (dd, *J* = 8.4, 7.0 Hz, 2H), 1.97-1.91

(m, 1H), 1.78-1.61 (m, 3H), 1.37-1.29 (m, 1H), 1.03 (qd, *J* = 13.3, 12.6 Hz, 1H), 0.98-0.81 (m, 8H), 0.70 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 133.2, 120.1, 111.6, 111.2, 74.2, 55.9, 55.80, 47.0, 41.0, 36.5, 34.3, 31.4, 30.7, 26.2, 23.4, 22.0, 20.8, 16.3.

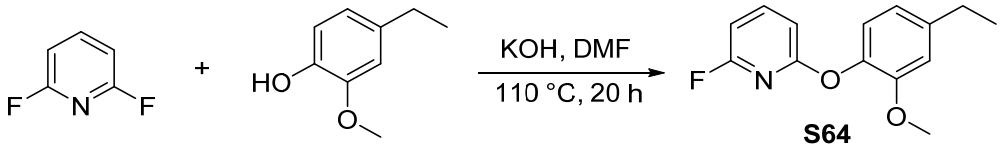
(*1R,2R,4S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl-5-ethyl-2-methoxybenzoate (S63)



S63

The product **S63** (0.39 g, 1.23 mmol, 85% yield) was obtained from 5-ethyl-2-methoxybenzoic acid (0.271 g, 1.5 mmol) and (+)-Borneol (0.23 g, 1.5 mmol) following the same procedure as **S61**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.4 Hz, 1H), 7.39-7.12 (m, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 5.10 (ddd, *J* = 9.9, 3.5, 2.1 Hz, 1H), 3.87 (s, 3H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.52-2.36 (m, 1H), 2.15 (ddd, *J* = 12.5, 9.0, 4.4 Hz, 1H), 1.85-1.64 (m, 2H), 1.41-1.26 (m, 2H), 1.23 (t, *J* = 7.6 Hz, 3H), 1.13 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.96 (s, 3H), 0.92 (s, 3H), 0.91 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 157.3, 135.8, 132.5, 130.6, 120.6, 112.1, 80.4, 56.0, 48.9, 47.8, 45.0, 36.9, 28.0, 27.7, 27.3, 19.7, 18.9, 15.6, 13.6.

2-(4-ethyl-2-methoxyphenoxy)-6-fluoropyridine (S64)

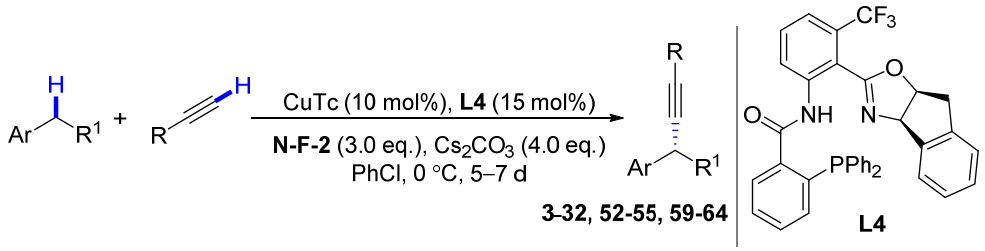


S64

A mixture of substituted 4-ethyl-2-methoxyphenol (1.62 mL, 10 mmol) and KOH (560 mg, 10 mmol) in DMF (5 mL) was treated slowly with 2,6-difluoropyridine (1.0 mL, 10 mmol) drop wise. After completion of addition, the reaction mixture was stirred for another 20 h at 110 ºC. After completion of reaction, , the reaction mixture was poured into water, extract with ethyl acetate. The extract was washed with water, brine solution, dried over $MgSO_4$ and concentrated. The crude compound was subjected to column chromatography on silica gel to obtained 2-(4-ethyl-2-methoxyphenoxy)-6-fluoropyridine (**S64**) in 35% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (q, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.89-6.75 (m, 2H), 6.68 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.54 (dd, *J* = 7.8, 2.7 Hz, 1H), 3.76 (s, 3H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -68.59.
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, $J_{C\text{-}F}$ = 240.3 Hz), 162.8 (d, $J_{C\text{-}F}$ = 67.6 Hz),

151.3, 143.1 (d, $J_{C\text{-}F}$ = 7.9 Hz), 142.7, 139.8, 122.6, 120.2, 112.7, 106.4 (d, $J_{C\text{-}F}$ = 5.1 Hz), 102.0, 101.7, 55.9, 28.8, 15.5.

Asymmetric oxidative radical C(sp^3)-H/C(sp)-H cross-coupling

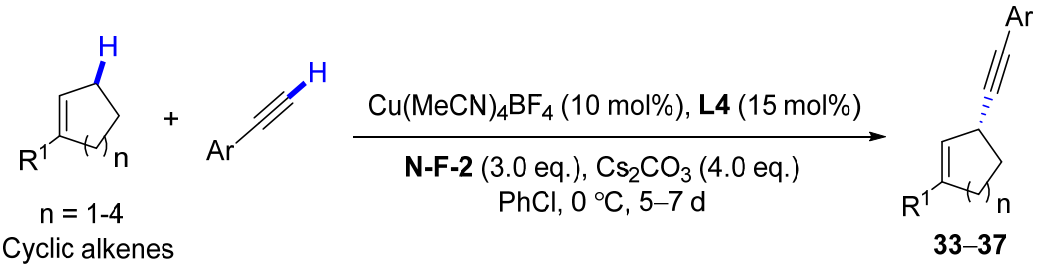


General procedure A:

To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuTc (1.9 mg, 0.010 mmol, 10 mol%), **L4** (9.2 mg, 0.015 mmol, 15 mol%), alkyne (0.10 mmol, 1.0 equiv., if solid), C(sp^3)-H substrate (1.0 mmol, 10 equiv., if solid), **N-F-2** (90.0 mg, 0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (130.4 mg, 0.40 mmol, 4.0 equiv.), The tube was evacuated and backfilled with argon for three times, anhydrous PhCl (0.8 mL), alkyne (0.10 mmol, 1.0 equiv., if liquid) and C(sp^3)-H substrate (1.0 mmol, 10 equiv., if liquid) were added into the mixture and the reaction mixture was stirred at 0 °C for 5-7 d. Upon alkyne completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure B:

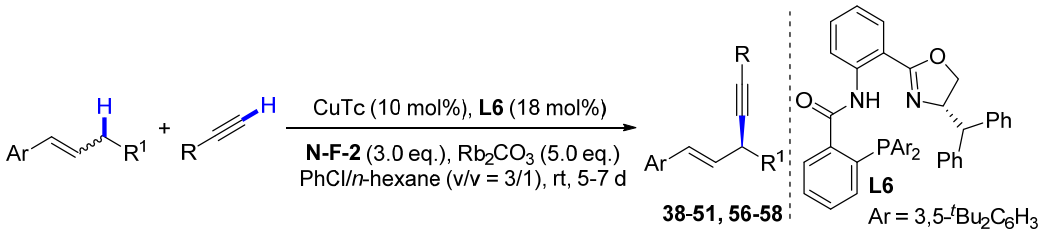
To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuTc (1.9 mg, 0.010 mmol, 10 mol%), **L4** (9.2 mg, 0.015 mmol, 15 mol%), alkyne (0.10 mmol, 1.0 equiv., if solid), C(sp^3)-H substrate (1.0 mmol, 10 equiv., if solid), **N-F-2** (90.0 mg, 0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (130.4 mg, 0.40 mmol, 4.0 equiv.), The tube was evacuated and backfilled with argon for three times, anhydrous PhCl (0.8 mL), alkyne (0.10 mmol, 1.0 equiv., if liquid) and C(sp^3)-H substrate (1.0 mmol, 10 equiv., if liquid) were added into the mixture and the reaction mixture was stirred at -15 °C under irradiation of blue LED (24 W) for 10 d. Upon alkyne completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.



General procedure C:

To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $Cu(MeCN)_4BF_4$ (3.2 mg, 0.010 mmol, 10 mol%), **L4** (9.2 mg, 0.015 mmol, 15 mol%),

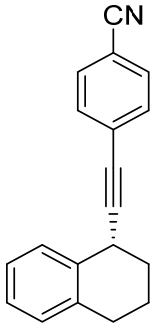
alkyne (0.10 mmol, 1.0 equiv., if solid), C(sp^3)-H substrate (1.0 mmol, 10 equiv., if solid), **N-F-2** (90.0 mg, 0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (130.4 mg, 0.40 mmol, 4.0 equiv.), The tube was evacuated and backfilled with argon for three times, anhydrous PhCl (0.8 mL), alkyne (0.10 mmol, 1.0 equiv., if liquid) and C(sp^3)-H substrate (1.0 mmol, 10 equiv., if liquid) were added into the mixture and the reaction mixture was stirred at 0 °C for 5–7 d. Upon alkyne completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.



General procedure D:

To a flame-dried Schlenk tube equipped with a magnetic stir bar were added CuTc (1.9 mg 10 mol%), **L6** (15.1 mg, 18 mol%), alkyne (0.10 mmol, 1.0 equiv., if solid), C(sp^3)-H substrate (1.0 mmol, 10 equiv., if solid), **N-F-2** (90 mg, 0.3 mmol), and Rb_2CO_3 (116 mg, 0.5 mmol). The tube was evacuated and backfilled with argon for three times, alkyne (0.10 mmol, 1.0 equiv., if liquid) and C(sp^3)-H substrate (1.0 mmol, 10 equiv., if liquid) and dry PhCl (0.6 mL), *n*-hexane (0.2 mL) were added *via* syringe. The tube was stirred at rt for 5-7 d, the reaction stopped and the reaction mixture was filtered through a short celite. The filtrate solvent was removed under reduced pressure, and the residue was purified by column chromatography to afford the desired product.

(*S*)-4-((1,2,3,4-tetrahydronaphthalen-1-yl)ethynyl)benzonitrile (3)



3

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1,2,3,4-tetrahydronaphthalene (136 μL, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **3** (17.2 mg) in 62% isolated yield.

Procedure for large-scale synthesis:

To a flame-dried Schlenk tube equipped with a magnetic stir bar were charged with

CuTc (152 mg, 0.8 mmol, 10 mol%), **L4** (736 mg, 1.2 mmol, 15 mol%), 4-cyanophenylacetylene (1.0160 g, 8 mmol, 1.0 equiv.), **N-F-2** (7.21 g, 24 mmol, 3.0 equiv.) and Cs_2CO_3 (10.4 g, 32 mmol, 4.0 equiv.), The tube was evacuated and backfilled with argon for three times, anhydrous PhCl (64 mL) and 1,2,3,4-tetrahydronaphthalene (10.9 mL, 80 mmol, 10 equiv.) were added into the mixture and the reaction mixture was stirred at 0 °C for 12 d. Upon alkyne completion (monitored by TLC), the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **3** (1.52 g, 5.92 mmol) in 74% isolated yield.

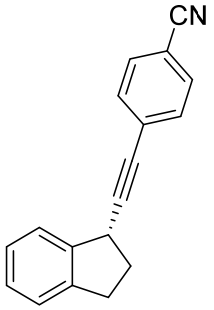
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.54 (m, 2H), 7.50-7.45 (m, 3H), 7.21-7.15 (m, 2H), 7.14-7.08 (m, 1H), 4.04 (t, *J* = 6.4 Hz, 1H), 2.87-2.78 (m, 2H), 2.26-2.13 (m, 1H), 2.13-1.94 (m, 2H), 1.87-1.78 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 135.5, 132.2, 131.9, 129.4, 129.0, 128.9, 126.8, 126.1, 118.6, 111.0, 98.1, 80.2, 32.1, 30.0, 29.1, 21.2.

HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{16}N$ $[M + H]^+$ 258.1277, found 258.1275.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 19.0 min, t(major) = 24.4 min, 93% ee (96.5:3.5 er).

***(S)*-4-((2,3-dihydro-1H-inden-1-yl)ethynyl)benzonitrile (4)**



4

According to **General Procedure B** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1,2-hydrindene (124 μL, 1 mmol, 10 equiv) for 10 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **4** (17.2 mg) in 71% isolated yield.

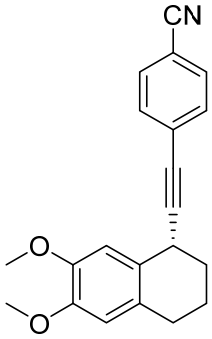
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.52 (m, 2H), 7.52-7.46 (m, 2H), 7.43 (dd, *J* = 4.3, 3.9 Hz, 1H), 7.30-7.20 (m, 3H), 4.21 (t, *J* = 8.4 Hz, 1H), 3.13-2.82 (m, 2H), 2.59-2.57 (m, 1H), 2.23-2-17 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 142.8, 132.2, 131.9, 128.7, 127.3, 126.7, 124.6, 124.1, 118.5, 111.0, 96.6, 80.3, 77.3, 77.0, 76.7, 36.8, 34.1, 31.5.

HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{14}N$ $[M + H]^+$ 244.1121, found 244.1119.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 20.5 min, t(major) = 29.2 min, 72% ee (86.1:13.9 er).

***(S)*-4-((6,7-dimethoxy-1,2,3,4-tetrahydronaphthalen-1-yl)ethynyl)benzonitrile (5)**



5

According to **General Procedure B** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (96.2 mg, 0.5 mmol, 5 equiv) for 10 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **5** (20.8 mg) in 66% isolated yield.

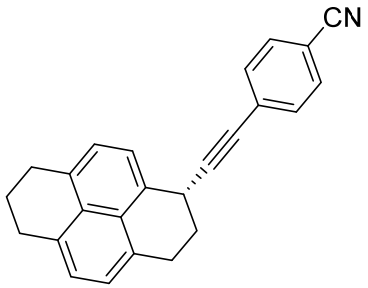
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.52 (m, 2H), 7.52-7.39 (m, 2H), 6.94 (s, 1H), 6.59 (s, 1H), 3.98 (t, *J* = 6.3 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.93-2.61 (m, 2H), 2.26-2.09 (m, 1H), 2.07-1.96 (m, 2H), 1.89-1.71 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.32, 132.1, 131.9, 128.8, 128.3, 127.0, 118.6, 111.8, 110.9, 98.3, 80.1, 56.0, 55.9, 31.7, 30.0, 28.7, 21.2.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{20}N$ $[M + H]^+$ 318.1489, found 318.1485.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 25.3 min, t(major) = 36.1 min, 92% ee (95.8:4.2 er).

(*S*)-4-((1,2,3,6,7,8-hexahydropyren-1-yl)ethynyl)benzonitrile (6)



6

According to **General Procedure A**, while $Cu(MeCN)_4BF_4$ (3.2 mg, 10 mol%) was used with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1,2,3,6,7,8-hexahydropyrene (208 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **6** (18.2 mg) in 54% isolated yield.

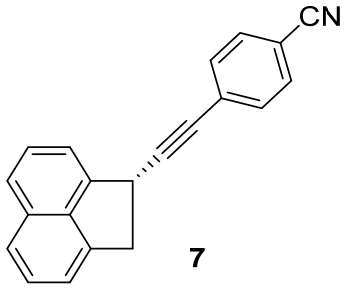
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.54 (m, 2H), 7.53-7.46 (m, 3H), 7.24-7.14 (m, 3H), 4.33 (dd, *J* = 7.9, 4.3 Hz, 1H), 3.32 (ddd, *J* = 16.1, 7.7, 4.2 Hz, 1H), 3.19-2.98 (m, 5H), 2.36 (ddt, *J* = 12.1, 8.2, 4.3 Hz, 1H), 2.25 (dtd, *J* = 12.4, 8.2, 4.2 Hz, 1H), 2.14-1.99 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 134.5, 132.5, 132.2, 131.9, 131.7, 130.2, 128.8, 124.0, 123.8, 123.7, 123.6, 118.6, 111.0, 96.9, 81.5, 33.7, 31.5, 31.4, 29.4, 29.0, 23.2.

HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{20}N$ $[M + H]^+$ 334.1590, found 334.1585.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 25.0 min, t(major) = 32.4 min, 84% ee (92.0:8.0 er).

***(S)*-4-((1,2-dihydroacenaphthylen-1-yl)ethynyl)benzonitrile (7)**



7

According to **General Procedure A**, while $Cu(MeCN)_4BF_4$ (3.2 mg, 10 mol%) was used with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1,2-dihydroacenaphthylene (154 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **7** (14.1 mg) in 50% isolated yield.

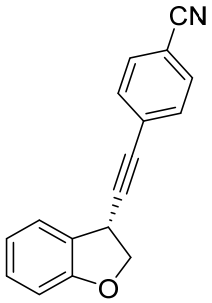
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.64 (m, 2H), 7.60-7.57 (m, 3H), 7.56-7.48 (m, 4H), 7.35 (dd, *J* = 6.9, 1.6 Hz, 1H), 4.83-4.79 (m, 1H), 3.99-3.92 (m, 1H), 3.66-3.61 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 142.4, 137.6, 132.2, 131.9, 131.6, 128.6, 128.2, 128.1, 123.7, 122.9, 119.6, 119.5, 118.5, 111.2, 96.2, 80.3, 39.4, 34.7.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{14}N$ $[M + H]^+$ 280.1121, found 280.1119.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 29.2 min, t(major) = 32.0 min, 75% ee (87.7:12.3 er).

***(S)*-4-((2,3-dihydrobenzofuran-3-yl)ethynyl)benzonitrile (8)**



8

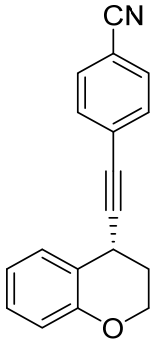
According to **General Procedure A**, while $Cu(MeCN)_4BF_4$ (3.2 mg, 10 mol%) was used with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 2,3-dihydrobenzofuran (113 μL, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **8** (11.2 mg) in 45% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.56 (m, 2H), 7.52-7.46 (m, 2H), 7.41-7.34 (m, 1H), 7.24-7.17 (m, 1H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 4.84 (dd, *J* = 9.1, 8.1 Hz, 1H), 4.61 (t, *J* = 8.8 Hz, 1H), 4.52 (t, *J* = 8.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 132.2, 132.0, 129.2, 127.9, 126.6, 124.7, 121.2,

118.4, 111.6, 110.1, 92.7, 81.4, 76.2, 34.5.
HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{12}NO$ $[M + H]^+$ 246.0913, found 246.0912.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 31.1 min, t(major) = 42.0 min, 83% ee (91.5:8.5 er).

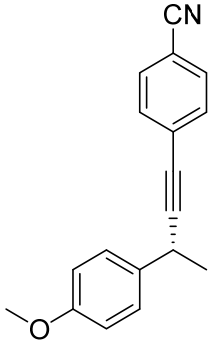
***(S)*-4-(chroman-4-ylethynyl)benzonitrile (9)**



9

According to **General Procedure A**, while $Cu(MeCN)_4BF_4$ (3.2 mg, 10 mol%) was used with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and chromane (125 μL, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **9** (15.5 mg) in 59% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.53 (m, 2H), 7.53-7.45 (m, 2H), 7.37 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 6.92 (td, *J* = 7.5, 1.3 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.3 Hz, 1H), 4.39 (ddd, *J* = 10.8, 7.5, 3.0 Hz, 1H), 4.24 (ddd, *J* = 10.7, 7.2, 3.0 Hz, 1H), 4.10 (t, *J* = 6.1 Hz, 1H), 2.45-2.27 (m, 1H), 2.25-2.21 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 132.2, 131.9, 129.6, 128.7, 128.3, 120.9, 120.7, 118.5, 117.2, 111.3, 96.0, 80.8, 64.2, 28.8, 28.1.
HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{14}NO$ $[M + H]^+$ 260.1070, found 260.1067.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 32.1 min, t(major) = 37.9 min, 86% ee (92.8:7.2 er).

***(R)*-4-(3-(4-methoxyphenyl)but-1-yn-1-yl)benzonitrile (10)**



10

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-ethyl-4-methoxybenzene (142 μL, 1 mmol, 10 equiv) for 7 d,

the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **10** (16.6 mg) in 63% isolated yield.

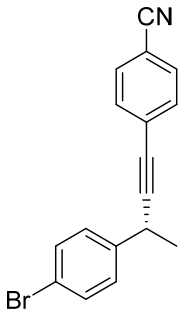
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.43-7.22 (m, 2H), 6.89 (d, *J* = 8.7 Hz, 1H), 3.95 (q, *J* = 7.1 Hz, 1H), 3.80 (s, 3H), 1.56 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 134.6, 132.1, 131.9, 128.8, 127.8, 118.6, 114.0, 111.0, 98.0, 80.9, 55.3, 31.7, 24.1.

HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{16}NO$ $[M + H]^+$ 262.1226, found 262.1223.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min. λ = 280 nm, t(major) = 25.8 min, t(minor) = 27.6 min, 85% ee (92.4:7.6 er).

***(R)*-4-(3-(4-bromophenyl)but-1-yn-1-yl)benzonitrile (11)**



11

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-bromo-4-ethylbenzene (185.1 mg, 1.0 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **11** (12.4 mg) in 47% isolated yield.

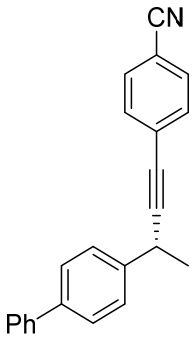
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 2H), 7.53-7.42 (m, 4H), 7.33-7.26 (m, 2H), 3.96 (q, *J* = 7.1 Hz, 1H), 1.57 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 132.2, 131.9, 131.8, 128.6, 128.4, 120.7, 118.5, 111.3, 96.8, 81.4, 32.1, 23.9.

HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{12}BrNNa$ $[M + Na]^+$ 332.0045, found 332.0042.

HPLC condition: Chiralcel AD-3, *n*-hexane/*i*-PrOH = 97/3, flow rate 0.8 mL/min. λ = 230 nm, t(minor) = 16.2 min, t(major) = 17.9 min, 78% ee (10.9:89.1 er).

***(R)*-4-(3-([1,1'-biphenyl]-4-yl)but-1-yn-1-yl)benzonitrile (12)**



12

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 4-ethyl-1,1'-biphenyl (182 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **12** (20.2 mg) in 65% isolated yield.

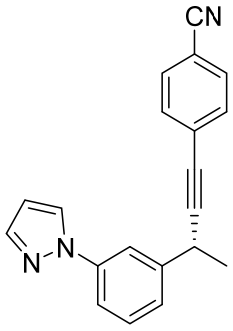
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.56 (m, 6H), 7.50 (dd, *J* = 12.7, 8.3 Hz, 4H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.38-7.31 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 1H), 1.63 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 140.7, 140.0, 132.2, 131.9, 128.8, 128.7, 127.4, 127.3, 127.0, 118.6, 111.1, 97.5, 81.1, 32.2, 24.0.

HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{18}N$ $[M + H]^+$ 308.1434, found 308.1438.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 39.9 min, t(major) = 51.0 min, 90% ee (95.1:4.9 er).

***(R)*-4-(3-(3-(1*H*-pyrazol-1-yl)phenyl)but-1-yn-1-yl)benzonitrile (13)**



13

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-(3-ethylphenyl)-1*H*-pyrazole (172 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **13** (25.1 mg) in 84% isolated yield.

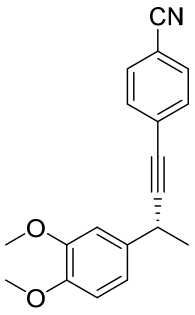
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.4 Hz, 1H), 7.81 (t, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.63-7.56 (m, 2H), 7.56 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 7.54-7.50 (m, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.36 (dt, *J* = 7.7, 1.4 Hz, 1H), 6.48 (t, *J* = 2.2 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 141.2, 140.5, 132.2, 131.9, 129.7, 128.5, 126.8, 124.9, 118.5, 118.1, 117.6, 111.2, 107.7, 96.9, 81.4, 32.6, 23.9.

HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{16}N_3$ $[M + H]^+$ 298.1339, found 298.1336.

HPLC condition: Chiralcel AD-3, *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 15.2 min, t(major) = 24.0 min, 81% ee (90.5:9.5 er).

***(R)*-4-(3-(3,4-dimethoxyphenyl)but-1-yn-1-yl)benzonitrile (14)**



14

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 4-ethyl-1,2-dimethoxybenzene (83 mg, 0.5 mmol, 5 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **14** (17.6 mg) in 61% isolated yield.

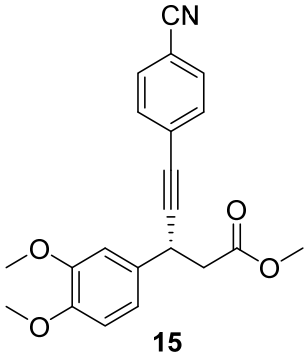
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.57 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.03-6.93 (m, 2H), 6.88 (d, *J* = 8.1 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 1.61 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 148.0, 135.1, 132.1, 131.9, 128.7, 118.8, 118.5, 111.3, 111.1, 110.3, 97.8, 81.0, 56.0, 55.9, 32.1, 24.1.

HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{18}NO_2$ $[M + H]^+$ 292.1332, found 292.1329.

HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 12.8 min, t(major) = 15.1 min, 88% ee (94.0:6.0 er).

methyl *(R)*-5-(4-cyanophenyl)-3-(3,4-dimethoxyphenyl)pent-4-ynoate (15)



15

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and methyl 3-(3,4-dimethoxyphenyl)propanoate (224 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **15** (14.9 mg) in 42% isolated yield.

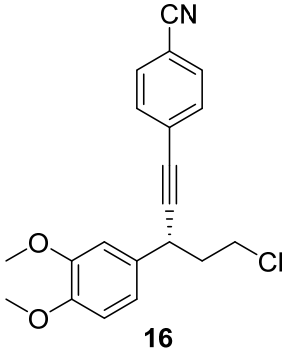
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.01-6.90 (m, 2H), 6.85 (d, *J* = 8.3 Hz, 1H), 4.36 (dd, *J* = 8.2, 6.9 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.70 (s, 3H), 2.92 (dd, *J* = 15.4, 8.3 Hz, 1H), 2.82 (dd, *J* = 15.4, 6.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 149.1, 148.4, 132.2, 132.1, 131.9, 131.5, 129.2, 128.2, 119.4, 118.5, 111.40, 111.35, 110.6, 94.9, 82.0, 77.2, 55.9, 51.9, 42.8, 34.4.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{20}NO_4$ $[M + H]^+$ 350.1387, found 350.1383.

HPLC condition: Chiralcel OD-3, *n*-hexane/*i*-PrOH = 97/3, flow rate 0.7 mL/min. λ = 254 nm, t(minor) = 84.0 min, t(major) = 88.0 min, 82% ee (91.1:8.9 er).

***(R)*-4-(5-chloro-3-(3,4-dimethoxyphenyl)pent-1-yn-1-yl)benzonitrile (16)**



16

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 4-(3-chloropropyl)-1,2-dimethoxybenzene (214 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **16** (14.1 mg) in 41% isolated yield.

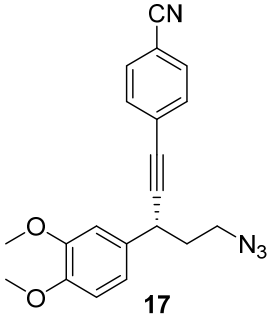
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 2H), 7.54-7.48 (m, 2H), 6.96 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.91 (d, *J* = 2.1 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 4.12 (dd, *J* = 8.2, 6.6 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.74 (ddd, *J* = 11.0, 7.6, 5.7 Hz, 1H), 3.58 (dt, *J* = 11.1, 6.1 Hz, 1H), 2.40-2.17 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 148.4, 132.2, 132.0, 128.2, 119.5, 118.4, 111.4, 110.7, 95.1, 82.3, 56.0, 42.4, 40.6, 35.2.

HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{19}ClNO_2$ $[M + H]^+$ 340.1099, found 340.1095.

HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 15.7 min, t(major) = 18.9 min, 93% ee (96.3:3.7 er).

***(R)*-4-(5-azido-3-(3,4-dimethoxyphenyl)pent-1-yn-1-yl)benzonitrile (17)**



17

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 4-(3-azidopropyl)-1,2-dimethoxybenzene (221 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **17** (12.0 mg) in 35% isolated yield.

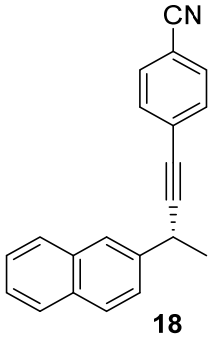
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.56-7.49 (m, 2H), 6.95 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.93-6.83 (m, 2H), 4.05-3.97 (m, 1H), 3.91 (s, 3H), 3.89 (s, 1H), 3.55-3.49 (m, 1H), 3.43-3.37 (m, 1H), 2.16-2.04 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 148.3, 132.4, 132.2, 132.0, 128.2, 119.5, 118.4, 111.43, 111.41, 110.6, 95.1, 82.4, 56.0, 49.2, 37.1, 35.2.

HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{19}N_4O_2$ $[M + H]^+$ 347.1503, found 347.1498.

HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 18.2 min, t(major) = 21.2 min, 94% ee (97.0:3.0 er).

***(R)*-4-(3-(naphthalen-2-yl)but-1-yn-1-yl)benzonitrile (18)**



18

According to **General Procedure A**, while $Cu(MeCN)_4BF_4$ (3.2 mg, 10 mol%) was used with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 2-ethylnaphthalene (157 μL, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **18** (16.0 mg) in 62% isolated yield.

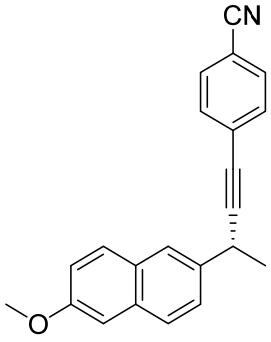
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.77 (m, 4H), 7.60-7.49 (m, 5H), 7.48-7.44 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 1H), 1.67 (dd, *J* = 7.2, 1.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 133.5, 132.5, 132.2, 131.9, 128.6, 128.5, 127.7, 127.6, 126.2, 125.8, 125.3, 125.1, 118.5, 111.1, 97.5, 81.3, 32.7, 23.9.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{16}N$ $[M + H]^+$ 282.1277, found 282.1275.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 31.4 min, t(major) = 44.4 min, 83% ee (91.6:8.4 er).

***(R)*-4-(3-(6-methoxynaphthalen-2-yl)but-1-yn-1-yl)benzonitrile (19)**



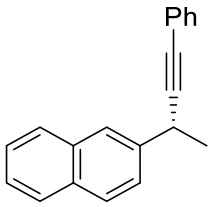
19

According to **General Procedure A**, while $Cu(MeCN)_4BF_4$ (3.2 mg, 10 mol%) was used with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 2-ethyl-6-methoxynaphthalene (186 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **19** (17.9 mg) in 57% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 1H), 7.73 (dd, *J* = 8.6, 5.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.51 (m, 3H), 7.18-7.10 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 1H), 3.92 (s,

3H), 1.66 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 137.5, 133.6, 132.2, 131.9, 129.2, 128.9, 128.7, 127.3, 125.8, 125.0, 119.0, 118.6, 111.1, 105.7, 97.8, 81.2, 55.3, 32.5, 23.9.
HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{18}NO$ $[M + H]^+$ 312.1383, found 282.1379.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 75/25, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 27.1 min, t(major) = 40.2 min, 86% ee (93.0:7.0 er).

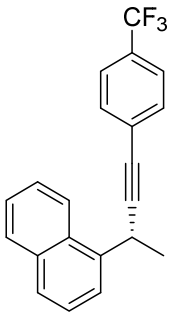
***(R)*-2-(4-phenylbut-3-yn-2-yl)naphthalene (20)**



20

According to **General Procedure A** with phenylacetylene (11.1 μL, 0.10 mmol, 1.0 equiv) and 2-ethylnaphthalene (157 μL, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **20** (10.2 mg) in 40% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.87 (m, 1H), 7.86-7.80 (m, 3H), 7.58 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.51-7.41 (m, 4H), 7.35-7.27 (m, 3H), 4.15 (q, *J* = 7.1 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 133.5, 132.4, 131.7, 128.3, 128.2, 127.79, 127.78, 127.6, 126.1, 125.6, 125.1, 123.7, 92.5, 82.7, 32.6, 24.3.
The NMR spectra was in accord with that reported in literature.[7]
HPLC condition: Chiralcel OD-3, *n*-hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 5.1 min, t(major) = 5.4 min, 90% ee (94.8:5.2 er).

***(S)*-1-(4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl)naphthalene (21)**

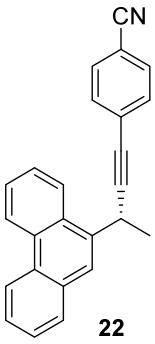


21

According to **General Procedure A** with 1-ethynyl-4-(trifluoromethyl)benzene (16.3 μL, 0.10 mmol, 1.0 equiv) and 1-ethylnaphthalene (155 μL, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **21** (12.1 mg) in 43% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.86-7.69 (m, 2H), 7.70-7.37 (m, 7H), 4.75 (q, *J* = 7.1 Hz, 1H), 1.75 (d, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.74.
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 134.0, 131.9, 130.5, 129.1, 127.7, 126.1, 125.64, 125.60, 125.1 (q, J_{C-F} = 3.8 Hz), 124.2, 123.1, 95.6, 81.5, 29.1, 23.1.
HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{16}F_3$ $[M + H]^+$ 325.1199, found 325.1195.
HPLC condition: Chiralcel OJ-3, *n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min. λ = 254 nm, t(minor) = 10.9 min, t(major) = 16.9 min, 92% ee (96.1:3.9 er).

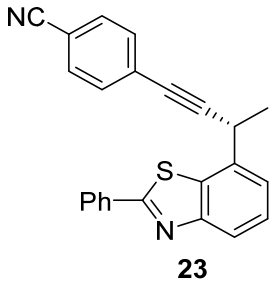
***(S)*-4-(3-(phenanthren-9-yl)but-1-yn-1-yl)benzonitrile (22)**



22

According to **General Procedure A**, while $Cu(MeCN)_4BF_4$ (3.2 mg, 10 mol%) was used with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 9-ethylphenanthrene (206.3 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **22** (17.2 mg) in 55% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85-8.76 (m, 1H), 8.71 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.32-8.23 (m, 1H), 8.03 (s, 1H), 7.98-7.90 (m, 1H), 7.79-7.69 (m, 2H), 7.70-7.62 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 4.80 (q, *J* = 7.0 Hz, 1H), 1.86 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 132.2, 131.9, 131.5, 131.0, 129.9, 129.7, 128.7, 128.5, 126.8, 126.7, 126.6, 126.4, 124.9, 123.8, 123.5, 122.4, 118.6, 111.1, 97.6, 81.6, 29.3, 22.4.
HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{18}N$ $[M + H]^+$ 332.1434, found 332.1430.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 29.3 min, t(major) = 47.9 min, 91% ee (95.7:4.3 er).

***(S)*-4-(3-(2-phenylbenzo[d]thiazol-7-yl)but-1-yn-1-yl)benzonitrile (23)**

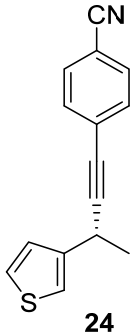


23

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 7-ethyl-2-phenylbenzo[*d*]thiazole[8] (240 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to

give the corresponding product **23** (16.7 mg) in 46% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.08 (m, 2H), 8.02 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.63-7.57 (m, 2H), 7.57-7.48 (m, 6H), 7.48-7.43 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 1H), 1.75 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 155.1, 136.1, 133.5, 133.1, 132.2, 132.0, 131.1, 129.1, 128.3, 127.6, 126.8, 123.2, 122.2, 118.5, 111.4, 95.6, 82.1, 33.1, 21.4.
HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{17}N_2S$ $[M + H]^+$ 365.1107, found 365.1104.
HPLC condition: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 16.5 min, t(major) = 22.2 min, 90% ee (95:5 er).

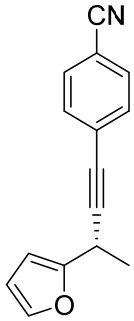
***(S)*-4-(3-(thiophen-3-yl)but-1-yn-1-yl)benzonitrile (24)**



24

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 3-ethylthiophene (112 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **24** (14.1 mg) in 59% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.55 (m, 2H), 7.53-7.47 (m, 2H), 7.31 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.20 (dt, *J* = 2.9, 1.2 Hz, 1H), 7.11 (dd, *J* = 5.0, 1.3 Hz, 1H), 4.08 (q, *J* = 7.0 Hz, 1H), 1.60 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 132.1, 131.9, 128.6, 126.7, 126.1, 120.4, 118.5, 111.1, 97.3, 80.4, 27.9, 22.8.
HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{12}NS$ $[M + H]^+$ 238.0685, found 238.0682.
HPLC condition: Chiralcel AD-3, *n*-hexane/*i*-PrOH = 97/3, flow rate 0.8 mL/min. λ = 254 nm, t(minor) = 12.3 min, t(major) = 14.5 min, 85% ee (92.3:7.7 er).

***(S)*-4-(3-(furan-2-yl)but-1-yn-1-yl)benzonitrile (25)**



25

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10

mmol, 1.0 equiv) and 2-ethylfuran (96 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **25** (10.0 mg) in 45% isolated yield.

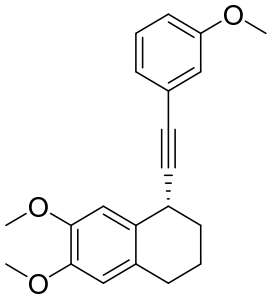
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 1.8 Hz, 1H), 6.34 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.23 (d, *J* = 3.1 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 1H), 1.61 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 141.8, 132.2, 131.9, 128.4, 118.5, 111.3, 110.3, 105.0, 94.8, 80.1, 26.4, 20.1.

HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{12}NO$ $[M + H]^+$ 222.0913, found 222.0911.

HPLC condition: Chiralcel AD-3, *n*-hexane/*i*-PrOH = 97/3, flow rate 0.8 mL/min. λ = 254 nm, t(minor) = 9.5 min, t(major) = 10.9 min, 84% ee (92.0:8.0 er).

(S)-6,7-dimethoxy-1-((3-methoxyphenyl)ethynyl)-1,2,3,4-tetrahydronaphthalene (26)



26

According to **General Procedure B** with 1-ethynyl-3-methoxybenzene (12.7 μL, 0.10 mmol, 1.0 equiv) and 6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (96.2 mg, 0.5 mmol, 5 equiv) for 10 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **26** (17.1 mg) in 53% isolated yield.

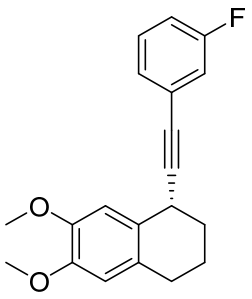
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.9 Hz, 1H), 7.06-6.97 (m, 2H), 6.94 (dd, *J* = 2.7, 1.4 Hz, 1H), 6.83 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 6.58 (s, 1H), 3.99-3.89 (m, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 2.85-2.64 (m, 2H), 2.24-2.11 (m, 1H), 2.06-1.96 (m, 2H), 1.78-1.73 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 147.7, 147.3, 129.2, 128.2, 127.9, 124.8, 124.1, 116.5, 114.2, 111.9, 111.7, 93.1, 81.3, 56.0, 55.9, 55.2, 31.7, 30.4, 28.8, 21.5.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{23}O_3$ $[M + H]^+$ 323.1642, found 323.1638.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min. λ = 254 nm, t(major) = 17.0 min, t(minor) = 21.6 min, 91% ee (95.6:4.4 er).

(S)-1-((3-fluorophenyl)ethynyl)-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (27)



27

According to **General Procedure B** with 1-ethynyl-3-fluorobenzene (11.6 μL, 0.10 mmol, 1.0 equiv) and 6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (96.2 mg, 0.5 mmol, 5 equiv) for 10 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **27** (27.4 mg) in 88% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 1H), 7.18 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.14 – 7.06 (m, 1H), 7.02-6.92 (m, 2H), 6.58 (s, 1H), 3.98-3.90 (m, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 2.85-2.65 (m, 2H), 2.22-2.08 (m, 1H), 2.10-1.90 (m, 2H), 1.86-1.67 (m, 1H).

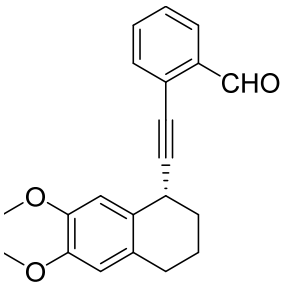
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.36.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$= 246.4 Hz), 161.1, 147.8, 147.3, 129.7 (d, $J_{C\text{-}F}$ = 8.7 Hz), 128.2, 127.6, 127.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 125.7 (d, $J_{C\text{-}F}$ = 9.6 Hz), 118.5, 118.3, 115.1, 114.9, 111.8, 111.7, 94.4, 80.3 (d, $J_{C\text{-}F}$ = 3.4 Hz), 55.9 (d, $J_{C\text{-}F}$ = 11.5 Hz), 31.6, 30.2, 28.7, 21.4.

HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{20}FO_2$ $[M + H]^+$ 311.1442, found 311.1438.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min. λ = 254 nm, t(major) = 8.7 min, t(minor) = 9.8 min, 90% ee (94.8:5.2 er).

***(S)*-2-((6,7-dimethoxy-1,2,3,4-tetrahydronaphthalen-1-yl)ethynyl)benzaldehyde (28)**



28

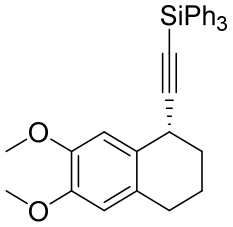
According to **General Procedure B** with 2-ethynylbenzaldehyde (13.0 mg, 0.10 mmol, 1.0 equiv) and 6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (96.2 mg, 0.5 mmol, 5 equiv) for 10 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **28** (28.7 mg) in 89% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 4.2 Hz, 3H), 7.39 (m, 1H), 6.97 (s, 1H), 6.59 (s, 1H), 4.03 (t, *J* = 6.4 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.84-2.69 (m, 2H), 2.20-2.15 (m, 1H), 2.08-1.99 (m, *2*H), 1.85-1.80 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 148.0, 147.4, 136.0, 133.7, 133.3, 128.3, 128.1,

127.6, 127.11, 127.07, 111.8, 111.7, 100.9, 56.0, 55.9, 31.9, 30.2, 28.7, 21.3.
HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{21}O_3$ $[M + H]^+$ 321.1485, found 321.1482.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min. λ = 254 nm, t(major) = 27.4 min, t(minor) = 30.1 min, 92% ee (96.0:4.0 er).

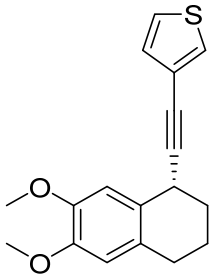
***(S)*-((6,7-dimethoxy-1,2,3,4-tetrahydronaphthalen-1-yl)ethynyl)triphenylsilane (29)**



29

According to **General Procedure A** with ethynyltriphenylsilane (28.4 mg, 0.10 mmol, 1.0 equiv) and 6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (96.2 mg, 0.5 mmol, 5 equiv) at 0 °C for 4 d and then at rt for 4 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **29** (21.2 mg) in 45% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dt, *J* = 6.7, 1.5 Hz, 6H), 7.52-7.29 (m, 9H), 7.05 (s, 1H), 6.56 (s, 1H), 3.91 (t, *J* = 7.0 Hz, 1H), 3.84 (s, 2H), 3.71 (s, 2H), 2.92-2.57 (m, 2H), 2.24-2.21 (m, 1H), 2.12-1.89 (m, 2H), 1.76-1.73 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 147.2, 135.5, 134.0, 129.8, 128.0, 127.9, 127.3, 115.2, 111.6, 111.5, 80.3, 55.9, 55.7, 32.5, 30.2, 28.7, 21.8.
HRMS (ESI) *m*/*z* calcd. for $C_{32}H_{31}O_2Si$ $[M + H]^+$ 475.2088, found 475.2087.
HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min. λ = 214 nm, t(major) = 13.7 min, t(minor) = 18.1 min, 92% ee (95.8:4.2 er).

***(S)*-3-((6,7-dimethoxy-1,2,3,4-tetrahydronaphthalen-1-yl)ethynyl)thiophene (30)**

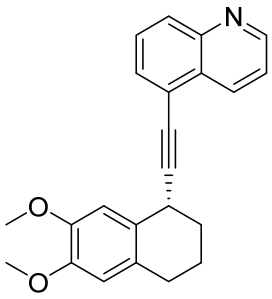


30

According to **General Procedure B** with 3-ethynylthiophene (10.8 mg, 0.10 mmol, 1.0 equiv) and 6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (96.2 mg, 0.5 mmol, 5 equiv) for 10 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **30** (17.6 mg) in 59% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.23 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.08 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.00 (s, 1H), 6.57 (s, 1H), 3.94-3.90 (m, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 2.78-2.68 (m, 2H), 2.16-2.11 (m, 1H), 2.10-1.91 (m, 2H), 1.85-

1.72 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 147.3, 130.0, 128.2, 127.9, 127.8, 125.0, 122.8, 111.9, 111.7, 92.7, 76.4, 56.0, 55.9, 31.7, 30.4, 28.8, 21.4.
HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{19}O_2S$ $[M + H]^+$ 299.1100, found 299.1098.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min. λ = 254 nm, t(major) = 20.2 min, t(minor) = 26.8 min, 92% ee (95.8:4.2 er).

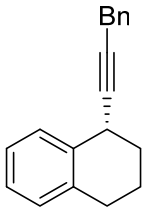
***(S)*-5-((6,7-dimethoxy-1,2,3,4-tetrahydronaphthalen-1-yl)ethynyl)quinoline (31)**



31

According to **General Procedure A** with 5-ethynylquinoline (15.3 mg, 0.10 mmol, 1.0 equiv) and 6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene (96.2 mg, 0.5 mmol, 5 equiv) for 10 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **31** (14.9 mg) in 43% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.5 Hz, 1H), 8.25 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.72 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.56 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.46 (d, *J* = 4.5 Hz, 1H), 7.08 (s, 1H), 6.62 (s, 1H), 4.14 (t, *J* = 6.4 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.84-2.77 (m, 2H), 2.36-2.20 (m, 1H), 2.15-2.07 (m, 2H), 1.95-1.79 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 148.0, 147.4, 129.8, 129.7, 128.4, 128.2, 127.03, 126.97, 126.0, 123.6, 111.8, 111.7, 103.6, 77.5, 56.0, 55.9, 32.1, 30.2, 28.7, 21.5.
HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{22}NO_2$ $[M + H]^+$ 344.1645, found 344.1641.
HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 22.7 min, t(major) = 23.7 min, 87% ee (93.3:6.7 er).

***(S)*-1-(3-phenylprop-1-yn-1-yl)-1,2,3,4-tetrahydronaphthalene (32)**

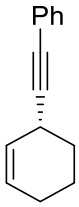


32

According to **General Procedure A** with prop-2-yn-1-ylbenzene (11.6 mg, 0.10 mmol, 1.0 equiv) and 1,2,3,4-tetrahydronaphthalene (132 mg, 1.0 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **32** (6.8 mg) in 28% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dt, *J* = 7.1, 1.4 Hz, 1H), 7.39-7.27 (m, 4H), 7.24-7.19 (m, 1H), 7.15 (tt, *J* = 7.2, 5.3 Hz, 2H), 7.07 (dd, *J* = 7.2, 1.9 Hz, 1H), 3.84 (td, *J* = 5.8, 2.8 Hz, 1H), 3.63 (d, *J* = 2.3 Hz, 2H), 2.90-2.66 (m, 2H), 2.17-2.08 (m, 1H), 2.08-1.97 (m, 1H), 1.97-1.87 (m, 1H), 1.84-1.70 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 136.8, 136.1, 129.1, 129.0, 128.4, 127.8, 126.39, 126.36, 125.9, 85.7, 78.6, 31.6, 30.5, 29.1, 25.2, 21.3.
HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{19}$ $[M + H]^+$ 247.1481, found 247.1479.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.7 mL/min. λ = 214 nm, t(major) = 42.5 min, t(minor) = 54.9 min, 78% ee (88.9:11.1 er).

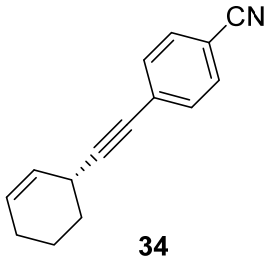
***(R)*-(cyclohex-2-en-1-ylethynyl)benzene (33)**



33

According to **General Procedure C** with phenylacetylene (11.1 μL, 0.10 mmol, 1.0 equiv) and cyclohexene (100 μL, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **33** (7.7 mg) in 42% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.33 (m, 2H), 7.28-7.25 (m,3H), 5.79-5.73 (m, 2H), 3.29 (td, *J* = 5.0, 2.6 Hz, 1H), 2.00 (m, *2*H), 1.93-1.72 (m, 2H), 1.62-1.52 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6, 128.1, 128.0, 127.5, 127.0, 123.9, 92.9, 80.3, 29.4, 28.0, 24.7, 20.6.
The NMR spectra were in accord with that reported in literature.[9]
HPLC condition: Chiralcel OD-3, *n*-hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 12.9 min, t(major) = 15.9 min, 89% ee (94.6:5.4 er).

***(R)*-4-(cyclohex-2-en-1-ylethynyl)benzonitrile (34)**

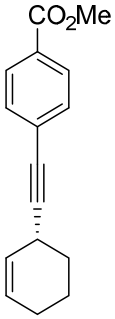


34

According to **General Procedure C** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and cyclohexene (101 μL, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **34** (13.5 mg) in 65% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 5.83-5.78 (m, 1H), 5.72-5.67 (m, 1H), 3.34-3.29 (m, 1H), 2.09-1.95 (m, 3H), 1.90-1.76 (m,

2H), 1.67-1.60 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 132.2, 131.9, 129.0, 128.7, 126.1, 118.7, 110.9, 97.9, 79.2, 29.1, 28.1, 24.6, 20.5.
HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{14}N$ $[M + H]^+$ 208.1121, found 208.1120.
HPLC condition: Chiralcel AD-3, *n*-hexane/*i*-PrOH = 99.3/0.7, flow rate 0.3 mL/min. λ = 254 nm, t(major) = 33.1 min, t(minor) = 35.4 min, 89% ee (94.3:5.7 er).

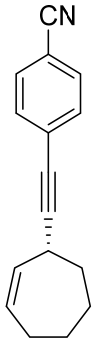
methyl-(*R*)-4-(cyclohex-2-en-1-ylethynyl)benzoate (35)



35

According to **General Procedure C** with 4-(methoxycarbonyl)phenylacetylene (16.0 mg, 0.10 mmol, 1.0 equiv) and cyclohexene (101 μL, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **35** (13.2 mg) in 55% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 5.83-5.78 (m, 1H), 5.74-5.69 (m, 1H), 3.91 (s, 3H), 3.34-3.29 (m, 1H), 2.08-1.95 (m, 3H), 1.91-1.77 (m, 2H), 1.67-1.58 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 131.6, 129.4, 128.9, 128.8, 128.4, 126.5, 96.3, 79.9, 52.2, 29.2, 28.1, 24.7, 20.6.
HRMS (ESI) m/z calcd. for $C_{16}H_{17}O_2$ $[M+H]^+$ 241.1223, found 241.2220.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min. λ = 254 nm, t(minor) =23.7 min, t(major) = 25.4 min, 85% ee (92.3:7.7 er).

***(R)*-4-(cyclohept-2-en-1-ylethynyl)benzonitrile (36)**

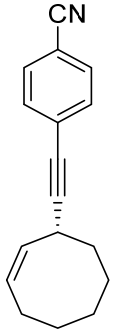


36

According to **General Procedure C** with 4-cyanophenylacetylene (12.8 mg , 0.10 mmol, 1.0 equiv) and cycloheptene (117 μL, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding

product **36** (12.0 mg) in 53% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 5.90-5.79 (m, 2H), 3.51 (td, *J* = 6.3, 5.6, 2.2 Hz, 1H), 2.26-2.23 (m, 1H), 2.19-1.99 (m, 2H), 1.97-1.86 (m, 1H), 1.83-1.66 (m, 2H), 1.67-1.44 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 133.3, 132.3, 132.1, 131.9, 129.0, 118.6, 110.8, 98.0, 79.6, 33.3, 32.5, 29.5, 28.3, 26.6.
HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{16}N$ $[M + H]^+$ 222.1277, found 222.1275.
HPLC condition: Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min. λ = 254 nm, t(major) = 33.2 min, t(minor) = 36.6 min, 89% ee (94.4:5.6 er).

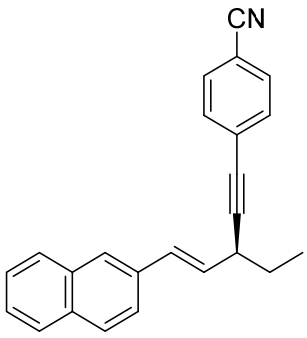
(*R*,*Z*)-4-(cyclooct-2-en-1-ylethynyl)benzonitrile (37)



37

According to **General Procedure C** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and (Z)-cyclooctene (130 μL, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **37** (8.9 mg) in 38% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 5.76-5.73 (m, 1H), 5.57-5,52 (m, 1H), 3.75-3.58 (m, 1H), 2.18-2.14 (m, 2H), 2.04-1.91 (m, 1H), 1.87-1.66 (m, 2H), 1.66-1.48 (m, 3H), 1.45-1.28 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 132.1, 131.9, 130.7, 130.0, 129.0, 118.6, 110.8, 98.7, 79.3, 36.7, 29.13, 29.10, 26.4, 26.2, 25.3.
HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{18}N$ $[M + H]^+$ 236.1434, found 236.1431.
HPLC condition: Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min. λ = 254 nm, t(minor) = 34.9 min, t(major) = 40.7 min, 86% ee (93.2:6.8 er).

(*S*,*E*)-4-(3-ethyl-5-(naphthalen-2-yl)pent-4-en-1-yn-1-yl)benzonitrile (38)



38

According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 2-(pent-1-en-1-yl)naphthalene (196 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **38** (16.2 mg) in 50% isolated yield.

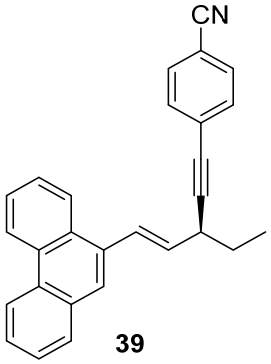
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.76 (m, 3H), 7.74 (s, 1H), 7.63-7.56 (m, 3H), 7.54 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.48-7.39 (m, 2H), 6.82 (dd, *J* = 15.8, 1.4 Hz, 1H), 6.30 (dd, *J* = 15.8, 6.6 Hz, 1H), 3.48-3.43 (m, 1H), 1.86-1.74 (m, 2H), 1.12 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4, 133.6, 133.0, 132.3, 132.0, 131.1, 129.3, 128.8, 128.2, 127.9, 127.7, 126.3, 126.2, 125.9, 123.6, 118.7, 111.1, 95.7, 82.5, 37.2, 28.9, 11.6.

HRMS (ESI) m/z calcd. for $C_{24}H_{20}N$ $[M+H]^+$ 322.1590, found 322.1587.

HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min. λ = 254 nm, t(minor) = 19.7 min, t(major) = 21.2 min, 88% ee (94:6 er).

(*S*,*E*)-4-(3-ethyl-5-(phenanthren-9-yl)pent-4-en-1-yn-1-yl)benzonitrile (39)



39

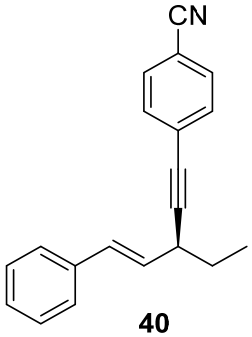
According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 9-(pent-1-en-1-yl)phenanthrene (246 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **39** (14.9 mg) in 40% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.68 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.15 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.88 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.81 (s, 1H), 7.72-7.53 (m, 8H), 7.42 (dt, *J* = 15.2, 1.2 Hz, 1H), 6.27 (dd, *J* = 15.2, 6.4 Hz, 1H), 3.61-3.55 (m, 1H), 1.94-1.82 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.8, 132.5, 132.3, 132.0, 131.8, 130.7, 130.4, 130.2,

129.0, 128.8, 128.6, 126.8, 126.7, 126.54, 126.51, 124.8, 124.7, 123.1, 122.6, 118.6, 111.2, 95.7, 82.7, 37.4, 28.9, 11.6.
HRMS (ESI) m/z calcd. for $C_{28}H_{22}N$ $[M+H]^+$ 372.1747, found 372.1746.
HPLC condition: Chiralcel AD-H, *n*-hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min. λ = 254 nm, t(major) = 13.4 min, t(minor) = 17.3 min, 80% ee (90.2:9.8 er).

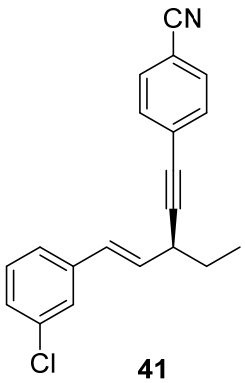
(*S,E*)-4-(3-ethyl-5-phenylpent-4-en-1-yn-1-yl)benzonitrile (40)



40

According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and pent-1-en-1-ylbenzene (146 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **40** (12.2 mg) in 45% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.8, 6.8 Hz, 1H), 3.44 (q, *J* = 6.8 Hz, 1H), 1.84-1.74 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 132.2, 131.7 131.0, 128.9, 128.8, 128.6, 127.5, 126.4, 118.6, 111.1, 95.6, 82.4, 37.1, 28.8, 11.5.
HRMS (ESI) m/z calcd. for $C_{20}H_{18}N$ $[M+H]^+$ 272.1434, found 272.1431.
HPLC condition: Chiralcel OJ-3, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min. λ = 270 nm, t(major) = 31.6 min, t(minor) = 40.7 min, 88% ee (93.8:6.2 er).

***(S,E)*-4-(5-(3-chlorophenyl)-3-ethylpent-4-en-1-yn-1-yl)benzonitrile (41)**

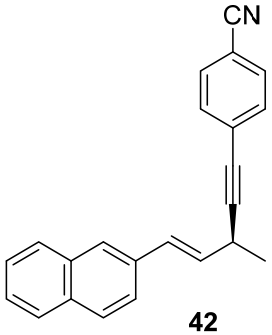


41

According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-chloro-3-(pent-1-en-1-yl)benzene (180.0 mg, 1.0 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica

gel to give the corresponding product **41** (13.9 mg) in 46% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.57 (m, 2H), 7.56-7.47 (m, 2H), 7.38 (q, *J* = 1.2 Hz, 1H), 7.31-7.17 (m, 3H), 6.61 (dd, *J* = 15.7, 1.4 Hz, 1H), 6.19 (dd, *J* = 15.7, 6.6 Hz, 1H), 3.45-3.39 (m, 1H), 1.84 – 1.66 (m, 2H), 1.09 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 134.5, 132.2, 132.0, 130.4, 129.8, 129.7, 128.6, 127.4, 126.2, 124.6, 118.6, 111.2, 95.1, 82.6, 37.0, 28.6, 11.5.
HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{17}ClN$ $[M + H]^+$ 306.1044, found 306.1041.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.7 mL/min. λ = 254 nm, t(major) = 19.3 min, t(minor) = 25.0 min, 83% ee (91.5:8.5 er).

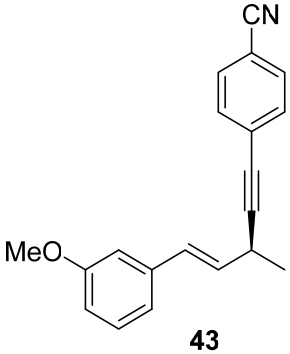
(*S*,*E*)-4-(3-methyl-5-(naphthalen-2-yl)pent-4-en-1-yn-1-yl)benzonitrile (42)



42

According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 2-(but-1-en-1-yl)naphthalene (182 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **42** (12.9 mg) in 42% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.77 (m, 3H), 7.77-7.71 (m, 1H), 7.64-7.57 (m, 3H), 7.57-7.51 (m, 2H), 7.50-7.41 (m, 2H), 6.81 (dd, *J* = 15.8, 1.6 Hz, 1H), 6.35 (dd, *J* = 15.8, 6.4 Hz, 1H), 3.71-3.55 (m, 1H), 1.50 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 133.6, 133.0, 132.2, 132.0, 130.6, 130.1, 128.7, 128.2, 127.9, 127.7, 126.3, 126.2, 125.9, 123.6, 118.6, 111.2, 96.7, 81.5, 29.8, 21.5.
HRMS (ESI) m/z calcd. for $C_{23}H_{18}N$ $[M+H]^+$ 308.1434, found 308.1431.
HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min. λ = 254 nm, t(minor) = 23.0 min, t(major) = 24.4 min, 84% ee (92.1:7.9 er).

(*S*,*E*)-4-(5-(3-methoxyphenyl)-3-methylpent-4-en-1-yn-1-yl)benzonitrile (43)



43

According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10

mmol, 1.0 equiv) and 1-(but-1-en-1-yl)-3-methoxybenzene (162 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **43** (13.8 mg) in 48% isolated yield.

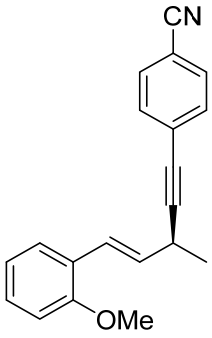
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.26-7.20 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 6.80 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.62 (dd, *J* = 15.8, 1.6 Hz, 1H), 6.26-6.16 (m, 1H), 3.82 (s, 3H), 3.62-3.51 (m, 1H), 1.45 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 138.3, 132.2, 132.0, 130.5, 129.9, 129.6, 128.7, 119.0, 118.6, 113.2, 111.8, 111.1, 96.6, 81.4, 55.3, 29.7, 21.5.

HRMS (ESI) m/z calcd. for $C_{20}H_{18}NO$ $[M+H]^+$ 288.1383, found 288.1381.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min. λ = 254 nm, t(major) = 28.1 min, t(minor) = 37.5min, 87% ee (93.5:6.5 er).

(*S*,*E*)-4-(5-(2-methoxyphenyl)-3-methylpent-4-en-1-yn-1-yl)benzonitrile (44)



44

According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-(but-1-en-1-yl)-2-methoxybenzene (162 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **44** (14.9 mg) in 52% isolated yield.

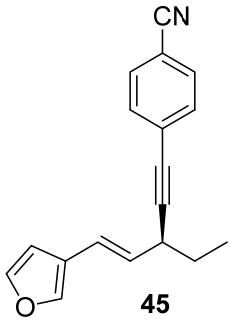
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.22 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 6.99-6.90 (m, 2H), 6.87 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.23 (dd, *J* = 15.9, 6.4 Hz, 1H), 3.85 (s, 3H), 3.62-3.54 (m, 1H), 1.46 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 132.2, 131.9, 130.8, 128.9, 128.6, 126.9, 125.8, 124.9, 120.7, 118.7, 111.0, 110.9, 97.2, 81.2, 55.5, 30.2, 21.5.

HRMS (ESI) m/z calcd. for $C_{20}H_{18}NO$ $[M+H]^+$ 288.1383, found 288.1381.

HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min. λ = 254 nm, t(minor) = 22.6 min, t(major) = 23.8 min, 84% ee (92.1:7.9 er).

(*S*,*E*)-4-(3-ethyl-5-(furan-3-yl)pent-4-en-1-yn-1-yl)benzonitrile (45)



45

According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 3-(pent-1-en-1-yl)furan (136 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **45** (10.5 mg) in 40% isolated yield.

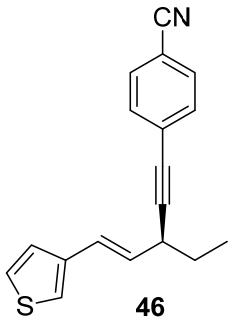
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.45 – 7.40 (m, 1H), 7.37 (td, *J* = 1.7, 0.7 Hz, 1H), 6.51 (ddd, *J* = 14.2, 1.7, 0.8 Hz, 2H), 5.90 (dd, *J* = 16.0, 6.6 Hz, 1H), 3.39-3.36 (m, 1H), 1.81-1.66 (m, 2H), 1.08 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 140.3, 132.2, 132.0, 128.8, 128.4, 123.7, 120.6, 118.7, 111.1, 107.5, 95.6, 82.3, 36.9, 28.8, 11.5.

HRMS (ESI) m/z calcd. for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1229.

HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 96/4, flow rate 0.8 mL/min. λ = 254 nm, t(major) = 23.4 min, t(minor) = 27.4 min, 85% ee (92.5:7.5 er).

(*S*,*E*)-4-(3-ethyl-5-(thiophen-3-yl)pent-4-en-1-yn-1-yl)benzonitrile (46)



46

According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 3-(pent-1-en-1-yl)thiophene (152 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **46** (10.0 mg) in 35% isolated yield.

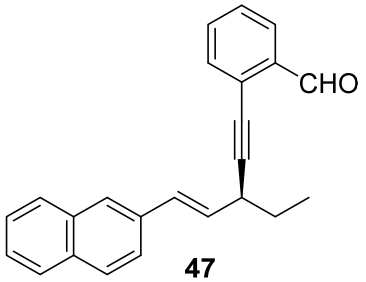
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 5.2, 3.2 Hz, 1H), 7.22 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.15 (dd, *J* = 3.2, 1.2 Hz, 1H), 6.66 (dd, *J* = 16.0, 1.4 Hz, 1H), 6.03 (dd, *J* = 16.0, 6.8 Hz, 1H), 3.41-3.35 (m, 1H), 1.79-1.69 (m, 2H), 1.09 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 132.2, 132.0, 128.8, 128.7, 126.1, 125.2, 125.0, 121.9, 118.6, 111.1, 95.7, 82.4, 37.0, 28.8, 11.6.

HRMS (ESI) m/z calcd. for $C_{18}H_{16}NS$ $[M+H]^+$ 278.0998, found 278.0996.

HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min. λ = 254 nm, t(major) = 14.6 min, t(minor) = 15.8 min, 87% ee (93.5:6.5 er).

(*S*,*E*)-2-(3-ethyl-5-(naphthalen-2-yl)pent-4-en-1-yn-1-yl)benzaldehyde (47)



47

According to **General Procedure D** with 2-ethynylbenzaldehyde (13.0 mg, 0.10 mmol, 1.0 equiv) and 2-(but-1-en-1-yl)naphthalene (182 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **47** (13.7 mg) in 42% isolated yield.

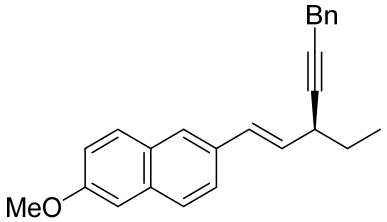
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (d, *J* = 0.8 Hz, 1H), 7.93 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.81-7.78 (m, 3H), 7.75 (s, 1H), 7.64-7.58 (m, 2H), 7.55 (td, *J* = 7.4, 1.2 Hz, 1H), 7.50-7.38 (m, 3H), 6.86 (dd, *J* = 15.8, 1.4 Hz, 1H), 6.33 (dd, *J* = 15.8, 6.6 Hz, 1H), 3.56-3.51 (m, 1H), 1.90-1.76 (m, 2H), 1.15 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 136.0, 134.4, 133.8, 133.6, 133.5, 133.0, 131.1, 129.3, 128.2, 128.2, 128.0, 127.7, 127.5, 127.1, 126.3, 126.2, 125.8, 123.6, 98.2, 79.5, 37.4, 28.9, 11.7.

HRMS (ESI) m/z calcd. for $C_{24}H_{21}O$ $[M+H]^+$ 325.1587, found 325.1587.

HPLC condition: Chiralcel AD-3, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min. λ = 254 nm, t(major) =11.6 min, t(minor) = 15.4 min, 91% ee (95.3:4.7 er).

(*S*,*E*)-2-(3-ethyl-6-phenylhex-1-en-4-yn-1-yl)-6-methoxynaphthalene (48)



48

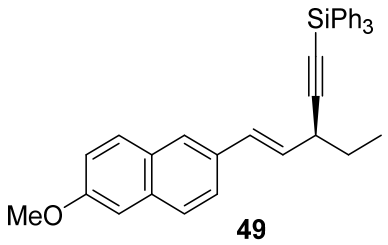
According to **General Procedure D** with prop-2-yn-1-ylbenzene (11.6 mg, 0.10 mmol, 1.0 equiv) and 2-(but-1-en-1-yl)-6-methoxynaphthalene (212 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **48** (10.3 mg) in 42% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 8.0 Hz, 2H), 7.64 (s, 1H), 7.55 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.35-7.32 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.13-7.10 (m, 2H), 6.77 (dd, *J* = 16.0, 1.6 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.4 Hz, 1H), 3.91 (s, 3H), 3.70 (d, *J* = 2.4 Hz, 2H), 3.29-3.26 (m, 1H), 1.76-1.64 (m, 2H), 1.07 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 137.5, 134.0, 132.7, 130.3, 129.8, 129.4, 129.1, 128.5, 127.9, 126.9, 126.5, 125.8, 124.3, 105.9, 83.3, 81.0, 55.3, 36.6, 29.2, 25.3, 11.6.

HRMS (ESI) m/z calcd. for $C_{25}H_{25}O$ $[M+H]^+$ 341.1900, found 341.1898.
HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min. λ = 254 nm, t(major) = 11.9 min, t(minor) = 13.7 min, 82% ee (91.2:8.8 er).

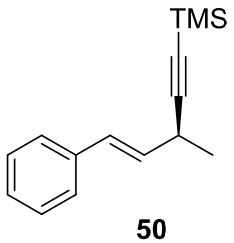
(*S,E*)-(3-ethyl-5-(6-methoxynaphthalen-2-yl)pent-4-en-1-yn-1-yl)triphenylsilane (49)



49

According to **General Procedure D** with ethynyltriphenylsilane (28.4 mg, 0.10 mmol, 1.0 equiv) and 2-(but-1-en-1-yl)-6-methoxynaphthalene (212 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **49** (13.8 mg) in 27% isolated yield (48% yield based on recovered alkyne).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.62 (m, 8H), 7.61-7.49 (m, 2H), 7.47-7.33 (m, 9H), 7.16-7.07 (m, 2H), 6.86 (dd, *J* = 15.8, 1.5 Hz, 1H), 6.25 (dd, *J* = 15.8, 6.2 Hz, 1H), 3.92 (s, 3H), 3.45-3.40 (m, 1H), 1.86-1.71 (m, 2H), 1.13 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 135.6, 134.1, 134.0, 132.4, 131.1, 129.8, 129.4, 129.0, 128.3, 128.0, 127.0, 126.0, 124.2, 118.9, 112.7, 105.9, 83.0, 55.3, 37.6, 28.9, 11.6.
HRMS (ESI) m/z calcd. for $C_{36}H_{33}OSi$ $[M+H]^+$ 509.2295, found 509.2299.
HPLC condition: Chiralcel AD-3, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.4 mL/min. λ = 254 nm, t(major) =12.2 min, t(minor) = 18.6 min, 91% ee (95.3:4.7 er).

***(S,E)*-trimethyl(3-methyl-5-phenylpent-4-en-1-yn-1-yl)silane (50)**

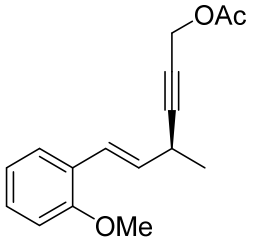


50

According to **General Procedure D** with trimethylsilylacetylene (9.8 mg, 0.10 mmol, 1.0 equiv) and but-1-en-1-ylbenzene (132 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **50** (5.5 mg) in 24% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.32-7.28 (m, 2H), 7.25-7.19 (m, 1H), 6.61 (dd, *J* = 15.8, 1.6 Hz, 1H), 6.15 (dd, *J* = 15.8, 6.0 Hz, 1H), 3.38-3.32 (m, 1H), 1.35 (d, *J* = 7.1 Hz, 3H), 0.19 (s, 9H).
The **^{1}H NMR** spectra were in accord with that reported in literature.[10]

HRMS (ESI) m/z calcd. for $C_{15}H_{21}Si$ $[M+H]^+$ 229.1407, found 229.1406.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min. λ = 214 nm, t(major) =11.8 min, t(minor) = 17.8 min, 84% ee (91.8:8.2 er).

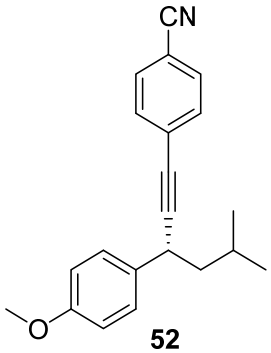
(*S*,*E*)-6-(2-methoxyphenyl)-4-methylhex-5-en-2-yn-1-yl acetate (51)



51

According to **General Procedure D** with prop-2-yn-1-yl acetate (9.8 mg, 0.10 mmol, 1.0 equiv) and 1-(but-1-en-1-yl)-2-methoxybenzene (162 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **51** (9.8 mg) in 38% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.21 (ddd, *J* = 8.1, 7.6, 2.0 Hz, 1H), 6.95-6.83 (m, 3H), 6.16 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.73 (d, *J* = 2.0 Hz, 2H), 3.85 (s, 3H), 3.42-3.35 (m, 1H), 2.10 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 156.6, 131.2, 128.5, 126.9, 126.0, 124.6, 120.6, 110.8, 89.5, 75.80, 55.5, 52.9, 29.5, 21.5, 20.9.
HRMS (ESI) m/z calcd. for $C_{16}H_{19}O_3$ $[M+H]^+$ 259.1329, found 259.1331.
HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min. λ = 254 nm, t(major) = 11.5 min, t(minor) = 12.6 min, 75% ee (87.4:12.6 er).

***(R)*-4-(3-(4-methoxyphenyl)-5-methylhex-1-yn-1-yl)benzonitrile (52)**

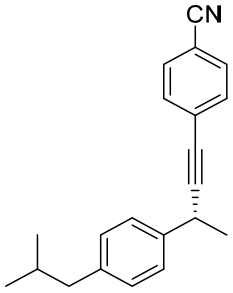


52

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-isopentyl-4-methoxybenzene (178 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **52** (14.8 mg) in 49% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.51-7.43 (m, 2H), 7.34-7.27 (m, 2H), 6.96-6.82 (m, 2H), 3.88-3.82 (m, 1H), 3.80 (s, 3H), 1.90-1.72 (m, 2H), 1.66-1.53 (m, 1H), 0.97 (dd, *J* = 6.4, 3.5 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 133.9, 132.7, 132.1, 132.0, 131.9, 128.9, 128.3, 118.6, 114.0, 111.0, 97.3, 81.5, 81.4, 55.3, 47.7, 35.7, 26.1, 22.9, 21.9.

HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{22}NO$ $[M + H]^+$ 304.1696, found 304.1694.
HPLC condition: Chiralcel OJ-3, *n*-hexane/*i*-PrOH = 97/3, flow rate 0.8 mL/min. λ = 254 nm, t(major) = 16.8 min, t(minor) = 18.8 min, 82% ee (91.0:9.0 er).

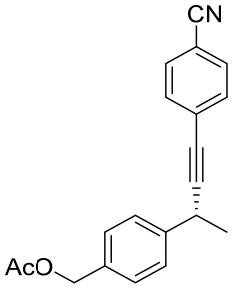
***(R)*-4-(3-(4-isobutylphenyl)but-1-yn-1-yl)benzonitrile (53)**



53

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-ethyl-4-isobutylbenzene (162 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **53** (18.5 mg) in 64% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.54-7.47 (m, 2H), 7.35-7.28 (m, 2H), 7.16-7.08 (m, 2H), 3.97 (q, *J* = 7.3 Hz, 1H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.98-1.74 (m, 1H), 1.57 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 139.7, 132.2, 131.9, 129.4, 128.8, 126.5, 118.6, 111.0, 98.0, 80.9, 45.0, 32.1, 30.2, 24.1, 22.4.
HRMS (ESI) *m*/*z* calcd. for $C_{21}H_{22}N$ $[M + H]^+$ 288.1747, found 288.1745.
HPLC condition: Chiralcel OJ-3, *n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min. λ = 254 nm, t(major) = 21.3 min, t(minor) = 23.7 min, 90% ee (95.0:5.0 er).

***(R)*-4-(4-(4-cyanophenyl)but-3-yn-2-yl)benzyl acetate (54)**

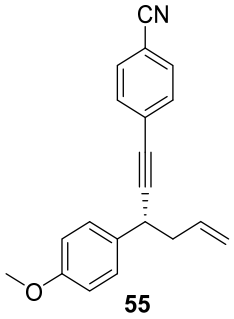


54

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 4-ethylbenzyl acetate (178 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **54** (9.1 mg) in 30% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.55 (m, 2H), 7.55-7.46 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 5.10 (s, 2H), 4.01 (q, *J* = 7.1 Hz, 1H), 2.10 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 142.6, 134.6, 132.2, 131.9, 128.7, 128.6, 127.1, 118.6, 111.2, 100.0, 97.3, 81.1, 66.0, 32.3, 30.2, 24.0, 21.0.

HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{18}NO_2$ $[M + H]^+$ 304.1332, found 304.1331.
HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 97/3, flow rate 0.8 mL/min. λ = 254 nm, t(major) = 48.9 min, t(minor) = 54.6 min, 85% ee (92.3:7.7 er).

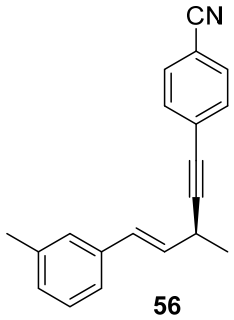
***(R)*-4-(3-(4-methoxyphenyl)hex-5-en-1-yn-1-yl)benzonitrile (55)**



55

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-(but-3-en-1-yl)-4-methoxybenzene (162 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **55** (10.0 mg) in 36% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 1H), 5.94-5.84 (m, 1H), 5.20-5.03 (m, 2H), 3.91 (t, *J* = 7.1 Hz, 1H), 3.83 (s, 3H), 2.80-2.34 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 135.1, 132.7, 132.2, 132.1, 131.9, 129.5, 128.7, 128.5, 118.6, 117.4, 114.0, 111.1, 96.4, 82.2, 55.3, 42.5, 37.8.
HRMS (ESI) *m*/*z* calcd. for $C_{20}H_{18}NO$ $[M + H]^+$ 288.1383, found 288.1380.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min. λ = 254 nm, t(major) = 27.3 min, t(minor) = 33.8 min, 93% ee (96.4:3.6 er).

(*S*,*E*)-4-(3-methyl-5-(m-tolyl)pent-4-en-1-yn-1-yl)benzonitrile (56)

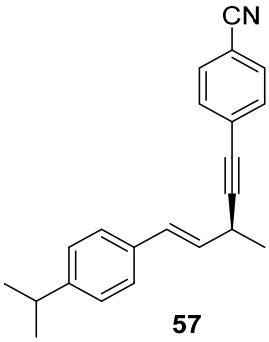


56

According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-(but-1-en-1-yl)-3-methylbenzene (146 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **56** (12.5 mg) in 46% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.23-7.17 (m, 3H), 7.09-7.03 (m, 1H), 6.61 (dd, *J* = 15.8, 1.6 Hz, 1H), 6.20 (dd, *J* = 15.8, 6.4 Hz, 1H), 3.59-3.53 (m, 1H), 2.34 (s, 3H), 1.45 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 136.8, 132.2, 132.0, 130.0, 130.0, 128.8, 128.5, 128.4, 127.1, 123.5, 118.6, 111.1, 96.8, 81.3, 29.7, 21.5, 21.4.

HRMS (ESI) m/z calcd. for $C_{20}H_{18}N$ $[M+H]^+$ 272.1434, found 272.1432.
HPLC condition: Chiralcel OJ-3, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min. λ = 254 nm, t(major) = 31.1 min, t(minor) = 39.3 min, 86% ee (93:7 er).

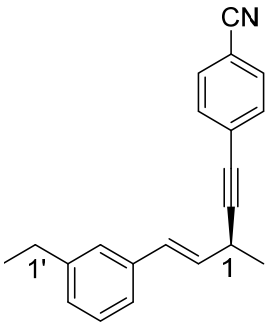
(*S*,*E*)-4-(5-(4-isopropylphenyl)-3-methylpent-4-en-1-yn-1-yl)benzonitrile (57)



57

According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-(but-1-en-1-yl)-4-isopropylbenzene (174 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **57** (13.2 mg) in 44% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.61 (dd, *J* = 15.8, 1.4 Hz, 1H), 6.16 (dd, *J* = 15.8, 6.4 Hz, 1H), 3.59-3.52 (m, 1H), 2.94-2.84 (m, 1H), 1.44 (d, *J* = 7.1 Hz, 3H), 1.25 (s, 3H), 1.23 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 134.5, 132.2, 132.0, 129.8, 129.3, 128.8, 126.7, 126.3, 118.6, 111.1, 96.9, 81.3, 33.9, 29.7, 24.0, 21.5.
HRMS (ESI) m/z calcd. for $C_{22}H_{22}N$ $[M+H]^+$300.1747, found 300.1745.
HPLC condition: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.6 mL/min. λ = 254 nm, t(major) = 28.7 min, t(minor) = 37.8 min, 80% ee (89.8:10.2 er).

(*S*,*E*)-4-(5-(3-ethylphenyl)-3-methylpent-4-en-1-yn-1-yl)benzonitrile (58)



58, (C1:C1'=4.0:1)

According to **General Procedure D** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-(but-1-en-1-yl)-3-ethylbenzene (160 mg, 1 mmol, 10 equiv) for 5 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **58** (12.8 mg) in 45% isolated yield.
^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 7.59 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* =

8.6 Hz, 2H), 7.25-7.16 (m, 3H), 7.08 (dt, *J* = 6.8, 2.0 Hz, 1H), 6.63 (dd, *J* = 16.0, 1.6 Hz, 1H), 6.21 (dd, *J* = 16.0, 6.4 Hz, 1H), 3.60-3.53 (m, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.45 (d, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.6 Hz, 4H).

^{1}H NMR (400 MHz, $CDCl_3$, minor isomer) δ 7.59 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.38-7.26 (m, 3H), 7.25-7.16 (m, 1H), 6.42-6.37 (m, 1H), 6.29 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.67 (dt, *J* = 11.6, 7.6 Hz, 1H), 4.02-3.95 (m, 1H), 2.39-2.32 (m, 2H), 2.28-2.20 (m, 2H), 1.59 (dd, *J* = 7.2, 2.8 Hz, 1H), 1.10 (t, *J* = 7.6 Hz, 1H), 1.06 (t, *J* = 7.6 Hz, 1H).

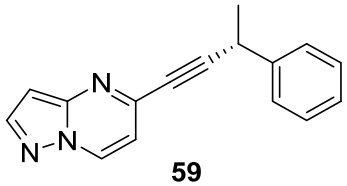
^{13}C NMR (101 MHz, $CDCl_3$, major isomer) δ 144.6, 136.8, 132.2, 132.0, 130.1, 130.0, 128.8, 128.6, 127.2, 125.9, 123.7, 118.6, 111.1, 96.8, 81.3, 29.7, 28.9, 21.5, 15.7.

HRMS (ESI) m/z calcd. for $C_{21}H_{20}N$ $[M+H]^+$286.1590, found 286.1589.

HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, flow rate 0.2 mL/min. λ = 214 nm, t(major) = 37.9 min, t(minor) = 39.9 min, 80% ee (89.7:10.3 er).

Procedure for synthetic application

***(R)*-5-(3-phenylbut-1-yn-1-yl)pyrazolo[1,5-a]pyrimidine (59)**



59

According to **General Procedure A** with 5-ethynylpyrazolo[1,5-*a*]pyrimidine[7] (14.3 mg, 0.10 mmol, 1.0 equiv) and ethylbenzene (212 mg, 2 mmol, 20 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **59** (10.2 mg) in 42% isolated yield.

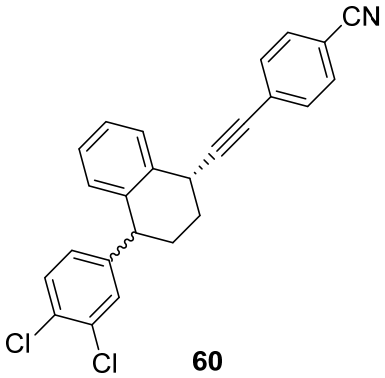
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 7.2, 0.9 Hz, 1H), 8.12 (d, *J* = 2.4 Hz, 1H), 7.47-7.41 (m, 2H), 7.39-7.33 (m, 2H), 7.31-7.24 (m, 1H), 6.85 (d, *J* = 7.2 Hz, 1H), 6.68 (dd, *J* = 2.4, 0.9 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.1, 145.6, 142.5, 141.8, 134.5, 128.7, 127.0, 126.9, 110.8, 97.3, 97.0, 81.0, 32.5, 23.7.

The NMR spectra were in accord with that reported in literature.[7]

HPLC condition: Chiralcel AD-3, *n*-hexane/*i*-PrOH = 96/4, flow rate 0.3 mL/min. λ = 240 nm, t(minor) = 59.5 min, t(major) = 62.3 min, 94% ee (97:3 er).

***(S)*-4-((4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)ethynyl)benzonitrile (60)**



60

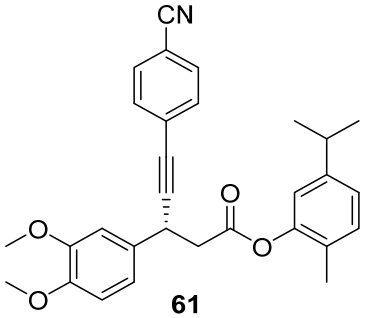
According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 1-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalene[11] (276 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **60** (20.8 mg) in 52% isolated yield and recover 223 mg C–H substrate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 2H), 7.53-7.46 (m, 2H), 7.36 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.27-7.22 (m, 2H), 7.20-7.10 (m, 2H), 6.94 (ddd, *J* = 11.7, 8.3, 2.1 Hz, 1H), 6.85 (ddd, *J* = 9.0, 7.8, 1.3 Hz, 1H), 4.22-4.09 (m, 2H), 2.38 (m, 1H), 2.26 (m, 1H), 2.22-2.12 (m, 1H), 2.12-1.95 (m, 1H), 1.85 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 147.0, 137.33, 137.3, 136.2, 135.9, 132.4, 132.2, 131.9, 130.64, 130.60, 130.4, 130.32, 130.29, 130.2, 129.2, 129.1, 128.61, 128.60,

128.2, 128.1, 127.4, 127.3, 127.0, 118.6, 111.1, 97.5, 97.4, 81.0, 80.4, 44.7, 44.4, 32.4, 32.1, 31.4, 30.4, 29.7, 28.0, 27.1.
HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{18}Cl_2N$ $[M + H]^+$ 402.0811, found 402.0807.
HPLC condition: Chiralcel OD-3, *n*-hexane/*i*-PrOH = 99.3/0.7, flow rate 0.7 mL/min. λ = 254 nm, t(major) = 28.2 min, t(minor) = 30.9 min, 90% ee; t(major) = 37.2 min, t(minor) = 48.7 min, 87% ee; dr = 1.2:1.

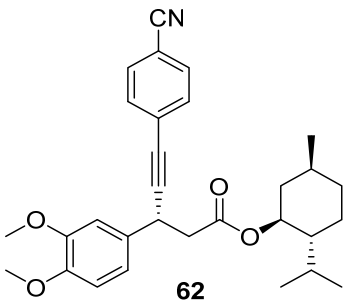
5-isopropyl-2-methylphenyl-(*R*)-5-(4-cyanophenyl)-3-(3,4-dimethoxyphenyl)pent-4-ynoate (61)



61

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 5-isopropyl-2-methylphenyl 3-(3,4-dimethoxyphenyl) propanoate (342 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **61** (20.2 mg) in 43% isolated yield and recover 277 mg C–H substrate.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.55 (m, 2H), 7.56-7.46 (m, 2H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.06-7.00 (m, 3H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 1.8 Hz, 1H), 4.56-4.45 (m, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.17-3.07 (m, 2H), 2.86-2.79 (m, 1H), 2.04 (s, 3H), 1.18 (d, *J* = 6.9 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 149.2, 149.1, 148.6, 148.1, 132.2, 132.0, 131.9, 130.9, 128.1, 127.1, 124.4, 119.6, 119.5, 118.4, 111.5, 111.4, 110.7, 94.8, 82.3, 56.0, 42.9, 34.7, 33.5, 23.84, 23.79, 15.7.
HRMS (ESI) *m*/*z* calcd. for $C_{30}H_{30}NO_4$ $[M + H]^+$ 468.2169, found 468.2170.
HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 93/7, flow rate 1.0 mL/min. λ = 254 nm, t(major) = 34.5 min, t(minor) = 42.9 min, 85% ee (92.4:7.6 er).

(*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl(*R*)-5-(4-cyanophenyl)-3-(3,4-dimethoxyphenyl)pent-4-ynoate (62)



62

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10

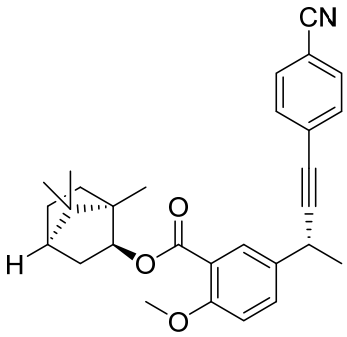
mmol, 1.0 equiv) and *(1S,2R,5S)*-2-isopropyl-5-methylcyclohexyl3-(3,4-dimethoxyphenyl)propanoate (348 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **62** (29.1 mg) in 62% isolated yield and recover 292 mg C–H substrate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.55 (m, 2H), 7.51-7.45 (m, 2H), 6.97 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.92 (d, *J* = 2.1 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 4.69 (td, *J* = 10.9, 4.4 Hz, 1H), 4.34 (t, *J* = 7.8 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 2.84 (ddd, *J* = 22.1, 14.8, 7.8 Hz, 2H), 1.96 (dd, *J* = 7.1, 4.8 Hz, 1H), 1.72-1.53 (m, 4H), 1.52-1.39 (m, 1H), 1.39-1.21 (m, 2H), 1.04-0.98 (m, 1H), 0.94 (d, *J* = 11.2 Hz, 1H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H), 0.62 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 149.1, 148.4, 132.2, 132.1, 131.9, 128.3, 119.5, 118.5, 111.4, 111.3, 110.6, 95.1, 82.0, 74.7, 55.9, 46.9, 43.5, 41.0, 34.7, 34.1, 31.3, 26.0, 23.3, 22.0, 20.7, 16.1.

HRMS (ESI) *m*/*z* calcd. for $C_{30}H_{36}NO_4$ $[M + H]^+$ 474.2639, found 474.2639.

(*1R,2R,4S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl-5-((*R*)-4-(4-cyanophenyl)but-3-yn-2-yl)-2-methoxybenzoate (63)



63

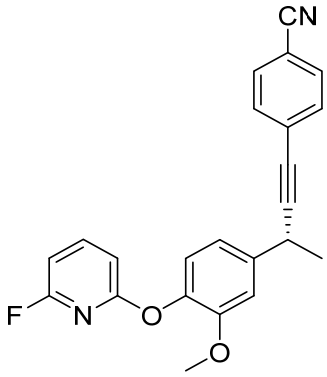
According to **General procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and *(1R,2R,4S)*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 5-ethyl-2-methoxybenzoate (316 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **63** (27.2 mg) in 62% isolated yield and recover 259 mg C–H substrate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.4 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.52-7.48 (m, 3H), 6.97 (d, *J* = 8.6 Hz, 1H), 5.16-4.97 (m, 1H), 3.98 (dd, *J* = 12.2, 6.3 Hz, 1H), 3.90 (s, 3H), 2.53-2.41 (m, 1H), 2.15-2.09 (m, 1H), 1.77-1.72 (m, 2H), 1.58 (d, *J* = 7.1 Hz, 3H), 1.37-1.18 (m, 3H), 1.15-1.07 (m, 1H), 0.96 (s, 3H), 0.90 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 158.2, 134.1, 132.2, 131.9, 131.6, 129.9, 128.5, 120.9, 118.5, 112.4, 111.2, 97.2, 81.3, 80.7, 56.0, 49.0, 47.8, 45.0, 37.0, 31.5, 28.1, 27.3, 24.0, 19.7, 18.9, 13.6.

HRMS (ESI) *m*/*z* calcd. for $C_{29}H_{31}NNaO_3$ $[M + Na]^+$ 464.2196, found 464.2194.

***(R)*-4-(3-(4-((6-fluoropyridin-2-yl)oxy)-3-methoxyphenyl)but-1-yn-1-yl)benzonitrile (64)**



64

According to **General Procedure A** with 4-cyanophenylacetylene (12.8 mg, 0.10 mmol, 1.0 equiv) and 2-(4-ethyl-2-methoxyphenoxy)-6-fluoropyridine (247 mg, 1 mmol, 10 equiv) for 7 d, the reaction mixture was purified by column chromatography on silica gel to give the corresponding product **64** (11.1 mg) in 32% isolated yield and recover 212 mg C–H substrate.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (q, *J* = 8.0 Hz, 1H), 7.64-7.57 (m, 2H), 7.55-7.49 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.07-6.99 (m, 2H), 6.74 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.57 (dd, *J* = 7.8, 2.6 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 1H), 3.79 (s, 3H), 1.63 (d, *J* = 7.1 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -68.69.

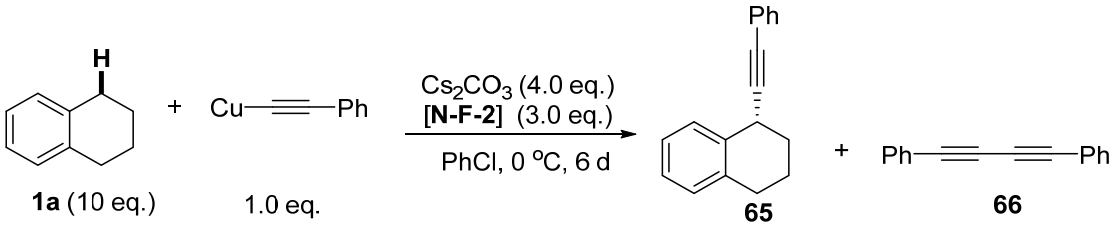
^{13}C NMR (101 MHz, $CDCl_3$) δ162.4 (d, $J_{C\text{-}F}$ = 14.1 Hz), 162.1 (d, $J_{C\text{-}F}$ = 242.4 Hz), 160.9, 151.6, 143.2, 143.1, 140.7, 140.7, 132.2, 132.0, 128.6, 122.9, 119.3, 118.5, 111.7, 111.2, 106.7 (d, $J_{C\text{-}F}$ = 4.9 Hz), 102.2, 101.8, 97.3, 81.2, 55.9, 32.5, 24.1.

HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{18}FN_2O_2$ $[M + H]^+$ 373.1347, found 373.1344.

HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 93/7, flow rate 0.8 mL/min. λ = 254 nm, t(minor) = 32.7 min, t(major) = 38.2 min, 88% ee (93.8:6.2 er).

Mechanistic studies

Control experiment with copper phenylacetylide:



1a (10 eq.) 1.0 eq. **65** **66**

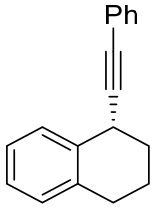
with **L4** (1.0 eq.), **65** (48%, 86% ee), **66** (11%)
without **L4**, **65** (0%), **66** (46%)

Copper phenylacetylide was synthesized according to literature.[13]

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.), **N-F-2** (90.0 mg, 0.30 mmol, 3.0 equiv.), **L4** (92 mg, 0.10 mmol, 1.0 equiv.), and anhydrous PhCl (0.8 mL). The resulting reaction mixture was stirred at room temperature for 4 d. Upon completion of reaction (monitored by TLC), the reaction mixture was filtered and washed by EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether) to afford **65** (11.1 mg, 48% yield, 86% ee) and **66** (2.2 mg, 11% yield).

The procedure for the reaction without **L4** was the same with that described above except that **L4** was not added. Upon completion of reaction (monitored by TLC), the reaction mixture was filtered and washed by EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether) to afford **66** (9.2 mg, 46% yield). No desired product **65** was observed.

***(S)*-1-(phenylethynyl)-1,2,3,4-tetrahydronaphthalene (65)**



65

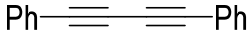
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 6.8, 2.1 Hz, 1H), 7.41 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.31-7.23 (m, 3H), 7.20-7.13 (m, 2H), 7.09 (d, *J* = 6.4 Hz, 1H), 4.02 (dd, *J* = 7.9, 5.4 Hz, 1H), 2.87-2.80 (m, 2H), 2.21-2.17 (m, 1H), 2.13-1.92 (m, 2H), 1.88-1.74 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 136.2, 131.6, 129.2, 129.1, 128.1, 127.6, 126.5, 126.0, 123.8, 93.0, 81.4, 32.1, 30.3, 29.1, 21.3.

The NMR spectra were in accord with that reported in literature.[12]

HPLC condition: Chiralcel OD-3, *n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 19.5 min, t(major) = 21.7 min, 86% ee (93:7 er).

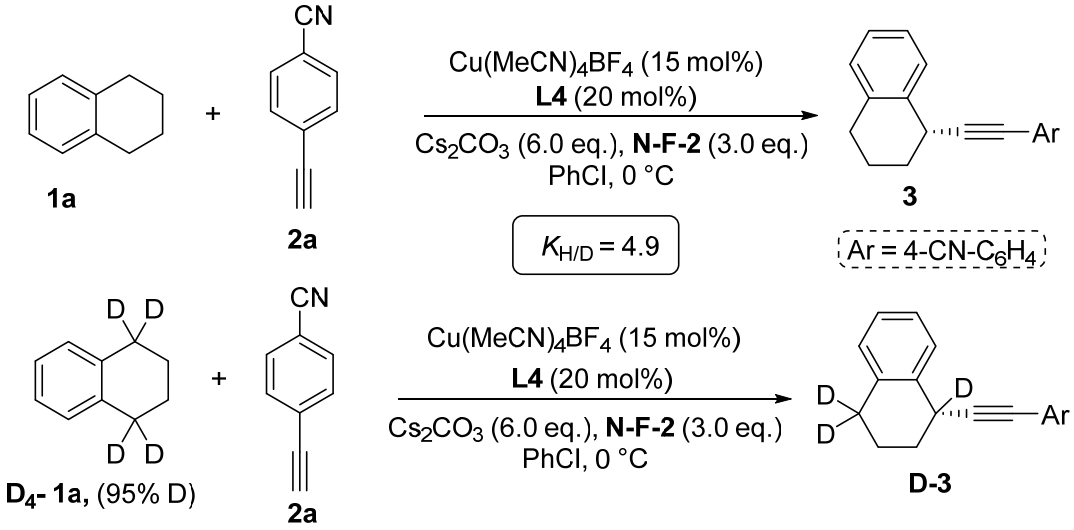
1,4-diphenylbuta-1,3-diyne (66)



66

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.46 (m, 2H), 7.45-7.28 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 129.2, 128.4, 121.8, 81.5, 73.9.
The NMR spectra were in accord with that reported in literature.[12]

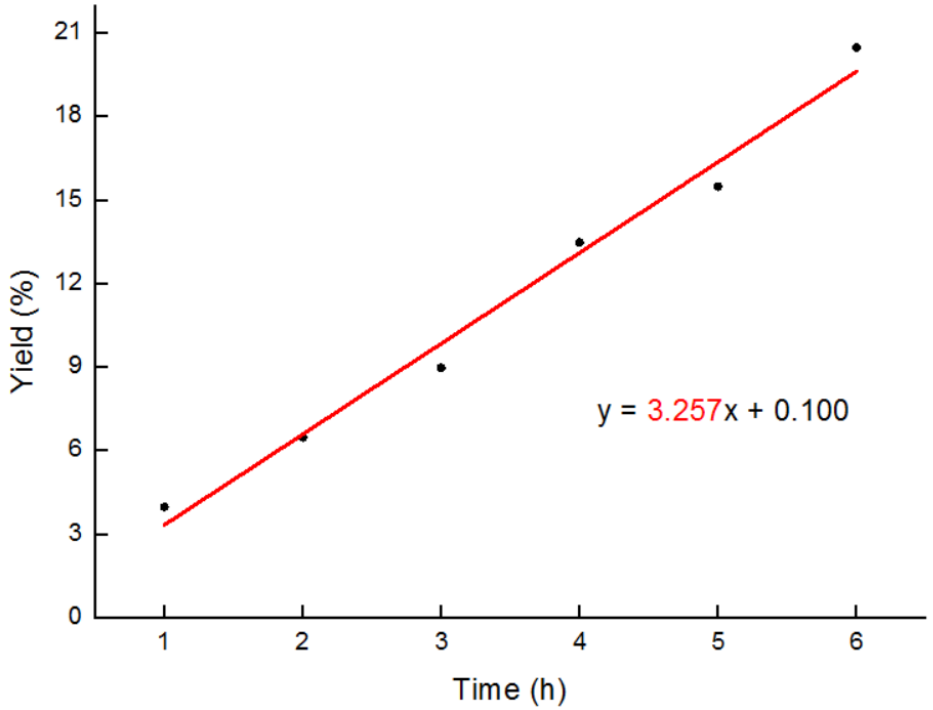
KIE Experiment:

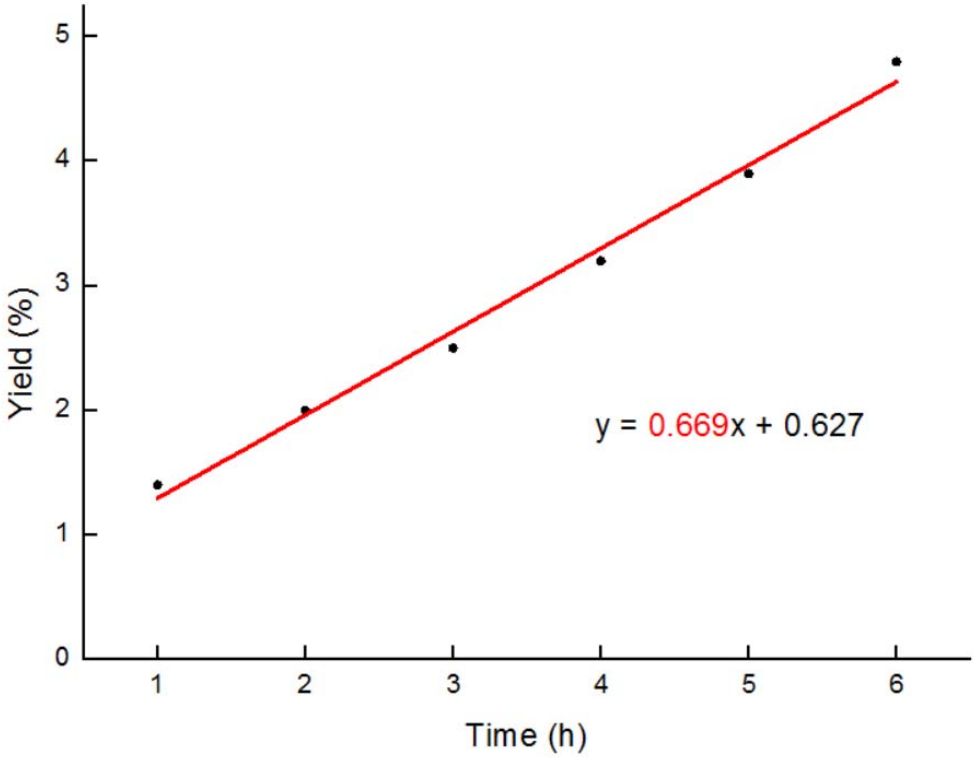


To a flame-dried Schlenk tube equipped with a magnetic stir bar were added 4-ethynylbenzonitrile (6.5 mg, 0.05 mmol), $Cu(MeCN)_4BF_4$ (2.4 mg, 15 mol%), **L4** (6.1 mg, 20 mol%), **N-F-2** (45 mg, 0.15 mmol, 3.0 eq.) and Cs_2CO_3 (97.5 mg, 0.3 mmol, 6.0 eq.). The tube were evacuated and backfilled with argon for three times, the **1a** (43.3 mg, 34 μL,0.25 mmol) or **D-1a** (43.5 mg, 35 μL, 0.25 mmol) and dry PhCl (0.5 mL) was added via syringe. The tube was stirred at 0 ºC and the yield of **3** and **D-3** were determined by crude ^1H NMR using CH_2Br_2 as internal standard at different times to determine the intermolecular KIE value.

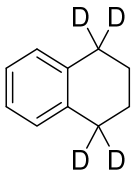
time (h)	1st run yield of **H** (%)	2nd run yield of **H** (%)	average (%)
1	5	3	4
2	8	5	6.5
3	9	9	9
4	14	13	13.5
5	18	13	15.5
6	21	20	20.5

time (h)	1st run yield of **D** (%)	2nd run yield of **D** (%)	average (%)
1	1.4	1.4	1.4
2	2.1	1.8	2.0
3	2.5	2.5	2.5
4	2.8	3.5	3.2
5	3.5	4.2	3.9
6	4.6	4.9	4.8





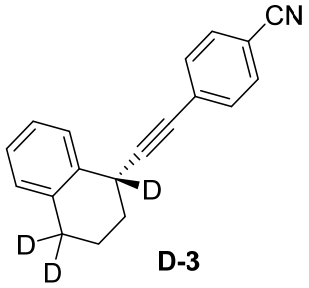
1,2,3,4-tetrahydronaphthalene-1,1,4,4-d$_4$ (D$_4$-1a)



D$_4$-1a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (p, *J* = 4.8 Hz, 4H), 2.76-2.70 (m, 0.2H), 1.77 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.1, 129.2, 125.5, 28.8 (dq, $J_{C\text{-}D}$ = 38.7, 19.4 Hz), 23.04.

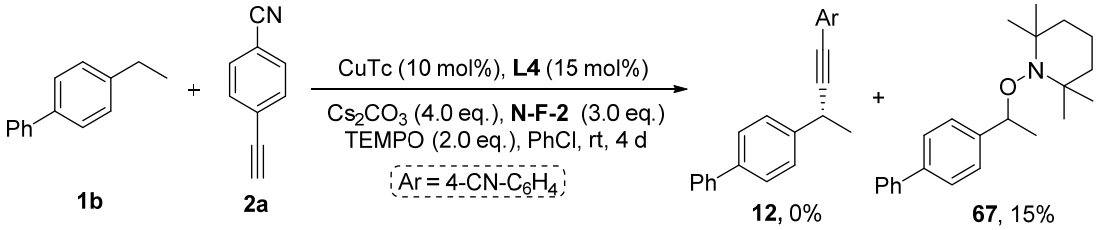
(*S*)-4-((1,2,3,4-tetrahydronaphthalen-1-yl-1,4,4-d_3)ethynyl)benzonitrile (D-3)



D-3

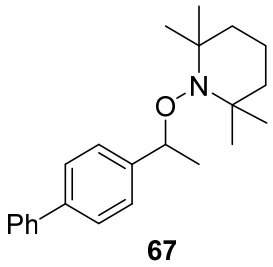
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.50-7.43 (m, 3H), 7.22-7.14 (m, 2H), 7.11 (dt, *J* = 4.4, 2.9 Hz, 1H), 2.22-2.12 (m, 1H), 2.09-1.95 (m, 2H), 1.80 (ddd, *J* = 13.8, 9.6, 3.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 135.5, 132.2, 131.9, 129.4, 129.0, 128.9, 126.8, 126.1, 118.6, 111.0, 98.1, 80.2, 32.3-31.2 (m, 1C), 29.9, 28.9-28.1 (m, 1C), 21.0.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{12}D_3NNa$ $[M + Na]^+$ 283.1285, found 283.1284.

Radical-trapping experiment:



To a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with CuTc (1.9 mg, 0.010 mmol, 10 mol%), **L4** (9.2 mg, 0.015 mmol, 15 mol%), 4-cyanophenylacetylene (**2a**, 12.8 mg, 0.10 mmol, 1.0 equiv), **1b** (364 mg, 1.0 mmol, 10 equiv.), TEMPO (62.5 mg, 0.2 mmol, 2.0 equiv.), **N-F-2** (90.0 mg, 0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (130.4 mg, 0.40 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon for three times, and anhydrous PhCl (0.8 mL) was then added. The reaction mixture was stirred at rt for 4 d. After the completion of reaction, the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was analyzed by **^{1}H NMR**, the desired product **12** was not detected in the reaction mixture. The residue was purified by column chromatography on basic alumina to afford the desired product **67** (5.2 mg) in 15% isolated yield.

1-(1-([1,1'-biphenyl]-4-yl)ethoxy)-2,2,6,6-tetramethylpiperidine (67)

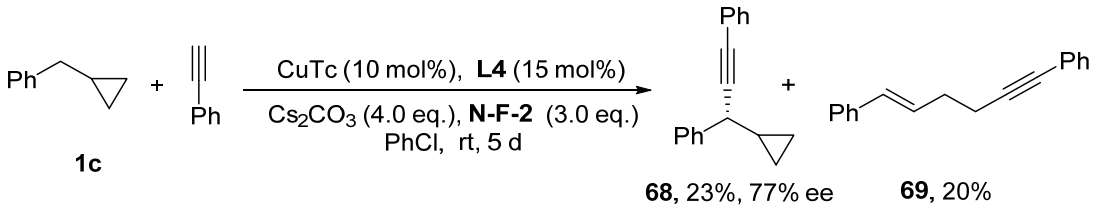


67

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.51 (m, 2H), 7.50-7.44 (m, 2H), 7.41-7.29 (m, 4H), 7.29-7.21 (m, 1H), 4.76 (q, *J* = 6.7 Hz, 1H), 1.52-1.45 (m, 6H), 1.44 (d, *J* = 6.6 Hz, 3H), 1.40-1.28 (m, 1H), 1.24 (s, 3H), 1.11 (s, 2H), 1.04 (s, 1H), 0.98 (s, 3H), 0.65 (s, 2H).

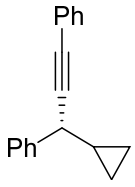
HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{32}NO$ $[M + H]^+$ 338.2478, found 338.2475.

Radical clock experiments:



Under argon atmosphere, an oven-dried Schlenk tube equipped with a magnetic stir bar were charged with CuTc (1.9 mg, 0.010 mmol, 10 mol%), **L4** (9.2 mg, 0.015 mmol, 15 mol%), **N-F-2** (90.0 mg, 0.3 mmol, 3.0 equiv.) and Cs_2CO_3 (130.4 mg, 0.40 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon for three times, and **1c** (132 mg, 1.0 mmol, 10 equiv.), phenylacetylene (11.1 μL, 0.10 mmol, 1.0 equiv) and anhydrous PhCl (0.8 mL) were then added successively. Then, the reaction mixture was stirred at rt for 5 d. After the completion of reaction, the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the product **68** (5.3 mg) in 23% isolated yield, and the ring-opening product **69** (4.6 mg) in 20% isolated yield.

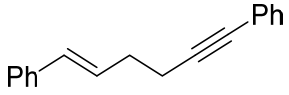
***(R)*-(3-cyclopropylprop-1-yne-1,3-diyl)dibenzene (68)**



68

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.43 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.32-7.24 (m, 4H), 3.69 (d, *J* = 6.6 Hz, 1H), 1.21 (dt, *J* = 7.7, 6.2 Hz, 1H), 0.68-0.42 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 131.7, 128.9, 128.4, 128.2, 127.8, 127.5, 126.8, 89.6, 83.2, 41.3, 17.5, 4.1, 3.1.
The NMR spectra were in accord with that reported in literature.[12]
HPLC condition: Chiralcel AD-3, *n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.8 mL/min. λ = 254 nm, t(minor) = 8.7 min, t(major) = 10.2 min, 77% ee (88.5:11.5 er).

***(E)*-hex-1-en-5-yne-1,6-diyldibenzene (69)**

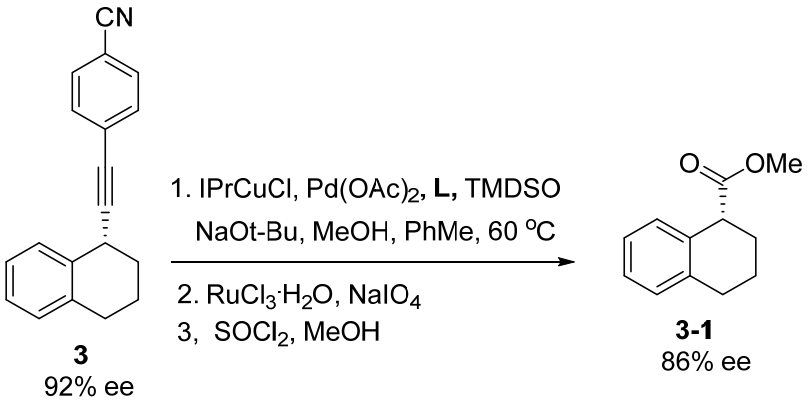


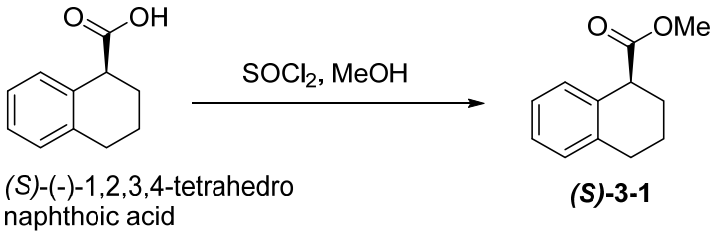
69

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.36 (m, 4H), 7.34-7.25 (m, 5H), 7.25-7.18 (m, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.41-6.18 (m, 1H), 2.94-2.18 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 131.6, 131.1, 128.8, 128.5, 128.2, 127.6, 127.1, 126.1, 123.9, 89.4, 81.2, 32.3, 19.8.
The NMR spectra were in accord with that reported in literature.[12]

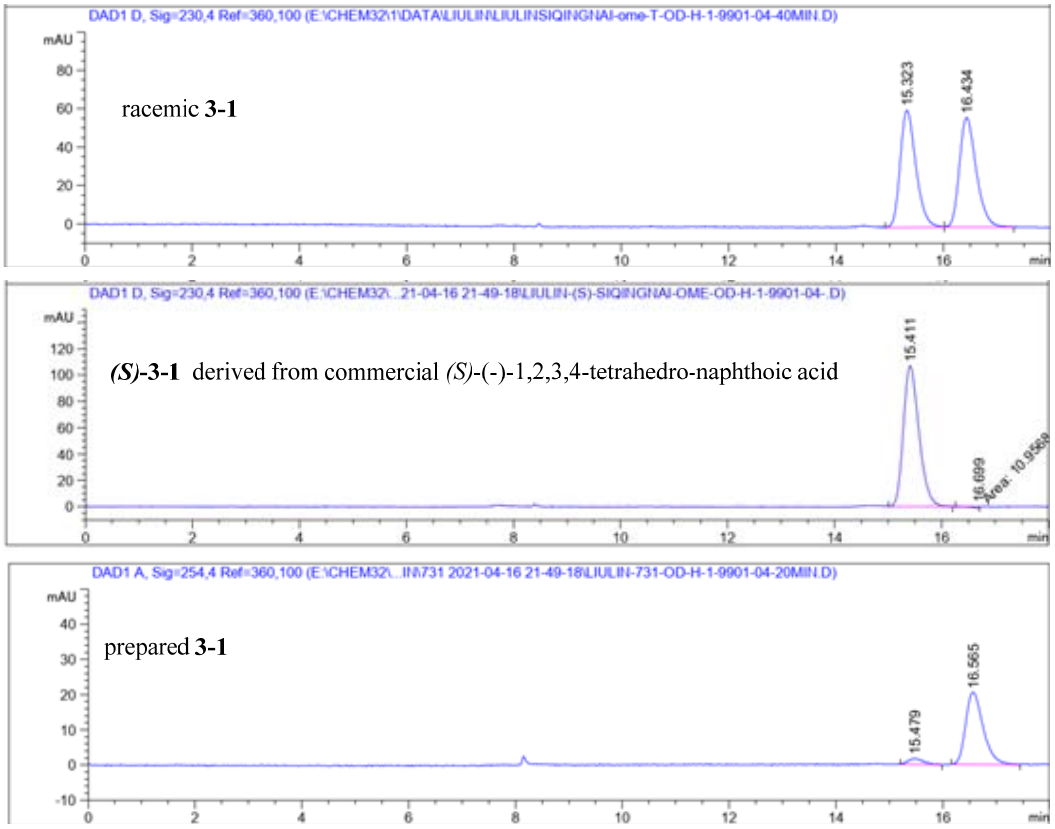
Assignment of absolute stereochemistry

For cyclic benzyl products:





The absolute configuration of **3** was assigned to be *S* by comparing HPLC spectra of **3-1** and the one deriving from commercial *(S)*-(-)-1,2,3,4-tetrahedro-naphthoic acid (*purchased from Shanghai Bidepharm) technology Ltd.*), as shown below.



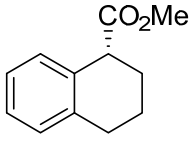
Entry	Sample	Absolute configuration	ee/%
1	**(S)-3-1** derived from commercial (S)-(-)-1,2,3,4-tetrahedro-naphthoic acid	(*S*)	-99
2	**3-1**	(*R*)	86

To a flamed Schlenk tube charged with a stir bar were added **3** (92% ee, 162.1 mg, 0.63 mmol, 1.0 equiv.), NaOt-Bu (121.2 mg, 1.26 mmol, 2.0 equiv.), $Pd(OAc)_2$ (7.1 mg, 0.032 mmol, 5 mol%), **L** (dicyclohexyl(2'-Methoxy-[1,1'-biphenyl] -2-yl)phosphine) (24.0 mg, 0.063 mmol, 10 mol%), IPrCuCl (30.7 mg, 0.063 mmol, 10 mol%), TMDSO (1,1,3,3-tetramethyldisiloxane) (223 μL, 1.26 mmol, 2.0 equiv.), MeOH (128 μL, 3.15 mmol, 5.0 equiv.), and toluene (5.0 mL). The reaction mixture was stirred at 60 °C for 10 h. Upon completion, the reaction mixture was filtered through a short plug of silica gel eluted with EtOAc and purified by column chromatography to afford olefin (140.5 mg, 0.54 mmol, 85% yield).

To a mixture of $RuCl_3$ (6.1 mg, 0.010 mmol, 5.0 mol%) and sodium periodate (464.0 mg, 0.80 mmol, 4.0 equiv.) in a mixed solvent of CCl_4 (2 mL) and water (3 mL) was added a solution of olefin (250.9 mg, 0.54 mmol, 1.0 equiv.) in MeCN (2 mL) in one portion. The reaction mixture was stirred at room temperature for 6 h, and then, was concentrated. The residue was purified by column chromatography on silica gel to afford the product *(R)*-1,2,3,4-tetrahydronaphthalene-1-carboxylic acid (80.0 mg, 0.45 mmol, 84% yield).

To a solution of *(R)*-1,2,3,4-tetrahydronaphthalene-1-carboxylic acid (80.0 mg, 0.45 mmol, 1.0 equiv.) in MeOH (2.0 mL) was added $SOCl_2$ (119.0 mg, 1.0 mmol, 2.0 equiv.) dropwise at 0 °C. Then, the reaction mixture was warmed up to room temperature and stirred for another 6 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 **3-1** (78.0 mg, 0.41 mmol, 91% yield) as a slight yellow oil.

methyl *(R)*-1,2,3,4-tetrahydronaphthalene-1-carboxylate (3-1)



3-1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-6.92 (m, 4H), 3.83 (t, *J* = 5.7 Hz, 1H), 3.70 (s, 3H), 2.85-2.72 (m, 2H), 2.16-2.11 (m, 1H), 2.06-1.88 (m, 2H), 1.86-1.60 (m, 1H).

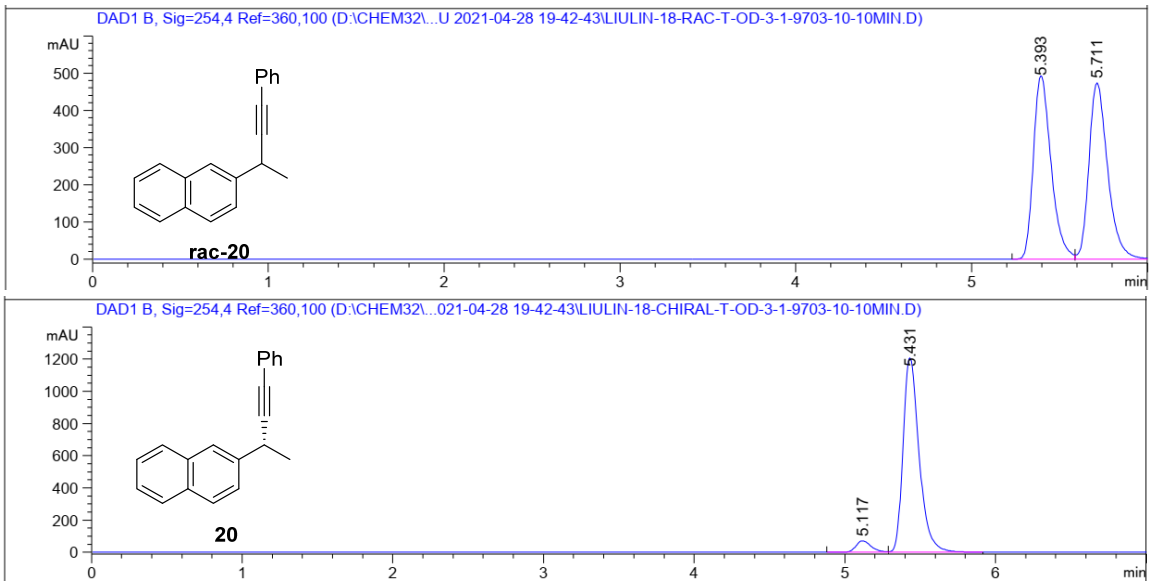
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 137.1, 133.2, 129.3, 129.2, 126.8, 125.7, 51.9, 44.7, 29.1, 26.6, 20.5.

The NMR spectra was in accord with that reported in literature.[14]

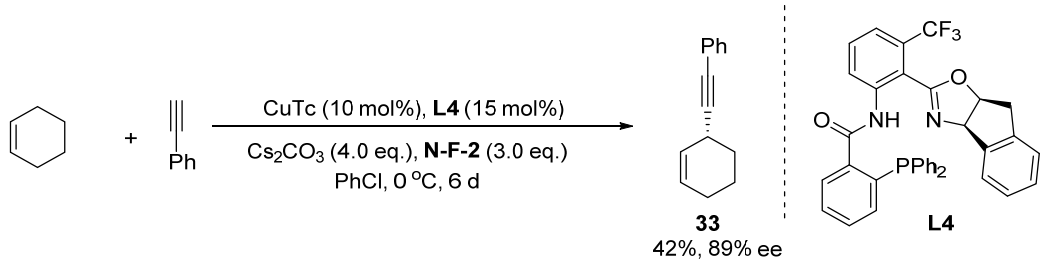
HPLC condition: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 99/1, flow rate 0.4 mL/min. λ = 214 nm, t(minor) = 15.5 min, t(major) = 16.6 min, 86% ee (93.2:6.8 er).

For acyclic benzyl products:

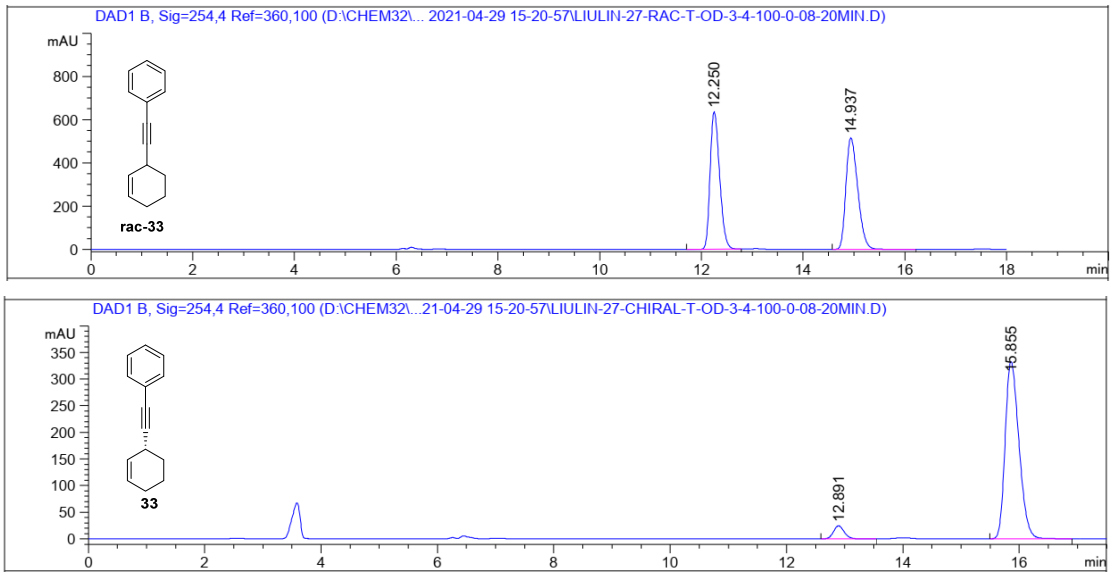
The absolute configuration of **20** was assigned to be *R* by comparing its HPLC spectra with the product **98** (90% ee) in the literature (see ref. *Nat. Chem.* **2019**, *11*, 1158.). Using the same HPLC condition: Chiralcel OD-3, *n*-hexane/*i*-PrOH = 97/3, flow rate 1.0 mL/min. λ = 254 nm, t(minor) = 5.1 min, t(major) = 5.4 min, 90% ee (94.8:5.2 er).



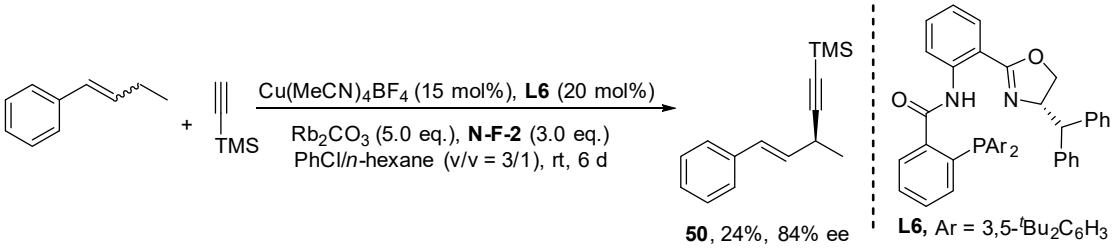
For cyclic allyl products:



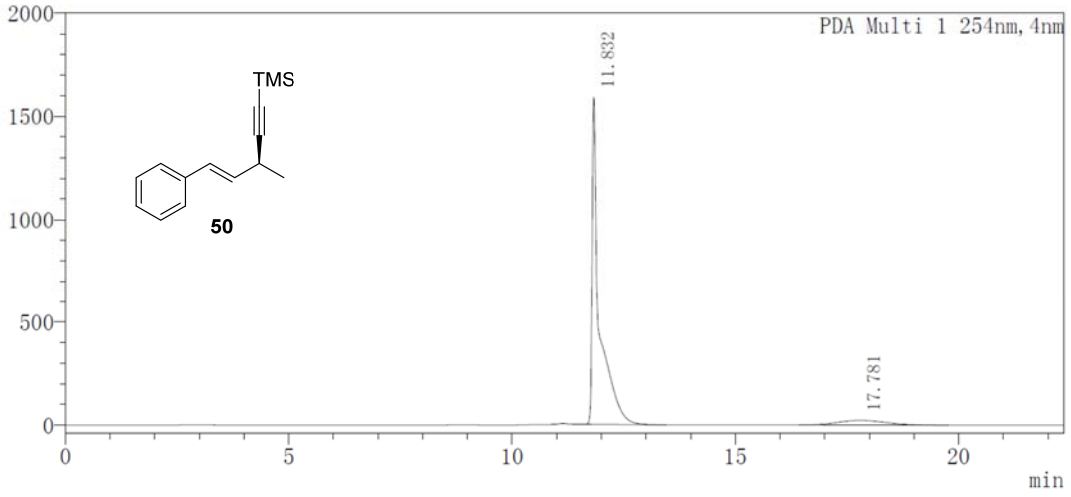
The absolute configuration of **33** was assigned to be *R* by comparing its optical rotation (**33**, 89% ee, $[\alpha]^{24.5}_D$ +190.7 (c 0.12 in CH_2Cl_2)) and the product **3a** (91% ee, $[\alpha]^{23}_D$ +260.8 (c 1.60 in CH_2Cl_2)) in the literature (see ref. *J. Am. Chem. Soc.* **2018**, *140*, 8448).



For acyclic allyl products:



The absolute configuration of **50** was assigned to be *S* by comparing its HPLC spectra with the product ***S*-5a** (99% ee) in the literature (see ref. *Tetrahedron Lett.* **2010**, *51*, 5592). HPLC condition of **50**: Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min., t(major) = 11.8 min, t(minor) = 17.8 min, 84% ee (91.8:8.2 er).



PDA Ch1 254nm

T	Hight	Area	Area%
11.832	1589654	17970116	91.823
17.781	22134	1600375	8.177

References

[1] W. J. Marshall, V. V. Grushin, *Organometallics,* **2003**, *22*, 555.

[2] S. A. Macgregor, D. C. Roe, W. J. Marshall, K. M. Bloch, V. I. Bakhmutov, V. V. Grushin. *J. Am. Chem. Soc.* **2005**, *127*, 15304.

[3] M. Arisawa, T. Suzuki, T. Ishikawa, M. Yamaguchi. *J. Am. Chem. Soc.,* **2008**, *130*, 12214.

[4] S. S. Bera, S. Debbarma, A.K. Ghosh, S. Chand, M. S. Maji. *J. Org. Chem.* **2017**, *82*, 420

[5] K. Born, S. Doye. *Eur. J. Org. Chem.* **2012**, 764.

[6] H. Zhang, C. Jiang, J.-P. Tan, H.-L. Hu, Y. Chen, X. Ren, H.-S. Zhang, T. Wang. *ACS Catal.* **2020**, *10*, 5698.

[7] X.-Y. Dong, Y.-F. Zhang, C.-L. Ma, Q.-S. Gu, F.-L. Wang, Z.-L. Li, S.-P. Jiang, X.-Y. Liu. *Nat. Chem.* **2019**, *11*, 1158.

[8] W. Zhang, F. Wang, S. D. McCann, D. Wang, P. Chen, S. S. Stahl. G. Liu. *Science* **2016**, *353*, 1014.

[9] X.-Y. Cui, Y. Ge, S. M. Tan, H. Jiang, D. Tan, Y. Lu, R. Lee, C.-H. Tan. *J. Am. Chem. Soc.,* **2018**, *140*, 8448

[10] Q. Wang, Y. Kobayashi. *Tetrahedron Lett.* **2010**, *51*, 5592.

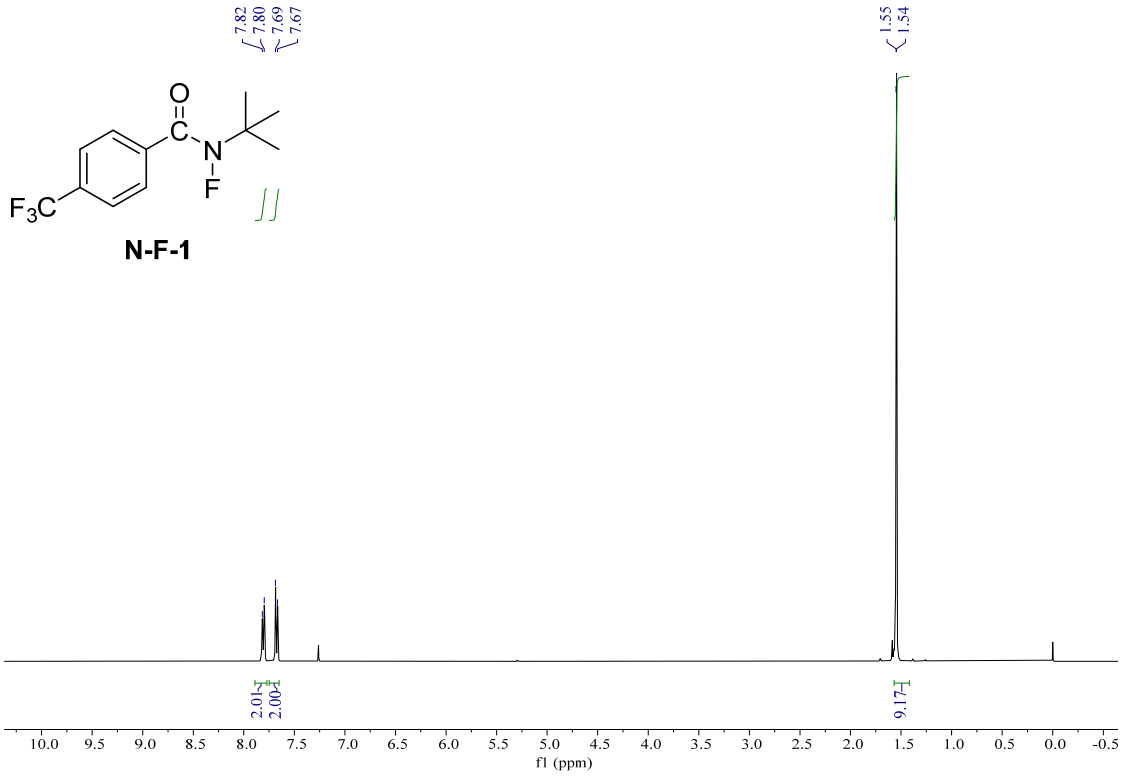
[11] J. R. Clark, K. Feng, A. Sookezian, M. C. White. *Nat. Chem.* **2018**, *10*, 583.

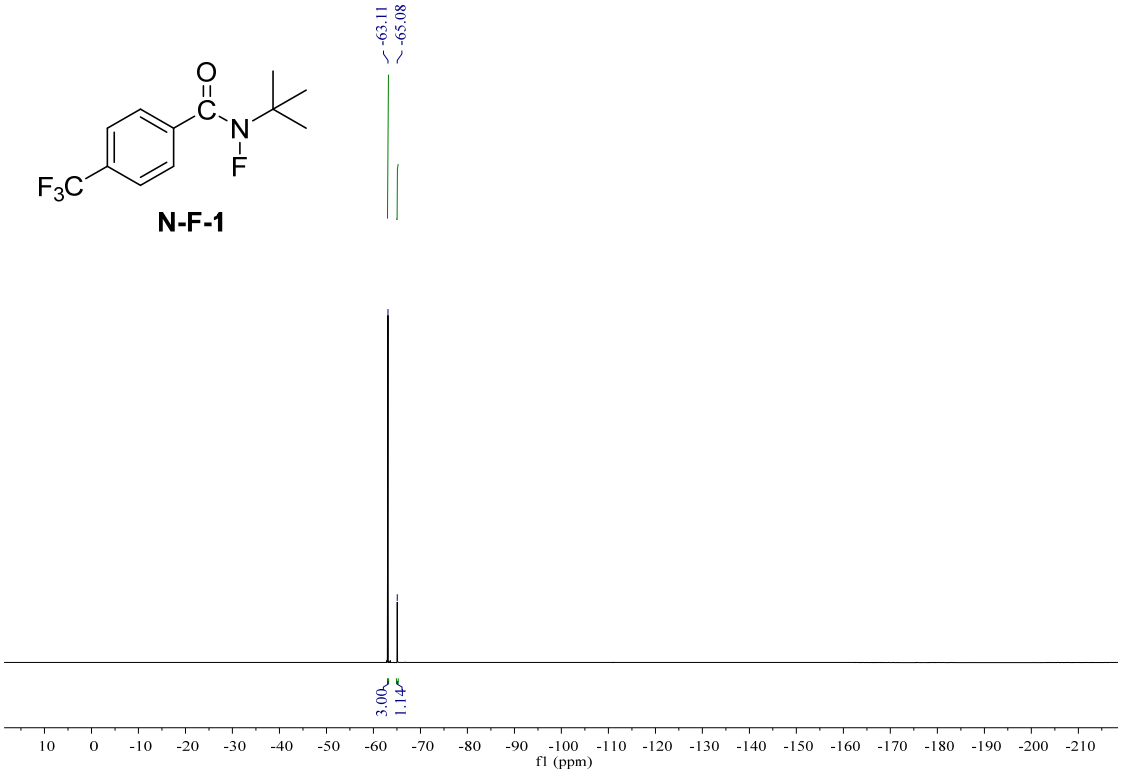
[12] H.-D. Xia, Z.-L. Li, Q.-S. Gu, X.-Y. Dong, J.-H. Fang, X.-Y. Du, L.-L. Wang, X.-Y. Liu. *Angew. Chem., Int. Ed.* **2020**, *59*, 16926; *Angew. Chem.,* **2020**, *132*, 17074.

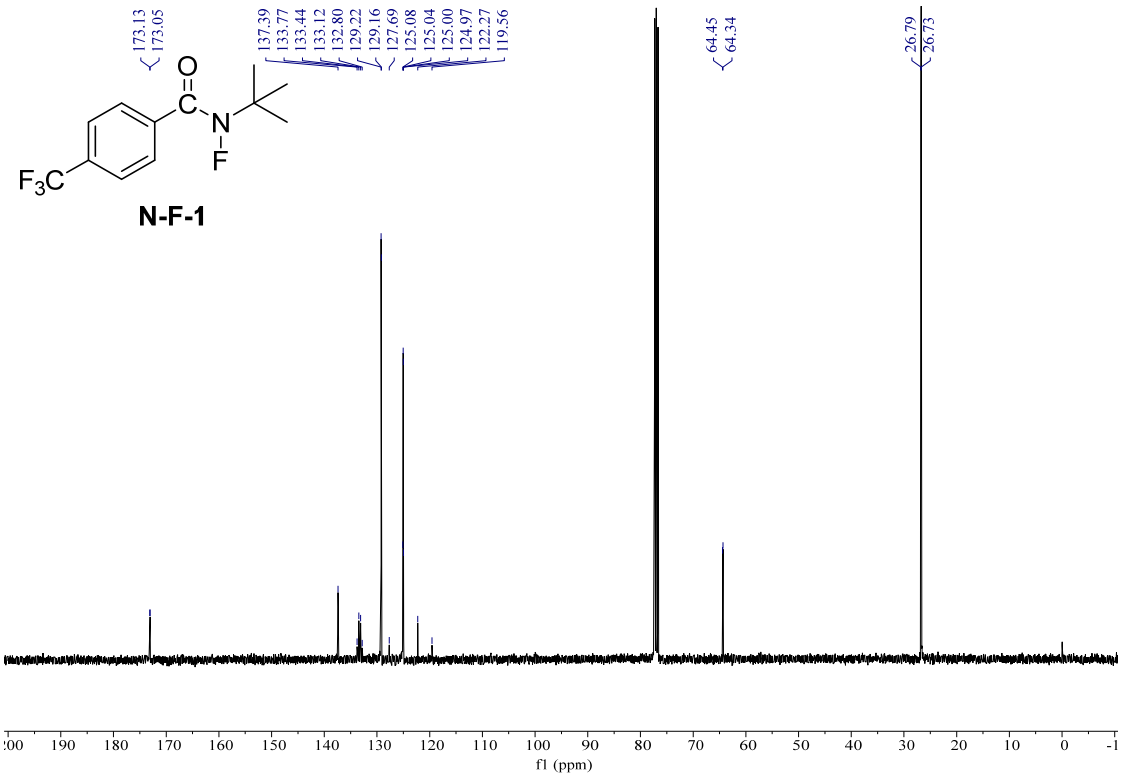
[13] A. Sagadevan, A. Ragupathi & K. C. Hwang. *Angew. Chem., Int. Ed.* **2015**, *54*, 13896; *Angew. Chem.,* **2015**, *127*, 14102.

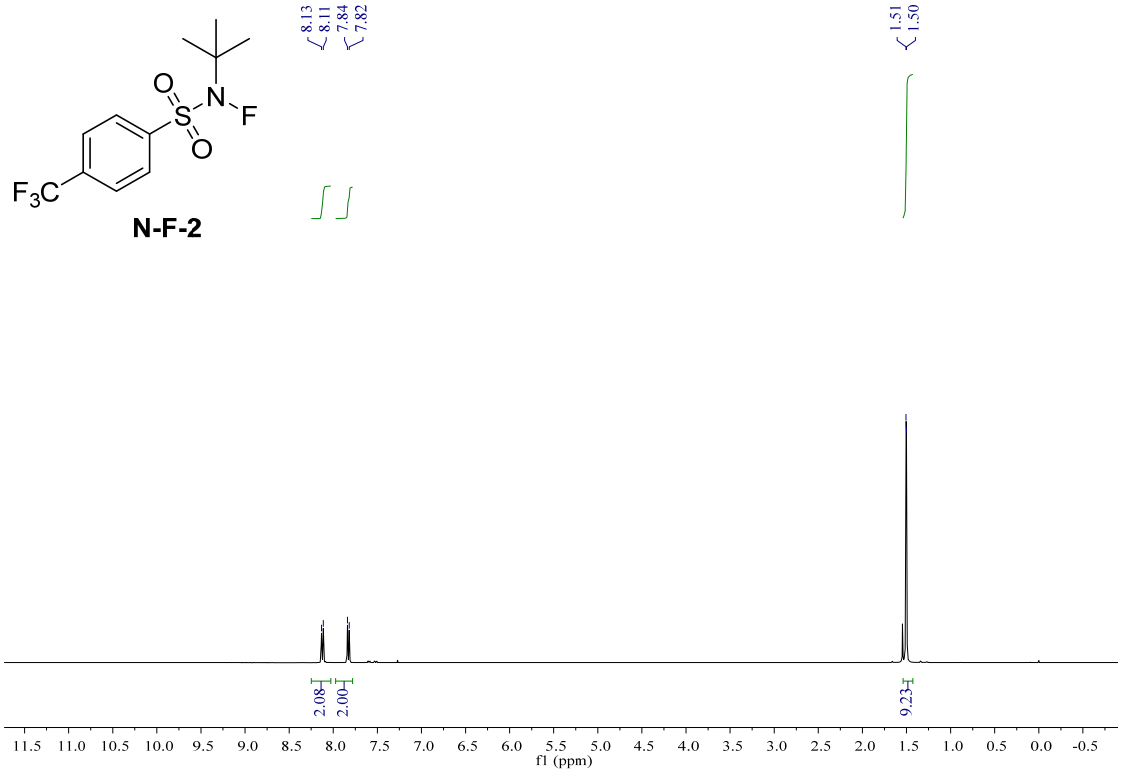
[14] B. A. Sandoval, A. J. Meichan, T. K. Hyster. *J. Am. Chem. Soc.,* **2017**, *139*, 11313.

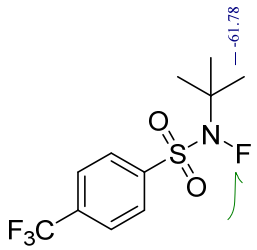
NMR Spectra


7.82
7.80
7.69
7.67
1.55
1.54
O
C
N
F
F3C
N-F-1
2.01
2.00
9.17
10.0 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)

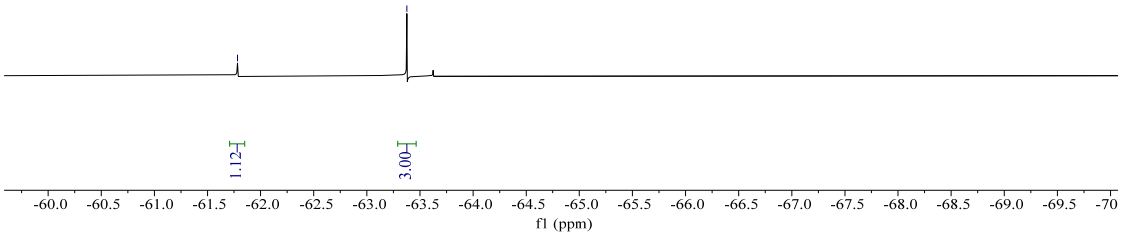

-63.11
-65.08
O
C
N
F
F3C
N-F-1
3.00
1.14
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

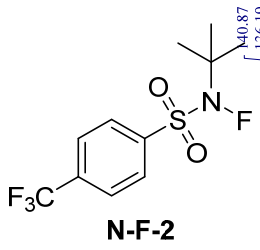

173.13
173.05
137.39
133.77
133.44
133.12
132.80
129.22
129.16
127.69
125.08
125.04
125.00
124.97
122.27
119.56
64.45
64.34
26.79
26.73
O
C
N
F
F3C
N-F-1
f1 (ppm)


8.13
8.11
7.84
7.82
1.51
1.50
O
S
N
F
F3C
N-F-2
2.08
2.00
9.23
f1 (ppm)


-61.78
-63.38
O
S
O
N
F
F3C

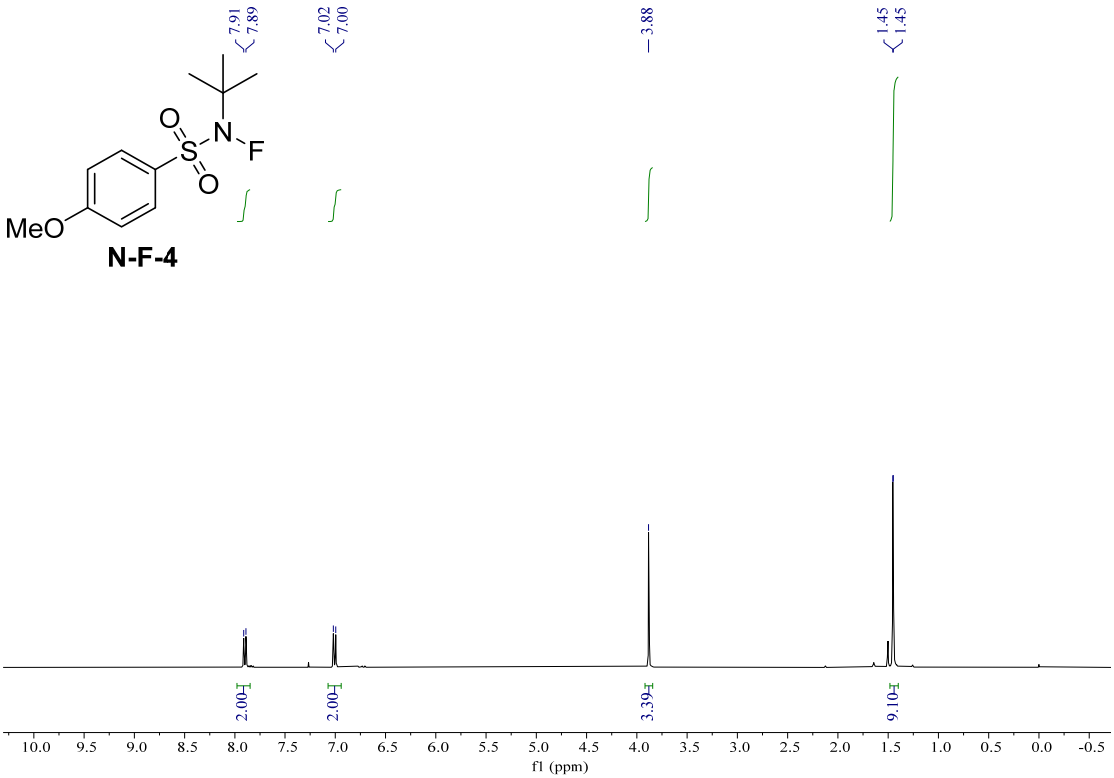
N-F-2

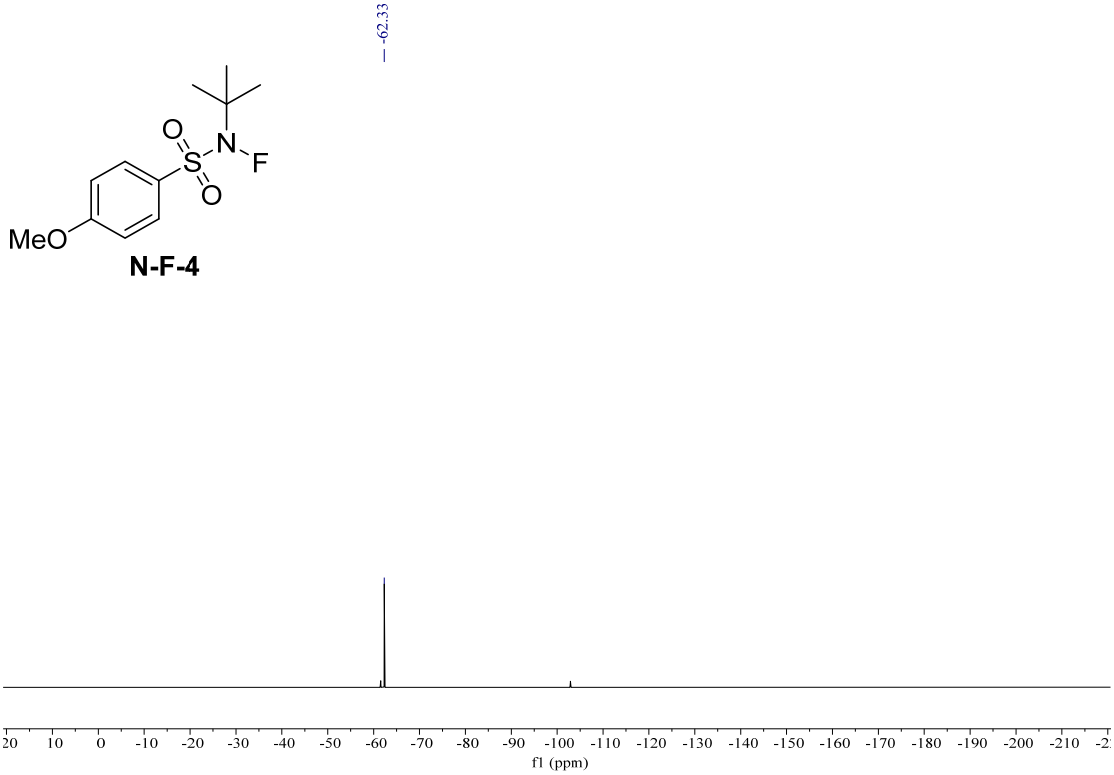

1.12
3.00
-60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5 -70
f1 (ppm)

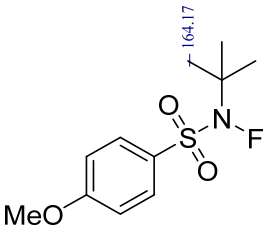

O
S
O
N
F
F3C

N-F-2

140.87
136.19
135.86
135.53
135.20
132.90
129.61
127.14
126.17
126.13
126.10
126.06
124.43
121.71
119.00
67.17
67.05
27.19
27.13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

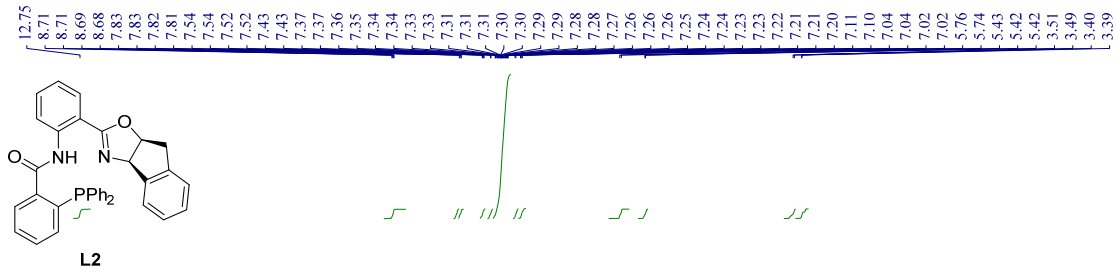

7.91
7.89
7.02
7.00
3.88
1.45
1.45
MeO
N-F-4
2.00
2.00
3.39
9.10
f1 (ppm)


-62.33
MeO
N-F-4
f1 (ppm)


MeO
O
S
O
N
F

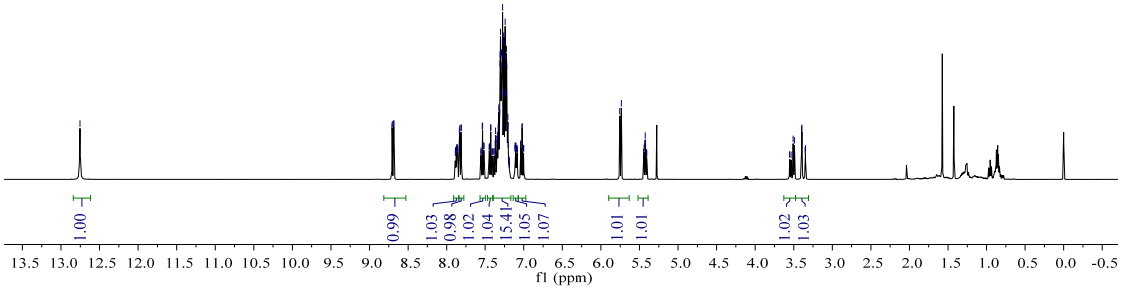
N-F-4

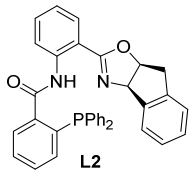
164.17
131.36
131.35
128.66
114.18
66.35
66.23
55.68
27.17
27.11
f1 (ppm)


12.75
8.71
8.71
8.69
8.68
7.83
7.83
7.82
7.81
7.54
7.54
7.52
7.52
7.43
7.43
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.11
7.10
7.04
7.04
7.02
7.02
5.76
5.74
5.43
5.42
5.42
3.51
3.49
3.40
3.39

O
NH
N
O
PPh2

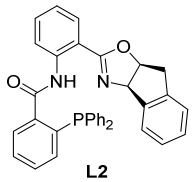
L2


1.00
0.99
1.03
0.98
1.02
1.04
15.41
1.05
1.07
1.01
1.01
1.02
1.03
f1 (ppm)


O
NH
N
PPh2

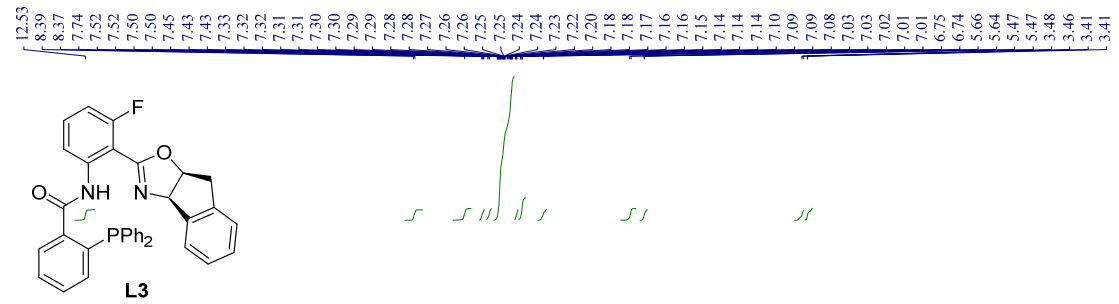
L2

7.84
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)


O
NH
N
PPh2

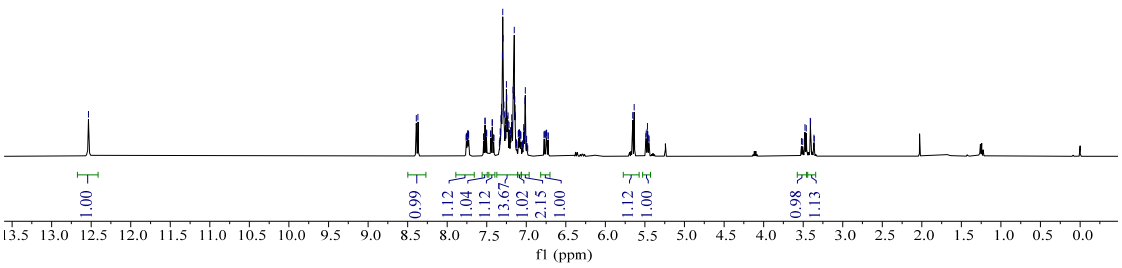
L2

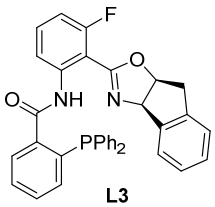
167.13
163.91
141.66
141.47
141.25
139.90
139.67
139.06
138.83
138.59
138.47
138.14
138.03
134.81
134.13
133.92
133.83
133.63
132.54
130.34
128.96
128.72
128.38
128.31
128.27
128.25
128.22
128.15
127.49
127.45
127.41
125.53
125.04
122.25
119.96
113.31
81.67
76.61
39.78
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


12.53
8.39
8.37
7.74
7.52
7.52
7.50
7.50
7.45
7.43
7.43
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.20
7.18
7.18
7.17
7.16
7.16
7.15
7.14
7.14
7.14
7.10
7.09
7.09
7.08
7.03
7.03
7.02
7.01
7.01
6.75
6.74
5.66
5.64
5.47
5.47
3.48
3.46
3.41
3.41

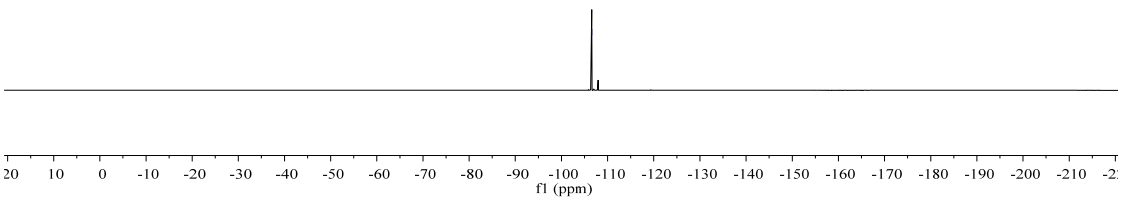
F
O
NH
N
PPh2

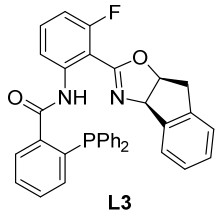
L3


1.00
0.99
1.12
1.04
1.12
13.67
1.02
2.15
1.00
1.12
1.00
0.98
1.13
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)


F
O
NH
N
PPh2

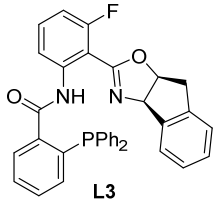
L3


-106.56
20 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)


F
O
NH
N
O
PPh2

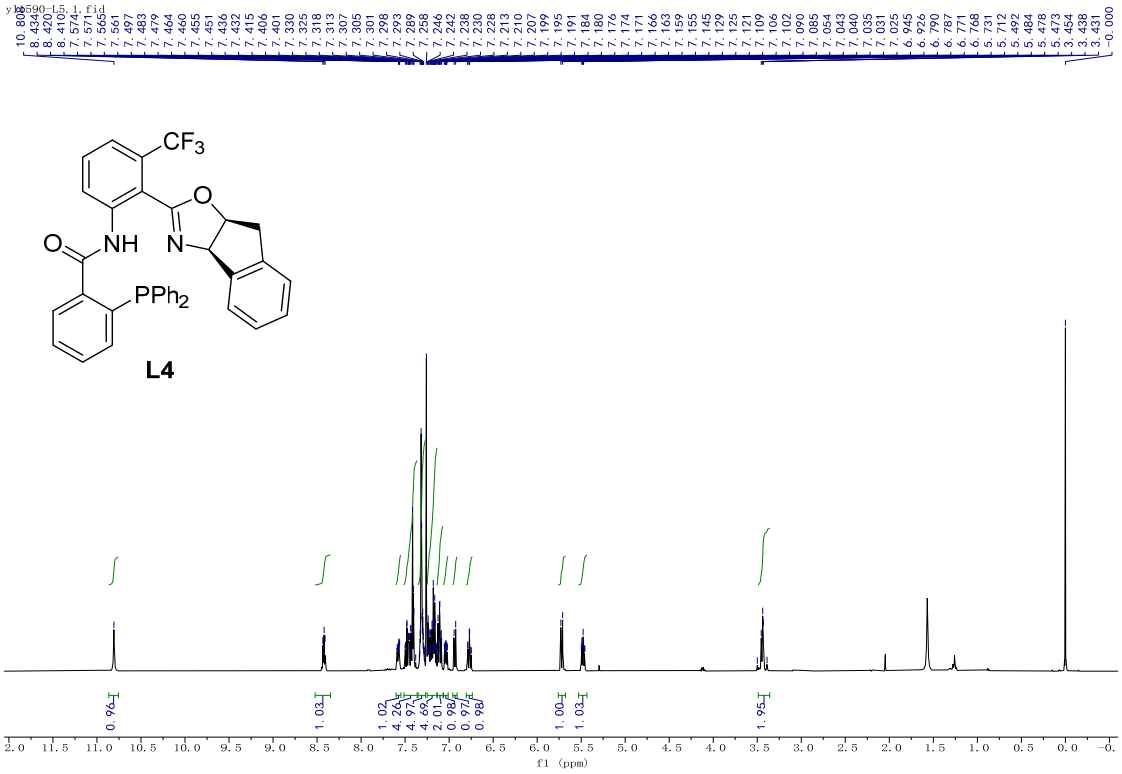
L3

-7.61
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)


F
O
NH
N
O
PPh2

L3

167.14
162.78
162.25
162.22
160.23
141.29
141.15
140.93
140.65
140.61
139.57
138.78
138.55
137.93
137.81
137.73
137.62
134.59
134.08
133.88
133.85
133.65
132.96
132.85
130.31
128.64
128.46
128.37
128.33
128.31
128.28
128.23
128.12
128.05
127.36
127.33
127.20
127.16
125.48
124.87
115.99
115.96
110.56
110.34
103.30
103.17
82.44
77.32
77.00
76.68
75.02
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)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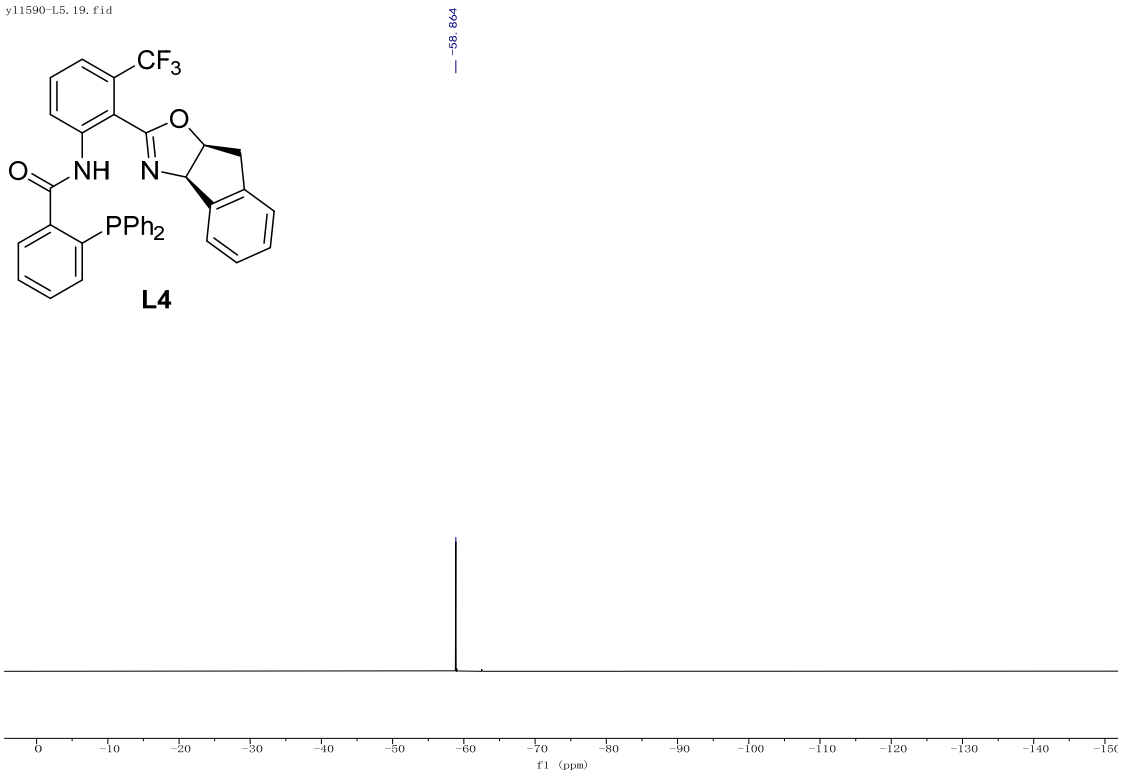
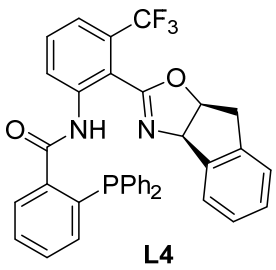
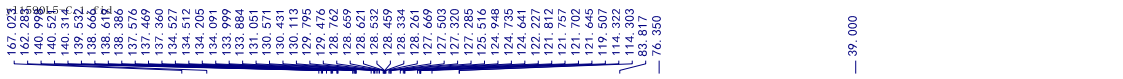
CF3
O
NH
N
PPh2
L4
f1 (ppm)

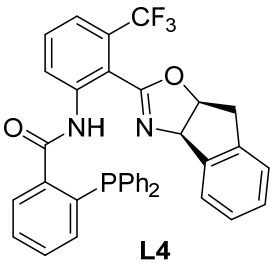

y11590-L5.19.fid
-58.864
CF3
O
NH
N
PPh2
L4
f1 (ppm)

y11590-L5.31.fid

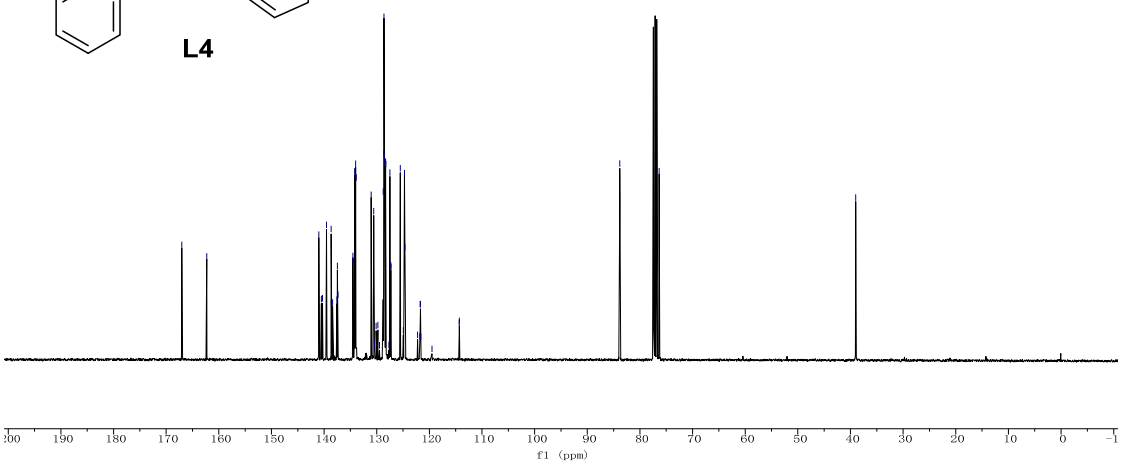


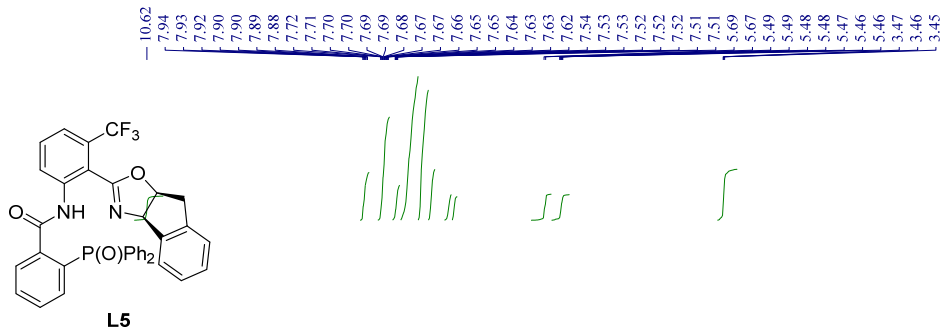
L4



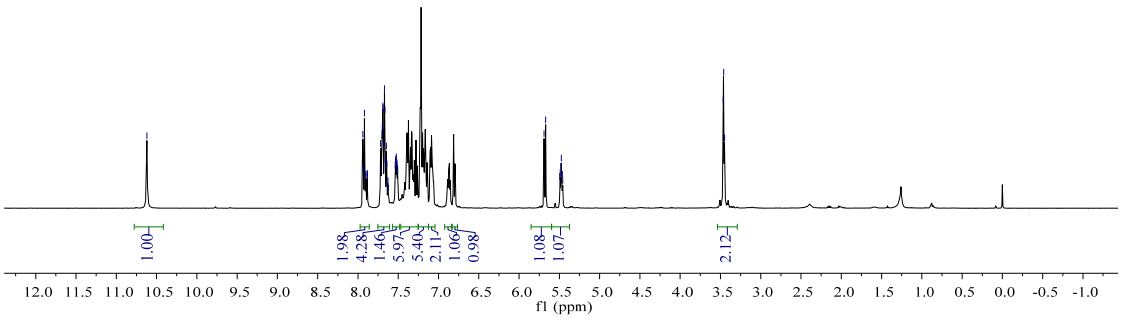


L4




10.62
7.94
7.93
7.92
7.90
7.90
7.89
7.88
7.72
7.71
7.70
7.70
7.69
7.69
7.68
7.67
7.67
7.66
7.65
7.65
7.64
7.63
7.63
7.62
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.51
5.69
5.67
5.49
5.49
5.48
5.48
5.47
5.46
5.46
3.47
3.46
3.45
CF3
O
NH
N
O
P(O)Ph2

L5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1.98
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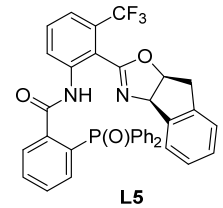
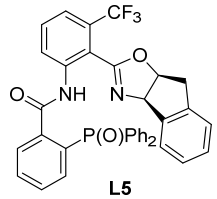
1.46
5.97
5.40
2.11
1.06
0.98
1.08
1.07
2.12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


CF3
O
NH
N
O
P(O)Ph2

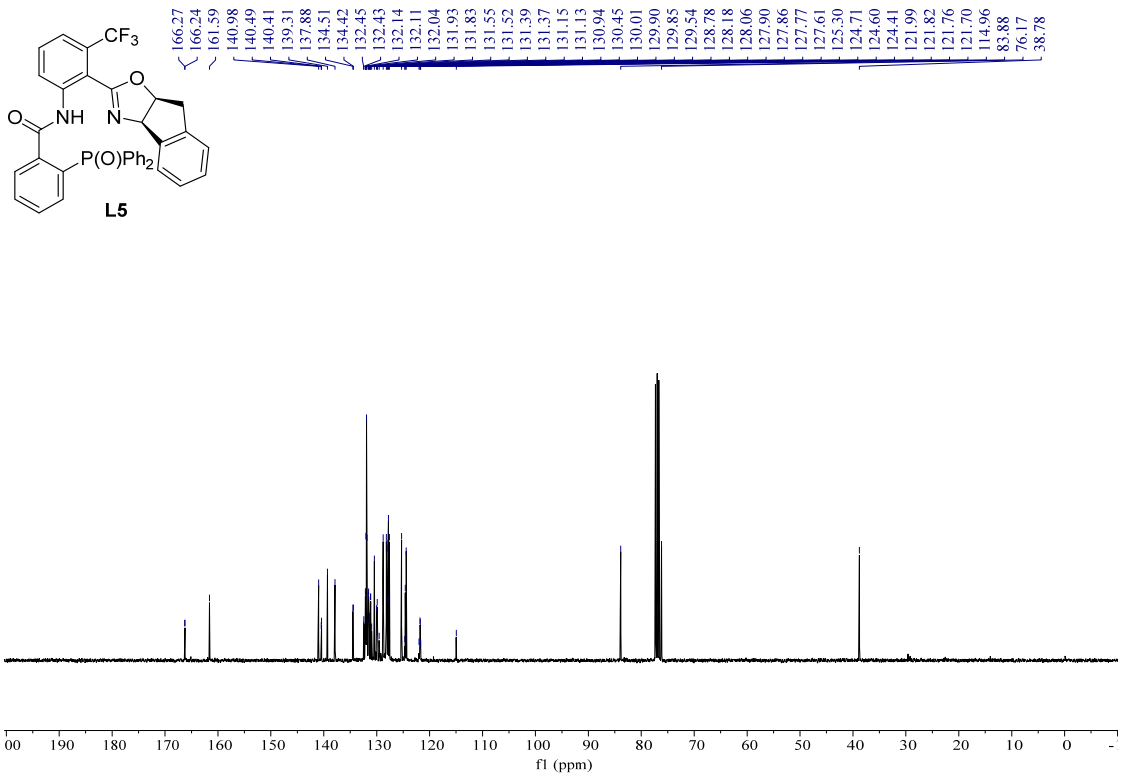
L5

-58.92
-52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71
f1 (ppm)


CF3
O
NH
N
P(O)Ph2

L5

29.95
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)


166.27
166.24
161.59
140.98
140.49
140.41
139.31
137.88
134.51
134.42
132.45
132.43
132.14
132.11
132.04
131.93
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131.55
131.52
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131.13
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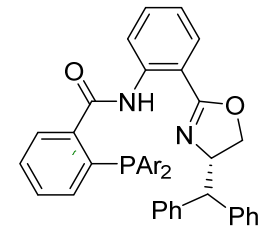
130.45
130.01
129.90
129.85
129.54
128.78
128.18
128.06
127.90
127.86
127.77
127.61
125.30
124.71
124.60
124.41
121.99
121.82
121.76
121.70
114.96
83.88
76.17
38.78
CF3
O
NH
N
P(O)Ph2
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)

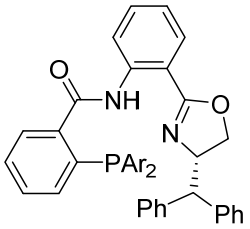
L5

GKX21-P-LIGANG/1

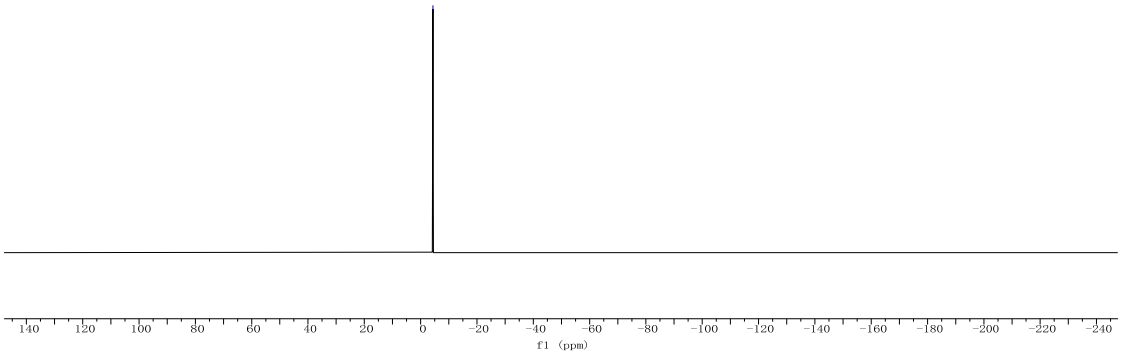


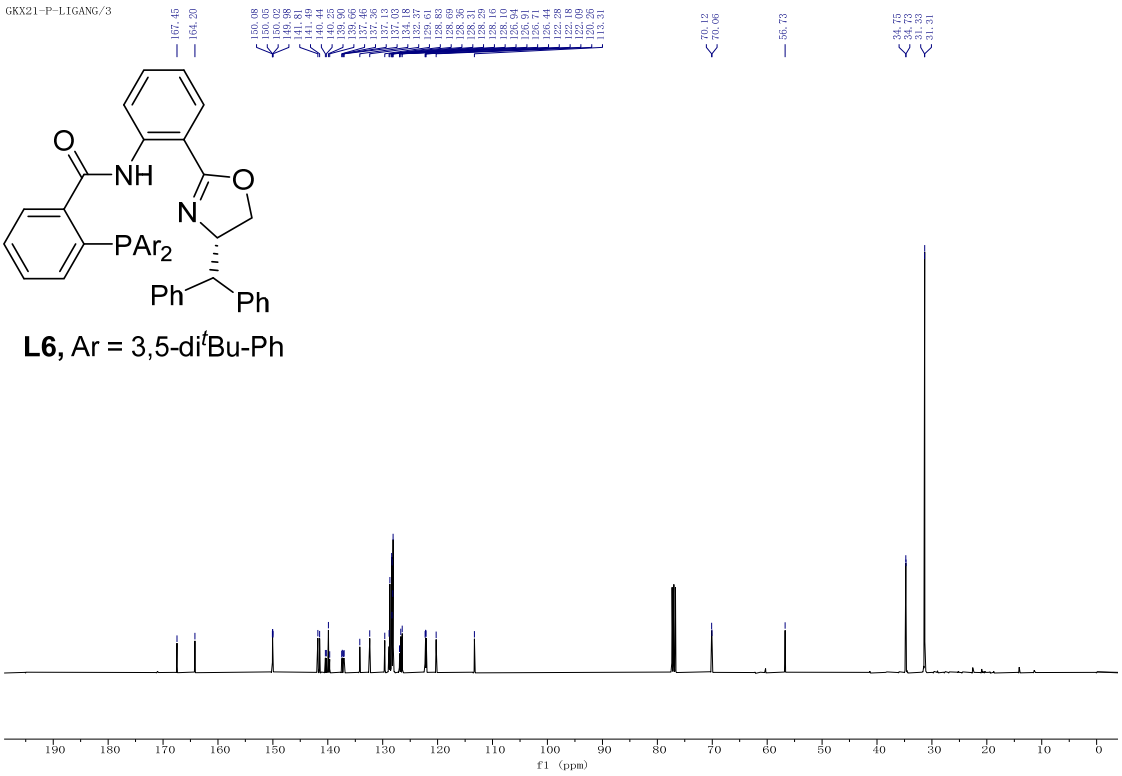
L6, Ar = 3,5-di^{t}Bu-Ph

GKX21-P-LIGANG/2

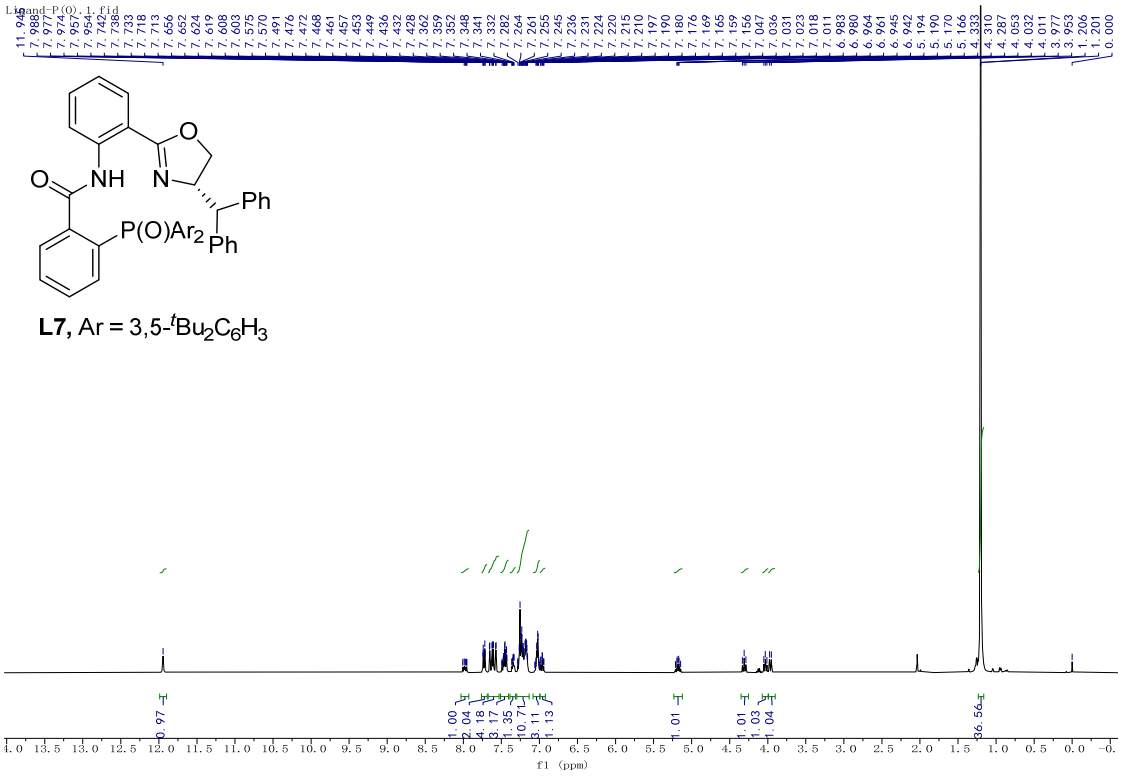


L6, Ar = 3,5-di^{t}Bu-Ph



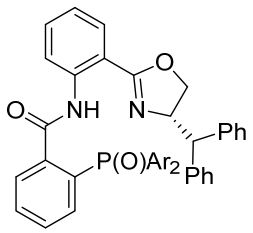


L6, Ar = 3,5-di^{t}Bu-Ph



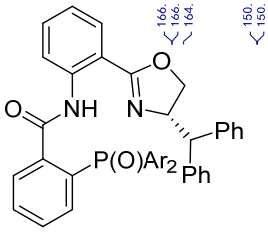
L7, Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$

Ligand-P(O).2.fid

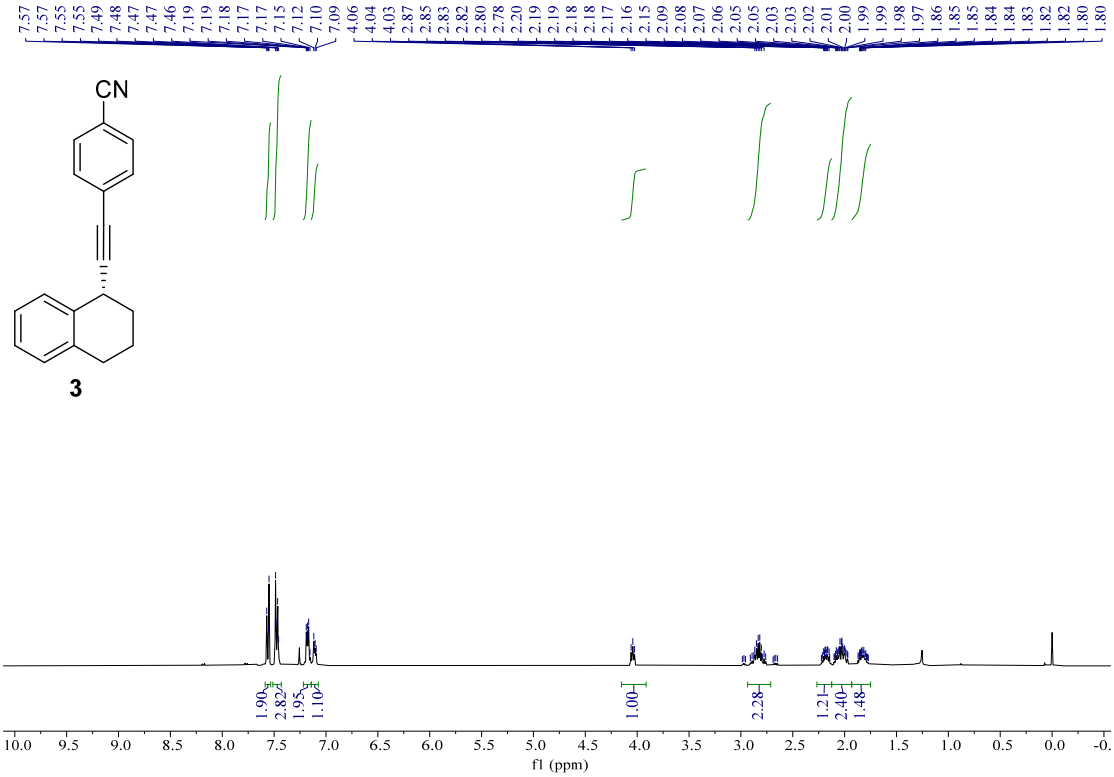


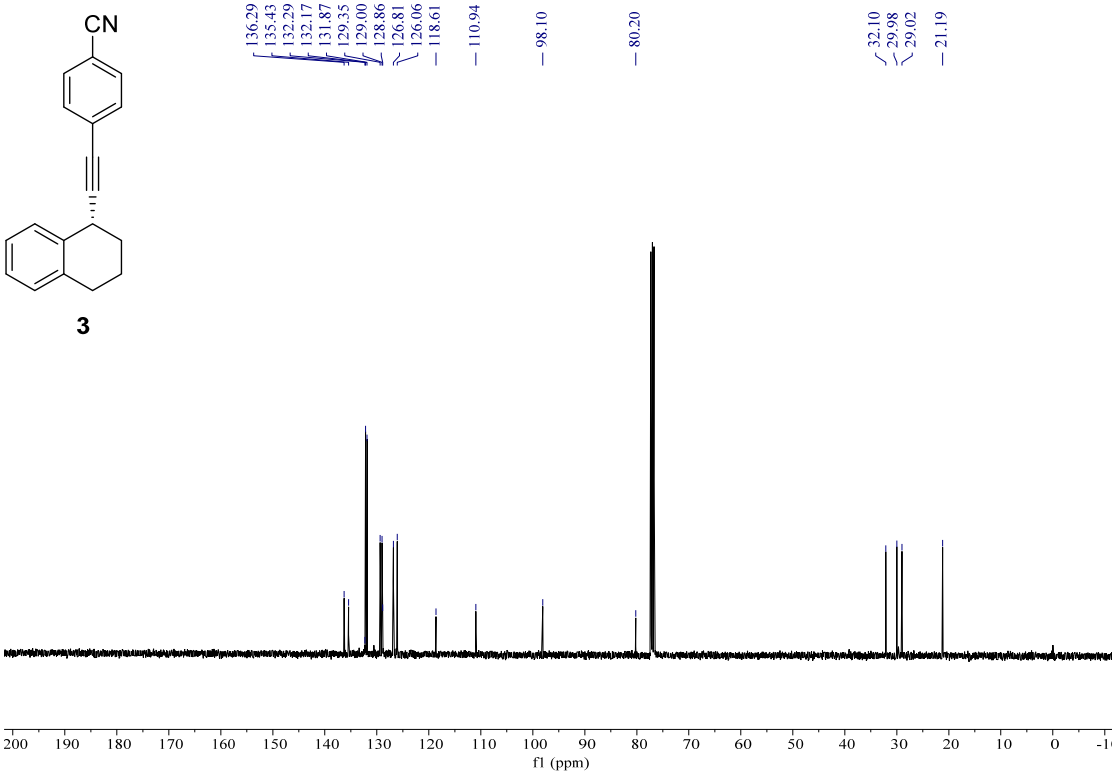
L7, Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$

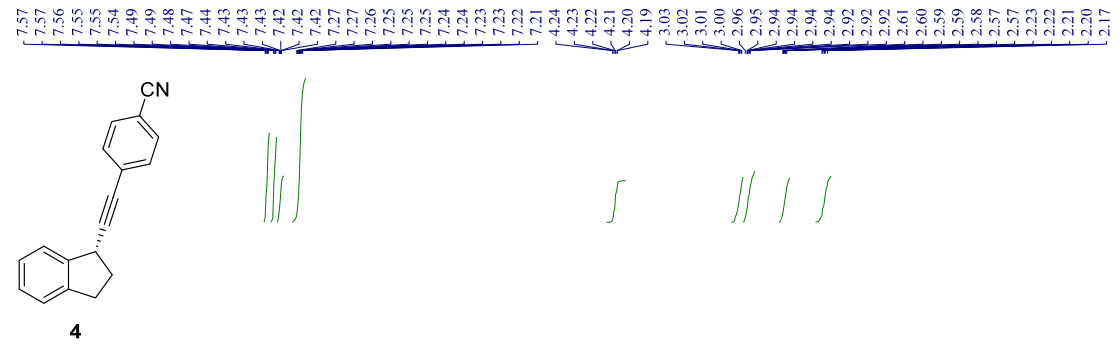
Ligand-P(O).3.fid



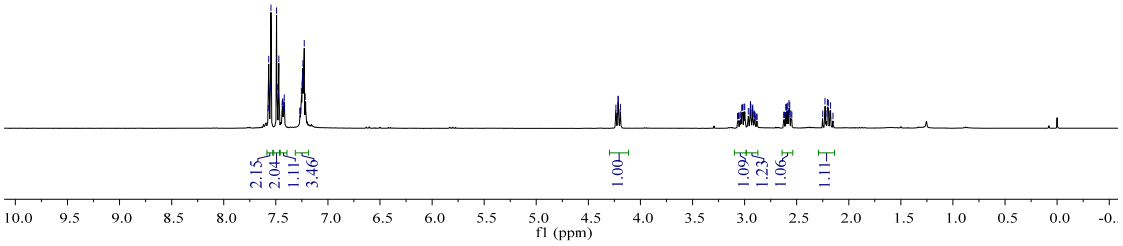
L7, Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$

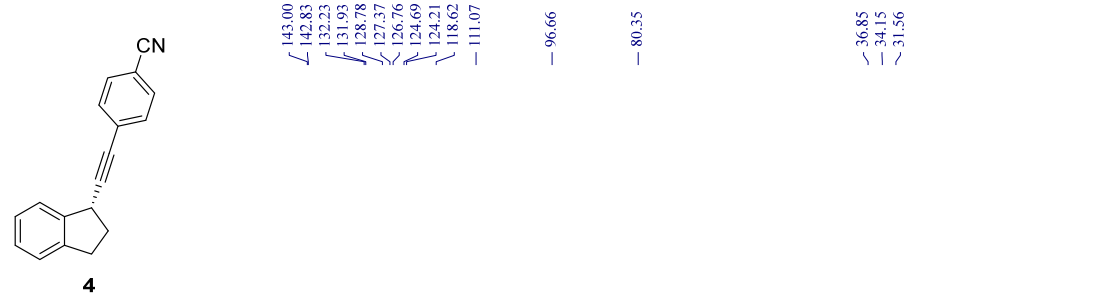

CN
3
7.57 7.57 7.55 7.55 7.49 7.48 7.47 7.47 7.46 7.19 7.19 7.18 7.17 7.17 7.15 7.12 7.10 7.09 4.06 4.04 4.03 2.87 2.85 2.83 2.82 2.80 2.78 2.20 2.19 2.19 2.18 2.18 2.17 2.16 2.15 2.09 2.08 2.07 2.06 2.05 2.05 2.03 2.03 2.02 2.01 2.00 1.99 1.99 1.98 1.97 1.86 1.85 1.85 1.84 1.84 1.83 1.82 1.82 1.80 1.80
1.90 2.82 1.95 1.10 1.00 2.28 1.21 2.40 1.48
10.0 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
f1 (ppm)


CN
3
136.29 135.43 132.29 132.17 131.87 129.35 129.00 128.86 126.81 126.06 118.61 110.94 98.10 80.20 32.10 29.98 29.02 21.19
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

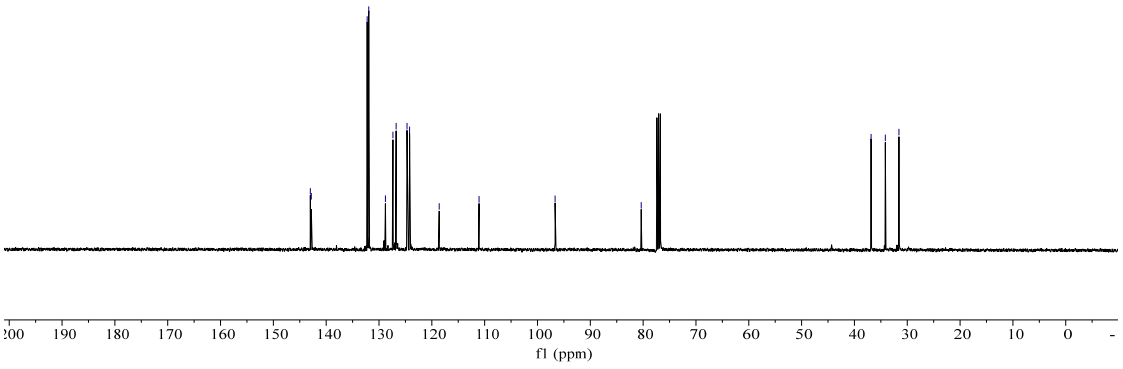


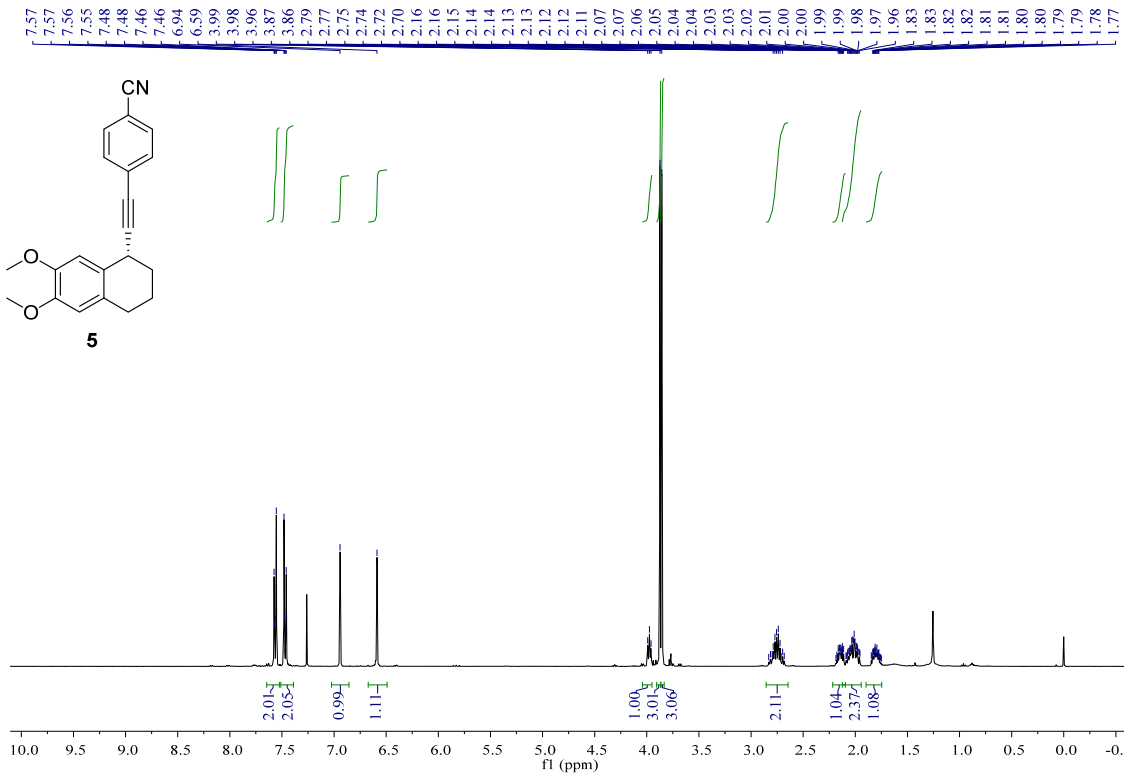
4

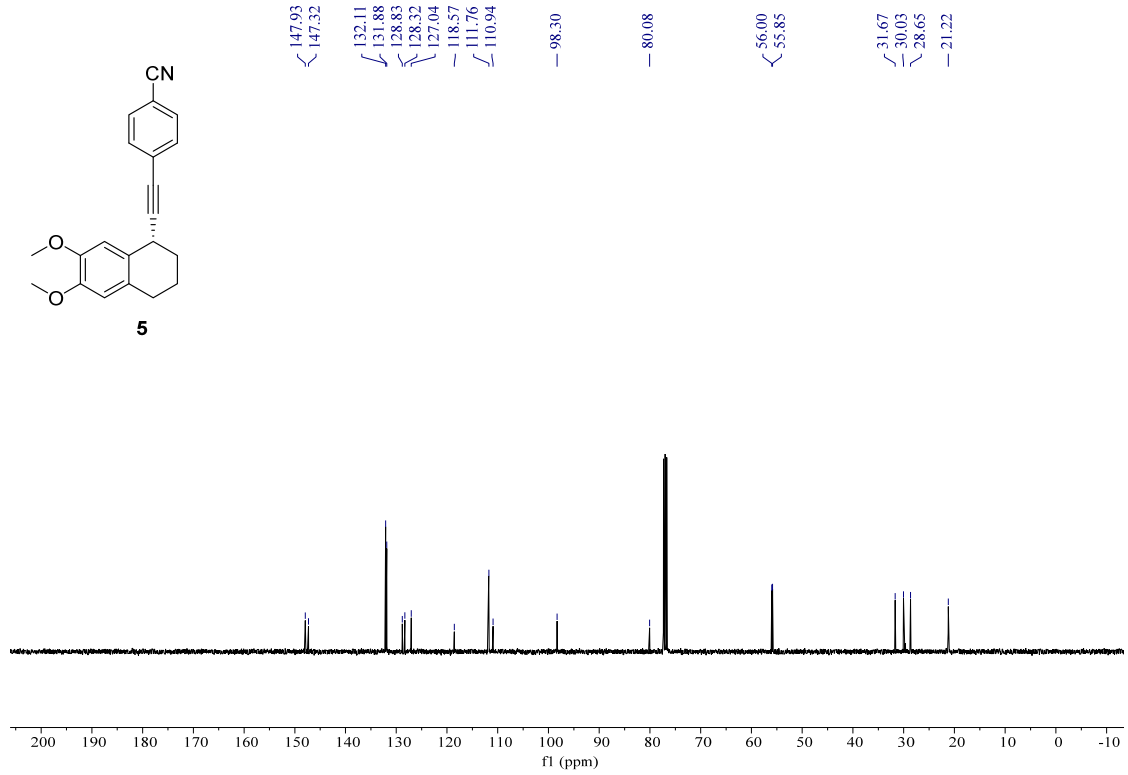


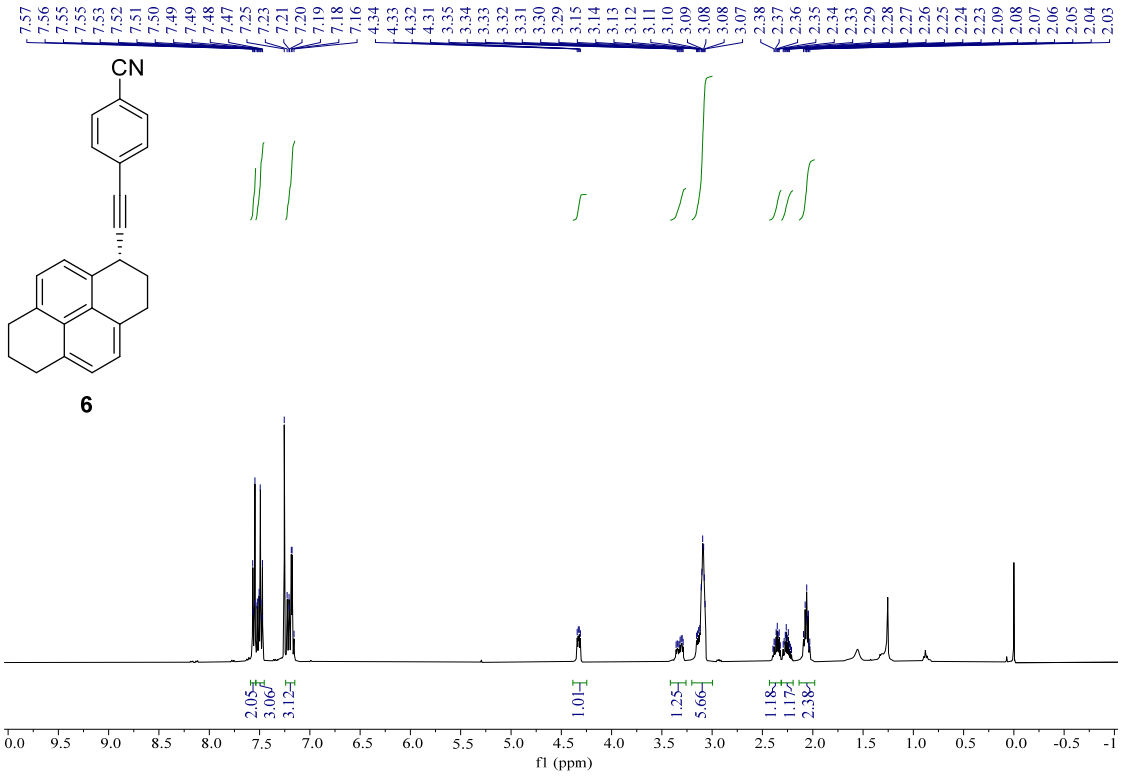


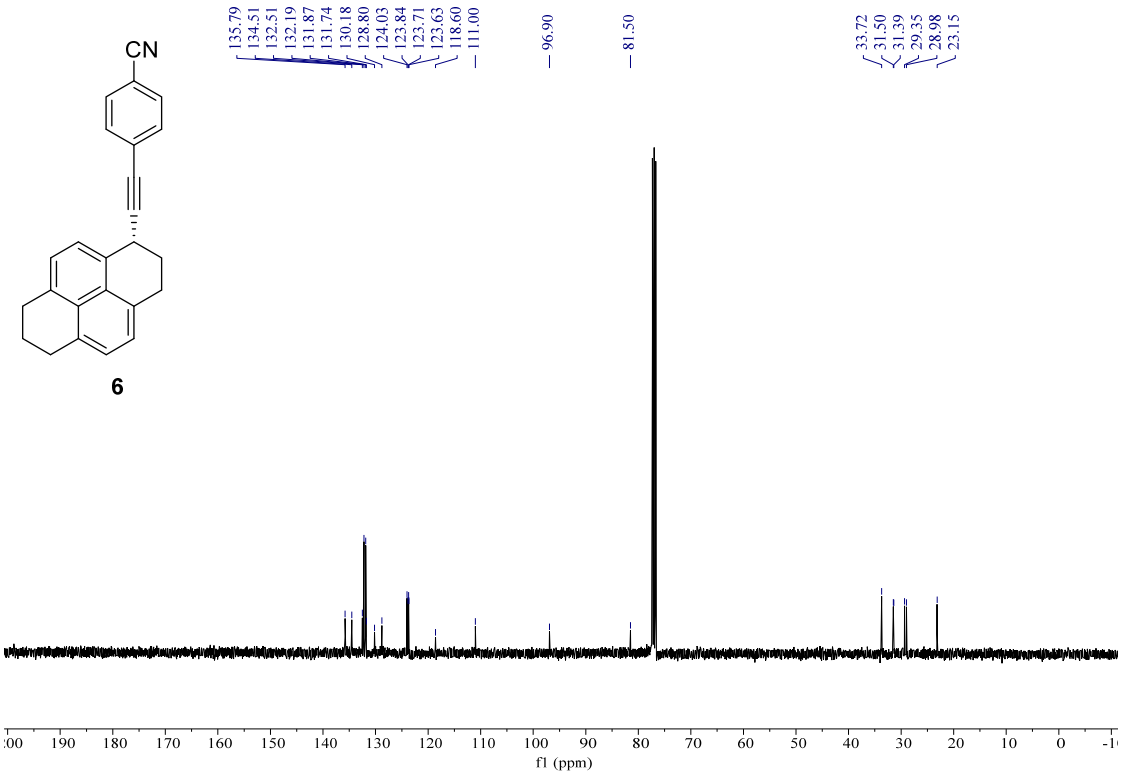
4

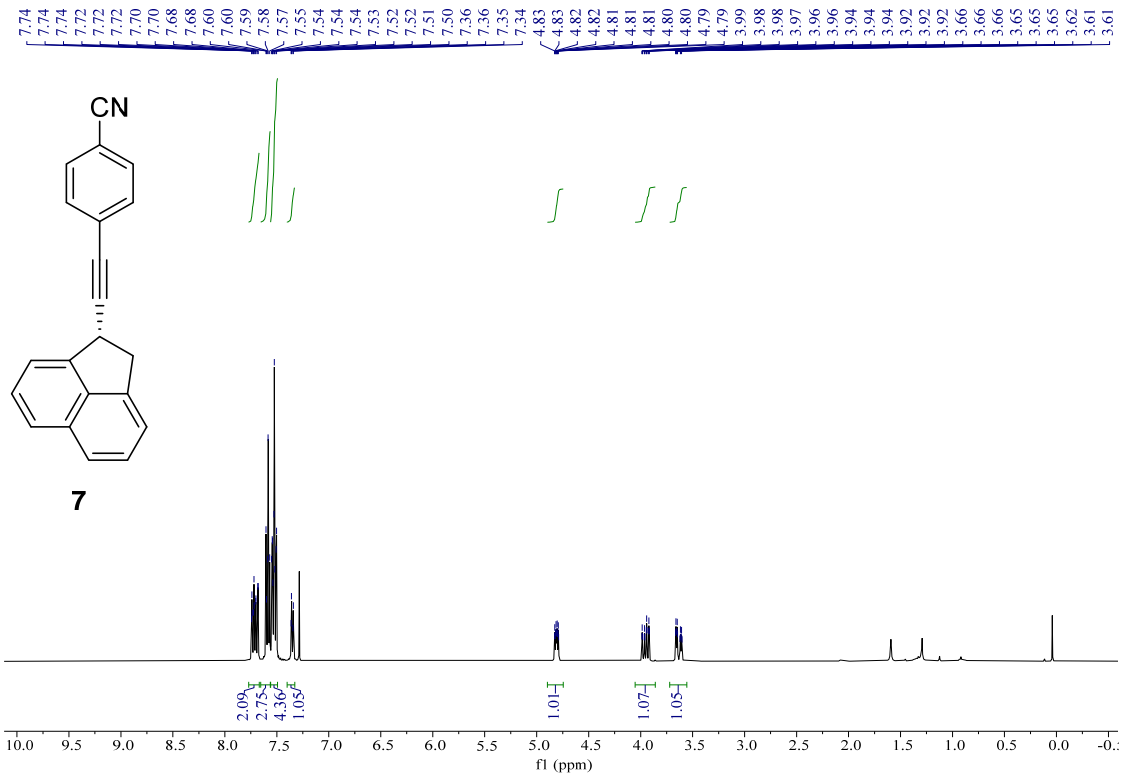


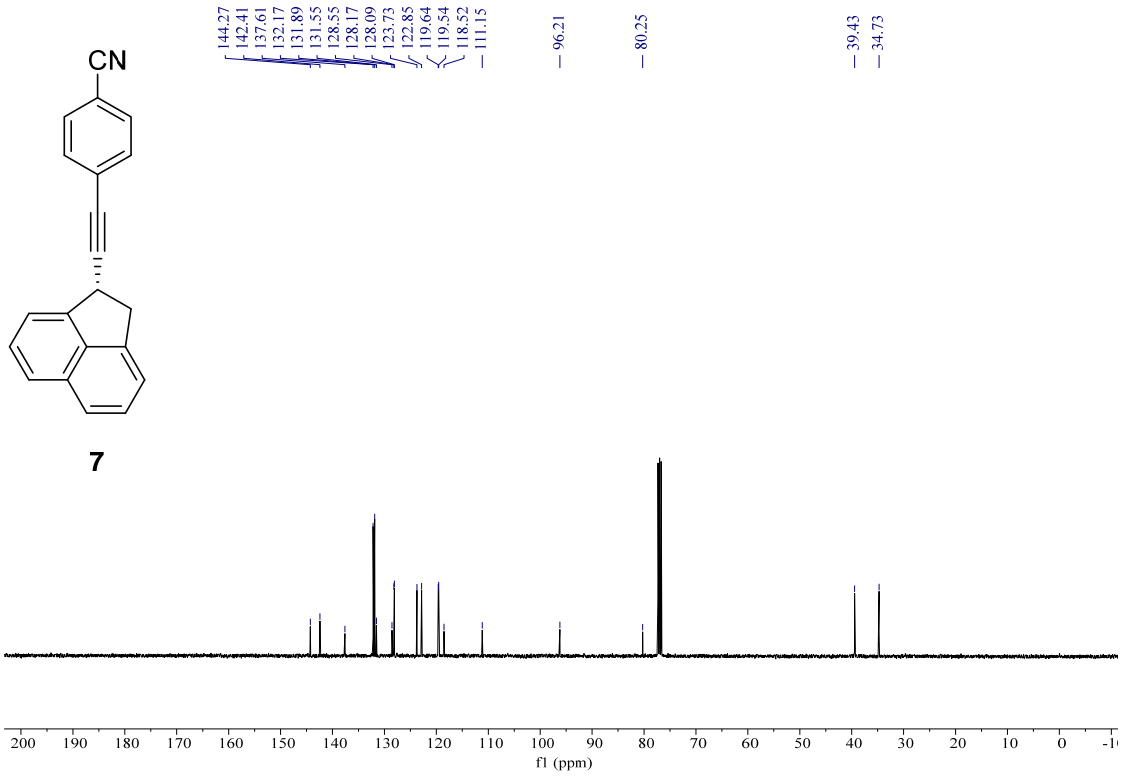

CN
O
O
5
fl (ppm)

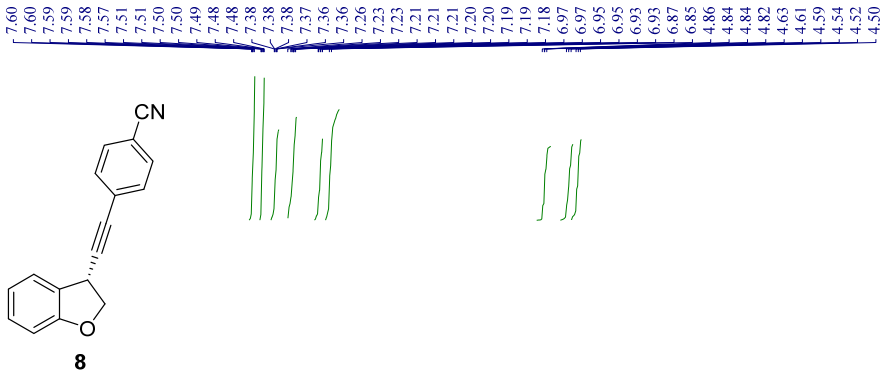

CN
O
O
5
fl (ppm)


CN
6
fl (ppm)


CN
6
fl (ppm)


CN
7
fl (ppm)


CN
7
fl (ppm)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7.60
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7.59
7.58
7.57
7.51
7.51
7.50
7.50
7.49
7.48
7.48
7.38
7.38
7.38
7.37
7.36
7.36
7.26
7.23
7.23
7.21
7.21
7.21
7.20
7.20
7.19
7.19
7.18
6.97
6.97
6.95
6.95
6.93
6.93
6.87
6.85
4.86
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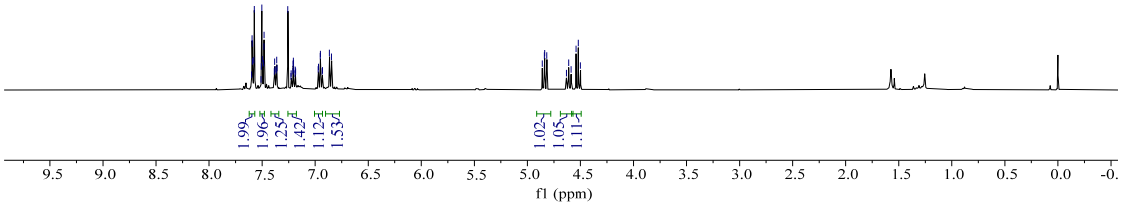
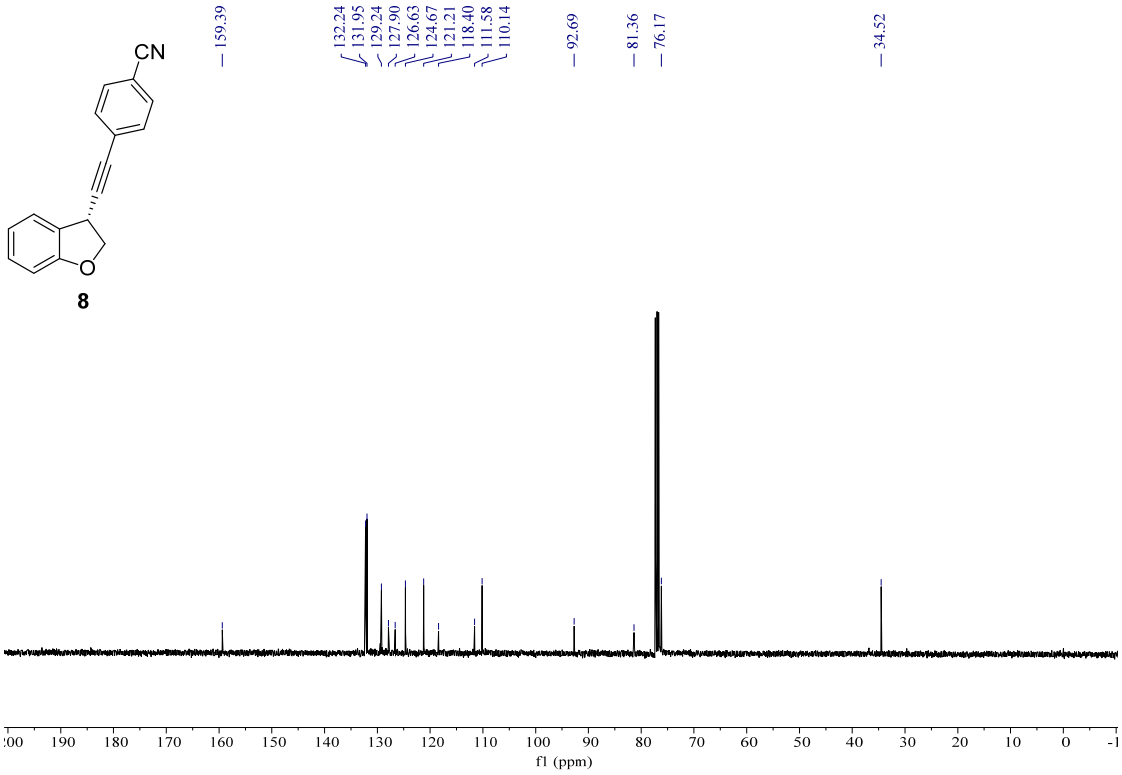
4.84
4.82
4.63
4.61
4.59
4.54
4.52
4.50
CN
O

8


1.90
1.96
1.25
1.42
1.12
1.53
1.02
1.05
1.11
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.
f1 (ppm)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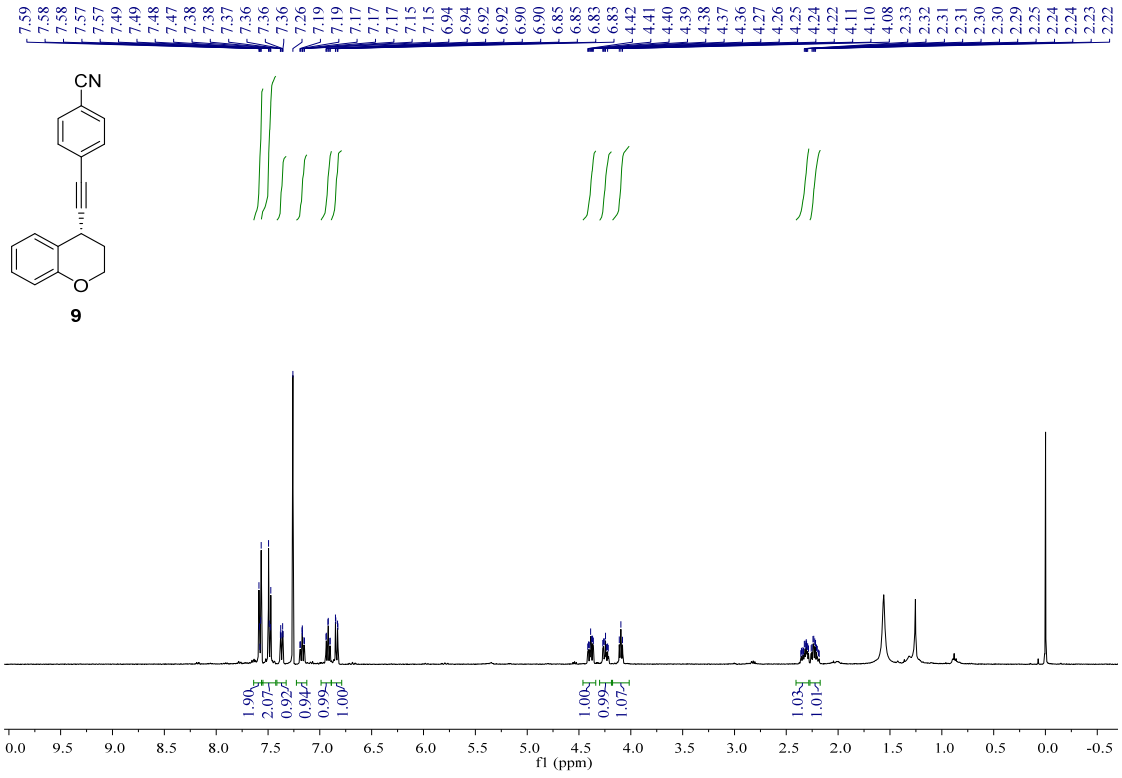
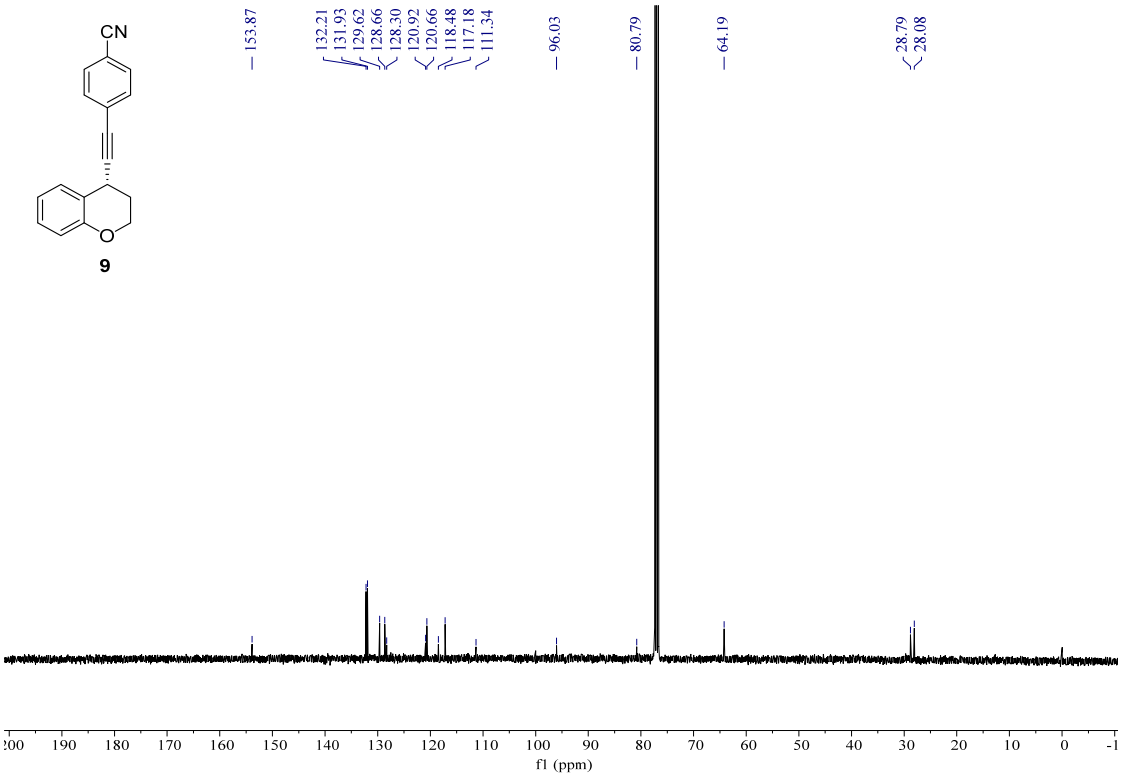
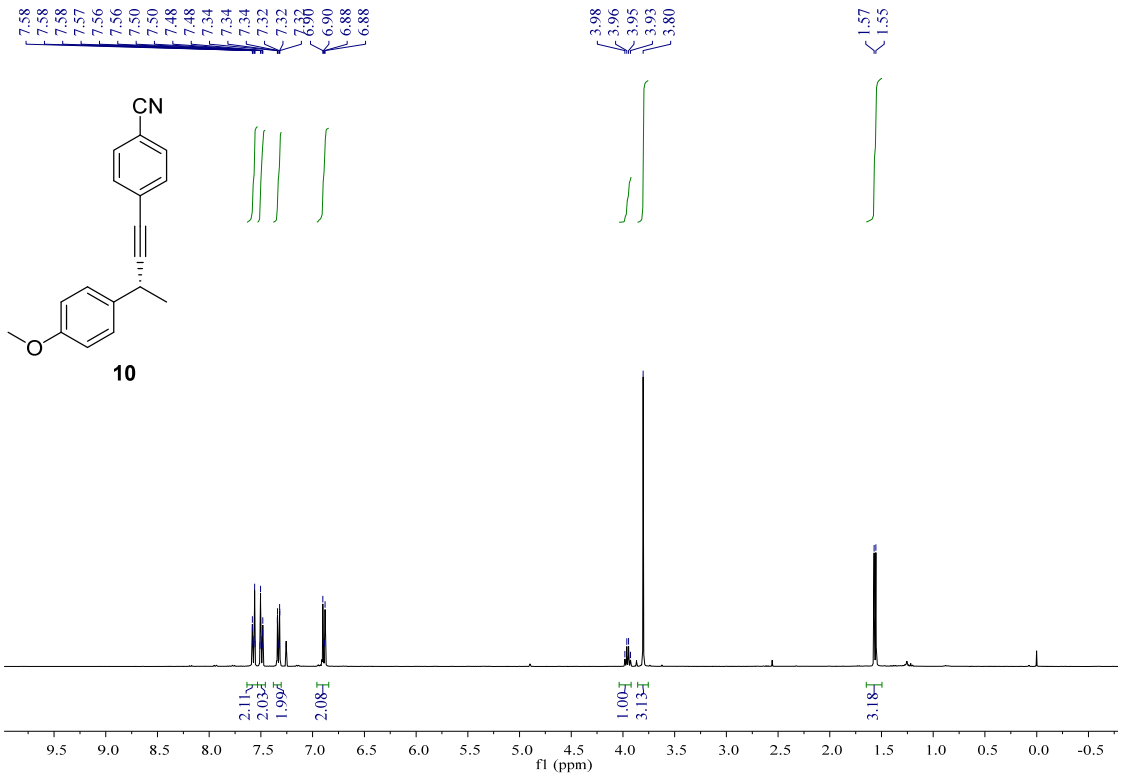
131.95
129.24
127.90
126.63
124.67
121.21
118.40
111.58
110.14
92.69
81.36
76.17
34.52
CN
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

8


CN
O
9
f1 (ppm)


CN
O
9
f1 (ppm)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7.50
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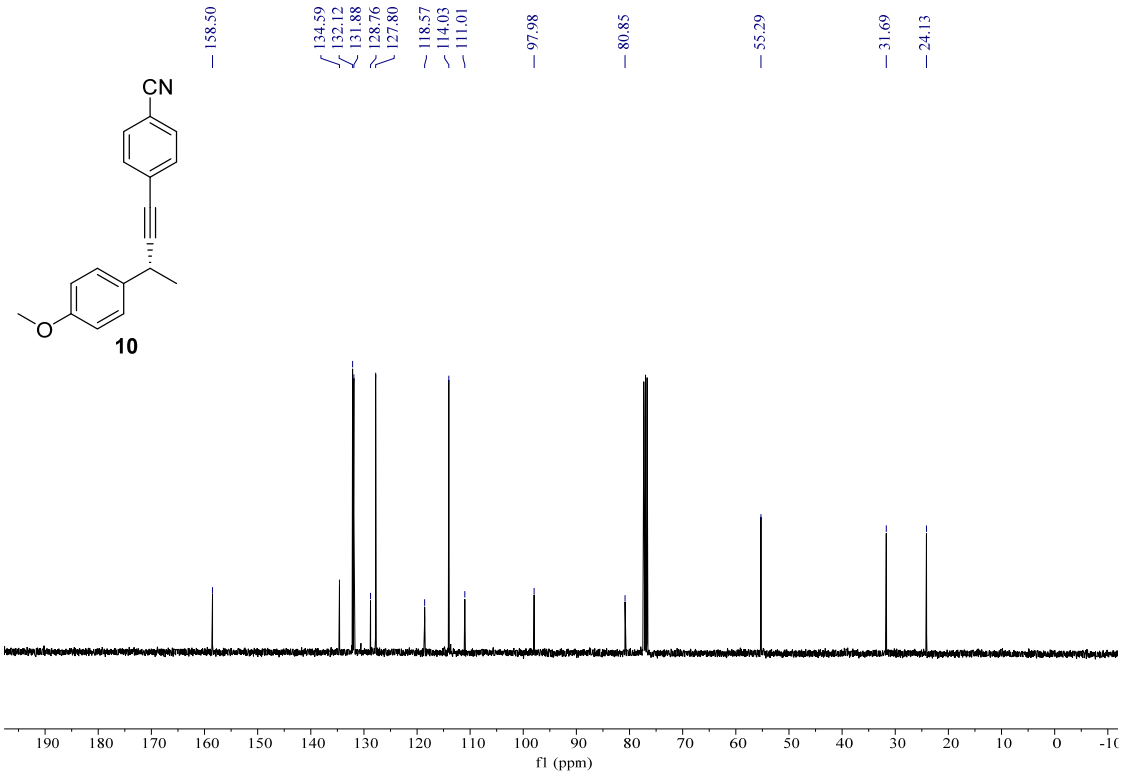
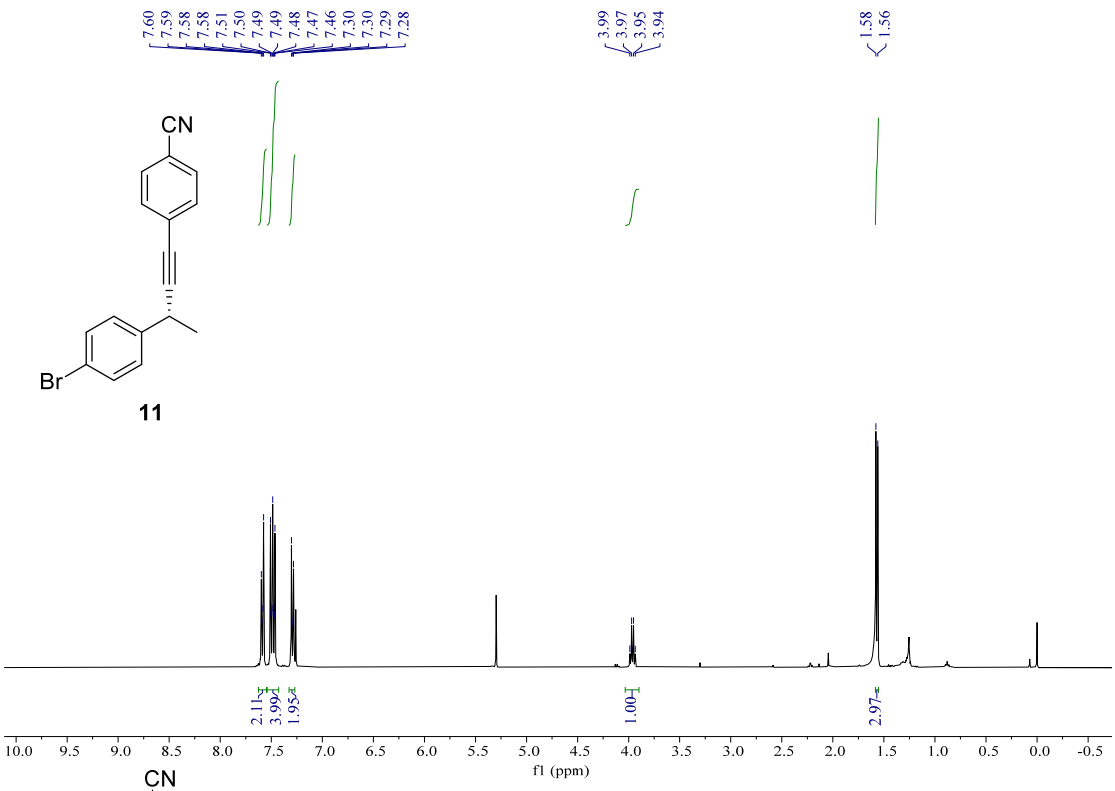
7.34
7.34
7.32
7.32
6.90
6.88
6.88
3.98
3.96
3.95
3.93
3.80
1.57
1.55
CN
O
10
2.11
2.03
1.99
2.08
1.00
3.13
3.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.50
134.59
132.12
131.88
128.76
127.80
118.57
114.03
111.01
97.98
80.85
55.29
31.69
24.13
CN
O
10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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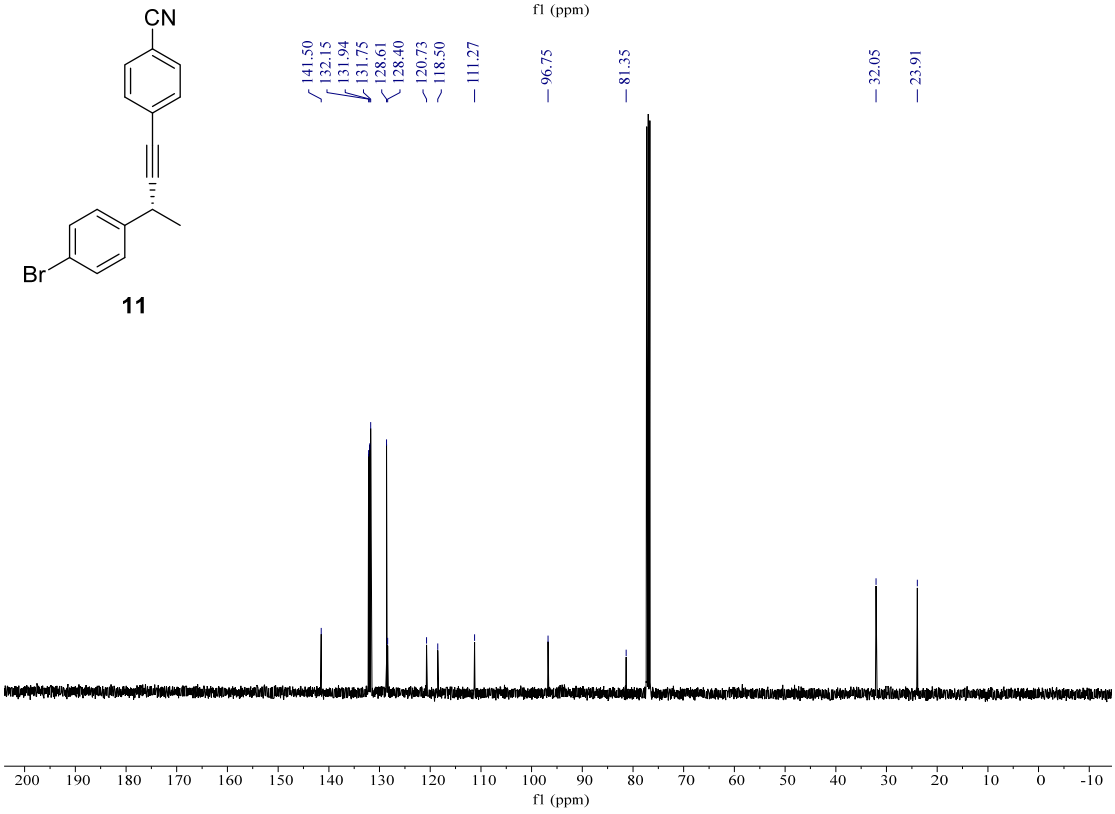
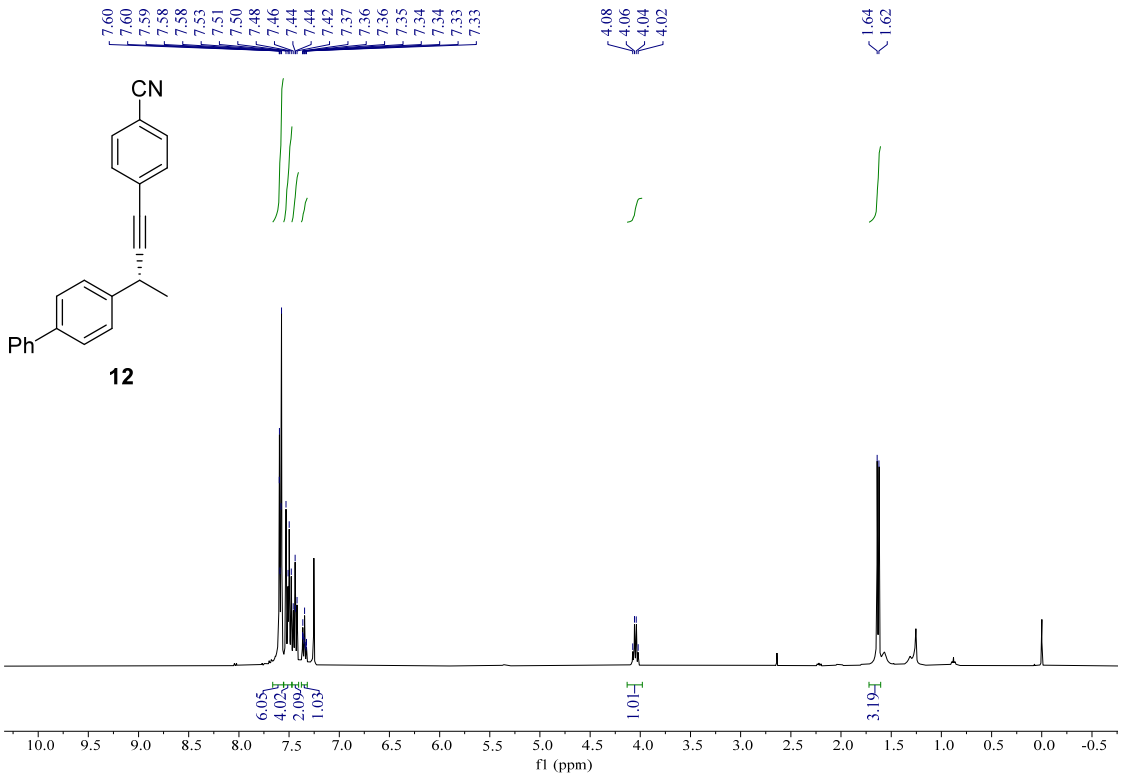
7.47
7.46
7.30
7.30
7.29
7.28
3.99
3.97
3.95
3.94
1.58
1.56
CN
Br
11
2.11
3.99
1.95
1.00
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


CN
Br
11
141.50
132.15
131.94
131.75
128.61
128.40
120.73
118.50
111.27
96.75
81.35
32.05
23.91
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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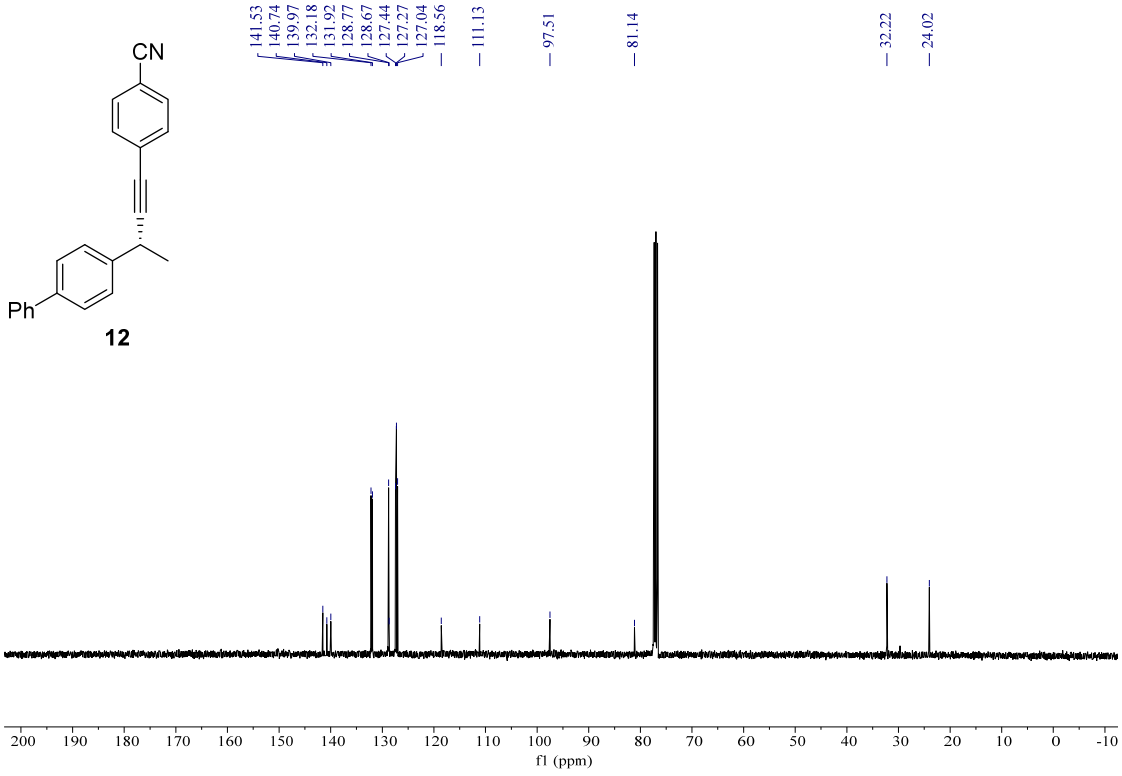
7.42
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.33
4.08
4.06
4.04
4.02
1.64
1.62
CN
Ph
12
6.05
4.02
2.09
1.03
1.01
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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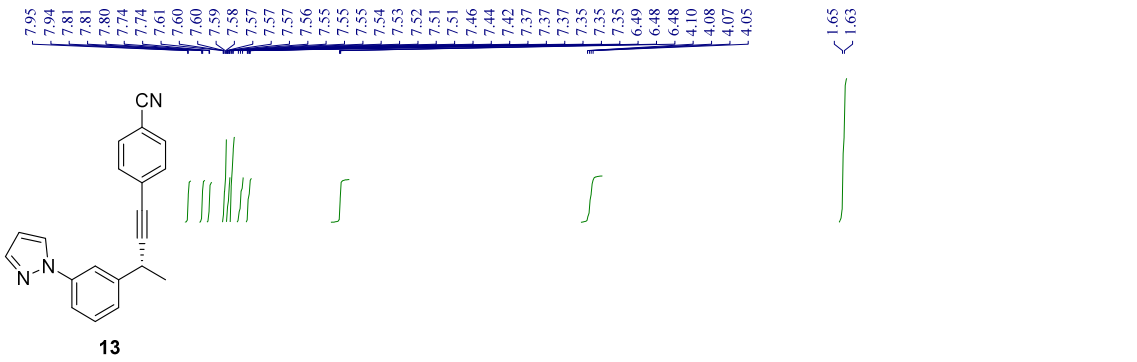
131.92
128.77
128.67
127.44
127.27
127.04
118.56
111.13
97.51
81.14
32.22
24.02
CN
Ph
12
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.74
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7.60
7.59
7.58
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7.57
7.57
7.56
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7.42
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7.35
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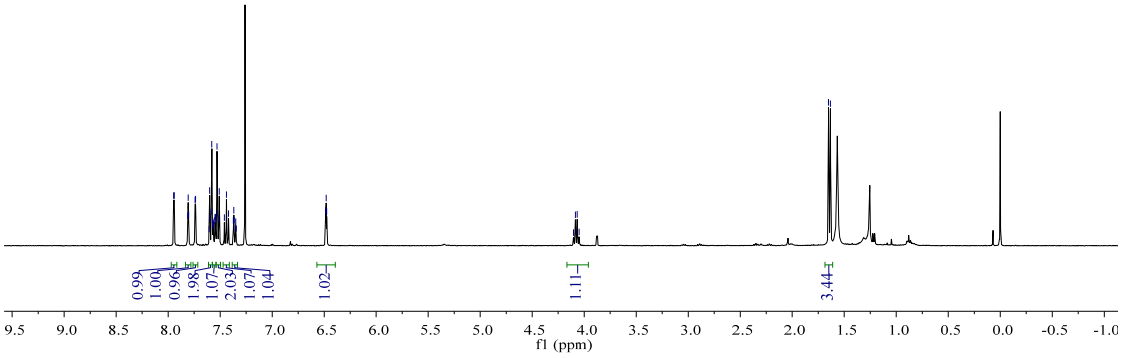
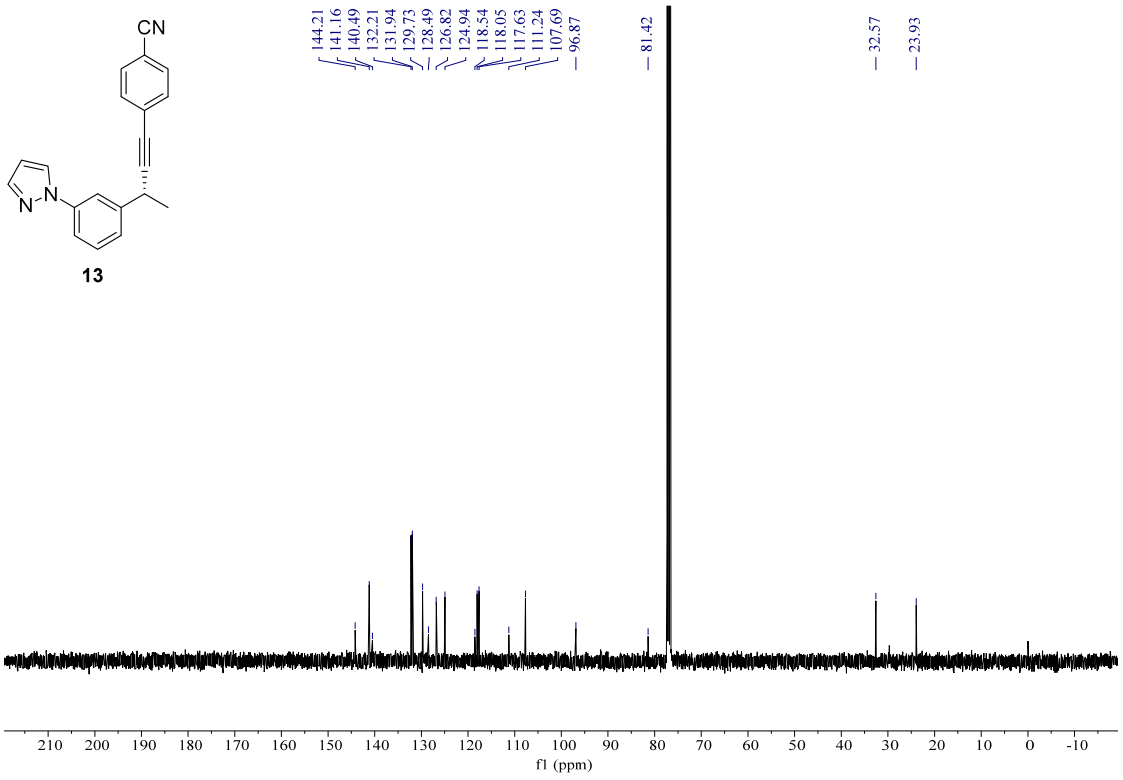
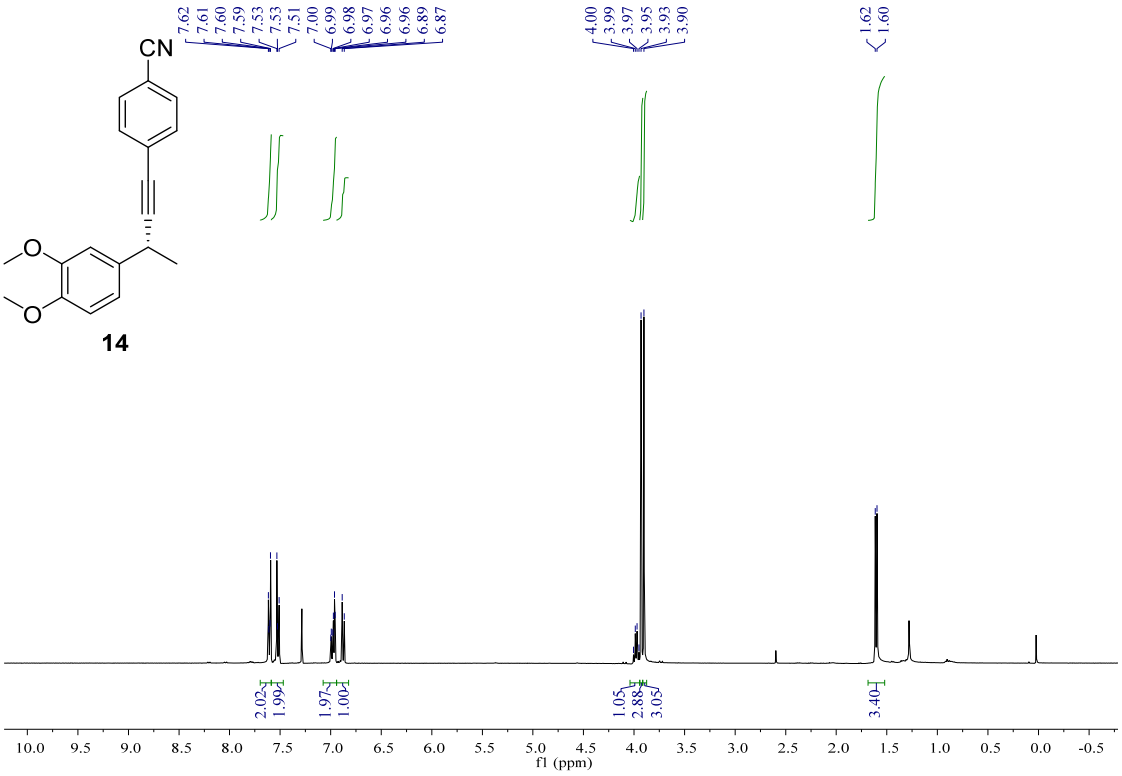
6.48
4.10
4.08
4.07
4.05
1.65
1.63
CN
N
N

13


0.99
1.00
0.96
1.98
1.07
2.03
1.07
1.04
1.02
1.11
3.44
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 -1.0
f1 (ppm)


144.21
141.16
140.49
132.21
131.94
129.73
128.49
126.82
124.94
118.54
118.05
117.63
111.24
107.69
96.87
81.42
32.57
23.93
CN
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

13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O
O
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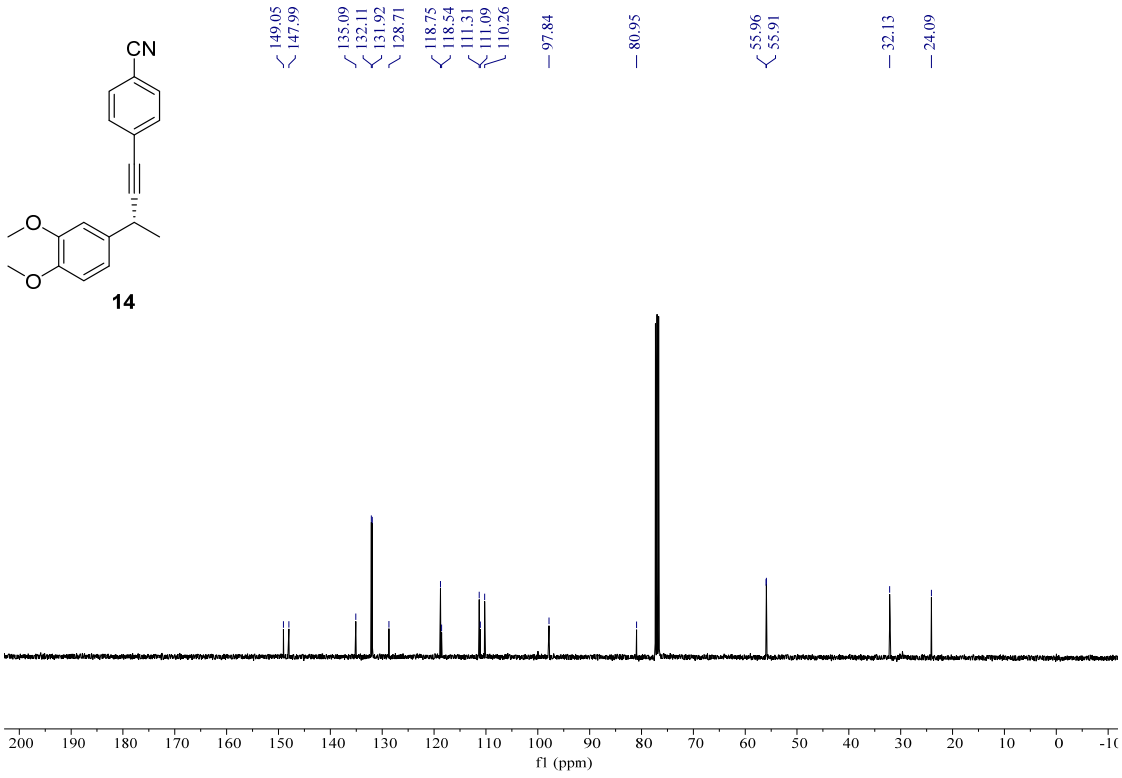
7.53
7.51
7.00
6.99
6.98
6.97
6.96
6.96
6.89
6.87
4.00
3.99
3.97
3.95
3.93
3.90
1.62
1.60
2.02
1.99
1.97
1.00
1.05
2.88
3.05
3.40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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O
O
14
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135.09
132.11
131.92
128.71
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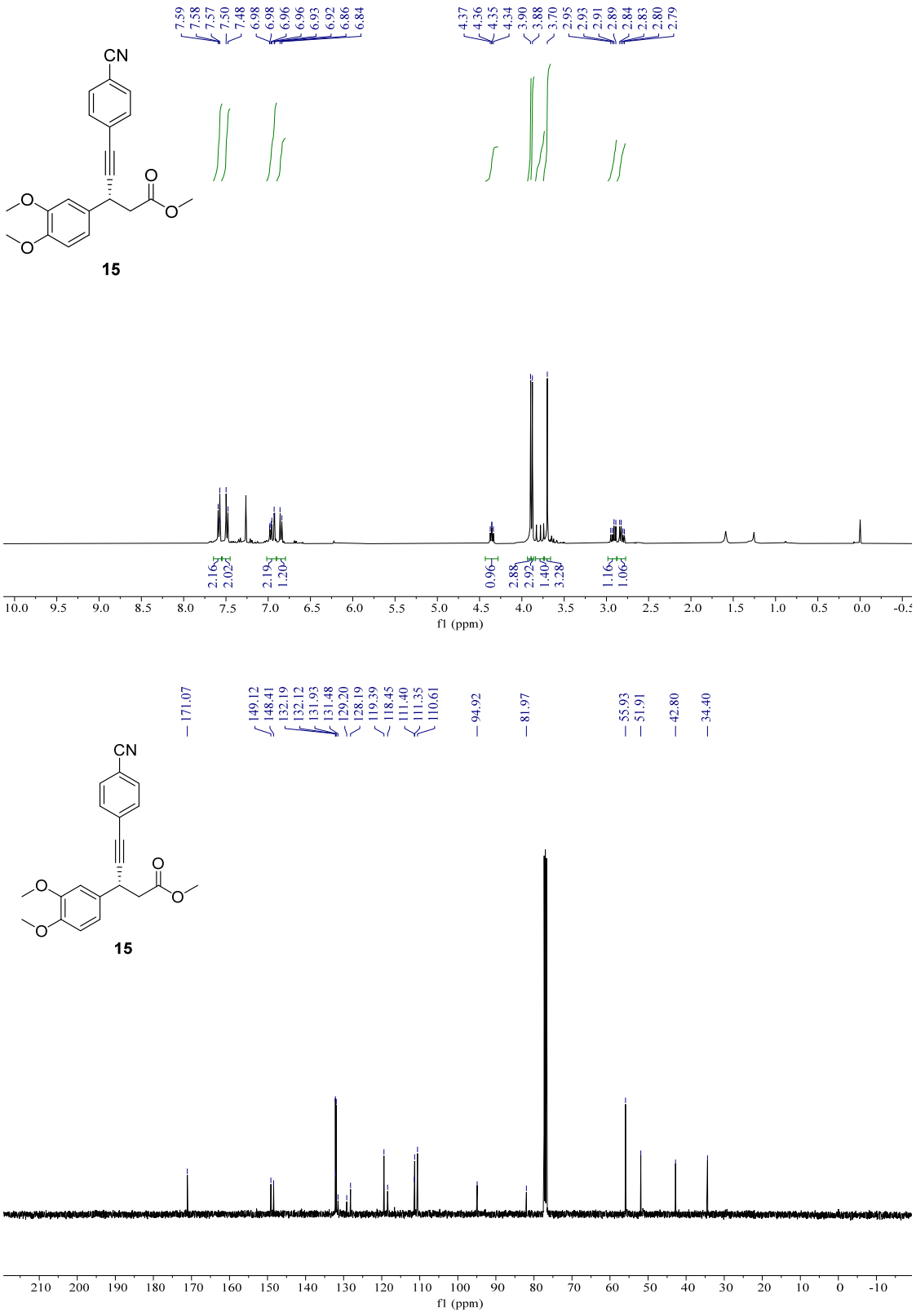
118.54
111.31
111.09
110.26
97.84
80.95
55.96
55.91
32.13
24.09
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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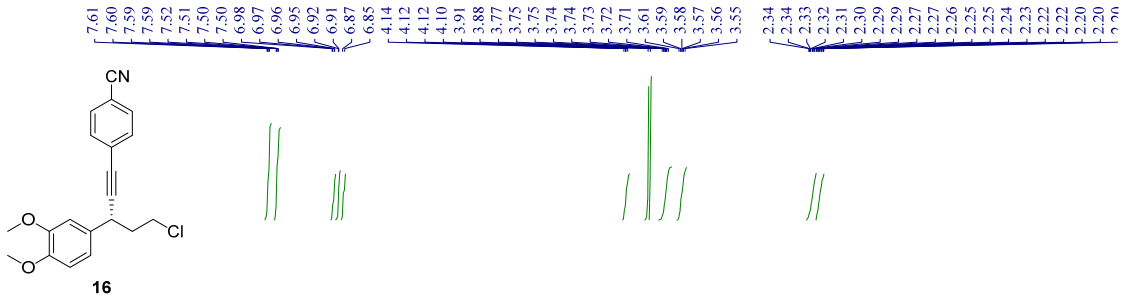
6.96
6.96
6.93
6.92
6.86
6.84
4.37
4.36
4.35
4.34
3.90
3.88
3.70
2.95
2.93
2.91
2.89
2.84
2.83
2.80
2.79
CN
O
O
O
O
15
2.16
2.02
2.19
1.20
0.96
2.88
2.92
1.40
3.28
1.16
1.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
171.07
149.12
148.41
132.19
132.12
131.93
131.48
129.20
128.19
119.39
118.45
111.40
111.35
110.61
94.92
81.97
55.93
51.91
42.80
34.40
CN
O
O
O
O
15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CN
O
O
Cl

16

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7.60
7.59
7.59
7.52
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7.50
7.50
6.98
6.97
6.96
6.95
6.92
6.91
6.87
6.85
4.14
4.12
4.12
4.10
3.91
3.88
3.77
3.75
3.75
3.74
3.74
3.73
3.72
3.71
3.61
3.59
3.58
3.57
3.56
3.55
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2.34
2.33
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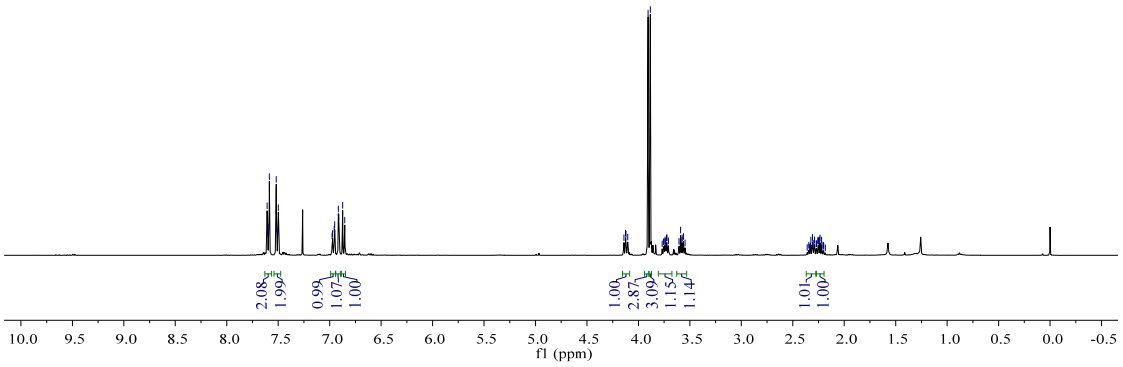
2.24
2.23
2.22
2.22
2.20
2.20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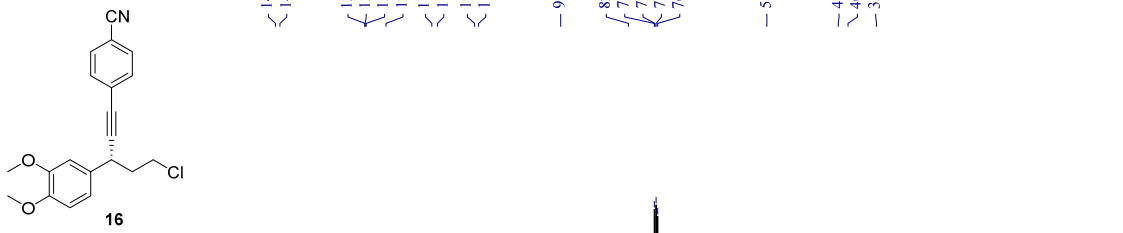
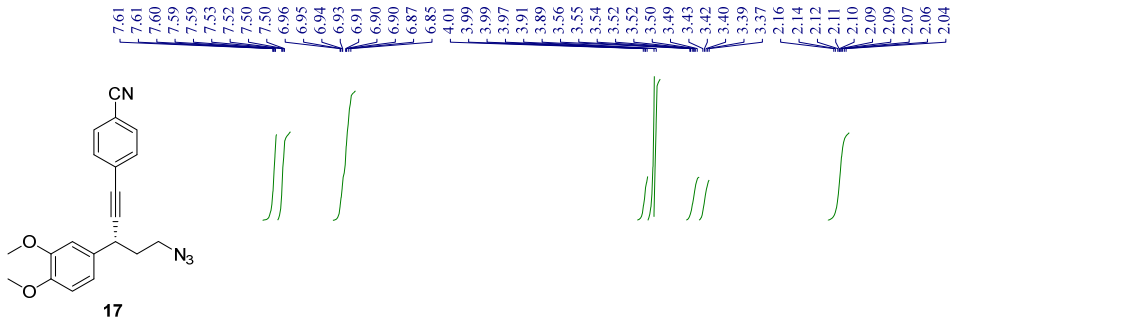
0.99
1.07
1.00
1.00
2.87
3.09
1.15
1.14
1.01
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


CN
O
O
Cl

16

149.20
148.35
132.22
132.18
131.98
128.23
119.53
118.44
111.41
110.66
95.10
82.25
77.32
77.20
77.00
76.68
55.96
42.44
40.58
35.18
:00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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6.95
6.94
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6.91
6.90
6.90
6.87
6.85
4.01
3.99
3.99
3.97
3.91
3.89
3.56
3.55
3.54
3.52
3.52
3.50
3.49
3.43
3.42
3.40
3.39
3.37
2.16
2.14
2.12
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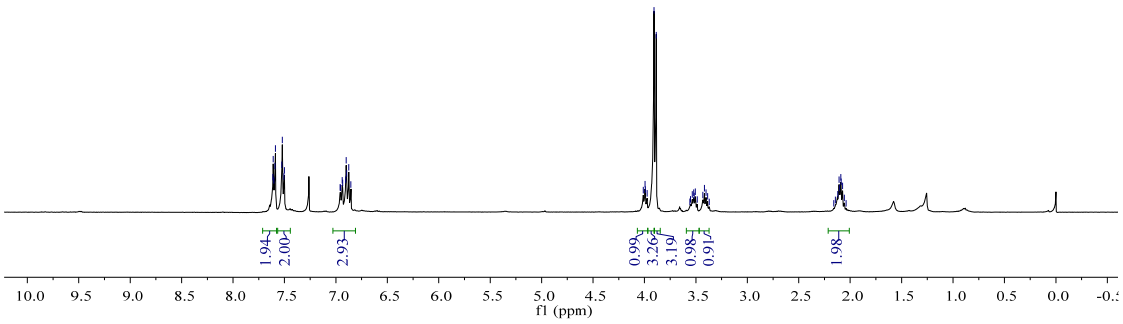
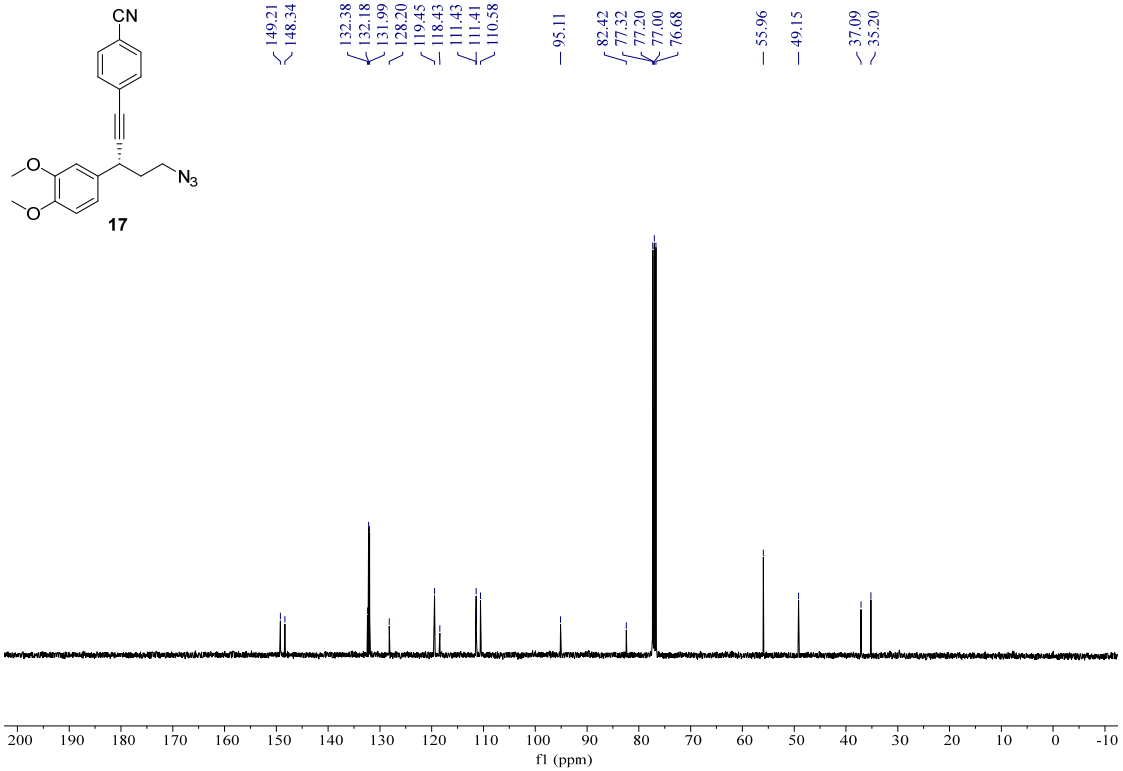
2.10
2.09
2.09
2.07
2.06
2.04
CN
O
O
N3
17


1.94
2.00
2.93
0.99
3.26
3.19
0.98
0.91
1.98
10.0 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
f1 (ppm)


CN
O
O
N3
17
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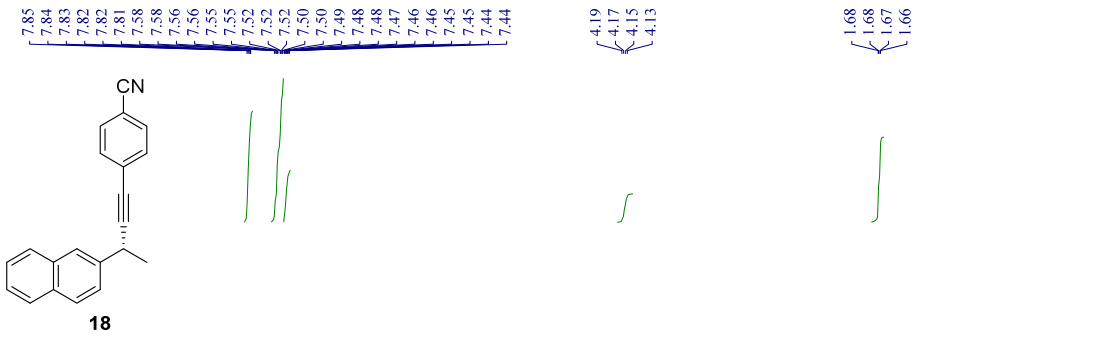
148.34
132.38
132.18
131.99
128.20
119.45
118.43
111.43
111.41
110.58
95.11
82.42
77.32
77.20
77.00
76.68
55.96
49.15
37.09
35.20
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.58
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7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.45
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7.44
4.19
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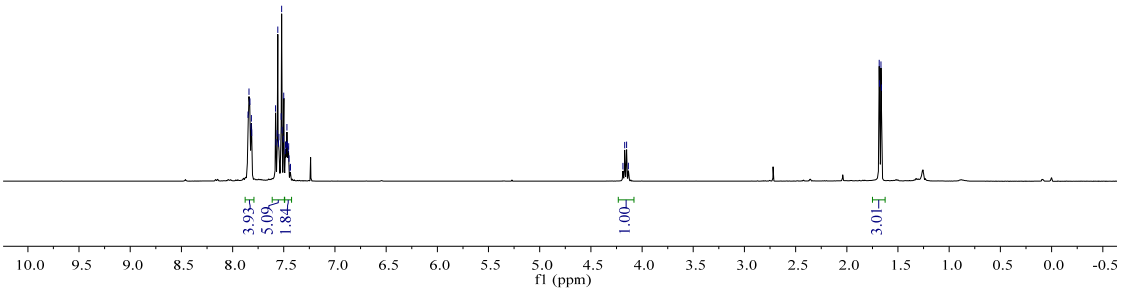
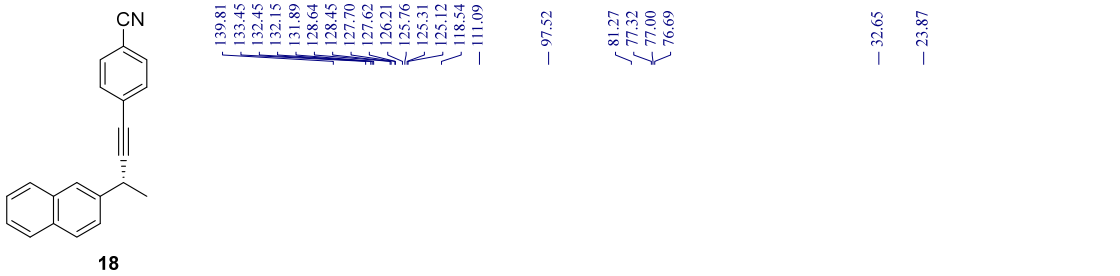
4.15
4.13
1.68
1.68
1.67
1.66
CN

18


3.93
5.09
1.84
1.00
3.01
10.0 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)


CN
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132.15
131.89
128.64
128.45
127.70
127.62
126.21
125.76
125.31
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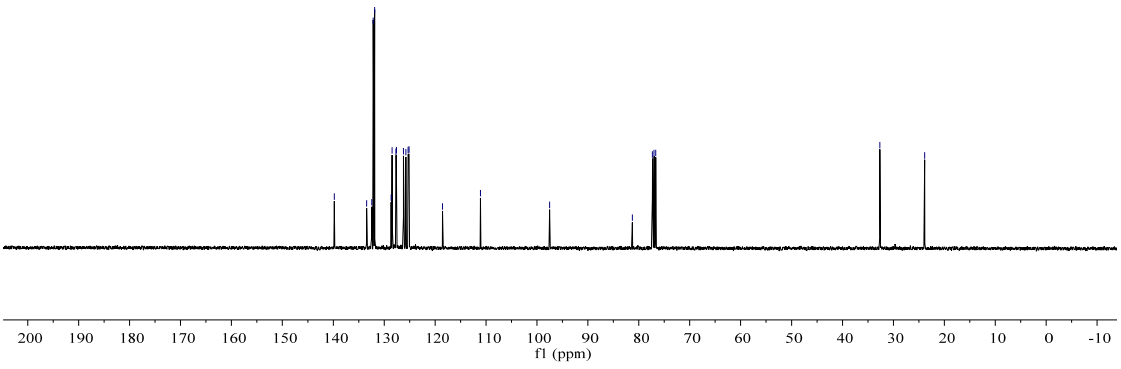
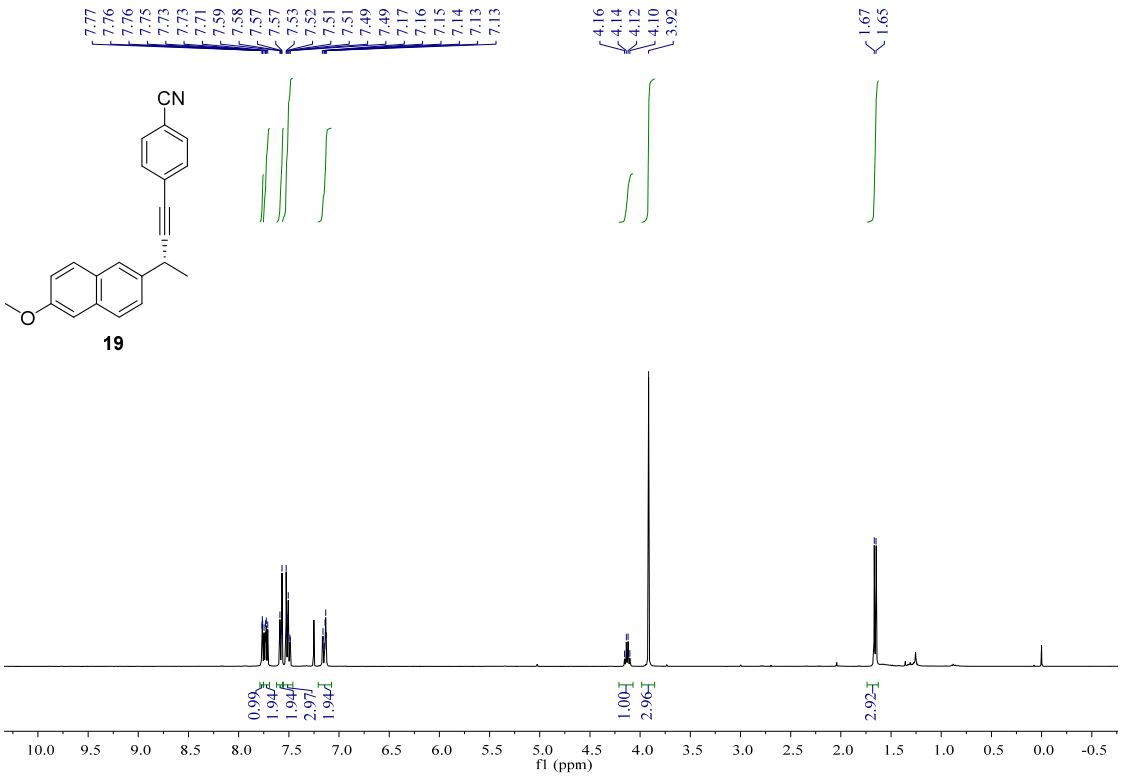
118.54
111.09
97.52
81.27
77.32
77.00
76.69
32.65
23.87

18


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.77
7.76
7.76
7.75
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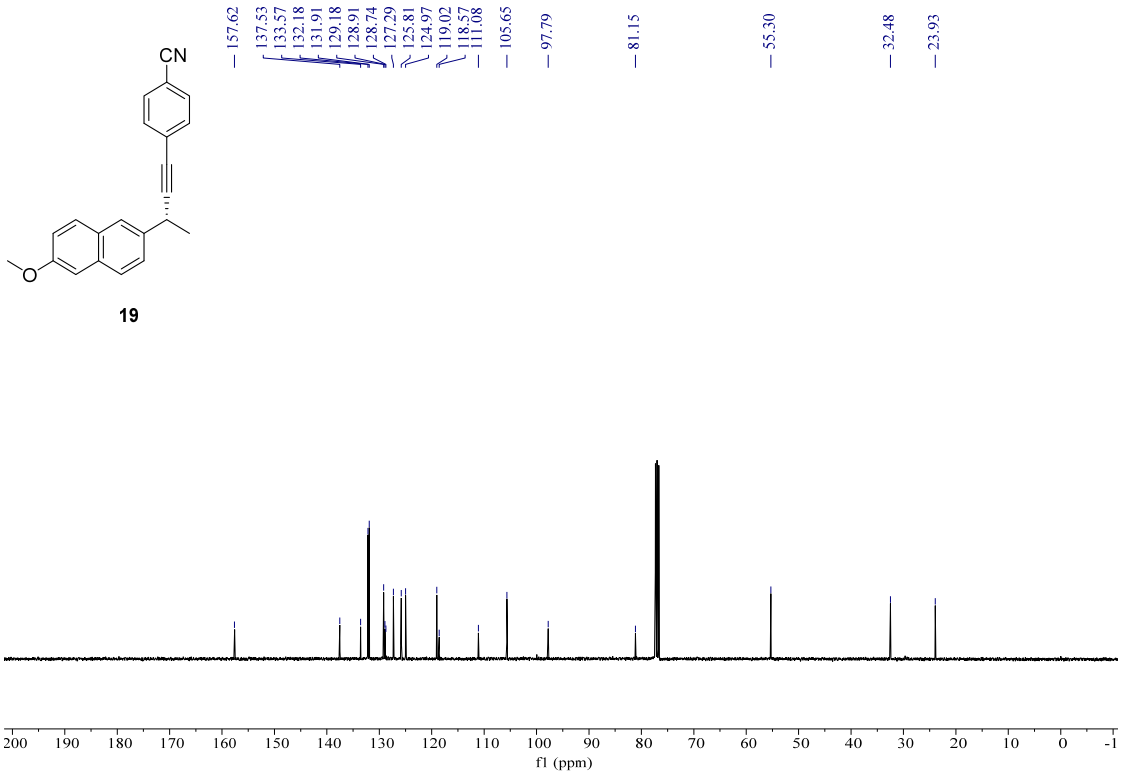
7.73
7.71
7.59
7.58
7.57
7.57
7.53
7.52
7.51
7.51
7.49
7.49
7.17
7.16
7.15
7.14
7.13
7.13
4.16
4.14
4.12
4.10
3.92
1.67
1.65
CN
O
0.99
1.94
1.94
2.97
1.94
1.00
2.96
2.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

19


157.62
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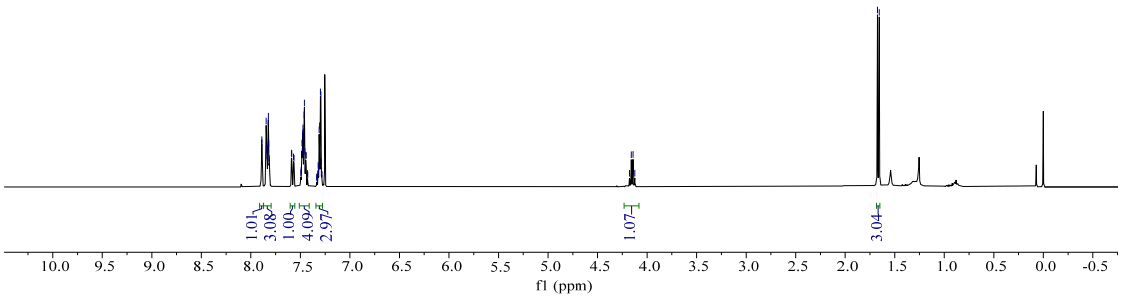
132.18
131.91
129.18
128.91
128.74
127.29
125.81
124.97
119.02
118.57
111.08
105.65
97.79
81.15
55.30
32.48
23.93
CN
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

19


Ph

20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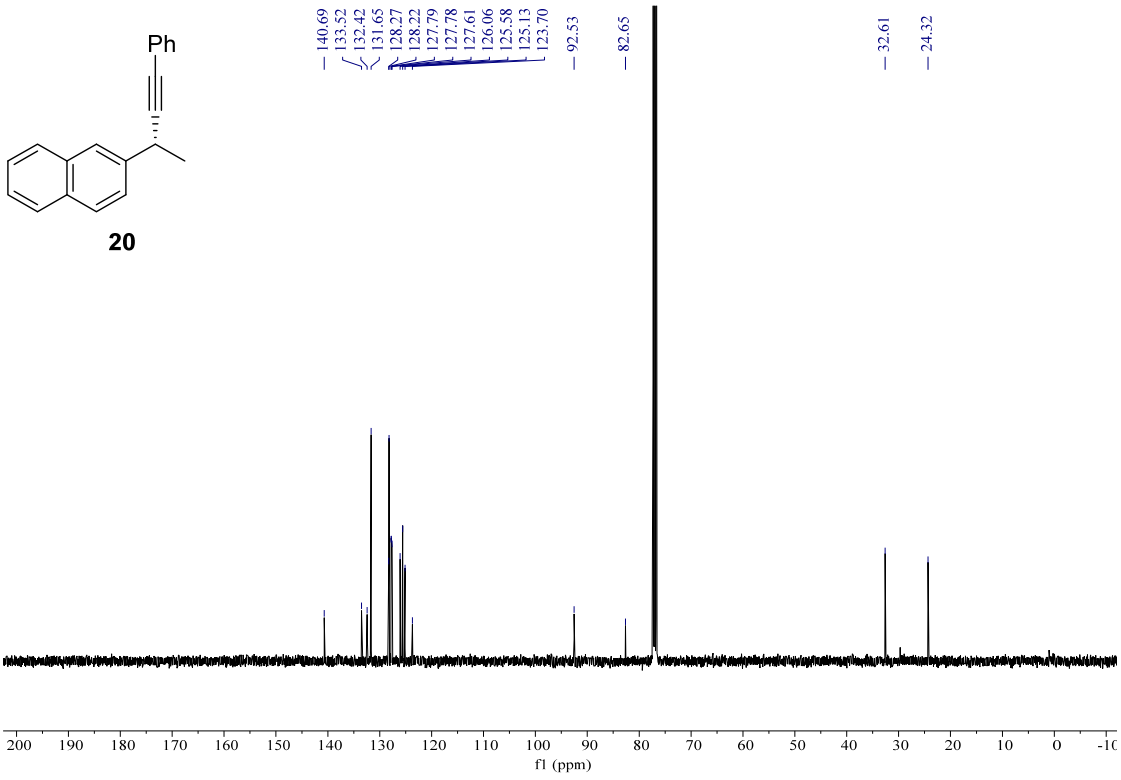
1.00
4.09
2.97
1.07
3.04
f1 (ppm)


Ph
140.69
133.52
132.42
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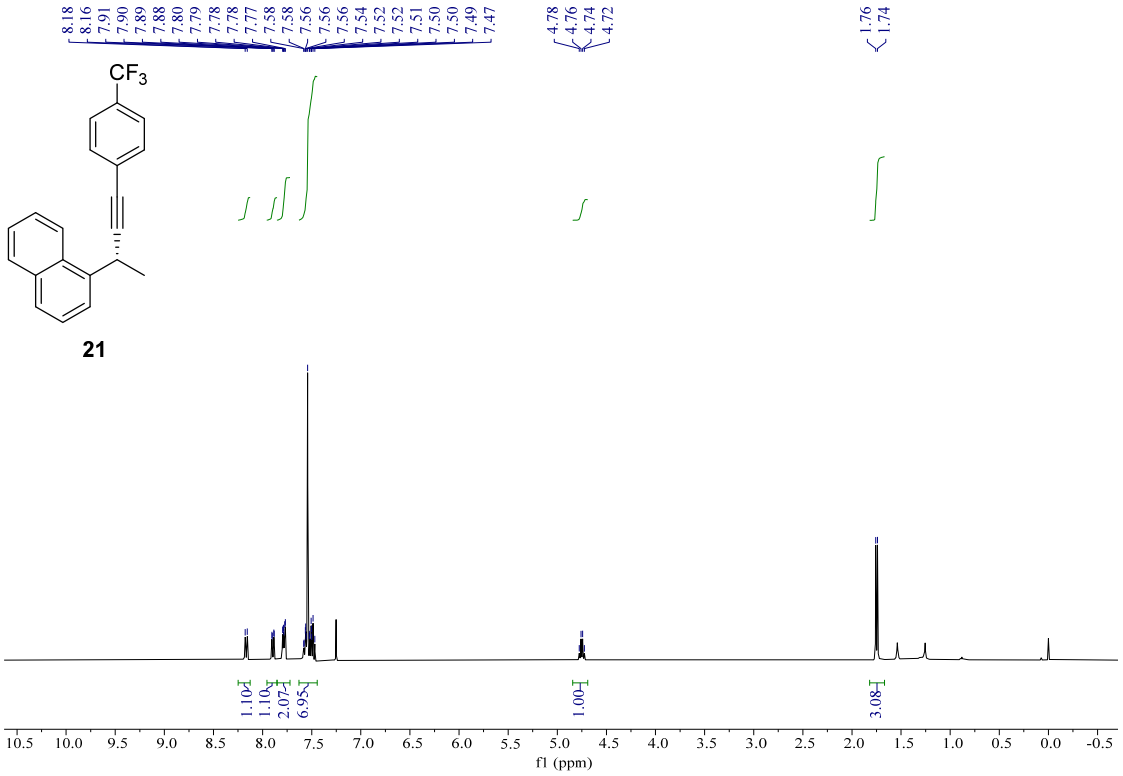
128.22
127.79
127.78
127.61
126.06
125.58
125.13
123.70
92.53
82.65
32.61
24.32
f1 (ppm)

20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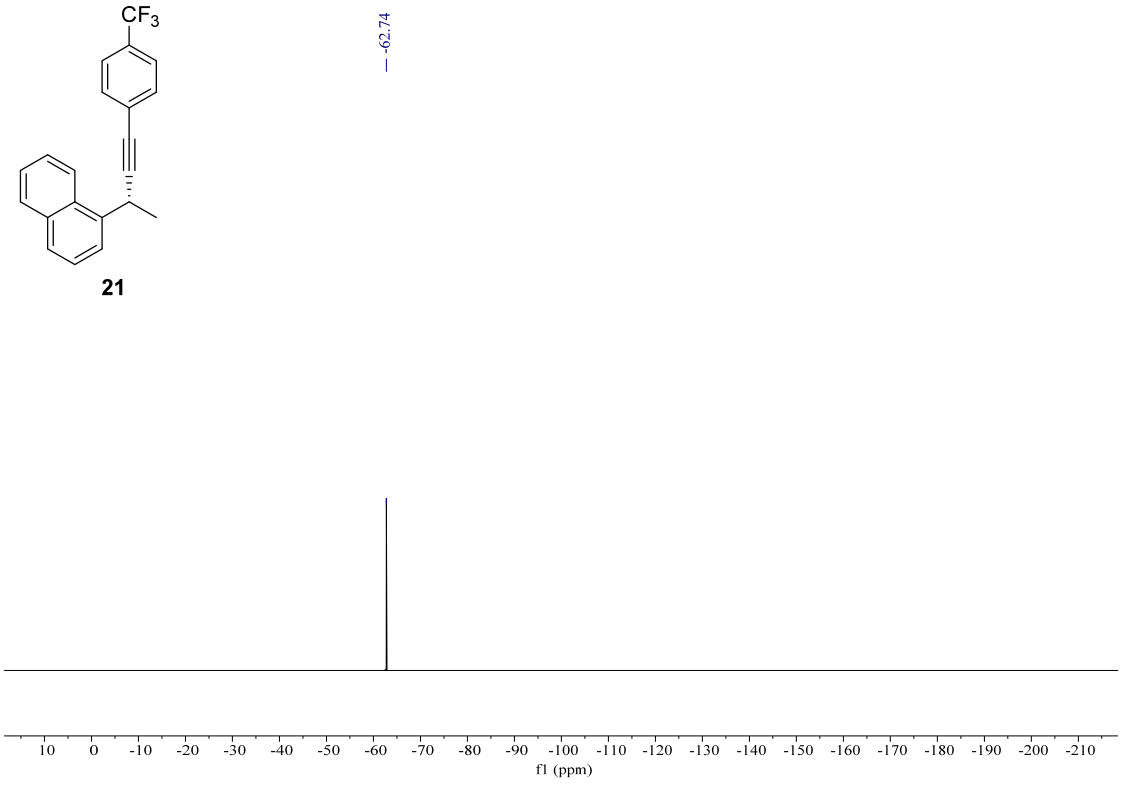
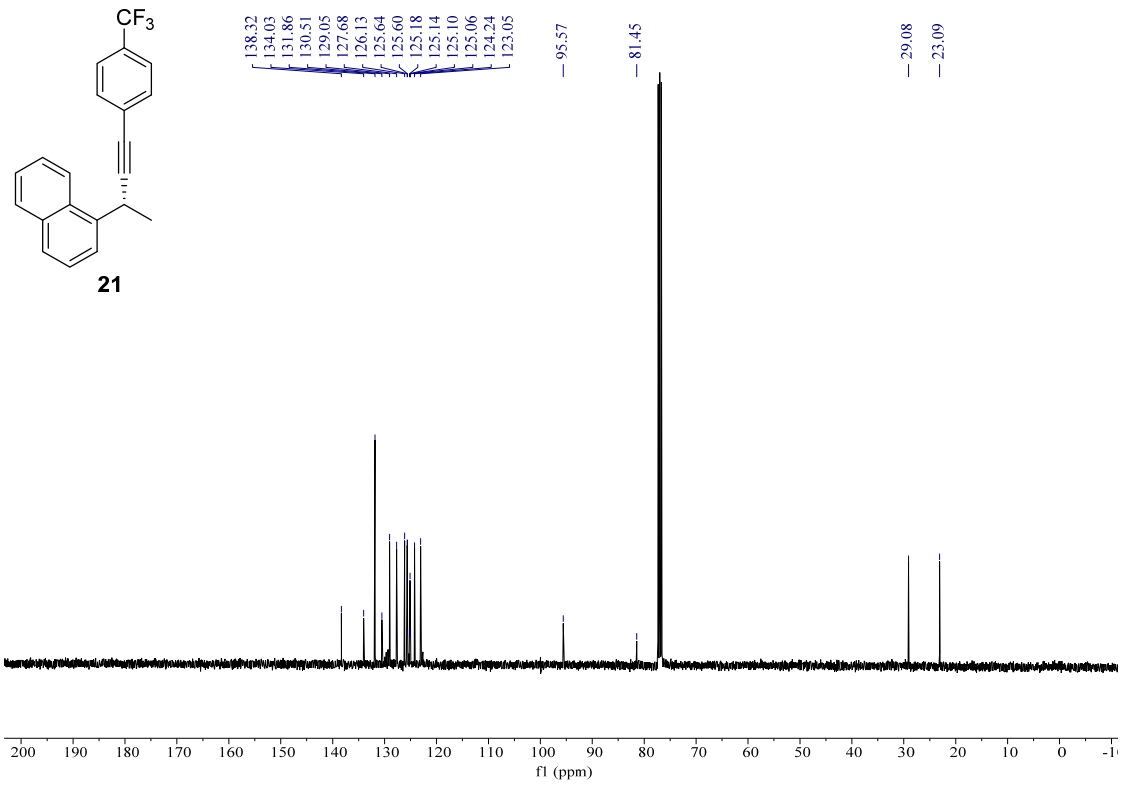
7.78
7.78
7.77
7.58
7.58
7.56
7.56
7.56
7.54
7.52
7.52
7.51
7.50
7.50
7.49
7.47
4.78
4.76
4.74
4.72
1.76
1.74
CF3
21
1.10
1.10
2.07
6.95
1.00
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


CF3
-62.74
21
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)


CF3
21
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126.13
125.64
125.60
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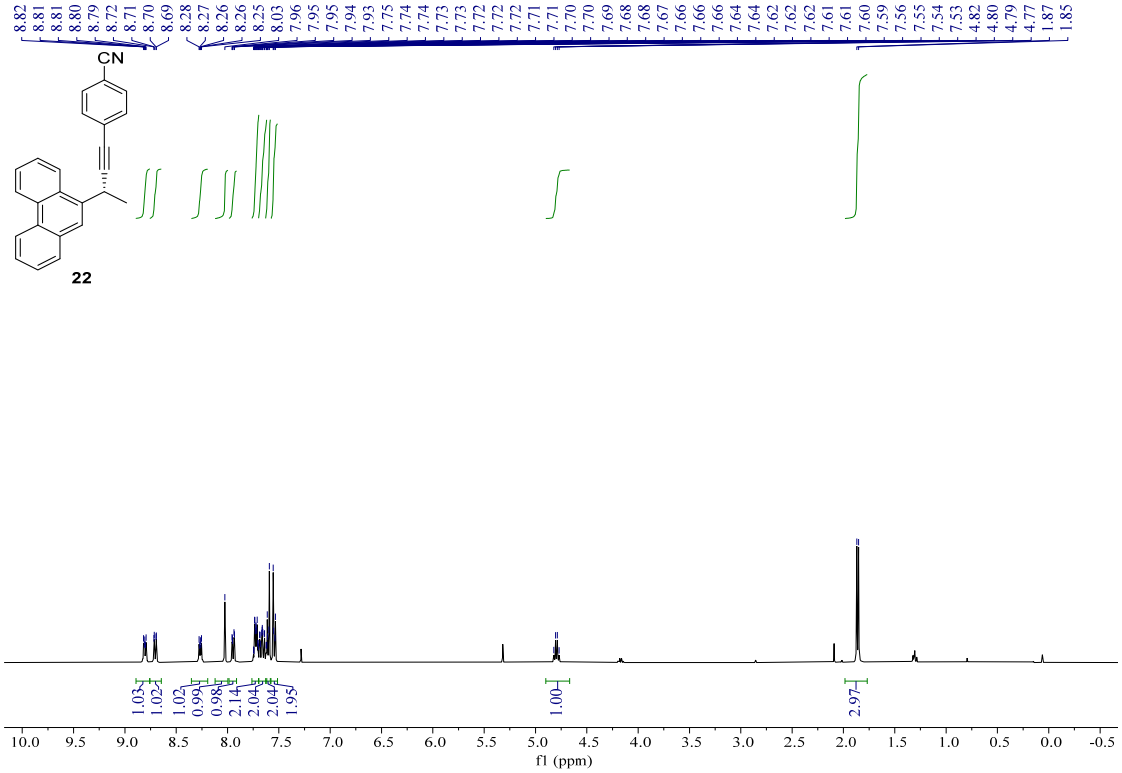
95.57
81.45
29.08
23.09
fl (ppm)


CN
22
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8.71
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8.69
8.28
8.27
8.26
8.26
8.25
8.03
7.96
7.95
7.95
7.94
7.93
7.75
7.74
7.74
7.73
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7.55
7.54
7.53
4.82
4.80
4.79
4.77
1.87
1.85
1.03
1.02
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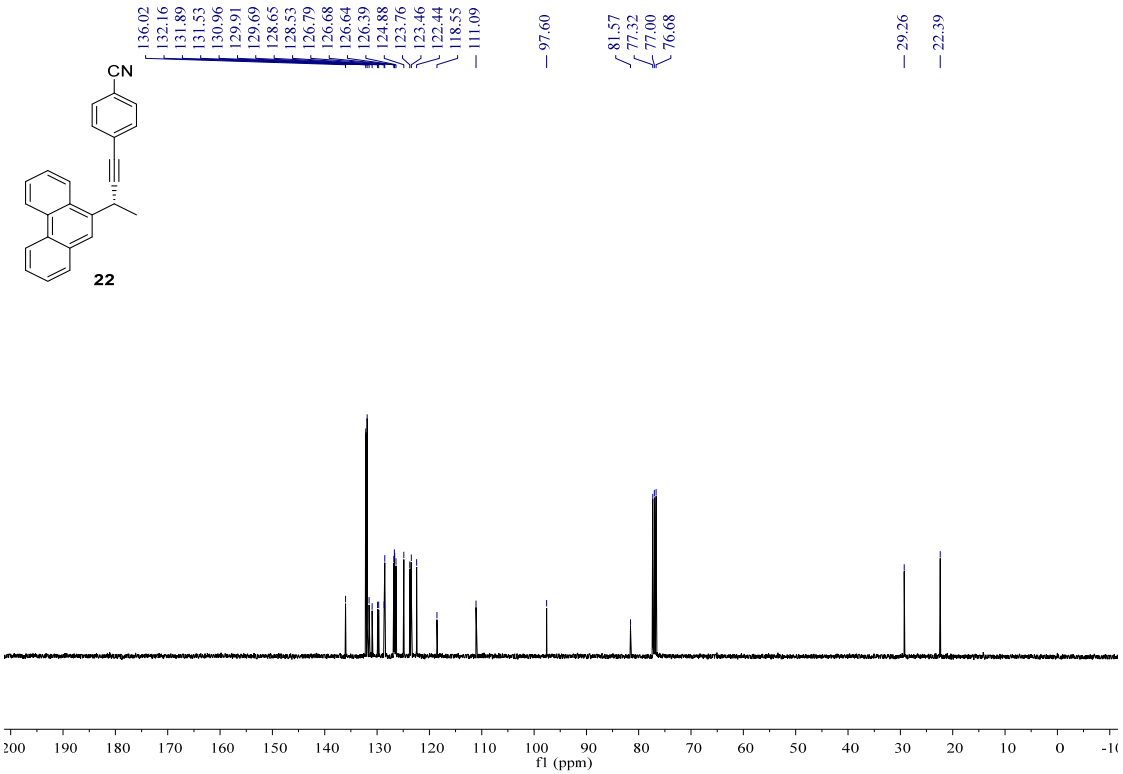
0.99
0.98
2.14
2.04
2.04
1.95
1.00
2.97
fl (ppm)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126.79
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126.39
124.88
123.76
123.46
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81.57
77.32
77.00
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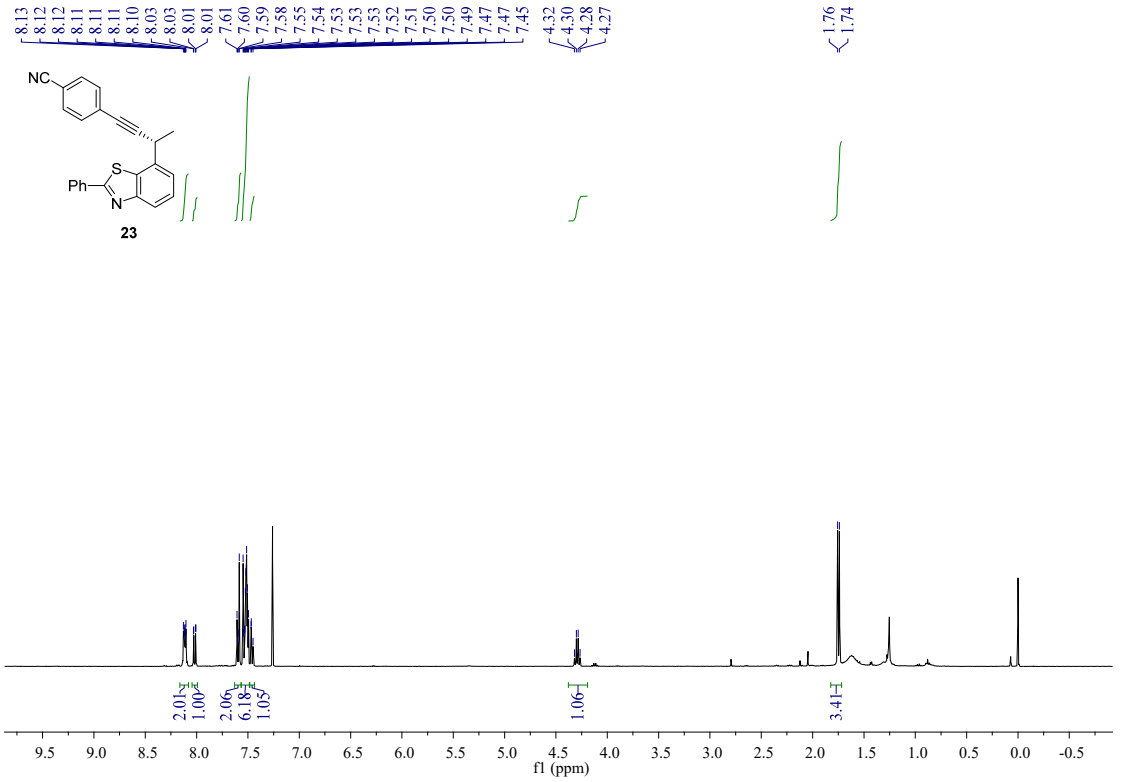
29.26
22.39
CN
22
f1 (ppm)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8.01
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7.50
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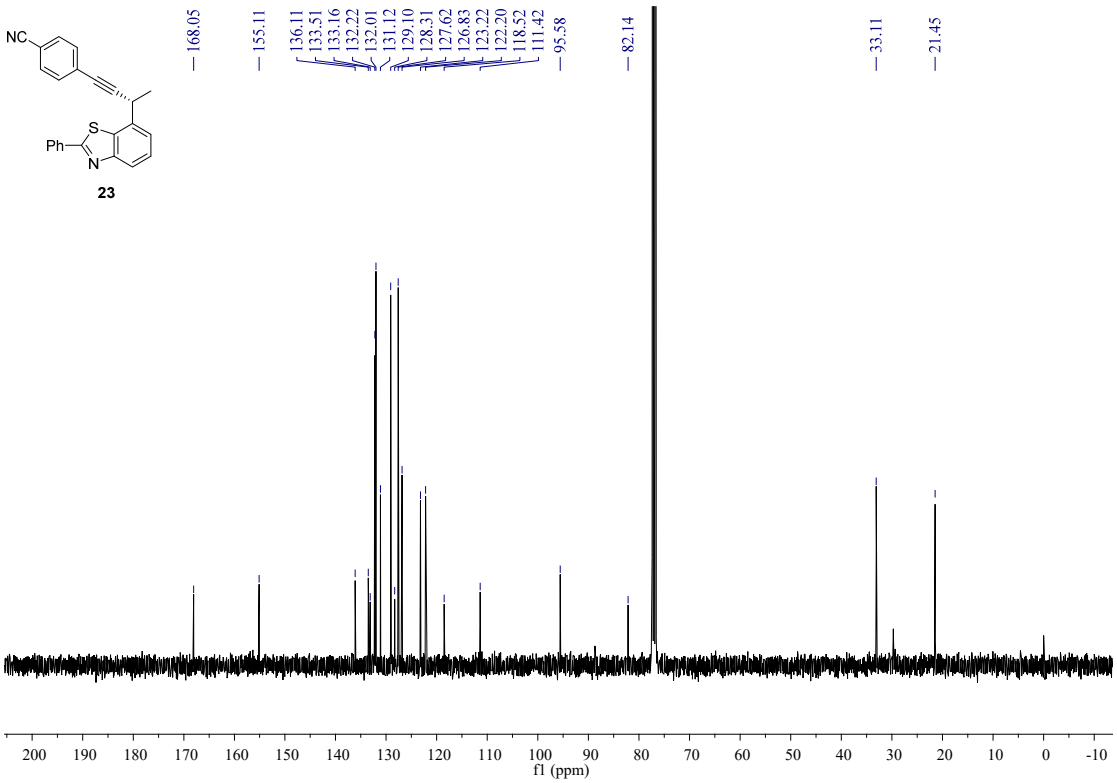
7.49
7.47
7.47
7.45
4.32
4.30
4.28
4.27
1.76
1.74
NC
Ph
S
N
23
2.01
1.00
2.06
6.18
1.05
1.06
3.41
f1 (ppm)


NC
Ph
S
N
23
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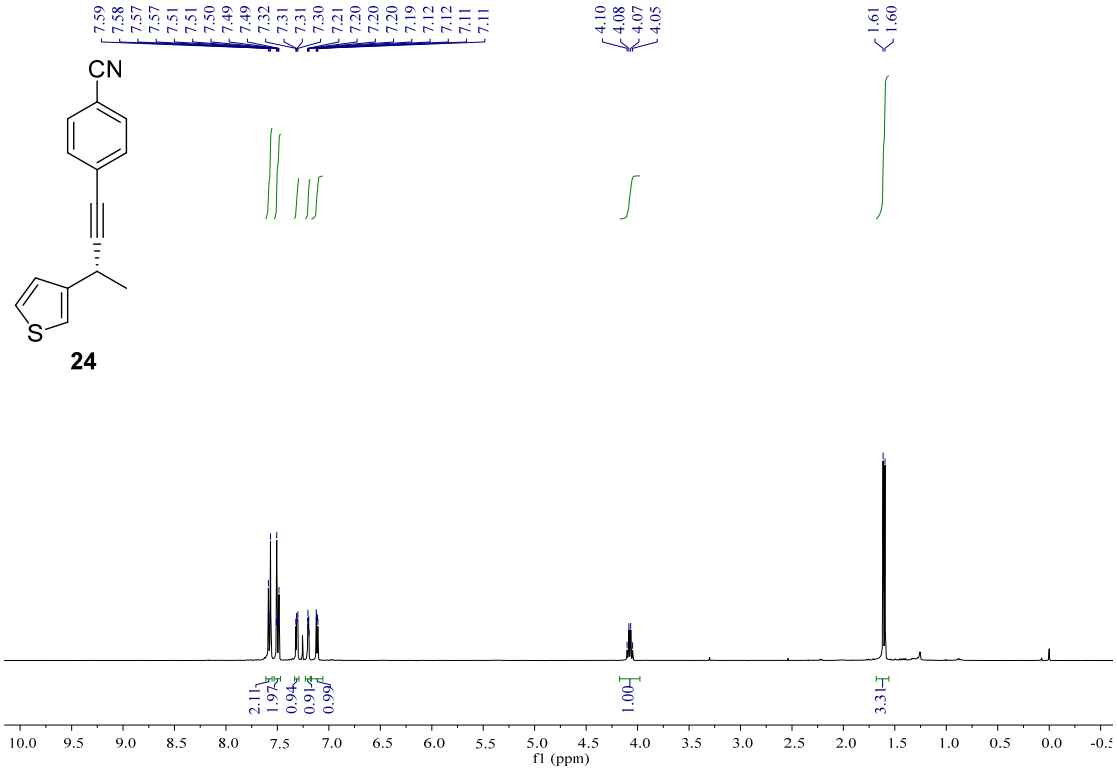
133.16
132.22
132.01
131.12
129.10
128.31
127.62
126.83
123.22
122.20
118.52
111.42
95.58
82.14
33.11
21.45
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.32
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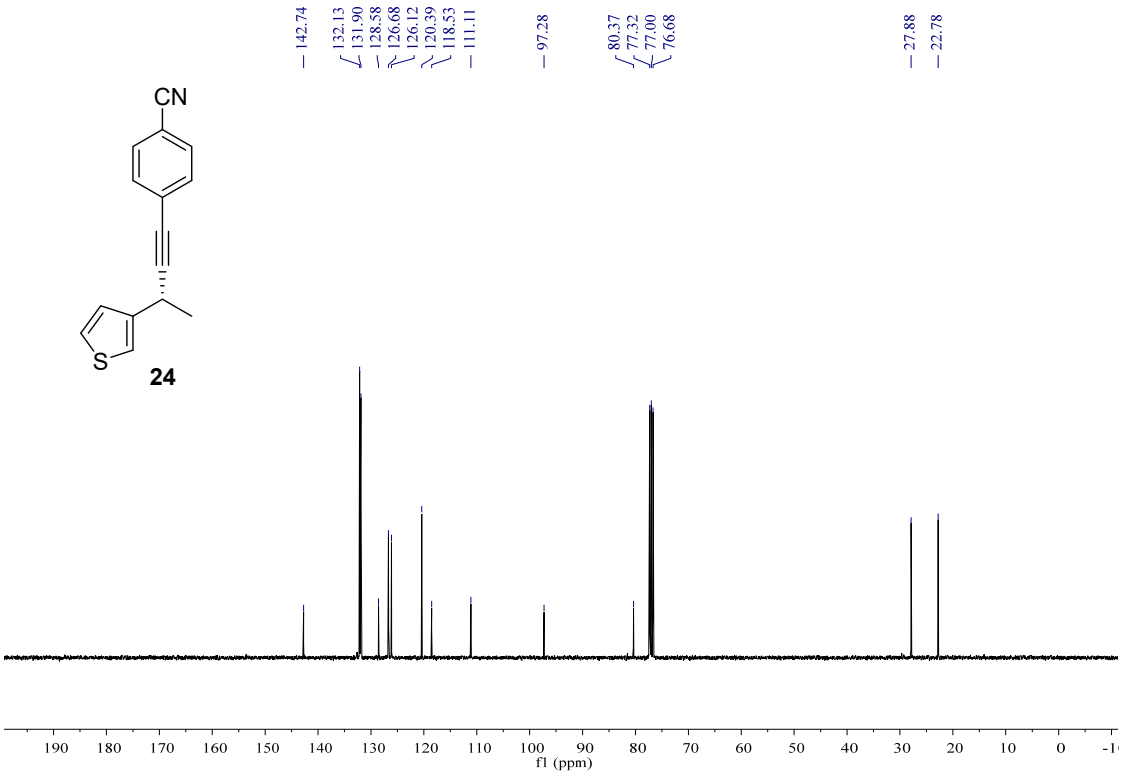
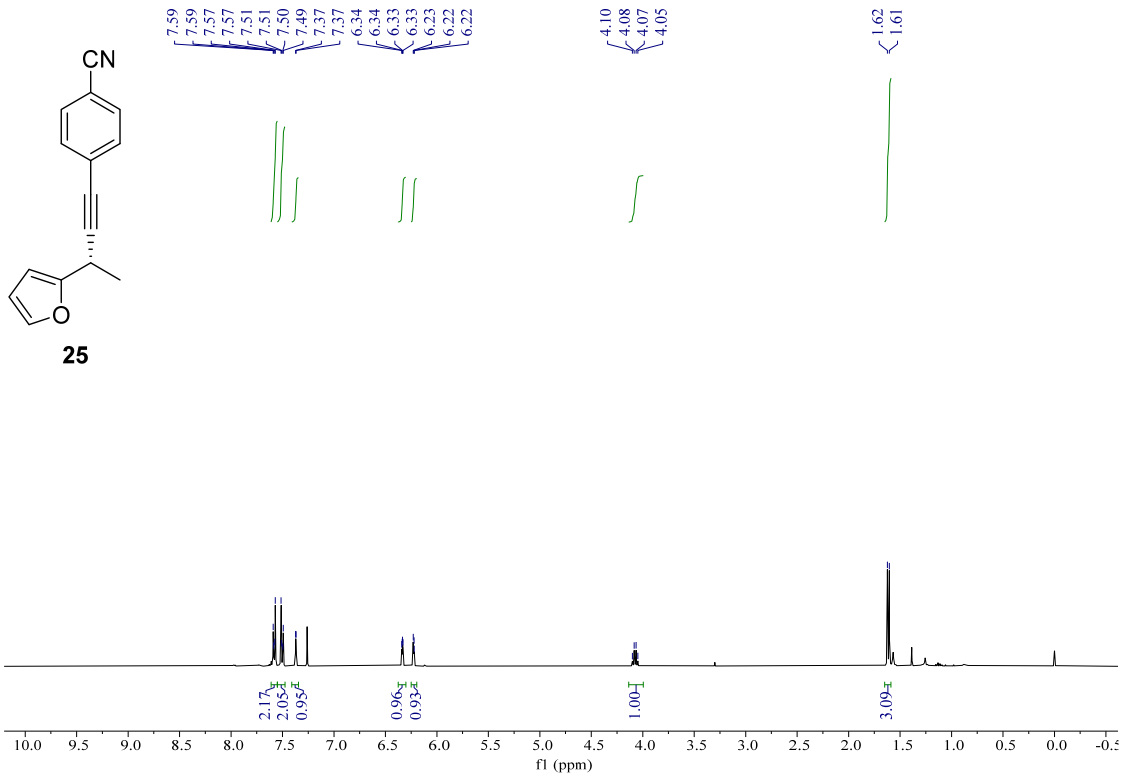
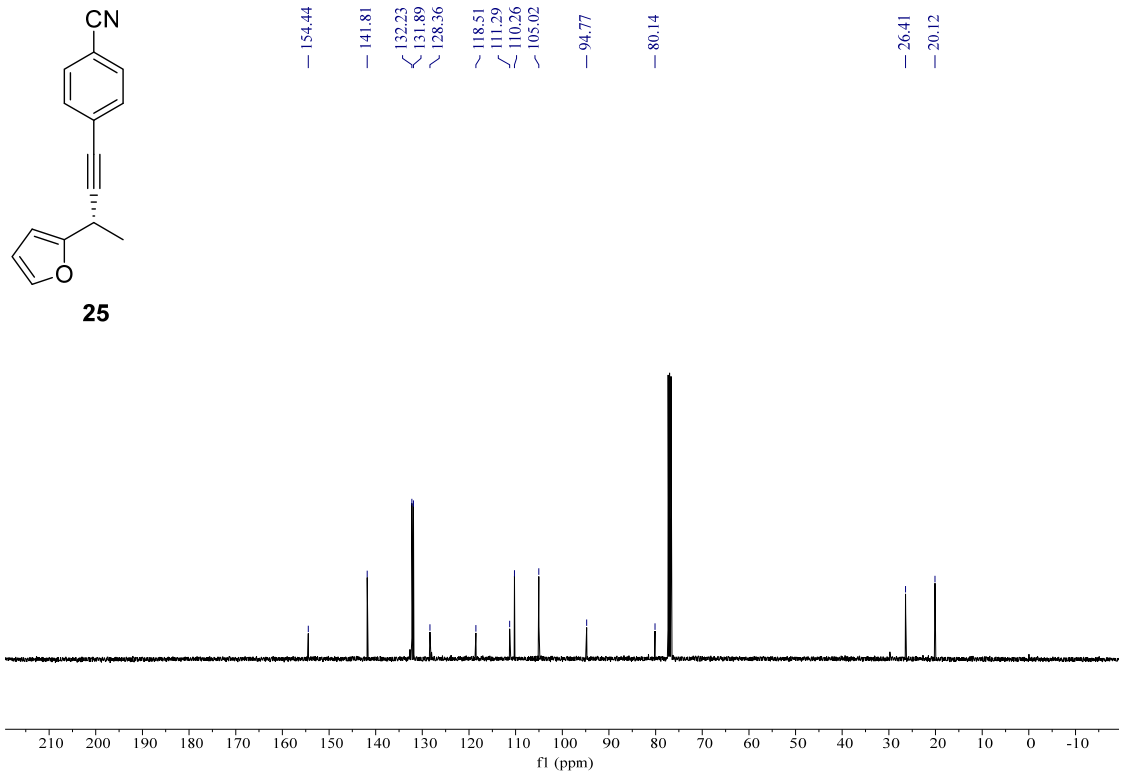
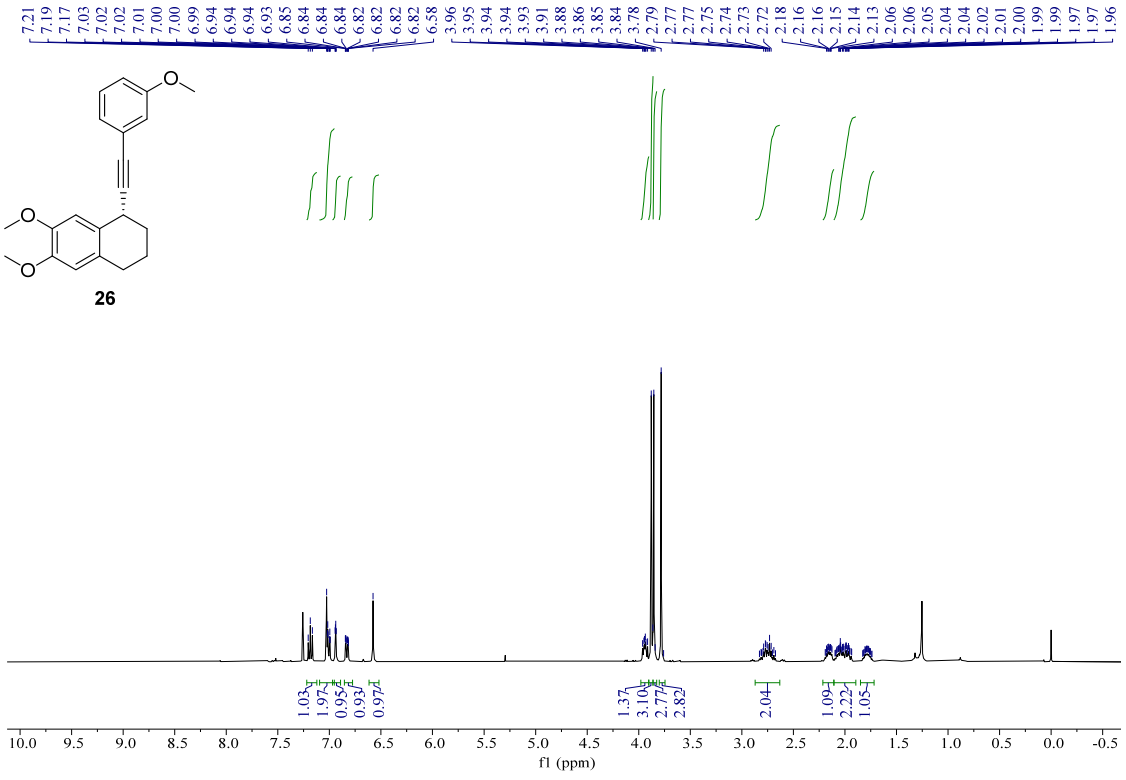
7.31
7.30
7.21
7.20
7.20
7.20
7.19
7.12
7.12
7.11
7.11
4.10
4.08
4.07
4.05
1.61
1.60
CN
S
24
2.11
1.97
0.94
0.91
0.99
1.00
3.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.74
132.13
131.90
128.58
126.68
126.12
120.39
118.53
111.11
97.28
80.37
77.32
77.00
76.68
27.88
22.78
CN
S
24
f1 (ppm)

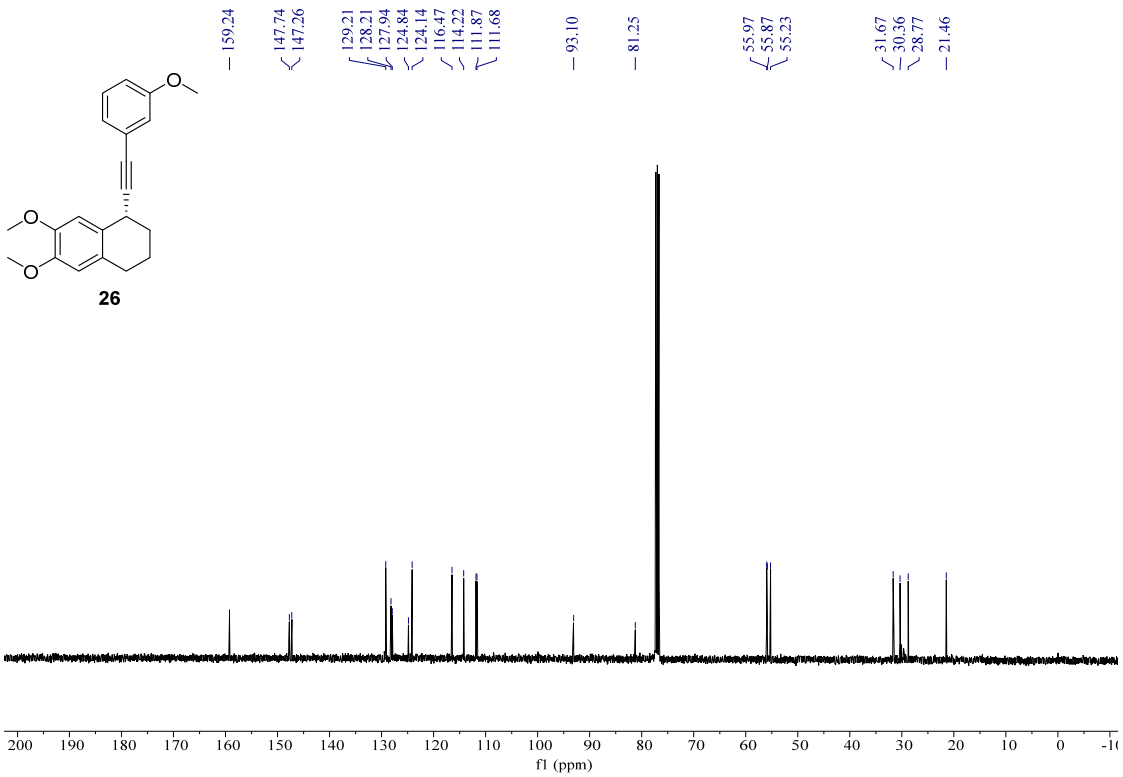

7.59
7.59
7.57
7.57
7.51
7.51
7.50
7.49
7.37
7.37
6.34
6.34
6.33
6.33
6.23
6.22
6.22
4.10
4.08
4.07
4.05
1.62
1.61
CN
O
25
2.17
2.05
0.95
0.96
0.93
1.00
3.09
f1 (ppm)

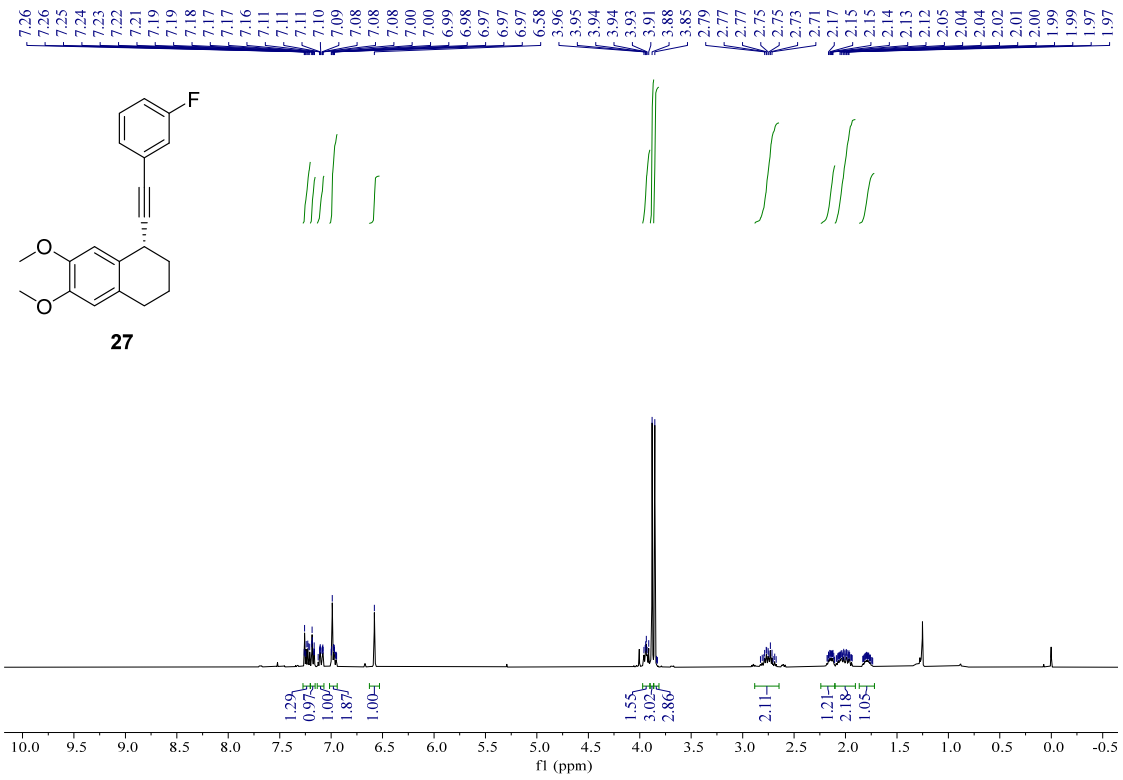

CN
O
154.44
141.81
132.23
131.89
128.36
118.51
111.29
110.26
105.02
94.77
80.14
26.41
20.12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

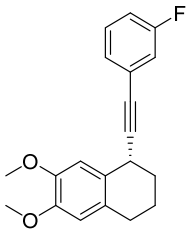
25


7.21 7.19 7.17 7.03 7.02 7.02 7.01 7.00 7.00 6.99 6.94 6.94 6.94 6.93 6.85 6.84 6.84 6.84 6.82 6.82 6.82 6.82 6.58
3.96 3.95 3.94 3.94 3.93 3.91 3.88 3.86 3.85 3.84 3.78 2.79 2.77 2.77 2.75 2.74 2.73 2.72 2.18 2.16 2.16 2.15 2.14 2.13 2.06 2.06 2.05 2.04 2.04 2.02 2.01 2.00 1.99 1.99 1.97 1.97 1.96
O
O
O
1.03 1.97 0.95 0.93 0.97
1.37 3.10 2.77 2.82 2.04 1.09 2.22 1.05
10.0 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)

26

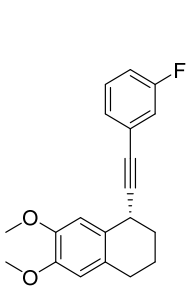

159.24
147.74
147.26
129.21
128.21
127.94
124.84
124.14
116.47
114.22
111.87
111.68
93.10
81.25
55.97
55.87
55.23
31.67
30.36
28.77
21.46
26
f1 (ppm)


F
27
1.29
0.97
1.00
1.87
1.00
1.55
3.02
2.86
2.11
1.21
2.18
1.05
f1 (ppm)


F
O
O

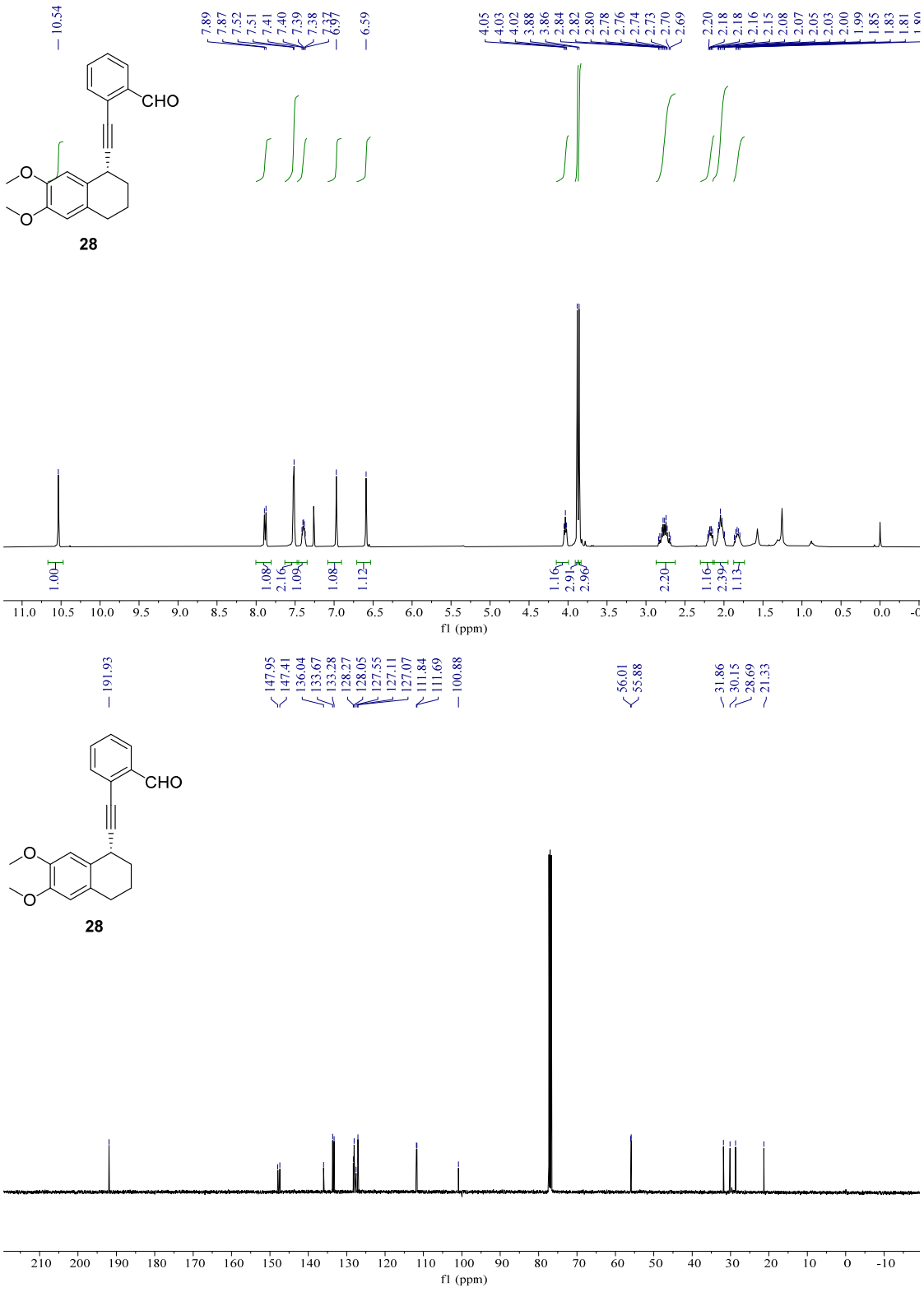
27

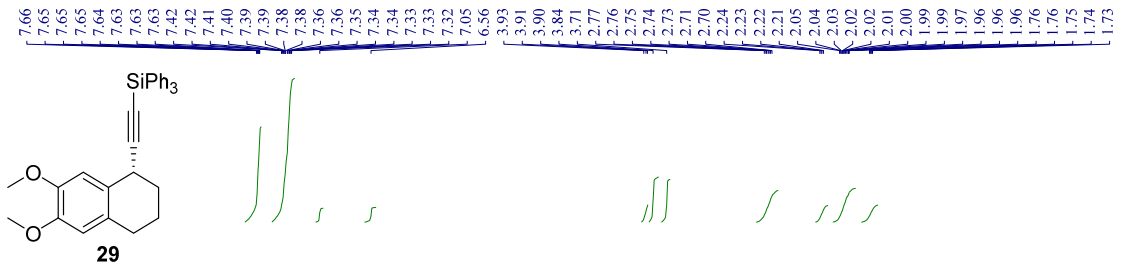
-113.36
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195
f1 (ppm)

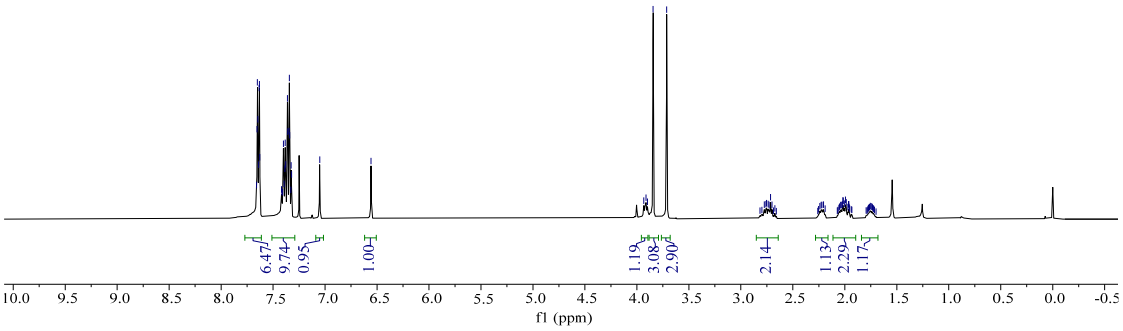

F
O
O

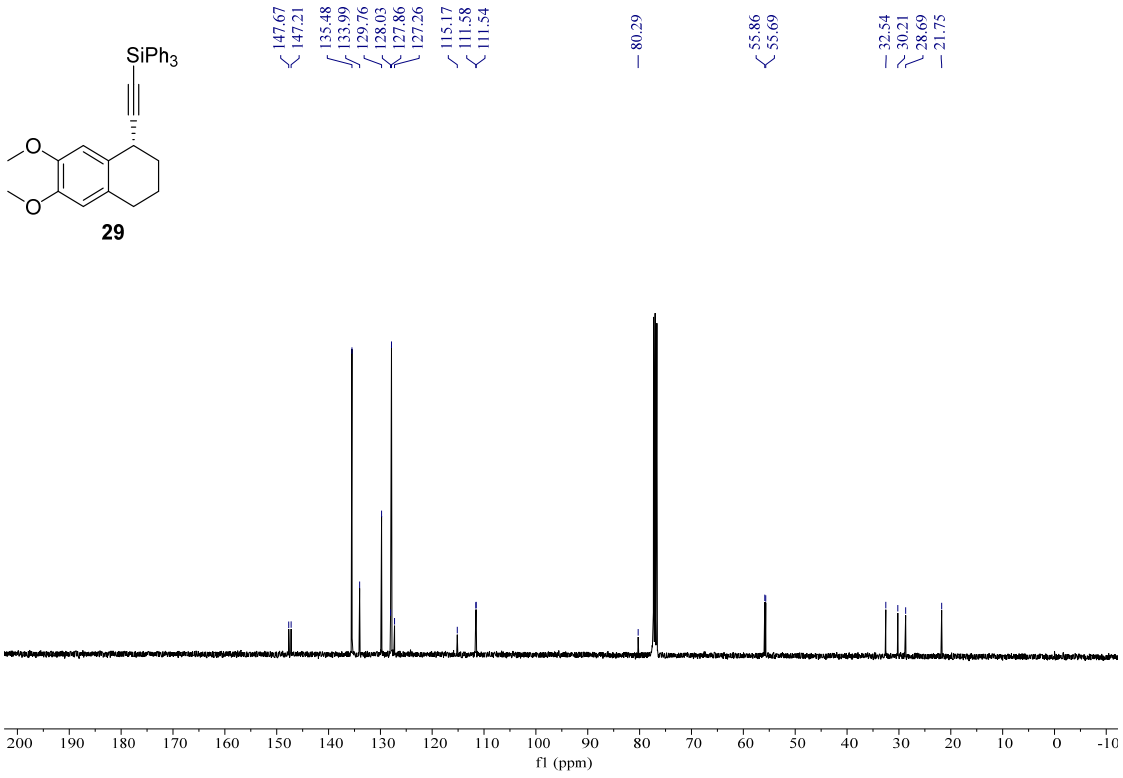
27

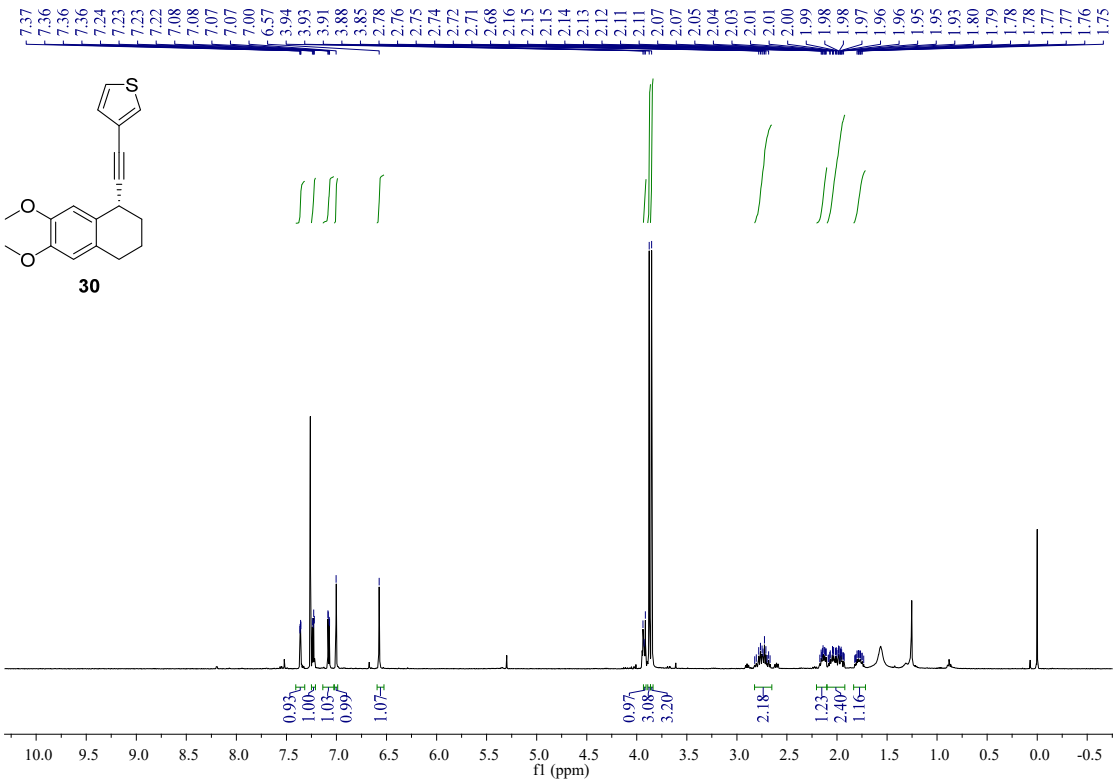
163.54
161.10
147.82
147.29
129.72
129.63
128.24
127.60
127.45
127.42
125.74
125.65
118.48
118.26
115.06
114.85
111.81
111.72
94.35
80.26
80.23
55.98
55.87
31.61
30.23
28.73
21.36
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

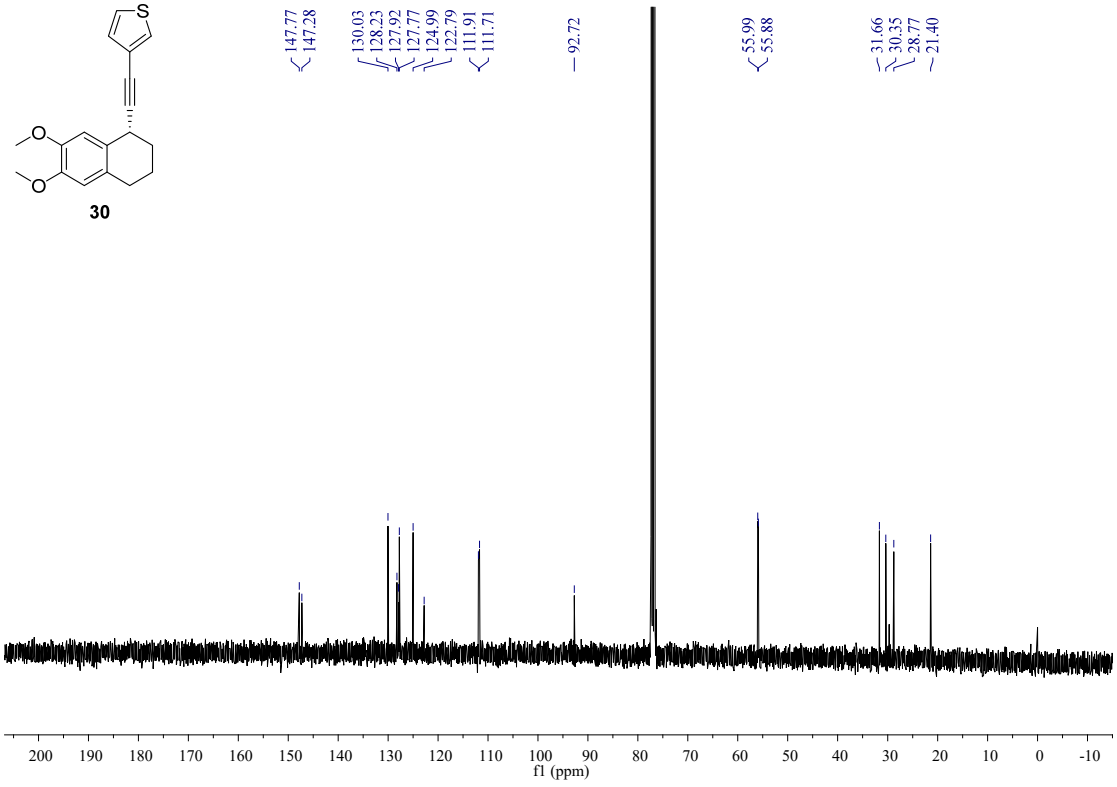

10.54
7.89
7.87
7.52
7.51
7.41
7.40
7.39
7.38
6.97
6.59
4.05
4.03
4.02
3.88
3.86
2.84
2.82
2.80
2.78
2.76
2.74
2.73
2.70
2.69
2.20
2.18
2.18
2.16
2.15
2.08
2.07
2.05
2.03
2.00
1.99
1.85
1.83
1.81
CHO
O
O
28
1.00
1.08
2.16
1.09
1.08
1.12
1.16
2.91
2.96
2.20
1.16
2.39
1.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 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
f1 (ppm)
191.93
147.95
147.41
136.04
133.67
133.28
128.27
128.05
127.55
127.11
127.07
111.84
111.69
100.88
56.01
55.88
31.86
30.15
28.69
21.33
CHO
O
O
28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.66 7.65 7.65 7.65 7.64 7.63 7.63 7.63 7.42 7.42 7.41 7.40 7.39 7.39 7.38 7.38 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.32 7.05 6.56
3.93 3.91 3.90 3.84 3.71 2.77 2.76 2.75 2.74 2.73 2.71 2.70 2.24 2.23 2.22 2.21 2.05 2.04 2.03 2.02 2.02 2.01 2.00 1.99 1.99 1.97 1.96 1.96 1.96 1.76 1.76 1.75 1.74 1.73
SiPh3
O
O
29


6.47
9.74
0.95
1.00
1.19
3.08
2.90
2.14
1.13
2.29
1.17
10.0 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)


147.67
147.21
135.48
133.99
129.76
128.03
127.86
127.26
115.17
111.58
111.54
80.29
55.86
55.69
32.54
30.21
28.69
21.75
SiPh3
O
O
29
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.37 7.36 7.36 7.36 7.24 7.23 7.23 7.22 7.08 7.08 7.07 7.07 7.00 6.57 3.94 3.93 3.91 3.88 3.85 2.78 2.76 2.75 2.74 2.72 2.71 2.68 2.16 2.15 2.15 2.14 2.13 2.12 2.11 2.11 2.07 2.07 2.05 2.04 2.03 2.01 2.01 2.00 1.99 1.98 1.98 1.97 1.96 1.96 1.95 1.95 1.93 1.80 1.79 1.78 1.78 1.77 1.77 1.76 1.75
30
0.93 1.00 1.03 0.99 1.07 0.97 3.08 3.20 2.18 1.23 2.40 1.16
10.0 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)


147.77 147.28 130.03 128.23 127.92 127.77 124.99 122.79 111.91 111.71 92.72 55.99 55.88 31.66 30.35 28.77 21.40
30
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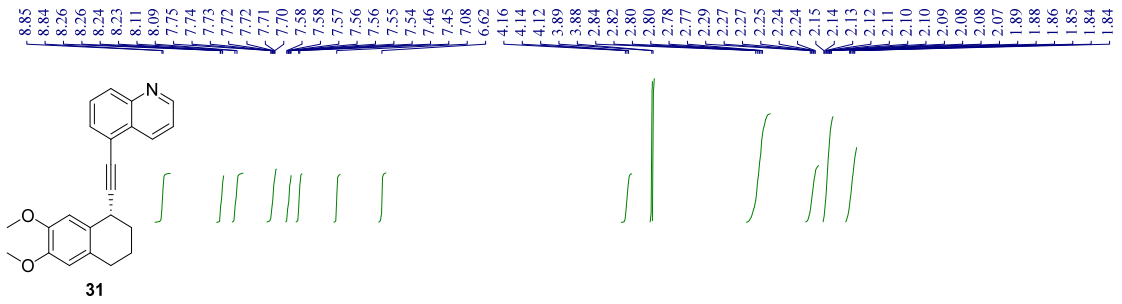
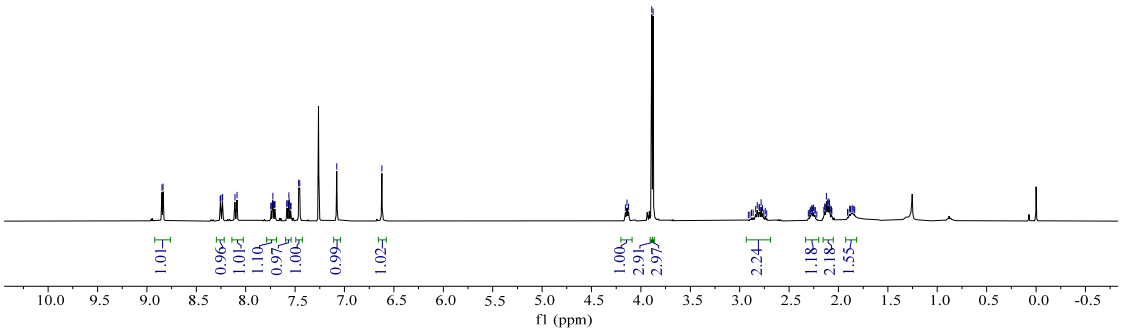
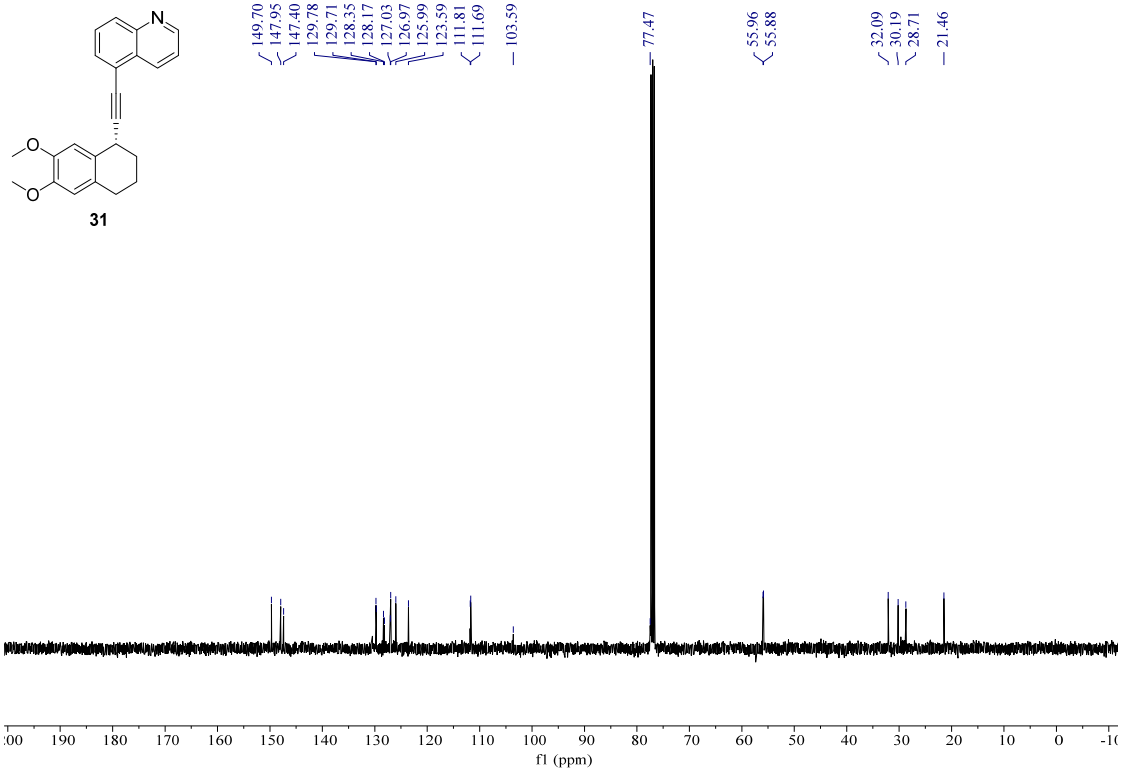
f1 (ppm)

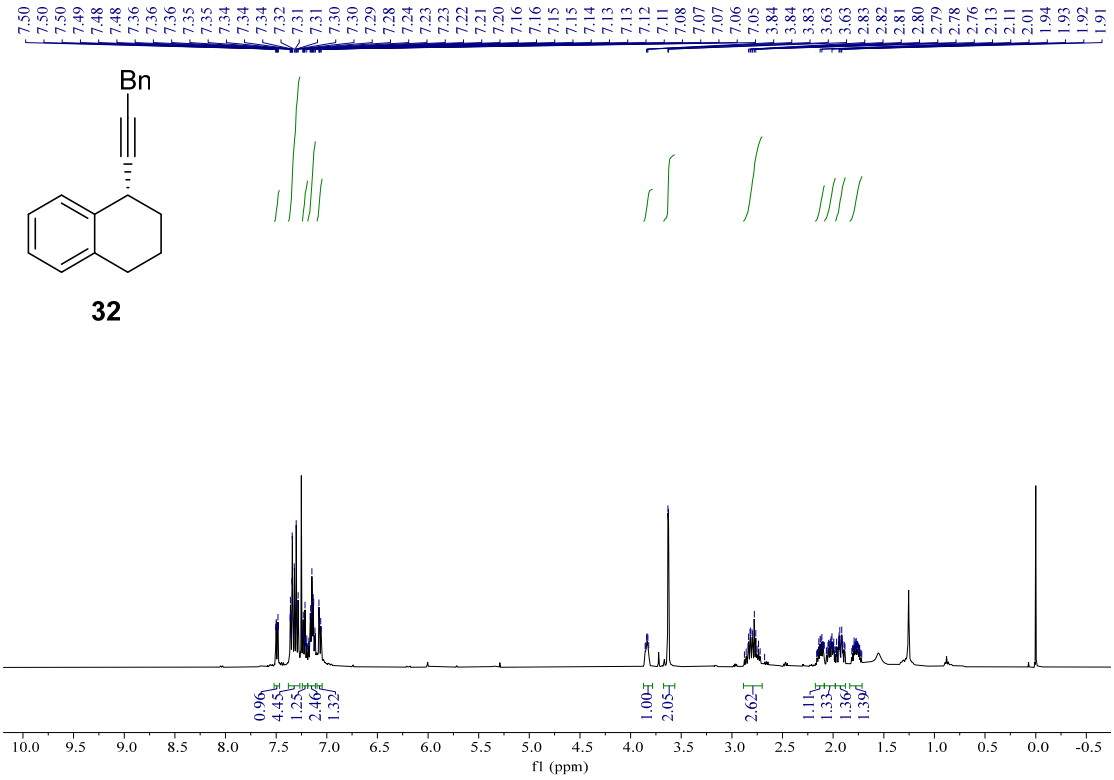

8.85
8.84
8.26
8.26
8.24
8.23
8.11
8.09
7.75
7.74
7.73
7.72
7.72
7.71
7.70
7.58
7.58
7.57
7.56
7.56
7.55
7.54
7.46
7.45
7.08
6.62
4.16
4.14
4.12
3.89
3.88
3.84
2.82
2.80
2.80
2.78
2.77
2.29
2.27
2.27
2.25
2.24
2.24
2.15
2.14
2.13
2.12
2.11
2.10
2.10
2.09
2.08
2.08
2.07
1.89
1.88
1.86
1.85
1.84
1.84
N
O
O

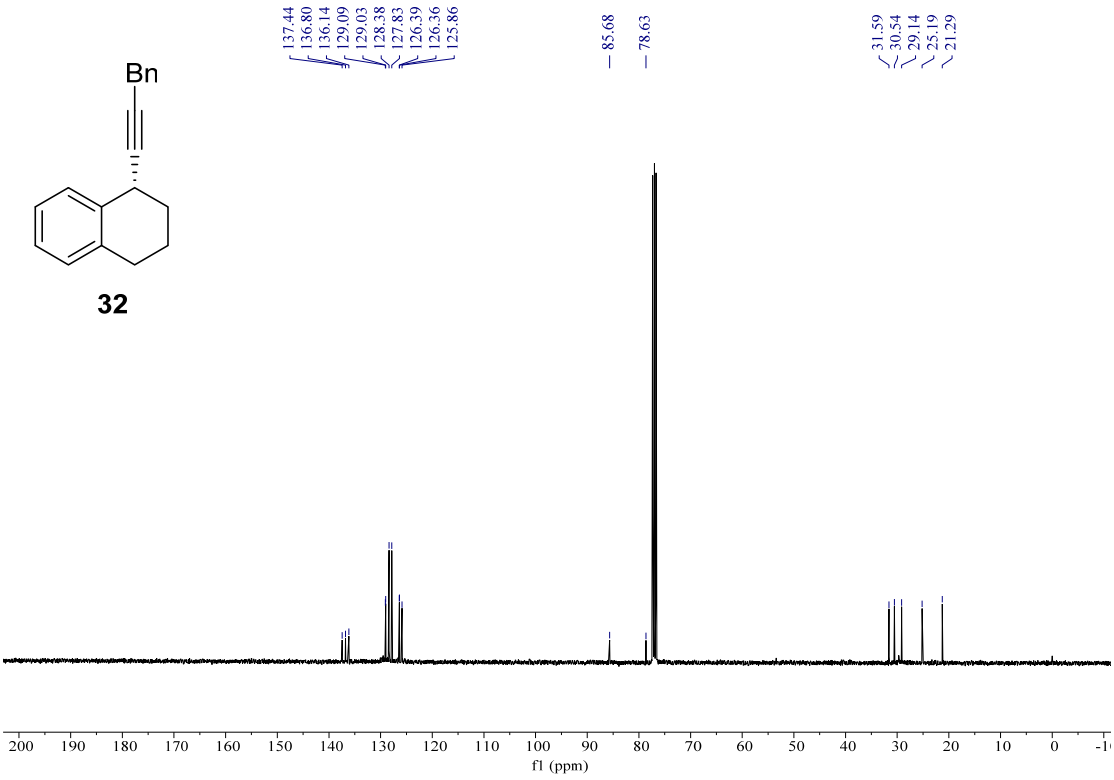
31

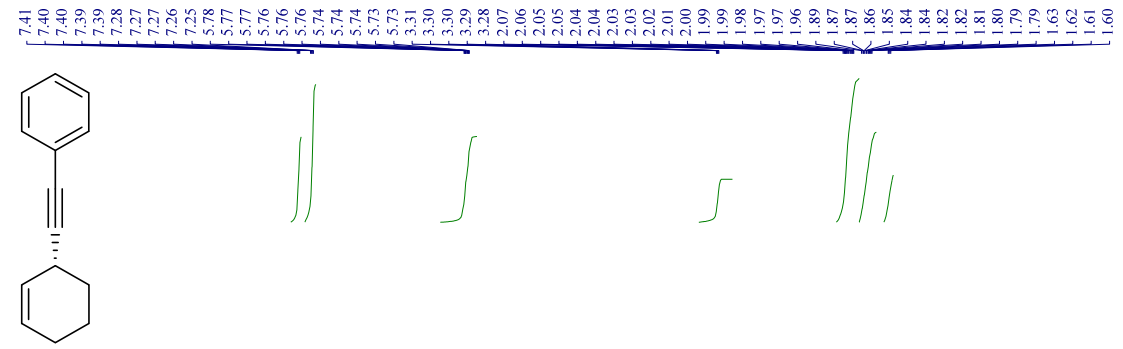

1.01
0.96
1.01
1.10
0.97
1.00
0.99
1.02
1.00
2.91
2.97
2.24
1.18
2.18
1.55
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


149.70
147.95
147.40
129.78
129.71
128.35
128.17
127.03
126.97
125.99
123.59
111.81
111.69
103.59
77.47
55.96
55.88
32.09
30.19
28.71
21.46
N
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

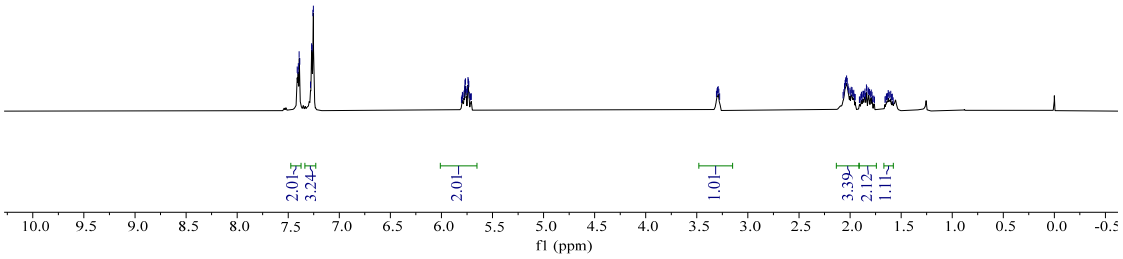
31

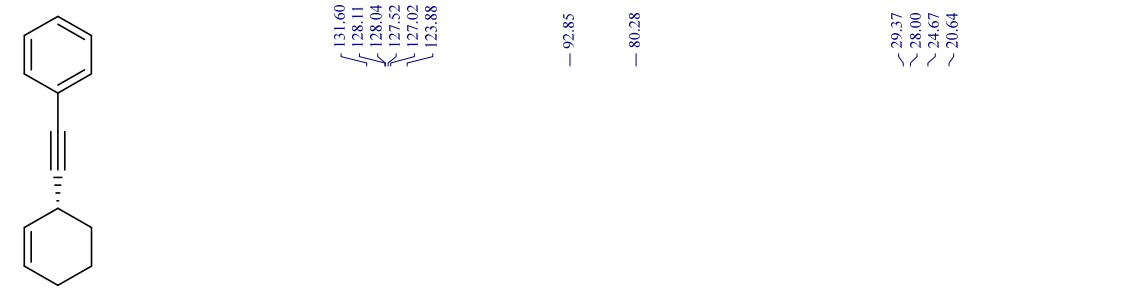

Bn
32
0.96
4.45
1.25
2.46
1.32
1.00
2.05
2.62
1.11
1.33
1.36
1.39
f1 (ppm)


Bn
32
137.44
136.80
136.14
129.09
129.03
128.38
127.83
126.39
126.36
125.86
85.68
78.63
31.59
30.54
29.14
25.19
21.29
f1 (ppm)

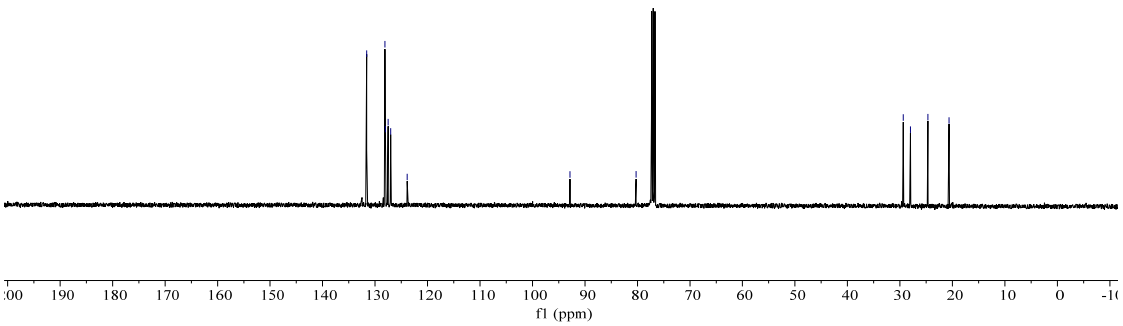


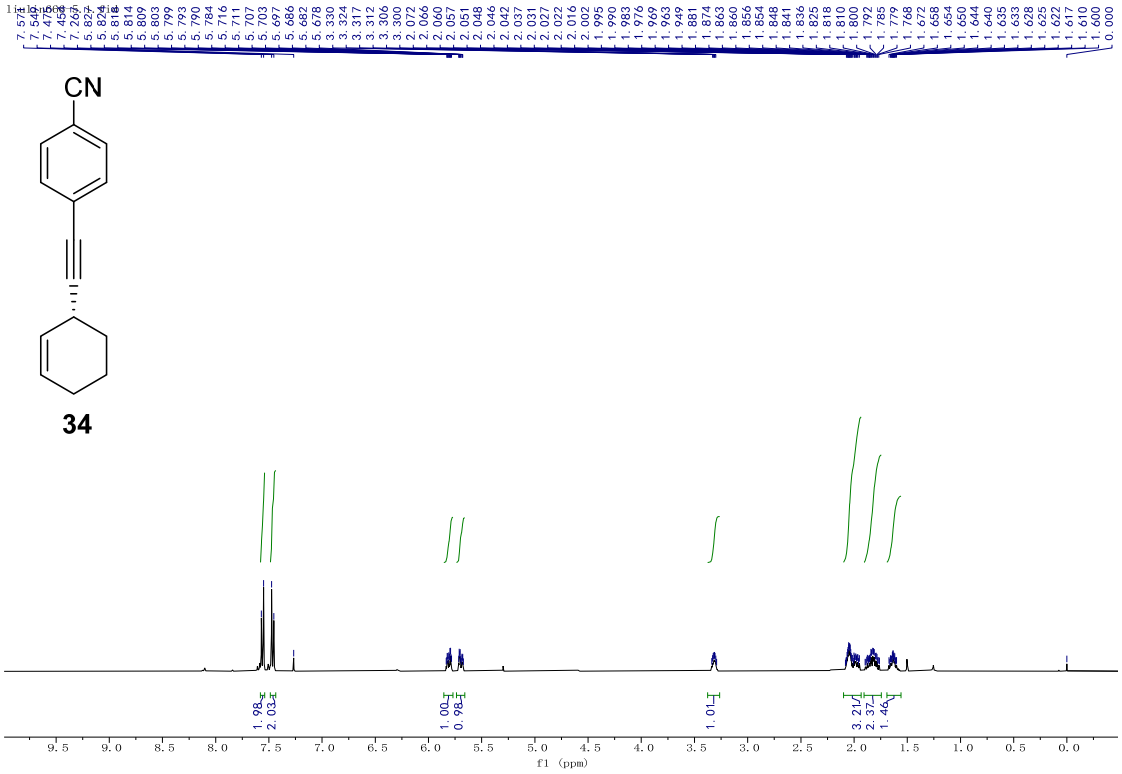
33

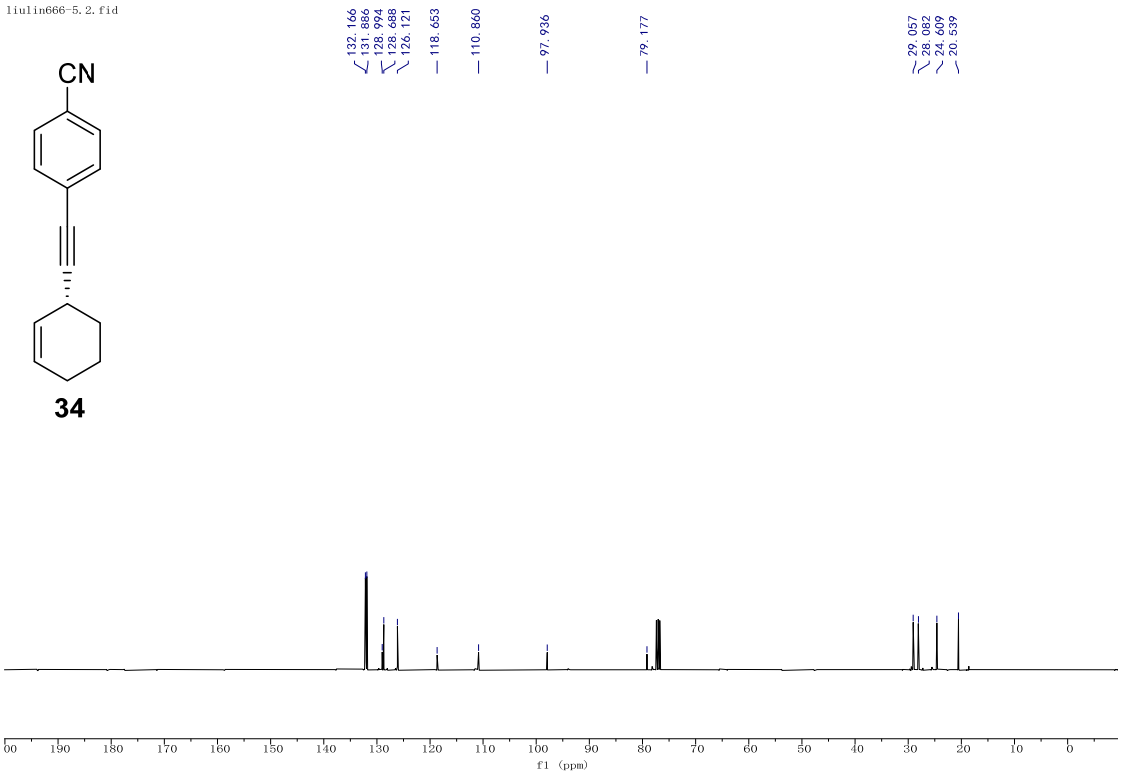

2.01
3.24
2.01
1.01
3.39
2.12
1.11
f1 (ppm)

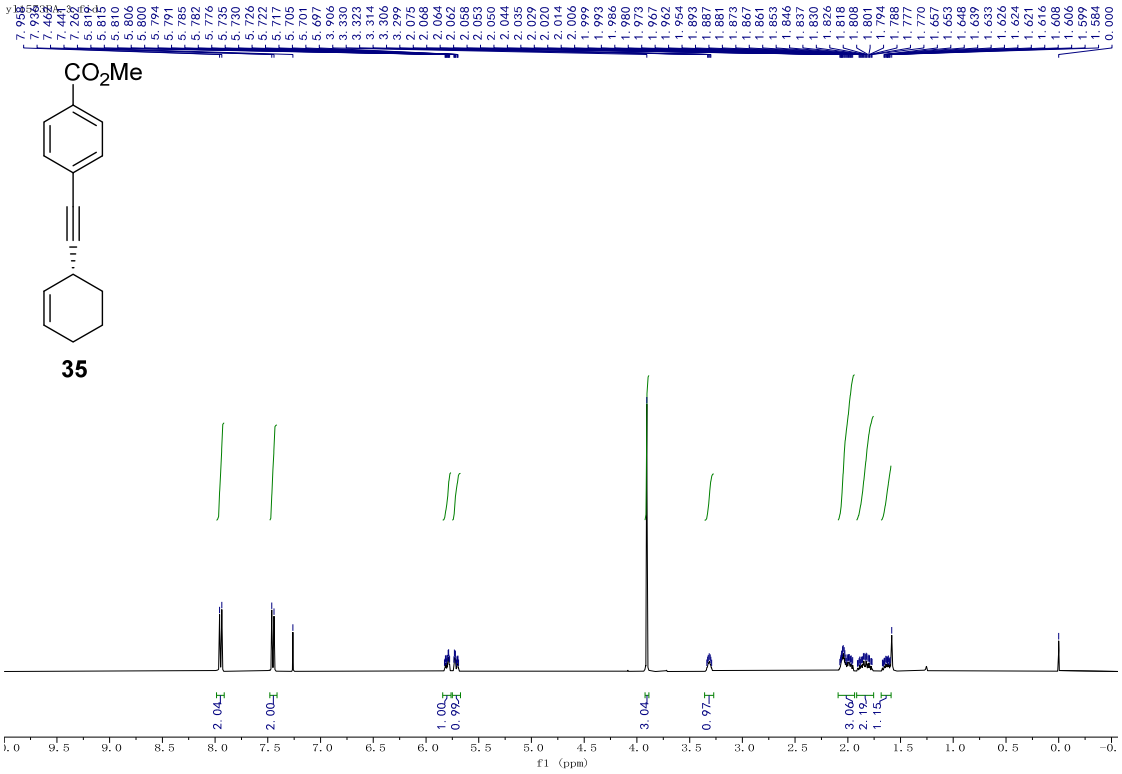


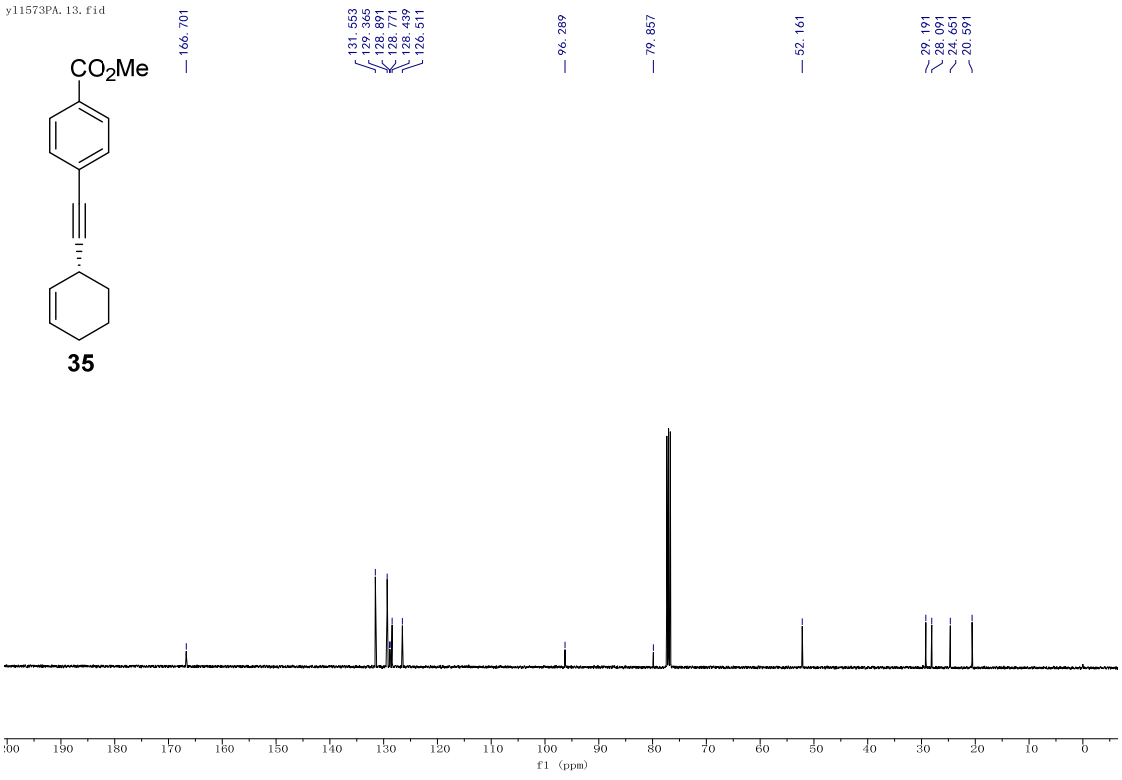
33

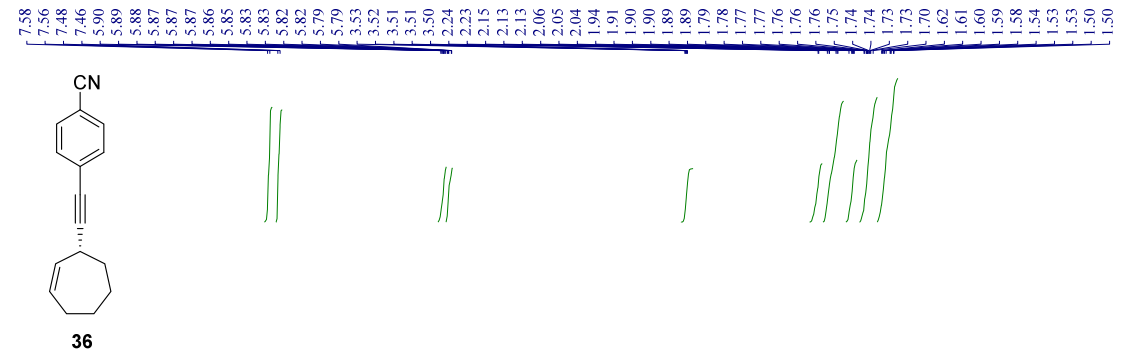

131.60
128.11
128.04
127.52
127.02
123.88
92.85
80.28
29.37
28.00
24.67
20.64
f1 (ppm)


CN
34
1.98
2.03
1.00
0.98
1.01
3.21
2.37
1.46
f1 (ppm)

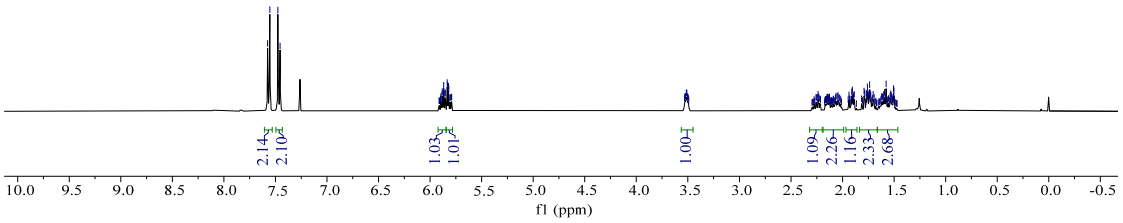

liulin666-5.2.fid
132.166
131.886
128.994
128.688
126.121
118.653
110.860
97.936
79.177
29.057
28.092
24.609
20.539
CN
34
f1 (ppm)

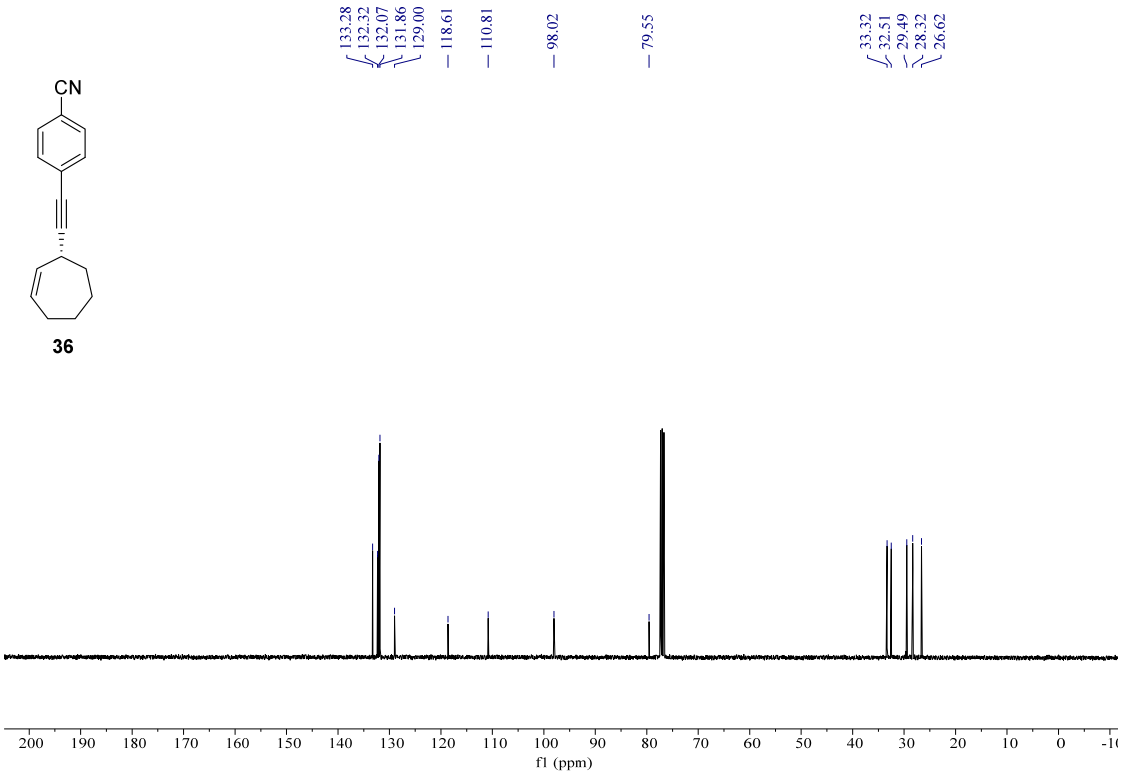

CO2Me
35
f1 (ppm)


y11573PA. 13. fid
CO2Me
35
166. 701
131. 553
131. 345
128. 891
128. 771
128. 439
126. 511
96. 289
79. 857
52. 161
29. 191
28. 091
24. 651
20. 591
f1 (ppm)

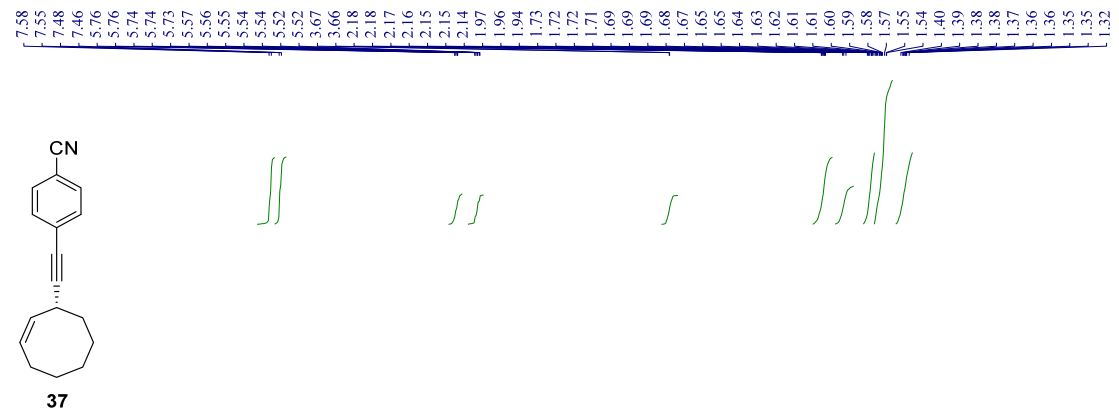

7.58 7.56 7.48 7.46 5.90 5.89 5.88 5.87 5.87 5.87 5.86 5.85 5.83 5.83 5.82 5.82 5.79 5.79 3.53 3.52 3.51 3.51 3.50 2.24 2.23 2.15 2.13 2.13 2.06 2.05 2.04 1.94 1.91 1.90 1.90 1.89 1.89 1.79 1.78 1.77 1.77 1.76 1.76 1.76 1.75 1.74 1.74 1.73 1.73 1.70 1.62 1.61 1.60 1.59 1.58 1.54 1.53 1.53 1.50 1.50
CN

36

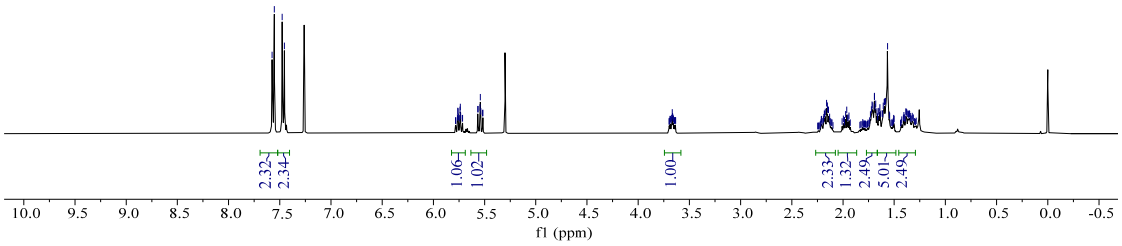

2.14 2.10 1.03 1.01 1.00 1.09 2.26 1.16 2.33 2.68
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

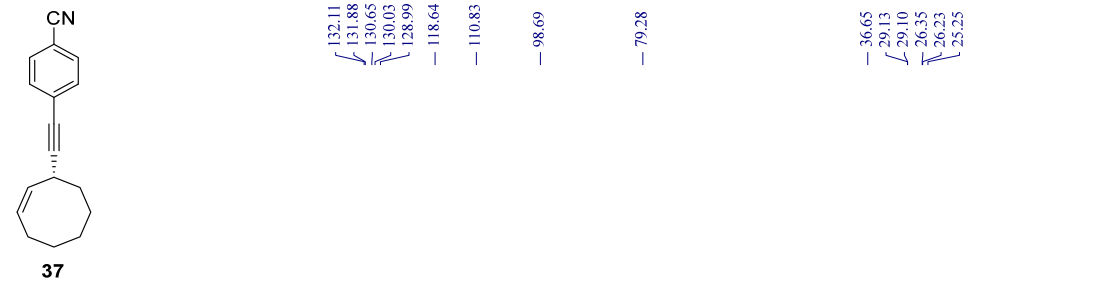

133.28 132.32 132.07 131.86 129.00 118.61 110.81 98.02 79.55 33.32 32.51 29.49 28.32 26.62
CN
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

36



37





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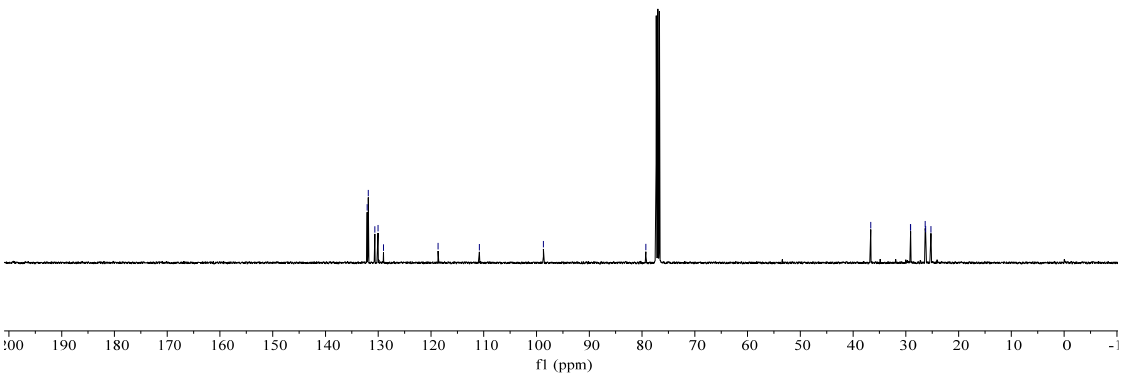
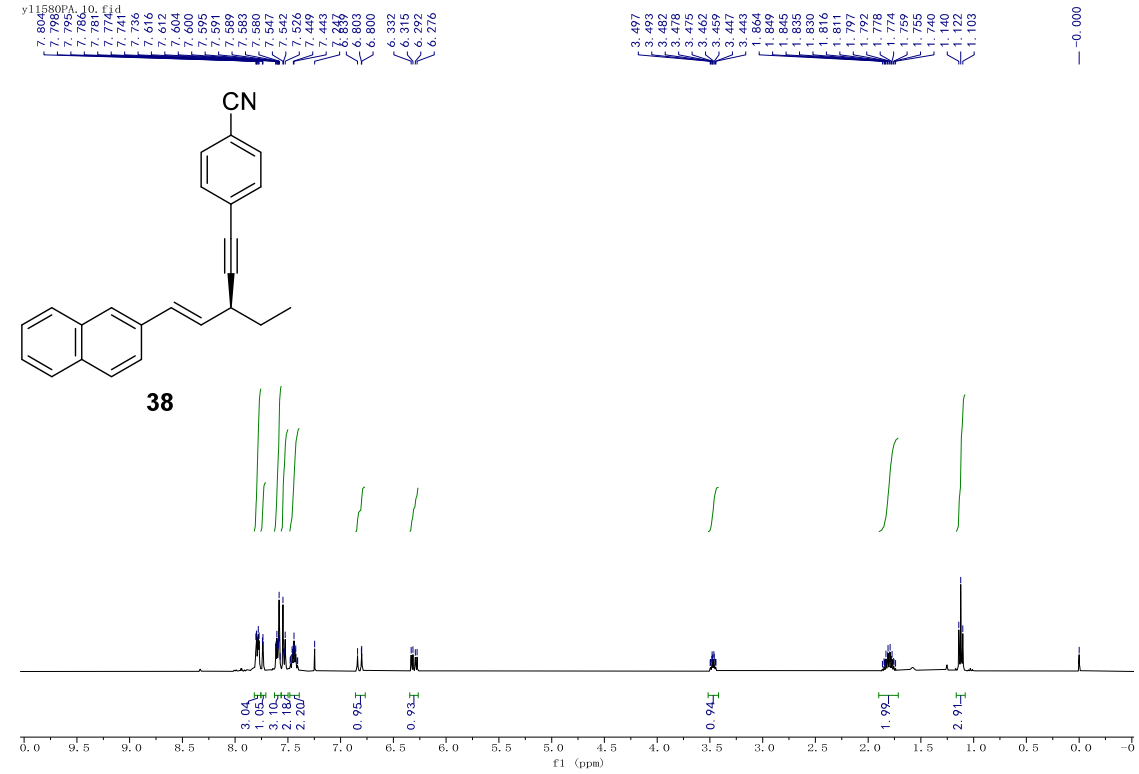
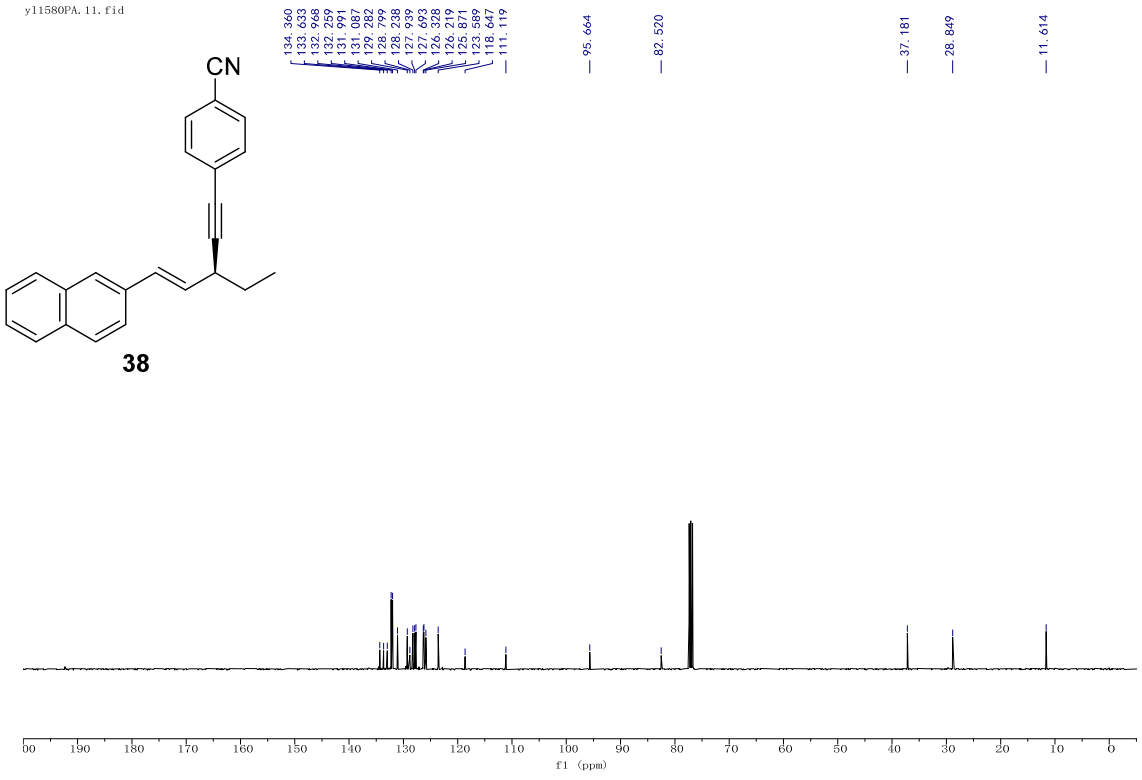
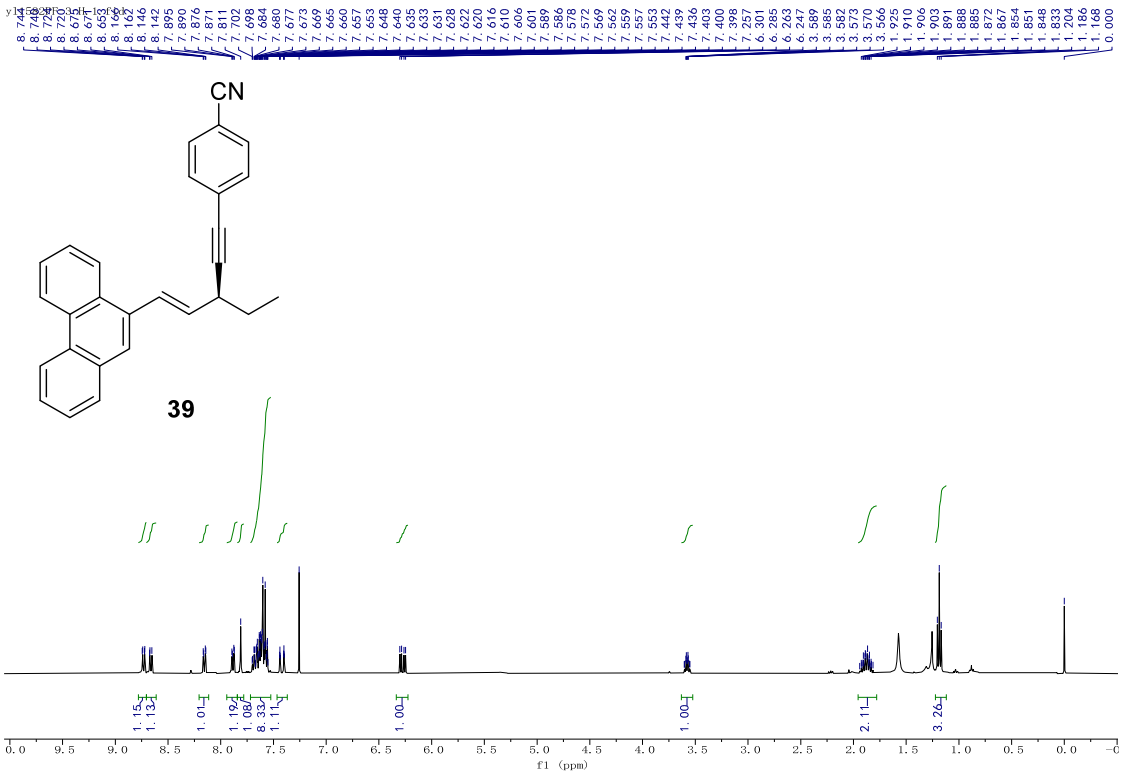



y11580PA.10.fid
CN
38
f1 (ppm)


y11580PA.11.fid
CN
38
f1 (ppm)


CN
39
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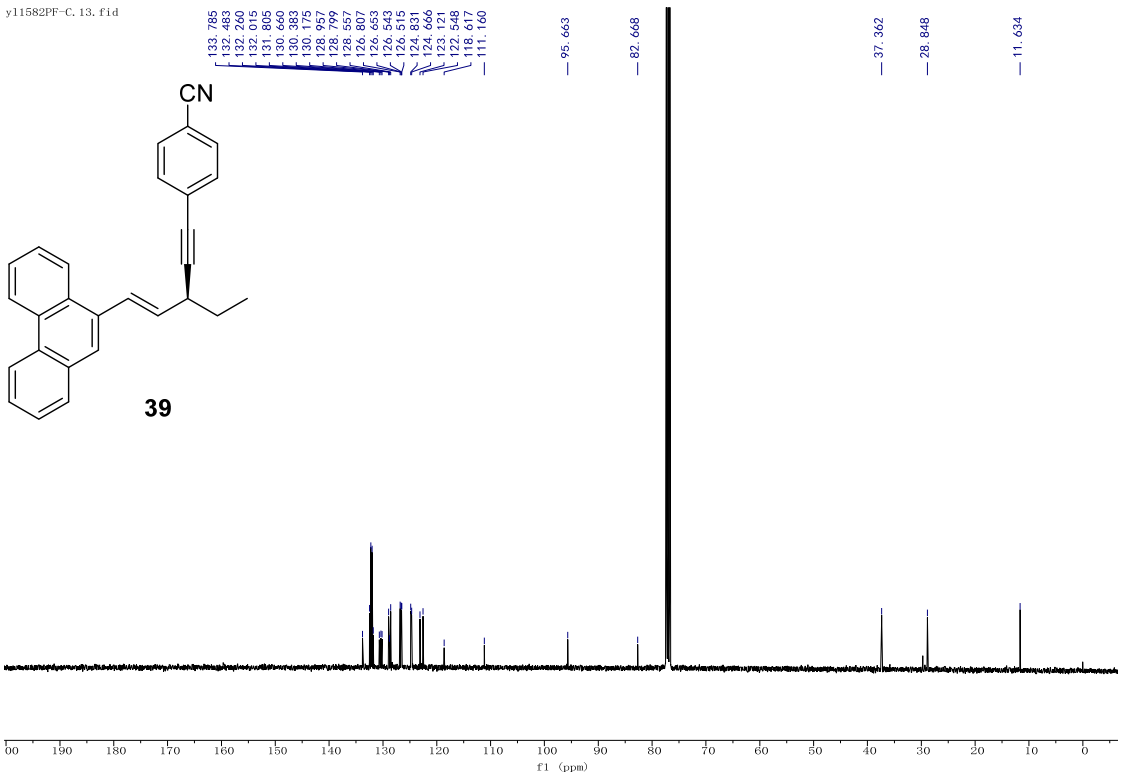
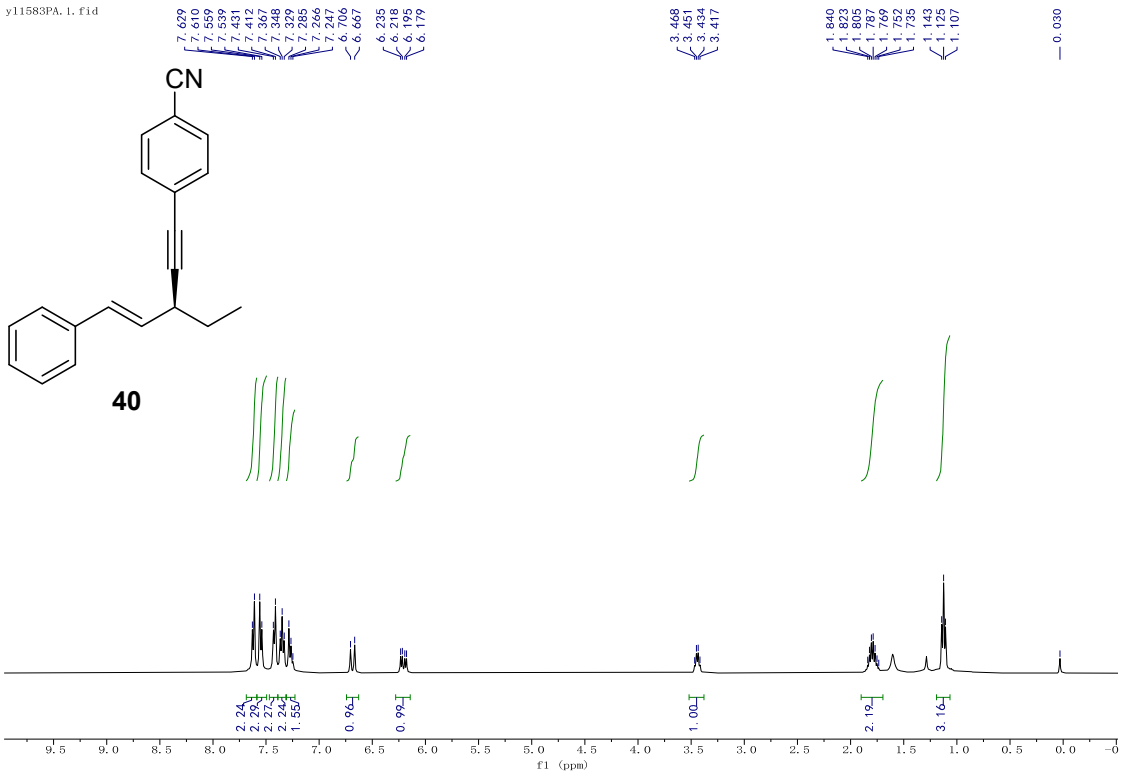
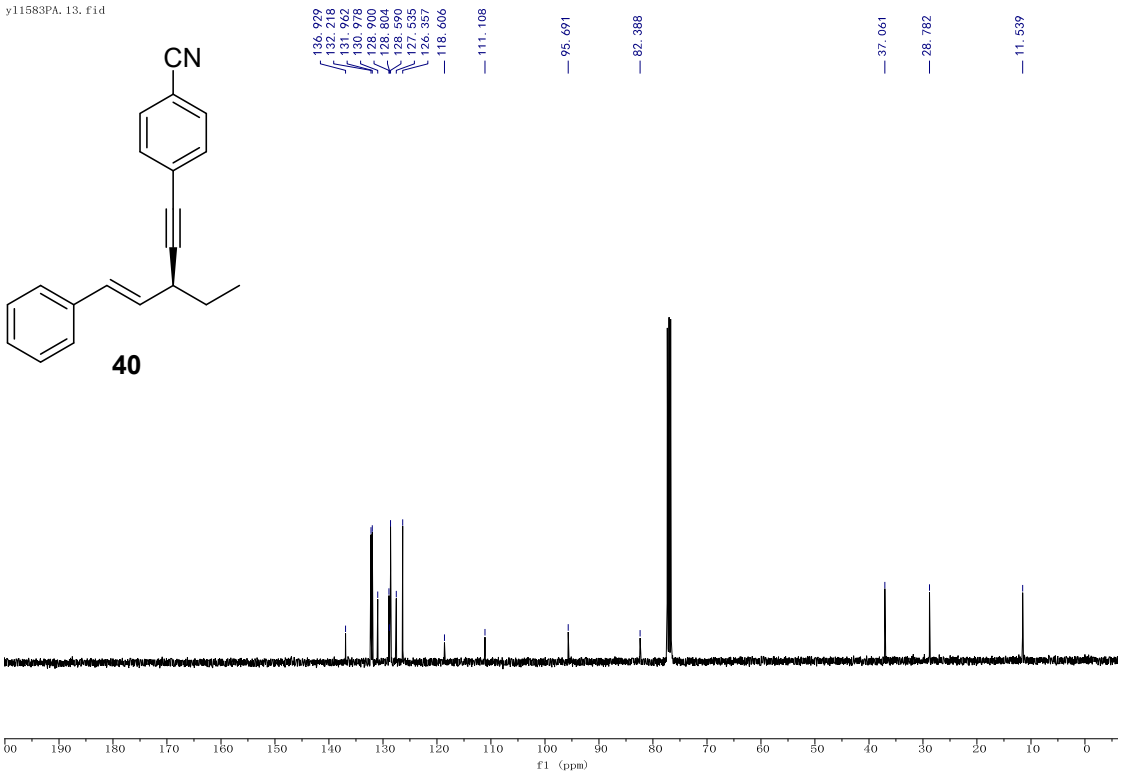
1.13
1.01
1.19
1.08
8.33
1.11
1.00
1.00
2.11
3.26
f1 (ppm)


y11582PF-C.13.fid
CN
39
95.663
82.668
37.362
28.848
11.634
f1 (ppm)


y11583PA.1.fid
7.629
7.610
7.559
7.539
7.431
7.412
7.367
7.348
7.329
7.285
7.266
7.247
6.706
6.667
6.235
6.218
6.195
6.179
3.468
3.451
3.434
3.417
1.840
1.823
1.805
1.787
1.769
1.752
1.735
1.143
1.125
1.107
0.030
CN
40
2.24
2.29
2.27
2.24
1.55
0.96
0.99
1.00
2.19
3.16
f1 (ppm)


y11583PA.13.fid
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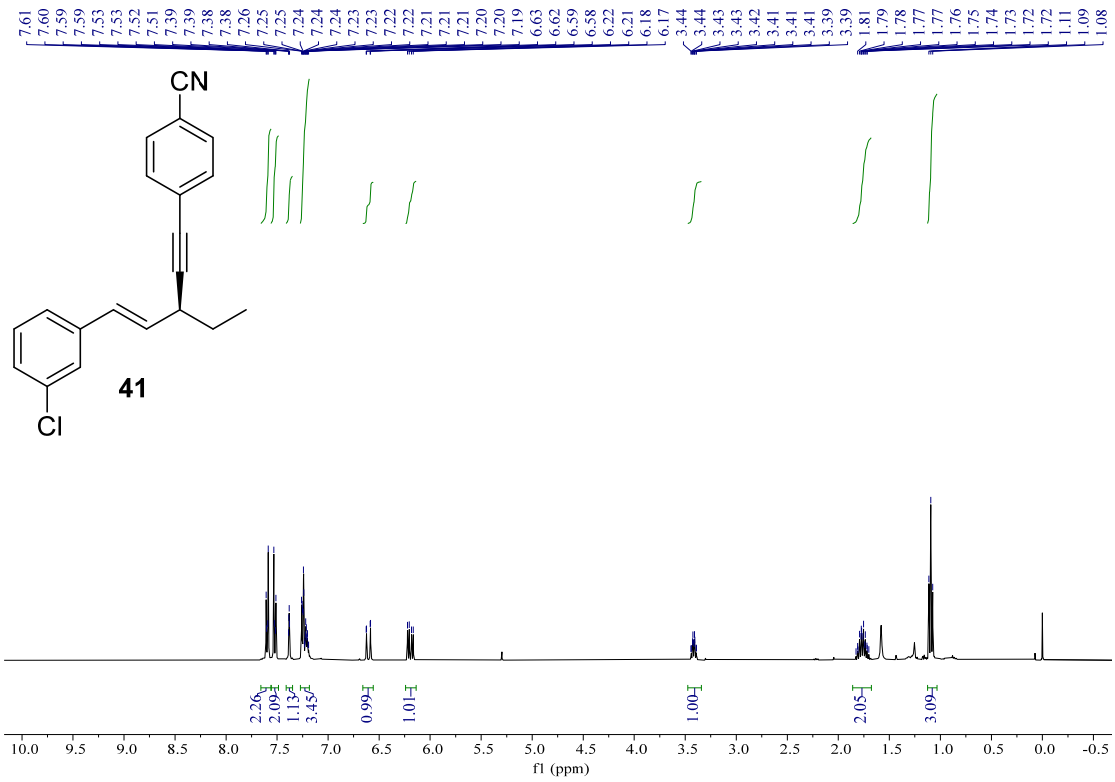
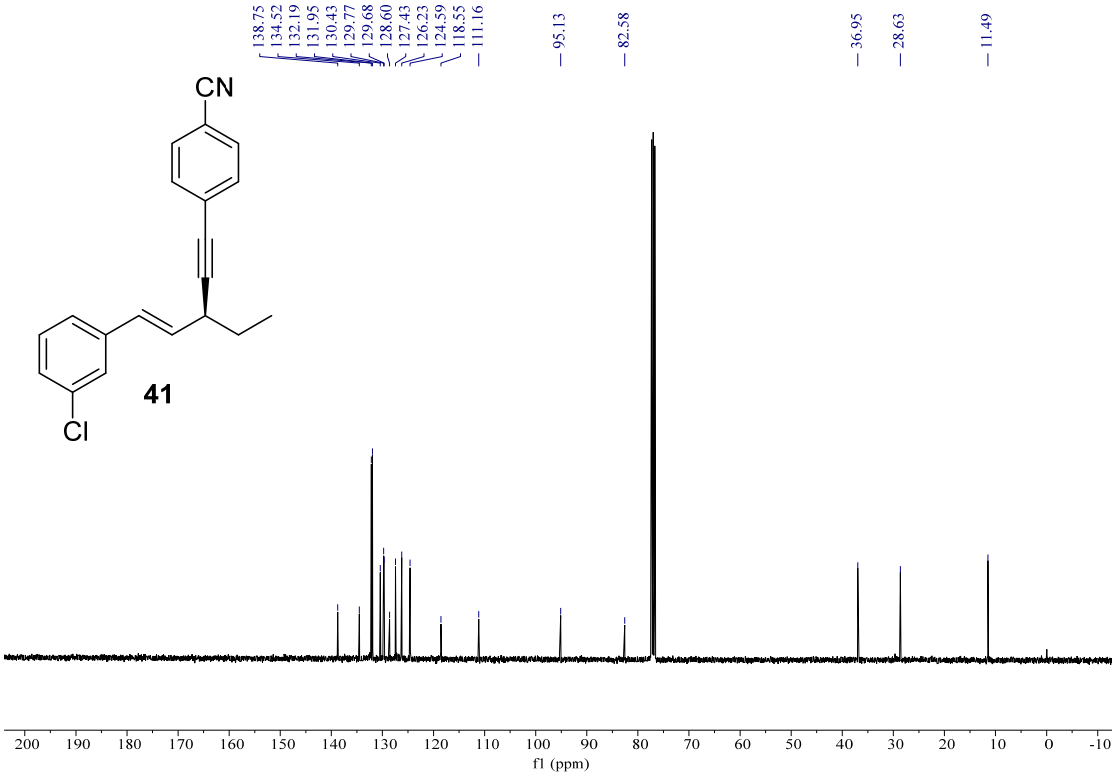
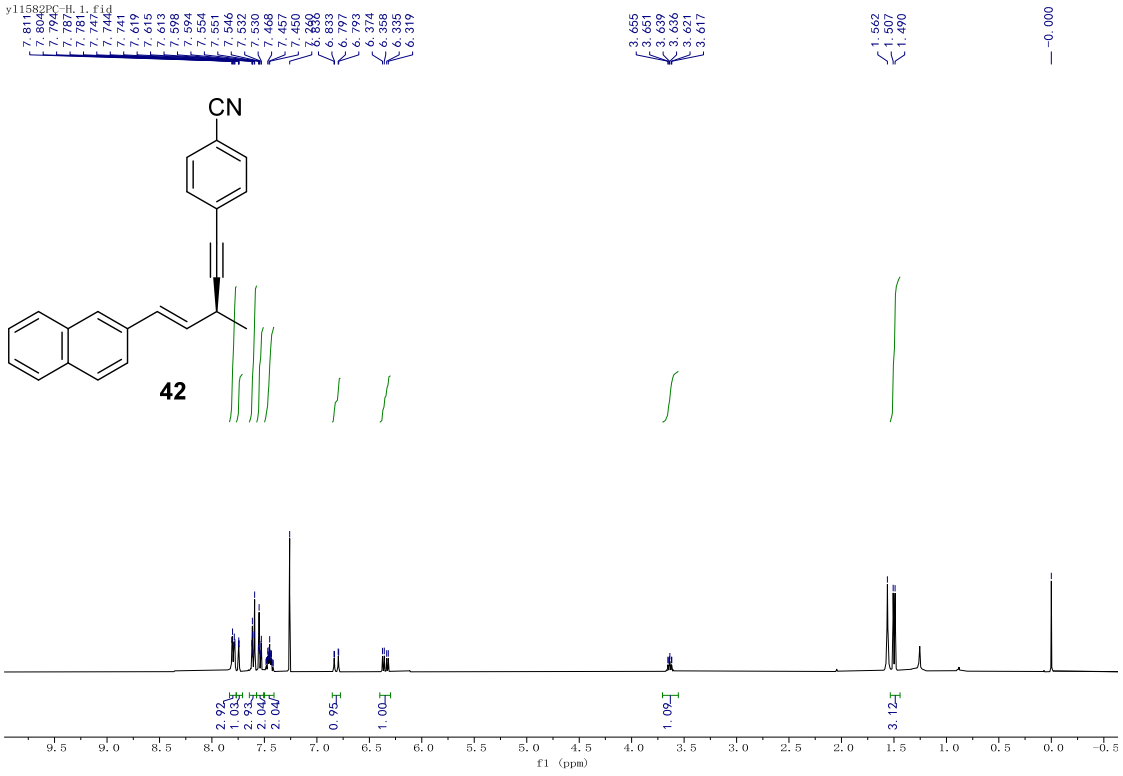
132.218
131.962
130.978
128.900
128.804
128.590
127.535
126.357
118.606
111.108
95.691
82.388
37.061
28.782
11.539
CN
40
f1 (ppm)


CN
41
Cl
fl (ppm)


CN
41
Cl
fl (ppm)


y11582PC-H.1.fid
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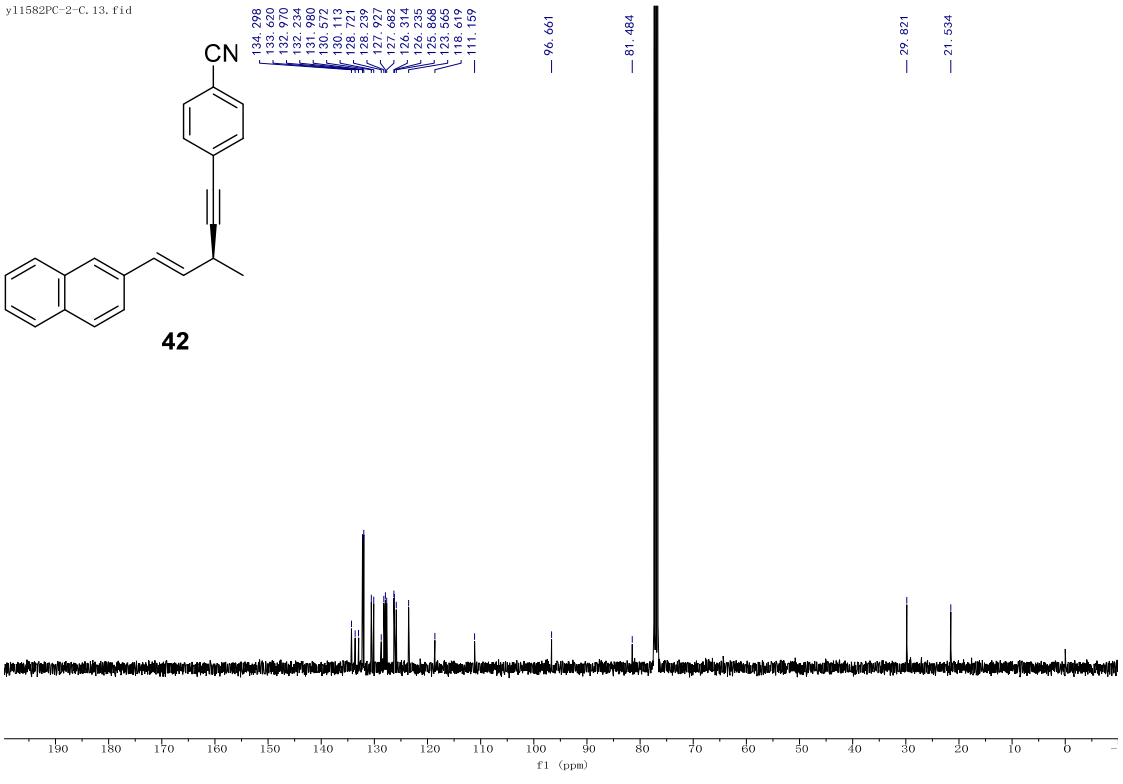
7.804
7.794
7.787
7.781
7.747
7.744
7.741
7.619
7.615
7.613
7.598
7.594
7.554
7.551
7.546
7.532
7.530
7.468
7.457
7.450
6.833
6.797
6.793
6.374
6.358
6.335
6.319
3.655
3.651
3.639
3.636
3.621
3.617
1.562
1.507
1.490
-0.000
CN
42
2.92
1.03
2.93
2.04
2.04
0.95
1.00
1.09
3.12
f1 (ppm)


y11582PC-2-C.13.fid
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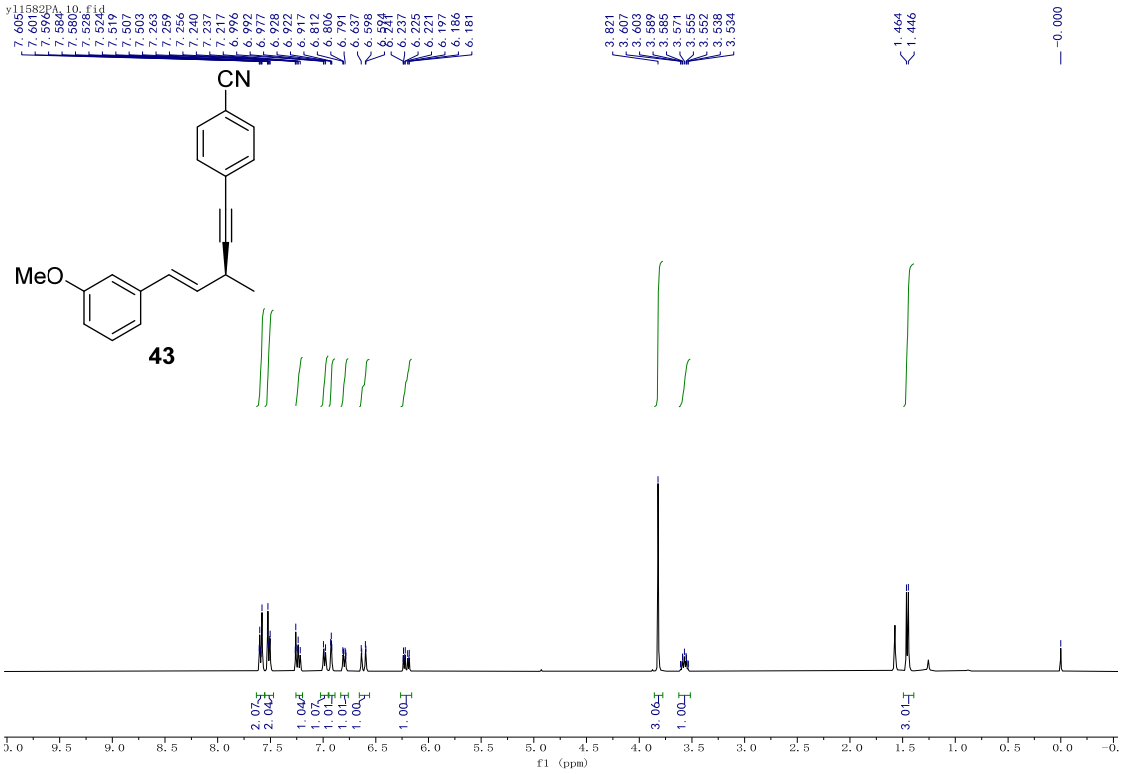
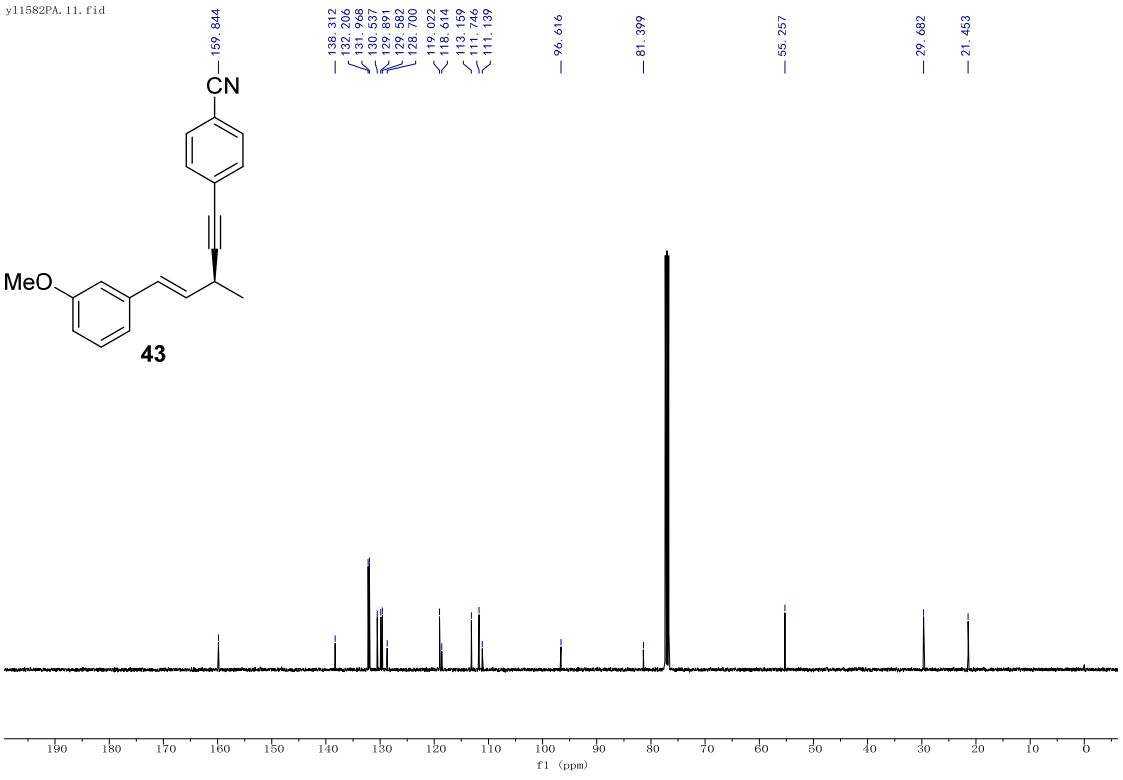
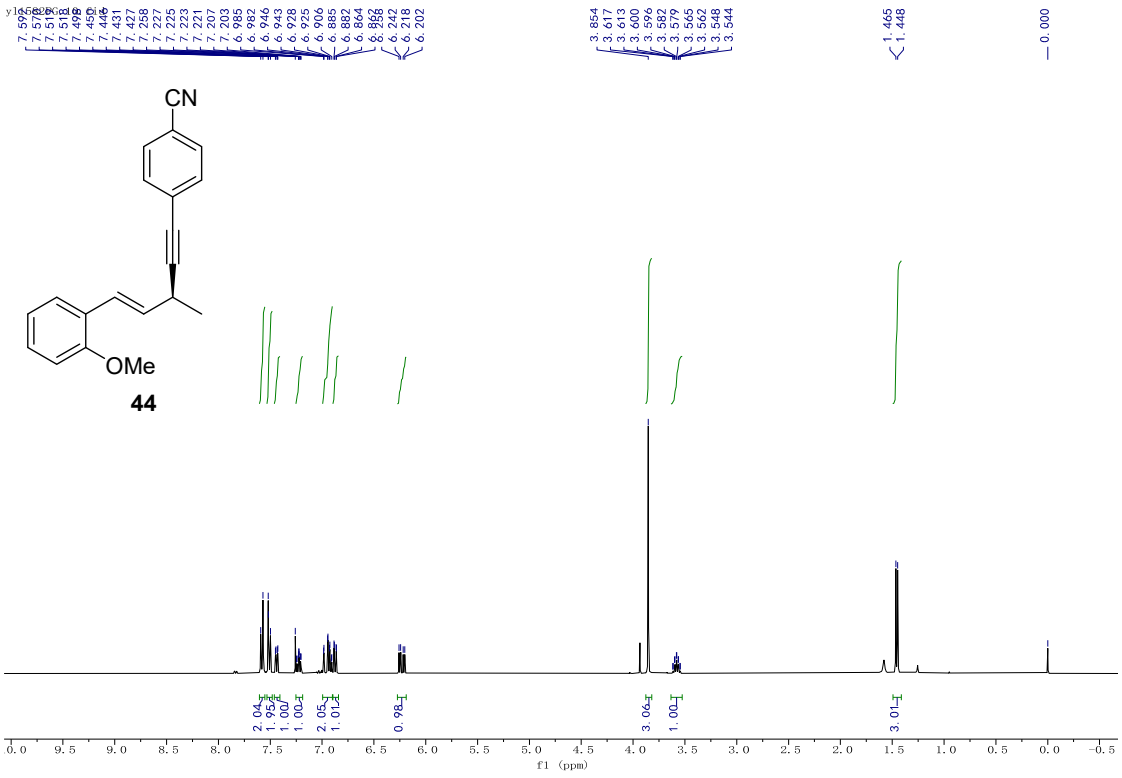
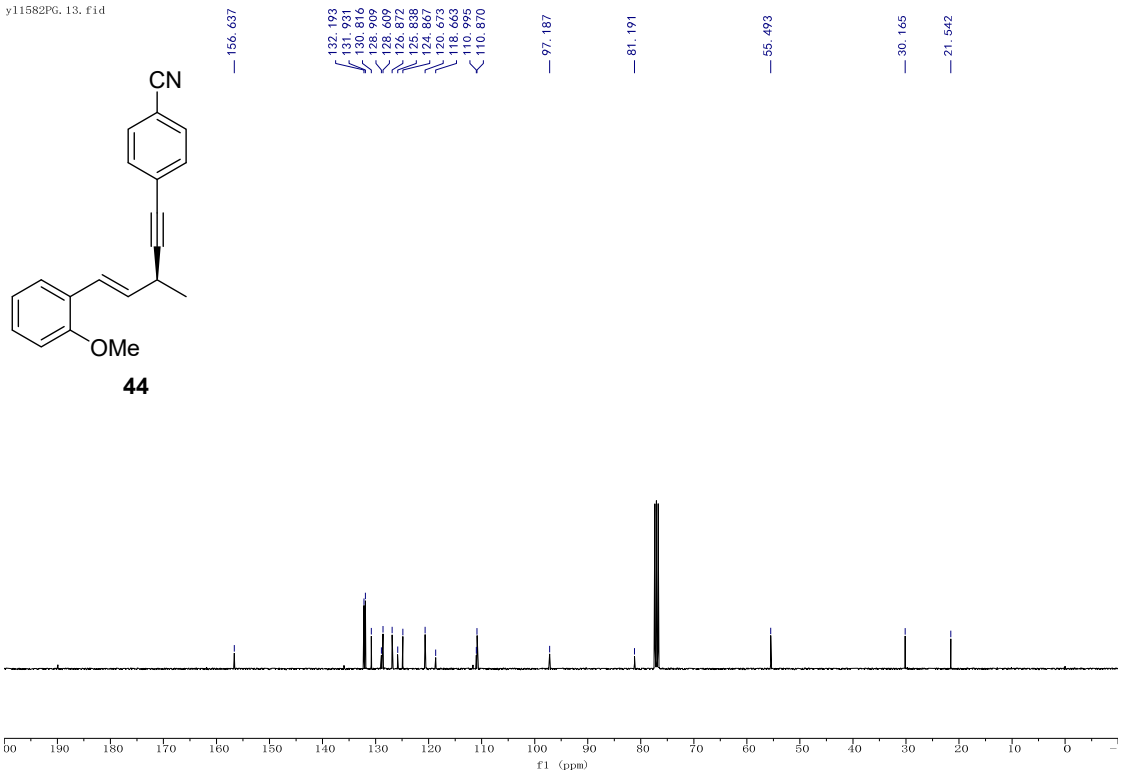
133.620
132.970
132.234
131.980
131.572
130.113
128.721
128.239
127.927
127.682
126.314
126.235
125.868
123.565
118.619
111.159
96.661
81.484
29.821
21.534
CN
42
f1 (ppm)

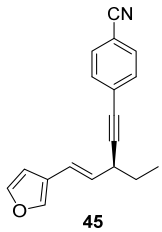

y11582PA.10.fid
CN
MeO
43
f1 (ppm)


y11582PA.11.fid
CN
MeO
43
f1 (ppm)


CN
OMe
44
f1 (ppm)


CN
OMe
44
f1 (ppm)

y11561PC-HC.10.fid



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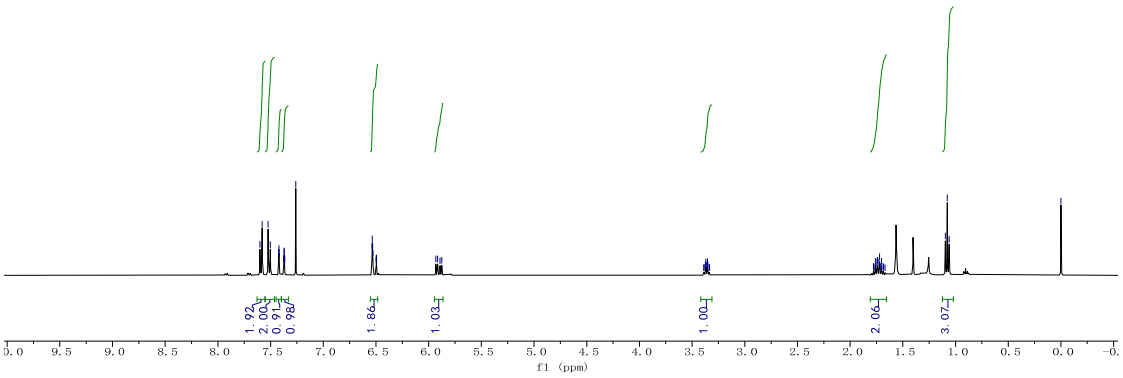
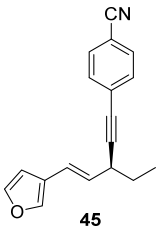


y11561PC-HC.13.fid



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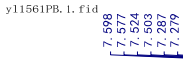
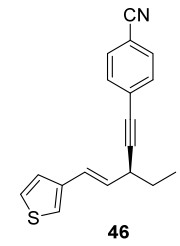
y11561PB.1.fid





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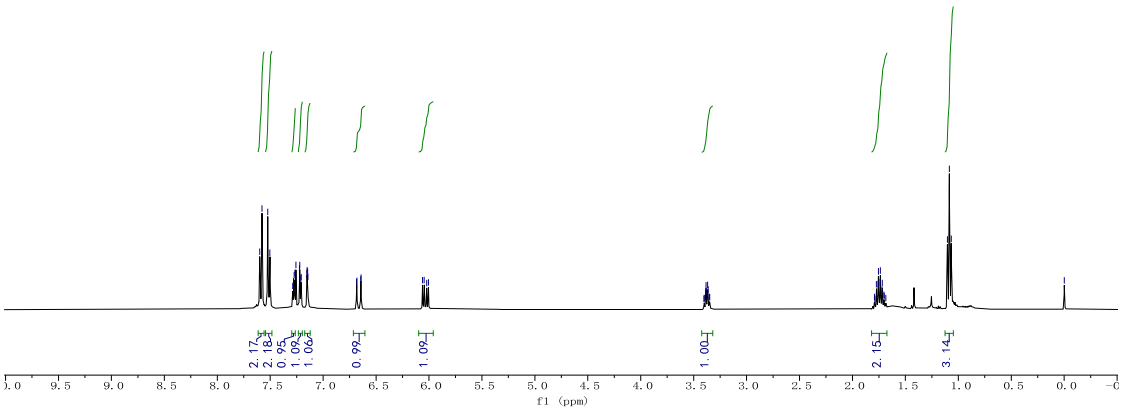

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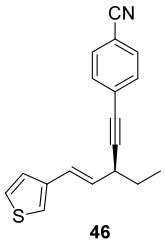

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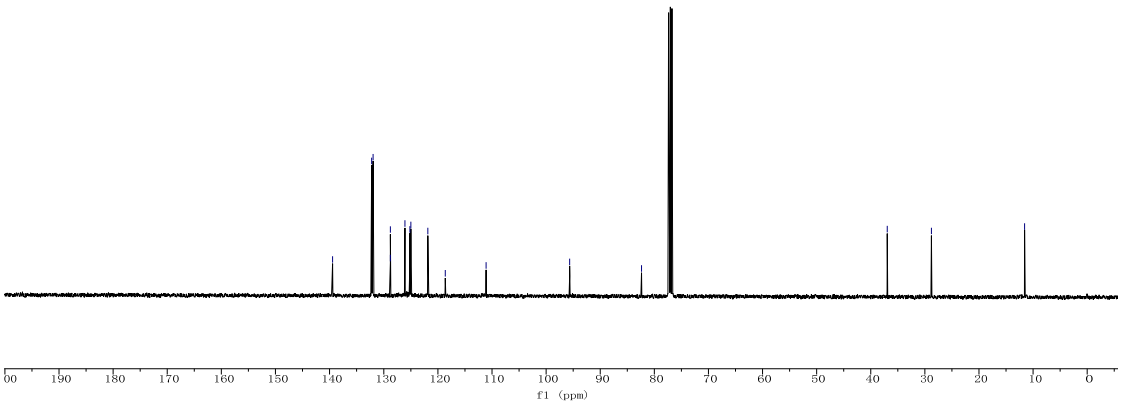

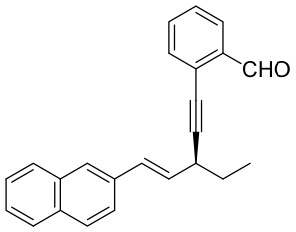

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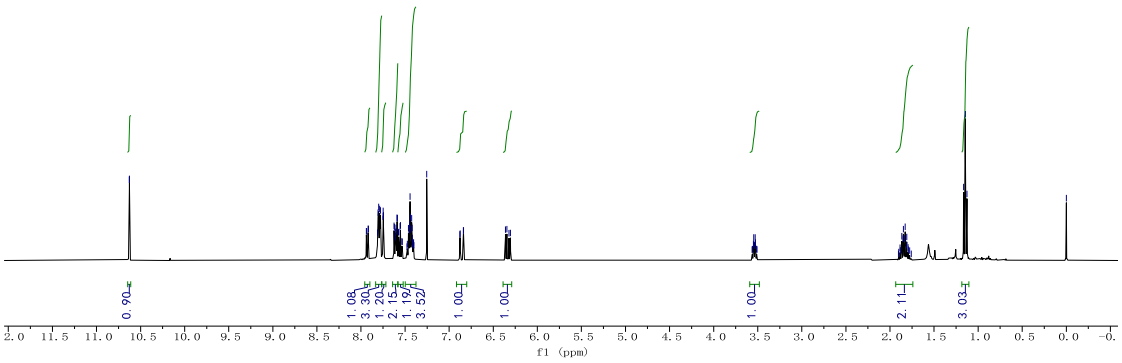
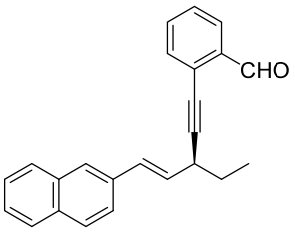
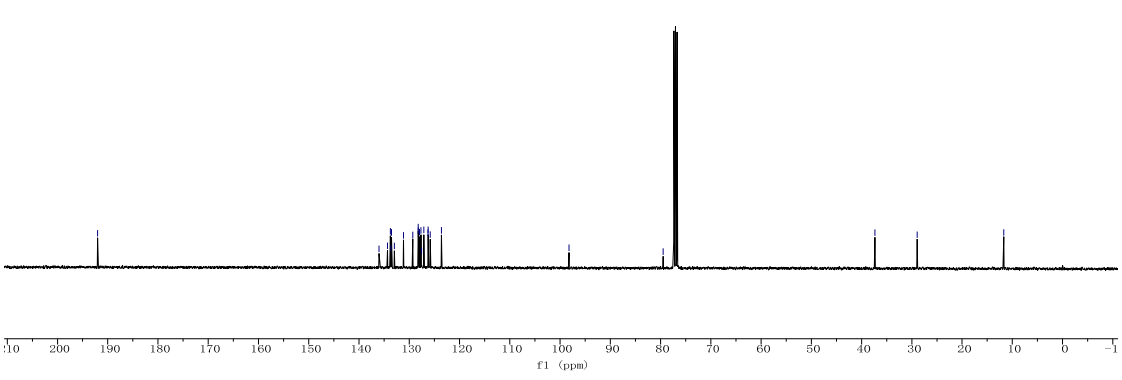
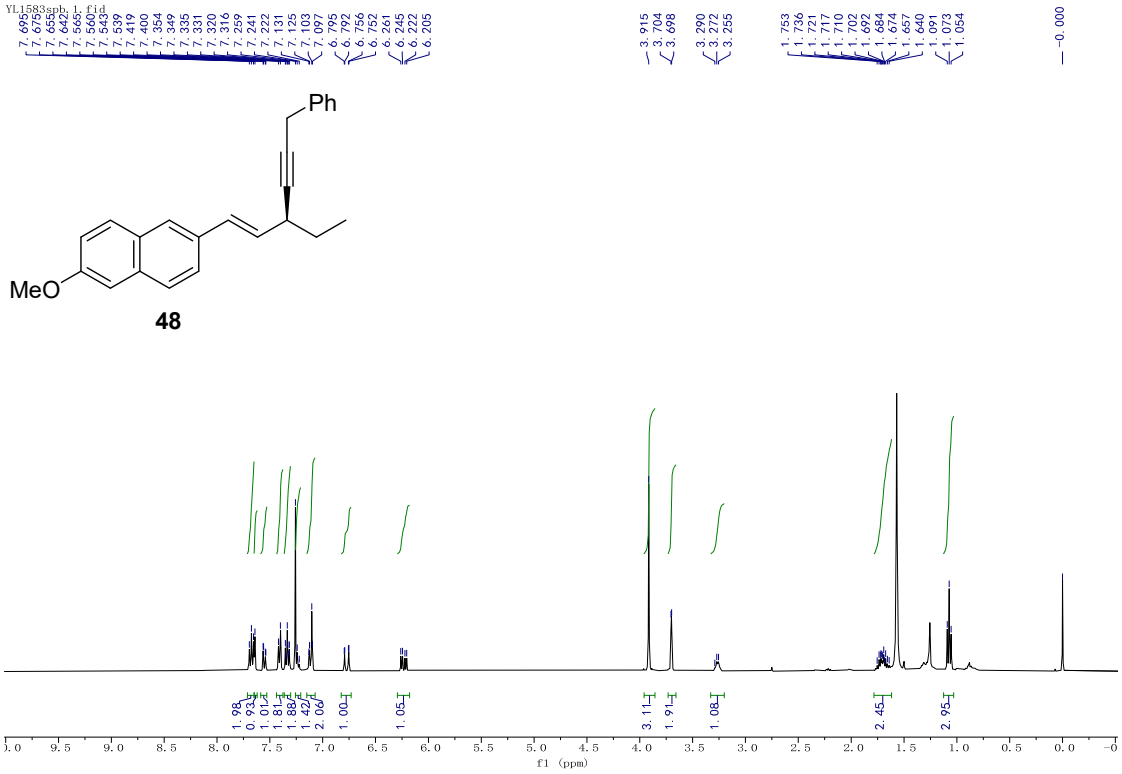
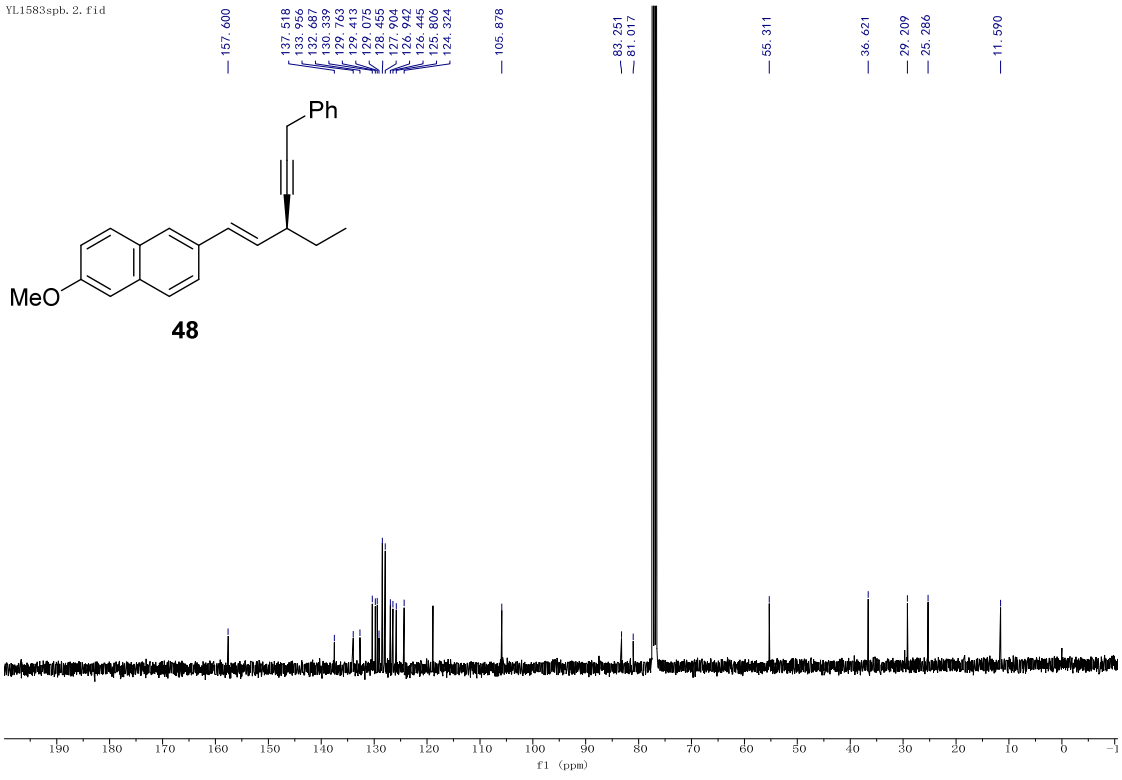


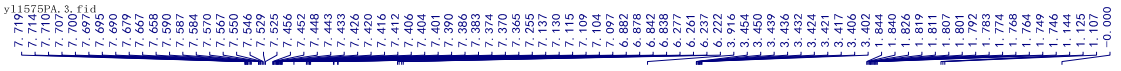


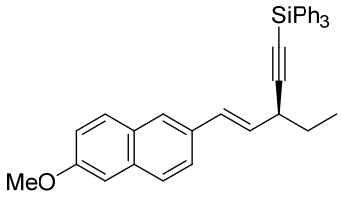
47



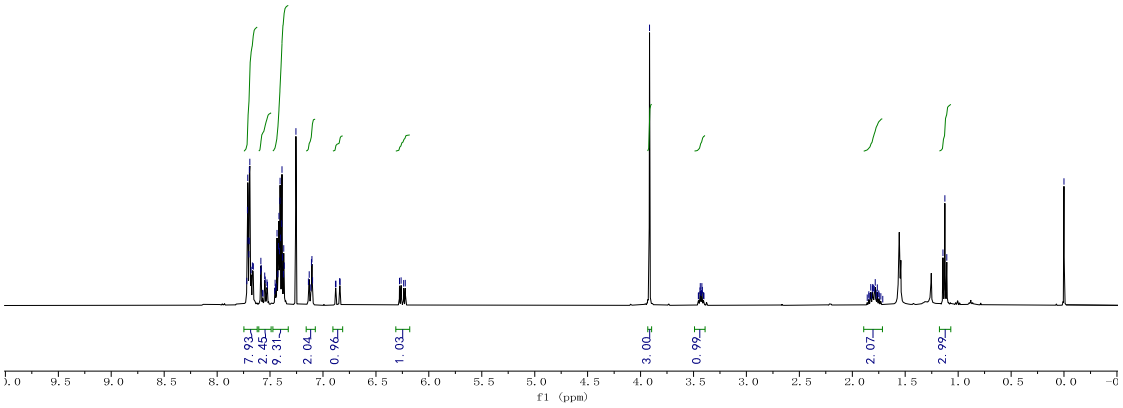

YL1583spb.1.fid
Ph
MeO
48
f1 (ppm)

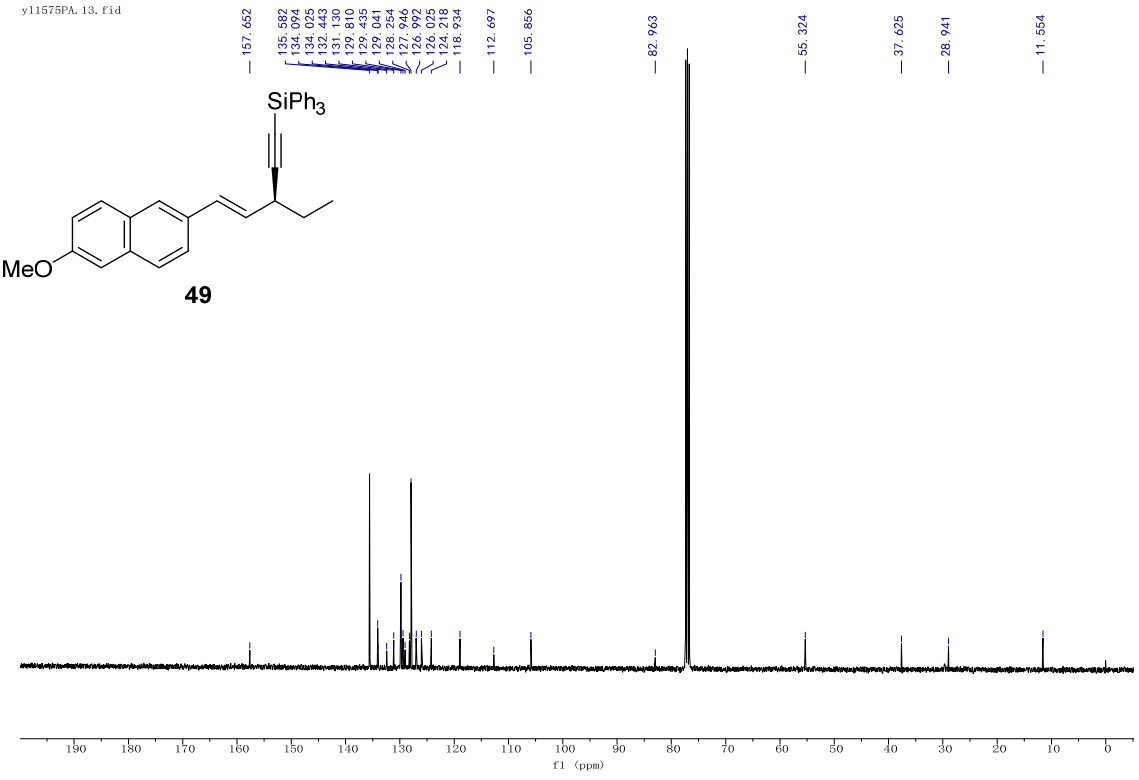

YL1583spb.2.fid
Ph
MeO
48
f1 (ppm)


y11575PA.3.fid


SiPh3
MeO

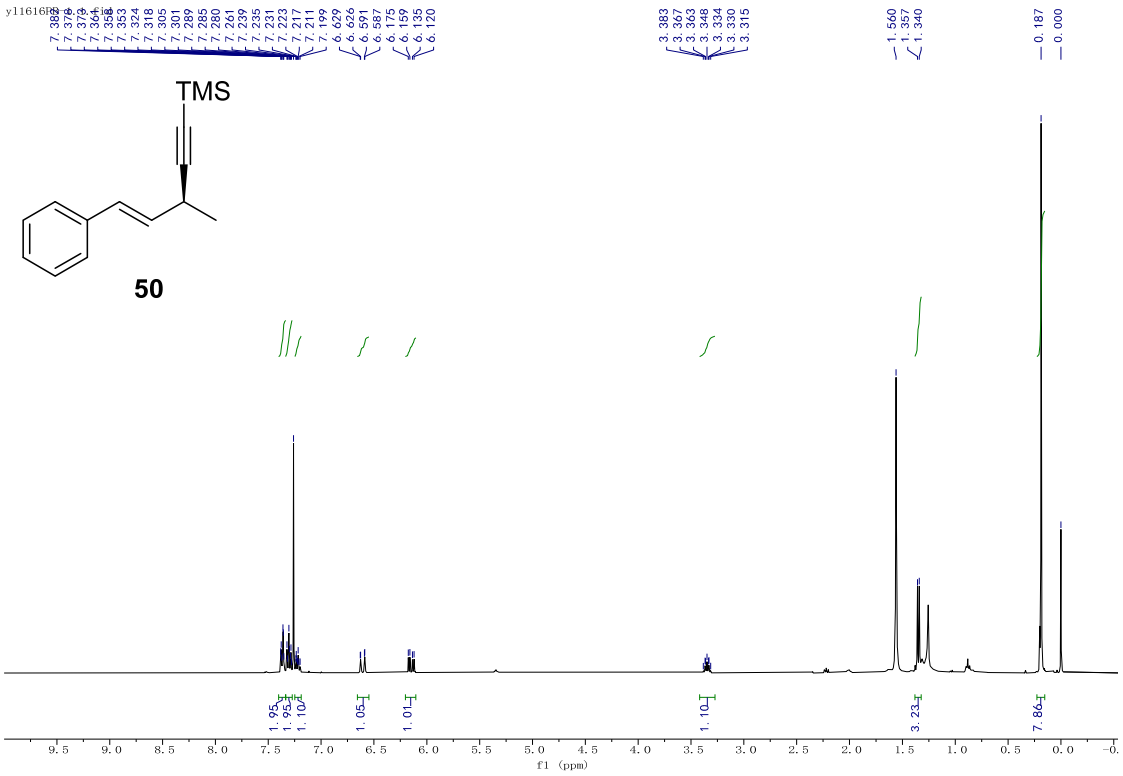
49

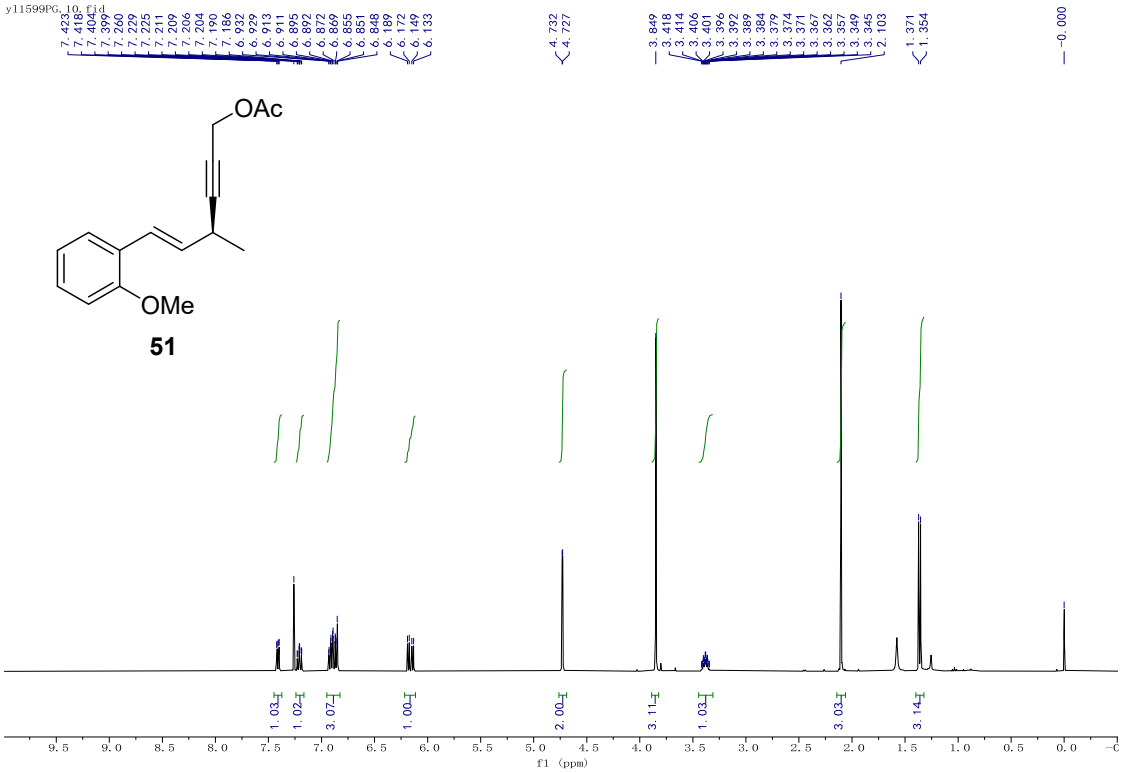

7.93
2.45
9.31
2.04
0.96
1.03
3.00
0.99
2.07
2.99
f1 (ppm)

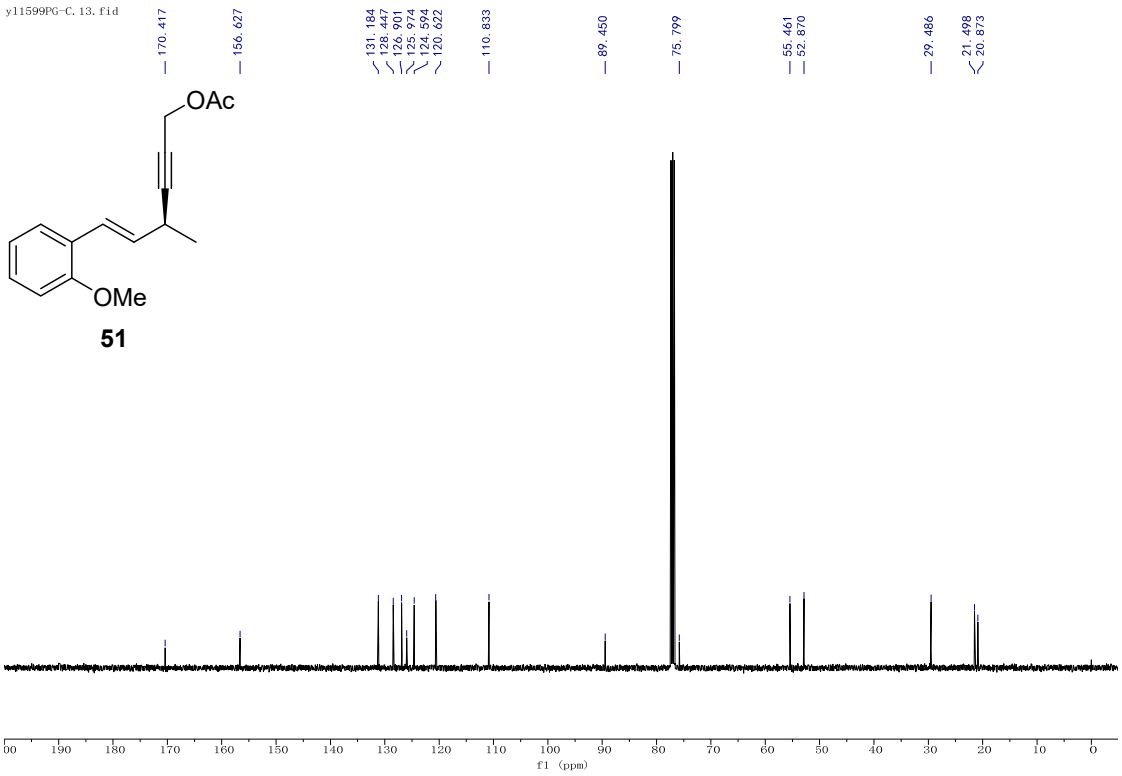

y11575PA.13.fid
157.652
135.582
134.094
134.025
132.443
131.130
129.810
129.435
129.041
128.254
127.946
126.992
126.025
124.218
118.934
112.697
105.856
82.963
55.324
37.625
28.941
11.554
f1 (ppm)

SiPh3
MeO

49


TMS
50
f1 (ppm)


OAc
OMe
51
f1 (ppm)


y11599PG-C.13.fid
170.417
156.627
131.184
128.447
126.901
125.974
124.594
120.622
110.833
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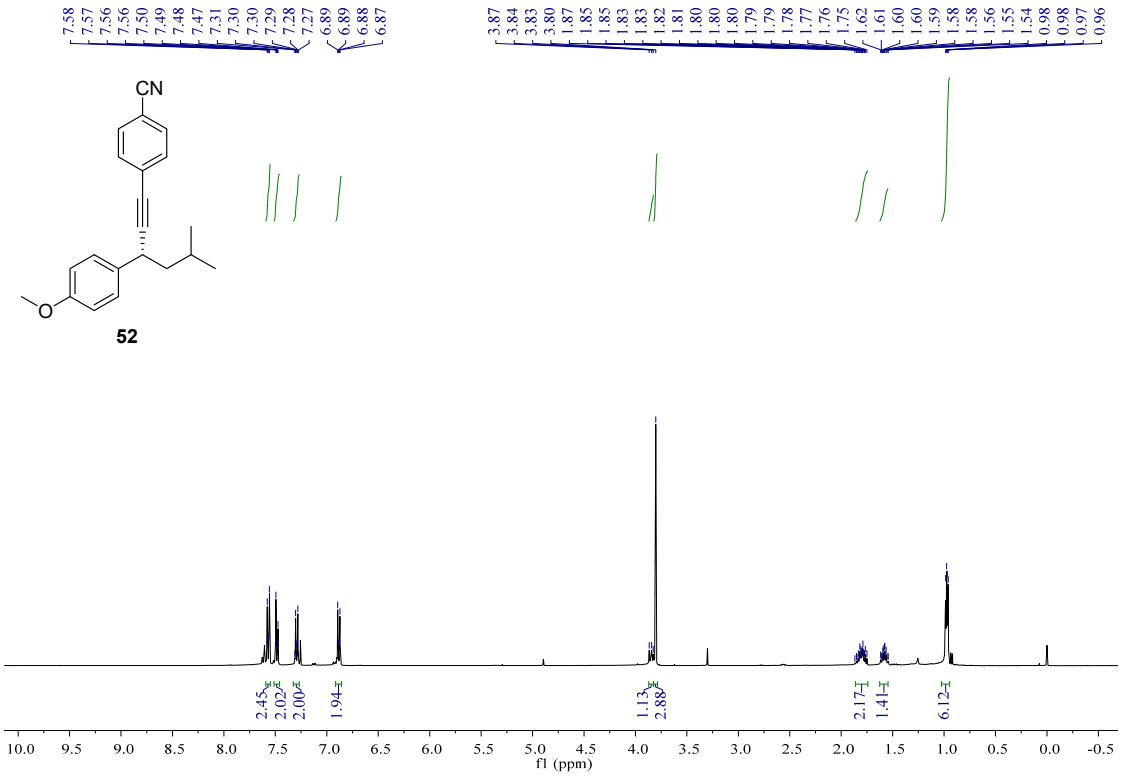
75.799
55.461
52.870
29.486
21.498
20.873
OAc
OMe
51
f1 (ppm)


7.58
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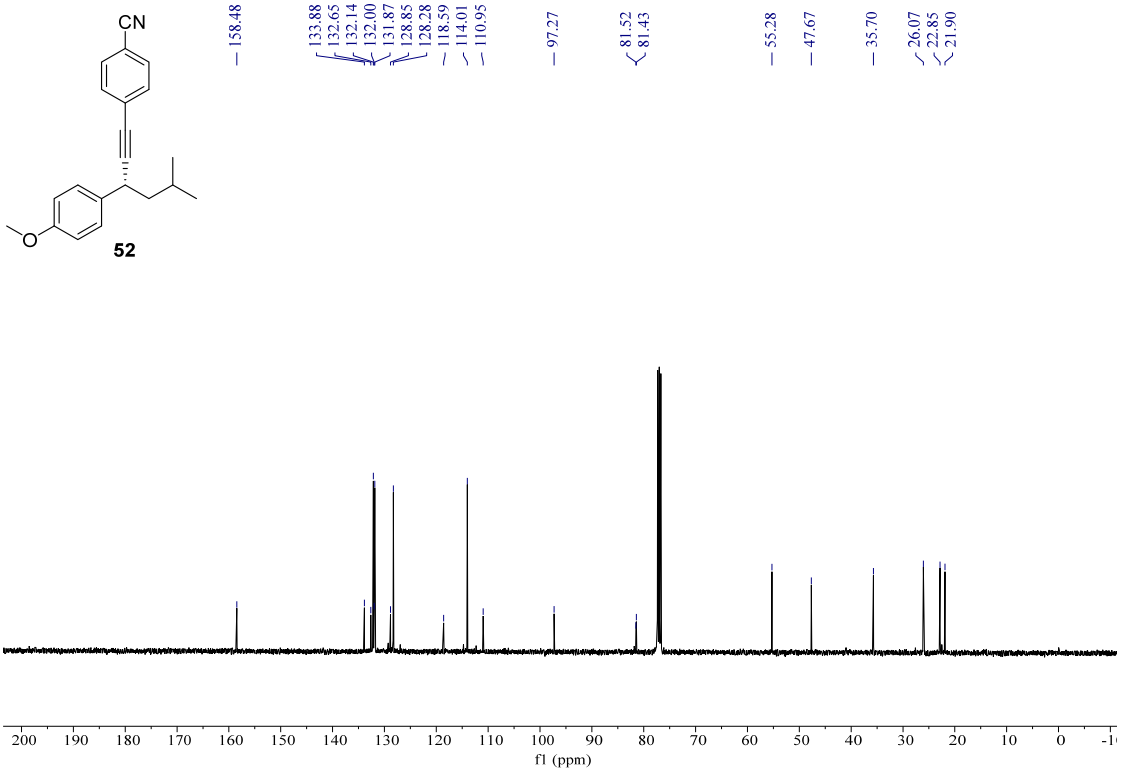
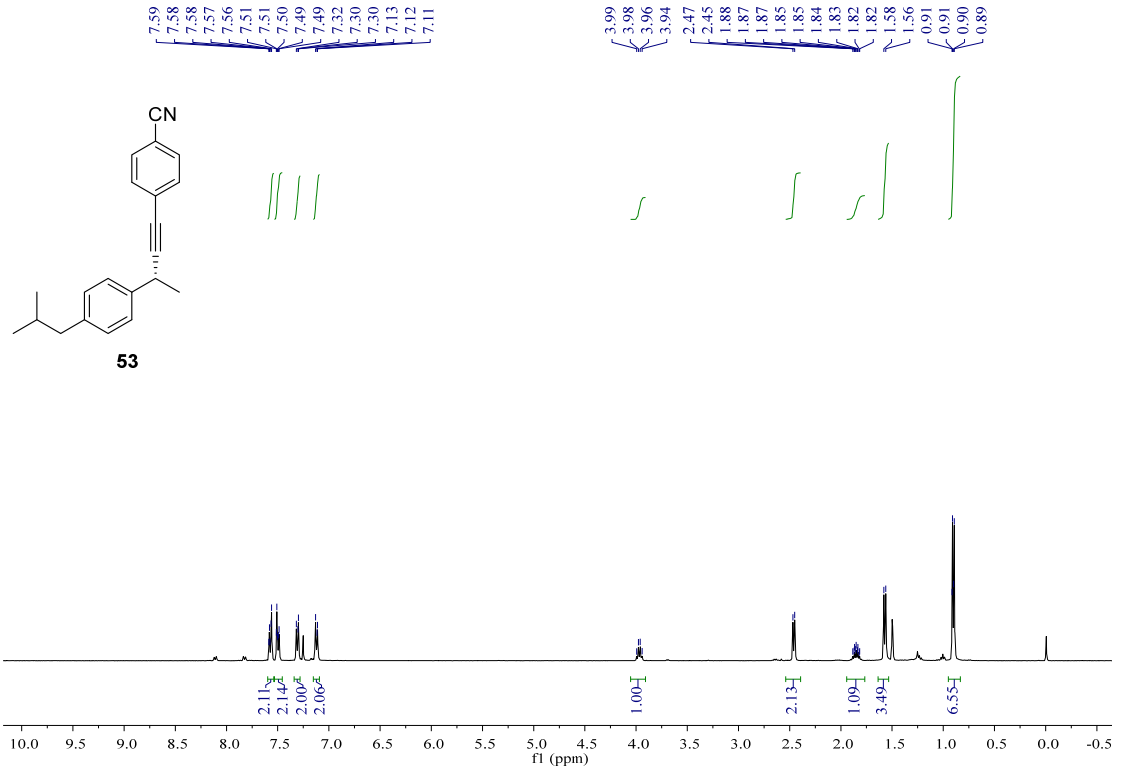
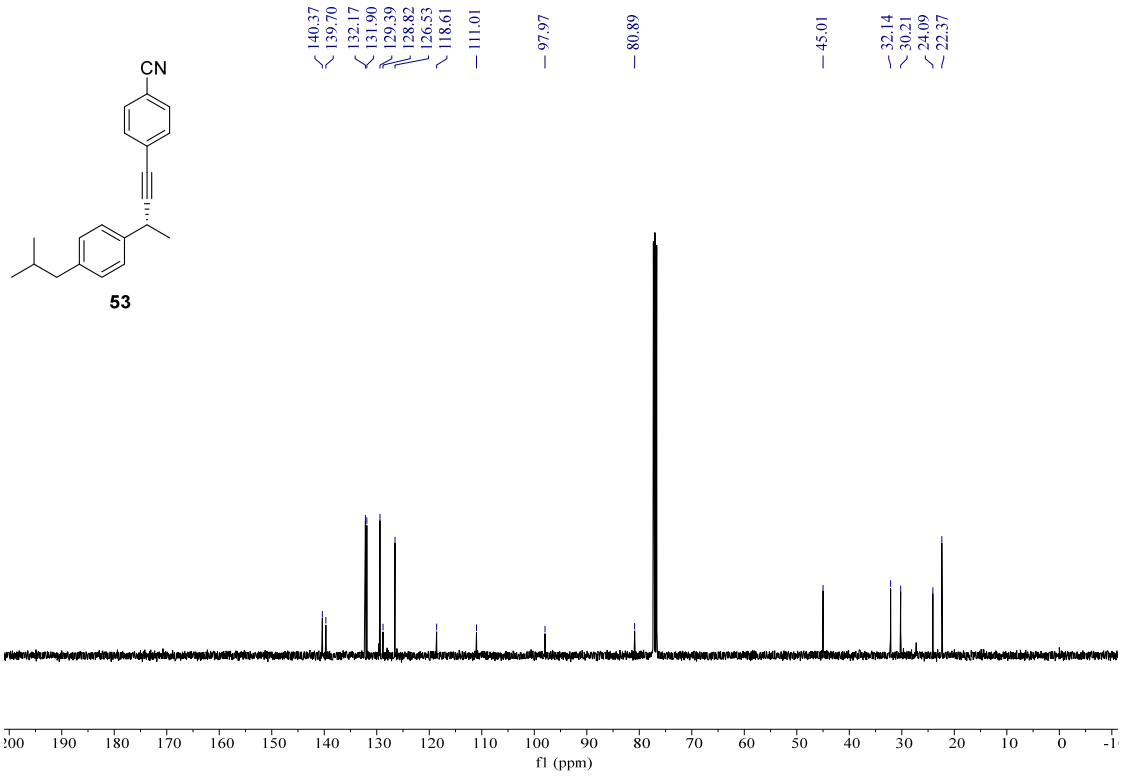
7.56
7.56
7.50
7.49
7.48
7.47
7.31
7.30
7.30
7.29
7.28
7.27
6.89
6.89
6.88
6.87
3.87
3.84
3.83
3.80
1.87
1.85
1.85
1.83
1.83
1.82
1.81
1.80
1.80
1.80
1.79
1.79
1.78
1.77
1.76
1.75
1.62
1.61
1.60
1.60
1.59
1.58
1.58
1.56
1.55
1.54
0.98
0.98
0.97
0.96
CN
O
52
2.45
2.02
2.00
1.94
1.13
2.88
2.17
1.41
6.12
f1 (ppm)

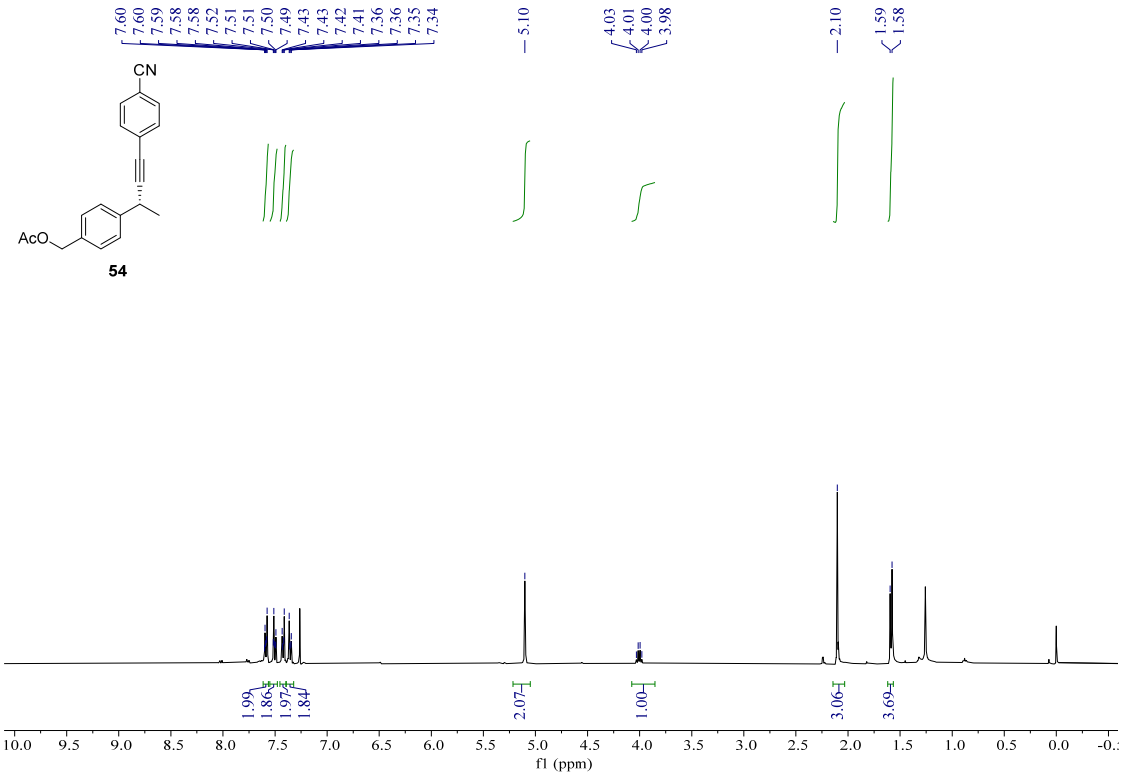

CN
O
158.48
133.88
132.65
132.14
132.00
131.87
128.85
128.28
118.59
114.01
110.95
97.27
81.52
81.43
55.28
47.67
35.70
26.07
22.85
21.90
f1 (ppm)

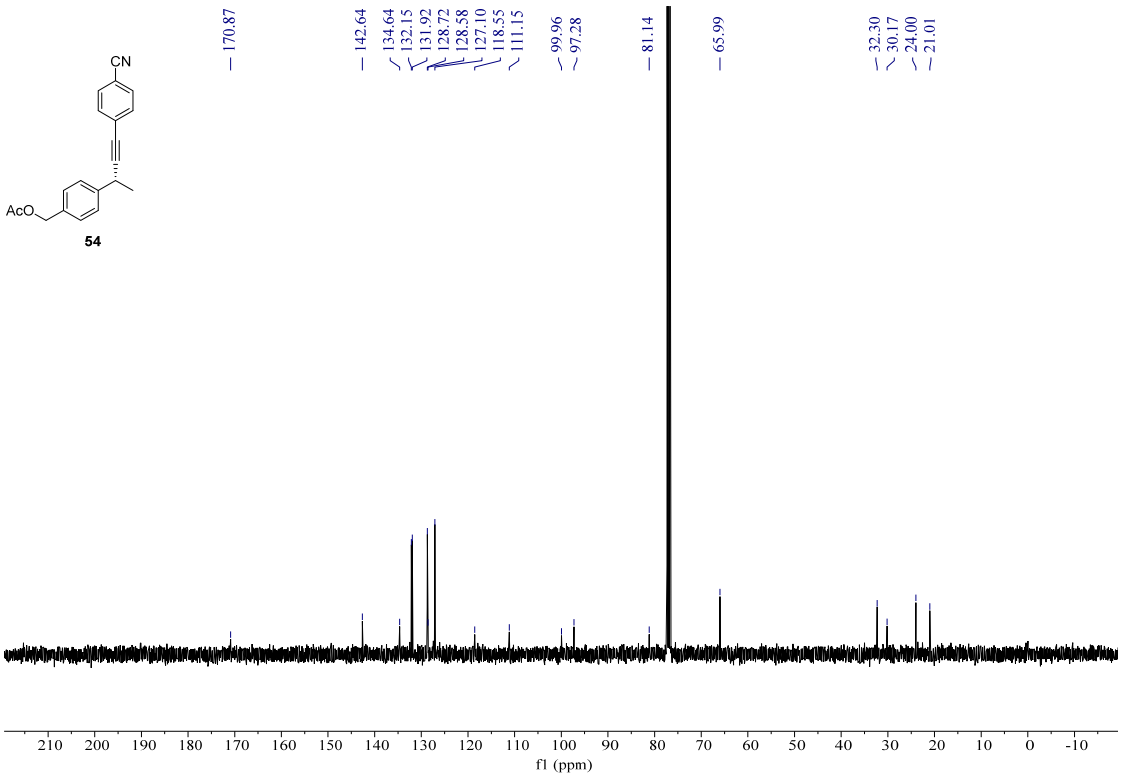
52

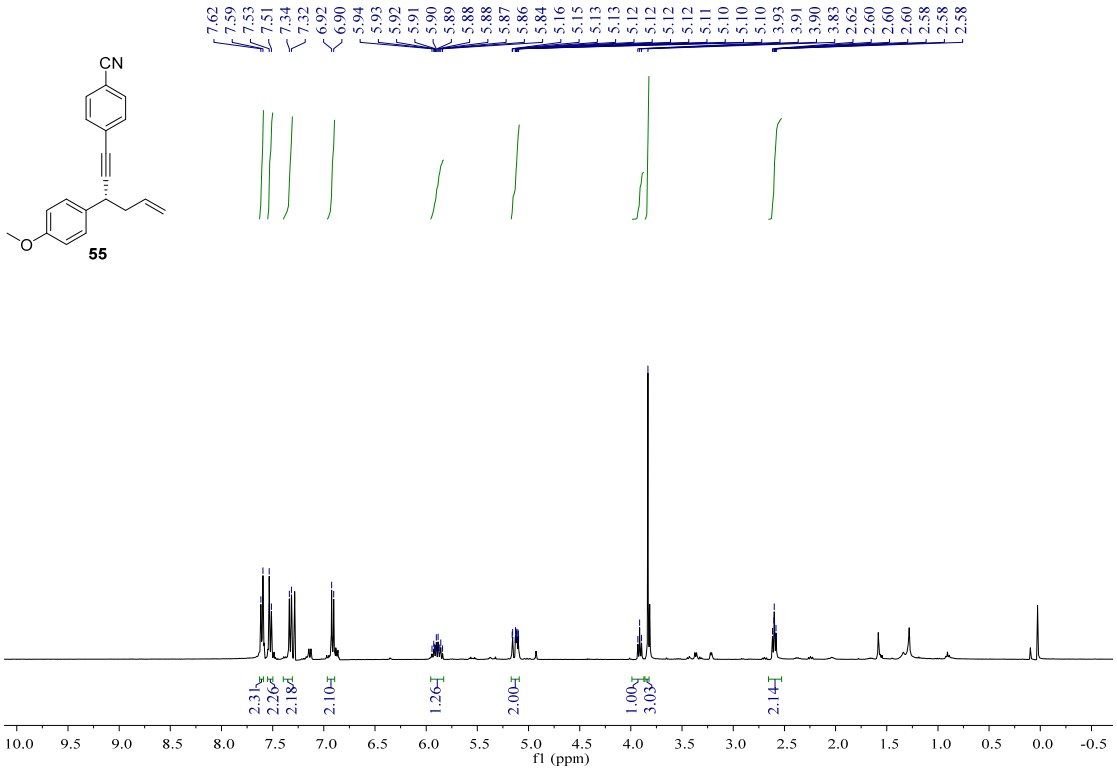

CN
7.59
7.58
7.58
7.57
7.56
7.51
7.51
7.50
7.49
7.49
7.32
7.30
7.30
7.13
7.12
7.11
3.99
3.98
3.96
3.94
2.47
2.45
1.88
1.87
1.87
1.85
1.85
1.84
1.83
1.82
1.82
1.58
1.56
0.91
0.90
0.89
2.11
2.14
2.00
2.06
1.00
2.13
1.09
3.49
6.55
f1 (ppm)

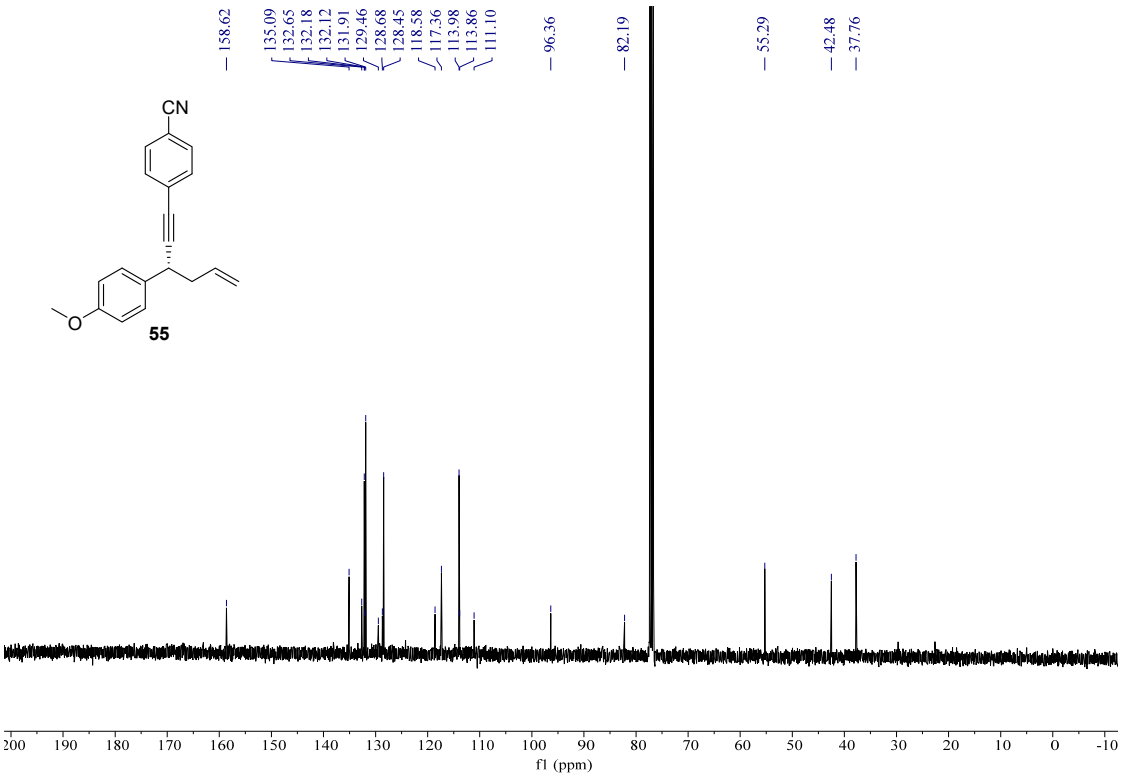
53

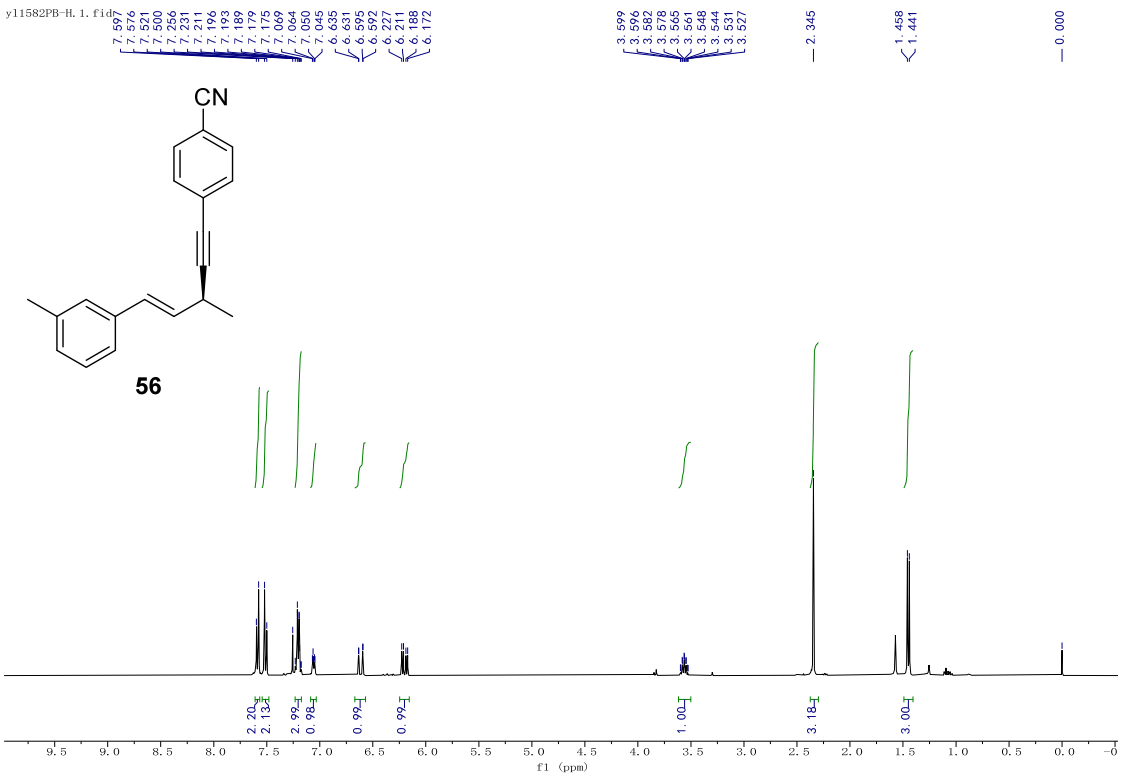

CN
53
140.37
139.70
132.17
131.90
129.39
128.82
126.53
118.61
111.01
97.97
80.89
45.01
32.14
30.21
24.09
22.37
f1 (ppm)


CN
AcO
54
7.60
7.60
7.59
7.58
7.58
7.52
7.51
7.51
7.50
7.49
7.43
7.43
7.42
7.41
7.36
7.36
7.35
7.34
5.10
4.03
4.01
4.00
3.98
2.10
1.59
1.58
1.99
1.86
1.97
1.84
2.07
1.00
3.06
3.69
f1 (ppm)

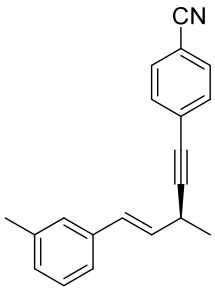

CN
AcO
54
170.87
142.64
134.64
132.15
131.92
128.72
128.58
127.10
118.55
111.15
99.96
97.28
81.14
65.99
32.30
30.17
24.00
21.01
fl (ppm)


CN
O
55
7.62
7.59
7.53
7.51
7.34
7.32
6.92
6.90
5.94
5.93
5.92
5.91
5.90
5.89
5.88
5.88
5.87
5.86
5.84
5.16
5.15
5.13
5.13
5.12
5.12
5.12
5.12
5.11
5.10
5.10
5.10
3.93
3.91
3.90
3.83
2.62
2.60
2.60
2.60
2.58
2.58
2.58
2.31
2.26
2.18
2.10
1.26
2.00
1.00
3.03
2.14
fl (ppm)


158.62
135.09
132.65
132.18
132.12
131.91
129.46
128.68
128.45
118.58
117.36
113.98
113.86
111.10
96.36
82.19
55.29
42.48
37.76
CN
O
55
f1 (ppm)

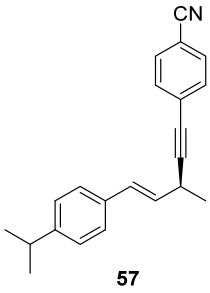

y11582PB-H.1.fid
7.597
7.576
7.521
7.500
7.236
7.231
7.211
7.196
7.193
7.189
7.179
7.175
7.069
7.064
7.050
7.045
6.635
6.631
6.595
6.592
6.227
6.211
6.188
6.172
3.599
3.596
3.582
3.578
3.565
3.561
3.548
3.544
3.531
3.527
2.345
1.458
1.441
0.000
CN
56
2.20
2.13
2.98
0.98
0.99
0.99
1.00
3.18
3.00
f1 (ppm)

y11582PB.11.fid

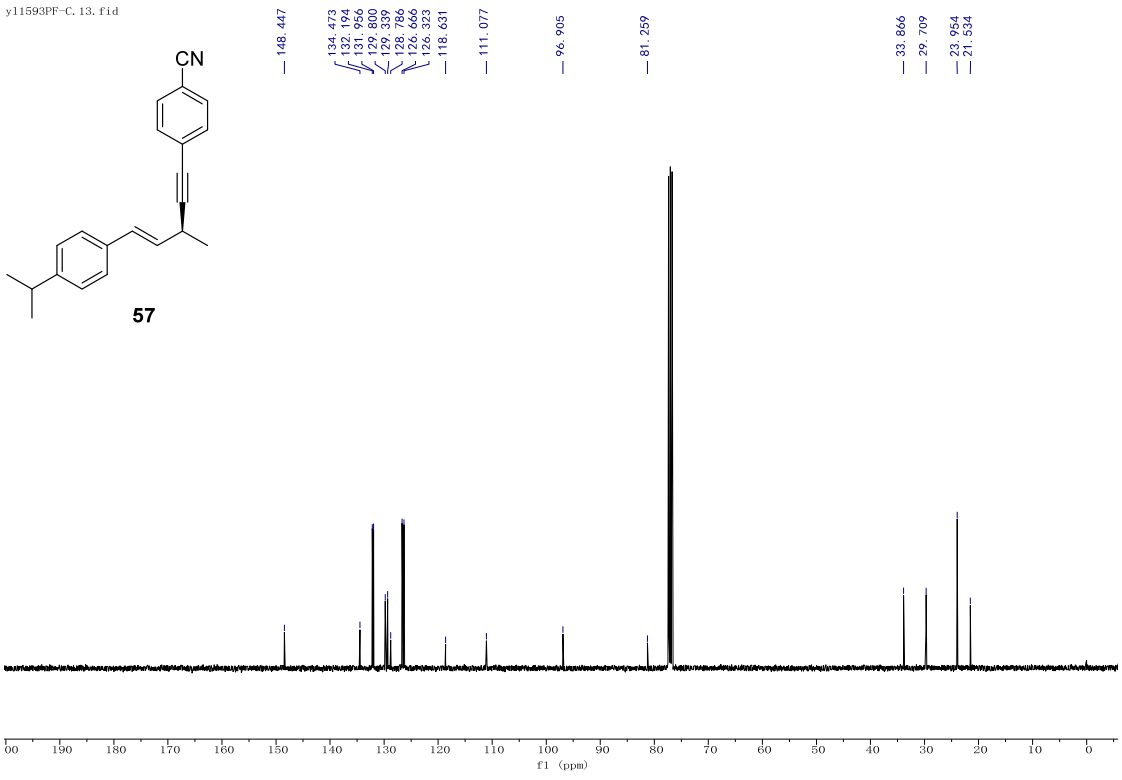


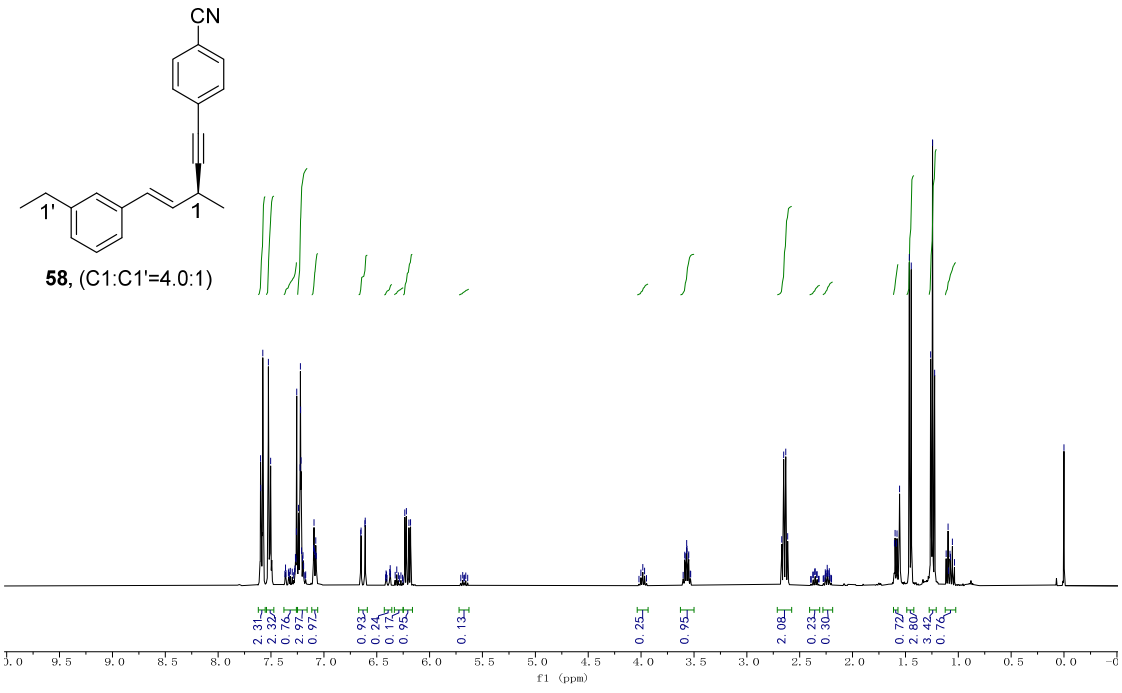
56

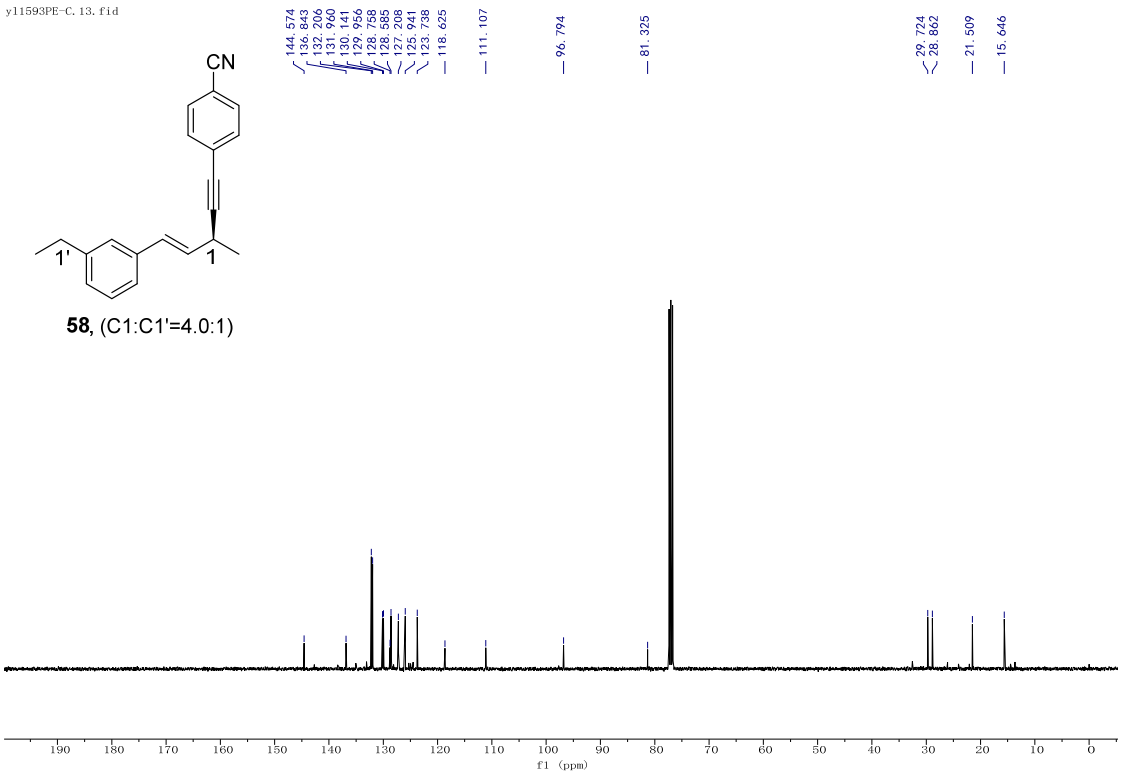
y11593PB.10.fid



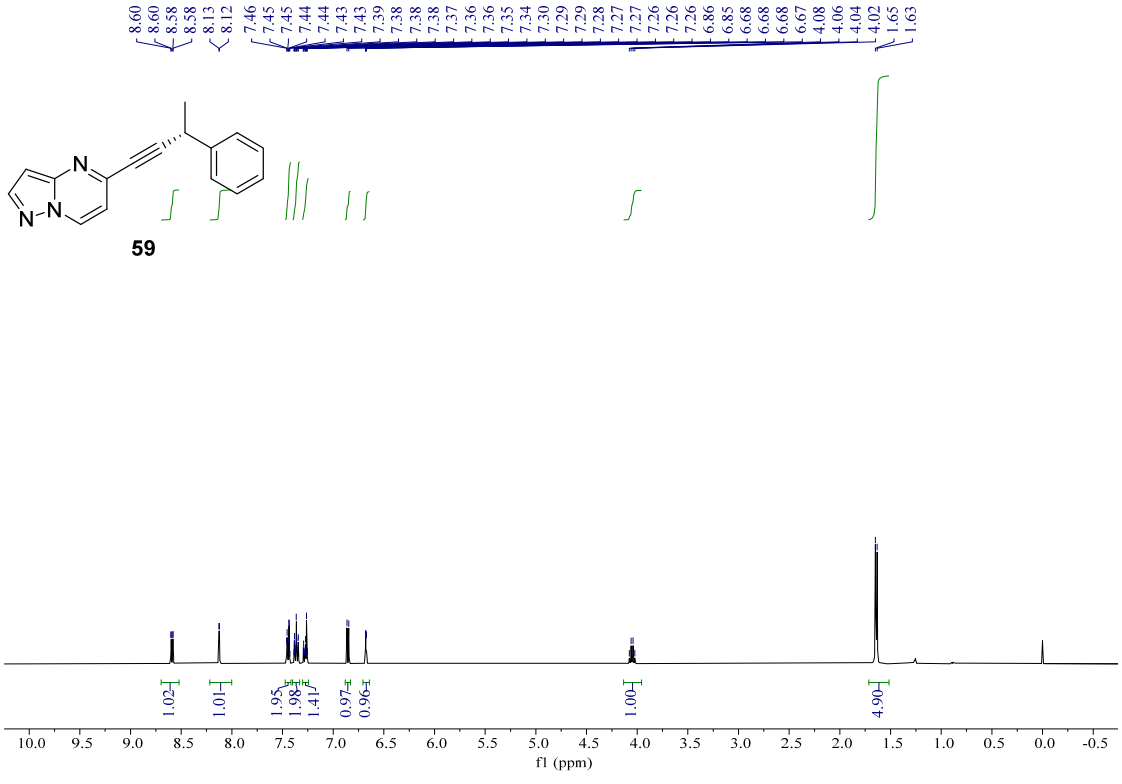
57


y11593PF-C.13.fid
CN
57
148.447
134.473
132.194
131.956
129.800
129.339
128.786
126.666
126.323
118.631
111.077
96.905
81.259
33.866
29.709
23.954
21.534
f1 (ppm)

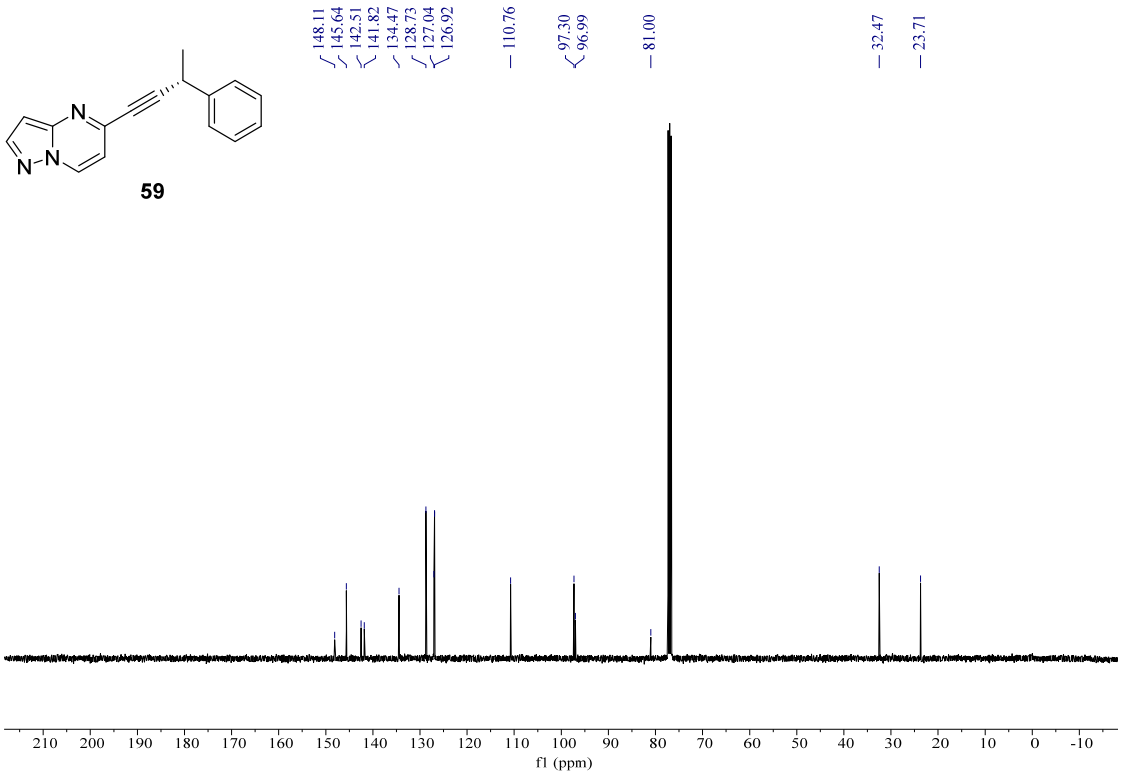

CN
1'
1
58, (C1:C1'=4.0:1)
2.31
2.32
0.76
2.97
0.97
0.93
0.24
0.17
0.95
0.13
0.25
0.95
2.08
0.23
0.30
0.72
2.80
3.42
0.76
f1 (ppm)

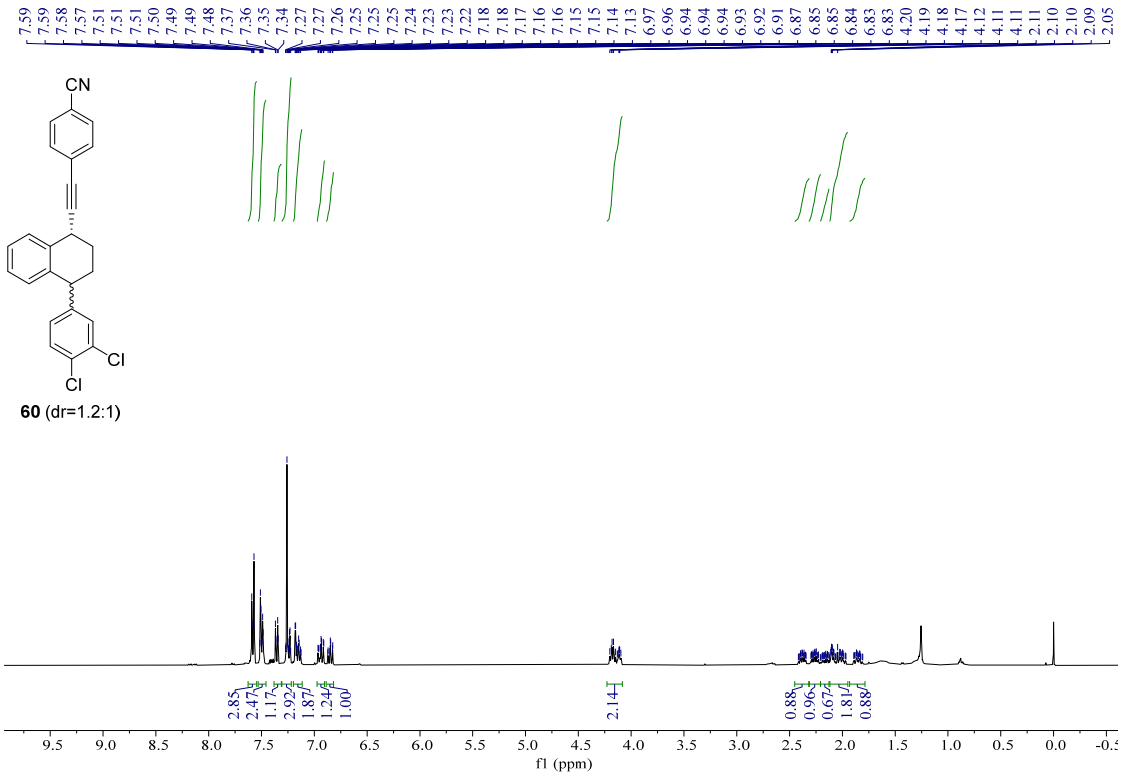


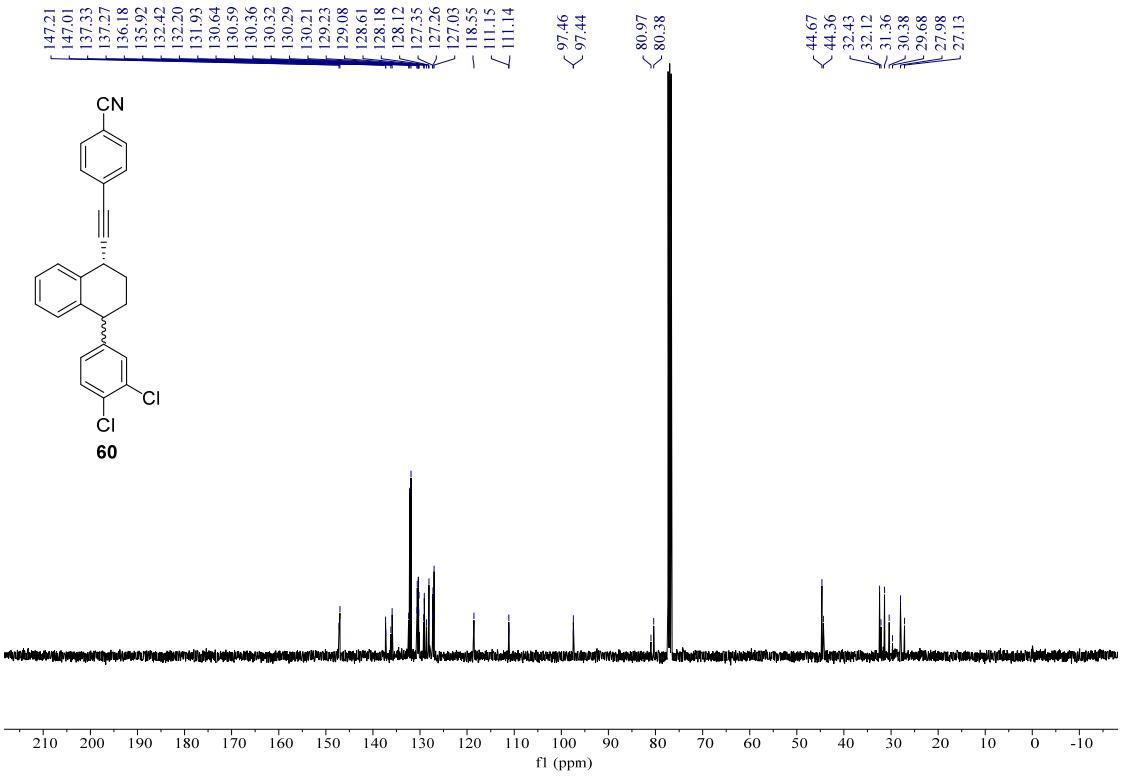
58, (C1:C1'=4.0:1)

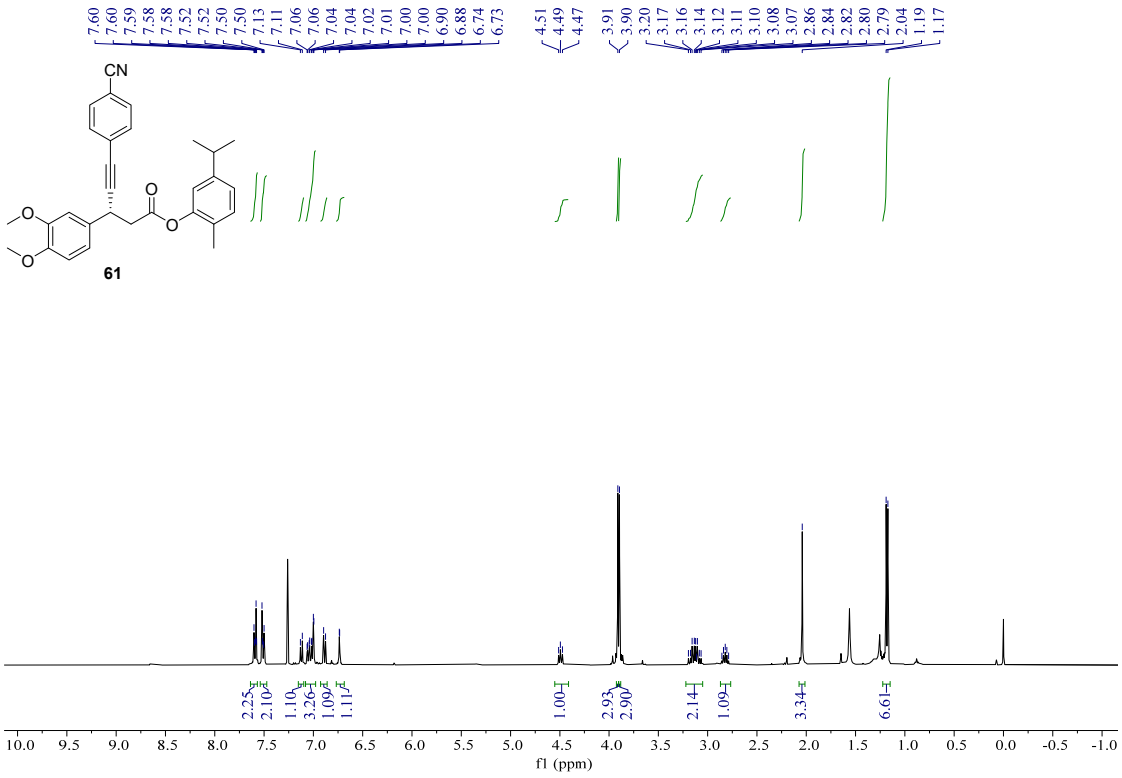


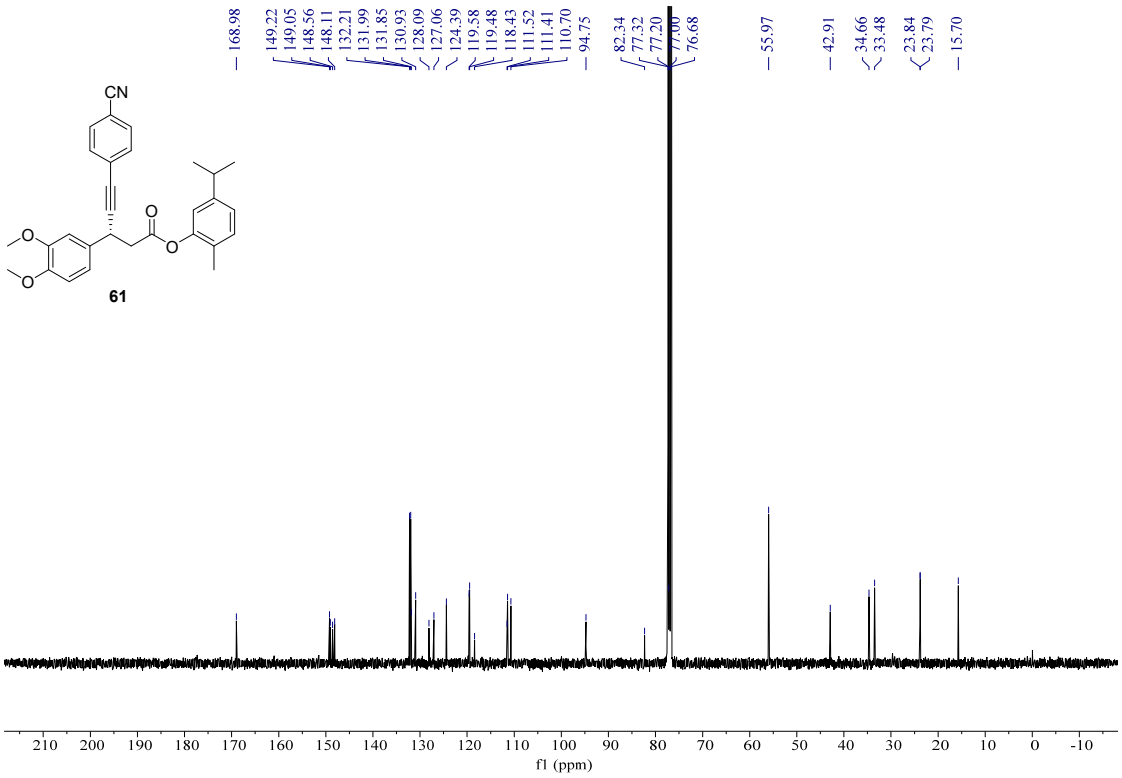
59

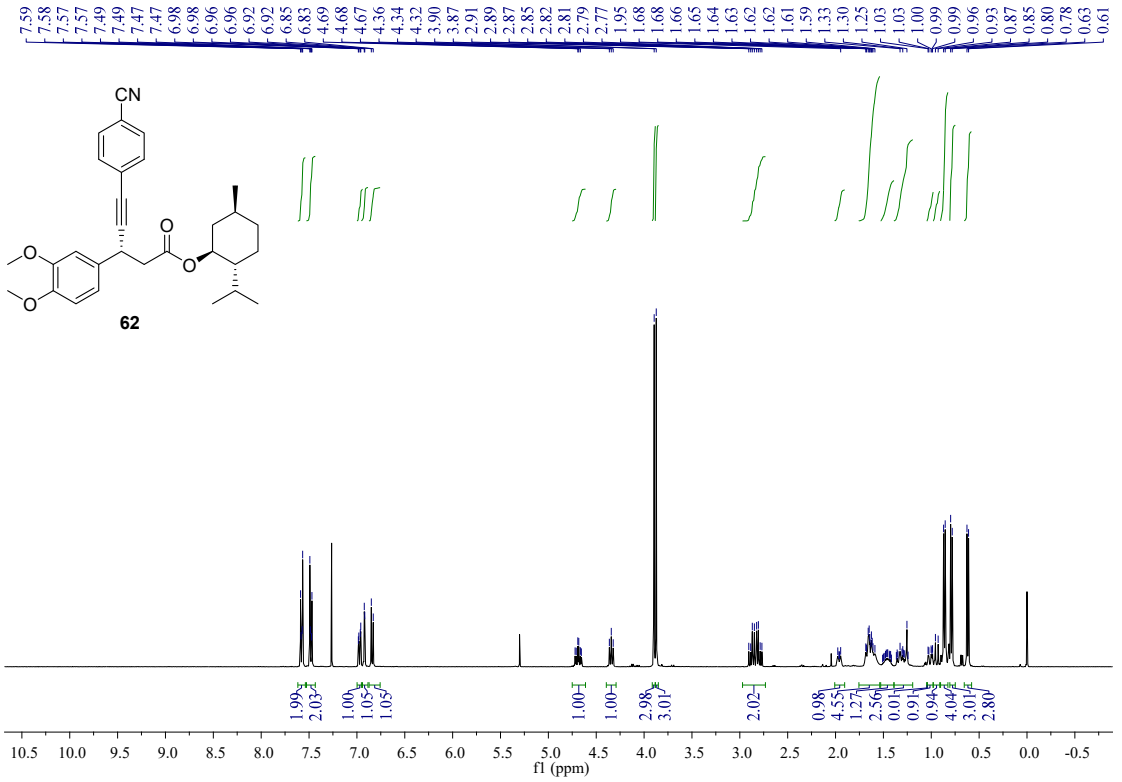

148.11
145.64
142.51
141.82
134.47
128.73
127.04
126.92
110.76
97.30
96.99
81.00
32.47
23.71
59
fl (ppm)

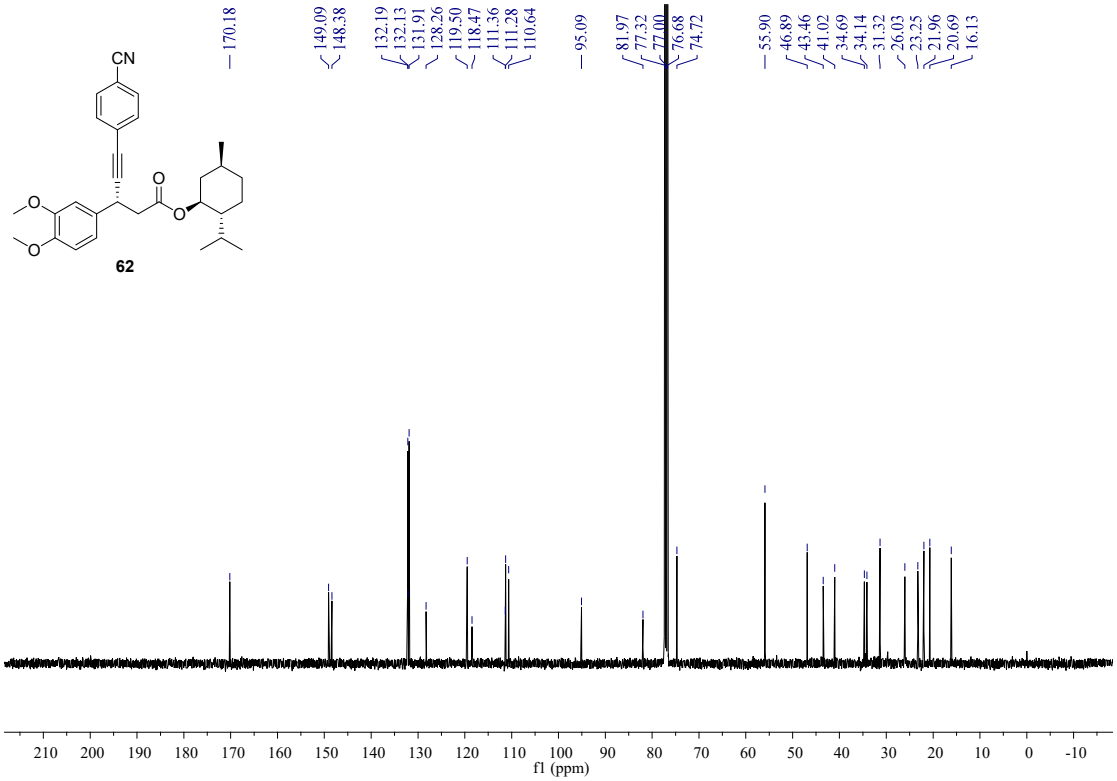

7.59
7.59
7.58
7.57
7.51
7.51
7.51
7.50
7.49
7.49
7.48
7.37
7.36
7.35
7.34
7.27
7.27
7.26
7.25
7.25
7.25
7.24
7.23
7.23
7.22
7.18
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.13
6.97
6.96
6.94
6.94
6.94
6.93
6.92
6.91
6.87
6.85
6.85
6.84
6.83
6.83
4.20
4.19
4.18
4.17
4.12
4.11
4.11
2.11
2.10
2.10
2.09
2.05
CN
Cl
Cl
60 (dr=1.2:1)
2.85
2.47
1.17
2.92
1.87
1.24
1.00
2.14
0.88
0.96
0.67
1.81
0.88
fl (ppm)

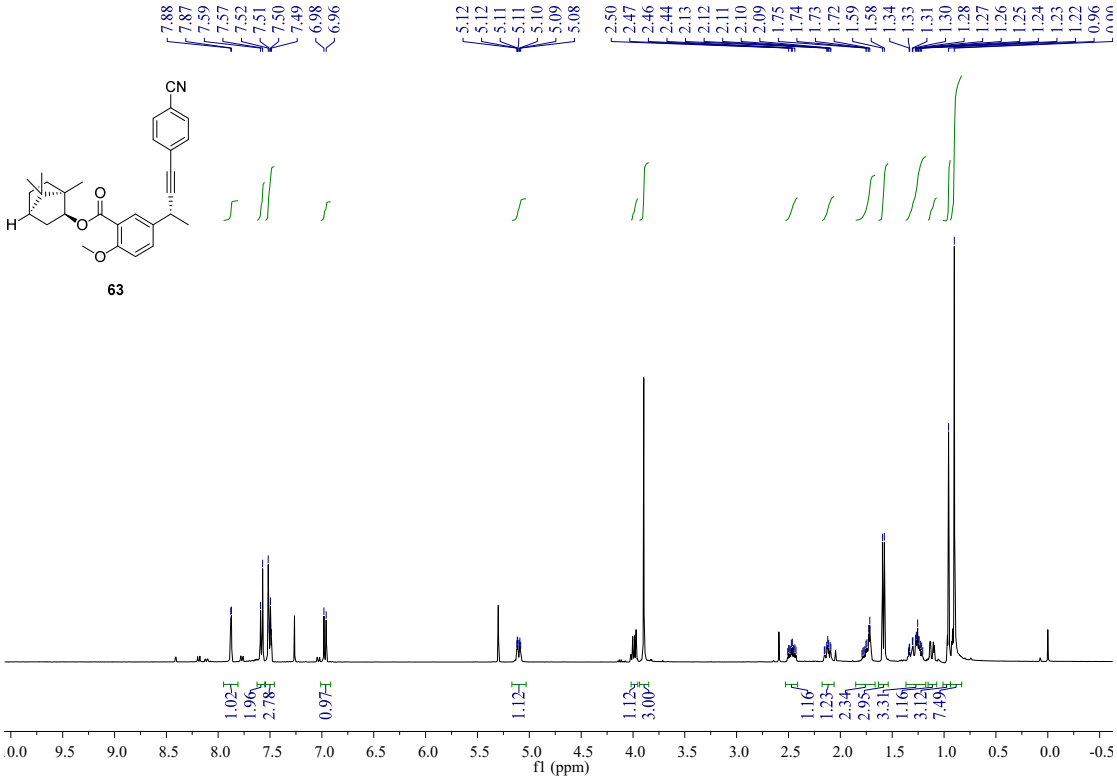

147.21
147.01
137.33
137.27
136.18
135.92
132.42
132.20
131.93
130.64
130.59
130.36
130.32
130.29
130.21
129.23
129.08
128.61
128.18
128.12
127.35
127.26
127.03
118.55
111.15
111.14
97.46
97.44
80.97
80.38
44.67
44.36
32.43
32.12
31.36
30.38
29.68
27.98
27.13
CN
Cl
Cl
60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

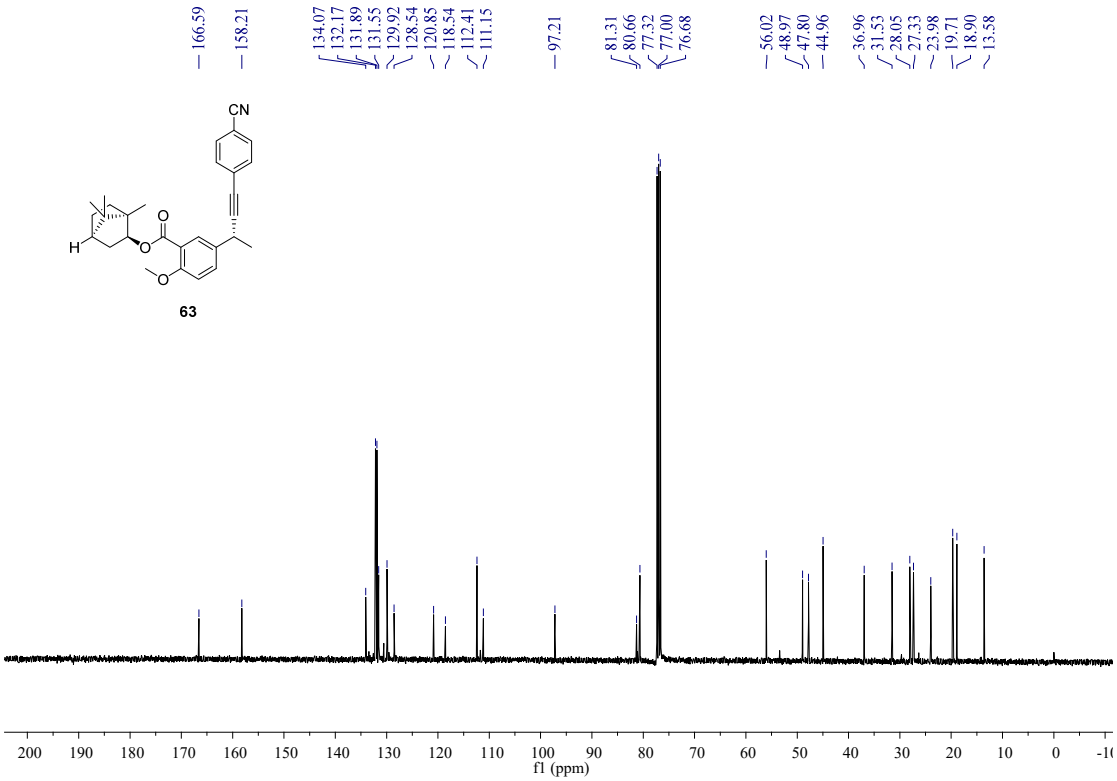

7.60
7.60
7.59
7.58
7.58
7.52
7.52
7.50
7.50
7.13
7.11
7.06
7.06
7.04
7.04
7.02
7.01
7.00
7.00
6.90
6.88
6.74
6.73
4.51
4.49
4.47
3.91
3.90
3.20
3.17
3.16
3.14
3.12
3.11
3.10
3.08
3.07
2.86
2.84
2.82
2.80
2.79
2.04
1.19
1.17
CN
O
O
O
O
61
2.25
2.10
1.10
3.26
1.09
1.11
1.00
2.93
2.90
2.14
1.09
3.34
6.61
10.0 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 -1.0
f1 (ppm)

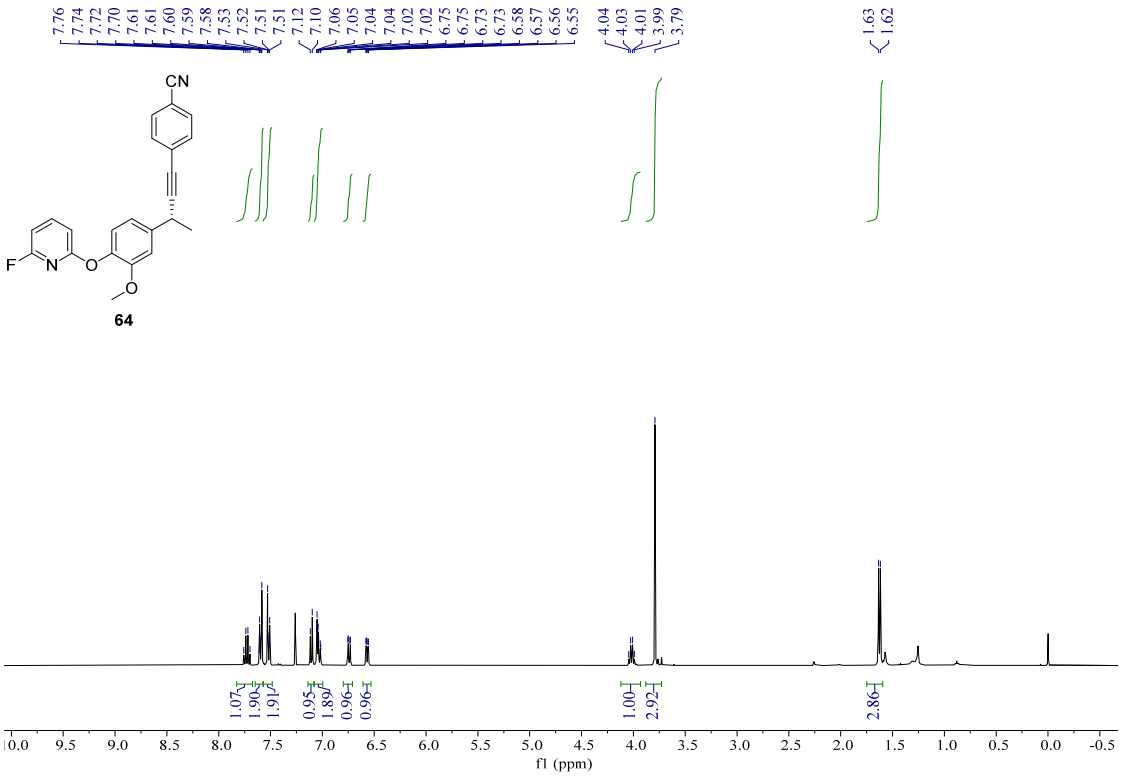

168.98
149.22
149.05
148.56
148.11
132.21
131.99
131.85
130.93
128.09
127.06
124.39
119.58
119.48
118.43
111.52
111.41
110.70
94.75
82.34
77.32
77.20
77.00
76.68
55.97
42.91
34.66
33.48
23.84
23.79
15.70
CN
O
O
O
61
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

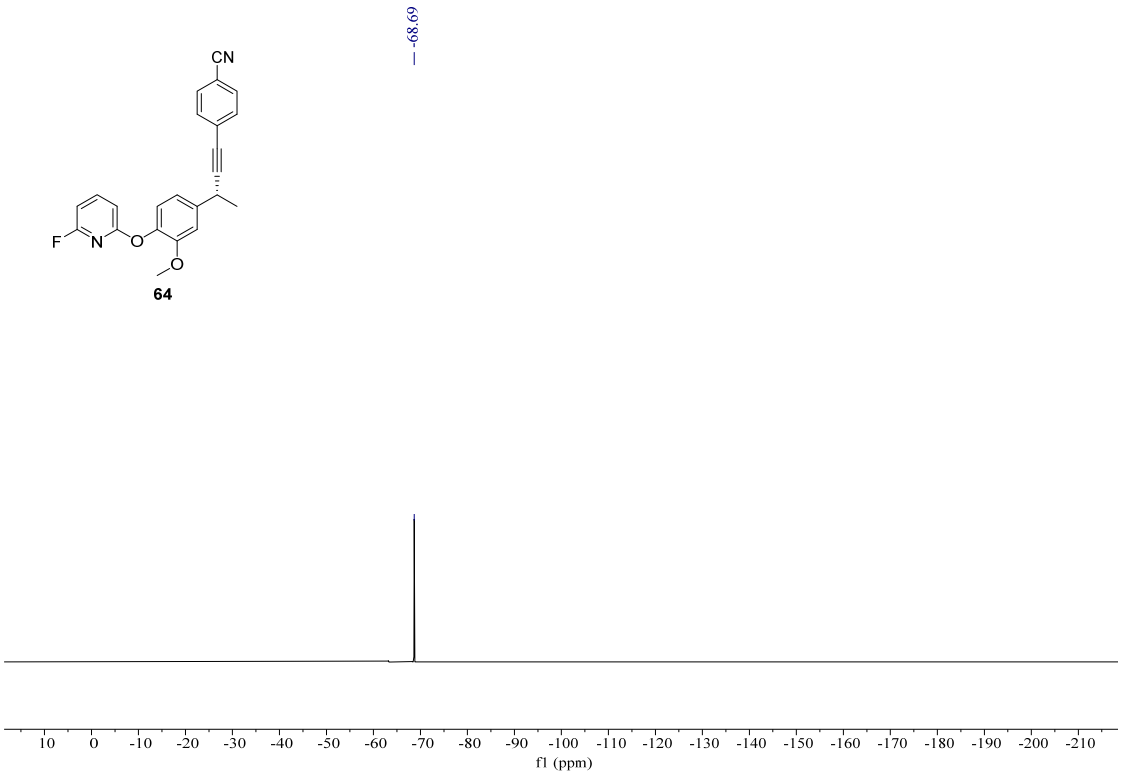

7.59
7.58
7.57
7.57
7.49
7.49
7.47
7.47
6.98
6.98
6.96
6.96
6.92
6.92
6.85
6.83
4.69
4.68
4.67
4.36
4.34
4.32
3.90
3.87
2.91
2.89
2.87
2.85
2.82
2.81
2.79
2.77
1.95
1.68
1.68
1.66
1.65
1.64
1.63
1.62
1.62
1.61
1.59
1.33
1.30
1.25
1.03
1.03
1.00
0.99
0.99
0.96
0.93
0.87
0.85
0.80
0.78
0.63
0.61
CN
O
O
O
62
1.99
2.03
1.00
1.05
1.05
1.00
1.00
2.98
3.01
2.02
0.98
4.55
1.27
2.56
0.01
0.91
0.94
4.04
3.01
2.80
10.5 10.0 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)

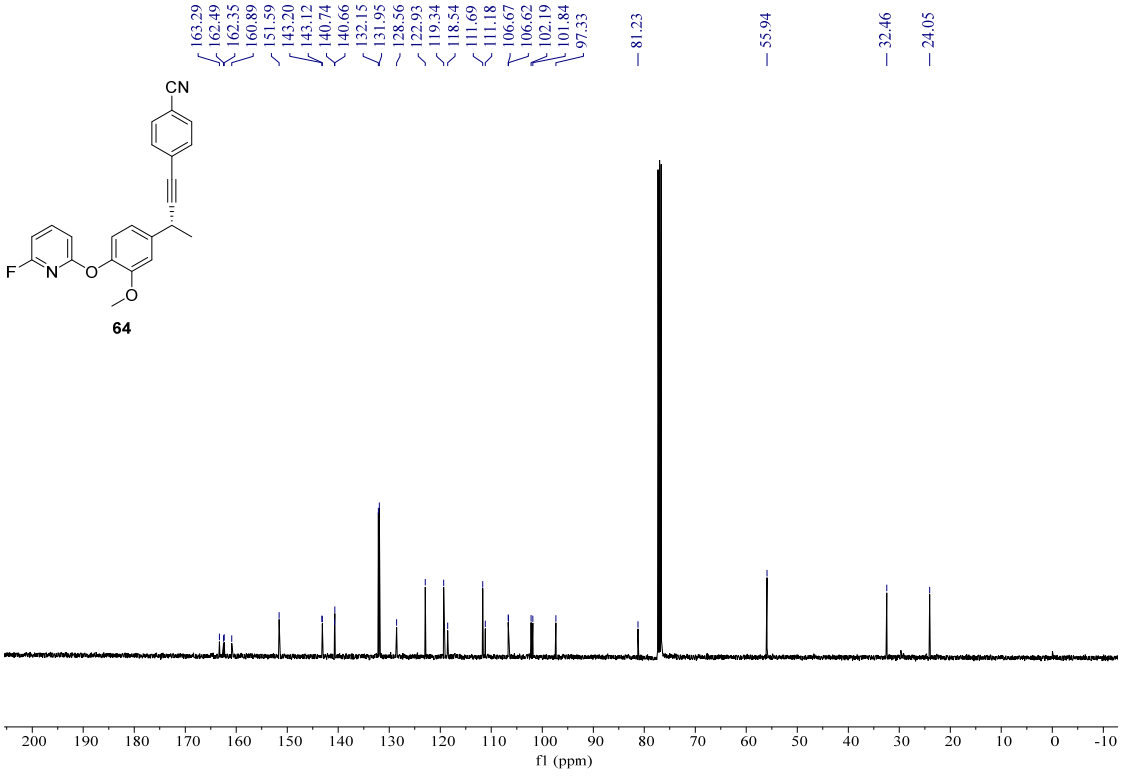

CN
O
O
O
62
170.18
149.09
148.38
132.19
132.13
131.91
128.26
119.50
118.47
111.36
111.28
110.64
95.09
81.97
77.32
77.00
76.68
74.72
55.90
46.89
43.46
41.02
34.69
34.14
31.32
26.03
23.25
21.96
20.69
16.13
f1 (ppm)

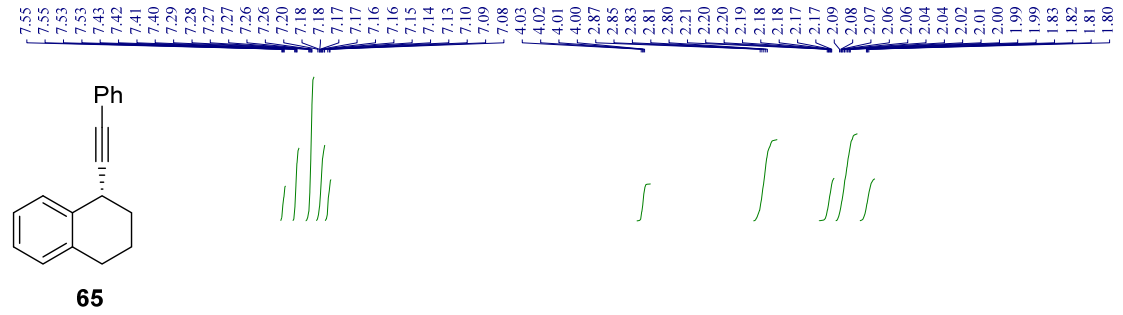

CN
H
O
O
O
63
7.88
7.87
7.59
7.57
7.52
7.51
7.50
7.49
6.98
6.96
5.12
5.12
5.11
5.11
5.10
5.09
5.08
2.50
2.47
2.46
2.44
2.13
2.12
2.11
2.10
2.09
1.75
1.74
1.73
1.72
1.59
1.58
1.34
1.33
1.31
1.30
1.28
1.27
1.26
1.25
1.24
1.23
1.22
0.96
1.02
1.96
2.78
0.97
1.12
1.12
3.00
1.16
1.23
2.34
2.95
3.31
1.16
3.12
7.49
f1 (ppm)


166.59
158.21
134.07
132.17
131.89
131.55
129.92
128.54
120.85
118.54
112.41
111.15
97.21
81.31
80.66
77.32
77.00
76.68
56.02
48.97
47.80
44.96
36.96
31.53
28.05
27.33
23.98
19.71
18.90
13.58
CN
H
O
O
O
63
f1 (ppm)


7.76
7.74
7.72
7.70
7.61
7.61
7.60
7.59
7.58
7.53
7.52
7.51
7.51
7.12
7.10
7.06
7.05
7.04
7.04
7.02
7.02
6.75
6.75
6.73
6.58
6.57
6.56
6.55
4.04
4.03
4.01
3.99
3.79
1.63
1.62
CN
F
N
O
O
64
1.07
1.90
1.91
0.95
1.89
0.96
0.96
1.00
2.92
2.86
f1 (ppm)

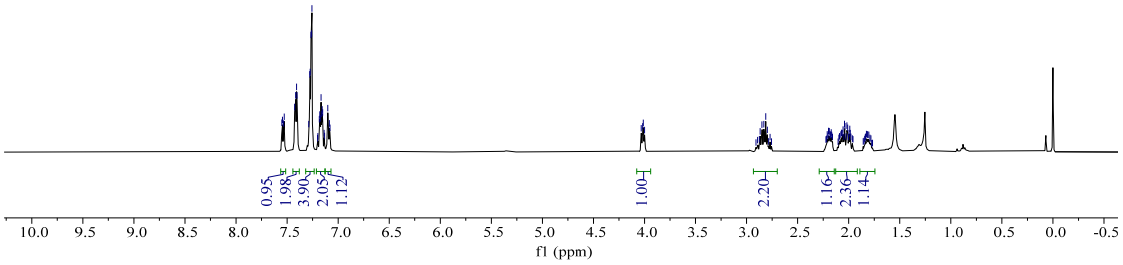

-68.69
CN
F
N
O
O
64
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

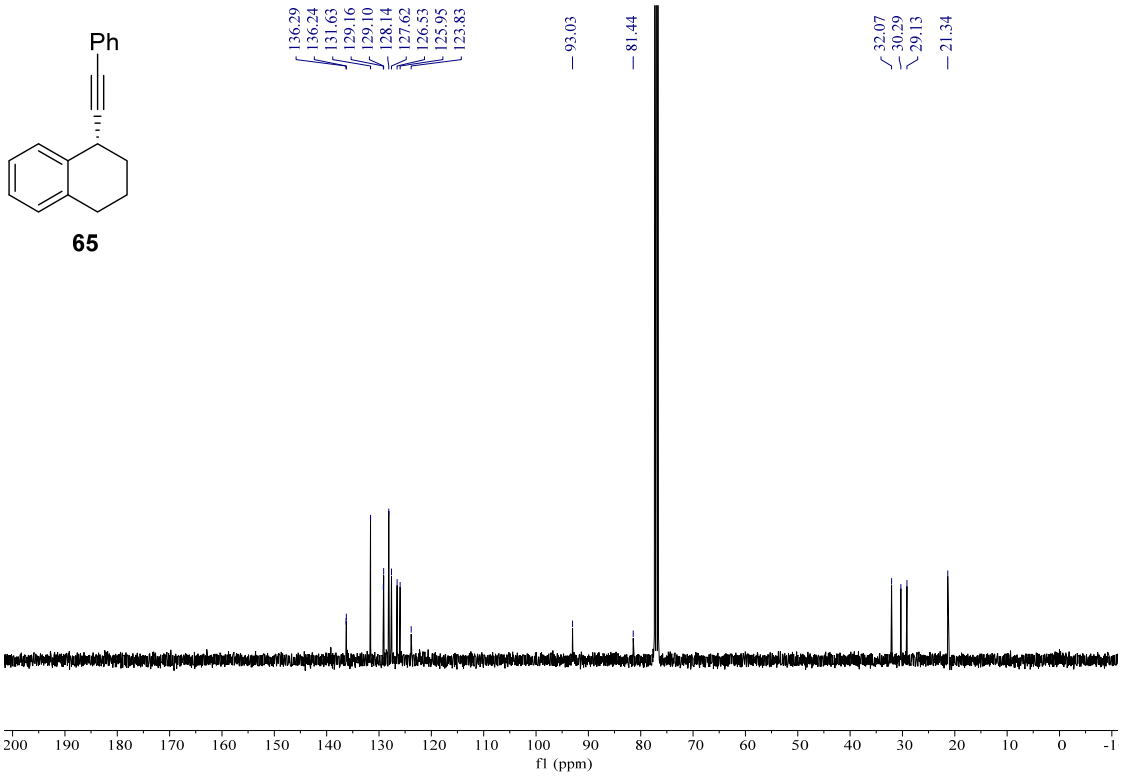

163.29
162.49
162.35
160.89
151.59
143.20
143.12
140.74
140.66
132.15
131.95
128.56
122.93
119.34
118.54
111.69
111.18
106.67
106.62
102.19
101.84
97.33
81.23
55.94
32.46
24.05
CN
F
N
O
O
64
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.55 7.55 7.53 7.53 7.43 7.42 7.41 7.40 7.29 7.28 7.27 7.27 7.26 7.26 7.20 7.18 7.18 7.17 7.17 7.16 7.16 7.15 7.14 7.13 7.10 7.09 7.08 4.03 4.02 4.01 4.00 2.87 2.85 2.83 2.81 2.80 2.21 2.20 2.20 2.19 2.18 2.18 2.17 2.17 2.09 2.08 2.07 2.06 2.06 2.04 2.04 2.02 2.01 2.00 1.99 1.99 1.83 1.82 1.81 1.80

Ph

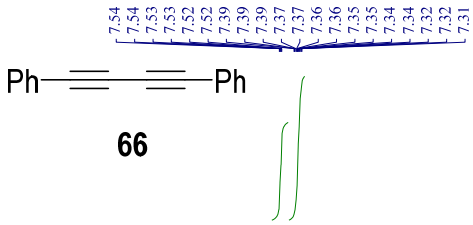
65


0.95 1.98 3.90 2.05 1.12 1.00 2.20 1.16 2.36 1.14
10.0 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)

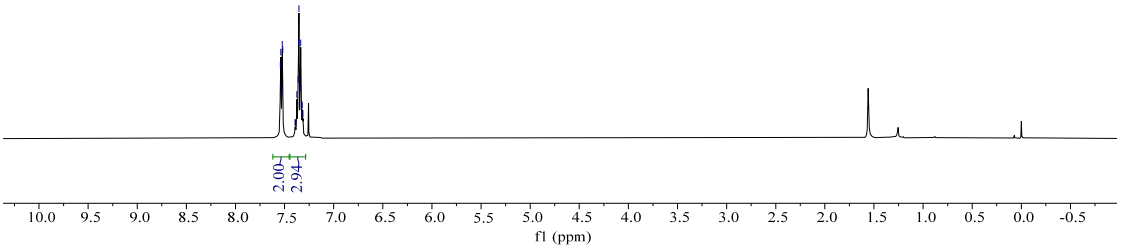

136.29 136.24 131.63 129.16 129.10 128.14 127.62 126.53 125.95 123.83 93.03 81.44 32.07 30.29 29.13 21.34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

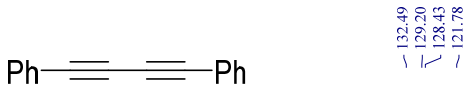
Ph

65


7.54
7.54
7.53
7.53
7.52
7.52
7.39
7.39
7.39
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.32
7.32
7.31
Ph
Ph

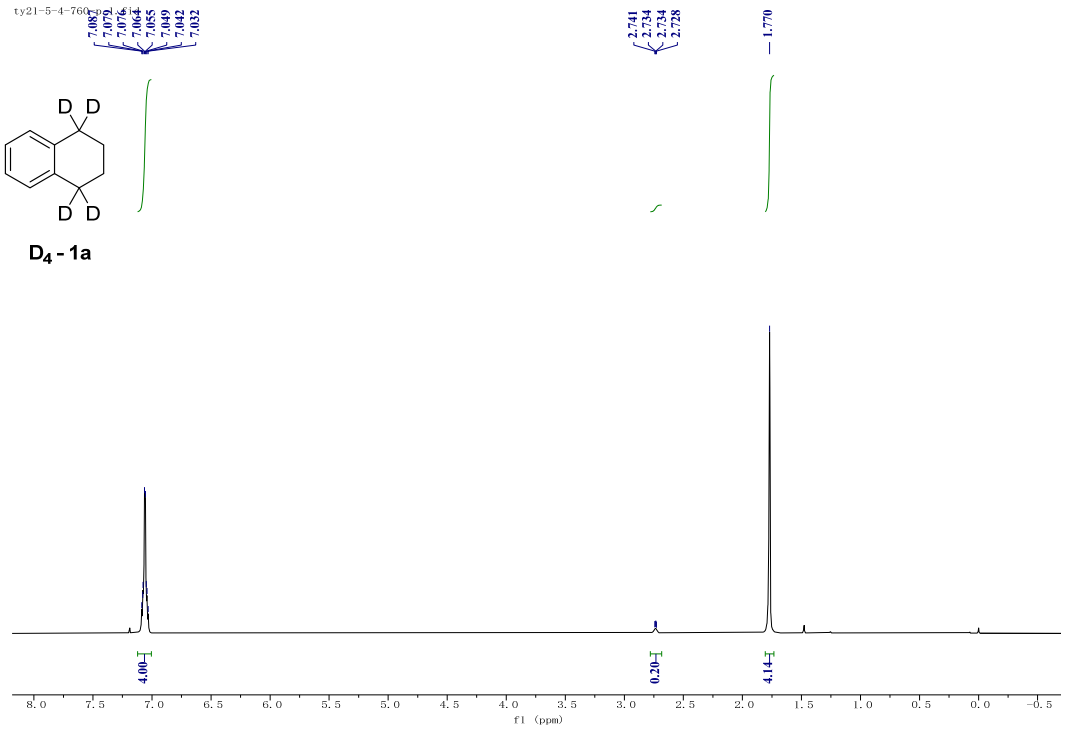
66


2.00
2.94
10.0 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)

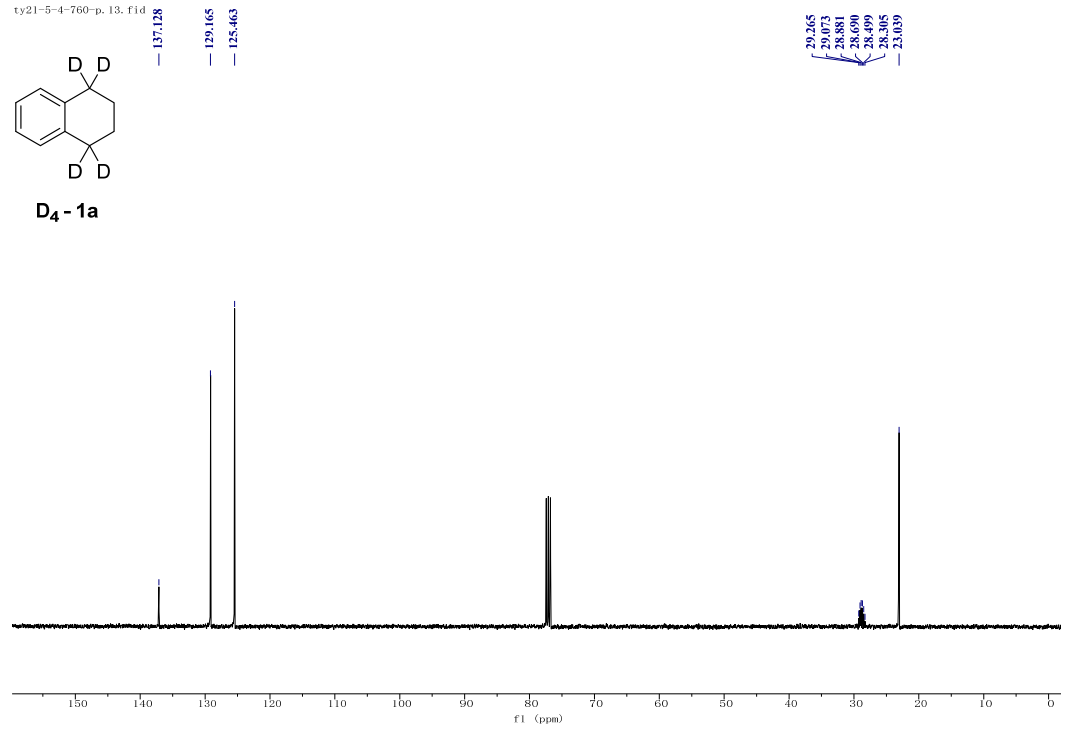

Ph
Ph

66

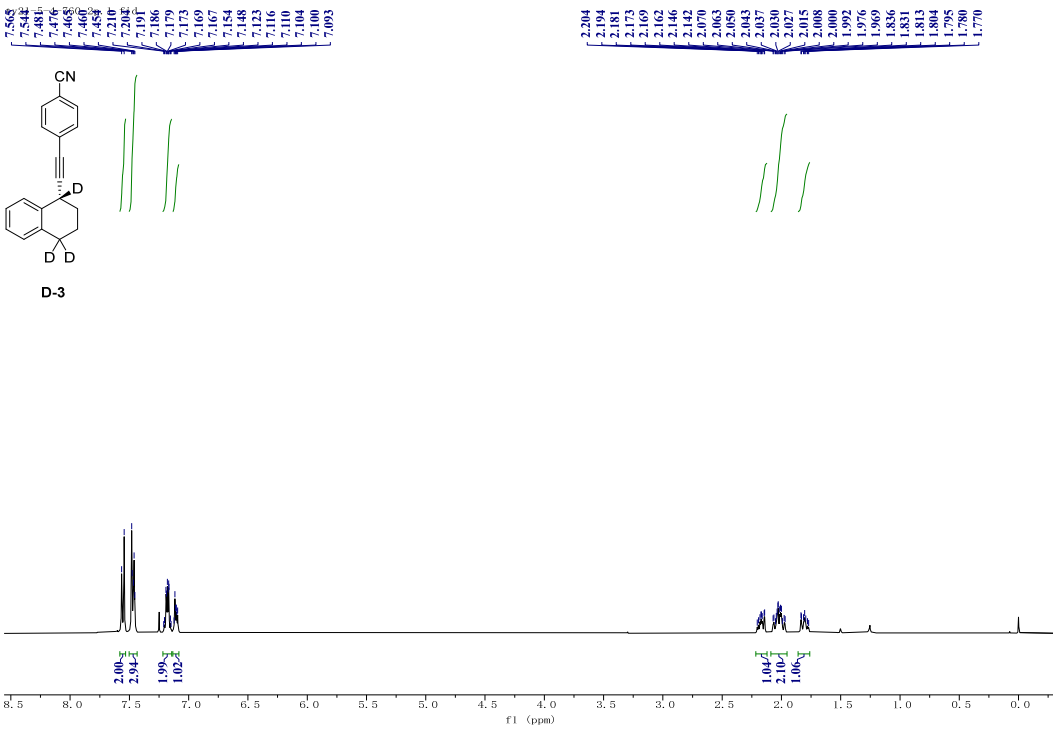
132.49
129.20
128.43
121.78
81.53
73.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.082
7.079
7.076
7.064
7.055
7.049
7.042
7.032
2.741
2.734
2.734
2.728
1.770
D D
D D
4.00
0.20
4.14
f1 (ppm)

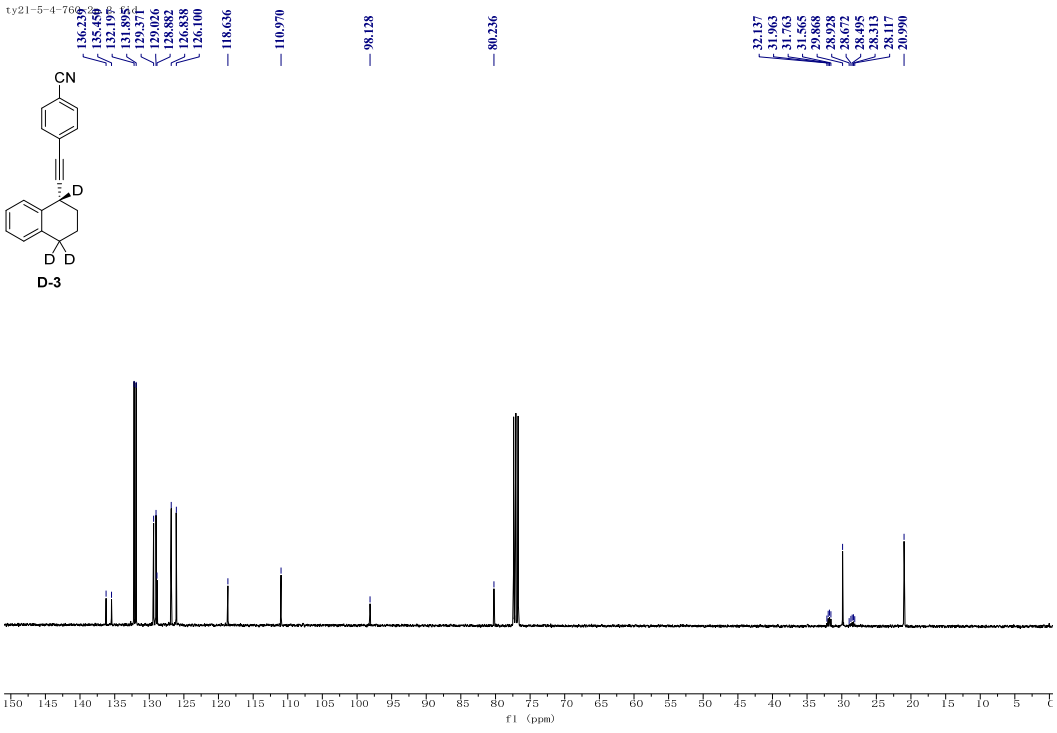
D_4 - 1a


ty21-5-4-760-p.13.fid
137.128
129.165
125.463
29.265
29.073
28.881
28.690
28.499
28.305
23.039
D D
D D
f1 (ppm)

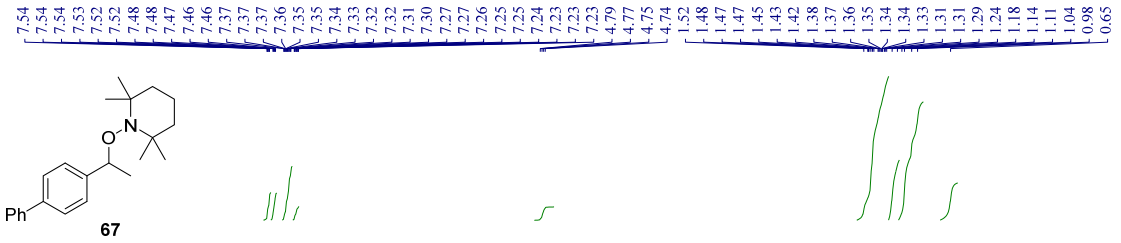
D_4 - 1a


7.568
7.544
7.481
7.476
7.465
7.460
7.454
7.210
7.204
7.191
7.186
7.179
7.173
7.169
7.167
7.154
7.148
7.123
7.116
7.110
7.104
7.100
7.093
2.204
2.194
2.181
2.173
2.169
2.162
2.146
2.142
2.070
2.065
2.050
2.043
2.037
2.030
2.027
2.015
2.008
2.000
1.992
1.976
1.969
1.836
1.831
1.813
1.804
1.795
1.780
1.770
CN
D
D D
2.00
2.94
1.99
1.02
1.04
2.10
1.06
f1 (ppm)

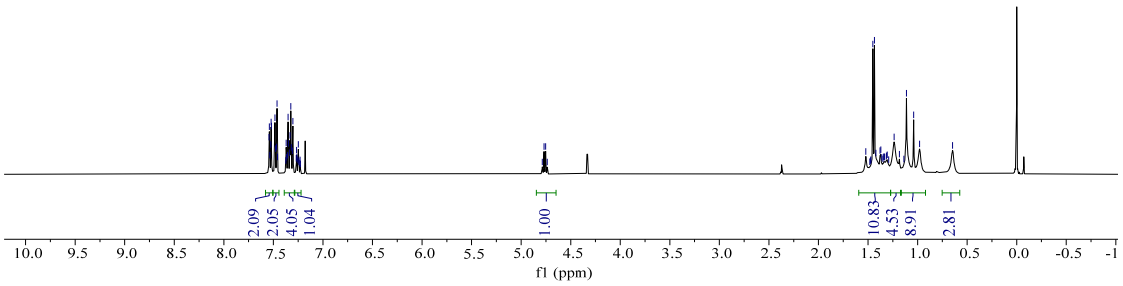
D-3

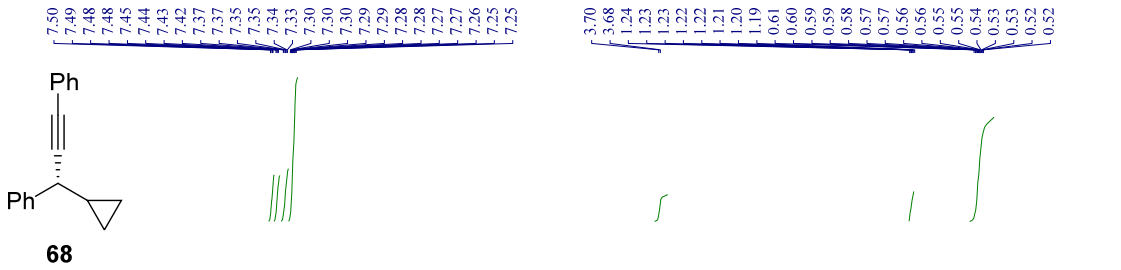

136.239
135.450
132.195
131.895
129.371
129.026
128.882
126.838
126.100
118.636
110.970
98.128
80.236
32.137
31.963
31.763
31.565
29.868
28.928
28.672
28.495
28.313
28.117
20.990
CN
D
D D
f1 (ppm)

D-3

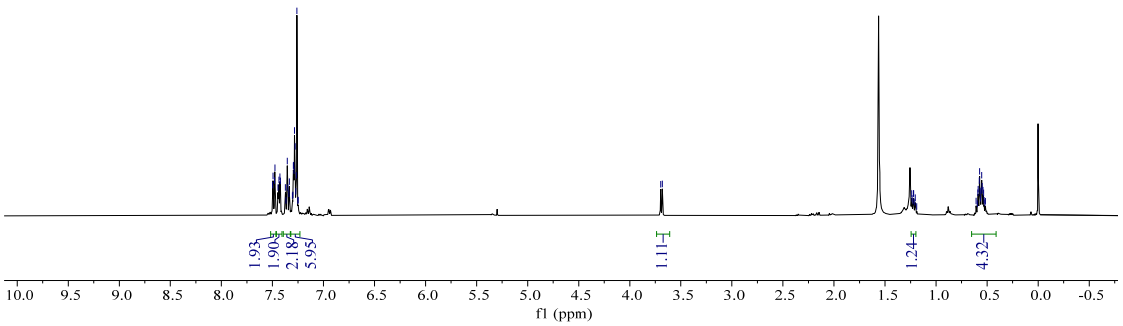

7.54 7.54 7.54 7.53 7.52 7.52 7.48 7.48 7.47 7.46 7.46 7.37 7.37 7.37 7.36 7.35 7.35 7.34 7.33 7.32 7.32 7.31 7.30 7.27 7.27 7.26 7.25 7.25 7.24 7.23 7.23 7.23 4.79 4.77 4.75 4.74 1.52 1.48 1.47 1.47 1.45 1.43 1.42 1.38 1.37 1.36 1.35 1.34 1.34 1.33 1.31 1.31 1.29 1.24 1.18 1.14 1.11 1.04 0.98 0.65
N
O
Ph

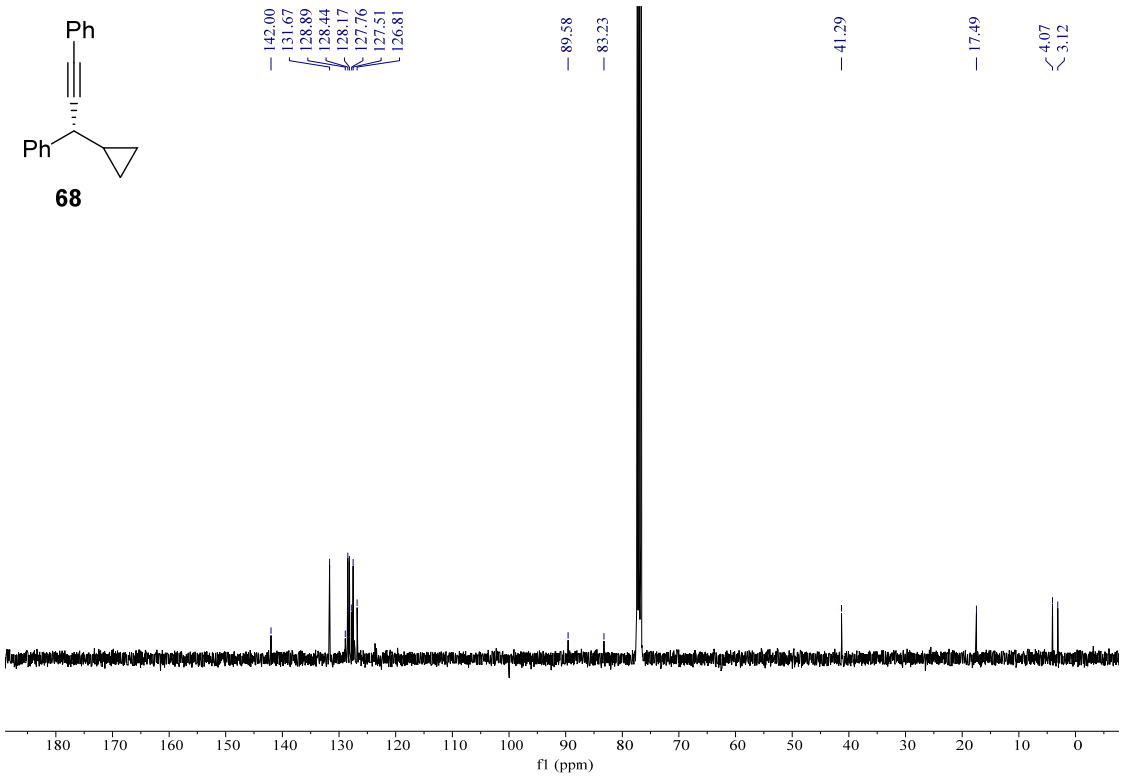
67

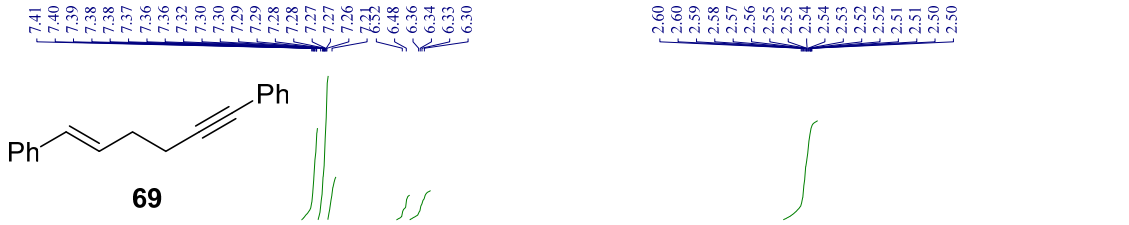

2.09 2.05 4.05 1.04 1.00 10.83 4.53 8.91 2.81
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

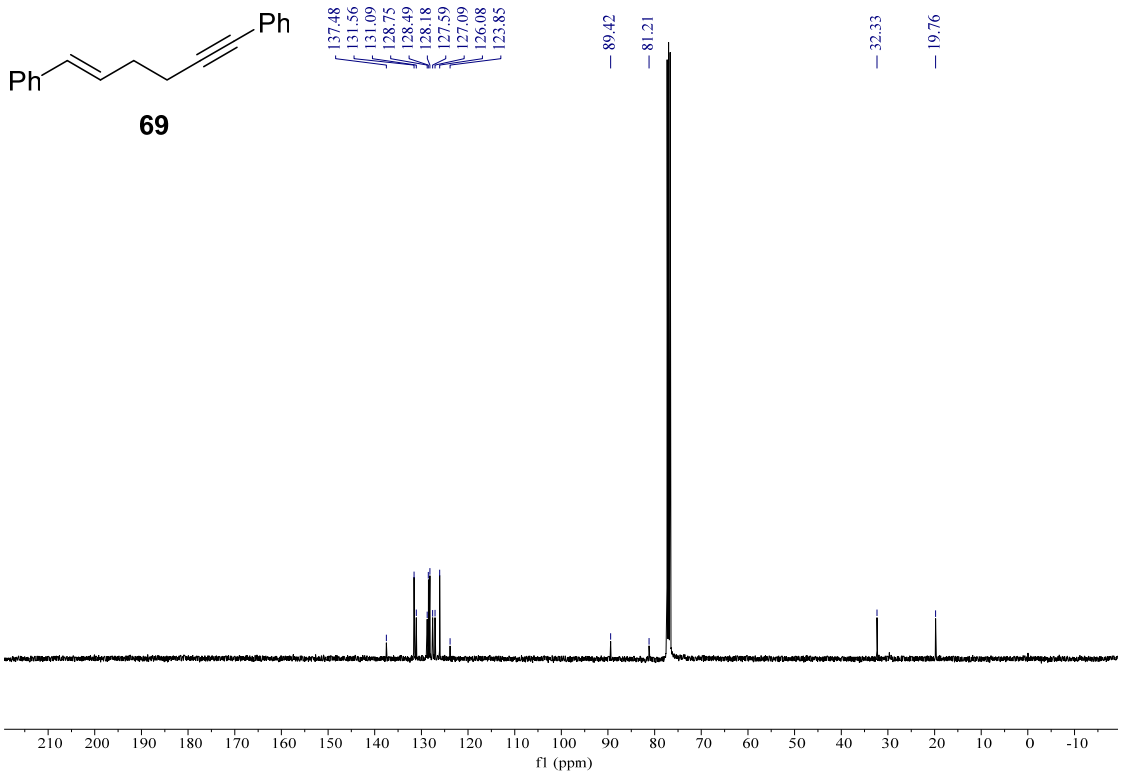

7.50 7.49 7.48 7.48 7.45 7.44 7.43 7.42 7.37 7.37 7.35 7.35 7.34 7.33 7.30 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.25 7.25
3.70 3.68 1.24 1.23 1.23 1.22 1.22 1.21 1.20 1.19 0.61 0.60 0.59 0.59 0.58 0.57 0.57 0.56 0.56 0.55 0.55 0.54 0.53 0.53 0.52 0.52
Ph
Ph

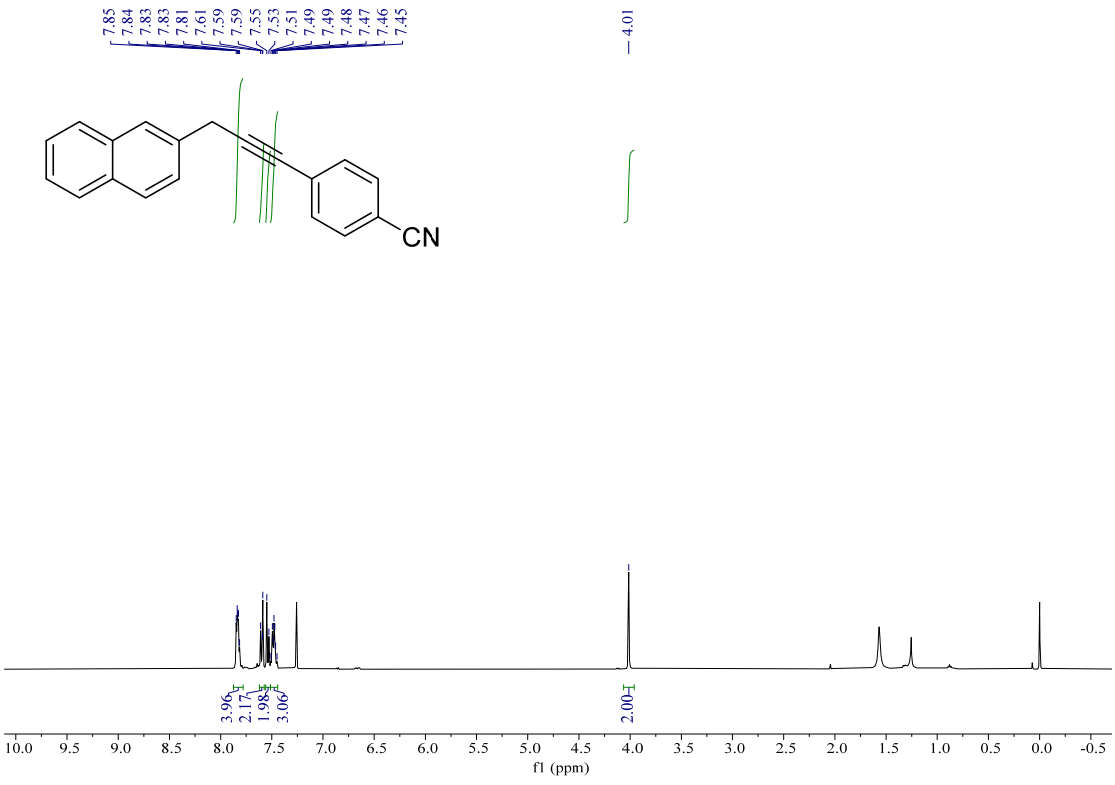
68

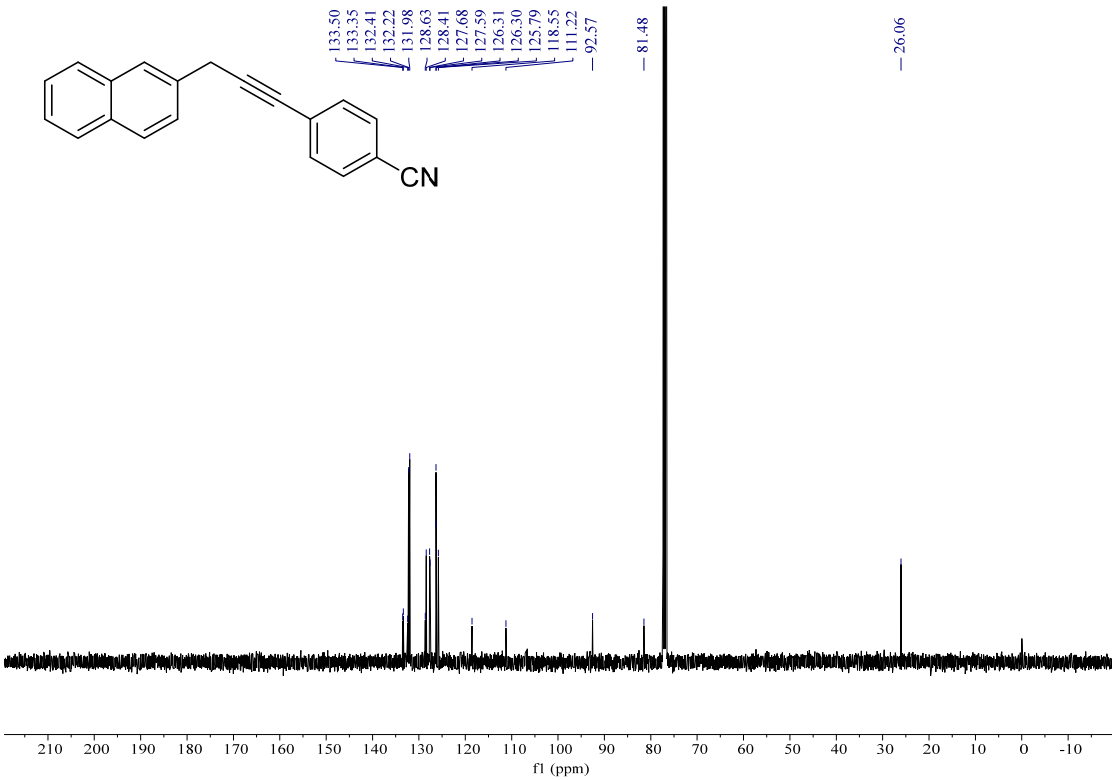

1.93 1.90 2.18 5.95 1.11 1.24 4.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

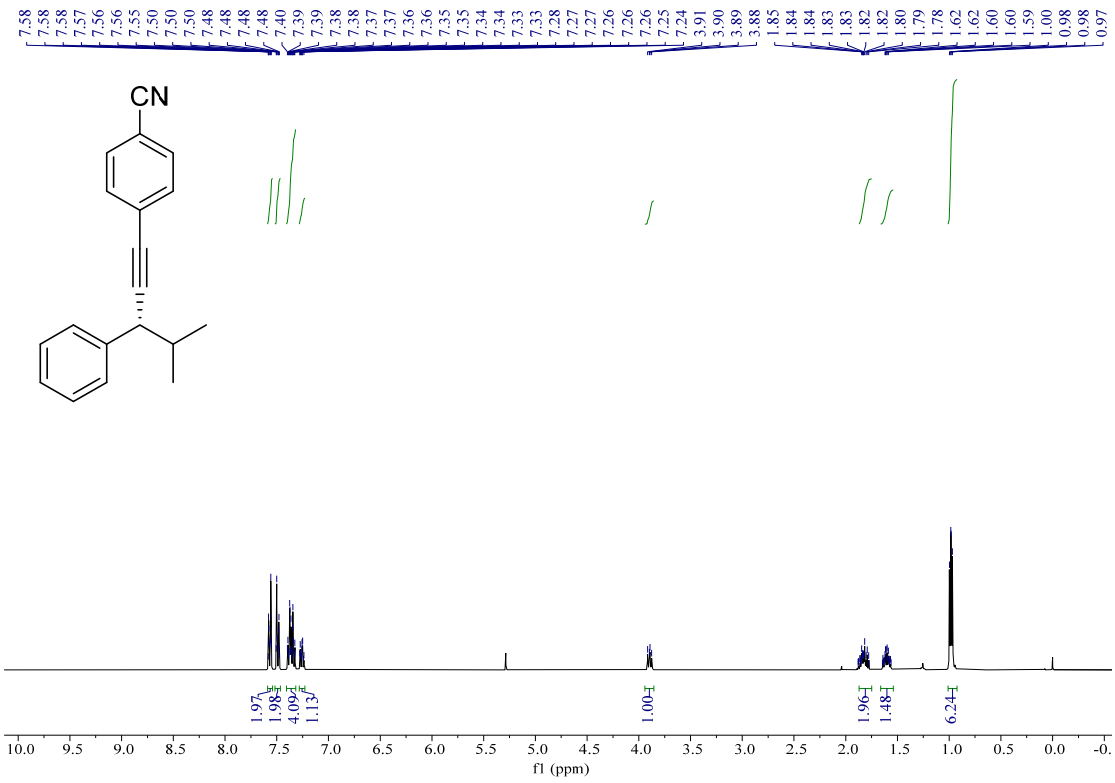

Ph
Ph
68
142.00
131.67
128.89
128.44
128.17
127.76
127.51
126.81
89.58
83.23
41.29
17.49
4.07
3.12
fl (ppm)

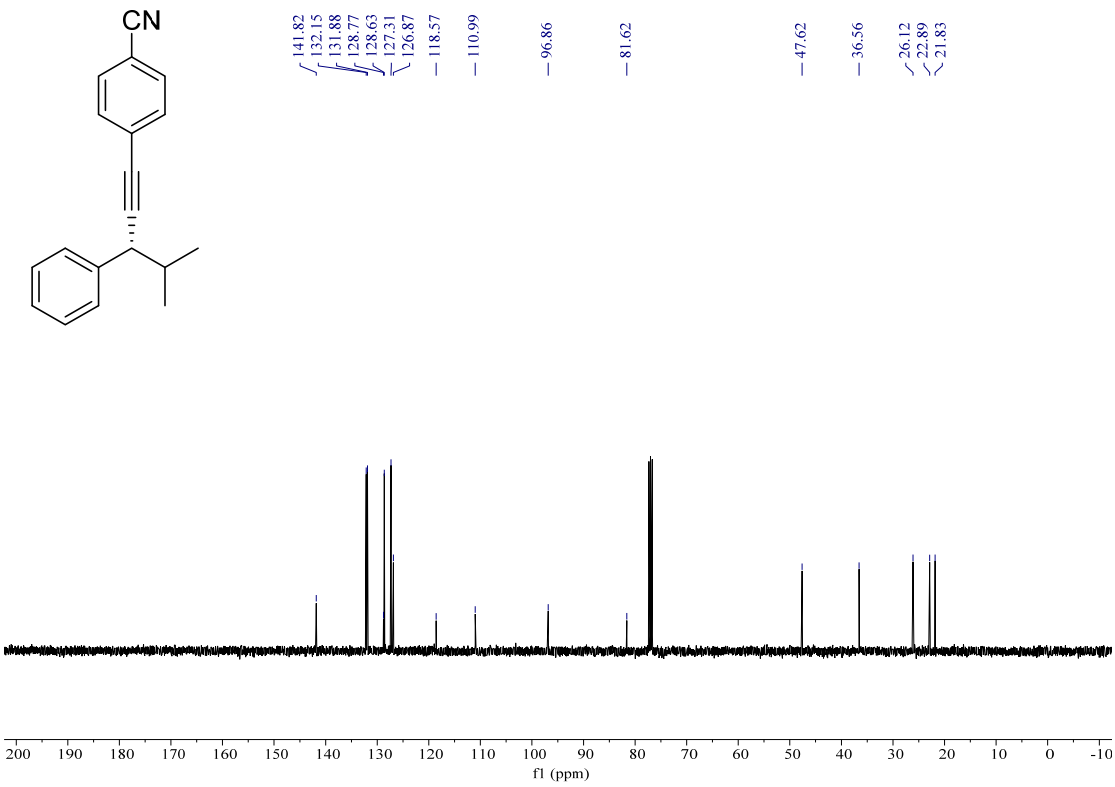

Ph
Ph
69
fl (ppm)


Ph
Ph
69
137.48
131.56
131.09
128.75
128.49
128.18
127.59
127.09
126.08
123.85
89.42
81.21
32.33
19.76
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

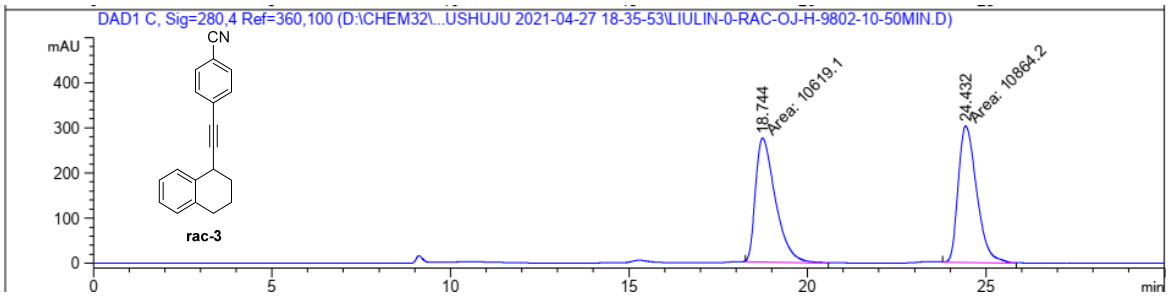

7.85
7.84
7.83
7.83
7.81
7.61
7.59
7.59
7.55
7.53
7.51
7.49
7.49
7.48
7.47
7.46
7.45
4.01
CN
3.96
2.17
1.98
3.06
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


133.50
133.35
132.41
132.22
131.98
128.63
128.41
127.68
127.59
126.31
126.30
125.79
118.55
111.22
92.57
81.48
26.06
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.58 7.58 7.58 7.57 7.56 7.56 7.55 7.50 7.50 7.50 7.48 7.48 7.48 7.48 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.28 7.27 7.27 7.26 7.26 7.26 7.25 7.24 3.91 3.90 3.89 3.88 1.85 1.84 1.84 1.83 1.83 1.82 1.82 1.80 1.79 1.78 1.62 1.62 1.60 1.60 1.59 1.00 0.98 0.98 0.97
CN
1.97
1.98
4.09
1.13
1.00
1.96
1.48
6.24
10.0 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.
f1 (ppm)

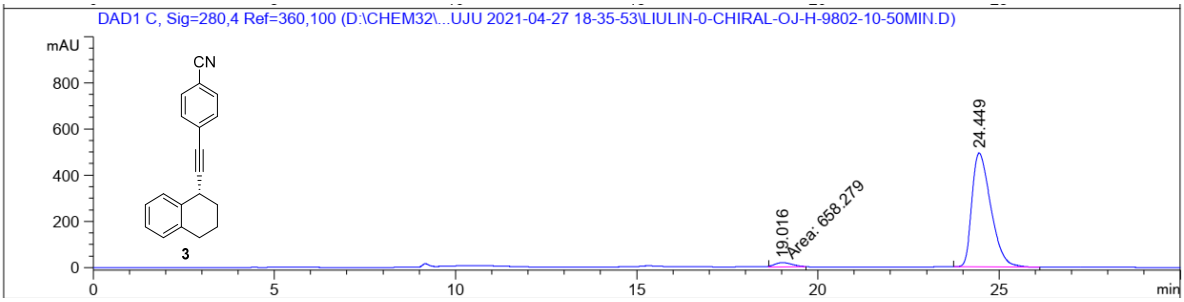

CN
141.82
132.15
131.88
128.77
128.63
127.31
126.87
118.57
110.99
96.86
81.62
47.62
36.56
26.12
22.89
21.83
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

HPLC Spectra



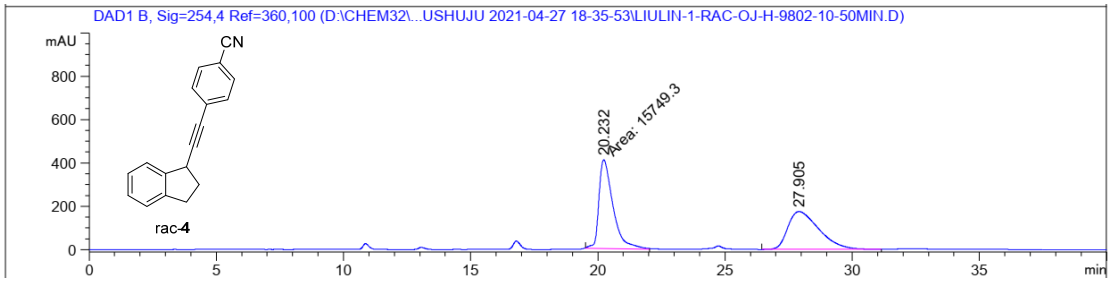
Signal 3: DAD1 C, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.744	MM	0.6453	1.06191e4	274.25906	49.4295
2	24.432	MM	0.5994	1.08642e4	302.06860	50.5705
Totals :				2.14832e4	576.32767	



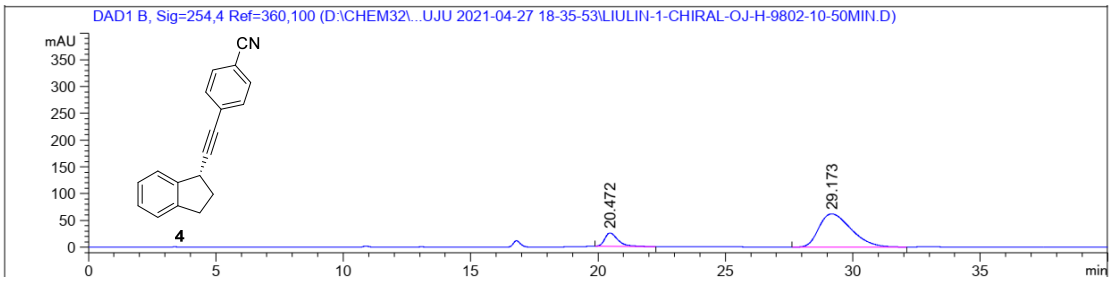
Signal 3: DAD1 C, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.016	MP	0.5678	658.27899	19.32092	3.5444
2	24.449	BB	0.5656	1.79140e4	493.32886	96.4556
Totals :				1.85723e4	512.64977	



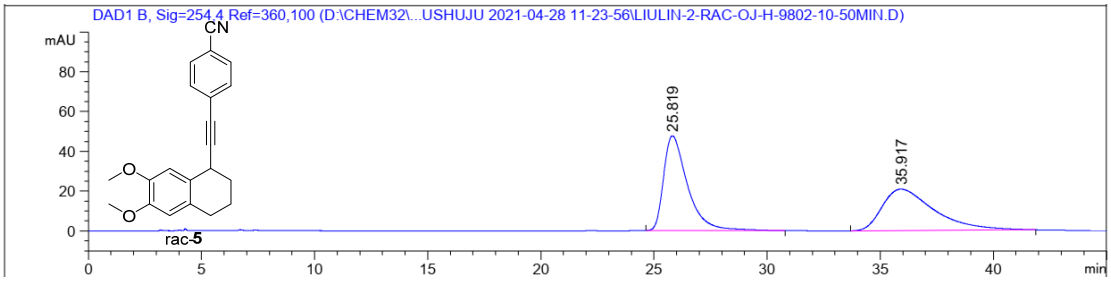
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.232	MM	0.6399	1.57493e4	410.20657	51.4867
2	27.905	BB	1.2662	1.48397e4	174.49814	48.5133
Totals :				3.05890e4	584.70471	



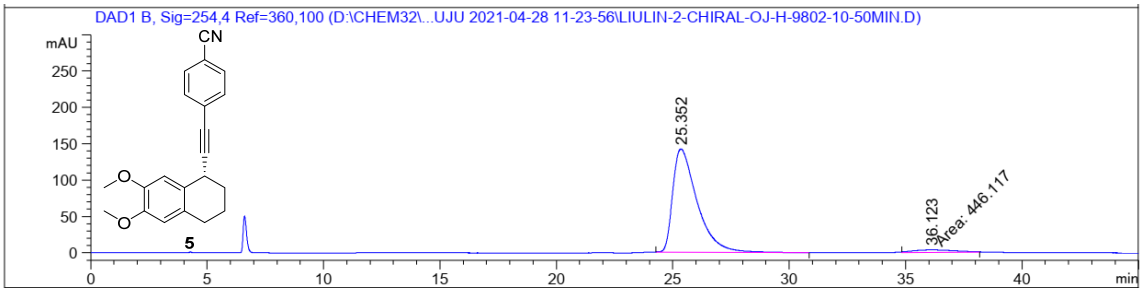
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.472	BB	0.5397	881.01862	24.84333	13.8924
2	29.173	BB	1.2960	5460.70654	62.09615	86.1076
Totals :				6341.72516	86.93948	



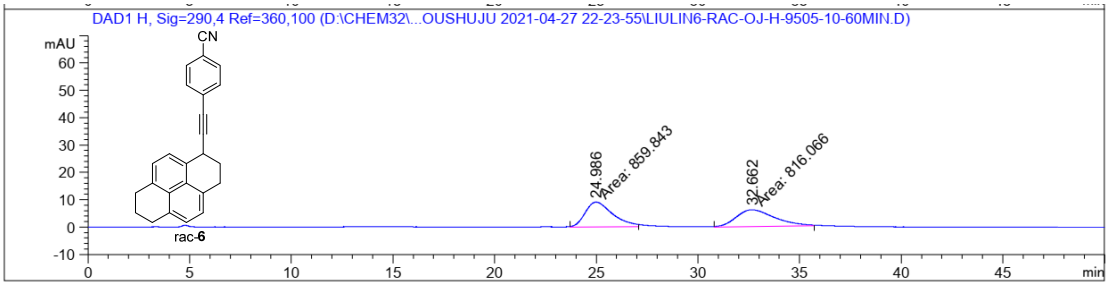
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.819	BB	1.0682	3480.47363	47.53834	51.1261
2	35.917	BB	1.8780	3327.15015	20.82483	48.8739
Totals :				6807.62378	68.36316	



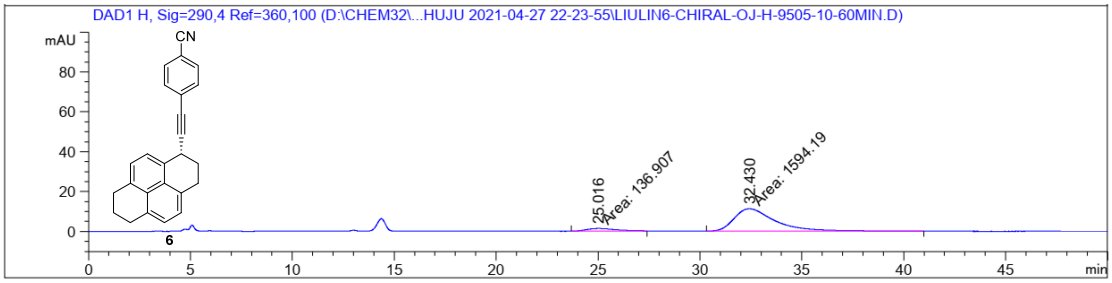
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.352	BB	1.0946	1.02878e4	141.77747	95.8438
2	36.123	MM	2.1118	446.11734	3.52075	4.1562
Totals :				1.07339e4	145.29822	



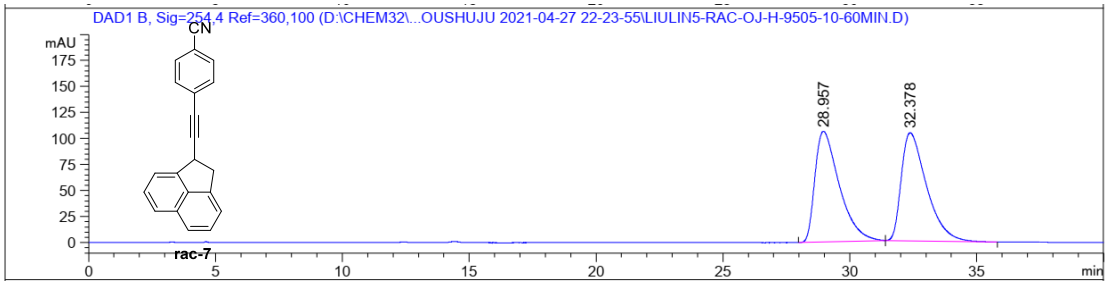
Signal 8: DAD1 H, Sig=290,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.986	MM	1.5773	859.84338	9.08578	51.3061
2	32.662	MM	2.2070	816.06635	6.16258	48.6939
Totals :				1675.90973	15.24836	



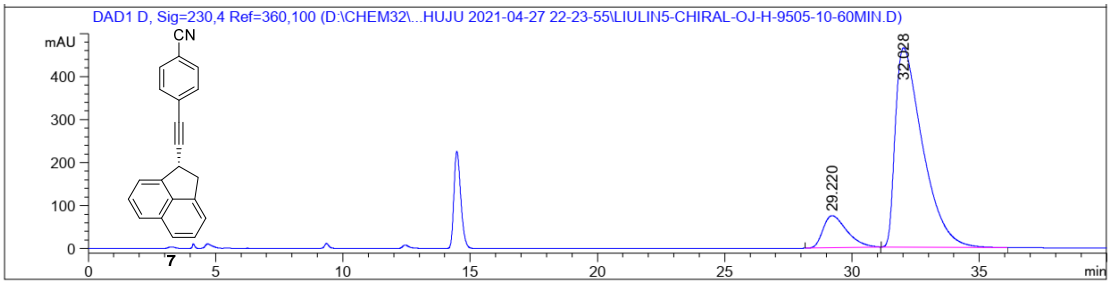
Signal 8: DAD1 H, Sig=290,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.016	MM	1.7006	136.90688	1.34173	7.9087
2	32.430	MM	2.3593	1594.18835	11.26183	92.0913
Totals :				1731.09523	12.60357	



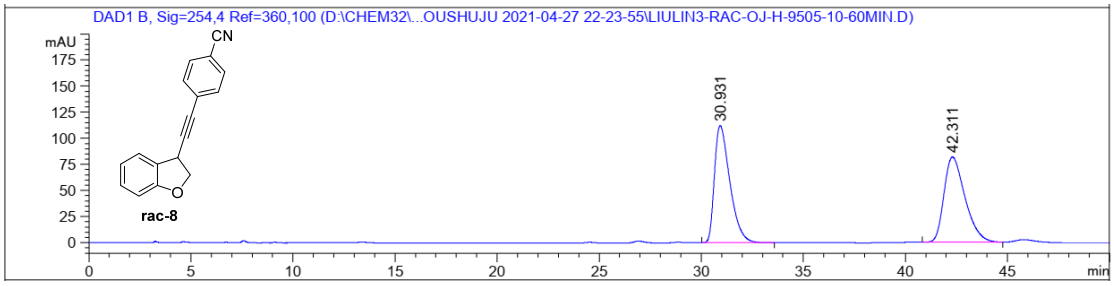
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.957	BB	0.9967	7101.71436	106.39526	49.7058
2	32.378	BB	1.0273	7185.78076	103.84354	50.2942
Totals :				1.42875e4	210.23879	



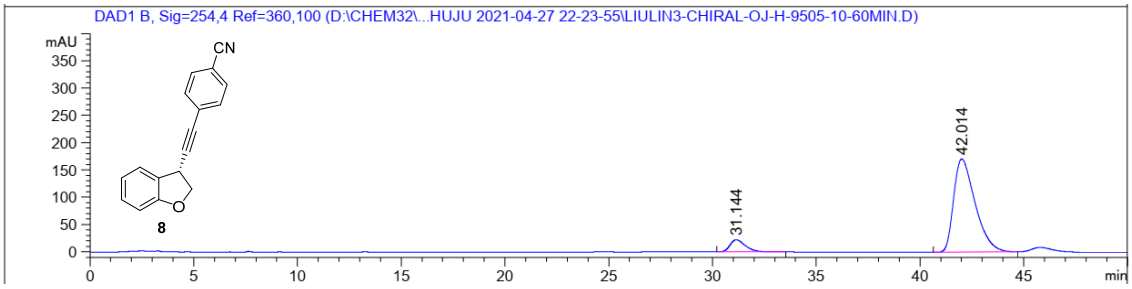
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.220	BB	0.9776	4835.99023	74.67343	12.2940
2	32.028	BB	1.1131	3.45002e4	463.15054	87.7060
Totals :				3.93362e4	537.82397	



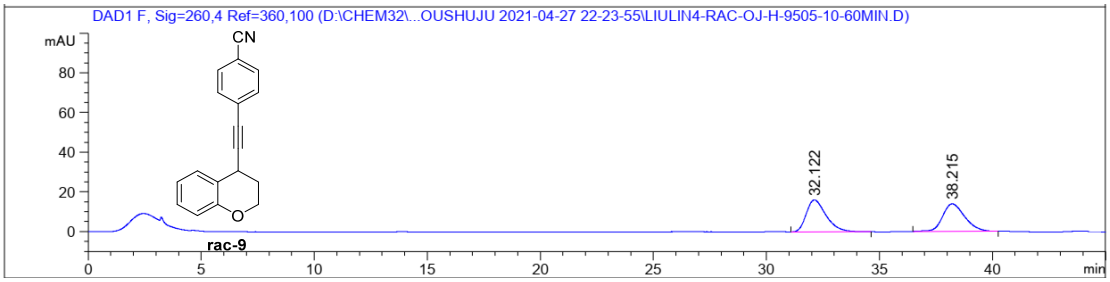
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.931	BB	0.8019	5892.03125	112.33083	50.1645
2	42.311	BB	1.0722	5853.39404	81.66998	49.8355
Totals :				1.17454e4	194.00082	



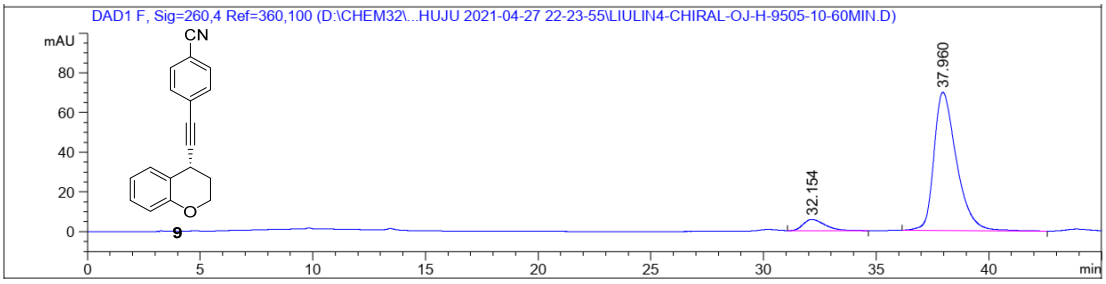
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.144	BB	0.7636	1141.87073	22.29045	8.4956
2	42.014	BB	1.0918	1.22989e4	170.86789	91.5044
Totals :				1.34407e4	193.15834	



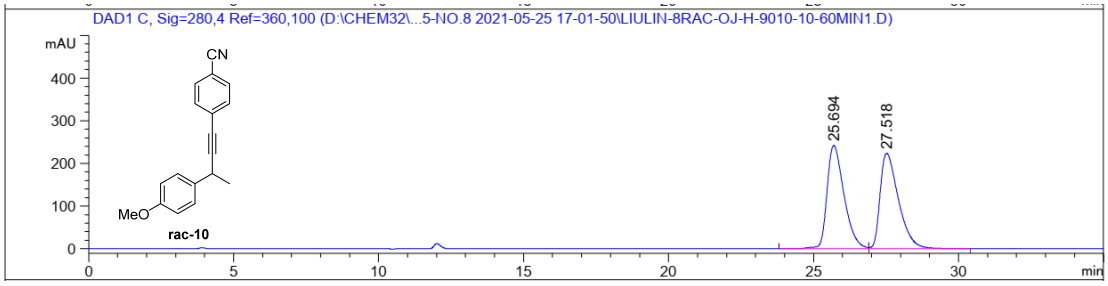
Signal 6: DAD1 F, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.122	BB	0.8889	983.72339	16.09814	51.0491
2	38.215	BB	0.9923	943.29181	13.85436	48.9509
Totals :				1927.01520	29.95250	



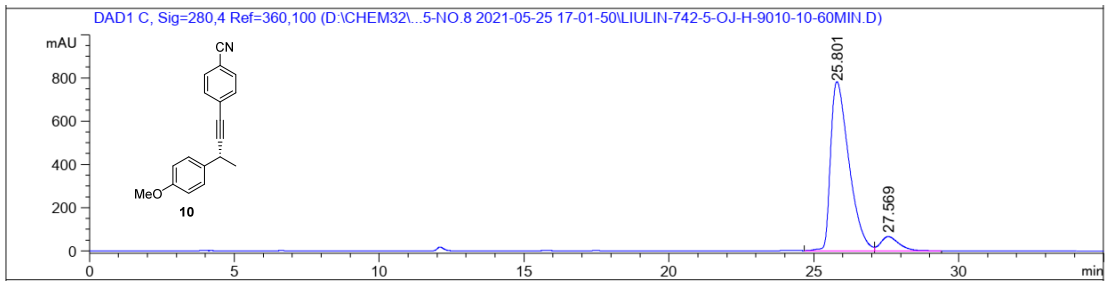
Signal 6: DAD1 F, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.154	BB	0.7928	374.17508	5.63410	7.1748
2	37.960	BB	1.0431	4840.98730	69.62732	92.8252
Totals :				5215.16238	75.26142	



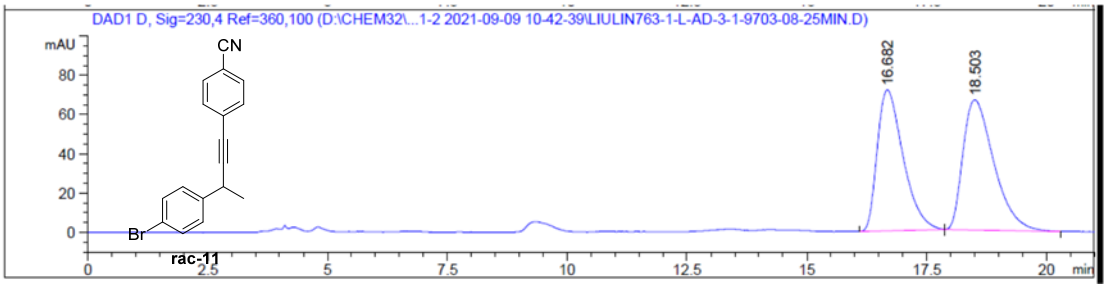
Signal 3: DAD1 C, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.694	BV	0.6223	9874.61035	241.89417	50.0526
2	27.518	VB	0.6697	9853.84863	223.78572	49.9474
Totals :				1.97285e4	465.67989	



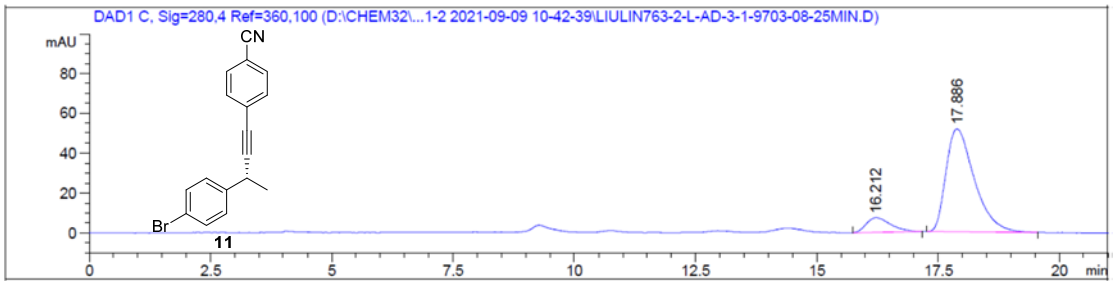
Signal 3: DAD1 C, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.801	BV	0.6727	3.43594e4	781.82532	92.3782
2	27.569	VB	0.6579	2834.87061	65.11900	7.6218
Totals :				3.71942e4	846.94432	



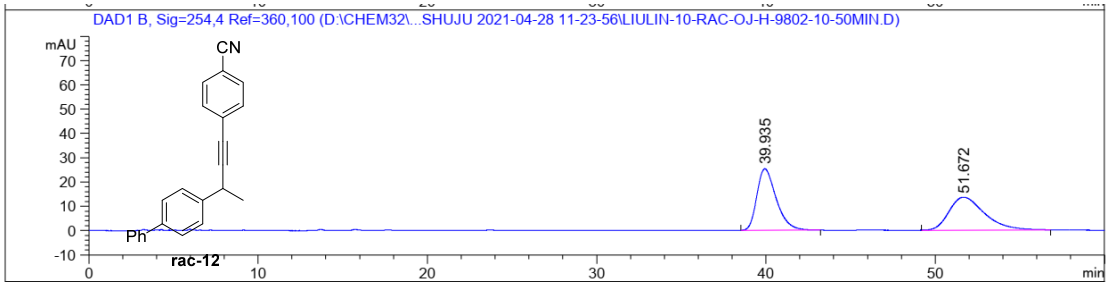
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.682	BB	0.5564	2699.37549	71.83487	47.5746
2	18.503	BB	0.6335	2974.60400	66.29469	52.4254
Totals :				5673.97949	138.12955	



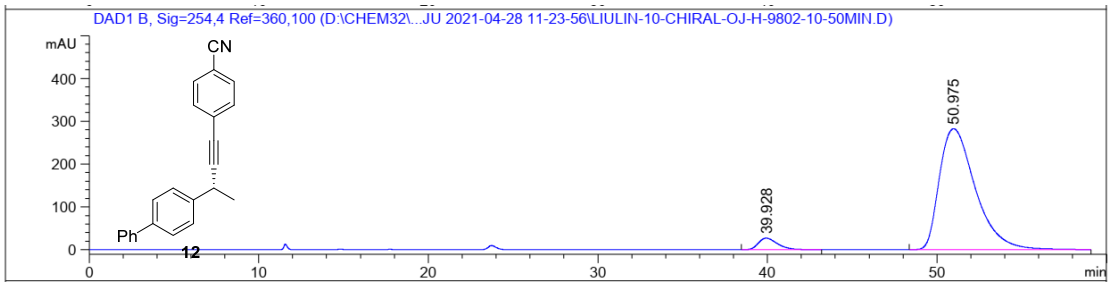
Signal 3: DAD1 C, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.212	BB	0.4185	259.66724	7.45337	10.9333
2	17.886	BB	0.5862	2115.34985	51.60865	89.0667
Totals :				2375.01709	59.06202	



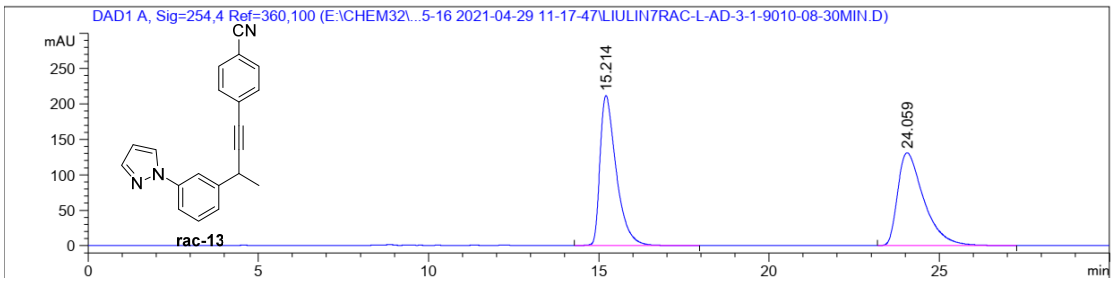
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.935	BB	1.1440	2011.45593	25.34231	50.5959
2	51.672	BB	1.7072	1964.07288	13.54894	49.4041
Totals :				3975.52881	38.89125	



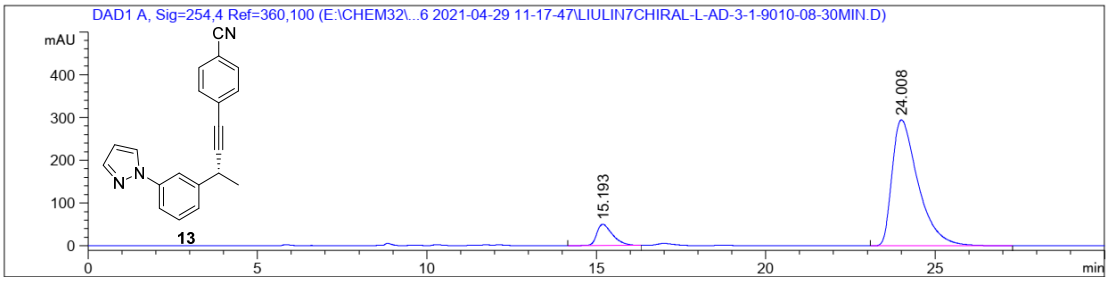
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.928	BB	1.1574	2133.40234	27.07096	4.8728
2	50.975	BBA	2.1892	4.16489e4	282.30133	95.1272
Totals :				4.37823e4	309.37230	



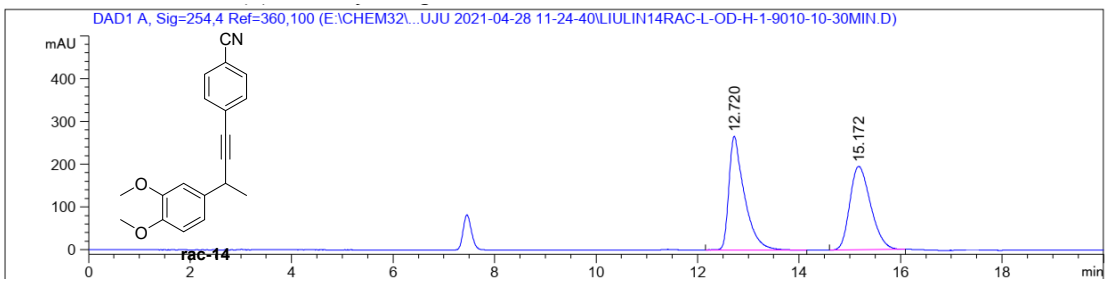
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.214	BB	0.4983	7009.51074	211.67659	50.1301
2	24.059	BB	0.8074	6973.13184	130.92867	49.8699
Totals :				1.39826e4	342.60526	



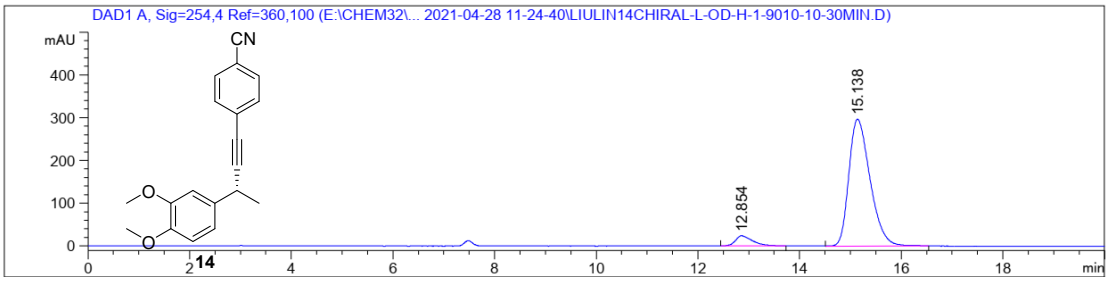
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.193	BB	0.4926	1637.15198	49.92568	9.4349
2	24.008	BB	0.8075	1.57150e4	294.07220	90.5651
Totals :				1.73521e4	343.99789	



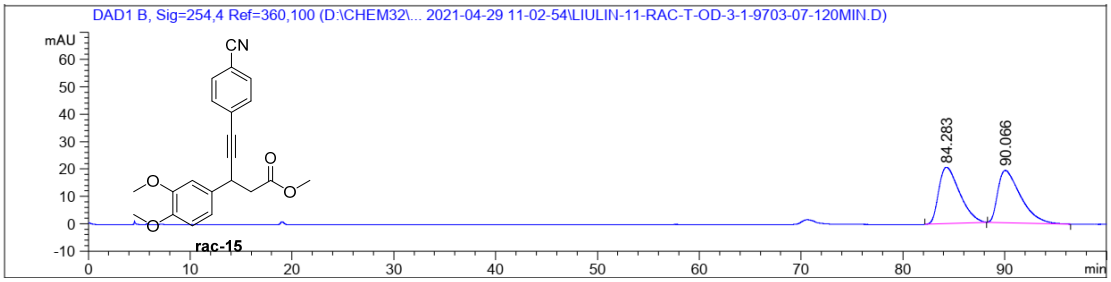
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.720	BB	0.2981	5656.65967	265.98544	50.3593
2	15.172	BB	0.4353	5575.94238	195.18159	49.6407
Totals :				1.12326e4	461.16704	



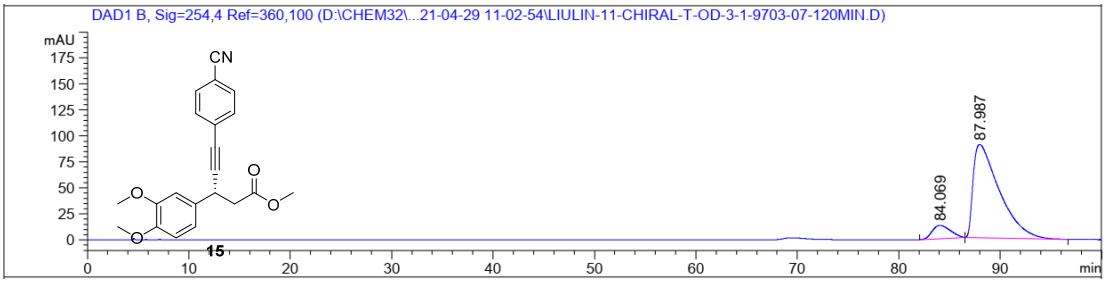
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.854	BB	0.3096	545.78674	23.79666	5.9766
2	15.138	BB	0.4401	8586.24707	296.29031	94.0234
Totals :				9132.03381	320.08697	



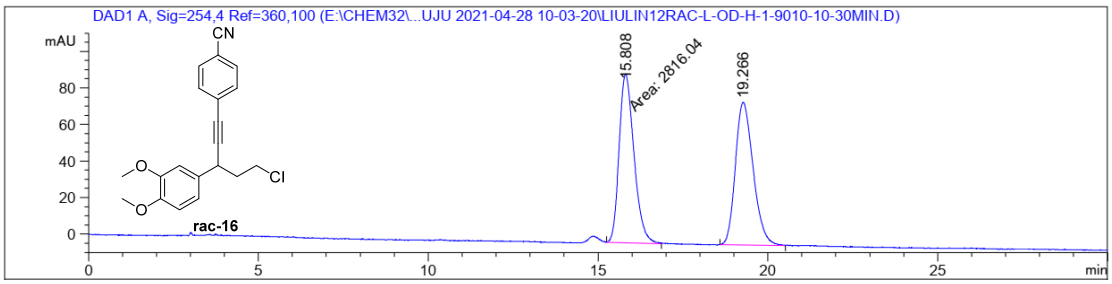
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	84.283	BB	1.6988	2939.90405	20.60299	49.9896
2	90.066	BB	1.8418	2941.12280	19.06445	50.0104
Totals :				5881.02686	39.66744	



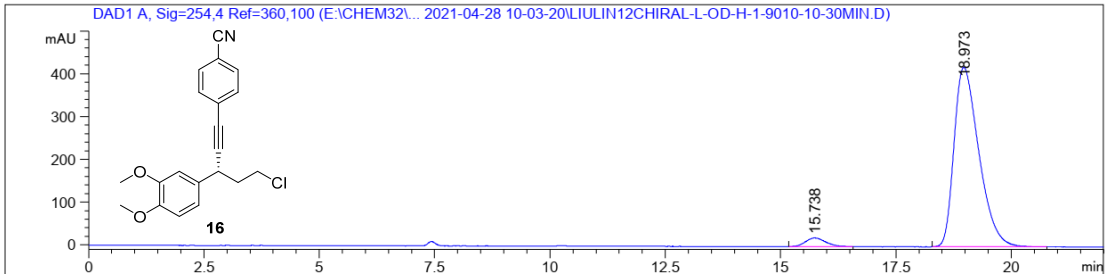
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	84.069	BB	1.4632	1583.22583	12.83423	8.9424
2	87.987	BB	2.4149	1.61216e4	89.78024	91.0576
Totals :				1.77048e4	102.61448	



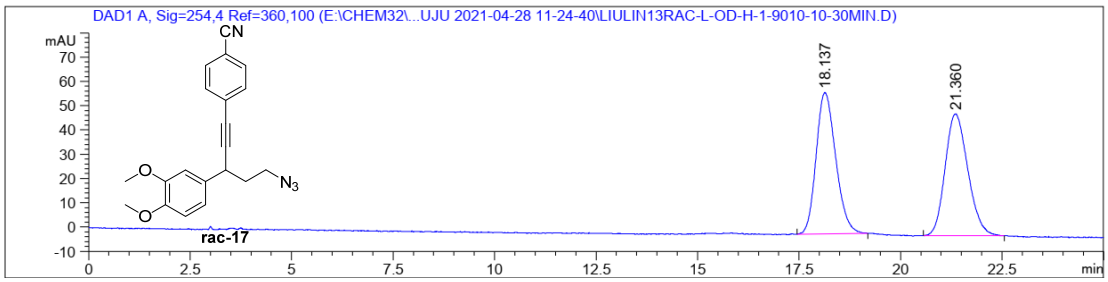
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.808	MM	0.5072	2816.04297	92.53878	49.7851
2	19.266	BB	0.5542	2840.35181	78.12350	50.2149
Totals :				5656.39478	170.66228	



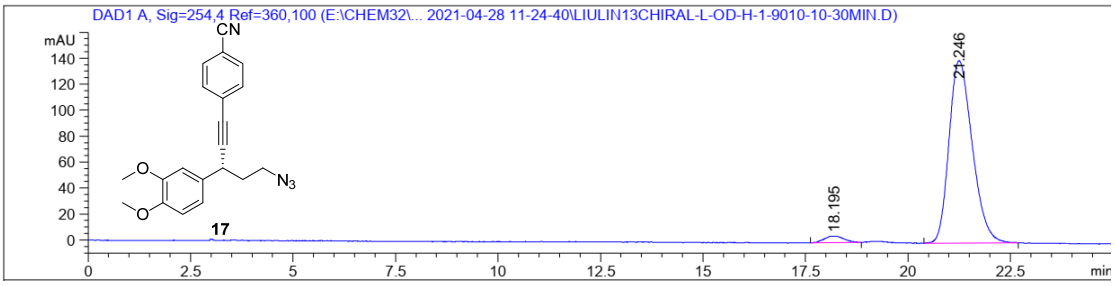
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.738	BB	0.3890	614.82294	20.20588	3.7744
2	18.973	BV R	0.5636	1.56747e4	419.82751	96.2256
Totals :				1.62895e4	440.03339	



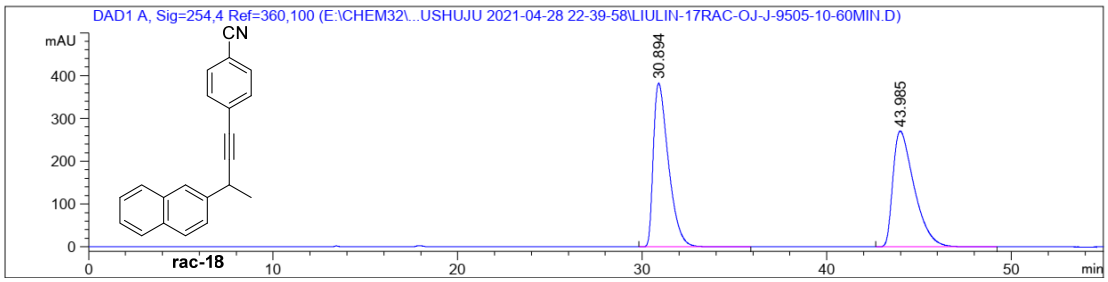
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.137	BB	0.5081	1958.29224	58.26832	49.9348
2	21.360	BB	0.5380	1963.40942	50.23597	50.0652
Totals :				3921.70166	108.50429	



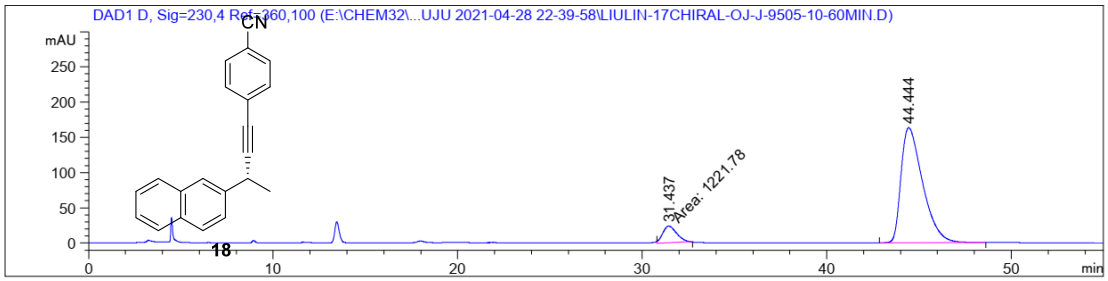
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.195	BB	0.3988	170.49489	5.08993	2.9836
2	21.246	BB	0.5686	5543.83008	140.42360	97.0164
Totals :				5714.32497	145.51353	



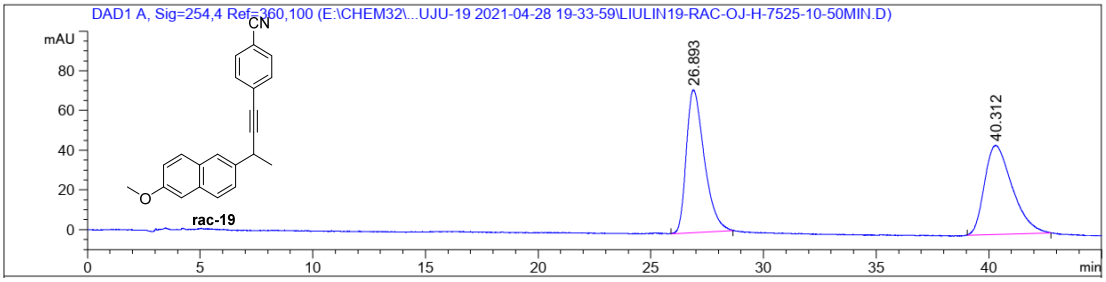
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.894	BB	0.8658	2.16758e4	382.09894	49.9964
2	43.985	BB	1.2124	2.16790e4	270.68146	50.0036
Totals :				4.33548e4	652.78040	



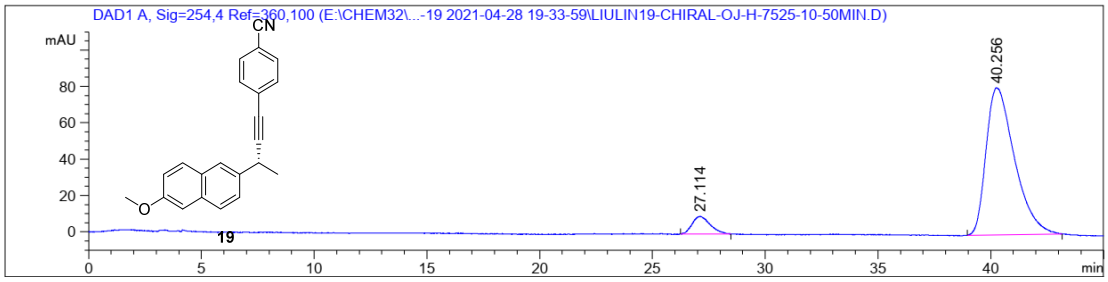
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.437	MM	0.8671	1221.78076	23.48451	8.4358
2	44.444	BB	1.2362	1.32616e4	163.16200	91.5642
Totals :				1.44833e4	186.64652	



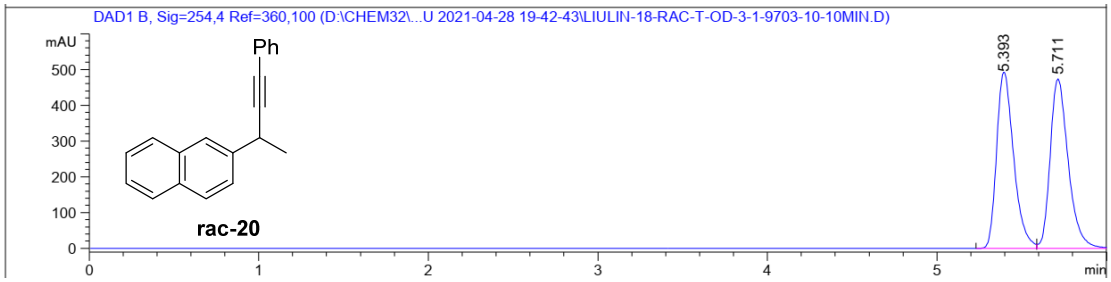
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.893	BB	0.7540	3991.10059	71.86034	50.9392
2	40.312	BB	1.0187	3843.93091	44.90318	49.0608
Totals :				7835.03149	116.76353	



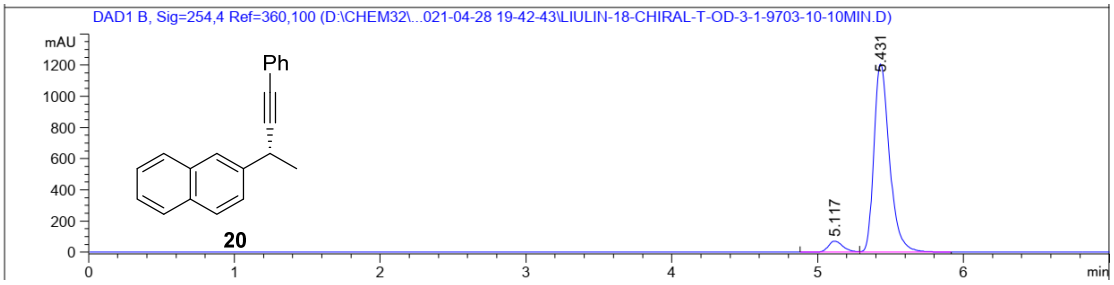
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.114	BB	0.6578	537.09344	9.70217	7.0268
2	40.256	BB	1.0623	7106.35352	80.93707	92.9732
Totals :				7643.44696	90.63923	



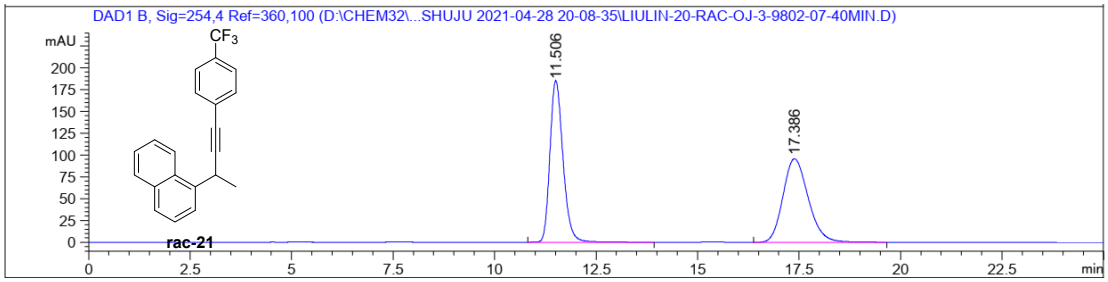
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.393	BV	0.1073	3439.54175	493.45621	49.5256
2	5.711	VB	0.1123	3505.43701	473.62903	50.4744
Totals :				6944.97876	967.08524	



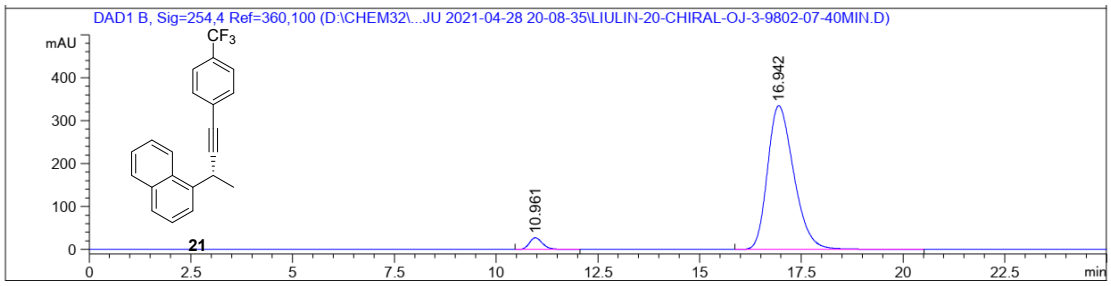
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.117	BV	0.1052	494.33380	71.04460	5.2466
2	5.431	VV	0.1122	8927.70605	1207.94934	94.7534
Totals :				9422.03986	1278.99394	



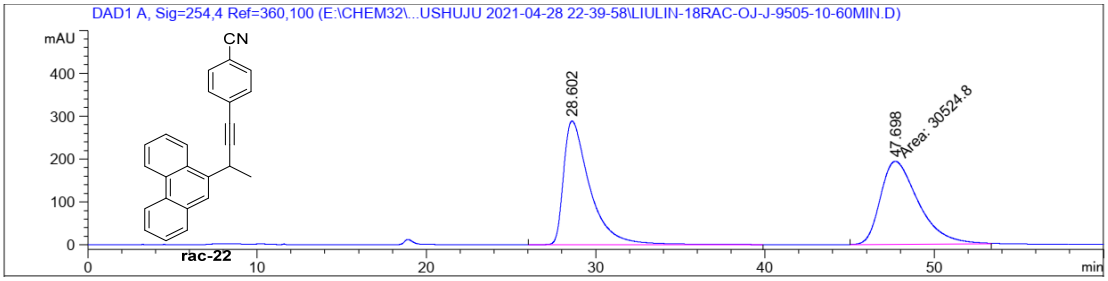
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.506	BB	0.3468	4139.64014	185.20062	50.0451
2	17.386	BB	0.6676	4132.17383	95.73479	49.9549
Totals :				8271.81396	280.93541	



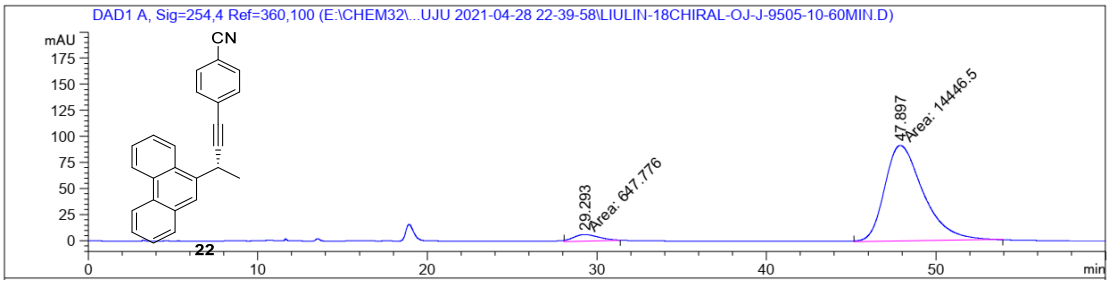
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.961	BB	0.3450	606.51294	27.11358	3.8847
2	16.942	BB	0.6913	1.50064e4	334.57190	96.1153
Totals :				1.56129e4	361.68548	



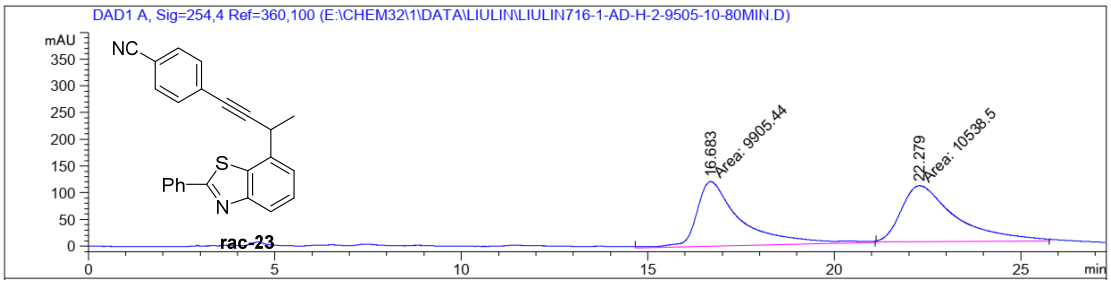
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.602	BB	1.5859	3.09708e4	288.16101	50.3627
2	47.698	MM	2.6190	3.05248e4	194.25427	49.6373
Totals :				6.14956e4	482.41528	



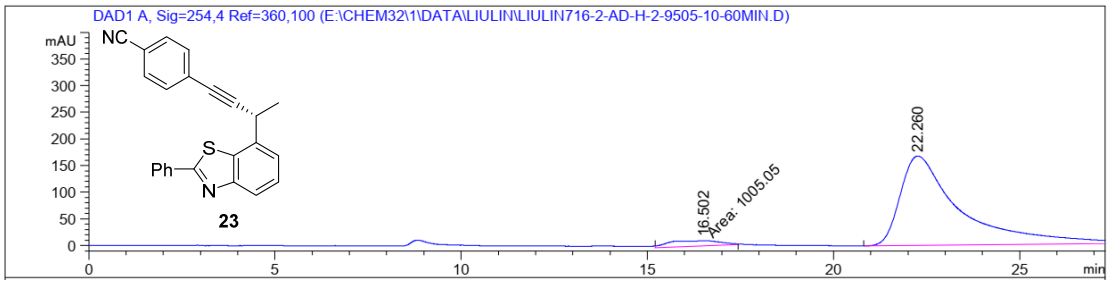
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.293	MM	1.7195	647.77594	6.27878	4.2915
2	47.897	MM	2.6313	1.44465e4	91.50255	95.7085
Totals :				1.50943e4	97.78133	



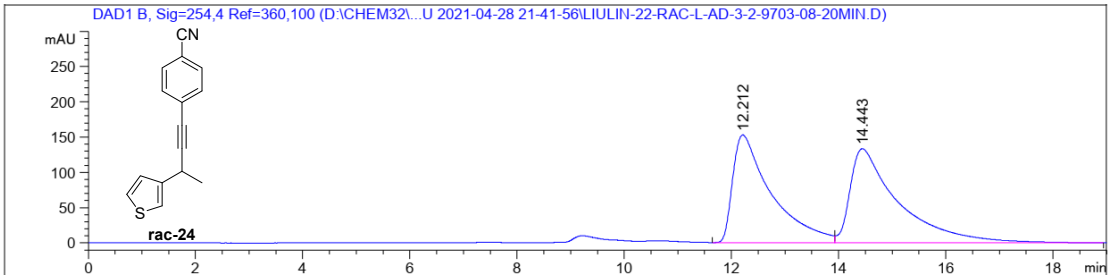
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.683	MM	1.3667	9905.44043	120.79878	48.4518
2	22.279	MM	1.6778	1.05385e4	104.68726	51.5482
Totals :				2.04439e4	225.48605	



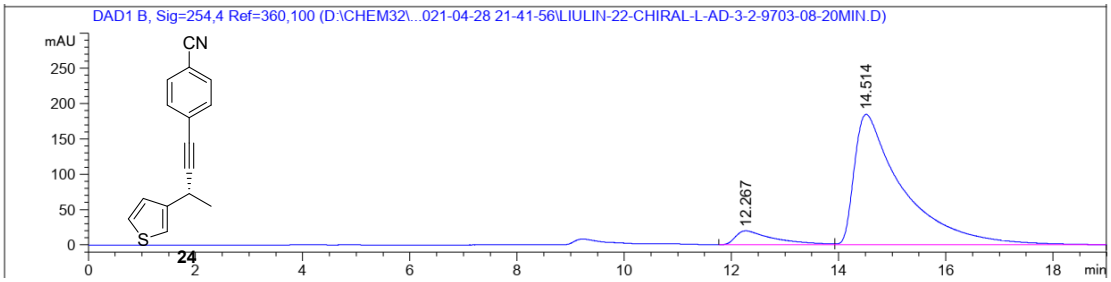
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.502	MM	1.2050	1005.04987	9.82534	4.9915
2	22.260	BB	1.5122	1.91300e4	167.77661	95.0085
Totals :				2.01350e4	177.60195	



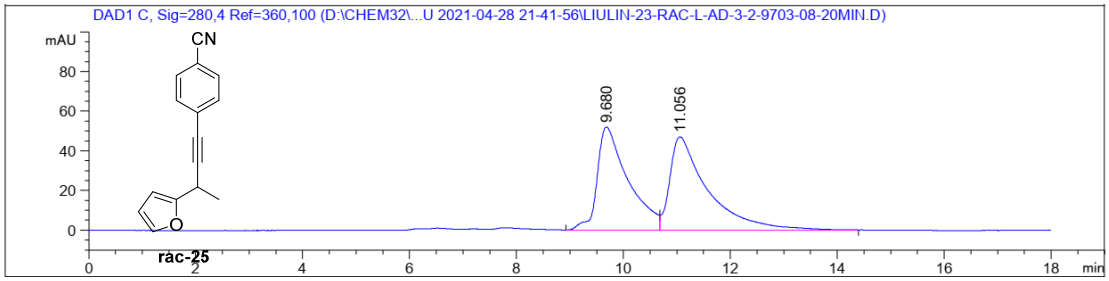
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.212	BV	0.7025	7621.47412	152.63591	47.8319
2	14.443	VBA	0.8604	8312.40039	133.13379	52.1681
Totals :				1.59339e4	285.76970	



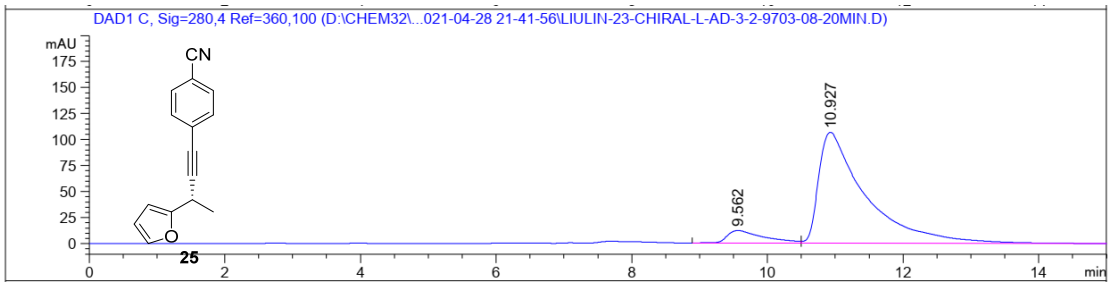
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.267	BV	0.6910	963.41077	19.61568	7.6947
2	14.514	VBA	0.8684	1.15571e4	184.58902	92.3053
Totals :				1.25205e4	204.20470	



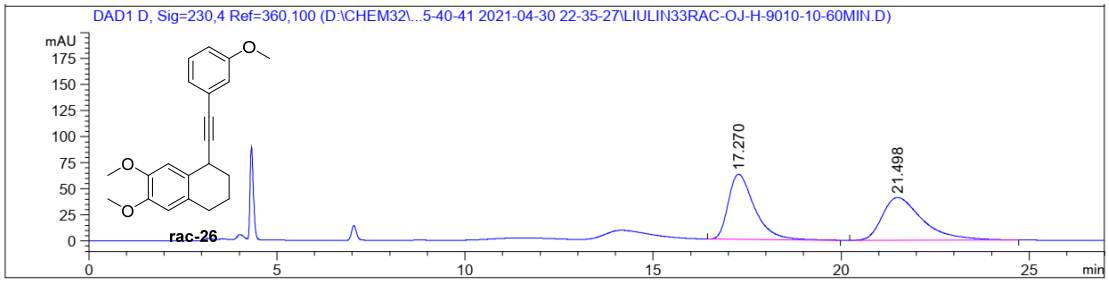
Signal 3: DAD1 C, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.680	BV	0.5595	2081.77734	51.94943	47.4325
2	11.056	VB	0.6771	2307.15039	46.97017	52.5675
Totals :				4388.92773	98.91959	



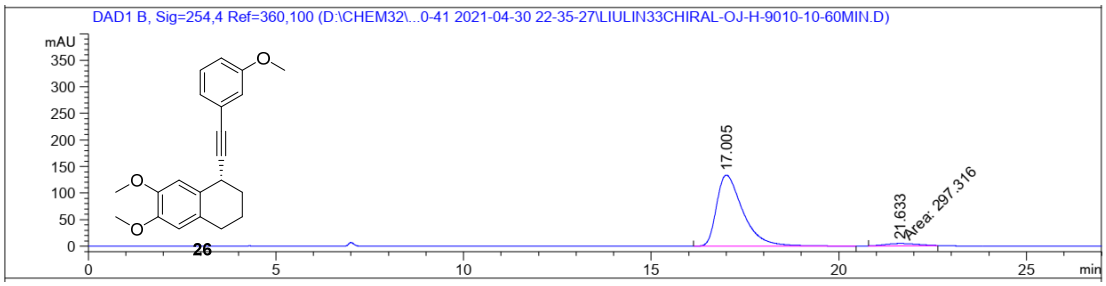
Signal 3: DAD1 C, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.562	BV	0.5165	448.87595	12.05347	8.0432
2	10.927	VBA	0.6638	5131.95264	106.57375	91.9568
Totals :				5580.82858	118.62722	



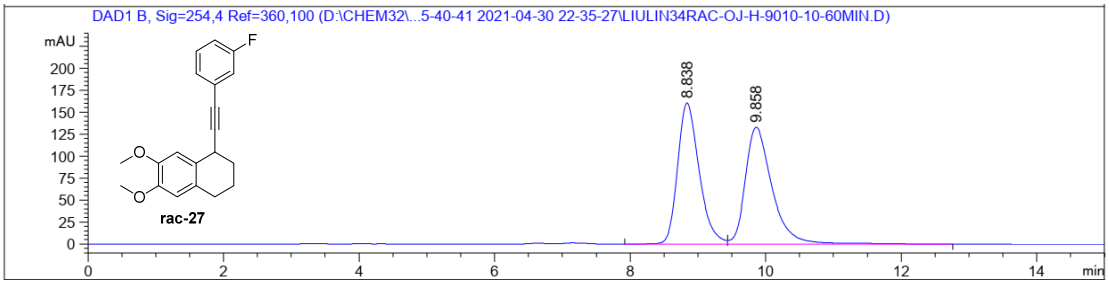
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.270	BB	0.7187	3013.56763	62.47997	49.7538
2	21.498	BB	1.0709	3043.38623	40.95895	50.2462
Totals :				6056.95386	103.43892	



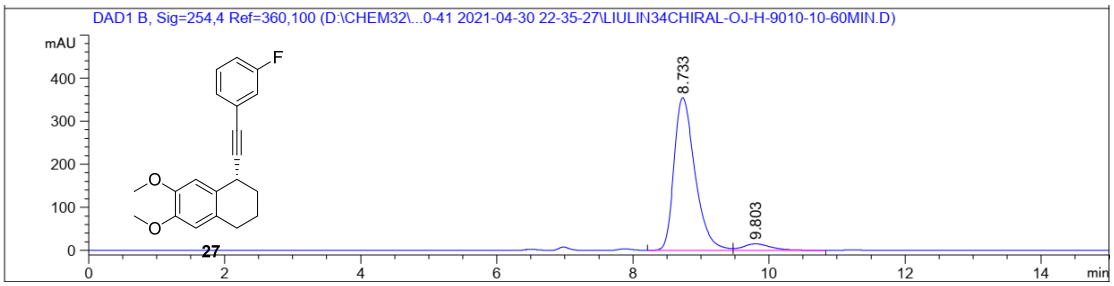
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.005	BB	0.7337	6507.14551	133.72081	95.6306
2	21.633	MM	1.0617	297.31555	4.66718	4.3694



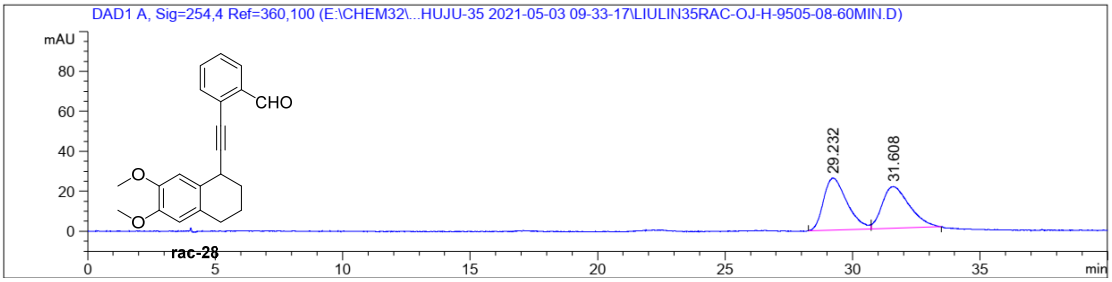
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.838	BV	0.3390	3539.99951	160.73064	49.2916
2	9.858	VB	0.4137	3641.75098	132.87816	50.7084
Totals :				7181.75049	293.60880	



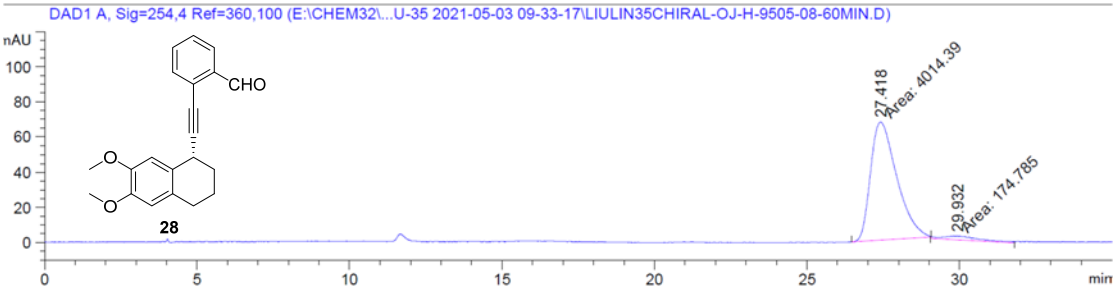
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.733	BV	0.3276	7567.80615	353.78061	94.7284
2	9.803	VB	0.4207	421.14703	14.94743	5.2716
Totals :				7988.95319	368.72804	



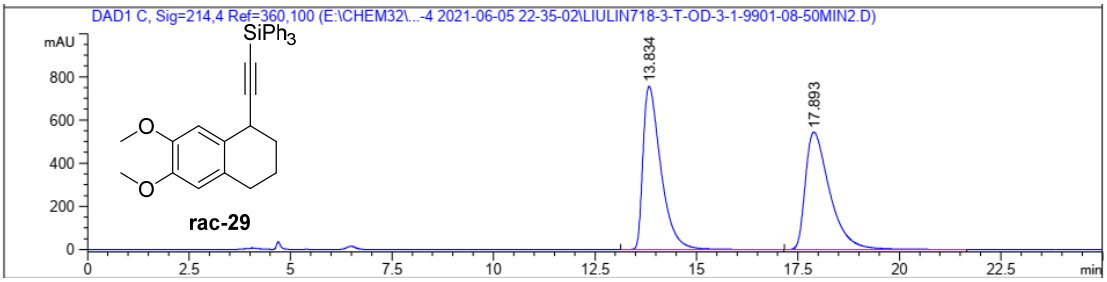
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.232	BV R	0.7732	1674.43567	26.07538	51.8193
2	31.608	VB	0.8788	1556.85999	20.85736	48.1807
Totals :				3231.29565	46.93274	



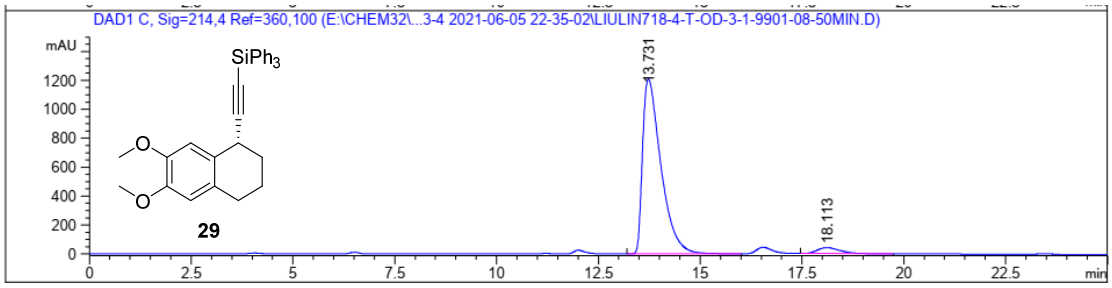
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.418	MM	0.9985	4014.38550	67.00638	95.8277
2	29.932	MM	1.3694	174.78462	2.12728	4.1723
Totals :				4189.17012	69.13366	



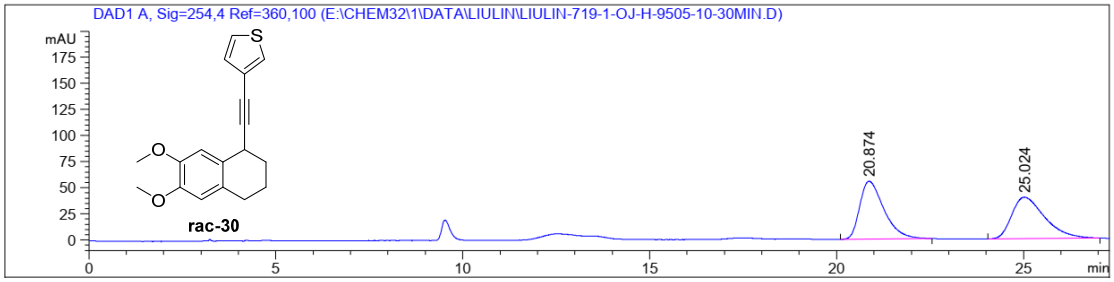
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.834	BB	0.4608	2.31174e4	755.79272	50.4983
2	17.893	BB	0.6284	2.26611e4	543.57141	49.5017
Totals :				4.57785e4	1299.36414	



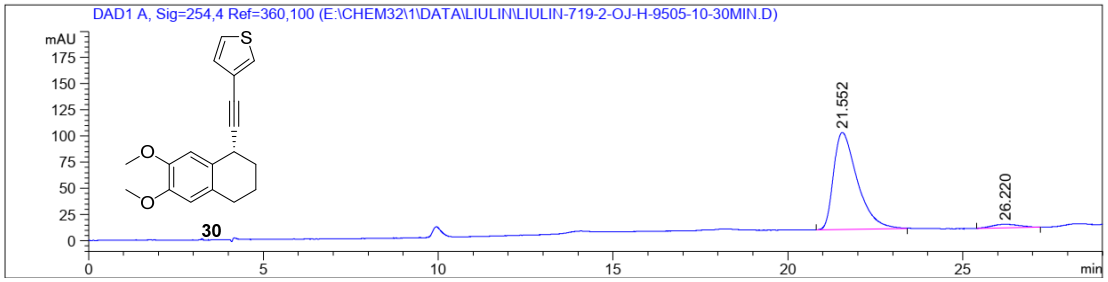
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.731	BB	0.4720	3.79327e4	1209.10510	95.7938
2	18.113	BB	0.6029	1665.56592	41.79293	4.2062
Totals :				3.95983e4	1250.89803	



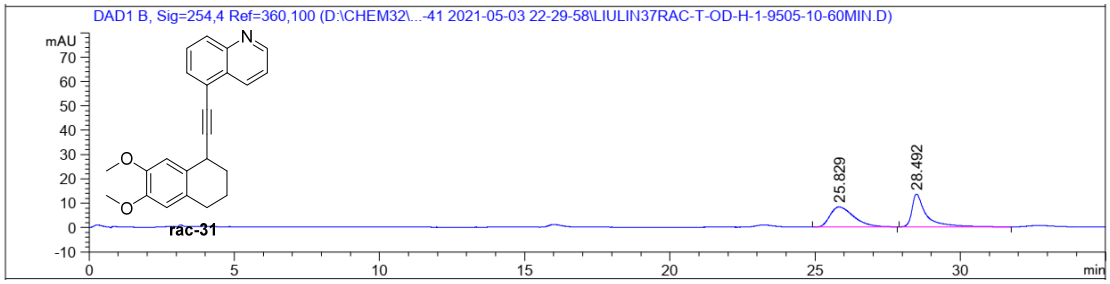
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.874	BB	0.6491	2503.91699	55.42449	50.5112
2	25.024	BB	0.7821	2453.23218	39.85449	49.4888
Totals :				4957.14917	95.27898	



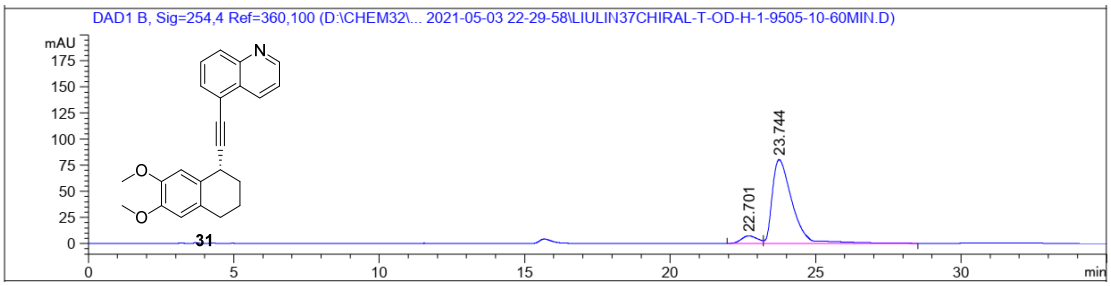
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.552	BB	0.7053	4373.75195	92.56031	95.8089
2	26.220	BB	0.6574	191.32921	3.45833	4.1911
Totals :				4565.08116	96.01864	



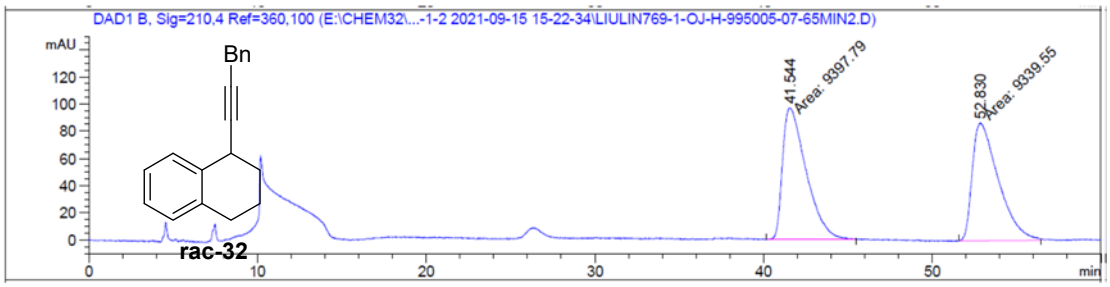
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.829	BB	0.8119	467.02777	8.23242	50.3962
2	28.492	BB	0.4827	459.68427	13.44975	49.6038
Totals :				926.71204	21.68218	



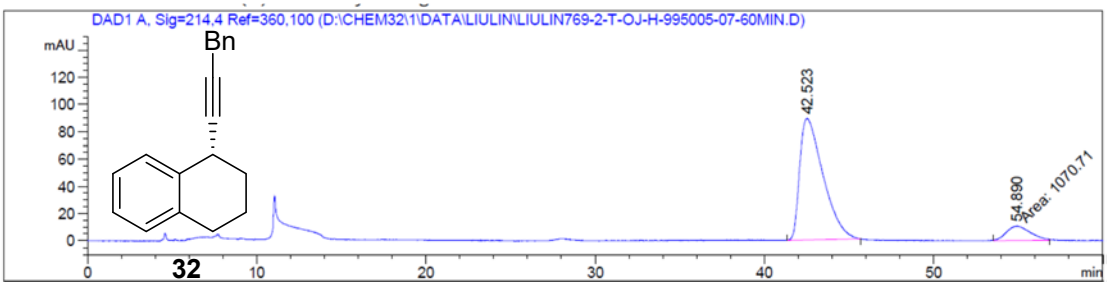
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.701	BV	0.5631	275.33337	7.18381	6.7315
2	23.744	VB	0.7229	3814.91162	80.20061	93.2685
Totals :				4090.24500	87.38443	



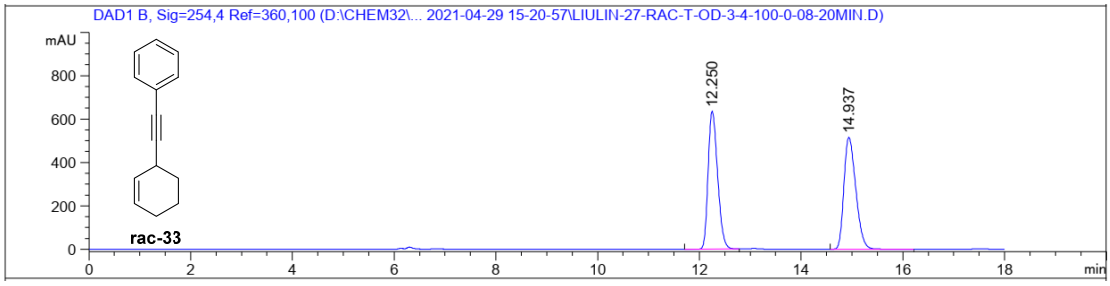
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.544	MM	1.6203	9397.79395	96.66846	50.1554
2	52.830	MM	1.8019	9339.55273	86.38586	49.8446
Totals :				1.87373e4	183.05433	



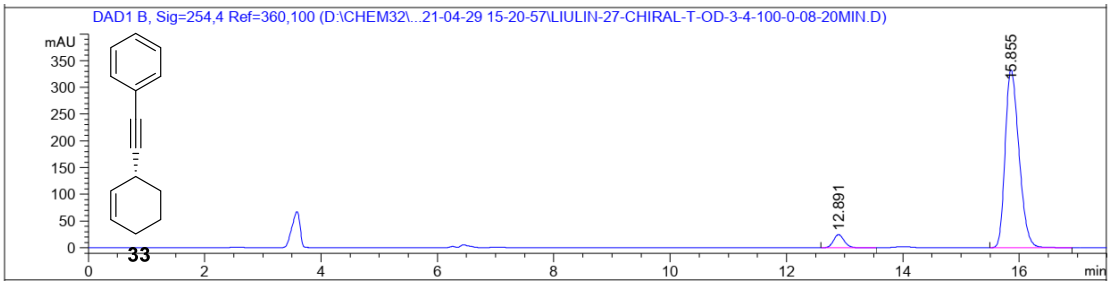
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.523	VB	1.1314	8599.57813	89.14636	88.9279
2	54.890	MM	1.6548	1070.70715	10.78371	11.0721
Totals :				9670.28528	99.93007	



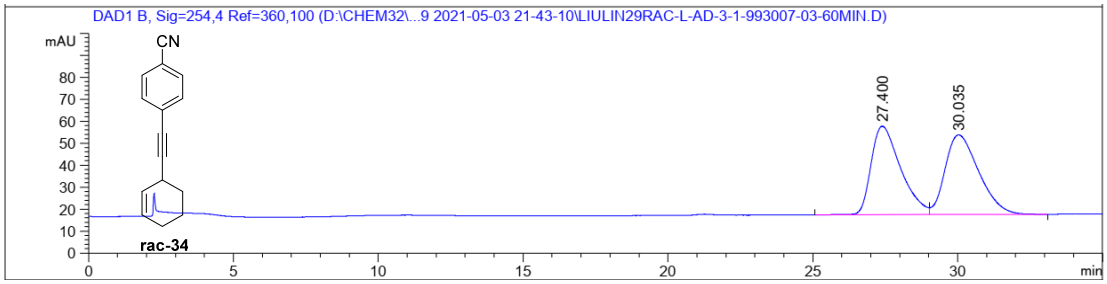
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.250	BB	0.2033	8226.61719	634.37061	49.6566
2	14.937	BB	0.2530	8340.39063	514.76636	50.3434
Totals :				1.65670e4	1149.13696	



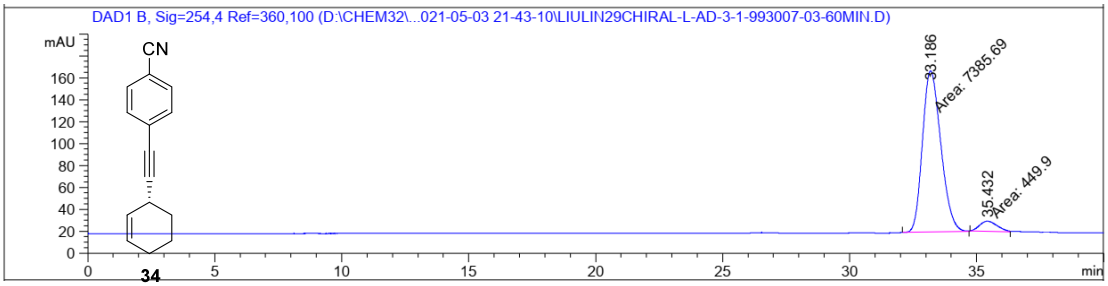
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.891	BB	0.1989	312.07657	24.45831	5.3816
2	15.855	BB	0.2565	5486.90967	332.55722	94.6184
Totals :				5798.98624	357.01553	



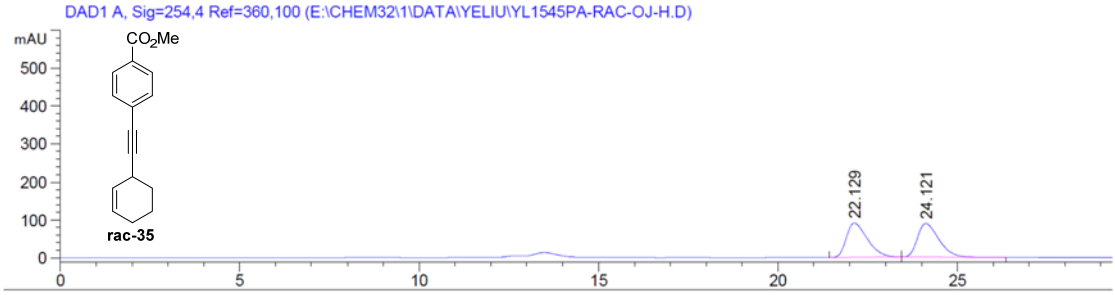
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.400	BV	1.0711	2854.00659	40.25534	49.3100
2	30.035	VB	1.2403	2933.87842	36.24854	50.6900
Totals :				5787.88501	76.50388	



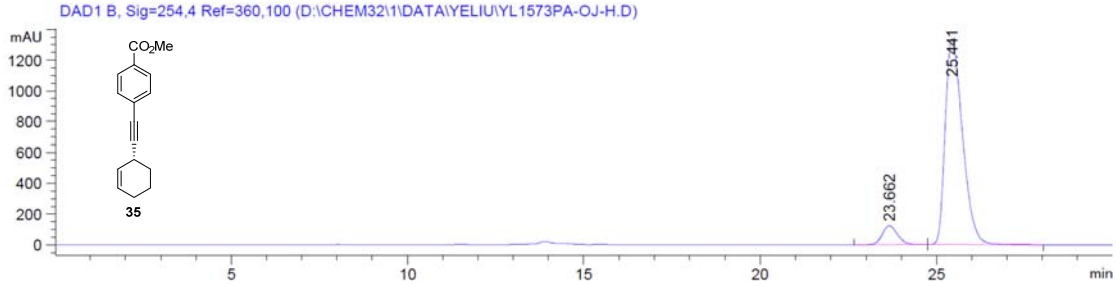
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.186	MM	0.8373	7385.69238	147.02200	94.2582
2	35.432	MM	0.8090	449.90024	9.26872	5.7418
Totals :				7835.59262	156.29072	



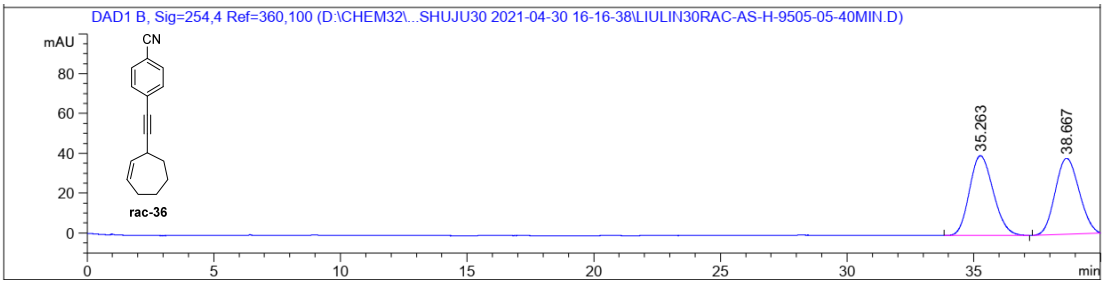
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.129	BB	0.6237	3703.46606	90.83044	49.9699
2	24.121	BB	0.6350	3707.93311	89.18979	50.0301



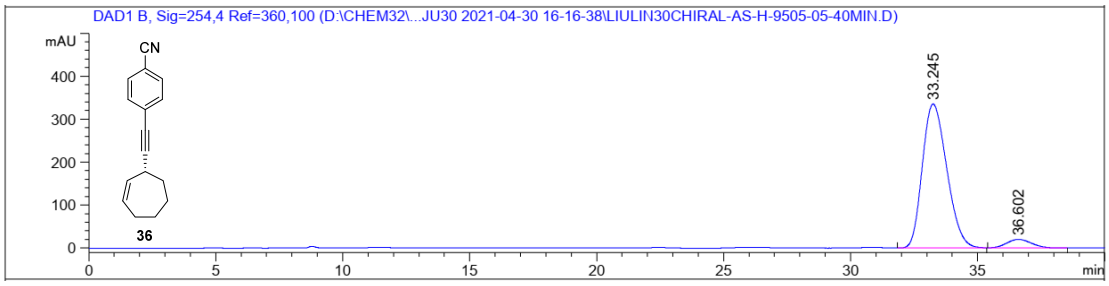
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.662	BB	0.4667	3737.74048	123.63723	7.5642
2	25.441	BB	0.5285	4.56760e4	1337.21387	92.4358



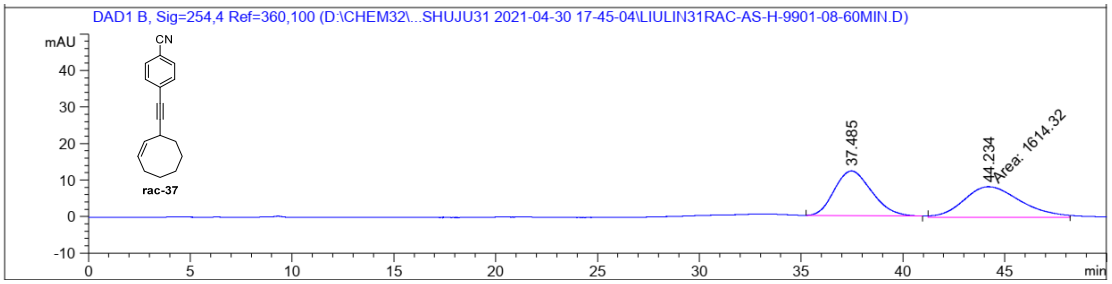
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.263	BB	0.9822	2622.28906	40.03397	51.2245
2	38.667	BBA	0.9920	2496.92285	38.12967	48.7755
Totals :				5119.21191	78.16364	



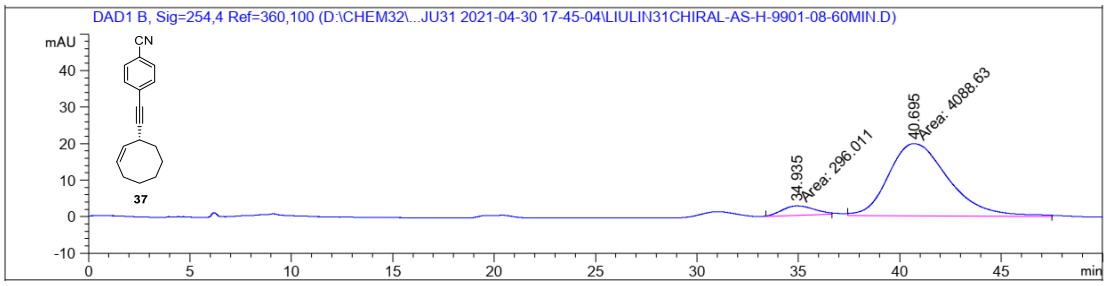
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.245	BB	1.0382	2.24029e4	334.99173	94.3956
2	36.602	BB	0.9760	1330.08228	19.69328	5.6044
Totals :				2.37330e4	354.68501	



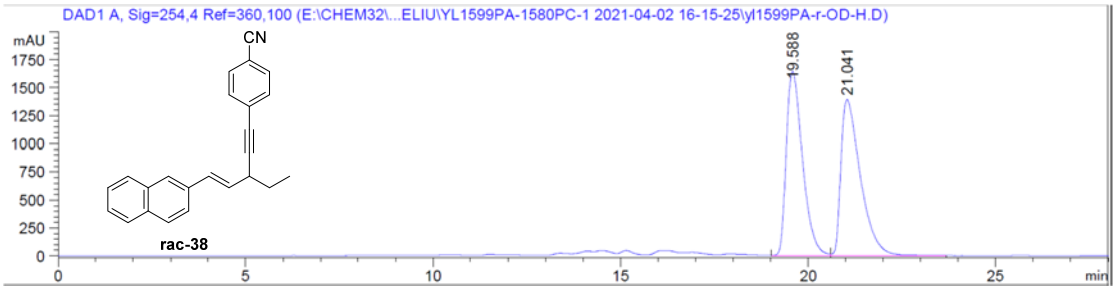
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.485	BB	1.4978	1549.72607	12.23448	48.9793
2	44.234	MM	3.2327	1614.31628	8.32276	51.0207
Totals :				3164.04236	20.55724	



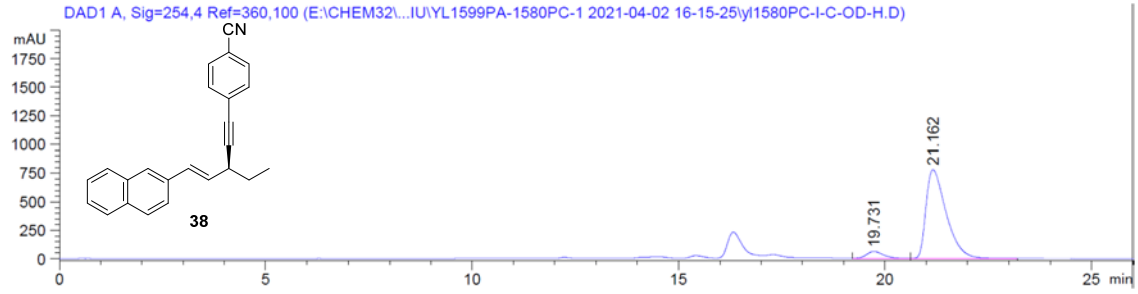
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.935	MM	1.8739	296.01071	2.63274	6.7511
2	40.695	MM	3.4432	4088.62769	19.79087	93.2489
Totals :				4384.63840	22.42361	



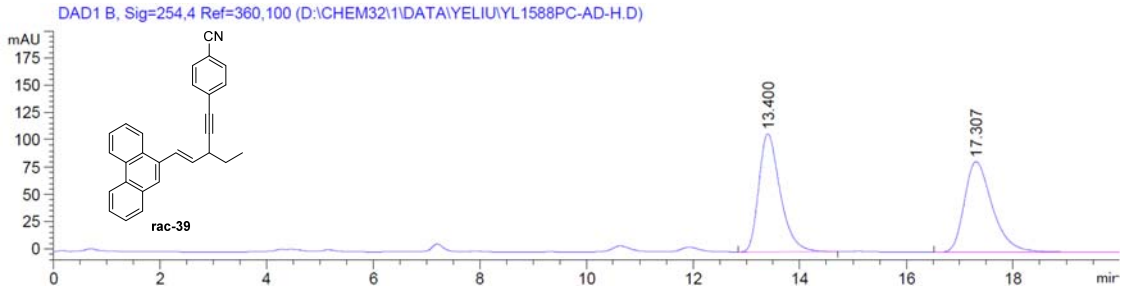
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.588	BV	0.4542	4.93333e4	1643.28809	49.4857
2	21.041	VB	0.5360	5.03588e4	1392.26843	50.5143



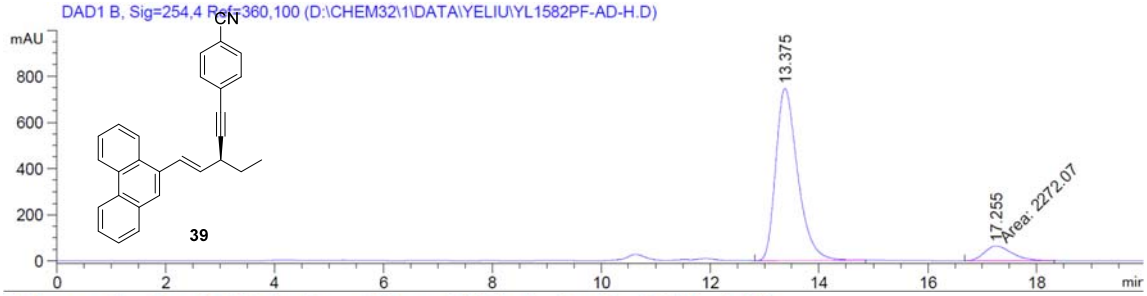
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.731	BB	0.4014	1703.13477	61.44896	6.0400
2	21.162	BB	0.5084	2.64944e4	779.74469	93.9600



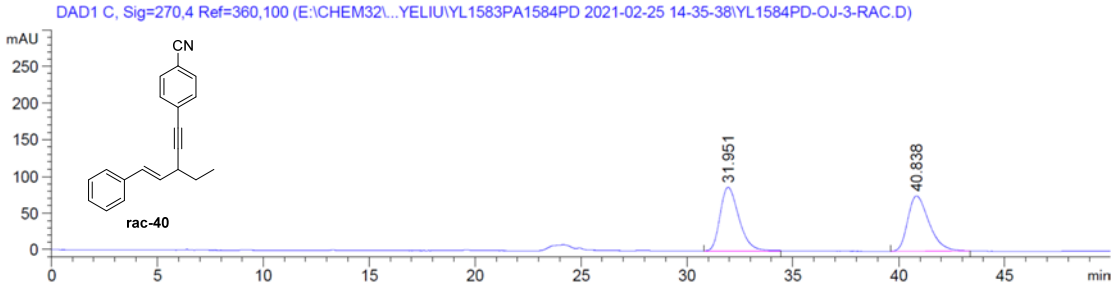
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.400	BB	0.4265	3025.88794	108.11101	49.7662
2	17.307	BB	0.5592	3054.31470	83.41529	50.2338



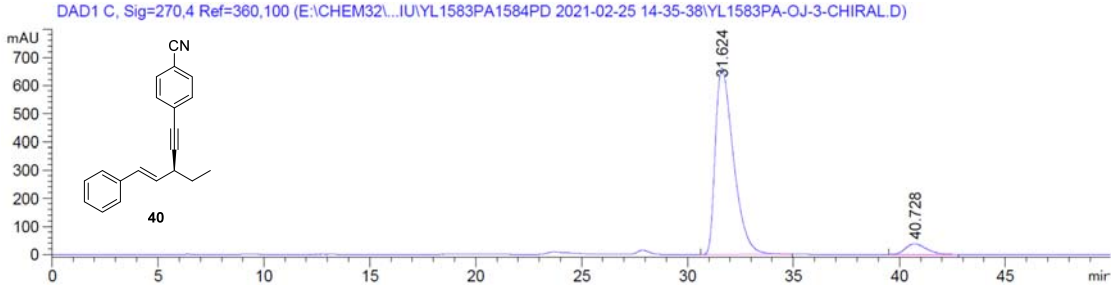
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.375	BB	0.4266	2.08804e4	745.86005	90.1865
2	17.255	MM	0.5922	2272.06665	63.94063	9.8135



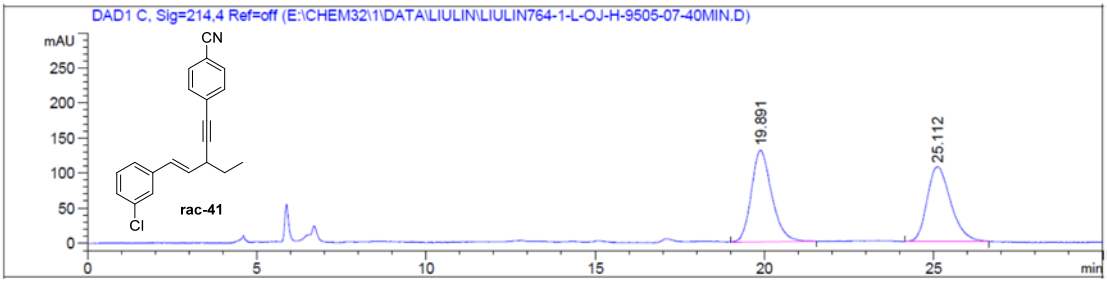
Signal 3: DAD1 C, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.951	BB	0.9020	5346.39893	87.11886	50.3625
2	40.838	BB	0.9731	5269.43799	75.61109	49.6375



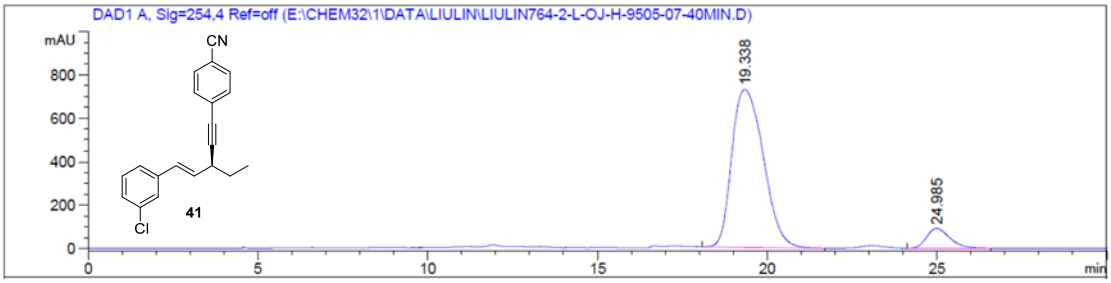
Signal 3: DAD1 C, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.624	BB	0.8847	3.93296e4	660.44812	93.7643
2	40.728	BB	0.8172	2615.57056	38.08457	6.2357



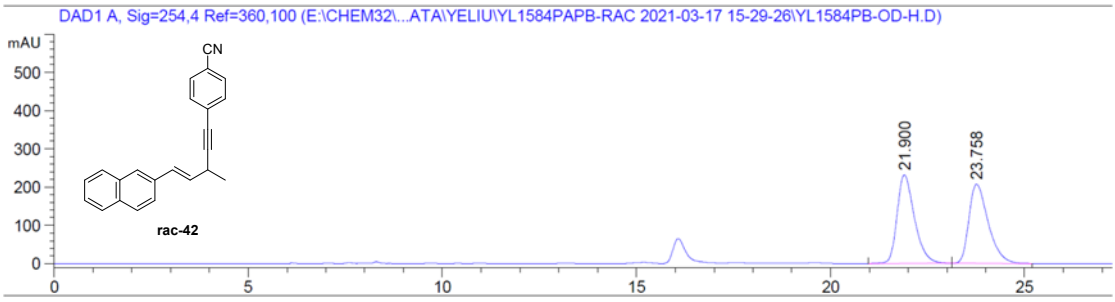
Signal 3: DAD1 C, Sig=214,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.891	VV R	0.5303	5473.40869	130.76518	51.2861
2	25.112	VV R	0.5966	5198.89600	106.66969	48.7139
Totals :				1.06723e4	237.43487	



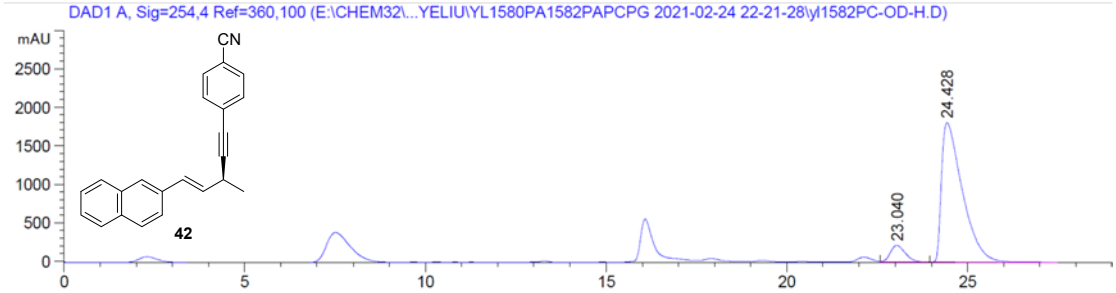
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.338	VB R	0.7929	4.70396e4	728.93915	91.4912
2	24.985	BV R	0.5813	4374.73242	91.91467	8.5088
Totals :				5.14144e4	820.85382	



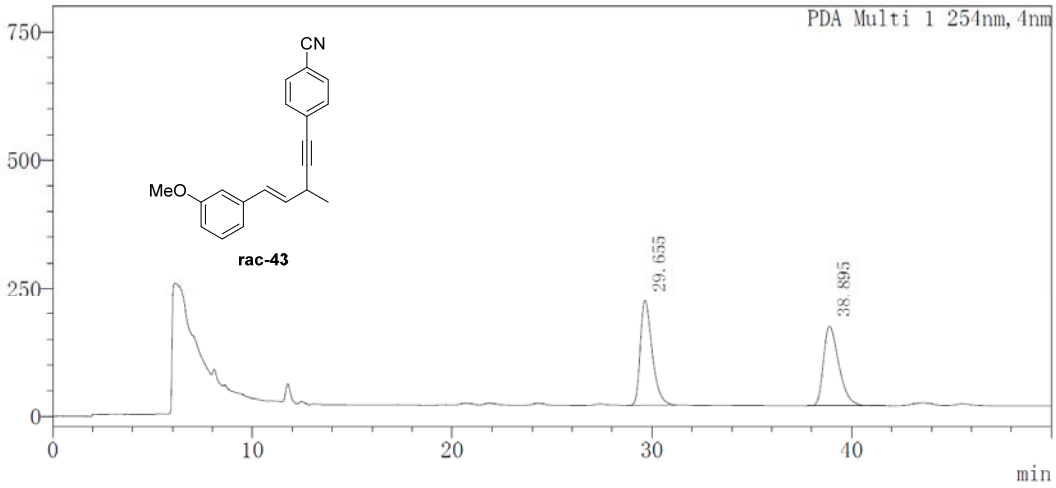
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.900	BB	0.4716	7206.18750	231.20390	50.2534
2	23.758	BB	0.5187	7133.50293	206.66875	49.7466



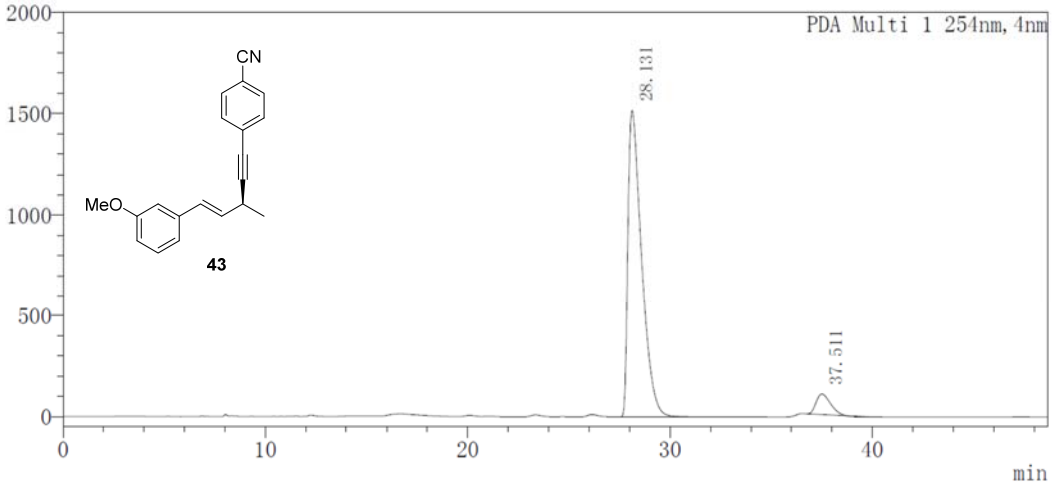
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.040	VB	0.4407	6186.67188	215.66946	7.8755
2	24.428	BB	0.5785	7.23690e4	1809.74536	92.1245



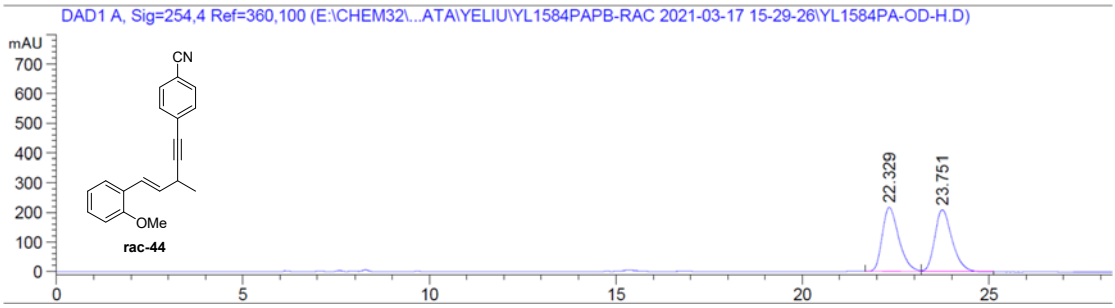
PDA Ch1 254nm

T	Hight	Area	Area%
29.655	204268	8394688	50.125
38.895	155353	8352921	49.875



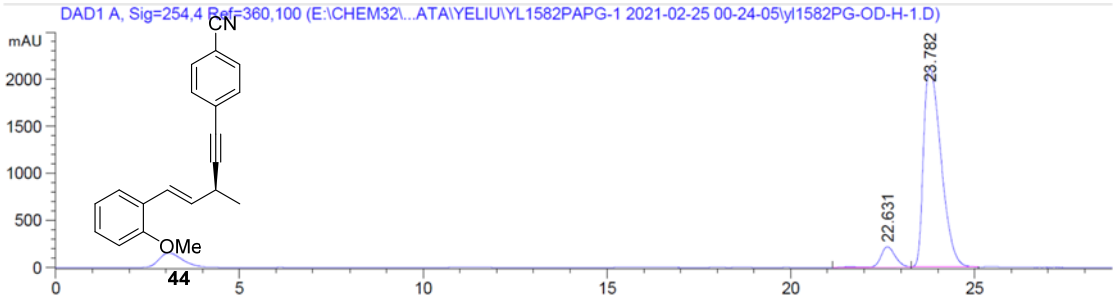
PDA Ch1 254nm

T	Hight	Area	Area%
28.131	1517734	71474606	93.507
37.511	101959	4963041	6.493



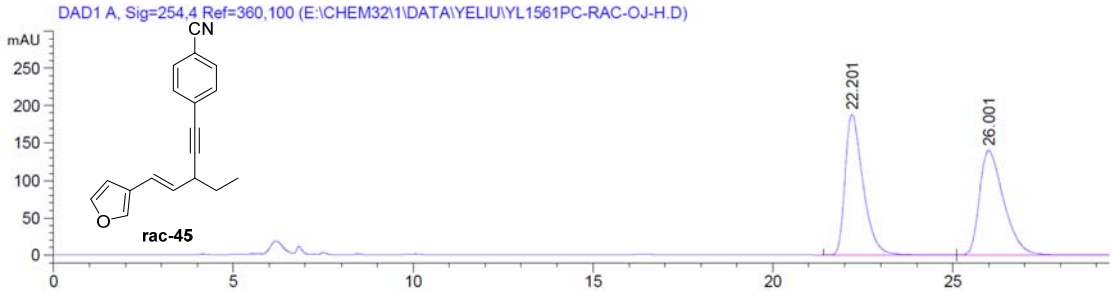
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.329	BV	0.4676	6687.55225	216.94937	49.7251
2	23.751	VB	0.4911	6761.50146	209.17957	50.2749



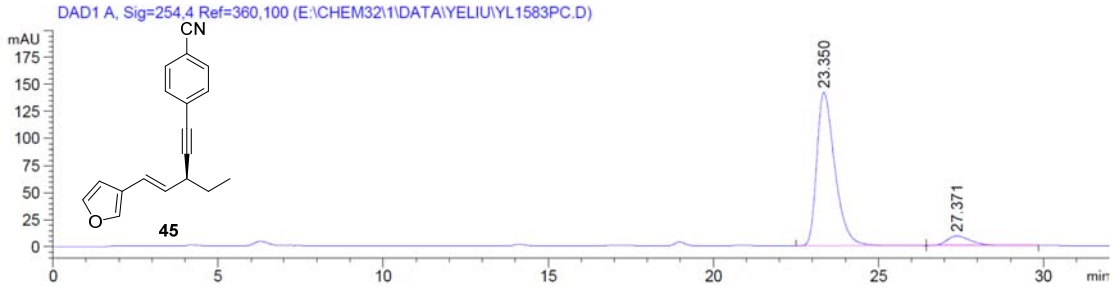
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.631	VV R	0.4185	5997.34570	216.64156	7.8957
2	23.782	VB	0.5077	6.99596e4	2105.18286	92.1043



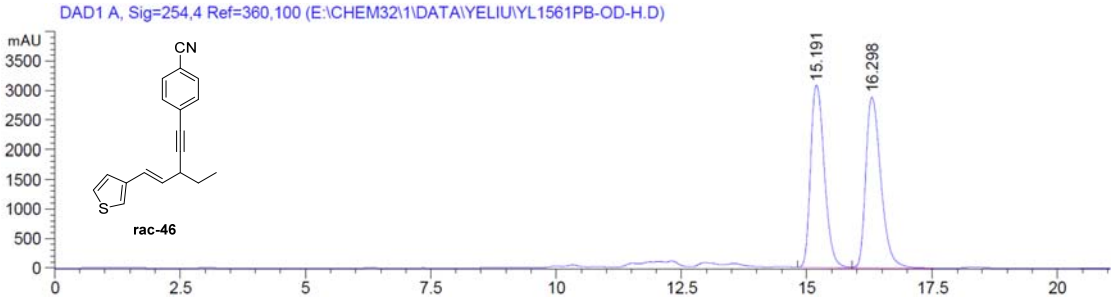
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.201	BB	0.5293	6564.82813	188.04828	50.0148
2	26.001	BB	0.7170	6560.94092	139.93434	49.9852



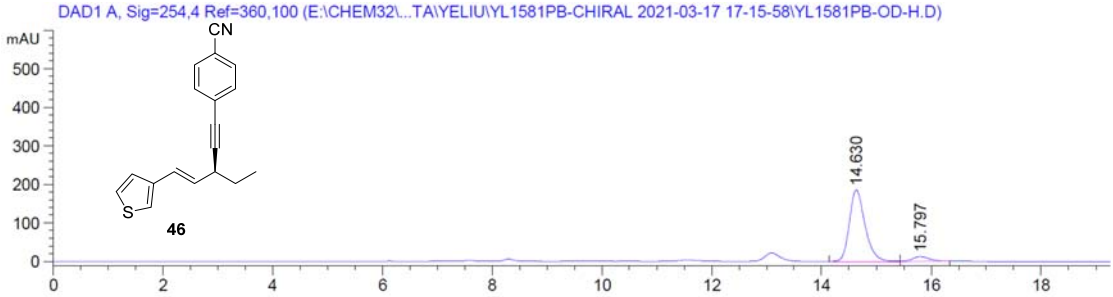
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.350	BB	0.5826	5416.79688	141.50156	92.4155
2	27.371	BB	0.7672	444.55246	8.92397	7.5845



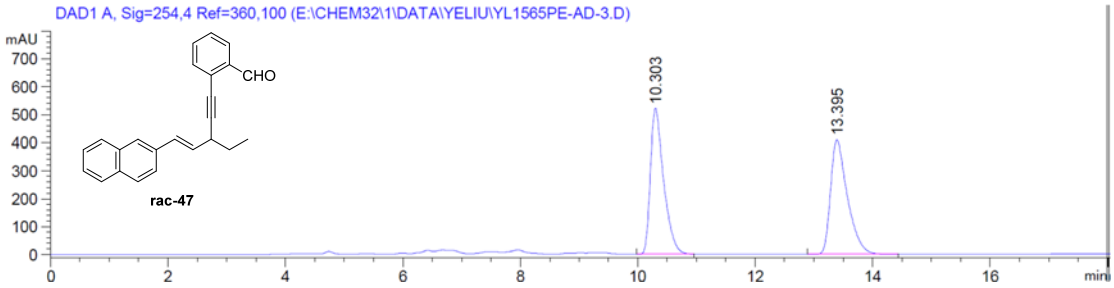
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.191	BV	0.2960	5.86472e4	3082.00659	49.3556
2	16.298	VB	0.3217	6.01787e4	2881.12524	50.6444



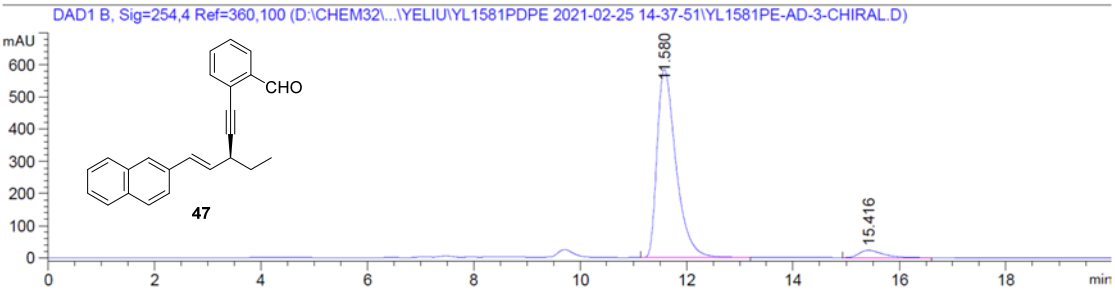
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.630	BV	0.2986	3670.37622	185.70300	93.5641
2	15.797	VB	0.3007	252.46906	11.93735	6.4359



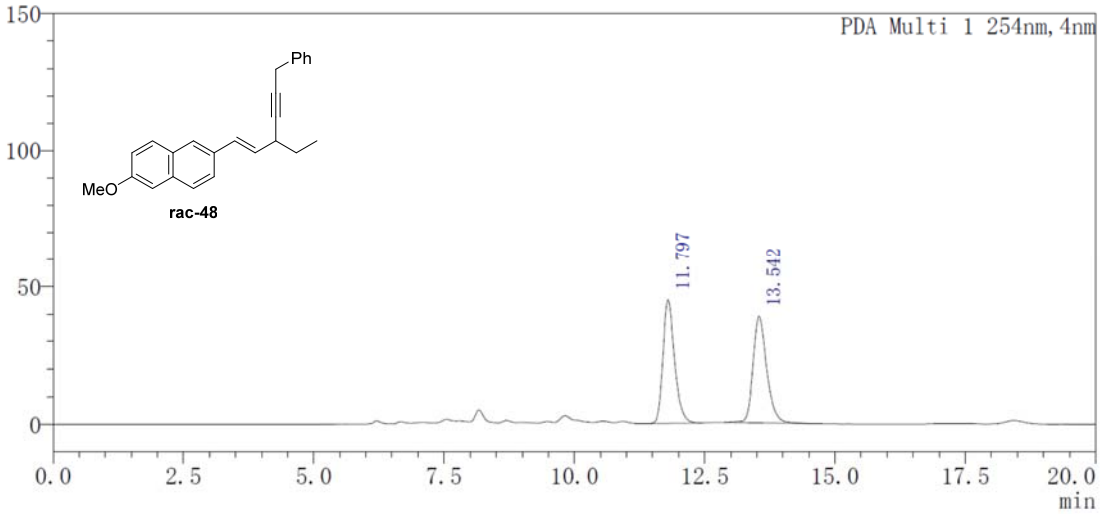
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.303	BB	0.2307	8154.72021	520.85895	49.9193
2	13.395	BB	0.2977	8181.09473	408.41983	50.0807



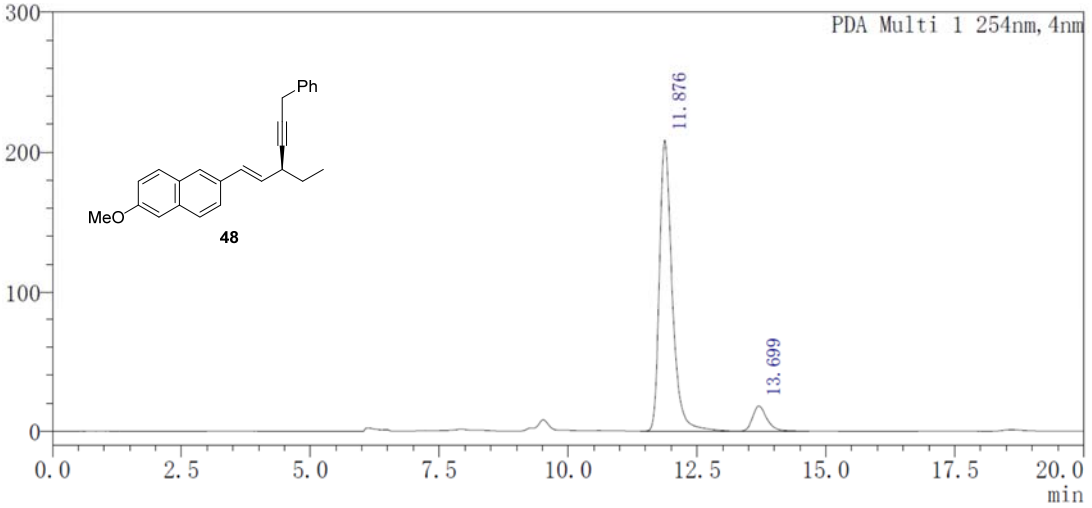
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.580	BB	0.3754	1.44255e4	585.53186	95.2783
2	15.416	BB	0.4422	714.88464	23.41740	4.7217



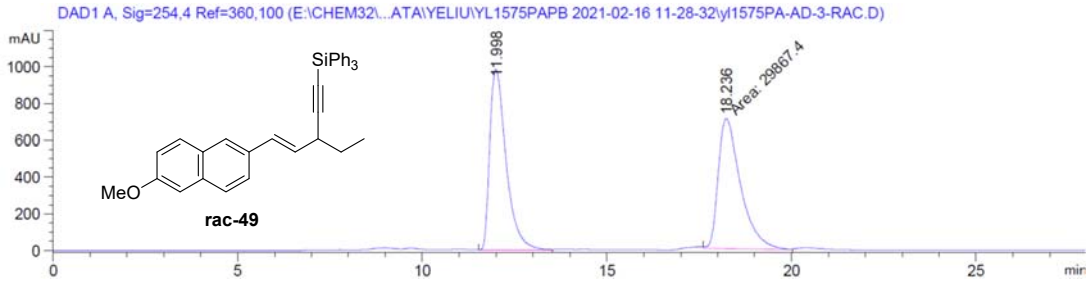
PDA Ch1 254nm

T	Hight	Area	Area%
11.797	44714	692134	49.413
13.542	38575	708582	50.587



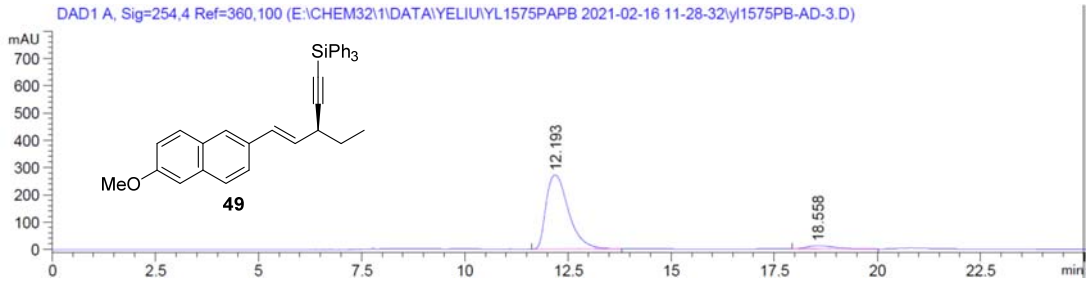
PDA Ch1 254nm

T	Hight	Area	Area%
11.876	207887	3571818	91.156
13.699	17908	346558	8.844



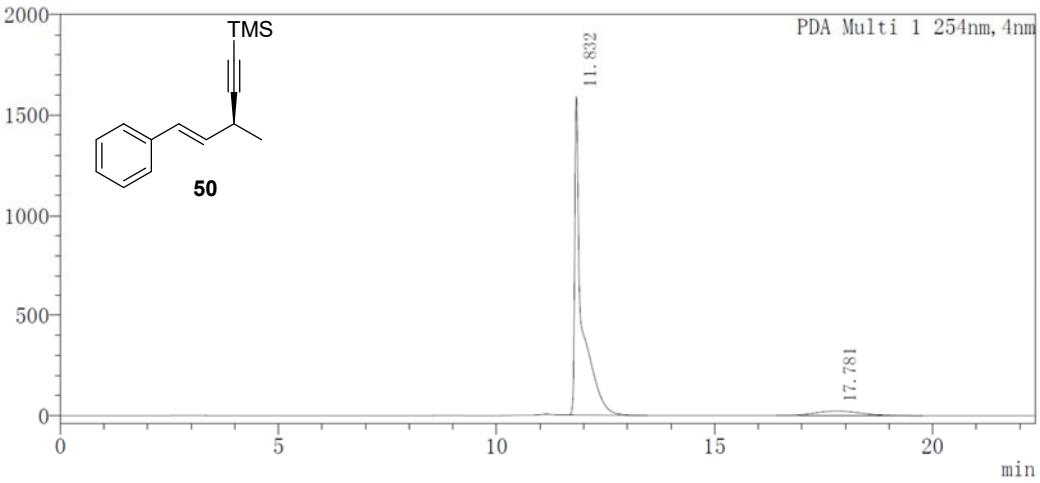
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.998	BB	0.4688	3.00689e4	983.05896	50.1681
2	18.236	MM	0.7031	2.98674e4	707.96588	49.8319



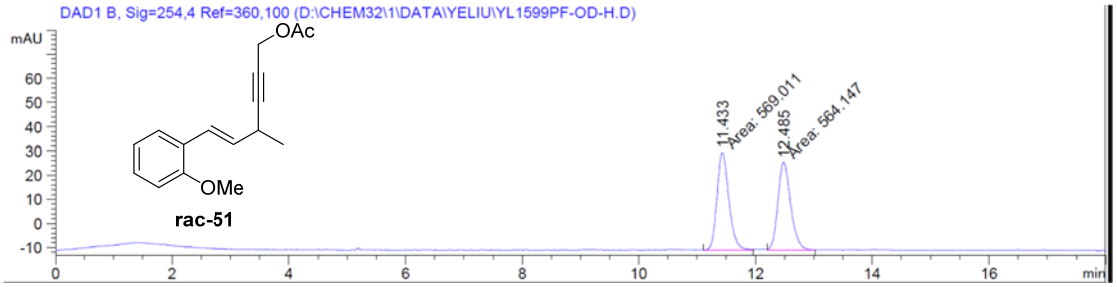
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.193	BB	0.5901	1.01998e4	270.40430	95.2523
2	18.558	BB	0.5482	508.39197	11.18711	4.7477



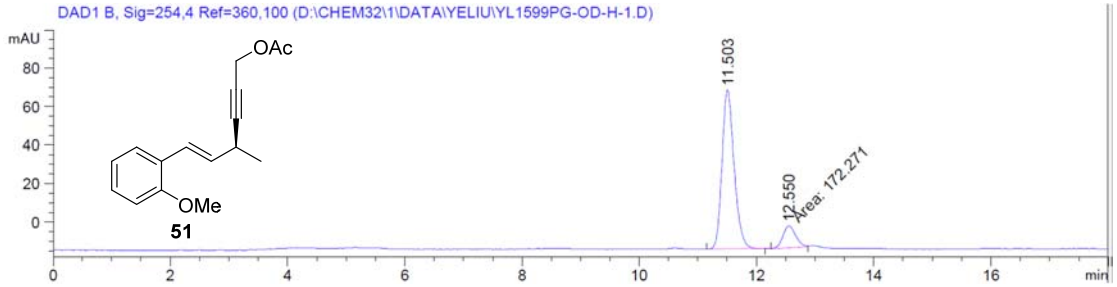
PDA Ch1 254nm

T	Hight	Area	Area%
11.832	1589654	17970116	91.823
17.781	22134	1600375	8.177



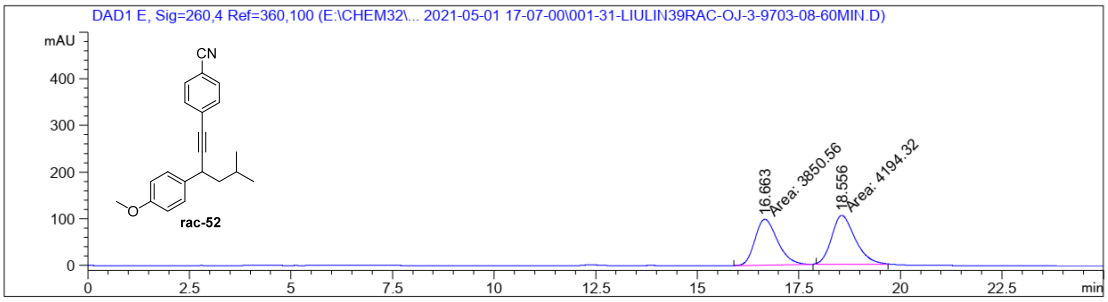
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.433	MM	0.2351	569.01068	40.33370	50.2146
2	12.485	MM	0.2565	564.14655	36.65808	49.7854



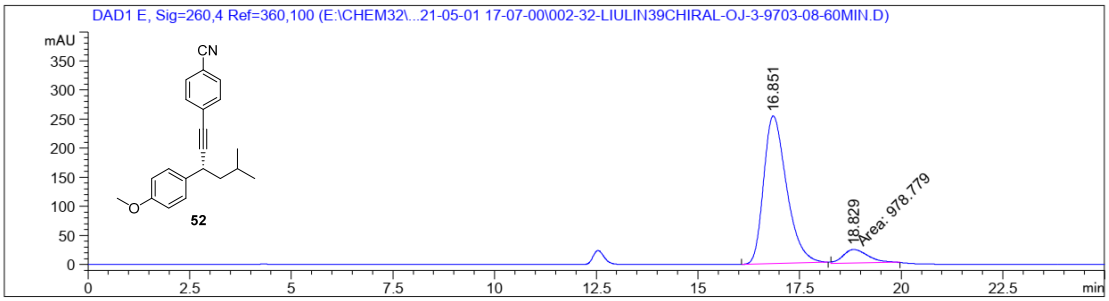
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.503	BB	0.2200	1190.02991	82.61703	87.3544
2	12.550	MM	0.2509	172.27078	11.44510	12.6456



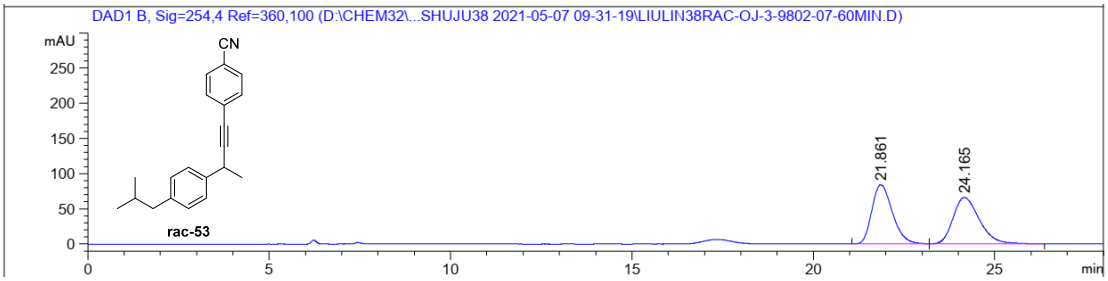
Signal 5: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.663	MM	0.6494	3850.55957	98.81837	47.8635
2	18.556	MM	0.6699	4194.31738	104.35616	52.1365
Totals :				8044.87695	203.17453	



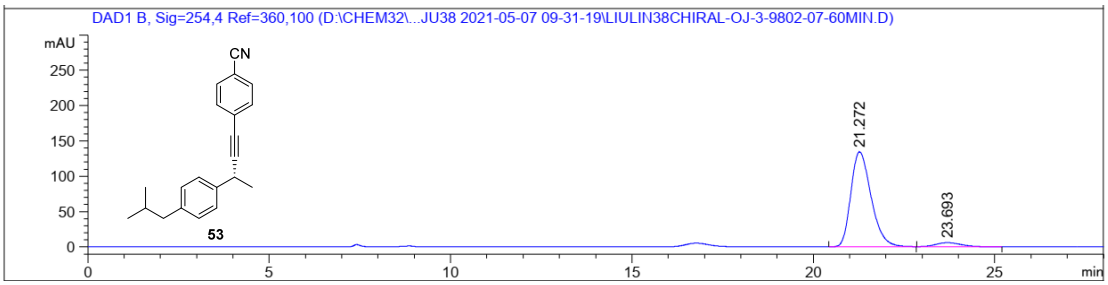
Signal 5: DAD1 E, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.851	BB	0.6008	9945.89258	253.99646	91.0407
2	18.829	MM	0.7002	978.77856	23.29738	8.9593
Totals :				1.09247e4	277.29384	



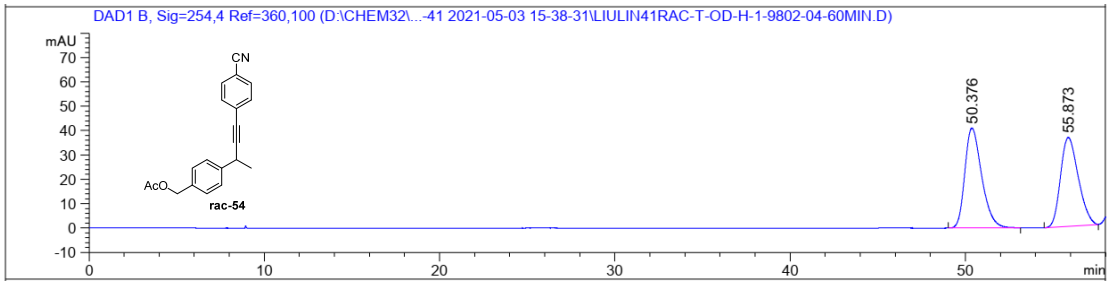
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.861	BB	0.6104	3299.30249	83.97447	49.9606
2	24.165	BB	0.7646	3304.51221	65.72065	50.0394
Totals :				6603.81470	149.69512	



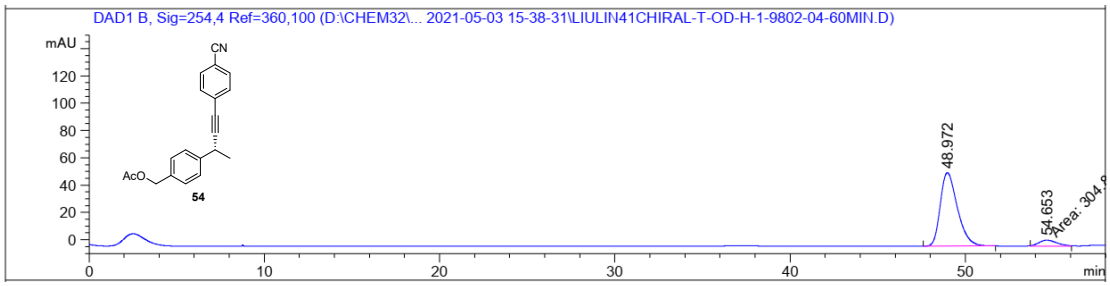
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.272	BB	0.5998	5195.53809	134.15295	95.0469
2	23.693	BB	0.6438	270.75308	5.64270	4.9531
Totals :				5466.29117	139.79565	



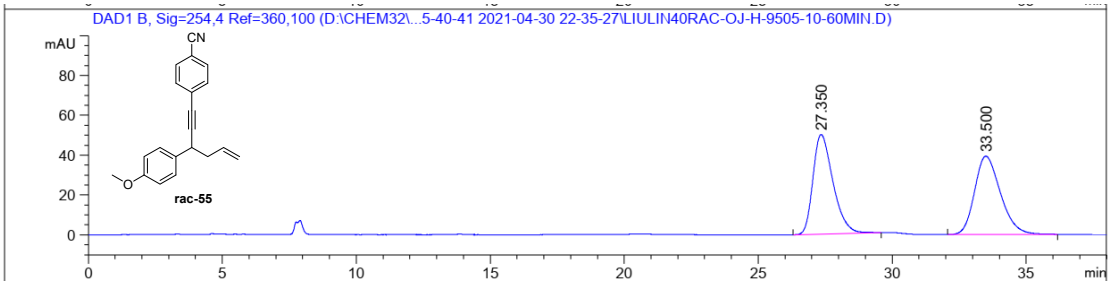
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	50.376	BB	0.9828	2735.78687	40.98225	51.5565
2	55.873	BB	1.0201	2570.60205	36.48064	48.4435
Totals :				5306.38892	77.46288	



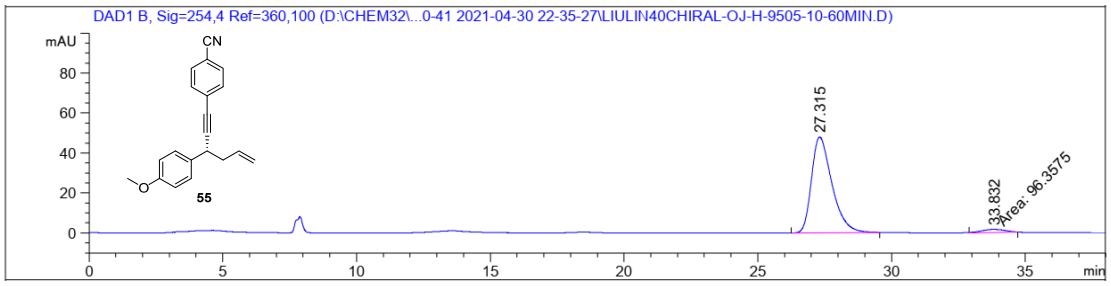
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.972	BB	1.0121	3652.34546	53.79363	92.2974
2	54.653	MM	1.1831	304.80457	4.29405	7.7026
Totals :				3957.15002	58.08768	



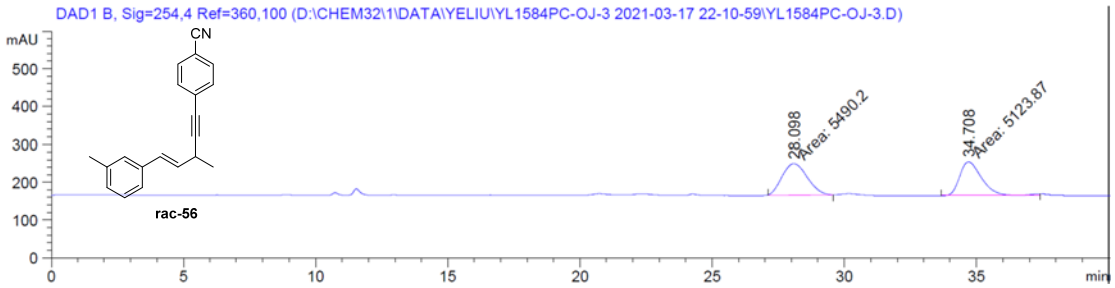
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.350	BB	0.8014	2604.68994	50.02668	49.6538
2	33.500	BB	0.9977	2641.01294	39.31342	50.3462
Totals :				5245.70288	89.34010	



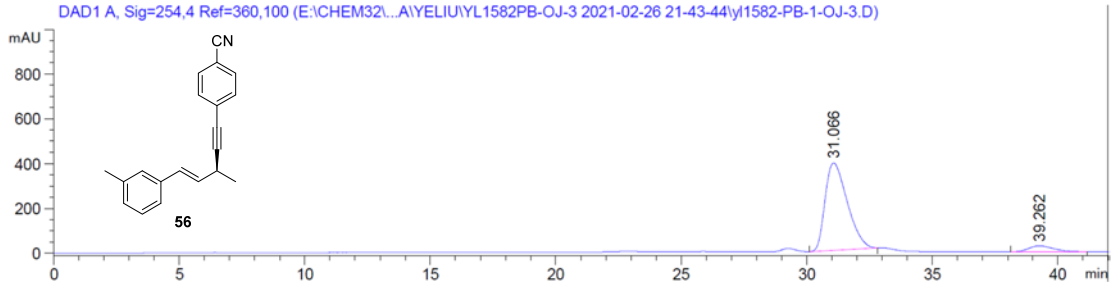
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.315	BB	0.7974	2545.39771	47.94524	96.3525
2	33.832	MM	1.0238	96.35753	1.56856	3.6475
Totals :				2641.75523	49.51380	



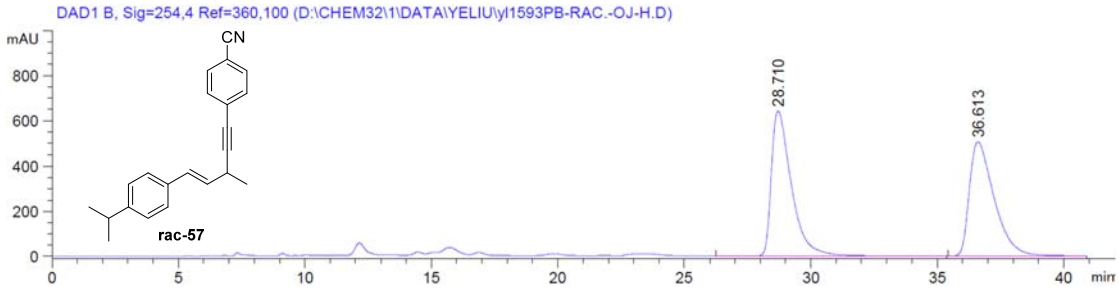
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.098	MM	1.0996	5490.19580	83.21301	51.7257
2	34.708	MM	0.9610	5123.86719	88.86179	48.2743



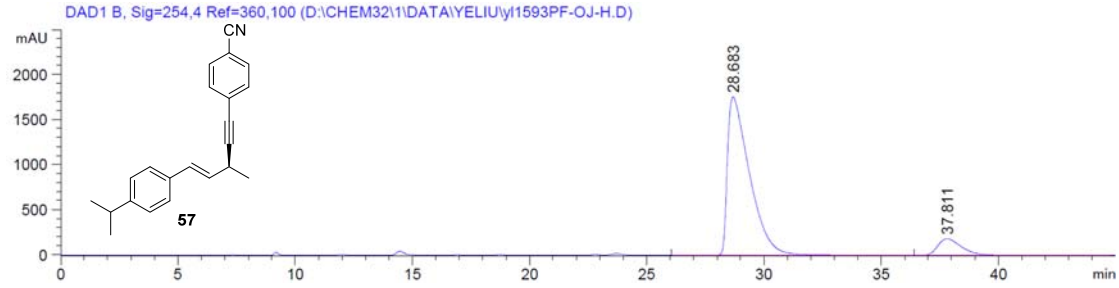
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.066	BB	0.9280	2.40301e4	391.54980	92.9496
2	39.262	BB	0.8187	1822.74170	26.42632	7.0504



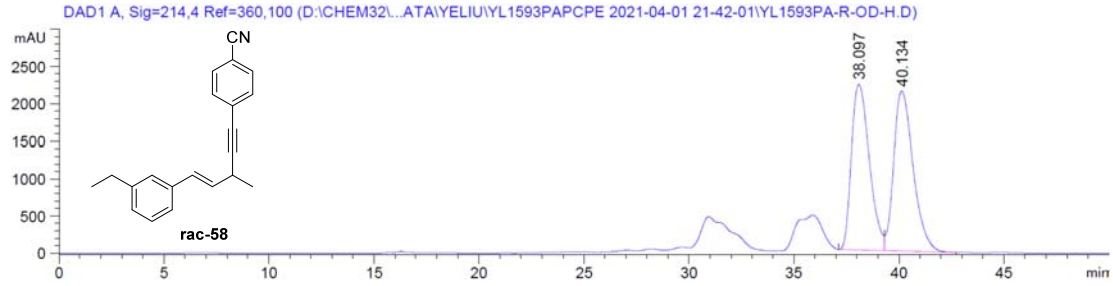
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.710	BB	0.8310	3.53816e4	641.93353	50.7071
2	36.613	BBA	1.0276	3.43948e4	504.38147	49.2929



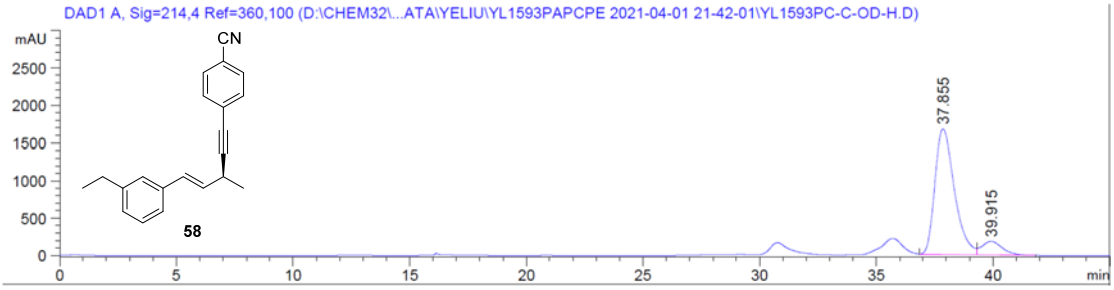
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.683	BB	0.9745	1.15901e5	1759.40808	89.7790
2	37.811	BB	1.0722	1.31950e4	184.53462	10.2210



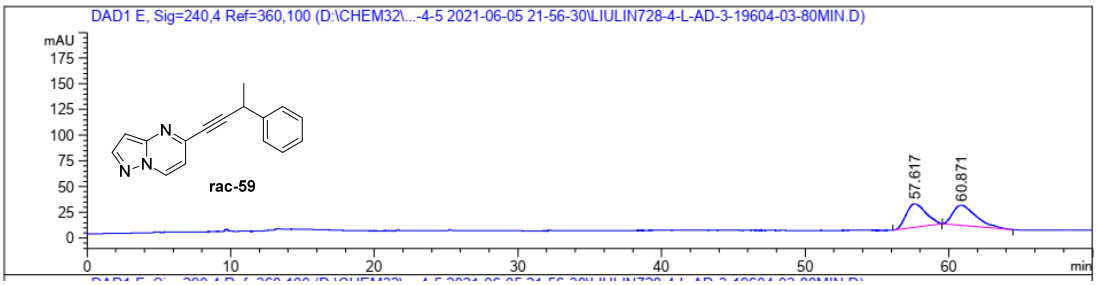
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.097	BV	0.9061	1.31327e5	2213.78784	48.6972
2	40.134	VB	0.9913	1.38354e5	2137.01245	51.3028



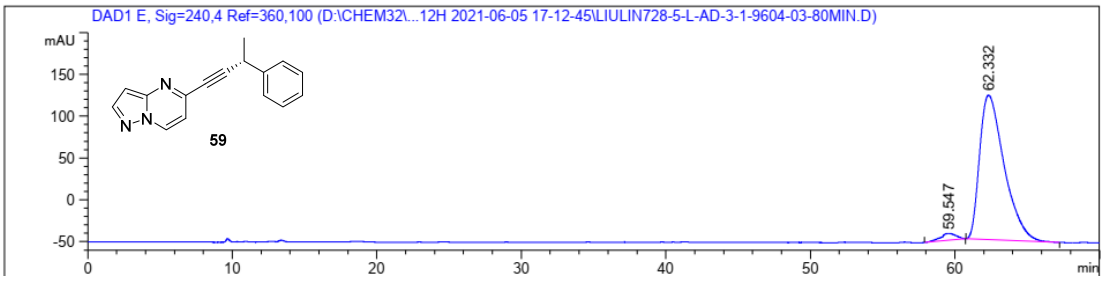
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.855	BV	0.9034	9.71088e4	1667.59058	89.7204
2	39.915	VB	0.9189	1.11261e4	181.56084	10.2796



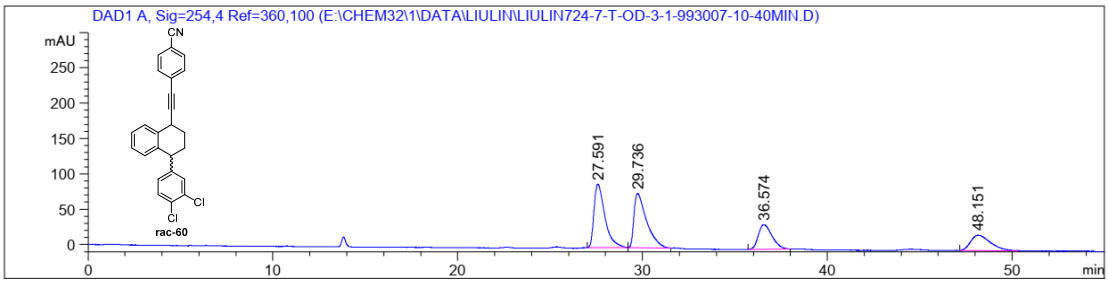
Signal 5: DAD1 E, Sig=240,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	57.617	BB	1.1269	2166.95190	22.83898	49.9061
2	60.871	BB	1.3352	2175.10449	19.47202	50.0939
Totals :				4342.05640	42.31100	



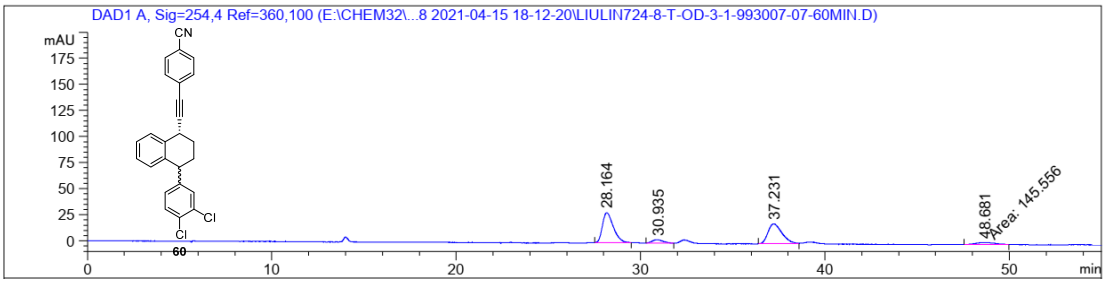
Signal 5: DAD1 E, Sig=240,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	59.547	BB	0.8942	624.01251	8.34686	2.9615
2	62.332	BB	1.6905	2.04470e4	172.80002	97.0385
Totals :				2.10710e4	181.14688	



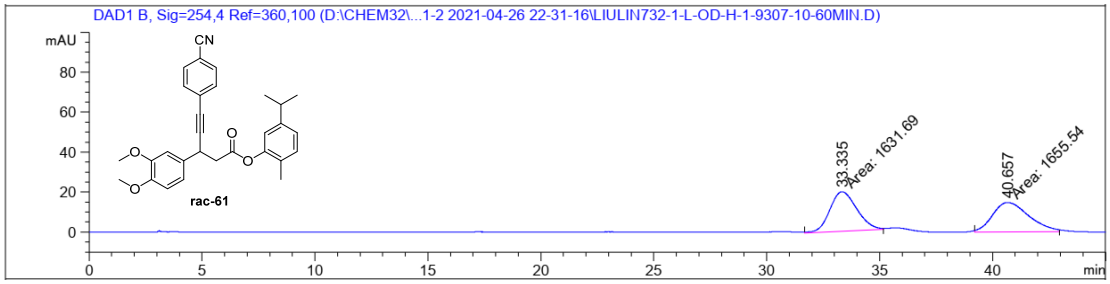
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.591	BV	0.5943	3716.23364	89.89716	34.4913
2	29.736	VB	0.6618	3652.67407	76.94755	33.9014
3	36.574	BB	0.6278	1787.47681	34.88399	16.5900
4	48.151	BV R	0.8853	1618.00867	21.76522	15.0172
Totals :				1.07744e4	223.49393	



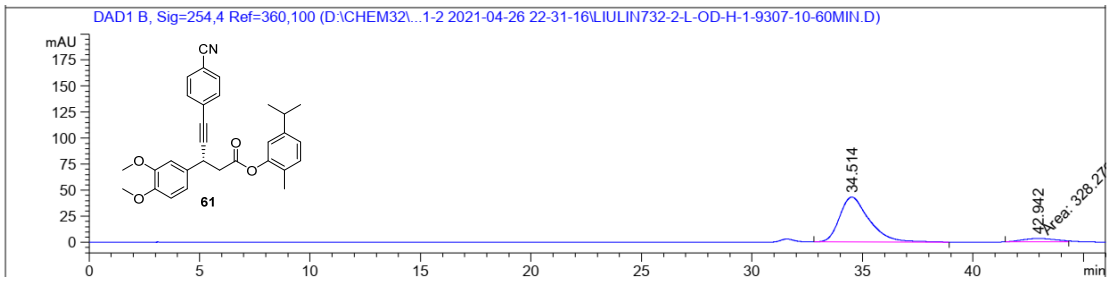
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.164	BB	0.5482	1181.90564	28.71334	48.2797
2	30.935	BB	0.4908	130.83554	3.18774	5.3445
3	37.231	BB	0.6186	989.73999	19.03477	40.4299
4	48.681	MM	1.1703	145.55620	2.07299	5.9458
Totals :				2448.03737	53.00884	



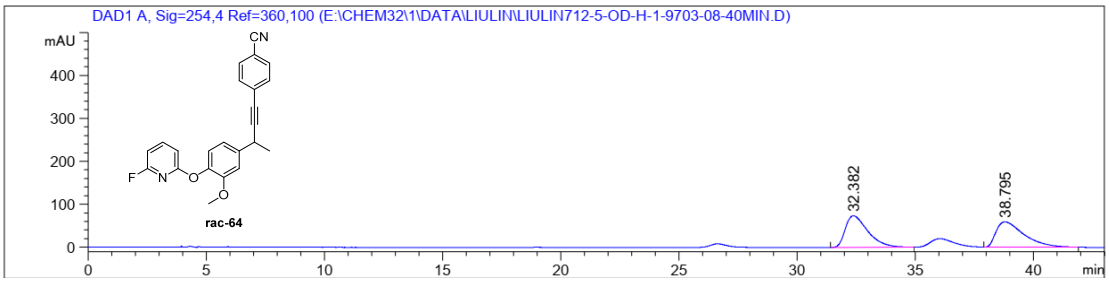
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.335	MM	1.3794	1631.69092	19.71524	49.6373
2	40.657	MM	1.8709	1655.53955	14.74791	50.3627
Totals :				3287.23047	34.46314	



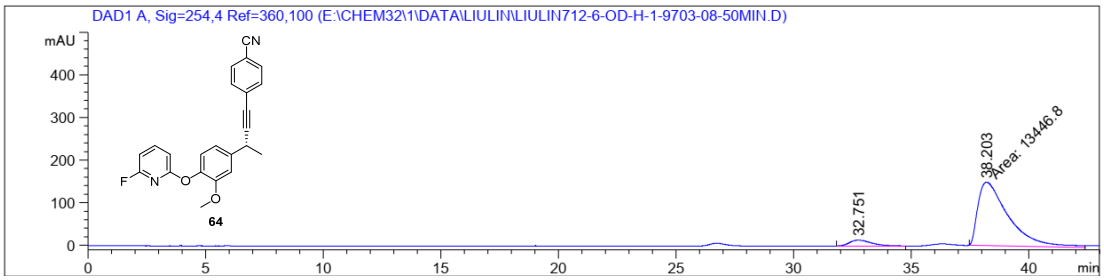
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.514	BB	1.3291	3983.74634	42.98977	92.3869
2	42.942	MM	1.7479	328.27893	3.13024	7.6131
Totals :				4312.02527	46.12001	



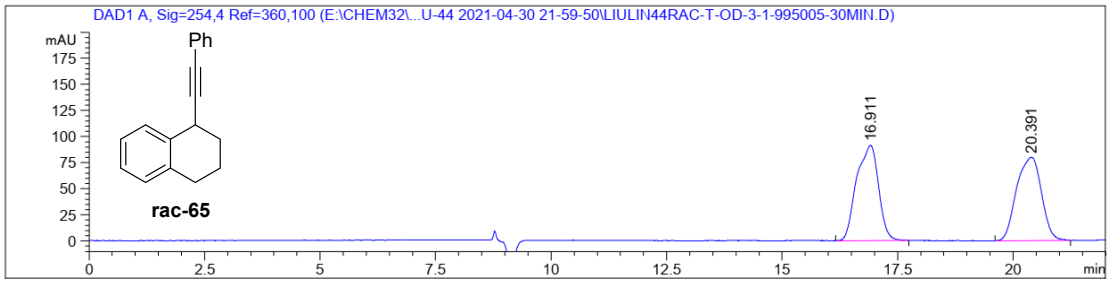
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.382	BB	0.9194	4877.32373	73.57573	50.1889
2	38.795	BB	0.9986	4840.60303	58.91498	49.8111
Totals :				9717.92676	132.49071	



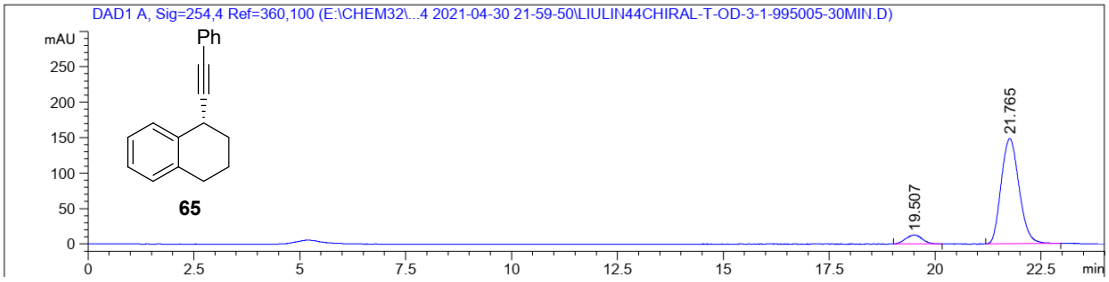
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.751	BB	0.7647	892.09424	13.75428	6.2215
2	38.203	MM	1.5028	1.34468e4	149.13438	93.7785
Totals :				1.43389e4	162.88866	



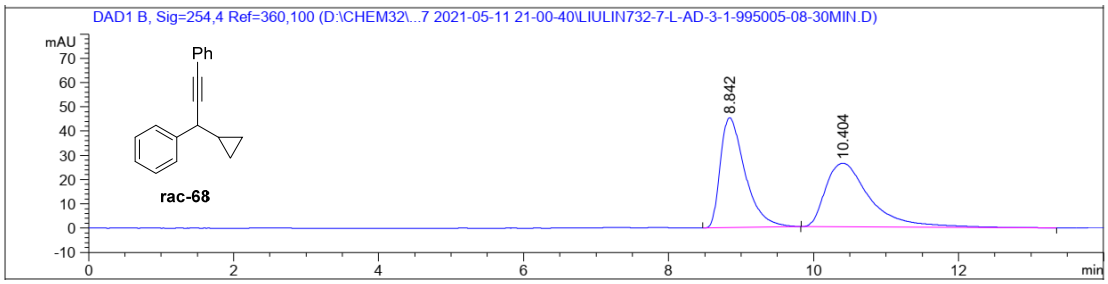
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.911	BB	0.4555	3011.47974	91.14550	50.3091
2	20.391	BB	0.5210	2974.47827	79.77512	49.6909
Totals :				5985.95801	170.92062	



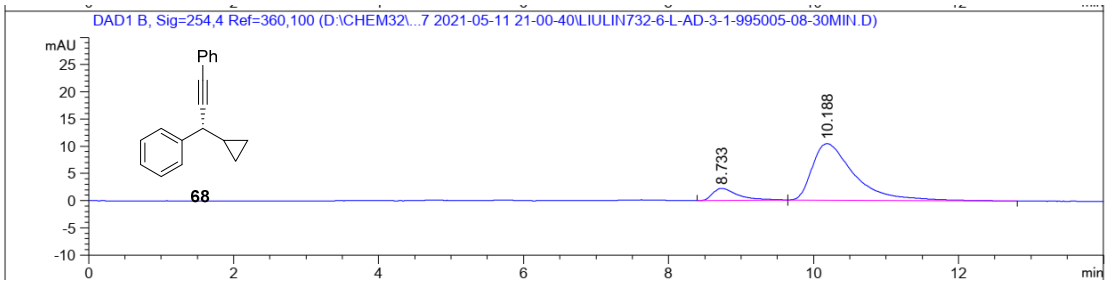
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.507	BB	0.3387	345.44034	12.56646	7.3173
2	21.765	BB	0.4632	4375.40820	148.75182	92.6827
Totals :				4720.84854	161.31828	



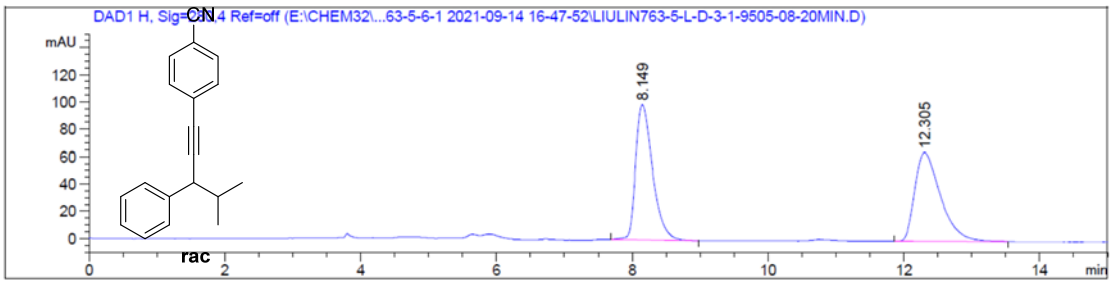
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.842	BB	0.3625	1073.78394	45.31363	49.0106
2	10.404	BB	0.6455	1117.13721	26.19519	50.9894



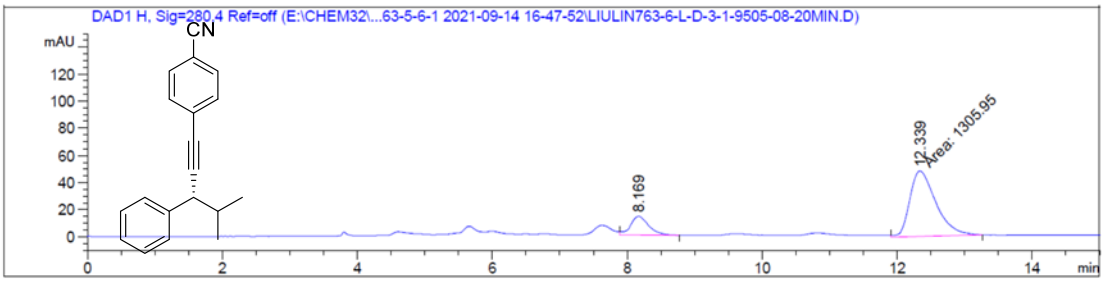
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.733	BB	0.3484	54.12192	2.23558	11.4552
2	10.188	BB	0.5898	418.34201	10.38952	88.5448
Totals :				472.46393	12.62510	



Signal 8: DAD1 H, Sig=280,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.149	BB	0.2702	1714.12891	98.92181	49.8364
2	12.305	BB	0.3866	1725.38501	65.22168	50.1636
Totals :				3439.51392	164.14349	



Signal 8: DAD1 H, Sig=280,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.169	VB	0.2830	261.47672	13.80089	16.6819
2	12.339	MM	0.4479	1305.94714	48.59459	83.3181
Totals :				1567.42386	62.39548	