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Supporting Information

Fused-Ring Formation by an Intramolecular "Cut-and-Sew" Reaction between Cyclobutanones and Alkynes

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1. General Information

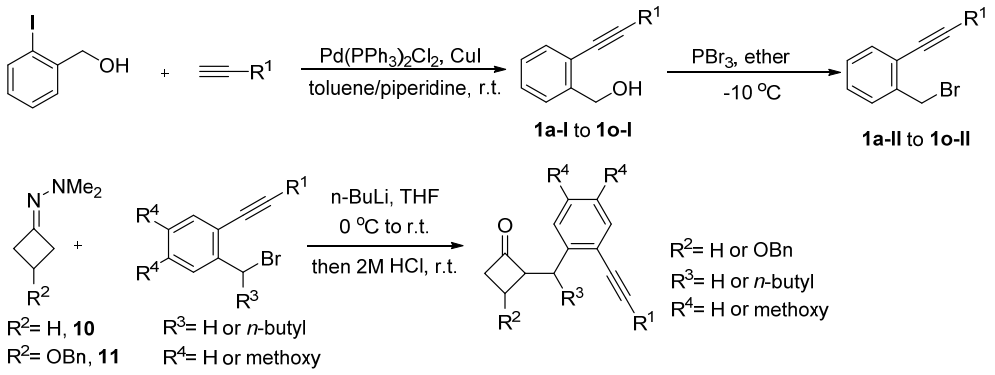
Unless noted otherwise, all solvents were dried by filtration through a Pure-Solv MD-5 Solvent Purification System (Innovative Technology). And the solvents for the C−C Activation reactions were distilled freshly over sodium or calcium hydride and carefully freeze-pump-thawed. All the C−C Activation reactions were carried out under nitrogen atmosphere with a stir bar in a sealed vial. Reaction temperatures were reported as the temperatures of the bather surrounding the flasks or vials. Sensitive ligands and rhodium catalysts and solvents were transferred under nitrogen into a nitrogen-filled glove-box with standard techniques. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD chemical). Vials (17 x 60 mm (7.5mL) with PTFE lined cap attached) were purchased from Qorpak and flame-dried or put in an oven overnight. High-resolution mass spectra (HRSM) were obtained on a Agilent 6224 Tof-MS and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$, $[M+H]^+$. Infrared spectra were recorded on a Nicolet 380 FTIR using neat thin film technique. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded with a Bruker Avance 500 instrument (500 MHz, ^{1}H at 500 MHz, ^{13}C at 126 MHz) and Bruker Avance 400 instrument (400 MHz, ^{1}H at 400 MHz, ^{13}C at 100 MHz). Unless otherwise noted, all spectra were acquired in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ=0.00ppm) and are referenced to residual solvent ($CDCl_3$, δ=7.26 ppm (^{1}H) and 77.00 ppm (^{13}C); CD_2Cl_2, δ=5.32 ppm (^{1}H) and 53.84 ppm (^{13}C)). Coupling constants were reported in Hertz (Hz). Data for ^{1}H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium; s = singlet, d = doublet, t = triplet, q = quartet, hept=heptuplet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration).

2. Experimental Procedure and Characterization Data

I. *General information about substrate synthesis*

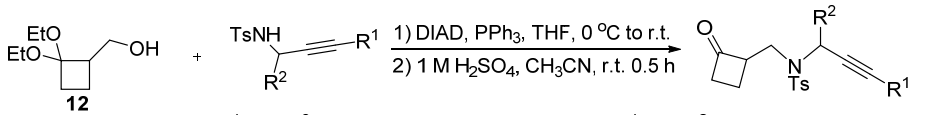
The substrates for the C−C Activation reactions were synthesized through two different routes.

Synthetic **Route I** for substrates with benzene linkage[1]



Substrates **1a** to **1o** and **1u** were synthesized through **Route I**.

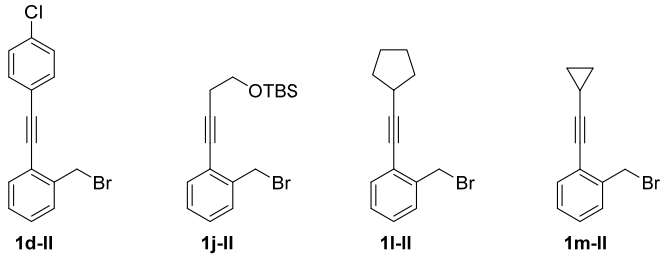
Synthetic route II for substrates with N-Ts linkage[2]



Substrates **1q** to **1s** were synthesized through **route II**. **1q-I**, **1r-I** and **1s-I** are known compounds.

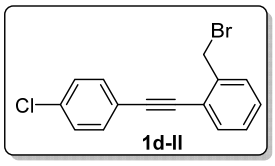
II. *Synthesis of precursors*

a) *Synthesis of unknown precursors*:



1d-II **1j-II** **1l-II** **1m-II** **1n-II** **1o-II** **1u-I**

Apart from what are reported here, all other alkyl bromide precursors are known compound.[3] Compound **1d-II**, **1j-II**, **1l-II**, **1m-II** and **1n-II** were synthesized using the previously reported procedure as shown in route I and the alcohol precursor **1d-I**, **1j-I**, **1l-I**, **1m-I** and **1n-I** are known compounds.[4] Compound **1o-II** was synthesized from the corresponding alcohol **1o-I** (literature known).[4] Because of the instability of compound **1o-II** towards column, it was subjected directly to the alkylation reaction.

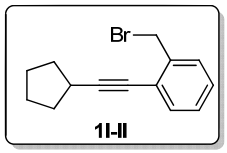


1d-II

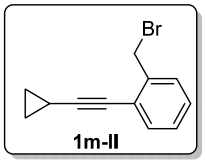
Compound **1d-II** was obtained as a white solid (M.P.: 74-75 ^{o}C) in 55% yield (1.65 g) over two steps. R_f = 0.8 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.56 – 7.50 (m, 3H), 7.45 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.37 – 7.28 (m, 4H), 4.72 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 139.22, 134.67, 132.81, 132.48, 129.75, 128.99, 128.80, 128.56, 122.98, 121.52, 94.06, 87.41, 31.94. **IR:** v 3065, 3028, 1492, 1450, 1397, 1220, 1090, 1013, 949, 827, 758, 606 532, 515 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 304.9727. Found: 304.9707.

1j-II

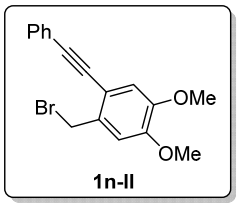
Compound **1j-II** was obtained as a colorless oil in 37% yield (1.1 g). R_f = 0.8 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.44 – 7.36 (m, 2H), 7.23 (td, *J* = 7.0, 1.6 Hz, 2H), 4.66 (s, 2H), 3.86 (t, *J* = 7.1 Hz, 2H), 2.69 (t, *J* = 7.1 Hz, 2H), 0.92 (s, 9H), 0.10 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 139.13, 132.48, 129.61, 128.33, 128.19, 123.66, 93.31, 78.70, 61.84, 32.21, 25.92, 24.10, 18.35, -5.23. **IR:** ν 2954, 2928, 2856, 1485, 1471, 1275, 1258, 1221, 1106, 1057, 916, 837, 750 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 353.0931. Found: 353.0940.



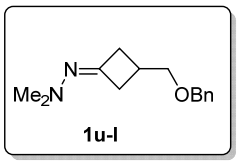
Compound **1l-II** was obtained as a light yellow oil in 68% yield (1.43 g). R_f = 0.8 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40 – 7.37 (m, 2H), 7.25 – 7.21 (m, 2H), 4.65 (s, 2H), 2.90 (dt, J = 10.9, 7.2 Hz, 1H), 2.05 – 1.98 (m, 2H), 1.84 – 1.76 (m, 4H), 1.67 – 1.60 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.98, 132.33, 129.53, 128.37, 127.92, 124.16, 101.00, 77.29, 33.88, 32.44, 31.02, 25.06. **IR:** ν 2961, 2868, 1485, 1499, 1275, 1260, 1220, 750, 607 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 263.0430. Found: 263.0435.



Compound **1m-II** was obtained as a light yellow oil in 36% yield (1.0 g) over two steps. R_f = 0.8 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38 (dt, *J* = 6.8, 2.2 Hz, 2H), 7.23 (ddd, *J* = 6.1, 3.3, 1.8 Hz, 2H), 4.63 (s, 2H), 1.55 – 1.46 (m, 1H), 0.96 – 0.86 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 139.08, 132.45, 129.52, 128.34, 127.89, 123.94, 99.75, 72.78, 32.38, 8.86, 0.42. **IR:** ν 3013, 2923, 2850, 1221, 1028, 955, 842, 809, 758, 607, 542 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 235.0117. Found: 235.0120.



Compound **1n-II** was obtained as a white solid (M.P.: 89-92 °C) in 74% yield (2.56 g) from corresponding alcohol. R_f = 0.4 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.62 – 7.53 (m, 2H), 7.42 – 7.31 (m, 3H), 7.01 (s, 1H), 6.92 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 149.49, 148.93, 132.38, 131.45, 128.40, 128.36, 123.15, 115.55, 114.35, 112.30, 93.76, 86.57, 56.05, 56.00, 32.79. **IR**: 3003, 2961, 2935, 2851, 2832, 1595, 1516, 1463, 1352, 1251, 1225, 1091, 1027, 863, 756, 691, 577, 529 cm^{-1}. **HRMS** calcd. For $[M+H]^+$: 331.0328. Found: 331.0328.



1u-I

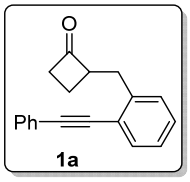
Compound **1u-I** was obtained as a light yellow oil in 23% yield (335 g) over 5 steps. R_f = 0.6 (EtOAc/Hexane=1/1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38 – 7.27 (m, 5H), 4.54 (s, 2H), 3.59 – 3.44 (m, 2H), 3.12 – 2.93 (m, 2H), 2.78 – 2.60 (m, 3H), 2.59 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 156.90, 138.26, 128.42, 127.69, 127.67, 73.59, 73.18, 46.83, 38.22, 27.92. **IR:** ν 2955, 2855, 2776, 1782, 1682, 1453, 1364, 1097, 1027, 988, 738, 698, 606 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 233.1648. Found: 233.1634.

III. *Synthesis of substrates*

a) *Synthesis of substrates with benzene linkage (In Route I)*:

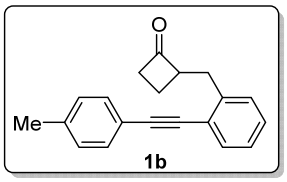
The procedure for the alkylation reaction is as follows (using substrate **1a** as an example):

n-BuLi (2.5 M in hexane, 0.9 mL, 1.1 equiv.) was added to a solution of known compound **10** (228.8 mg, 2.04 mmol, 1 equiv.) in freshly distilled THF (5 mL). The reaction mixture was stirred for 1 h at 0 °C until a yellow suspension was generated. After that, a solution of **1a-II** (608.9 mg, 2.25 mmol, 1.1 equiv.) in THF (2 mL) was added dropwise to the stirring mixture at -78 °C. The mixture was further stirred for 15 min at -78 °C, then overnight at room temperature. 2 M HCl (3.6 mL) was then added to the reaction system and the reaction was stirred vigorously for 1 h at room temperature. A mixture of diethyl ether (25 mL) and water (10 mL) was added to the reaction mixture. The aqueous phase was extracted by diethyl ether (2×25 mL). Then the organic phase was washed with brine (2×10 mL) and dried using Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/Hexane=1/10) to obtain the desired substrate **1a** (457.3 mg) as a light yellow oil in 86% yield.



1a

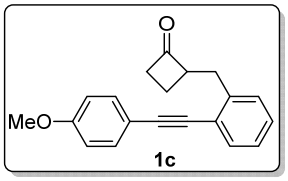
Compound **1a** was obtained as a light yellow oil in 86% yield (457.3 mg). R_f = 0.5 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.53 (ddd, *J* = 7.2, 3.6, 1.7 Hz, 3H), 7.41 – 7.31 (m, 3H), 7.32 – 7.18 (m, 3H), 3.79 (tdd, *J* = 9.9, 7.4, 5.8 Hz, 1H), 3.35 (dd, *J* = 14.0, 5.7 Hz, 1H), 3.11 – 3.01 (m, 1H), 3.05 – 2.97 (m, 1H), 2.93 (dddd, *J* = 17.6, 9.7, 5.1, 2.7 Hz, 1H), 2.21 – 2.09 (m, 1H), 1.84 (ddt, *J* = 11.2, 9.6, 7.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 210.70, 140.93, 132.31, 131.52, 129.24, 128.58, 128.48, 128.42, 126.43, 123.24, 122.89, 93.76, 87.91, 60.58, 44.55, 34.04, 16.80. **IR:** ν 3059, 2922, 1777, 1599, 1479, 1443, 1089, 1071, 757, 691, 553 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 261.1274. Found: 261.1283.



1b

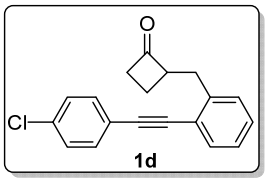
Compound **1b** was obtained as light yellow oil in 27% yield (118.9 mg). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.51 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.30 – 7.14 (m, 5H), 3.78 (dtq, *J* = 12.6, 8.2, 2.7 Hz,

1H), 3.34 (dd, *J* = 14.0, 5.7 Hz, 1H), 3.10 – 3.00 (m, 1H), 3.04 – 2.97 (m, 1H), 2.92 (dddd, *J* = 17.5, 9.6, 5.1, 2.7 Hz, 1H), 2.38 (s, 3H), 2.14 (qd, *J* = 10.5, 5.1 Hz, 1H), 1.83 (ddt, *J* = 11.2, 9.6, 7.7 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 210.73, 140.80, 138.55, 132.20, 131.38, 129.20, 129.18, 128.34, 126.37, 123.11, 120.16, 93.92, 87.23, 60.60, 44.51, 34.01, 21.52, 16.76, 6.96. **IR:** v 2922, 2853, 1778, 1510, 1448, 1393, 1073, 817, 757, 522 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 275.1430. Found: 275.1438.



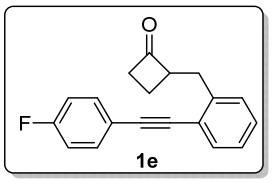
1c

Compound **1c** was obtained as colorless oil in 68% yield (246.7 mg). R_f = 0.5 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 – 7.42 (m, 3H), 7.30 – 7.16 (m, 3H), 6.93 – 6.85 (m, 2H), 3.83 (s, 3H), 3.82 – 3.73 (m, 1H), 3.35 (dd, *J* = 14.0, 5.6 Hz, 1H), 3.12 – 2.85 (m, 3H), 2.14 (dtd, *J* = 11.3, 10.2, 5.2 Hz, 1H), 1.90 – 1.76 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 210.98, 159.70, 140.62, 132.94, 132.05, 129.14, 128.17, 126.36, 123.18, 115.30, 114.09, 93.76, 86.55, 60.55, 55.33, 44.51, 34.03, 16.76. **IR:** v 3062, 2997, 2954, 2837, 1777, 1606, 1510, 1442, 1287, 1249, 1175, 1029, 832, 757, 532 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 291.1380. Found: 291.1384.



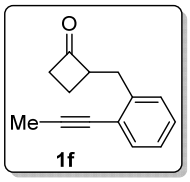
1d

Compound **1d** was obtained as colorless oil in 48% yield (225.5 mg). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51 (ddd, *J* = 7.5, 1.5, 0.6 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 1H), 7.26 – 7.20 (m, 2H), 3.84 – 3.69 (m, 1H), 3.35 (dd, *J* = 14.0, 5.6 Hz, 1H), 3.13 – 2.86 (m, 3H), 2.15 (dtd, *J* = 11.3, 10.3, 5.2 Hz, 1H), 1.82 (ddt, *J* = 11.2, 9.7, 7.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 210.69, 140.93, 134.40, 132.69, 132.30, 129.21, 128.79, 128.76, 126.45, 122.52, 121.68, 92.57, 88.78, 60.51, 44.56, 34.02, 16.82. **IR:** v 3059, 2923, 2852, 1778, 1492, 1447, 1397, 1090, 1014, 828, 757, 520 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 295.0884. Found: 295.0893.

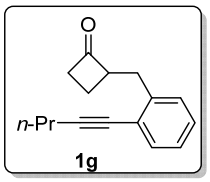


1e

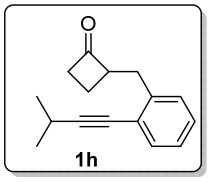
Compound **1e** was obtained as colorless oil in 67% yield (277.2mg). R_f = 0.5 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 (ddt, *J* = 8.5, 5.3, 3.1 Hz, 3H), 7.35 – 7.19 (m, 3H), 7.13 – 7.01 (m, 2H), 3.79 (dtq, *J* = 12.7, 8.1, 2.8 Hz, 1H), 3.38 (dd, *J* = 14.1, 5.6 Hz, 1H), 3.08 (dddd, *J* = 18.3, 10.6, 8.0, 2.7 Hz, 1H), 3.05 – 2.90 (m, 2H), 2.17 (ddt, *J* = 15.7, 10.6, 5.5 Hz, 1H), 1.85 (ddt, *J* = 11.3, 9.6, 7.8 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 210.74, 162.56 (d, *J* = 249.8 Hz), 140.85, 133.37 (d, *J* = 8.4 Hz), 132.24, 129.19, 128.60, 126.43, 122.68, 119.29 (d, *J* = 3.5 Hz), 115.75 (d, *J* = 22.1 Hz), 92.64, 87.51 (d, *J* = 1.5 Hz), 60.52, 44.54, 34.03, 16.82. **IR:** v 3065, 2924, 2853, 1778, 1597, 1508, 1229, 1156, 1092, 836, 757, 525 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 279.1180. Found: 279.1190.



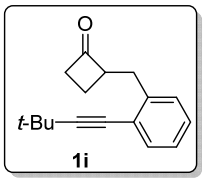
Compound **1f** was obtained as a light yellow oil in 63 % yield (850 mg). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 – 7.35 (m, 1H), 7.23 – 7.11 (m, 3H), 3.77 – 3.65 (m, 1H), 3.24 (dd, *J* = 14.1, 5.7 Hz, 1H), 3.04 (dddd, *J* = 17.6, 10.6, 8.0, 2.7 Hz, 1H), 2.97 – 2.84 (m, 2H), 2.18 – 2.04 (m, 1H), 2.08 (s, 3H), 1.78 (ddt, *J* = 11.2, 9.6, 7.7 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 211.15, 140.61, 132.33, 128.91, 127.73, 126.23, 123.70, 90.11, 78.17, 60.47, 44.47, 33.73, 16.72, 4.50. **IR:** ν 3063, 2971, 2851, 1778, 1485, 1446, 1091, 1073, 758 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 199.1117. Found: 199.1122.



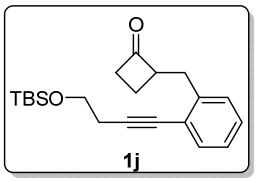
Compound **1g** was obtained as a colorless oil in 70% yield (420 mg). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.38 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.23 – 7.11 (m, 3H), 3.78 – 3.67 (m, 1H), 3.24 (dd, *J* = 14.0, 5.8 Hz, 1H), 3.10 – 2.98 (m, 1H), 2.97 – 2.85 (m, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.15 – 2.06 (m, 1H), 1.79 (ddt, *J* = 11.3, 9.6, 7.7 Hz, 1H), 1.64 (q, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 210.91, 140.56, 132.30, 128.96, 127.68, 126.22, 126.20, 123.74, 94.64, 79.17, 60.54, 60.54, 44.43, 33.83, 22.29, 21.55, 16.65, 13.60. **IR:** ν 3064, 2962, 2832, 1779, 1484, 1448, 1091, 1073, 758 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 227.1430. Found: 227.1435.



Compound **1h** was obtained as a colorless oil in 74% yield (566 mg). R_f = 0.5 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.37 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.23 – 7.11 (m, 3H), 3.72 (dq, *J* = 8.0, 2.8 Hz, 1H), 3.23 (dd, *J* = 13.9, 5.7 Hz, 1H), 3.09 – 2.97 (m, 1H), 2.91 (dd, *J* = 13.8, 9.5 Hz, 2H), 2.81 (p, *J* = 6.9 Hz, 1H), 2.09 (dt, *J* = 10.5, 5.2 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 210.92, 140.61, 132.13, 129.01, 127.70, 126.20, 123.59, 100.24, 78.26, 60.57, 44.43, 33.89, 23.09, 21.31, 16.65. **IR:** ν 2975, 2930, 1777, 1485, 1448, 1362, 1174, 963, 912, 759 cm^{-1}; **HRMS** calcd. For $[M+Na]^+$: 249.1250. Found: 249.1254.

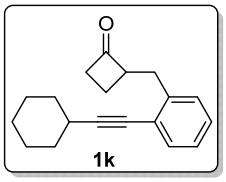


Compound **1i** was obtained as white solid (M.P.: 63-64 ^{o}C) in 77% yield (885 mg). R_f = 0.5 (EtOAc/Hexane=1/5). M. P.= . **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.39 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.26 – 7.13 (m, 3H), 3.82 – 3.68 (m, 1H), 3.25 (dd, *J* = 13.8, 5.7 Hz, 1H), 3.11 – 3.00 (m, 1H), 3.00 – 2.88 (m, 2H), 2.12 (qd, *J* = 10.5, 5.2 Hz, 1H), 1.84 (ddt, *J* = 11.3, 9.8, 7.7 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 210.91, 140.59, 132.03, 129.05, 127.67, 126.19, 123.59, 103.03, 60.60, 44.41, 33.97, 31.04, 28.19, 16.61. **IR:** ν 3065, 2968, 2867, 1780, 1474, 1448, 1291, 1203, 1089, 1072, 757 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 241.1587. Found: 241.1596.



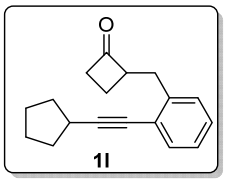
1j

Compound **1j** was obtained as a colorless oil in 33% yield (288 mg). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.38 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.24 – 7.12 (m, 3H), 3.82 (t, *J* = 7.1 Hz, 2H), 3.77 – 3.65 (m, 1H), 3.22 (dd, *J* = 14.1, 5.7 Hz, 1H), 3.03 (dddd, *J* = 18.3, 10.5, 8.0, 2.7 Hz, 1H), 2.97 – 2.84 (m, 2H), 2.66 (t, *J* = 7.1 Hz, 2H), 2.10 (qd, *J* = 10.6, 5.1 Hz, 1H), 1.84 – 1.71 (m, 1H), 0.91 (s, 9H), 0.10 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 210.76, 140.70, 132.35, 128.96, 127.88, 126.20, 123.43, 91.47, 80.03, 61.99, 60.51, 44.46, 33.78, 25.90, 25.90, 24.00, 18.33, 16.70, -5.25, -5.48. **IR:** ν 2927, 2855, 1779, 1485, 1390, 1254, 1098, 1055, 837, 758, 668 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 343.2088. Found: 343.2102.



1k

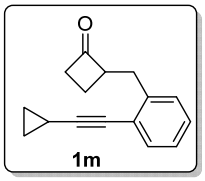
Compound **1k** was obtained as a light yellow oil in 54% yield (603 mg). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.41 – 7.36 (m, 1H), 7.23 – 7.10 (m, 3H), 3.81 – 3.67 (m, 1H), 3.23 (dd, *J* = 13.9, 5.8 Hz, 1H), 3.03 (dddd, *J* = 18.4, 10.6, 8.0, 2.8 Hz, 1H), 2.96 – 2.86 (m, 2H), 2.64 (dt, *J* = 9.7, 5.2 Hz, 1H), 2.16 – 2.03 (m, 1H), 1.95 – 1.69 (m, 5H), 1.60 – 1.51 (m, 3H), 1.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 211.04, 140.56, 132.19, 129.01, 127.64, 126.19, 123.71, 98.89, 78.97, 60.55, 44.43, 33.90, 32.73, 29.78, 25.91, 24.87, 16.61. **IR:** ν 2929, 2853, 1779, 1484, 1447, 1072, 953, 886, 757 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 267.1743. Found: 267.1753.



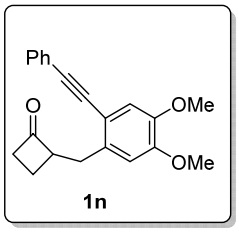
1l

Compound **1l** was obtained as a light yellow oil in 34% yield (315 mg). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (ddd, *J* = 7.4, 1.5, 0.7 Hz, 1H), 7.24 – 7.09 (m, 3H), 3.79 – 3.64 (m, 1H), 3.22 (dd, *J* = 13.9, 5.7 Hz, 1H), 3.09 – 2.98 (m, 1H), 2.96 – 2.82 (m, 3H), 2.09 (dtd, *J* = 11.3, 10.3, 5.2 Hz, 1H), 2.04 – 1.92 (m, 2H), 1.88 – 1.56 (m, 7H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 211.02, 140.55, 132.11, 129.00, 127.62, 126.19, 123.73, 99.09, 78.57, 60.55, 44.43,

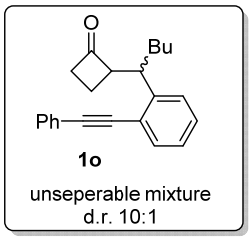
34.00, 33.98, 33.90, 30.95, 24.99, 16.63. **IR:** ν 2958, 2869, 1777, 1484, 14448, 1353, 1177, 1072, 994, 919, 758 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 253.1587. Found: 253.1595.



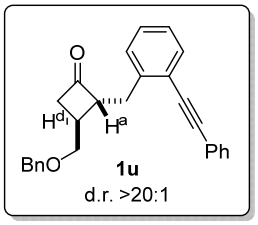
Compound **1m** was obtained as a light yellow oil in 47% yield (411.4 mg). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38 – 7.34 (m, 1H), 7.22 – 7.09 (m, 3H), 3.69 (ddd, *J* = 9.5, 5.6, 2.7 Hz, 1H), 3.21 (dd, *J* = 14.0, 5.6 Hz, 1H), 3.10 – 2.97 (m, 1H), 2.97 – 2.83 (m, 2H), 2.10 (dtd, *J* = 11.2, 10.2, 5.2 Hz, 1H), 1.84 – 1.72 (m, 1H), 1.47 (tt, *J* = 8.2, 5.0 Hz, 1H), 0.93 – 0.77 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 211.05, 140.71, 132.27, 128.94, 127.63, 126.20, 123.53, 97.93, 77.33, 74.10, 60.49, 44.45, 33.84, 16.69, 8.82, 8.78, 0.31. **IR:** ν 3010, 2923, 2852, 1778, 1485, 1447, 1392, 1178, 1087, 1072, 954, 757 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 225.1274. Found: 225.1285.



Compound **1n** was obtained as a light yellow solid (M.P.: 91-92 °C) in 66% yield (695 mg). R_f = 0.4 (EtOAc/Hexane=1/3). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.54 – 7.48 (m, 2H), 7.38 – 7.30 (m, 3H), 7.01 (s, 1H), 6.77 (s, 1H), 3.90 (d, *J* = 4.6 Hz, 6H), 3.78 – 3.68 (m, 1H), 3.24 (dd, *J* = 14.0, 6.1 Hz, 1H), 3.09 – 2.97 (m, 2H), 2.95 – 2.83 (m, 1H), 2.15 (qd, *J* = 10.6, 5.1 Hz, 1H), 1.86 (ddt, *J* = 11.1, 9.5, 7.7 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 210.97, 149.45, 147.26, 134.43, 131.31, 128.41, 128.10, 123.45, 114.59, 114.52, 112.45, 92.12, 88.17, 60.97, 56.00, 55.95, 44.55, 33.57, 16.48. **IR:** ν 3004, 2360, 1775, 1512, 1464, 1349, 1275, 1260, 1091, 913, 764, 750, 691 cm^{-1}. **HRMS** calcd. For $[M+H]^+$: 321.1485. Found: 321.1485.

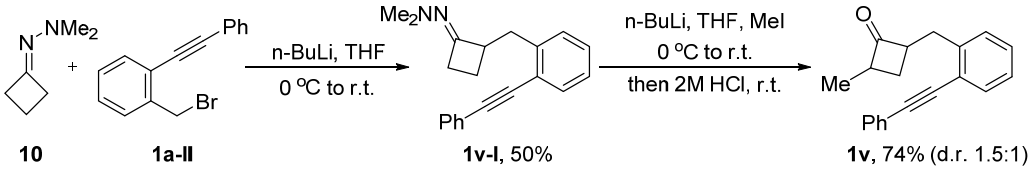


Compound **1o** was obtained as a light yellow oil in 32% yield (64 mg). R_f = 0.5 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ (major) 7.57 – 7.50 (m, 3H), 7.40 – 7.32 (m, 3H), 7.32 – 7.18 (m, 3H), 3.71 (dd, *J* = 6.8, 3.6 Hz, 2H), 2.92 (dddd, *J* = 17.8, 10.3, 7.6, 2.9 Hz, 1H), 2.74 (dddd, *J* = 17.9, 10.0, 5.3, 2.6 Hz, 1H), 2.19 – 2.02 (m, 1H), 1.99 – 1.83 (m, 2H), 1.78 (tdd, *J* = 13.5, 5.9, 4.4 Hz, 1H), 1.41 – 1.08 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ (major) 210.99, 144.30, 132.40, 131.47, 128.61, 128.41, 128.27, 126.75, 126.18, 123.56, 123.41, 93.61, 88.18, 65.51, 44.58, 42.50, 32.00, 29.49, 22.67, 14.60, 13.99. **IR:** ν 3059, 2956, 2928, 2859, 1777, 1599, 1493, 1443, 1072, 913, 756, 690 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 317.1900. Found: 317.1900.



Compound **1u** was obtained as a light yellow oil in 66% yield (361.5 mg) from **11**. R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 – 7.48 (m, 3H), 7.37 – 7.31 (m, 3H), 7.31 – 7.26 (m, 2H), 7.25 – 7.14 (m, 6H), 4.34 (td, *J* = 12.4, 8.2 Hz, 2H), 3.62 (ddd, *J* = 9.1, 7.3, 5.9 Hz, 1H), 3.44 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.34 (dd, *J* = 13.8, 6.0 Hz, 1H), 3.30 (dd, *J* = 9.50, 6.27 Hz, 1H), 3.03 (dd, *J* = 13.8, 9.1 Hz, 1H), 2.95 (d, *J* = 8.3 Hz, 2H), 2.52 – 2.41 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 208.85, 140.68, 138.11, 132.31, 131.49, 129.44, 128.58, 128.44, 128.39, 128.32, 127.54, 127.45, 126.44, 123.14, 122.74, 93.63, 87.88, 72.94, 71.93, 61.78, 47.42, 33.15, 30.81. **IR:** v 3060, 3030, 2922, 2851, 1776, 1494, 1451, 1364, 1097, 914, 757, 691 cm^{-1}; **HRMS** calcd. For $[M+Na]^+$: 403.1669. Found: 403.1671. The diastereomer was assigned by characteristic *J* coupling constant (7.3) of H^a and H^d at four-membered ring[17].

b) *Synthesis of substrate **1v***:



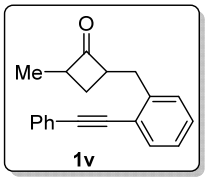
The Procedure for the synthesis of **1v-I**:

n-BuLi (2.5 M in hexane, 3.8 mL, 1.1 equiv.) was added to a solution of known compound **10** (977.7 mg, 8.7 mmol, 1 equiv.) in freshly distilled THF (10 mL). Then the reaction mixture was stirred for 1 h at 0 °C until a yellow suspension was generated. After that, a solution of **1a-II** (2.6 g, 9.6 mmol, 1.1 equiv.) in THF (10 mL) was added dropwise to the stirring mixture at -78 °C. The mixture was stirred at -78 °C for 15 min before warmed up to room temperature and stirred overnight. The reaction was quenched with a mixture of diethyl ether (25 mL) and water (10 mL) and the aqueous phase was extracted by diethyl ether (2×25 mL). Then the organic phase was washed with brine (2×10 mL) and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/Hexane=1/10 to 1/5 to 1/2) to obtain the desired product **1v-I** with a small amount of impurity due to its instability. **1v-I** was subjected to the next step without further purification.

The procedure for the synthesis of **1v**:

n-BuLi (2.5 M in hexane, 0.73 mL, 1.1 equiv.) was added to a solution of compound **1v-I** (500 mg, 1.65 mmol, 1 equiv.) in freshly distilled THF (10 mL). Then the reaction mixture was stirred for 1 h at 0 °C until a yellow suspension was generated. After that, MeI (258.1 mg, 1.82 mmol, 1.1 equiv.) was added dropwise to the stirring mixture at -78 °C. The mixture was stirred at -78 °C for 15 min before warmed up to room temperature. After starting material was fully converted as shown by TLC, 2 M HCl (1 mL) was added to the reaction system and the reaction was stirred vigorously for 1 h at room temperature. A mixture of diethyl ether (10 mL) and water (10 mL) was added to the reaction mixture. The aqueous phase was extracted by diethyl ether (2×25 mL). Then the organic phase was washed with brine (2×20 mL)

and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/Hexane=1/10) to obtain the desired substrate **1v** (335 mg) as a light yellow oil in 74% yield.



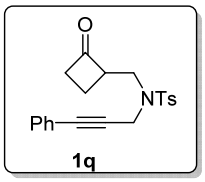
3:2 mixture of diastereomers

Compound **1v** was obtained as a yellow oil in 74% yield (335 mg). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.53 (ddt, *J* = 9.2, 4.5, 2.6 Hz, 3H), 7.36 (td, *J* = 4.9, 2.9 Hz, 3H), 7.31 – 7.26 (m, 1H), 7.26 – 7.17 (m, 2H), 3.73 (ddd, *J* = 9.4, 6.3, 3.2 Hz, 1H), 3.34 (ddd, *J* = 14.0, 12.4, 5.8 Hz, 1H), 3.30 – 3.17 (m, 1H), 3.05 (dd, *J* = 14.0, 9.5 Hz, 0.6H), 2.97 (dd, *J* = 14.0, 9.1 Hz, 0.4H), 2.38 (d, *J* = 10.5 Hz, 0.4H), 2.10 (ddd, *J* = 11.5, 10.0, 6.1 Hz, 0.6H), 1.73 (ddd, *J* = 11.4, 9.7, 6.3 Hz, 0.6H), 1.41 (dt, *J* = 10.7, 8.4 Hz, 0.4H), 1.19 (d, *J* = 7.6 Hz, 1.8H), 1.12 (d, *J* = 7.3 Hz, 1.2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 214.63, 212.92, 141.25, 140.95, 132.32, 132.25, 131.50, 131.48, 129.28, 129.16, 128.53, 128.44, 128.37, 128.35, 126.43, 126.30, 123.26, 122.98, 122.83, 93.69, 93.62, 87.97, 87.90, 57.88, 57.81, 52.11, 51.57, 34.46, 33.78, 25.91, 25.19, 24.93, 14.86, 13.51. **IR:** ν 3059, 2960, 2867, 1772, 1599, 1493, 1443, 1372, 1101, 1070, 914, 756, 690 cm^{-1}; **HRMS** calcd. For $[M+Na]^+$: 297.1250. Found: 297.1258.

c) *Synthesis of substrates with NTs linkage (In Route II):*

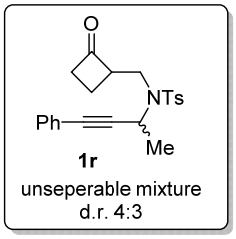
The procedure for Mitsunobu reaction and deprotection cascade is as follows (using substrate **1q** as an example):

A solution of **12** (174.2 mg, 1.0 mmol, 1 equiv.) and DIAD (208.3 mg, 1.03 mmol, 1.03 equiv.) in THF (5 mL) was added to a solution of known[5] compound **1q-I** (313.9 mg, 1.1 mmol, 1.1 equiv.) and triphenylphosphine (270.0 mg, 1.03 mmol, 1.03 equiv.) in THF (5 mL) at 0 °C. Then the reaction mixture was warmed up to room temperature and stirred overnight. After the reaction finished, solvent was removed by rotavap and the residue was dissolved in 5 mL acetonitrile and 3 mL 1M H_2SO_4 was added to the solution. The resulting mixture was stirred at room temperature for 0.5 h and the progress of the reaction was monitored by TLC. When the starting material was fully consumed, the reaction mixture was diluted with ether and washed by water, saturated $NaHCO_3$ solution and brine successively. Then the organic phase was dried over magnesium sulfate, then filtered and concentrated. The residue was purified by silica gel flash column chromatography (EtOAc/Hexane=1/10 to 1/5) to obtain the desired substrate **1q** (258.3 mg) as a white solid in 74% yield.

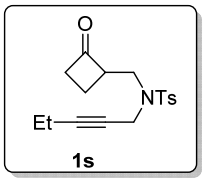


Compound **1q** was obtained as a white solid (M.P.: 102-104 °C) in 74% yield (258.3 mg). R_f = 0.4 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.20 (m, 5H), 7.05 (dd, *J* = 8.2, 1.5 Hz, 2H), 4.44 (dd, *J* = 18.7, 0.8 Hz, 1H), 4.31 (dd, *J* = 18.7, 0.6 Hz, 1H), 3.72 – 3.61 (m, 1H), 3.58 – 3.40 (m, 2H), 3.19 – 3.06 (m, 1H), 3.05 – 2.93 (m, 1H), 2.33 (s, 3H), 2.32 – 2.22 (m, 1H), 2.02 (ddt, *J* = 11.5, 9.7, 7.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 208.48, 143.71, 135.59, 131.50, 129.59, 128.48, 128.12, 127.80, 121.99, 85.90, 81.58, 59.13, 45.39, 45.06, 38.31, 21.42, 15.49. **IR:**

v 2960, 2923, 2858, 1778, 1597, 1490, 1442, 1348, 1162, 1090, 1024, 903, 815, 758, 658, 571, 544 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 368.1315. Found: 368.1319.

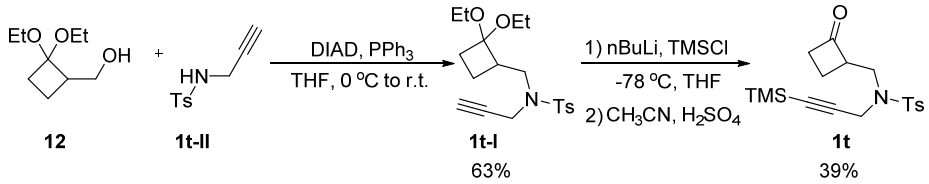


Compound **1r** was obtained as an oil in 79% yield (53.1 mg). R_f = 0.4 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (dd, *J* = 9.8, 8.1 Hz, 2H), 7.27 (dd, *J* = 7.5, 3.6 Hz, 3H), 7.26 – 7.20 (m, 2H), 7.09 – 7.02 (m, 2H), 5.10 – 4.98 (m, 1H), 4.01 (s, 0.42H), 3.77 – 3.63 (m, 0.56H), 3.55 – 3.37 (m, 1.58H), 3.28 (dd, *J* = 15.5, 9.6 Hz, 0.44H), 3.14 – 3.00 (m, 1H), 3.01 – 2.85 (m, 1H), 2.35 (d, *J* = 3.3 Hz, 3H), 2.34 – 2.26 (m, 1H), 2.24 – 2.10 (m, 0.60H), 1.99 – 1.85 (m, 0.43H), 1.52 (d, *J* = 7.1 Hz, 1.77H), 1.47 (d, *J* = 7.0 Hz, 1.32H) . **^{13}C NMR (100 MHz, $CDCl_3$):** δ 208.71, 208.53, 143.75, 143.67, 135.47, 135.23, 131.51, 131.49, 129.63, 129.61, 128.50, 128.18, 128.16, 127.88, 127.79, 121.98, 86.25, 86.00, 85.25, 84.96, 61.34, 61.15, 47.27, 46.58, 44.50, 43.53, 43.40, 22.50, 22.04, 21.48, 21.47, 16.95, 16.28. **IR:** v 2968, 2863, 1777, 1275, 1165, 1121, 913, 748, 658 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 382.1471. Found: 382.1472.



Compound **1s** was obtained as a colorless oil in 59% yield (396.7 mg). R_f = 0.3 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 – 7.69 (m, 2H), 7.29 (dq, *J* = 8.0, 0.6 Hz, 2H), 4.24 – 4.12 (m, 1H), 4.02 (dtd, *J* = 18.3, 2.2, 0.6 Hz, 1H), 3.72 – 3.55 (m, 1H), 3.50 – 3.30 (m, 2H), 3.10 (dddd, *J* = 18.6, 10.6, 8.2, 2.5 Hz, 1H), 2.98 (dddd, *J* = 17.7, 9.7, 5.2, 2.6 Hz, 1H), 2.24 (dtd, *J* = 11.5, 10.3, 5.2 Hz, 1H), 1.99 (ddt, *J* = 11.5, 9.7, 7.9 Hz, 1H), 1.90 (qt, *J* = 7.5, 2.3 Hz, 2H), 0.94 – 0.82 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 208.67, 143.47, 135.75, 129.38, 127.83, 87.89, 71.61, 59.03, 45.07, 45.02, 37.81, 21.50, 15.52, 13.42, 12.10. **IR:** v 2977, 2923, 1778, 1597, 1442, 1347, 1161, 1089, 1014, 903, 815, 750, 656, 569, 544 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 342.1134. Found: 342.1151.

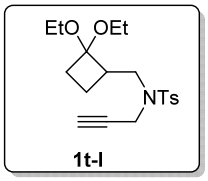
Synthesis of substrate 1t



The procedures for synthesis of **1t-I**:

A solution of **6** (261.3 mg, 1.5 mmol, 1 equiv.) and DIAD (313.4 mg, 1.55 mmol, 1.03 equiv.) in THF (5 mL) was added to a solution of known[5a] compound **1t-II** (345.3 mg, 1.65 mmol, 1.1 equiv.) and triphenylphosphine (406.2 mg, 1.55 mmol, 1.03 equiv.) in THF (5 mL) at 0 °C. Then the reaction mixture was warmed up to room temperature and stirred overnight. After the reaction finished, solvent was removed by rotavap and the residue was purified by silica gel flash

column chromatography (EtOAc/Hexane=1/15 to 1/10) to obtain the desired coumpound **1t-I** (346 mg) as a colorless oil in 63% yield.

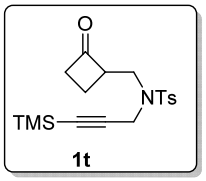


1t-I

Compound **1t-I** was obtained as a colorless oil in 63% yield (346 mg). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.29 (dt, *J* = 8.0, 0.7 Hz, 2H), 4.27 (ddd, *J* = 18.4, 2.5, 1.0 Hz, 1H), 4.09 (dd, *J* = 18.4, 2.5 Hz, 1H), 3.48 – 3.31 (m, 5H), 3.24 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.74 (ddd, *J* = 8.7, 6.8, 1.4 Hz, 1H), 2.42 (s, 3H), 2.19 (dddd, *J* = 12.2, 10.0, 4.6, 1.0 Hz, 1H), 2.04 – 1.94 (m, 2H), 1.91 – 1.80 (m, 1H), 1.46 (ddt, *J* = 11.3, 10.2, 7.7 Hz, 1H), 1.18 (td, *J* = 7.1, 1.2 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.35, 135.97, 129.38, 127.81, 102.10, 77.11, 73.33, 56.62, 56.28, 46.76, 43.71, 37.19, 29.42, 21.54, 16.76, 15.28, 15.24. **IR:** v 3271, 2976, 1930, 2883, 1598, 1445, 1348, 1260, 1162, 1049, 911, 749, 660, 580, 545 cm^{-1}; **HRMS** calcd. For $[M+Na]^+$: 388.1553. Found: 388.1560.

The procedures for synthesis of **1t**:

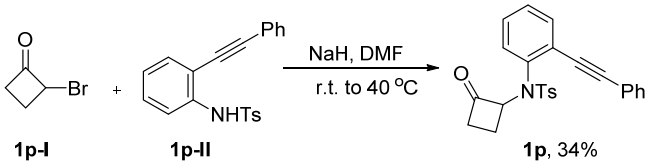
A 10 mL Schlenk flask charged with solution of **1t-I** (185 mg, 0.51 mmol, 1 equiv.) in THF (5 mL) was cooled to -78 ^oC by acetone-dry ice bath, then n-BuLi (2.5 M, 0.34 mL, 1.05 equiv.) was added to the mixture. The mixture was stirred at -78 ^oC for 1.5 h before TMSCl (60.5 mg, 0.56 mmol, 1.1 equiv.) was added to the reaction. The mixture was further stirred for 15 min at -78 ^oC, then overnight at room temperature. The reaction was quenched with a mixture of diethyl ether (15 mL) and water (10 mL) and the aqueous phase was extracted by diethyl ether (2×15 mL). Then the organic phase was washed with brine (2×10 mL) and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in 5 mL acetonitrile and 3 mL 1M H_2SO_4 was added to the solution. The resulting mixture was stirred at room temperature for 0.5 h and the progress of the reaction was monitored by TLC. When the starting material was fully consumed, reaction mixture was diluted with ether and washed with water, saturated $NaHCO_3$ solution and brine successively. Then the organic phase was dried over $MgSO_4$, then filtered and concentrated. The residue was purified by silica gel flash column chromatography (EtOAc/Hexane=1/10 to 1/5) to obtain the desired substrate **1t** (258.3 mg) as a white solid in 60% yield (70 mg).



1t

Compound **1t** was obtained as a light yellow oil in 60% yield (70 mg) from **1t-I**. R_f = 0.5 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.77 – 7.70 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.30 – 4.20 (m, 1H), 4.10 (d, *J* = 18.7 Hz, 1H), 3.71 – 3.57 (m, 1H), 3.46 (dd, *J* = 14.0, 8.8 Hz, 1H), 3.38 (dd, *J* = 14.0, 5.9 Hz, 1H), 3.12 (dddd, *J* = 18.7, 10.6, 8.2, 2.5 Hz, 1H), 3.00 (dddd, *J* = 17.7, 9.7, 5.1, 2.7 Hz, 1H), 2.43 (s, 3H), 2.32 – 2.19 (m, 1H), 2.06 – 1.93 (m, 1H), -0.00 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 208.35, 143.54, 135.53, 129.53, 127.72, 97.63, 91.23, 58.96, 45.08, 44.96, 38.22, 21.48, 15.46, -0.50. **IR:** v 2959, 2923, 2853, 1780, 1598, 1445, 1349, 1250, 1162, 1090, 1027, 991, 845, 759, 665, 546 cm^{-1}; **HRMS** calcd. For $[M+Na]^+$: 386.1217. Found: 386.1217.

d) *Synthesis of substrate **1p***:

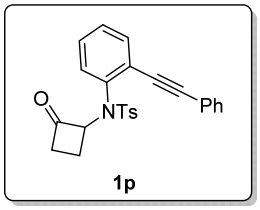


1p-I **1p-II** **1p**, 34%

Substrates **1p** were synthesized through alkylation of **1p-II** as shown above. **1p-I** and **1p-II** are known compounds.[6]

Procedure:

NaH (86.4 mg, 3.6 mmol, 1.2 equiv.) was added to a 20 mL vial with solution of known compound **1p-II** (978.6 mg, 3 mmol, 1 equiv.) in DMF (10 mL) at room temperature. After the mixture was stirred for 30 min at room temperature, **1p-I** (536.4 mg, 3.6 mmol, 1.2 equiv.) in DMF (2 mL) was added. Then the reaction mixture was heated to 40 °C for 5 h. The progress of the reaction was monitored by TLC. When the starting material was fully consumed, reaction mixture was diluted with ether and water was added slowly to the vial. The organic phase was dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel flash column chromatography (EtOAc/Hexane=1/10 to 1/5) to obtain the desired substrate **1p** (400 mg) as an orange oil in 34% yield.

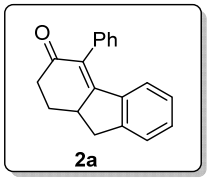


Compound **1p** was obtained as a light yellow oil in 34% yield (400 g) from known compound. R_f = 0.4 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.39 – 7.26 (m, 6H), 7.15 (d, *J* = 8.5 Hz, 2H), 5.34 (s, 1H), 2.82 – 2.70 (m, 1H), 2.70 – 2.56 (m, 1H), 2.48 (qd, *J* = 10.5, 4.6 Hz, 1H), 2.30 (m, 1H), 2.30 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 204.65, 143.53, 138.24, 137.43, 133.25, 132.27, 131.78, 129.38, 129.07, 128.91, 128.58, 128.28, 127.83, 125.95, 122.91, 94.43, 86.08, 72.63, 40.23, 21.52, 19.40. **IR:** ν 3063, 2968, 2255, 2219, 1793, 1598, 1494, 1444, 1346, 1161, 1091, 912, 758, 669, 544 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 416.1315. Found: 416.1316.

IV. *Rh-catalyzed Intramolecular Coupling between Cyclobutanones and Alkynes*

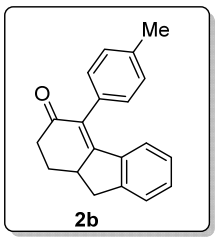
General procedure:

In a nitrogen-filled glove box, a 4 mL vial was charged with the cyclobutanone substrates (0.1 mmol), followed by 800 μL 1,4-dioxane. 100 μL of PMe_2Ph stock solution (22.1 mg/1000 μL , 2.21 mg, 0.016 mmol, 16 mol%) and 100 μL of $[Rh(CO)_2Cl]_2$ stock solution (19.4 mg/1000 μL, 1.94 mg, 0.005 mmol, 5 mol%) were added sequentially to the vial. After stirring to a homogeneous solution, the vial was capped and the reaction was maintained at 125 °C (**1a** to **1t**) and 140 °C (**1u** and **1v**) for 60 h. After the reaction was complete, solvent was removed by rotavap and the residue was directly purified by silica gel flash chromatography.



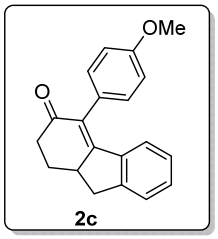
2a

Compound **2a** was isolated as a white solid (M.P.: 118-120 ^{o}C) in 82% yield. R_f = 0.4 (EtOAc/Hexane=1/2). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.39 (q, *J* = 9.9, 7.2 Hz, 3H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.15 (s, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 3.37 – 3.22 (m, 2H), 2.86 – 2.73 (m, 2H), 2.61 (ddd, *J* = 17.3, 14.3, 5.0 Hz, 1H), 2.43 (dtd, *J* = 12.0, 4.7, 2.2 Hz, 1H), 2.06 (dtd, *J* = 16.4, 12.5, 4.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.28, 162.69, 148.84, 138.46, 135.34, 132.51, 130.72, 129.67, 128.70, 127.66, 126.62, 125.14, 43.13, 38.44, 37.31, 29.14. **IR:** ν 3057, 2938, 2860, 1654, 1620, 1593, 1463, 1359, 1326, 1182, 1002, 910, 829, 732, 699, 578 cm^{-1}; **HRMS** calcd. For $[M+Na]^+$: 283.1093. Found: 283.1094.



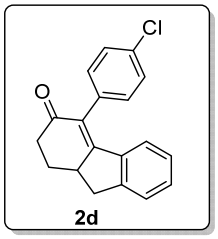
2b

Compound **2b** was isolated as a white solid (M.P.: 168-172 ^{o}C) in 82% yield. R_f = 0.4 (EtOAc/Hexane=1/2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.18 (m, 3H), 7.04 (s, 2H), 6.98 – 6.89 (m, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 3.38 – 3.21 (m, 2H), 2.87 – 2.72 (m, 2H), 2.59 (ddd, *J* = 17.1, 14.2, 5.0 Hz, 1H), 2.41 (m, 4H), 2.11 – 1.98 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.47, 162.51, 148.78, 138.58, 137.25, 132.46, 132.19, 130.63, 129.47, 129.35, 126.65, 126.59, 125.10, 43.10, 38.46, 37.30, 29.15, 21.40. **IR:** ν 3023, 2922, 2859, 1657, 1597, 1510, 1462, 1358, 1335, 1206, 1092, 980, 811, 773, 734, 678, 518 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 297.1250. Found: 297.1255.



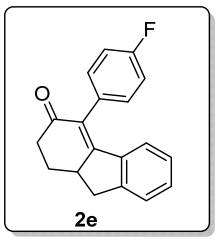
2c

Compound **2c** was isolated as a white solid (M.P.: 132-135 ^{o}C) in 65% yield. R_f = 0.4 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34 – 7.29 (m, 1H), 7.28 – 7.23 (m, 1H), 7.21 – 6.89 (m, 5H), 6.56 – 6.50 (m, 1H), 3.86 (s, 3H), 3.36 – 3.20 (m, 2H), 2.87 – 2.71 (m, 2H), 2.60 (ddd, *J* = 17.2, 14.2, 5.0 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.12 – 1.96 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.71, 162.84, 159.05, 148.81, 138.59, 132.02, 130.84, 130.66, 127.37, 126.63, 126.62, 125.13, 114.23, 55.24, 43.16, 38.45, 37.32, 29.11. **IR:** ν 2934, 1655, 1603, 1509, 1463, 1334, 1245, 1174, 1030, 979, 823, 774, 734, 578 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 291.1380. Found: 291.1395.



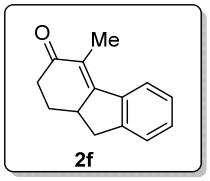
2d

Compound **2d** was isolated as a white solid (M.P.: 145-147 °C) in 76% yield. R_f = 0.4 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.11 (s, 2H), 7.00 – 6.93 (m, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 3.38 – 3.21 (m, 2H), 2.87 – 2.72 (m, 2H), 2.60 (ddd, *J* = 17.2, 14.2, 5.0 Hz, 1H), 2.48 – 2.38 (m, 1H), 2.12 – 1.98 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.04, 163.20, 149.02, 138.12, 133.76, 133.65, 131.27, 131.16, 131.03, 128.99, 126.76, 126.51, 125.31, 43.26, 38.35, 37.29, 29.01. **IR:** ν 3010, 2922, 1657, 1588, 1489, 1335, 1183, 1069, 816, 734, 578 cm^{-1}; **HRMS** calcd. For $[M+Na]^+$: 317.0704. Found: 317.0710.



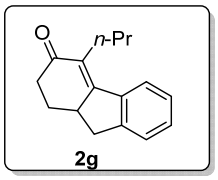
2e

Compound **2e** was isolated as a white solid (M.P.: 120-121 °C) in 78% yield. R_f = 0.3 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38 – 7.33 (m, 1H), 7.33 – 7.27 (m, 1H), 7.15 (s, 4H), 6.98 (dd, *J* = 8.2, 7.0 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 3.40 – 3.23 (m, 2H), 2.90 – 2.75 (m, 2H), 2.63 (ddd, *J* = 17.2, 14.2, 4.9 Hz, 1H), 2.46 (ddt, *J* = 12.6, 5.1, 2.1 Hz, 1H), 2.07 (dddd, *J* = 14.3, 12.8, 11.9, 4.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.36, 163.32, 162.39 (d, *J* = 246.2 Hz), 148.98, 138.23, 131.33, 131.08 (d, *J* = 3.5 Hz), 130.94, 126.58 (d, *J* = 21.6 Hz), 125.28, 115.76 (d, *J* = 21.3 Hz), 43.21, 38.35, 37.29, 29.02. **IR:** ν 2943, 1656, 1597, 1507, 1335, 1223, 1182, 911, 826, 773, 733, 584 cm^{-1}; **HRMS** calcd. For $[M+Na]^+$: 301.0999. Found: 301.1000.

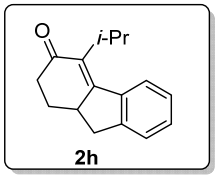


2f

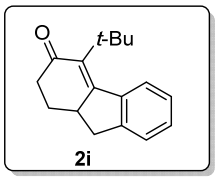
Compound **2f** was isolated as a colorless oil in 77% yield. R_f = 0.5 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 7.4 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 3.25 – 3.11 (m, 2H), 2.79 – 2.69 (m, 1H), 2.66 (ddd, *J* = 17.1, 4.2, 2.3 Hz, 1H), 2.46 (ddd, *J* = 17.1, 14.4, 4.9 Hz, 1H), 2.32 (dtd, *J* = 12.5, 4.5, 2.3 Hz, 1H), 2.13 (d, *J* = 2.2 Hz, 3H), 1.88 (dddd, *J* = 14.4, 12.5, 11.7, 4.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.76, 161.02, 148.55, 139.71, 130.24, 127.10, 126.92, 126.78, 125.32, 43.26, 37.95, 37.64, 29.27, 11.12. **IR:** ν 3304, 2954, 1720, 1632, 1463, 1330, 1276, 1205, 1070, 925, 849, 749, 580 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 199.1117. Found: 199.1121.



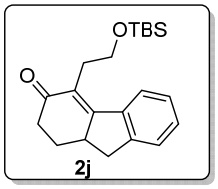
Compound **2g** was isolated as a colorless oil in 80% yield. R_f = 0.5 (EtOAc/Hexane=1/3). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.27 (m, 3H), 3.26 – 3.09 (m, 2H), 2.77 – 2.59 (m, 3H), 2.52 – 2.38 (m, 2H), 2.37 – 2.26 (m, 1H), 1.87 (dd, *J* = 14.5, 4.1 Hz, 1H), 1.59 (dd, *J* = 9.4, 3.8 Hz, 1H), 1.50 – 1.38 (m, 1H), 1.03 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.49, 160.65, 148.53, 139.18, 132.50, 130.23, 127.08, 126.29, 125.35, 43.28, 38.15, 37.69, 29.40, 27.00, 22.08, 14.33. **IR:** ν 2956, 2868, 1665, 1598, 1462, 1362, 1327, 1183, 1114, 770, 733 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 227.1430. Found: 227.1442.



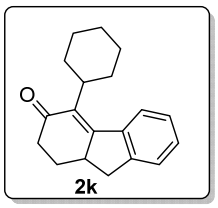
Compound **2h** was isolated as an oily solid (M.P.: 63-65 °C) in 70% yield. R_f = 0.6 (EtOAc/Hexane=1/3). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.69 – 7.64 (m, 1H), 7.35 (dd, *J* = 5.6, 1.1 Hz, 2H), 7.31 – 7.26 (m, 1H), 3.31 (hept, *J* = 6.9 Hz, 1H), 3.19 – 3.01 (m, 2H), 2.74 (dd, *J* = 14.9, 7.3 Hz, 1H), 2.55 (ddd, *J* = 17.6, 4.4, 2.2 Hz, 1H), 2.35 (ddd, *J* = 17.6, 14.4, 4.9 Hz, 1H), 2.27 – 2.18 (m, 1H), 1.82 (dddd, *J* = 14.4, 12.5, 11.7, 4.4 Hz, 1H), 1.43 (d, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.39, 159.77, 148.41, 139.27, 137.11, 130.09, 126.73, 126.46, 125.31, 44.32, 38.90, 37.88, 28.47, 28.01, 20.80, 20.70. **IR:** ν 2952, 2869, 1658, 1598, 1461, 1357, 1325, 995, 771, 733 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 227.1430. Found: 227.1444.



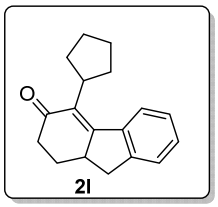
Compound **2i** was isolated as a light yellow oil in 49% yield. R_f = 0.6 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.26 – 7.19 (m, 1H), 3.11 – 2.93 (m, 2H), 2.76 (dd, *J* = 14.4, 7.9 Hz, 1H), 2.51 (ddd, *J* = 18.7, 5.7, 1.6 Hz, 1H), 2.31 (ddd, *J* = 18.7, 13.8, 5.6 Hz, 1H), 2.15 – 2.06 (m, 1H), 1.84 – 1.71 (m, 1H), 1.38 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.70, 157.81, 148.62, 143.12, 140.15, 129.41, 129.28, 125.58, 124.62, 48.19, 38.49, 38.34, 34.91, 30.61, 27.23. **IR:** ν 2957, 2863, 1660, 1576, 1461, 1362, 1318, 1203, 991, 768, 737 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 241.1587. Found: 241.1601.



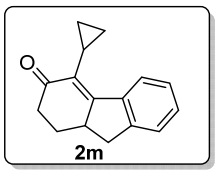
Compound **2j** was isolated as a colorless oil in 89% yield. R_f = 0.6 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.26 (m, 3H), 3.85 (ddd, *J* = 9.9, 8.0, 5.2 Hz, 1H), 3.72 (dt, *J* = 9.9, 7.5 Hz, 1H), 3.24 – 3.12 (m, 2H), 2.99 – 2.80 (m, 2H), 2.72 (d, *J* = 8.3 Hz, 1H), 2.63 (ddd, *J* = 16.9, 4.1, 2.4 Hz, 1H), 2.44 (ddd, *J* = 16.9, 14.4, 4.9 Hz, 1H), 2.37 – 2.26 (m, 1H), 1.96 – 1.80 (m, 1H), 0.84 (s, 9H), 0.03 (d, *J* = 0.3 Hz, 3H), 0.00 (d, *J* = 0.7 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.57, 162.98, 148.38, 139.05, 130.51, 128.36, 127.05, 126.90, 125.14, 61.97, 43.56, 38.07, 37.74, 29.29, 28.78, 25.94, 18.32, -5.28, -5.31. **IR:** ν 2882, 1659, 1600, 1471, 1360, 1337, 1254, 1100, 1076, 928, 836, 774, 732 cm^{-1}; **HRMS** calcd. For $[M+Na]^+$: 365.1907. Found: 365.1909.



Compound **2k** was isolated as a white solid (M.P.: 103-105 °C) in 61% yield. R_f = 0.6 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 26.6, 4.0 Hz, 3H), 3.14 (dd, *J* = 15.2, 8.0 Hz, 1H), 3.06 (ddt, *J* = 11.7, 7.8, 3.8 Hz, 1H), 2.88 (td, *J* = 10.3, 8.6, 6.0 Hz, 1H), 2.74 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.59 – 2.49 (m, 1H), 2.41 – 2.29 (m, 1H), 2.29 – 2.17 (m, 2H), 2.17 – 2.03 (m, 1H), 1.92 – 1.66 (m, 5H), 1.49 – 1.31 (m, 3H), 1.24 – 1.09 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.55, 160.23, 148.49, 139.38, 136.71, 130.07, 126.78, 126.42, 125.30, 44.36, 39.18, 38.87, 37.90, 30.41, 29.92, 28.43, 27.27, 26.90, 25.97. **IR:** ν 2933, 2862, 1655, 1598, 1450, 1325, 1276, 1181, 986, 769, 733 cm^{-1}; **HRMS** calcd. For $[M+Na]^+$: 289.1563. Found: 289.15774.

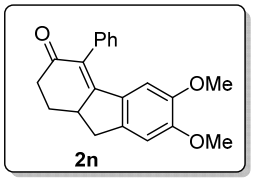


Compound **2l** was isolated as a colorless oil in 74% yield. R_f = 0.6 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.31 – 7.24 (m, 1H), 3.45 – 3.31 (m, 1H), 3.19 – 3.02 (m, 2H), 2.80 – 2.71 (m, 1H), 2.56 (ddd, *J* = 17.5, 4.3, 2.3 Hz, 1H), 2.42 – 2.31 (m, 1H), 2.23 (ddt, *J* = 10.1, 4.3, 2.3 Hz, 1H), 2.03 – 1.88 (m, 5H), 1.71 – 1.52 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.12, 160.93, 148.41, 139.53, 134.75, 130.09, 126.69, 126.20, 125.30, 44.58, 38.93, 38.52, 37.94, 31.24, 30.79, 28.35, 27.05, 26.91. **IR:** ν 2938, 2863, 1658, 1597, 1462, 1326, 1274, 1153, 943, 769, 733 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 253.1587. Found: 253.1602.



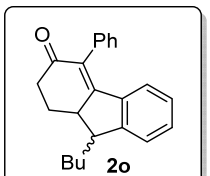
Compound **2m** was isolated as a colorless oil in 58% yield. R_f = 0.6 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.40 – 7.26 (m, 3H), 3.22 – 3.08 (m, 2H), 2.78 – 2.66 (m, 1H), 2.58 (ddd, *J* = 17.6, 4.4,

2.3 Hz, 1H), 2.41 (ddd, *J* = 17.6, 14.2, 5.0 Hz, 1H), 2.29 – 2.21 (m, 1H), 1.79 (dddd, *J* = 14.2, 12.6, 11.8, 4.5 Hz, 1H), 1.61 (ddt, *J* = 8.5, 5.6, 2.9 Hz, 1H), 1.13 – 1.02 (m, 1H), 0.86 (dddd, *J* = 9.1, 7.9, 6.1, 4.5 Hz, 1H), 0.49 – 0.42 (m, 1H), 0.35 – 0.26 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.80, 164.00, 148.67, 138.66, 131.93, 130.47, 127.91, 126.35, 124.94, 43.98, 38.41, 37.56, 28.54, 9.59, 8.05, 7.91. **IR:** v 2925, 2855, 1657, 1597, 1462, 1306, 1204, 1027, 997, 770, 734 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 225.1274. Found: 225.1290.



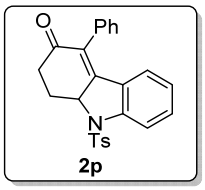
2n

Compound **2n** was isolated as a colorless oil in 75% yield. R_f = 0.3 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.57 – 7.27 (m, 4H), 7.05 (s, 1H), 6.78 (s, 1H), 5.85 (s, 1H), 3.87 (s, 3H), 3.38 – 3.26 (m, 1H), 3.31 (s, 3H), 3.20 (dd, *J* = 15.8, 7.9 Hz, 1H), 2.78 (dd, *J* = 6.5, 2.3 Hz, 1H), 2.74 (dd, *J* = 4.4, 2.2 Hz, 1H), 2.60 (ddd, *J* = 17.2, 14.0, 4.9 Hz, 1H), 2.39 (dtd, *J* = 12.0, 4.7, 2.4 Hz, 1H), 2.02 (dtd, *J* = 13.7, 12.4, 4.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.05, 163.76, 152.01, 147.88, 142.99, 135.74, 130.55, 130.36, 129.74, 128.70, 127.50, 108.16, 106.92, 55.96, 55.17, 43.42, 38.42, 37.04, 29.12. **IR:** v 2937, 2835, 2250, 1647, 1590, 1490, 1464, 1322, 1293, 1220, 1189, 977, 750, 701 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 321.1485. Found: 321.1487.



2o
unseperable mixture
d.r. 9:1

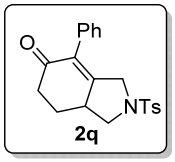
Compound **2o** was isolated as a colorless oil in 33% yield. R_f = 0.5 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.50 – 7.34 (m, 3H), 7.28 (dd, *J* = 13.8, 7.4 Hz, 2H), 7.14 (s, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 3.45 – 3.24 (m, 0.21H), 3.04 – 2.84 (m, 1.87H), 2.82 – 2.69 (m, 1H), 2.59 (ddd, *J* = 17.4, 14.2, 4.9 Hz, 1H), 2.52 – 2.36 (m, 1H), 2.26 – 2.14 (m, 0.23H), 2.11 – 1.92 (m, 1.88H), 1.80 – 1.63 (m, 1H), 1.54 – 1.35 (m, 3.94H), 1.35 – 1.18 (m, 0.83H), 0.96 (t, *J* = 7.1 Hz, 2.78H), 0.88 (t, *J* = 6.9 Hz, 0.41H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ (major) 198.46, 161.95, 152.42, 137.91, 135.41, 132.23, 130.80, 129.75, 128.75, 127.67, 126.68, 126.45, 123.97, 49.41, 48.05, 38.49, 33.19, 29.23, 28.97, 23.20, 14.09. **IR:** v 2928, 2858, 1661, 1594, 1463, 1330, 1274, 1179, 750, 700 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 317.1900. Found: 317.1900.



2p

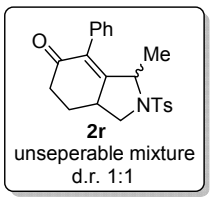
Compound **2p** was isolated as a light yellow oil in 42% yield. R_f = 0.5 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.20 (dt, *J* = 8.5, 0.8 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.29 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.26 – 7.22 (m, 5H), 7.15 – 7.11 (m, 2H), 7.09 (ddd, *J* = 8.2, 7.3, 1.0 Hz, 1H), 6.93 – 6.84 (m, 1H), 4.74 – 4.69 (m, 1H), 3.77 (dddd, *J* = 17.6, 7.5, 3.5,

0.8 Hz, 1H), 3.34 (dddd, *J* = 18.1, 10.0, 6.5, 1.9 Hz, 1H), 2.89 (ddd, *J* = 13.9, 10.0, 7.8 Hz, 1H), 2.55 (dddd, *J* = 13.9, 6.5, 3.5, 1.1 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 207.24, 145.18, 137.45, 136.74, 135.72, 134.49, 130.06, 128.85, 128.42, 128.01, 127.65, 126.40, 124.93, 123.72, 119.22, 118.58, 114.82, 53.23, 35.14, 24.64, 21.65. **IR:** v 3028, 2921, 1718, 1597, 1451, 1371, 1247, 1170, 1149, 1090, 910, 746, 707, 659, 576, 541 cm^{-1}; **HRMS** calcd. For [M+H]$^+$: 416.1315. Found: 416.1315.



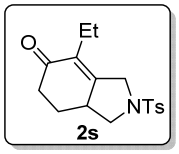
2q

Compound **2q** was isolated as a white solid (M.P.: 158-160 ^{o}C) in 73% yield. R_f = 0.3 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.29 (m, 5H), 7.03 (d, *J* = 8.1 Hz, 2H), 4.32 (dd, *J* = 17.6, 1.6 Hz, 1H), 3.95 (dd, *J* = 9.5, 8.2 Hz, 1H), 3.65 (dd, *J* = 17.6, 2.2 Hz, 1H), 3.19 – 3.05 (m, 1H), 2.71 (dd, *J* = 10.5, 9.5 Hz, 1H), 2.65 (ddd, *J* = 17.3, 4.4, 2.5 Hz, 1H), 2.52 – 2.43 (m, 4H), 2.43 (s, 4H), 2.24 (ddt, *J* = 12.8, 4.9, 2.5 Hz, 1H), 1.72 (dddd, *J* = 14.7, 12.9, 11.6, 4.4 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 195.98, 158.93, 144.05, 134.48, 133.32, 132.91, 129.91, 129.01, 128.34, 128.11, 127.64, 127.35, 53.12, 51.13, 40.86, 36.93, 26.37, 21.59. **IR:** v 3056, 2950, 2869, 1674, 1598, 1493, 1443, 1346, 1272, 1163, 1094, 1038, 912, 816, 733, 701, 679, 596, 550 cm^{-1}; **HRMS** calcd. For [M+Na]$^+$: 390.1134. Found: 390.1143.



2r
unseperable mixture
d.r. 1:1

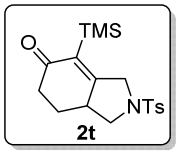
Compound **2r** was isolated as a colorless oil in 70% yield. R_f = 0.5 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, CDCl$_3$):** δ (major) 7.65 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.34 (m, 5H), 6.83 – 6.74 (m, 2H), 4.24 (qd, *J* = 6.6, 1.9 Hz, 1H), 3.92 (dd, *J* = 9.2, 8.3 Hz, 1H), 3.24 (ddd, *J* = 8.1, 4.8, 2.5 Hz, 1H), 2.73 (dd, *J* = 10.4, 9.3 Hz, 1H), 2.60 – 2.49 (m, 2H), 2.48 (s, 3H), 2.30 – 2.22 (m, 1H), 1.64 – 1.48 (m, 1H), 1.23 (d, *J* = 6.6 Hz, 3H). δ (minor) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.73 (m, 2H), 7.41 – 7.29 (m, 5H), 7.07 – 6.99 (m, 2H), 4.97 (q, *J* = 6.8 Hz, 1H), 3.98 (dd, *J* = 12.1, 8.3 Hz, 1H), 3.05 (t, *J* = 11.8 Hz, 1H), 2.65 (ddd, *J* = 17.7, 4.5, 2.2 Hz, 1H), 2.45 (s, 3H), 2.44 – 2.30 (m, 2H), 2.13 (dtd, *J* = 12.1, 5.0, 2.2 Hz, 1H), 1.71 (dtd, *J* = 14.5, 12.4, 4.5 Hz, 1H), 0.87 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ (mixture) 196.74, 196.67, 165.85, 162.51, 144.10, 143.90, 136.56, 134.72, 133.97, 133.68, 133.18, 132.94, 130.07, 129.78, 129.18, 129.00, 128.49, 128.48, 128.05, 128.01, 127.82, 127.02, 58.52, 58.48, 54.11, 50.55, 42.07, 37.84, 36.97, 36.61, 26.56, 26.45, 22.19, 21.63, 21.60, 18.89. **IR:** v 2931, 2869, 1675, 1597, 1493, 1344, 1275, 1162, 1093, 915, 817, 751, 701, 659, 575, 550 cm^{-1}; **HRMS** calcd. For [M+H]$^+$: 382.1471. Found: 382.1475.



2s

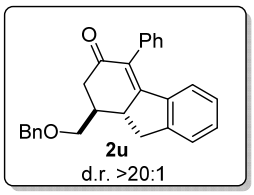
Compound **2s** was isolated as a colorless oil in 71% yield. R_f = 0.3 (EtOAc/Hexane=1/3). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 4.26 (d, *J* = 16.6 Hz, 1H), 3.89 (dd, *J* = 9.2, 7.9 Hz, 1H), 3.82 (dd, *J* =

16.9, 2.5 Hz, 1H), 2.96 (q, *J* = 11.7 Hz, 1H), 2.59 (dd, *J* = 10.9, 9.2 Hz, 1H), 2.49 (ddd, *J* = 17.1, 4.3, 2.3 Hz, 5H), 2.45 (s, 4H), 2.30 (ddd, *J* = 17.2, 14.6, 4.9 Hz, 1H), 2.23 – 2.08 (m, 2H), 2.03 (qd, *J* = 7.5, 6.1 Hz, 1H), 1.55 (dddd, *J* = 14.5, 12.6, 11.7, 4.4 Hz, 1H), 0.91 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 196.95, 156.63, 144.11, 134.63, 132.56, 129.92, 127.73, 53.42, 50.11, 40.57, 36.73, 26.54, 21.60, 19.58, 12.89. **IR:** ν 2965, 2872, 1667, 1598, 1453, 1346, 1164, 1094, 1041, 913, 815, 732, 675, 593, 550 457 cm^{-1}; **HRMS** calcd. For [M+Na]$^+$: 320.1315. Found: 320.1308.



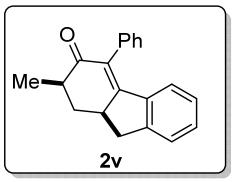
2t

Compound **2t** was isolated as a white solid (M.P.: 138-140 °C) in 37% yield. R_f = 0.4 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.37 (dd, *J* = 8.6, 0.7 Hz, 2H), 4.30 (dd, *J* = 17.3, 1.3 Hz, 1H), 3.87 (dd, *J* = 9.0, 8.1 Hz, 1H), 3.81 (dd, *J* = 17.3, 2.4 Hz, 1H), 2.86 (dd, *J* = 12.3, 6.6 Hz, 1H), 2.51 (dd, *J* = 11.0, 9.3 Hz, 1H), 2.46 (s, 3H), 2.45 – 2.40 (m, 1H), 2.27 (ddd, *J* = 17.2, 14.4, 5.2 Hz, 1H), 2.12 (dtd, *J* = 12.4, 5.0, 2.3 Hz, 1H), 1.54 (dtd, *J* = 14.4, 12.3, 4.6 Hz, 1H), 0.15 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 201.09, 170.41, 144.14, 134.08, 132.34, 129.92, 127.80, 52.42, 52.22, 42.05, 36.75, 25.99, 21.61, 0.39. **IR:** ν 2924, 2852, 1659, 1600, 1453, 1349, 1262, 1165, 1094, 875, 841, 665, 597, 550 cm^{-1}; **HRMS** calcd. For [M+Na]$^+$: 364.1397. Found: 364.1400.



2u
d.r. >20:1

Compound **2u** was isolated as a colorless oil in 40% yield (d.r. >20:1). R_f = 0.3 (EtOAc/Hexane=1/4). **^{1}H NMR (500 MHz, CDCl$_3$):** δ 7.55 – 7.27 (m, 9H), 7.23 (m, 3H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 3.69 – 3.58 (m, 2H), 3.27 (ddt, *J* = 30.5, 15.5, 7.9 Hz, 2H), 2.84 (ddd, *J* = 21.2, 16.2, 5.4 Hz, 2H), 2.64 (dd, *J* = 16.9, 13.3 Hz, 1H), 2.52 – 2.39 (m, 1H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 198.40, 162.04, 148.43, 138.26, 138.23, 135.23, 132.40, 130.75, 129.62, 128.72, 128.45, 127.69, 127.52, 126.60, 125.14, 73.32, 72.20, 45.31, 41.76, 41.62, 35.86. **IR:** ν 3060, 2856, 1657, 1594, 1463, 1313, 1108, 1073, 776, 737, 699 cm^{-1}; **HRMS** calcd. For [M+H]$^+$: 381.1849. Found: 381.1848. The stereochemistry was tentatively assigned according to the stereochemistry of starting material **1v**.



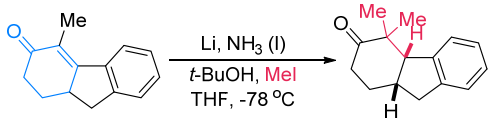
2v

Compound **2v** (major) was isolated as a white solid (M.P.: 123-125 °C) in 33% yield and 2v (minor) was isolated as a white solid in 13% (d.r. =2.5:1 based on isolated yield). R_f = 0.4 (EtOAc/Hexane=1/4). **^{1}H NMR (500 MHz, CDCl$_3$):** δ (major) 7.49 – 7.33 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.25 – 6.96 (m, 3H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 7.9 Hz, 1H), 3.41 – 3.32 (m, 1H), 3.24 (dd, *J* = 15.8, 8.1 Hz, 1H), 2.80 (dd, *J* = 15.8, 7.3 Hz, 1H), 2.59 (dqd, *J* = 13.5, 6.7, 4.3 Hz, 1H), 2.44 (dt, *J* = 12.5, 4.4 Hz, 1H), 1.85 (q, *J* = 12.6 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 3H). δ (minor) 7.48 – 7.35 (m, 3H), 7.34 – 7.27

(m, 2H), 7.25 – 7.08 (m, 2H), 6.91 (t, J = 7.6 Hz, 1H), 6.40 (d, J = 7.9 Hz, 1H), 3.56 – 3.42 (m, 1H), 3.24 (dd, J = 15.8, 8.0 Hz, 1H), 2.85 – 2.71 (m, 2H), 2.35 – 2.15 (m, 2H), 1.38 (d, J = 7.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ (major) 200.66, 161.82, 148.52, 138.56, 135.61, 132.05, 130.54, 129.73, 128.59, 127.50, 126.55, 126.46, 125.10, 43.03, 42.25, 37.66, 37.34, 16.20. **IR:** ν 3020, 2928, 2852, 1658, 1595, 1462, 1372, 1330, 1179, 1093, 774, 731, 699 cm^{-1}; **HRMS** calcd. For $[M+Na]^+$: 297.1250. Found: 297.1253. The major diastereomer's stereochemistry was assigned according to 2-D NMR (see in **2-D NMR spectra**).

V. *Procedures and data for synthetic applications*

a) *Dissolving metal reduction followed by alkylation of **2f**: synthesis of **3***



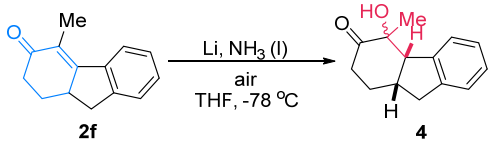
2f → **3**: 93%, >20:1 d.r.

Procedure:[7]

1 mL liquid ammonia was condensed in a 10 mL Schlenk flask at -78 °C and nitrogen atmosphere was introduced after condensation. A solution of **2f** (20.0 mg, 0.1 mmol, 1 equiv.) and *t*-BuOH (8.2 mg, 0.11 mmol, 1.1 equiv.) in anhydrous tetrahydrofuran (1 mL) was added dropwise to the stirring liquid ammonia at -78 °C. Under N_2 flow, the rubber stopper of Schlenk flask was removed and pieces of lithium (6.9 mg, 1.0 mmol, 10 equiv.) was added to the stirring mixture. After stirring at -78 °C for 3 h, iodomethane (851.3 mg, 6 mmol, 60 equiv.) was injected into the flask and stirred for another 3 h. 1 mL of saturated aqueous ammonia chloride solution was injected to the flask and the system was opened and slowly warmed up to room temperature. After the ammonia was removed, the reaction was diluted with ether (10 mL) and washed with sat. NH_4Cl (aq.) solution (20 mL) and brine (20 mL). The combined organic extract was dried by $MgSO_4$ and concentrated under reduced pressure. The crude product was purified with silica gel flash column chromatography (EtOAc/Hexane= 1/10 to 1/5) to afford compound **3** as a white solid in 93% yield (20.0 mg).

Compound **3** was isolated as a white solid (M.P.: 70-72 °C) in 93% yield (d.r. >20:1). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 1H), 7.25 – 7.14 (m, 3H), 3.30 (d, J = 8.7 Hz, 1H), 3.16 – 3.02 (m, 1H), 2.98 – 2.81 (m, 2H), 2.60 (ddd, J = 15.7, 6.2, 4.4 Hz, 1H), 2.41 (ddd, J = 15.7, 11.4, 5.2 Hz, 1H), 2.26 (dddd, J = 13.7, 7.4, 6.1, 5.1 Hz, 1H), 1.98 (dddd, J = 14.0, 11.5, 7.9, 4.4 Hz, 1H), 1.28 (s, 3H), 0.81 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 217.10, 144.29, 143.28, 127.11, 126.13, 125.74, 124.78, 53.78, 48.12, 39.59, 38.03, 36.68, 26.37, 24.90, 22.63. **IR:** ν 2969, 2932, 1707, 1458, 1378, 1319, 1224, 1177, 1098, 940, 754, 735 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 215.1430. Found: 215.1430.

b) *Dissolving metal reduction followed by oxidation of **2f**: synthesis of **4***



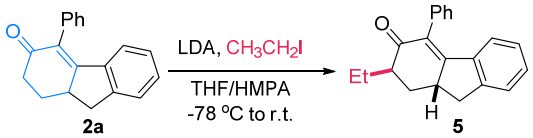
2f → **4**: 59%, 12:1 d.r.

Procedure:[8]

1 mL liquid ammonia was condensed in a 10 mL Schlenk flask at -78 °C and nitrogen atmosphere was introduced after condensation. A solution of **2f** (12.0 mg, 0.06 mmol, 1 equiv.) in anhydrous tetrahydrofuran (1 mL) was added dropwise to the stirring liquid ammonia at -78 °C. Under N_2 flow, the rubber stopper of Schlenk flask was removed and pieces of lithium (1.8 mg, 0.27 mmol, 4.4 equiv.) was added to the stirring mixture. After stirring at -78 °C for 3 h, 1 mL of saturated aqueous ammonia chloride solution was injected to the flask and the system was opened and slowly warmed up to room temperature. After the ammonia was removed, the reaction was diluted with ether (10 mL) and washed with sat. NH_4Cl (aq.) solution (20 mL) and brine (20 mL). The combined organic extract was dried by $MgSO_4$ and concentrated under reduced pressure. The crude product was purified with silica gel flash column chromatography (EtOAc/Hexane= 1/10 to 1/5) to afford compound **4** as a colorless oil in 59% yield (7.7 mg). (note: The d.r. of **4** decreased if being kept in chloroform).

Compound **4** was isolated as a colorless oil in 59% yield (d.r.=12:1). R_f = 0.4 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.37 – 9.22 (m, 1H), 7.44 – 7.38 (m, 1H), 7.26 – 7.19 (m, 3H), 4.00 (d, *J* = 9.6 Hz, 1H), 3.18 (dd, *J* = 15.7, 8.7 Hz, 1H), 3.07 – 2.94 (m, 1H), 2.87 (dd, *J* = 15.7, 8.9 Hz, 1H), 2.68 (ddd, *J* = 16.8, 6.6, 5.1 Hz, 1H), 2.49 (ddd, *J* = 16.7, 10.2, 5.4 Hz, 1H), 2.23 (ddd, *J* = 13.8, 6.8, 1.4 Hz, 1H), 2.02 (ddd, *J* = 10.3, 8.5, 5.0 Hz, 1H), 1.02 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 214.20, 143.31, 141.09, 127.50, 126.72, 126.61, 124.51, 88.91, 48.99, 38.87, 37.11, 36.74, 26.43, 18.25. **IR:** ν 3300, 2934, 1717, 1458, 1275, 1260, 913, 764, 749 cm^{-1}; **HRMS** calcd. For $[M+H-(H_2O)]^+$: 199.1117. Found: 199.1114.

c) *α-alkylation of **2a**: synthesis of **5***



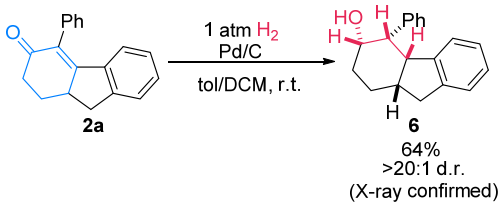
Procedure:

To a 10 mL flamed-dried Schlenk flask equipped with a nitrogen-filled balloon was added THF (2.3 mL) and freshly distilled *i*-Pr_2NH (506.0 mg, 0.7 mL, 5.0 mmol, 1 equiv.). The reaction mixture was cooled to -78 °C with an acetone-dry ice bath and *n*-BuLi (2.5 M in hexane, 2.0 mL, 5 mmol, 1 equiv.) was added dropwise. Upon completion, the system was warmed to 0 °C and stirred for 0.5 h under nitrogen atmosphere. Meanwhile, to another 10 mL flamed-dried flask equipped with a nitrogen-filled balloon were added compound **2a** (26 mg, 0.1 mmol, 1 equiv.) and THF (5 mL). After cooling to -78 °C with an acetone-dry ice bath, the newly made LDA solution as indicated above (1 M in THF/Hexane, 2.0 ml, 2.00 mmol, 20 equiv.) was added dropwise and the reaction was warmed up to -20 °C for 0.5 h. After that, the reaction was cooled to -78 °C again and EtI (779.9 mg, 0.4 mL, 5 mmol, 50 equiv.) was added dropwise. The reaction was gradually warmed up to room temperature for 3 h and was quenched by adding NH_4Cl (sat.) 5 mL. The mixture was extracted with diethyl ether (10 mL×3), washed with brine, and dried with Na_2SO_4. The combined organic extract was concentrated under reduced pressure and purified by silica gel flash column chromatography (EtOAc/Hexane=1/10) on silica gel to afford compound **5** as a colorless oil in 60% yield (d.r. >20:1). The relative stereochemistry was determined by 2-D NMR (see in **2-D NMR spectra**).

Compound **5** was isolated as a colorless oil in 60% yield (d.r. >20:1). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 – 7.34 (m, 3H), 7.33 – 7.29 (m, 1H), 7.23 (td, *J* = 7.5, 1.2 Hz, 1H), 7.14 (s, 2H), 6.95 – 6.88 (m, 1H),

6.41 (dt, J = 8.0, 0.9 Hz, 1H), 3.43 (ddt, J = 12.3, 7.7, 3.9 Hz, 1H), 3.22 (dd, J = 15.7, 8.0 Hz, 1H), 2.80 (dd, J = 15.7, 7.5 Hz, 1H), 2.51 (dtt, J = 6.7, 4.9, 2.5 Hz, 1H), 2.38 (ddd, J = 13.1, 4.6, 2.0 Hz, 1H), 2.26 – 2.12 (m, 1H), 1.93 – 1.68 (m, 2H), 1.09 (t, J = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.10, 161.14, 148.74, 138.54, 135.64, 131.73, 130.53, 129.82, 128.65, 127.56, 126.57, 126.56, 125.08, 47.45, 38.38, 37.54, 32.18, 23.05, 12.39. **IR:** v 2930, 1654, 1462, 1337, 1275, 1260, 1177, 764, 749, 699 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 289.1587. Found: 289.1589.

d) *H_2/ (Pd/C) reduction of **2a**: synthesis of **6***

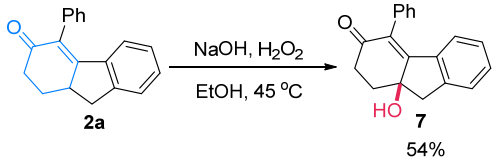


Procedure:

A 10 mL Schlenk flask was charged with **2a** (26 mg, 0.1 mmol, 1 equiv.) and Pd/C (26.0 mg, 0.24 mmol, 2.4 equiv.) before it was degassed and backfilled with hydrogen three times. After that, toluene (1 mL) and dichloromethane (1 mL) were injected into the flask. A balloon of hydrogen was kept on top of the flask. After stirring at room temperature overnight, the reaction was diluted with dichloromethane (10 mL) and filtered through a filtration paper. The resulting solution was concentrated under reduced pressure and purified by silica gel flash column chromatography (EtOAc/Hexane= 1/10 to 1/5) to afford compound **6** as a bright yellow oil in 64% yield (17.0 mg). The stereochemistry was determined by X-ray crystallography.

Compound **6** was isolated as a white solid (M.P.: 110-112 °C) in 64% yield (d.r.>20:1). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (dt, J = 8.4, 1.1 Hz, 2H), 7.42 (dd, J = 8.4, 7.0 Hz, 2H), 7.30 (td, J = 7.5, 1.0 Hz, 1H), 7.20 (t, J = 6.6 Hz, 1H), 7.08 – 7.02 (m, 1H), 6.88 – 6.82 (m, 1H), 6.48 (d, J = 7.6 Hz, 1H), 4.72 – 4.62 (m, 1H), 3.97 (t, J = 5.7 Hz, 1H), 3.34 (d, J = 4.3 Hz, 1H), 3.08 – 2.77 (m, 1H), 2.69 – 2.57 (m, 1H), 2.59 (d, J = 15.5 Hz, 1H), 1.95 (dq, J = 13.6, 3.5 Hz, 1H), 1.65 (tdd, J = 13.5, 4.6, 2.2 Hz, 1H), 1.56 – 1.42 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.16, 143.77, 142.35, 128.58, 127.66, 126.48, 126.16, 126.14, 125.74, 125.46, 68.36, 47.01, 45.13, 40.95, 38.60, 32.89, 21.50. **IR:** v 3580, 3022, 2926, 2854, 1456, 1275, 973, 913, 763, 748, 698 cm^{-1}; **HRMS** calcd. For $[M+H-(H_2O)]^+$:247.1481. Found: 247.1484.

e) *Epoxidation of **2a**: synthesis of **7***



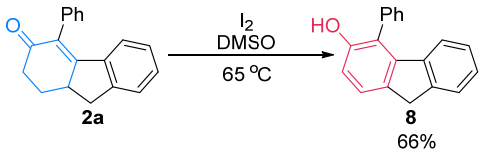
Procedure:

A 20 mL vial was charged with **2a** (26 mg, 0.1 mmol, 1 equiv.) in 10 mL anhydrous ethanol, NaOH (12 mg, 0.3 mmol, 3.0 equiv.) and H_2O_2 (28 L, 1 mmol, 10 equiv.). After stirring at 45 °C overnight, the reaction was diluted with dichloromethane and filtered through a pad of silica gel and $MgSO_4$. The combined organic extract was concentrated under reduced pressure and purified by silica gel flash column chromatography (EtOAc/Hexane=1/5 to 1/1) to afford

compound **7** as a colorless oil in 54% yield.

Compound **7** was isolated as a colorless oil in 54% yield (14.9 mg). R_f = 0.2 (EtOAc/Hexane=1/1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 – 7.37 (m, 3H), 7.38 – 7.23 (m, 2H), 7.16 (s, 2H), 7.00 – 6.92 (m, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 3.24 (d, *J* = 16.6 Hz, 1H), 3.18 (d, *J* = 16.6 Hz, 1H), 3.09 (ddd, *J* = 17.7, 13.3, 5.4 Hz, 1H), 2.66 (ddd, *J* = 17.7, 4.9, 1.9 Hz, 1H), 2.55 (ddd, *J* = 13.6, 5.4, 1.9 Hz, 1H), 2.36 (td, *J* = 13.4, 4.9 Hz, 1H), 2.29 – 2.09 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.30, 158.52, 146.11, 136.32, 134.40, 133.35, 131.36, 129.30, 128.80, 128.05, 127.56, 127.17, 125.95, 77.21, 46.43, 33.65, 33.53. **IR:** v 3404, 3058, 2924, 2245, 1647, 1595, 1463, 1442, 1331, 1275, 1192, 1064, 1004, 960, 906, 750, 733, 699 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 277.1223. Found: 277.1225.

f) *Oxidation of **2a**: synthesis of **8***

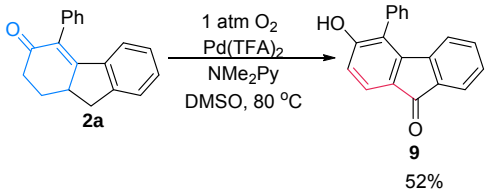


Procedure:[9]

A 4 mL vial was charged with **2a** (20 mg, 0.077 mmol, 1 equiv.) in 0.5 mL anhydrous DMSO and I_2 (4.9 mg, 0.038 mmol, 0.5 equiv.) under nitrogen atmosphere. After stirring at 65 °C overnight, the reaction was diluted with ethyl acetate (10 mL) and washed with saturated $Na_2S_2O_3$ aqueous solution (10 mL). Then the organic phase was washed with brine (10 mL) and dried by a pad of $MgSO_4$. The combined organic extract was concentrated under reduced pressure and purified by silica gel flash column chromatography (EtOAc/Hexane=1/10 to 1/5) to afford compound **8** as a light yellow oil in 66% yield (13.2 mg).

Compound **8** was isolated as a colorless oil in 66% yield (13.2 mg). R_f = 0.6 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 – 7.53 (m, 3H), 7.52 – 7.41 (m, 4H), 7.19 (td, *J* = 7.4, 1.1 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.51 (dt, *J* = 7.9, 0.9 Hz, 1H), 4.82 (t, *J* = 0.8 Hz, 1H), 3.88 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 152.04, 144.71, 141.52, 140.03, 135.52, 134.44, 130.45, 129.90, 128.88, 126.33, 126.23, 125.11, 124.84, 122.92, 122.33, 113.66, 36.22. **IR:** v 3511, 3050, 2887, 1595, 1478, 1444, 1424, 1276, 1231, 1170, 912, 763, 747, 701 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 259.1117. Found: 259.1117.

g) *Aerobic Oxidation of **2a**: synthesis of **9***



Procedure:[10]

A 8 mL rubber-head test tube was charged with **2a** (26 mg, 0.1 mmol, 1 equiv.) in 0.5 mL anhydrous DMSO, $Pd(TFA)_2$ (1.7 mg, 0.005 mmol, 5 mol%), 2-Me_2NPy (1.2 mg, 0.01 mmol, 10 mol%) and TsOH (3.8 mg, 0.02 mmol, 20 mol%) before purging oxygen through the solution for 5 min. A balloon of oxygen was kept on top of the test tube through the rubber. After stirring at 80 °C overnight, the reaction was diluted with ethyl acetate (10 mL) and washed with brine (10 mL) and dried by a pad of $MgSO_4$. The combined organic extract was concentrated under reduced pressure and purified

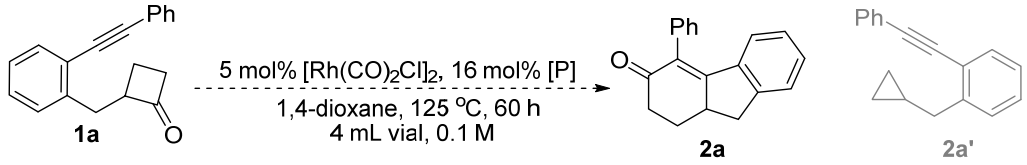
by silica gel flash column chromatography (EtOAc/Hexane= 1/5) to afford compound **9** as a bright yellow oil in 52% yield (13.5 mg).

Compound **9** was isolated as a yellow oil in 52% yield (13.5 mg). R_f = 0.3 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.68 – 7.57 (m, 5H), 7.45 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.17 (td, *J* = 7.4, 1.1 Hz, 1H), 7.10 (td, *J* = 7.6, 1.3 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.27 (dt, *J* = 7.5, 0.9 Hz, 1H), 5.53 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 192.61, 159.14, 144.11, 143.32, 135.55, 133.86, 132.63, 130.16, 130.11, 129.57, 128.86, 127.30, 125.90, 124.28, 123.80, 122.60, 114.91. **IR:** v 3246, 1685, 1603 ,1575, 1420, 1380, 1275, 1184, 1097, 942, 903, 834, 763, 749, 699 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 273.0910. Found: 273.0914.

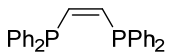
3. Additional Condition Screening

Following the general procedure for Rh-catalyzed intramolecular coupling between cyclobutanones and alkynes (2-IV), additional condition screening of different ligands and precatalyst to ligand ratios are shown below.

a. Screening of ligands

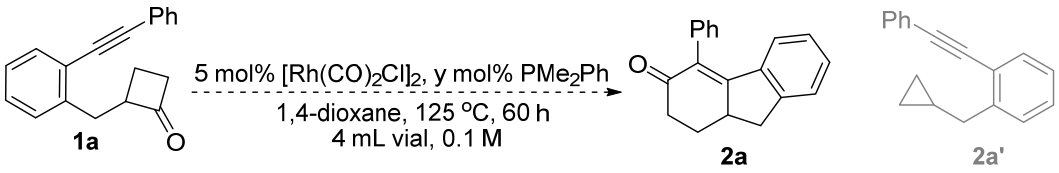


entry	ligands	results (**2a**: **1a**: **2a'**)
1[a]	PMe_3	57%: trace: 10%
2[a]	$PMePh_2$	50%: 22%: 8%
3[a]	PPh_3	35%: 50%: 12%
4[a]	$P(tol)_3$	47%: 12%: 19%
5[a]	$P(4\text{-}F\ Ph)_3$	64%: 16%; 22%
6[a]	$P(4\text{-}MeOPh)_3$	53%: trace: 17%
7[a]	PCy_3	37%: 23%: 18%
8[a]	PBu_3	39%: 6%: 15%
9[a]	$P(t\text{-}Bu)_3$	65%: trace: 16%
10[b]	$P(OMe)_3$	decomp.
11[b]	$P(OPh)_3$	SM recovered 70%
12[a]	dppb	45%: 40%: 9%
13[a]	dppe	67%: 8%: trace
14[b]	dppbz	9%: 77%: 10%
15[b]	binap	48%: 33%: trace
16[b]	biphep	31%: 52%: trace
17[b]	L	17%: 70%: trace
18[a]	$P(3,5\text{-}CF_3C_6H_3)_3$	50%: 25%: 10%

L: 

[a] isolated yield. [b] NMR yield using mesitylene as internal standard

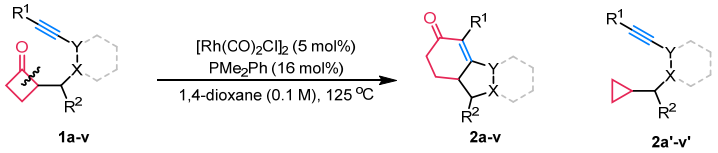
b. Screening of the [Rh]/P ratio

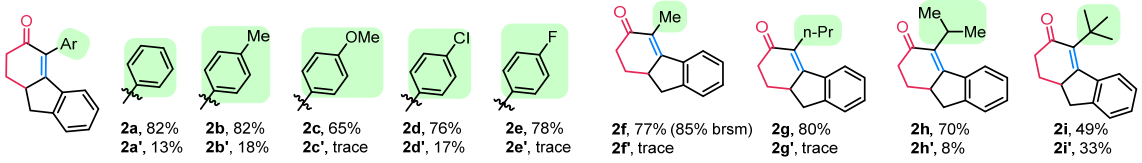


entry[a]	y	results (**2a**: **1a**: **2a'**)
1	10 mol%	64%: trace: 24%
2	13 mol%	71%: trace: 20%
3	14 mol%	73%: trace: 20%
4	15 mol%	76%: trace: 18%
5	16 mol%	82%: trace: 13%
6	17 mol%	77%: 5%: 15%
7	18 mol%	53%: 30%: 8%
8	20 mol%	trace: 92%: trace

[a] All the yields are NMR yield using mesitylene as internal standard

4. Substrate Table (with decarbonylation side product yield indicated)



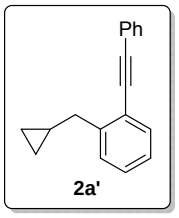


2a, 82% **2a'**, 13%
2b, 82% **2b'**, 18%
2c, 65% **2c'**, trace
2d, 76% **2d'**, 17%
2e, 78% **2e'**, trace
2f, 77% (85% brsm) **2f'**, trace
2g, 80% **2g'**, trace
2h, 70% **2h'**, 8%
2i, 49% **2i'**, 33%
2j, 89% **2j'**, trace
2k, 61% **2k'**, 17%
2l, 74% **2l'**, 5%
2m, 60% **2m'**, trace
2n, 75% **2n'**, 8%
2o, 33% (39% brsm) **2o'**, 28%
2p, 42% **2p'**, trace
2q, 73% **2q'**, trace
2r, 70% **2r'**, trace
2s, 71% **2s'**, trace
2t, 37% **2t'**, trace
2u(±), 40% **2u'**, 33%
2v(±), 46% (72% brsm) **2v'**, 6%

5. Mechanistic Study

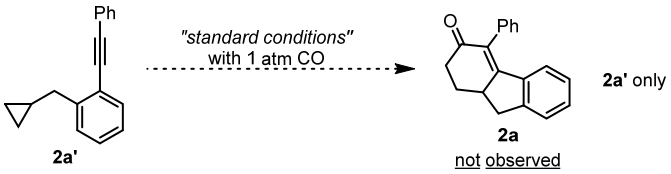
*I. Subjecting **2a'** to carbonylative (3+2+1) conditions*

2a' was obtained as a side product from the key reaction of **1a**.



Compound **2a'** was isolated as a colorless oil. R_f = 0.8 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 (ddd, *J* = 6.6, 5.2, 1.9 Hz, 3H), 7.40 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 7.21 (dd, *J* = 7.5, 1.4 Hz, 1H), 2.81 (d, *J* = 6.9 Hz, 2H), 1.20 – 1.07 (m, 1H), 0.58 – 0.49 (m, 2H), 0.29 (dt, *J* = 6.0, 4.5 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.19, 132.06, 131.46, 128.55, 128.40, 128.36, 128.16, 125.81, 123.56, 122.54, 92.91, 88.45, 38.79, 11.27, 4.67. **IR:** v 3060, 3000, 2923, 1599, 1492, 1442, 1016, 754, 689 cm^{-1}; **HRMS** calcd. For $[M+H]^+$: 233.1325. Found: 233.1311.

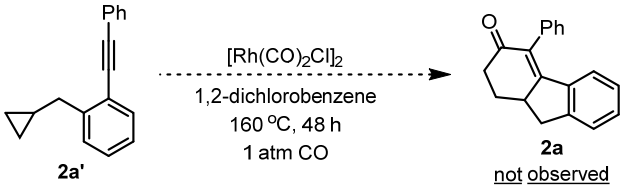
a) Utilizing "standard conditions" with 1 atm CO



Procedure:

In a nitrogen-filled glovebox, a flame dried reaction tube, containing a magnetic stirrer, was charged with **2a'** (19.0 mg, 0.082 mmol, 1 equiv.) in FPT 1,4-dioxane (0.8 mL). PMe_2Ph (1.81 mg, 0.0131 mmol, 16 mol%) and $[Rh(CO)_2Cl]_2$ (1.6 mg, 0.0041 mmol, 5 mol%) were added as a stock solution to the system. The tube was sealed with a rubber septum and the reaction mixture was sparged with CO for 2 minutes, then heated at 125 °C under a CO atmosphere (1 atm.) for 60 h. The mixture was cooled to room temperature and filtered through a pad of silica gel to afford >90% recovery of **2a'** indicated by crude ^{1}H-NMR.

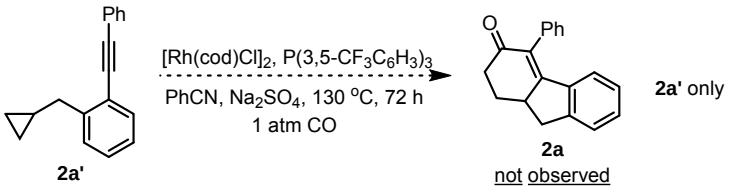
b) Narasaka's (3+2+1) condition



Procedure:[11]

A flame-dried reaction tube, fitted with a magnetic stirrer, was charged with $[Rh(CO)_2Cl]_2$ (3.0 mg, 0.0075 mmol, 10 mol%) in a nitrogen-filled glovebox. Compound **2a'** (18.0 mg, 0.077 mmol, 1 equiv.) in a nitrogen sparged anhydrous 1,2-dichlorobenzene (300 μL) was added via syringe. The reaction mixture was sparged with CO for 2 minutes, and then heated at 160 °C under a CO atmosphere (1 atm.) for 48 h. The mixture was cooled to r.t. and filtered through a pad of silica gel to afford a crude mixture which has no NMR signal from 2a' or 2a indicated by crude NMR.

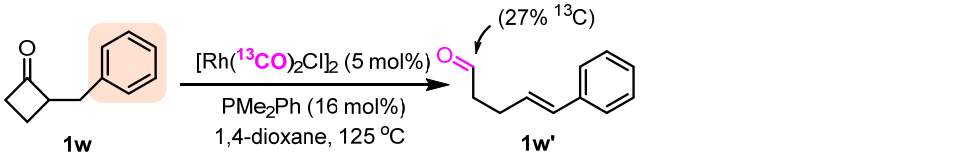
c) Bower's (3+2+1) condition



Procedure:[12]

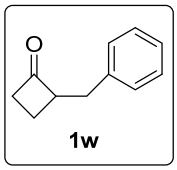
An oven-dried reaction tube, fitted with a magnetic stirrer, was charged with $[Rh(cod)Cl]_2$ (1.0 mg, 0.002 mmol, 3.75 mol%), $P(3,5\text{-}(CF_3)_2Ph)_3$ (5.5 mg, 0.0082 mmol, 15 mol%) and Na_2SO_4 (1.6 mg, 0.011, 20 mol%). The tube was fitted with a rubber septum and purged with nitrogen. Compound **2a'** (12.8 mg, 0.055 mmol, 1 equiv.) in a nitrogen sparged anhydrous benzonitrile solution (0.07 M) was added via syringe. The reaction mixture was sparged with CO for 2 minutes, and then heated at 130 °C under a CO atmosphere (1 atm.) for 72 h. The mixture was cooled to r.t. and filtered through a pad of silica gel to afford >90% recovery of **2a'** indicated by crude NMR.

*II. Subjecting **1w** to standard conditions*

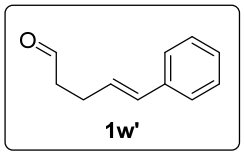


22% yield + several unidentifiable decomposition products

Compound **1w** was synthesized according to literature known procedure and matched the reported characterization data[13]. Adopting the aforementioned standard procedure for C−C activation reaction but using $[Rh(^{13}CO)_2Cl]_2$ as the precatalyst, full conversion of **1w** was observed and **1w'** was isolated as the only characterizable product, which spectra matched the reported data[14]. Along with **1w'**, there are several unidentifiable decomposition products. This result suggests that C−C activation of cyclobutanone does not require the alkyne moiety serving as a directing group.



Compound **1w**[13] was isolated as a colorless oil in 56% yield from compound **10** and benzyl bromide (**Route I**, page S5). R_f = 0.7 (EtOAc/Hexane=1/5). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.29 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.22 (s, 1H), 7.20 – 7.16 (m, 2H), 3.71 – 3.53 (m, 1H), 3.11 – 2.98 (m, 2H), 2.89 (ddd, *J* = 9.7, 5.1, 2.8 Hz, 1H), 2.81 (dd, *J* = 14.4, 9.0 Hz, 1H), 2.23 – 2.10 (m, 1H), 1.75 (ddt, *J* = 11.2, 9.6, 7.6 Hz, 1H).



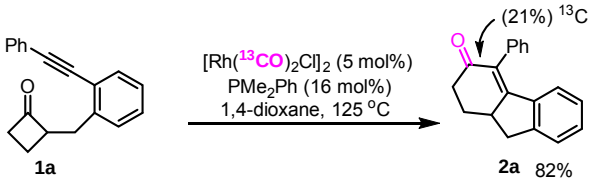
Compound **1w'** was isolated as a colorless oil in 22% yield from **1w**.[14] R_f = 0.5 (EtOAc/Hexane=1/5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.83 (s, 1H), 7.38 – 7.28 (m, 3H), 7.21 (t, *J* = 8.7 Hz, 2H), 6.44 (d, *J* = 15.9 Hz, 2H), 6.21 (dt, *J* = 15.4, 6.4

Hz, 2H), 2.70 – 2.60 (t, J = 7.1 Hz, 2H), 2.61 – 2.53 (t, J = 7.0 Hz, 2H). The characterization of ^{13}CO incorporation ratio was demonstrated in **5.III**.

III. ^{13}CO labeling study

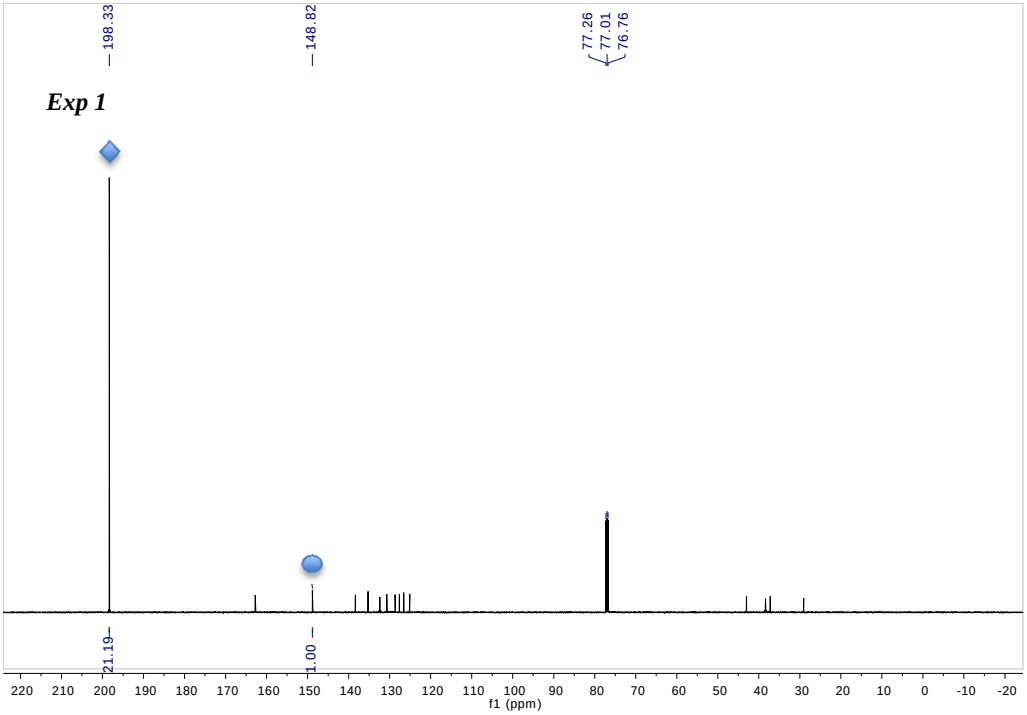
$[Rh(^{13}CO)_2Cl]_2$ was prepared according to literature procedure (using ^{13}CO atmosphere instead of CO) and its characterization matched the reported data.[15]

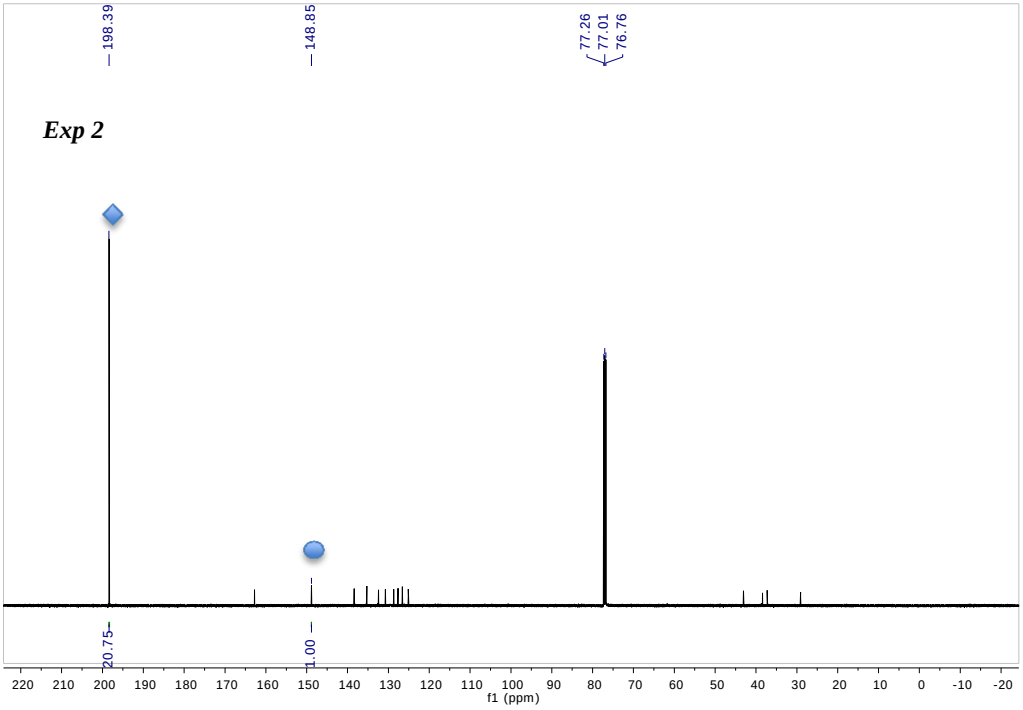
The reaction below adopted the standard procedure of C– C activation and **2a** (^{13}CO incorporated) was isolated in 82% yield. Using this entry as an example to demonstrate how we measure the ^{13}CO incorporation ratio.



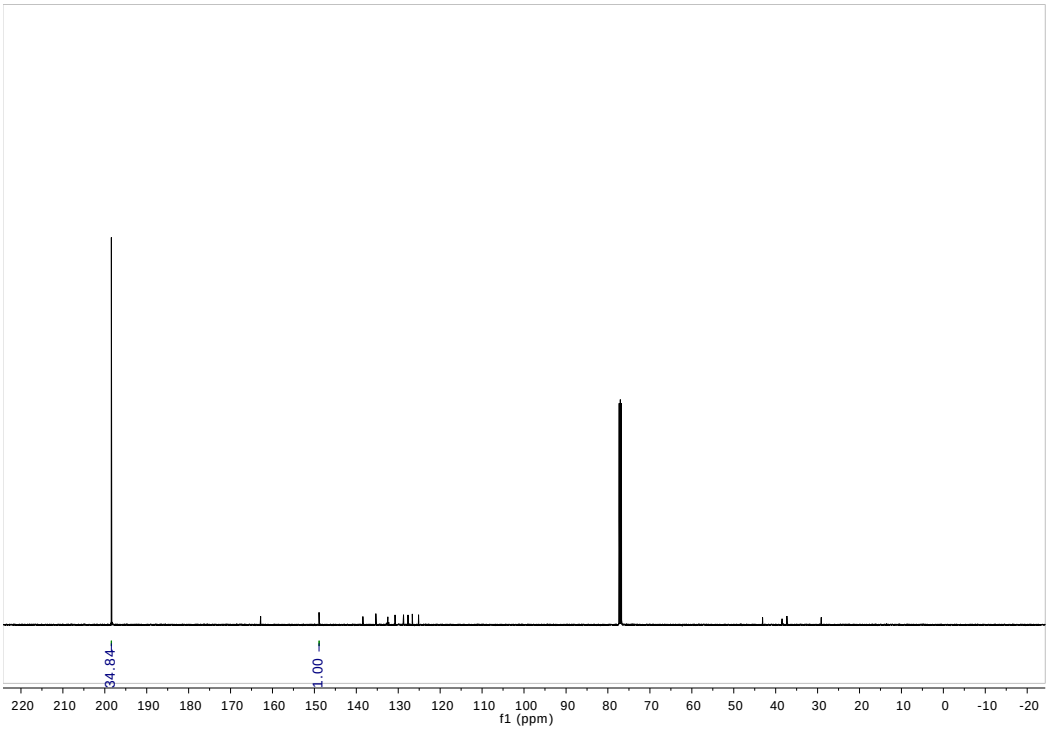
Method A: Quantitative ^{13}C-NMR experiment:[16]

The ^{13}C NMR spectra were acquired on a Bruker AVANCE III HD 500 MHz; 11.7 Tesla NMR spectrometer (126 MHz for ^{13}C, $CDCl_3$) at 295 K with inverse-gated decoupling. T_1 values of enriched carbon (marked with diamond shape in the spectra below) and the reference carbon (marked with oval shape in the spectra below) were determined to be 5.7 second and 8.7 second prior to the acquisitions, and delays of 50 s (50 s > 5 × T_1) were utilized between scans. The reaction was repeated twice and the spectra are shown below. 21% ^{13}C was found to be incorporated as an average of two experiments (Exp 1 and Exp 2).





at 52% conversion:



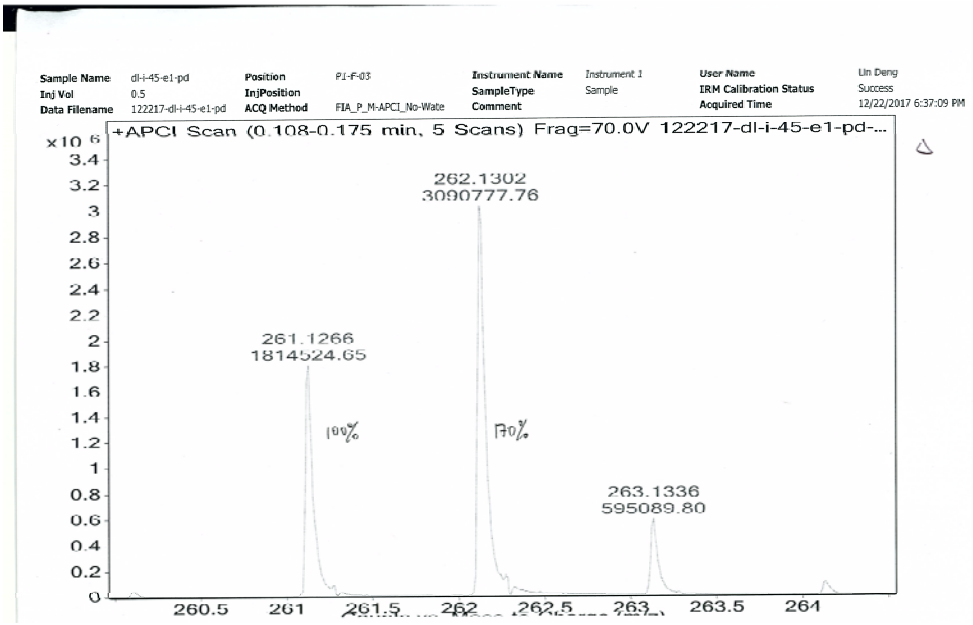
Method B: Using high resolution mass spectroscopy to determine the incorporation ratio of ^{13}C

For compound 2a without ^{13}CO incorporation, the native isotope peak can be calculated according to the natural abundance of ^{13}C. We obtained this ratio from chemdraw as $[M+H+1]^+$ (262.1307) equals 20.5% when setting the

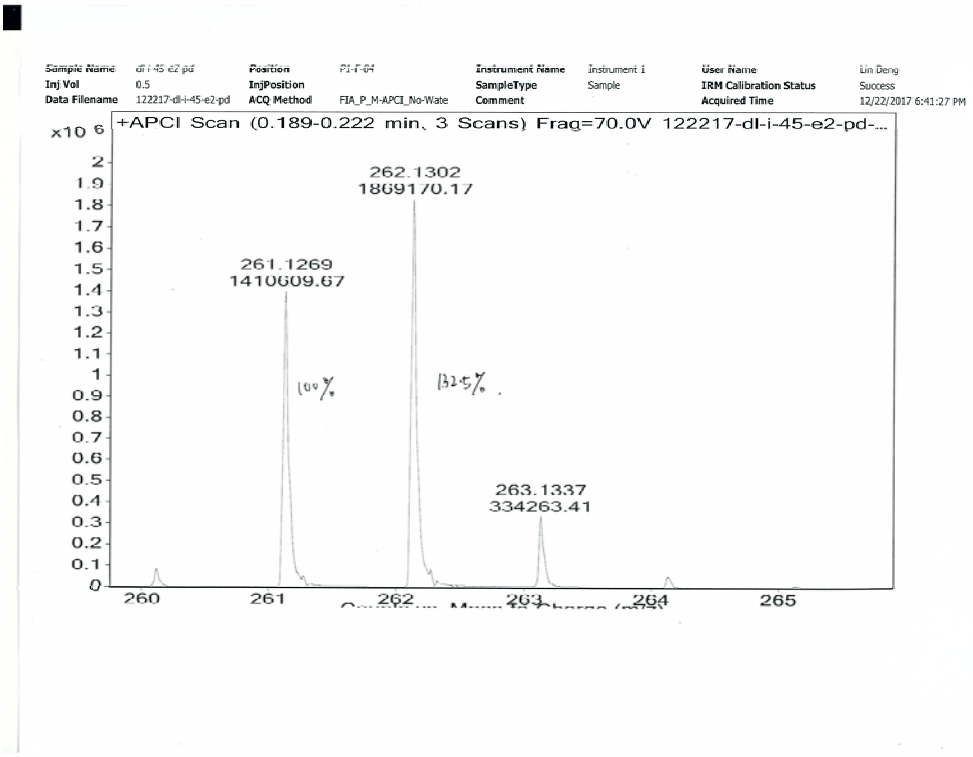
$[M+H]^+$ (261.1274) as 100%. From this ratio, we can derive a function between the experimental $[M+H+1]^+$ (y) and incorporation ratio (x). The function is $y = (20.5 + 0.795x)/(100 - x) \times 100$

Using Agilent TOF LCMS, we acquired the mass spectrum of column purified product 2a at different conversion and obtained the experimental $[M+H+1]^+$ (y), then the incorporation ratio can be calculated accordingly.

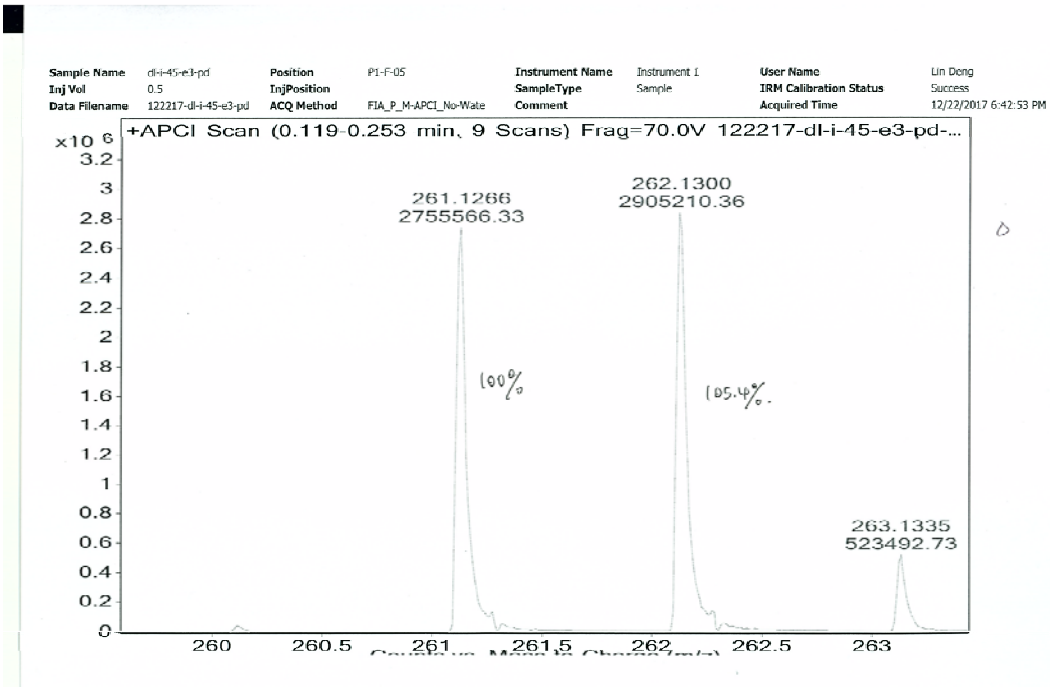
10% conversion:



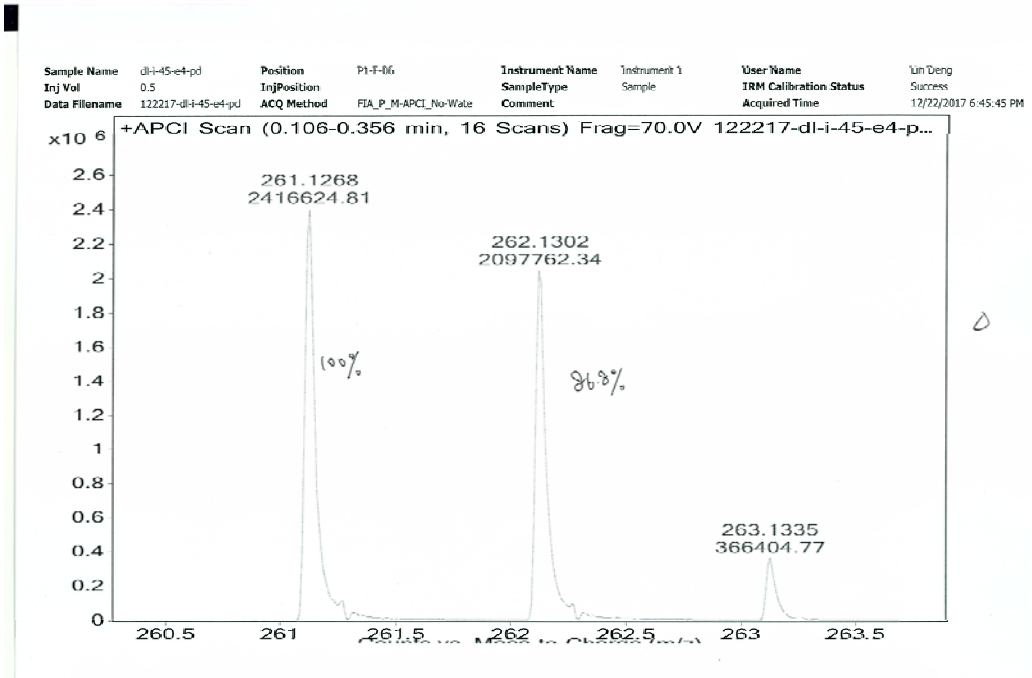
15% conversion:



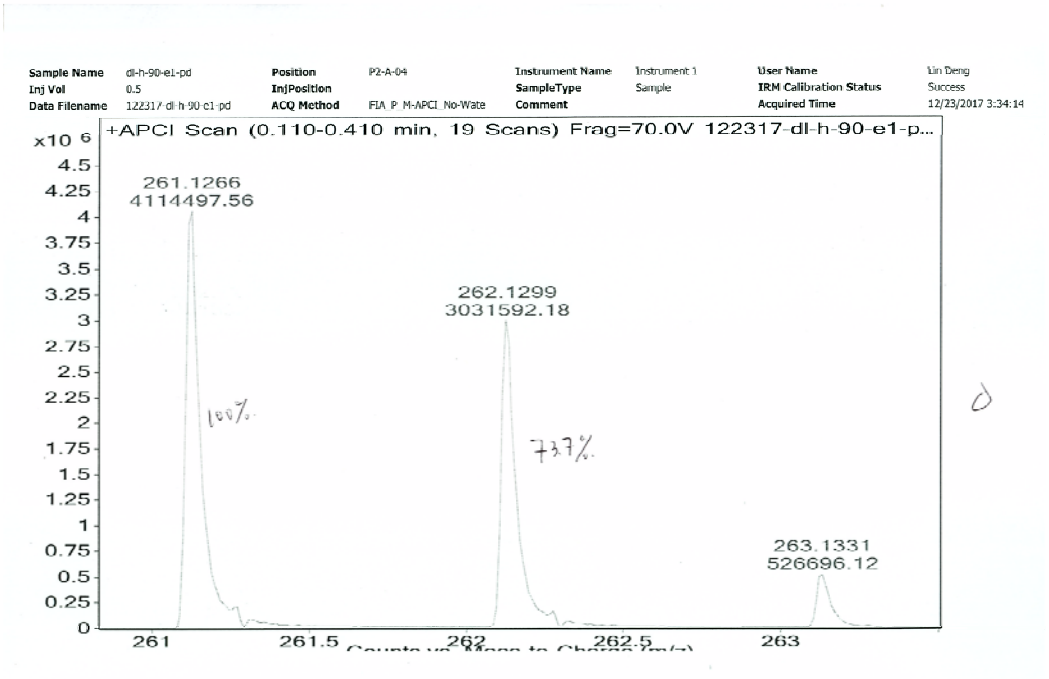
30% conversion:



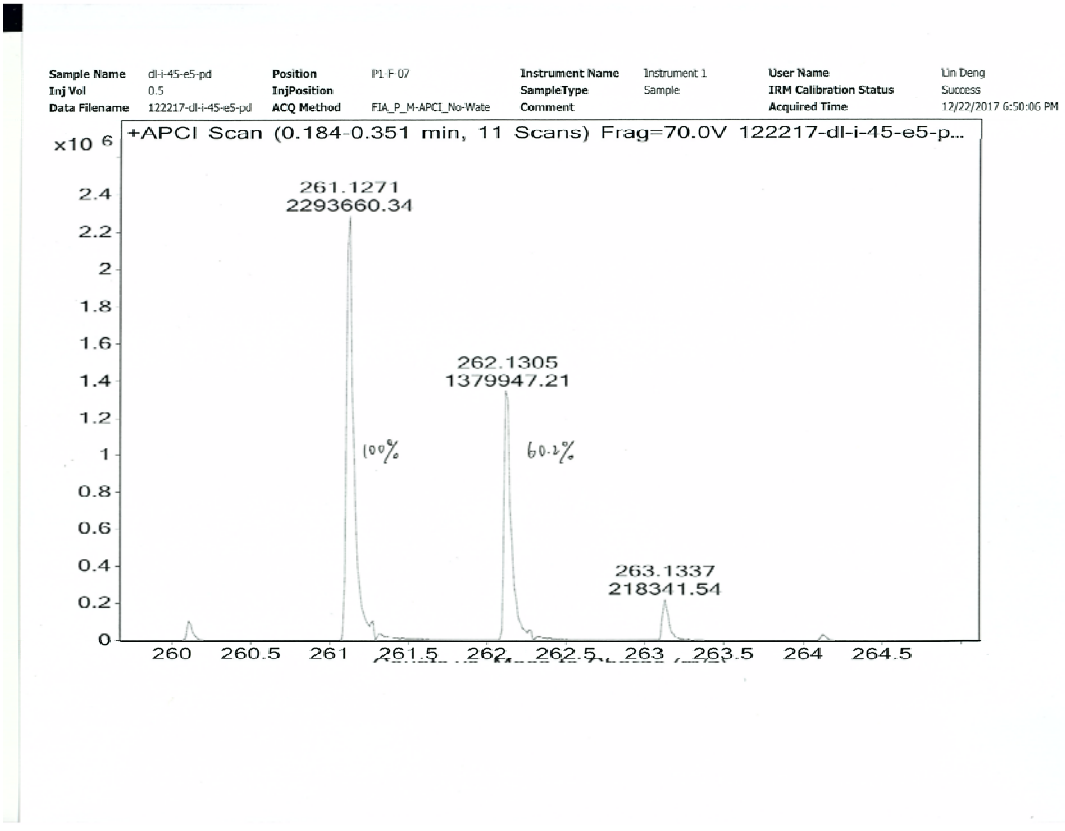
36% conversion:



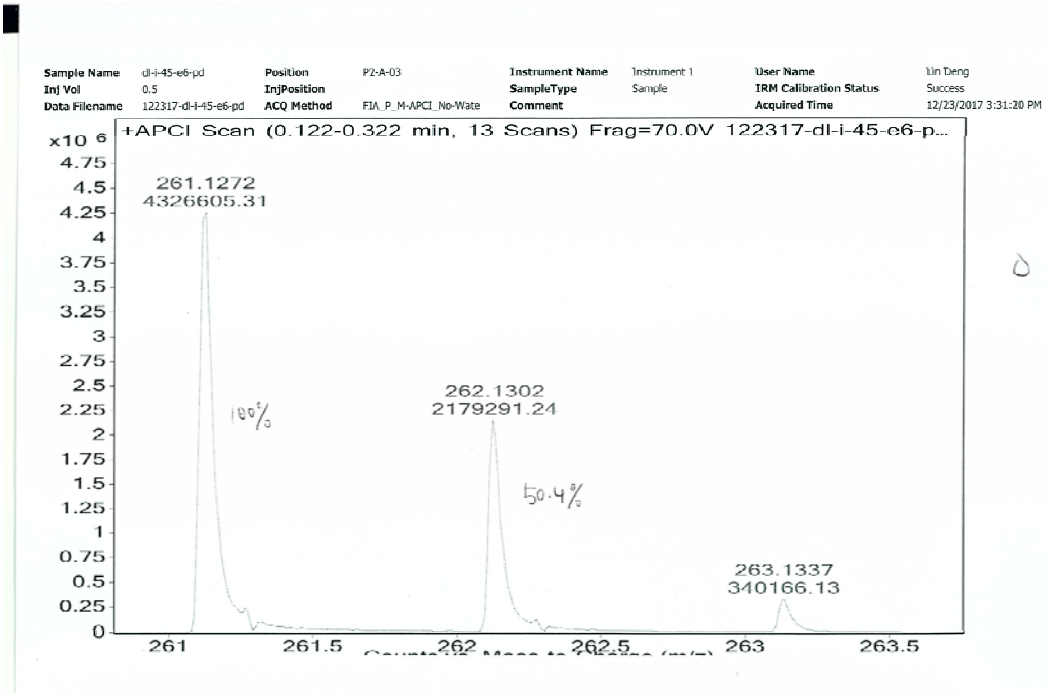
52% conversion:



67% conversion:



79% conversion:

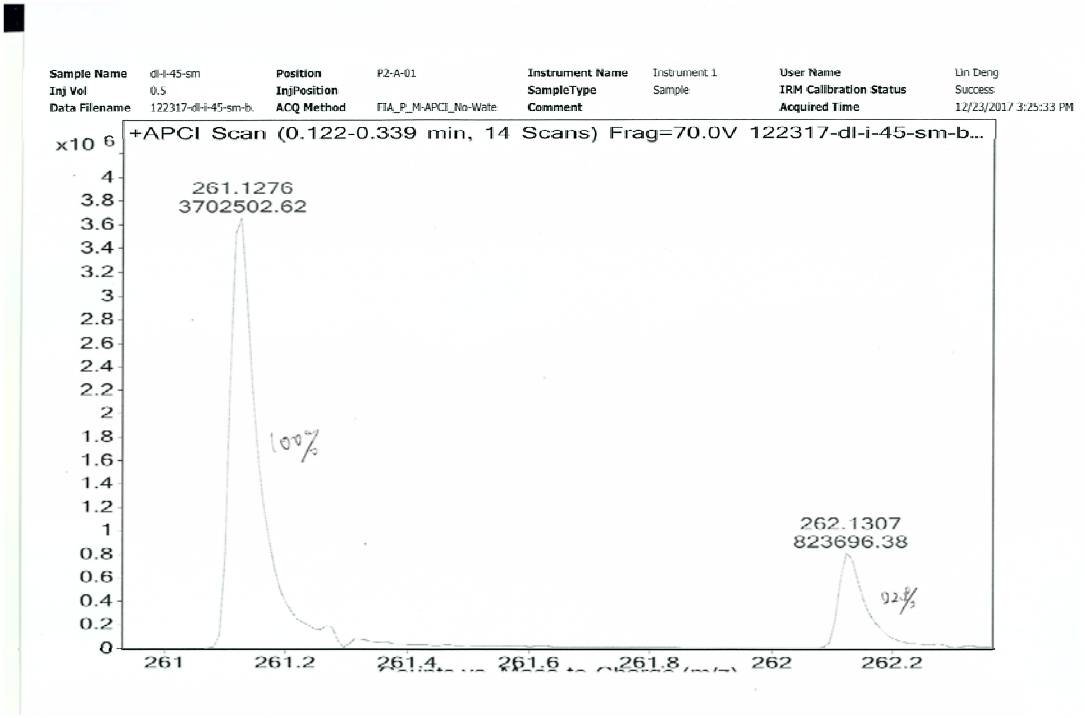


Shown below are the ^{13}C-incorporation ratio obtained from this study.

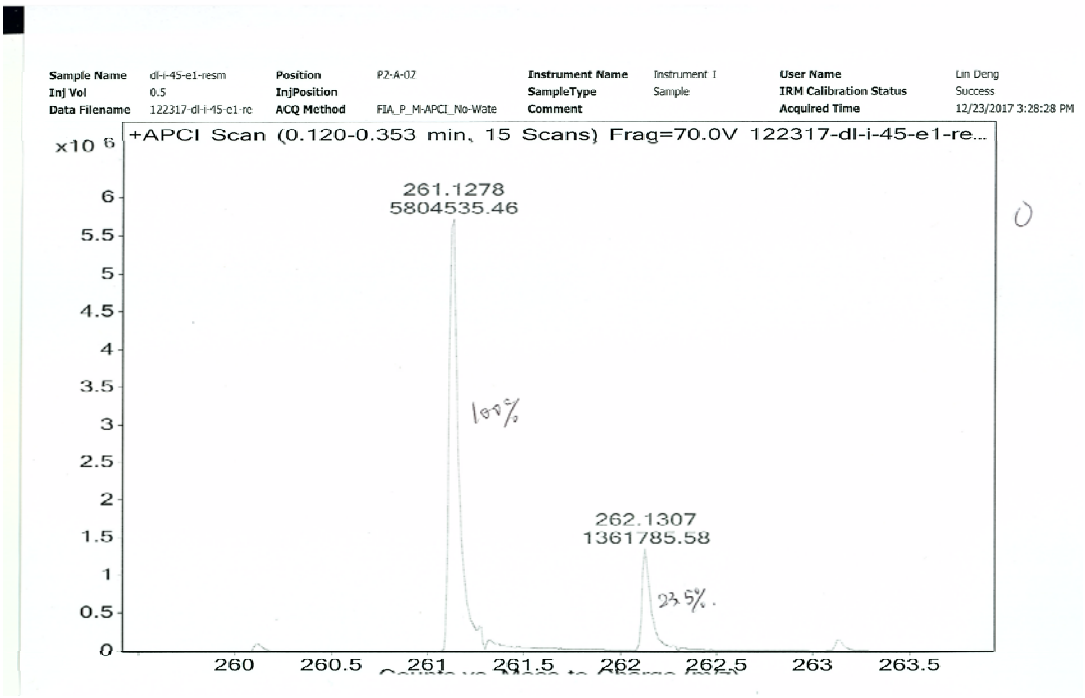
conversion	10%	15%	30%	36%	52%	67%	79%	100%
yield of **2a**	9%	13%	29%	32%	46%	52%	67%	82%
^{13}C incorporation	60%	53%	45%	39%	34%	28%	24%	21%

Starting material was also recycled at 10% and 52% conversion. Both of them did not show significant ^{13}C incorporation compared with the original starting material through comparing their isotope peaks in mass spectroscopy.

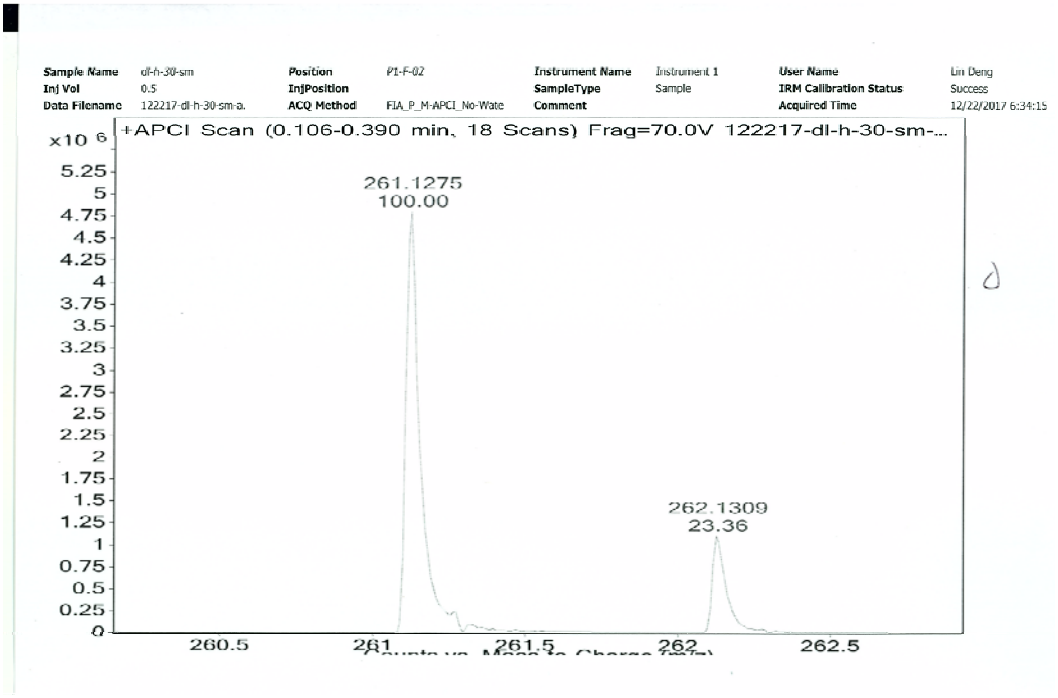
Original starting material:



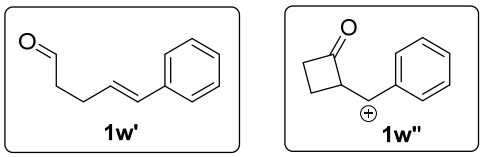
Recycled starting material at 10% conversion:



Recycled starting material at 52% conversion:

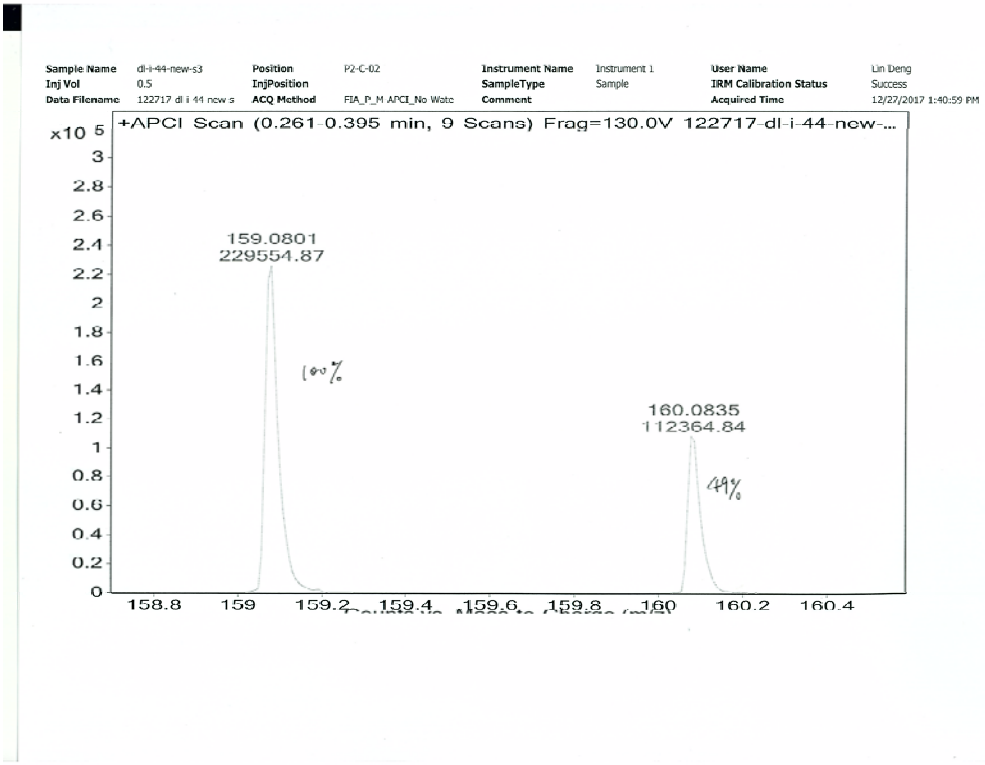


Measurement of ^{13}CO incorporation in **1w'**:



For compound **1w'** without ^{13}CO incorporation, the native isotope peak can be calculated according to the natural abundance of ^{13}C. Because of the weak aldehyde C-H bond under the mass spectroscopy condition, **1w** will cyclize to form carbocation **1w''** as shown. In mass spectrum, the m/z we observed is **1w''**(m/z=159.0804). We obtained the ratio for **1w''** from chemdraw as $[M+1]^+$ equals 11.9% when setting the $[M]^+$ as 100%. From this ratio, we can derive a function between the experimental $[M+1]^+$ (y) and incorporation ratio (x). The function is $y = (11.9 + 0.88x)/(100 - x) \times 100$

Using Agilent TOF LCMS, we acquired the mass spectrum of column purified product **1w'** and obtained the experimental $[M+1]^+$ (y) equals 49%, then the incorporation ratio can be calculated as 27%.



6. References

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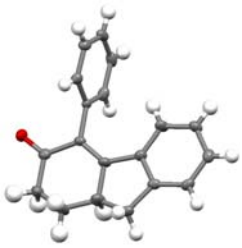
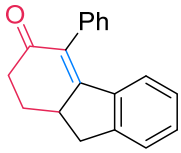
7. X-ray Data

a) X-ray data for **2a**





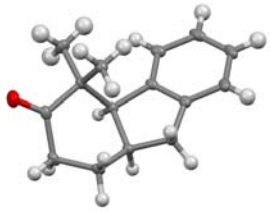
2a

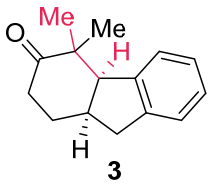
Table 6-1. Crystal data and structure refinement for **2a**

Identification code	Complex
Empirical formula	$C_{19}H_{16}O$
Formula weight	260.32
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.6293(4)
b/Å	7.8160(3)
c/Å	16.5040(6)
α/°	90
β/°	91.724(2)
γ/°	90
Volume/Å^3	1370.51(9)
Z	4
ρ_{calc}g/cm^3	1.262
μ/mm^{-1}	0.076
F(000)	552.0
Crystal size/mm^3	0.03 × 0.02 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.498 to 48.88
Index ranges	-12 ≤ h ≤ 12, -9 ≤ k ≤ 9, -19 ≤ l ≤ 19
Reflections collected	13330
Independent reflections	2261 [R_{int} = 0.0495, R_{sigma} = 0.0306]
Data/restraints/parameters	2261/57/209

Goodness-of-fit on F^2	1.161
Final R indexes [I>=2σ (I)]	R_1 = 0.0624, wR_2 = 0.1612
Final R indexes [all data]	R_1 = 0.0808, wR_2 = 0.1708
Largest diff. peak/hole / e $Å^{-3}$	0.36/-0.32

b) X-ray data for **3**





3

Table 6-2 Crystal data and structure refinement for **3**.

Identification code	DL-h-116
Empirical formula	$C_{15}H_{18}O$
Formula weight	214.29
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.9732(5)
b/Å	7.5678(5)
c/Å	19.3603(13)
α/°	90
β/°	92.343(2)
γ/°	90
Volume/$Å^3$	1167.22(13)
Z	4
$\rho_{calc}g/cm^3$	1.219
μ/mm^{-1}	0.074
F(000)	464.0
Crystal size/mm^3	0.1 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.114 to 60.214
Index ranges	$-11 \le h \le 11$, $-10 \le k \le 10$, $-27 \le l \le 27$
Reflections collected	24376

Independent reflections	3431 [R_{int} = 0.0447, R_{sigma} = 0.0342]
Data/restraints/parameters	3431/0/147
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0474, wR_2 = 0.1055
Final R indexes [all data]	R_1 = 0.0729, wR_2 = 0.1166
Largest diff. peak/hole / e $Å^{-3}$	0.47/-0.18

c) X-ray data for **6**

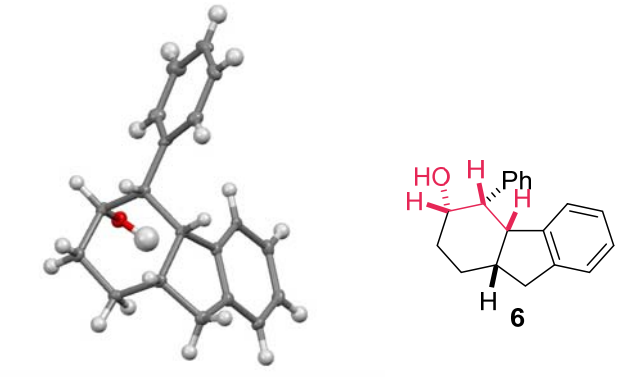
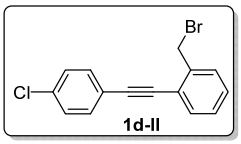


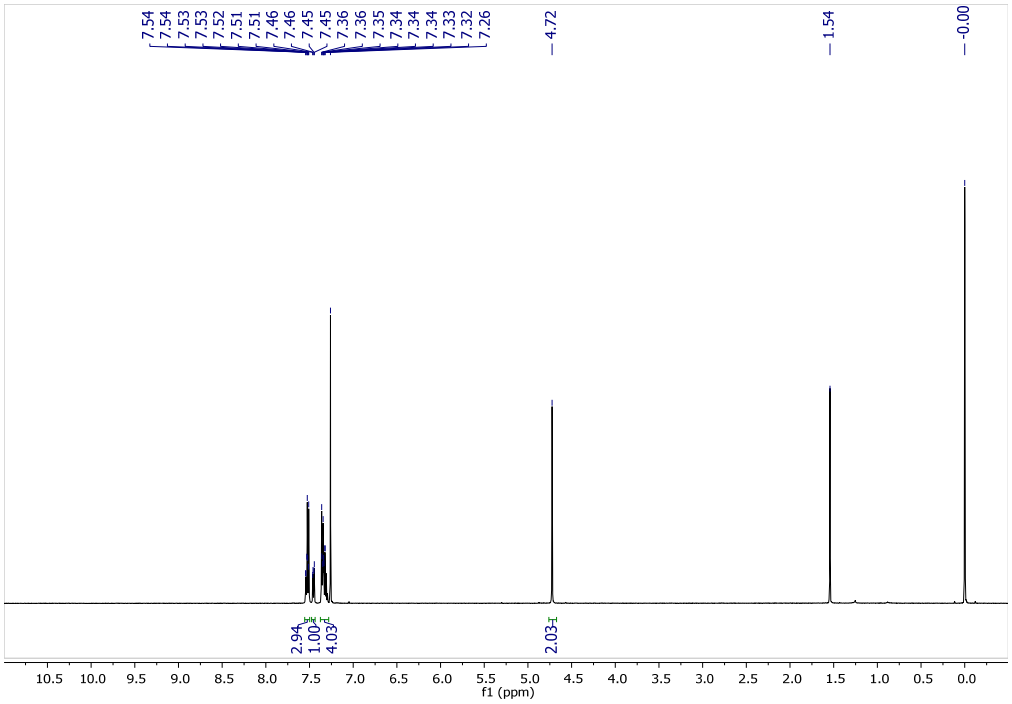
Table 6-3. Crystal data and structure refinement for **6**.

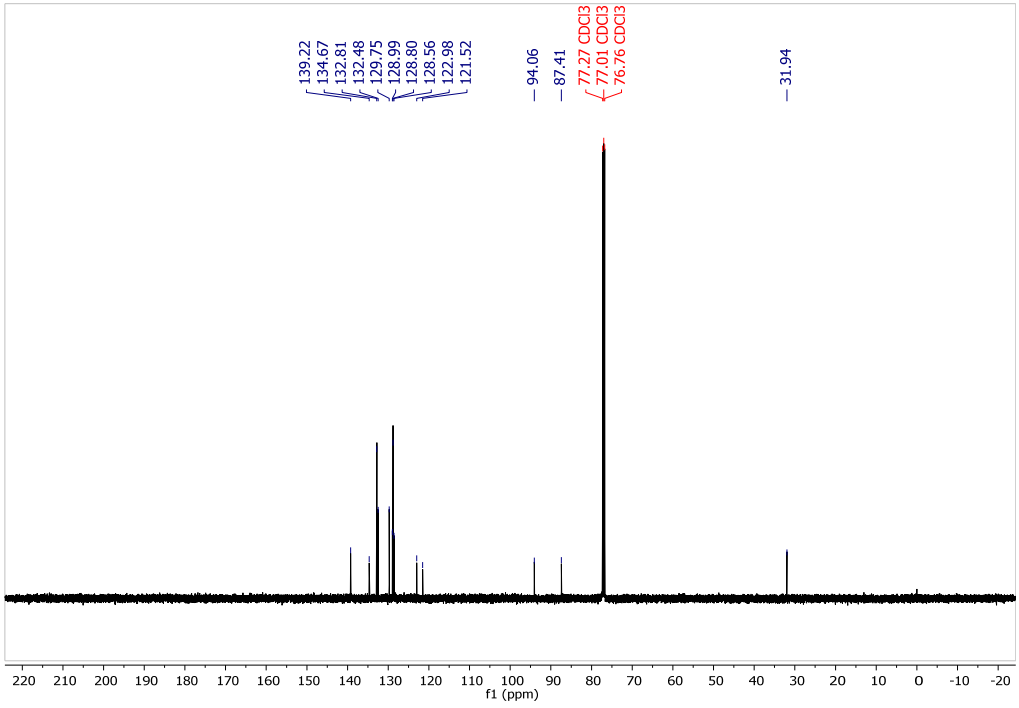
Identification code	DL-h-59
Empirical formula	$C_{19}H_{20}O$
Formula weight	264.35
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.8407(4)
b/Å	22.3977(15)
c/Å	10.7014(7)
α/°	90
β/°	97.123(2)
γ/°	90
Volume/$Å^3$	1389.13(16)
Z	4
ρ_{calc}g/cm^3	1.264
μ/mm^{-1}	0.076
F(000)	568.0
Crystal size/mm^3	0.02 × 0.02 × 0.01

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.246 to 54.354
Index ranges	$-7 \leq h \leq 7$, $-28 \leq k \leq 28$, $-13 \leq l \leq 13$
Reflections collected	18648
Independent reflections	6167 [R_{int} = 0.0417, R_{sigma} = 0.0592]
Data/restraints/parameters	6167/1/369
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0468, wR_2 = 0.0988
Final R indexes [all data]	R_1 = 0.0749, wR_2 = 0.1096
Largest diff. peak/hole / e $Å^{-3}$	0.28/-0.21
Flack parameter	0.2(7)

8. Spectra


Br
Cl
1d-II


7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.46
7.46
7.45
7.45
7.36
7.36
7.35
7.34
7.34
7.34
7.33
7.32
7.26
4.72
1.54
0.00
2.94
1.00
4.03
2.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.67
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132.48
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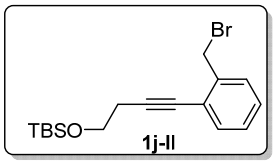
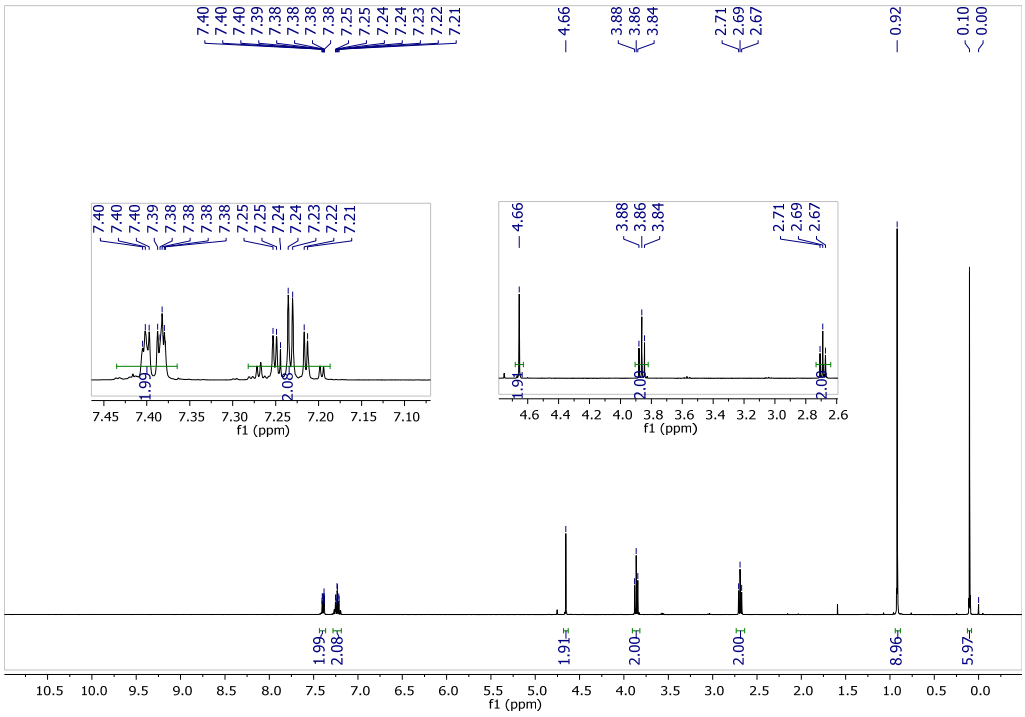
128.99
128.80
128.56
122.98
121.52
94.06
87.41
77.27 CDCl3
77.01 CDCl3
76.76 CDCl3
31.94
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


Br
TBSO
1j-II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7.40
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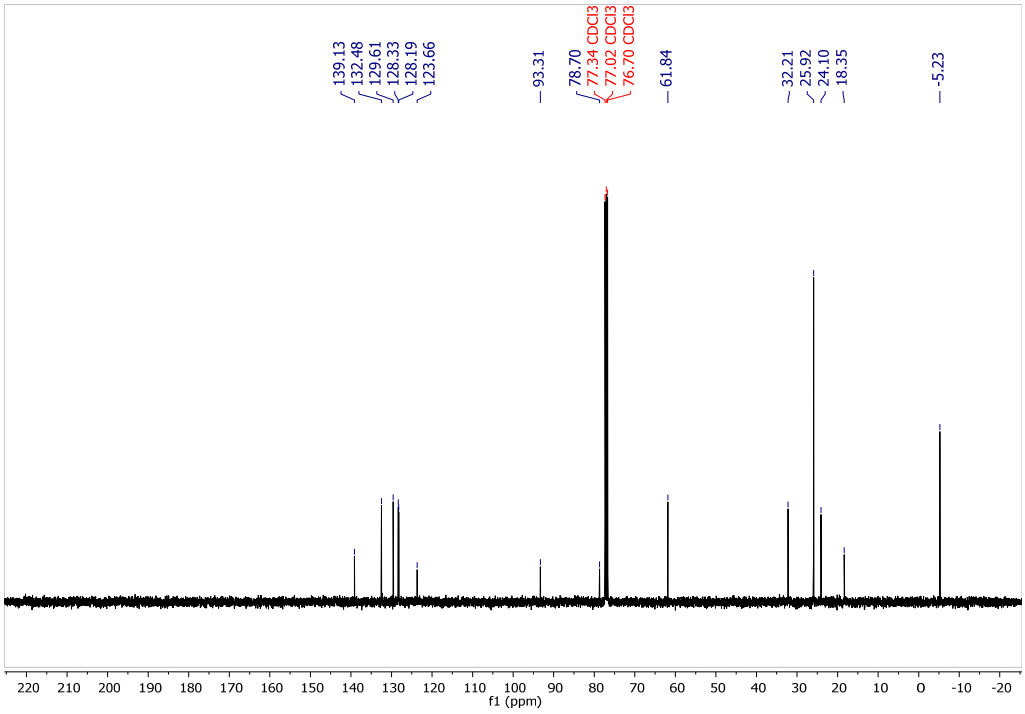
7.38
7.38
7.25
7.25
7.24
7.24
7.23
7.22
7.21
4.66
3.88
3.86
3.84
2.71
2.69
2.67
0.92
0.10
0.00
1.99
2.08
1.91
2.00
2.00
8.96
5.97
f1 (ppm)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132.48
129.61
128.33
128.19
123.66
93.31
78.70
77.34 CDCl3
77.02 CDCl3
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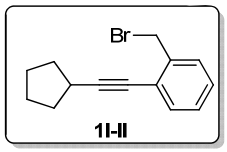
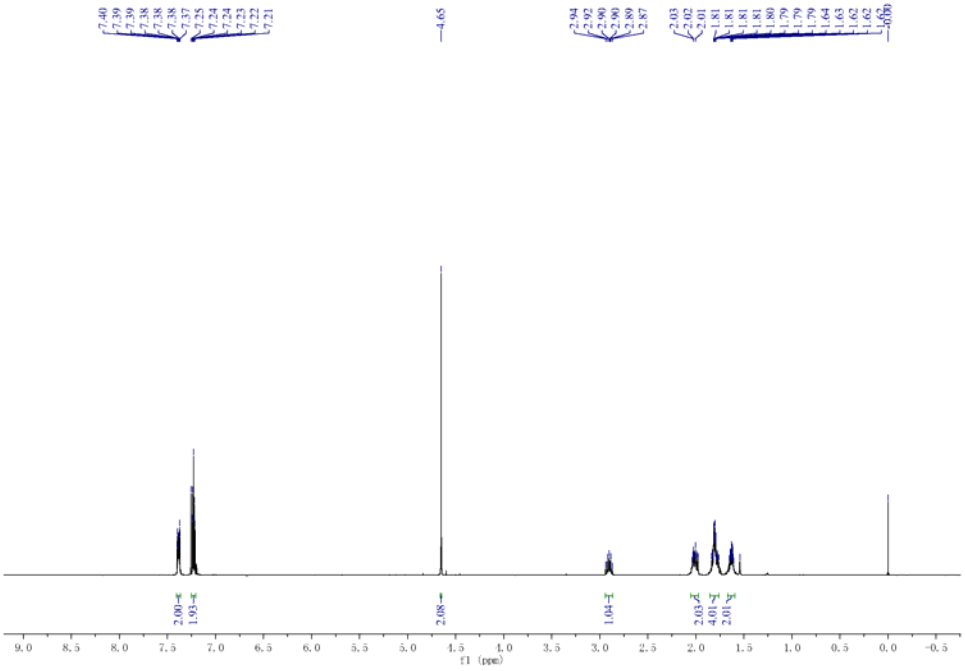
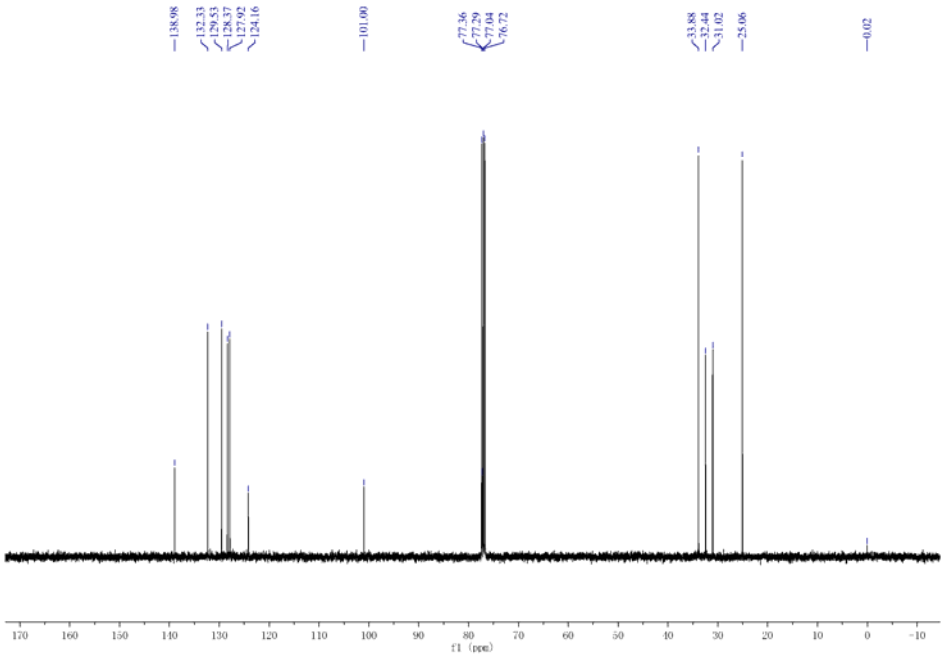
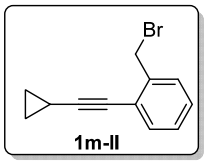
25.92
24.10
18.35
-5.23
f1 (ppm)


Br
1l-II



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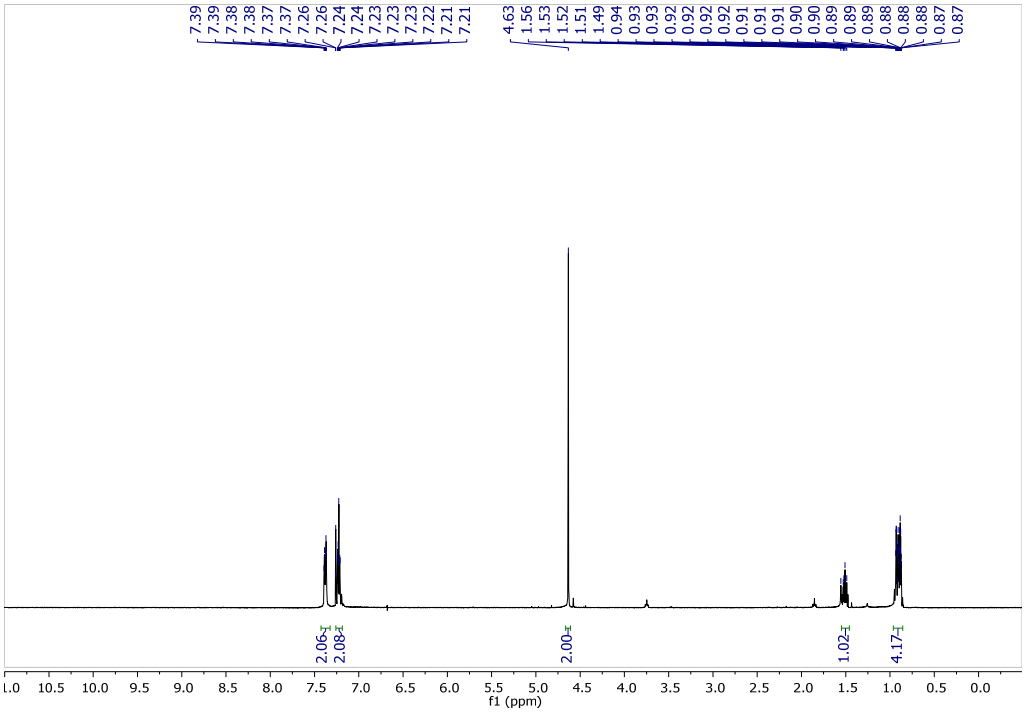
1m-II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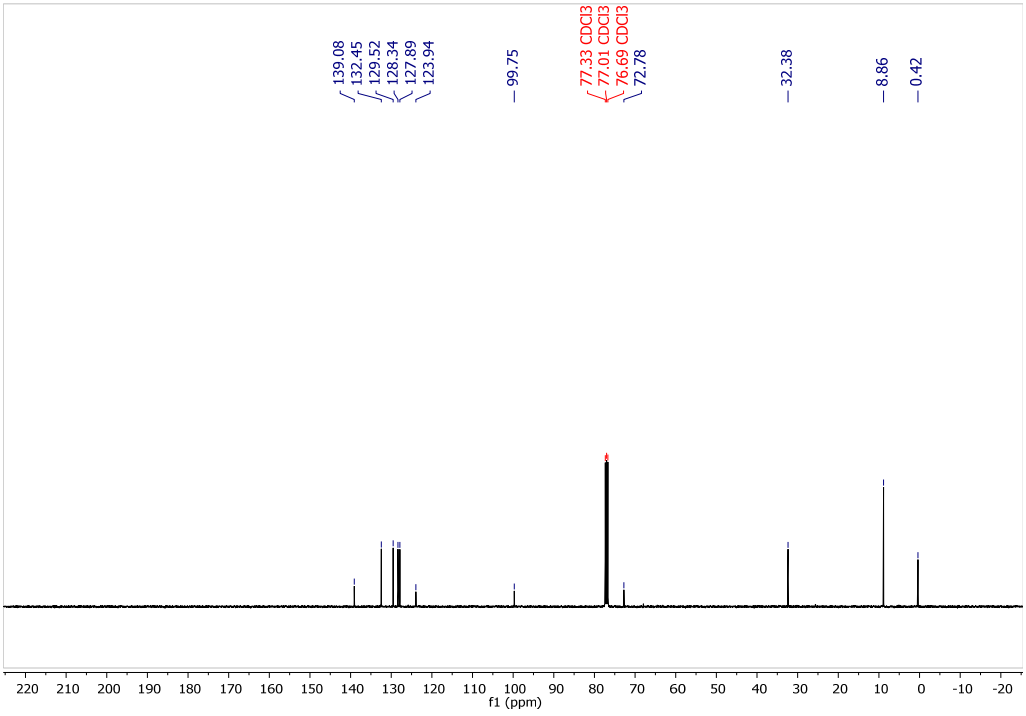
7.37
7.26
7.26
7.24
7.24
7.23
7.23
7.23
7.22
7.21
7.21
4.63
1.56
1.53
1.52
1.51
1.49
0.94
0.93
0.93
0.92
0.92
0.92
0.92
0.91
0.91
0.91
0.90
0.90
0.89
0.89
0.89
0.88
0.88
0.88
0.87
0.87
2.06
2.08
2.00
1.02
4.17
f1 (ppm)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129.52
128.34
127.89
123.94
99.75
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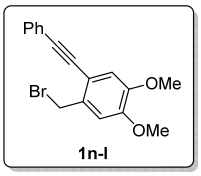
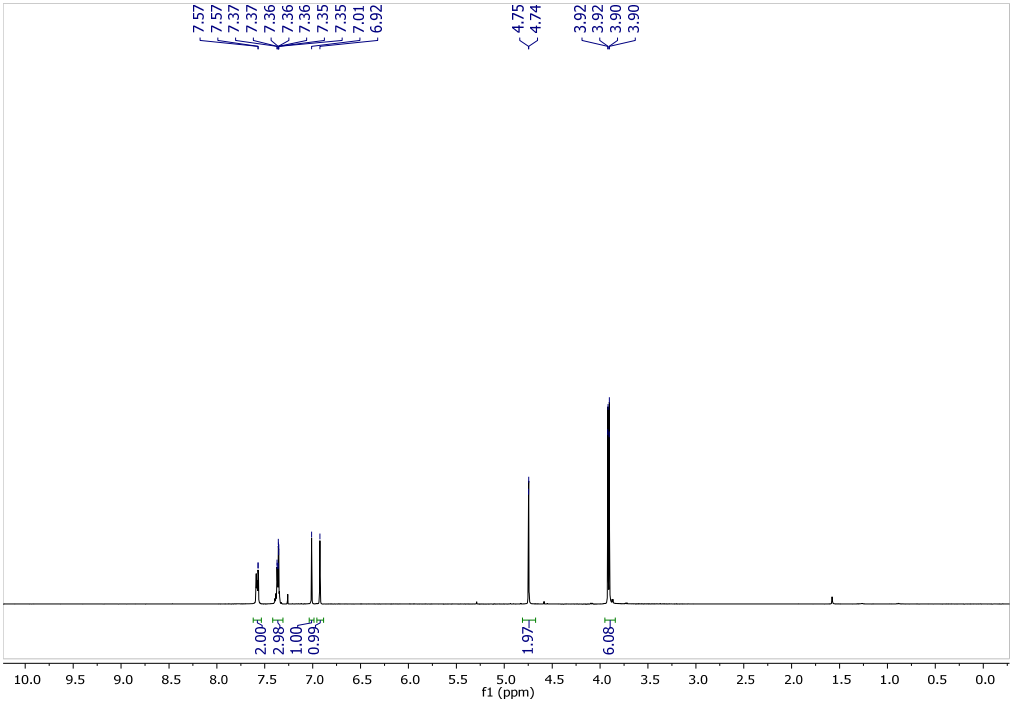
77.01 CDCl3
76.69 CDCl3
72.78
32.38
8.86
0.42
f1 (ppm)


Ph
Br
OMe
OMe
1n-l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7.57
7.37
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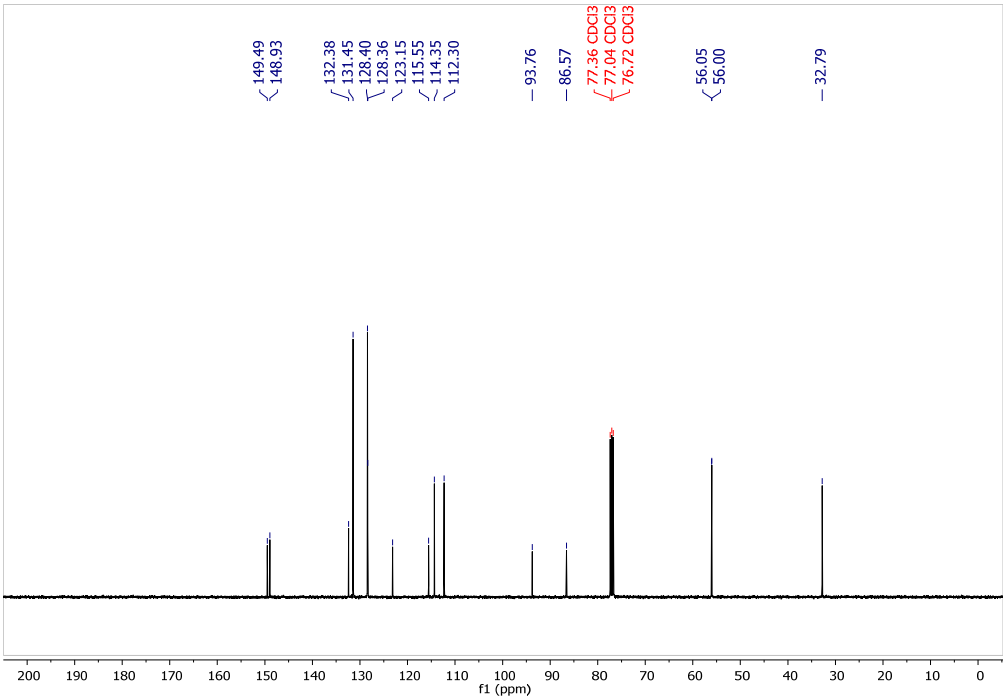
7.36
7.36
7.35
7.35
7.01
6.92
4.75
4.74
3.92
3.92
3.90
3.90
2.00
2.98
1.00
0.99
1.97
6.08
f1 (ppm)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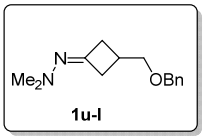
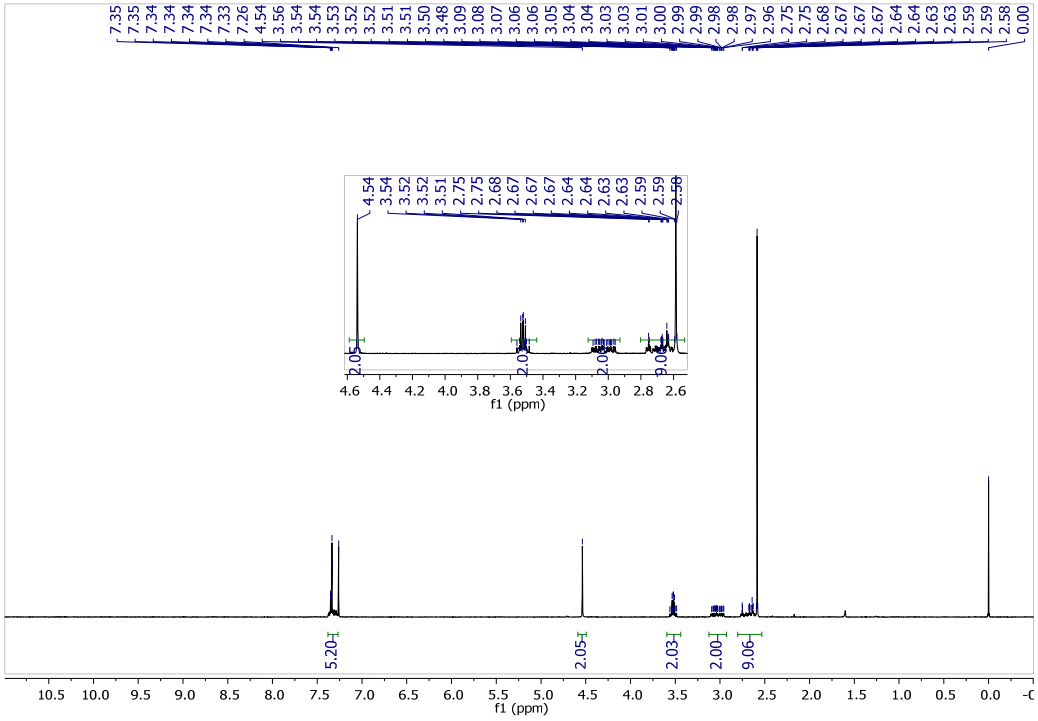
148.93
132.38
131.45
128.40
128.36
123.15
115.55
114.35
112.30
93.76
86.57
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
56.05
56.00
32.79
f1 (ppm)


N
Me2N
OBn

1u-l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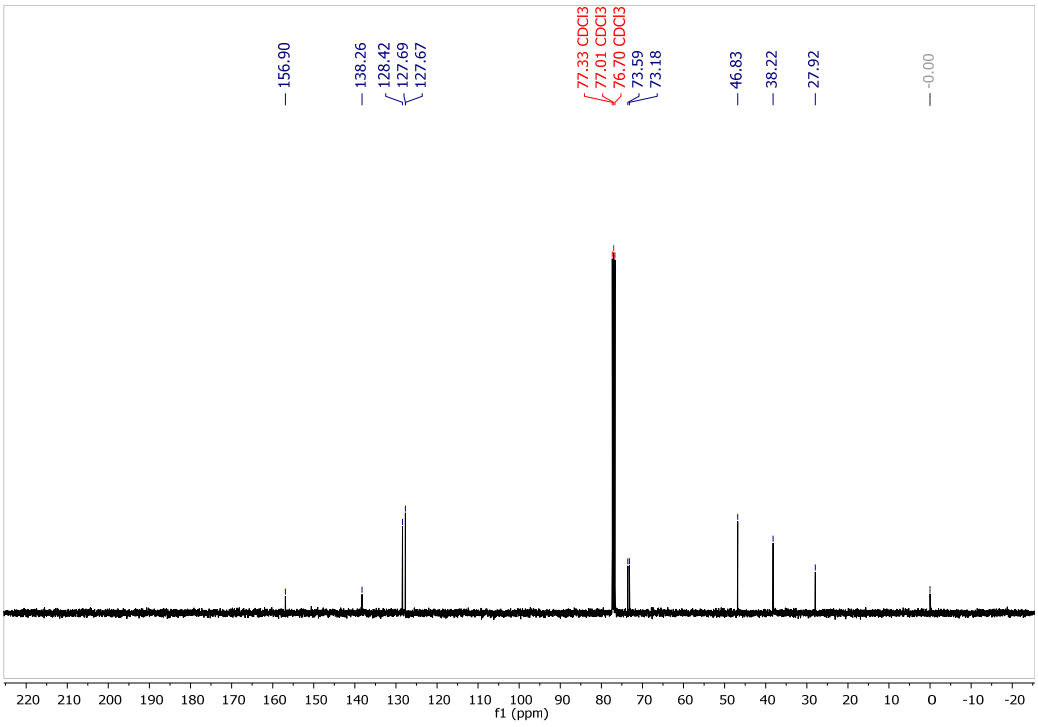
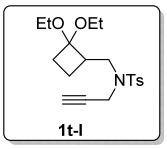
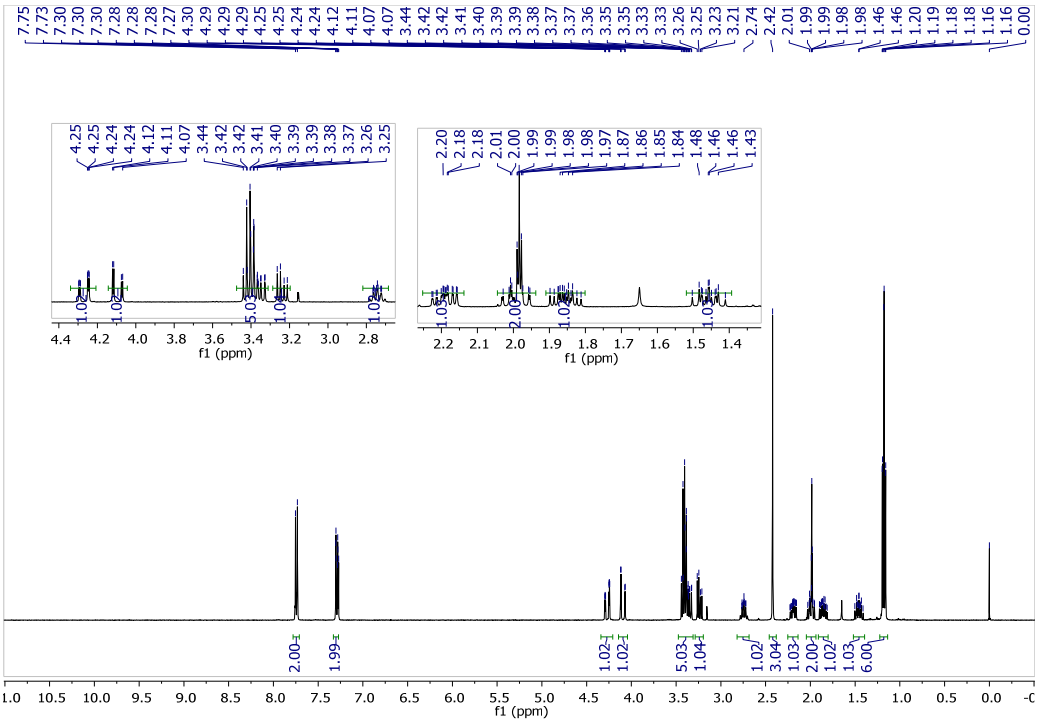
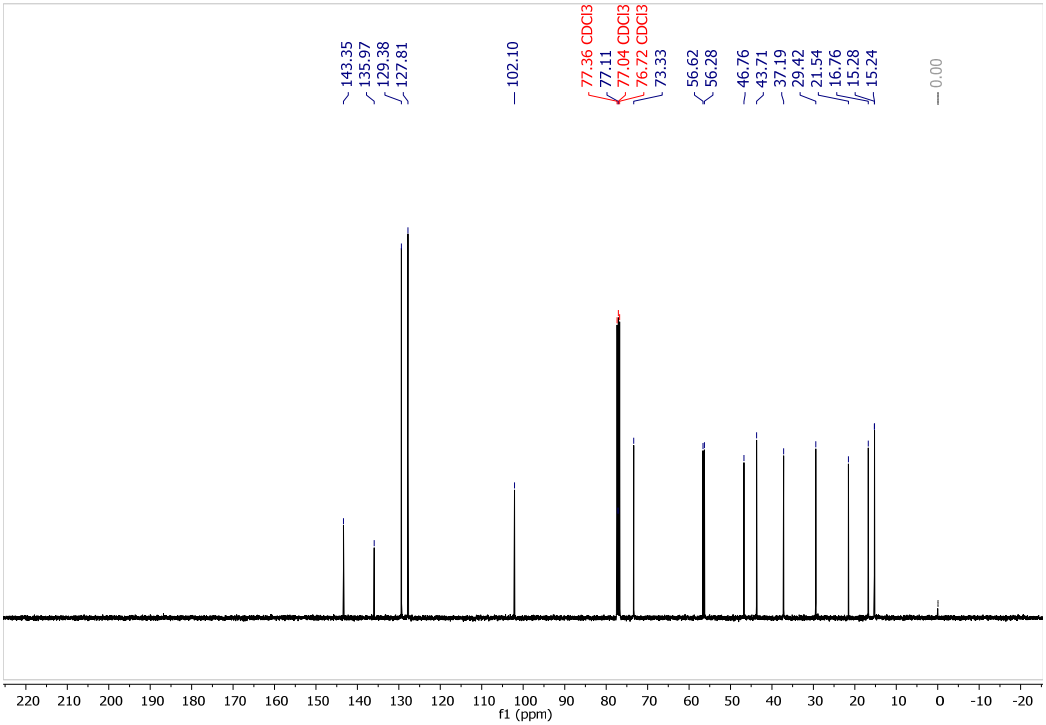
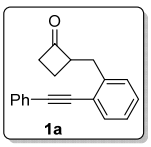
4.54 3.54 3.52 3.52 3.51 2.75 2.75 2.68 2.67 2.67 2.67 2.64 2.64 2.63 2.63 2.59 2.59 2.58
2.05 2.01 2.06 9.06
4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6
f1 (ppm)
5.20 2.05 2.03 2.00 9.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

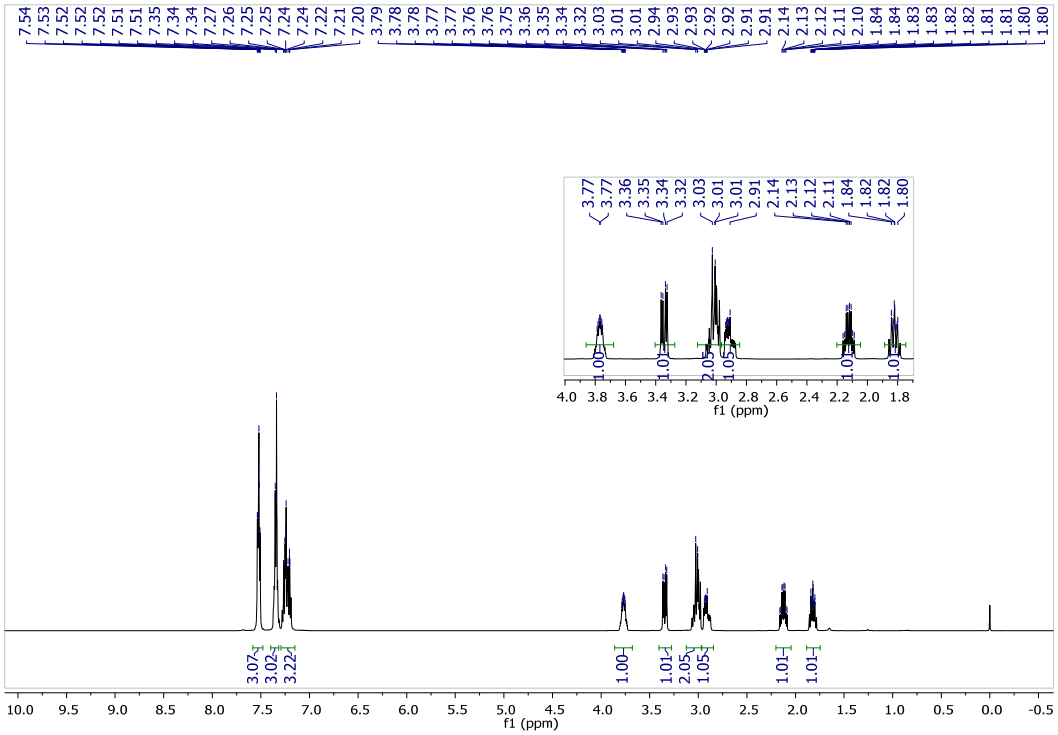

156.90
138.26
128.42
127.69
127.67
77.33 CDCl3
77.01 CDCl3
76.70 CDCl3
73.59
73.18
46.83
38.22
27.92
-0.00
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

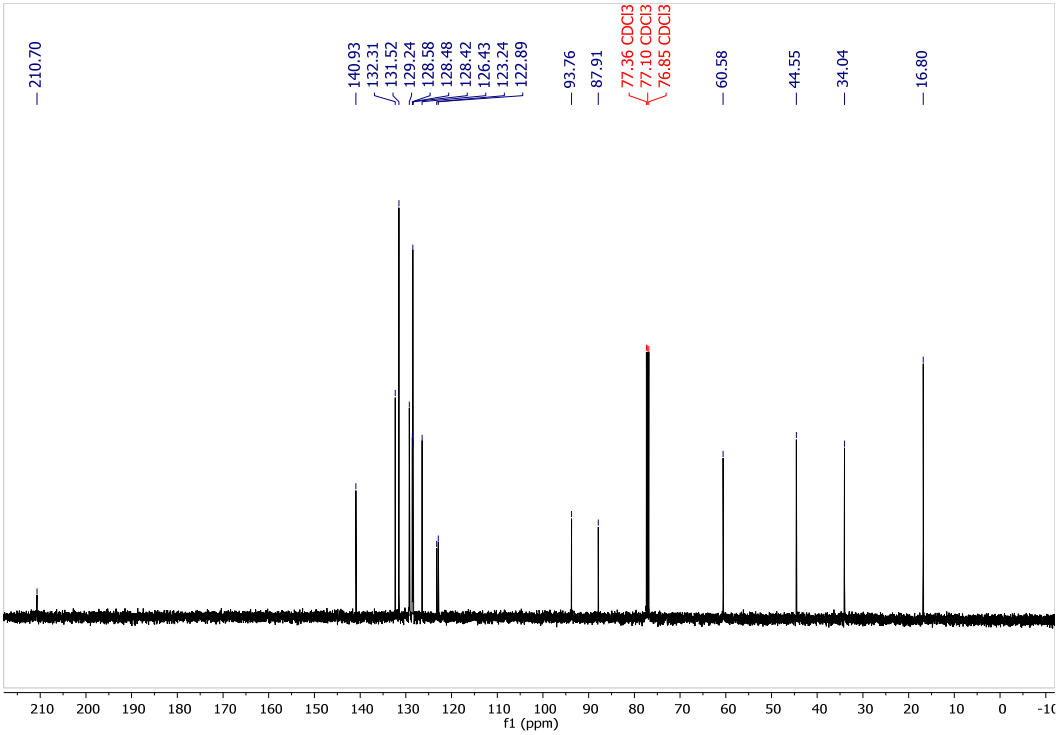

EtO
OEt
NTs
1t-l

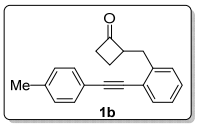





O
Ph
1a


7.54 7.53 7.52 7.52 7.52 7.51 7.51 7.35 7.34 7.34 7.27 7.26 7.25 7.25 7.24 7.24 7.22 7.21 7.20
3.79 3.78 3.78 3.77 3.77 3.76 3.76 3.75 3.36 3.35 3.34 3.32 3.03 3.01 3.01 2.94 2.93 2.93 2.92 2.92 2.91 2.91
2.14 2.13 2.12 2.11 2.10 1.84 1.84 1.83 1.83 1.82 1.82 1.81 1.81 1.80 1.80
3.77 3.77 3.36 3.35 3.34 3.32 3.03 3.01 3.01 2.91 2.14 2.13 2.12 2.11 1.84 1.82 1.82 1.80
1.00 1.01 2.05 1.05 1.01 1.01
4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)
3.07 3.02 3.22 1.00 1.01 2.05 1.05 1.01 1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


210.70
140.93 132.31 131.52 129.24 128.58 128.48 128.42 126.43 123.24 122.89
93.76 87.91
77.36 CDCl3 77.10 CDCl3 76.85 CDCl3
60.58 44.55 34.04 16.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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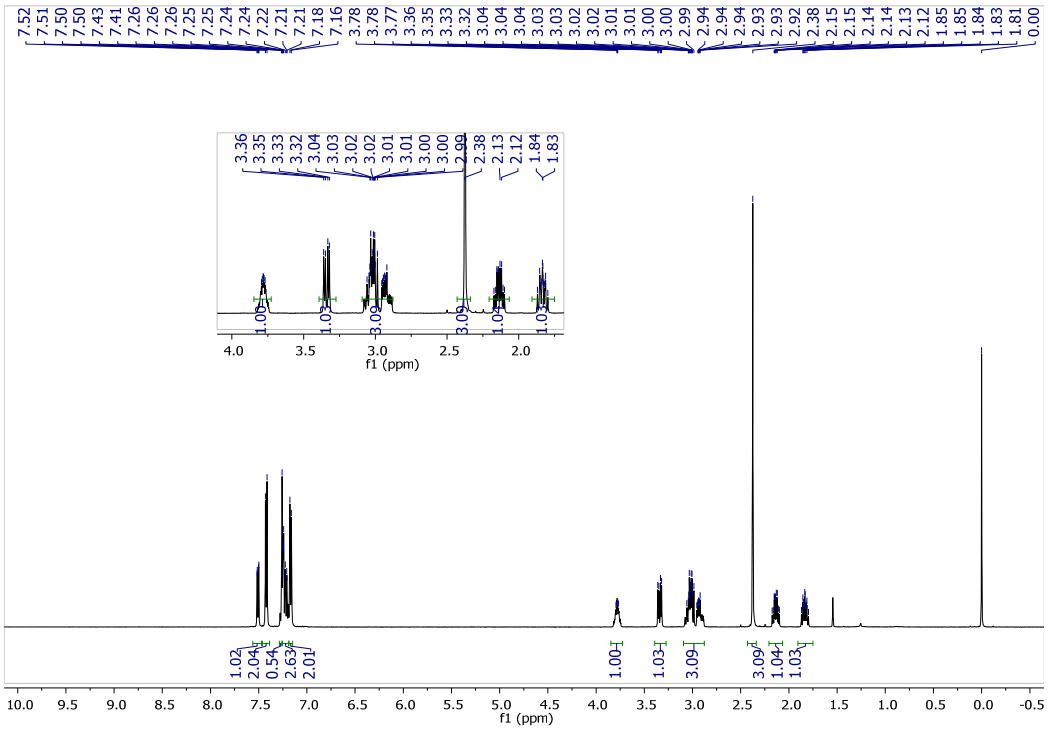
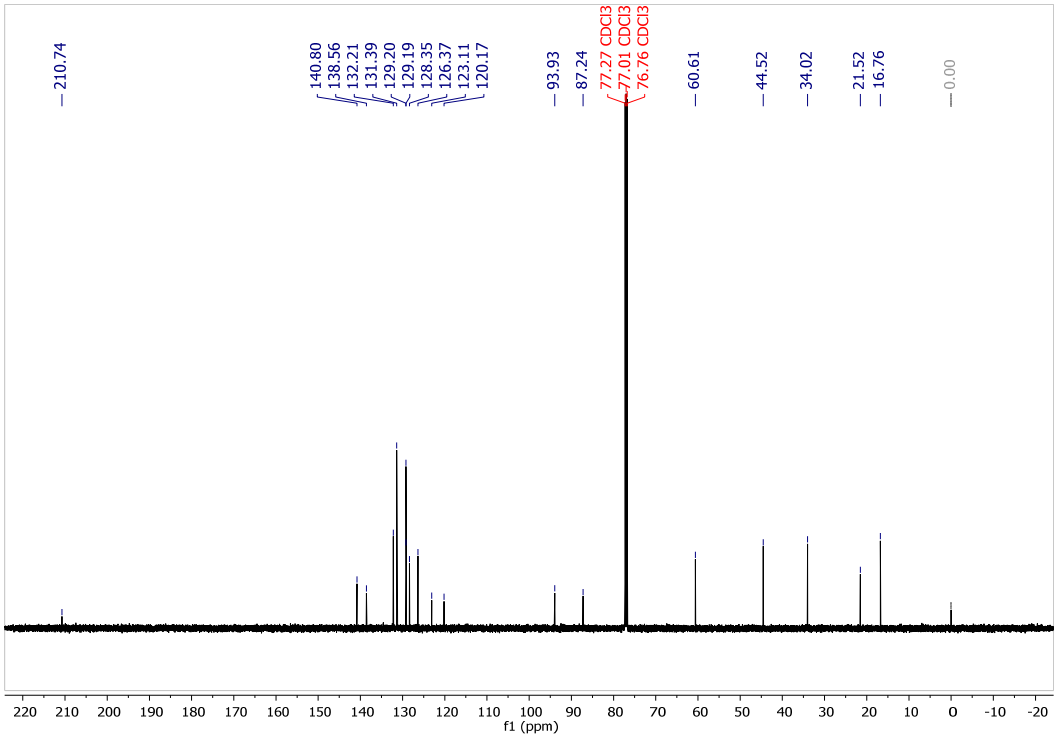
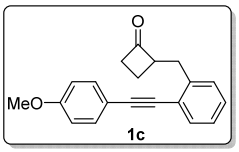

7.52 7.51 7.50 7.50 7.43 7.41 7.26 7.26 7.25 7.25 7.24 7.24 7.22 7.21 7.21 7.18 7.16 3.78 3.78 3.77 3.36 3.35 3.33 3.32 3.04 3.04 3.03 3.03 3.02 3.02 3.01 3.01 3.00 3.00 2.99 2.94 2.94 2.94 2.93 2.93 2.92 2.38 2.15 2.15 2.14 2.14 2.13 2.12 1.85 1.85 1.84 1.83 1.81 0.00
3.36 3.35 3.33 3.32 3.04 3.03 3.02 3.02 3.01 3.01 3.00 3.00 2.99 2.38 2.13 2.12 1.84 1.83
1.00 1.02 3.09 3.09 1.03 1.02
4.0 3.5 3.0 2.5 2.0
f1 (ppm)
1.02 2.04 0.54 2.63 2.01 1.00 1.03 3.09 3.09 1.04 1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


210.74
140.80 138.56 132.21 131.39 129.20 129.19 128.35 126.37 123.11 120.17
93.93 87.24 77.27 CDCl3 77.01 CDCl3 76.76 CDCl3 60.61 44.52 34.02 21.52 16.76 0.00
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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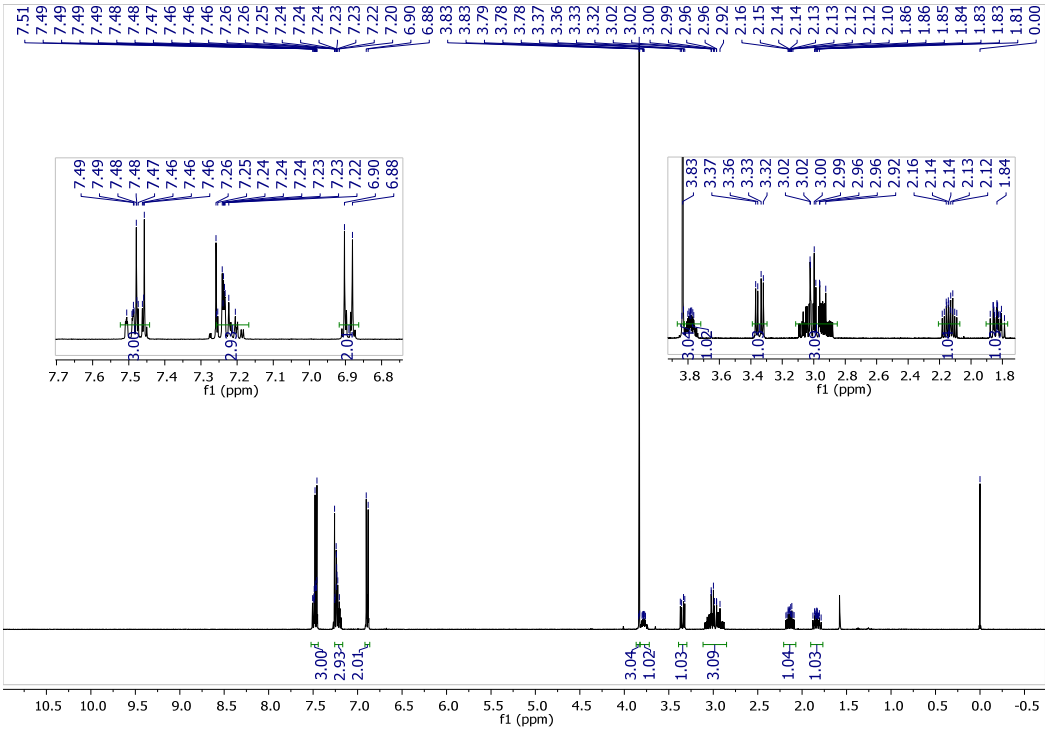
MeO

1c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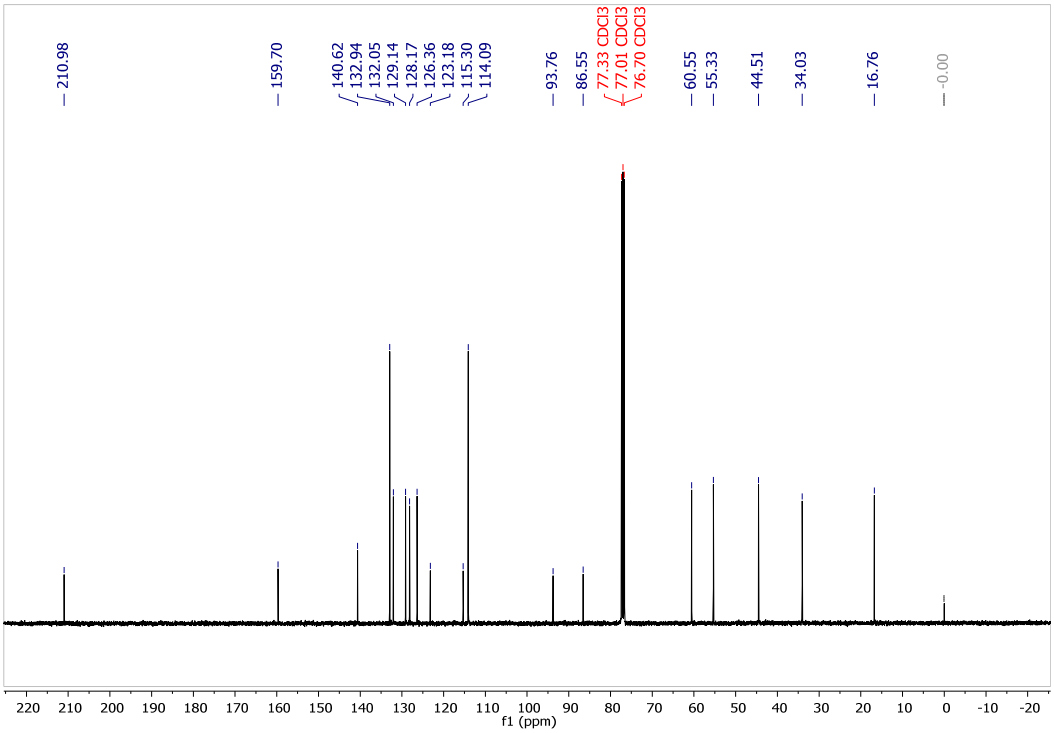
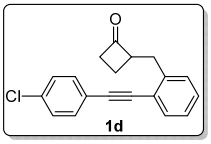
3.83 3.83 3.79 3.78 3.78 3.37 3.36 3.33 3.32 3.02 3.02 3.00 2.99 2.96 2.96 2.92 2.16 2.15 2.14 2.14 2.13 2.12 2.12 2.10 1.86 1.86 1.85 1.84 1.83 1.81 0.00
3.00 2.93 2.01 3.04 1.02 1.03 3.09 1.04 1.03
f1 (ppm)


210.98 159.70 140.62 132.94 132.05 129.14 128.17 126.36 123.18 115.30 114.09 93.76 86.55 77.33 CDCl3 77.01 CDCl3 76.70 CDCl3 60.55 55.33 44.51 34.03 16.76 -0.00
f1 (ppm)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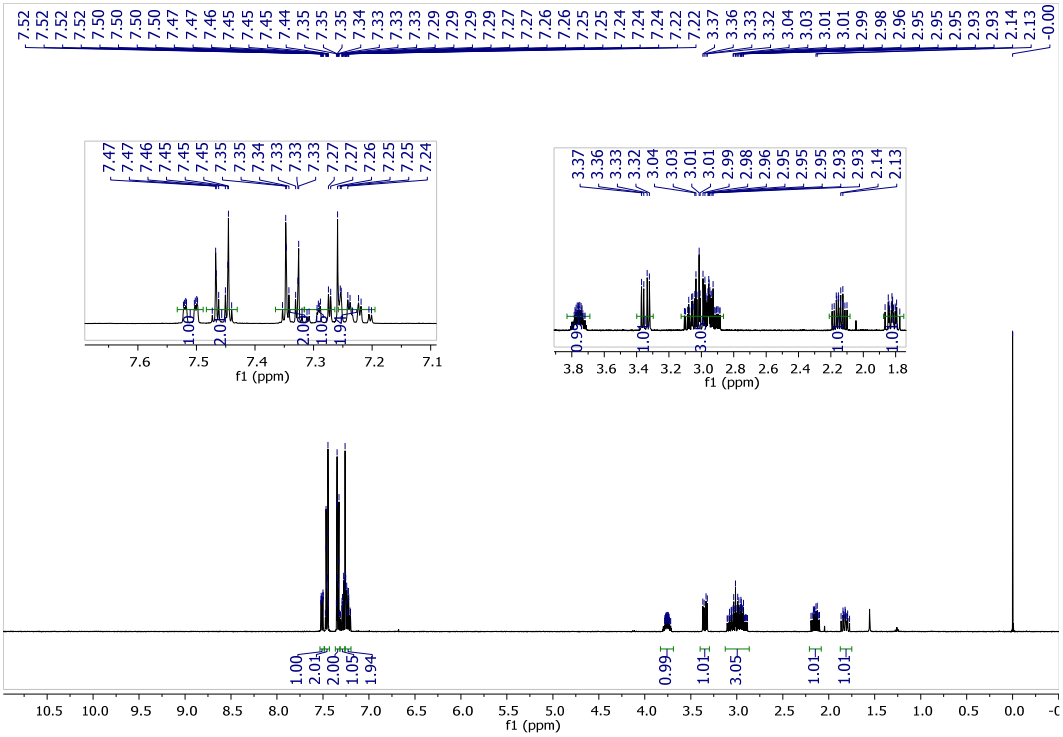
1d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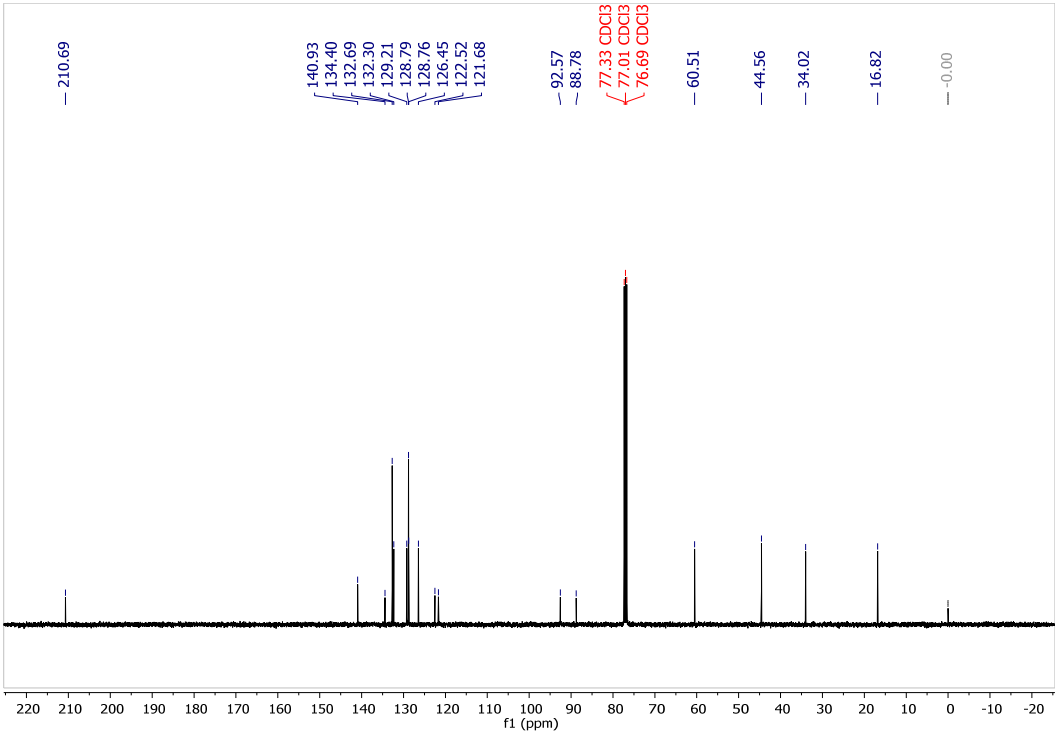
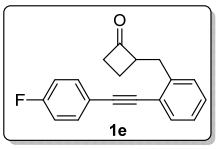

f1 (ppm)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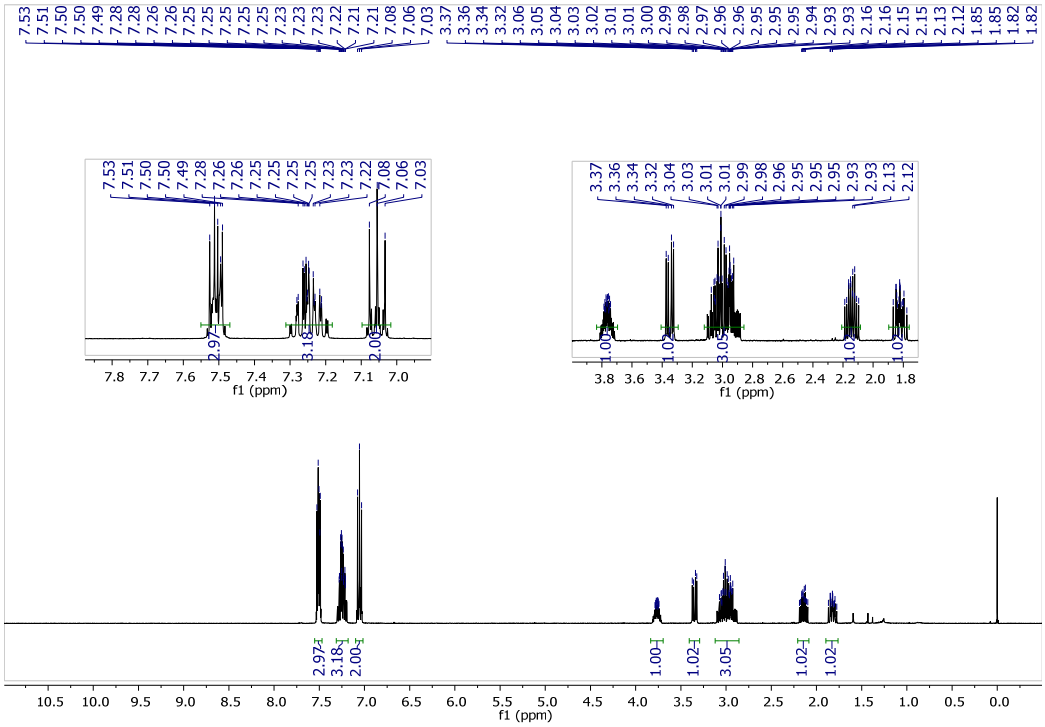
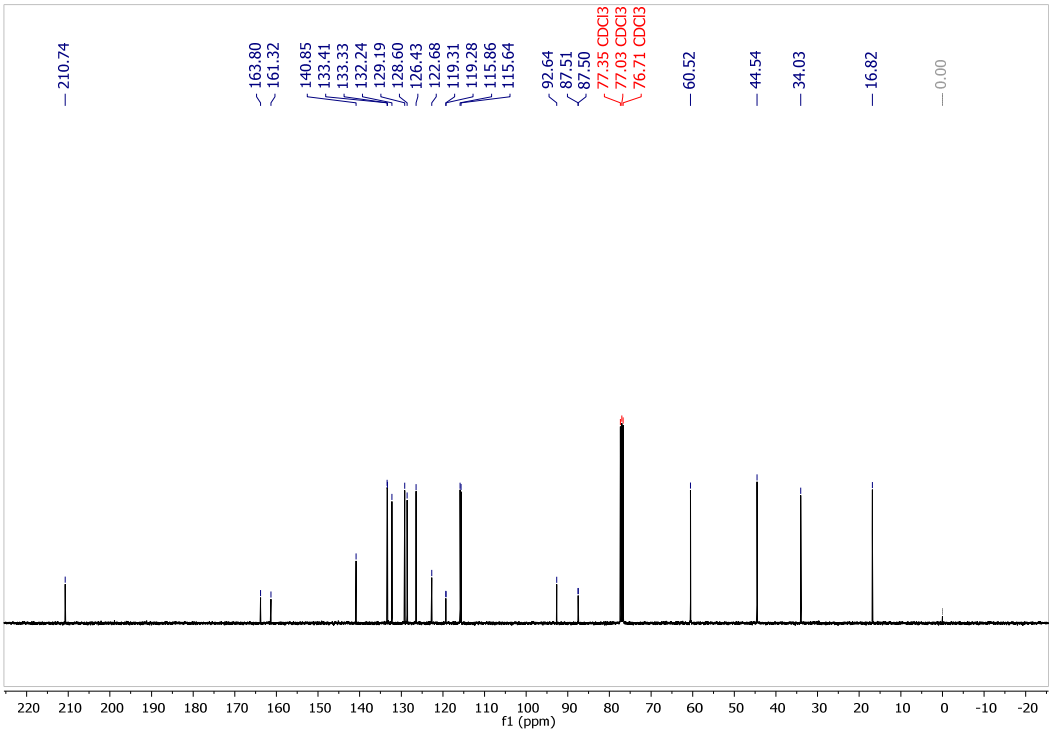
F
1e


7.53 7.51 7.50 7.50 7.49 7.28 7.26 7.26 7.25 7.25 7.25 7.25 7.25 7.23 7.23 7.23 7.22 7.21 7.21 7.08 7.06 7.03
3.37 3.36 3.36 3.34 3.32 3.06 3.05 3.04 3.03 3.02 3.01 3.01 3.00 2.99 2.98 2.97 2.96 2.96 2.95 2.95 2.95 2.94 2.93 2.93 2.16 2.15 2.15 2.13 2.12 1.85 1.85 1.82 1.82
2.97
3.18
2.00
1.00
1.02
3.05
1.02
1.02
f1 (ppm)


210.74
163.80 161.32 140.85 133.41 133.33 132.24 129.19 128.60 126.43 122.68 119.31 119.28 115.86 115.64
92.64 87.51 87.50
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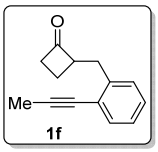
44.54
34.03
16.82
0.00
f1 (ppm)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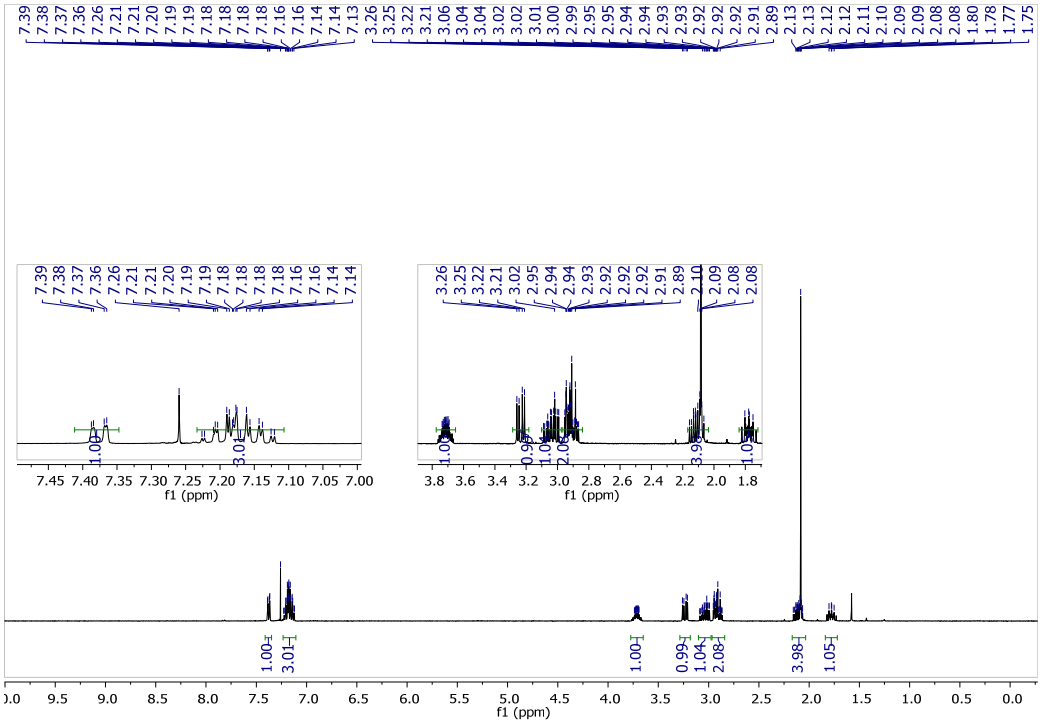
Me

1f


7.39 7.38 7.37 7.36 7.26 7.21 7.21 7.20 7.19 7.19 7.18 7.18 7.18 7.18 7.16 7.16 7.14 7.14 7.13
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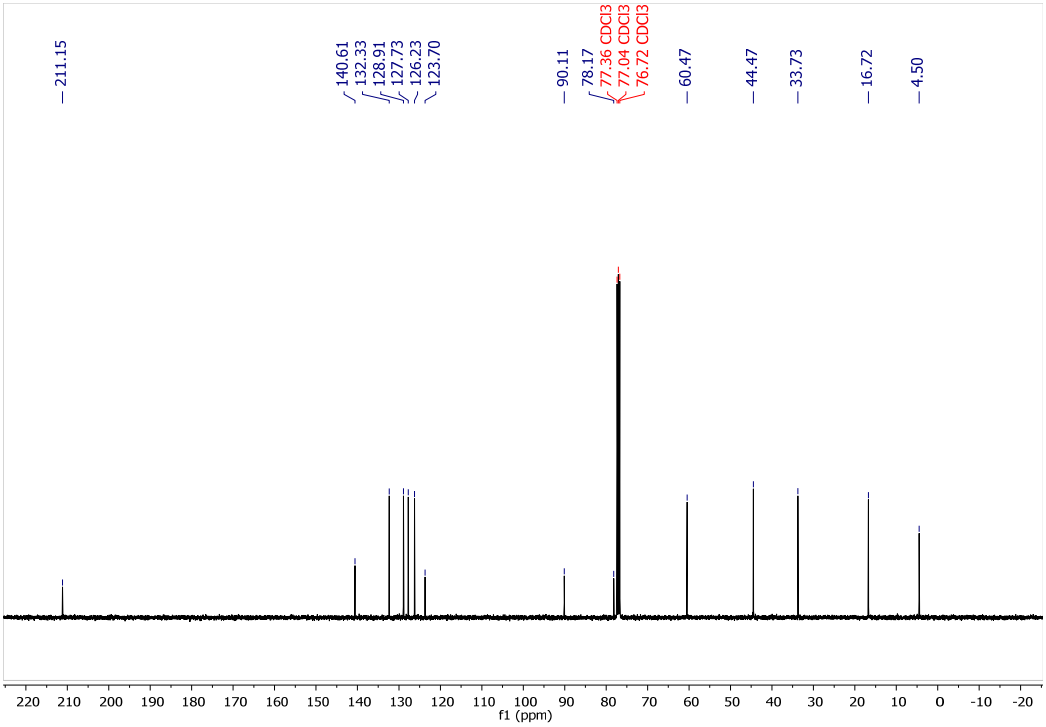
2.13 2.13 2.12 2.12 2.11 2.10 2.09 2.09 2.08 2.08 1.80 1.78 1.77 1.75
1.00 3.01
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
1.00 0.99 1.04 2.08 3.98 1.05
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)
1.00 0.99 1.04 2.08 3.98 1.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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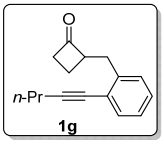
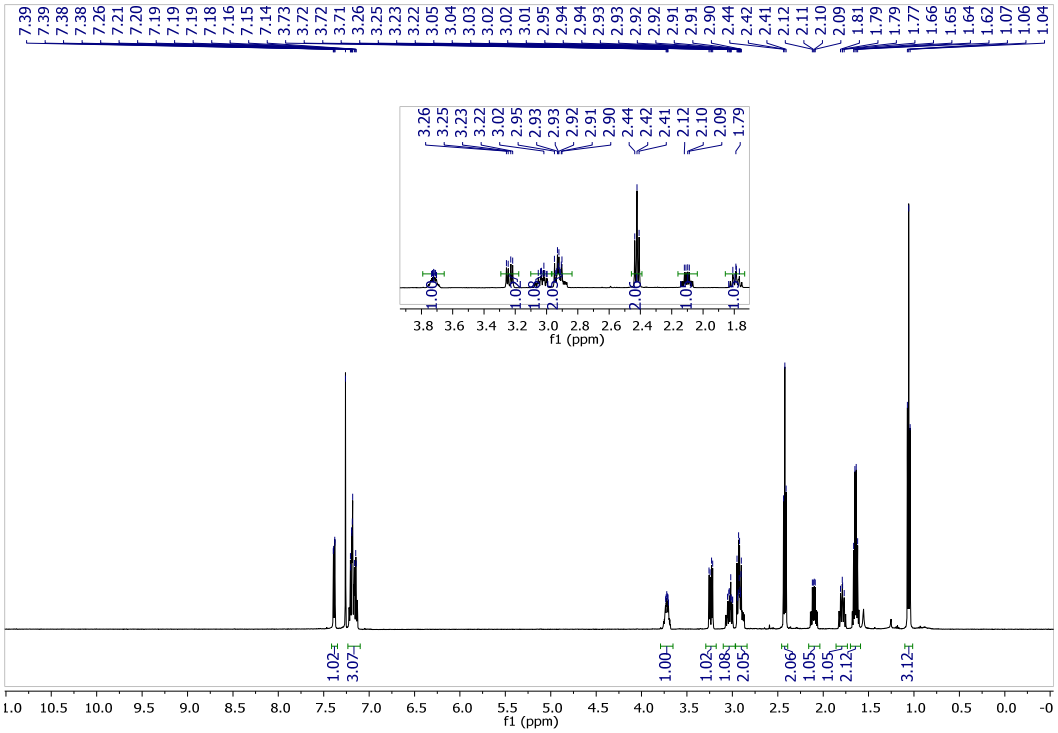
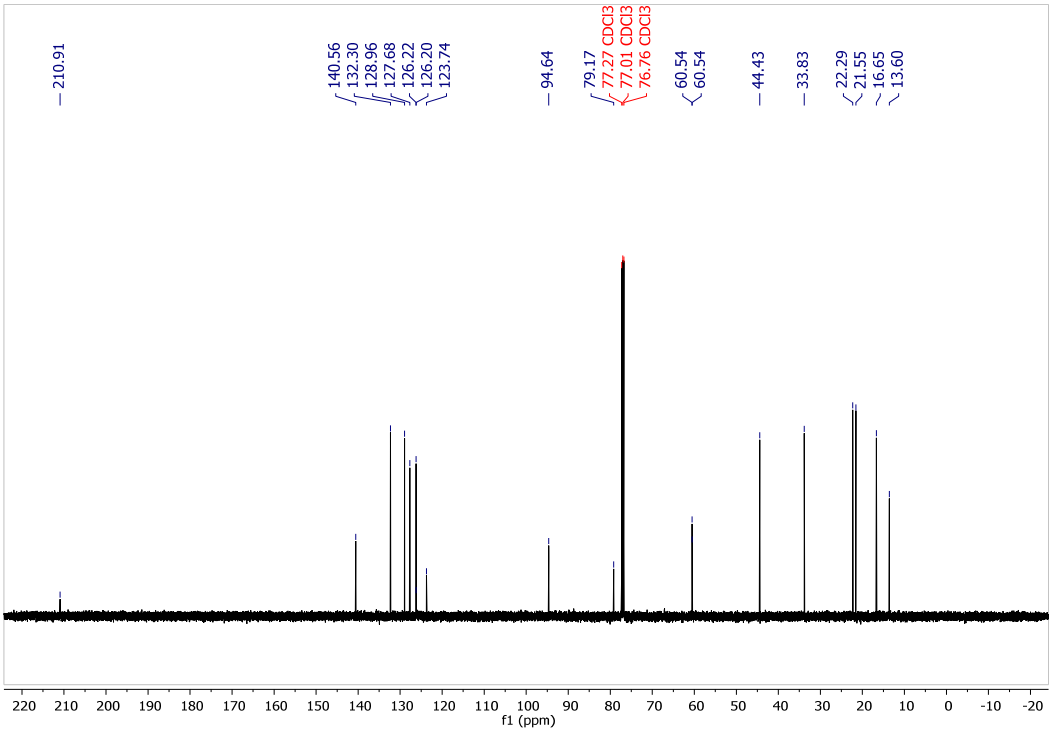
140.61
132.33
128.91
127.73
126.23
123.70
90.11
78.17
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
60.47
44.47
33.73
16.72
4.50
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O
n-Pr
1g


7.39 7.39 7.38 7.38 7.26 7.21 7.20 7.19 7.19 7.19 7.18 7.16 7.15 7.14 3.73 3.72 3.72 3.71 3.26 3.25 3.23 3.22 3.05 3.04 3.03 3.02 3.02 3.01 2.95 2.94 2.94 2.93 2.93 2.92 2.92 2.91 2.91 2.90 2.44 2.42 2.41 2.12 2.11 2.10 2.09 1.81 1.79 1.79 1.77 1.66 1.65 1.64 1.62 1.07 1.06 1.04
3.26 3.25 3.23 3.22 3.02 2.95 2.93 2.93 2.92 2.91 2.90 2.44 2.42 2.41 2.12 2.10 2.09 1.79
1.02 1.06 1.02 1.06 2.05 2.05 1.03 1.05
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)
1.02 3.07 1.00 1.02 1.08 2.05 2.06 1.05 1.05 2.12 3.12
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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140.56 132.30 128.96 127.68 126.22 126.20 123.74
94.64
79.17 77.27 CDCl3 77.01 CDCl3 76.76 CDCl3
60.54 60.54
44.43
33.83
22.29 21.55 16.65 13.60
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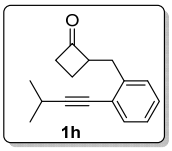
f1 (ppm)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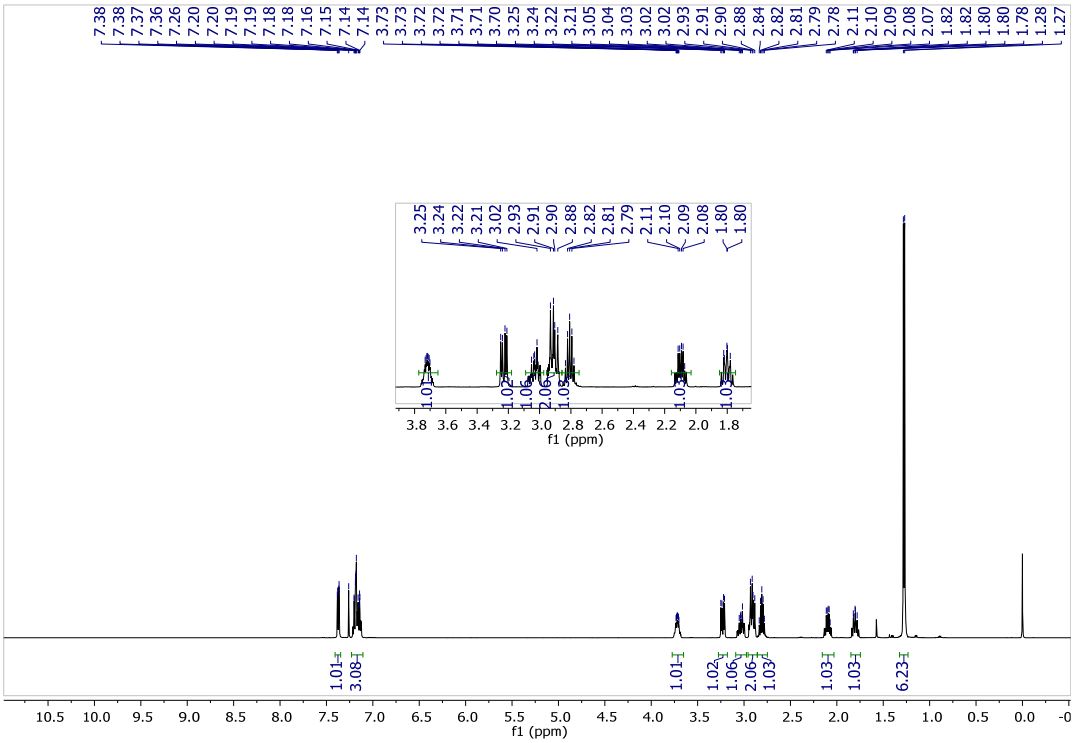
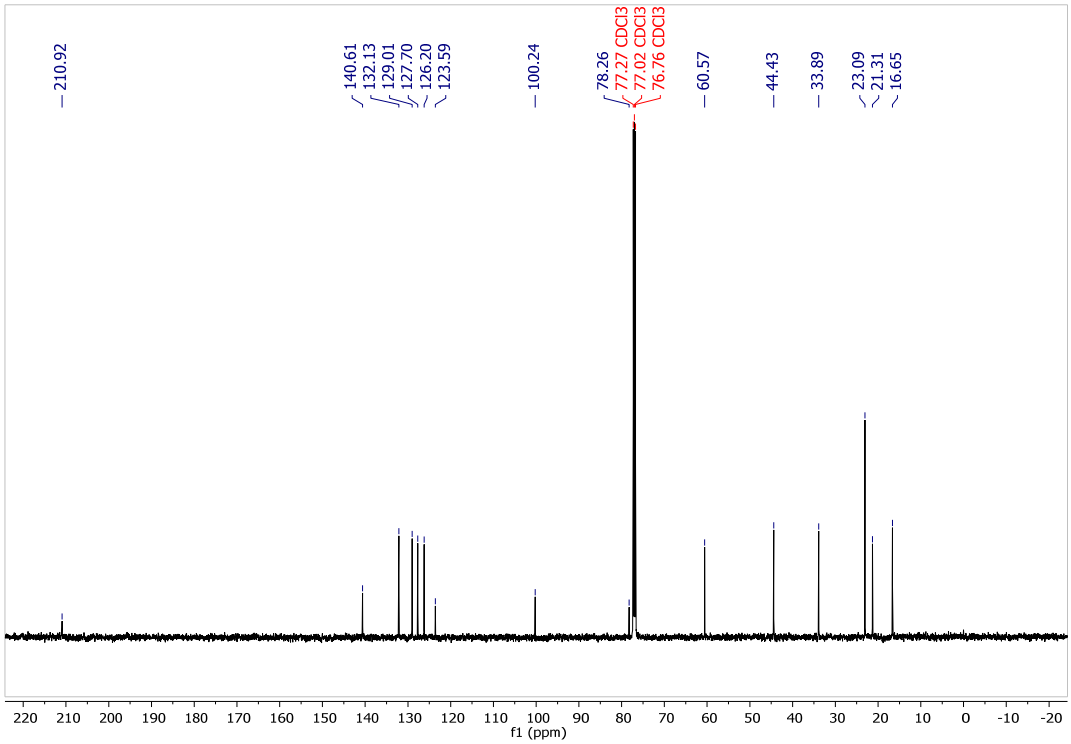
1h


7.38 7.38 7.37 7.36 7.26 7.20 7.20 7.19 7.19 7.18 7.18 7.16 7.15 7.14 7.14
3.73 3.73 3.72 3.72 3.71 3.71 3.70 3.25 3.24 3.22 3.21 3.05 3.04 3.03 3.02 3.02 2.93 2.91 2.90 2.88 2.84 2.82 2.81 2.79 2.78 2.11 2.10 2.09 2.08 2.07 1.82 1.82 1.80 1.80 1.78 1.28 1.27
3.25 3.24 3.22 3.21 3.02 2.93 2.91 2.90 2.88 2.82 2.81 2.79 2.11 2.10 2.09 2.08 1.80 1.80
1.01 1.02 1.06 2.06 1.03 1.03 1.03
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)
1.01 3.08 1.01 1.02 1.06 2.06 1.03 1.03 1.03 6.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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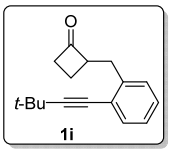
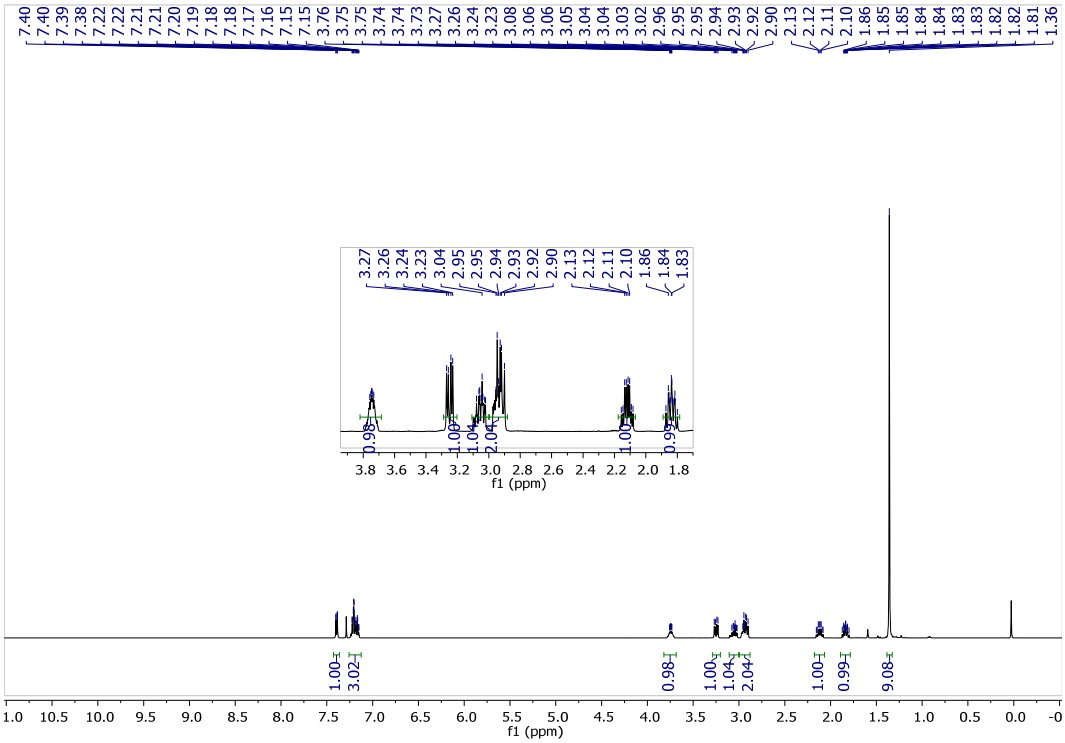
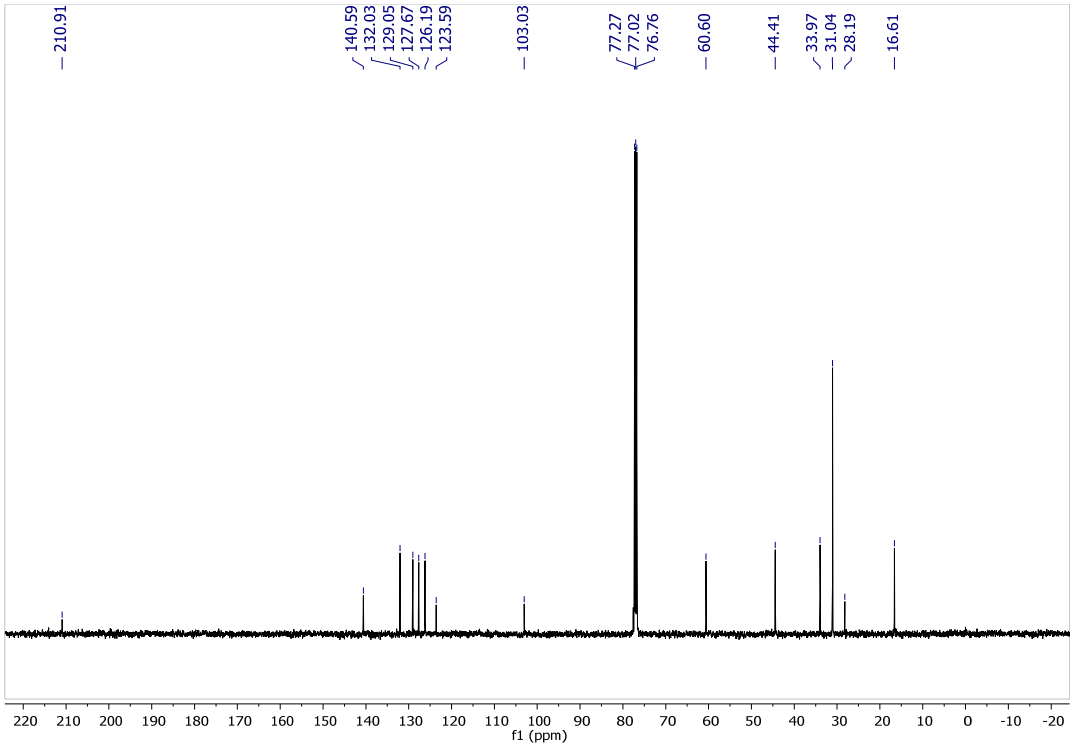
100.24
78.26 77.27 CDCl3 77.02 CDCl3 76.76 CDCl3
60.57
44.43
33.89
23.09 21.31 16.65
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O
t-Bu

1i


7.40 7.40 7.39 7.38 7.22 7.22 7.21 7.21 7.20 7.19 7.18 7.18 7.17 7.16 7.15 7.15 3.76 3.75 3.75 3.74 3.74 3.73 3.27 3.26 3.26 3.24 3.23 3.08 3.06 3.06 3.05 3.04 3.04 3.03 3.02 2.96 2.95 2.95 2.94 2.93 2.92 2.90 2.13 2.12 2.11 2.10 1.86 1.85 1.85 1.84 1.84 1.83 1.83 1.82 1.82 1.81 1.36
3.27 3.26 3.24 3.23 3.04 2.95 2.95 2.94 2.93 2.92 2.90 2.13 2.12 2.11 2.10 1.86 1.84 1.83
0.98 1.00 1.04 2.04 1.03 0.95
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)
1.00 3.02 0.98 1.00 1.04 2.04 1.00 0.99 9.08
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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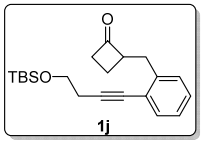
140.59 132.03 129.05 127.67 126.19 123.59
103.03
77.27 77.02 76.76
60.60
44.41
33.97 31.04 28.19
16.61
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


TBSO
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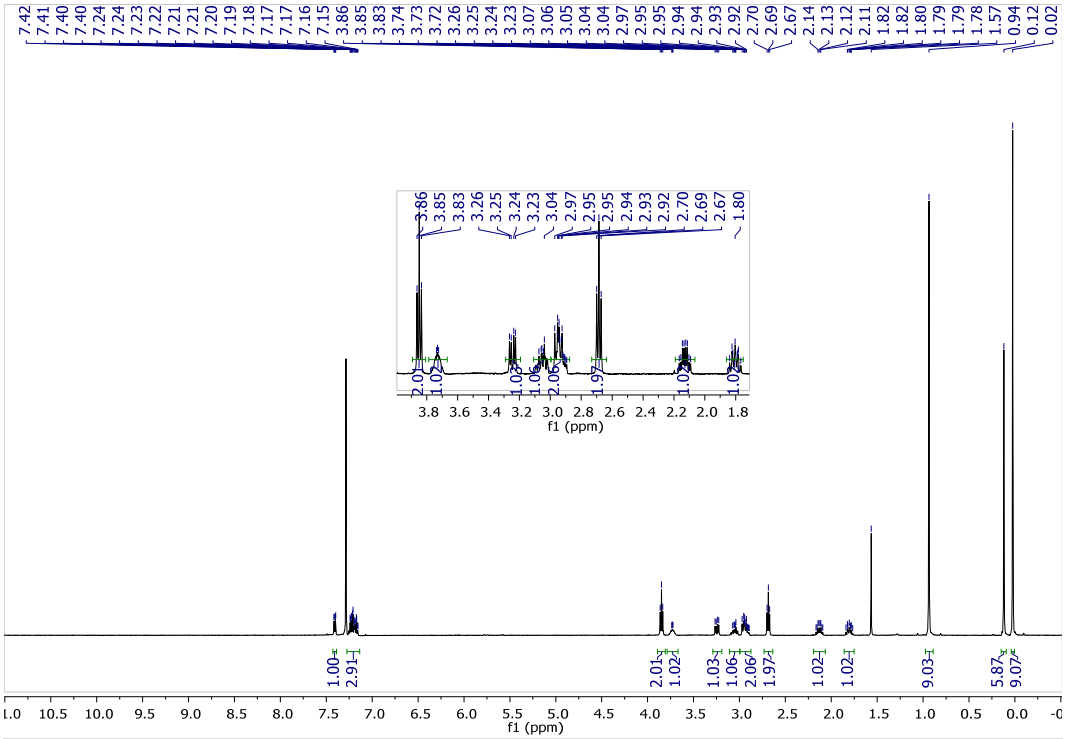
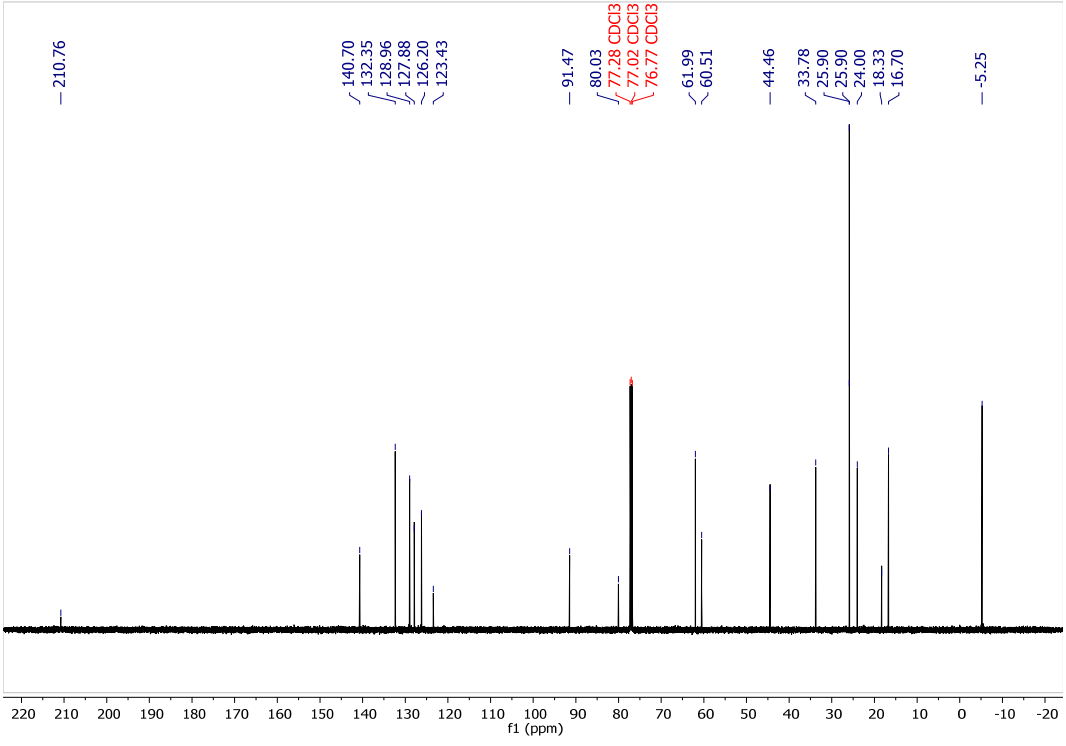
1j


7.42 7.41 7.40 7.40 7.24 7.24 7.23 7.22 7.21 7.21 7.20 7.19 7.18 7.17 7.17 7.16 7.15 3.86 3.85 3.83 3.74 3.73 3.72 3.26 3.25 3.24 3.23 3.07 3.06 3.05 3.04 3.04 2.97 2.95 2.95 2.94 2.94 2.93 2.92 2.70 2.69 2.67 2.14 2.13 2.12 2.11 1.82 1.82 1.80 1.79 1.79 1.78 1.57 0.94 0.12 0.02
3.86 3.85 3.83 3.26 3.25 3.24 3.23 3.04 2.97 2.95 2.95 2.94 2.93 2.92 2.70 2.69 2.67 1.80
2.01 1.02 1.02 1.06 2.05 1.97 1.02 1.03
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)
1.00 2.91 2.01 1.02 1.03 1.06 2.06 1.97 1.02 1.02 9.03 5.87 9.07
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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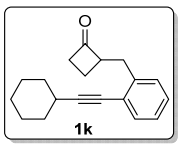
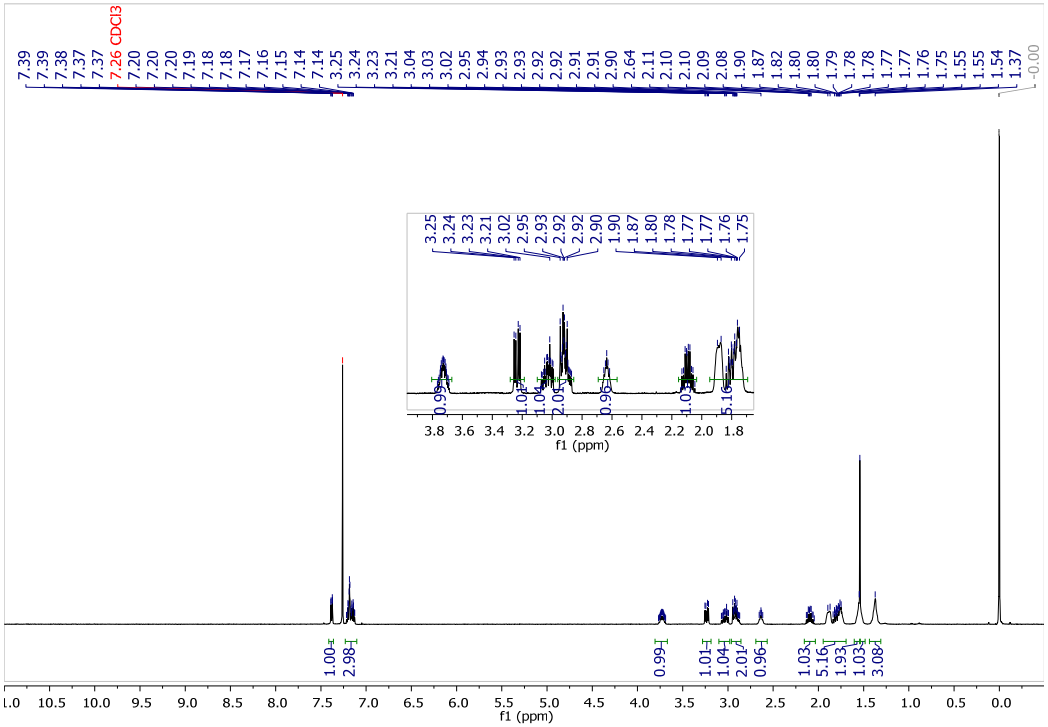
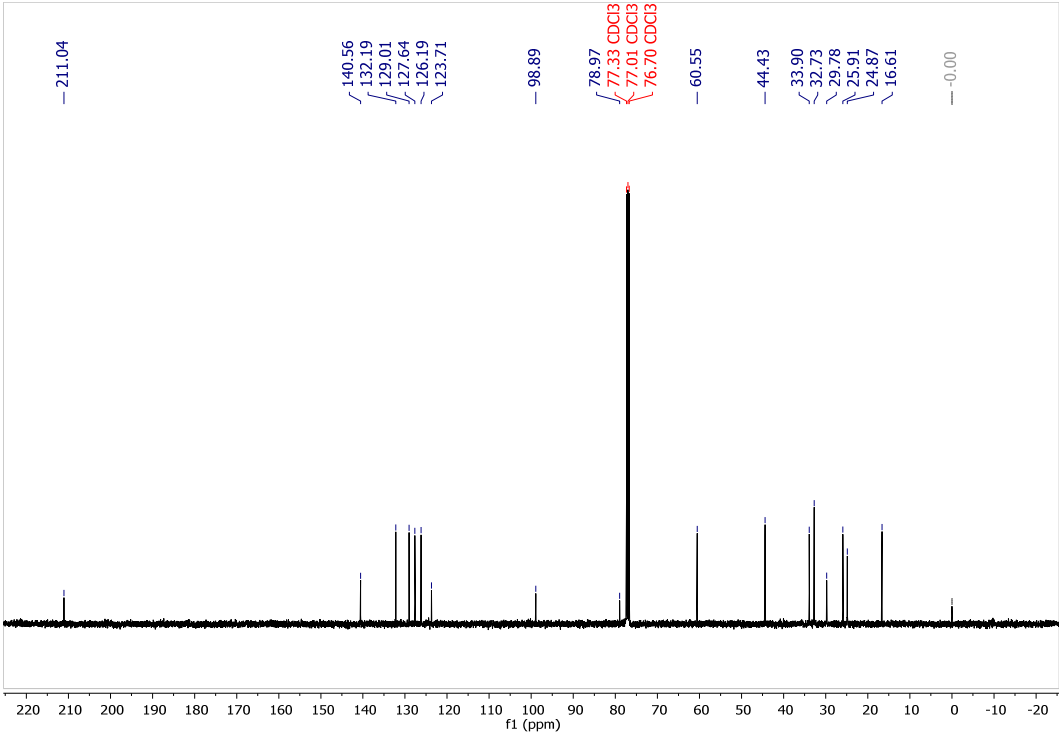
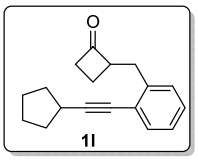
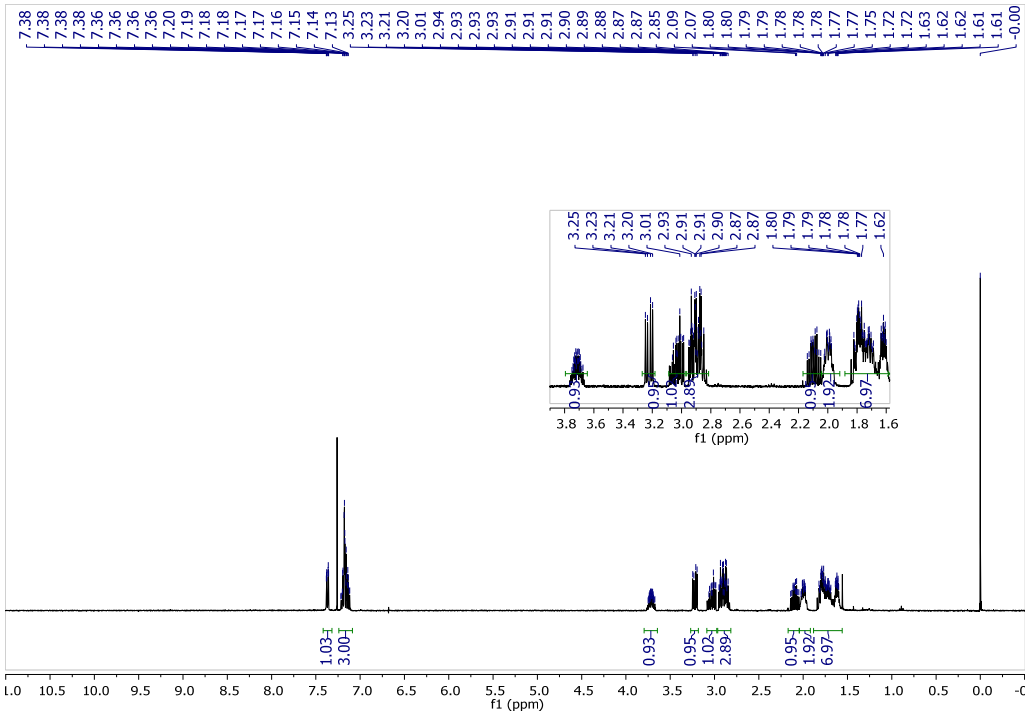
91.47
80.03 77.28 CDCl3 77.02 CDCl3 76.77 CDCl3
61.99 60.51
44.46
33.78 25.90 25.90 24.00 18.33 16.70
-5.25
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

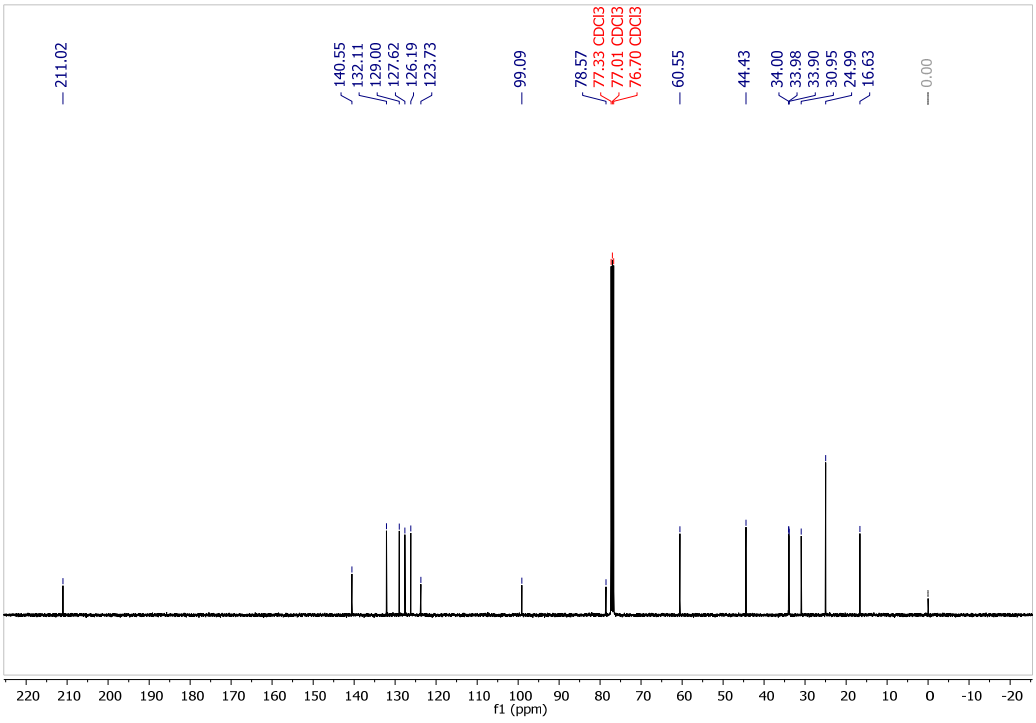

O
1k

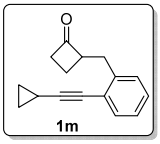

7.39 7.39 7.38 7.37 7.37 7.26 CDCl3 7.20 7.20 7.20 7.19 7.18 7.18 7.17 7.16 7.15 7.14 7.14 3.25 3.24 3.23 3.21 3.04 3.03 3.02 2.95 2.94 2.93 2.93 2.92 2.92 2.91 2.91 2.90 2.64 2.11 2.10 2.10 2.09 2.08 1.90 1.87 1.82 1.80 1.80 1.79 1.78 1.78 1.77 1.77 1.76 1.75 1.55 1.55 1.54 1.37 -0.00
1.00 2.98 0.99 1.01 1.04 2.01 0.96 1.03 5.16 1.93 1.03 3.08
f1 (ppm)

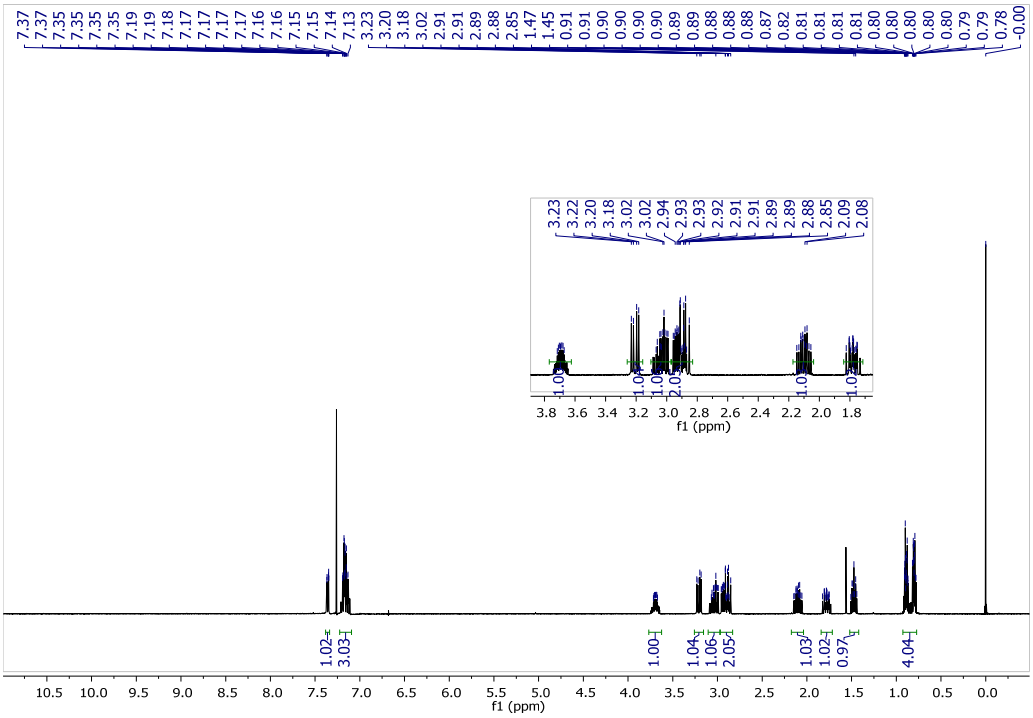

211.04 140.56 132.19 129.01 127.64 126.19 123.71 98.89 78.97 77.33 CDCl3 77.01 CDCl3 76.70 CDCl3 60.55 44.43 33.90 32.73 29.78 25.91 24.87 16.61 -0.00
f1 (ppm)

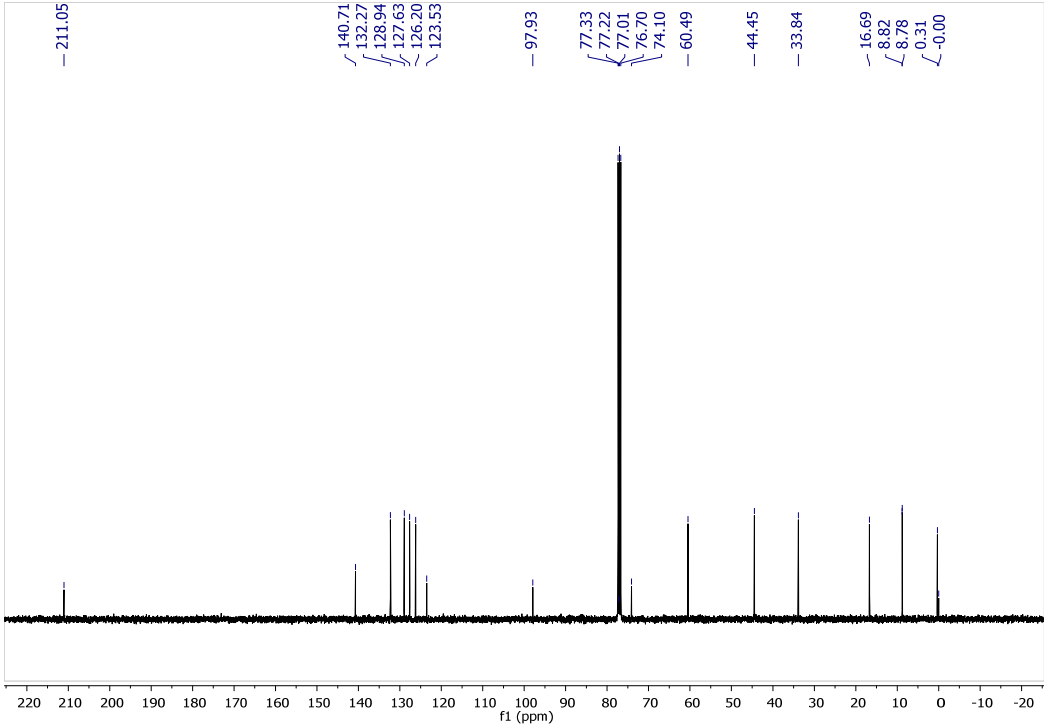

O
1l

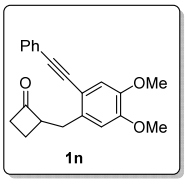

7.38 7.38 7.38 7.38 7.36 7.36 7.36 7.36 7.20 7.19 7.18 7.18 7.17 7.17 7.16 7.15 7.14 7.13 3.25 3.23 3.21 3.20 3.01 2.94 2.93 2.93 2.93 2.91 2.91 2.91 2.90 2.89 2.88 2.87 2.87 2.85 2.09 2.07 1.80 1.80 1.79 1.79 1.78 1.78 1.78 1.77 1.77 1.75 1.72 1.72 1.63 1.62 1.62 1.61 1.61 -0.00
3.25 3.23 3.21 3.20 3.01 2.93 2.91 2.91 2.90 2.87 2.87 1.80 1.79 1.79 1.78 1.78 1.77 1.62
0.93 0.98 1.02 2.89 0.95 1.92 6.97
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)
1.03 3.00 0.93 0.95 1.02 2.89 0.95 1.92 6.97
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

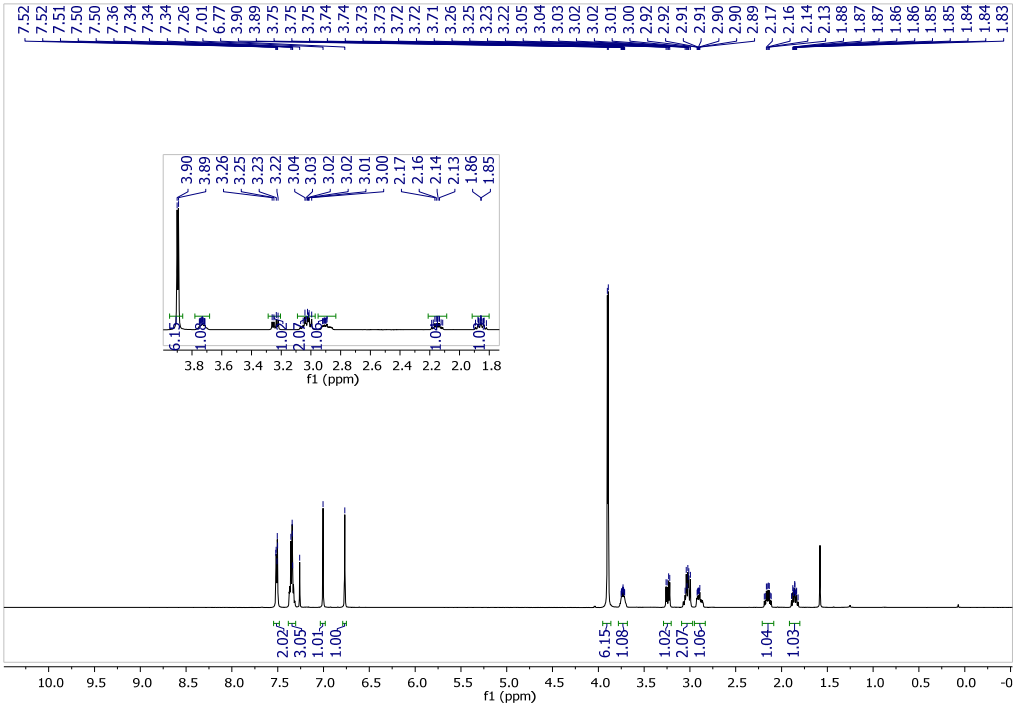

211.02
140.55 132.11 129.00 127.62 126.19 123.73
99.09
78.57 77.33 CDCl3 77.01 CDCl3 76.70 CDCl3
60.55
44.43
34.00 33.98 33.90 30.95 24.99 16.63
0.00
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

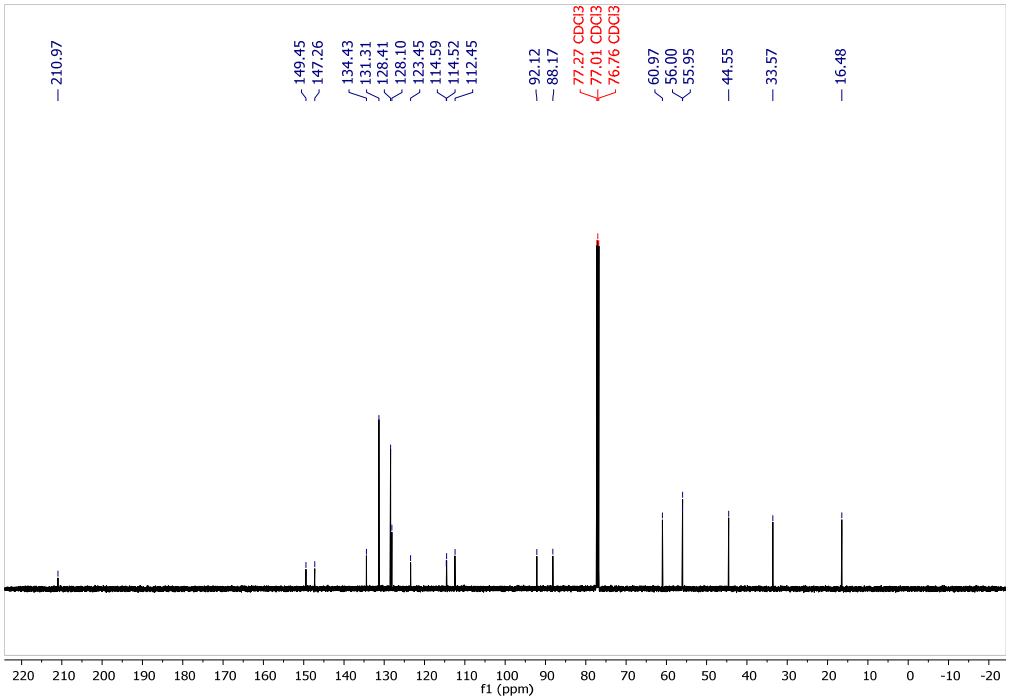

1m

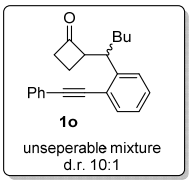

f1 (ppm)

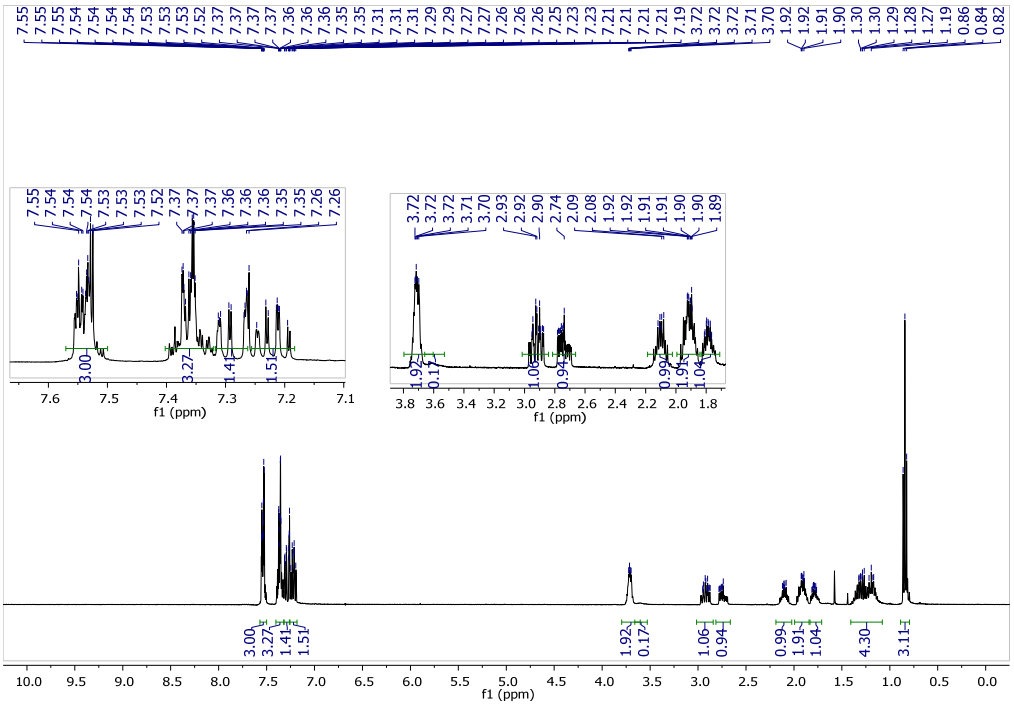

f1 (ppm)

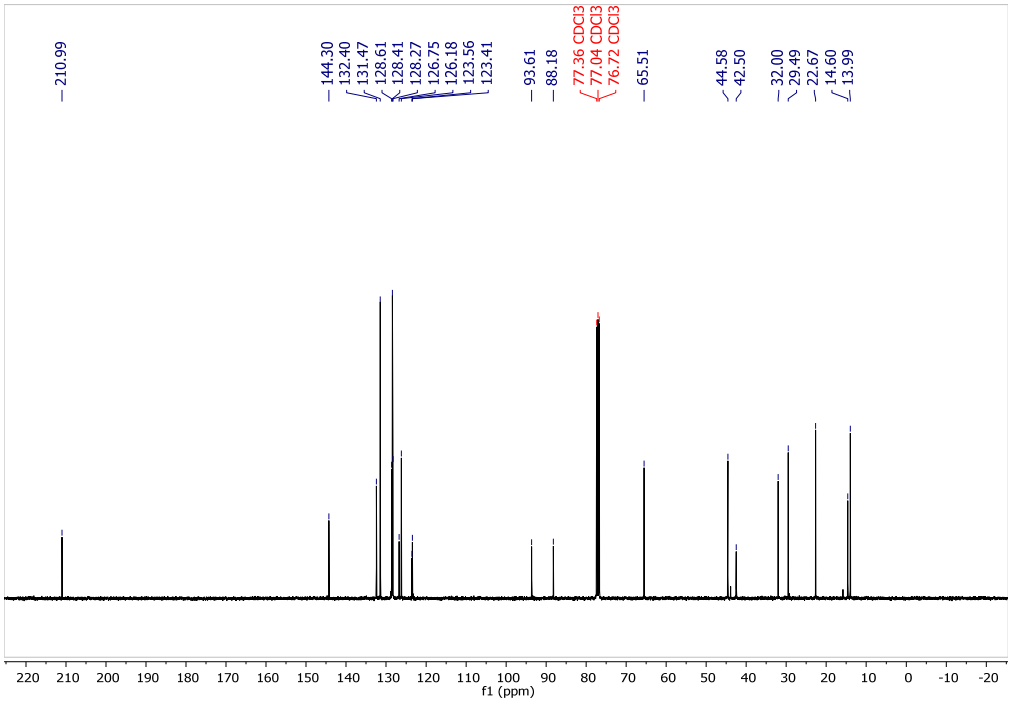

Ph
O
OMe
OMe
1n

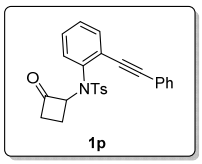

f1 (ppm)

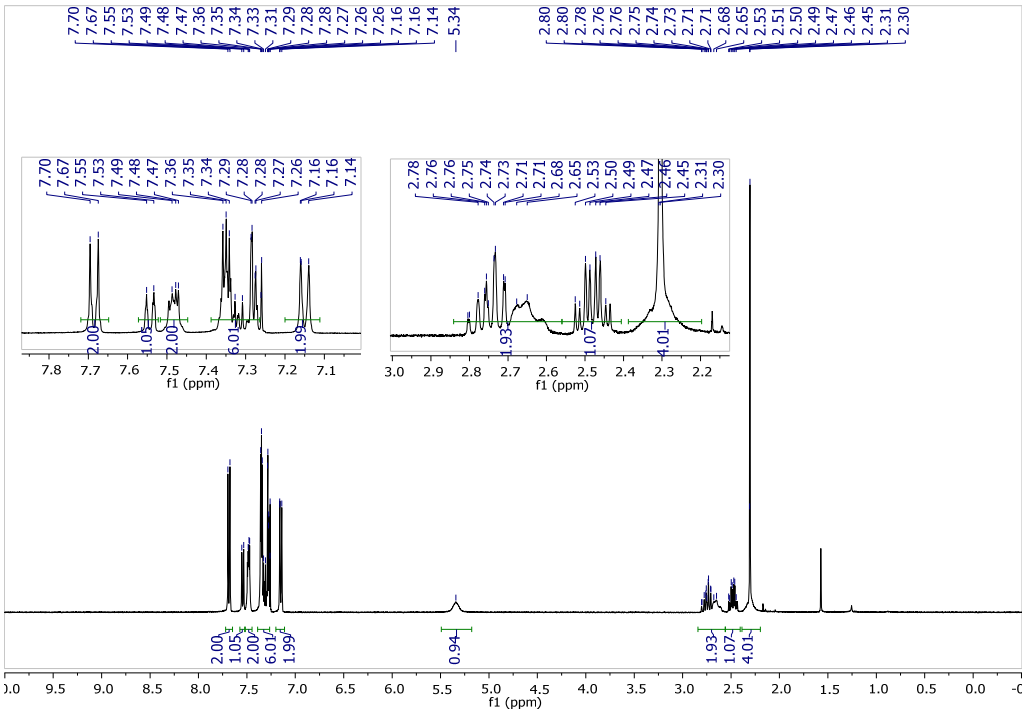

f1 (ppm)

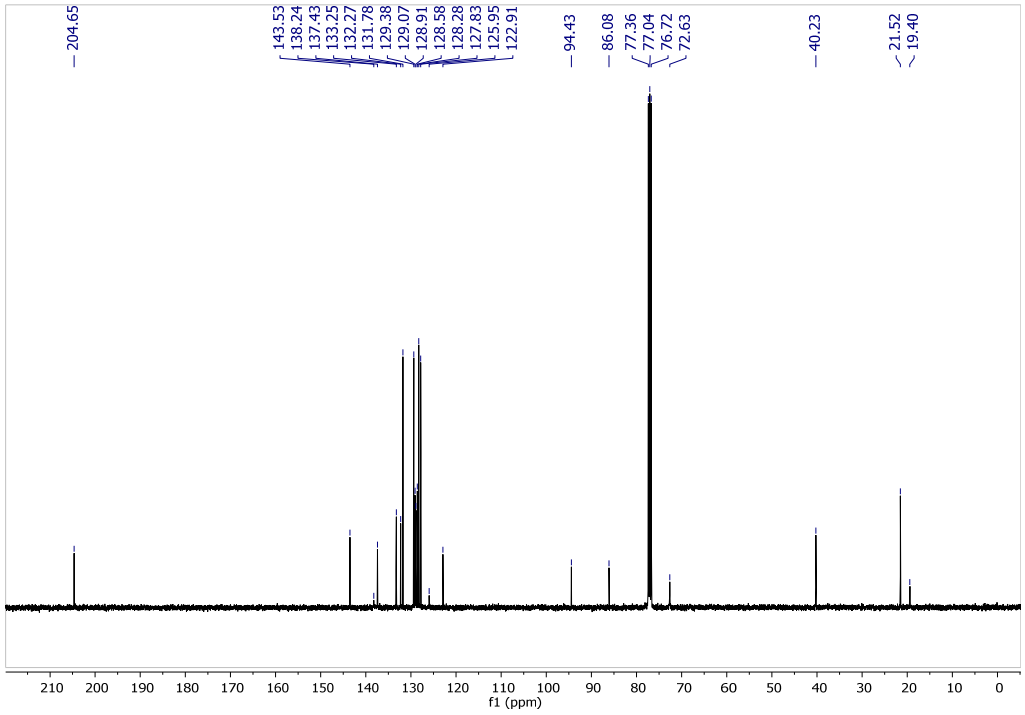

O
Bu
Ph
1o
unseperable mixture
d.r. 10:1

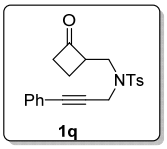

f1 (ppm)

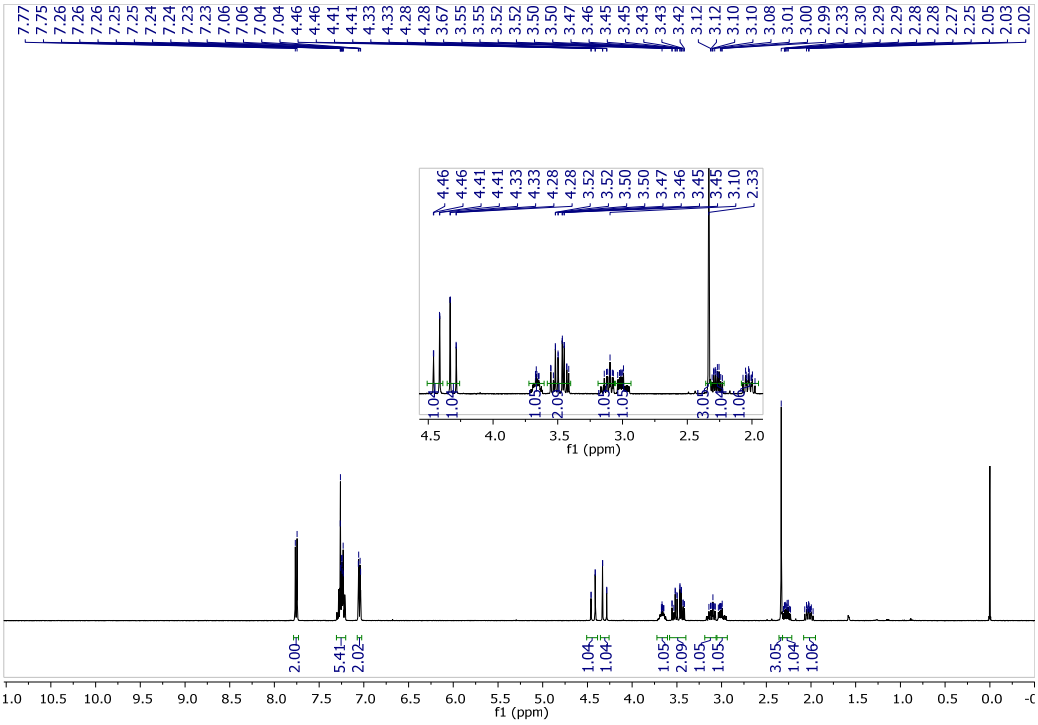

f1 (ppm)

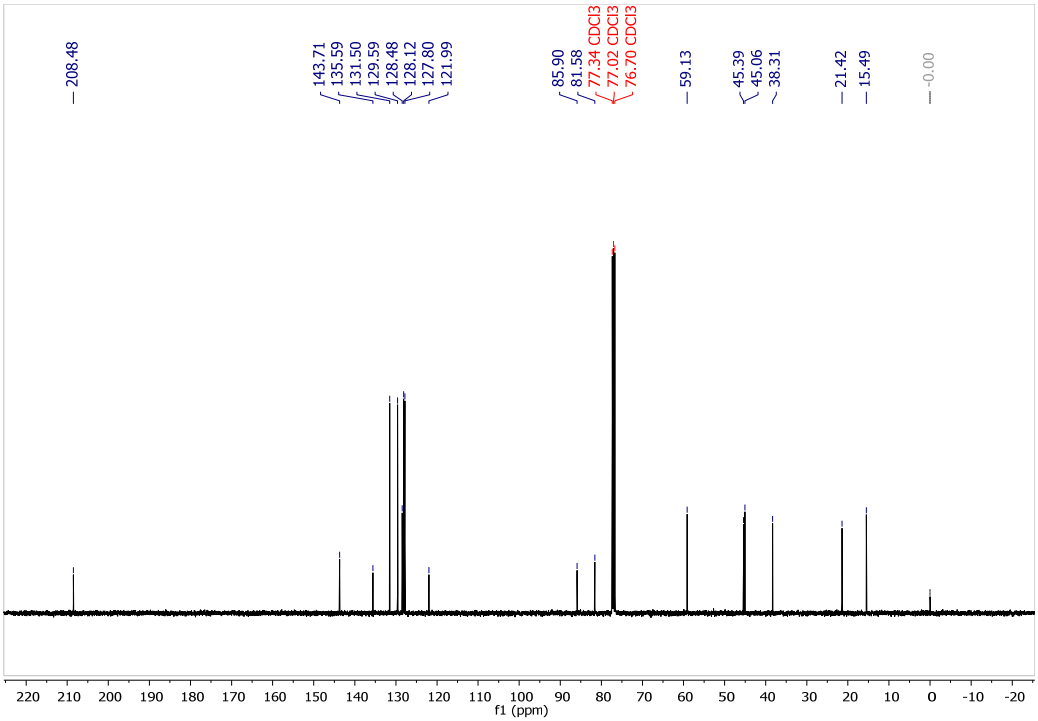

O
NTs
Ph
1p

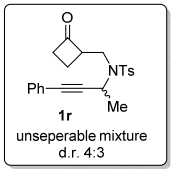

7.70 7.67 7.55 7.53 7.49 7.48 7.47 7.36 7.35 7.34 7.33 7.31 7.29 7.28 7.28 7.27 7.26 7.26 7.16 7.16 7.14 5.34
2.80 2.80 2.78 2.76 2.76 2.75 2.74 2.73 2.71 2.71 2.68 2.65 2.53 2.51 2.50 2.49 2.47 2.46 2.45 2.31 2.30
2.00 1.05 2.00 6.01 1.99 0.94 1.93 1.07 4.01
f1 (ppm)

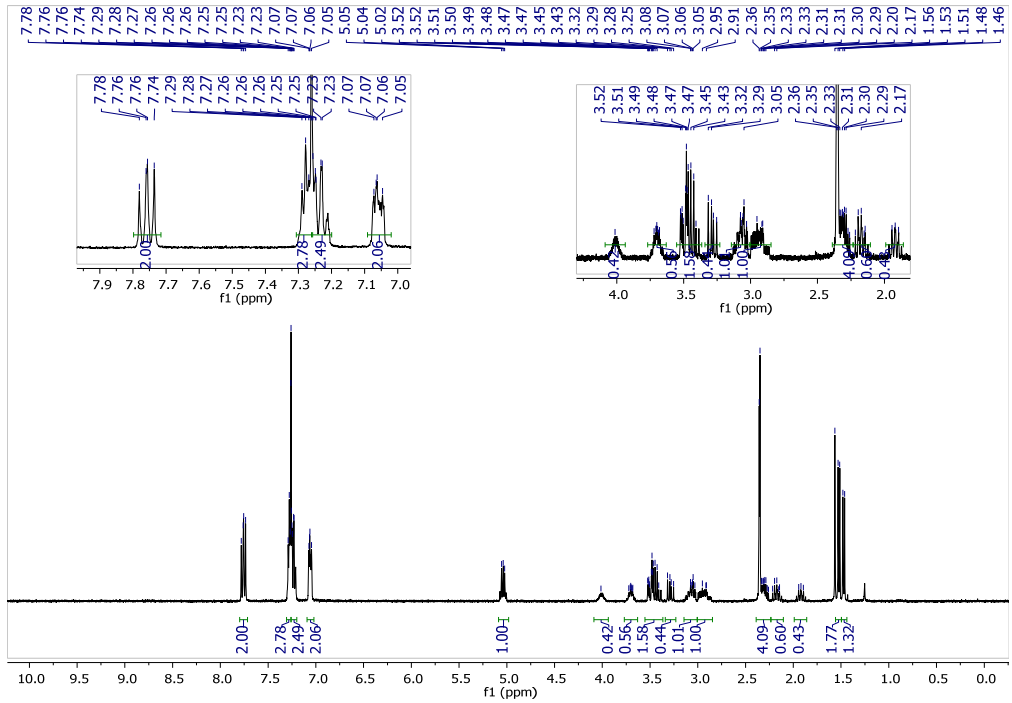

204.65
143.53 138.24 137.43 133.25 132.27 131.78 129.38 129.07 128.91 128.58 128.28 127.83 125.95 122.91
94.43
86.08
77.36 77.04 76.72 72.63
40.23
21.52 19.40
f1 (ppm)

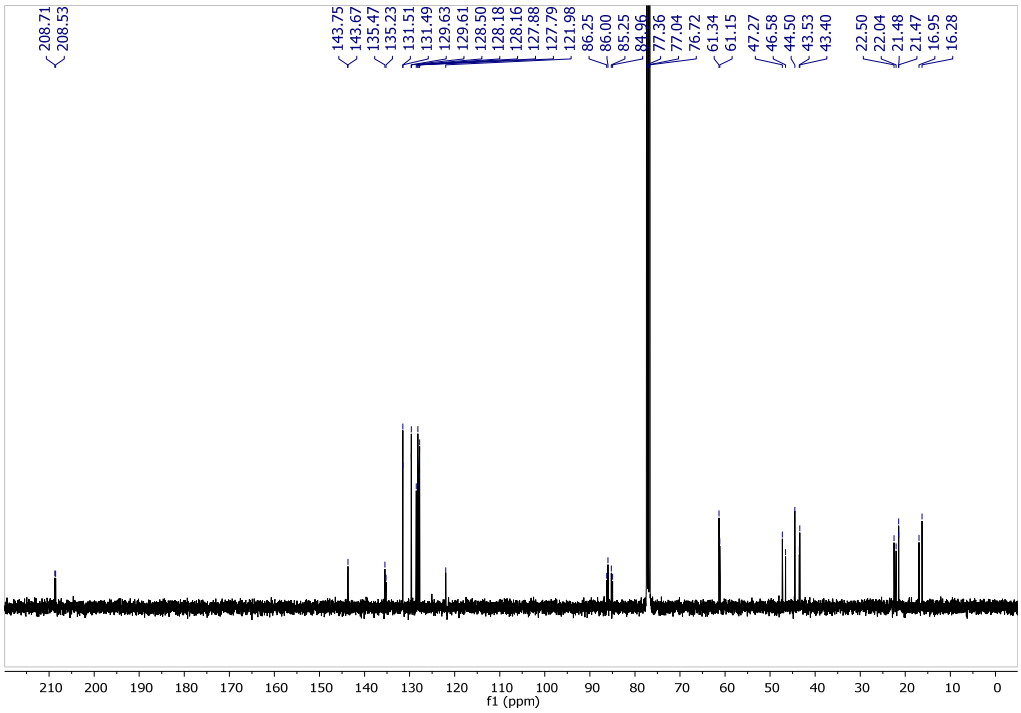

O
NTs
Ph
1q

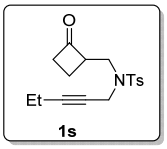

f1 (ppm)


208.48
143.71
135.59
131.50
129.59
128.48
128.12
127.80
121.99
85.90
81.58
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
59.13
45.39
45.06
38.31
21.42
15.49
-0.00
f1 (ppm)

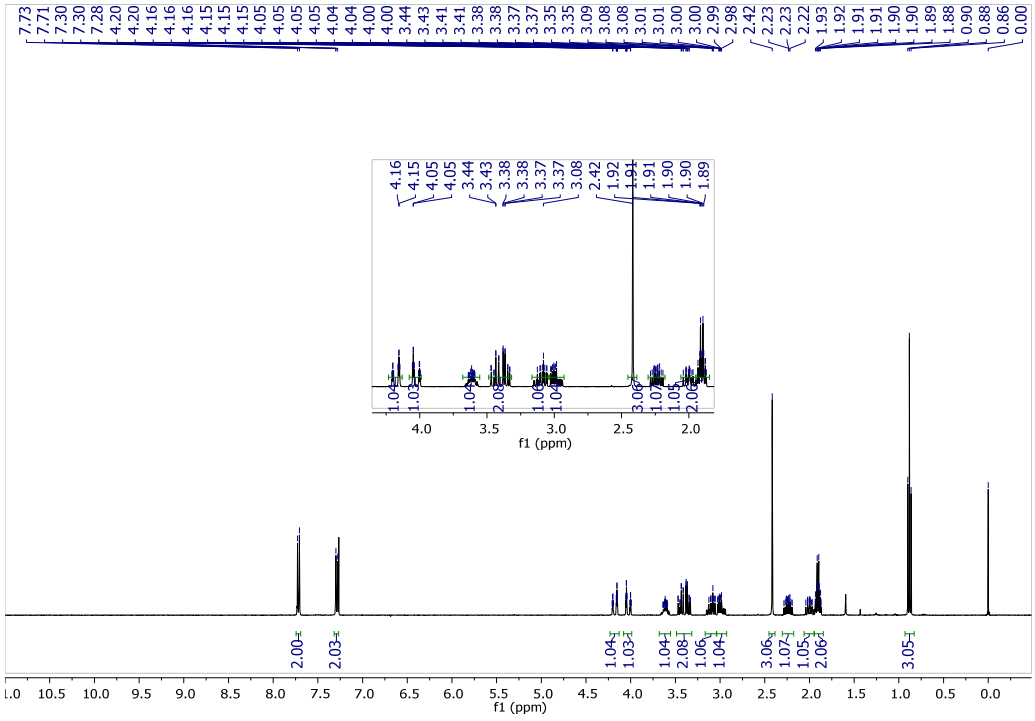

O
NTs
Ph
Me
1r
unseperable mixture
d.r. 4:3

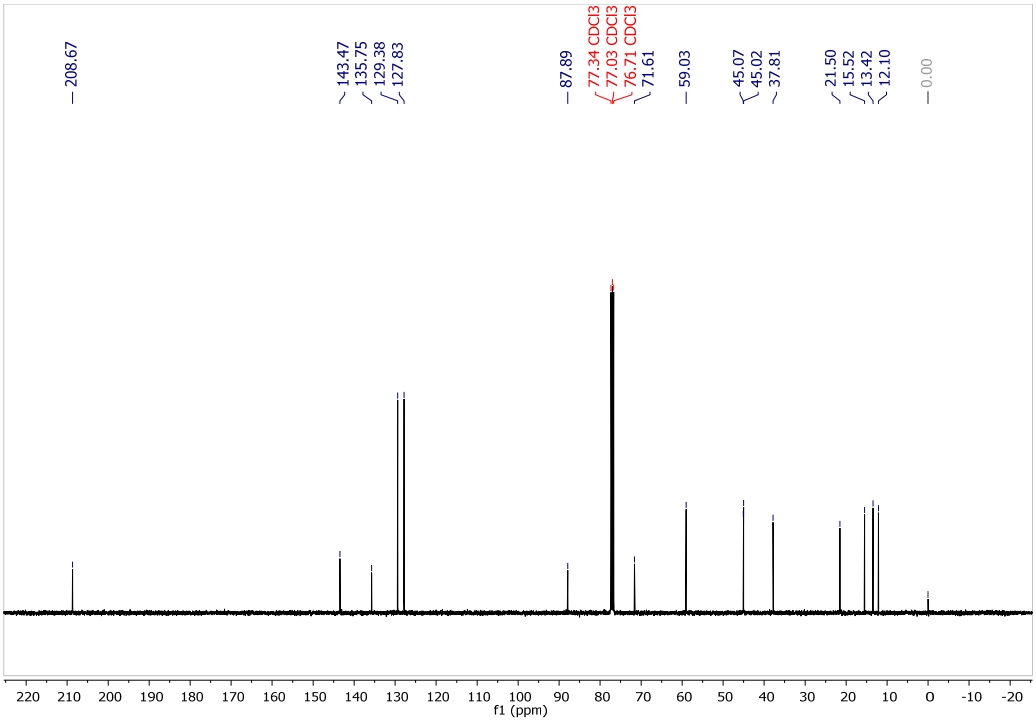

f1 (ppm)

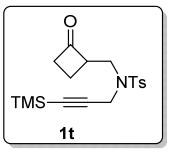

f1 (ppm)

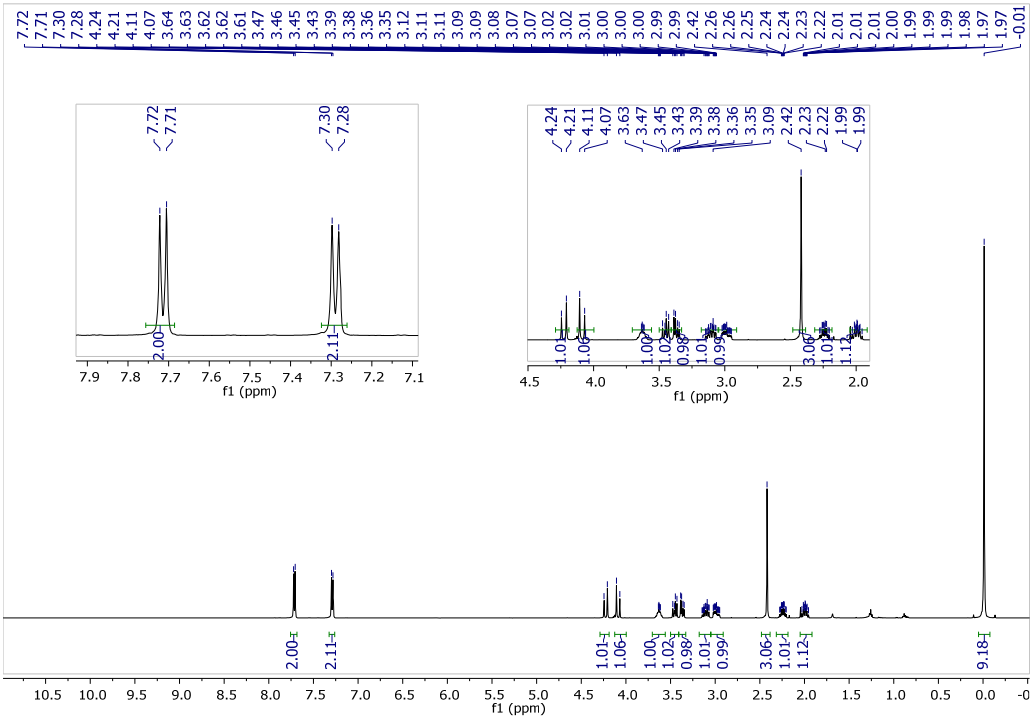

O
NTs
Et

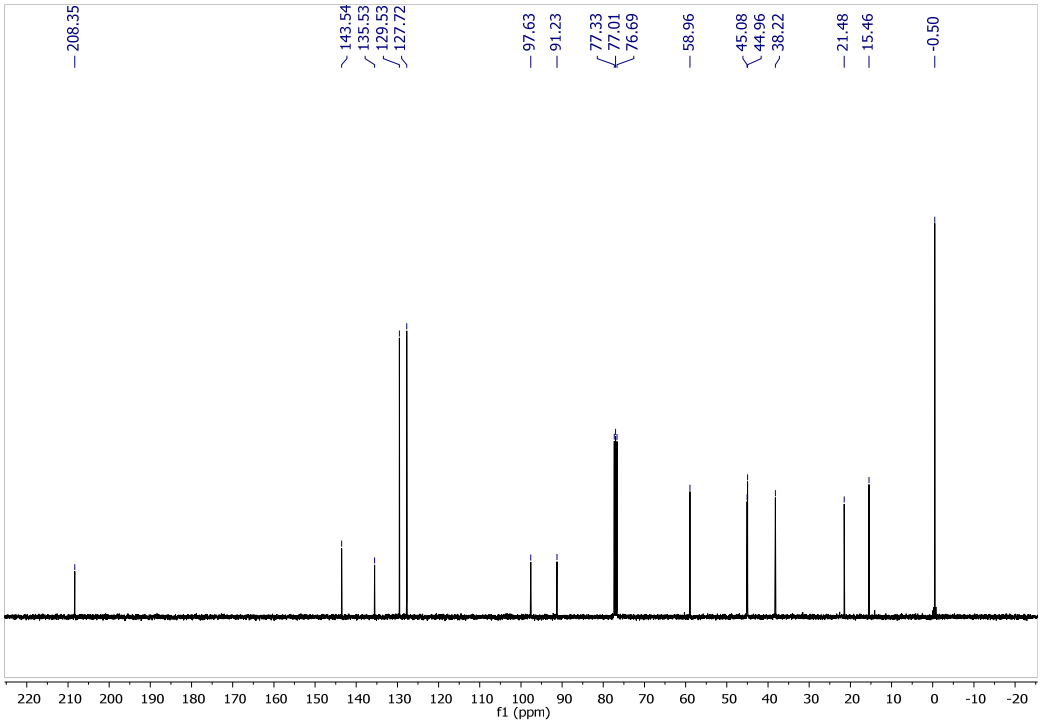
1s

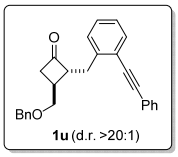

f1 (ppm)


208.67
143.47
135.75
129.38
127.83
87.89
77.34 CDCl3
77.03 CDCl3
76.71 CDCl3
71.61
59.03
45.07
45.02
37.81
21.50
15.52
13.42
12.10
0.00
f1 (ppm)

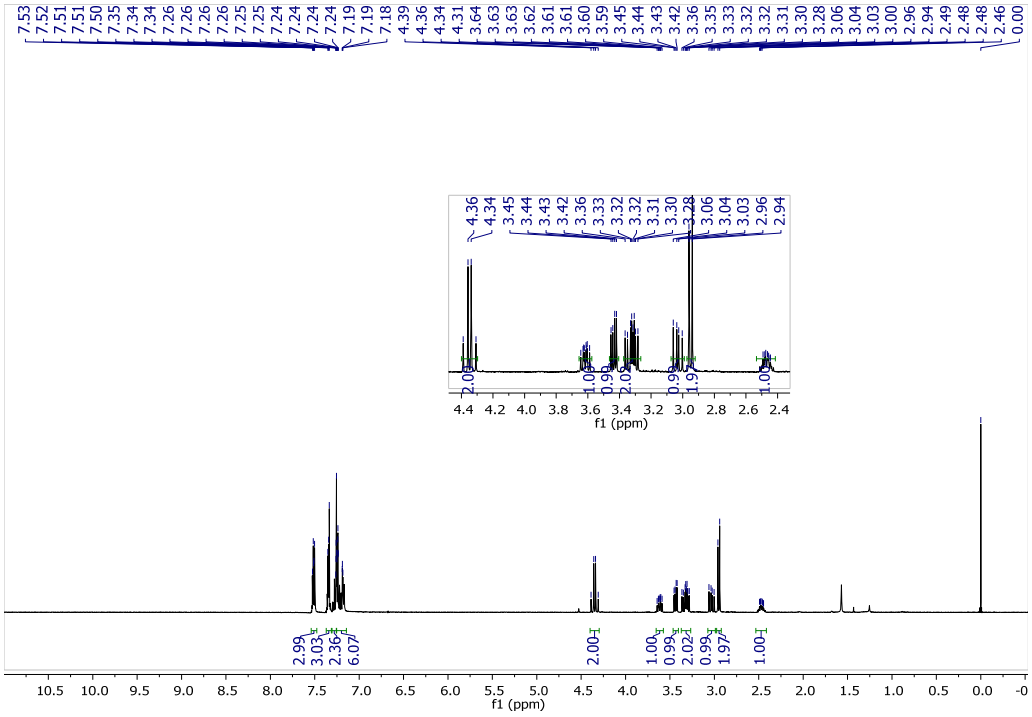

O
NTs
TMS
1t

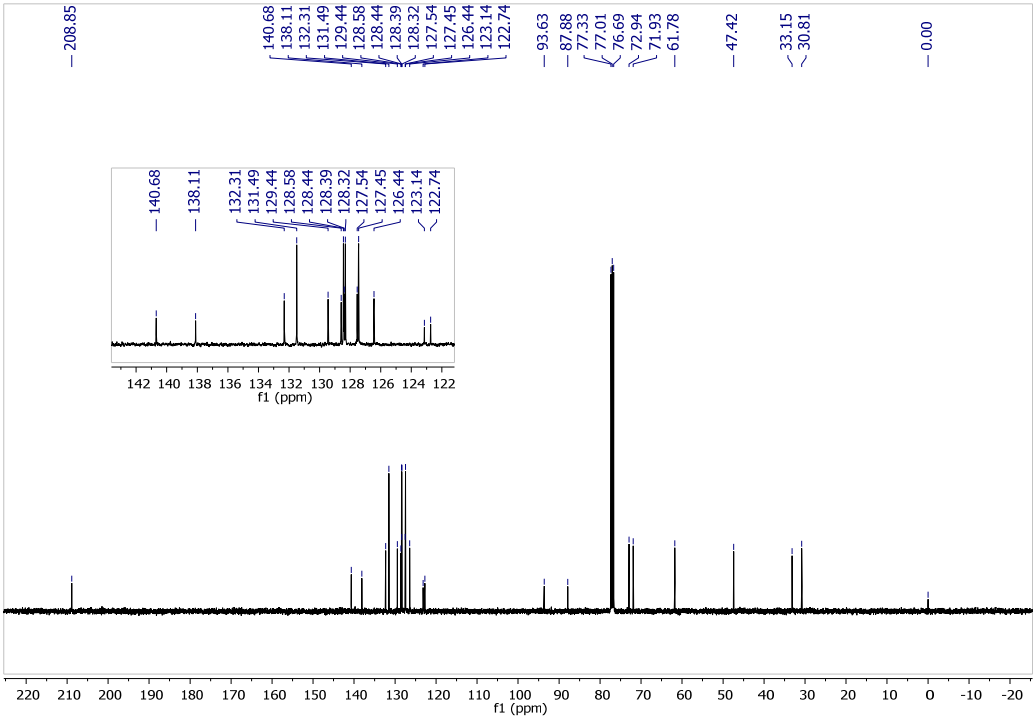


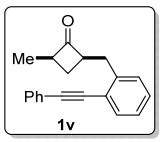




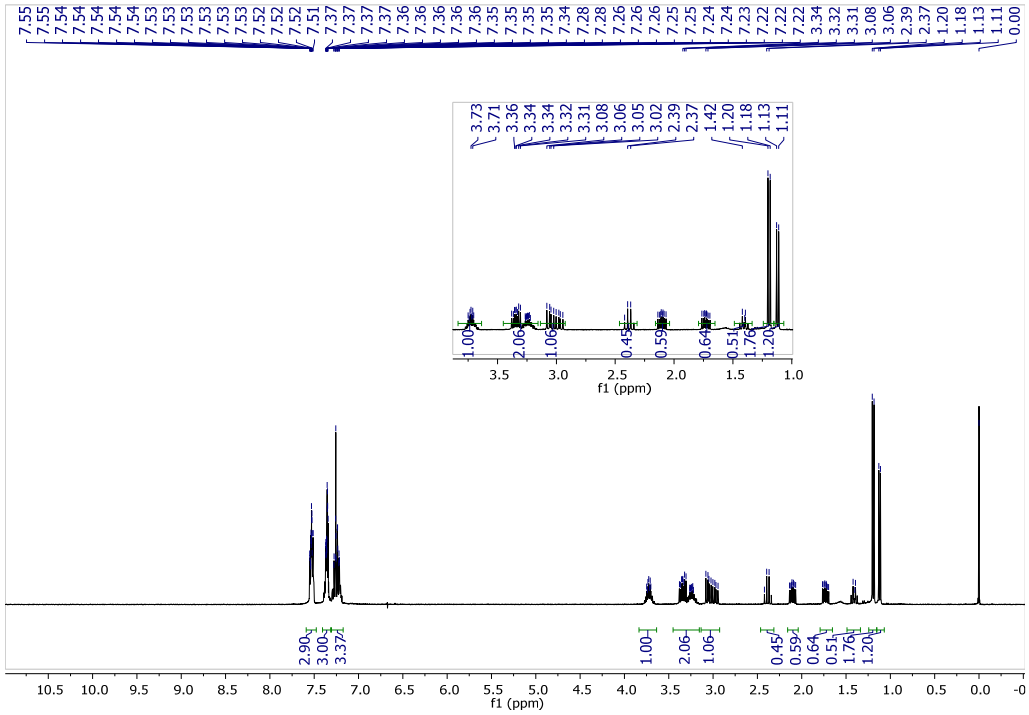
1u (d.r. >20:1)

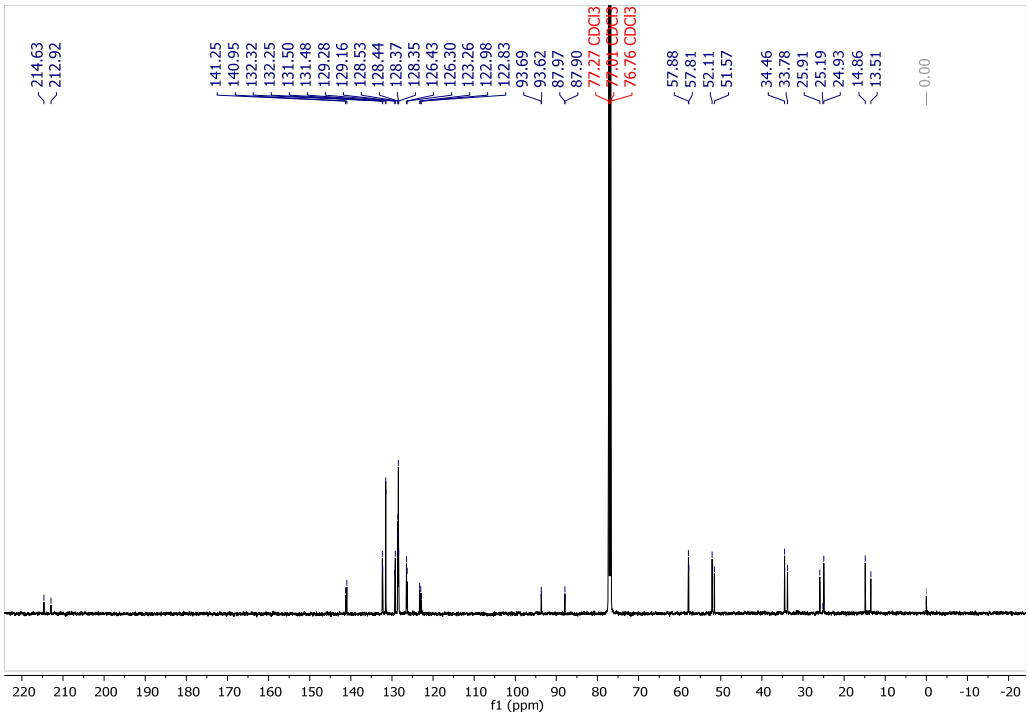


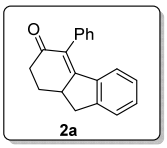


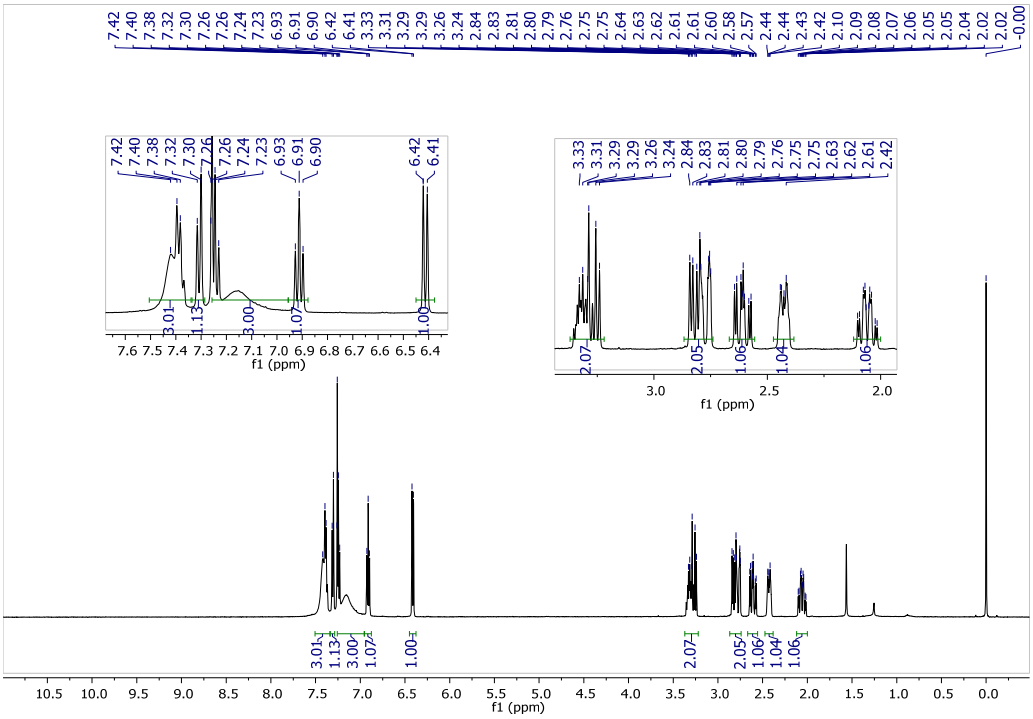


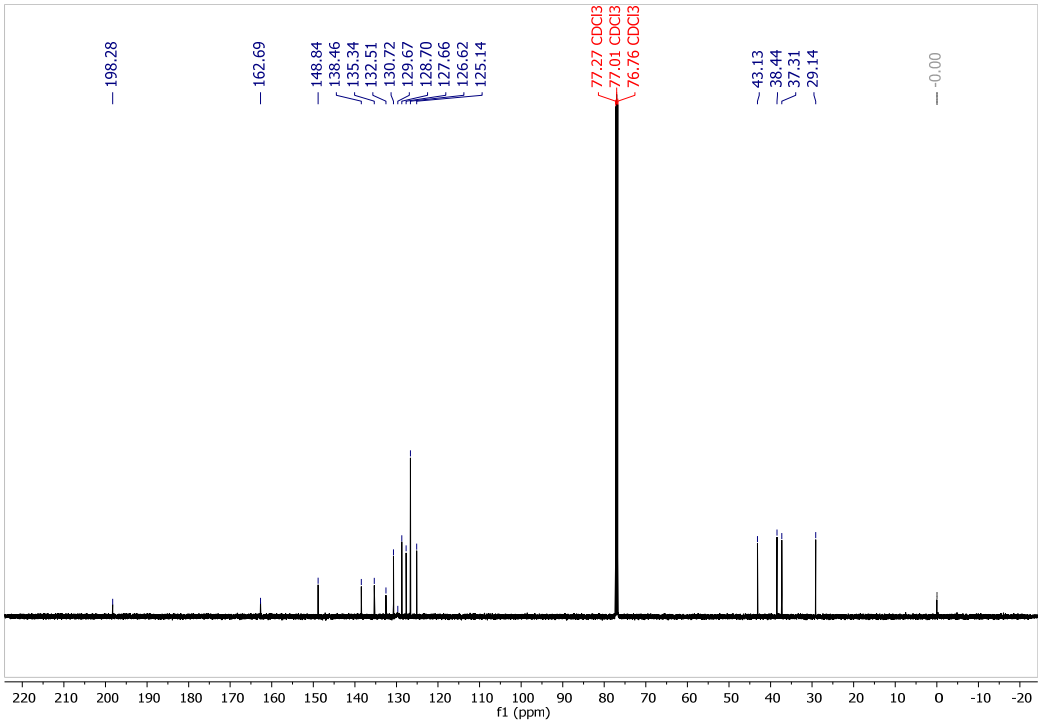
3:2 mixture of diastereomers

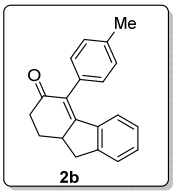


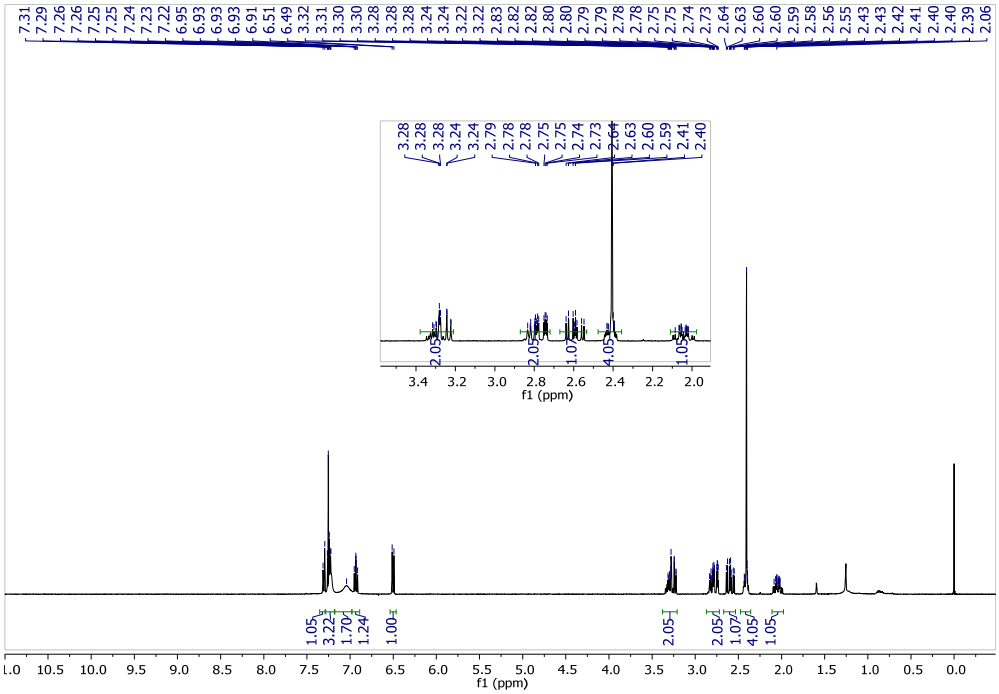


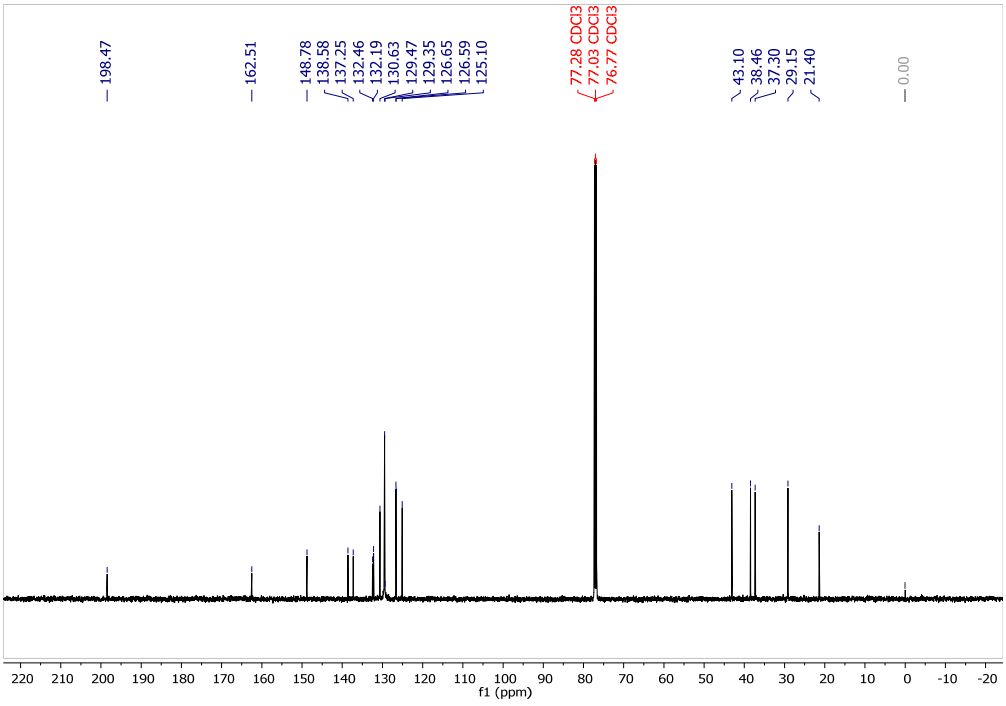

O
Ph
2a

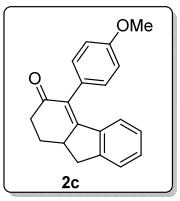

7.42 7.40 7.38 7.32 7.30 7.26 7.26 7.24 7.23 6.93 6.91 6.90 6.42 6.41 3.33 3.31 3.29 3.26 3.24 2.84 2.83 2.81 2.80 2.79 2.76 2.75 2.63 2.62 2.61 2.42 -0.00
3.01 1.13 3.00 1.07 1.00 2.07 2.05 1.06 1.04 1.06
f1 (ppm)

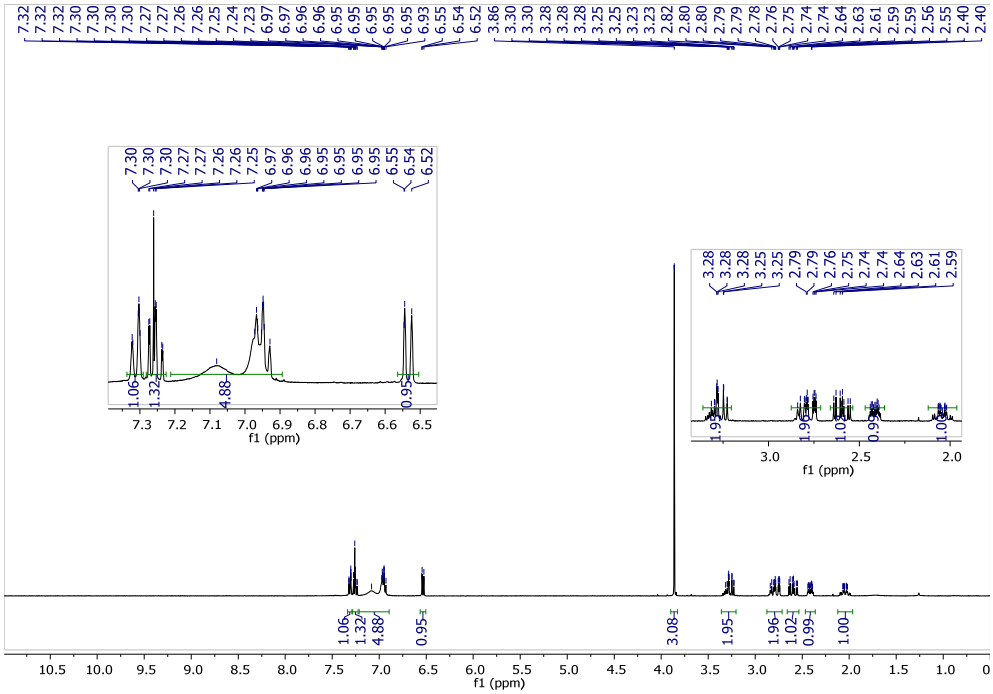

198.28 162.69 148.84 138.46 135.34 132.51 130.72 129.67 128.70 127.66 126.62 125.14 77.27 CDCl3 77.01 CDCl3 76.76 CDCl3 43.13 38.44 37.31 29.14 -0.00
f1 (ppm)

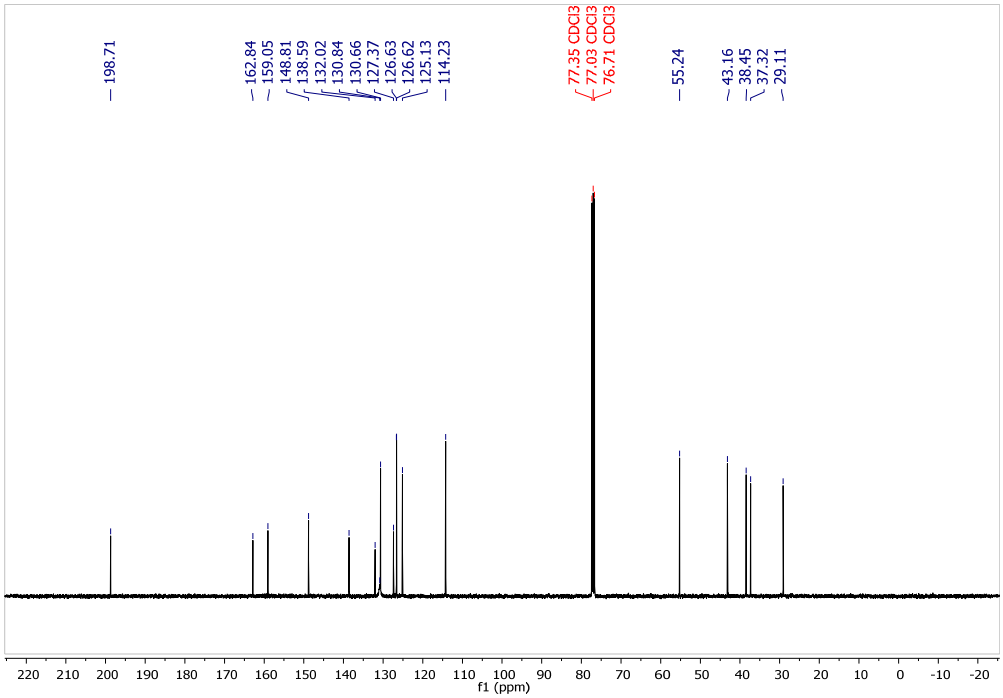

Me
O
2b


7.31 7.29 7.26 7.26 7.25 7.25 7.24 7.23 7.22 6.95 6.93 6.93 6.93 6.91 6.51 6.49 3.32 3.31 3.30 3.30 3.28 3.28 3.28 3.24 3.24 3.22 3.22 2.83 2.82 2.82 2.80 2.80 2.79 2.79 2.78 2.78 2.75 2.75 2.74 2.73 2.64 2.63 2.63 2.60 2.60 2.59 2.58 2.56 2.55 2.43 2.43 2.42 2.41 2.40 2.40 2.39 2.06
3.28 3.28 3.28 3.24 3.24 2.79 2.78 2.78 2.75 2.75 2.74 2.73 2.64 2.63 2.60 2.59 2.41 2.40
2.05 2.05 1.07 4.05 1.05
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)
1.05 3.22 1.70 1.24 1.00 2.05 2.05 1.07 4.05 1.05
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


198.47
162.51
148.78 138.58 137.25 132.46 132.19 130.63 129.47 129.35 126.65 126.59 125.10
77.28 CDCl3 77.03 CDCl3 76.77 CDCl3
43.10 38.46 37.30 29.15 21.40
0.00
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


OMe
O
2c


f1 (ppm)


198.71
162.84
159.05
148.81
138.59
132.02
130.84
130.66
127.37
126.63
126.62
125.13
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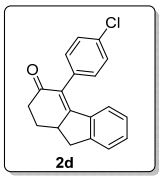
38.45
37.32
29.11
f1 (ppm)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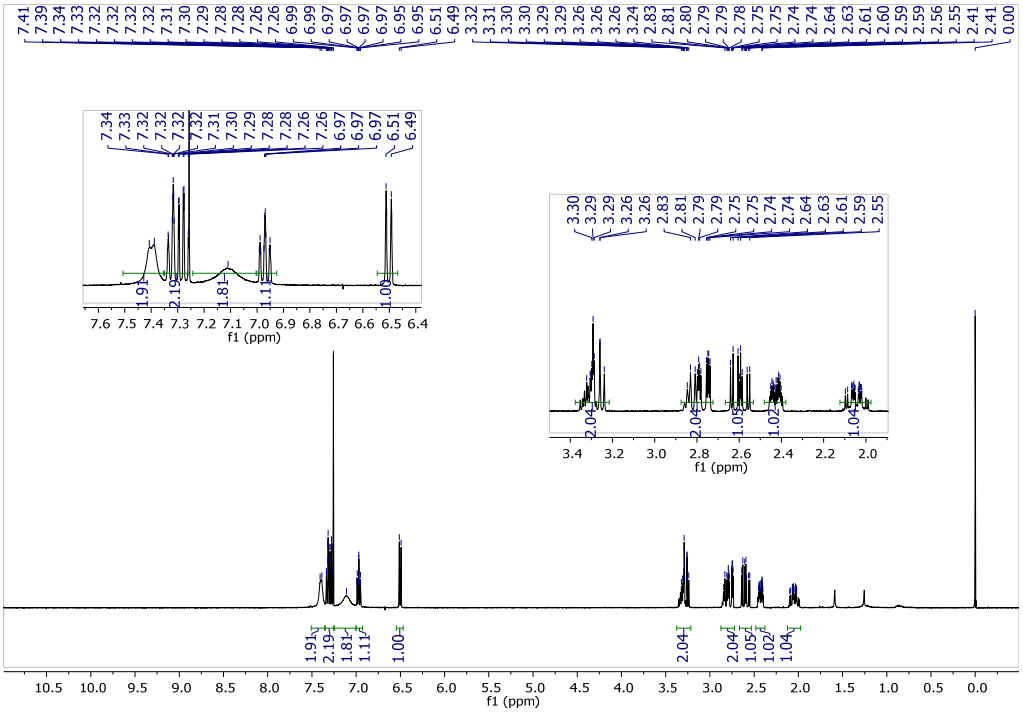
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3.32 3.31 3.30 3.30 3.29 3.29 3.26 3.26 3.24 2.83 2.81 2.80 2.79 2.79 2.78 2.75 2.75 2.74 2.74 2.64 2.63 2.61 2.60 2.59 2.59 2.56 2.55 2.41 2.41 0.00
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2.04 2.04 1.05 1.02 1.04
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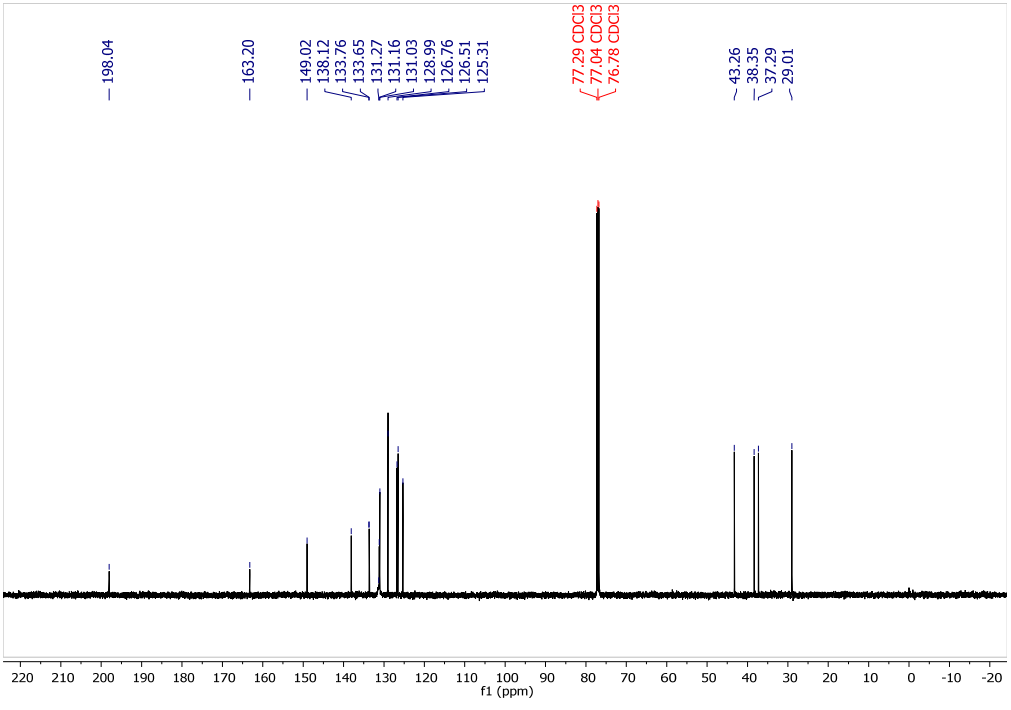
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163.20
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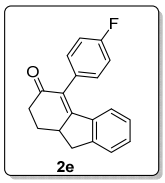
43.26 38.35 37.29 29.01
f1 (ppm)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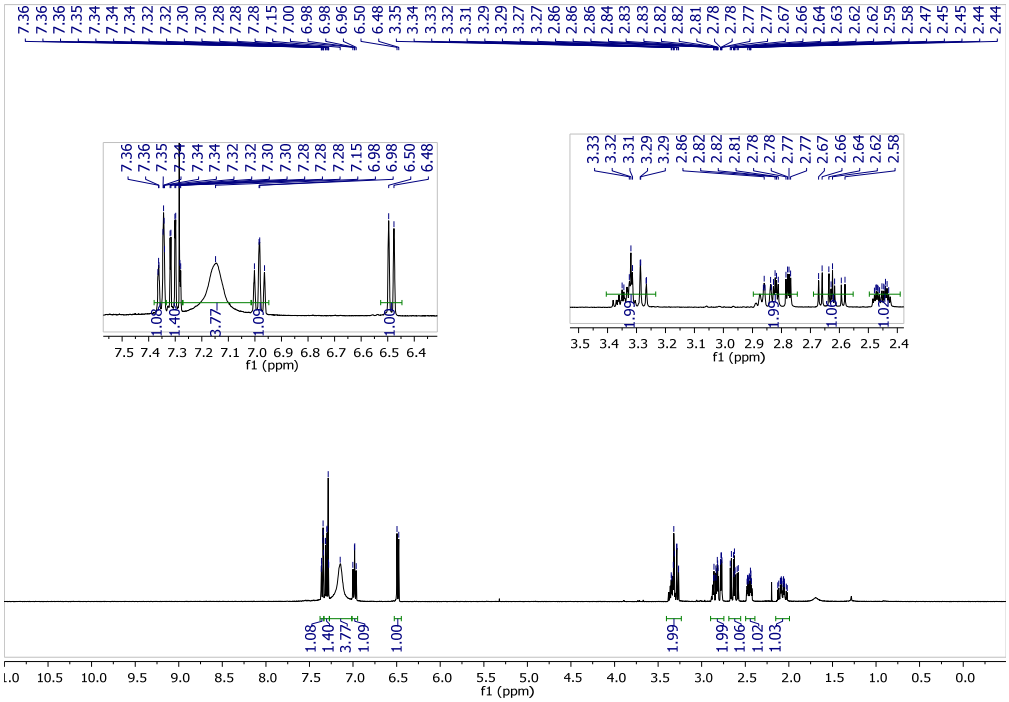
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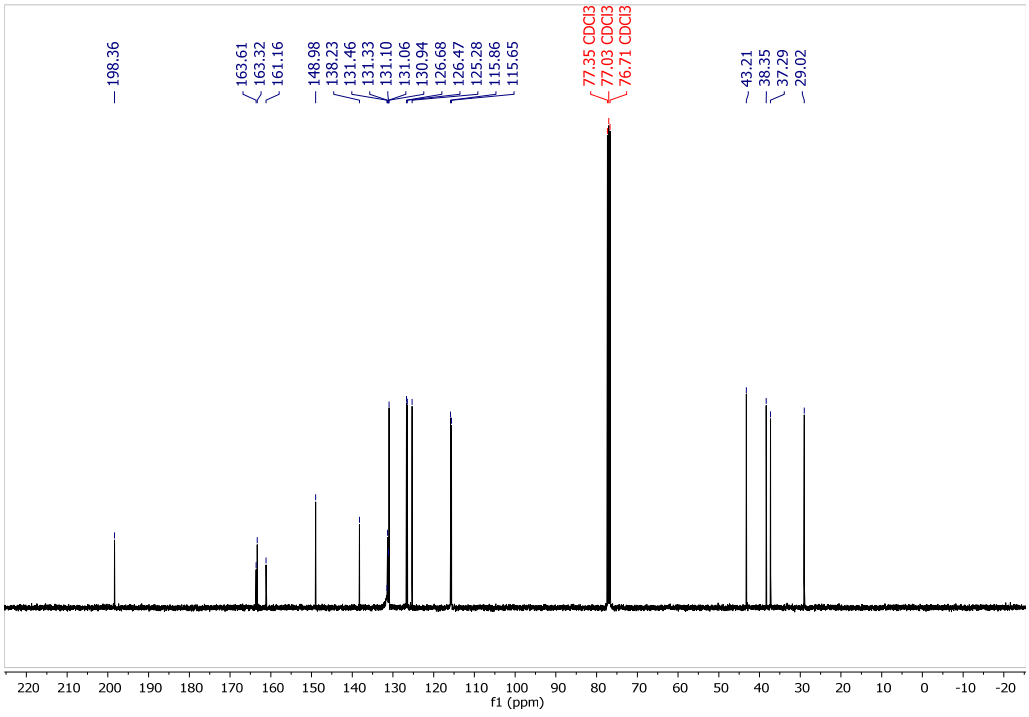
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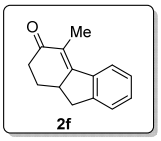
f1 (ppm)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Me
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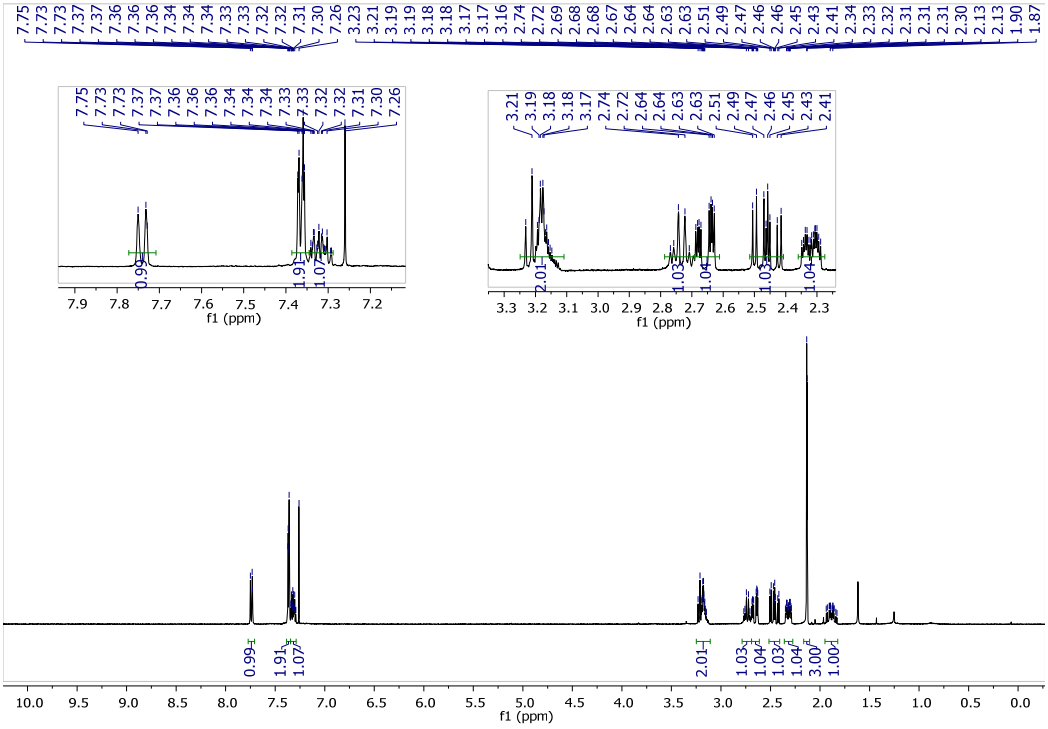
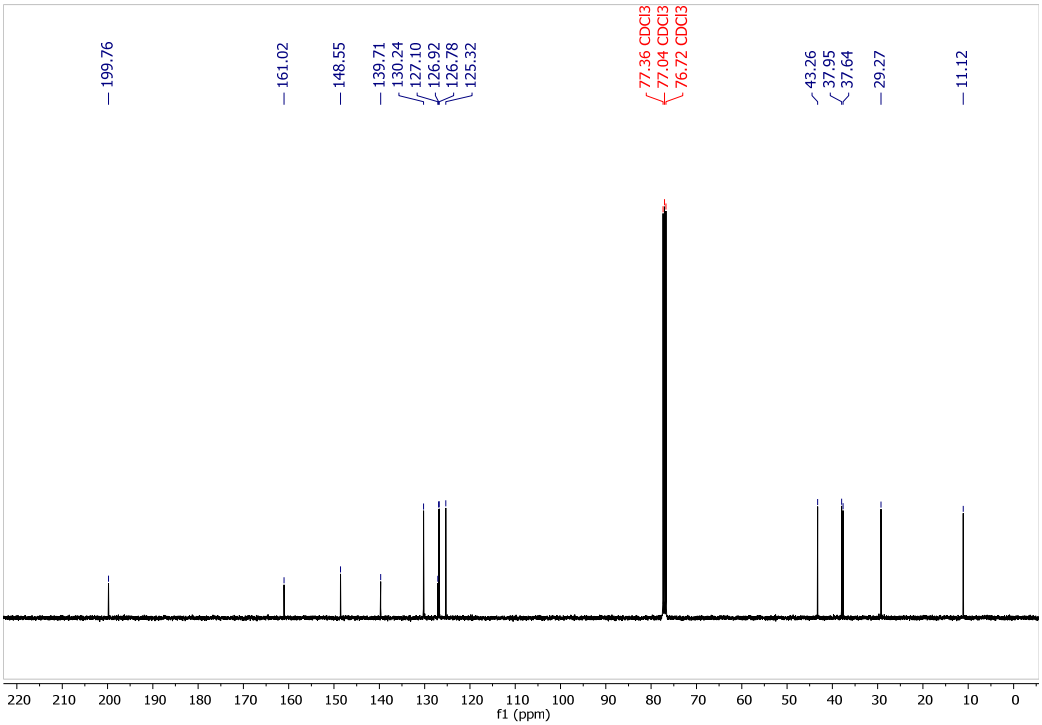

f1 (ppm)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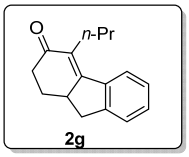
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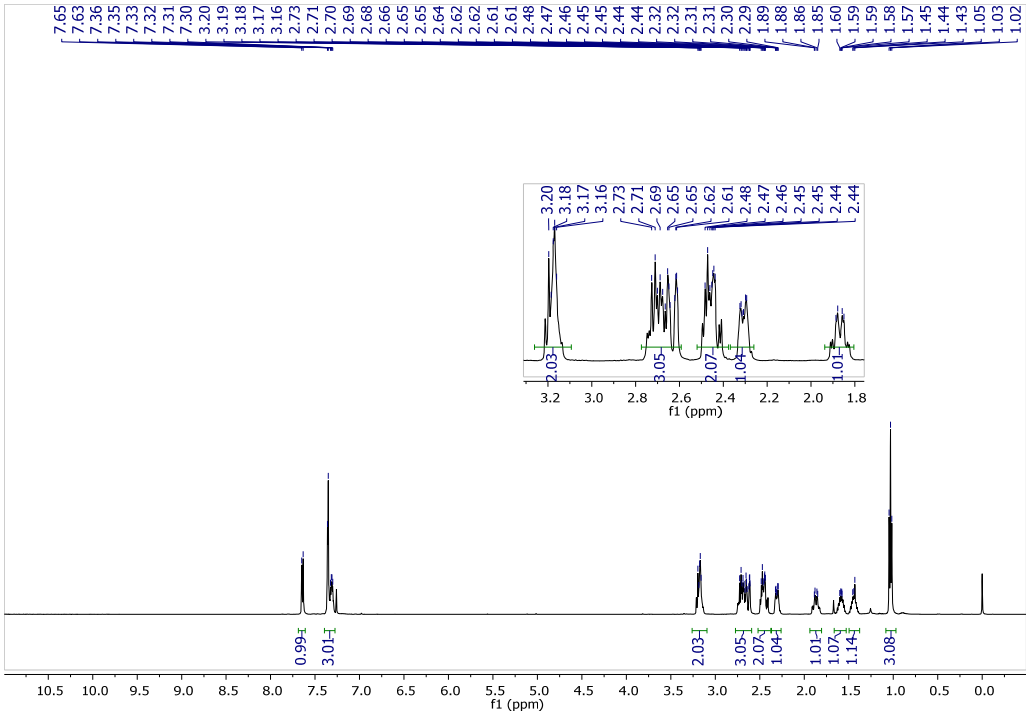
n-Pr
2g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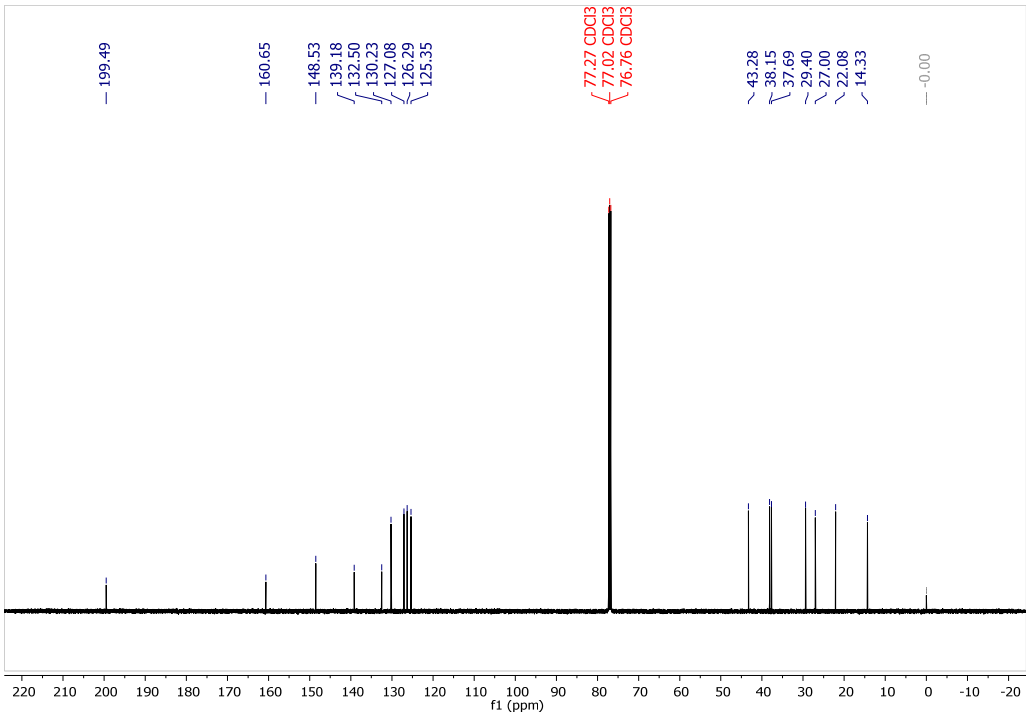
3.20 3.18 3.17 3.16 2.73 2.71 2.69 2.65 2.65 2.62 2.61 2.48 2.47 2.46 2.45 2.45 2.44 2.44
2.03 3.05 2.07 1.04 1.01
f1 (ppm)
0.99 3.01 2.03 3.05 2.07 1.04 1.01 1.07 1.14 3.08
f1 (ppm)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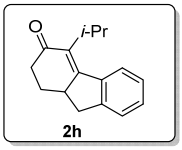
43.28 38.15 37.69 29.40 27.00 22.08 14.33
-0.00
f1 (ppm)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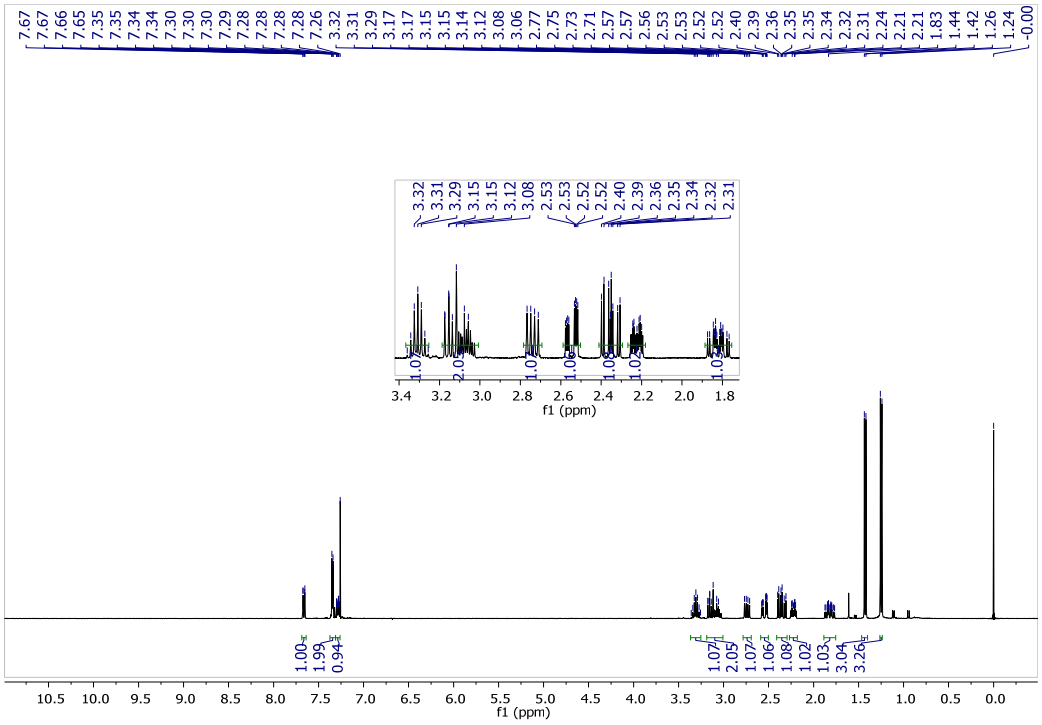
i-Pr
2h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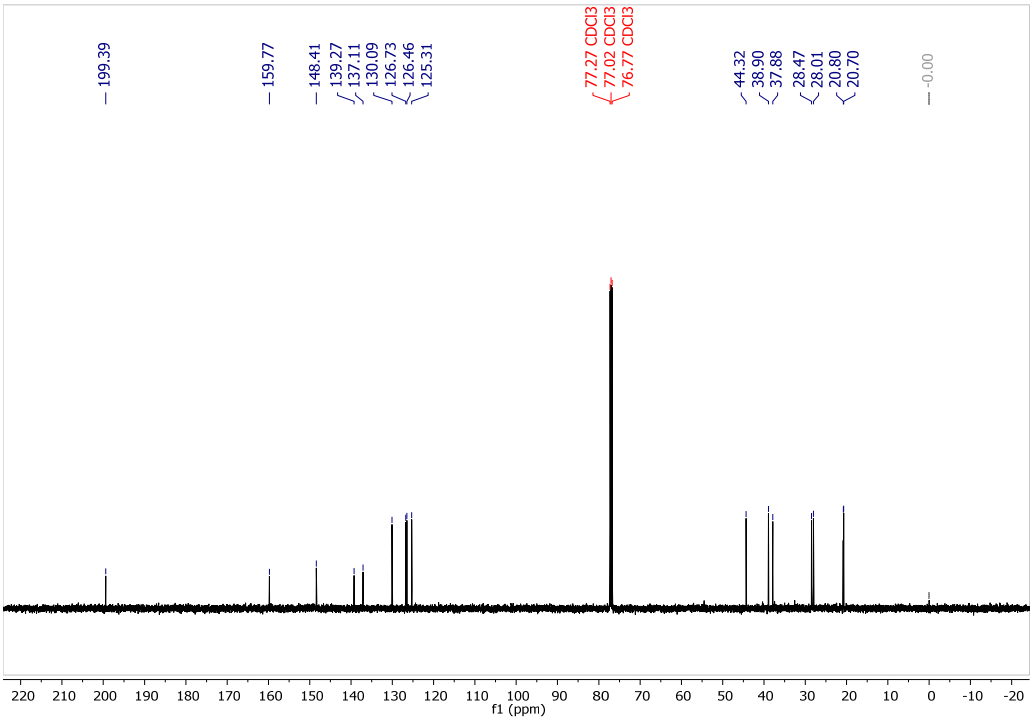
3.32 3.31 3.29 3.15 3.15 3.12 3.08 2.53 2.53 2.52 2.52 2.40 2.39 2.36 2.35 2.34 2.32 2.31
1.00 2.05 1.07 1.06 1.02 1.03
3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)
1.00 1.99 0.94 1.07 2.05 1.07 1.06 1.08 1.02 1.03 3.04 3.26
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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125.31
77.27 CDCl3
77.02 CDCl3
76.77 CDCl3
44.32
38.90
37.88
28.47
28.01
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20.70
-0.00
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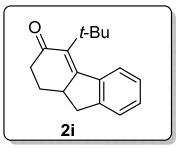
f1 (ppm)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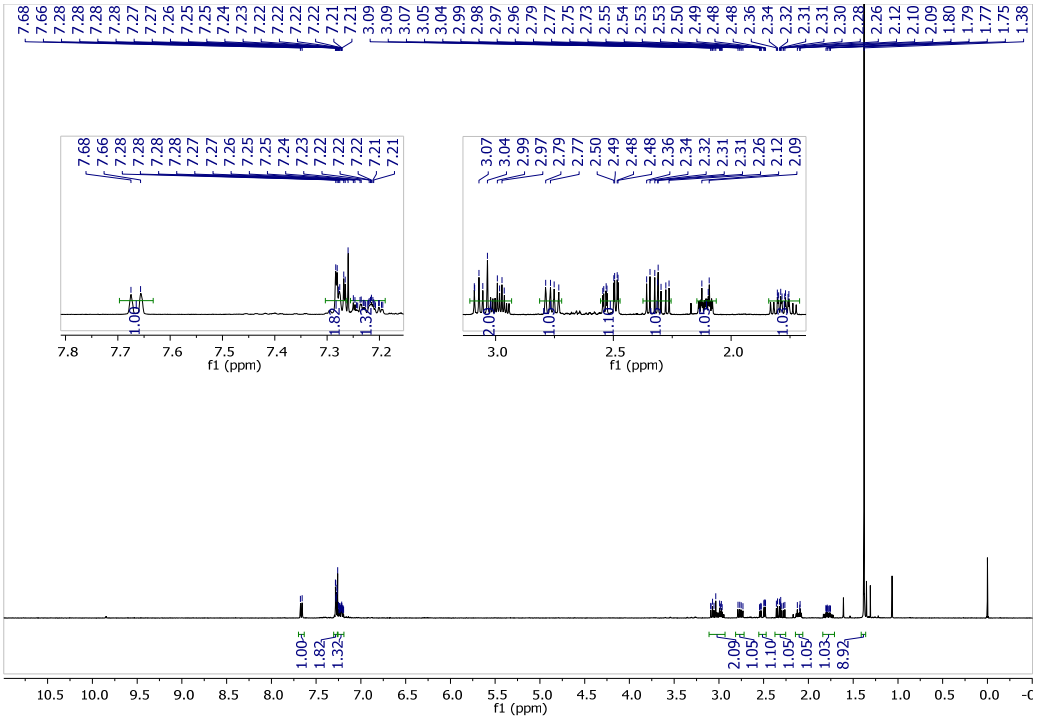
2i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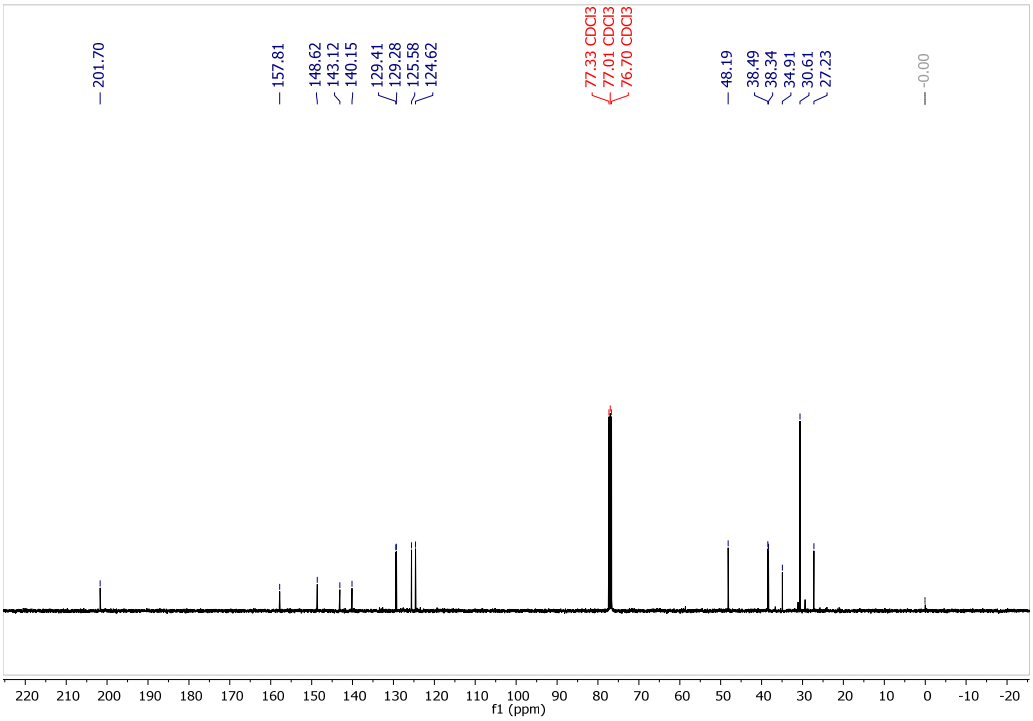
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125.58
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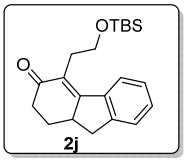
48.19
38.49
38.34
34.91
30.61
27.23
-0.00
f1 (ppm)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O
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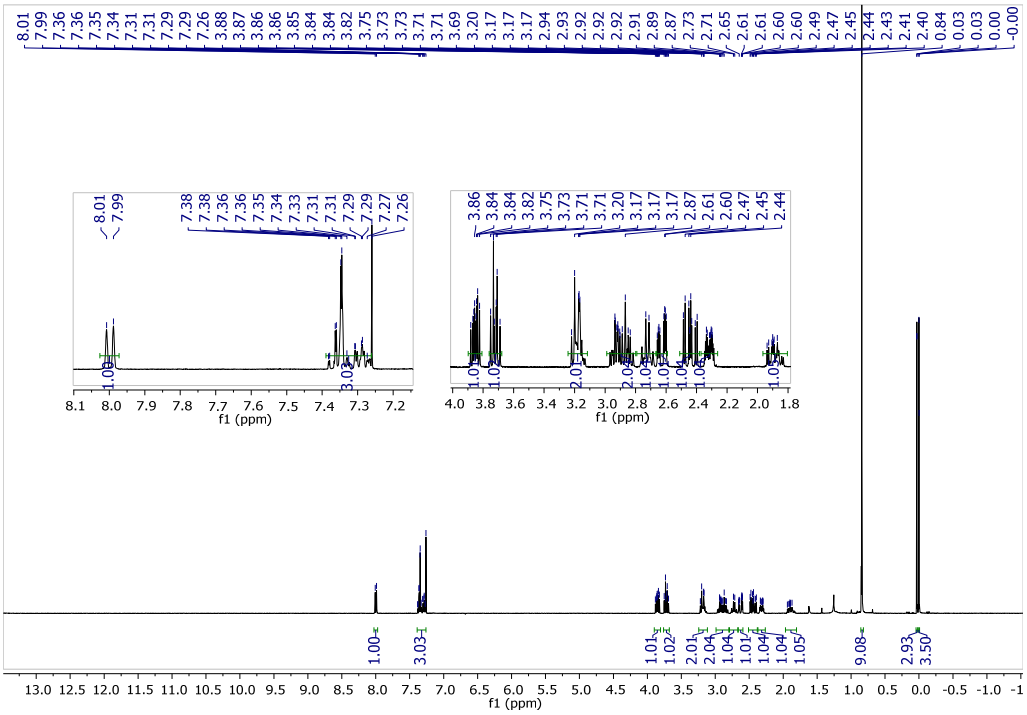
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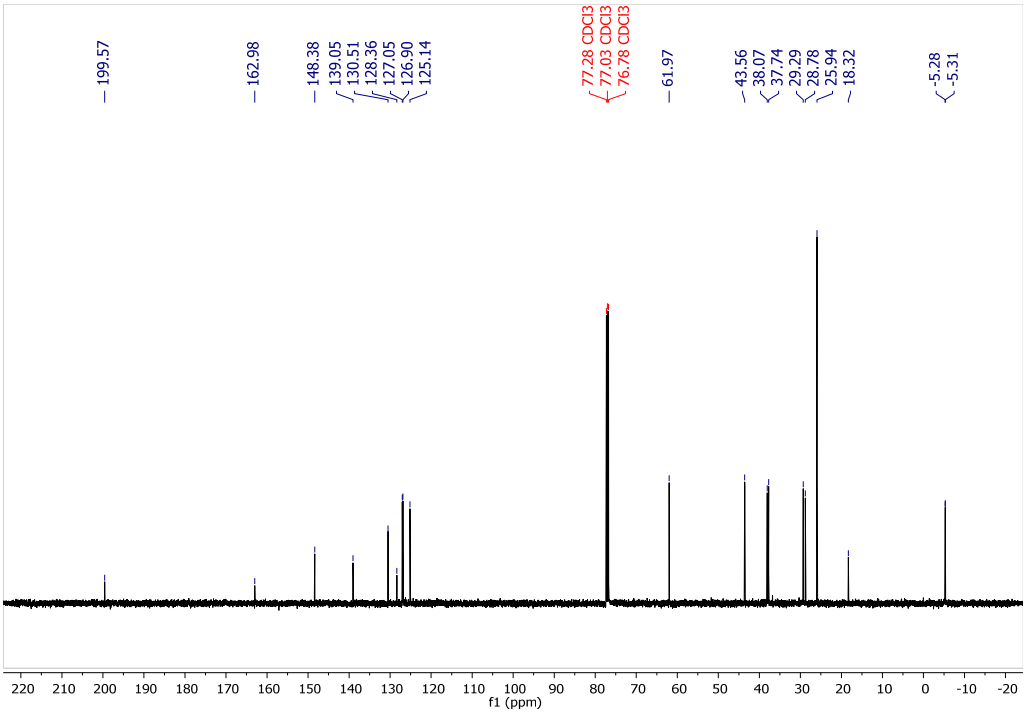
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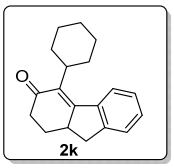
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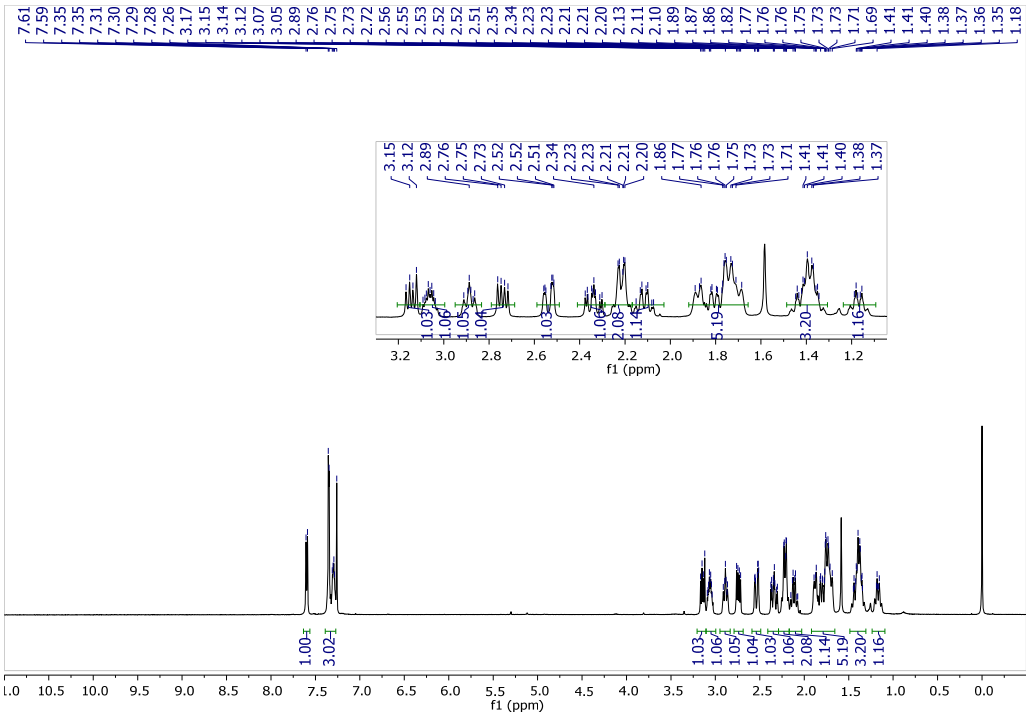
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3.15 3.12 2.89 2.76 2.75 2.73 2.52 2.52 2.51 2.34 2.23 2.23 2.21 2.21 2.20 1.86 1.77 1.76 1.76 1.75 1.73 1.71 1.41 1.41 1.40 1.38 1.37
1.03 1.06 1.05 1.04 1.03 1.06 2.08 1.14 5.19 3.20 1.16
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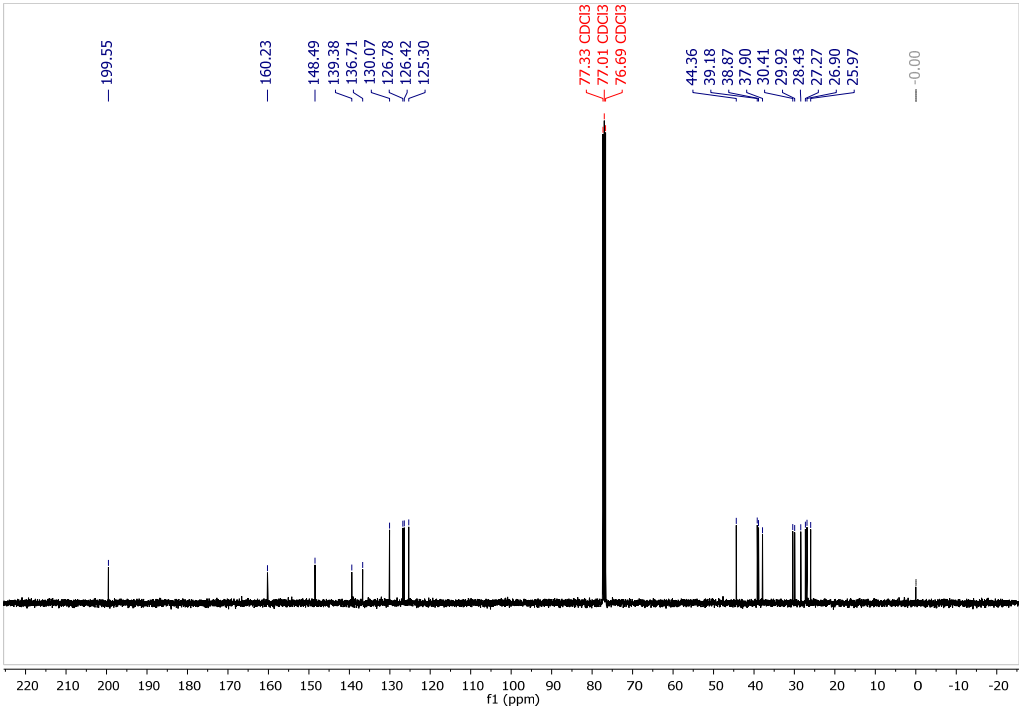
f1 (ppm)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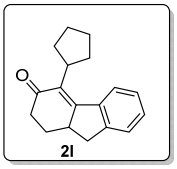
f1 (ppm)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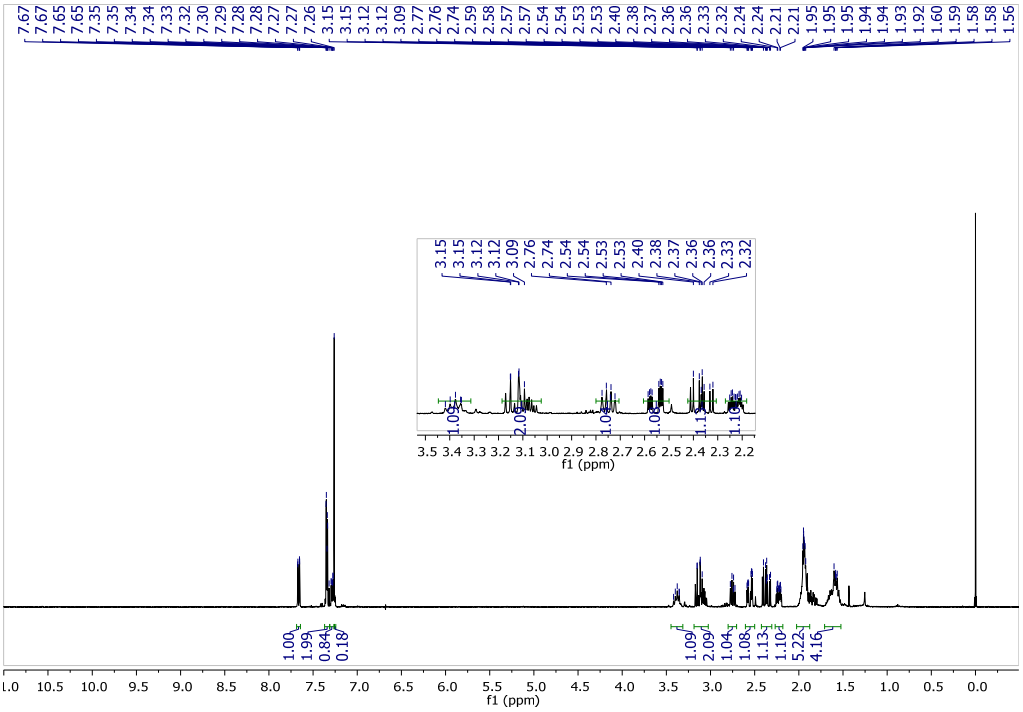
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3.15 3.15 3.12 3.12 3.09 2.76 2.74 2.54 2.54 2.53 2.53 2.40 2.38 2.37 2.36 2.36 2.33 2.32
1.00 2.09 0.84 1.08
3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2
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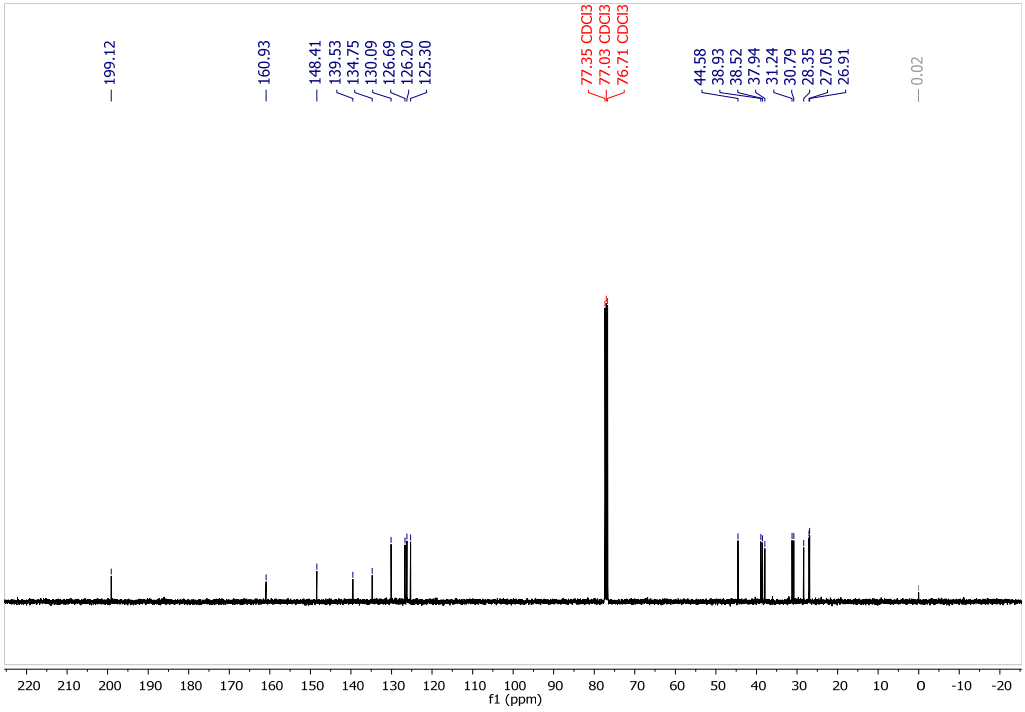
f1 (ppm)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76.71 CDCl3
44.58
38.93
38.52
37.94
31.24
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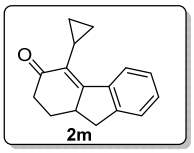
f1 (ppm)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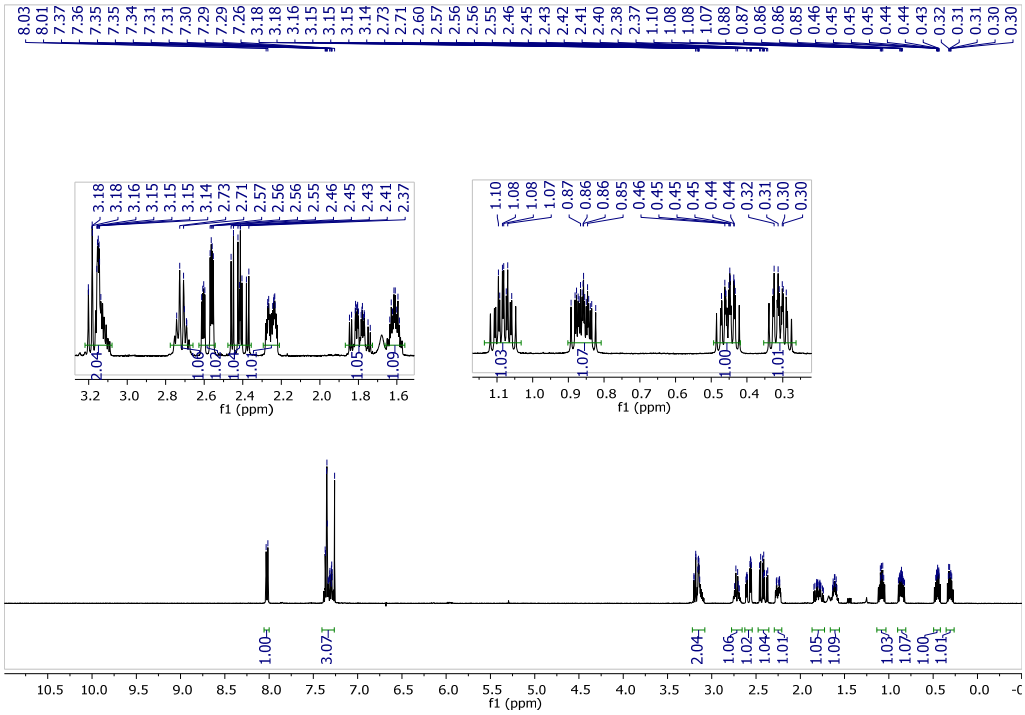
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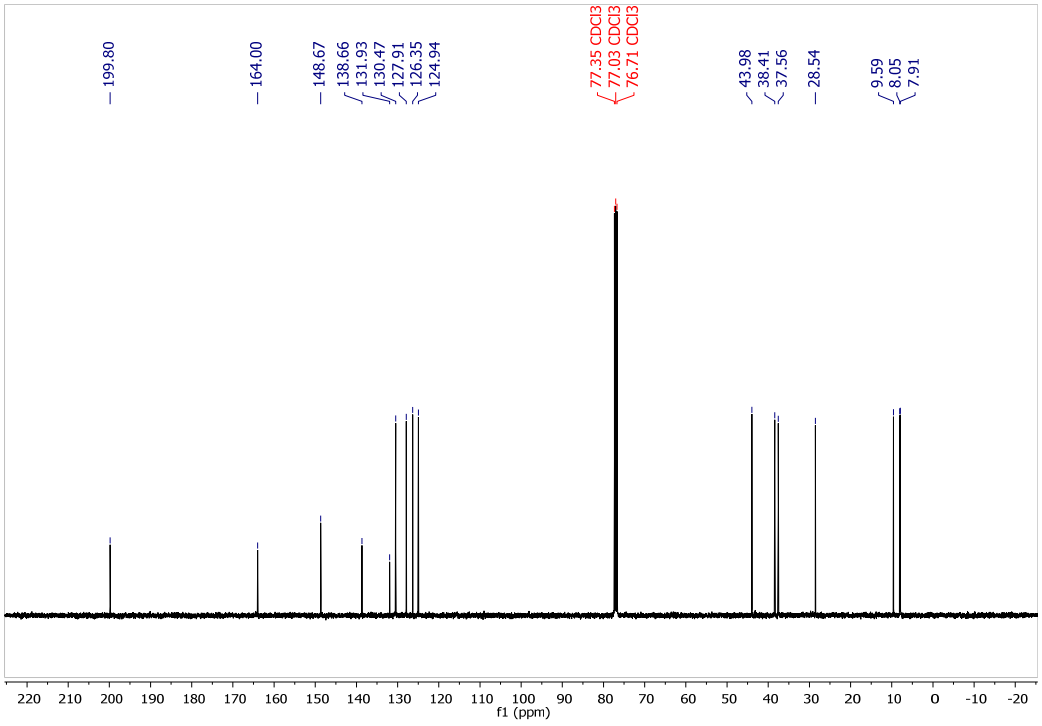
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77.35 CDCl3
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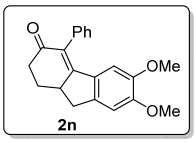
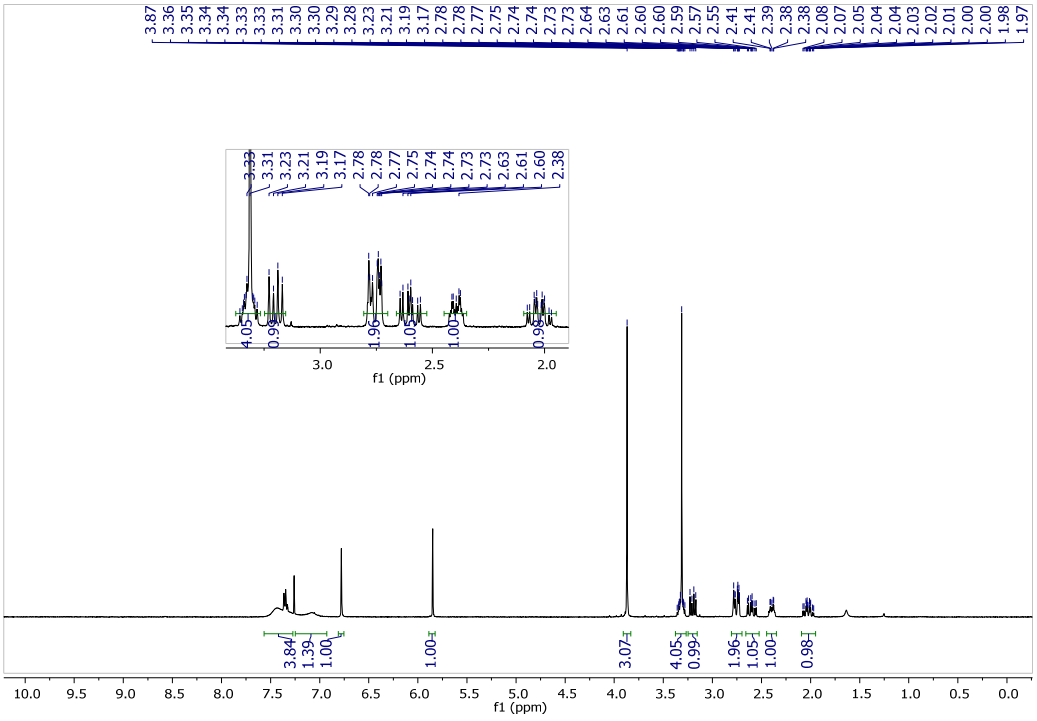
43.98
38.41
37.56
28.54
9.59
8.05
7.91
f1 (ppm)


O
Ph
OMe
OMe
2n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3.33 3.31 3.23 3.21 3.19 3.17 2.78 2.78 2.77 2.75 2.74 2.74 2.73 2.73 2.63 2.61 2.60 2.38
4.05 0.99 1.96 1.05 1.00 0.98
3.0 2.5 2.0
f1 (ppm)
3.84 1.39 1.00 1.00 3.07 4.05 0.99 1.96 1.05 1.00 0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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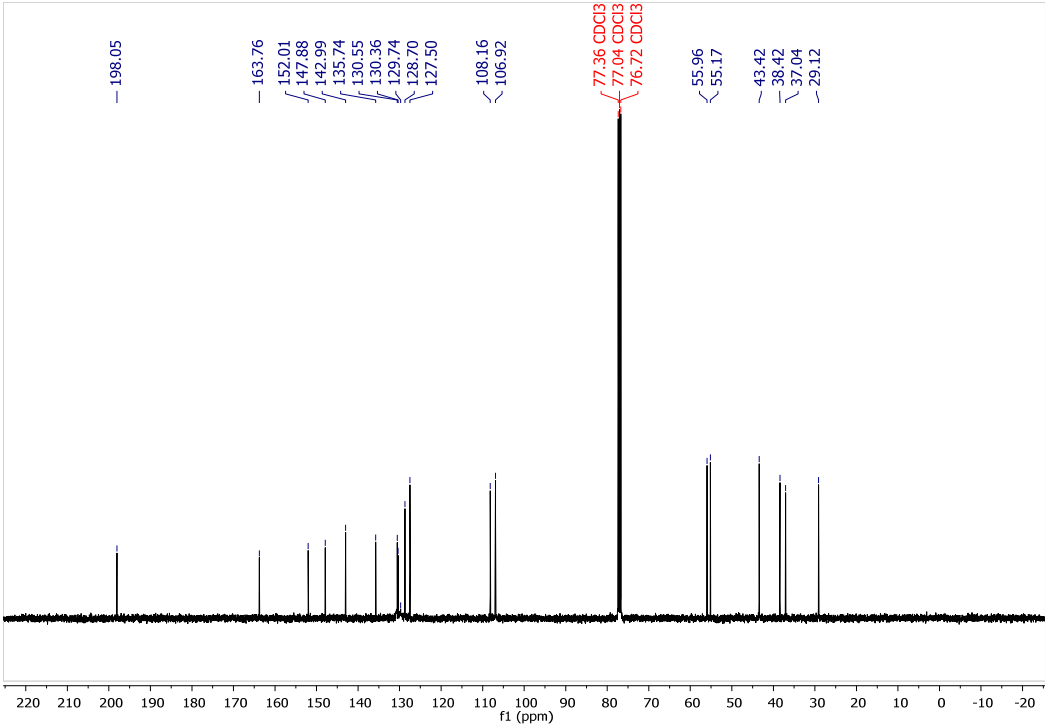
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108.16 106.92
77.36 CDCl3 77.04 CDCl3 76.72 CDCl3
55.96 55.17
43.42 38.42 37.04 29.12
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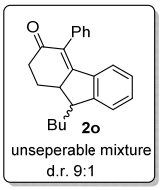
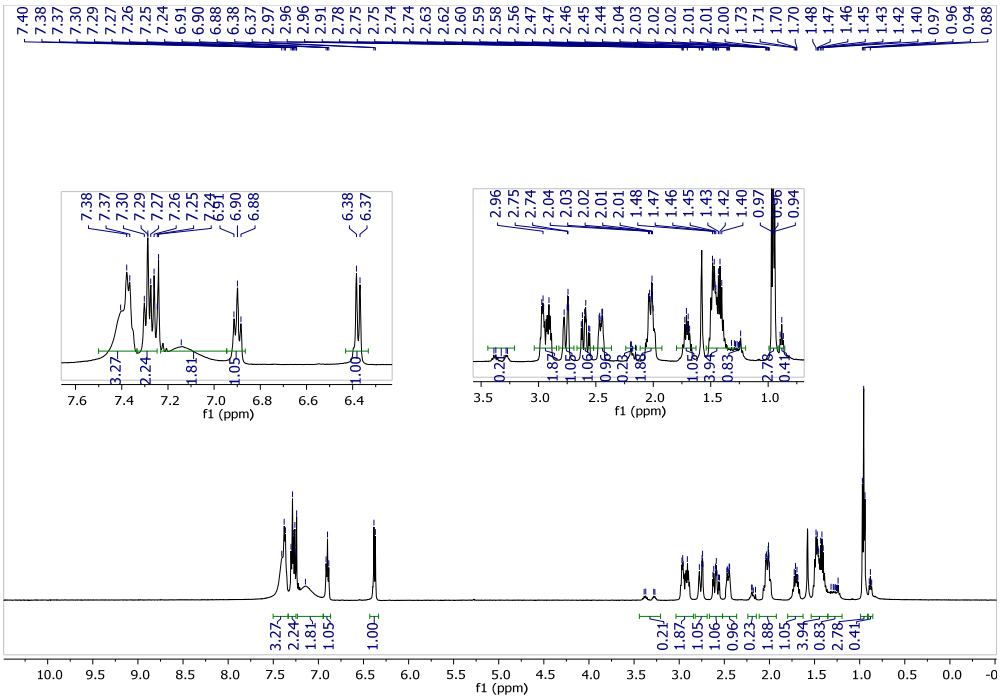
f1 (ppm)


O
Ph
Bu
2o
unseperable mixture
d.r. 9:1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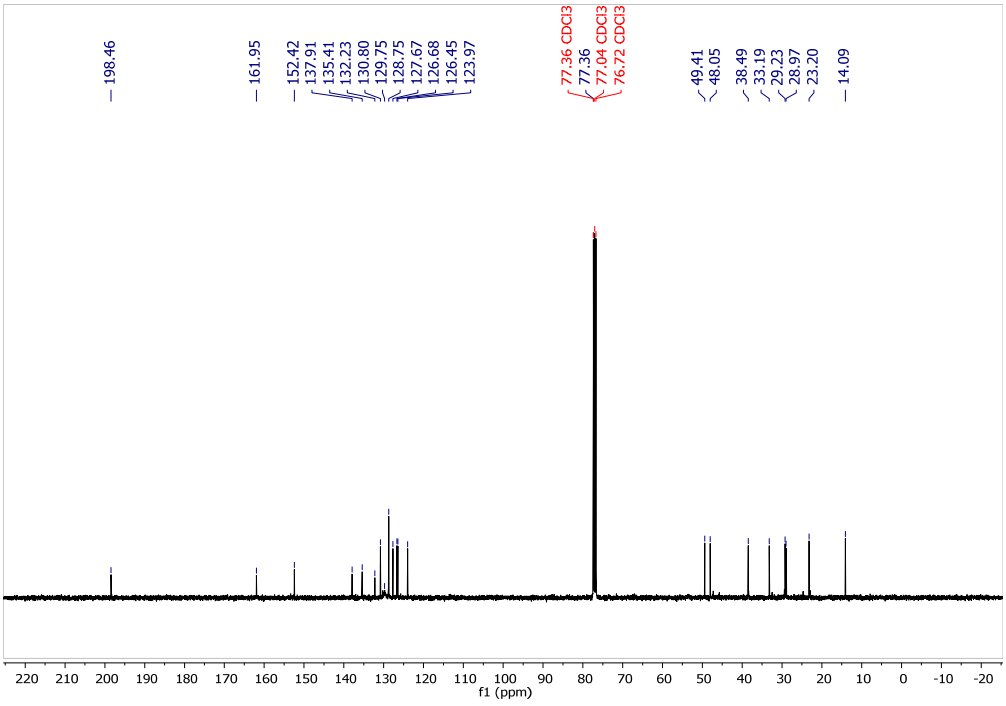
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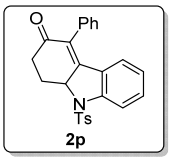
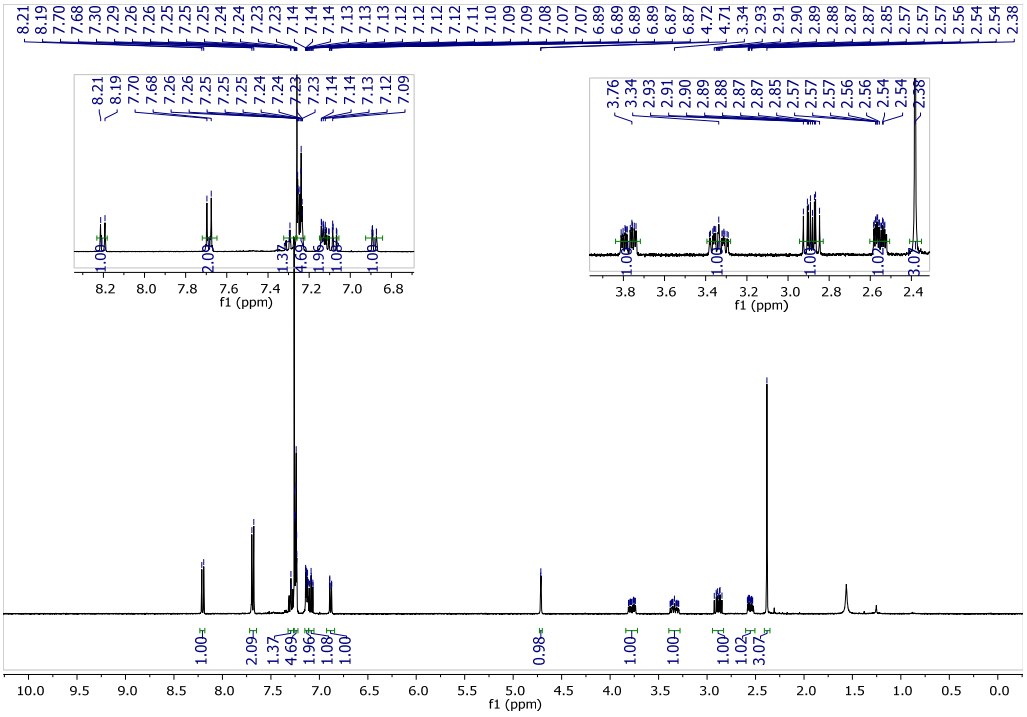
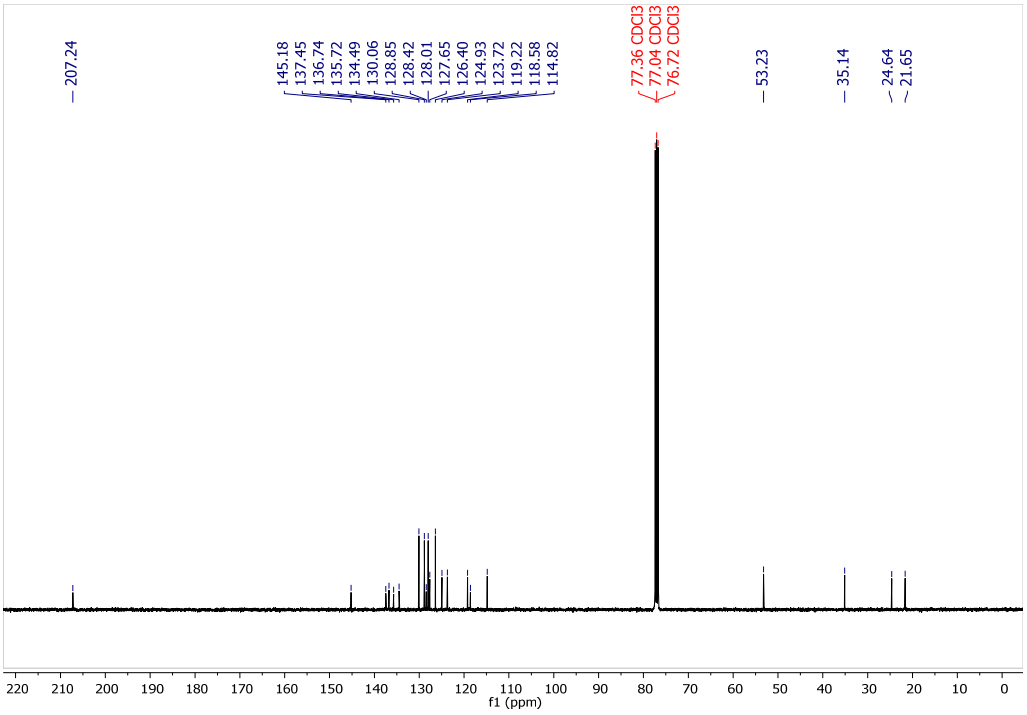
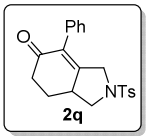
49.41
48.05
38.49
33.19
29.23
28.97
23.20
14.09
f1 (ppm)

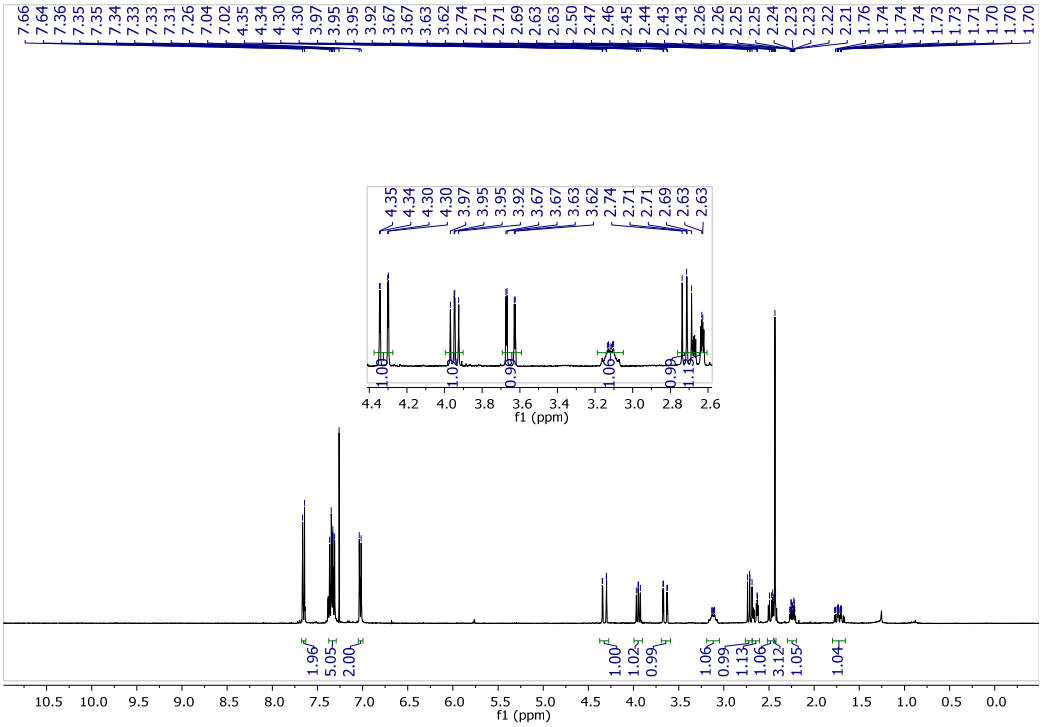

O
Ph
N
Ts

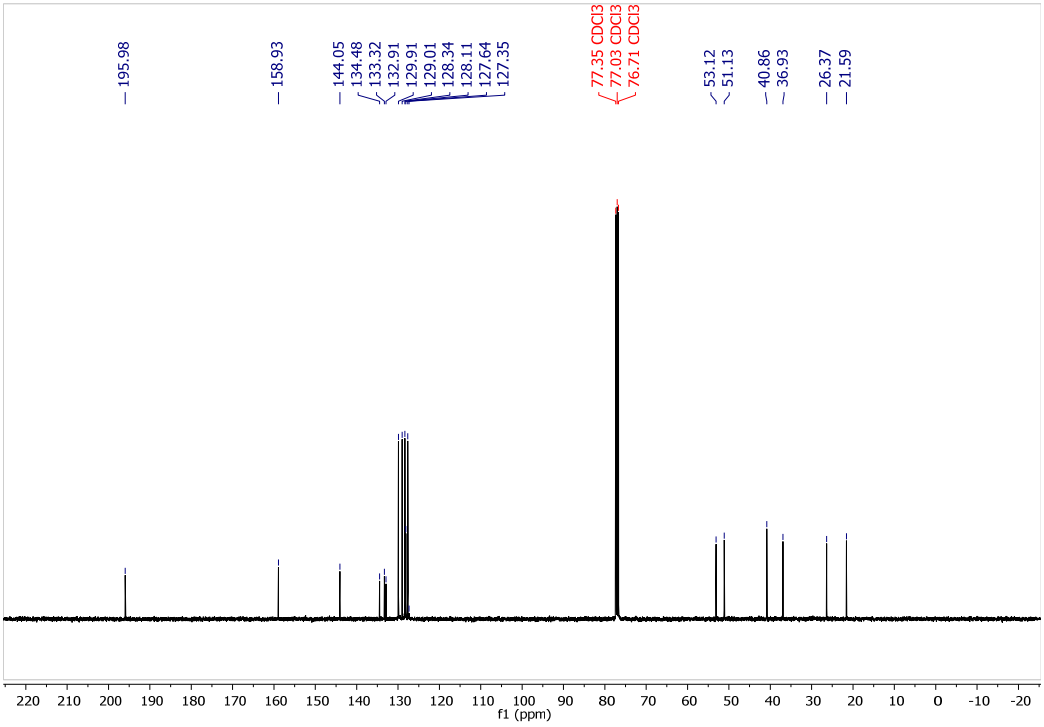
2p

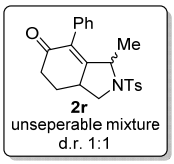

f1 (ppm)

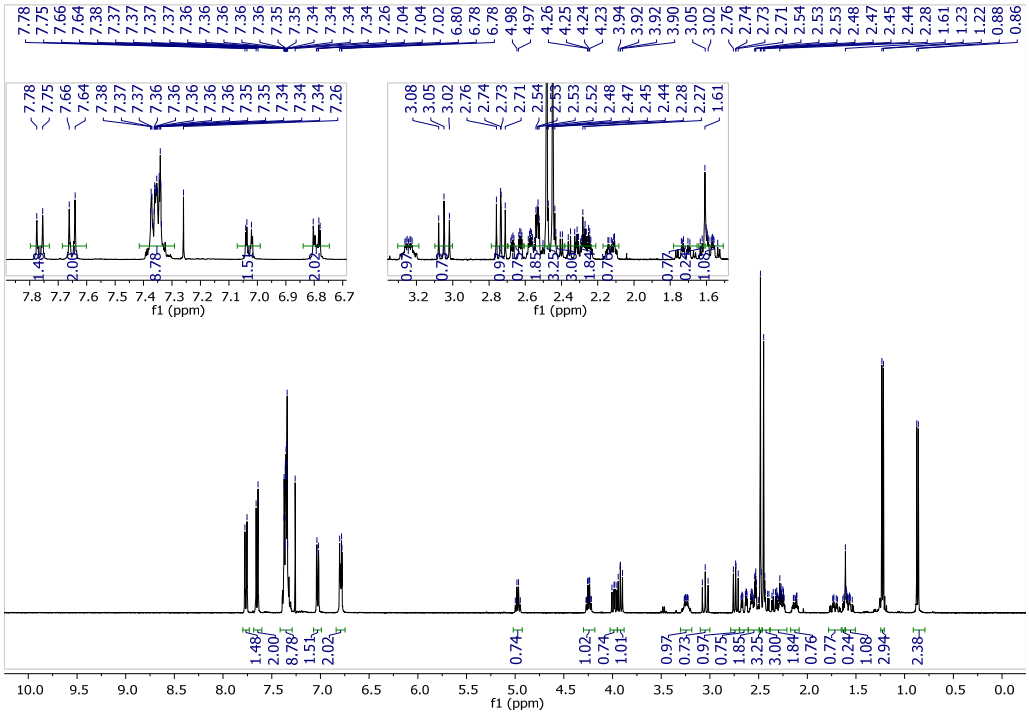

207.24
145.18
137.45
136.74
135.72
134.49
130.06
128.85
128.42
128.01
127.65
126.40
124.93
123.72
119.22
118.58
114.82
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
53.23
35.14
24.64
21.65
f1 (ppm)

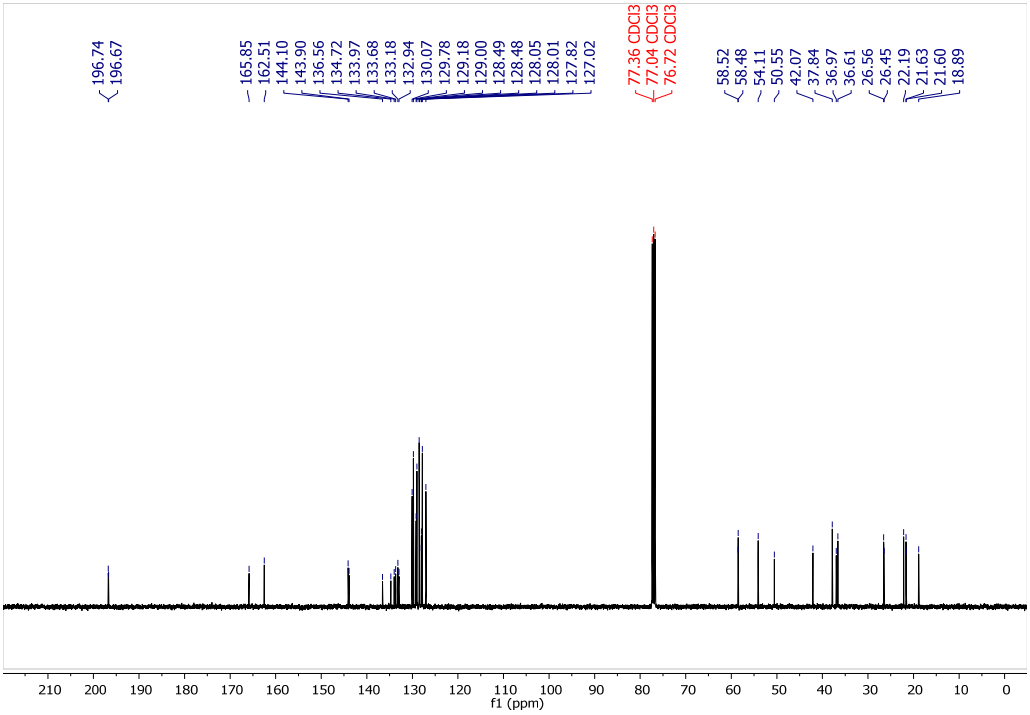

Ph
O
NTs
2q

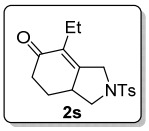

7.66 7.64 7.36 7.35 7.35 7.34 7.33 7.33 7.31 7.26 7.04 7.02 4.35 4.34 4.30 4.30 3.97 3.95 3.95 3.92 3.67 3.63 3.62 2.74 2.71 2.71 2.69 2.63 2.63 2.50 2.47 2.46 2.45 2.44 2.43 2.43 2.26 2.25 2.25 2.24 2.23 2.23 2.22 2.21 1.76 1.74 1.74 1.74 1.73 1.73 1.71 1.70 1.70 1.70
4.35 4.34 4.30 4.30 3.97 3.95 3.95 3.92 3.67 3.67 3.63 3.62 2.74 2.71 2.71 2.69 2.63 2.63
1.00 1.02 0.99 1.06 0.99 1.13
4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6
f1 (ppm)
1.96 5.05 2.00 1.00 1.02 0.99 1.06 0.99 1.13 1.06 3.12 1.05 1.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

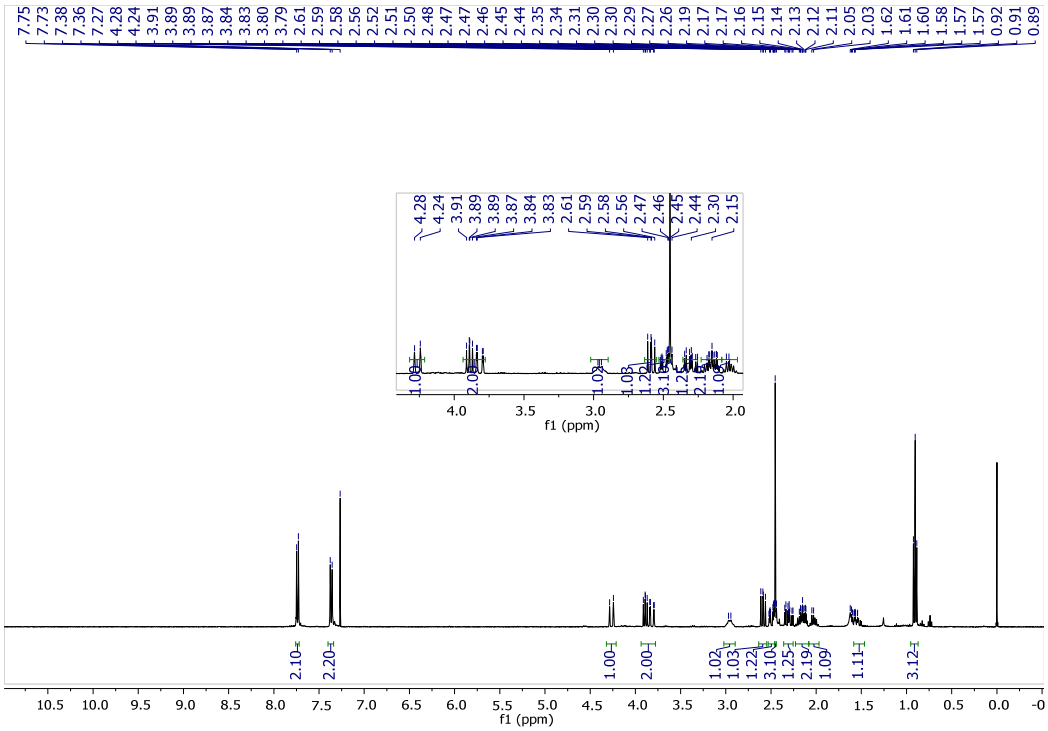

195.98
158.93
144.05
134.48
133.32
132.91
129.91
129.01
128.34
128.11
127.64
127.35
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
53.12
51.13
40.86
36.93
26.37
21.59
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

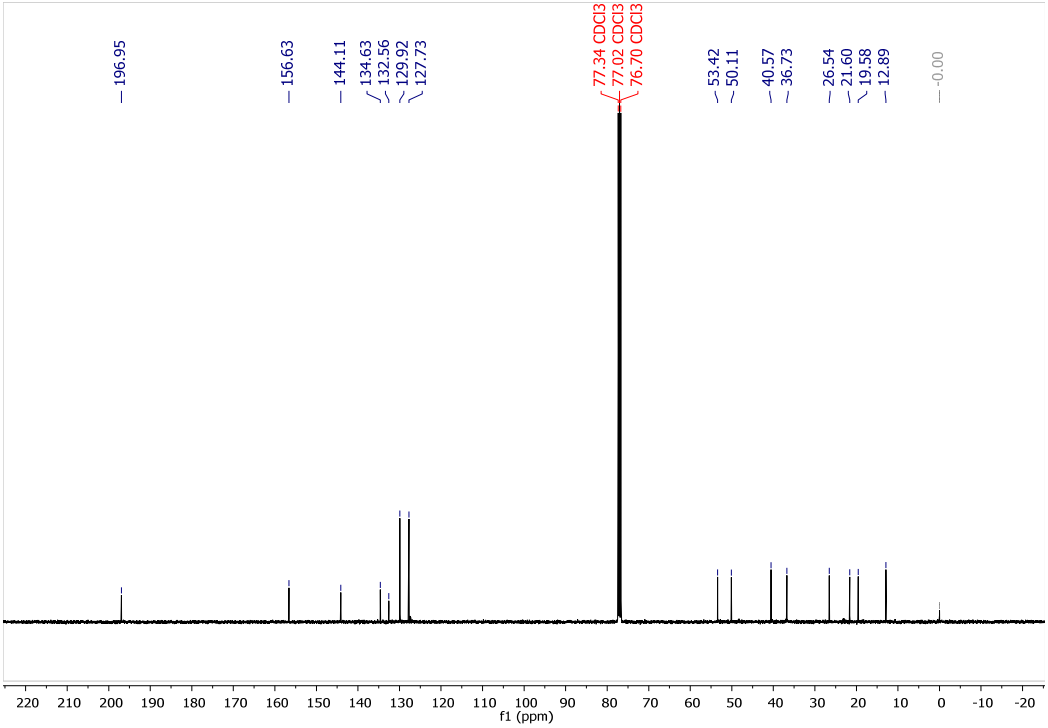

Ph
O
Me
NTs
2r
unseperable mixture
d.r. 1:1

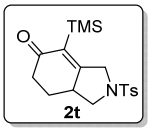

f1 (ppm)

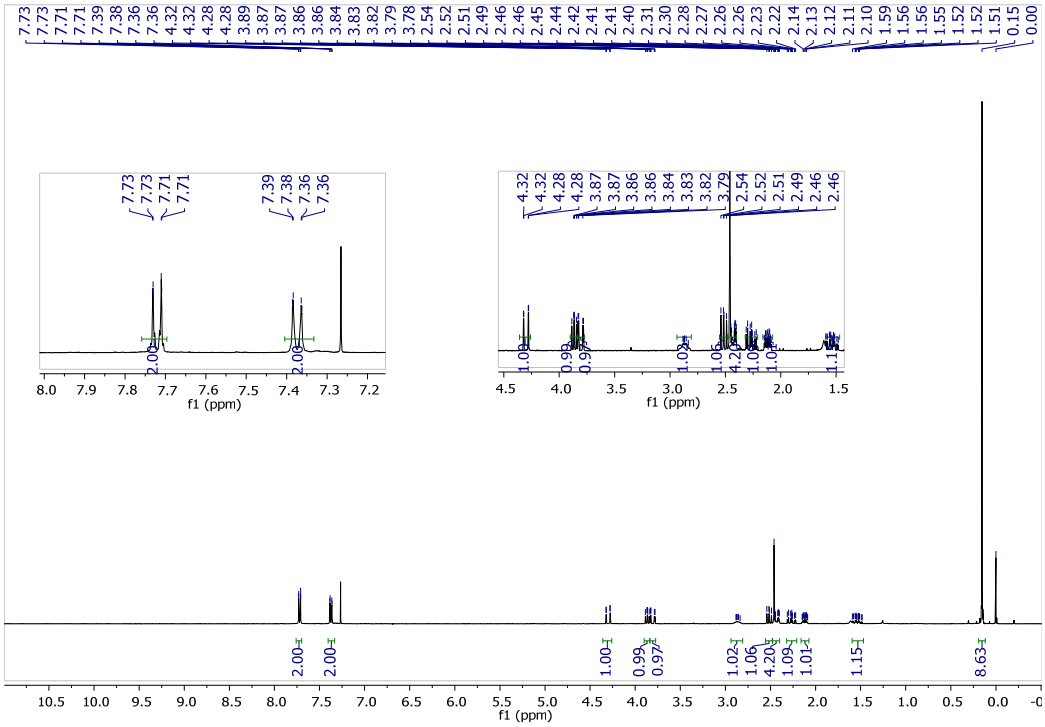

77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
f1 (ppm)

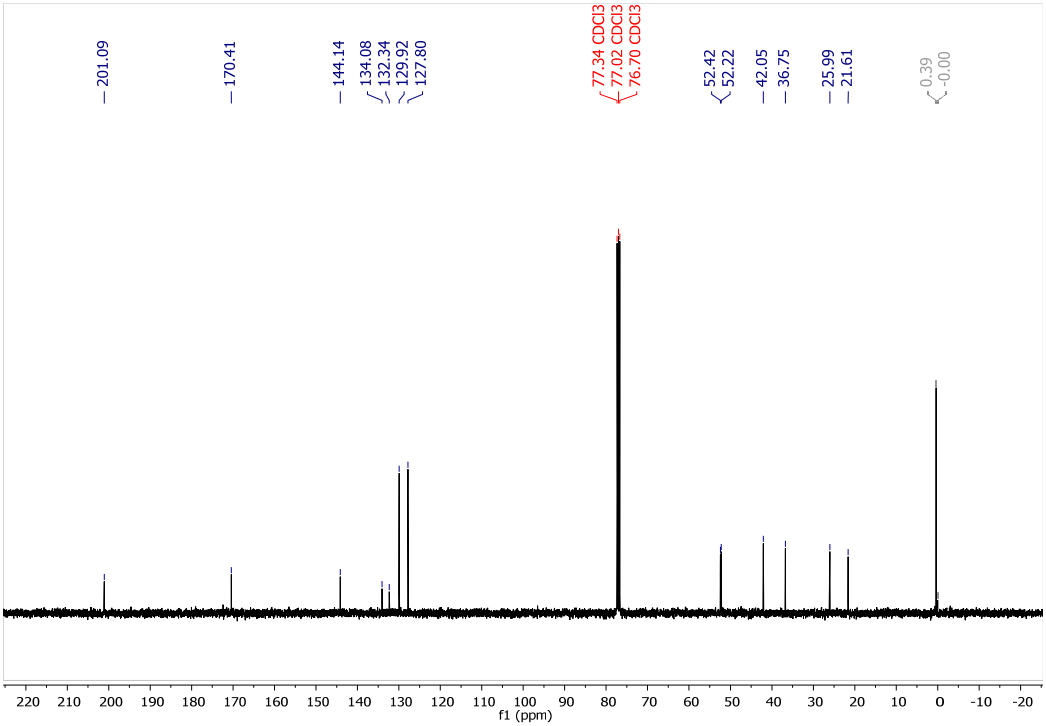

Et
O
NTs
2s

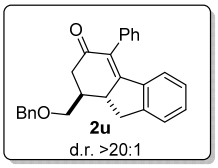

7.75 7.73 7.38 7.36 7.27 4.28 4.24 3.91 3.89 3.89 3.87 3.84 3.83 3.80 3.79 2.61 2.59 2.58 2.56 2.52 2.51 2.50 2.48 2.47 2.47 2.46 2.45 2.44 2.35 2.34 2.31 2.30 2.30 2.29 2.27 2.26 2.19 2.17 2.17 2.16 2.15 2.14 2.13 2.12 2.11 2.05 2.03 1.62 1.61 1.60 1.58 1.57 1.57 0.92 0.91 0.89
4.28 4.24 3.91 3.89 3.89 3.87 3.84 3.83 2.61 2.59 2.58 2.56 2.47 2.46 2.45 2.44 2.30 2.15
1.06 2.05 1.03 1.05 1.22 3.15 2.19 1.04
4.0 3.5 3.0 2.5 2.0
f1 (ppm)
2.10 2.20 1.00 2.00 1.02 1.03 1.22 3.10 1.25 2.19 1.09 1.11 3.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

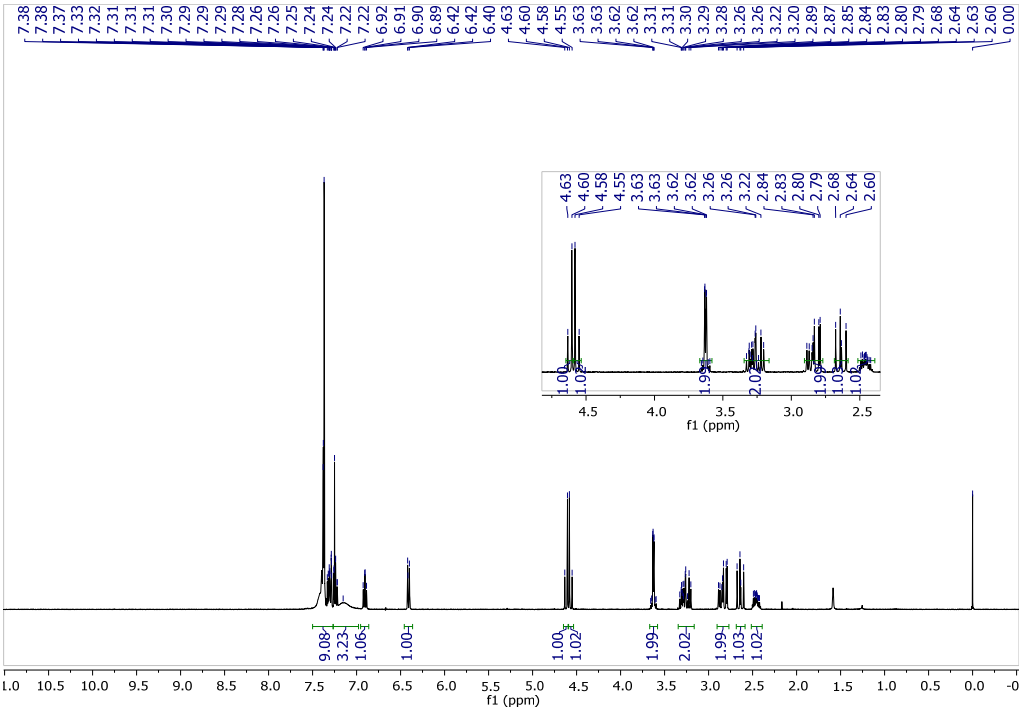

196.95
156.63
144.11
134.63
132.56
129.92
127.73
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
53.42
50.11
40.57
36.73
26.54
21.60
19.58
12.89
-0.00
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

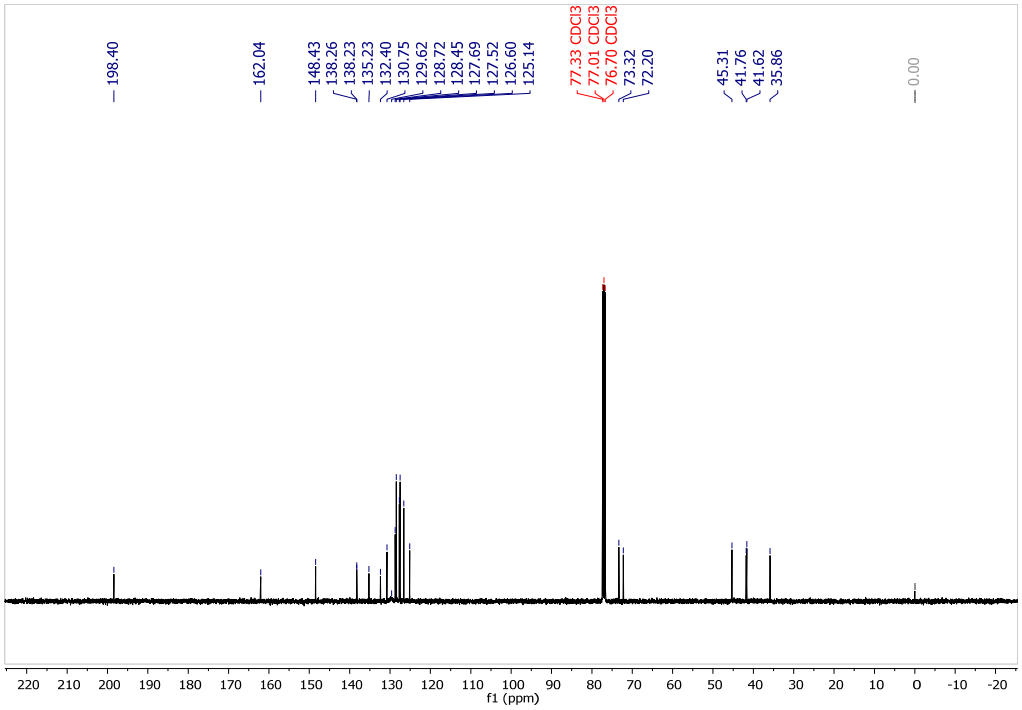

TMS
O
NTs
2t

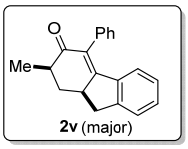

f1 (ppm)

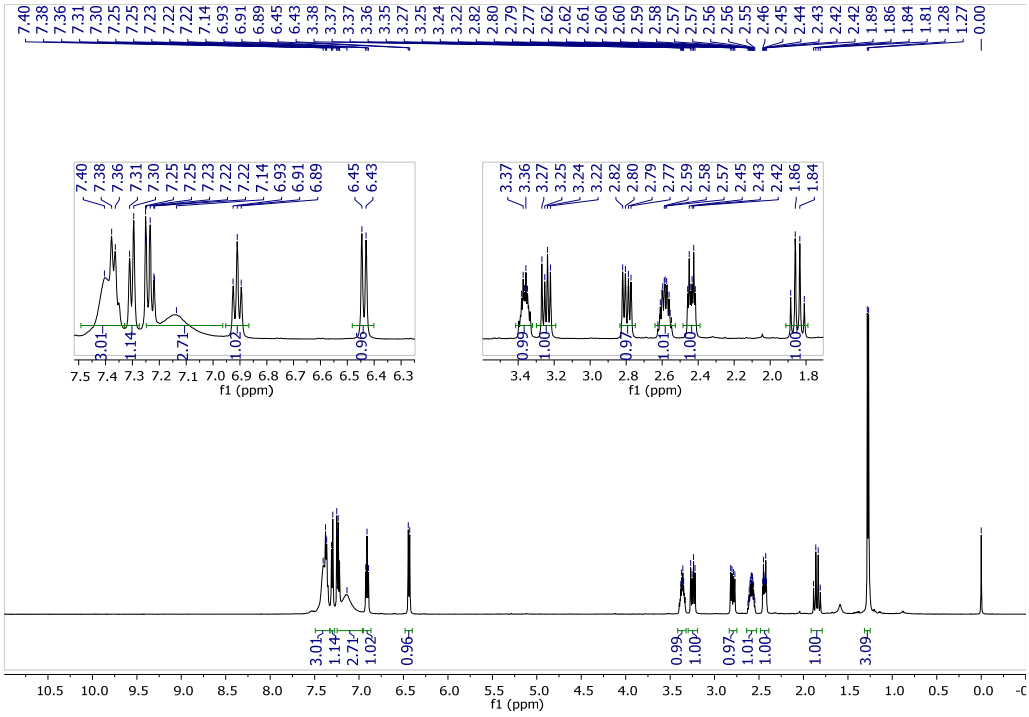

201.09
170.41
144.14
134.08
132.34
129.92
127.80
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
52.42
52.22
42.05
36.75
25.99
21.61
0.39
-0.00
f1 (ppm)

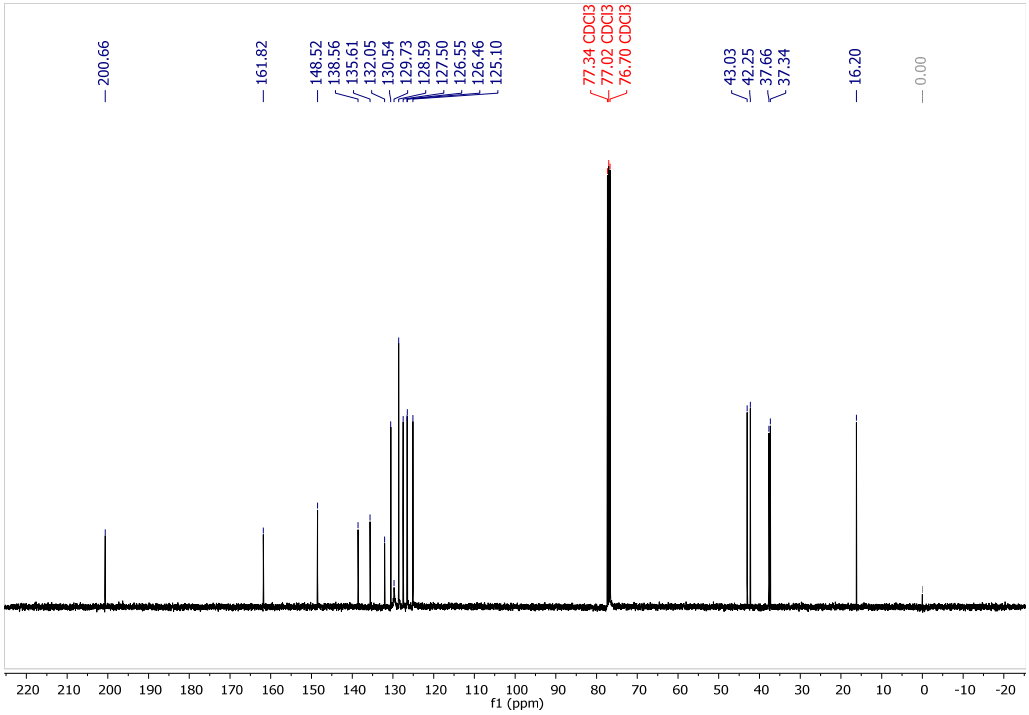

O
Ph
BnO
2u
d.r. >20:1

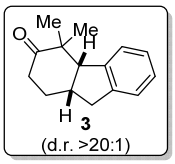

7.38 7.38 7.37 7.33 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.26 7.26 7.25 7.24 7.24 7.22 7.22 6.92 6.91 6.90 6.89 6.42 6.42 6.40 4.63 4.60 4.58 4.55 3.63 3.63 3.62 3.62 3.31 3.31 3.30 3.29 3.28 3.26 3.26 3.22 3.20 2.89 2.87 2.85 2.84 2.83 2.80 2.79 2.68 2.64 2.63 2.60 0.00
4.63 4.60 4.58 4.55 3.63 3.63 3.62 3.62 3.26 3.26 3.22 2.84 2.83 2.80 2.79 2.68 2.64 2.60
1.00 1.02 1.99 2.02 1.99 1.03 1.02
4.5 4.0 3.5 3.0 2.5
f1 (ppm)
9.08 3.23 1.06 1.00 1.00 1.02 1.99 2.02 1.99 1.03 1.02
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

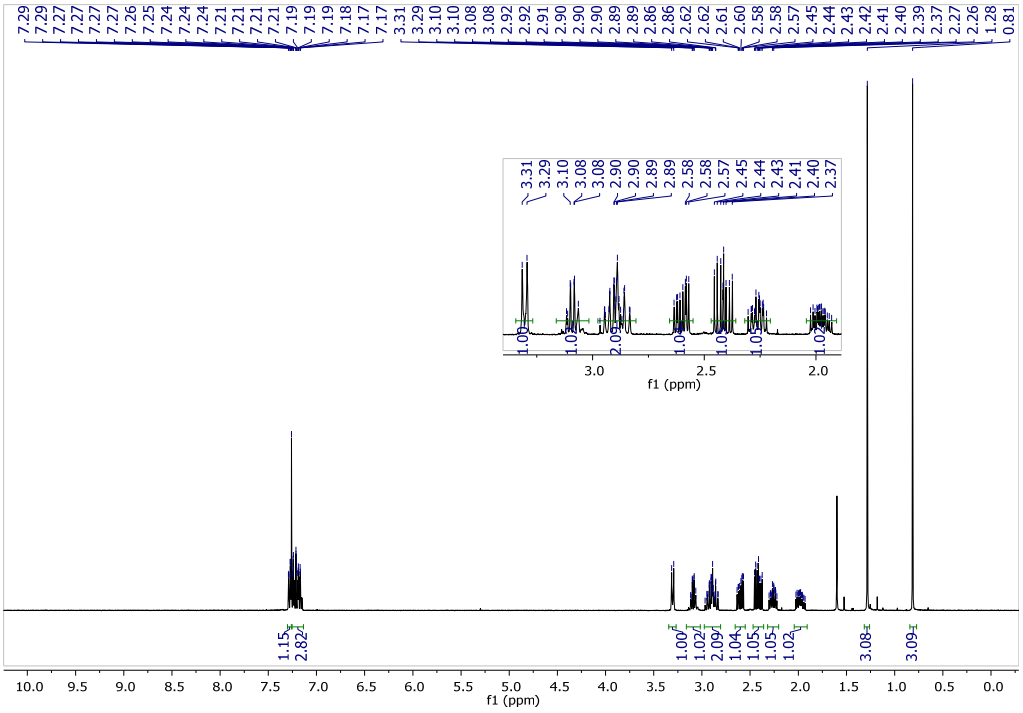

198.40
162.04
148.43 138.26 138.23 135.23 132.40 130.75 129.62 128.72 128.45 127.69 127.52 126.60 125.14
77.33 CDCl3 77.01 CDCl3 76.70 CDCl3
73.32 72.20
45.31 41.76 41.62 35.86
0.00
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

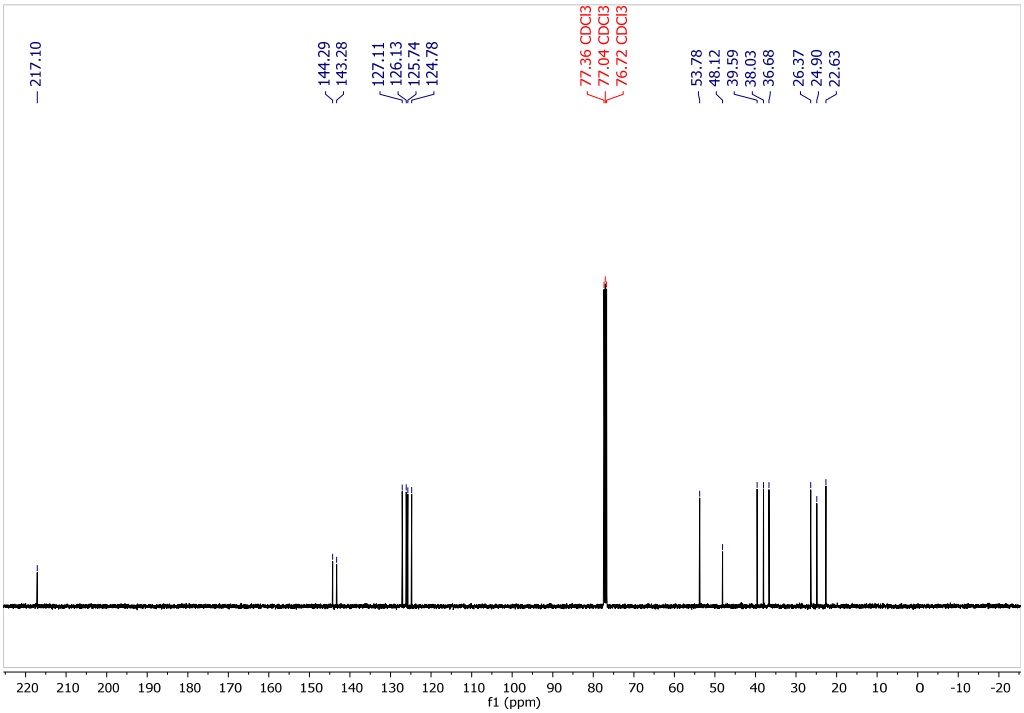

O
Ph
Me
2v (major)

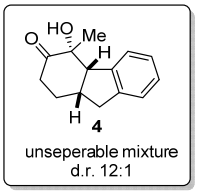

f1 (ppm)


f1 (ppm)

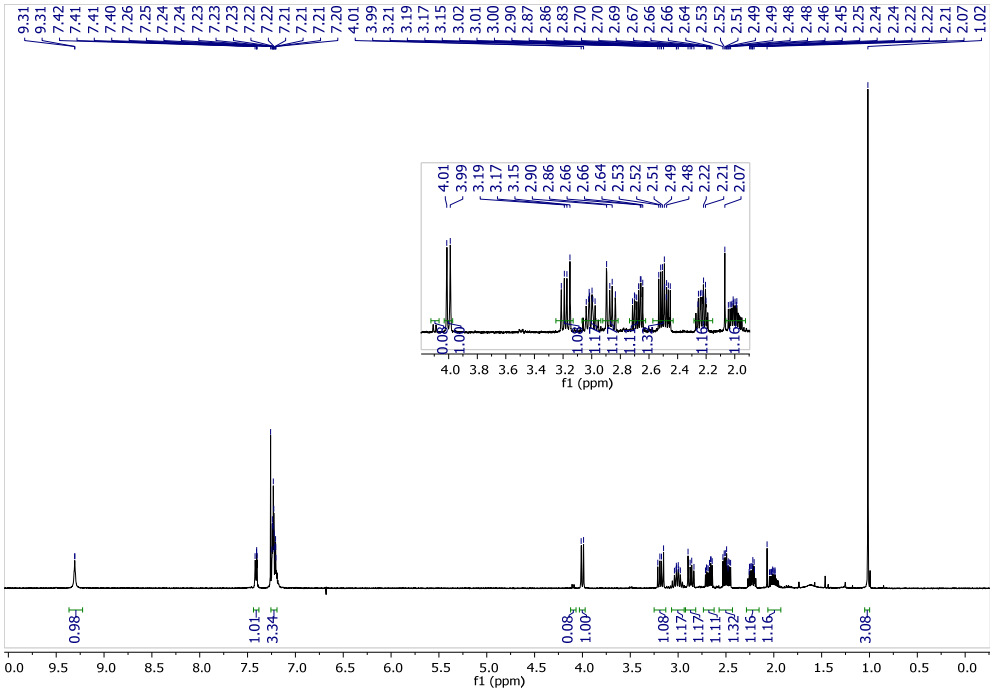

Me
Me
H
O
H
3
(d.r. >20:1)

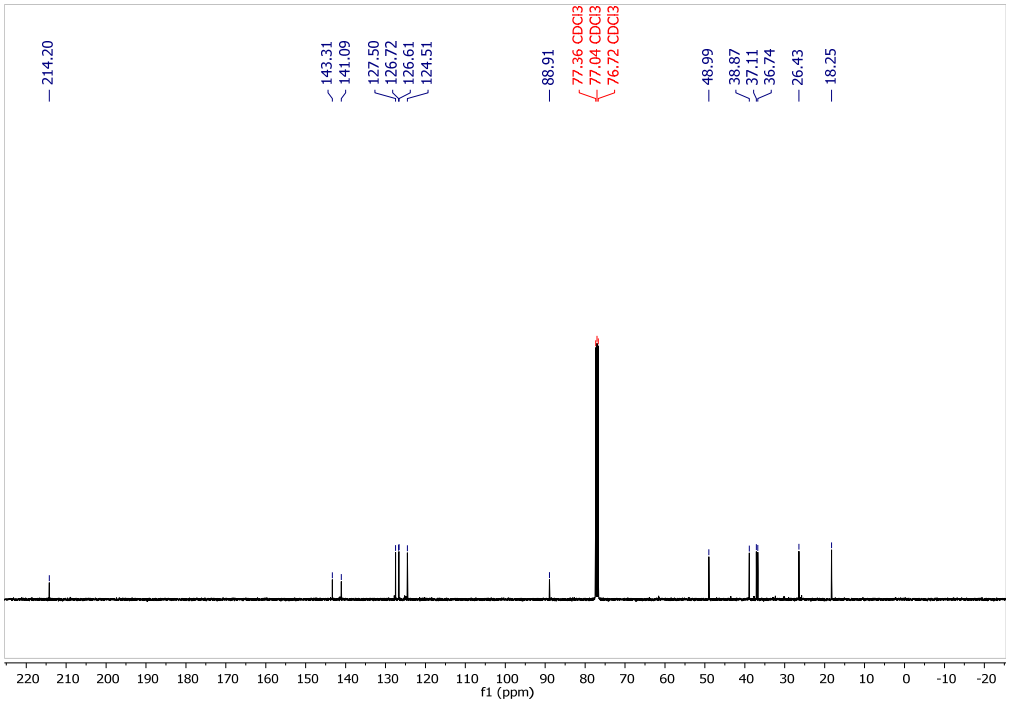

7.29 7.29 7.27 7.27 7.27 7.27 7.26 7.25 7.24 7.24 7.24 7.21 7.21 7.21 7.21 7.19 7.19 7.19 7.18 7.17 7.17
3.31 3.29 3.10 3.10 3.08 3.08 2.92 2.92 2.91 2.90 2.90 2.90 2.89 2.89 2.86 2.86 2.62 2.62 2.61 2.60 2.58 2.58 2.57 2.45 2.44 2.43 2.42 2.41 2.40 2.39 2.37 2.27 2.26 1.28 0.81
1.15
2.82
1.00
1.02
2.09
1.04
1.05
1.05
1.02
3.08
3.09
f1 (ppm)

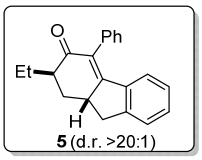

217.10
144.29
143.28
127.11
126.13
125.74
124.78
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
53.78
48.12
39.59
38.03
36.68
26.37
24.90
22.63
f1 (ppm)



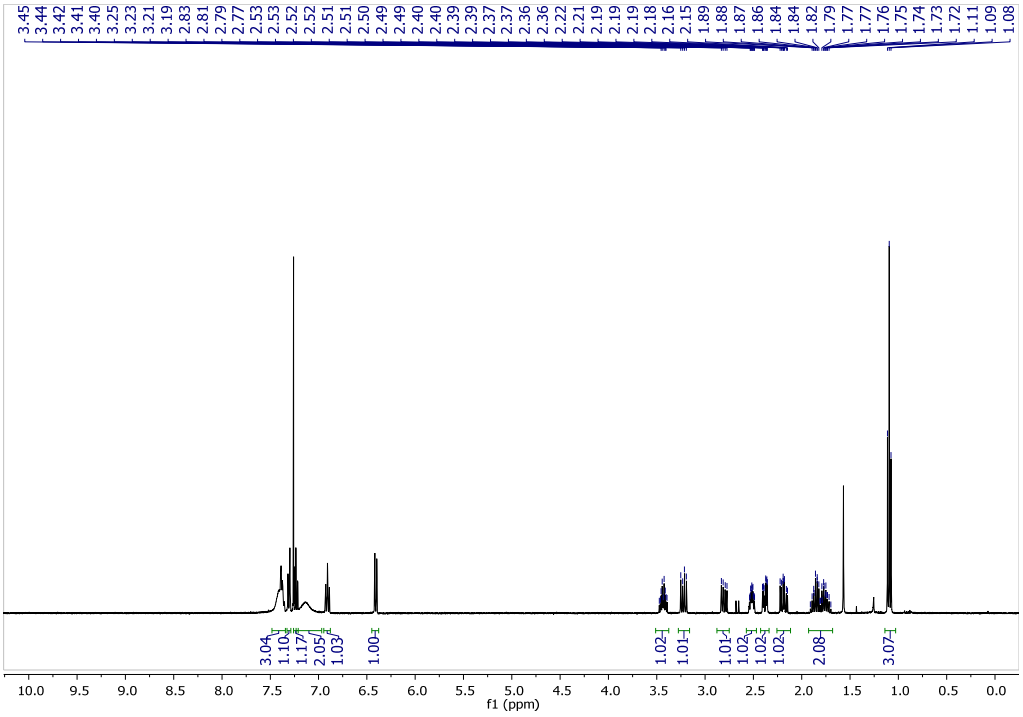
unseperable mixture
d.r. 12:1

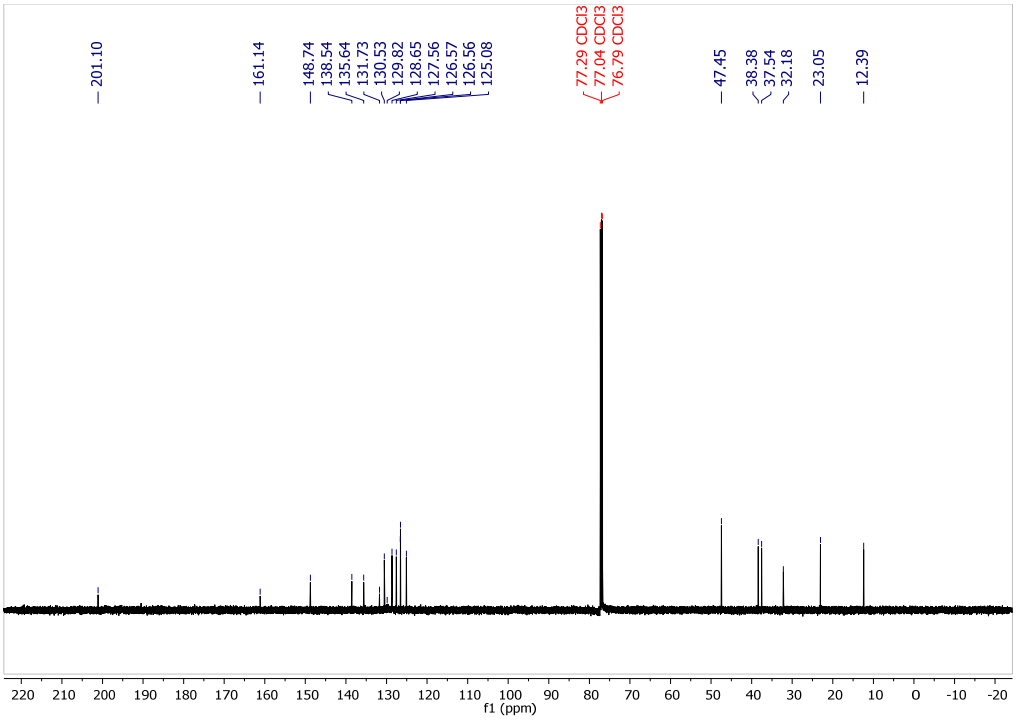


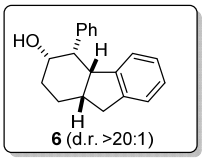



O
Ph
Et
H

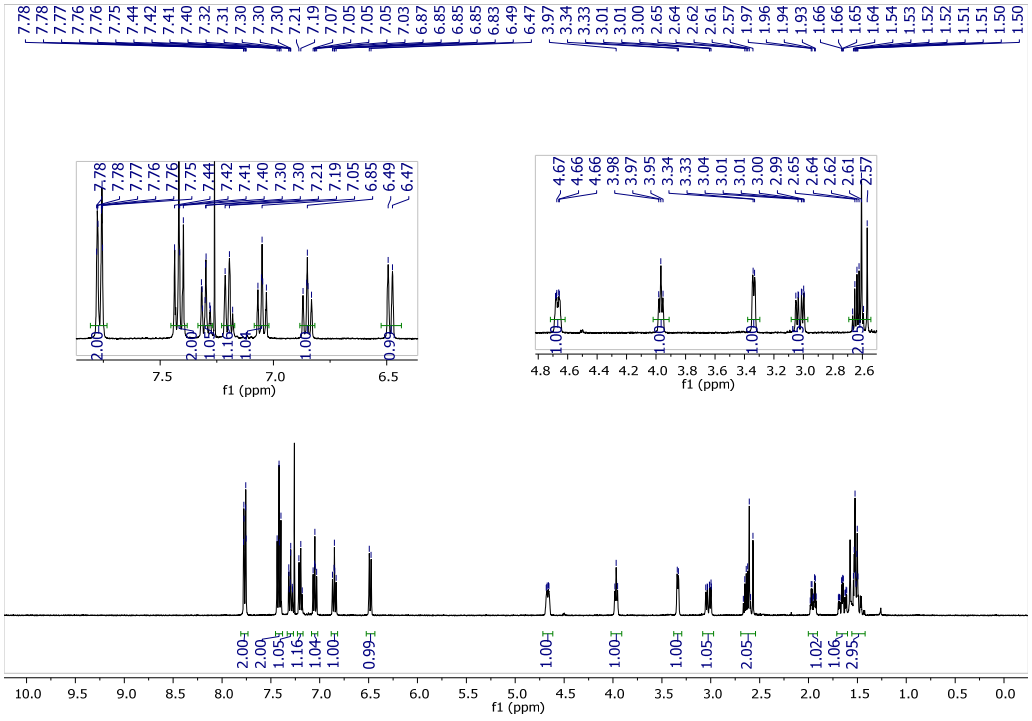
5 (d.r. >20:1)

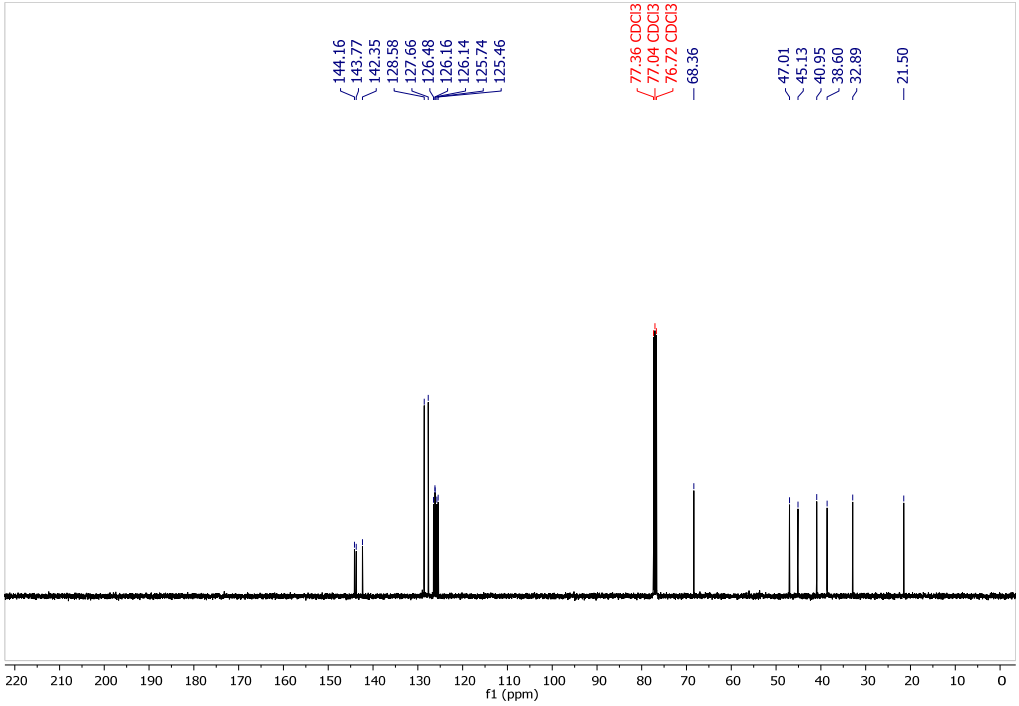

3.45 3.44 3.42 3.41 3.40 3.25 3.23 3.21 3.19 2.83 2.81 2.79 2.77 2.53 2.53 2.52 2.52 2.51 2.51 2.50 2.49 2.40 2.40 2.39 2.39 2.37 2.36 2.36 2.22 2.21 2.19 2.19 2.19 2.18 2.16 2.15 1.89 1.88 1.87 1.86 1.84 1.84 1.82 1.79 1.77 1.77 1.76 1.75 1.74 1.73 1.72 1.11 1.09 1.08
3.04 1.10 1.17 2.05 1.03 1.00 1.02 1.01 1.01 1.02 1.02 1.02 2.08 3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

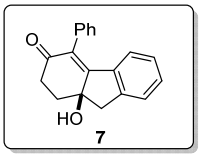

201.10
161.14
148.74
138.54
135.64
131.73
130.53
129.82
128.65
127.56
126.57
126.56
125.08
77.29 CDCl3
77.04 CDCl3
76.79 CDCl3
47.45
38.38
37.54
32.18
23.05
12.39
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

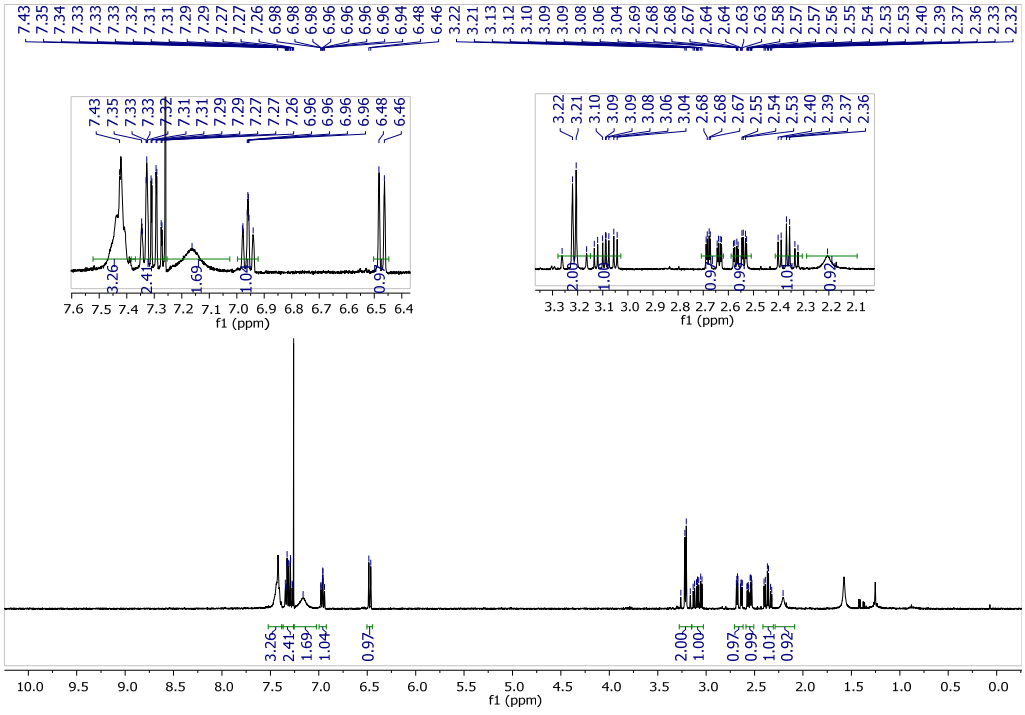


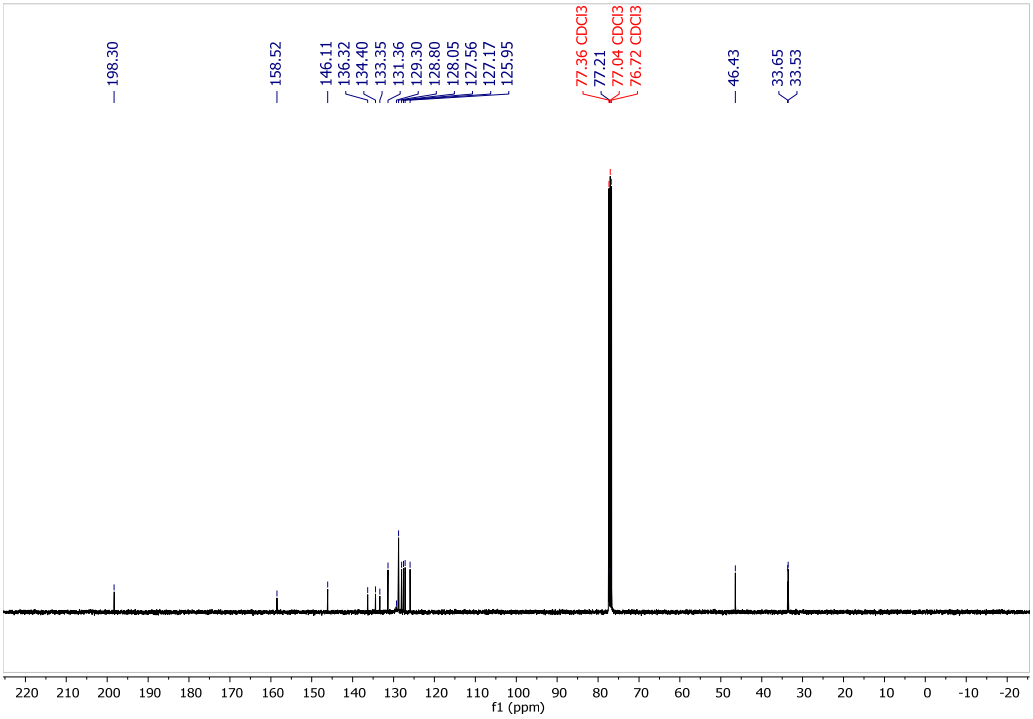
6 (d.r. >20:1)

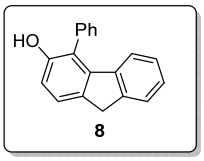




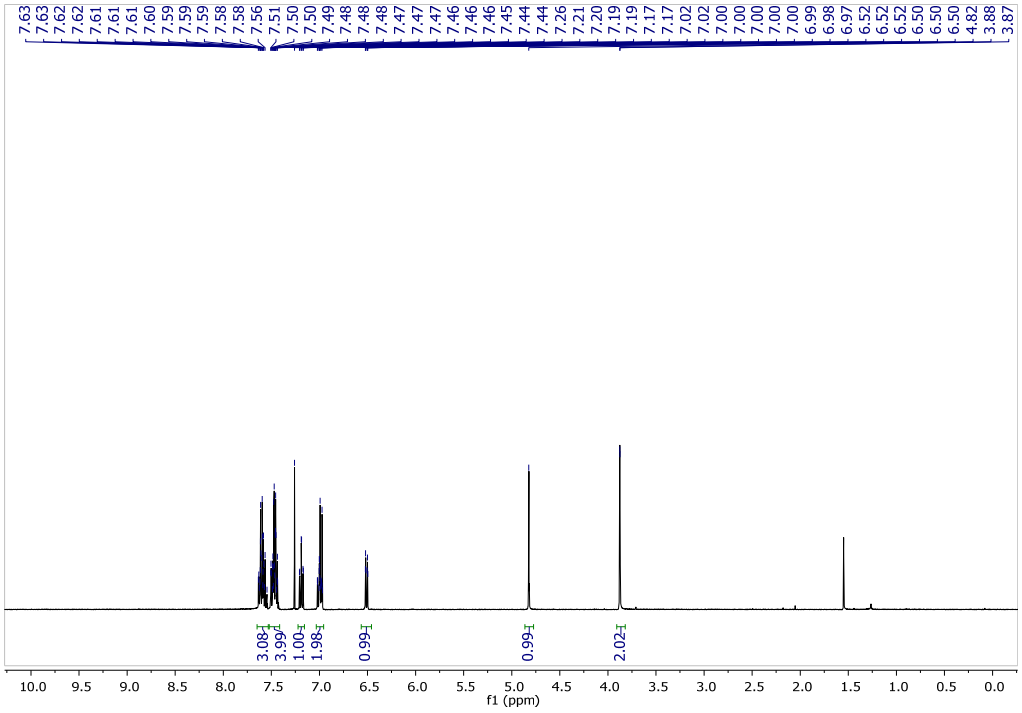

Ph
O
HO
7

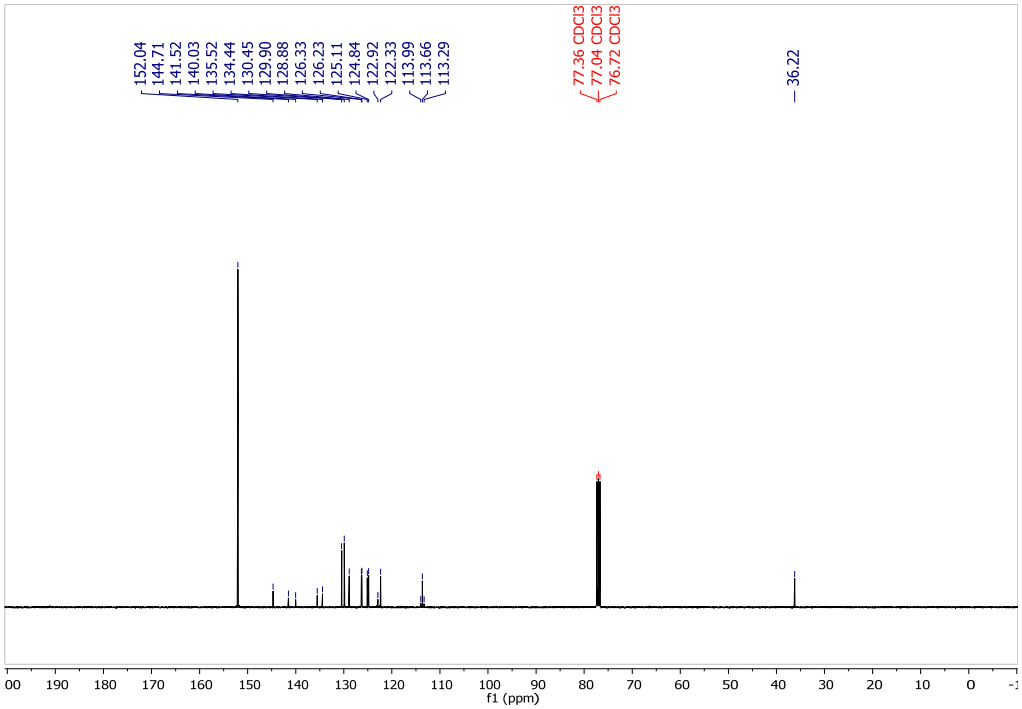

f1 (ppm)

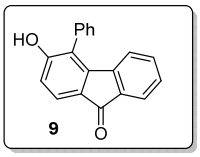

198.30
158.52
146.11
136.32
134.40
133.35
131.36
129.30
128.80
128.05
127.56
127.17
125.95
77.36 CDCl3
77.21
77.04 CDCl3
76.72 CDCl3
46.43
33.65
33.53
f1 (ppm)

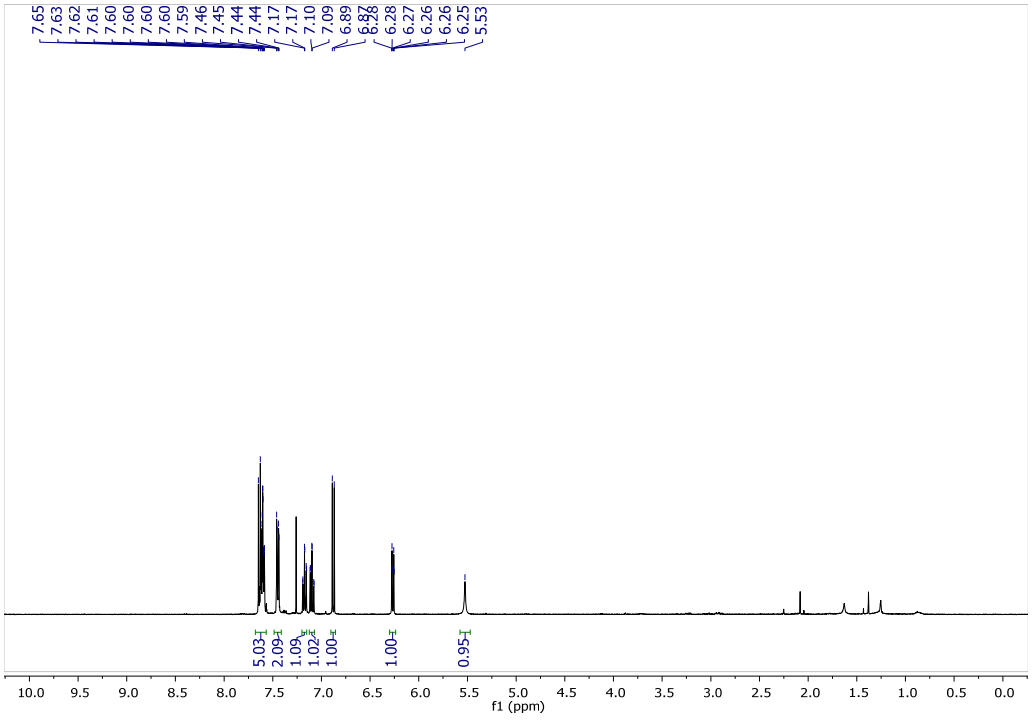

HO
Ph

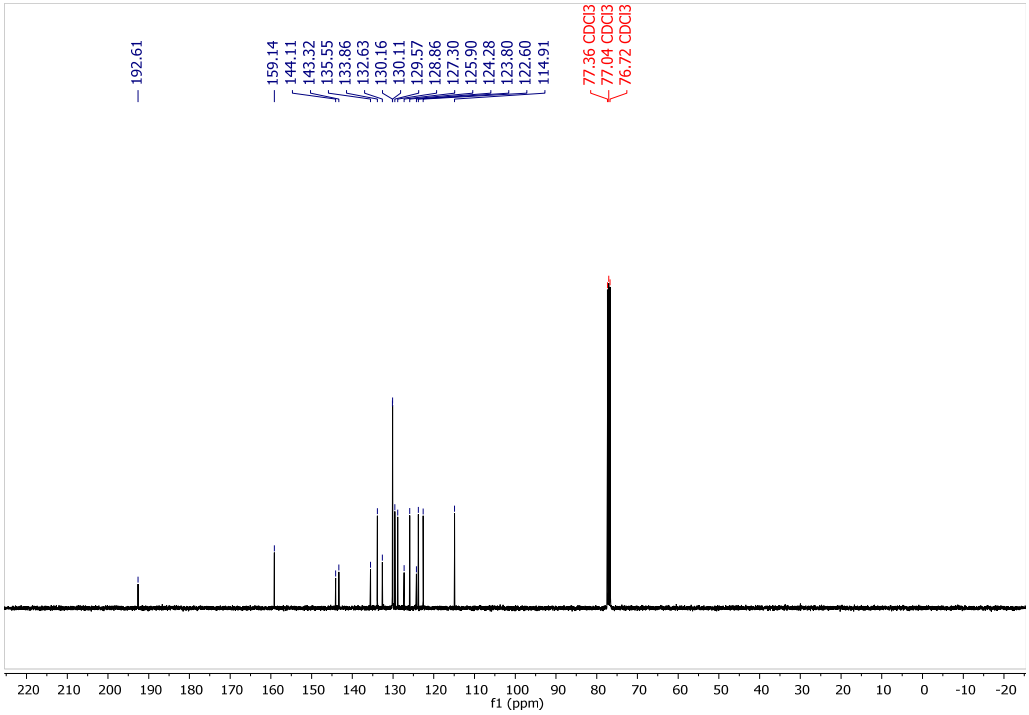
8

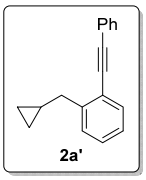

7.63 7.63 7.62 7.62 7.61 7.61 7.61 7.60 7.59 7.59 7.59 7.58 7.58 7.56 7.51 7.50 7.50 7.49 7.48 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.44 7.44 7.26 7.21 7.20 7.19 7.19 7.17 7.17 7.02 7.02 7.00 7.00 7.00 7.00 7.00 6.99 6.98 6.97 6.52 6.52 6.52 6.50 6.50 6.50 6.50 4.82 3.88 3.87
3.08 3.99 1.00 1.98 0.99 0.99 2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

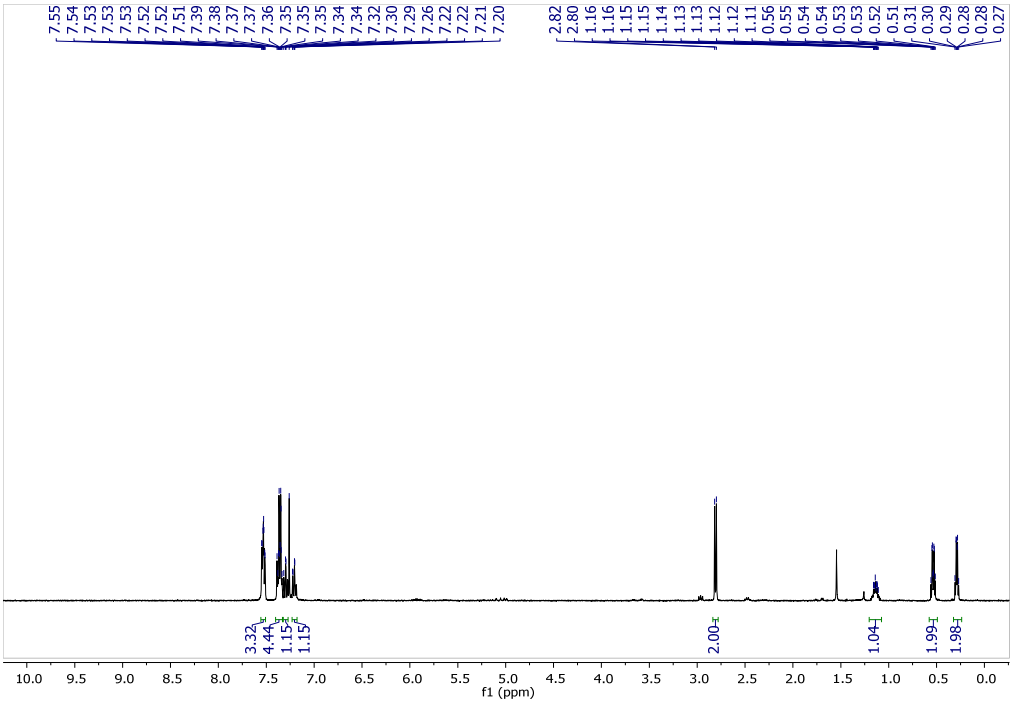

152.04 144.71 141.52 140.03 135.52 134.44 130.45 129.90 128.88 126.33 126.23 125.11 124.84 122.92 122.33 113.99 113.66 113.29
77.36 CDCl3 77.04 CDCl3 76.72 CDCl3
36.22
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

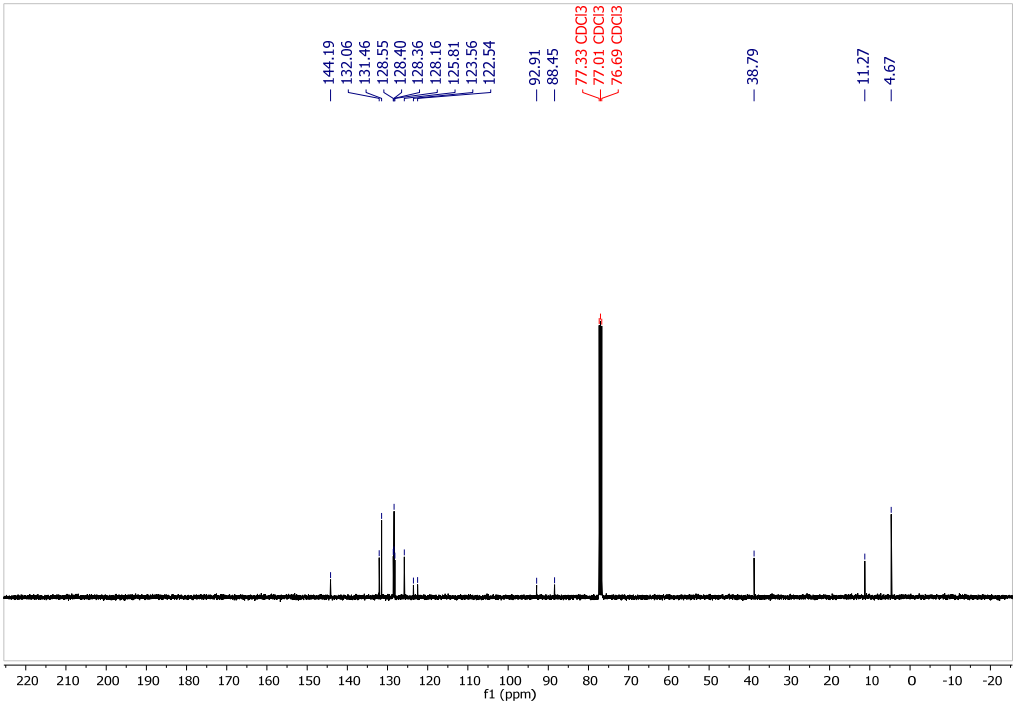

HO
Ph
O
9


7.65
7.63
7.62
7.61
7.60
7.60
7.60
7.60
7.59
7.46
7.45
7.44
7.44
7.17
7.17
7.10
7.09
6.89
6.87
6.28
6.27
6.26
6.26
6.25
5.53
5.03
2.09
1.09
1.02
1.00
1.00
0.95
f1 (ppm)

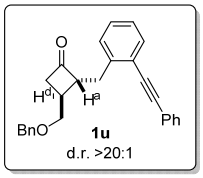

192.61
159.14
144.11
143.32
135.55
133.86
132.63
130.16
130.11
129.57
128.86
127.30
125.90
124.28
123.80
122.60
114.91
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
f1 (ppm)

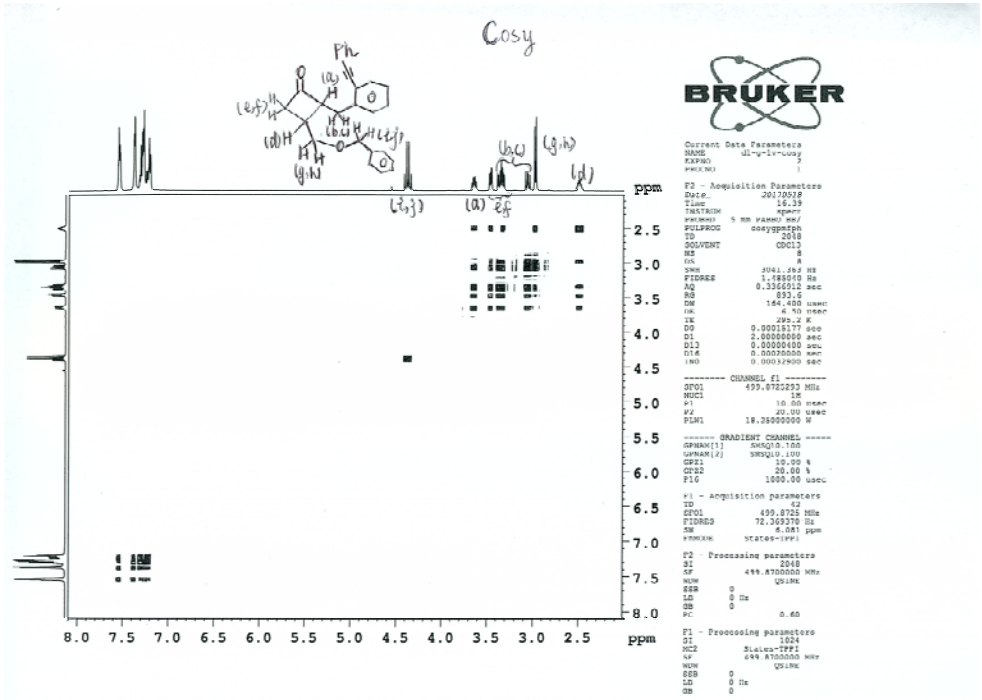

Ph
2a'

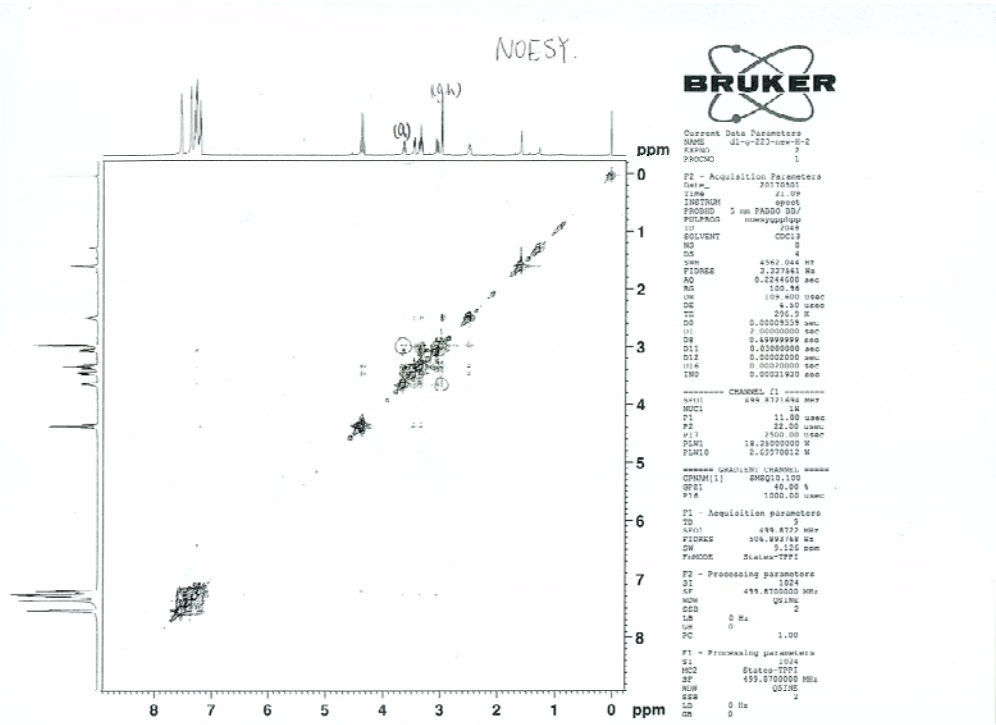

7.55 7.54 7.53 7.53 7.53 7.52 7.52 7.51 7.39 7.38 7.37 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.32 7.30 7.29 7.26 7.22 7.22 7.21 7.20
2.82 2.80 1.16 1.16 1.15 1.15 1.14 1.13 1.13 1.12 1.12 1.11 0.56 0.55 0.54 0.54 0.53 0.53 0.52 0.51 0.31 0.30 0.29 0.28 0.28 0.27
3.32 4.44 1.15 1.15 2.00 1.04 1.99 1.98
f1 (ppm)

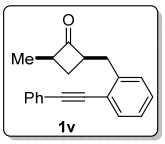

144.19 132.06 131.46 128.55 128.40 128.36 128.16 125.81 123.56 122.54 92.91 88.45 77.33 CDCl3 77.01 CDCl3 76.69 CDCl3 38.79 11.27 4.67
f1 (ppm)

b) 2D-NMR spectra

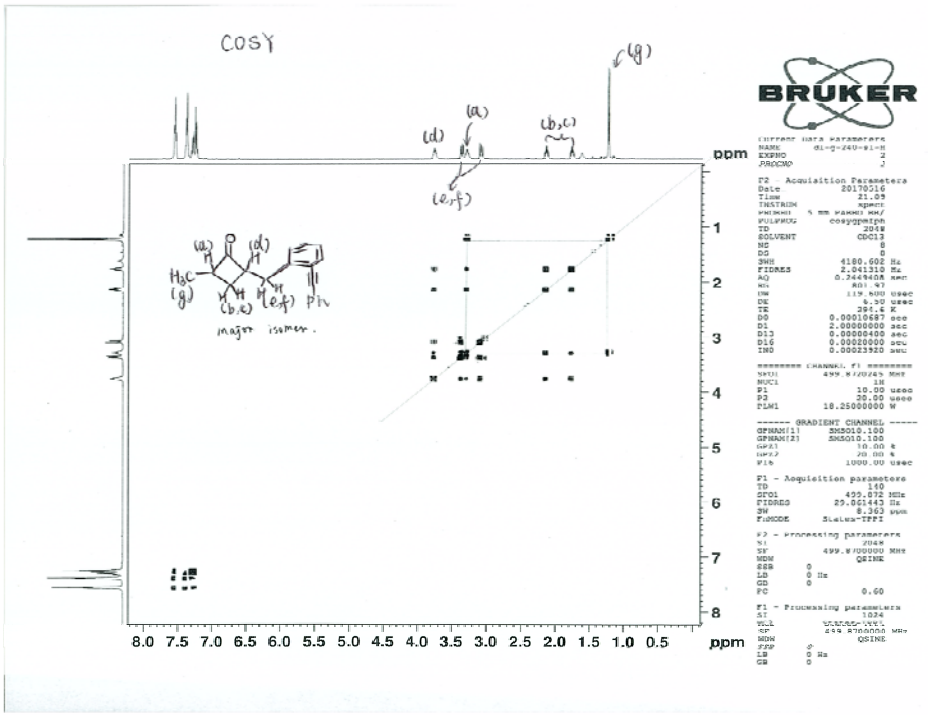


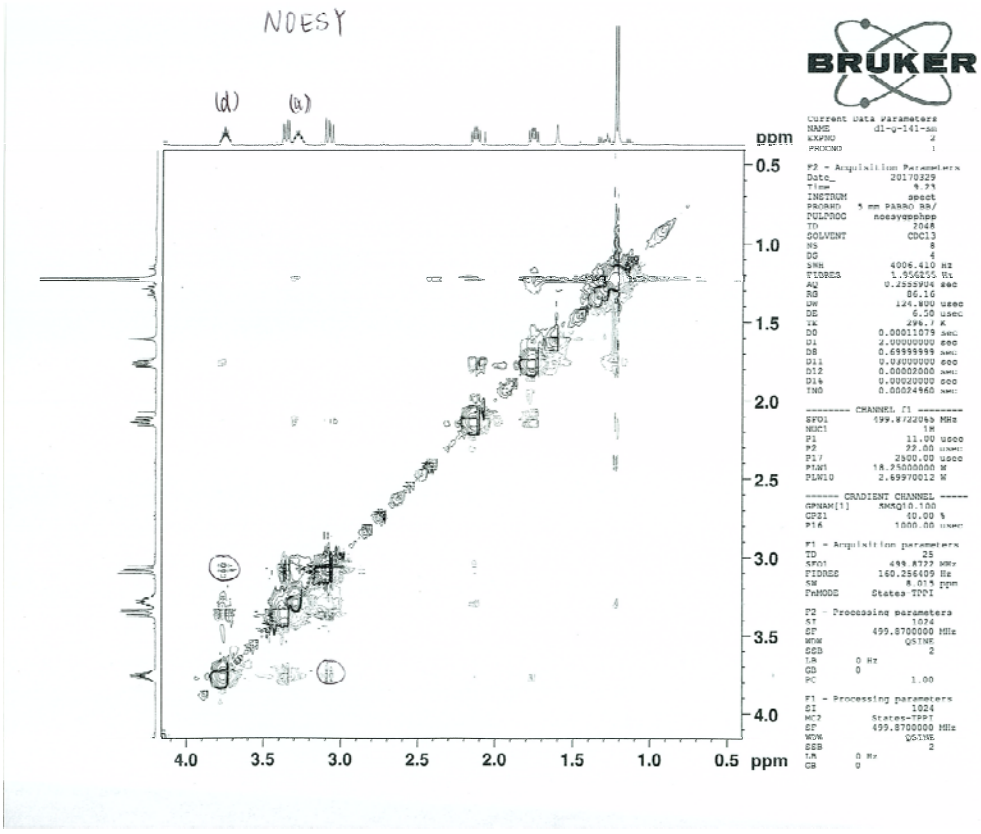


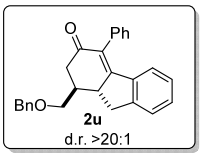


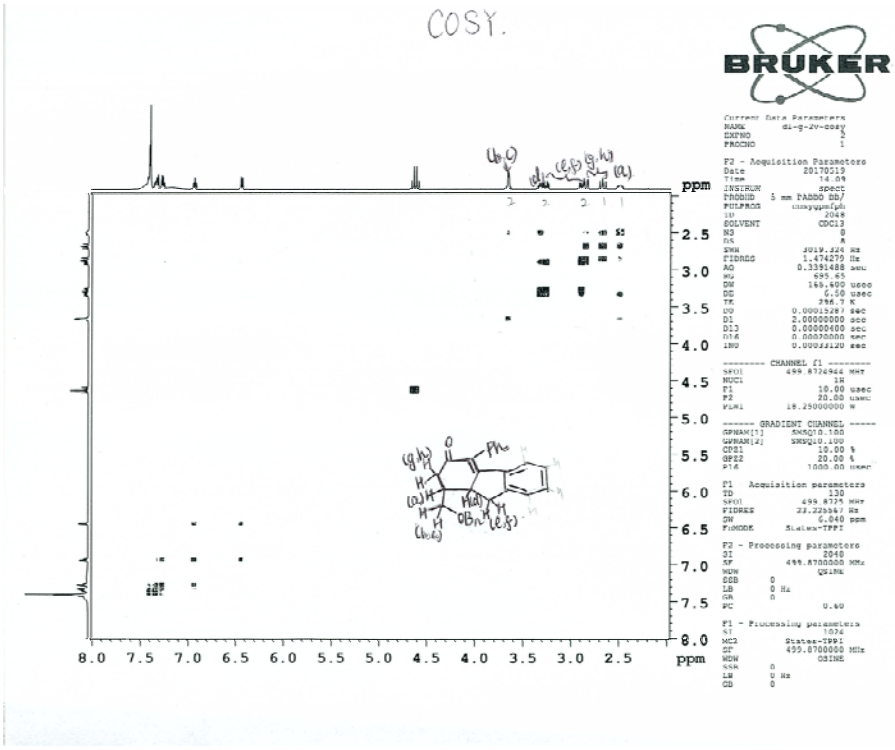


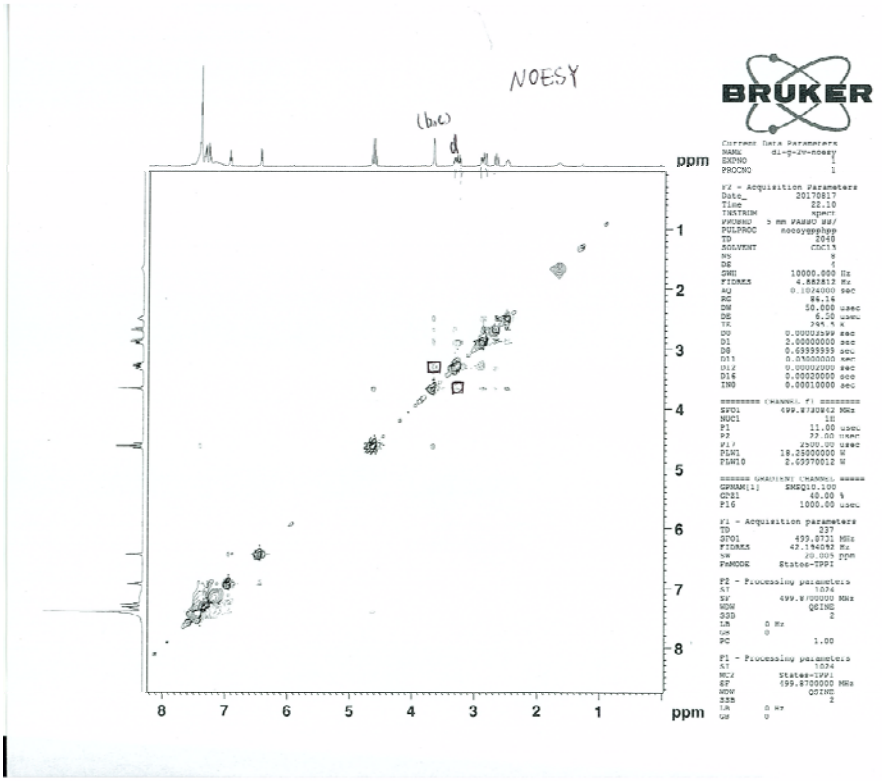
major diastereomer

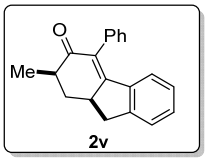




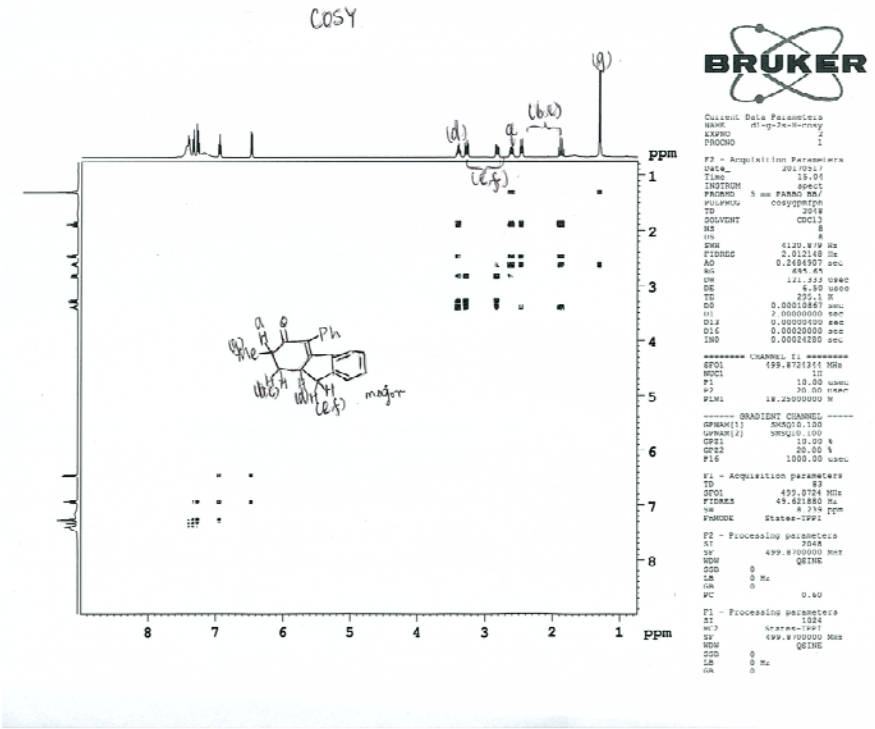

O
Ph
BnO
2u
d.r. >20:1

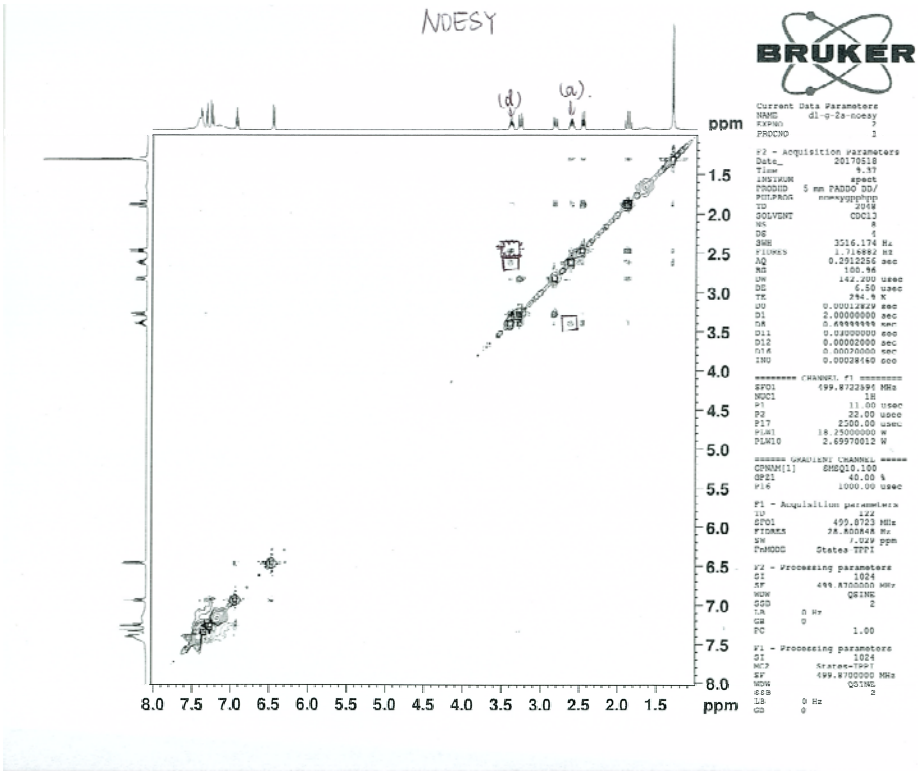

COSY.
BRUKER
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5
2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0

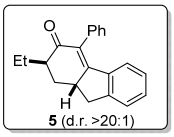

NOESY
BRUKER
ppm
8 7 6 5 4 3 2 1
1 2 3 4 5 6 7 8



major diastereomer







5 (d.r. >20:1)