Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information for

Asymmetric Sonogashira C(sp^3)-C(sp) Bond Coupling Enabled by Copper(I) Complex of New Guanidine-Hybrid Ligand

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1. General Information

Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Column chromatography was generally performed on silica gel (300–400 mesh) and reactions were monitored with thin-layer chromatography (TLC) using 254 nm UV light and basic $KMnO_4$ aqueous.

NMR characterization data were collected on bruker ASCENDTM operating at 400 MHz for ^1H NMR, 101 MHz for $^{13}C\{1H\}$ NMR (with complete proton decoupling), and 376 MHz for $^{19}F\{1H\}$ NMR (with complete proton decoupling). ^1H NMR chemical shifts were reported in ppm from tetramethylsilane with the TMS resonance as the internal standard (δ = 0.00). ^{13}C NMR spectra chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0, CD_2Cl_2, δ = 53.8, $(CD_3)_2CO$, δ = 206.3, δ = 29.8, CD_3CN, δ = 118.3, δ = 1.3). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment.

Enantiomeric ratios (er) were determined by high-performance liquid chromatography (HPLC) analysis using the corresponding commercial chiral column as stated in the experimental procedures at 25 ºC.

Optical rotations were measured on Rudolph Research Analytic Automatic Polarimeter, and reported as follows: $[\alpha]_D^T$ (c g/100 mL, in solvent).

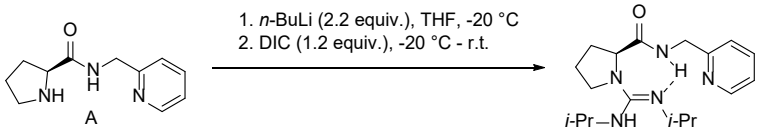
High-resolution mass spectra (HRMS) were performed on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z).

Infrared spectra (IR) were recorded on Bruker Tensor II spectrometer with Plantium ATR accessory and the peaks are reported as absorption maxima (v, cm^{-1}).

All catalytic reactions were run in over-dried glassware. Tetrahydrofuran (THF), toluene, and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Ethyl acetate (EtOAc), and dichloromethane (DCM) were distilled over CaH_2.

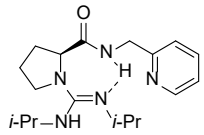
The preparation of alkyl halide[1] followed the literature.

2. General procedure for the synthesis of 2-picolylamine-based guanidine-amide ligands



General Procedure for the synthesis of guanidine G. In an over-dried RB flask, amide A (1.0 mmol,1.0 equiv.) was dissolved in THF (20 mL) and cooled to -20 °C under nitrogen atmosphere. *n*-BuLi (2.4 M in hexane, 2.2 mmol, 2.2 equiv.) was added dropwise. After stirring at -20 °C for 20 mins, *N*,*N*'-diisopropylcarbodiimide (1.2 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was slowly warmed up to rt and further stirred for 48 h. The reaction was quenched with water (25 mL) at 0 °C and extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with brine, then dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel (eluent: DCM/MeOH/NEt_3 = 85:15:1) to afford the corresponding guanidine.

***Guanidine* G-PrPy**



1.0 mmol scale, 130 mg, pale yellow oil, 39% yield. $[\alpha]_D^{20}$ = -15.0 (*c* 0.60, CH_2Cl_2).

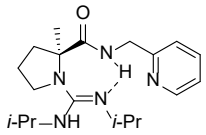
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (brs, 1H), 8.56 (t, *J* = 5.9 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 12.4, 8.0 Hz, 1H), 7.25 - 7.13 (m, 1H), 5.88 (brs, 1H), 4.15 - 3.42 (m, 4H), 3.10 - 2.92 (m, 2H), 2.14 - 2.07 (m, 1H), 1.95 - 1.83 (m, 1H), 1.76 - 1.67 (m, 2H), 1.22 - 0.88 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 152.2, 149.1, 149.0, 136.9, 122.57, 121.96, 60.7, 60.6, 47.3, 47.2, 30.8, 30.6, 26.1, 26.0, 24.8, 23.3.

HR-MS (ESI) calcd for $C_{18}H_{30}N_5O^+$ ([M+H]$^+$): 332.2445, found 332.2441;

IR (neat) 13326, 2964, 2868, 1639, 1589, 1499, 1436, 1169, 1124, 995, 735 cm^{-1}.

***Guanidine* G-qPrPy**



1.0 mmol scale, 157 mg, pale yellow oil, 45% yield. $[\alpha]_D^{20}$ = -16.3 (*c* 0.44, CH_2Cl_2).

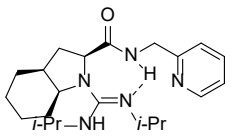
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (brs, 1H), 8.58 - 8.56 (m, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 6.2 Hz, 1H), 5.90 (brs, 1H), 4.17 (m, 3H), 3.15 - 3.07 (m, 1H), 3.00 - 2.83 (m, 1H), 2.29 - 2.22 (m, 1H), 1.86 - 1.55 (m, 4H), 1.40 (d, *J* = 16.8 Hz, 3H), 1.11 - 1.01 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 156.9, 152.1, 149.1, 136.9, 122.5, 122.0, 66.4, 47.2, 47.1, 38.0, 37.4, 26.5, 26.4, 25.8, 25.7, 25.0, 22.4.

HR-MS (ESI) calcd for $C_{19}H_{32}N_5O^+$ ([M+H]$^+$): 346.2601, found 346.2600;

IR (neat) 3326, 2963, 2688, 1643, 1590, 1570, 1495, 1365, 1170, 1052, 753 cm^{-1}.

***Guanidine* G-PePy**



3.0 mmol scale, 719 mg, pale yellow oil, 62% yield. $[\alpha]_D^{20}$ = +8.2 (*c* 0.33, CH_2Cl_2).

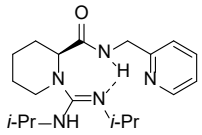
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (brs, 1H), 8.57 - 8.53 (m, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.37 - 7.32 (m, 1H), 7.20 - 7.17 (m, 1H), 5.96 (s, 1H), 4.61 - 3.47 (m, 4H), 3.31 (dt, *J* = 9.6, 4.8 Hz, 1H), 2.34 - 2.20(m, 1H), 1.99 - 1.89 (m, 1H), 1.83 - 1.60 (m, 4H), 1.55 - 1.43 (m, 2H), 1.39 - 1.23 (m, 4H), 1.18 - 0.94 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 157.4, 152.2, 149.1, 136.9, 122.4, 122.2, 58.9, 57.4, 38.0, 37.6, 35.9, 35.6, 29.4, 29.3, 27.8, 27.4, 25.0, 24.2, 23.8, 22.6, 21.6, 20.9.

HR-MS (ESI) calcd for $C_{22}H_{35}N_5O^+$ ([M+H]$^+$):386.2914, found 386.2910;

IR (neat) 3323, 2961, 2927, 2858, 1642, 1590, 1570, 1496, 1378, 1305, 1172, 1124, 751, 624 cm^{-1}.

***Guanidine* G-PiPy**



1.4 mmol scale, 243 mg, pale yellow oil, 49% yield. $[\alpha]_D^{20}$ = -14.0 (*c* 0.60, CH_2Cl_2).

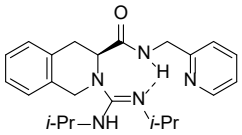
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.8 Hz, 1H), 8.24 (brs, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.25 - 7.12 (m, 1H), 5.85 (brs, 1H), 3.99 (brs, 3H), 3.28 - 3.23 (m, 1H), 3.13 - 3.03 (m, 1H), 2.75 - 2.61 (m, 1H), 1.96 - 1.89 (m, 1H), 1.81 - 1.78 (m, 1H), 1.57 - 1.55 (m, 1H), 1.52 - 1.38 (m, 3H), 1.19 - 0.92 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 152.2, 148.9, 148.8, 136.9, 122.6, 121.8, 60.1, 45.9, 45.8, 29.8, 26.1, 26.0, 24.8, 24.1, 24.0, 23.3, 22.6.

HR-MS (ESI) calcd for $C_{19}H_{32}N_5O^+$ ($[M+H]^+$): 346.2601, found 346.2596;

IR (neat) 3344, 2961, 2929, 2857, 1638, 2589, 1498, 1436, 1378, 1171, 1126, 752, 619 cm^{-1}.

***Guanidine* G-TqPy**



2.0 mmol scale, 258 mg, pale yellow oil, 33% yield. $[\alpha]_D^{21}$ = -58.3 (*c* 0.40, CH_2Cl_2).

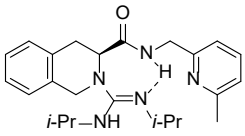
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.61 - 8.50 (m, 1H), 7.65 (q, *J* = 8.0 Hz, 1H), 7.41 - 7.31 m, 1H), 7.21 - 7.20 (m, 1H), 7.17 - 7.13 (m, 3H), 7.08 - 7.02 (m, 1H), 5.88 (s, 1H), 4.23 - 3.36 (m, 6H), 3.24 - 3.12 (m, 1H), 2.92 - 2.81 (m, 1H), 1.20 - 0.93 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 152.4, 149.0, 148.9, 137.0, 135.9, 135.8, 134.2, 134.1, 129.2, 126.4, 126.3, 126.1, 125.7, 125.6, 122.7, 121.8, 56.6, 56.5, 47.6, 47.5, 45.0, 31.1, 24.8, 23.3.

HR-MS (ESI) calcd for $C_{23}H_{32}N_5O^+$ ($[M+H]^+$): 394.2601, found 394.2599;

IR (neat) 3338, 2963, 2927, 1638, 1589, 1495, 1435, 1379, 1249, 1172, 1125, 996, 747, 626 cm^{-1}.

***Guanidine* G-TqPy-*o*Me**



1.0 mmol scale, 283 mg, pale yellow oil, 70% yield. $[\alpha]_D^{21}$ = -59.8 (*c* 0.40, CH_2Cl_2).

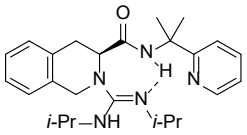
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.52 (q, *J* = 8.2 Hz, 1H), 7.21 - 7.08 (m, 4H), 7.06 - 7.02 (m, 2H), 5.85 (s, 1H), 4.43 - 3.37 (m, 7H), 3.16 (dt, *J* = 12.8, 4.4 Hz, 1H), 2.87 (dt, *J* = 16.4, 10.8 Hz, 1H), 2.54 (d, *J* = 4.8 Hz, 3H), 1.18 - 0.96 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 157.7, 152.2, 137.2, 135.8, 135.7, 134.2, 134.1, 129.3, 129.2, 126.4, 126.1, 125.6, 122.1, 118.6, 56.6, 47.6, 31.1, 24.4, 24.4, 24.4, 22.4.

HR-MS (ESI) calcd for $C_{24}H_{34}N_5O^+$ ($[M+H]^+$): 408.2758, found 408.2752;

IR (neat) 3335, 2963, 2926, 1640, 1576, 1496, 1455, 1377, 1257, 1173, 1125, 747 cm^{-1}.

***Guanidine* G-TqPy^{Me2}**



2.0 mmol scale, 455 mg, white solid, m. p. 88.3-89.3 °C, 54% yield. $[\alpha]_D^{21}$ = -69.0 (*c* 0.20, CH_2Cl_2).

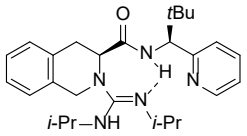
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.51 - 8.42 (m, 1H), 7.53 (td, *J* = 7.6, 2.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.15 - 7.09 (m, 3H), 7.06 - 7.01 (m 2H), 4.81 (d, *J* = 6.0 Hz, 1H), 4.47 - 4.28 (m, 2H), 3.55 - 3.22 (m, 4H), 2.95 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.66 (s, 3H), 1.63 (s, 3H), 1.13 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 165.2, 155.5, 148.1, 136.2, 134.4, 132.8, 128.8, 126.5, 125.6, 125.4, 121.1, 119.3, 57.0, 55.5, 47.2, 47.0, 29.4, 28.5, 27.9, 24.4.

HR-MS (ESI) calcd for $C_{25}H_{36}N_5O^+$ ($[M+H]^+$):422.2914, found 422.2909;

IR (neat) 3346, 2964, 1672, 1620, 1502, 1457, 1398, 1360, 1310, 1274, 1237, 1125, 1084, 990, 748 cm^{-1}.

***Guanidine* G-TqPy$^{(S)\text{-}tBu}$**



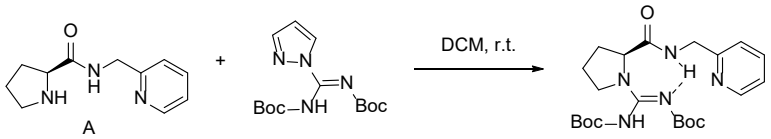
2.0 mmol scale, 433 mg, white solid, m. p. 150.1-151.7 °C, 48% yield. $[\alpha]_D^{21}$ = -112.5 (*c* 0.20, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 9.2 Hz, 1H), 8.54 (dd, *J* = 4.8, 1.8 Hz, 1H), 7.55 (td, *J* = 7.6, 1.9 Hz, 1H), 7.21 - 7.08 (m, 5H), 7.06 - 7.03 (m, 1H), 4.85 - 4.80 (m, 2H), 4.56 - 4.28 (m, 2H), 3.46 (s, 1H), 3.37 - 3.31 (m, 3H), 2.91 (dd, *J* = 15.9, 6.4 Hz, 1H), 1.25 - 1.23 (m, 6H),1.15 - 1.13 (m, 3H), 1.09 - 0.98 (m, 3H), 0.85 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 159.9, 155.2, 148.4, 135.2, 134.6, 132.7, 128.9, 126.4, 125.7, 125.4, 123.4, 121.6, 62.5, 55.4, 47.6, 47.1, 46.7, 35.2, 29.6, 27.2, 25.5, 24.4, 24.2, 23.2.

HR-MS (ESI) calcd for $C_{27}H_{40}N_5O^+$ ($[M+H]^+$): 450.3227, found 450.3225;

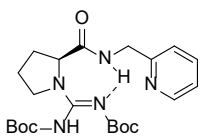
IR (neat) 13354, 2963, 2867, 1667, 1624, 1537, 1472, 1398, 1362, 1309, 1228, 1164, 1084, 992, 749 cm^{-1}.



A

General Procedure for the synthesis of N-EWG guanidine. In an over-dried RB flask, amide A (1.0 mmol,1.0 equiv.) and *N*,*N*'-di-Boc-pyrazole-1-carbodiimide (1 mmol, 1.0 equiv.) was dissolved in DCM (10 mL). The reaction mixture was stirred for 48 h. Then, concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel (eluent: PE/EtOAc = 2:1) afforded the corresponding guanidine.

***Guanidine* G^3-PrPy**



1.0 mmol scale, 173 mg, colorless oil, 39% yield. $[\alpha]_D^{22}$ = -84.0 (*c* 0.20, CH_2Cl_2).

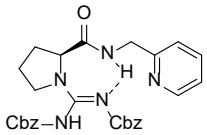
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.52 (d, *J* = 4.8 Hz, 1H), 7.81 (s, 1H), 7.65 - 7.61(m, 1H), 7.34 - 7.25 (m, 1H), 7.17 - 7.14 (m, 1H), 4.96 (s, 1H), 4.70 (dd, *J* = 16.2, 6.4 Hz, 1H), 4.48 (dd, *J* = 16.2, 5.2 Hz, 1H), 3.71 (dt, *J* = 11.2, 7.2 Hz, 1H), 3.55 (dt, *J* = 12.0, 6.6 Hz, 1H), 2.47 (s, 1H), 2.30 - 2.17 (m, 2H), 2.06 - 1.99 (m, 1H), 1.94 - 1.83 (m, 1H), 1.45 (s, 18H).

^{13}C NMR δ 171.5, 157.4, 154.6, 148.9, 136.6, 122.0, 121.3, 61.6, 49.7, 44.8, 29.2, 28.0, 24.4.

HR-MS (ESI) calcd for $C_{22}H_{34}N_5O_5^+$ ([M+H]$^+$): 448.2554, found 448.2548;

IR (neat) 3299, 2976, 1726, 1649, 1595, 1544, 1453, 1389, 1364, 1304, 1252, 1169, 1132, 803, 755 cm^{-1}.

***Guanidine* G^4-PrPy**



1.0 mmol scale, 195 mg, white solid, m. p. 136.2-137.6 °C, 38% yield. $[\alpha]_D^{21}$ = -87.0 (*c* 0.20, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.41 (d, *J* = 4.8 Hz, 1H), 7.58 (s, 1H), 7.42 - 7.19 (m, 12H), 7.05 (t, *J* = 6.2 Hz, 1H), 5.11 (s, 4H), 4.89 (t, *J* = 7.2 Hz, 1H), 4.63 (dd, *J* = 16.2, 6.0 Hz, 1H), 4.46 (dd, *J* = 16.2, 5.2 Hz, 1H), 3.78 - 3.72 (m, 1H), 3.65 - 3.50 (m, 1H), 2.28 - 2.18 (m, 2H), 2.10 - 1.98 (m, 1H), 1.91 - 1.86 (m, 1H).

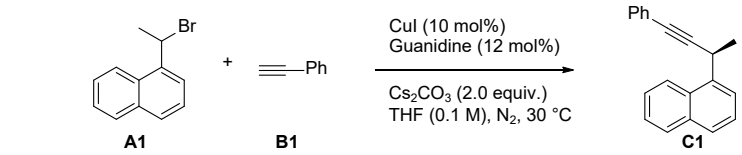
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 156.9, 154.8, 148.9, 136.7, 128.4, 128.1, 122.0, 121.3, 67.8, 62.1, 50.1, 44.6, 29.3, 24.4.

HR-MS (ESI) calcd for $C_{28}H_{30}N_5O_5^+$ ([M+H]$^+$): 516.2241, found516.2239;

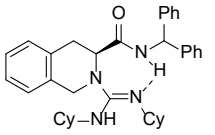
IR (neat) 2951, 1751, 1677, 1599, 1503, 1454, 1376, 1268, 1219, 1192, 1128, 1049, 751, 698 cm^{-1}.

3. Optimization of reaction conditions

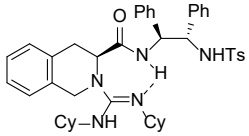
Table S1: Screening of chiral guanidines[a].



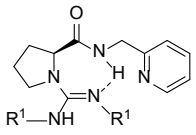
A1 **B1** **C1**



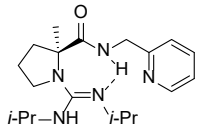
G2



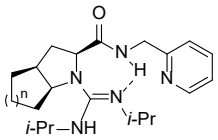
G3



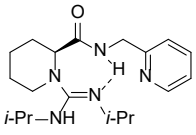
G-PrPy, R^1 = *i*-Pr
G²-PrPy, R^1 = Boc
G³-PrPy, R^1 = Cbz



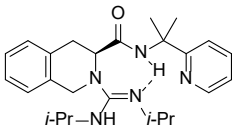
G-qPrPy



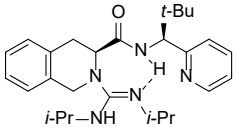
G-RaPy, n = 1
G-PePy, n = 2



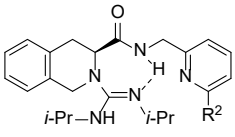
G-PiPy



G-TqPy^{Me2}



G-TqPy$^{(S)\text{-}tBu}$

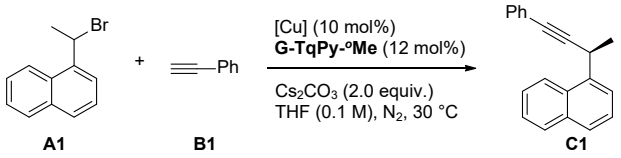


G-TqPy, R^2 = H
G-TqPy-^{o}Me, R^2 = Me
G-TqPy-^{o}Et, R^2 = Et
G-TqPy-$^{o n}$Pr, R^2 = *n*-Pr
G-TqPy-$^{o i}$Pr, R^2 = *i*-Pr

Entry[a]	guanidine	Yield [%][b]	*er*[c]
1	**G_2**	-	-
2	**G_3**	-	-
3	**G-PrPy**	34	85:15
4	**G²-PrPy**	-	-
5	**G³-PrPy**	-	-
6	**G-qPrPy**	15	78:22
7	**G-RaPy**	33	82:18
8	**G-PePy**	22	83:17
9	**G-PiPy**	55	82:18
10	**G-TqPy**	60	92:8
11	**G-TqPy-*o*Me**	81	94:6
12	**G-TqPy-*o*Et**	72	93.5:6.5
13	**G-TqPy-*o^{n}*Pr**	53	93.5:6.5
14	**G-TqPy-*o^{i}*Pr**	47	93.5:6.5
15	**G-TqPy^{Me2}**	-	-
16	**G-TqPy$^{(S)\text{-}tBu}$**	-	-

[a] Reaction conditions: CuI (10 mol %), Guanidine (12 mol %), **A1** (0.05 mmol), **B1** (0.075 mmol) and Cs_2CO_3 (0.1 mmol) in THF (0.1 M) under N_2 at 30 °C. [b] ^{1}H NMR yields using CH_2Br_2 as an internal standard. [c] the *er* value was determined by HPLC on a chiral stationary phase.

Table S2: Screening of copper salts and other metal salts.

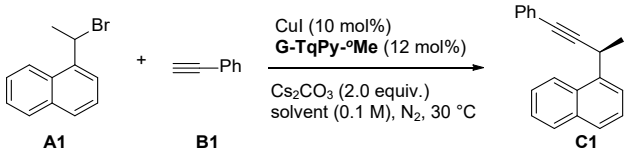


A1 **B1** **C1**

Entry[a]	metal salts	Yield [%][b]	*er* [c]
1	CuCl	40	93.5:6.5
2	CuBr	69	93.5:6.5
3	CuI	81	94:6
4	CuTc	53	94:6
5	CuOAc	35	93:7
6	$(CuOTf)_2$ PhH	8	93:7
7	$Cu(CH_3CN)_4BF_4$	61	94:6
8	$Cu(CH_3CN)_4PF_6$	51	94:6
9	$Cu(PPh_3)_2BH_4$	50	94:6
10	CuPhenylethynyl	48	94:6
11	$CuBr_2$	41	94:6
12	$FeCl_2$	-	-
13	$CoCl_2$	-	-
14	$NiCl_2$	-	-

[a] Reaction conditions: [M] (10 mol %), **G²-TqPy-*o*Me** (12 mol %), **A1** (0.05 mmol), **B1** (0.075 mmol) and Cs_2CO_3 (0.1 mmol) in THF (0.1 M) under N_2 at 30 °C. [b] ^1H NMR yields using CH_2Br_2 as an internal standard. [c] the *er* value was determined by HPLC on a chiral stationary phase.

Table S3: Screening of solvent.

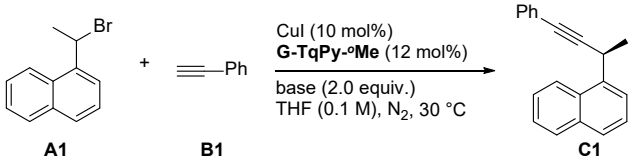


A1 **B1** **C1**

Entry[a]	Solvent	Yield [%][b]	*er* [c]
1	THF	81	94:6
2	Et_2O	trace	ND
3	DCM	54	91:9
4	Toluene	trace	ND
5	MeCN	57	79:21
6	EtOAc	66	88:12
7	1,4-dioxane	63	93:7
8	DME	45	91:9

[a] Reaction conditions: CuI (10 mol %), **G²-TqPy-*o*Me** (12 mol %), **A1** (0.05 mmol), **B1** (0.075 mmol) and Cs_2CO_3 (0.1 mmol) in solvent (0.1 M) under N_2 at 30 °C. [b] 1H NMR yields using CH_2Br_2 as an internal standard. [c] the *er* value was determined by HPLC on a chiral stationary phase.

Table S4: Screening of base.



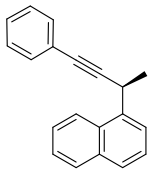
A1 **B1** **C1**

Entry[a]	base	Yield [%][b]	*er* [c]
1	Na_2CO_3	trace	ND
2	K_2CO_3	36	91:9
3	K_3PO_4	50	93:7
4	Cs_2CO_3	81	94:6
5	Cs_2CO_3 + KI (0.5 eq)	-	-
6	KO^{t}Bu	-	-
7	KOH	19	77:23
8	DABCO	-	-
9	DIPEA	-	-

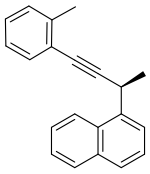
[a] Reaction conditions: CuI (10 mol %), **G^2-TqPy-oMe** (12 mol %), **A1** (0.05 mmol), **B1** (0.075 mmol) and base (0.1 mmol) in THF (0.1 M) under N_2 at 30 °C. [b] 1H NMR yields using CH_2Br_2 as an internal standard. [c] the *er* value was determined by HPLC on a chiral stationary phase.

4. Full list of the coupling products.

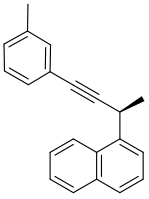
Table S5: Full list of the scope of alkynes.



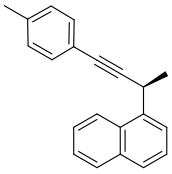
C1, 96%, 94:6 er



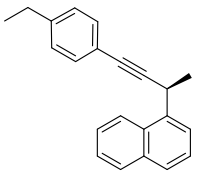
C2, 90%, 94:6 er



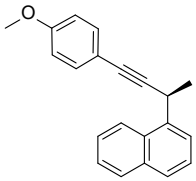
C3, 87%, 94:6 er



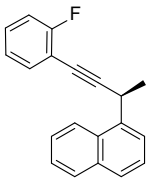
C4, 95%, 95.5:4.5 er



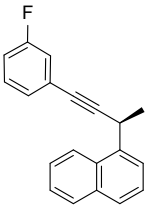
C5, 81%, 93.5:6.5 er



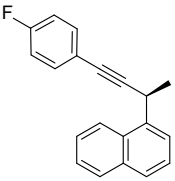
C6, 74%, 94.5:5.5 er



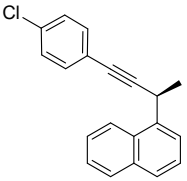
C7, 74%, 92.5:7.5 er



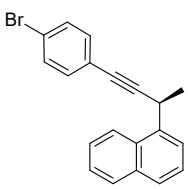
C8, 92%, 91.5:8.5 er



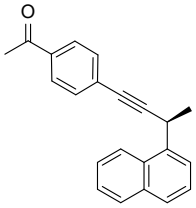
C9, 83%, 93:7 er



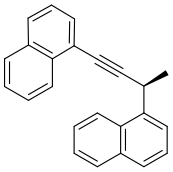
C10, 90%, 92:8 er



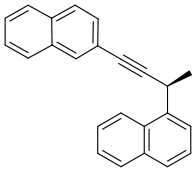
C11, 85%, 91:9 er



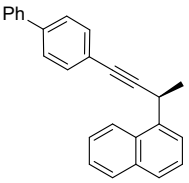
C12, 63%, 89:11 er



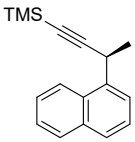
C13, 96%, 94:6 er



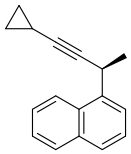
C14, 96%, 93:7 er



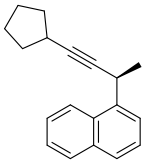
C15, 80%, 92:8 er



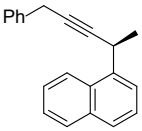
C16, 87%, 93:7 er



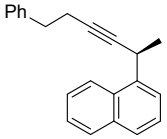
C17, 71%, 94:6 er



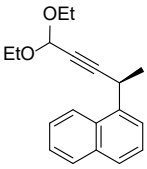
C18, 67%, 93:7 er



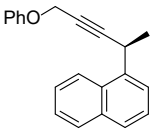
C19, 85%, 93:7 er



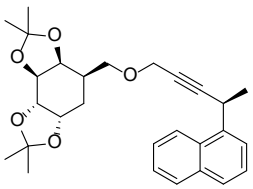
C20, 82%, 92:8 er



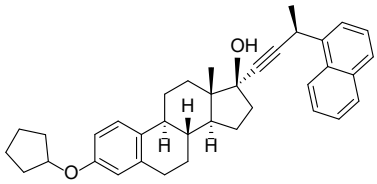
C21, 94%, 94:6 er



C22, 67%, 94:6 er

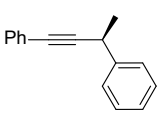


C23, 66%, 95:5 dr

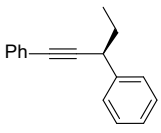


C24, 71%, 91:9 dr

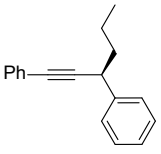
Table S6: Full list of the scope of alkyl bromides.



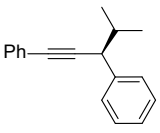
C25, 86%, 82.5:17.5 er



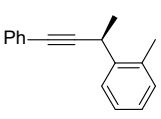
C26, 89%, 85:15 er



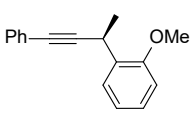
C27, 92%, 82:18 er



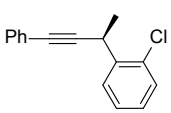
C28, 58%, 90:10 er



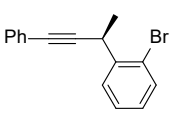
C29, 87%, 93:7 er



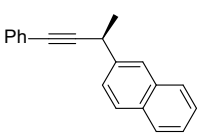
C30, 61%, 95:5 er



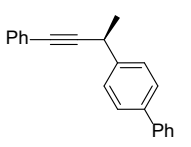
C31, 84%, 95:5 er



C32, 85%, 95.5:4.5 er

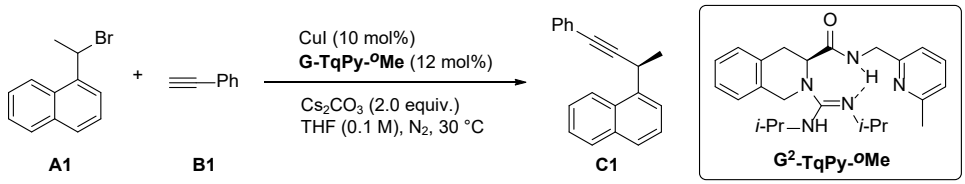


C33, 87%, 85:15 er



C34, 86%, 80.5:19.5 er

5. General procedure for the catalytic reactions

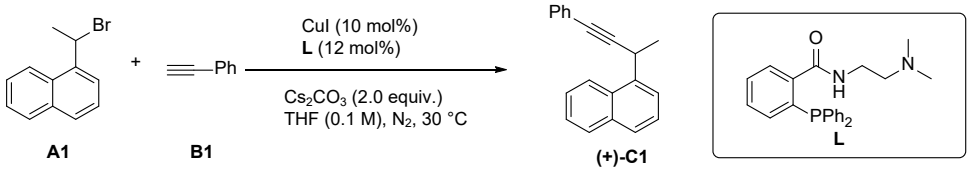


1. General procedure A:

Under nitrogen atmosphere, an over-dried reaction tube charged with alkyl halide (0.20 mmol, 1.0 equiv.), CuI (10 mol %), **G^2-TqPy-*o*Me** (12 mol %), Cs_2CO_3 (2.0 equiv.), and anhydrous THF (1.0 mL). Then, alkyne (0.24 mmol, 1.2 equiv.) was sequentially added to the mixture and the reaction mixture was stirred at 30 °C for 24 to 72 h. Upon completion (monitored by TLC), THF was evaporated in vacuo, then the crude mixture was purified by flash chromatography on silica gel (eluent: PE) to afford the desired product.

2. General procedure B:

Under nitrogen atmosphere, an over-dried reaction tube charged with alkyl halide (0.24 mmol, 1.2 equiv.), CuI (10 mol %), **G^2-TqPy-*o*Me** (12 mol %), Cs_2CO_3 (2.0 equiv.), and anhydrous THF (1.0 mL). Then, alkyne (0.20 mmol, 1.0 equiv.) was sequentially added to the mixture and the reaction mixture was stirred at 30 °C for 24 to 72 h. Upon completion (monitored by TLC), THF was evaporated in vacuo, then the crude mixture was purified by flash chromatography on silica gel (eluent: PE) to afford the desired product.

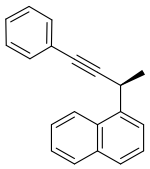


3. General procedure for the racemic coupling reaction:

Under nitrogen atmosphere, an over-dried reaction tube charged with alkyl halide (0.10 mmol, 1.0 equiv.), CuI (10 mol %), **L** (12 mol %), Cs_2CO_3 (2.0 equiv.), and anhydrous THF (1.0 mL). Then, alkyne (0.15 mmol, 1.5 equiv.) was sequentially added to the mixture and the reaction mixture was stirred at 30 °C for 24 h. Upon completion (monitored by TLC), THF was evaporated in vacuo, then the crude mixture was purified by flash chromatography on silica gel (eluent: PE) to afford the desired product.

6. Characterization of the products

_(S)_-1-(4-phenylbut-3-yn-2-yl)naphthalene (C1)



General procedure A for 48 h.

0.2 mmol scale; 49.1 mg, colorless oil, 96% yield, 94:6 *er*; $[\alpha]_D^{20}$ = +73.4 (*c* 0.98, CH_2Cl_2).

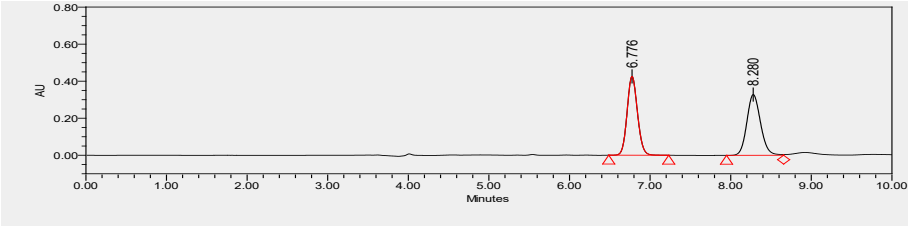
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 6.70 min, t_2 = 8.10 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.55 - 7.50 (m, 1H), 7.49 - 7.43 (m, 4H), 7.27 - 7.26 (m, 3H), 4.72 (q, *J* = 7.2 Hz, 1H), 1.72 (d, *J* = 7.2 Hz, 3H).

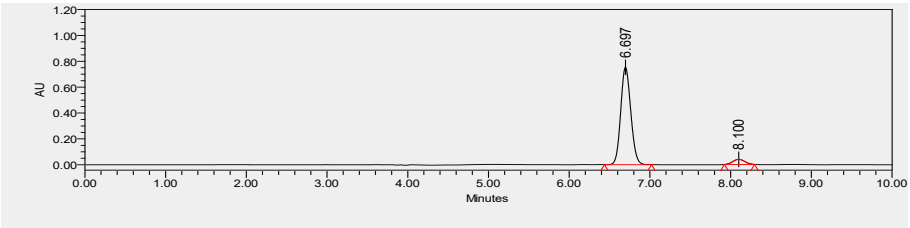
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 134.0, 131.6, 130.5, 129.0, 128.2, 127.7, 127.5, 126.0, 125.7, 125.5, 124.3, 123.8, 123.2, 92.8, 82.7, 29.1, 23.4.

HR-MS (ESI) calcd for $C_{16}H_{17}^+$ ([M+H]$^+$): 257.1325, found 257.1329;

IR (neat) 3054, 2977, 2929, 1597, 1489, 1445, 1395, 1263, 896, 798, 776, 731, 701, 456 cm^{-1}.

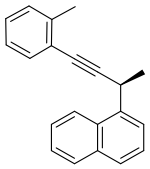


	Retention Time	Area	% Area
1	6.776	3806864	49.53
2	8.280	3879831	50.47



	Retention Time	Area	% Area
1	6.697	6523769	94.05
2	8.100	413072	5.95

***(S)*-1-(4-(o-tolyl)but-3-yn-2-yl)naphthalene (C2)**



General procedure A for 48 h.

0.2 mmol scale; 48.9 mg, colorless oil, 90% yield, 94:6 *er*; $[\alpha]_D^{20}$ = +72.3 (*c* 0.98, CH_2Cl_2).

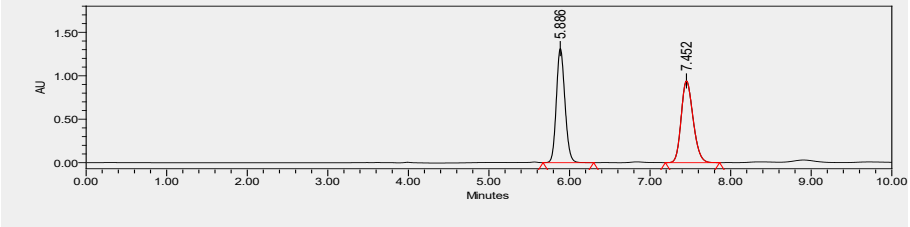
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 5.75 min, t_2 = 7.21 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.55 - 7.51 (m, 1H), 7.49 - 7.44 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.17 - 7.16 (m, 2H), 7.12 - 7.08 (m, 1H), 4.77 (q, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 1.74 (d, *J* = 7.2 Hz, 3H).

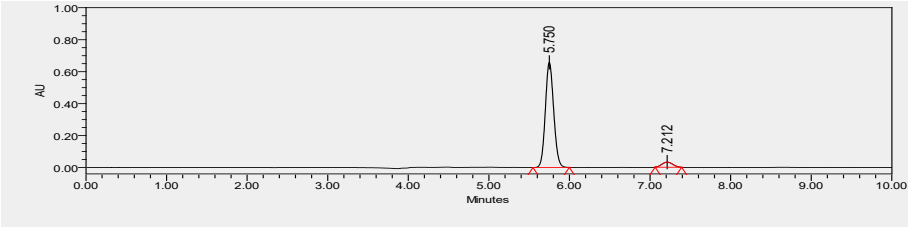
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 139.0, 134.0, 131.9, 130.6, 129.3, 129.0, 127.7, 127.4, 126.0, 125.6, 125.5, 125.4, 124.3, 123.5, 123.2, 96.8, 81.6, 29.3, 23.5, 20.8.

HR-MS (ESI) calcd for $C_{21}H_{19}^+$ ([M+H]$^+$): 271.1481, found 271.1489;

IR (neat) 3058, 2975, 2928, 1597, 1510, 1485, 1452, 1395, 1309, 1164, 1118, 985, 797, 776, 756, 451 cm^{-1}.

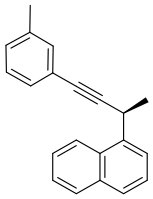


	Retention Time	Area	% Area
1	5.886	9713938	50.12
2	7.452	9666508	49.88



	Retention Time	Area	% Area
1	5.750	4731770	94.05
2	7.212	299471	5.95

***(S)*-1-(4-(m-tolyl)but-3-yn-2-yl)naphthalene (C3)**



General procedure A for 48 h.

0.2 mmol scale; 46.9 mg, colorless oil, 87% yield, 94:6 *er*; $[\alpha]_D^{20}$ = +76.4 (*c* 0.94, CH_2Cl_2).

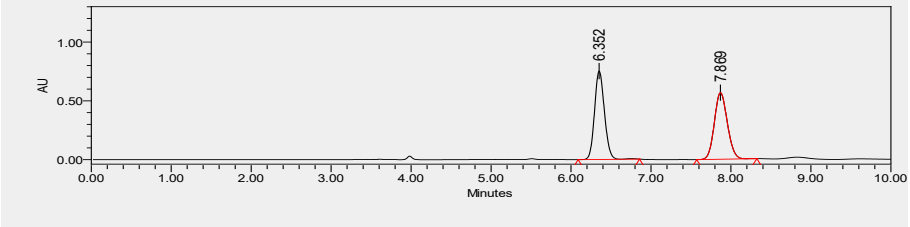
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 6.27 min, t_2 = 7.66 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.49 - 7.44 (m, 2H), 7.28 - 7.25 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.08 - 7.07 (m, 1H), 4.72 (q, *J* = 7.2 Hz, 1H), 2.30 (s, 3H), 1.72 (d, *J* = 7.2 Hz, 3H).

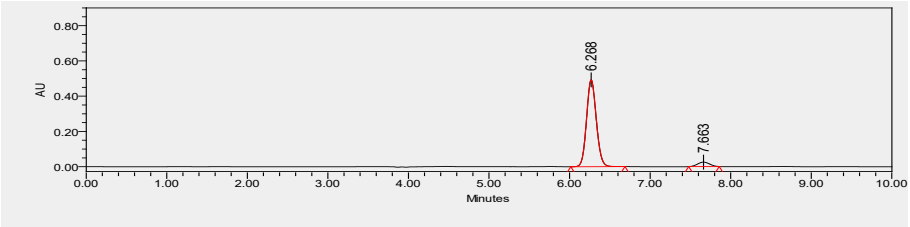
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 137.8, 134.0, 132.2, 130.6, 129.0, 128.7, 128.6, 128.1, 127.4, 126.0, 125.7, 125.5, 124.3, 123.5, 123.2, 92.4, 82.8, 29.1, 23.4, 21.2.

HR-MS (ESI) calcd for $C_{21}H_{19}^+$ ([M+H]$^+$): 271.1481, found 271.1487;

IR (neat) 3044, 2975, 2927, 1599, 1510, 1484, 1450, 1395, 1372, 1309, 1000, 860, 777, 691, 503, 455 cm^{-1}.

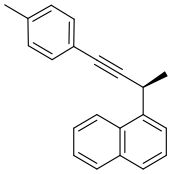


	Retention Time	Area	% Area
1	6.352	6482340	50.40
2	7.869	6378385	49.60



	Retention Time	Area	% Area
1	6.268	4144309	94.03
2	7.663	263231	5.97

***(S)*-1-(4-(p-tolyl)but-3-yn-2-yl)naphthalene (C4)**



General procedure A for 48 h.

0.2 mmol scale; 51.1 mg, colorless oil, 95% yield, 94.5:5.5 *er*; $[\alpha]_D^{20}$ = +81.1 (*c* 1.02, CH_2Cl_2).

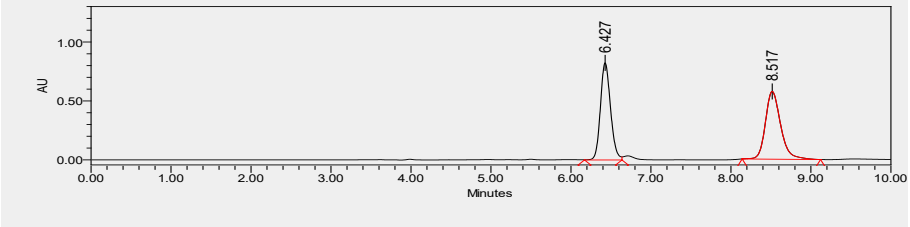
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 6.42 min, t_2 = 8.36 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.87 - 7.85 (m, 1H), 7.82 - 7.80 (m, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.55 - 7.50 (m, 1H), 7.49 - 7.44 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.71 (q, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 1.71 (d, *J* = 7.2 Hz, 3H).

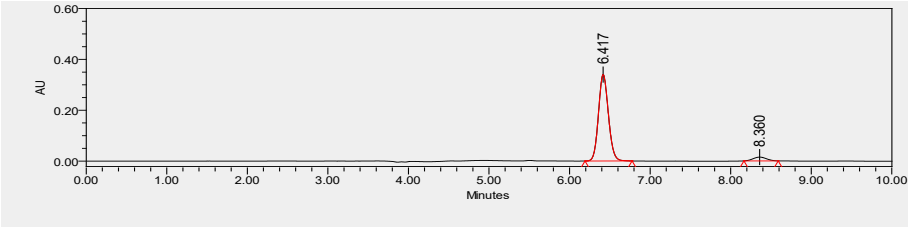
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 137.7, 134.0, 131.5, 130.6, 128.9, 127.4, 126.0, 125.7, 125.4, 124.3, 123.2, 120.7, 92.0, 82.7, 29.1, 23.4, 21.4.

HR-MS (ESI) calcd for $C_{21}H_{19}^+$ ([M+H]$^+$): 271.1481, found 271.1482;

IR (neat) 3047, 2975, 2926, 1596, 1509, 1450, 1395, 1372, 1308, 1103, 816, 797, 776, 533, 447 cm^{-1}.

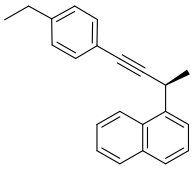


	Retention Time	Area	% Area
1	6.427	7238632	48.83
2	8.517	7584342	51.17



	Retention Time	Area	% Area
1	6.417	2911585	94.47
2	8.360	170302	5.53

***(S)*-1-(4-(4-ethylphenyl)but-3-yn-2-yl)naphthalene (C5)**



General procedure A for 48 h.

0.2 mmol scale; 46.2 mg, colorless oil, 81% yield, 93.5:6.5 *er*; $[\alpha]_D^{20}$ = +77.8 (c 0.92, CH_2Cl_2).

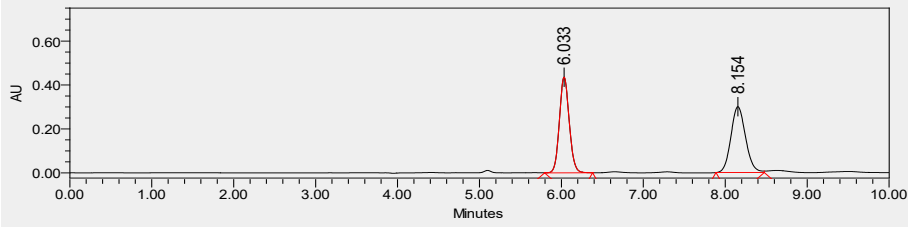
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 6.03 min, t_2 = 8.15 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.88 - 7.81 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.55 - 7.51 (m, 1H), 7.50 - 7.44 (m, 2H), 7.41 - 7.34 (m, 2H), 7.12 - 7.10 (m, 2H), 4.72 (q, *J* = 7.2 Hz, 1H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.72 (d, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.6 Hz, 3H).

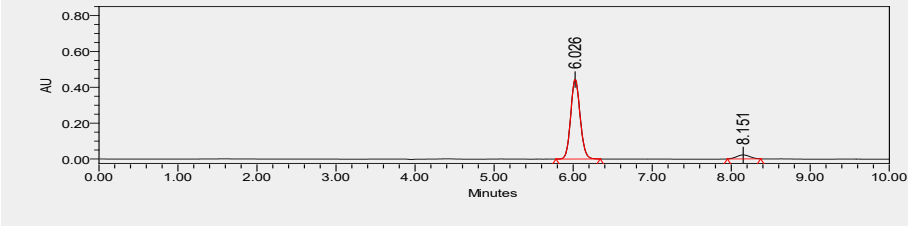
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 139.0, 133.9, 131.6, 130.5, 128.9, 127.8, 127.4, 126.0, 125.7, 125.4, 124.3, 123.2, 120.9, 92.0, 82.7, 29.1, 28.7, 23.4, 15.4.

HR-MS (ESI) calcd for $C_{22}H_{21}^+$ ([M+H]$^+$): 285.1638, found 285.1635;

IR (neat) 3051, 2968, 2930, 1596, 1510, 1451, 1395, 1263, 833, 798, 776, 733, 703, 553,436 cm^{-1}.

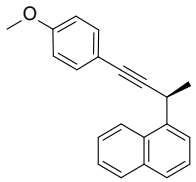


	Retention Time	Area	% Area
1	6.033	3630806	49.33
2	8.154	3728751	50.67



	Retention Time	Area	% Area
1	6.026	3694660	93.49
2	8.151	257202	6.51

***(S)*-1-(4-(4-methoxyphenyl)but-3-yn-2-yl)naphthalene (C6)**



General procedure A for 48 h.

0.2 mmol scale; 41.4 mg, colorless oil, 74% yield, 94.5:5.5 *er*; $[\alpha]_D^{20}$ = +85.7 (*c* 0.83, CH_2Cl_2).

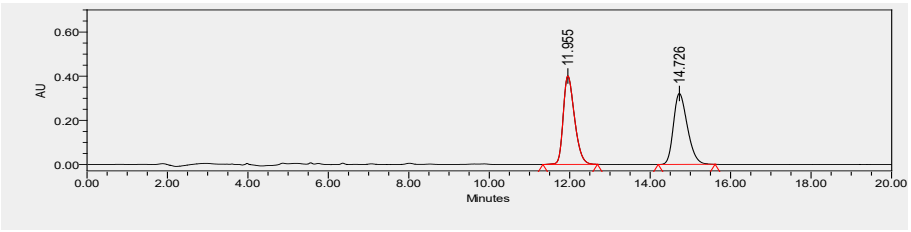
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 11.58 min, t_2 = 14.41 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.56 - 7.52 (m, 1H), 7.51 - 7.45 (m, 2H), 7.43 - 7.36 (m, 2H), 6.87 - 6.78 (m, 2H), 4.72 (q, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 1.72 (d, *J* = 7.2 Hz, 3H).

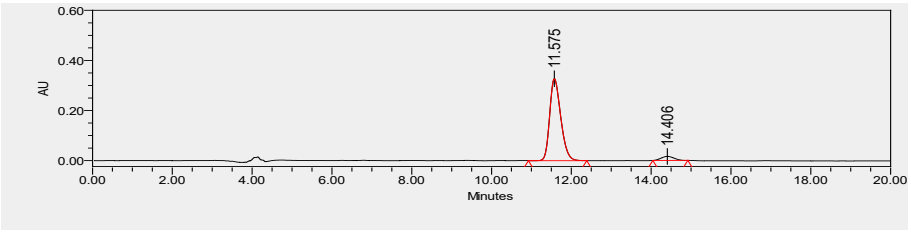
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 139.0, 133.9, 133.0, 130.5, 128.9, 127.4, 126.0, 125.6, 125.4, 124.3, 123.2, 115.8, 113.8, 91.2, 82.4, 55.2, 29.0, 23.4.

HR-MS (ESI) calcd for $C_{21}H_{19}O^+$ ([M+H]$^+$): 287.1430, found 287.1429;

IR (neat) 3045, 2974, 2931, 1604, 1508, 1459, 1287, 1247, 1173, 1031, 832, 797, 777, 538, 436 cm^{-1}.

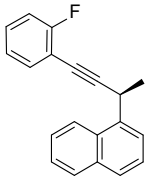


	Retention Time	Area	% Area
1	11.955	7811420	50.23
2	14.726	7740419	49.77



	Retention Time	Area	% Area
1	11.575	6294102	94.58
2	14.406	360499	5.42

***(S)*-1-(4-(2-fluorophenyl)but-3-yn-2-yl)naphthalene (C7)**



General procedure B for 48 h.

0.2 mmol scale; 40.5 mg, colorless oil, 74% yield, 92.5:7.5 *er*; $[\alpha]_D^{20}$ = +65.1(c 0.81, CH_2Cl_2).

HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 6.71 min, t_2 = 7.70 min

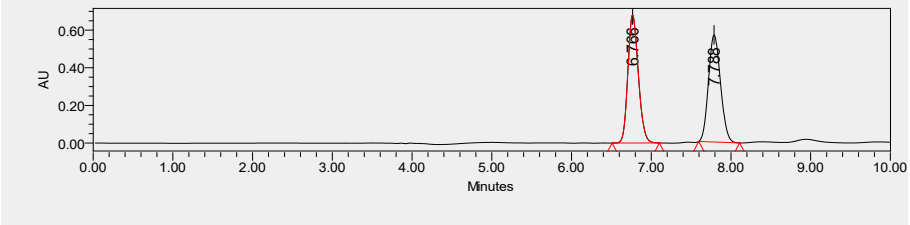
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.88 - 7.83 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.56 - 7.52 (m, 1H), 7.50 - 7.41 (m, 3H), 7.29 - 7.20 (m, 1H), 7.10 - 7.00 (m, 2H), 4.77 (q, *J* = 7.2 Hz, 1H), 1.74 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (d, *J* = 251.6 Hz, 1C), 138.4, 134.0, 133.5, 130.4, 129.4 (d, *J* = 8.1 Hz, 1C), 129.0, 127.5, 126.0, 125.7, 125.5, 124.4, 123.8 (d, *J* = 3.7 Hz, 1C), 123.1, 115.5 (d, *J* = 21.0 Hz), 112.3 (d, *J* = 15.5 Hz, 1C), 98.2 (d, *J* = 3.5 Hz, 1C), 76.1, 29.3, 23.3.

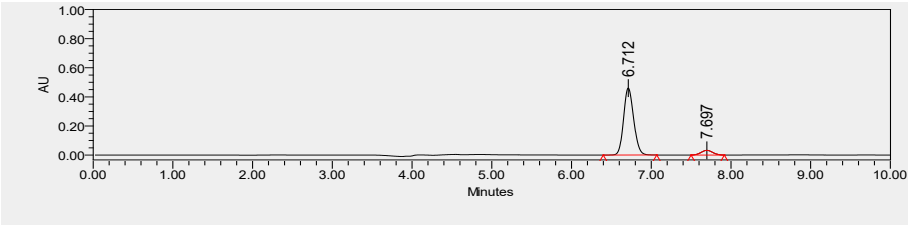
^{19}F NMR (377 MHz, $CDCl_3$) δ -110.42.

HR-MS (ESI) calcd for $C_{20}H_{16}F^+$ ([M+H]$^+$): 275.1231, found 275.1239;

IR (neat) 3058, 2977, 2932, 1573, 1491, 1450, 1256, 1214, 1106, 800, 776, 756, 571, 449 cm^{-1}.

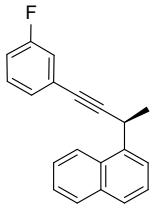


	Retention Time	Area	% Area
1	6.766	6194964	50.87
2	7.788	5984229	49.13



	Retention Time	Area	% Area
1	6.712	4041019	92.58
2	7.697	323851	7.42

***(S)*-1-(4-(3-fluorophenyl)but-3-yn-2-yl)naphthalene (C8)**



General procedure B for 48 h.

0.2 mmol scale; 50.4 mg, colorless oil, 92% yield, 91.5:8.5 *er*; $[\alpha]_D^{20}$ = +80.5 (c 1.0, CH_2Cl_2).

HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 6.81 min, t_2 = 8.26 min

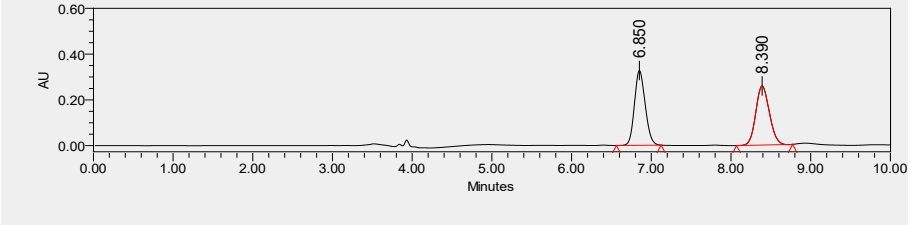
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.88 - 7.86 (m, 1H), 7.81 – 7.72 (m, 2H), 7.56 - 7.52 (m, 1H), 7.50 - 7.44 (m, 2H), 7.24 - 7.19 (m, 2H), 7.18 - 7.09 (m, 1H), 7.03 - 6.92 (m, 1H), 4.71 (q, *J* = 7.2 Hz, 1H), 1.72 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (d, *J* = 246.7 Hz, 1C), 138.4, 134.0, 130.5, 129.8 (d, *J* = 8.7 Hz, 1C), 129.0, 127.6, 127.50(d, *J* = 3.0 Hz, 1C), 126.1, 125.6, 125.4, 124.2, 123.1, 118.5 (d, *J* = 22.5 Hz, 1C), 115.2 (d, *J* = 21.4 Hz,1C), 93.9, 81.5 (d, *J* = 3.5 Hz, 1C), 29.0, 23.2.

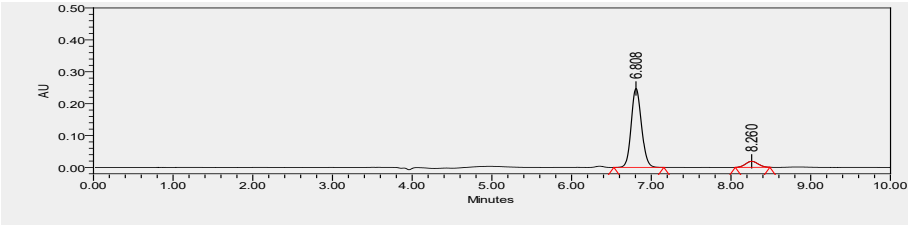
^{19}F NMR (377 MHz, $CDCl_3$) δ -113.16

HR-MS (ESI) calcd for $C_{20}H_{16}F^+$ ([M+H]$^+$): 275.1231, found 275.1232;

IR (neat) 3064, 2977, 2931, 1606, 1578, 1485, 1431, 1265, 1150, 1000, 945, 868, 777, 681, 519 cm^{-1}.

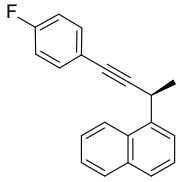


	Retention Time	Area	% Area
1	6.850	3060489	50.07
2	8.390	3051688	49.93



	Retention Time	Area	% Area
1	6.808	2216069	91.49
2	8.260	206148	8.51

***(S)*-1-(4-(4-fluorophenyl)but-3-yn-2-yl)naphthalene (C9)**



General procedure B for 48 h.

0.2 mmol scale; 45.7 mg, colorless oil, 83% yield, 93:7 *er*; $[\alpha]_D^{20}$ = +67.6 (c 0.91, CH_2Cl_2).

HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 6.57 min, t_2 = 8.64 min

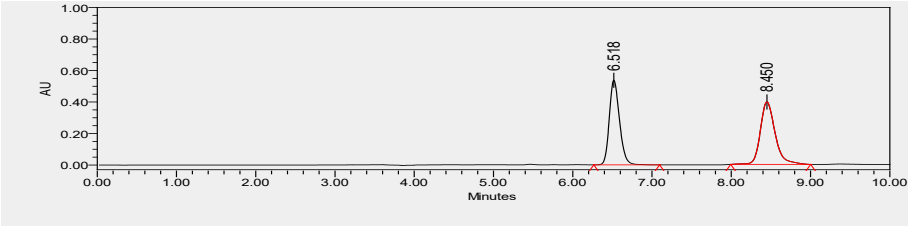
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.88 - 7.86 (m, 1H), 7.82 - 7.73 (m, 2H), 7.56 - 7.52 (m, 1H), 7.51 - 7.45 (m, 2H), 7.44 - 7.38 (m, 2H), 6.99 - 6.95 (m, 2H), 4.71 (q, *J* = 7.2 Hz, 1H), 1.72 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.39 (d, *J* = 249.3 Hz, 1C), 138.69, 133.96, 133.45 (d, *J* = 8.1 Hz, 1C), 130.50, 128.99, 127.53, 126.04, 125.64, 125.52, 124.22, 123.11, 119.77 (d, *J* = 3.6 Hz, 1C), 115.51 (d, *J* = 21.9 Hz, 2C), 92.43, 81.53, 28.98, 23.26.

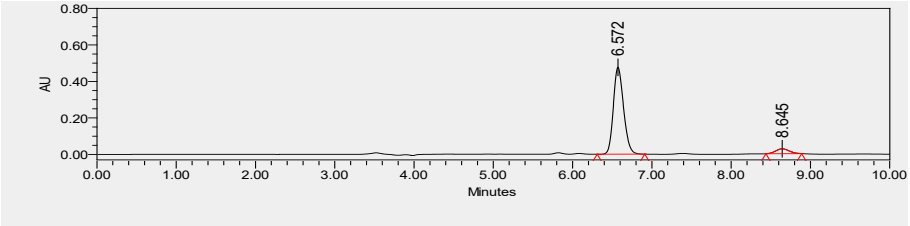
^{19}F NMR (377 MHz, $CDCl_3$) δ -111.81

HR-MS (ESI) calcd for $C_{20}H_{16}F^+$ ([M+H]$^+$): 275.1231, found 275.1237;

IR (neat) 3050, 2976, 2929, 1598, 1506, 1451, 1228, 1156, 1094, 835, 798, 776, 532, 446 cm^{-1}.

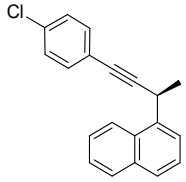


	Retention Time	Area	% Area
1	6.518	4814040	48.34
2	8.450	5144257	51.66



	Retention Time	Area	% Area
1	6.572	4256561	93.07
2	8.645	317051	6.93

***(S)*-1-(4-(4-chlorophenyl)but-3-yn-2-yl)naphthalene (C10)**



General procedure B for 48 h.

0.2 mmol scale; 52.5 mg, colorless oil, 90% yield, 92:8 *er*; $[\alpha]_D^{20}$ = +82.8 (c 1.05, CH_2Cl_2).

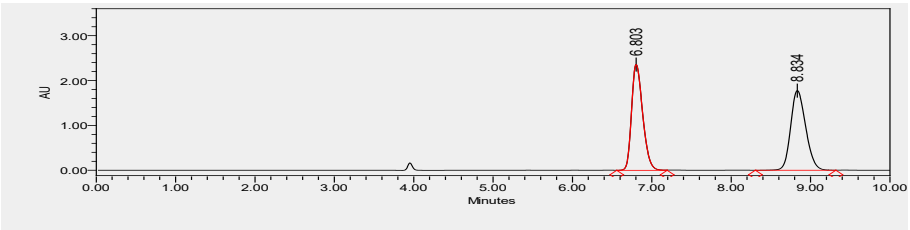
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 6.74 min, t_2 = 8.96 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 6.8 Hz, 2H), 7.56 - 7.51 (m, 1H), 7.50 - 7.44 (m, 2H), 7.36 - 7.34 (m, 2H), 7.25 - 7.23 (m, 2H), 4.71 (q, *J* = 7.2 Hz, 1H), 1.71 (d, *J* = 7.2 Hz, 3H).

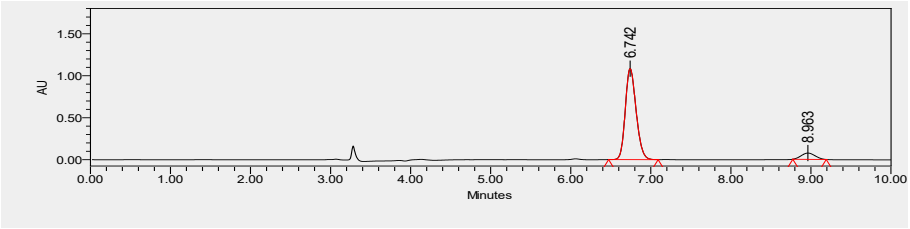
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 134.0, 133.7, 132.8, 130.5, 129.0, 128.5, 127.6, 126.1, 125.6, 125.5, 124.2, 123.1, 122.2, 93.8, 81.5, 29.0, 23.2.

HR-MS (ESI) calcd for $C_{20}H_{16}Cl^+$ ([M+H]$^+$): 291.0935, found 291.0927;

IR (neat) 3052, 2976, 2929, 1595, 1510, 1488, 1395, 1090, 1013, 827, 797, 776, 748, 525, 428 cm^{-1}.

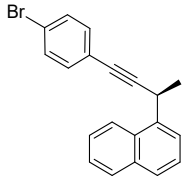


	Retention Time	Area	% Area
1	6.803	23034943	49.56
2	8.834	23444272	50.44



	Retention Time	Area	% Area
1	6.742	10180453	91.92
2	8.963	894764	8.08

***(S)*-1-(4-(4-bromophenyl)but-3-yn-2-yl)naphthalene (C11)**



General procedure B for 48 h.

0.2 mmol scale; 56.8 mg, colorless oil, 85% yield, 91:9 *er*; $[\alpha]_D^{20}$ = +77.0 (c 1.14, CH_2Cl_2).

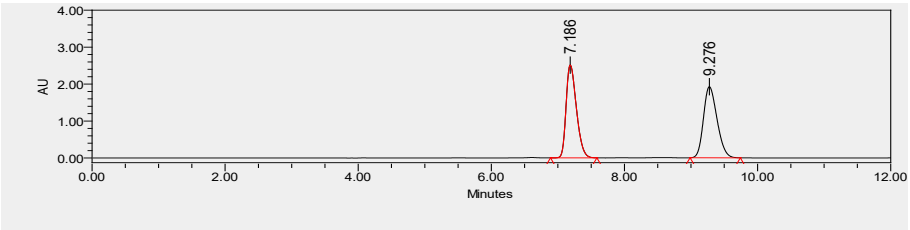
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 7.35 min, t_2 = 9.83 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.80 - 7.74 (m, 2H), 7.56 - 7.51 (m, 1H), 7.50 - 7.44 (m, 2H), 7.42 - 7.37 (m, 2H), 7.30 - 7.28 (m, 2H), 4.70 (q, *J* = 7.2 Hz, 1H), 1.71 (d, *J* = 7.2 Hz, 3H).

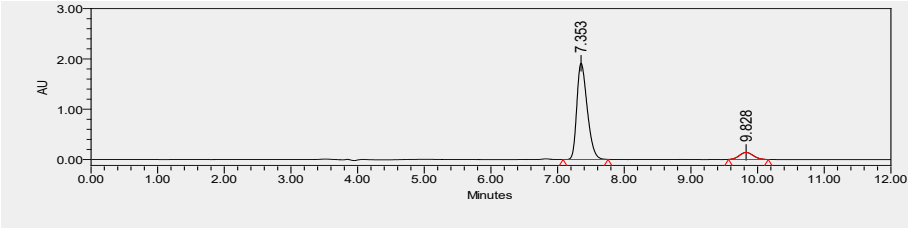
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 134.0, 133.1, 131.4, 130.5, 129.0, 127.6, 126.1, 125.6, 125.5, 124.2, 123.1, 122.6, 121.9, 94.0, 81.6, 29.0, 23.2.

HR-MS (ESI) calcd for $C_{20}H_{16}Br^+$ ([M+H]$^+$): 335.0430, 337.0409, found 335.0438, 337.0400;

IR (neat) 3050, 2978, 2920, 2850, 1595, 1510, 1394, 1263, 1069, 1009, 824, 798, 777, 738, 523 cm^{-1}.

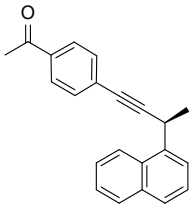


	Retention Time	Area	% Area
1	7.186	27157463	49.80
2	9.276	27371338	50.20



	Retention Time	Area	% Area
1	7.353	20705183	91.10
2	9.828	2023100	8.90

***(S)*-1-(4-(3-(naphthalen-1-yl)but-1-yn-1-yl)phenyl)ethan-1-one (C12)**



General procedure B for 48 h.

0.2 mmol scale; 37.9 mg, colorless oil, 63% yield, 89:11 *er*; $[\alpha]_D^{20}$ = +98.7 (c 0.76, CH_2Cl_2).

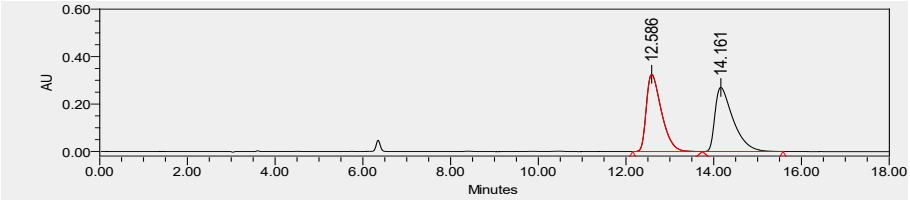
HPLC Chiralcel OD-H, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 254 nm, t_1 = 12.55 min, t_2 = 14.33 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.92 - 7.84 (m, 3H), 7.80 - 7.77 (m, 2H), 7.58 - 7.44 (m, 5H), 4.75 (q, *J* = 7.2 Hz, 1H), 2.57 (s, 3H), 1.74 (d, *J* = 7.2 Hz, 3H).

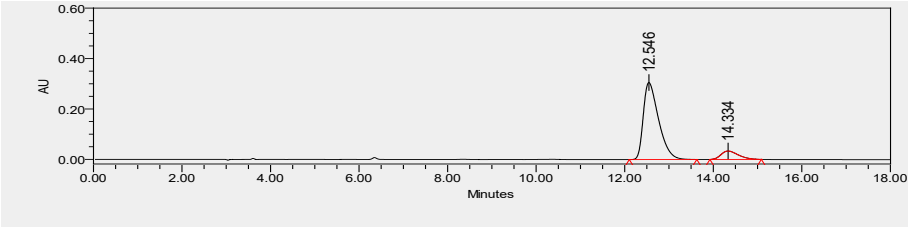
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 138.3, 135.8, 134.0, 131.7, 130.4, 129.0, 128.7, 128.1, 127.6, 126.1, 125.6, 125.6, 124.2, 123.0, 96.5, 82.0, 29.1, 26.6, 23.1.

HR-MS (ESI) calcd for $C_{22}H_{19}O^+$ ([M+H]$^+$): 299.1430, found 299.1430;

IR (neat) 3048, 2977, 2931, 2231, 1682, 1600, 1510, 1400, 1357, 1262, 836, 799, 777, 592 cm^{-1}.

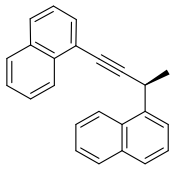


	Retention Time	Area	% Area
1	12.586	7785414	50.10
2	14.161	7754731	49.90



	Retention Time	Area	% Area
1	12.546	7318545	88.97
2	14.334	907579	11.03

***(S)*-1,1'-(but-1-yne-1,3-diyl)dinaphthalene (C13)**



General procedure A for 48 h.

0.2 mmol scale; 59.0 mg, colorless oil, 96% yield, 94:6 *er*; $[\alpha]_D^{20}$ = +80.1 (c 1.18, CH_2Cl_2).

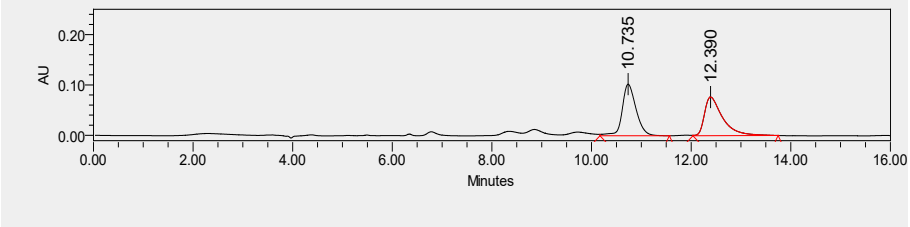
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 10.70 min, t_2 = 12.41 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.92 - 7.86 (m, 2H), 7.81 - 7.45 (m, 3H), 7.68 - 7.66 (m, 1H), 7.58 - 7.44 (m, 5H), 7.39 - 7.36 (m, 1H), 4.88 (q, *J* = 7.2 Hz, 1H), 1.83 (d, *J* = 7.2 Hz, 3H).

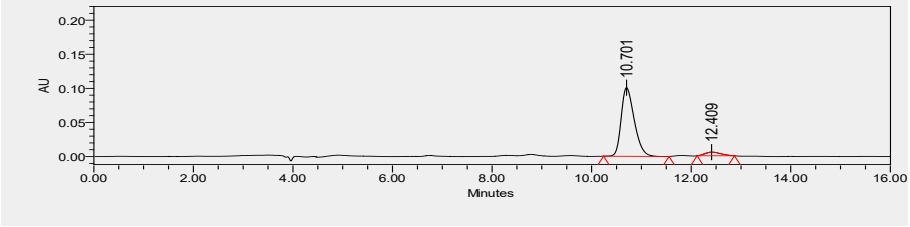
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 134.0, 133.5, 133.2, 130.6, 130.2, 129.0, 128.2, 127.5, 126.6, 126.3, 126.2, 126.1, 125.7, 125.5, 125.2, 124.3, 123.2, 121.4, 97.8, 80.8, 29.4, 23.5.

HR-MS (ESI) calcd for $C_{24}H_{19}^+$ ([M+H]$^+$): 307.1481, found 304.1485;

IR (neat) 3054, 2976, 2930, 1591, 1508, 1394, 861, 797, 773, 736, 568, 452 cm^{-1}.

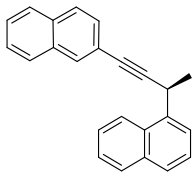


	Retention Time	Area	% Area
1	10.735	1979438	50.48
2	12.390	1941582	49.52



	Retention Time	Area	% Area
1	10.701	1835615	93.88
2	12.409	119582	6.12

***(S)*-1-(4-(naphthalen-2-yl)but-3-yn-2-yl)naphthalene (C14)**



General procedure A for 48 h.

0.2 mmol scale; 58.7 mg, colorless oil, 96% yield, 93:7 *er*; $[\alpha]_D^{20}$ = +117.5 (c 1.17, CH_2Cl_2).

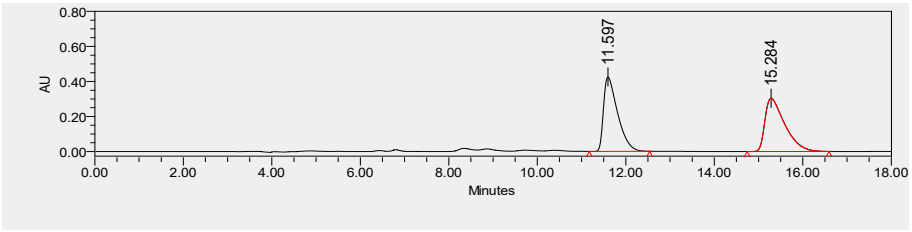
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 10.70 min, t_2 = 12.41 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.96 - 7.95 (m, 1H), 7.87 - 7.85 (m, 2H), 7.79 - 7.69 (m, 4H), 7.59 - 7.39 (m, 6H), 4.76 (q, *J* = 7.2 Hz, 1H), 1.76 - 1.74 (m, 3H).

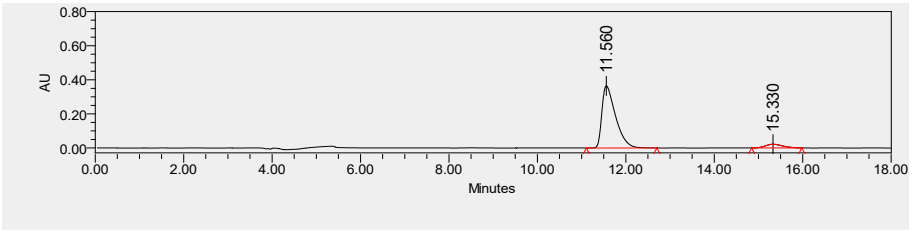
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 134.0, 133.0, 132.5, 131.2, 130.5, 129.0, 128.7, 127.8, 127.7, 127.6, 127.5, 126.4, 126.3, 126.0, 125.7, 125.5, 124.3, 123.2, 121.0, 93.2, 83.0, 29.1, 23.4.

HR-MS (ESI) calcd for $C_{24}H_{19}^+$ ([M+H]$^+$): 307.1481, found 307.1485;

IR (neat) 3054, 2976, 2930, 1596, 1505, 1451, 1395, 1264, 893, 858, 797, 776, 754, 475, 445 cm^{-1}.

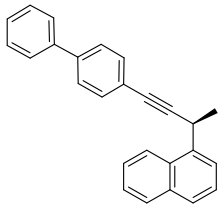


	Retention Time	Area	% Area
1	11.597	9374701	49.85
2	15.284	9431577	50.15



	Retention Time	Area	% Area
1	11.560	7823080	93.01
2	15.330	588343	6.99

***(S)*-1-(4-([1,1'-biphenyl]-4-yl)but-3-yn-2-yl)naphthalene (C15)**



General procedure A for 48 h.

0.2 mmol scale; 53.2 mg, colorless oil, 80% yield, 92:8 *er*; $[\alpha]_D^{20}$ = +99.1 (c 1.06, CH_2Cl_2).

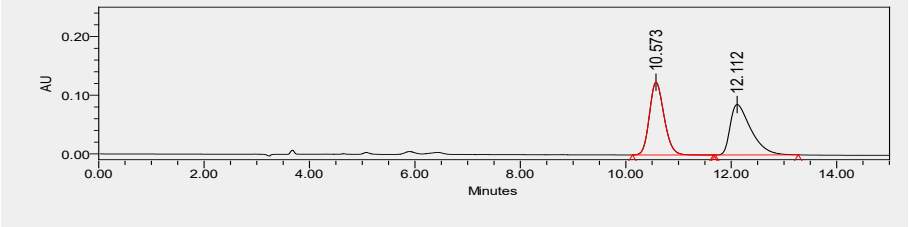
HPLC Chiralcel OD-H, hexane/isopropanol = 97/3, 1.0 mL/min, λ = 254 nm, t_1 = 10.70 min, t_2 = 12.41 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.91 - 7.81 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.60 - 7.53 (m, 3H), 7.52 (s, 4H), 7.50 - 7.46(m, 2H), 7.43 - 7.40 (m, 2H), 7.36 - 7.30 (m, 1H), 4.75 (q, *J* = 7.2 Hz, 1H), 1.74 (d, *J* = 7.2 Hz, 3H).

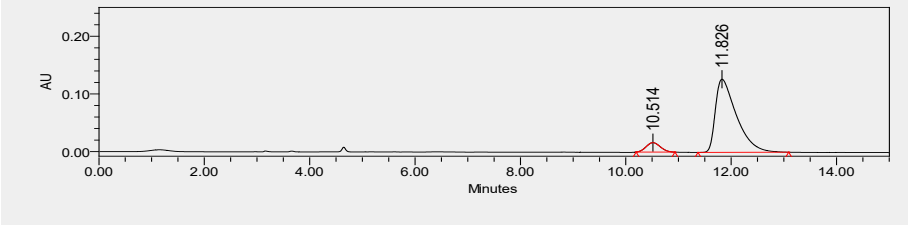
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 138.8, 134.0, 132.0, 130.5, 129.0, 128.8, 127.5, 127.0 126.9, 126.0, 125.7, 125.5, 124.3, 123.2, 122.6, 93.5, 82.5, 29.1, 23.4.

HR-MS (ESI) calcd for $C_{26}H_{21}^+$ ([M+H]$^+$): 333.1638, found 333.1642;

IR (neat) 3055, 2976, 2929, 1597, 1485, 1396, 1308, 1004, 840, 798, 764, 724, 696, 558, 501 cm^{-1}.

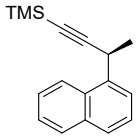


	Retention Time	Area	% Area
1	10.573	2390465	50.47
2	12.112	2345706	49.53



	Retention Time	Area	% Area
1	10.514	306253	8.00
2	11.826	3520541	92.00

***(S)*-trimethyl(3-(naphthalen-1-yl)but-1-yn-1-yl)silane (C16)**



General procedure A for 72 h.

0.2 mmol scale; 43.7 mg, colorless oil, 87% yield, 93:7 *er*; $[\alpha]_D^{20}$ = +5.6 (c 0.87, CH_2Cl_2).

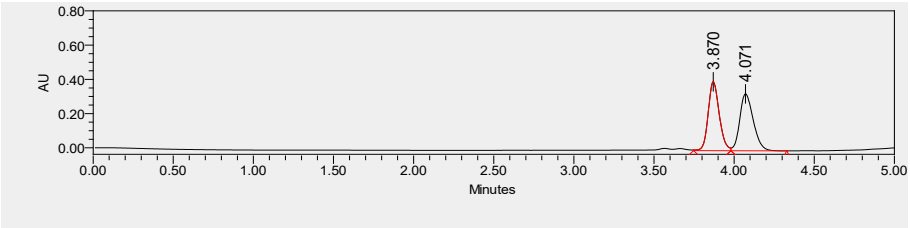
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 3.86 min, t_2 = 4.08 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.91 - 7.83 (m, 1H), 7.80 - 7.70 (m, 2H), 7.57 - 7.40 (m, 3H), 4.53 (q, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H), 0.19 (s, 9H).

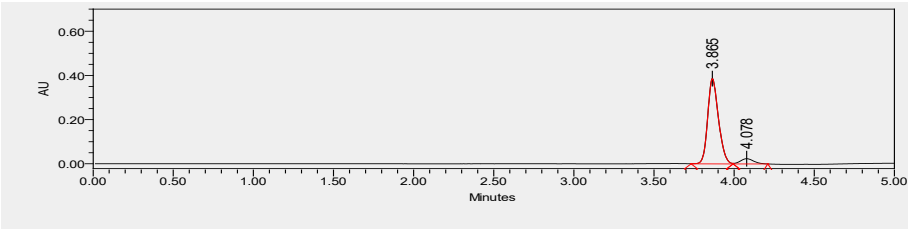
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 133.9, 130.4, 128.9, 127.4, 125.9, 125.6, 125.4, 124.3, 123.1, 109.7, 86.55, 29.5, 23.6, 0.2.

HR-MS (ESI) calcd for $C_{17}H_{21}Si^+$ ([M+H]$^+$): 253.1407, found 253.1411;

IR (neat) 2960, 2166, 1263, 1114, 1005, 913, 844, 798, 775, 732, 703 cm^{-1}.

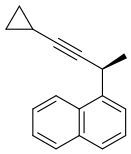


	Retention Time	Area	% Area
1	3.870	1933852	49.72
2	4.071	1955355	50.28



	Retention Time	Area	% Area
1	3.865	1810589	93.02
2	4.078	135852	6.98

***(S)*-1-(4-cyclopropylbut-3-yn-2-yl)naphthalene (C17)**



General procedure A for 72 h.

0.2 mmol scale; 31.4 mg, colorless oil, 71% yield, 94:6 *er*; $[\alpha]_D^{20}$ = +14.3 (c 0.63, CH_2Cl_2).

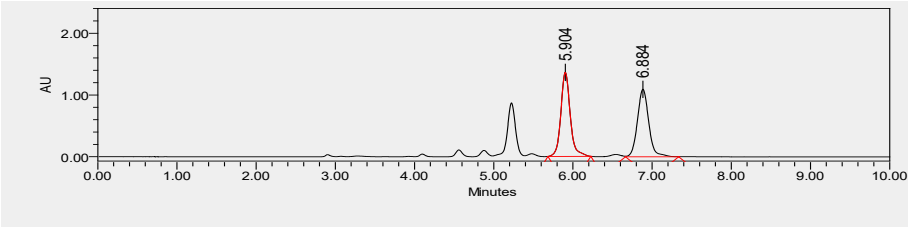
HPLC Chiralcel AD-H, hexane/isopropanol = 99.5/0.5, 1.0 mL/min, λ = 214 nm, t_1 = 6.01 min, t_2 = 9.30 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.86 - 7.84 (m, 1H), 7.74- 7.70 (m, 2H), 7.54 - 7.42 (m, 3H), 4.46 (qd, *J* = 7.2, 1.6 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H), 1.33 - 1.25 (m, 1H), 0.78 - 0.71 (m, 2H), 0.71 - 0.64 (m, 2H).

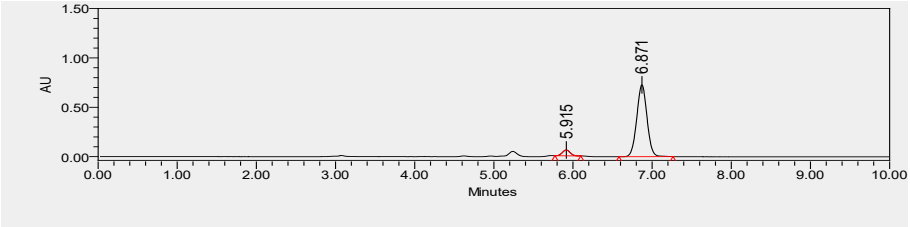
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 133.9, 130.5, 128.9, 127.2, 125.8, 125.6, 125.4, 124.1, 123.2, 85.5, 78.32 28.4, 23.7, 8.2, 8.1, -0.3.

HR-MS (ESI) calcd for $C_{17}H_{17}^+$ ([M+H]$^+$): 221.1325, found 221.1326;

IR (neat) 3051, 2976, 2931, 1596, 1510, 1450, 1395, 1362, 1264, 1052, 1026, 798, 777, 736, 704 cm^{-1}.

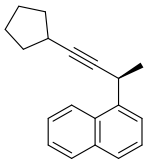


	Retention Time	Area	% Area
1	5.904	11214667	50.73
2	6.884	10891985	49.27



	Retention Time	Area	% Area
1	5.915	403566	5.78
2	6.871	6578801	94.22

***(S)*-1-(4-cyclopentylbut-3-yn-2-yl)naphthalene (C18)**



General procedure A for 72 h.

0.2 mmol scale; 33.3 mg, colorless oil, 67% yield, 93:7 *er*; $[\alpha]_D^{20}$ = +4.1 (c 0.67, CH_2Cl_2).

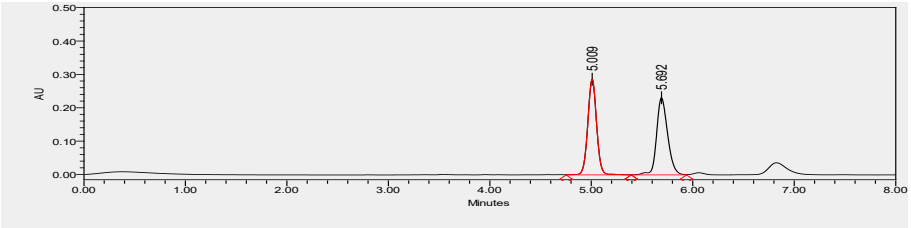
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 214 nm, t_1 = 4.98 min, t_2 = 5.71 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.86 - 7.84 (m, 1H), 7.76 - 7.72 (m, 2H), 7.53 - 7.42 (m, 3H), 4.49 (qd, *J* = 7.2, 2.0 Hz, 1H), 2.67 (pd, *J* = 7.2, 2.0 Hz, 1H), 2.00 - 1.85 (m, 2H), 1.75 - 1.69 (m, 2H), 1.67 - 1.47 (m, 7H).

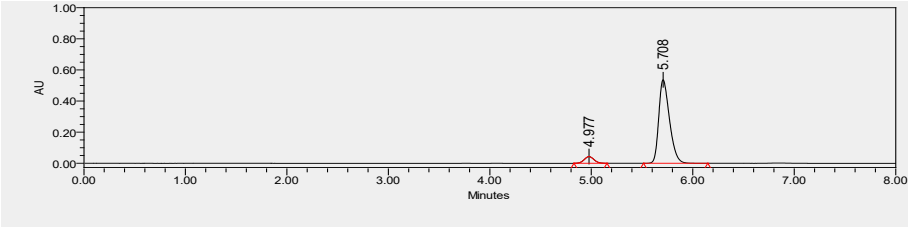
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 133. 9, 130.5, 128.9, 127.2, 125.8, 125.6, 125.3, 124.1, 123.2, 87.0, 82.6, 34.1, 30.4, 28.6, 24.9, 23.9.

HR-MS (ESI) calcd for $C_{19}H_{21}^+$ ([M+H]$^+$): 249.1638, found 249.1638;

IR (neat) 2962, 1263, 895, 731, 703 cm^{-1}.

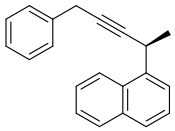


	Retention Time	Area	% Area
1	5.009	1733216	49.77
2	5.692	1749523	50.23



	Retention Time	Area	% Area
1	4.977	286553	6.80
2	5.708	3930035	93.20

***(S)*-1-(5-phenylpent-3-yn-2-yl)naphthalene (C19)**



General procedure B for 72 h.

0.2 mmol scale; 46.0 mg, colorless oil, 85% yield, 93:7 *er*; $[\alpha]_D^{20}$ = +16.4 (c 0.92, CH_2Cl_2).

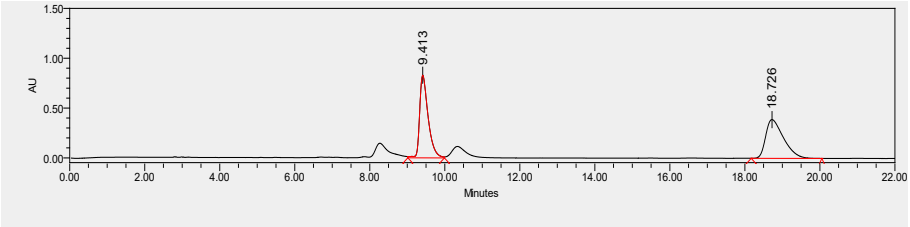
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 214 nm, t_1 = 9.96 min, t_2 = 18.40 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.89 - 7.83 (m, 1H), 7.78 - 7.73 (m, 2H), 7.54 - 7.44 (m, 3H), 7.38 - 7.36 (m, 2H), 7.32 - 7.28 (m, 2H), 7.25 - 7.19 (m, 1H), 4.57 (qt, *J* = 7.2, 2.0 Hz, 1H), 3.67 (d, *J* = 2.4 Hz, 2H), 1.65 (d, *J* = 7.2 Hz, 3H).

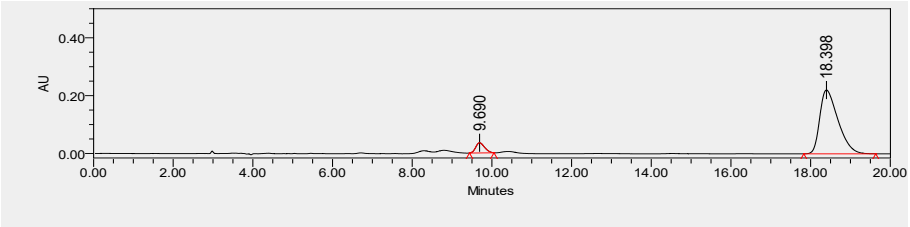
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 137.3, 133.9, 130.5, 128.9, 128.4, 127.9, 127.3, 126.4, 125.9, 125.6, 125.4, 124.1, 123.2, 85.4, 79.9, 28.5, 25.2, 23.5.

HR-MS (ESI) calcd for $C_{21}H_{19}^+$ ([M+H]$^+$): 271.1481, found 271.1489;

IR (neat) 3057, 2975, 1598, 1494, 1451, 1263, 1029, 798, 777, 729, 700 cm^{-1}.

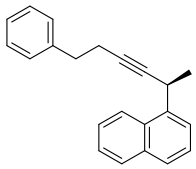


	Retention Time	Area	% Area
1	9.413	13024397	50.38
2	18.726	12830277	49.62



	Retention Time	Area	% Area
1	9.690	540199	7.16
2	18.398	7001993	92.84

***(S)*-1-(6-phenylhex-3-yn-2-yl)naphthalene (C20)**



General procedure B for 72 h.

0.2 mmol scale; 46.5 mg, colorless oil, 82% yield, 92:8 *er*; $[\alpha]_D^{20}$ = +14.6 (c 0.93, CH_2Cl_2).

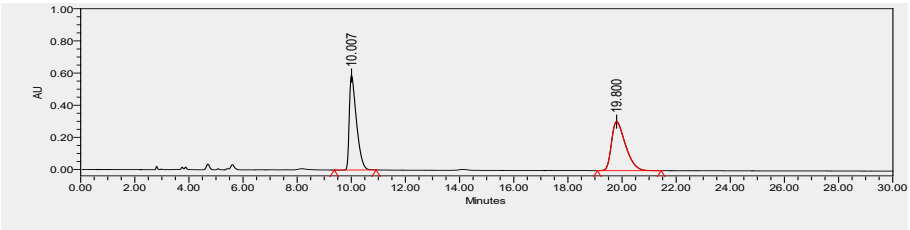
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 214 nm, t_1 = 10.64 min, t_2 = 20.36 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.87 - 7.82 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 6.8 Hz, 1H), 7.52 - 7.39 (m, 3H), 7.31 - 7.24 (m, 2H), 7.24 - 7.17 (m, 3H), 4.52 - 4.42 (m, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.53 (td, *J* = 7.6, 2.4 Hz, 2H), 1.58 (d, *J* = 7.2 Hz, 3H).

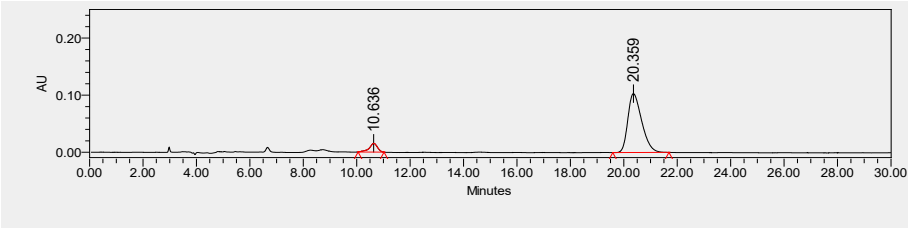
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 139.3, 133.9, 130.5, 128.9, 128.6, 128.3, 127.2, 126.1, 125.8, 125.6, 125.4, 124.1, 123.2, 83.9, 81.8, 35.4, 28.4, 23.6, 21.1.

HR-MS (ESI) calcd for $C_{22}H_{21}^+$ ([M+H]$^+$): 285.1638, found 285.1644;

IR (neat) 3059, 2974, 2928, 1598, 1495, 1451, 1394, 1029, 798, 777, 745, 698, 577, 499 cm^{-1}.

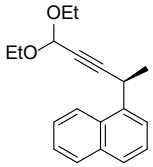


	Retention Time	Area	% Area
1	10.007	10780042	49.67
2	19.800	10922504	50.33



	Retention Time	Area	% Area
1	10.636	324528	8.02
2	20.359	3723608	91.98

***(S)*-1-(5,5-diethoxypent-3-yn-2-yl)naphthalene (C21)**



General procedure B for 72 h.

0.2 mmol scale; 53.0 mg, colorless oil, 94% yield, 94:6 *er*; $[\alpha]_D^{20}$ = +16.2 (c 1.06, CH_2Cl_2).

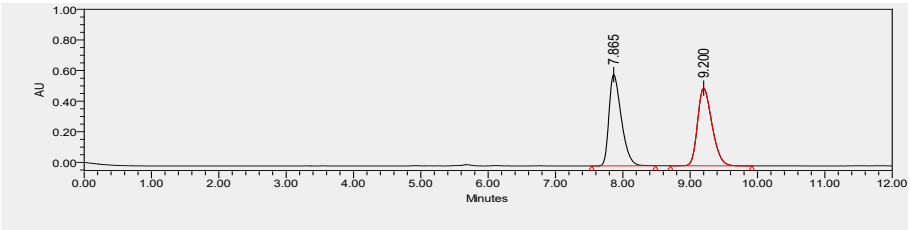
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 280 nm, t_1 = 7.86 min, t_2 = 9.33 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.89 - 7.83 (m, 1H), 7.76 - 7.71 (m, 2H), 7.54 - 7.43 (m, 3H), 5.35 (s, 1H), 4.59 (q, *J* = 6.8 Hz, 1H), 3.76 (dp, *J* = 9.6, 7.2 Hz, 2H), 3.59 (dp, *J* = 9.6, 7.2 Hz, 2H), 1.65 (d, *J* = 7.2 Hz, 3H), 1.23 (q, *J* = 7.2 Hz, 6H).

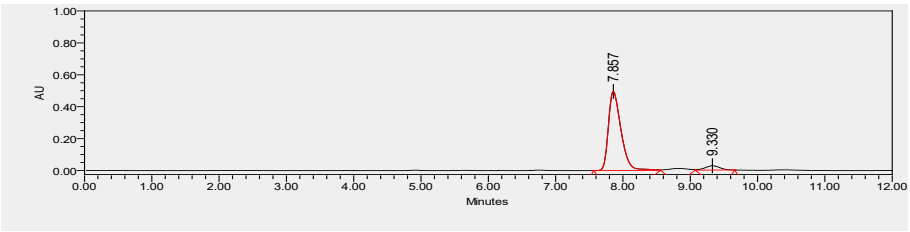
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 133.9, 130.4, 128.9, 127.5, 126.0, 125.6, 125.5, 124.2, 123.0, 91.5, 88.7, 77.8, 60.7, 60.6, 28.3, 22.9, 15.1, 15.0.

HR-MS (ESI) calcd for $C_{19}H_{23}O_2^+$ ([M+H]$^+$): 283.1693, found 283.1690;

IR (neat) 2975, 2930, 2881, 2246, 1597, 1511, 1448, 1394, 1356, 1329, 1149, 1097, 1051, 1007, 799, 777 cm^{-1}.

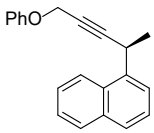


	Retention Time	Area	% Area
1	7.865	7587706	50.13
2	9.200	7547750	49.87



	Retention Time	Area	% Area
1	7.857	6448420	93.99
2	9.330	412629	6.01

***(S)*-1-(5-phenoxypent-3-yn-2-yl)naphthalene (C22)**



General procedure B for 48 h.

0.2 mmol scale; 38.7 mg, colorless oil, 67% yield, 94:6 *er*; $[\alpha]_D^{20}$ = +15.2 (c 0.77, CH_2Cl_2).

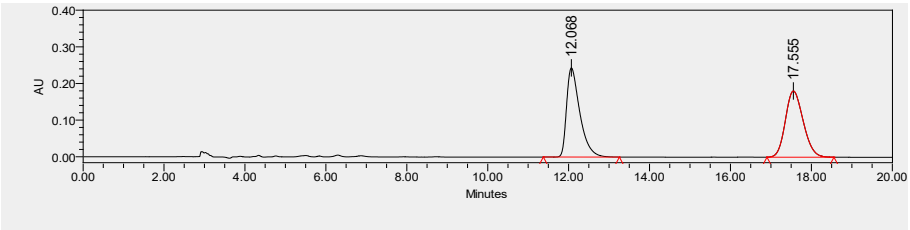
HPLC Chiralcel OD-H, hexane/isopropanol = 95/5, 1.0 mL/min, λ = 220 nm, t_1 = 12.32 min, t_2 = 17.61 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.00 (m, 1H), 7.86 - 7.84 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 6.8 Hz, 1H), 7.52 - 7.38 (m, 3H), 7.31 - 7.26 (m, 2H), 7.00 - 6.96 (m, 3H), 4.74 (d, *J* = 2.0 Hz, 2H), 4.54 (q, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H).

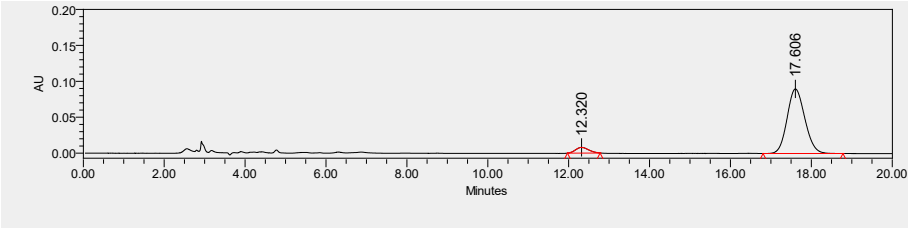
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 138.2, 133.9, 130.4, 129.4, 128.9, 127.5, 126.0, 125.6, 125.4, 124.2, 123.0, 121.2, 115.0, 90.7, 56.4, 28.4, 22.9.

HR-MS (ESI) calcd for $C_{21}H_{18}ONa^+$ ([M+Na]$^+$): 309.1250, found 309.1246;

IR (neat) 3059, 2977, 2931, 2870, 2246, 1595, 1493, 1452, 1372, 1215, 1174, 1030, 1009, 799, 777, 753, 690, 506, 432 cm^{-1}.

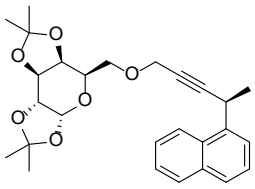


	Retention Time	Area	% Area
1	12.068	5528583	50.02
2	17.555	5523197	49.98



	Retention Time	Area	% Area
1	12.320	177576	6.12
2	17.606	2725414	93.88

(3*aS*,4*R*,5*aS*,8*aS*,8*bS*)-2,2,7,7-tetramethyl-4-((((*S*)-4-(naphthalen-1-yl)pent-2-yn-1-yl)oxy)methyl)hexahydrobenzo[1,2-d:3,4-d']bis([1,3]dioxole) (C23)



General procedure B for 72 h.

0.1 mmol scale; 29.9 mg, colorless oil, 66% yield, 95:5 *dr*; $[\alpha]_D^{20}$ = -40.8 (c 0.60, CH_2Cl_2).

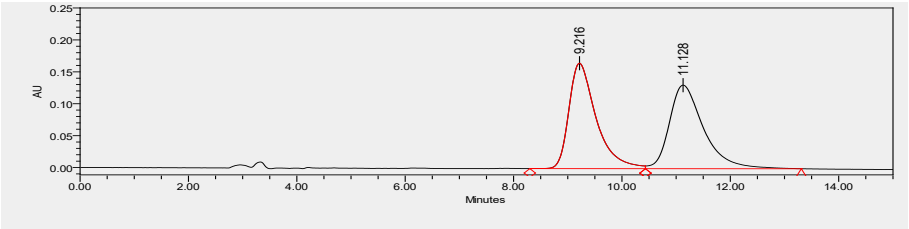
HPLC Chiralcel OD-H, hexane/isopropanol = 80/20, 1.0 mL/min, λ = 220 nm, t_1 = 9.33 min, t_2 = 11.17 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 2H), 7.57 - 7.42 (m, 3H), 5.55 (d, *J* = 5.2 Hz, 1H), 4.63 - 4.52 (m, 2H), 4.36 - 4.20 (m, 4H), 4.04 - 3.97 (m, 1H), 3.80 - (dd, *J* = 10.0, 5.2 Hz, 1H), 3.69 (dd, *J* = 10.0, 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H), 1.53 (s, 3H), 1.44 (s, 3H), 1.33 (d, *J* = 4.4 Hz, 6H).

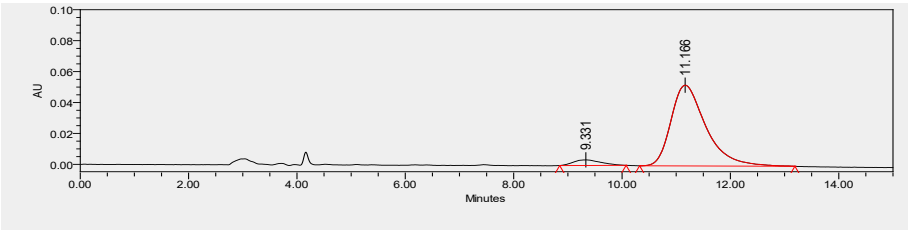
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 133.9, 130.4, 128.9, 127.4, 126.0, 125.6, 125.4, 124.2, 123., 109.2, 108.6, 96.3, 89.7, 78.0, 71.1, 70.6, 70.4, 68.3, 66.6, 59.0, 28.4, 26.0, 25.9, 24.9, 24.4, 23.1.

HR-MS (ESI) calcd for $C_{27}H_{32}O_6Na^+$ ([M+Na]$^+$): 475.2091, found 475.2086;

IR (neat) 2983, 2932, 1511, 1454, 1377, 1254, 1211, 1171, 1102, 1070, 1004, 891, 862, 801, 777, 511 cm^{-1}.

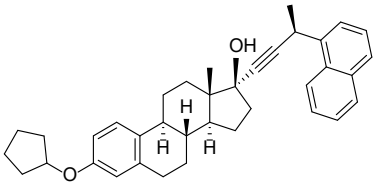


	Retention Time	Area	% Area
1	9.216	5776675	50.12
2	11.128	5749801	49.88



	Retention Time	Area	% Area
1	9.331	128837	5.21
2	11.166	2342912	94.79

(8*R*,9*S*,13*S*,14*S*,17*S*)-3-(cyclopentyloxy)-13-methyl-17-((*S*)-3-(naphthalen-1-yl)but-1-yn-1-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-ol (C24)



General procedure B for 72 h.

0.1 mmol scale; 36.9 mg, colorless oil, 71% yield, 91:9 *dr*; $[\alpha]_D^{20}$ = +4.9 (c 0.74, CH_2Cl_2).

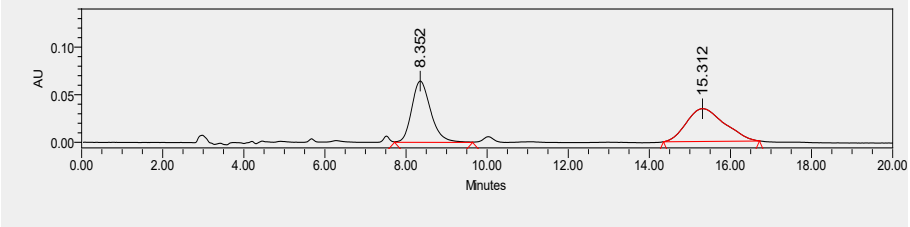
HPLC Chiralcel OD-H, hexane/isopropanol = 90/10, 1.0 mL/min, λ = 220 nm, t_1 = 12.32 min, t_2 = 17.61 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.77 - 7.69 (m, 2H), 7.57 - 7.40 (m, 3H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.67 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 4.71 (dt, *J* = 5.6, 2.8 Hz, 1H), 4.58 (q, *J* = 7.2 Hz, 1H), 3.74 (brs, 1H), 2.83 - 2.81 (m, 2H), 2.36 - 2.26 (m, 2H), 2.12 - 1.99 (m, 2H), 1.90 - 1.82 (m, 6H), 1.81 - 1.71 (m, 4H), 1.70 - 1.64 (m, 5H), 1.61 - 1.57 (m, *J* = 7.1, 6.7, 3.6 Hz, 2H), 1.50 - 1.28 (m, 4H), 0.87 (s, 3H).

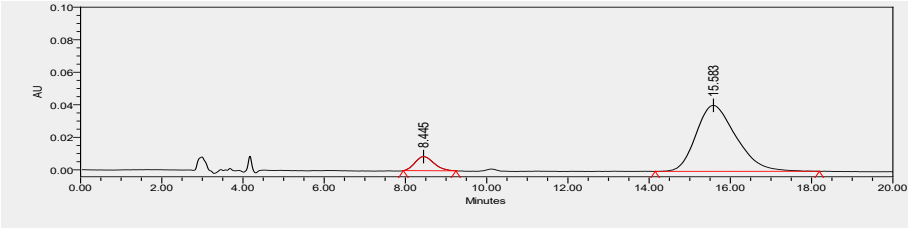
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 138.9, 137.8, 133.9, 132.1, 130.4, 128.9, 127.4, 126.2, 125.9, 125.5, 125.4, 124.1, 123.2, 115.5, 112.8, 89.0, 86.0, 80.0, 78.9, 49.5, 47.4, 43.6, 39.4, 39.1, 32.8, 29.8, 28.6, 27.3, 26.4, 24.0, 23.4, 22.8, 12.8.

HR-MS (ESI) calcd for $C_{37}H_{42}O_2Na^+$ ([M+Na]$^+$): 541.3077, found 541.3083;

IR (neat) 3446, 2932, 2869, 1609, 1497, 1450, 1280, 1251, 1166, 1047, 1001, 867, 798, 777, 452 cm^{-1}.

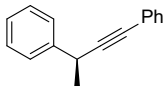


	Retention Time	Area	% Area
1	8.352	2095898	48.37
2	15.312	2237060	51.63



	Retention Time	Area	% Area
1	8.445	279036	9.15
2	15.583	2769399	90.85

***(S)*-but-1-yne-1,3-diyldibenzene (C25)**



General procedure A for 24 h.

0.2 mmol scale; 35.5 mg, colorless oil, 86% yield, 82.5:17.5 *er*; $[\alpha]_D^{20}$ = +25.5 (c 0.71, CH_2Cl_2).

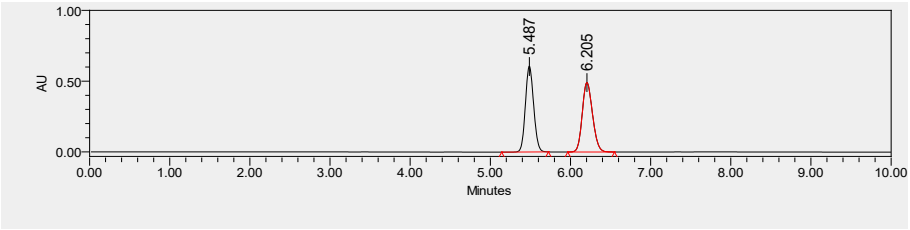
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 5.46 min, t_2 = 6.19 min

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 - 7.43 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.30 - 7.21 (m, 4H), 3.98 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H).

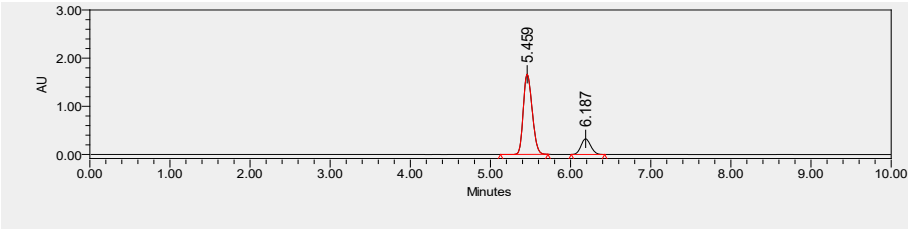
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 131.6, 128.5, 128.2, 127.7, 126.9, 126.6, 123.7, 92.6, 82.4, 32.4, 24.5.

HR-MS (ESI) calcd for $C_{16}H_{15}^+$ ([M+H]$^+$): 207.1168, found 207.1166;

IR (neat) 3059, 3027, 2975, 2929, 2870, 1598, 1489, 1448, 1299, 1071, 1028, 911, 755, 694, 556, 527 cm^{-1}.

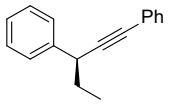


	Retention Time	Area	% Area
1	5.487	4342230	49.79
2	6.205	4378735	50.21



	Retention Time	Area	% Area
1	5.459	12792927	82.42
2	6.187	2728630	17.58

***(S)*-pent-1-yne-1,3-diyldibenzene (C26)**



General procedure A for 48 h.

0.2 mmol scale; 39.1 mg, colorless oil, 89% yield, 85:15 *er*; $[\alpha]_D^{20}$ = +15.9 (c 0.78, CH_2Cl_2).

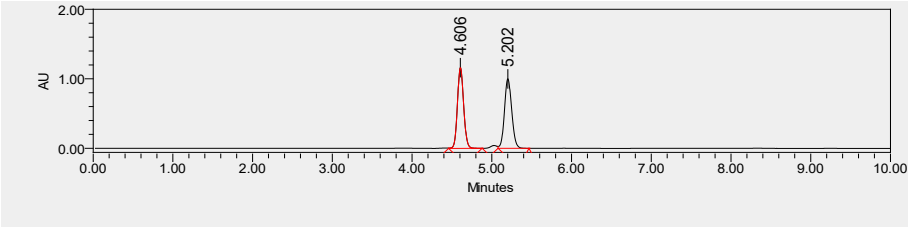
HPLC Chiralcel OD-H, hexane/isopropanol = 99.5/0.5, 1.0 mL/min, λ = 254 nm, t_1 = 4.63 min, t_2 = 5.26 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 - 7.38 (m, 4H), 7.35 - 7.31 (m, 2H), 7.31 - 7.19 (m, 4H), 3.83 - 3.75 (m, 1H), 1.94 - 1.78 (m, 2H), 1.05 (t, *J* = 7.2 Hz, 3H).

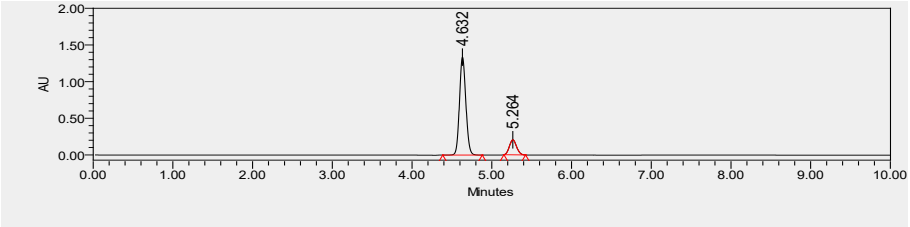
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 131.6, 128.4, 128.2, 127.7, 127.5, 126.6, 123.8, 91.4, 83.3, 39.9, 31.7, 11.8.

HR-MS (ESI) calcd for $C_{17}H_{17}^+$ ([M+H]$^+$): 221.1325, found 221.1321;

IR (neat) 3060, 3028, 2965, 2930, 2871, 1599, 1490, 1450, 1378, 1344, 1070, 1027, 913, 754, 694, 543 cm^{-1}.

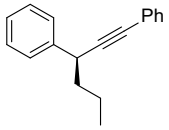


	Retention Time	Area	% Area
1	4.606	6292936	49.78
2	5.202	6348174	50.22



	Retention Time	Area	% Area
1	4.632	7422572	85.26
2	5.264	1282884	14.74

***(S)*-hex-1-yne-1,3-diyldibenzene (C27)**



General procedure A for 48 h.

0.2 mmol scale; 43.2 mg, colorless oil, 92% yield, 82:18 *er*; $[\alpha]_D^{20}$ = +13.0 (c 0.86, CH_2Cl_2).

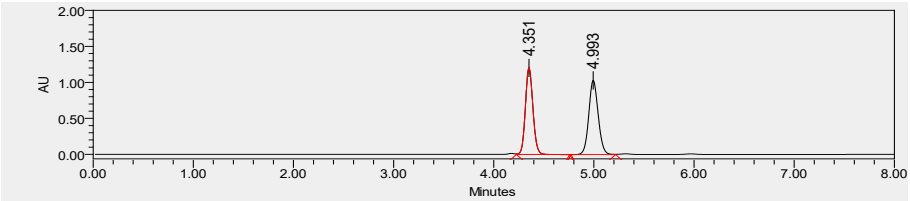
HPLC Chiralcel OD-H, hexane/isopropanol = 99.5/0.5, 1.0 mL/min, λ = 254 nm, t_1 = 4.34 min, t_2 = 4.99 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 - 7.40 (m, 4H), 7.35 - 7.31 (m, 2H), 7.30 - 7.20 (m, 4H), 3.84 (dd, *J* = 8.0, 6.0 Hz, 1H), 1.84 - 1.76 (m, 2H), 1.63 - 1.44 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

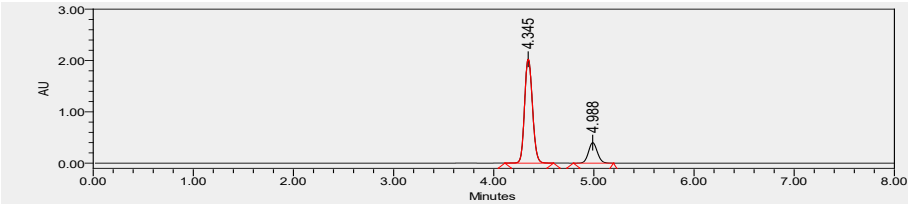
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 131.6, 128.4, 128.2, 127.7, 127.4, 126.6, 123.8, 91.6, 83.1, 40.8, 38.2, 20.6, 13.8.

HR-MS (ESI) calcd for $C_{18}H_{19}^+$ ([M+H]$^+$): 235.1481, found 235.1477;

IR (neat) 2958, 2931, 2869, 1599, 1490, 1453, 1342, 1070, 1028, 754, 694, 539 cm^{-1}.

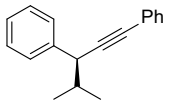


	Retention Time	Area	% Area
1	4.351	6317732	48.41
2	4.993	6733481	51.59



	Retention Time	Area	% Area
1	4.345	11136935	81.97
2	4.988	2449216	18.03

***(S)*-(4-methylpent-1-yne-1,3-diyl)dibenzene (C28)**



General procedure A for 48 h.

0.2 mmol scale; 27.0 mg, colorless oil, 58% yield, 90:10 *er*; $[\alpha]_D^{20}$ = +28.3 (c 0.54, CH_2Cl_2).

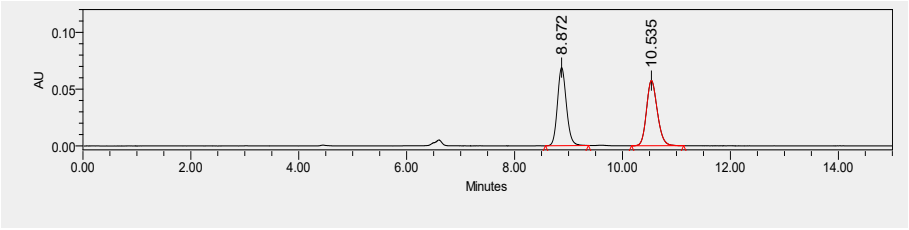
HPLC Chiralcel OD-H, hexane/isopropanol = 100/0, 1.0 mL/min, λ = 254 nm, t_1 = 8.84 min, t_2 = 10.55 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 - 7.43 (m, 2H), 7.42 - 7.36 (m, 2H), 7.35 - 7.21 (m, 6H), 3.73 (d, *J* = 6.0 Hz, 1H), 2.05 (dq, *J* = 13.2, 6.4 Hz, 1H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H).

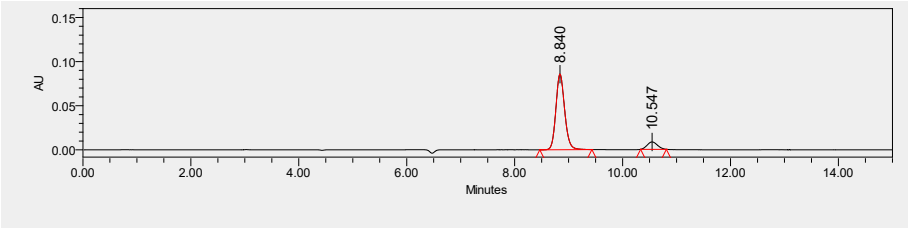
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 131.6, 128.2, 128.2, 127.7, 126.6, 123.9, 90.2, 84.2, 45.7, 35.2, 21.3, 18.7.

HR-MS (ESI) calcd for $C_{18}H_{19}^+$ ([M+H]$^+$): 235.1481, found 235.1471;

IR (neat) 3028, 2960, 2927, 2869, 2361, 1599, 1490, 1450, 1384, 1348, 1273, 1069, 1029, 912, 754, 694, 542 cm^{-1}.

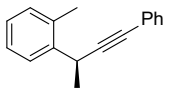


	Retention Time	Area	% Area
1	8.872	788779	49.59
2	10.535	801851	50.41



	Retention Time	Area	% Area
1	8.840	971793	89.86
2	10.547	109710	10.14

***(S)*-1-methyl-2-(4-phenylbut-3-yn-2-yl)benzene (C29)**



General procedure A for 48 h.

0.2 mmol scale; 38.2 mg, colorless oil, 87% yield, 93:7 *er*; $[\alpha]_D^{20}$ = +36.1 (c 0.76, CH_2Cl_2).

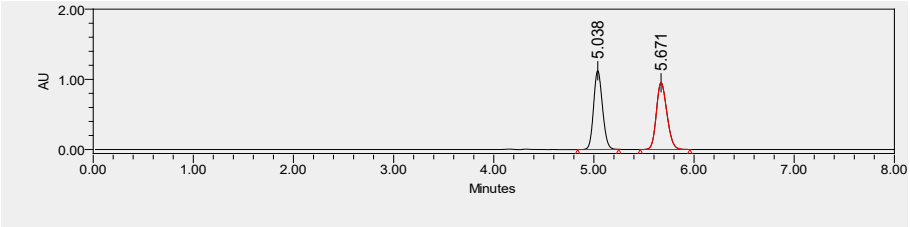
HPLC Chiralcel OD-H, hexane/isopropanol = 99.5/0.5, 1.0 mL/min, λ = 254 nm, t_1 = 5.04 min, t_2 = 5.66 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 1H), 7.45 - 7.39 (m, 2H), 7.30 - 7.24 (m, 3H), 7.24 - 7.19 (m, 1H), 7.18 - 7.14 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 1H), 2.40 (s, 3H), 1.54 (d, *J* = 7.2 Hz, 3H).

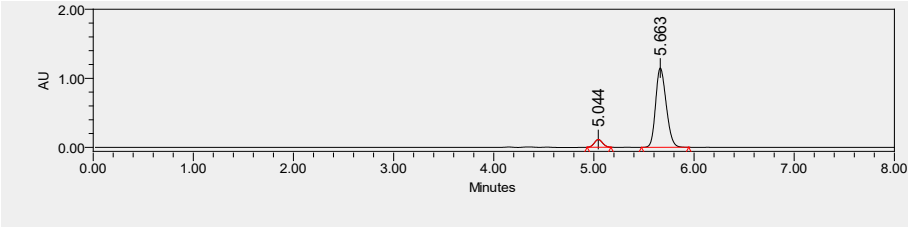
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 134.7, 131.6, 130.4, 128.2, 127.7, 126.8, 126.6, 126.4, 123.8, 92.9, 81.7, 29.1, 22.8, 19.1.

HR-MS (ESI) calcd for $C_{17}H_{17}^+$ ([M+H]$^+$): 221.1325, found 221.1322;

IR (neat) 3021, 2974, 2930, 1599, 1488, 1458, 1374, 1327, 1290, 1073, 912, 756, 728, 691, 563, 465 cm^{-1}.

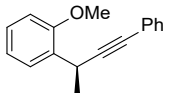


	Retention Time	Area	% Area
1	5.038	6908571	49.72
2	5.671	6985366	50.28



	Retention Time	Area	% Area
1	5.044	642035	7.09
2	5.663	8409506	92.91

***(S)*-1-methoxy-2-(4-phenylbut-3-yn-2-yl)benzene (C30)**



General procedure A for 48 h.

0.2 mmol scale; 28.8 mg, colorless oil, 61% yield, 95:5 *er*; $[\alpha]_D^{20}$ = +53.5 (c 0.58, CH_2Cl_2).

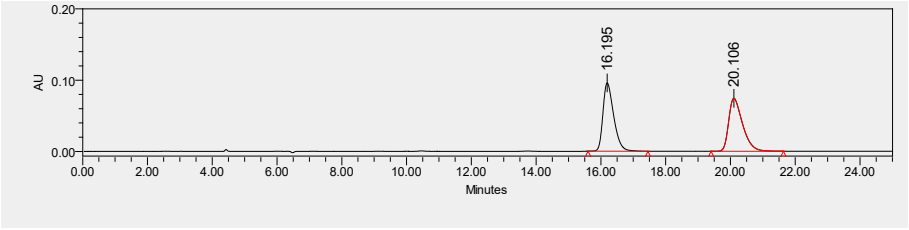
HPLC Chiralcel OD-H, hexane/isopropanol = 100/0, 1.0 mL/min, λ = 254 nm, t_1 = 16.25 min, t_2 = 20.34 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 - 7.64 (m, 1H), 7.48 - 7.40 (m, 2H), 7.32 - 7.19 (m, 4H), 7.00 - 6.96 (m, 1H), 6.91 – 6.82 (m, 1H), 4.39 (q, *J* = 7.2 Hz, 1H), 3.84 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H).

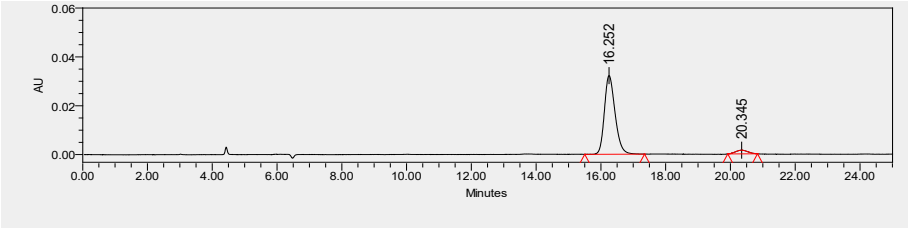
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 131.6, 131.6, 128.1, 127.8, 127.7, 127.6, 123.9, 120.7, 110.3, 93.1, 81.7, 55.3, 26.1, 22.9.

HR-MS (ESI) calcd for $C_{17}H_{17}O^+$ ([M+H]$^+$): 237.1274, found 237.1269;

IR (neat) 2973, 2932, 2836, 1596, 1491, 1459, 1242, 1115, 1075, 1051, 1029, 753, 691, 502 cm^{-1}.

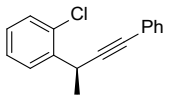


	Retention Time	Area	% Area
1	16.195	2210758	50.01
2	20.106	2210017	49.99



	Retention Time	Area	% Area
1	16.252	736009	94.80
2	20.345	40408	5.20

***(S)*-1-chloro-2-(4-phenylbut-3-yn-2-yl)benzene (C31)**



General procedure A for 48 h.

0.2 mmol scale; 40.2 mg, colorless oil, 84% yield, 95:5 *er*; $[\alpha]_D^{20}$ = +55.8 (c 0.80, CH2Cl2).

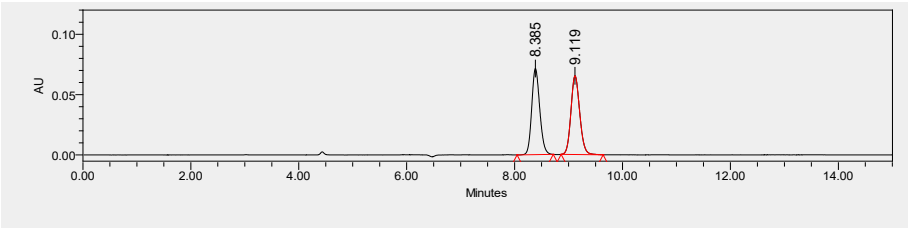
HPLC Chiralcel OD-H, hexane/isopropanol = 100/0, 1.0 mL/min, λ = 254 nm, t_1 = 8.05 min, t_2 = 8.85 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.48 - 7.41 (m, 2H), 7.36 - 7.33 (m, 1H), 7.32 - 7.25 (m, 4H), 7.20 - 7.15 (m, 1H), 4.44 (q, *J* = 7.2 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H).

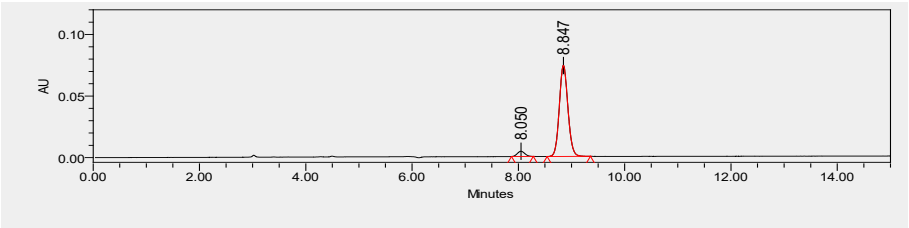
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 132.5, 131.6, 129.5, 128.6, 128.2, 128.0, 127.9, 127.2, 123.5, 91.8, 82.4, 29.7, 22.9.

HR-MS (APCI) calcd for $C_{16}H_{14}Cl^+$ ($[M+H]^+$): 241.0779, 243.0749, found 241.0780, 243.0752;

IR (neat)3060, 2978, 2931, 1596, 1472, 1440, 1324, 1036, 753, 691, 562, 469 cm^{-1}.

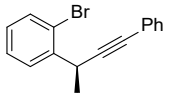


	Retention Time	Area	% Area
1	8.385	738749	49.97
2	9.119	739767	50.03



	Retention Time	Area	% Area
1	8.050	41657	4.77
2	8.847	832202	95.23

***(S)*-1-bromo-2-(4-phenylbut-3-yn-2-yl)benzene (C32)**



General procedure A for 48 h.

0.2 mmol scale; 48.6 mg, colorless oil, 85% yield, 95.5:4.5 *er*; $[\alpha]_D^{20}$ = +62.3 (c 0.97, CH_2Cl_2).

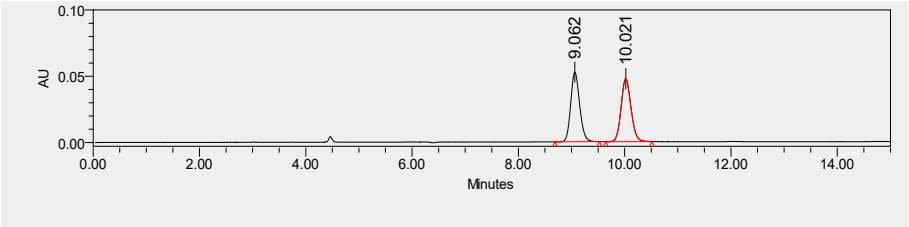
HPLC Chiralcel OD-H, hexane/isopropanol = 100/0, 1.0 mL/min, λ = 254 nm, t_1 = 8.05 min, t_2 = 8.85 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.53 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.48 - 7.41 (m, 2H), 7.36 - 7.25 (m, 4H), 7.14 - 7.06 (m, 1H), 4.42 (q, *J* = 7.2 Hz, 1H), 1.54 (d, *J* = 7.2 Hz, 3H).

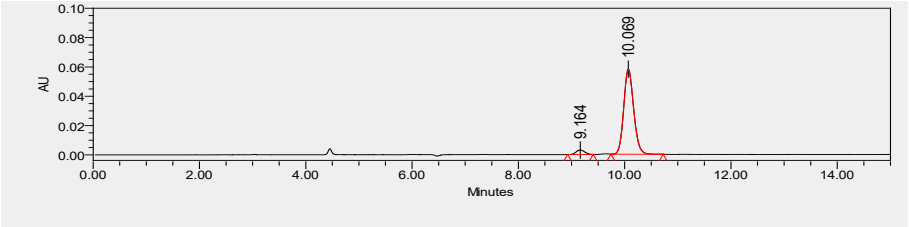
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 132.8, 131.6, 128.8, 128.3, 128.2, 127.9, 123.5, 123.0, 91.9, 82.5, 32.3, 23.1.

HR-MS (ESI) calcd for $C_{16}H_{14}Br^+$ ([M+H]$^+$): 285.0273, found 285.0268;

IR (neat) 3058, 2977, 2930, 1595, 1567, 1489, 1469, 1438, 1323, 1023, 753, 691, 561, 461 cm^{-1}.

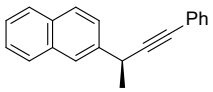


	Retention Time	Area	% Area
1	9.062	615860	50.00
2	10.021	615763	50.00



	Retention Time	Area	% Area
1	9.164	35119	4.46
2	10.069	751486	95.54

***(S)*-2-(4-phenylbut-3-yn-2-yl)naphthalene (C33)**



General procedure A for 48 h.

0.2 mmol scale; 44.4 mg, white solid, m.p. 81.9-83.1 °C, 87% yield, 85:15 *er*; $[\alpha]_D^{20}$ = +17.1 (c 0.89, CH_2Cl_2).

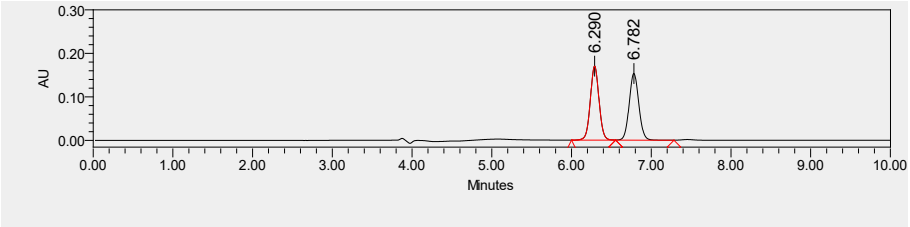
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 6.18 min, t_2 = 6.68 min

^{1}H NMR (400 MHz, $CDCl_3$) 7.88 - 7.87(m, 1H), 7.85 - 7.78 (m, 3H), 7.58 - 7.55 (m, 1H), 7.45 (m, 4H), 4.13 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H).

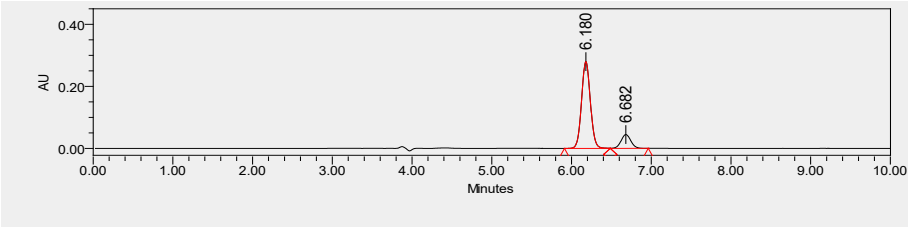
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 133.5, 132.4, 131.6, 131.4, 128.3, 128.2, 127.8, 127.7, 127.6, 126.0, 125.6, 125.1, 123.7, 92.5, 82.6, 32.6, 24.3.

HR-MS (ESI) calcd for $C_{20}H_{17}^+$ ([M+H]$^+$): 257.1325, found 257.1335;

IR (neat) 3054,2975, 2929, 1599, 1489, 1445, 1368, 1302, 1072, 856, 818, 751, 691, 478 cm^{-1}.

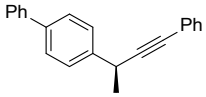


	Retention Time	Area	% Area
1	6.290	1300656	50.09
2	6.782	1296053	49.91



	Retention Time	Area	% Area
1	6.180	2159212	85.00
2	6.682	381110	15.00

***(S)*-4-(4-phenylbut-3-yn-2-yl)-1,1'-biphenyl (C34)**



General procedure A for 48 h.

0.2 mmol scale; 48.7 mg, colorless oil, 86% yield, 80.5:19.5 *er*; $[\alpha]_D^{20}$ = +12.3 (c 0.97, CH_2Cl_2).

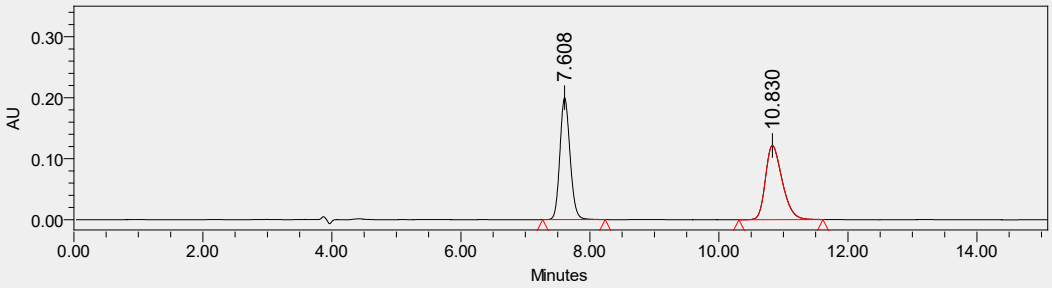
HPLC Chiralcel OD-H, hexane/isopropanol = 99/1, 1.0 mL/min, λ = 254 nm, t_1 = 7.58 min, t_2 = 10.75 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 - 7.55 (m, 4H), 7.53 - 7.50 (m, 2H), 7.48 - 7.39 (m, 4H), 7.36 - 7.24 (m, 4H), 4.02 (q, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H).

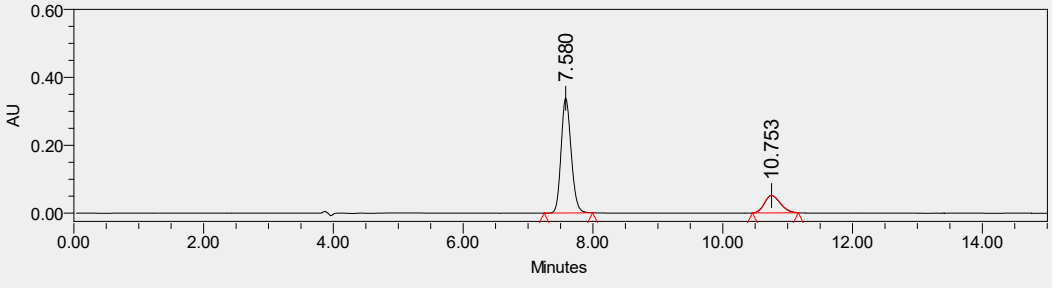
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 140.9, 139.6, 131.6, 128.7, 128.5, 128.2, 127.8, 127.4, 127.3, 127.1, 127.0, 123.6, 92.5, 82.5, 32.1, 24.4.

HR-MS (ESI) calcd for $C_{22}H_{19}^+$ ([M+H]$^+$): 283.1481, found 283.1490;

IR (neat) 3028, 2975, 2929, 1685, 1599, 1486, 1447, 1299, 1075, 1005, 838, 759, 694, 570, 510 cm^{-1}.



	Retention Time	Area	% Area
1	7.608	2185618	50.03
2	10.830	2182923	49.97



	Retention Time	Area	% Area
1	7.580	3637457	80.66
2	10.753	872335	19.34

7. X-ray crystal data

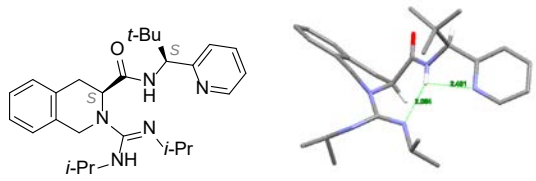
The structure of the catalyst **G-TqPy$^{(S)\text{-}tBu}$** was determined by X-ray chromatography analysis.

Single crystal of **G-TqPy$^{(S)\text{-}tBu}$** was obtained by recrystallization in petroleum ether and ethyl acetate at room temperature in a 10 mL glassware bottle.

The crystal data and further details are listed in Table S8.

CCDC 2182833 (**G-TqPy$^{(S)\text{-}tBu}$**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

The colourless crystal in block-shape, with approximate dimensions of 0.279 × 0.234 × 0.160 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[a, b, c, d]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[e].



Datablock ljj008 - ellipsoid plot

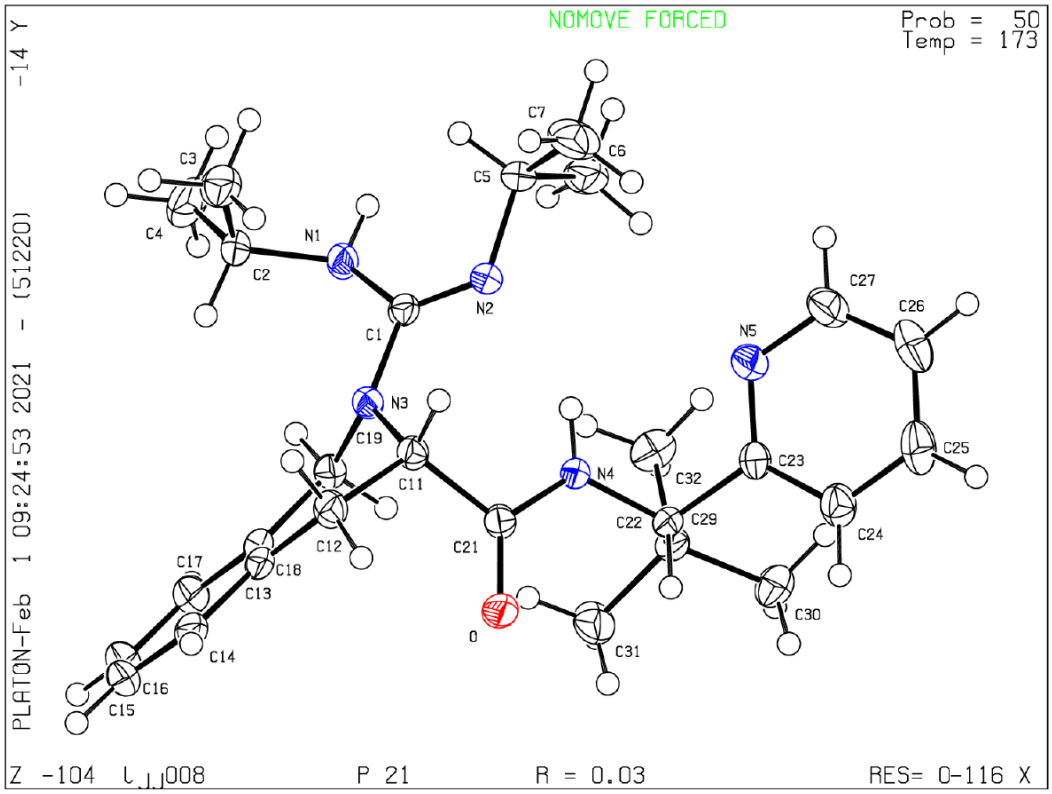


Figure S7. the thermal ellipsoid figure of **G-TqPy$^{(S)\text{-}tBu}$** with 50% probabilities

Table S8. Crystallographic Data for $C_{27}H_{39}N_5O$

Formula	C27H39N5O
Formula mass (amu)	449.63
Space group	P 21
a (Å)	9.0124(2)
c (Å)	14.6098(4)
c (Å)	10.7090(3)
α (deg)	90
β (deg)	110.238(1)
γ (deg)	90
V (Å^3)	1323.00(6)
Z	2
λ (Å)	1.54178
T (K)	173 K
ρ_{calcd} (g cm^{-3})	1.129
μ (mm^{-1})	0.548
Transmission factors	0.860, 0.970
$2\theta_{max}$ (deg)	68.264
No. of unique data, including $F_o^2 < 0$	4774
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	4722
No. of variables	313
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0261
$R_w(F_o^2)$ [b]	0.0669
Goodness of fit	1.083

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

References:

[a] Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122.

[b] Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3–8.

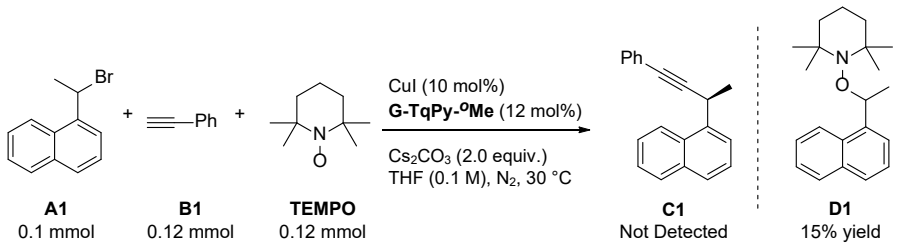
[c] Sheldrick, G. M. *Acta Cryst*. **2015**, *C71*, 3–8.

[d] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J. A. K., Puschmann, H. *J. Appl. Cryst*. **2009**, *42*, 339-341.

[e] Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7–13.

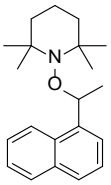
8. Mechanistic Studies

8.1 Radical trapping experiment with TEMPO:



A1	**B1**	**TEMPO**	**C1**	**D1**
0.1 mmol	0.12 mmol	0.12 mmol	Not Detected	15% yield

Under nitrogen atmosphere, an over-dried reaction tube charged with alkyl halide (0.10 mmol, 1.0 equiv.), TEMPO (0.12 mmol, 0.2 equiv.), CuI (10 mol %), **G^2-TqPy-*o*Me** (12 mol %), Cs_2CO_3 (2.0 equiv.), and anhydrous THF (1.0 mL). Then, alkyne (0.12 mmol, 1.2 equiv.) was sequentially added to the mixture and the reaction mixture was stirred at 30 °C for 24 h. Upon completion (monitored by TLC), THF was evaporated in vacuo, then the crude mixture was purified by flash chromatography on silica gel (eluent: PE/EtOAc = 19:1) to afford the TEMPO adduct (4.6 mg, 15%yield).

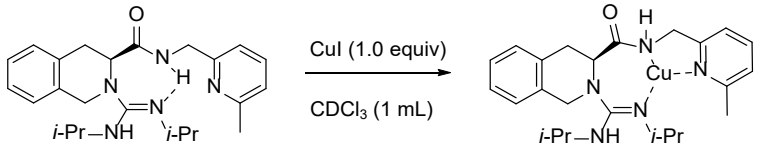


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 - 8.16 (m 1H), 7.88 - 7.82 (m, 1H), 7.74 -7.71 (m, 1H), 7.57 - 7.55 (m, 1H), 7.51 - 7.42 (m, 3H), 5.45 (q, *J* = 6.8 Hz, 1H), 1.65 (d, *J* = 6.8 Hz, 3H), 1.53 (brs, 3H), 1.42 - 1.40 (m, 5H), 1.25 - 1.24 (m, 4H), 1.01 (brs, 3H), 0.62 (brs, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 133.8, 130.3, 128.7, 127.0, 125.5, 125.4, 125.2, 124.4, 123.8, 82.2, 59.80, 40.3, 34.7, 33.6, 23.8, 20.5, 17.18.

HR-MS (ESI) calcd for $C_{21}H_{30}NO^+$ ([M+H]$^+$): 312.2322, found 312.2317;

8.2 NMR Analysis of G and G/Cu^{I}:



G-TqPy-^{oMe} **G/Cu^{I}**

Under nitrogen atmosphere, an over-dried reaction tube charged with CuI (7.6 mg, 0.04 mmol), **G-TqPy-*o*Me** (16.3 mg, 0.04 mmol) and $CDCl_3$ (1.0 mL). The mixture was stirred at r.t. for 30 mins. The mixture was filtered through a syringe filter and transferred into an NMR tube for recording the ^{1}H NMR.

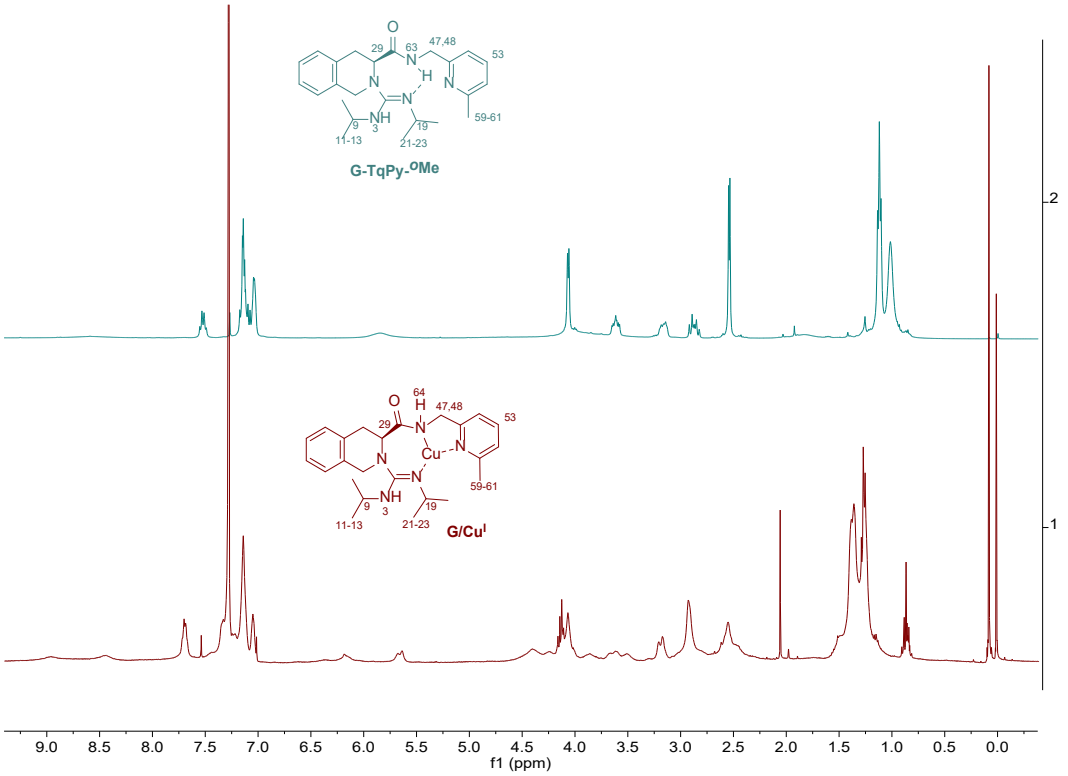


Figure S9. Stacking ^{1}H NMR spectrum of G and CuI/G . (green color: G; red color: CuI/G)

	H_3	H_9	$H_{11\text{-}13}$	H_{19}	$H_{21\text{-}23}$	H_{53}	$H_{59\text{-}61}$	H_{64}
G	5.86	~	1.02	~	1.12	7.52	2.54	8.58
G/Cu^{I}	6.16, 5.63	2.94	1.28	2.94	1.39	7.68	2.56	8.98, 8.45
δ		~	0.26	~	0.27	0.16	0.02	

8.3 ESI-MS analysis of catalytic system:

Under nitrogen atmosphere, an over-dried reaction tube charged with **A1** (11.7 mg, 0.05 mmol, 1.0 equiv.), CuI (0.9 mg, 0.005 mmol, 10 mol %), **G-TqPy-*o*Me** (2.4 mg, 0.006 mmol, 12 mol %), Cs_2CO_3 (32.6 mg, 0.1 mmol, 2.0 equiv.), and anhydrous THF (0.5 mL). Then, alkyne **B1** (8.4 μL, 0.075 mmol, 1.5 equiv.) was sequentially added to the mixture. The reaction mixture was stirred at 30 °C for 30 mins. An aliquot was taken up with the syringe through the filter and diluted 1000 times in the dilution vial. Lastly, the mixture was transferred to a glass syringe and taken for mass measurement. The mass spectra are listed in accordance as: the free catalyst **G-TqPy-*o*Me**, G^-/Cu^{II}, $G/Cu^{II}Br$, $G/Cu^{II}I$, G/Cu^{III}/A1/B1 adduct.

ESI-MS (m/z) calculated for [**G-TqPy-*o*Me**/H^+]$^+$ ($C_{24}H_{34}N_5O^+$): 408.28, found 408.37;

ESI-MS (m/z) calculated for [(**G-H$^+$**)$^-$/Cu^{2+}]$^+$ ($C_{24}H_{32}CuN_5O^+$): 469.19, found 469.28;

ESI-MS (m/z) calculated for [**G**/$Cu^{2+}Br$]$^+$ ($C_{24}H_{33}BrCuN_5O^+$): 549.11, 551.11, found 549.18, 551.23;

ESI-MS (m/z) calculated for [**G**/$Cu^{2+}I$]$^+$ ($C_{24}H_{33}ICuN_5O^+$): 597.10, 599.10; found 597.18, 599.22;

ESI-MS (m/z) calculated for [(G-H^+)$^-$/Cu^{3+}/PhCC$^-$**/R$^•$**]$^{+•}$ ($C_{44}H_{48}CuN_5O^{•+}$): 725.32, found 725.54;

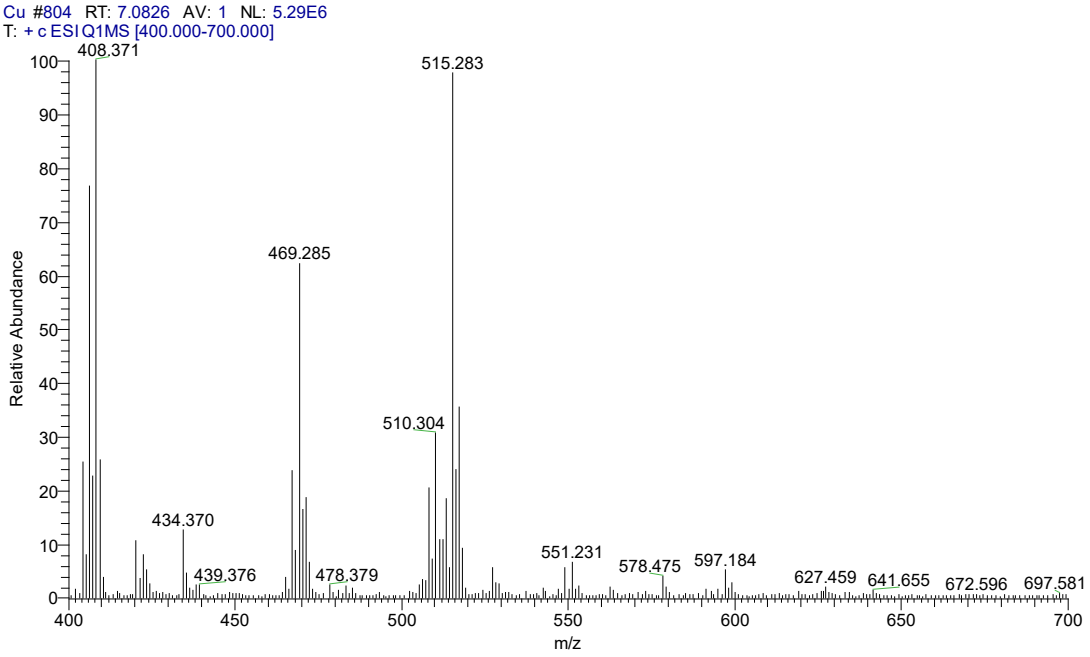


Figure S10. Overview of the ESI-MS (positive mode) of catalytic system.

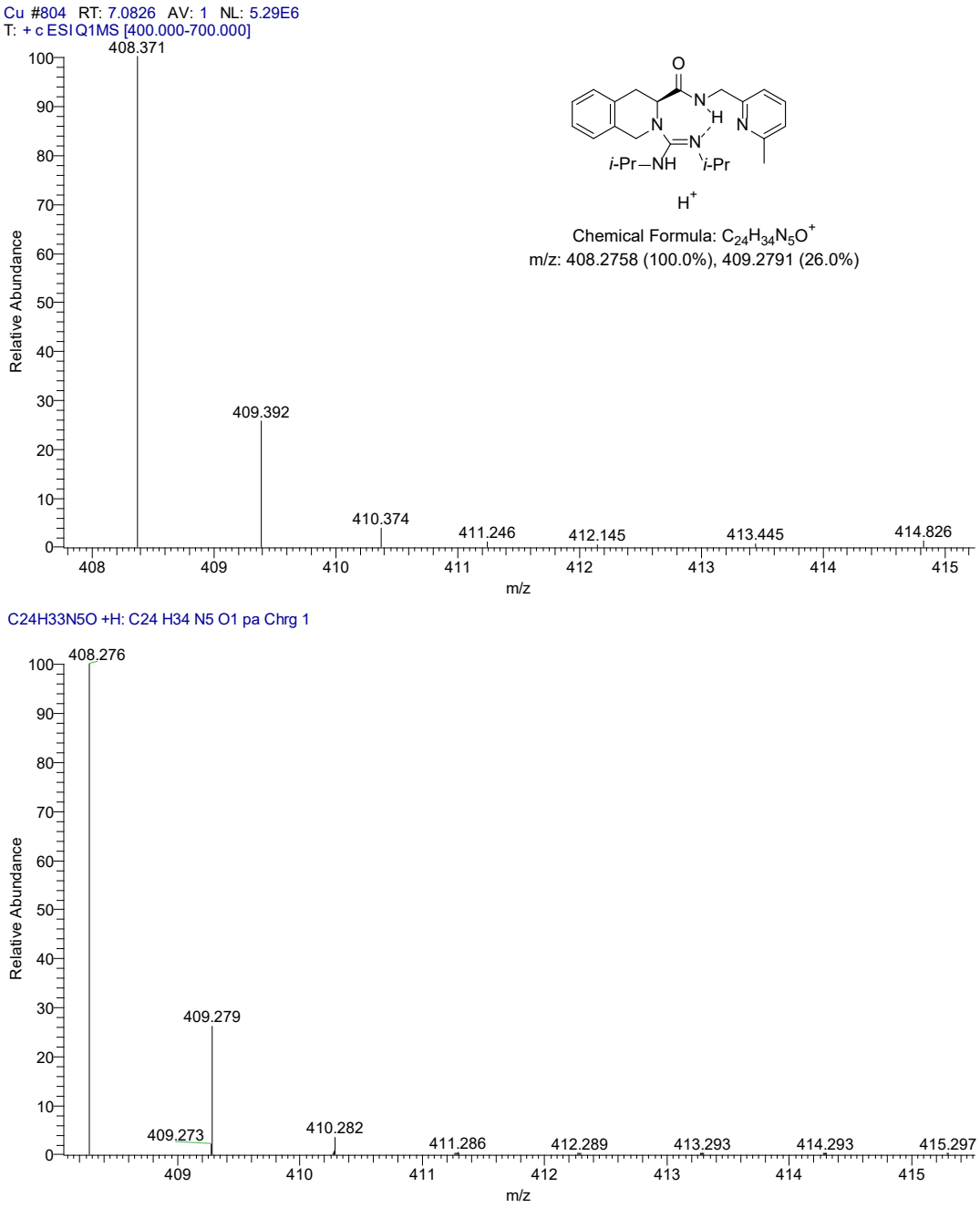


Figure S11. Zoomed-in view of the ESI-MS (positive mode) of **G²-TqPy-*o*Me** (top) and simulation of $[M]^+$ below.

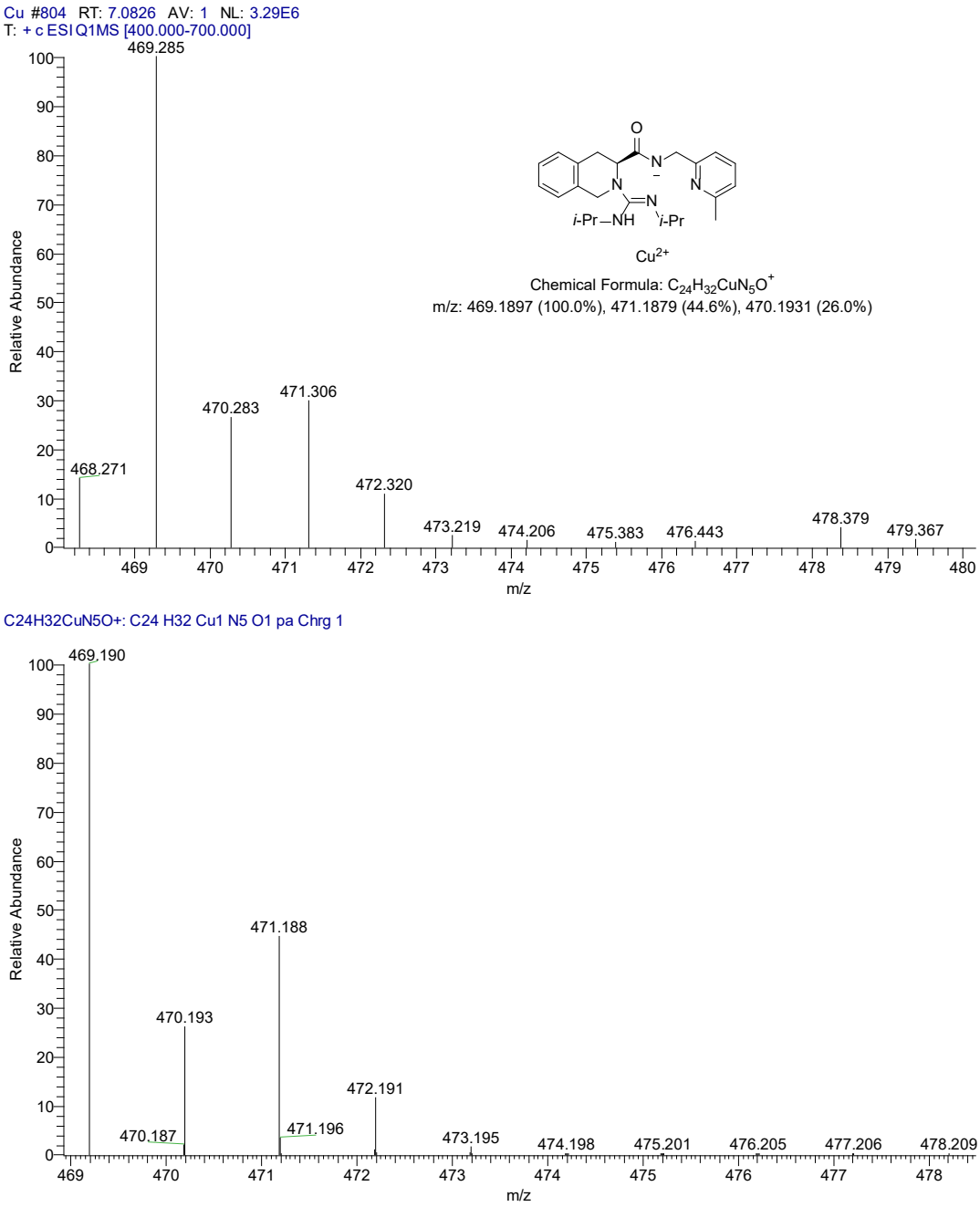


Figure S12. Zoomed-in view of the ESI-MS (positive mode) of **(G-H$^+$)$^-$/Cu^{2+}** (top) and simulation of [M]$^+$ below.

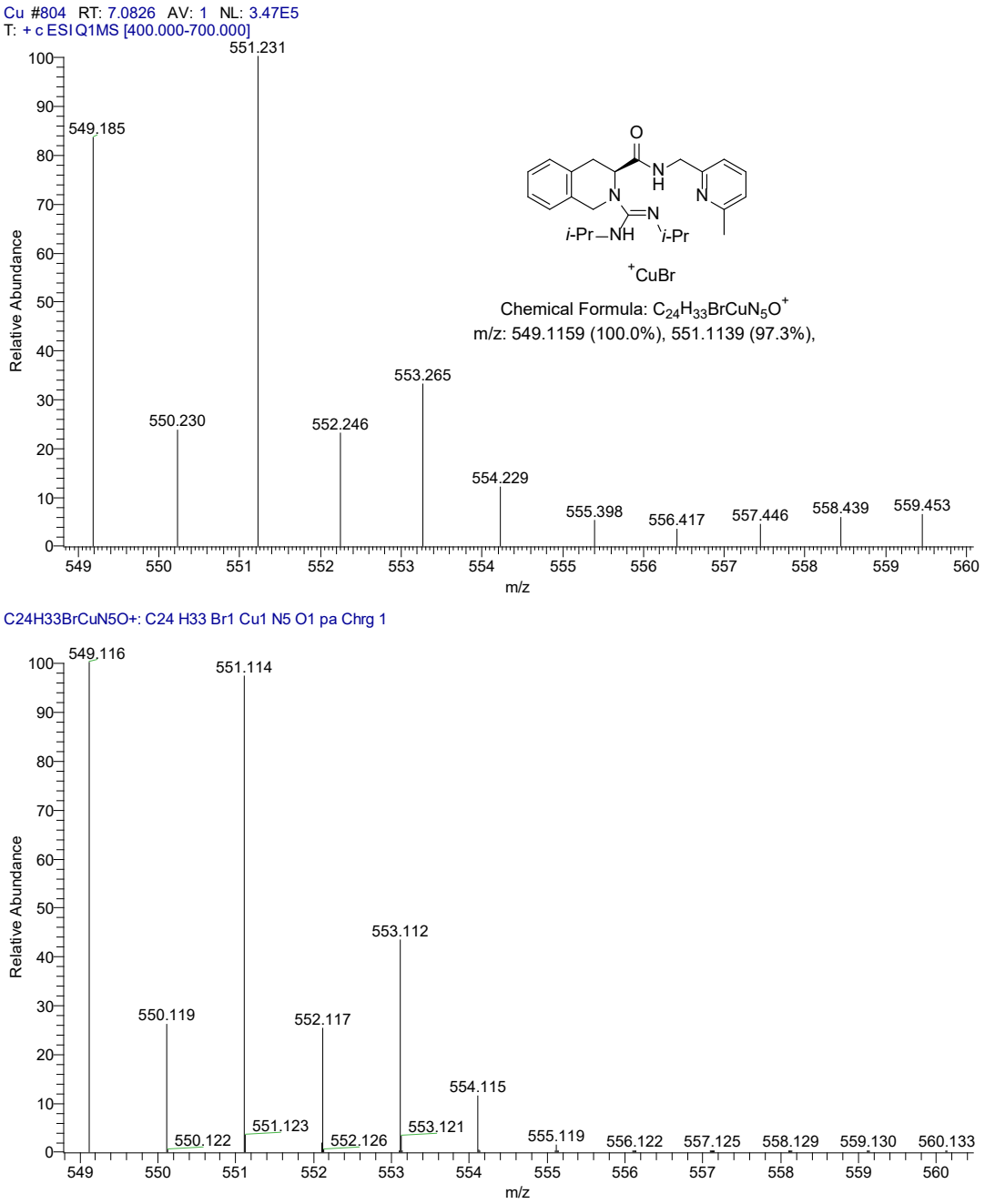


Figure S13. Zoomed-in view of the ESI-MS (positive mode) of **G/Cu^{2+}Br** (top) and simulation of $[M]^+$ below.

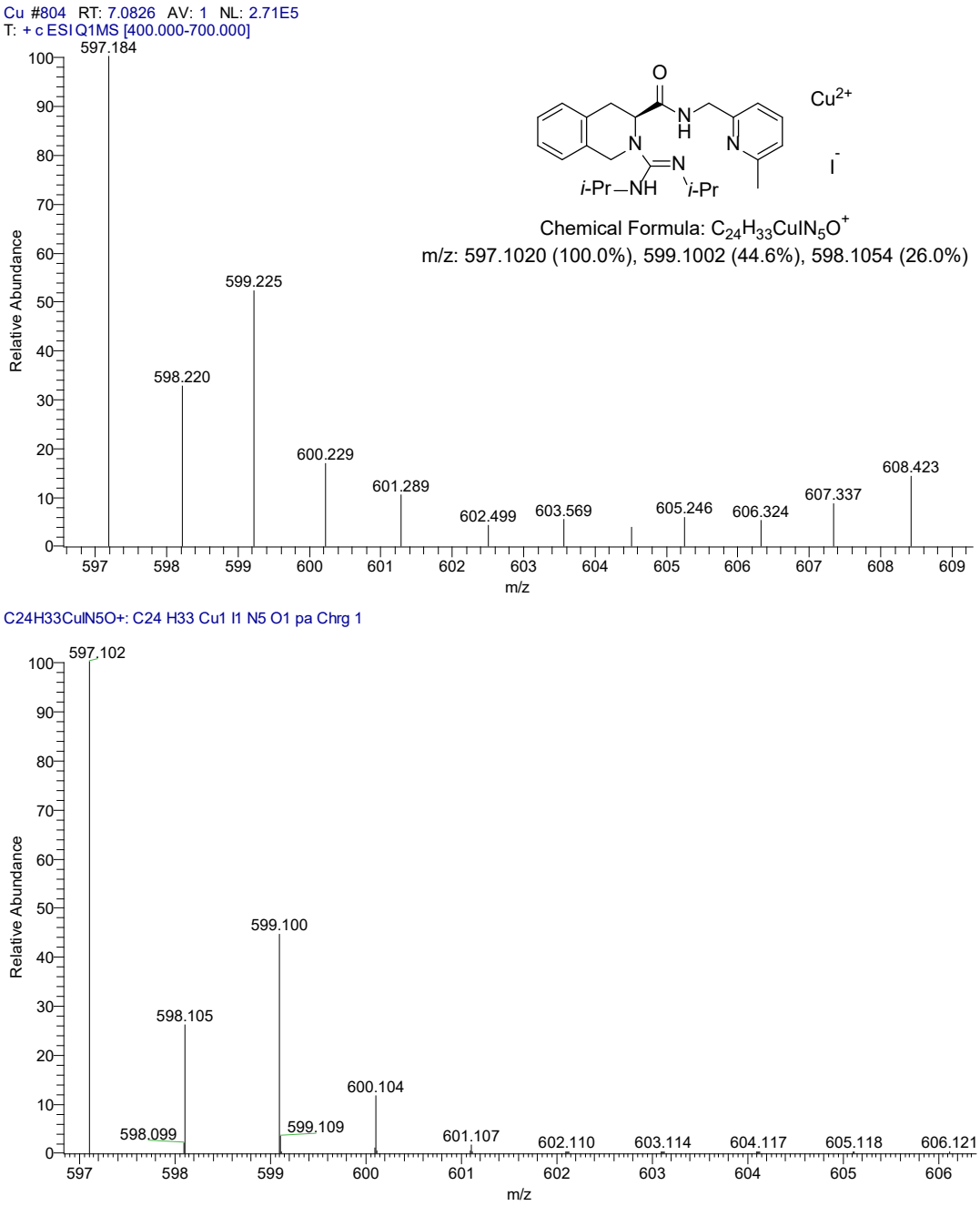


Figure S13. Zoomed-in view of the ESI-MS (positive mode) of **G/Cu^{2+}I** (top) and simulation of [M]$^{+}$ below.

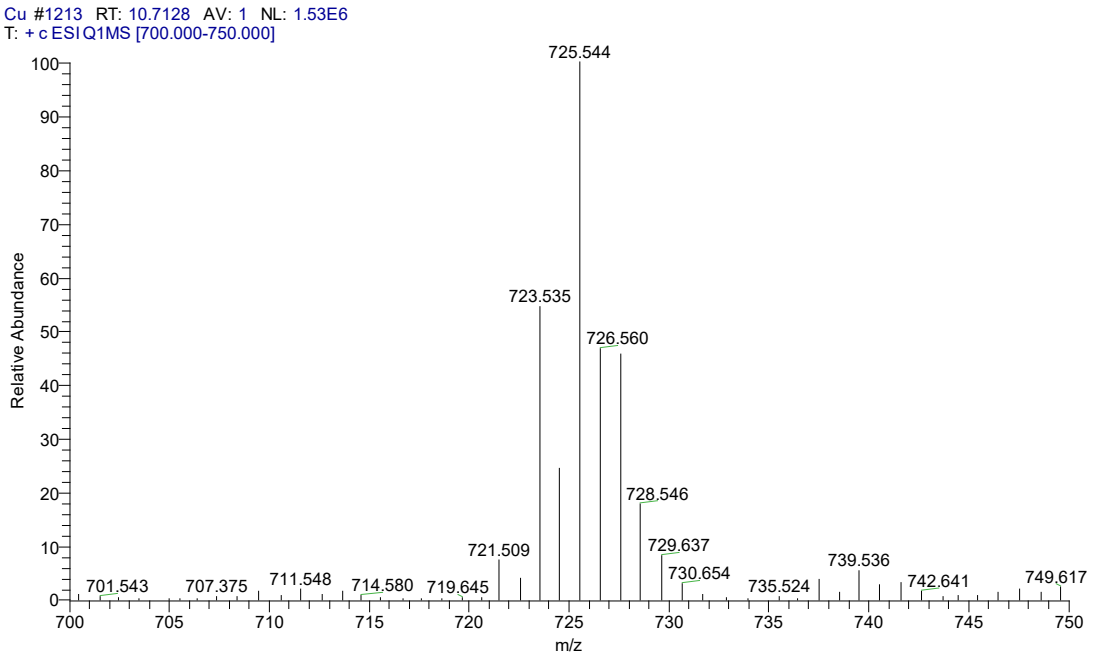


Figure S14. Overview of the ESI-MS (positive mode) of catalytic system.

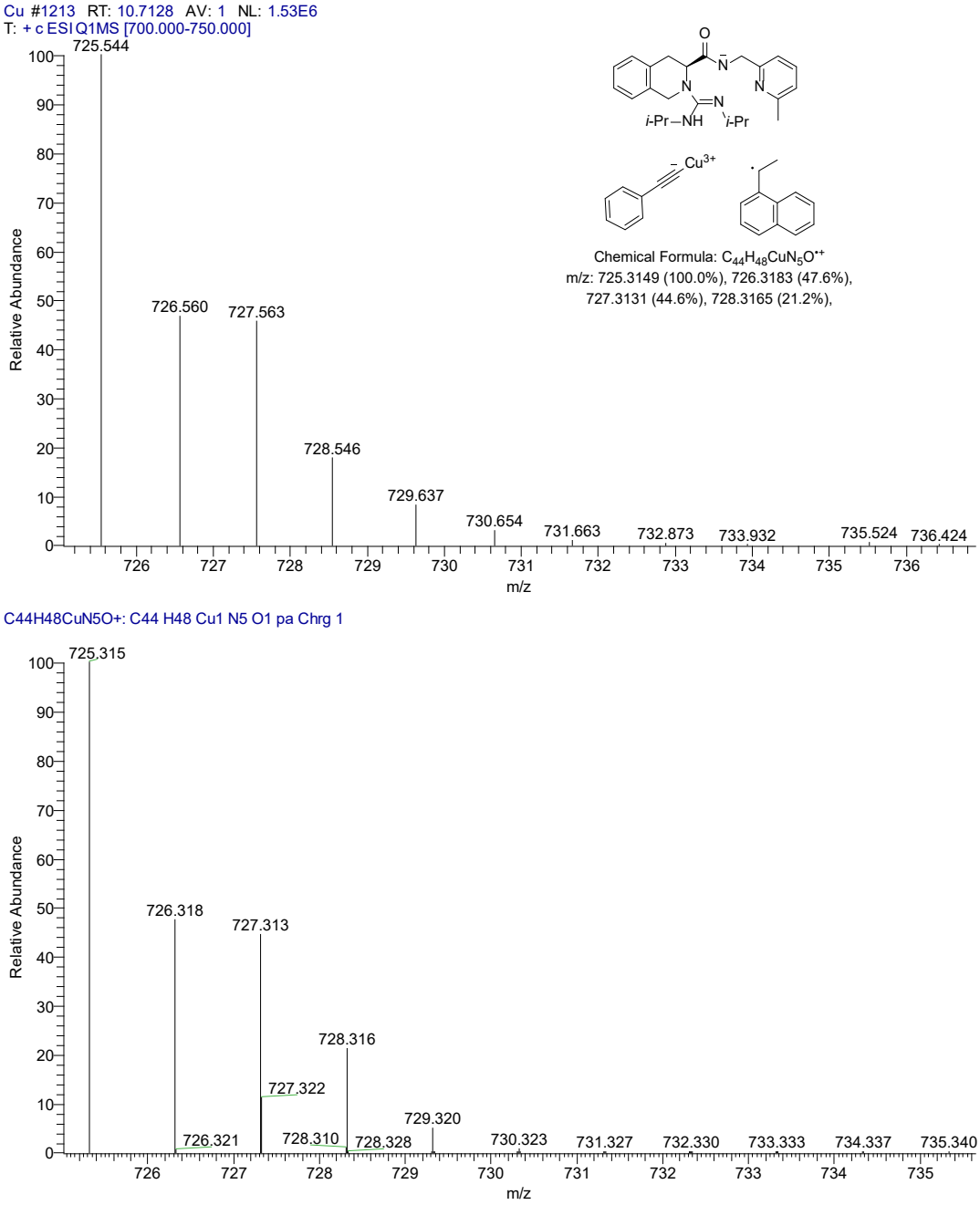


Figure S15. Zoomed-in view of the ESI-MS (positive mode) of **(G-H$^+$)$^-$/Cu^{3+}/PhCC$^-$/R$^•$** (top) and simulation of [M]$^+$ below.

8.4 EPR analysis of catalytic system:

Experiment for independent synthesis of the Cu^{II} intermediate.

Under nitrogen atmosphere, an over-dried reaction tube charged with $CuBr_2$ (1.1 mg, 0.005 mmol), **G-TqPy-*o*Me** (2.0 mg, 0.005 mmol), alkyne **B1** (8.4 μL, 0.075 mmol, 15.0 equiv.) and anhydrous THF (0.5 mL). The reaction mixture was stirred at 30 °C for 30 mins. An aliquot of the reaction mixture (0.50 mL) was transferred to an EPR tube under a nitrogen atmosphere for X-band EPR measurement at 100K.

Experiment for detection of the Cu^{II} species in the reaction system without B1.

Under nitrogen atmosphere, an over-dried reaction tube charged with **A1** (11.7 mg, 0.05 mmol, 1.0 equiv.), CuBr (0.6 mg, 0.005 mmol, 10 mol %), **G-TqPy-*o*Me** (2.4 mg, 0.006 mmol, 12 mol %), Cs_2CO_3 (32.6 mg, 0.1 mmol, 2.0 equiv.), and anhydrous THF (0.5 mL). The reaction mixture was stirred at 30 °C for 30 mins. An aliquot of the reaction mixture (0.50 mL) was transferred to an EPR tube under a nitrogen atmosphere for X-band EPR measurement at 100K.

Experiment for detection of the Cu^{II} species in the reaction system.

Under nitrogen atmosphere, an over-dried reaction tube charged with **A1** (11.7 mg, 0.05 mmol, 1.0 equiv.), CuBr (0.6 mg, 0.005 mmol, 10 mol %), **G-TqPy-*o*Me** (2.4 mg, 0.006 mmol, 12 mol %), Cs_2CO_3 (32.6 mg, 0.1 mmol, 2.0 equiv.), and anhydrous THF (0.5 mL). Then, alkyne **B1** (8.4 μL, 0.075 mmol, 1.5 equiv.) was sequentially added to the mixture. The reaction mixture was stirred at 30 °C for 30 mins. An aliquot of the reaction mixture (0.50 mL) was transferred to an EPR tube under a nitrogen atmosphere for X-band EPR measurement at 100K.

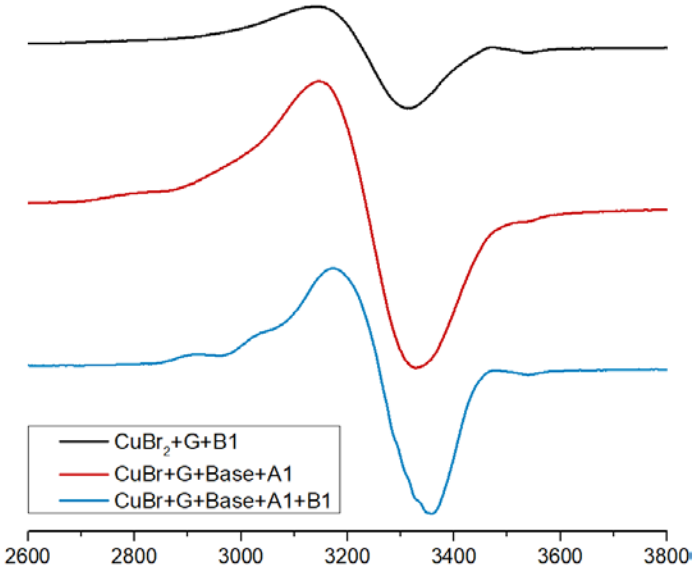


Figure S16. X-band EPR spectrum (9.42 GHz, 100K). Black: a mixture of $CuBr_2$, **G-TqPy-*o*Me** and **B1**. Red: a a mixture of CuBr, **G-TqPy-*o*Me**, Cs_2CO_3 and **A1**. Blue: a mixture of CuBr, **G-TqPy-oMe**, Cs_2CO_3, **A1** and **B1**.

8.5 Cyclic voltammogram (CV) analysis of the catalysts

Cyclic Voltammetry experiments were performed using a CH Instruments Electrochemical Workstation model CHI620E, scan rate = 0. 1V/s, 2 sweep segments, sample interval = 0.001 V. The electrochemical cell was equipped with a glassy carbon disk working electrode (3mm diameter) and a Pt wire counter electrode and the potentials were calibrated with Fc as an internal standard. The samples(CuBr 10nM, CuBr/G 5nM) were

prepared under the protection of the N_2 by dissolving them in degassed CH_3CN (0.1 M Bu_4NPF_6) directly and stirred for 1min.

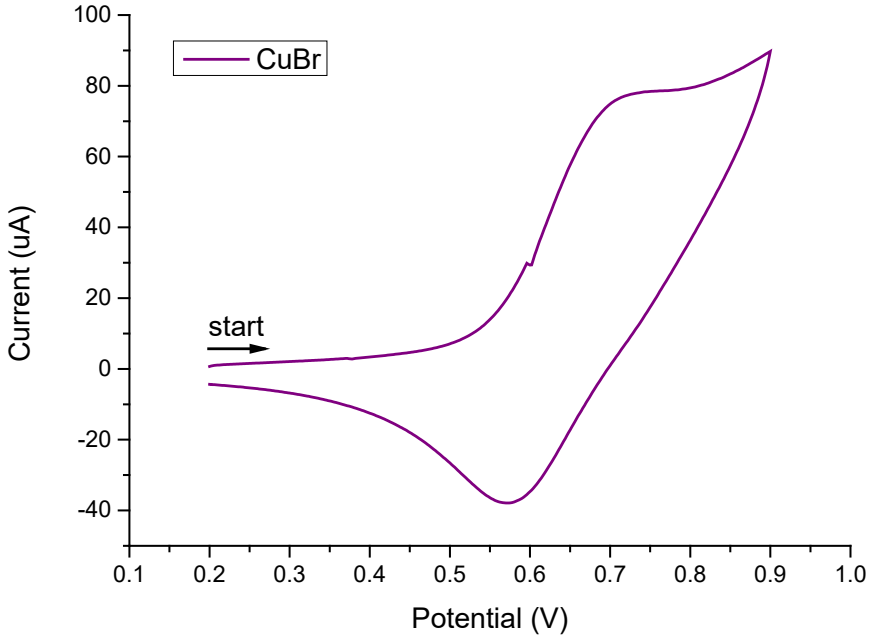


Figure S17. CVs of the CuBr (10 mM), calibrated with Fc as an internal standard.

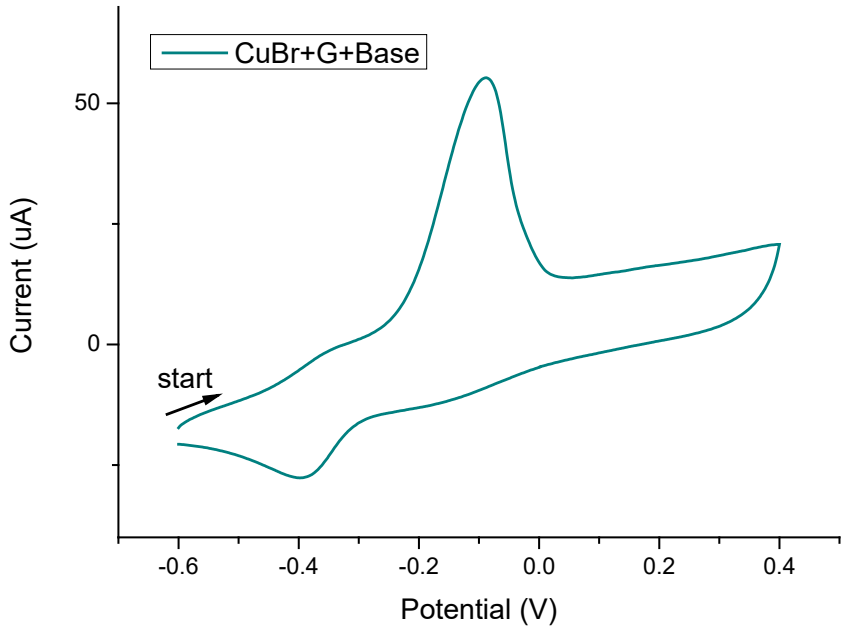
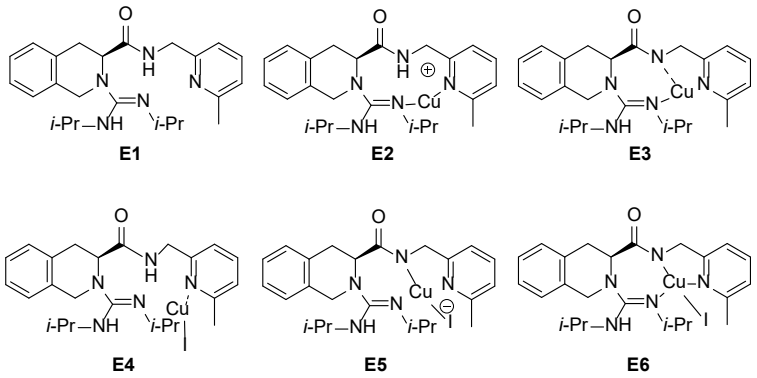


Figure S18. CVs of the CuBr/guanidine complex (5 mM), calibrated with Fc as an internal standard.

9. Computational details

9.1 DFT caculations of guanidine and possible guanidine-metal complex structures.

DFT caculations were conducted to evaluate the coordination of guanidine-CuI complexes, as listed in Scheme S19. Various coordination form and valence states were involved [Cu(I) in **E1**-**E5**, Cu(II) in **E6**], and the simulated ^{1}H NMR of **E1** & **E2** are consistent with the experimental results (see 9.1).



Scheme S19. Possible coordination structures of guanidine and CuI.

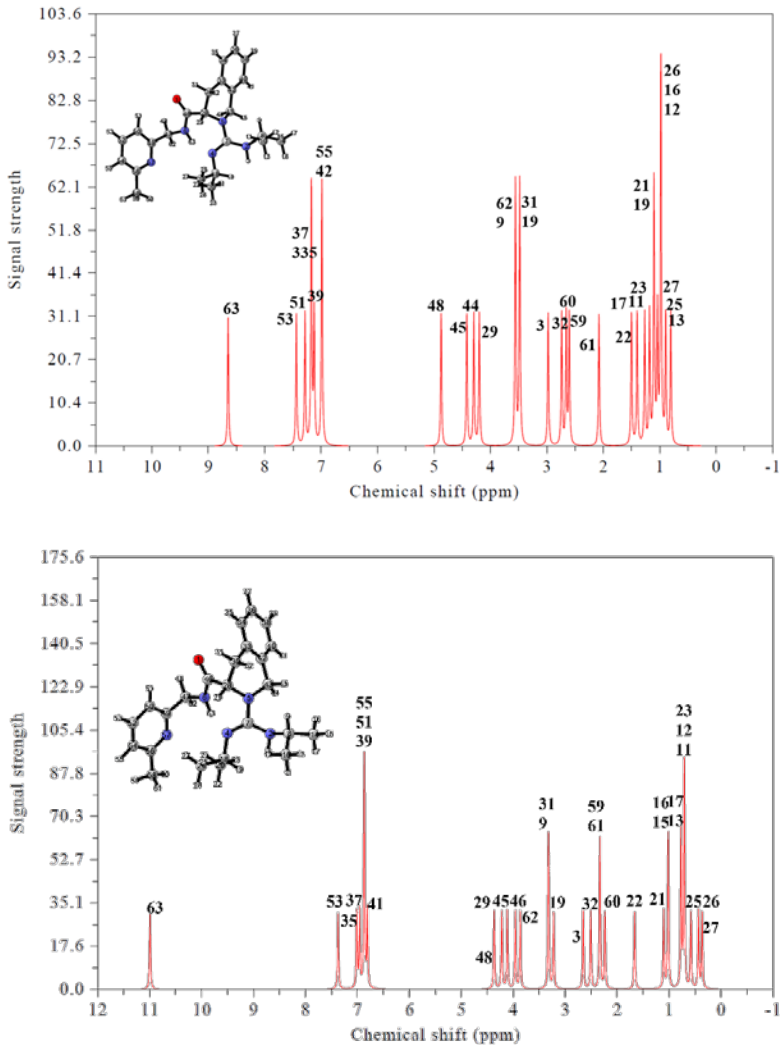


Figure S20.Simulated ^{1}H NMR of E1 (up: basic structure, down: Boltzmann-weighted chemical shifts)

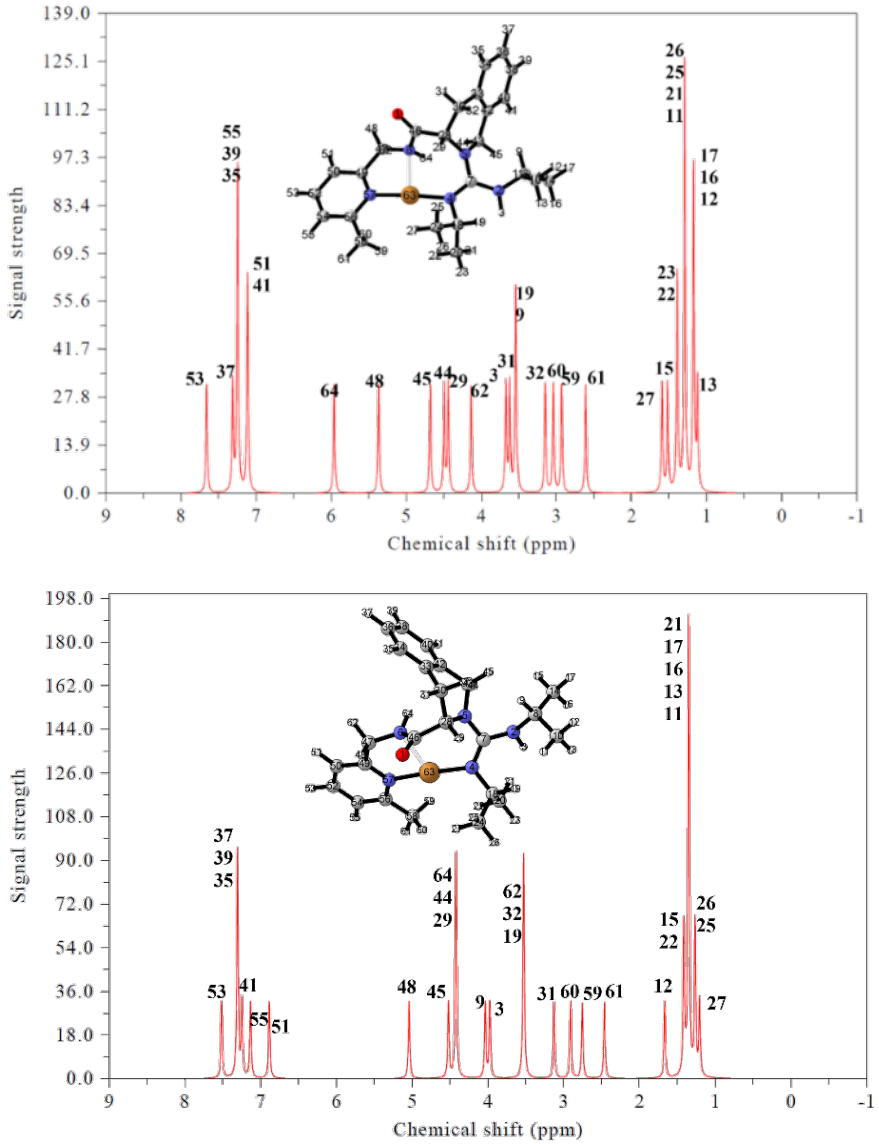


Figure S21. Simulated ^{1}H NMR of E2. (up: basic structure, down: Boltzmann-weighted chemical shifts)

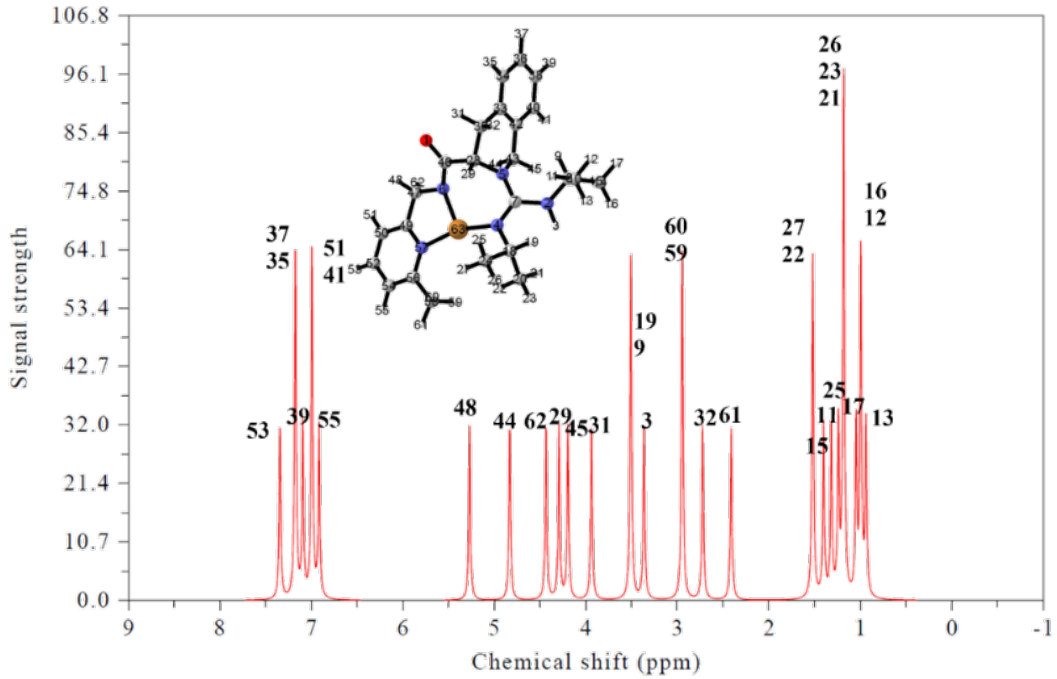


Figure S22. Simulated ^{1}H NMR of E3.

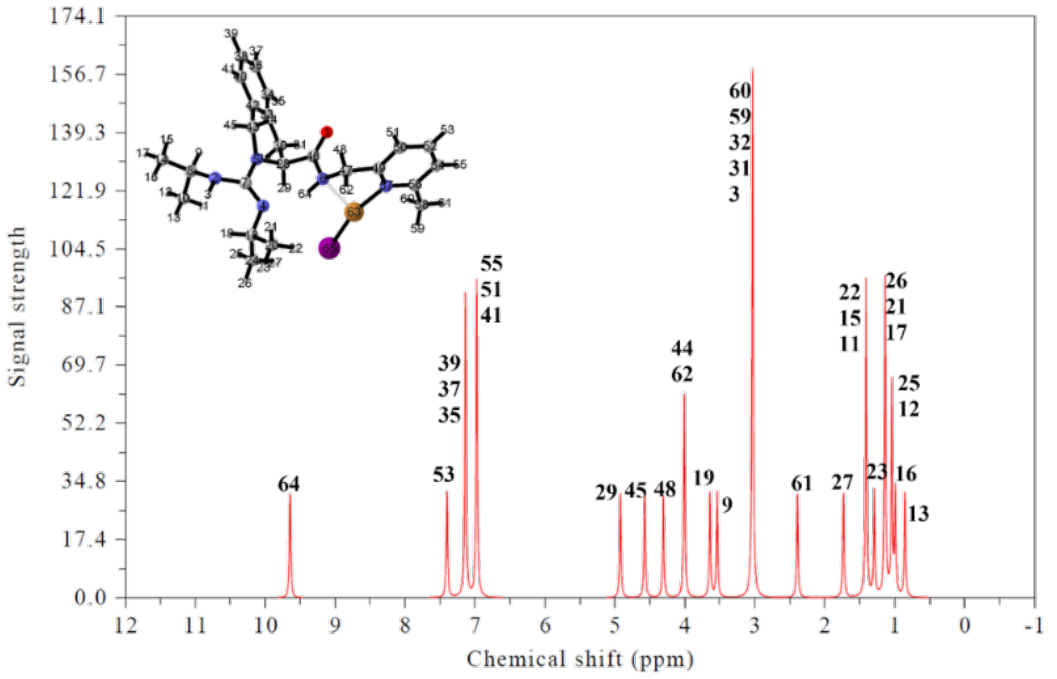


Figure S23. Simulated ^{1}H NMR of E4.

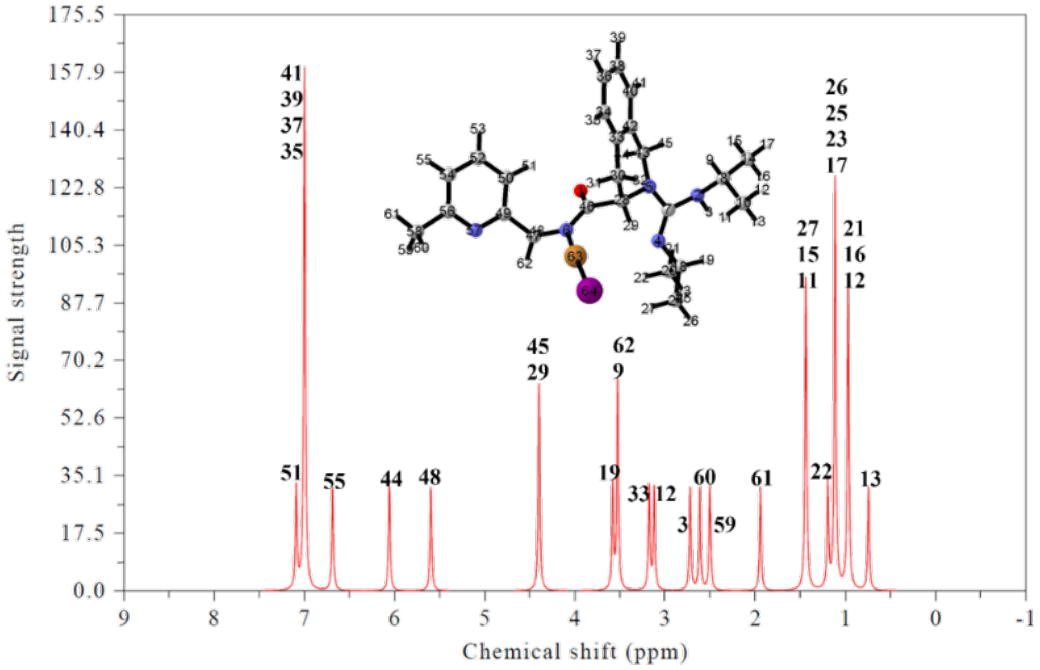


Figure S24. Simulated ^{1}H NMR of E5.

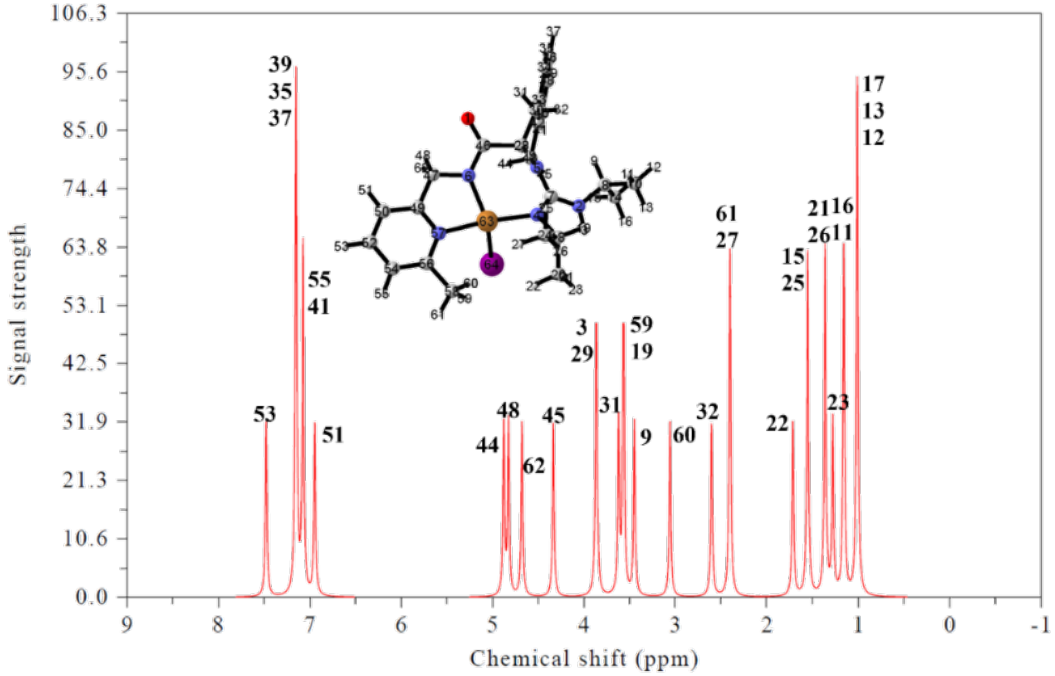


Figure S25. Simulated ^{1}H NMR of E6.

Table S26. The NMR comparison of simulated structures

	E1	E1'		E2	E2'	E3	E4	E5	E6
No.	CS	CS	No.	CS	CS	CS	CS	CS	CS
3(H)	2.977	2.654	3(H)	3.671	3.974	3.364	3.032	2.720	3.864
9(H)	3.557	3.322	9(H)	3.540	4.033	3.507	3.539	3.524	3.448
11(H)	1.266	0.710	11(H)	1.289	1.349	1.316	1.410	1.438	1.157
12(H)	0.979	0.738	12(H)	1.172	1.665	0.993	1.042	0.969	1.010
13(H)	0.804	0.769	13(H)	1.118	1.328	0.937	0.854	0.743	1.008
15(H)	1.401	1.016	15(H)	1.517	1.413	1.400	1.404	1.426	1.552
16(H)	0.986	1.000	16(H)	1.135	1.316	0.999	0.991	0.945	1.109
17(H)	1.101	0.767	17(H)	1.156	1.362	1.045	1.138	1.113	1.059
19(H)	3.482	3.224	19(H)	3.587	3.526	3.503	3.641	3.579	3.566
21(H)	1.107	1.103	21(H)	1.274	1.326	1.181	1.143	0.934	1.361
22(H)	1.500	1.663	22(H)	1.390	1.401	1.519	1.403	1.194	1.714
23(H)	1.180	0.757	23(H)	1.378	1.301	1.173	1.292	1.063	1.277
25(H)	0.895	0.580	25(H)	1.318	1.264	1.239	1.014	1.154	1.584
26(H)	1.014	0.435	26(H)	1.335	1.274	1.161	1.143	1.075	1.398
27(H)	1.040	0.364	27(H)	1.590	1.205	1.526	1.732	1.440	2.402
29(H)	4.197	4.220	29(H)	4.439	4.420	4.292	4.923	4.396	3.914
31(H)	3.449	3.316	31(H)	3.619	3.126	3.937	3.024	3.174	3.620
32(H)	2.737	2.508	32(H)	3.147	3.497	2.722	3.061	3.119	2.603
35(H)	7.173	7.014	35(H)	7.244	7.304	7.174	7.139	6.996	7.150
37(H)	7.180	6.958	37(H)	7.309	7.327	7.163	7.156	6.997	7.159
39(H)	7.123	6.868	39(H)	7.290	7.264	7.092	7.098	7.041	7.116
41(H)	6.987	6.807	41(H)	7.112	7.244	6.992	6.977	6.991	7.073
44(H)	4.295	3.960	44(H)	4.494	4.400	4.830	4.009	6.055	4.877
45(H)	4.419	4.115	45(H)	4.678	4.520	4.195	4.575	4.415	4.334
48(H)	4.874	4.367	48(H)	5.365	5.039	5.269	4.308	5.595	4.825
51(H)	7.286	6.873	51(H)	7.127	6.883	6.966	6.996	7.088	6.945
53(H)	7.440	7.372	53(H)	7.657	7.513	~~7.341~~	~~7.401~~	~~6.992~~	7.476
55(H)	6.961	6.866	55(H)	7.208	7.131	6.915	7.021	6.684	7.063
59(H)	2.604	2.331	59(H)	2.929	2.753	2.945	2.995	2.501	3.553
60(H)	2.658	2.235	60(H)	3.039	2.908	2.908	2.995	2.613	3.058
61(H)	2.076	2.367	61(H)	2.609	2.460	2.410	2.391	1.942	2.357
62(H)	3.587	3.865	62(H)	4.133	3.540	4.434	4.007	3.554	4.678
63(H)	8.649	10.992	64(H)	5.958	4.388	10.992	9.645		

It was found that protons related to *N*-isopropyl substituents (H 11-13, 15-17) and *para*-proton at pyridine ring (H 53) of the ligand appeared to significant downfield shift upon mixing CuI with the ligand G-TqPy-*o*Me, which E1 and E2 were well consistent with the ^{1}H NMR experiments. While the Boltzmann-weighted chemical shifts of E1' were inconsistent with the ^{1}H NMR experiments bearing a wider range of chemical shifts. It reveals the coordination of two sp^{2}-N of the ligand to the copper center.

9.2 Computational methods

Geometries were fully optimized by using B3LYP density functional, as implemented in Gaussian 09 program package[2]. The aug-cc-pVTZ-PP basis set was used for the I atom and LANL2DZ basis set and pseudopotential for the Cu atom, and the 6-31g(d) for C, H, O and N atom. The scaling method[3] was used to obtain the NMR shifts. Based on the optimized structures, the NMR shift was calculated at the same level using the gauge-invariant atomic orbital (GIAO) method. The SMD solvent model of chloroform was used during the calculation. The Boltzmann-weighted chemical shifts were calculated by using Multiwfn software[4] combined with xtb program[5] to generate the conformers. The cartesian coordinates of lowest free energy structures were given in this study.

9.3 Cartesian coordinats

E1

O	0.305680000	-2.796609000	0.154354000
N	-1.777995000	2.591989000	-0.483276000

H	-1.326516000	3.475644000	-0.690789000
N	0.395685000	1.784402000	0.134044000
N	-1.418844000	0.338536000	0.040274000
N	1.085461000	-0.864320000	-0.793762000
H	1.117657000	0.147701000	-0.625586000
C	-0.865386000	1.614563000	-0.084542000
C	-3.077192000	2.775459000	0.199120000
H	-3.519875000	1.781448000	0.303564000
C	-2.913879000	3.378930000	1.601850000
H	-2.264889000	2.752241000	2.222815000
H	-3.884366000	3.465260000	2.104549000
H	-2.472107000	4.382368000	1.549025000
C	-3.983264000	3.630511000	-0.690347000
H	-4.112321000	3.172233000	-1.676099000
H	-3.559533000	4.633339000	-0.834964000
H	-4.969975000	3.753051000	-0.231343000
C	1.014937000	3.098501000	0.241227000
H	0.267853000	3.891877000	0.424473000
C	1.761383000	3.426523000	-1.062968000
H	1.075027000	3.457332000	-1.917505000
H	2.515822000	2.657465000	-1.266271000
H	2.265878000	4.397573000	-0.992920000
C	1.977181000	3.088836000	1.436999000
H	1.439529000	2.868160000	2.365443000
H	2.475152000	4.059356000	1.548037000
H	2.742413000	2.316979000	1.297229000
C	-0.731232000	-0.690160000	0.830642000
H	-0.124382000	-0.156290000	1.568800000
C	-1.782993000	-1.543510000	1.551736000
H	-1.297863000	-2.445696000	1.935021000
H	-2.151202000	-0.973695000	2.415664000
C	-2.958372000	-1.927783000	0.674956000
C	-3.840892000	-2.936348000	1.084518000
H	-3.651849000	-3.453067000	2.023198000
C	-4.943343000	-3.289463000	0.310668000
H	-5.612911000	-4.077233000	0.645838000
C	-5.180770000	-2.630533000	-0.898300000
H	-6.039085000	-2.895898000	-1.509824000
C	-4.310052000	-1.627121000	-1.315265000
H	-4.489423000	-1.112224000	-2.257531000
C	-3.201054000	-1.268471000	-0.538688000
C	-2.247192000	-0.204859000	-1.041534000
H	-1.595897000	-0.634162000	-1.822767000
H	-2.794436000	0.614402000	-1.510955000
C	0.265969000	-1.574369000	0.025584000
C	2.199557000	-1.493960000	-1.493629000
H	1.907674000	-2.523841000	-1.710657000
C	3.480943000	-1.458384000	-0.679669000
C	3.780460000	-2.476235000	0.235116000
H	3.093531000	-3.306990000	0.360536000
C	4.954968000	-2.374183000	0.973996000
H	5.225952000	-3.145715000	1.690375000
C	5.782174000	-1.267938000	0.781053000
H	6.707928000	-1.160363000	1.339159000
C	5.402659000	-0.289840000	-0.144932000
N	4.269264000	-0.388961000	-0.862005000
C	6.245700000	0.936790000	-0.395677000
H	6.520293000	1.002819000	-1.454474000
H	5.681542000	1.845463000	-0.155069000
H	7.161805000	0.929332000	0.202781000
H	2.366281000	-0.959257000	-2.432998000

E1'

O	-0.538345000	-2.807878000	0.590005000
N	-1.230892000	2.786319000	-0.470132000
H	-0.531777000	3.392559000	-0.883010000
N	0.597844000	1.439629000	0.252870000
N	-1.518420000	0.615089000	0.339761000
N	0.591853000	-1.139776000	-0.446587000
C	-0.653391000	1.635486000	0.061674000
C	-2.195183000	3.565381000	0.297284000
H	-2.760501000	2.872604000	0.926033000
C	-1.492326000	4.572002000	1.212743000
H	-0.935951000	5.299481000	0.623206000
H	-0.799685000	4.058013000	1.877030000
H	-2.220656000	5.105457000	1.818308000
C	-3.144097000	4.273250000	-0.666822000
H	-3.898195000	4.828115000	-0.115163000
H	-3.639711000	3.549132000	-1.307774000
H	-2.591470000	4.968162000	-1.295331000
C	1.624461000	2.431606000	0.076860000
H	1.243645000	3.461029000	0.214370000
C	2.223657000	2.303333000	-1.328046000
H	2.651037000	1.310458000	-1.451677000
H	3.004744000	3.046269000	-1.473030000
H	1.456726000	2.446888000	-2.087621000
C	2.699915000	2.172981000	1.133059000
H	2.278617000	2.264664000	2.131537000
H	3.513791000	2.886207000	1.027289000
H	3.089799000	1.165463000	1.015121000
C	-1.095317000	-0.509721000	1.152651000
H	-0.396430000	-0.111890000	1.900333000
C	-2.326361000	-1.134748000	1.815875000
H	-2.014268000	-1.929793000	2.491237000
H	-2.865617000	-0.372304000	2.385255000
C	-3.178888000	-1.684986000	0.713882000
C	-3.738624000	-2.950997000	0.735542000
H	-3.601881000	-3.578807000	1.602875000
C	-4.456018000	-3.411573000	-0.354359000
H	-4.891572000	-4.399598000	-0.334209000
C	-4.602648000	-2.614043000	-1.476712000
H	-5.151183000	-2.978583000	-2.332806000
C	-4.040611000	-1.349747000	-1.506020000
H	-4.152366000	-0.725544000	-2.381555000
C	-3.330708000	-0.880999000	-0.411968000
C	-2.786324000	0.517386000	-0.366638000
H	-2.657825000	0.917331000	-1.377041000
H	-3.548315000	1.134216000	0.136858000
C	-0.324731000	-1.625662000	0.398134000
C	1.561599000	-1.976981000	-1.120783000
H	1.232748000	-3.014367000	-1.022825000
C	2.907457000	-1.768505000	-0.477601000
C	3.229705000	-2.392914000	0.721626000
H	2.534570000	-3.081468000	1.175484000
C	4.450678000	-2.101618000	1.306941000
H	4.739002000	-2.568584000	2.238028000
C	5.295778000	-1.200960000	0.681944000
H	6.254116000	-0.947501000	1.109728000
C	4.887389000	-0.617644000	-0.514645000
N	3.718346000	-0.902832000	-1.071278000
C	5.744890000	0.382470000	-1.226314000
H	6.758028000	0.003679000	-1.344253000

H	5.320928000	0.598077000	-2.202453000
H	5.792833000	1.306254000	-0.650956000
H	1.612228000	-1.692110000	-2.175151000
H	0.808419000	-0.136261000	-0.340150000

E2

O	0.361146000	-2.603899000	1.609357000
N	-1.790945000	2.364074000	-0.705243000
H	-1.378450000	3.238706000	-1.005005000
N	0.327655000	1.770281000	0.174212000
N	-1.345865000	0.148261000	-0.098834000
N	0.785086000	-1.616362000	-0.408552000
C	-0.904293000	1.458020000	-0.194888000
C	-3.230987000	2.471787000	-0.355989000
H	-3.555824000	1.474102000	-0.051391000
C	-3.429406000	3.430612000	0.826272000
H	-2.869213000	3.097350000	1.706684000
H	-4.488881000	3.483441000	1.098457000
H	-3.101216000	4.445887000	0.571272000
C	-4.024242000	2.910073000	-1.590069000
H	-3.899318000	2.207909000	-2.420777000
H	-3.702790000	3.901460000	-1.933145000
H	-5.090386000	2.972813000	-1.351743000
C	0.651161000	3.184882000	0.484580000
H	-0.283449000	3.719288000	0.698645000
C	1.347900000	3.871964000	-0.699072000
H	0.732930000	3.854986000	-1.606921000
H	2.292354000	3.368059000	-0.937172000
H	1.573095000	4.917214000	-0.461994000
C	1.502210000	3.248734000	1.757363000
H	0.987694000	2.770862000	2.597227000
H	1.706639000	4.290329000	2.027427000
H	2.464723000	2.743990000	1.614133000
C	-0.983209000	-0.679309000	1.055127000
H	-0.475047000	-0.016078000	1.762509000
C	-2.235364000	-1.243127000	1.748530000
H	-1.916066000	-2.043321000	2.423357000
H	-2.656918000	-0.449287000	2.379401000
C	-3.298164000	-1.738684000	0.790498000
C	-4.314682000	-2.587386000	1.252545000
H	-4.304973000	-2.908001000	2.291550000
C	-5.326895000	-3.023051000	0.402353000
H	-6.104043000	-3.682254000	0.777657000
C	-5.337282000	-2.613095000	-0.934668000
H	-6.124492000	-2.946218000	-1.604411000
C	-4.331785000	-1.773854000	-1.404760000
H	-4.334130000	-1.458676000	-2.446441000
C	-3.312658000	-1.330786000	-0.549713000
C	-2.205492000	-0.468282000	-1.121285000
H	-1.587823000	-1.093333000	-1.791580000
H	-2.609878000	0.321010000	-1.755231000
C	0.074696000	-1.764842000	0.776168000
C	1.873534000	-2.520902000	-0.727937000
H	1.776653000	-3.396973000	-0.079050000
C	3.270409000	-1.932851000	-0.545619000
C	4.359630000	-2.789557000	-0.713043000
H	4.186593000	-3.835783000	-0.946018000
C	5.647246000	-2.288579000	-0.574365000
H	6.509708000	-2.936326000	-0.698982000
C	5.811978000	-0.938866000	-0.268910000
H	6.802003000	-0.512093000	-0.151766000

C	4.692280000	-0.125897000	-0.106984000
N	3.432345000	-0.624891000	-0.247461000
C	4.839523000	1.330357000	0.238746000
H	4.292510000	1.961535000	-0.470709000
H	4.447167000	1.533496000	1.242378000
H	5.889560000	1.632923000	0.222574000
H	1.767966000	-2.863503000	-1.763656000
Cu	1.833529000	0.530009000	0.003151000
H	0.317211000	-1.146292000	-1.171659000

E2’

O	-0.465078000	0.971386000	2.824108000
N	2.526190000	-2.022018000	-0.735785000
H	2.255784000	-2.922264000	-1.113883000
N	0.367547000	-1.895184000	0.218229000
N	1.700547000	0.027195000	0.067144000
N	-0.808965000	1.357616000	0.593004000
C	1.510756000	-1.335006000	-0.130640000
C	3.970310000	-1.935424000	-0.405063000
H	4.113109000	-0.986460000	0.117016000
C	4.370788000	-3.071772000	0.546672000
H	3.789502000	-3.039305000	1.474407000
H	5.431499000	-2.992386000	0.807127000
H	4.218683000	-4.051486000	0.076950000
C	4.800739000	-1.945873000	-1.691787000
H	4.524944000	-1.119225000	-2.353495000
H	4.655147000	-2.883881000	-2.241416000
H	5.866908000	-1.862058000	-1.458622000
C	0.305359000	-3.363933000	0.414112000
H	1.317385000	-3.727940000	0.637103000
C	-0.209200000	-4.087136000	-0.840058000
H	0.414857000	-3.894514000	-1.721454000
H	-1.225802000	-3.759323000	-1.083552000
H	-0.233413000	-5.169656000	-0.675515000
C	-0.570175000	-3.670966000	1.634043000
H	-0.191121000	-3.163550000	2.526536000
H	-0.589468000	-4.748480000	1.829652000
H	-1.603631000	-3.339711000	1.469566000
C	1.429502000	0.604751000	1.398003000
H	1.660195000	-0.144483000	2.160375000
C	2.325601000	1.848643000	1.626207000
H	2.078289000	2.283936000	2.598532000
H	3.371185000	1.514091000	1.679773000
C	2.132616000	2.834679000	0.499800000
C	1.911992000	4.200539000	0.687220000
H	1.905816000	4.613112000	1.692965000
C	1.704916000	5.035396000	-0.414473000
H	1.543979000	6.098741000	-0.263085000
C	1.697874000	4.504301000	-1.705942000
H	1.531344000	5.152177000	-2.561392000
C	1.905317000	3.135774000	-1.899675000
H	1.905169000	2.721912000	-2.905434000
C	2.130262000	2.301957000	-0.800851000
C	2.433510000	0.829039000	-0.944901000
H	2.150549000	0.464013000	-1.935947000
H	3.519620000	0.687750000	-0.852512000
C	-0.031404000	0.995941000	1.685361000
C	-2.126493000	1.937032000	0.805328000
H	-2.298172000	1.914016000	1.887959000
C	-3.258646000	1.198500000	0.109095000
C	-4.454732000	1.873580000	-0.135447000

H	-4.541840000	2.924091000	0.123465000
C	-5.519695000	1.183051000	-0.702778000
H	-6.461779000	1.685722000	-0.899943000
C	-5.356571000	-0.164007000	-1.018021000
H	-6.165486000	-0.733066000	-1.462874000
C	-4.136046000	-0.789253000	-0.764606000
N	-3.101625000	-0.106689000	-0.205728000
C	-3.919472000	-2.238274000	-1.104590000
H	-3.128355000	-2.347303000	-1.856112000
H	-3.618877000	-2.806608000	-0.217007000
H	-4.831106000	-2.688991000	-1.504801000
H	-2.135204000	2.987468000	0.494509000
Cu	-1.319690000	-0.926823000	0.087771000
H	-0.306593000	1.624782000	-0.247227000

E3

O	-0.246781000	-2.951833000	1.495174000
N	-1.678621000	2.345599000	-0.731337000
H	-1.232702000	3.217691000	-0.985153000
N	0.342909000	1.775237000	0.378551000
N	-1.336557000	0.173141000	0.035773000
N	0.954011000	-1.533002000	0.107850000
C	-0.851524000	1.450152000	-0.079018000
C	-3.133364000	2.461396000	-0.509297000
H	-3.512623000	1.448599000	-0.357582000
C	-3.449309000	3.289942000	0.745355000
H	-2.980839000	2.848913000	1.631821000
H	-4.530876000	3.333232000	0.918621000
H	-3.084358000	4.319797000	0.640194000
C	-3.785106000	3.051943000	-1.763231000
H	-3.578107000	2.434876000	-2.643476000
H	-3.410938000	4.065287000	-1.961675000
H	-4.870503000	3.119992000	-1.635523000
C	0.662239000	3.183882000	0.660223000
H	-0.270897000	3.743671000	0.826837000
C	1.418901000	3.840763000	-0.505754000
H	0.838217000	3.822789000	-1.436343000
H	2.353856000	3.302659000	-0.696628000
H	1.661578000	4.885185000	-0.276600000
C	1.476058000	3.263131000	1.957481000
H	0.920162000	2.819331000	2.789790000
H	1.708651000	4.304758000	2.209307000
H	2.418213000	2.712415000	1.851545000
C	-1.059168000	-0.695970000	1.190789000
H	-0.589273000	-0.063651000	1.950096000
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H	-2.177108000	-2.052139000	2.401795000
H	-2.868060000	-0.420294000	2.344721000
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C	-4.507463000	-2.407567000	1.009762000
H	-4.654271000	-2.690815000	2.049932000
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C	-5.237043000	-2.452429000	-1.291003000
H	-5.952029000	-2.757786000	-2.050487000
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H	-3.959699000	-1.424964000	-2.686327000
C	-3.188923000	-1.296874000	-0.678559000
C	-1.957298000	-0.519081000	-1.095404000
H	-1.206363000	-1.203785000	-1.519261000
H	-2.198892000	0.211795000	-1.870039000

C	-0.061574000	-1.867713000	0.913563000
C	1.971887000	-2.539950000	-0.043892000
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H	6.524332000	-2.881072000	-1.060287000
C	5.838623000	-0.859474000	-0.723775000
H	6.808695000	-0.398083000	-0.878906000
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N	3.507504000	-0.606008000	-0.218263000
C	4.854532000	1.430548000	-0.315088000
H	4.273818000	1.920760000	-1.105586000
H	4.457964000	1.781938000	0.643760000
H	5.896223000	1.753554000	-0.403220000
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Cu	1.721202000	0.362555000	0.139587000

E4

O	0.067499000	2.397277000	0.301569000
N	-3.688961000	-1.449161000	1.408613000
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N	-1.304434000	-1.741709000	1.308288000
N	-2.327441000	0.101923000	0.316263000
N	0.650699000	0.368605000	1.181534000
C	-2.390581000	-1.097406000	1.032972000
C	-4.788435000	-1.517935000	0.418878000
H	-4.749200000	-0.591238000	-0.159985000
C	-4.624357000	-2.698005000	-0.549818000
H	-3.668114000	-2.638441000	-1.080343000
H	-5.426749000	-2.701678000	-1.296803000
H	-4.659749000	-3.655112000	-0.013701000
C	-6.120167000	-1.575241000	1.171989000
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H	-6.187349000	-2.485505000	1.782813000
H	-6.959755000	-1.587715000	0.469000000
C	-1.291617000	-3.120068000	1.793012000
H	-2.292682000	-3.467927000	2.101164000
C	-0.379683000	-3.207298000	3.024823000
H	-0.727135000	-2.537754000	3.820199000
H	0.645860000	-2.924256000	2.758894000
H	-0.356737000	-4.229089000	3.420500000
C	-0.807898000	-4.053018000	0.671873000
H	-1.502132000	-4.033229000	-0.175400000
H	-0.735837000	-5.086342000	1.032565000
H	0.173983000	-3.737416000	0.303784000
C	-1.137683000	0.414651000	-0.488625000
H	-0.689937000	-0.537048000	-0.785404000
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C	-2.635382000	2.234461000	-1.502842000
C	-2.932805000	3.176659000	-2.496636000
H	-2.360858000	3.166778000	-3.422171000
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H	-4.151870000	4.845867000	-3.098392000
C	-4.673320000	4.135733000	-1.126564000
H	-5.464134000	4.865826000	-0.976480000
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H	-4.953847000	3.208855000	0.795838000
C	-3.374256000	2.251165000	-0.311697000

C	-3.048401000	1.284236000	0.806030000
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H	-3.956257000	0.952976000	1.311578000
C	-0.092032000	1.184446000	0.348397000
C	1.390672000	0.985862000	2.272033000
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C	2.660763000	1.697709000	1.836304000
C	3.114140000	2.813043000	2.541068000
H	2.522890000	3.208393000	3.360773000
C	4.314472000	3.406062000	2.165673000
H	4.688268000	4.278095000	2.694877000
C	5.025926000	2.871735000	1.093660000
H	5.962680000	3.313159000	0.770120000
C	4.521507000	1.758474000	0.419120000
N	3.353061000	1.186098000	0.800577000
C	5.243179000	1.152200000	-0.753660000
H	5.441579000	0.088271000	-0.582049000
H	4.631590000	1.216852000	-1.661062000
H	6.193069000	1.662341000	-0.937675000
H	1.661218000	0.185222000	2.971453000
Cu	2.567783000	-0.341759000	-0.241051000
H	0.205275000	-0.550167000	1.349406000
I	2.276381000	-2.171806000	-1.847481000

E5

O	-0.338762000	1.550943000	1.831305000
N	-4.555829000	-0.083732000	0.872624000
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N	-2.580161000	-1.288631000	1.543887000
N	-2.416760000	0.569654000	0.156317000
N	1.133488000	-0.036120000	1.030576000
C	-3.162705000	-0.334567000	0.909641000
C	-5.248683000	-0.016850000	-0.429465000
H	-4.684742000	0.685898000	-1.048894000
C	-5.278892000	-1.369964000	-1.158452000
H	-4.263964000	-1.757763000	-1.293533000
H	-5.742109000	-1.273819000	-2.148704000
H	-5.854496000	-2.110691000	-0.587443000
C	-6.657511000	0.542538000	-0.208304000
H	-6.615384000	1.521235000	0.281024000
H	-7.250242000	-0.128799000	0.428612000
H	-7.190245000	0.649180000	-1.160412000
C	-3.314471000	-2.374077000	2.164967000
H	-4.323621000	-2.511642000	1.726995000
C	-3.488811000	-2.093611000	3.668878000
H	-4.075363000	-1.182138000	3.837291000
H	-2.507423000	-1.944368000	4.132196000
H	-3.993299000	-2.928151000	4.173272000
C	-2.542129000	-3.681701000	1.937639000
H	-2.425770000	-3.878304000	0.866676000
H	-3.061821000	-4.533772000	2.395359000
H	-1.538687000	-3.604981000	2.370049000
C	-1.010373000	0.236651000	-0.103062000
H	-0.961737000	-0.848960000	-0.198872000
C	-0.621773000	0.859412000	-1.461211000
H	0.462301000	0.782306000	-1.597802000
H	-1.075719000	0.248080000	-2.254447000
C	-1.075249000	2.292418000	-1.637115000
C	-0.497844000	3.104924000	-2.624018000
H	0.310233000	2.699515000	-3.230072000
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H	-0.473843000	5.022853000	-3.605943000

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C	-2.111840000	2.813744000	-0.848067000
C	-2.716282000	2.005792000	0.277591000
H	-2.310161000	2.373493000	1.228037000
H	-3.799574000	2.142237000	0.293845000
C	-0.030012000	0.638778000	1.033462000
C	2.075858000	0.336177000	2.092700000
H	1.507354000	0.720207000	2.951150000
C	3.084212000	1.389382000	1.667576000
C	2.652556000	2.646081000	1.202967000
H	1.589430000	2.860181000	1.172851000
C	3.608679000	3.575567000	0.817341000
H	3.308729000	4.557503000	0.457052000
C	4.962939000	3.236845000	0.900377000
H	5.736100000	3.940251000	0.601226000
C	5.307777000	1.970713000	1.376943000
N	4.383216000	1.068893000	1.755485000
C	6.748459000	1.528120000	1.487537000
H	6.970177000	1.192916000	2.507509000
H	6.938922000	0.676094000	0.823925000
H	7.442404000	2.334072000	1.224556000
H	2.638778000	-0.546999000	2.407571000
Cu	1.638795000	-1.440153000	-0.178823000
I	2.227834000	-3.241295000	-1.759711000

E6

O	1.054249000	3.433306000	0.914964000
N	1.820056000	-2.340561000	0.261232000
H	1.241319000	-3.168147000	0.195233000
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N	1.769368000	-0.001304000	0.353603000
N	-0.513614000	1.843970000	0.394968000
C	1.160703000	-1.199796000	0.620770000
C	3.274405000	-2.570295000	0.256337000
H	3.745979000	-1.585128000	0.235743000
C	3.713432000	-3.295279000	1.538002000
H	3.439629000	-2.717991000	2.427563000
H	4.799637000	-3.440822000	1.545230000
H	3.242020000	-4.283462000	1.611521000
C	3.674844000	-3.348039000	-1.002488000
H	3.377786000	-2.815140000	-1.911085000
H	3.198381000	-4.336605000	-1.020060000
H	4.758923000	-3.500805000	-1.028635000
C	-0.424060000	-2.340741000	2.060579000
H	0.498091000	-2.831560000	2.407160000
C	-1.287867000	-3.406493000	1.367983000
H	-0.803718000	-3.831918000	0.482542000
H	-2.241294000	-2.990323000	1.030892000
H	-1.495372000	-4.223516000	2.069749000
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H	-0.509106000	-1.065734000	3.828149000
H	-1.414754000	-2.588548000	3.986812000
H	-2.064483000	-1.262083000	3.003387000
C	1.653024000	1.121303000	1.292690000
H	1.217916000	0.708785000	2.207087000
C	3.063930000	1.648614000	1.601864000
H	2.966206000	2.633797000	2.065403000
H	3.527394000	0.979012000	2.340408000
C	3.970210000	1.743920000	0.388881000

C	5.165582000	2.472637000	0.464003000
H	5.411001000	2.987571000	1.390427000
C	6.032495000	2.553151000	-0.622976000
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C	5.712586000	1.898798000	-1.815893000
H	6.382079000	1.954376000	-2.670011000
C	4.527461000	1.172599000	-1.903697000
H	4.270438000	0.664995000	-2.831674000
C	3.655093000	1.087488000	-0.810792000
C	2.350856000	0.328560000	-0.948139000
H	1.620604000	0.934546000	-1.507720000
H	2.485401000	-0.592786000	-1.518376000
C	0.696571000	2.249446000	0.830960000
C	-1.429892000	2.928898000	0.099013000
H	-1.330558000	3.742626000	0.833126000
C	-2.864954000	2.469582000	0.071579000
C	-3.898333000	3.383205000	-0.163322000
H	-3.656982000	4.423151000	-0.360923000
C	-5.212114000	2.939033000	-0.126279000
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C	-5.465695000	1.597361000	0.162164000
H	-6.482193000	1.223070000	0.223457000
C	-4.400742000	0.724604000	0.378797000
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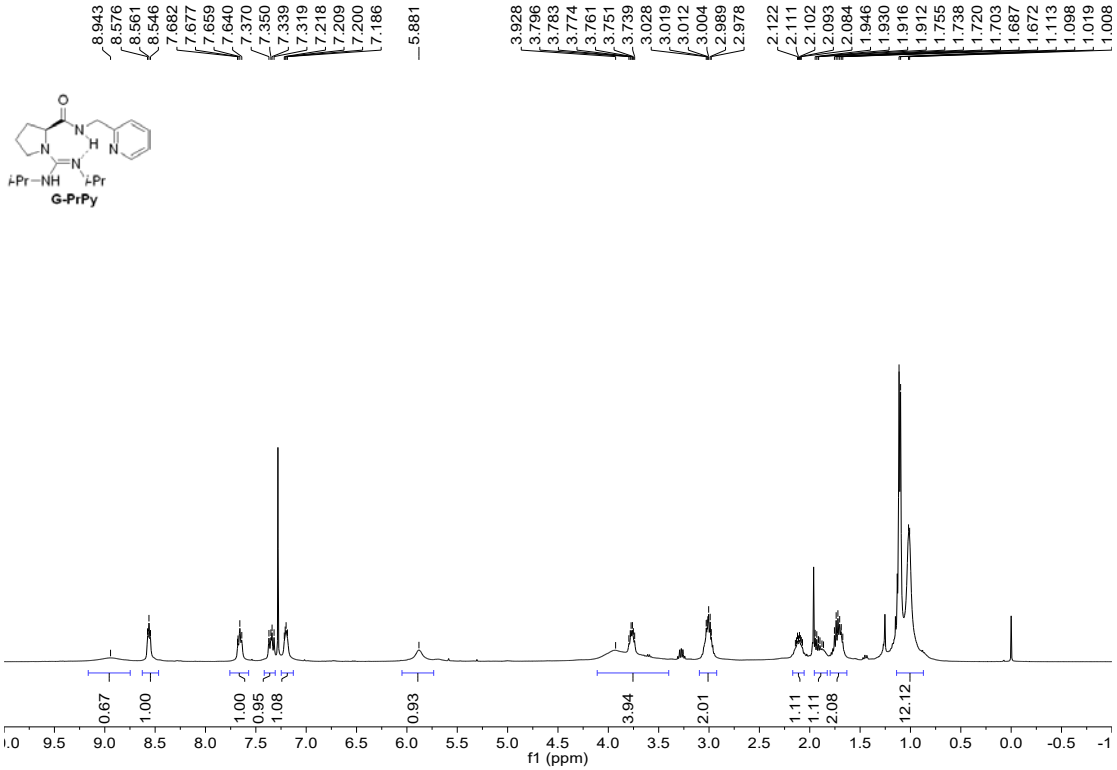
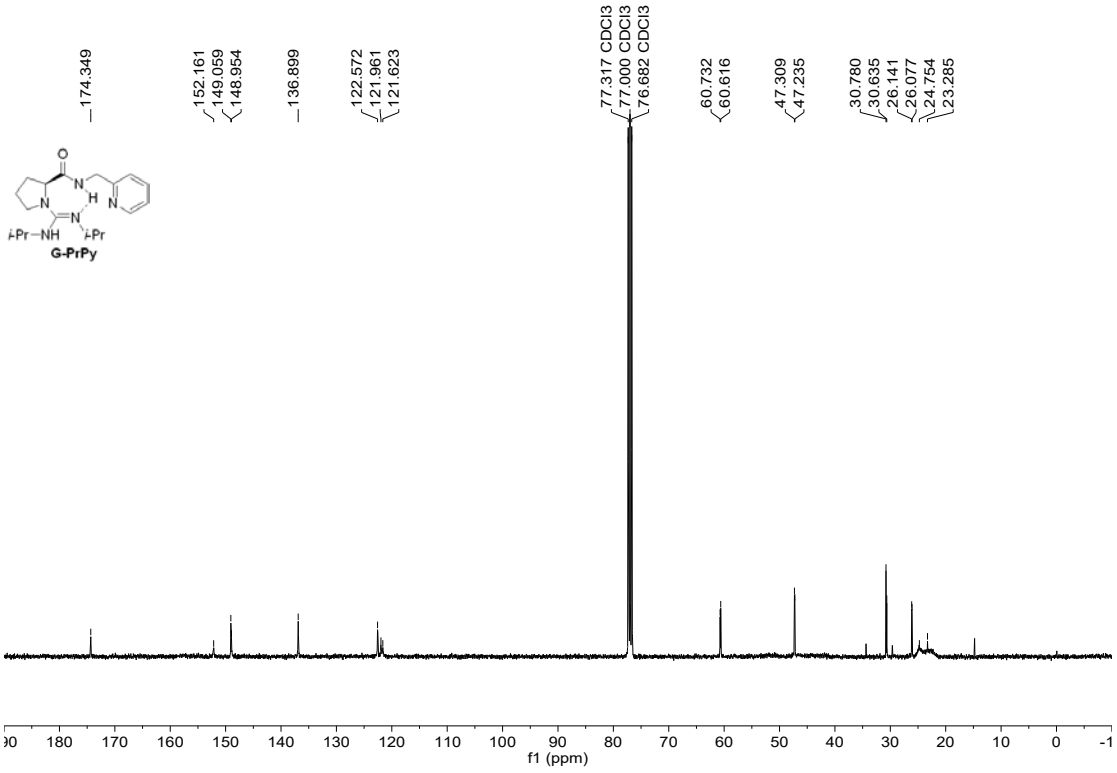
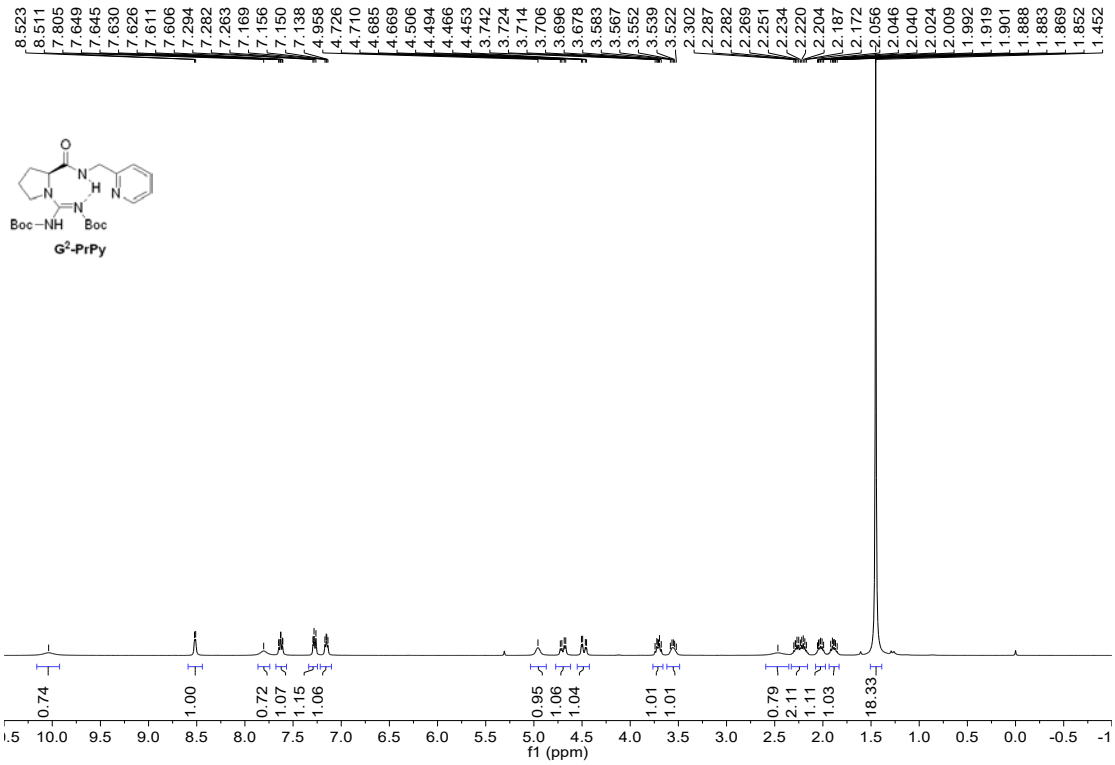
C	-4.635280000	-0.721834000	0.714067000
H	-4.244626000	-1.368498000	-0.079135000
H	-4.120988000	-0.992010000	1.643919000
H	-5.702710000	-0.922555000	0.841483000
H	-1.186419000	3.391098000	-0.872233000
Cu	-1.352334000	0.048520000	0.283564000
I	-1.847702000	-1.451643000	-1.876227000

10. Copies of NMR spectra for the ligands and the products



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2.269
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2.172
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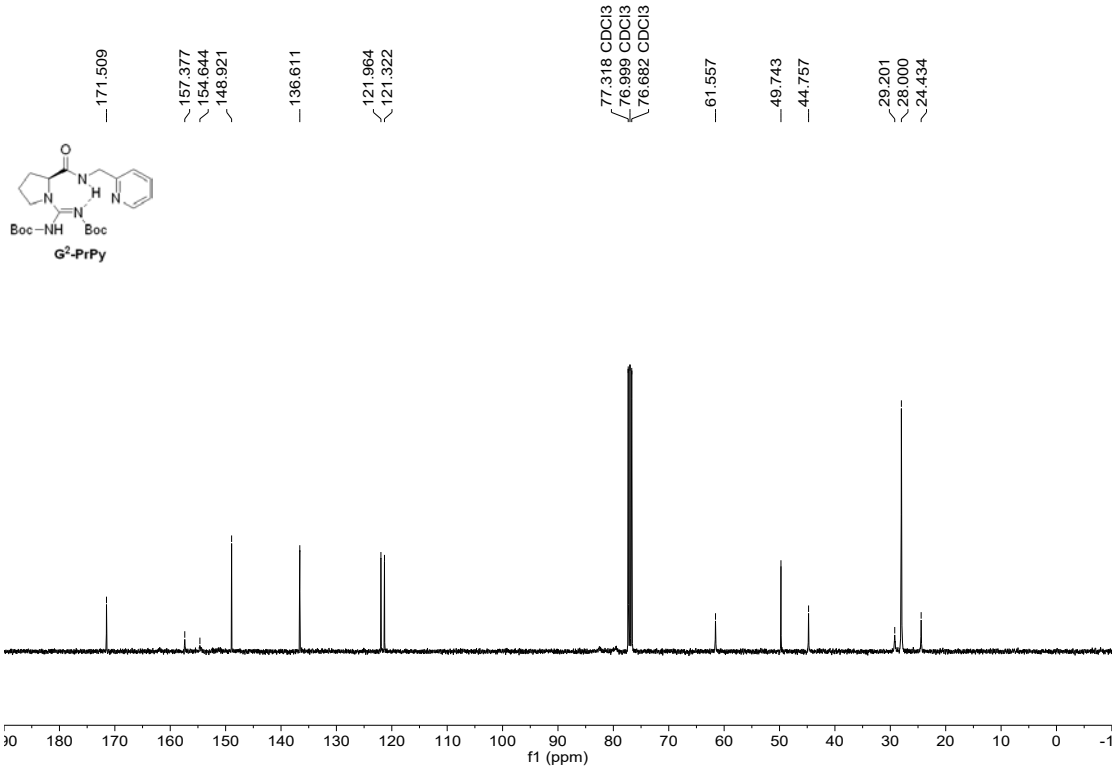
2.046
2.040
2.024
2.009
1.992
1.919
1.901
1.888
1.883
1.869
1.852
1.452
Boc–NH
Boc
G2-PrPy
0.74
1.00
0.72
1.07
1.15
1.06
0.95
1.06
1.04
1.01
1.01
0.79
2.11
1.11
1.03
18.33
f1 (ppm)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76.999 CDCl3
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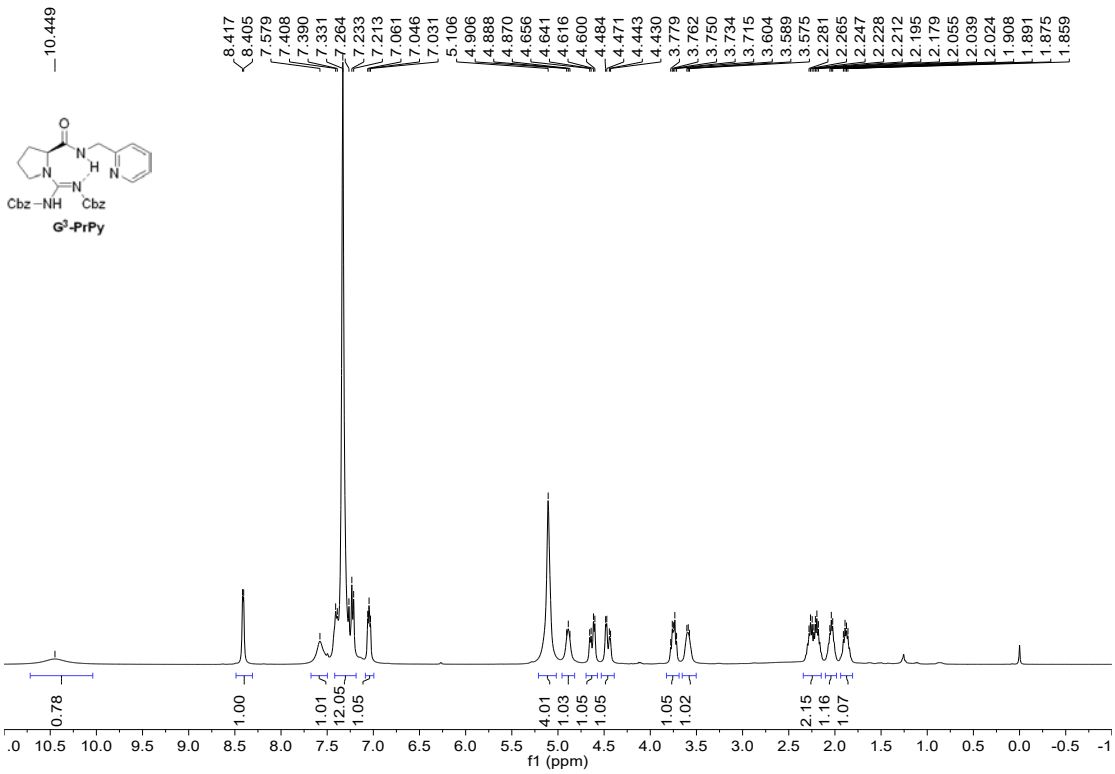
49.743
44.757
29.201
28.000
24.434
Boc–NH
Boc
G2-PrPy
f1 (ppm)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3.779
3.762
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3.715
3.604
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2.195
2.179
2.055
2.039
2.024
1.908
1.891
1.875
1.859
Cbz–NH Cbz
G3-PrPy
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1.00
1.01
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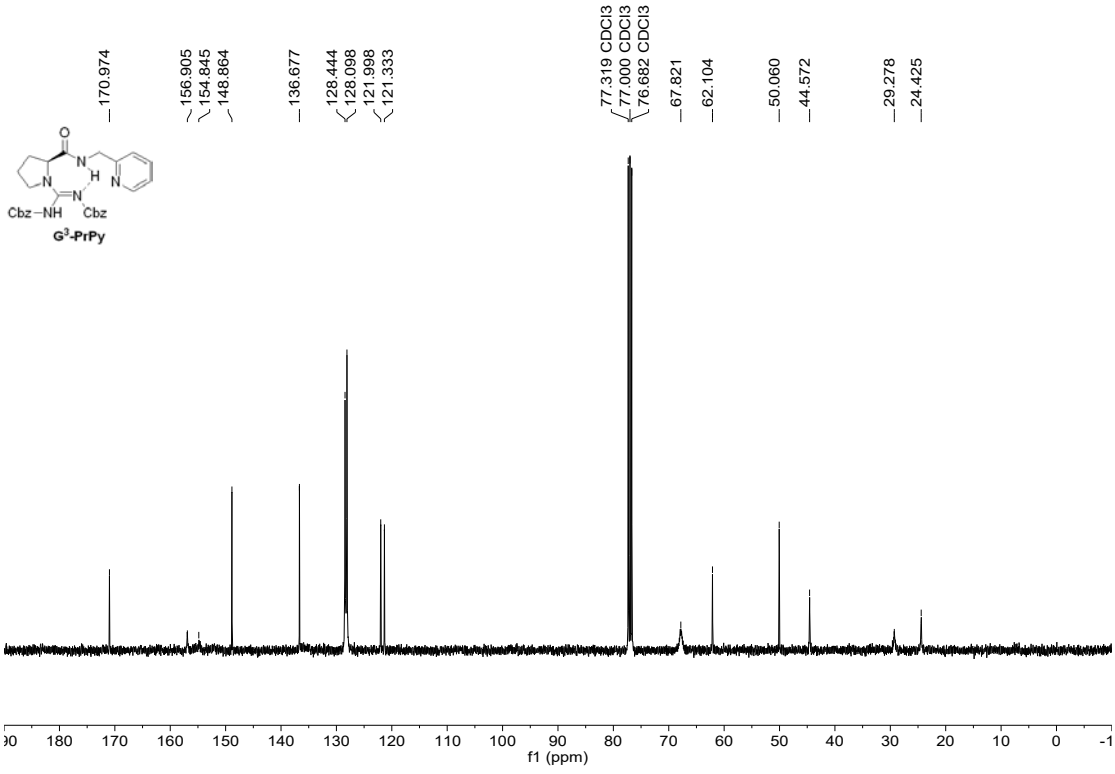
1.05
1.05
1.05
1.02
2.15
1.16
1.07
f1 (ppm)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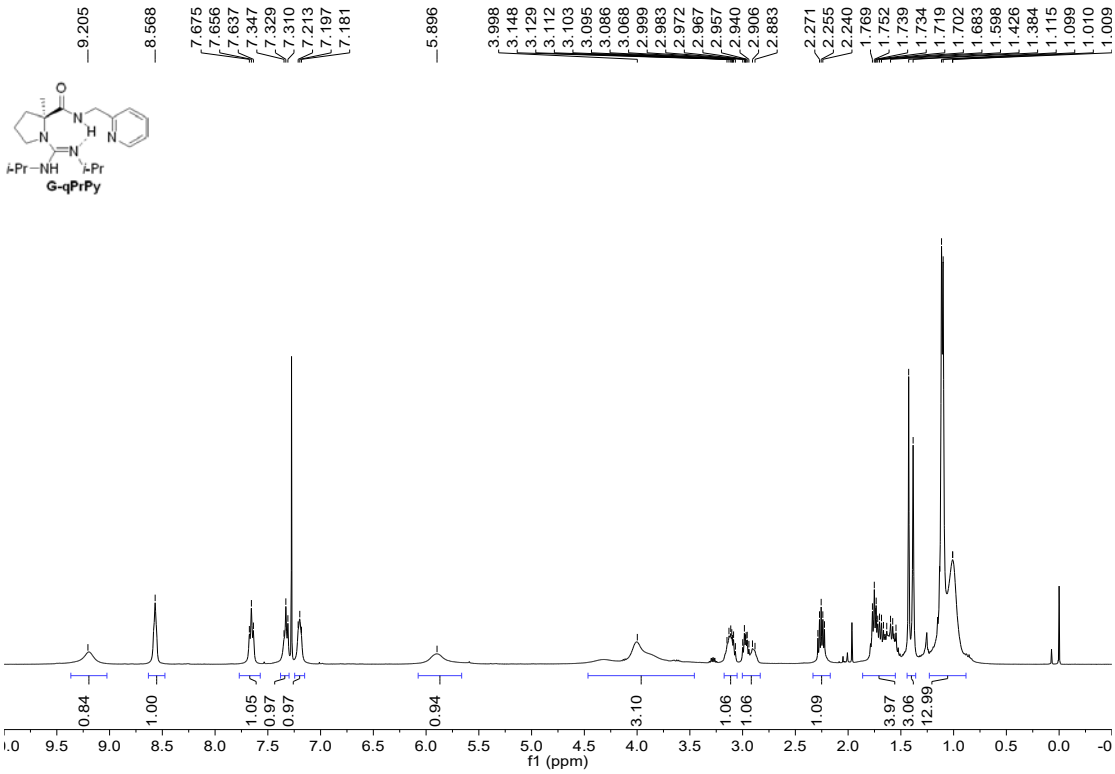
62.104
50.060
44.572
29.278
24.425
Cbz–NH Cbz
G3-PrPy
f1 (ppm)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3.095
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1.115
1.099
1.010
1.009
i-Pr—NH
i-Pr
G-qPrPy
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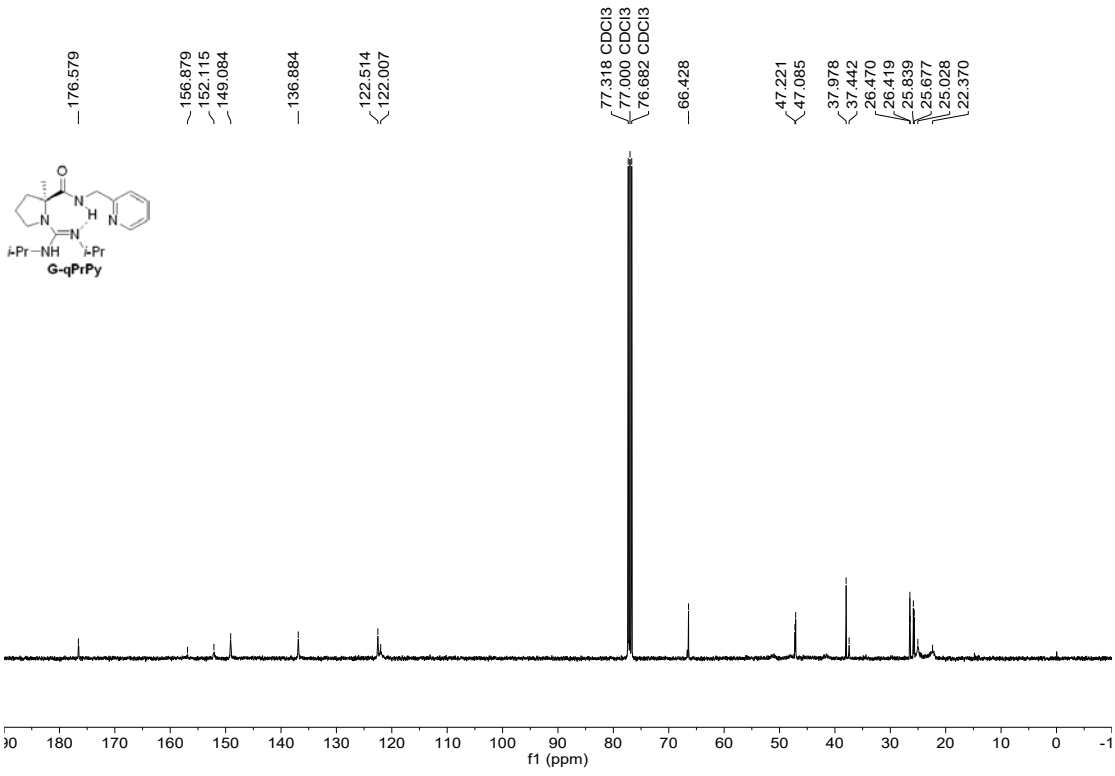
1.05
0.97
0.97
0.94
3.10
1.06
1.06
1.09
3.97
3.06
12.99
f1 (ppm)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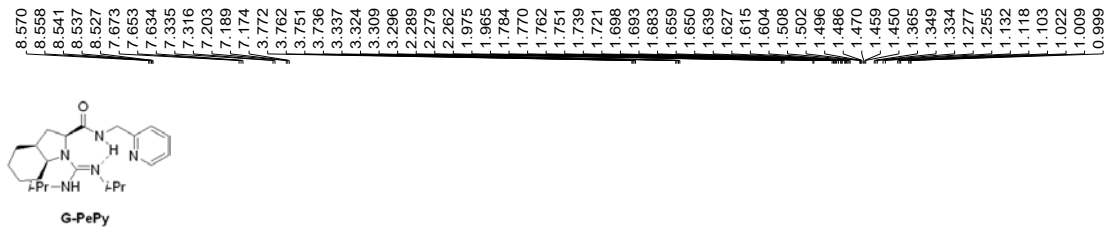
156.879
152.115
149.084
136.884
122.514
122.007
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
66.428
47.221
47.085
37.978
37.442
26.470
26.419
25.839
25.677
25.028
22.370
i-Pr—NH
i-Pr
G-qPrPy
f1 (ppm)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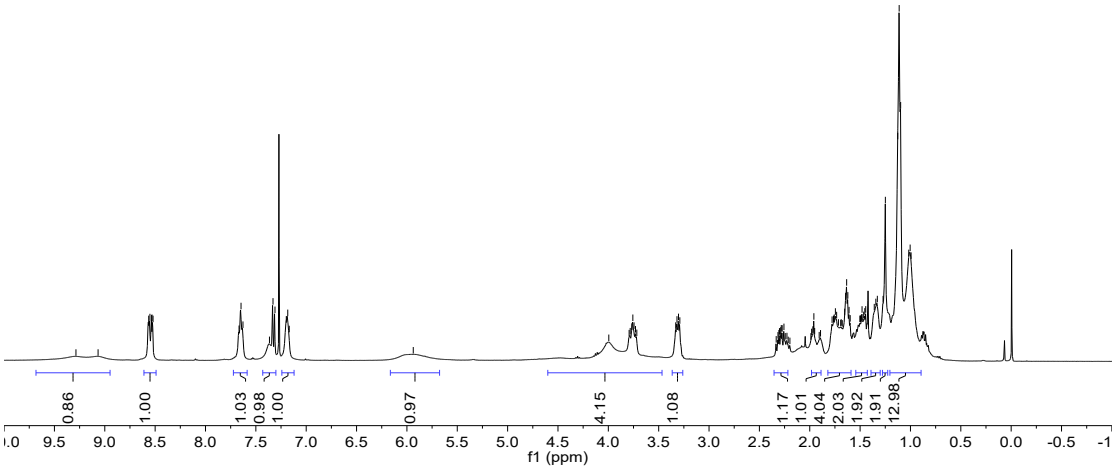
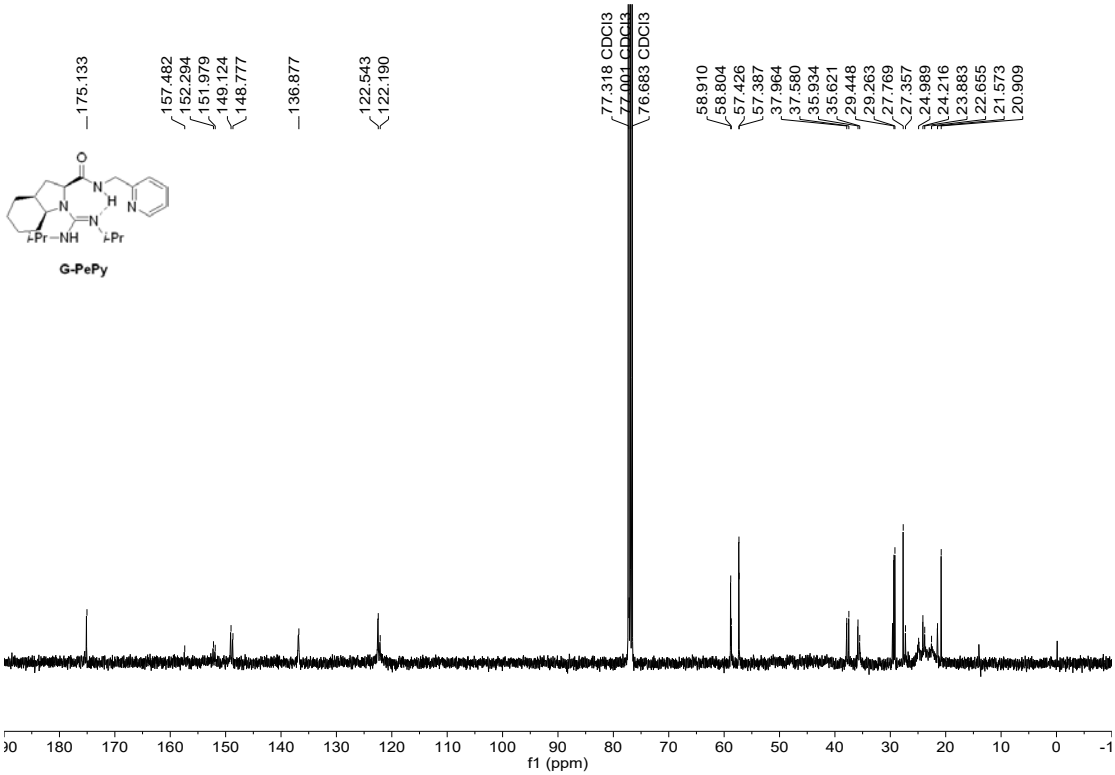
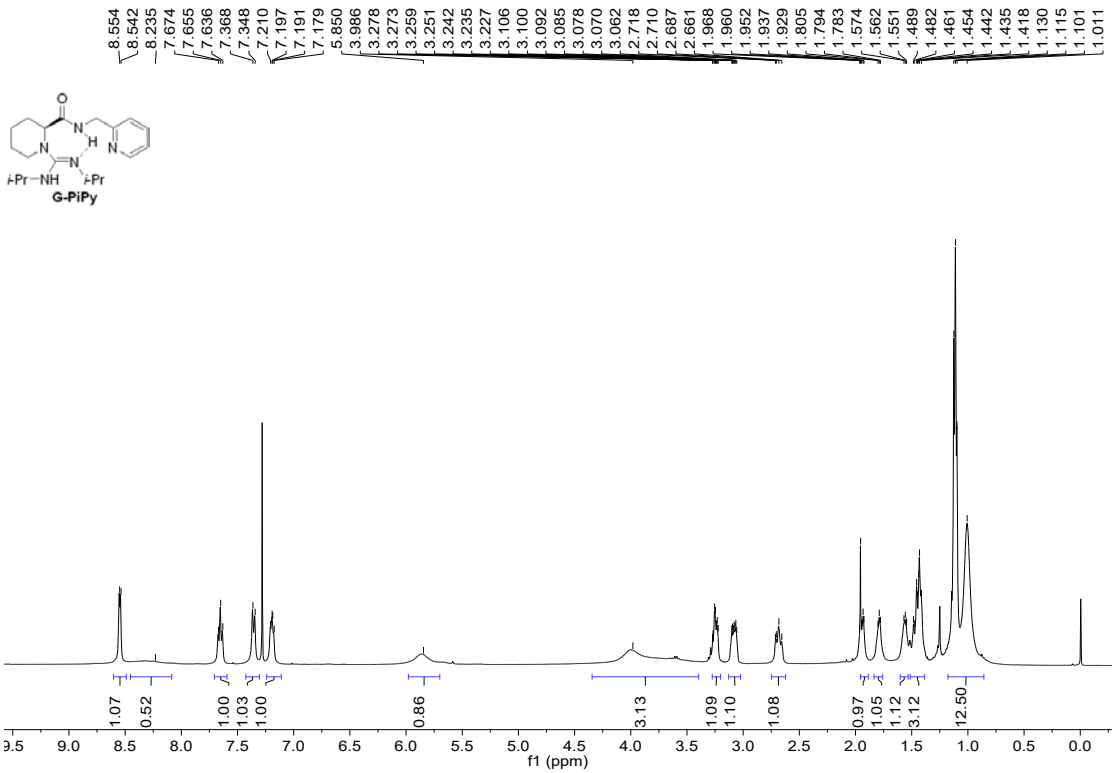
8.558
8.541
8.537
8.527
7.673
7.653
7.634
7.335
7.316
7.203
7.189
7.174
3.772
3.762
3.751
3.736
3.337
3.324
3.309
3.296
2.289
2.279
2.262
1.975
1.965
1.784
1.770
1.762
1.751
1.739
1.721
1.698
1.693
1.683
1.659
1.650
1.639
1.627
1.615
1.604
1.508
1.502
1.496
1.486
1.470
1.459
1.450
1.365
1.349
1.334
1.277
1.255
1.132
1.118
1.103
1.022
1.009
0.999

G-PePy


0.86
1.00
1.03
0.98
1.00
0.97
4.15
1.08
1.17
1.01
4.04
2.03
1.92
1.91
12.98
f1 (ppm)


175.133
157.482
152.294
151.979
149.124
148.777
136.877
122.543
122.190
77.318 CDCl3
77.001 CDCl3
76.683 CDCl3
58.910
58.804
57.426
57.387
37.964
37.580
35.934
35.621
29.448
29.263
27.769
27.357
24.989
24.216
23.883
22.655
21.573
20.909
f1 (ppm)

G-PePy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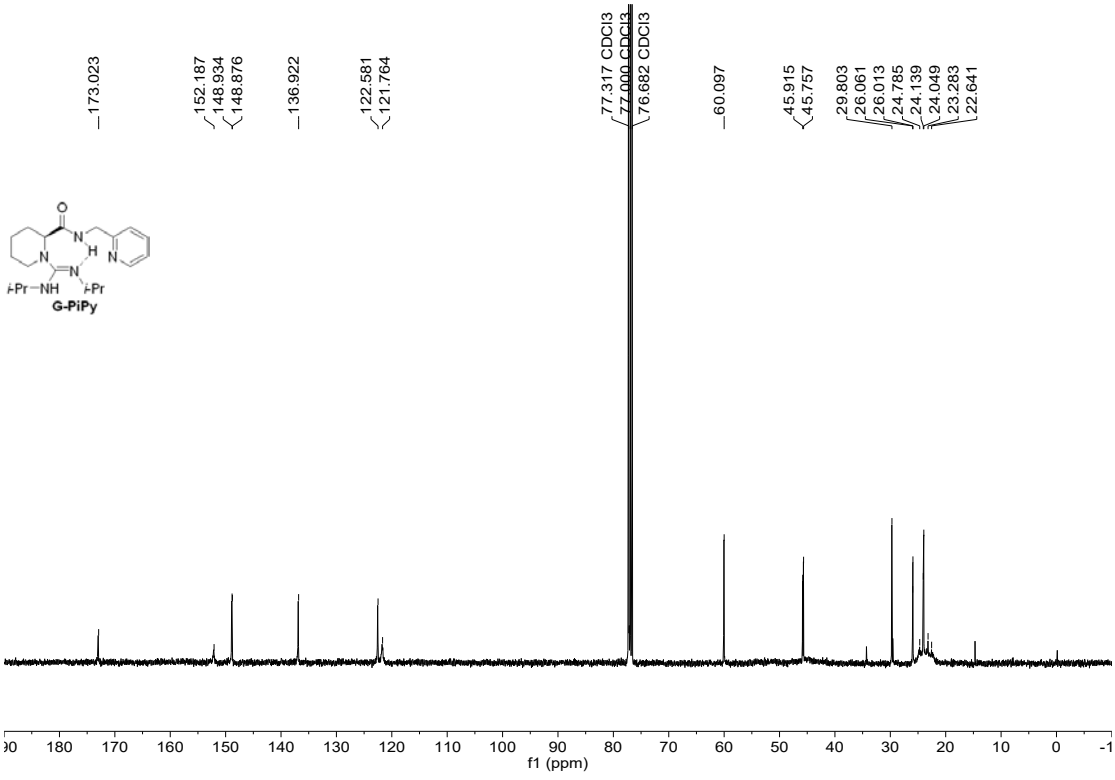
8.542
8.235
7.674
7.655
7.636
7.368
7.348
7.210
7.197
7.191
7.179
5.850
3.986
3.278
3.273
3.259
3.251
3.242
3.235
3.227
3.106
3.100
3.092
3.085
3.078
3.070
3.062
2.718
2.710
2.687
2.661
1.968
1.960
1.952
1.937
1.929
1.805
1.794
1.783
1.574
1.562
1.551
1.489
1.482
1.461
1.454
1.442
1.435
1.418
1.130
1.115
1.101
1.011
i-Pr
NH
i-Pr
G-PiPy
1.07
0.52
1.00
1.03
1.00
0.86
3.13
1.09
1.10
1.08
0.97
1.05
1.12
3.12
12.50
f1 (ppm)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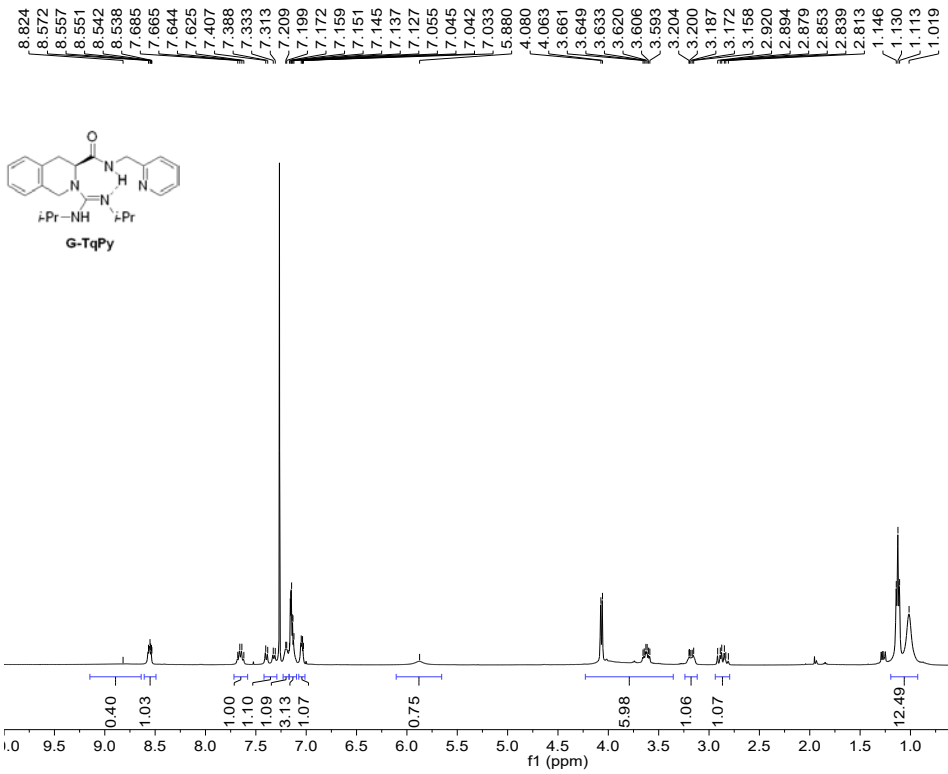
152.187
148.934
148.876
136.922
122.581
121.764
77.317 CDCl3
77.000 CDCl3
76.682 CDCl3
60.097
45.915
45.757
29.803
26.061
26.013
24.785
24.139
24.049
23.283
22.641
i-Pr
NH
i-Pr
G-PiPy
f1 (ppm)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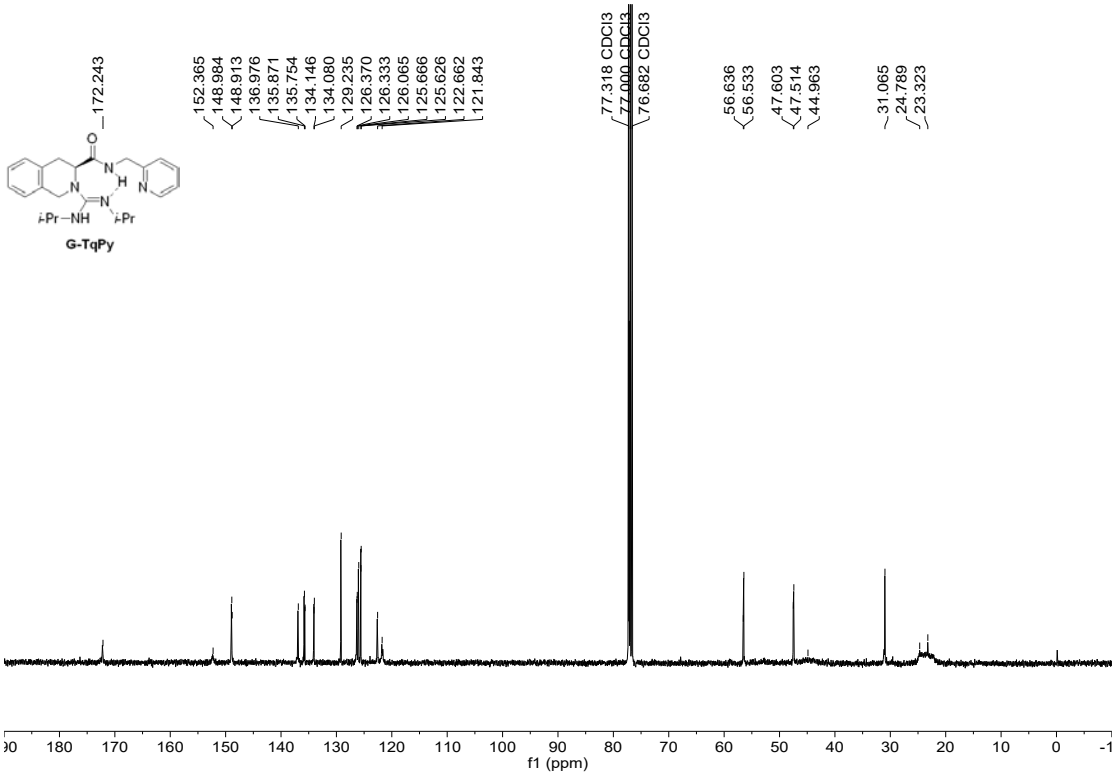
8.572
8.557
8.551
8.542
8.538
7.685
7.665
7.644
7.625
7.407
7.388
7.333
7.313
7.209
7.199
7.172
7.159
7.151
7.145
7.137
7.127
7.055
7.045
7.042
7.033
5.880
4.080
4.063
3.661
3.649
3.633
3.620
3.606
3.593
3.204
3.200
3.187
3.172
3.158
2.920
2.894
2.879
2.853
2.839
2.813
1.146
1.130
1.113
1.019
G-TqPy
0.40
1.03
1.00
1.10
1.09
3.13
1.07
0.75
5.98
1.06
1.07
12.49
f1 (ppm)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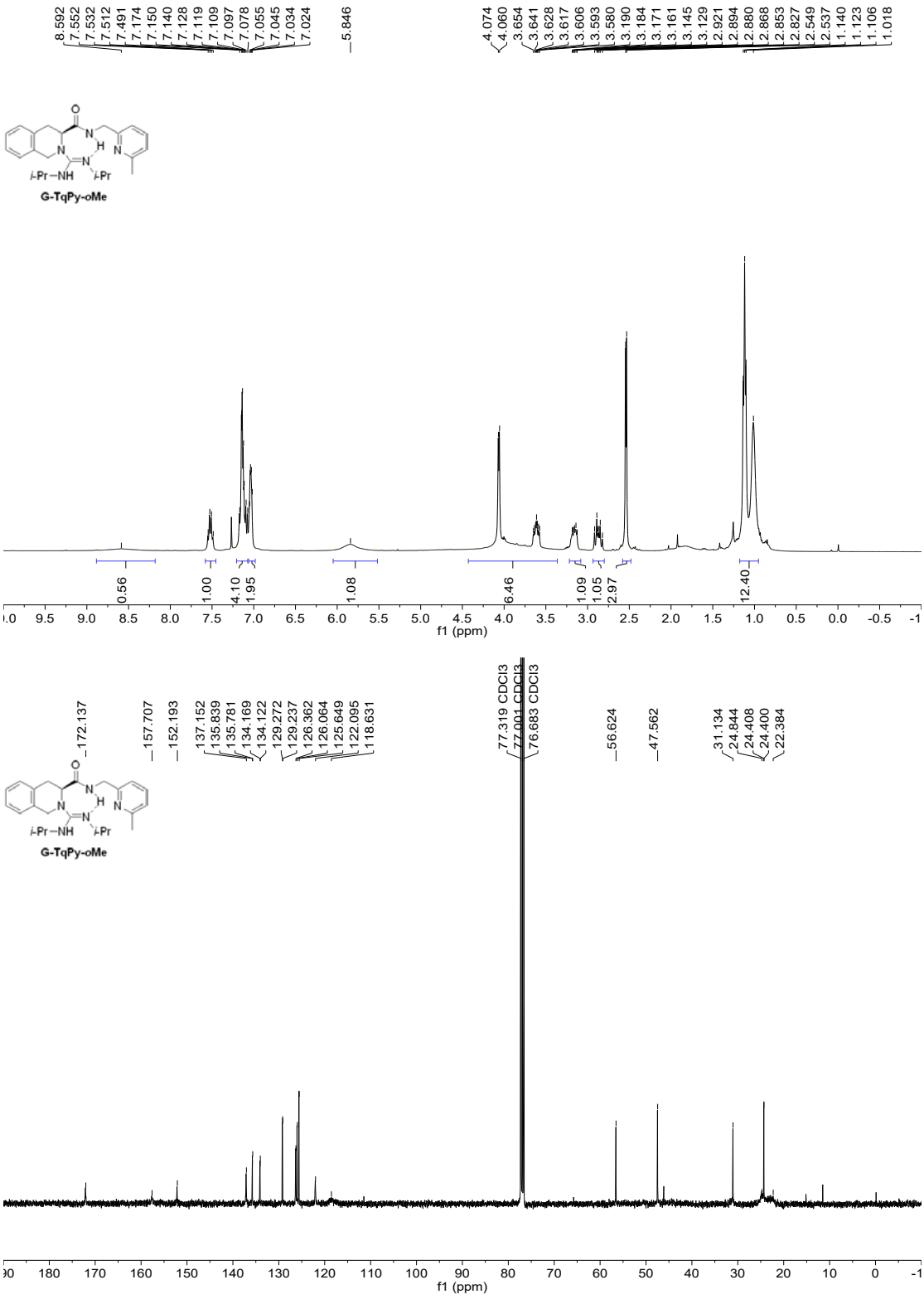
152.365
148.984
148.913
136.976
135.871
135.754
134.146
134.080
129.235
126.370
126.333
126.065
125.666
125.626
122.662
121.843
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
56.636
56.533
47.603
47.514
44.963
31.065
24.789
23.323
G-TqPy
f1 (ppm)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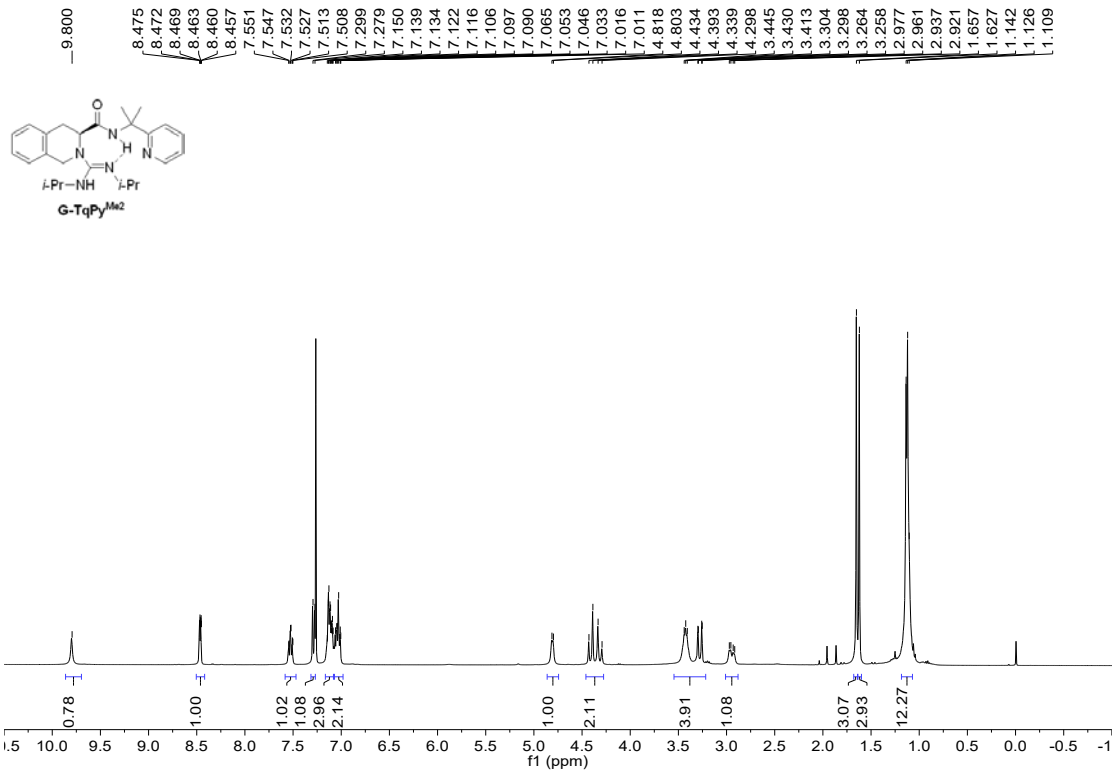
7.532
7.512
7.491
7.174
7.150
7.140
7.128
7.119
7.109
7.097
7.078
7.055
7.045
7.034
7.024
5.846
4.074
4.060
3.654
3.641
3.628
3.617
3.606
3.593
3.580
3.190
3.184
3.171
3.161
3.145
3.129
2.921
2.894
2.880
2.868
2.853
2.827
2.549
2.537
1.140
1.123
1.106
1.018
G-TqPy-oMe
0.56
1.00
4.10
1.95
1.08
6.46
1.09
1.05
2.97
12.40
f1 (ppm)
172.137
157.707
152.193
137.152
135.839
135.781
134.169
134.122
129.272
129.237
126.362
126.064
125.649
122.095
118.631
77.319 CDCl3
77.001 CDCl3
76.683 CDCl3
56.624
47.562
31.134
24.844
24.408
24.400
22.384
G-TqPy-oMe
f1 (ppm)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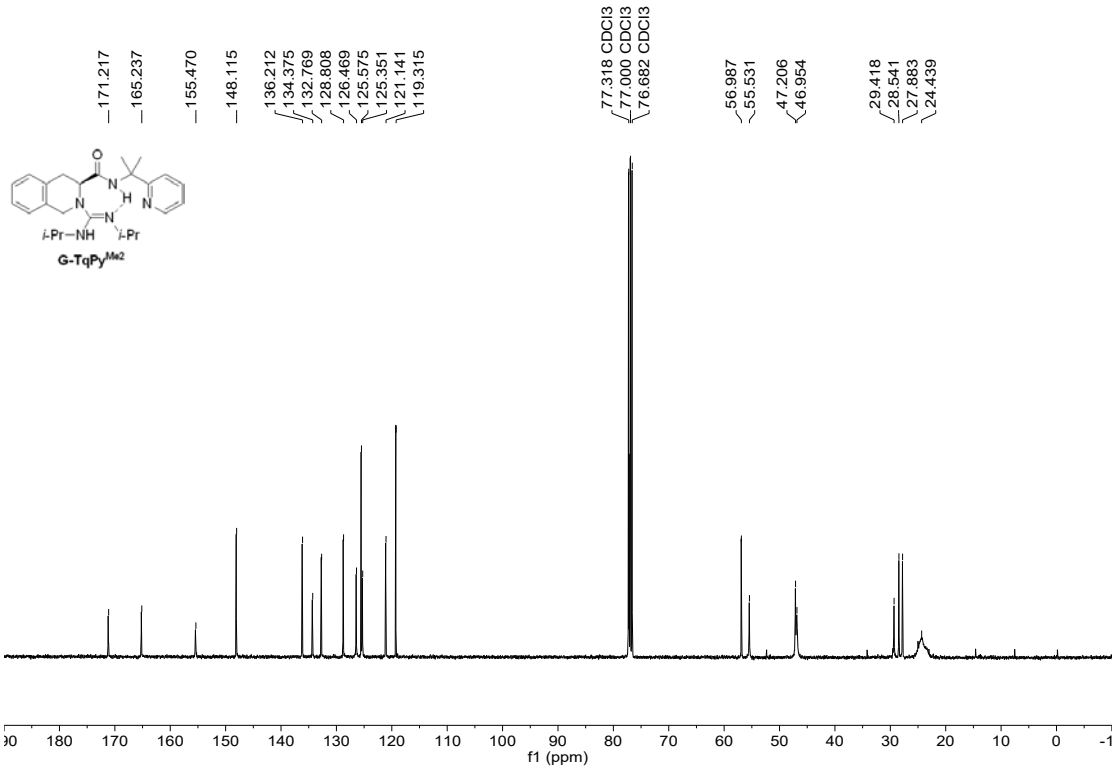
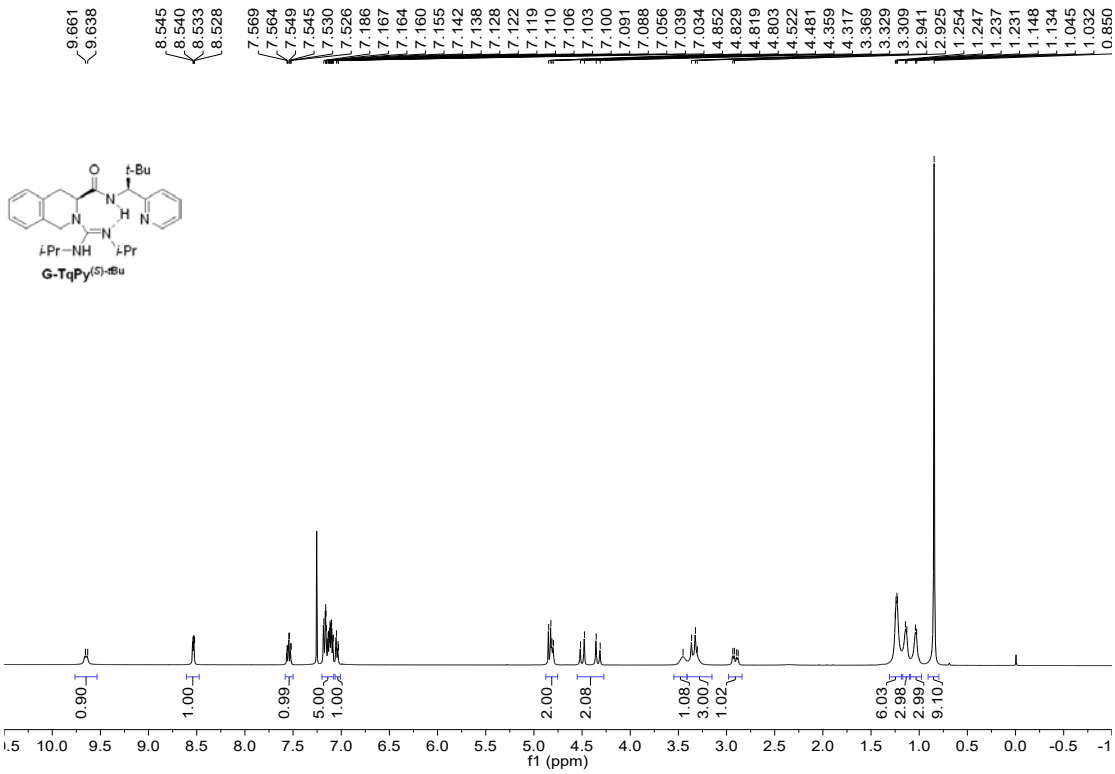
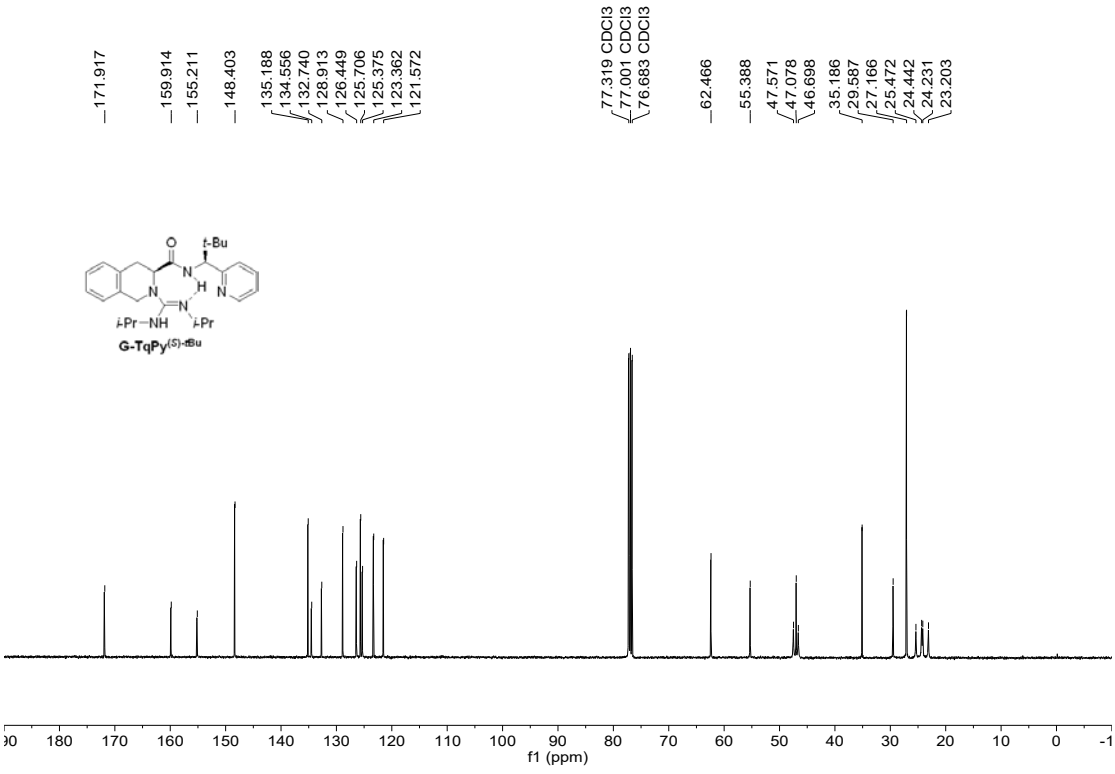
8.472
8.469
8.463
8.460
8.457
7.551
7.547
7.532
7.527
7.513
7.508
7.299
7.279
7.150
7.139
7.134
7.122
7.116
7.106
7.097
7.090
7.065
7.053
7.046
7.033
7.016
7.011
4.818
4.803
4.434
4.393
4.339
4.298
3.445
3.430
3.413
3.304
3.298
3.264
3.258
2.977
2.961
2.937
2.921
1.657
1.627
1.142
1.126
1.109
i-Pr–NH
i-Pr
G-TqPyMe2
0.78
1.00
1.02
1.08
2.96
2.14
1.00
2.11
3.91
1.08
3.07
2.93
12.27
f1 (ppm)


171.217
165.237
155.470
148.115
136.212
134.375
132.769
128.808
126.469
125.575
125.351
121.141
119.315
77.318 CDCl3
77.000 CDCl3
76.682 CDCl3
56.987
55.531
47.206
46.954
29.418
28.541
27.883
24.439
i-Pr–NH
i-Pr
G-TqPyMe2
f1 (ppm)


9.661
9.638
8.545
8.540
8.533
8.528
7.569
7.564
7.549
7.545
7.530
7.526
7.186
7.167
7.164
7.160
7.155
7.142
7.138
7.128
7.122
7.119
7.110
7.106
7.103
7.100
7.091
7.088
7.056
7.039
7.034
4.852
4.829
4.819
4.803
4.522
4.481
4.359
4.317
3.369
3.329
3.309
2.941
2.925
1.254
1.247
1.237
1.231
1.148
1.134
1.045
1.032
0.850
t-Bu
i-Pr—NH
i-Pr
G-TqPy(S)-tBu
0.90
1.00
0.99
5.00
1.00
2.00
2.08
1.08
3.00
1.02
6.03
2.98
2.99
9.10
f1 (ppm)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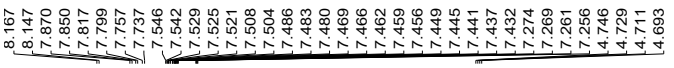
155.211
148.403
135.188
134.556
132.740
128.913
126.449
125.706
125.375
123.362
121.572
77.319 CDCl3
77.001 CDCl3
76.683 CDCl3
62.466
55.388
47.571
47.078
46.698
35.186
29.587
27.166
25.472
24.442
24.231
23.203
t-Bu
i-Pr—NH
i-Pr
G-TqPy(S)-tBu
f1 (ppm)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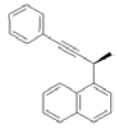
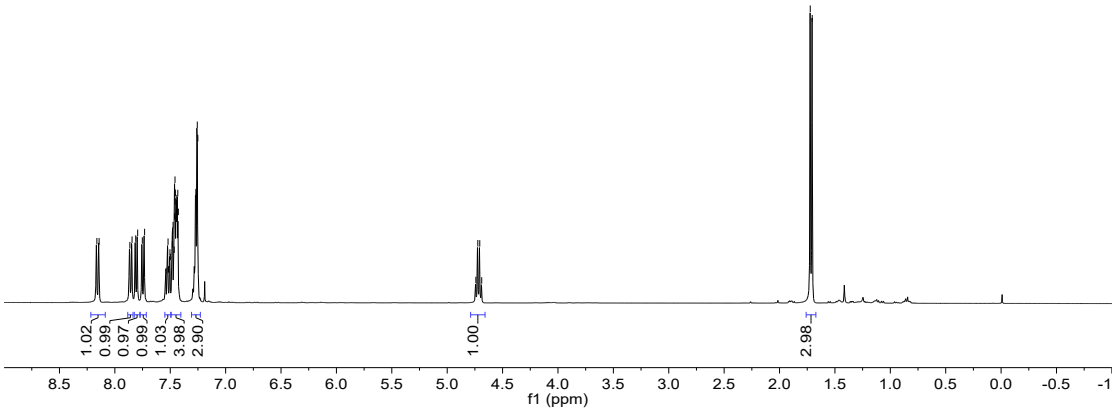
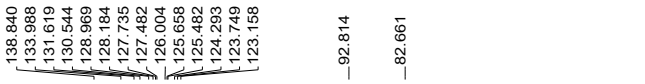
7.817
7.799
7.757
7.737
7.546
7.542
7.529
7.525
7.521
7.508
7.504
7.486
7.483
7.480
7.469
7.466
7.462
7.459
7.456
7.449
7.445
7.441
7.437
7.432
7.274
7.269
7.261
7.256
4.746
4.729
4.711
4.693
1.728
1.710



C1


1.02
0.99
0.97
0.99
1.03
3.98
2.90
1.00
2.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


138.840
133.988
131.619
130.544
128.969
128.184
127.735
127.482
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125.658
125.482
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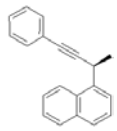
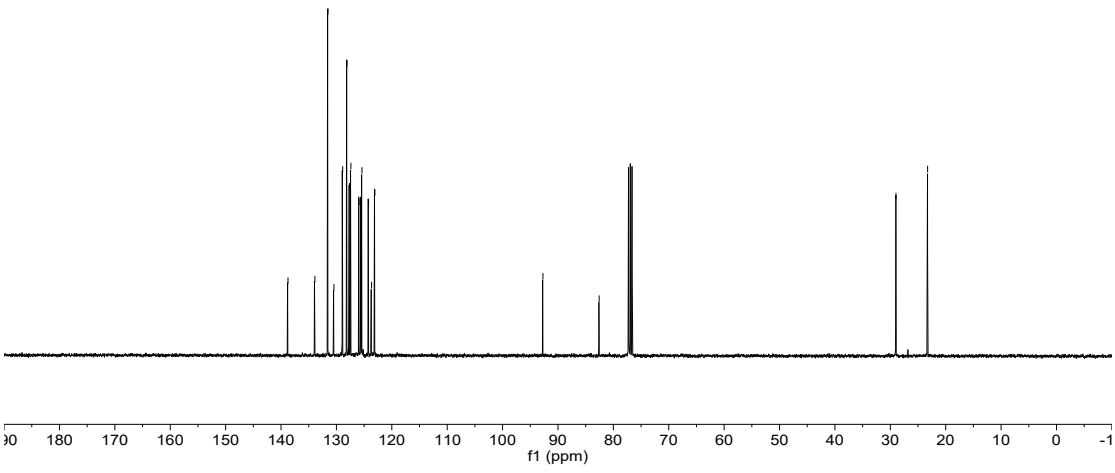
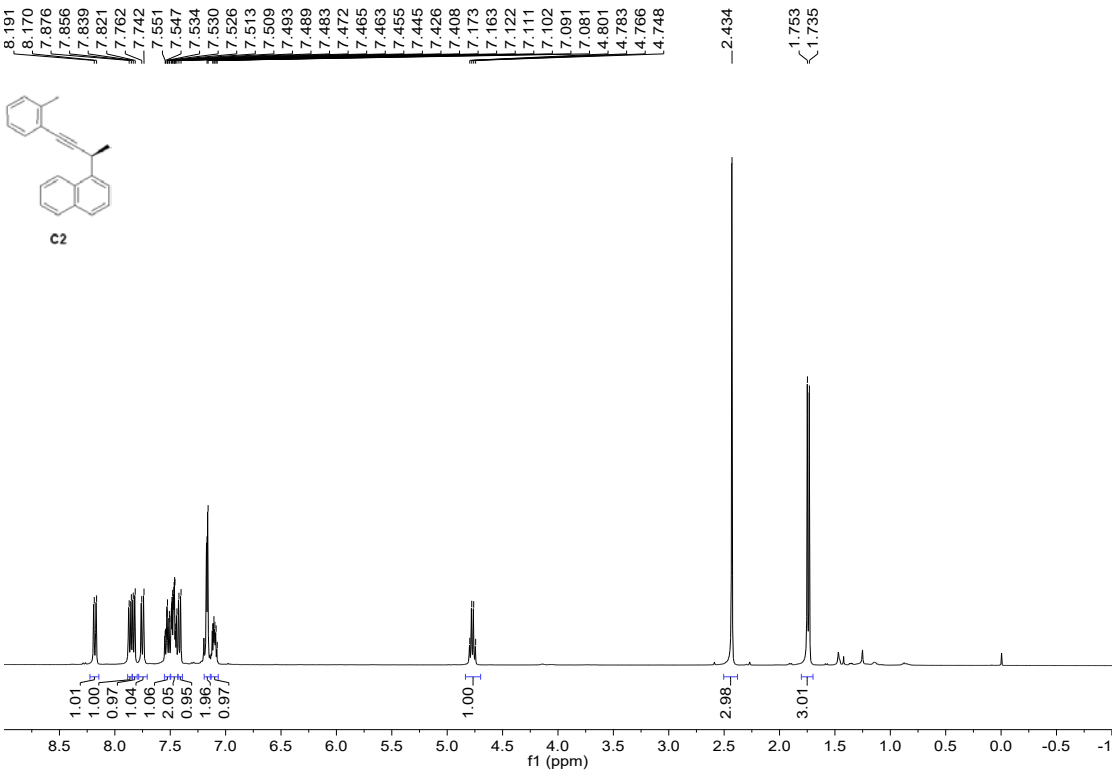
123.158
92.814
82.661
29.076
23.363



C1


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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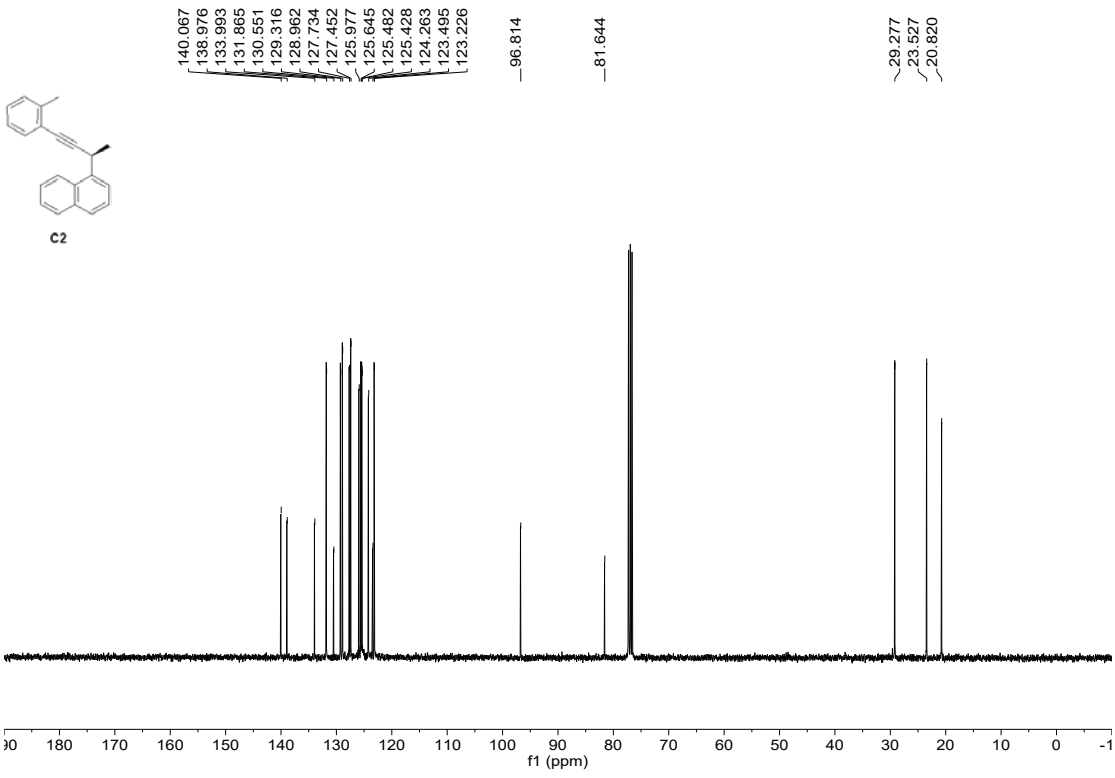
7.876
7.856
7.839
7.821
7.762
7.742
7.551
7.547
7.534
7.530
7.526
7.513
7.509
7.493
7.489
7.483
7.472
7.465
7.463
7.455
7.445
7.426
7.408
7.173
7.163
7.122
7.111
7.102
7.091
7.081
4.801
4.783
4.766
4.748
2.434
1.753
1.735
C2
1.01
1.00
0.97
1.04
1.06
2.05
0.95
1.96
0.97
1.00
2.98
3.01
f1 (ppm)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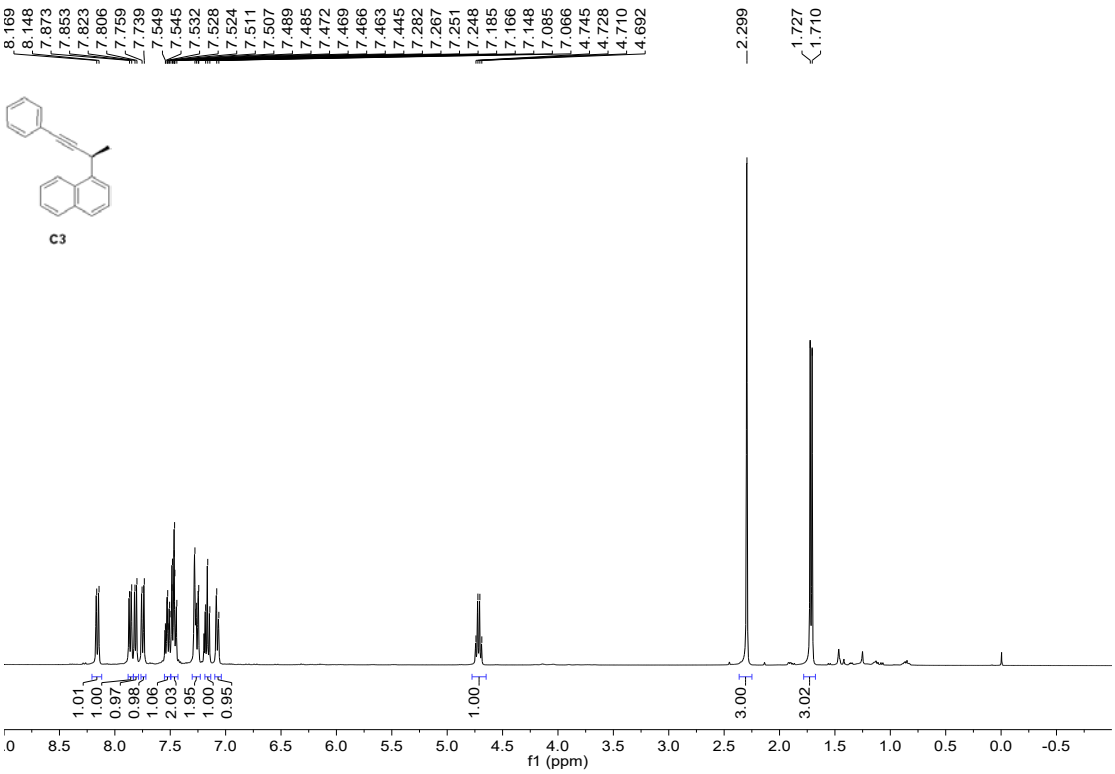
131.865
130.551
129.316
128.962
127.734
127.452
125.977
125.645
125.482
125.428
124.263
123.495
123.226
96.814
81.644
29.277
23.527
20.820
C2
f1 (ppm)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8.148
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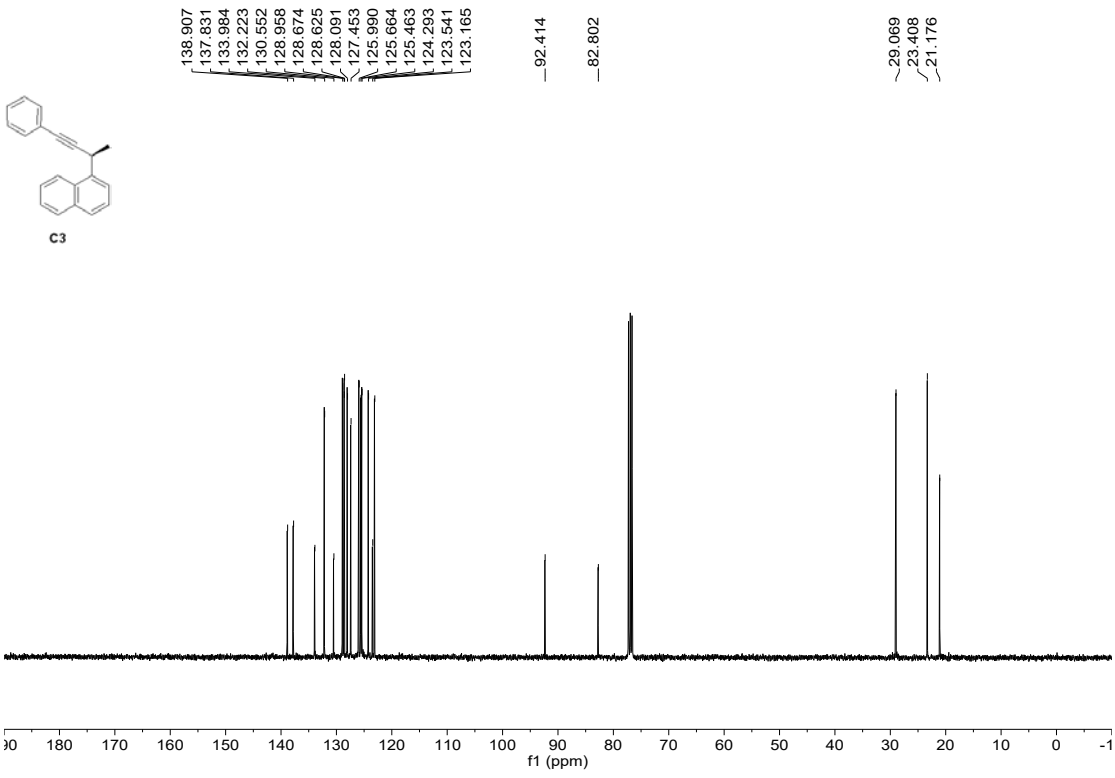
7.853
7.823
7.806
7.759
7.739
7.549
7.545
7.532
7.528
7.524
7.511
7.507
7.489
7.485
7.472
7.469
7.466
7.463
7.445
7.282
7.267
7.251
7.248
7.185
7.166
7.148
7.085
7.066
4.745
4.728
4.710
4.692
2.299
1.727
1.710
C3
1.01
1.00
0.97
0.98
1.06
2.03
1.95
1.00
0.95
1.00
3.00
3.02
f1 (ppm)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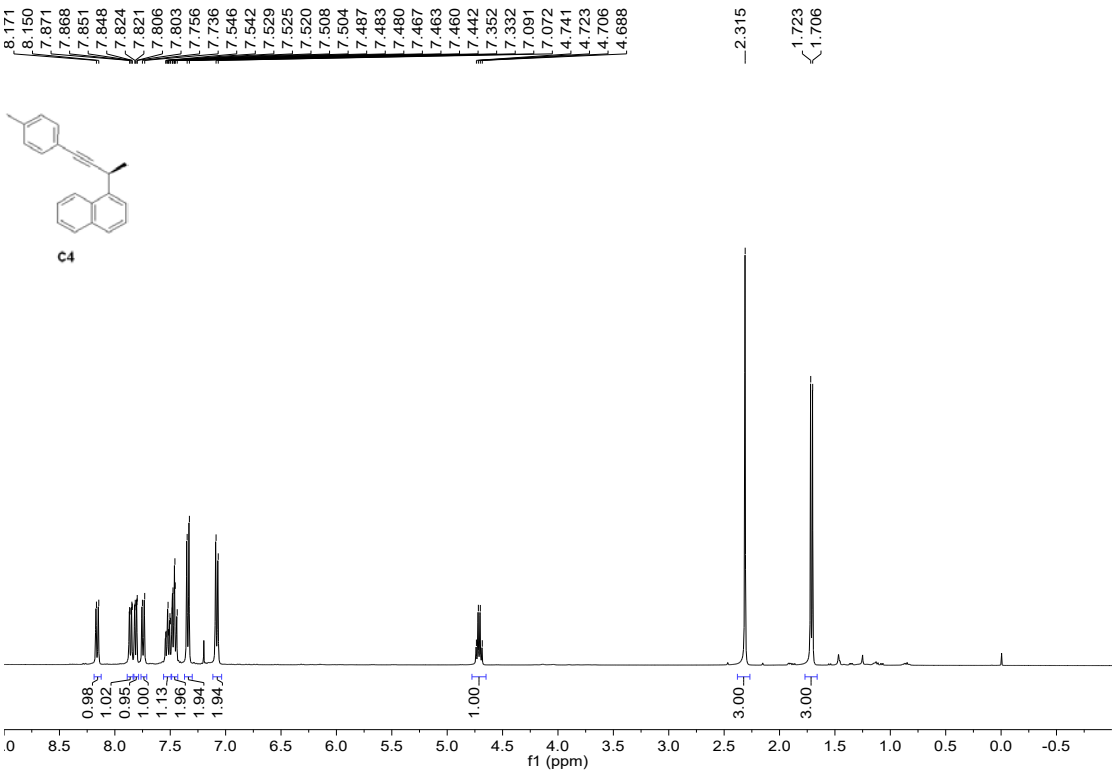
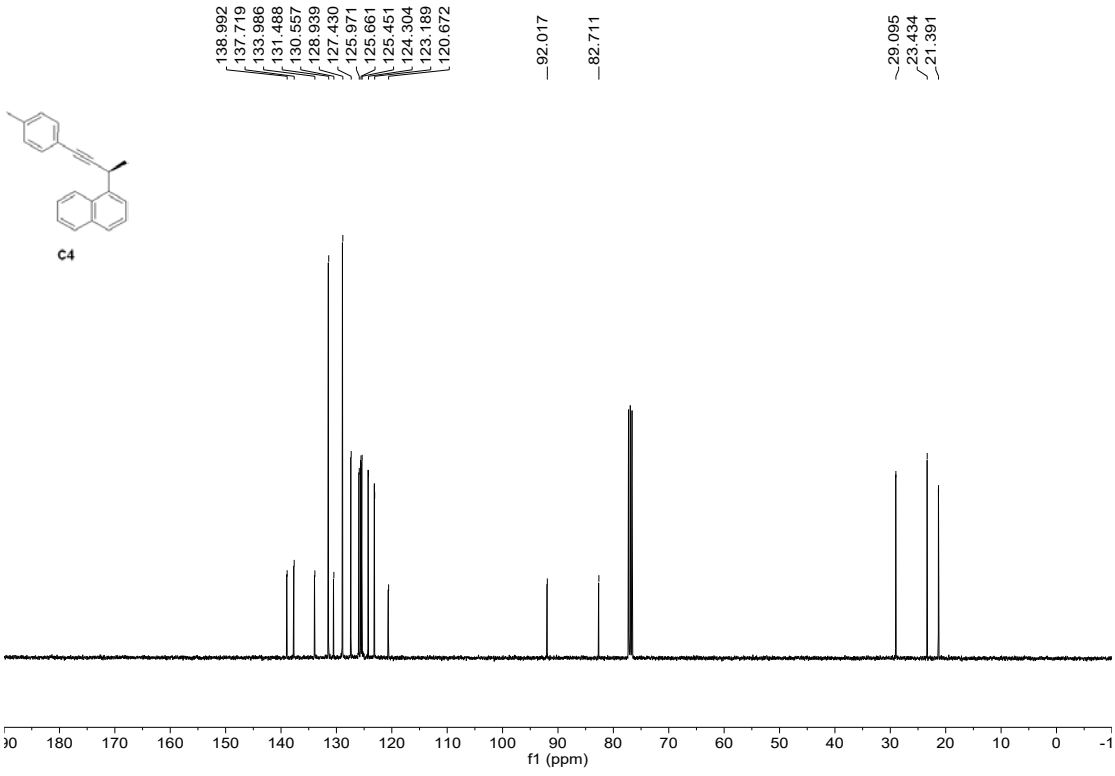
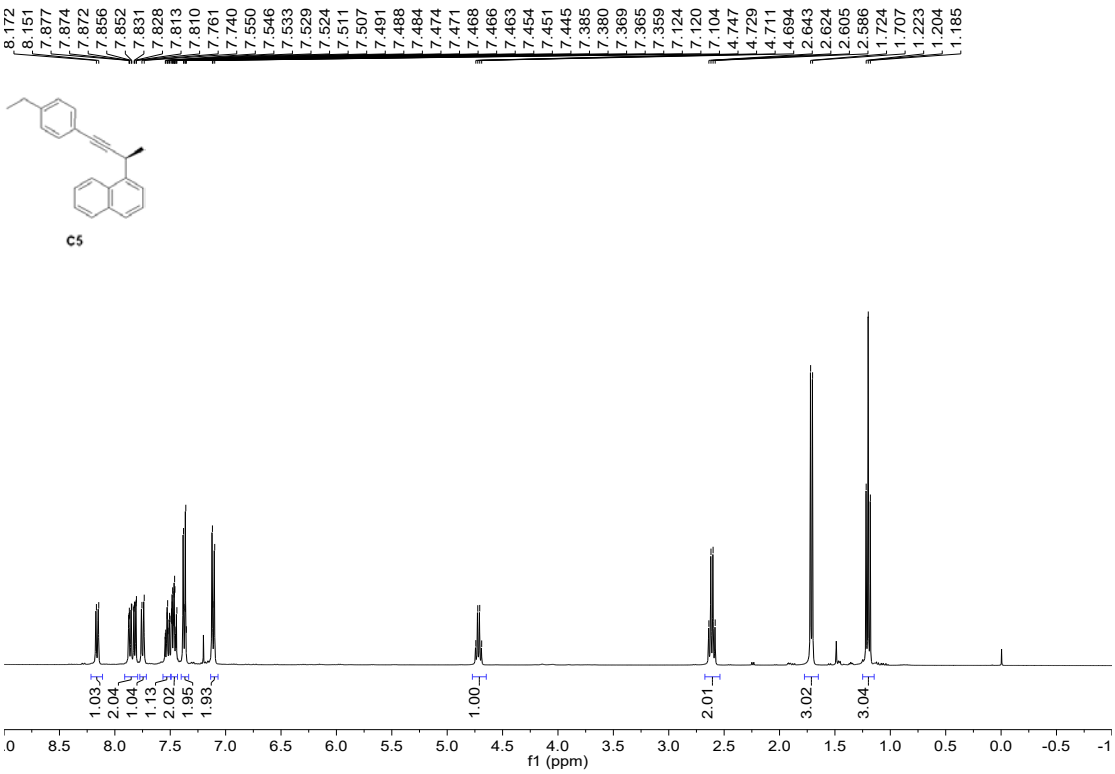
137.831
133.984
132.223
130.552
128.958
128.674
128.625
128.091
127.453
125.990
125.664
125.463
124.293
123.541
123.165
92.414
82.802
29.069
23.408
21.176
C3
f1 (ppm)


8.171
8.150
7.871
7.868
7.851
7.848
7.824
7.821
7.806
7.803
7.756
7.736
7.546
7.542
7.529
7.525
7.520
7.508
7.504
7.487
7.483
7.480
7.467
7.463
7.460
7.442
7.352
7.332
7.091
7.072
4.741
4.723
4.706
4.688
2.315
1.723
1.706
C4
0.98
1.02
0.95
1.00
1.13
1.96
1.94
1.94
1.00
3.00
3.00
f1 (ppm)


138.992
137.719
133.986
131.488
130.557
128.939
127.430
125.971
125.661
125.451
124.304
123.189
120.672
92.017
82.711
29.095
23.434
21.391
C4
f1 (ppm)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7.831
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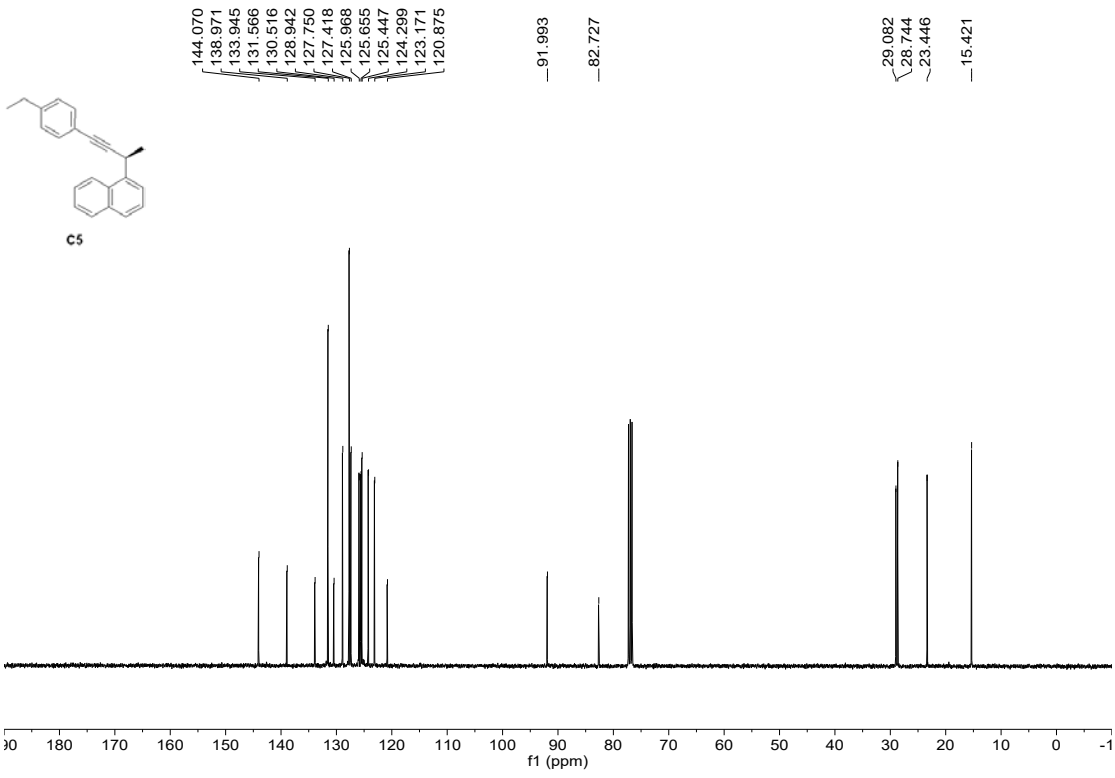
7.813
7.810
7.761
7.740
7.550
7.546
7.533
7.529
7.524
7.511
7.507
7.491
7.488
7.484
7.474
7.471
7.468
7.466
7.463
7.454
7.451
7.445
7.385
7.380
7.369
7.365
7.359
7.124
7.120
7.104
4.747
4.729
4.711
4.694
2.643
2.624
2.605
2.586
1.724
1.707
1.223
1.204
1.185
C5
1.03
2.04
1.04
1.13
2.02
1.95
1.93
1.00
2.01
3.02
3.04
f1 (ppm)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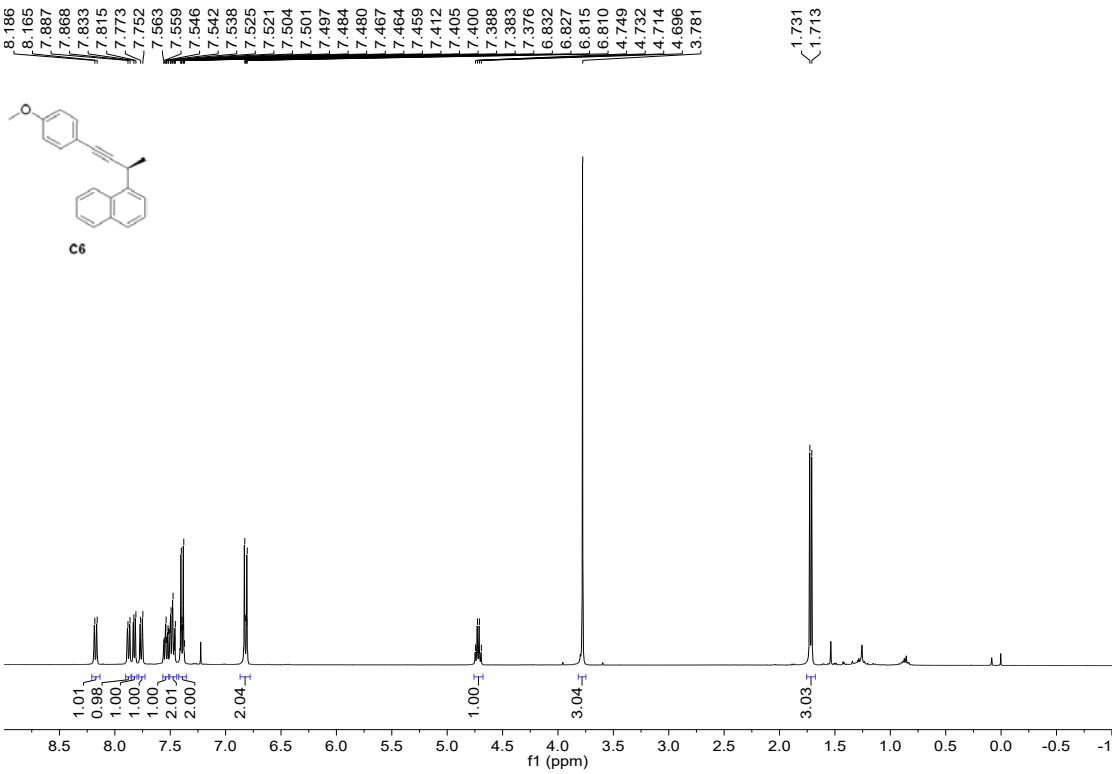
133.945
131.566
130.516
128.942
127.750
127.418
125.968
125.655
125.447
124.299
123.171
120.875
91.993
82.727
29.082
28.744
23.446
15.421
C5
f1 (ppm)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7.815
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7.752
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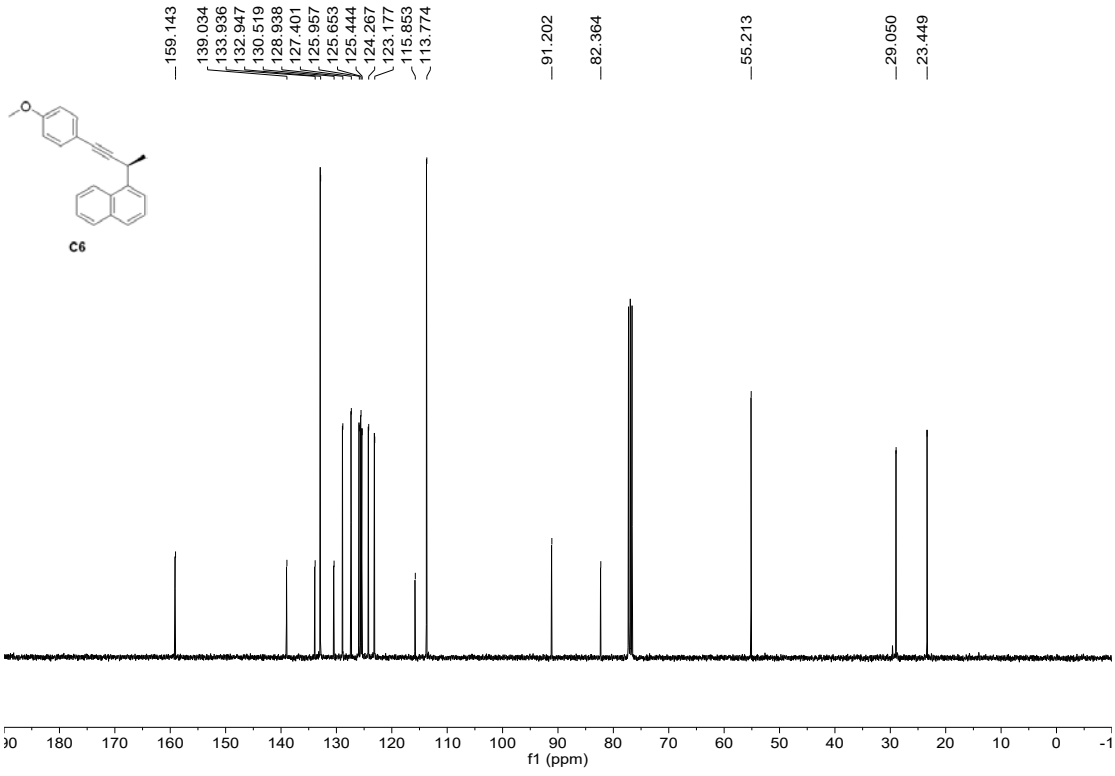
7.559
7.546
7.542
7.538
7.525
7.521
7.504
7.501
7.497
7.484
7.480
7.467
7.464
7.459
7.412
7.405
7.400
7.388
7.383
7.376
6.832
6.827
6.815
6.810
4.749
4.732
4.714
4.696
3.781
1.731
1.713
C6
1.01
0.98
1.00
1.00
1.00
2.01
2.00
2.04
1.00
3.04
3.03
f1 (ppm)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132.947
130.519
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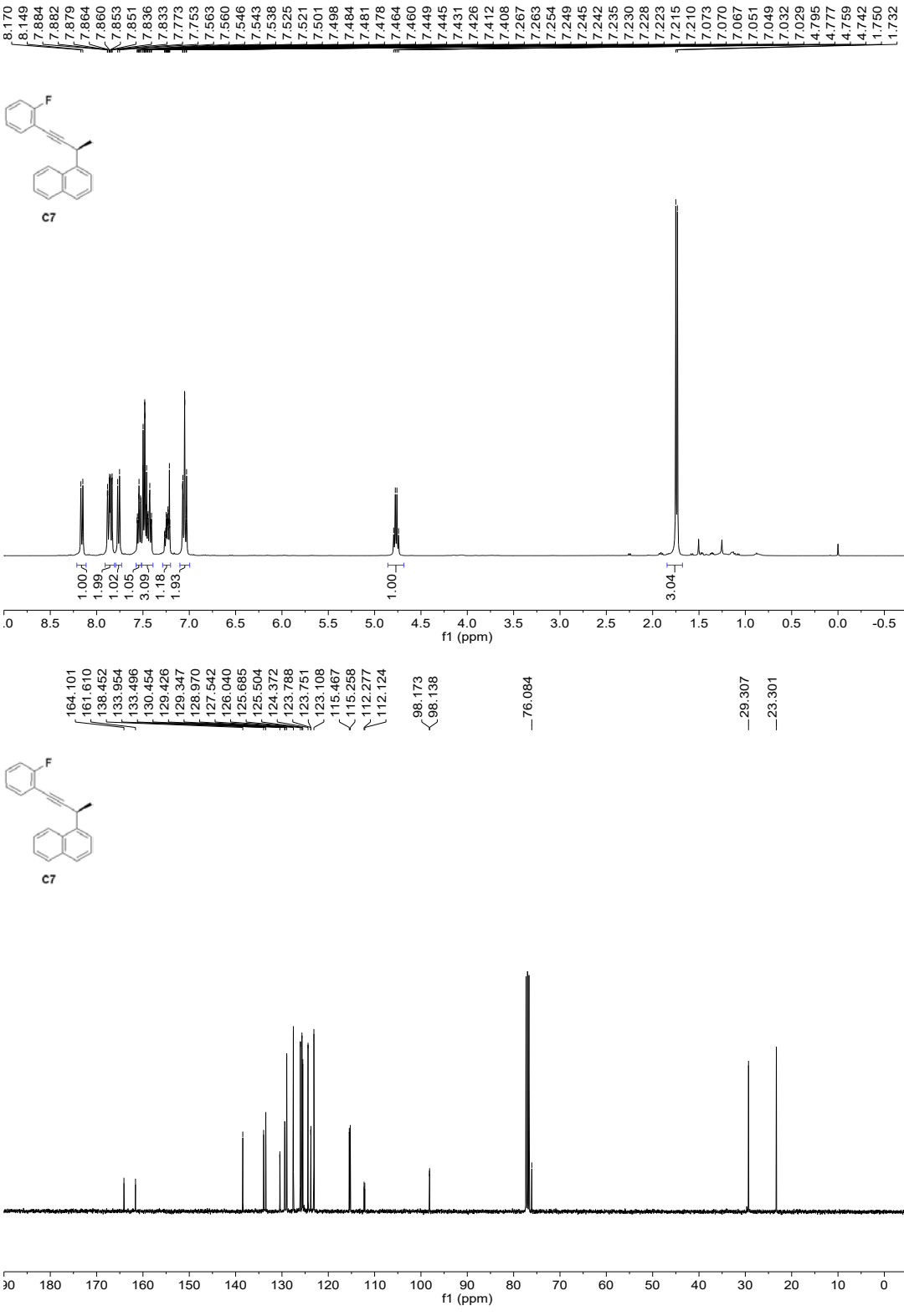
127.401
125.957
125.653
125.444
124.267
123.177
115.853
113.774
91.202
82.364
55.213
29.050
23.449
C6
f1 (ppm)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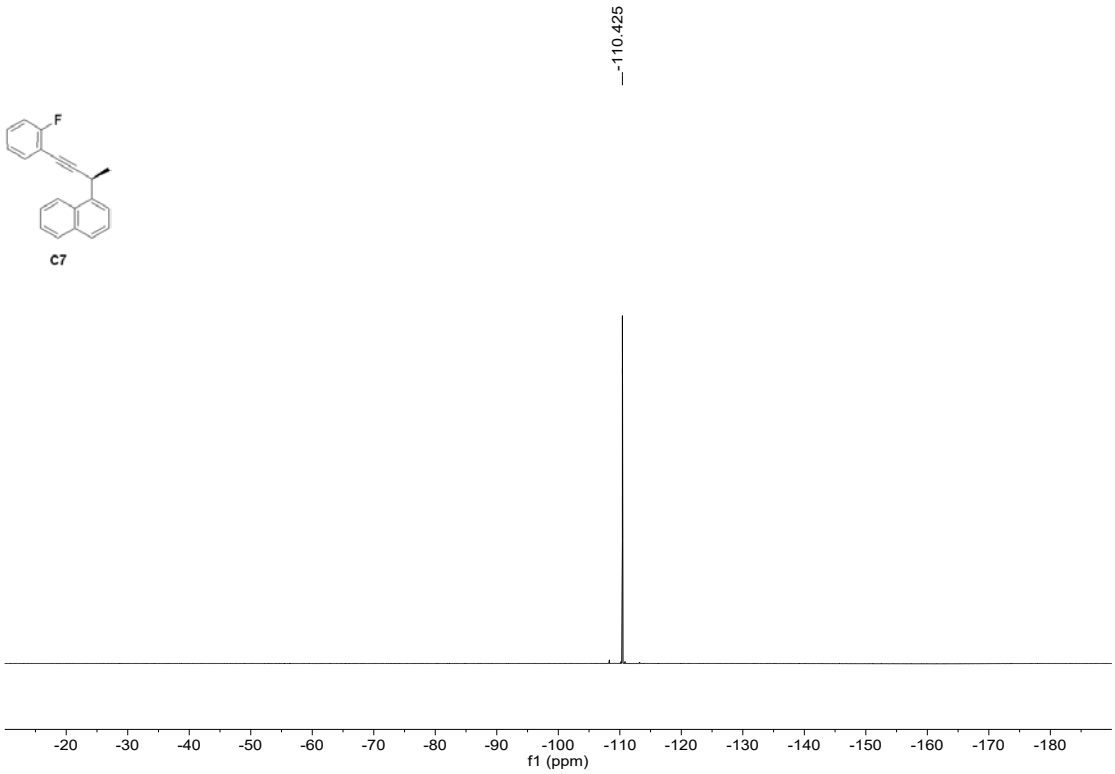
8.149
7.884
7.882
7.879
7.864
7.860
7.853
7.851
7.836
7.833
7.773
7.753
7.563
7.560
7.546
7.543
7.538
7.525
7.521
7.501
7.498
7.484
7.481
7.478
7.464
7.460
7.449
7.445
7.431
7.426
7.412
7.408
7.267
7.263
7.254
7.249
7.245
7.242
7.235
7.230
7.228
7.223
7.215
7.210
7.073
7.070
7.067
7.051
7.049
7.032
7.029
4.795
4.777
4.759
4.742
1.750
1.732
F
C7
1.00
1.99
1.02
1.05
3.09
1.18
1.93
1.00
3.04
f1 (ppm)
164.101
161.610
138.452
133.954
133.496
130.454
129.426
129.347
128.970
127.542
126.040
125.685
125.504
124.372
123.788
123.751
123.108
115.467
115.258
112.277
112.124
98.173
98.138
76.084
29.307
23.301
F
C7
f1 (ppm)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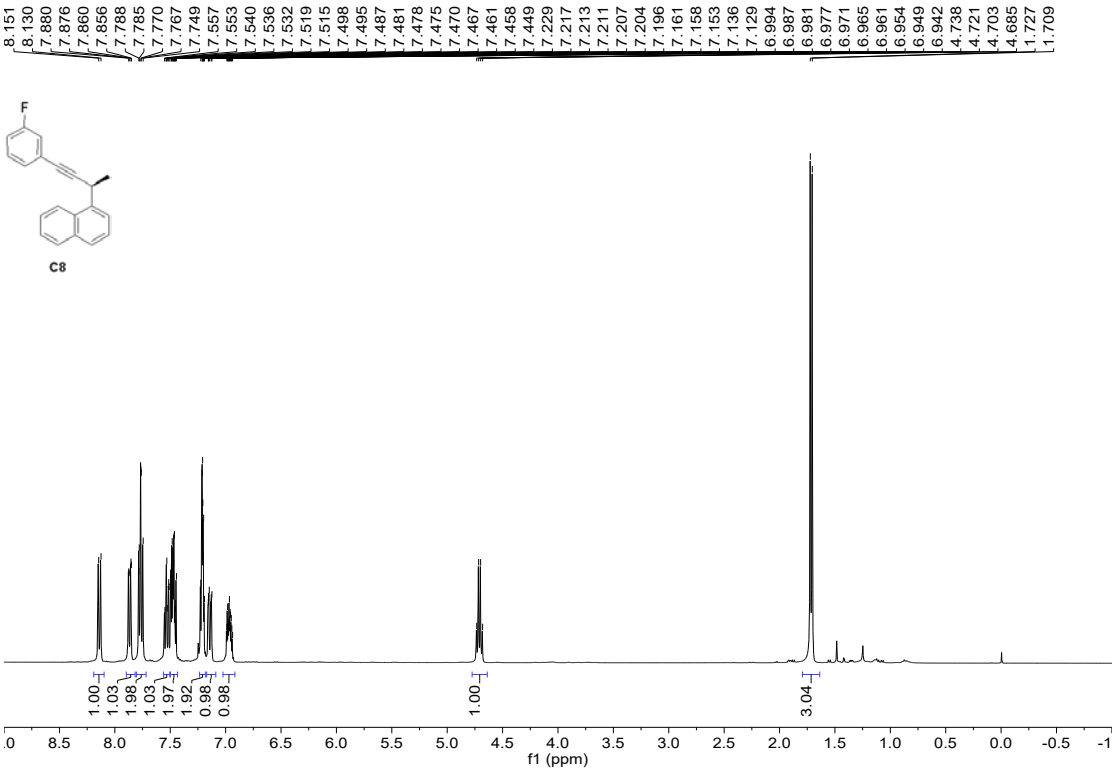
F
C7
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)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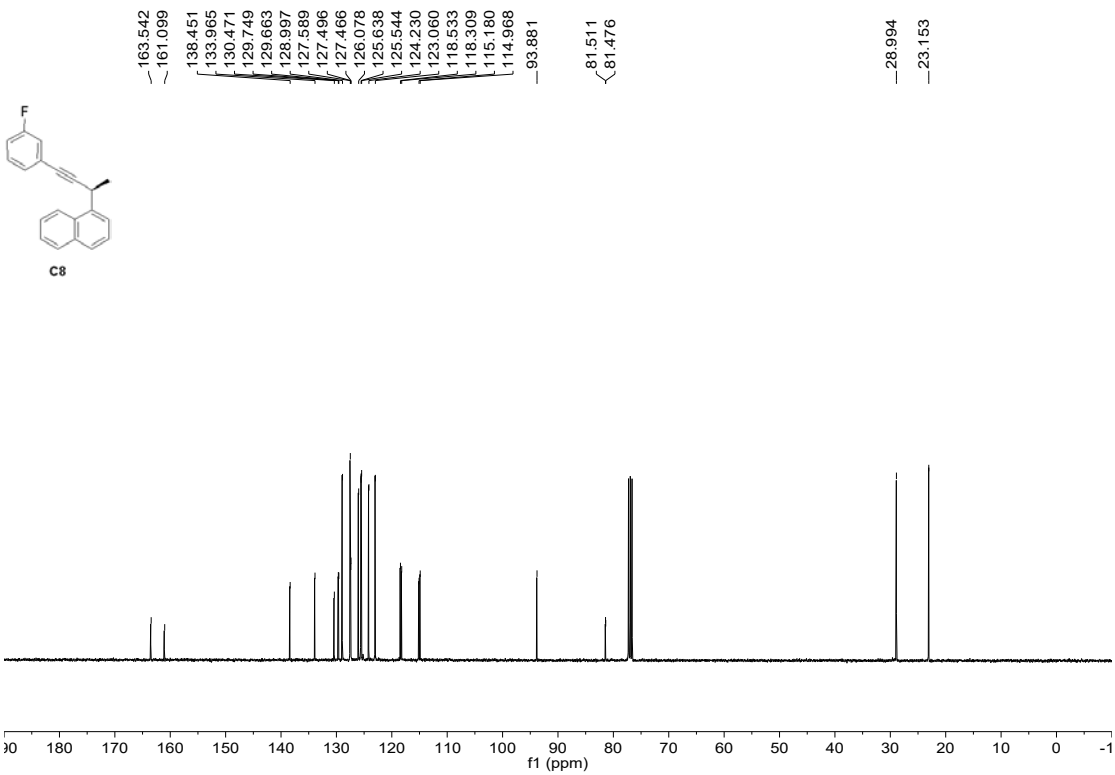
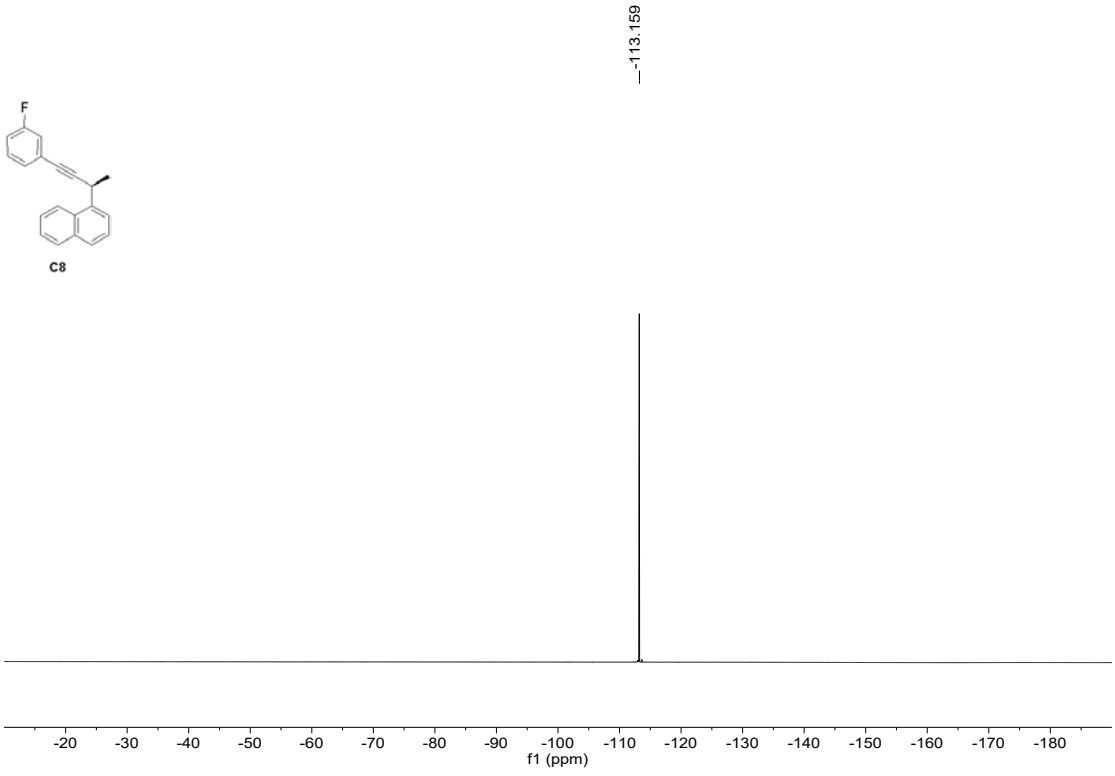
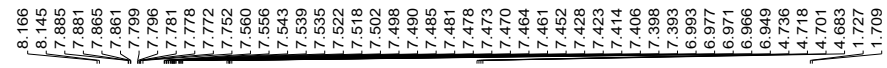
7.856
7.788
7.785
7.770
7.767
7.749
7.557
7.553
7.540
7.536
7.532
7.519
7.515
7.498
7.495
7.487
7.481
7.478
7.475
7.470
7.467
7.461
7.458
7.449
7.229
7.217
7.213
7.211
7.207
7.204
7.196
7.161
7.158
7.153
7.136
7.129
6.994
6.987
6.981
6.977
6.971
6.965
6.961
6.954
6.949
6.942
4.738
4.721
4.703
4.685
1.727
1.709
F
C8
1.00
1.03
1.98
1.03
1.97
1.92
0.98
0.98
1.00
3.04
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


163.542
161.099
138.451
133.965
130.471
129.749
129.663
128.997
127.589
127.496
127.466
126.078
125.638
125.544
124.230
123.060
118.533
118.309
115.180
114.968
93.881
81.511
81.476
28.994
23.153
F
C8
f1 (ppm)


-113.159
F
C8
f1 (ppm)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7.885
7.881
7.865
7.861
7.799
7.796
7.781
7.778
7.772
7.752
7.560
7.556
7.543
7.539
7.535
7.522
7.518
7.502
7.498
7.490
7.485
7.481
7.478
7.473
7.470
7.464
7.461
7.452
7.428
7.423
7.414
7.406
7.398
7.393
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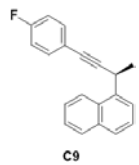
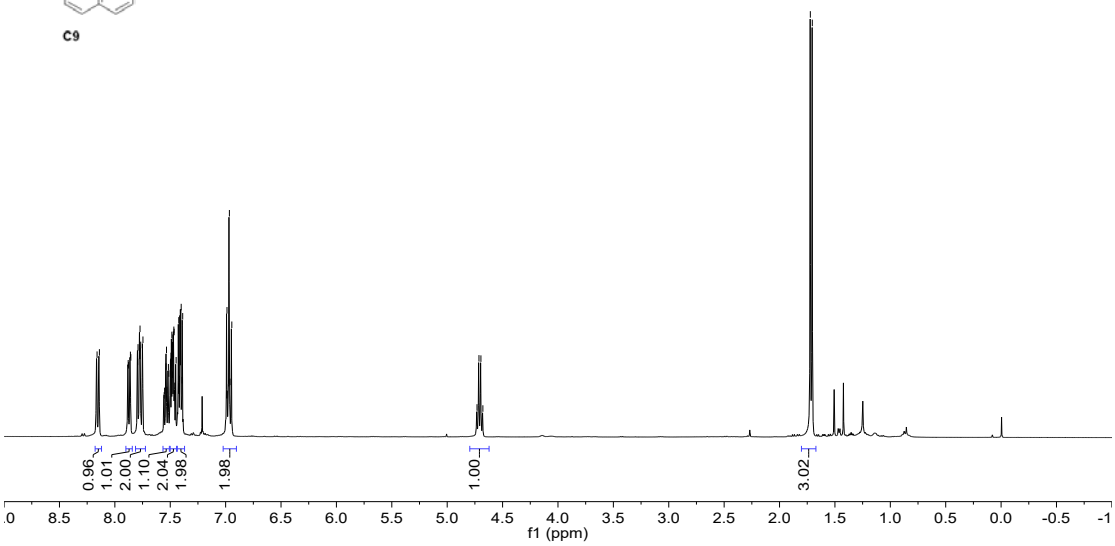
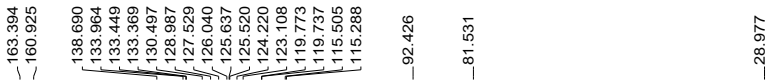
4.718
4.701
4.683
1.727
1.709


F

C9


0.96
1.01
2.00
1.10
2.04
1.98
1.98
1.00
3.02
f1 (ppm)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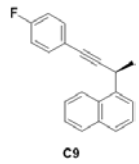
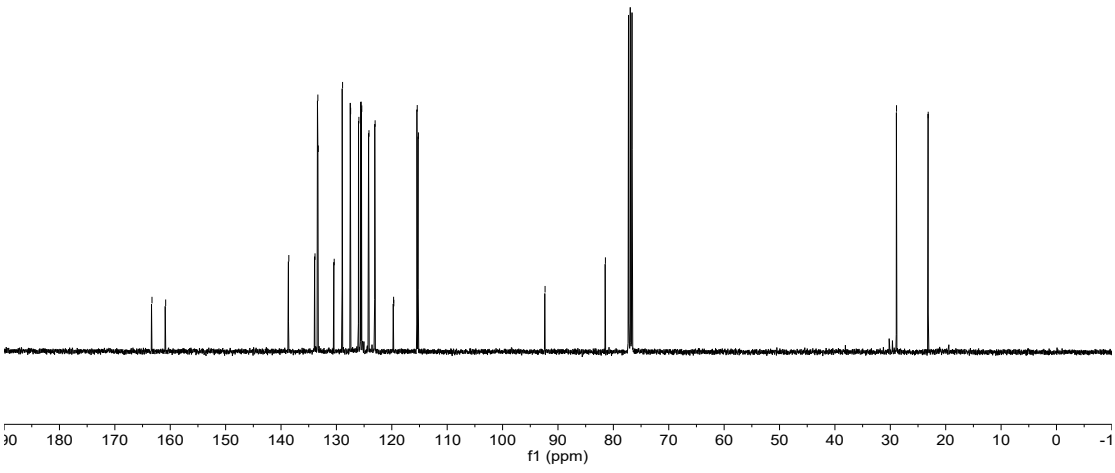
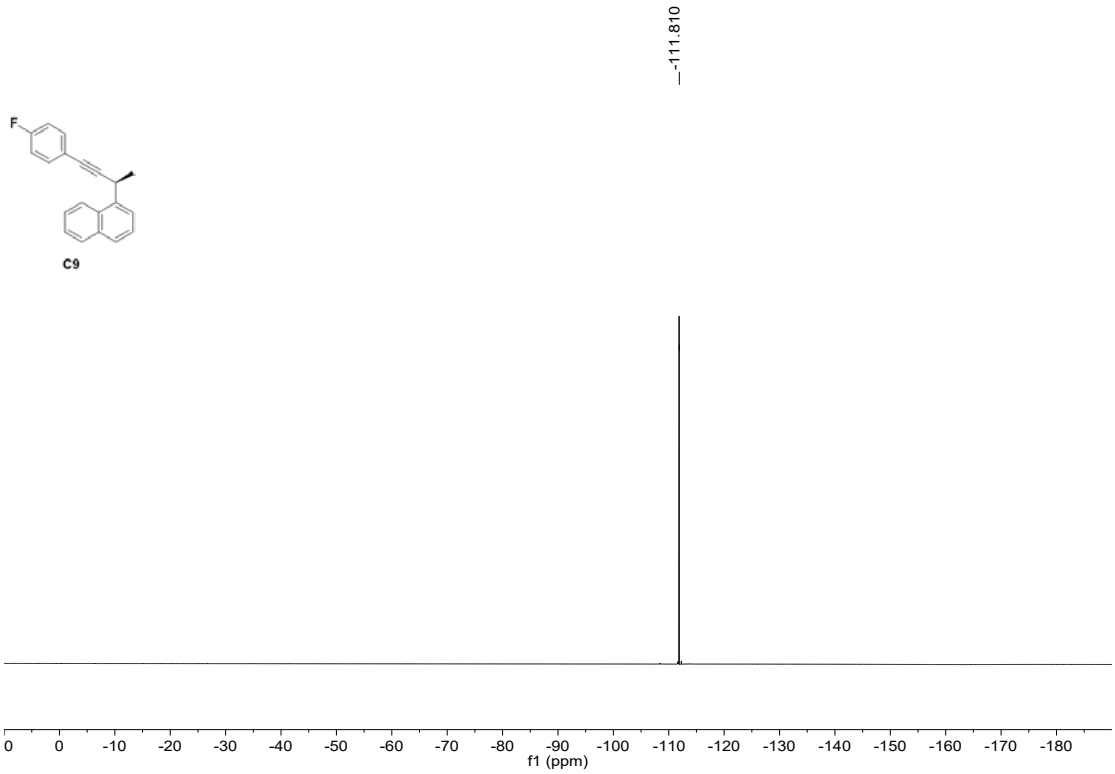
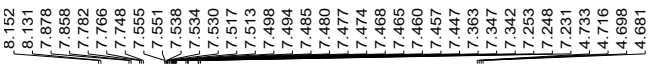
160.925
138.690
133.964
133.449
133.369
130.497
128.987
127.529
126.040
125.637
125.520
124.220
123.108
119.773
119.737
115.505
115.288
92.426
81.531
28.977
23.257


F

C9


f1 (ppm)


-111.810
F
C9
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)


8.152
8.131
7.878
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7.782
7.766
7.748
7.555
7.551
7.538
7.534
7.530
7.517
7.513
7.498
7.494
7.485
7.480
7.477
7.474
7.468
7.465
7.460
7.457
7.447
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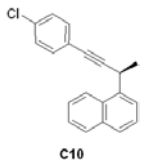
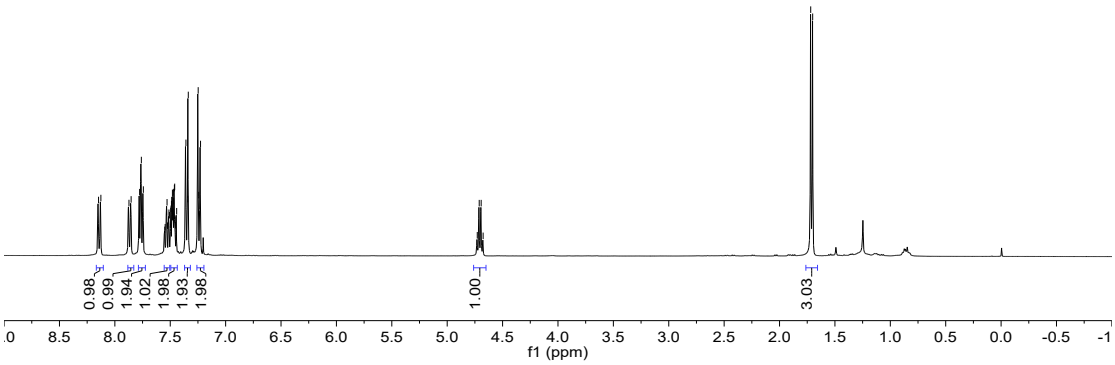
4.716
4.698
4.681
1.724
1.706

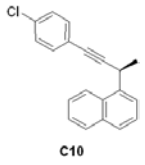

Cl

C10

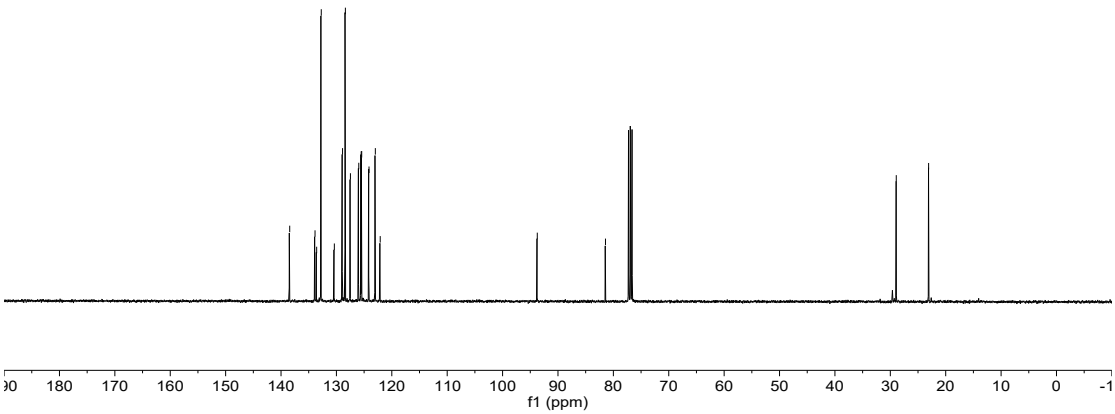

0.98
0.99
1.94
1.02
1.98
1.93
1.98
1.00
3.03
f1 (ppm)

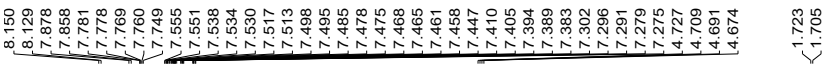

138.530
133.959
133.665
132.833
130.472
128.991
128.479
127.567
126.059
125.627
125.533
124.212
123.070
122.189


93.833
81.521
29.023
23.182


Cl

C10


f1 (ppm)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7.878
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7.781
7.778
7.769
7.760
7.749
7.555
7.551
7.538
7.534
7.530
7.517
7.513
7.498
7.495
7.485
7.478
7.475
7.468
7.465
7.461
7.458
7.447
7.410
7.405
7.394
7.389
7.383
7.302
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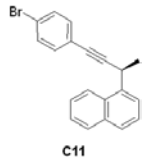
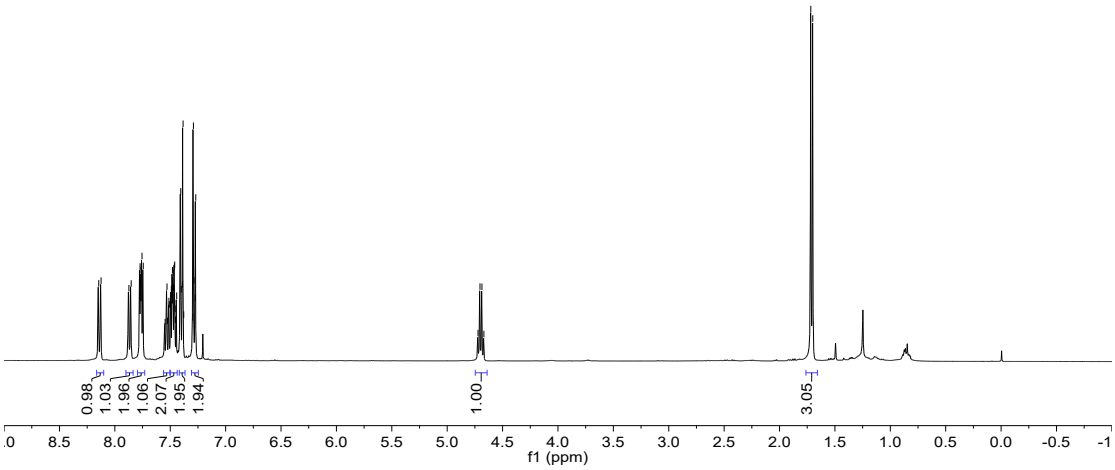
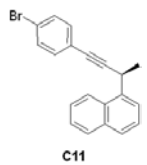
4.709
4.691
4.674
1.723
1.705


Br

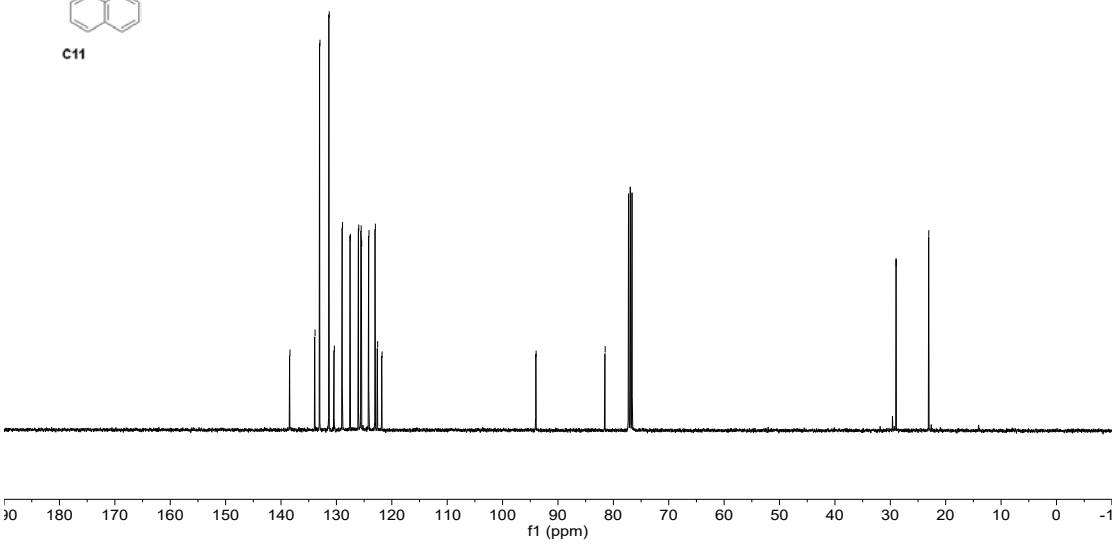
C11

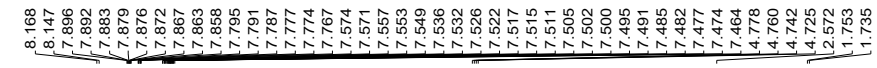

0.98
1.03
1.96
1.06
2.07
1.95
1.94
1.00
3.05
f1 (ppm)


138.481
133.951
133.070
131.395
130.464
128.990
127.568
126.059
125.625
125.532
124.210
123.062
122.650
121.857
94.043
81.578
29.040
23.153


Br

C11


f1 (ppm)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7.876
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7.867
7.863
7.858
7.795
7.791
7.787
7.777
7.774
7.767
7.574
7.571
7.557
7.553
7.549
7.536
7.532
7.526
7.522
7.517
7.515
7.511
7.505
7.502
7.500
7.495
7.491
7.485
7.482
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7.474
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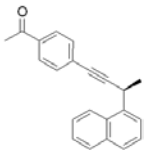
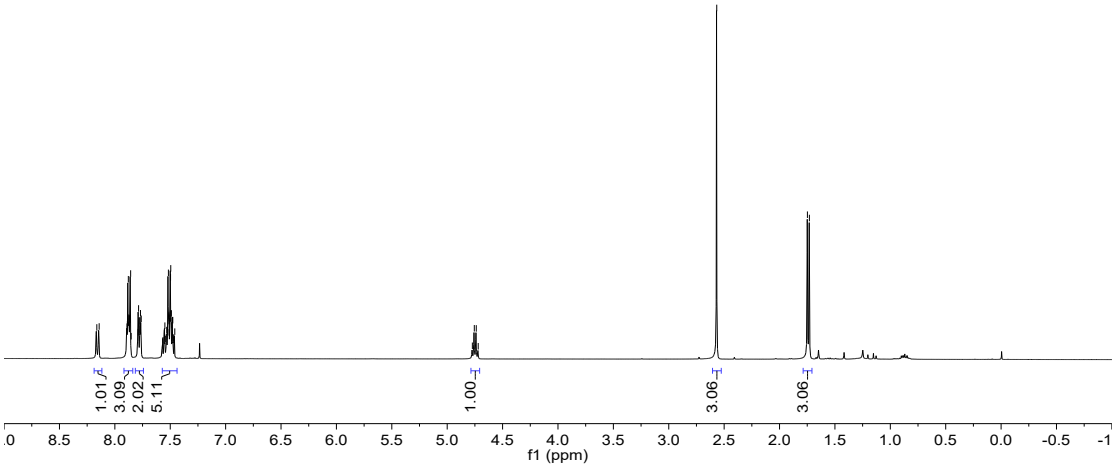
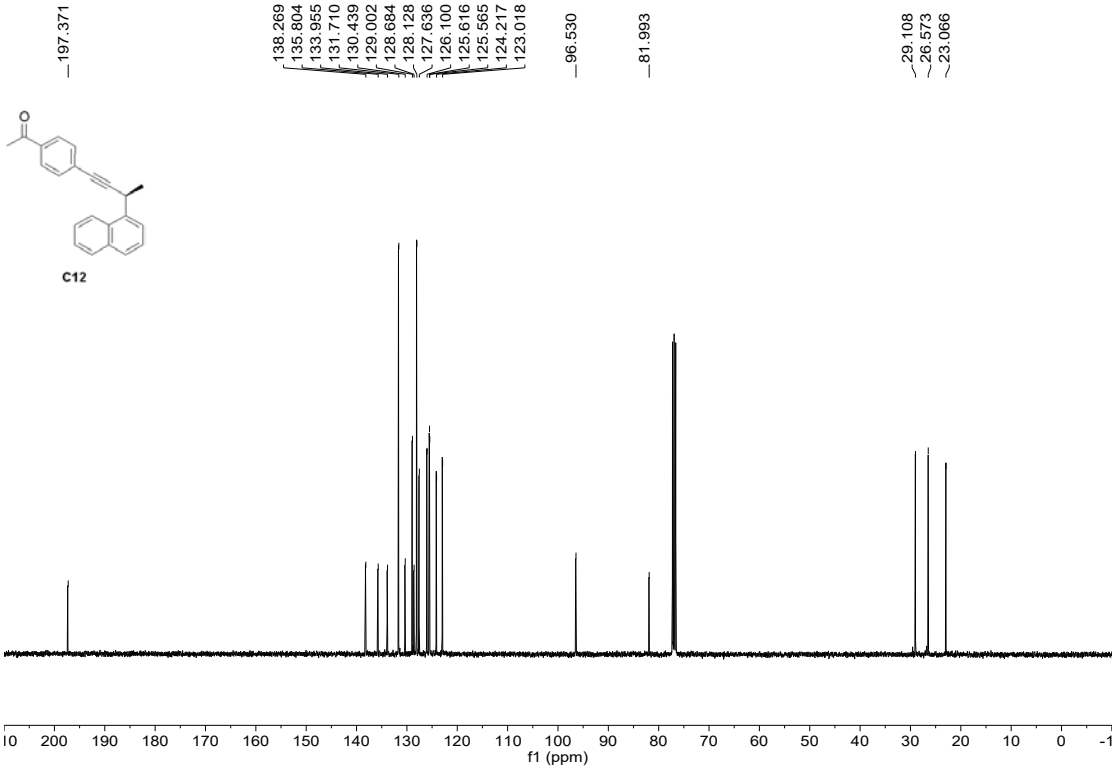
4.778
4.760
4.742
4.725
2.572
1.753
1.735

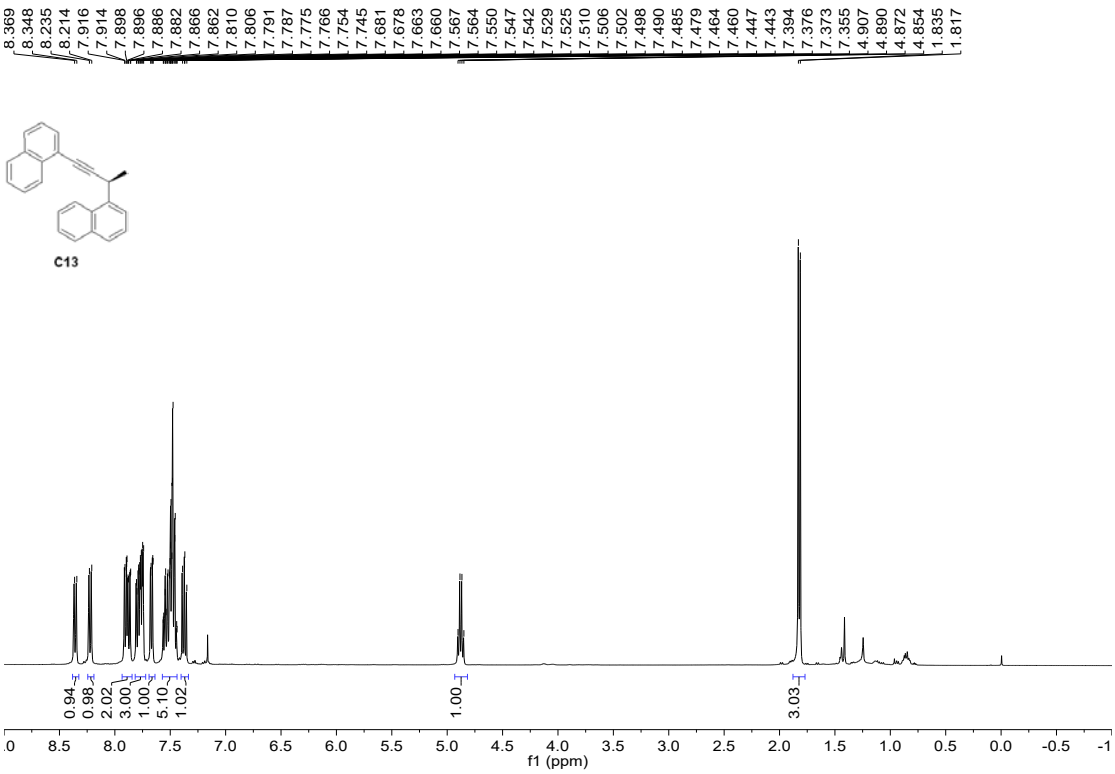


C12


1.01
3.09
2.02
5.11
1.00
3.06
3.06
f1 (ppm)


197.371
138.269
135.804
133.955
131.710
130.439
129.002
128.684
128.128
127.636
126.100
125.616
125.565
124.217
123.018
96.530
81.993
29.108
26.573
23.066
f1 (ppm)

C12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7.914
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7.896
7.886
7.882
7.866
7.862
7.810
7.806
7.791
7.787
7.775
7.766
7.754
7.745
7.681
7.678
7.663
7.660
7.567
7.564
7.550
7.547
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7.510
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7.485
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7.447
7.443
7.394
7.376
7.373
7.355
4.907
4.890
4.872
4.854
1.835
1.817
C13
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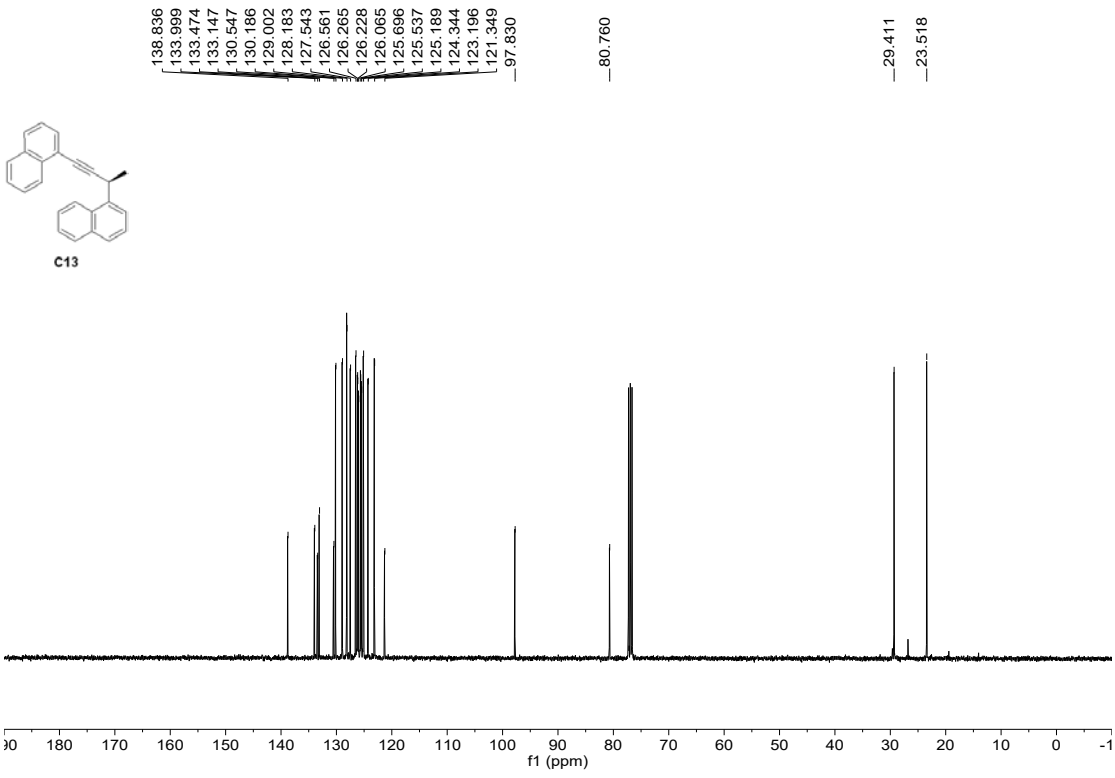
0.98
2.02
3.00
1.00
5.10
1.02
1.00
3.03
f1 (ppm)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133.999
133.474
133.147
130.547
130.186
129.002
128.183
127.543
126.561
126.265
126.228
126.065
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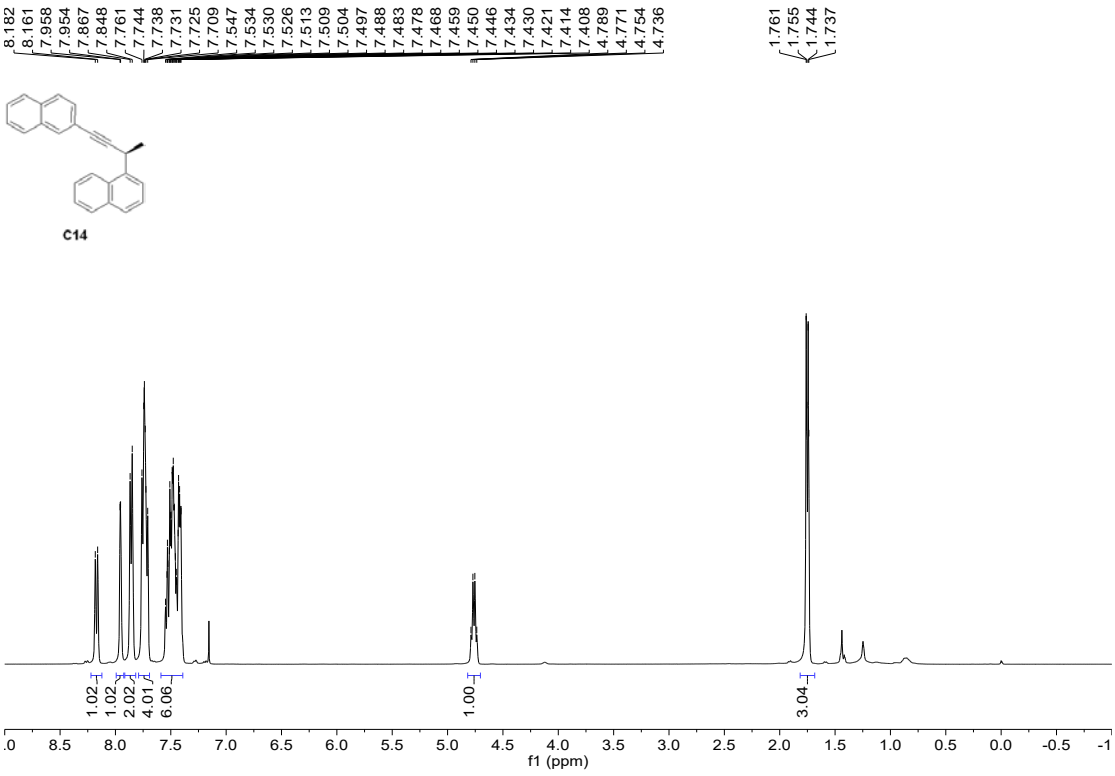
C13
f1 (ppm)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7.530
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7.513
7.509
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7.468
7.459
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7.446
7.434
7.430
7.421
7.414
7.408
4.789
4.771
4.754
4.736
1.761
1.755
1.744
1.737
C14
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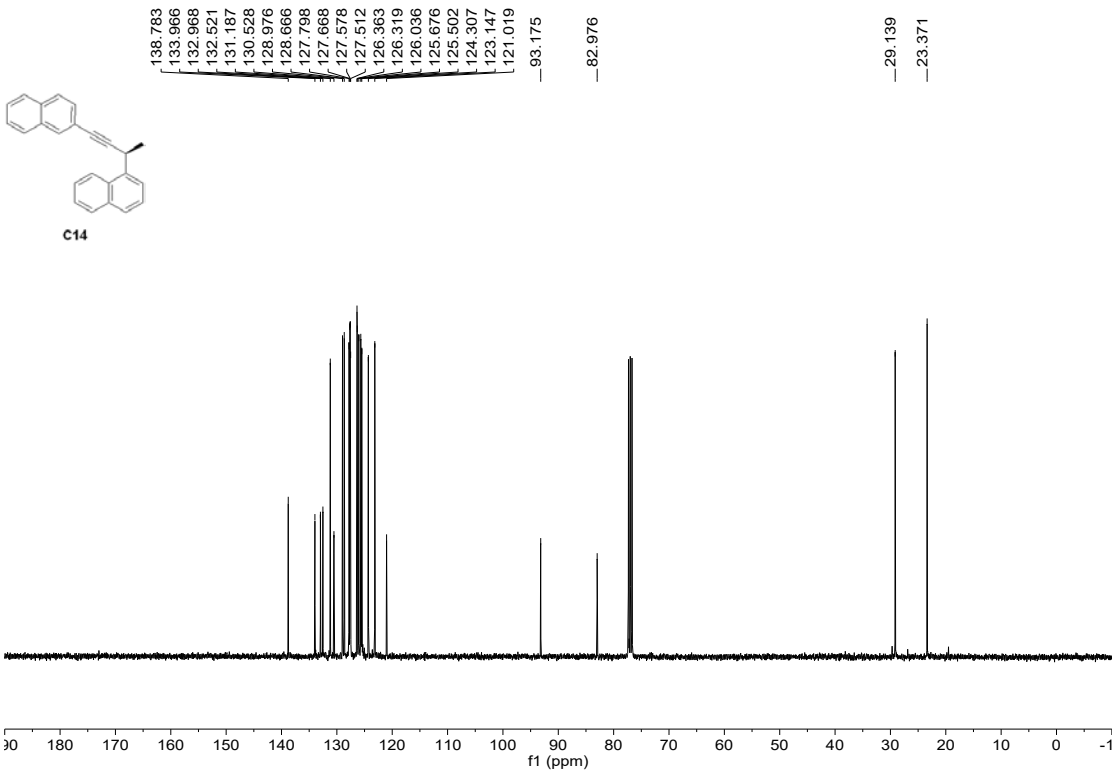
1.02
2.02
4.01
6.06
1.00
3.04
f1 (ppm)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126.363
126.319
126.036
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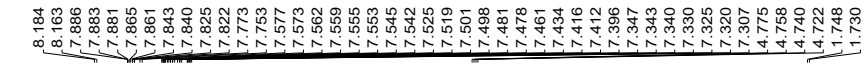
124.307
123.147
121.019
93.175
82.976
29.139
23.371
C14
f1 (ppm)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7.573
7.562
7.559
7.555
7.553
7.545
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7.525
7.519
7.501
7.498
7.481
7.478
7.461
7.434
7.416
7.412
7.396
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7.320
7.307
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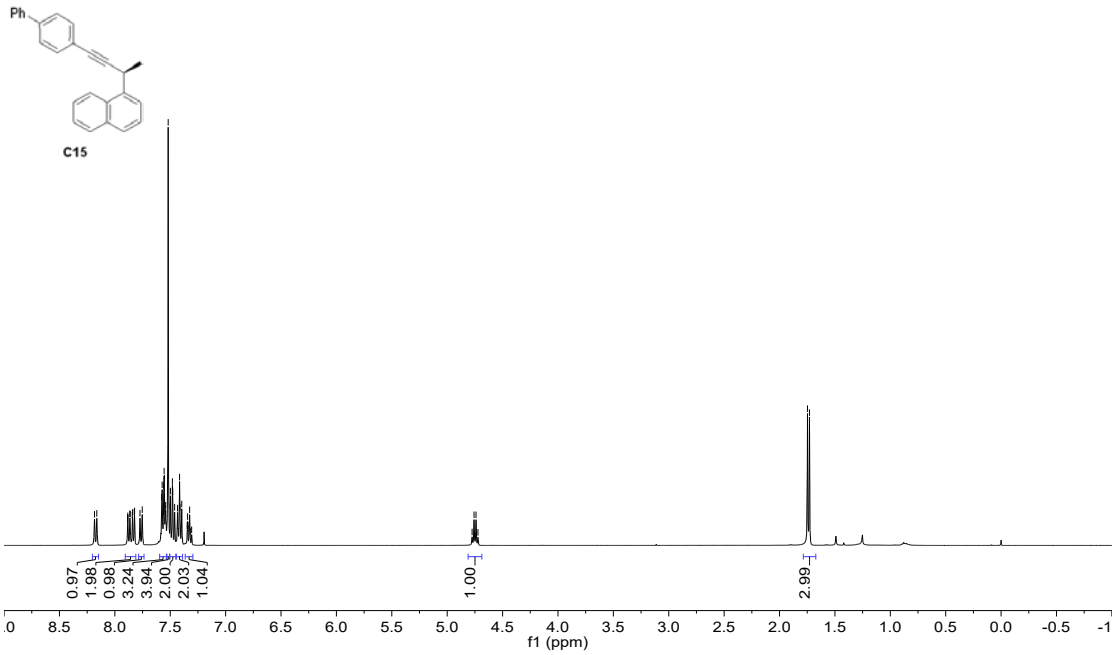
4.740
4.722
1.748
1.730


Ph
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0.98
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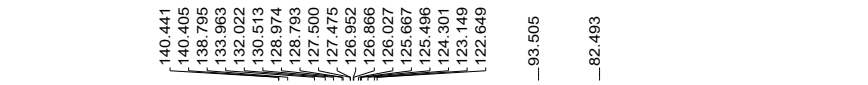
2.00
2.03
1.04
1.00
2.99
f1 (ppm)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140.405
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127.475
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126.027
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122.649
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82.493
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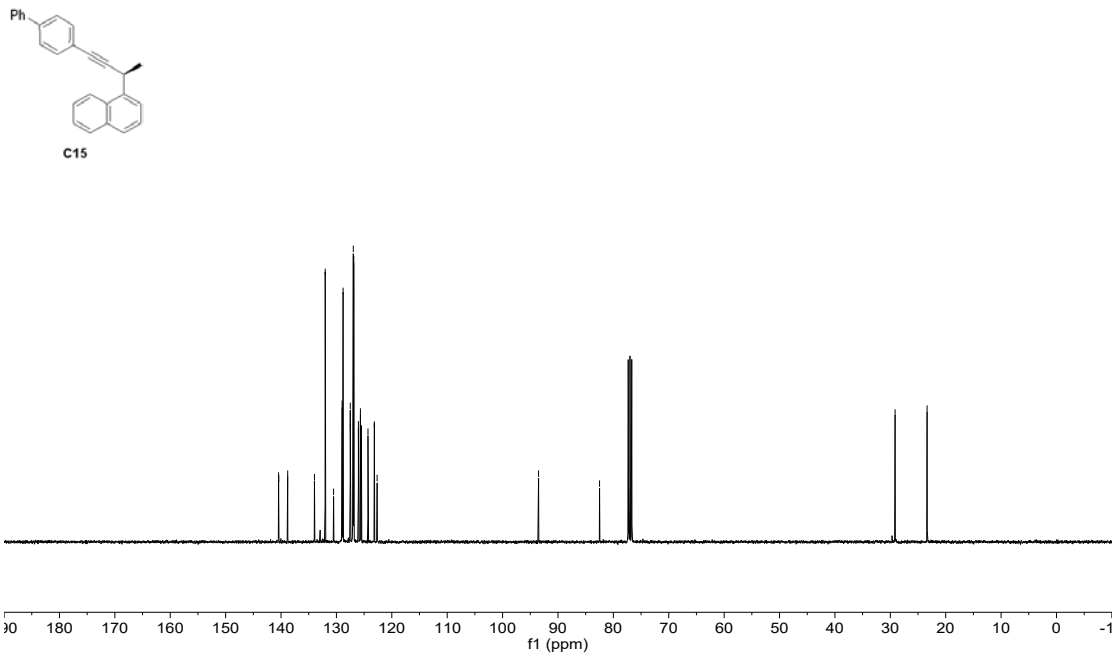
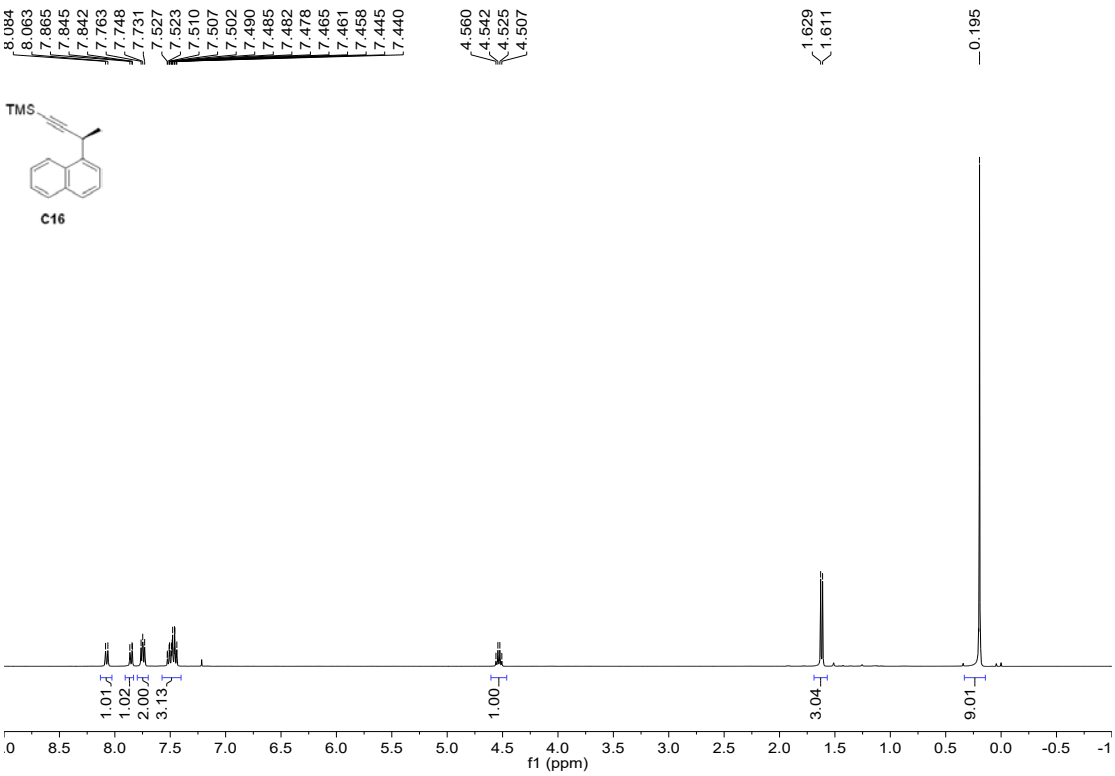
23.361


Ph
C15
f1 (ppm)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7.731
7.527
7.523
7.510
7.507
7.502
7.490
7.485
7.482
7.478
7.465
7.461
7.458
7.445
7.440
4.560
4.542
4.525
4.507
1.629
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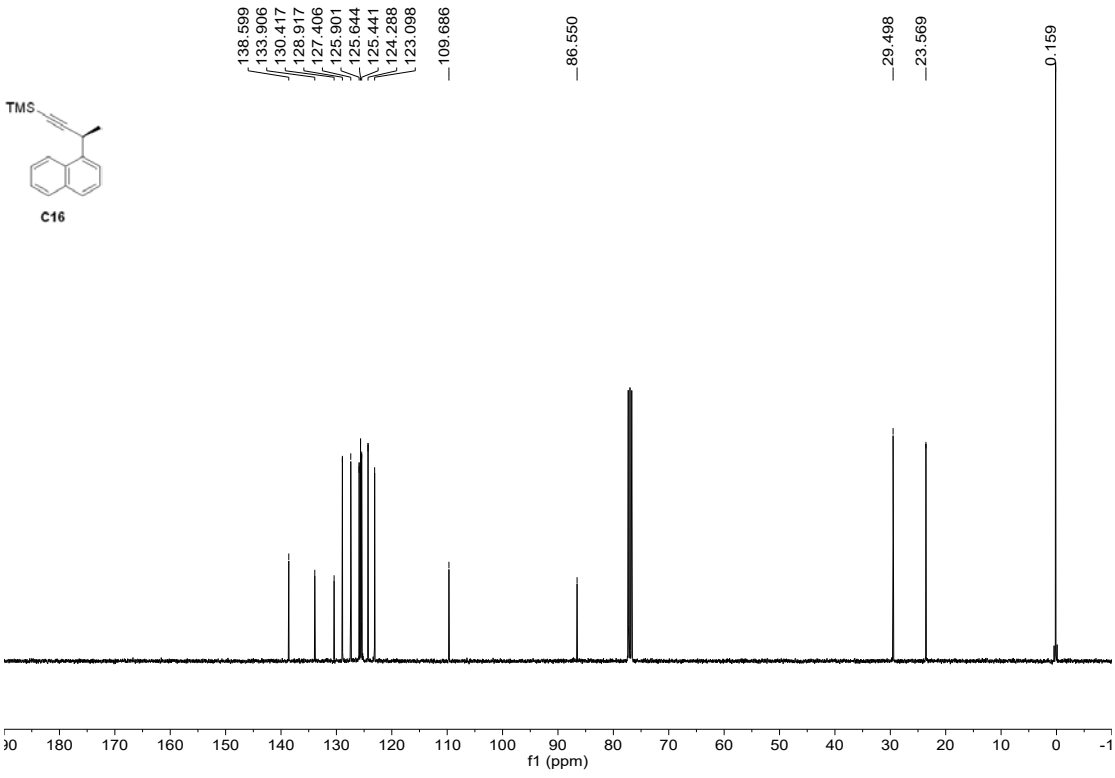
TMS
C16
1.01
1.02
2.00
3.13
1.00
3.04
9.01
f1 (ppm)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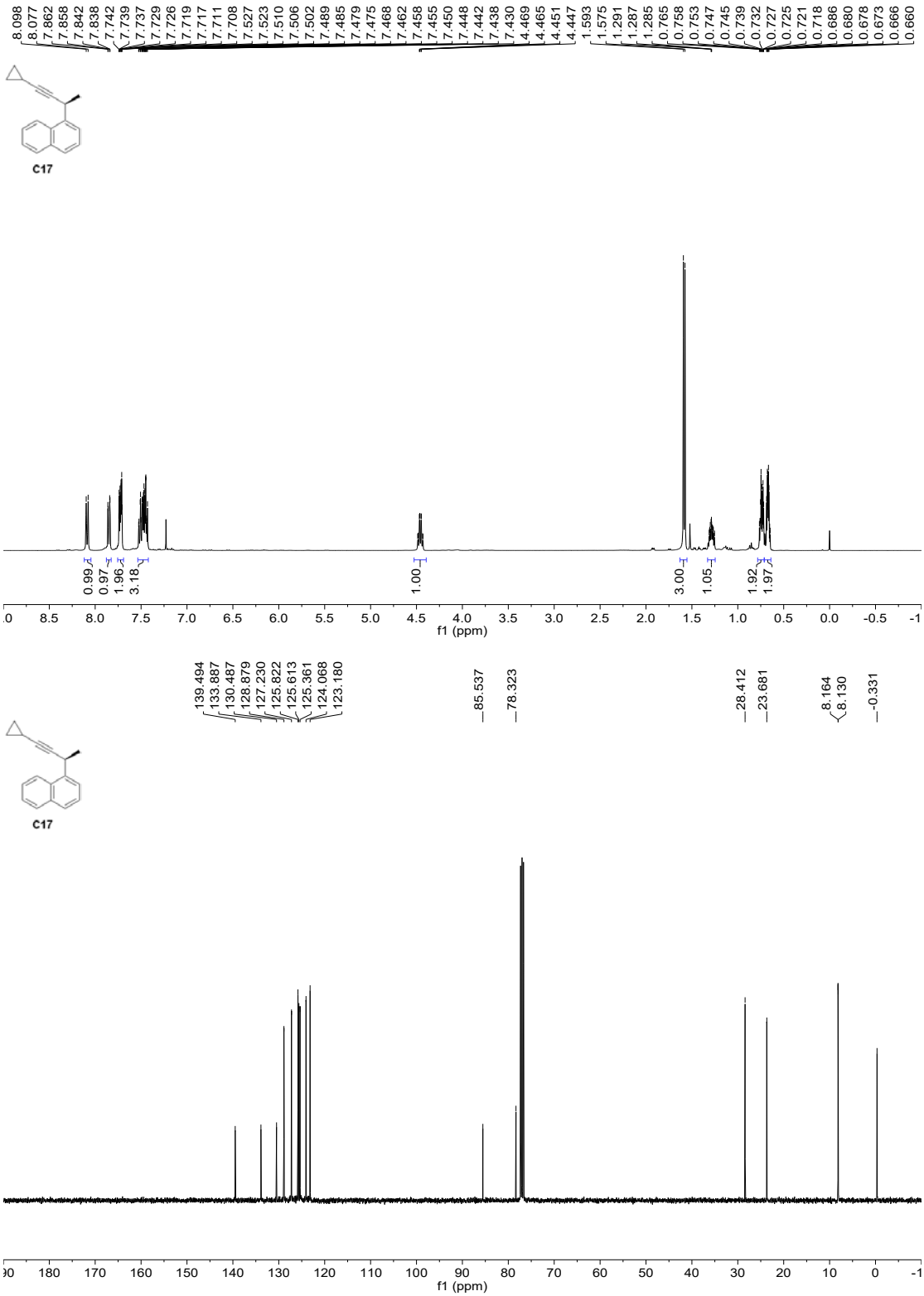
86.550
29.498
23.569
0.159
TMS
C16
f1 (ppm)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7.838
7.742
7.739
7.737
7.729
7.726
7.719
7.717
7.711
7.708
7.527
7.523
7.510
7.506
7.502
7.489
7.485
7.479
7.475
7.468
7.462
7.458
7.455
7.450
7.448
7.442
7.438
7.430
4.469
4.465
4.451
4.447
1.593
1.575
1.291
1.287
1.285
0.765
0.758
0.753
0.747
0.745
0.739
0.732
0.727
0.725
0.721
0.718
0.686
0.680
0.678
0.673
0.666
0.660
C17
0.99
0.97
1.96
3.18
1.00
3.00
1.05
1.92
1.97
f1 (ppm)
139.494
133.887
130.487
128.879
127.230
125.822
125.613
125.361
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85.537
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28.412
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8.130
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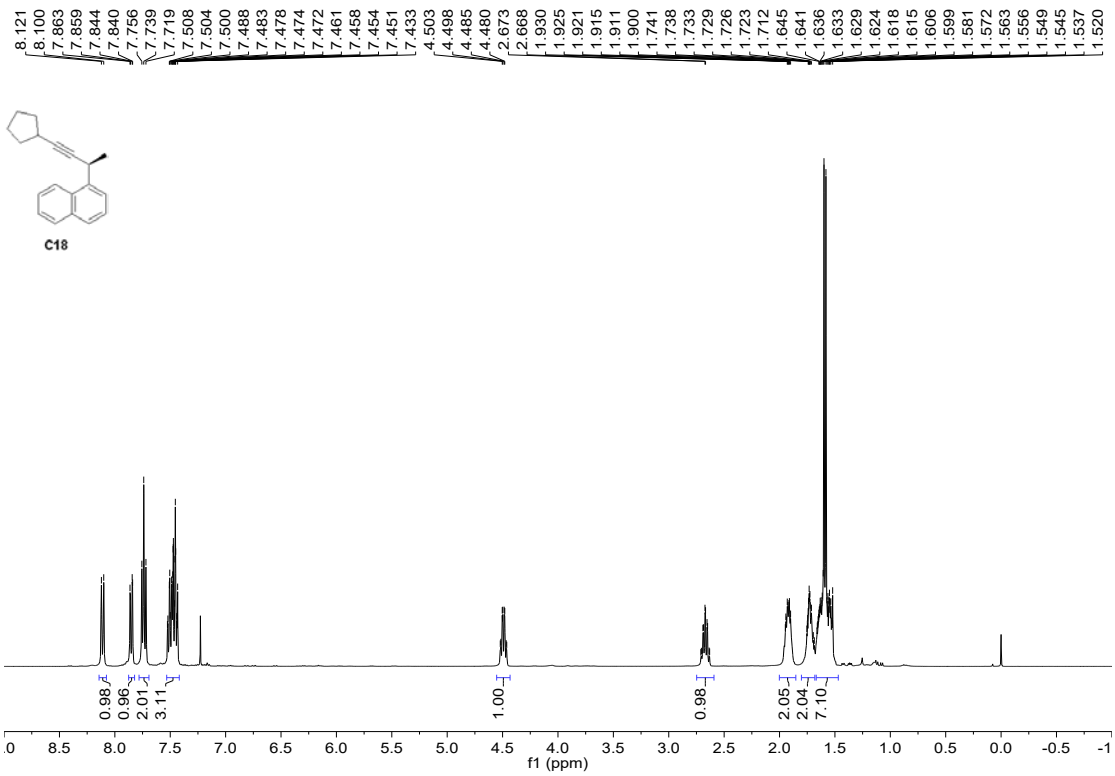
C17
f1 (ppm)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7.483
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7.474
7.472
7.461
7.458
7.454
7.451
7.433
4.503
4.498
4.485
4.480
2.673
2.668
1.930
1.925
1.921
1.915
1.911
1.900
1.741
1.738
1.733
1.729
1.726
1.723
1.712
1.645
1.641
1.636
1.633
1.629
1.624
1.618
1.615
1.606
1.599
1.581
1.572
1.563
1.556
1.549
1.545
1.537
1.520
C18
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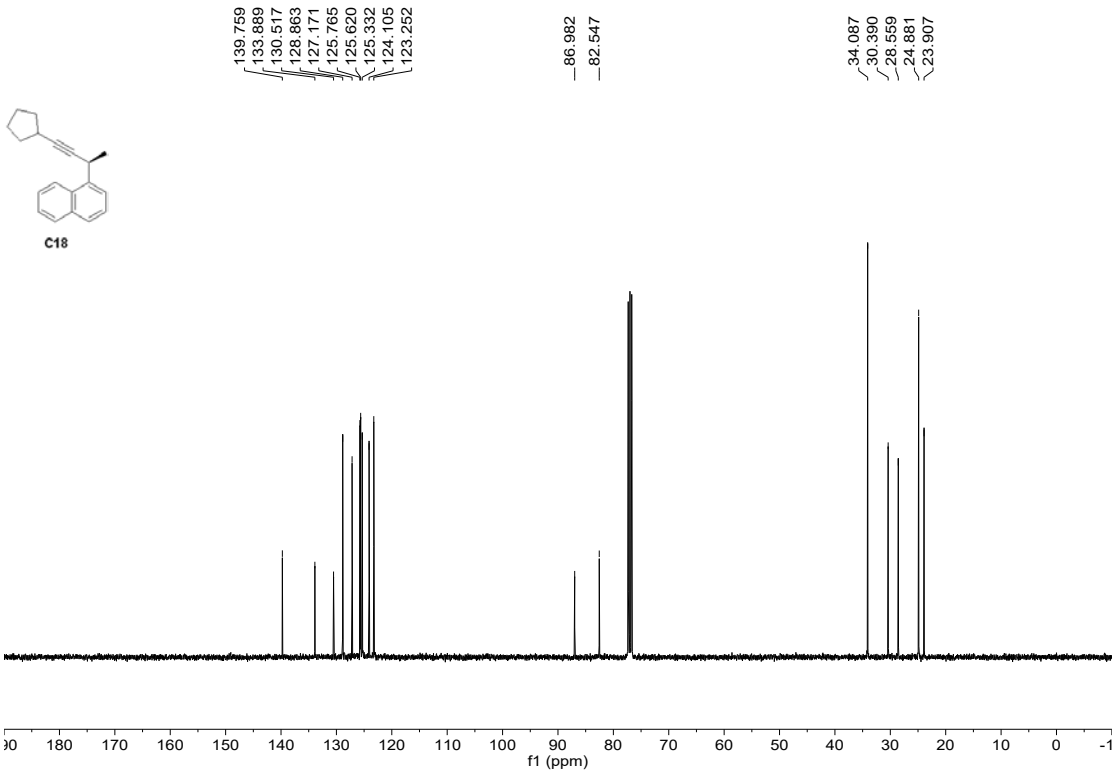
0.96
2.01
3.11
1.00
0.98
2.05
2.04
7.10
f1 (ppm)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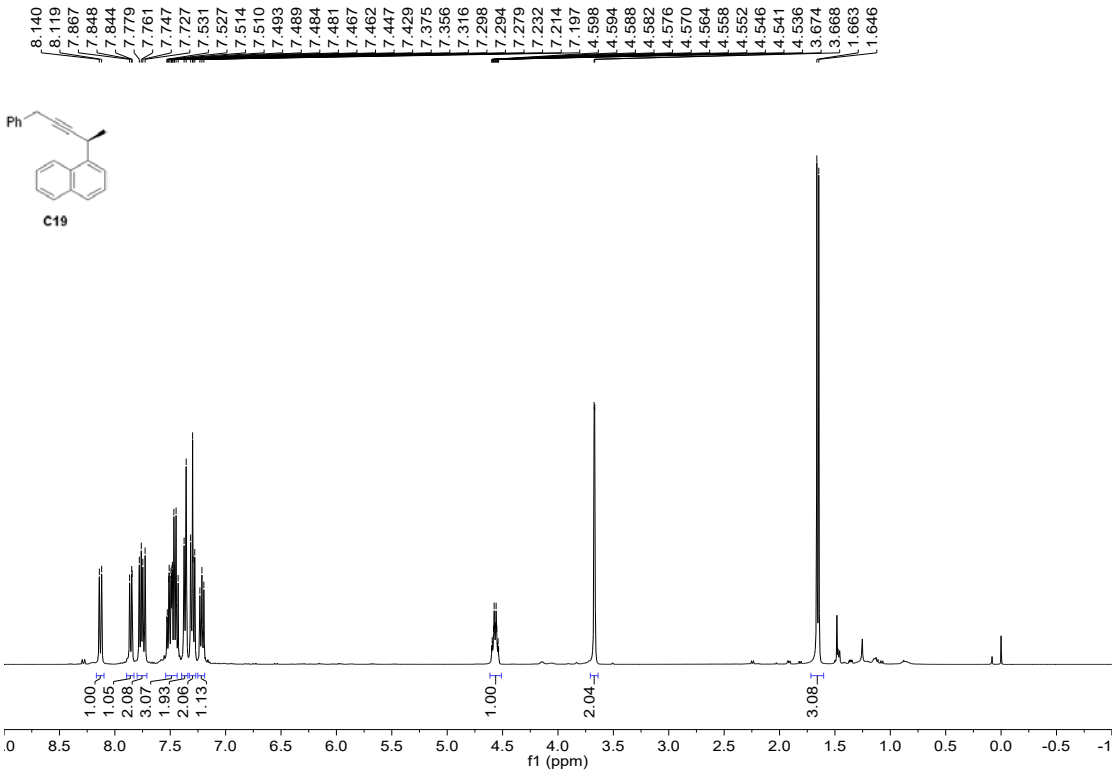
24.881
23.907
C18
f1 (ppm)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7.727
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7.527
7.514
7.510
7.493
7.489
7.484
7.481
7.467
7.462
7.447
7.429
7.375
7.356
7.316
7.298
7.294
7.279
7.232
7.214
7.197
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4.594
4.588
4.582
4.576
4.570
4.564
4.558
4.552
4.546
4.541
4.536
3.674
3.668
1.663
1.646
Ph
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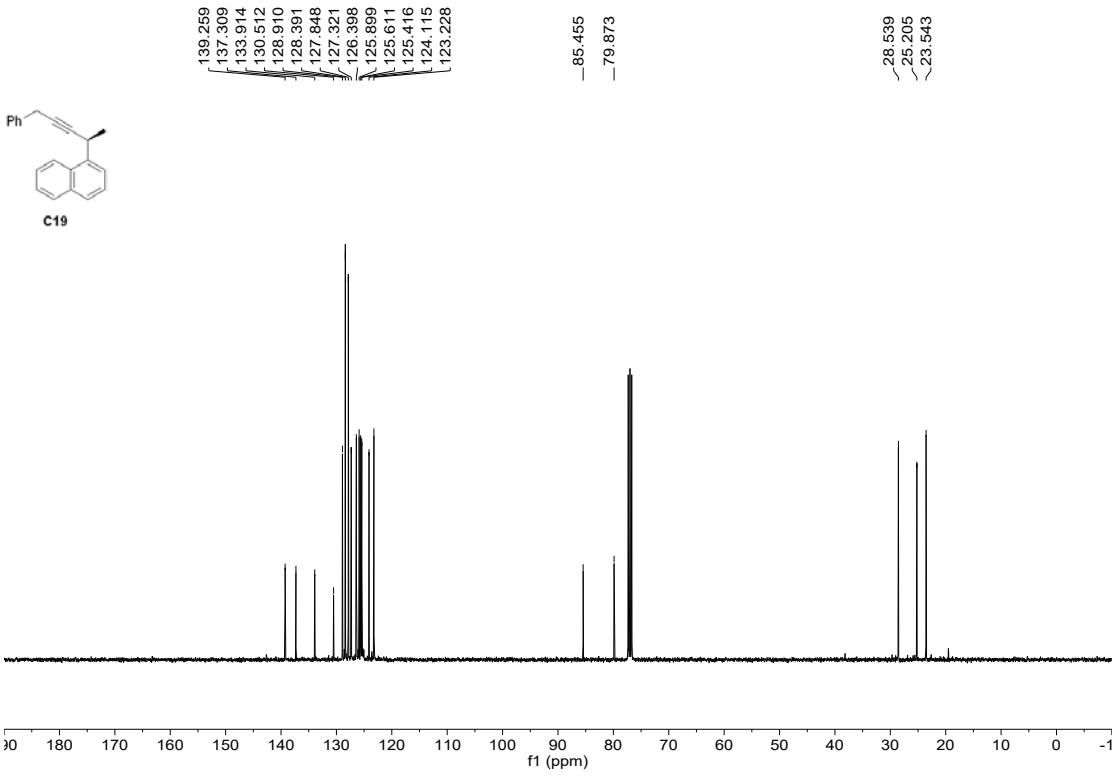
2.08
3.07
1.93
2.06
1.13
1.00
2.04
3.08
f1 (ppm)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124.115
123.228
85.455
79.873
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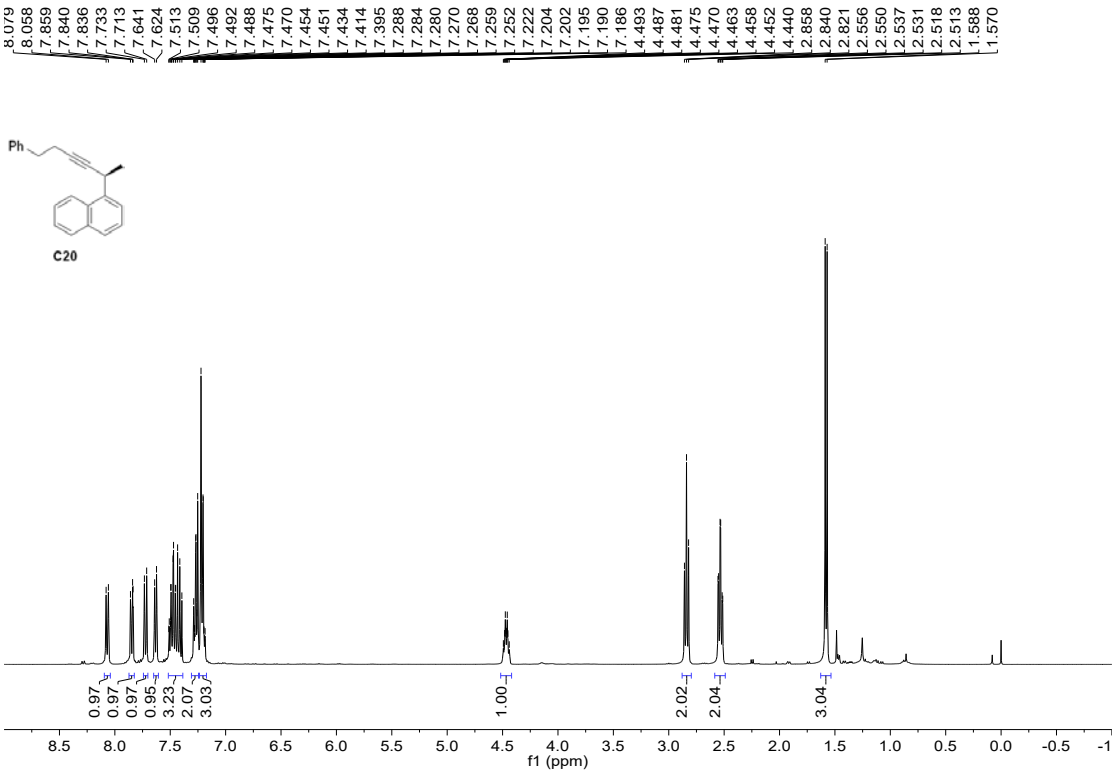
25.205
23.543
Ph
C19
f1 (ppm)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7.509
7.496
7.492
7.488
7.475
7.470
7.454
7.451
7.434
7.414
7.395
7.288
7.284
7.280
7.270
7.268
7.259
7.252
7.222
7.204
7.202
7.195
7.190
7.186
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4.487
4.481
4.475
4.470
4.463
4.458
4.452
4.440
2.858
2.840
2.821
2.556
2.550
2.537
2.531
2.518
2.513
1.588
1.570
Ph
C20
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0.95
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2.07
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2.02
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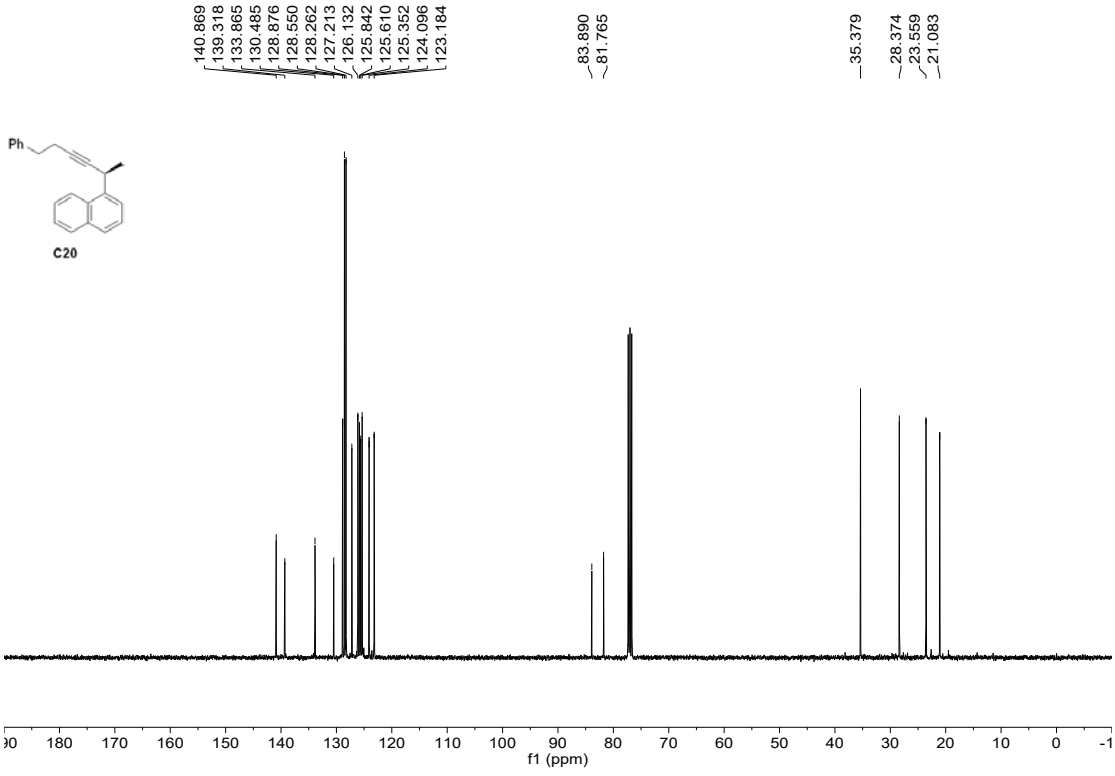
3.04
f1 (ppm)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127.213
126.132
125.842
125.610
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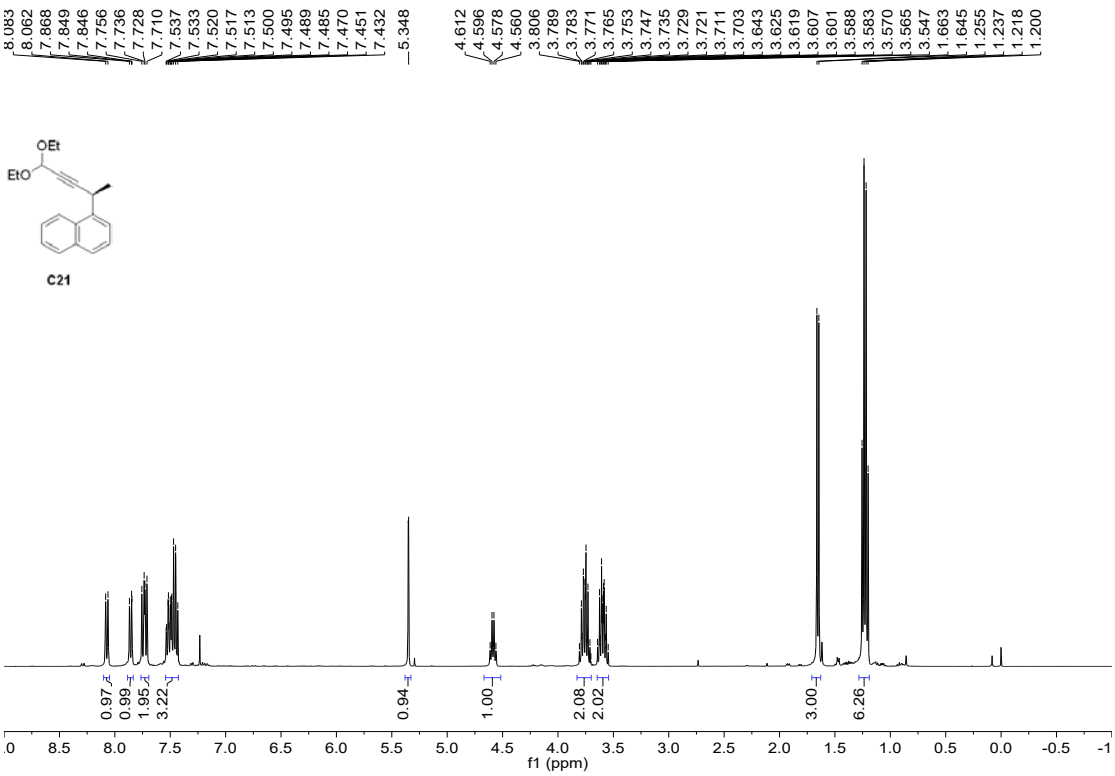
123.184
83.890
81.765
35.379
28.374
23.559
21.083
Ph
C20
f1 (ppm)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7.520
7.517
7.513
7.500
7.495
7.489
7.485
7.470
7.451
7.432
5.348
4.612
4.596
4.578
4.560
3.806
3.789
3.783
3.771
3.765
3.753
3.747
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3.729
3.721
3.711
3.703
3.643
3.625
3.619
3.607
3.601
3.588
3.583
3.570
3.565
3.547
1.663
1.645
1.255
1.237
1.218
1.200
OEt
EtO
C21
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1.95
3.22
0.94
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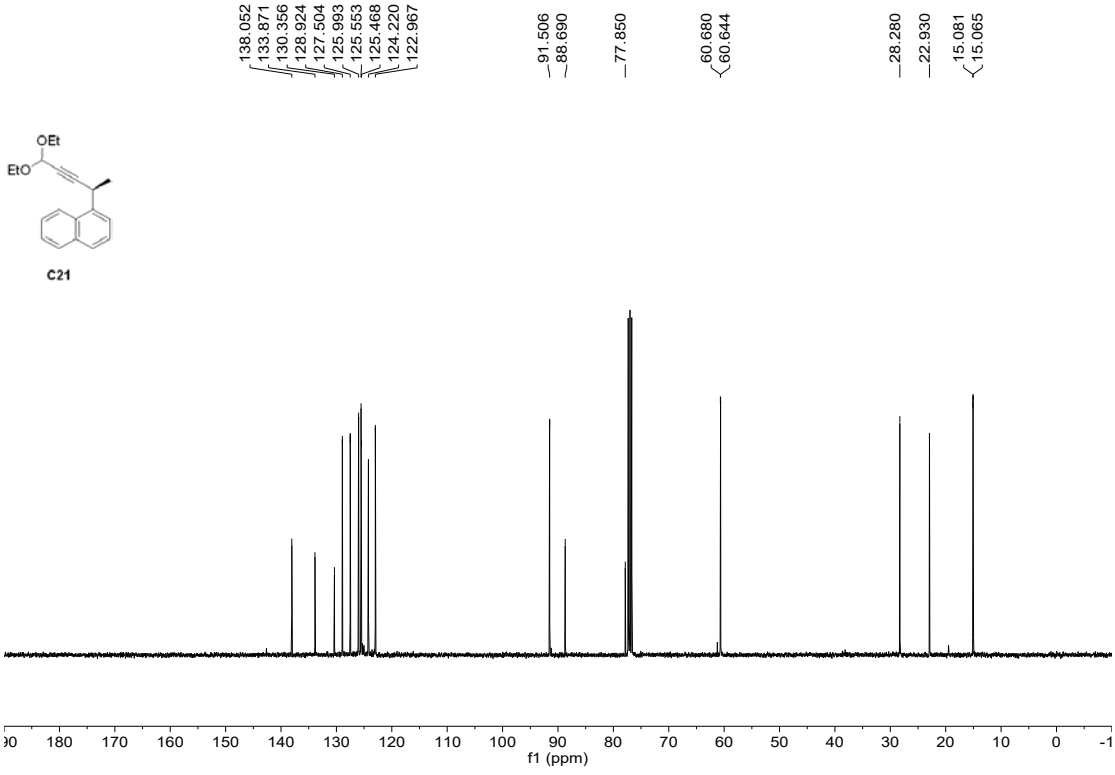
2.02
3.00
6.26
f1 (ppm)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122.967
91.506
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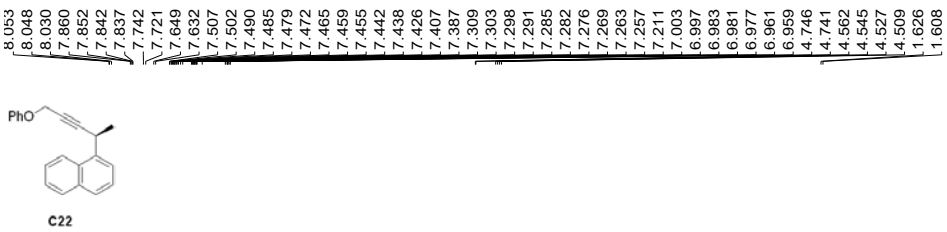
60.644
28.280
22.930
15.081
15.065
OEt
EtO
C21
f1 (ppm)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7.507
7.502
7.490
7.485
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7.472
7.465
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7.438
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7.387
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7.303
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7.291
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7.276
7.269
7.263
7.257
7.211
7.003
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6.981
6.977
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4.741
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4.545
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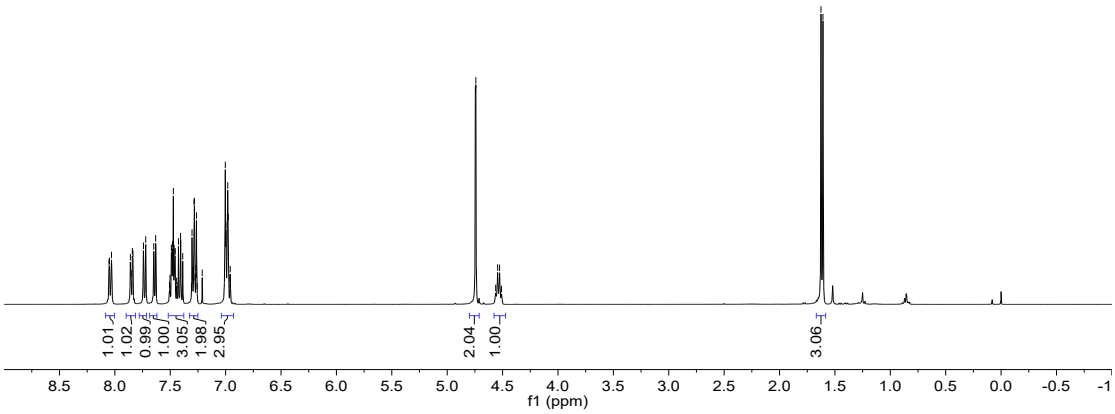
4.509
1.626
1.608

PhO

C22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2.04
1.00
3.06
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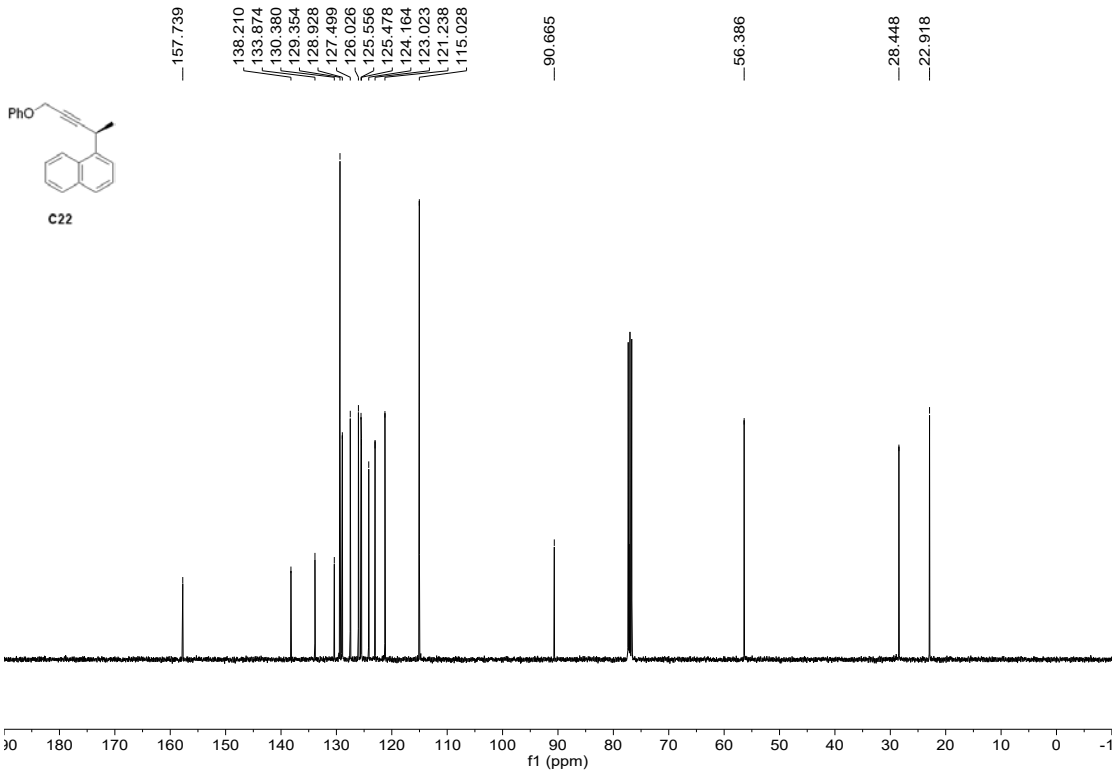
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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125.478
124.164
123.023
121.238
115.028
90.665
56.386
28.448
22.918
PhO
C22
180
170
160
150
140
130
120
110
100
90
80
70
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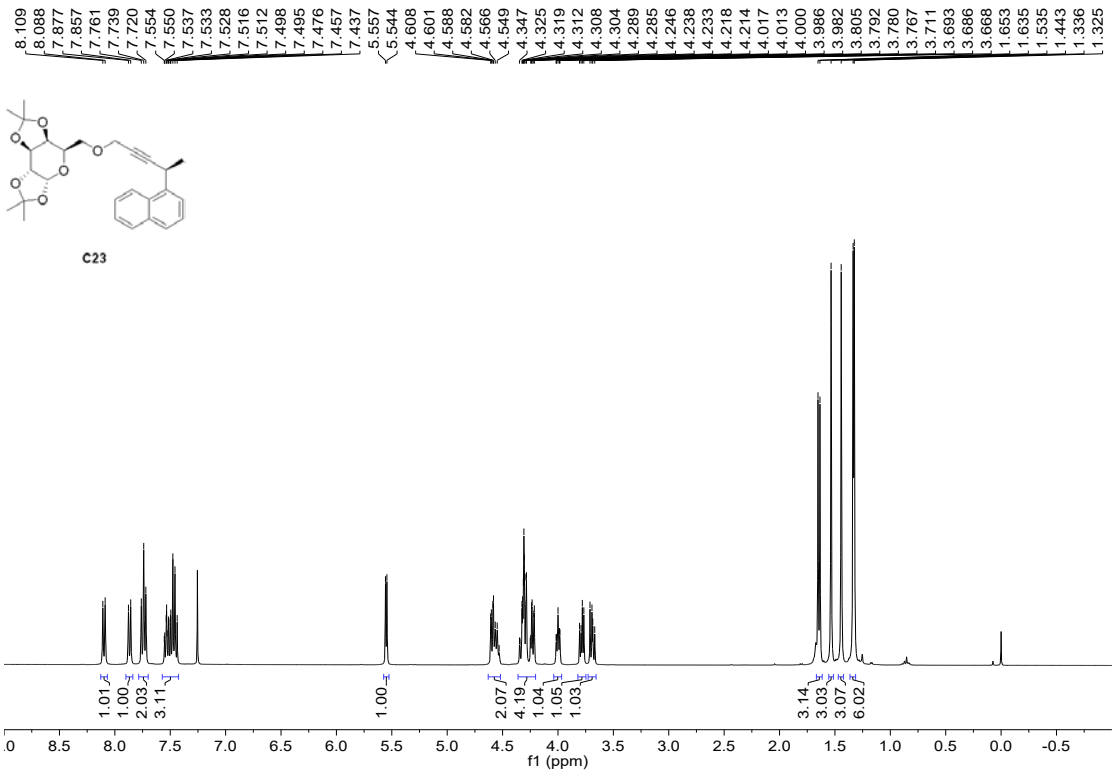
50
40
30
20
10
0
-1
f1 (ppm)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7.512
7.498
7.495
7.476
7.457
7.437
5.557
5.544
4.608
4.601
4.588
4.582
4.566
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3.711
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3.686
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1.635
1.535
1.443
1.336
1.325
C23
1.01
1.00
2.03
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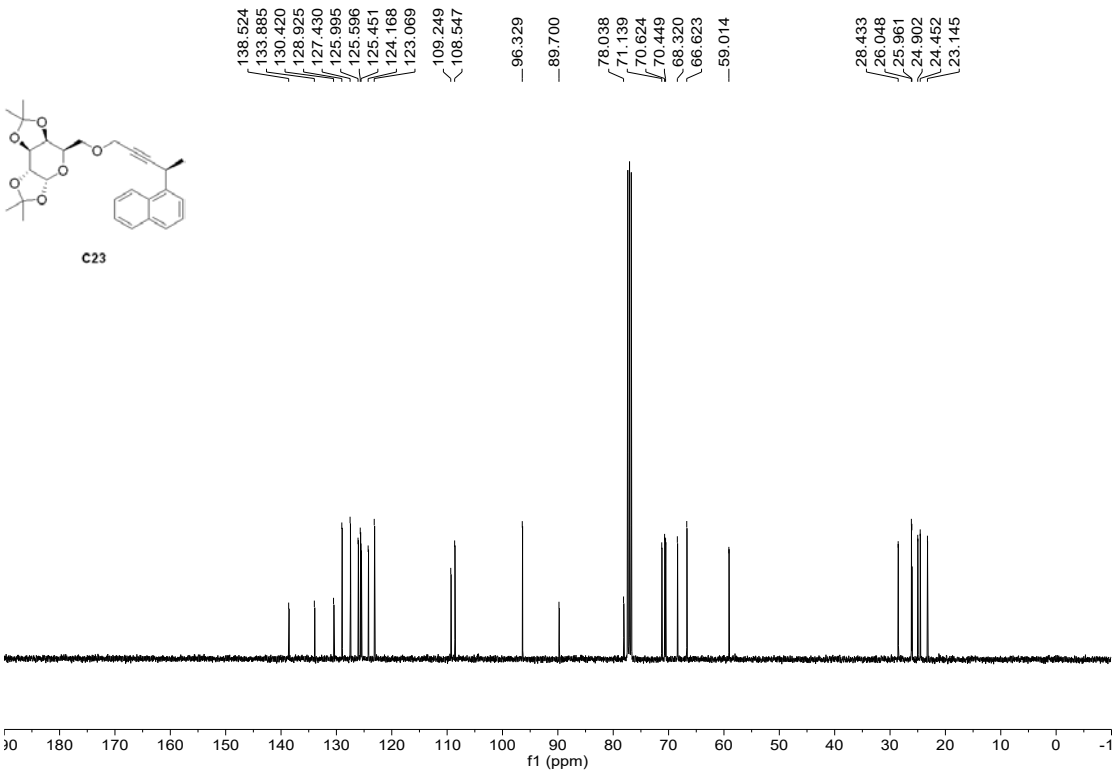
3.03
3.07
6.02
f1 (ppm)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78.038
71.139
70.624
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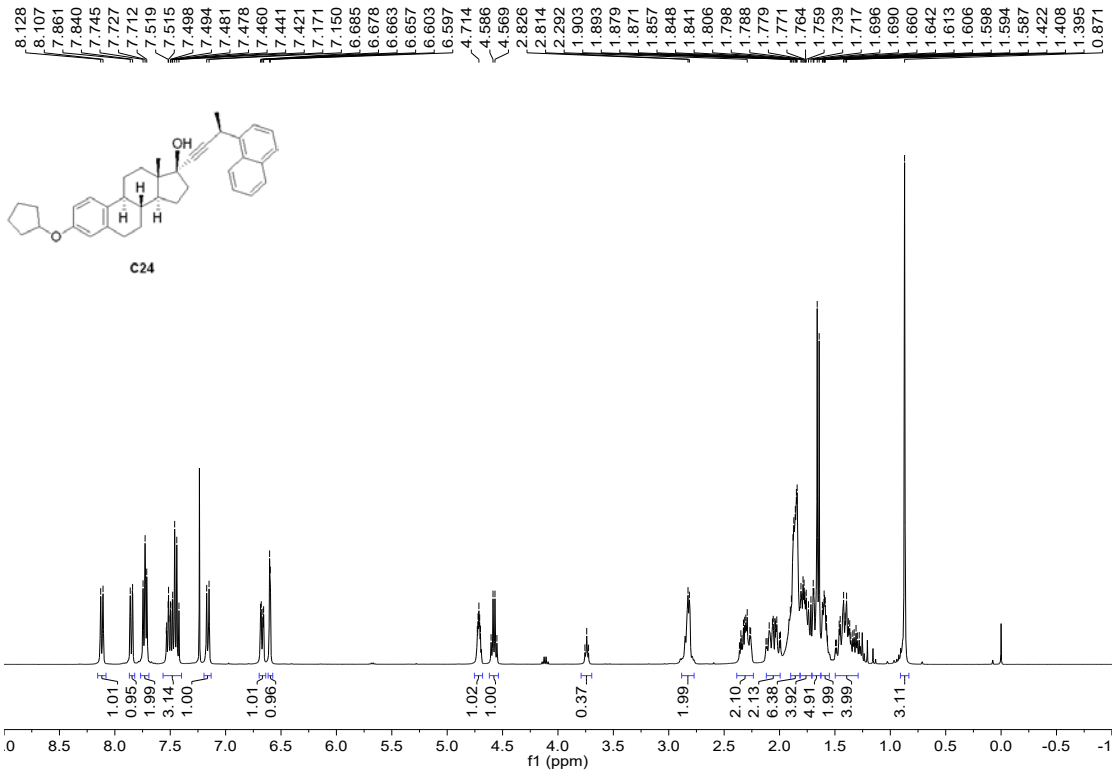
23.145
C23
f1 (ppm)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7.171
7.150
6.685
6.678
6.663
6.657
6.603
6.597
4.714
4.586
4.569
2.826
2.814
2.292
1.903
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1.422
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OH
H
H
H
O
C24
1.01
0.95
1.99
3.14
1.00
1.01
0.96
1.02
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1.99
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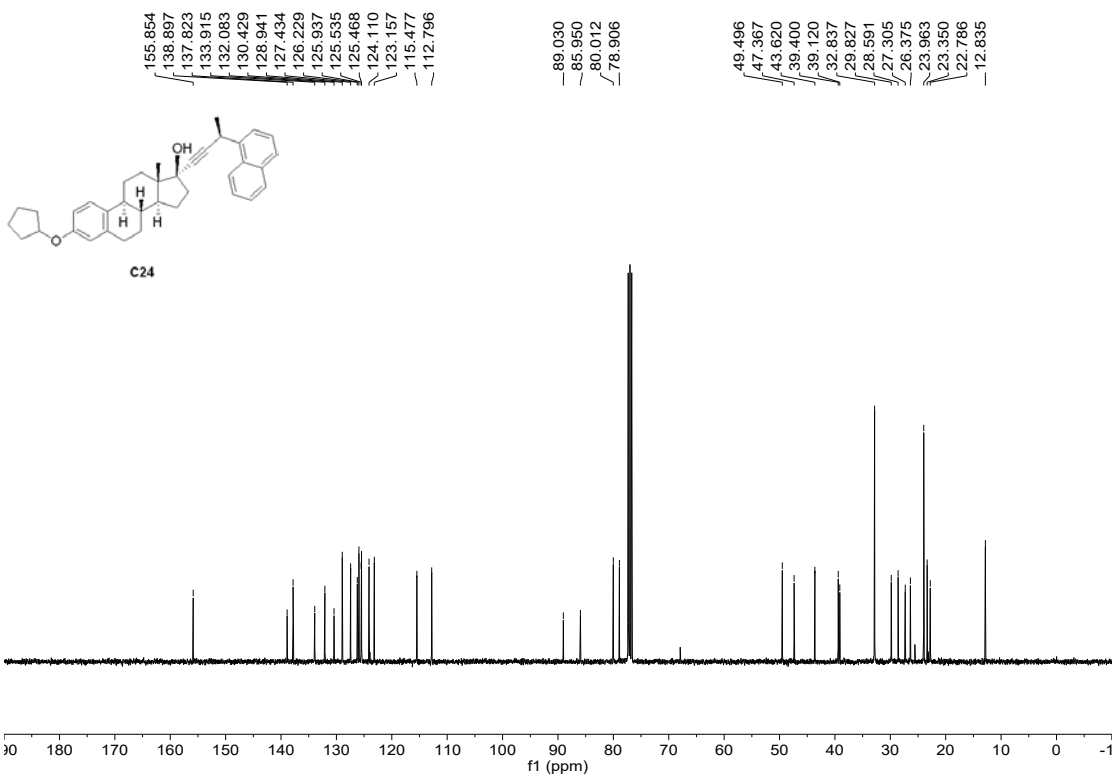
3.11
f1 (ppm)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127.434
126.229
125.937
125.535
125.468
124.110
123.157
115.477
112.796
89.030
85.950
80.012
78.906
49.496
47.367
43.620
39.400
39.120
32.837
29.827
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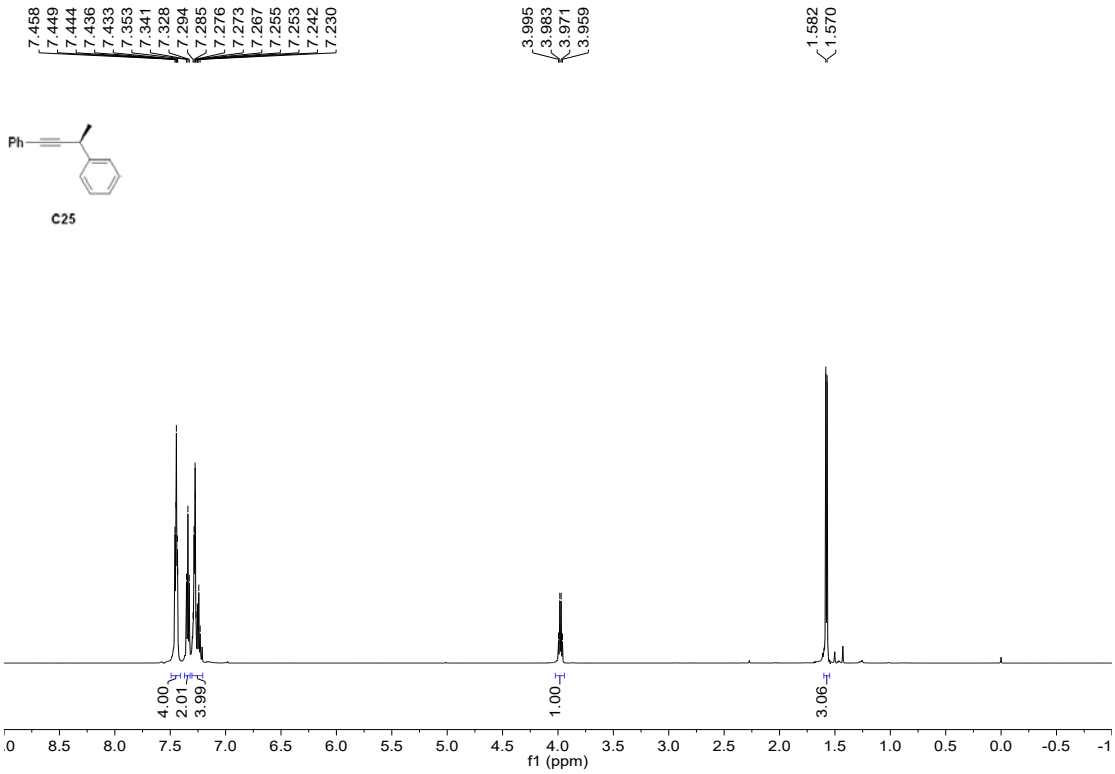
23.963
23.350
22.786
12.835
OH
H
H
H
O
C24
f1 (ppm)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7.436
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7.328
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7.285
7.276
7.273
7.267
7.255
7.253
7.242
7.230
3.995
3.983
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1.570
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C25
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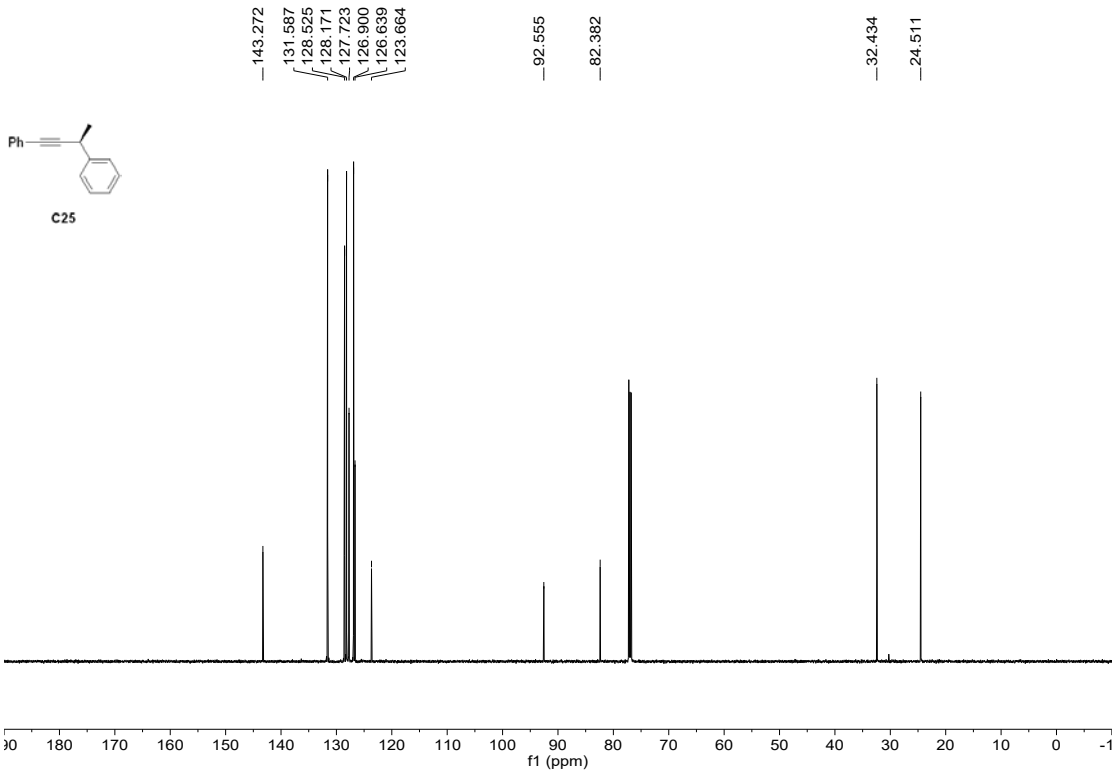
2.01
3.99
1.00
3.06
f1 (ppm)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126.639
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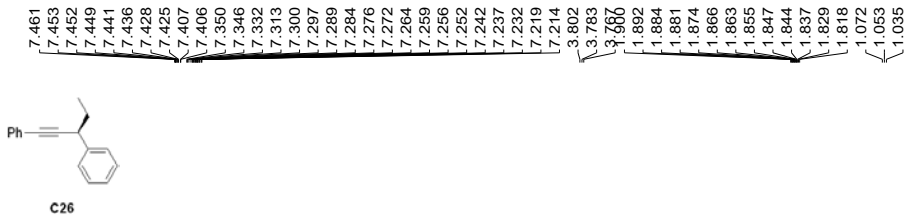
32.434
24.511
Ph
C25
f1 (ppm)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7.425
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7.406
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7.346
7.332
7.313
7.300
7.297
7.289
7.284
7.276
7.272
7.264
7.259
7.256
7.252
7.242
7.237
7.232
7.219
7.214
3.802
3.783
3.767
1.900
1.892
1.884
1.881
1.874
1.866
1.863
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1.844
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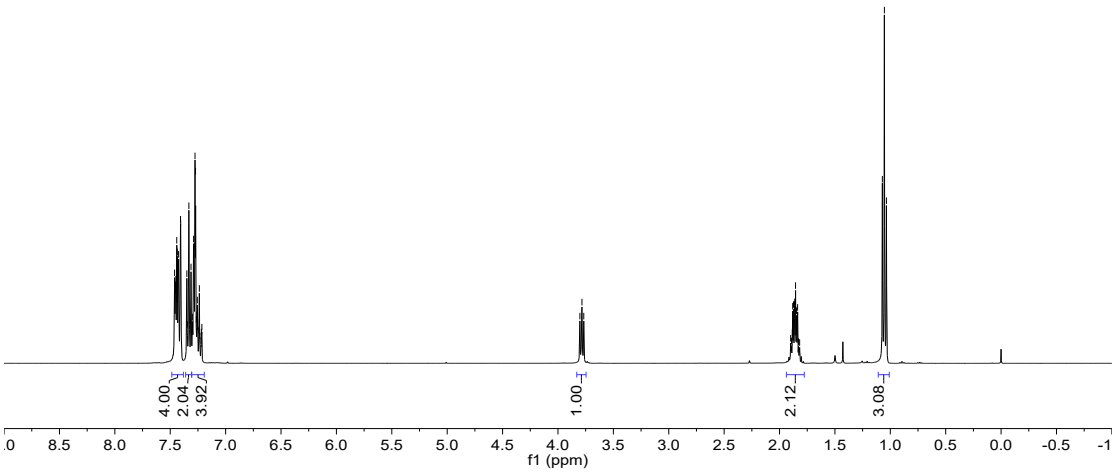
1.072
1.053
1.035

Ph

C26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8.5
8.0
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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
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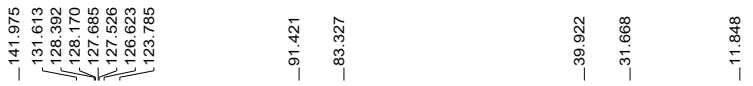
-1
f1 (ppm)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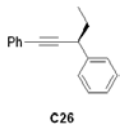
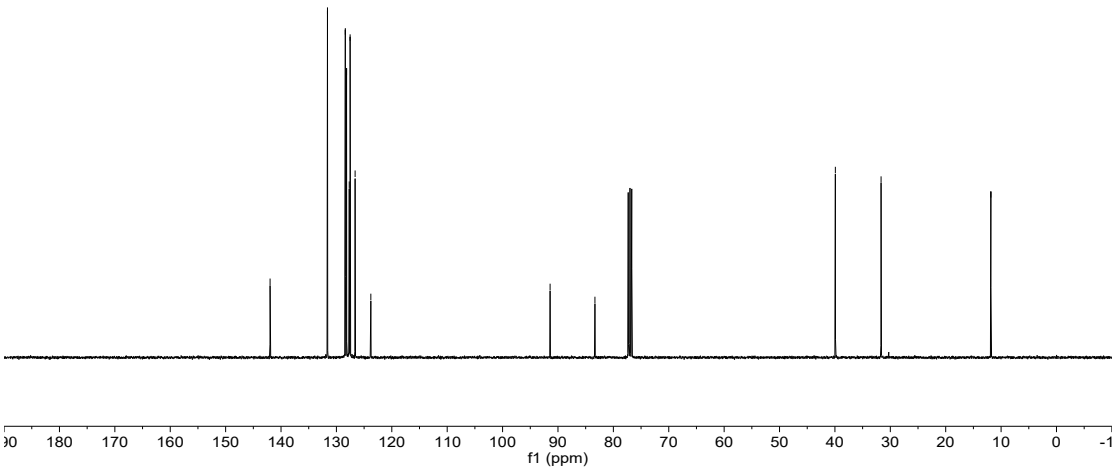
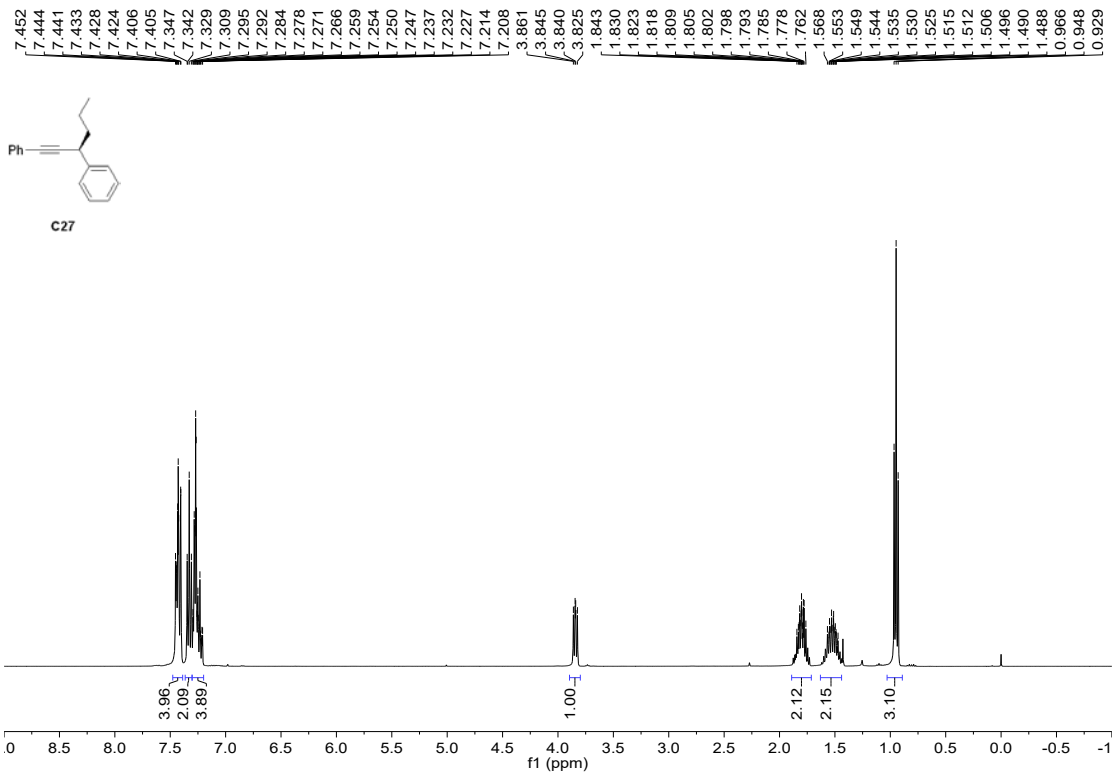
11.848


Ph

C26


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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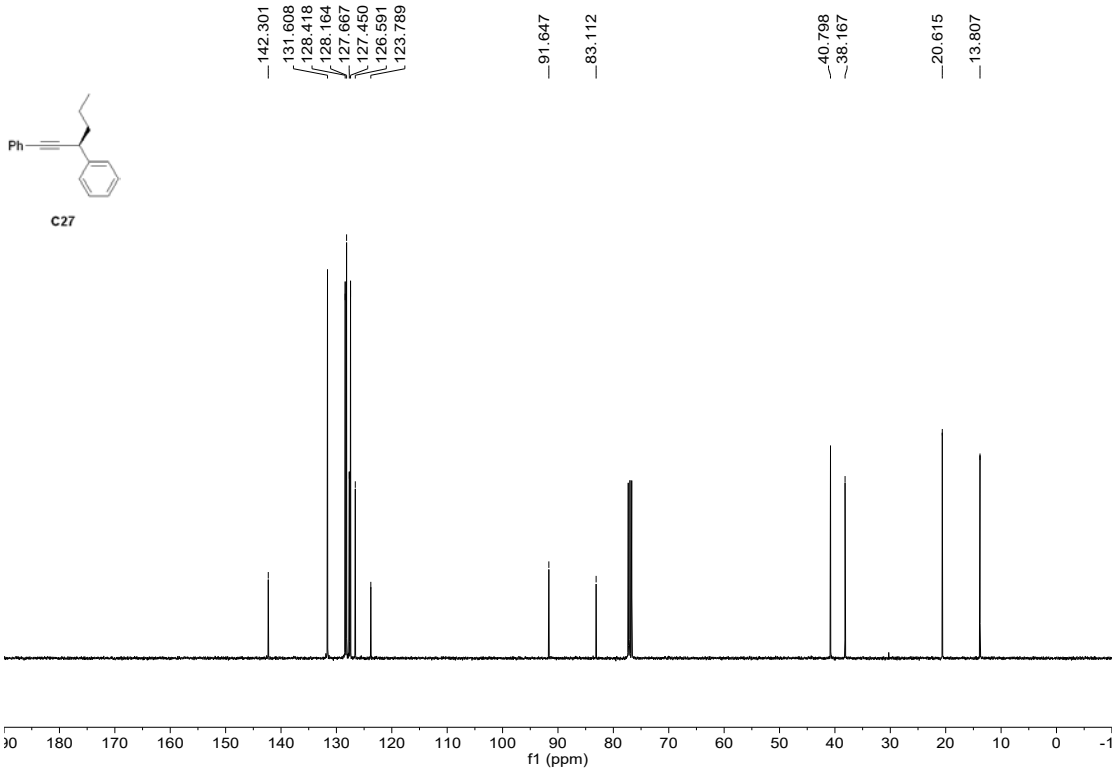
7.309
7.295
7.292
7.284
7.278
7.271
7.266
7.259
7.254
7.250
7.247
7.237
7.232
7.227
7.214
7.208
3.861
3.845
3.840
3.825
1.843
1.830
1.823
1.818
1.809
1.805
1.802
1.798
1.793
1.785
1.778
1.762
1.568
1.553
1.549
1.544
1.535
1.530
1.525
1.515
1.512
1.506
1.496
1.490
1.488
0.966
0.948
0.929
Ph
C27
3.96
2.09
3.89
1.00
2.12
2.15
3.10
f1 (ppm)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123.789
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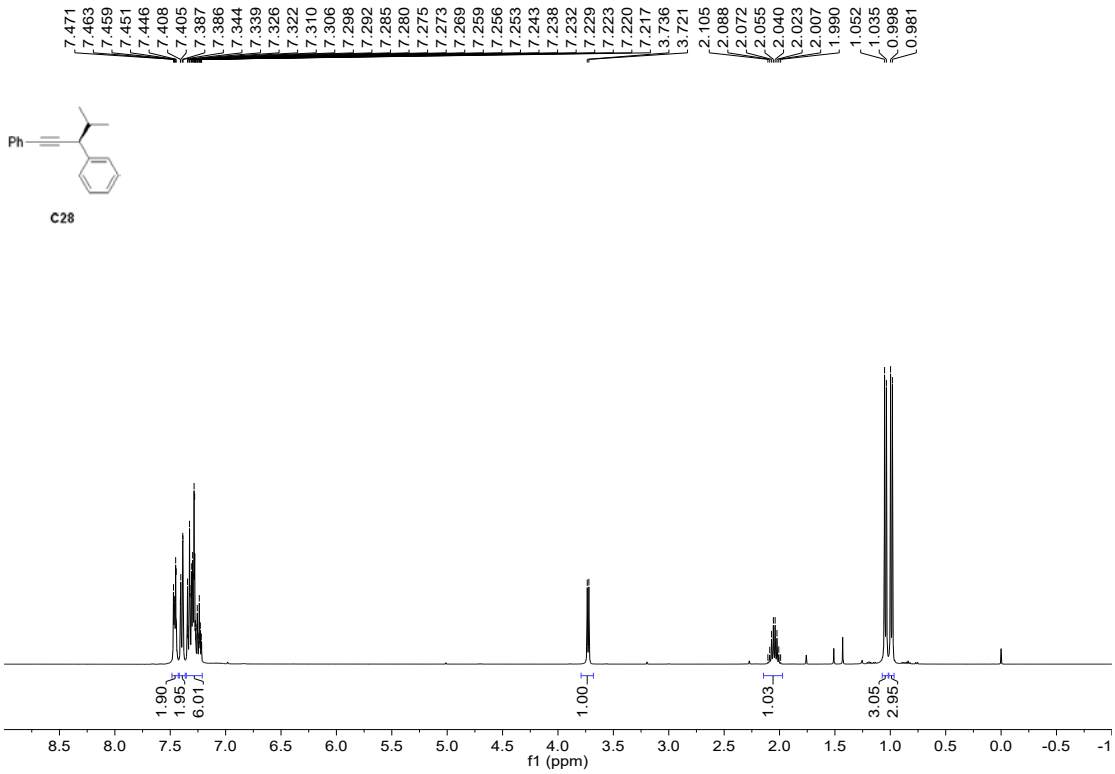
38.167
20.615
13.807
Ph
C27
f1 (ppm)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7.446
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7.322
7.310
7.306
7.298
7.292
7.285
7.280
7.275
7.273
7.269
7.259
7.256
7.253
7.243
7.238
7.232
7.229
7.223
7.220
7.217
3.736
3.721
2.105
2.088
2.072
2.055
2.040
2.023
2.007
1.990
1.052
1.035
0.998
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Ph
C28
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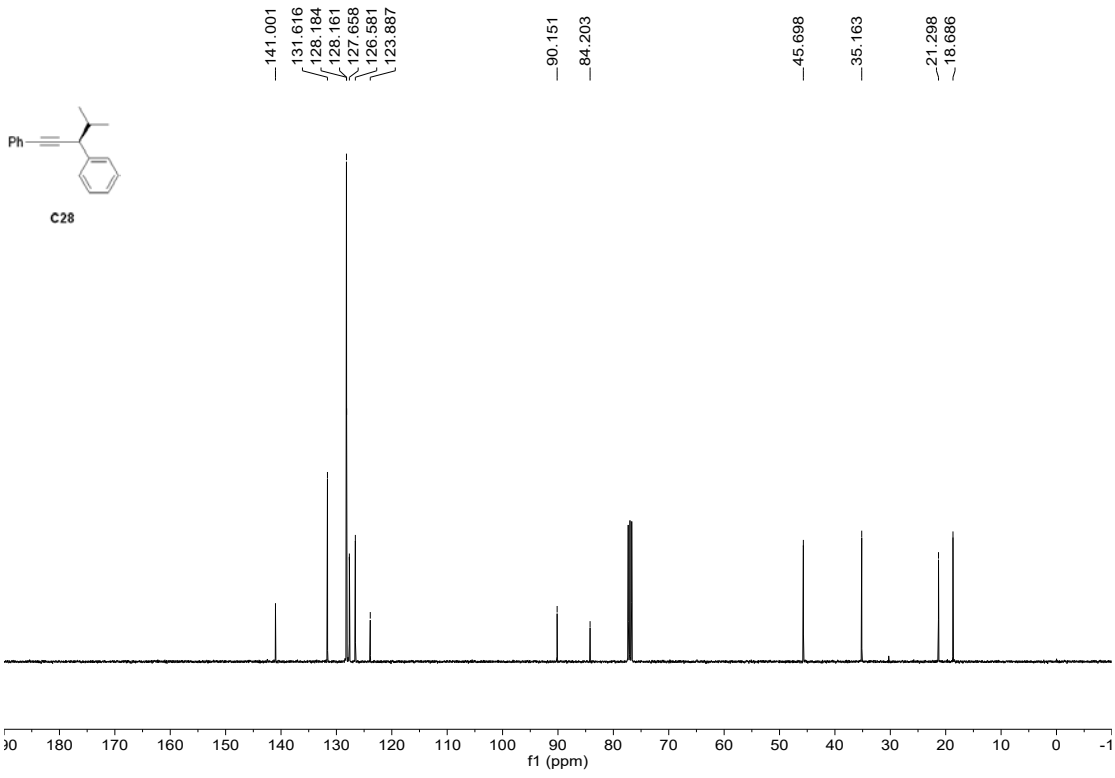
1.00
1.03
3.05
2.95
f1 (ppm)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90.151
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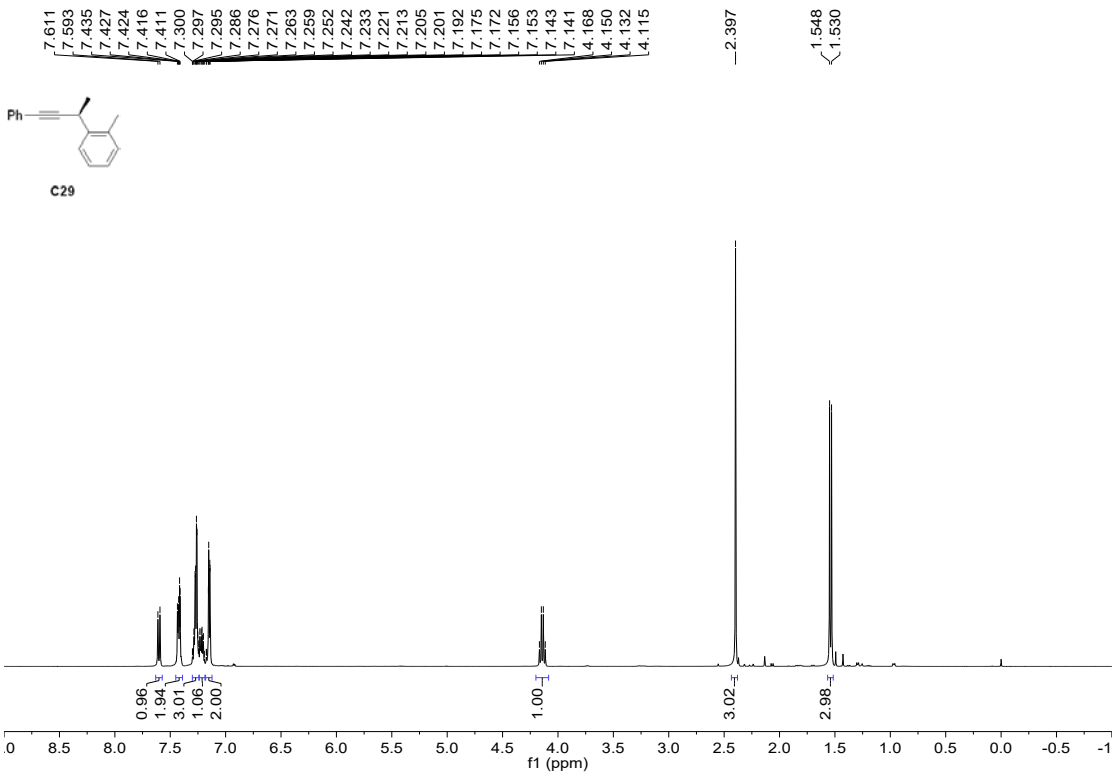
45.698
35.163
21.298
18.686
Ph
C28
f1 (ppm)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7.300
7.297
7.295
7.286
7.276
7.271
7.263
7.259
7.252
7.242
7.233
7.221
7.213
7.205
7.201
7.192
7.175
7.172
7.156
7.153
7.143
7.141
4.168
4.150
4.132
4.115
2.397
1.548
1.530
Ph
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0.96
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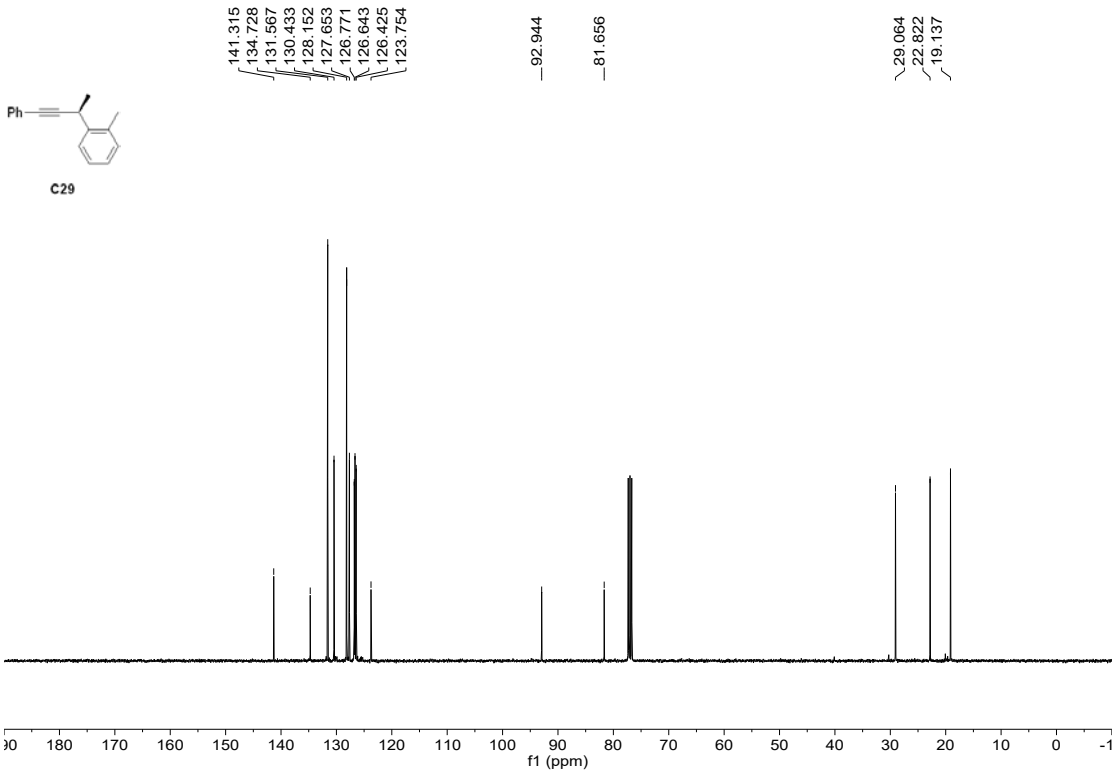
1.06
2.00
1.00
3.02
2.98
f1 (ppm)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126.643
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81.656
29.064
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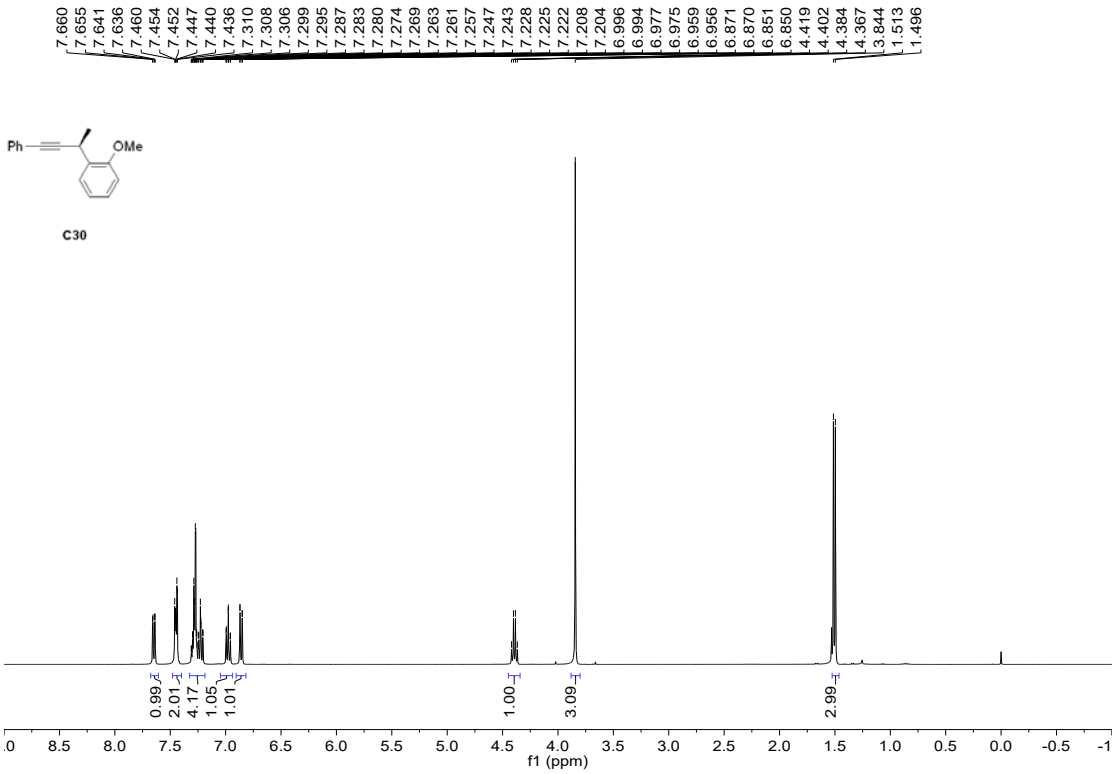
Ph
C29
f1 (ppm)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7.636
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7.440
7.436
7.310
7.308
7.306
7.299
7.295
7.287
7.283
7.280
7.274
7.269
7.263
7.261
7.257
7.247
7.243
7.228
7.225
7.222
7.208
7.204
6.996
6.994
6.977
6.975
6.959
6.956
6.871
6.870
6.851
6.850
4.419
4.402
4.384
4.367
3.844
1.513
1.496
Ph
OMe
C30
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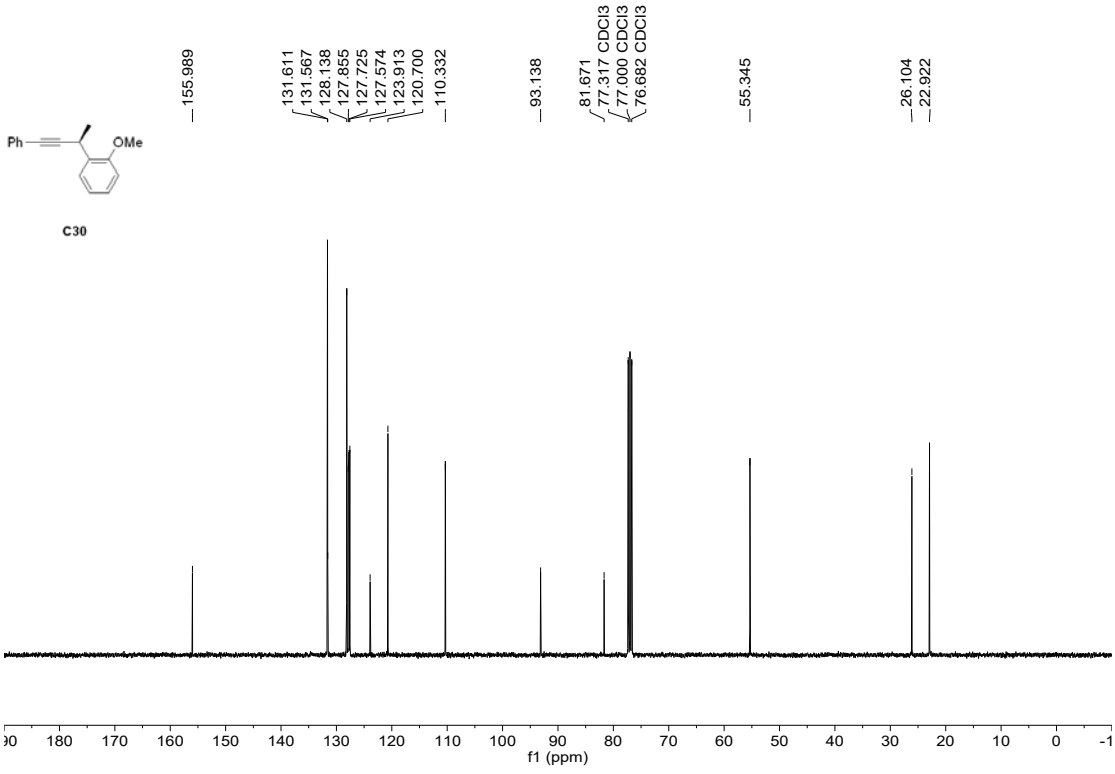
4.17
1.05
1.01
1.00
3.09
2.99
f1 (ppm)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131.567
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127.725
127.574
123.913
120.700
110.332
93.138
81.671
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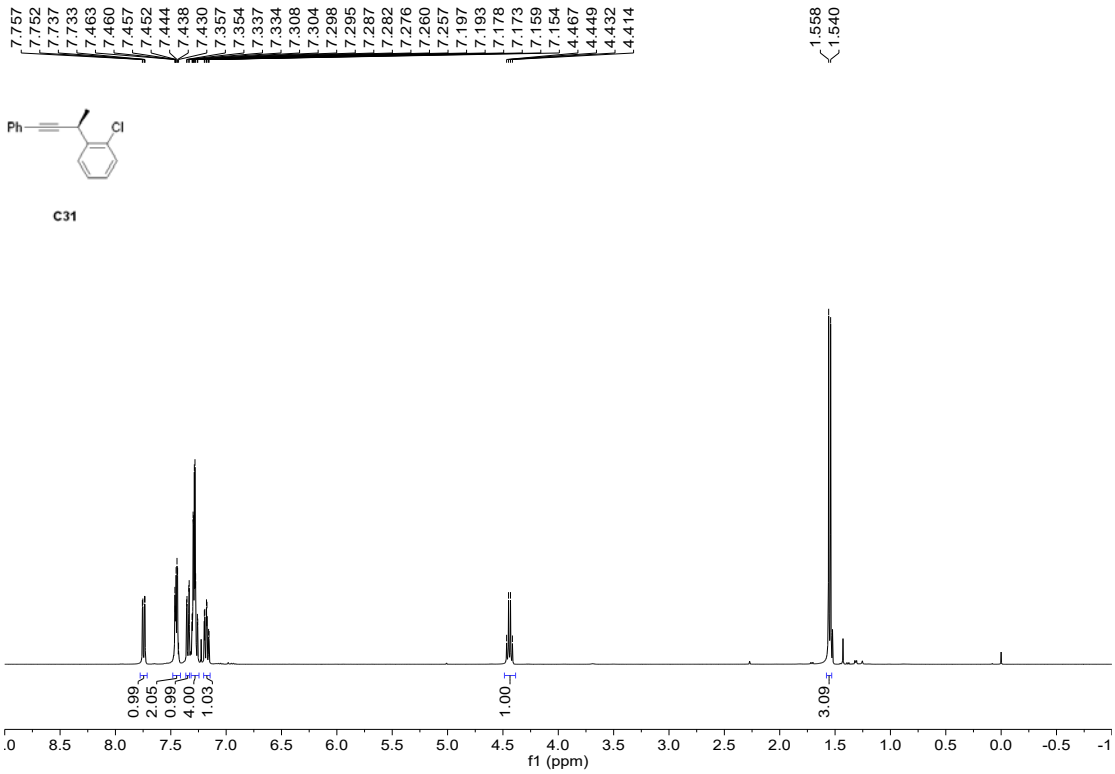
77.000 CDCl3
76.682 CDCl3
55.345
26.104
22.922
Ph
OMe
C30
f1 (ppm)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7.354
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7.308
7.304
7.298
7.295
7.287
7.282
7.276
7.260
7.257
7.197
7.193
7.178
7.173
7.159
7.154
4.467
4.449
4.432
4.414
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Cl
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0.99
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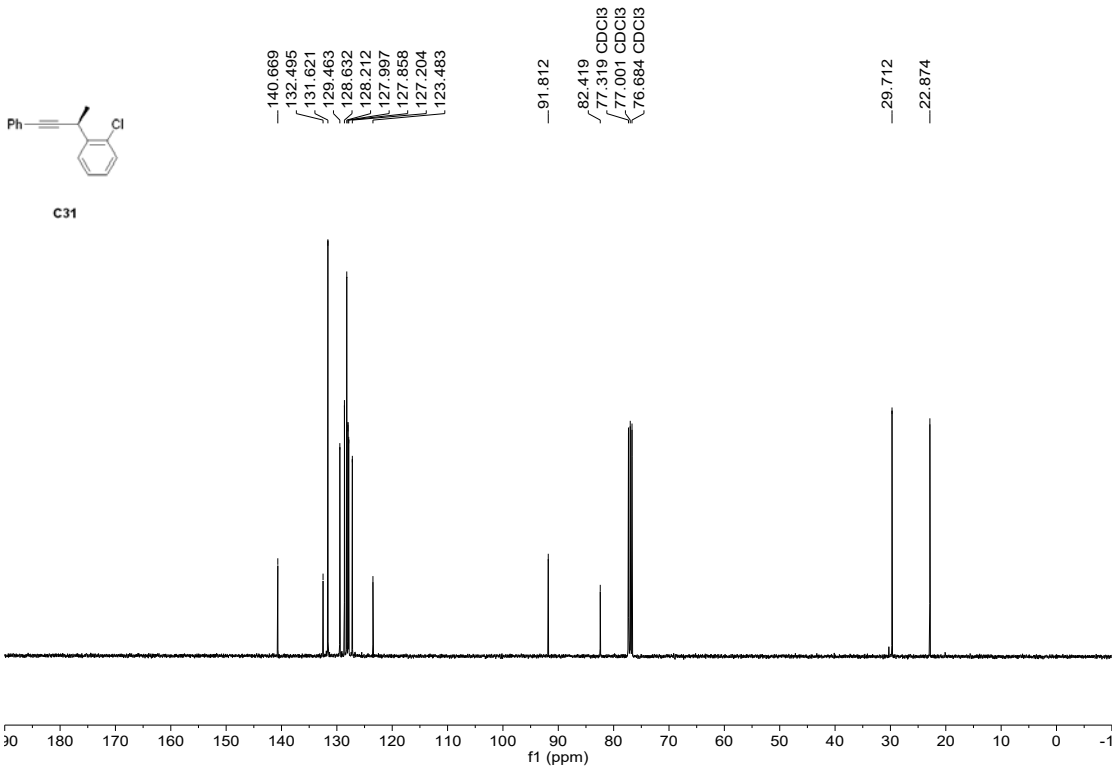
1.00
3.09
f1 (ppm)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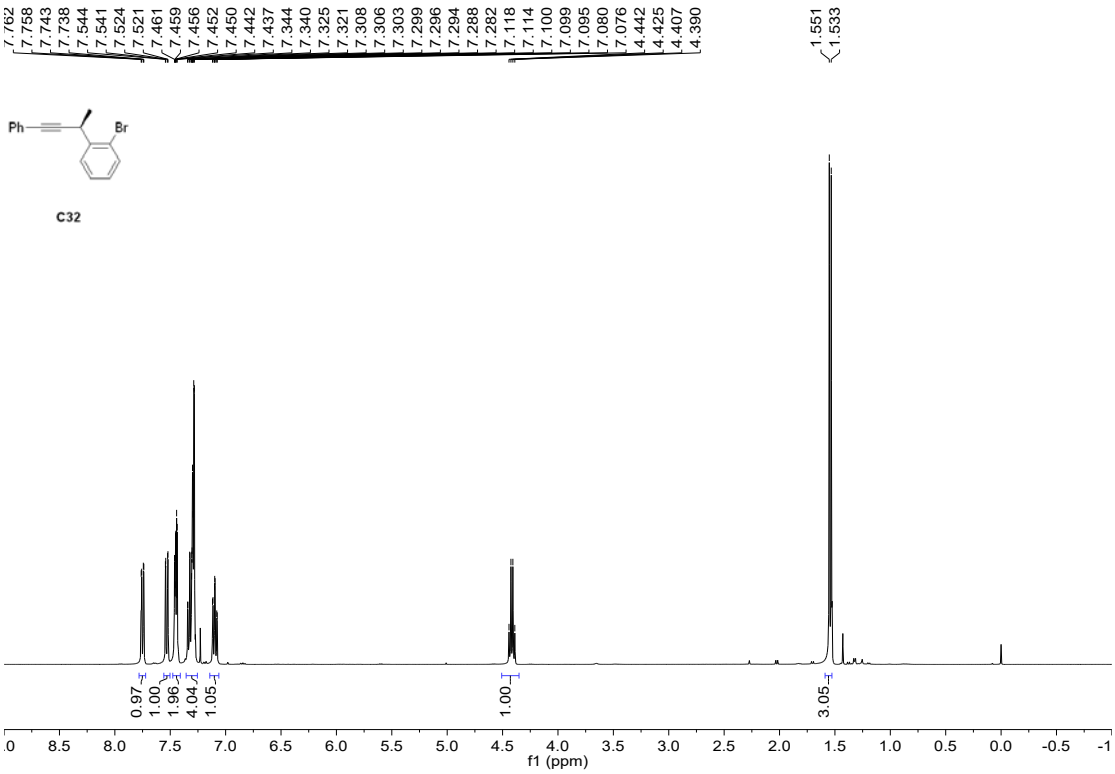
22.874
Ph
Cl
C31
f1 (ppm)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7.452
7.450
7.442
7.437
7.344
7.340
7.325
7.321
7.308
7.306
7.303
7.299
7.296
7.294
7.288
7.282
7.118
7.114
7.100
7.099
7.095
7.080
7.076
4.442
4.425
4.407
4.390
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Br
C32
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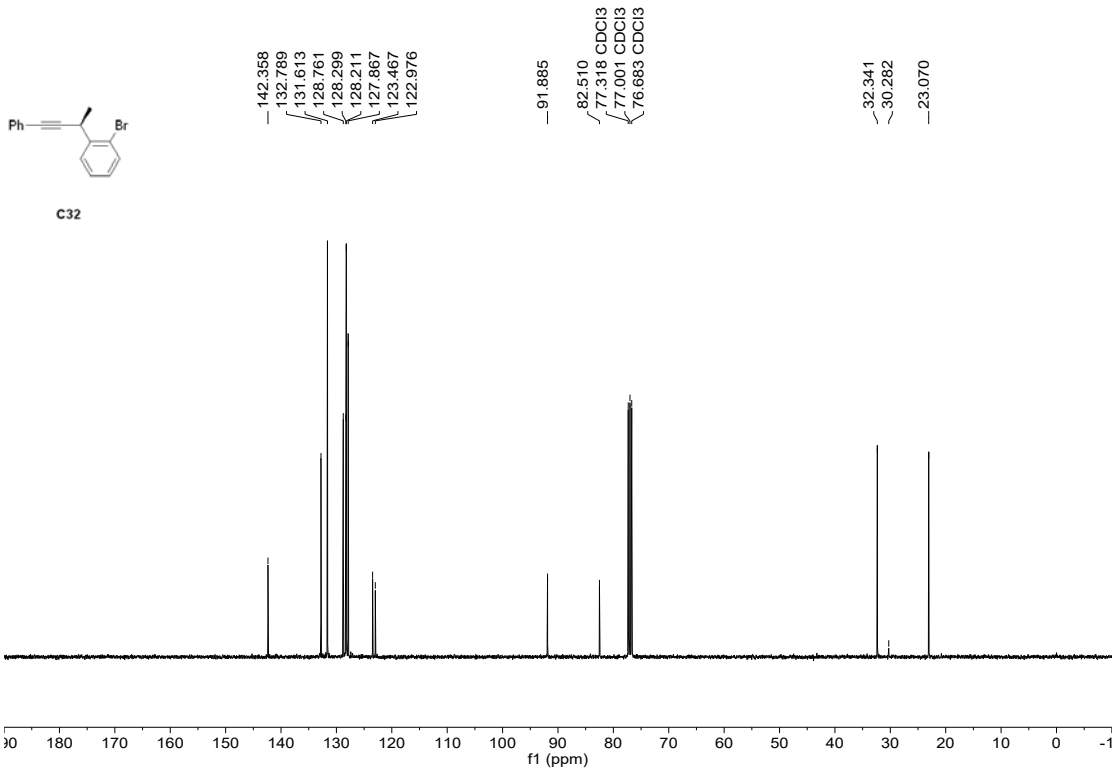
1.00
3.05
f1 (ppm)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128.211
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91.885
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77.001 CDCl3
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32.341
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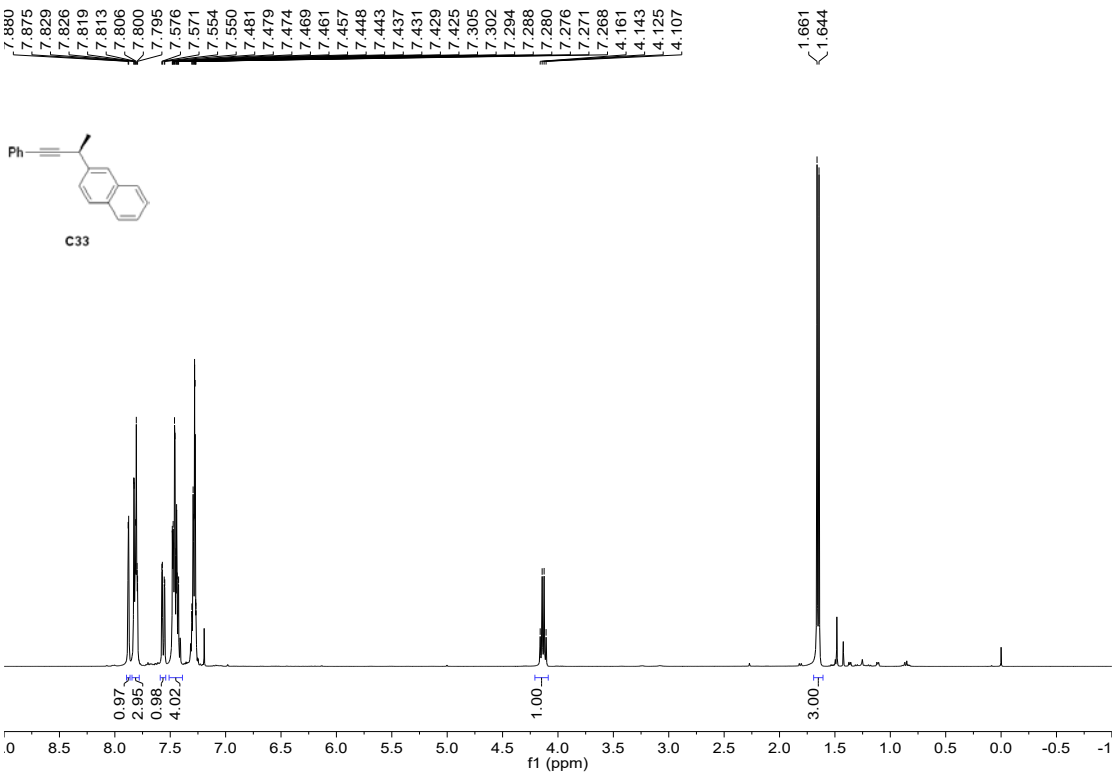
23.070
Ph
Br
C32
f1 (ppm)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7.437
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7.429
7.425
7.305
7.302
7.294
7.288
7.280
7.276
7.271
7.268
4.161
4.143
4.125
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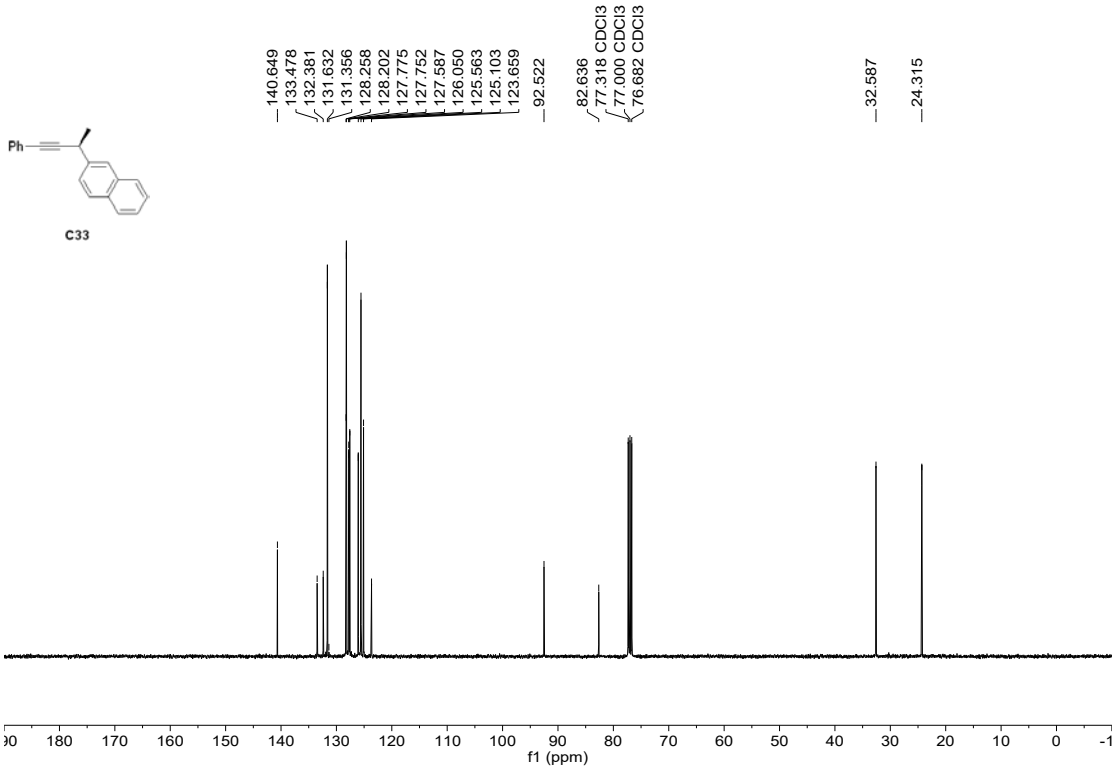
3.00
f1 (ppm)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77.318 CDCl3
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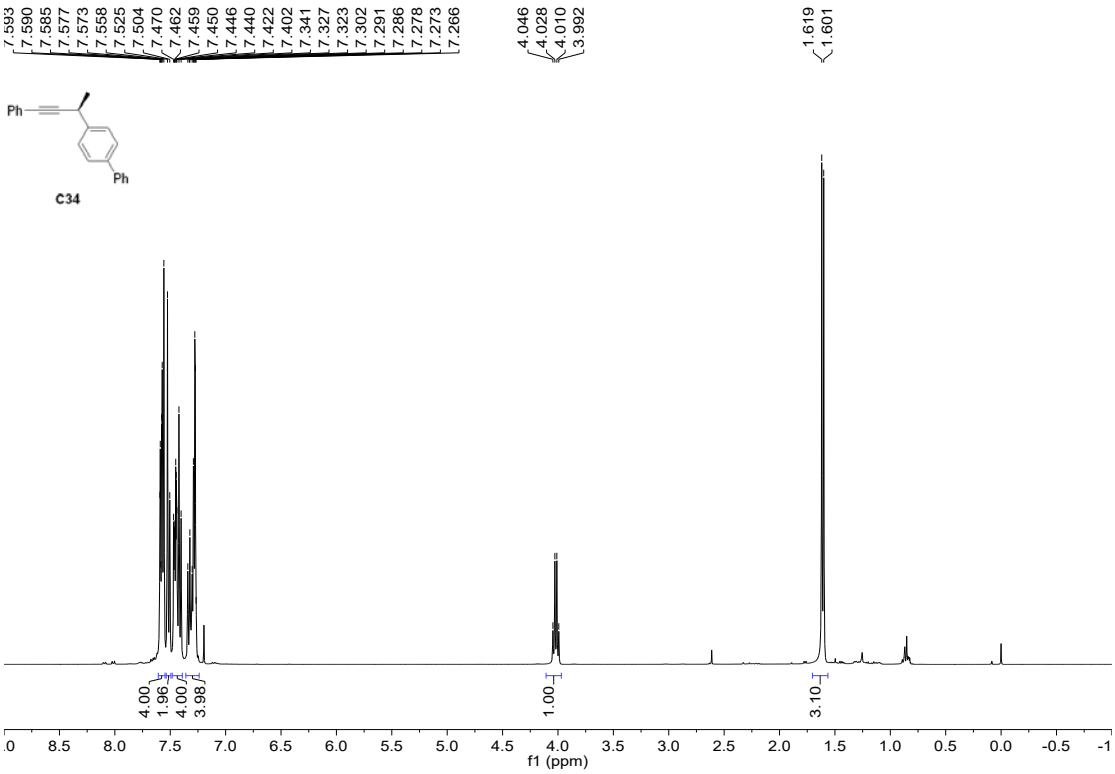
32.587
24.315
Ph
C33
f1 (ppm)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7.459
7.450
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7.440
7.422
7.402
7.341
7.327
7.323
7.302
7.291
7.286
7.278
7.273
7.266
4.046
4.028
4.010
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1.619
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Ph
Ph
C34
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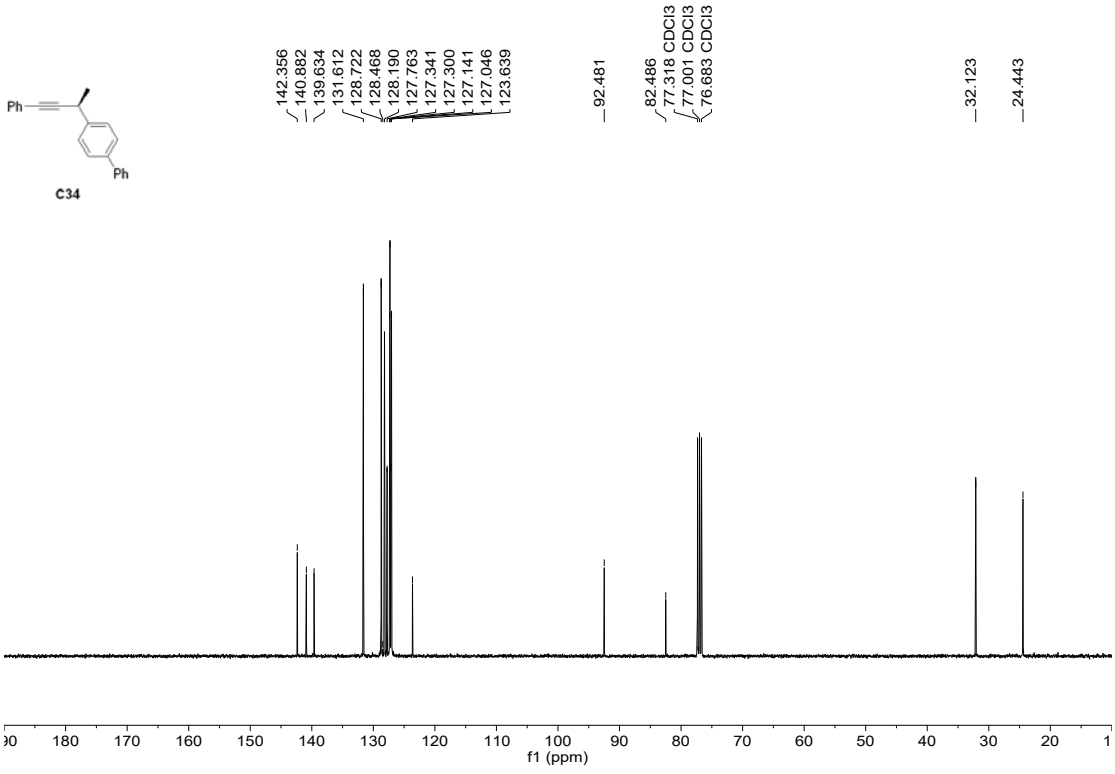
f1 (ppm)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127.141
127.046
123.639
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77.001 CDCl3
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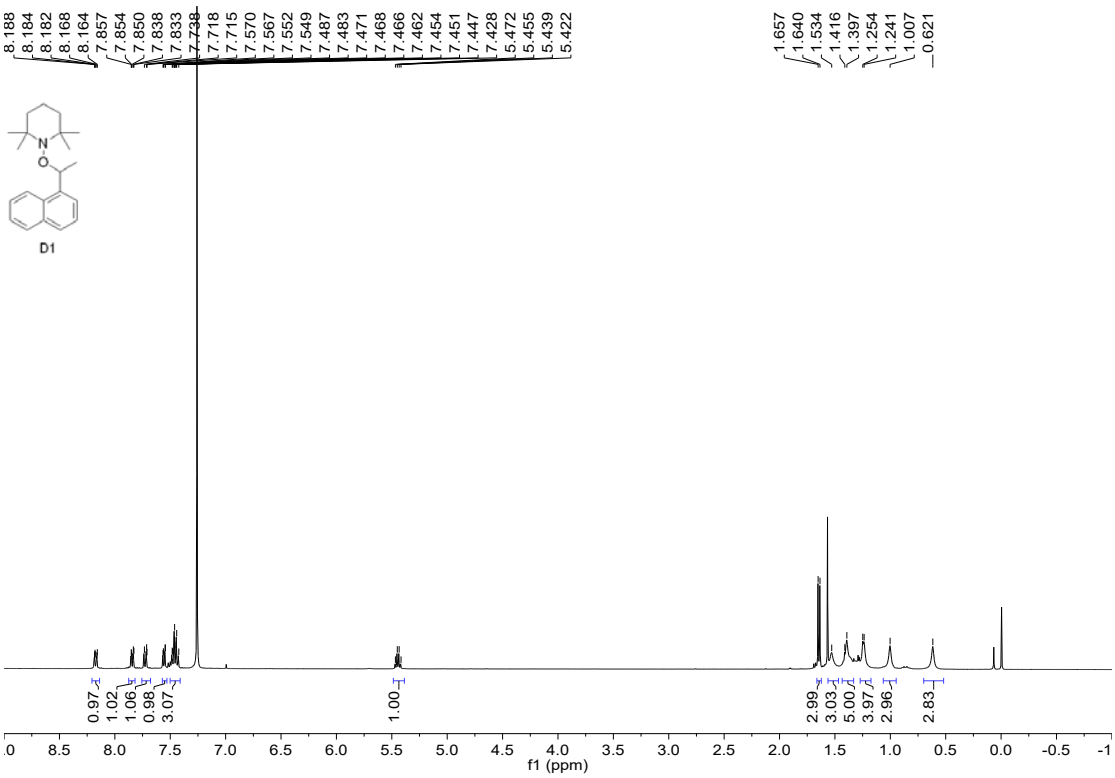
C34
f1 (ppm)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7.549
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7.471
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7.466
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7.428
5.472
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5.439
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1.640
1.534
1.416
1.397
1.254
1.241
1.007
0.621
D1
0.97
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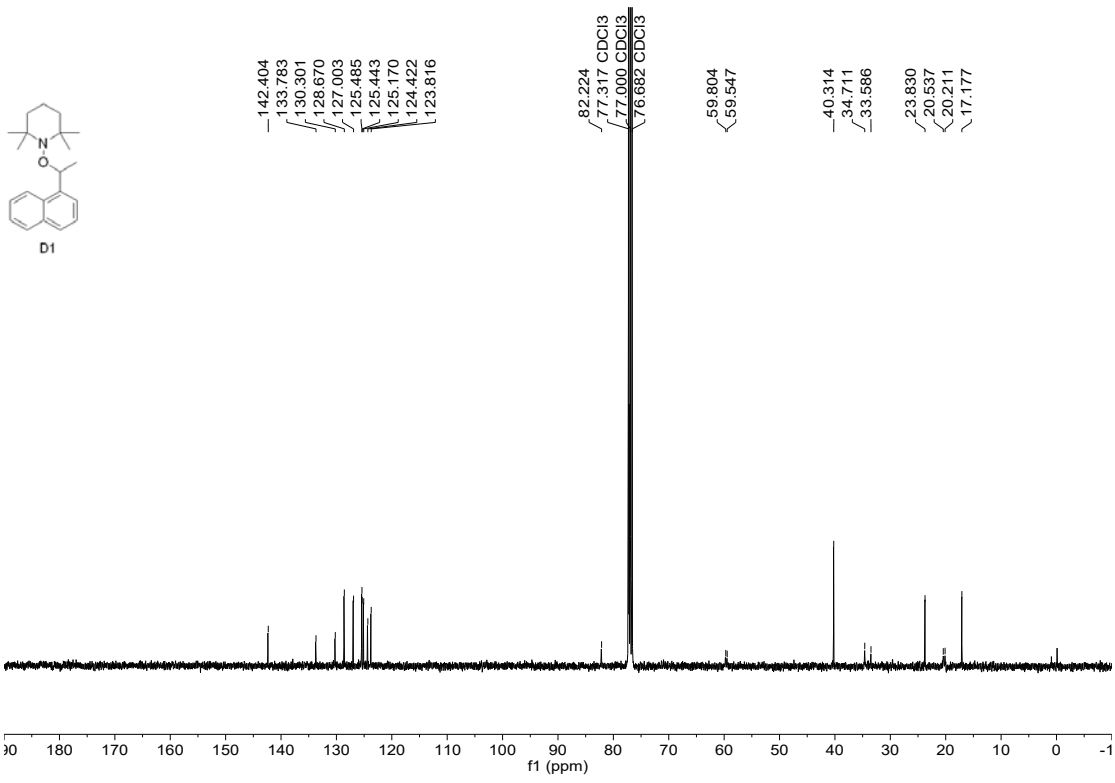
f1 (ppm)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125.170
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123.816
82.224
77.317 CDCl3
77.000 CDCl3
76.682 CDCl3
59.804
59.547
40.314
34.711
33.586
23.830
20.537
20.211
17.177
D1
f1 (ppm)

11. References

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12. Author Contributions

X. H. L. guided the research. J. Z. L conducted the experiments, analyzed the results, and wrote the Supplementary Information and manuscript. L. C. N. conducted the DFT calculations. Q. F. T. repeated some experiments. X. H. L. and X. M. F. helped revise the Supplementary Information and manuscript. All the authors contributed to the discussion.