Supporting Information

Gold(I)-Catalyzed Ring Expansions of Unactivated Alkynylcyclopropanes to (*E*)-2-Alkylidenecyclobutanamines in the Presence of Sulfonamides

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1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Tetrahydrofuran and toluene were distilled from sodium and benzophenone prior to use. 1,2-Dichloroethane was distilled from CaH_2 prior to use. 1,1,2,2-tetrachloroethane was dried over anhydrous K_2CO_3 and distilled prior to use. Dioxane (extra dry, water < 50 ppm) was commercially available and used as received. Synthetic reagents purchased from Acros and Alfa Aesar were used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates containing a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash column chromatography on silica gel and the purified compounds show a single spot by analytical TLC.

NMR spectra were measured on Varian Mercury Plus 300 (^{1}H at 300 MHz, ^{13}C at 75 MHz) or Bruker ARX400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dt = doublet of triplets, tt = triplet of triplets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm, d_6-DMSO: 39.5 ppm). Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) with an OMNI sampler and are reported in wavenumbers (cm^{-1}). Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on Waters micromass GCT (EI, 70 eV) and Bruker APEX IV (ESI) mass spectrometers.

Abbreviations:

THF = tetrehydrofuran
PE = petroleum ether
EA = ethyl acetate
DCE = 1,2-dichloroethane
TCE = 1,1,2,2-tetrachloroethane
DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone
PDC = pyridinium dichromate
m.p. = melting point

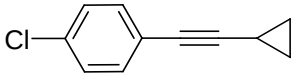
2. Experimental procedures and characterization data

2.1 Synthesis of alkynylcyclopropanes

Alkynylcyclopropanes **1a**—**1o** and **1v**—**1x** were prepared by following the reported Sonogashira cross-coupling procedures. And **1a**[1], **1b**[1,2], **1c**[1], and **1e**[1] are known compounds. **1t** and **1u** are also known compounds, which were prepared by following the literature procedures.[2]

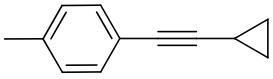
General Sonogashira procedure for the preparation of aryl alkynylcyclopropanes: $Pd(PPh_3)_4$ (0.10 mmol) and CuI (0.20 mmol) were dissolved in 30 mL dry THF at room temperature under argon atmosphere. Then aryl iodide (10 mmol), $(i\text{-Pr})_2NH$ (15 mmol), and cyclopropylacetylene (11 mmol) was added successively. The reaction was stirred at room temperature and a brown precipitate appeared. When TLC indicated the reaction was complete, the reaction mixture was filtered through a thin pad of neutral Al_2O_3. The filter cake was washed with Et_2O and the combined filtrate was concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE) to afford the corresponding alkynylcyclopropane.

1-Chloro-4-cyclopropylethynylbenzene (1a):



colorless oil, 97% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.9 Hz, 2H), 7.23 (d, J = 8.9 Hz, 2H), 1.43 (tt, J = 8.2 and 5.1 Hz, 1H), 0.90—0.84 (m, 2H), 0.82—0.78 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 133.3, 132.8, 128.4, 122.4, 94.5, 74.7, 8.6, 0.1.
FT-IR (neat): ν 2925, 2234, 1490, 1362 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 176 (M^+, 74), 141 (100), 113 (14), 99 (2).
HRMS (EI) calcd for $C_{11}H_9Cl$: 176.0393. Found: 176.0395.

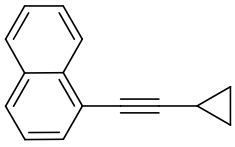
1-Cyclopropylethynyl-4-methylbenzene (1c)



colorless oil, 99% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 2.32 (s, 3H), 1.43 (tt, J = 8.2 and 5.0 Hz, 1H), 0.87—0.81 (m, 2H), 0.80—0.76 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 131.5, 128.9, 120.8, 92.5, 75.8, 21.4, 8.5, 0.2.
FT-IR (neat): ν 3010, 2234, 1511, 1452, 1363 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 156 (M^+, 100), 141 (86), 128 (31), 115 (41), 101 (2), 91 (2).
HRMS (EI) calcd for $C_{12}H_{12}$: 156.0939. Found: 156.0941.

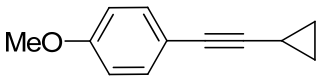
(1) Takeuchi, K.; Kitagawa, T.; Miyabo, A.; Hori, H.; Komatsu, K. *J. Org. Chem.* **1993**, *58*, 5802.
(2) Ma, S.; He, Q. *Tetrahedron* **2006**, *62*, 2769.

1-Cyclopropylethynylnaphthalene (1d):



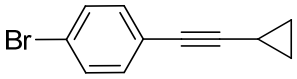
colorless oil, 79% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.60 (dd, J = 7.1 and 1.0 Hz, 1H), 7.56—7.46 (m, 2H), 7.37 (dd, J = 8.2 and 7.1 Hz, 1H), 1.59 (tt, J = 8.2 and 5.2 Hz, 1H), 0.97—0.89 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 133.5, 133.1, 130.0, 128.2, 127.8, 126.4, 126.21, 126.17, 125.2, 121.6, 98.6, 73.7, 8.9, 0.5.
FT-IR (neat): ν 3059, 3009, 2224, 1585, 1506, 1398 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 192 (M^+, 100), 165 (54), 163 (32), 152 (6), 149 (7), 115 (3).
HRMS (EI) calcd for $C_{15}H_{12}$: 192.0939. Found: 192.0942.

1-Cyclopropylethynyl-4-methoxybenzene (1e):



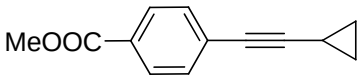
colorless oil, 91% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 9.1 Hz, 2H), 6.79 (d, J = 9.1 Hz, 2H), 3.79 (s, 3H), 1.43 (tt, J = 8.2 and 5.1 Hz, 1H), 0.86—0.81 (m, 2H), 0.79—0.75 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 132.9, 116.0, 113.8, 91.7, 75.5, 55.2, 8.4, 0.1.
FT-IR (neat): ν 3008, 2837, 2233, 1606, 1509 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 172 (M^+, 100), 157 (45), 141 (3), 128 (41), 127 (18), 115 (6), 101 (3).
HRMS (EI) calcd for $C_{12}H_{12}O$: 172.0888. Found: 172.0890.

1-Bromo-4-cyclopropylethynylbenzene (1f)



colorless oil, 85% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 1.43 (tt, J = 8.4 and 5.1 Hz, 1H), 0.90—0.83 (m, 2H), 0.82—0.78 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 133.0, 131.4, 122.9, 121.5, 94.7, 74.8, 8.6, 0.1.
FT-IR (neat): ν 3014, 2234, 1485, 1393, 1361 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 220 (M^+, 59), 141 (100), 115 (56), 113 (22), 87 (6).
HRMS (EI) calcd for $C_{11}H_9Br$: 219.9888. Found: 219.9889.

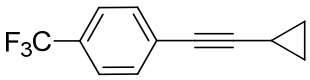
Methyl 4-cyclopropylethynylbenzoate (1g):



white solid, 99% yield, m.p.: 46—47 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 3.90 (s, 3H),

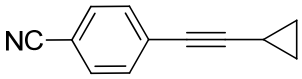
1.47 (tt, J = 8.3 and 5.2 Hz, 1H), 0.92－0.86 (m, 2H), 0.85－0.81 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 131.4, 129.3, 128.8, 128.7, 97.0, 52.1, 8.8, 0.2.
FT-IR (neat): ν 2950, 2232, 1720, 1605 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 200 (M^+, 69), 169 (100), 141 (19), 115 (22), 101 (2).
HRMS (EI) calcd for $C_{13}H_{12}O_2$: 200.0837. Found: 200.0840.

1-Cyclopropylethynyl-4-trifluoromethylbenzene (1h):



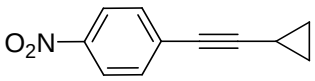
colorless oil, 97% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 1.46 (tt, J = 8.1 and 5.2 Hz, 1H), 0.93－0.87 (m, 2H), 0.85－0.81 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 131.8, 129.1 (q, J = 32.8 Hz), 127.8, 125.1 (q, J = 4.6 Hz), 124.0 (q, J = 270.9 Hz), 96.3, 74.7, 8.7, 0.2.
FT-IR (neat): ν 2930, 2235, 1615, 1408, 1323 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 210 (M^+, 100), 191 (8), 182 (12), 141 (56), 115 (12).
HRMS (EI) calcd for $C_{12}H_9F_3$: 210.0656. Found: 210.0659.

4-Cyclopropylethynylbenzonitrile (1i):



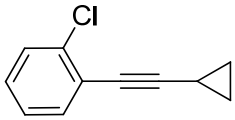
white solid, 99% yield, m.p.: 47 ^{o}C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 1.47 (tt, J = 8.2 and 5.0 Hz, 1H), 0.95－0.88 (m, 2H), 0.87－0.82 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 132.0, 131.8, 129.0, 118.6, 110.6, 98.7, 74.6, 8.8, 0.2.
FT-IR (neat): ν 3016, 2232, 2222, 1601, 1499 cm^{-1}.
HRMS (ESI) calcd for $C_{12}H_{10}N$ [M+H$^+$]: 168.0808. Found: 168.0806.

1-Cyclopropylethynyl-4-nitrobenzene (1j):



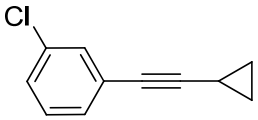
light yellow solid, 97% yield, m.p.: 56－57 ^{o}C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 9.0 Hz, 2H), 7.48 (d, J = 9.0 Hz, 2H), 1.49 (tt, J = 8.3 and 5.1 Hz, 1H), 0.97－0.92 (m, 2H), 0.89－0.84 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 132.1, 131.1, 123.4, 99.9, 74.5, 9.0, 0.3.
FT-IR (neat): ν 3016, 2930, 2230, 2212, 1594, 1507 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 187 (M^+, 100), 171 (8), 157 (25), 141 (28), 139 (30), 128 (21), 115 (70).
HRMS (EI) calcd for $C_{11}H_9NO_2$: 187.0633. Found: 187.0636.

1-Chloro-2-cyclopropylethynylbenzene (1k):



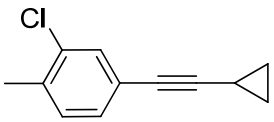
colorless oil, 99% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41－7.39 (m, 1H), 7.36－7.34 (m, 1H), 7.20－7.13 (m, 2H), 1.51 (tt, J = 8.2 and 5.1 Hz, 1H), 0.93－0.88 (m, 2H), 0.87－0.83 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 135.7, 133.2, 129.1, 128.4, 126.3, 123.7, 99.2, 72.6, 8.9, 0.3.
FT-IR (neat): ν 3018, 2232, 1475, 1437 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 176 (M^+, 100), 141 (97), 115 (39), 113 (22), 99 (2).
HRMS (EI) calcd for $C_{11}H_9Cl$: 176.0393. Found: 176.0395.

1-Chloro-3-cyclopropylethynylbenzene (1l):



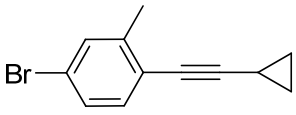
colorless oil, 99% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36－7.35 (m, 1H), 7.25－7.16 (m, 3H), 1.44 (tt, J = 8.2 and 5.2 Hz, 1H), 0.90－0.84 (m, 2H), 0.82－0.78 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 134.0, 131.5, 129.7, 129.4, 127.7, 125.7, 94.9, 74.5, 8.7, 0.1.
FT-IR (neat): ν 3011, 2228, 1593, 1560, 1475 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 176 (M^+, 79), 141 (100), 115 (31), 113 (12), 99 (2).
HRMS (EI) calcd for $C_{11}H_9Cl$: 176.0393. Found: 176.0396.

2-Chloro-4-cyclopropylethynyl-1-methylbenzene (1m):



colorless oil, 99% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 1.9 Hz, 1H), 7.15 (dd, J = 8.0 and 1.9 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 2.33 (s, 3H), 1.42 (tt, J = 8.3 and 5.0 Hz, 1H), 0.88－0.82 (m, 2H), 0.81－0.77 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 135.5, 134.0, 131.9, 130.6, 129.7, 122.9, 93.9, 74.5, 19.9, 8.6, 0.1.
FT-IR (neat): ν 3012, 2922, 2233, 1548, 1495 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 190 (M^+, 100), 175 (10), 155 (75), 127 (20), 115 (10), 101 (3).
HRMS (EI) calcd for $C_{12}H_{11}Cl$: 190.0549. Found: 190.0551.

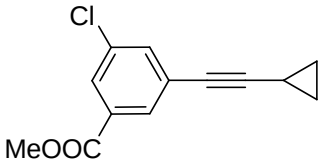
4-Bromo-1-cyclopropylethynyl-2-methylbenzene (1n):



colorless oil, 98% yield.

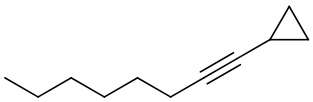
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (s, 1H), 7.21 (d, J = 8.3 Hz, 1H), 7.18 (d, J = 8.3 Hz, 1H), 2.35 (s, 3H), 1.47 (tt, J = 8.2 and 5.1 Hz, 1H), 0.91－0.83 (m, 2H), 0.81－0.77 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 133.0, 132.2, 128.6, 122.7, 121.2, 98.7, 73.6, 20.5, 8.8, 0.3.
FT-IR (neat): ν 3009, 2916, 2231, 1587, 1479 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 234 (M^+, 100), 206 (13), 193 (28), 155 (26), 153 (50), 127 (38), 115 (18), 101 (4), 77 (7).
HRMS (EI) calcd for $C_{12}H_{11}Br$: 234.0044. Found: 234.0042.

Methyl 3-chloro-5-cyclopropylethynylbenzoate (1o):



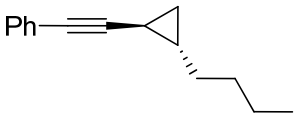
colorless oil, 99% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (t, J = 1.5 Hz, 1H), 7.88 (t, J = 1.5 Hz, 1H), 7.51 (t, J = 1.5 Hz, 1H), 3.91 (s, 3H), 1.45 (tt, J = 8.3 and 5.1 Hz, 1H), 0.93－0.86 (m, 2H), 0.84－0.80 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 135.4, 134.2, 131.7, 130.8, 128.4, 126.0, 96.1, 73.7, 52.4, 8.7, 0.1.
FT-IR (neat): ν 3013, 2952, 2227, 1728, 1595, 1571, 1439 cm^{-1}.
HRMS (ESI) calcd for $C_{13}H_{12}ClO_2$ [M+H$^+$]: 235.0520. Found: 235.0520.

Oct-1-ynylcyclopropane (1p):



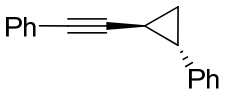
To a solution of cyclopropylacetylene (606 mg, 9.2 mmol) in 10 mL dry THF was added *n*-BuLi (1.6 M hexane solution, 5.6 mL, 9 mmol) at －78 ^{o}C. And then the mixture was warmed to room temperature by removal of the cooling bath. After stirred for 1 h, the solution was cooled to －78 ^{o}C again, and DMPU (1.15 g, 9 mmol) and 1-iodohexane (1.27 g, 6 mmol) were added. The resulting mixture was warmed to room temperature and stirred for 3 h. The mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic phase was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluted with hexane) to afford **1p** as a colorless oil (599 mg, 66%).
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.11 (td, J = 7.0 and 1.9 Hz, 2H), 1.50－1.16 (m, 9H), 0.89 (t, J = 6.9 Hz, 3H), 0.73－0.65 (m, 2H), 0.62－0.57 (m, 2H).
^{13}C NMR (75.5 MHz, $CDCl_3$): δ 83.1, 75.8, 31.4, 29.1, 28.5, 22.5, 18.7, 14.0, 7.9, -0.5.
FT-IR (neat): ν 3013, 2956, 2930, 2858, 1467, 1360 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 150 (M^+, 6), 121 (17), 107 (20), 93 (30), 79 (100).
HRMS (EI) calcd for $C_{11}H_{18}$: 150.1409. Found: 150.1411.

(±)-[(1*S*,2*S*)-2-butylcyclopropyl]ethynylbenzene (1v):



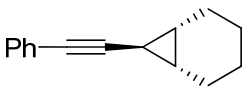
colorless oil, 99% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37－7.35 (m, 2H), 7.26－7.23 (m, 3H), 1.45－1.31 (m, 5H), 1.27－1.12 (m, 3H), 0.95－0.90 (m, 1H), 0.91 (t, J = 7.1 Hz, 3H), 0.65 (ddd, J = 7.9, 5.9, and 4.4 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 131.5, 128.1, 127.3, 124.1, 93.4, 75.9, 33.4, 31.3, 22.9, 22.4, 15.8, 14.1, 7.2.
FT-IR (neat): ν 2957, 2926, 2857, 2226, 1598, 1491, 1442 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 198 (M^+, 36), 155 (19), 141 (35), 128 (100), 115 (21).
HRMS (EI) calcd for $C_{15}H_{18}$: 198.1409. Found: 198.1412.

(±)-[(1*S*,2*S*)-2-phenylcyclopropyl]ethynylbenzene (1w):



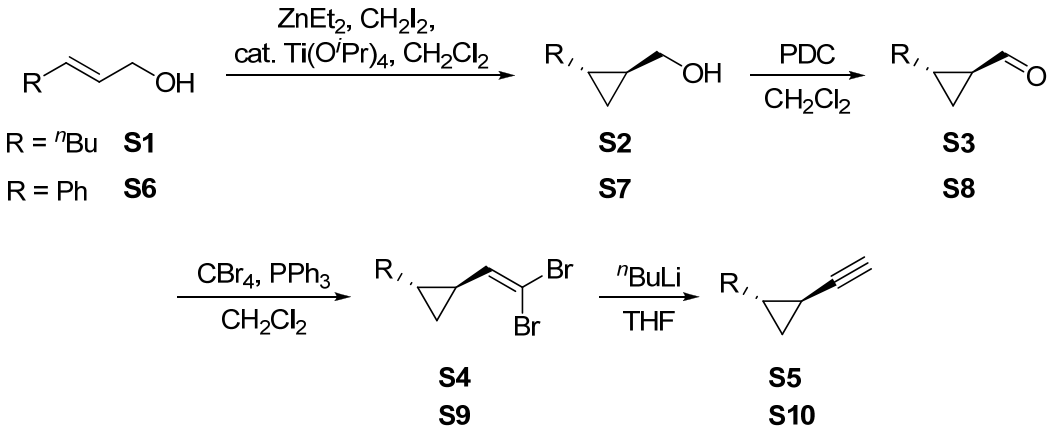
colorless oil, 79% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41－7.39 (m, 2H), 7.29－7.25 (m, 5H), 7.22－7.16 (m, 1H), 7.12－7.10 (m, 2H), 3.36 (ddd, J = 8.9, 6.2, and 4.4 Hz, 1H), 1.70 (ddd, J = 8.4, 5.3, and 4.4 Hz, 1H), 1.41 (ddd, J = 8.9, 5.3, and 4.4 Hz, 1H), 1.33 (ddd, J = 8.4, 6.2, and 4.4 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 131.6, 128.4, 128.2, 127.6, 126.2, 125.9, 123.7, 91.9, 77.03, 26.6, 18.0, 12.1.
FT-IR (neat): ν 3028, 2226, 1598, 1491, 1458, 1441 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 218 (M^+, 62), 217 (61), 203 (38), 202 (100), 141 (13), 115 (12).
HRMS (EI) calcd for $C_{17}H_{14}$: 218.1096. Found: 218.1099.

(1*R*,6*S*,7*r*)-7-(phenylethynyl)bicyclo[4.1.0]heptane (1x):



white solid, 93% yield, m.p.: 33－35 ^{o}C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36－7.34 (m, 2H), 7.29－7.21 (m, 3H), 1.96－1.87 (m, 2H), 1.78－1.71 (m, 2H), 1.37－1.35 (m, 2H), 1.31－1.21 (m, 2H), 1.19－1.13 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 131.5, 128.1, 127.2, 124.1, 93.6, 76.4, 22.9, 21.8, 21.0, 12.4.
FT-IR (neat): ν 2926, 2856, 2223, 1598, 1490, 1447 cm^{-1}.
MS (EI, 70 eV): *m/z* (%) 196 (M^+, 90), 167 (100), 153 (48), 141 (53), 128 (95), 115 (66), 91 (27).
HRMS (EI) calcd for $C_{15}H_{16}$: 196.1252. Found: 196.1255.

2.2 Synthesis of substituted cyclopropylacetylenes S5, S10, and S14



To a solution of $ZnEt_2$ (1 M hexane solution, 26 mL, 26 mmol) in 100 mL dry CH_2Cl_2 at −10 °C was added dropwise CH_2I_2 (13.0 g, 49 mmol). The resulting solution was stirred at that temperature for 15 min and a white precipitate was formed. Then the alcohol **S1** (2.37 g, 20.7 mmol) and $Ti(O^iPr)_4$ (0.35 g, 1.2 mmol) were added successively. The reaction mixture was warmed to room temperature and stirred over night. The reaction was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/AE = 4:1) to afford alcohol **S2** as a colorless oil (2.15 g, 81%).

S2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.48−3.40 (m, 2H), 1.41−1.20 (m, 7H), 0.89 (t, J = 7.0 Hz, 3H), 0.86−0.80 (m, 1H), 0.63−0.56 (m, 1H), 0.38−0.28 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 67.3, 33.3, 31.8, 22.5, 21.2, 17.2, 14.1, 9.9.

To a solution of **S2** (2.15 g, 16.8 mmol) in 60 mL CH_2Cl_2 was added PDC powder (12.6 g, 33.6 mmol). The reaction mixture was stirred at room temperature over night, diluted with 100 mL PE, and stirred for another 1 h. The resulting mixture was filtered through a pad of neutral Al_2O_3, and the filter cake was washed with Et_2O. The combined filtrate was concentrated to afford the crude aldehyde **S3**. To a solution of PPh_3 (16.8 g, 64 mmol) in 30 mL CH_2Cl_2 was added a solution of CBr_4 (10.6 g, 32 mmol) in 20 mL CH_2Cl_2 at 0 °C under argon. After stirred for 10 min, the crude aldehyde **S3** was added. The resulting mixture was stirred for 30 min at room temperature and diluted with 100 mL PE. The precipitate was removed by filtration through a pad of neutral Al_2O_3 and washed with PE. The combined filtrate was concentrated and purified by flash column chromatography on silica gel (eluted with PE) to afford compound **S4** as a colorless oil (3.28 g, 69%).

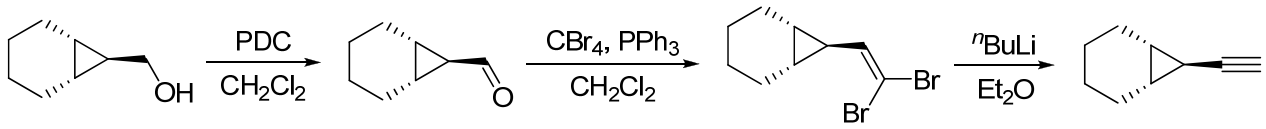
S4: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (d, J = 9.4 Hz, 1H), 1.41−1.24 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H), 0.71−0.65 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 84.5, 33.2, 31.4, 22.7, 22.4, 21.1, 14.06, 14.04.

To a solution of **S4** (3.28 g, 11.6 mmol) in 15 mL dry Et_2O was added *n*-BuLi (1.6 M hexane solution, 15 mL, 24 mmol) at −78 °C. The reaction mixture was allowed to stir at −78 °C for 1 h and at room temperature for 4 h, and then quenched with water and extracted with Et_2O. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated. The crude product was purified by flash column chromatography on silica gel

(eluted with pentane) to afford alkyne **S5** as a colorless oil (0.93 mg, 65%).
S5: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.78 (d, J = 2.0 Hz, 1H), 1.43－1.16 (m, 6H), 1.12－1.04 (m, 1H), 0.97－0.92 (m, 1H), 0.90 (t, J = 7.2 Hz, 3H), 0.86－0.82 (m, 1H), 0.56 (ddd, J = 8.3, 5.9, and 4.3 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 87.6, 63.5, 33.3, 31.2, 22.5, 22.4, 15.2, 14.1, 6.1.

S6 was converted to **S10** following the procedures for the preparation of **S5**. Compounds **S7**, **S9**, and **S10** are known compounds.[3]
S7: colorless oil, 86% yield.
S9: colorless oil, 62% yield.
S10: colorless oil, 77% yield.



S11 **S12** **S13** **S14**

Alcohol **S11** is a known compound[4] and was prepared by following the literature procedures. **S11** was converted to **S14** following the procedures for the preparation of **S5**.

S13: colorless oil, a 5.6 : 1 mixture of two inseparable diastereomers, 61% yield.
^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ 5.80 (d, J = 9.4 Hz, 1H), 1.92－1.84 (m, 2H), 1.74－1.67 (m, 2H), 1.30－1.18 (m, 5H), 1.12－1.09 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ 142.6, 83.8, 28.1, 23.0, 21.2, 20.0.

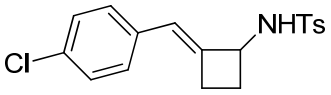
S14: colorless oil, the major isomer obtained by flash column chromatography on silica gel (eluted with pentane), 59% yield. No attempt was taken to get the minor isomer from the reaction mixture.
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93－1.84 (m, 2H), 1.82 (d, J = 2.0 Hz, 1H), 1.73－1.67 (m, 2H), 1.29－1.20 (m, 4H), 1.16－1.07 (m, 2H), 0.94 (td, J = 4.6 and 2.0 Hz,1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 88.0, 63.8, 22.8, 21.2, 20.9, 11.3.

(3) Schmittel, M.; Mahajan, A. A.; Bucher, G.; Bats, J. W. *J. Org. Chem.* **2007**, *72*, 2166.
(4) Trost, B. M.; Shen, H. C.; Horne, D. B.; Toste, F. D.; Steinmetz, B. G.; Koradin, C. *Chem. Eur. J.* **2005**, *11*, 2577.

2.3 General procedure for the ring expansion reaction

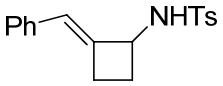
$AuPPh_3Cl$ (12 mg, 0.025 mmol, 5 mol %) and AgOTf (6 mg, 0.025 mmol, 5 mol %) were mixed in 1 mL dry DCE (or TCE) under argon atmosphere. The mixture was stirred at room temperature (or 80 °C, TCE as solvent) for 30 min with sufficient precipitation of AgCl, and then was added to a solution of alkynylcyclopropane derivative (0.5 mmol) and sulfonamide (0.6 mmol) in 4 mL dry DCE (or TCE). The resulting mixture was heated at the indicated temperature. When TLC indicated the disappearance of the alkynylcyclopropane derivative, the reaction mixture was cooled to room temperature and purified by flash column chromatography on silica gel (eluted with PE to PE/EA = 7:1) to afford the corresponding alkylidenecyclobutyl sulfonamide product. All the products were assigned to have an *E*-olefinic configuration by compared to product **3h**, which was determined by X-ray crystallographic analysis.

(*E*)-*N*-[2-(4-Chlorobenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3a):



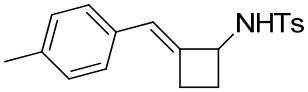
white solid (76% yield, DCE as solvent, 80 °C, 14 h), m.p.: 145－146 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 6.05－6.03 (m, 1H), 5.13 (d, J = 9.7 Hz, 1H), 4.63－4.54 (m, 1H), 2.68－2.62 (m, 2H), 2.43 (s, 3H), 2.33－2.25 (m, 1H), 1.84－1.74 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 143.6, 138.1, 134.7, 132.4, 129.8, 128.8, 128.5, 127.0, 120.3, 54.5, 29.8, 27.0, 21.5.
FT-IR (neat): ν 3277, 2925, 1598, 1491, 1329 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{18}ClNNaO_2S$ [M+Na^+]: 370.0639. Found: 370.0632.

(*E*)-*N*-(2-Benzylidenecyclobutyl)-4-methylbenzenesulfonamide (3b):



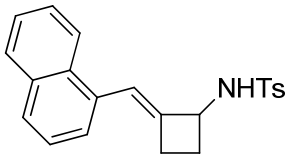
white solid (63% yield, DCE as solvent, 80 °C, 6 h), m.p.: 141－142 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.2 Hz, 2H), 7.32－7.26 (m, 4H), 7.18 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.0 Hz, 2H), 6.06－6.04 (m, 1H), 5.09 (d, J = 10.2 Hz, 1H), 4.64－4.56 (m, 1H), 2.70－2.65 (m, 2H), 2.42 (s, 3H), 2.32－2.24 (m, 1H), 1.82－1.73 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 143.5, 138.2, 136.2, 129.8, 128.4, 127.7, 127.0, 126.9, 121.4, 54.6, 30.0, 27.1, 21.5.
FT-IR (neat): ν 3273, 2923, 1598, 1492, 1334 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{19}NNaO_2S$ [M+Na^+]: 336.1029. Found: 336.1024.

(*E*)-4-Methyl-*N*-[2-(4-methylbenzylidene)cyclobutyl]benzenesulfonamide (3c):



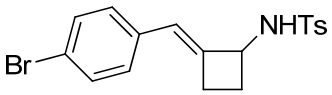
white solid (46% yield, DCE as solvent, 80 °C, 20 h), m.p.: 144－145 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 7.01 (d, J = 7.8 Hz, 2H), 6.01－5.99 (m, 1H), 5.02 (d, J = 10.1 Hz, 1H), 4.63－4.55 (m, 1H), 2.69－2.64 (m, 2H), 2.42 (s, 3H), 2.31 (s, 3H), 2.33－2.24 (m, 1H), 1.81－1.71 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 142.7, 138.2, 136.6, 133.4, 129.7, 129.1, 127.6, 127.0, 121.2, 54.5, 29.9, 27.1, 21.4, 21.1.
FT-IR (neat): ν 3288, 2916, 2849, 1667, 1598, 1438 cm^{-1}.
HRMS (ESI) calcd for $C_{19}H_{21}NNaO_2S$ [M+Na$^+$]: 350.1185. Found: 350.1181.

(*E*)-4-Methyl-*N*-[2-(naphthalen-1-ylmethylene)cyclobutyl]benzenesulfonamide (3d):



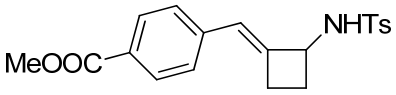
white solid (14% yield, TCE as solvent, 100 °C, 14 h), m.p. = 140－141 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89－7.87 (m, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.82－7.79 (m, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.48－7.43 (m, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.1 Hz, 1H), 6.78－6.76 (m, 1H), 5.35 (d, J = 10.2 Hz, 1H), 4.74－4.66 (m, 1H), 2.70－2.61 (m, 1H), 2.56－2.48 (m, 1H), 2.38 (s, 3H), 2.32－2.24 (m, 1H), 1.81－1.71 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 143.6, 138.2, 133.6, 132.3, 131.2, 129.8, 128.4, 127.4, 127.0, 125.9, 125.7, 125.2, 123.8, 117.7, 54.6, 29.8, 26.8, 21.5.
FT-IR (neat): ν 3276, 3047, 2948, 1598, 1433 cm^{-1}.
HRMS (ESI) calcd for $C_{22}H_{21}NNaO_2S$ [M+Na$^+$]: 386.1185. Found: 386.1185.

(*E*)-*N*-[2-(4-Bromobenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3f):



white solid (66% yield, TCE as solvent, 100 °C, 7 h), m.p. = 143－144 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 6.03－6.01 (m, 1H), 5.23 (d, J = 10.3 Hz, 1H), 4.61－4.52 (m, 1H), 2.66－2.60 (m, 2H), 2.42 (s, 3H), 2.32－2.24 (m, 1H), 1.84－1.74 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 143.5, 138.1, 135.1, 131.5, 129.7, 129.1, 127.0, 120.5, 120.3, 54.5, 29.7, 27.0, 21.5.
FT-IR (neat): ν 3210, 2924, 1491, 1434, 1236 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{18}BrNNaO_2S$ [M+Na$^+$]: 414.0134. Found: 414.0132.

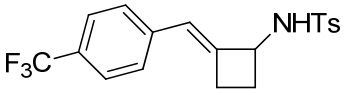
(*E*)-Methyl 4-[2-(4-methylphenylsulfonamido)cyclobutylidene]methylbenzoate (3g):



white solid (77% yield, TCE as solvent, 100 °C, 7 h), m.p. = 157－158 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2

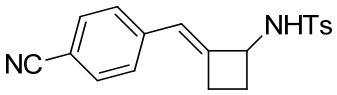
Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 6.12－6.10 (m, 1H), 5.36 (d, J = 9.7 Hz, 1H), 4.65－4.57 (m, 1H), 3.89 (s, 3H), 2.73－2.66 (m, 2H), 2.42 (s, 3H), 2.34－2.26 (m, 1H), 1.87－1.77 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 147.3, 143.6, 140.8, 138.1, 129.8, 129.7, 128.1, 127.4, 127.0, 120.6, 54.6, 52.0, 29.6, 27.3, 21.5.
FT-IR (neat): ν 3255, 2953, 1702, 1609, 1438 cm^{-1}.
HRMS (ESI) calcd for $C_{20}H_{21}NNaO_4S$ [M+Na$^+$]: 394.1084. Found: 394.1082.

(*E*)-4-Methyl-*N*-[2-(4-trifluoromethylbenzylidene)cyclobutyl]benzene sulfonamide (3h):



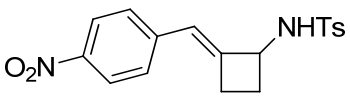
white solid (84% yield, TCE as solvent, 100 ^{o}C, 13 h), m.p. = 127－128 ^{o}C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.15－6.13 (m, 1H), 5.44 (d, J = 9.9 Hz, 1H), 4.65－4.56 (m, 1H), 2.73－2.65 (m, 2H), 2.41 (s, 3H), 2.33－2.25 (m, 1H), 1.87－1.78 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 143.6, 139.7, 138.0, 129.7, 128.4 (q, J = 32.4 Hz), 127.7, 127.0, 125.2 (q, J = 4.6 Hz), 124.1 (q, J = 272.1 Hz), 120.2, 54.5, 29.5, 27.1, 21.4.
FT-IR (neat): ν 3270, 2955, 1615, 1438, 1324 cm^{-1}.
HRMS (ESI) calcd for $C_{19}H_{18}F_3NNaO_2S$ [M+Na$^+$]: 404.0903. Found: 404.0903.

(*E*)-*N*-[2-(4-Cyanobenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3i):



white solid (70% yield, TCE as solvent, 100 ^{o}C, 13 h), m.p. = 172－174 ^{o}C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 6.16－6.14 (m, 1H), 5.26 (d, J = 9.8 Hz, 1H), 4.66－4.58 (m, 1H), 2.75－2.65 (m, 2H), 2.44 (s, 3H), 2.36－2.28 (m, 1H), 1.88－1.78 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 143.7, 140.8, 137.9, 132.2, 129.8, 128.0, 127.0, 120.1, 118.9, 109.9, 54.5, 29.6, 27.3, 21.5.
FT-IR (neat): ν 3270, 2952, 2225, 1604, 1437 cm^{-1}.
HRMS (ESI) calcd for $C_{19}H_{18}N_2NaO_2S$ [M+Na$^+$]: 361.0981. Found: 361.0973.

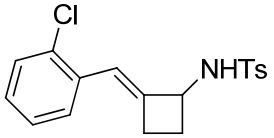
(*E*)-4-Methyl-*N*-[2-(4-nitrobenzylidene)cyclobutyl]benzenesulfonamide (3j):



white solid (54% yield, TCE as solvent, 100 ^{o}C, 13 h), m.p. = 204－206 ^{o}C.
^{1}H NMR (400 MHz, d_6-DMSO): δ 8.31 (d, J = 7.8 Hz, 1H), 8.16 (d, J = 6.8 Hz, 2H), 7.75 (d, J = 6.8 Hz, 2H), 7.44－7.37 (m, 4H), 6.12 (s, 1H), 4.48 (br s, 1H), 2.79－2.69 (m, 1H), 2.69－2.58 (m, 1H), 2.40 (s, 3H), 2.11－2.02 (m, 1H), 1.82－1.71 (m, 1H).
^{13}C NMR (100 MHz, d_6-DMSO): δ 151.7, 145.4, 143.1, 142.8, 138.9, 129.7, 128.1, 126.5, 123.9, 118.5, 54.2, 28.0, 27.1, 21.0.

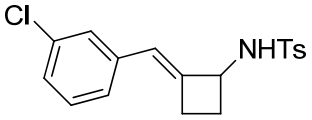
FT-IR (neat): *v* 3270, 2951, 2927, 1595, 1512 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{18}N_2NaO_4S$ [M+Na^+]: 381.0880. Found: 381.0873.

(*E*)-*N*-[2-(2-Chlorobenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3k):



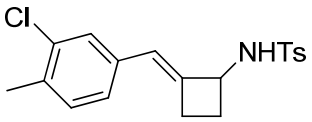
white solid (75% yield, TCE as solvent, 100 °C, 7 h), m.p. = 134－135 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.32－7.28 (m, 1H), 7.20－7.08 (m, 3H), 6.38－6.36 (m, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.67－4.59 (m, 1H), 2.69－2.51 (m, 2H), 2.41 (s, 3H), 2.34－2.26 (m, 1H), 1.85－1.75 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 143.5, 138.1, 133.8, 133.0, 129.8, 129.6, 128.5, 127.9, 126.9, 126.4, 117.3, 54.6, 29.8, 26.8, 21.5.
FT-IR (neat): *v* 3243, 2957, 2917, 2849, 1436, 1327 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{18}ClNNaO_2S$ [M+Na^+]: 370.0639. Found: 370.0637.

(*E*)-*N*-[2-(3-Chlorobenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3l):



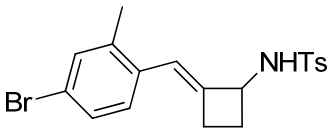
white solid (88% yield, TCE as solvent, 100 °C, 7 h), m.p. = 105－106 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.22－7.13 (m, 2H), 7.06 (s, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.00－5.98 (m, 1H), 5.15 (d, *J* = 9.9 Hz, 1H), 4.64－4.56 (m, 1H), 2.71－2.64 (m, 2H), 2.44 (s, 3H), 2.34－2.26 (m, 1H), 1.85－1.75 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 143.6, 138.1, 138.0, 134.2, 129.8, 129.6, 127.5, 127.0, 126.8, 125.8, 120.2, 54.5, 29.7, 27.0, 21.5.
FT-IR (neat): *v* 3267, 2949, 1593, 1563, 1434, 1332 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{18}ClNNaO_2S$ [M+Na^+]: 370.0639. Found: 370.0637.

(*E*)-*N*-[2-(3-Chloro-4-methylbenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3m):



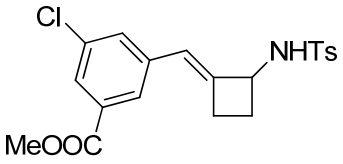
white solid (87% yield, DCE as solvent, 100 °C, 36 h), m.p. = 119－120 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 1.1 Hz, 1H), 6.89 (dd, *J* = 7.9 and 1.1 Hz, 1H), 5.95－5.93 (m, 1H), 5.17 (d, *J* = 9.7 Hz, 1H), 4.62－4.54 (m, 1H), 2.68－2.63 (m, 2H), 2.43 (s, 3H), 2.32 (s, 3H), 2.31－2.24 (m, 1H), 1.84－1.69 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 143.5, 138.1, 135.5, 134.4, 134.3, 130.8, 139.8, 127.9, 127.0, 125.8, 120.1, 54.5, 29.7, 27.0, 21.5, 19.7.
FT-IR (neat): *v* 3274, 2989, 2949, 2919, 1598, 1553, 1495, 1438 cm^{-1}.
HRMS (ESI) calcd for $C_{19}H_{20}ClNNaO_2S$ [M+Na^+]: 384.0796. Found: 384.0791.

(*E*)-*N*-[2-(4-Bromo-2-methylbenzylidene)cyclobutyl]-4-methylbenzenesulfonamide (3n):



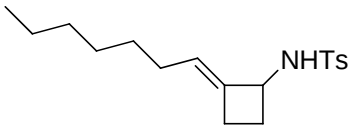
white solid (59% yield, TCE as solvent, 100 °C, 13 h), m.p. = 140－141 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.26 (s, 1H), 7.22 (dd, J = 8.2 and 1.6 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.15－6.13 (m, 1H), 5.09 (d, J = 10.1 Hz, 1H), 4.65－4.56 (m, 1H), 2.66－2.47 (m, 2H), 2.42 (s, 3H), 2.32－2.24 (m, 1H), 2.14 (s, 3H), 1.80－1.71 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 143.5, 138.1, 137.8, 133.5, 132.9, 129.8, 128.66, 128.63, 126.9, 120.5, 117.7, 54.5, 29.7, 26.8, 21.5, 19.5.
FT-IR (neat): ν 3270, 2986, 2950, 2920, 1598, 1586, 1478, 1438 cm^{-1}.
HRMS (ESI) calcd for $C_{19}H_{20}BrNNaO_2S$ [M+Na$^+$]: 428.0290. Found: 428.0293.

(*E*)-Methyl 3-chloro-5-[2-(4-methylphenylsulfonamido)cyclobutylidene]methylbenzoate (3o):



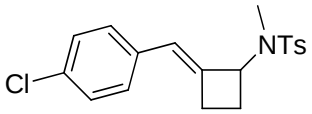
white solid (85% yield, TCE as solvent, 100 °C, 13 h), m.p. = 165－166 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.2 Hz, 2H), 7.81－7.79 (m, 1H), 7.63 (s, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.23－7.22 (m, 1H), 5.99－5.97 (m, 1H), 5.21 (d, J = 10.3 Hz, 1H), 4.65－4.57 (m, 1H), 3.91 (s, 3H), 2.75－2.68 (m, 2H), 2.45 (s, 3H), 2.38－2.29 (m, 1H), 1.89－1.79 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 147.3, 143.7, 138.2, 138.1, 134.5, 131.8, 131.4, 129.8, 127.6, 127.0, 126.9, 119.5, 54.5, 52.5, 29.6, 27.0, 21.5.
FT-IR (neat): ν 3276, 2952, 1725, 1597, 1574, 1437 cm^{-1}.
HRMS (ESI) calcd for $C_{20}H_{20}ClNNaO_4S$ [M+Na$^+$]: 428.0694. Found: 428.0691.

(*E*)-*N*-(2-Heptylidenecyclobutyl)-4-methylbenzenesulfonamide (3p):



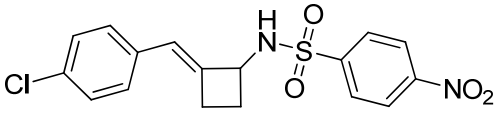
light brown oil (45% yield, DCE as solvent, 50 °C, 20 h).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 5.08 －5.02 (m, 1H), 4.82 (d, J = 9.8 Hz, 1H), 4.41－4.34 (m, 1H), 2.43 (s, 3H), 2.41－2.33 (m, 1H), 2.27－2.09 (m, 2H), 1.84－1.79 (m, 2H), 1.65－1.56 (m, 1H), 1.31－1.17 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 140.6, 138.2, 129.6, 127.0, 121.9, 53.8, 31.7, 29.2, 28.74, 28.68, 27.5, 23.9, 22.6, 21.5, 14.0.
FT-IR (neat): ν 3267, 2955, 2926, 2854, 1599, 1437 cm^{-1}.
HRMS (ESI) calcd for $C_{18}H_{27}NNaO_2S$ [M+Na$^+$]: 344.1655. Found: 344.1652.

(*E*)-*N*-[2-(4-Chlorobenzylidene)cyclobutyl]-*N*,4-dimethylbenzenesulfonamide (3r):



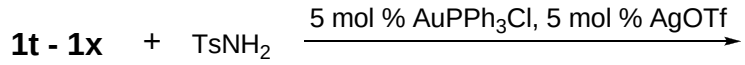
white solid (84% yield, DCE as solvent, 80 °C, 12 h), m.p. = 110－111 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 5.79－5.76 (m, 1H), 5.31 (t, J = 7.0 Hz, 1H), 2.77 (s, 3H), 2.72－2.60 (m, 2H), 2.44 (s, 3H), 2.15－1.98 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 142.3, 136.0, 134.8, 132.4, 129.7, 128.7, 128.6, 127.2, 121.3, 58.6, 29.2, 26.9, 23.3, 21.5.
FT-IR (neat): ν 2957, 1597, 1491, 1338 cm^{-1}.
HRMS (ESI) calcd for $C_{19}H_{20}ClNNaO_2S$ [M+Na$^+$]: 384.0796. Found: 384.0795.

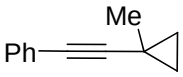
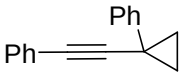
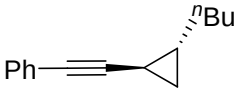
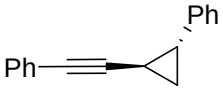
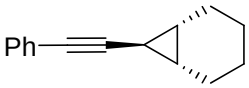
(*E*)-*N*-[2-(4-Chlorobenzylidene)cyclobutyl]-4-nitrobenzenesulfonamide (3s):



white solid (47% yield, TCE as solvent, 100 °C, 14 h), m.p. = 161－162 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 9.0 Hz, 2H), 8.09 (d, J = 9.0 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 6.17－6.15 (m, 1H), 5.15 (d, J = 9.3 Hz, 1H), 4.68－4.60 (m, 1H), 2.75－2.69 (m, 2H), 2.42－2.34 (m, 1H), 1.91－1.82 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 147.1, 143.7, 134.4, 133.0, 128.9, 128.8, 128.2, 124.4, 121.1, 54.7, 29.8, 27.2.
FT-IR (neat): ν 3273, 3108, 2987, 1607, 1529, 1491 cm^{-1}.
HRMS (ESI) calcd for $C_{17}H_{15}ClN_2NaO_4S$ [M+Na$^+$]: 401.0333. Found: 401.0330.

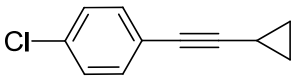
3. Effect of substituents on the cyclopropane rings



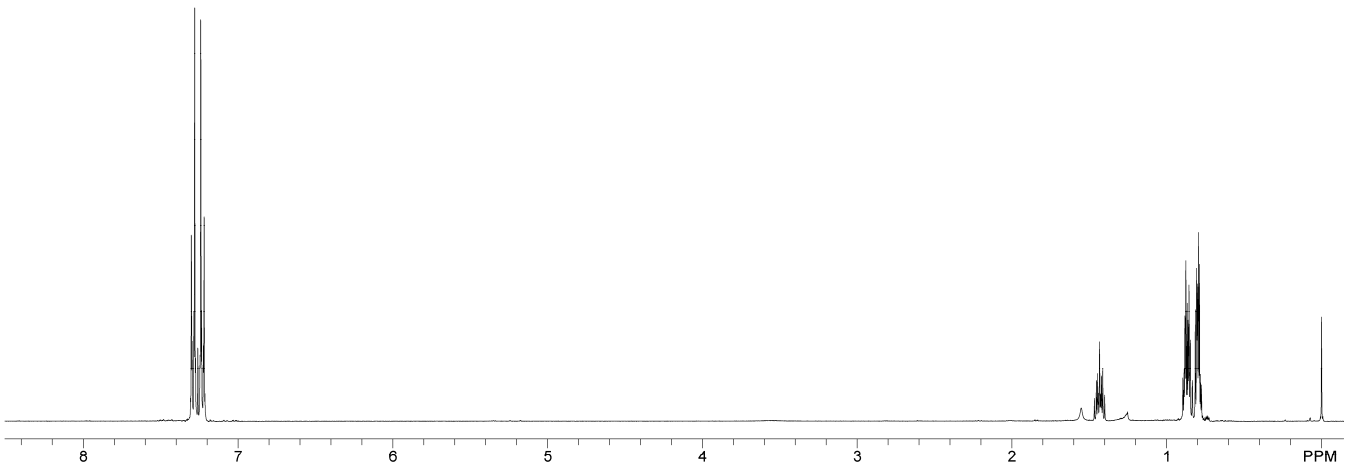
entry[a]	substrate		solvent	temp (°C)	time (h)	yield (%)	conversion (%)
1		(**1t**)	DCE	80	14	ND[b]	>99
2		(**1t**)	TCE	100	14	ND[b]	>99
3		(**1u**)	TCE	100	14	ND[b]	>99
4		(**1v**)	DCE	80	14	ND[b]	>99
5		(**1w**)	DCE	80	14	ND[b]	>99
6		(**1x**)	DCE	80	14	ND[b]	>99

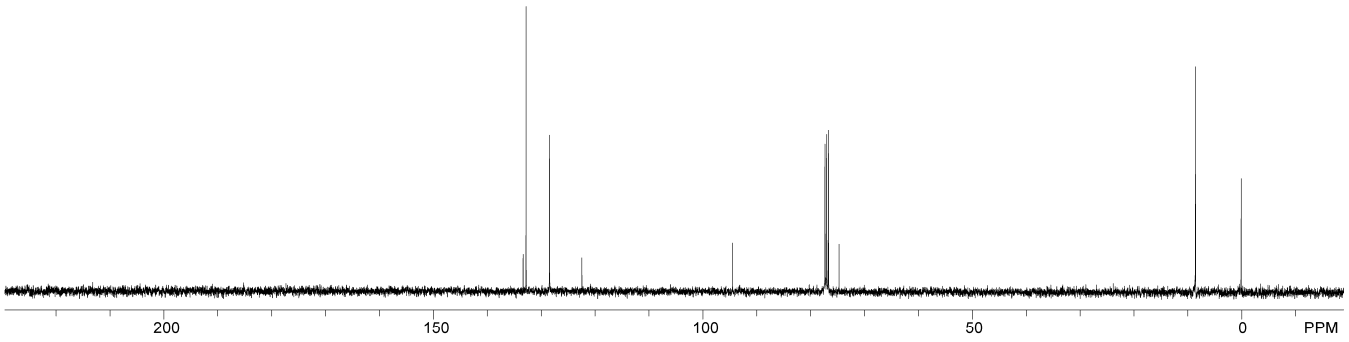
[a] Reaction condition: substrate (0.5 mmol), $TsNH_2$ (0.6 mmol), catalyst (0.05 mmol), solvent (5 mL). [b] ND = product not detected. Mixtures of unidentified products were obtained.

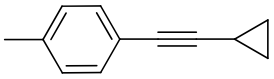
4. ^{1}H and ^{13}C-NMR spectra for new compounds



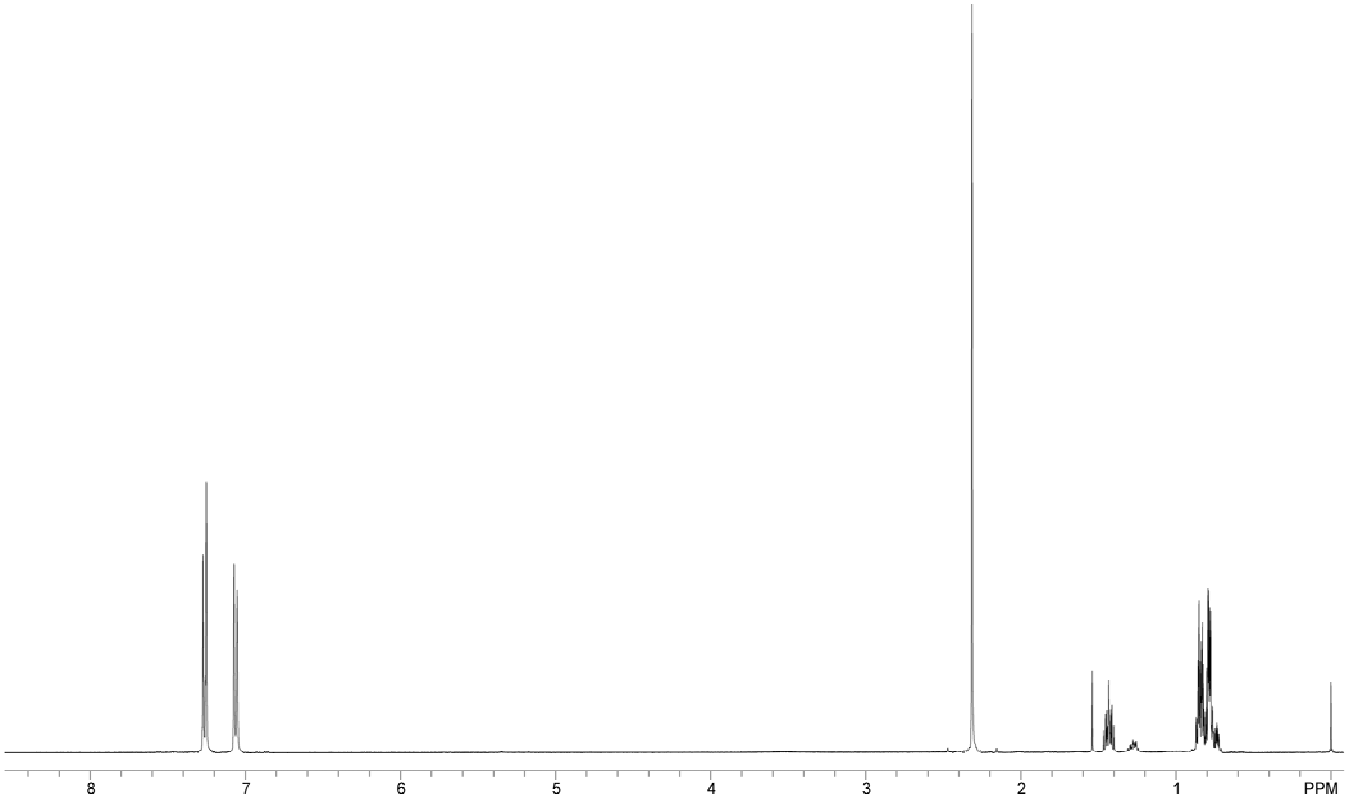
1a

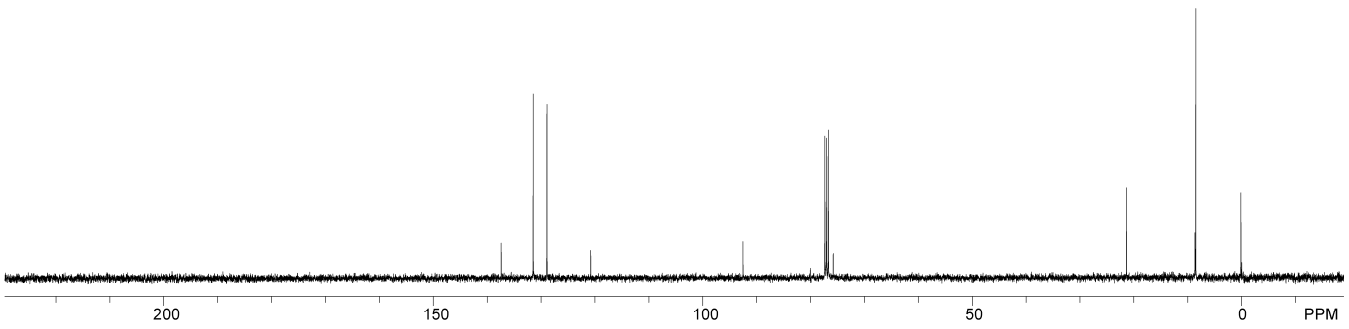


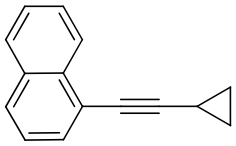




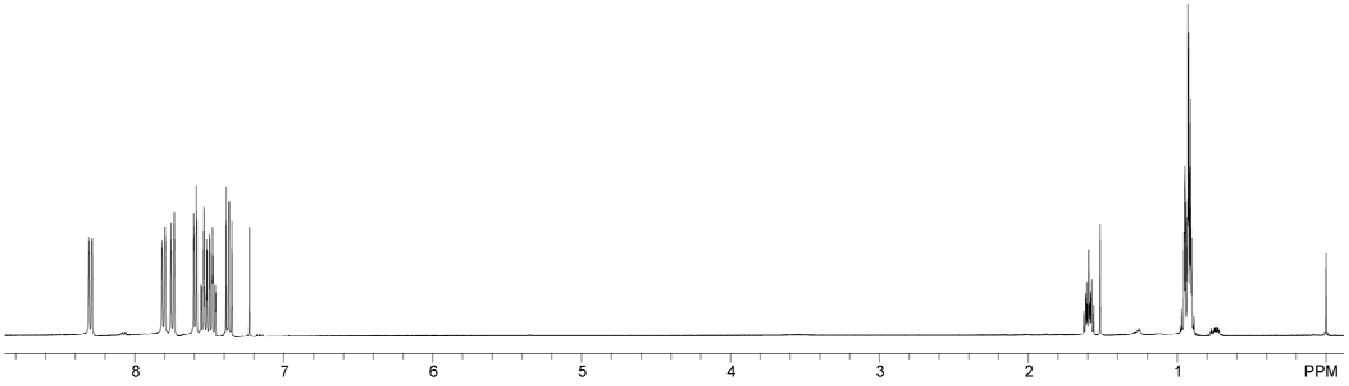
1c

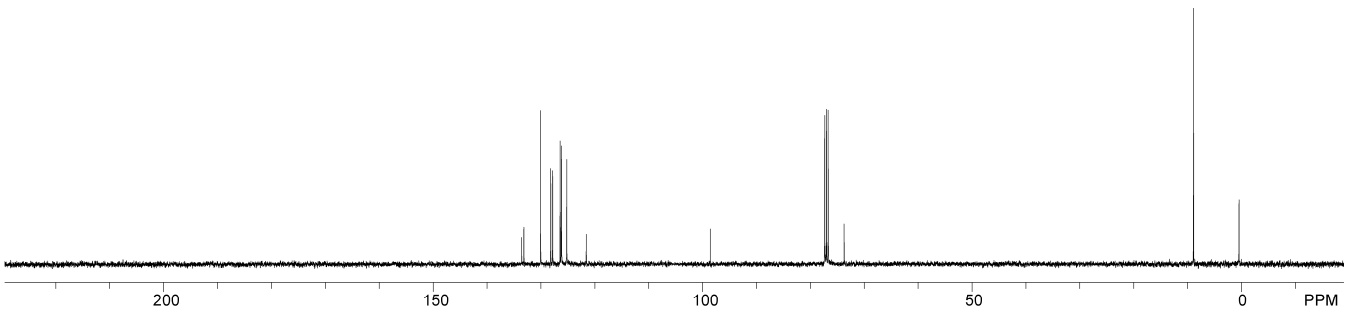


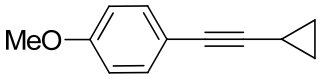




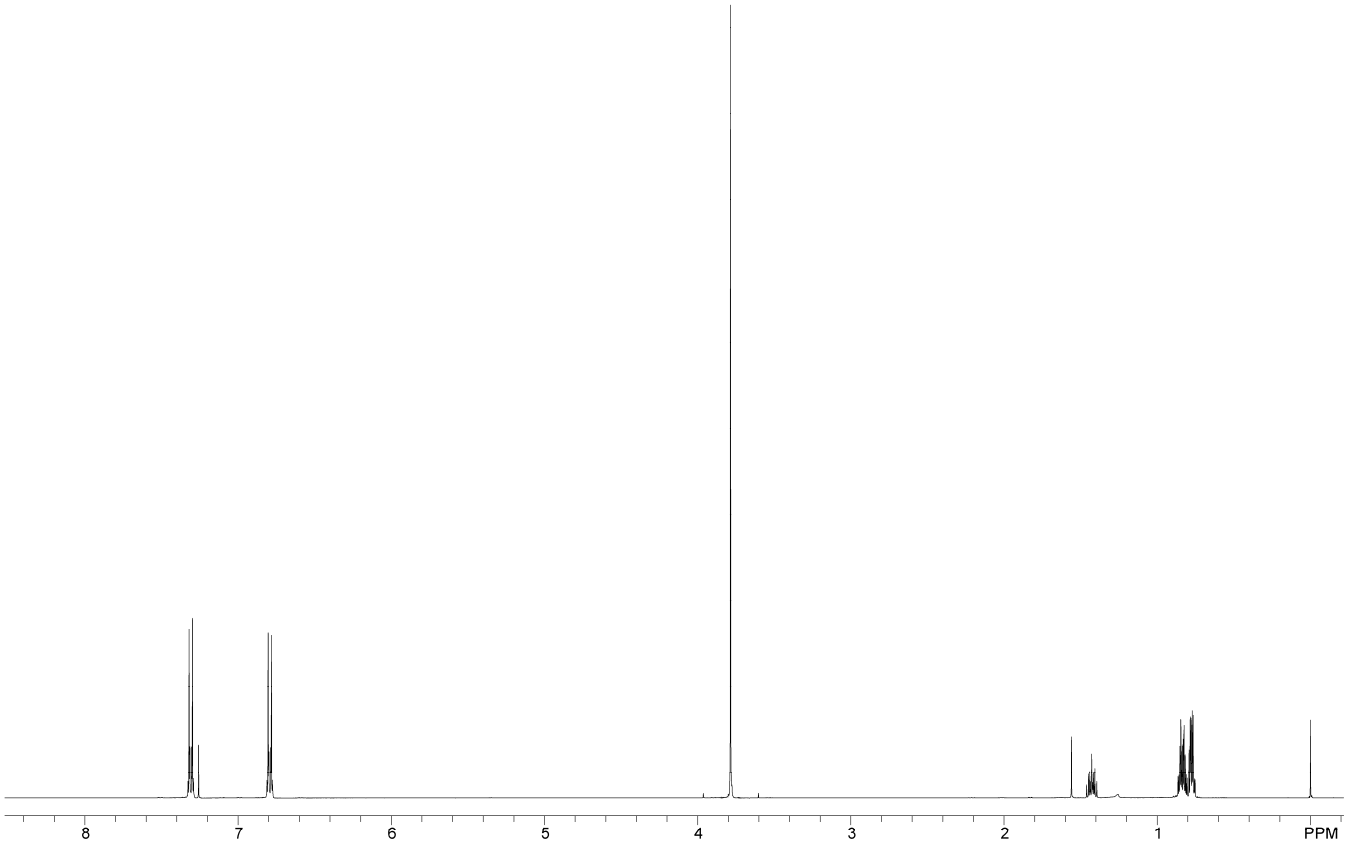
1d

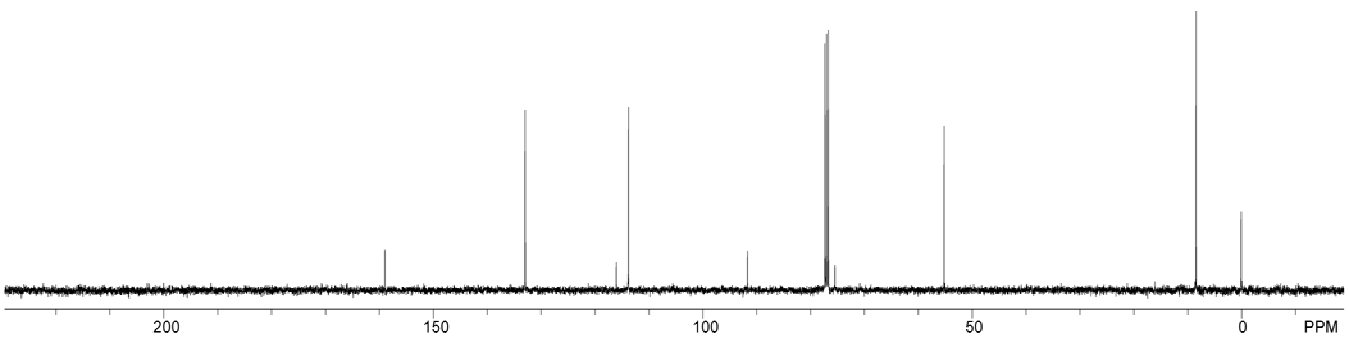


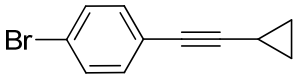




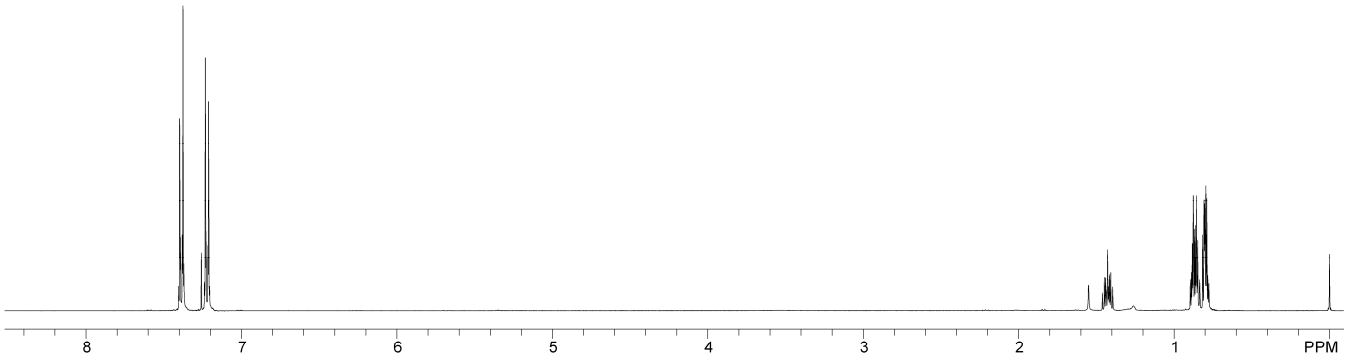
1e

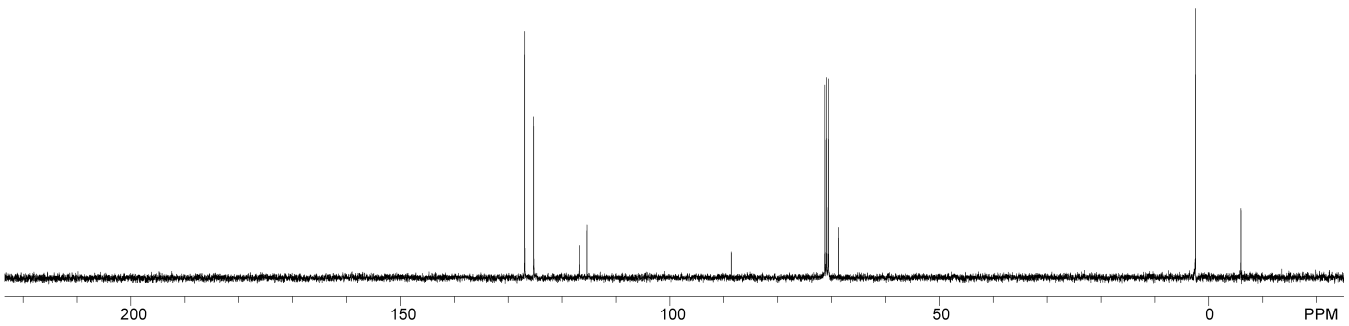


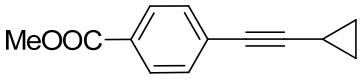




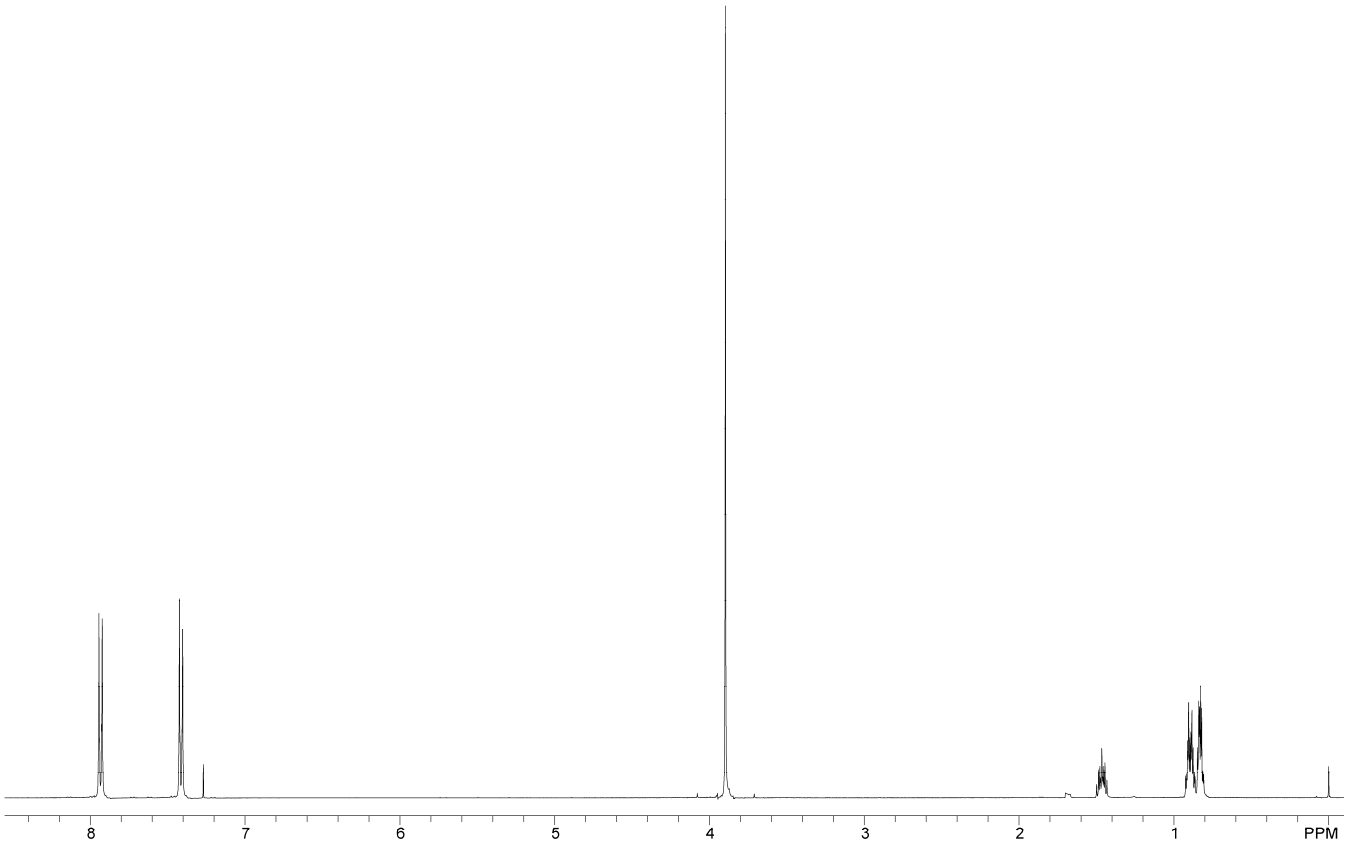
1f

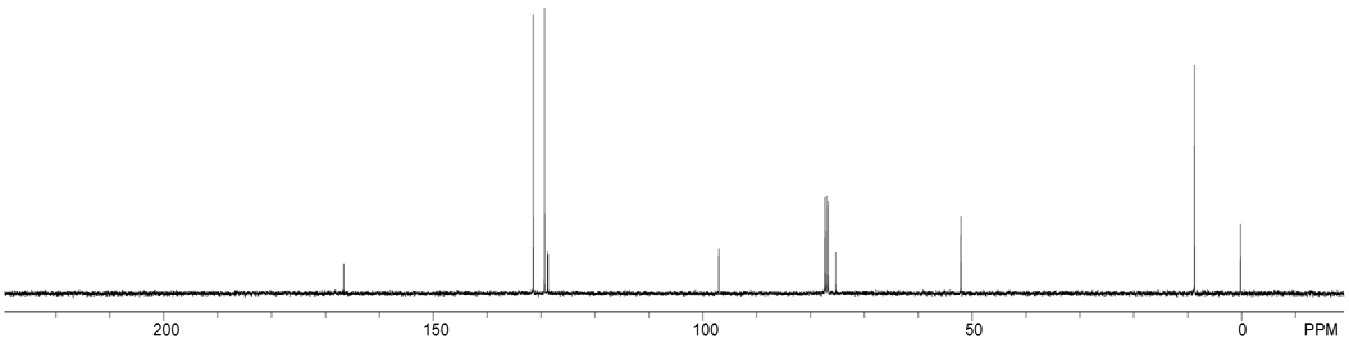


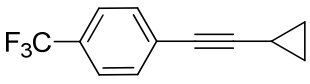




1g







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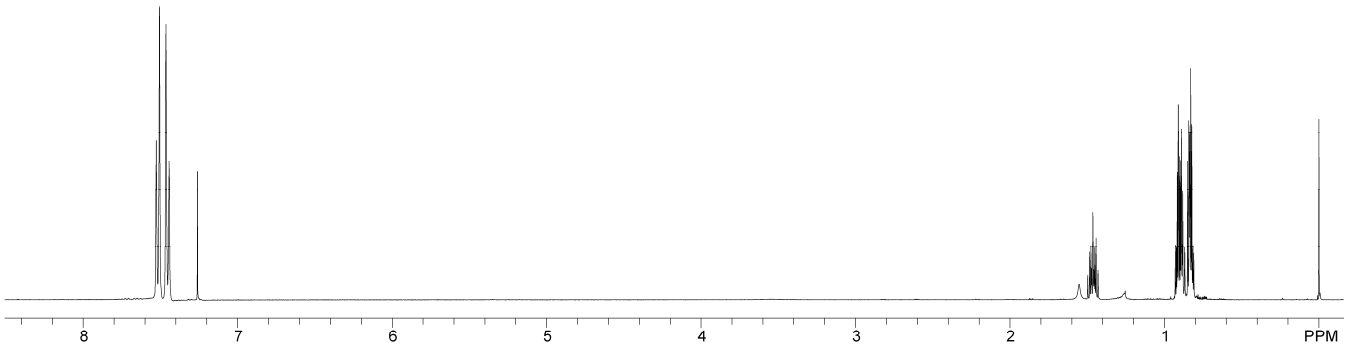

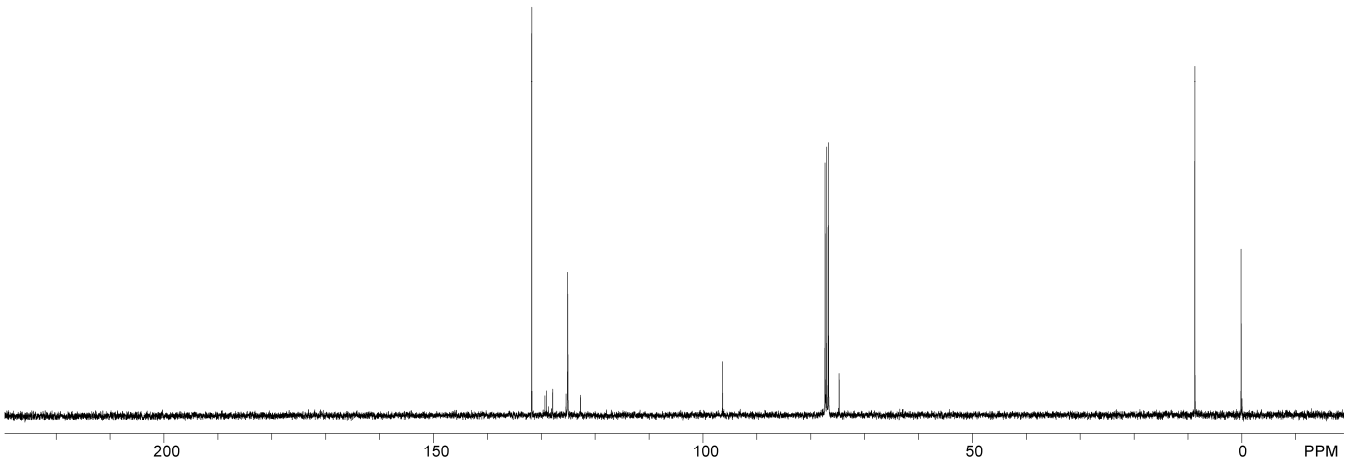

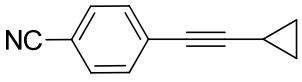

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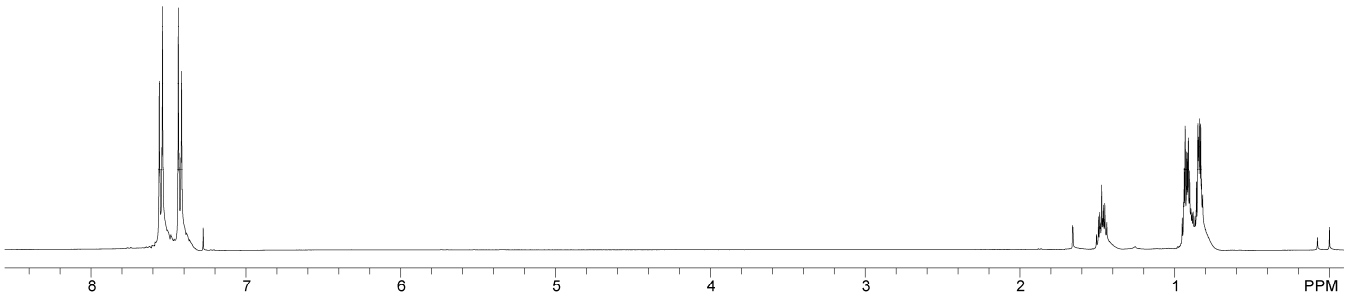

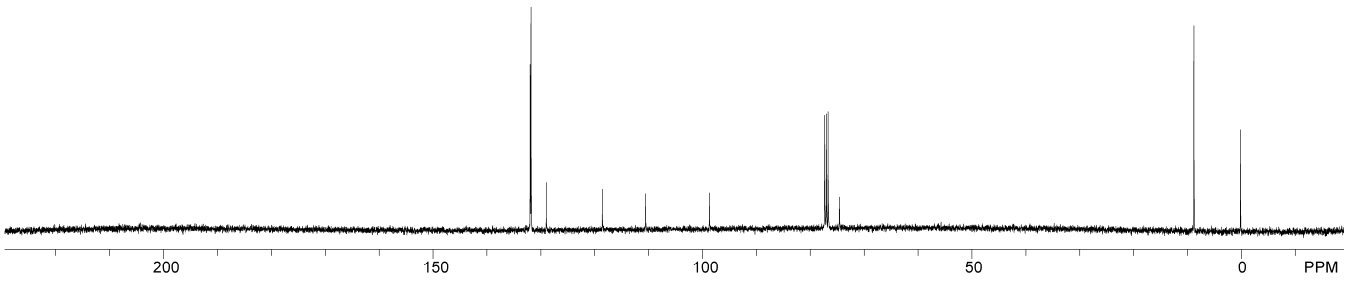

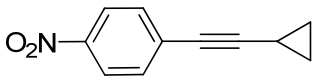

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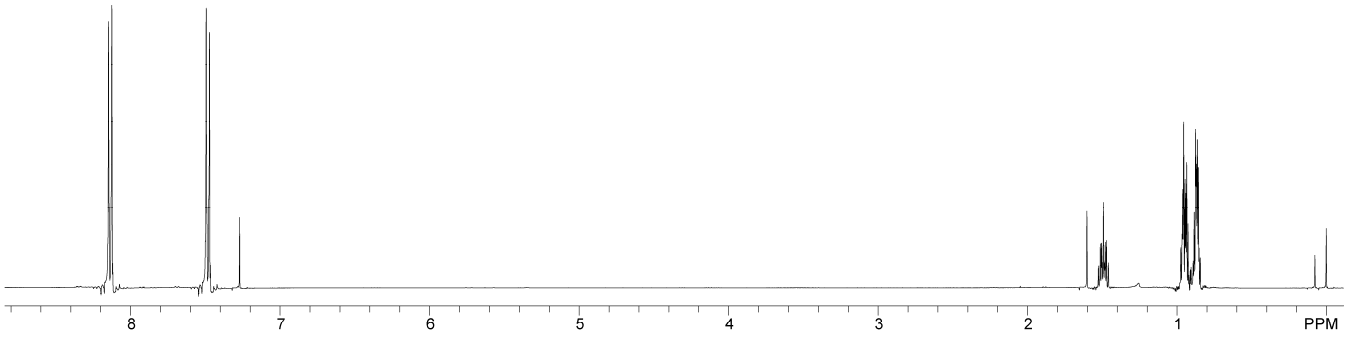

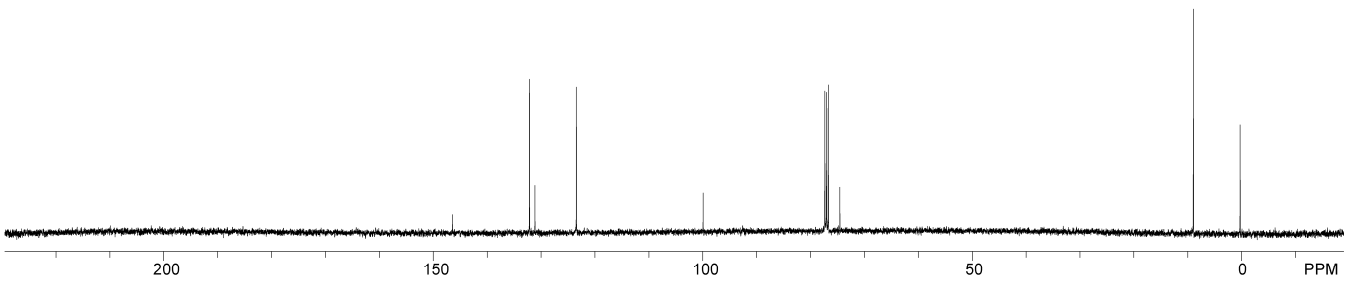

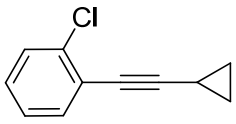

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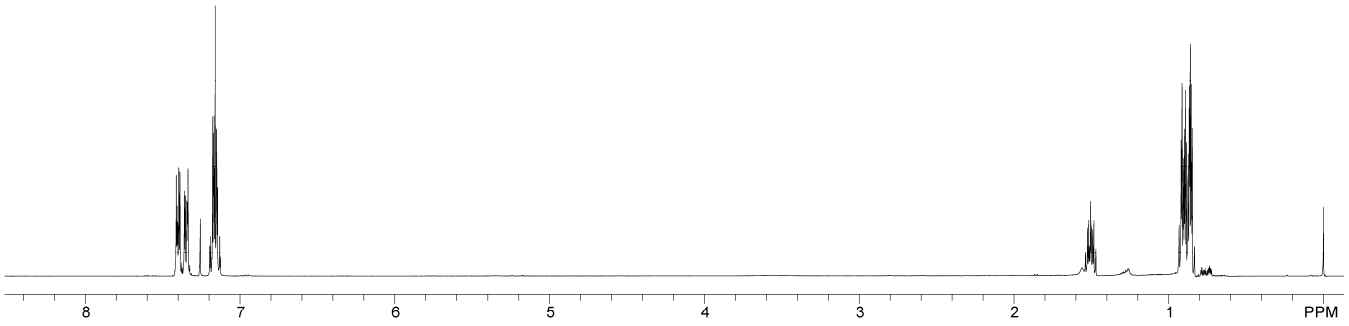

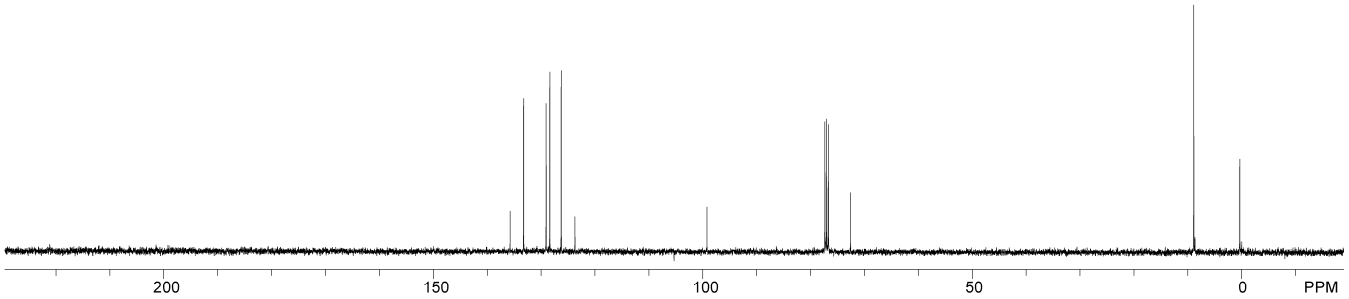

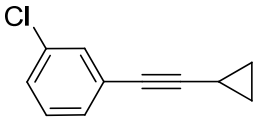

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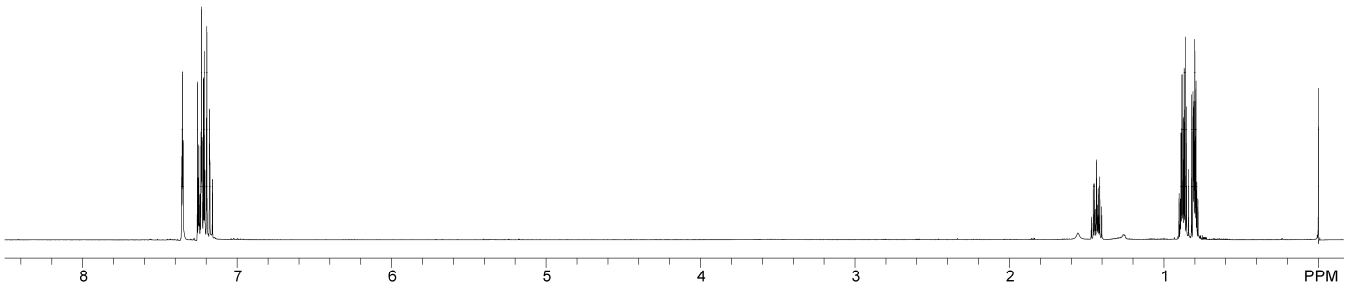

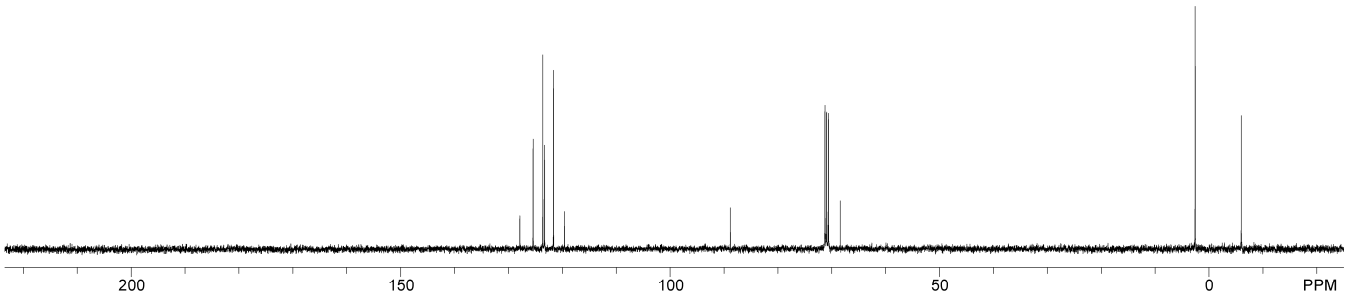

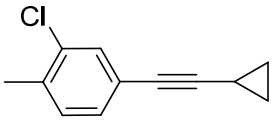

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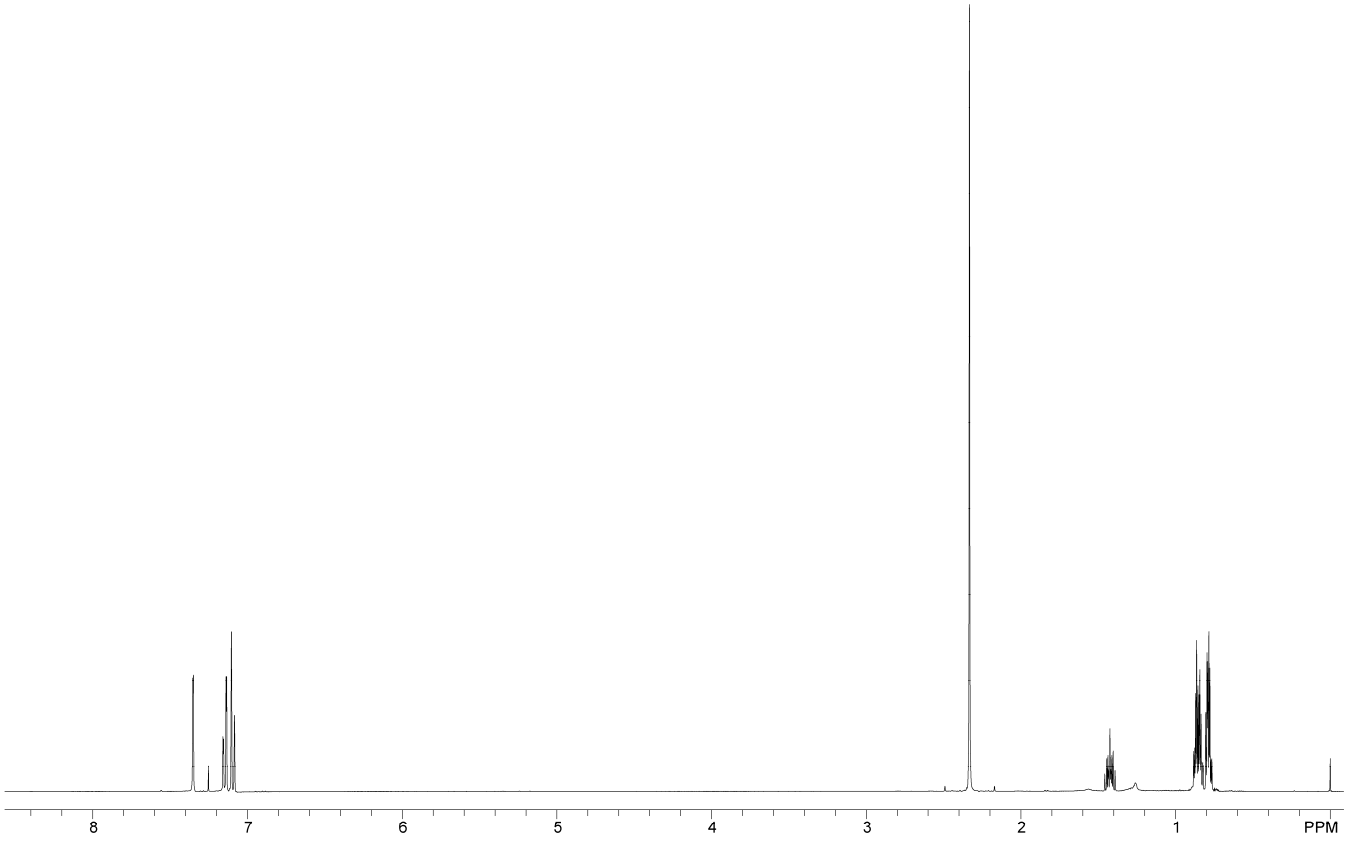

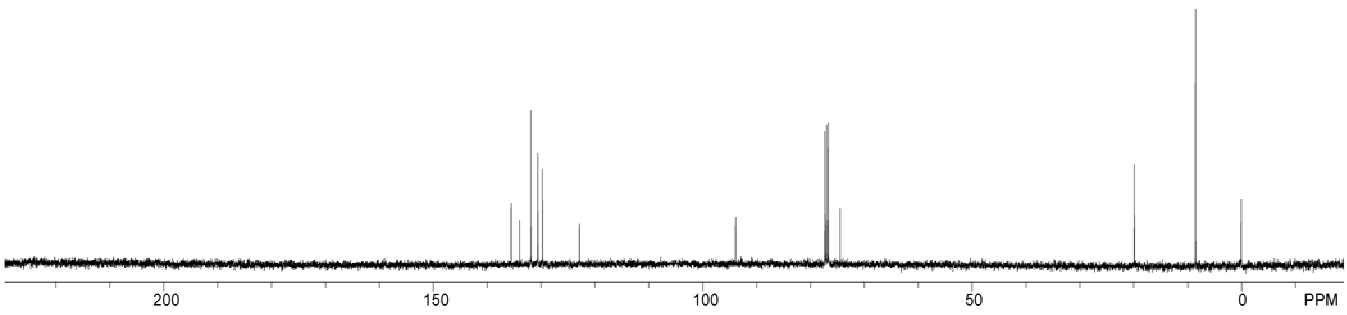

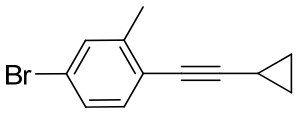

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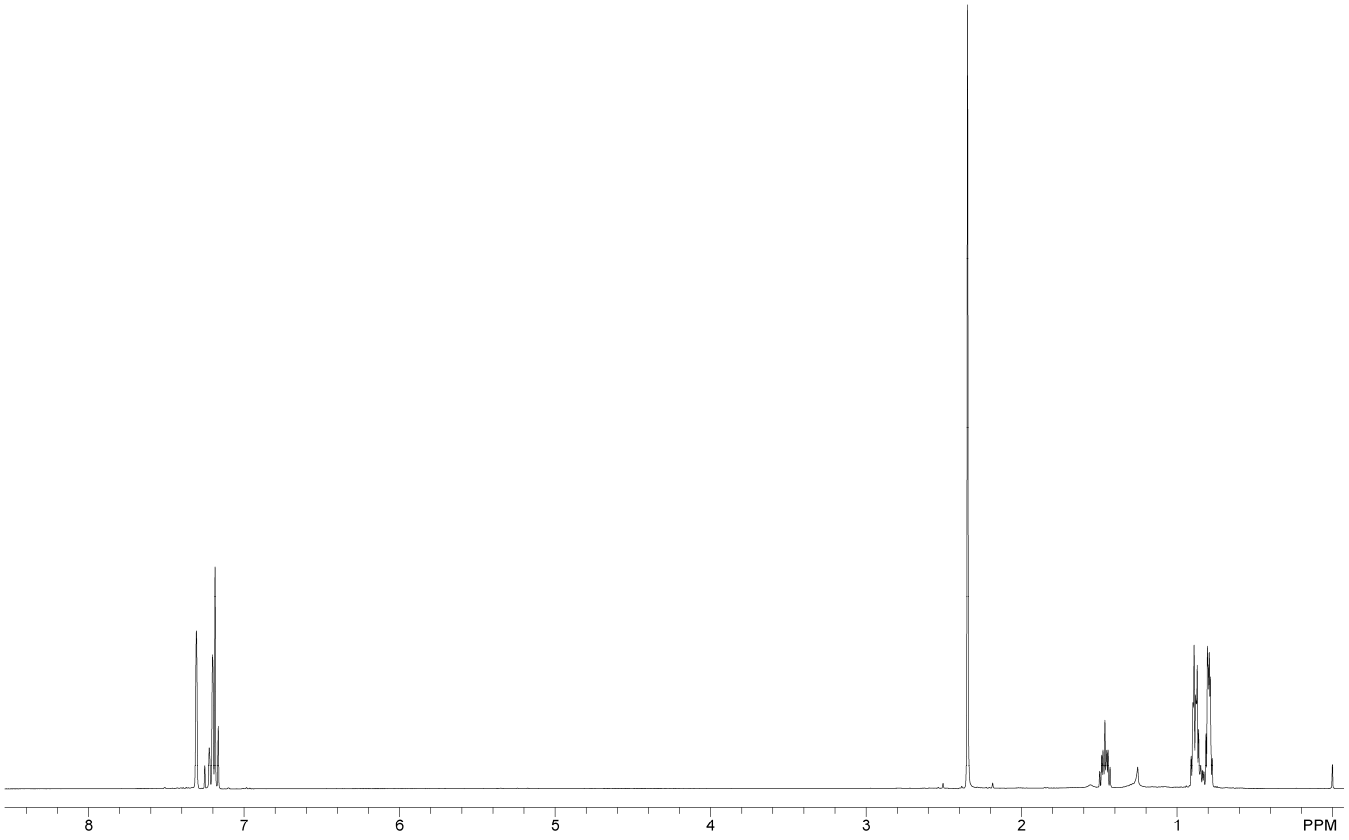

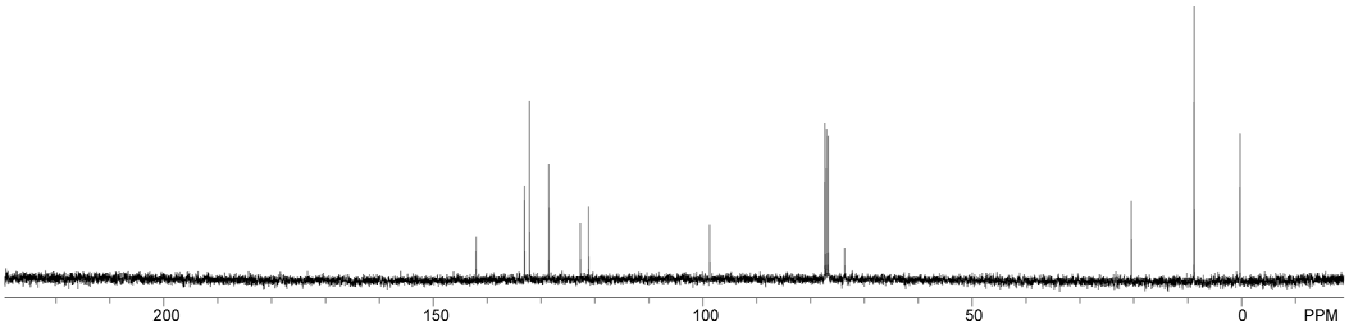

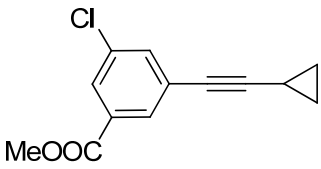

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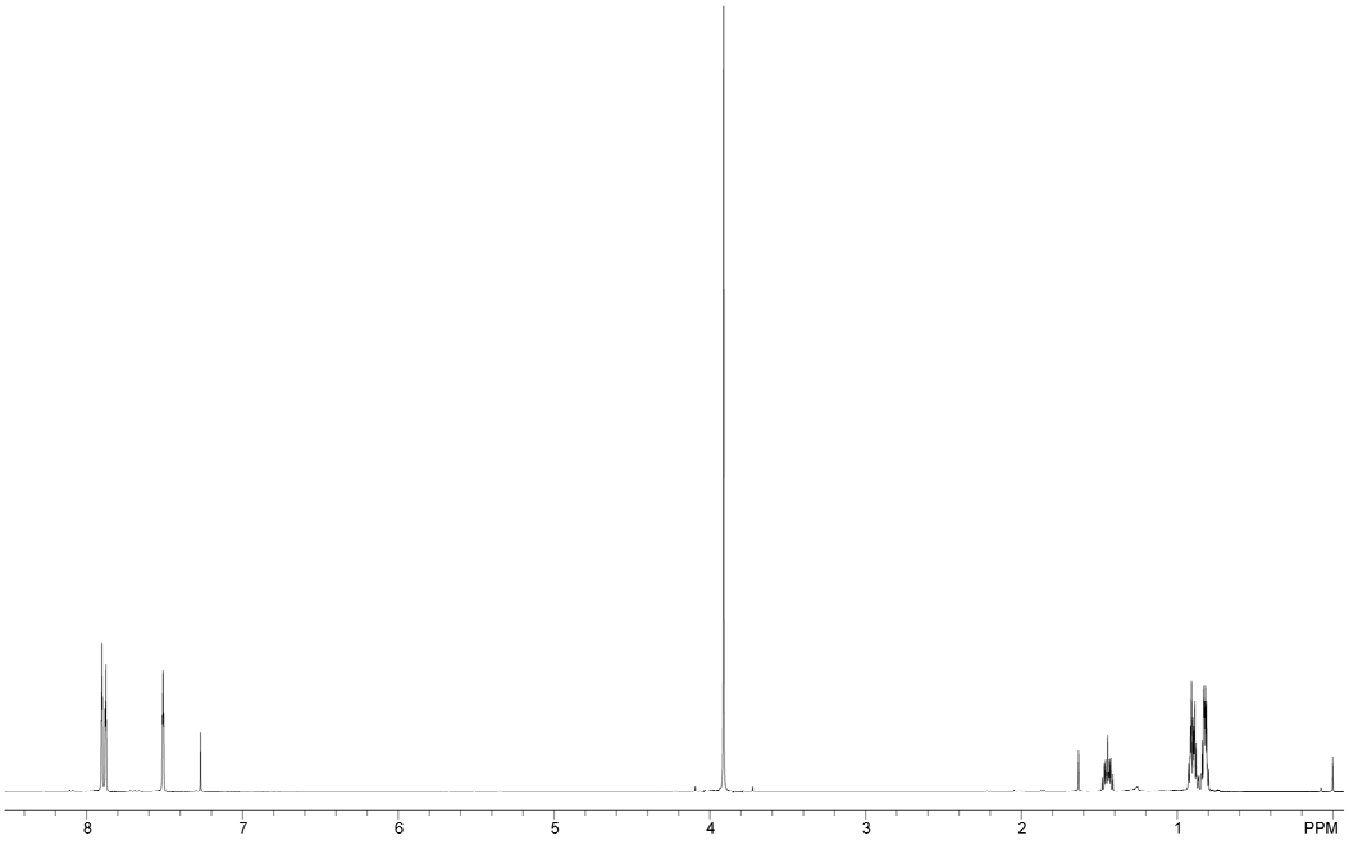

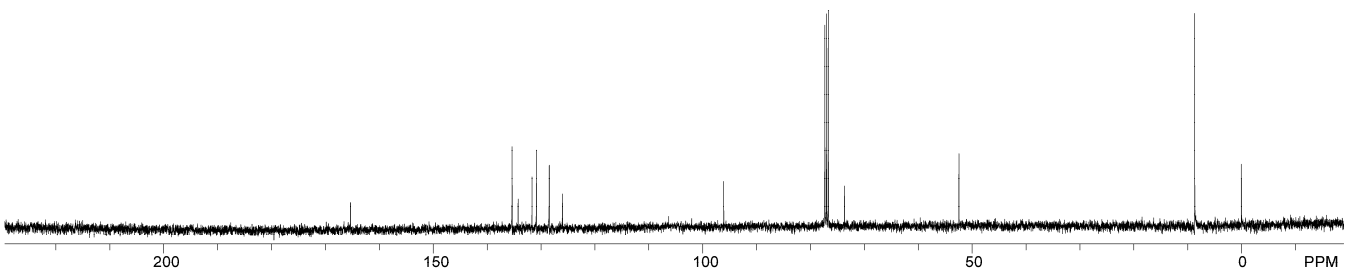

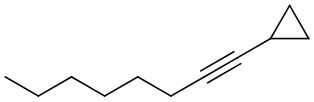

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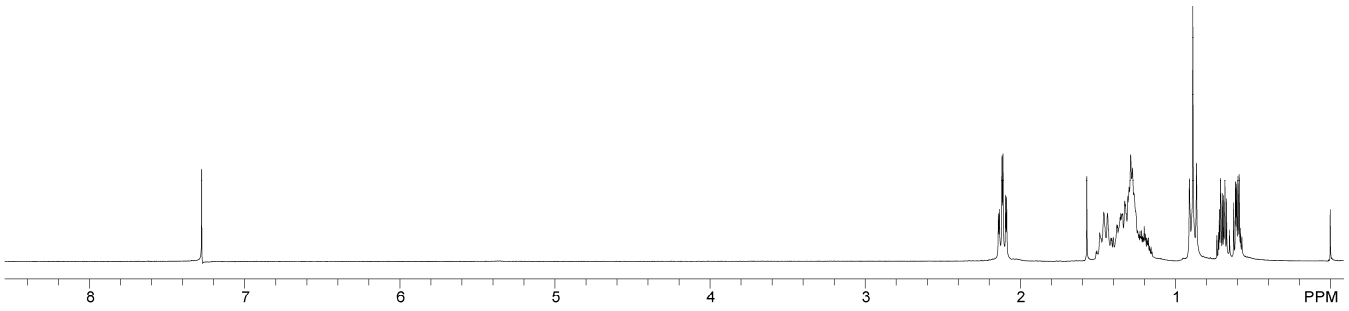

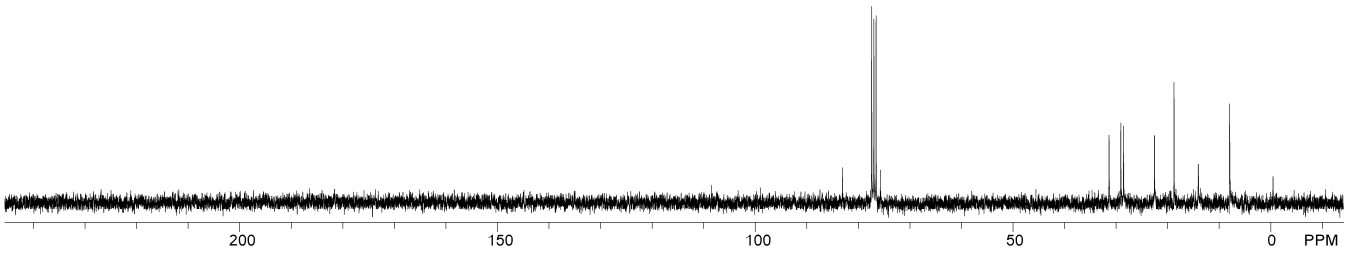

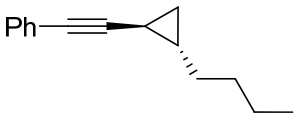

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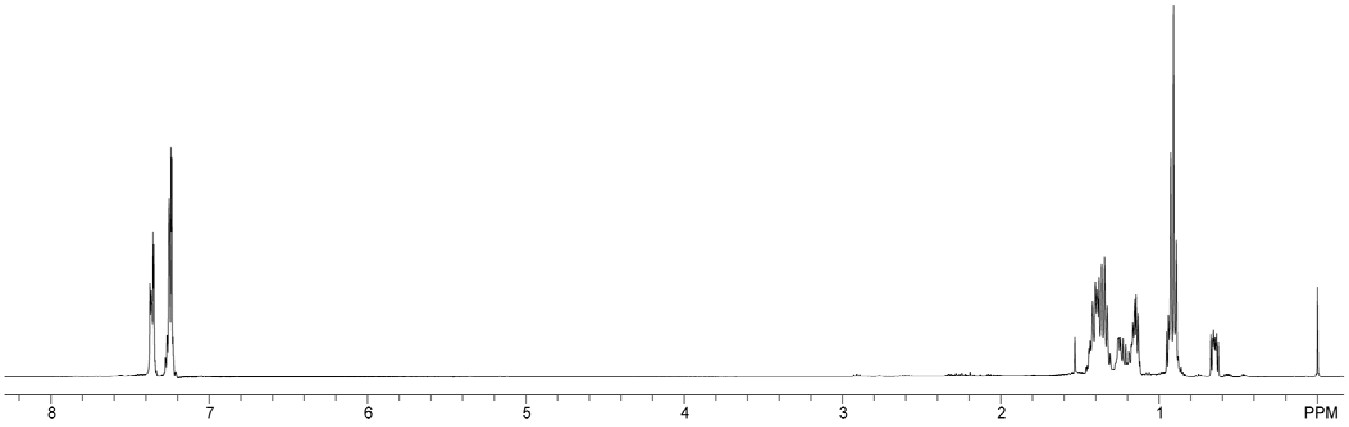

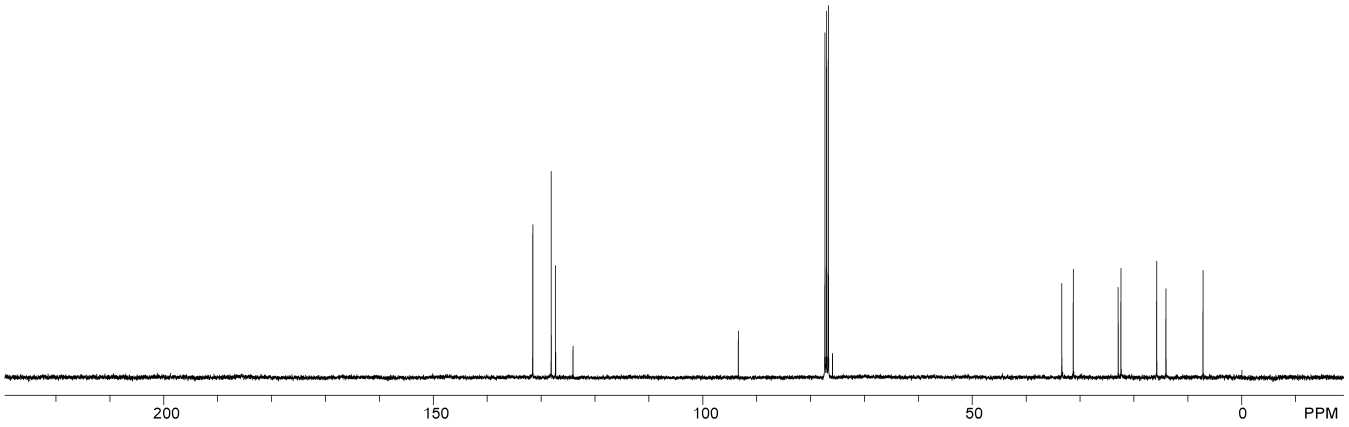

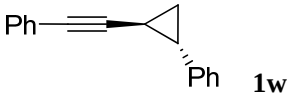

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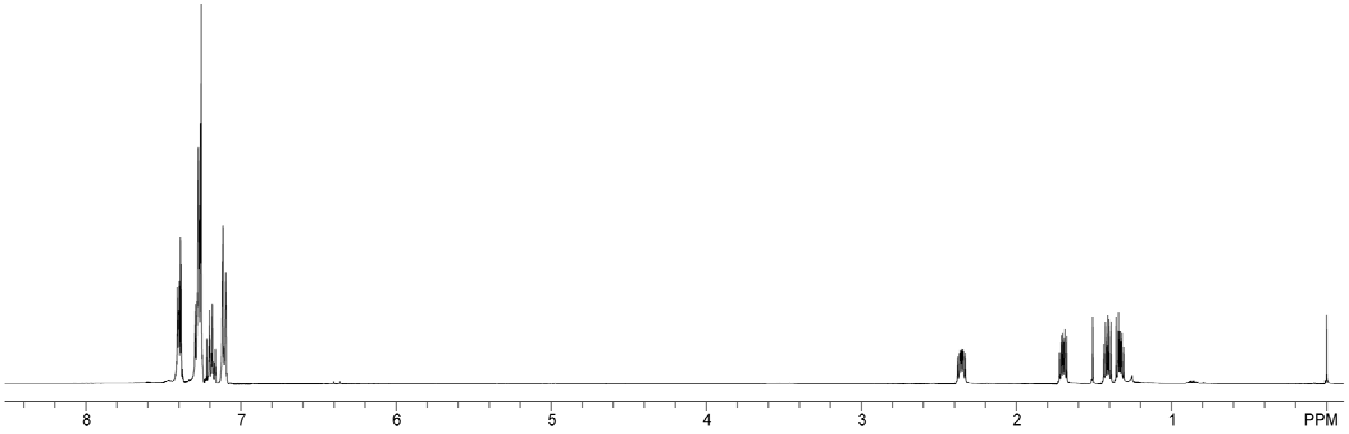

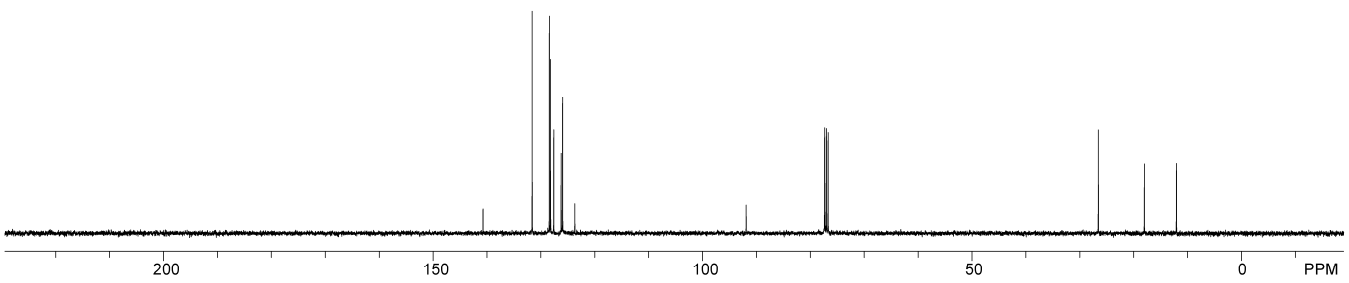

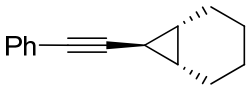

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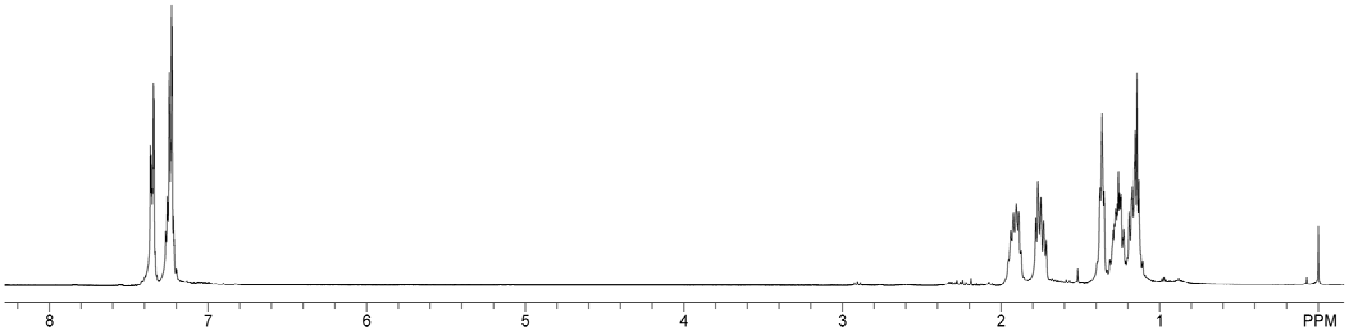

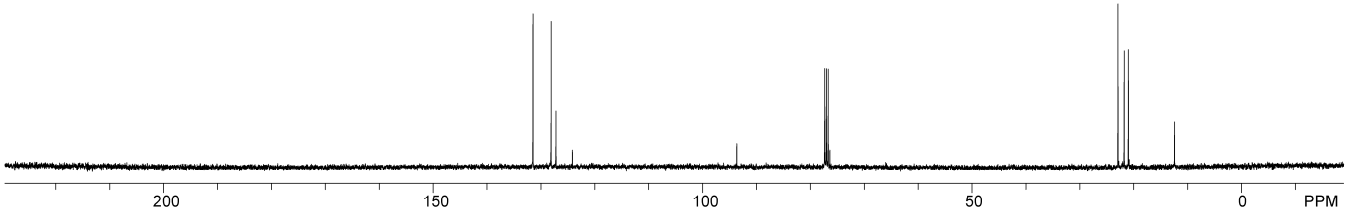

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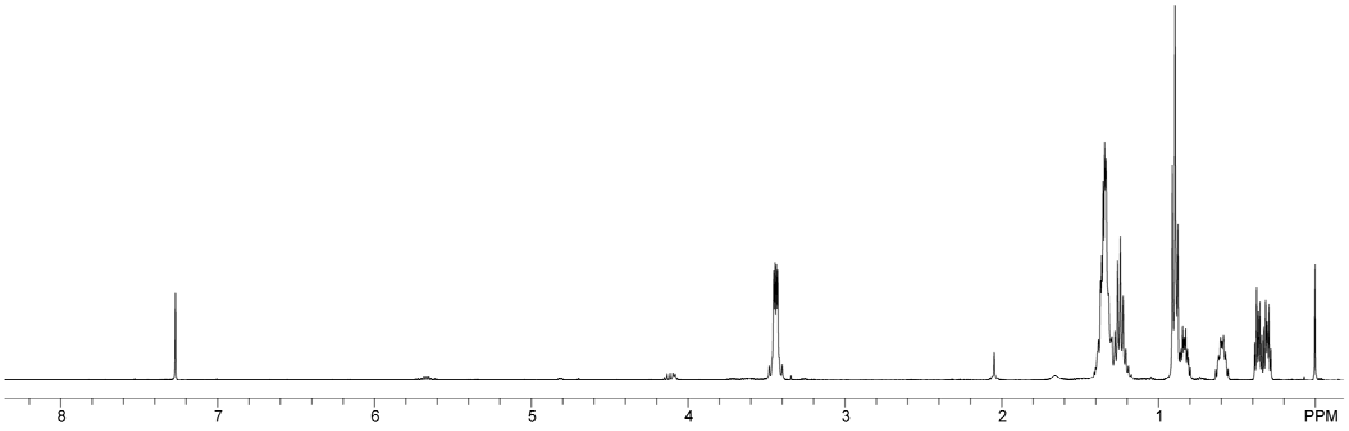

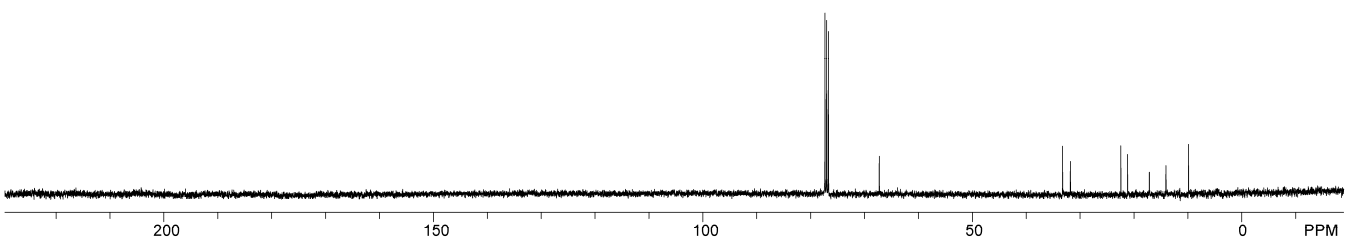

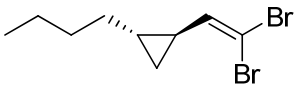

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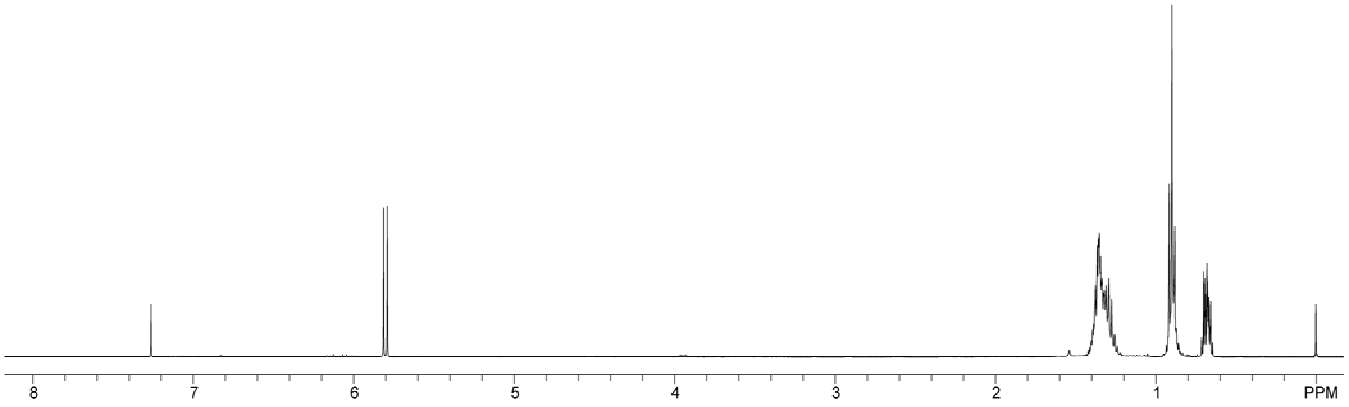

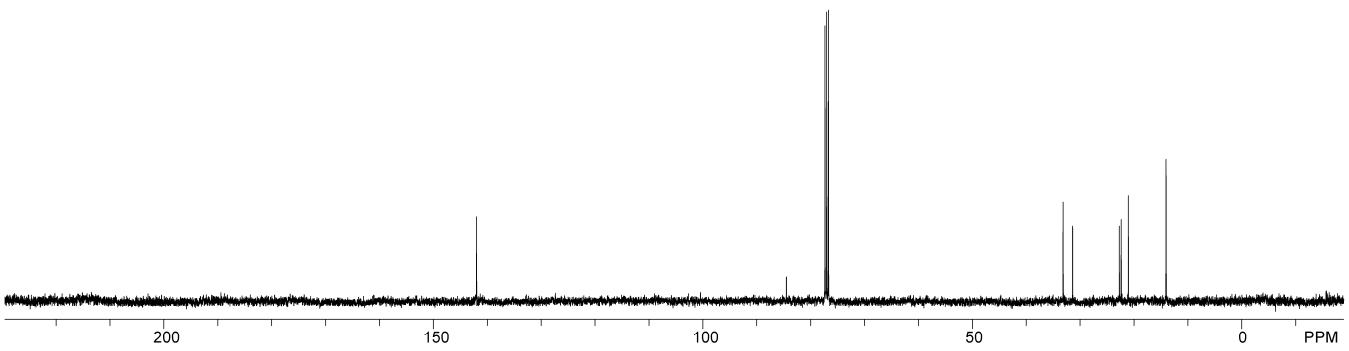

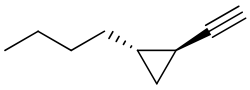

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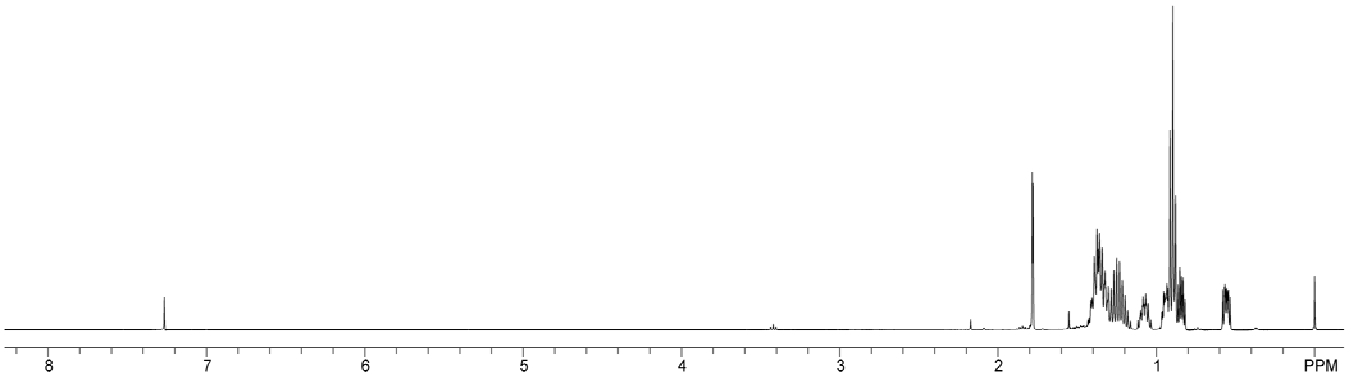

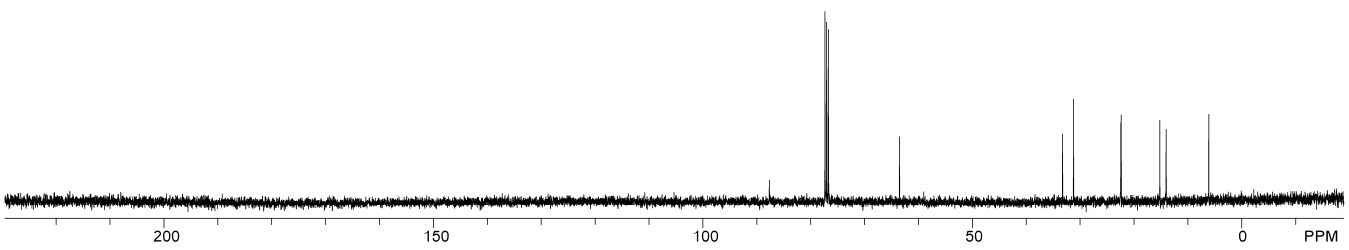

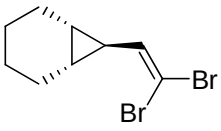

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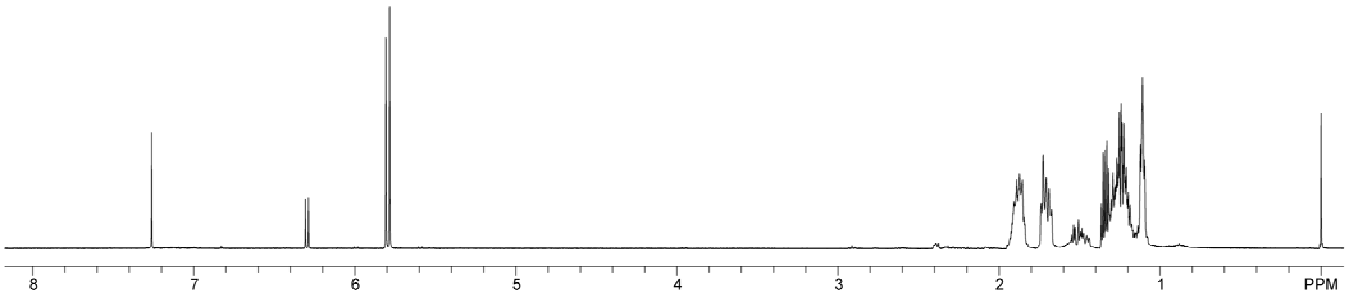

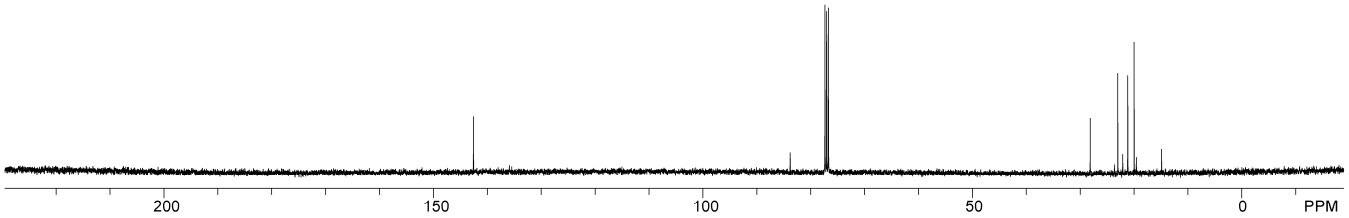

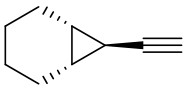

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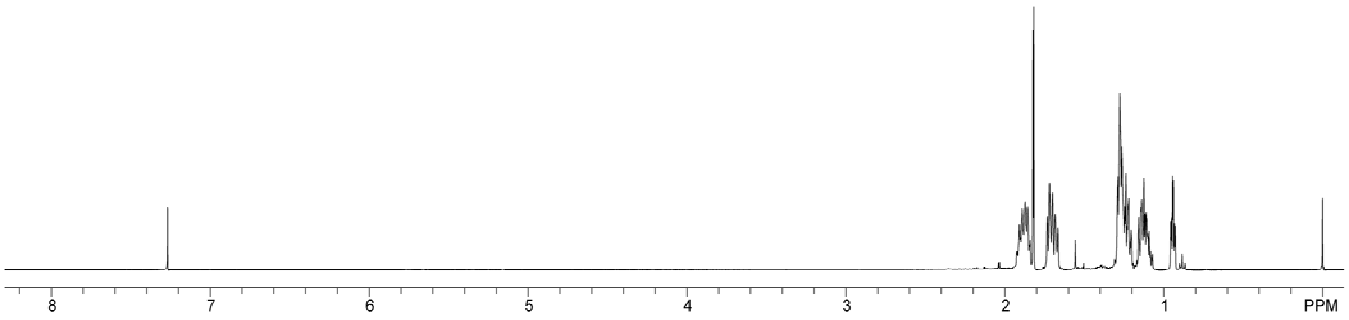

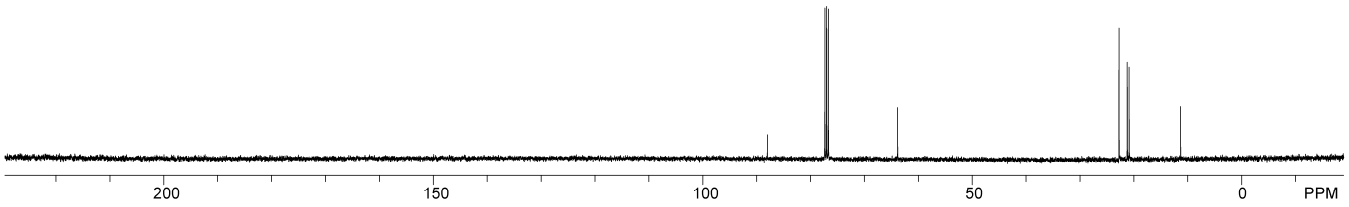

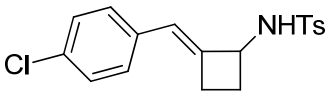

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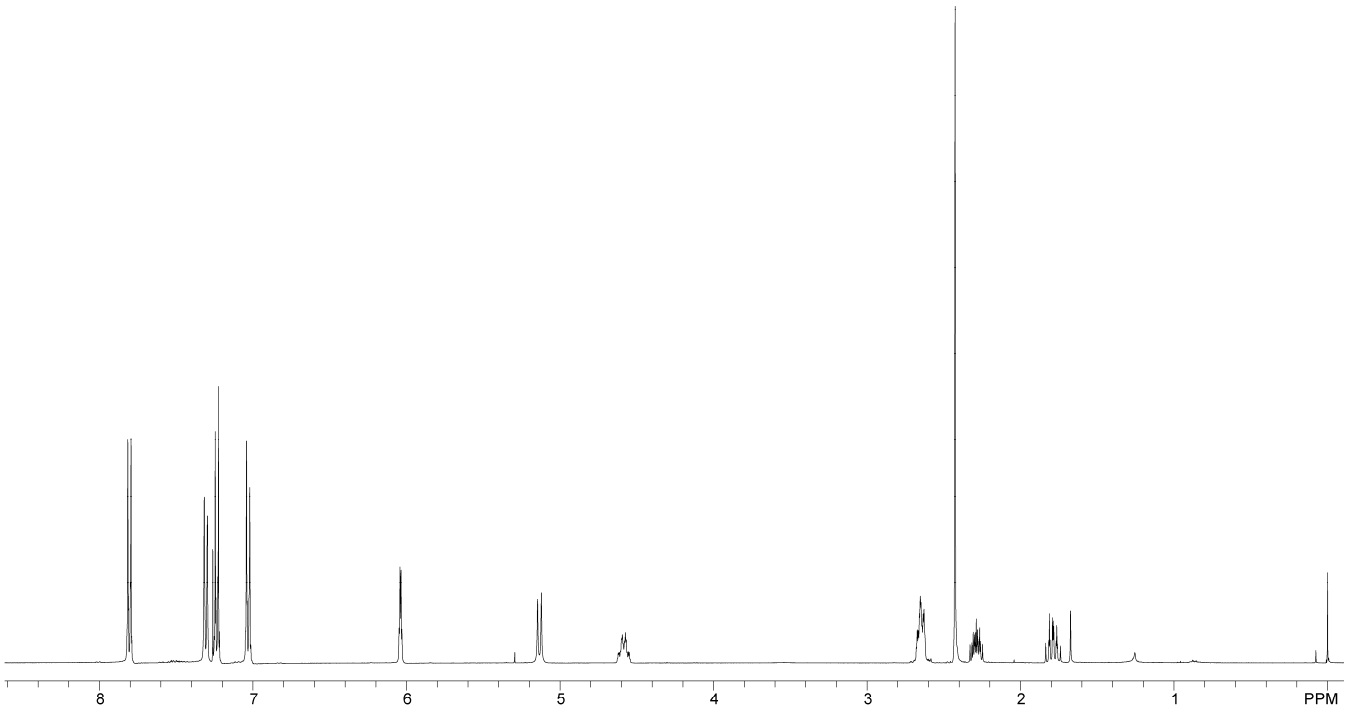

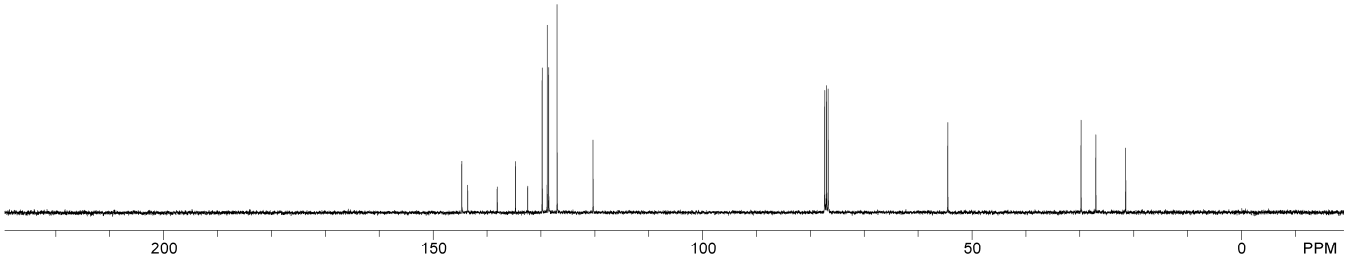

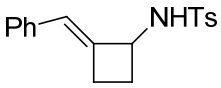

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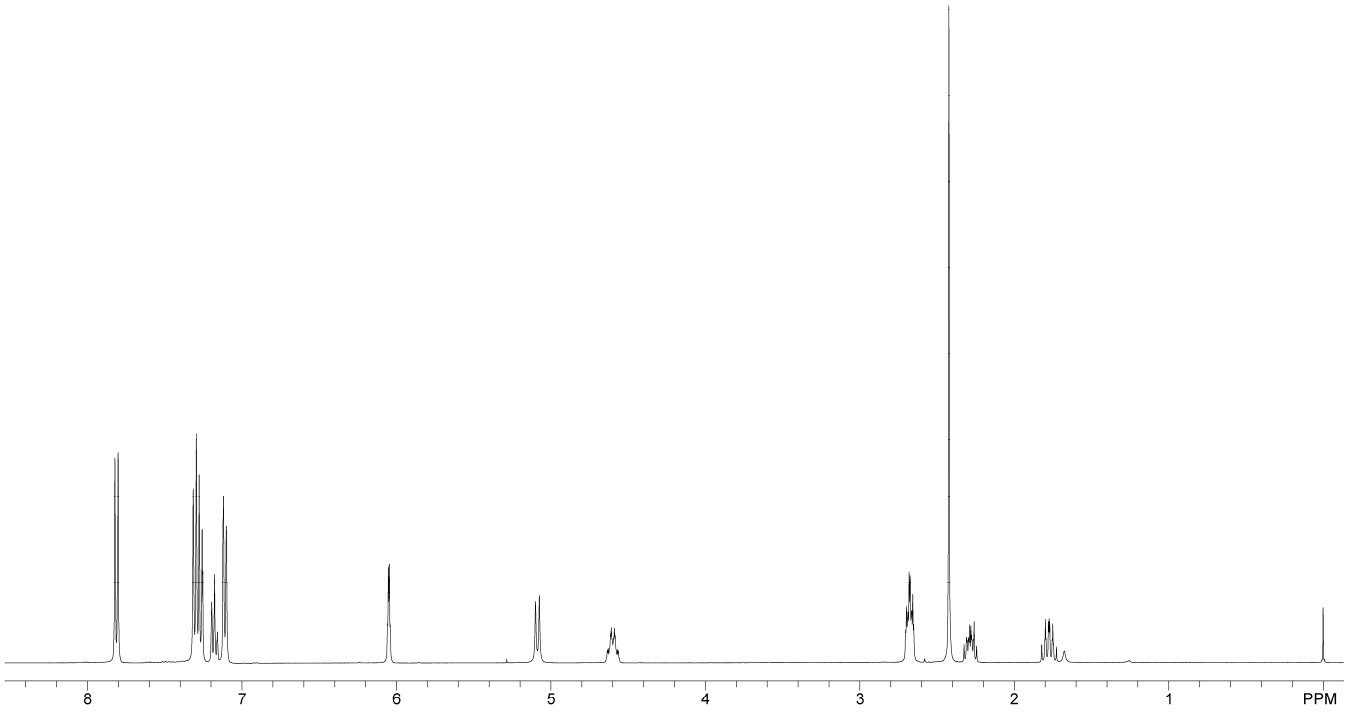

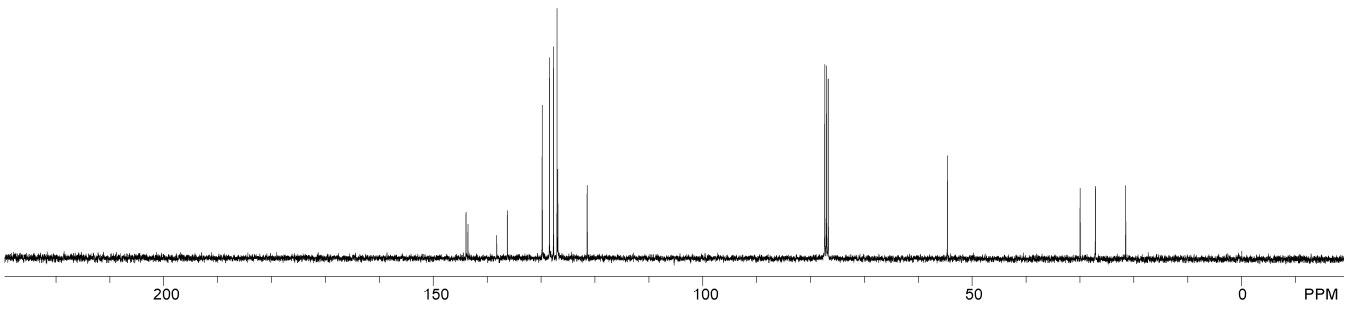

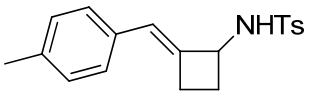

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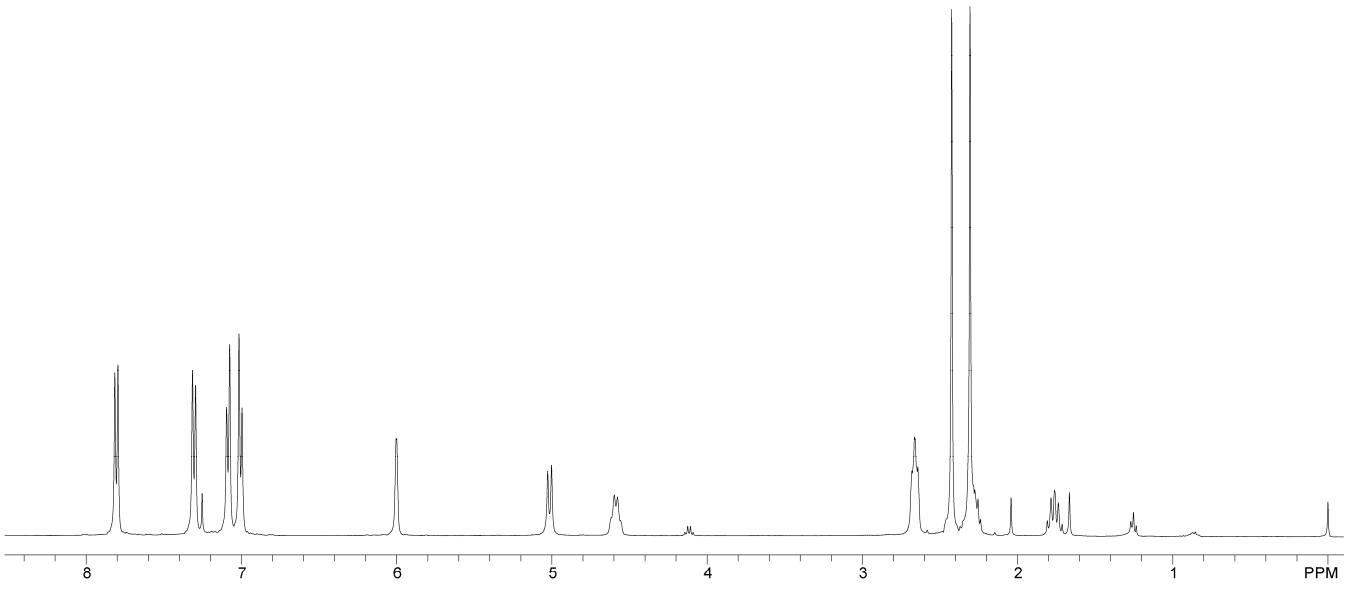

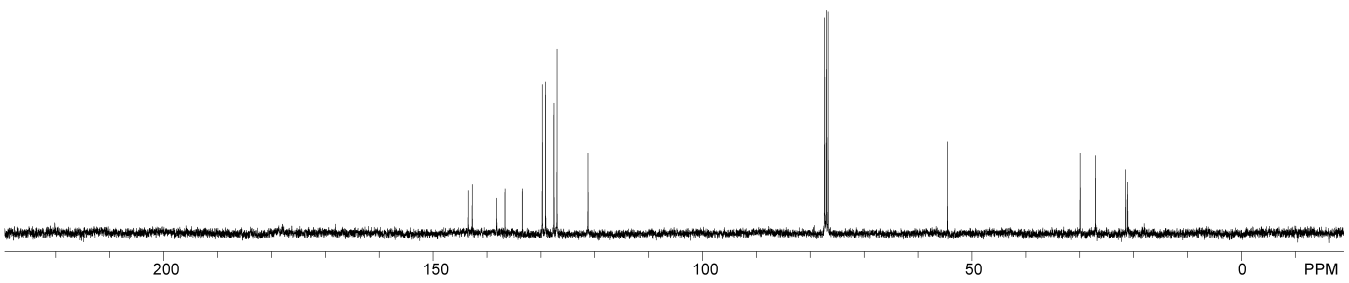

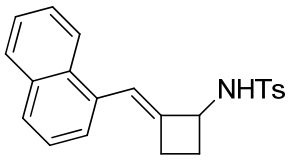

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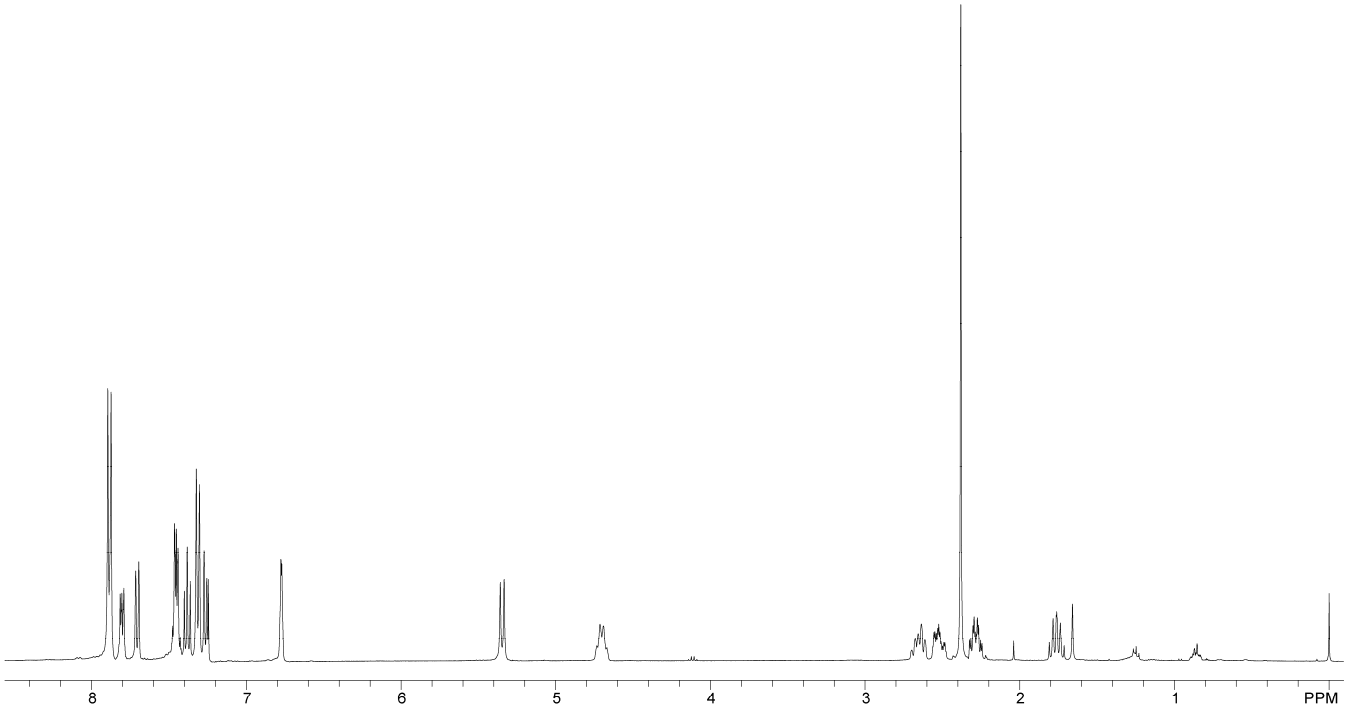

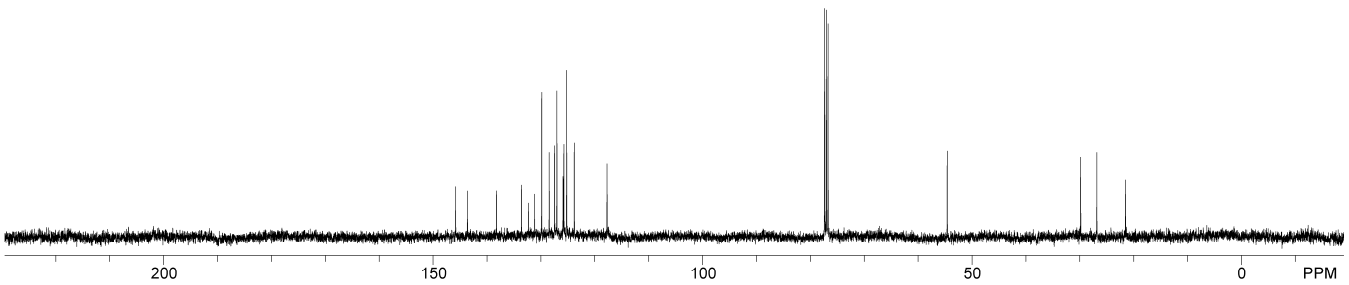

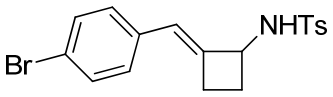

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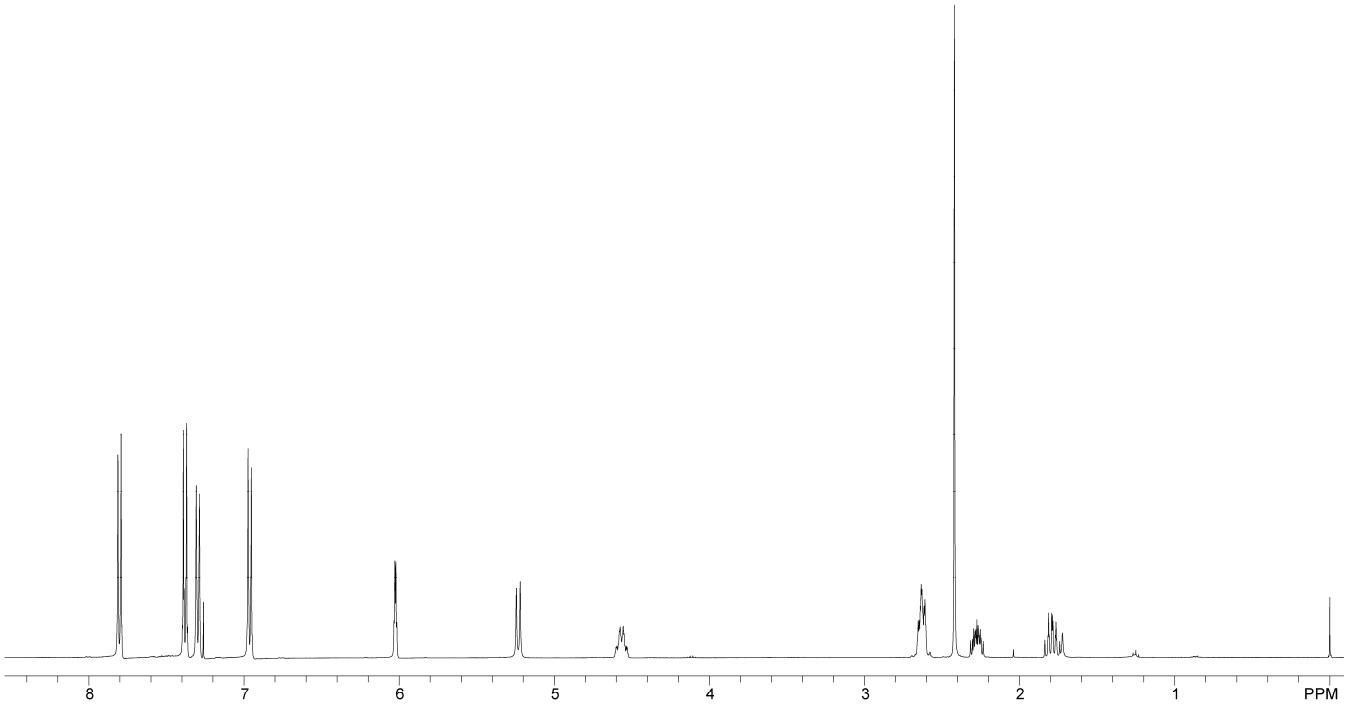

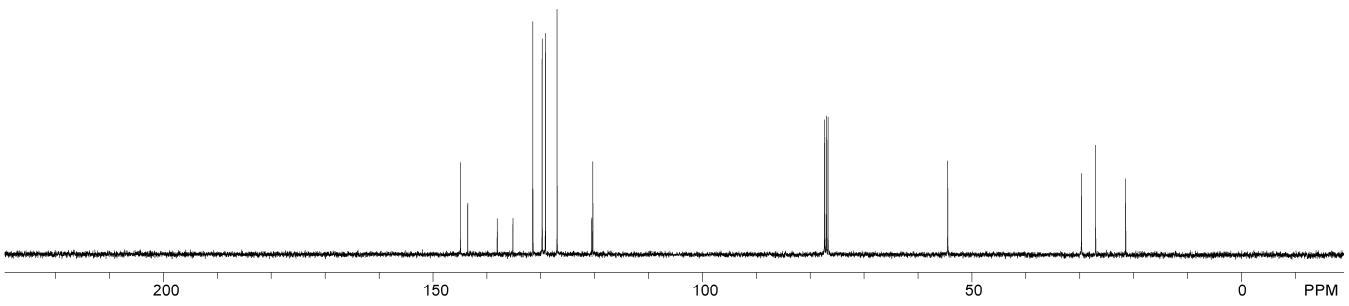

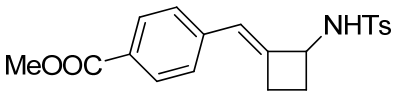

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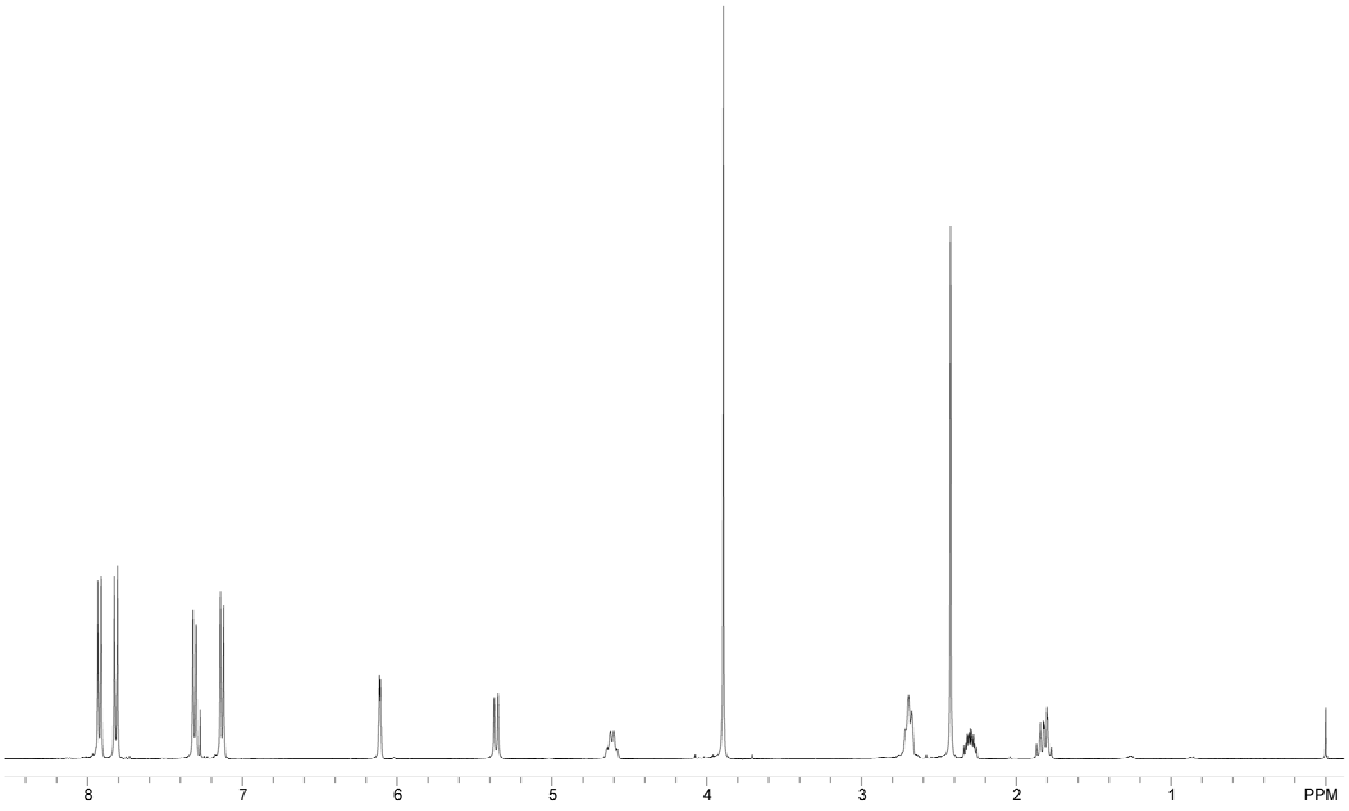

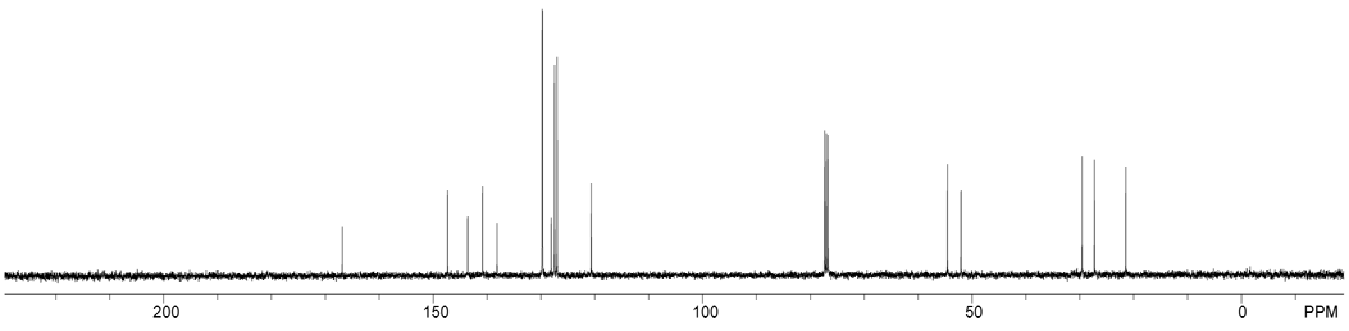

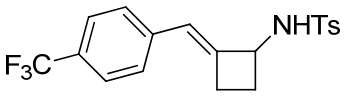

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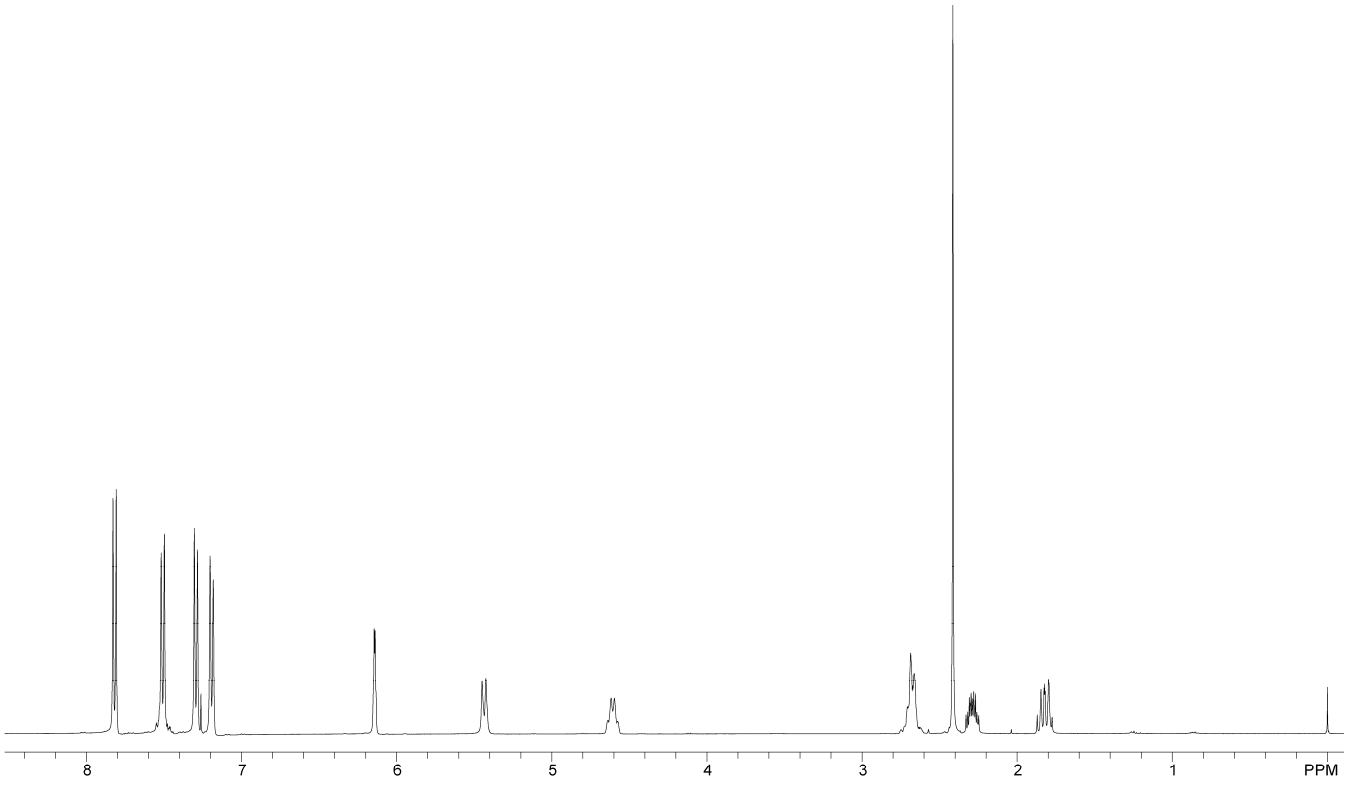

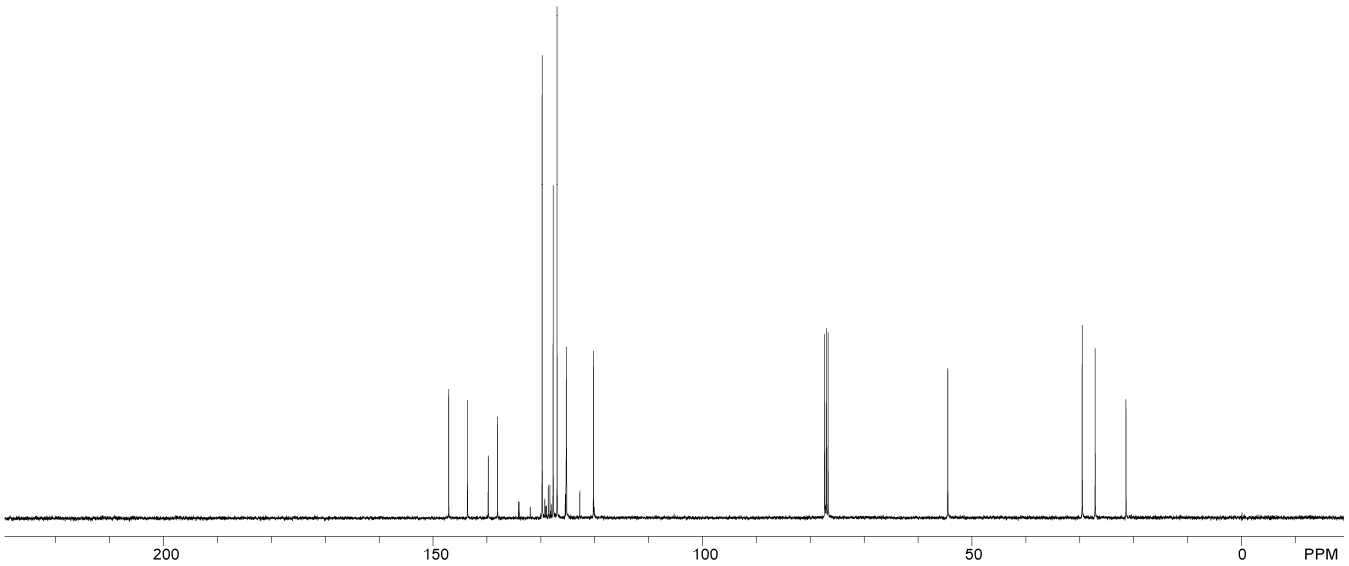

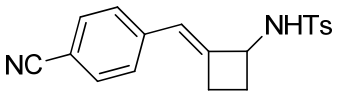

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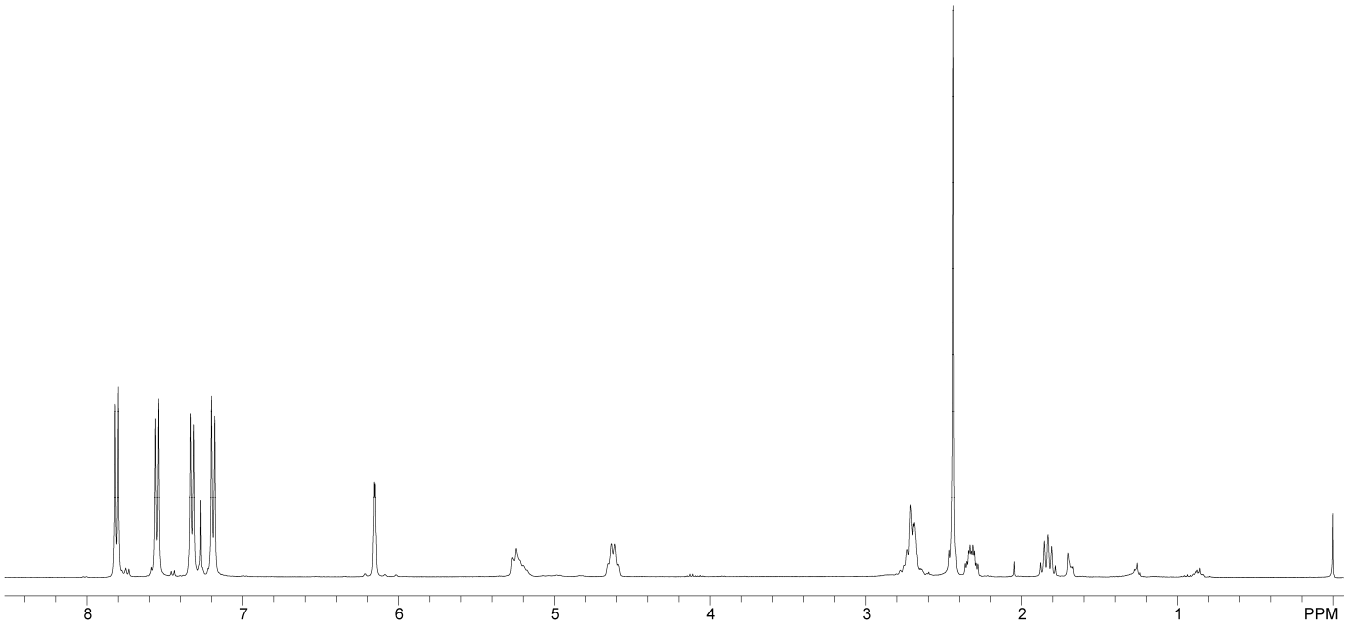

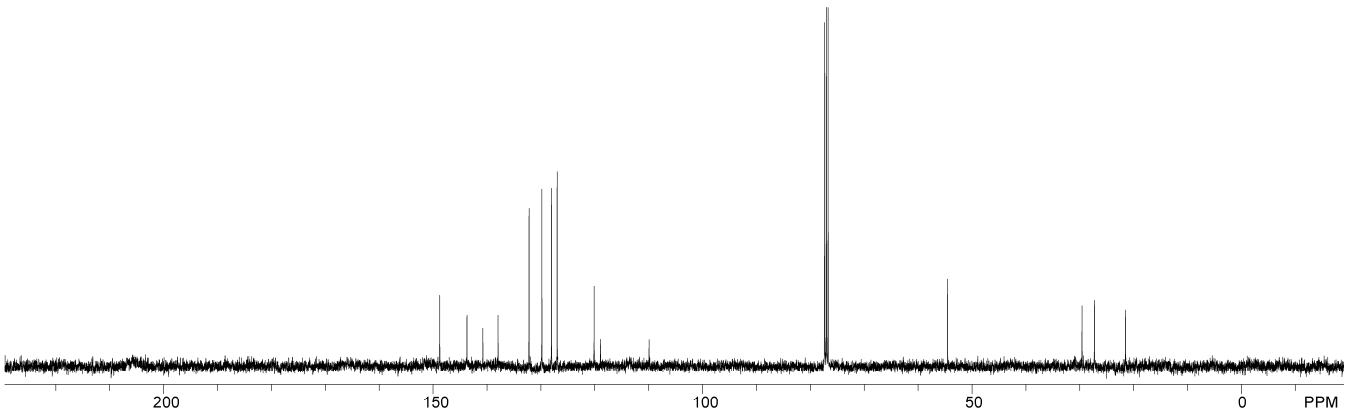

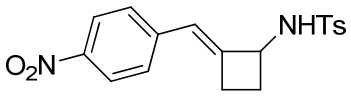

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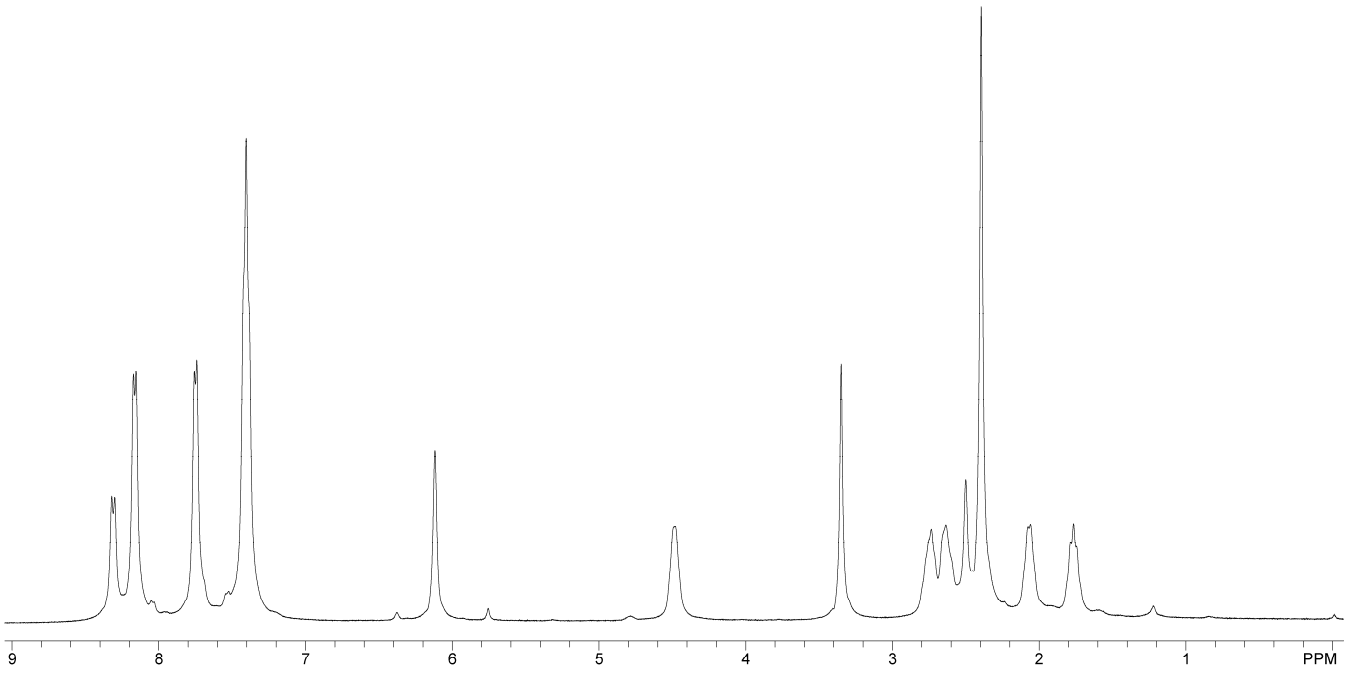

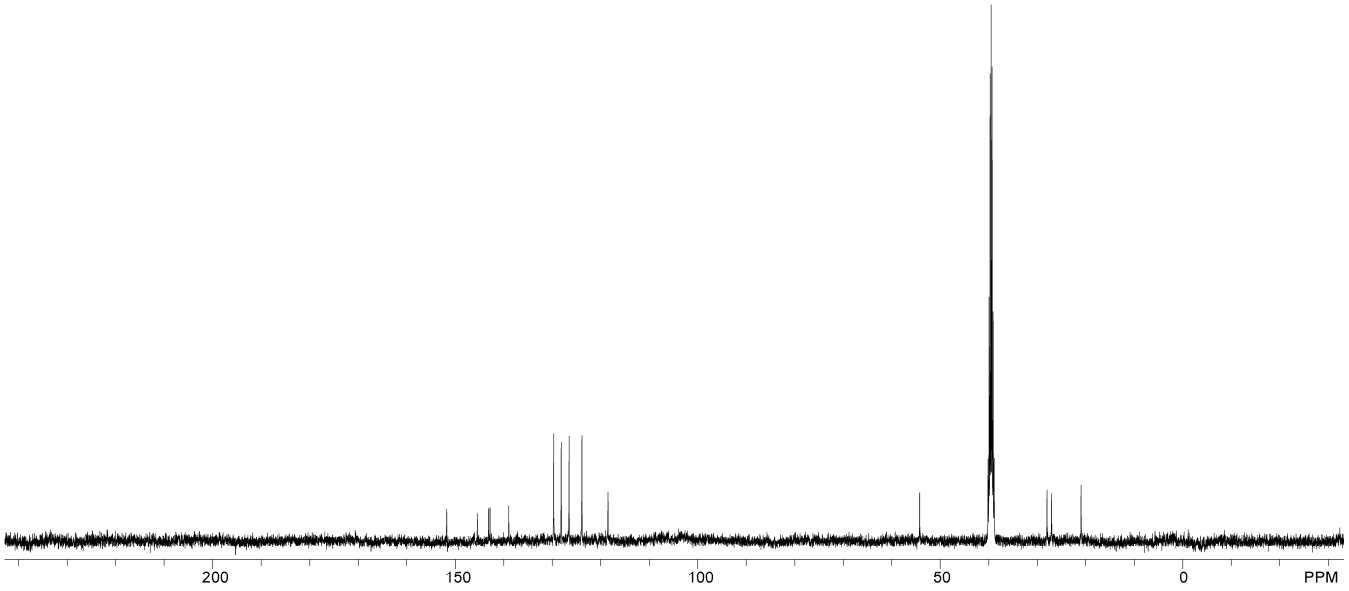

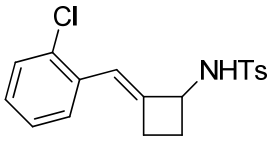

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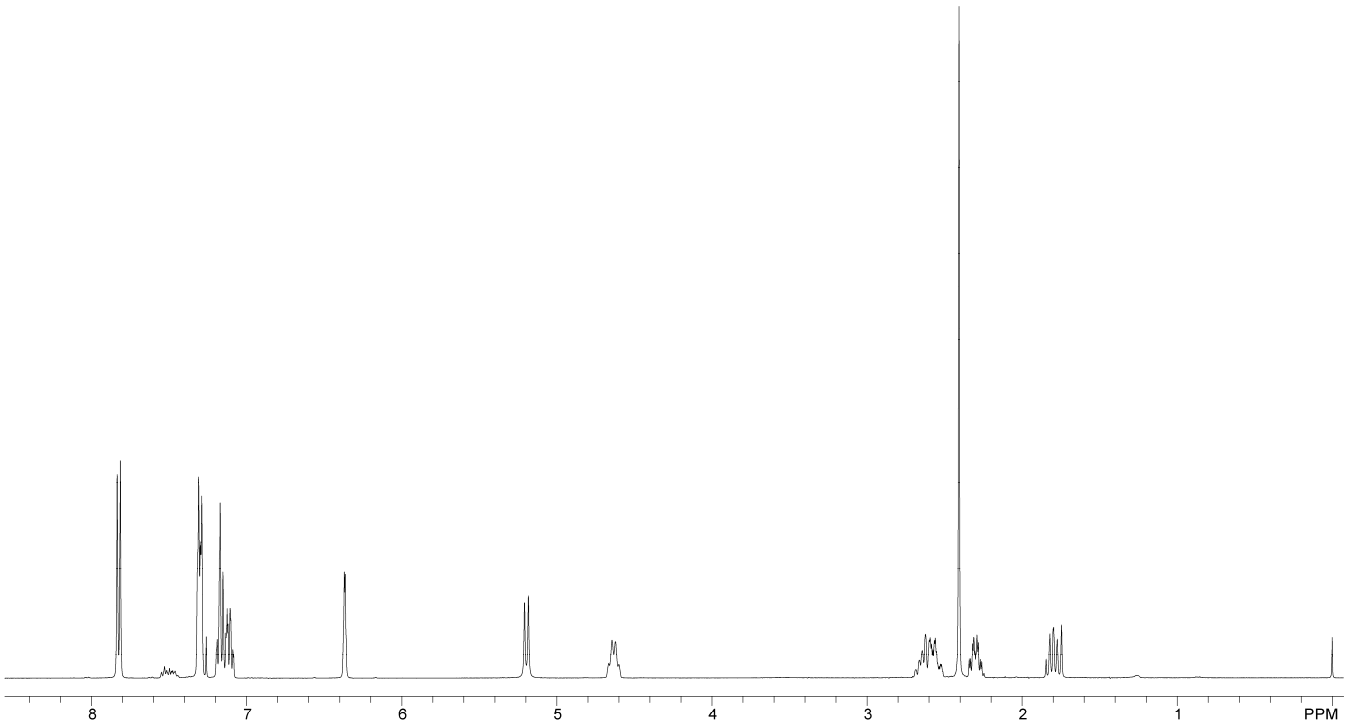

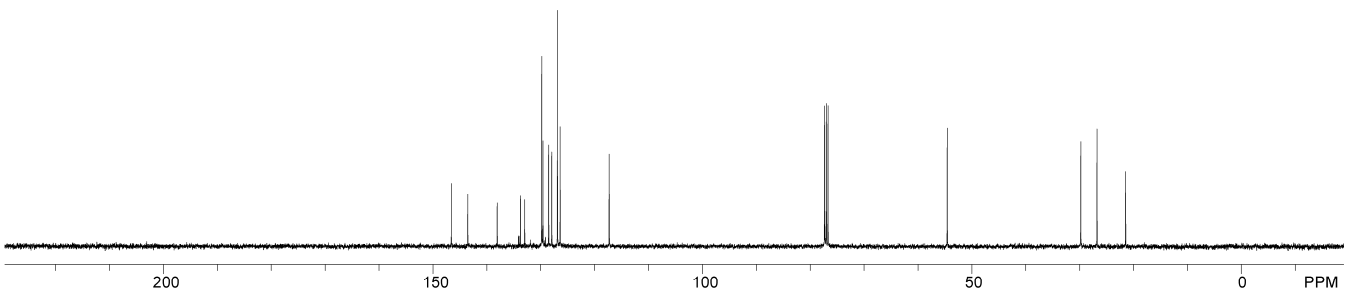

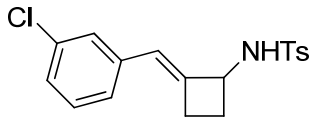

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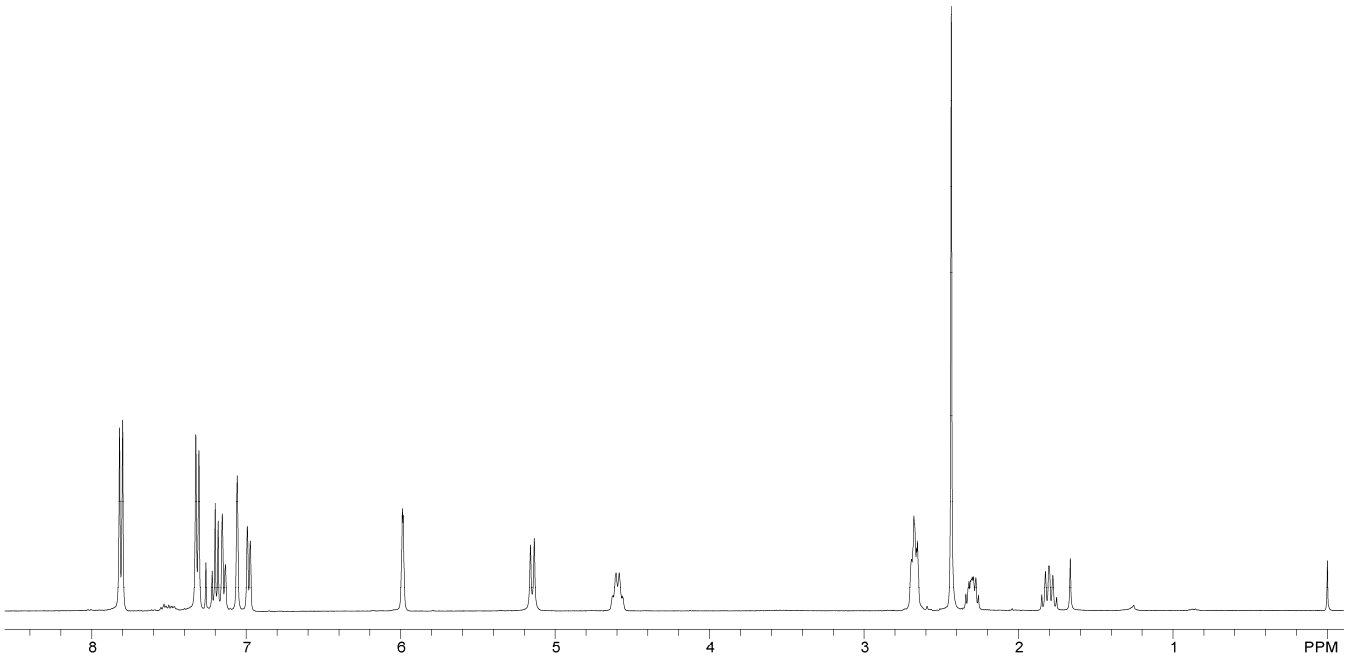

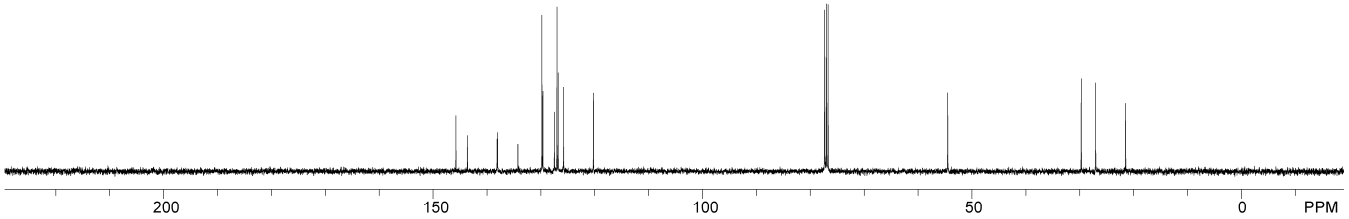

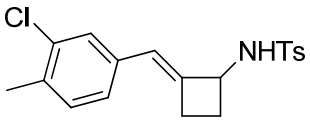

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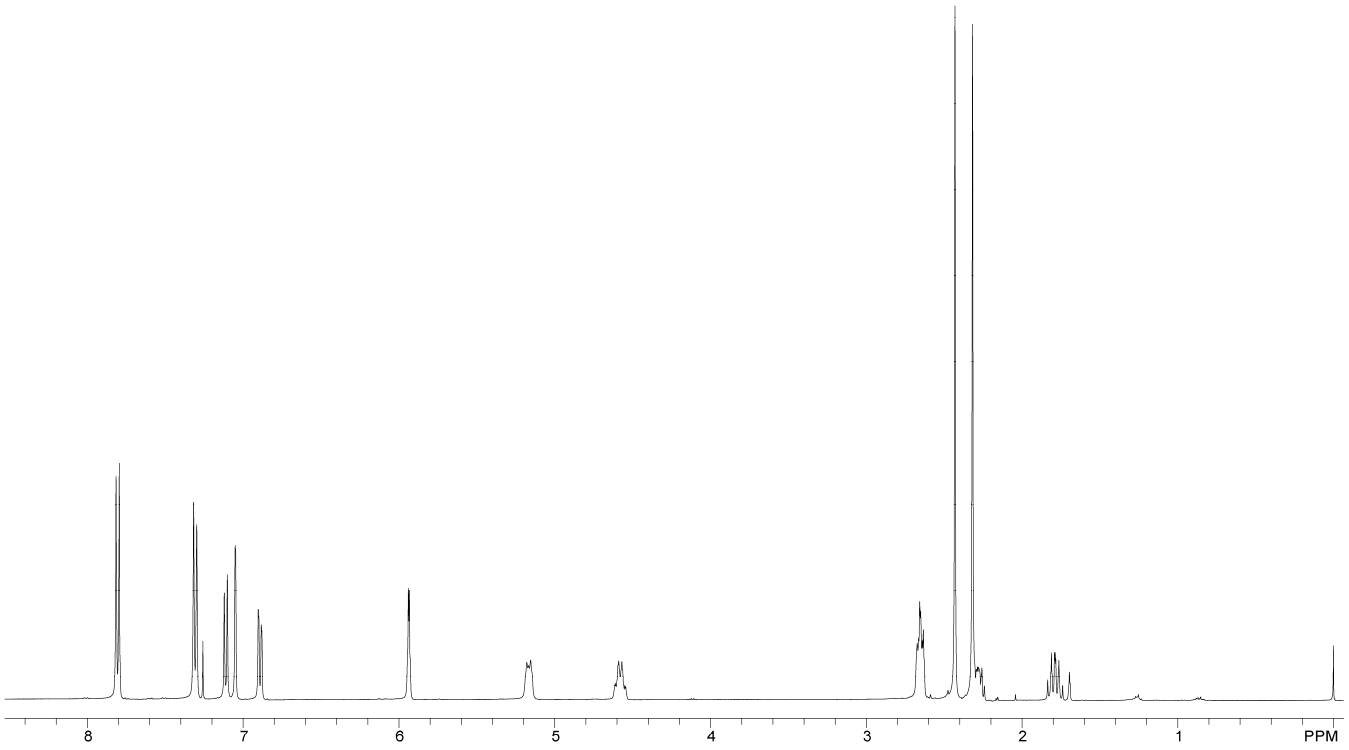

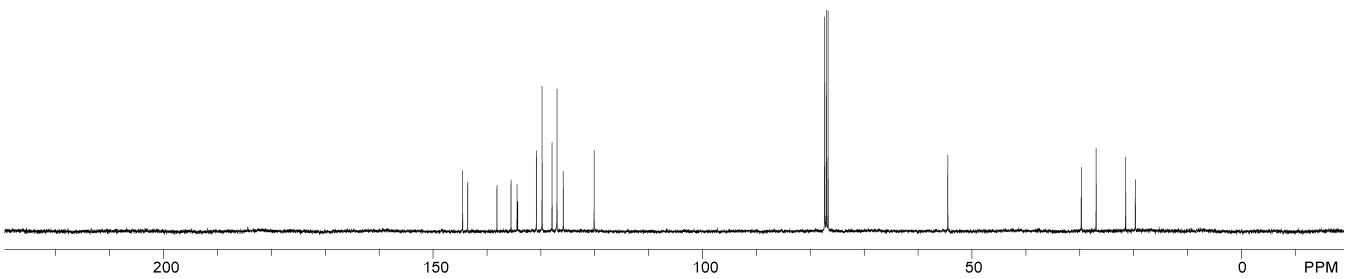

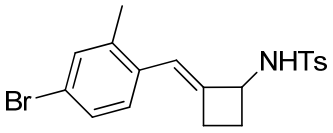

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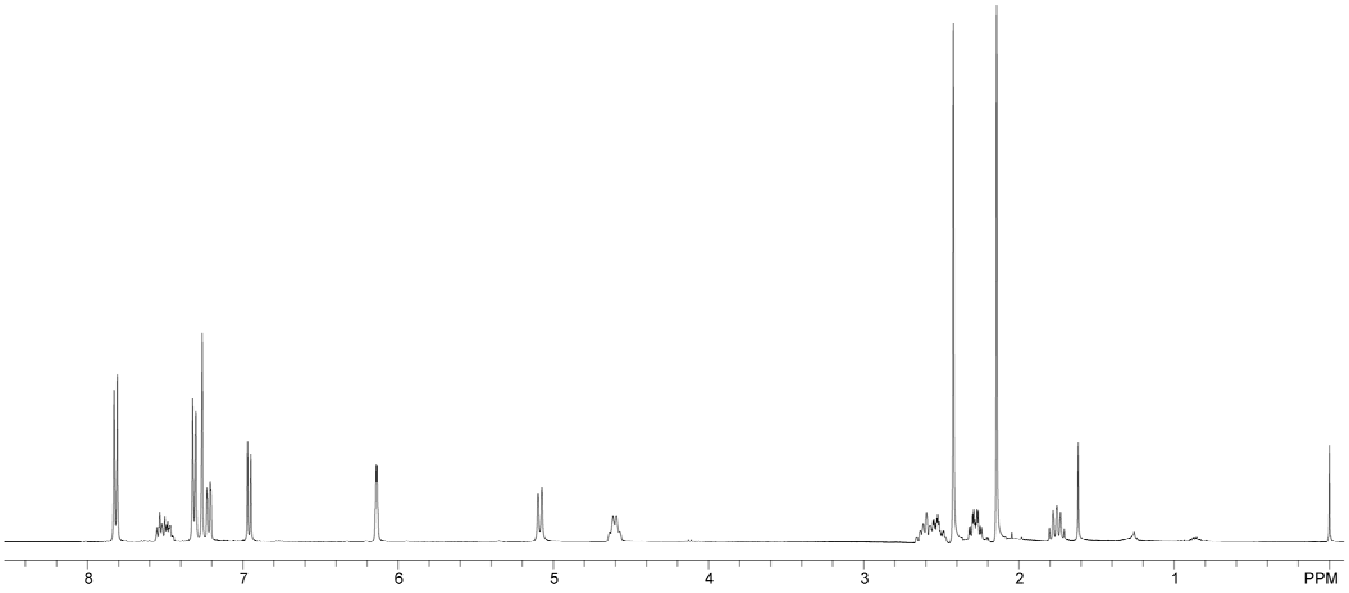

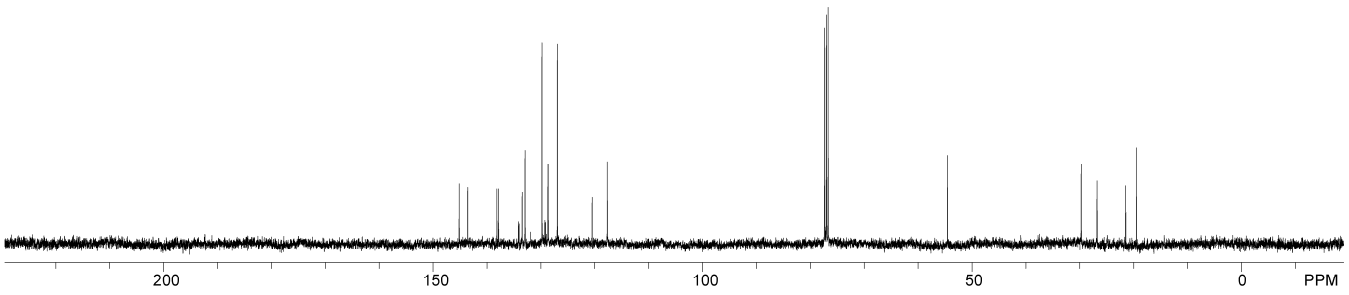

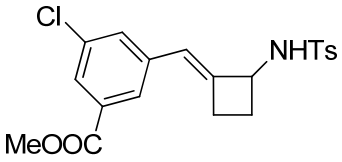

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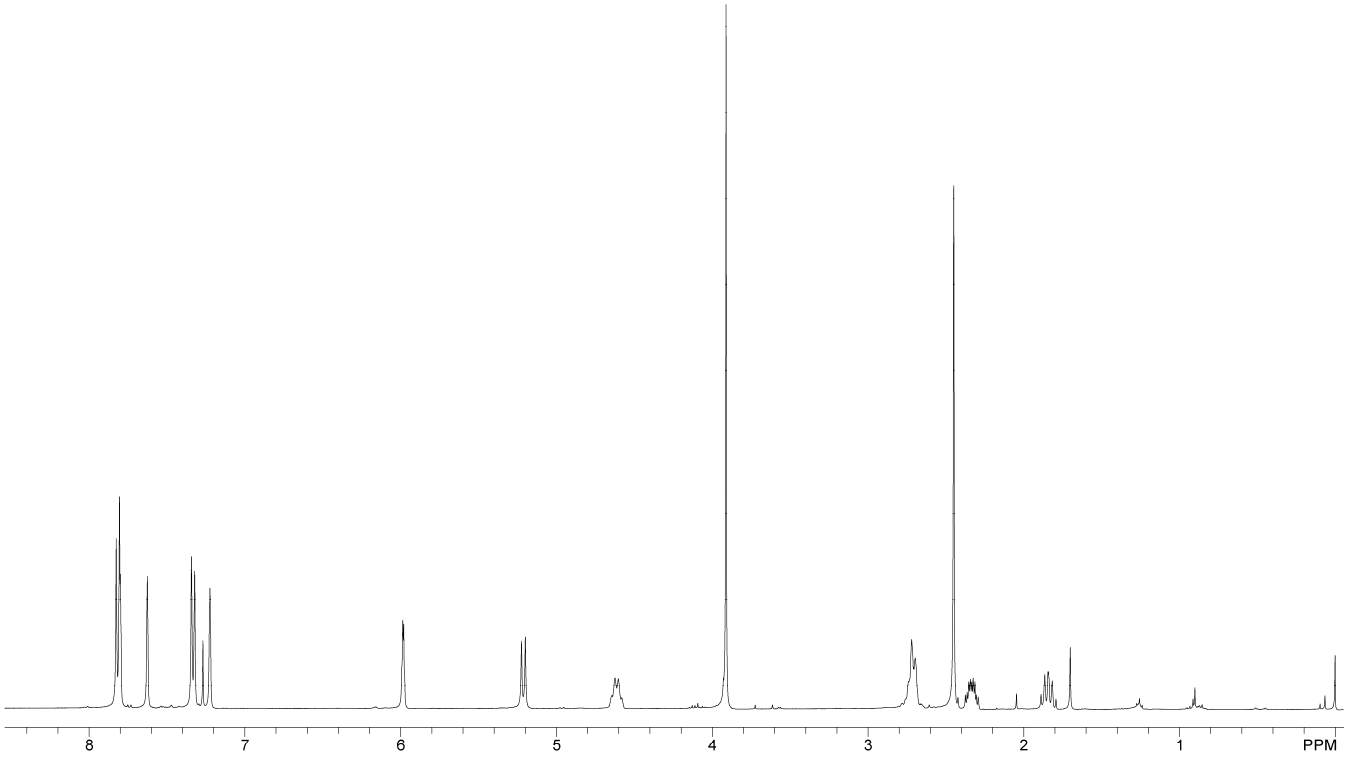

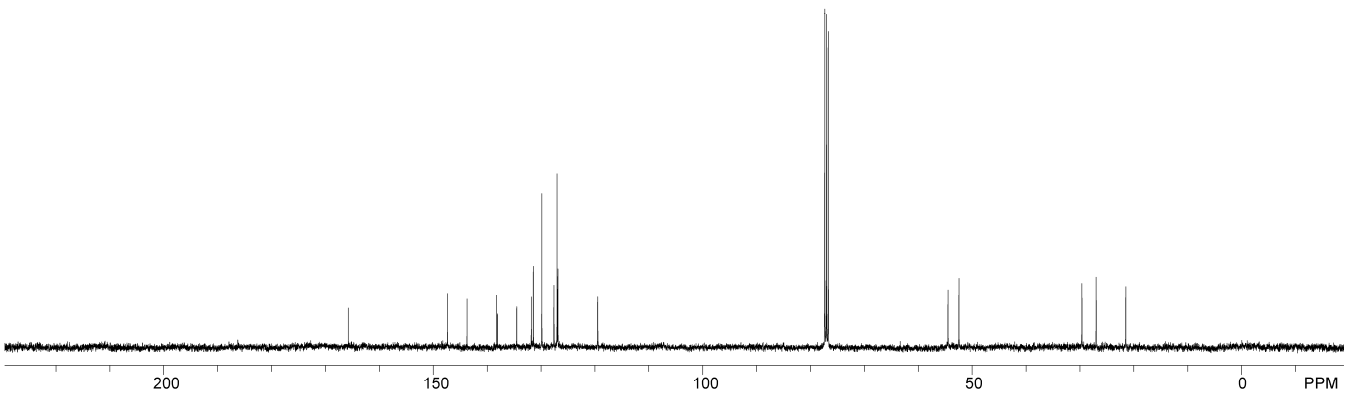

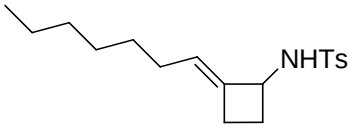

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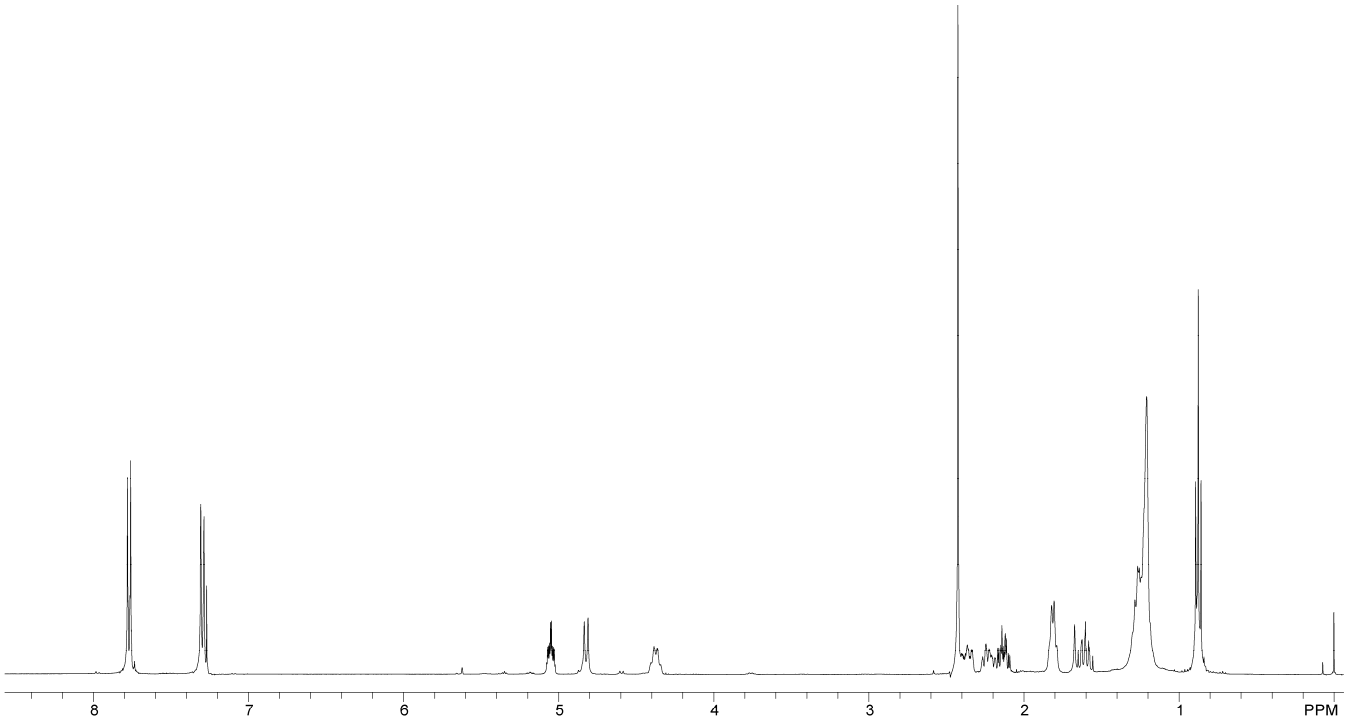

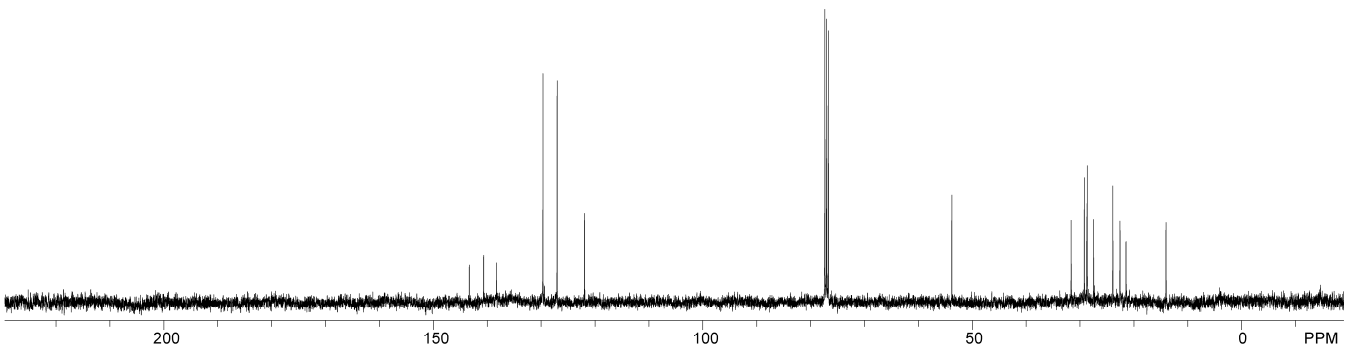

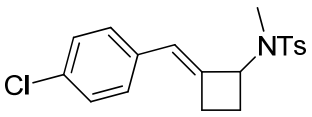

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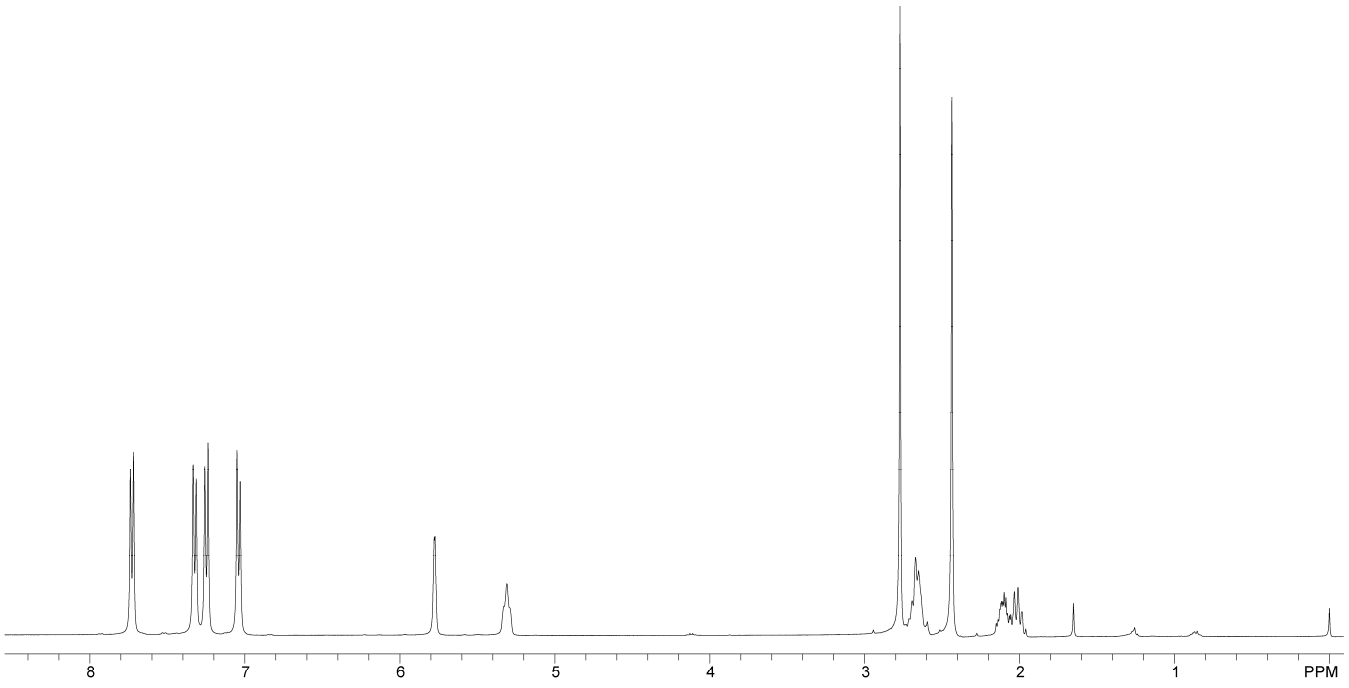

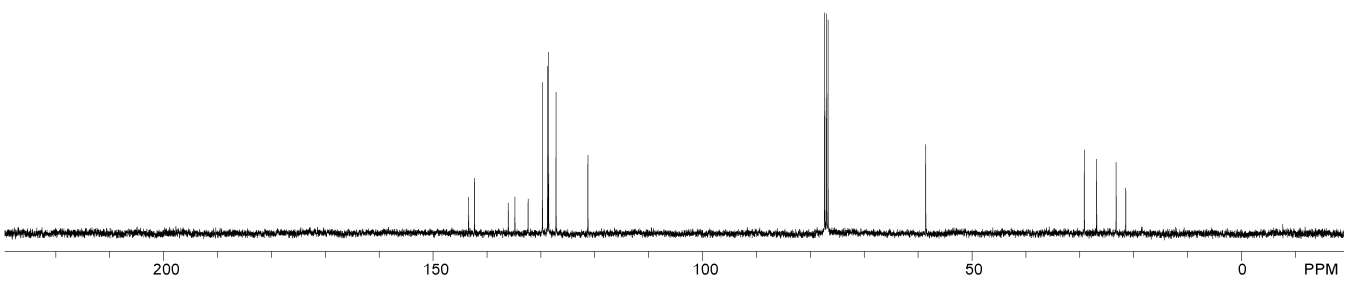

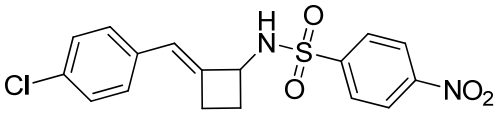

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