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Supplementary information

Mechanism-based ligand design for copper-catalysed enantioconvergent C(sp^3)–C(sp) cross-coupling of tertiary electrophiles with alkynes

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Supplementary information for

Mechanism-based ligand design for copper-catalysed enantioconvergent C(sp^3)–C(sp) cross-coupling of tertiary electrophiles with alkynes

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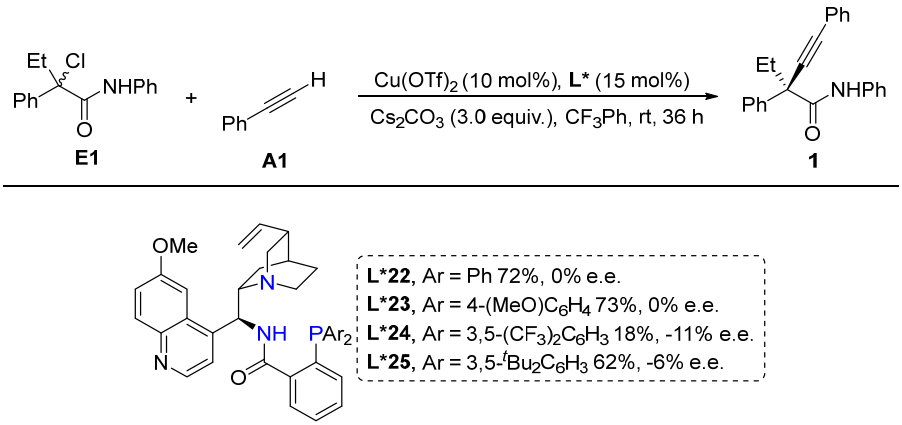
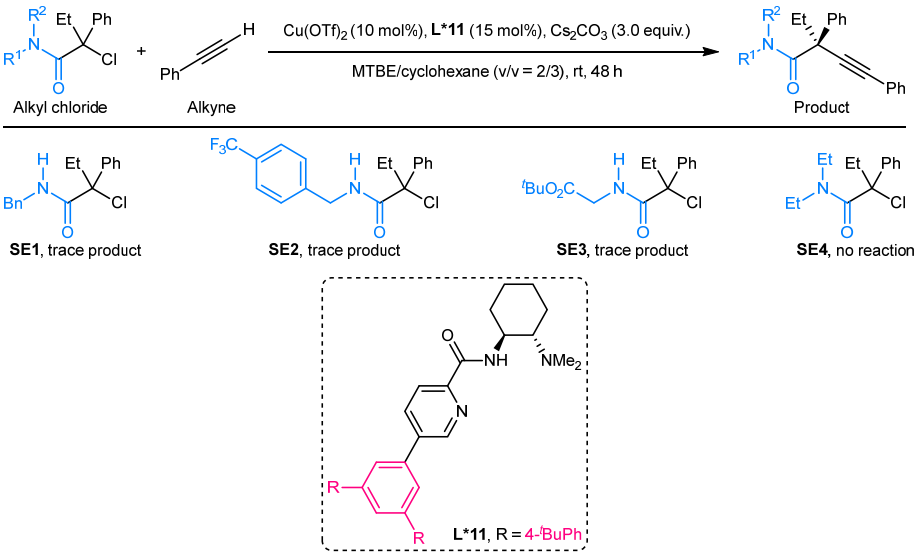
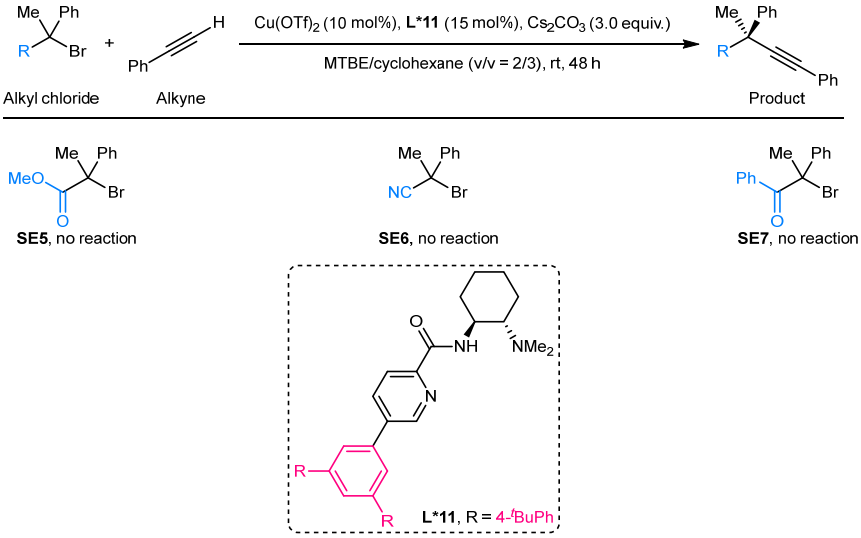
Supplementary figures for experiments



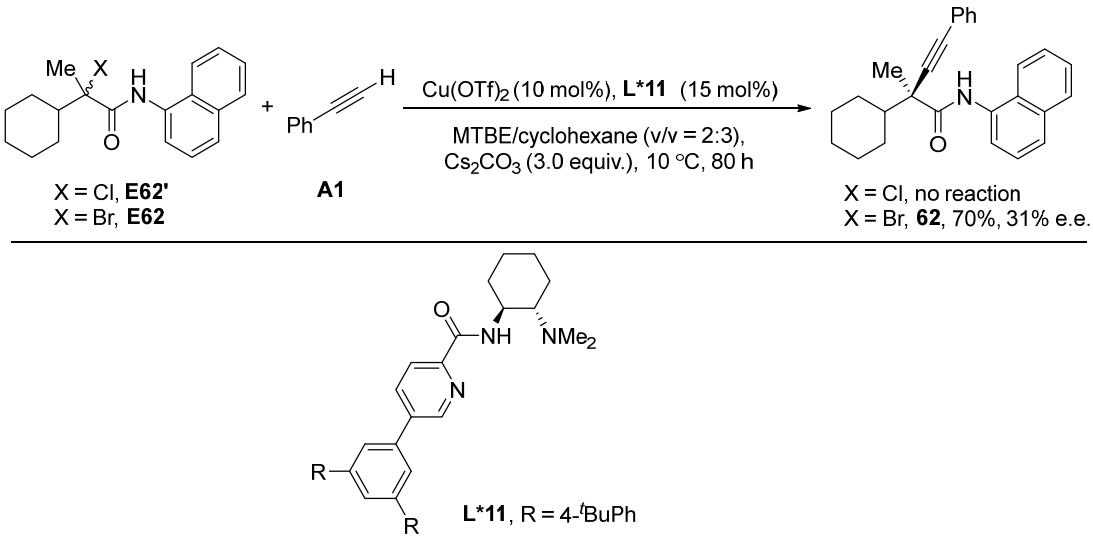
Supplementary Fig. 1 The effect of quinine-derived N,N,P-ligands in the model reaction. Reaction conditions: **E1** (0.025 mmol), phenylacetylene **A1** (1.5 equiv.), $Cu(OTf)_2$ (10 mol%), **L*** (15 mol%) and Cs_2CO_3 (3.0 equiv.) in dry CF_3Ph (0.50 mL) under argon at room temperature for 36 h. Yield is based on ^{1}HNMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. E.e. of **1** is based on HPLC analysis.



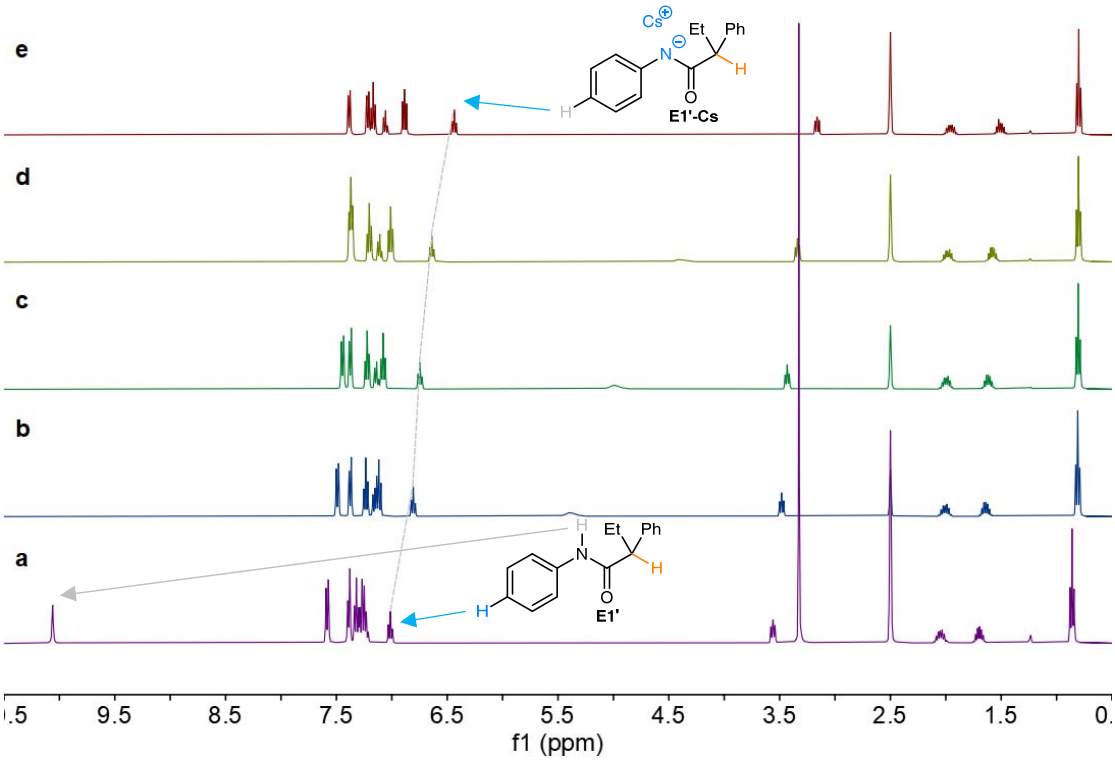
Supplementary Fig. 2 Results of *N*-alkyl and *N,N*-dialkyl substituted substrates.
MTBE, methyl *tert*-butyl ether



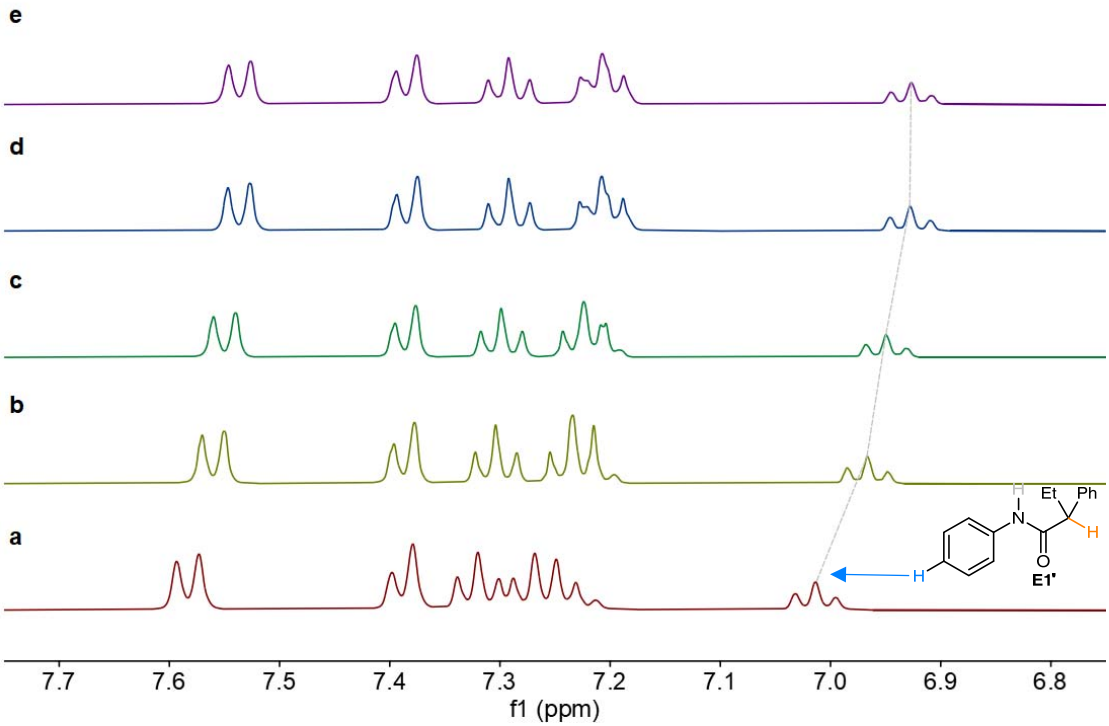
Supplementary Fig. 3 Results of other types of alkyl bromides. MTBE, methyl *tert*-butyl ether.



Supplementary Fig. 4 The effect of *α*,*α*-dialkyl-substituted tertiary *α*-haloamides. Reaction conditions: alkyl halide **E** (0.025 mmol), phenylacetylene **A1** (1.5 equiv.), $Cu(OTf)_2$ (10 mol%), **L*11** (15 mol%) and Cs_2CO_3 (3.0 equiv.) in MTBE/cyclohexane (v/v = 2/3, 0.50 mL) under argon at 10 °C for 80 h. Yield is based on ^{1}HNMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. E.e. of **62** is based on HPLC analysis. MTBE, methyl *tert*-butyl ether.



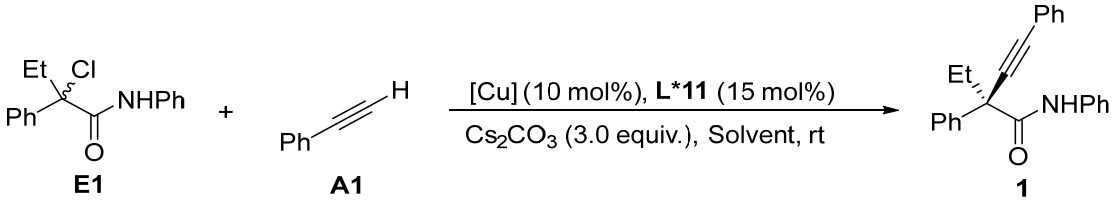
Supplementary Fig. 5 ^{1}H-NMR studies of E1' with E1'-Cs (298K, 400 MHz, DMSO-d_6). a, **E1'** (25 mM). **b**, **E1'** (75 mM) with 0.67 equiv. of **E1'-Cs** (50 mM). **c**, **E1'** (50 mM) with 1.0 equiv. of **E1'-Cs** (50 mM). **d**, **E1'** (25 mM) with 2.0 equiv. of **E1'-Cs** (50 mM). **e**, **E1'-Cs** (50 mM).



Supplementary Fig. 6 ^{1}H-NMR studies of E1' (25 mM, 298K, 400 MHz, DMSO-d_6) with Cs_2CO_3. a, **E1'**. **b**, **E1'** with 0.50 equiv. of Cs_2CO_3. **c**, **E1'** with 1.0 equiv. of Cs_2CO_3. **d**, **E1'** with 2.0 equiv. of Cs_2CO_3. **e**, **E1'** with 3.0 equiv. of Cs_2CO_3.

Supplementary tables for experiments

Supplementary Table 1 Screening of reaction conditions[a]

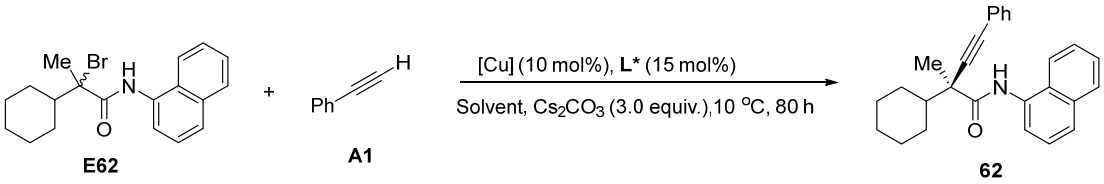


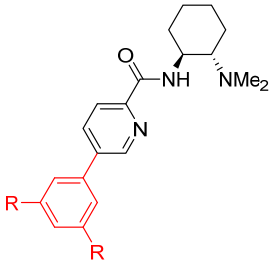
Entry	[Cu]	Solvent	Time (h)	Yield (%)[b]	E.e. (%)[c]
1	$Cu(OTf)_2$	CF_3Ph	36	80	86
2	CuI	CF_3Ph	36	73	78
3	CuBr	CF_3Ph	36	63	81
4	CuCN	CF_3Ph	36	25	80
5	$Cu(CH_3CN)_4PF_6$	CF_3Ph	36	80	79
6	$Cu(OAc)_2$	CF_3Ph	36	72	86
7	$Cu(OTf)_2$	PhCl	48	63	85
8	$Cu(OTf)_2$	Et_2O	48	75	74
9	$Cu(OTf)_2$	MTBE	48	83	77
10	$Cu(OTf)_2$	cyclohexane	48	45	88
11	$Cu(OTf)_2$	CF_3Ph/cyclohexane (v/v = 2/3)	60	71	88
12	$Cu(OTf)_2$	MTBE/cyclohexane (v/v = 2/3)	60	76	88
13[d]	$Cu(OTf)_2$	MTBE/cyclohexane (v/v = 2/3)	60	70	89
14[e]	$Cu(OTf)_2$	MTBE/cyclohexane (v/v = 2/3)	60	55	53
15[f]	$Cu(OTf)_2$	MTBE/cyclohexane (v/v = 2/3)	60	53	89
16[g]	$Cu(OTf)_2$	MTBE/cyclohexane (v/v = 2/3)	80	21	91
17[h]	$Cu(OTf)_2$	MTBE/cyclohexane (v/v = 2/3)	80	13	91
18[i,j]	$Cu(OTf)_2$	MTBE/cyclohexane (v/v = 2/3)	80	8	89
21[k]	$Cu(OTf)_2$	CF_3Ph/cyclohexane (v/v = 2/3)	80	72	91
22[k]	$Cu(OTf)_2$	MTBE/cyclohexane (v/v = 2/3)	80	75	92

[a]Reaction conditions: **E1** (0.025 mmol), phenylacetylene **A1** (1.5 equiv.), [Cu] (10 mol%), **L*11** (15 mol%) and Cs_2CO_3 (3.0 equiv.) in solvent (0.50 mL) under argon at room temperature. [b]Yield is based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard, [c]E.e. of **1** is based on HPLC analysis. [d]The reaction was carried out in the dark. [e]The

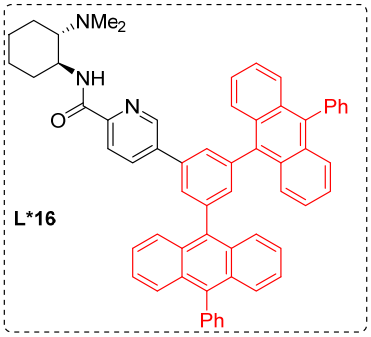
reaction was carried out under irradiation of blue LED (24 W). [f][Cu] (5 mol%), **L*11** (7.5 mol%). [g][Cu] (3 mol%), **L*11** (4.5 mol%). [h][Cu] (2 mol%), **L*11** (3 mol%). [i][Cu] (1 mol%), **L*11** (1.5 mol%). [j]**E1** (0.05 mmol) scale. [k]The reaction was carried out at 10 °C for 80 h. MTBE, methyl *tert*-butyl ether.

Supplementary Table 2 Screening of reaction conditions[a]





L*10, R = 1-Naphthyl
L*11, R = 4-^{t}BuPh
L*26, R = 3,5-Diphenylphenyl
L*27, R = 1-Pyrenyl
L*28, R = 9-Phenanthracenyl
L*29, R = 9-Anthryl

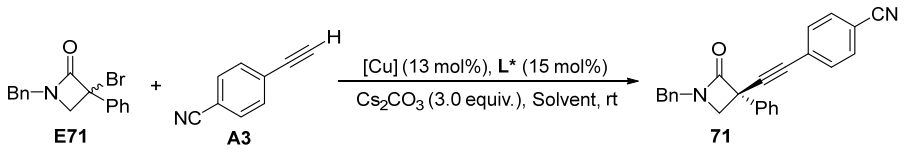


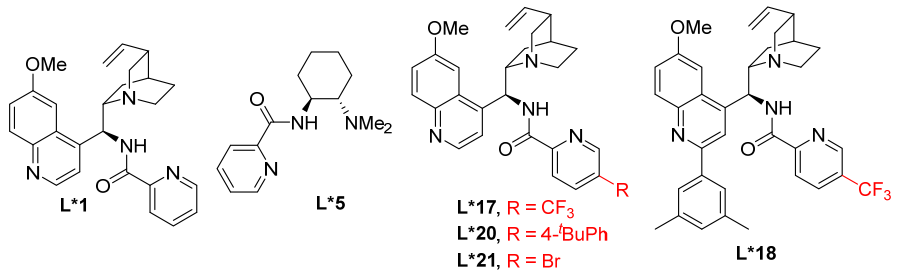
L*16

Entry	[Cu]	Ligand	Solvent	Yield (%)[b]	E.e. (%)[c]
1	$Cu(OTf)_2$	**L*11**	MTBE/cyclohexane (v/v = 2/3)	70	31
2	$Cu(OTf)_2$	**L*11**	CF_3Ph	54	45
3	$Cu(OAc)_2$	**L*11**	CF_3Ph	61	55
4	$Cu(OAc)_2$	**L*10**	CF_3Ph	65	68
5	$Cu(OAc)_2$	**L*26**	CF_3Ph	47	28
6	$Cu(OAc)_2$	**L*27**	CF_3Ph	45	71
7	$Cu(OAc)_2$	**L*28**	CF_3Ph	65	76
8	$Cu(OAc)_2$	**L*29**	CF_3Ph	67	87
9	$Cu(OAc)_2$	**L*16**	CF_3Ph	67	90

[a]Reaction conditions: **E62** (0.025 mmol), phenylacetylene **A1** (1.5 equiv.), [Cu] (10 mol%), ligand (15 mol%) and Cs_2CO_3 (3.0 equiv.) in solvent (0.50 mL) under argon at 10 °C for 80 h. [b]Yield is based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. [c]E.e. value is based on HPLC analysis. MTBE, methyl *tert*-butyl ether.

Supplementary Table 3 Screening of reaction conditions[a]





Entry	[Cu]	Ligand	Solvent	Time (h)	Yield (%)[b]	E.e. (%)[c]
1	CuTc	**L*1**	Et_2O	36	75	73
2	CuTc	**L*5**	Et_2O	36	50	28
3	CuTc	**L*17**	Et_2O	36	82	86
4	CuTc	**L*18**	Et_2O	36	76	92
5	CuTc	**L*20**	Et_2O	36	70	72
6	CuTc	**L*21**	Et_2O	36	75	85
7[d]	CuTc	**L*17**	Et_2O	60	85	90

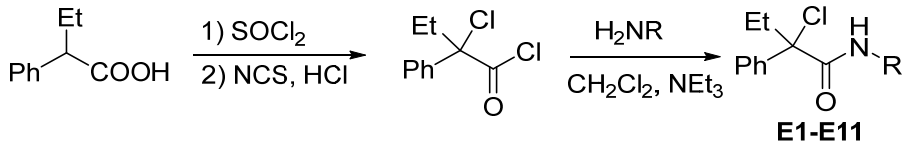
[a]Reaction conditions: **E71** (0.025 mmol), 4-cyanophenylacetylene **A3** (1.2 equiv.), [Cu] (13 mol%), **L*** (15 mol%) and Cs_2CO_3 (3.0 equiv.) in dry solvent (0.50 mL) under argon at room temperature for 36 h. [b]Yield is based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. [c]E.e. of **71** is based on HPLC analysis. [d]The reaction was carried out at 10 °C for 60 h.

General information

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. $Cu(OTf)_2$ was purchased from Alfa Aesar. $Cu(OAc)_2$ was purchased from Sigma-Aldrich. CuTc was purchased from Bide Pharmatech Ltd. Anhydrous diethyl ether (Et_2O) was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd, which was directly used without further treatment. Anhydrous MTBE, CF_3Ph and cyclohexane were purchased from J&K Chemical Ltd. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm), iodine or basic $KMnO_4$ indicator. NMR spectra were recorded on Bruker DRX-400 and DPX-500 spectrometers at 400 or 500 MHz for ^1H NMR, 100 or 125 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts were expressed in ppm and coupling constants were given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR were reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (e.e.) was determined using SHIMADZU LC-20AD with SPD-20AV detector or Agilent high-performance liquid chromatography (HPLC) with Hatachi detector (at appropriate wavelength). Column conditions were reported in the experimental section below. Specific optical rotation was measured on a Rudolph-Autopol I. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu–Kα radiation.

General procedure for synthesis of substrates

General procedure SM-A for the synthesis of tertiary *α*-chloroamides (E1–E11)

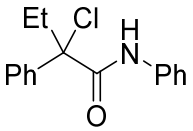


E1-E11

According to the literature reported procedure[1] with slightly modification: 2-phenylbutanoic acid (1.64 g, 10 mmol) was dissolved in $SOCl_2$ (5.0 mL), and the resulting solution was heated at 80 °C for 30 min with vigorous stirring ($CaCl_2$ drying tube). The mixture was allowed to cool to room temperature, and then *N*-chlorosuccinimide (3.34 g, 25 mmol), $SOCl_2$ (3.0 mL), and HCl (concentrated; 3 drops) were added. The resulting mixture was heated at 90 °C for 2.5 h and then allowed to cool to room temperature. The precipitate was removed by filtration, washed by CCl_4 (5.0 mL) and the filtrate was concentrated by evaporation. The resulting liquid residue was used directly in the next step.

The *α*-chloro acid chloride in anhydrous CH_2Cl_2 (5.0 mL) was added dropwise to a solution of the corresponding amine (10 mmol) and triethylamine (4.2 mL, 30 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The reaction was stirred at 0 °C for 15 min and then warmed up to room temperature. After completion (monitored by TLC), the reaction was quenched by the addition of 1.0 M HCl, the organic layer was washed by brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude material, which was purified by flash chromatography to yield the tertiary α-chloroamide.

2-Chloro-*N*,2-diphenylbutanamide (E1)



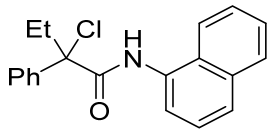
According to general procedure **SM-A** with aniline (0.93 g, 10 mmol, 1.0 equiv.) to afford **E1** as a white amorphous solid (2.16 g, 79% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.65 – 7.58 (m, 2H), 7.57 – 7.51 (m, 2H), 7.43 – 7.30 (m, 5H), 7.18 – 7.10 (m, 1H), 2.67 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.43 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 140.4, 137.2, 129.0, 128.6, 128.5, 126.3, 124.9, 119.9, 79.4, 34.9, 9.5.

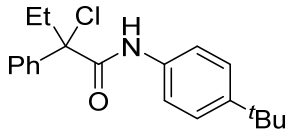
HRMS (ESI) *m/z* calcd. for $C_{16}H_{17}ClNO$ $[M + H]^+$ 274.0993, found 274.0993.

2-Chloro-*N*-(naphthalen-1-yl)-2-phenylbutanamide (E2)



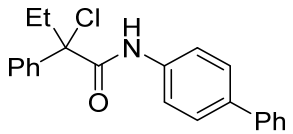
According to general procedure **SM-A** with 1-naphthylamine (1.43 g, 10 mmol, 1.0 equiv.) to afford **E2** as a white solid (2.69 g, 83% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.92 – 7.82 (m, 1H), 7.79 – 7.63 (m, 4H), 7.57 – 7.32 (m, 6H), 2.74 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.50 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 140.5, 134.1, 131.7, 128.8, 128.7, 128.6, 127.1, 126.6, 126.4, 126.1, 125.7, 120.2, 80.1, 34.9, 9.6.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}ClNO$ $[M + H]^+$ 324.1150, found 324.1150.

***N*-(4-(*tert*-Butyl)phenyl)-2-chloro-2-phenylbutanamide (E3)**



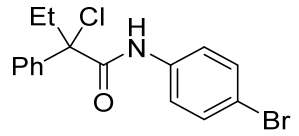
According to general procedure **SM-A** with 4-*tert*-butylaniline (1.49 g, 10 mmol, 1.0 equiv.) to afford **E3** as a white solid (2.70 g, 82% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.64 – 7.56 (m, 2H), 7.51 – 7.43 (m, 2H), 7.41 – 7.29 (m, 5H), 2.67 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.41 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.30 (s, 9H), 1.08 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 148.0, 140.6, 134.6, 128.5, 128.4, 126.3, 125.9, 119.6, 79.4, 34.9, 34.4, 31.3, 9.5.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{25}ClNO$ $[M + H]^+$ 330.1619, found 330.1619.

***N*-([1,1'-Biphenyl]-4-yl)-2-chloro-2-phenylbutanamide (E4)**



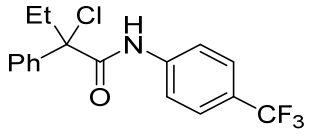
According to general procedure **SM-A** with 4-phenylbenzylamine (1.83 g, 10 mmol, 1.0 equiv.) to afford **E4** as a slightly yellow solid (2.69 g, 77% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.66 – 7.60 (m, 4H), 7.60 – 7.54 (m, 4H), 7.47 – 7.29 (m, 6H), 2.69 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.44 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 140.3, 137.8, 136.4, 128.8, 128.6, 128.5, 127.7, 127.2, 126.9, 126.3, 120.2, 79.4, 34.9, 9.5.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{21}ClNO$ $[M + H]^+$ 350.1306, found 350.1306.

***N*-(4-Bromophenyl)-2-chloro-2-phenylbutanamide (E5)**



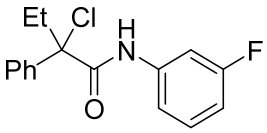
According to general procedure **SM-A** with 4-bromoaniline (1.72 g, 10 mmol, 1.0 equiv.) to afford **E5** as a slightly yellow solid (2.54 g, 72% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.63 – 7.54 (m, 2H), 7.44 (s, 4H), 7.41 – 7.31 (m, 3H), 2.64 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.41 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.06 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 140.0, 136.2, 132.0, 128.61, 128.56, 126.3, 121.5, 117.6, 79.4, 34.9, 9.4.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}BrClNO$ $[M + H]^+$ 352.0098, found 352.0099.

2-Chloro-2-phenyl-*N*-(4-(trifluoromethyl)phenyl)butanamide (E6)



According to general procedure **SM-A** with 4-aminobenzotrifluoride (1.61 g, 10 mmol, 1.0 equiv.) to afford **E6** as a white solid (2.39 g, 70% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.63 – 7.54 (m, 4H), 7.44 – 7.30 (m, 3H), 2.65 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.43 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.06 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 140.2, 139.8, 128.7, 128.6, 126.7 (q, *J* = 32.7 Hz), 126.3, 126.2, 123.9 (q, *J* = 270.2 Hz), 119.5, 79.3, 34.9, 9.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.22 (s, 3F).
HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}ClF_3NO$ $[M + H]^+$ 342.0867, found 342.0869.

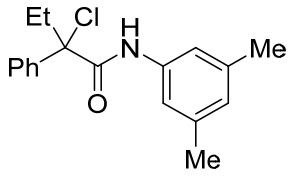
2-Chloro-*N*-(3-fluorophenyl)-2-phenylbutanamide (E7)



According to general procedure **SM-A** with 3-fluoroaniline (1.11 g, 10 mmol, 1.0 equiv.) to afford **E7** as a white solid (2.22 g, 76% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.63 – 7.56 (m, 2H), 7.53 (dt, *J* = 10.8, 2.3 Hz, 1H), 7.42 – 7.31 (m, 3H), 7.31 – 7.23 (m, 1H), 7.15 (ddd, *J* = 8.1, 2.1, 1.0 Hz, 1H), 6.84 (tdd, *J* = 8.3, 2.5, 0.9 Hz, 1H), 2.65 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.42 (dq, *J* = 14.5, 7.2 Hz, 1H), 1.06 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 163.0 (d, *J* = 245.5 Hz), 140.0, 138.7 (d, *J* = 11.1 Hz), 130.1 (d, *J* = 9.4 Hz), 128.63, 128.58, 126.3, 115.1 (d, *J* = 3.0 Hz), 111.6 (d, *J* = 21.4 Hz), 107.4 (d, *J* = 26.5 Hz), 79.4, 34.9, 9.4.

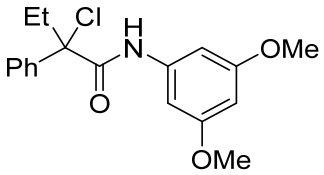
^{19}F NMR (376 MHz, $CDCl_3$) δ −111.14 (s, 1F).
HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}ClFNO$ $[M + H]^+$ 292.0899, found 292.0898.

2-Chloro-*N*-(3,5-dimethylphenyl)-2-phenylbutanamide (E8)



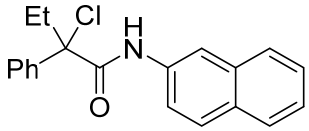
According to general procedure **SM-A** with 3,5-dimethylaniline (1.21 g, 10 mmol, 1.0 equiv.) to afford **E8** as a white solid (2.47 g, 82% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.65 – 7.55 (m, 2H), 7.43 – 7.28 (m, 3H), 7.20 (s, 2H), 6.79 (s, 1H), 2.67 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.42 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.30 (s, 6H), 1.08 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 140.5, 138.8, 137.0, 128.5, 128.4, 126.6, 126.3, 117.7, 79.4, 34.8, 21.3, 9.5.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}ClNO$ $[M + H]^+$ 302.1306, found 302.1307.

2-Chloro-*N*-(3,5-dimethoxyphenyl)-2-phenylbutanamide (E9)



According to general procedure **SM-A** with 3,5-dimethoxyaniline (1.53 g, 10 mmol, 1.0 equiv.) to afford **E9** as a white solid (2.50 g, 75% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.69 – 7.52 (m, 2H), 7.44 – 7.29 (m, 3H), 6.79 (d, *J* = 2.2 Hz, 2H), 6.27 (t, *J* = 2.3 Hz, 1H), 3.78 (s, 6H), 2.66 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.42 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.08 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 161.0, 140.3, 138.9, 128.6, 128.5, 126.3, 97.9, 97.4, 79.3, 55.4, 34.8, 9.5.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}ClNO_3$ $[M + H]^+$ 334.1204, found 334.1205.

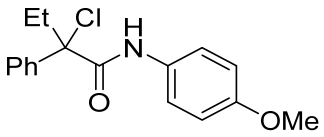
2-Chloro-*N*-(naphthalen-2-yl)-2-phenylbutanamide (E10)



According to general procedure **SM-A** with 2-naphthylamine (1.43 g, 10 mmol, 1.0 equiv.) to afford **E10** as a white solid (2.59 g, 80% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.31 (d, *J* = 2.1 Hz, 1H), 7.87 – 7.76 (m, 3H), 7.72 – 7.62 (m, 2H), 7.54 – 7.32 (m, 6H), 2.74 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.49 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.14 (t, *J* = 7.2 Hz, 3H).

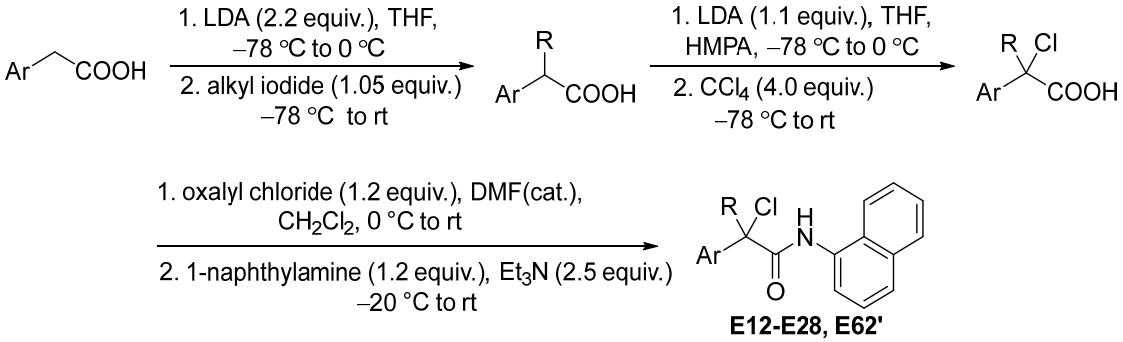
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 140.4, 134.6, 133.7, 130.9, 128.8, 128.6, 128.5, 127.7, 127.6, 126.6, 126.4, 125.3, 119.7, 116.8, 79.5, 35.0, 9.5.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}ClNO$ $[M + H]^+$ 324.1150, found 324.1151.

2-Chloro-*N*-(4-methoxyphenyl)-2-phenylbutanamide (E11)



According to general procedure **SM-A** with *p*-anisidine (1.23 g, 10 mmol, 1.0 equiv.) to afford **E11** as a slightly yellow solid (2.61 g, 86% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.69 – 7.57 (m, 2H), 7.49 – 7.42 (m, 2H), 7.41 – 7.29 (m, 3H), 6.93 – 6.82 (m, 2H), 3.79 (s, 3H), 2.67 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.42 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 156.8, 140.6, 130.2, 128.5, 128.4, 126.3, 121.8, 114.1, 79.4, 55.5, 34.9, 9.5.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}ClNO_2$ $[M + H]^+$ 304.1099, found 304.1098.

General procedure SM-B for the synthesis of tertiary *α*-chloroamides (E12–E28, E62′)



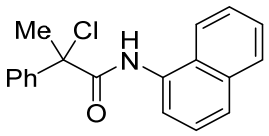
To a solution of corresponding aryl acetic acid (20.0 mmol, 1.0 equiv.) in anhydrous THF (40.0 mL) was added LDA (44.0 mL, 44.0 mmol, 2.2 equiv., 1.0 M in THF) via syringe at −78 °C under argon. The reaction was stirred at −78 °C for 30 min, warmed up to 0 °C and stirred for another 1 h. The solution was then cooled to −78 °C again and the corresponding alkyl iodide (21.0 mmol, 1.05 equiv.) was added in one portion. The reaction was warmed up to room temperature slowly and stirred overnight. The resulting solution was used directly in the next step.

To the resulting solution was added hexamethylphosphoramide (HMPA, 6.0 mL) and LDA (22.0 mL, 22.0 mmol, 1.1 equiv., 1.0 M in THF) via syringe at −78 °C under argon. The reaction was slowly warmed up to 0 °C and stirred for another 1 h. Then the solution was cooled to −78 °C again and carbon tetrachloride (26.24 g, 80.0 mmol, 4.0 equiv.) was added in one portion. The reaction was stirred at −78 °C for 2 h, warmed up to room temperature slowly and stirred overnight. Then, the reaction was quenched with 1.0 M HCl (60 mL) at 0 °C, extracted with ethyl acetate twice and the combined organic layer was washed by brine, dried over Na_2SO_4 and filtered. The filtrate was

then concentrated under reduced pressure to afford the crude tertiary α-chloroacetic acid, which was directly used in the next step.

To a solution of the crude acetic acid in anhydrous CH_2Cl_2 (80.0 mL) was added oxalyl chloride (3.02 g, 24.0 mmol, 1.2 equiv.) at 0 °C, and then few drops of DMF was added as catalyst. After warmed up to room temperature and stirred for 30 min, the resulting acyl chloride was cooled to –20 °C. Anhydrous triethylamine (5.05 g, 50.0 mmol, 2.5 equiv.) and 1-naphthylamine (3.43 g, 24.0 mmol, 1.2 equiv.) were added, then the reaction mixture was warmed up to room temperature and stirred at that temperature. After completion (monitored by TLC), the reaction was quenched by addition of 1.0 M HCl. The organic layer was washed by brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude material which was purified by flash chromatography to yield the tertiary α-chloroamide.

2-Chloro-*N*-(naphthalen-1-yl)-2-phenylpropanamide (E12)



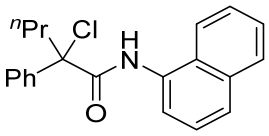
According to general procedure **SM-B** with 2-phenylacetic acid (2.72 g, 20 mmol, 1.0 equiv.) and iodomethane (2.98 g, 21 mmol, 1.05 equiv.) to afford **E12** as a white amorphous solid (1.21 g, 19% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.94 – 7.86 (m, 1H), 7.78 – 7.72 (m, 4H), 7.59 – 7.37 (m, 6H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 141.5, 134.1, 131.7, 128.9, 128.8, 128.7, 127.0, 126.6, 126.14, 126.10, 125.7, 120.2, 73.9, 30.4.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{17}ClNO$ $[M + H]^+$ 310.0993, found 310.0992.

2-Chloro-*N*-(naphthalen-1-yl)-2-phenylpentanamide (E13)



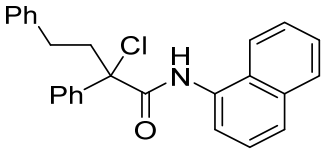
According to general procedure **SM-B** with 2-phenylacetic acid (2.72 g, 20 mmol, 1.0 equiv.) and 1-iodopropane (3.57 g, 21 mmol, 1.05 equiv.) to afford **E13** as a yellowish amorphous solid (0.85 g, 13% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.76 – 7.68 (m, 4H), 7.60 – 7.29 (m, 6H), 2.74 – 2.60 (m, 1H), 2.48 – 2.38 (m, 1H), 1.69 – 1.56 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 140.8, 134.1, 131.7, 128.8, 128.7, 128.6, 127.0, 126.6, 126.4, 126.11, 126.07, 125.7, 120.2, 120.1, 79.3, 43.8, 18.5, 13.9.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}ClNO$ $[M + H]^+$ 338.1306, found 338.1306

2-Chloro-*N*-(naphthalen-1-yl)-2,4-diphenylbutanamide (E14)



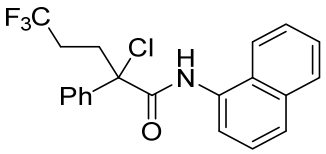
According to general procedure **SM-B** with 2-phenylacetic acid (1.36 g, 10 mmol, 1.0 equiv.) and (2-iodoethyl)benzene (2.44 g, 10.5 mmol, 1.05 equiv.) to afford **E14** as a yellow amorphous solid (0.85 g, 21% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.05 (d, *J* = 7.4 Hz, 1H), 7.94 – 7.89 (m, 1H), 7.82 – 7.75 (m, 4H), 7.59 – 7.51 (m, 3H), 7.50 – 7.39 (m, 3H), 7.36 – 7.21 (m, 5H), 3.12 – 3.02 (m, 1H), 2.99 – 2.90 (m, 2H), 2.82 – 2.71 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 141.0, 140.4, 134.1, 132.0, 128.9, 128.83, 128.76, 128.6, 128.5, 127.1, 126.7, 126.35, 126.25, 126.18, 126.15, 125.7, 120.4, 120.2, 78.8, 44.0, 31.7.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{23}ClNO$ $[M + H]^+$ 400.1463, found 400.1464.

2-Chloro-5,5,5-trifluoro-*N*-(naphthalen-1-yl)-2-phenylpentanamide (E15)



According to general procedure **SM-B** with 2-phenylacetic acid (1.36 g, 10 mmol, 1.0 equiv.) and 1,1,1-trifluoro-3-iodopropane (2.35 g, 10.5 mmol, 1.05 equiv.) to afford **E15** as an off-white amorphous solid (0.61 g, 16% yield over three steps).

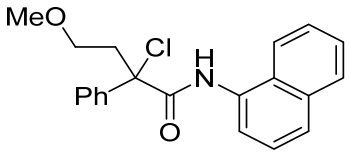
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.94 – 7.86 (m, 1H), 7.81 – 7.71 (m, 3H), 7.68 – 7.60 (m, 1H), 7.57 – 7.42 (m, 6H), 3.01 – 2.89 (m, 1H), 2.79 – 2.67 (m, 1H), 2.57 – 2.24 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 139.0, 134.1, 131.3, 129.2, 129.1, 128.9, 128.2 (q, *J* = 276.5 Hz), 127.1, 126.7, 126.5, 126.2, 126.1, 125.7, 120.5, 120.1, 76.8, 34.8 (q, *J* = 3.3 Hz), 30.3 (q, *J* = 29.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ −66.06 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{21}H_{18}ClF_3NO$ $[M + H]^+$ 392.1024, found 392.1023.

2-Chloro-4-methoxy-*N*-(naphthalen-1-yl)-2-phenylbutanamide (E16)

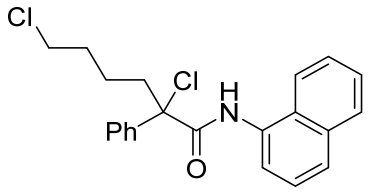


According to general procedure **SM-B** with 2-phenylacetic acid (1.36 g, 10 mmol, 1.0 equiv.) and 1-iodo-2-methoxyethane (1.95 g, 10.5 mmol, 1.05 equiv.) to afford **E16** as a brown amorphous solid (0.96 g, 27% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.93 – 7.88 (m, 1H), 7.79 – 7.72 (m, 4H), 7.57 – 7.38 (m, 6H), 3.81 – 3.63 (m, 2H), 3.34 (s, 3H), 3.15

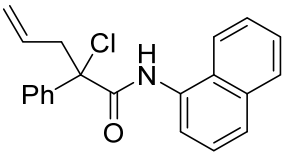
(ddd, *J* = 14.6, 8.4, 6.5 Hz, 1H), 2.74 (ddd, *J* = 14.3, 8.2, 4.6 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 140.4, 134.1, 131.7, 128.83, 128.82, 128.77, 127.1, 126.6, 126.3, 126.2, 126.1. 125.7, 120.3, 120.2, 76.6, 69.2, 58.8, 40.8.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{21}ClNO_2$ $[M + H]^+$ 354.1255, found 354.1256.

2,6-Dichloro-*N*-(naphthalen-1-yl)-2-phenylhexanamide (E17)



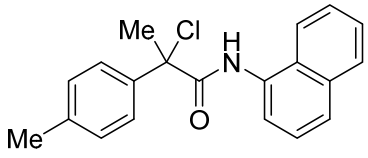
According to general procedure **SM-B** with 2-phenylacetic acid (1.36 g, 10 mmol, 1.0 equiv.) and 1-chloro-4-iodobutane (2.29 g, 10.5 mmol, 1.05 equiv.) to afford **E17** as a brown amorphous solid (0.63 g, 16% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.00 (d, *J* = 7.4 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.78 – 7.69 (m, 4H), 7.58 – 7.37 (m, 6H), 3.62 – 3.51 (m, 2H), 2.79 – 2.65 (m, 1H), 2.56 – 2.41 (m, 1H), 1.98 – 1.69 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 140.3, 134.1, 131.6, 128.8, 128.8, 128.7, 127.1, 126.7, 126.3, 126.24, 126.16, 125.7, 120.3, 120.2, 78.9 44.6, 41.1, 32.4, 22.7.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}Cl_2NO$ $[M + H]^+$ 386.1073, found 386.1075

2-Chloro-*N*-(naphthalen-1-yl)-2-phenylpent-4-enamide (E18)



According to general procedure **SM-B** with 2-phenylacetic acid (1.36 g, 10 mmol, 1.0 equiv.) and 3-bromoprop-1-ene (1.27 g, 10.5 mmol, 1.05 equiv.) to afford **E18** as a yellow amorphous solid (0.51 g, 14% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.73 – 7.67 (m, 4H), 7.52 – 7.32 (m, 6H), 5.89 (ddt, *J* = 17.1, 10.3, 6.9 Hz, 1H), 5.32 – 5.11 (m, 2H), 3.45 (dd, *J* = 14.5, 6.9 Hz, 1H), 3.21 (dd, *J* = 14.6, 7.0 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 140.1, 134.1, 132.1, 131.7, 128.8, 128.76, 128.74, 127.2, 126.6, 126.5, 126.2, 126.1, 125.7, 120.4, 120.3, 77.7, 45.9.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{19}ClNO$ $[M + H]^+$ 336.1150, found 336.1149

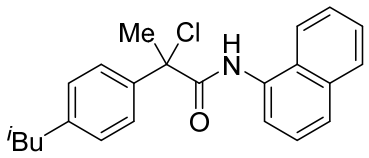
2-Chloro-*N*-(naphthalen-1-yl)-2-(*p*-tolyl)propenamide (E19)



According to general procedure **SM-B** with 2-(*p*-tolyl)acetic acid (3.00 g, 20 mmol, 1.0 equiv.) and iodomethane (2.98 g, 21 mmol, 1.05 equiv.) to afford **E19** as a white

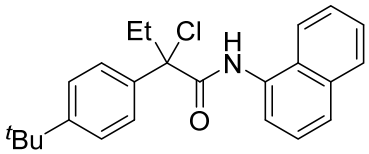
amorphous solid (0.96 g, 15% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.11 – 8.05 (m, 1H), 7.95 – 7.88 (m, 1H), 7.83 – 7.73 (m, 2H), 7.70 – 7.63 (m, 2H), 7.63 – 7.47 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.36 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 138.71, 138.69, 134.1, 131.9, 129.5, 128.9, 127.1, 126.6, 126.2, 126.10, 126.09, 125.8, 120.3, 120.2, 74.0, 30.4, 21.1.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}ClNO$ $[M + H]^+$ 324.1150, found 324.1153.

2-Chloro-2-(4-isobutylphenyl)-*N*-(naphthalen-1-yl)propenamide (E20)



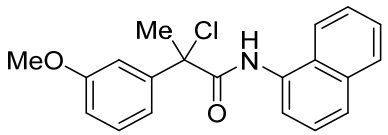
According to general procedure **SM-B** with slightly modification. 2-(4-isobutylphenyl)propanoic acid (2.06 g, 10 mmol, 1.0 equiv.) and LDA (22.0 mL, 22.0 mmol, 2.2 equiv.,1.0 M in THF) to afford **E20** as a white amorphous solid (1.27 g, 35% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.00 (d, *J* = 7.6, 1.0 Hz, 1H), 7.88 – 7.79 (m, 1H), 7.70 – 7.56 (m, 4H), 7.50 – 7.40 (m, 3H), 7.18 (d, *J* = 7.5 Hz, 2H), 2.48 (d, *J* = 7.1 Hz, 2H), 2.27 (s, 3H), 1.87 (dp, *J* = 13.6, 6.7 Hz, 1H), 0.91 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 142.5, 138.8, 134.1, 131.8, 129.6, 128.9, 127.0, 126.6, 126.1, 126.1, 125.9, 125.8, 120.2, 120.1, 73.9, 45.0, 30.3, 30.2, 22.5.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{25}ClNO$ $[M + H]^+$ 366.1619, found 366.1624.

2-(4-(*tert*-Butyl)phenyl)-2-chloro-*N*-(naphthalen-1-yl)butanamide(E21)



According to general procedure **SM-B** with 2-(4-(*tert*-butyl)phenyl)acetic acid (1.92 g, 10 mmol, 1.0 equiv.) and iodoethane (1.64 g, 10.5 mmol, 1.05 equiv.) to afford **E21** as a yellow amorphous solid (1.25 g, 33% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.91 – 7.83 (m, 1H), 7.75 – 7.68 (m, 2H), 7.65 – 7.59 (m, 2H), 7.54 – 7.40 (m, 5H), 2.76 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.49 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.33 (s, 9H), 1.16 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 151.6, 137.5, 134.0, 131.7, 128.8, 127.0, 126.9, 126.5, 126.14, 126.05, 125.96, 125.8, 125.7, 125.6, 120.2, 120.0, 80.1, 34.6, 34.6, 31.3, 31.2, 9.6.
HRMS (ESI) *m/z* calcd. For $C_{24}H_{27}ClNO$ $[M + H]^+$ 380.1776, found 380.1775.

2-Chloro-2-(3-methoxyphenyl)-*N*-(naphthalen-1-yl)propenamide (E22)



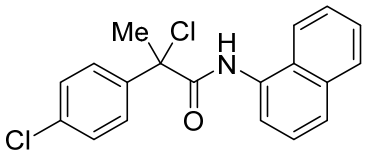
According to general procedure **SM-B** with 2-(4-methoxyphenyl)acetic acid (3.32 g, 20 mmol, 1.0 equiv.) and iodomethane (2.98 g, 21 mmol, 1.05 equiv.) to afford **E22** as a white amorphous solid (0.74 g, 11% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.06 – 8.00 (m, 1H), 7.94 – 7.86 (m, 1H), 7.78 – 7.70 (m, 2H), 7.57 – 7.47 (m, 3H), 7.43 – 7.35 (m, 1H), 7.35 – 7.26 (m, 2H), 6.98 – 6.91 (m, 1H), 3.86 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 159.8, 142.9, 134.1, 131.7, 129.9, 128.8, 127.1, 126.6, 126.1, 125.7, 120.21, 120.20,118.4, 113.9, 112.4, 73.6, 55.4, 30.3.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{19}ClNO_2$ $[M + H]^+$ 340.1099, found 340.1101.

2-Chloro-2-(4-chlorophenyl)-*N*-(naphthalen-1-yl)propenamide (E23)



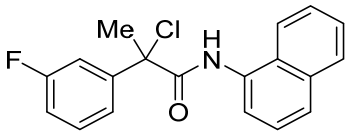
According to general procedure **SM-B** with 2-(4-chlorophenyl)acetic acid (3.41 g, 20 mmol, 1.0 equiv.) and iodomethane (2.98 g, 21 mmol, 1.05 equiv.) to afford **E23** as a white amorphous solid (1.27 g, 18% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.99 (d, J = 7.4 Hz, 1H), 7.94 – 7.85 (m, 1H), 7.77 – 7.70 (m, 2H), 7.67 – 7.61 (m, 2H), 7.57 – 7.46 (m, 3H), 7.42 – 7.36 (m, 2H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 140.1, 134.8, 134.1, 131.5, 128.9, 127.6, 127.0, 126.7, 126.3, 126.2, 125.7, 120.2, 120.1, 73.3, 30.4.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{16}Cl_2NO$ $[M + H]^+$ 344.0603, found 344.0606.

2-Chloro-2-(3-fluorophenyl)-*N*-(naphthalen-1-yl)propenamide (E24)



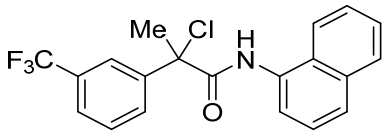
According to general procedure **SM-B** with 2-(3-fluorophenyl)acetic acid (3.08 g, 20 mmol, 1.0 equiv.) and iodomethane (2.98 g, 21 mmol, 1.05 equiv.) to afford **E24** as a yellowish amorphous solid (1.32 g, 20% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.94 – 7.87 (m, 1H), 7.80 – 7.73 (m, 2H), 7.61 – 7.37 (m, 6H), 7.15 – 7.06 (m, 1H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 162.8 (d, J = 247.0 Hz), 143.9 (d, J = 7.3 Hz), 134.1, 131.5, 130.4 (d, J = 8.3 Hz), 128.9, 127.0, 126.7, 126.3, 126.2, 125.7, 121.8 (d, J = 3.1 Hz), 120.3, 120.1, 115.7 (d, J = 21.1 Hz), 113.7 (d, J = 23.9 Hz), 73.1, 30.4.

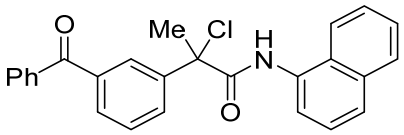
^{19}F NMR (376 MHz, $CDCl_3$) δ −111.75 – −111.85 (m, 1F).
HRMS (ESI) *m/z* calcd. for $C_{19}H_{16}ClFNO$ $[M + H]^+$ 328.0899, found 328.0901.

2-Chloro-*N*-(naphthalen-1-yl)-2-(3-(trifluoromethyl)phenyl)propenamide (E25)



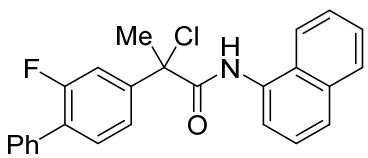
According to general procedure **SM-B** with 2-(3-(trifluoromethyl)phenyl)acetic acid (4.08 g, 20 mmol, 1.0 equiv.) and iodomethane (2.98 g, 21 mmol, 1.05 equiv.) to afford **E25** as a yellowish amorphous solid (2.4 g, 32% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.00 (s, 1H), 7.91 (d, *J* = 7.5, 1.1 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.75 – 7.68 (m, 2H), 7.64 – 7.59 (m, 1H), 7.55 – 7.42 (m, 4H), 2.30 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 142.6, 134.1, 131.5, 131.2 (q, *J* = 32.5 Hz), 129.7, 129.4, 128.9, 127.3, 126.8, 126.6, 126.3, 125.7, 125.6 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.6 Hz), 123.1 (q, *J* = 3.9 Hz), 120.7, 120.2, 73.0, 30.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.51 (s, 3F).
HRMS (ESI) *m/z* calcd. for $C_{20}H_{16}ClF_3NO$ $[M + H]^+$ 378.0867, found 378.0870.

2-(3-Benzoylphenyl)-2-chloro-N-(naphthalen-1-yl)propenamide (E26)



According to general procedure **SM-A** with 2-(4-benzoylphenyl)propanoic acid (2.54 g, 10 mmol, 1.0 equiv.) and naphthalen-1-amine (1.43 g, 10 mmol, 1.0 equiv.) to afford **E26** as a brown viscous liquid (0.91 g, 22% yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.18 (t, *J* = 1.9 Hz, 1H), 7.97 – 7.83 (m, 3H), 7.81 – 7.69 (m, 5H), 7.61 – 7.38 (m, 7H), 2.33 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 168.8, 142.0, 138.0, 137.2, 134.1, 132.7, 131.5, 130.3, 130.08, 130.06, 128.9, 128.8, 128.4, 127.8, 127.2, 126.7, 126.4, 126.2, 125.7, 120.5, 120.2, 73.3, 30.3.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{21}ClNO_2$ $[M + H]^+$ 414.1255, found 414.1259.

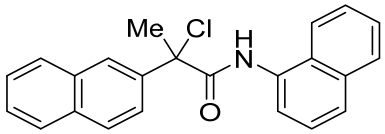
2-Chloro-2-(2-fluoro-[1,1'-biphenyl]-4-yl)-*N*-(naphthalen-1-yl)propenamide (E27)



According to general procedure **SM-B** with slightly modification. 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (2.44 g, 10 mmol, 1.0 equiv.) and LDA (22.0 mL, 22.0 mmol, 2.2 equiv.,1.0 M in THF) to afford **E27** as a white amorphous solid (2.30 g, 57%

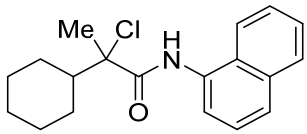
yield over two steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.97 – 7.88 (m, 1H), 7.87 – 7.81 (m, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.64 – 7.39 (m, 11H), 2.38 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 159.6 (d, *J* = 249.3 Hz), 142.7 (d, *J* = 7.5 Hz), 134.9, 134.1, 131.6, 131.1 (d, *J* = 4.0 Hz), 129.5 (d, *J* = 13.6 Hz), 129.02, 129.00, 128.9, 128.6, 128.1, 127.1, 126.8, 126.4, 126.2, 125.7, 122.1 (d, *J* = 3.5 Hz), 120.2 (d, *J* = 15.7 Hz), 114.5 (d, *J* = 25.6 Hz), 73.0 (d, *J* = 1.5 Hz), 30.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ −116.18 – −116.27 (m, 1F).
HRMS (ESI) *m/z* calcd. for $C_{25}H_{20}ClFNO$ $[M + H]^+$ 404.1212, found 404.1215.

2-Chloro-*N*-(naphthalen-1-yl)-2-(naphthalen-2-yl)propenamide (E28)



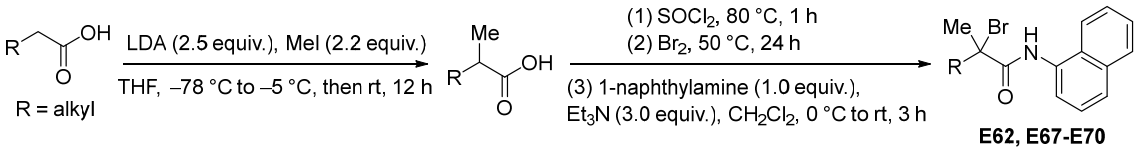
According to general procedure **SM-B** with 2-(naphthalen-2-yl)acetic acid (3.64 g, 20 mmol, 1.0 equiv.) and iodomethane (2.98 g, 21 mmol, 1.05 equiv.) to afford **E28** as a white solid (1.66 g, 23% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.16 (d, *J* = 2.1 Hz, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.92 – 7.80 (m, 4H), 7.78 – 7.66 (m, 3H), 7.54 – 7.42 (m, 5H), 2.38 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 138.6, 134.0, 133.0, 132.8, 131.6, 128.8, 128.5, 127.5, 127.0, 126.9, 126.7, 126.6, 126.14, 126.07, 125.6, 125.0, 123.9, 120.23, 120.16, 74.0, 30.2.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{19}ClNO$ $[M + H]^+$ 360.1150, found 360.1154.

2-Chloro-2-cyclohexyl-*N*-(naphthalen-1-yl)propenamide (E62′)



According to general procedure **SM-B** with 2-cyclohexylacetic acid (2.84 g, 20 mmol, 1.0 equiv.) and iodomethane (2.98 g, 21 mmol, 1.05 equiv.) to afford **E62′** as a white solid (2.58 g, 41% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.44 (m, 3H), 2.20 – 2.13 (m, 1H), 2.01 – 1.94 (m, 1H), 1.90 (s, 3H), 1.86 – 1.67 (m, 4H), 1.46 – 1.14 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 134.0, 131.7, 128.8, 126.8, 126.6, 126.0, 125.8, 125.7, 120.1, 119.8, 80.3, 47.1, 28.5, 27.5, 26.8, 26.1, 26.04, 26.02.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}ClNO$ $[M + H]^+$ 316.1463, found 316.1461.

General procedure SM-C for the synthesis of tertiary *α*-methyl-*α*-alkyl-*α*-bromoamides (E62, E67–E70)

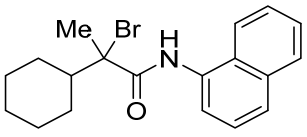


E62, E67-E70

To a solution of corresponding alkyl acetic acid (20.0 mmol, 1.0 equiv.) in anhydrous THF (40 mL) was added LDA (1.0 M solution in THF, 50 mL, 50.0 mmol, 2.5 equiv.) dropwise via syringe at –78 °C under argon atmosphere. The resulting mixture was warmed up to –5 °C and stirred for 2 h. Then MeI (2.74 mL, 44.0 mmol, 2.2 equiv.) in anhydrous THF (10 mL) was added dropwise into the reaction mixture, and the resulting mixture was warmed up to room temperature and stirred for 12 h. The reaction mixture was quenched by saturated NH_4Cl (40 mL) and concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (50 mL × 2). The combined organic layers were washed with brine (40 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude substituted carboxylic acid, which was directly used in the next step without further purification.

The crude substituted acetic acid was dissolved in $SOCl_2$ (5.0 mL), and the mixture was stirred at 80 °C for 0.5 h. The reaction was cooled to room temperature, and then Br_2 (2.20 mL, 40.0 mmol, 2.0 equiv.) and $SOCl_2$ (4.0 mL) were added. The resulting mixture was stirred at 50 °C for 24 h. The reaction mixture was concentrated under reduced pressure to remove the solvent and excess Br_2 to afford the crude *α*-bromo acyl chloride, which was subsequently dissolved in CH_2Cl_2 (40 mL) followed by the addition of 1-naphthylamine (2.86 g, 20.0 mmol, 1.0 equiv.) and triethylamine (8.34 mL, 60.0 mmol, 3.0 equiv.) at 0 °C. The resulting mixture was warmed up to room temperature and stirred for 3 h. The reaction was quenched by HCl (1 M, 40 mL) and extracted with CH_2Cl_2 (30 mL × 2). The combined organic layers were washed with HCl (50 mL × 2) and brine (100 mL × 2), dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 100/1–50/1) to give the desired product as a white solid.

2-Bromo-2-cyclohexyl-*N*-(naphthalen-1-yl)propenamide (E62)

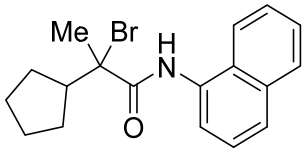


According to general procedure **SM-C** with 2-cyclohexylacetic acid (2.84 g, 20 mmol) to afford **E62** as a white solid (2.30 g, 32% yield over four steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.03 (d, J = 7.3 Hz, 1H), 7.88 (t, J = 8.9 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.60 – 7.43 (m, 3H), 2.07 (s, 3H), 2.01 – 1.56 (m, 6H), 1.43 – 1.14 (m, 5H).

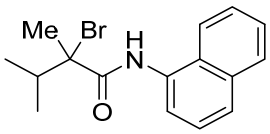
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 134.0, 132.0, 128.8, 126.9, 126.6, 126.0, 125.8, 125.7, 120.2, 119.8, 78.2, 48.2, 29.7, 28.6, 28.1, 26.08, 26.05, 26.03.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{23}BrNO$ $[M + H]^+$ 360.0958, found 360.3959.

2-Bromo-2-cyclopentyl-*N*-(naphthalen-1-yl)propenamide (E67)



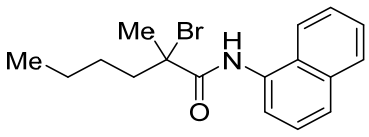
According to general procedure **SM-C** with 2-cyclohexylacetic acid (2.56 g, 20 mmol) to afford **E67** as a white solid (2.84 g, 41% yield over four steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.48 (m, 3H), 2.68 – 2.55 (m, 1H), 2.14 (s, 3H), 2.01 – 1.84 (m, 2H), 1.82 – 1.57 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 134.1, 132.1, 128.9, 127.1, 126.6, 126.1, 126.0, 125.7, 120.4, 120.0, 78.5, 50.4, 30.2, 30.1, 29.0, 25.7, 25.6.
HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}BrNO$ $[M + H]^+$ 346.0801, found 346.0802.

2-Bromo-2,3-dimethyl-*N*-(naphthalen-1-yl)butanamide (E68)



According to general procedure **SM-C** with 3-methylbutanoic acid (2.04 g, 20 mmol) to afford **E68** as a white solid (2.95 g, 46% yield over four steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.01 (d, *J* = 7.4 Hz, 1H), 7.88 (t, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.43 (m, 3H), 2.41 – 2.30 (m, 1H), 2.08 (s, 3H), 1.17 – 1.10 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 134.0, 132.0, 128.8, 127.0, 126.6, 126.1, 125.9, 125.7, 120.3, 119.9, 79.5, 38.4, 29.1, 19.9, 18.0.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{19}BrNO$ $[M + H]^+$ 320.0645, found 320.0645.

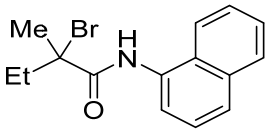
2-Bromo-2-methyl-*N*-(naphthalen-1-yl)hexanamide (E69)



According to general procedure **SM-C** with hexanoic acid (2.32 g, 20 mmol) to afford **E69** as a white solid (2.47 g, 37% yield over four steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.45 (m, 3H), 2.37 – 2.28 (m, 1H), 2.12 (s, 3H), 2.10 – 2.03 (m, 1H), 1.69 – 1.58 (m, 1H), 1.55 – 1.45 (m, 1H), 1.44 – 1.33 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

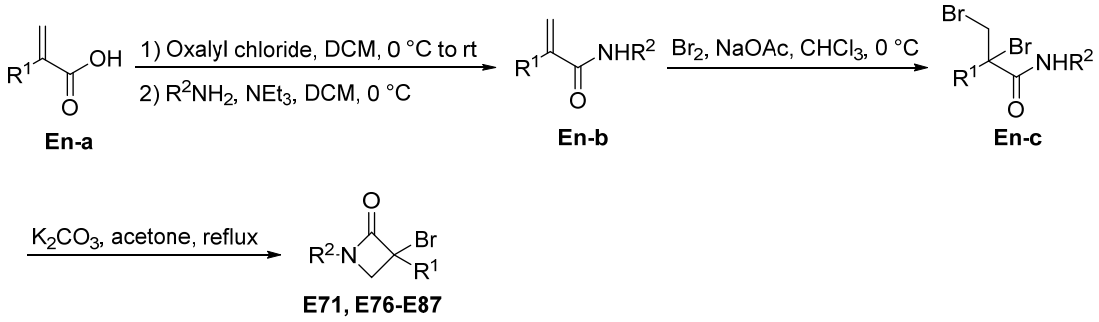
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 134.0, 132.0, 128.8, 127.0, 126.6, 126.1, 126.0, 125.7, 120.3, 119.9, 71.5, 44.2, 31.4, 28.5, 22.4, 13.9.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{21}BrNO$ $[M + H]^+$ 334.0801, found 334.0800.

2-Bromo-2-methyl-*N*-(naphthalen-1-yl)butanamide (E70)

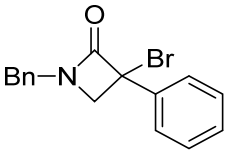


According to general procedure **SM-C** with hexanoic acid (1.76 g, 20 mmol) to afford **E70** as a white solid (2.66 g, 43% yield over four steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.88 (t, *J* = 7.0 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.46 (m, 3H), 2.37 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.17 – 2.05 (m, 4H), 1.15 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 134.0, 132.0, 128.8, 127.0, 126.6, 126.1, 126.0, 125.6, 120.3, 120.0, 72.4, 37.6, 31.0, 10.9.
HRMS (ESI) *m/z* calcd. for $C_{15}H_{17}BrNO$ $[M + H]^+$ 306.0488, found 306.0488.

General procedure SM-D for preparation of *β*-lactam of E71, E76–E87



1-Benzyl-3-bromo-3-phenylazetidin-2-one (E71)



To a solution of the atropic acid (1.48 g, 10.0 mmol) in anhydrous CH_2Cl_2 (30 mL) was added oxalyl chloride (1.51 g, 12.0 mmol, 1.2 equiv.) at 0 °C, and then a few drops of DMF was added as catalyst. After warmed up to room temperature and stirred for 30 min, the resulting acyl chloride was cooled to –20 °C. Anhydrous triethylamine (2.53 g, 25.0 mmol, 2.5 equiv.) and benzylamine (1.18 g, 11.0 mmol, 1.1 equiv.) were added, and then the reaction mixture was warmed up to room temperature and stirred at that temperature. After completion (monitored by TLC), the reaction was quenched by addition of 1.0 M HCl. The organic layer was washed by brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude material, which was purified by flash chromatography to yield acrylamide **E71-b** (2.14 g, 90%).

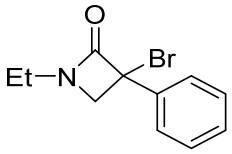
E71 was synthesized according to a modified literature procedure[2]: to a mixture of **E71-b** (1.19 g, 5.0 mmol) and sodium acetate (1.23 g, 15.0 mmol) in chloroform (30 mL) was added bromine (0.10 mL, 10.0 mmol) dropwise at 0 °C under argon atmosphere. After being stirred for 40 min, the mixture was poured into a solution of 10% sodium thiosulfate, and then extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over sodium sulfate, filtered and concentrated under reduced pressure to give **E71-c**. The crude product was used directly in the next step. A mixture of the dibromide **E71-c** and potassium carbonate (2.07 g, 15.0 mmol) in acetone (20 mL) was heated to reflux for 24 h under argon atmosphere. After being cooled to room temperature, the mixture was filtered through a short pat of silica gel column. The filtrate was concentrated under reduced pressure, and then the residue was purified by column chromatography on silica gel to afford the *β*-lactam **E71** as a white solid (1.00 g, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.52 (m, 2H), 7.42 – 7.28 (m, 6H), 7.25 – 7.18 (m, 2H), 4.56 (d, J = 15.1 Hz, 1H), 4.39 (d, J = 15.2 Hz, 1H), 3.88 (d, J = 6.0 Hz, 1H), 3.86 (d, J = 6.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 137.5, 134.3, 129.1, 129.0, 128.9, 128.1, 127.1, 60.5, 57.6, 46.2.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}BrNO$ $[M + H]^+$ 316.0332, found 316.0334.

3-Bromo-1-ethyl-3-phenylazetidin-2-one (E76)



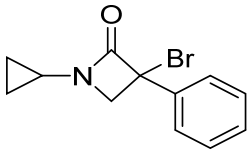
According to **general procedure SM-D** with atropic acid (0.74 g, 5.0 mmol, 1.0 equiv.) and ethylamine (0.25 g, 5.5 mmol, 1.1 equiv.) to afford **E76** as a colorless oil (0.902 g, 71% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 2H), 7.42 – 7.29 (m, 3H), 4.00 (d, *J* = 6.0 Hz, 1H), 3.98 (d, *J* = 6.0 Hz, 1H), 3.44 – 3.24 (m, 2H), 1.19 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 137.8, 129.0, 128.8, 127.1, 60.1, 57.4, 36.9, 12.3.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{13}BrNO$ $[M + H]^+$ 254.0175, found 254.0173.

3-Bromo-1-cyclopropyl-3-phenylazetidin-2-one (E77)



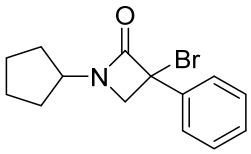
According to **general procedure SM-D** with atropic acid (0.74 g, 5.0 mmol, 1.0 equiv.) and cyclopropylamine (0.31 g, 5.5 mmol, 1.1 equiv.) to afford **E77** as a yellowish solid (0.931 g, 70% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.41 – 7.29 (m, 3H), 3.95 (d, *J* = 6.0 Hz, 1H), 3.92 (d, *J* = 5.9 Hz, 1H), 2.61 (tt, *J* = 7.2, 3.8 Hz, 1H), 0.91 – 0.72 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 137.7, 129.1, 128.9, 127.1, 59.6, 58.6, 24.6, 5.3.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{13}BrNO$ $[M + H]^+$ 266.0175, found 266.0174.

3-Bromo-1-cyclopentyl-3-phenylazetidin-2-one (E78)



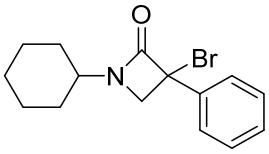
According to **general procedure SM-D** with atropic acid (0.742 g, 5.0 mmol, 1.0 equiv.) and cyclopentylamine (0.47 g, 5.5 mmol, 1.1 equiv.) to afford **E78** as a yellow oil (0.956 g, 65% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.41 – 7.29 (m, 3H), 4.18 – 4.03 (m, 1H), 3.96 (d, *J* = 5.9 Hz, 1H), 3.94 (d, *J* = 5.8 Hz, 1H), 1.99 – 1.53 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 137.8, 129.0, 128.8, 127.1, 59.3, 56.2, 53.7, 30.0, 29.9, 23.99, 23.95.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{17}BrNO$ $[M + H]^+$ 294.0488, found 294.0490.

3-Bromo-1-cyclohexyl-3-phenylazetidin-2-one (E79)



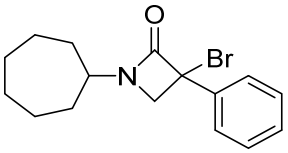
According to **general procedure SM D** with atropic acid (0.74 g, 5.0 mmol, 1.0 equiv.) and cyclohexylamine (0.55 g, 5.5 mmol, 1.1 equiv.) to afford **E79** as a yellowish solid (0.924 g, 60% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 2H), 7.44 – 7.30 (m, 3H), 3.98 (s, 2H), 3.64 (tt, *J* = 11.0, 3.9 Hz, 1H), 2.03 – 1.93 (m, 1H), 1.91 – 1.72 (m, 3H), 1.69 – 1.60 (m, 1H), 1.48 – 1.25 (m, 4H), 1.22 – 1.08 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 137.8, 129.0, 128.8, 127.1, 59.4, 55.7, 51.5, 30.4, 30.2, 25.2, 24.64, 24.62.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{19}BrNO$ $[M + H]^+$ 308.0645, found 308.0647.

3-Bromo-1-cycloheptyl-3-phenylazetidin-2-one (E80)



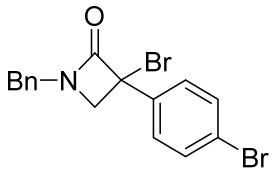
According to **general procedure SM D** with atropic acid (0.74 g, 5.0 mmol, 1.0 equiv.) and cycloheptylamine (0.62 g, 5.5 mmol, 1.1 equiv.) to afford **E80** as a yellowish-brown solid (1.03 g, 64% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 2H), 7.44 – 7.31 (m, 3H), 3.99 (s, 2H), 3.90 – 3.77 (m, 1H), 2.06 – 1.96 (m, 1H), 1.95 – 1.83 (m, 1H), 1.78 – 1.40 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 137.8, 129.0, 128.8, 127.1, 59.7, 55.9, 53.5, 32.5, 32.2, 27.9, 27.8, 24.1.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{21}BrNO$ $[M + H]^+$ 322.0801, found 322.0804.

1-Benzyl-3-bromo-3-(4-bromophenyl)azetidin-2-one (E81)



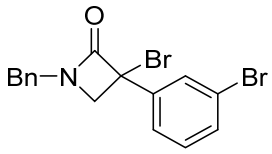
According to **general procedure SM-D** with 2-(4-bromophenyl)acrylic acid (1.14 g, 5.0 mmol, 1.0 equiv.) and benzylamine (0.59 g, 5.5 mmol, 1.1 equiv.) to afford **E81** as a white solid (1.32 g, 67% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 4H), 7.40 – 7.28 (m, 3H), 7.24 – 7.20 (m, 2H), 4.53 (d, *J* = 15.1 Hz, 1H), 4.40 (d, *J* = 15.1 Hz, 1H), 3.85 (d, *J* = 6.1 Hz, 1H), 3.83 (d, *J* = 6.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 136.6, 134.1, 132.1, 129.0, 128.8, 128.2, 128.1, 123.4, 59.4, 57.4, 46.3.

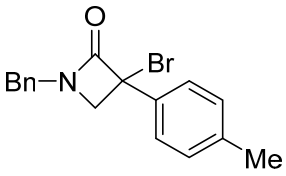
HRMS (ESI) *m/z* calcd. for $C_{16}H_{14}Br_2NO$ $[M + H]^+$ 393.9437, found 393.9435.

1-Benzyl-3-bromo-3-(3-bromophenyl)azetidin-2-one (E82)



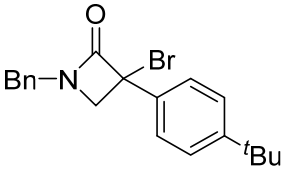
According to **general procedure SM-D** with 2-(3-bromophenyl)acrylic acid (1.14 g, 5.0 mmol, 1.0 equiv.) and benzylamine (0.59 g, 5.5 mmol, 1.1 equiv.) to afford **E82** as a white solid (1.40 g, 71% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 1.8 Hz, 1H), 7.55 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.47 (ddd, *J* = 8.1, 1.9, 1.0 Hz, 1H), 7.36 (m, 3H), 7.25 – 7.20 (m, 3H), 4.55 (d, *J* = 15.1 Hz, 1H), 4.39 (d, *J* = 15.0 Hz, 1H), 3.84 (s, 2H).
^{13}C NMR (10 MHz, $CDCl_3$) δ 164.5, 139.7, 134.1, 132.3, 130.5, 130.2, 129.1, 128.23, 128.15, 125.8, 122.8, 59.1, 57.5, 46.3.
HRMS (ESI) *m/z* calcd. for $C_{16}H_{14}Br_2NO$ $[M + H]^+$ 393.9437, found 393.9435.

1-Benzyl-3-bromo-3-(*p*-tolyl)azetidin-2-one (E83)



According to **general procedure SM-D** with 2-(*p*-tolyl)acrylic acid (0.81 g, 5.0 mmol, 1.0 equiv.) and benzylamine (0.59 g, 5.5 mmol, 1.1 equiv.) to afford **E83** as a white solid (1.14 g, 69% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.38 – 7.28 (m, 3H), 7.25 – 7.21 (m, 2H), 7.20 – 7.15 (m, 2H), 4.54 (d, *J* = 15.1 Hz, 1H), 4.39 (d, *J* = 15.1 Hz, 1H), 3.87 (d, *J* = 6.0 Hz, 1H), 3.85 (d, *J* = 6.0 Hz, 1H), 2.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 139.2, 134.3, 129.6, 129.0, 128.07, 128.05, 127.0, 60.7, 57.6, 46.2, 21.2.
HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}BrNO$ $[M + H]^+$ 330.0488, found 330.0485.

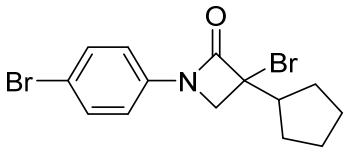
1-Benzyl-3-bromo-3-(4-(*tert*-butyl)phenyl)azetidin-2-one (E84)



According to **general procedure SM-D** with 2-(4-(*tert*-butyl)phenyl)acrylic acid (1.02 g, 5.0 mmol, 1.0 equiv.) and benzylamine (0.59 g, 5.5 mmol, 1.1 equiv.) to afford **E84** as a white solid (1.02 g, 55% yield over three steps).

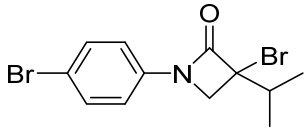
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.41 – 7.29 (m, 5H), 7.25 – 7.21 (m, 2H), 4.56 (d, *J* = 15.2 Hz, 1H), 4.35 (d, *J* = 15.2 Hz, 1H), 3.89 (d, *J* = 6.0 Hz, 1H), 3.85 (d, *J* = 6.0 Hz, 1H), 1.31 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 152.3, 134.3, 129.0, 128.1, 128.1, 126.9, 125.9, 60.7, 57.6, 46.2, 34.7, 31.2.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}BrNO$ $[M + H]^+$ 372.0958, found 372.0956.

3-Bromo-1-(4-bromophenyl)-3-cyclopentylazetidin-2-one (E85)



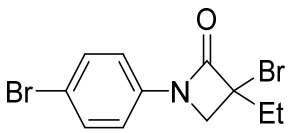
According to **general procedure SM-D** with 2-cyclopentylacrylic acid (0.70 g, 5.0 mmol, 1.0 equiv.) and 4-bromoaniline (0.95 g, 5.5 mmol, 1.1 equiv.) to afford **E85** as a white solid (1.31 g, 70% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.25 – 7.20 (m, 2H), 3.94 (d, *J* = 6.4 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 1H), 2.58 – 2.42 (m, 1H), 2.06 – 1.93 (m, 1H), 1.91 – 1.80 (m, 1H), 1.79 – 1.61 (m, 4H), 1.56 – 1.44 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 136.5, 132.3, 118.2, 117.4, 66.6, 54.3, 45.6, 29.3, 29.1, 25.7, 25.6.
HRMS (ESI) *m/z* calcd. for $C_{14}H_{16}Br_2NO$ $[M + H]^+$ 371.9593, found 371.9596.

3-Bromo-1-(4-bromophenyl)-3-isopropylazetidin-2-one (E86)



According to **general procedure SM-D** with 3-methyl-2-methylenebutanoic acid (0.57 g, 5.0 mmol, 1.0 equiv.) and 4-bromoaniline (0.95 g, 5.5 mmol, 1.1 equiv.) to afford **E86** as a white solid (1.28 g, 74% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.28 – 7.22 (m, 2H), 3.91 (d, *J* = 6.8 Hz, 1H), 3.90 (d, *J* = 6.8 Hz, 1H)，2.20 – 2.10 (m, 1H), 1.19 (d, *J* = 6.5 Hz, 3H), 1.08 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 136.5, 132.3, 118.2, 117.4, 69.4, 54.2, 34.5, 18.6, 18.5.
HRMS (ESI) *m/z* calcd. for $C_{12}H_{14}Br_2NO$ $[M + H]^+$ 345.9437, found 345.9438.

3-Bromo-1-(4-bromophenyl)-3-ethylazetidin-2-one (E87)

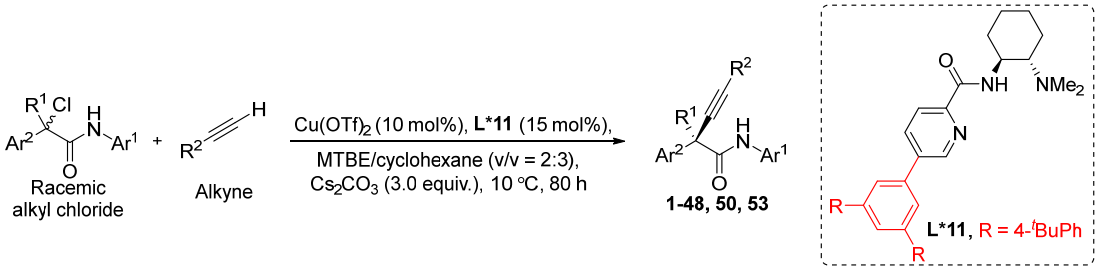


According to **general procedure SM-D** with 2-methylenebutanoic acid (0.50 g, 5.0

mmol, 1.0 equiv.) and 4-bromoaniline (0.95 g, 5.5 mmol, 1.1 equiv.) to afford **E87** as a white solid (1.33 g, 80% yield over three steps).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.30 – 7.24 (m, 2H), 3.98 (d, *J* = 6.4 Hz, 1H), 3.93 (d, *J* = 6.4 Hz, 1H), 2.27 – 2.10 (m, 2H), 1.19 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 136.5, 132.3, 118.2, 117.4, 63.4, 55.0, 30.7, 10.1.
HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}Br_2NO$ $[M + H]^+$ 331.9280, found 331.9281.

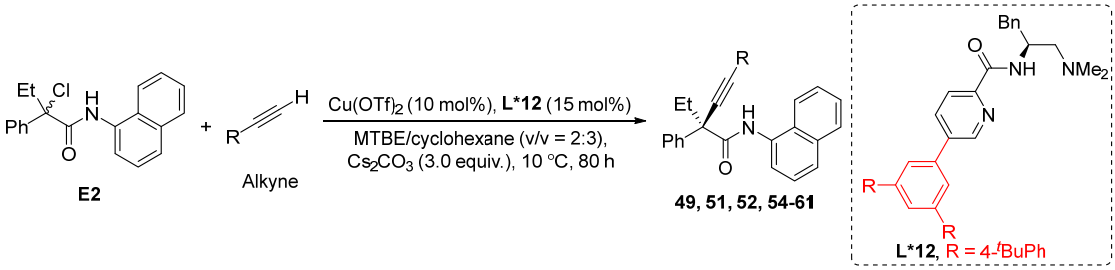
Enantioconvergent cross-coupling of tertiary electrophiles with alkynes

General procedure A: Substrate scope of α-aminocarbonyl-α-aryl alkyl chlorides and alkynes (Table 2, 1–48, 50 and 53)



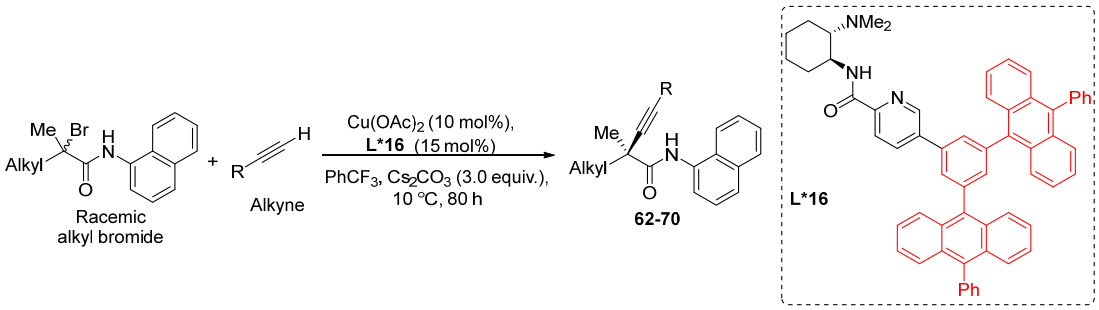
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OTf)_2$ (3.6 mg, 0.010 mmol, 10 mol%), **L*11** (8.8 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and MTBE/cyclohexane (v/v = 2/3, 2.0 mL). Then, alkyl halide (0.10 mmol, 1.0 equiv.) and alkyne (0.15 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 10 °C for 80 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure B: Substrate scope of alkynes (Table 2, 49, 51, 52, 54–61)



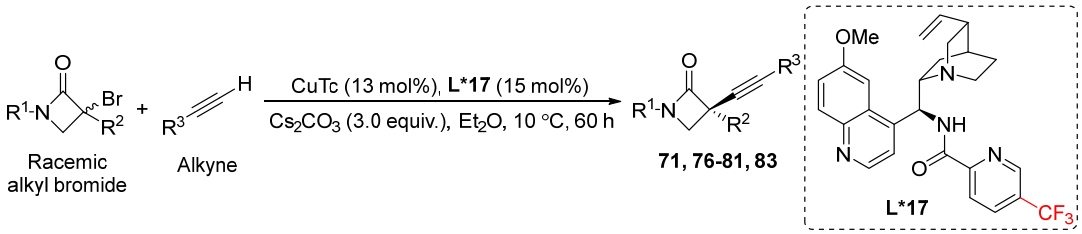
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OTf)_2$ (3.6 mg, 0.010 mmol, 10 mol%), **L*12** (9.4 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and MTBE/cyclohexane (v/v = 2/3, 2.0 mL). Then, alkyl halide (0.10 mmol, 1.0 equiv.) and alkyne (0.15 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 10 °C for 80 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure C: Substrate scope of racemic tertiary alkyl halides. (Table 3, 62–70)



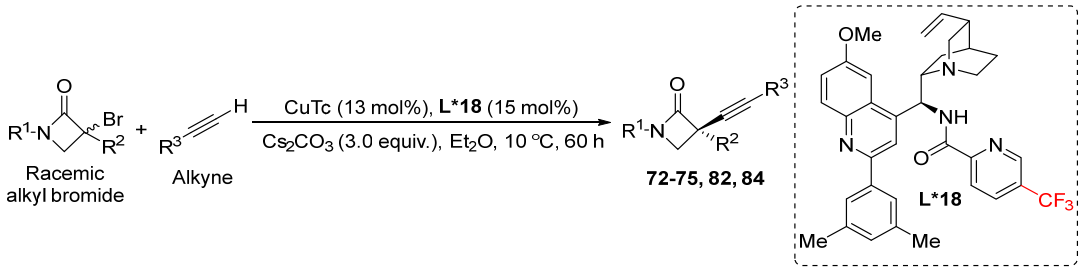
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (1.8 mg, 0.010 mmol, 10 mol%), **L*16** (12.4 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and CF_3Ph (2.0 mL). Then, alkyl halide (0.10 mmol, 1.0 equiv.) and alkyne (0.15 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 10 °C for 80 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure D: Substrate scope of racemic *α*-bromo-*β*-lactams. (Table 4, 71, 76–81, and 83)



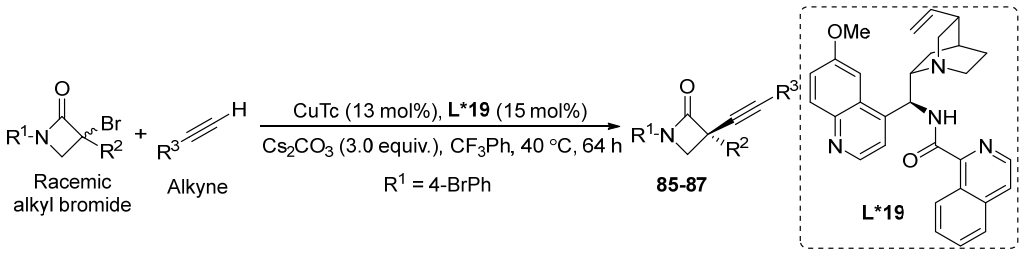
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (2.5 mg, 0.013 mmol, 10 mol%), **L*17** (7.4 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and Et_2O (2.0 mL). Then, alkyl halide (0.10 mmol, 1.0 equiv.) and alkyne (0.12 mmol, 1.2 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 10 °C for 60 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure E: Substrate scope of racemic *α*-bromo-*β*-lactams. (Table 4, 72–75, 82, and 84)



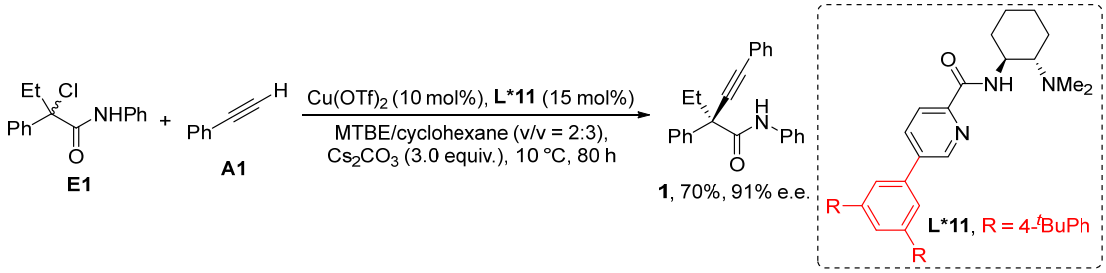
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (2.5 mg, 0.013 mmol, 10 mol%), **L*18** (9.0 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and Et_2O (2.0 mL). Then, alkyl halide (0.10 mmol, 1.0 equiv.) and alkyne (0.12 mmol, 1.2 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 10 °C for 60 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure F: Substrate scope of racemic *α*-bromo-*β*-lactams. (Table 4, 85–87)



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (2.5 mg, 0.013 mmol, 10 mol%), **L*19** (7.2 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and CF_3Ph (2.0 mL). Then, alkyl halide (0.10 mmol, 1.0 equiv.) and alkyne (0.12 mmol, 1.2 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 40 °C for 64 h. Upon completion, the mixture was then allowed to cool to room temperature, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

The procedure for the large-scale reaction (Table 2, 1)

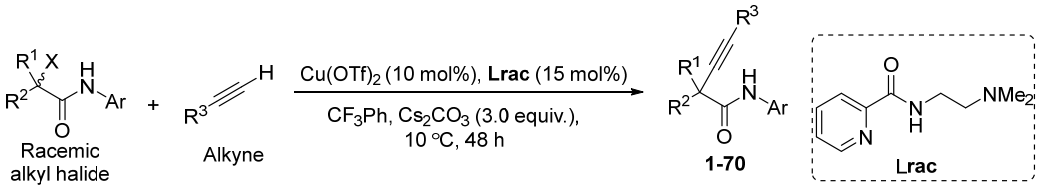


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OTf)_2$ (72.3 mg, 0.20 mmol, 10 mol%), **L*11** (176.4 mg, 0.30 mmol, 15 mol%), Cs_2CO_3 (1.95 g, 6.0 mmol, 3.0 equiv.), and MTBE/cyclohexane (v/v = 2/3, 40 mL). Then, alkyl halide **E1** (547.5 mg, 2.0 mmol, 1.0 equiv.) and alkyne **A1** (329 μL, 3.0 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 10 °C for 80 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 40/1) to afford the desired product **1** as a slightly yellow solid (475.2 mg, 70% yield, 91% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 18.963 min, t_R (major) = 21.592 min.

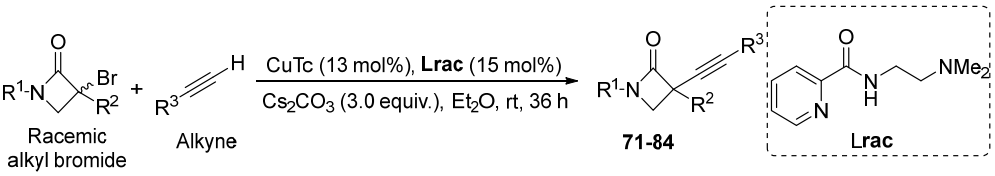
General procedure for the synthesis of racemates

General procedure G for the synthesis of racemates 1–70



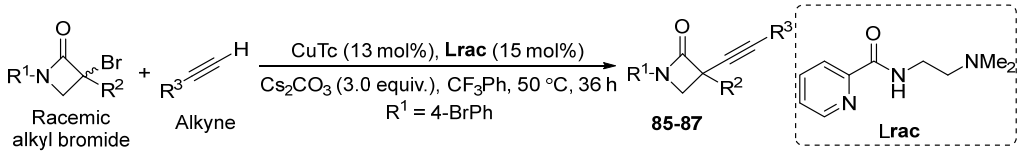
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OTf)_2$ (3.6 mg, 0.010 mmol, 10 mol%), **Lrac** (2.9 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and CF_3Ph (2.0 mL). Then, alkyl halide (0.10 mmol, 1.0 equiv.) and alkyne (0.15 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 10 °C for 48 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure H for the synthesis of racemates 71–84



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (2.5 mg, 0.013 mmol, 10 mol%), **Lrac** (2.9 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and Et_2O (2.0 mL). Then, alkyl halide (0.10 mmol, 1.0 equiv.) and alkyne (0.12 mmol, 1.2 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for 36 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure I for the synthesis of racemates 85–87

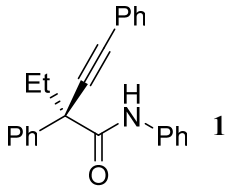


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuTc (2.5 mg, 0.013 mmol, 10 mol%), **Lrac** (2.9 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and CF_3Ph (2.0 mL). Then, alkyl halide (0.10 mmol, 1.0 equiv.) and alkyne (0.12 mmol, 1.2 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 50 °C for 36 h. Upon completion, the mixture was then allowed to cool to room temperature,

the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Analytical data for products 1–87

(*S*)-2-Ethyl-*N*,2,4-triphenylbut-3-ynamide (1)



1

According to the **general procedure A**, substrate **E1** (27.4 mg, 0.10 mmol) was employed to yield the product **1** as a slightly yellow solid (24.8 mg, 73% yield, 91% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 24.71 min, t_R (major) = 28.34 min.

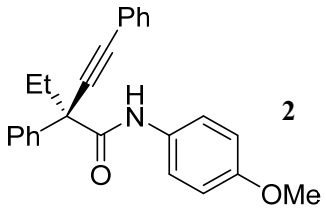
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.83 – 7.74 (m, 2H), 7.64 – 7.56 (m, 2H), 7.55 – 7.48 (m, 2H), 7.44 – 7.35 (m, 5H), 7.34 – 7.27 (m, 3H), 7.14 – 7.05 (m, 1H), 2.53 (dq, *J* = 13.5, 7.3 Hz, 1H), 2.19 (dq, *J* = 13.5, 7.3 Hz, 1H), 1.08 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 139.8, 137.7, 131.7, 129.0, 128.9, 128.6, 128.5, 127.66, 126.62, 124.4, 122.2, 119.7, 89.9, 88.7, 55.3, 33.3, 10.2.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{22}NO$ $[M + H]^+$ 340.1696, found 340.1691.

$[\alpha]_D^{27}$ = +50.0 (*c* 0.50, CH_2Cl_2).

(*S*)-2-Ethyl-*N*-(4-methoxyphenyl)-2,4-diphenylbut-3-ynamide (2)



2

According to the **general procedure A**, substrate **E11** (30.4 mg, 0.10 mmol) was employed to yield the product **2** as a white solid (20.0 mg, 54% yield, 91% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 0.60 mL/min, λ = 254 nm), t_R (major) = 18.37 min, t_R (minor) = 21.05 min.

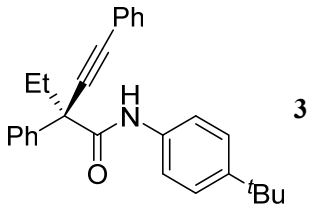
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.85 – 7.71 (m, 2H), 7.67 – 7.51 (m, 2H), 7.49 – 7.34 (m, 7H), 7.34 – 7.28 (m, 1H), 6.89 – 6.79 (m, 2H), 3.77 (s, 3H), 2.51 (dq, *J* = 13.3, 7.1 Hz, 1H), 2.19 (dq, *J* = 13.3, 7.1 Hz, 1H), 1.08 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 156.5, 139.9, 131.7, 130.8, 128.9, 128.6, 128.5, 127.6, 126.6, 122.2, 121.5, 114.1, 89.8, 88.9, 55.5, 55.1, 33.3, 10.2.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{24}NO_2$ $[M + H]^+$ 370.1802, found 370.1795.

$[\alpha]_D^{27}$ = +45.0 (*c* 1.00, CH_2Cl_2).

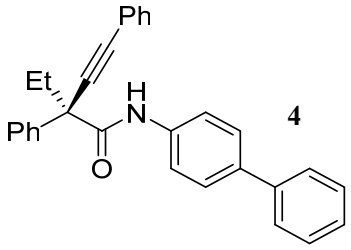
(*S*)-*N*-(4-(tert-Butyl)phenyl)-2-ethyl-2,4-diphenylbut-3-ynamide (3)



3

According to the **general procedure A**, substrate **E3** (33.0 mg, 0.10 mmol) was employed to yield the product **3** as a colorless oil (20.6 mg, 52% yield, 92% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 33.33 min, t_R (major) = 50.27 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.86 – 7.72 (m, 2H), 7.63 – 7.54 (m, 2H), 7.48 – 7.27 (m, 10H), 2.53 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.19 (dq, *J* = 13.2, 7.3 Hz, 1H), 1.29 (s, 9H), 1.08 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 147.4, 139.9, 135.1, 131.7, 128.9, 128.6, 128.5, 127.6, 126.6, 125.7, 122.2, 119.4, 89.7, 88.9, 55.2, 34.3, 33.3, 31.3, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{30}NO$ $[M + H]^+$ 396.2322, found 396.2315.
$[\alpha]_D^{27}$ = +46.0 (*c* 1.00, CH_2Cl_2).

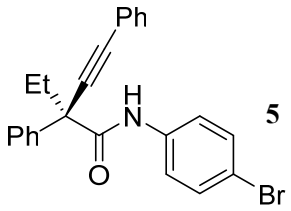
(*S*)-*N*-([1,1'-Biphenyl]-4-yl)-2-ethyl-2,4-diphenylbut-3-ynamide (4)



4

According to the **general procedure A**, substrate **E4** (35.0 mg, 0.10 mmol) was employed to yield the product **4** as a slightly yellow solid (26.2 mg, 63% yield, 91% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 33.37 min, t_R (minor) = 36.15 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.85 – 7.76 (m, 2H), 7.68 – 7.49 (m, 8H), 7.47 – 7.35 (m, 7H), 7.35 – 7.29 (m, 2H), 2.55 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.21 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.10 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 140.5, 139.8, 137.4, 137.0, 131.8, 129.0, 128.8, 128.64, 128.61, 127.7, 127.6, 127.1, 126.9, 126.7, 122.2, 120.0, 90.0, 88.8, 55.4, 33.4, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{26}NO$ $[M + H]^+$ 416.2009, found 416.2003.
$[\alpha]_D^{27}$ = +28.0 (*c* 1.00, CH_2Cl_2).

(*S*)-*N*-(4-Bromophenyl)-2-ethyl-2,4-diphenylbut-3-ynamide (5)



5

According to the **general procedure A**, substrate **E5** (35.3 mg, 0.10 mmol) was employed to yield the product **5** as a slightly yellow solid (19.2 mg, 46% yield, 92% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 99/1, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 25.06 min, t_R (minor) = 26.41 min.

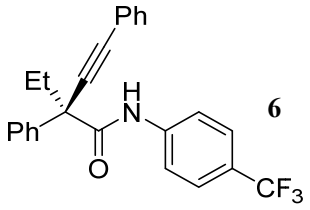
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.82 – 7.70 (m, 2H), 7.64 – 7.53 (m, 2H), 7.45 – 7.34 (m, 9H), 7.34 – 7.28 (m, 1H), 2.51 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.20 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.06 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 139.5, 136.8, 131.9, 131.8, 129.0, 128.62, 128.60, 127.8, 126.6, 122.1, 121.3, 117.0, 90.1, 88.5, 55.3, 33.3, 10.1.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{21}BrNO$ $[M + H]^+$ 418.0801, found 418.0794.

$[\alpha]_D^{27}$ = +48.8 (*c* 0.80, CH_2Cl_2).

(*S*)-2-Ethyl-2,4-diphenyl-*N*-(4-(trifluoromethyl)phenyl)but-3-ynamide (6)



6

According to the **general procedure A**, substrate **E6** (34.2 mg, 0.10 mmol) was employed to yield the product **6** as a white solid (15.9 mg, 39% yield, 94% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 21.37 min, t_R (major) = 23.86 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.82 – 7.72 (m, 2H), 7.67 – 7.51 (m, 6H), 7.46 – 7.36 (m, 5H), 7.35 – 7.29 (m, 1H), 2.52 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.20 (dq, *J* = 14.4, 7.3 Hz, 1H), 1.07 (t, *J* = 7.3 Hz, 3H).

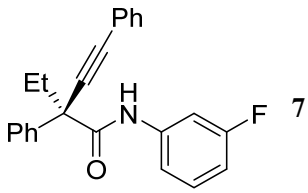
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 140.7, 139.4, 131.8, 129.1, 128.67, 128.65, 127.9, 126.6, 126.2 (q, *J* = 3.9 Hz), 124.0 (q, *J* = 271.5 Hz),122.0, 119.3, 90.2, 88.3, 55.4, 33.3, 10.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.15 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{25}H_{21}F_3NO$ $[M + H]^+$ 408.1570, found 408.1564.

$[\alpha]_D^{27}$ = +19.0 (*c* 1.00, CH_2Cl_2).

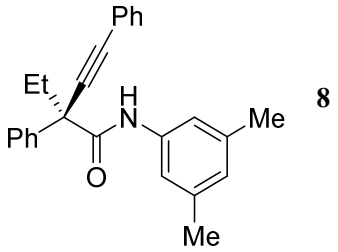
(*S*)-2-Ethyl-*N*-(3-fluorophenyl)-2,4-diphenylbut-3-ynamide (7)



7

According to the **general procedure A**, substrate **E7** (29.2 mg, 0.10 mmol) was employed to yield the product **7** as a slightly yellow oil (13.9 mg, 39% yield, 94% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 99/1, flow rate 0.30 mL/min, λ = 254 nm), t_R (minor) = 23.78 min, t_R (major) = 27.20 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.85 – 7.75 (m, 2H), 7.66 – 7.58 (m, 2H), 7.53 (dt, *J* = 10.9, 2.3 Hz, 1H), 7.48 – 7.39 (m, 5H), 7.37 – 7.31 (m, 1H), 7.27 – 7.21 (m, 1H), 7.13 (ddd, *J* = 8.3, 2.0, 0.9 Hz, 1H), 6.82 (tdd, *J* = 8.4, 2.6, 0.9 Hz, 1H), 2.54 (dq, *J* = 13.6, 7.2 Hz, 1H), 2.22 (dq, *J* = 13.5, 7.3 Hz, 1H), 1.10 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 163.0 (d, *J* = 245.1 Hz), 139.5, 139.2 (d, *J* = 10.6 Hz), 131.8, 130.0 (d, *J* = 9.5 Hz), 129.0, 128.6, 127.8, 126.6, 122.0, 114.9 (d, *J* = 3.0 Hz), 111.1 (d, *J* = 21.2 Hz), 107.2 (d, *J* = 26.3 Hz), 90.1, 88.4, 55.3, 33.3, 10.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ −111.39 (s, 1F).
HRMS (ESI) *m/z* calcd. for $C_{24}H_{21}FNO$ $[M + H]^+$ 358.1602, found 358.1595.
$[\alpha]_D^{27}$ = +33.0 (*c* 1.00, CH_2Cl_2).

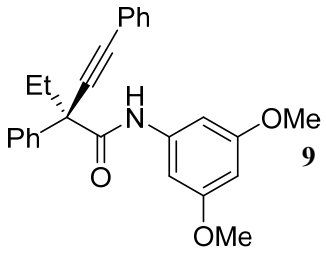
(*S*)-*N*-(3,5-Dimethylphenyl)-2-ethyl-2,4-diphenylbut-3-ynamide (8)



8

According to the **general procedure A**, substrate **E8** (30.2 mg, 0.10 mmol) was employed to yield the product **8** as a colorless oil (23.2 mg, 63% yield, 91% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 99/1, flow rate 0.30 mL/min, λ = 254 nm), t_R (minor) = 21.76 min, t_R (major) = 25.79 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.84 – 7.73 (m, 2H), 7.64 – 7.55 (m, 2H), 7.45 – 7.34 (m, 5H), 7.34 – 7.27 (m, 1H), 7.16 (s, 2H), 6.74 (s, 1H), 2.53 (dq, *J* = 13.7, 7.4 Hz, 1H), 2.28 (s, 6H), 2.19 (dq, *J* = 13.7, 7.4 Hz, 1H), 1.08 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 139.9, 138.7, 137.5, 131.8, 128.9, 128.6, 128.5, 127.6, 126.6, 126.1, 122.3, 117.4, 89.8, 88.8, 55.2, 33.3, 21.3, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{26}NO$ $[M + H]^+$ 368.2009, found 368.2002.
$[\alpha]_D^{27}$ = +62.0 (*c* 1.00, CH_2Cl_2).

(*S*)-*N*-(3,5-Dimethoxyphenyl)-2-ethyl-2,4-diphenylbut-3-ynamide (9)



9

According to the **general procedure A**, substrate **E9** (33.4 mg, 0.10 mmol) was employed to yield the product **9** as a slightly yellow solid (17.2 mg, 43% yield, 93% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 96/4, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 14.39 min, t_R (minor) = 24.76 min.

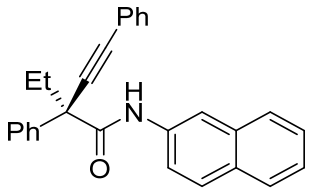
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.83 – 7.69 (m, 2H), 7.63 – 7.53 (m, 2H), 7.44 – 7.34 (m, 5H), 7.33 – 7.28 (m, 1H), 6.76 (d, *J* = 2.2 Hz, 2H), 6.22 (t, *J* = 2.2 Hz, 1H), 3.76 (s, 6H), 2.52 (dq, *J* = 13.1, 7.2 Hz, 1H), 2.19 (dq, *J* = 13.4, 7.3 Hz, 1H), 1.07 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 161.0, 139.7, 139.5, 131.7, 128.9, 128.59, 128.57, 127.7, 126.6, 122.1, 97.8, 96.9, 90.0, 88.6, 55.4, 33.2, 10.2.

HRMS (ESI) *m/z* calcd. for $C_{26}H_{26}NO_3$ $[M + H]^+$ 400.1907, found 400.1900.

$[\alpha]_D^{27}$ = +31.0 (*c* 1.00, CH_2Cl_2).

(*S*)-2-Ethyl-*N*-(naphthalen-2-yl)-2,4-diphenylbut-3-ynamide (10)



10

According to the **general procedure A**, substrate **E10** (32.4 mg, 0.10 mmol) was employed to yield the product **10** as a slightly yellow solid (28.8 mg, 74% yield, 86% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 19.15 min, t_R (minor) = 26.21 min.

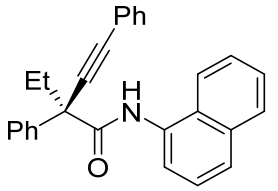
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.26 (s, 1H), 7.86 – 7.80 (m, 2H), 7.80 – 7.72 (m, 3H), 7.67 – 7.58 (m, 2H), 7.48 – 7.35 (m, 8H), 7.35 – 7.28 (m, 1H), 2.58 (dq, *J* = 14.3, 7.3 Hz, 1H), 2.24 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.11 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 139.8, 135.1, 133.8, 131.8, 130.7, 129.0, 128.7, 128.62, 128.58, 127.71, 127.65, 127.5, 126.7, 126.5, 125.0, 122.2, 119.6, 116.5, 90.0, 88.7, 55.4, 33.4, 10.2.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{24}NO$ $[M + H]^+$ 390.1852, found 390.1845.

$[\alpha]_D^{27}$ = +65.0 (*c* 1.00, CH_2Cl_2).

(*S*)-2-Ethyl-*N*-(naphthalen-1-yl)-2,4-diphenylbut-3-ynamide (11)



11

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **11** as a colorless oil (32.0 mg, 82% yield, 93% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 214 nm), t_R (major) = 24.62 min, t_R (minor) = 29.46 min.

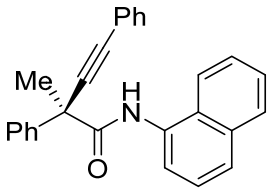
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.90 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.85 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.71 – 7.64 (m, 3H), 7.51 – 7.31 (m, 9H), 2.63 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.30 (dq, *J* = 13.6, 7.2 Hz, 1H), 1.16 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 139.9, 134.0, 132.1, 131.8, 129.0, 128.8, 128.6, 128.6, 127.7, 126.7, 126.6, 126.3, 125.9, 125.8, 125.4, 122.1, 120.0, 119.5, 90.2, 89.2, 55.6, 33.2, 10.2.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{24}NO$ $[M + H]^+$ 390.1852, found 390.1845.

$[\alpha]_D^{27}$ = –7.0 (*c* 1.00, CH_2Cl_2).

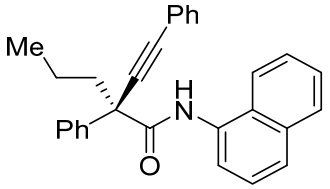
(*S*)-2-Methyl-*N*-(naphthalen-1-yl)-2,4-diphenylbut-3-ynamide (12)



12

According to the **general procedure A**, substrate **E12** (30.9 mg, 0.10 mmol) was employed to yield the product **12** as a colorless oil (31.2 mg, 83% yield, 93% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 27.82 min, t_R (minor) = 34.39 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.62 (m, 3H), 7.51 – 7.34 (m, 9H), 2.09 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 141.3, 134.0, 132.1, 131.7, 128.9, 128.79, 128.76, 128.6, 127.8, 126.7, 126.3, 126.2, 125.9, 125.7, 125.5, 122.1, 120.0, 119.6, 90.6, 88.3, 49.6, 27.4.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{22}NO$ $[M + H]^+$ 376.1696, found 376.1690.
$[\alpha]_D^{27}$ = +5.0 (*c* 1.00, CH_2Cl_2).

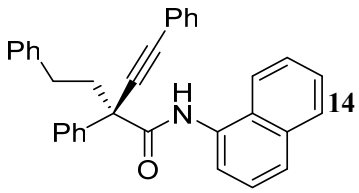
(*S*)-*N*-(Naphthalen-1-yl)-2-phenyl-2-(phenylethynyl)pentanamide (13)



13

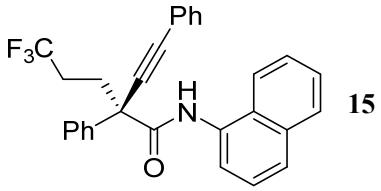
According to the **general procedure A**, substrate **E13** (33.8 mg, 0.10 mmol) was employed to yield the product **13** as a colorless oil (24.9 mg, 62% yield, 86% e.e.).
HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.06 min, t_R (minor) = 9.76 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.06 (d, *J* = 7.4 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.63 (m, 3H), 7.48 – 7.29 (m, 9H), 2.54 (ddd, *J* = 13.2, 11.8, 4.8 Hz, 1H), 2.20 (ddd, *J* = 13.2, 12.0, 4.8 Hz, 1H), 1.70 – 1.49 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 140.2, 134.0, 132.2, 131.8, 129.0, 128.8, 128.7, 128.6, 127.7, 126.7, 126.6, 126.3, 125.9, 125.8, 125.4, 122.2, 120.0, 119.5, 90.2, 89.5, 54.9, 42.1, 19.3, 14.2.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{26}NO$ $[M + H]^+$ 404.2009, found 404.2003.
$[\alpha]_D^{27}$ = –3.0 (*c* 1.00, CH_2Cl_2).

(*S*)-*N*-(Naphthalen-1-yl)-2-phenethyl-2,4-diphenylbut-3-ynamide (14)



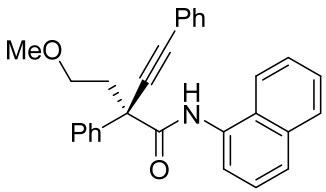
According to the **general procedure A**, substrate **E14** (40.0 mg, 0.10 mmol) was employed to yield the product **14** as a yellow oil (28.9 mg, 62% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.81 min, t_R (minor) = 25.47 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.48 – 7.40 (m, 7H), 7.39 – 7.32 (m, 2H), 7.29 – 7.23 (m, 4H), 7.18 – 7.13 (m, 1H), 2.98 – 2.83 (m, 3H), 2.55 – 2.44 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 141.6, 139.8, 134.0, 132.1, 131.8, 129.1, 128.9, 128.8, 128.7, 128.5, 128.3, 127.9, 126.7, 126.6, 126.3, 125.9, 125.8, 125.5, 122.0, 120.0, 119.6, 90.6, 89.0, 54.7, 41.9, 32.4.
HRMS (ESI) *m/z* calcd. for $C_{34}H_{28}NO$ $[M + H]^+$ 466.2165, found 466.2160.
$[\alpha]_D^{27}$ = –1.5 (*c* 1.00, CH_2Cl_2).

(*S*)-5,5,5-Trifluoro-*N*-(naphthalen-1-yl)-2-phenyl-2-(phenylethynyl)pentanamide (15)



According to the **general procedure A**, substrate **E15** (39.2 mg, 0.10 mmol) was employed to yield the product **15** as a colorless oil (33.7 mg, 74% yield, 89% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 18.82 min, t_R (minor) = 22.30 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.99 (d, *J* = 7.4 Hz, 1H), 7.88 – 7.83 (m, 3H), 7.69 – 7.62 (m, 4H), 7.49 – 7.42 (m, 7H), 7.41 – 7.34 (m, 2H), 2.83 – 2.72 (m, 1H), 2.54 – 2.41 (m, 2H), 2.29 – 2.18 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 138.8, 134.0, 131.9, 131.8, 129.4, 129.1, 128.9, 128.8, 128.4, 126.8, 126.42, 126.39, 126.0, 125.9, 125.7, 121.5, 119.92, 119.88, 90.9, 87.5, 53.5, 32.3 (q, *J* = 2.8 Hz), 30.8 (q, *J* = 29.1 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ –66.03 (s, 3F).
HRMS (ESI) *m/z* calcd. for $C_{29}H_{23}F_3NO$ $[M + H]^+$ 458.1726, found 458.1717.
$[\alpha]_D^{27}$ = +4.9 (*c* 1.00, CH_2Cl_2).

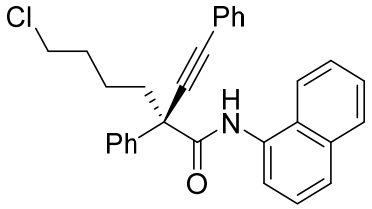
(*S*)-2-(2-Methoxyethyl)-*N*-(naphthalen-1-yl)-2,4-diphenylbut-3-ynamide (16)



16

According to the **general procedure A**, substrate **E16** (35.4 mg, 0.10 mmol) was employed to yield the product **16** as a yellow oil (32.0 mg, 76% yield, 91% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 10.16 min, t_R (minor) = 31.59 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.01 (d, *J* = 7.4 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.63 (m, 3H), 7.47 – 7.38 (m, 7H), 7.37 – 7.31 (m, 2H), 3.77 (td, *J* = 9.2, 6.7 Hz, 1H), 3.60 (td, *J* = 9.2, 4.6 Hz, 1H), 3.32 (s, 3H), 2.99 (ddd, *J* = 13.4, 8.8, 6.7 Hz, 1H), 2.46 (ddd, *J* = 13.4, 8.7, 4.6 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 139.8, 133.9, 132.1, 131.7, 129.1, 128.8, 128.7, 128.6, 127.9, 126.7, 126.5, 126.2, 125.8, 125.7, 125.5, 121.9, 120.0, 119.6, 90.4, 88.5, 70.0, 58.7, 52.4, 38.7.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{26}NO_2$ $[M + H]^+$ 420.1958, found 420.1950.
$[\alpha]_D^{27}$ = +5.0 (*c* 1.00, CH_2Cl_2).

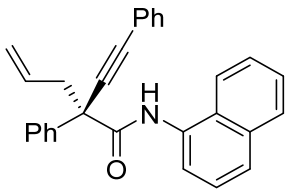
(*S*)-6-Chloro-*N*-(naphthalen-1-yl)-2-phenyl-2-(phenylethynyl)hexanamide (17)



17

According to the **general procedure A**, substrate **E17** (38.6 mg, 0.10 mmol) was employed to yield the product **17** as a slightly yellow oil (29.8 mg, 66% yield, 89% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 33.53 min, t_R (minor) = 35.15 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.64 (m, 3H), 7.50 – 7.32 (m, 9H), 3.55 (t, *J* = 6.6 Hz, 2H), 2.63 – 2.52 (m, 1H), 2.30 – 2.19 (m, 1H), 1.96 – 1.63 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 139.8, 134.0, 132.0, 131.8, 129.1, 128.8, 128.7, 128.6, 127.8, 126.7, 126.5, 126.3, 125.9, 125.7, 125.5, 122.0, 120.0, 119.6, 90.4, 88.9, 54.7, 44.7, 39.1, 32.5, 23.3.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{27}ClNO$ $[M + H]^+$ 452.1776, found 452.1777.
$[\alpha]_D^{27}$ = +3.0 (*c* 1.00, CH_2Cl_2).

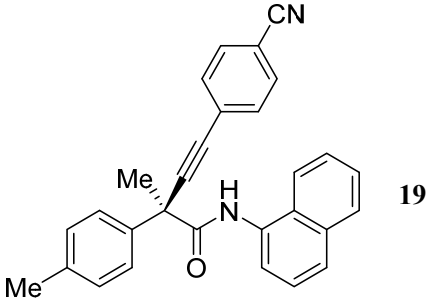
(*S*)-*N*-(Naphthalen-1-yl)-2-phenyl-2-(phenylethynyl)pent-4-enamide (18)



18

According to the **general procedure A**, substrate **E18** (33.6 mg, 0.10 mmol) was employed to yield the product **18** as a slightly yellow oil (26.1 mg, 65% yield, 92% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 22.78 min, t_R (minor) = 26.55 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.03 (d, *J* = 7.4 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.68 – 7.61 (m, 3H), 7.47 – 7.39 (m, 7H), 7.39 – 7.31 (m, 2H), 5.94 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.28 – 5.20 (m, 1H), 5.18 – 5.12 (m, 1H), 3.32 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.99 (dd, *J* = 13.6, 7.1 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 139.5, 134.0, 133.5, 132.0, 131.8, 129.0, 128.8, 128.7, 128.6, 127.8, 126.8, 126.7, 126.3, 125.9, 125.8, 125.5, 122.1, 120.0, 119.6, 119.1, 90.7, 88.9, 54.5, 44.3.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{24}NO$ $[M + H]^+$ 402.1852, found 402.1845.
$[\alpha]_D^{27}$ = +2.0 (*c* 1.00, CH_2Cl_2).

(*S*)-4-(4-Cyanophenyl)-2-methyl-*N*-(naphthalen-1-yl)-2-(*p*-tolyl)but-3-ynamide (19)

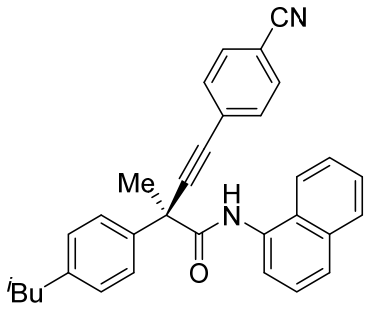


19

According to the **general procedure A**, substrate **E19** (32.4 mg, 0.10 mmol) was employed to yield the product **19** as a yellow oil (26.0 mg, 63% yield, 94% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 14.74 min, t_R (minor) = 19.27 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.65 (m, 7H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.28 – 7.23 (m, 2H), 2.38 (s, 3H), 2.04 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 137.9, 137.8, 134.0, 132.3, 132.2, 132.0, 129.7, 128.9, 127.1, 126.8, 126.3, 126.1, 125.9, 125.8, 125.7, 120.0, 119.8, 118.2, 112.3, 95.3, 86.0, 49.4, 27.2, 21.0.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{23}N_2O$ $[M + H]^+$ 415.1805, found 415.1797.
$[\alpha]_D^{27}$ = +2.2 (*c* 1.00, CH_2Cl_2).

(*S*)-4-(4-Cyanophenyl)-2-(4-*iso*butylphenyl)-2-methyl-*N*-(naphthalen-1-yl)but-3-

ynamide (20)



20

According to the **general procedure A**, substrate **E20** (36.6 mg, 0.10 mmol) was employed to yield the product **20** as a slightly yellow solid (24.1 mg, 53% yield, 91% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.09 min, t_R (minor) = 13.69 min.

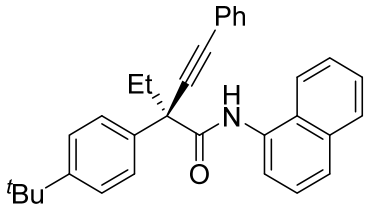
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.65 (m, 7H), 7.51 – 7.43 (m, 3H), 7.36 – 7.31 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 2.51 (d, *J* = 7.2 Hz, 2H), 2.05 (s, 3H), 1.93 – 1.84 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 141.8, 138.0, 134.0, 132.3, 132.2, 131.9, 129.8, 128.9, 127.2, 126.8, 126.3, 126.0, 125.9, 125.8, 125.7, 119.9, 119.7, 118.2, 112.3, 95.3, 85.9, 49.4, 44.9, 30.2, 27.1, 22.4.

HRMS (ESI) *m/z* calcd. for $C_{32}H_{29}N_2O$ $[M + H]^+$ 457.2274, found 457.2265.

$[\alpha]_D^{27}$ = +5.0 (*c* 1.00, CH_2Cl_2).

(*S*)-2-(4-(*tert*-Butyl)phenyl)-2-ethyl-*N*-(naphthalen-1-yl)-4-phenylbut-3-ynamide (21)



21

According to the **general procedure A**, substrate **E21** (38.0 mg, 0.10 mmol) was employed to yield the product **21** as a slightly yellow oil (30.2 mg, 68% yield, 82% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 11.81 min, t_R (minor) = 13.40 min.

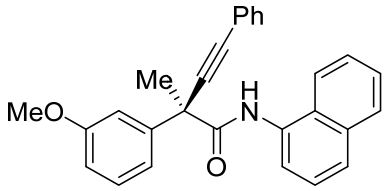
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.68 – 7.62 (m, 3H), 7.48 – 7.40 (m, 7H), 7.39 – 7.34 (m, 1H), 2.61 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.24 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.33 (s, 9H), 1.15 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 150.6, 136.9, 134.0, 132.2, 131.8, 128.9, 128.8, 128.6, 126.6, 126.4, 126.2, 125.9, 125.8, 125.6, 125.3, 122.3, 120.0, 119.3, 89.9, 89.5, 55.2, 34.5, 33.0, 31.3, 10.3.

HRMS (ESI) *m/z* calcd. for $C_{32}H_{32}NO$ $[M + H]^+$ 446.2478, found 446.2470.

$[\alpha]_D^{27}$ = –10.0 (*c* 0.80, CH_2Cl_2).

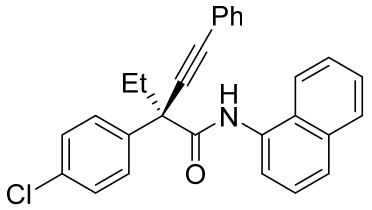
(*S*)-2-(3-Methoxyphenyl)-2-methyl-*N*-(naphthalen-1-yl)-4-phenylbut-3-ynamide (22)



22

According to the **general procedure A**, substrate **E22** (34.0 mg, 0.10 mmol) was employed to yield the product **22** as a yellow oil (19.3 mg, 48% yield, 94% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 32.39 min, t_R (minor) = 35.96 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.64 – 7.60 (m, 2H), 7.49 – 7.39 (m, 7H), 7.38 – 7.32 (m, 2H), 6.92 – 6.85 (m, 1H), 3.84 (s, 3H), 2.05 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 159.9, 143.0, 134.0, 132.2, 131.8, 129.8, 128.9, 128.8, 128.6, 126.8, 126.3, 125.9, 125.8, 125.5, 122.2, 120.1, 119.7, 118.6, 113.0, 112.5, 90.5, 88.2, 55.3, 49.6, 27.4.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{24}NO_2$ $[M + H]^+$ 406.1802, found 406.1794.
$[\alpha]_D^{27}$ = –6.4 (*c* 1.00, CH_2Cl_2).

(*S*)-2-(4-Chlorophenyl)-2-methyl-*N*-(naphthalen-1-yl)-4-phenylbut-3-ynamide (23)

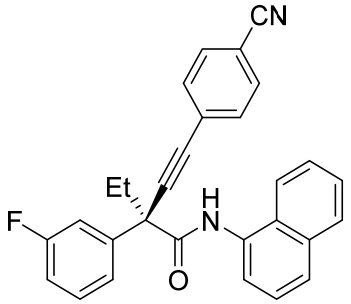


23

According to the **general procedure A**, substrate **E23** (35.8 mg, 0.10 mmol) was employed to yield the product **23** as a white solid (23.2 mg, 55% yield, 87% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 26.46 min, t_R (minor) = 39.66 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.88 – 7.80 (m, 3H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.63 (m, 3H), 7.50 – 7.35 (m, 8H), 2.57 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.24 (dq, *J* = 14.5, 7.4 Hz, 1H), 1.14 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 138.4, 134.0, 133.7, 132.0, 131.8, 129.2, 128.9, 128.70, 128.68, 128.2, 126.7, 126.4, 125.9, 125.8, 125.6, 121.9, 119.9, 119.6, 90.8, 88.6, 55.2, 33.5, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{23}ClNO$ $[M + H]^+$ 424.1463, found 424.1463.
$[\alpha]_D^{27}$ = –5.4 (*c* 0.50, CH_2Cl_2).

(*S*)-4-(4-Cyanophenyl)-2-ethyl-2-(3-fluorophenyl)-*N*-(naphthalen-1-yl)but-3-

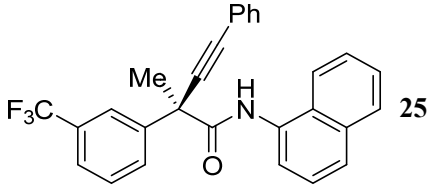
ynamide (24)



24

According to the **general procedure A**, substrate **E24** (34.2 mg, 0.10 mmol) was employed to yield the product **24** as a yellow oil (24.5 mg, 57% yield, 89% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 16.59 min, t_R (minor) = 19.17 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.78 – 7.68 (m, 5H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 – 7.37 (m, 2H), 7.10 – 7.03 (m, 1H), 2.59 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.27 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.13 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 162.9 (d, *J* = 246.5 Hz), 141.8 (d, *J* = 7.2 Hz), 134.0, 132.4, 131.7, 130.3 (d, *J* = 8.1 Hz), 129.0, 126.8, 126.6, 126.5, 126.0, 125.9, 125.8, 122.2 (d, *J* = 2.9 Hz), 120.1, 119.7, 118.1, 115.0 (d, *J* = 21.1 Hz), 114.0 (d, *J* = 23.3 Hz), 112.7, 93.0, 88.6, 55.4, 33.2, 10.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ −111.75 (s, 1F).
HRMS (ESI) *m/z* calcd. for $C_{29}H_{22}FN_2O$ $[M + H]^+$ 433.1711, found 433.1703.
$[\alpha]_D^{27}$ = −6.0 (*c* 1.00, CH_2Cl_2).

(*S*)-2-Methyl-*N*-(naphthalen-1-yl)-4-phenyl-2-(3-(trifluoromethyl)phenyl)but-3-ynamide (25)

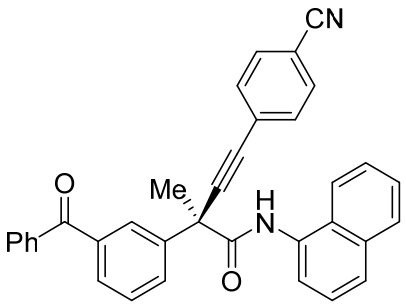


25

According to the **general procedure A**, substrate **E25** (37.8 mg, 0.10 mmol) was employed to yield the product **25** as a yellow oil (32.6 mg, 74% yield, 80% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 99/1, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 20.99 min, t_R (minor) = 25.53 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.17 (s, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.66 – 7.60 (m, 3H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.49 – 7.36 (m, 6H), 2.09 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 142.3, 134.0, 131.9, 131.8, 131.0 (q, *J* = 32.3 Hz), 129.9, 129.3, 129.2, 128.9, 128.7, 126.8, 126.4, 126.0, 125.8, 125.7, 124.7 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.6 Hz), 123.3 (q, *J* = 3.8 Hz), 121.7, 119.9, 119.8, 89.6, 89.3, 49.5, 27.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ −62.46 (s, 3F).

HRMS (ESI) *m/z* calcd. for $C_{28}H_{21}F_3NO$ $[M + H]^+$ 444.1570, found 444.1563.
$[\alpha]_D^{27}$ = –5.0 (*c* 1.00, CH_2Cl_2).

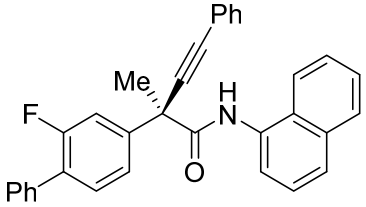
(*S*)-2-(3-Benzoylphenyl)-4-(4-cyanophenyl)-2-methyl-*N*-(naphthalen-1-yl)but-3-ynamide (26)



26

According to the **general procedure A**, substrate **E26** (41.4 mg, 0.10 mmol) was employed to yield the product **26** as a yellow solid (50.5 mg, 51% yield, 88% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 13.66 min, t_R (minor) = 15.62 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.34 (t, *J* = 1.7 Hz, 1H), 8.02 (ddd, *J* = 7.9, 1.9, 1.0 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.84 – 7.78 (m, 3H), 7.71 – 7.59 (m, 7H), 7.58 – 7.55 (m, 1H), 7.48 (d, *J* = 7.3 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.39 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 2.10 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 168.7, 141.2, 138.1, 137.3, 134.0, 132.6, 132.3, 132.3, 131.7, 130.2, 130.1, 129.8, 129.0, 128.9, 128.4, 127.9, 126.8, 126.6, 126.5, 126.1, 126.0, 125.7, 120.1, 119.7, 118.1, 112.6, 94.3, 87.1, 49.6, 27.3.
HRMS (ESI) *m/z* calcd. for $C_{35}H_{25}N_2O_2$ $[M + H]^+$ 505.1911, found 505.1902.
$[\alpha]_D^{27}$ = +13.2 (*c* 1.00, CH_2Cl_2).

(*S*)-2-(2-Fluoro-[1,1'-biphenyl]-4-yl)-2-methyl-*N*-(naphthalen-1-yl)-4-phenylbut-3-ynamide (27)

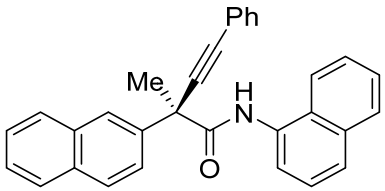


27

According to the **general procedure A**, substrate **E27** (40.4 mg, 0.10 mmol) was employed to yield the product **27** as a white solid (25.0 mg, 53% yield, 88% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 10.34 min, t_R (minor) = 12.85 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.67 – 7.64 (m, 3H), 7.58 – 7.54 (m, 2H), 7.52 – 7.35 (m, 10H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 159.7 (d, *J* = 248.5 Hz), 142.7 (d, *J* = 7.4 Hz), 135.3, 134.0, 132.0, 131.8, 130.9 (d, *J* = 3.9 Hz), 129.1 (d, *J* = 28.8 Hz), 129.0 (d, *J* = 2.9 Hz), 128.7, 128.5, 128.5, 128.4, 127.8, 126.6, 126.4, 126.0, 125.8, 125.7, 122.3 (d, *J* = 3.4 Hz), 121.8, 119.9, 119.6, 114.5 (d, *J* = 25.1 Hz), 89.9, 88.8, 49.3 (d, *J* = 1.4 Hz), 27.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ −116.71 (s, 1F).
HRMS (ESI) *m/z* calcd. for $C_{33}H_{25}FNO$ $[M + H]^+$ 470.1915, found 470.1907.
$[\alpha]_D^{27}$ = –23.0 (*c* 1.00, CH_2Cl_2).

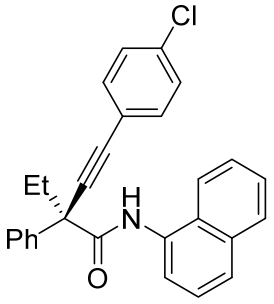
(*S*)-2-Methyl-*N*-(naphthalen-1-yl)-2-(naphthalen-2-yl)-4-phenylbut-3-ynamide (28)



28

According to the **general procedure A**, substrate **E28** (36.0 mg, 0.10 mmol) was employed to yield the product **28** as a yellow oil (24.3 mg, 57% yield, 82% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 10.39 min, t_R (minor) = 13.67 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.33 (s, 1H), 8.03 (d, *J* = 7.4 Hz, 1H), 7.95 – 7.89 (m, 3H), 7.87 – 7.81 (m, 2H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.69 – 7.64 (m, 3H), 7.53 – 7.41 (m, 7H), 7.37 – 7.31 (m, 1H), 2.15 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 138.7, 134.0, 133.3, 132.8, 132.1, 131.8, 129.0, 128.8, 128.6, 128.3, 127.6, 126.8, 126.4, 126.3, 125.9, 125.8, 125.6, 125.2, 124.3, 122.2, 120.1, 119.8, 90.6, 88.5, 49.8, 27.4.
HRMS (ESI) *m/z* calcd. for $C_{31}H_{24}NO$ $[M + H]^+$ 426.1852, found 426.1846.
$[\alpha]_D^{27}$ = +8.4 (*c* 0.50, CH_2Cl_2).

(*S*)-4-(4-Chlorophenyl)-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (29)

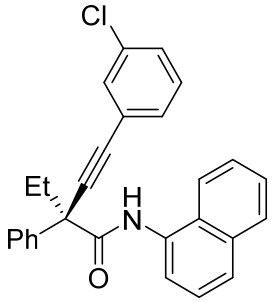


29

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **29** as a colorless oil (33.0 mg, 78% yield, 94% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 21.83 min, t_R (minor) = 28.34 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.92 – 7.81 (m, 3H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.53 – 7.31

(m, 8H), 2.62 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.29 (dq, *J* = 14.4, 7.3 Hz, 1H), 1.15 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 139.7, 135.1, 134.0, 133.0, 132.0, 129.0, 128.8, 128.7, 127.8, 126.7, 126.6, 126.3, 125.9, 125.8, 125.5, 120.6, 119.8, 119.6, 90.2, 88.9, 55.5, 33.1, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{23}ClNO$ $[M + H]^+$ 424.1463, found 424.1455.
$[\alpha]_D^{27}$ = –4.0 (*c* 1.00, CH_2Cl_2).

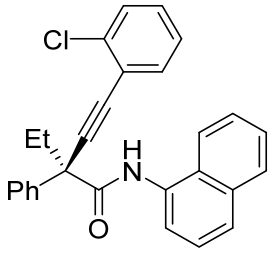
(*S*)-4-(3-Chlorophenyl)-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (30)



30

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **30** as a colorless oil (27.6 mg, 65% yield, 92% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 214 nm), t_R (major) = 23.73 min, t_R (minor) = 29.81 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.05 (d, *J* = 7.4 Hz, 1H), 7.90 – 7.82 (m, 3H), 7.75 – 7.63 (m, 3H), 7.57 – 7.52 (m, 1H), 7.51 – 7.39 (m, 6H), 7.39 – 7.32 (m, 2H), 2.62 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.29 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.14 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 139.6, 134.5, 134.0, 132.0, 131.6, 129.9, 129.3, 128.9, 128.7, 127.8, 126.7, 126.6, 126.3, 125.9, 125.8, 125.5, 123.8, 119.9, 119.7, 90.5, 88.6, 55.5, 33.1, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{23}ClNO$ $[M + H]^+$ 424.1463, found 424.1455.
$[\alpha]_D^{27}$ = –3.0 (*c* 1.00, CH_2Cl_2).

(*S*)-4-(2-Chlorophenyl)-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (31)

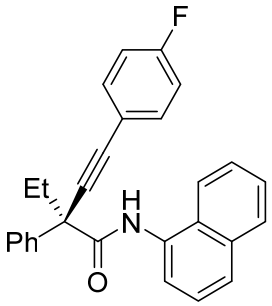


31

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **31** as a slightly yellow oil (22.5 mg, 53% yield, 91% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 214 nm), t_R (major) = 32.62 min, t_R (minor) = 38.23 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.02 – 7.88 (m, 3H), 7.84 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.55 – 7.28 (m, 9H), 2.65 (dq, *J* = 13.2, 7.2 Hz, 1H), 2.32 (dq, *J* = 13.5, 7.3 Hz, 1H), 1.19 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 139.7, 136.2, 134.0, 133.4, 132.2, 129.9, 129.4, 128.6, 127.7, 127.2, 126.8, 126.2, 125.9, 125.8, 125.6, 122.2, 120.6, 120.4, 94.5, 86.9, 55.6, 33.0, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{23}ClNO$ $[M + H]^+$ 424.1463, found 424.1455.
$[\alpha]_D^{27}$ = +1.2 (*c* 1.00, CH_2Cl_2).

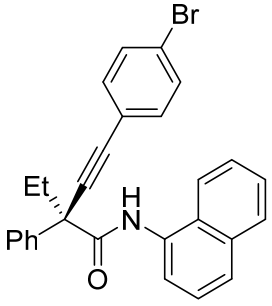
(*S*)-2-Ethyl-4-(4-fluorophenyl)-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (32)



32

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **32** as a slightly yellow oil (30.6 mg, 75% yield, 93% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 21.87 min, t_R (minor) = 27.08 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.93 – 7.79 (m, 3H), 7.76 – 7.59 (m, 4H), 7.52 – 7.29 (m, 6H), 7.13 (t, *J* = 8.5 Hz, 2H), 2.61 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.28 (dq, *J* = 14.4, 7.3 Hz, 1H), 1.14 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 162.9 (d, *J* = 250.5 Hz), 139.8, 134.0, 133.7 (d, *J* = 8.4 Hz), 132.1, 128.9, 128.7, 127.8, 126.68, 126.65, 126.3, 125.9, 125.8, 125.5, 119.9, 119.6, 118.3 (d, *J* = 3.6 Hz), 116.0 (d, *J* = 22.1 Hz), 89.02, 88.98 (d, *J* = 1.5 Hz), 55.5, 33.1, 10.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ −109.60 (s, 1F).
HRMS (ESI) *m/z* calcd. for $C_{28}H_{23}FNO$ $[M + H]^+$ 408.1758, found 408.1752.
$[\alpha]_D^{27}$ = −2.0 (*c* 1.00, CH_2Cl_2).

(*S*)-4-(4-Bromophenyl)-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (33)

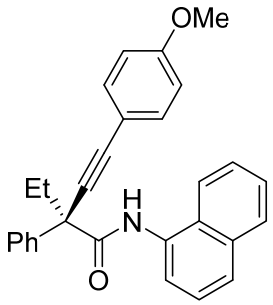


33

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **33** as a slightly yellow oil (40.2 mg, 86% yield, 94% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 22.92 min, t_R (minor) = 30.79 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.91 – 7.81 (m, 3H), 7.74 – 7.63 (m, 2H), 7.60 – 7.51 (m, 4H), 7.50 – 7.32 (m, 6H), 2.62 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.29 (dq, *J* = 14.3, 7.3 Hz, 1H), 1.15 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 139.6, 134.0, 133.1, 132.0, 131.9, 128.8, 128.7, 127.8, 126.7, 126.6, 126.3, 125.9, 125.8, 125.5, 123.3, 121.0, 119.8, 119.6, 90.4, 88.9, 55.6, 33.1, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{23}BrNO$ $[M + H]^+$ 468.0958, found 468.0952.
$[\alpha]_D^{27}$ = –5.0 (*c* 1.00, CH_2Cl_2).

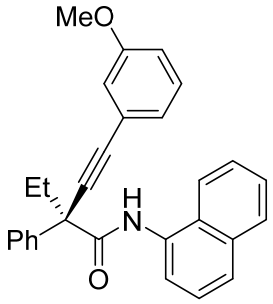
(*S*)-2-Ethyl-4-(4-methoxyphenyl)-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (34)



34

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **34** as a slightly yellow oil (35.2 mg, 84% yield, 91% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 18.44 min, t_R (minor) = 24.03 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.09 (dd, *J* = 7.6, 2.5 Hz, 1H), 7.97 – 7.87 (m, 2H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.52 – 7.31 (m, 6H), 6.99 – 6.93 (m, 2H), 3.87 (s, 3H), 2.62 (dq, *J* = 14.2, 7.4 Hz, 1H), 2.29 (dq, *J* = 14.2, 7.4 Hz, 1H), 1.16 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 160.1, 140.1, 133.9, 133.2, 132.2, 128.8, 128.5, 127.6, 126.7, 126.6, 126.2, 125.82, 125.76, 125.3, 120.0, 119.3, 114.22, 114.16, 90.2, 87.7, 55.6, 55.3, 33.2, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{26}ClNO_2$ $[M + H]^+$ 420.1958, found 420.1950.
$[\alpha]_D^{27}$ = –6.0 (*c* 1.00, CH_2Cl_2).

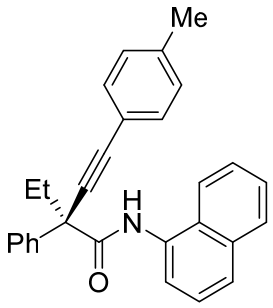
(*S*)-2-Ethyl-4-(3-methoxyphenyl)-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (35)



35

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **35** as a slightly yellow oil (28.5 mg, 68% yield, 93% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 29.36 min, t_R (minor) = 38.05 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.38 (m, 5H), 7.38 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 7.18 (dd, *J* = 2.7, 1.4 Hz, 1H), 7.00 (ddd, *J* = 8.4, 2.6, 1.1 Hz, 1H), 3.86 (s, 3H), 2.61 (dq, *J* = 13.2, 7.4 Hz, 1H), 2.29 (dq, *J* = 13.2, 7.4 Hz, 1H), 1.16 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 160.1, 140.1, 133.9, 133.2, 132.2, 128.8, 128.5, 127.6, 126.7, 126.6, 126.2, 125.82, 125.77, 125.3, 120.0, 119.3, 114.2, 114.2, 90.2, 87.7, 55.6, 55.3, 33.2, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{26}ClNO_2$ $[M + H]^+$ 420.1958, found 420.1951.
$[\alpha]_D^{27}$ = –5.0 (*c* 1.00, CH_2Cl_2).

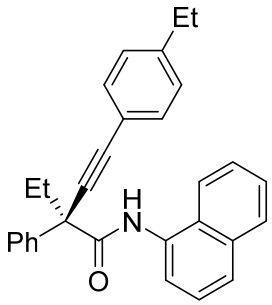
(*S*)-2-Ethyl-*N*-(naphthalen-1-yl)-2-phenyl-4-(*p*-tolyl)but-3-ynamide (36)



36

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **36** as a white solid (25.3 mg, 63% yield, 95% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 18.38 min, t_R (minor) = 22.54 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.07 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.49 – 7.30 (m, 6H), 7.24 (d, *J* = 7.9 Hz, 2H), 2.60 (dq, *J* = 13.2, 7.3 Hz, 1H), 2.42 (s, 3H), 2.27 (dq, *J* = 13.4, 7.4 Hz, 1H), 1.14 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 140.0, 139.2, 134.0, 132.2, 131.6, 129.4, 128.8, 128.6, 127.7, 126.7, 126.6, 126.3, 125.84, 125.78, 125.4, 120.0, 119.4, 119.1, 90.4, 88.4, 55.6, 33.2, 21.5, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{26}NO$ $[M + H]^+$ 404.2009, found 404.2003.
$[\alpha]_D^{27}$ = –7.0 (*c* 1.00, CH_2Cl_2).

(*S*)-2-Ethyl-4-(4-ethylphenyl)-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (37)



37

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **37** as a yellow oil (34.2 mg, 82% yield, 90% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 21.45 min, t_R (minor) = 26.03 min.

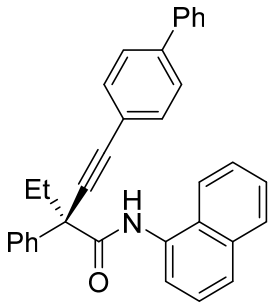
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.09 (d, *J* = 7.5 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.51 – 7.32 (m, 6H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.69 – 2.57 (m, 1H), 2.36 – 2.23 (m, 1H), 1.30 (t, *J* = 7.6 Hz, 3H), 1.17 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 145.5, 140.0, 133.9, 132.2, 131.7, 128.8, 128.6, 128.2, 127.6, 126.7, 126.6, 126.2, 125.83, 125.76, 125.3, 120.0, 119.4, 119.3, 90.4, 88.4, 55.6, 33.2, 28.9, 15.4, 10.2.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{27}NO$ $[M + H]^+$ 418.2165, found 418.2159.

$[\alpha]_D^{27}$ = –7.0 (*c* 1.00, CH_2Cl_2).

(*S*)-4-([1,1'-Biphenyl]-4-yl)-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (38)



38

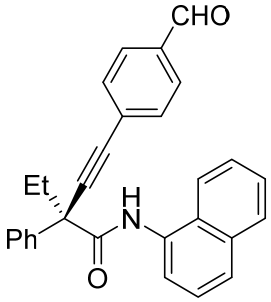
According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **38** as a slightly yellow solid (35.8 mg, 77% yield, 93% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 28.28 min, t_R (minor) = 48.38 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 7.96 – 7.90 (m, 2H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1), 7.78 – 7.74 (m, 2H), 7.72 – 7.63 (m, 5H), 7.54 – 7.34 (m, 9H), 2.66 (dq, *J* = 13.3, 7.3 Hz, 1H), 2.32 (dq, *J* = 13.3, 7.3 Hz, 1H), 1.19 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 141.8, 140.1, 139.9, 134.0, 132.2, 132.1, 128.9, 128.8, 128.6, 127.8, 127.7, 127.3, 127.0, 126.69, 126.66, 126.3, 125.9, 125.8, 125.4, 121.0, 120.0, 119.5, 90.1, 89.8, 55.6, 33.2, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{34}H_{28}NO$ $[M + H]^+$ 466.2165, found 466.2159.
$[\alpha]_D^{27}$ = −14.0 (*c* 1.00, CH_2Cl_2).

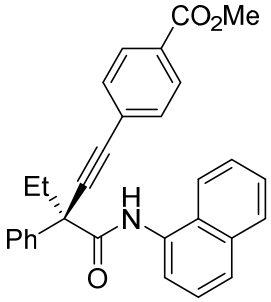
(*S*)-2-Ethyl-4-(4-formylphenyl)-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (39)



39

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **39** as a slightly yellow solid (25.4 mg, 61% yield, 94% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 0.80 mL/min, λ = 276 nm), t_R (major) = 13.93 min, t_R (minor) = 18.47 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.79 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.88 – 7.77 (m, 5H), 7.71 – 7.63 (m, 2H), 7.51 – 7.41 (m, 4H), 7.41 – 7.32 (m, 2H), 2.63 (dq, *J* = 14.4, 7.3 Hz, 1H), 2.30 (dq, *J* = 14.4, 7.3 Hz, 1H), 1.15 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 168.8, 139.4, 136.0, 134.0, 132.3, 131.9, 129.8, 128.9, 128.8, 128.3, 127.9, 126.8, 126.6, 126.3, 125.9, 125.8, 125.7, 119.9, 119.8, 93.3, 88.9, 55.6, 33.0, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{24}NO_2$ $[M + H]^+$ 418.1802, found 418.1802.
$[\alpha]_D^{27}$ = −7.5 (*c* 1.00, CH_2Cl_2).

Methyl (*S*)-4-(3-(Naphthalen-1-ylcarbamoyl)-3-phenylpent-1-yn-1-yl)benzoate (40)

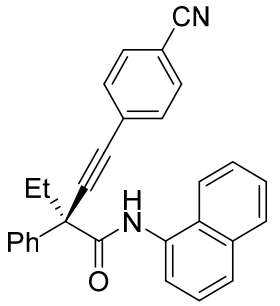


40

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **40** as a white solid (21.0 mg, 47% yield, 93% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 0.80 mL/min, λ = 254 nm), t_R (major) = 9.36 min, t_R (minor) = 12.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.09 (d, *J* = 8.3 Hz, 2H), 8.03 (d, *J* = 7.4 Hz, 1H), 7.88 – 7.82 (m, 3H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.67 (t, *J* = 8.7 Hz, 2H), 7.48 – 7.41 (m, 4H), 7.39 – 7.32 (m, 2H), 3.95 (s, 3H), 2.61 (dq, *J* = 14.6, 7.3 Hz, 1H), 2.28 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.14 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 166.3, 139.6, 134.0, 132.0, 131.7, 130.3, 129.8, 128.9, 128.7, 127.9, 126.8, 126.7, 126.6, 126.3, 125.9, 125.8, 125.6, 119.9, 119.7, 92.2, 89.2, 55.6, 52.3, 33.1, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{26}NO_3$ $[M + H]^+$ 448.1907, found 448.1901.
$[\alpha]_D^{27}$ = –5.0 (*c* 1.00, CH_2Cl_2).

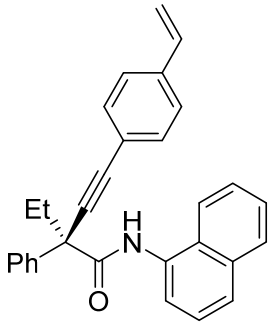
(*S*)-4-(4-Cyanophenyl)-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (41)



41

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **41** as a slightly yellow solid (22.7 mg, 55% yield, 94% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 0.80 mL/min, λ = 254 nm), t_R (major) = 15.10 min, t_R (minor) = 18.79 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.82 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.76 – 7.66 (m, 5H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.50 – 7.41 (m, 4H), 7.40 – 7.34 (m, 2H), 2.62 (dq, *J* = 14.4, 7.3 Hz, 1H), 2.29 (dq, *J* = 14.4, 7.4 Hz, 1H), 1.12 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 139.3, 134.0, 132.34, 132.30, 131.9, 128.9, 128.8, 128.0, 127.0, 126.8, 126.5, 126.3, 126.0, 125.78, 125.76, 120.0, 119.8, 118.2, 112.4, 93.8, 88.1, 55.6, 33.0, 10.1.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{23}N_2O$ $[M + H]^+$ 415.1805, found 415.1797.
$[\alpha]_D^{27}$ = –3.3 (*c* 1.00, CH_2Cl_2).

(*S*)-2-Ethyl-*N*-(naphthalen-1-yl)-2-phenyl-4-(4-vinylphenyl)but-3-ynamide (42)

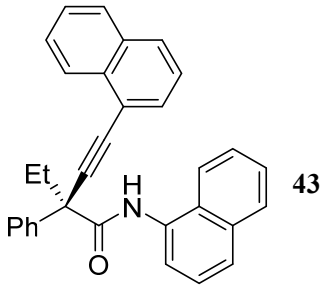


42

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was

employed to yield the product **42** as a slightly yellow oil (30.0 mg, 72% yield, 92% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 14.10 min, t_R (minor) = 18.41 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.08 (d, *J* = 7.2 Hz, 1H), 7.93 – 7.88 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.52 – 7.32 (m, 8H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.85 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.37 (dd, *J* = 10.9, 0.7 Hz, 1H), 2.63 (dq, *J* = 13.2, 7.2 Hz, 1H), 2.30 (dq, *J* = 13.3, 7.3 Hz, 1H), 1.16 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 139.9, 138.2, 136.0, 134.0, 132.1, 131.9, 128.8, 128.6, 127.7, 126.7, 126.6, 126.4, 126.3, 125.9, 125.8, 125.4, 121.3, 120.0, 119.5, 115.3, 90.2, 89.8, 55.6, 33.2, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{26}NO$ $[M + H]^+$ 416.2009, found 416.2001.
$[\alpha]_D^{27}$ = −8.0 (*c* 1.00, CH_2Cl_2).

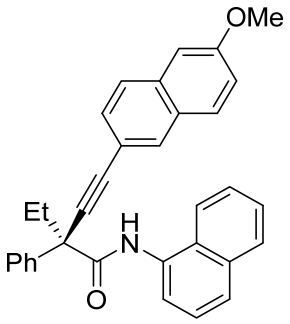
(*S*)-2-Ethyl-*N*,4-di(naphthalen-1-yl)-2-phenylbut-3-ynamide (43)



43

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **43** as a white solid (32.0 mg, 73% yield, 88% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 36.73 min, t_R (minor) = 39.36 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.57 – 8.43 (m, 1H), 8.12 (d, *J* = 7.5 Hz, 1H), 8.04 – 8.00 (m, 2H), 7.98 – 7.92 (m, 3H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.57 – 7.45 (m, 4H), 7.44 – 7.37 (m, 2H), 7.24 – 7.18 (m, 1H), 2.75 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.42 (dq, *J* = 14.4, 7.3 Hz, 1H), 1.28 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 140.0, 133.9, 133.30, 133.28, 132.1, 131.0, 129.5, 128.72, 128.70, 128.6, 127.8, 127.3, 126.7, 126.64, 126.63, 126.2, 125.8, 125.73, 125.71, 125.5, 125.2, 120.1, 119.8, 119.5, 94.0, 88.3, 56.0, 33.3, 10.4.
HRMS (ESI) *m/z* calcd. for $C_{32}H_{26}NO$ $[M + H]^+$ 440.2009, found 440.2001.
$[\alpha]_D^{27}$ = +5.0 (*c* 1.00, CH_2Cl_2).

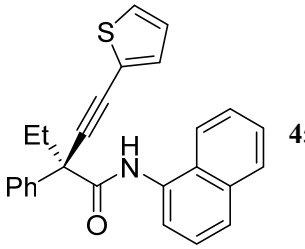
(*S*)-2-Ethyl-4-(6-methoxynaphthalen-2-yl)-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (44)



44

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **44** as a white solid (37.9 mg, 81% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 0.60 mL/min, λ = 254 nm), t_R (major) = 17.66 min, t_R (minor) = 23.07 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.13 – 8.07 (m, 2H), 7.94 – 7.91 (m, 2H), 7.83 – 7.73 (m, 4H), 7.67 – 7.62 (m, 2H), 7.48 – 7.40 (m, 4H), 7.36 – 7.31 (m, 2H), 7.20 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 3.93 (s, 3H), 2.63 (dq, *J* = 14.6, 7.3 Hz, 1H), 2.30 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.18 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 158.6, 140.0, 134.5, 134.0, 132.2, 131.6, 129.3, 128.9, 128.8, 128.6, 128.5, 127.7, 127.2, 126.7, 126.6, 126.3, 125.9, 125.8, 125.3, 120.0, 119.8, 119.4, 116.9, 105.9, 90.8, 88.7, 55.7, 55.4, 33.2, 10.3.
HRMS (ESI) *m/z* calcd. for $C_{33}H_{28}NO_2$ $[M + H]^+$ 470.2115, found 470.2107.
$[\alpha]_D^{27}$ = –22.0 (*c* 1.00, CH_2Cl_2).

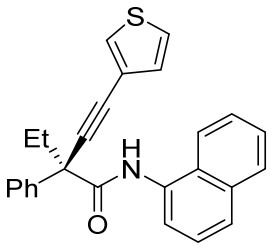
(*S*)-2-Ethyl-*N*-(naphthalen-1-yl)-2-phenyl-4-(thiophen-2-yl)but-3-ynamide (45)



45

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **45** as a colorless oil (24.4 mg, 62% yield, 94% e.e.).
HPLC analysis: Nu-Analytical Solutions INA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 24.72 min, t_R (minor) = 31.18 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.89 – 7.83 (m, 3H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.40 (m, 6H), 7.40 – 7.33 (m, 2H), 7.10 (dd, *J* = 5.2, 3.6 Hz, 1H), 2.62 (dq, *J* = 14.3, 7.3 Hz, 1H), 2.29 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.15 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 139.7, 134.0, 132.6, 132.1, 128.8, 128.7, 127.8, 127.7, 127.3, 126.6, 126.6, 126.3, 125.9, 125.7, 125.4, 121.9, 120.0, 119.5, 93.0, 83.3, 55.8, 33.1, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{22}NOS$ $[M + H]^+$ 396.1417, found 396.1410.
$[\alpha]_D^{27}$ = –6.0 (*c* 0.50, CH_2Cl_2).

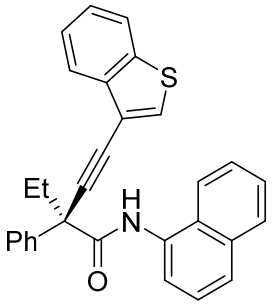
(*S*)-2-Ethyl-*N*-(naphthalen-1-yl)-2-phenyl-4-(thiophen-3-yl)but-3-ynamide (46)



46

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **46** as a colorless oil (34.0 mg, 86% yield, 94% e.e.).
HPLC analysis: Nu-Analytical Solutions INA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 27.88 min, t_R (minor) = 35.71 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.52 – 7.30 (m, 8H), 2.61 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.28 (dq, *J* = 14.4, 7.4 Hz, 1H), 1.15 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 139.8, 134.0, 132.1, 129.8, 129.4, 128.8, 128.6, 127.7, 126.7, 126.6, 126.3, 125.93, 125.86, 125.78, 125.4, 121.1, 119.9, 119.5, 88.8, 85.3, 55.6, 33.1, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{22}NOS$ $[M + H]^+$ 396.1417, found 396.1411.
$[\alpha]_D^{27}$ = –6.3 (*c* 1.00, CH_2Cl_2).

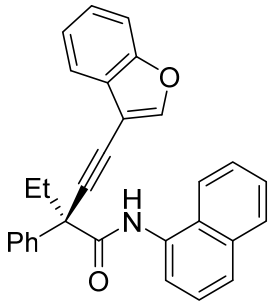
(*S*)-4-(Benzo[b]thiophen-3-yl)-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (47)



47

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **47** as a colorless oil (33.7 mg, 76% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 214 nm), t_R (major) = 36.56 min, t_R (minor) = 42.25 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.12 – 8.02 (m, 2H), 7.96 – 7.88 (m, 3H), 7.82 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.31 (m, 7H), 7.23 (t, *J* = 7.7 Hz, 1H), 2.67 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.34 (dq, *J* = 14.4, 7.4 Hz, 1H), 1.21 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 139.8, 139.0, 138.9, 133.9, 132.1, 130.9, 128.8, 128.7, 127.8, 126.69, 126.65, 126.3, 125.9, 125.7, 125.5, 125.3, 125.1, 122.9, 122.8, 120.0, 119.6, 117.2, 91.8, 83.9, 55.9, 33.2, 10.4.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{24}NOS$ $[M + H]^+$ 446.1573, found 446.1566.
$[\alpha]_D^{27}$ = –1.2 (*c* 1.00, CH_2Cl_2).

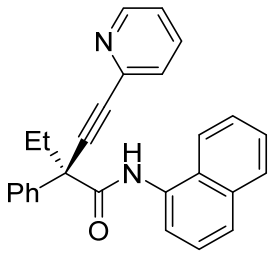
(*S*)-4-(Benzofuran-3-yl)-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (48)



48

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **48** as a yellow oil (26.2 mg, 61% yield, 92% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 28.88 min, t_R (minor) = 33.66 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 8.02 (s, 1H), 7.95 – 7.88 (m, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.39 (m, 5H), 7.39 – 7.33 (m, 2H), 7.31 – 7.26 (m, 1H), 2.66 (dq, *J* = 14.3, 7.3 Hz, 1H), 2.31 (dq, *J* = 13.5, 7.3 Hz, 1H), 1.19 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 154.7, 148.0, 139.7, 134.0, 132.1, 128.8, 128.7, 127.8, 127.5, 126.70, 126.67, 126.3, 125.9, 125.8, 125.6, 125.5, 123.7, 120.3, 119.9, 119.6, 111.9, 103.6, 94.1, 79.8, 55.9, 33.2, 10.3.
HRMS (ESI) *m/z* calcd. for $C_{30}H_{24}NO_2$ $[M + H]^+$ 430.1802, found 430.1794.
$[\alpha]_D^{27}$ = –1.0 (*c* 1.00, CH_2Cl_2).

(*S*)-2-Ethyl-*N*-(naphthalen-1-yl)-2-phenyl-4-(pyridin-2-yl)but-3-ynamide (49)

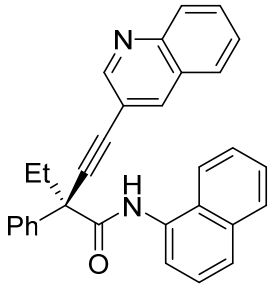


49

According to the **general procedure B**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **49** as a slightly yellow oil (25.0 mg, 64% yield, 93% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 0.60 mL/min, λ = 254 nm), t_R (major) = 15.09 min, t_R (minor) = 18.78 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.71 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 8.03 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.92 – 7.86 (m, 3H), 7.85 – 7.81 (m, 1H), 7.74 (td, *J* = 7.7, 1.8 Hz, 1H), 7.66 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.62 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.49 – 7.39 (m, 5H), 7.37 – 7.30 (m, 2H), 2.64 (dq, *J* = 13.4, 7.3 Hz, 1H), 2.32 (dq, *J* = 13.4, 7.3 Hz, 1H), 1.17 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 150.3, 142.5, 139.4, 136.4, 134.0, 132.2, 128.7, 128.6, 127.8, 127.3, 126.9, 126.7, 126.3, 125.9, 125.63, 125.57, 123.5, 120.6, 119.8, 89.5, 89.0, 55.4, 32.9, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{23}N_2O$ $[M + H]^+$ 391.1805, found 391.1797.
$[\alpha]_D^{27}$ = –9.3 (*c* 1.00, CH_2Cl_2).

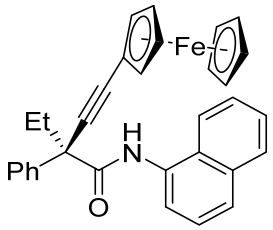
(*S*)-2-Ethyl-*N*-(naphthalen-1-yl)-2-phenyl-4-(quinolin-3-yl)but-3-ynamide (50)



50

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **50** as a white solid (30.7 mg, 70% yield, 94% e.e.).
HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 93/7, flow rate 0.80 mL/min, λ = 254 nm), t_R (minor) = 53.93 min, t_R (major) = 59.41 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 2.1 Hz, 1H), 8.86 (s, 1H), 8.45 (d, *J* = 2.1 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 7.4 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.79 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.63 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.50 – 7.35 (m, 6H), 2.66 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.33 (dq, *J* = 14.3, 7.3 Hz, 1H), 1.18 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 151.8, 147.2, 139.6, 138.9, 134.0, 132.0, 130.6, 129.5, 128.9, 128.8, 127.9, 127.6, 127.6, 127.2, 126.8, 126.6, 126.4, 126.0, 125.8, 125.7, 119.9, 119.8, 116.3, 92.7, 87.1, 55.7, 33.1, 10.3.
HRMS (ESI) *m/z* calcd. for $C_{31}H_{25}N_2O$ $[M + H]^+$ 441.1961, found 441.1955.
$[\alpha]_D^{27}$ = –2.3 (*c* 1.00, CH_2Cl_2).

(*S*)-2-Ethyl-*N*-(naphthalen-1-yl)-4-(ferrocenyl)-2-phenylbut-3-ynamide (51)

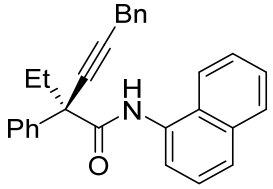


51

According to the **general procedure B**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **51** as a slightly yellow oil (44.7 mg, 90% yield, 91% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 36.07 min, t_R (minor) = 39.29 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.12 (d, *J* = 7.5 Hz, 1H), 7.95 – 7.83 (m, 4H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.41 (m, 5H), 7.39 – 7.32 (m, 1H), 4.76 – 4.56 (m, 2H), 4.33 (t, *J* = 1.9 Hz, 2H), 4.29 (s, 5H), 2.61 (dq, *J* = 13.3, 7.2 Hz, 1H), 2.26 (dq, *J* = 13.1, 7.4 Hz, 1H), 1.18 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 140.2, 134.0, 132.2, 128.9, 128.5, 127.6, 126.7, 126.5, 126.2, 125.9, 125.8, 125.3, 120.0, 119.2, 89.1, 85.3, 71.5, 71.4, 69.8, 69.0, 64.0, 55.7, 33.1, 10.3.
HRMS (ESI) *m/z* calcd. for $C_{32}H_{28}FeNO$ $[M + H]^+$ 498.1515, found 498.1506.
$[\alpha]_D^{27}$ = –8.0 (*c* 1.00, CH_2Cl_2).

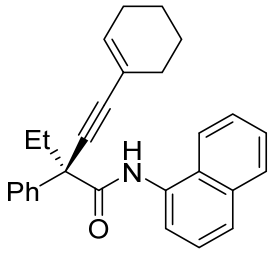
(*S*)-2-Ethyl-*N*-(naphthalen-1-yl)-2,5-diphenylpent-3-ynamide (52)



52

According to the **general procedure B**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **52** as a colorless oil (19.0 mg, 47% yield, 88% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 214 nm), t_R (major) = 28.25 min, t_R (minor) = 36.47 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.87 – 7.79 (m, 3H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.23 (m, 12H), 3.96 (s, 2H), 2.54 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.21 (dq, *J* = 14.4, 7.4 Hz, 1H), 1.10 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 140.2, 136.3, 133.9, 132.2, 128.9, 128.7, 128.5, 127.9, 127.6, 127.0, 126.70, 126.65, 126.2, 125.8, 125.7, 125.4, 120.0, 119.5, 88.2, 82.3, 55.1, 33.2, 25.5, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{26}NO$ $[M + H]^+$ 404.2009, found 404.2002.
$[\alpha]_D^{27}$ = +7.7 (*c* 1.00, CH_2Cl_2).

(*S*)-4-(Cyclohex-1-en-1-yl)-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (53)

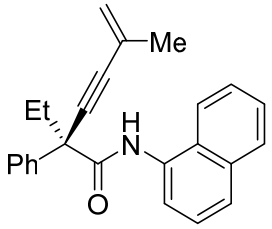


53

According to the **general procedure A**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **53** as a slightly yellow oil (28.7 mg, 73% yield, 92% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 221 nm), t_R (major) = 18.68 min, t_R (minor) = 22.12 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.07 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.89 – 7.76 (m, 4H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.42 – 7.36 (m, 2H), 7.34 – 7.28 (m, 1H), 6.42 – 6.36 (m, 1H), 2.52 (dq, *J* = 13.3, 7.3 Hz, 1H), 2.41 – 2.30 (m, 2H), 2.27 – 2.11 (m, 3H), 1.80 – 1.73 (m, 2H), 1.72 – 1.65 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 140.2, 136.1, 134.0, 132.3, 128.8, 128.5, 127.5, 126.7, 126.6, 126.1, 125.8, 125.2, 120.1, 120.0, 119.3, 92.2, 86.3, 55.5, 33.2, 29.5, 25.7, 22.3, 21.5, 10.2.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{28}NO$ $[M + H]^+$ 394.2165, found 394.2160.
$[\alpha]_D^{27}$ = –4.0 (*c* 1.00, CH_2Cl_2).

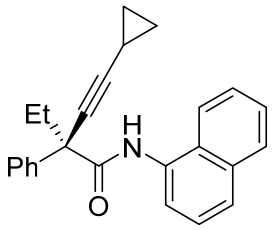
(*S*)-2-Ethyl-5-methyl-*N*-(naphthalen-1-yl)-2-phenylhex-5-en-3-ynamide (54)



54

According to the **general procedure B**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **54** as a slightly yellow oil (24.0 mg, 68% yield, 92% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 221 nm), t_R (major) = 17.07 min, t_R (minor) = 23.46 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.06 (d, *J* = 7.4 Hz, 1H), 7.88 – 7.72 (m, 4H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.36 (m, 5H), 7.35 – 7.29 (m, 1H), 5.57 (dq, *J* = 2.1, 1.1 Hz, 1H), 5.48 – 5.40 (m, 1H), 2.54 (dq, *J* = 13.3, 7.2 Hz, 1H), 2.20 (dq, *J* = 13.3, 7.3 Hz, 1H), 2.14 – 2.08 (m, 3H), 1.08 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 139.9, 134.0, 132.2, 128.8, 128.6, 127.6, 126.6, 126.6, 126.2, 126.0, 125.9, 125.8, 125.3, 123.0, 119.9, 119.4, 91.4, 88.1, 55.4, 33.1, 23.6, 10.1.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{24}NO$ $[M + H]^+$ 354.1852, found 354.1848.
$[\alpha]_D^{27}$ = –4.3 (*c* 1.00, CH_2Cl_2).

(*S*)-4-Cyclopropyl-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylbut-3-ynamide (55)

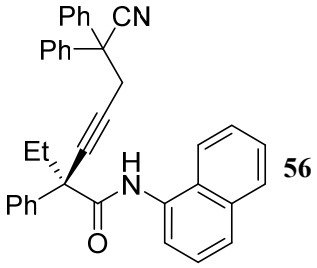


55

According to the **general procedure B**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **55** as a white solid (18.0 mg, 51% yield, 89% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 303 nm), t_R (major) = 21.41 min, t_R (minor) = 30.17 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.82 – 7.75 (m, 3H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.43 (m, 3H), 7.42 – 7.35 (m, 2H), 7.34 – 7.28 (m, 1H), 2.47 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.14 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.60 – 1.53 (m, 1H), 1.04 (t, *J* = 7.3 Hz, 3H), 1.01 – 0.87 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 140.6, 134.3, 132.6, 129.1, 128. 7, 127.7, 126.9, 126.9, 126.4, 126.12, 126.11, 125.5, 120.3, 119.5, 94.2, 75.6, 55.3, 33.5, 10.4, 8.9, 8.8, 0.0.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{24}NO$ $[M + H]^+$ 354.1852, found 354.1847.
$[\alpha]_D^{27}$ = –3.0 (*c* 1.00, CH_2Cl_2).

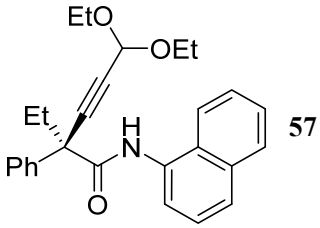
(*S*)-6-Cyano-2-ethyl-*N*-(naphthalen-1-yl)-2,6,6-triphenylhex-3-ynamide (56)



56

According to the **general procedure B**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **56** as a white solid (32.6 mg, 63% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 14.71 min, t_R (minor) = 19.52 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.89 – 7.83 (m, 1H), 7.75 – 7.68 (m, 2H), 7.65 – 7.59 (m, 2H), 7.53 – 7.42 (m, 8H), 7.38 – 7.15 (m, 9H), 3.63 (d, *J* = 16.8 Hz, 1H), 3.61 (d, *J* = 16.8 Hz, 1H), 2.45 (dq, *J* = 14.3, 7.3 Hz, 1H), 2.13 (dq, *J* = 14.3, 7.3 Hz, 1H), 0.98 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 139.7, 138.5, 134.0, 132.1, 129.02, 128.99, 128.45, 128.40, 128.37, 127.9, 127.5, 126.9, 126.80, 126.6, 126.3, 126.1, 125.9, 125.4, 121.9, 121.6, 121.1, 85.0, 84.2, 54.6, 51.8, 32.9, 31.7, 9.9.
HRMS (ESI) *m/z* calcd. for $C_{37}H_{31}N_2O$ $[M + H]^+$ 519.2431, found 519.2425.
$[\alpha]_D^{27}$ = +7.0 (*c* 1.00, CH_2Cl_2).

(*S*)-5,5-Diethoxy-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylpent-3-ynamide (57)

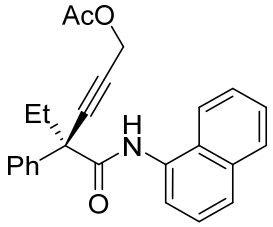


57

According to the **general procedure B**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **57** as a colorless oil (22.9 mg, 55% yield, 94% e.e.).
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 95/5, flow rate 0.60 mL/min, λ = 220 nm), t_R (major) = 16.15 min, t_R (minor) = 35.61 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.88 – 7.76 (m, 4H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.36 (m, 5H), 7.35 – 7.29 (m, 1H), 5.59 (s, 1H), 3.95 – 3.83 (m, 2H), 3.80 – 3.69 (m, 2H), 2.54 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.22 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.34 – 1.28 (m, 6H), 1.08 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 139.3, 134.0, 132.1, 128.7, 128.6, 127.7, 126.63, 126.60, 126.3, 125.9, 125.7, 125.4, 120.3, 119.3, 91.5, 86.1, 85.1, 61.3, 61.1, 54.9, 32.8, 15.18, 15.17, 10.1.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{29}NNaO_3$ $[M + Na]^+$ 438.2040, found 438.2040.
$[\alpha]_D^{27}$ = –3.0 (*c* 1.00, CH_2Cl_2).

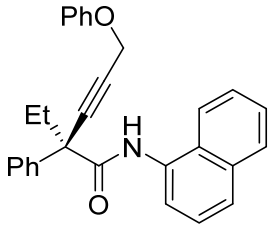
(*S*)-4-(Naphthalen-1-ylcarbamoyl)-4-phenylhex-2-yn-1-yl acetate (58)



58

According to the **general procedure B**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **58** as a colorless oil (18.8 mg, 49% yield, 83% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 0.60 mL/min, λ = 254 nm), t_R (major) = 11.32 min, t_R (minor) = 13.85 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.80 – 7.71 (m, 3H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.37 (m, 5H), 7.36 – 7.29 (m, 1H), 4.98 (s, 2H), 2.52 (dq, *J* = 13.3, 7.3 Hz, 1H), 2.24 – 2.15 (m, 1H), 2.14 (s, 3H), 1.06 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 169.0, 139.4, 134.0, 132.1, 128.7, 128.6, 127.8, 127.0, 126.6, 126.3, 125.9, 125.7, 120.3, 120.1, 86.8, 84.1, 54.9, 52.4, 32.8, 20.7, 10.0.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{24}NO_3$ $[M + H]^+$ 386.1751, found 386.1743.
$[\alpha]_D^{27}$ = +3.0 (*c* 1.00, CH_2Cl_2).

(*S*)-2-Ethyl-*N*-(naphthalen-1-yl)-5-phenoxy-2-phenylpent-3-ynamide (59)

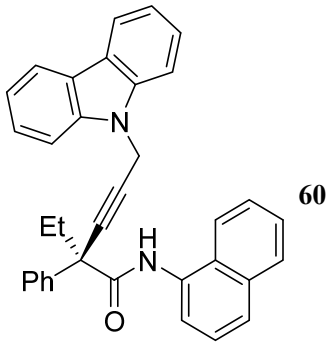


59

According to the **general procedure B**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **59** as a slightly yellow oil (26.4 mg, 63% yield, 87% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 21.29 min, t_R (minor) = 27.93 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.48 – 7.20 (m, 8H), 7.09 – 7.03 (m, 2H), 6.92 (tt, *J* = 7.4, 1.1 Hz, 1H), 5.02 (d, *J* = 15.6 Hz, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 2.48 (dq, *J* = 13.3, 7.3 Hz, 1H), 2.17 (dq, *J* = 13.3, 7.3 Hz, 1H), 1.02 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 157.4, 139.4, 133.9, 132.0, 129.6, 128.63, 128.58, 127.7, 127.0, 126.6, 126.4, 125.9, 125.7, 125.6, 121.8, 120.3, 120.1, 115.1, 87.5, 85.0, 56.3, 54.9, 32.7, 10.0.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{26}NO_2$ $[M + H]^+$ 420.1958, found 420.1949.
$[\alpha]_D^{27}$ = –4.0 (*c* 1.00, CH_2Cl_2).

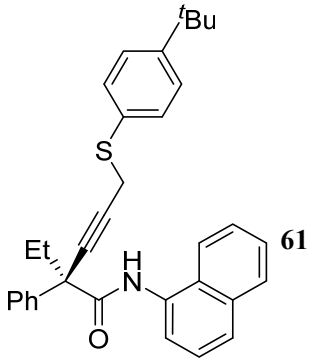
(*S*)-5-(9*H*-Carbazol-9-yl)-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylpent-3-ynamide (60)



60

According to the **general procedure B**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **60** as a slightly yellow solid (31.0 mg, 63% yield, 90% e.e.). **HPLC** analysis: Chiralcel IA (hexane/*i*-PrOH = 90/10, flow rate 0.60 mL/min, λ = 254 nm), t_R (major) = 21.62 min, t_R (minor) = 24.43 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.06 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.65 – 7.60 (m, 2H), 7.59 – 7.52 (m, 3H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.16 (m, 7H), 7.10 (d, *J* = 8.5 Hz, 1H), 6.91 (t, *J* = 7.3 Hz, 1H), 5.30 (s, 2H), 2.44 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.12 (dq, *J* = 14.3, 7.2 Hz, 1H), 0.96 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 139.9, 139.4, 133.8, 131.8, 128.5, 128.5, 127.7, 126.8, 126.5, 126.2, 126.1, 125.7, 125.6, 125.4, 123.5, 120.6, 120.0, 119.8, 119.8, 108.6, 84.3, 84.2, 54.8, 33.0, 32.8, 10.0.
HRMS (ESI) *m/z* calcd. for $C_{35}H_{29}N_2O$ $[M + H]^+$ 493.2274, found 493.2270.
$[\alpha]_D^{27}$ = +6.0 (*c* 1.00, CH_2Cl_2).

(*S*)-5-((4-(*tert*-Butyl)phenyl)thio)-2-ethyl-*N*-(naphthalen-1-yl)-2-phenylpent-3-ynamide (61)

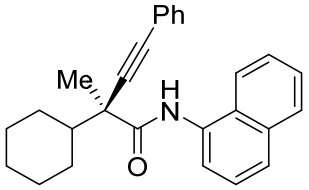


61

According to the **general procedure B**, substrate **E2** (32.4 mg, 0.10 mmol) was employed to yield the product **61** as a slightly yellow oil (25.0 mg, 51% yield, 90% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (major) = 31.77 min, t_R (minor) = 38.37 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.88 – 7.80 (m, 2H), 7.69 – 7.56 (m, 5H), 7.48 – 7.36 (m, 3H), 7.35 – 7.24 (m, 4H), 7.09 – 7.03 (m, 1H), 7.03 – 6.97 (m, 1H), 3.98 (s, 2H), 2.43 (dq, *J* = 14.3, 7.2 Hz, 1H), 2.10 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.48 (s, 9H), 0.96 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 150.3, 139.8, 134.0, 133.6, 132.6, 132.2, 128.6, 128.5, 127.5, 127.2, 127.0, 126.8, 126.60, 126.56, 126.3, 125.9, 125.8, 125.7, 125.6, 120.5, 120.4, 85.9, 83.1, 54.9, 36.5, 33.0, 30.6, 24.5, 10.0.
HRMS (ESI) *m/z* calcd. for $C_{33}H_{34}NOS$ $[M + H]^+$ 492.2356, found 492.2350.
$[\alpha]_D^{27}$ = −5.7 (*c* 1.00, CH_2Cl_2).

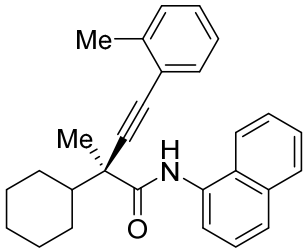
(*S*)-2-Cyclohexyl-2-methyl-*N*-(naphthalen-1-yl)-4-phenylbut-3-ynamide (62)



62

According to the **general procedure C**, substrate **E62** (35.9 mg, 0.10 mmol) was employed to yield the product **62** as a colorless oil (23.5 mg, 62% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (major) = 19.20 min, t_R (minor) = 22.51 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.22 (d, *J* = 7.5 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.52 – 7.37 (m, 6H), 2.04 – 1.96 (m, 2H), 1.87 – 1.72 (m, 3H), 1.67 (s, 3H), 1.51 – 1.16 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 134.0, 132.1, 131.7, 128.9, 128.7, 128.6, 126.3, 125.9, 125.9, 125.1, 122.3, 119.9, 118.8, 90.2, 88.6, 50.3, 45.4, 29.5, 27.6, 26.4, 26.2, 24.2.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{28}NO$ $[M + H]^+$ 382.2165, found 382.2161.
$[\alpha]_D^{27}$ = +12.2 (*c* 0.90, CH_2Cl_2).

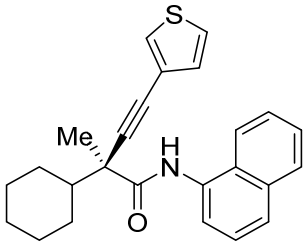
(*S*)-2-Cyclohexyl-2-methyl-*N*-(naphthalen-1-yl)-4-(*o*-tolyl)but-3-ynamide (63)



63

According to the **general procedure C**, substrate **E62** (35.9 mg, 0.10 mmol) was employed to yield the product **63** as a colorless oil (20.5 mg, 52% yield, 92% e.e.).
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.59 min, t_R (minor) = 17.27 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.19 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.44 – 7.39 (m, 1H), 7.32 – 7.25 (m, 2H), 7.24 – 7.18 (m, 1H), 2.53 (s, 3H), 2.07 – 1.98 (m, 2H), 1.89 – 1.72 (m, 3H), 1.69 (s, 3H), 1.54 – 1.12 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 140.1, 134.0, 132.1, 132.1, 129.7, 128.9, 128.7, 126.5, 126.3, 125.90, 125.87, 125.80, 125.2, 122.2, 120.0, 119.1, 94.0, 87.5, 50.6, 45.4, 29.6, 27.6, 26.4, 26.3, 26.2, 24.5, 21.1.
HRMS (ESI) *m/z* calcd. for $C_{28}H_{30}NO$ $[M + H]^+$ 396.2322, found 396.2328.
$[\alpha]_D^{27}$ = +16.0 (*c* 1.00, CH_2Cl_2).

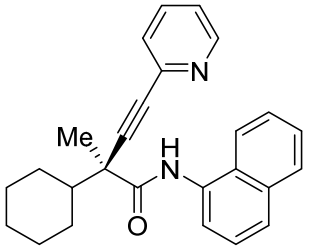
(*S*)-2-Cyclohexyl-2-methyl-*N*-(naphthalen-1-yl)-4-(thiophen-3-yl)but-3-ynamide (64)



64

According to the **general procedure C**, substrate **E62** (35.9 mg, 0.10 mmol) was employed to yield the product **64** as a colorless oil (22.0 mg, 57% yield, 89% e.e.).
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.38 min, t_R (minor) = 15.76 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.22 (d, *J* = 7.5 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.57 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.35 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.23 (dd, *J* = 5.0, 1.1 Hz, 1H), 2.03 – 1.94 (m, 2H), 1.88 – 1.70 (m, 3H), 1.66 (s, 3H), 1.48 – 1.15 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 134.0, 132.1, 129.8, 129.0, 128.9, 126.3, 126.0, 125.9, 125.8, 125.1, 121.3, 119.8, 118.8, 89.8, 83.6, 50.4, 45.4, 29.5, 27.6, 26.3, 26.2, 24.2.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{26}NOS$ $[M + H]^+$ 388.1730, found 388.1726.
$[\alpha]_D^{27}$ = +6.6 (*c* 0.50, CH_2Cl_2).

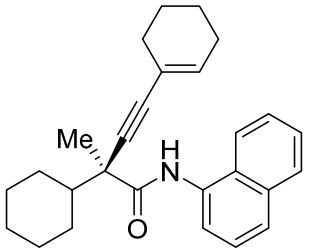
(*S*)-2-Cyclohexyl-2-methyl-*N*-(naphthalen-1-yl)-4-(pyridin-2-yl)but-3-ynamide (65)



65

According to the **general procedure C**, substrate **E62** (35.9 mg, 0.10 mmol) was employed to yield the product **65** as a colorless oil (25.6 mg, 67% yield, 86% e.e.).
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 9.05 min, t_R (minor) = 14.07 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.67 (ddd, *J* = 4.9, 1.6, 0.9 Hz, 1H), 8.19 (d, *J* = 7.0 Hz, 1H), 8.09 – 8.04 (m, 1H), 7.89 – 7.83 (m, 1H), 7.74 – 7.67 (m, 2H), 7.55 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.30 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 2.08 – 1.97 (m, 2H), 1.89 – 1.80 (m, 2H), 1.78 – 1.72 (m, 1H), 1.70 (s, 3H), 1.53 – 1.17 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 150.3, 142.6, 136.3, 134.0, 132.2, 128.7, 127.1, 126.5, 126.4, 125.9, 125.8, 125.3, 123.3, 120.5, 119.1, 90.1, 88.1, 50.1, 45.4, 29.5, 27.6, 26.3, 26.2, 26.1, 24.0.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{27}N_2O$ $[M + H]^+$ 383.2118, found 383.2121.
$[\alpha]_D^{27}$ = +8.0 (*c* 1.00, CH_2Cl_2).

(*S*)-4-(Cyclohex-1-en-1-yl)-2-cyclohexyl-2-methyl-*N*-(naphthalen-1-yl)but-3-ynamide (66)

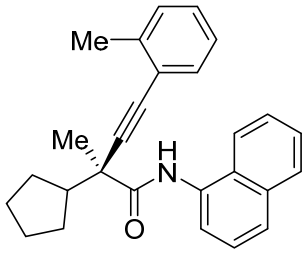


66

According to the **general procedure C**, substrate **E62** (35.9 mg, 0.10 mmol) was employed to yield the product **66** as a colorless oil (8.8 mg, 23% yield, 88% e.e.).
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.23 min, t_R (minor) = 8.61 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.21 (dd, *J* = 7.5, 0.6 Hz, 1H), 7.94 – 7.85 (m, 2H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.48 (m, 3H), 6.27 (tt, *J* = 3.9, 1.8 Hz, 1H), 2.29 – 2.24 (m, 2H), 2.20 – 2.13 (m, 2H), 1.97 – 1.81 (m, 3H), 1.75 – 1.64 (m, 6H), 1.57 (s, 3H), 1.41 – 1.14 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 135.5, 134.0, 132.3, 128.9, 126.3, 126.2, 126.0, 125.8, 124.9, 120.0, 118.6, 90.4, 87.3, 50.2, 45.3, 29.6, 29.4, 27.5, 26.4, 26.3, 26.2, 25.7, 24.3, 22.3, 21.5.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{32}NO$ $[M + H]^+$ 386.2478, found 386.2474.
$[\alpha]_D^{27}$ = +20.5 (*c* 1.00, CH_2Cl_2).

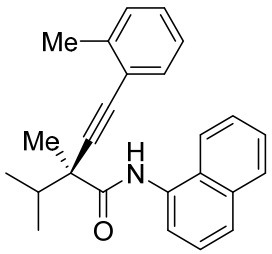
(*S*)-2-Cyclopentyl-2-methyl-*N*-(naphthalen-1-yl)-4-(*o*-tolyl)but-3-ynamide (67)



67

According to the **general procedure C**, substrate **E67** (34.6 mg, 0.10 mmol) was employed to yield the product **67** as a colorless oil (21.0 mg, 55% yield, 72% e.e.).
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 6.27 min, t_R (minor) = 14.63 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 7.87 (dd, *J* = 7.9, 3.6 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.40 (m, 4H), 7.32 – 7.25 (m, 2H), 7.23 – 7.18 (m, 1H), 2.61 – 2.51 (m, 1H), 2.52 (s, 3H), 1.98 – 1.90 (m, 1H), 1.89 – 1.81 (m, 1H), 1.72 (s, 3H), 1.71 – 1.57 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 140.1, 134.0, 132.3, 132.1, 129.7, 128.9, 128.8, 126.6, 126.3, 125.9, 125.8, 125.3, 122.1, 120.1, 119.4, 93.8, 87.3, 49.8, 47.9, 29.4, 28.2, 25.9, 25.7, 25.5, 21.0.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{28}NO$ $[M + H]^+$ 382.2165, found 382.2170.
$[\alpha]_D^{27}$ = +6.0 (*c* 1.00, CH_2Cl_2).

(*S*)-2-Isopropyl-2-methyl-*N*-(naphthalen-1-yl)-4-(*o*-tolyl)but-3-ynamide (68)

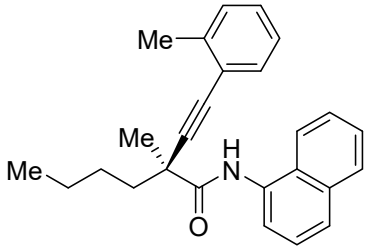


68

According to the **general procedure C**, substrate **E68** (32.0 mg, 0.10 mmol) was employed to yield the product **68** as a colorless oil (18.0 mg, 51% yield, 62% e.e.).
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.23 min, t_R (minor) = 14.48 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.16 (d, *J* = 7.5 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.52 – 7.39 (m, 3H), 7.31 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 2.53 (s, 3H), 2.44 – 2.32 (m, 1H), 1.70 (s, 3H), 1.19 (d, *J* = 6.6 Hz, 3H), 1.15 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 140.1, 134.0, 132.2, 132.1, 129.7, 128.9, 128.8, 126.6, 126.3, 125.9, 125.8, 125.3, 122.1, 120.0, 119.3, 93.2, 87.7, 51.1, 35.9, 25.1, 21.1, 19.6, 17.7.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{26}NO$ $[M + H]^+$ 356.2009, found 356.2013.
$[\alpha]_D^{27}$ = +11.0 (*c* 1.00, CH_2Cl_2).

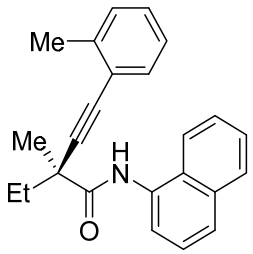
(*S*)-2-Methyl-*N*-(naphthalen-1-yl)-2-(*o*-tolylethynyl)hexanamide (69)



69

According to the **general procedure C**, substrate **E69** (33.4 mg, 0.10 mmol) was employed to yield the product **69** as a colorless oil (18.1 mg, 49% yield, 64% e.e.).
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.17 min, t_R (minor) = 12.76 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.16 (d, *J* = 7.2 Hz, 1H), 7.91 – 7.82 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.39 (m, 4H), 7.32 – 7.26 (m, 2H), 7.23 – 7.18 (m, 1H), 2.51 (s, 3H), 2.19 – 2.11 (m, 1H), 1.85 – 1.77 (m, 1H), 1.72 (s, 3H), 1.71 – 1.66 (m, 1H), 1.55 – 1.36 (m, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 140.2, 134.0, 132.2, 132.0, 129.7, 128.9, 128.8, 126.5, 126.3, 125.9, 125.8, 125.3, 122.0, 120.0, 119.3, 95.2, 86.4, 45.9, 40.4, 28.1, 27.0, 22.8, 20.9, 14.0.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{28}NO$ $[M + H]^+$ 370.2165, found 370.2172.
$[\alpha]_D^{27}$ = +1.0 (*c* 1.00, CH_2Cl_2).

(*S*)-2-Ethyl-2-methyl-*N*-(naphthalen-1-yl)-4-(*o*-tolyl)but-3-ynamide (70)

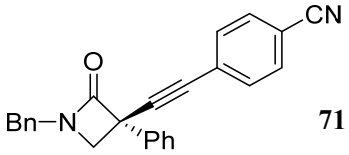


70

According to the **general procedure C**, substrate **E70** (30.6 mg, 0.10 mmol) was employed to yield the product **70** as a colorless oil (14.6 mg, 43% yield, 32% e.e.).
HPLC analysis: Chiralcel IB (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.33 min, t_R (minor) = 12.98 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.15 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.52 – 7.39 (m, 3H), 7.32 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 2.52 (s, 3H), 2.19 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.86 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.72 (s, 3H), 1.19 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 140.1, 134.0, 132.2, 132.1, 129.7, 128.9, 128.8, 126.6, 126.3, 125.9, 125.9, 125.8, 125.4, 122.0, 120.0, 119.4, 94.9, 86.5, 46.6, 33.8, 26.6, 20.9, 10.3.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}NO$ $[M + H]^+$ 342.1852, found 342.1857.
$[\alpha]_D^{27}$ = +3.3 (*c* 0.60, CH_2Cl_2).

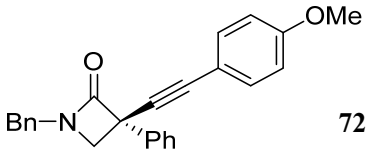
(*S*)-4-((1-Benzyl-2-oxo-3-phenylazetidin-3-yl)ethynyl)benzonitrile (71)



71

According to the **general procedure D**, substrate **E71** (31.6 mg, 0.10 mmol) was employed to yield the product **71** as a yellowish solid (29.7 mg, 82% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 270 nm), t_R (minor) = 24.72 min, t_R (major) = 32.47 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.43 – 7.29 (m, 8H), 4.60 (d, *J* = 15.0 Hz, 1H), 4.50 (d, *J* = 15.0 Hz, 1H), 3.75 (d, *J* = 5.4 Hz, 1H), 3.53 (d, *J* = 5.4 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 135.8, 134.7, 132.3, 131.9, 129.0, 128.9, 128.21, 128.16, 128.1, 127.4, 126.1, 118.3, 111.8, 90.2, 85.0, 56.7, 55.4, 46.5.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{19}N_2O$ $[M + H]^+$ 363.1492, found 363.1488.
$[\alpha]_D^{27}$ = –81.0 (*c* 1.00, CH_2Cl_2).

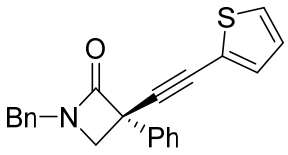
(*S*)-1-Benzyl-3-((4-methoxyphenyl)ethynyl)-3-phenylazetidin-2-one (72)



72

According to the **general procedure E**, substrate **E71** (31.6 mg, 0.10 mmol) was employed to yield the product **72** as a yellowish solid (31.2 mg, 85% yield, 89% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 260 nm), t_R (minor) = 13.93 min, t_R (major) = 22.08 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.46 – 7.28 (m, 10H), 6.88 – 6.81 (m, 2H), 4.62 (d, *J* = 15.0 Hz, 1H), 4.49 (d, *J* = 15.0 Hz, 1H), 3.81 (s, 3H), 3.73 (d, *J* = 5.3 Hz, 1H), 3.49 (d, *J* = 5.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 159.7, 136.6, 135.0, 133.3, 128.9, 128.8, 128.2, 128.0, 127.9, 126.2, 114.7, 113.8, 86.7, 84.0, 56.9, 56.0, 55.3, 46.4.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{22}NO_2$ $[M + H]^+$ 368.1645, found 368.1642.
$[\alpha]_D^{27}$ = –48.0 (*c* 1.00, CH_2Cl_2).

(*S*)-1-Benzyl-3-phenyl-3-(thiophen-2-ylethynyl)azetidin-2-one (73)

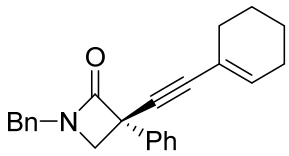


73

According to the **general procedure E**, substrate **E71** (31.6 mg, 0.10 mmol) was employed to yield the product **73** as yellow oil (26.7 mg, 78% yield, 92% e.e.).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 270 nm), t_R (minor) = 11.03 min, t_R (major) = 14.39 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.43 – 7.29 (m, 8H), 7.28 – 7.24 (m, 2H), 6.98 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.62 (d, *J* = 15.0 Hz, 1H), 4.49 (d, *J* = 15.0 Hz, 1H), 3.74 (d, *J* = 5.3 Hz, 1H), 3.50 (d, *J* = 5.3 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 136.2, 134.8, 132.4, 129.0, 128.9, 128.2, 128.0, 127.3, 126.9, 126.2, 122.5, 89.3, 80.1, 57.0, 55.7, 46.5.
HRMS (ESI) *m/z* calcd. for $C_{22}H_{18}NOS$ $[M + H]^+$ 344.1104, found 344.1102.
$[\alpha]_D^{27}$ = –50.7 (*c* 1.00, CH_2Cl_2).

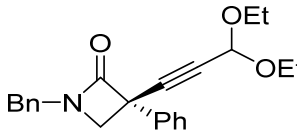
(*S*)-1-Benzyl-3-(cyclohex-1-en-1-ylethynyl)-3-phenylazetidin-2-one (74)



74

According to the **general procedure E**, substrate **E71** (31.6 mg, 0.10 mmol) was employed to yield the product **74** as a colorless oil (16.0 mg, 47% yield, 87% e.e.).
HPLC analysis: Nu-Analytical Solutions INA (hexane/*i*-PrOH = 85/15, flow rate 0.70 mL/min, λ = 240 nm), t_R (minor) = 10.62 min, t_R (major) = 14.30 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.41 – 7.26 (m, 8H), 6.17 (tt, *J* = 3.9, 1.8 Hz, 1H), 4.58 (d, *J* = 15.0 Hz, 1H), 4.46 (d, *J* = 15.0 Hz, 1H), 3.62 (d, *J* = 5.2 Hz, 1H), 3.43 (d, *J* = 5.2 Hz, 1H), 2.20 – 2.06 (m, 4H), 1.67 – 1.56 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 136.7, 135.5, 135.0, 128.9, 128.7, 128.2, 127.9, 127.8, 126.2, 120.2, 88.7, 82.6, 56.8, 56.2, 46.4, 29.2, 25.6, 22.2, 21.4.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}NO$ $[M + H]^+$ 342.1852, found 342.1850.
$[\alpha]_D^{27}$ = –22.0 (*c* 1.00, CH_2Cl_2).

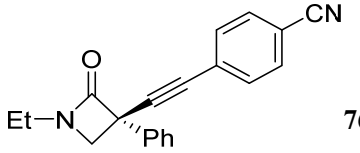
(*S*)-1-Benzyl-3-(3,3-diethoxyprop-1-yn-1-yl)-3-phenylazetidin-2-one (75)



75

According to the **general procedure E**, substrate **E71** (31.6 mg, 0.10 mmol) was employed to yield the product **75** as a colorless oil (26.0 mg, 72% yield, 84% e.e.).
HPLC analysis: Nu-Analytical Solutions INA (hexane/*i*-PrOH = 85/15, flow rate 0.70 mL/min, λ = 214 nm), t_R (minor) = 9.11 min, t_R (major) = 11.22 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.40 – 7.27 (m, 8H), 5.37 (s, 1H), 4.56 (d, *J* = 15.0 Hz, 1H), 4.45 (d, *J* = 15.0 Hz, 1H), 3.80 – 3.70 (m, 2H), 3.68 (d, *J* = 5.4 Hz, 1H), 3.66 – 3.55 (m, 2H), 3.41 (d, *J* = 5.4 Hz, 1H), 1.24 (t, *J* = 7.2, 3H), 1.23 (t, *J* = 7.2, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 135.8, 134.8, 128.9, 128.8, 128.2, 128.0, 126.1, 91.4, 82.3, 81.7, 61.0, 56.1, 55.3, 46.4, 15.1.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{25}NNaO_3$ $[M + Na]^+$ 386.1727, found 386.1723.
$[\alpha]_D^{27}$ = –8.0 (*c* 0.50, CH_2Cl_2).

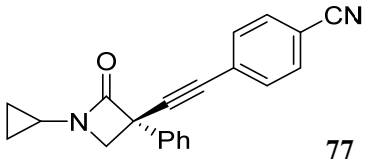
(*S*)-4-((1-Ethyl-2-oxo-3-phenylazetidin-3-yl)ethynyl)benzonitrile (76)



76

According to the **general procedure D**, substrate **E76** (25.4 mg, 0.10 mmol) was employed to yield the product **76** as a colorless oil (27.0 mg, 90% yield, 85% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 270 nm), t_R (minor) = 14.34 min, t_R (major) = 17.96 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 6H), 7.43 – 7.37 (m, 2H), 7.36 – 7.30 (m, 1H), 3.83 (d, *J* = 5.2 Hz, 1H), 3.62 (d, *J* = 5.2 Hz, 1H), 3.54 – 3.32 (m, 2H), 1.27 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 136.0, 132.3, 131.9, 129.0, 128.2, 127.5, 126.1, 118.3, 111.8, 90.4, 85.0, 56.2, 55.3, 37.0, 12.6.
HRMS (ESI) *m/z* calcd. for $C_{20}H_{17}N_2O$ $[M + H]^+$ 301.1335, found 301.1334.
$[\alpha]_D^{27}$ = –19.0 (*c* 1.00, CH_2Cl_2).

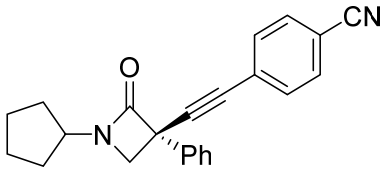
(*S*)-4-((1-Cyclopropyl-2-oxo-3-phenylazetidin-3-yl)ethynyl)benzonitrile (77)



77

According to the **general procedure D**, substrate **E77** (26.6 mg, 0.10 mmol) was employed to yield the product **77** as a colorless oil (27.5 mg, 88% yield, 84% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 270 nm), t_R (minor) = 16.20 min, t_R (major) = 27.89 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 4H), 7.52 – 7.48 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m, 1H), 3.79 (d, *J* = 5.3 Hz, 1H), 3.56 (d, *J* = 5.3 Hz, 1H), 2.76 – 2.66 (m, 1H), 0.98 – 0.76 (m, 4H).
^{13}C NMR (10MHz, $CDCl_3$) δ 165.5, 136.0, 132.3, 131.9, 129.0, 128.1, 127.5, 126.1, 118.3, 111.8, 90.3, 85.0, 56.4, 55.4, 24.7, 5.6, 5.4.
HRMS (ESI) *m/z* calcd. for $C_{21}H_{17}N_2O$ $[M + H]^+$ 313.1335, found 313.1334.
$[\alpha]_D^{27}$ = –12.0 (*c* 1.00, CH_2Cl_2).

(*S*)-4-((1-Cyclopentyl-2-oxo-3-phenylazetidin-3-yl)ethynyl)benzonitrile (78)

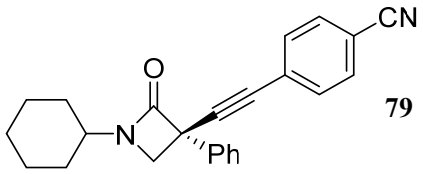


78

According to the **general procedure D**, substrate **E78** (29.4 mg, 0.10 mmol) was employed to yield the product **78** as a white solid (28.2 mg, 83% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 270

nm), t_R (minor) = 15.45 min, t_R (major) = 22.07 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.50 (m, 6H), 7.43 – 7.36 (m, 2H), 7.36 – 7.30 (m, 1H), 4.27 – 4.13 (m, 1H), 3.81 (d, *J* = 5.2 Hz, 1H), 3.57 (d, *J* = 5.2 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.85 – 1.58 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 136.2, 132.4, 131.9, 129.0, 128.1, 127.5, 126.1, 118.3, 111.7, 90.5, 84.9, 55.1, 54.0, 53.8, 30.4, 30.0, 23.98, 23.95.
HRMS (ESI) *m/z* calcd. for $C_{23}H_{21}N_2O$ $[M + H]^+$ 341.1648, found 341.1646.
$[\alpha]_D^{27}$ = –29.0 (*c* 1.00, CH_2Cl_2).

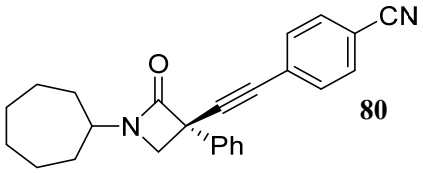
(*S*)-4-((1-Cyclohexyl-2-oxo-3-phenylazetidin-3-yl)ethynyl)benzonitrile (79)



79

According to the **general procedure D**, substrate **E79** (30.8 mg, 0.10 mmol) was employed to yield the product **79** as a white solid (30.0 mg, 85% yield, 91% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 270 nm), t_R (minor) = 17.31 min, t_R (major) = 23.56 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 6H), 7.43 – 7.36 (m, 2H), 7.35 – 7.29 (m, 1H), 3.81 (d, *J* = 5.2 Hz, 1H), 3.69 (tt, *J* = 11.3, 3.9 Hz, 1H), 3.57 (d, *J* = 5.2 Hz, 1H), 2.05 – 1.93 (m, 2H), 1.86 – 1.75 (m, 2H), 1.71 – 1.61 (m, 1H), 1.53 – 1.41 (m, 2H), 1.39 – 1.28 (m, 2H), 1.17 (qt, *J* = 12.4, 3.6 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 136.1, 132.4, 131.9, 128.9, 128.1, 127.6, 126.0, 118.3, 111.7, 90.5, 84.9, 55.1, 53.6, 51.7, 30.8, 30.4, 25.2, 24.73, 24.72.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{23}N_2O$ $[M + H]^+$ 355.1805, found 355.1802.
$[\alpha]_D^{27}$ = –18.0 (*c* 1.00, CH_2Cl_2).

(*S*)-4-((1-Cycloheptyl-2-oxo-3-phenylazetidin-3-yl)ethynyl)benzonitrile (80)

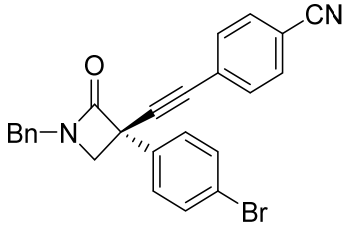


80

According to the **general procedure D**, substrate **E80** (32.2 mg, 0.10 mmol) was employed to yield the product **80** as a white solid (32.0 mg, 87% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 270 nm), t_R (minor) = 19.03 min, t_R (major) = 25.22 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.50 (m, 6H), 7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m, 1H), 3.90 (tt, *J* = 9.4, 4.4 Hz, 1H), 3.82 (d, *J* = 5.2 Hz, 1H), 3.59 (d, *J* = 5.2 Hz, 1H), 2.10 – 1.97 (m, 2H), 1.78 – 1.43 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 136.1, 132.4, 131.9, 128.9, 128.1, 127.5, 126.0, 118.3, 111.7, 90.5, 84.9, 55.2, 53.8, 53.7, 32.9, 32.5, 27.9, 27.8, 24.17, 24.15.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{25}N_2O$ $[M + H]^+$ 369.1961, found 369.1959.

$[\alpha]_D^{27}$ = –24.0 (*c* 1.00, CH_2Cl_2).

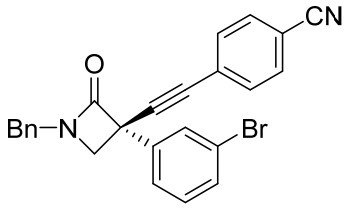
(*S*)-4-((1-Benzyl-3-(4-bromophenyl)-2-oxoazetidin-3-yl)ethynyl)benzonitrile (81)



81

According to the **general procedure D**, substrate **E81** (39.5 mg, 0.10 mmol) was employed to yield the product **81** as a white solid (37.5 mg, 85% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 270 nm), t_R (minor) = 28.21 min, t_R (major) = 31.68 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.56 – 7.52 (m, 2H), 7.52 – 7.48 (m, 2H), 7.42 – 7.28 (m, 7H), 4.60 (d, *J* = 15.0 Hz, 1H), 4.47 (d, *J* = 15.0 Hz, 1H), 3.74 (d, *J* = 5.5 Hz, 1H), 3.48 (d, *J* = 5.5 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 135.0, 134.5, 132.3, 132.1, 132.0, 129.0, 128.19, 128.16, 127.9, 127.1, 122.3, 118.2, 112.0, 89.5, 85.3, 56.2, 55.2, 46.6.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{18}BrN_2O$ $[M + H]^+$ 441.0597, found 441.0593.
$[\alpha]_D^{27}$ = –48.0 (*c* 1.00, CH_2Cl_2).

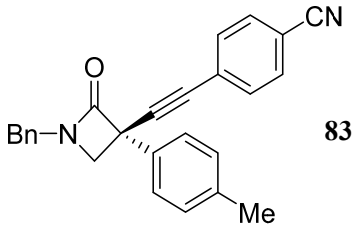
(*S*)-4-((1-Benzyl-3-(3-bromophenyl)-2-oxoazetidin-3-yl)ethynyl)benzonitrile (82)



82

According to the **general procedure E**, substrate **E82** (39.5 mg, 0.10 mmol) was employed to yield the product **82** as a white solid (37.0 mg, 84% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 270 nm), t_R (minor) = 17.38 min, t_R (major) = 21.42 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 3H), 7.58 – 7.53 (m, 2H), 7.49 – 7.29 (m, 7H), 7.28 – 7.23 (m, 1H), 4.60 (d, *J* = 14.9 Hz, 1H), 4.48 (d, *J* = 15.0 Hz, 1H), 3.74 (d, *J* = 5.5 Hz, 1H), 3.49 (d, *J* = 5.5 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 138.0, 134.5, 132.4, 132.0, 131.4, 130.5, 129.3, 129.1, 128.3, 128.2, 127.1, 124.8, 123.0, 118.3, 112.0, 89.3, 85.5, 56.2, 55.2, 46.6.
HRMS (ESI) *m/z* calcd. for $C_{25}H_{18}BrN_2O$ $[M + H]^+$ 441.0597, found 441.0593.
$[\alpha]_D^{27}$ = –56.0 (*c* 1.00, CH_2Cl_2).

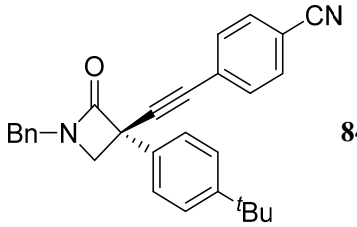
(*S*)-4-((1-Benzyl-2-oxo-3-(*p*-tolyl)azetidin-3-yl)ethynyl)benzonitrile (83)



83

According to the **general procedure D**, substrate **E83** (33.0 mg, 0.10 mmol) was employed to yield the product **83** as a white solid (33.0 mg, 88% yield, 90% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 270 nm), t_R (minor) = 30.53 min, t_R (major) = 42.69 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.29 (m, 7H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.60 (d, *J* = 15.0 Hz, 1H), 4.49 (d, *J* = 15.0 Hz, 1H), 3.73 (d, *J* = 5.4 Hz, 1H), 3.50 (d, *J* = 5.3 Hz, 1H), 2.35 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 138.0, 134.3, 132.9, 132.3, 131.9, 129.6, 128.9, 128.2, 128.0, 127.5, 126.0, 118.3, 111.7, 90.5, 84.8, 56.4, 55.5, 46.5, 21.0.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{21}N_2O$ $[M + H]^+$ 377.1648, found 377.1645.
$[\alpha]_D^{27}$ = –72.0 (*c* 1.00, CH_2Cl_2).

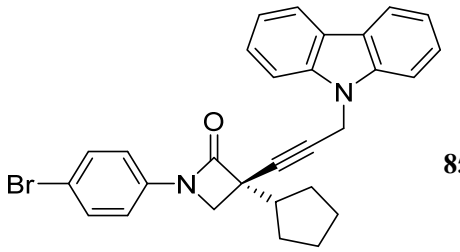
(*S*)-4-((1-Benzyl-3-(4-(*tert*-butyl)phenyl)-2-oxoazetidin-3-yl)ethynyl)benzonitrile (84)



84

According to the **general procedure E**, substrate **E84** (37.2 mg, 0.10 mmol) was employed to yield the product **84** as a white solid (27.2 mg, 65% yield, 92% e.e.).
HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 80/20, flow rate 0.80 mL/min, λ = 254 nm), t_R (minor) = 14.81 min, t_R (major) = 17.04 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.58 – 7.53 (m, 2H), 7.46 – 7.30 (m, 9H), 4.60 (d, *J* = 15.0 Hz, 1H), 4.50 (d, *J* = 14.9 Hz, 1H), 3.73 (d, *J* = 5.4 Hz, 1H), 3.53 (d, *J* = 5.3 Hz, 1H), 1.31 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 151.2, 134.8, 132.7, 132.3, 131.9, 129.0, 128.3, 128.1, 127.5, 125.9, 125.8, 118.4, 111.8, 90.5, 84.9, 56.4, 55.4, 46.5, 34.5, 31.2.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{27}N_2O$ $[M + H]^+$ 419.2118, found 419.2113.
$[\alpha]_D^{27}$ = –52.0 (*c* 1.00, CH_2Cl_2).

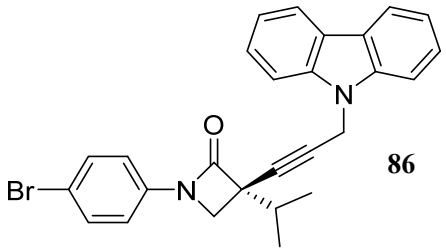
(*S*)-3-(3-(9*H*-Carbazol-9-yl)prop-1-yn-1-yl)-1-(4-bromophenyl)-3-cyclopentylazetidin-2-one (85)



85

According to the **general procedure F**, substrate **E85** (37.3 mg, 0.10 mmol) was employed to yield the product **85** as a white solid (41.2 mg, 83% yield, 86% e.e.).
HPLC analysis: Nu-Analytical Solutions INB (hexane/*i*-PrOH = 90/10, flow rate 0.80 mL/min, λ = 230 nm), t_R (major) = 26.52 min, t_R (minor) = 30.63 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.44 (m, 4H), 7.43 – 7.38 (m, 2H), 7.29 – 7.21 (m, 2H), 7.18 – 7.12 (m, 2H), 5.09 (s, 2H), 3.55 (d, *J* = 5.5 Hz, 1H), 3.41 (d, *J* = 5.5 Hz, 1H), 2.30 – 2.16 (m, 1H), 1.89 – 1.78 (m, 1H), 1.71 – 1.31 (m, 7H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 139.9, 136.9, 132.1, 125.8, 123.2, 120.4, 119.5, 118.0, 116.8, 108.8, 80.1, 80.0, 55.0, 50.7, 44.0, 32.8, 28.6, 28.5, 25.5, 25.1.
HRMS (ESI) *m/z* calcd. for $C_{29}H_{26}BrN_2O$ $[M + H]^+$ 497.1223, found 497.1225.
$[\alpha]_D^{27}$ = −18.0 (*c* 1.00, CH_2Cl_2).

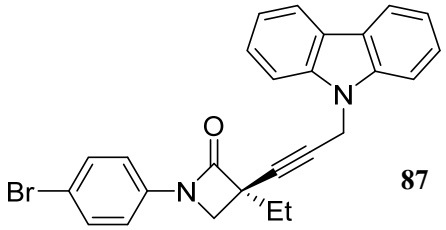
(*S*)-3-(3-(9*H*-Carbazol-9-yl)prop-1-yn-1-yl)-1-(4-bromophenyl)-3-isopropylazetidin-2-one (86)



86

According to the **general procedure F**, substrate **E86** (34.7 mg, 0.10 mmol) was employed to yield the product **86** as a white solid (42.0 mg, 89% yield, 86% e.e.).
HPLC analysis: Nu-Analytical Solutions INB (hexane/*i*-PrOH = 90/10, flow rate 0.80 mL/min, λ = 230 nm), t_R (major) = 26.09 min, t_R (minor) = 30.78 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.8 Hz, 2H), 7.54 – 7.47 (m, 4H), 7.47 – 7.41 (m, 2H), 7.33 – 7.24 (m, 2H), 7.22 – 7.16 (m, 2H), 5.13 (s, 2H), 3.54 (d, *J* = 5.6 Hz, 1H), 3.45 (d, *J* = 5.6 Hz, 1H), 2.14 – 2.02 (m, 1H), 1.13 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 139.8, 136.9, 132.1, 125.8, 123.2, 120.4, 119.5, 117.9, 116.8, 108.8, 80.6, 79.2, 56.7, 50.1, 33.1, 32.8, 18.4, 18.1.
HRMS (ESI) *m/z* calcd. for $C_{27}H_{24}BrN_2O$ $[M + H]^+$ 471.1067, found 471.1068.
$[\alpha]_D^{27}$ = −18.0 (*c* 1.00, CH_2Cl_2).

(*S*)-3-(3-(9*H*-Carbazol-9-yl)prop-1-yn-1-yl)-1-(4-bromophenyl)-3-ethylazetidin-2-one (87)

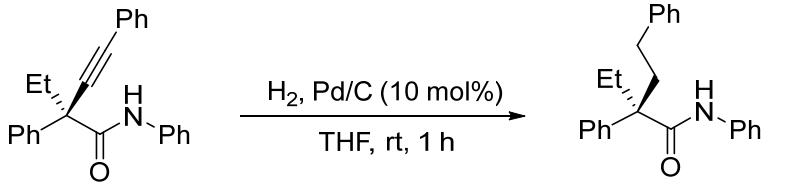


87

According to the **general procedure F**, substrate **E87** (33.3 mg, 0.10 mmol) was employed to yield the product **87** as a white solid (39.8 mg, 87% yield, 79% e.e.).
HPLC analysis: Nu-Analytical Solutions INB (hexane/*i*-PrOH = 90/10, flow rate 0.80 mL/min, λ = 230 nm), t_R (major) = 30.47 min, t_R (minor) = 37.70 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.52 – 7.45 (m, 4H), 7.45 – 7.39 (m, 2H), 7.31 – 7.23 (m, 2H), 7.19 – 7.12 (m, 2H), 5.10 (s, 2H), 3.57 (d, *J* = 5.5 Hz, 1H), 3.41 (d, *J* = 5.5 Hz, 1H), 1.99 – 1.76 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 139.8, 136.9, 132.1, 125.8, 123.1, 120.4, 119.5, 118.0, 116.8, 108.7, 80.1, 52.3, 51.1, 32.7, 28.2, 9.5.
HRMS (ESI) *m/z* calcd. for $C_{26}H_{22}BrN_2O$ $[M + H]^+$ 457.0910, found 457.0911.
$[\alpha]_D^{27}$ = –27.0 (*c* 1.00, CH_2Cl_2).

Procedure for synthetic applications (88–99)

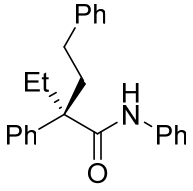
The synthesis of 88



1, 91% e.e. **88**, 96%, 91% e.e.

To a solution of **1** (33.9 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) in THF (2.0 mL) was added Pd/C (10% palladium on carbon, wet with ca. 50% water, 10.6 mg, 10 mol%). Then the reaction flask was evacuated and refilled with hydrogen through a balloon, and the mixture was stirred under a hydrogen atmosphere at room temperature for 1 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5.0 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 50/1–20/1) to give the product **88** as a white solid (32.8 mg, 96% yield, 91% e.e.).

(*R*)-2-Ethyl-*N*,2,4-triphenylbutanamide (88)



88

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 10.36 min, t_R (major) = 11.87 min.

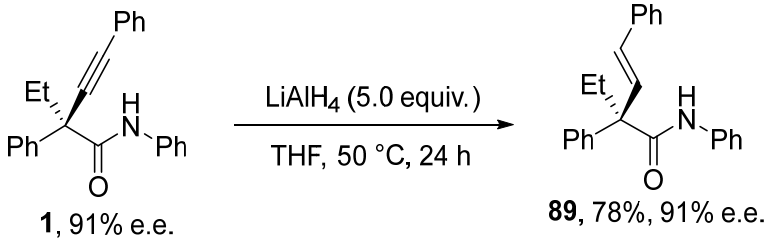
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 6H), 7.34 – 7.30 (m, 1H), 7.30 – 7.23 (m, 4H), 7.20 – 7.12 (m, 3H), 7.09 – 7.04 (m, 1H), 6.83 (s, 1H), 2.54 – 2.28 (m, 4H), 2.27 – 2.11 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 142.6, 142.1, 137.9, 128.9, 128.8, 128.4, 128.3, 127.4, 127.3, 125.9, 124.2, 119.9, 55.4, 36.9, 30.5, 28.0, 8.5.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{26}NO$ $[M + H]^+$ 344.2009, found 344.2004.

$[\alpha]_D^{27}$ = –13.0 (*c* 1.00, CH_2Cl_2).

The synthesis of 89

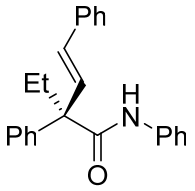


1, 91% e.e. **89**, 78%, 91% e.e.

To a solution of **1** (33.9 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) in anhydrous THF (2.0 mL) was added $LiAlH_4$ (19.0 mg, 0.50 mmol, 5.0 equiv.) in portions at 0 °C under argon

atmosphere. The resulting mixture was stirred at 50 °C for 24 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated NH_4Cl (5.0 mL), filtered through a short pad of celite and rinsed with EtOAc (5.0 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (5.0 mL × 2). The combined organic layer was washed with water (10 mL) and brine (10 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 50/1–20/1) to give **89** as a white solid (26.5 mg, 78% yield, 91% e.e.).

(*R*, *E*)-2-Ethyl-*N*,2,4-triphenylbut-3-enamide (89)



89

(*R*, *E*)-2-Ethyl-*N*,2,4-triphenylbut-3-enamide (89)

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 15.59 min, t_R (major) = 17.23 min.

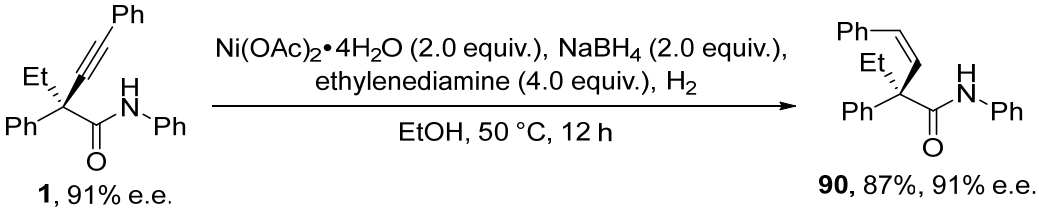
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 8H), 7.36 – 7.24 (m, 6H), 7.10 – 7.05 (m, 2H), 6.89 (d, *J* = 16.4 Hz, 1H), 6.41 (d, *J* = 16.4 Hz, 1H), 2.45 – 2.25 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 142.0, 137.8, 136.9, 132.3, 131.6, 128.93, 128.88, 128.6, 128.2, 127.8, 127.5, 126.5, 124.3, 119.8, 59.0, 31.2, 9.3.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}NO$ $[M + H]^+$ 342.1852, found 342.1847.

$[\alpha]_D^{27}$ = +1.2 (*c* 1.00, CH_2Cl_2).

The synthesis of 90



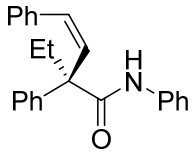
1, 91% e.e.

90, 87%, 91% e.e.

To a solution of **1** (33.9 mg, 0.10 mmol, 91% e.e.) in EtOH (2.0 mL) was added nickel(II) acetate tetrahydrate (49.8 mg, 0.20 mmol, 2.0 equiv.) and ethylenediamine (27 μL, 0.40 mmol, 4.0 equiv.) under argon atmosphere. The resulting mixture was cooled to 0 °C and $NaBH_4$ (7.6 mg, 0.20 mmol, 2.0 equiv.) was added in portions. Then the reaction flask was evacuated and refilled with hydrogen through a balloon, and the mixture was stirred under a hydrogen atmosphere at 50 °C for 12 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated NH_4Cl (5.0 mL), filtered through a short pad of celite and rinsed with EtOAc (5.0 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (5.0 mL × 2). The combined organic layer was washed with

water (10 mL) and brine (10 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 50/1–20/1) to give **90** as a colorless oil (29.7 mg, 87% yield, 91% e.e.).

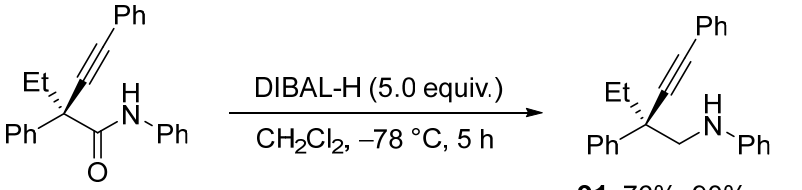
(*R*, *Z*)-2-Ethyl-*N*,2,4-triphenylbut-3-enamide (90)



90

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 9.42 min, t_R (minor) = 10.86 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.32 – 7.26 (m, 2H), 7.24 – 7.20 (m, 1H), 7.20 – 7.11 (m, 5H), 7.10 – 7.03 (m, 3H), 7.02 – 6.97 (m, 3H), 6.87 (d, *J* = 12.8 Hz, 1H), 6.46 (d, *J* = 12.8 Hz, 1H), 2.34 – 2.18 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 142.5, 137.7, 136.4, 133.0, 132.8, 128.60, 128.55, 128.5, 127.8, 127.7, 127.02, 127.00, 124.0, 119.8, 57.5, 32.3, 9.2.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}NO$ $[M + H]^+$ 342.1852, found 342.1849.
$[\alpha]_D^{27}$ = +9.5 (*c* 1.00, CH_2Cl_2).

The synthesis of 91

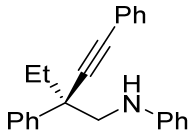


1, 91% e.e.

91, 76%, 90% e.e.

To a solution of **1** (33.9 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) in anhydrous CH_2Cl_2 (2.0 mL) was added diisobutylaluminium hydride (DIBAL-H, 1.0 M solution in *n*-hexane, 0.50 mL, 0.50 mmol, 5.0 equiv.) at −78 °C under argon atmosphere. The resulting mixture was stirred at −78 °C for 5 h. Upon completion (monitored by TLC), the reaction mixture was warmed up to room temperature and quenched by saturated NH_4Cl (5.0 mL), filtered through a short pad of celite and rinsed with CH_2Cl_2 (5.0 mL), and the filtrate was extracted with CH_2Cl_2 (5.0 mL × 2). The combined organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on neutral aluminium oxide (200–300 mesh, petroleum ether/ethyl acetate 200/1 as eluent) to give **91** as a slightly yellow oil (24.8 mg, 76% yield, 90% e.e.).

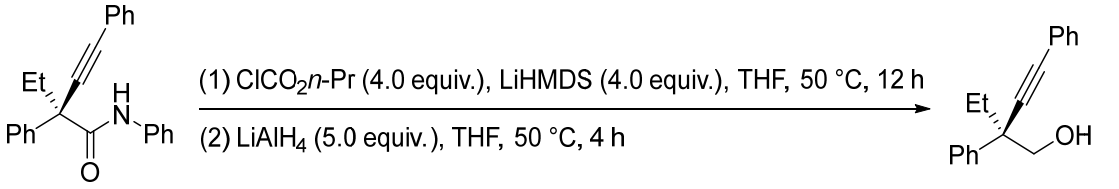
(*S*)-*N*-(2-Ethyl-2,4-diphenylbut-3-yn-1-yl)aniline (91)



91

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 99/1, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 12.10 min, t_R (major) = 13.37 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.47 – 7.43 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.29 (m, 3H), 7.29 – 7.24 (m, 1H), 7.16 – 7.10 (m, 2H), 6.69 – 6.64 (m, 1H), 6.62 – 6.59 (m, 2H), 3.83 (s, 1H), 3.60 (d, *J* = 11.7 Hz, 1H), 3.51 (d, *J* = 11.7 Hz, 1H), 2.12 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.99 (dq, *J* = 14.6, 7.3 Hz, 1H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 141.4, 131.8, 129.1, 128.5, 128.3, 128.1, 127.0, 126.9, 123.3, 117.3, 113.1, 91.6, 86.5, 54.5, 48.0, 33.0, 9.5.
HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}N$ $[M + H]^+$ 326.1903, found 326.1898.
$[\alpha]_D^{27}$ = −1.6 (*c* 1.00, CH_2Cl_2).

The synthesis of 92

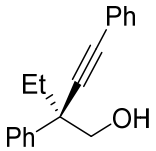


1, 91% e.e. **92**, 72%, 91% e.e.

To a solution of **1** (33.9 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) in anhydrous THF (1.0 mL) was added lithium bis(trimethylsilyl)amide (LiHMDS, 1.0 M solution in THF, 0.40 mL, 0.40 mmol, 4.0 equiv.) at room temperature under argon atmosphere. The reaction mixture was stirred for 15 min. Then the solution of propyl chloroformate (45 μL, 0.40 mmol, 4.0 equiv.) in anhydrous THF (0.60 mL) was added into the mixture dropwise via syringe. The resulting mixture was stirred at 50 °C for 12 h. Upon completion (monitored by TLC), the mixture was quenched by saturated NH_4Cl (5.0 mL), filtered through a short pad of celite and rinsed with EtOAc (5.0 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (5.0 mL × 2). The combined organic layer was washed with brine (10 mL × 2). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was directly used in the next step without further purification.

The above residue was dissolved in THF (2.0 mL), and then $LiAlH_4$ (19.0 mg, 0.50 mmol, 5.0 equiv.) was added in portions at 0 °C under argon atmosphere. The resulting mixture was stirred at 50 °C for 4 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated NH_4Cl (5.0 mL), filtered through a short pad of celite and rinsed with EtOAc (5.0 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (5.0 mL × 2). The combined organic layer was washed with water (10 mL) and brine (10 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 50/1–20/1) to give **92** as a colorless oil (18.1 mg, 72% yield over two steps, 91% e.e.).

(*S*)-2-Ethyl-2,4-diphenylbut-3-yn-1-ol (92)



92

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.41 min, t_R (major) = 8.07 min.

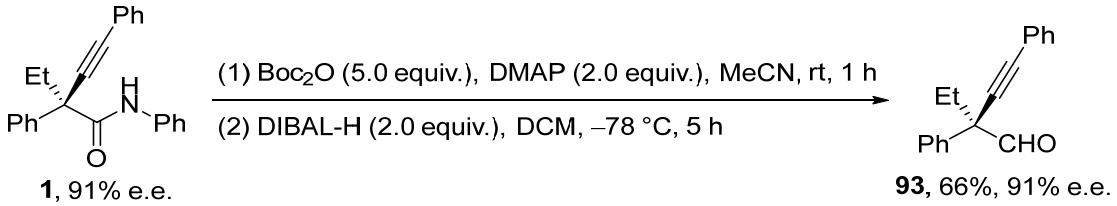
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.54 – 7.49 (m, 2H), 7.40 – 7.31 (m, 5H), 7.30 – 7.25 (m, 1H), 3.85 (d, *J* = 10.7 Hz, 1H), 3.82 (d, *J* = 10.7 Hz, 1H), 2.09 (dq, *J* = 14.5, 7.4 Hz, 1H), 1.94 (dq, *J* = 14.5, 7.4 Hz, 1H), 1.77 (br s, 1H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 131.8, 128.5, 128.3, 128.2, 127.1, 127.0, 123.2, 91.0, 86.6, 71.1, 49.9, 30.7, 9.4.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{19}O$ $[M + H]^+$ 251.1430, found 251.1433.

$[\alpha]_D^{27}$ = +1.6 (*c* 0.50, CH_2Cl_2).

The synthesis of 93



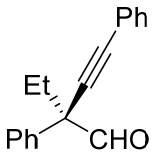
1, 91% e.e.

93, 66%, 91% e.e.

To a solution of **1** (33.9 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) and 4-dimethylamino pyridine (DMAP, 24.4 mg, 0.20 mmol, 2.0 equiv.) in anhydrous MeCN (2.0 mL) was added Boc_2O (115 μL, 0.50 mmol, 5.0 equiv.) under argon atmosphere. The resulting mixture was stirred at room temperature for 1 h. Upon completion (monitored by TLC), the reaction mixture was quenched by HCl (0.5 M, 5.0 mL) and concentrated under reduced pressure to remove the organic solvent. The remaining aqueous phase was extracted with DCM (5.0 mL × 2). The combined organic layers were washed with water (10 mL) and brine (10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was directly used in the next step without further purification.

The above residue was dissolved in anhydrous DCM (2.0 mL) and diisobutylaluminium hydride (DIBAL-H, 1.0 M solution in *n*-hexane, 0.20 mL, 0.20 mmol, 2.0 equiv.) was added at −78 °C under argon atmosphere. The resulting mixture was stirred at −78 °C for 5 h. Upon completion (monitored by TLC), the reaction mixture was warmed up to room temperature, quenched by saturated NH_4Cl (5.0 mL), filtered through a short pad of celite, and rinsed with DCM (5.0 mL). The filtrate was extracted with DCM (5.0 mL × 2). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 100/1) to give **93** as a white solid (16.3 mg, 66% yield over two steps, 91% e.e.).

(*S*)-2-Ethyl-2,4-diphenylbut-3-ynal (93)



93

HPLC analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 13.49 min, t_R (major) = 16.27 min.

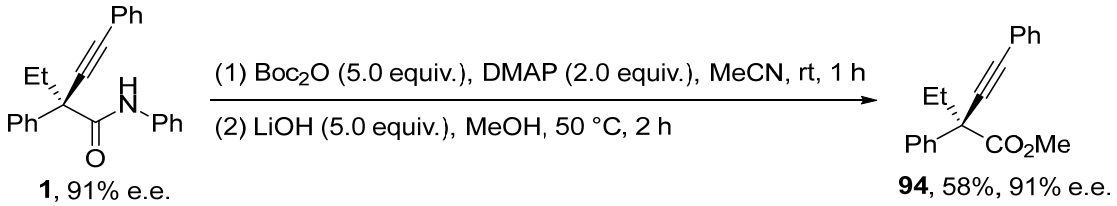
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.56 – 7.49 (m, 4H), 7.44 – 7.39 (m, 2H), 7.37 – 7.31 (m, 4H), 2.26 (dq, *J* = 14.6, 7.4 Hz, 1H), 2.05 (dq, *J* = 14.6, 7.4 Hz, 1H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 135.8, 131.9, 128.9, 128.6, 128.4, 128.0, 127.8, 122.6, 89.9, 85.8, 58.9, 29.0, 9.3.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}O_2$ $[M + H]^+$ 249.1274, found 249.1272

$[\alpha]_D^{27}$ = –21.2 (*c* 1.00, CH_2Cl_2).

The synthesis of 94

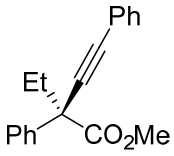


1, 91% e.e. **94**, 58%, 91% e.e.

To a solution of **1** (33.9 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) and 4-dimethylamino pyridine (DMAP, 24.4 mg, 0.20 mmol, 2.0 equiv.) in anhydrous MeCN (2.0 mL) was added Boc_2O (115 μL, 0.50 mmol, 5.0 equiv.) under argon atmosphere. The resulting mixture was stirred at room temperature for 1 h. Upon completion (monitored by TLC), the reaction mixture was quenched by HCl (0.5 M, 5.0 mL) and concentrated under reduced pressure to remove the organic solvent. The remaining aqueous phase was extracted with DCM (5.0 mL × 2). The combined organic layers were washed with water (10 mL) and brine (10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was directly used in the next step without further purification.

The above residue was dissolved in anhydrous MeOH (2.0 mL) and LiOH (12.0 mg, 0.50 mmol, 5.0 equiv.) was added at room temperature under argon atmosphere. The resulting mixture was stirred at 50 °C for 2 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated NH_4Cl (5.0 mL), filtered through a short pad of celite, and rinsed with EtOAc (5.0 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (5.0 mL × 2). The combined organic layers were washed with water (10 mL) and brine (10 mL × 2), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 100/1) to give **94** as a white solid (16.1 mg, 58% yield over two steps, 91% e.e.).

Methyl (*S*)-2-ethyl-2,4-diphenylbut-3-ynoate (94)



94

HPLC analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 98/2, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 30.92 min, t_R (major) = 34.31 min.

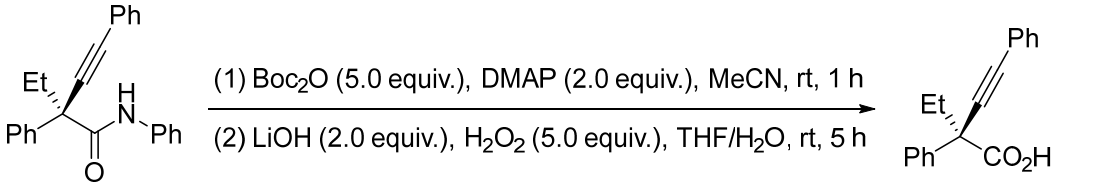
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.56 – 7.52 (m, 2H), 7.39 – 7.27 (m, 6H), 3.73 (s, 3H), 2.40 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.12 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.00 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 139.4, 131.8, 128.5, 128.3, 127.5, 126.6, 123.1, 87.9, 86.8, 53.7, 53.1, 33.4, 9.7.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{19}O_2$ $[M + H]^+$ 279.1380, found 279.1378

$[\alpha]_D^{27}$ = −7.4 (*c* 1.00, CH_2Cl_2).

The synthesis of 95



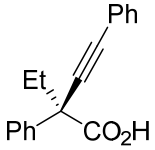
1, 91% e.e. **95**, 79%, 91% e.e.

To a solution of **1** (33.9 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) and 4-dimethylamino pyridine (DMAP, 24.4 mg, 0.20 mmol, 2.0 equiv.) in anhydrous MeCN (2.0 mL) was added Boc_2O (115 μL, 0.50 mmol, 5.0 equiv.) under argon atmosphere. The resulting mixture was stirred at room temperature for 1 h. Upon completion (monitored by TLC), the reaction mixture was quenched by HCl (0.5 M, 5.0 mL) and concentrated under reduced pressure to remove the organic solvent. The remaining aqueous phase was extracted with DCM (5.0 mL × 2). The combined organic layers were washed with water (10 mL) and brine (10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was directly used in the next step without further purification.

To a solution of the above residue in THF (1.5 mL) and H_2O (0.50 mL) was added LiOH (4.8 mg, 0.20 mmol, 2.0 equiv.) and H_2O_2 (51 μL, wt. 30% in water, 0.50 mmol, 5.0 equiv.) under argon atmosphere. The resulting mixture was stirred at room temperature for 5 h. Upon completion (monitored by TLC), the reaction mixture was quenched by aqueous solution of Na_2SO_3 (1.0 M, 0.50 mL, 0.50 mmol, 5.0 equiv.) and concentrated under reduced pressure to remove the organic solvent. The remaining aqueous phase was diluted with HCl (1.0 M, 5.0 mL) and extracted with DCM (5.0 mL × 2). The combined organic layers were washed with water (10 mL) and brine (10 mL × 2), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 5/1−3/1) to give **95** as a white solid (20.8 mg, 79% yield

over two steps, 91% e.e. and the e.e. value was determined by analyzing the esterified product **94** as described below).

(*S*)-2-Ethyl-2,4-diphenylbut-3-ynoic Acid (95)



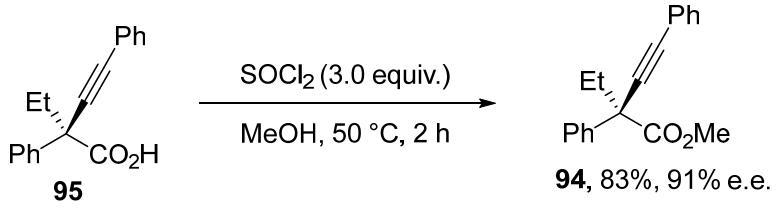
95

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 (d, J = 7.7 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.43 – 7.38 (m, 5H), 7.31 (t, J = 7.3 Hz, 1H), 2.28 (dq, J = 14.4, 7.3 Hz, 1H), 2.02 (dq, J = 14.4, 7.3 Hz, 1H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 172.8, 140.3, 131.9, 129.2, 129.0, 128.9, 127.8, 126.9, 123.0, 89.8, 86.1, 53.8, 32.9, 10.3.

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

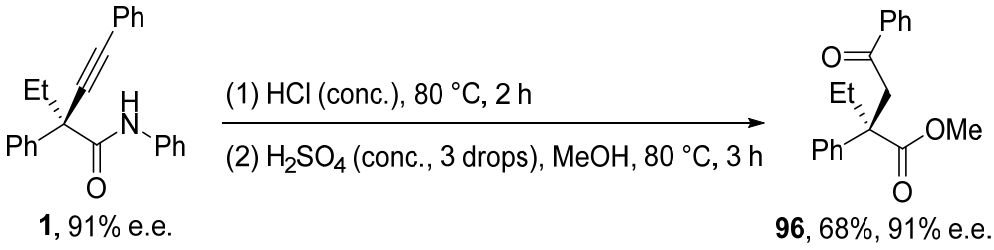
$[\alpha]_D^{27}$ = −15.0 (*c* 1.00, CH_2Cl_2).



To a solution of **95** (13.2 mg, 0.05 mmol, 1.0 equiv.) in anhydrous MeOH (1.0 mL) was slowly added $SOCl_2$ (10.9 μL, 0.15 mmol, 3.0 equiv.) at 0 °C under argon atmosphere. The resulting mixture was stirred at 50 °C for 2 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated NH_4Cl (5.0 mL) and concentrated under reduced pressure to remove the organic solvent. The remaining aqueous phase was extracted with EtOAc (5.0 mL × 2). The combined organic layers were washed with water (10 mL) and brine (10 mL × 2), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 100/1) to give **94** as a white solid (11.5 mg, 83% yield, 91% e.e.).

HPLC analysis: Chiralcel OJ-H (hexane/*i*-PrOH = 98/2, flow rate 0.40 mL/min, λ = 254 nm), t_R (minor) = 30.52 min, t_R (major) = 33.83 min.

The synthesis of 96

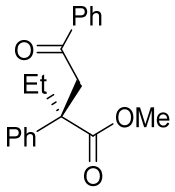


To compound **1** (33.9 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) in a reaction flask was

added concentrated hydrochloric acid (1.0 mL), and the mixture was stirred at 80 °C for 2 h. Upon completion (monitored by TLC), the reaction mixture was slowly quenched by water (5.0 mL) and extracted with CH_2Cl_2 (5.0 mL × 2). The combined organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude quaternary carboxylic acid, which was directly used in the next step without further purification.

The crude carboxylic acid was dissolved in MeOH (1.0 mL), and 3 drops of concentrated sulfuric acid was added. The resulting mixture was stirred at 80 °C for 3 h. Upon completion (monitored by TLC), the reaction mixture was diluted with water (5.0 mL) and concentrated under reduced pressure to remove the organic solvent. The remaining aqueous phase was extracted with EtOAc (5.0 mL × 2). The combined organic layer was washed with brine (10 mL × 2), dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30/1) to give **96** as a white solid (20.1 mg, 68% yield over two steps, 91% e.e.).

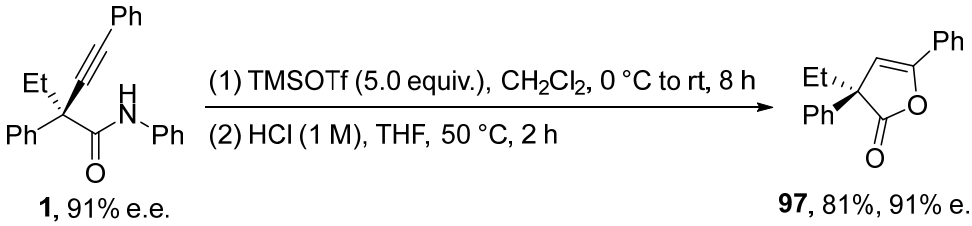
Methyl (*R*)-2-ethyl-4-oxo-2,4-diphenylbutanoate (96)



96

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.14 min, t_R (major) = 9.94 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.60 – 7.54 (m, 1H), 7.49 – 7.44 (m, 2H), 7.40 – 7.32 (m, 4H), 7.28 – 7.22 (m, 1H), 3.82 (s, 2H), 3.66 (s, 3H), 2.38 (dq, *J* = 14.8, 7.5 Hz, 1H), 2.25 (dq, *J* = 14.8, 7.5 Hz, 1H), 0.67 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 175.7, 141.4, 137.1, 133.2, 128.6, 128.5, 127.9, 127.0, 126.3, 52.2, 51.8, 42.2, 28.3, 8.7.
HRMS (ESI) *m/z* calcd. for $C_{19}H_{21}O_3$ $[M + H]^+$ 297.1485, found 297.1482.
$[\alpha]_D^{27}$ = –5.8 (*c* 1.00, CH_2Cl_2).

The synthesis of 97



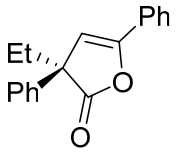
1, 91% e.e. **97**, 81%, 91% e.e.

To a solution of **1** (33.9 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) in anhydrous CH_2Cl_2 (2.0 mL) was added trimethylsilyl trifluoromethanesulfonate (TMSOTf, 90 μL, 0.50 mmol, 5.0 equiv.) at 0 °C under argon atmosphere. The resulting mixture was warmed up to room temperature and stirred for 8 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated NH_4Cl (5.0 mL), filtered through a short

pad of celite and rinsed with CH_2Cl_2 (5.0 mL). The filtrate was extracted with CH_2Cl_2 (5.0 mL × 2). The combined organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was directly used in the next step without further purification.

The above residue was dissolved in THF (1.0 mL), and then HCl (1 M, 1.0 mL) was added. The resulting mixture was stirred at 50 °C for 2 h. Upon completion (monitored by TLC), the reaction mixture was quenched by saturated NH_4Cl (5.0 mL), filtered through a short pad of celite and rinsed with EtOAc (5.0 mL). The filtrate was concentrated under reduced pressure to remove the organic solvent, and the remaining aqueous phase was extracted with EtOAc (5.0 mL × 2). The combined organic layer was washed with water (10 mL) and brine (10 mL × 2), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 100/1–50/1) to give **97** as a white solid (21.3 mg, 81% yield over two steps, 91% e.e.).

(*R*)-3-Ethyl-3,5-diphenylfuran-2(3*H*)-one (97)



97

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 7.98 min, t_R (major) = 13.99 min.

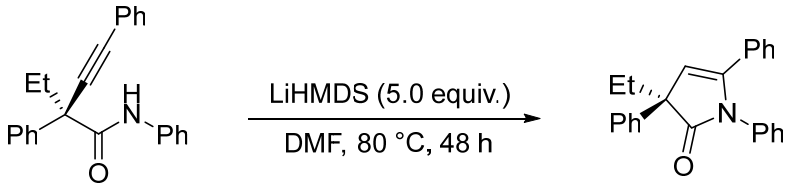
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.53 – 7.49 (m, 2H), 7.46 – 7.39 (m, 3H), 7.39 – 7.34 (m, 2H), 7.31 – 7.26 (m, 1H), 6.12 (s, 1H), 2.28 – 2.10 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 152.2, 139.0, 129.8, 128.8, 128.7, 128.2, 127.7, 126.5, 125.0, 105.7, 57.7, 32.6, 9.5.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}O_2$ $[M + H]^+$ 265.1223, found 265.1219.

$[\alpha]_D^{27}$ = –52.0 (*c* 1.00, CH_2Cl_2).

The synthesis of 98

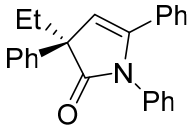


1, 91% e.e. → **98**, 83%, 91% e.e.

To a solution of **1** (33.9 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) in anhydrous DMF (2.0 mL) was added lithium hexamethyldisilazide (LiHMDS, 1.0 M solution in THF, 0.50 mL, 0.50 mmol, 5.0 equiv.) at room temperature under argon atmosphere. Then the reaction mixture was stirred at 80 °C for 48 h. After cooling down to room temperature, the mixture was quenched by saturated NH_4Cl (5.0 mL), filtered through a short pad of celite and rinsed with EtOAc (5.0 mL). The filtrate was extracted with EtOAc (5.0 mL × 2). The combined organic layers were washed with brine (10 mL × 3). The organic

layer was separated, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 50/1 as eluent) to give **98** as a white solid (28.0 mg, 83% yield, 91% e.e.).

(*R*)-3-Ethyl-1,3,5-triphenyl-1,3-dihydro-2*H*-pyrrol-2-one (98)



98

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 15.84 min, t_R (minor) = 19.22 min.

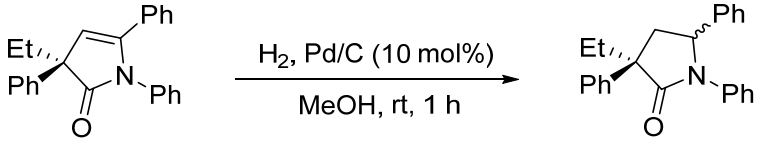
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.38 – 7.33 (m, 2H), 7.29 – 7.23 (m, 6H), 7.21 – 7.16 (m, 3H), 7.06 – 7.02 (m, 2H), 5.87 (s, 1H), 2.30 – 2.11 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 144.3, 140.2, 135.6, 131.2, 128.6, 128.5, 128.2, 127.6, 127.1, 126.9, 126.8, 126.7, 112.3, 58.3, 32.4, 9.4.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{22}NO$ $[M + H]^+$ 340.1696, found 340.1691.

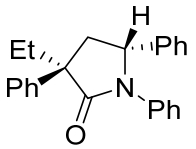
$[\alpha]_D^{27}$ = +33.0 (*c* 1.00, CH_2Cl_2).

The synthesis of 99



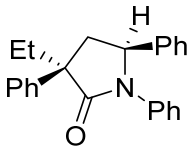
98, 91% e.e. **99**, 92%, 3.4:1 d.r., 91%/91% e.e.

To a solution of **98** (33.9 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) in MeOH (2.0 mL) was added Pd/C (10% palladium on carbon, wet with ca. 50% water, 10.6 mg, 10 mol%). Then the reaction flask was evacuated and refilled with hydrogen through a balloon, and the mixture was stirred under a hydrogen atmosphere at room temperature for 1 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short pad of celite and rinsed with EtOAc (5.0 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (gradient eluent: petroleum ether/ethyl acetate 30/1–20/1) to give the product **99** as two diastereoisomers (31.3 mg, d.r. = 3.4:1, 92% total yield).



99-1

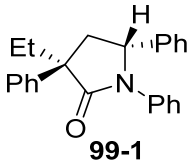
The major isomer, as a white solid, 24.2 mg, 71% yield, 91% e.e.



99-2

The minor isomer, as a white solid, 7.1 mg, 21% yield, 91% e.e.

(3*R*,5*R*)-3-Ethyl-1,3,5-triphenylpyrrolidin-2-one (99-1)



99-1

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 22.42 min, t_R (minor) = 25.32 min.

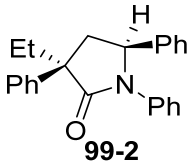
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.22 (m, 5H), 7.21 – 7.14 (m, 5H), 7.00 (t, *J* = 7.4 Hz, 1H), 5.03 (dd, *J* = 9.9, 6.1 Hz, 1H), 2.99 (dd, *J* = 13.2, 6.1 Hz, 1H), 2.19 (dd, *J* = 13.2, 9.9 Hz, 1H), 2.17 – 2.01 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 140.72, 140.71, 137.8, 128.8, 128.7, 128.4, 127.7, 127.1, 126.7, 126.6, 125.0, 123.2, 60.4, 54.0, 42.0, 32.3, 9.2.

HRMS (ESI) *m/z* calcd. For $C_{24}H_{24}NO$ $[M + H]^+$ 342.1852, found 342.1847.

$[\alpha]_D^{27}$ = +18.6 (*c* 0.50, CH_2Cl_2).

(3*R*,5*S*)-3-Ethyl-1,3,5-triphenylpyrrolidin-2-one (99-2)



99-2

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 23.46 min, t_R (major) = 26.18 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.43 – 7.39 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.20 (m, 3H), 7.18 – 7.08 (m, 5H), 7.07 – 7.02 (m, 1H), 5.27 (t, *J* = 7.3 Hz, 1H), 2.87 (dd, *J* = 13.2, 7.8 Hz, 1H), 2.52 (dd, *J* = 13.2, 6.9 Hz, 1H), 2.15 – 1.95 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

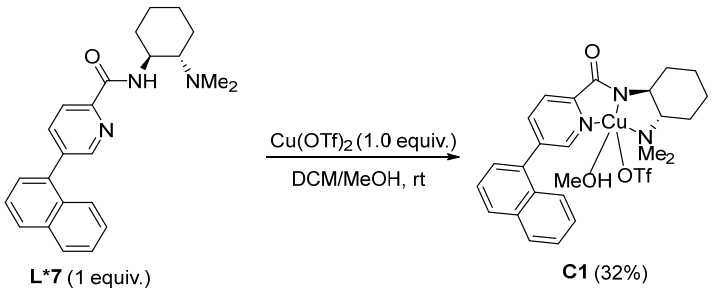
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 142.3, 140.9, 138.1, 128.59, 128.55, 128.1, 127.5, 126.8, 126.6, 126.5, 125.1, 122.9, 60.5, 52.7, 41.2, 32.9, 9.2.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}NO$ $[M + H]^+$ 342.1852, found 342.1849.

$[\alpha]_D^{27}$ = +30.0 (*c* 1.00, CH_2Cl_2).

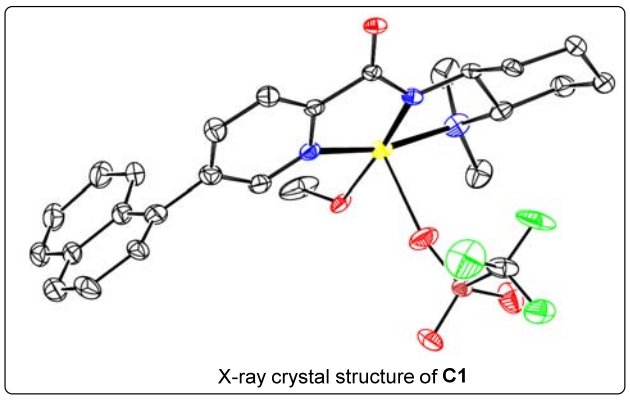
Mechanistic studies

1. Preparation and X-ray crystal structure of complex C1.



L*7 (1 equiv.)

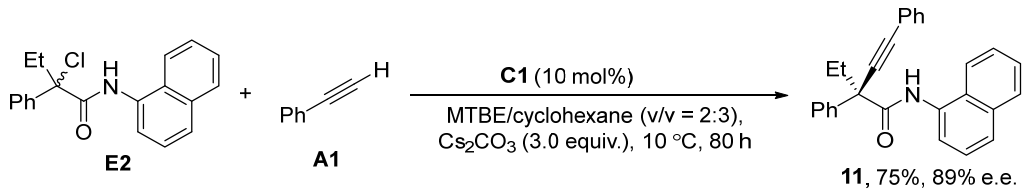
C1 (32%)



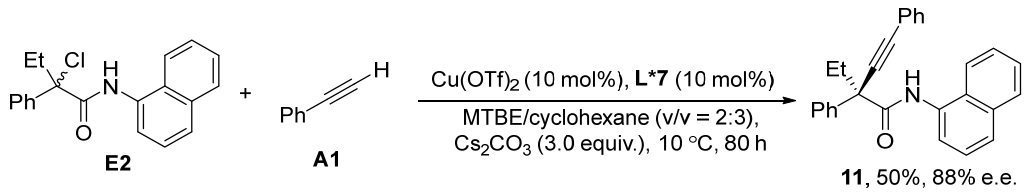
X-ray crystal structure of **C1**

A CH_2Cl_2/MeOH solution (v/v = 6/1, 3.5 mL) of $Cu(OTf)_2$ (18.1 mg, 0.05 mmol, 1.0 equiv.) and **L*7** (18.7 mg, 0.05 mmol, 1.0 equiv.) was stirred at room temperature for 0.5 h, to give a clear solution. Slow diffusion of Et_2O into the obtained solution to give blue crystals. The product was filtered and washed by a small amount of Et_2O (9.9 mg 32% yield).

2. The catalytic activity of complex C1.

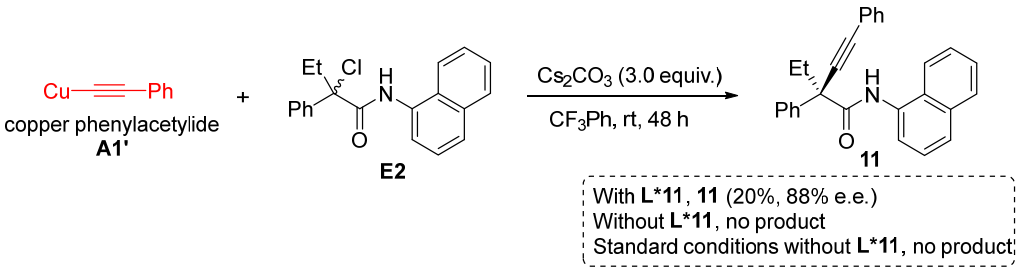


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **C1** (6.2 mg, 0.010 mmol, 10 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and MTBE/cyclohexane (v/v = 2/3, 2.0 mL). Then, **E2** (0.10 mmol, 1.0 equiv.) and **A1** (0.15 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 10 °C for 80 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to afford the desired product **11** as a colorless oil (29.2 mg, 75%, 89% e.e.).



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OTf)_2$ (3.6 mg, 0.010 mmol, 10 mol%), **L*7** (3.7 mg, 0.010 mmol, 10 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and MTBE/cyclohexane (v/v = 2/3, 2.0 mL). Then, **E2** (0.10 mmol, 1.0 equiv.) and **A1** (0.15 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 10 °C for 80 h. Upon completion, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to afford the desired product **11** as a colorless oil (19.5 mg, 50%, 88% e.e.).

3. The effect of ligand and copper phenylacetylide on the reaction initiation.

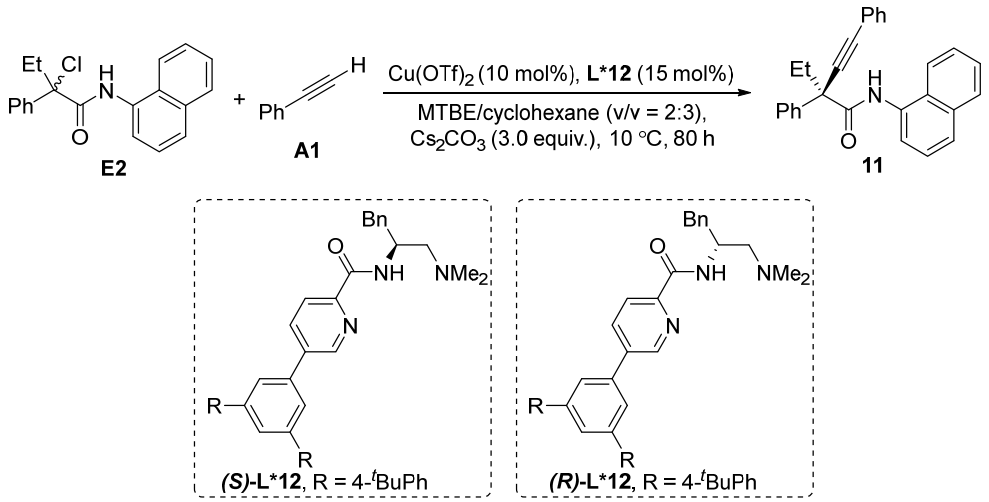


Copper phenylacetylide **98** was synthesized according to literature[3].

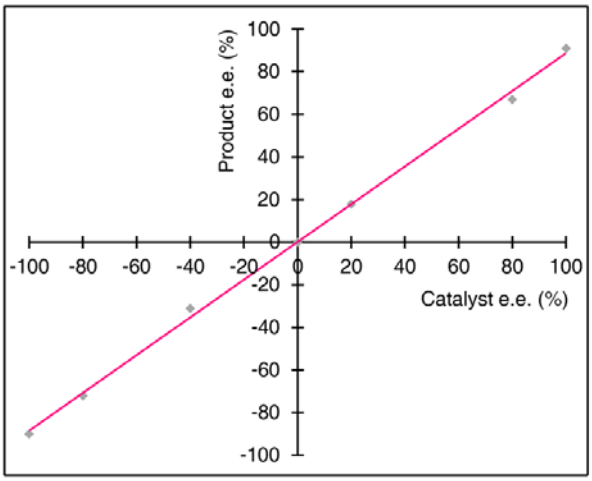
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with copper phenylacetylide **A1′** (16.5 mg, 0.10 mmol, 1.0 equiv.), **E2** (32.4 mg, 0.10 mmol, 1.0 equiv.), **L*11** (58.8 mg, 0.10 mmol, 1.0 equiv.), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and anhydrous CF_3Ph (2.0 mL). The resulting reaction mixture was stirred at room temperature for 48 h. Upon completion, the reaction mixture was filtered and washed by CH_2Cl_2. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to afford **11** (7.8 mg, 20% yield, 88% e.e.).

The procedure for the reaction without **L*11** was the same with that described above except that **L*11** was not added. No desired product **11** was observed.

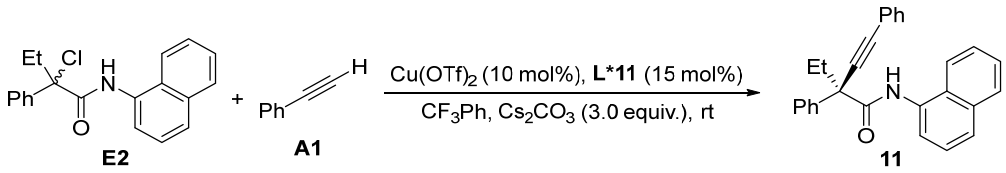
4. The non-linear effect of catalyst.



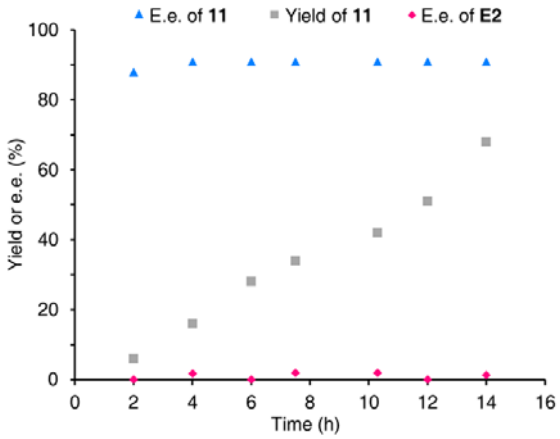
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OTf)_2$ (1.8 mg, 0.005 mmol, 10 mol%), **L*12** (4.7 mg, 0.0075 mmol, 15 mol%), Cs_2CO_3 (49.0 mg, 0.15 mmol, 3.0 equiv.), and MTBE/cyclohexane (v/v = 2/3, 1.0 mL). Then, alkyl halide **E2** (0.05 mmol, 1.0 equiv.) and alkyne **A1** (0.075 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 10 °C for 80 h. Upon completion, the product was separated by preparative TLC. The e.e. values of products were then determined by HPLC, which indicated a linear relationship between e.e. values of products and corresponding catalysts. The catalyst **L*12** with different e.e. values were prepared by mixing **(*S*)-L*12** (99% e.e.) and ***(R)*-L*12** (99% e.e.) in appropriate ratios.



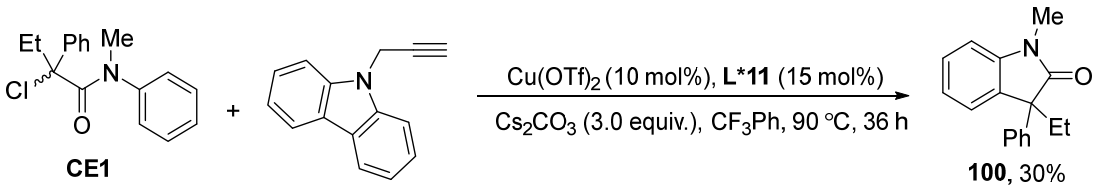
5. The stereochemistry of alkyl halide and product during the reaction.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OTf)_2$ (1.8 mg, 0.005 mmol, 10 mol%), **L*11** (4.4 mg, 0.0075 mmol, 15 mol%), Cs_2CO_3 (49.0 mg, 0.15 mmol, 3.0 equiv.), and CF_3Ph (1.0 mL). Then, alkyl halide **E2** (0.05 mmol, 1.0 equiv.) and alkyne **A1** (0.075 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at room temperature for appropriate time. Upon completion, the reaction was quenched with H_2O and extracted with EtOAc. The combined organic layer was concentrated to afford crude product. The residue was analyzed by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. The product was then separated by preparative TLC. The e.e. values of **11** and recovered **E2** were determined by HPLC analysis.



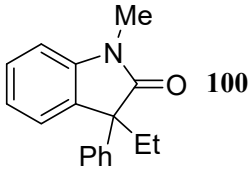
6. Radical clock experiments.



Substrate **CE1** is a known compound and was prepared according to the literature procedure[1].

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OTf)_2$ (3.6 mg, 0.010 mmol, 10 mol%), **L*11** (8.8 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and CF_3Ph (2.0 mL). Then, **CE1** (0.10 mmol, 1.0 equiv.) and alkyne (0.15 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 90 °C for 36 h. The mixture was then allowed to cool to room temperature, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **100** (7.5 mg, 30% yield). Characterization data is consistent with the reported one[4].

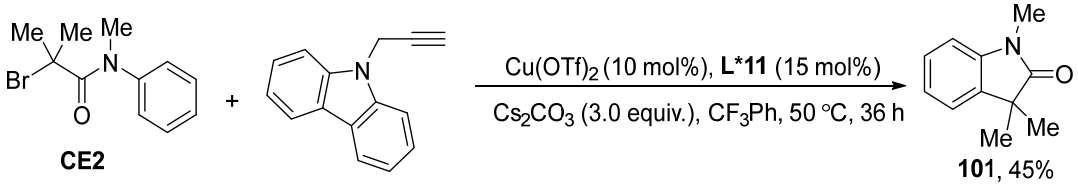
3-Ethyl-1-methyl-3-phenylindolin-2-one (100)



100

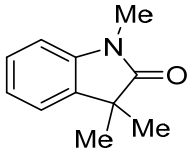
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 5H), 7.25 – 7.20 (m, 2H), 7.12 (td, J = 7.5, 1.0 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 3.23 (s, 3H), 2.43 (dq, J = 13.3, 7.3 Hz, 1H), 2.24 (dq, J = 13.3, 7.4 Hz, 1H), 0.69 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 144.1, 140.2, 132.0, 128.5, 128.1, 127.2, 126.9, 124.8, 122.5, 108.1, 57.3, 30.9, 26.3, 9.0.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $Cu(OTf)_2$ (3.6 mg, 0.010 mmol, 10 mol%), **L*11** (8.8 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (98.0 mg, 0.30 mmol, 3.0 equiv.), and CF_3Ph (2.0 mL). Then, **CE2** (0.10 mmol, 1.0 equiv.) and alkyne (0.15 mmol, 1.5 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at 50 °C for 36 h. The mixture was then allowed to cool to room temperature, the precipitate was filtered off and washed by CH_2Cl_2. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **101** (7.9 mg, 45% yield). Characterization data is consistent with the reported one[5].

1,3,3-Trimethylindolin-2-one (101)



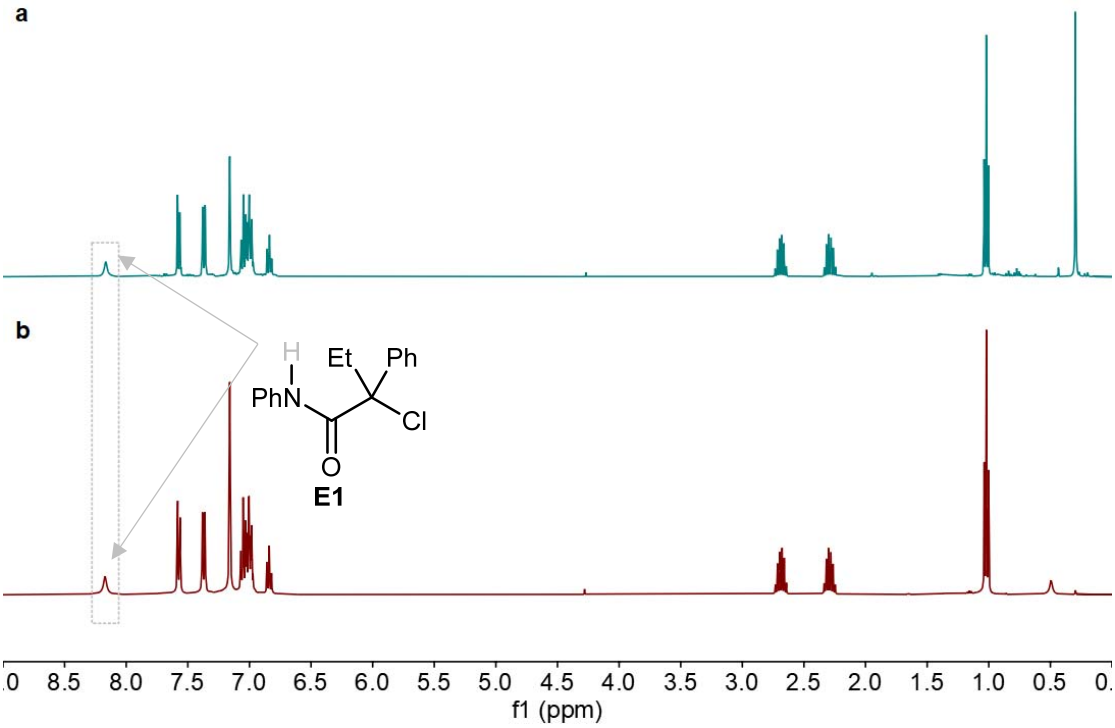
101

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.06 (t, *J* = 7.5, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.21 (s, 3H), 1.37 (s, 6H).

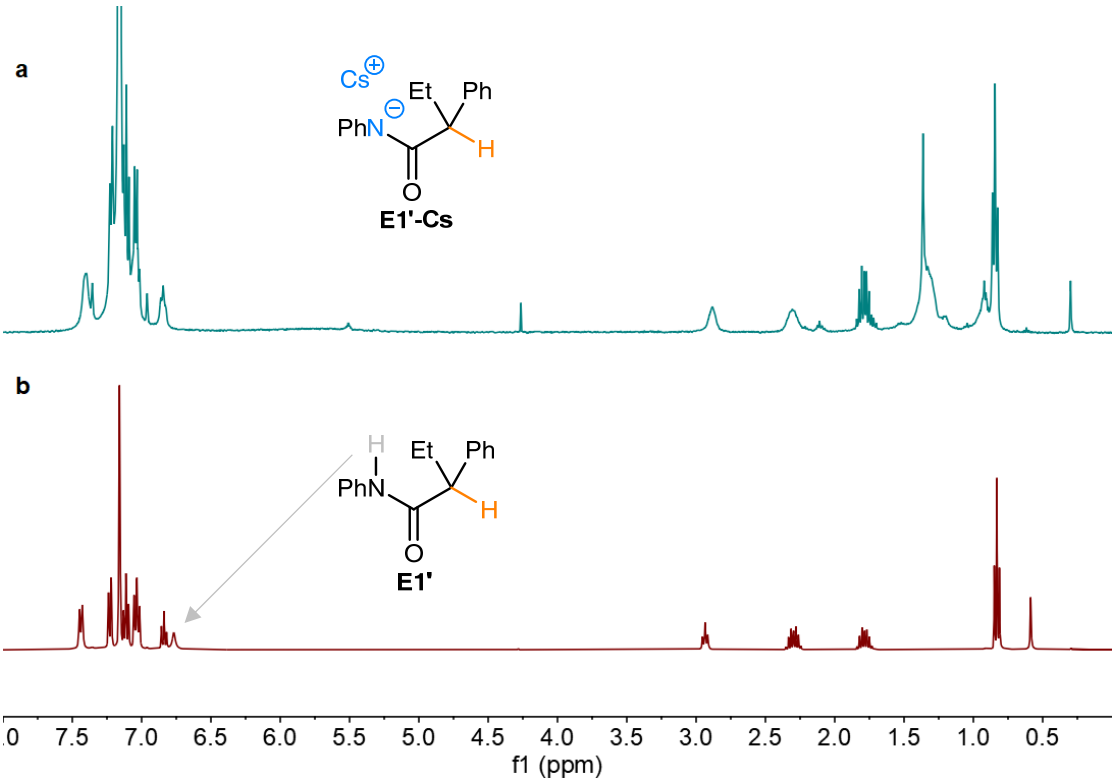
^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 142.6, 135.8, 127.6, 122.4, 122.2, 108.0, 44.1, 26.2, 24.3.

7. NMR experiments.

We initially failed to observe the disappearance of the NH peak in the ^{1}H NMR spectrum of the reaction mixture of **E1** and Cs_2CO_3 in benzene-d_6 after stirring for 2.0 h and filtration (Supplementary Fig. 7-1). In fact, only tiny new peaks belonging to trace amounts of unidentified compounds appeared in the ^{1}H NMR spectrum of the reaction mixture. We further took the ^{1}H NMR spectrum of a model cesium salt **E1'-Cs** in benzene-d_6 and observed only tiny peaks corresponding to the CH moieties in **E1'** (Supplementary Fig. 7-2). The NH peak of **E1'** was missing, likely due to relatively fast proton exchange processes that resulted in significant peak broadening. The **E1'** might be the residual starting material in the cesium salt or might be in situ generated through reprotonation of the cesium salt by adventitious water. All in all, these results indicate very low solubility of the cesium salt, which might have prevented us from observing corresponding peaks in the ^{1}H NMR spectrum.

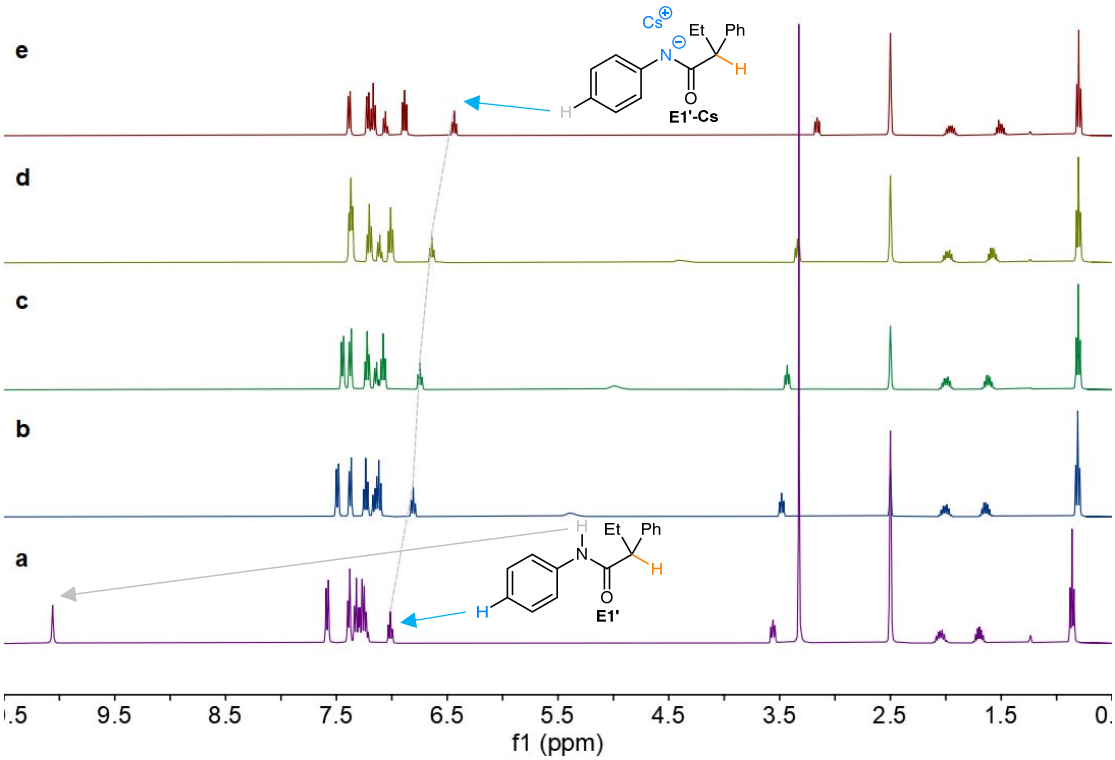


Supplementary Fig. 7-1 ^{1}H-NMR studies (400 MHz) of E1 with Cs_2CO_3 in benzene-d_6. a, ^{1}H-NMR spectrum of the reaction mixture of **E1** (0.025 mmol) with Cs_2CO_3 (3.0 equiv.) in benzene-d_6 (0.50 mL) after stirring at room temperature for 2.0 h followed by filtration under argon. **b**, ^{1}H-NMR spectrum of **E1** (50 mM) in benzene-d_6.

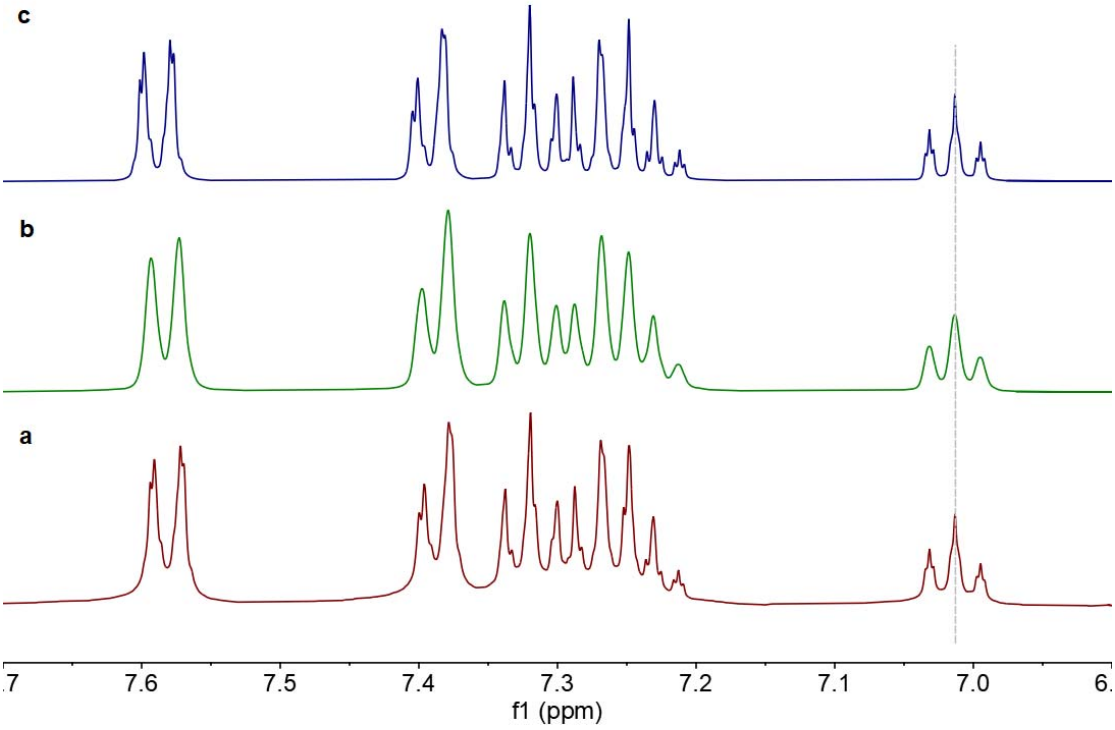


Supplementary Fig. 7-2 ^{1}H-NMR studies of E1'-Cs in benzene-d_6. a, ^{1}H-NMR spectrum of **E1'-Cs** in benzene-d_6. **b**, ^{1}H-NMR spectrum of **E1'** in benzene-d_6.

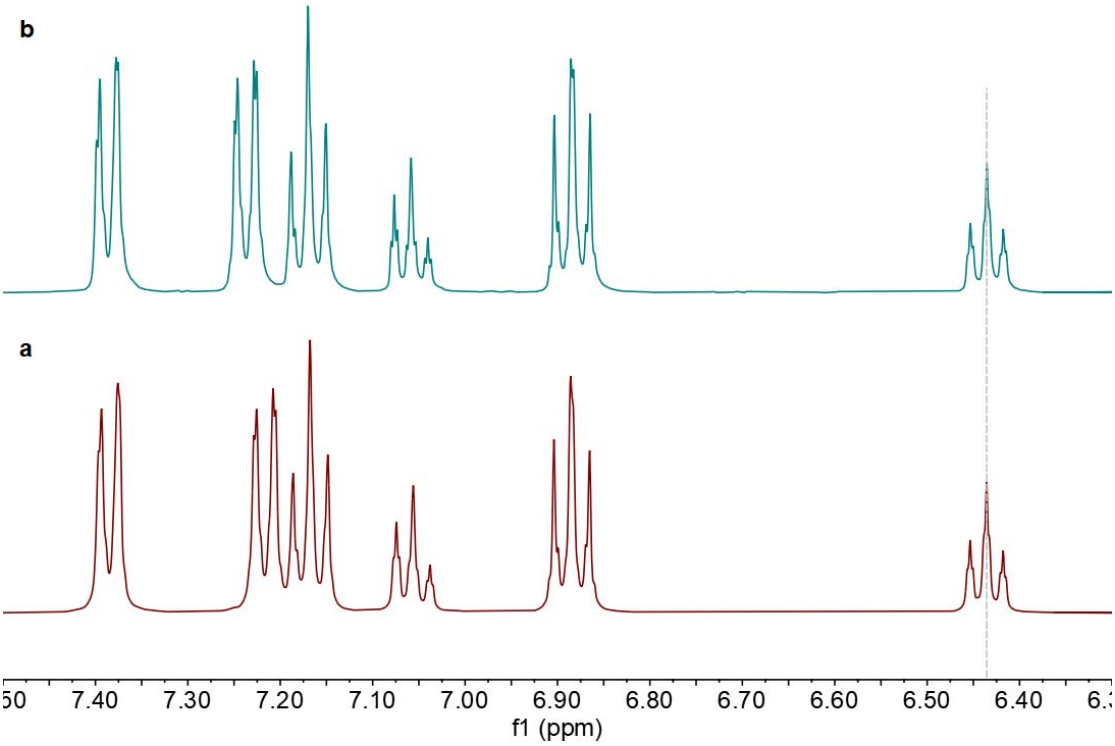
In view of the low solubility issue above mentioned, we next changed the deuterated solvent to DMSO-d_6 given its commonly high capacity for dissolving salts. Besides, DMSO is also one of the most used solvent for determining and reporting p*K*a values[6]. However, α-halo amides are not stable in strongly polar solvents such like DMSO and can readily undergo side reactions, e.g., elimination in the presence of base. Accordingly, we employed the model compound **E1'** again for the following NMR studies to give a lower estimate of the acidity of **E1**[7]. We found that the cesium salt **E1'-Cs** readily dissolved in DMSO-d_6. The subsequent ^{1}H NMR spectra (Supplementary Fig. 7-3) of a series of mixtures of **E1'** with increasing amounts (0.67 to 2.0 equiv.) of **E1'-Cs** revealed gradual upfield shifting of the peak corresponding to the *para*-CH on the aniline ring (7.01 to 6.64 ppm). The appearance of only one set of ^{1}H NMR peaks in the spectra of the mixtures indicated very fast exchange between **E1'** and **E1'-Cs**. The absence of the NH peak in the spectra of the mixtures was due to fast exchange of the proton with deuterium or Cs. We further confirmed that the chemical shift of this CH moiety was not concentration-dependent for either **E1'** or **E1'-Cs** alone (Supplementary Figs. 7-4 and 7-5). In summary, the chemical shift of the *para*-CH on the aniline ring proved to be a good indicator for the formation of **E1'-Cs** in the presence of **E1'**[6].



Supplementary Fig. 7-3 ^{1}H-NMR studies of E1' with E1'-Cs (298K, 400 MHz, DMSO-*d*$_6$). a, **E1'** (25 mM). **b**, **E1'** (75 mM) with 0.67 equiv. of **E1'-Cs** (50 mM). **c**, **E1'** (50 mM) with 1.0 equiv. of **E1'-Cs** (50 mM). **d**, **E1'** (25 mM) with 2.0 equiv. of **E1'-Cs** (50 mM). **e**, **E1'-Cs** (50 mM).

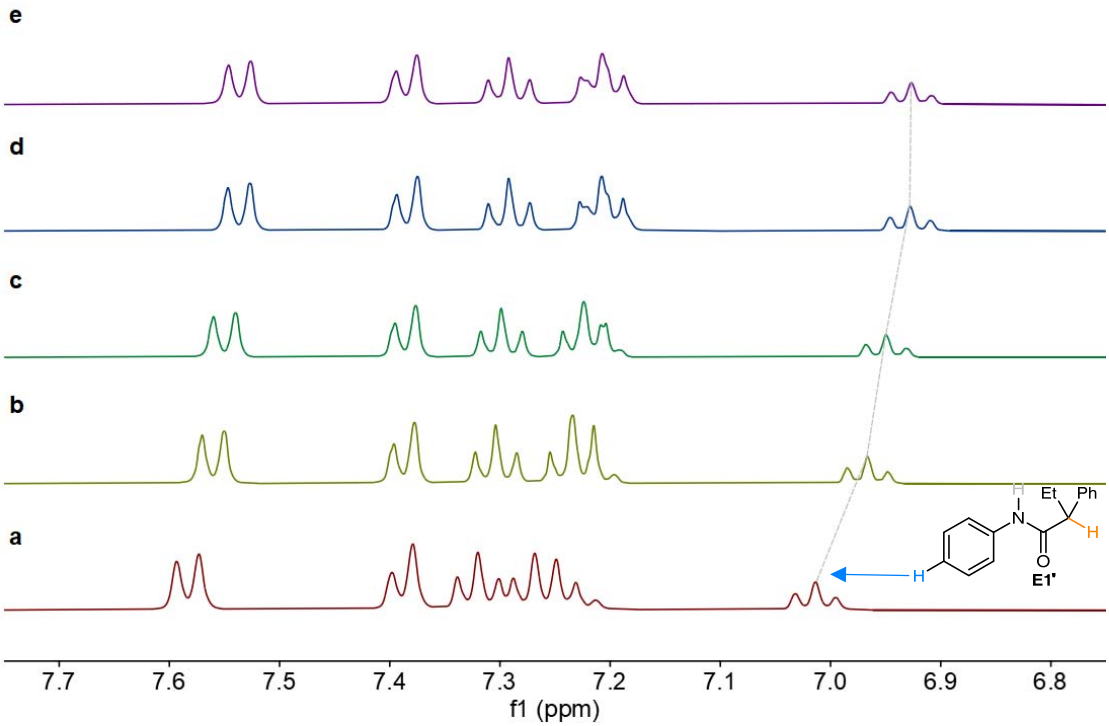


Supplementary Fig. 7-4 ^{1}H-NMR studies of different concentrations of E1' (298K, 400 MHz, DMSO-*d*$_6$). a, 5.0 mM. **b**, 25 mM. **c**, 75 mM.



Supplementary Fig. 7-5 ^{1}H-NMR studies of different concentrations of E1'-Cs (298K, 400 MHz, DMSO-d_6). a, 50 mM. **b**, 10 mM.

In the following study, we observed gradual up-field shifting (7.01 to 6.93 ppm) of this CH peak in the ^{1}H NMR spectra of a series of mixtures containing **E1'** and increasing amounts (0.50 to 3.0 equiv.) of Cs_2CO_3 (Supplementary Fig. 7-6). The trend leveled off from 2.0 to 3.0 equiv. of Cs_2CO_3, possibly due to the saturation of this salt or $CsHCO_3$ in DMSO-d_6. By fitting the data shown in Supplementary Fig. 7-3 using an exponential decay model (Supplementary Table 7-1 and Fig. 7-7)[6], we estimated that ca. 19% of the **E1'** was deprotonated to form **E1'-Cs** in the presence of 3.0 equiv. of Cs_2CO_3 (chemical shift: 6.93 ppm; ratio: 0.24). Due to the electron-withdrawing inductive effect of the chloro group in **E1**, its acidity is likely higher than that of **E1'**[7]. And thus, under the same conditions, a higher portion of **E1** should be deprotonated by 3.0 equiv. of Cs_2CO_3. To sum up, these ^{1}H NMR studies indicate that Cs_2CO_3 is indeed basic enough to at least partially deprotonate the substrate, leading to the corresponding cesium salt for subsequent reactions.

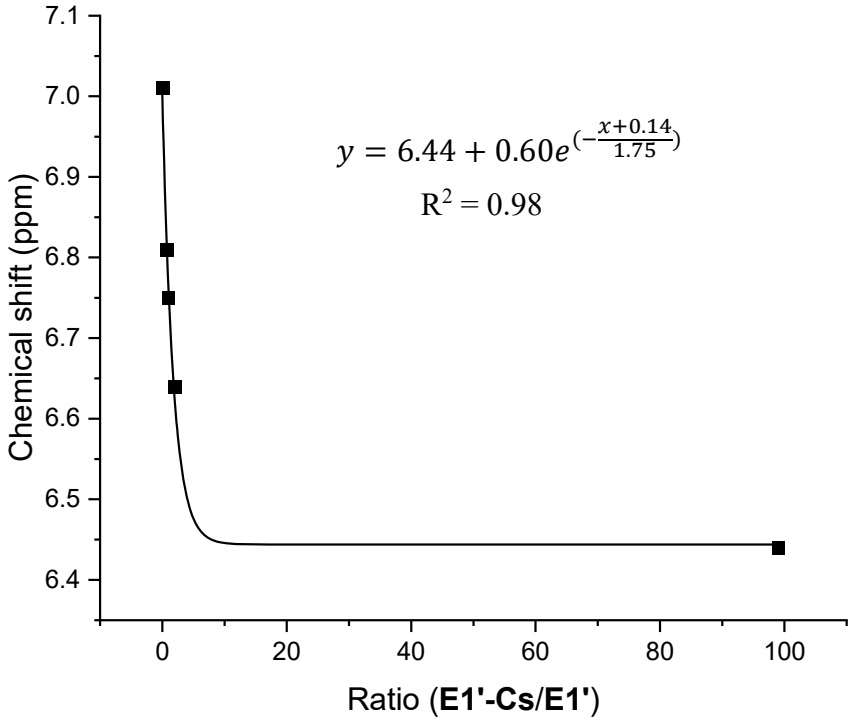


Supplementary Fig. 7-6 ^{1}H-NMR studies of E1' (25 mM, 298K, 400 MHz, DMSO-*d*$_6$) with Cs_2CO_3. a, E1'. b, E1' with 0.50 equiv. of Cs_2CO_3. **c, E1'** with 1.0 equiv. of Cs_2CO_3. **d, E1'** with 2.0 equiv. of Cs_2CO_3. **e, E1'** with 3.0 equiv. of Cs_2CO_3.

Supplementary Table 7-1 The ratio-dependent chemical shifts of the *para*-CH on the aniline ring

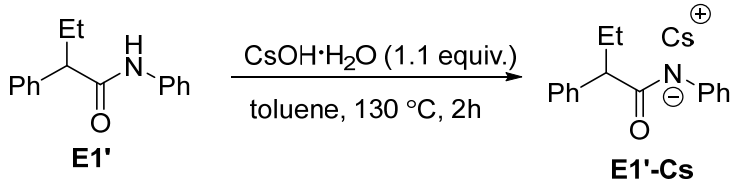
Ratio (**E1'-Cs/E1'**)	Chemical shifts/ppm
0	7.01
0.67	6.81
1.0	6.75
2.0	6.64
99[a]	6.44

[a]The ratio for pure **E1'-Cs** was presumed to be 99 as a lower estimation for the ease of data fitting.



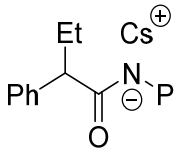
Supplementary Fig. 7-7 Data fitting using an exponential decay model.

The synthesis of E1'-Cs



A 100 mL round bottom flask equipped with a magnetic stir bar and Dean-Stark apparatus was charged with **E1'** (239 mg, 1.0 mmol), CsOH·H_2O (185 mg, 1.1 mmol), and toluene (40 mL). Then the resulting mixture was refluxed at 130 °C for 2 h to remove water. Upon completion, the reaction mixture was concentrated to afford the crude product. The residue was analyzed by ^{1}H NMR spectroscopy without further purification.

Cesium phenyl(2-phenylbutanoyl)amide (E1'-Cs)



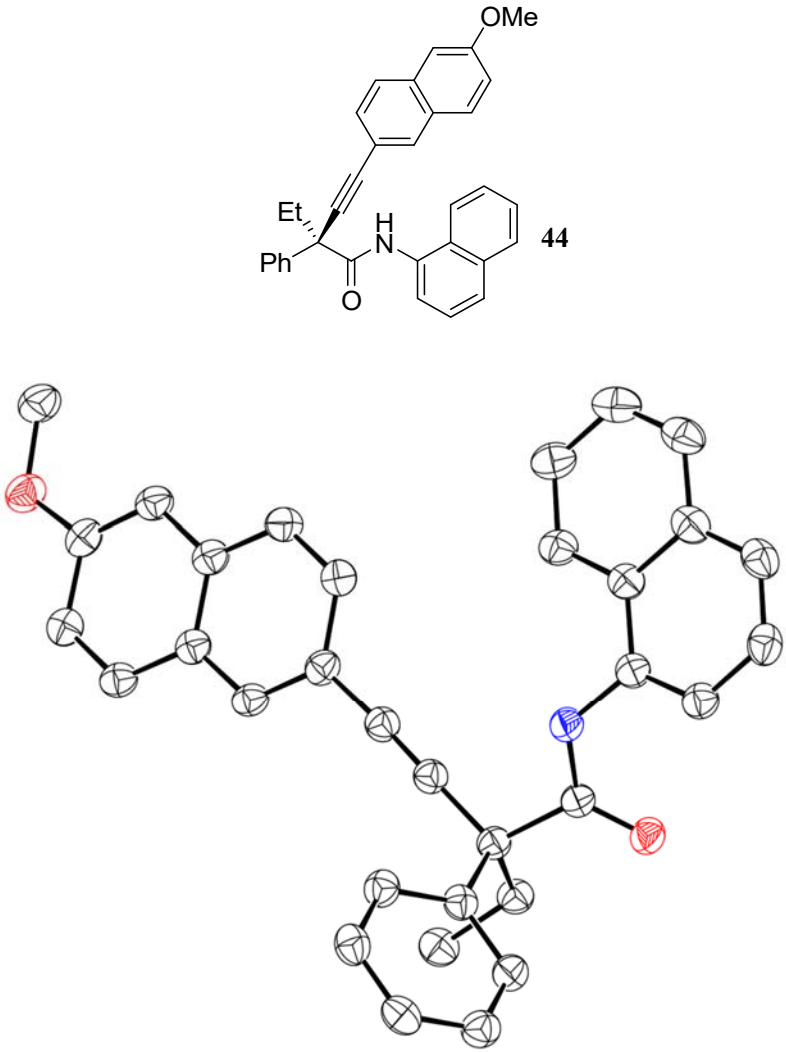
E1'-Cs

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 – 7.33 (m, 2H), 7.25 – 7.19 (m, 2H), 7.17 (t, J = 7.6 Hz, 2H), 7.09 – 7.02 (m, 1H), 6.93 – 6.84 (m, 2H), 6.44 (tt, J = 7.1, 1.3 Hz, 1H),

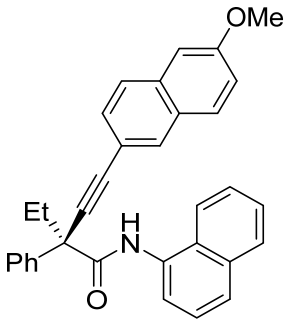
3.16 (dd, J = 8.5, 6.6 Hz, 1H), 2.03 – 1.88 (m, 1H), 1.57 – 1.44 (m, 1H), 0.80 (t, J = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 173.5, 155.4, 146.3, 128.0, 127.2, 127.0, 124.7, 123.7, 116.2, 58.1, 27.9, 13.1.

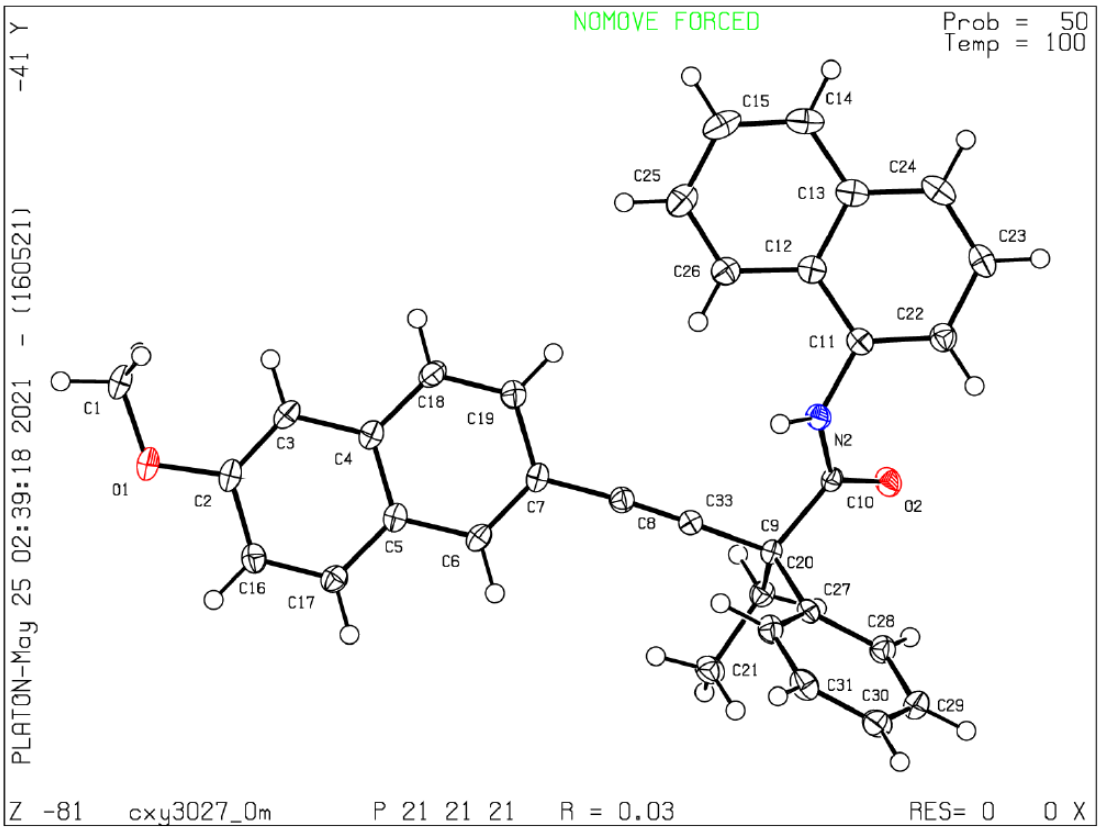
X-ray crystallography



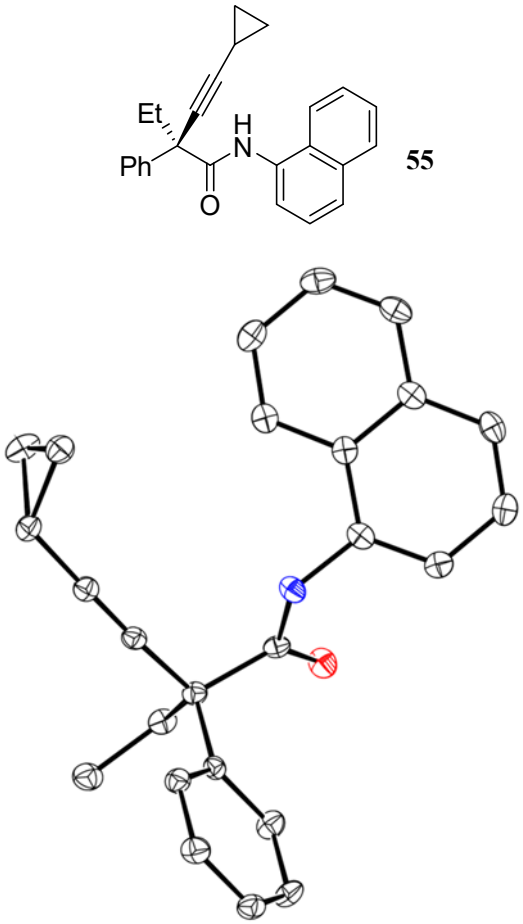
Supplementary Fig. 7 The X-ray structure of 44.



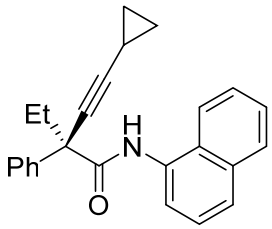
44, CCDC 2074298



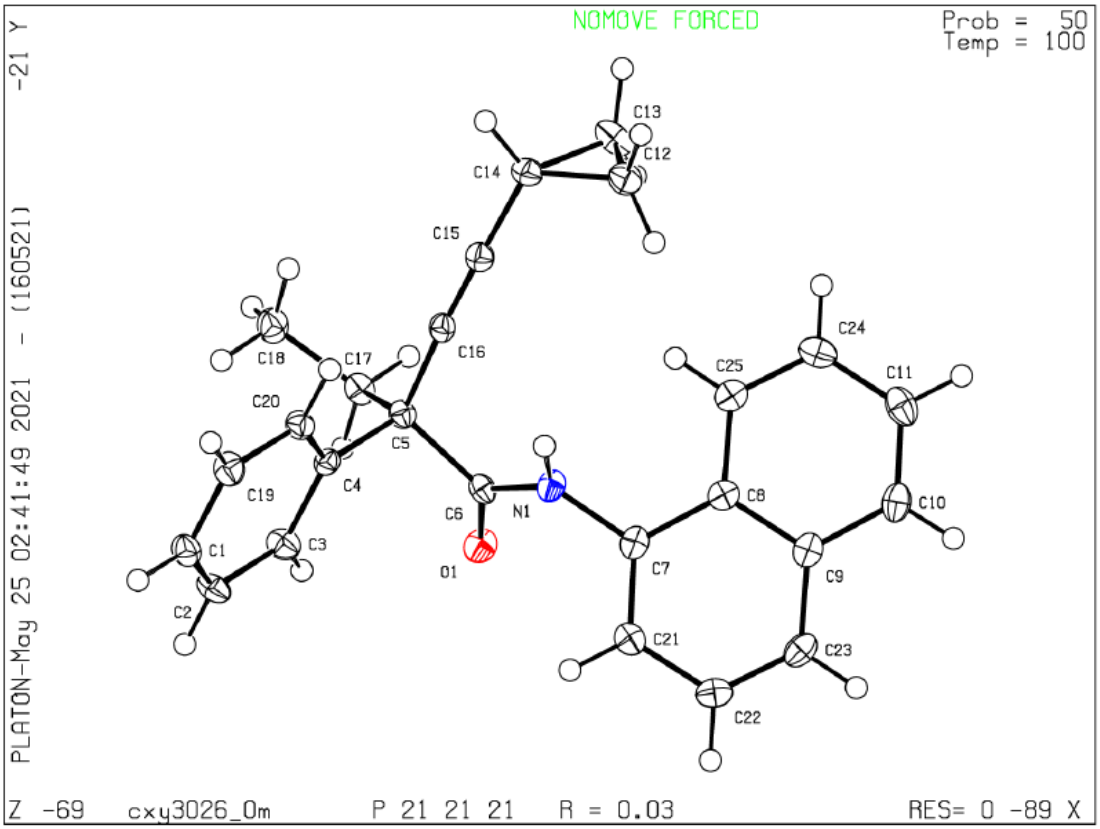
Supplementary Fig. 7' The X-ray structure of **44** (CCDC 2074298, 50% probability ellipsoids).



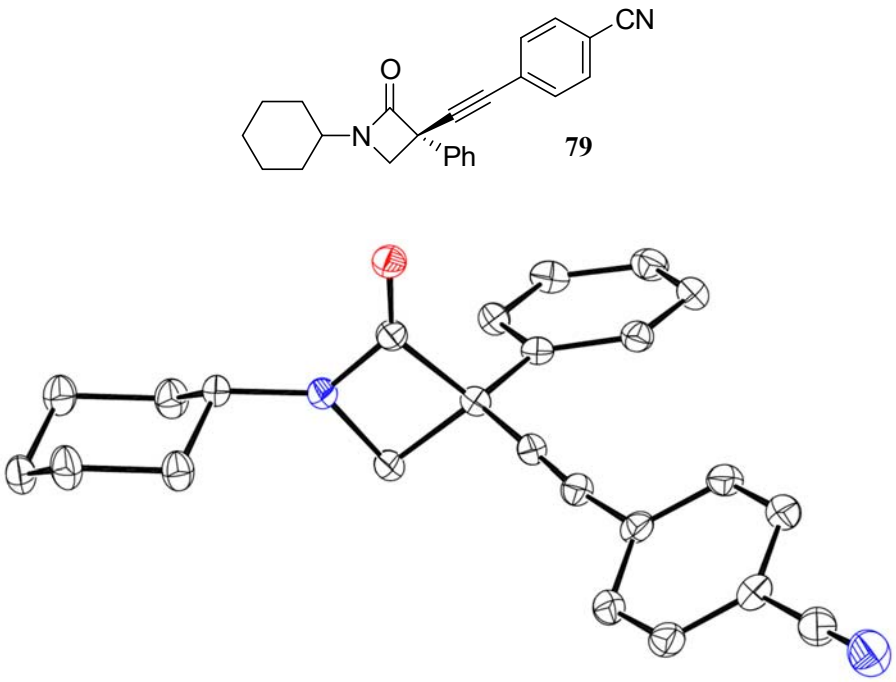
Supplementary Fig. 8 The X-ray structure of 55.



55, CCDC 2074300

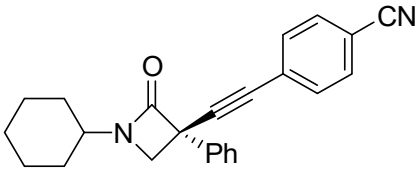


Supplementary Fig. 8' The X-ray structure of **55** (CCDC 2074300, 50% probability ellipsoids).

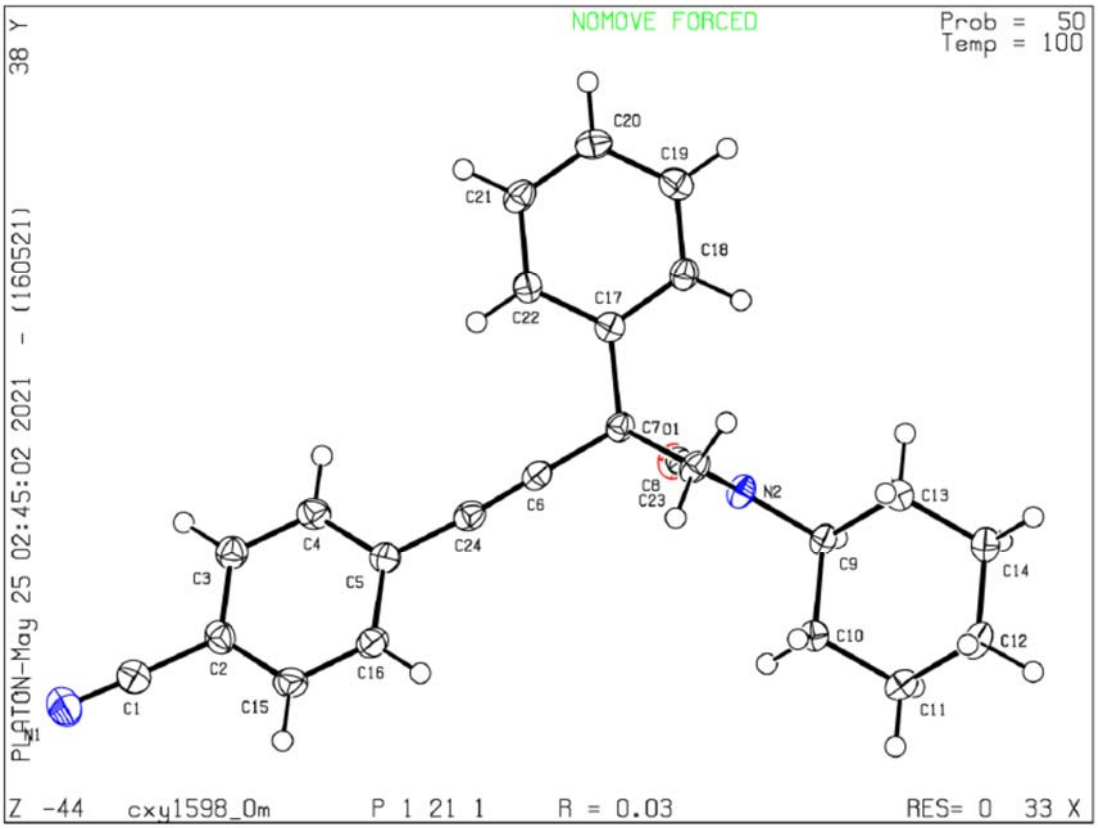


79

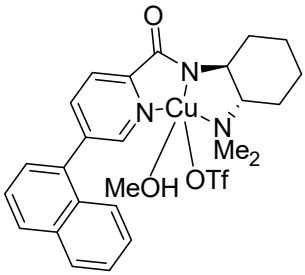
Supplementary Fig. 9 The X-ray structure of 79.



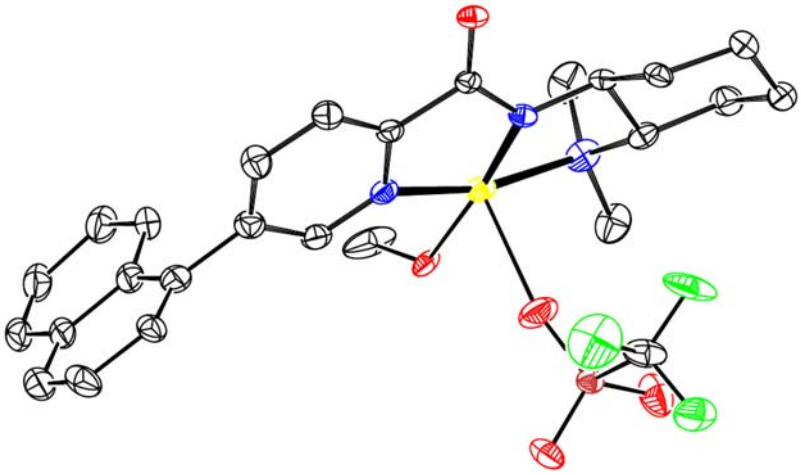
79, CCDC 2074301



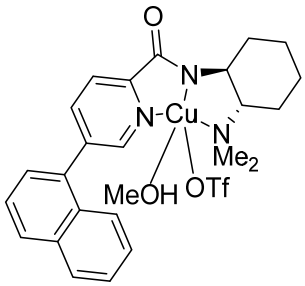
Supplementary Fig. 9' The X-ray structure of **79** (CCDC 2074301, 50% probability ellipsoids).



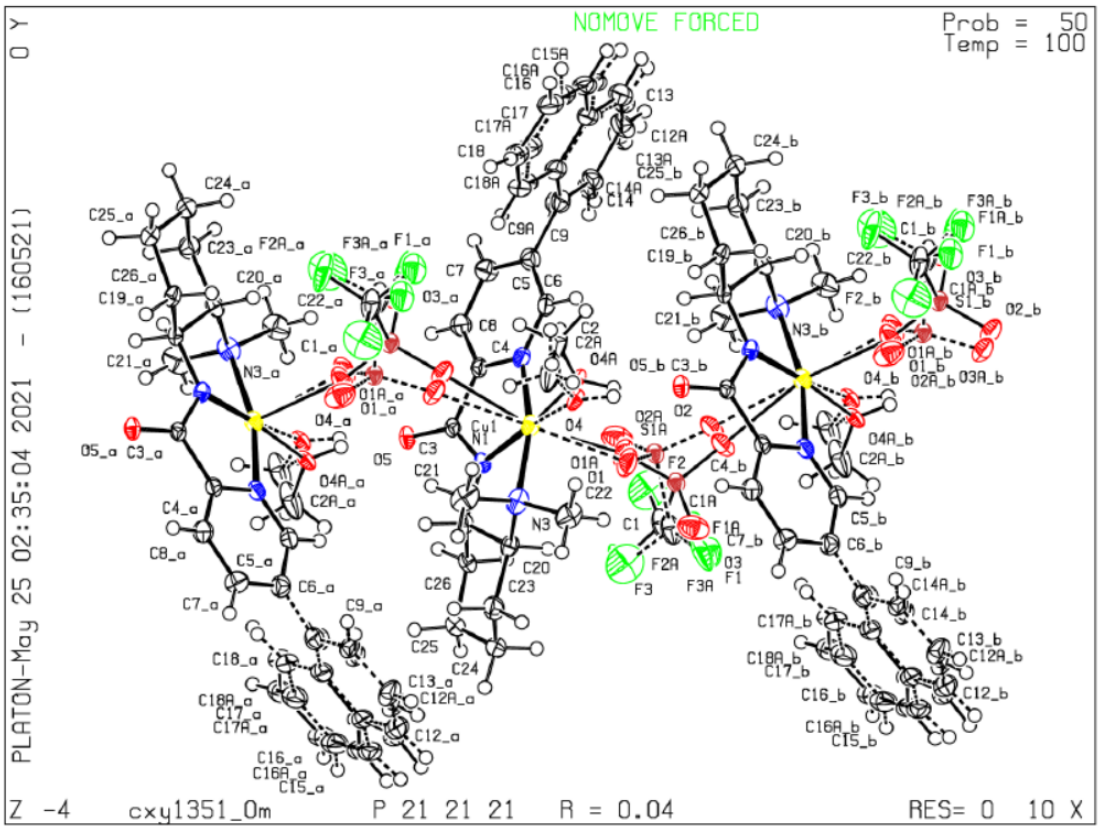
C1



Supplementary Fig. 10 The X-ray structure of C1.



C1, CCDC 2074302



Supplementary Fig. 10' The X-ray structure of **C1** (CCDC 2074302, 50% probability ellipsoids).

Computational studies

1. Computational details

All density functional theory (DFT) calculations were performed using Gaussian 16 program[8] Geometry optimizations were conducted with B3LYP functional[9], employing the D3 version of Grimme's dispersion corrections[10] with Becke-Johnson damping[11]. And LANL2DZ basis set[12] was used for copper and 6-31G* basis set was used for all other atoms. Frequency analysis was also performed at the same level of theory as geometry optimization to confirm whether optimized stationary points were either local minimum or transition state, as well as to evaluate zero-point vibrational energies and thermal corrections for enthalpies and free energies at 298.15 K. Mulliken spin distribution was acquired at the same level of theory as geometry optimization.

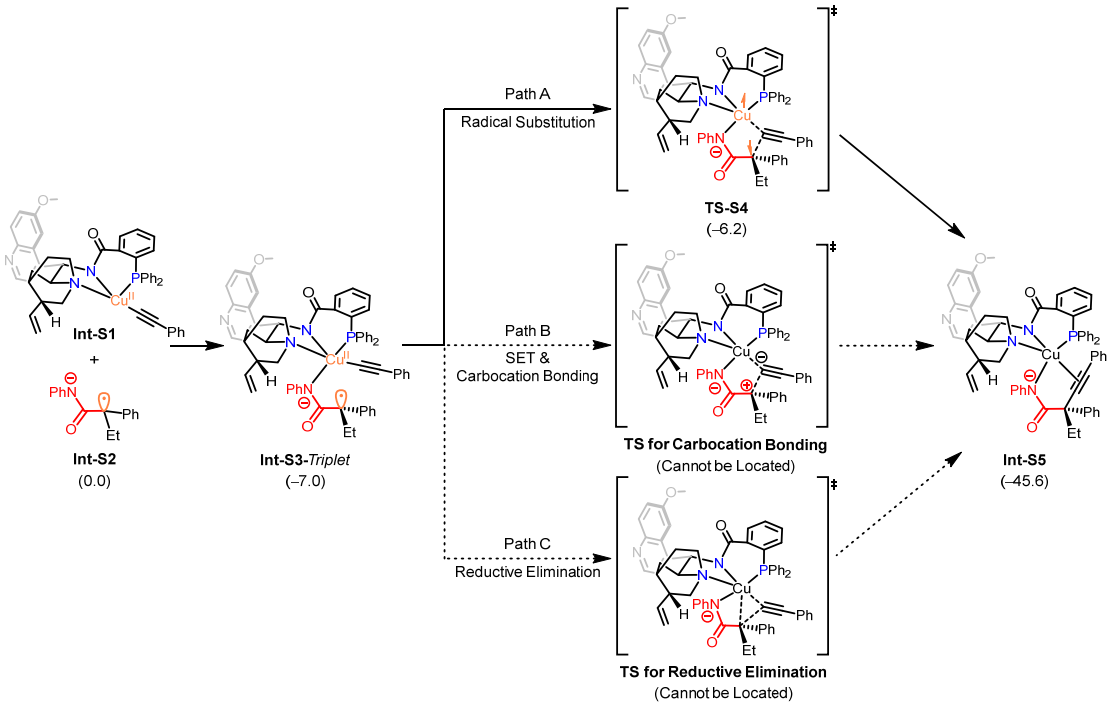
Single-point energies and solvent effects at cyclohexane were evaluated with B3LYP functional[9] with D3 version of Grimme's dispersion corrections[10] with Becke-Johnson damping[11]. SDD basis set[13] was used for copper and 6-311+G(d,p) basis set was used for all other atoms. The solvation energies were calculated with a self-consistent reaction field (SCRF) using the SMD implicit solvent model[14].

In addition, geometry optimization, frequency analysis and single point energy of open-shell local minimums were calculated with unrestricted DFT methods, while same computations for close-shell transition states and local minimum were performed with restricted DFT methods. Wavefunction stability test at the same level of theory as geometry optimizations was employed to ensure that the SCF converged wavefunction was stable.

To correct the Gibbs free energies under 1 atm to the standard state in solution (1 mol/L), a correction of $RT\ln(c_s/c_g)$ is added to energies of all species. c_s stands for the standard molar concentration in solution (1 mol/L), c_g stands for the standard molar concentration in gas phase (about 0.040876 mol/L), and R is the gas constant. For calculated intermediates at the standard state of 1 mol/L at 298.15 K, the correction value equaling to 1.89 kcal/mol was used.

The calculation and visualization of RMSD (root-mean-square deviation) analysis results are presented with VMD[15] visualization software. The 3D diagrams of optimized structures shown in the main text and below here in supplementary information for computations were generated with CYLview software[16].

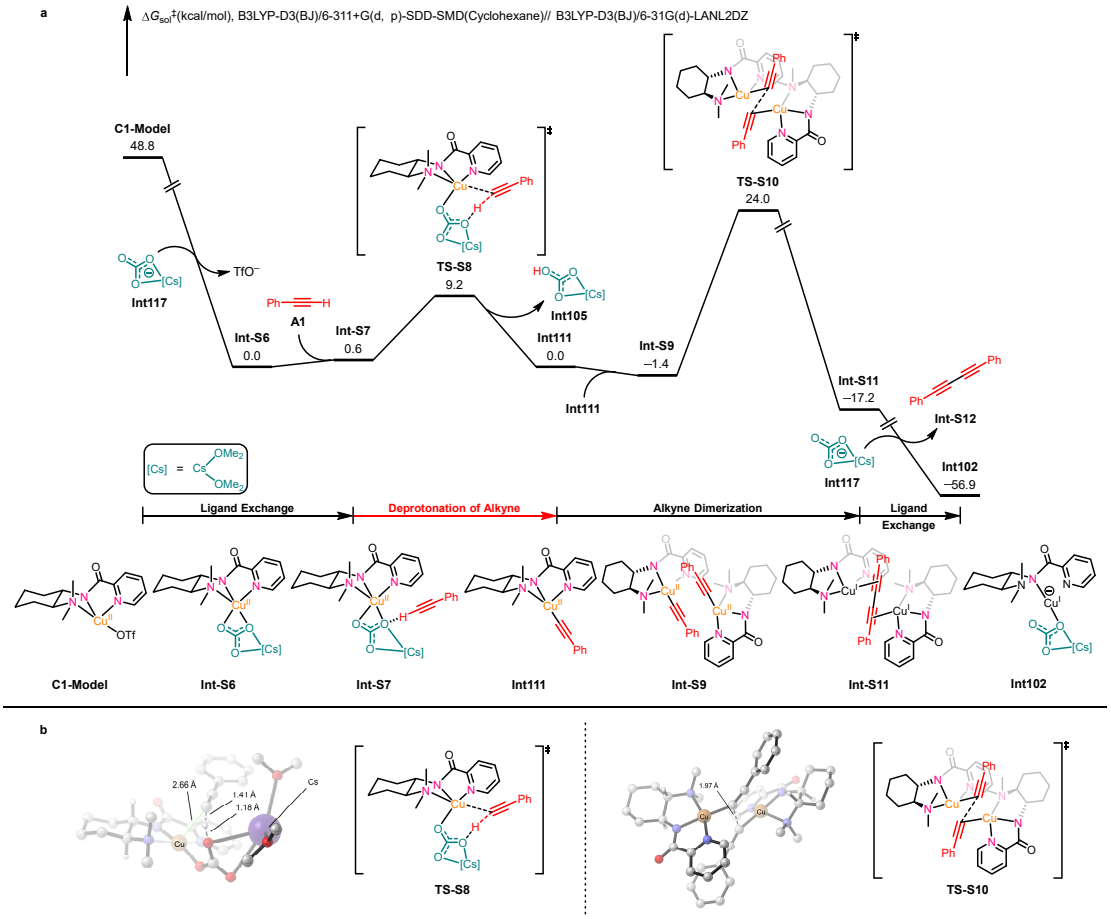
2. Initial computational study on the C–C bond formation pathway with N,N,P-ligand



Supplementary Fig. 11 DFT-computed free energy profile of C–C bonding pathway with N,N,P-ligand.

Prior to the ligand design and screening, we performed DFT calculations on the C–C bond formation pathway of LCu(II)-alkynyl species **Int-S1** with deprotonated tertiary radical **Int-S2** (Supplementary Fig. 11). The calculations led to the radical substitution-type C–C bond formation pathway (Path A) via **TS-S4**. The alternative mechanistic pathways, sequential SET and carbocation bonding as well as Cu(III)-mediated reductive elimination, cannot be located despite extensive efforts. We believe that the radical substitution-type C–C bond formation pathway is generally operative for the LCu(II)-alkynyl species and tertiary carbon radical.

3. Generation of the active Cu(I) catalyst from the LCu(II)OTf.

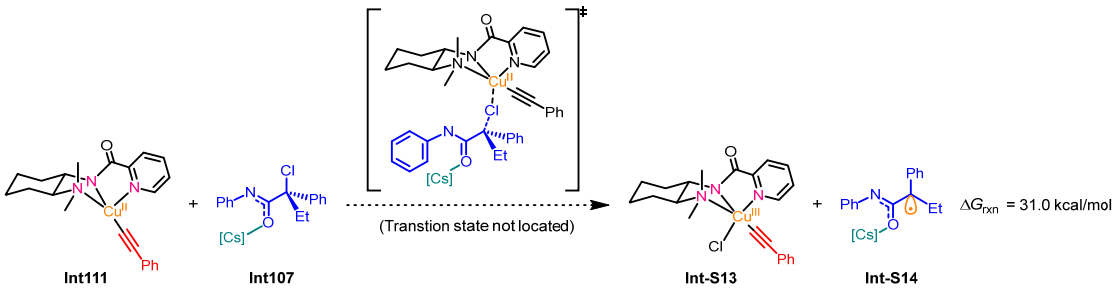


Supplementary Fig. 12 a, DFT-computed free energy changes for the generation of the active Cu(I) catalyst from the **LCu(II)OTf**. **b**, Transition state structures for **TS-S8** and **TS-S10**. Trivial hydrogen atoms are omitted for clarity.

The generation of the Cu(I) active catalyst from pre-catalyst LCu(II)OTf species **C1** is studied by DFT calculations, and the results are shown in Supplementary Fig. 12. A truncated model of the Cu(II)/N,N,N-ligand catalyst, **C1-Model**, is used in our DFT calculations. From **C1-Model**, an exergonic ligand exchange with cesium carbonate leads to **Int-S6**. From **Int-S6**, complexation with ethynylbenzene generates the weak hydrogen-bonding complex **Int-S7**, which undergoes subsequent concerted metalation-deprotonation via **TS-S8** to give the alkynylCu(II) intermediate **Int111**. This alkynylation process (**Int-S6** to **Int111**) is facile with a 9.2 kcal/mol barrier and thermoneutral, which suggests that the pre-catalyst LCu(II)OTf is efficiently *in situ* alkynylated.

From the alkynylCu(II) intermediate **Int111**, two equivalents of **Int111** can form a dinuclear complex **Int-S9**, which is able to undergo a dinuclear alkynyl–alkynyl bond formation via **TS-S10**. This process requires a barrier of 25.4 kcal/mol from **Int-S9** to **TS-S10** and irreversibly produces the diyne-coordinated Cu(I) complex **Int-S11**. This

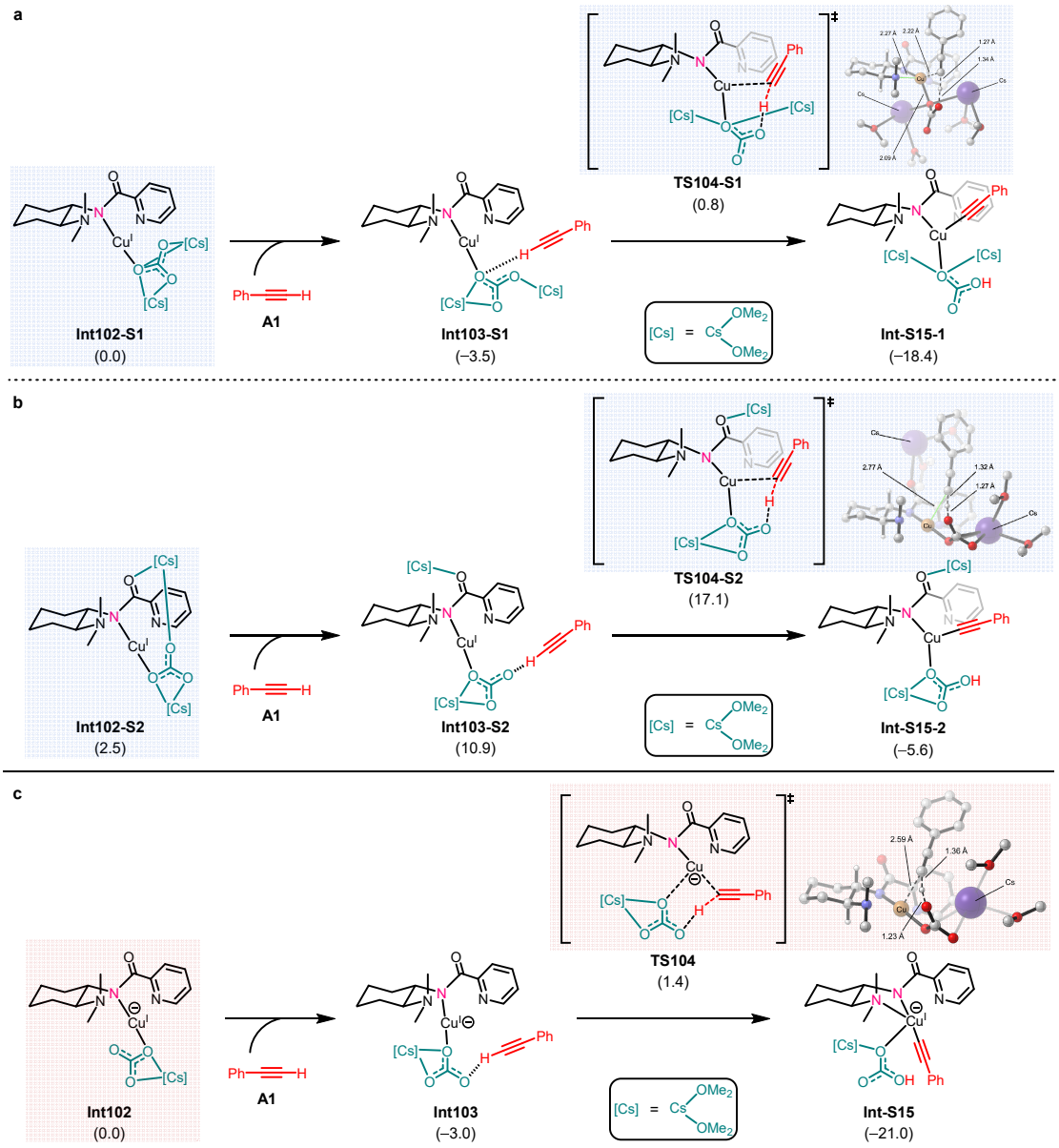
dinuclear reductive elimination pathway was also identified by Lan and co-workers in a related mechanistic study on copper catalysis[17]. From **Int-S11**, the exergonic ligand exchange with cesium carbonate liberates the diyne and produces the catalytically active Cu(I) species **Int102**.



Supplementary Fig. 13 DFT-computed free energy changes of the Cu(II)-mediated radical generation.

The possibility that the alkynylCu(II) species **Int111** acts as active catalyst to cleave the C–Cl bond of alkyl halide, which may lead to an alternative mechanism for the generation of alkyl radical, is also considered. This process is thermodynamically unfavorable (Supplementary Fig. 13). DFT calculations suggested that the LCu^{III}(alkynyl)Cl **Int-S13** together with alkyl radical **Int-S14** is 31.0 kcal/mol higher than the LCu^{II}(alkynyl) **Int111** together with deprotonated alkyl halide **Int107** in terms of free energy. The highly endergonic nature of this transformation indicates that the Cu(II) species is not responsible for C–Cl bond cleavage.

4. Effects for Neutral and Anionic Models on the Kinetics and Thermodynamics of Deprotometallation of Alkyne A1



Supplementary Fig. 14 DFT calculations on deprotometallation of alkyne A1 using various models of cesium carbonate. a, Cs_2CO_3-mediated deprotometallation with both cesium ions binding to carbonate (pathway 1). Free energies are compared to **Int102-S1**. **b**, Cs_2CO_3-mediated deprotometallation with one cesium ion binding to the ligand carbonyl group (pathway 2). Free energies are compared to **Int102-S1**. **c**, Original model of $CsCO_3^-$-mediated deprotometallation (pathway 3). Free energies are compared to **Int102**.

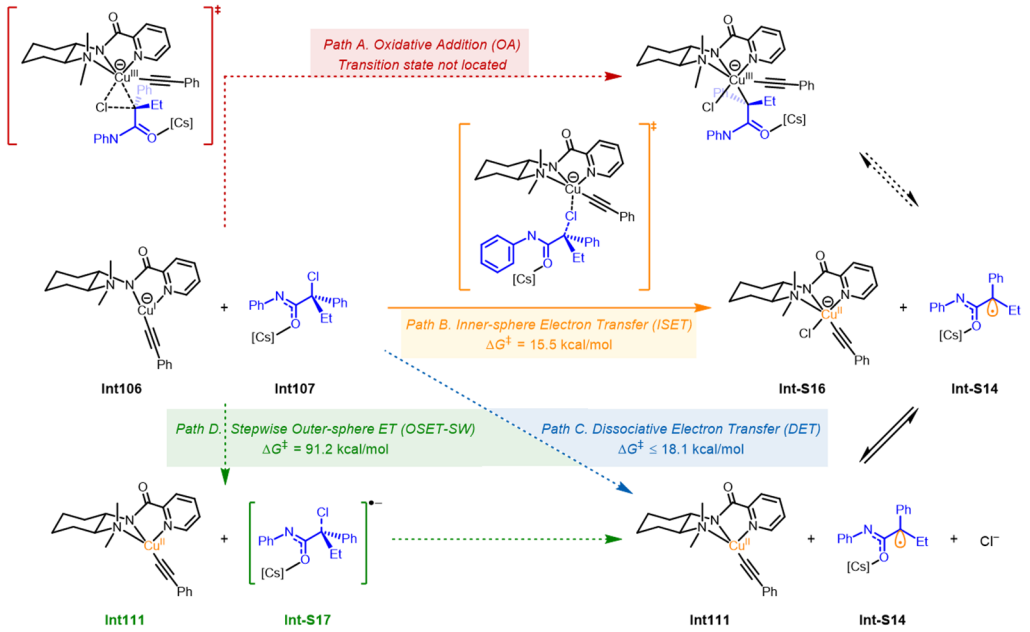
For the neutral Cs_2CO_3-mediated deprotometallation of alkyne, two models were considered. Pathway 1 has both cesium ions binding to carbonate, starting from the neutral complex **Int102-S1** (Supplementary Fig. 14a). **Int102-S1** first complexes with

alkyne **A1** to form the hydrogen bonding complex **Int103-S1**. Subsequent deprotometallation occurs via **TS104-S1** to generate the alkynylCu(I) species **Int-S15-1**. This process is facile with a 4.3 kcal/mol free energy barrier (**Int103-S1** to **TS104-S1**) and irreversible (**Int-S15-1** is 14.9 kcal/mol more stable than **Int103-S1**). This mechanistic picture of deprotometallation is consistent with our early model using anionic $CsCO_3^-$; the deprotometallation barrier and thermodynamics do not change significantly (*vide infra*).

Alternatively, one cesium ion can bind to the carbonyl group of the ligand, leading to pathway 2 (Supplementary Fig. 14b). In comparison to **Int102-S1**, **Int102-S2** with one cesium ion binding to the ligand carbonyl group is less favorable by 2.5 kcal/mol. From **Int102-S2**, a similar deprotometallation pathway can occur, but requiring a higher barrier. Pathway 2 is 16.3 kcal/mol kinetically less favorable compared with pathway 1 (**TS104-S2** vs. **TS104-S1**). Therefore, the neutral Cs_2CO_3-mediated deprotometallation prefers to occur via pathway 1 with both cesium ions binding to carbonate.

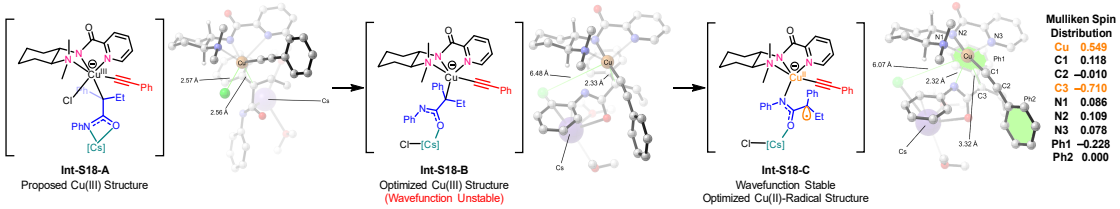
The anionic model of $CsCO_3^-$-mediated deprotometallation is shown in Supplementary Fig. 14c. The free energy barrier and reaction free energy change of the deprotometallation process are very close to that of the neutral model (Supplementary Fig. 14c vs. Supplementary Fig. 14a). Therefore, having one additional cesium ion in simulation does not significantly affect the deprotometallation kinetics and thermodynamics. Both models give consistent mechanistic understandings that the deprotometallation process is facile and irreversibly leads to the alkynylCu(I) active catalyst.

5. Exploration of the activation mechanisms of alkyl halide



Supplementary Fig. 15 Four possible pathways of the ATRP (atom transfer radical polymerization)-like Cu(I)-mediated C–Cl bond cleavage of alkyl halide.

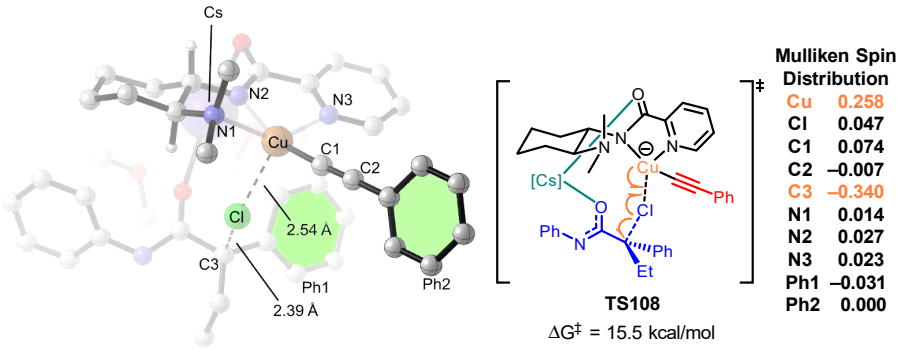
Based on former studies on the mechanism for Cu-mediated C–X bond cleavage[18–20], four possible C–Cl bond cleavage pathways (oxidative addition, inner-sphere electron transfer, stepwise outer-sphere electron transfer and dissociative electron transfer) were explored. The computational results are summarized in Supplementary Fig. 15. The inner-sphere electron transfer pathway and the dissociative electron transfer pathway are operative, while the oxidative addition and the stepwise out-sphere electron transfer pathways are unfeasible. Detailed explanations of each pathway are provided below.



Supplementary Fig. 16 Results of optimization of the post-oxidative addition Cu(III) intermediate.

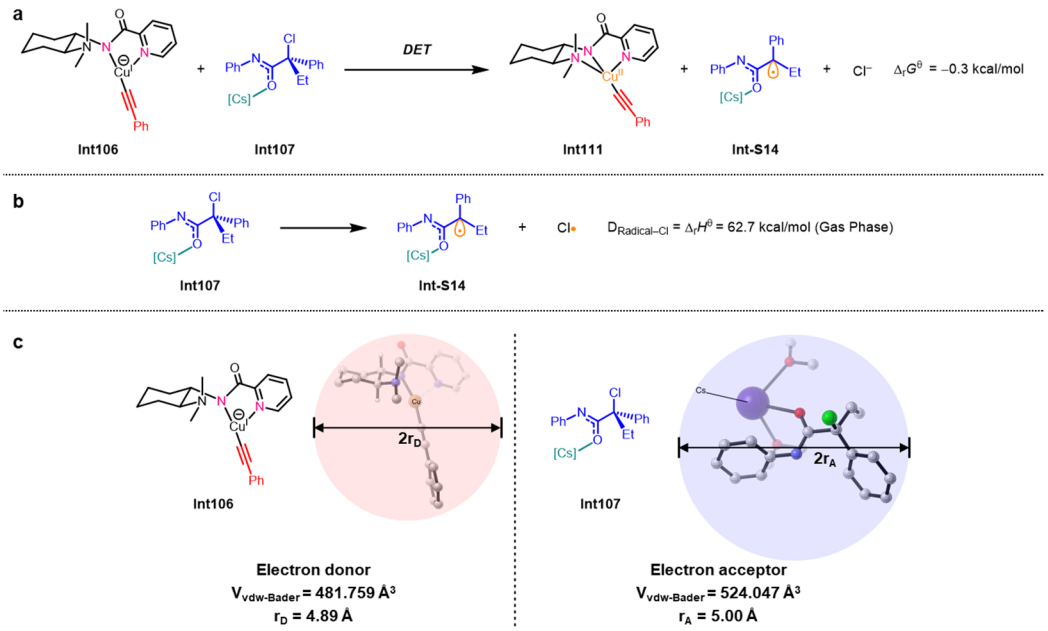
For the oxidative addition pathway, the transition state of oxidative addition cannot be located despite extensive efforts. The post-intermediate of oxidative addition, the LCu^{III}(alkynyl)(alkyl)Cl species, is not a stable intermediate based on our computations.

All the attempts to locate the proposed Cu(III) species were eventually optimized to the open-shell singlet complex of Cu(II) and pendant alkyl radical (Supplementary Fig. 16), which is the post-intermediate of radical-type C–Cl bond cleavage. Therefore, we believe that the Cu(I)-Cu(III) oxidative addition pathway is unlikely for the studied transformation.



Supplementary Fig. 17 Located transition state for inner-sphere electron transfer mechanism.

For the inner-sphere electron transfer pathway, the transition state was successfully located as **TS108**, which requires a free energy barrier of 15.5 kcal/mol (Supplementary Fig. 17). Mulliken spin population of **TS108** confirms its open-shell singlet nature, which is consistent with previous computational study[20].



Supplementary Fig. 18 a, Reaction free energy of DET (dissociative electron transfer) mechanism for **Int106** and **Int107**. **b**, C–Cl bond dissociation energy of radical

precursor **Int107**. **c**, Van der Waals radii for electron donor **Int106** and electron acceptor **Int107**.

For the dissociative electron transfer (DET) and stepwise outer-sphere electron transfer (OSET-SW) pathways, modified Marcus theory[21] was used to estimate the free energy barriers following the studies from by Coote, Matyjaszewski and Liu[20].

The DET barrier is estimated by the following equations:

$$\Delta G_{DET}^{\ddagger} = \Delta G_0^{\ddagger}\left(1+\frac{\Delta_r G^{\ominus}-D_p}{4\Delta G_0^{\ddagger}}\right)^2 \quad (1)$$

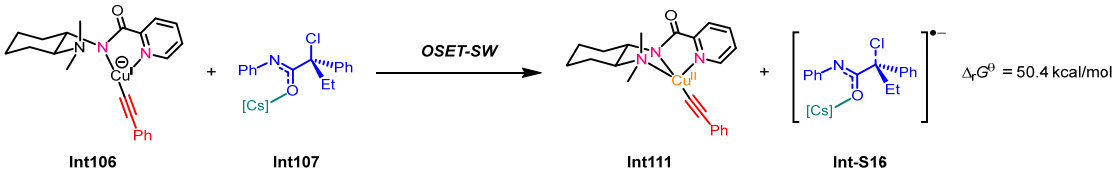
$$\Delta G_0^{\ddagger} = \frac{\left(\sqrt{D_{Radical-Cl}}-\sqrt{D_p}\right)^2+\lambda_0}{4} \quad (2)$$

$$\lambda_0 = A\times\left[(2r_D)^{-1}+(2r_A)^{-1}-(r_D+r_A)^{-1}\right] = 10.0\ kcal/mol \quad (3)$$

where $\Delta_r G^{\ominus}$ = −0.3 kcal/mol is the reaction energy of DET pathway (Supplementary Fig. 18a). $\Delta G_0^{\ddagger}$ is the intrinsic barrier, which is estimated using formula (2). λ_0 is the solvent reorganization energy that can be calculated with formula (3). D_p represents the interaction energy between the radical and Cl^- in the solvent cage. D_p = 0 gives the upper boundary of the estimated barrier. $D_{Radical\text{-}Cl}$ represents the C–Cl BDE of radical precursor **Int107** (Supplementary Fig. 18b). A equals to 99 kcal/mol as suggested in the previous studies by Coote, Matyjaszewski and Liu[18,20]. r_D represents the van der Waals radius updated by Bader[22] for electron donor **Int106**. r_A represents the same van der Waals radius for electron acceptor **Int107** (Supplementary Fig. 18c). By including the above values into the formulas (1), (2) and (3), the upper boundary of free energy barrier for DET is given as 18.1 kcal/mol.

$$\Delta G_0^{\ddagger} \approx \frac{\left(\sqrt{D_{Radical-Cl}}-\sqrt{D_p}\right)^2+\lambda_0}{4} = \frac{\left(\sqrt{62.7}-\sqrt{0}\right)^2+10.0}{4} = 18.2\ kcal/mol \quad (4)$$

$$\Delta G_{DET}^{\ddagger} \approx 18.2\times\left(1+\frac{-0.3-0}{4\times18.2}\right)^2 = 18.1\ kcal/mol \quad (5)$$



Supplementary Fig. 19 Free energy change for OSET-SW (stepwise outer-sphere electron-transfer) mechanism.

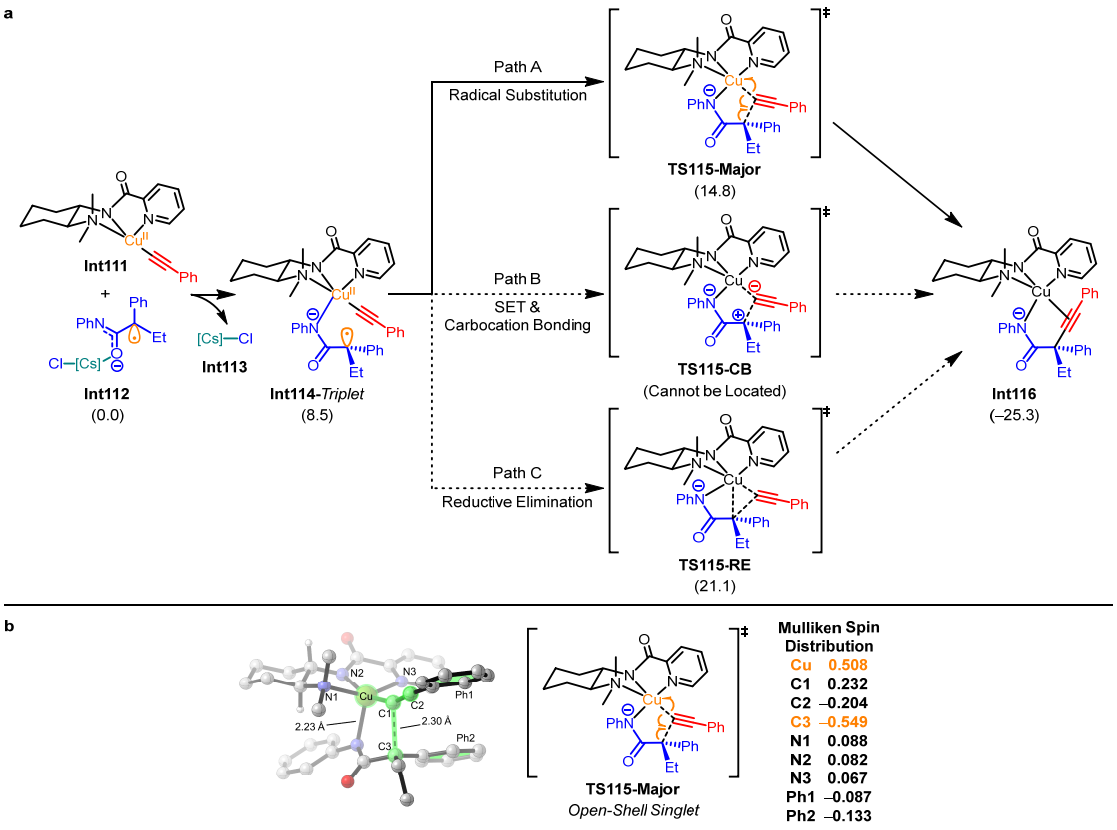
The barrier of OSET-SW is estimated using the following equation (6) (Supplementary Fig. 19), where λ_0 is calculated by the above equation (3). By including the above values into the equation (6), the free energy barrier for OSET-SW is estimated as 91.2 kcal/mol.

$$\Delta G_{OSET-SW}^{\ddagger} = \Delta G_0^{\ddagger}\left(1+\frac{\Delta_r G^{\ominus}}{4\Delta G_0^{\ddagger}}\right)^2 = \frac{\lambda_0}{4}\left(1+\frac{\Delta_r G^{\ominus}}{\lambda_0}\right)^2 \quad (6)$$

$$\Delta G^{\ddagger}_{OSET-SW} = 2.5 \times (1 + \frac{50.4}{4\times2.5})^2 = 91.2\ kcal/mol \quad (7)$$

Based on the above calculations and estimations, the inner-sphere electron transfer pathway (15.5 kcal/mol barrier via **TS108**) and dissociative electron transfer pathways (18.1 kcal/mol upper boundary barrier estimation) have surmountable barriers under the experimental conditions, which may both contribute to the generation of alkyl radical. These results support the generation of the proposed alkyl radical and the outer-sphere radical-type C–C bond formation.

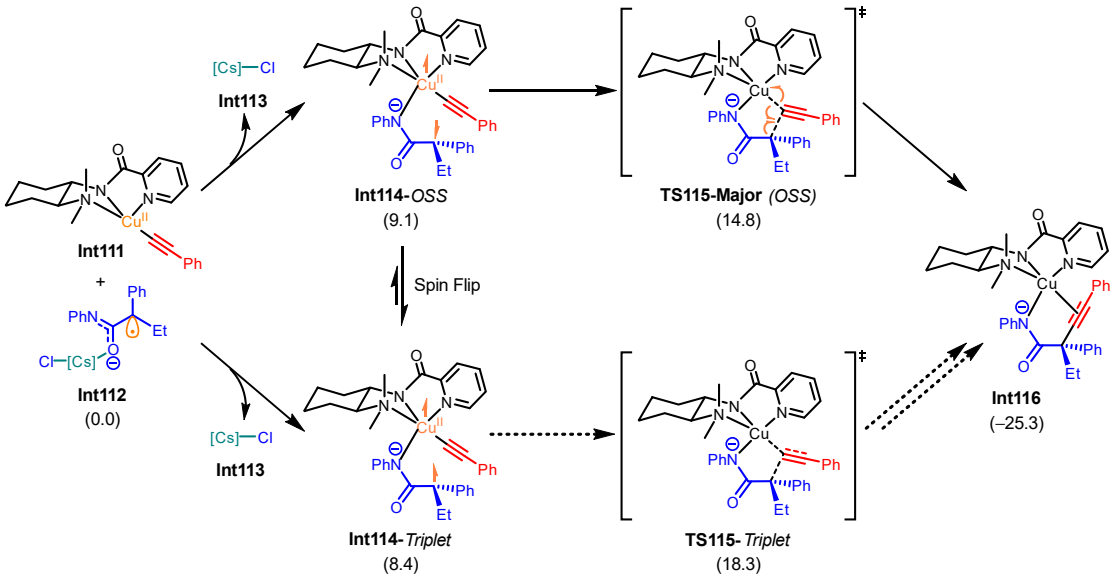
6. Discussion on C–C bond formation mechanism



Supplementary Fig. 20 DFT calculations on C–C bond formation pathways. **a**, Exploration of C–C bond formation pathways with **L*5Cu(II)(alkynyl)** species **Int111** and anionic tertiary radical **Int112**. Free energies in kcal/mol are shown in parentheses, which are compared to **Int111** and **Int112**. **b**, Optimized structure and Mulliken spin distribution of located open-shell singlet C–C bond formation transition state **TS115-Major**. RS, radical substitution; SET, single electron transfer; CB, carbocation bonding; RE, reductive elimination.

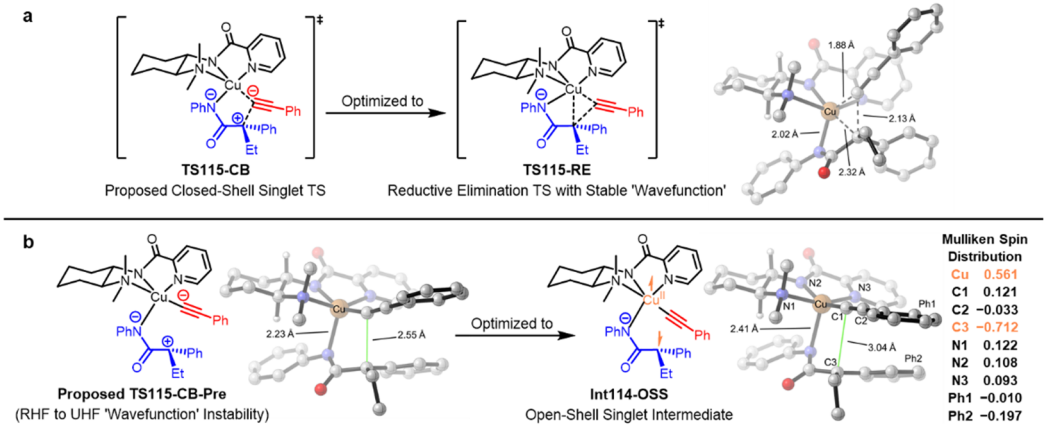
The C–C bond formation pathways for **Int111** and **Int112** including outer-sphere radical-substitution-type C–C bond formation via **TS115-Major** (path A in Supplementary Fig. 20a), sequential SET and carbocation bonding via **TS115-CB** (path B in Supplementary Fig. 20a) and reductive elimination via **TS115-RE** (path C in Supplementary Fig. 20a) were explored.

For path A, the radical substitution path via **TS115-Major** is operative for the C–C bond formation and it is an open-shell diradical singlet C–C bond formation transition state, whose nature of radical substitution is confirmed by the computed spin distribution. Significant radical character is identified on the carbons of the forming C–C bond, the adjacent alkynyl carbon and the copper centre (Supplementary Fig. 20b).



Supplementary Fig. 21 Triplet and open-shell singlet C–C bond formation processes with **L*5.** Free energies in kcal/mol are compared to **Int111** and **Int112**.

The radical-type C–C bond formation pathway can involve open-shell singlet or triplet transition state. The pre-intermediate for outer-sphere radical-substitution-type C–C bond formation via **TS115-Major**, **Int114**, has triplet and open-shell singlet states with comparable stabilities. The triplet state **Int114-***Triplet* is more stable than **Int114-***OSS* by 0.7 kcal/mol. The triplet C–C bond formation transition state **TS115-***Triplet* is 3.5 kcal/mol less favorable than open-shell singlet **TS115-Major**. (Supplementary Fig. 21) Therefore, we believe that the radical-type C–C bond formation pathway proceeds via the open-shell singlet **TS115-Major**, instead of the triplet transition state **TS115-***Triplet*.



Supplementary Fig. 22 a, The proposed closed-shell singlet carbocation bonding transition state structure **TS115-CB** and the actually located Cu(III)-mediated reductive elimination transition state **TS115-RE**. **b**, The located closed-shell singlet pre-intermediate structure (with an RHF to UHF 'wavefunction' instability) in the proposed

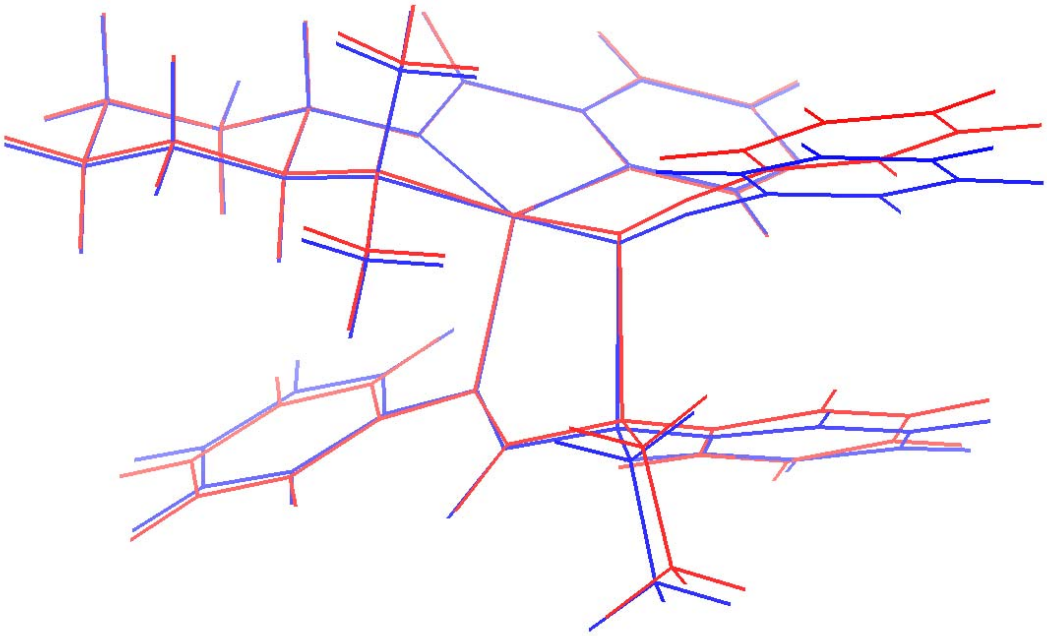
carbocation bonding C–C bond formation pathway, the located open-shell singlet intermediate **Int114-OSS** (with a stable 'wavefunction') upon further optimization, and the Mulliken spin distribution of the open-shell singlet **Int114-OSS**.

Regarding path B, the transition state **TS115-CB** cannot be located after extensive efforts (Supplementary Fig. 22). All the optimizations led to the closed-shell singlet Cu(III)-mediated reductive elimination transition state **TS115-RE**. To further probe the possibility of the carbocation bonding pathway, we tried to optimize the structure of the pre-intermediate prior to the proposed carbocation bonding transition state. A structure with an RHF to UHF 'wavefunction' instability, **TS115-CB-Pre**, was located. This also indicated that such a closed-shell singlet intermediate does not exist and the unfeasibility of the proposed carbocation bonding pathway. Further open-shell singlet optimization of the **TS115-CB-Pre** led to the open-shell singlet intermediate **Int114-OSS**, which is the pre-intermediate for the radical substitution C–C bond formation pathway. Based on these results, we believe that the carbocation bonding pathway is not operative.

As for path C, the transition state **TS115-RE** was located, whose free energy is 6.3 kcal/mol higher than that of **TS115-Major** (Supplementary Fig. 20a).

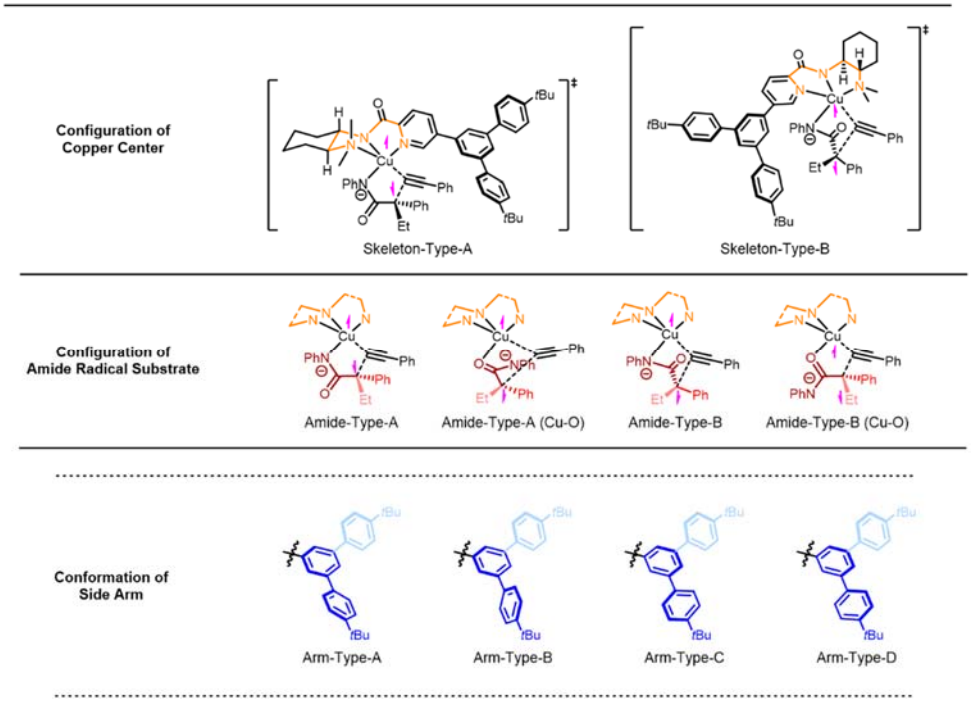
Therefore, we believe that C–C bond formation undergoes an outer-sphere singlet radical-substitution-type C–C bond formation via **TS115-Major**.

7. Geometry overlay between TS115-Major and corresponding fragment of TS119-Major-C1



Supplementary Fig. 23 Geometry overlay between **TS115-Major** and the corresponding fragment of **TS119-Major-C1.** The red lines represent the fragment of **TS115-Major** with the hydrogen atom deleted at the corresponding position of the side arm in **TS119-Major-C1** and the blue lines represent the corresponding fragment of **TS119-Major-C1** without the side arm. Calculated RMSD (root-mean-square deviation) between the two fragments is 0.0182 Å.

8. Conformational search of stereo-determining C–C bond formation transition state.



Supplementary Fig. 24 Details of conformational search of C–C bond formation transition state.

Supplementary Table 4. Conformational search of C–C bond formation transition state with L*5 (no side arm). Free energies are compared to TS115-Major.

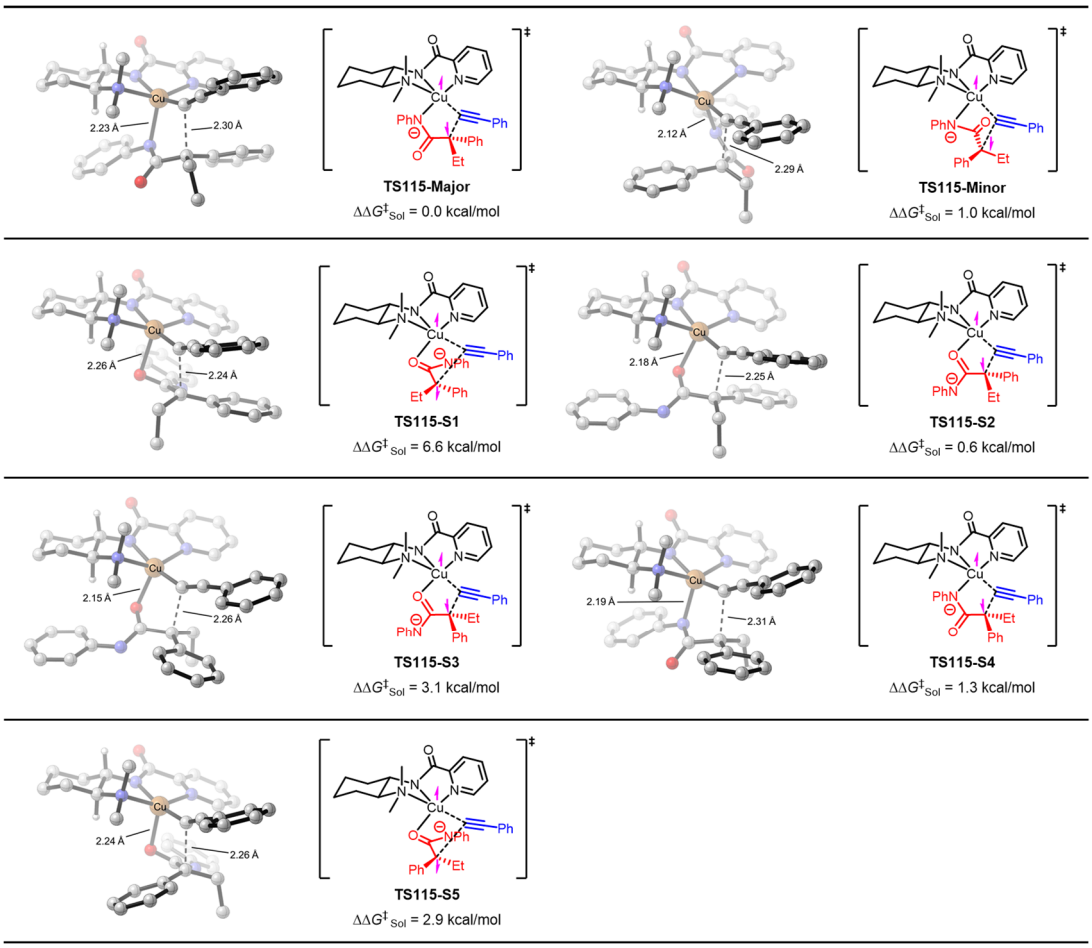
Configuration of Product	Copper Skeleton	Amide Configuration	No.	$\Delta\Delta G_{sol}^{\ddagger}$ (kcal/mol)
(S)	A	A	**TS115-Major**	0.0
(S)	A	A (Cu-O)	**TS115-S1**	6.6
(S)	A	B	/	optimized to **TS115-Major**
(S)	A	B (Cu-O)	**TS115-S2**	0.6
(R)	A	A	**TS115-Minor**	1.0
(R)	A	A (Cu-O)	**TS115-S3**	3.1
(R)	A	B	**TS115-S4**	1.3
(R)	A	B (Cu-O)	**TS115-S5**	2.9

Supplementary Table 5. Conformational search of C–C bond formation transition state with L*11 (with bulky side arm). Free energies are compared to TS119-Major-C1.

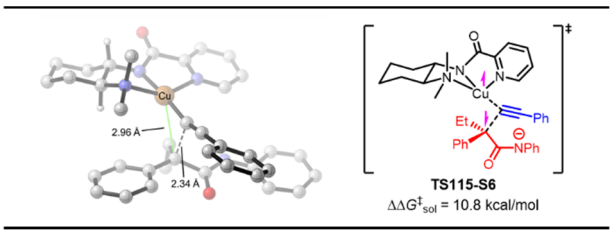
Configuration of Product	Copper Skeleton	Amide Configuration	Arm Conformation	No.	$\Delta\Delta G_{sol}^{\ddagger}$ (kcal/mol)
(S)	A	A	A	**TS119-Major-C1**	0.0
(S)	A	A	B	**TS119-S1**	0.7
(S)	A	A	C		optimized to **TS119-S2**
(S)	A	A	D	**TS119-S2**	3.4
(S)	A	A (Cu-O)	A	**TS119-S3**	5.3
(S)	A	A (Cu-O)	B	**TS119-S4**	4.0
(S)	A	A (Cu-O)	C		optimized to **TS119-S3**
(S)	A	A (Cu-O)	D	**TS119-S5**	5.1
(S)	A	B	A	**TS119-S6**	3.4
(S)	A	B (Cu-O)	A	**TS119-S7**	0.3
(S)	A	B (Cu-O)	B	**TS119-S8**	1.2
(S)	A	B (Cu-O)	C	**TS119-S9**	1.8
(S)	A	B (Cu-O)	D	**TS119-Major-C2**	2.7
(S)	B	A	A	**TS119-S10**	7.4
(S)	B	A	D	**TS119-S11**	8.7
(S)	B	A (Cu-O)	A	**TS119-S12**	9.0
(S)	B	A (Cu-O)	D	**TS119-S13**	8.9
(S)	B	B	A	**TS119-S14**	8.0
(S)	B	B	D	**TS119-S15**	7.5
(S)	B	B (Cu-O)	A	**TS119-S16**	5.2
(S)	B	B (Cu-O)	D	**TS119-S17**	5.0
(R)	A	A	A	**TS119-Minor-C1**	3.2
(R)	A	A	B	**TS119-S18**	3.0
(R)	A	A	C	**TS119-S19**	2.4
(R)	A	A	D	**TS119-S20**	3.8
(R)	A	A (Cu-O)	A	**TS119-S21**	4.7
(R)	A	A (Cu-O)	C	**TS119-S22**	4.6
(R)	A	B	A	**TS119-S23**	3.0
(R)	A	B	B	**TS119-S24**	3.7
(R)	A	B	C	**TS119-S25**	4.2
(R)	A	B	D	**TS119-S26**	3.7
(R)	A	B (Cu-O)	A	**TS119-S27**	2.4
(R)	A	B (Cu-O)	B	**TS119-S28**	2.5
(R)	A	B (Cu-O)	C	**TS119-S29**	2.6
(R)	A	B (Cu-O)	D	**TS119-Minor-C2**	2.1
(R)	B	A	A	**TS119-S30**	7.6
(R)	B	A	D	**TS119-S31**	4.7

(R)	B	A (Cu-O)	A	**TS119-S32**	5.9
(R)	B	A (Cu-O)	D	**TS119-S33**	6.3
(R)	B	B	D	**TS119-S34**	7.0
(R)	B	B (Cu-O)	A	**TS119-S35**	6.9
(R)	B	B (Cu-O)	D	**TS119-S36**	5.8

9. Key conformers of C–C bond formation transition state with L*5 (no side arm)

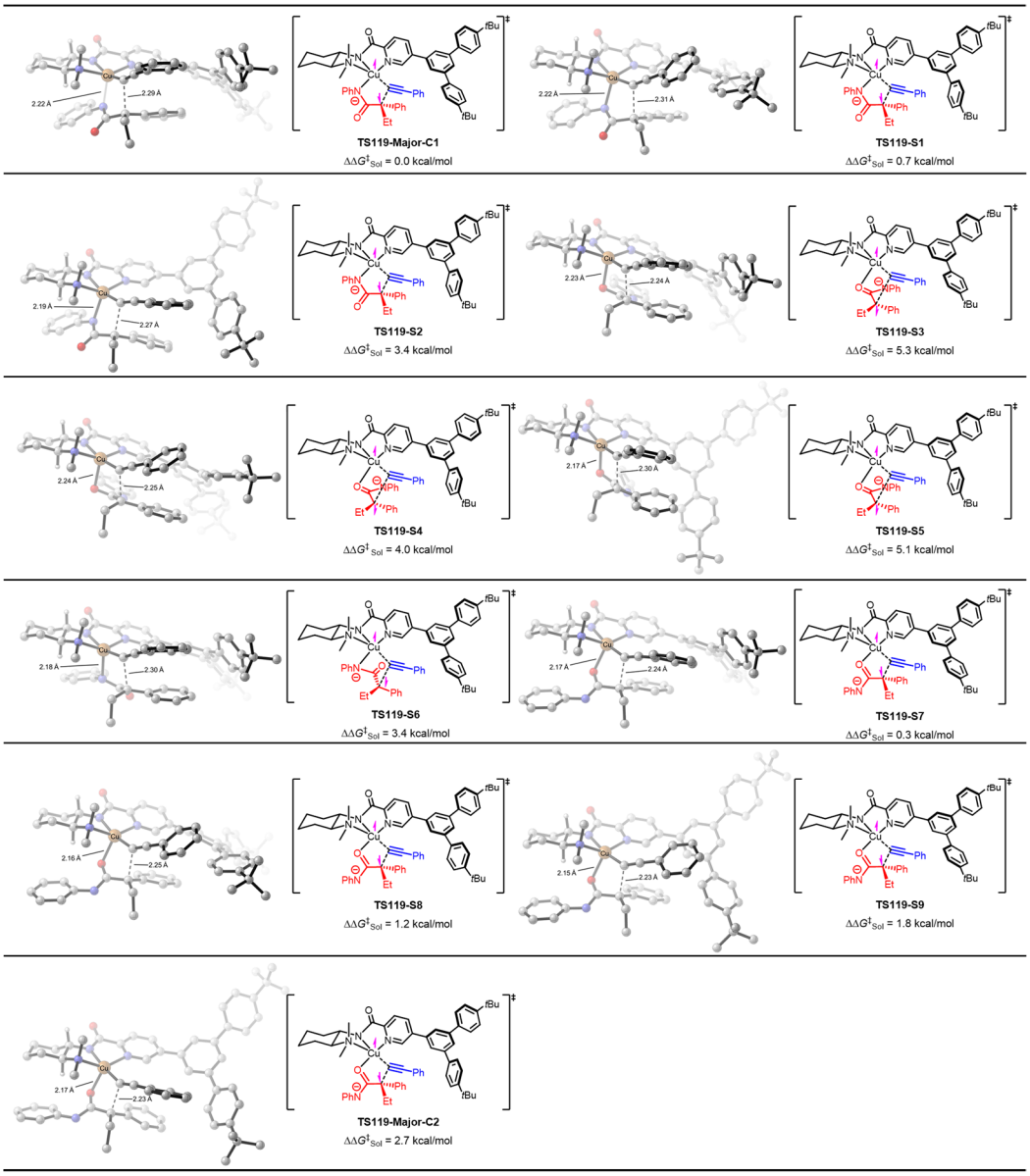


Supplementary Fig. 25 Key conformers of C–C bond formation transition states with L*5 (no bulky side arm). Free energies are compared to **TS115-Major**. Trivial hydrogen atoms are omitted for clarity.

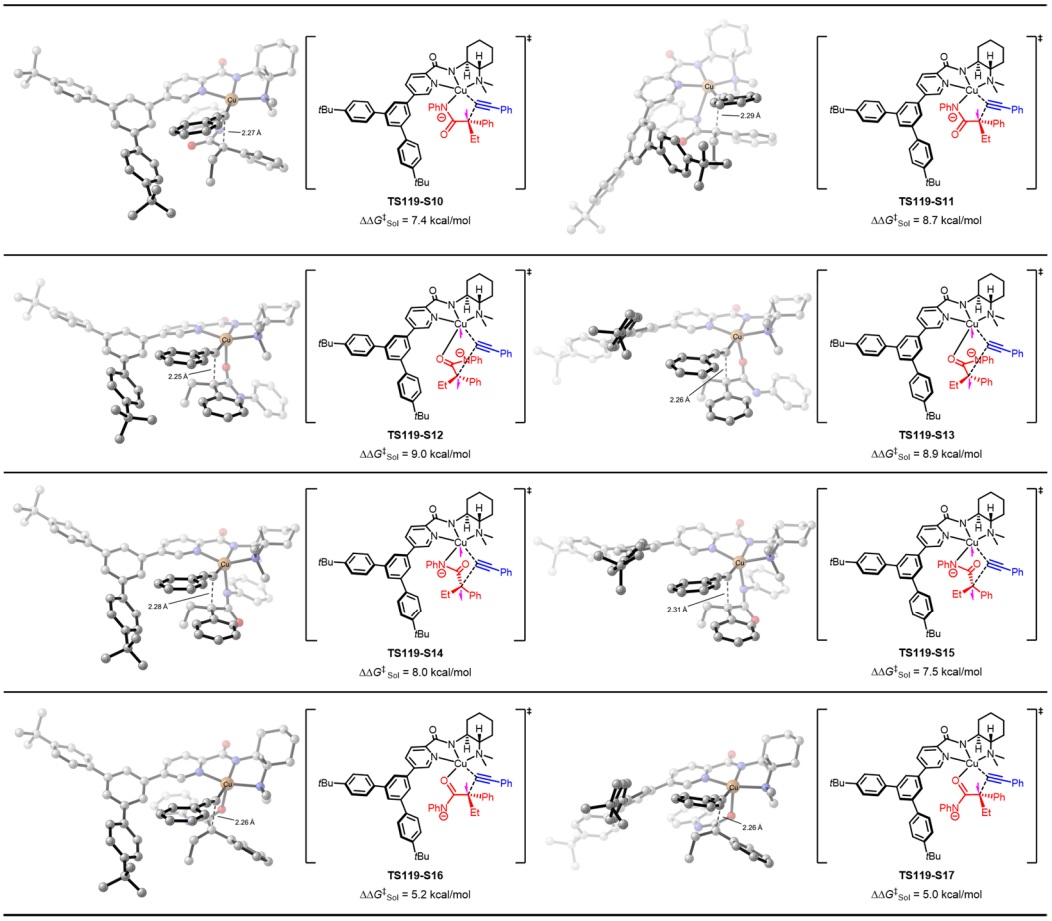


Supplementary Fig. 26 Considered conformers of C–C bond formation transition states with L*5 (no bulky side arm) without coordination between Cu and anionic amide substrate. Free energy is compared to **TS115-Major**. Trivial hydrogen atoms are omitted for clarity.

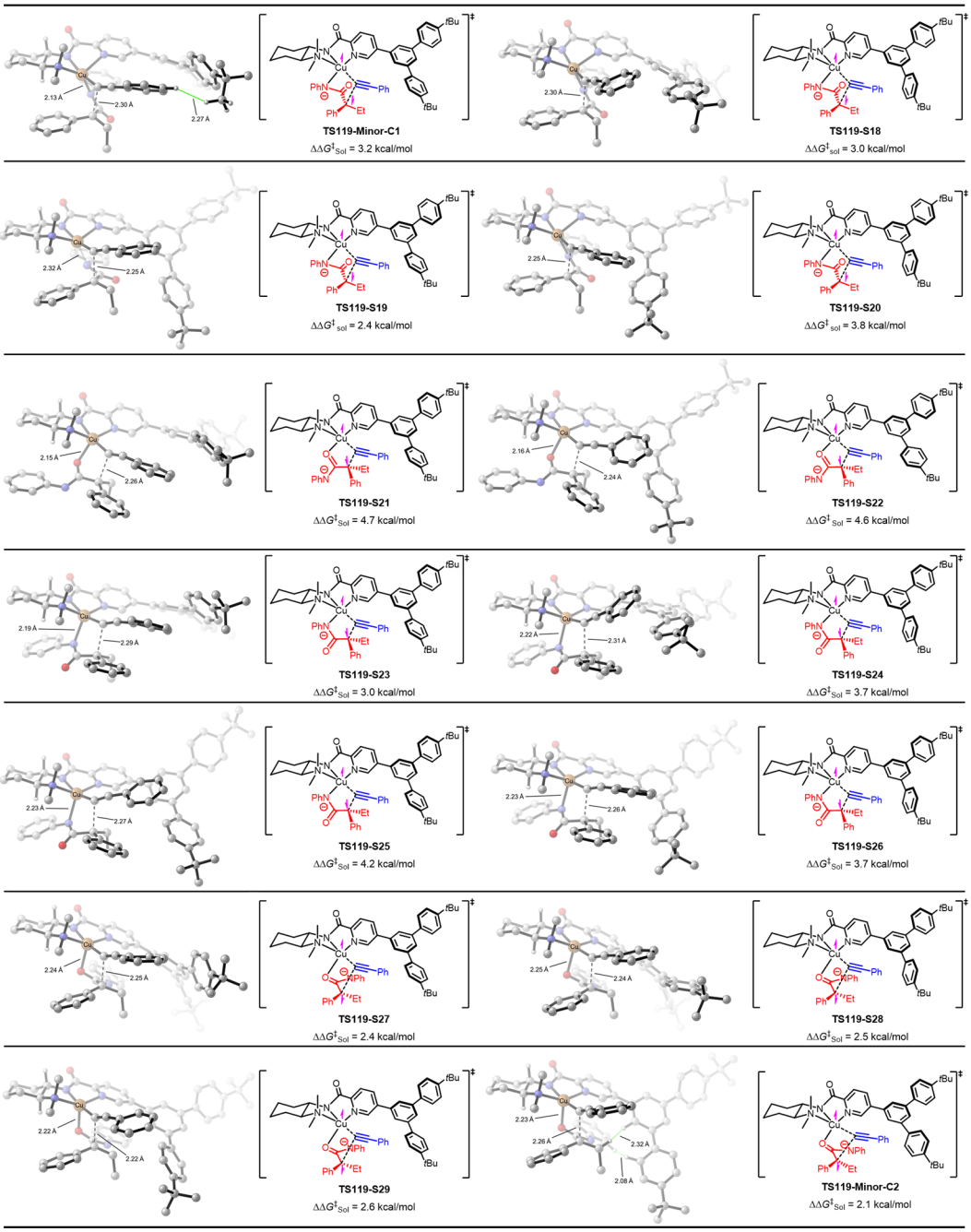
10. Key conformers of C–C bond formation transition state with L*11 (with bulky side arm)



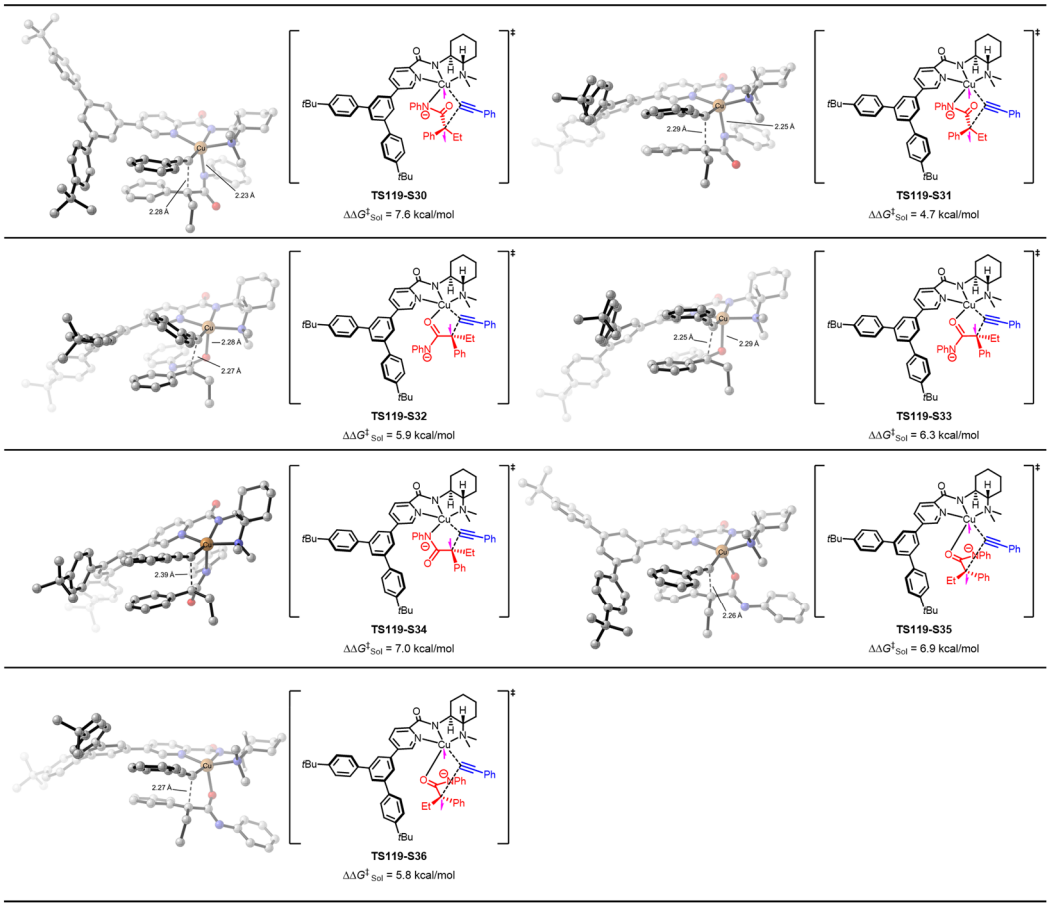
Supplementary Fig. 27 Key conformers of C–C bond formation transition states with L*11 (with bulky side arm) and A-type of copper skeleton, leading to the major product. Free energies are compared to **TS119-Major**. Trivial hydrogen atoms are omitted for clarity.



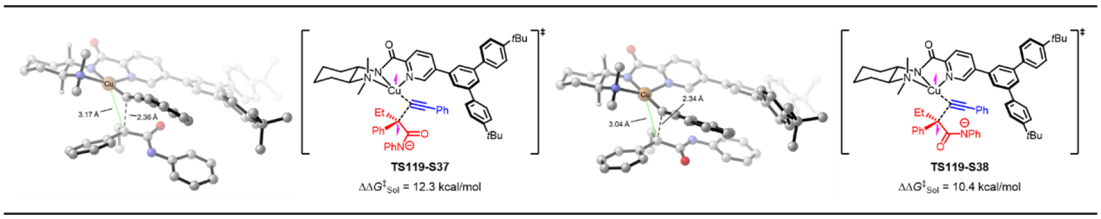
Supplementary Fig. 28 Key conformers of C–C bond formation transition states with L*11 (with bulky side arm) and B-type of copper skeleton, leading to the major product. Free energies are compared to **TS119-Major**. Trivial hydrogen atoms are omitted for clarity.



Supplementary Fig. 29 Key conformers of C–C bond formation transition states with L*11 (with bulky side arm) and A-type of copper skeleton, leading to the minor product. Free energies are compared to **TS119-Major**. Trivial hydrogen atoms are omitted for clarity.



Supplementary Fig. 30 Key conformers of C–C bond formation transition states with L*11 (with bulky side arm) and B-type of copper skeleton, leading to the minor product. Free energies are compared to **TS119-Major**. Trivial hydrogen atoms are omitted for clarity.



Supplementary Fig. 31 Considered conformers of C–C bond formation transition states with L*11 (with bulky side arm) without coordination between Cu and anionic amide substrate. Free energies are compared to **TS119-Major**. Trivial hydrogen atoms are omitted for clarity.

11. Summary of Archived Files

The xyz structures for all computed local minimums, transition states and proposed structures are included in the “Computational Archive” file folder. The second row in each xyz structure indicates the charge and multiplicity of the corresponding species. Also, the tables of energies are included again in a single document for readers to read key energies and frequencies.

12. Table of energies

Supplementary Table 6. Energies in Figs. 3 and 4 and Supplementary Figs. 11 to 31. Zero-point correction (***ZPE***), thermal correction to enthalpy (***TCH***), thermal correction to Gibbs free energy (***TCG***), energies (***E***), enthalpies (***H***), and Gibbs free energies (***G***) (in Hartree) of the structures calculated at B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cyclohexane)// B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory.

Structure	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
Int-S1	0.781749	0.829927	0.694564	−2670.535622	−2669.705695	−2669.841058	
Int-S2	0.267686	0.284154	0.222441	−749.059077	−748.774923	−748.836636	
Int-S3-*OSS*	1.051665	1.116721	0.948553	−3419.634198	−3418.517477	−3418.685645	
Int-S3- *Triplet*	1.051739	1.116747	0.948089	−3419.633907	−3418.517160	−3418.685818	
TS-S4	1.051071	1.115539	0.948040	−3419.632541	−3418.517002	−3418.684501	198.2*i*
Int-S5	1.054054	1.118627	0.952690	−3419.699969	−3418.581342	−3418.747279	
A1	0.109633	0.117058	0.079847	−308.509934	−308.392876	−308.430087	
C1-Model	0.362959	0.390111	0.305533	−1944.436944	−1944.046833	−1944.131411	
OTf-Anion	0.027345	0.035445	−0.005136	−961.782117	−961.746672	−961.787253	
Int-S6	0.514605	0.551086	0.444024	−1577.105119	−1576.554033	−1576.661095	
Int-S7	0.625027	0.670301	0.540297	−1885.627519	−1884.957218	−1885.087222	
TS-S8	0.621423	0.666083	0.536207	−1885.609786	−1884.943703	−1885.073579	755.8*i*
Int-S9	0.870256	0.923037	0.781224	−2581.357962	−2580.434925	−2580.576738	
TS-S10	0.866886	0.919491	0.778553	−2581.314695	−2580.395204	−2580.536142	512.9*i*
Int-S11	0.868363	0.921703	0.777196	−2581.379093	−2580.457390	−2580.601897	
Int-S12	0.202989	0.216857	0.161019	−615.8453746	−615.628518	−615.684356	
Int-S13	0.435965	0.463924	0.375602	−1750.882630	−1750.418706	−1750.507028	
Int-S14	0.432662	0.463727	0.362742	−1079.395703	−1078.931976	−1079.032961	
Int-S15	0.623344	0.669335	0.536235	−1885.726442	−1885.057107	−1885.190207	
Int-S15-1	0.789768	0.849642	0.685221	−2216.08735	−2215.237708	−2215.402129	
Int-S15-2	0.789288	0.849175	0.685771	−2216.067463	−2215.218288	−2215.381692	
Int-S16	0.433435	0.461856	0.370907	−1751.038181	−1750.576325	−1750.667274	
Int-S17	0.435168	0.467617	0.364514	−1539.687878	−1539.220261	−1539.323364	
Chloride Anion	0.000000	0.002360	−0.015023	−460.246371	−460.263754	−460.359213	
Chlorine Radical	0.000000	0.00236	−0.015677	−460.130428	−460.148465	−460.169234	
Int102	0.512055	0.548719	0.442263	−1577.171877	−1576.623158	−1576.729614	
Int102-S1	0.676737	0.728197	0.583706	−1907.529394	−1906.801197	−1906.945688	
Int102-S2	0.675774	0.727631	0.582199	−1907.523878	−1906.796247	−1906.941679	
Int103	0.621678	0.66718	0.537426	−1885.698924	−1885.031744	−1885.161498	
Int103-S1	0.787745	0.847539	0.682327	−2216.060627	−2215.213088	−2215.378300	

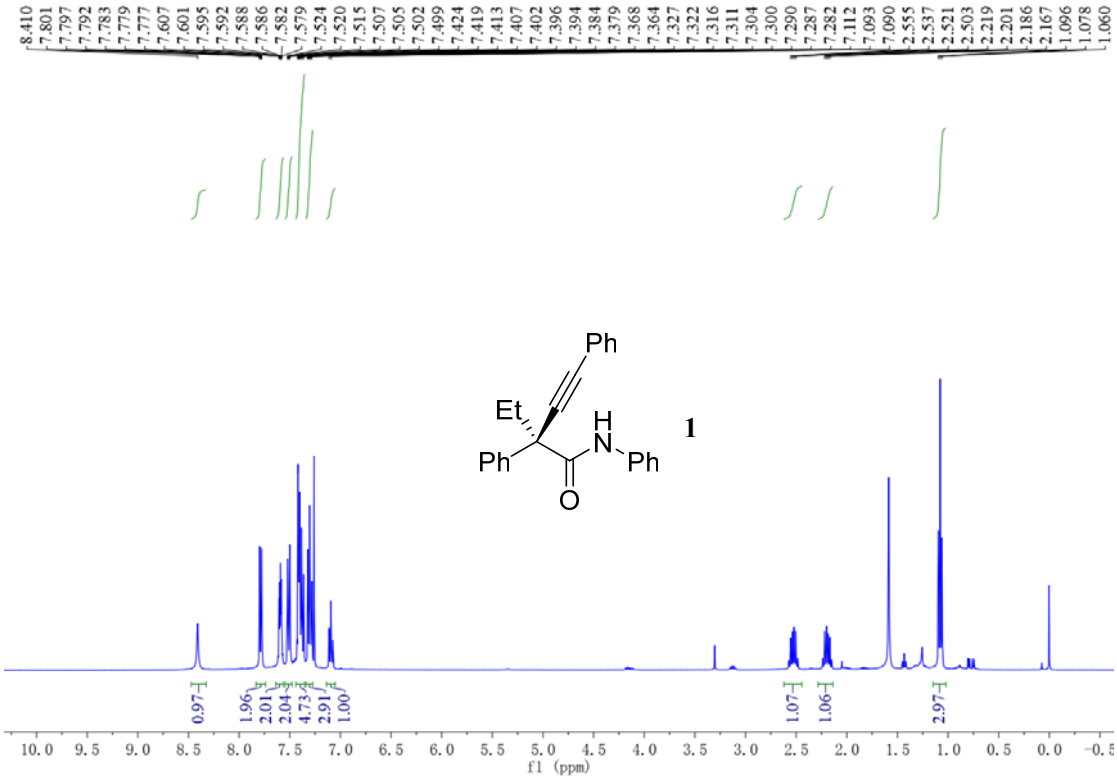
Int103-S2	0.787218	0.846854	0.68077	−2216.036153	−2215.189299	−2215.355383	
TS104	0.617311	0.662732	0.532283	−1885.686767	−1885.024035	−1885.154484	1120.7*i*
TS104-S1	0.783601	0.842690	0.682442	−2216.053923	−2215.211233	−2215.371481	982.0*i*
TS104-S2	0.782548	0.842256	0.676698	−2216.022195	−2215.179939	−2215.345497	1093.4*i*
Int105	0.191260	0.209858	0.138859	−594.941315	−594.731457	−594.802456	
Int106	0.429366	0.456774	0.367023	−1290.758575	−1290.301801	−1290.391552	
Int107	0.435514	0.468002	0.365381	−1539.666149	−1539.198147	−1539.300768	
TS108	0.866069	0.926023	0.761418	−2830.425949	−2829.499926	−2829.664531	297.0*i*
Int109-OSS	0.868003	0.927888	0.763861	−2830.464752	−2829.536864	−2829.700891	
Int109- *Triplet*	0.868004	0.927888	0.762838	−2830.464746	−2829.536858	−2829.701908	
Int110-OSS	0.867912	0.92818	0.761096	−2830.480312	−2829.552132	−2829.719216	
Int110- *Triplet*	0.867911	0.928179	0.760060	−2830.480311	−2829.552132	−2829.720251	
Int111	0.434100	0.460201	0.375053	−1290.663723	−1290.203522	−1290.288670	
Int112	0.433250	0.466342	0.361885	−1539.788093	−1539.321751	−1539.426208	
Int113	0.164154	0.179561	0.119161	−790.6910555	−790.511495	−790.571895	
Int114-*OSS*	0.703930	0.746932	0.627895	−2039.756353	−2039.009421	−2039.128458	
Int114- *Triplet*	0.703926	0.746929	0.626843	−2039.756367	−2039.009438	−2039.129524	
TS115-Major	0.702955	0.745403	0.627768	−2039.747211	−2039.001808	−2039.119443	319.0*i*
TS115-Minor	0.702153	0.744806	0.626004	−2039.743792	−2038.998986	−2039.117788	322.7*i*
TS115-S1	0.702310	0.744772	0.626312	−2039.735159	−2038.990387	−2039.108847	373.4*i*
TS115-S2	0.702613	0.745157	0.626279	−2039.744734	−2038.999577	−2039.118455	350.0*i*
TS115-S3	0.702059	0.744865	0.624549	−2039.739063	−2038.994198	−2039.114514	358.3*i*
TS115-S4	0.702461	0.745160	0.626187	−2039.743505	−2038.998345	−2039.117318	330.1*i*
TS115-S5	0.702322	0.744796	0.625750	−2039.740613	−2038.995817	−2039.114863	348.2*i*
TS115-S6	0.702109	0.745046	0.624079	−2039.726235	−2038.981189	−2039.102156	293.5*i*
TS115- *Triplet*	0.702652	0.745000	0.626909	−2039.740757	−2038.995757	−2039.113848	399.4*i*
TS115-RE	0.702820	0.745536	0.626593	−2039.735902	−2038.990366	−2039.109309	233.0*i*
Int116	0.703945	0.747137	0.625864	−2039.809229	−2039.062092	−2039.183365	
Int117	0.178275	0.195482	0.131973	−594.371191	−594.175709	−594.239218	
Int118	0.371074	0.394698	0.314530	−1057.012475	−1056.617777	−1056.697945	
TS119-Major-C1	1.173394	1.240906	1.068602	−3047.831364	−3046.590458	−3046.762762	335.1*i*
TS119-Major-C2	1.173196	1.240879	1.066842	−3047.825277	−3046.584398	−3046.758435	367.0*i*
TS119-Minor-C1	1.172809	1.240428	1.067792	−3047.825443	−3046.585015	−3046.757651	311.1*i*

TS119-Minor-C2	1.173409	1.240864	1.066560	−3047.826035	−3046.585171	−3046.759475	350.8*i*
TS119-S1	1.173781	1.241205	1.069469	−3047.831160	−3046.589955	−3046.761691	308.6*i*
TS119-S2	1.173372	1.240998	1.068003	−3047.825422	−3046.584424	−3046.757419	346.0*i*
TS119-S3	1.172900	1.240357	1.068252	−3047.822602	−3046.582245	−3046.754350	377.7*i*
TS119-S4	1.172765	1.240328	1.066843	−3047.823226	−3046.582898	−3046.756383	361.2*i*
TS119-S5	1.172504	1.240404	1.064982	−3047.819664	−3046.579260	−3046.754682	343.0*i*
TS119-S6	1.172367	1.240212	1.065765	−3047.823068	−3046.582856	−3046.757303	345.4*i*
TS119-S7	1.173172	1.240783	1.066461	−3047.828785	−3046.588002	−3046.762324	359.7*i*
TS119-S8	1.173423	1.240944	1.067852	−3047.828763	−3046.587819	−3046.760911	344.7*i*
TS119-S9	1.173333	1.240974	1.066769	−3047.826647	−3046.585673	−3046.759878	356.1*i*
TS119-S10	1.173547	1.240939	1.070486	−3047.821467	−3046.580528	−3046.750981	358.0*i*
TS119-S11	1.172470	1.240145	1.067227	−3047.816155	−3046.576010	−3046.748928	340.2*i*
TS119-S12	1.172704	1.240370	1.066251	−3047.814706	−3046.574336	−3046.748455	367.3*i*
TS119-S13	1.172361	1.240198	1.063973	−3047.812591	−3046.572393	−3046.748618	361.0*i*
TS119-S14	1.173018	1.240578	1.068564	−3047.818535	−3046.577957	−3046.749971	350.3*i*
TS119-S15	1.172690	1.240480	1.065581	−3047.816333	−3046.575853	−3046.750752	324.7*i*
TS119-S16	1.173066	1.240598	1.068642	−3047.823161	−3046.582563	−3046.754519	354.2*i*
TS119-S17	1.172908	1.240467	1.067675	−3047.822482	−3046.582015	−3046.754807	352.4*i*
TS119-S18	1.172735	1.240420	1.066227	−3047.824175	−3046.583755	−3046.757948	308.9*i*
TS119-S19	1.172836	1.240517	1.065899	−3047.824887	−3046.584370	−3046.758988	354.7*i*
TS119-S20	1.173663	1.240958	1.070871	−3047.827592	−3046.586634	−3046.756721	351.7*i*
TS119-S21	1.172304	1.240240	1.065170	−3047.820398	−3046.580158	−3046.755228	364.0*i*
TS119-S22	1.172828	1.240641	1.065781	−3047.821235	−3046.580594	−3046.755454	369.6*i*
TS119-S23	1.172711	1.240526	1.065992	−3047.823902	−3046.583376	−3046.757910	343.7*i*
TS119-S24	1.173675	1.241221	1.069288	−3047.826076	−3046.584855	−3046.756788	321.7*i*
TS119-S25	1.173305	1.240982	1.067615	−3047.823674	−3046.582692	−3046.756059	354.3*i*
TS119-S26	1.173075	1.240699	1.068707	−3047.825616	−3046.584917	−3046.756909	363.5*i*
TS119-S27	1.172704	1.240314	1.065563	−3047.824433	−3046.584119	−3046.758870	358.9*i*
TS119-S28	1.173128	1.240595	1.067280	−3047.826044	−3046.585449	−3046.758764	357.3*i*
TS119-S29	1.172857	1.240433	1.066177	−3047.824823	−3046.584390	−3046.758646	366.1*i*
TS119-S30	1.173218	1.240769	1.068078	−3047.818790	−3046.578021	−3046.750712	337.6*i*
TS119-S31	1.173356	1.240803	1.067826	−3047.823163	−3046.582360	−3046.755337	332.9*i*
TS119-S32	1.172622	1.240282	1.067246	−3047.820606	−3046.580324	−3046.753360	358.9*i*
TS119-S33	1.172725	1.240313	1.068432	−3047.821173	−3046.580860	−3046.752741	375.1*i*
TS119-S34	1.172204	1.240028	1.066949	−3047.818520	−3046.578492	−3046.751571	288.2*i*
TS119-S35	1.173199	1.240643	1.067113	−3047.818903	−3046.578260	−3046.751790	347.0*i*
TS119-S36	1.173232	1.240641	1.067145	−3047.820595	−3046.579954	−3046.753450	344.8*i*
TS119-S37	1.172962	1.240790	1.066834	−3047.809982	−3046.569192	−3046.743148	300.7*i*
TS119-S38	1.172648	1.240410	1.067137	−3047.813321	−3046.572911	−3046.746184	312.6*i*

Supplementary Table 7. Energies in Fig. 4 and Supplementary Fig. 18. Gas-phase energies (***E***) (in Hartree) of the structures calculated at B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Gas Phase)// B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory

Structure	*E*
Int107	−1539.643588
Int-S14	−1079.374828
Chlorine Radical	−460.166882
TS115-Major	−2039.691650
TS115-Minor	−2039.685943
TS119-Major-C1	−3047.760060
TS119-Major-C2	−3047.753616
TS119-Minor-C1	−3047.752012
TS119-Minor-C2	−3047.754165

NMR spectra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7.779
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7.595
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7.579
7.524
7.520
7.515
7.507
7.505
7.502
7.499
7.424
7.419
7.413
7.407
7.402
7.396
7.394
7.384
7.379
7.368
7.364
7.327
7.322
7.316
7.311
7.304
7.300
7.290
7.287
7.282
7.112
7.093
7.090
2.555
2.537
2.521
2.503
2.219
2.201
2.186
2.167
1.096
1.078
1.060
Ph
Et
H
N
Ph
Ph
O
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0.97
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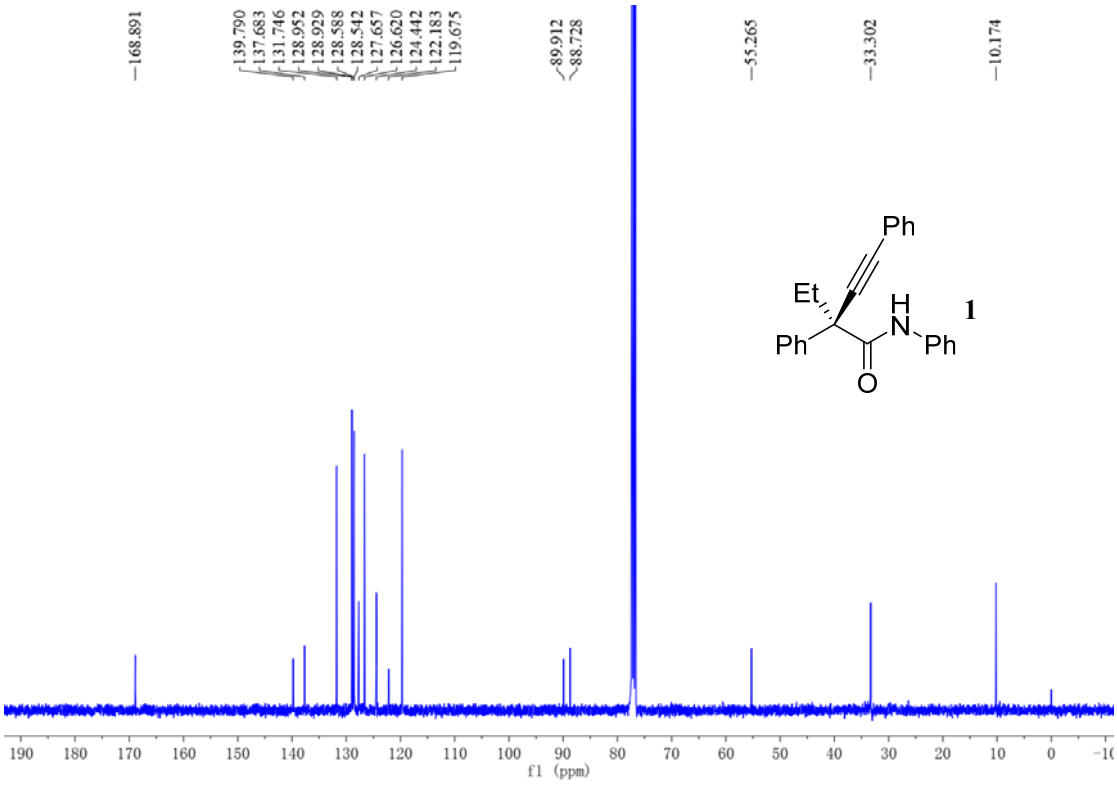
2.04
4.73
2.91
1.00
1.07
1.06
2.97
f1 (ppm)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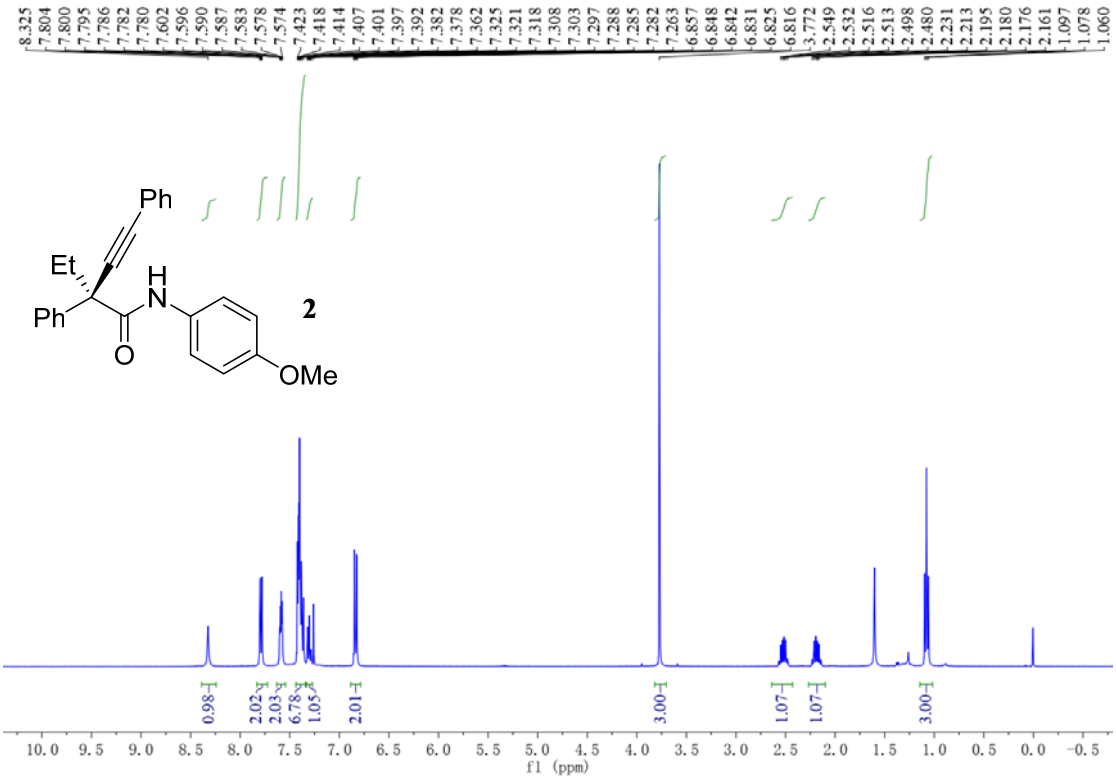
139.790
137.683
131.746
128.952
128.929
128.588
128.542
127.657
126.620
124.442
122.183
119.675
89.912
88.728
55.265
33.302
10.174
Ph
Et
H
N
Ph
Ph
O
1
f1 (ppm)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7.800
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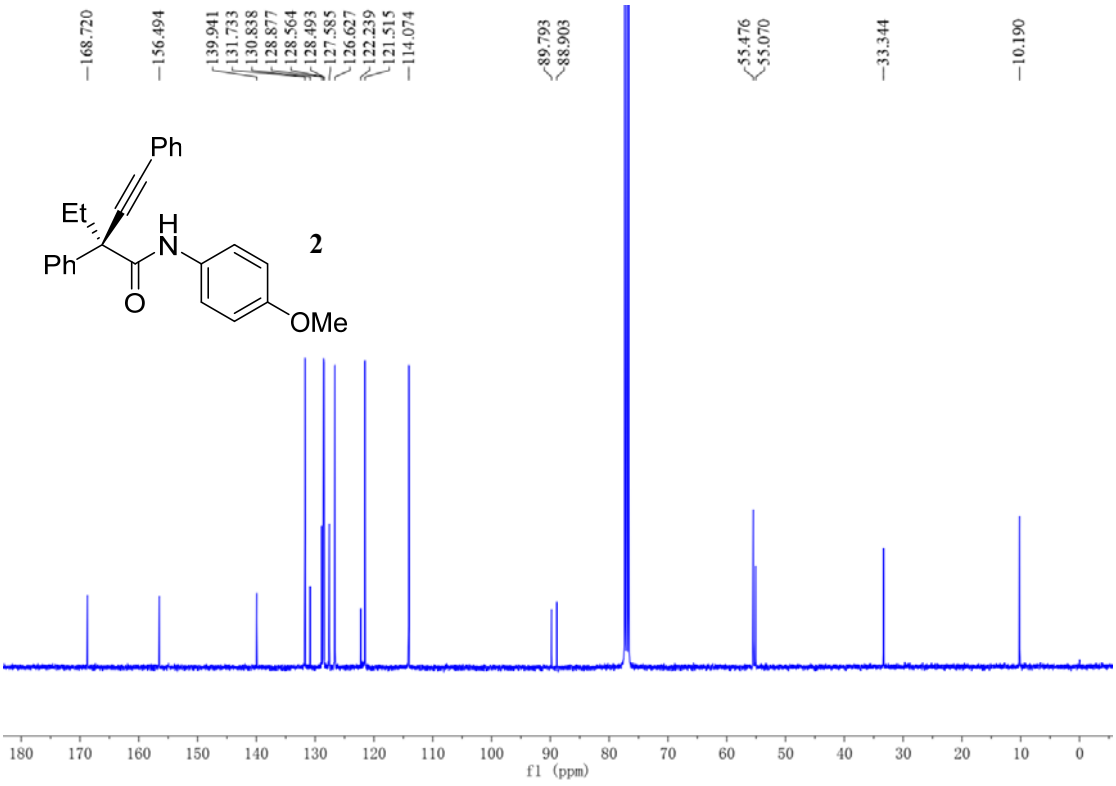
7.578
7.574
7.423
7.418
7.414
7.407
7.401
7.397
7.392
7.382
7.378
7.362
7.325
7.321
7.318
7.308
7.303
7.297
7.288
7.285
7.282
7.263
6.857
6.848
6.842
6.831
6.825
6.816
3.772
2.549
2.532
2.516
2.513
2.498
2.480
2.231
2.213
2.195
2.180
2.176
2.161
1.097
1.078
1.060
Ph
Et
Ph
H
N
O
2
OMe
0.98
2.02
2.03
6.78
1.05
2.01
3.00
1.07
1.07
3.00
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)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128.564
128.493
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121.515
114.074
89.793
88.903
55.476
55.070
33.344
10.190
Ph
Et
Ph
H
N
O
2
OMe
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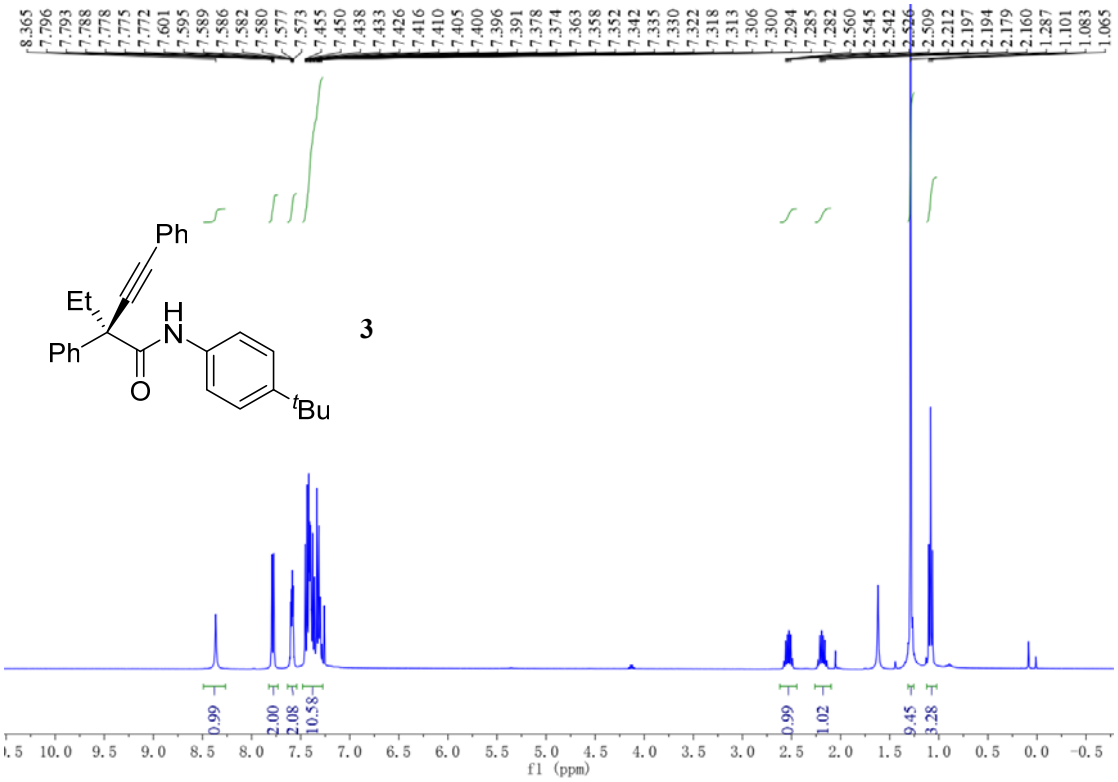
f1 (ppm)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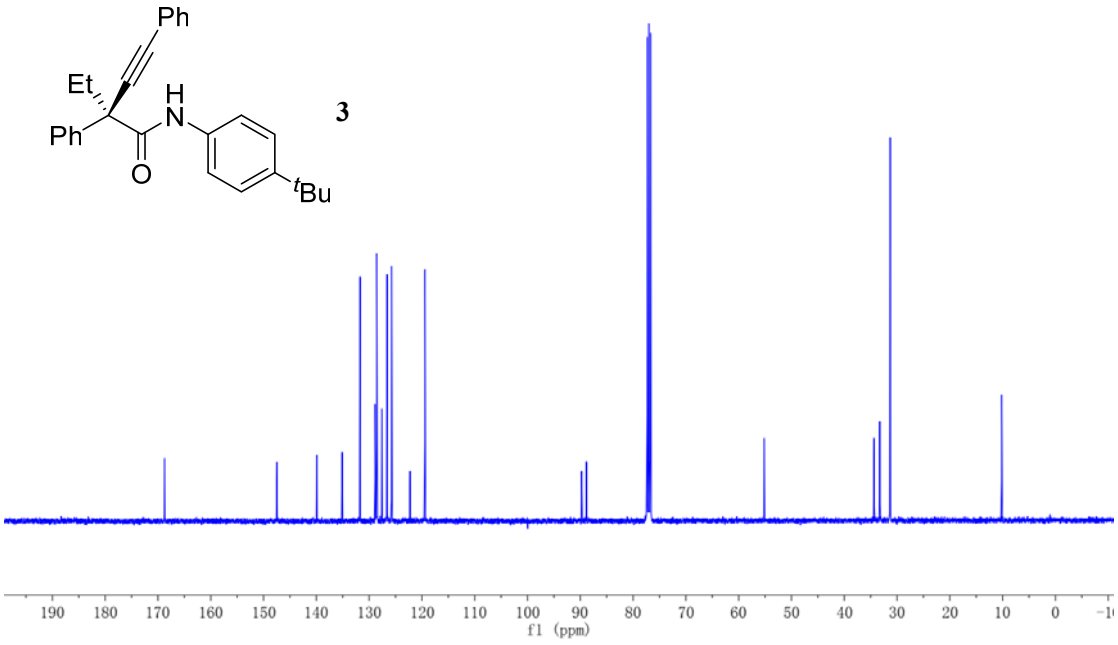
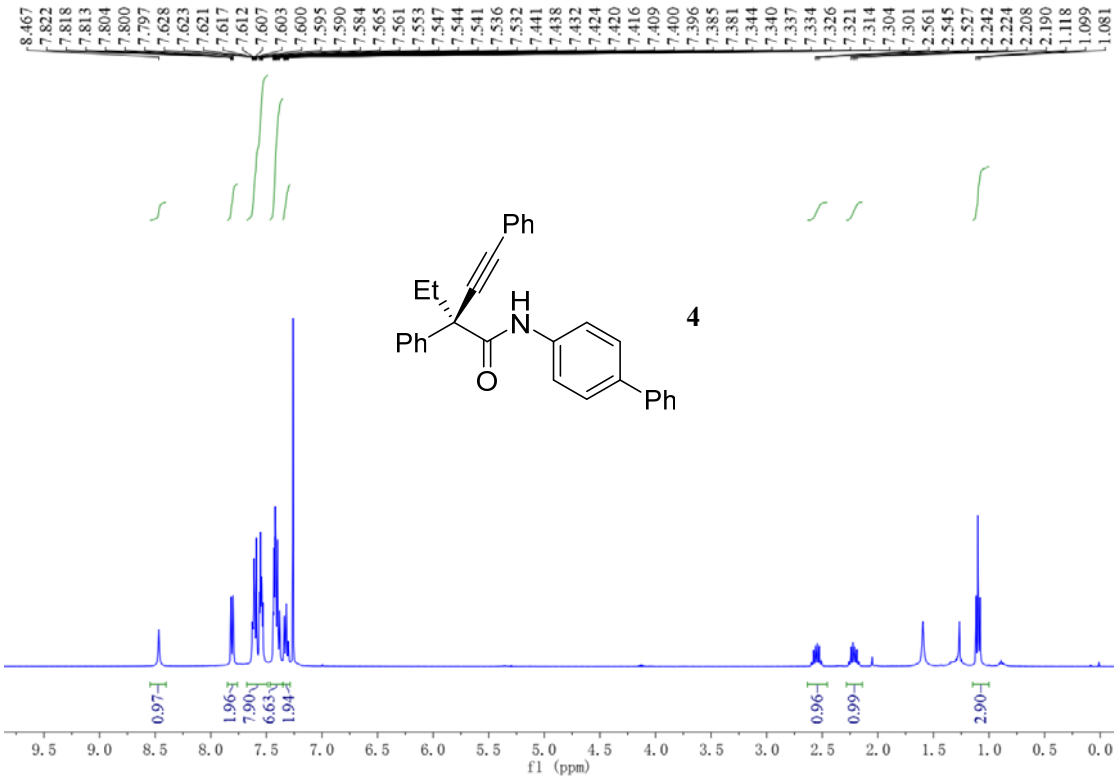
Et
Ph
H
N
O
tBu
3
f1 (ppm)


Ph
Et
Ph
H
N
O
tBu
3
f1 (ppm)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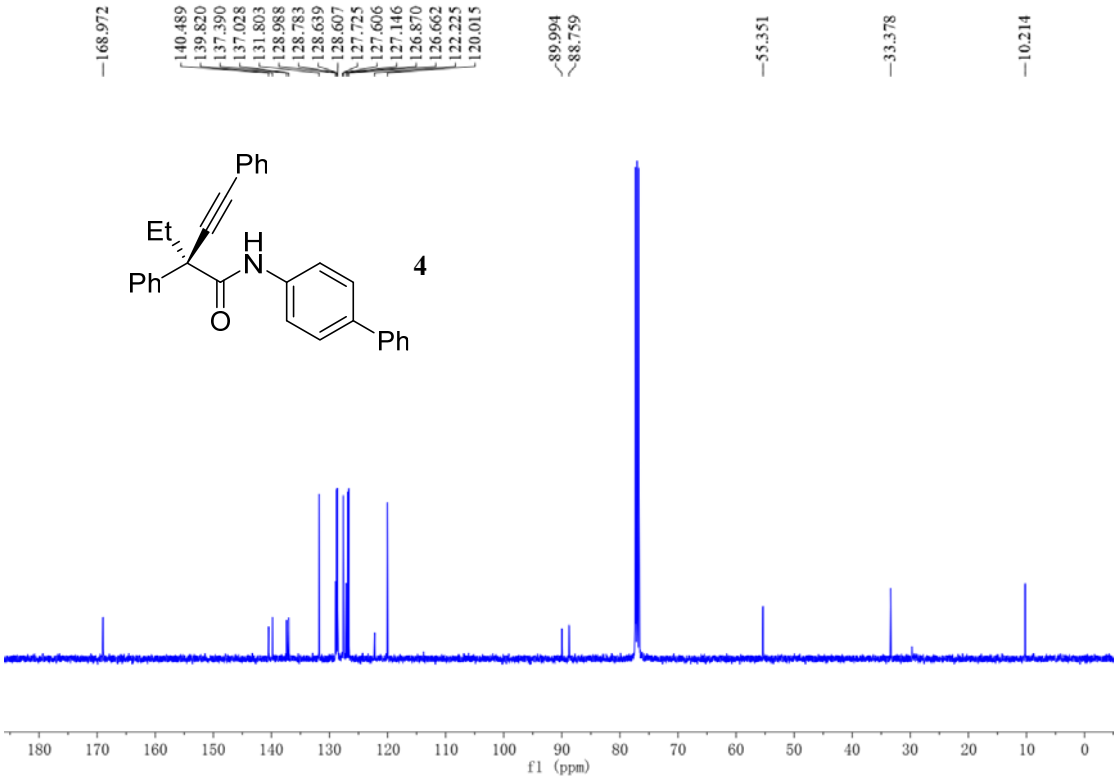
7.607
7.603
7.600
7.595
7.590
7.584
7.565
7.561
7.553
7.547
7.544
7.541
7.536
7.532
7.441
7.438
7.432
7.424
7.420
7.416
7.409
7.400
7.396
7.385
7.381
7.344
7.340
7.337
7.334
7.326
7.321
7.314
7.304
7.301
2.561
2.545
2.527
2.242
2.224
2.208
2.190
1.118
1.099
1.081
Ph
Et
H
N
Ph
O
Ph
4
0.97
1.96
7.90
6.63
1.94
0.96
0.99
2.90
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)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127.146
126.870
126.662
122.225
120.015
89.994
88.759
55.351
33.378
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Ph
Et
H
N
Ph
O
Ph
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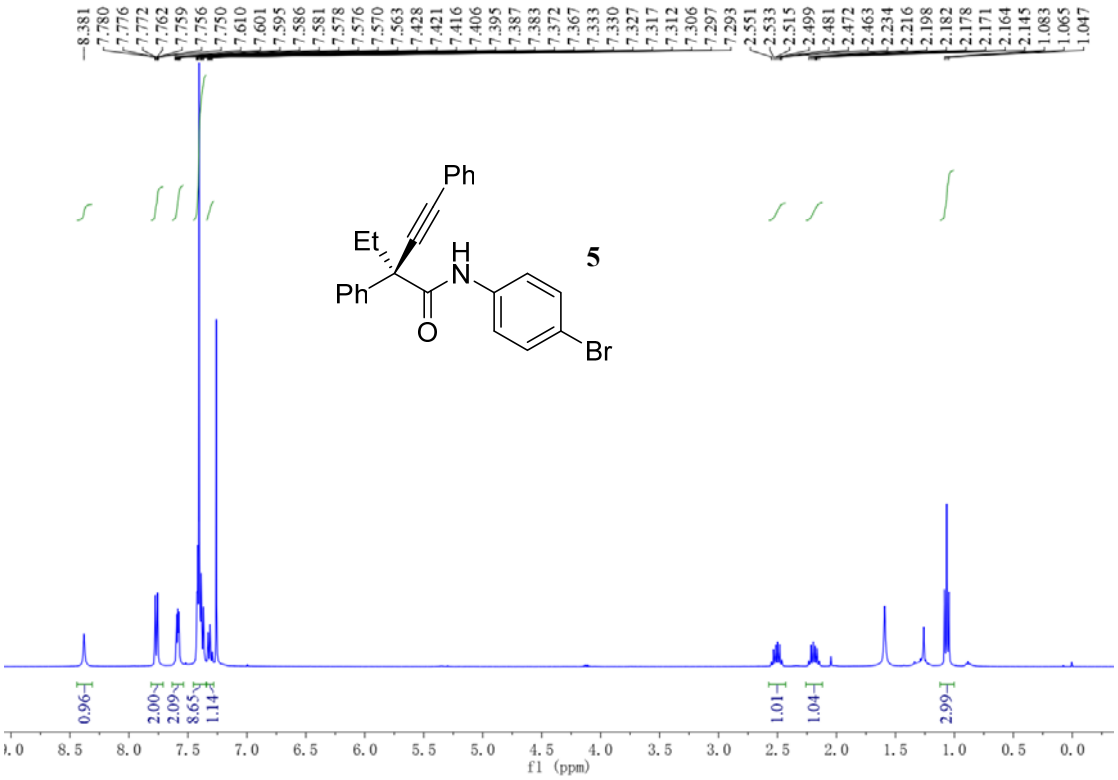
f1 (ppm)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7.570
7.563
7.428
7.421
7.416
7.406
7.395
7.387
7.383
7.372
7.367
7.333
7.330
7.327
7.317
7.312
7.306
7.297
7.293
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2.533
2.515
2.499
2.481
2.472
2.463
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2.198
2.182
2.178
2.171
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1.065
1.047
Ph
Et
H
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Ph
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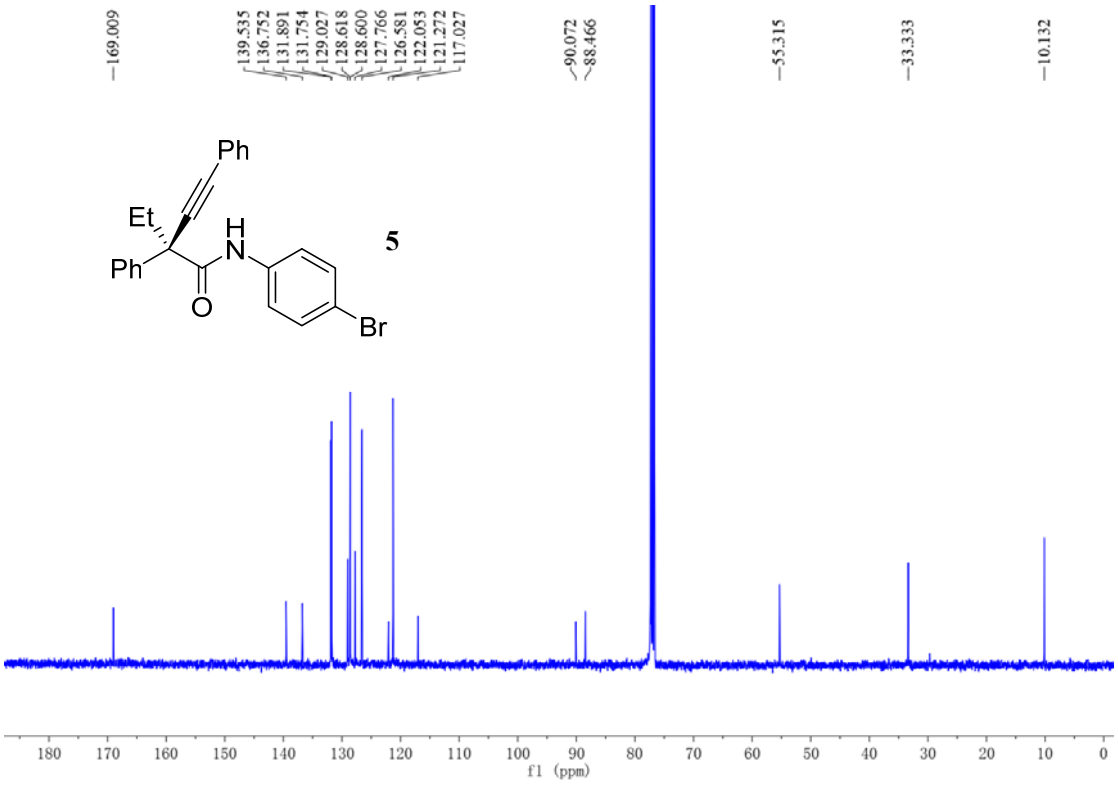
1.01
1.04
2.99
f1 (ppm)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126.581
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121.272
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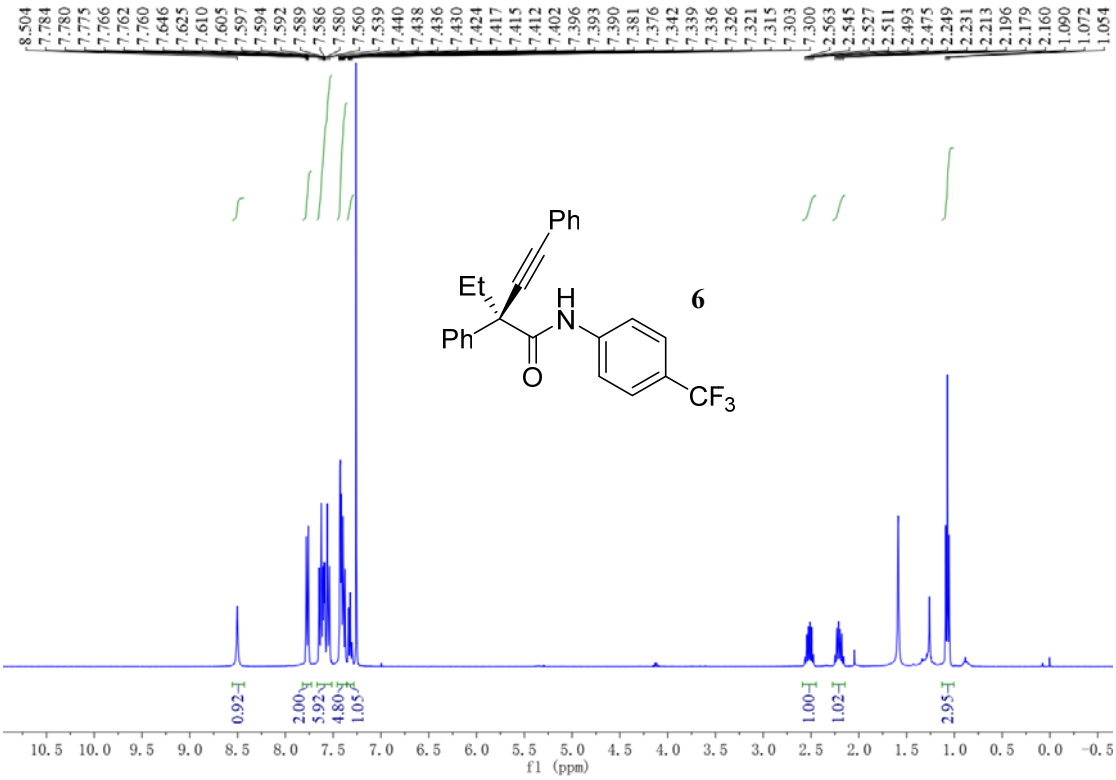
H
N
Ph
O
Br
5
f1 (ppm)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Et
Ph
H
N
O
CF3
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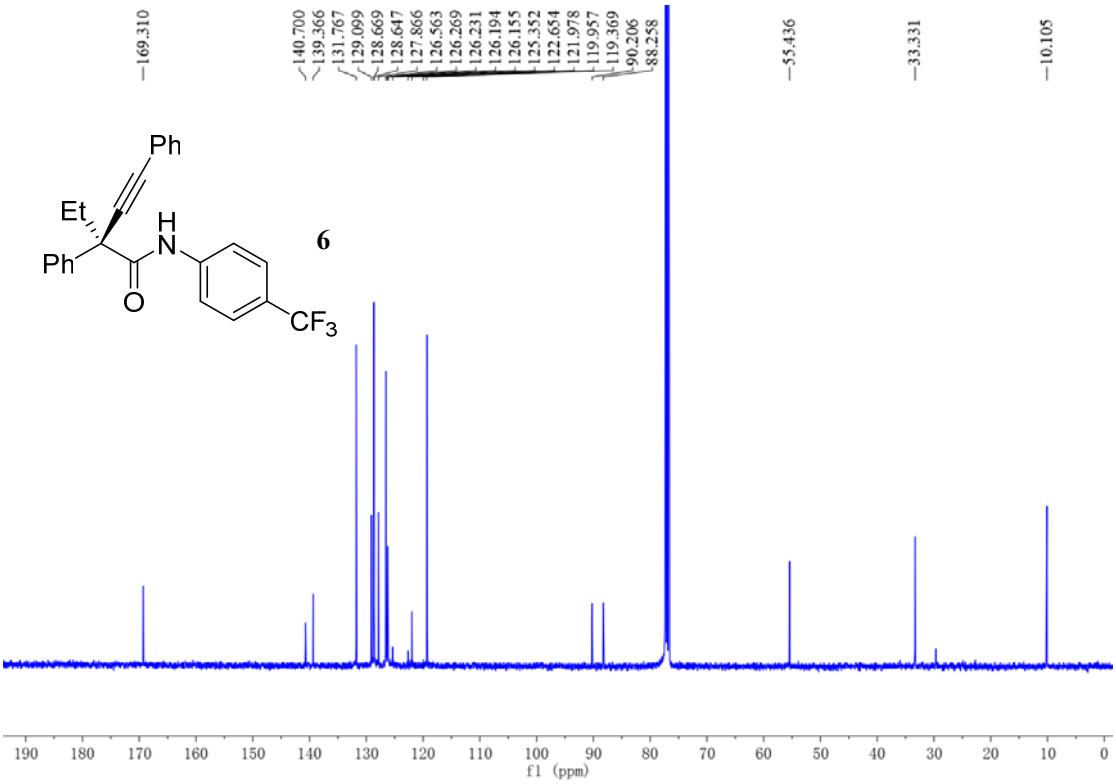
f1 (ppm)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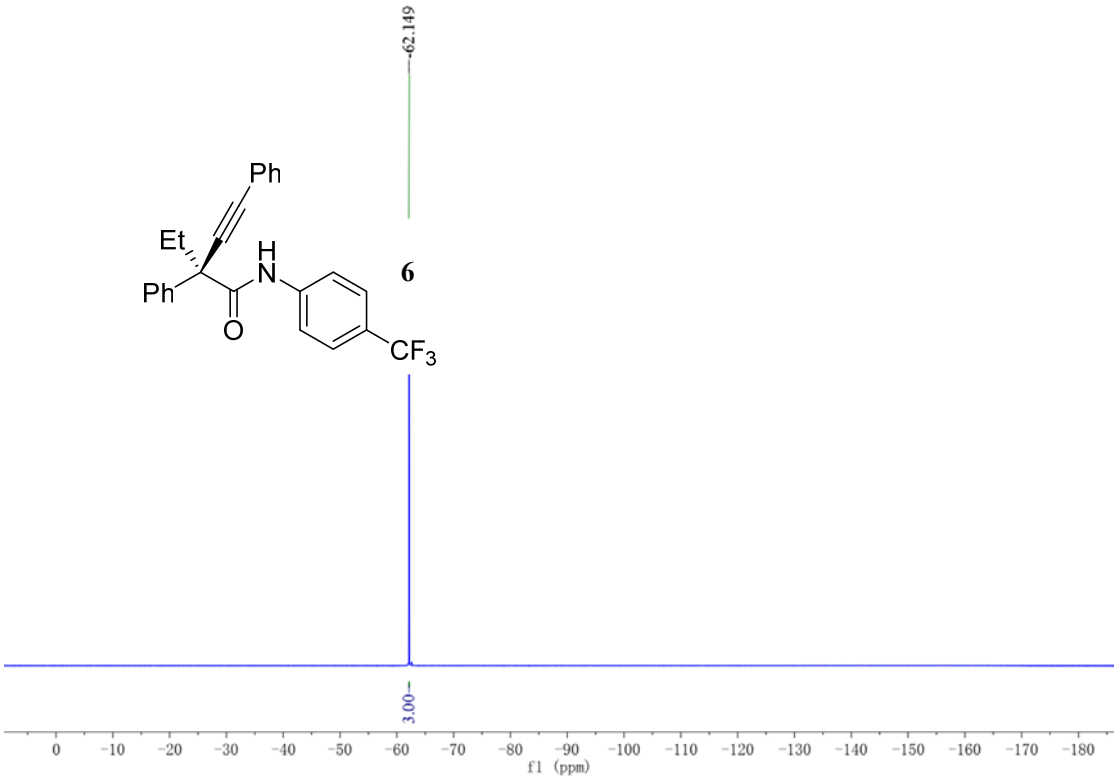
Et
Ph
H
N
O
CF3
6
f1 (ppm)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H
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O
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CF3
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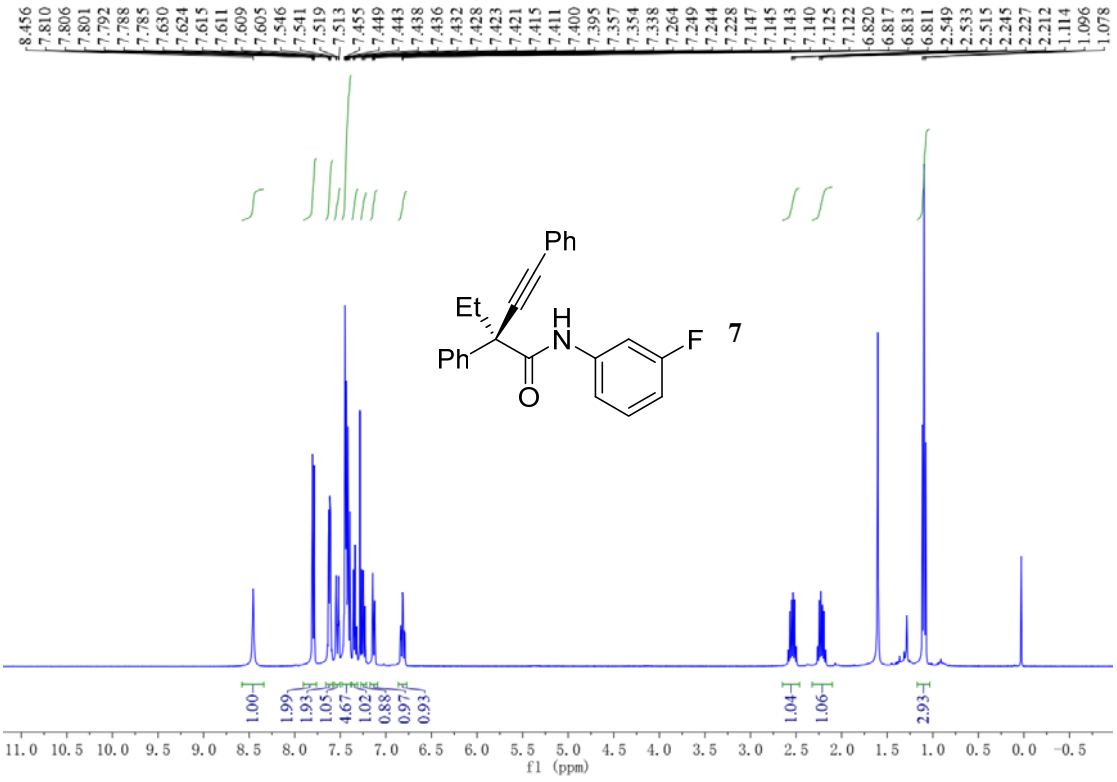
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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7.546
7.541
7.519
7.513
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7.449
7.443
7.438
7.436
7.432
7.428
7.423
7.421
7.415
7.411
7.400
7.395
7.357
7.354
7.338
7.264
7.249
7.244
7.228
7.147
7.145
7.143
7.140
7.125
7.122
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6.813
6.811
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2.515
2.245
2.227
2.212
1.114
1.096
1.078
Ph
Et
H
N
Ph
O
F
7
1.00
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0.93
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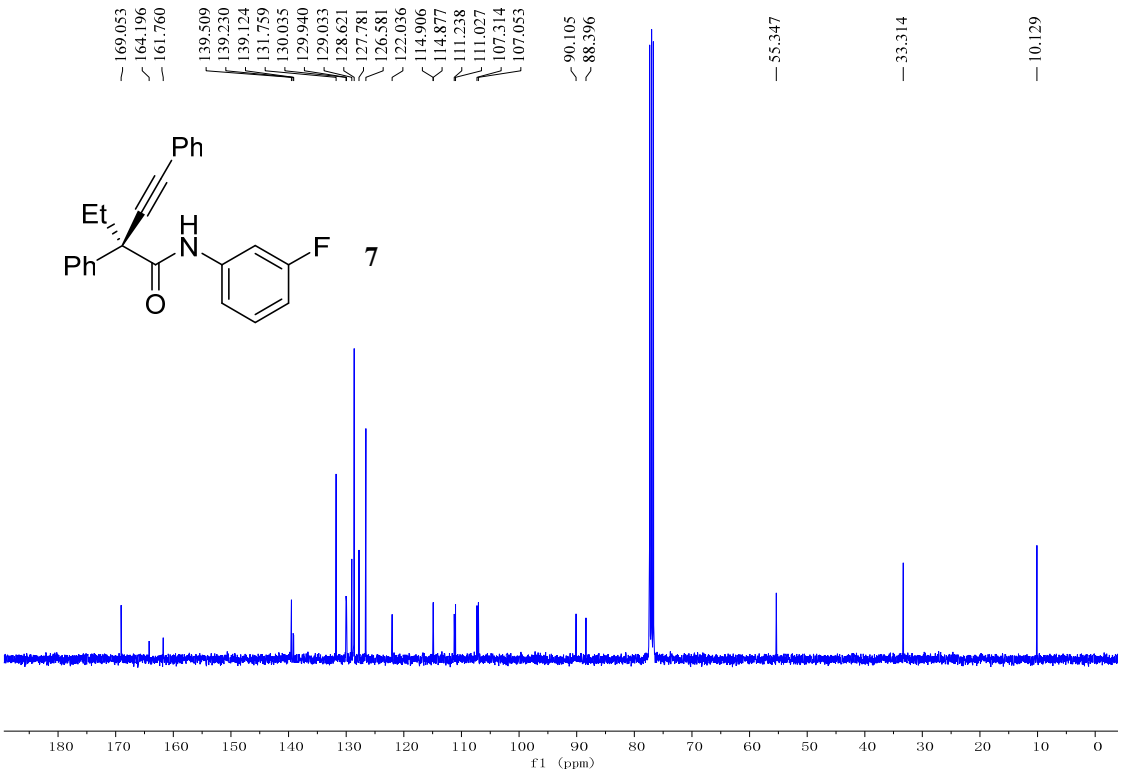
1.06
2.93
f1 (ppm)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111.027
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Et
H
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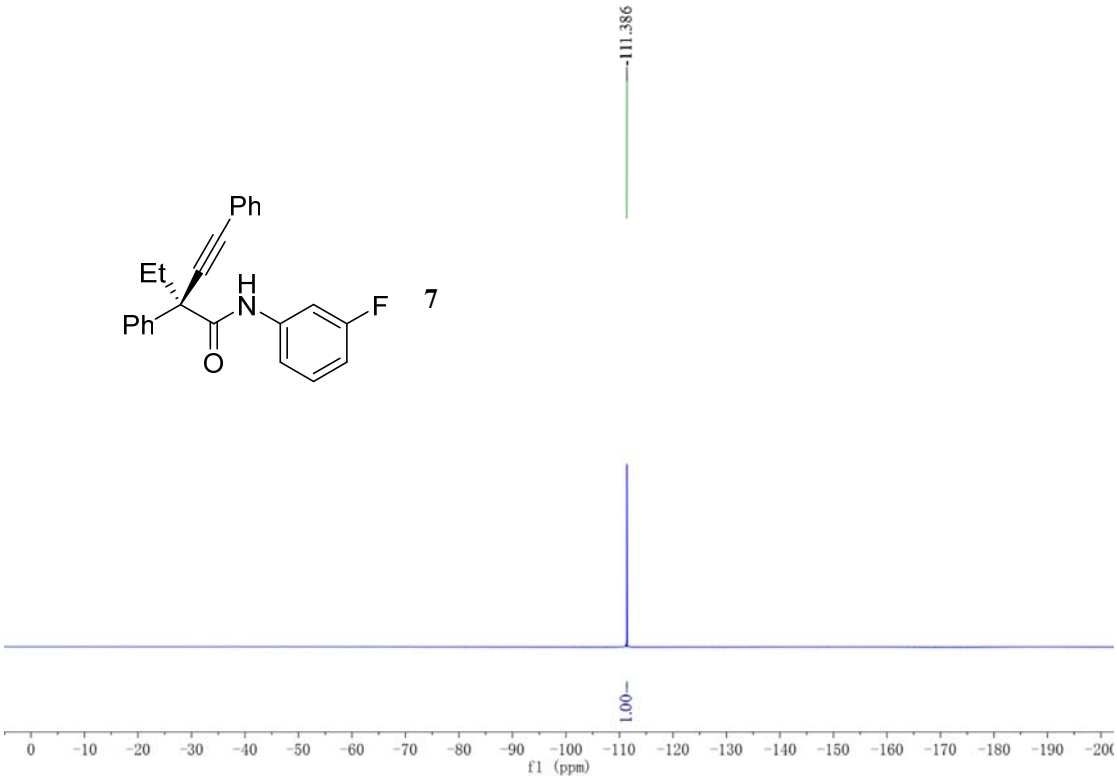
Ph
O
F
7
f1 (ppm)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-160
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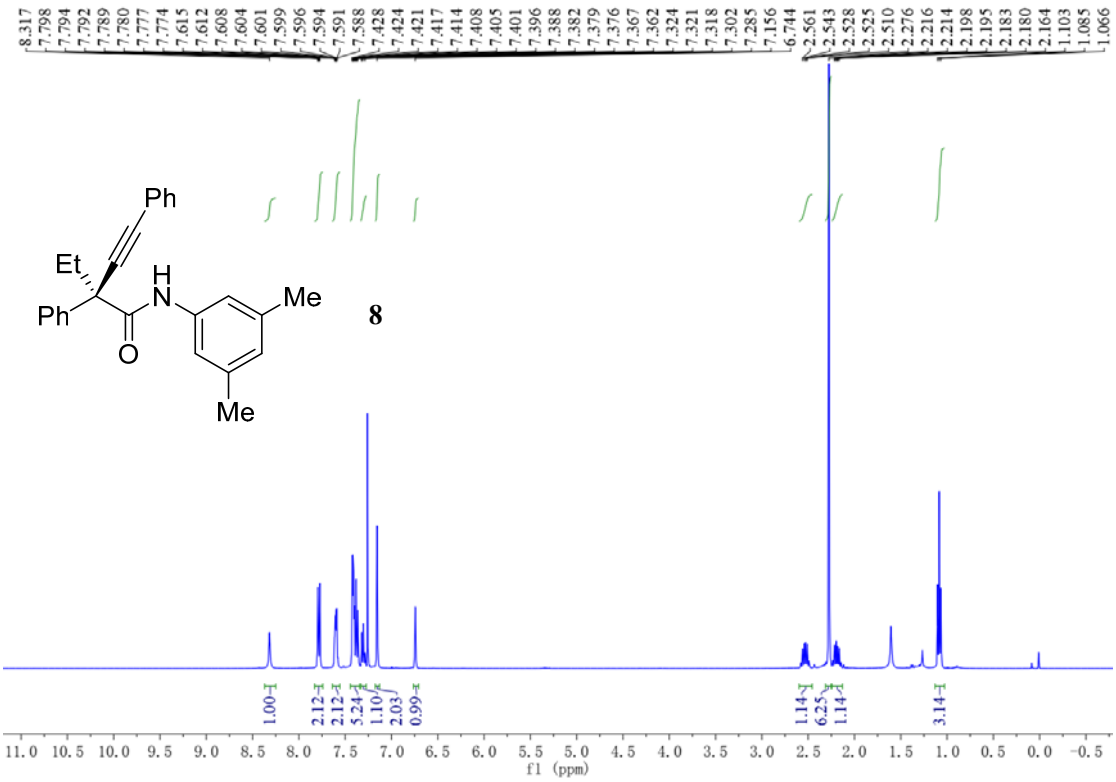
f1 (ppm)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7.591
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7.424
7.421
7.417
7.414
7.408
7.405
7.401
7.396
7.388
7.382
7.379
7.376
7.367
7.362
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7.321
7.318
7.302
7.285
7.156
6.744
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2.543
2.528
2.525
2.510
2.276
2.216
2.214
2.198
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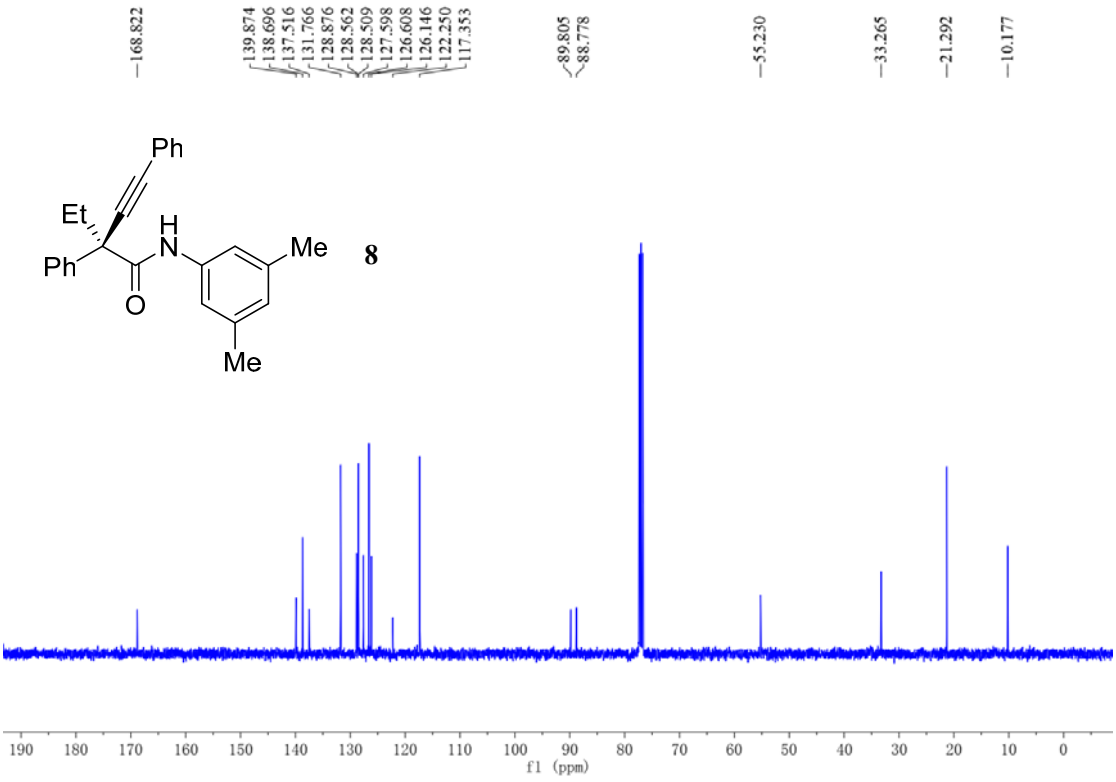
2.183
2.180
2.164
1.103
1.085
1.066
Ph
Et
H
N
Me
Ph
O
Me
8
1.00
2.12
2.12
5.24
1.10
2.03
0.99
1.14
6.25
1.14
3.14
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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138.696
137.516
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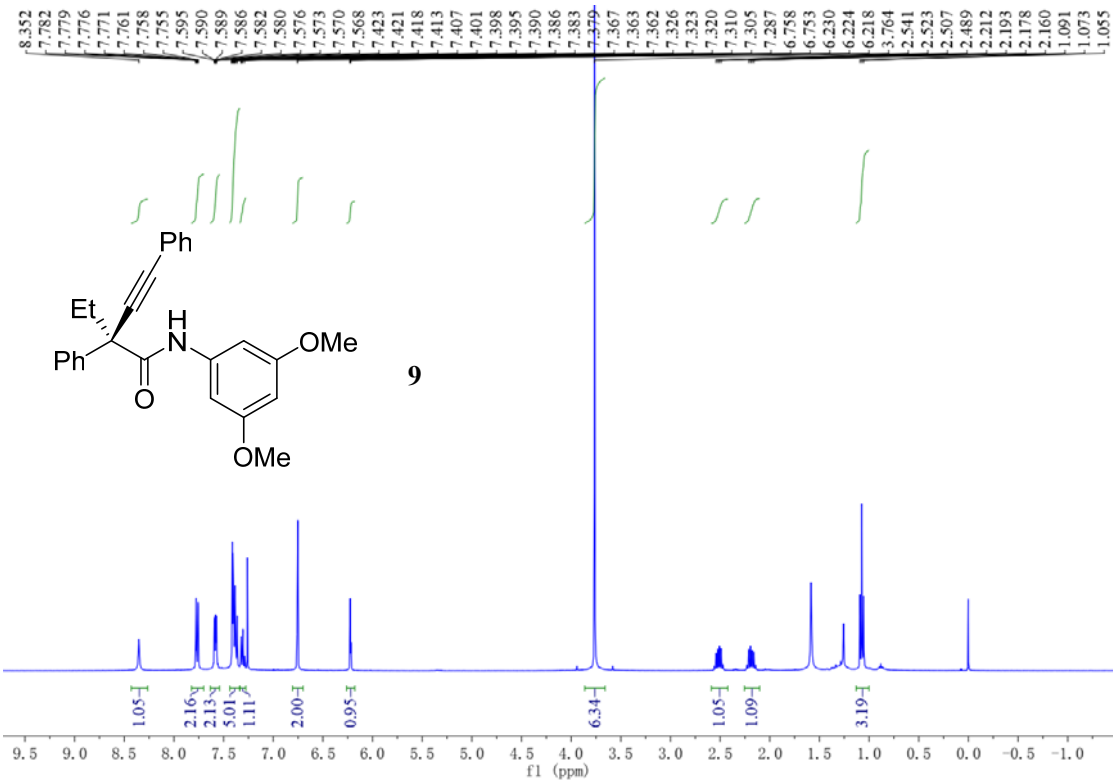
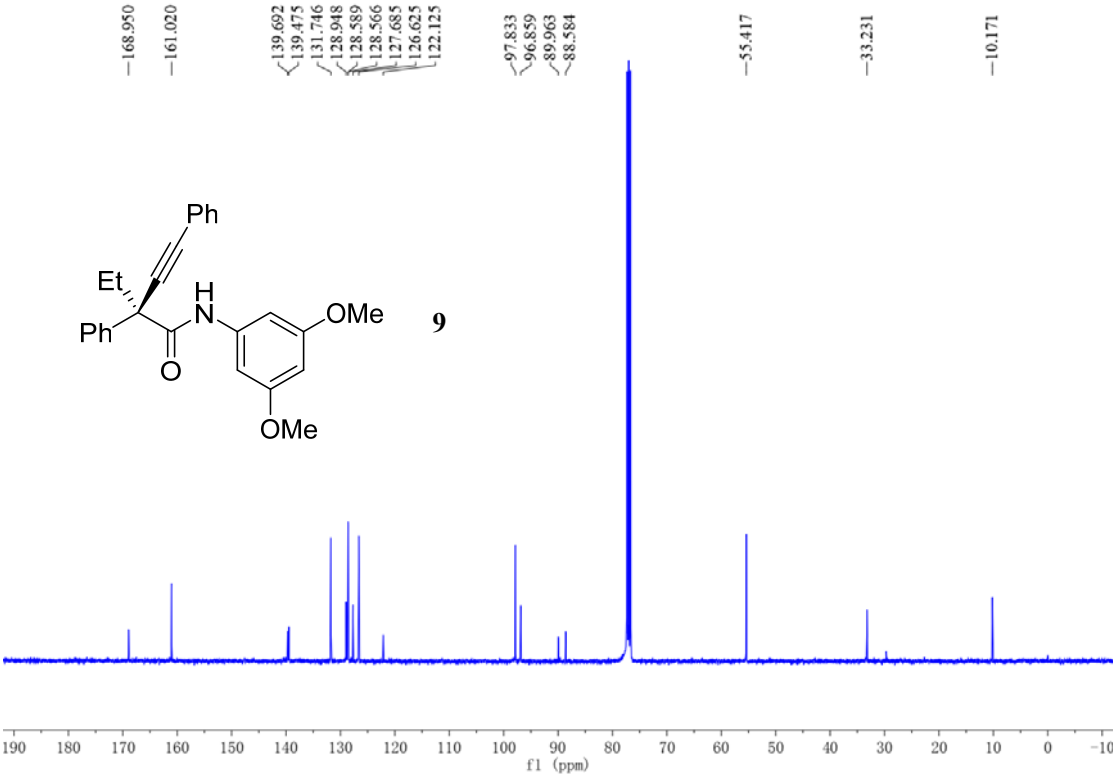
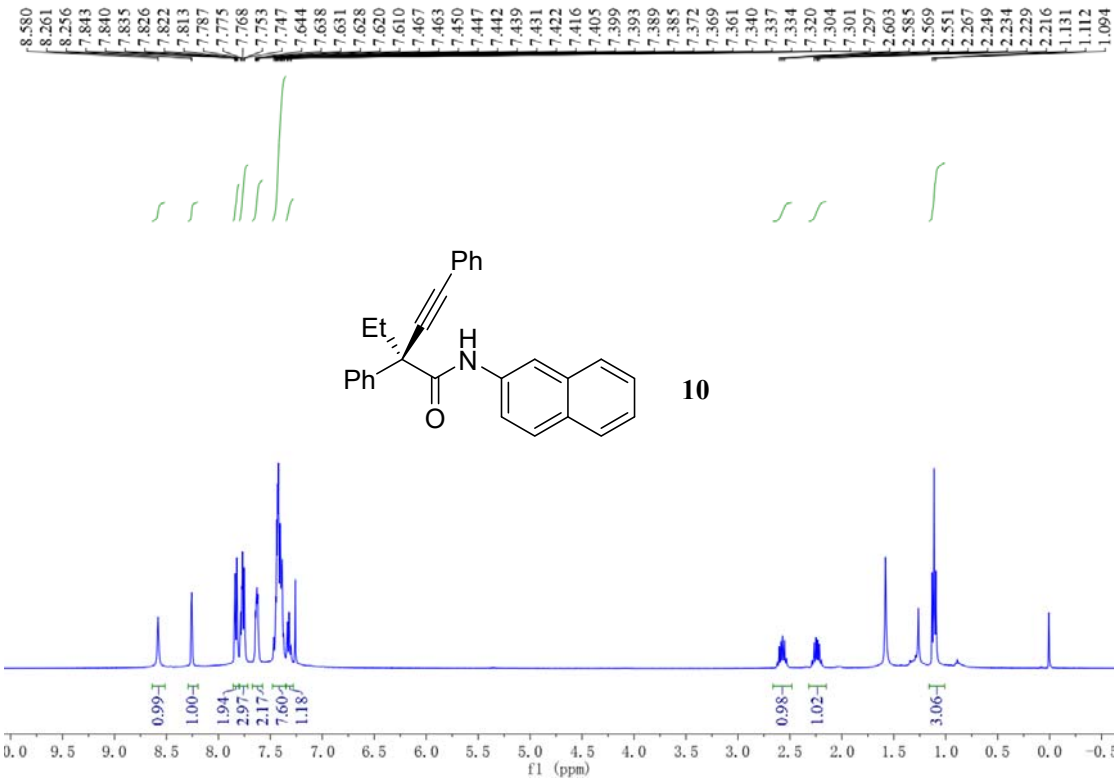
128.876
128.562
128.509
127.598
126.608
126.146
122.250
117.353
89.805
88.778
55.230
33.265
21.292
10.177
Ph
Et
H
N
Me
Ph
O
Me
8
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Et
H
N
Ph
O
OMe
OMe
9
f1 (ppm)


Ph
Et
H
N
Ph
O
OMe
OMe
9
f1 (ppm)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8.256
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7.840
7.835
7.826
7.822
7.813
7.787
7.775
7.768
7.753
7.747
7.644
7.638
7.631
7.628
7.620
7.610
7.467
7.463
7.450
7.447
7.442
7.439
7.431
7.422
7.416
7.405
7.399
7.393
7.389
7.385
7.372
7.369
7.361
7.340
7.337
7.334
7.320
7.304
7.301
7.297
2.603
2.585
2.569
2.551
2.267
2.249
2.234
2.229
2.216
1.131
1.112
1.094
Ph
Et
H
N
Ph
O
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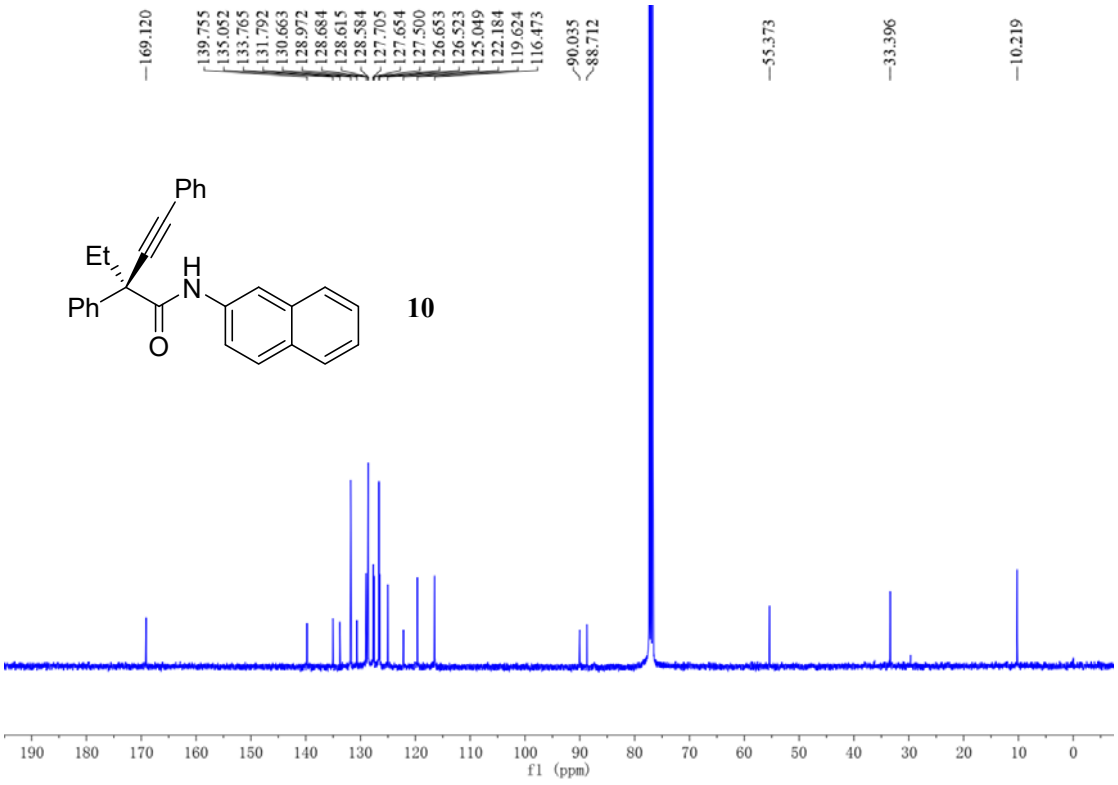
0.99
1.00
1.94
2.97
2.17
7.60
1.18
0.98
1.02
3.06
f1 (ppm)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135.052
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128.684
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128.584
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127.654
127.500
126.653
126.523
125.049
122.184
119.624
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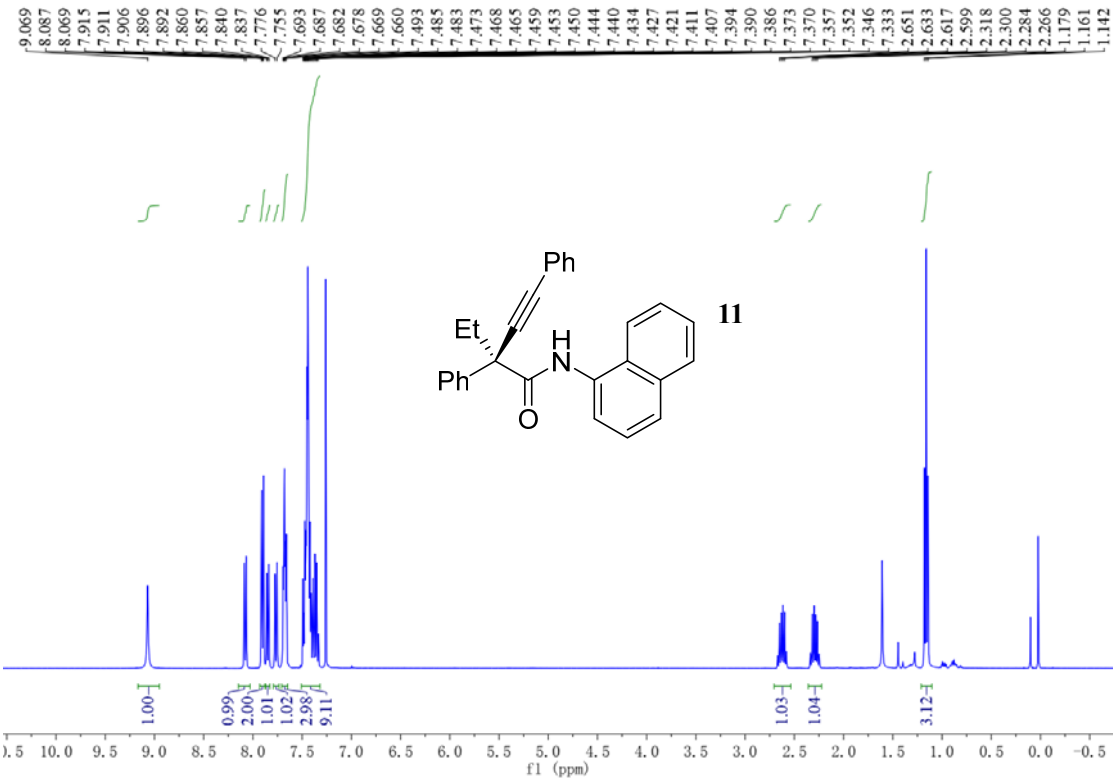
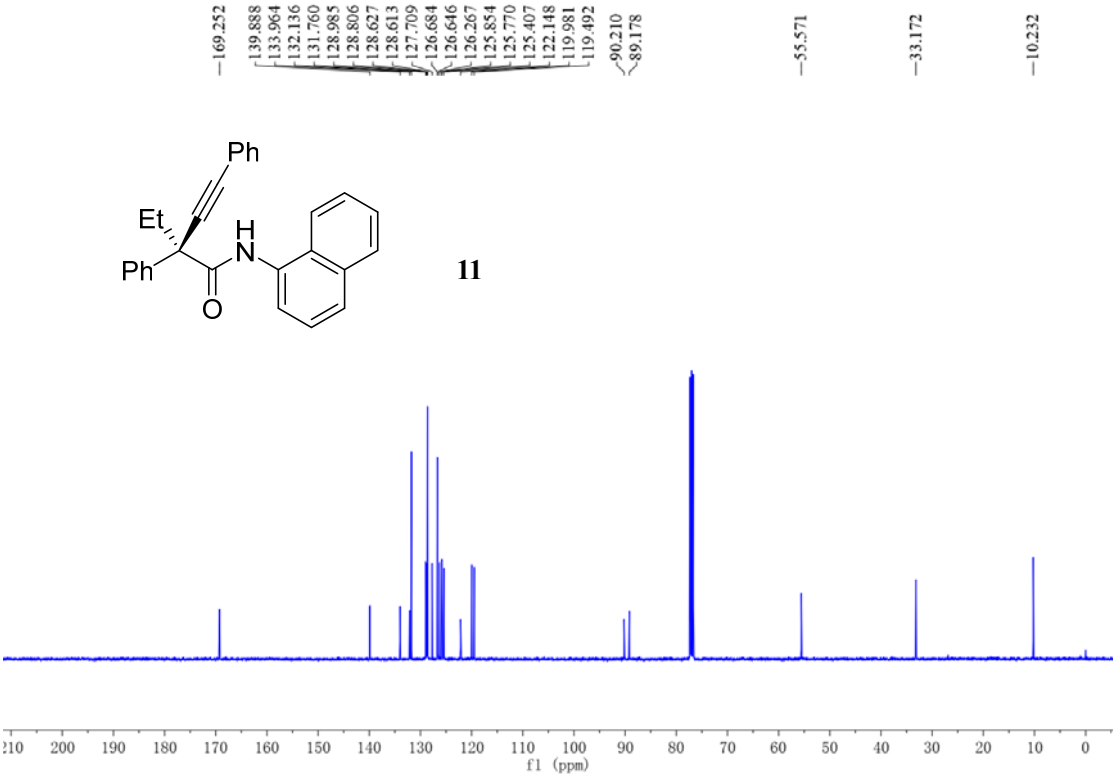
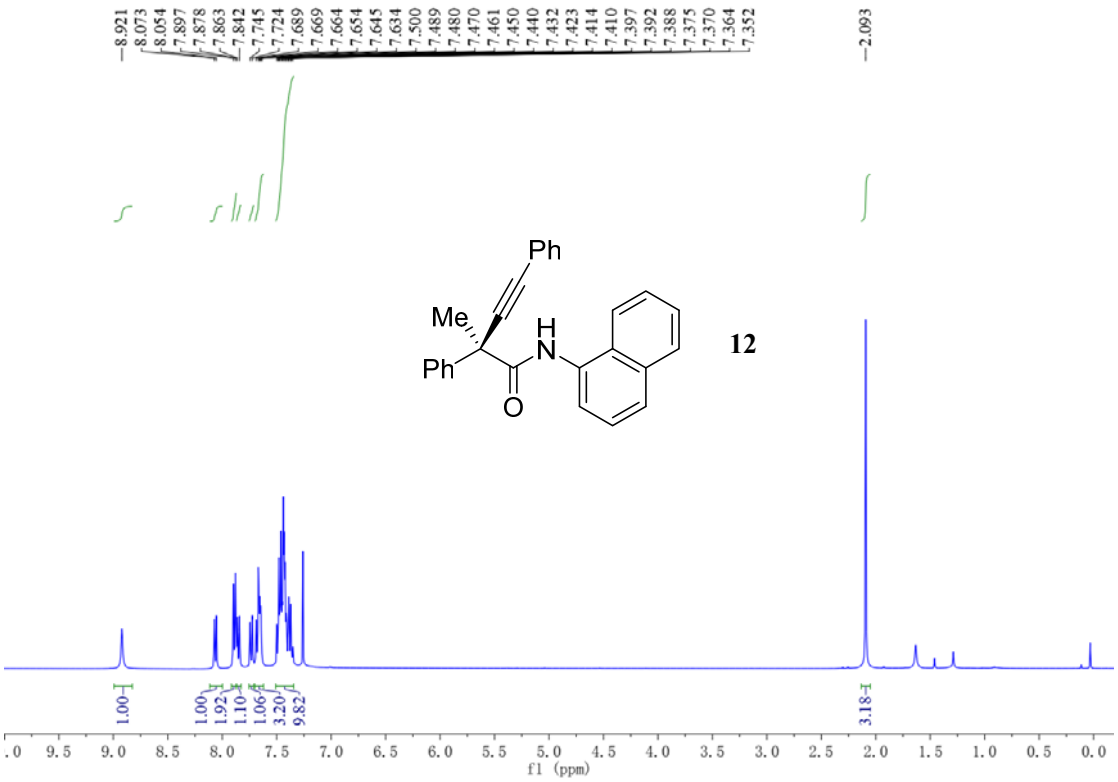
90.035
88.712
55.373
33.396
10.219
Ph
Et
H
N
Ph
O
10
f1 (ppm)


Ph
Et
H
N
Ph
O
11
1.00
0.99
2.00
1.01
1.02
2.98
9.11
1.03
1.04
3.12
f1 (ppm)


Ph
Et
H
N
Ph
O
11
f1 (ppm)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8.054
7.897
7.878
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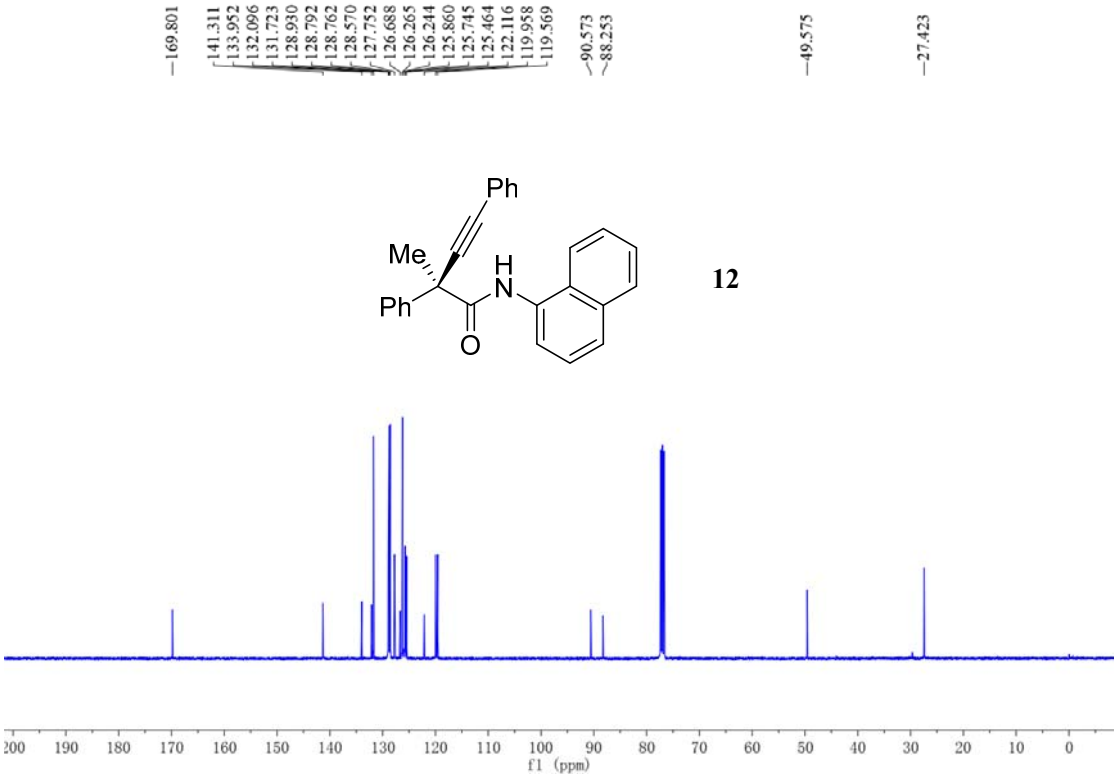
7.842
7.745
7.724
7.689
7.669
7.664
7.654
7.645
7.634
7.500
7.489
7.480
7.470
7.461
7.450
7.440
7.432
7.423
7.414
7.410
7.397
7.392
7.388
7.375
7.370
7.364
7.352
2.093
Ph
Me
Ph
H
N
O
12
1.00
1.00
1.92
1.10
1.06
3.20
9.82
3.18
f1 (ppm)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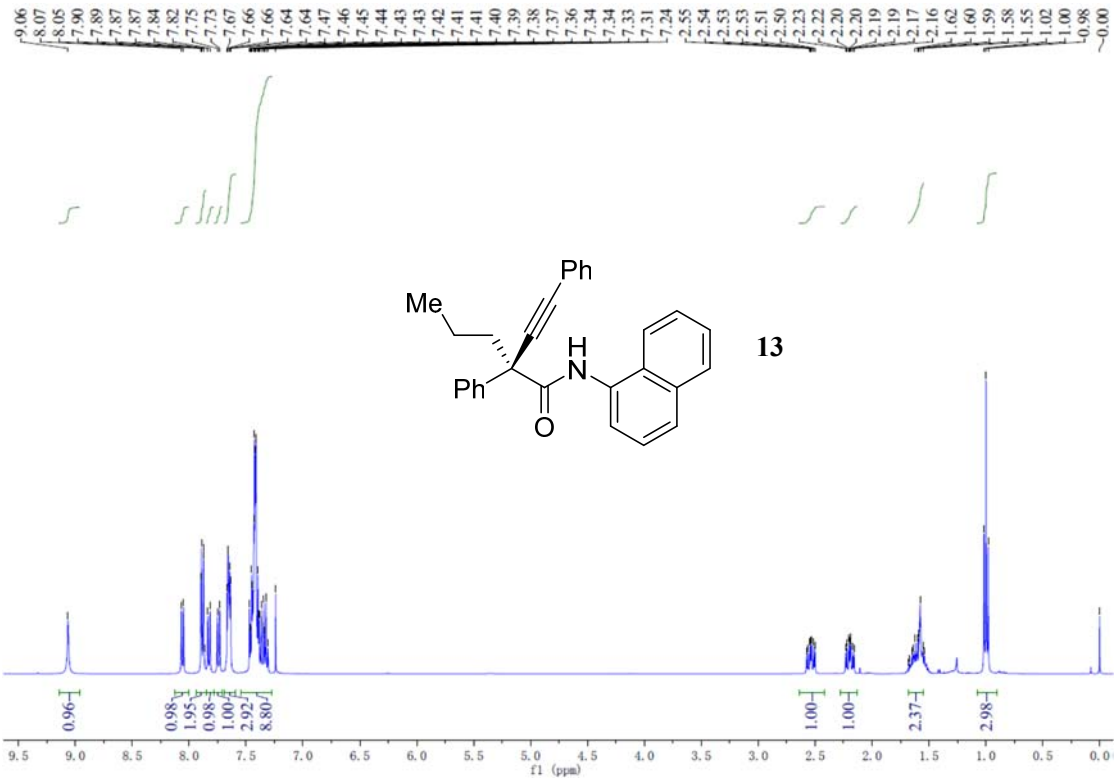
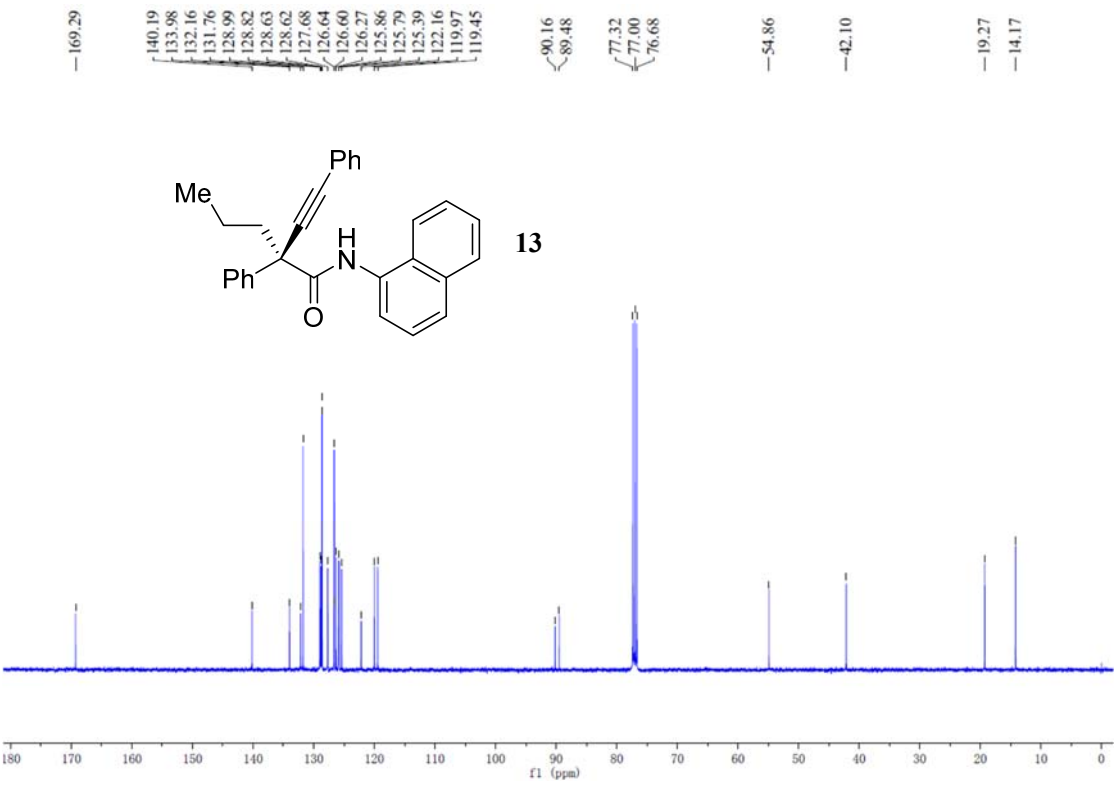
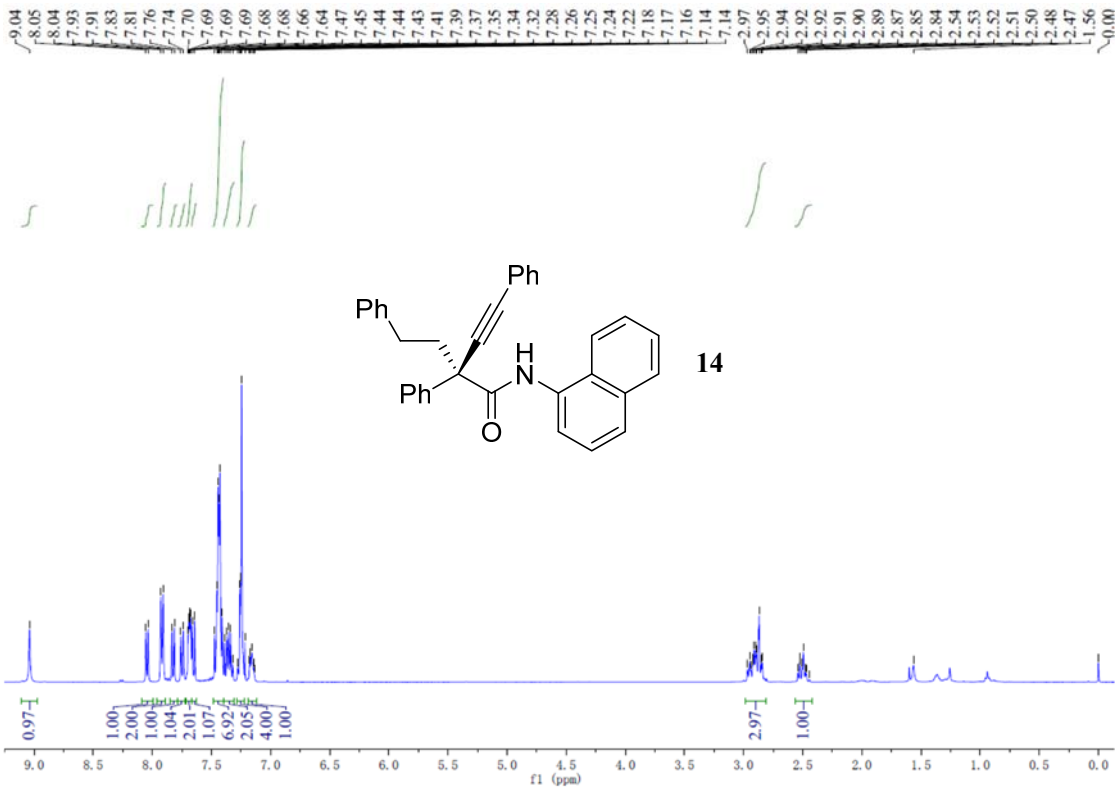
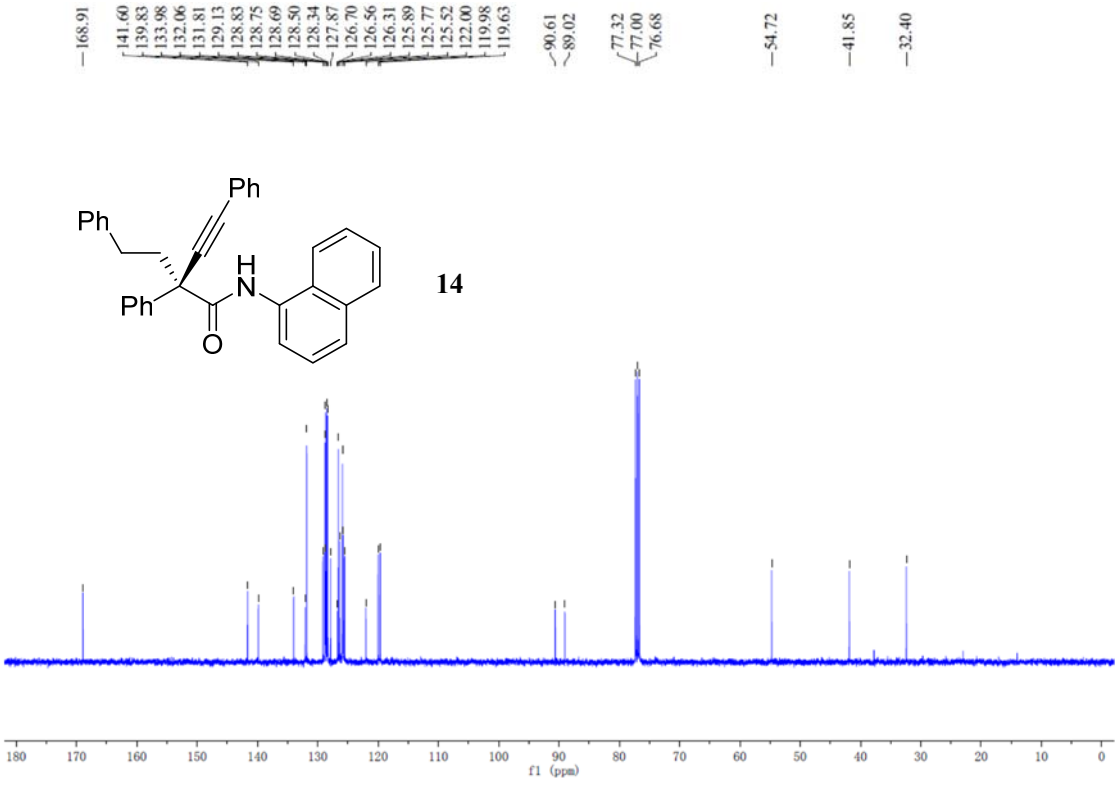
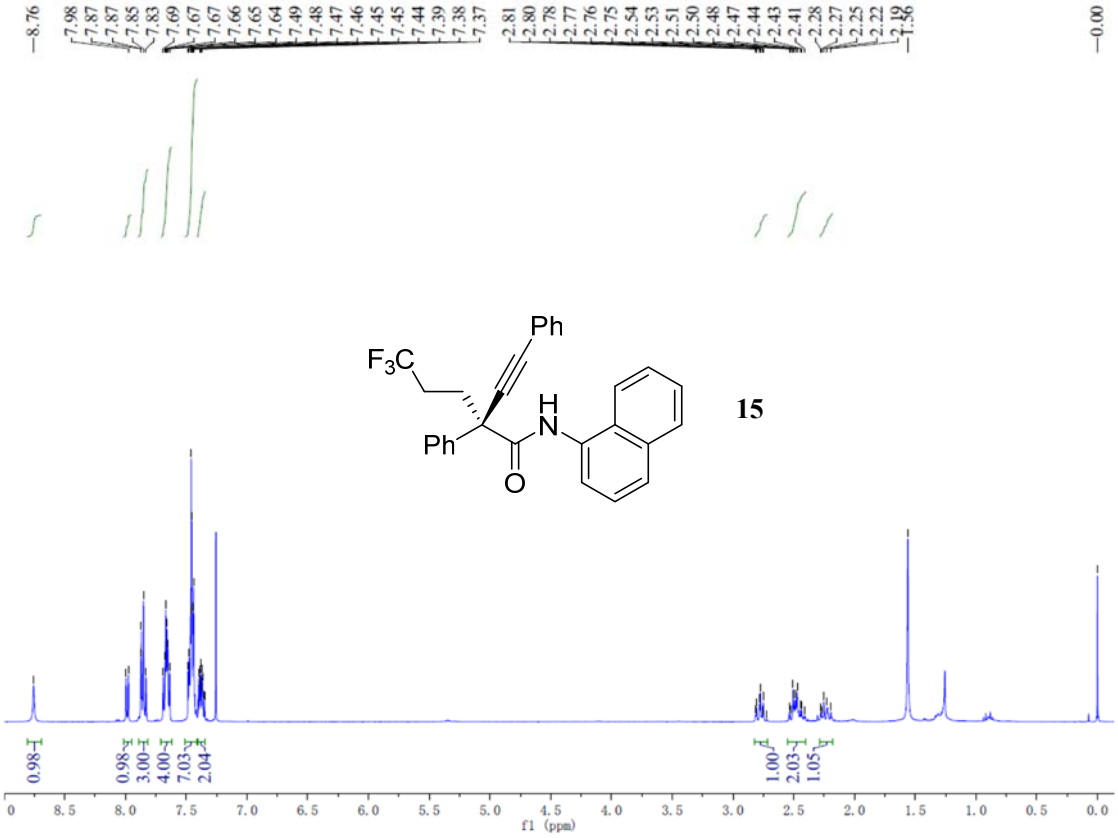
132.096
131.723
128.930
128.792
128.762
128.570
127.752
126.688
126.265
126.244
125.860
125.745
125.464
122.116
119.958
119.569
90.573
88.253
49.575
27.423
Ph
Me
Ph
H
N
O
12
f1 (ppm)


Ph
Me
H
N
Ph
O
13
0.96
0.98
1.95
0.98
1.00
2.92
8.80
1.00
1.00
2.37
2.98
f1 (ppm)


Ph
Me
H
N
Ph
O
13
f1 (ppm)


Ph
Ph
Ph
H
N
O
14


Ph
Ph
Ph
H
N
O
14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7.87
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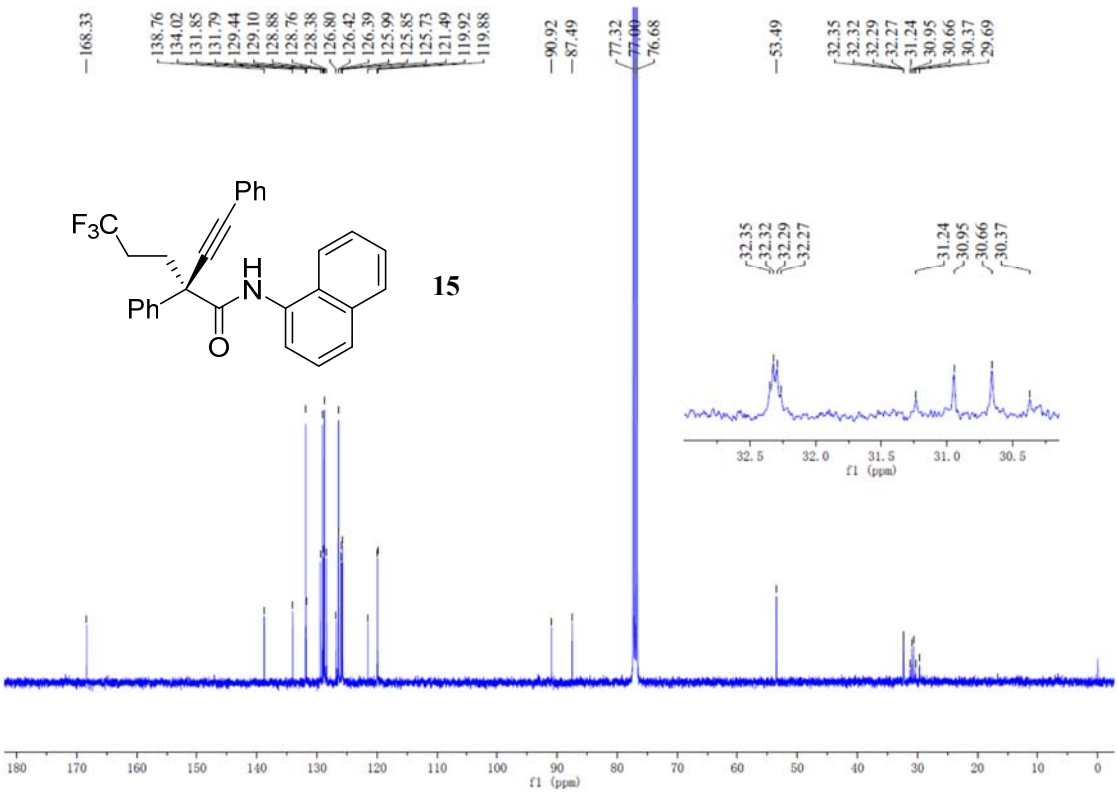
7.83
7.69
7.67
7.67
7.66
7.65
7.64
7.49
7.48
7.47
7.46
7.45
7.45
7.44
7.39
7.38
7.37
2.81
2.80
2.78
2.77
2.76
2.75
2.54
2.53
2.51
2.50
2.48
2.47
2.44
2.43
2.41
2.28
2.27
2.25
2.22
1.58
0.00
Ph
F3C
H
N
Ph
O
15
0.98
0.98
3.00
4.00
7.03
2.04
1.00
2.03
1.05
f1 (ppm)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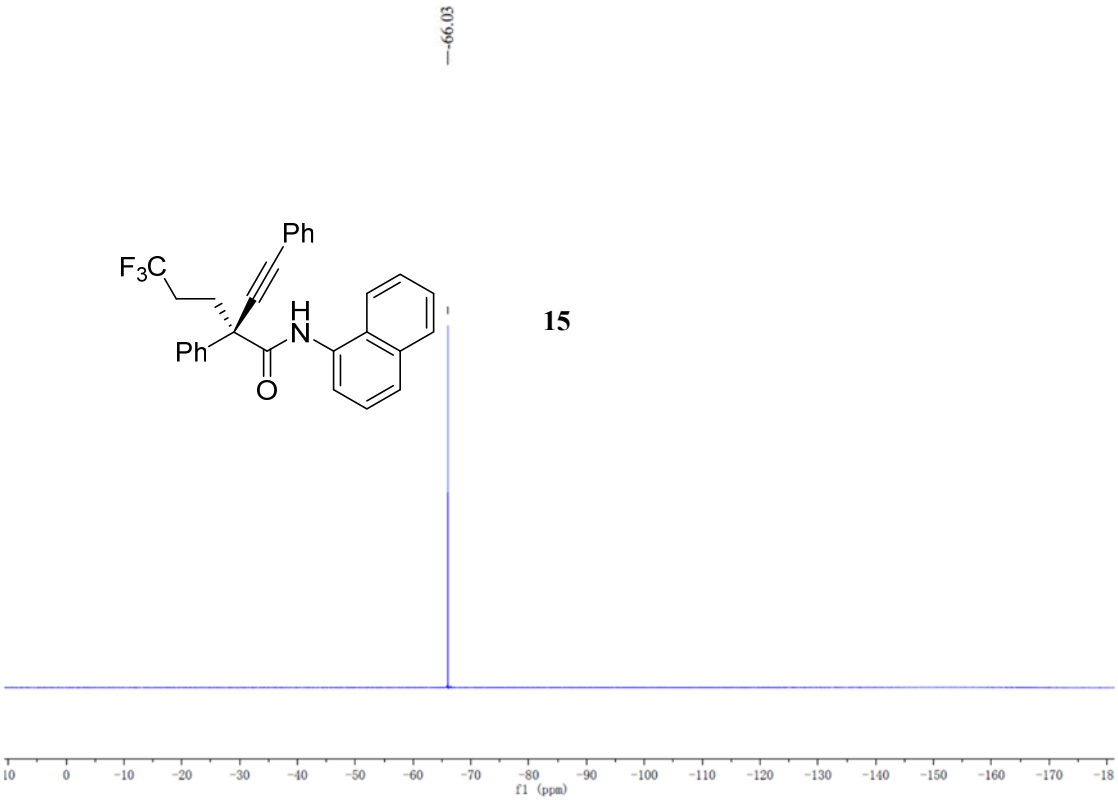
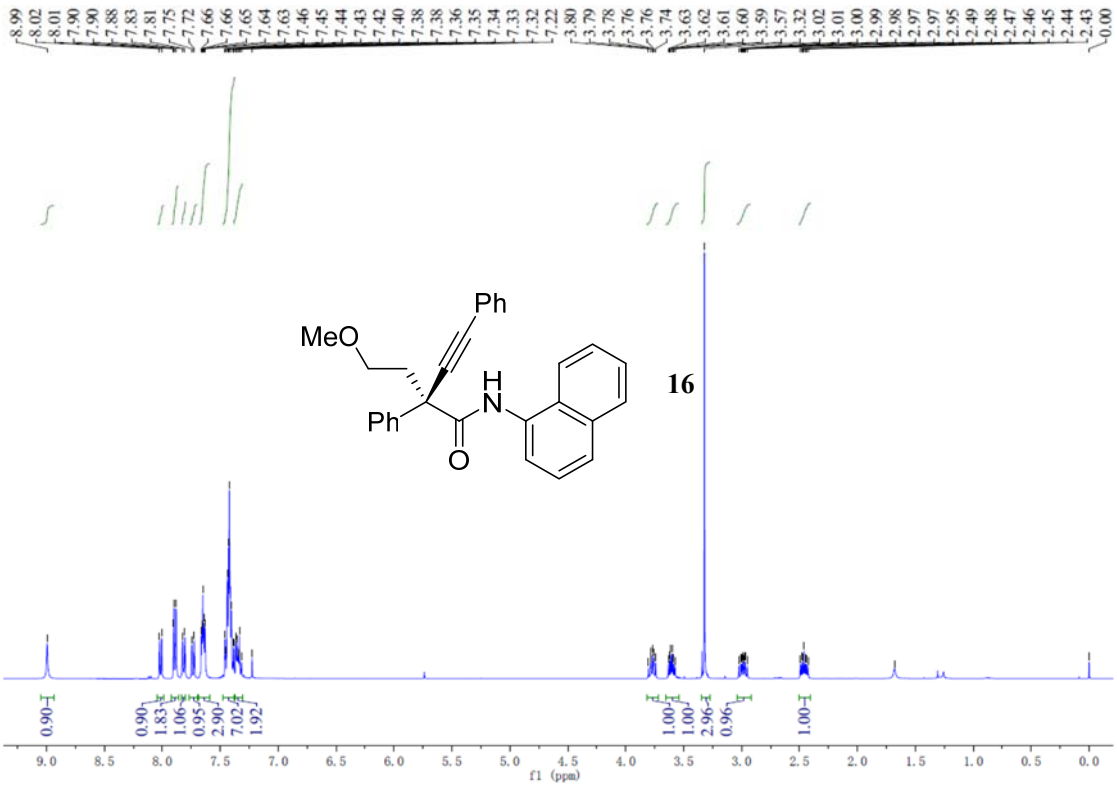
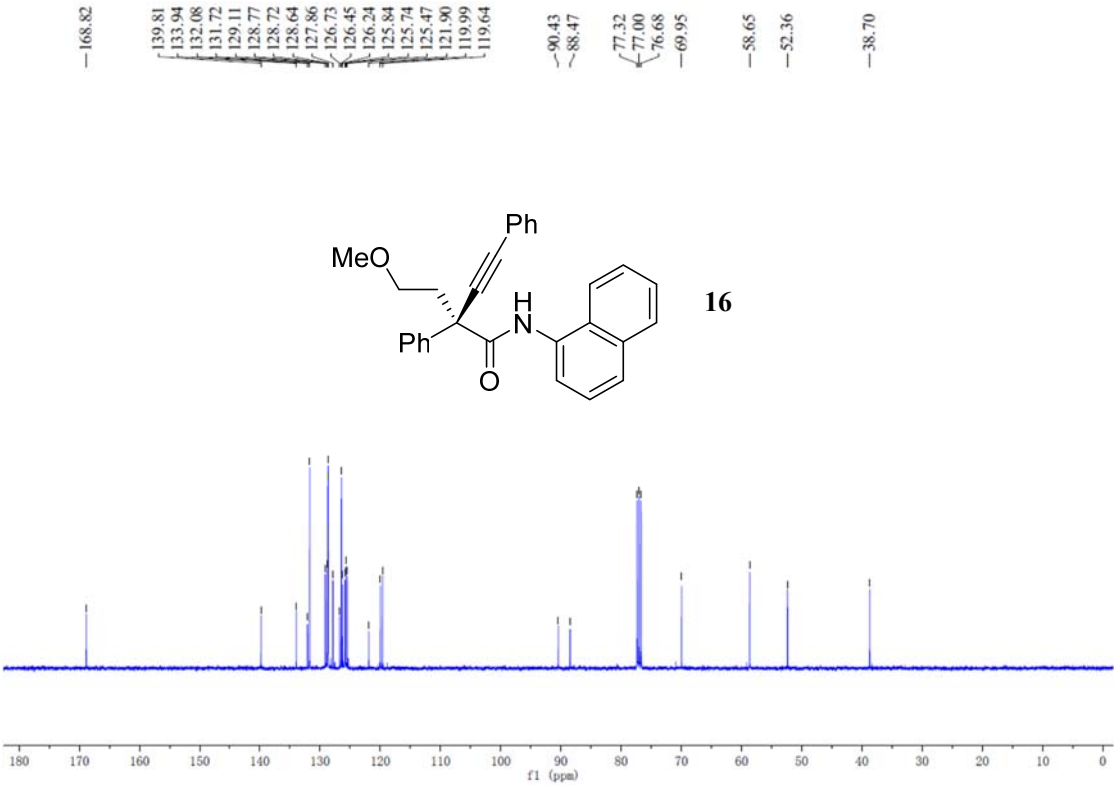
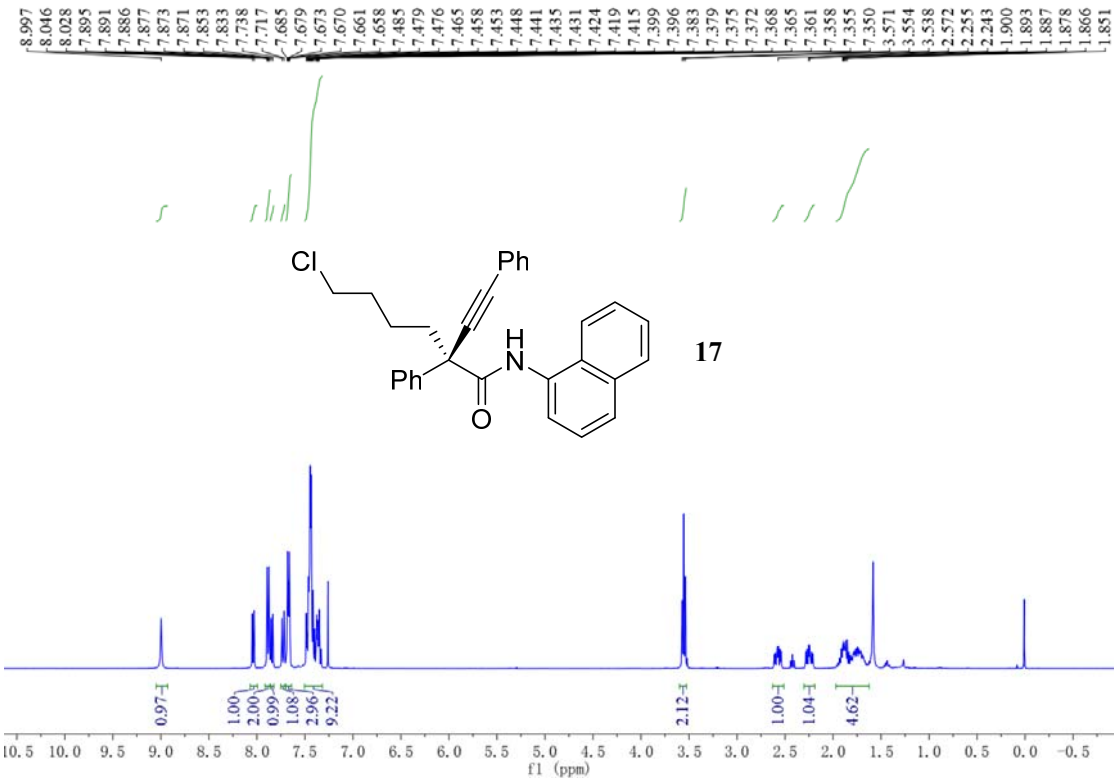
134.02
131.85
131.79
129.44
129.10
128.88
128.76
128.38
126.80
126.42
126.39
125.99
125.85
125.73
121.49
119.92
119.88
90.92
87.49
77.32
77.00
76.68
53.49
32.35
32.32
32.29
32.27
31.24
30.95
30.66
30.37
29.69
Ph
F3C
H
N
Ph
O
15
f1 (ppm)


-66.03
Ph
F3C
H
N
Ph
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-18
f1 (ppm)

15


MeO
Ph
Ph
H
N
O
16


MeO
Ph
Ph
H
N
O
16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7.479
7.476
7.465
7.458
7.453
7.448
7.441
7.435
7.431
7.424
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7.415
7.399
7.396
7.383
7.379
7.375
7.372
7.368
7.365
7.361
7.358
7.355
7.350
3.571
3.554
3.538
2.572
2.255
2.243
1.900
1.893
1.887
1.878
1.866
1.851
Cl
Ph
Ph
H
N
O
17
0.97
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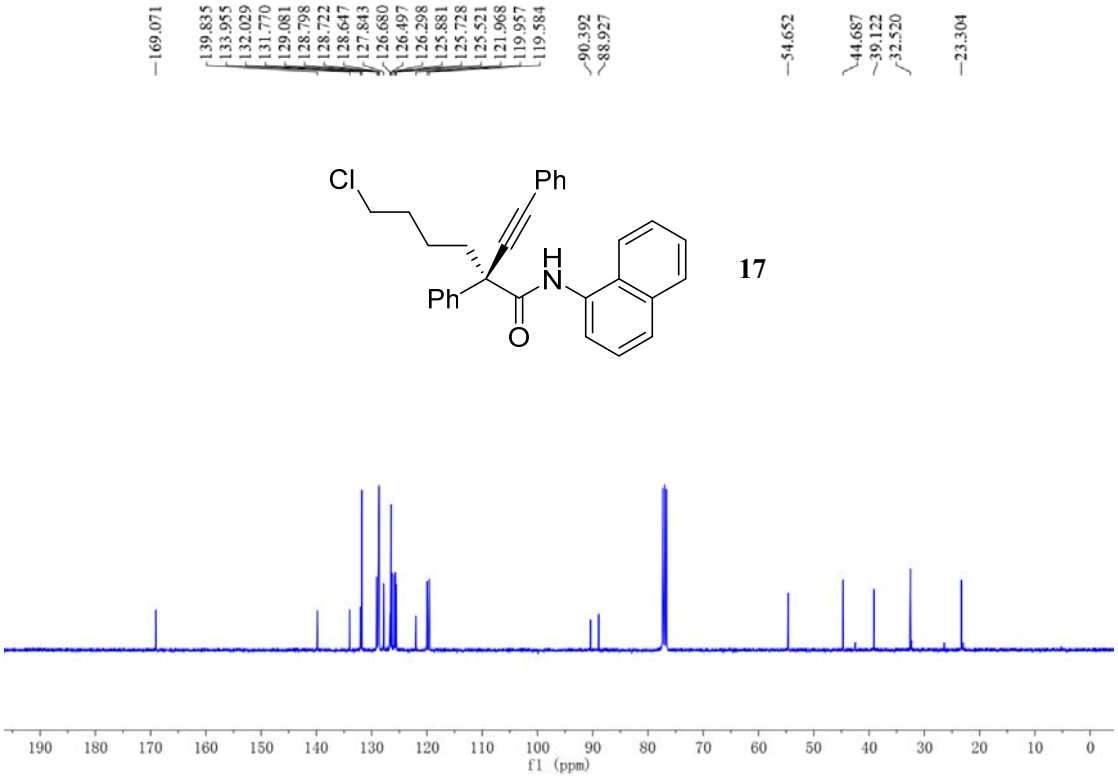
1.08
2.96
9.22
2.12
1.00
1.04
4.62
f1 (ppm)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119.957
119.584
90.392
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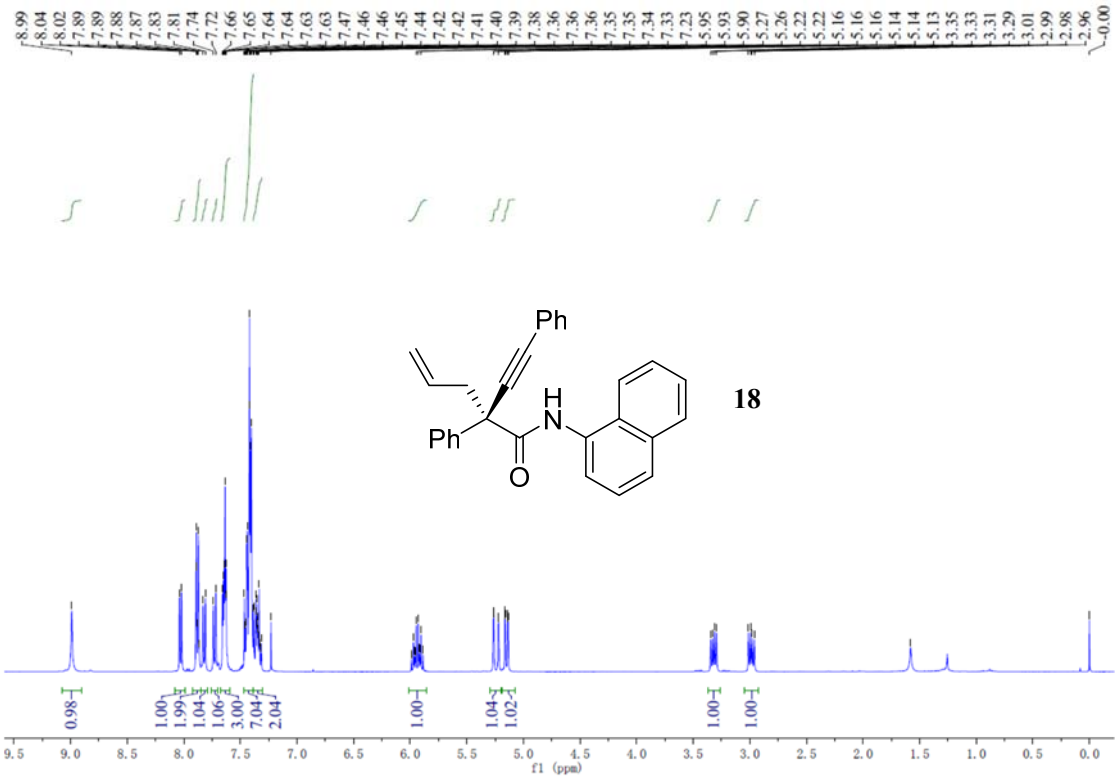
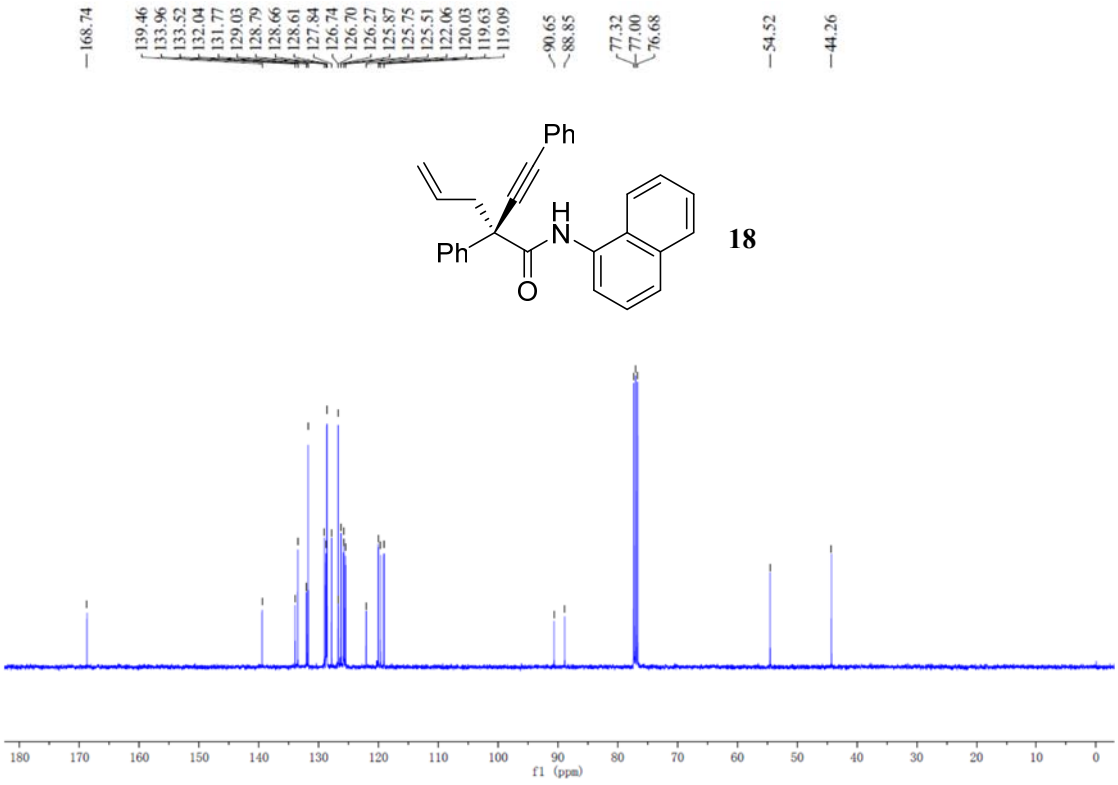
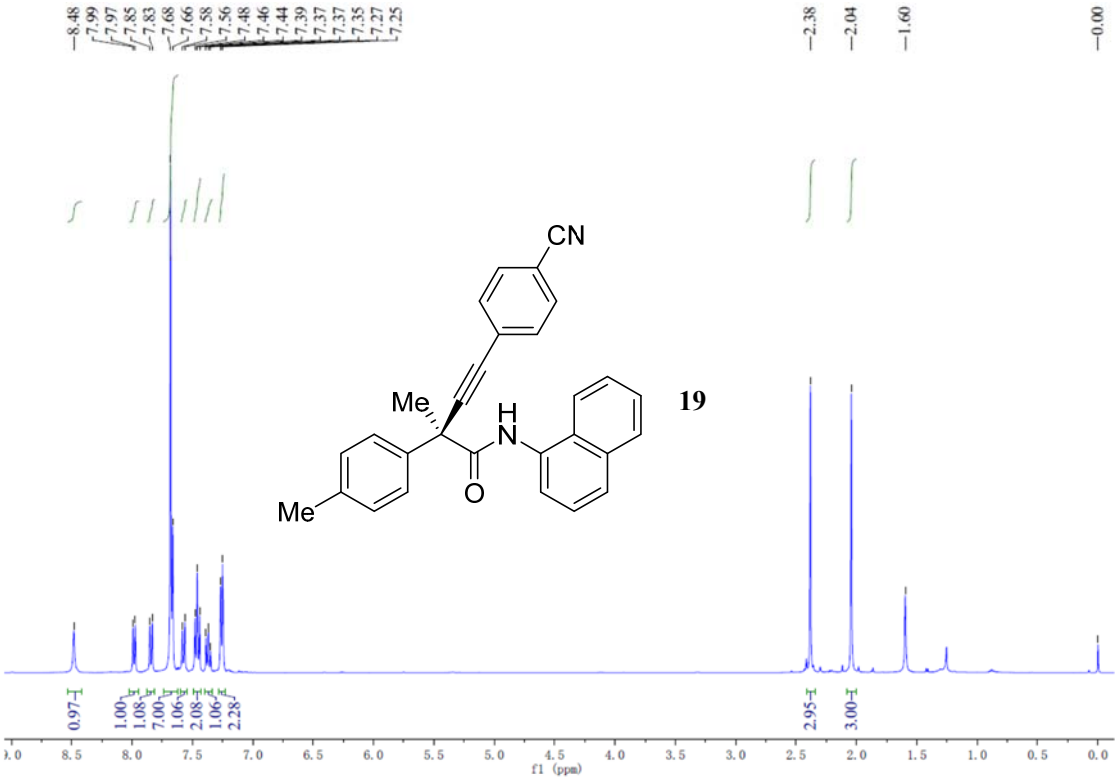
44.687
39.122
32.520
23.304
Cl
Ph
Ph
H
N
O
17
f1 (ppm)


Ph
H
N
Ph
O
18
0.98
1.00
1.99
1.04
1.06
3.00
7.04
2.04
1.00
1.04
1.02
1.00
1.00
f1 (ppm)


Ph
H
N
Ph
O
18
f1 (ppm)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7.56
7.48
7.46
7.44
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7.37
7.37
7.35
7.27
7.25
2.38
2.04
1.60
0.00
CN
Me
H
N
O
Me
19
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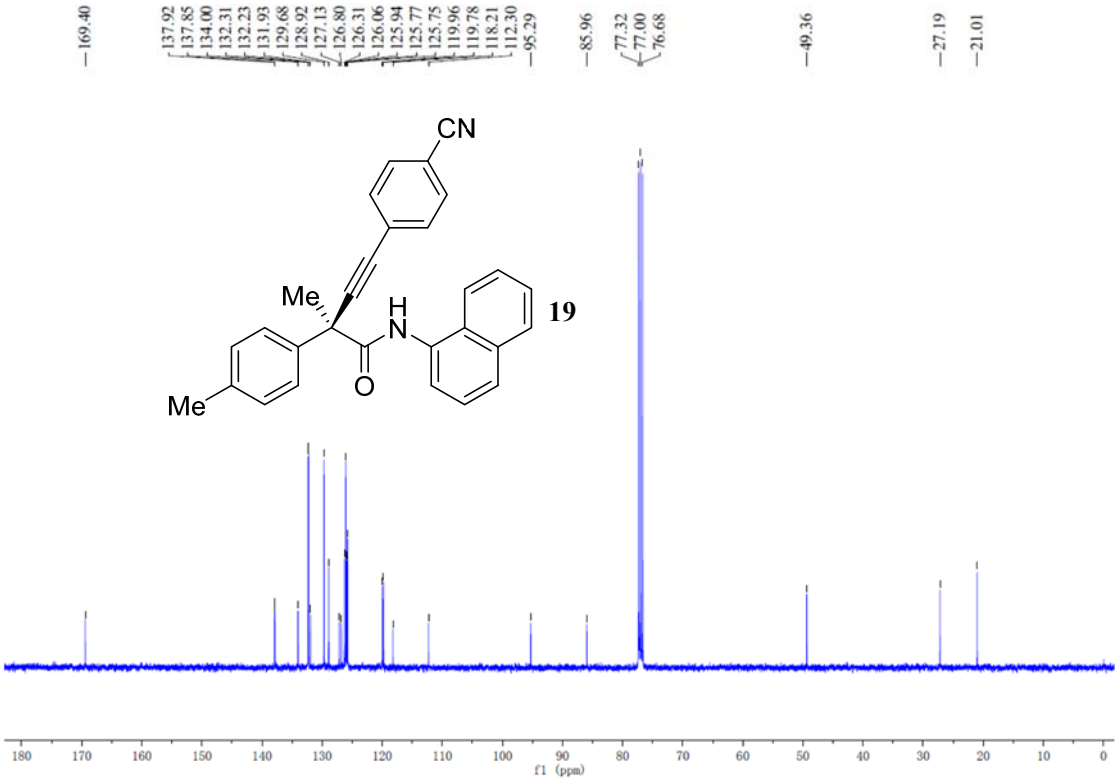
1.06
2.08
1.06
2.28
2.95
3.00
f1 (ppm)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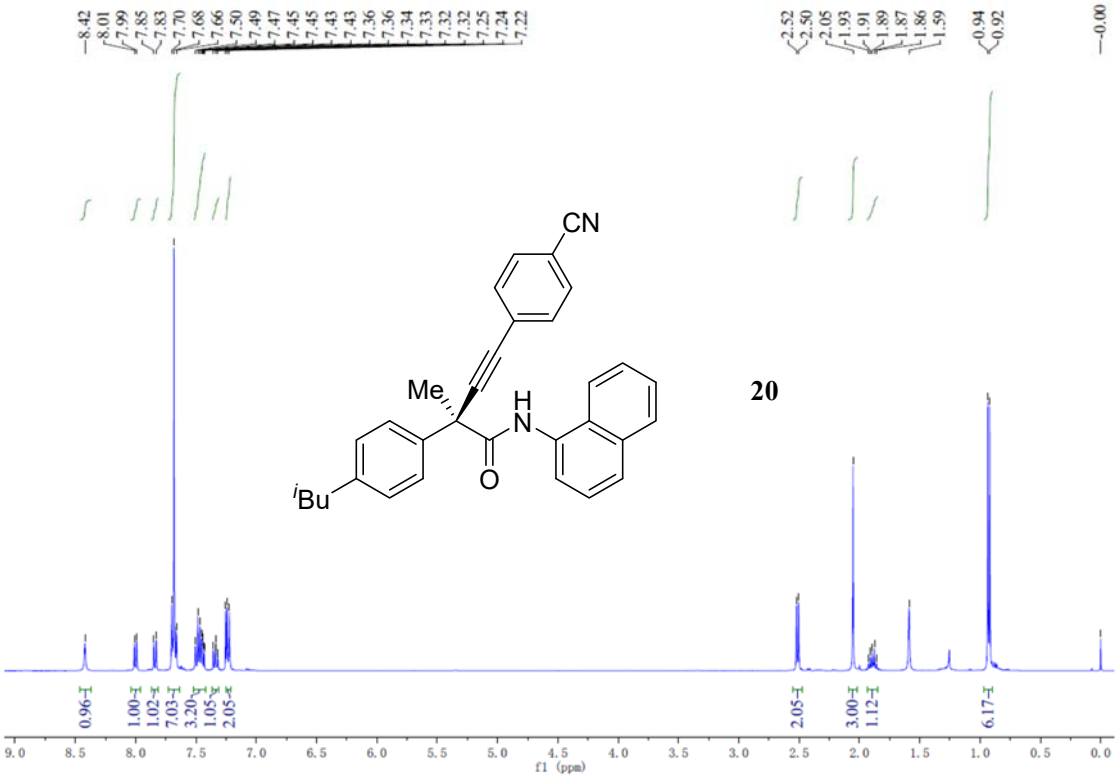
132.31
132.23
131.93
129.68
128.92
127.13
126.80
126.31
126.06
125.94
125.77
125.75
119.96
119.78
118.21
112.30
95.29
85.96
77.32
77.00
76.68
49.36
27.19
21.01
CN
Me
H
N
O
Me
19
f1 (ppm)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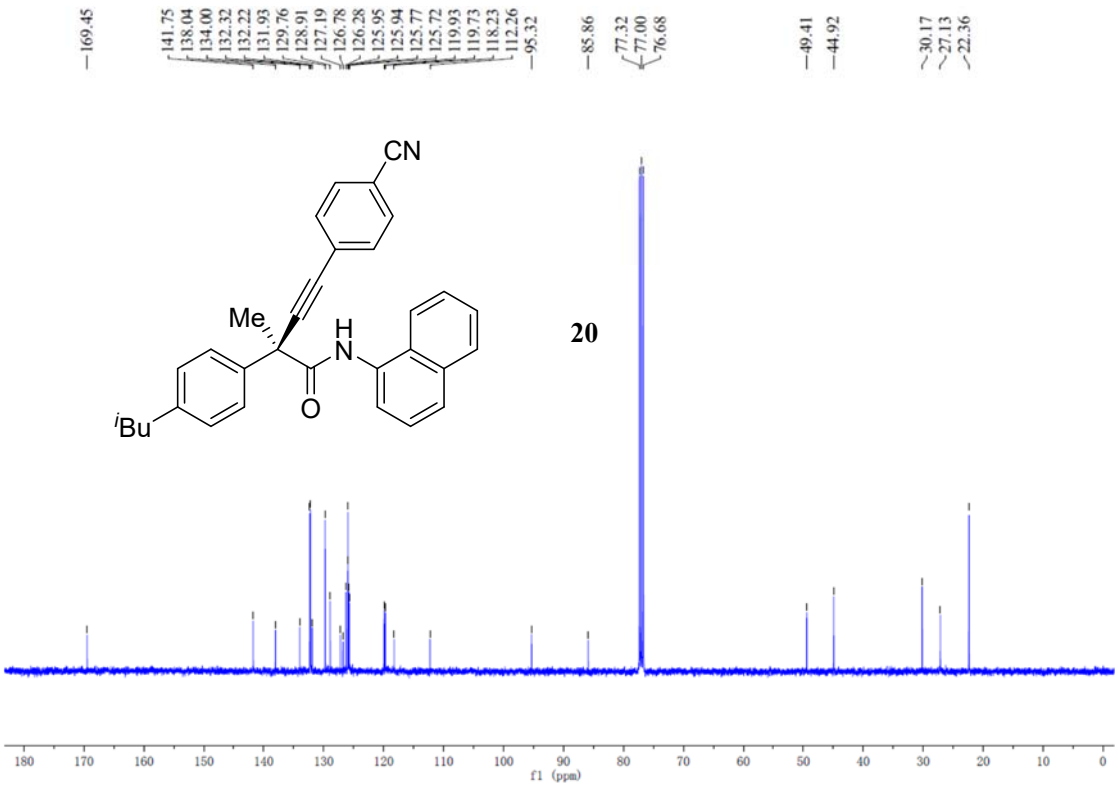
7.45
7.43
7.43
7.36
7.36
7.34
7.33
7.32
7.32
7.25
7.24
7.22
2.52
2.50
2.05
1.93
1.91
1.89
1.87
1.86
1.59
0.94
0.92
0.00
CN
Me
H
N
O
iBu
20
0.96
1.00
1.02
7.03
3.20
1.05
2.05
2.05
3.00
1.12
6.17
f1 (ppm)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129.76
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127.19
126.78
126.28
125.95
125.94
125.77
125.72
119.93
119.73
118.23
112.26
95.32
85.86
77.32
77.00
76.68
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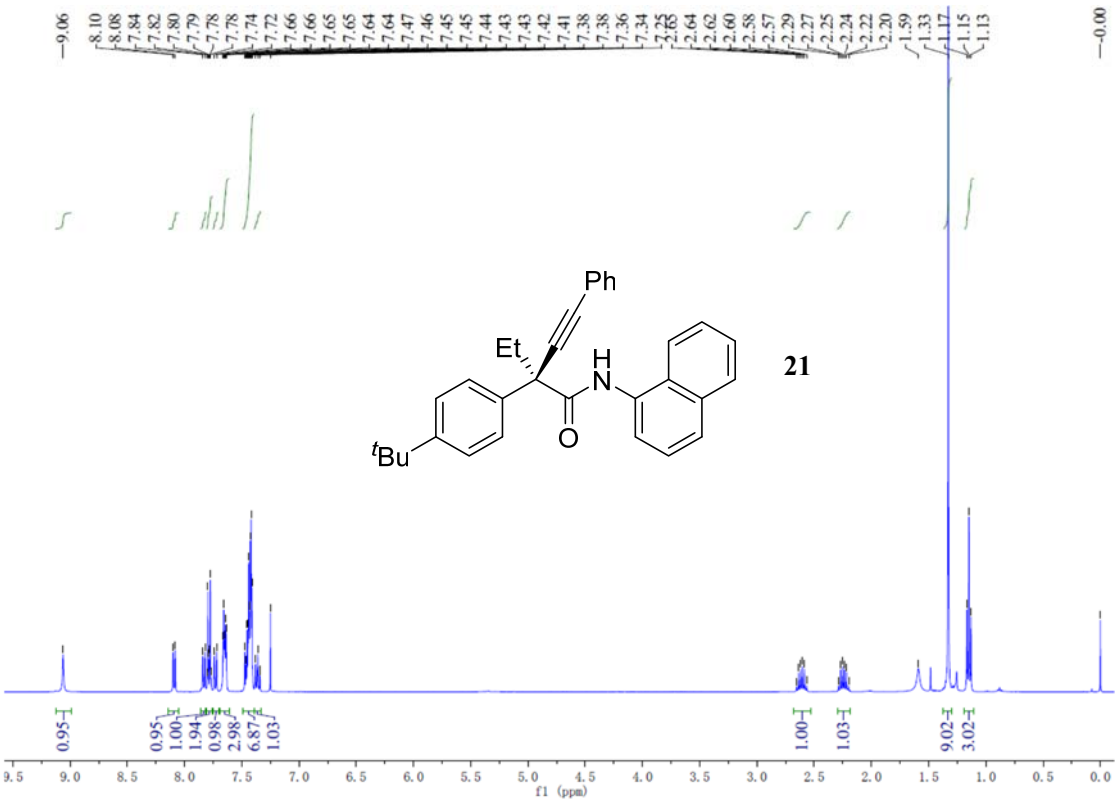
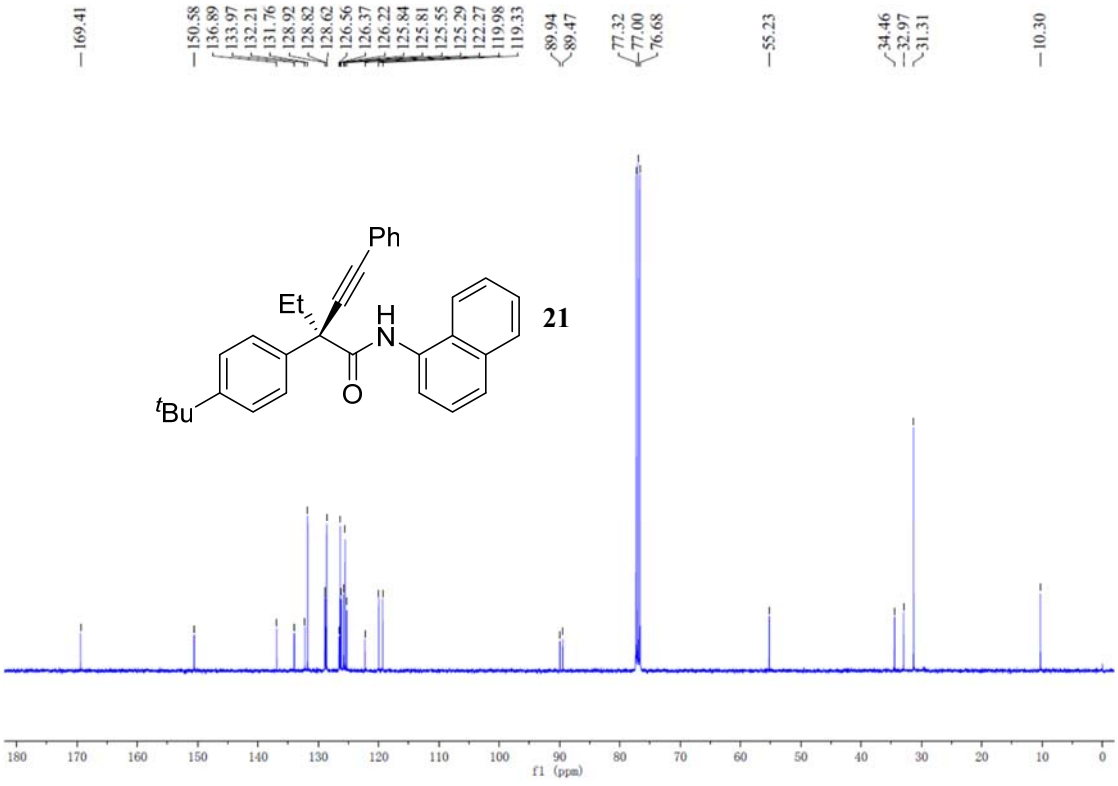
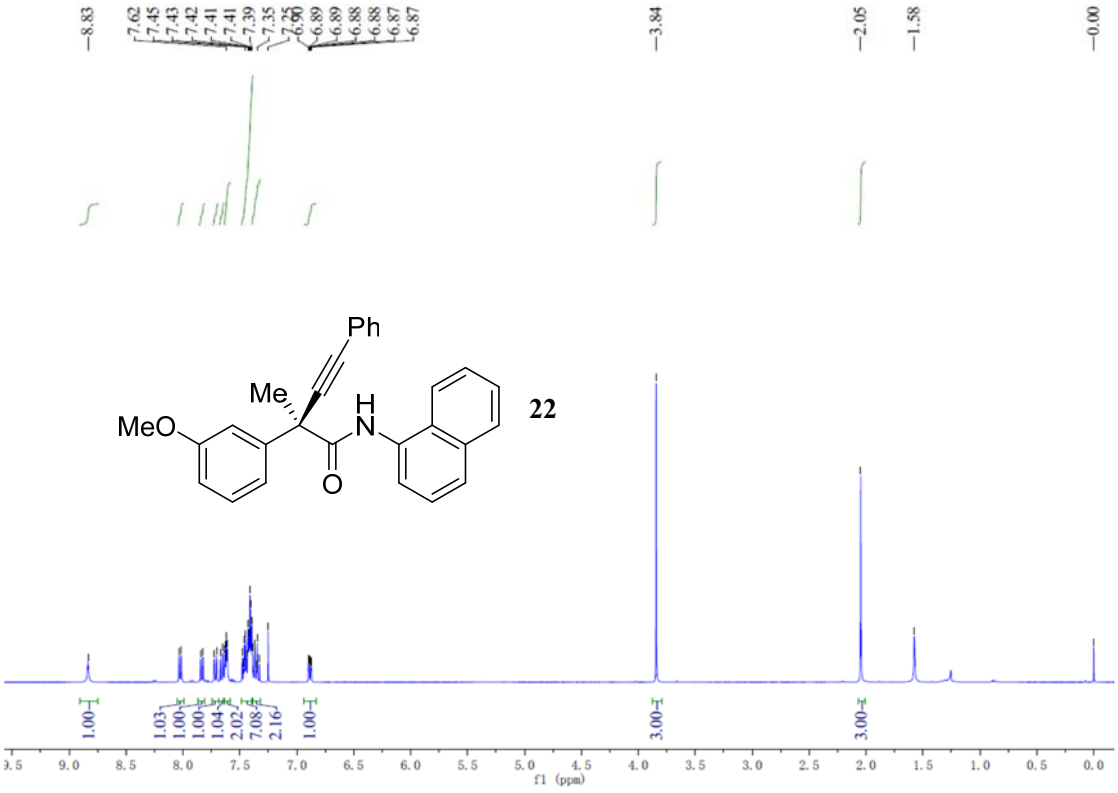
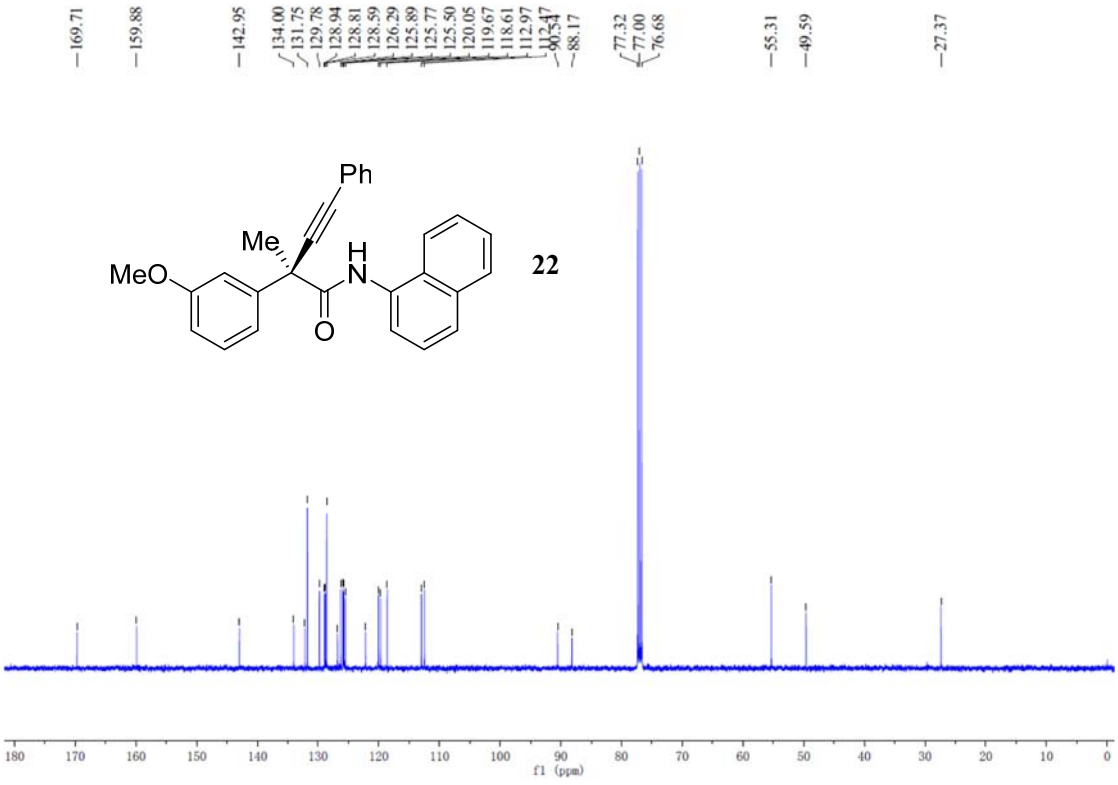
44.92
30.17
27.13
22.36
CN
Me
H
N
O
iBu
20
f1 (ppm)


Ph
Et
H
N
O
tBu
21
f1 (ppm)


Ph
Et
H
N
O
tBu
21
f1 (ppm)


8.83
7.62
7.45
7.43
7.42
7.41
7.41
7.39
7.35
6.90
6.89
6.89
6.88
6.88
6.87
6.87
3.84
2.05
1.58
0.00
Ph
Me
MeO
H
N
O
22
1.00
1.03
1.00
1.00
1.04
2.02
7.08
2.16
1.00
3.00
3.00
f1 (ppm)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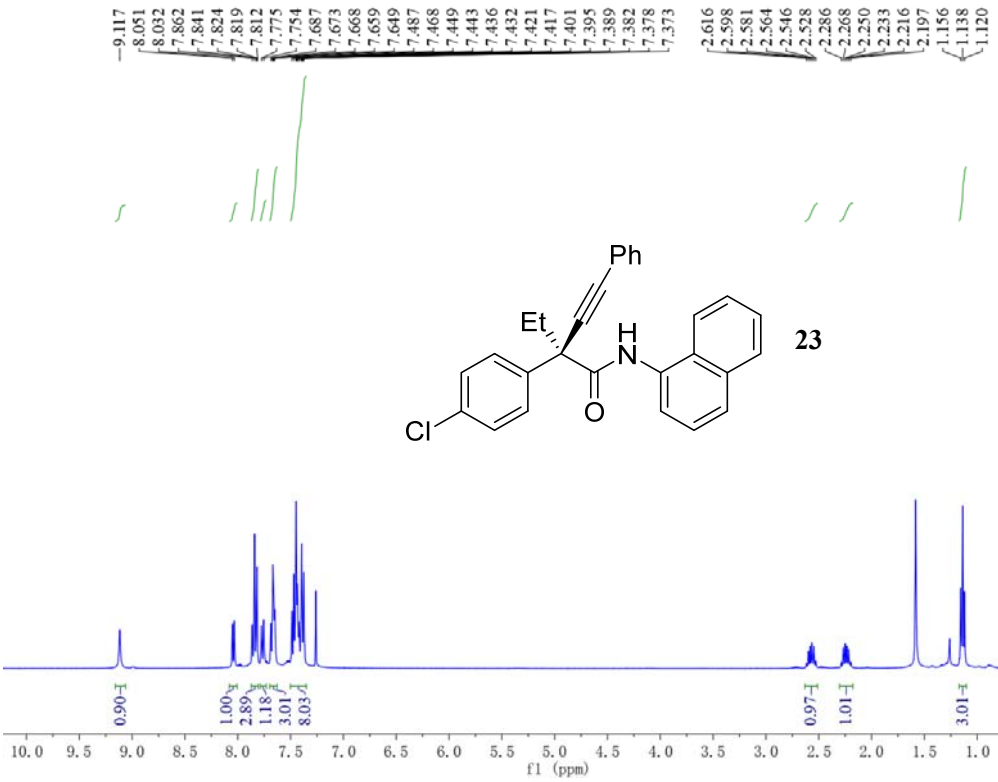
159.88
142.95
134.00
131.75
129.78
128.94
128.81
128.59
126.29
125.89
125.77
125.50
120.05
119.67
118.61
112.97
112.47
90.54
88.17
77.32
77.00
76.68
55.31
49.59
27.37
Ph
Me
MeO
H
N
O
22
f1 (ppm)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8.032
7.862
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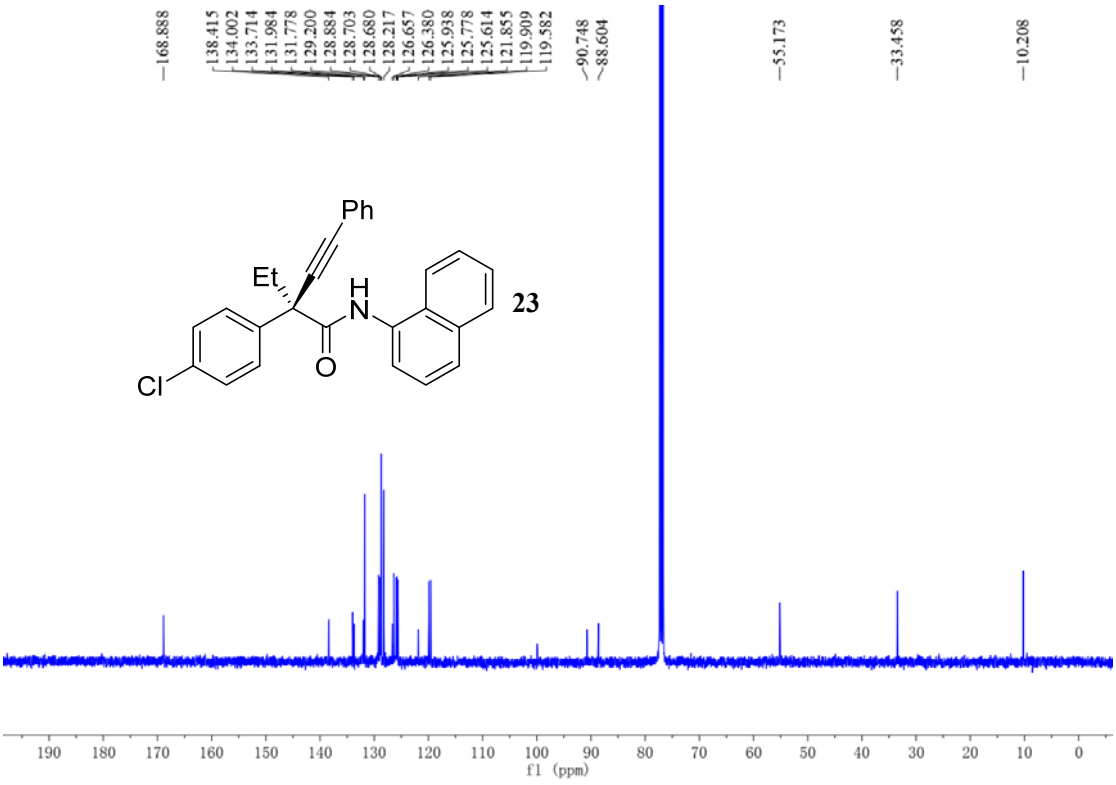
7.824
7.819
7.812
7.775
7.754
7.687
7.673
7.668
7.659
7.649
7.487
7.468
7.449
7.443
7.436
7.432
7.421
7.417
7.401
7.395
7.389
7.382
7.378
7.373
2.616
2.598
2.581
2.564
2.546
2.528
2.286
2.268
2.250
2.233
2.216
2.197
1.156
1.138
1.120
Ph
Et
H
N
O
Cl
23
0.90
1.00
2.89
1.18
3.01
8.03
0.97
1.01
3.01
10.0 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
f1 (ppm)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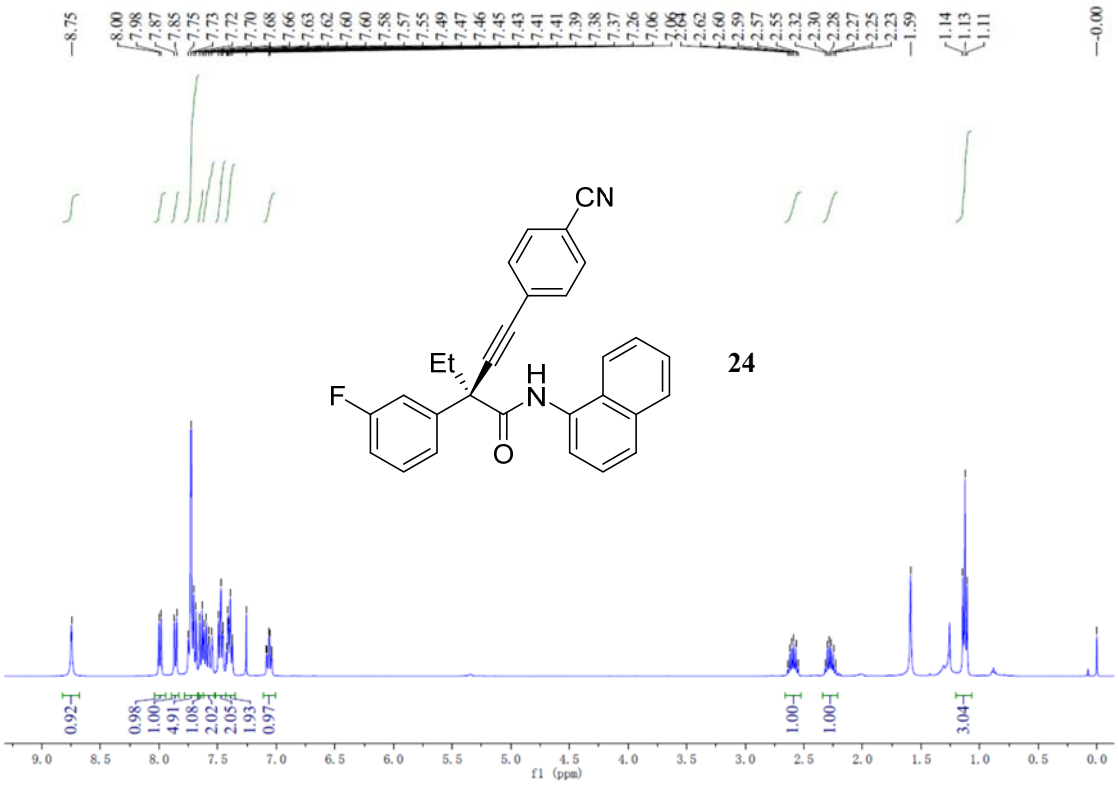
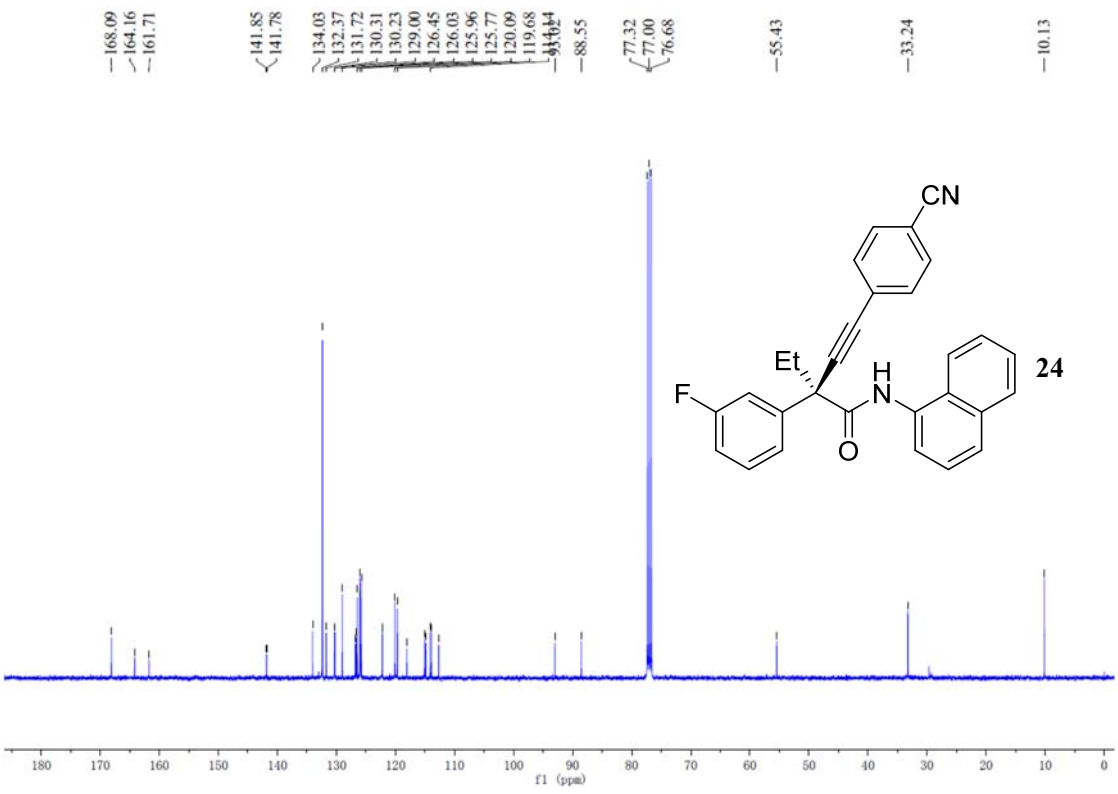
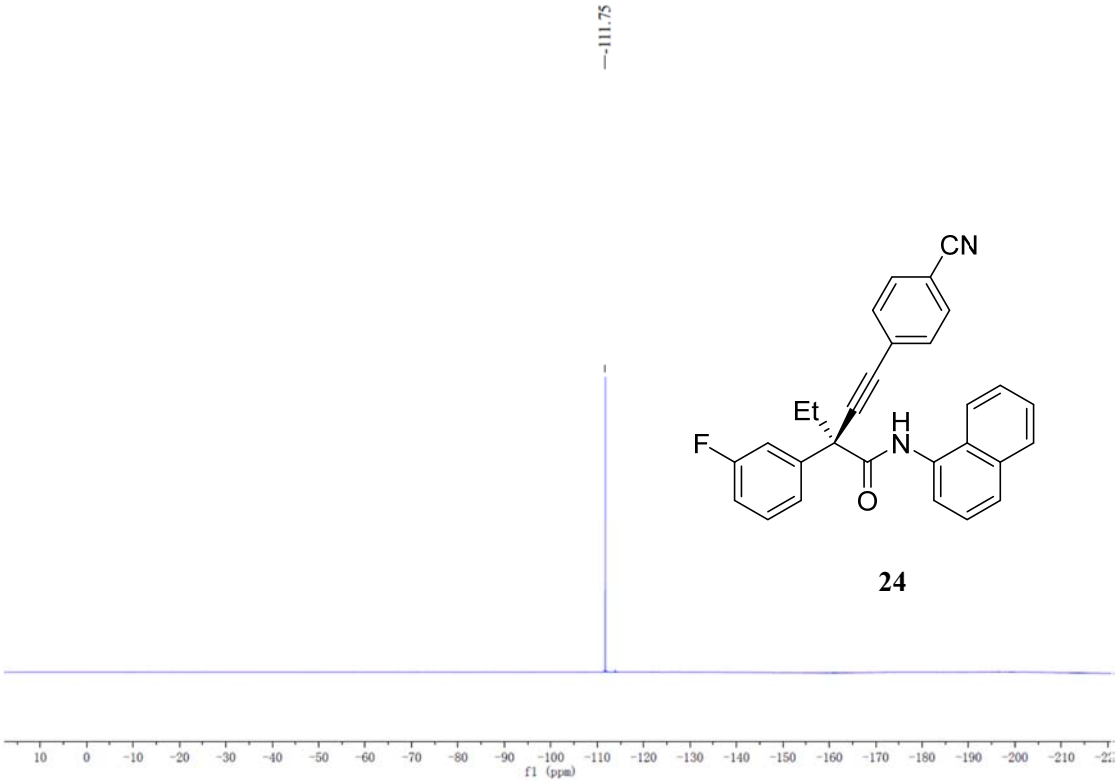
128.217
126.657
126.380
125.938
125.778
125.614
121.855
119.909
119.582
90.748
88.604
55.173
33.458
10.208
Ph
Et
H
N
O
Cl
23
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CN
Et
F
H
N
O
24
f1 (ppm)


CN
Et
F
H
N
O
24
f1 (ppm)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CN
Et
H
N
F
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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-130
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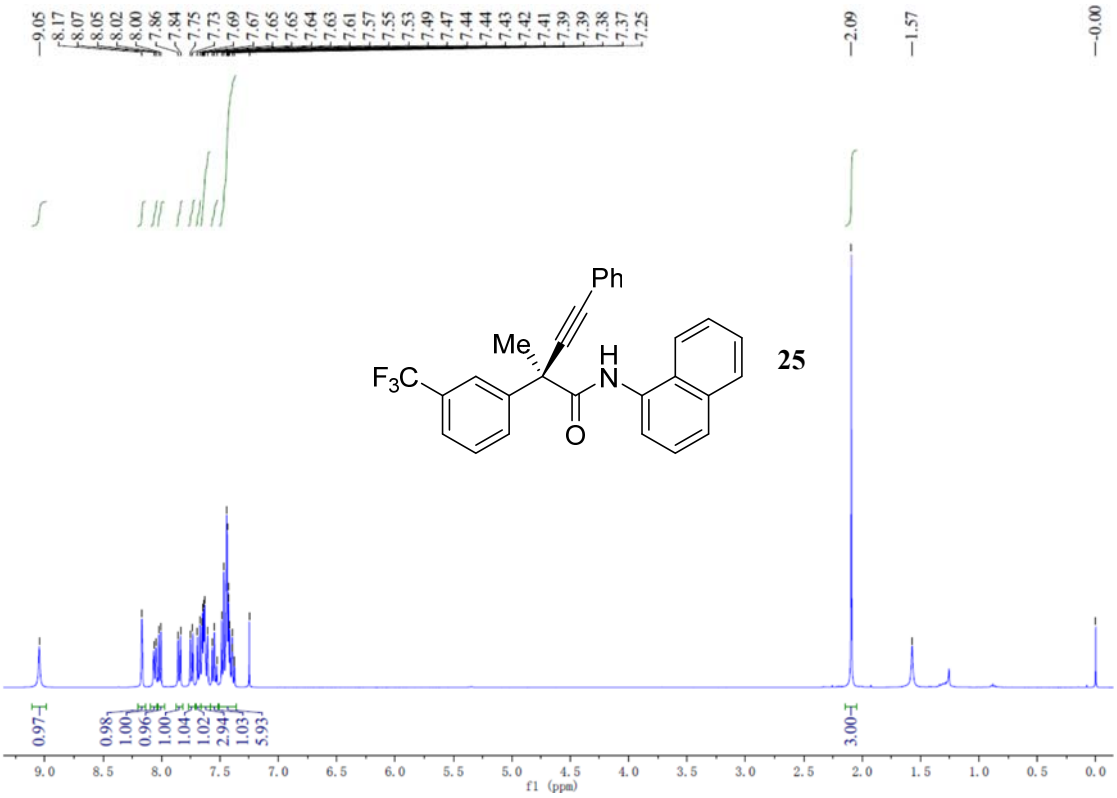
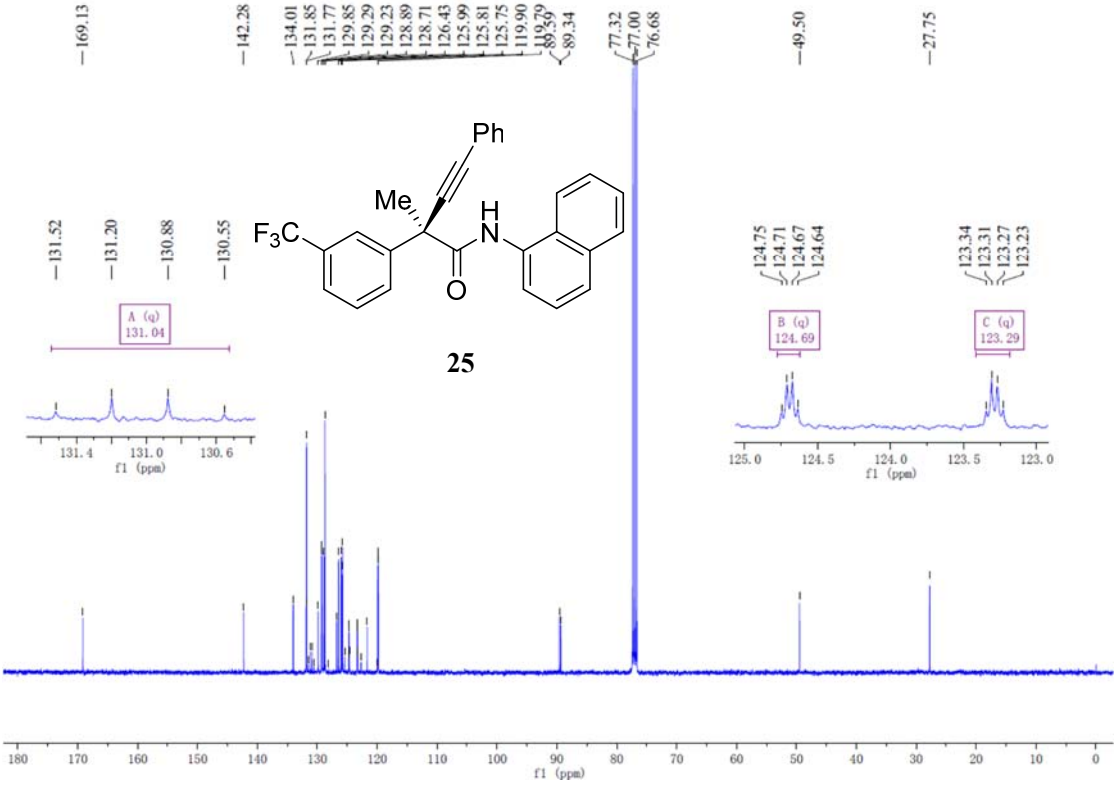
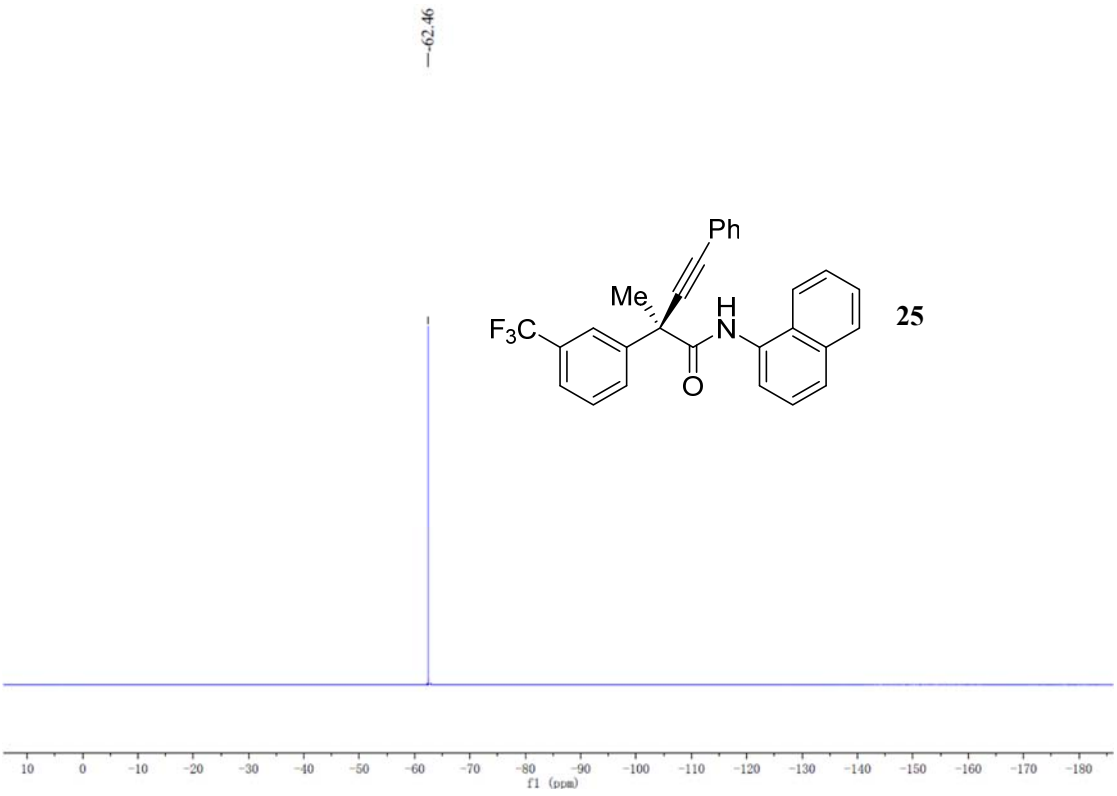
-170
-180
-190
-200
-210
f1 (ppm)

24


Ph
Me
H
N
O
F3C
25


Ph
Me
H
N
O
F3C
25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Me
H
N
F3C
O
10
0
-10
-20
-30
-40
-50
-60
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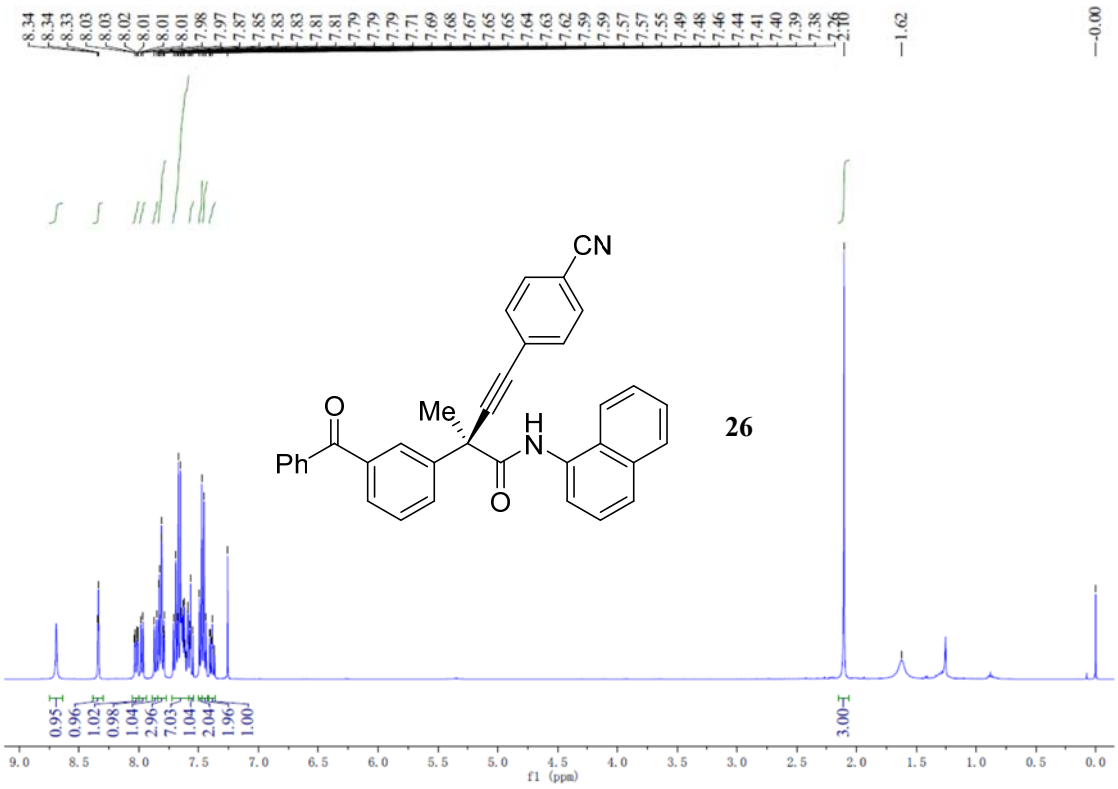
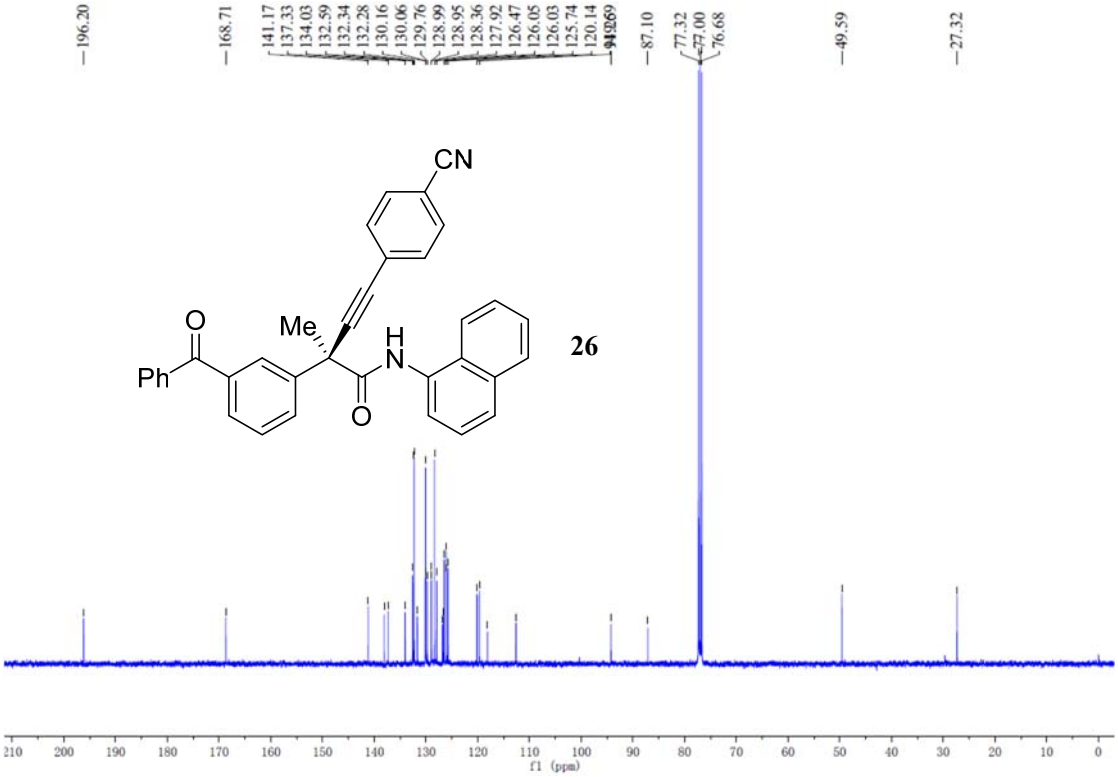
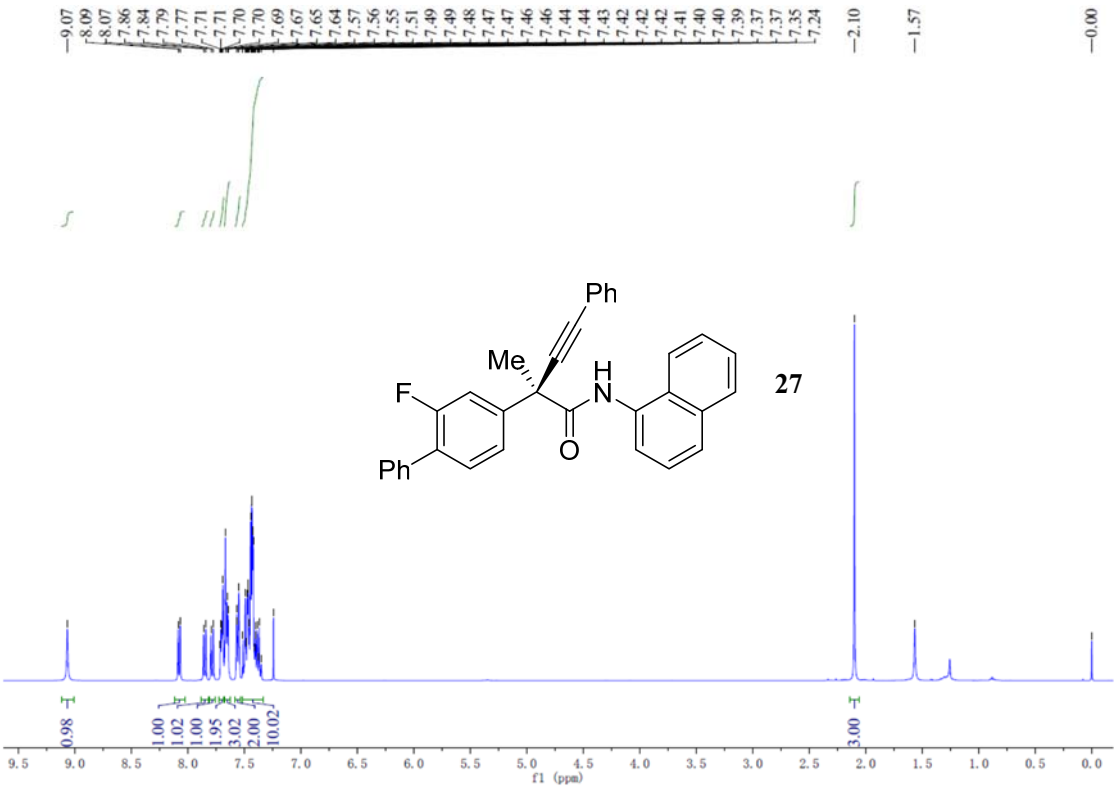
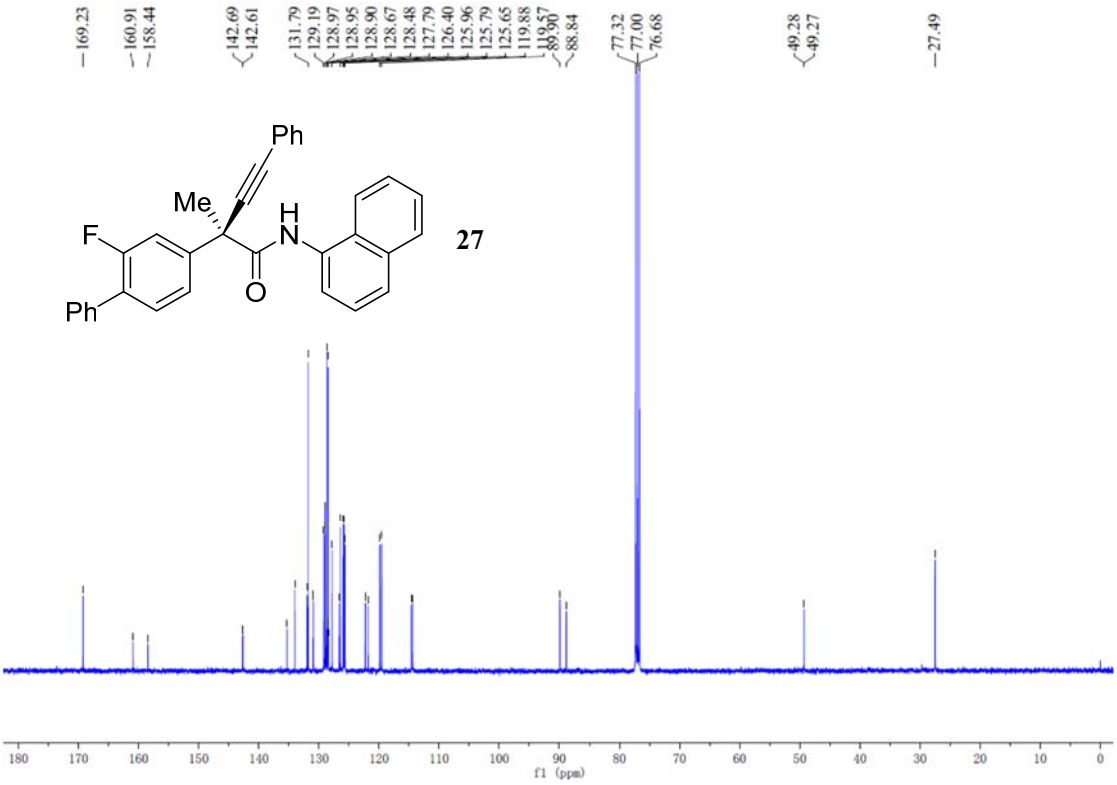
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

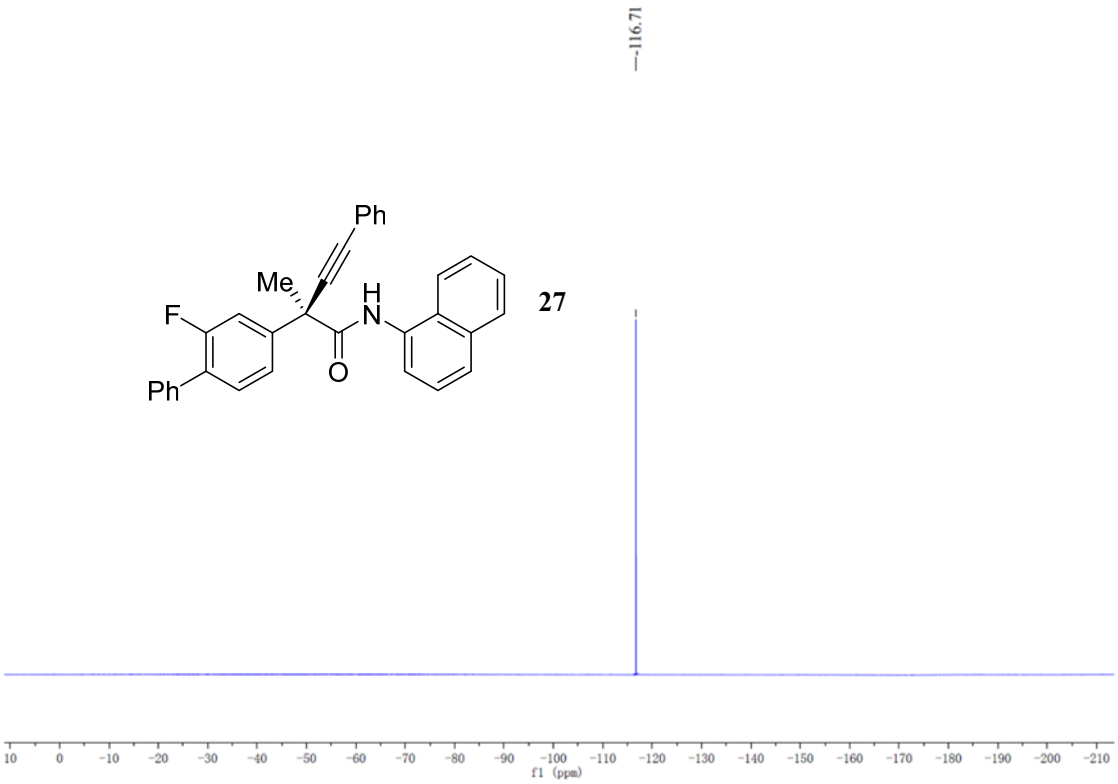
25


CN
O
Me
H
N
Ph
O
26
f1 (ppm)

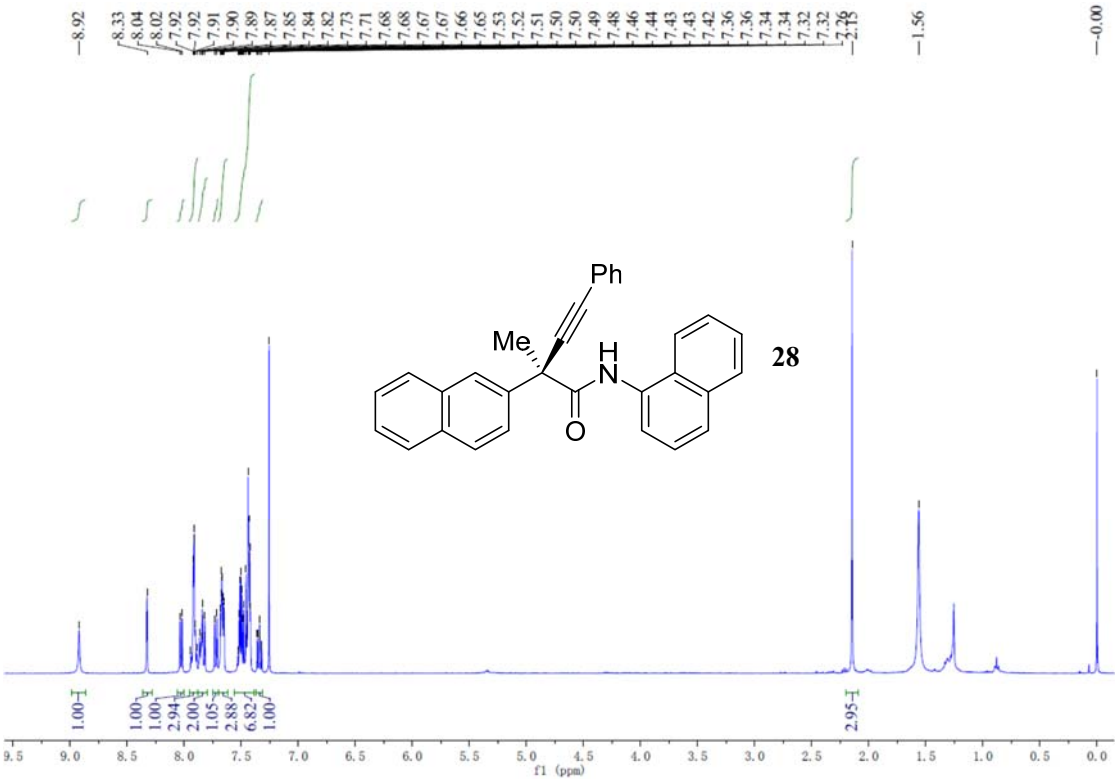

CN
O
Me
H
N
Ph
O
26
f1 (ppm)

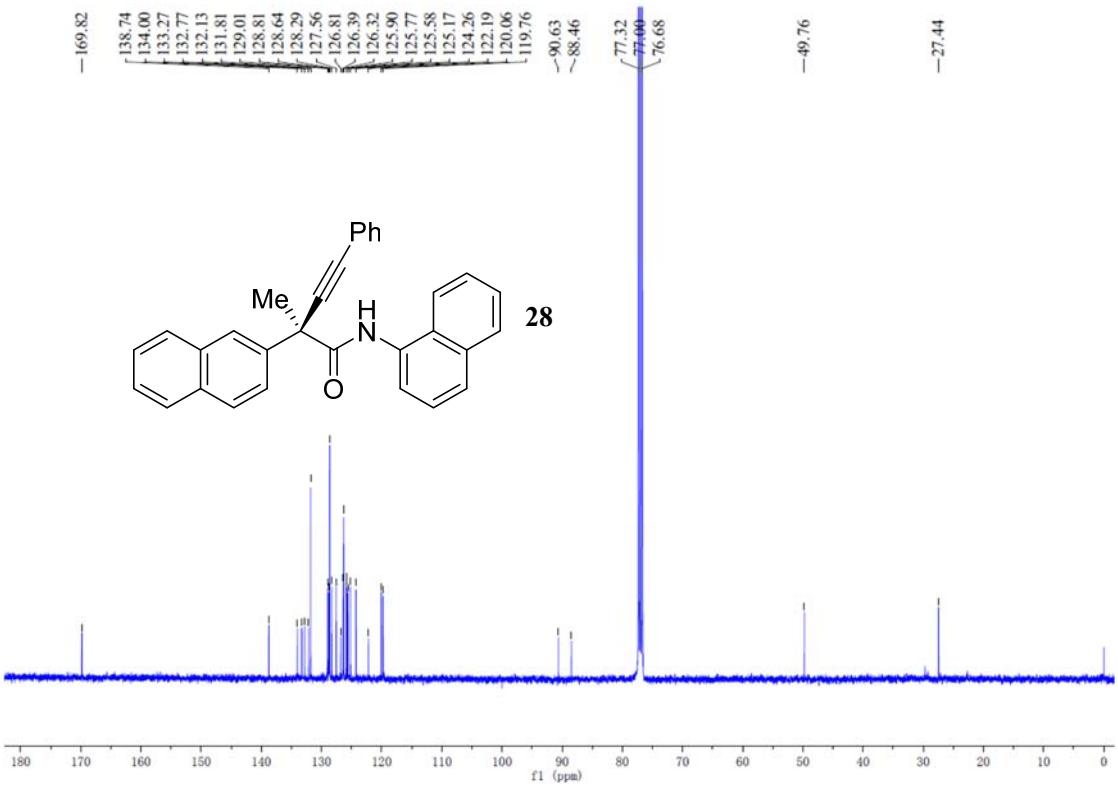

Ph
Me
H
N
F
O
Ph
27

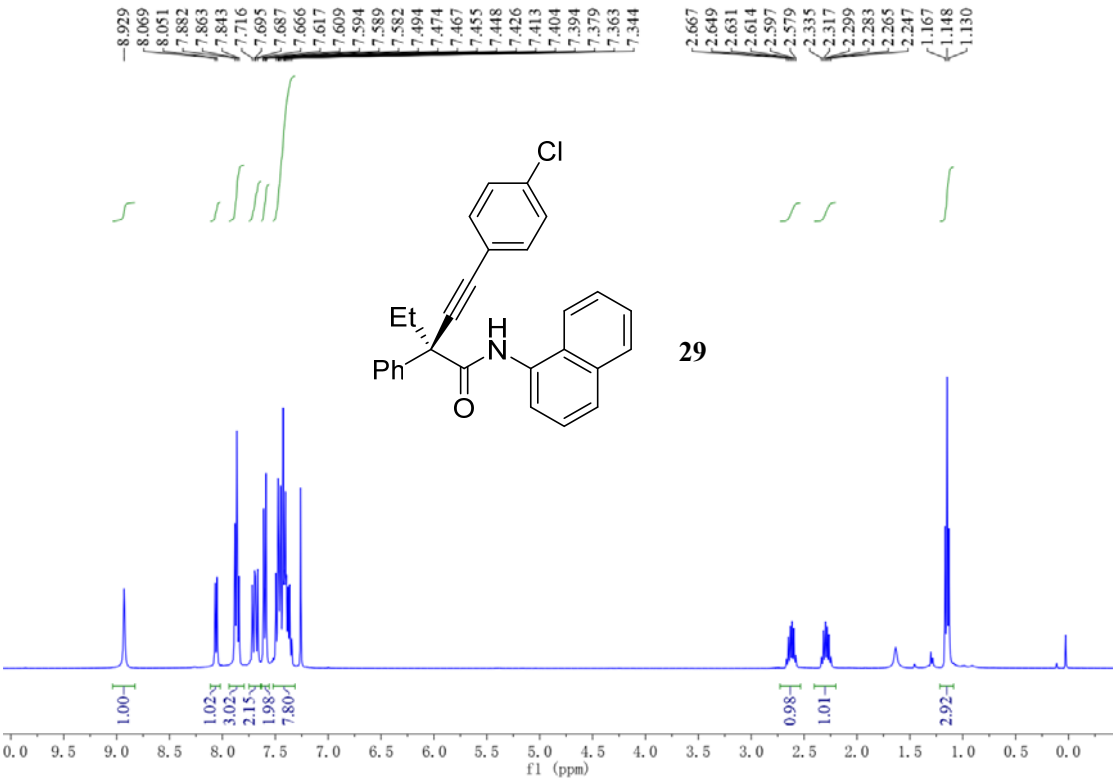

Ph
Me
H
N
F
O
Ph
27


-116.71
Ph
Me
H
N
F
O
Ph
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)

27


Ph
Me
H
N
O
28


Ph
Me
H
N
O
28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7.882
7.863
7.843
7.716
7.695
7.687
7.666
7.617
7.609
7.594
7.589
7.582
7.494
7.474
7.467
7.455
7.448
7.426
7.413
7.404
7.394
7.379
7.363
7.344
2.667
2.649
2.631
2.614
2.597
2.579
2.335
2.317
2.299
2.283
2.265
2.247
1.167
1.148
1.130
Cl
Et
Ph
H
N
O
29
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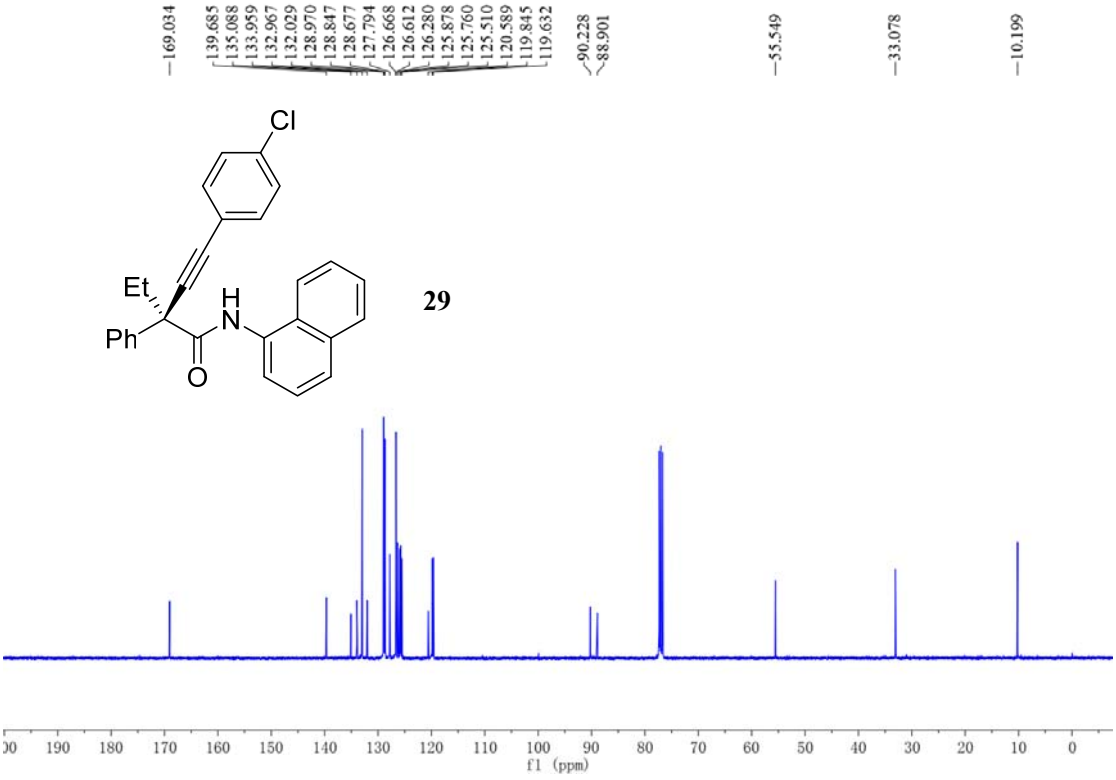
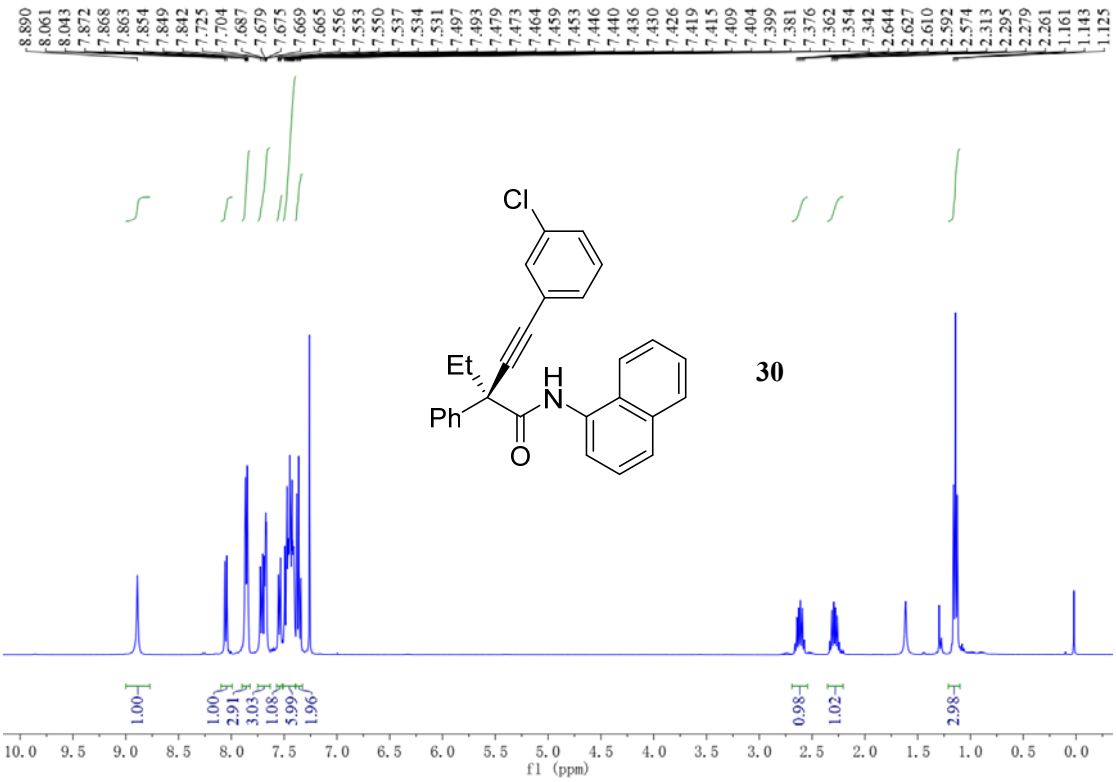
1.02
3.02
2.15
1.98
7.80
0.98
1.01
2.92
f1 (ppm)


169.034
139.685
135.088
133.959
132.967
132.029
128.970
128.847
128.677
127.794
126.668
126.612
126.280
125.878
125.760
125.510
120.589
119.845
119.632
90.228
88.901
55.549
33.078
10.199
Cl
Et
Ph
H
N
O
29
f1 (ppm)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7.868
7.863
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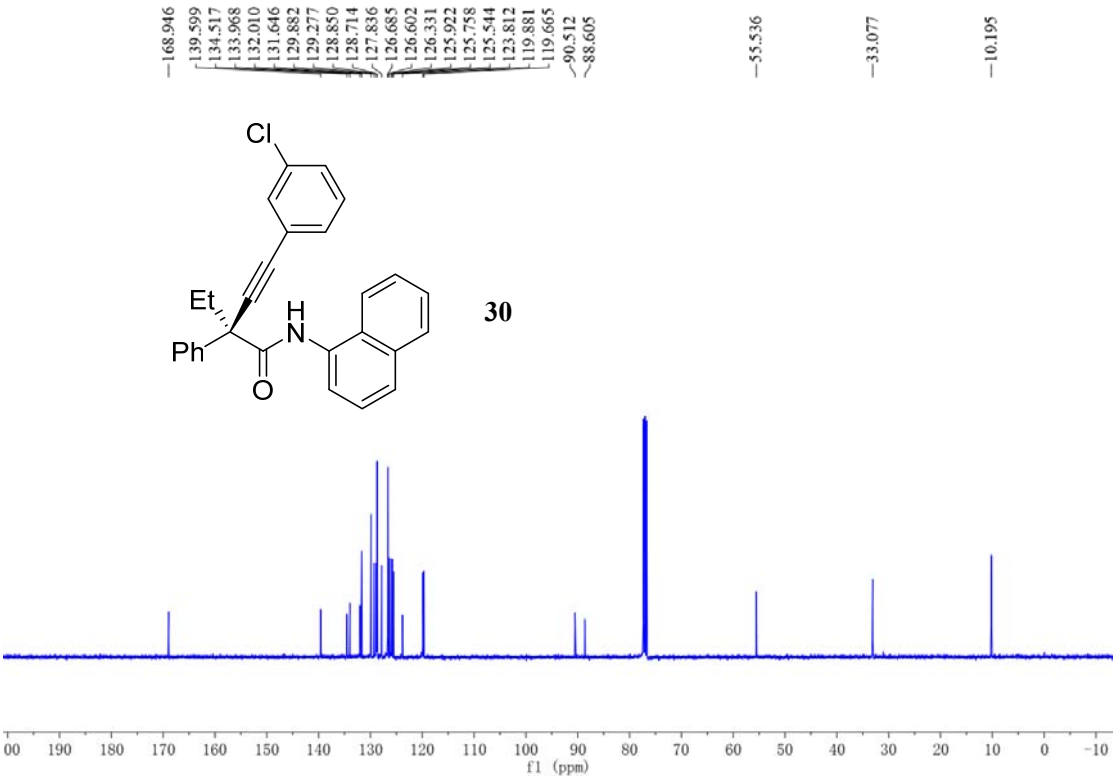
7.849
7.842
7.725
7.704
7.687
7.679
7.675
7.669
7.665
7.556
7.553
7.550
7.537
7.534
7.531
7.497
7.493
7.479
7.473
7.464
7.459
7.453
7.446
7.440
7.436
7.430
7.426
7.419
7.415
7.409
7.404
7.399
7.381
7.376
7.362
7.354
7.342
2.644
2.627
2.610
2.592
2.574
2.313
2.295
2.279
2.261
1.161
1.143
1.125
Cl
Et
Ph
H
N
O
30
1.00
1.00
2.91
3.03
1.08
5.99
1.96
0.98
1.02
2.98
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)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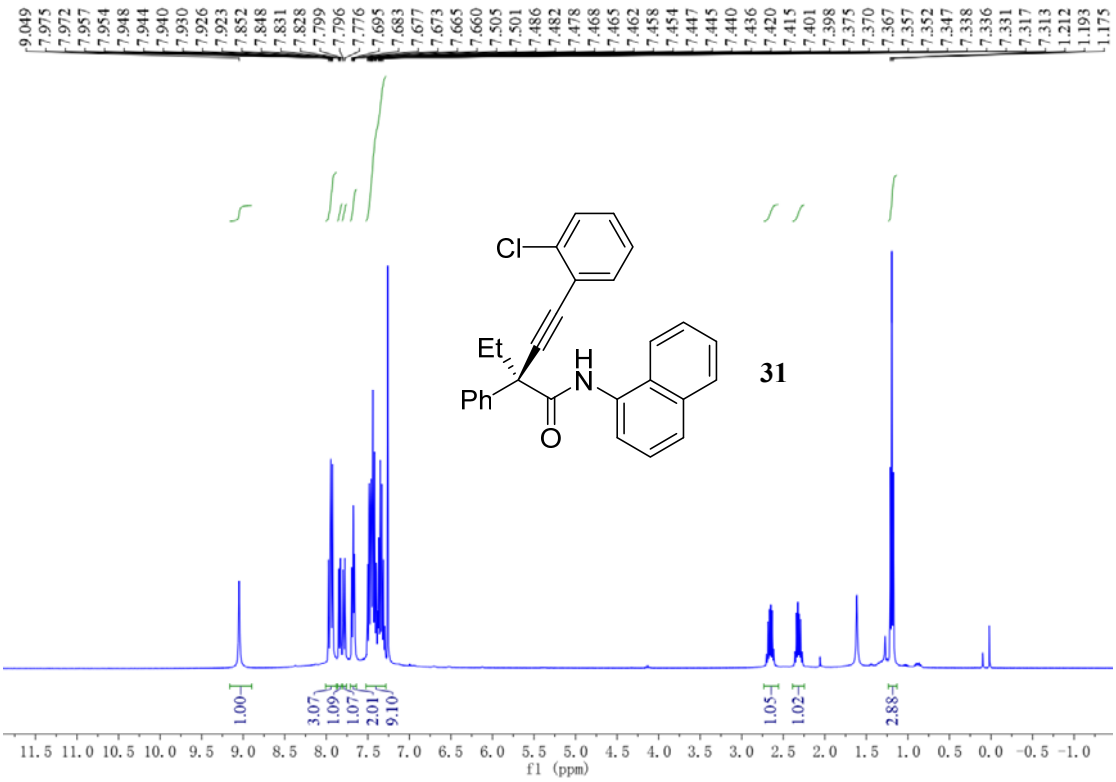
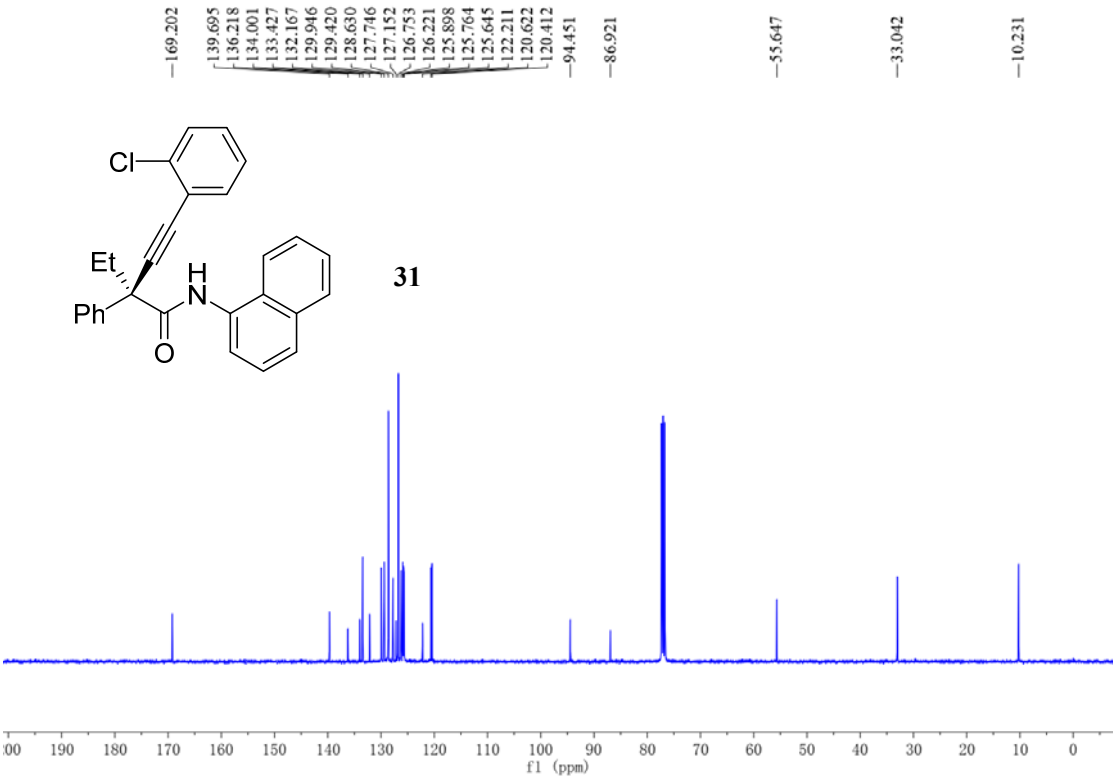
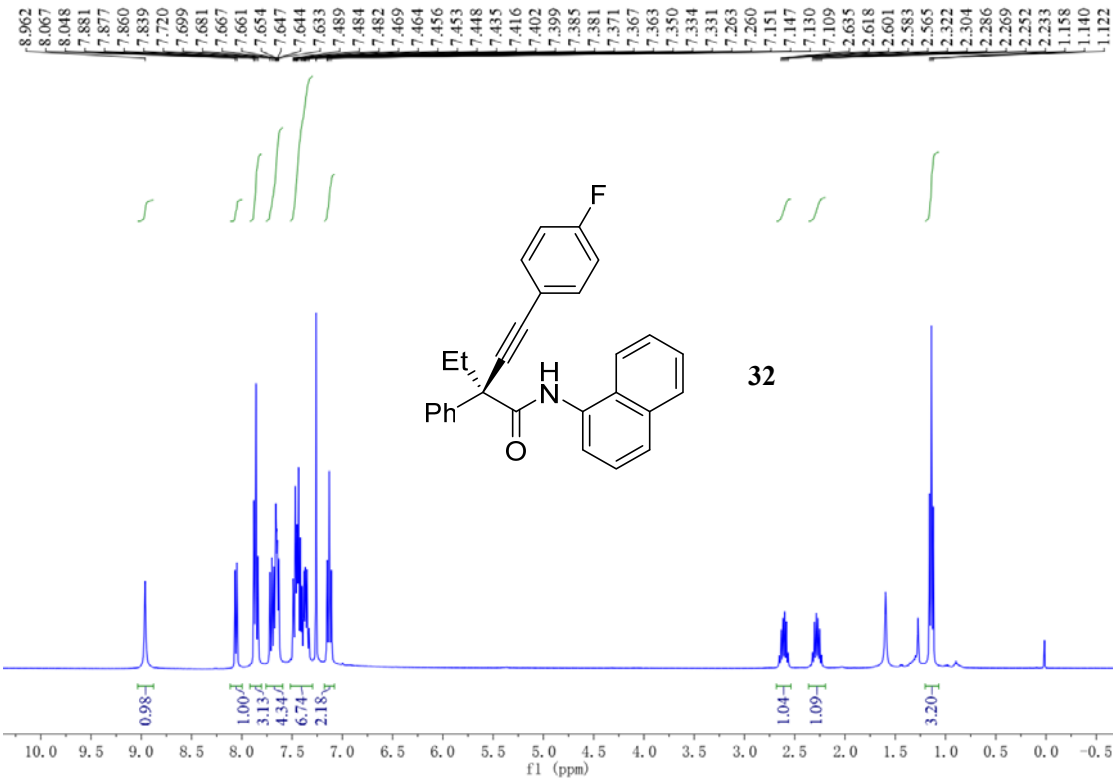
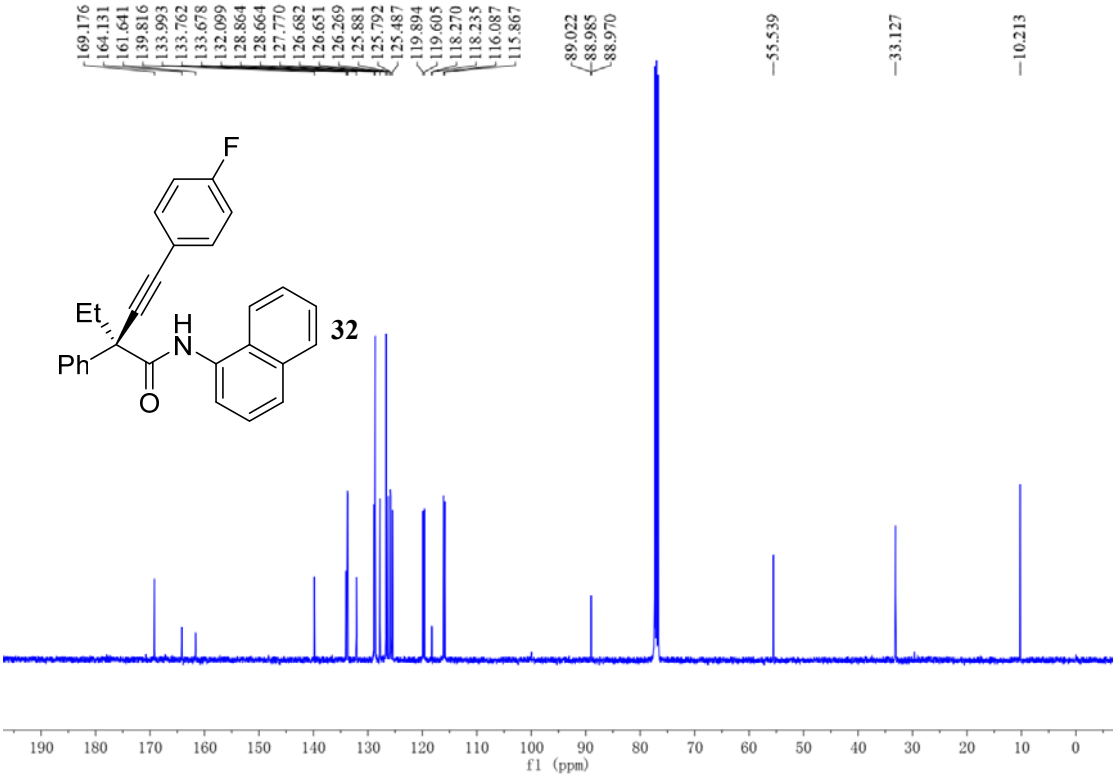
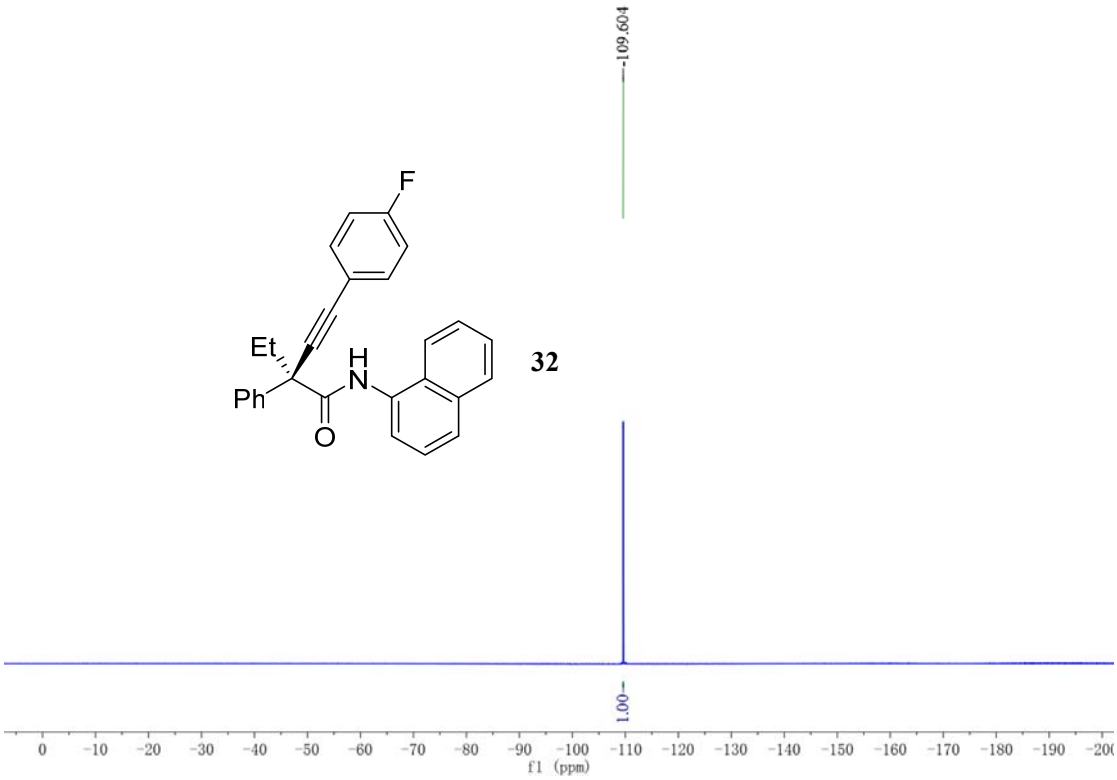
134.517
133.968
132.010
131.646
129.882
129.277
128.850
128.714
127.836
126.685
126.602
126.331
125.922
125.758
125.544
123.812
119.881
119.665
90.512
88.605
55.536
33.077
10.195
Cl
Et
Ph
H
N
O
30
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
Et
Ph
H
N
O
31
f1 (ppm)


Cl
Et
Ph
H
N
O
31
f1 (ppm)


F
Et
Ph
H
N
O
32
f1 (ppm)


F
Et
Ph
H
N
O
32
f1 (ppm)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F
Et
H
N
Ph
O
1.00
0
-10
-20
-30
-40
-50
-60
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-90
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-110
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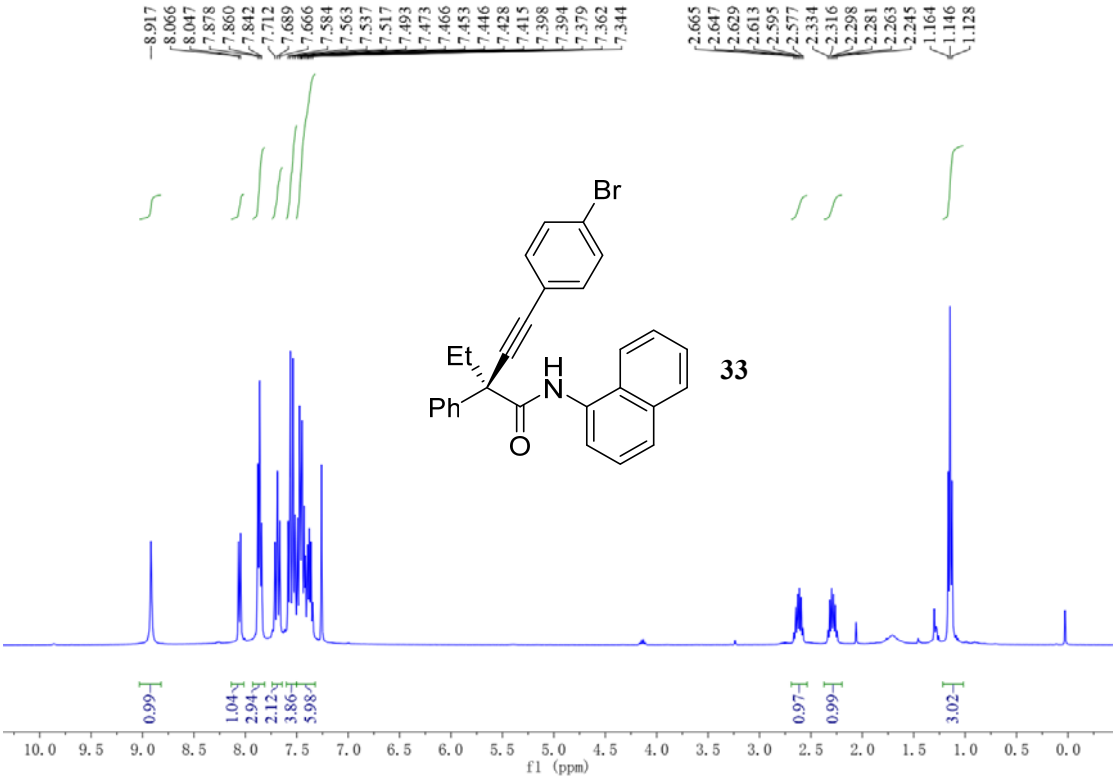
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

32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7.689
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7.517
7.493
7.473
7.466
7.453
7.446
7.428
7.415
7.398
7.394
7.379
7.362
7.344
2.665
2.647
2.629
2.613
2.595
2.577
2.334
2.316
2.298
2.281
2.263
2.245
1.164
1.146
1.128
Br
Et
Ph
H
N
O
33
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1.04
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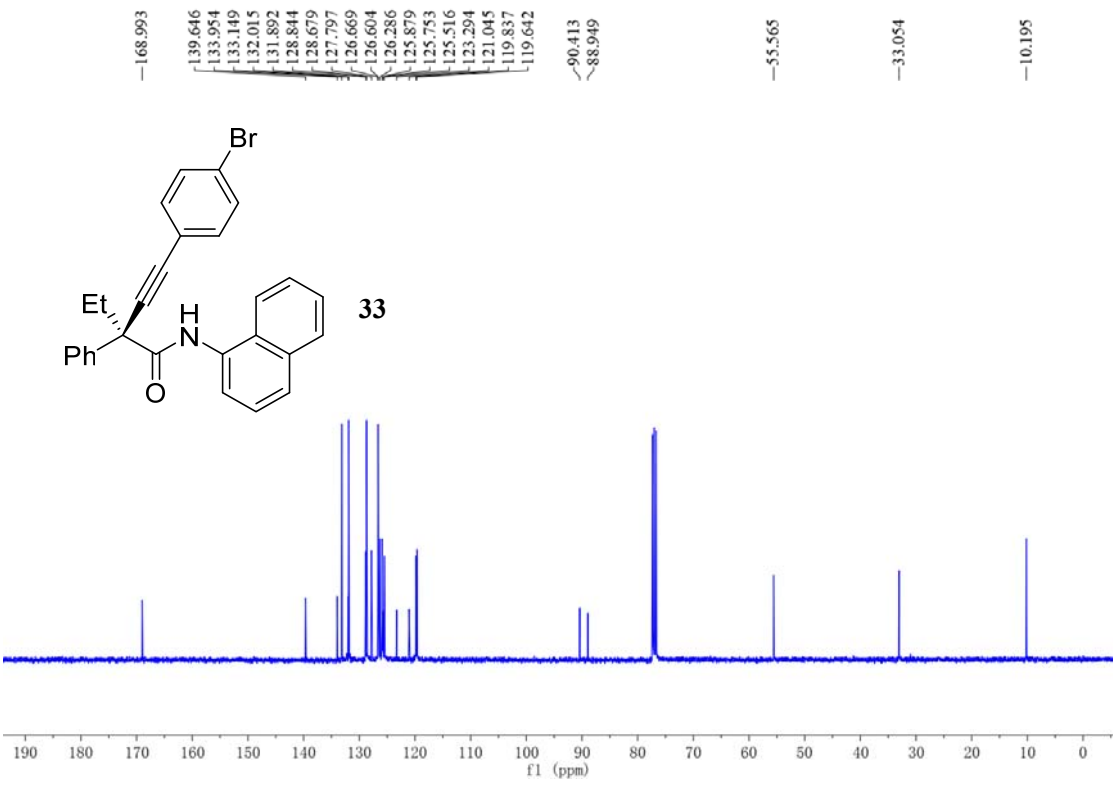
2.12
3.86
5.98
0.97
0.99
3.02
f1 (ppm)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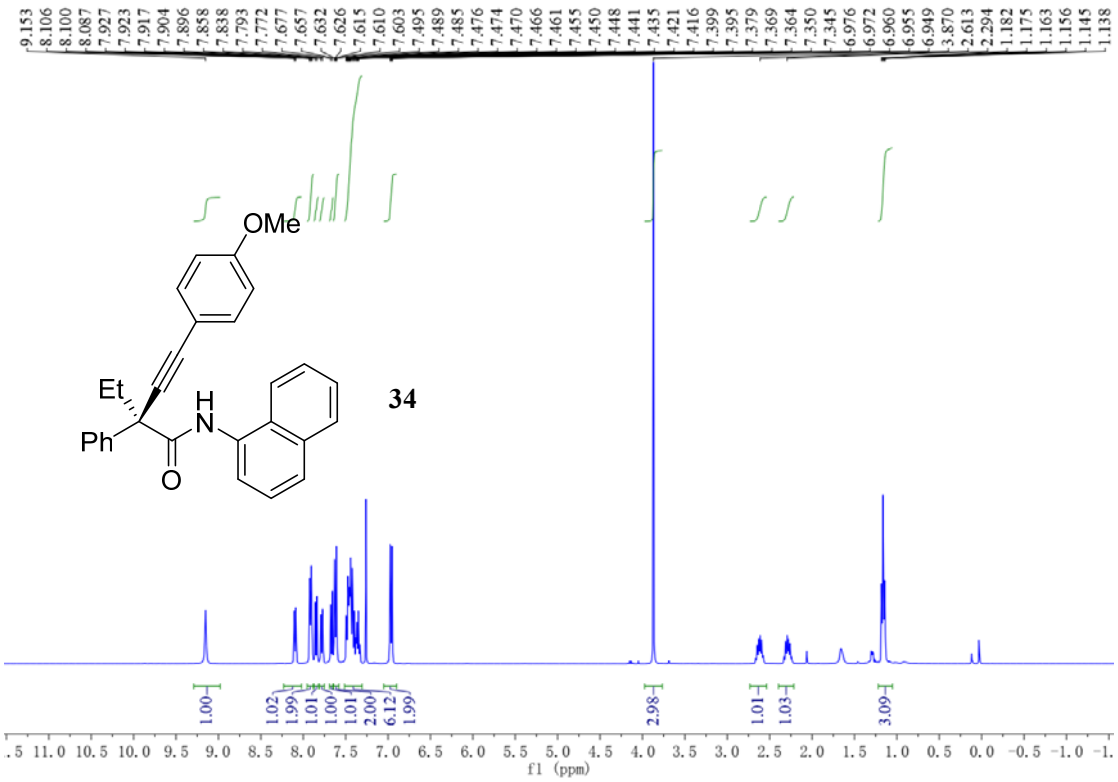
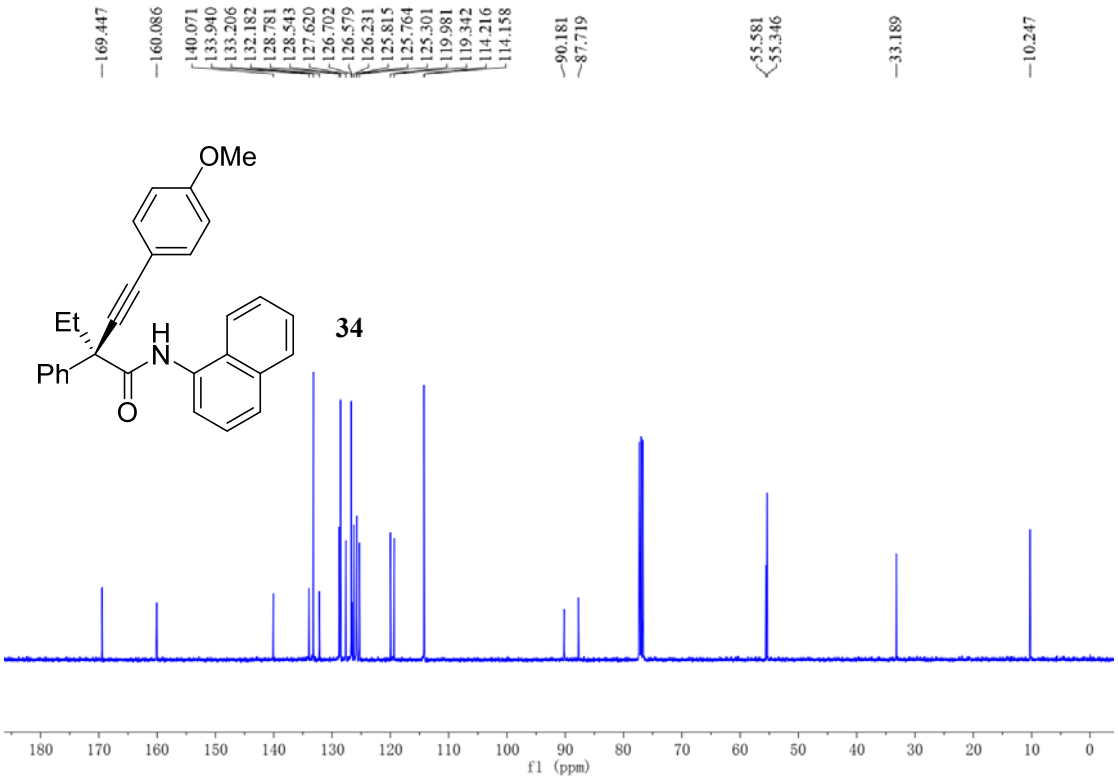
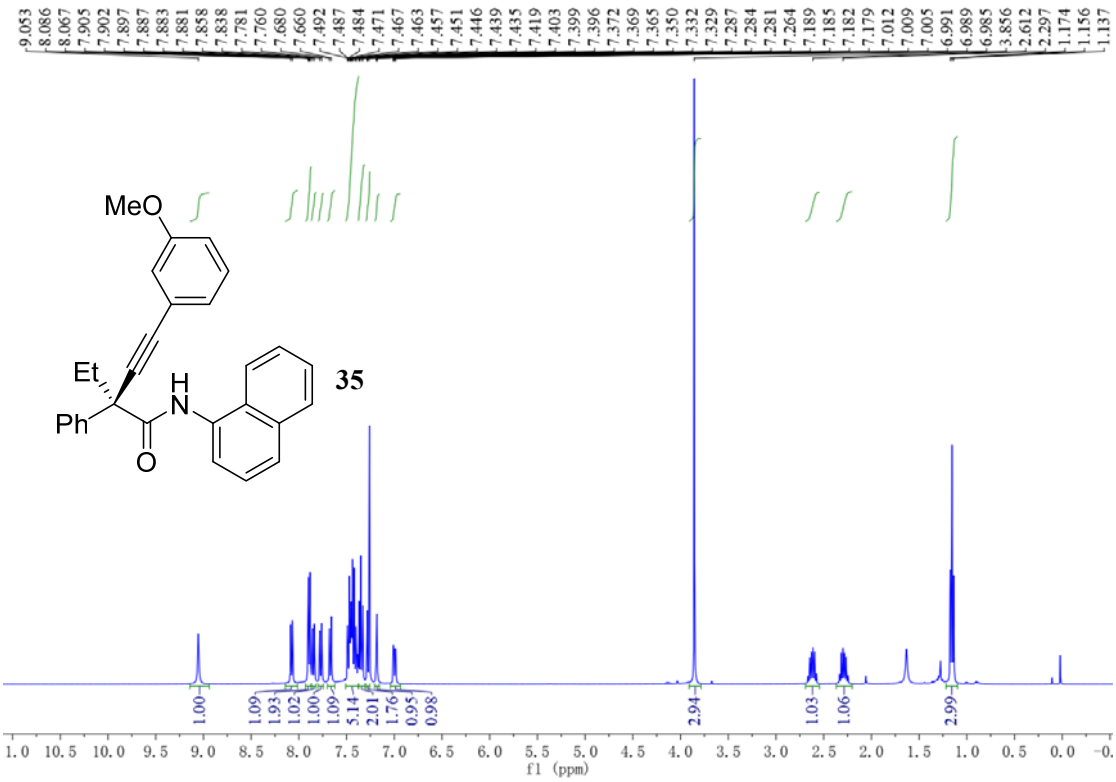
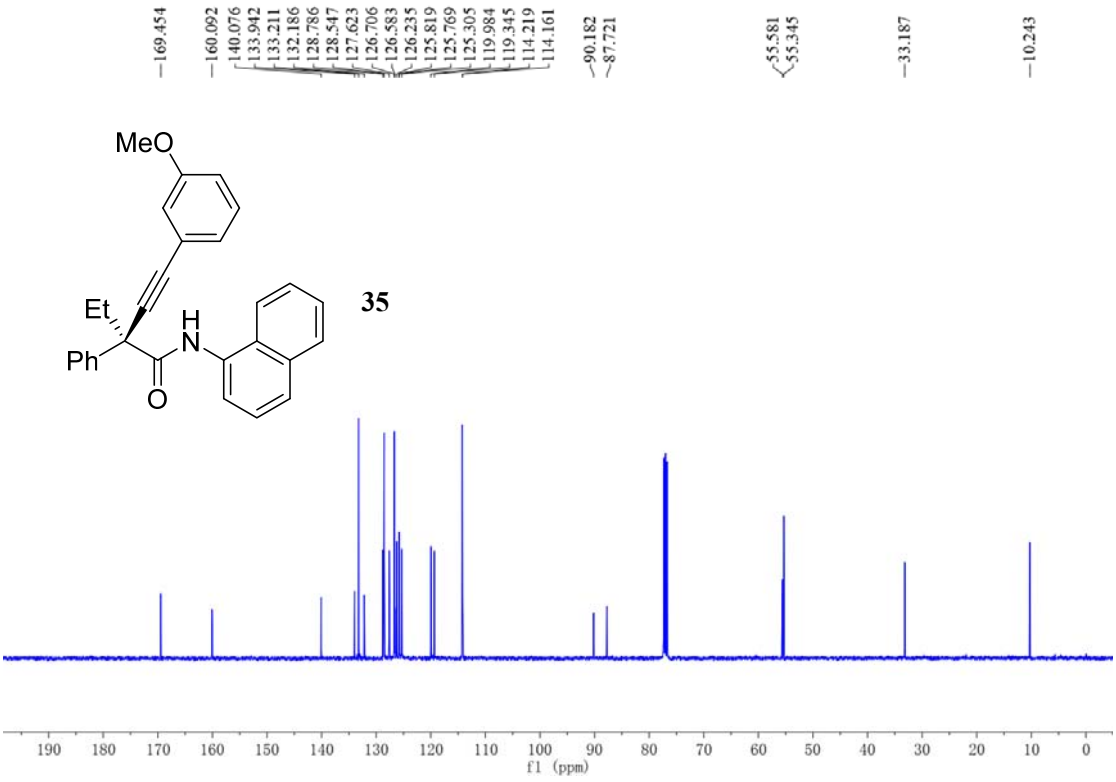
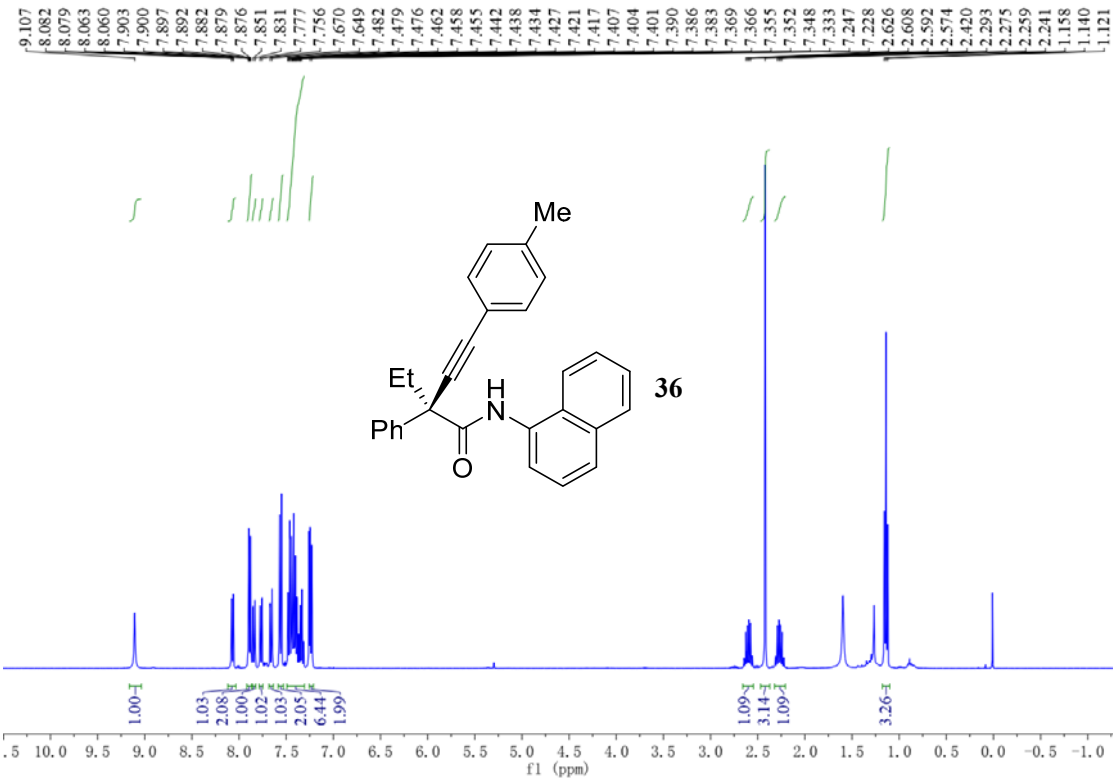
133.954
133.149
132.015
131.892
128.844
128.679
127.797
126.669
126.604
126.286
125.879
125.753
125.516
123.294
121.045
119.837
119.642
90.413
88.949
55.565
33.054
10.195
Br
Et
Ph
H
N
O
33
f1 (ppm)

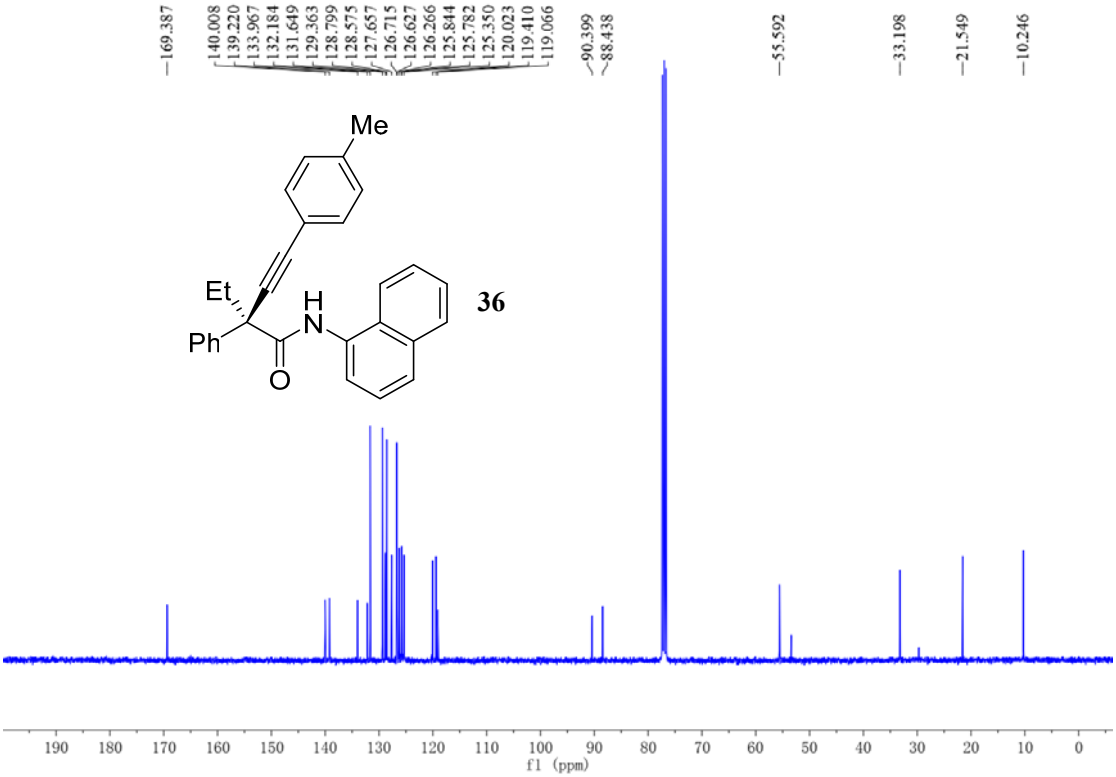

OMe
Et
Ph
H
N
O
34
f1 (ppm)

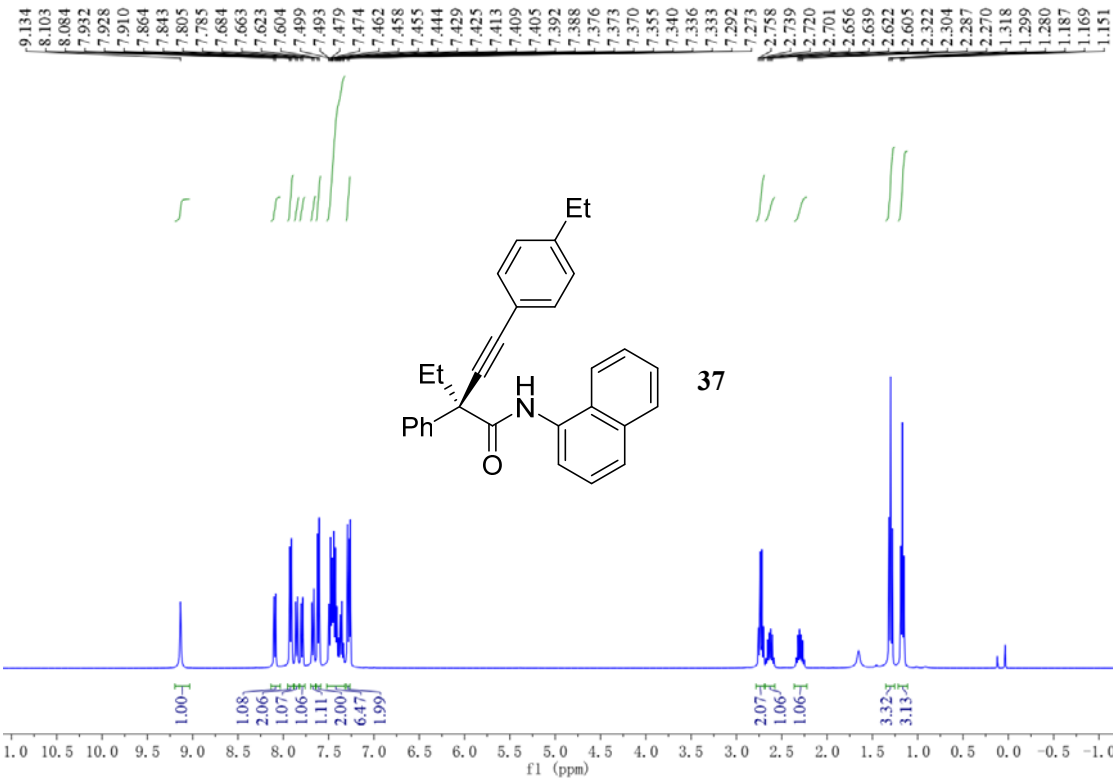

OMe
Et
Ph
H
N
O
34
f1 (ppm)

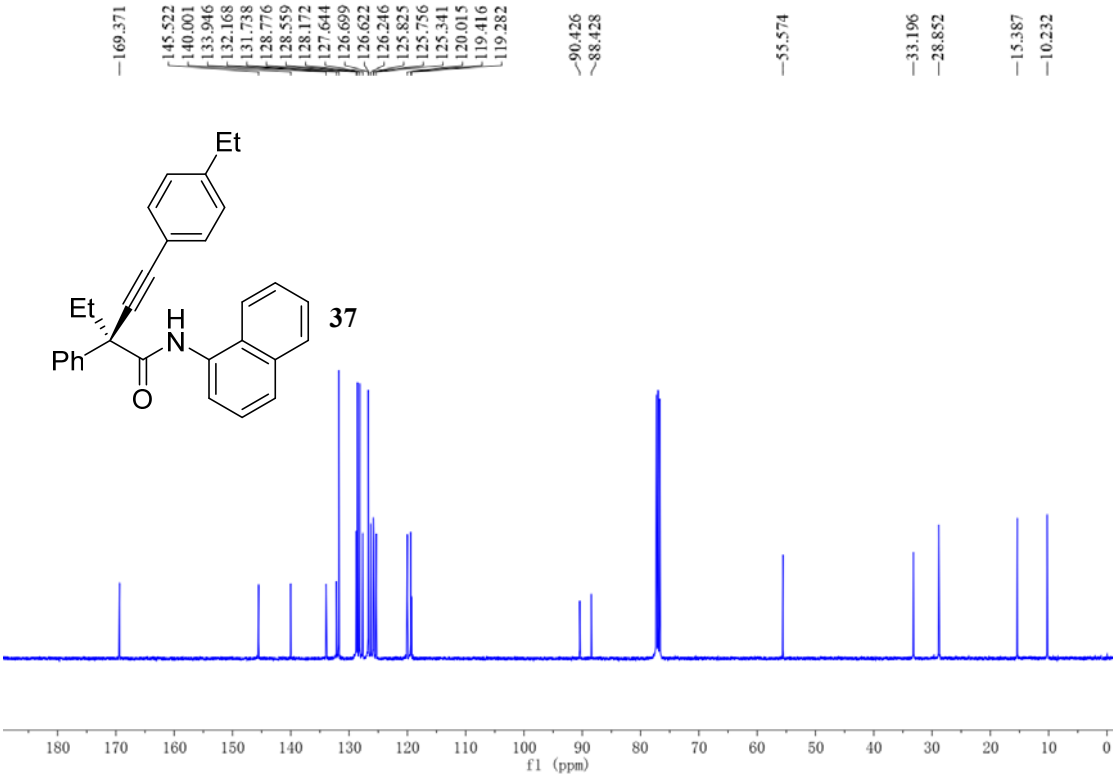

MeO
Et
Ph
H
N
O
35
f1 (ppm)

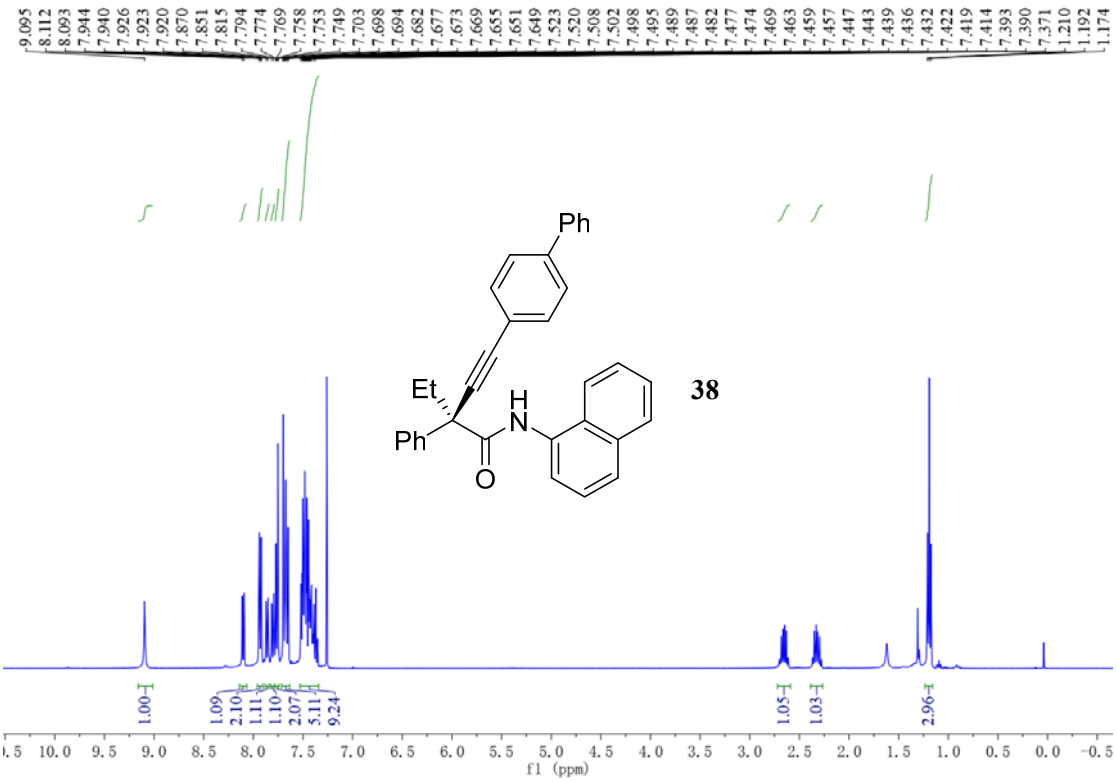

MeO
Et
Ph
H
N
O
35
f1 (ppm)

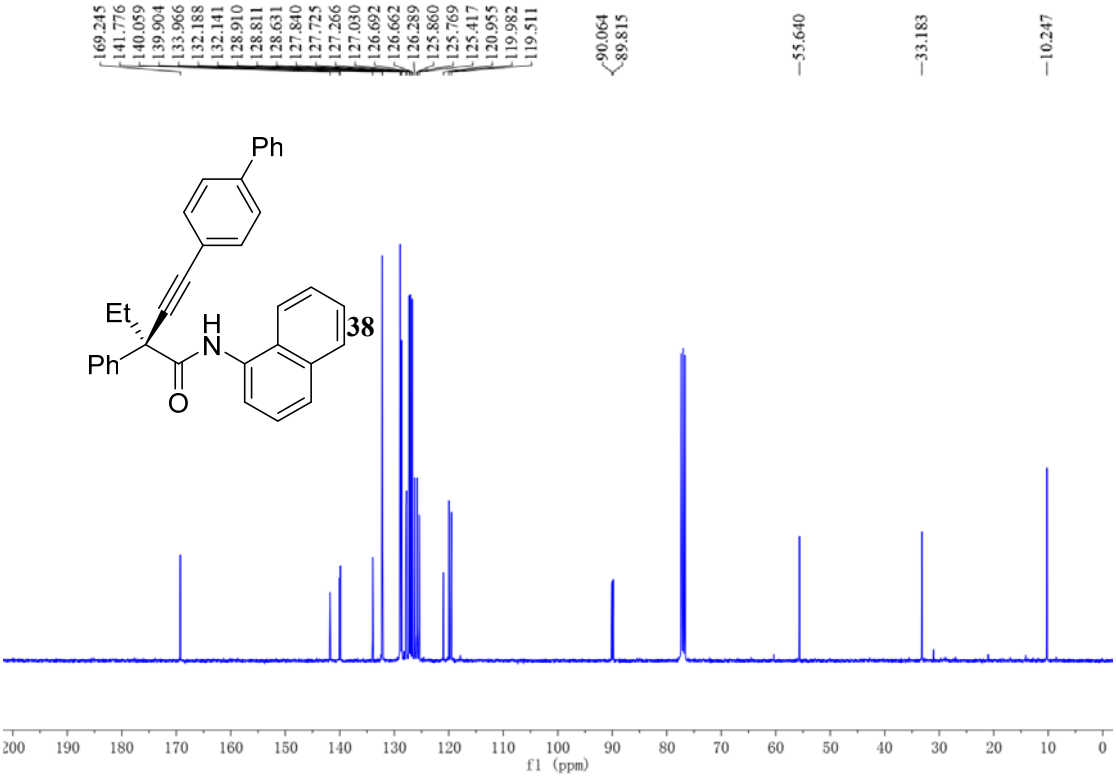

Me
Et
H
N
Ph
O
36
f1 (ppm)

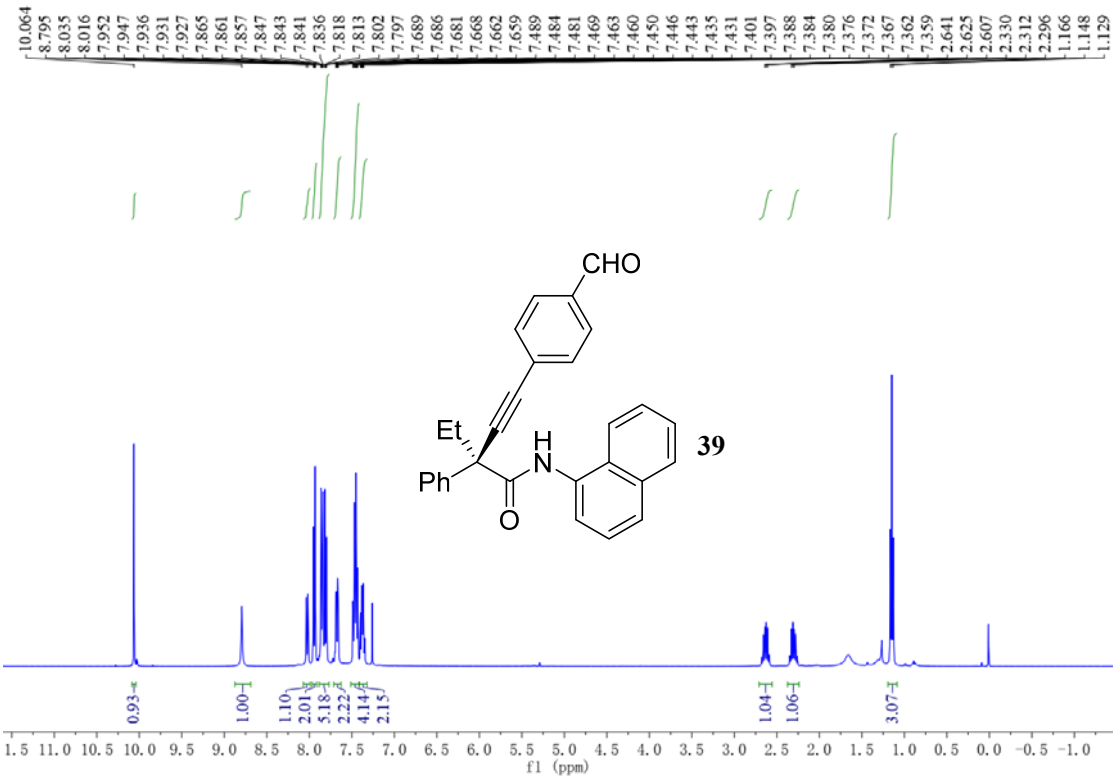

Me
Et
H
N
Ph
O
36
f1 (ppm)

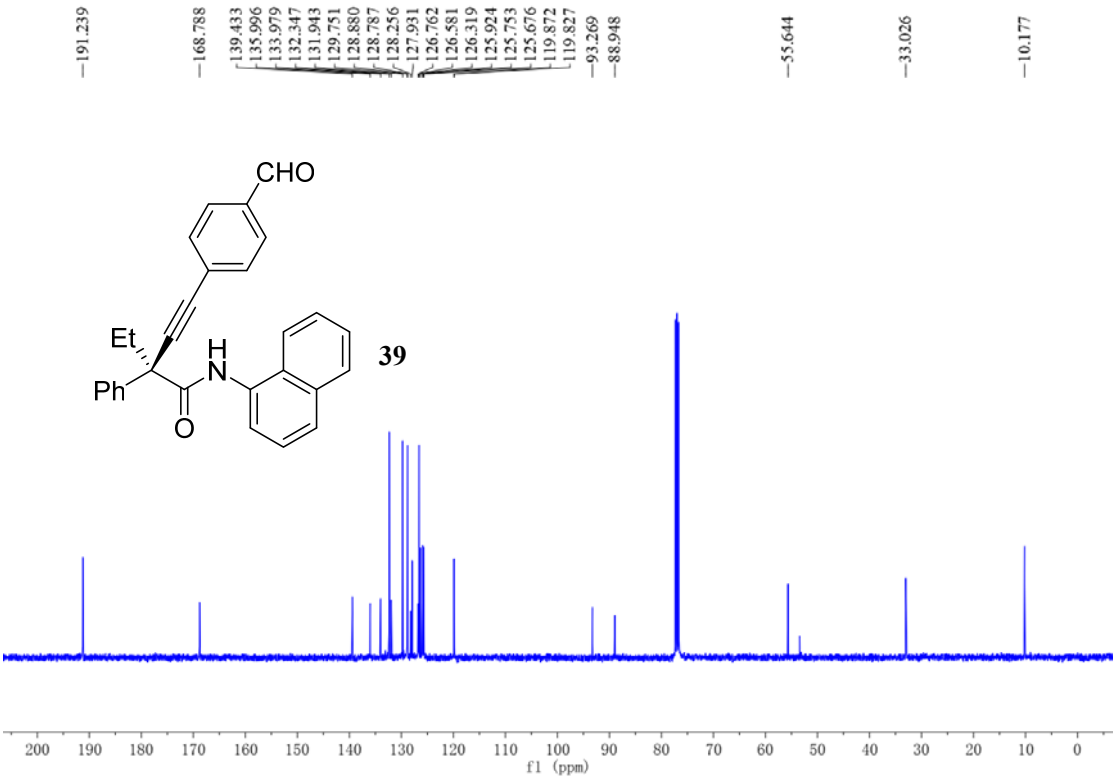

Et
Et
Ph
H
N
O
37
f1 (ppm)

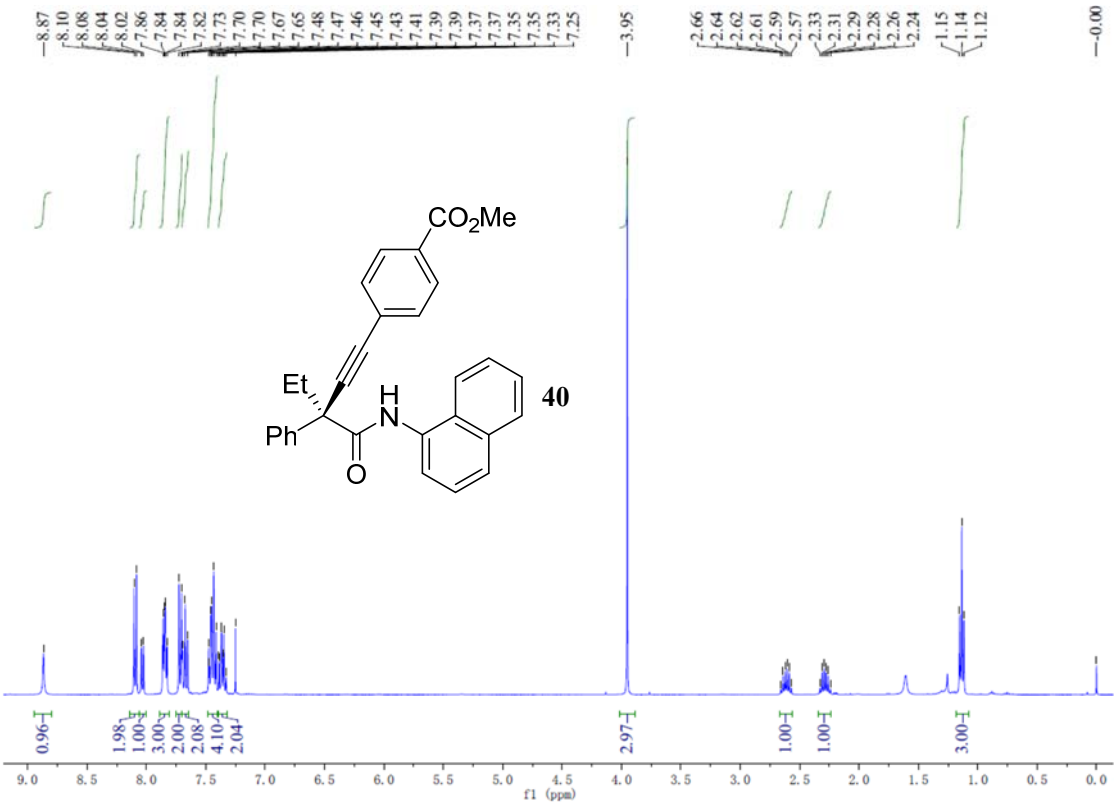

Et
Et
Ph
H
N
O
37
f1 (ppm)


Ph
Et
H
N
Ph
O
38
1.00
1.09
2.10
1.11
1.10
2.07
5.11
9.24
1.05
1.03
2.96
f1 (ppm)


Ph
Et
H
N
Ph
O
38
55.640
33.183
10.247
f1 (ppm)


CHO
Et
Ph
H
N
O
39
f1 (ppm)


CHO
Et
Ph
H
N
O
39
f1 (ppm)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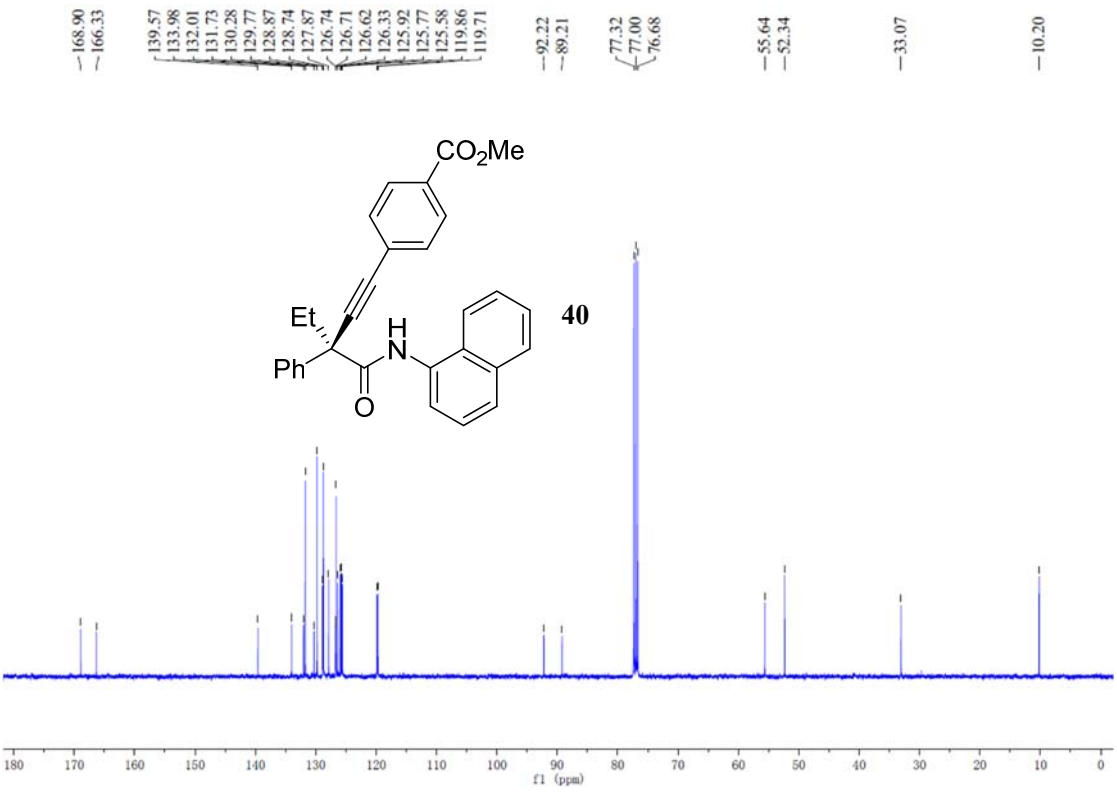
8.10
8.08
8.04
8.02
7.86
7.84
7.84
7.82
7.73
7.70
7.70
7.67
7.65
7.48
7.47
7.46
7.45
7.43
7.41
7.39
7.39
7.37
7.37
7.35
7.35
7.33
7.25
3.95
2.66
2.64
2.62
2.61
2.59
2.57
2.33
2.31
2.29
2.28
2.26
2.24
1.15
1.14
1.12
0.00
CO2Me
Et
Ph
H
N
O
40
0.96
1.98
1.00
3.00
2.00
2.08
4.10
2.04
2.97
1.00
1.00
3.00
f1 (ppm)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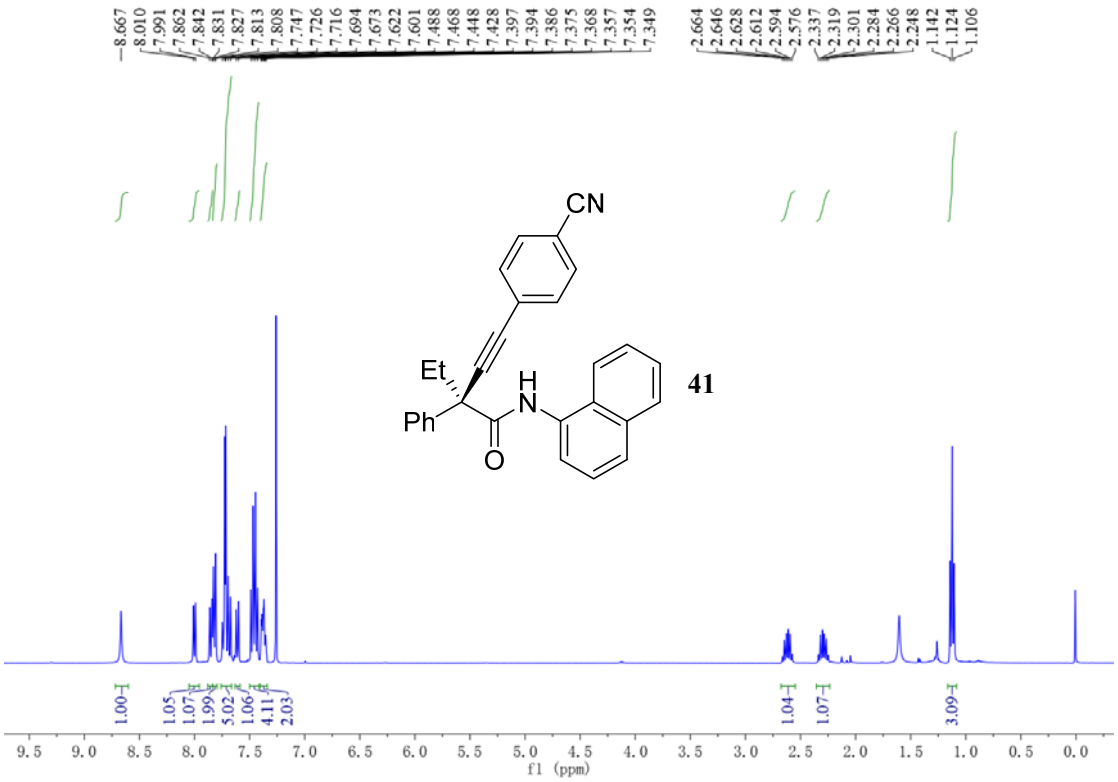
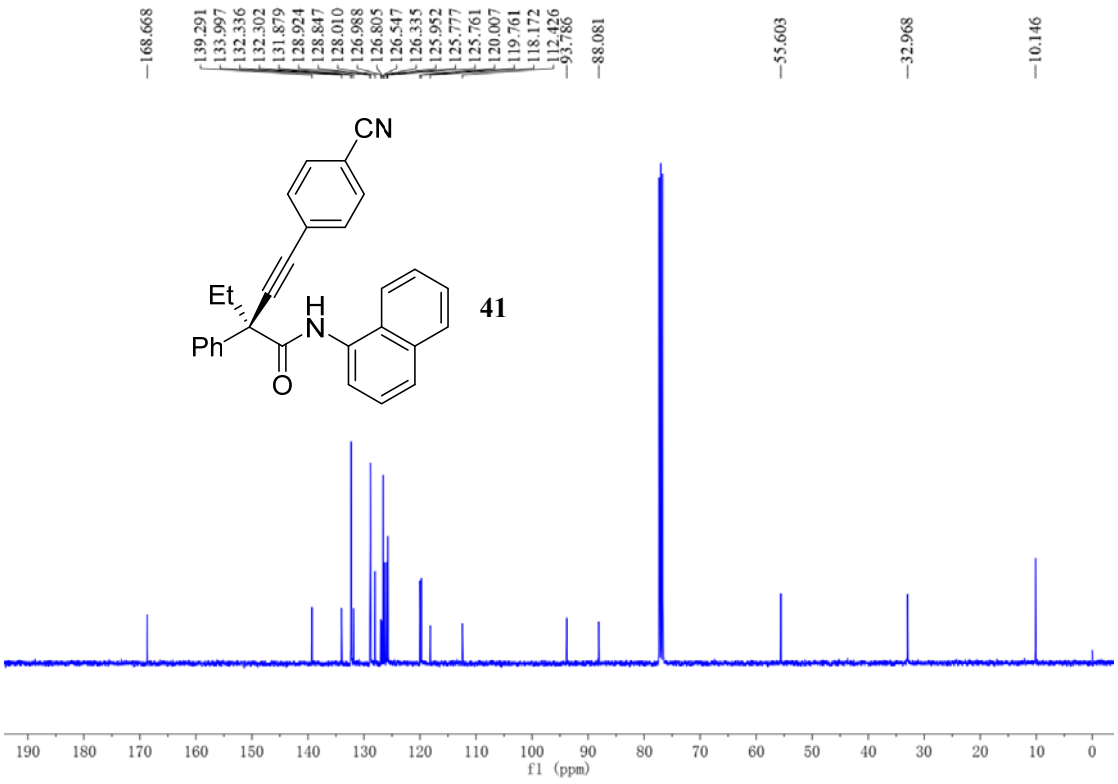
166.33
139.57
133.98
132.01
131.73
130.28
129.77
128.87
128.74
127.87
126.74
126.71
126.62
126.33
125.92
125.77
125.58
119.86
119.71
92.22
89.21
77.32
77.00
76.68
55.64
52.34
33.07
10.20
CO2Me
Et
Ph
H
N
O
40
f1 (ppm)


8.667
8.010
7.991
7.862
7.842
7.831
7.827
7.813
7.808
7.747
7.726
7.716
7.694
7.673
7.622
7.601
7.488
7.468
7.448
7.428
7.397
7.394
7.386
7.375
7.368
7.357
7.354
7.349
2.664
2.646
2.628
2.612
2.594
2.576
2.337
2.319
2.301
2.284
2.266
2.248
1.142
1.124
1.106
CN
Et
Ph
H
N
O
41
1.00
1.05
1.07
1.99
5.02
1.06
4.11
2.03
1.04
1.07
3.09
f1 (ppm)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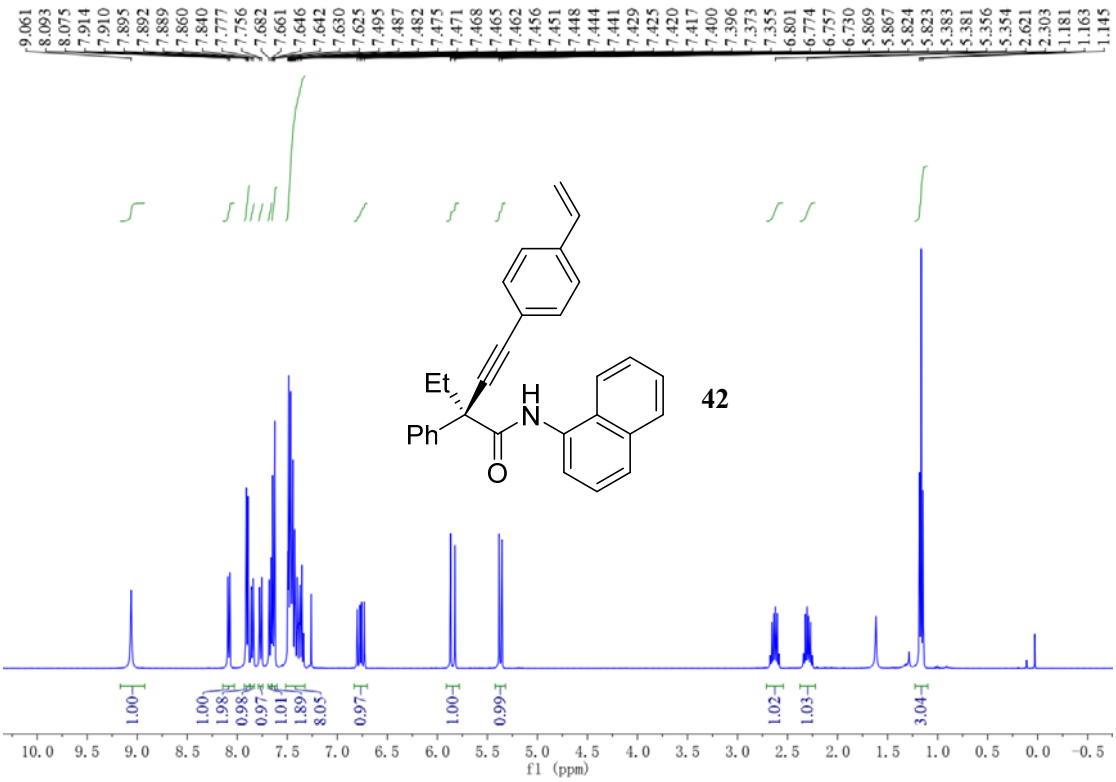
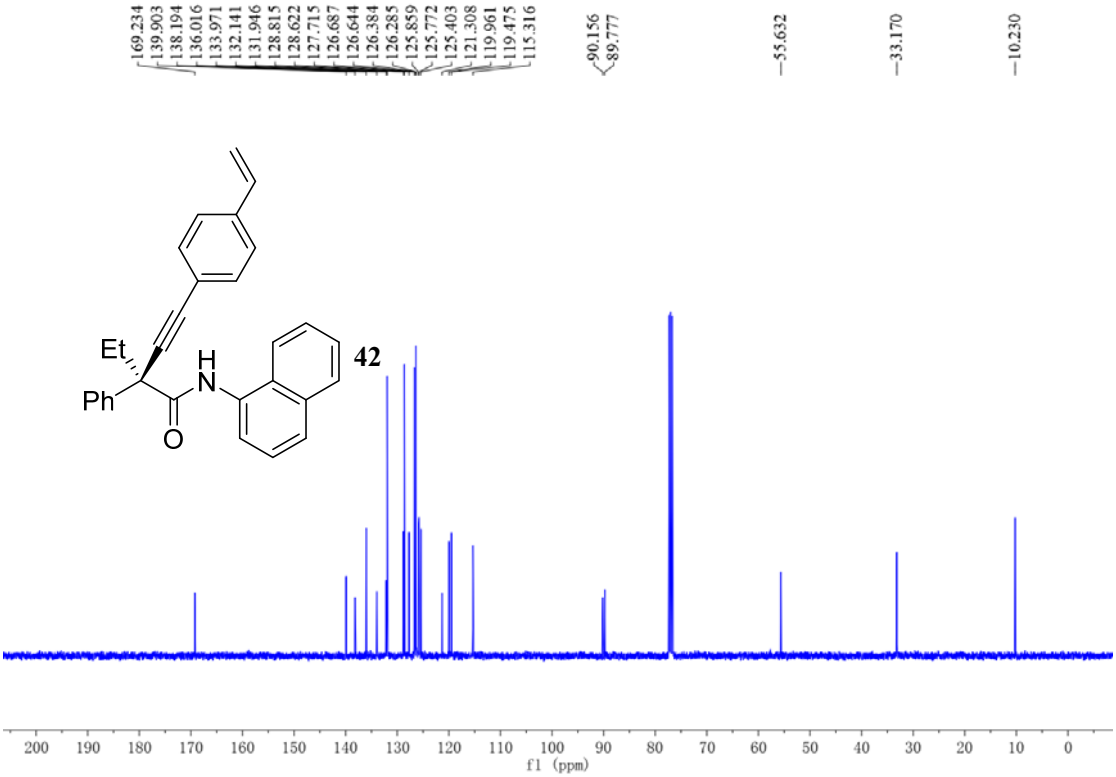
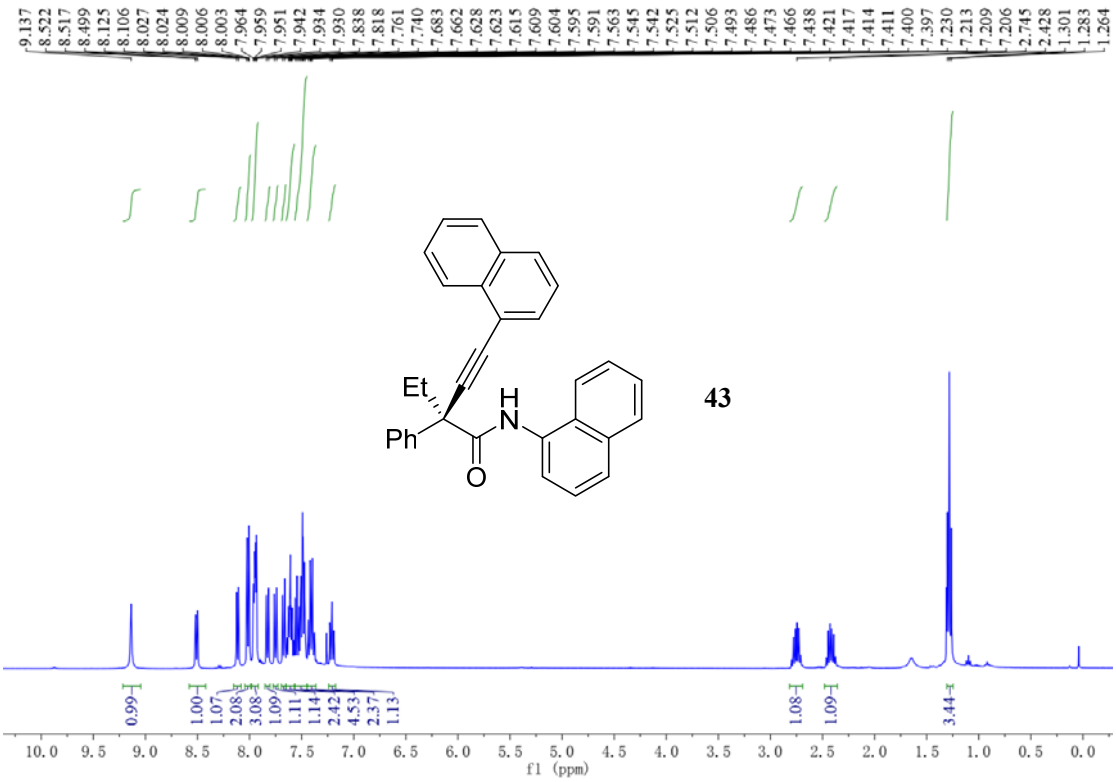
133.997
132.336
132.302
131.879
128.924
128.847
128.010
126.988
126.805
126.547
126.335
125.952
125.777
125.761
120.007
119.761
118.172
112.426
93.786
88.081
55.603
32.968
10.146
CN
Et
Ph
H
N
O
41
f1 (ppm)


Et
Ph
H
N
O
42
f1 (ppm)


Et
Ph
H
N
O
42
f1 (ppm)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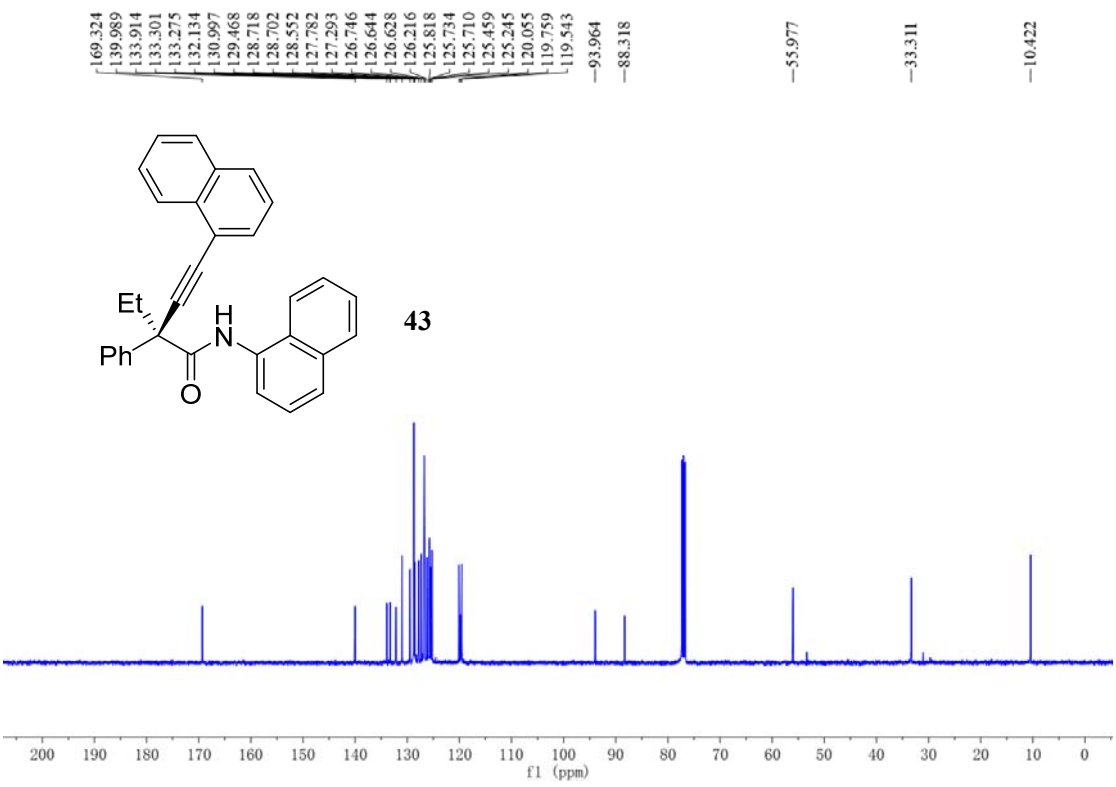
8.522
8.517
8.499
8.125
8.106
8.027
8.024
8.009
8.006
8.003
7.964
7.959
7.951
7.942
7.934
7.930
7.838
7.818
7.761
7.740
7.683
7.662
7.628
7.623
7.615
7.609
7.604
7.595
7.591
7.563
7.545
7.542
7.525
7.512
7.506
7.493
7.486
7.473
7.466
7.438
7.421
7.417
7.414
7.411
7.400
7.397
7.230
7.213
7.209
7.206
2.745
2.428
1.301
1.283
1.264
Et
H
N
Ph
O
43
0.99
1.00
1.07
2.08
3.08
1.09
1.11
1.14
2.42
4.53
2.37
1.13
1.08
1.09
3.44
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)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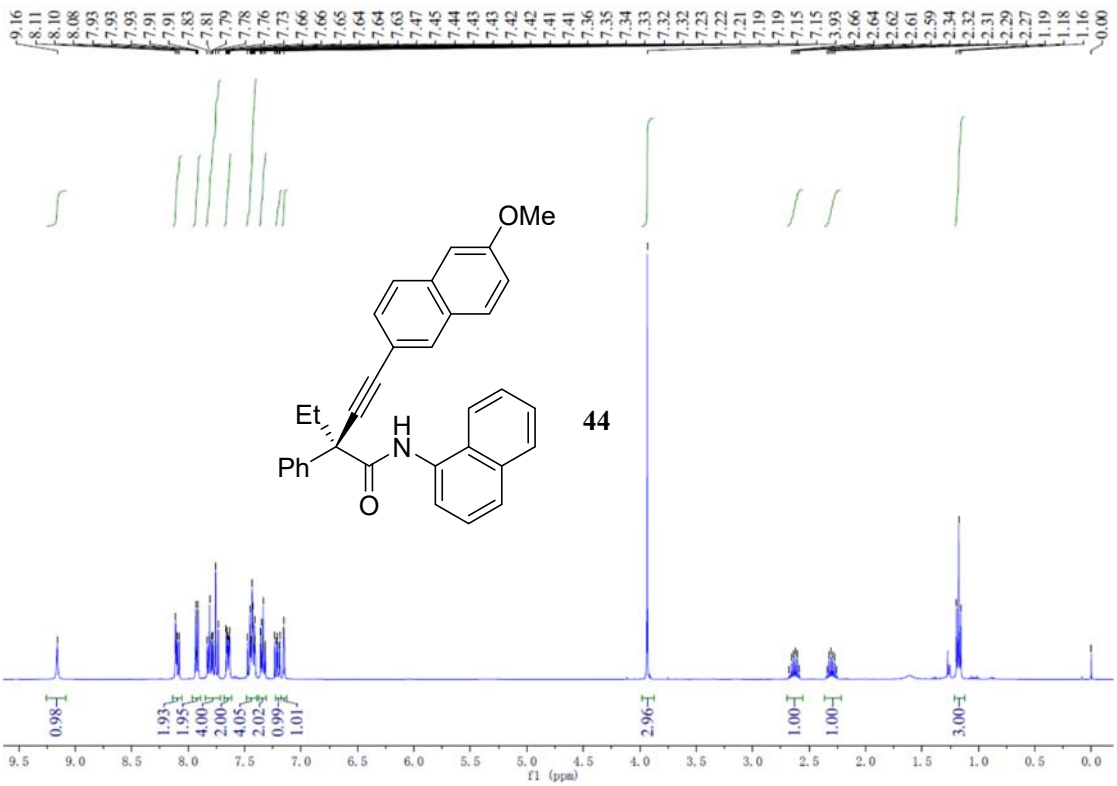
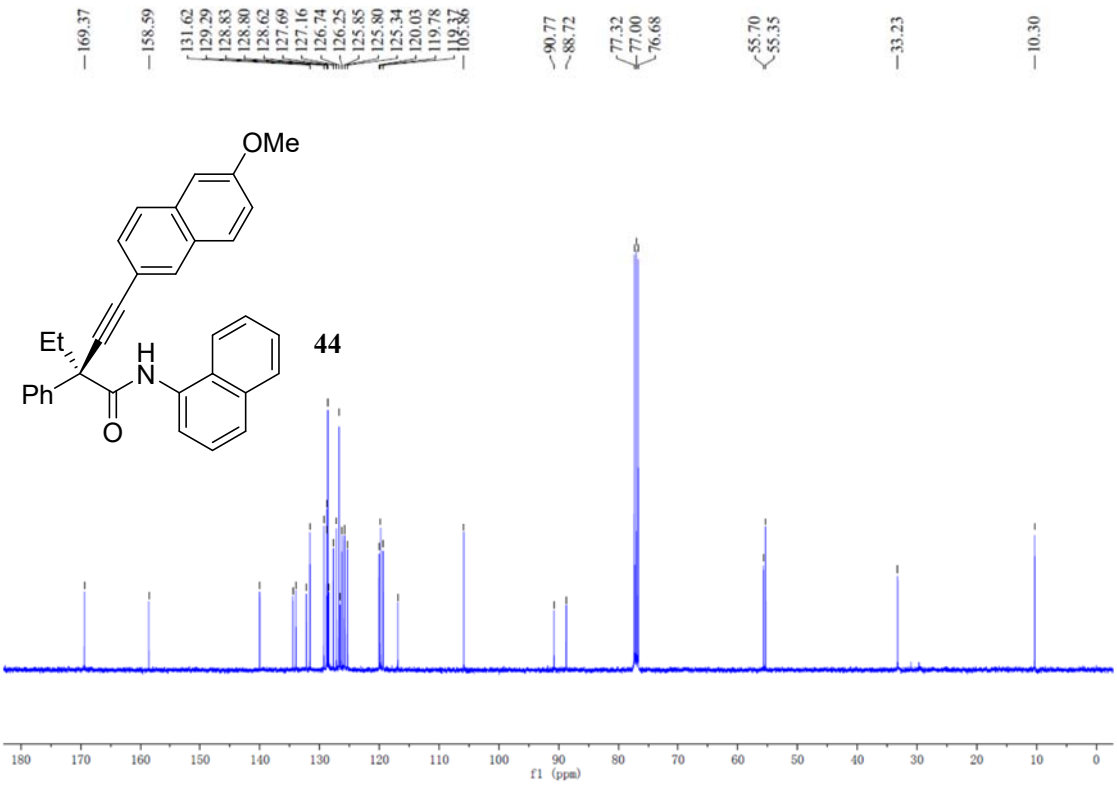
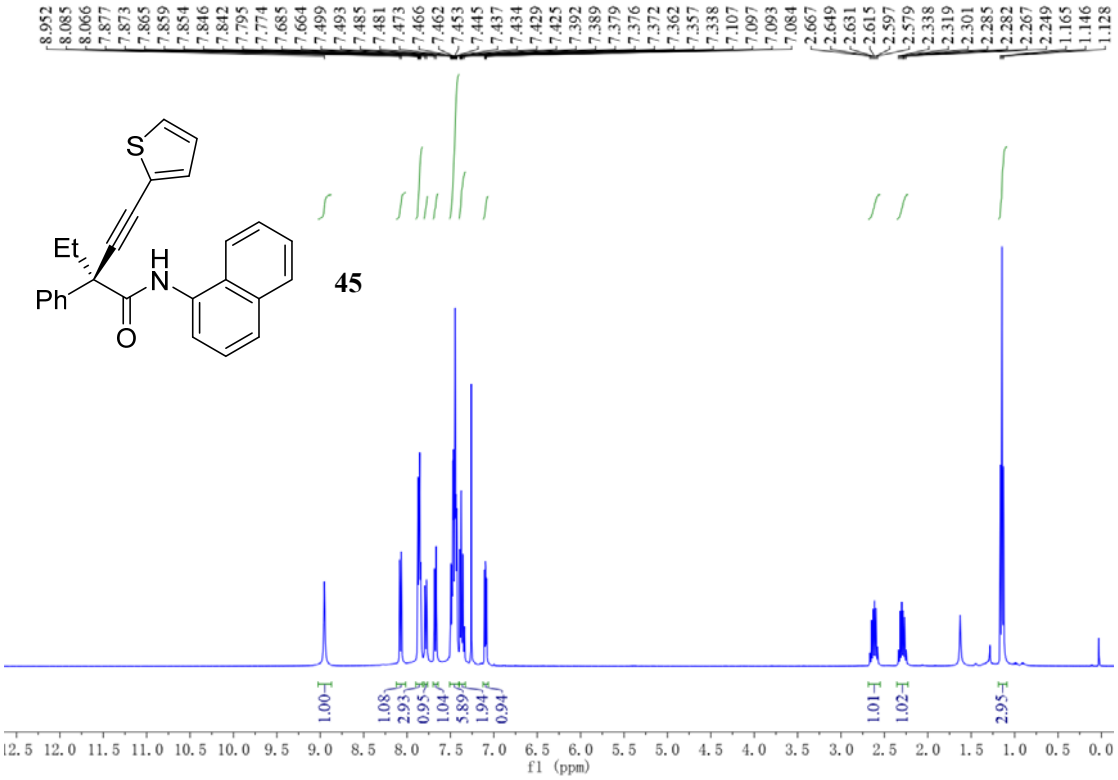
133.914
133.301
133.275
132.134
130.997
129.468
128.718
128.702
128.552
127.782
127.293
126.746
126.644
126.628
126.216
125.818
125.734
125.710
125.459
125.245
120.055
119.759
119.543
93.964
88.318
55.977
33.311
10.422
Et
H
N
Ph
O
43
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OMe
Et
Ph
H
N
O
44
0.98
1.93
1.95
4.00
2.00
4.05
2.02
0.99
1.01
2.96
1.00
1.00
3.00
f1 (ppm)


OMe
Et
Ph
H
N
O
44
f1 (ppm)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7.842
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7.774
7.685
7.664
7.499
7.493
7.485
7.481
7.473
7.466
7.462
7.453
7.445
7.437
7.434
7.429
7.425
7.392
7.389
7.379
7.376
7.372
7.362
7.357
7.338
7.107
7.097
7.093
7.084
2.667
2.649
2.631
2.615
2.597
2.579
2.338
2.319
2.301
2.285
2.282
2.267
2.249
1.165
1.146
1.128
S
Et
Ph
H
N
O
45
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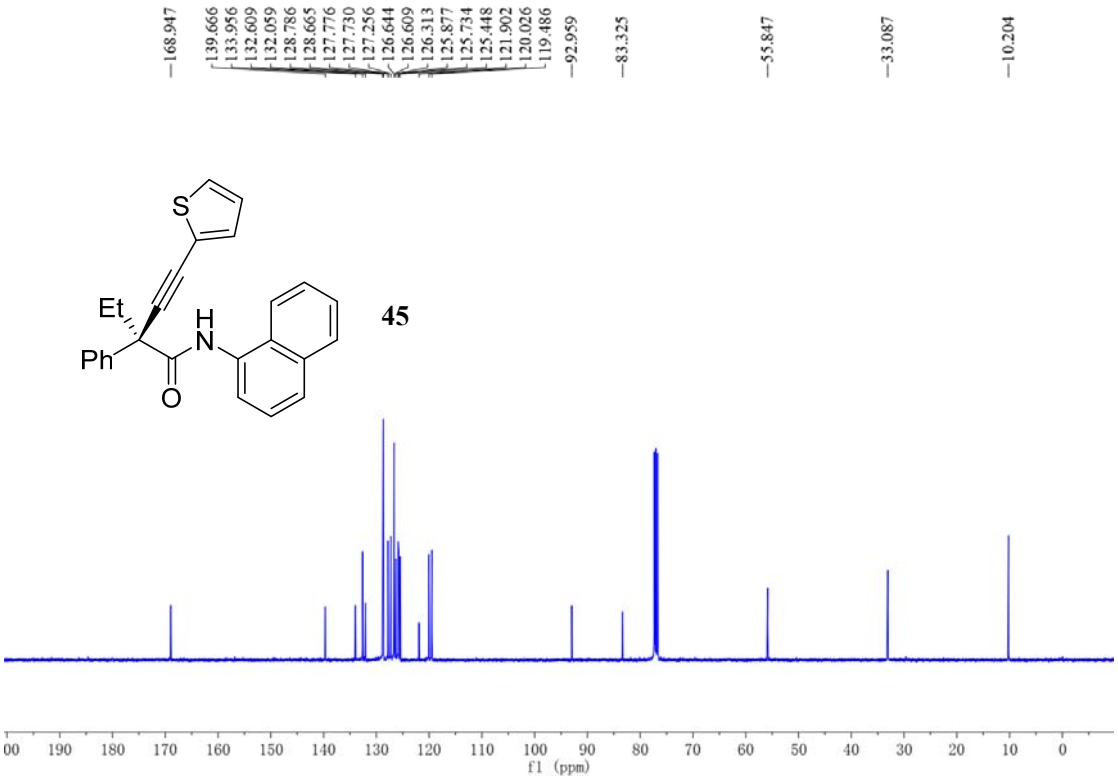
0.95
1.04
5.89
1.94
0.94
1.01
1.02
2.95
f1 (ppm)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133.956
132.609
132.059
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128.665
127.776
127.730
127.256
126.644
126.609
126.313
125.877
125.734
125.448
121.902
120.026
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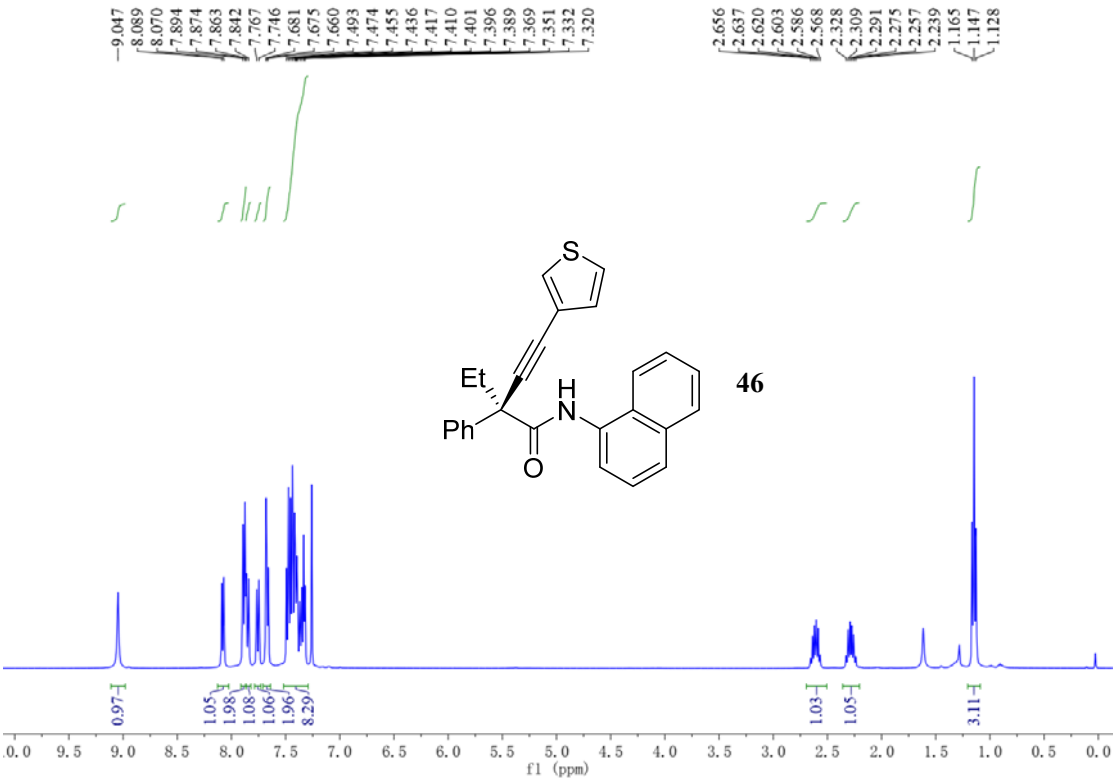
92.959
83.325
55.847
33.087
10.204
S
Et
Ph
H
N
O
45
f1 (ppm)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7.767
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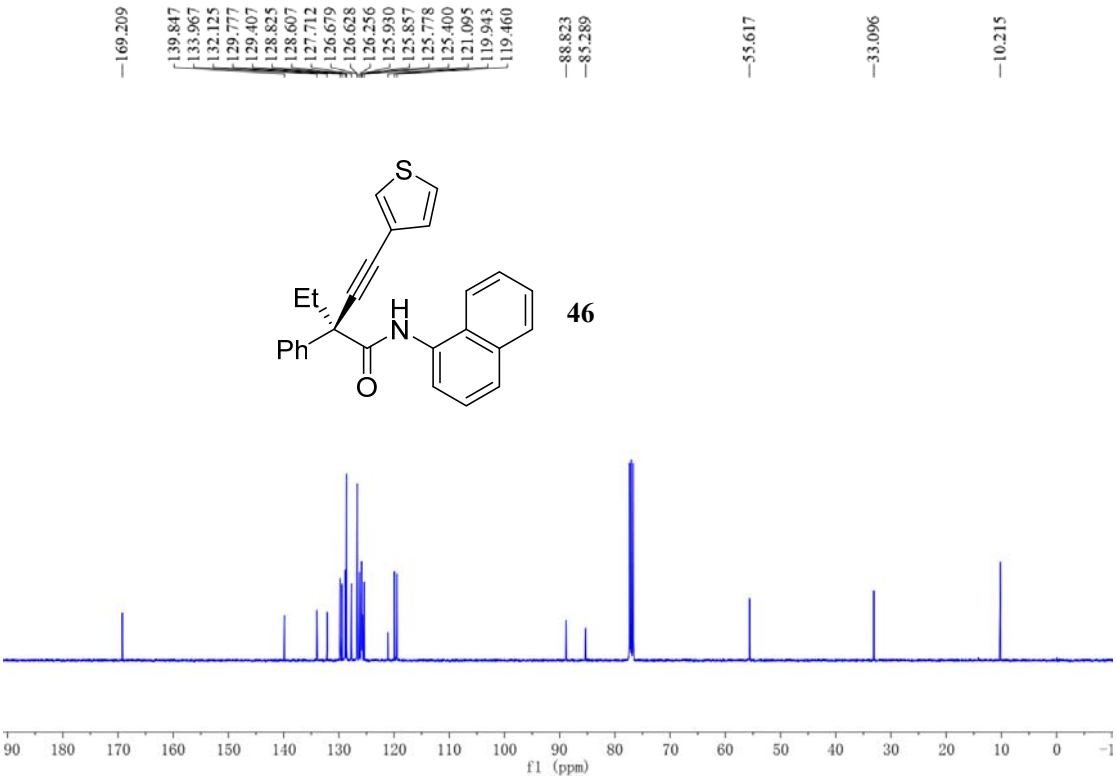
7.681
7.675
7.660
7.493
7.474
7.455
7.436
7.417
7.410
7.401
7.396
7.389
7.369
7.351
7.332
7.320
2.656
2.637
2.620
2.603
2.586
2.568
2.328
2.309
2.291
2.275
2.257
2.239
1.165
1.147
1.128
S
Et
Ph
H
N
O
46
0.97
1.05
1.98
1.08
1.06
1.96
8.29
1.03
1.05
3.11
f1 (ppm)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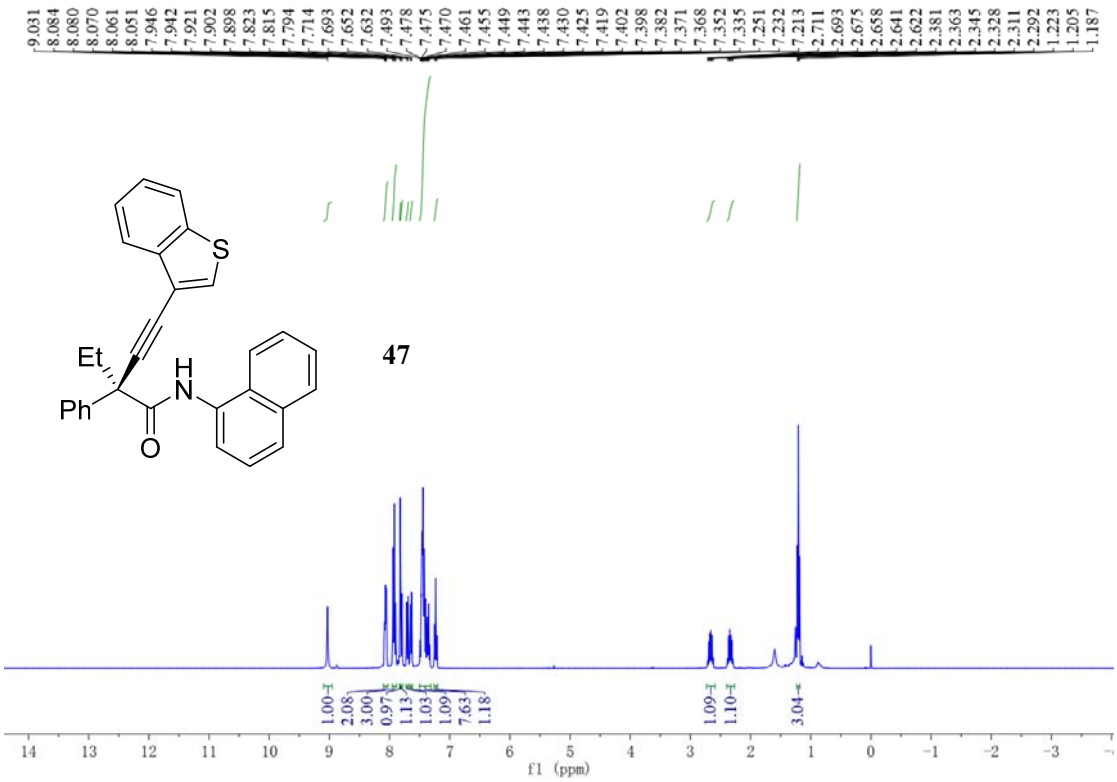
139.847
133.967
132.125
129.777
129.407
128.825
128.607
127.712
126.679
126.628
126.256
125.930
125.857
125.778
125.400
121.095
119.943
119.460
88.823
85.289
55.617
33.096
10.215
S
Et
Ph
H
N
O
46
f1 (ppm)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8.080
8.070
8.061
8.051
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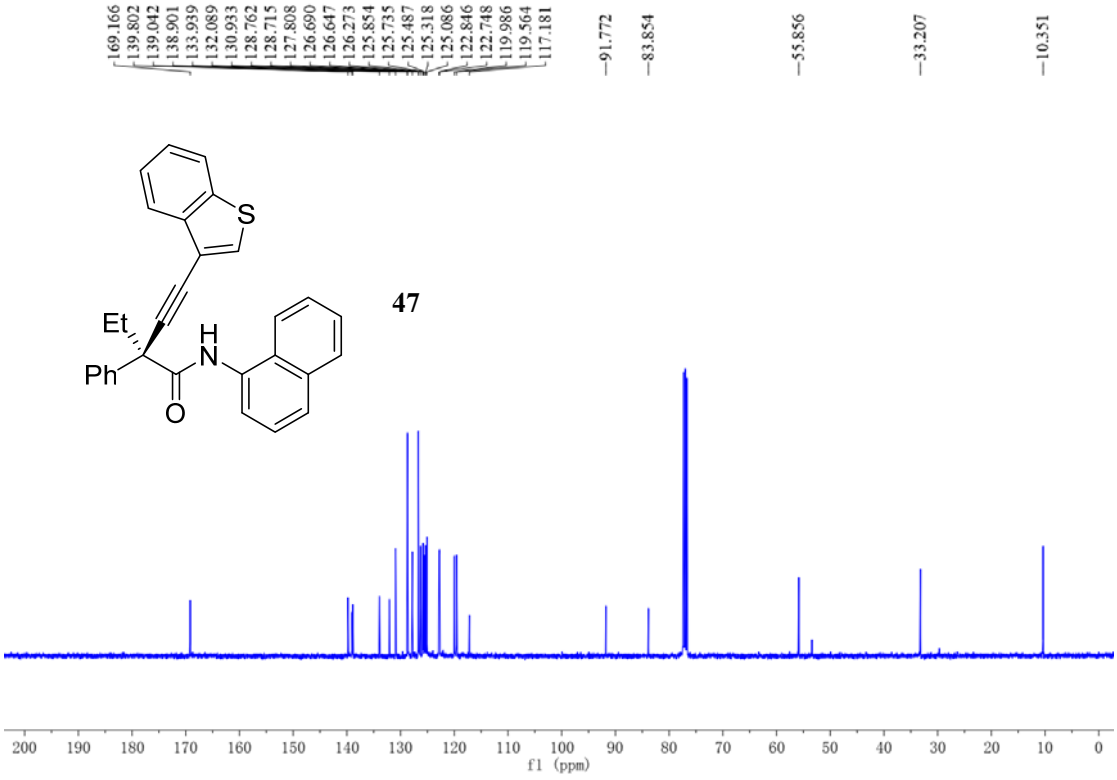
7.942
7.921
7.902
7.898
7.823
7.815
7.794
7.714
7.693
7.652
7.632
7.493
7.478
7.475
7.470
7.461
7.455
7.449
7.443
7.438
7.430
7.425
7.419
7.402
7.398
7.382
7.371
7.368
7.352
7.335
7.251
7.232
7.213
2.711
2.693
2.675
2.658
2.641
2.622
2.381
2.363
2.345
2.328
2.311
2.292
1.223
1.205
1.187
S
Et
Ph
H
N
O
47
1.00
2.08
3.00
0.97
1.13
1.03
1.09
7.63
1.18
1.09
1.10
3.04
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)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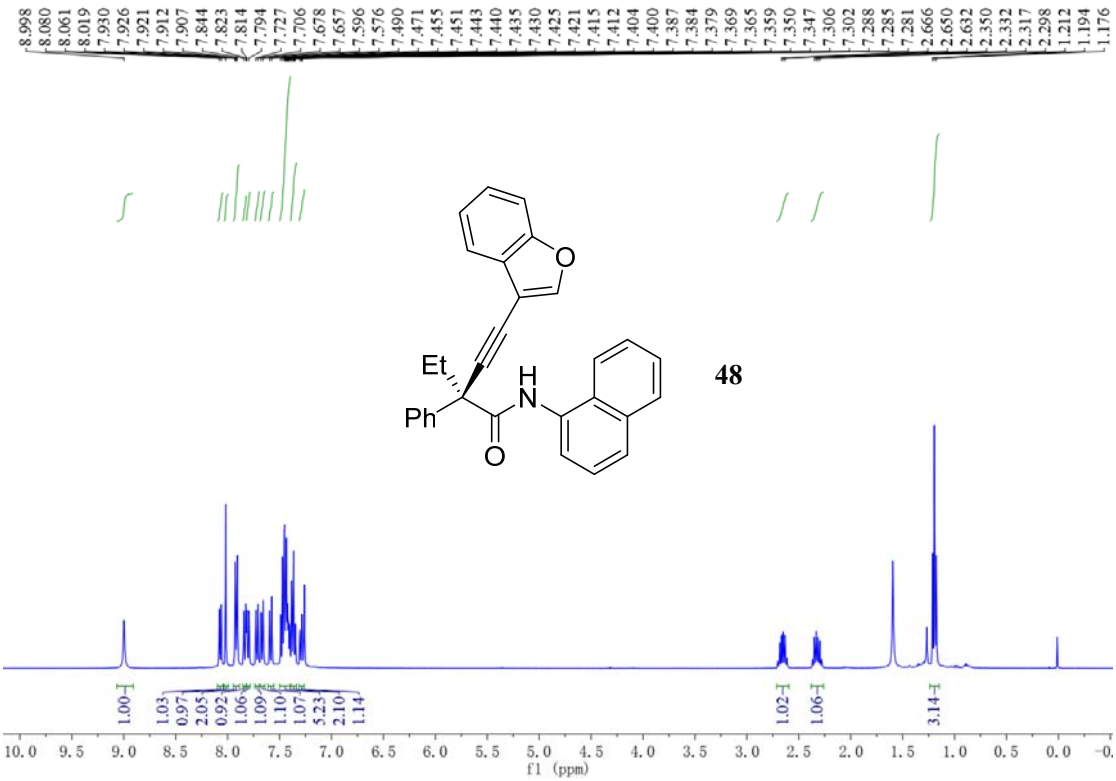
139.042
138.901
133.939
132.089
130.933
128.762
128.715
127.808
126.690
126.647
126.273
125.854
125.735
125.487
125.318
125.086
122.846
122.748
119.986
119.564
117.181
91.772
83.854
55.856
33.207
10.351
S
Et
Ph
H
N
O
47
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.019
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7.926
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7.907
7.844
7.823
7.814
7.794
7.727
7.706
7.678
7.657
7.596
7.576
7.490
7.471
7.455
7.451
7.443
7.440
7.435
7.430
7.425
7.421
7.415
7.412
7.404
7.400
7.387
7.384
7.379
7.369
7.365
7.359
7.350
7.347
7.306
7.302
7.288
7.285
7.281
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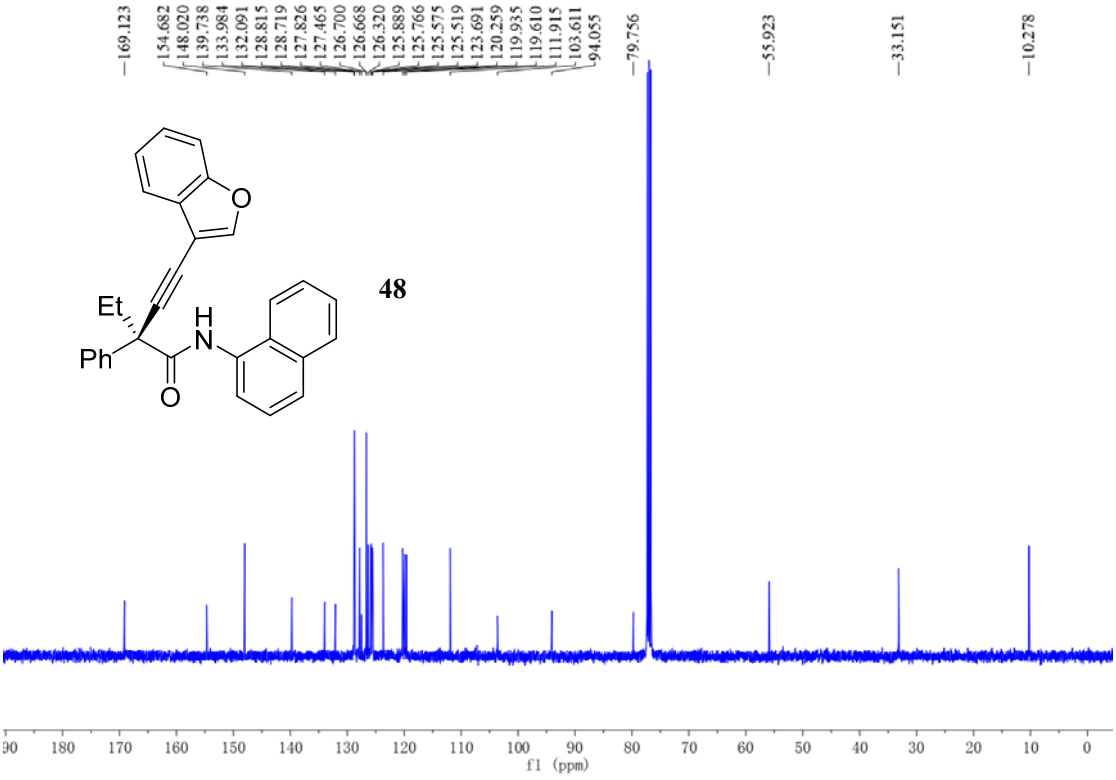
2.650
2.632
2.350
2.332
2.317
2.298
1.212
1.194
1.176
O
Et
H
N
Ph
O
48
1.00
1.03
0.97
2.05
0.92
1.06
1.09
1.10
1.07
5.23
2.10
1.14
1.02
1.06
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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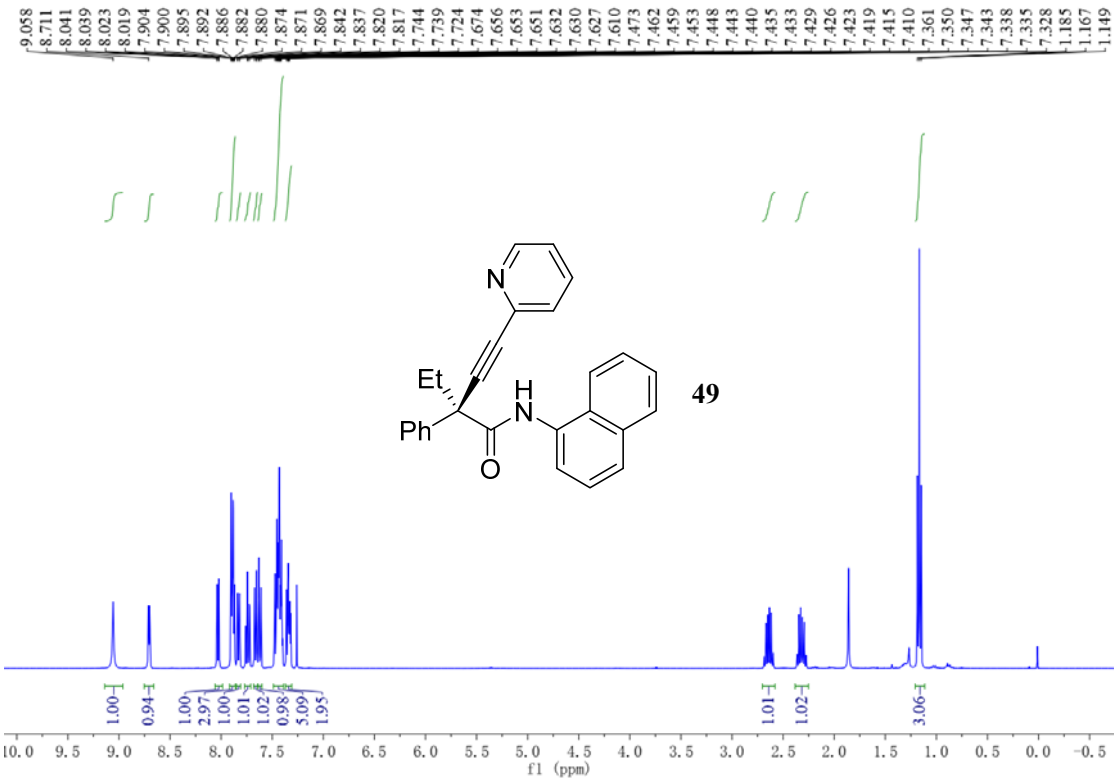
148.020
139.738
133.984
132.091
128.815
128.719
127.826
127.465
126.700
126.668
126.320
125.889
125.766
125.575
125.519
123.691
120.259
119.935
119.610
111.915
103.611
94.055
79.756
55.923
33.151
10.278
O
Et
H
N
Ph
O
48
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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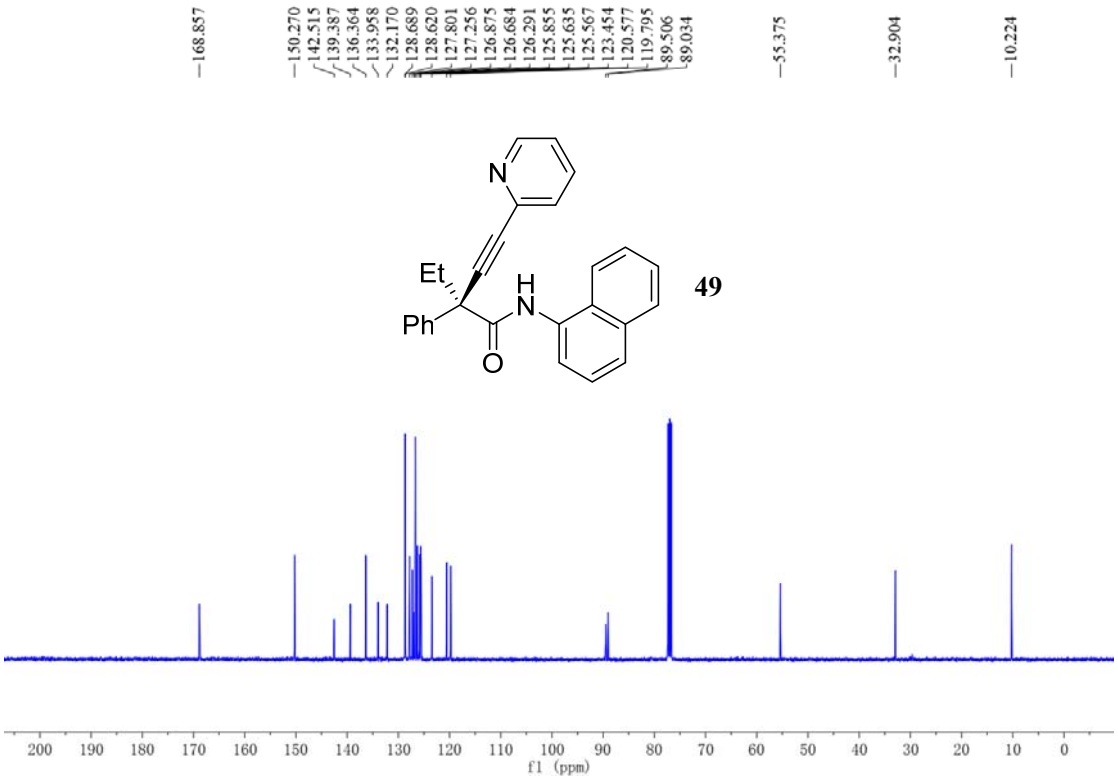
8.711
8.041
8.039
8.023
8.019
7.904
7.900
7.895
7.892
7.886
7.882
7.880
7.874
7.871
7.869
7.842
7.837
7.820
7.817
7.744
7.739
7.724
7.674
7.656
7.653
7.651
7.632
7.630
7.627
7.610
7.473
7.462
7.459
7.453
7.448
7.443
7.440
7.435
7.433
7.429
7.426
7.423
7.419
7.415
7.410
7.361
7.350
7.347
7.343
7.338
7.335
7.328
1.185
1.167
1.149
N
Et
H
N
Ph
O
49
1.00
0.94
1.00
2.97
1.00
1.01
1.02
0.98
5.09
1.95
1.01
1.02
3.06
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 -0.5
f1 (ppm)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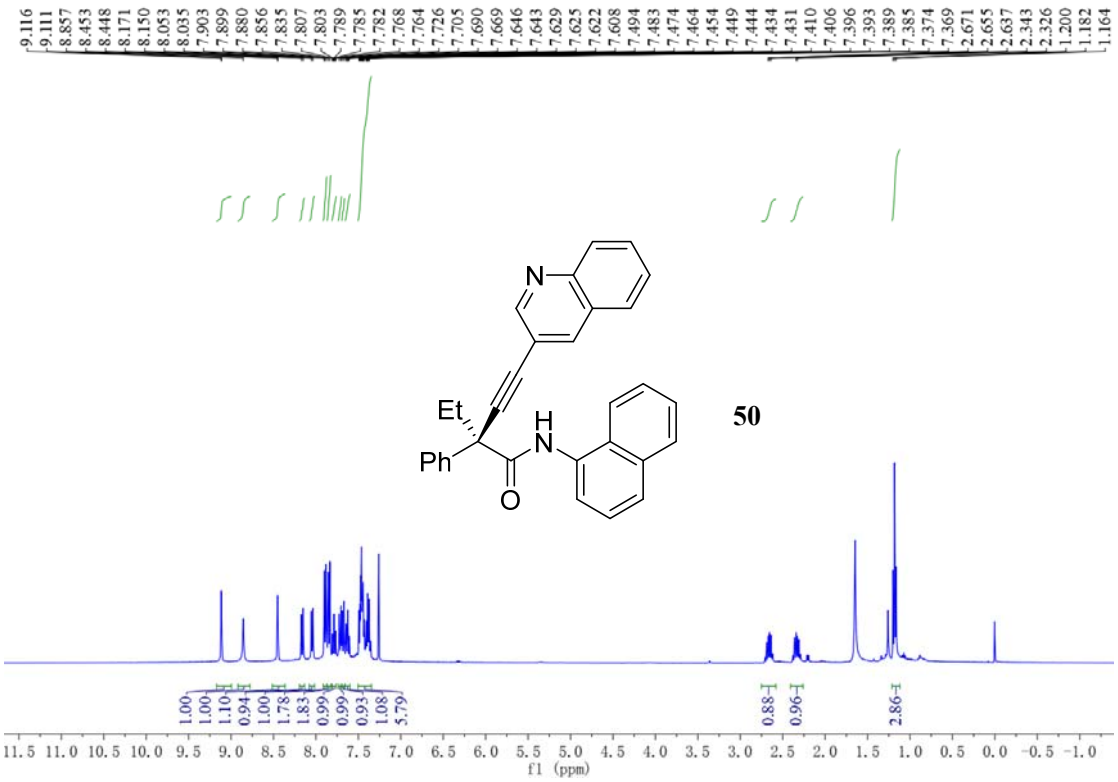
142.515
139.387
136.364
133.958
132.170
128.689
128.620
127.801
127.256
126.875
126.684
126.291
125.855
125.635
125.567
123.454
120.577
119.795
89.506
89.034
55.375
32.904
10.224
N
Et
H
N
Ph
O
49
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.857
8.453
8.448
8.171
8.150
8.053
8.035
7.903
7.899
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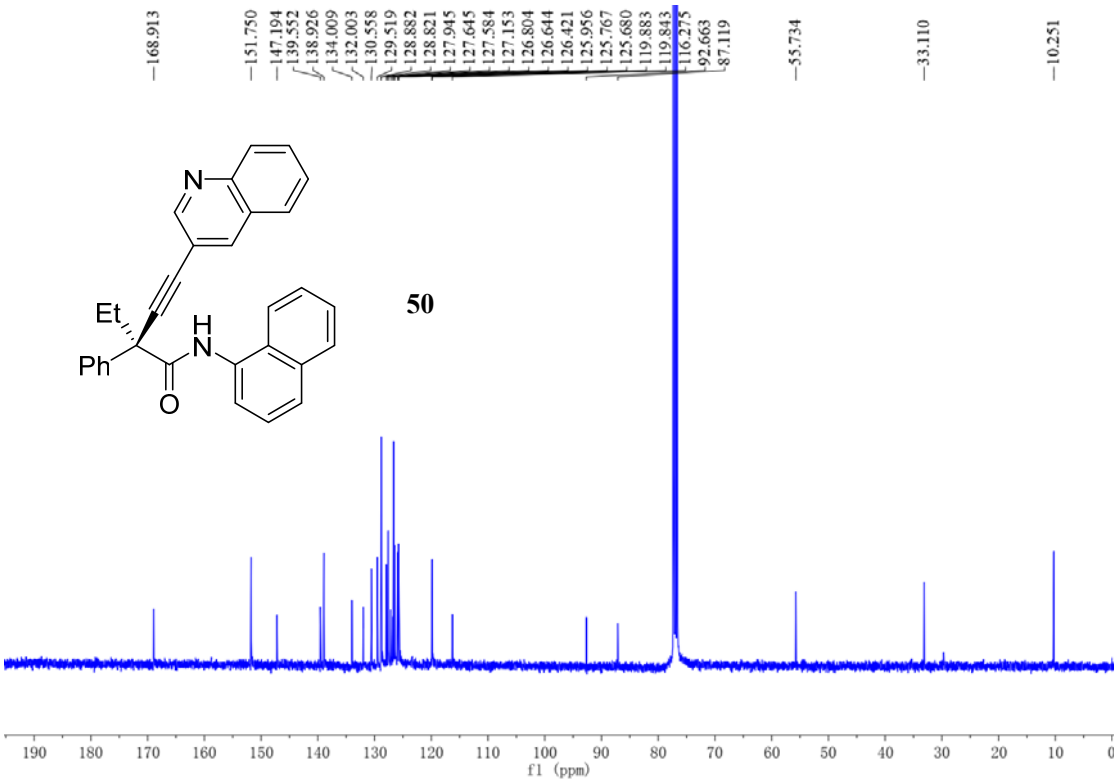
7.856
7.835
7.807
7.803
7.789
7.785
7.782
7.768
7.764
7.726
7.705
7.690
7.669
7.646
7.643
7.629
7.625
7.622
7.608
7.494
7.483
7.474
7.464
7.454
7.449
7.444
7.434
7.431
7.410
7.406
7.396
7.393
7.389
7.385
7.374
7.369
2.671
2.655
2.637
2.343
2.326
1.200
1.182
1.164
N
Et
Ph
H
N
O
50
1.00
1.00
1.10
0.94
1.00
1.78
1.83
0.99
0.99
0.93
1.08
3.79
0.88
0.96
2.86
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)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147.194
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138.926
134.009
132.003
130.558
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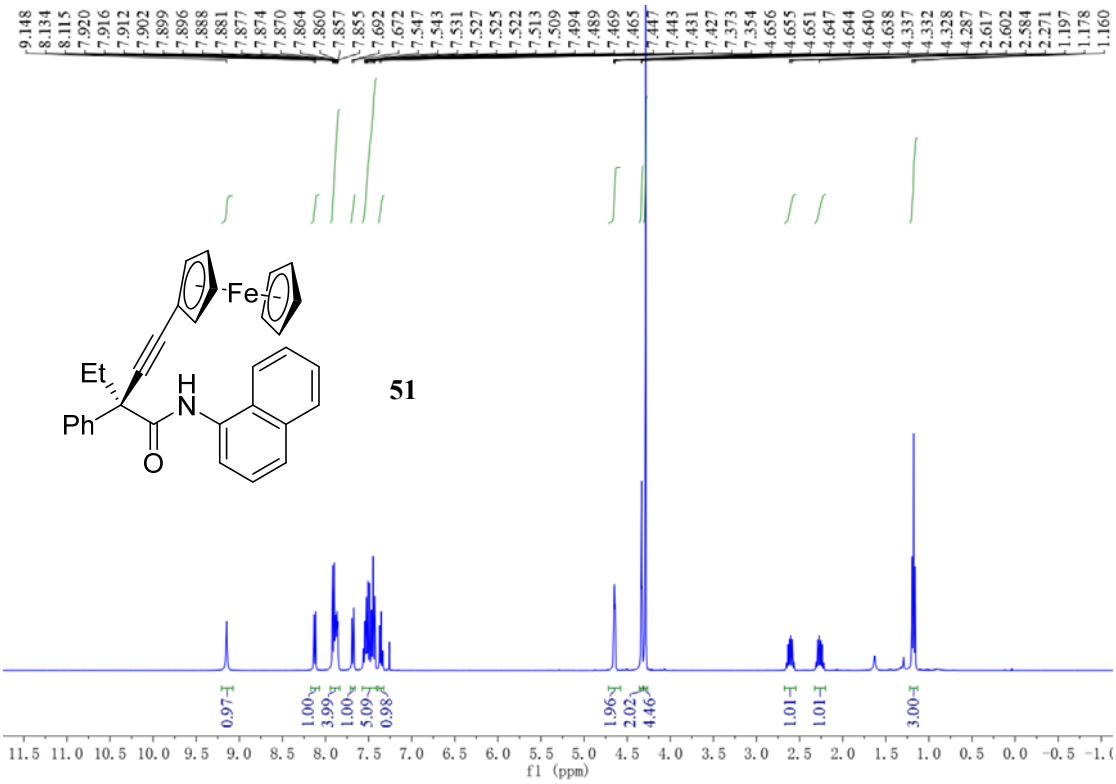
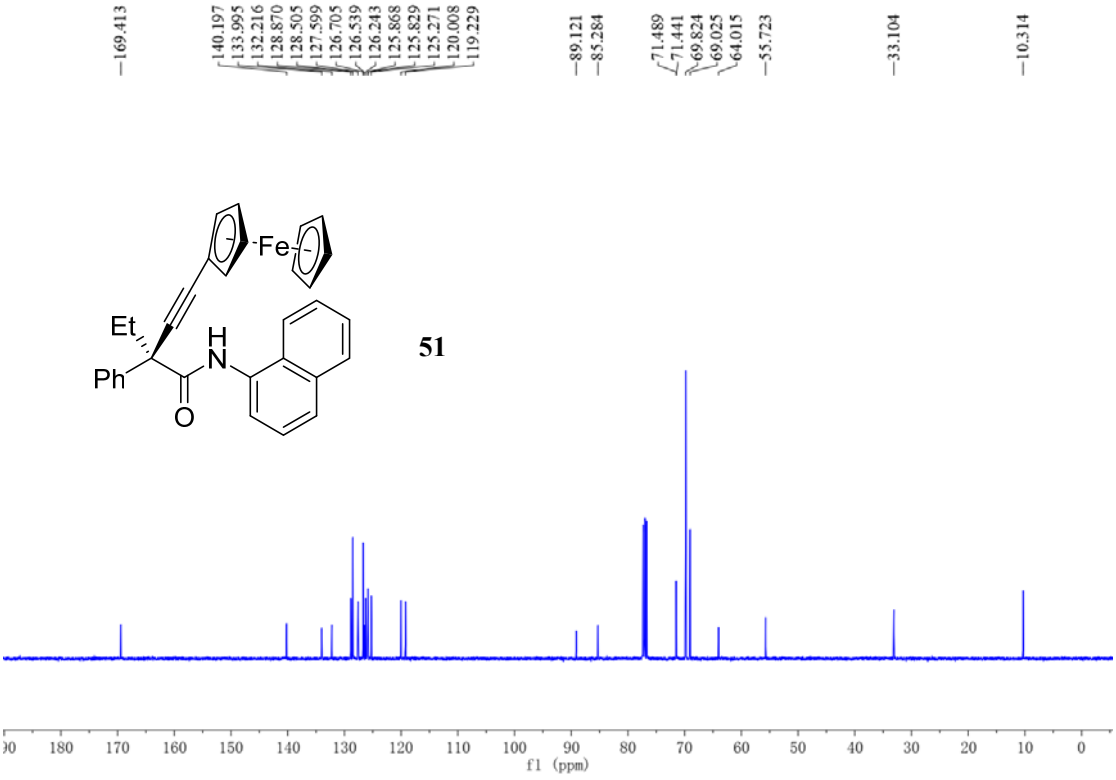
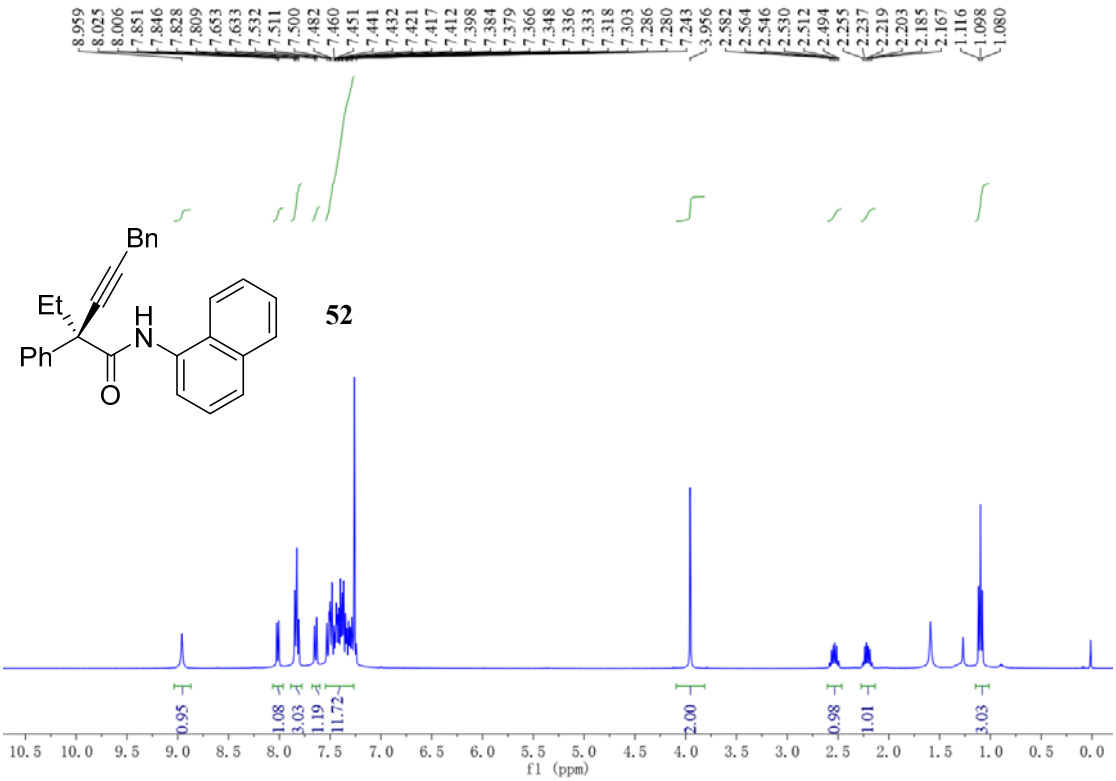
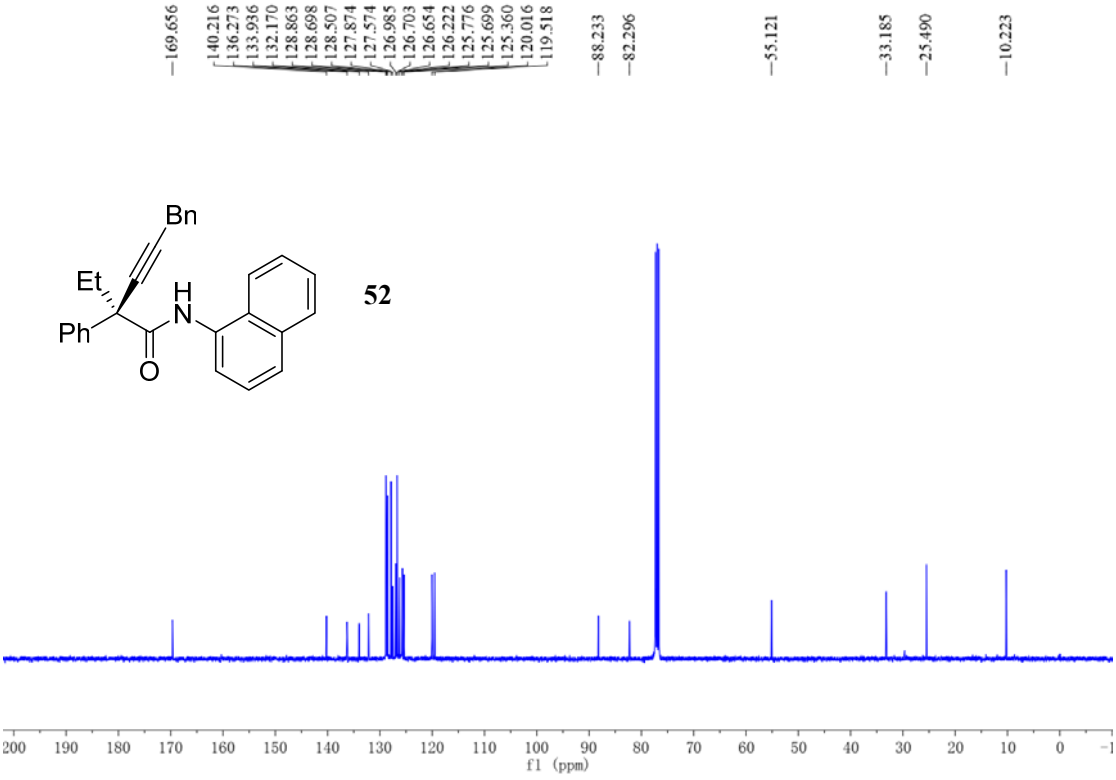
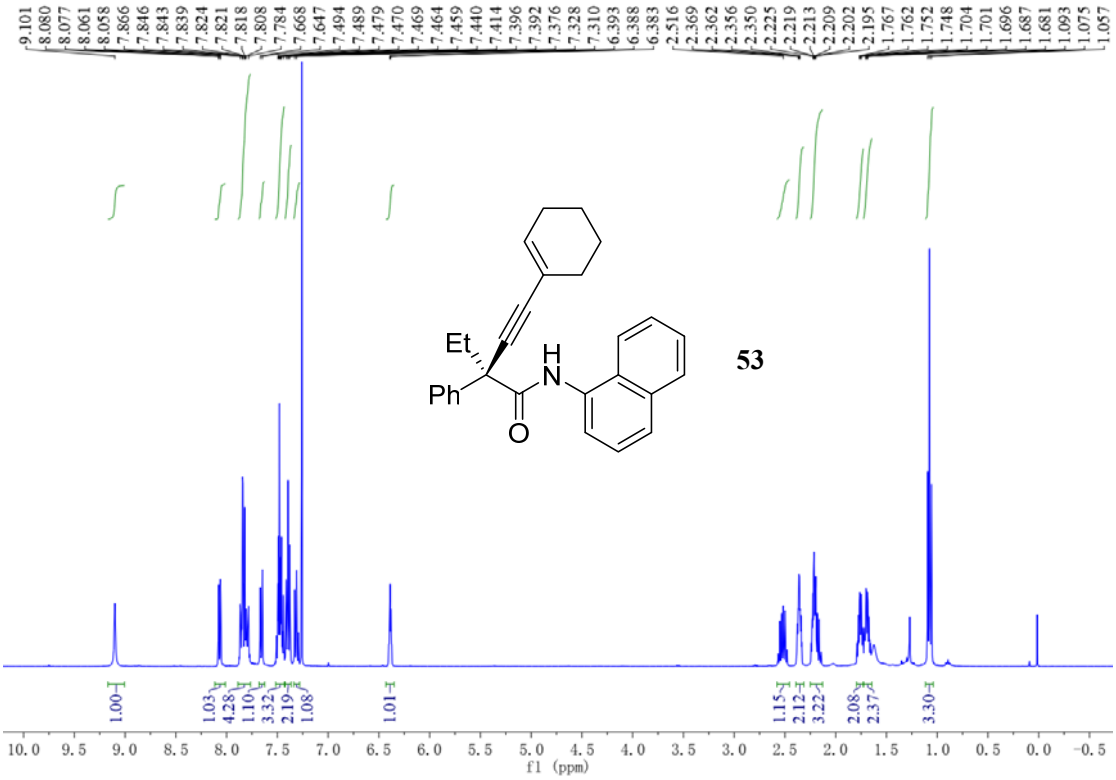
128.821
127.945
127.645
127.584
127.153
126.804
126.644
126.421
125.956
125.767
125.680
119.883
119.843
116.275
92.663
87.119
55.734
33.110
10.251
N
Et
Ph
H
N
O
50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

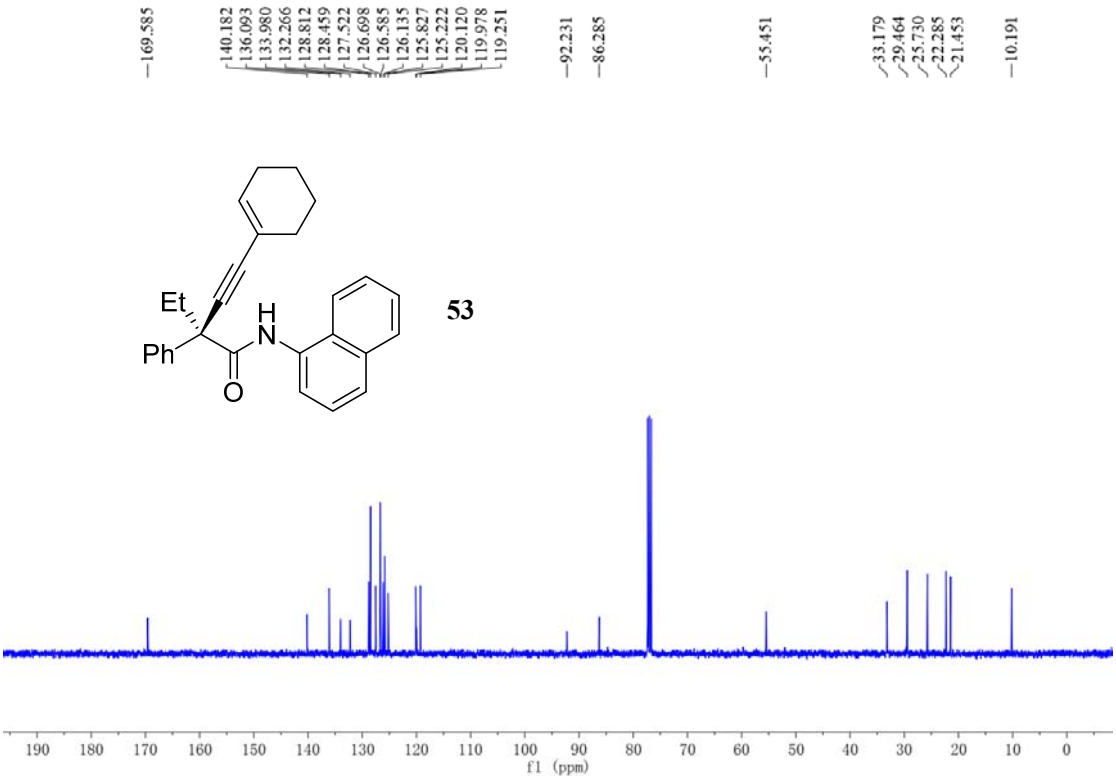

Fe
Et
Ph
H
N
O
51
f1 (ppm)

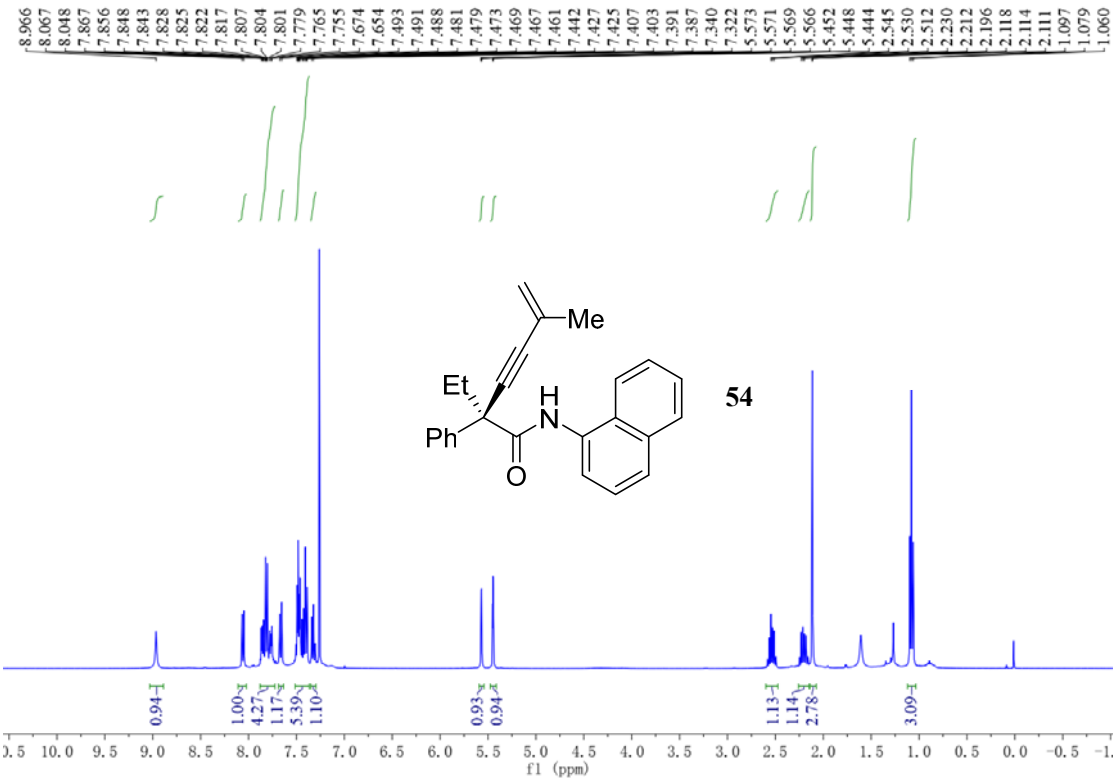

Fe
Et
Ph
H
N
O
51
f1 (ppm)

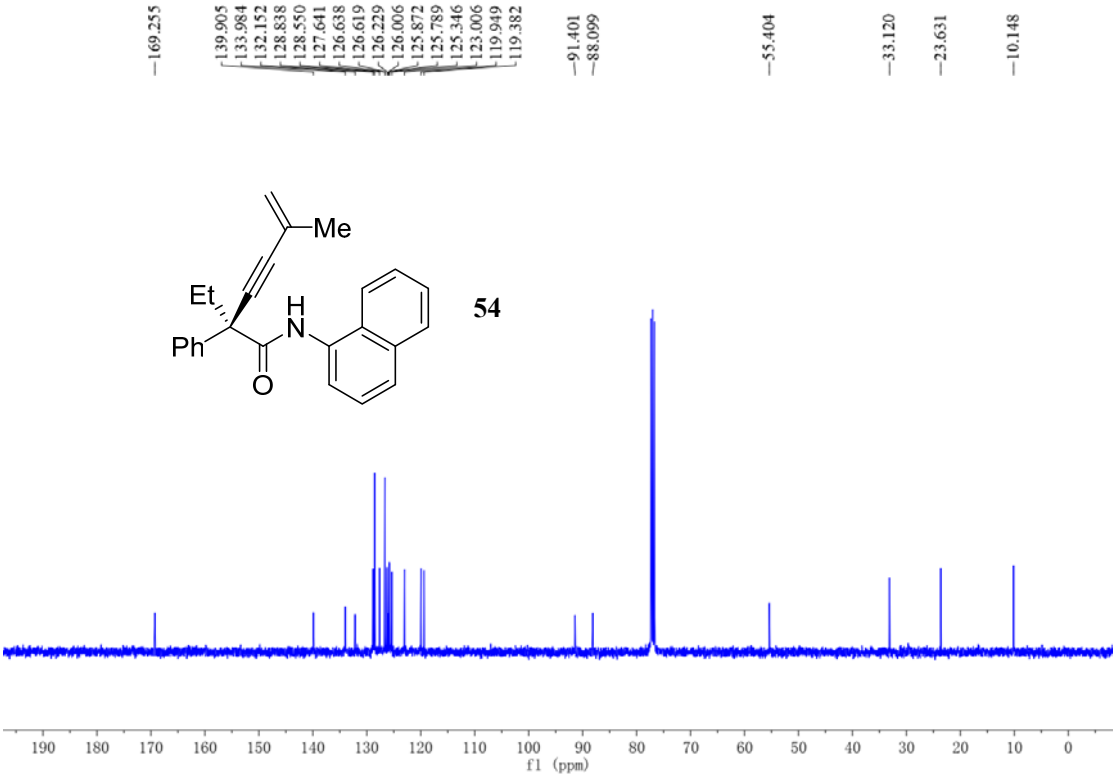

Bn
Et
Ph
H
N
O
52
f1 (ppm)

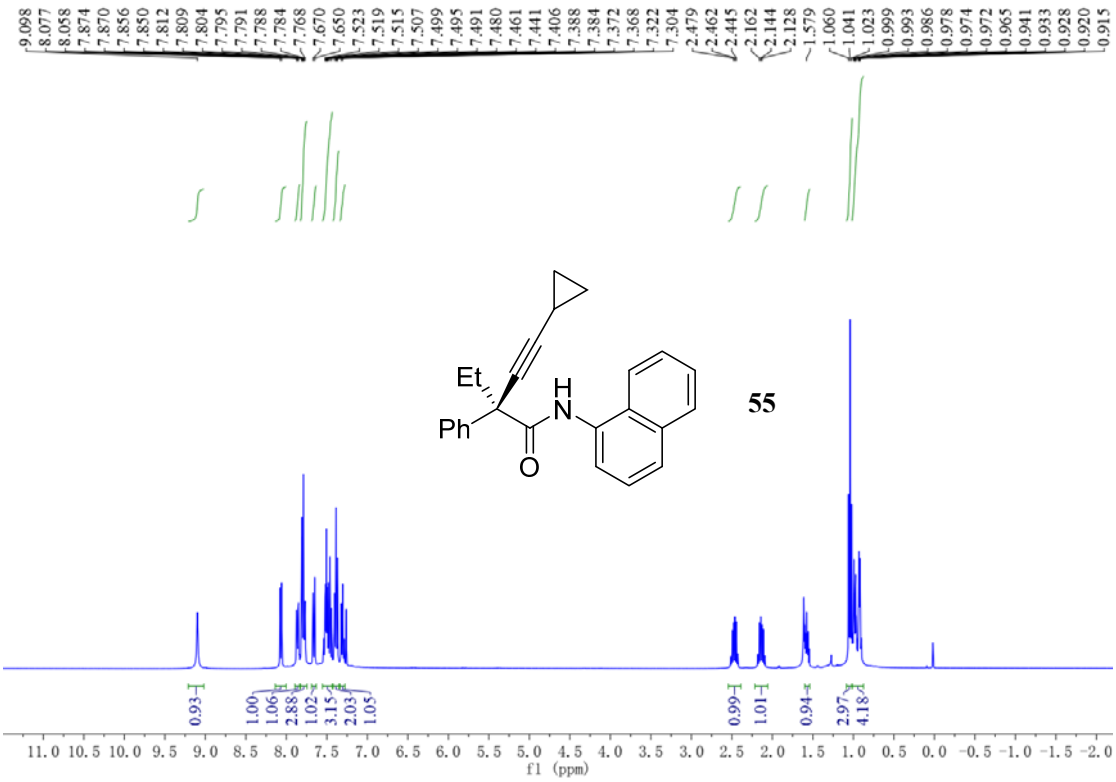

Bn
Et
Ph
H
N
O
52
f1 (ppm)


Et
Ph
H
N
O
53
f1 (ppm)


Et
Ph
H
N
O
53
f1 (ppm)


Me
Et
Ph
H
N
O
54
f1 (ppm)


Me
Et
Ph
H
N
O
54
f1 (ppm)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7.812
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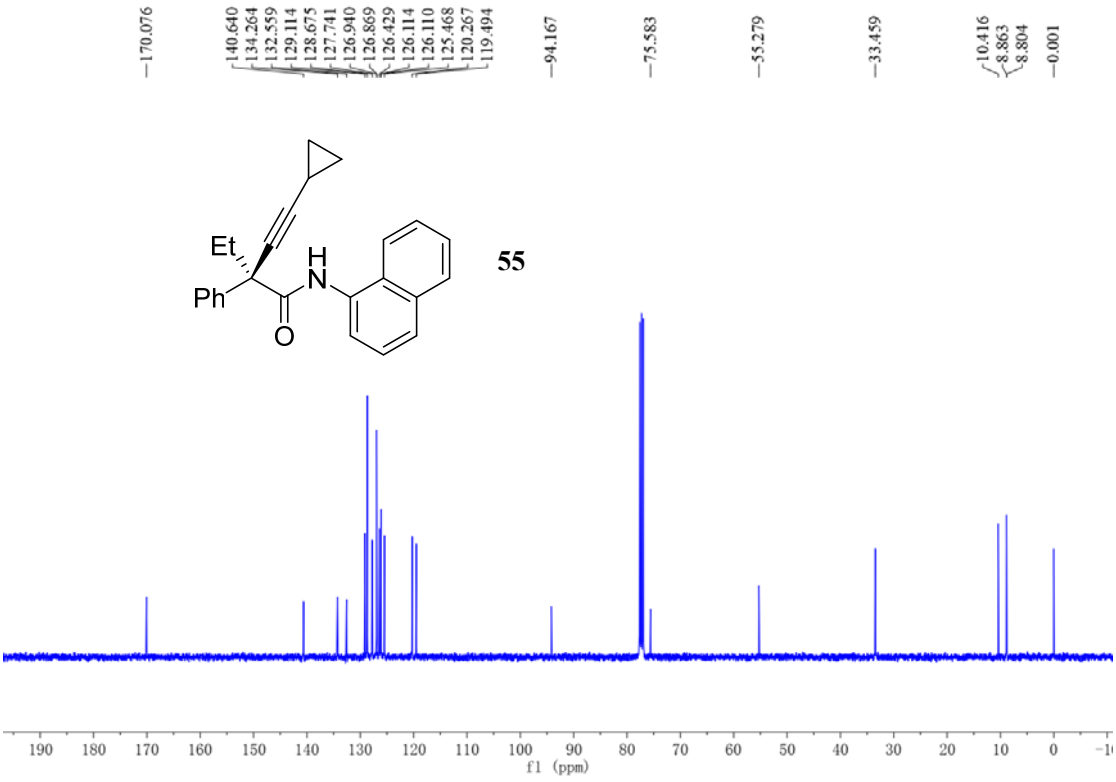
7.804
7.795
7.791
7.788
7.784
7.768
7.670
7.650
7.523
7.519
7.515
7.507
7.499
7.495
7.491
7.480
7.461
7.441
7.406
7.388
7.384
7.372
7.368
7.322
7.304
2.479
2.462
2.445
2.162
2.144
2.128
1.579
1.060
1.041
1.023
0.999
0.993
0.986
0.978
0.974
0.972
0.965
0.941
0.933
0.928
0.920
0.915
Et
Ph
H
N
O
55
0.93
1.00
1.06
2.88
1.02
3.15
2.03
1.05
0.99
1.01
0.94
2.97
4.18
f1 (ppm)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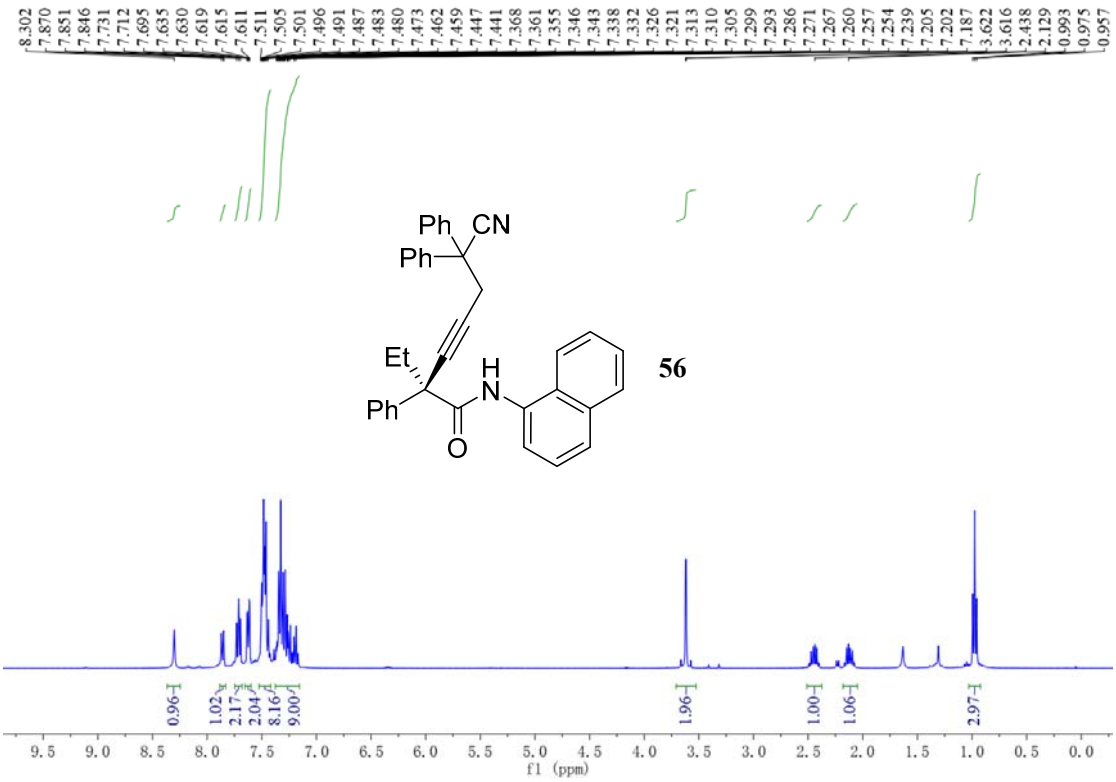
132.559
129.114
128.675
127.741
126.940
126.869
126.429
126.114
126.110
125.468
120.267
119.494
94.167
75.583
55.279
33.459
10.416
8.863
8.804
0.001
Et
Ph
H
N
O
55
f1 (ppm)


Ph
CN
Ph
Et
H
N
Ph
O
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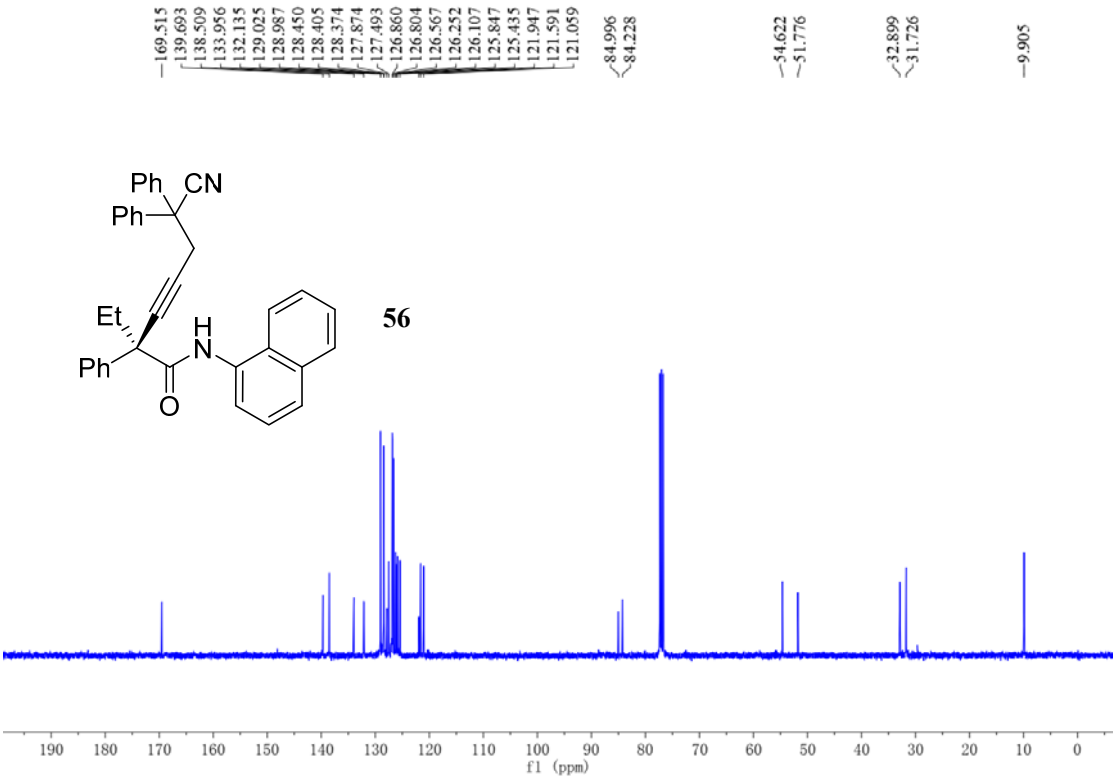
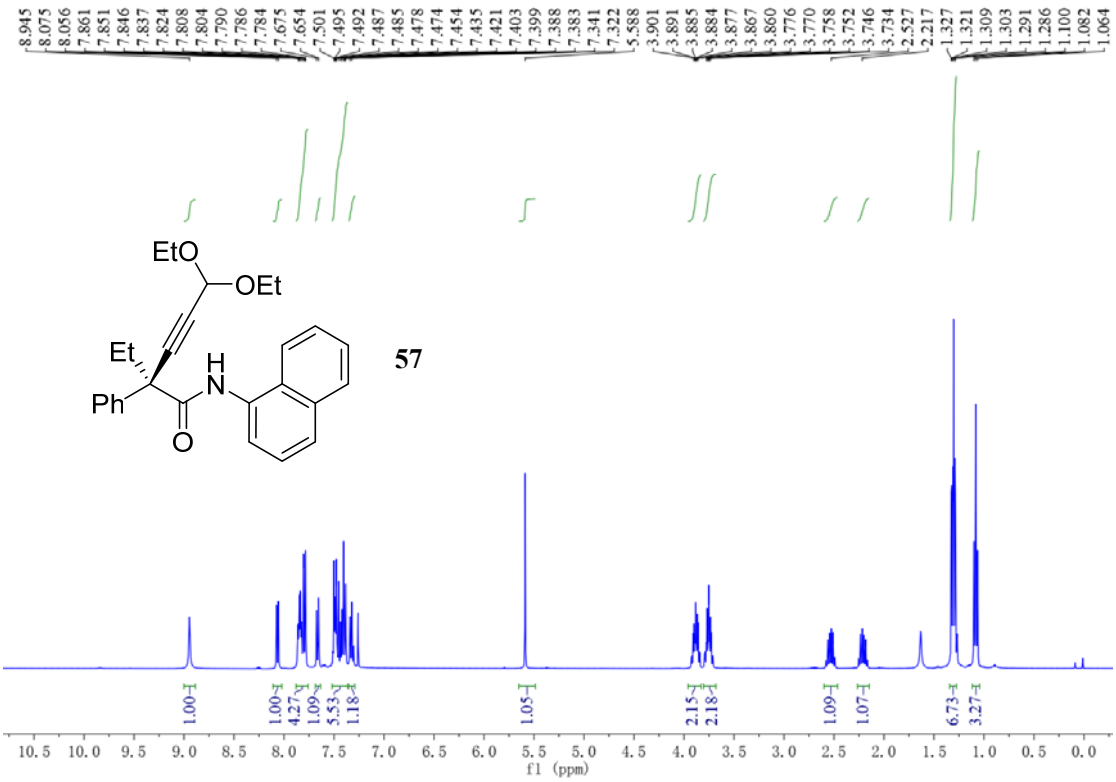
2.17
2.04
8.16
9.00
1.96
1.00
1.06
2.97
f1 (ppm)


Ph
CN
Ph
Et
H
N
Ph
O
56
f1 (ppm)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7.846
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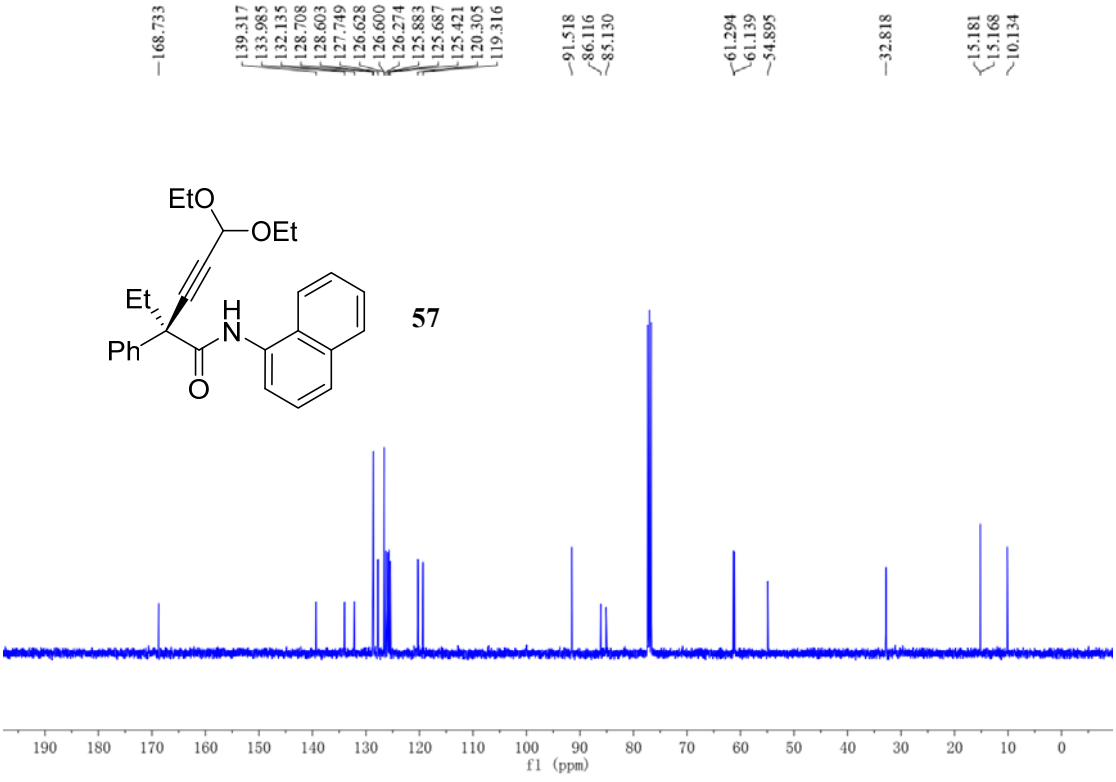
7.824
7.808
7.804
7.790
7.786
7.784
7.675
7.654
7.501
7.495
7.492
7.487
7.485
7.478
7.474
7.454
7.435
7.421
7.403
7.399
7.388
7.383
7.341
7.322
5.588
3.901
3.891
3.885
3.884
3.877
3.867
3.860
3.776
3.770
3.758
3.752
3.746
3.734
2.527
2.217
1.327
1.321
1.309
1.303
1.291
1.286
1.100
1.082
1.064
EtO
OEt
Et
Ph
H
N
O
57
1.00
1.00
4.27
1.09
5.53
1.18
1.05
2.15
2.18
1.09
1.07
6.73
3.27
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)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132.135
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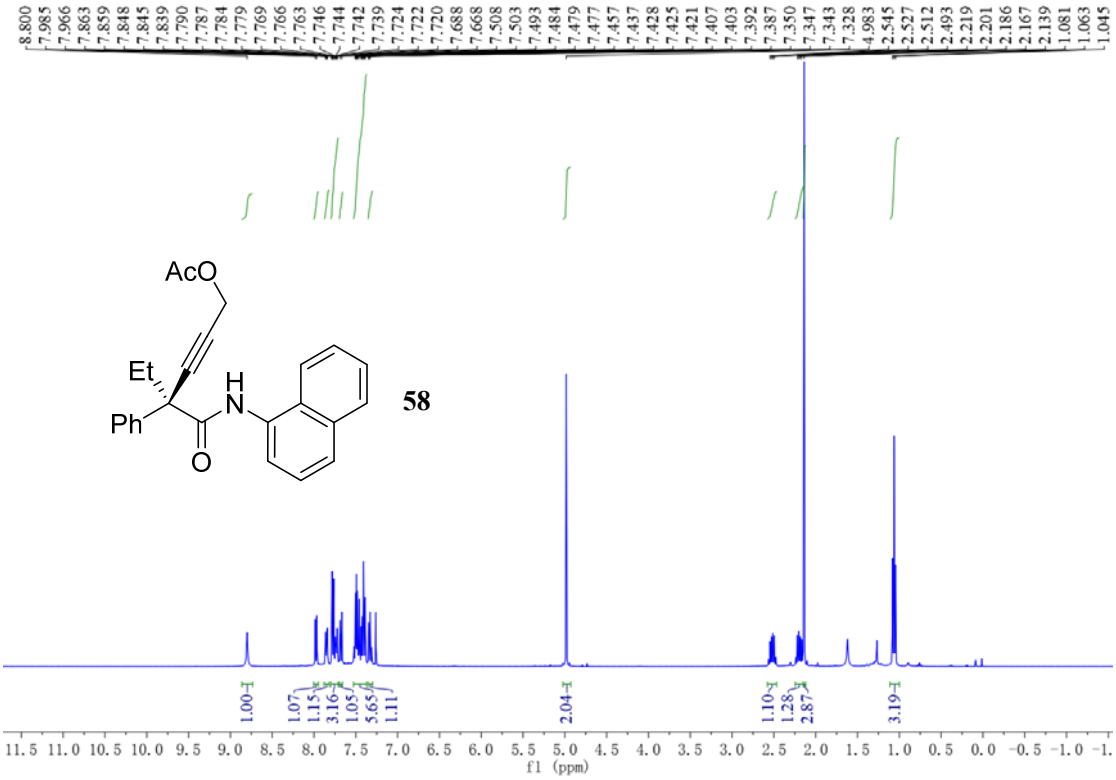
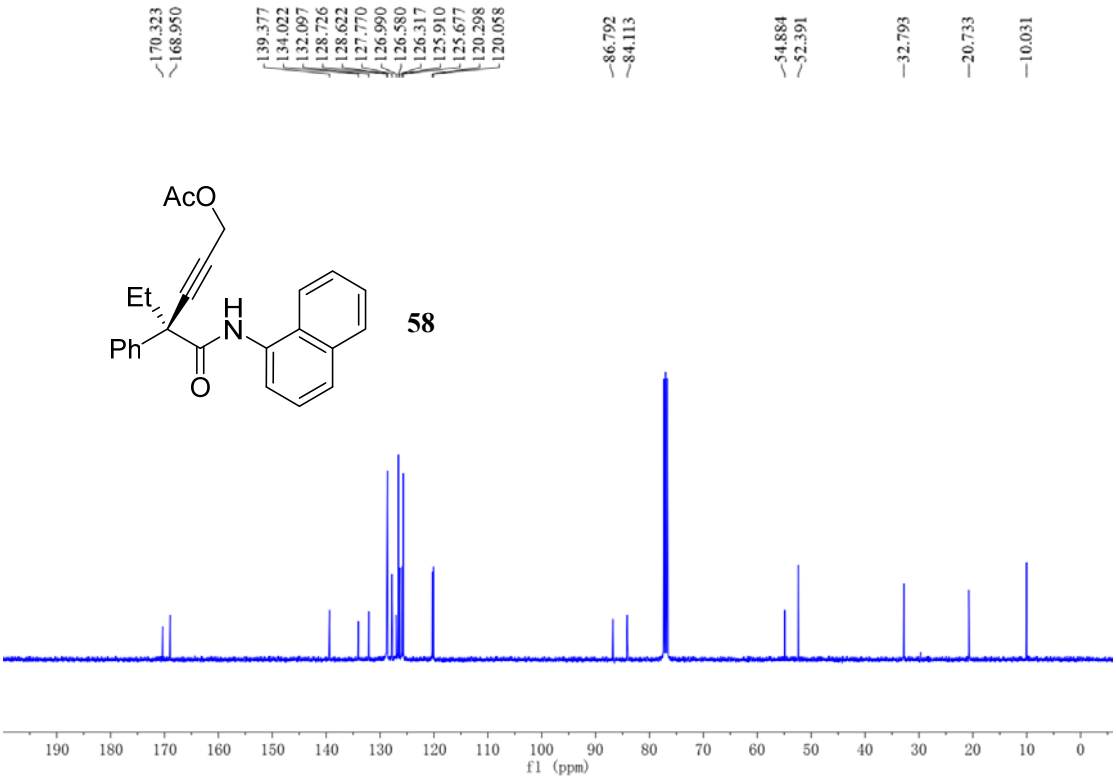
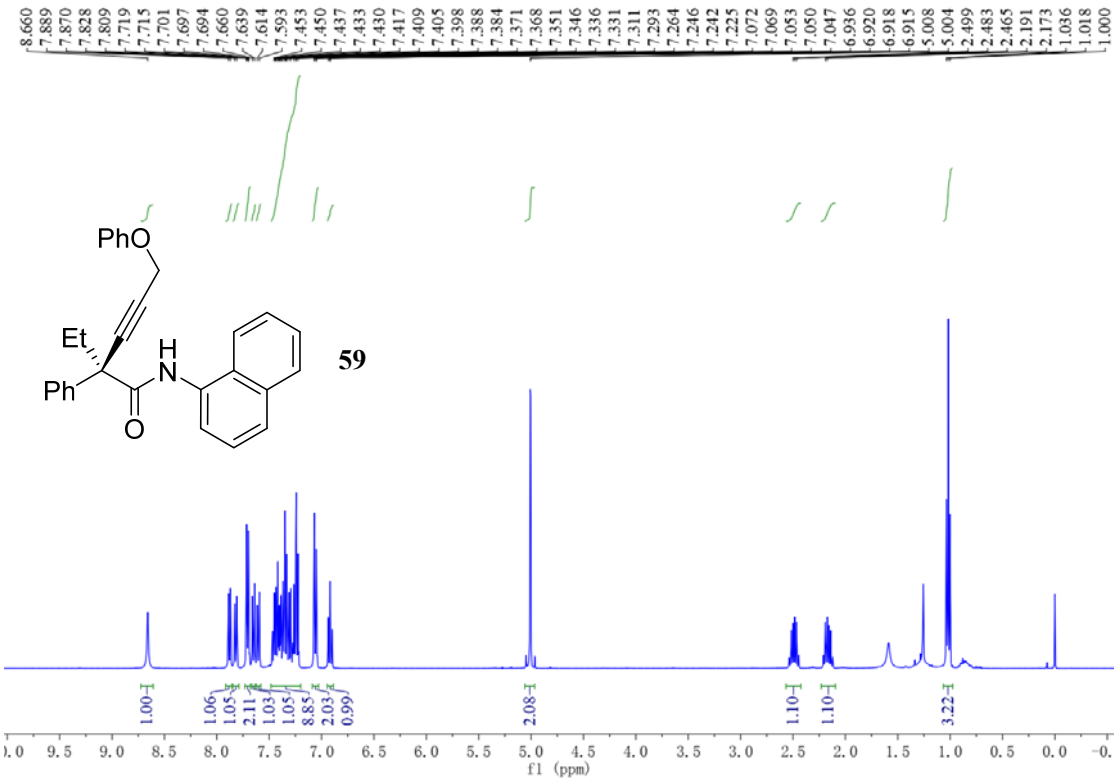
126.628
126.600
126.274
125.883
125.687
125.421
120.305
119.316
91.518
86.116
85.130
61.294
61.139
54.895
32.818
15.181
15.168
10.134
EtO
OEt
Et
Ph
H
N
O
57
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


AcO
Et
Ph
H
N
O
58
f1 (ppm)


AcO
Et
Ph
H
N
O
58
f1 (ppm)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Et
Ph
H
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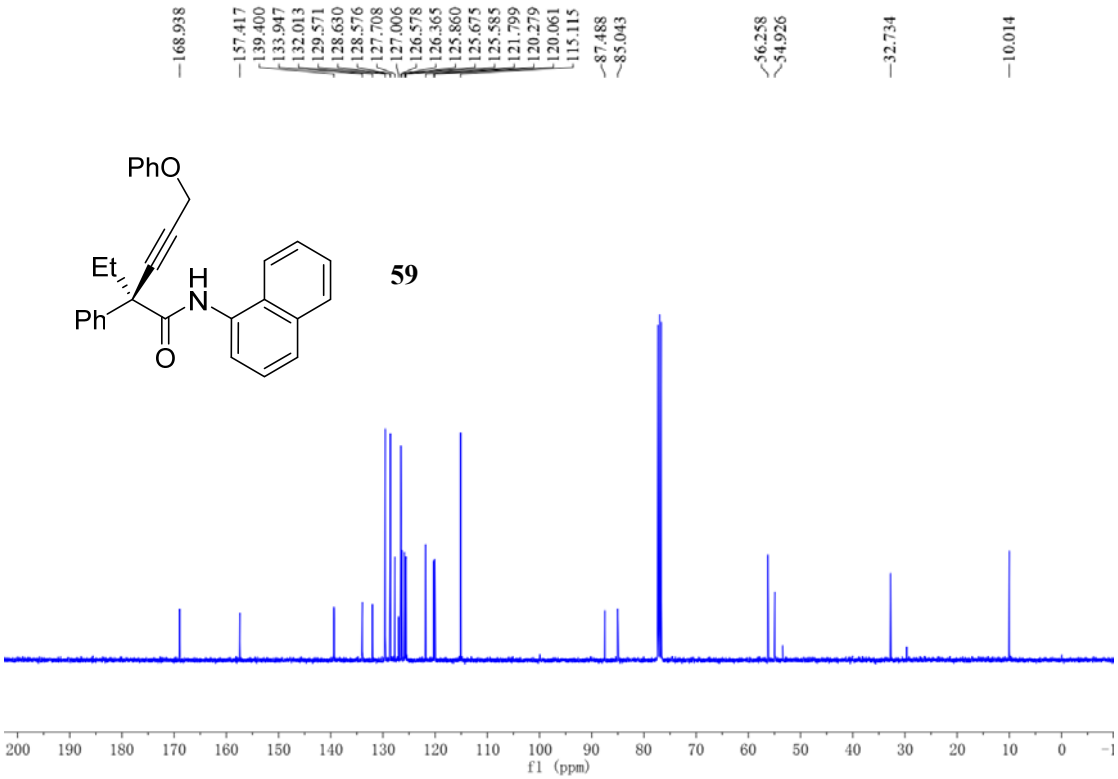
O
59
f1 (ppm)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Et
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H
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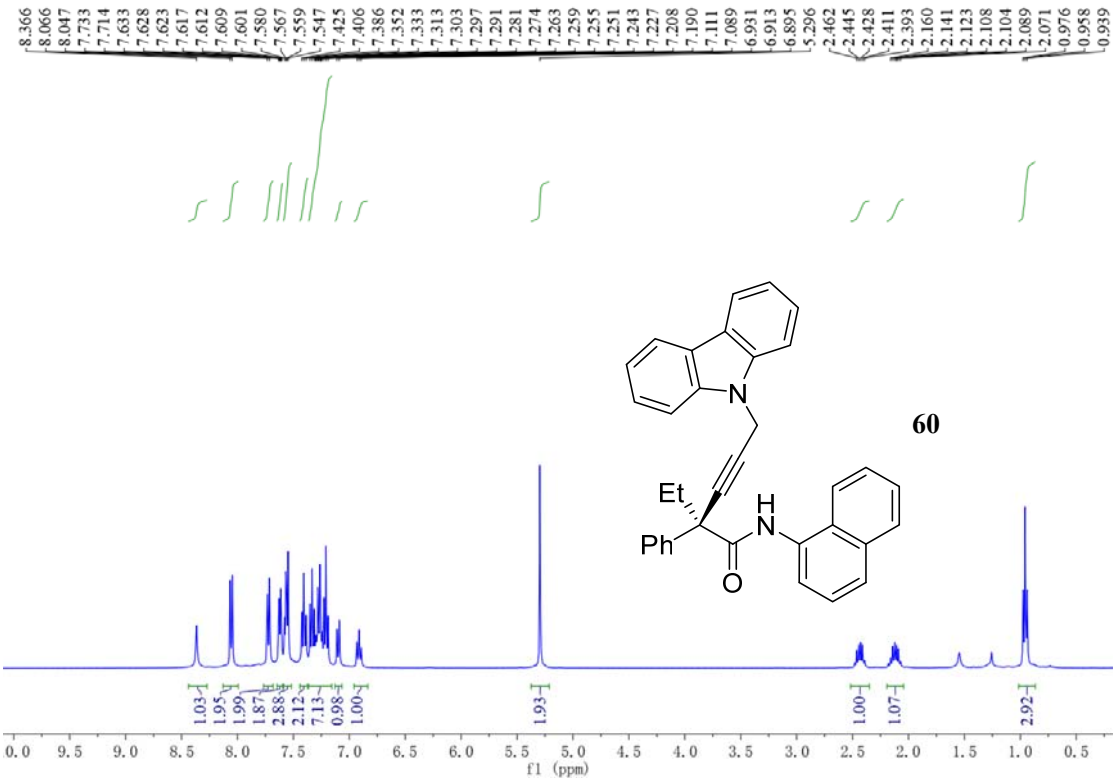
f1 (ppm)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7.303
7.297
7.291
7.281
7.274
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7.259
7.255
7.251
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7.208
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7.111
7.089
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6.913
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2.428
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2.160
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0.958
0.939
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Ph
H
N
O
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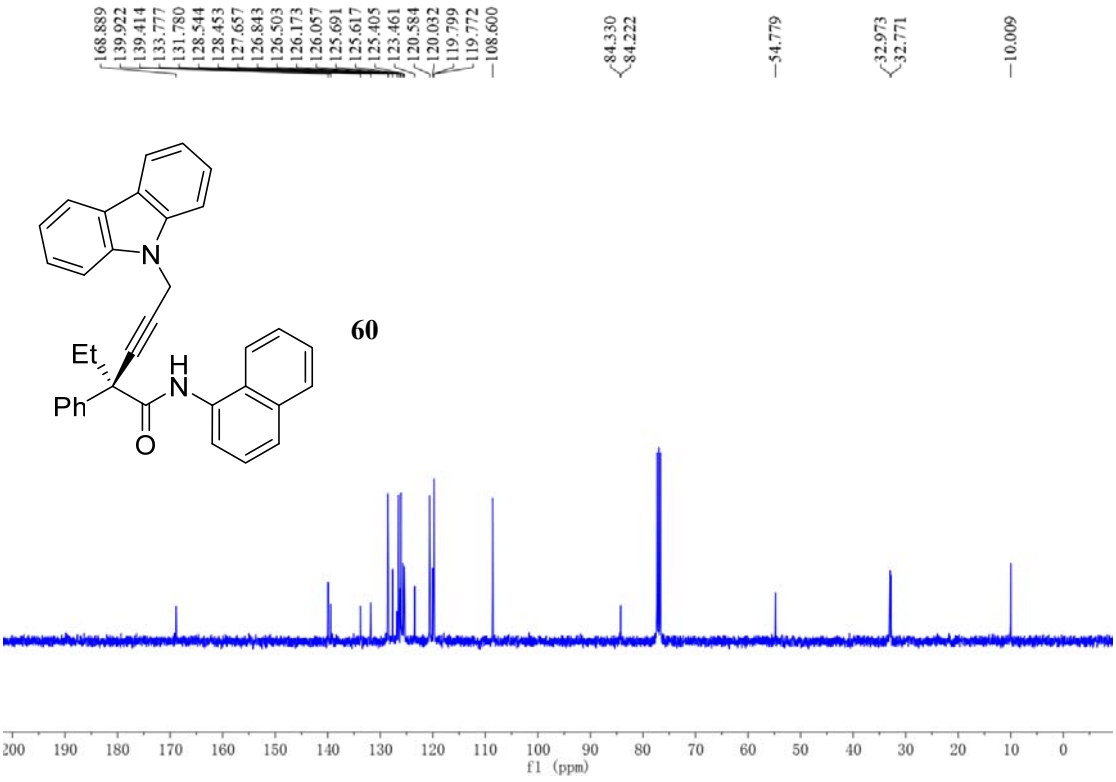
1.95
1.99
1.87
2.88
2.12
7.13
0.98
1.00
1.93
1.00
1.07
2.92
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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127.657
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126.503
126.173
126.057
125.691
125.617
125.405
123.461
120.584
120.032
119.799
119.772
108.600
84.330
84.222
54.779
32.973
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Et
Ph
H
N
O
60
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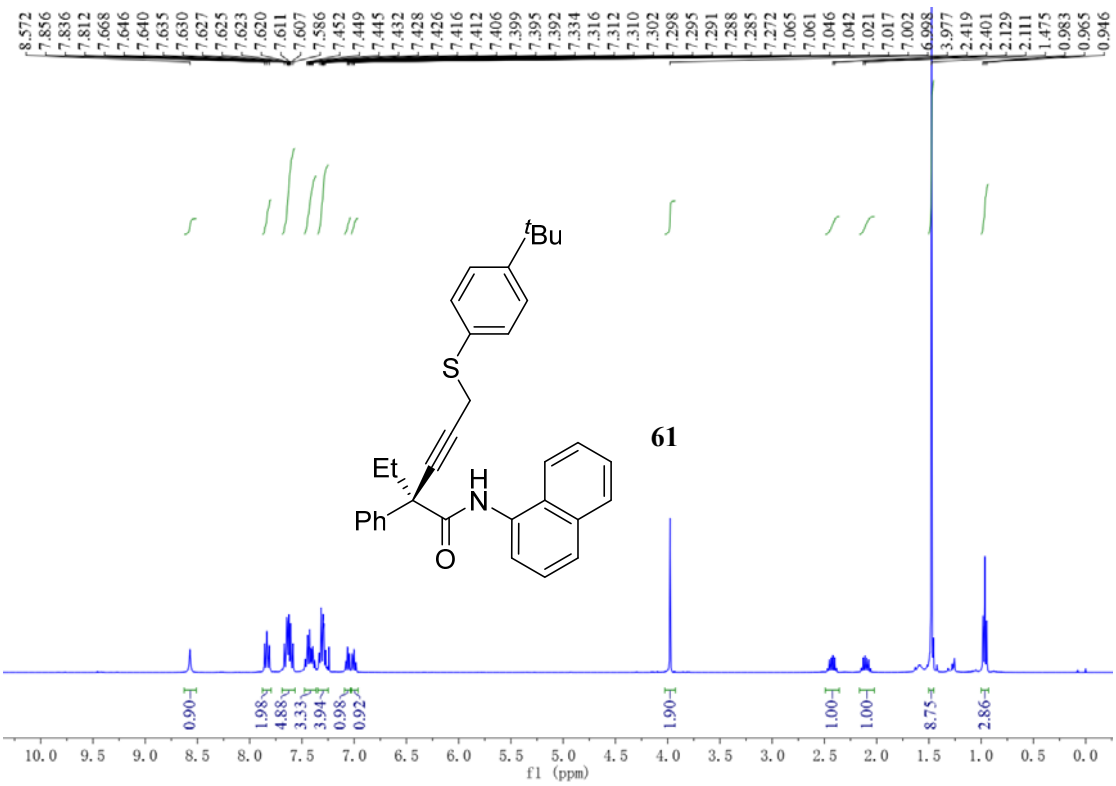
f1 (ppm)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7.611
7.607
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7.285
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7.017
7.002
6.998
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2.401
2.129
2.111
1.475
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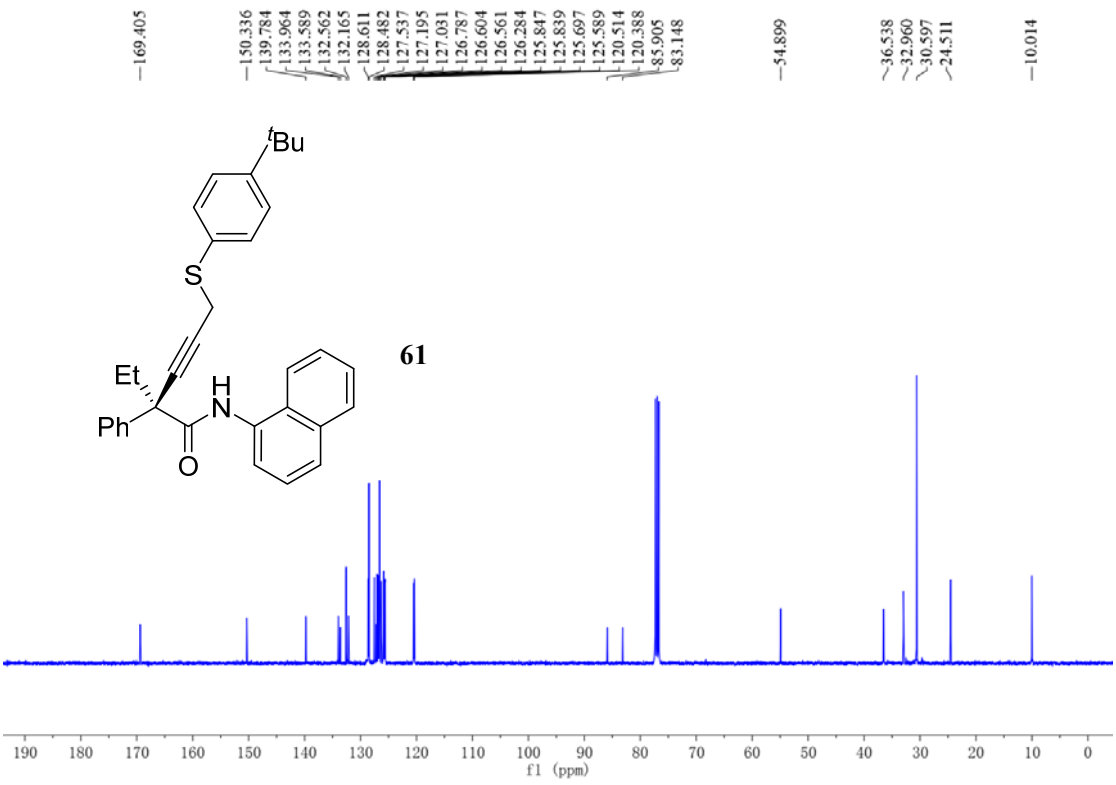
0.946
tBu
S
Et
Ph
H
N
O
61
0.90
1.98
4.88
3.33
3.94
0.98
0.92
1.90
1.00
1.00
8.75
2.86
f1 (ppm)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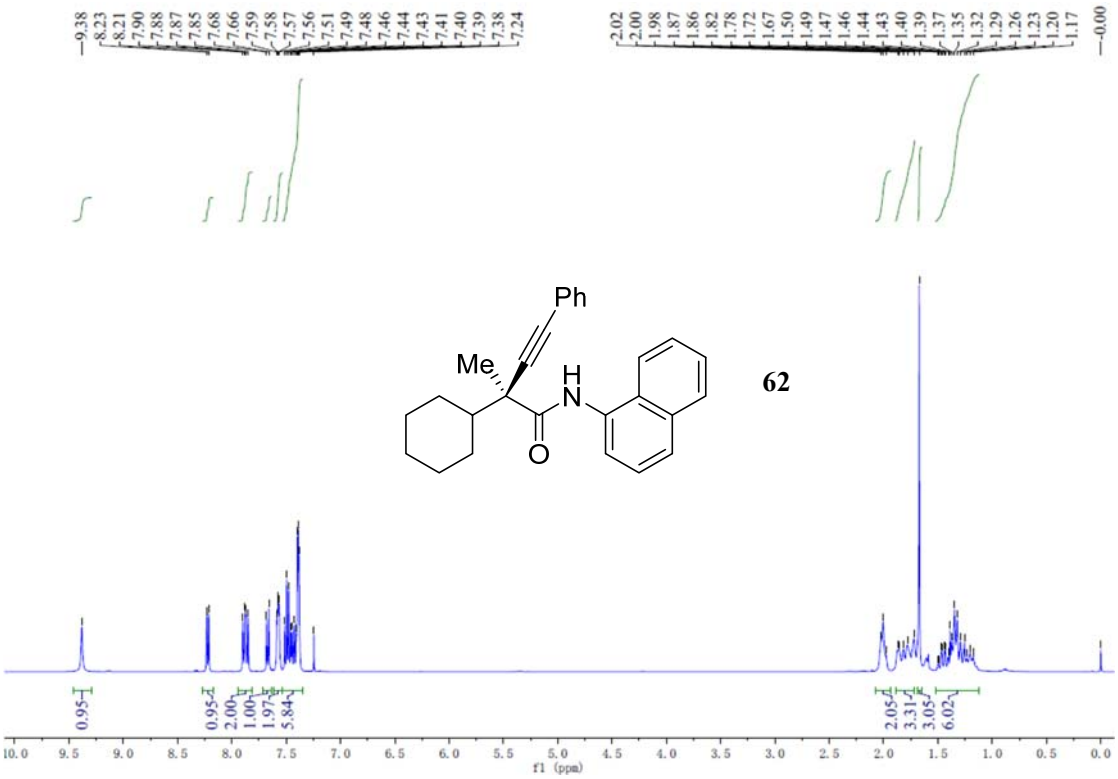
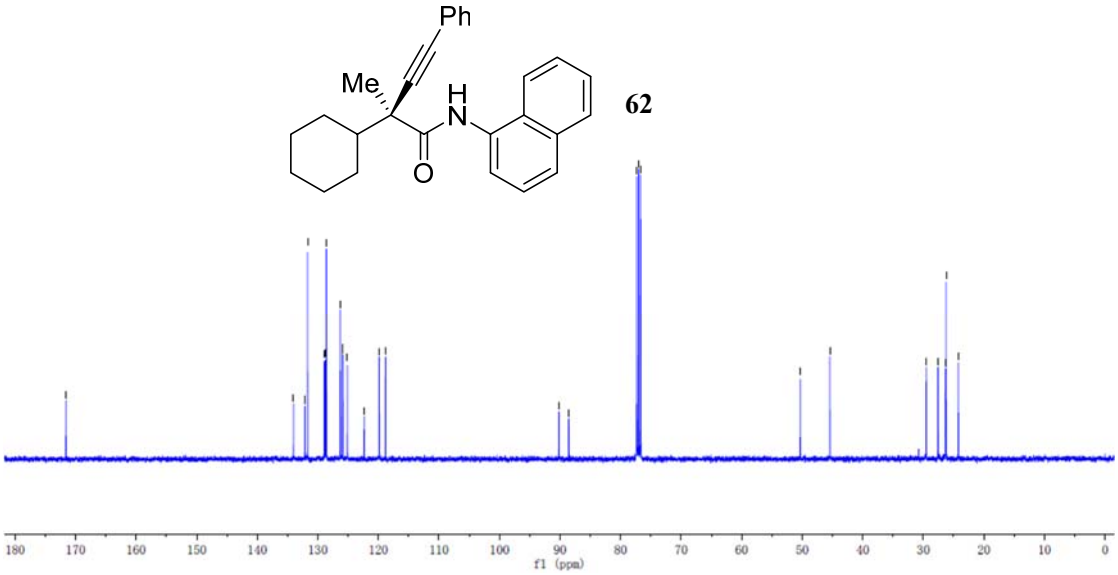
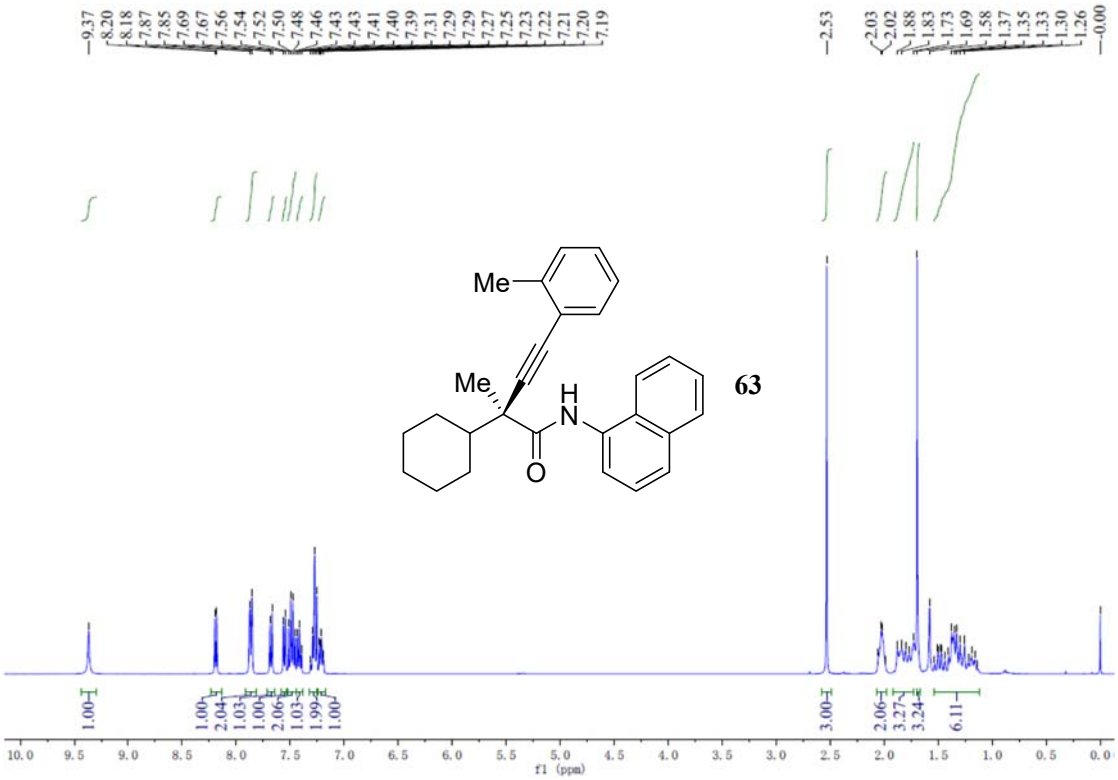
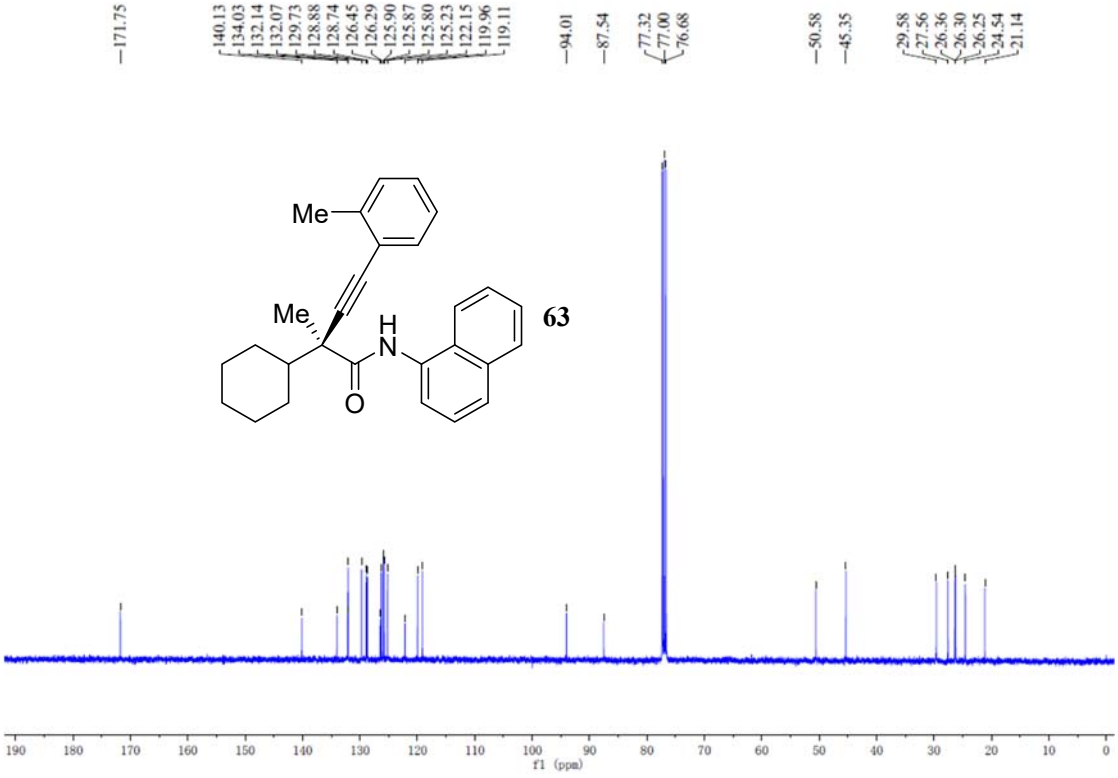
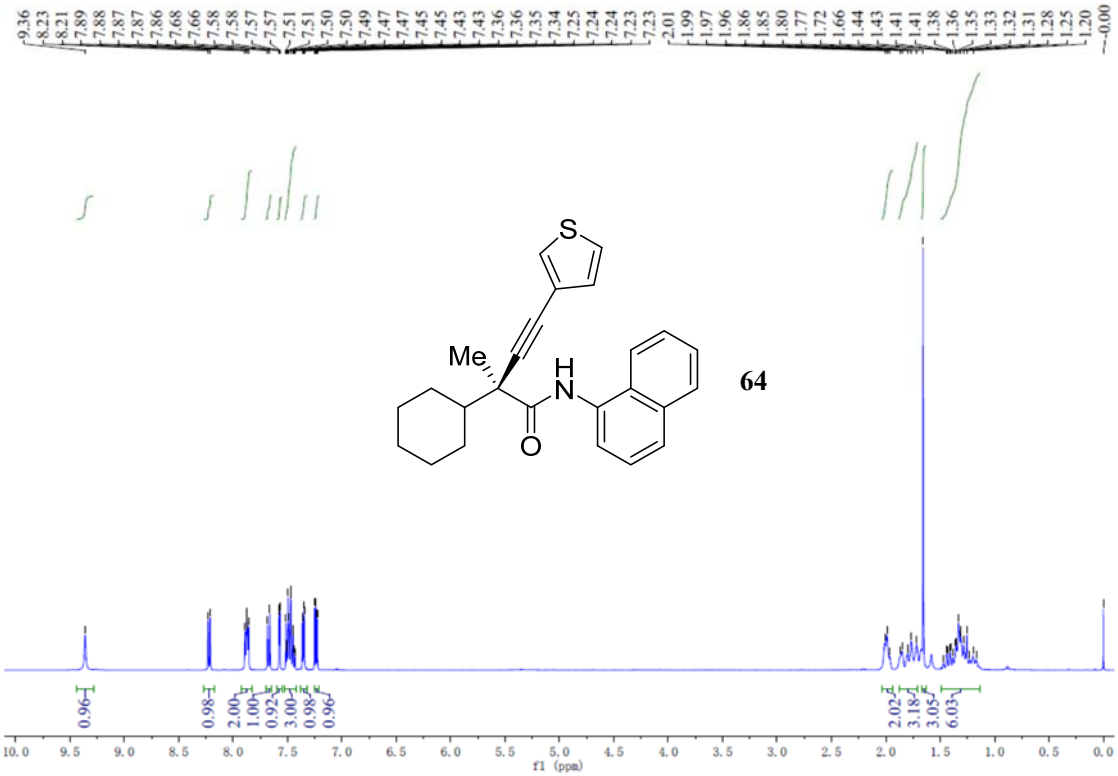
150.336
139.784
133.964
133.589
132.562
132.165
128.611
128.482
127.537
127.195
127.031
126.787
126.604
126.561
126.284
125.847
125.839
125.697
125.589
120.514
120.388
85.905
83.148
54.899
36.538
32.960
30.597
24.511
10.014
tBu
S
Et
Ph
H
N
O
61
f1 (ppm)


Ph
Me
H
N
O
62
f1 (ppm)


Ph
Me
H
N
O
62
f1 (ppm)


Me
Me
H
N
O
63


Me
Me
H
N
O
63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7.87
7.87
7.86
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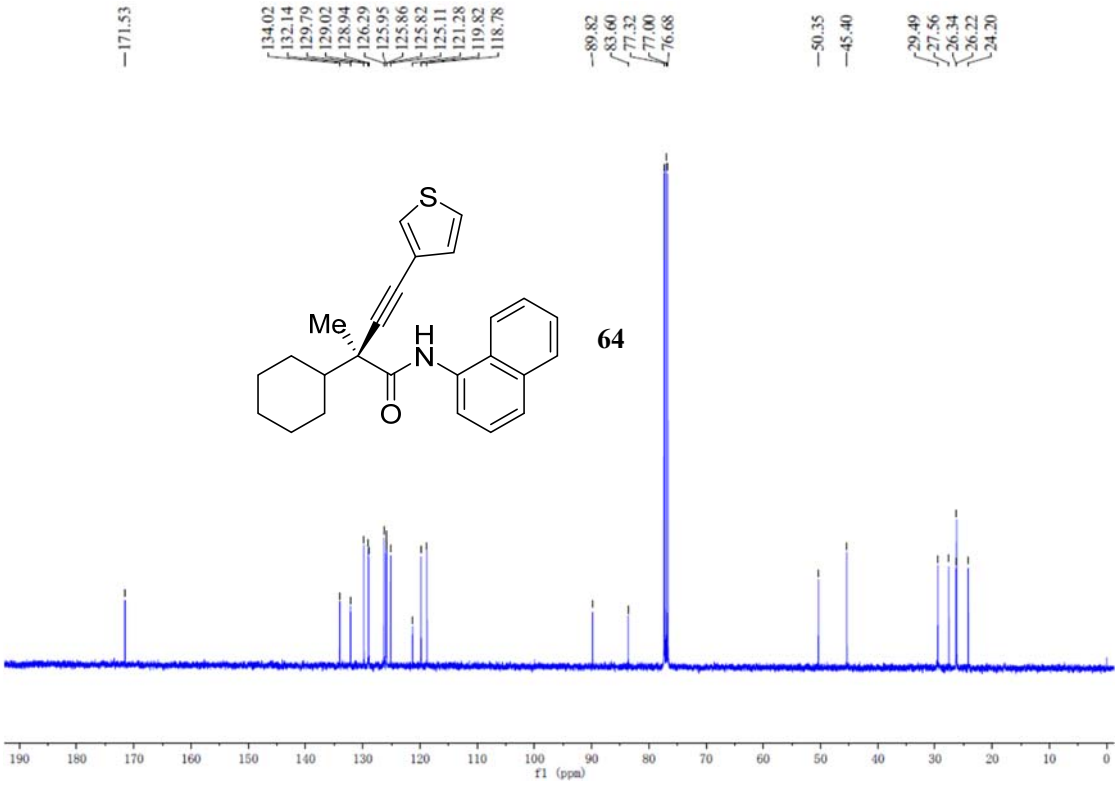
7.66
7.58
7.58
7.57
7.57
7.51
7.51
7.50
7.50
7.49
7.47
7.47
7.45
7.45
7.43
7.43
7.36
7.36
7.35
7.34
7.25
7.24
7.24
7.23
7.23
2.01
1.99
1.97
1.96
1.86
1.85
1.80
1.77
1.72
1.66
1.44
1.43
1.41
1.41
1.38
1.36
1.35
1.33
1.32
1.31
1.28
1.25
1.20
0.00
S
Me
H
N
O
64
0.96
0.98
2.00
1.00
0.92
3.00
0.98
0.96
2.02
3.18
3.05
6.03
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)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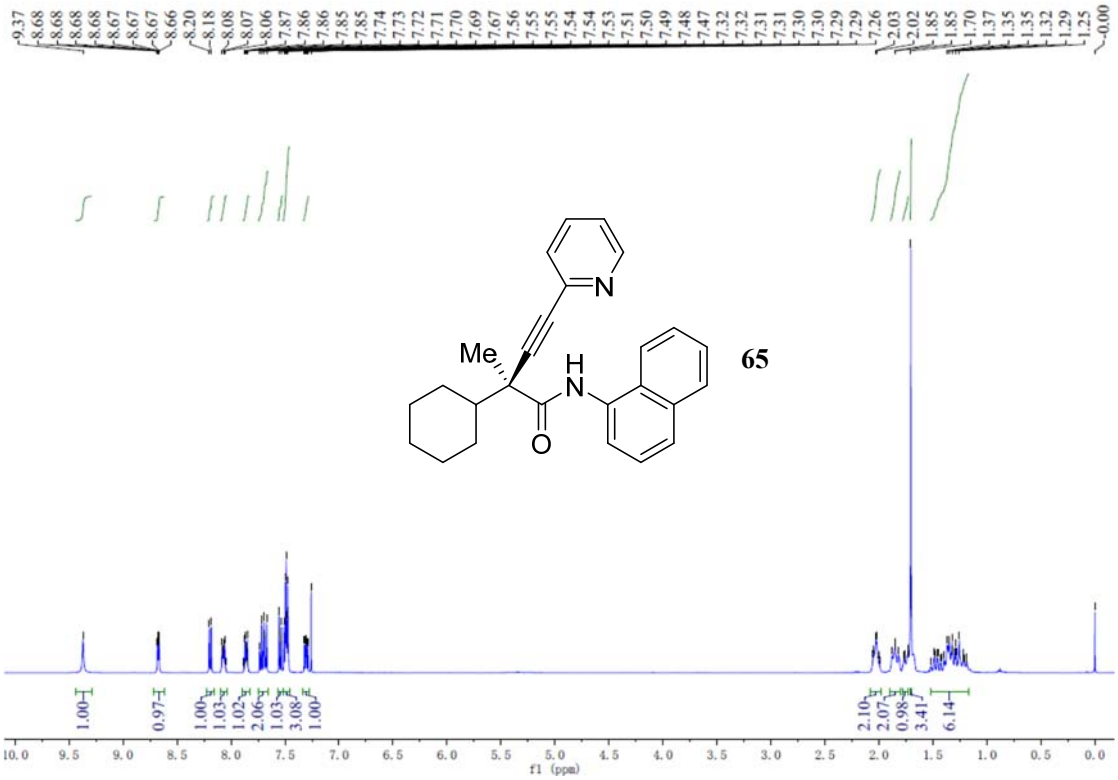
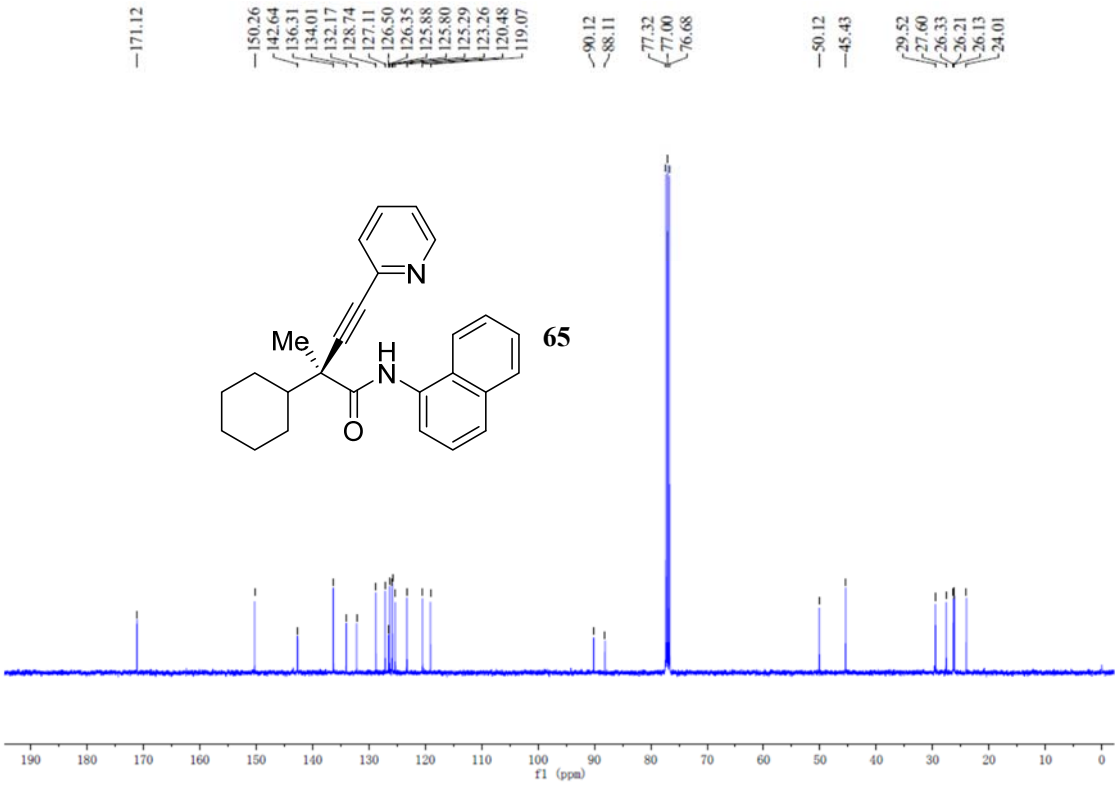
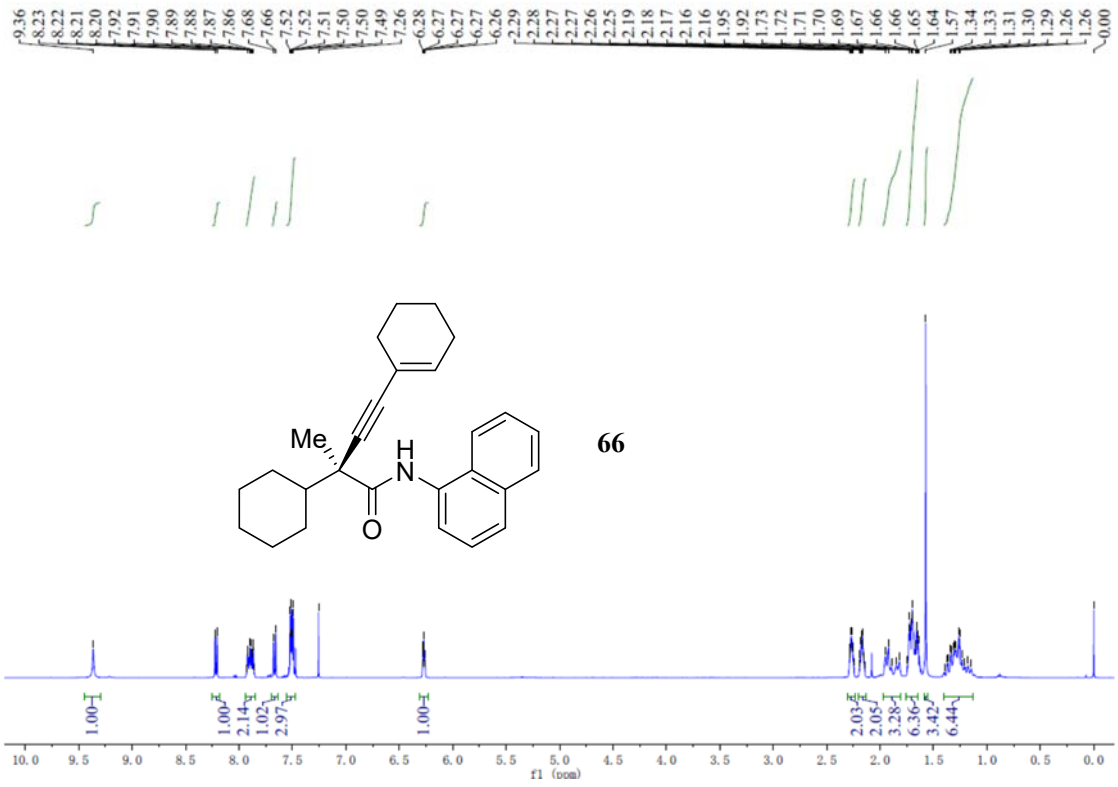
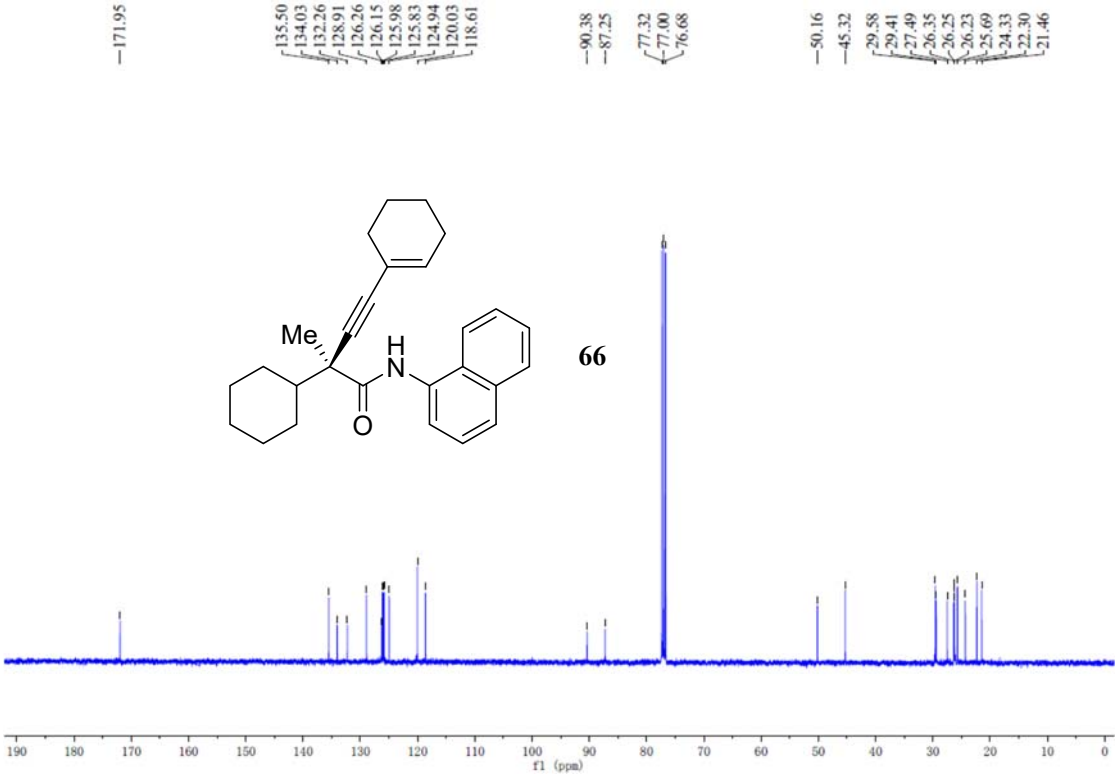
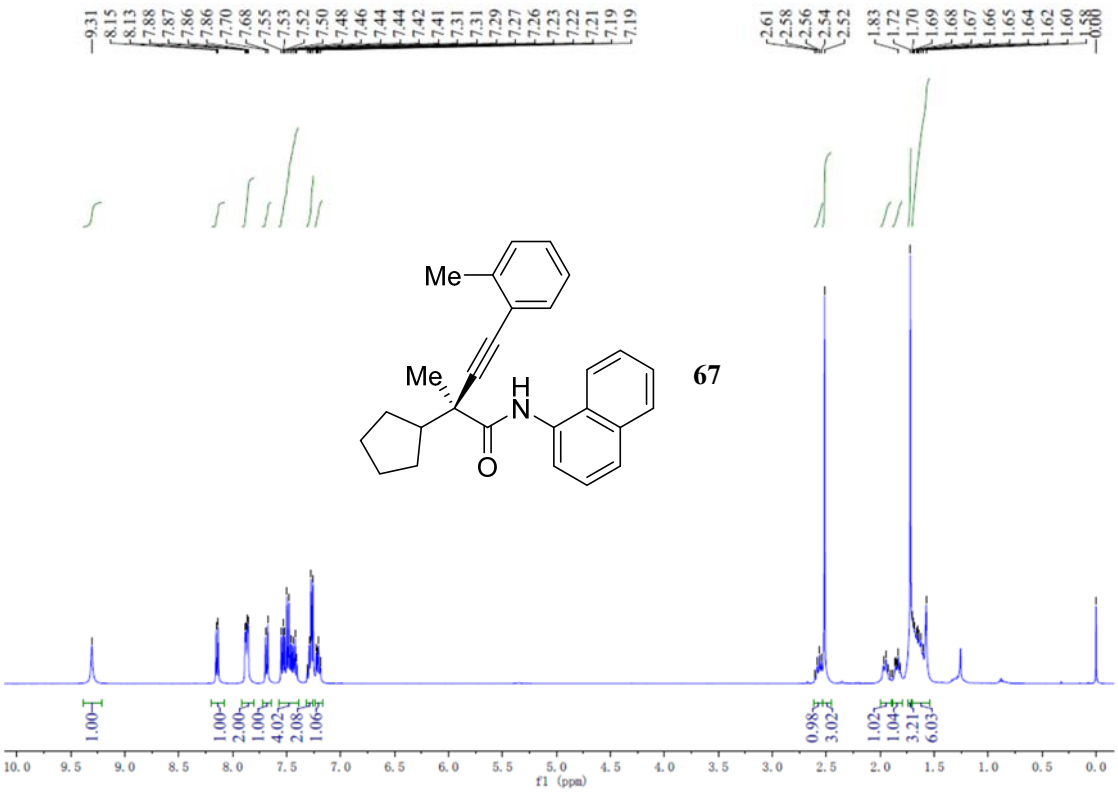
134.02
132.14
129.79
129.02
128.94
126.29
125.95
125.86
125.82
125.11
121.28
119.82
118.78
89.82
83.60
77.32
77.00
76.68
50.35
45.40
29.49
27.56
26.34
26.22
24.20
S
Me
H
N
O
64
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

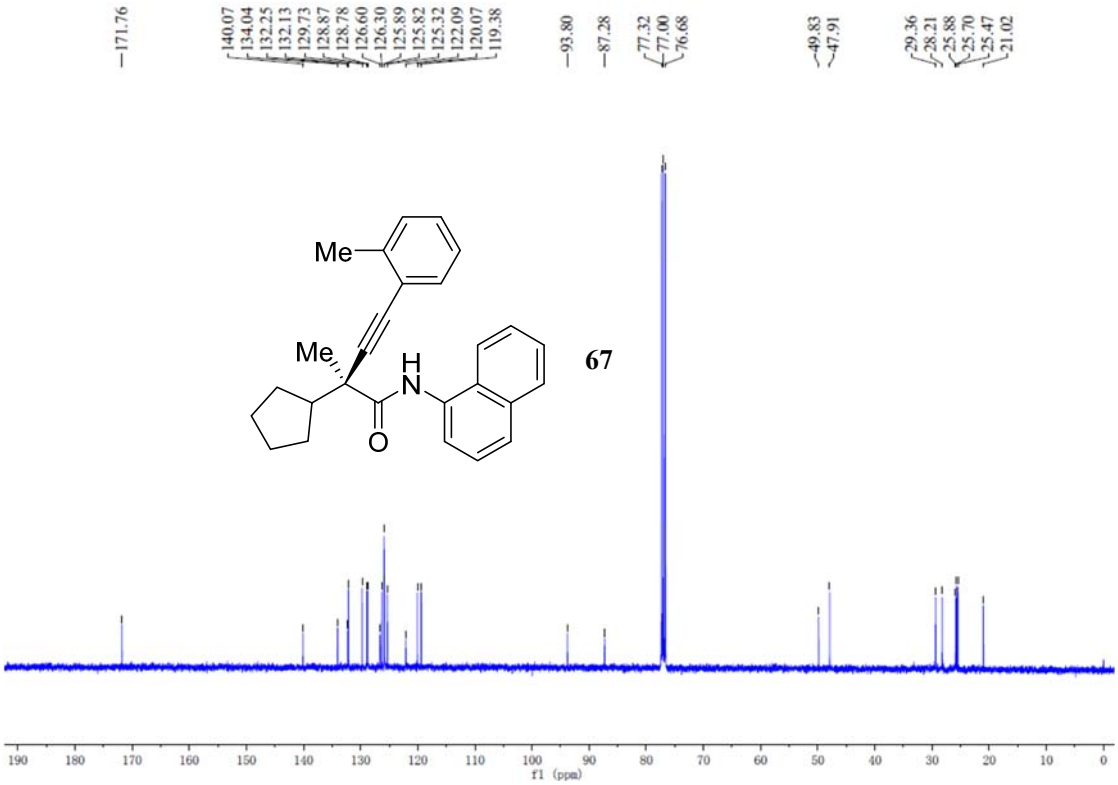

Me
H
N
O
N
65
f1 (ppm)

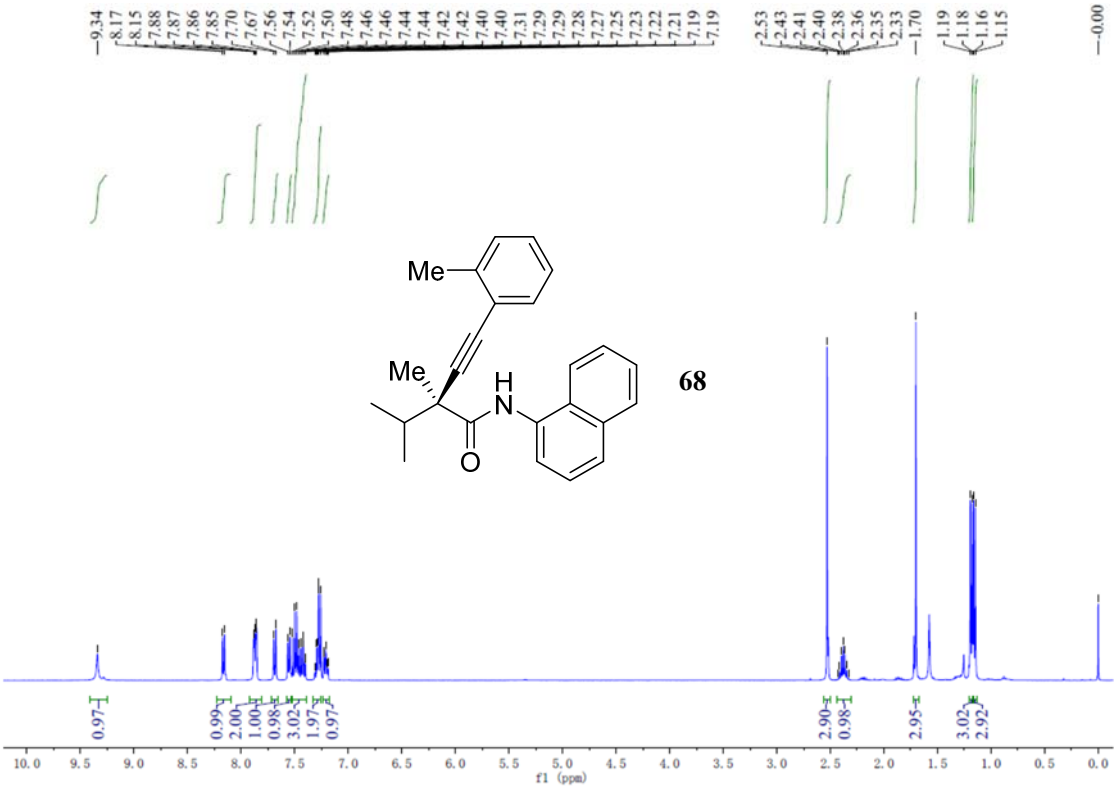

Me
H
N
O
N
65
f1 (ppm)

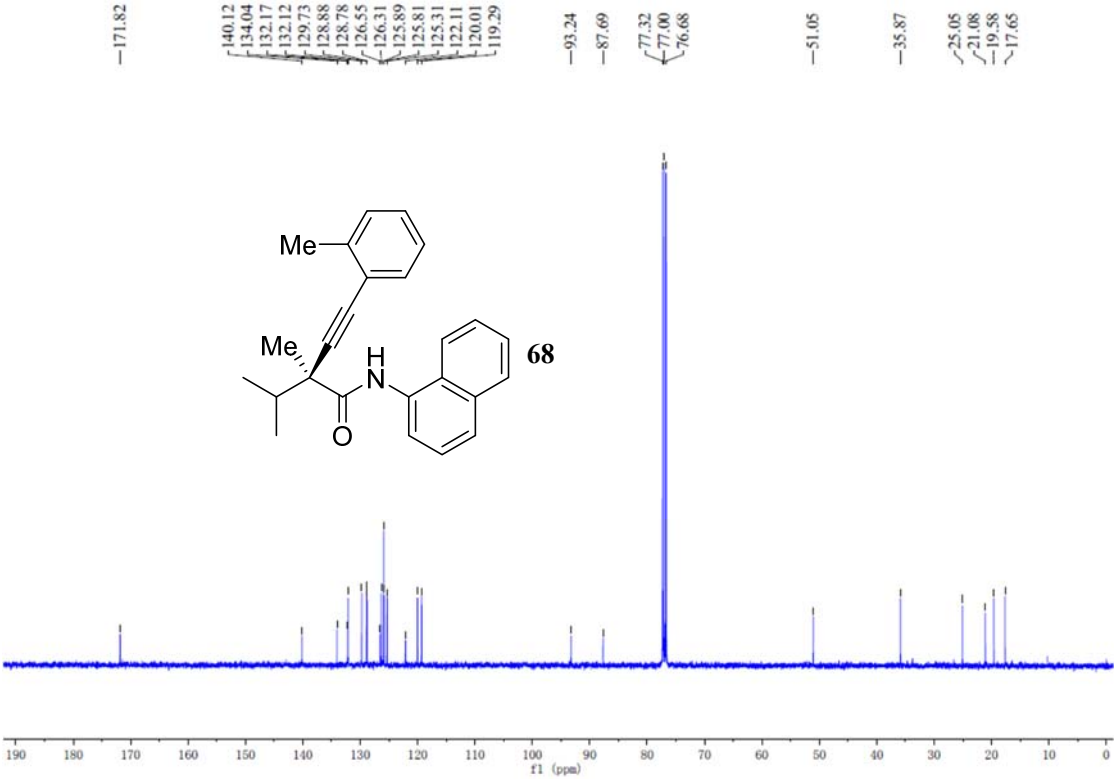

Me
H
N
O
66
f1 (ppm)

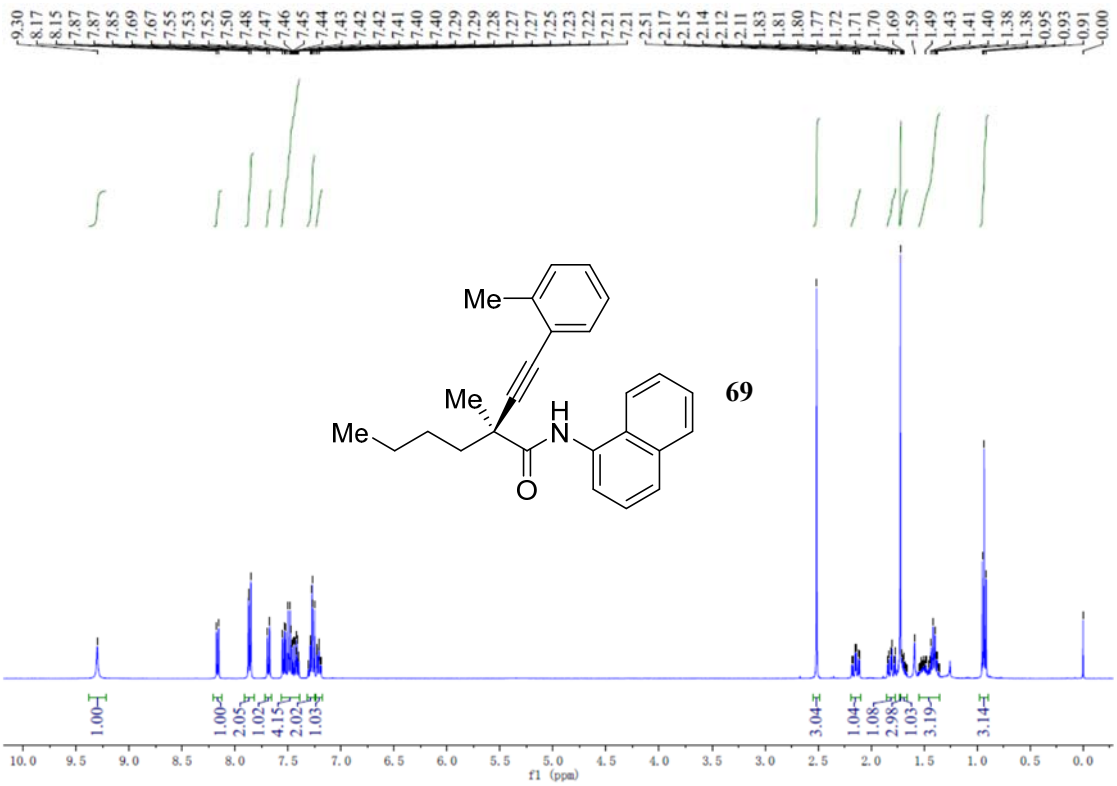

Me
H
N
O
66
f1 (ppm)

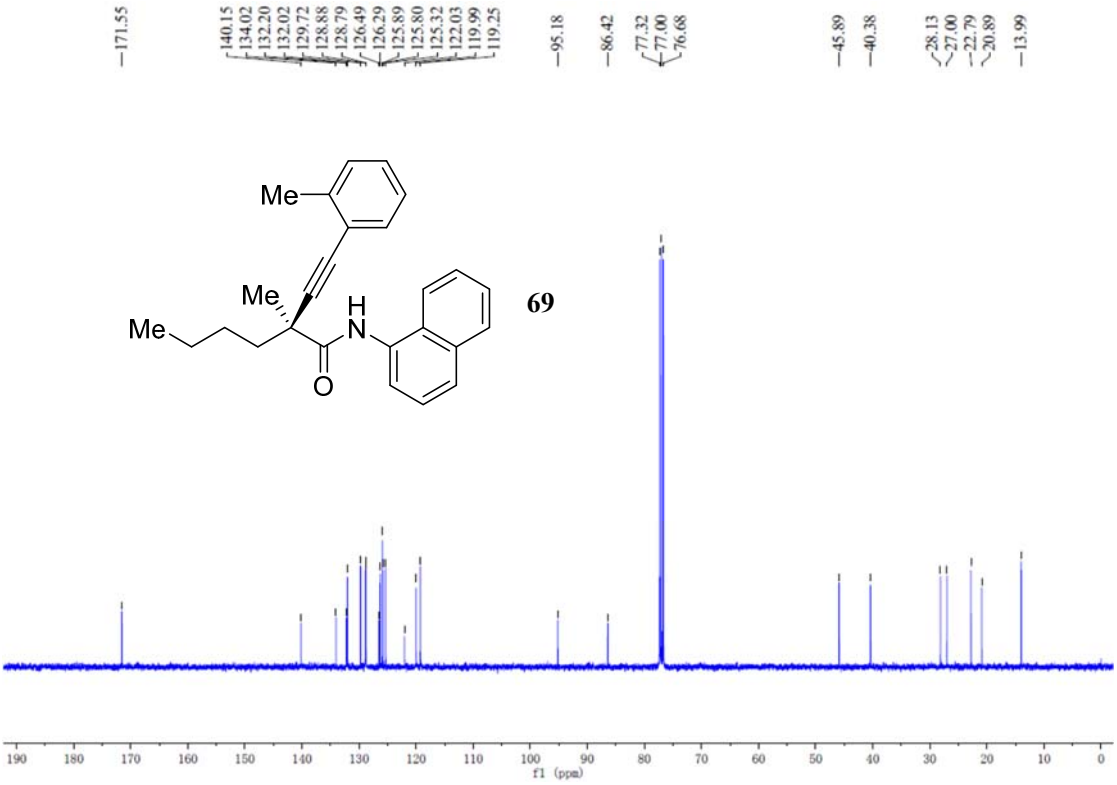

Me
Me
H
N
O
67

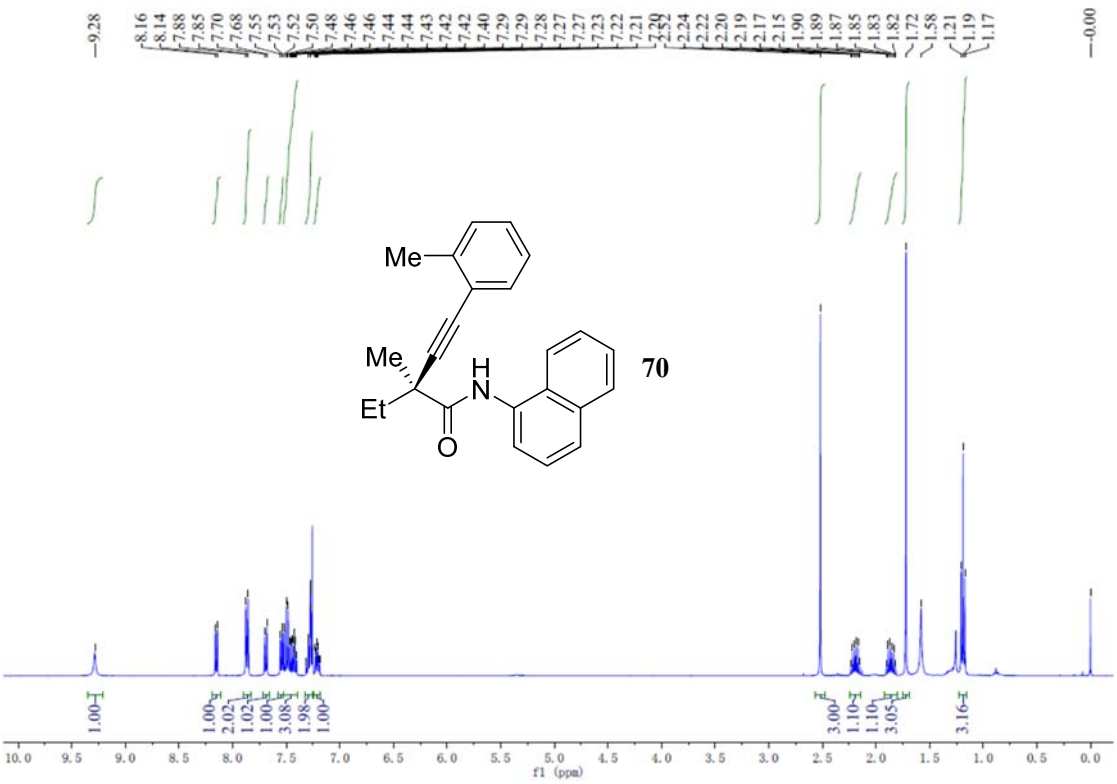

Me
Me
H
N
O
67

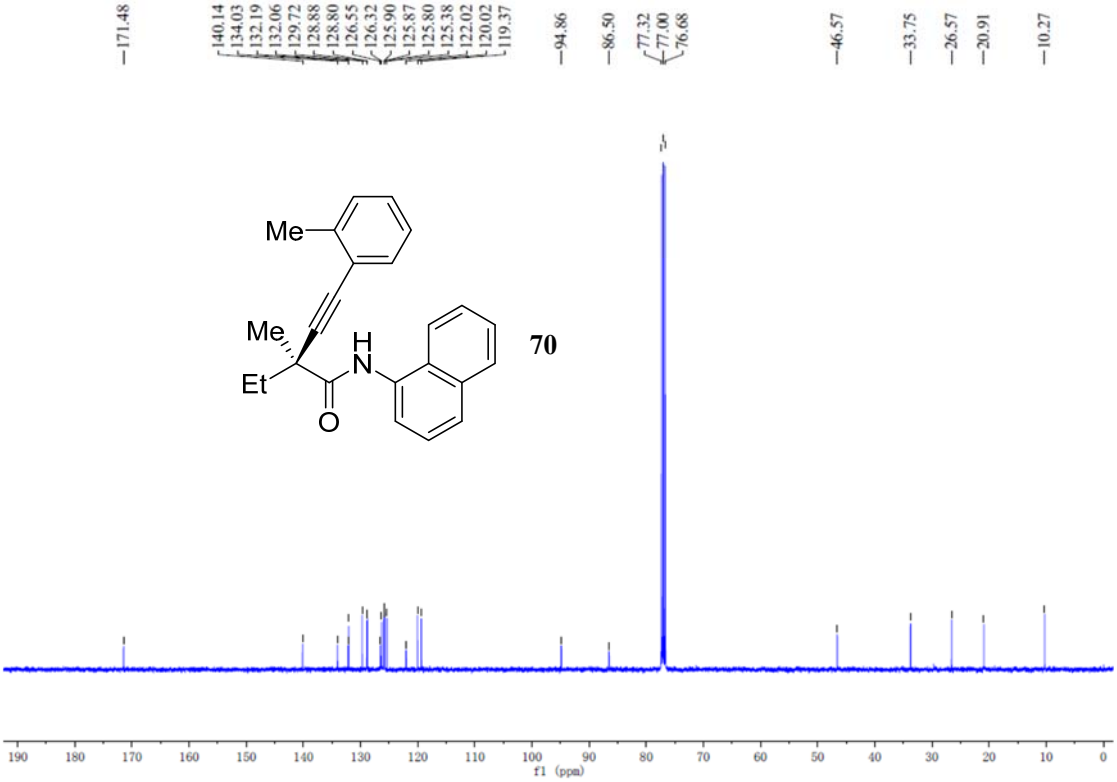

Me
Me
H
N
O
68

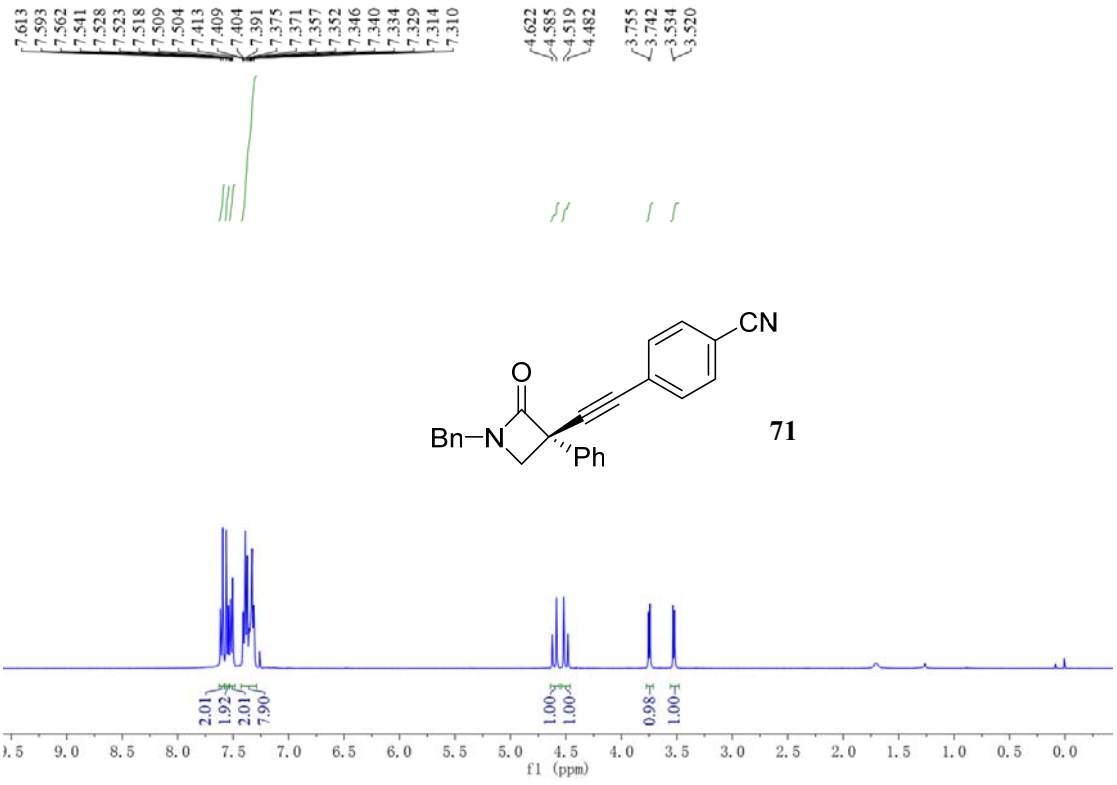

Me
Me
H
N
O
68


Me
Me
Me
H
N
O
69


Me
Me
Me
H
N
O
69


Me
Me
Et
H
N
O
70
f1 (ppm)


Me
Me
Et
H
N
O
70
f1 (ppm)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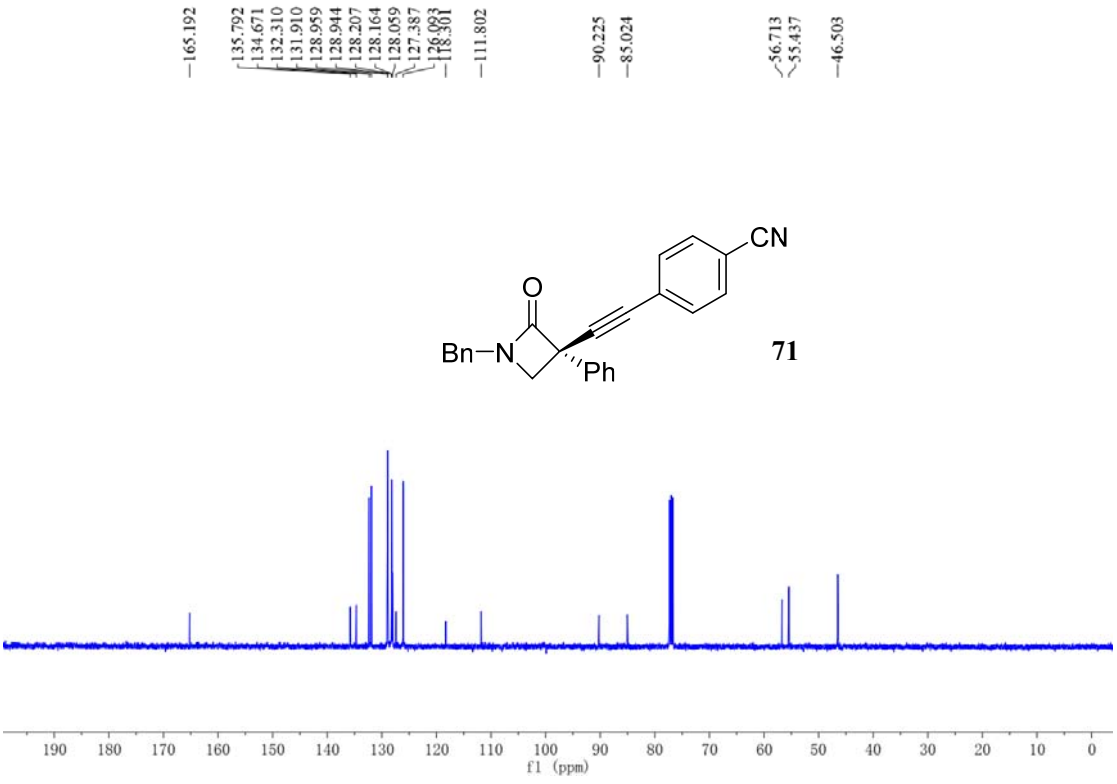
7.562
7.541
7.528
7.523
7.518
7.509
7.504
7.413
7.409
7.404
7.391
7.375
7.371
7.357
7.352
7.346
7.340
7.334
7.329
7.314
7.310
4.622
4.585
4.519
4.482
3.755
3.742
3.534
3.520
CN
O
Bn–N
Ph
71
2.01
1.92
2.01
7.90
1.00
1.00
0.98
1.00
f1 (ppm)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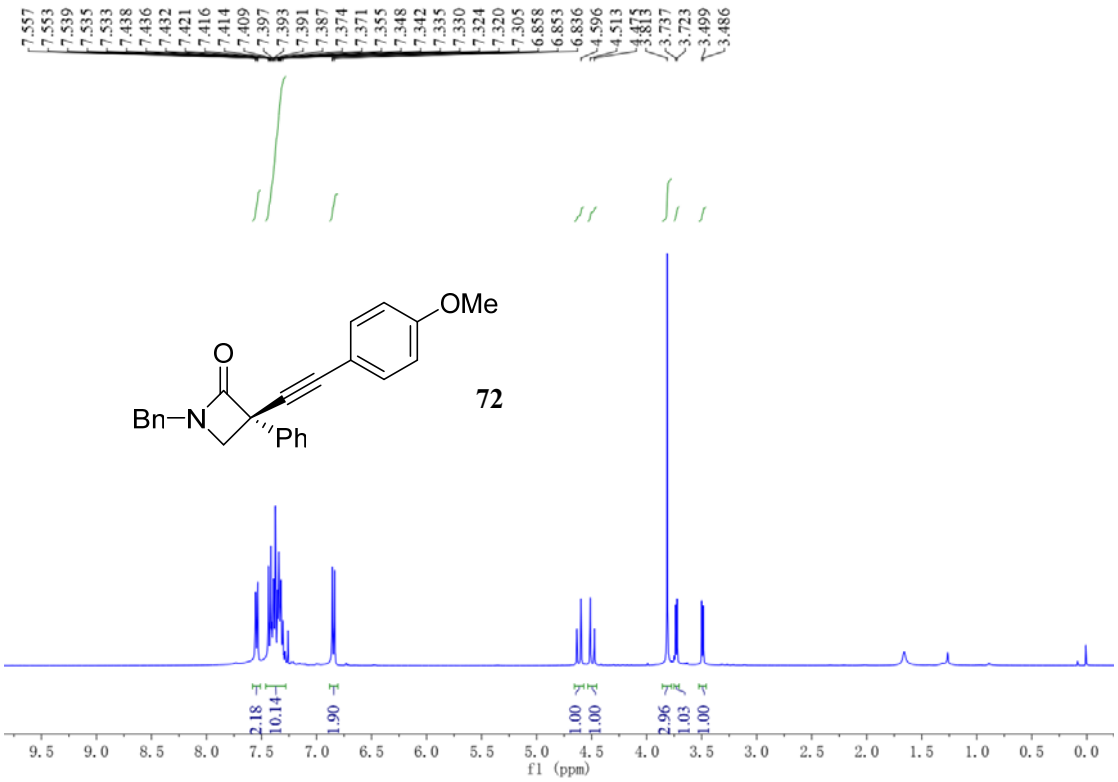
128.207
128.164
128.059
127.387
126.093
118.301
111.802
90.225
85.024
56.713
55.437
46.503
CN
O
Bn–N
Ph
71
f1 (ppm)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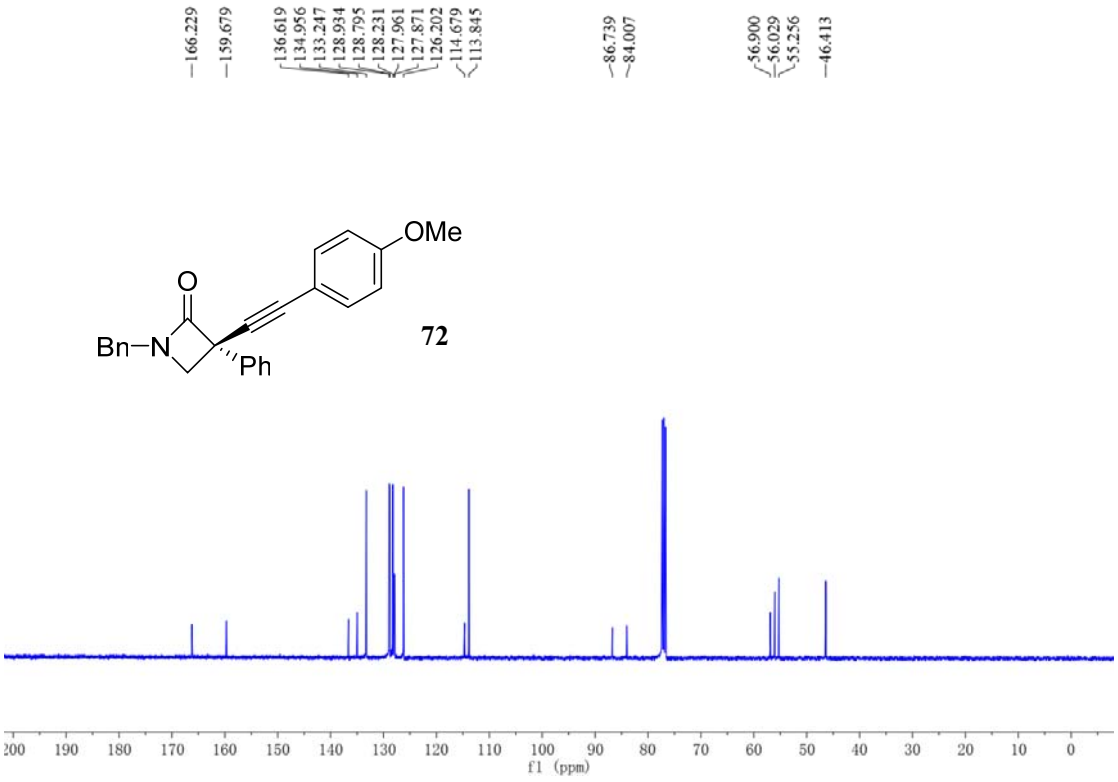
7.553
7.539
7.535
7.533
7.438
7.436
7.432
7.421
7.416
7.414
7.409
7.397
7.393
7.391
7.387
7.374
7.371
7.355
7.348
7.342
7.335
7.330
7.324
7.320
7.305
6.858
6.853
6.836
4.596
4.513
3.813
3.737
3.723
3.499
3.486
OMe
O
Bn–N
Ph
72
2.18
10.14
1.90
1.00
1.00
2.96
1.03
1.00
f1 (ppm)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128.934
128.795
128.231
127.961
127.871
126.202
114.679
113.845
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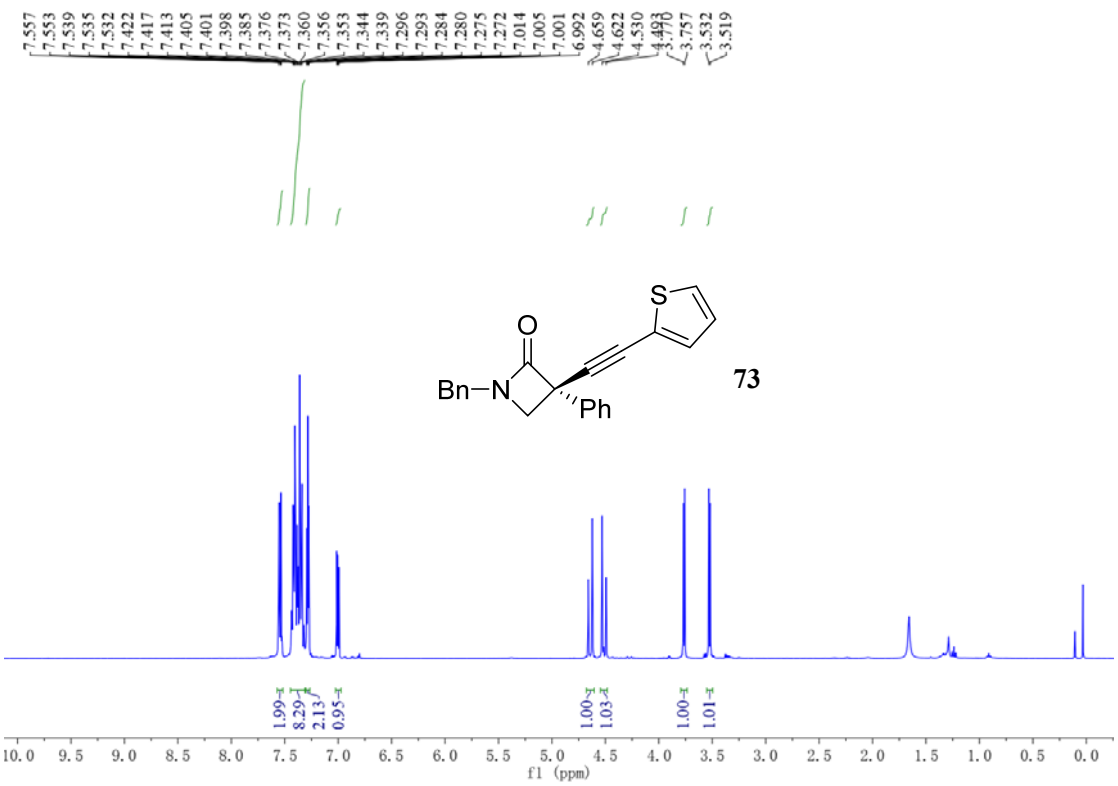
84.007
56.900
56.029
55.256
46.413
OMe
O
Bn–N
Ph
72
f1 (ppm)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7.553
7.539
7.535
7.532
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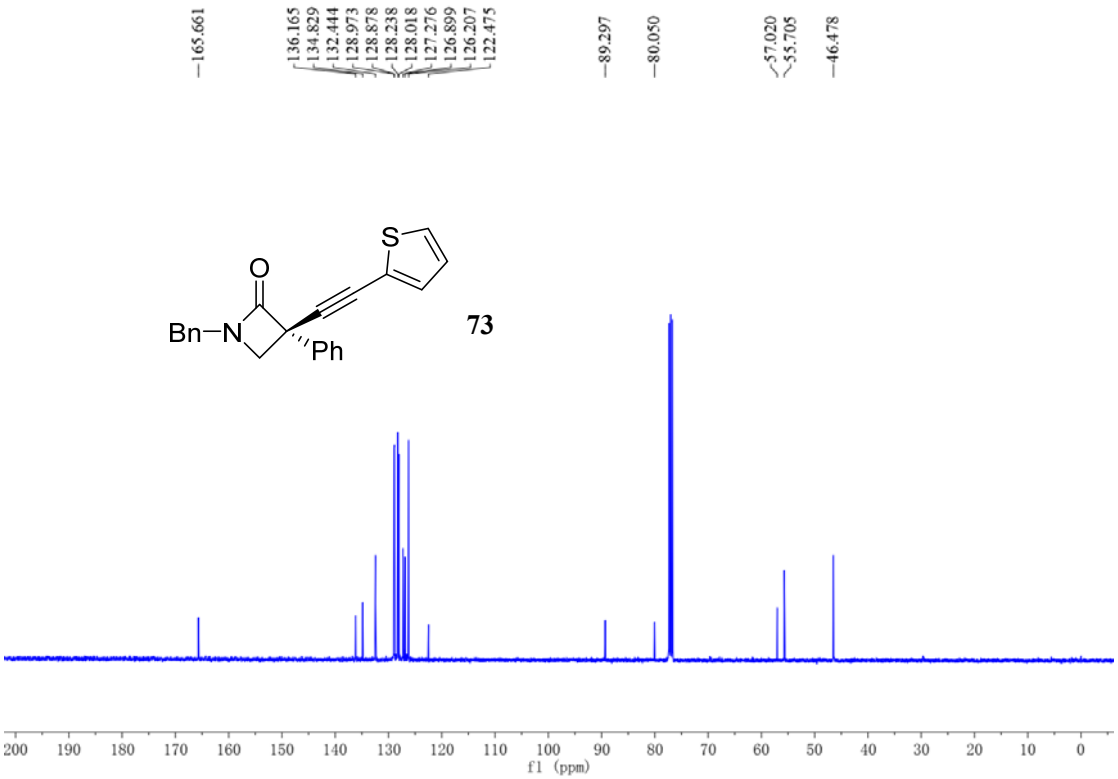
7.413
7.405
7.401
7.398
7.385
7.376
7.373
7.360
7.356
7.353
7.344
7.339
7.296
7.293
7.284
7.280
7.275
7.272
7.014
7.005
7.001
6.992
4.659
4.622
4.530
4.493
3.770
3.757
3.532
3.519
S
O
Bn—N
Ph
73
1.99
8.29
2.13
0.95
1.00
1.03
1.00
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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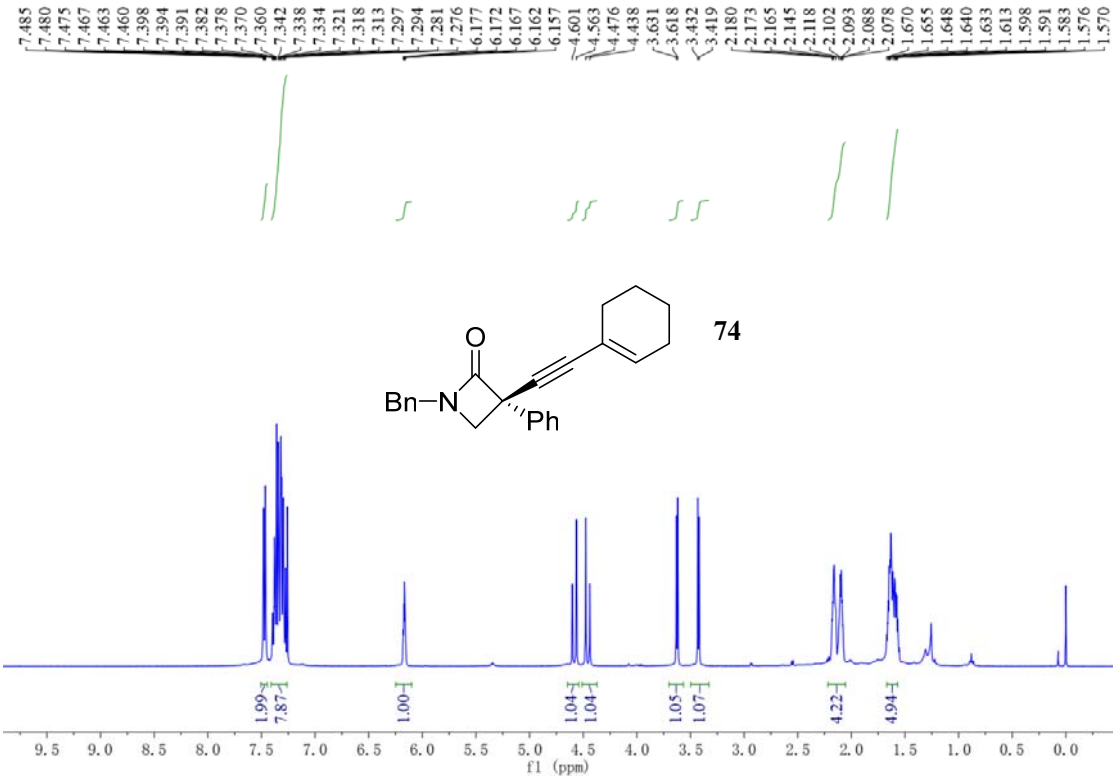
126.899
126.207
122.475
89.297
80.050
57.020
55.705
46.478
S
O
Bn—N
Ph
73
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.360
7.342
7.338
7.334
7.321
7.318
7.313
7.297
7.294
7.281
7.276
6.177
6.172
6.167
6.162
6.157
4.601
4.563
4.476
4.438
3.631
3.618
3.432
3.419
2.180
2.173
2.165
2.145
2.118
2.102
2.093
2.088
2.078
1.670
1.655
1.648
1.640
1.633
1.613
1.598
1.591
1.583
1.576
1.570
O
Bn—N
Ph
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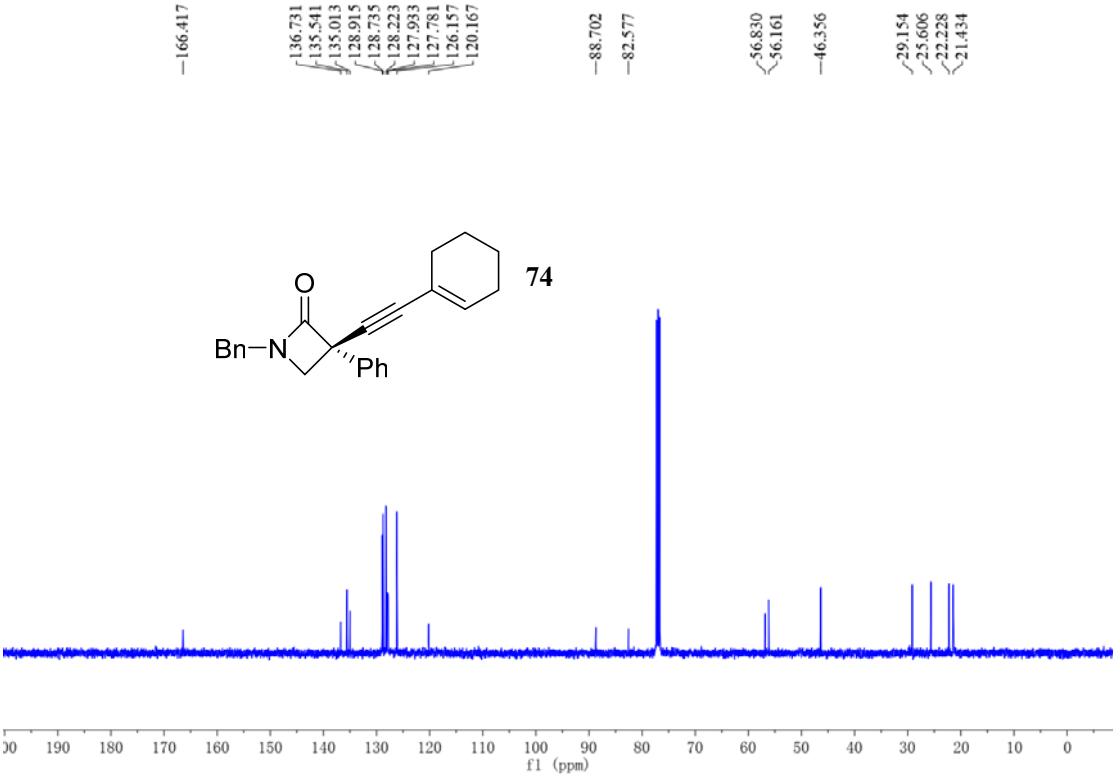
7.87
1.00
1.04
1.04
1.05
1.07
4.22
4.94
f1 (ppm)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135.541
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127.781
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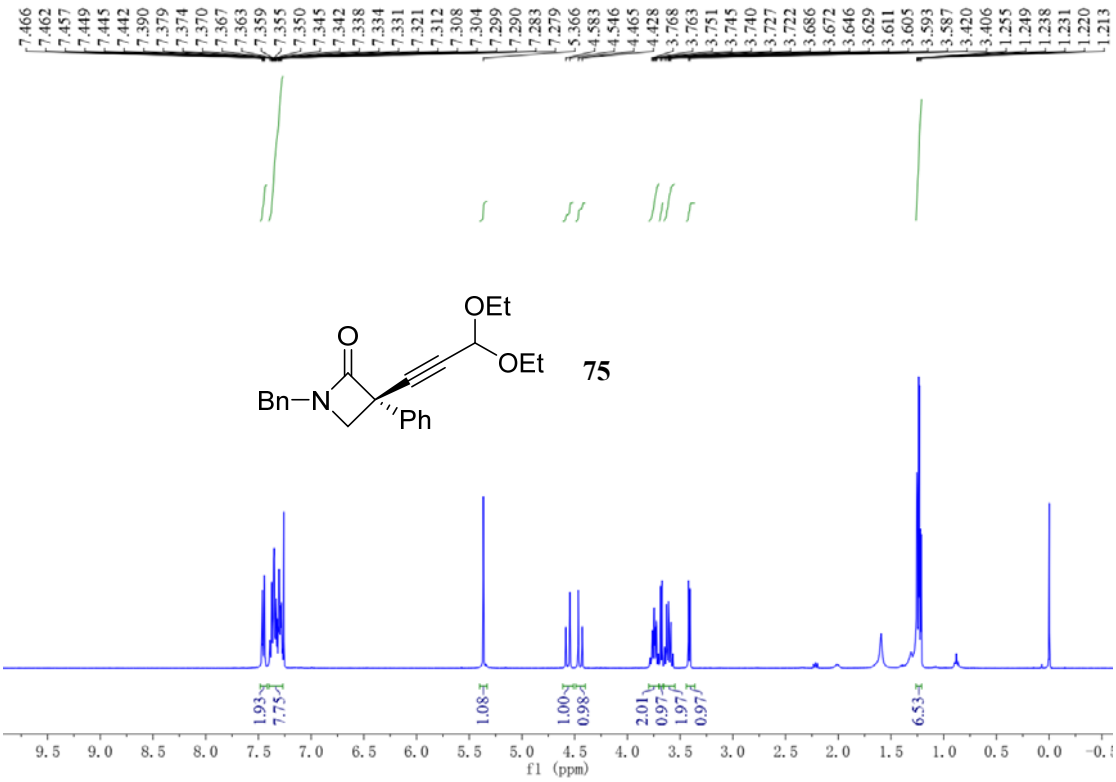
120.167
88.702
82.577
56.830
56.161
46.356
29.154
25.606
22.228
21.434
O
Bn—N
Ph
74
f1 (ppm)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7.359
7.355
7.350
7.345
7.342
7.338
7.334
7.331
7.321
7.312
7.308
7.304
7.299
7.290
7.283
7.279
5.366
4.583
4.546
4.465
4.428
3.768
3.763
3.751
3.745
3.740
3.727
3.722
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3.672
3.646
3.629
3.611
3.605
3.593
3.587
3.420
3.406
1.255
1.249
1.238
1.231
1.220
1.213
OEt
OEt
O
Bn—N
Ph
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1.08
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2.01
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1.97
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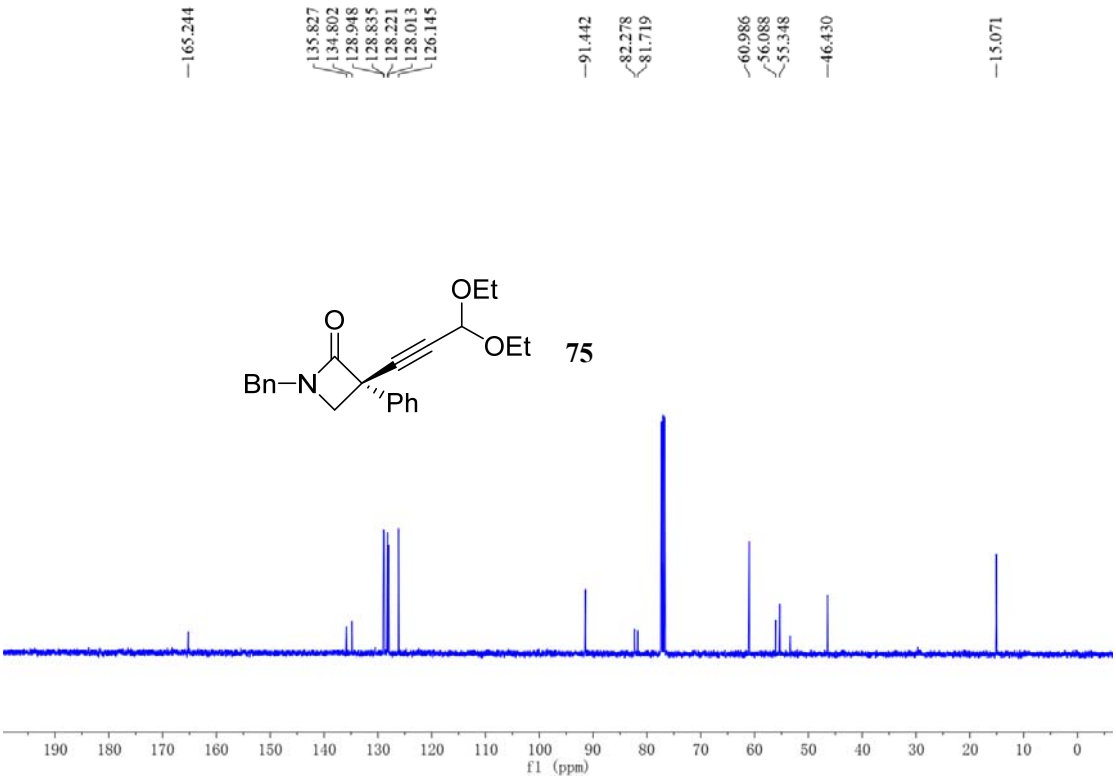
6.53
f1 (ppm)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126.145
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82.278
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55.348
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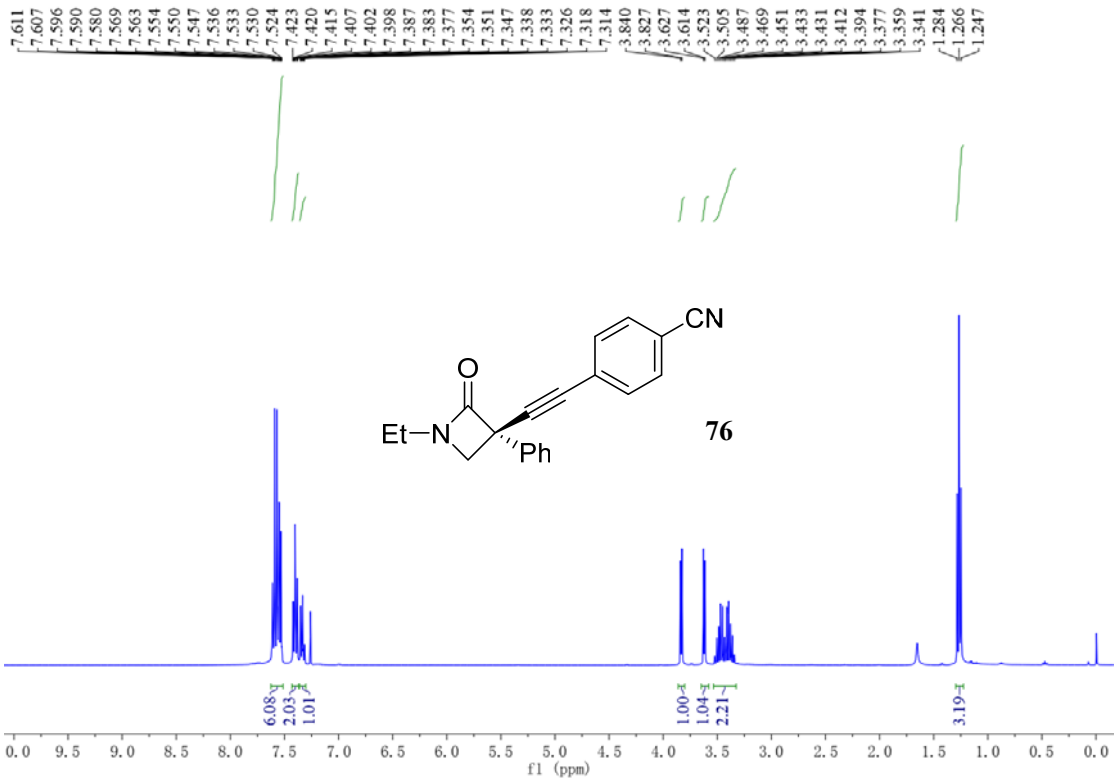
OEt
OEt
O
Bn—N
Ph
75
f1 (ppm)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7.530
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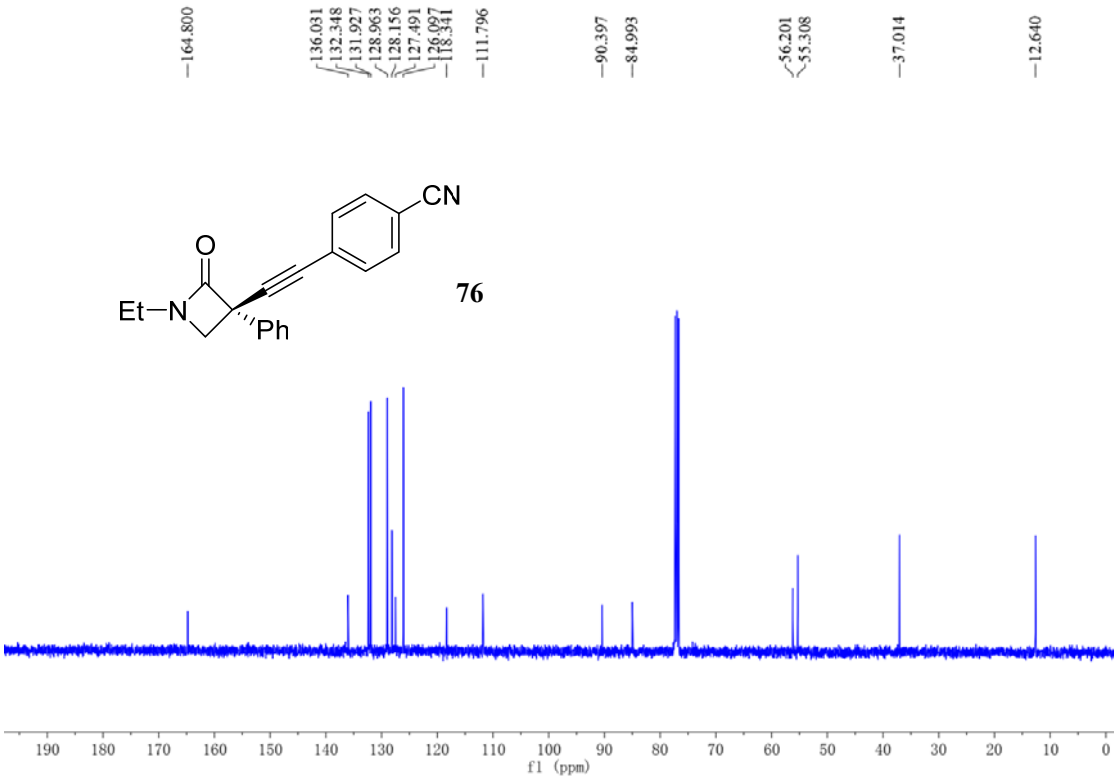
3.840
3.827
3.627
3.614
3.523
3.505
3.487
3.469
3.451
3.433
3.431
3.412
3.394
3.377
3.359
3.341
1.284
1.266
1.247
CN
O
Et—N
Ph
76
6.08
2.03
1.01
1.00
1.04
2.21
3.19
f1 (ppm)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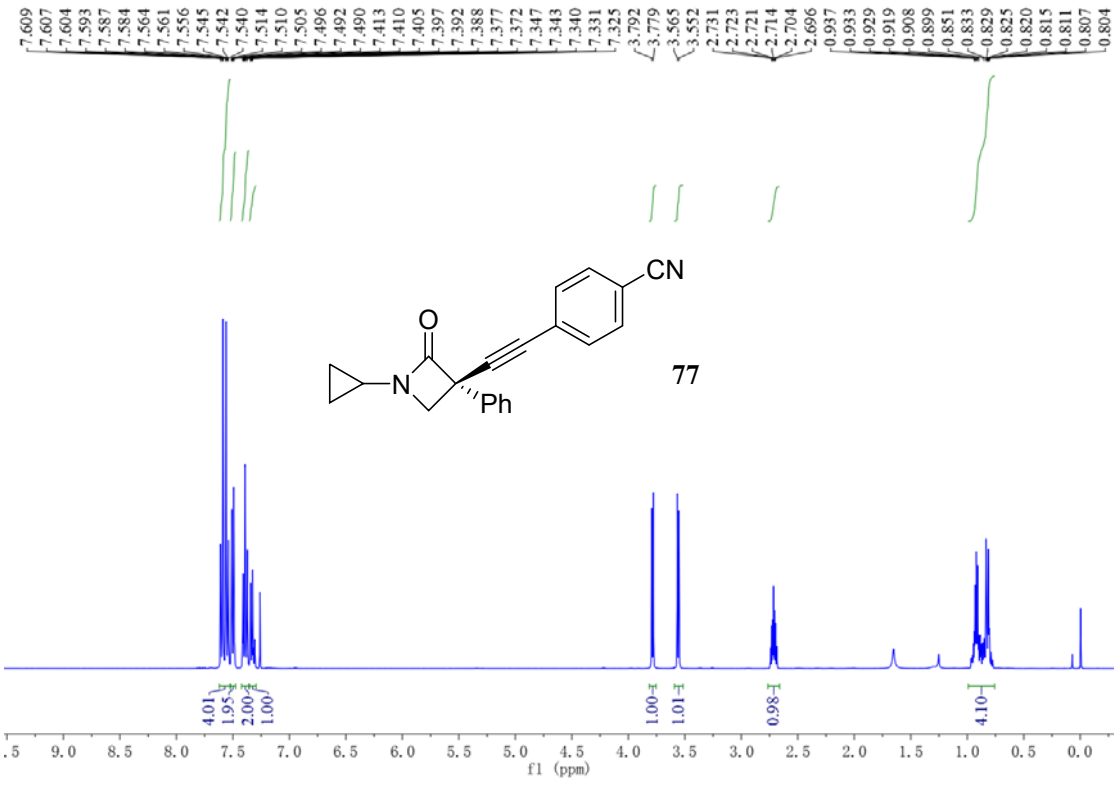
56.201
55.308
37.014
12.640
CN
O
Et—N
Ph
76
f1 (ppm)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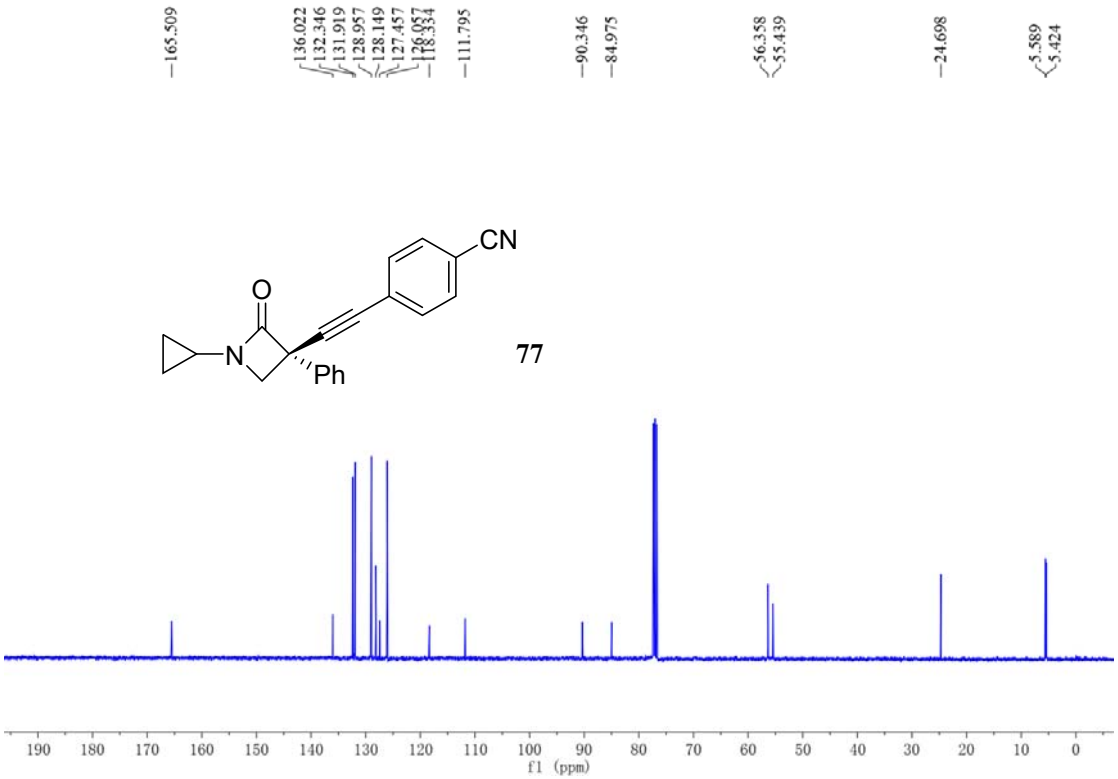
7.514
7.510
7.505
7.496
7.492
7.490
7.413
7.410
7.405
7.397
7.392
7.388
7.377
7.372
7.347
7.343
7.340
7.331
7.325
3.792
3.779
3.565
3.552
2.731
2.723
2.721
2.714
2.704
2.696
0.937
0.933
0.929
0.919
0.908
0.899
0.851
0.833
0.829
0.825
0.820
0.815
0.811
0.807
0.804
CN
O
N
Ph
77
4.01
1.95
2.00
1.00
1.00
1.01
0.98
4.10
f1 (ppm)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55.439
24.698
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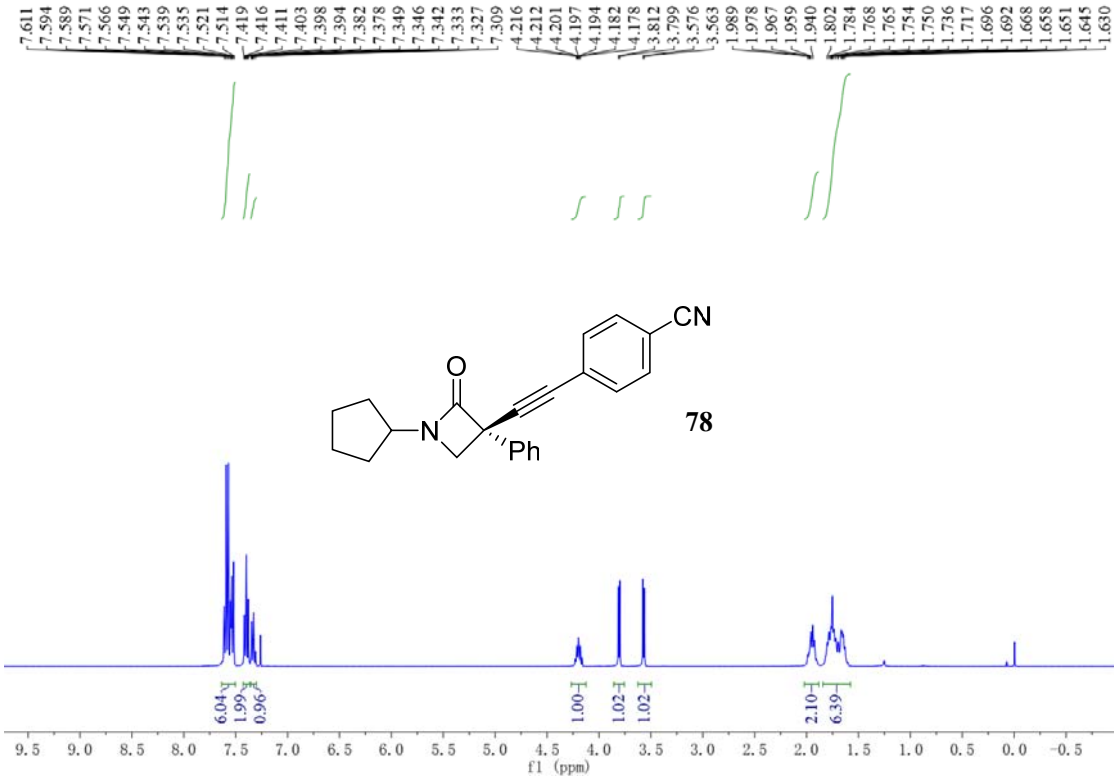
5.424
CN
O
N
Ph
77
f1 (ppm)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7.594
7.589
7.571
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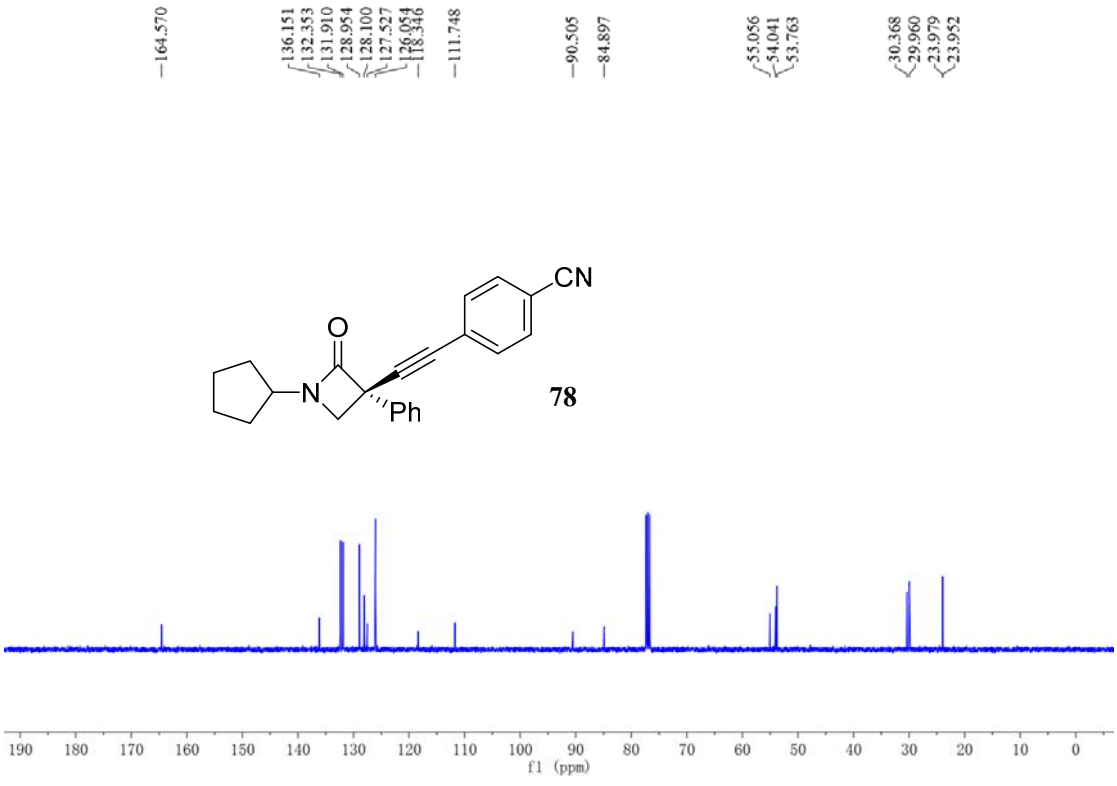
7.549
7.543
7.539
7.535
7.521
7.514
7.419
7.416
7.411
7.403
7.398
7.394
7.382
7.378
7.349
7.346
7.342
7.333
7.327
7.309
4.216
4.212
4.201
4.197
4.194
4.182
4.178
3.812
3.799
3.576
3.563
1.989
1.978
1.967
1.959
1.940
1.802
1.784
1.768
1.765
1.754
1.750
1.736
1.717
1.696
1.692
1.668
1.658
1.651
1.645
1.630
CN
O
N
Ph
78
6.04
1.99
0.96
1.00
1.02
1.02
2.10
6.39
f1 (ppm)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132.353
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126.054
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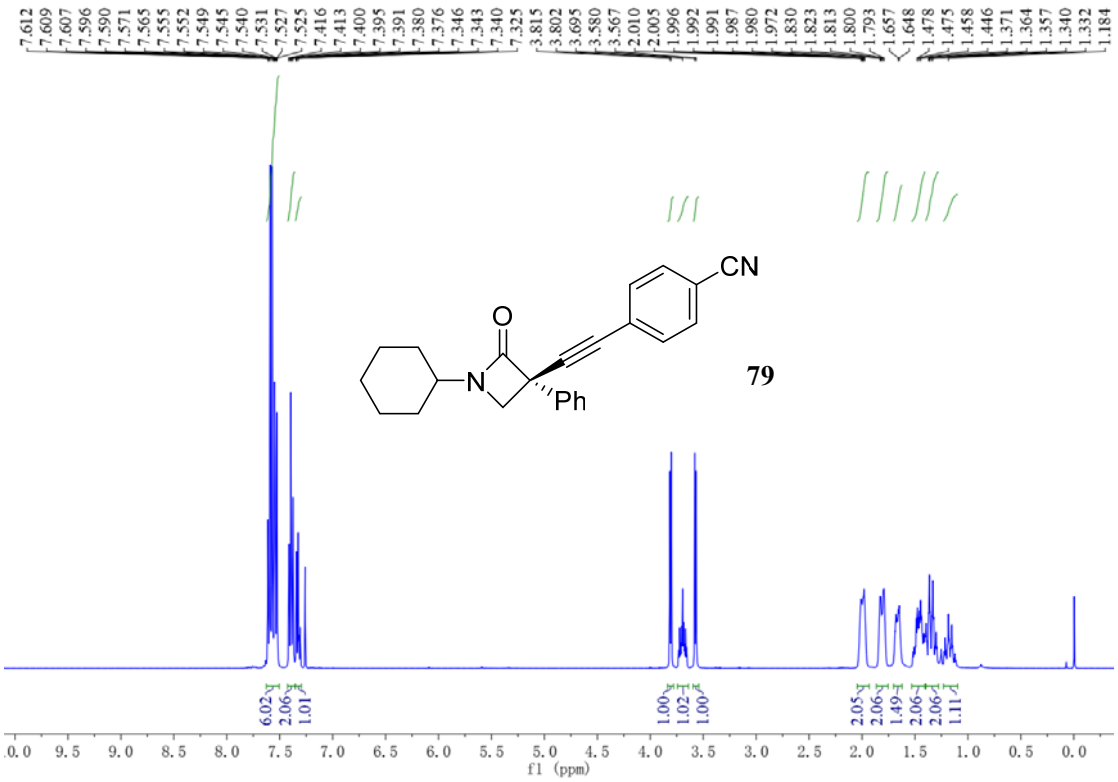
55.056
54.041
53.763
30.368
29.960
23.979
23.952
CN
O
N
Ph
78
f1 (ppm)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7.590
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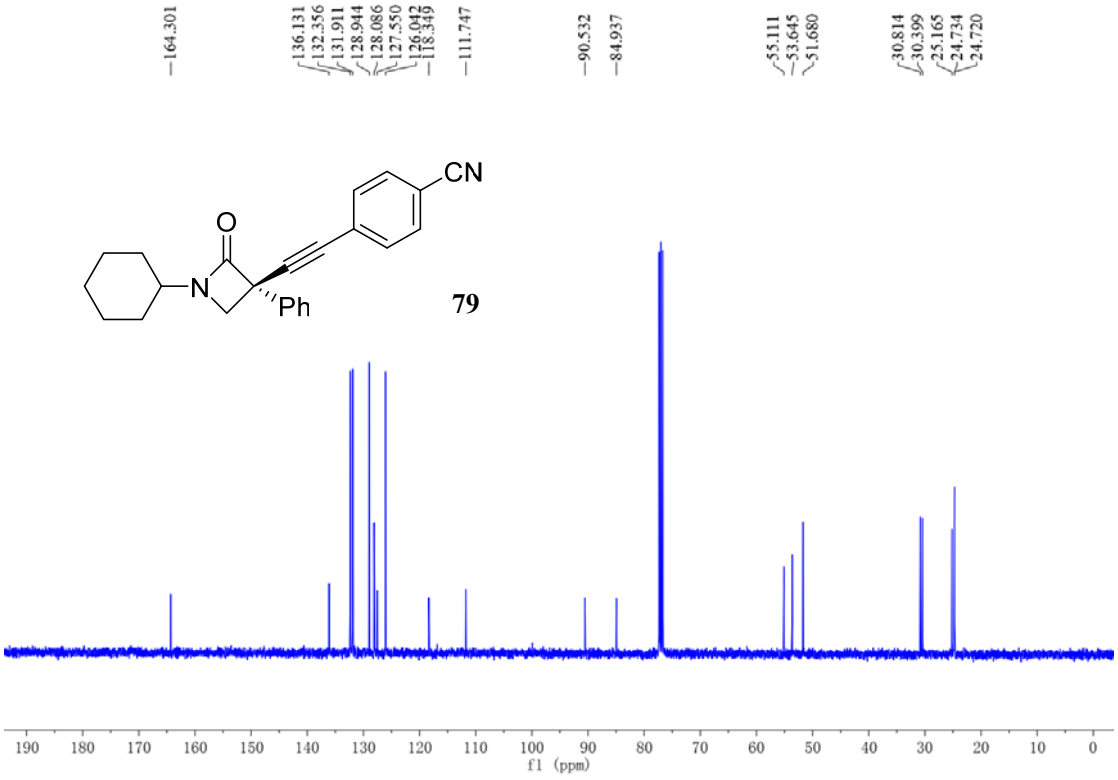
7.555
7.552
7.549
7.545
7.540
7.531
7.527
7.525
7.416
7.413
7.400
7.395
7.391
7.380
7.376
7.346
7.343
7.340
7.325
3.815
3.802
3.695
3.580
3.567
2.010
2.005
1.996
1.992
1.991
1.987
1.980
1.972
1.830
1.823
1.813
1.800
1.793
1.657
1.648
1.478
1.475
1.458
1.446
1.371
1.364
1.357
1.340
1.332
1.184
CN
O
N
Ph
79
6.02
2.06
1.01
1.00
1.02
1.00
2.05
2.06
1.49
2.06
2.06
1.11
f1 (ppm)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136.131
132.356
131.911
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128.086
127.550
126.042
118.349
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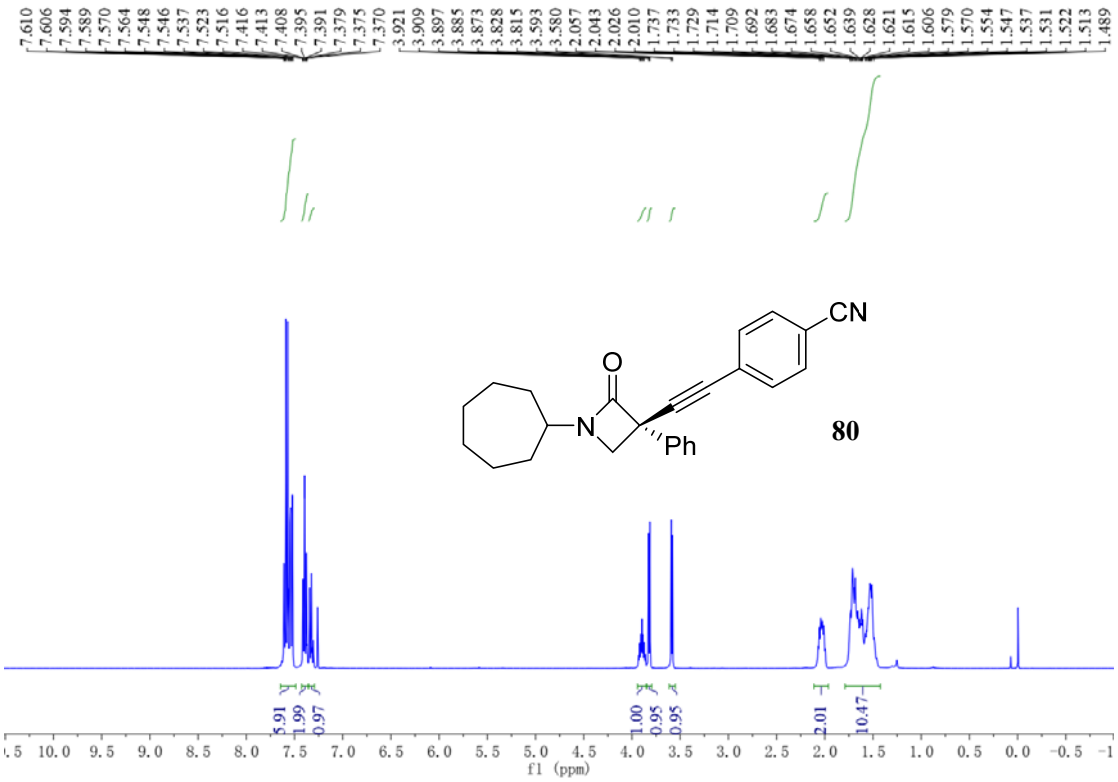
90.532
84.937
55.111
53.645
51.680
30.814
30.399
25.165
24.734
24.720
CN
O
N
Ph
79
f1 (ppm)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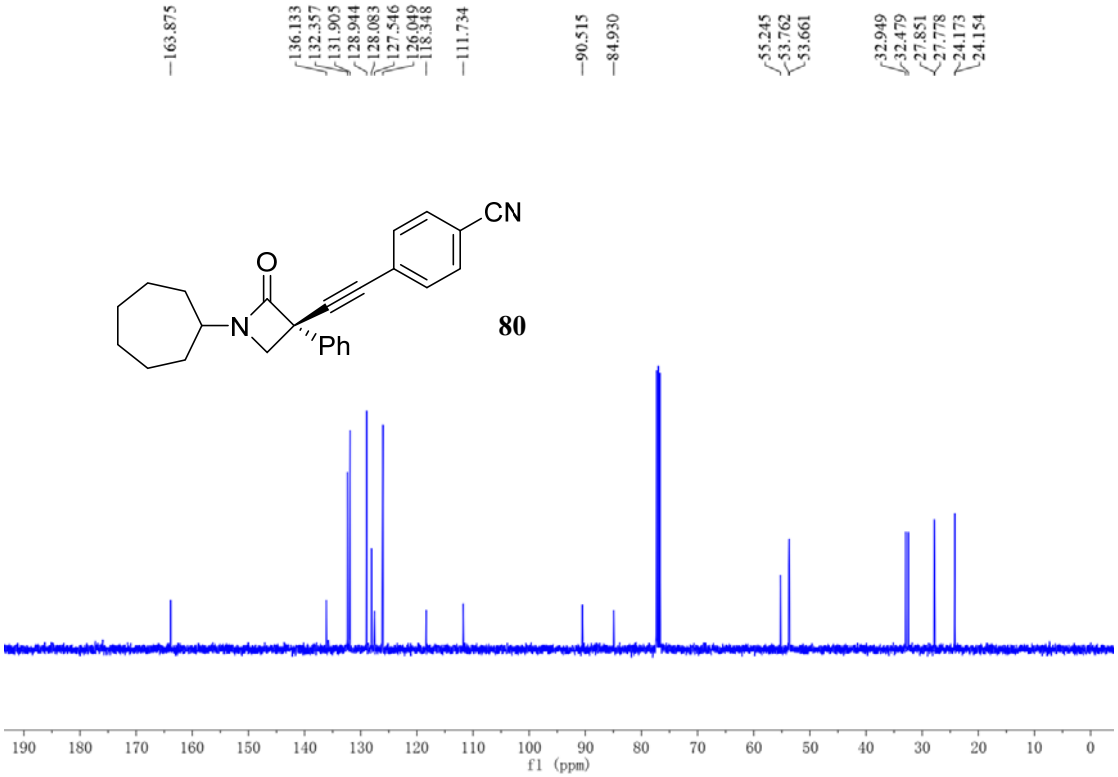
7.606
7.594
7.589
7.570
7.564
7.548
7.546
7.537
7.523
7.516
7.416
7.413
7.408
7.395
7.391
7.379
7.375
7.370
3.921
3.909
3.897
3.885
3.873
3.828
3.815
3.593
3.580
2.057
2.043
2.026
2.010
1.737
1.733
1.729
1.714
1.709
1.692
1.683
1.674
1.658
1.652
1.639
1.628
1.621
1.615
1.606
1.579
1.570
1.554
1.547
1.537
1.531
1.522
1.513
1.489
CN
O
N
Ph
80
5.91
1.99
0.97
1.00
0.95
0.95
2.01
10.47
f1 (ppm)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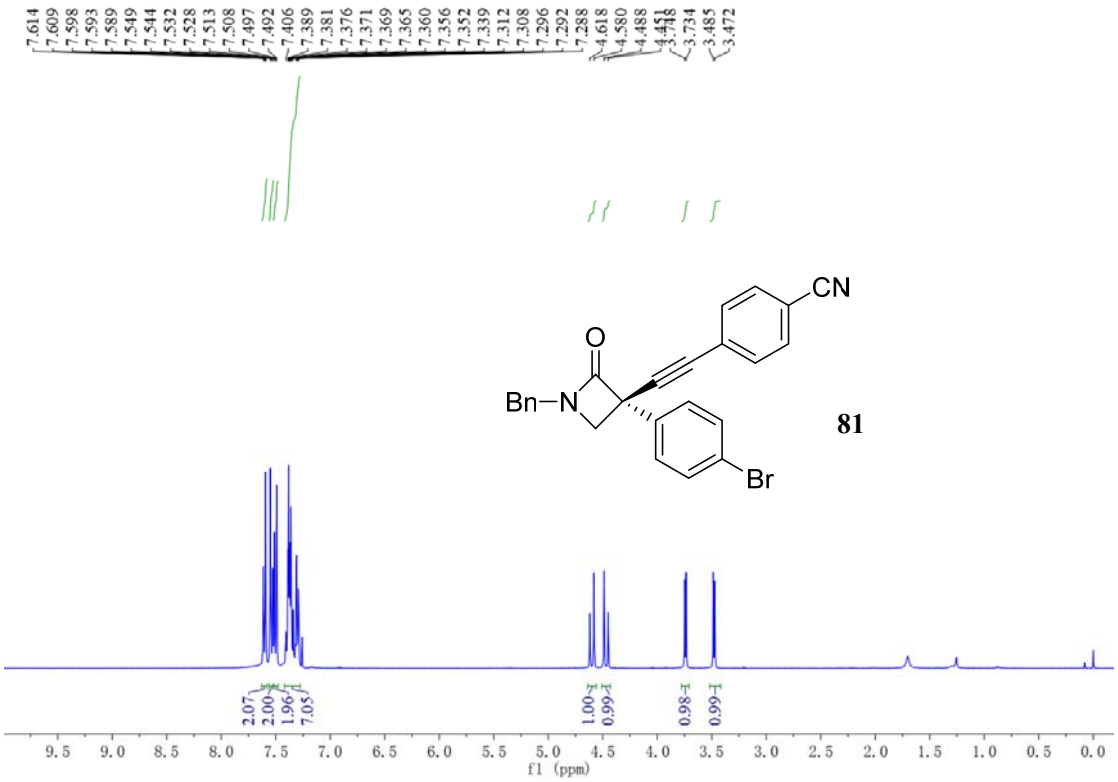
84.930
55.245
53.762
53.661
32.949
32.479
27.851
27.778
24.173
24.154
CN
O
N
Ph
80
f1 (ppm)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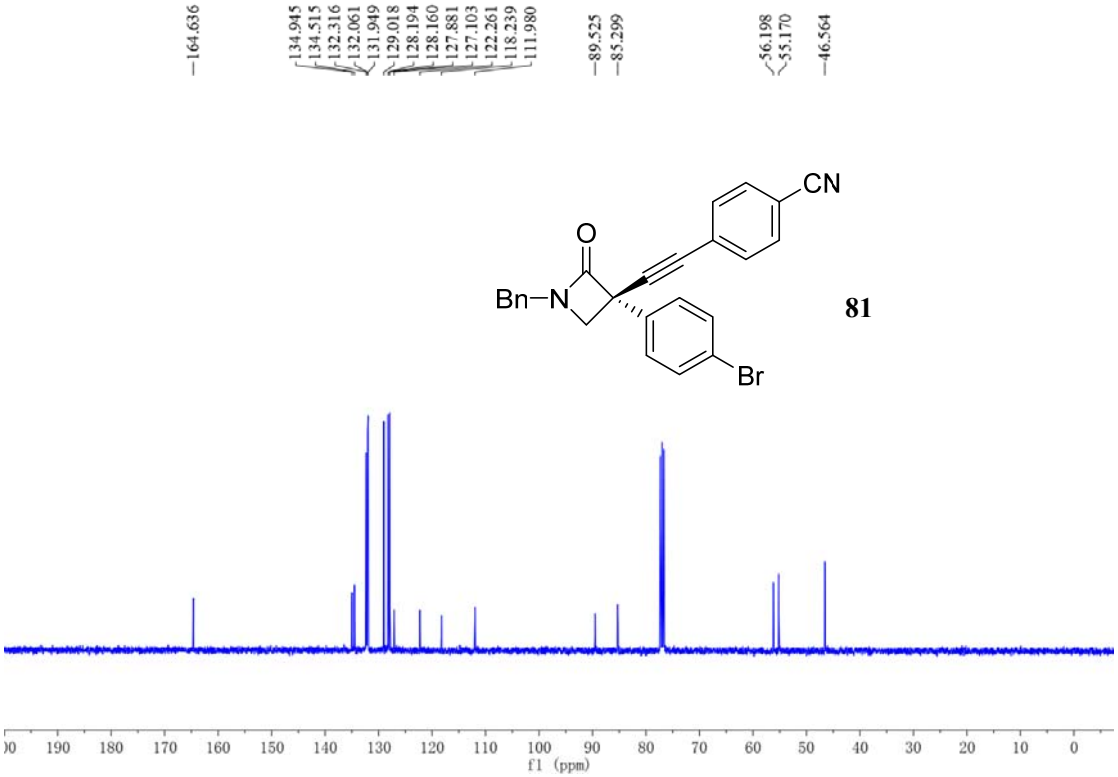
7.609
7.598
7.593
7.589
7.549
7.544
7.532
7.528
7.513
7.508
7.497
7.492
7.406
7.389
7.381
7.376
7.371
7.369
7.365
7.360
7.356
7.352
7.339
7.312
7.308
7.296
7.292
7.288
4.618
4.580
4.488
4.451
3.734
3.485
3.472
CN
O
Bn—N
Br
81
2.07
2.00
1.96
7.05
1.00
0.99
0.98
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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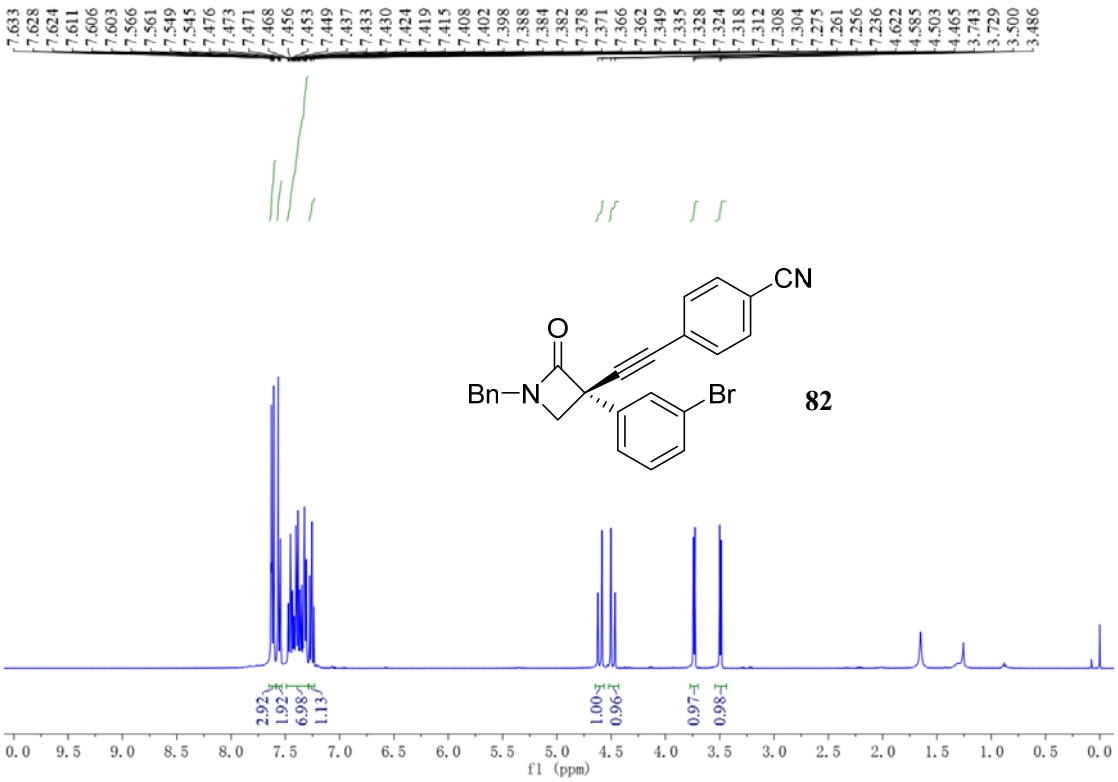
134.515
132.316
132.061
131.949
129.018
128.194
128.160
127.881
127.103
122.261
118.239
111.980
89.525
85.299
56.198
55.170
46.564
CN
O
Bn—N
Br
81
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.545
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7.468
7.456
7.453
7.449
7.437
7.433
7.430
7.424
7.419
7.415
7.408
7.402
7.398
7.388
7.384
7.382
7.378
7.371
7.366
7.362
7.349
7.335
7.328
7.324
7.318
7.312
7.308
7.304
7.275
7.261
7.256
7.236
4.622
4.585
4.503
4.465
3.743
3.729
3.500
3.486
CN
O
Bn—N
Br
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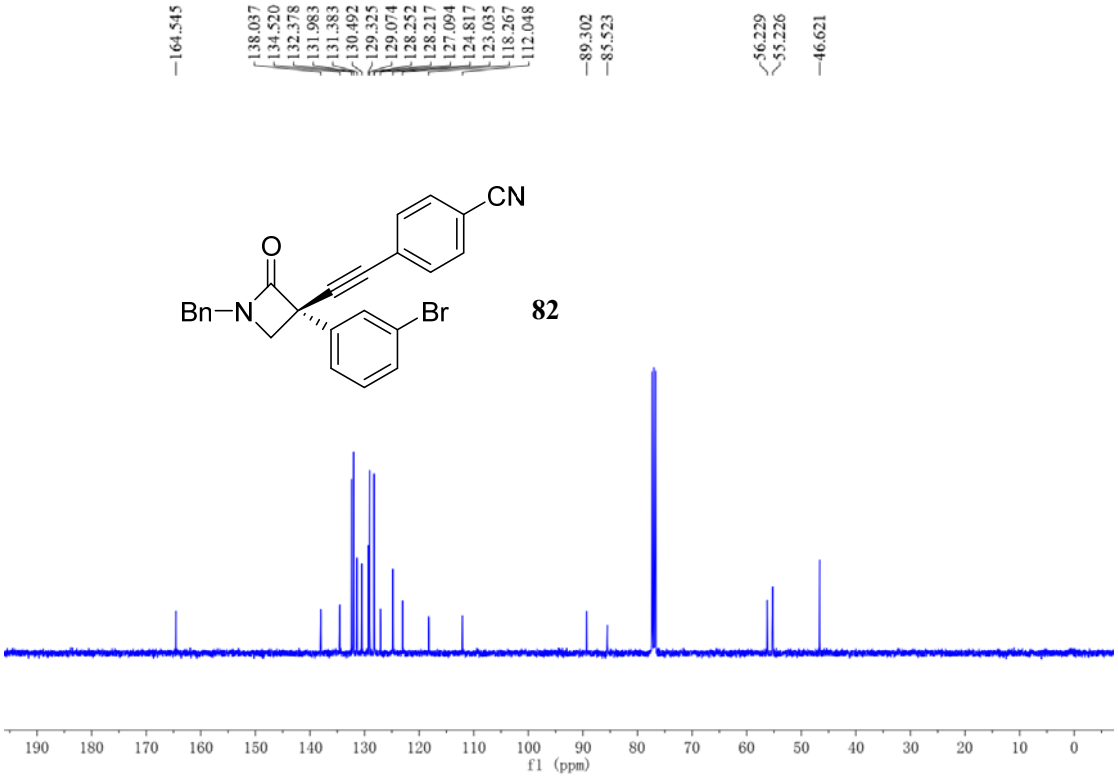
2.92
1.92
6.98
1.13
1.00
0.96
0.97
0.98
f1 (ppm)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130.492
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127.094
124.817
123.035
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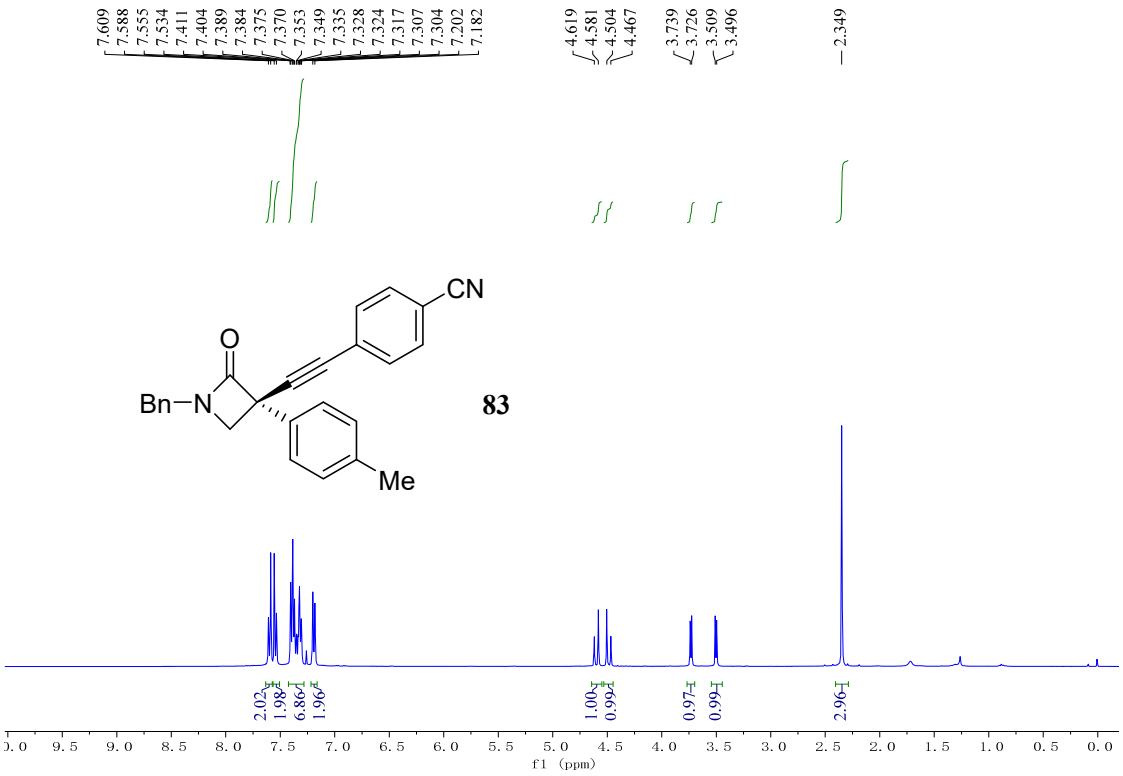
89.302
85.523
56.229
55.226
46.621
CN
O
Bn—N
Br
82
f1 (ppm)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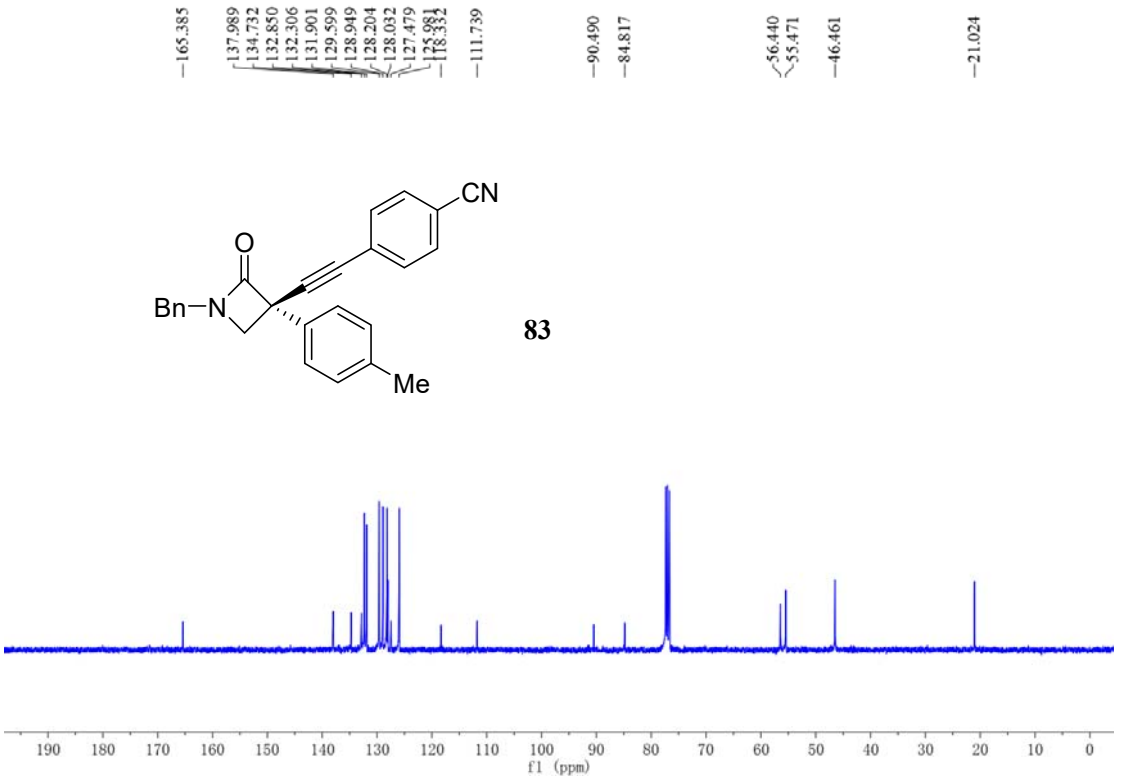
7.328
7.324
7.317
7.307
7.304
7.202
7.182
4.619
4.581
4.504
4.467
3.739
3.726
3.509
3.496
2.349
CN
O
Bn—N
Me
2.02
1.98
6.86
1.96
1.00
0.99
0.97
0.99
2.96
f1 (ppm)

83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128.949
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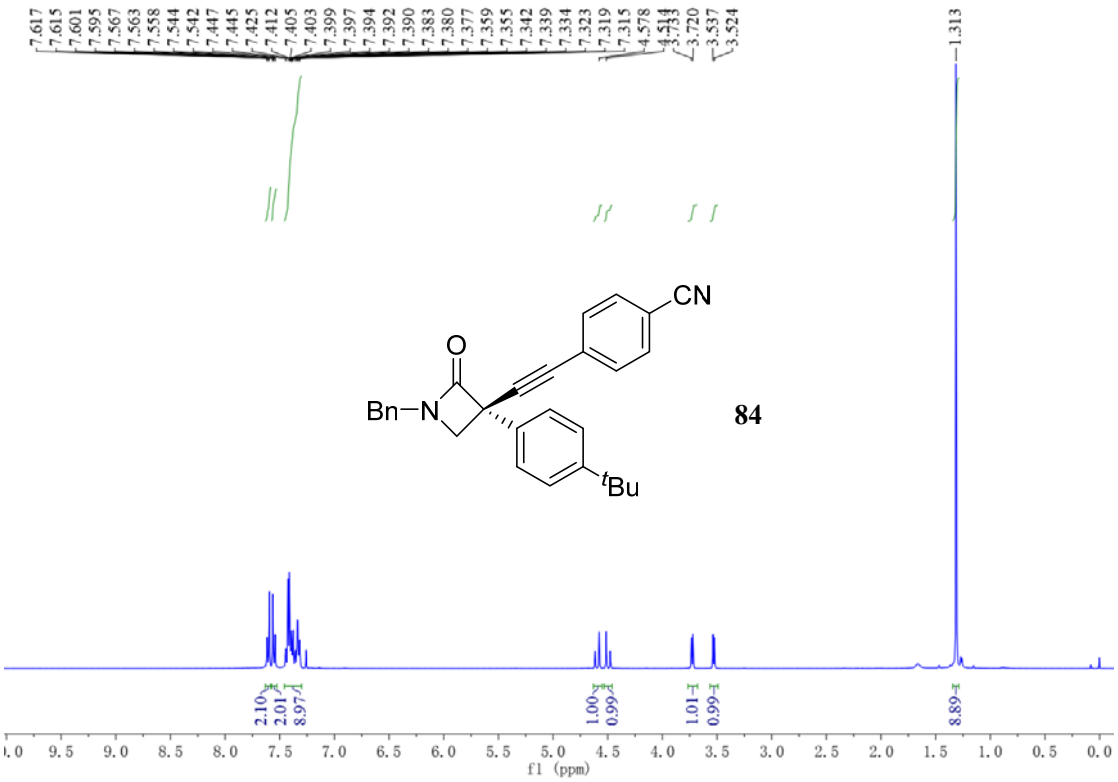
128.032
127.479
125.981
118.332
111.739
90.490
84.817
56.440
55.471
46.461
21.024
CN
O
Bn—N
Me
f1 (ppm)

83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7.595
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7.563
7.558
7.544
7.542
7.447
7.445
7.425
7.412
7.405
7.403
7.399
7.397
7.394
7.392
7.390
7.383
7.380
7.377
7.359
7.355
7.342
7.339
7.334
7.323
7.319
7.315
4.578
3.720
3.537
3.524
1.313
CN
O
Bn—N
tBu
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1.00
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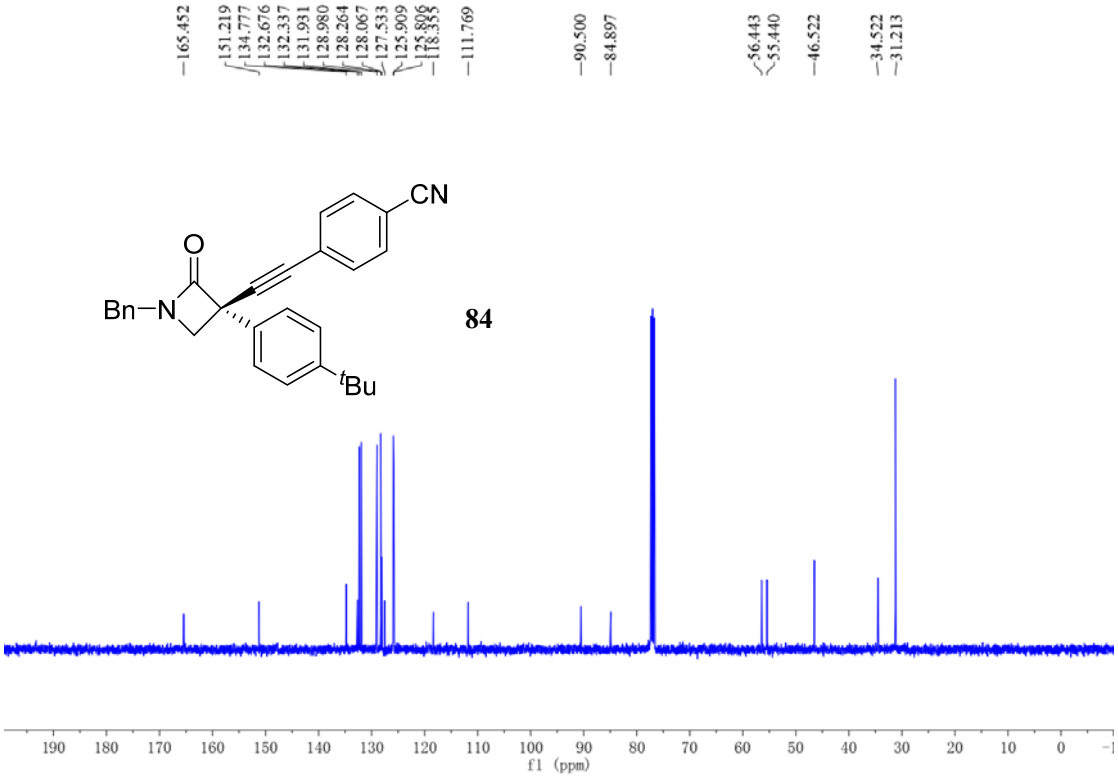
1.01
0.99
8.89
f1 (ppm)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128.980
128.264
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127.533
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118.355
111.769
90.500
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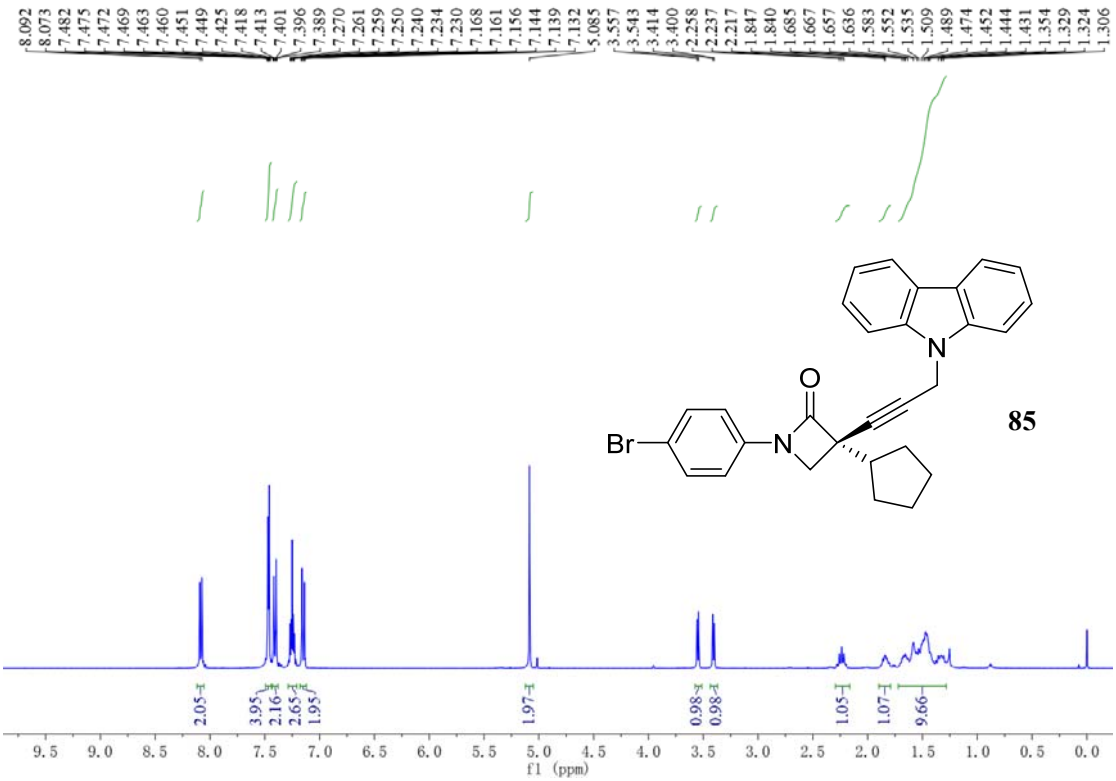
55.440
46.522
34.522
31.213
CN
O
Bn—N
tBu
84
f1 (ppm)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7.425
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7.413
7.401
7.396
7.389
7.270
7.261
7.259
7.250
7.240
7.234
7.230
7.168
7.161
7.156
7.144
7.139
7.132
5.085
3.557
3.543
3.414
3.400
2.258
2.237
2.217
1.847
1.840
1.685
1.667
1.657
1.636
1.583
1.552
1.535
1.509
1.489
1.474
1.452
1.444
1.431
1.354
1.329
1.324
1.306
Br
N
O
N
85
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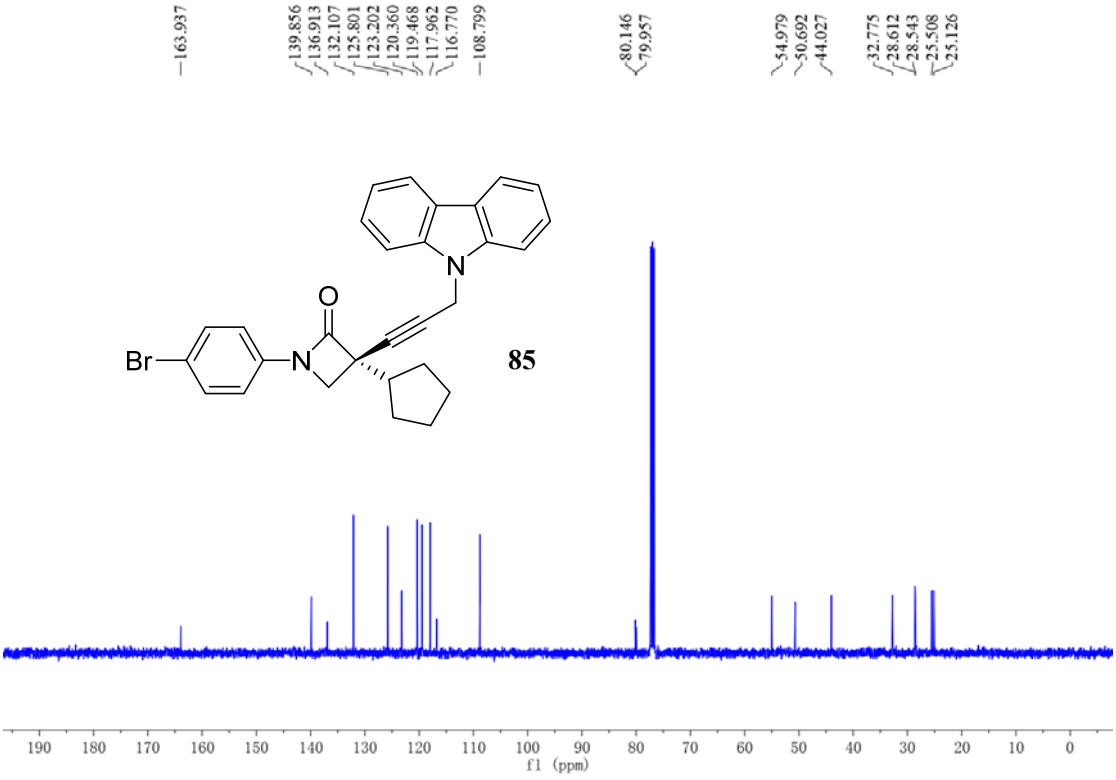
1.97
0.98
0.98
1.05
1.07
9.66
f1 (ppm)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119.468
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108.799
80.146
79.957
54.979
50.692
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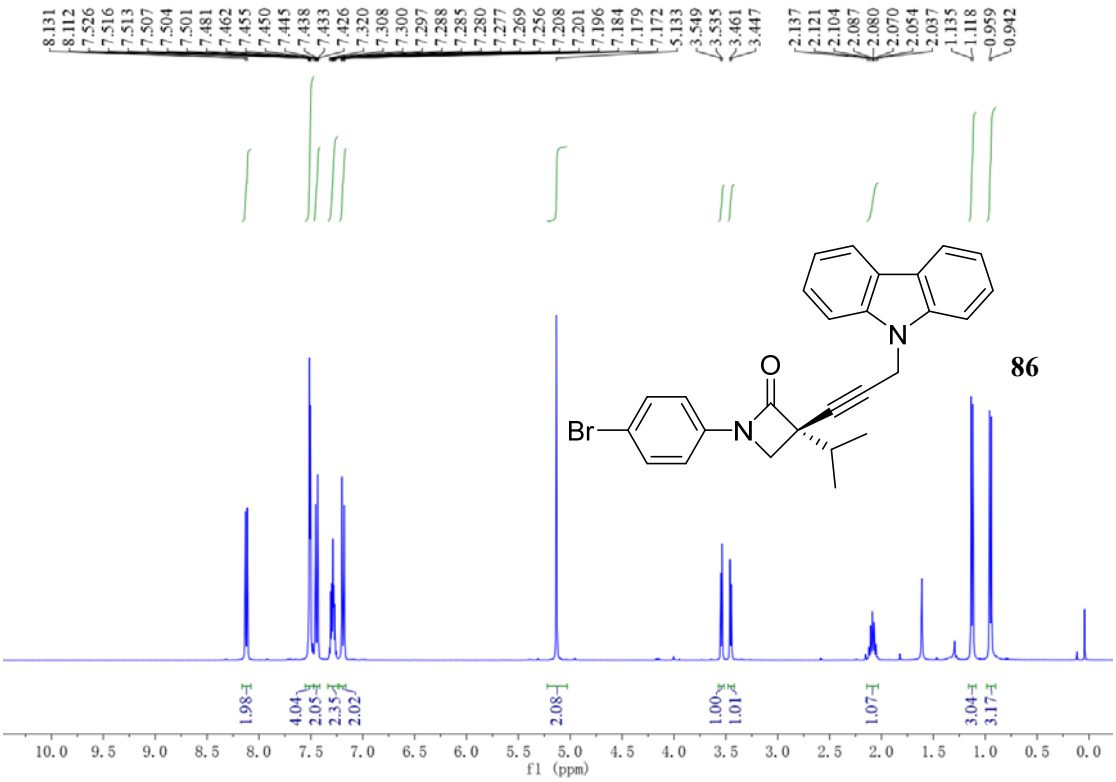
32.775
28.612
28.543
25.508
25.126
Br
N
O
N
85
f1 (ppm)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7.455
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7.445
7.438
7.433
7.426
7.320
7.308
7.300
7.297
7.288
7.285
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7.277
7.269
7.256
7.208
7.201
7.196
7.184
7.179
7.172
5.133
3.549
3.535
3.461
3.447
2.137
2.121
2.104
2.087
2.080
2.070
2.054
2.037
1.135
1.118
0.959
0.942
Br
N
O
86
1.98
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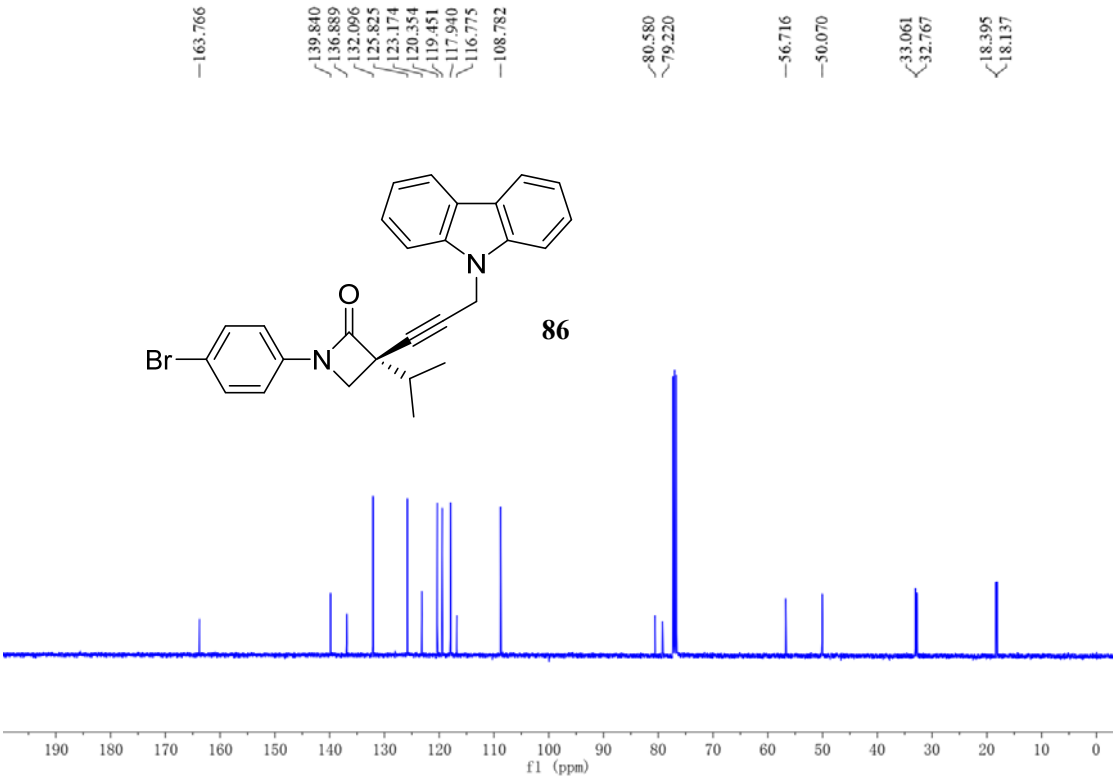
2.35
2.02
2.08
1.00
1.01
1.07
3.04
3.17
f1 (ppm)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125.825
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120.354
119.451
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116.775
108.782
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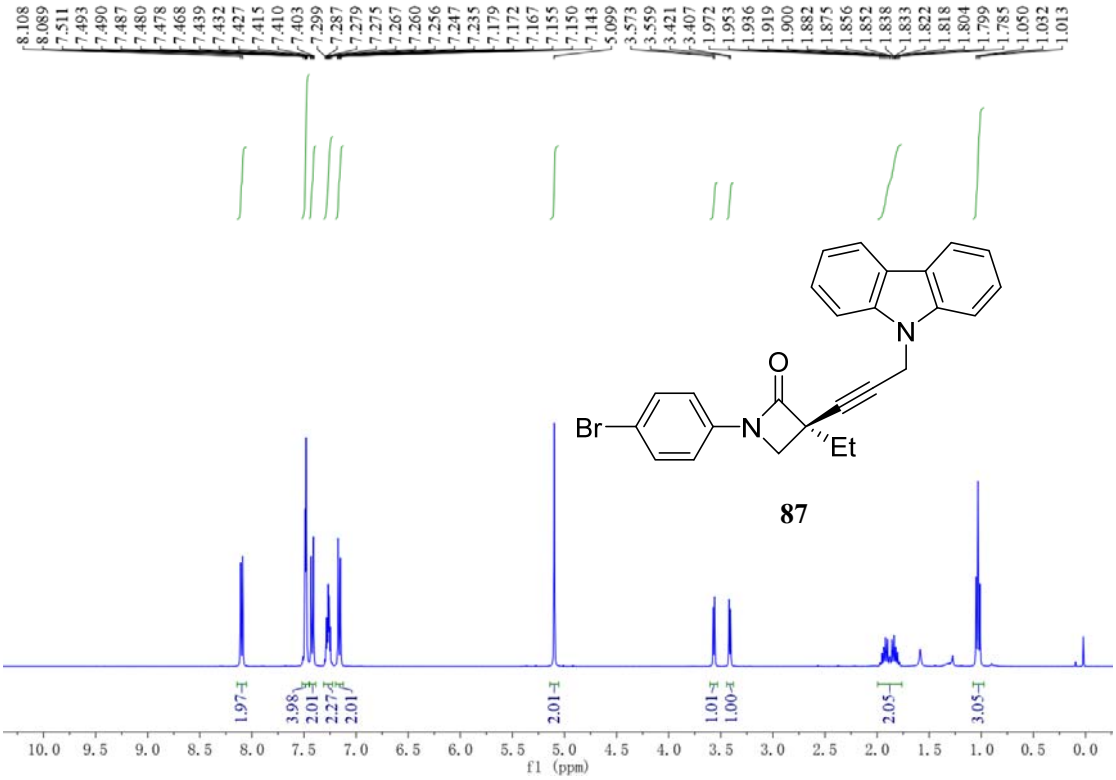
79.220
56.716
50.070
33.061
32.767
18.395
18.137
Br
N
O
86
f1 (ppm)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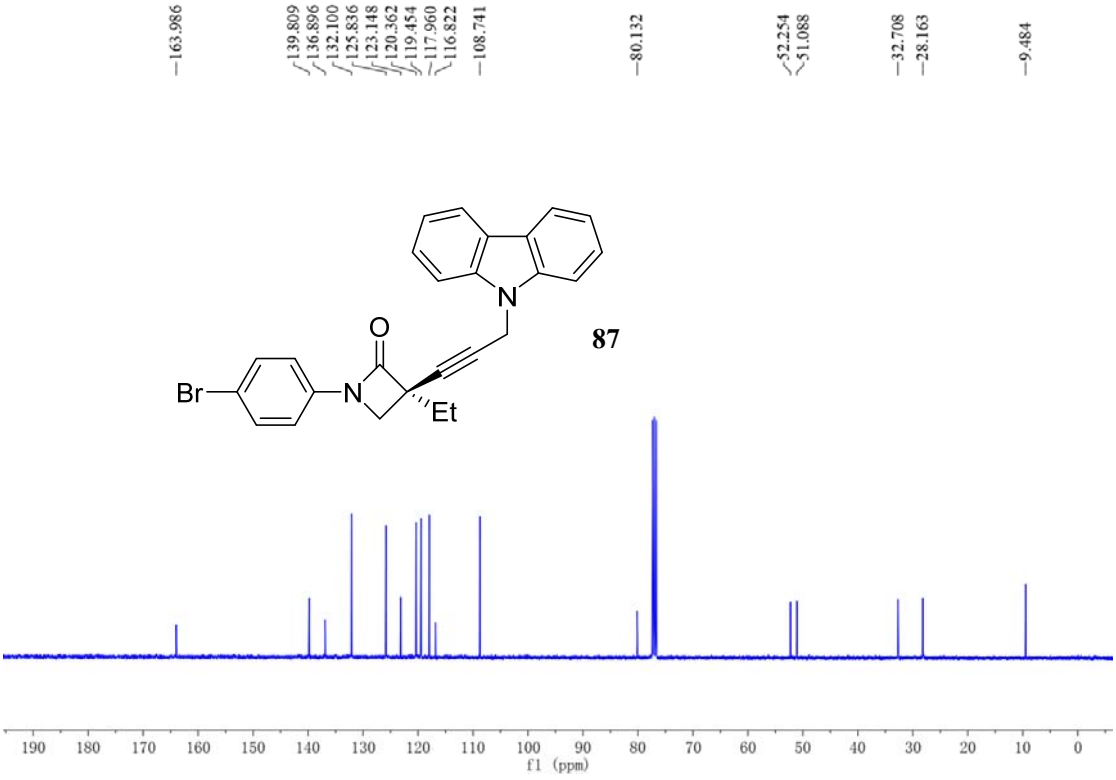
7.511
7.493
7.490
7.487
7.480
7.478
7.468
7.439
7.432
7.427
7.415
7.410
7.403
7.299
7.287
7.279
7.275
7.267
7.260
7.256
7.247
7.235
7.179
7.172
7.167
7.155
7.150
7.143
5.099
3.573
3.559
3.421
3.407
1.972
1.953
1.936
1.919
1.900
1.882
1.875
1.856
1.852
1.838
1.833
1.822
1.818
1.804
1.799
1.785
1.050
1.032
1.013
O
N
Br
N
Et
87
1.97
3.98
2.01
2.27
2.01
2.01
1.01
1.00
2.05
3.05
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
f1 (ppm)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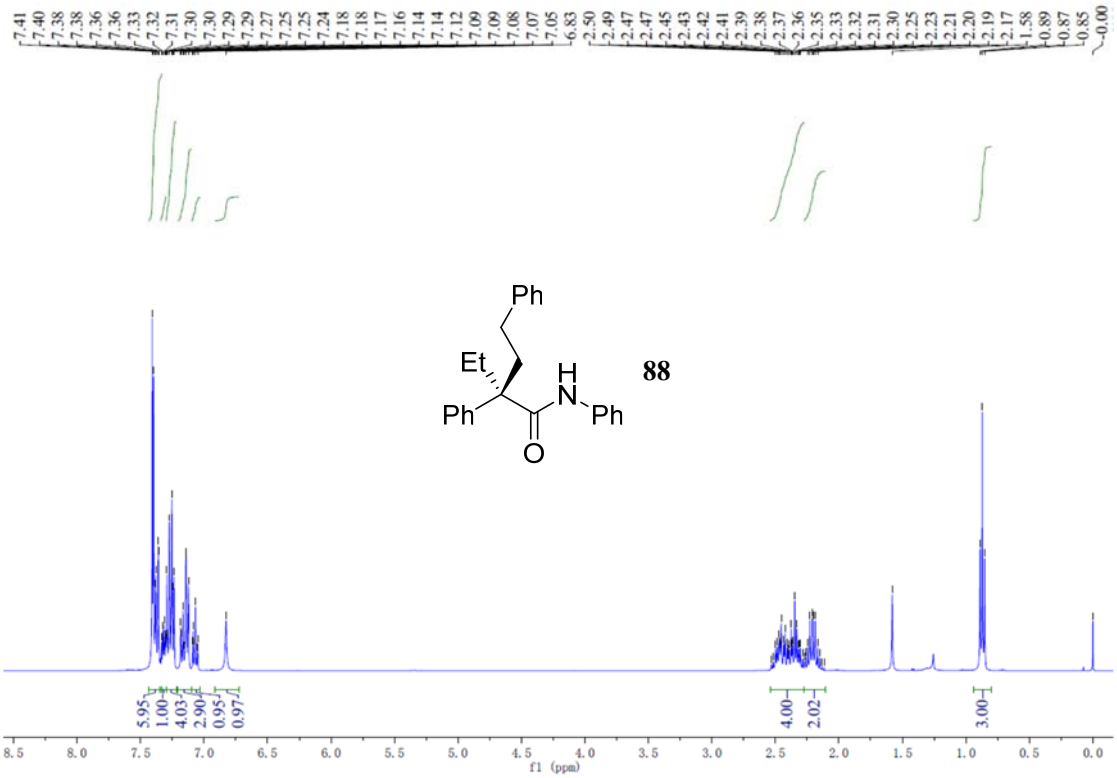
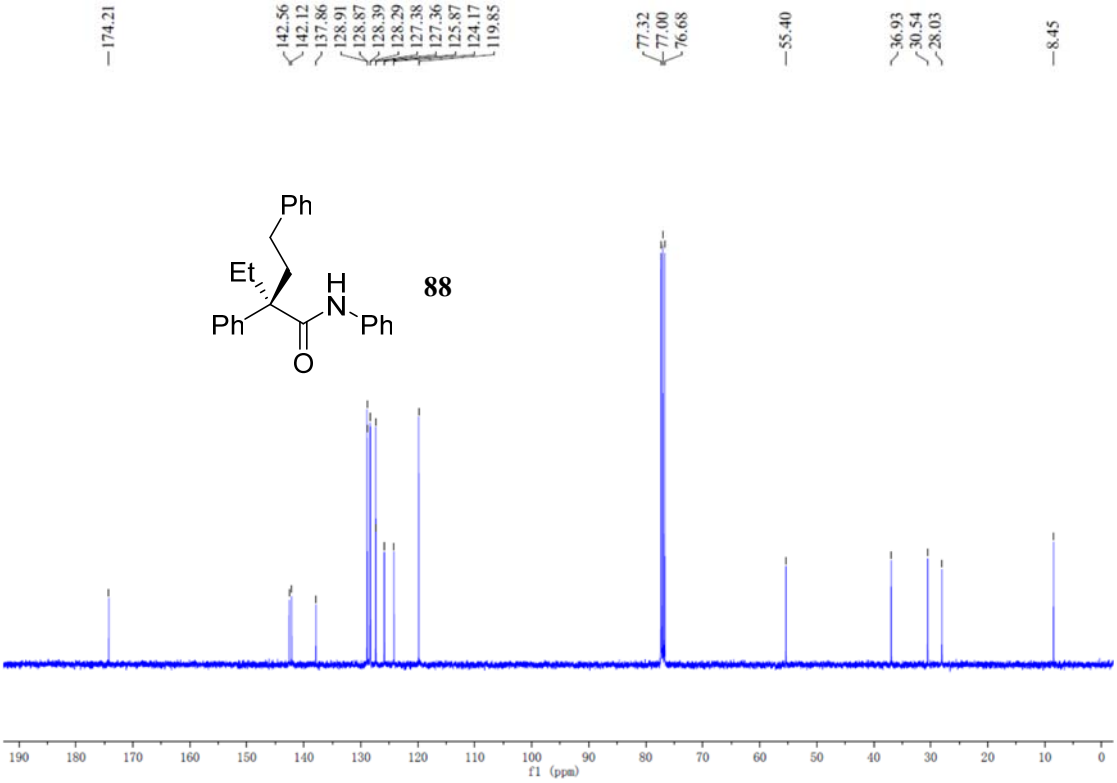
136.896
132.100
125.836
123.148
120.362
119.454
117.960
116.822
108.741
80.132
52.254
51.088
32.708
28.163
9.484
O
N
Br
N
Et
87
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Et
H
N
Ph
Ph
O
88
f1 (ppm)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Et
H
N
Ph
Ph
O
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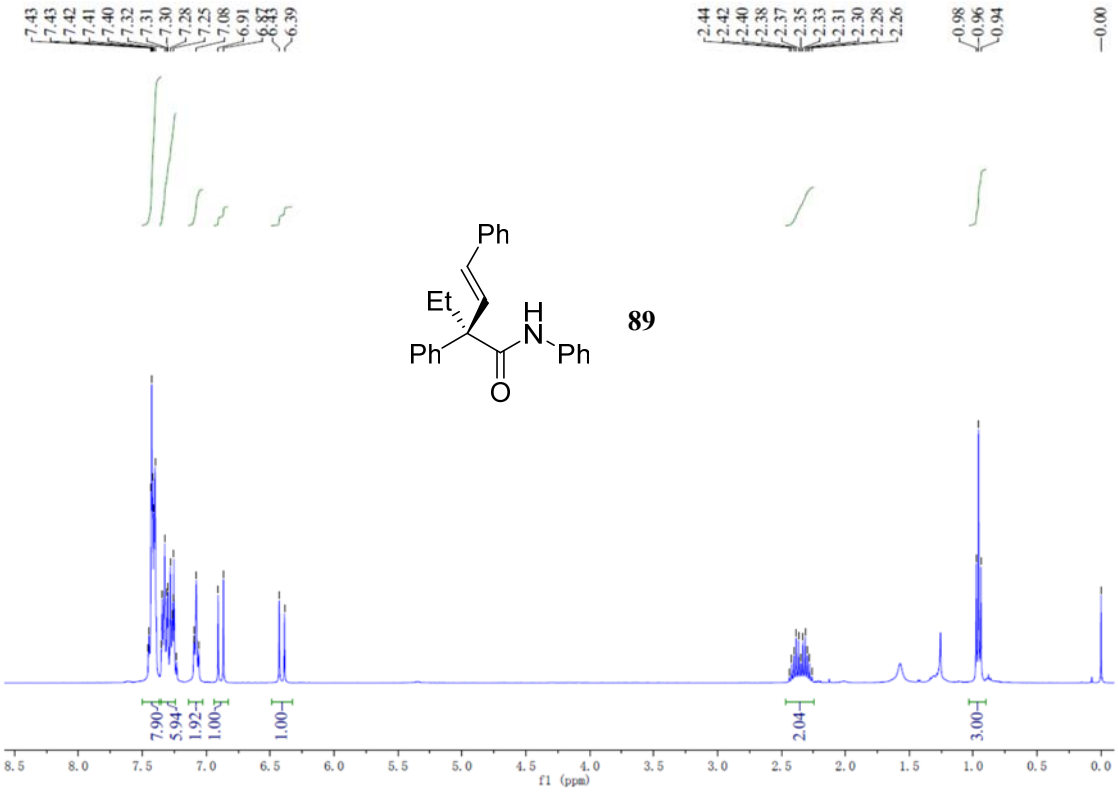
f1 (ppm)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7.43
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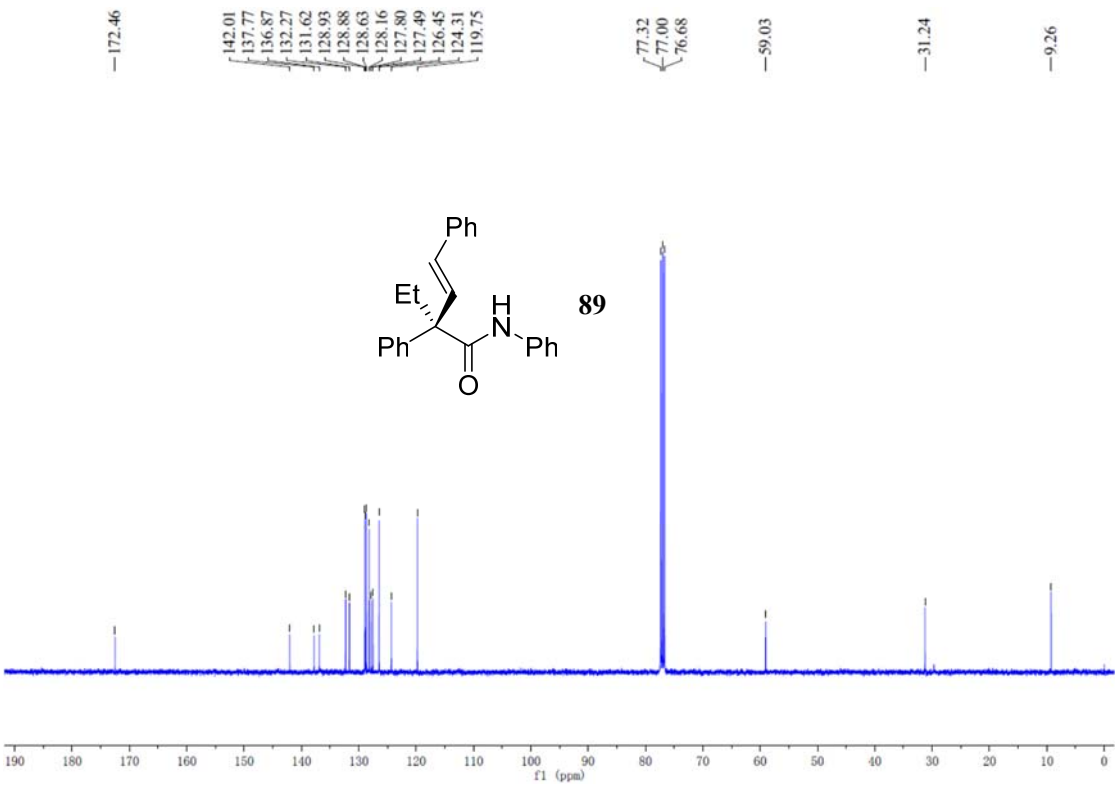
7.32
7.31
7.30
7.28
7.25
7.08
6.91
6.87
6.43
6.39
2.44
2.42
2.40
2.38
2.37
2.35
2.33
2.31
2.30
2.28
2.26
0.98
0.96
0.94
0.00
Ph
Et
Ph
H
N
Ph
O
89
7.90
5.94
1.92
1.00
1.00
2.04
3.00
f1 (ppm)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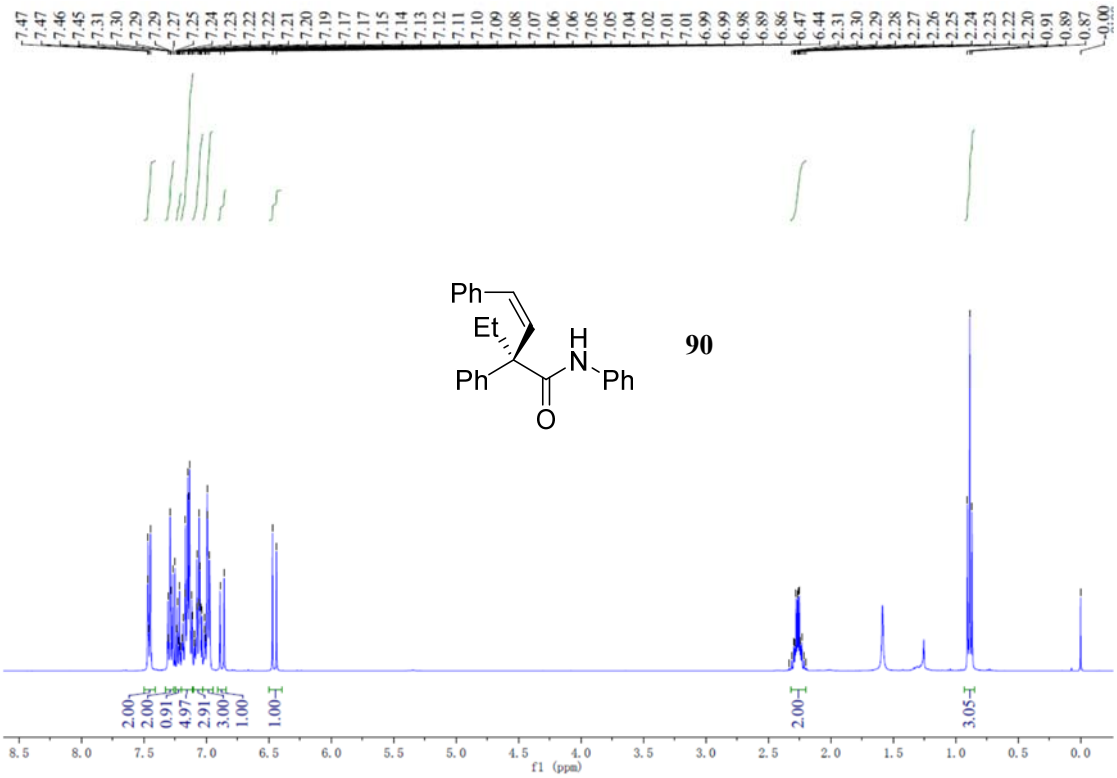
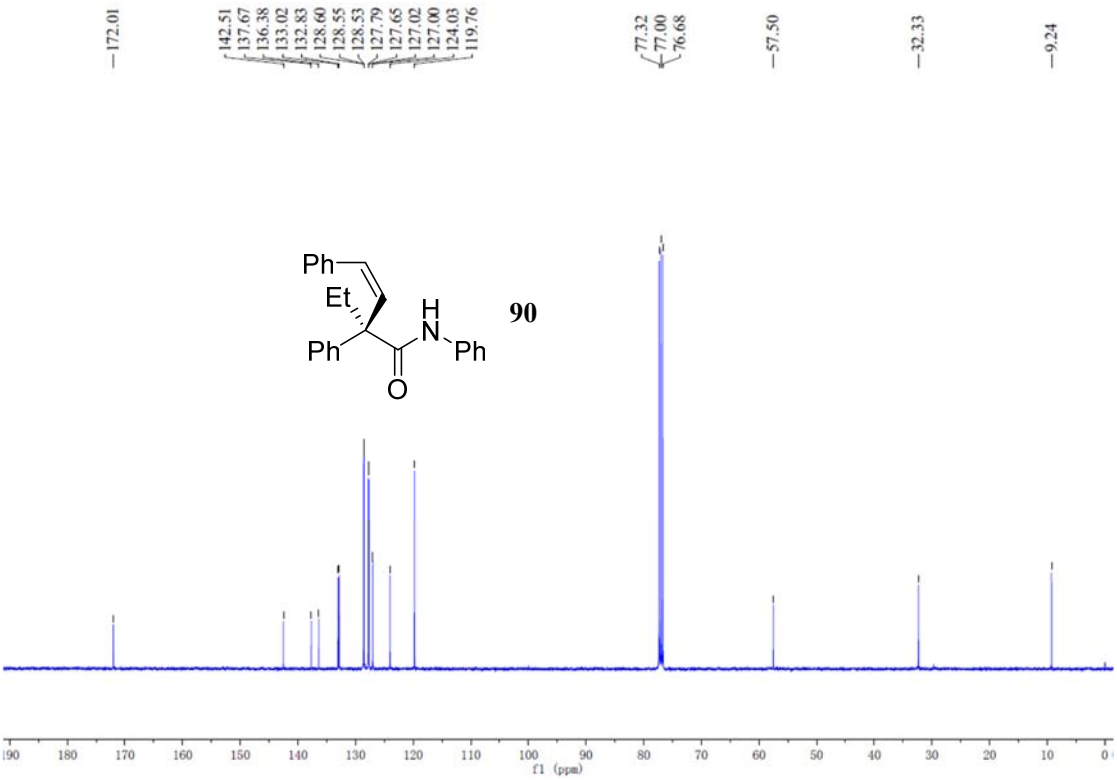
128.88
128.63
128.16
127.80
127.49
126.45
124.31
119.75
77.32
77.00
76.68
59.03
31.24
9.26
Ph
Et
Ph
H
N
Ph
O
89
f1 (ppm)


Ph
Et
Ph
H
N
Ph
O
90
f1 (ppm)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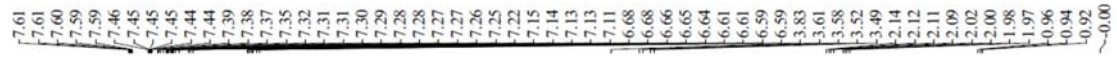
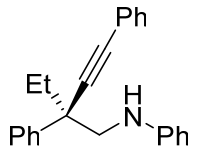
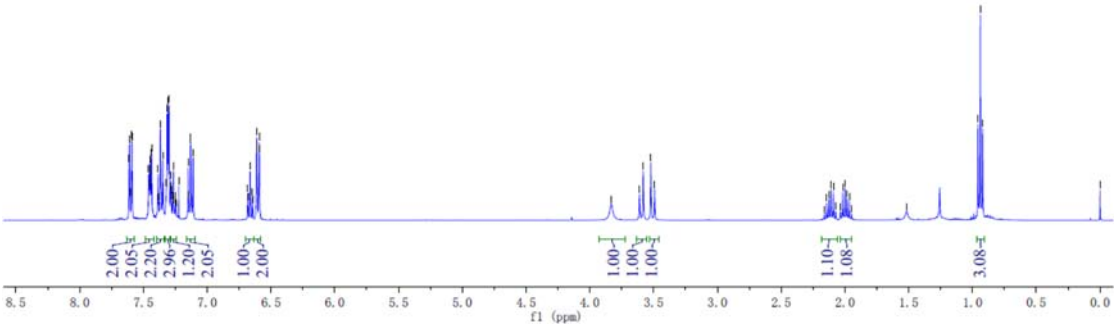
Et
Ph
H
N
Ph
O
90
f1 (ppm)




Ph
Et
H
N
Ph
Ph

91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2.05
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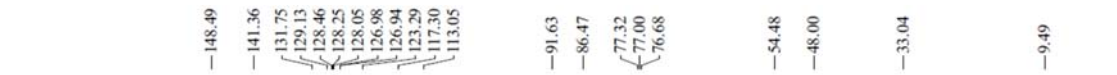
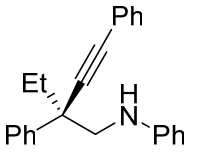
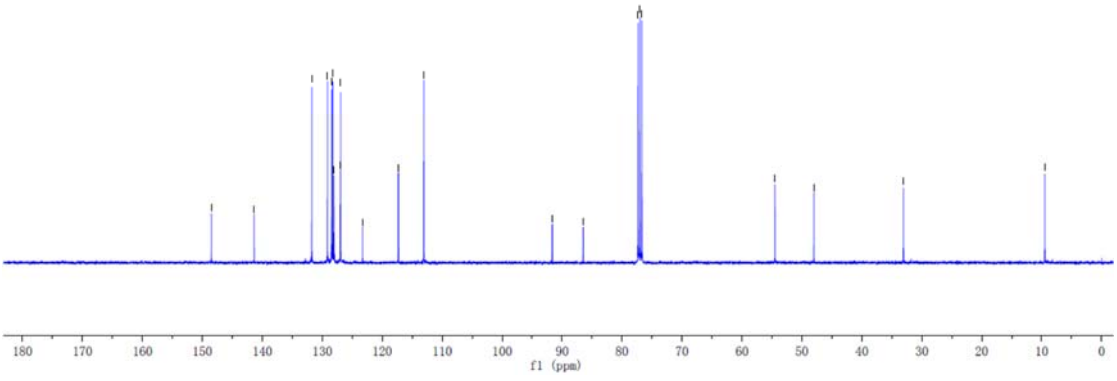
1.20
2.05
1.00
2.00
1.00
1.00
1.00
1.10
1.08
3.08
f1 (ppm)




Ph
Et
H
N
Ph
Ph

91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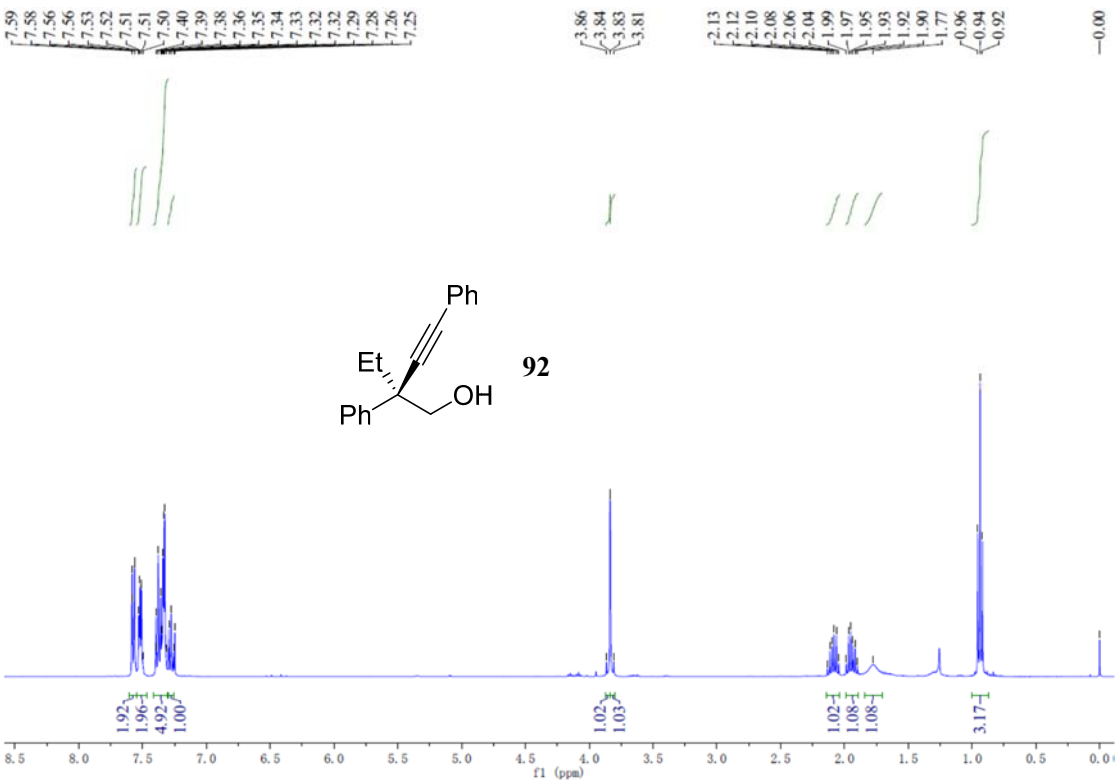
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7.56
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7.51
7.50
7.40
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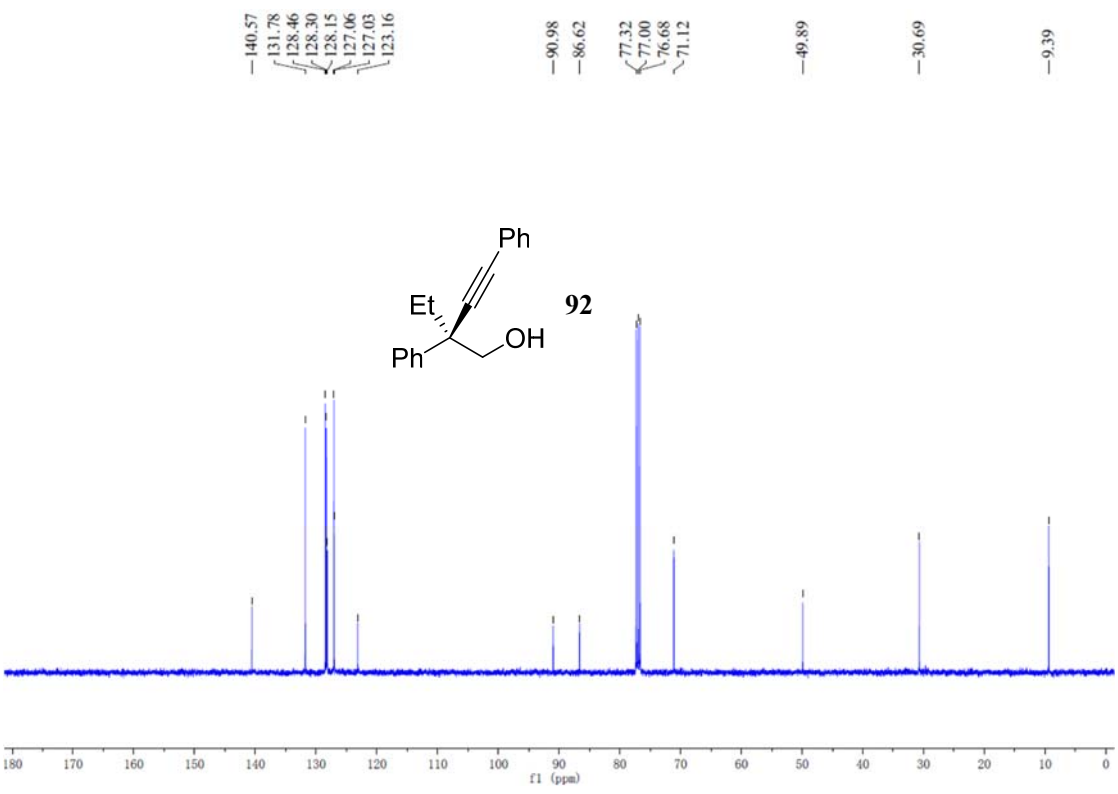
7.38
7.36
7.35
7.34
7.33
7.32
7.32
7.29
7.28
7.26
7.25
3.86
3.84
3.83
3.81
2.13
2.12
2.10
2.08
2.06
2.04
1.99
1.97
1.95
1.93
1.92
1.90
1.77
0.96
0.94
0.92
0.00
Ph
Et
OH
Ph
92
1.92
1.96
4.92
1.00
1.02
1.03
1.02
1.08
1.08
3.17
f1 (ppm)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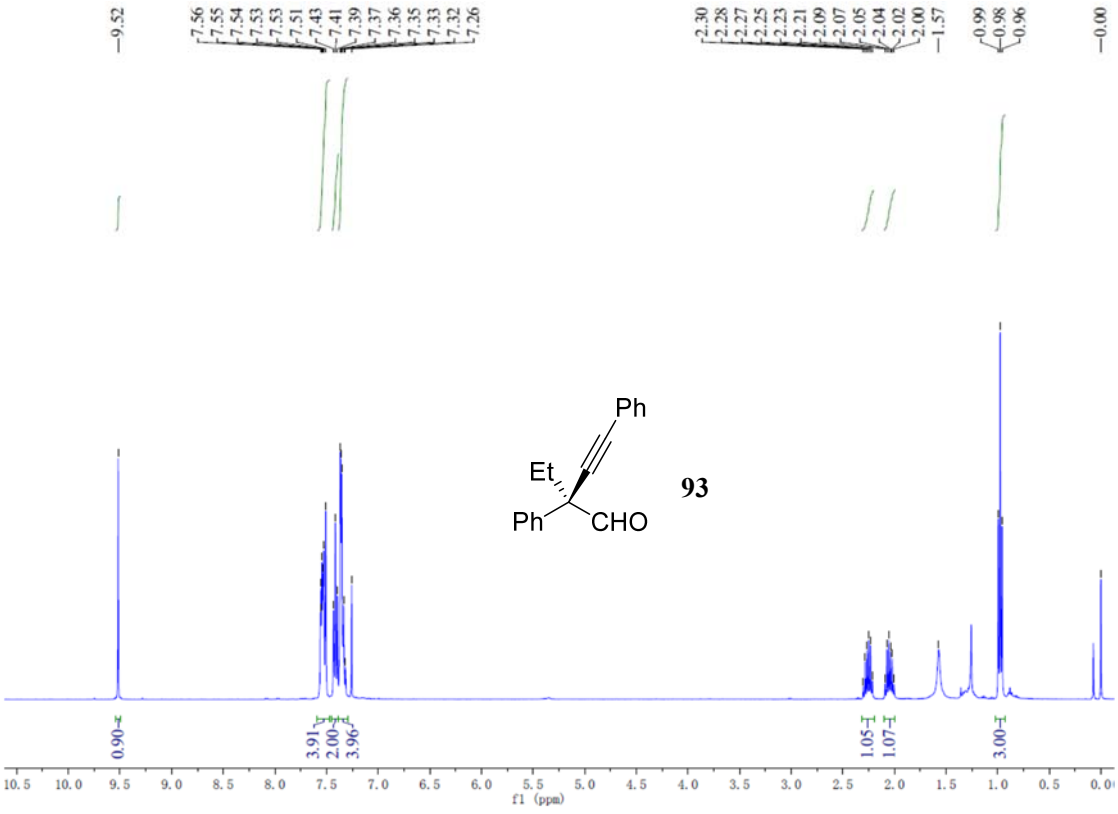
131.78
128.46
128.30
128.15
127.06
127.03
123.16
90.98
86.62
77.32
77.00
76.68
71.12
49.89
30.69
9.39
Ph
Et
OH
Ph
92
f1 (ppm)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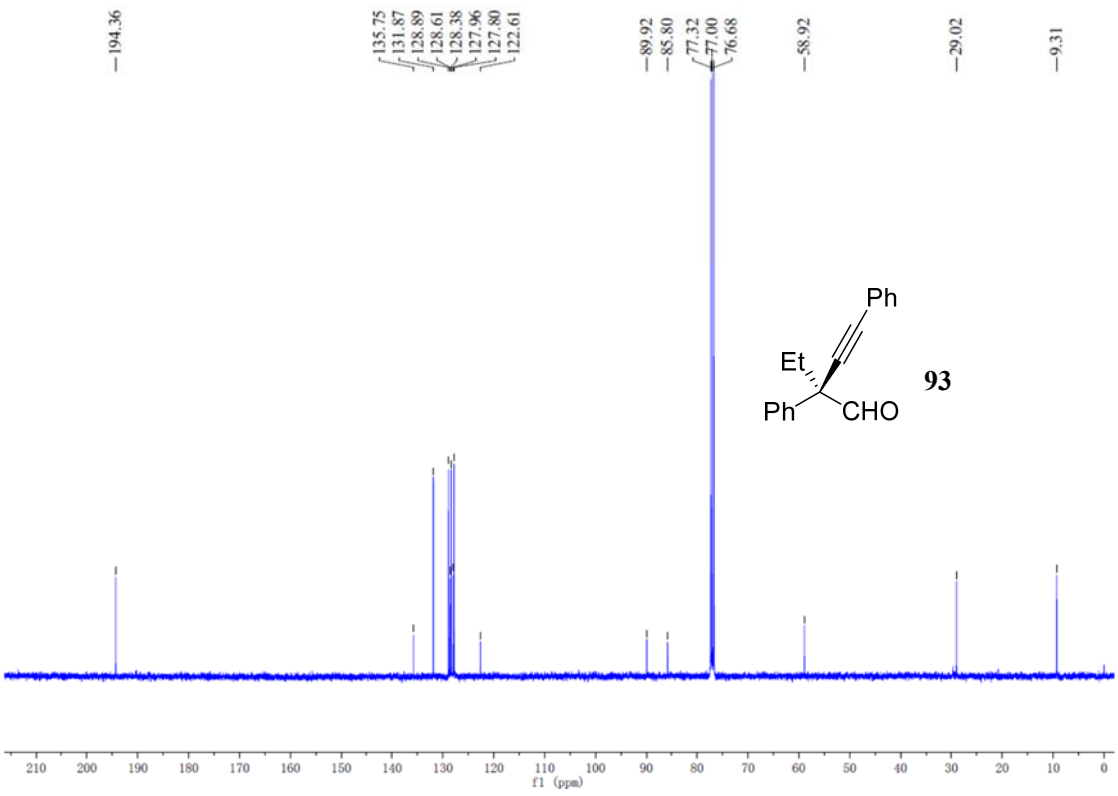
7.55
7.54
7.53
7.53
7.51
7.43
7.41
7.39
7.37
7.36
7.35
7.33
7.32
7.26
2.30
2.28
2.27
2.25
2.23
2.21
2.09
2.07
2.05
2.04
2.02
2.00
1.57
0.99
0.98
0.96
0.00
Ph
Et
Ph
CHO
93
0.90
3.91
2.00
3.96
1.05
1.07
3.00
f1 (ppm)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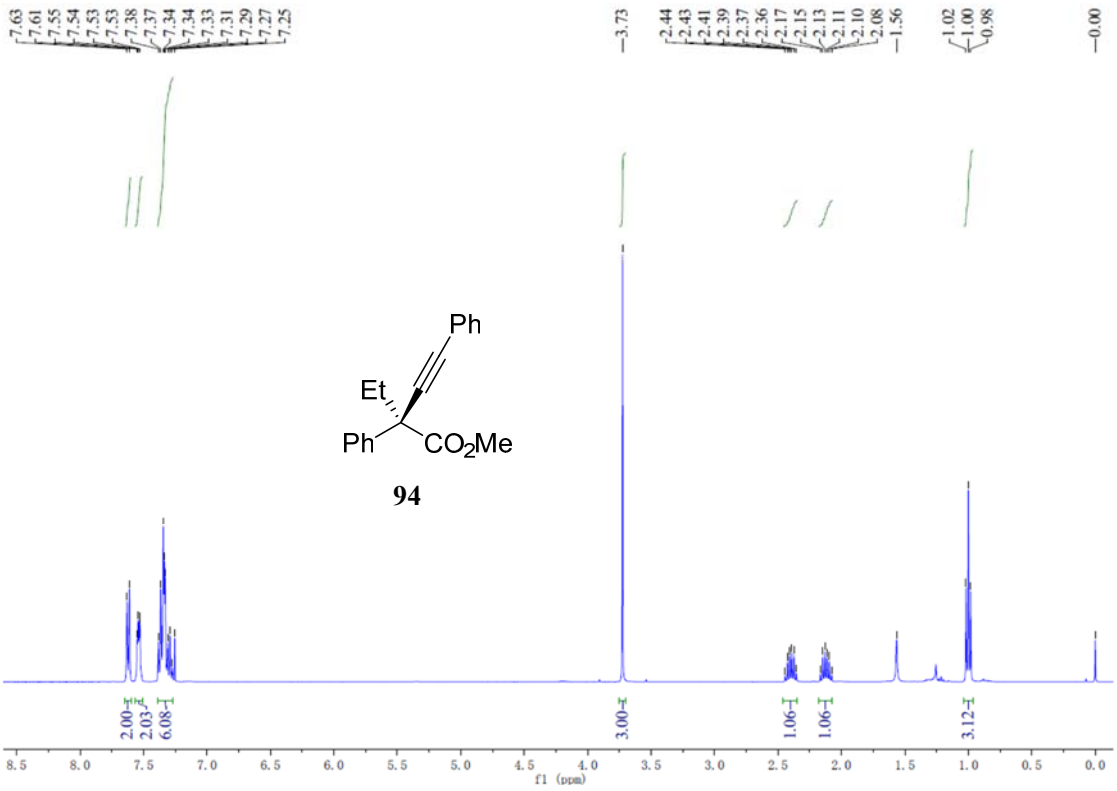
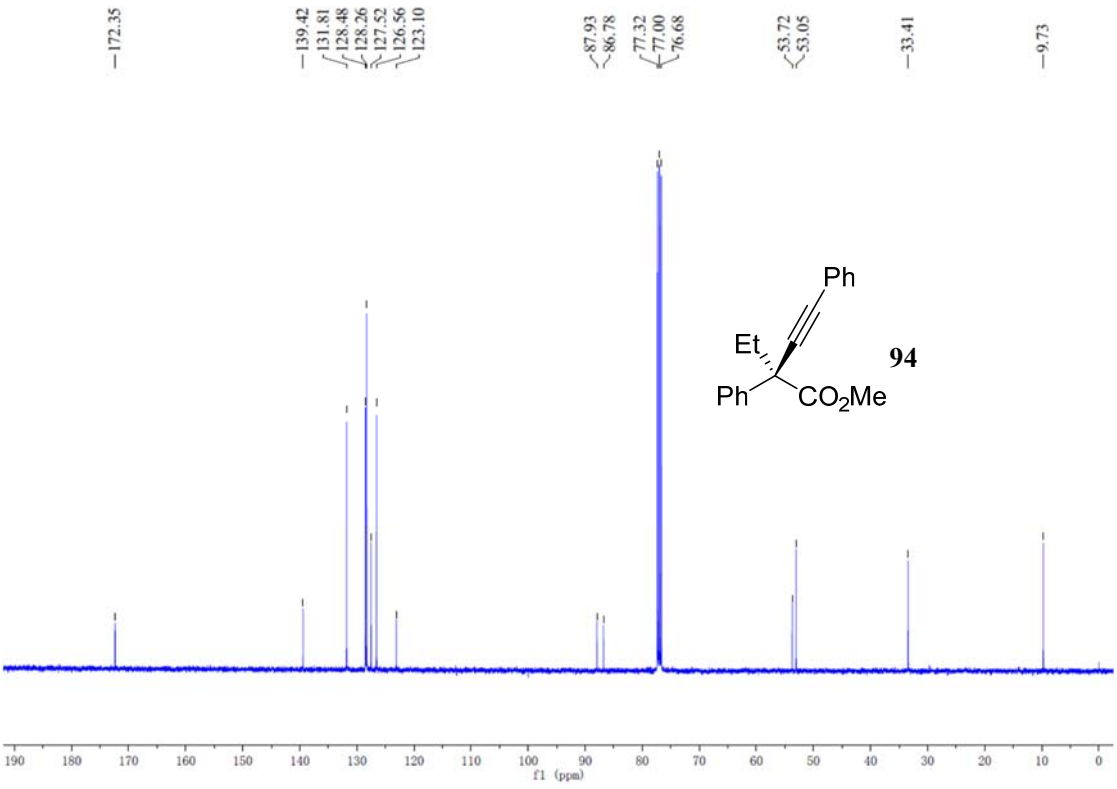
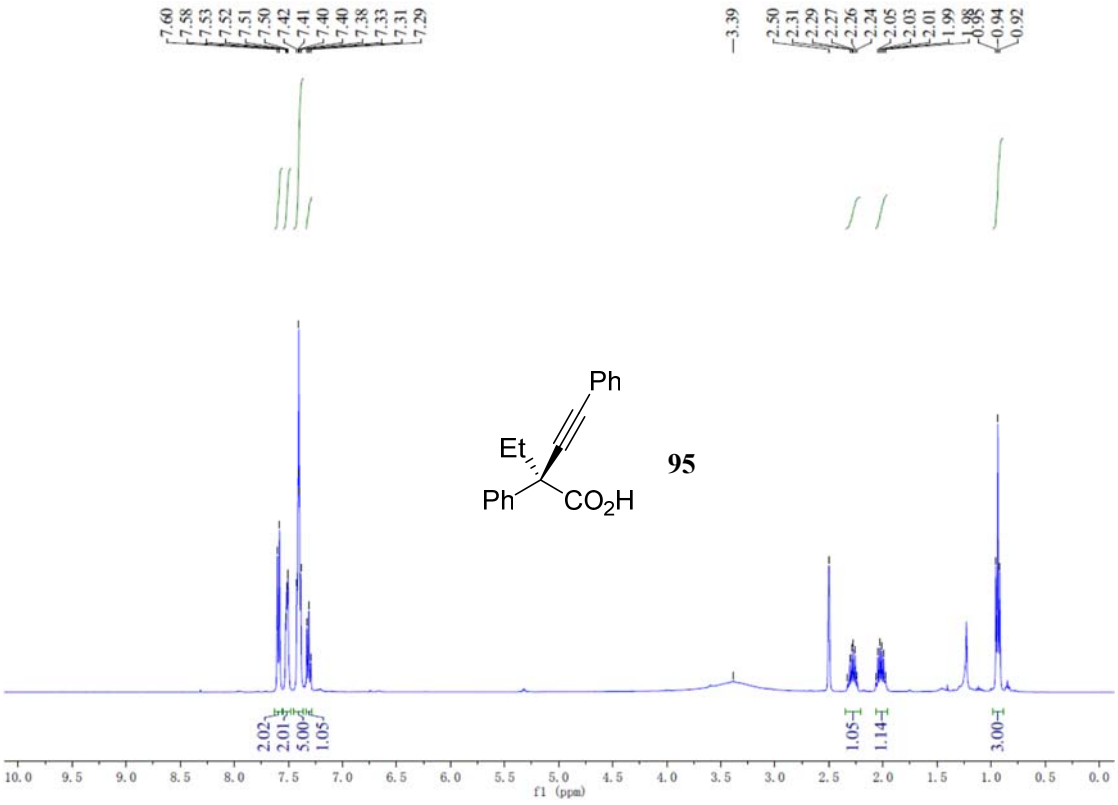
128.89
128.61
128.38
127.96
127.80
122.61
89.92
85.80
77.32
77.00
76.68
58.92
29.02
9.31
Ph
Et
Ph
CHO
93
f1 (ppm)


Ph
Et
Ph
CO2Me
94
f1 (ppm)


Ph
Et
Ph
CO2Me
94
f1 (ppm)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7.50
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7.41
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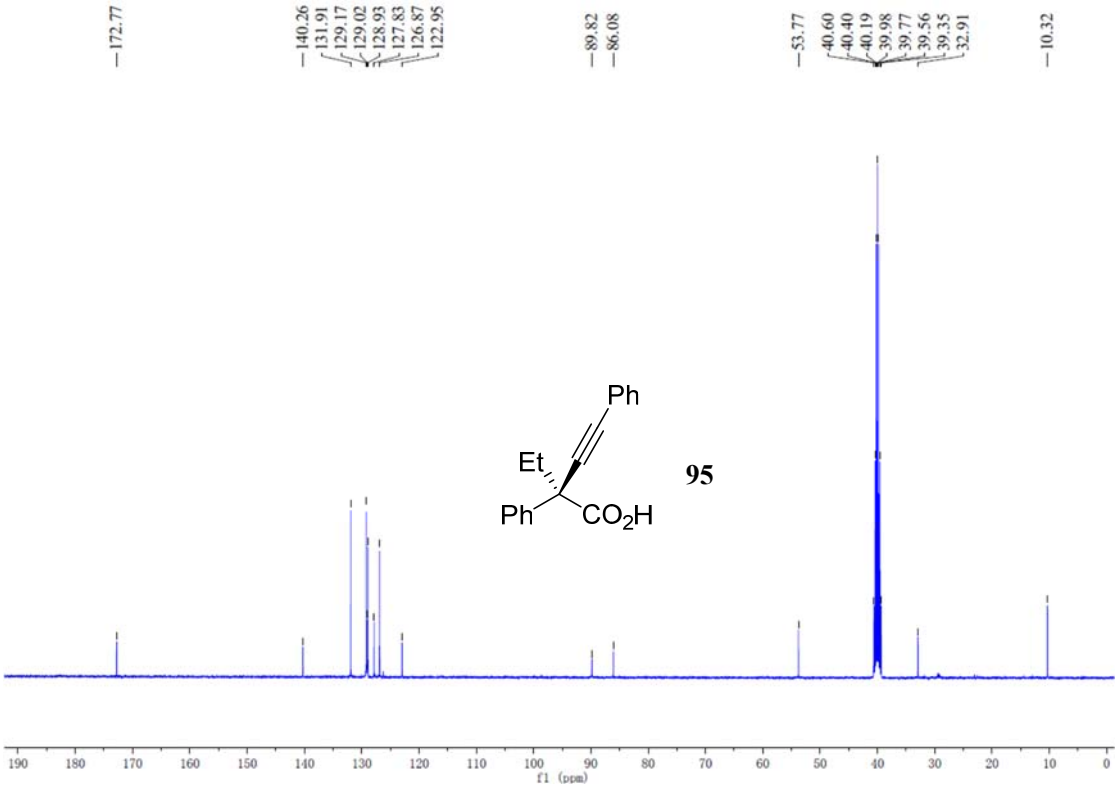
7.40
7.38
7.33
7.31
7.29
3.39
2.50
2.31
2.29
2.27
2.26
2.24
2.05
2.03
2.01
1.99
1.98
0.96
0.94
0.92
Ph
Et
Ph
CO2H
95
2.02
2.01
5.00
1.05
1.05
1.14
3.00
f1 (ppm)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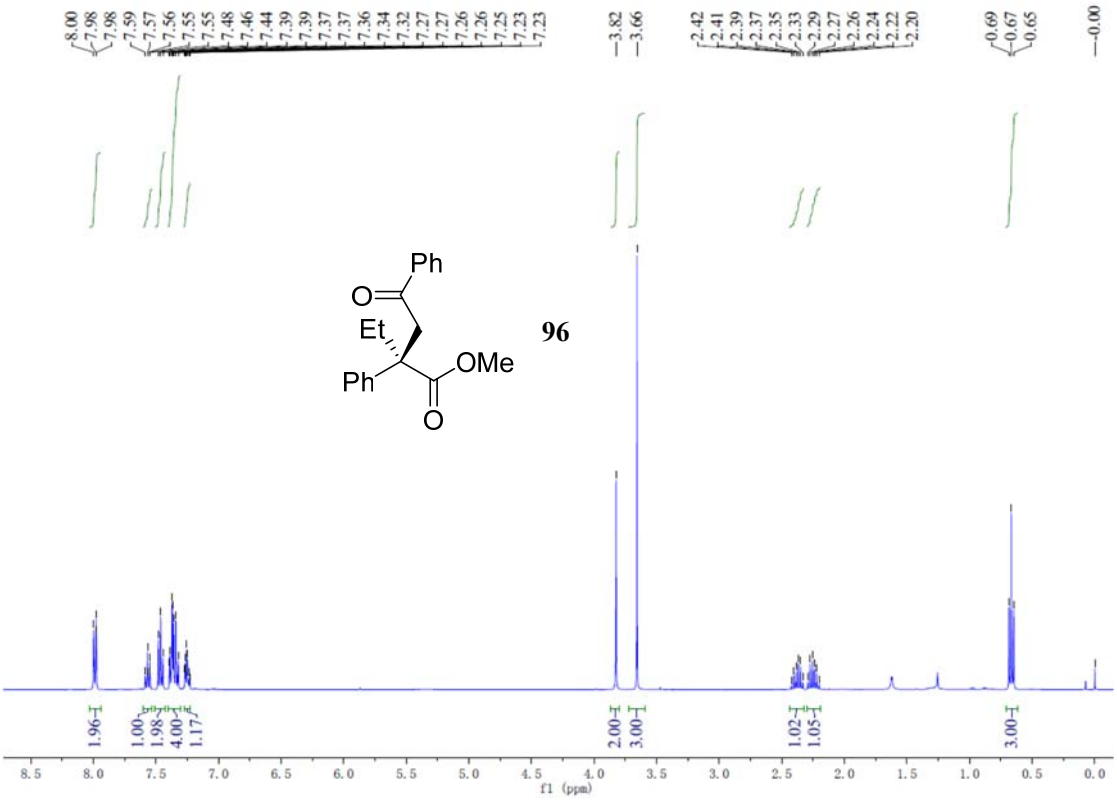
140.26
131.91
129.17
129.02
128.93
127.83
126.87
122.95
89.82
86.08
53.77
40.60
40.40
40.19
39.98
39.77
39.56
39.35
32.91
10.32
Ph
Et
Ph
CO2H
95
f1 (ppm)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7.56
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7.55
7.48
7.46
7.44
7.39
7.39
7.37
7.37
7.36
7.34
7.32
7.27
7.27
7.26
7.26
7.25
7.23
7.23
3.82
3.66
2.42
2.41
2.39
2.37
2.35
2.33
2.29
2.27
2.26
2.24
2.22
2.20
0.69
0.67
0.65
0.00
Ph
O
Et
Ph
OMe
O
96
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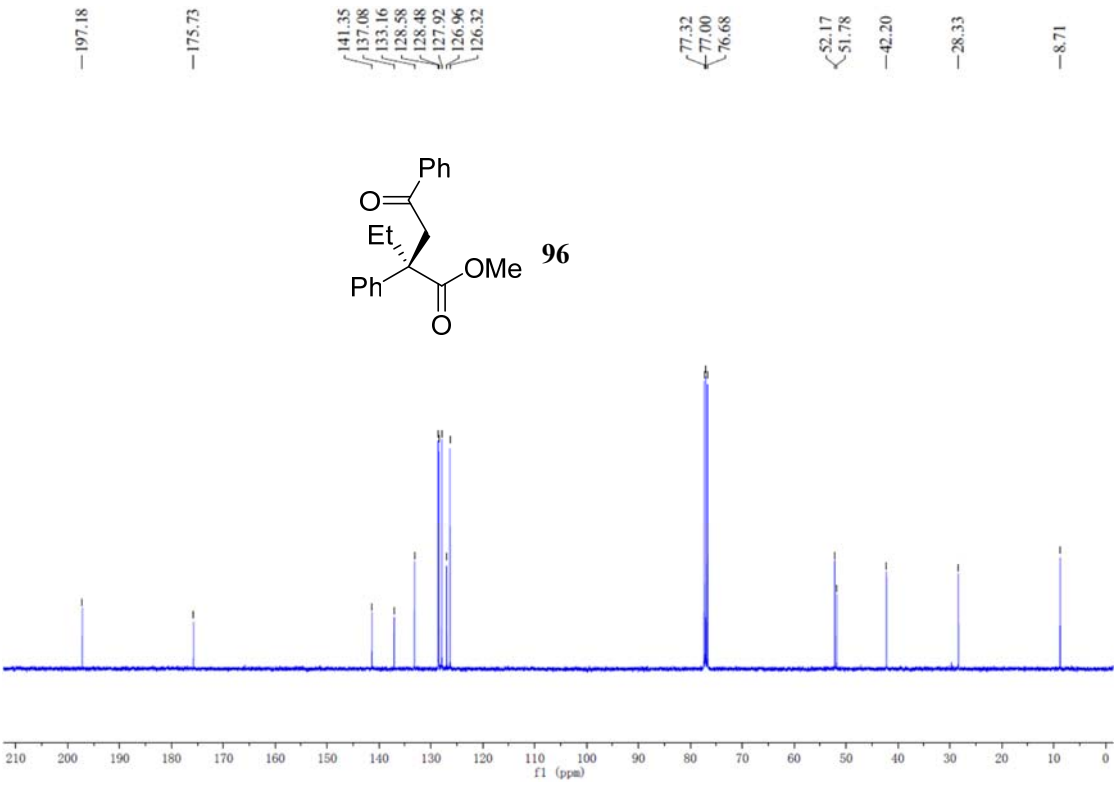
1.00
1.98
4.00
1.17
2.00
3.00
1.02
1.05
3.00
f1 (ppm)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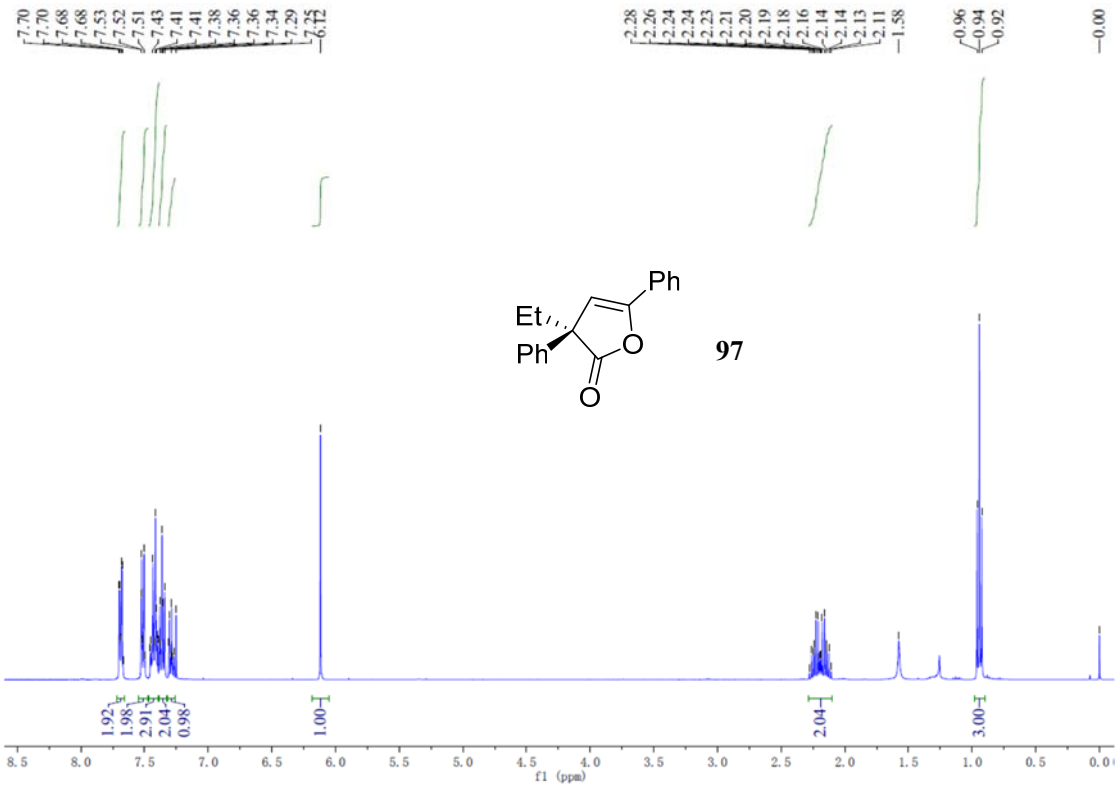
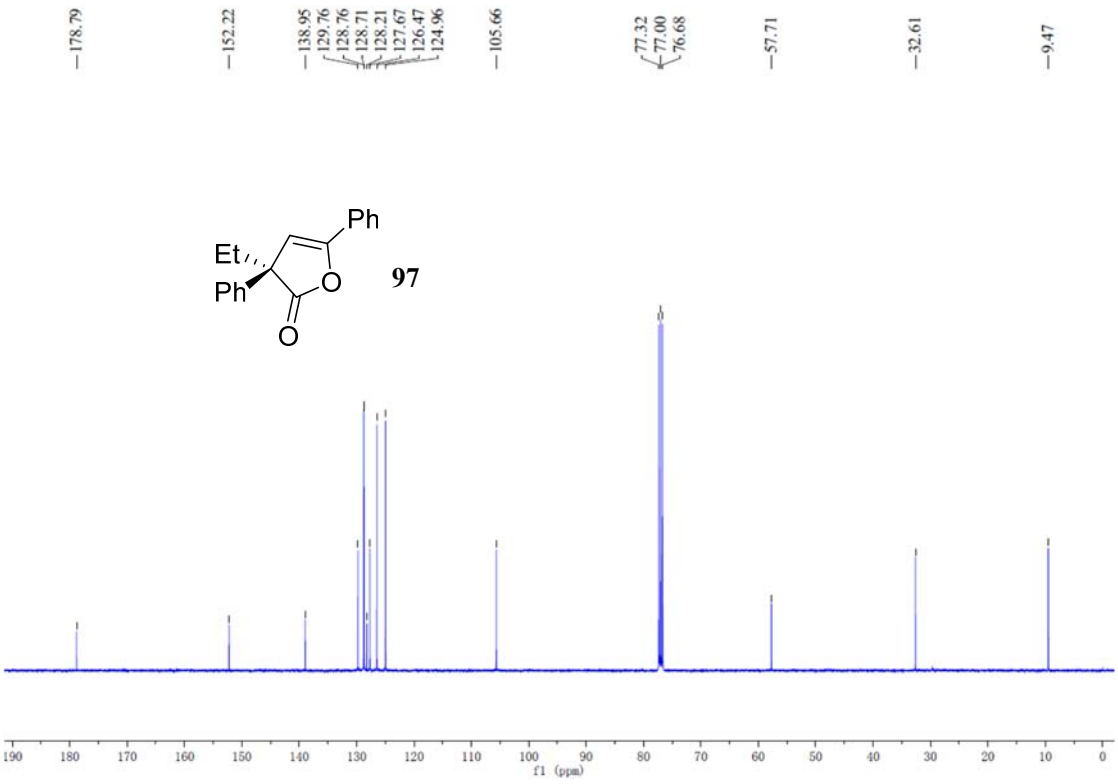
128.58
128.48
127.92
126.96
126.32
77.32
77.00
76.68
52.17
51.78
42.20
28.33
8.71
Ph
O
Et
Ph
OMe
O
96
f1 (ppm)


Et
Ph
Ph
O
O
97
f1 (ppm)


Et
Ph
Ph
O
O
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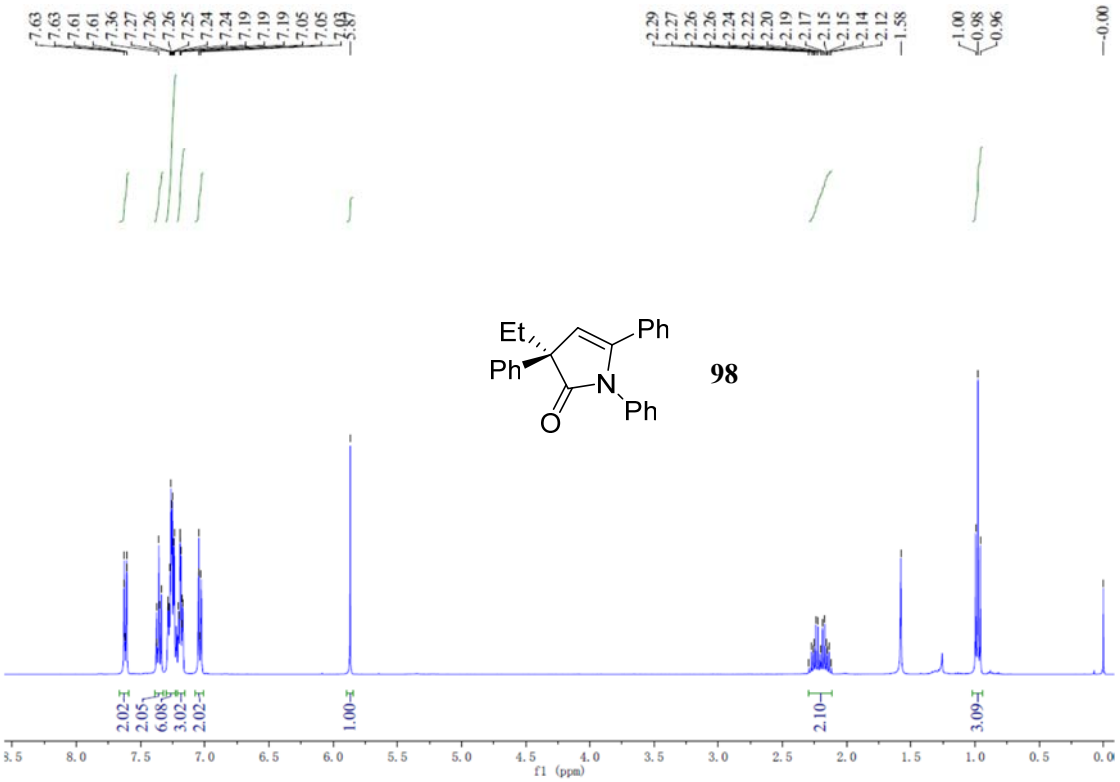
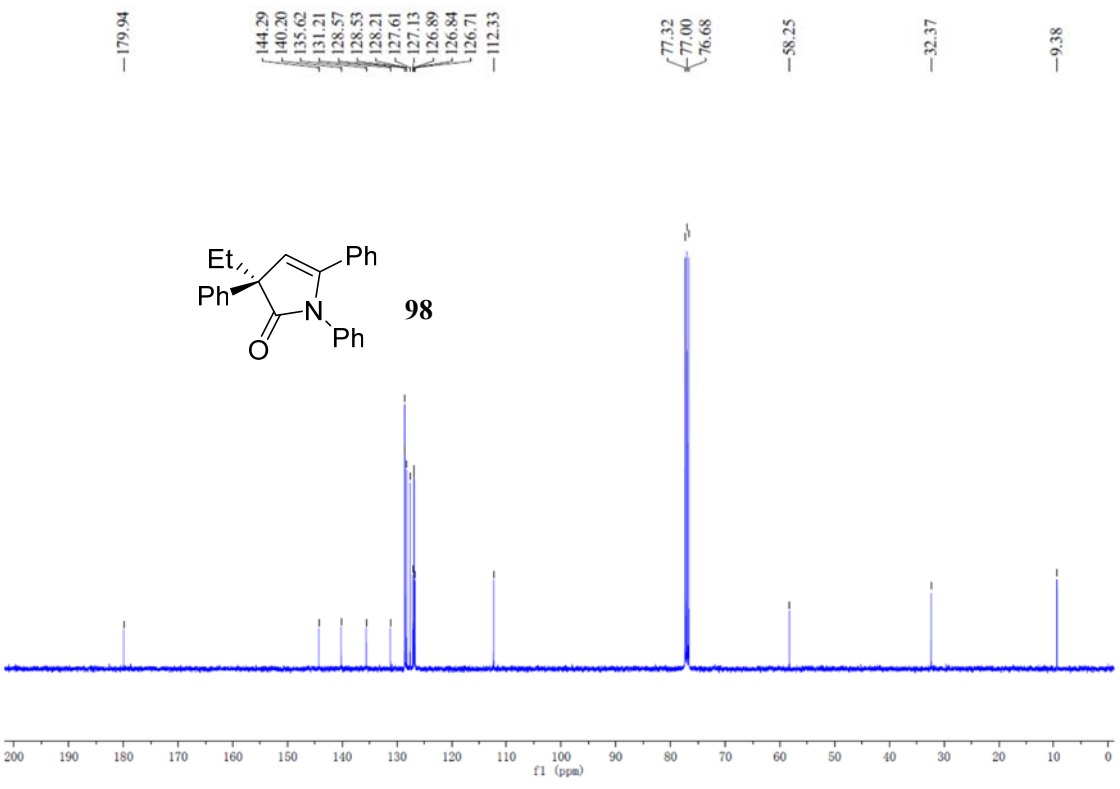
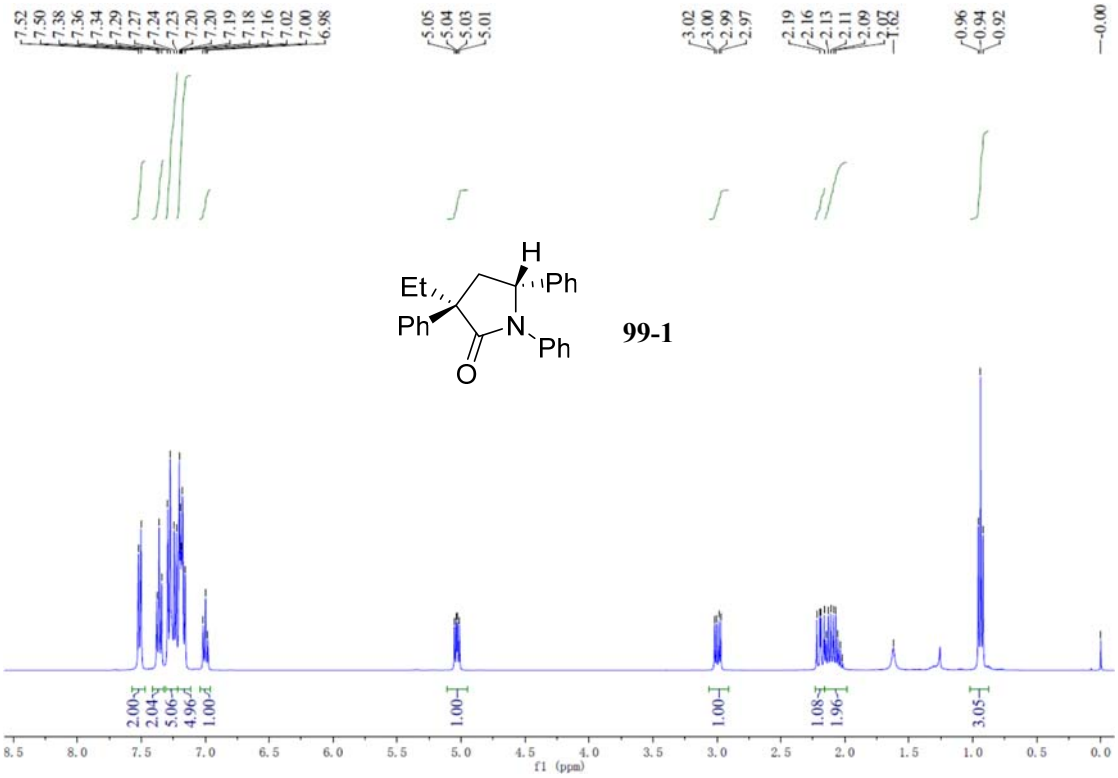
f1 (ppm)


Et
Ph
Ph
N
Ph
O
98


Et
Ph
Ph
N
Ph
O
98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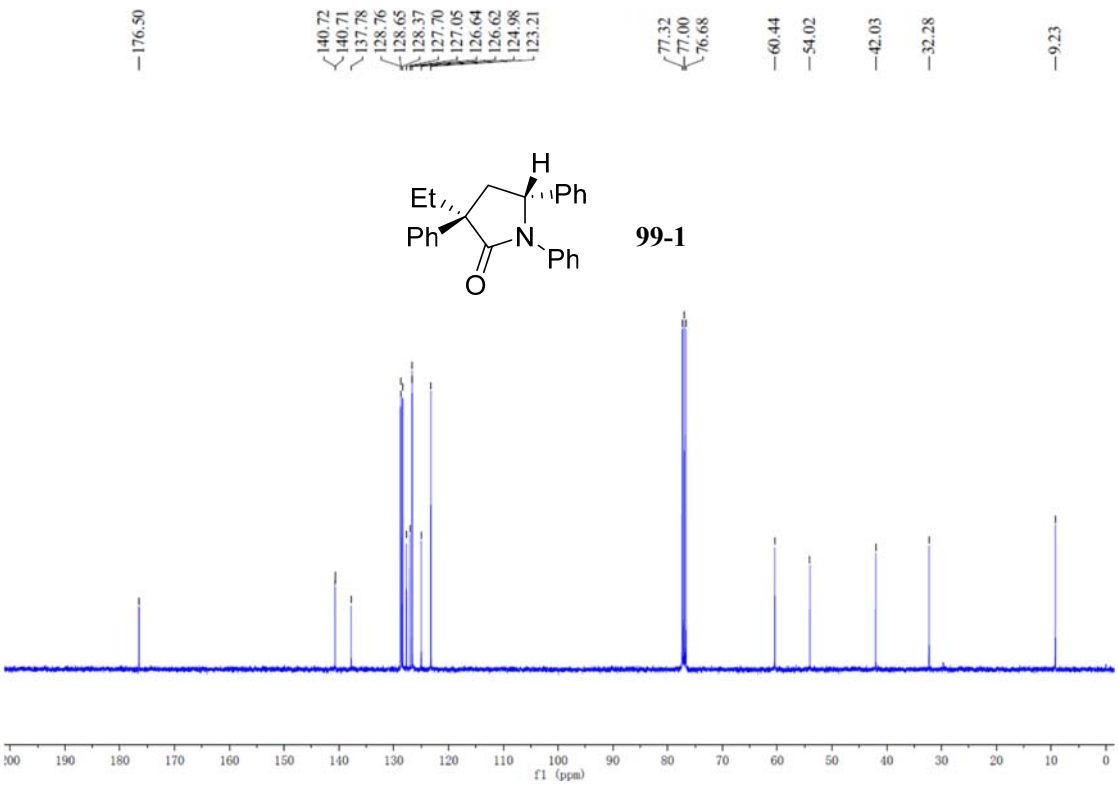
7.38
7.36
7.34
7.29
7.27
7.24
7.23
7.20
7.20
7.19
7.18
7.16
7.02
7.00
6.98
5.05
5.04
5.03
5.01
3.02
3.00
2.99
2.97
2.19
2.16
2.13
2.11
2.09
2.07
1.62
0.96
0.94
0.92
0.00
H
Et
Ph
Ph
N
Ph
O
99-1
2.00
2.04
5.06
4.96
1.00
1.00
1.00
1.08
1.96
3.05
f1 (ppm)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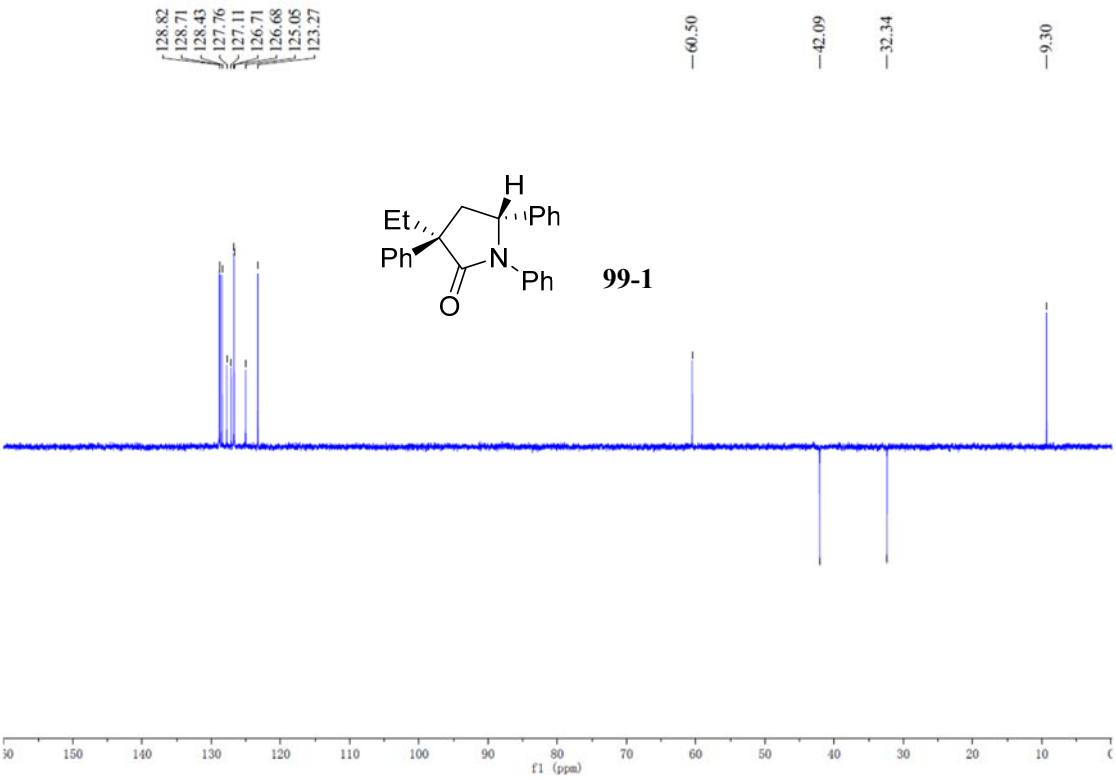
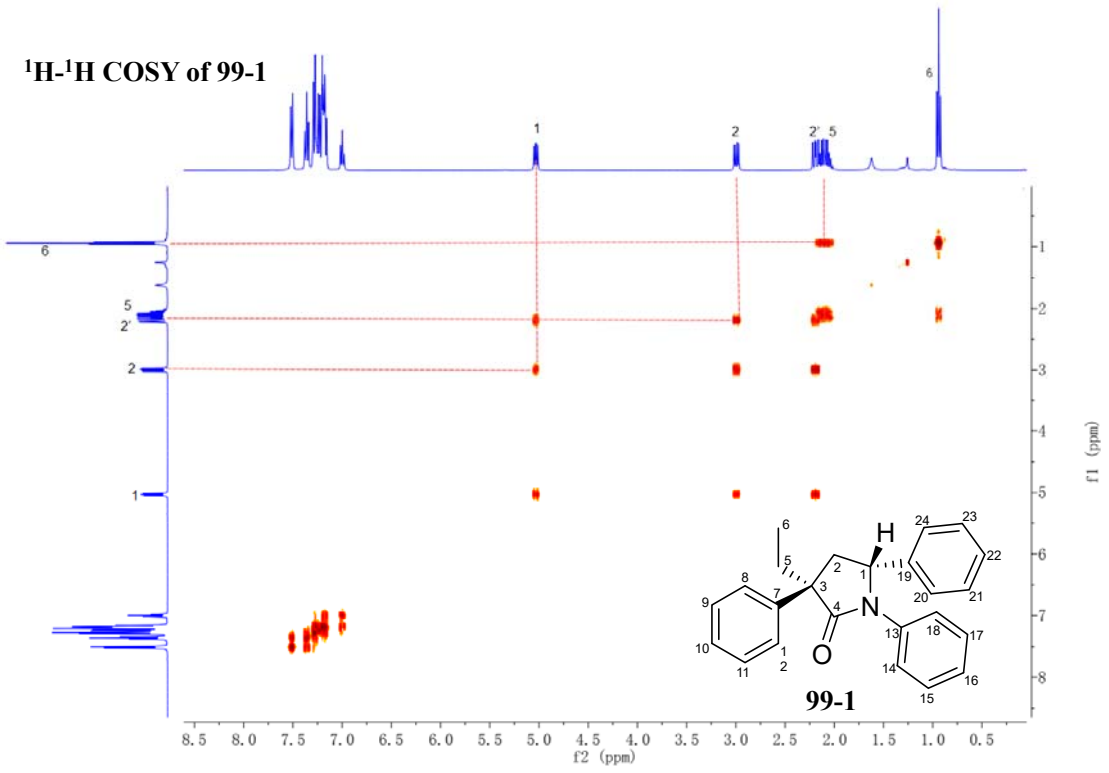
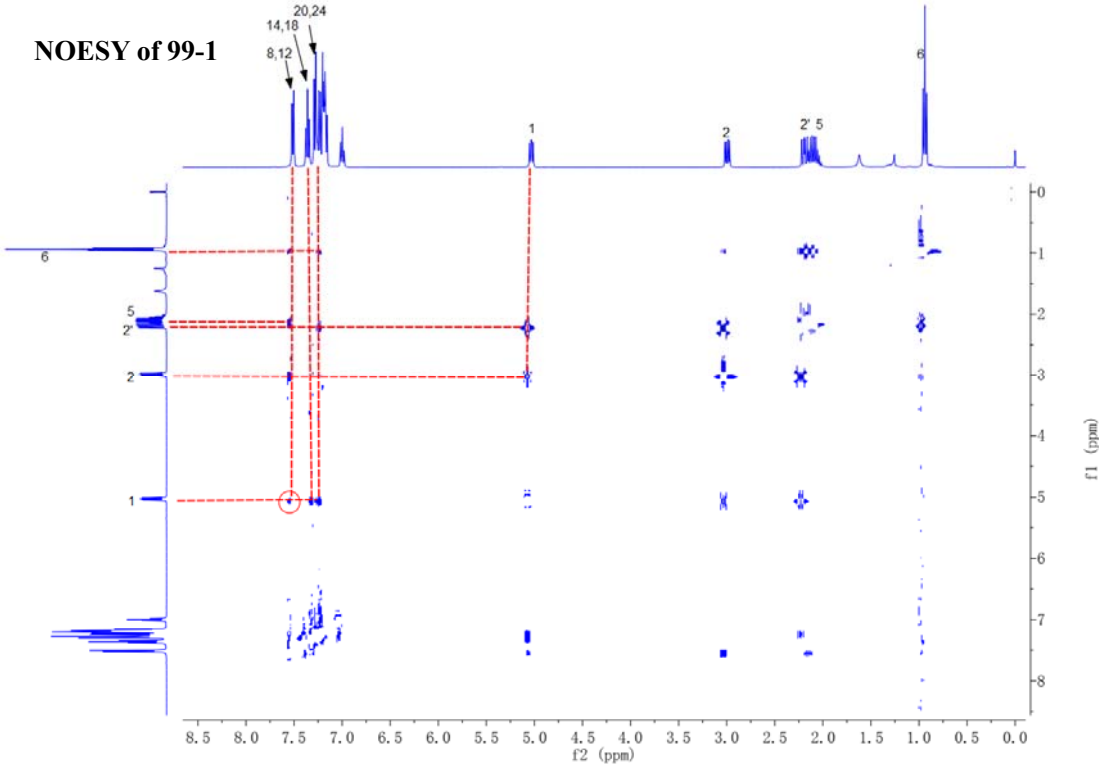
128.65
128.37
127.70
127.05
126.64
126.62
124.98
123.21
77.32
77.00
76.68
60.44
54.02
42.03
32.28
9.23
H
Et
Ph
Ph
N
Ph
O
99-1
f1 (ppm)

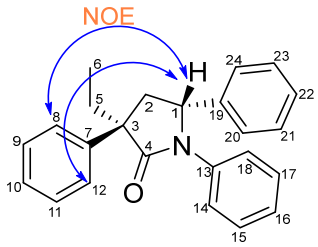


^{1}H-^{1}H COSY of 99-1

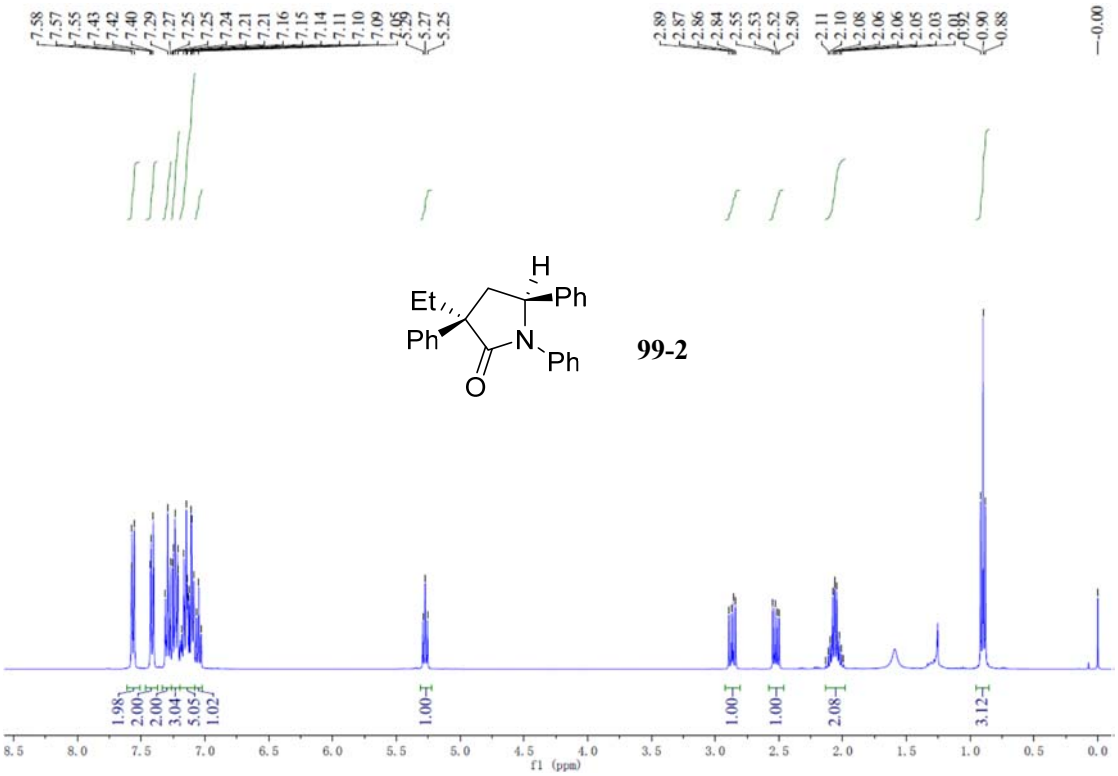


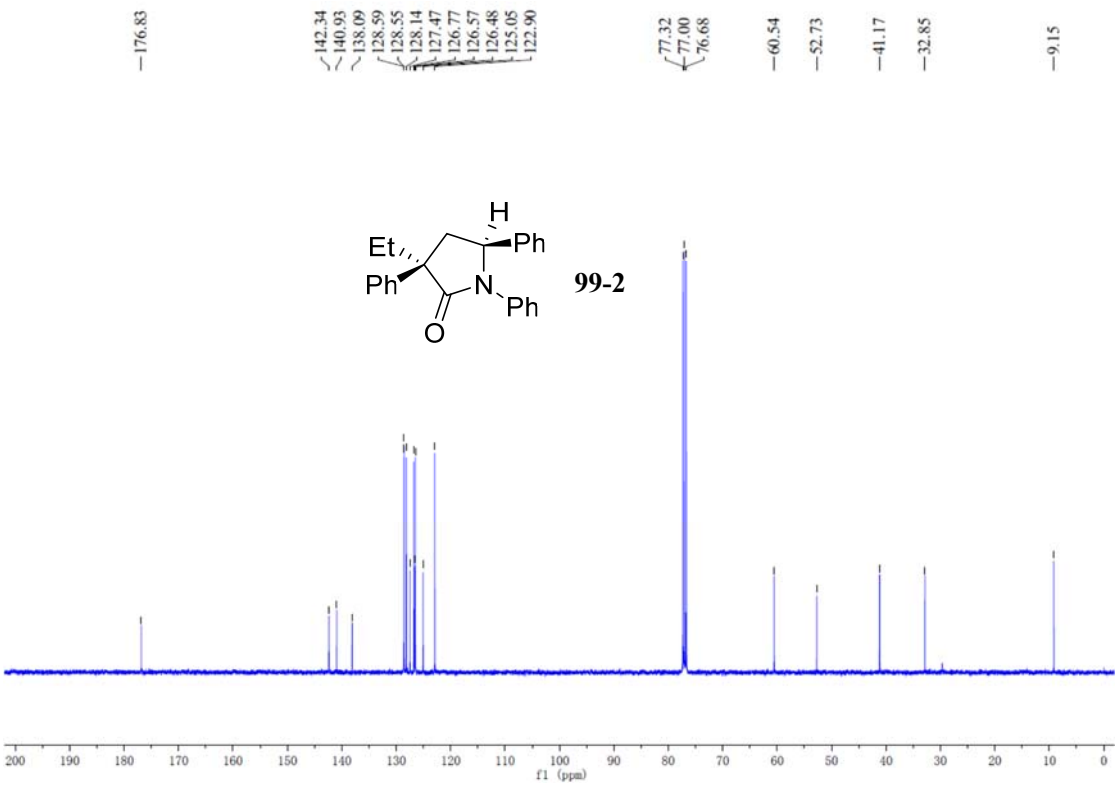
NOESY of 99-1





99-1


7.58
7.57
7.55
7.43
7.42
7.40
7.29
7.27
7.25
7.25
7.24
7.21
7.21
7.16
7.15
7.14
7.11
7.10
7.09
5.27
5.25
2.89
2.87
2.86
2.84
2.55
2.53
2.52
2.50
2.11
2.10
2.08
2.06
2.06
2.05
2.03
0.90
0.88
0.00
H
Et
Ph
Ph
N
Ph
O
99-2
1.98
2.00
2.00
3.04
5.05
1.02
1.00
1.00
1.00
2.08
3.12
f1 (ppm)


176.83
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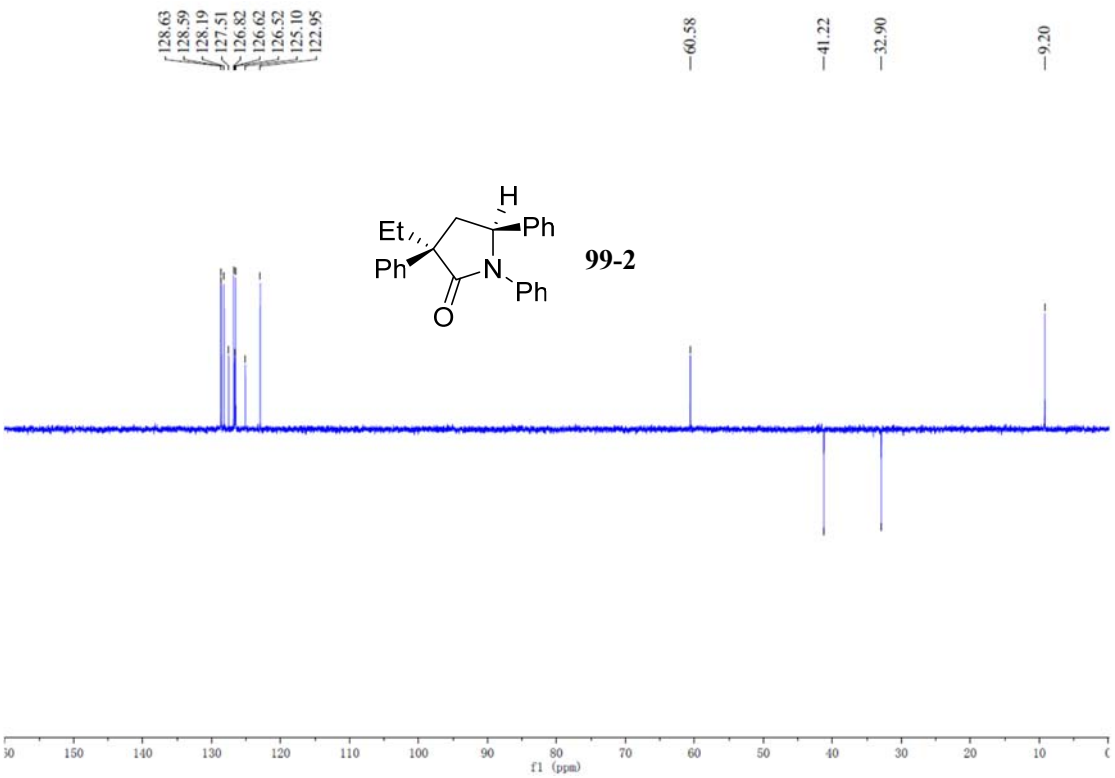
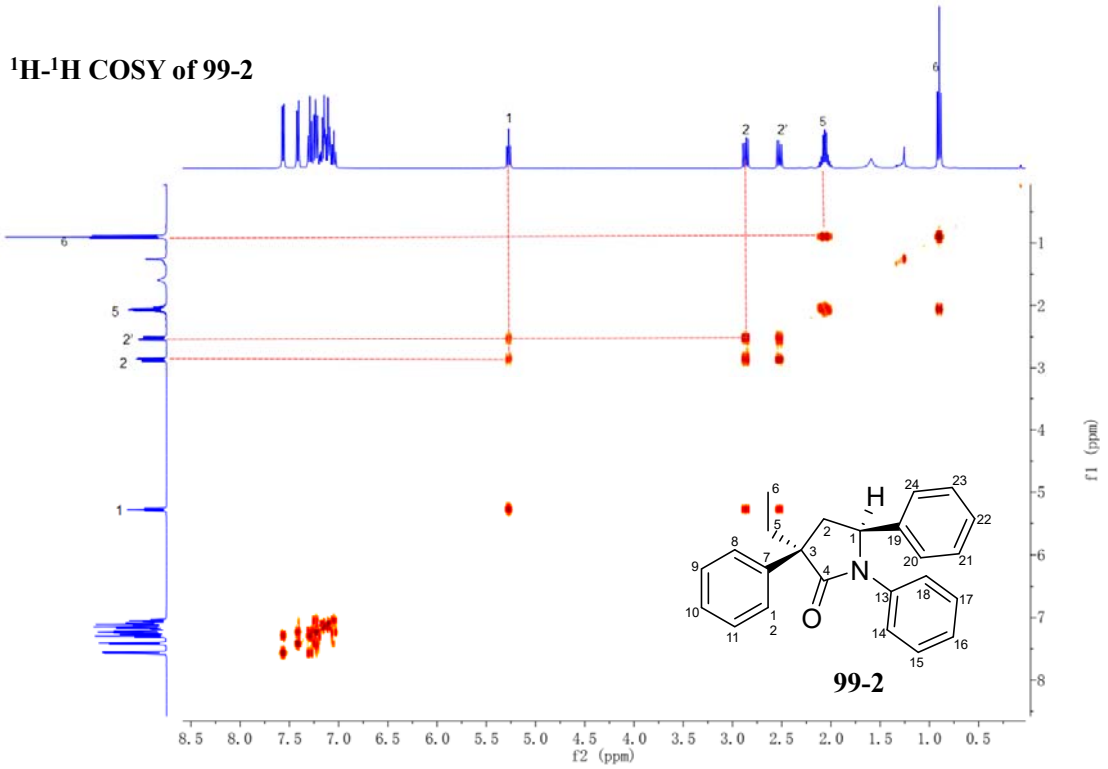
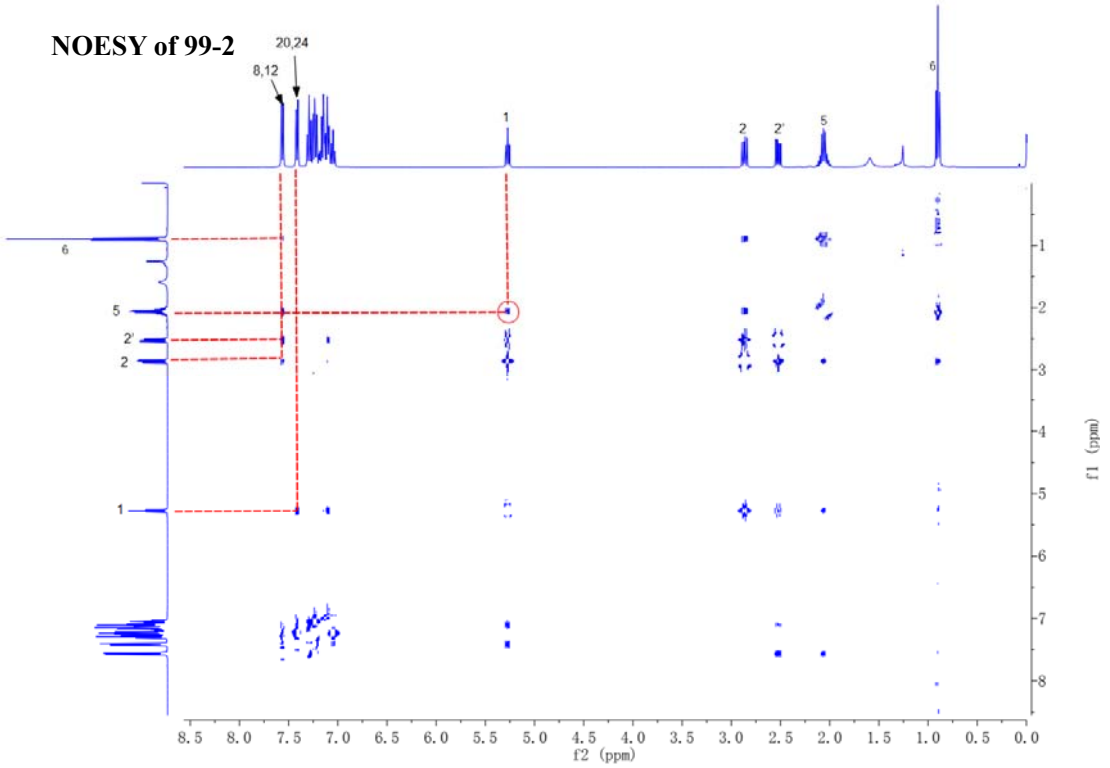
140.93
138.09
128.59
128.55
128.14
127.47
126.77
126.57
126.48
125.05
122.90
77.32
77.00
76.68
60.54
52.73
41.17
32.85
9.15
H
Et
Ph
Ph
N
Ph
O
99-2
f1 (ppm)

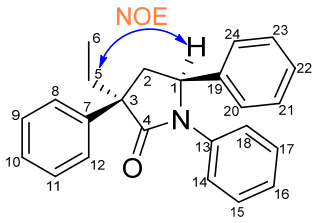


^{1}H-^{1}H COSY of 99-2



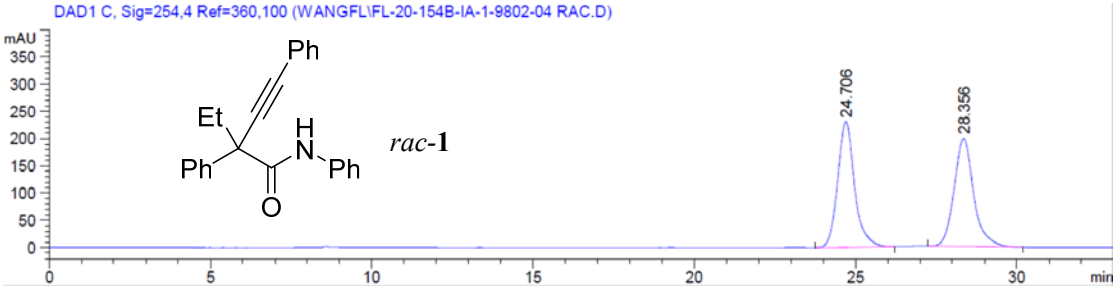
NOESY of 99-2





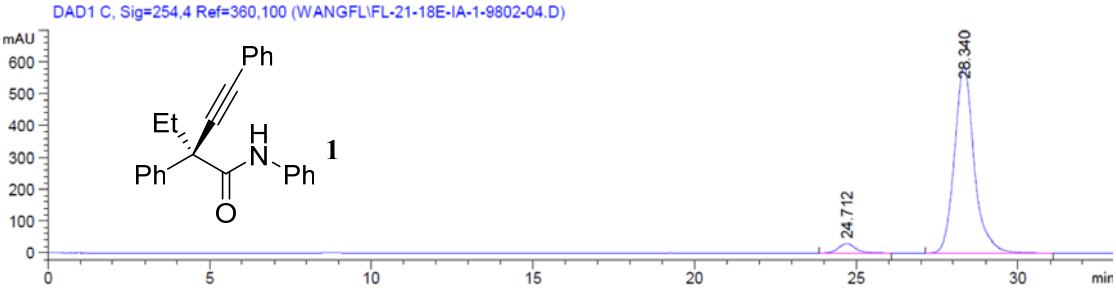
99-2

HPLC spectra



Signal 3: DAD1 C, Sig=254,4 Ref=360,100

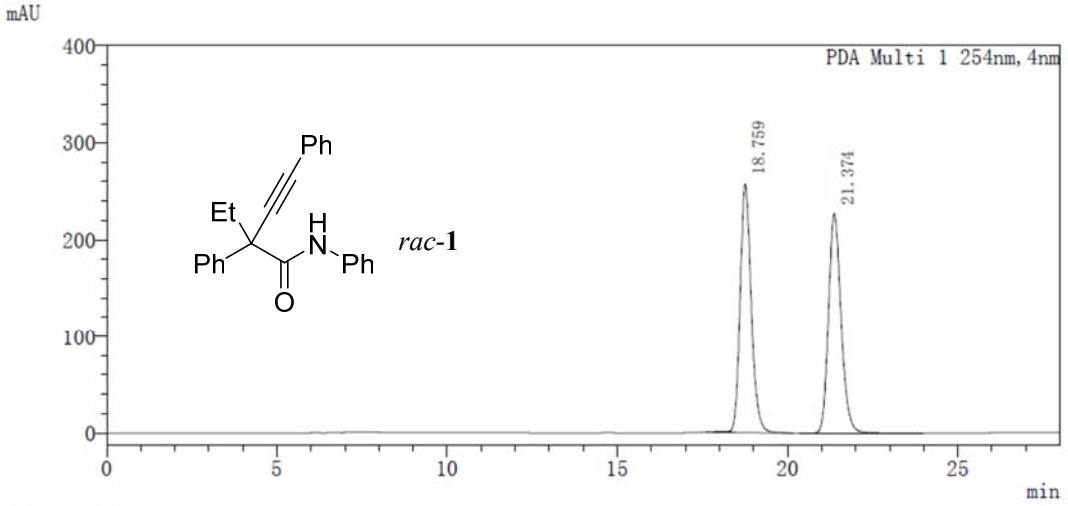
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.706	BB	0.5561	8401.95117	231.15485	50.0495
2	28.356	BB	0.6365	8385.31934	198.64166	49.9505
Totals :				1.67873e4	429.79651	



Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.712	BB	0.5540	1133.80811	30.90537	4.3521
2	28.340	BB	0.6389	2.49183e4	587.45514	95.6479
Totals :				2.60522e4	618.36051	

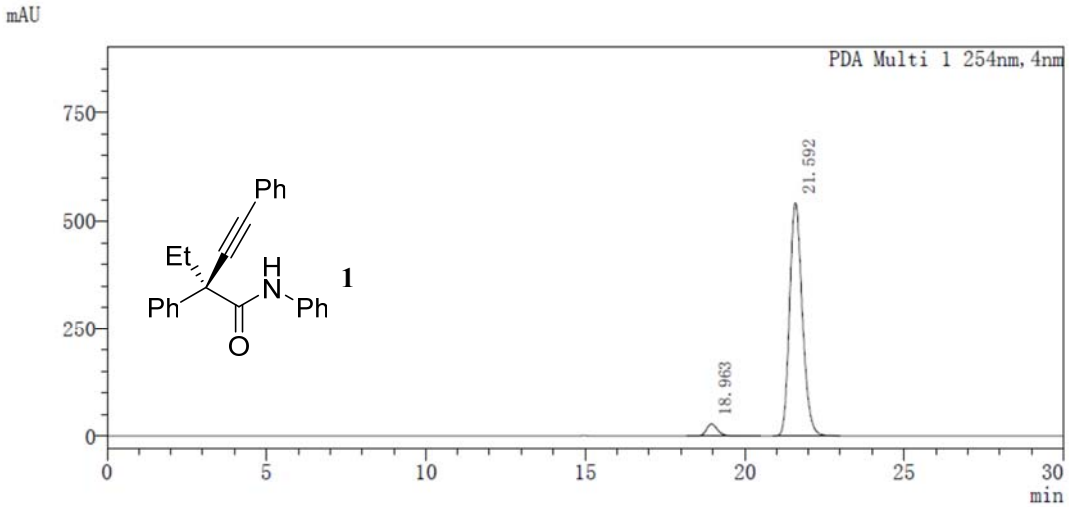
1 from large scale preparation



Peak Table

PDA Ch1 254nm

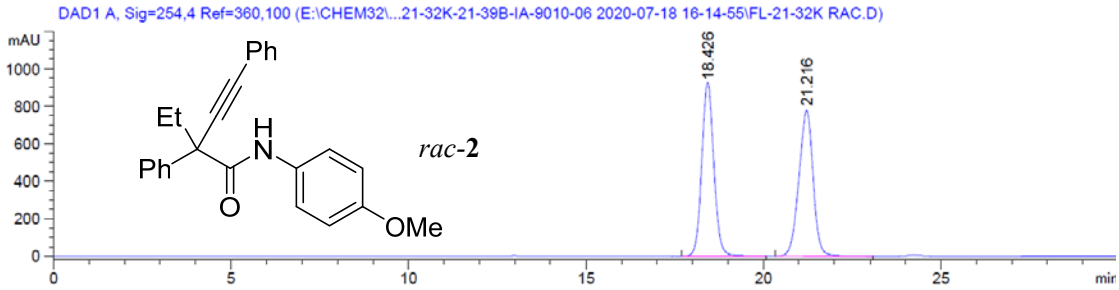
Peak#	Ret. Time	Area	Area%
1	18.759	5834820	49.937
2	21.374	5849467	50.063



Peak Table

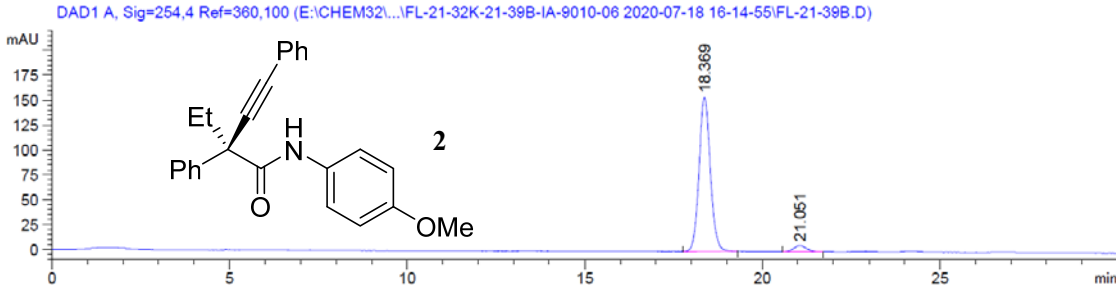
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.963	678458	4.296
2	21.592	15113256	95.704



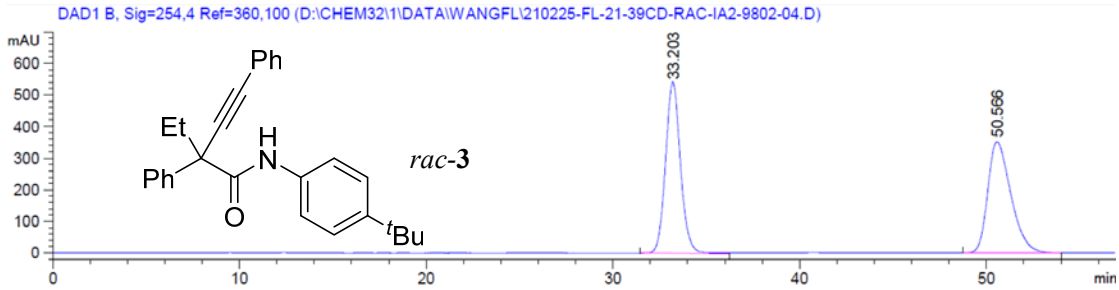
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.426	BB	0.3650	2.18935e4	928.96722	50.2725
2	21.216	BB	0.4263	2.16562e4	779.02808	49.7275
Totals :				4.35496e4	1707.99530	



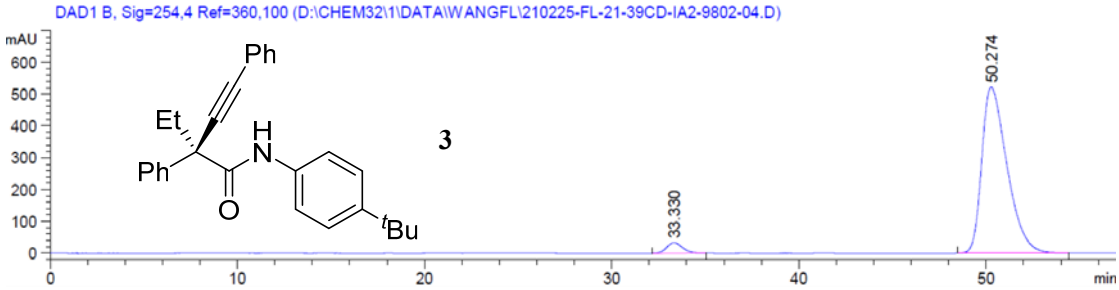
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.369	BB	0.3400	3431.55347	155.15408	95.2955
2	21.051	BB	0.3271	169.40799	6.65243	4.7045
Totals :				3600.96146	161.80652	



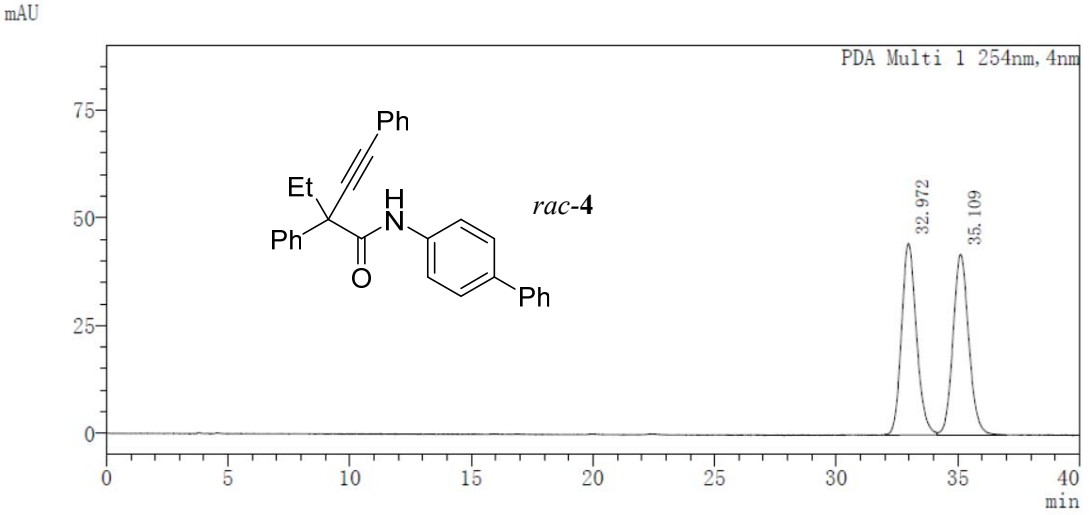
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.203	MM R	0.9254	3.00325e4	540.86737	49.8603
2	50.566	BB	1.2212	3.02008e4	351.90753	50.1397
Totals :				6.02333e4	892.77490	



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

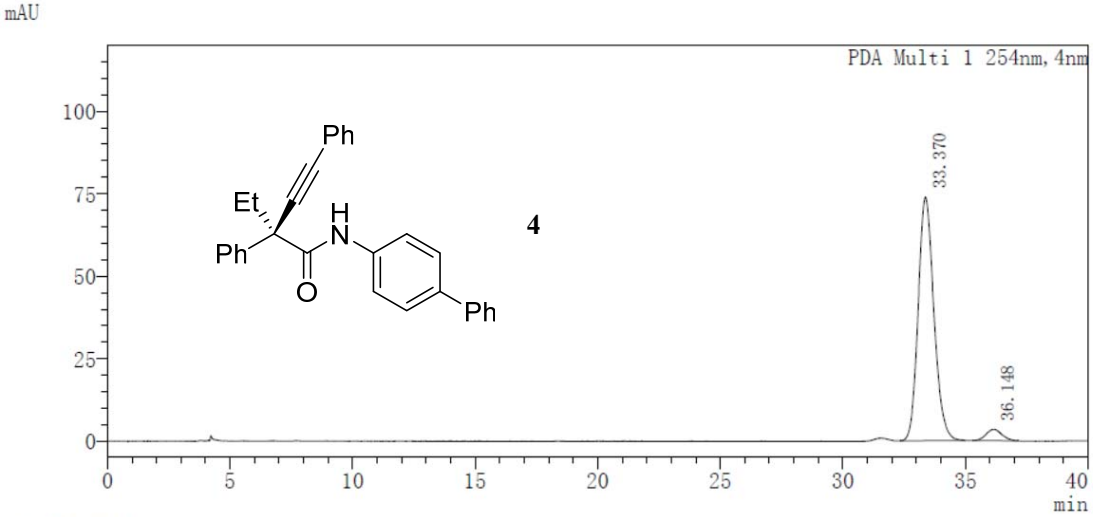
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.330	BB	0.7992	1935.86084	33.15507	3.8129
2	50.274	BB	1.3520	4.88361e4	521.73450	96.1871
Totals :				5.07719e4	554.88957	



Peak Table

PDA Ch1 254nm

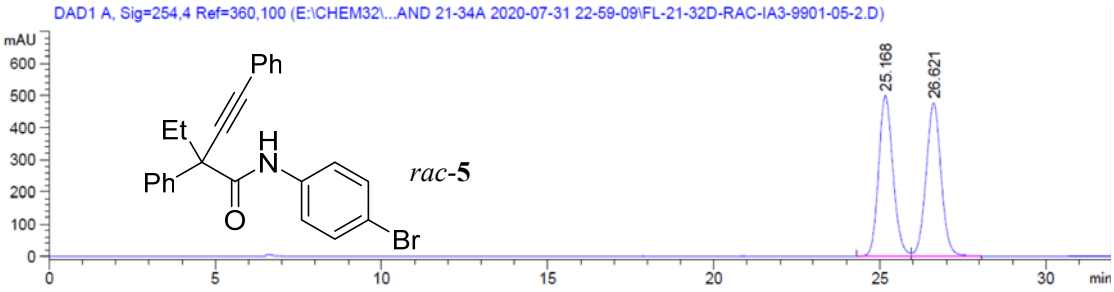
Peak#	Ret. Time	Area	Area%
1	32.972	1902966	50.159
2	35.109	1890876	49.841



Peak Table

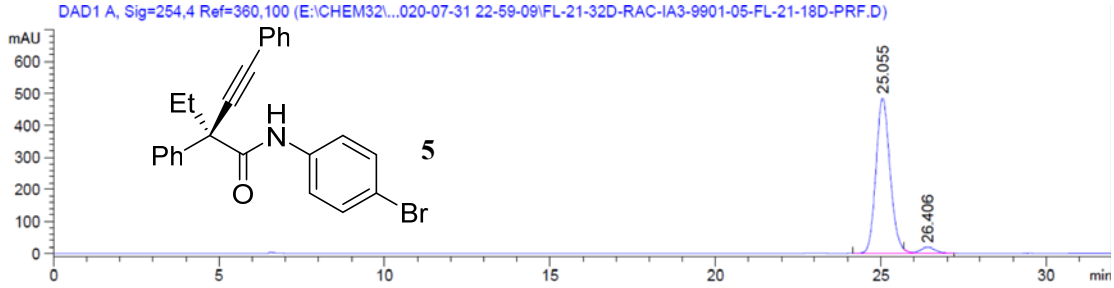
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	33.370	3296065	95.530
2	36.148	154240	4.470



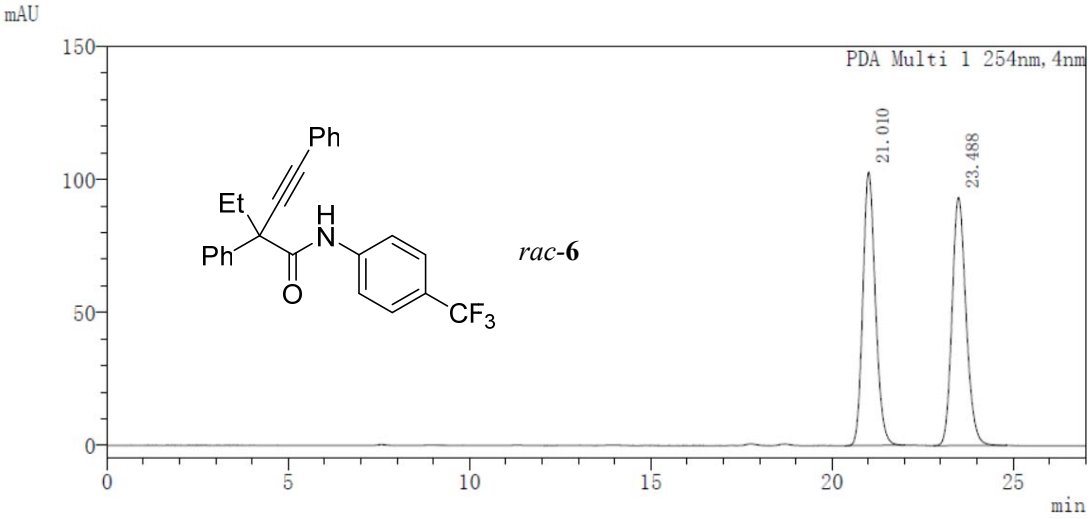
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.168	BV	0.4644	1.50184e4	499.98044	50.0713
2	26.621	VB	0.4840	1.49756e4	477.34042	49.9287
Totals :				2.99940e4	977.32086	



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

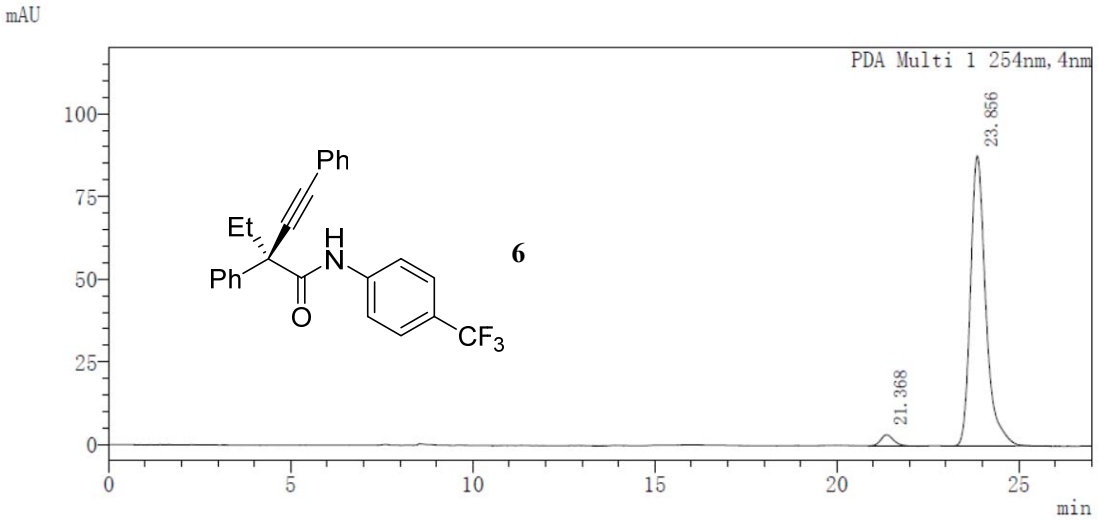
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.055	BV R	0.4569	1.44153e4	484.82382	95.9773
2	26.406	VB E	0.4055	604.18890	18.97512	4.0227
Totals :				1.50195e4	503.79894	



Peak Table

PDA Ch1 254nm

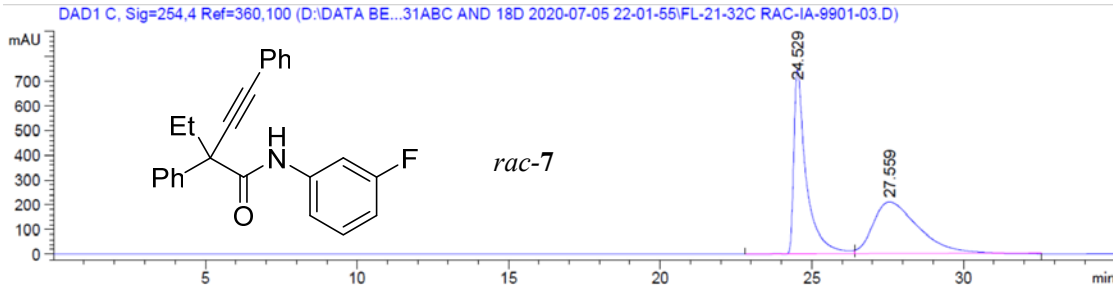
Peak#	Ret. Time	Area	Area%
1	21.010	2478014	49.685
2	23.488	2509403	50.315



Peak Table

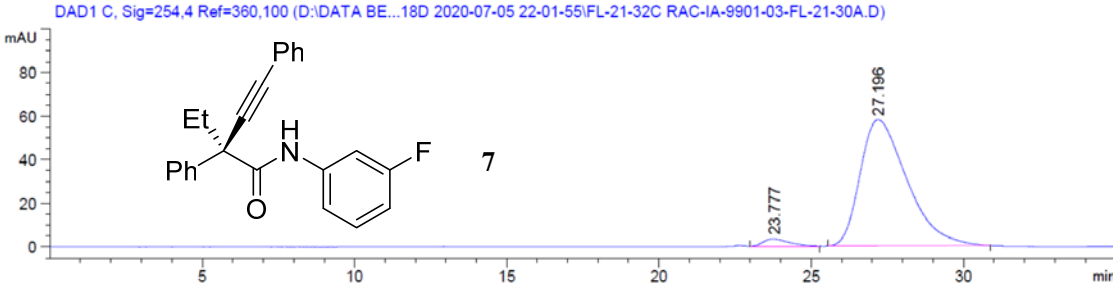
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.368	84882	3.198
2	23.856	2569457	96.802



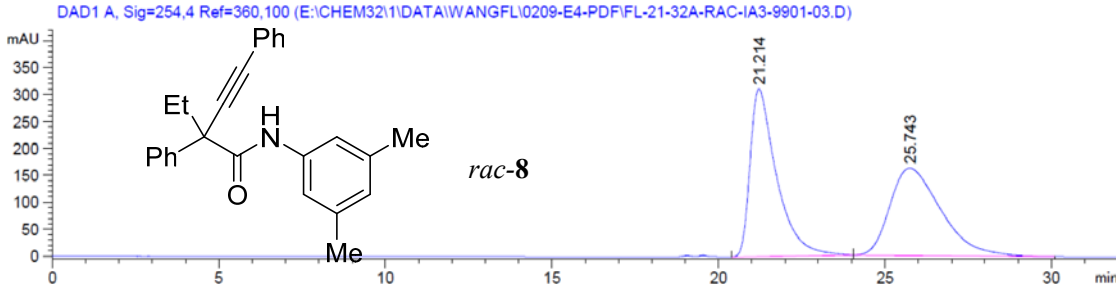
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.529	MF R	0.4757	2.12541e4	744.69348	49.3411
2	27.559	FM R	1.7331	2.18217e4	209.85619	50.6589
Totals :				4.30758e4	954.54967	



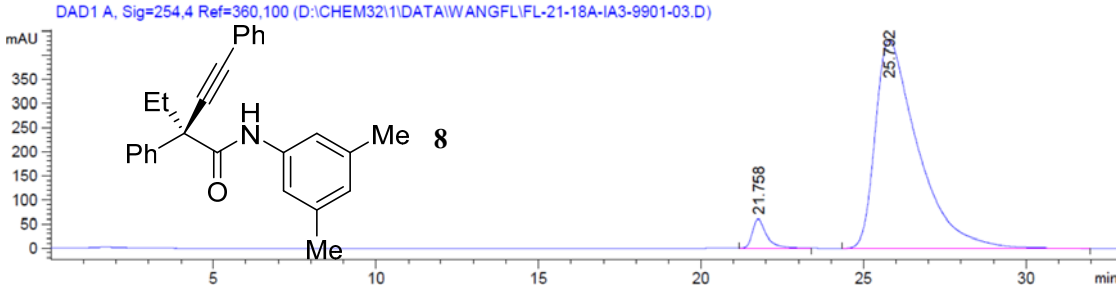
Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.777	BB	0.6941	194.17046	3.32130	3.0384
2	27.196	BB	1.2956	6196.30029	57.94130	96.9616
Totals :				6390.47075	61.26260	



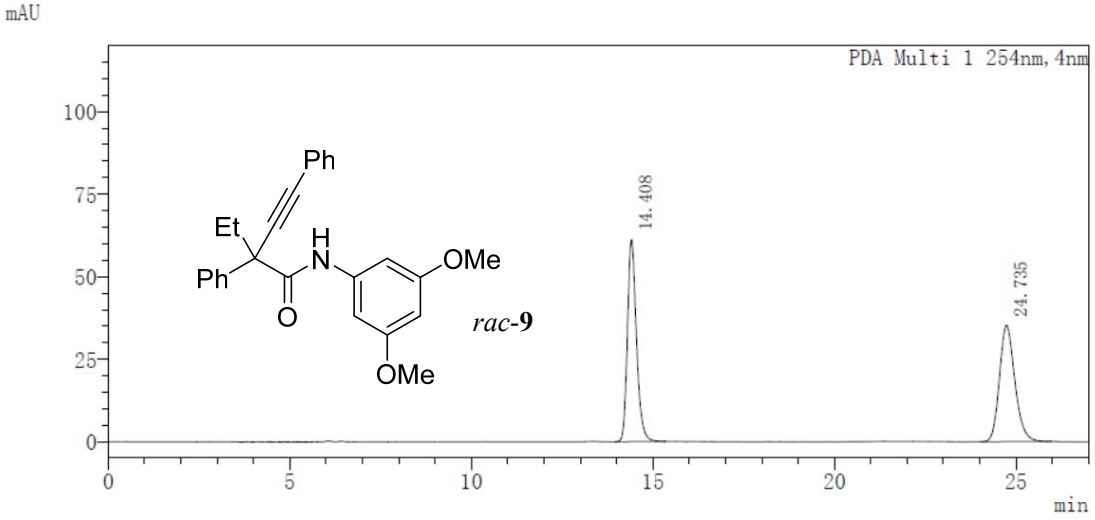
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.214	BB	0.7928	1.71445e4	311.18860	49.8868
2	25.743	BB	1.4625	1.72223e4	162.23572	50.1132
Totals :				3.43668e4	473.42432	



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

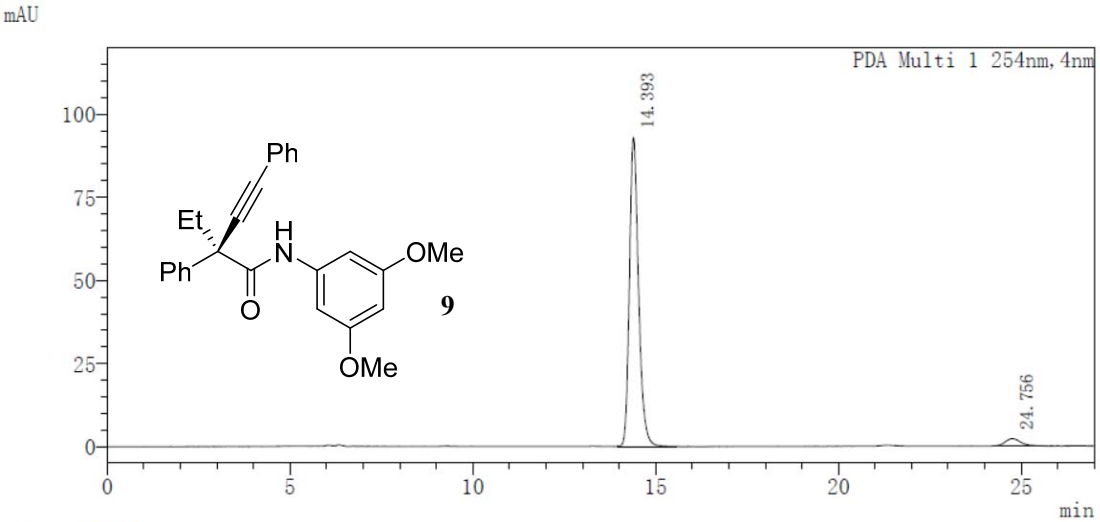
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.758	BB	0.4399	1798.43945	60.30443	4.3643
2	25.792	BB	1.2971	3.94092e4	431.68207	95.6357
Totals :				4.12077e4	491.98650	



Peak Table

PDA Ch1 254nm

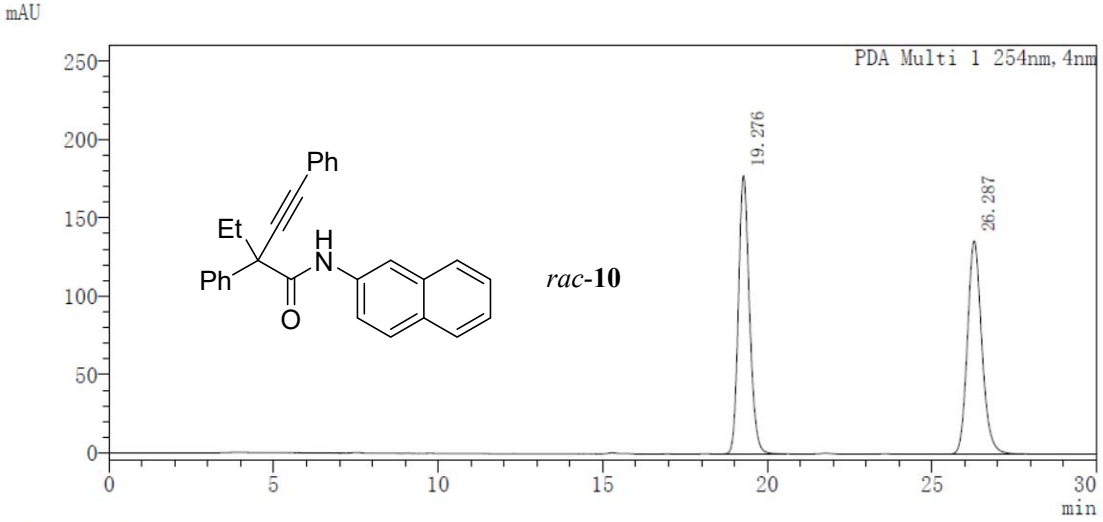
Peak#	Ret. Time	Area	Area%
1	14.408	1054969	50.268
2	24.735	1043722	49.732



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.393	1616784	96.262
2	24.756	62779	3.738

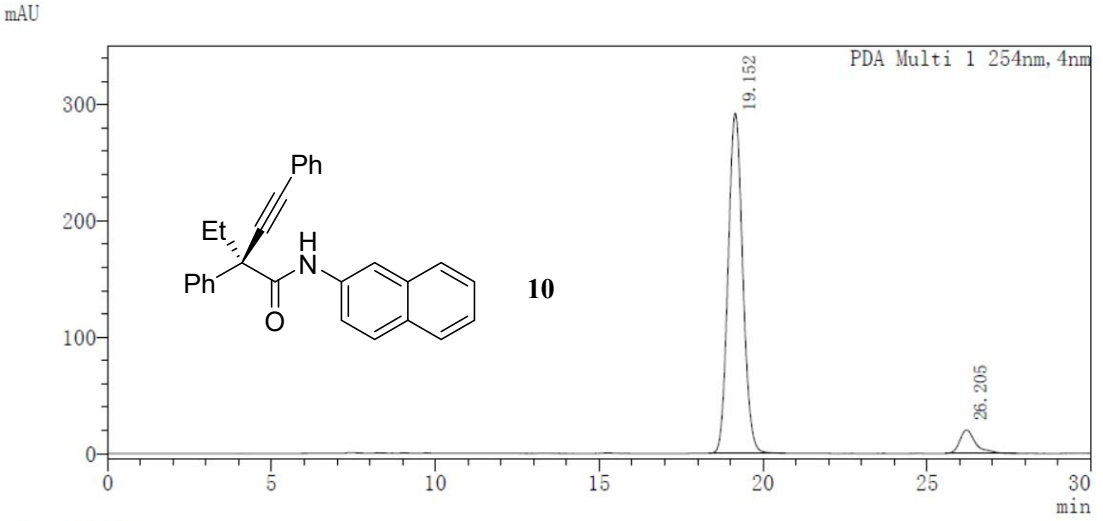


rac-**10**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.276	4147675	50.106
2	26.287	4130195	49.894



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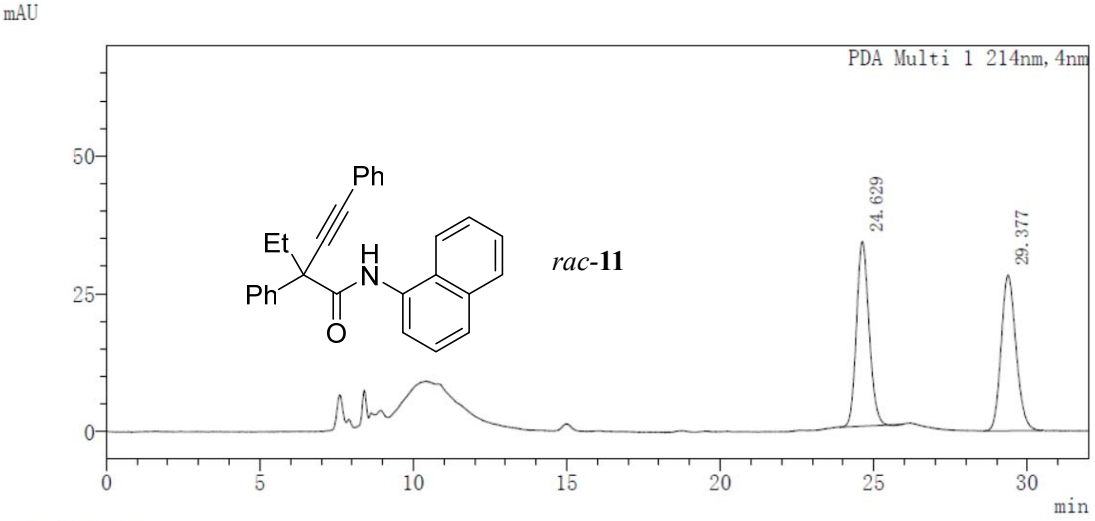
Peak Table

PDA Ch1 254nm

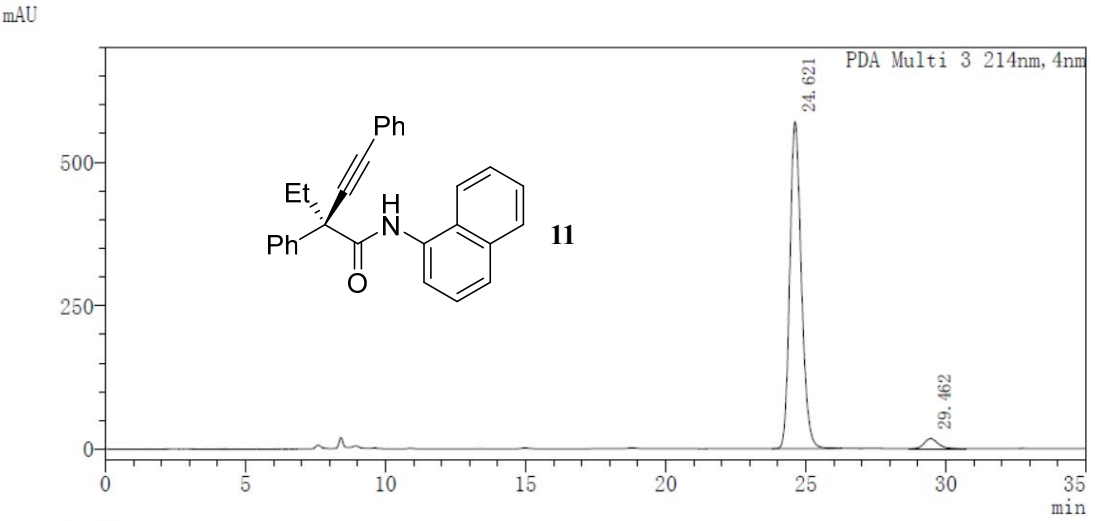
Peak#	Ret. Time	Area	Area%
1	19.152	9050130	93.079
2	26.205	672904	6.921



Peak Table

PDA Ch1 214nm

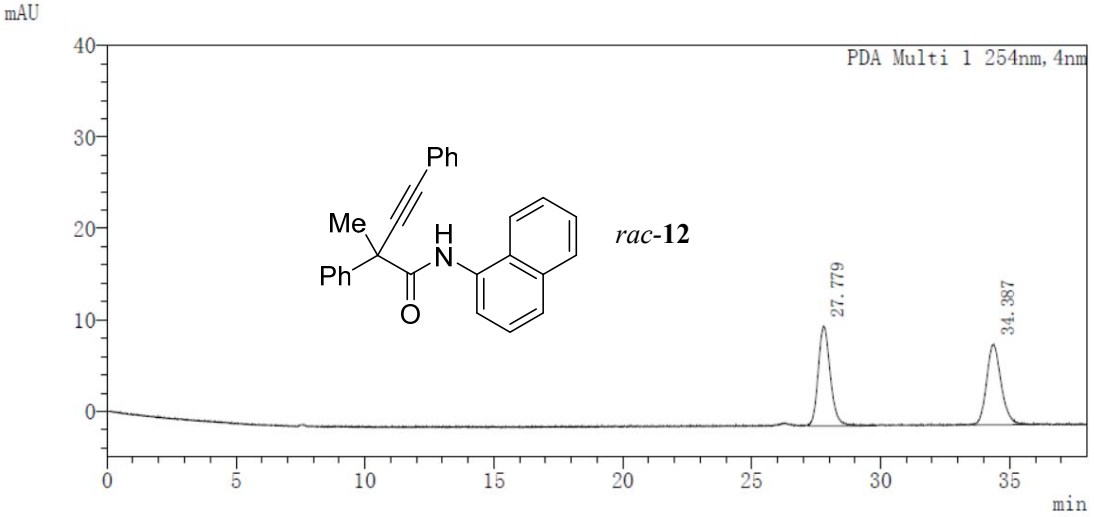
Peak#	Ret. Time	Area	Area%
1	24.629	954711	50.015
2	29.377	954145	49.985



Peak Table

PDA Ch3 214nm

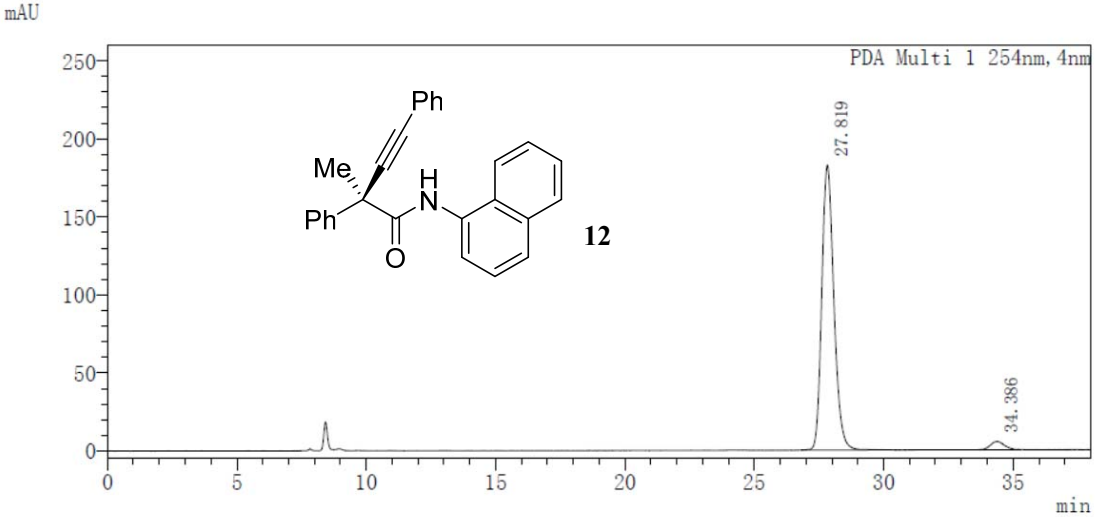
Peak#	Ret. Time	Area	Area%
1	24.621	16343603	96.470
2	29.462	598021	3.530



Peak Table

PDA Ch1 254nm

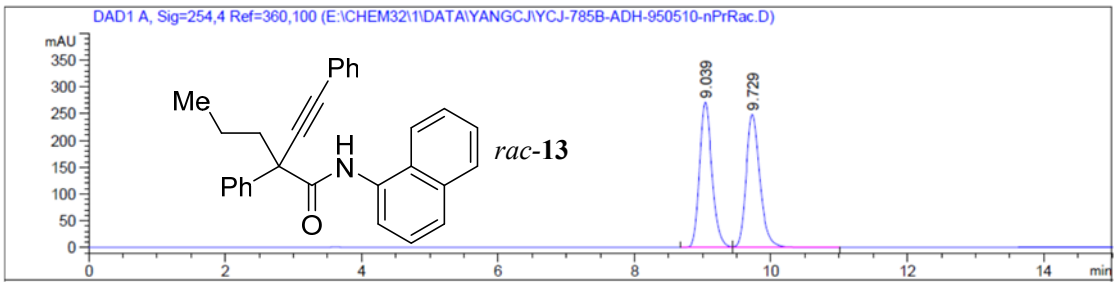
Peak#	Ret. Time	Area	Area%
1	27.779	350990	50.391
2	34.387	345537	49.609



Peak Table

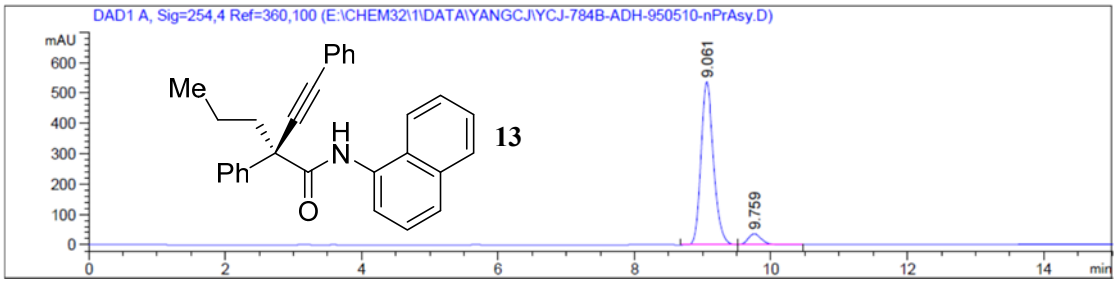
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	27.819	5905965	96.587
2	34.386	208674	3.413



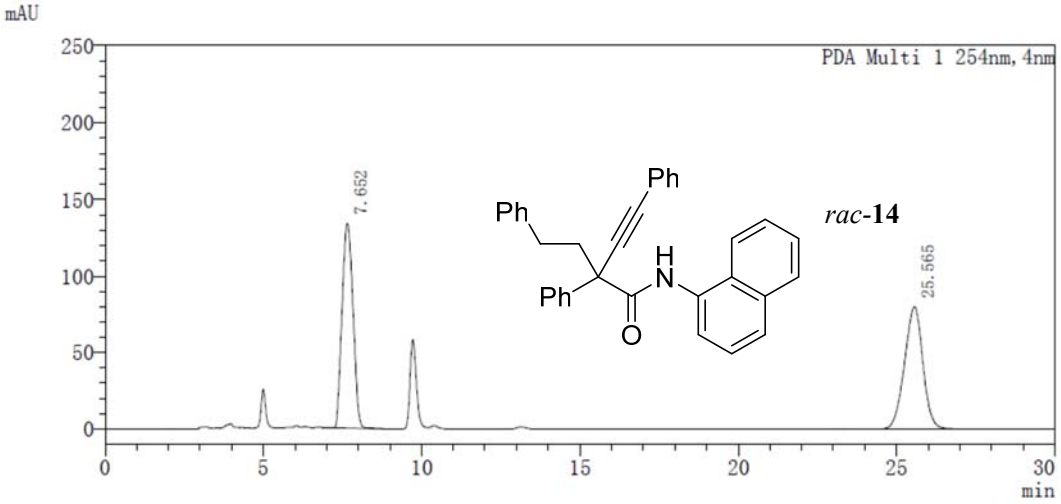
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.039	BV	0.1955	3431.75342	271.37070	49.6957
2	9.729	VB	0.2131	3473.77515	248.42046	50.3043
Totals :				6905.52856	519.79115	



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

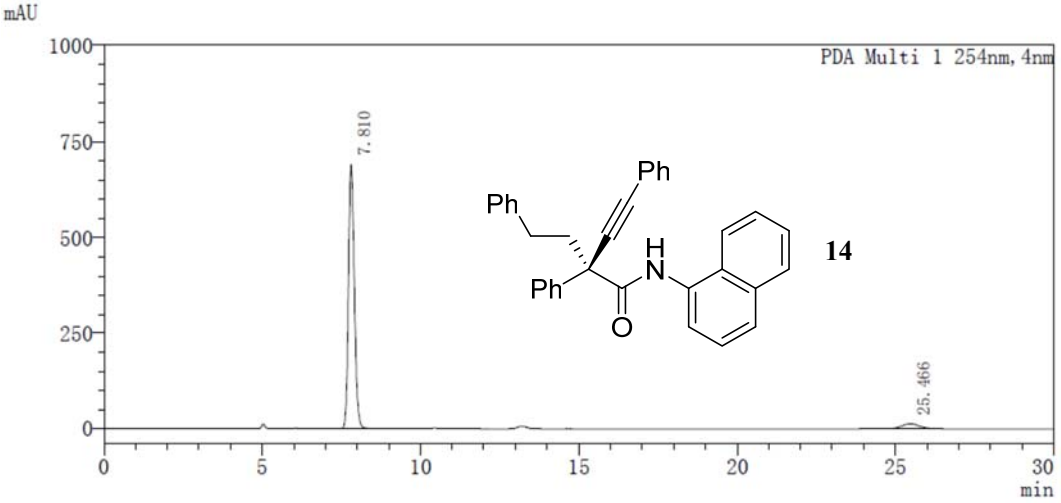
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.061	BV	0.1968	6838.96484	536.30304	93.1197
2	9.759	VB	0.2117	505.30582	36.45385	6.8803
Totals :				7344.27066	572.75689	



Peak Table

PDA Ch1 254nm

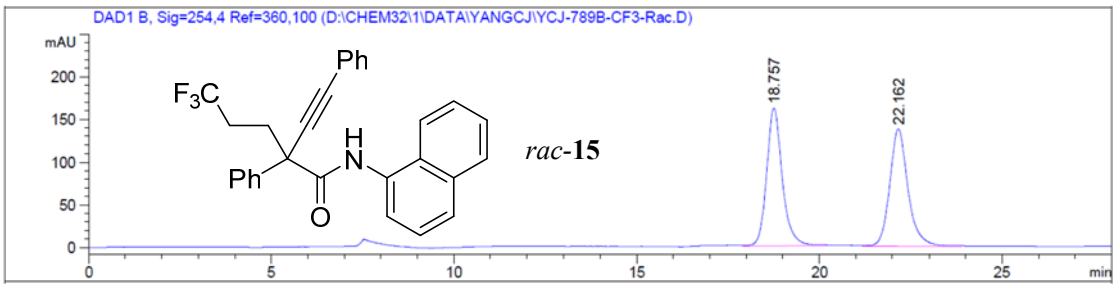
Peak#	Ret. Time	Area	Area%
1	7.652	3207695	49.925
2	25.565	3217299	50.075



Peak Table

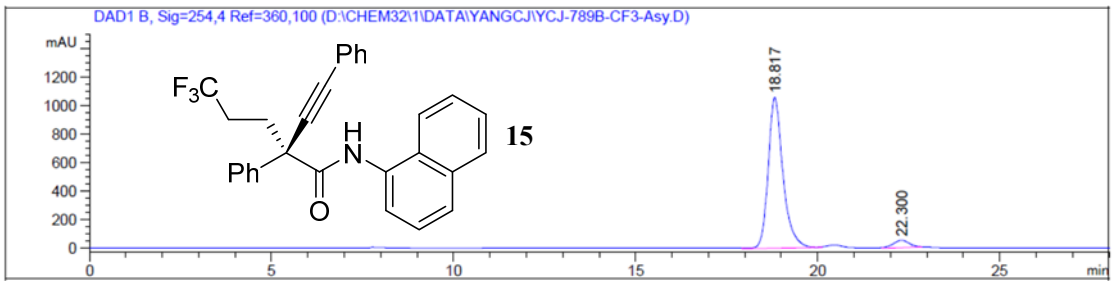
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.810	8888081	94.987
2	25.466	469096	5.013



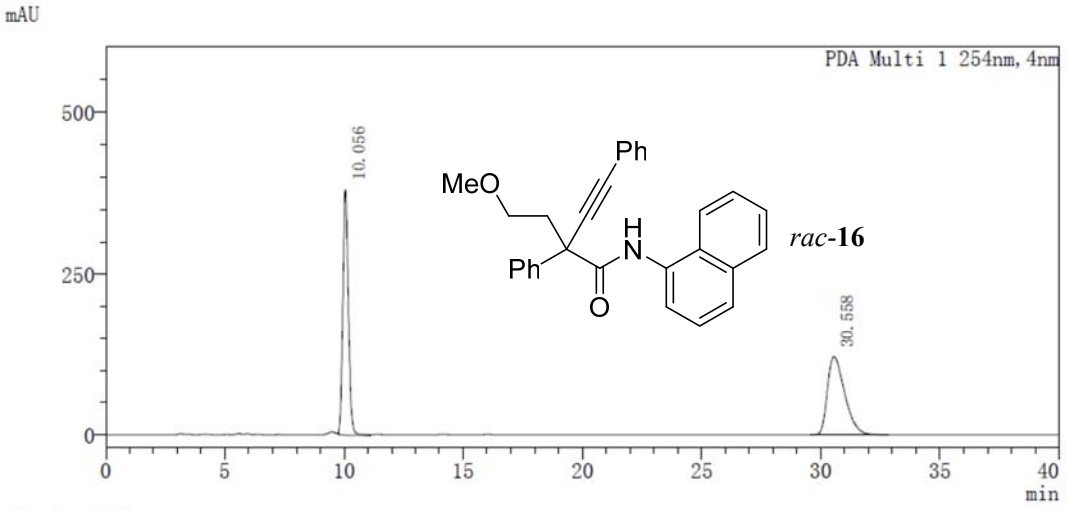
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.757	MM R	0.4973	4807.73047	161.11740	50.0266
2	22.162	MM R	0.5839	4802.62158	137.09305	49.9734
Totals :				9610.35205	298.21045	



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

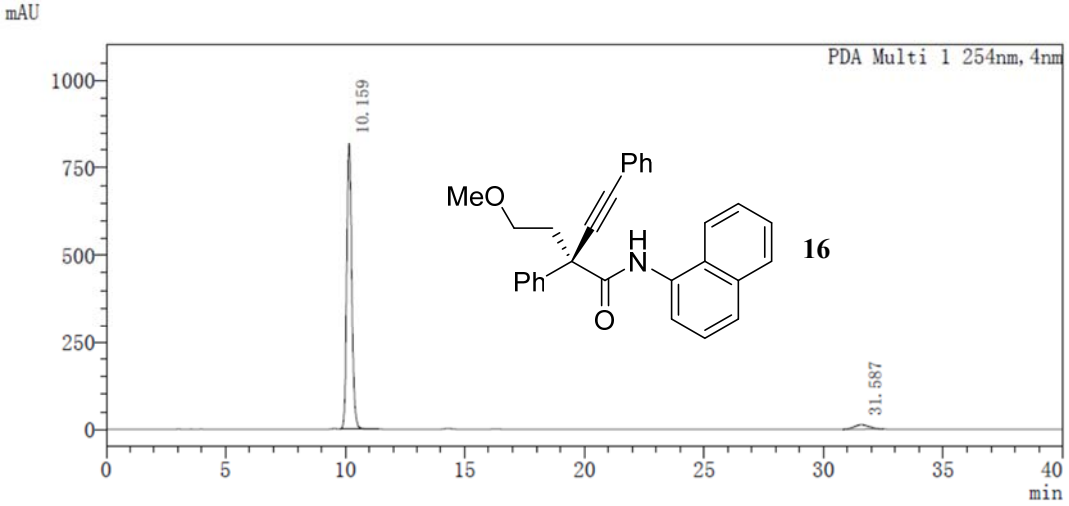
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.817	MM R	0.4710	2.98635e4	1056.83252	95.0673
2	22.300	MM R	0.5050	1549.52124	51.14184	4.9327
Totals :				3.14131e4	1107.97436	



Peak Table

PDA Ch1 254nm

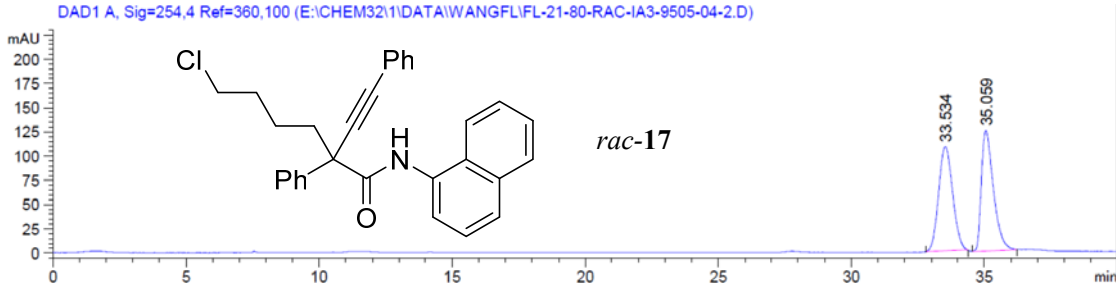
Peak#	Ret. Time	Area	Area%
1	10.056	6168709	50.048
2	30.558	6156833	49.952



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	10.159	12026375	95.586
2	31.587	555333	4.414



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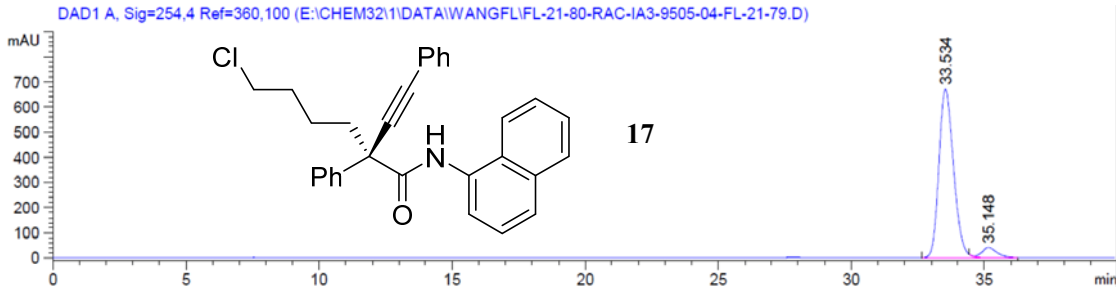
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.534	MM R	0.6072	3925.82275	107.76435	50.1245
2	35.059	MM R	0.5239	3906.32446	124.27023	49.8755
Totals :				7832.14722	232.03458	



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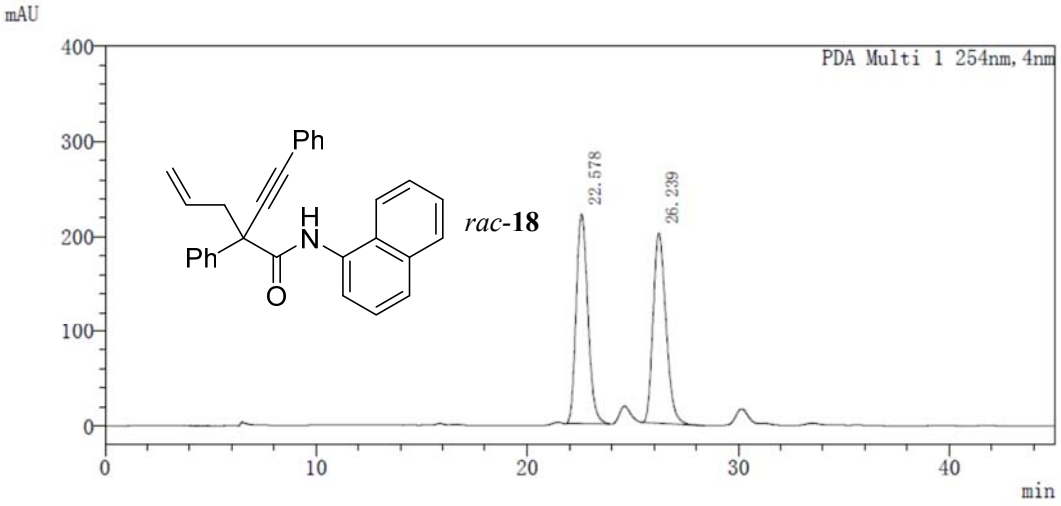
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

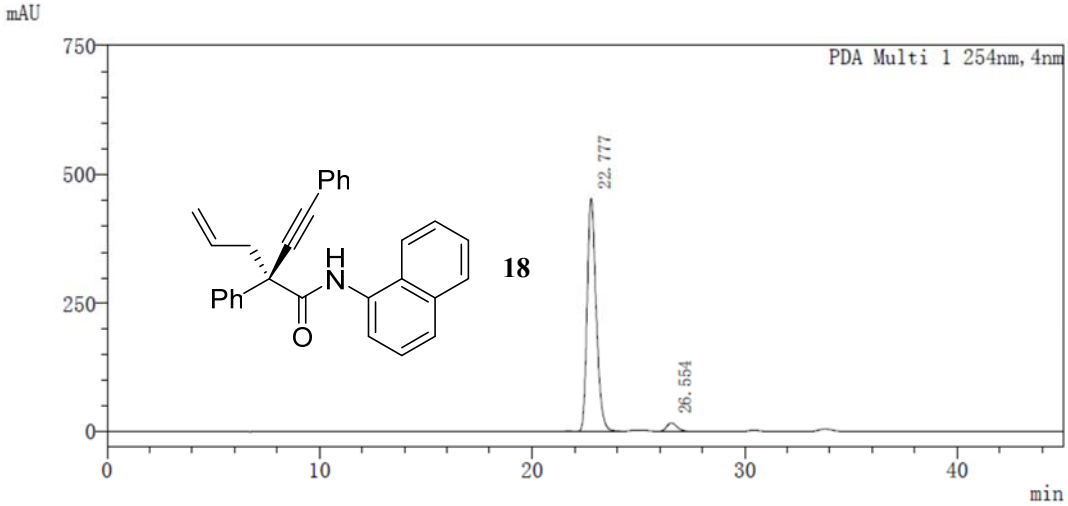
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.534	BV R	0.5944	2.56075e4	669.29022	94.3347
2	35.148	VB E	0.5370	1537.84985	40.68315	5.6653
Totals :				2.71453e4	709.97337	



Peak Table

PDA Ch1 254nm

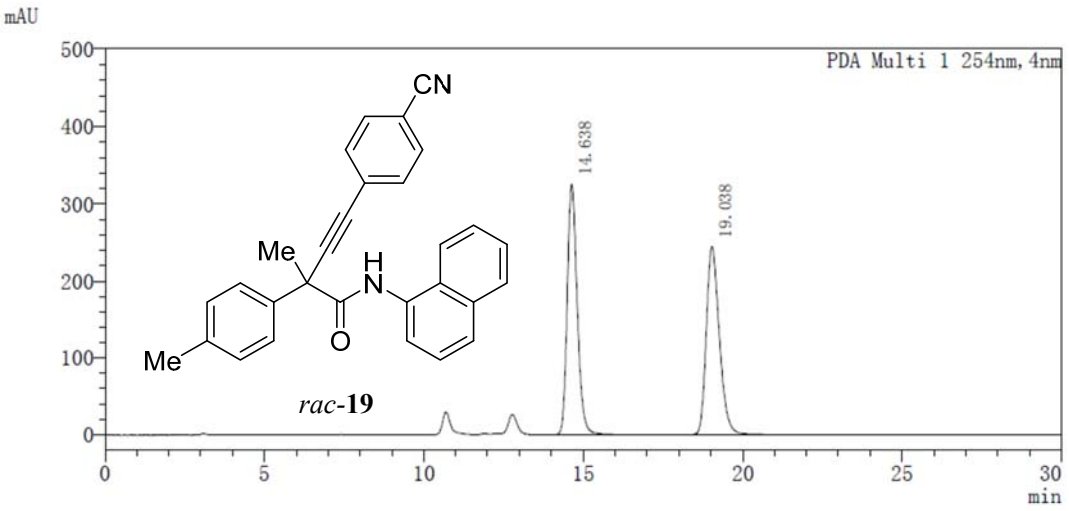
Peak#	Ret. Time	Area	Area%
1	22.578	8517157	50.009
2	26.239	8513923	49.991



Peak Table

PDA Ch1 254nm

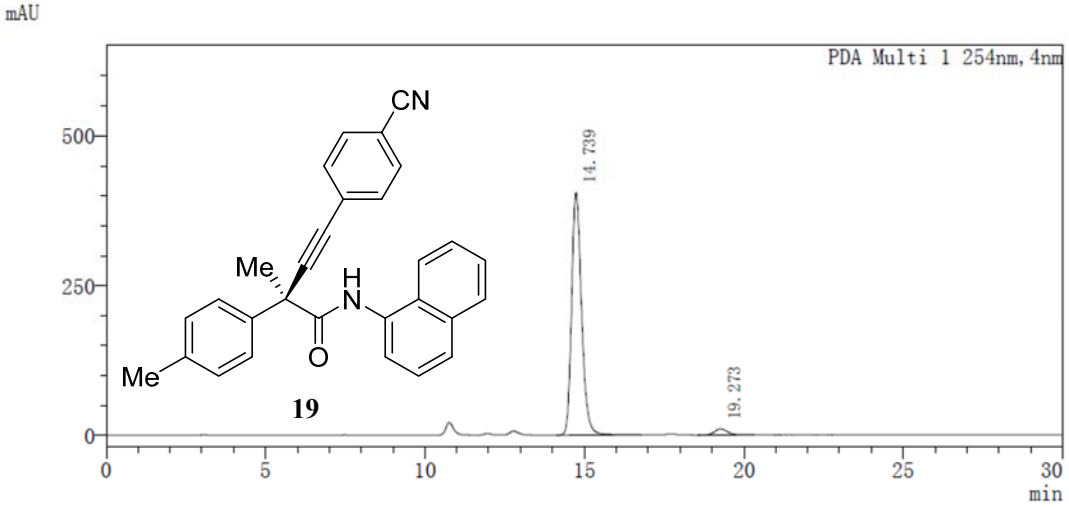
Peak#	Ret. Time	Area	Area%
1	22.777	13427352	95.990
2	26.554	560939	4.010



Peak Table

PDA Ch1 254nm

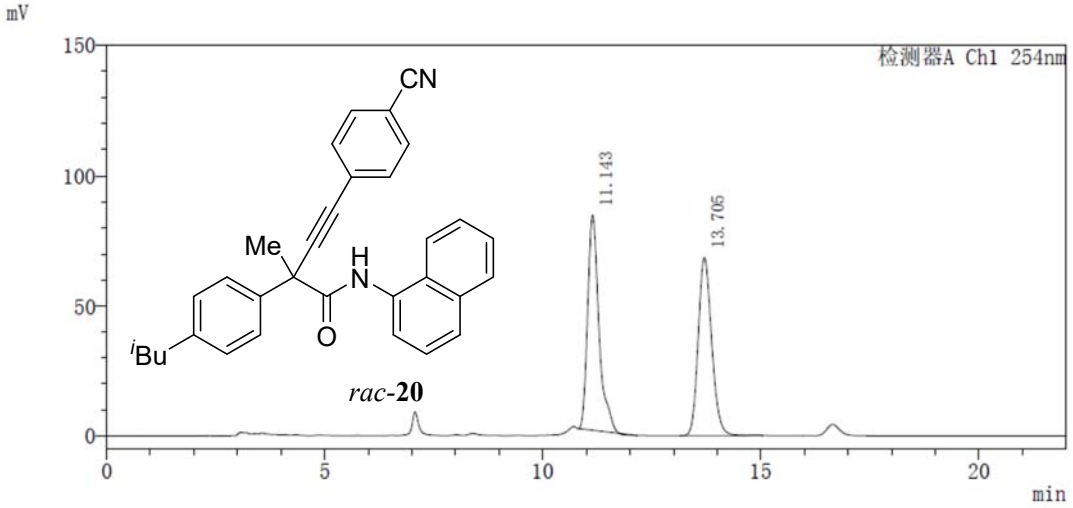
Peak#	Ret. Time	Area	Area%
1	14.638	7064647	50.359
2	19.038	6963913	49.641



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.739	8773293	96.892
2	19.273	281377	3.108



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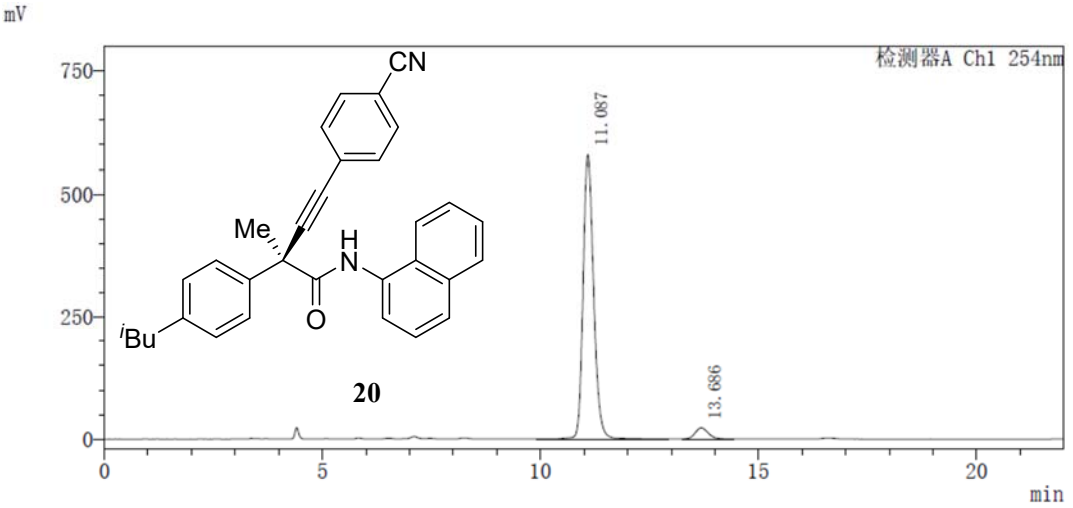
Peak Table

检测器A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.143	1492154	50.379
2	13.705	1469681	49.621



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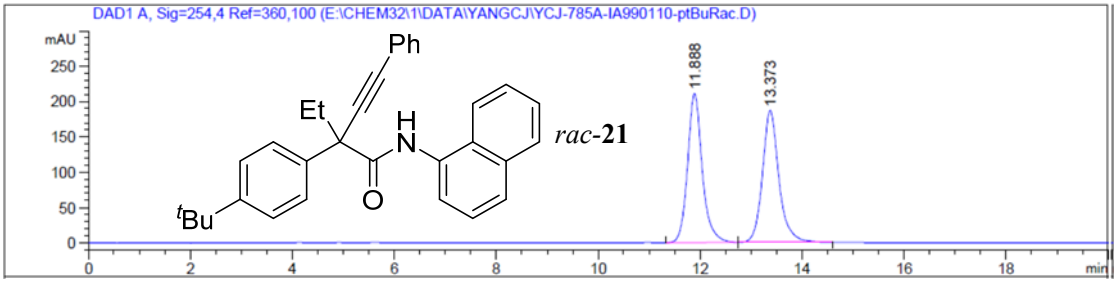
Peak Table

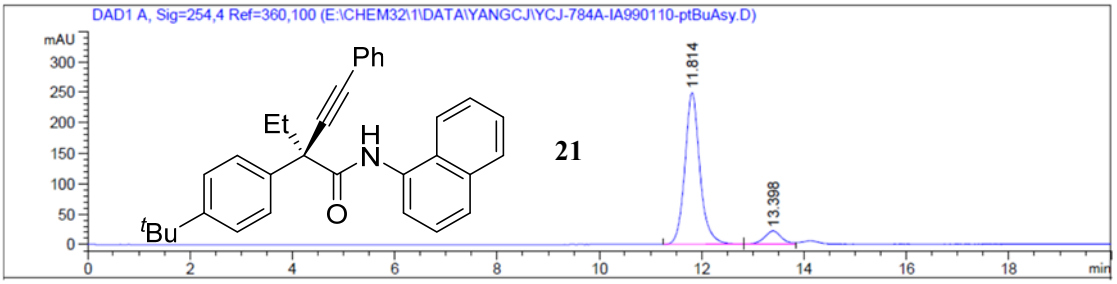
检测器A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	11.087	9740511	95.403
2	13.686	469363	4.597



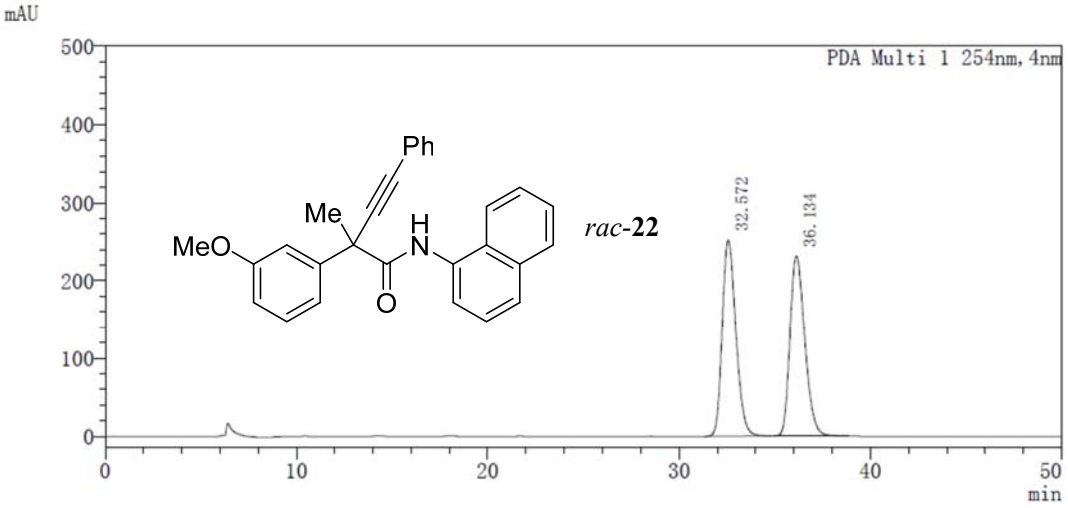
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.888	BB	0.2968	4212.00049	211.05446	50.1243
2	13.373	BB	0.3381	4191.11182	186.55934	49.8757
Totals :				8403.11230	397.61380	



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

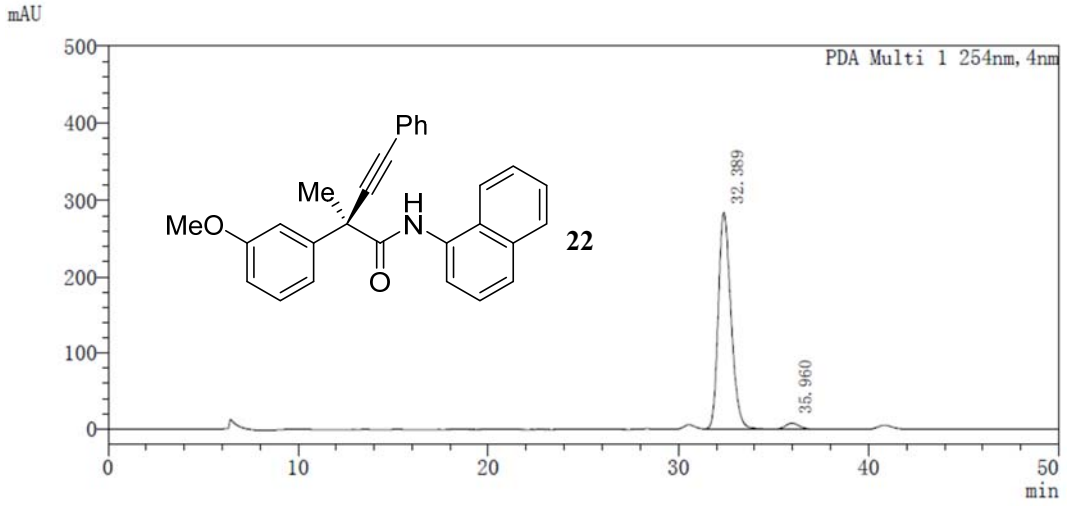
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.814	BB	0.3042	5081.12598	248.87680	91.0441
2	13.398	BV	0.3371	499.82486	21.66844	8.9559
Totals :				5580.95084	270.54524	



Peak Table

PDA Ch1 254nm

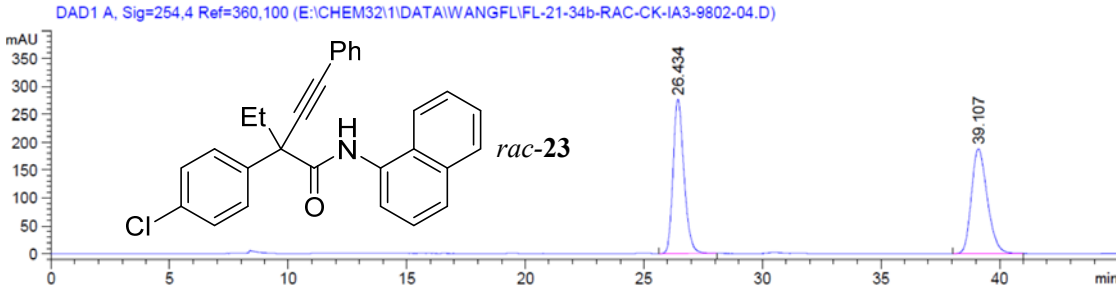
Peak#	Ret. Time	Area	Area%
1	32.572	12489416	50.022
2	36.134	12478203	49.978



Peak Table

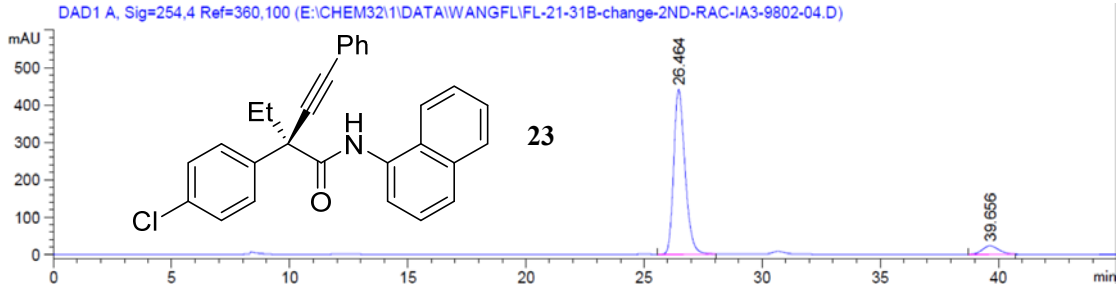
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	32.389	13127999	97.159
2	35.960	383808	2.841



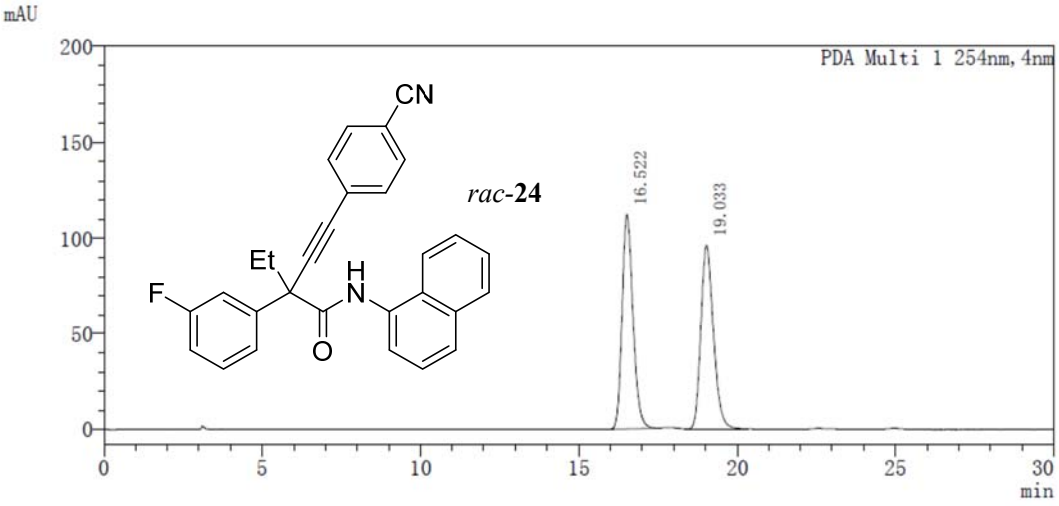
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.434	BB	0.4921	8868.66211	276.54718	50.2386
2	39.107	BV R	0.7058	8784.40625	187.76146	49.7614
Totals :				1.76531e4	464.30864	



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

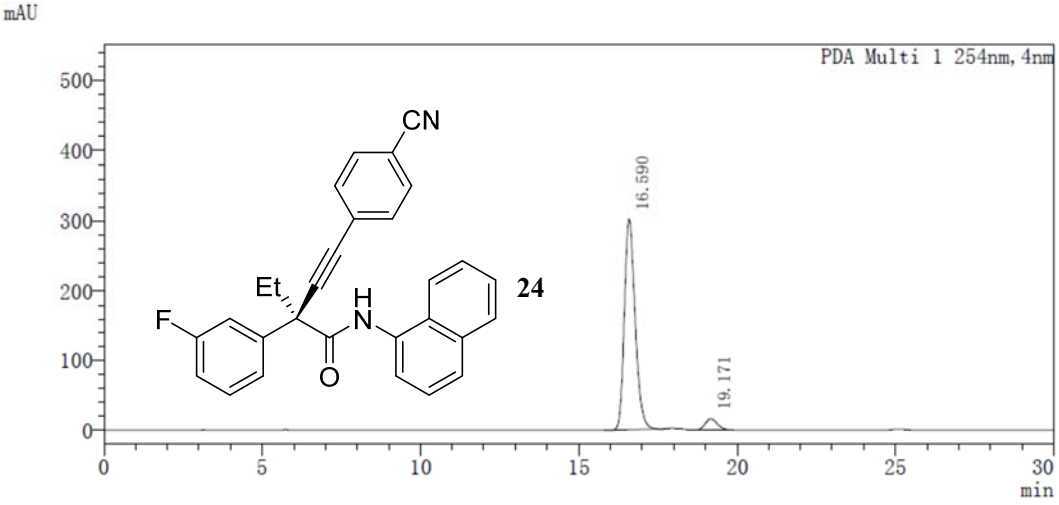
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.464	BB	0.5106	1.46653e4	440.29556	93.2564
2	39.656	MM R	0.7826	1060.48047	22.58313	6.7436
Totals :				1.57258e4	462.87869	



Peak Table

PDA Ch1 254nm

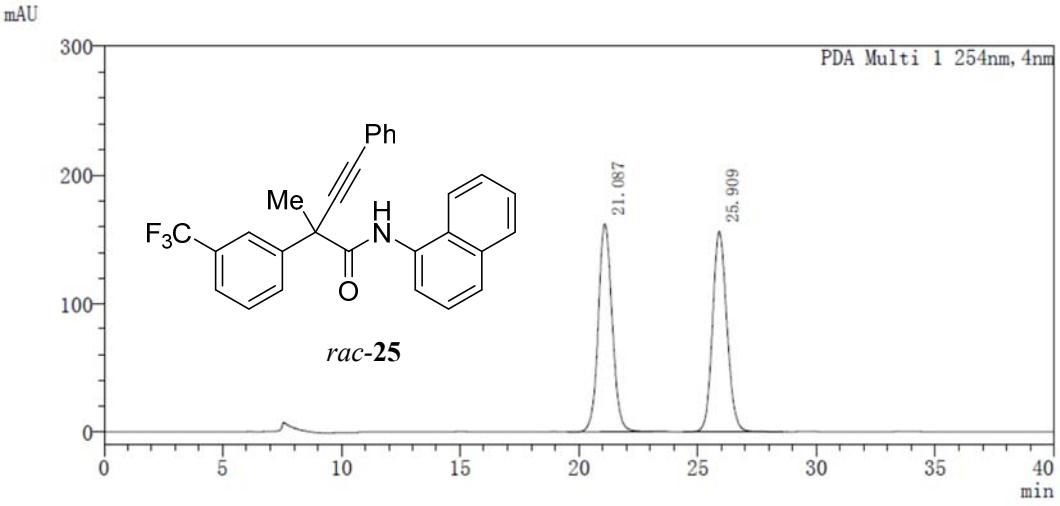
Peak#	Ret. Time	Area	Area%
1	16.522	2680574	50.235
2	19.033	2655526	49.765



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.590	7134103	94.388
2	19.171	424164	5.612



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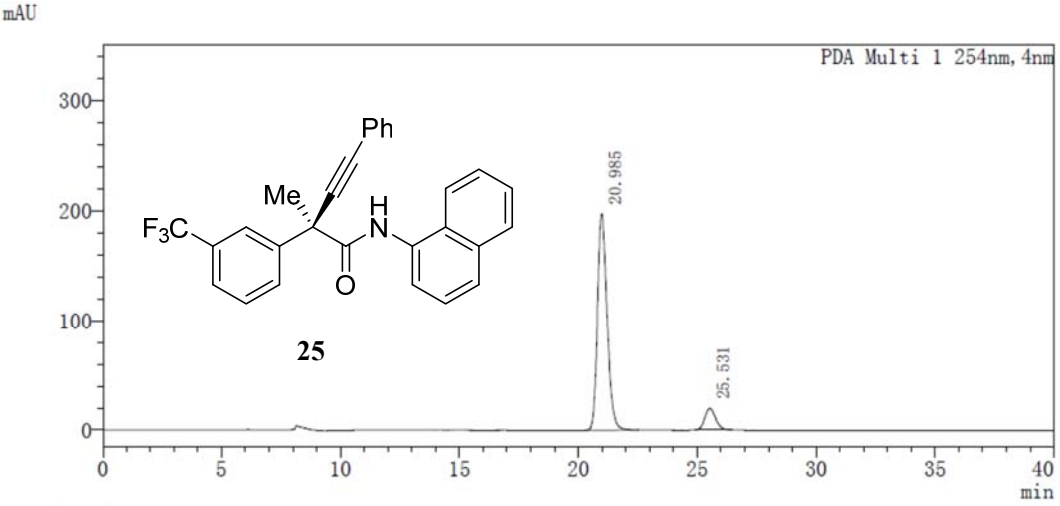
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.087	6591248	50.065
2	25.909	6574239	49.935



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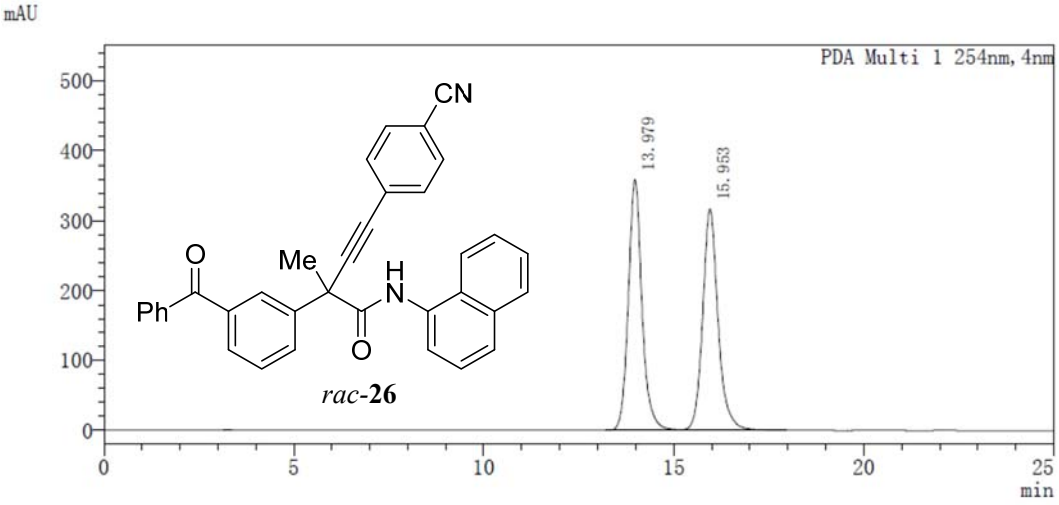
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.985	5557583	89.820
2	25.531	629902	10.180



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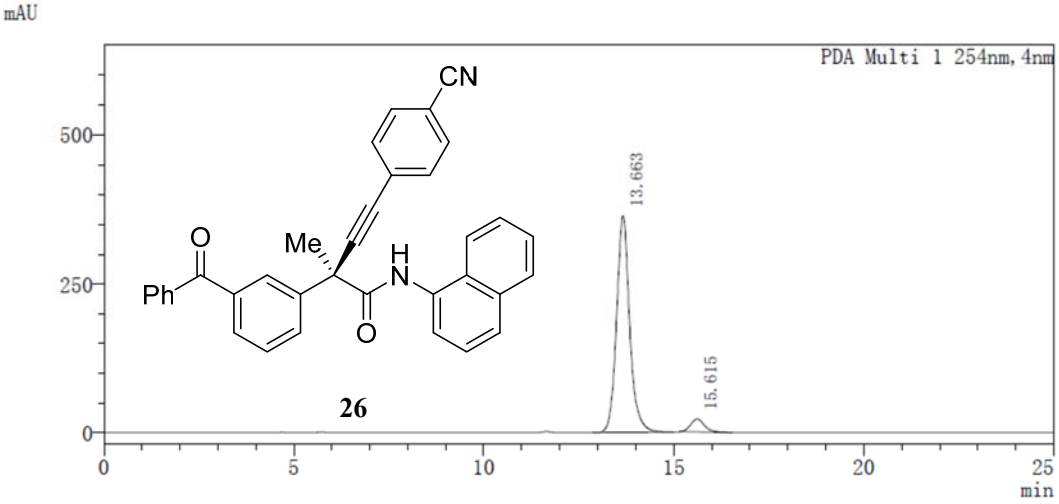
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.979	9015963	50.165
2	15.953	8956654	49.835



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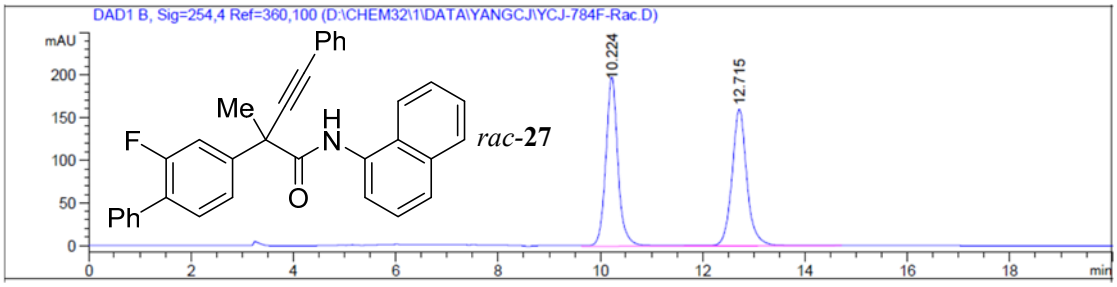
Peak Table

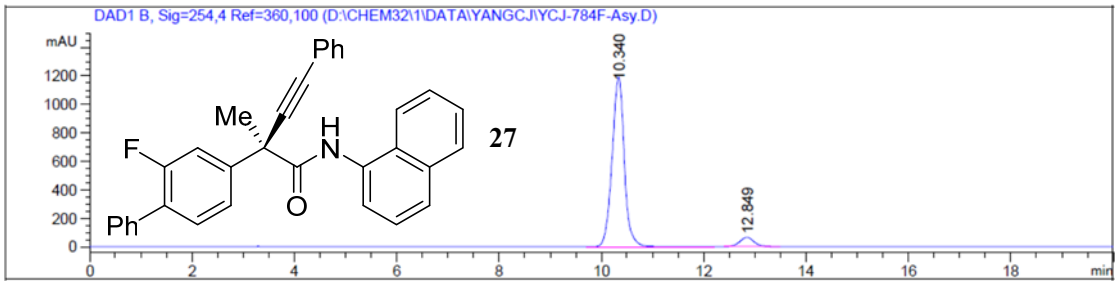
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.663	8775351	94.046
2	15.615	555515	5.954



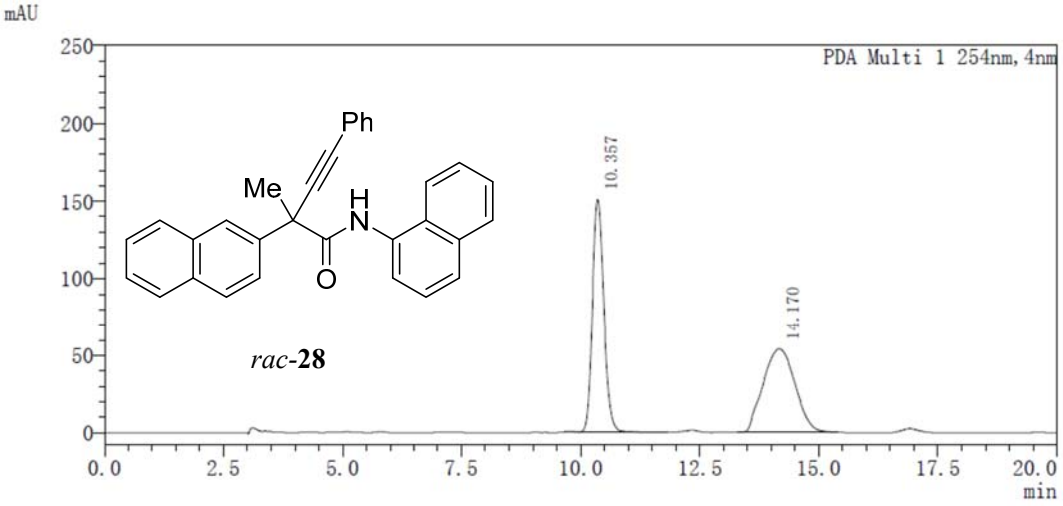
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.224	VV	0.2550	3318.31152	198.48392	50.4013
2	12.715	VV	0.3058	3265.46606	160.17561	49.5987
Totals :				6583.77759	358.65953	



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

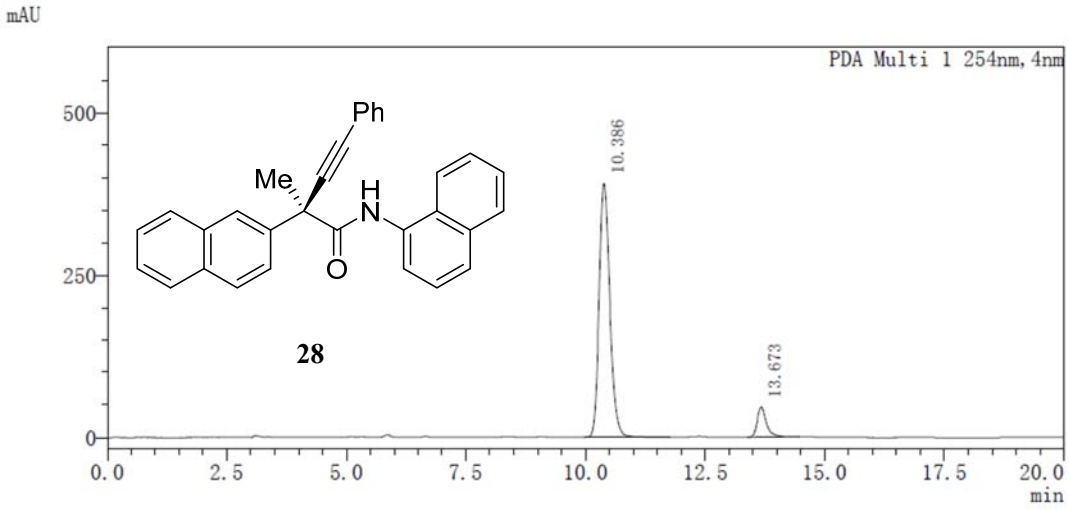
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.340	BV	0.2583	1.98235e4	1190.32178	93.9243
2	12.849	MM R	0.3258	1282.32556	65.60004	6.0757
Totals :				2.11058e4	1255.92181	



Peak Table

PDA Ch1 254nm

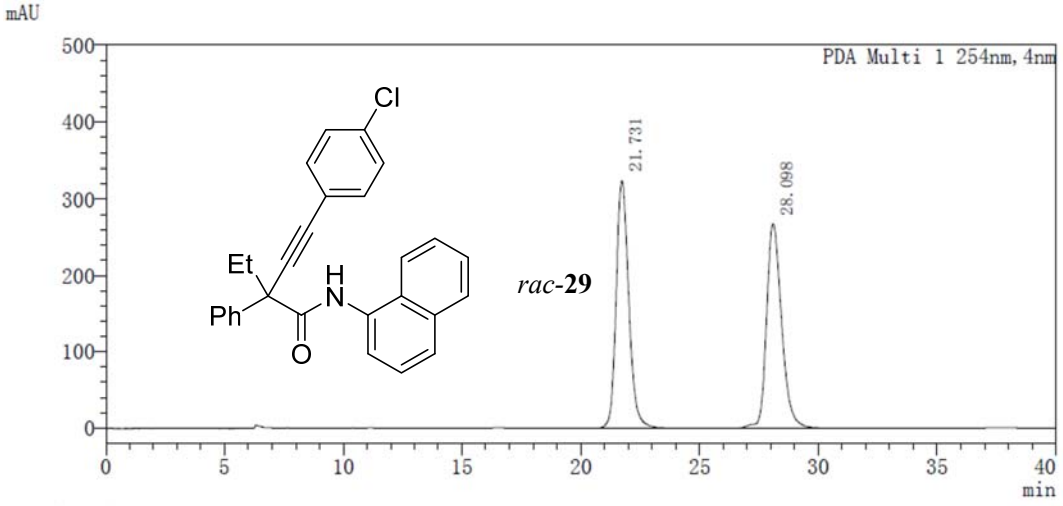
Peak#	Ret. Time	Area	Area%
1	10.357	2507178	49.818
2	14.170	2525495	50.182



Peak Table

PDA Ch1 254nm

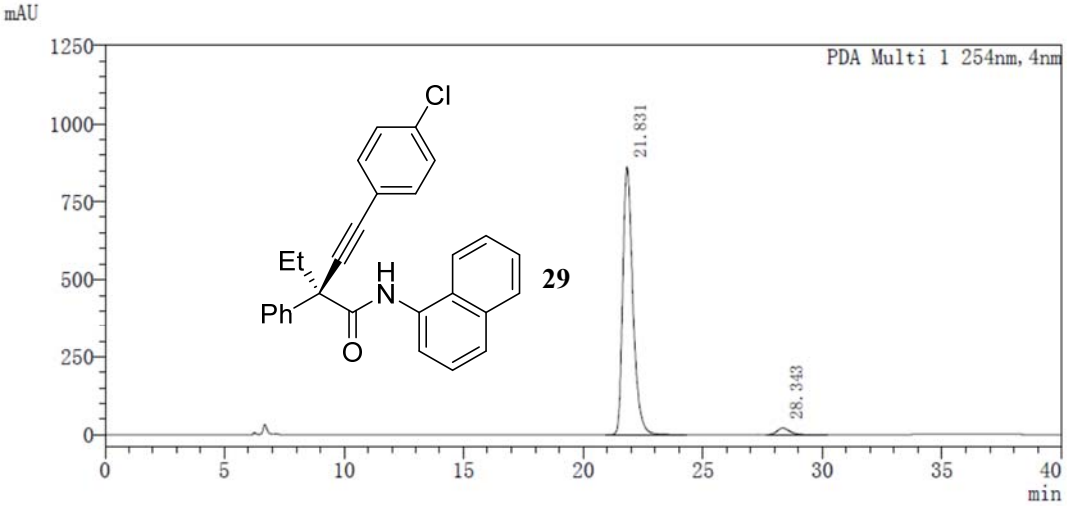
Peak#	Ret. Time	Area	Area%
1	10.386	6098874	90.826
2	13.673	616004	9.174



Peak Table

PDA Ch1 254nm

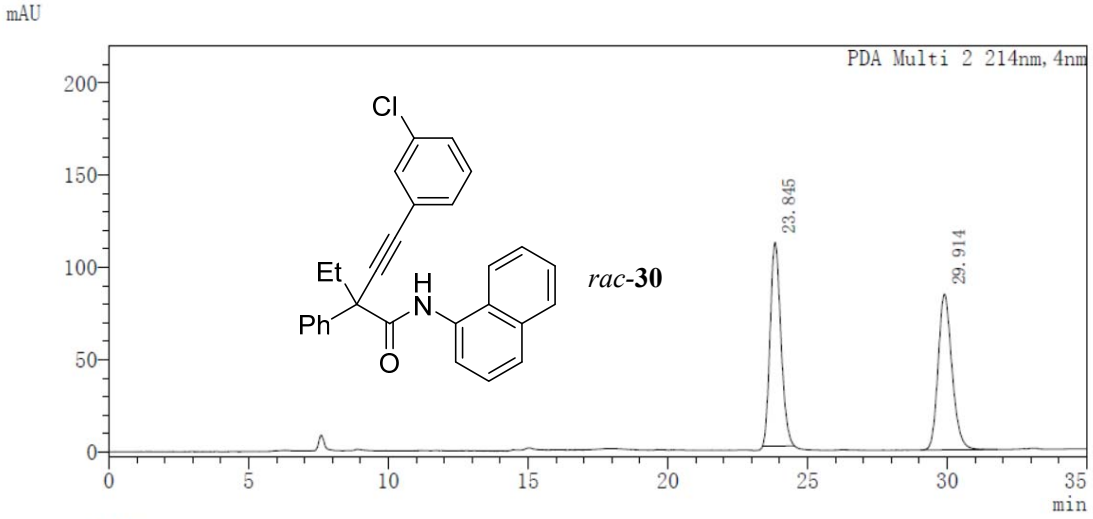
Peak#	Ret. Time	Area	Area%
1	21.731	11950290	50.337
2	28.098	11790154	49.663



Peak Table

PDA Ch1 254nm

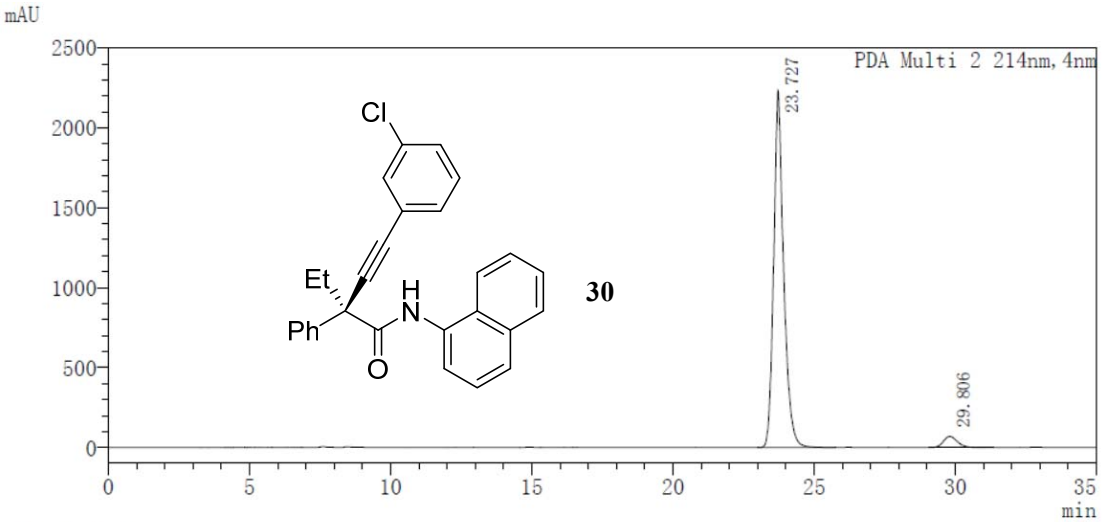
Peak#	Ret. Time	Area	Area%
1	21.831	25405531	97.023
2	28.343	779452	2.977



Peak Table

PDA Ch2 214nm

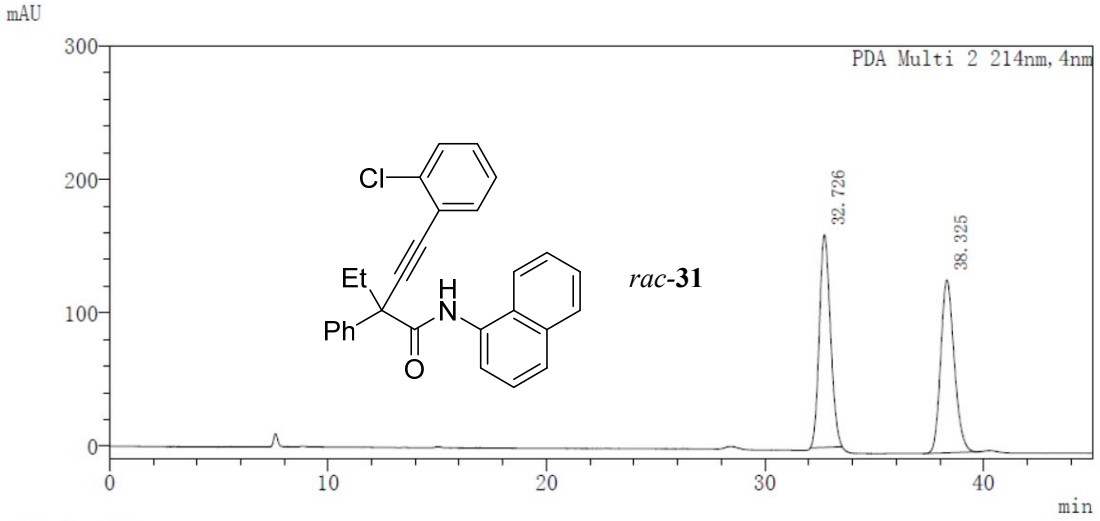
Peak#	Ret. Time	Area	Area%
1	23.845	2958912	50.359
2	29.914	2916719	49.641



Peak Table

PDA Ch2 214nm

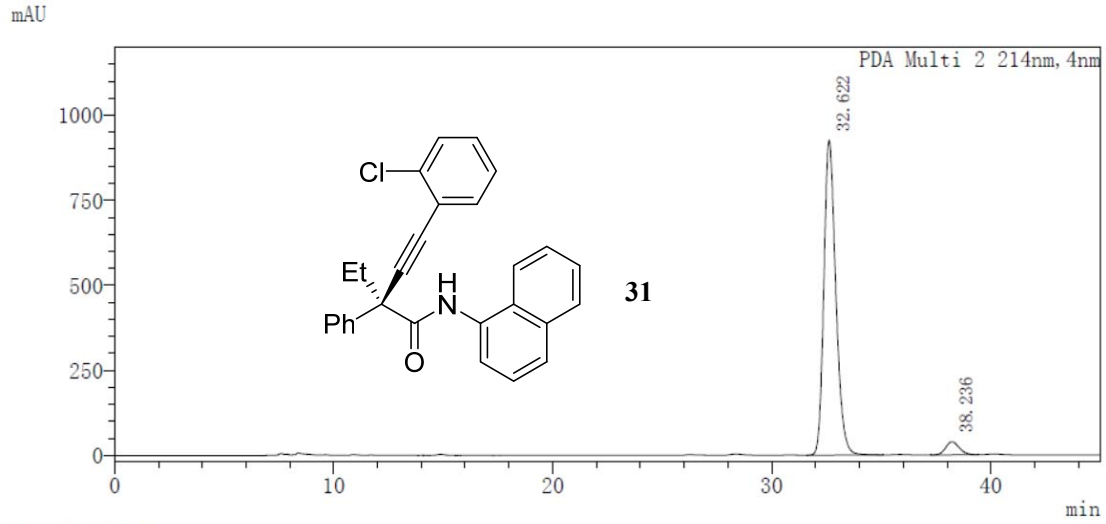
Peak#	Ret. Time	Area	Area%
1	23.727	54771764	95.739
2	29.806	2437974	4.261



Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	32.726	5638940	50.152
2	38.325	5604737	49.848

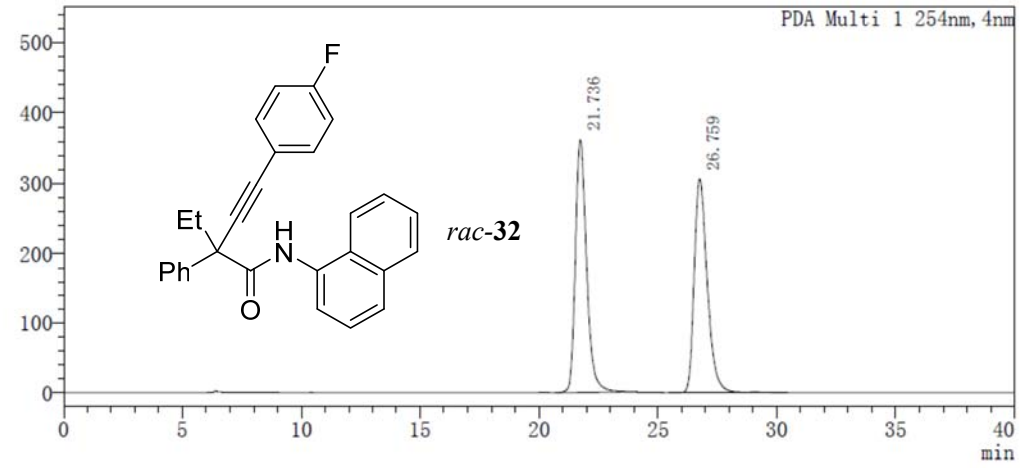


Peak Table

PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	32.622	35102692	95.447
2	38.236	1674517	4.553

mAU



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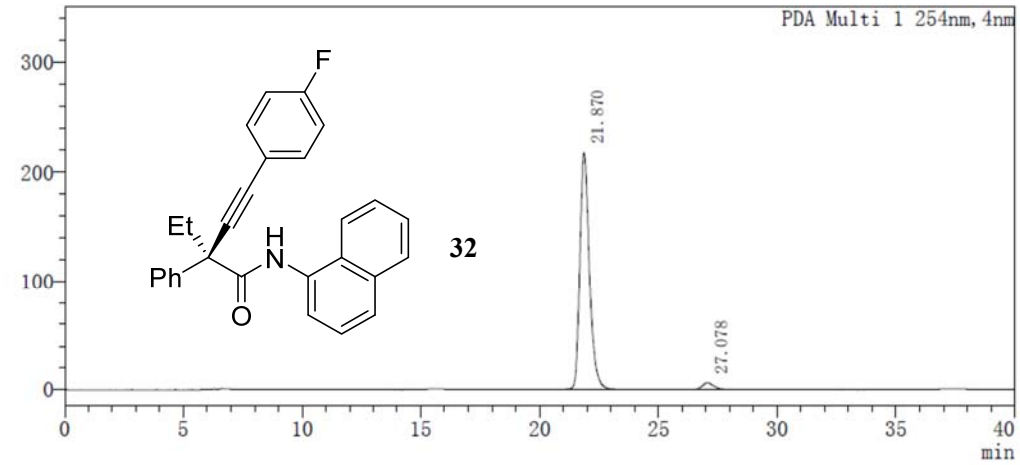
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	21.736	11924844	50.377
2	26.759	11746514	49.623

mAU



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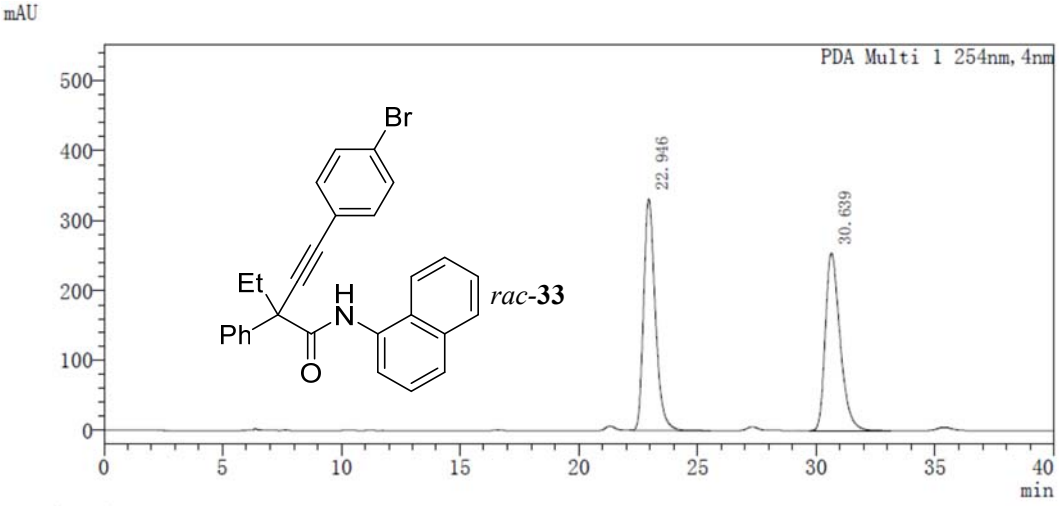
Peak Table

PDA Ch1 254nm

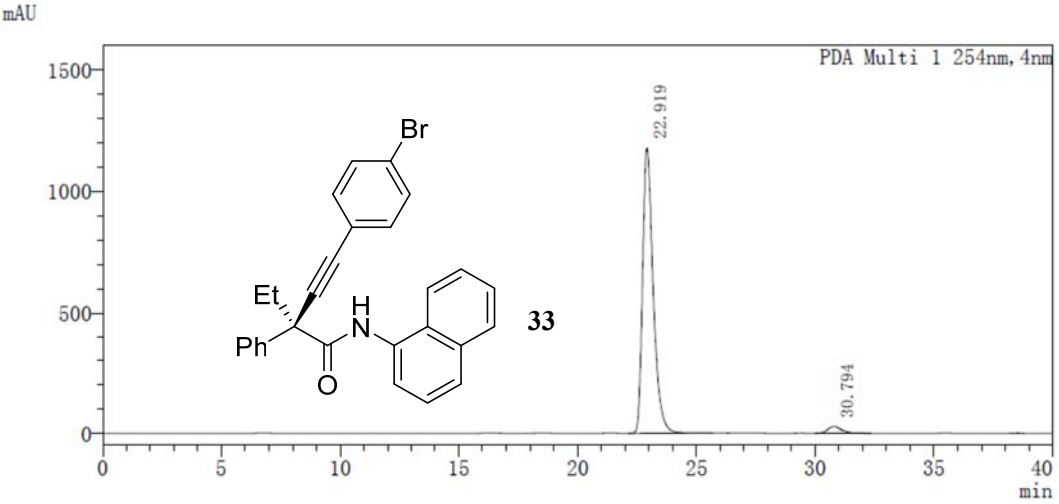
Peak#	Ret. Time	Area	Area%
1	21.870	6138226	96.646
2	27.078	213037	3.354



Peak Table

PDA Ch1 254nm

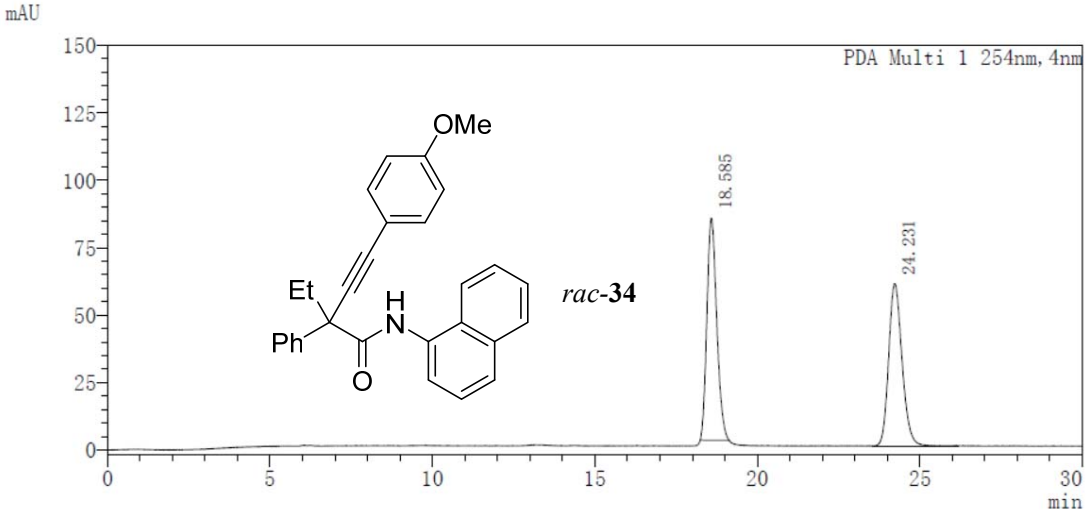
Peak#	Ret. Time	Area	Area%
1	22.946	11367043	50.825
2	30.639	10997974	49.175



Peak Table

PDA Ch1 254nm

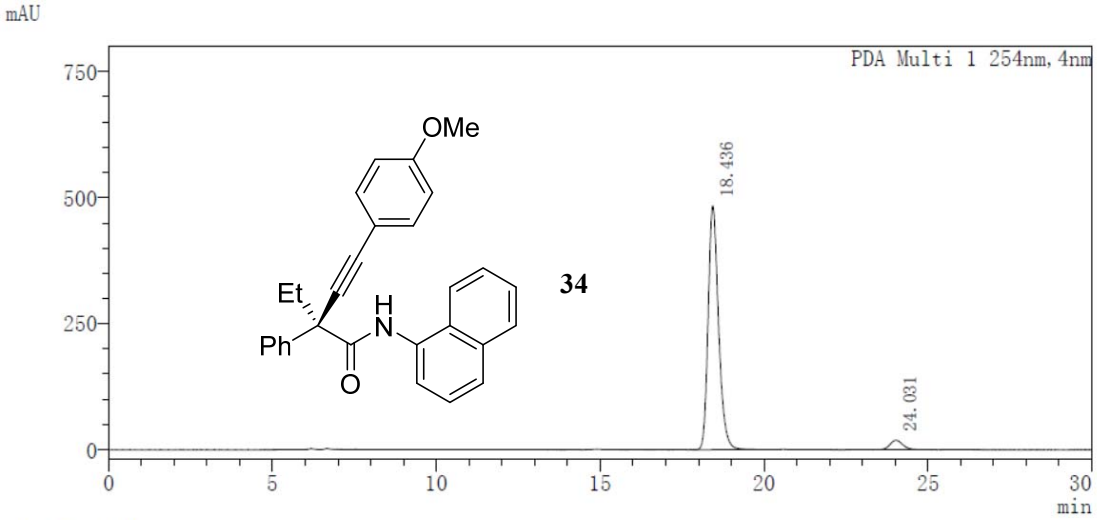
Peak#	Ret. Time	Area	Area%
1	22.919	36655851	97.094
2	30.794	1097166	2.906



Peak Table

PDA Ch1 254nm

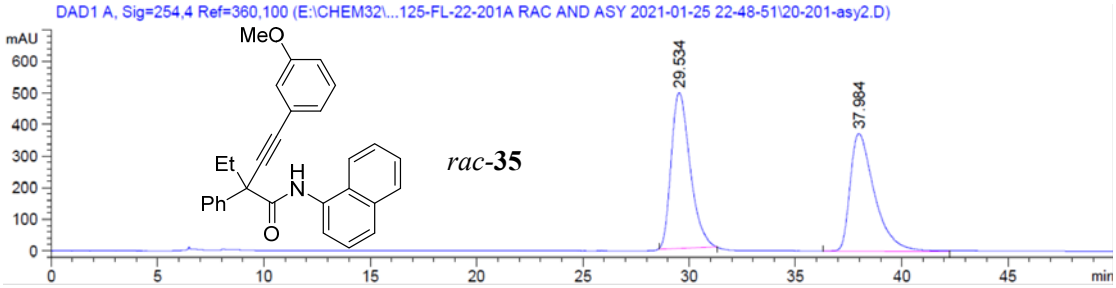
Peak#	Ret. Time	Area	Area%
1	18.585	1735614	50.133
2	24.231	1726407	49.867



Peak Table

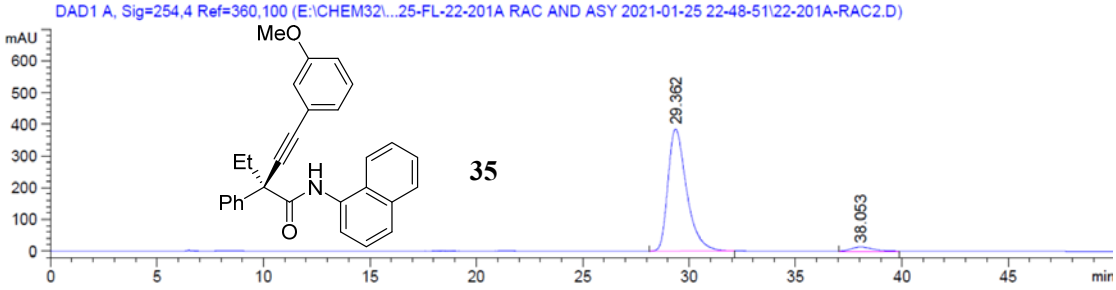
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	18.436	10665817	95.448
2	24.031	508678	4.552



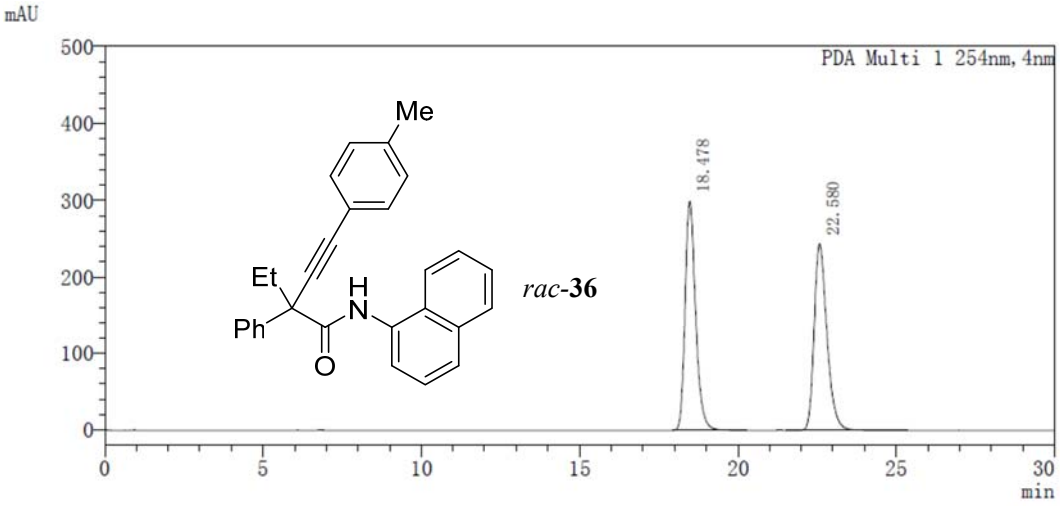
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.534	MM R	1.0334	3.06337e4	494.05920	50.5327
2	37.984	MM R	1.3415	2.99879e4	372.56265	49.4673
Totals :				6.06216e4	866.62186	



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

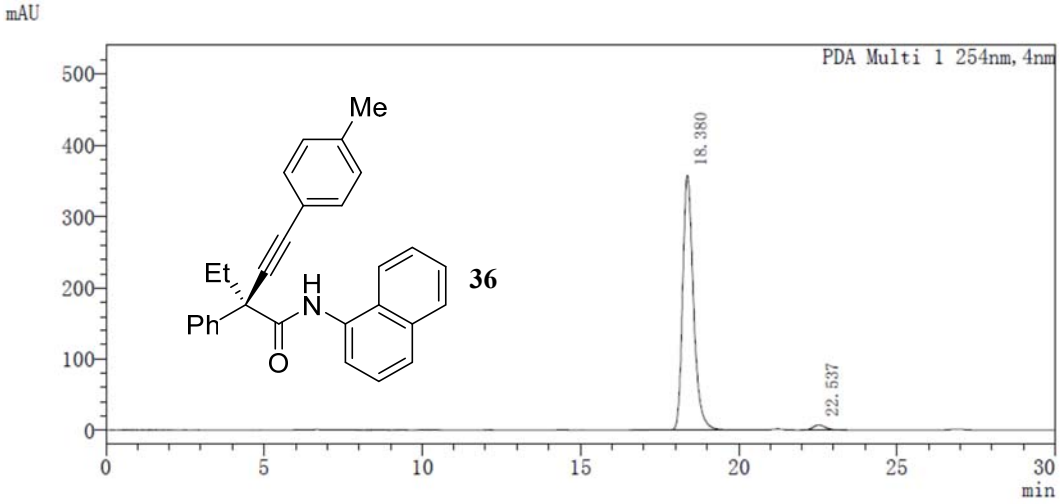
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.362	BB	0.9092	2.35864e4	385.80484	96.2443
2	38.053	BB	0.8150	920.38971	13.37287	3.7557
Totals :				2.45067e4	399.17771	



Peak Table

PDA Ch1 254nm

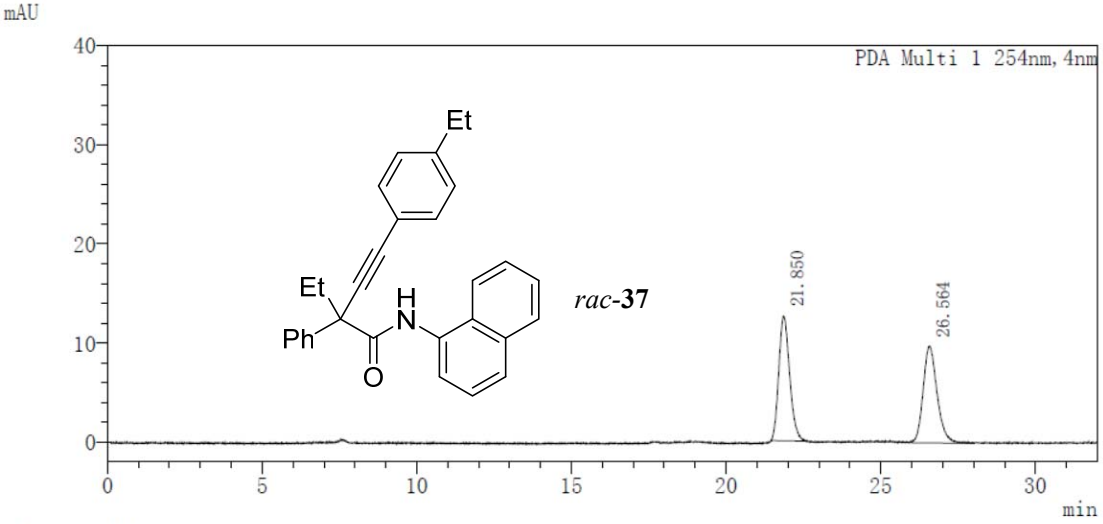
Peak#	Ret. Time	Area	Area%
1	18.478	6916597	50.335
2	22.580	6824634	49.665



Peak Table

PDA Ch1 254nm

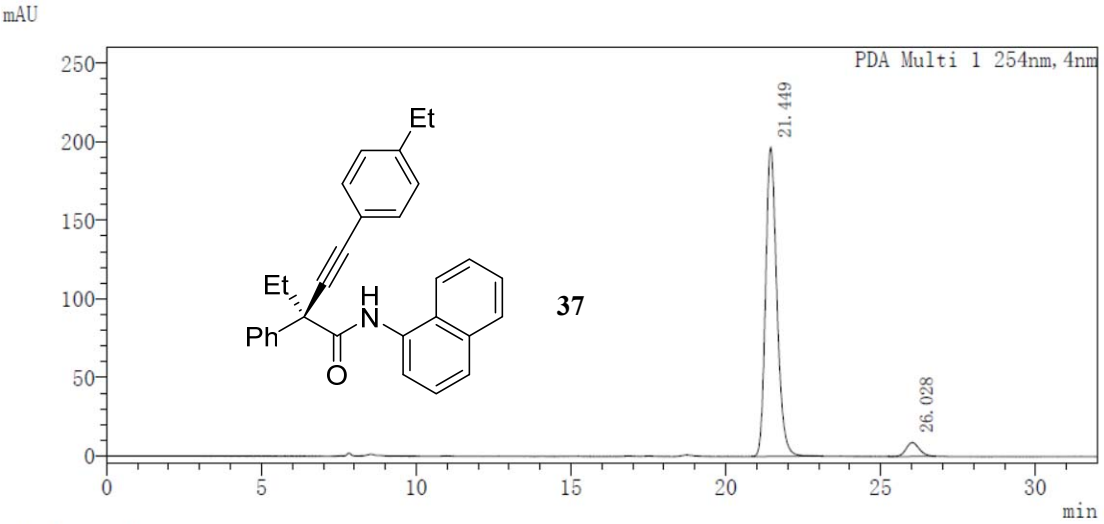
Peak#	Ret. Time	Area	Area%
1	18.380	8509027	97.689
2	22.537	201274	2.311



Peak Table

PDA Ch1 254nm

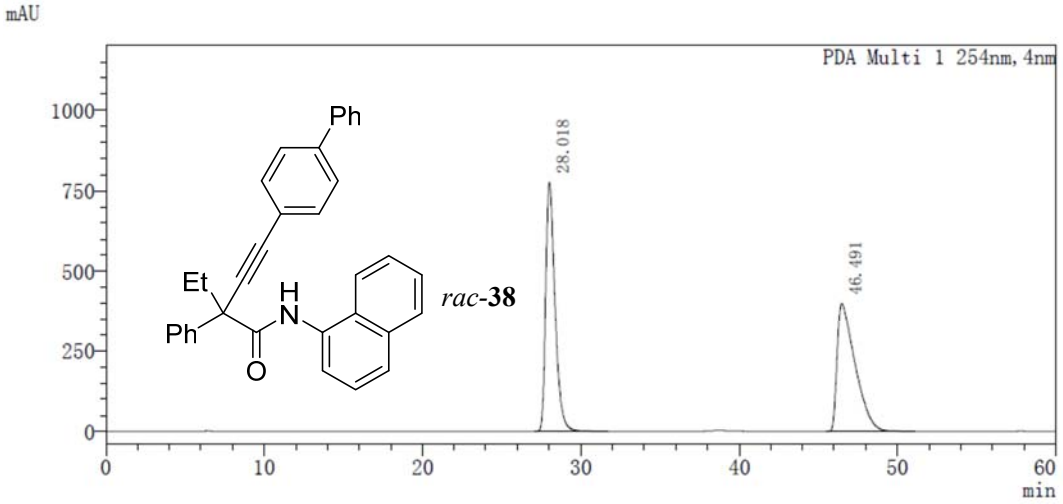
Peak#	Ret. Time	Area	Area%
1	21.850	306140	49.985
2	26.564	306326	50.015



Peak Table

PDA Ch1 254nm

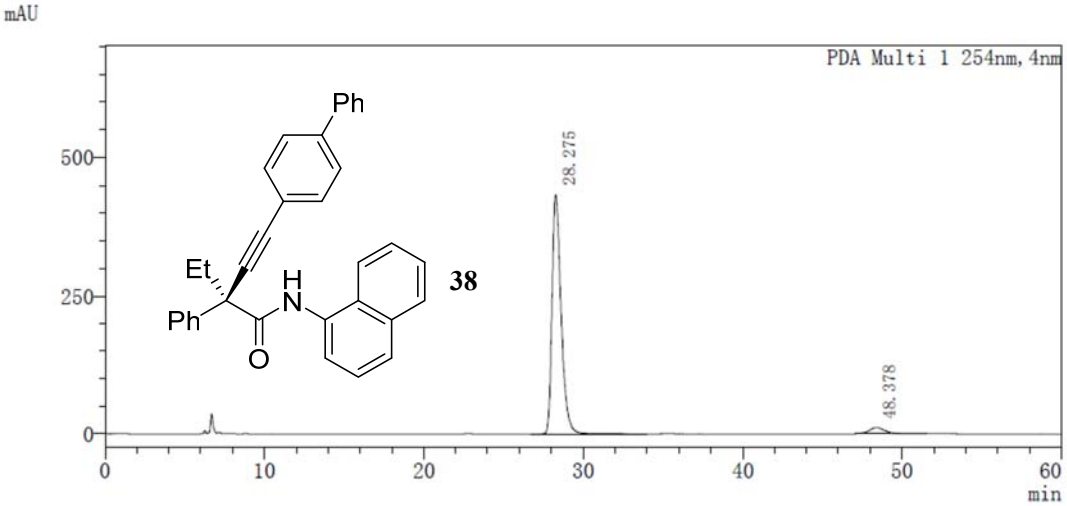
Peak#	Ret. Time	Area	Area%
1	21.449	4965194	94.951
2	26.028	264010	5.049



Peak Table

PDA Ch1 254nm

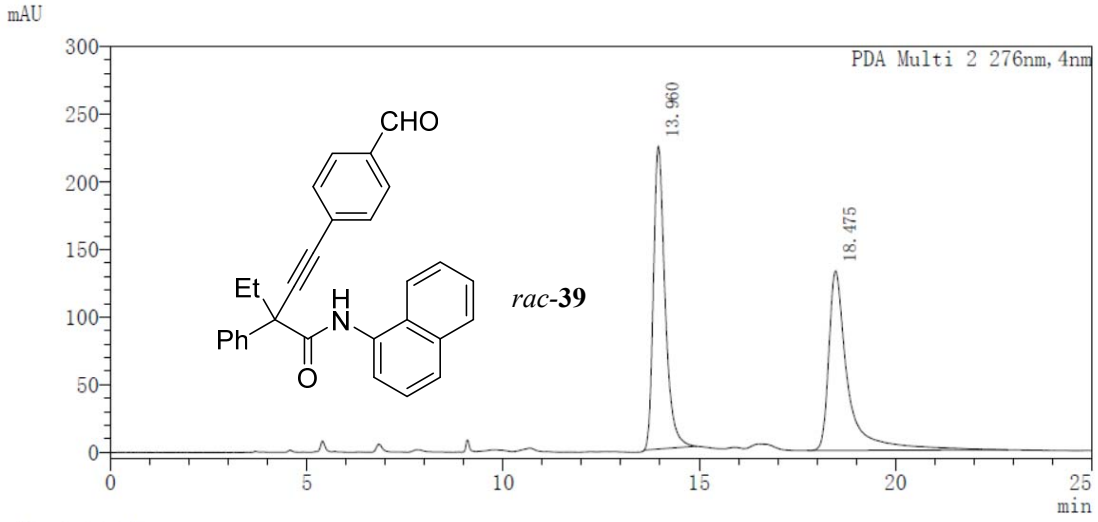
Peak#	Ret. Time	Area	Area%
1	28.018	31789071	50.281
2	46.491	31433661	49.719



Peak Table

PDA Ch1 254nm

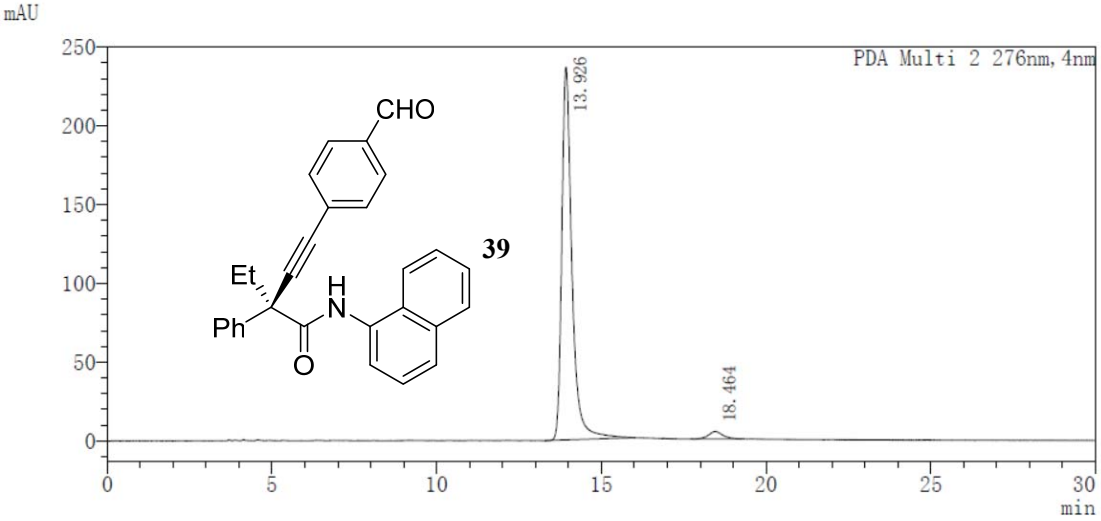
Peak#	Ret. Time	Area	Area%
1	28.275	17231665	96.468
2	48.378	630860	3.532



Peak Table

PDA Ch2 276nm

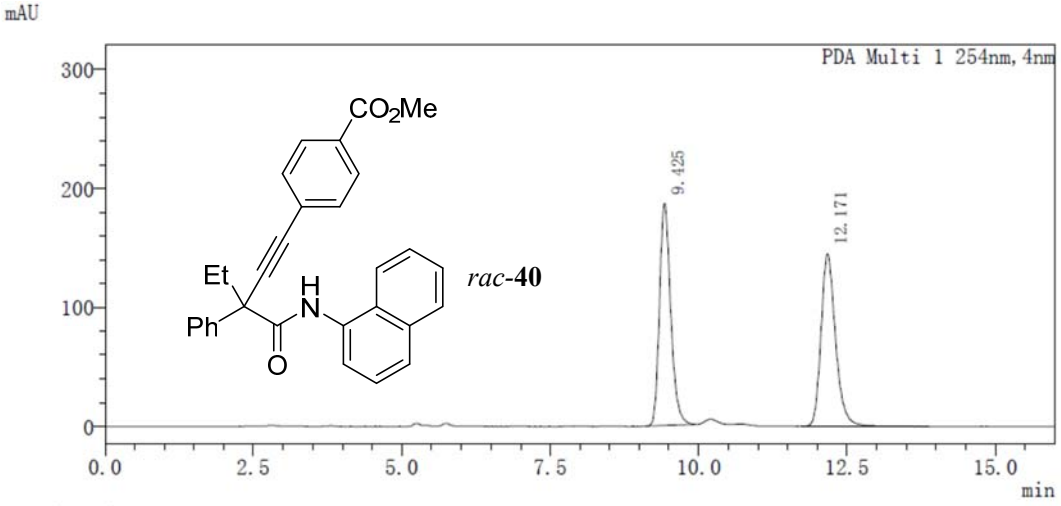
Peak#	Ret. Time	Area	Area%
1	13.960	4619317	50.457
2	18.475	4535605	49.543



Peak Table

PDA Ch2 276nm

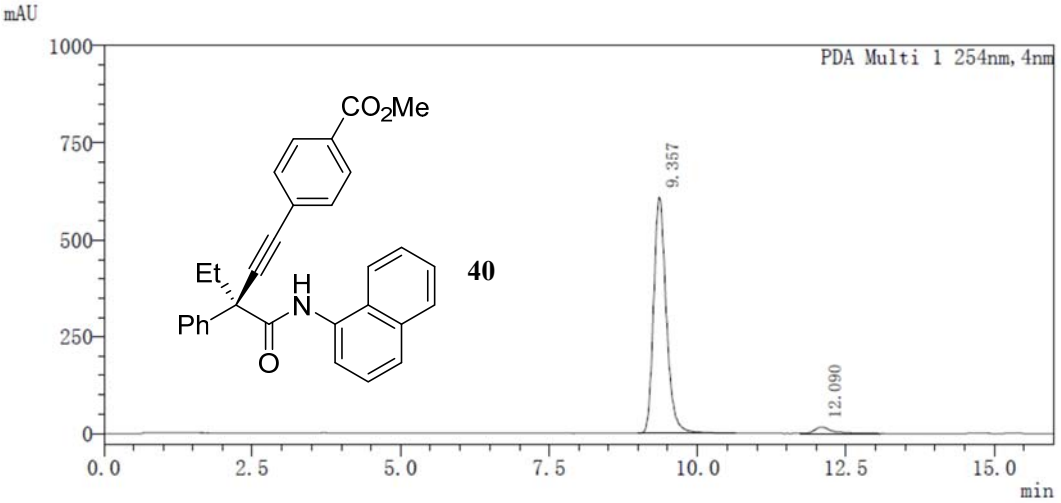
Peak#	Ret. Time	Area	Area%
1	13.926	5092504	97.219
2	18.464	145674	2.781



Peak Table

PDA Ch1 254nm

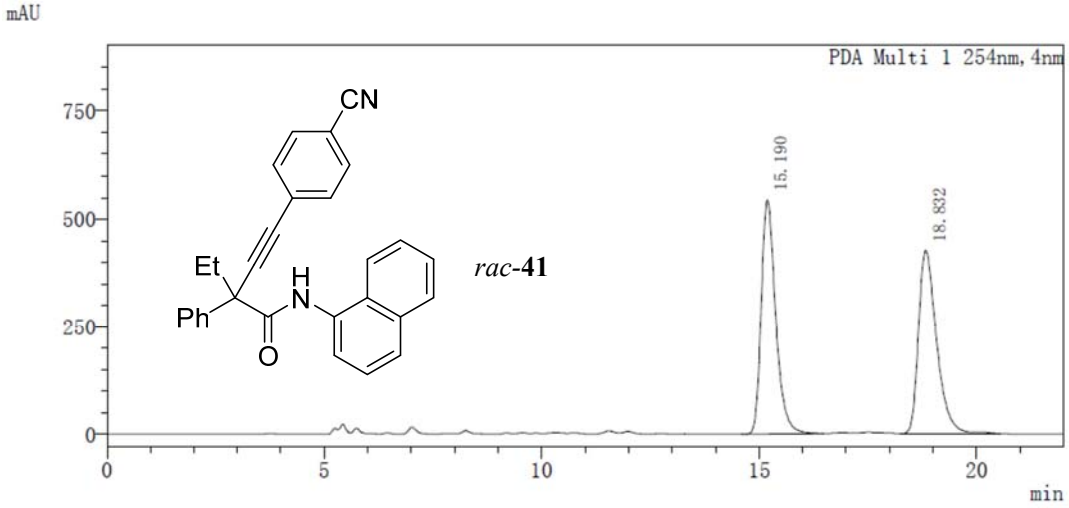
Peak#	Ret. Time	Area	Area%
1	9.425	2448735	49.804
2	12.171	2467983	50.196



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.357	9093329	96.595
2	12.090	320588	3.405



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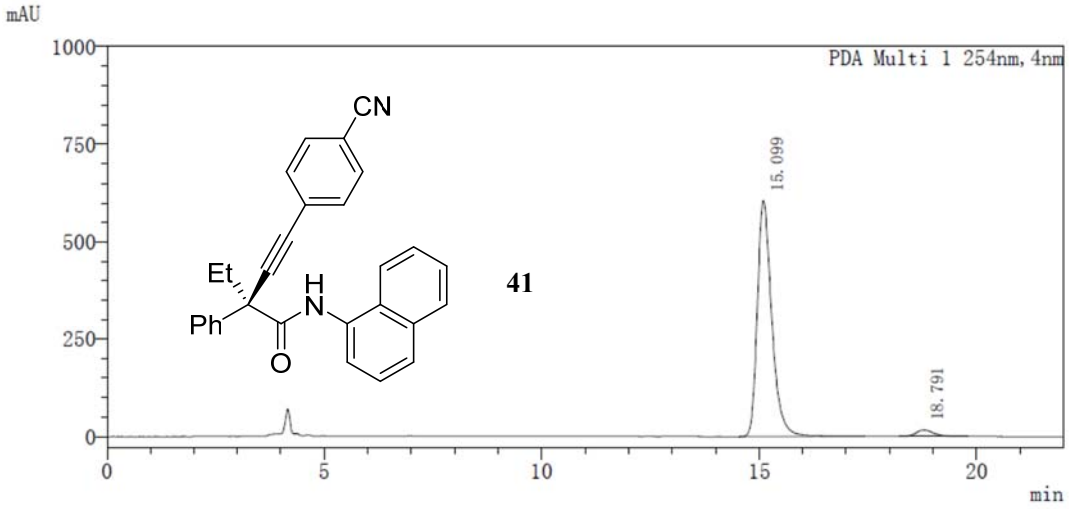
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.190	12575813	50.350
2	18.832	12400738	49.650

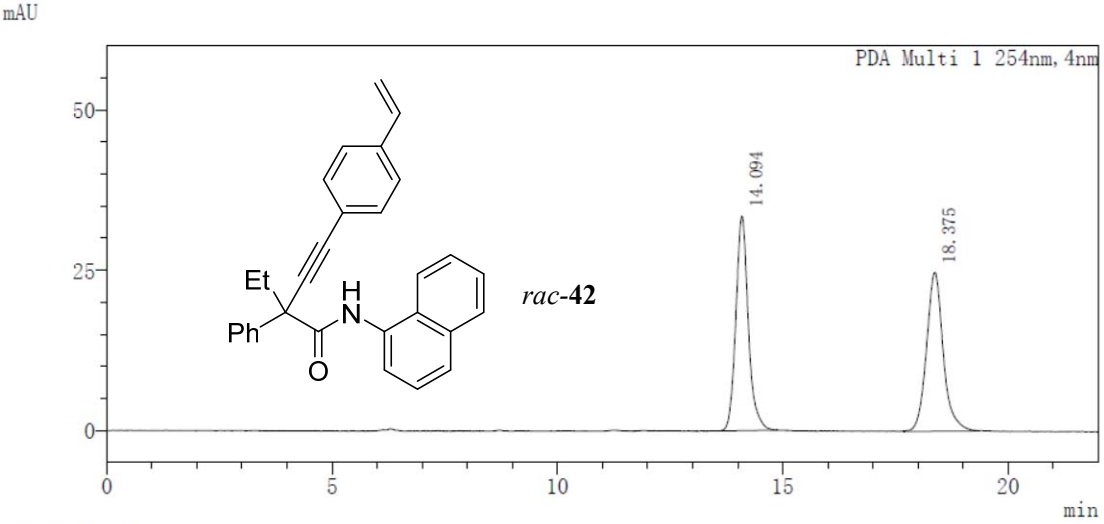


41

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.099	13983469	96.858
2	18.791	453646	3.142

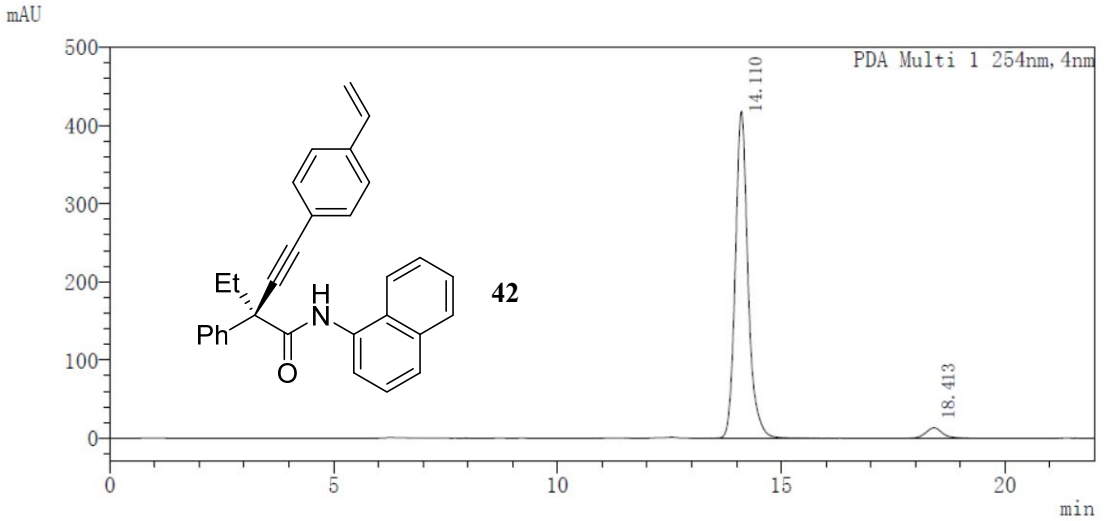


rac-**42**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	14.094	643906	50.231
2	18.375	637985	49.769

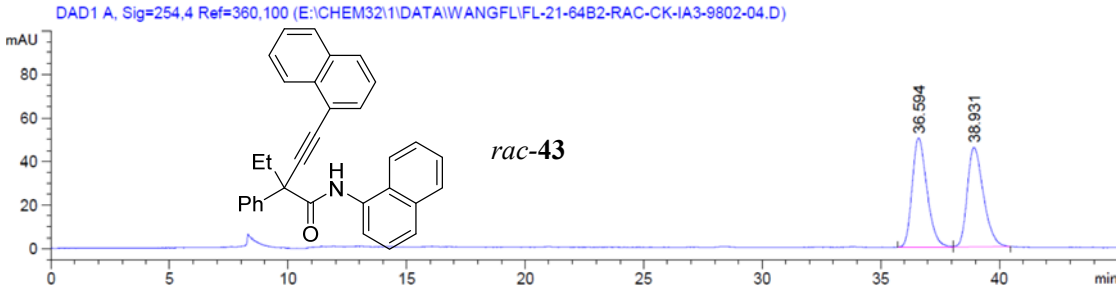


42

Peak Table

PDA Ch1 254nm

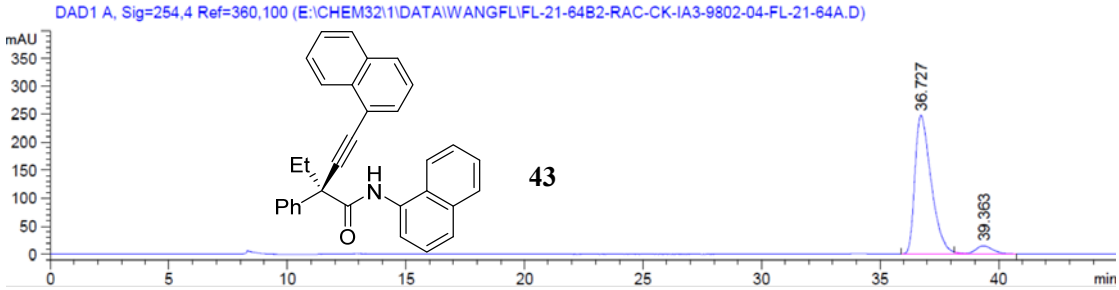
Peak#	Ret. Time	Area	Area%
1	14.110	8255876	95.982
2	18.413	345567	4.018



rac-**43**

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

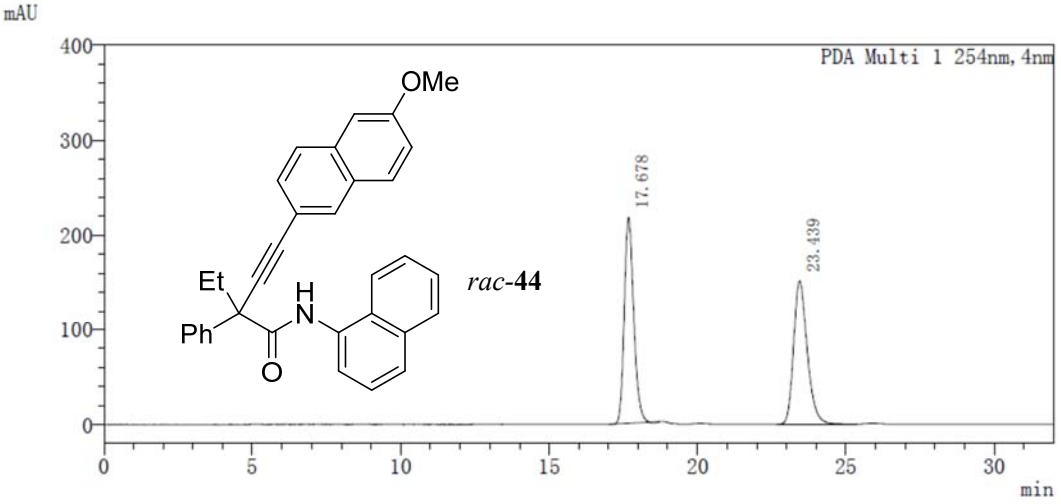
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.594	BV	0.6320	2188.33984	50.06032	50.2191
2	38.931	VB	0.6751	2169.24780	45.75777	49.7809
Totals :				4357.58765	95.81809	



43

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

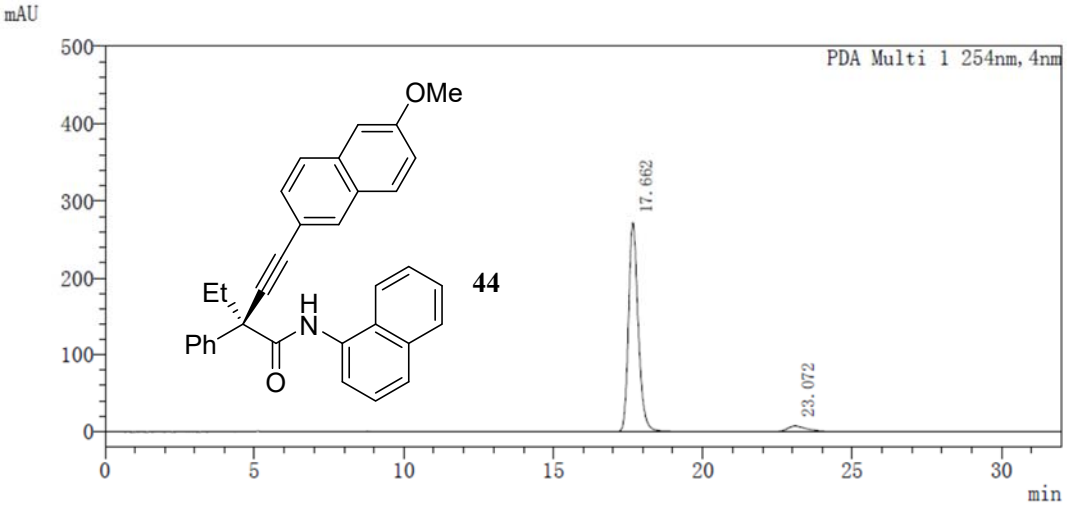
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.727	BV R	0.7381	1.19055e4	247.98300	94.0316
2	39.363	VB E	0.6129	755.66742	15.07373	5.9684
Totals :				1.26612e4	263.05673	



Peak Table

PDA Ch1 254nm

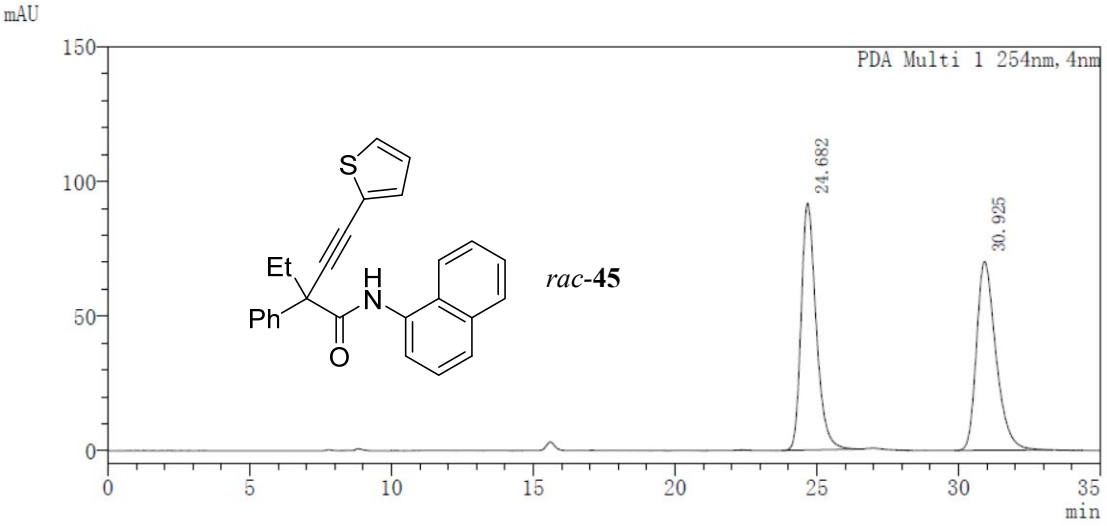
Peak#	Ret. Time	Area	Area%
1	17.678	4788888	49.573
2	23.439	4871439	50.427



Peak Table

PDA Ch1 254nm

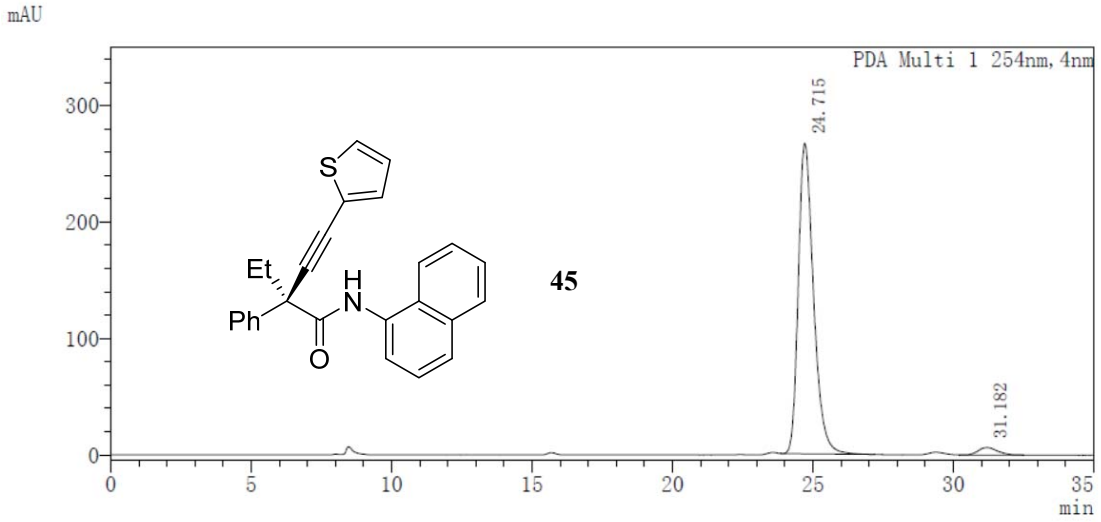
Peak#	Ret. Time	Area	Area%
1	17.662	6152543	94.789
2	23.072	338205	5.211



Peak Table

PDA Ch1 254nm

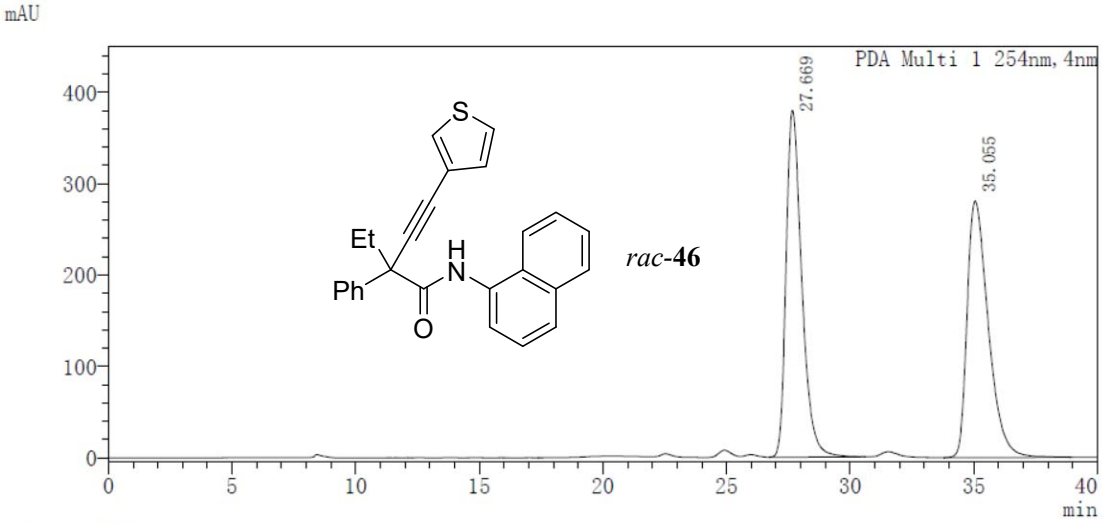
Peak#	Ret. Time	Area	Area%
1	24.682	3378151	50.166
2	30.925	3355839	49.834



Peak Table

PDA Ch1 254nm

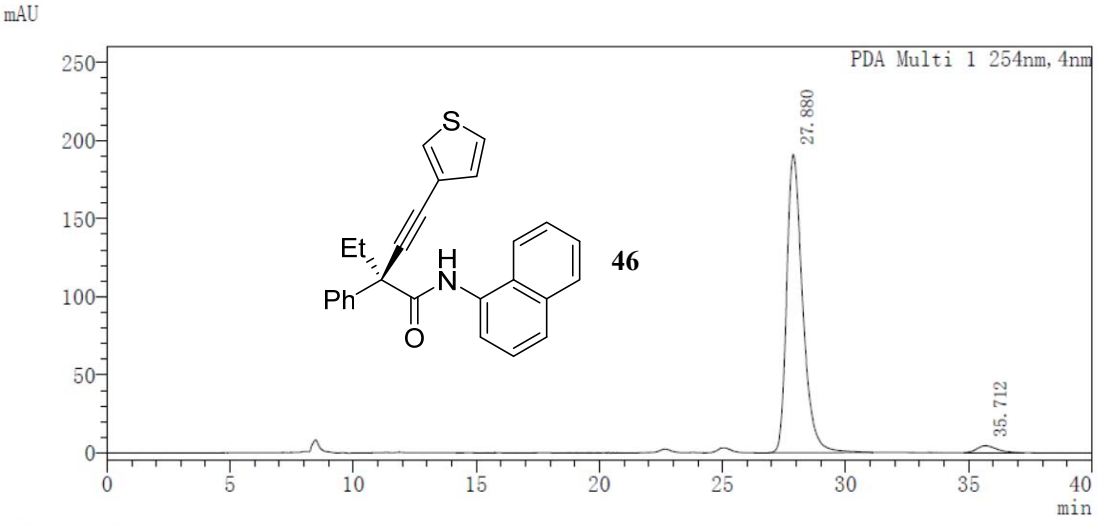
Peak#	Ret. Time	Area	Area%
1	24.715	10069467	97.031
2	31.182	308101	2.969



Peak Table

PDA Ch1 254nm

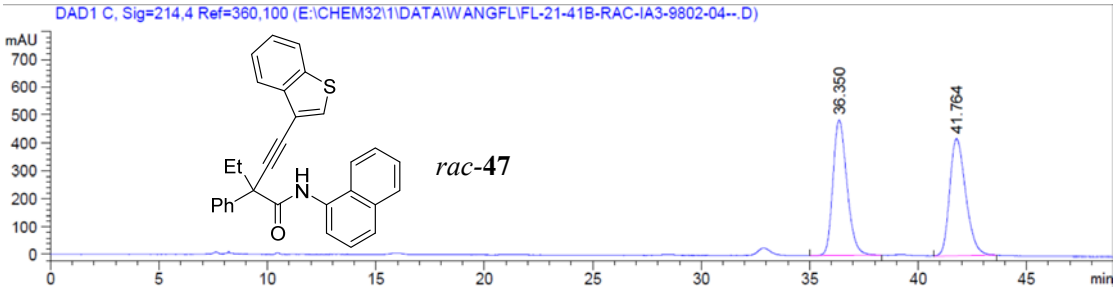
Peak#	Ret. Time	Area	Area%
1	27.669	16795452	50.134
2	35.055	16705942	49.866



Peak Table

PDA Ch1 254nm

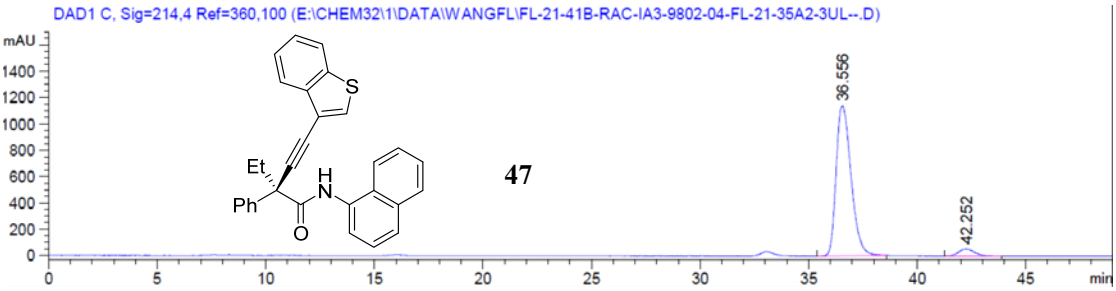
Peak#	Ret. Time	Area	Area%
1	27.880	8615628	97.121
2	35.712	255440	2.879



rac-**47**

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

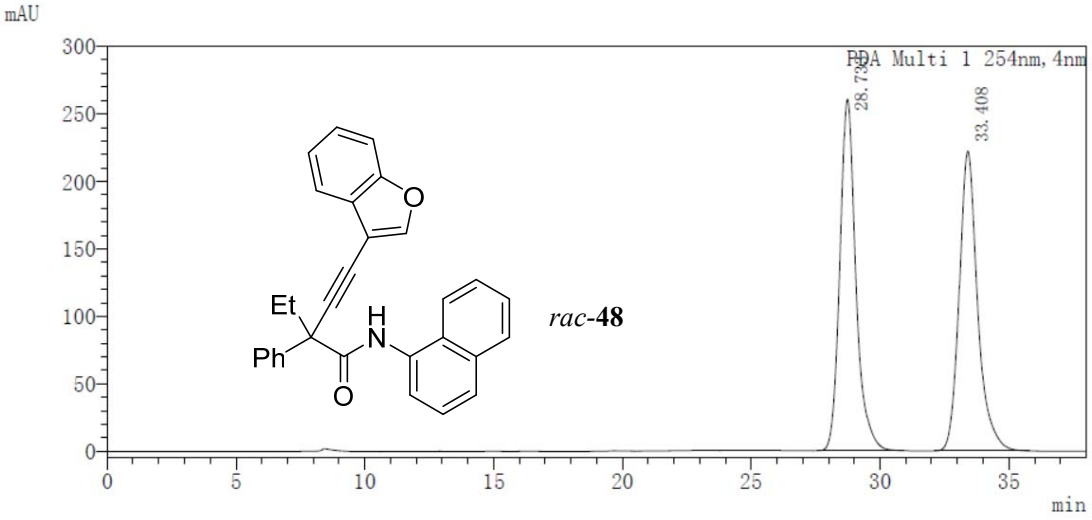
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.350	VV R	0.6540	2.20998e4	488.31244	50.3495
2	41.764	BV R	0.7009	2.17930e4	421.68924	49.6505
Totals :				4.38928e4	910.00168	



47

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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.556	VV R	0.5808	5.44887e4	1141.63599	94.9978
2	42.252	VV R	0.6202	2869.16187	56.14051	5.0022
Totals :				5.73578e4	1197.77649	

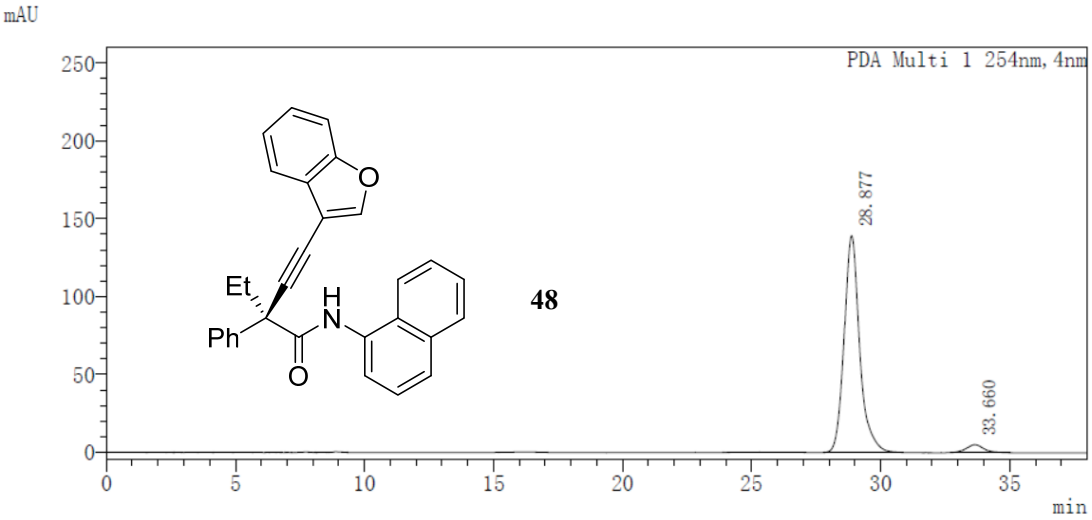


rac-**48**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	28.733	11248089	50.341
2	33.408	11095499	49.659

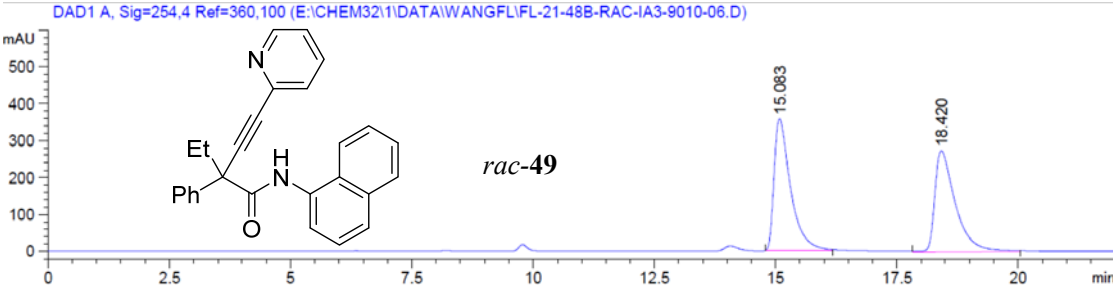


48

Peak Table

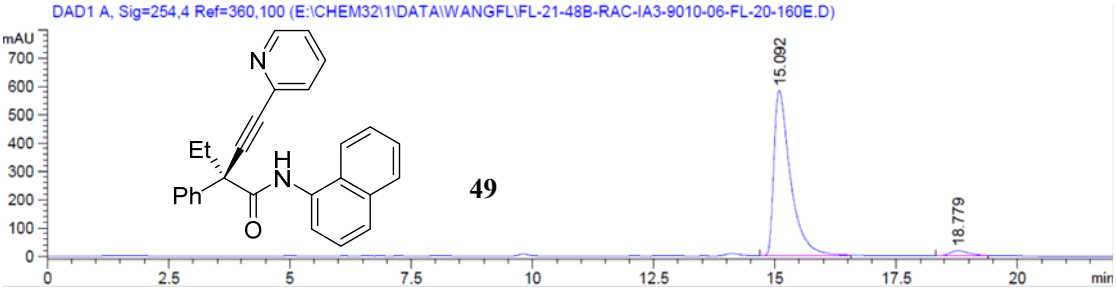
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	28.877	5846778	95.950
2	33.660	246769	4.050



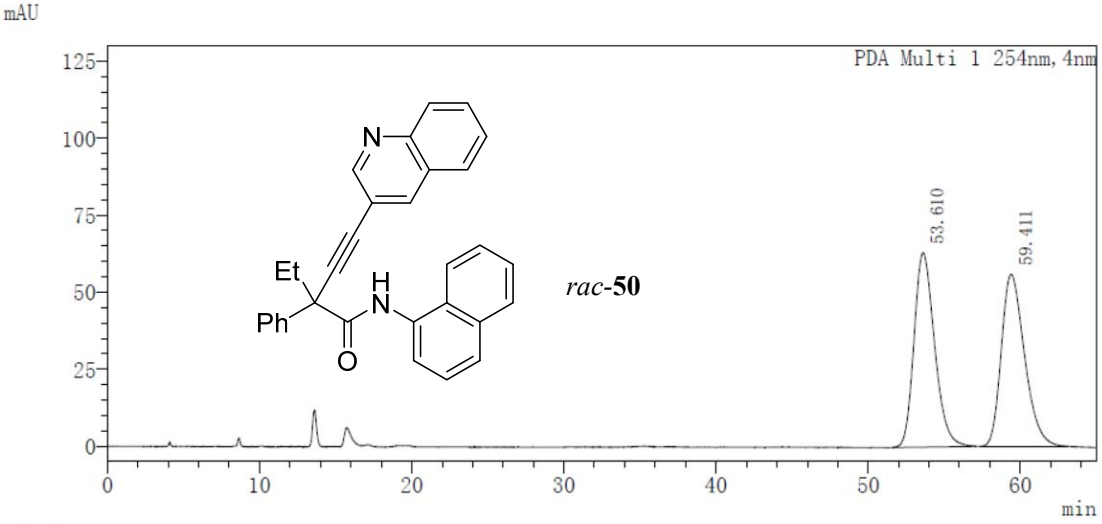
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.083	MF R	0.3916	8388.45117	356.98901	50.7557
2	18.420	MM R	0.4947	8138.64795	274.17709	49.2443
Totals :				1.65271e4	631.16611	



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.092	MF R	0.3968	1.39139e4	584.39966	96.2615
2	18.779	MF R	0.4700	540.37555	19.16306	3.7385
Totals :				1.44543e4	603.56272	

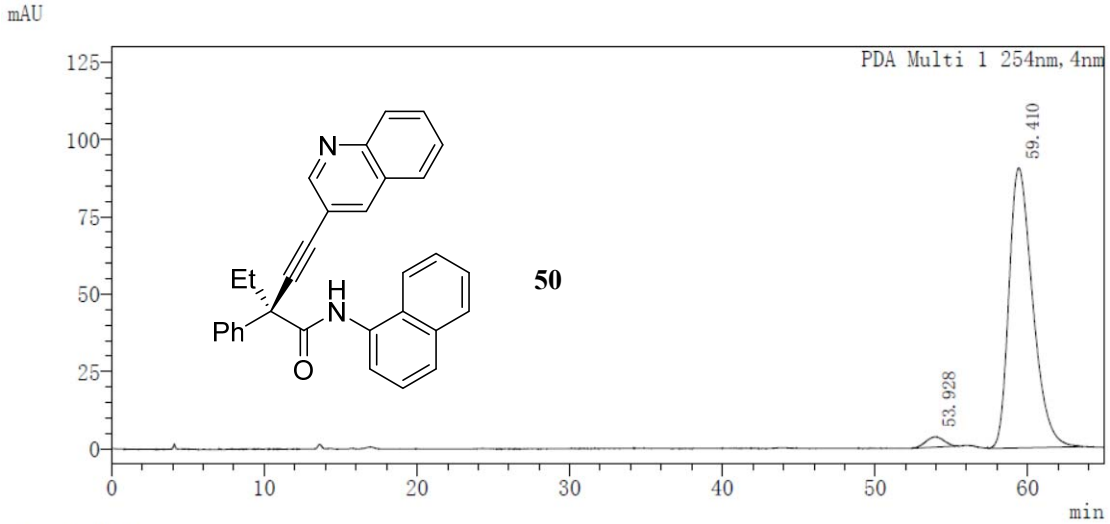


rac-**50**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	53.610	5928662	49.951
2	59.411	5940216	50.049



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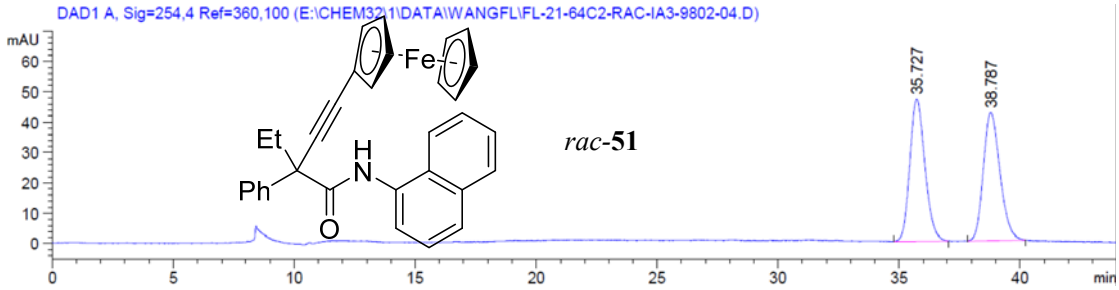
Peak Table

PDA Ch1 254nm

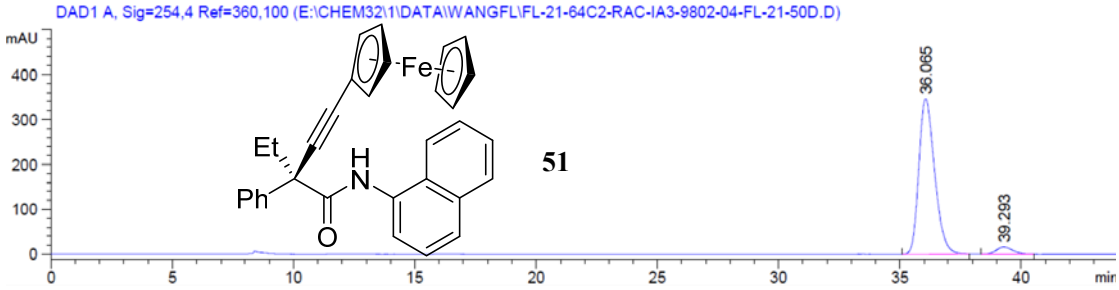
Peak#	Ret. Time	Area	Area%
1	53.928	278646	2.776
2	59.410	9760147	97.224



rac-**51**

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

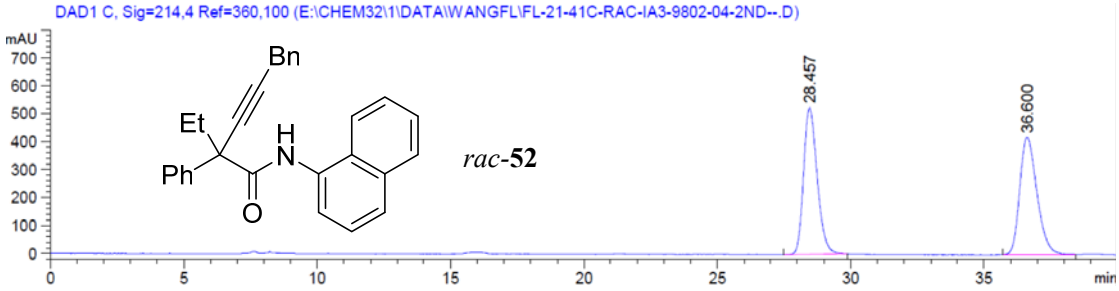
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.727	BB	0.6195	2031.46228	46.88345	50.0988
2	38.787	BV R	0.6744	2023.45105	42.12154	49.9012
Totals :				4054.91333	89.00499	



51

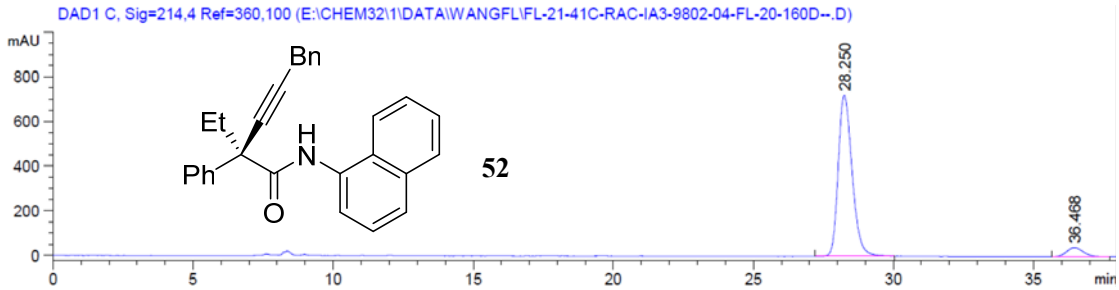
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.065	BB	0.6867	1.56808e4	346.02008	95.2485
2	39.293	BV R	0.5668	782.23718	16.44920	4.7515
Totals :				1.64631e4	362.46928	



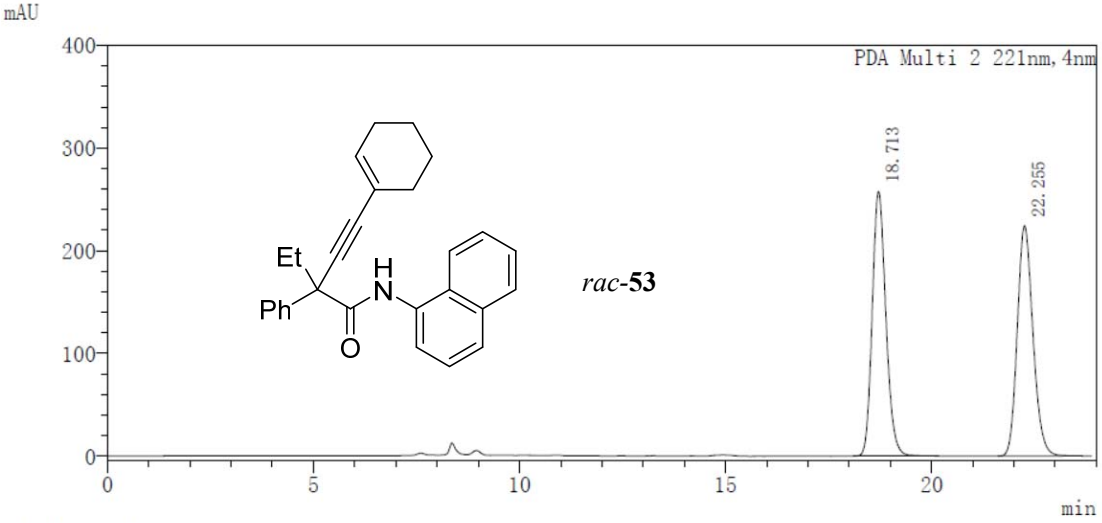
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.457	VV R	0.5311	1.86900e4	525.23694	49.6694
2	36.600	BV R	0.5681	1.89388e4	421.35876	50.3306
Totals :				3.76288e4	946.59570	



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

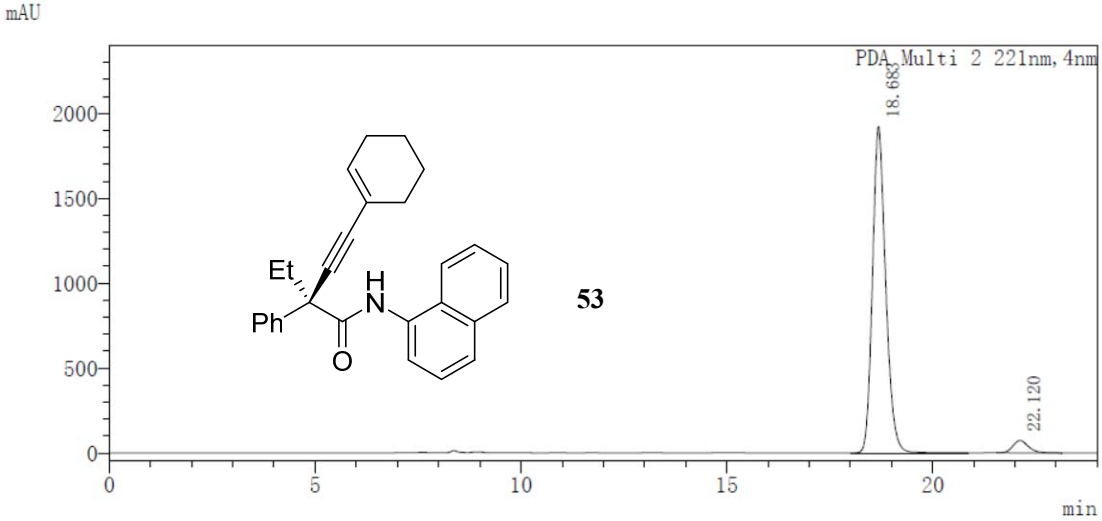
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.250	VV R	0.5146	2.48992e4	721.54572	93.3919
2	36.468	BV R	0.5101	1761.78625	42.46127	6.6081
Totals :				2.66610e4	764.00699	



Peak Table

PDA Ch2 221nm

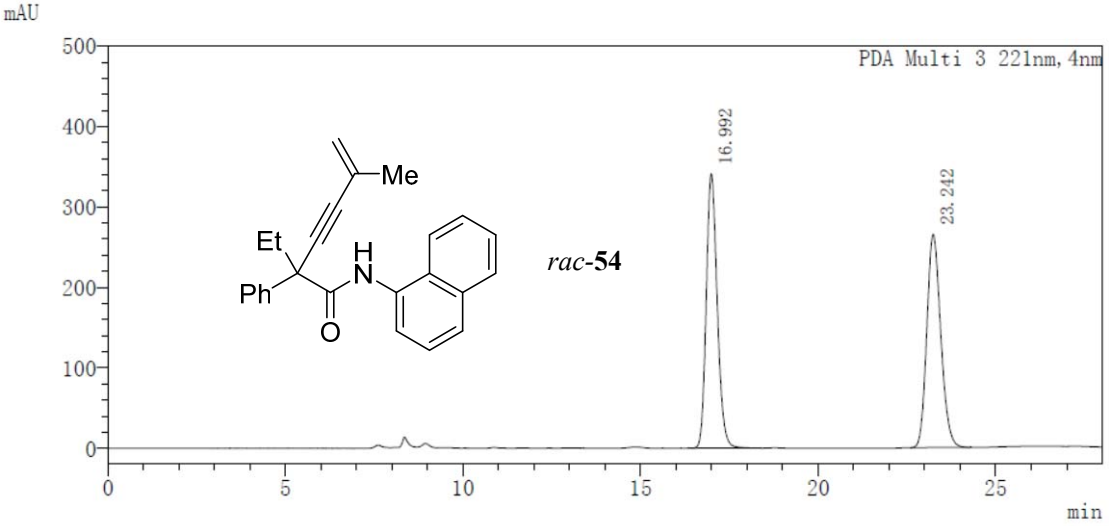
Peak#	Ret. Time	Area	Area%
1	18.713	5950205	50.048
2	22.255	5938796	49.952



Peak Table

PDA Ch2 221nm

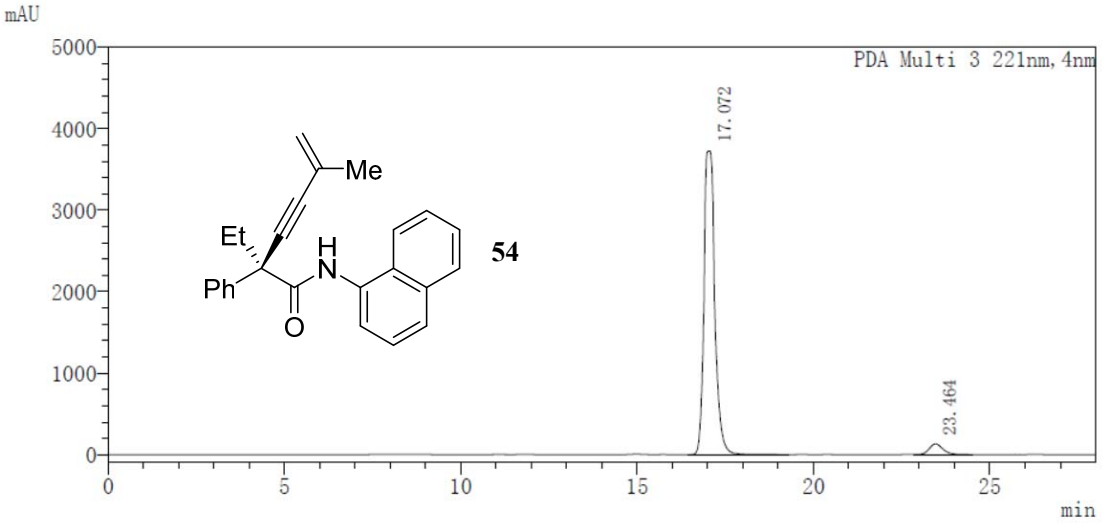
Peak#	Ret. Time	Area	Area%
1	18.683	43021564	95.745
2	22.120	1912148	4.255



Peak Table

PDA Ch3 221nm

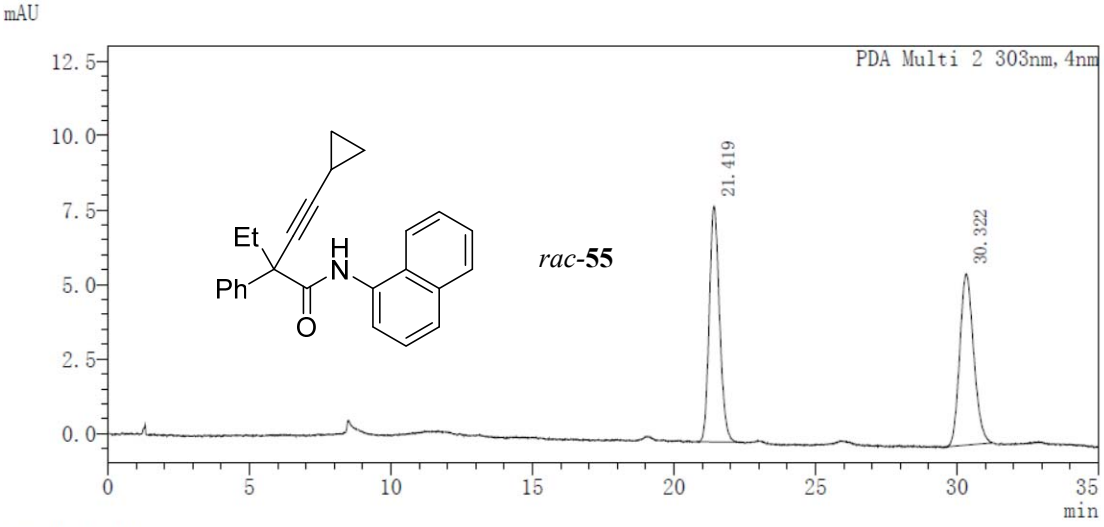
Peak#	Ret. Time	Area	Area%
1	16.992	7324314	50.271
2	23.242	7245424	49.729



Peak Table

PDA Ch3 221nm

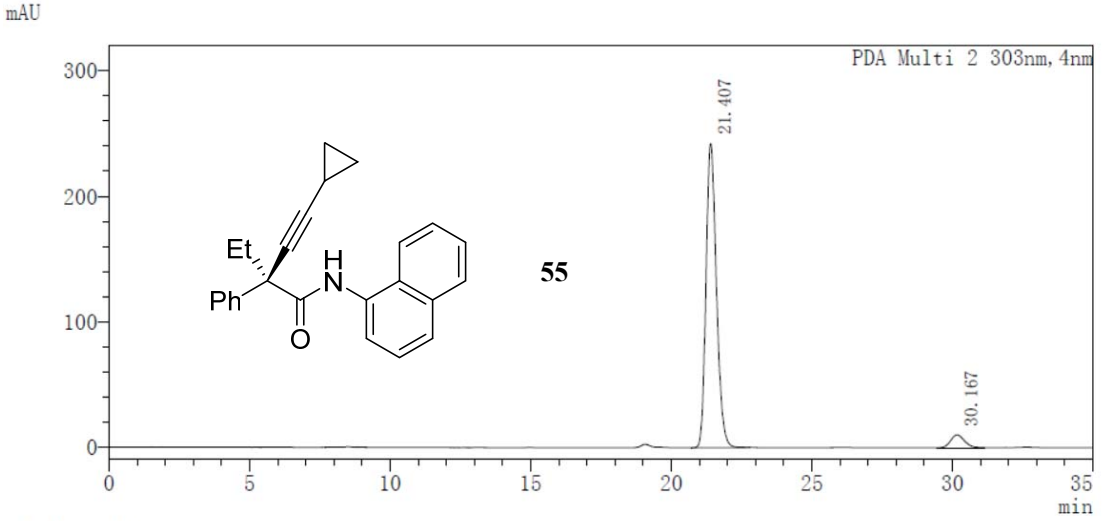
Peak#	Ret. Time	Area	Area%
1	17.072	79491256	95.747
2	23.464	3530611	4.253



Peak Table

PDA Ch2 303nm

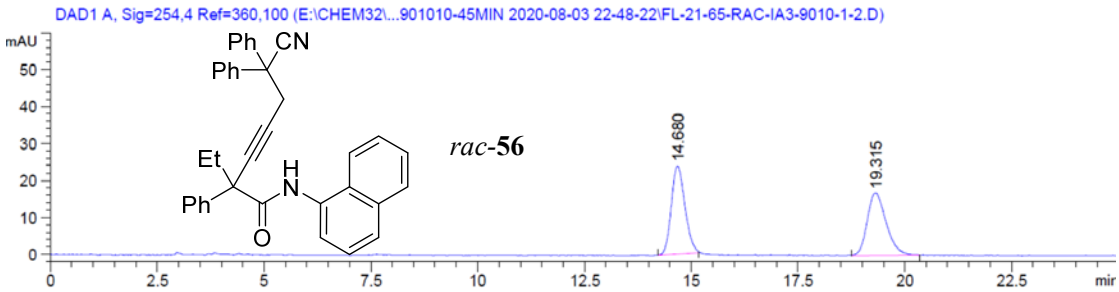
Peak#	Ret. Time	Area	Area%
1	21.419	199542	50.307
2	30.322	197104	49.693



Peak Table

PDA Ch2 303nm

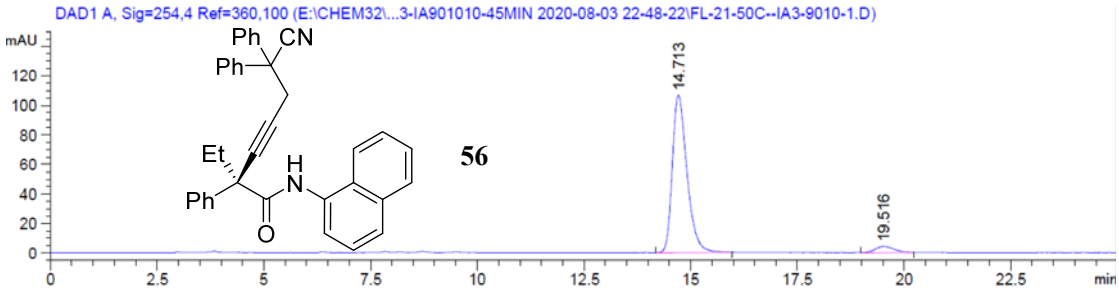
Peak#	Ret. Time	Area	Area%
1	21.407	6241275	94.634
2	30.167	353917	5.366



rac-**56**

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

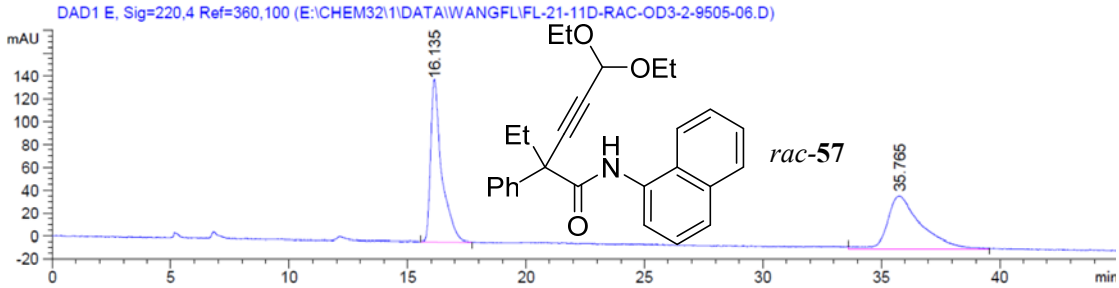
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.680	MM R	0.3671	524.11285	23.79375	50.1889
2	19.315	BB	0.4466	520.16772	16.82778	49.8111
Totals :				1044.28058	40.62153	



56

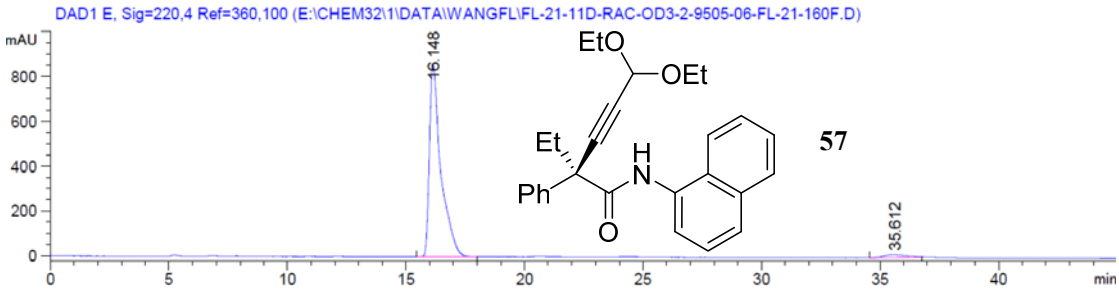
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.713	BB	0.3681	2542.18896	106.65381	95.1352
2	19.516	BB	0.3580	129.99744	4.38303	4.8648
Totals :				2672.18640	111.03684	



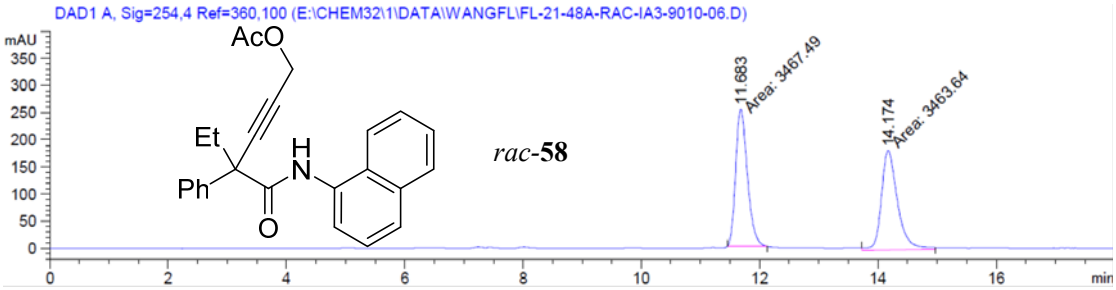
Signal 5: DAD1 E, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.135	VV R	0.4525	4584.40186	142.05020	50.0493
2	35.765	MM R	1.6423	4575.36426	46.43118	49.9507
Totals :				9159.76611	188.48138	



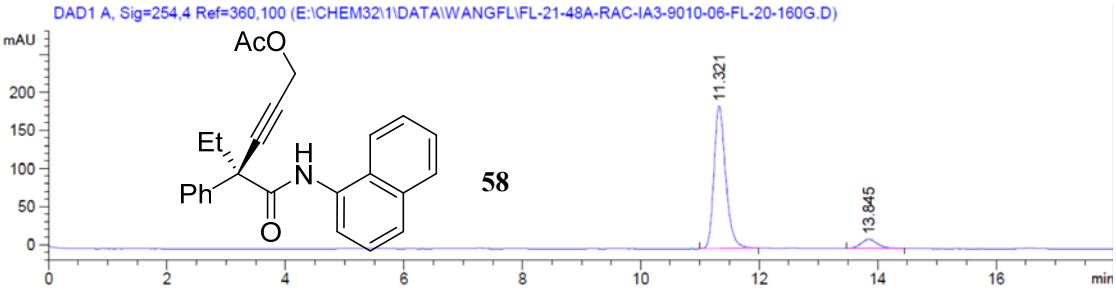
Signal 5: DAD1 E, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.148	VV R	0.4787	2.88451e4	852.55579	97.0140
2	35.612	MM R	1.1591	887.83380	12.76659	2.9860
Totals :				2.97329e4	865.32238	



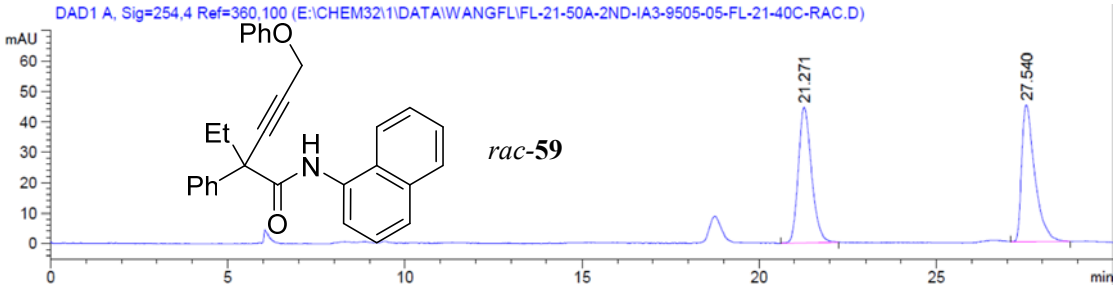
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.683	MM	0.2286	3467.49341	252.84680	50.0278
2	14.174	MM	0.3166	3463.64355	182.31435	49.9722
Totals :				6931.13696	435.16115	



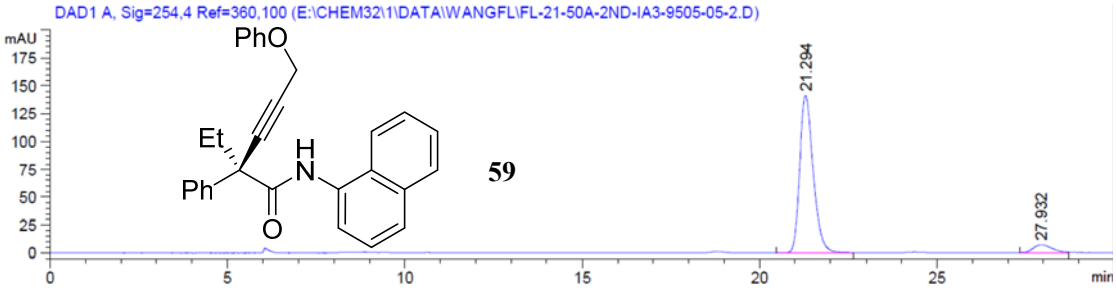
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.321	BB	0.2112	2578.16577	186.57191	91.6303
2	13.845	BB	0.2921	235.49533	11.93786	8.3697
Totals :				2813.66110	198.50978	



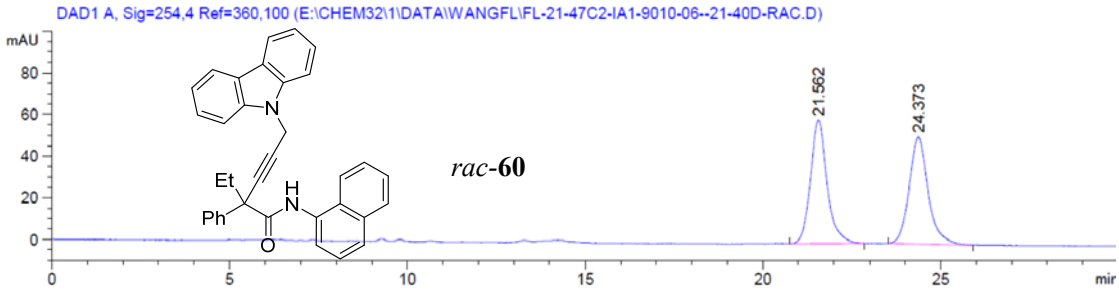
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.271	BV R	0.3958	1157.19617	44.44218	49.8997
2	27.540	BB	0.3832	1161.84668	45.00842	50.1003
Totals :				2319.04285	89.45060	



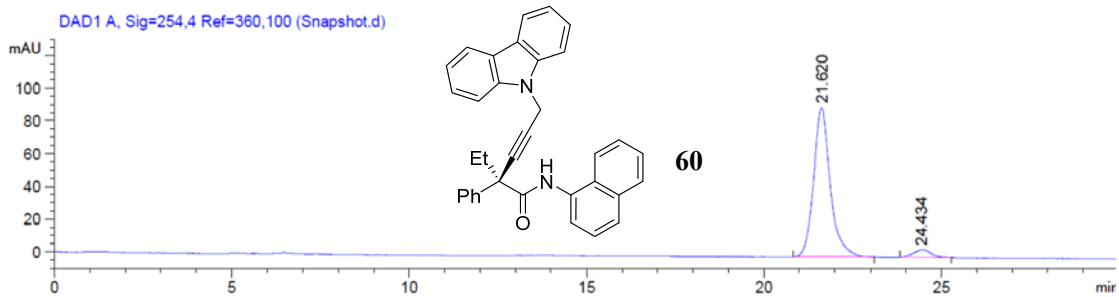
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.294	MM R	0.4479	3817.91309	142.07283	93.5938
2	27.932	MM R	0.5958	261.32422	7.30966	6.4062
Totals :				4079.23730	149.38249	



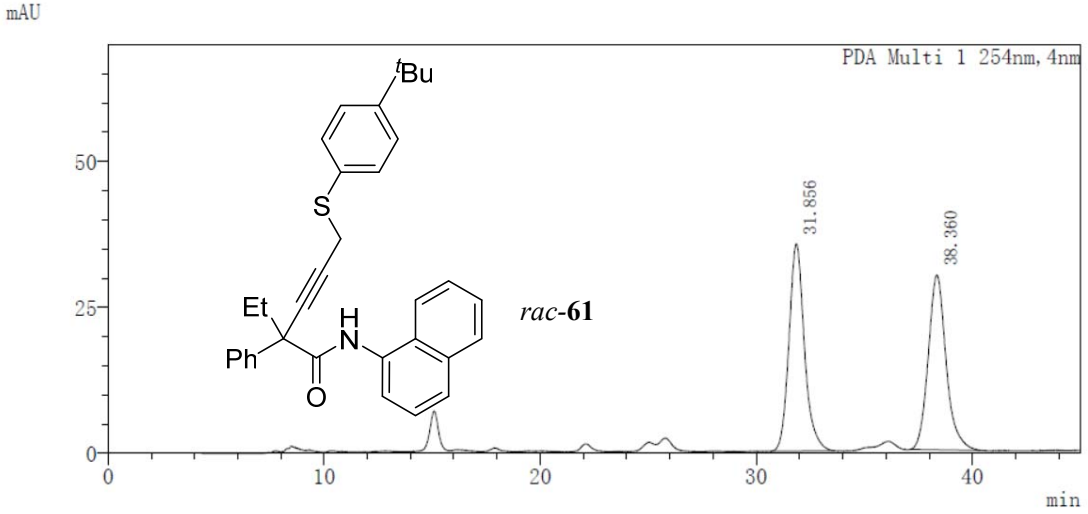
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.562	BB	0.4778	1934.63696	59.43175	50.3071
2	24.373	BB	0.5508	1911.01648	51.51911	49.6929
Totals :				3845.65344	110.95086	



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

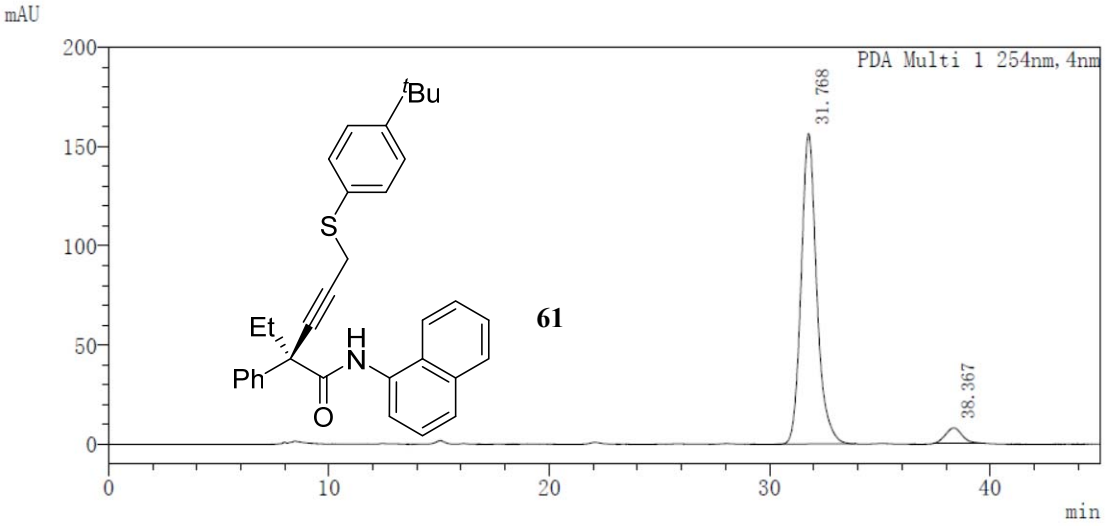
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.620	BB	0.4907	2998.73730	91.40713	94.8067
2	24.434	BB	0.4118	164.26338	4.76984	5.1933
Totals :				3163.00069	96.17697	



Peak Table

PDA Ch1 254nm

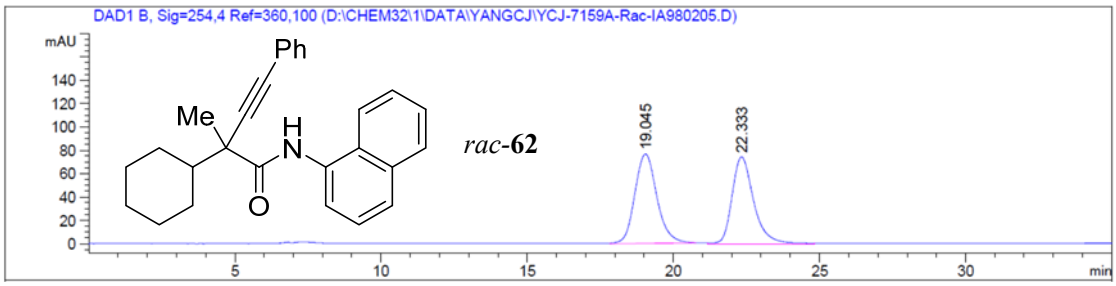
Peak#	Ret. Time	Area	Area%
1	31.856	1766478	50.599
2	38.360	1724675	49.401



Peak Table

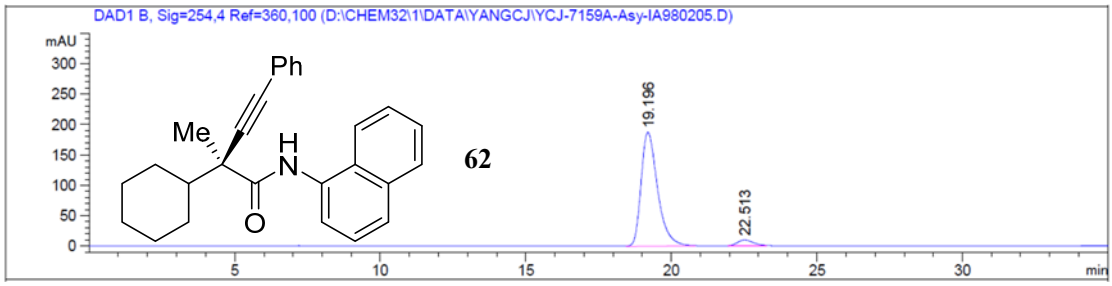
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	31.768	7680158	94.825
2	38.367	419159	5.175



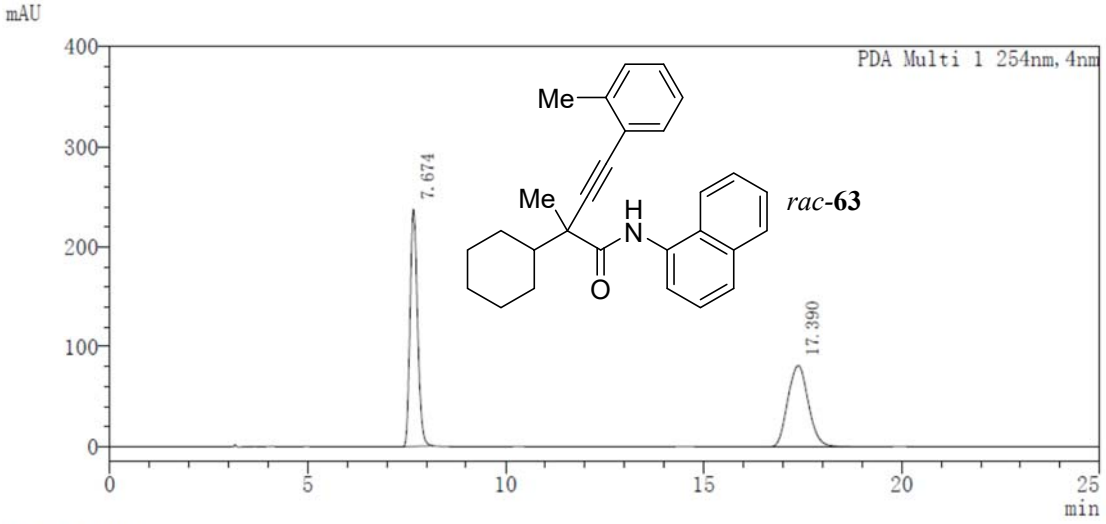
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.045	MM R	0.8787	4031.96948	76.47878	51.4973
2	22.333	MM R	0.8529	3797.50879	74.20380	48.5027
Totals :				7829.47827	150.68259	



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

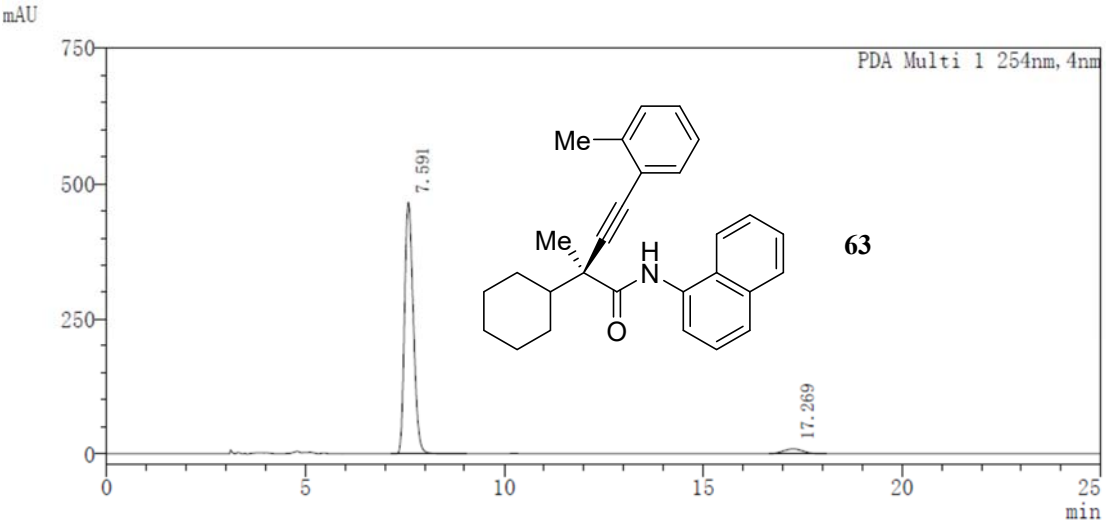
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.196	MM R	0.6595	7418.17578	187.46294	95.0129
2	22.513	MM R	0.6582	389.37146	9.85947	4.9871
Totals :				7807.54724	197.32241	



Peak Table

PDA Ch1 254nm

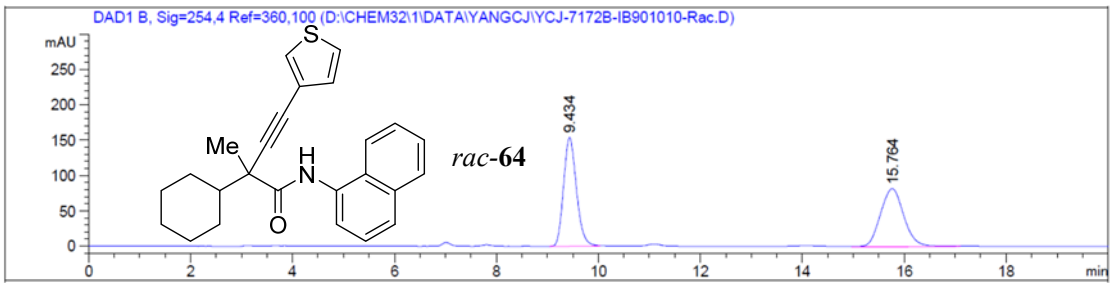
Peak#	Ret. Time	Area	Area%
1	7.674	3113373	51.562
2	17.390	2924737	48.438



Peak Table

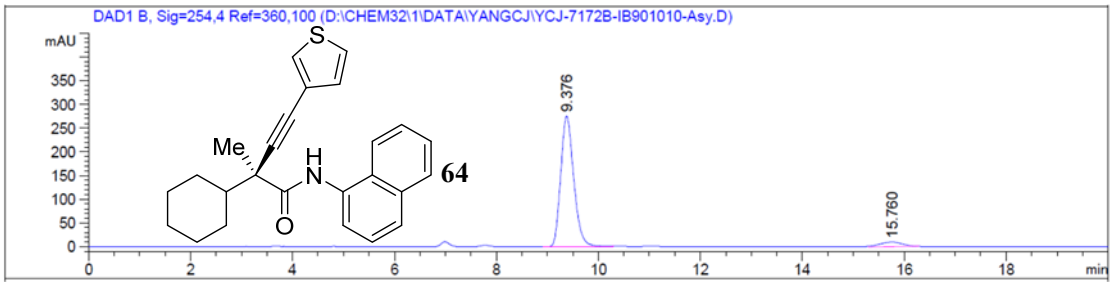
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.591	7166751	95.795
2	17.269	314611	4.205



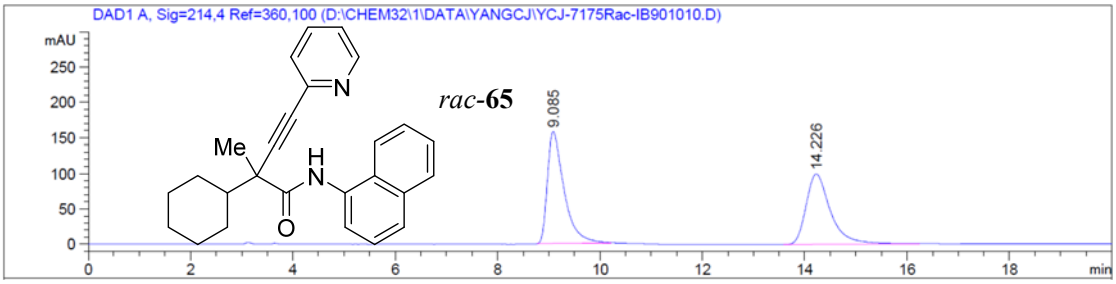
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.434	MM R	0.2926	2705.23267	154.08582	50.5028
2	15.764	MM R	0.5355	2651.36938	82.52261	49.4972
Totals :				5356.60205	236.60842	



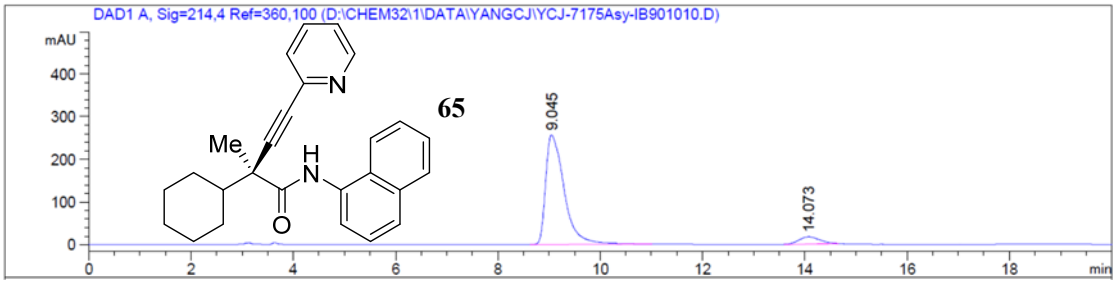
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.376	MM R	0.2979	4930.86279	275.87363	94.3592
2	15.760	MM R	0.5080	294.76471	9.67038	5.6408
Totals :				5225.62750	285.54400	



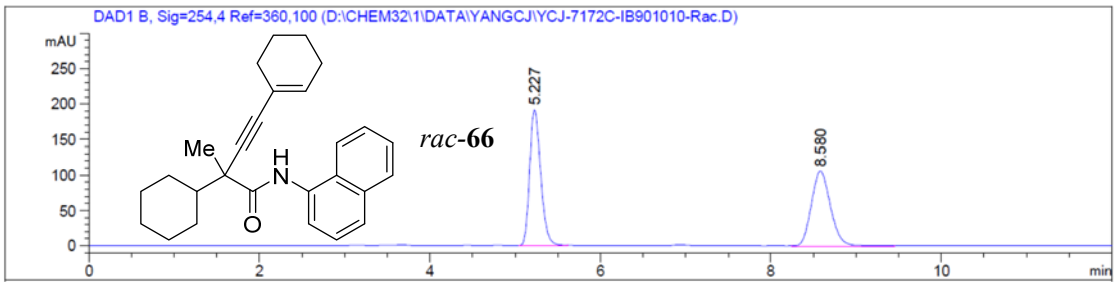
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.085	MM R	0.3783	3570.77393	157.30754	51.8172
2	14.226	MM R	0.5547	3320.32886	99.76469	48.1828
Totals :				6891.10278	257.07224	



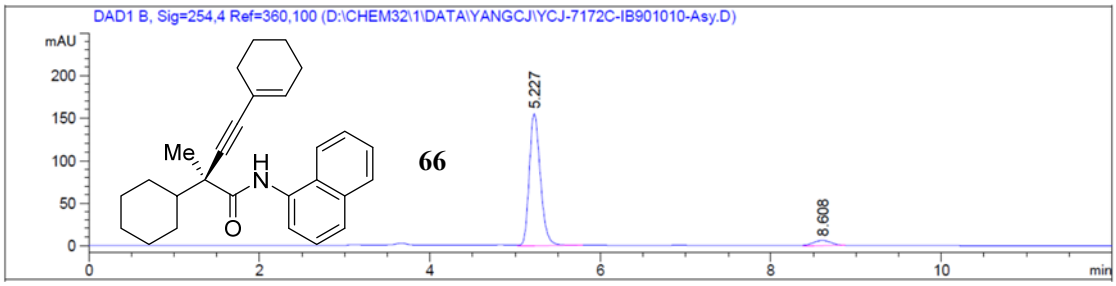
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.045	MM R	0.4234	6528.08252	256.95010	93.0012
2	14.073	MM R	0.4776	491.26944	17.14308	6.9988
Totals :				7019.35196	274.09318	



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

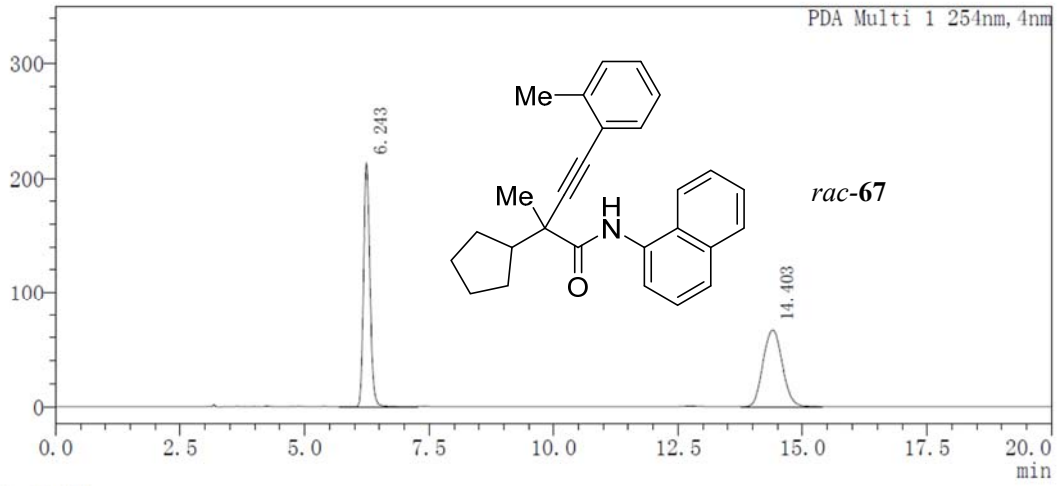
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.227	MM R	0.1502	1725.55029	191.45863	50.5740
2	8.580	MM R	0.2633	1686.37830	106.73345	49.4260
Totals :				3411.92859	298.19209	



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.227	MM R	0.1514	1412.17310	155.44176	93.9168
2	8.608	MM R	0.2450	91.46997	6.22205	6.0832
Totals :				1503.64307	161.66381	

mAU



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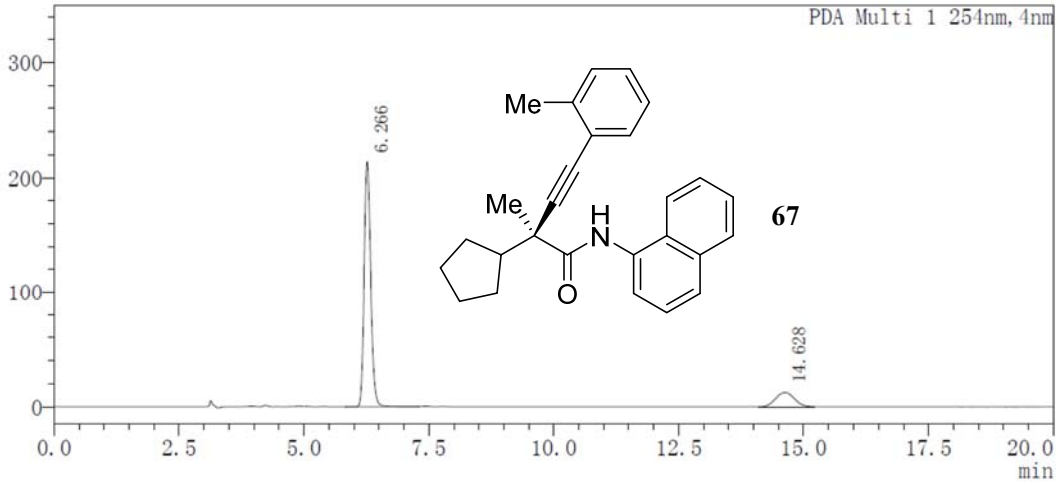
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.243	1895446	51.375
2	14.403	1794013	48.625

mAU



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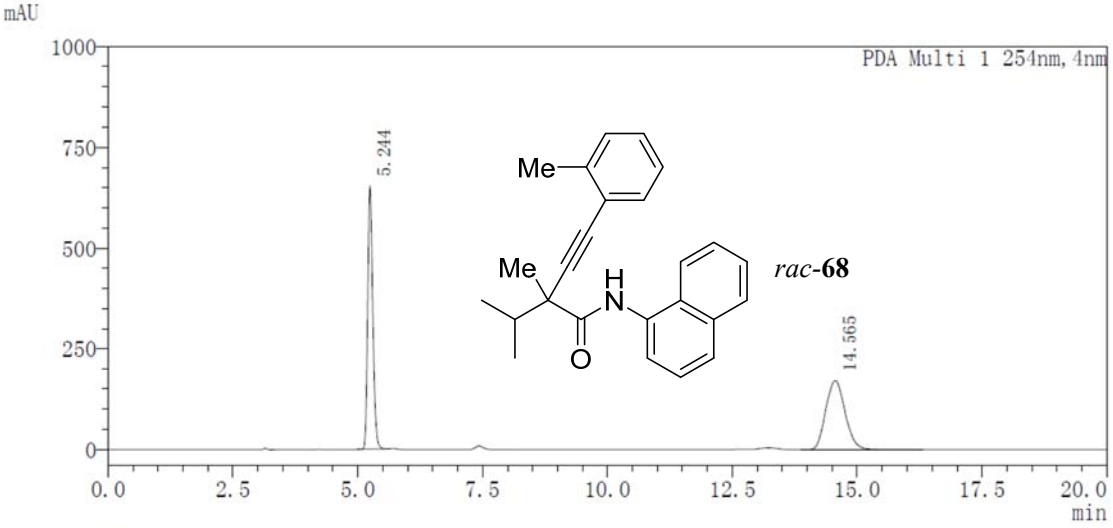
Peak Table

PDA Ch1 254nm

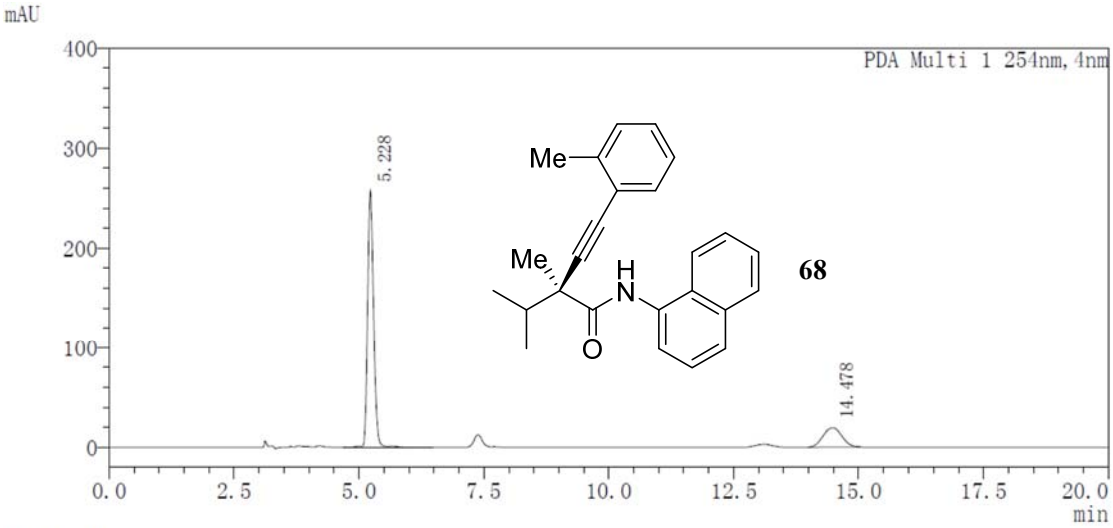
Peak#	Ret. Time	Area	Area%
1	6.266	1947183	85.759
2	14.628	323334	14.241



Peak Table

PDA Ch1 254nm

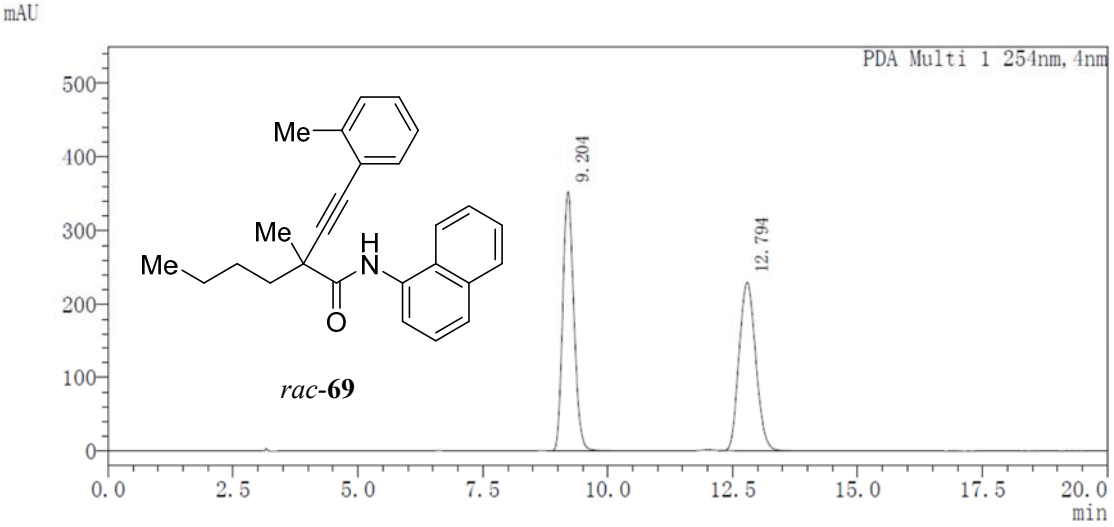
Peak#	Ret. Time	Area	Area%
1	5.244	4639822	50.450
2	14.565	4557110	49.550



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.228	2139729	80.989
2	14.478	502262	19.011

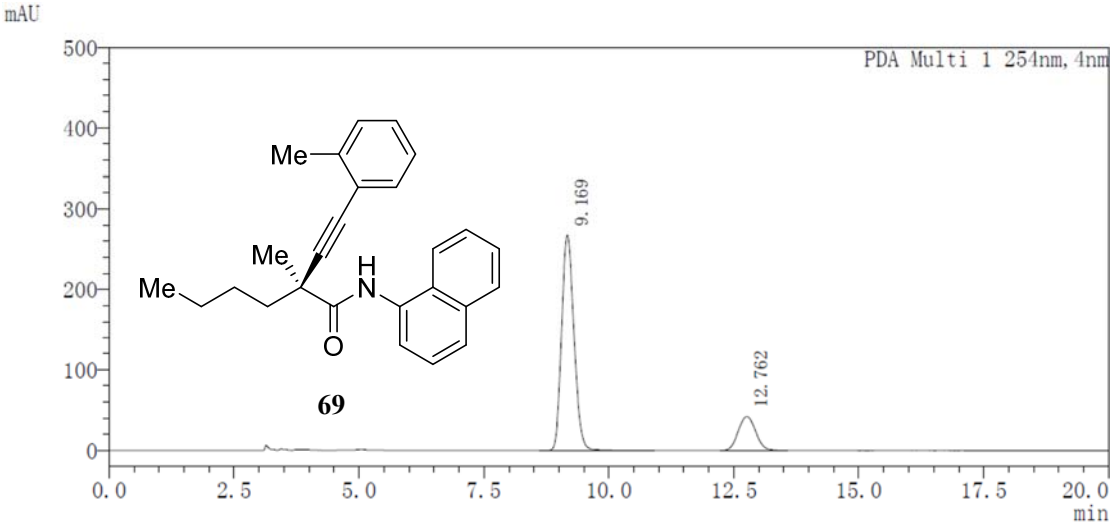


rac-**69**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.204	5464073	50.632
2	12.794	5327630	49.368



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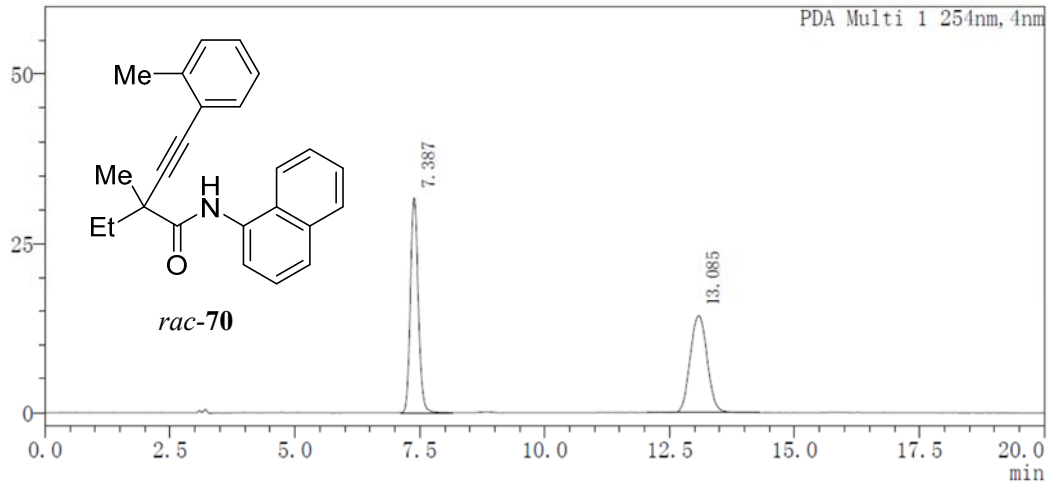
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	9.169	4596326	82.049
2	12.762	1005603	17.951

mAU



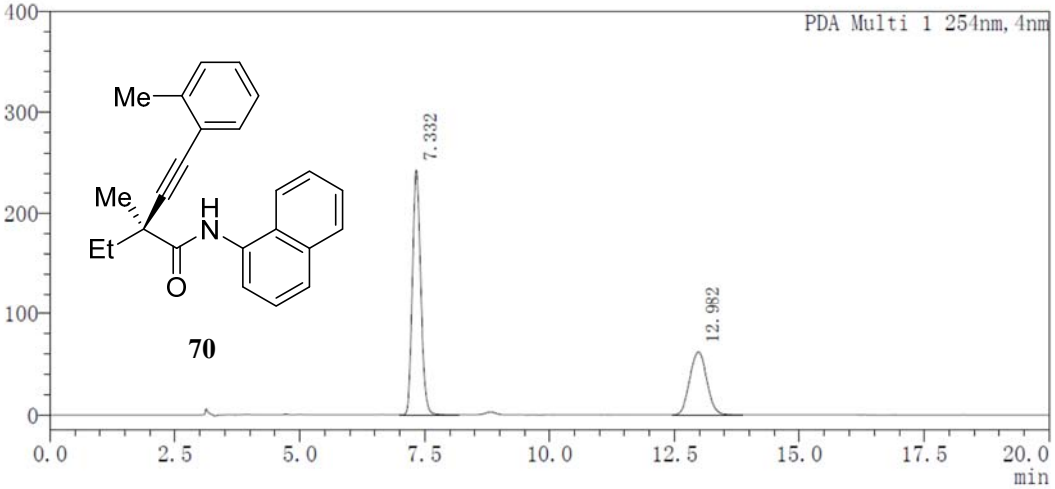
rac-**70**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.387	348269	50.728
2	13.085	338267	49.272

mAU

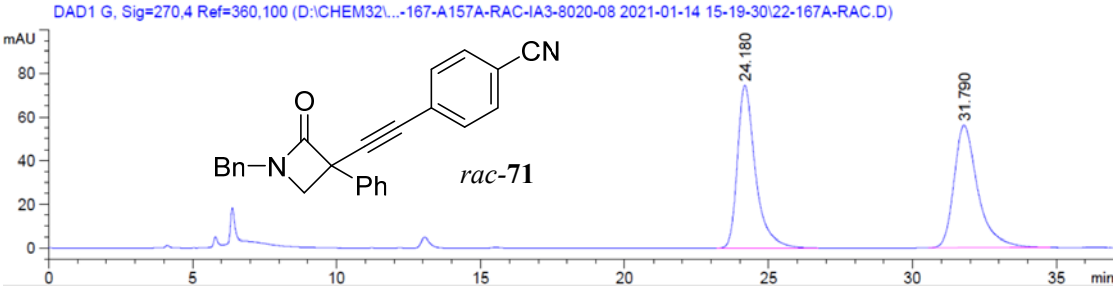


70

Peak Table

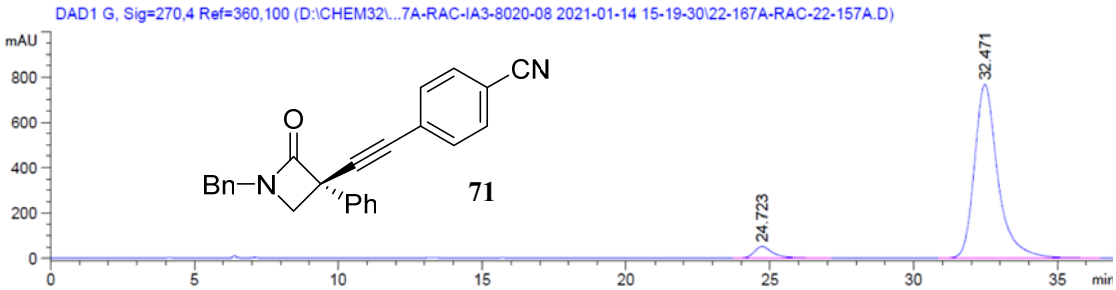
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.332	2824028	65.828
2	12.982	1465983	34.172



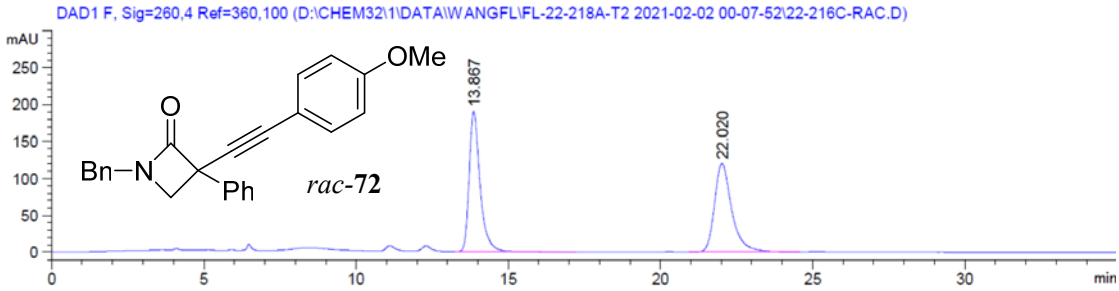
Signal 7: DAD1 G, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.180	BB	0.6473	3258.02832	74.62998	50.1885
2	31.790	BB	0.8467	3233.55566	56.07759	49.8115
Totals :				6491.58398	130.70758	



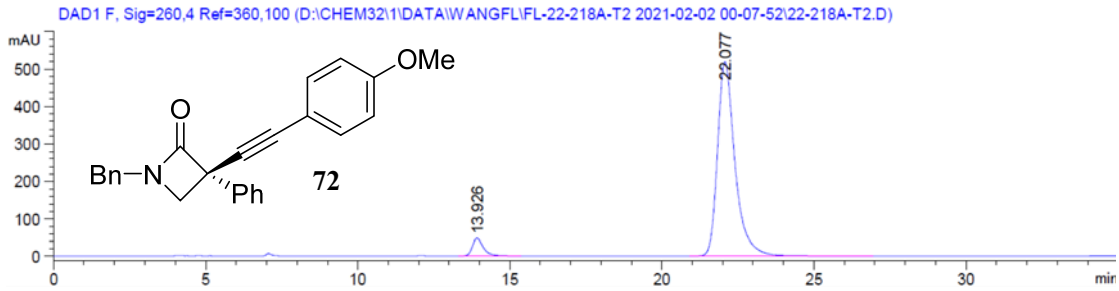
Signal 7: DAD1 G, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.723	BB	0.6530	2280.88428	51.46987	4.9985
2	32.471	BB	0.8540	4.33504e4	766.33301	95.0015
Totals :				4.56313e4	817.80288	



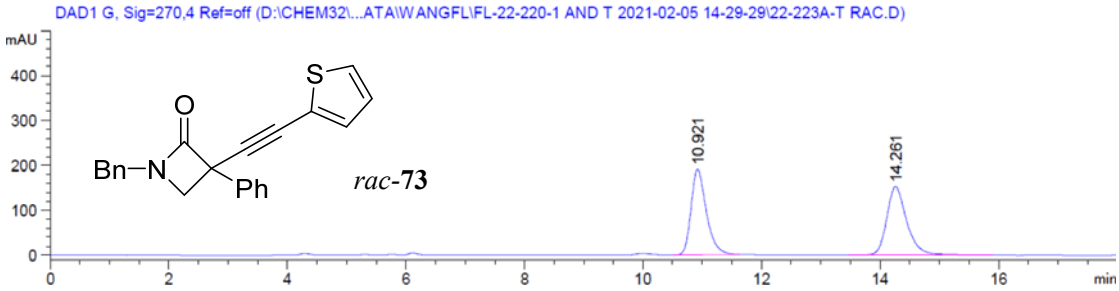
Signal 6: DAD1 F, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.867	BB	0.3760	4752.87012	189.91422	49.9195
2	22.020	BV	0.5953	4768.20605	120.06029	50.0805
Totals :				9521.07617	309.97450	



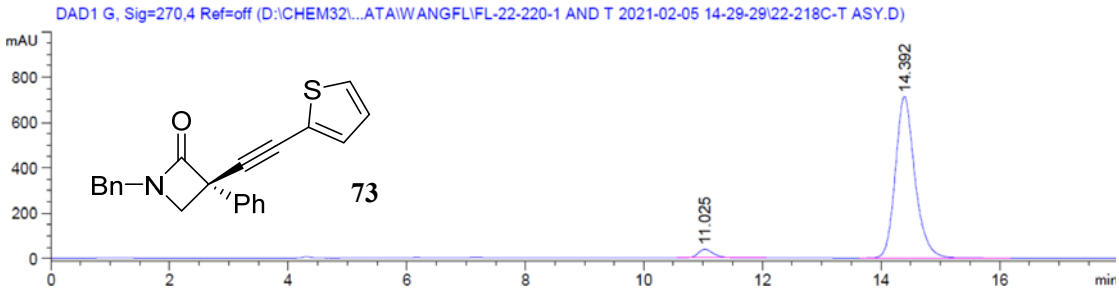
Signal 6: DAD1 F, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.926	BV	0.3793	1226.32422	48.45020	5.5746
2	22.077	VV	0.6021	2.07722e4	519.97595	94.4254
Totals :				2.19985e4	568.42615	



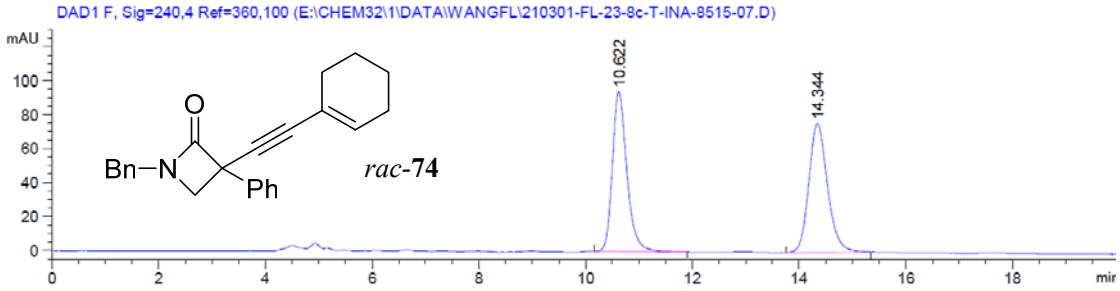
Signal 7: DAD1 G, Sig=270,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.921	BB	0.2718	3431.95850	190.88959	48.7749
2	14.261	BB	0.3558	3604.36768	152.44797	51.2251
Totals :				7036.32617	343.33755	



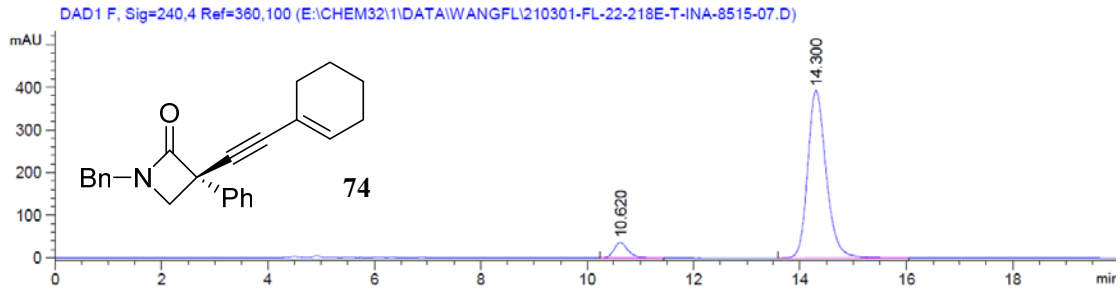
Signal 7: DAD1 G, Sig=270,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.025	BB	0.2737	708.72266	39.06460	4.1442
2	14.392	BB	0.3464	1.63930e4	712.67108	95.8558
Totals :				1.71018e4	751.73568	



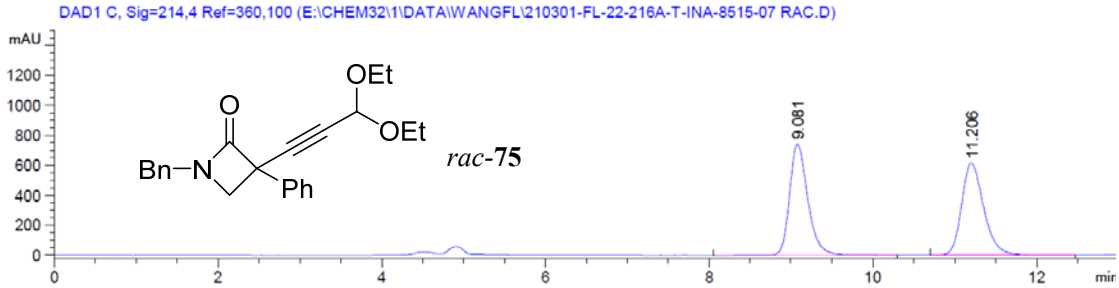
Signal 6: DAD1 F, Sig=240,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.622	BB	0.2861	1779.74622	94.35244	49.0425
2	14.344	BB	0.3705	1849.24097	75.84090	50.9575
Totals :				3628.98718	170.19334	



Signal 6: DAD1 F, Sig=240,4 Ref=360,100

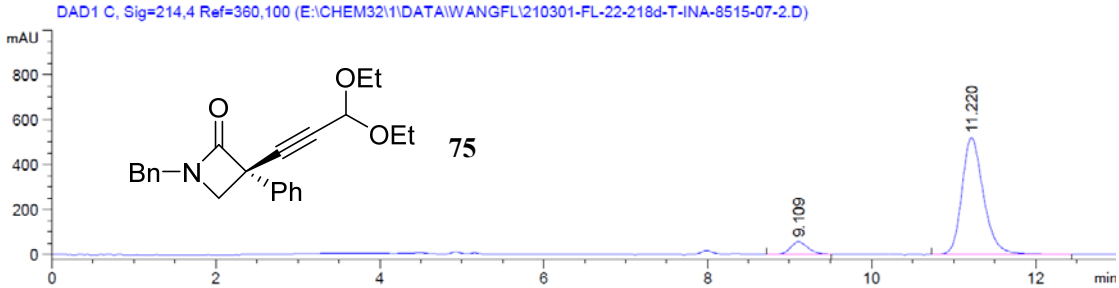
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.620	BB	0.2820	669.79370	36.51484	6.6051
2	14.300	BB	0.3698	9470.81152	392.12418	93.3949
Totals :				1.01406e4	428.63901	



rac-**75**

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

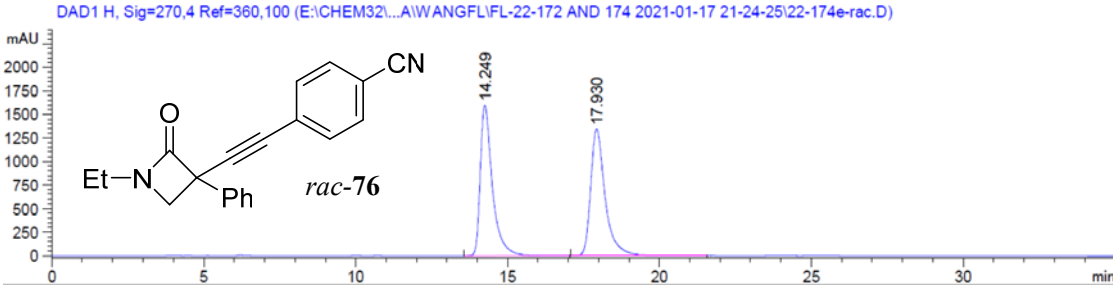
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.081	VV R	0.2381	1.16349e4	741.43060	50.0790
2	11.206	BB	0.2883	1.15981e4	614.33698	49.9210
Totals :				2.32330e4	1355.76758	



75

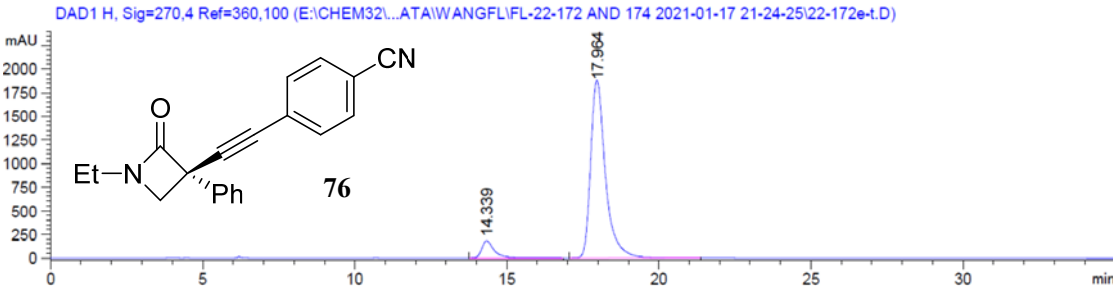
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.109	MF R	0.2470	849.63440	57.31901	8.1953
2	11.220	BB	0.2775	9517.74805	520.02155	91.8047
Totals :				1.03674e4	577.34055	



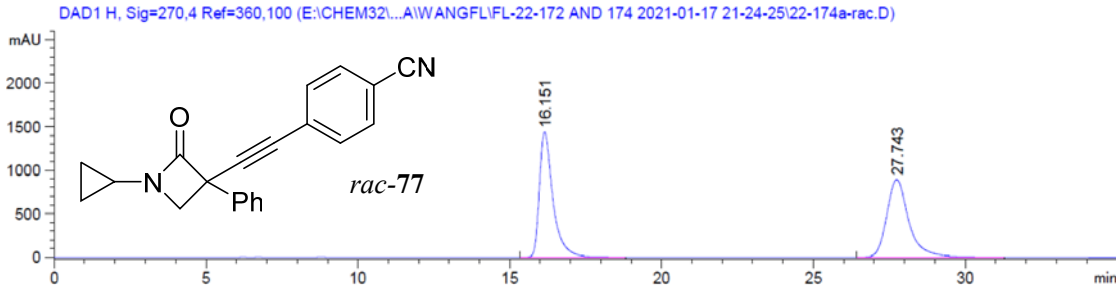
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.249	BB	0.4124	4.41319e4	1597.05701	49.8693
2	17.930	BB	0.4956	4.43632e4	1342.22156	50.1307
Totals :				8.84951e4	2939.27856	



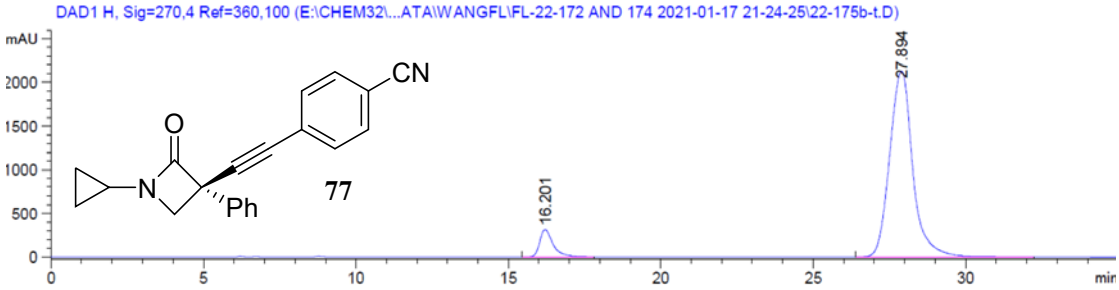
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.339	BB	0.4179	5148.47363	183.19617	7.4939
2	17.964	BB	0.5084	6.35539e4	1880.08008	92.5061
Totals :				6.87024e4	2063.27625	



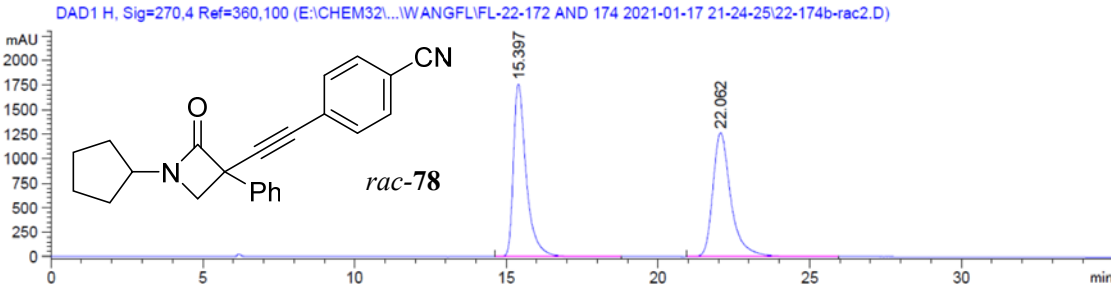
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.151	BB	0.4641	4.46220e4	1437.60535	49.8352
2	27.743	BB	0.7618	4.49171e4	891.59045	50.1648
Totals :				8.95391e4	2329.19580	



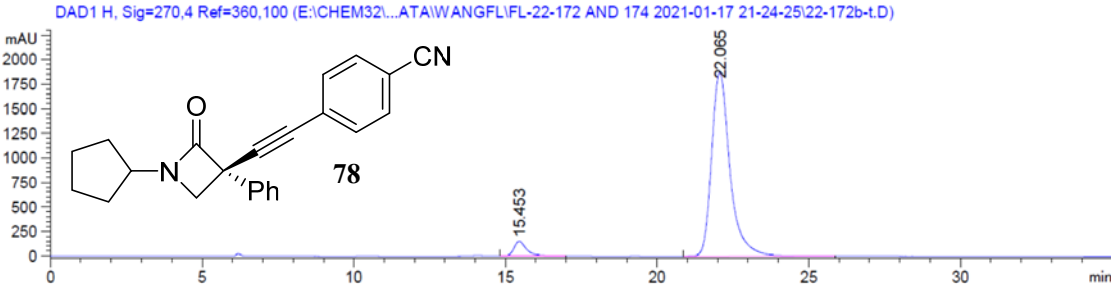
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.201	BB	0.4561	9677.37793	317.02151	7.9541
2	27.894	BB	0.7983	1.11988e5	2126.79102	92.0459
Totals :				1.21666e5	2443.81253	



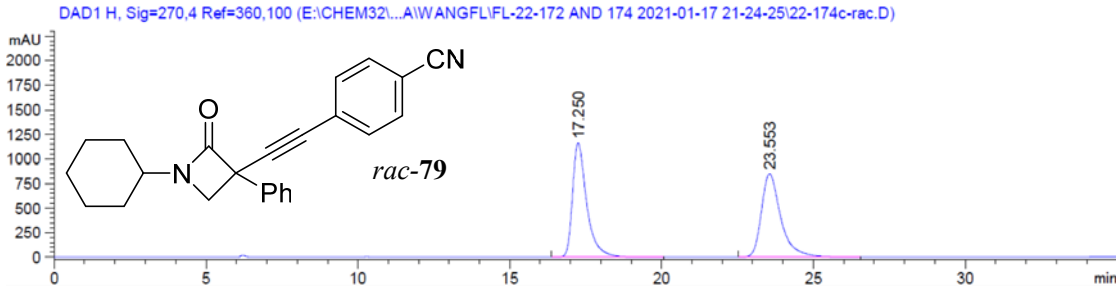
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.397	BB	0.4383	5.15564e4	1757.29468	49.7276
2	22.062	BB	0.6217	5.21212e4	1262.43994	50.2724
Totals :				1.03678e5	3019.73462	



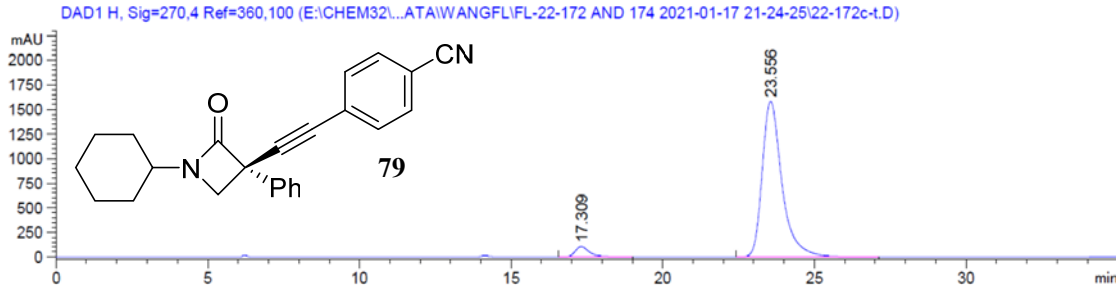
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.453	BB	0.4283	4285.20996	150.45261	5.1805
2	22.065	BB	0.6383	7.84326e4	1866.43823	94.8195
Totals :				8.27178e4	2016.89084	



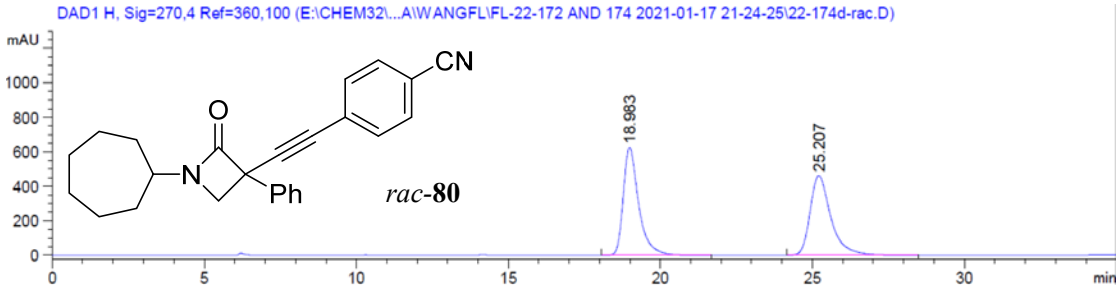
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.250	BB	0.4875	3.76986e4	1158.83545	50.0067
2	23.553	BB	0.6693	3.76885e4	846.76105	49.9933
Totals :				7.53871e4	2005.59650	



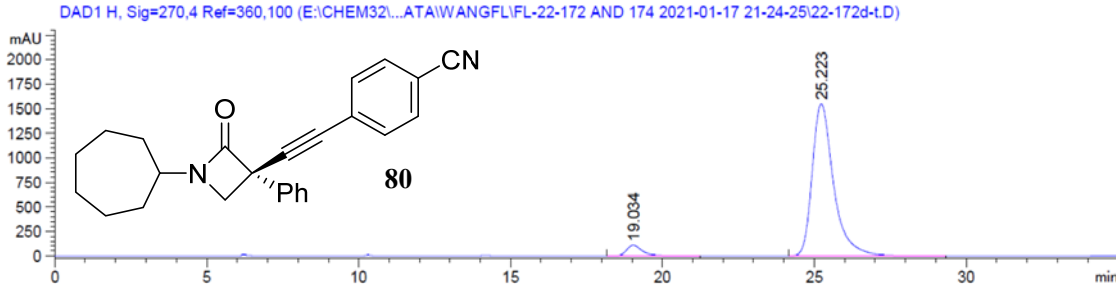
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.309	BB	0.4815	3432.35059	106.63303	4.5737
2	23.556	BB	0.6840	7.16132e4	1582.47388	95.4263
Totals :				7.50455e4	1689.10691	



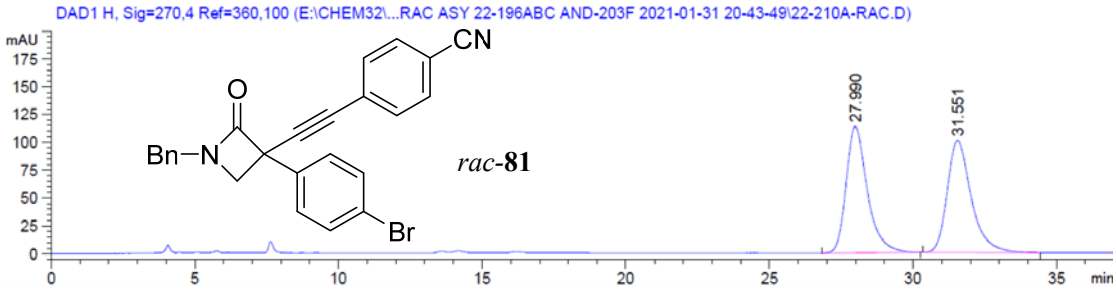
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.983	BB	0.5318	2.21684e4	625.05048	50.0887
2	25.207	BB	0.7156	2.20899e4	462.20224	49.9113
Totals :				4.42582e4	1087.25272	



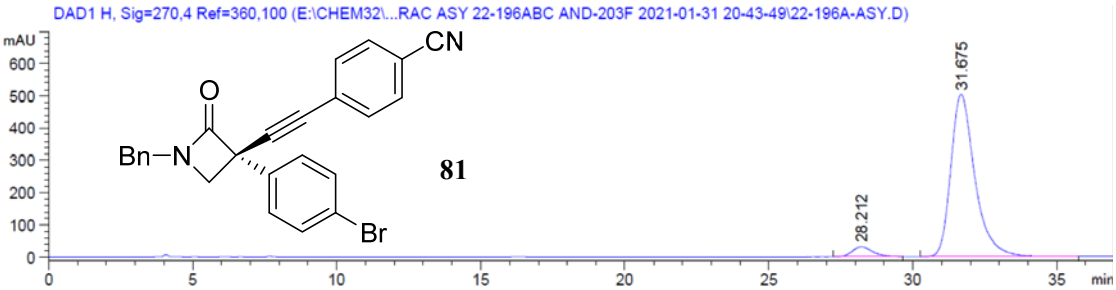
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.034	BB	0.5288	3929.24707	110.50815	4.9375
2	25.223	BB	0.7406	7.56505e4	1546.75452	95.0625
Totals :				7.95797e4	1657.26266	



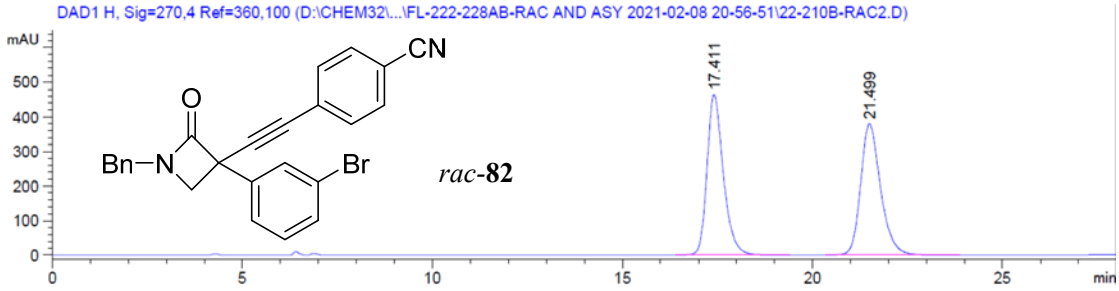
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.990	BB	0.7668	5845.26660	113.51472	49.9868
2	31.551	BB	0.8695	5848.35107	100.41972	50.0132
Totals :				1.16936e4	213.93444	



Signal 8: DAD1 H, Sig=270,4 Ref=360,100

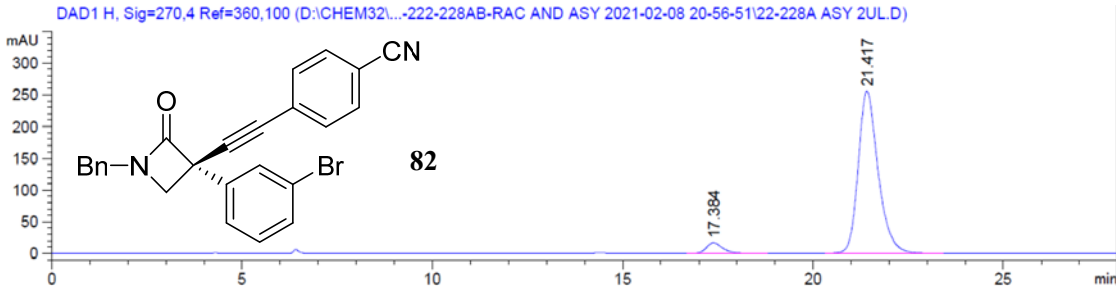
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.212	MM R	0.8221	1575.09155	31.93051	5.0815
2	31.675	BB	0.8791	2.94217e4	503.93869	94.9185
Totals :				3.09968e4	535.86920	



rac-**82**

Signal 8: DAD1 H, Sig=270,4 Ref=360,100

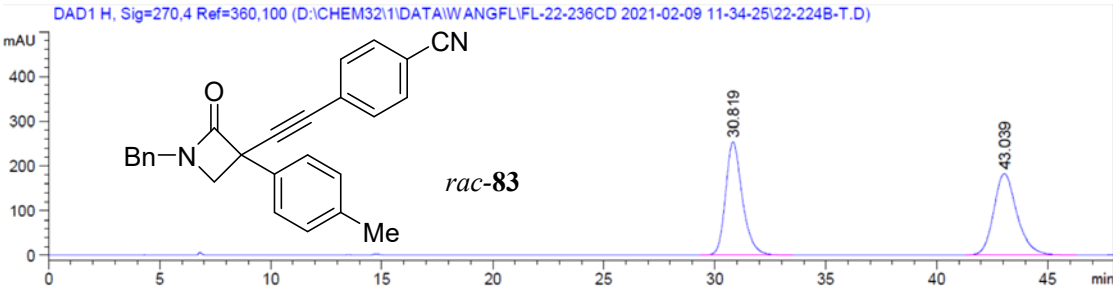
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.411	BB	0.4518	1.39198e4	464.31589	49.9764
2	21.499	BB	0.5541	1.39329e4	379.72327	50.0236
Totals :				2.78528e4	844.03915	



82

Signal 8: DAD1 H, Sig=270,4 Ref=360,100

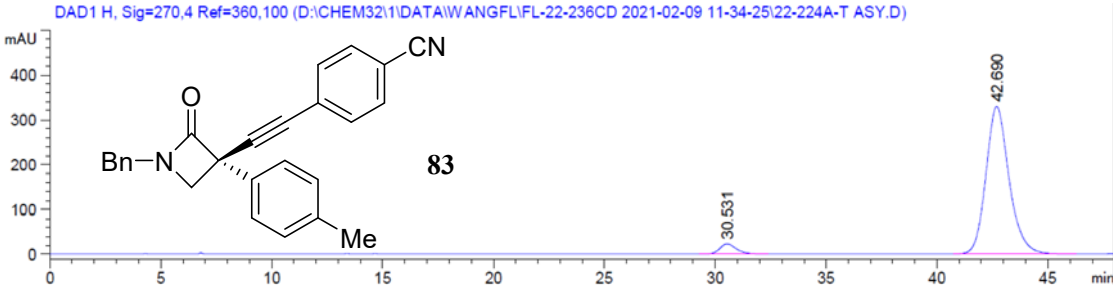
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.384	BB	0.4564	513.89026	17.11072	5.2198
2	21.417	BB	0.5496	9331.10254	255.78978	94.7802
Totals :				9844.99280	272.90050	



rac-**83**

Signal 8: DAD1 H, Sig=270,4 Ref=360,100

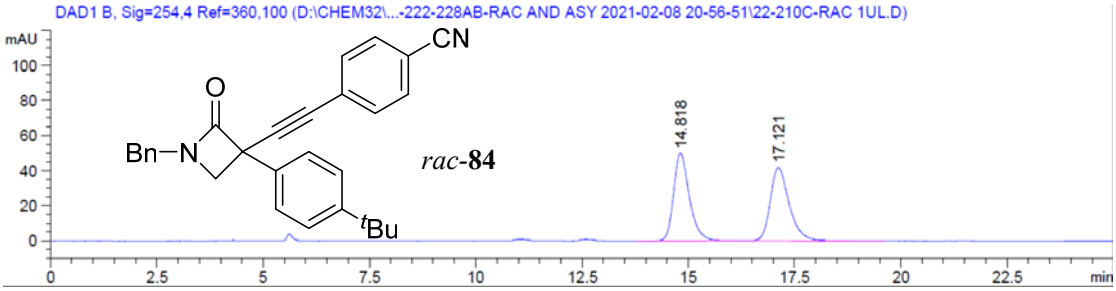
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.819	BB	0.7999	1.34329e4	252.82068	50.0597
2	43.039	BB	1.0934	1.34008e4	182.33847	49.9403
Totals :				2.68337e4	435.15915	



83

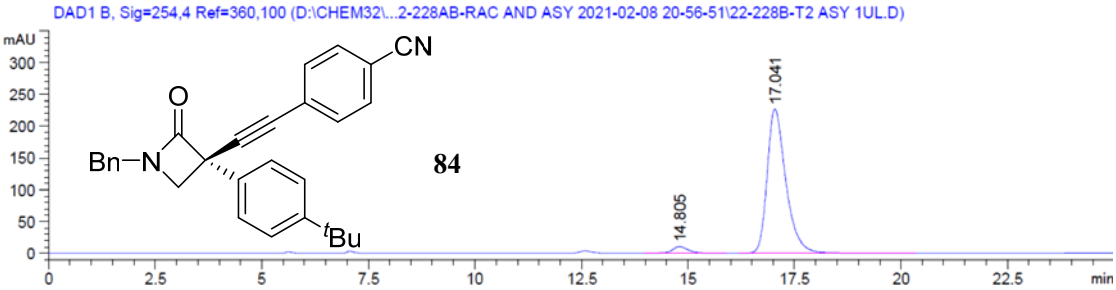
Signal 8: DAD1 H, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.531	BB	0.7578	1240.84790	23.58369	4.9096
2	42.690	BB	1.0971	2.40332e4	329.44360	95.0904
Totals :				2.52740e4	353.02729	



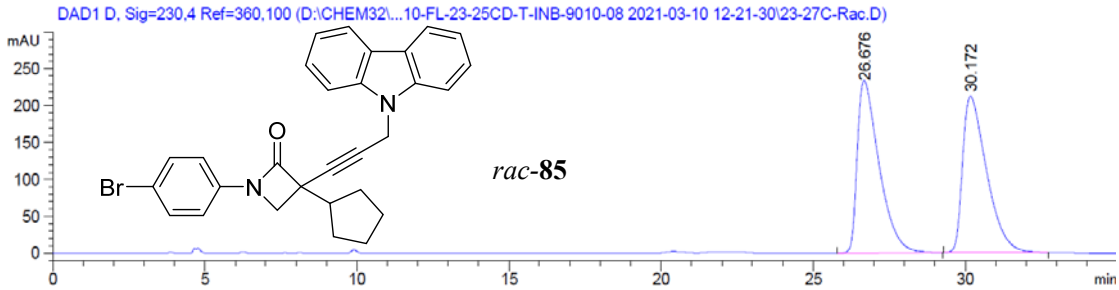
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.818	BB	0.3886	1293.64893	50.20746	49.8936
2	17.121	BV	0.4662	1299.16504	41.84780	50.1064
Totals :				2592.81396	92.05526	



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

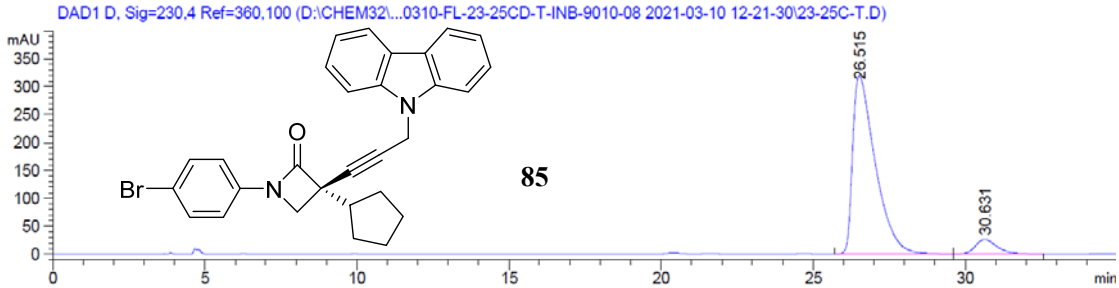
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.805	BB	0.4009	295.52316	11.01780	4.0662
2	17.041	BV	0.4623	6972.21973	227.04407	95.9338
Totals :				7267.74289	238.06187	



rac-**85**

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

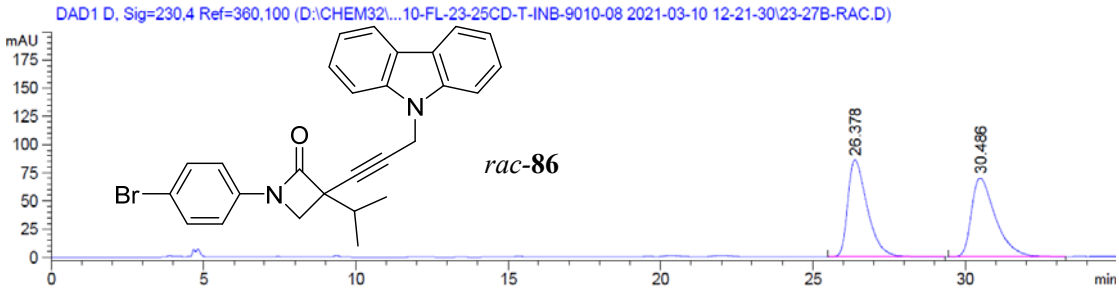
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.676	BB	0.7503	1.16647e4	233.70891	50.0485
2	30.172	BB	0.8290	1.16421e4	211.89503	49.9515
Totals :				2.33068e4	445.60394	



85

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

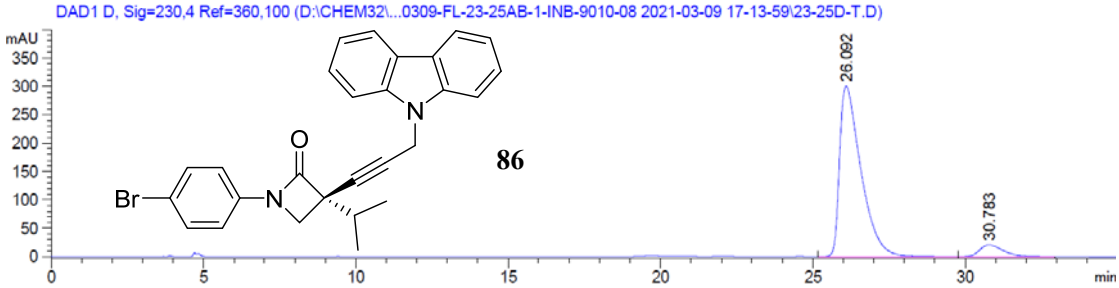
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.515	BB	0.7709	1.65300e4	319.84747	92.8328
2	30.631	BB	0.7374	1276.20117	26.05826	7.1672



rac-**86**

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

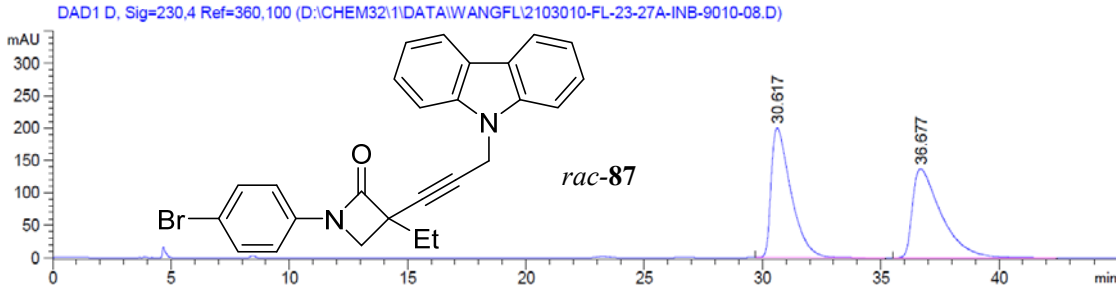
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.378	BB	0.6757	3858.73120	86.29017	49.9931
2	30.486	BB	0.8240	3859.79297	70.13635	50.0069



86

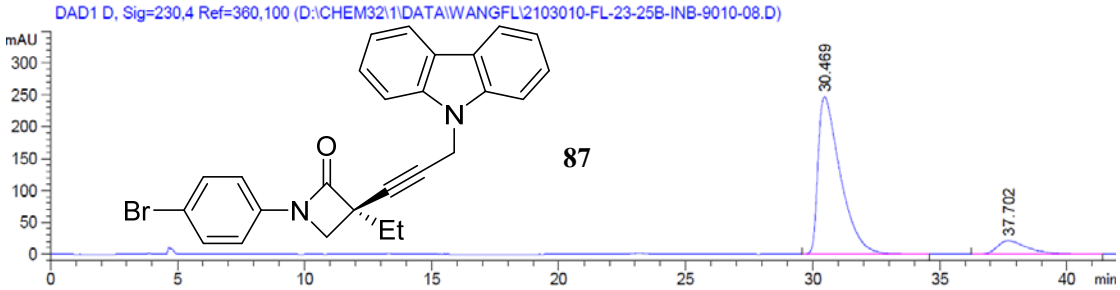
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.092	BB	0.7184	1.12299e4	231.29427	93.0271
2	30.782	BB	0.7976	841.74402	15.84896	6.9729
Totals :				1.20716e4	247.14323	



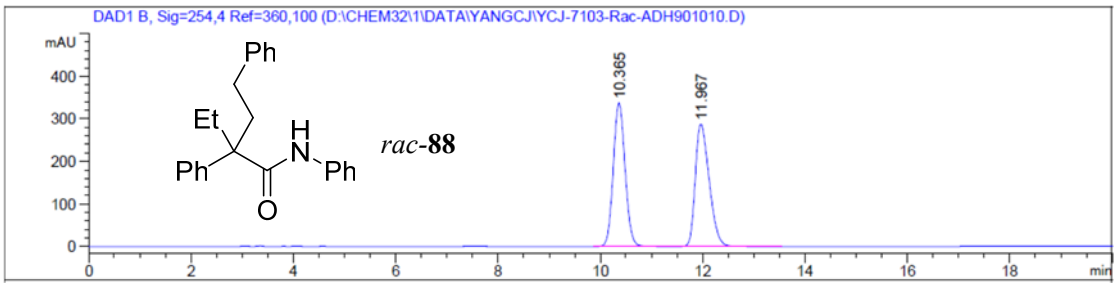
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.617	BB	0.8653	1.16421e4	199.95204	50.0366
2	36.677	BB	1.2386	1.16251e4	137.46515	49.9634
Totals :				2.32672e4	337.41719	



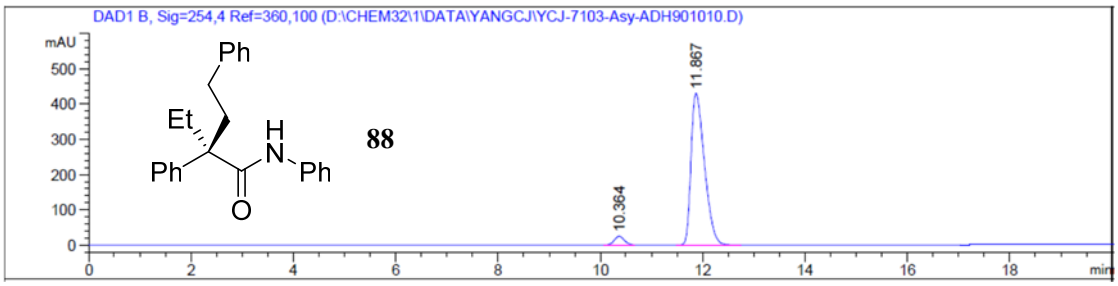
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.469	BB	0.9135	1.50350e4	246.54140	89.4364
2	37.702	MF R	1.3843	1775.82593	21.38046	10.5636
Totals :				1.68108e4	267.92185	



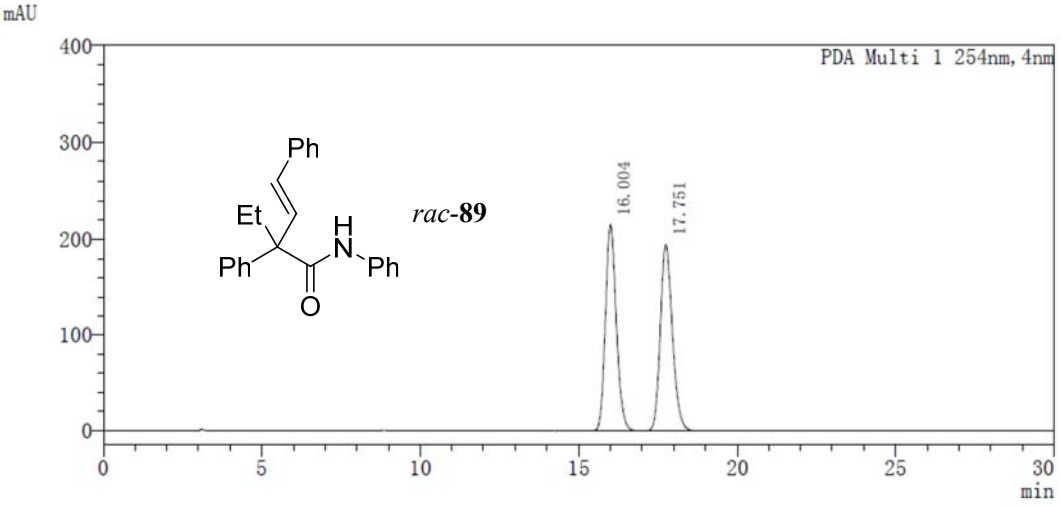
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.365	BB	0.2514	5408.89746	336.79150	49.9387
2	11.967	BV	0.2962	5422.18066	287.32394	50.0613
Totals :				1.08311e4	624.11545	



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.364	MM R	0.2443	383.12515	26.14209	4.6137
2	11.867	MM R	0.3055	7920.97070	432.15262	95.3863
Totals :				8304.09586	458.29471	

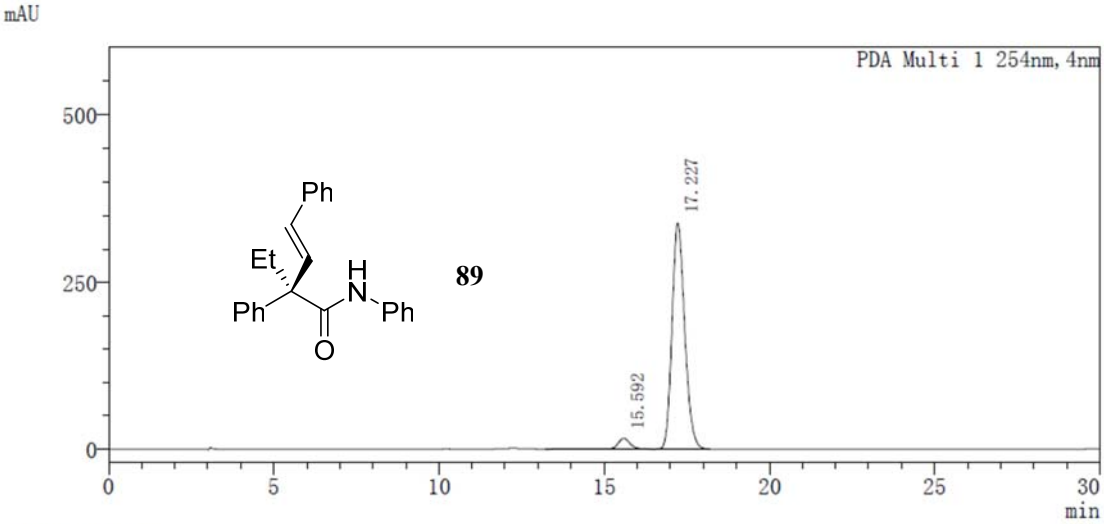


rac-**89**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	16.004	5127352	49.914
2	17.751	5144983	50.086

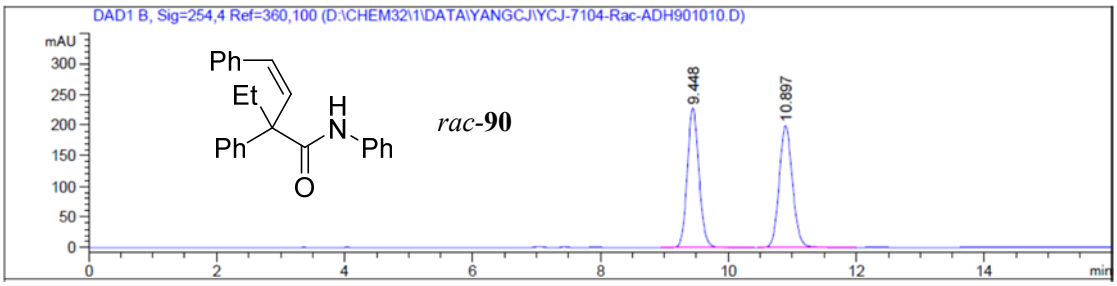


89

Peak Table

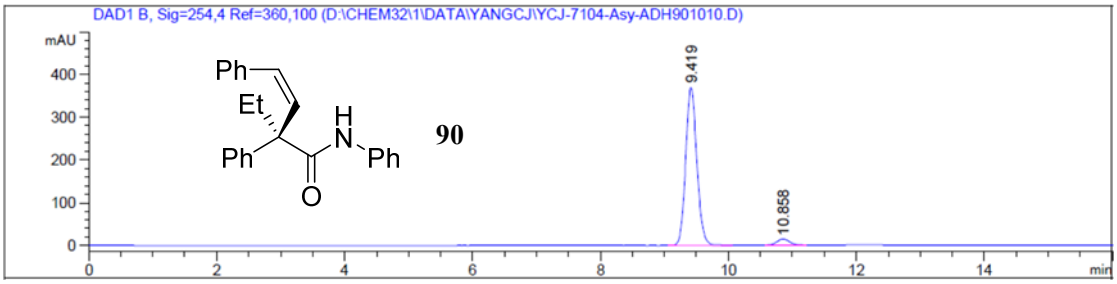
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.592	406450	4.306
2	17.227	9033631	95.694



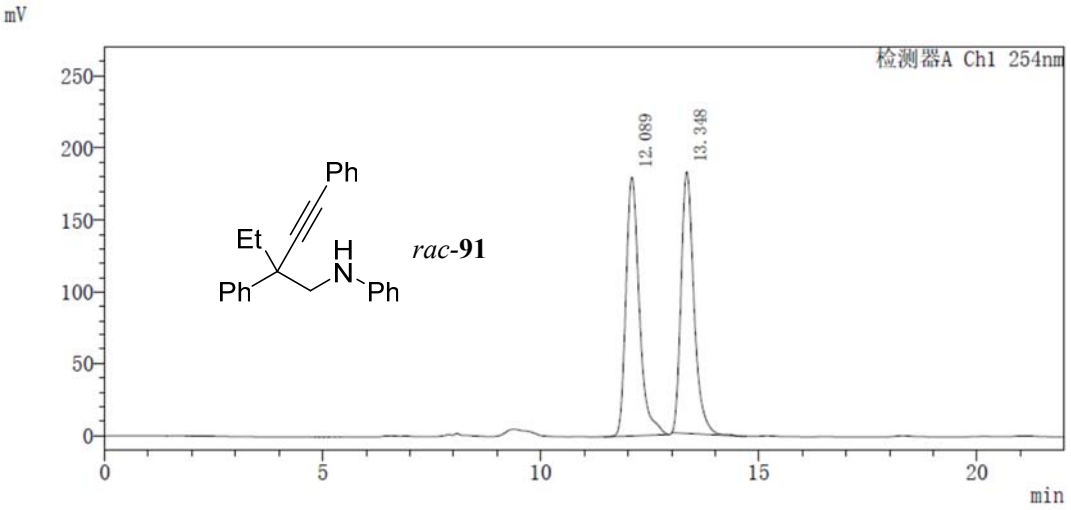
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.448	BB	0.2003	2885.86108	227.07635	50.0782
2	10.897	BV	0.2290	2876.84546	198.62880	49.9218
Totals :				5762.70654	425.70515	



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

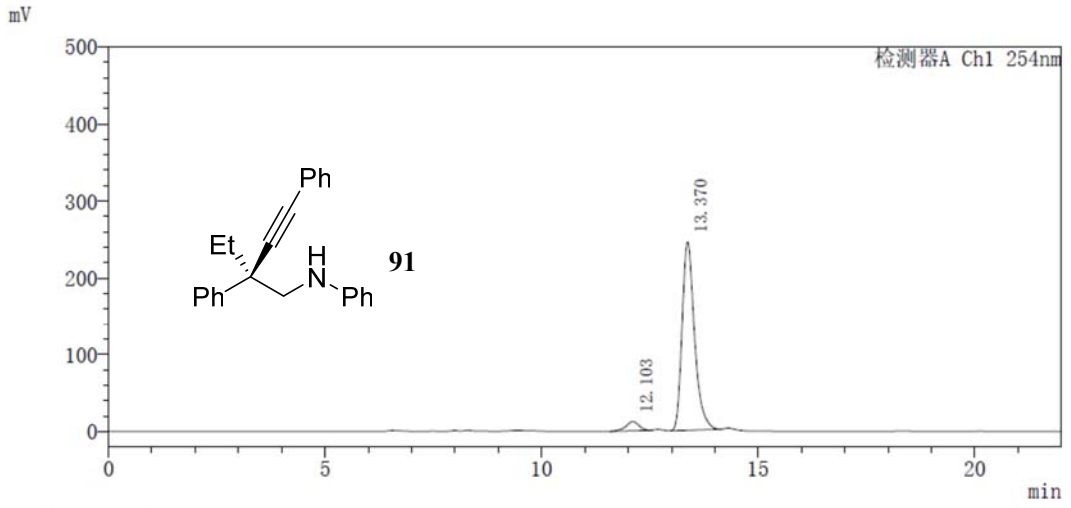
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.419	MM R	0.2038	4535.71045	370.94101	95.4220
2	10.858	MM R	0.2445	217.60536	14.83123	4.5780
Totals :				4753.31581	385.77224	



Peak Table

检测器A Ch1 254nm

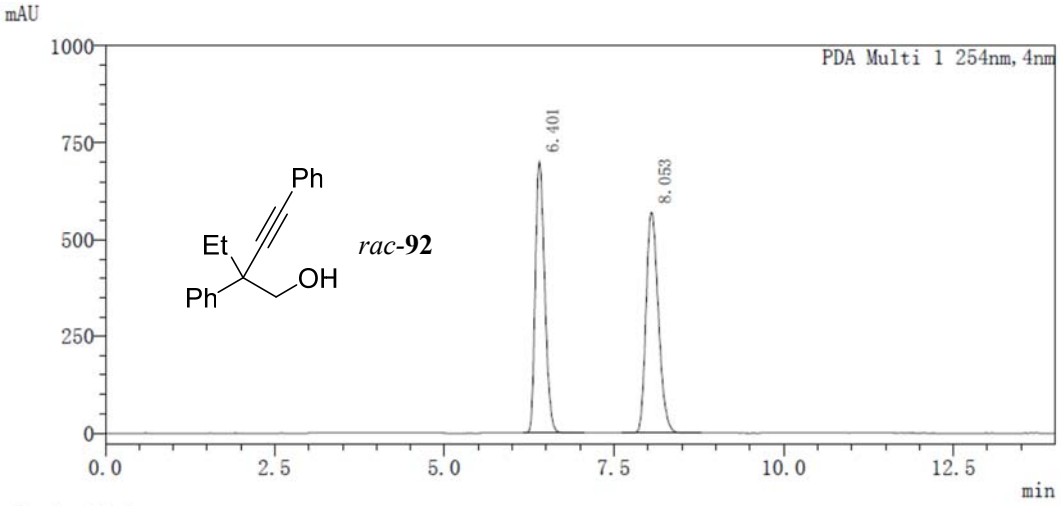
Peak#	Ret. Time	Area	Area%
1	12.089	3851771	50.650
2	13.348	3752853	49.350



Peak Table

检测器A Ch1 254nm

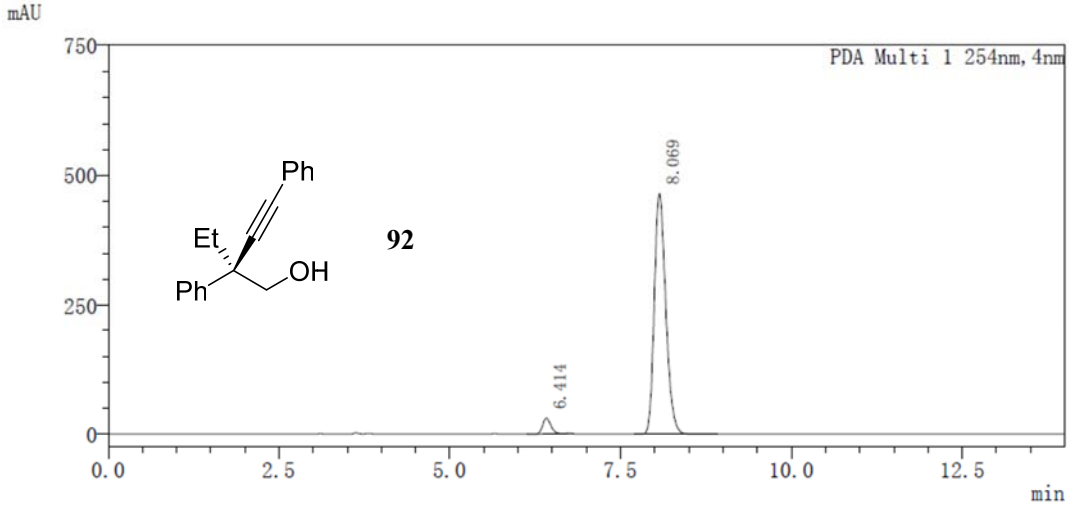
Peak#	Ret. Time	Area	Area%
1	12.103	245884	4.787
2	13.370	4890794	95.213



Peak Table

PDA Ch1 254nm

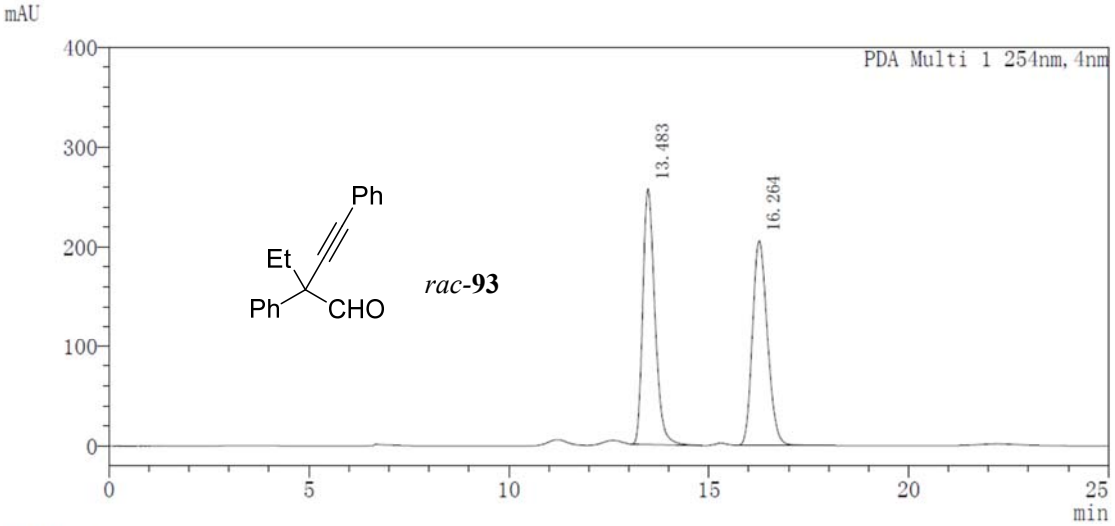
Peak#	Ret. Time	Area	Area%
1	6.401	6792491	48.429
2	8.053	7233063	51.571



Peak Table

PDA Ch1 254nm

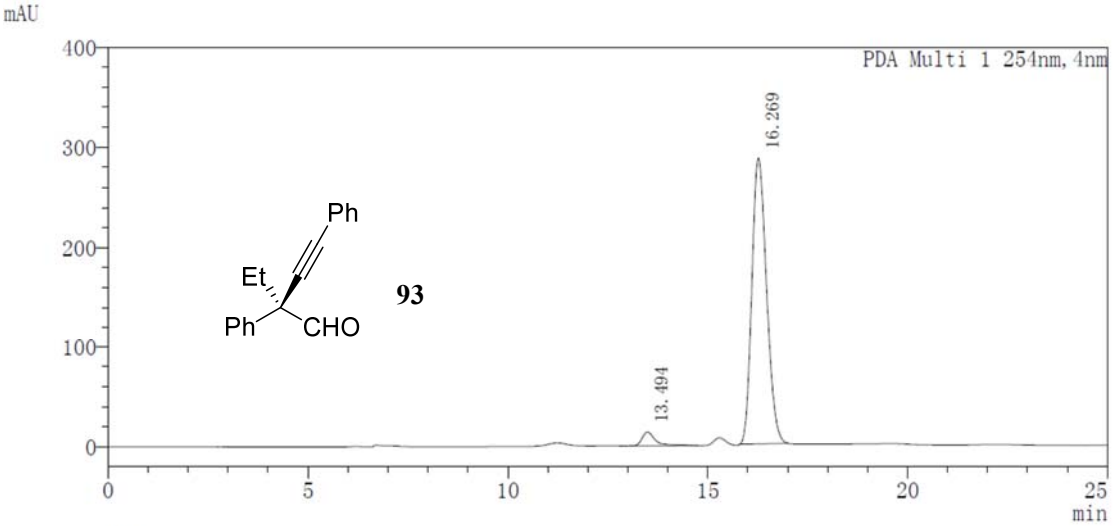
Peak#	Ret. Time	Area	Area%
1	6.414	260244	4.568
2	8.069	5436357	95.432



Peak Table

PDA Ch1 254nm

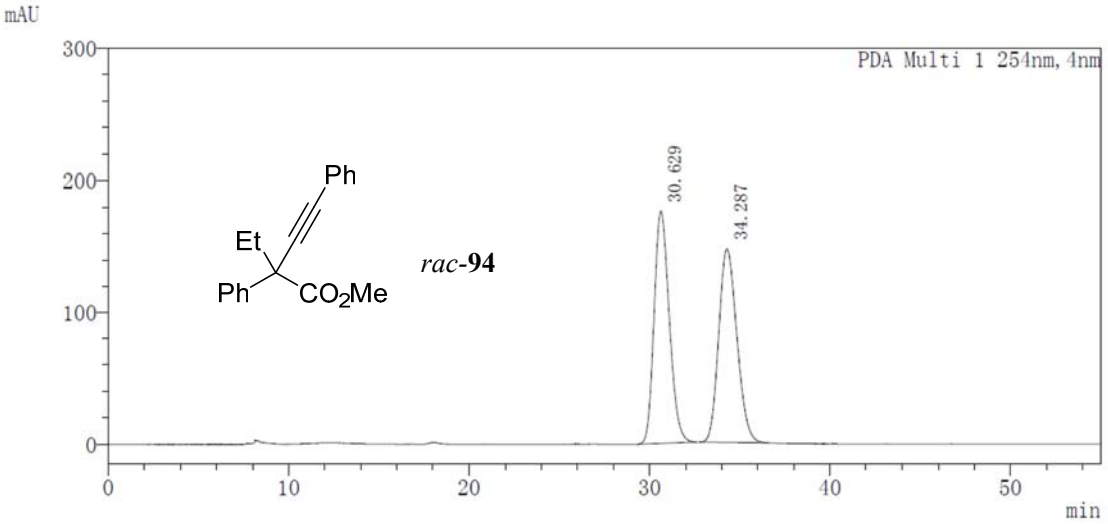
Peak#	Ret. Time	Area	Area%
1	13.483	5402594	50.302
2	16.264	5337625	49.698



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	13.494	328900	4.306
2	16.269	7309307	95.694

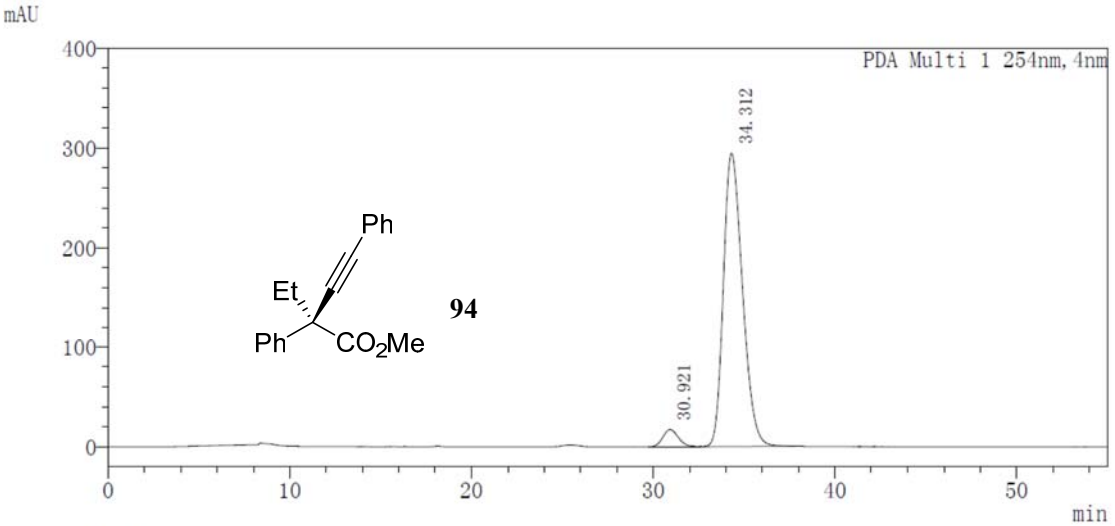


rac-**94**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	30.629	10274345	49.980
2	34.287	10282630	50.020



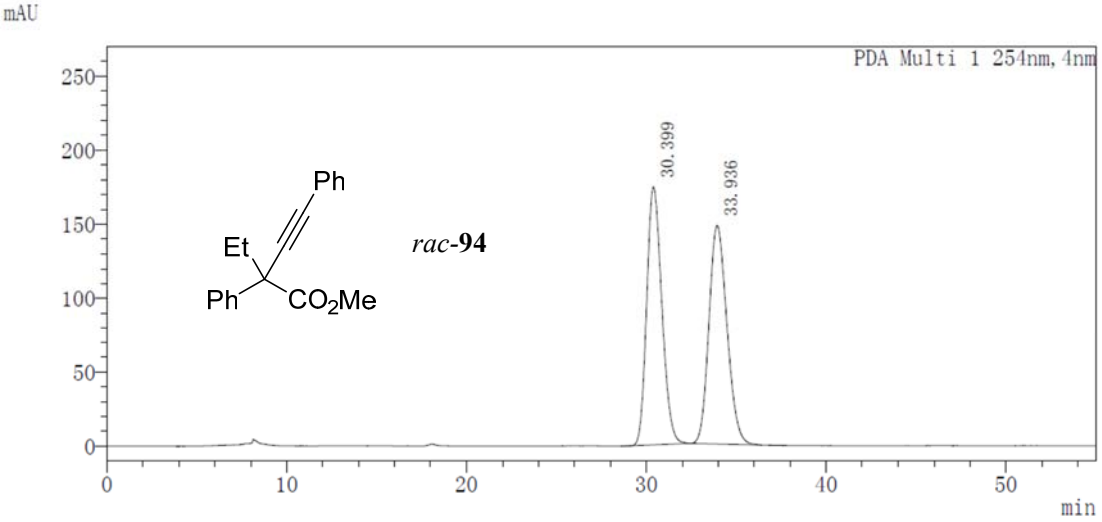
94

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	30.921	1009908	4.486
2	34.312	21501961	95.514

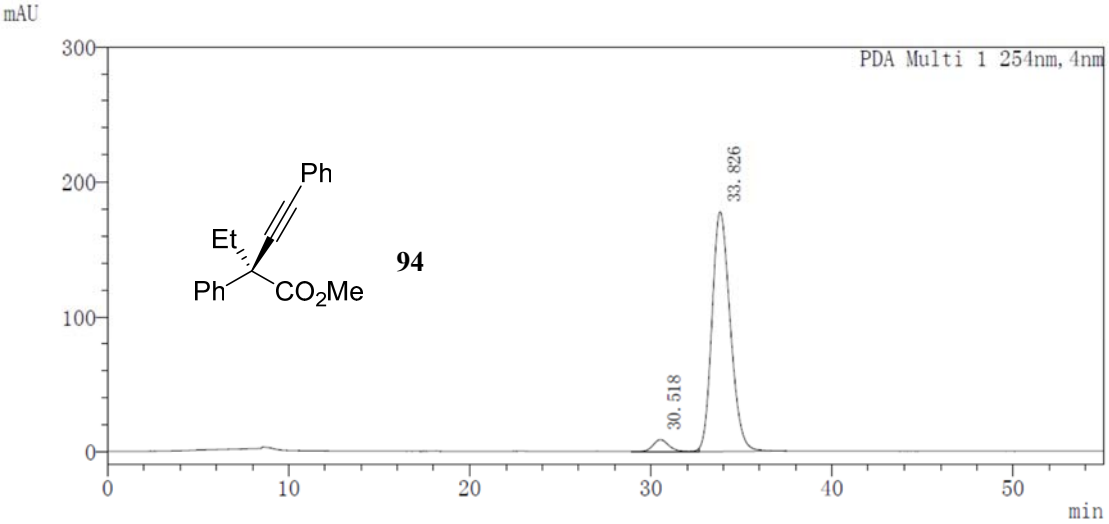
The e.e. value of **95** was determined by analyzing the esterified product **94**.



Peak Table

PDA Ch1 254nm

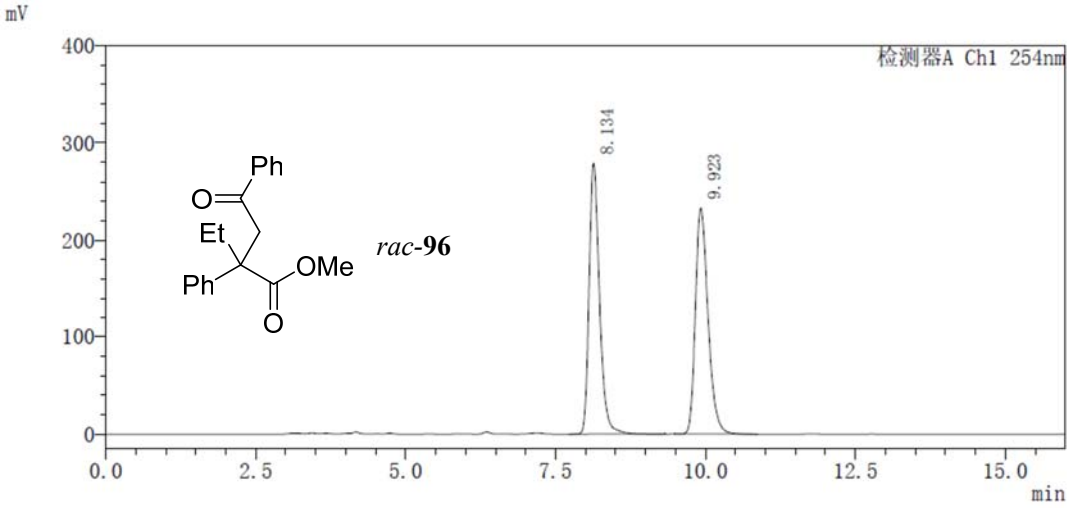
Peak#	Ret. Time	Area	Area%
1	30.399	10192111	49.787
2	33.936	10279389	50.213



Peak Table

PDA Ch1 254nm

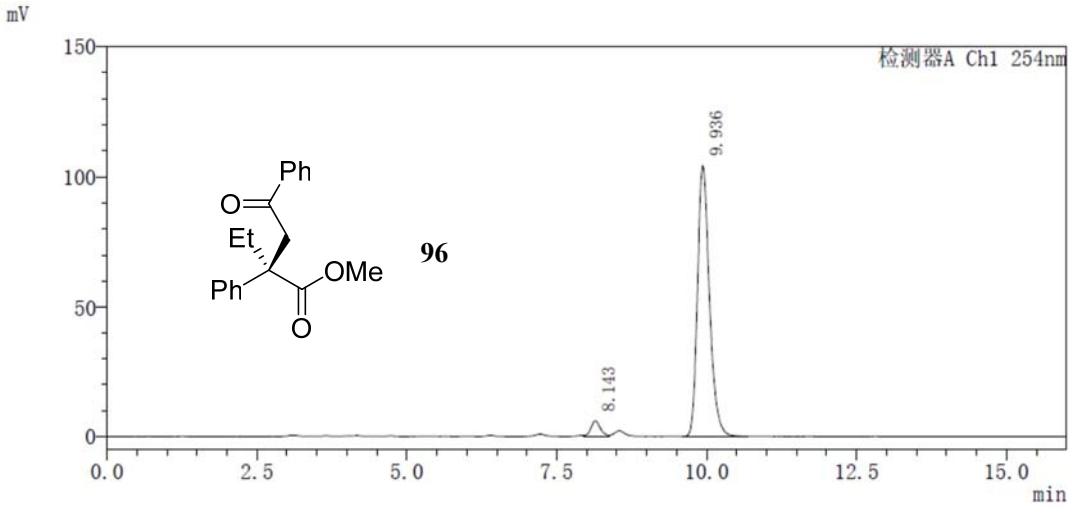
Peak#	Ret. Time	Area	Area%
1	30.518	563188	4.320
2	33.826	12474830	95.680



Peak Table

检测器A Ch1 254nm

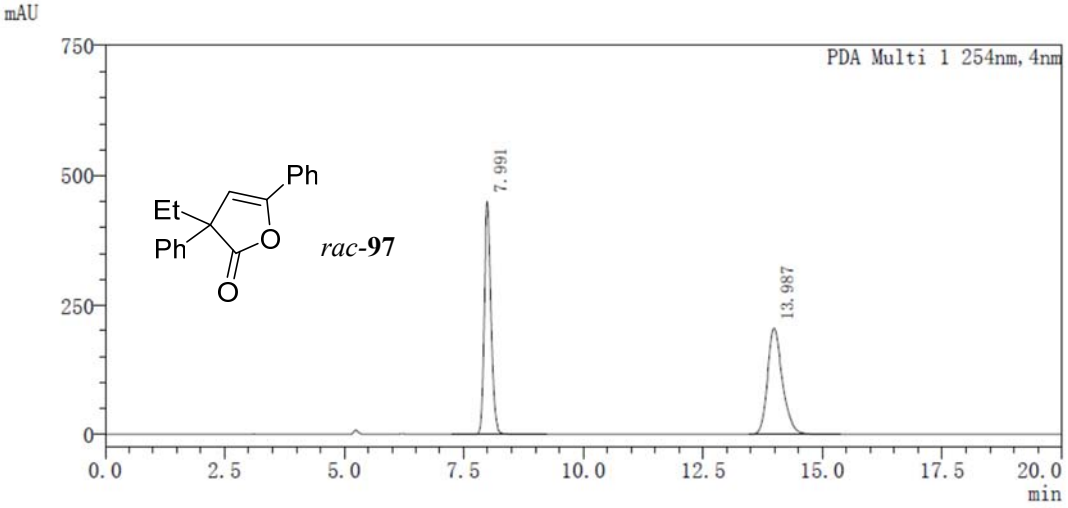
Peak#	Ret. Time	Area	Area%
1	8.134	3370173	49.678
2	9.923	3413907	50.322



Peak Table

检测器A Ch1 254nm

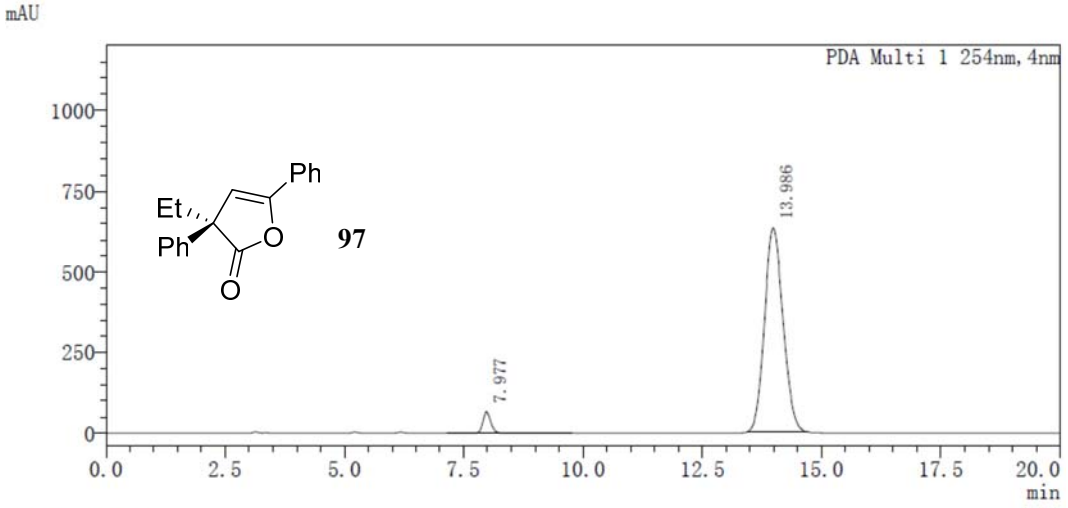
Peak#	Ret. Time	Area	Area%
1	8.143	67747	4.480
2	9.936	1444559	95.520



Peak Table

PDA Ch1 254nm

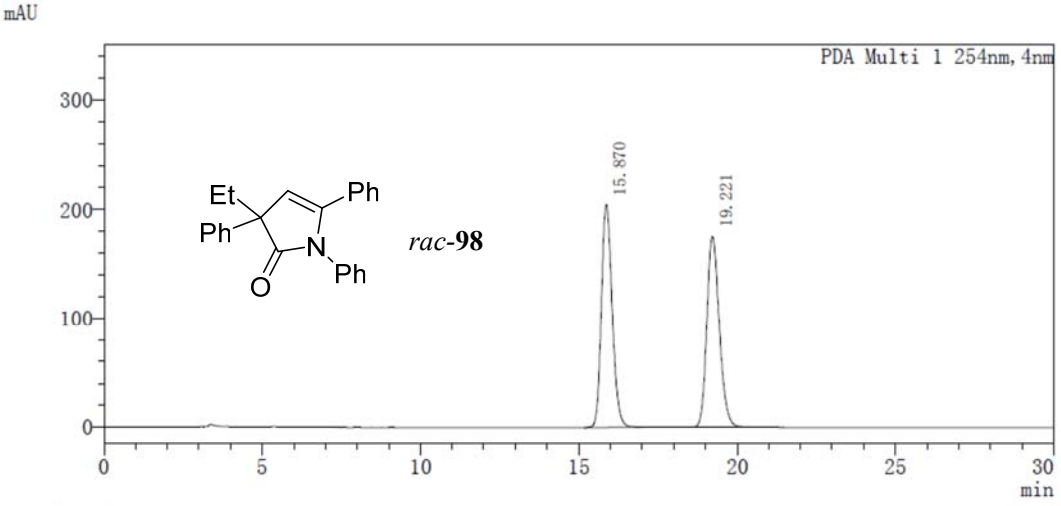
Peak#	Ret. Time	Area	Area%
1	7.991	4430996	50.023
2	13.987	4426887	49.977



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.977	763339	4.270
2	13.986	17115408	95.730

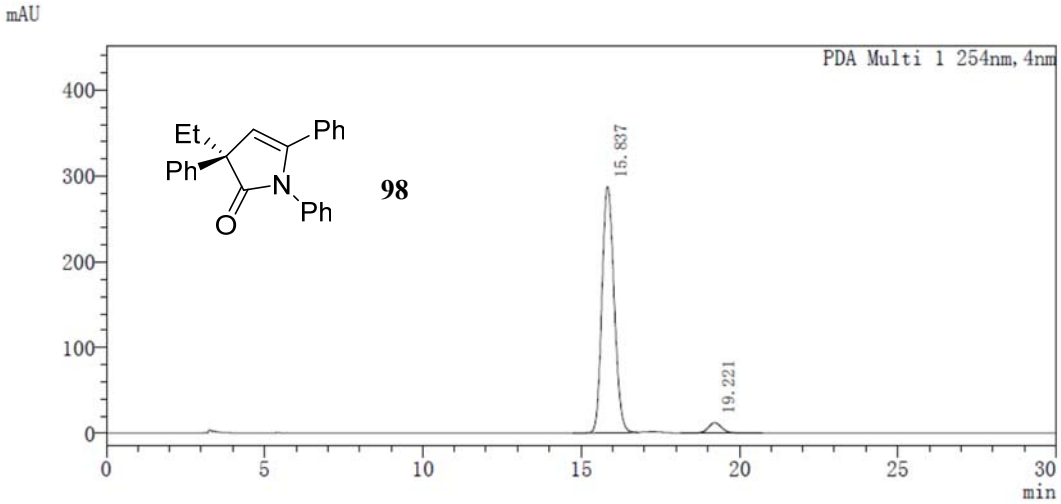


rac-**98**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.870	4820985	50.046
2	19.221	4812206	49.954

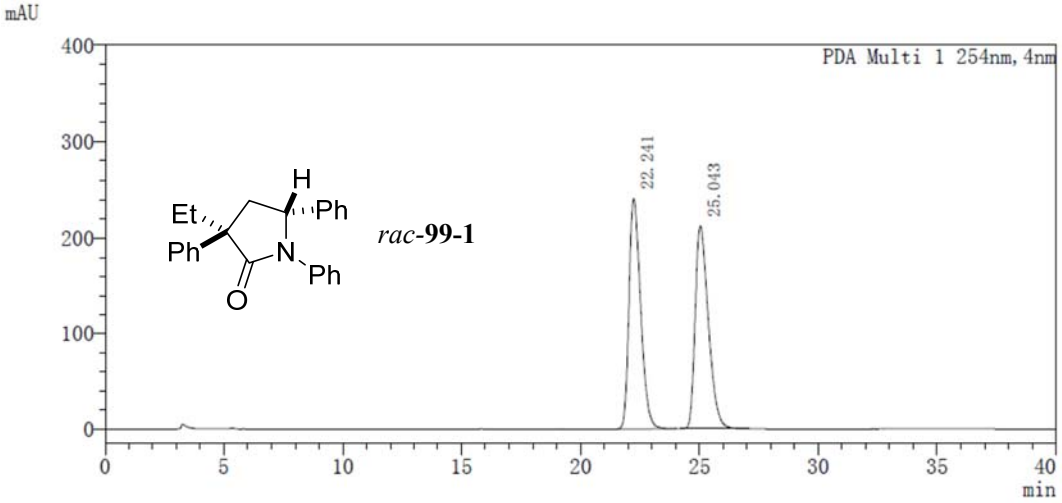


98

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.837	7666479	95.695
2	19.221	344891	4.305

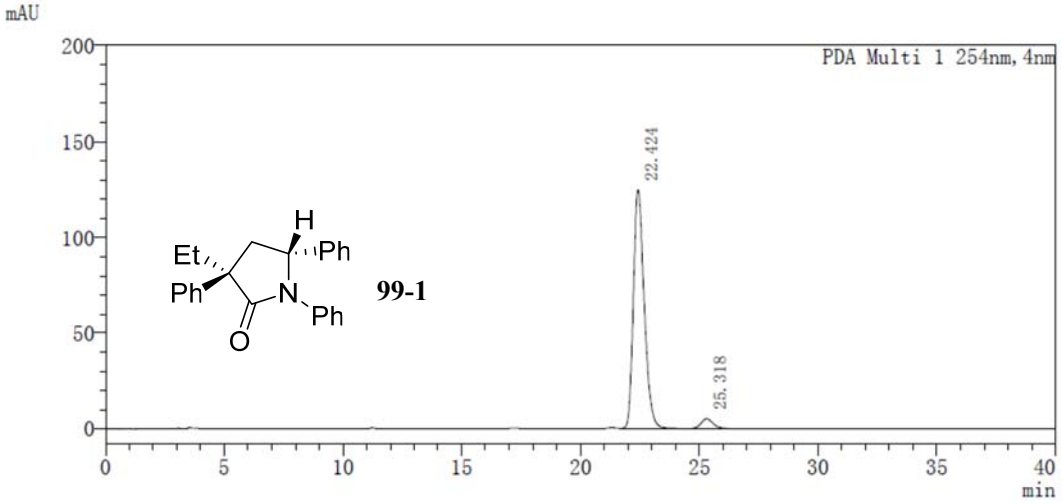


rac-**99-1**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.241	8201143	50.014
2	25.043	8196483	49.986

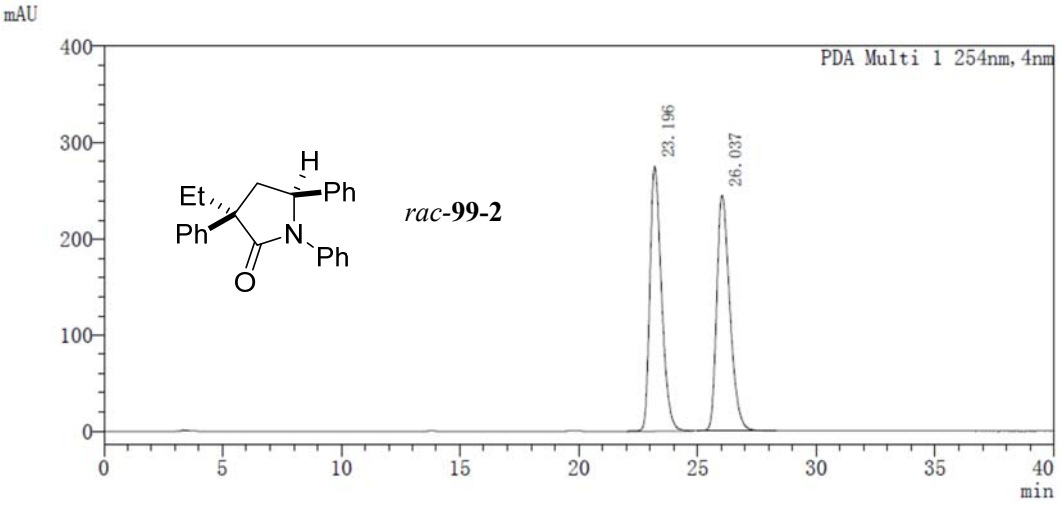


99-1

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.424	3949332	95.577
2	25.318	182769	4.423

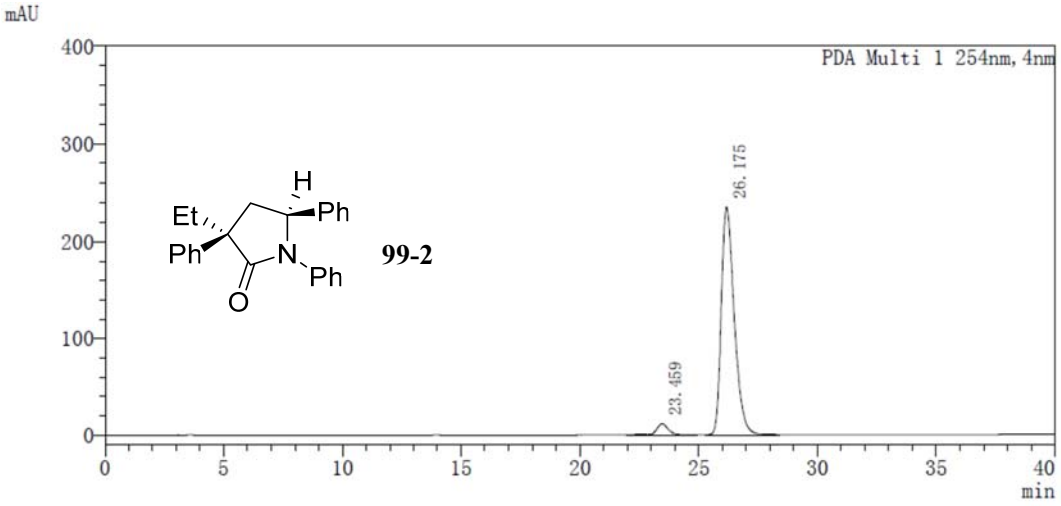


rac-**99-2**

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.196	9373498	49.888
2	26.037	9415418	50.112



99-2

Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.459	405178	4.342
2	26.175	8925358	95.658

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