

Gold-Catalyzed Formation of Oxonium Ions from Enynes and Their Intra- and Intermolecular Trapping with Allylsilanes

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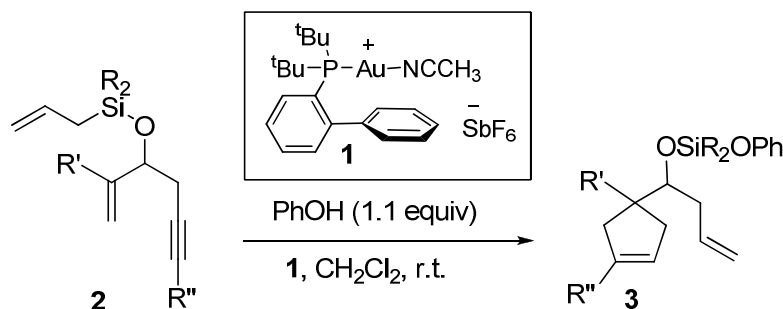
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I. General Information:

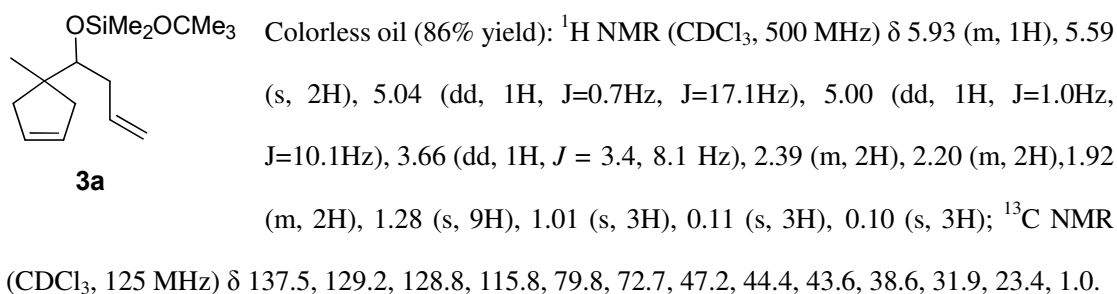
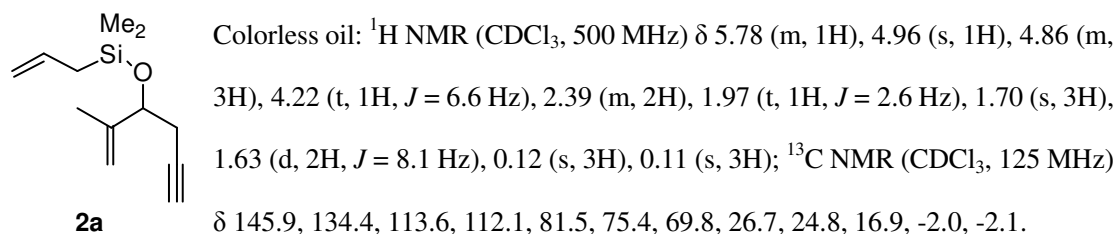
Reactions were carried out in vials or glassware under air. Compounds were purchased from Aldrich or Acros or TCI America unless otherwise noted. Dichloromethane (DCM) was distilled from calcium hydride (CaH_2) under nitrogen atmosphere. Flash chromatography was performed using silica gel 60 Å (32–63 mesh) purchased from Silicycle Inc. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck precoated silica gel 60 (particle size 0.040–0.063 mm). Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet), b (broad), and app (apparent). ^1H NMR signals that fall within a ca. 0.3 ppm, range are generally reported as a multiplet, with a single chemical shift value corresponding to the center of the peak. Coupling constants, J , are reported in Hz (Hertz). Electron impact (EI) mass spectra and Chemical Ionization (CI) mass spectra were obtained using a Micromass 70-VSE in the University of Illinois at Urbana-Champaign. IR spectra were recorded using JASCO FT-IR-4100 with GLADiATRTM Attenuated Total Reflectance (ATR) FT-IR accessory.

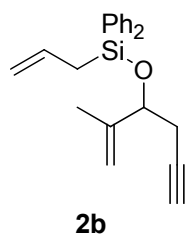
II. Procedure for Au(I)-catalyzed reaction with intramolecular allylation



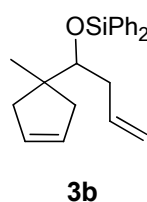
To a solution of 3-allylsilyloxy-1,5-enyne **2b** (60.1 mg, 0.18 mmol) and phenol (18.8 mg, 0.20 mmol) in CH₂Cl₂ (0.5 mL) was added the Au(I) catalyst **1** (1 mol%). The resulting solution was stirred at room temperature for 1 hour, at which point TLC indicated the consumption of the starting material. The reaction mixture was concentrated to afford the crude product, which was purified by column chromatography with hexane and ethyl acetate (30:1) to give the desired cyclopentene product **3b** (colorless oil, 73.7 mg, 96% yield).

III. Characterization data for Table 1

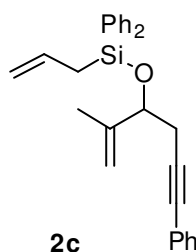




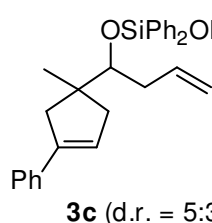
Colorless oil: IR (ATR diamond crystal, cm^{-1}) 3300, 3068, 2918, 1634, 1428, 1070; ^1H NMR (CDCl_3 , 500 MHz) δ 7.64 (m, 4H), 7.44 (m, 2H), 7.38 (m, 4H), 5.84 (m, 1H), 4.93 (m, 3H), 4.86 (s, 1H), 4.35 (m, 1H), 2.47 (m, 2H), 2.24 (m, 2H), 1.96 (s, 1H), 1.73 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 145.1, 135.0, 134.9, 134.4, 133.0, 130.0, 129.9, 127.8, 127.7, 115.2, 112.9, 81.1, 70.1, 26.5, 22.2, 17.0; HRMS (CI) calcd for $\text{C}_{22}\text{H}_{24}\text{OSi}$ $[\text{M}+1]^+$ 333.1674, found 333.1666.



Colorless oil (78% yield): IR (ATR diamond crystal, cm^{-1}) 3052, 2961, 1598, 1493, 1091, 913; ^1H NMR (CDCl_3 , 500 MHz) δ 7.72 (m, 2H), 7.43 (m, 2H), 7.37 (m, 4H), 7.15 (m, 3H), 6.91 (m, 4H), 5.77 (m, 1H), 5.53 (m, 2H), 4.92 (d, 1H, $J = 17.1$ Hz) ppm 4.90 (d, 1H, $J = 10.7$ Hz), 3.79 (m, 1H), 2.39 (m, 2H), 2.26 (m, 2H), 1.94 (m, 2H), 1.07 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 152.1, 136.3, 135.3, 130.4, 129.2, 128.6, 127.7, 121.3, 119.6, 116.7, 81.5, 47.3, 44.5, 43.8, 38.6, 23.3; HRMS (CI) calcd for $\text{C}_{28}\text{H}_{30}\text{O}_2\text{Si}$ $[\text{M}+1]^+$ 427.2093, found 427.2113.

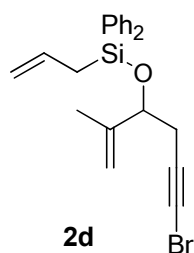


Colorless oil: IR (ATR diamond crystal, cm^{-1}) 3068, 3052, 2963, 2328, 1628, 1428, 1064; ^1H NMR (CDCl_3 , 500 MHz) δ 7.63 (m, 4H), 7.41 (m, 2H), 7.34 (m, 6H), 7.26 (m, 3H), 5.83 (m, 1H), 1H-NMR (501 MHz), 4.90 (m, 3H), 4.85 (s, 1H), 4.41 (t, 1H, $J = 6.4$ Hz), 2.67 (m, 2H), 2.24 (m, 2H), 1.75 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 147.1, 135.0, 134.9, 133.1, 129.9, 129.8, 128.1, 127.7, 127.69, 127.64, 124.5, 115.1, 87.1, 82.2, 27.6, 22.2, 17.1; HRMS (EI) calcd for $\text{C}_{28}\text{H}_{28}\text{OSi}$ $[\text{M}]^+$ 408.1909, found 408.1897.



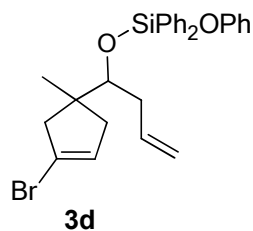
Colorless oil (81% yield): IR (ATR diamond crystal, cm^{-1}) 3052, 2915, 2835, 1591, 1487, 1118, 921, 695; Major: ^1H NMR (CDCl_3 , 500 MHz) δ 7.79 (m, 4H), 7.47 (m, 2H), 7.40 (m, 4H), 7.32 (m, 3H), 7.24 (m, 2H), 7.19 (m, 2H), 6.99 (m, 2H), 6.94 (m, 1H), 6.03 (s, 1H), 5.82 (m, 1H), 4.98 (m, 2H), 3.93 (s, 1H), 2.73 (m, 2H), 2.41 (m, 2H), 2.31 (m, 2H), 1.19 (d, 3H, $J = 9.7$ Hz); Minor: ^1H NMR (CDCl_3 , 500 MHz) δ 7.79 (m, 4H), 7.47 (m, 2H), 7.40 (m, 4H), 7.32 (m, 3H), 7.24 (m, 2H), 7.19 (m, 2H), 6.99 (m, 2H), 6.94 (m, 1H), 6.03 (s, 1H), 5.82 (m, 1H), 4.98 (m, 2H), 3.52 (q, 1H, $J =$

7.0 Hz), 2.70 (m, 2H), 2.41 (m, 2H), 2.10 (m, 2H), 1.19 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.5, 140.1, 136.7, 135.5, 132.4, 130.5, 129.3, 128.2, 127.8, 126.9, 125.5, 124.5, 123.6, 121.4, 119.7, 116.9, 81.4, 47.4, 45.0, 44.5, 44.3, 38.6, 23.6, 23.1; HRMS (CI) calcd for $\text{C}_{34}\text{H}_{34}\text{O}_2\text{Si}$ $[\text{M}]^+$ 502.2328, found 502.2333.

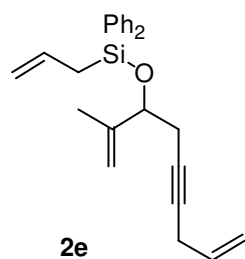


Colorless oil: IR (ATR diamond crystal, cm^{-1}) 3071, 3052, 2966, 2328, 1628, 1428, 1064; ^1H NMR (CDCl_3 , 500 MHz) δ 7.62 (m, 4H), 7.46 (m, 2H), 7.40 (dd, 4H, $J = 4.0, 10.5$ Hz), 5.85 (m, 1H), 4.95 (m, 3H), 4.86 (s, 1H), 4.34 (t, 1H, $J = 6.4$ Hz), 2.49 (m, 2H), 2.25 (m, 2H), 1.72 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 145.3, 135.1, 134.4, 133.1, 130.0, 127.8, 115.2, 112.8, 77.3, 75.7, 39.9, 27.8,

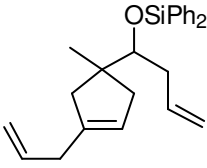
22.2, 17.1.

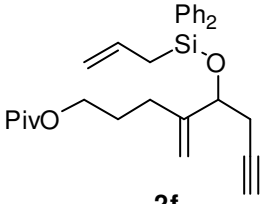


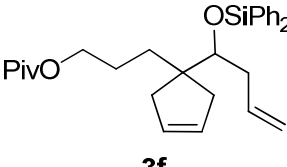
Colorless oil (69% yield): IR (ATR diamond crystal, cm^{-1}) 3071, 2928, 1591, 1428, 1067, 916; ^1H NMR (CDCl_3 , 500 MHz) diastereomer A: δ 7.71 (m, 4H), 7.46 (m, 2H), 7.39 (m, 4H), 7.16 (m, 2H), 6.91 (m, 3H), 5.75 (m, 1H), 5.71 (s, 1H), 4.93 (m, 2H), 3.78 (m, 1H), 1.8-3.0 (m, 6H), 1.13 (s, 3H); diastereomer B: δ 7.71 (m, 4H), 7.46 (m, 2H), 7.39 (m, 4H), 7.16 (m, 2H), 6.91 (m, 3H), 5.75 (m, 1H), 5.63 (s, 1H), 4.93 (m, 2H), 3.78 (m, 1H), 1.8-3.0 (m, 6H), 1.13 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.4, 135.6, 132.2, 130.6, 129.7, 129.3, 127.9, 121.5, 119.6, 118.9, 118.2, 117.1, 80.5, 50.4, 48.0, 44.6, 38.4, 24.0; HRMS (CI) calcd for $\text{C}_{28}\text{H}_{29}\text{BrO}_2\text{Si}$ $[\text{M}+1]^+$ 505.1198, found 505.1179.

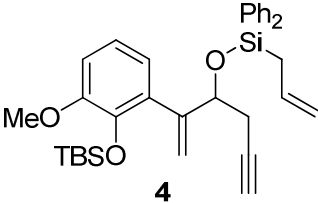


Colorless oil: IR (ATR diamond crystal, cm^{-1}) 3068, 3046, 2978, 1631, 1428, 1070; ^1H NMR (CDCl_3 , 500 MHz) δ 7.63 (m, 4H), 7.43 (m, 2H), 7.38 (m, 4H), 5.81 (m, 2H), 5.30 (dd, 1H, $J = 1.8, 17.0$ Hz), 5.08 (dd, 1H, $J = 1.7, 10.0$ Hz), 4.92 (m, 3H) ppm 4.83 (s, 1H), 4.33 (t, 1H, $J = 6.6$ Hz), 2.90 (m, 2H), 2.49 (m, 2H), 2.23 (m, 2H), 1.73 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.9, 145.6, 136.0, 134.9, 134.6, 133.1, 129.9, 127.7, 115.8, 112.6, 79.4, 78.5, 76.4, 27.0, 23.2, 22.2, 17.1; HRMS (CI) calcd for $\text{C}_{25}\text{H}_{28}\text{OSi}$ $[\text{M}+1]^+$ 373.1987, found 373.1976.

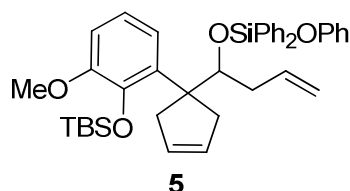

3e
 Colorless oil (78% yield): IR (ATR diamond crystal, cm^{-1}) 3071, 2910, 1643, 1490, 1070, 913; ^1H NMR (CDCl_3 , 500 MHz) δ 7.71 (m, 4H), 7.43 (m, 2H), 7.36 (m, 4H), 7.14 (t, 2H, $J = 7.8$ Hz), 6.90 (m, 3H), 5.76 (m, 2H), 5.19 (s, 1H), 4.94 (m, 4H), 3.76 (dd, 1H, $J = 3.3, 7.9$ Hz), 2.69 (m, 2H), 2.26 (m, 2H), 1.6-2.6 (m, 4H), 1.06 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.5, 140.5, 136.3, 136.1, 135.3, 130.3, 129.2, 127.7, 122.8, 121.3, 119.6, 116.7, 116.6, 115.5, 81.5, 47.5, 46.2, 44.2, 38.5, 35.8, 23.5; HRMS (EI) calcd for $\text{C}_{31}\text{H}_{34}\text{O}_2\text{Si}$ $[\text{M}]^+$ 466.2328, found 466.2334.


2f
 Colorless oil: IR (ATR diamond crystal, cm^{-1}) 3291, 3071, 2918, 1726, 1634, 1425, 1070; ^1H NMR (CDCl_3 , 500 MHz) δ 7.59 (m, 4H), 7.42 (m, 2H), 7.36 (m, 4H), 5.80 (m, 1H), 5.04 (s, 1H), 4.90 (m, 3H), 4.34 (t, 1H, $J = 6.4$ Hz), 4.01 (t, 2H, $J = 6.5$ Hz), 2.45 (m, 2H), 2.22 (m, 2H), 2.08 (m, 2H) ppm 1.92 (m, 1H) ppm 1.70 (m, 1H), 1.93 (t, 1H, $J = 2.6$ Hz), 1.68 (m, 2H), 1.19 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 178.5, 148.2, 135.0, 134.2, 132.9, 130.0, 127.8, 115.2, 111.9, 80.9, 75.5, 70.2, 63.9, 38.7, 27.2, 26.9, 26.7, 26.5, 22.1; HRMS (EI) calcd for $\text{C}_{29}\text{H}_{36}\text{O}_3\text{Si}$ $[\text{M}+\text{Na}]^+$ 483.2, found 483.2.


3f
 Colorless oil (81% yield): IR (ATR diamond crystal, cm^{-1}) 3073, 2904, 1726, 1591, 1490, 1070, 916; ^1H NMR (CDCl_3 , 500 MHz) δ 7.70 (m, 4H), 7.44 (m, 2H), 7.36 (m, 4H), 7.15 (m, 2H), 6.90 (m, 3H), 5.74 (m, 1H), 5.54 (m, 2H), 4.90 (m, 2H), 3.95 (t, 2H, $J = 6.4$ Hz), 3.83 (dd, 1H, $J = 3.7, 7.1$ Hz), 2.45 (m, 2H), 2.30 (m, 2H), 2.03 (m, 2H), 1.60 (m, 1H), 1.50 (m, 2H), 1.40 (m, 1H), 1.19 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 178.5, 154.4, 136.2, 135.3, 132.4, 132.3, 130.4, 129.4, 127.8, 127.7, 121.4, 119.6, 116.7, 80.6, 65.1, 49.3, 41.3, 38.7, 38.2, 30.6, 27.2, 23.6; HRMS (CI) calcd for $\text{C}_{35}\text{H}_{42}\text{O}_4\text{Si}$ $[\text{M}+1]^+$ 555.2930, found 555.2948.

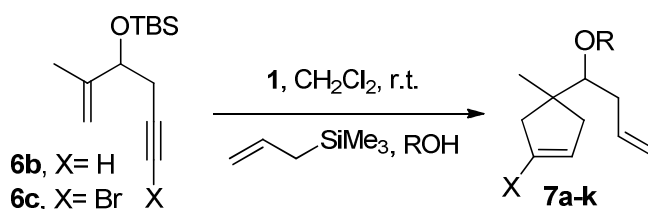

4
 Colorless oil: IR (ATR diamond crystal, cm^{-1}) 3309, 3068, 3052, 2954, 1631, 1470, 1055, 910; ^1H NMR (CDCl_3 , 500 MHz) δ 7.68 (m, 4H), 7.44 (m, 2H), 7.38 (m, 4H), 6.79 (m, 2H), 6.66 (m, 1H), 5.87 (m, 1H), 5.73 (s, 1H), 5.25 (s, 1H), 4.93 (m, 3H), 3.78 (s, 3H),

2.42 (dd, 1H, $J = 2.7, 4.1$ Hz), 2.38 (m, 2H), 2.27 (m, 2H), 1.93 (s, 1H), 0.94 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 150.2, 147.4, 142.1, 135.3, 134.6, 133.3, 132.4, 129.9, 127.6, 122.8, 120.8, 115.9, 115.1, 110.5, 81.7, 73.2, 70.4, 54.7, 26.5, 22.6, 18.8, -3.4, -3.8; HRMS (EI) calcd for $\text{C}_{34}\text{H}_{42}\text{O}_3\text{Si}_2$ $[\text{M}+1]^+$ 555.2751, found 555.2756.



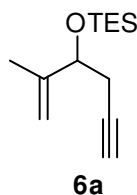
Colorless oil (76% yield): IR (ATR diamond crystal, cm^{-1}) 3073, 3049, 2931, 2853, 1951, 1457, 1070, 910, 733, 692; ^1H NMR (CDCl_3 , 500 MHz) δ 7.56 (m, 4H), 7.45 (m, 2H), 7.37 (m, 4H), 7.10 (m, 2H), 6.86 (m, 4H), 6.68 (m, 2H), 5.62 (m, 2H), 4.73 (m, 2H), 4.63 (s, 1H), 3.72 (s, 3H), 3.07 (m, 2H), 2.77 (m, 2H), 2.30 (m, 1H), 2.13 (m, 1H), 0.86 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 156.2, 149.1, 144.3, 136.4, 135.4, 133.1, 130.1, 129.0, 127.5, 122.5, 121.1, 119.2, 116.3, 108.8, 78.0, 55.3, 54.1, 38.7, 27.1, 19.7, 1.0, -1.5; HRMS (EI) calcd for $\text{C}_{40}\text{H}_{48}\text{O}_4\text{Si}_2$ $[\text{M}]^+$ 648.3091, found 648.3071.

IV. Procedure for Au(I)-catalyzed reaction with intermolecular allylation

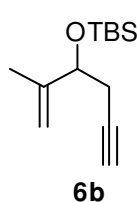


To a solution of 3-*t*-butyldimethylsilyloxy-1,5-enyne **6b** (40.5 mg, 0.18 mmol) and ethanol (9.2 mg, 0.20 mmol) in CH_2Cl_2 (0.5 mL) was added the Au(I) catalyst **1** (1 mol%). The resulting clean solution was stirred at room temperature for 1 hour, at which point TLC indicated the consumption of the starting material. The reaction mixture was concentrated to afford the crude product, which was purified by column chromatography with hexane and ethyl acetate (30:1) to give the desired cyclopentene product **7a** (colorless oil, 23.3 mg, 72% yield)

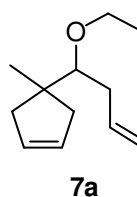
V. Characterization data for Table 2



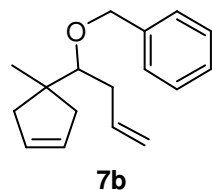
Colorless oil: ^1H NMR (CDCl_3 , 500 MHz) δ 4.96 (s, 1H), 4.85 (s, 1H), 4.22 (t, 1H, J = 6.6 Hz), 2.40 (m, 2H), 1.97 (t, 1H, J = 2.7 Hz), 1.71 (s, 3H), 0.96 (t, 9H, J = 7.94 Hz), 0.61 (q, 6H, J = 7.6 Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 146.1, 111.9, 81.5, 75.2, 69.7, 26.8, 16.8, 6.8, 4.7.



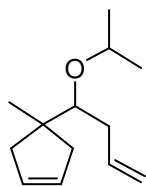
Colorless oil: IR (ATR diamond crystal, cm^{-1}) 3300, 3680, 2918, 2180, 1070; ^1H NMR (CDCl_3 , 500 MHz) δ 4.95 (s, 1H), 4.83 (s, 1H), 4.21 (t, 1H, J = 6.5 Hz), 2.37 (m, 2H), 1.95 (t, 1H, J = 2.5 Hz), 1.70 (s, 3H), 0.90 (s, 9H), 0.60 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 146.2, 111.9, 81.7, 75.6, 69.7, 26.9, 25.8, 18.2, 16.8, -5.0, -4.9; HRMS (CI) calcd for $\text{C}_{13}\text{H}_{24}\text{OSi}$ $[\text{M}+1]^+$ 225.1674, found 225.1682.



Colorless oil (72% yield): IR (ATR diamond crystal, cm^{-1}) 3052, 2966, 1623, 1055; ^1H NMR (CDCl_3 , 500 MHz) δ 5.93 (m, 1H), 5.59 (s, 2H), 5.08 (d, 1H, J = 17.1 Hz), 5.00 (dd, 1H, J = 0.9, 10.1 Hz), 3.62 (m, 1H), 3.50 (m, 1H), 3.12 (dd, 1H, J = 3.8, 7.7 Hz), 2.38 (m, 2H), 2.23 (m, 2H), 2.02 (m, 2H), 1.15 (t, 3H, J = 6.8 Hz), 1.03 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 137.3, 129.2, 128.9, 86.9, 67.4, 46.8, 44.1, 43.6, 36.9, 24.0, 15.7; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{20}\text{O}$ $[\text{M}-1]^+$ 179.1800, found 179.1817.

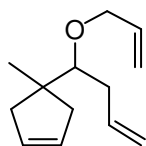


Colorless oil (85% yield): IR (ATR diamond crystal, cm^{-1}) 3055, 2910, 2847, 1645, 1094, 730, 700, 685; ^1H NMR (CDCl_3 , 500 MHz) δ 7.33 (m, 5H), 5.98 (m, 1H), 5.60 (s, 2H), 5.12 (dd, 1H, J = 1.5, 17.1 Hz), 5.03 (d, 1H, J = 10.1 Hz), 4.71 (d, 1H, J = 11.5 Hz), 4.53 (d, 1H, J = 11.5 Hz), 3.33 (t, 1H, J = 5.6 Hz), 2.43 (m, 2H), 2.35 (m, 2H), 2.01 (m, 2H), 1.07 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 139.2, 137.2, 129.3, 128.8, 128.2, 127.4, 127.3, 116.1, 86.6, 73.4, 46.9, 44.4, 43.8, 36.8, 23.9; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 242.1671, found 242.1666.



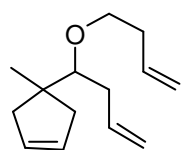
7d

Colorless oil (92% yield): IR (ATR diamond crystal, cm^{-1}) 3052, 2966, 1623, 1055; ^1H NMR (CDCl_3 , 500 MHz) δ 5.93 (m, 1H), 5.58 (s, 2H), 5.06 (dd, 1H, $J = 2.0$, 17.1 Hz) ppm 4.98 (dd, 1H, $J = 1.0$, 10.1 Hz), 3.68 (m, 1H), 3.24 (dd, 1H, $J = 3.9$, 7.1 Hz), 2.41 (m, 2H), 2.29 (m, 2H), 1.94 (m, 2H), 1.12 (s, 3H), 1.11 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 137.6, 129.3, 128.9, 115.6, 83.7, 70.6, 46.9, 44.2, 43.7, 37.6, 24.0, 23.4; MS (EI) calcd for $\text{C}_{13}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 194.17, found 194.13.



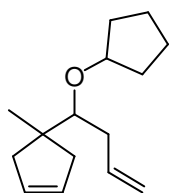
7e

Colorless oil (91% yield): IR (ATR diamond crystal, cm^{-1}) 3049, 3052, 2931, 1640, 1094; ^1H NMR (CDCl_3 , 500 MHz) δ 5.92 (m, 1H), 5.59 (s, 2H), 5.25 (dd, 1H, $J = 1.6$, 17.2 Hz), 5.10 (m, 2H), 5.01 (d, 1H, $J = 10.1$ Hz), 4.16 (dd, 1H, $J = 5.3$, 12.7 Hz), 3.99 (dd, 1H, $J = 5.6$, 12.6 Hz), 3.20 (dd, 1H, $J = 4.3$, 7.0 Hz), 2.40 (m, 2H), 2.27 (m, 2H), 1.97 (m, 2H), 1.04 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 137.8, 136.7, 129.2, 128.8, 116.0, 115.9, 86.6, 72.8, 44.2, 43.7, 43.5, 36.8, 23.9; HRMS (CI) calcd for $\text{C}_{13}\text{H}_{20}\text{O}$ $[\text{M}+1]^+$ 193.1514, found 193.2007.



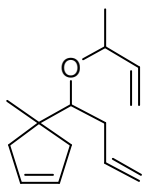
7f

Colorless oil (66% yield): IR (ATR diamond crystal, cm^{-1}) 3079, 3052, 2931, 1637, 1094; ^1H NMR (CDCl_3 , 500 MHz) δ 5.93 (m, 1H), 5.83 (m, 1H), 5.59 (s, 2H), 5.07 (ddd, 2H, $J = 1.7$, 9.3, 17.2 Hz), 5.00 (d, 2H, $J = 10.7$ Hz), 3.65 (td, 1H, $J = 6.8$, 8.8 Hz), 3.46 (td, 1H, $J = 7.0$, 8.8 Hz), 3.13 (dd, 1H, $J = 4.1$, 7.3 Hz), 2.38 (m, 2H), 2.30 (m, 2H), 2.24 (m, 2H), 1.96 (m, 2H), 1.02 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 137.3, 135.7, 129.2, 128.8, 115.9, 115.8, 87.0, 71.3, 46.8, 44.2, 43.7, 36.8, 34.8, 23.8; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 206.1671, found 206.1661.



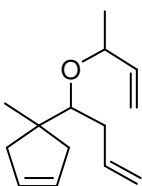
7g

Colorless oil (81% yield): IR (ATR diamond crystal, cm^{-1}) 3055, 2957, 1643; ^1H NMR (CDCl_3 , 500 MHz) δ 5.93 (m, 1H), 5.59 (s, 2H), 5.05 (dd, 1H, $J = 1.9$, 17.1 Hz) ppm 4.98 (dd, 1H, $J = 0.9$, 10.1 Hz), 4.01 (m, 1H), 3.22 (dd, 1H, $J = 4.0$, 6.8 Hz), 2.38 (m, 2H), 2.27 (m, 2H), 1.94 (m, 2H), 1.67 (m, 4H), 1.60 (m, 2H), 1.48 (m, 2H), 1.01 (m, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 137.6, 129.2, 128.9, 115.4, 84.3, 80.8, 46.9, 44.3, 43.7, 37.1, 33.3, 32.1, 23.9, 23.3, 23.2; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{24}\text{O}$ $[\text{M}]^+$ 220.1827, found 220.1817.



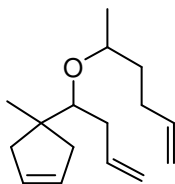
7h (less polar)

Colorless oil (44% yield): IR (ATR diamond crystal, cm^{-1}) 3055, 2954, 1631, 1077; ^1H NMR (CDCl_3 , 500 MHz) δ 5.92 (m, 1H), 5.69 (m, 1H), 5.57 (s, 2H), 5.08 (m, 3H), 4.99 (d, 1H, $J = 10.1$ Hz), 3.96 (m, 1H), 3.29 (dd, 1H, $J = 4.1, 6.6$ Hz), 2.29 (m, 4H), 1.91 (m, 2H), 1.19 (d, 3H, $J = 6.4$ Hz), 1.01 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 141.3, 137.4, 129.3, 128.7, 115.6, 115.4, 82.3, 75.3, 46.6, 44.3, 43.8, 37.0, 24.0, 21.9.



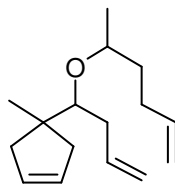
7h (more polar)

Colorless oil (40% yield): IR (ATR diamond crystal, cm^{-1}) 3055, 2954, 1631, 1077; ^1H NMR (CDCl_3 , 500 MHz) δ 5.88 (m, 1H), 5.79 (m, 1H), 5.60 (s, 2H), 5.13 (d, 1H, $J = 17.2$ Hz), 5.05 (d, 1H, $J = 5.4$ Hz), 5.02 (d, 1H, $J = 12.4$ Hz), 4.96 (d, 1H, $J = 9.2$ Hz), 3.98 (m, 1H), 3.30 (dd, 1H, $J = 4.5, 6.5$ Hz), 2.39 (m, 2H), 2.23 (m, 2H), 1.95 (m, 2H), 1.20 (d, 3H, $J = 6.3$ Hz), 1.04 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 141.8, 137.5, 129.2, 128.9, 115.5, 114.4, 83.7, 76.6, 47.1, 44.4, 43.7, 37.4, 23.8, 21.1; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 206.2034, found 206.2045.



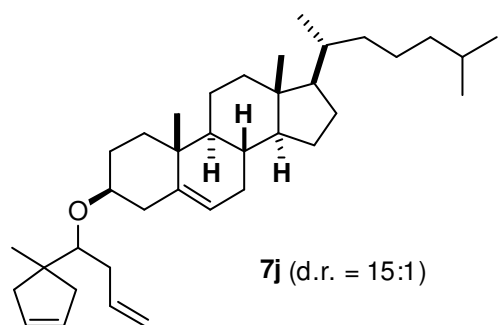
7i (less polar)

Colorless oil (49% yield): IR (ATR diamond crystal, cm^{-1}) 3055, 2928, 1640, 1064; ^1H NMR (CDCl_3 , 500 MHz) δ 5.92 (m, 1H), 5.83 (m, 1H), 5.58 (s, 2H), 5.00 (m, 4H), 3.58 (m, 1H), 3.28 (dd, 1H, $J = 4.5, 5.8$ Hz), 2.42 (m, 2H), 2.28 (m, 2H), 2.09 (m, 2H) ppm 1.93 (m, 2H), 1.61 (m, 1H), 1.46 (m, 1H), 1.09 (d, 3H, $J = 6.1$ Hz), 1.02 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 139.1, 137.7, 137.4, 129.3, 128.8, 115.5, 82.2, 72.3, 46.8, 44.2, 43.8, 37.1, 36.7, 29.8, 24.1, 19.4; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{26}\text{O}$ $[\text{M}]^+$ 234.1045, found 234.1034.



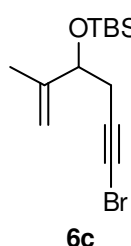
7i (more polar)

Colorless oil (40% yield): IR (ATR diamond crystal, cm^{-1}) 3055, 2928, 1640, 1064; ^1H NMR (CDCl_3 , 500 MHz) δ 5.94 (m, 1H), 5.82 (m, 1H), 5.59 (s, 2H), 5.00 (m, 4H), 3.55 (m, 1H), 3.26 (dd, 1H, $J = 4.1, 6.8$ Hz), 2.39 (m, 2H), 2.26 (m, 2H), 2.10 (m, 2H), 1.95 (m, 2H), 1.66 (m, 1H), 1.46 (m, 1H), 1.11 (d, 3H, $J = 6.1$ Hz), 1.03 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 139.1, 137.8, 129.0, 128.4, 115.8, 114.3, 85.2, 74.3, 47.1, 44.3, 43.9, 37.9, 36.3, 30.1, 24.3, 22.7.

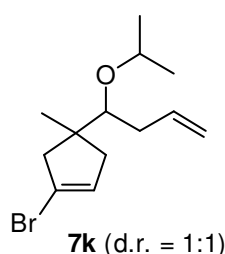


White solid (72% yield): IR (ATR diamond crystal, cm^{-1}) 3052, 2934, 1643; 3071, 2910, 1643, 1490, 1070; ^1H NMR (CDCl_3 , 500 MHz) δ 5.92 (m, 1H), 5.59 (s, 2H), 5.32 (s, 1H), 5.04 (m, 2H), 3.29 (dd, 1H, $J = 3.9, 7.2$ Hz), 3.22 (m, 1H), 2.29 (m, 6H), 2.00 (m, 4H), 1.85 (m, 6H), 1.53 (m, 5H), 1.29 (m, 5H), 1.11

(m, 3H), 1.00 (m, 6H), 0.90 (m, 6H), 0.68 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 141.6, 141.5, 137.3, 129.2, 121.1, 115.7, 83.9, 78.9, 56.8, 56.2, 50.2, 46.9, 44.2, 43.7, 42.3, 40.6, 39.5, 37.6, 36.8, 35.8, 32.0, 31.9, 31.6, 28.9, 28.2, 24.3, 24.0, 23.8, 22.8, 22.7, 22.6, 21.1, 19.4, 18.7, 14.1, 11.9; HRMS (EI) calcd for $\text{C}_{37}\text{H}_{60}\text{O}$ $[\text{M}]^+$ 520.4644, found 520.4658.



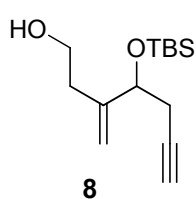
Colorless oil: ^1H NMR (CDCl_3 , 500 MHz) δ 4.94 (s, 1H), 4.83 (s, 1H), 4.21 (m, 1H), 2.38 (m, 2H), 1.69 (s, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 146.2, 111.8, 77.9, 75.3, 39.3, 28.2, 25.7, 18.2, 16.9, -4.8, -5.0; HRMS (CI) calcd for $\text{C}_{13}\text{H}_{23}\text{BrOSi}$ $[\text{M}+1]^+$ 303.0779, found 303.0799.



Colorless oil (73% yield): IR (ATR diamond crystal, cm^{-1}) 3071, 2969, 1643, 1624, 1058; ^1H NMR (CDCl_3 , 500 MHz) δ 5.89 (m, 1H), 5.71 (s, 1H), 5.03 (dd, 2H, $J = 1.2, 5.3$ Hz), 3.67 (m, 1H), 3.23 (td, 1H, $J = 4.2, 8.0$ Hz), 1.80-2.80 (m, 6H), 1.10 (m, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 136.8, 129.6, 129.2, 116.0, 82.4, 70.7, 50.5, 47.6, 43.6, 37.0, 24.5, 23.5, 22.1;

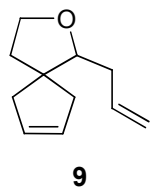
HRMS (CI) calcd for $\text{C}_{13}\text{H}_{21}\text{BrO}$ $[\text{M}+1]^+$ 273.0854, found 273.0836.

VI. Characterization data for Scheme 3

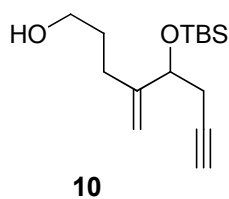


Colorless oil: IR (ATR diamond crystal, cm^{-1}) 3401, 3312, 2951, 1651, 1077; ^1H NMR (CDCl_3 , 500 MHz) δ 5.10 (s, 1H), 4.96 (s, 1H), 4.27 (t, 1H, $J = 6.7$ Hz), 3.74 (m, 1H), 3.68 (m, 1H), 2.47 (s, 1H), 2.44 (m, 2H), 2.34 (m, 2H), 1.97 (t, 1H, $J = 2.6$ Hz), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz)

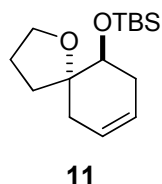
δ 146.8, 114.6, 81.1, 75.5, 70.3, 61.7, 34.3, 26.8, 25.7, 18.1, -4.7, -4.8; HRMS (CI) calcd for $C_{14}H_{26}O_2Si$ $[M+1]^+$ 255.1780, found 255.1794.



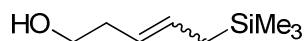
Colorless oil (72% yield): IR (ATR diamond crystal, cm^{-1}) 3049, 2919, 1634; 1H NMR ($CDCl_3$, 500 MHz) δ 5.88 (m, 1H), 5.67 (m, 2H), 5.10 (dd, 1H, $J = 1.5, 17.1$ Hz) 5.04 (d, 1H, $J = 10.1$ Hz), 3.86 (m, 2H), 3.62 (dd, 1H, $J = 3.6, 9.2$ Hz), 2.54 (m, 1H), 2.35 (m, 2H), 2.18 (m, 2H), 2.03 (m, 1H), 1.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.1, 129.6, 129.1, 116.2, 85.3, 65.7, 50.8, 42.2, 41.2, 39.0, 35.4; HRMS (EI) calcd for $C_{11}H_{16}O$ $[M-1]^+$ 163.1123, found 163.1109.



Colorless oil: IR (ATR diamond crystal, cm^{-1}) 3402, 3312, 3103, 2951, 1651, 1061; 1H NMR ($CDCl_3$, 500 MHz) δ 5.08 (s, 1H), 4.88 (s, 1H), 4.24 (t, 1H, $J = 6.4$ Hz), 3.67 (t, 2H, $J = 6.4$ Hz), 2.39 (m, 2H), 2.11 (m, 2H), 1.96 (s, 1H), 1.75 (m, 2H), 1.61 (s, 1H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.5, 110.9, 81.7, 75.2, 69.8, 62.6, 30.8, 27.3, 26.3, 25.8, 18.2, -4.7, -4.9; HRMS (CI) calcd for $C_{15}H_{28}O_2Si$ $[M+1]^+$ 269.1936, found 269.1947.

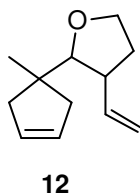


Colorless oil (56% yield): 1H NMR ($CDCl_3$, 500 MHz) δ 5.55 (m, 2H), 3.87 (t, 2H, $J = 6.3$ Hz), 3.72 (dd, 1H, $J = 5.5, 7.1$ Hz), 2.25 (m, 3H), 2.08 (m, 1H), 1.91 (m, 4H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 125.1, 124.8, 83.2, 72.8, 68.3, 37.2, 34.0, 33.2, 26.4, 25.9, 18.6, -4.3, -4.6; HRMS (CI) calcd for $C_{15}H_{28}O_2Si$ $[M+1]^+$ 269.1936, found 269.1917.



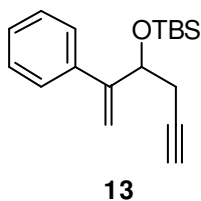
Compound **SI-1** was obtained from cross metathesis reaction between 3-buten-1-ol and allyltrimethylsilane. Colorless oil: (Major) 1H NMR ($CDCl_3$, 500 MHz) δ 5.49 (m, 1H), 5.20 (m, 1H), 3.57 (t, 2H, $J = 6.3$ Hz), 2.24 (m, 2H), 1.42 (m, 2H), -0.02 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 130.2, 124.1, 62.2, 36.2, 22.9, -1.8; (Minor) 1H NMR ($CDCl_3$, 500 MHz) δ 5.57 (m, 1H), 5.26 (m, 1H), 3.61 (t, 2H, $J = 6.5$ Hz),

2.28 (m, 2H), 1.50 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 128.9, 122.5, 62.4, 30.6, 18.7, -1.9.

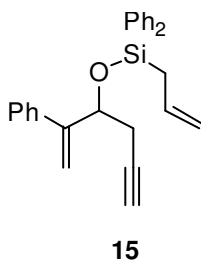


Colorless oil (87% yield): Major: ^1H NMR (CDCl_3 , 500 MHz) δ 5.90 (m, 1H), 5.58 (m, 2H), 5.03 (d, 1H, $J = 17.0$ Hz), 4.96 (d, 1H, $J = 10.1$ Hz), 4.01 (m, 2H), 3.83 (m, 1H), 2.59 (m, 2H), 2.17 (m, 1H), 1.96 (m, 2H), 1.78 (m, 2H), 1.04 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 138.9, 129.3, 127.9, 114.3, 88.4, 66.3, 46.3, 45.9, 42.5, 33.3, 25.4; Minor: ^1H NMR (500 MHz) δ 5.77 (m, 1H), 5.55 (d, 2H, $J = 8.6$ Hz), 5.04 (d, 1H, $J = 17.0$ Hz), 4.96 (m, 1H), 3.70 (m, 2H), 3.56 (m, 1H), 2.83 (m, 2H), 2.45 (m, 1H), 2.17 (m, 2H), 2.07 (m, 2H), 1.05 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 141.1, 129.0, 128.9, 114.4, 90.3, 67.5, 45.5, 44.1, 43.6, 43.3, 34.9, 24.7.

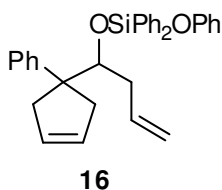
VII. Characterization data for Scheme 4



^1H NMR (CDCl_3 , 500 MHz) δ 7.43 (m, 2H), 7.33 (m, 3H), 5.44 (s, 1H), 5.35 (s, 1H), 4.77 (m, 1H), 2.38 (m, 2H), 1.97 (s, 1H), 0.99 (s, 9H), 0.21 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 150.3, 139.4, 128.3, 127.6, 127.1, 114.3, 81.8, 73.8, 69.8, 27.8, 25.9, 18.4, -4.5, -4.7.

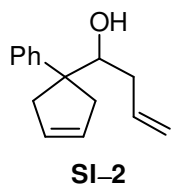


Colorless oil: IR (ATR diamond crystal, cm^{-1}) 3306, 3088, 2937, 1711, 1482, 1028; ^1H NMR (CDCl_3 , 500 MHz) δ 7.68 (m, 4H), 7.45 (m, 2H), 7.39 (m, 4H), 7.26 (m, 5H), 5.87 (m, 1H), 5.45 (s, 1H), 5.32 (s, 1H), 4.96 (dd, 1H, $J = 1.5$, 17.0 Hz), 4.90 (d, 1H, $J = 10.1$ Hz), 4.82 (t, 1H, $J = 5.8$ Hz), 2.41 (m, 2H), 2.29 (m, 2H), 1.92 (t, 1H, $J = 2.6$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 149.1, 139.1, 135.1, 133.0, 130.0, 128.2, 127.7, 127.6, 127.2, 115.3, 115.0, 81.3, 74.2, 70.2, 27.3, 22.3; HRMS (EI) calcd for $\text{C}_{27}\text{H}_{26}\text{OSi}$ $[\text{M}]^+$ 394.3631, found 394.3613.



Colorless oil (85% yield): IR (ATR diamond crystal, cm^{-1}) 3071, 2910, 1601, 1493, 1070, 916; ^1H NMR (CDCl_3 , 500 MHz) δ 7.63 (m, 4H), 7.43 (m, 2H), 7.37 (m, 4H), 7.24 (m, 4H), 7.17 (m, 3H), 6.89 (m, 3H), 5.65 (m, 1H), 5.58 (m,

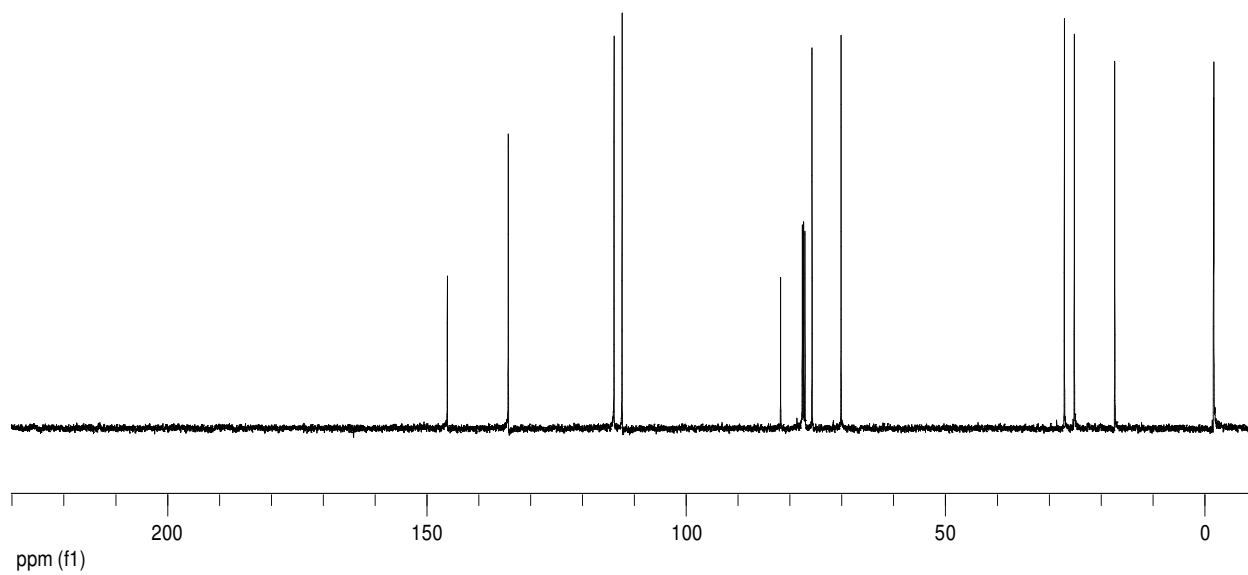
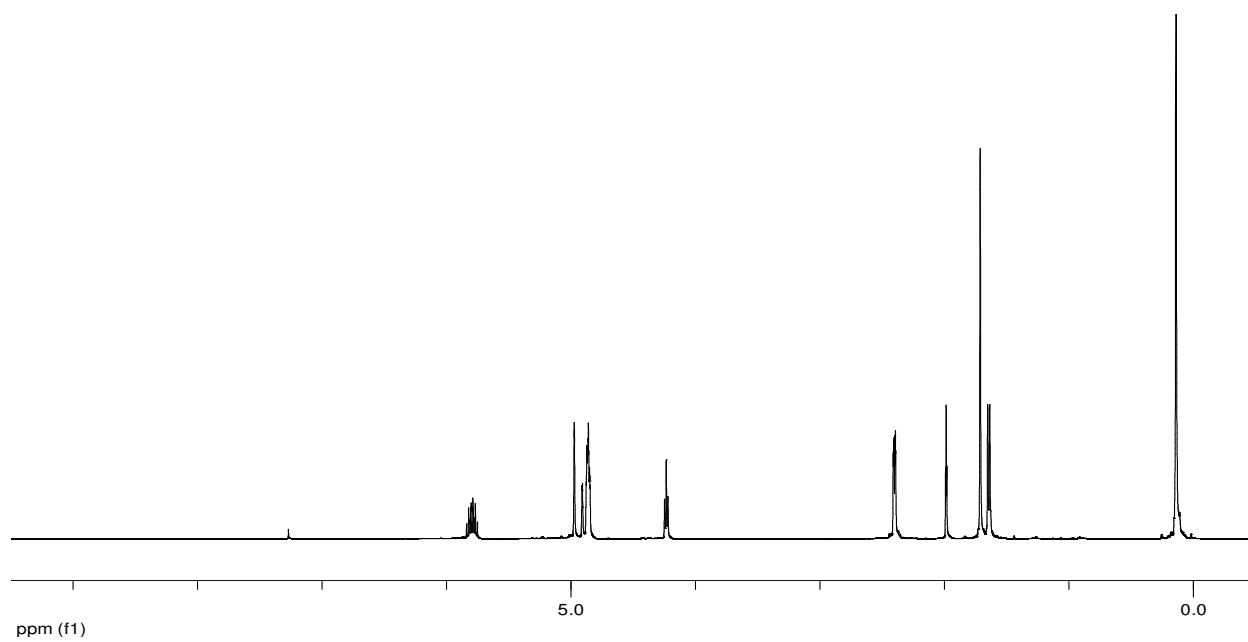
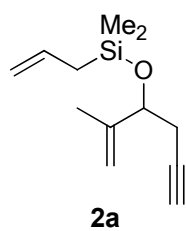
2H), 4.75 (m, 2H), 4.11 (dd, 1H, $J = 2.8, 7.8$ Hz), 2.91 (m, 2H), 2.66 (m, 2H), 2.10 (m, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.4, 146.7, 136.2, 135.4, 134.5, 132.3, 130.4, 129.2, 129.1, 129.0, 128.0, 127.7, 125.8, 121.4, 119.7, 116.6, 80.0, 56.1, 42.2, 41.0, 38.8; HRMS (CI) calcd for $\text{C}_{33}\text{H}_{32}\text{O}_2\text{Si}$ $[\text{M}+1]^+$ 489.2249, found 489.2236.

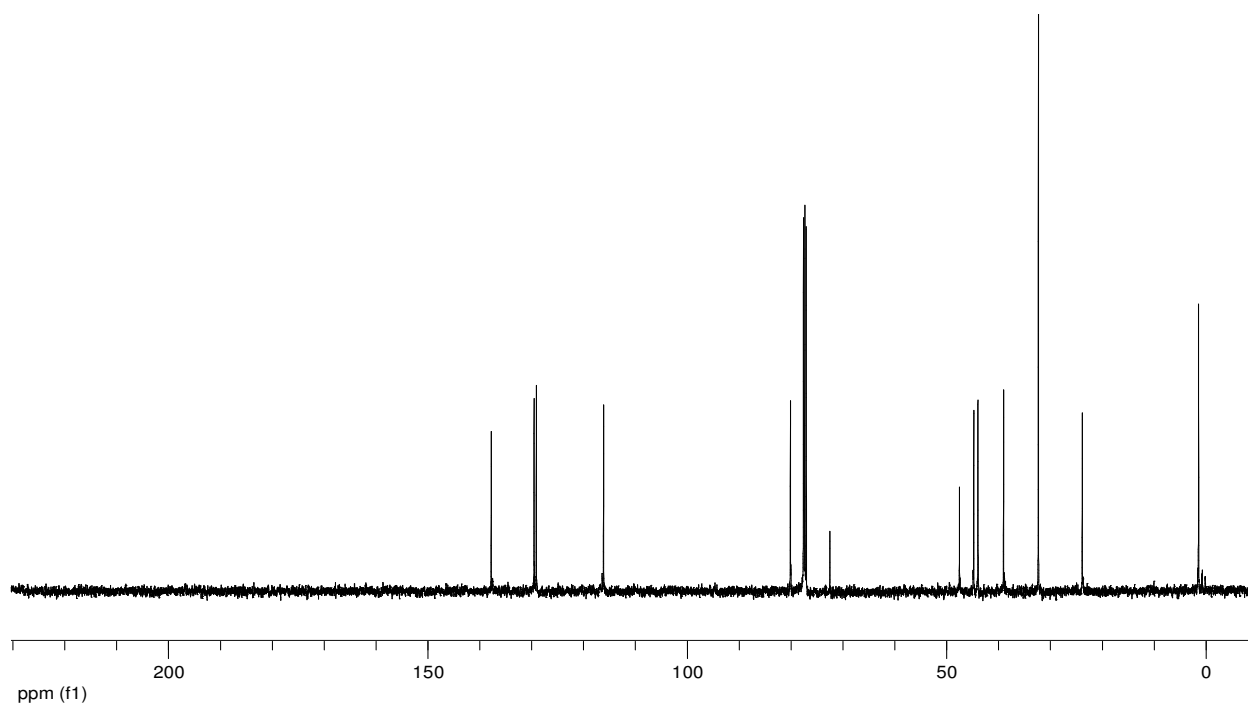
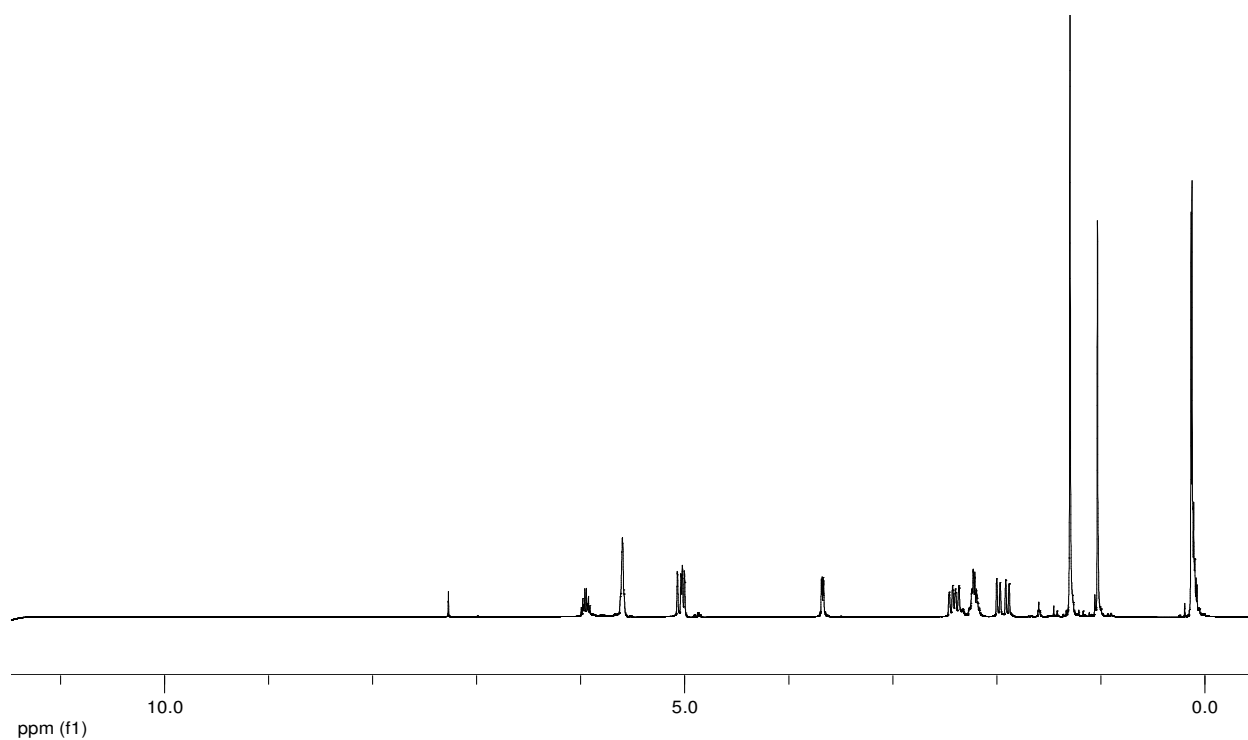
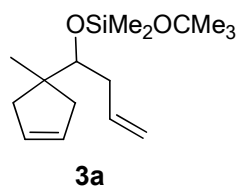


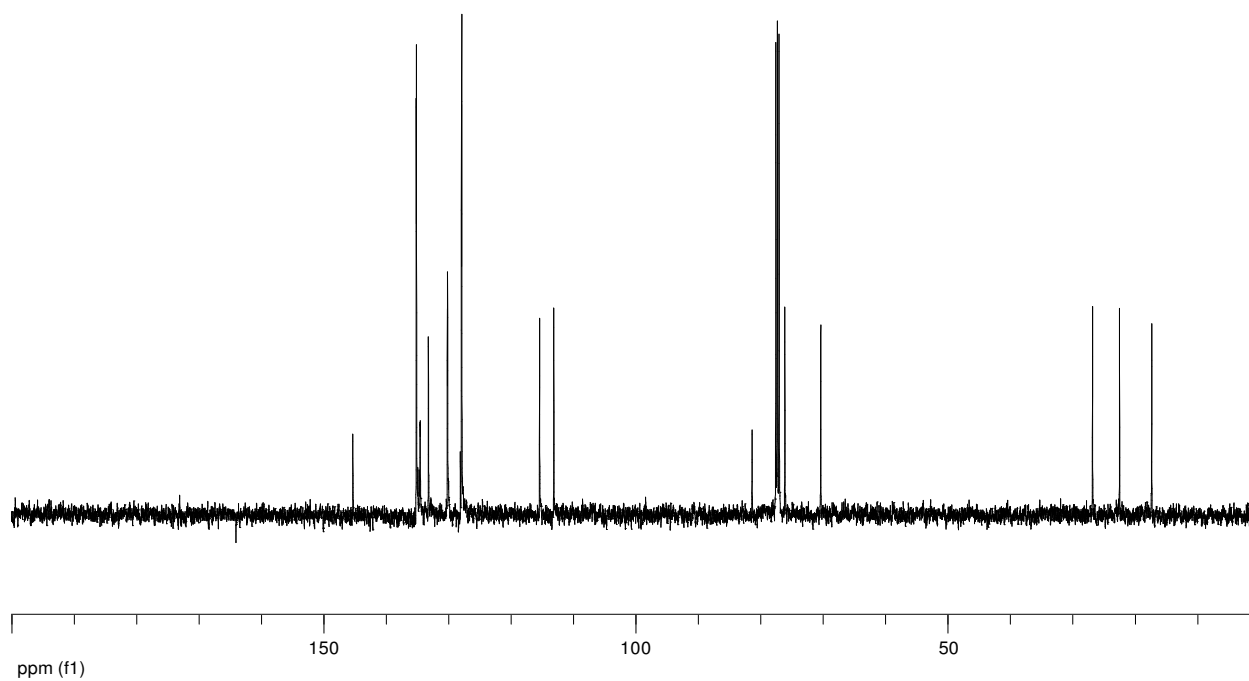
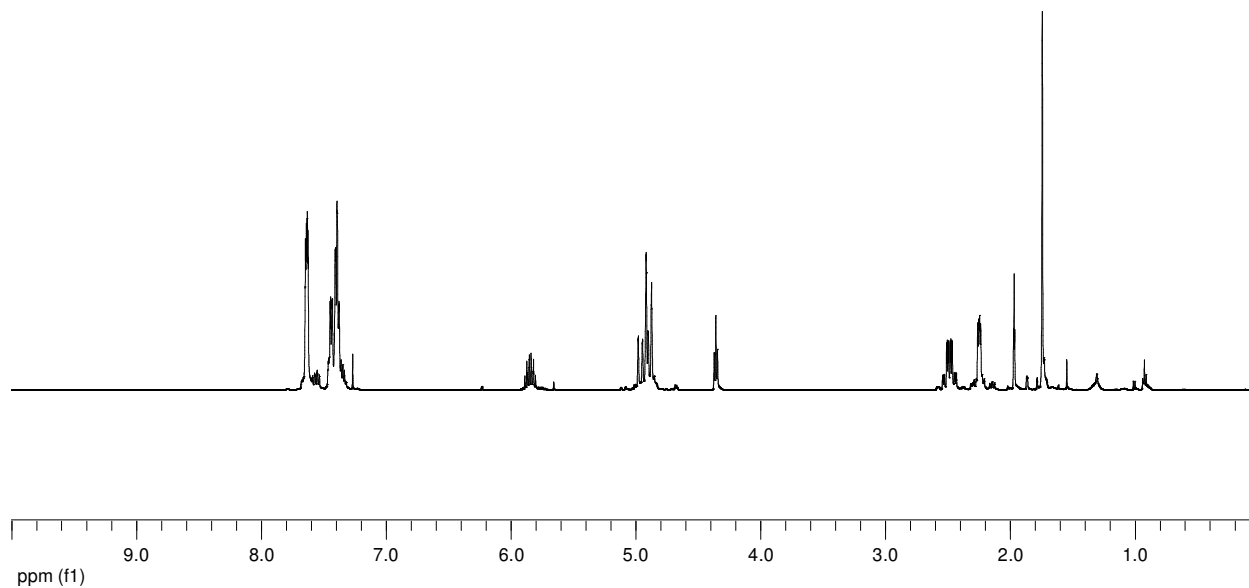
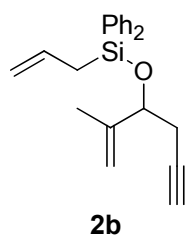
Compound **SI-2** was obtained from desilylation of compound **16** using TBAF.

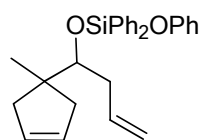
Colorless oil: ^1H NMR (CDCl_3 , 500 MHz) δ 7.32 (m, 2H), 7.23 (m, 3H), 5.80 (m, 1H), 5.75 (s, 2H), 5.04 (m, 2H), 3.64 (ddd, 1H, $J = 2.0, 4.3, 10.4$ Hz), 2.85 (m, 2H), 2.76 (m, 2H), 2.27 (m, 1H), 1.78 (m, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ

146.7, 136.4, 129.5, 129.3, 128.2, 127.9, 126.1, 117.2, 77.0, 54.9, 41.6, 40.7, 37.2.

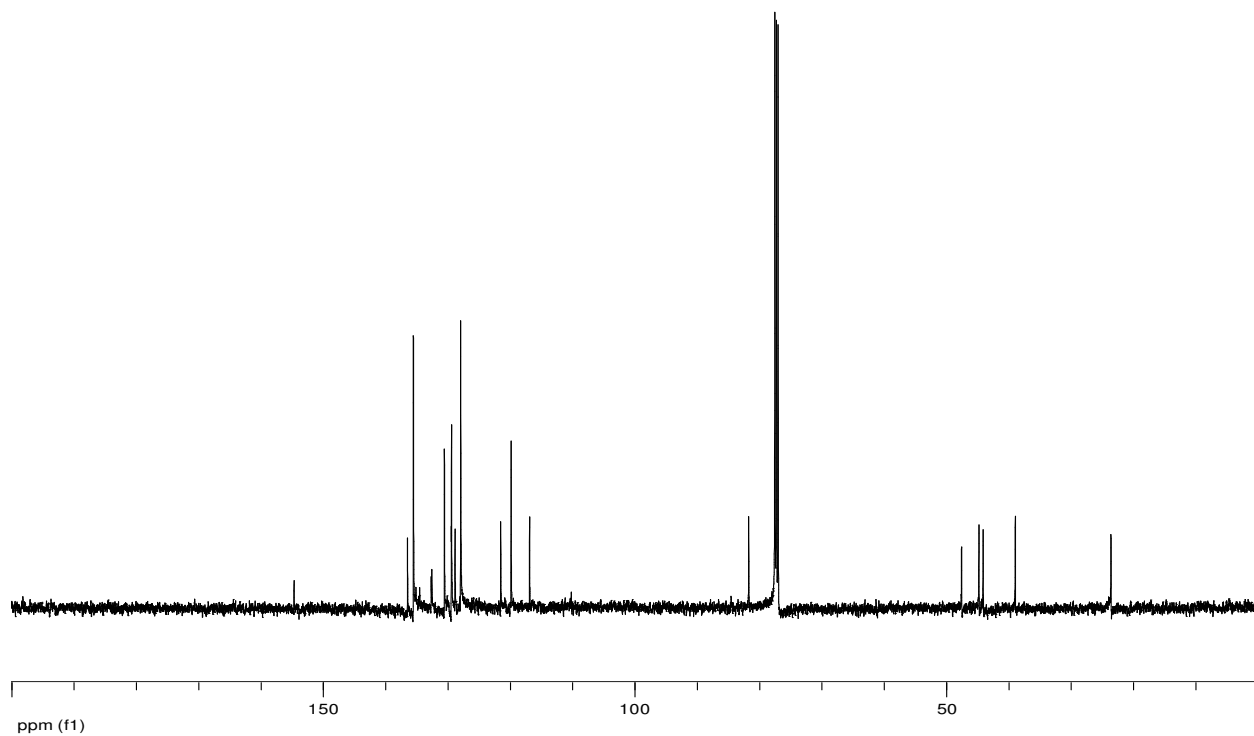
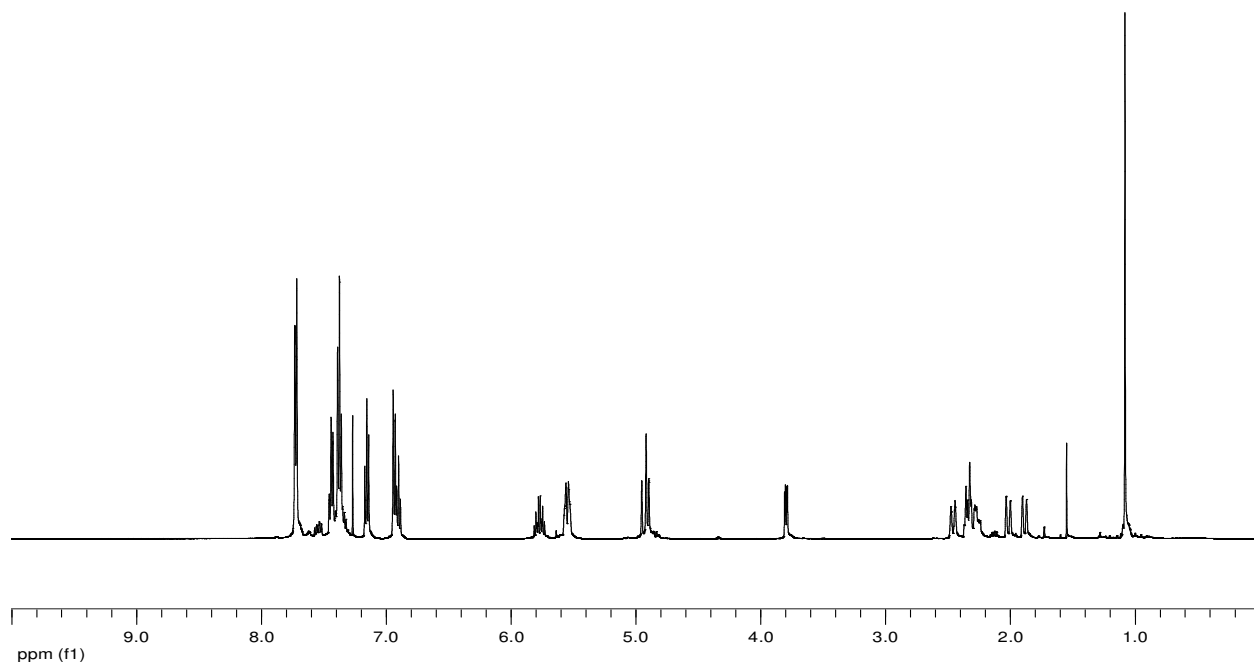


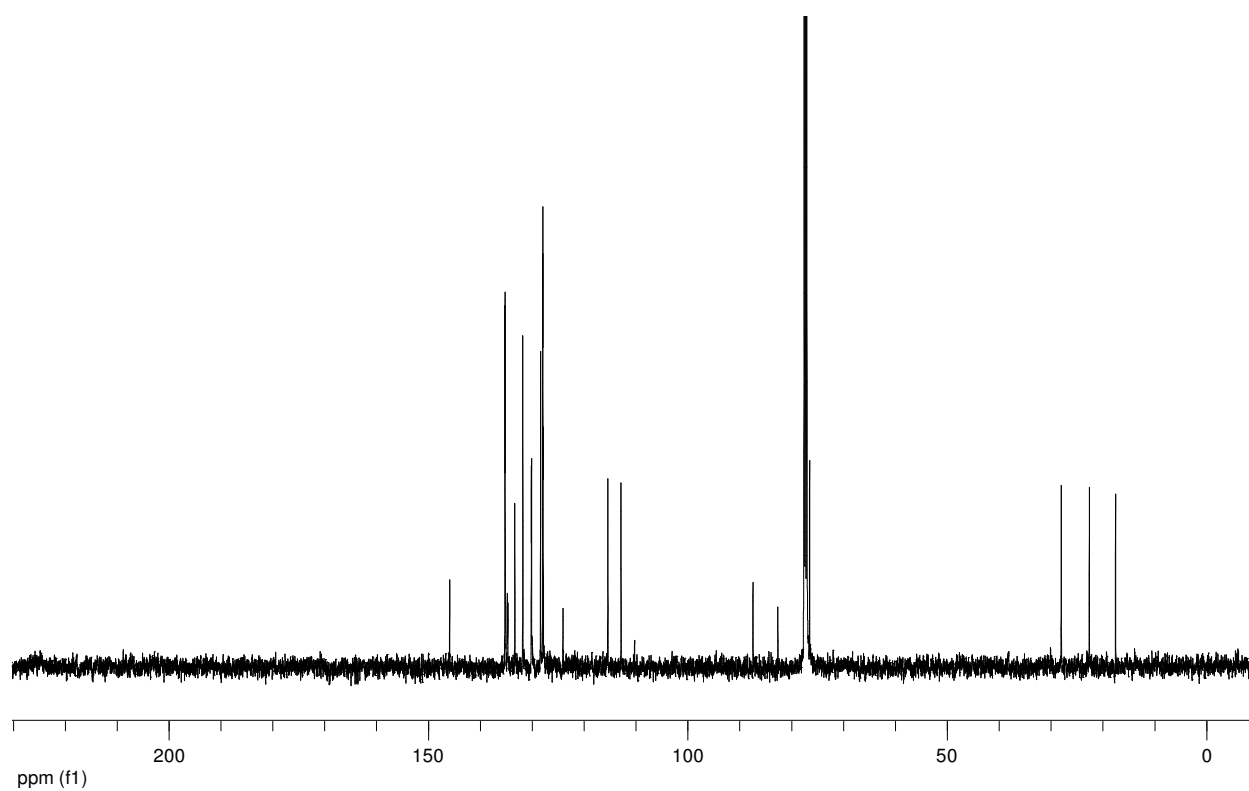
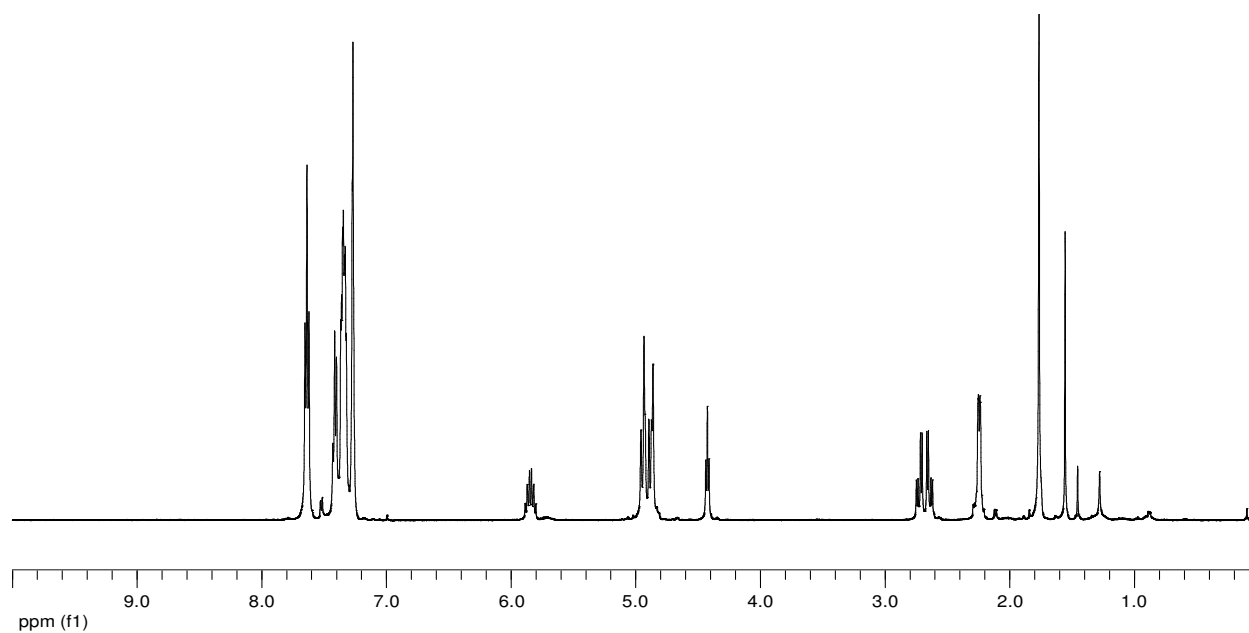
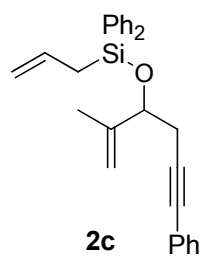


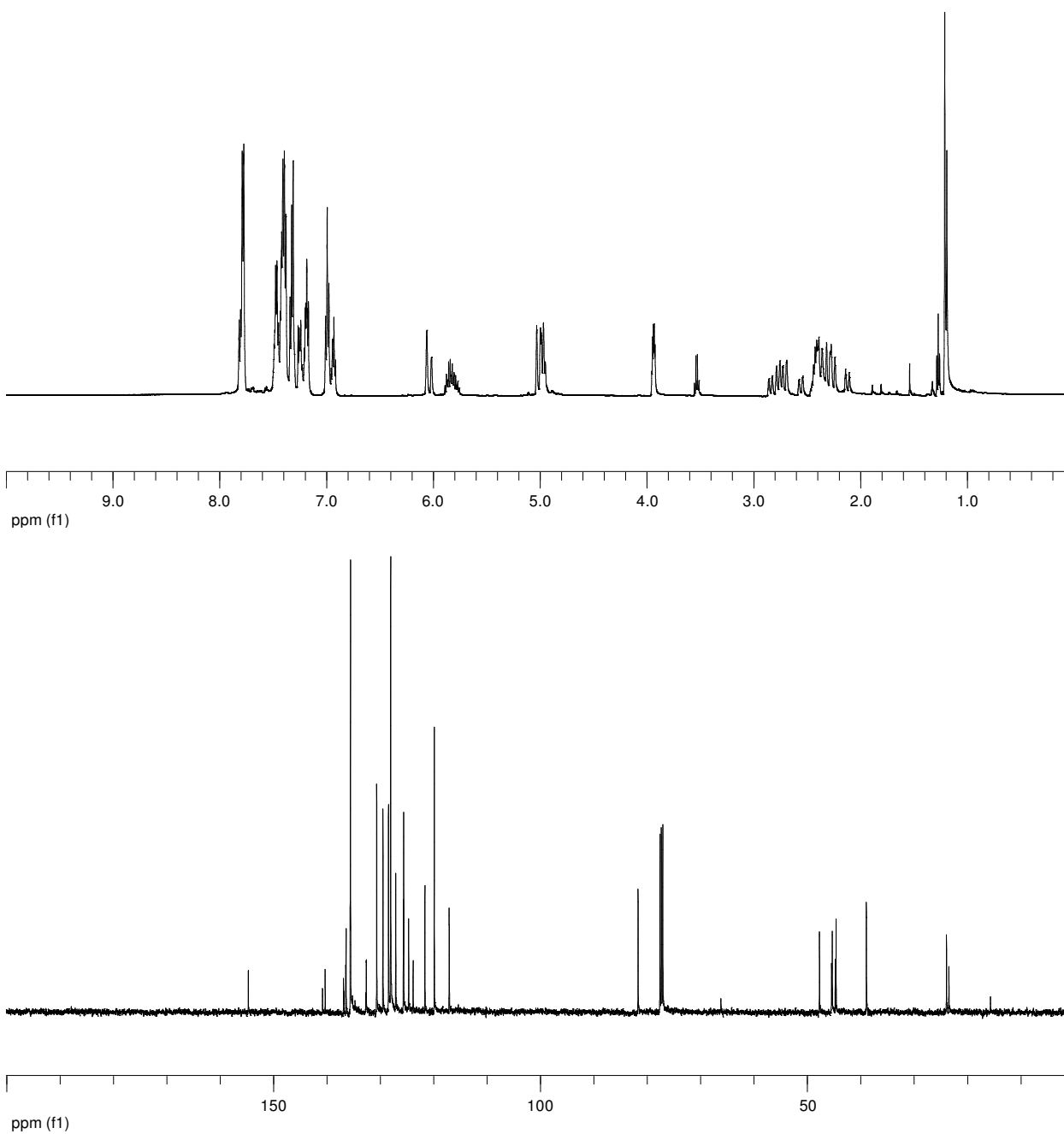


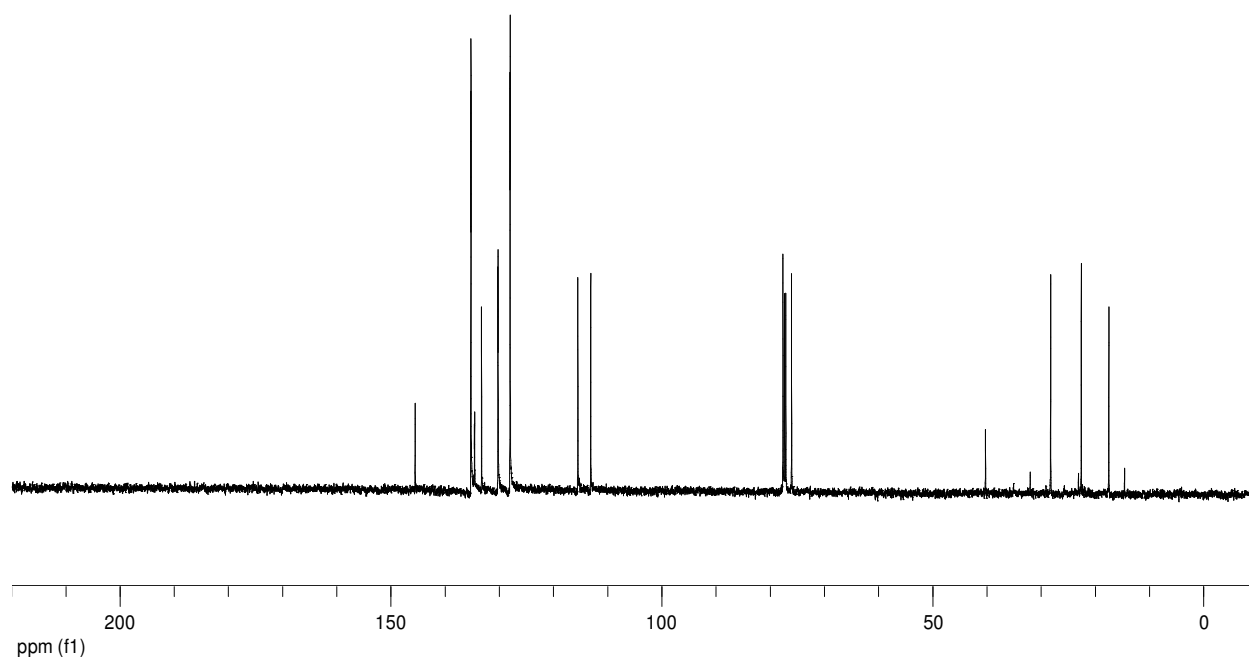
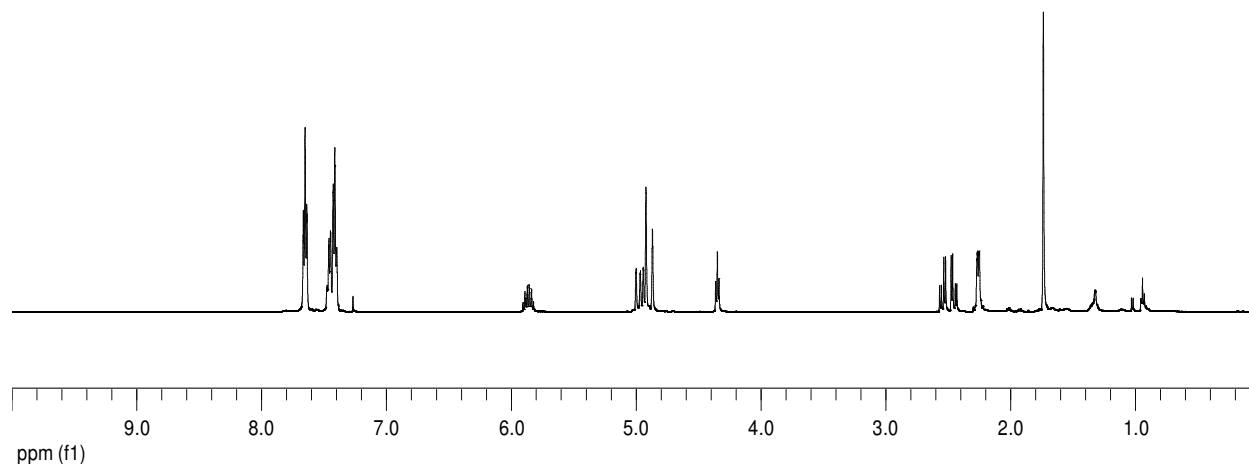
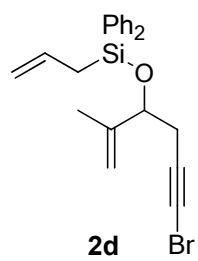


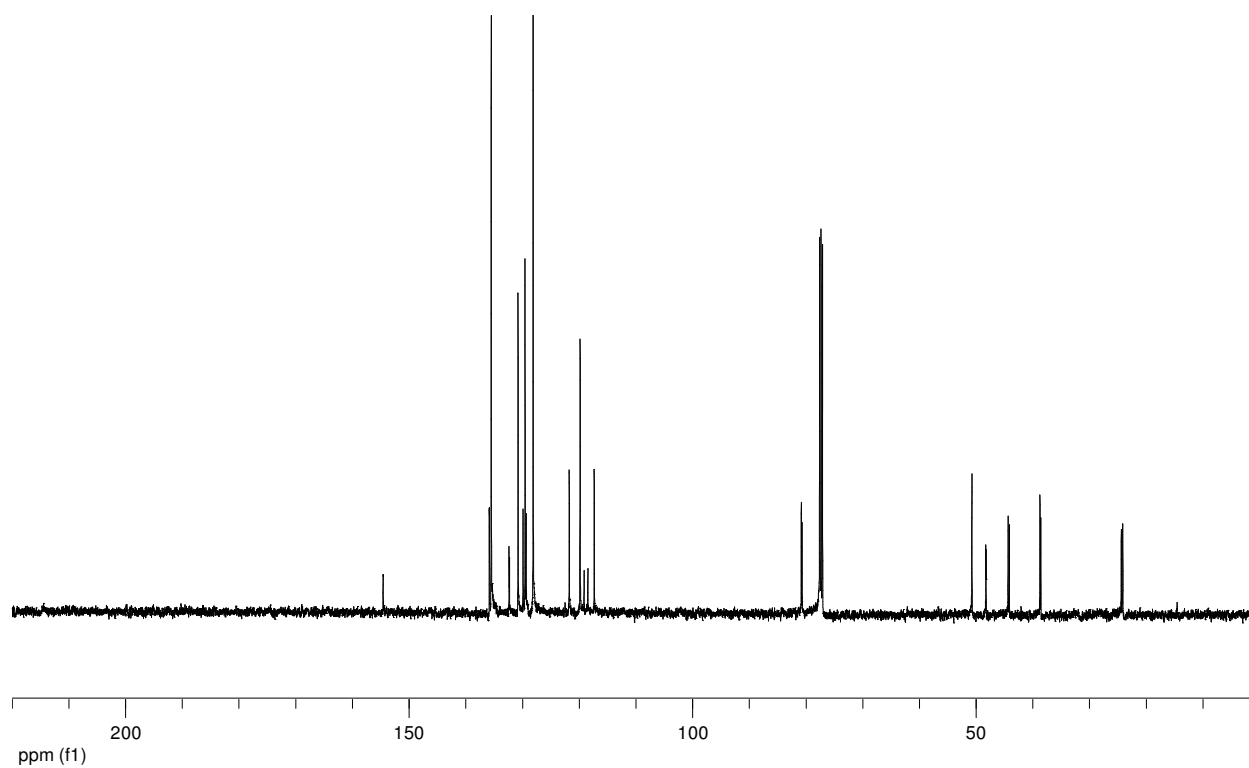
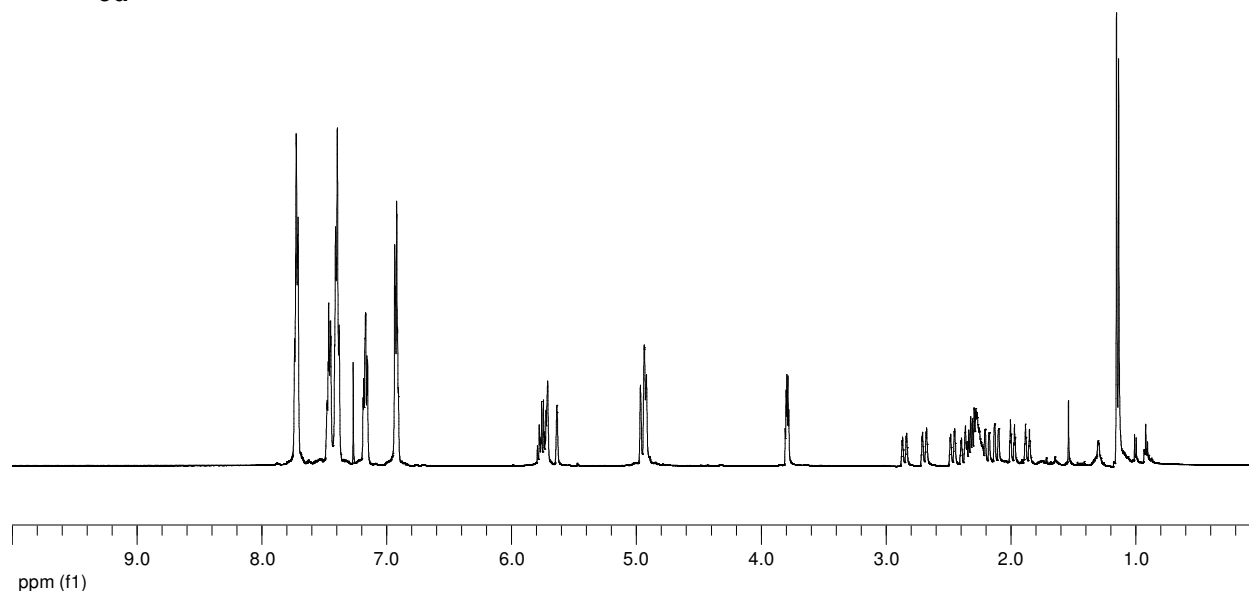
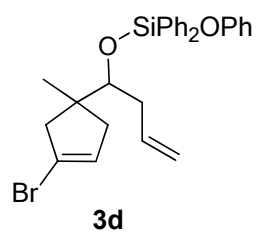
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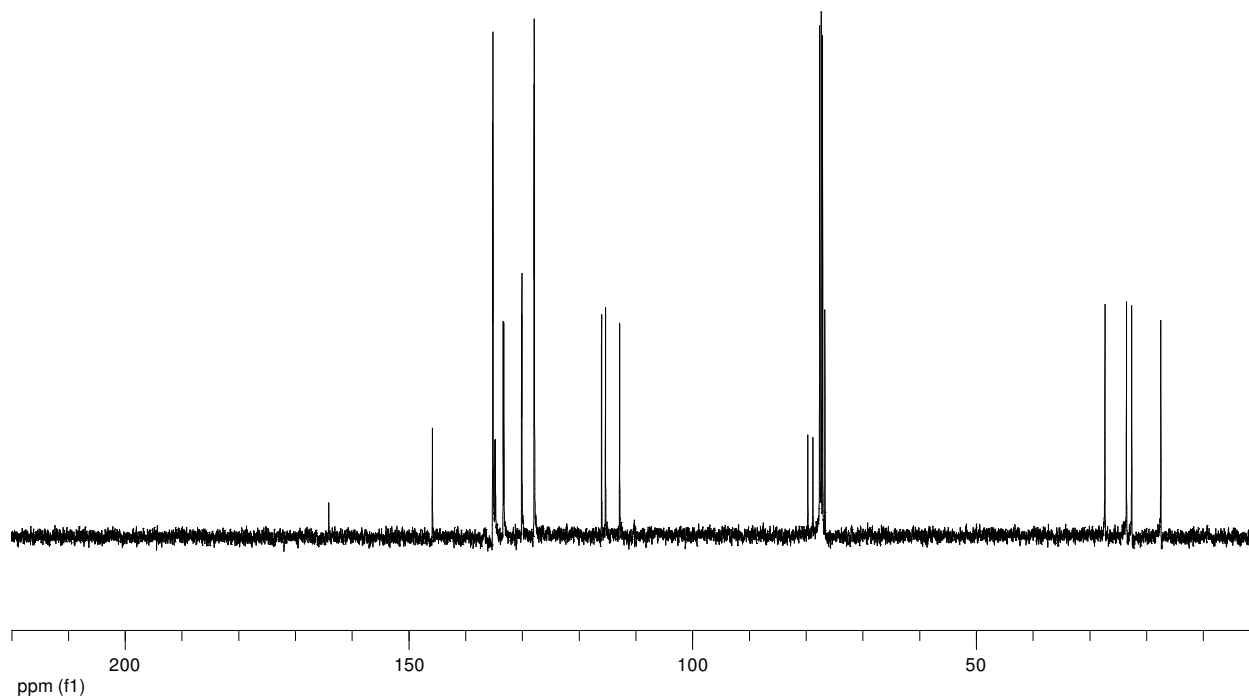
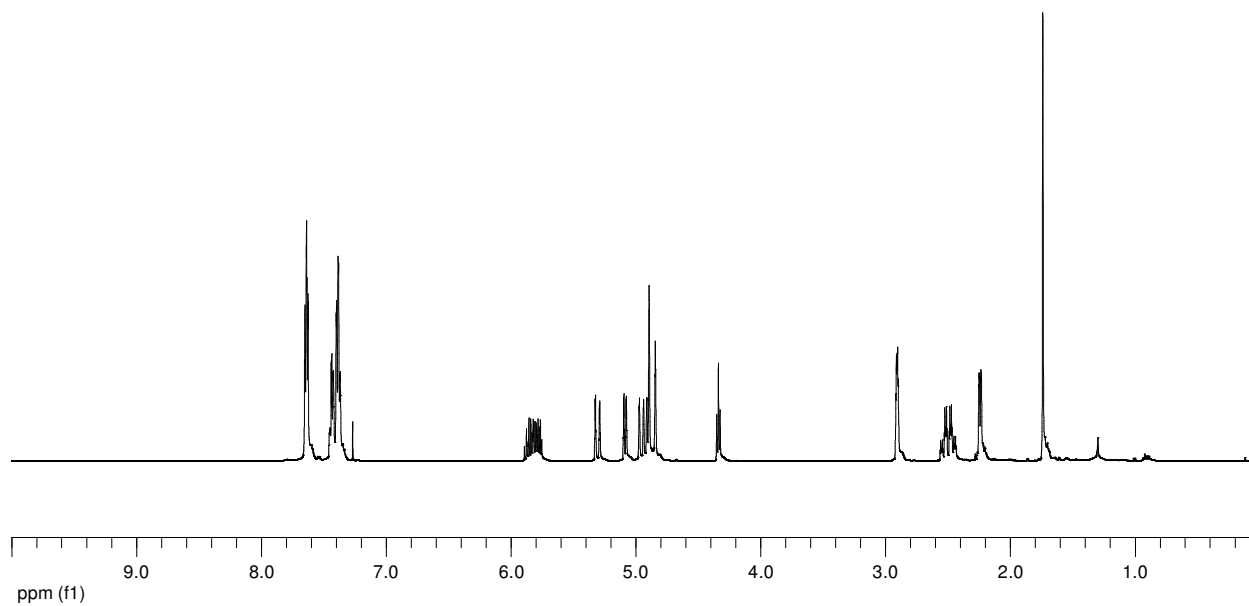
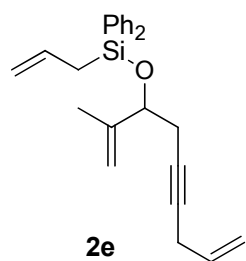


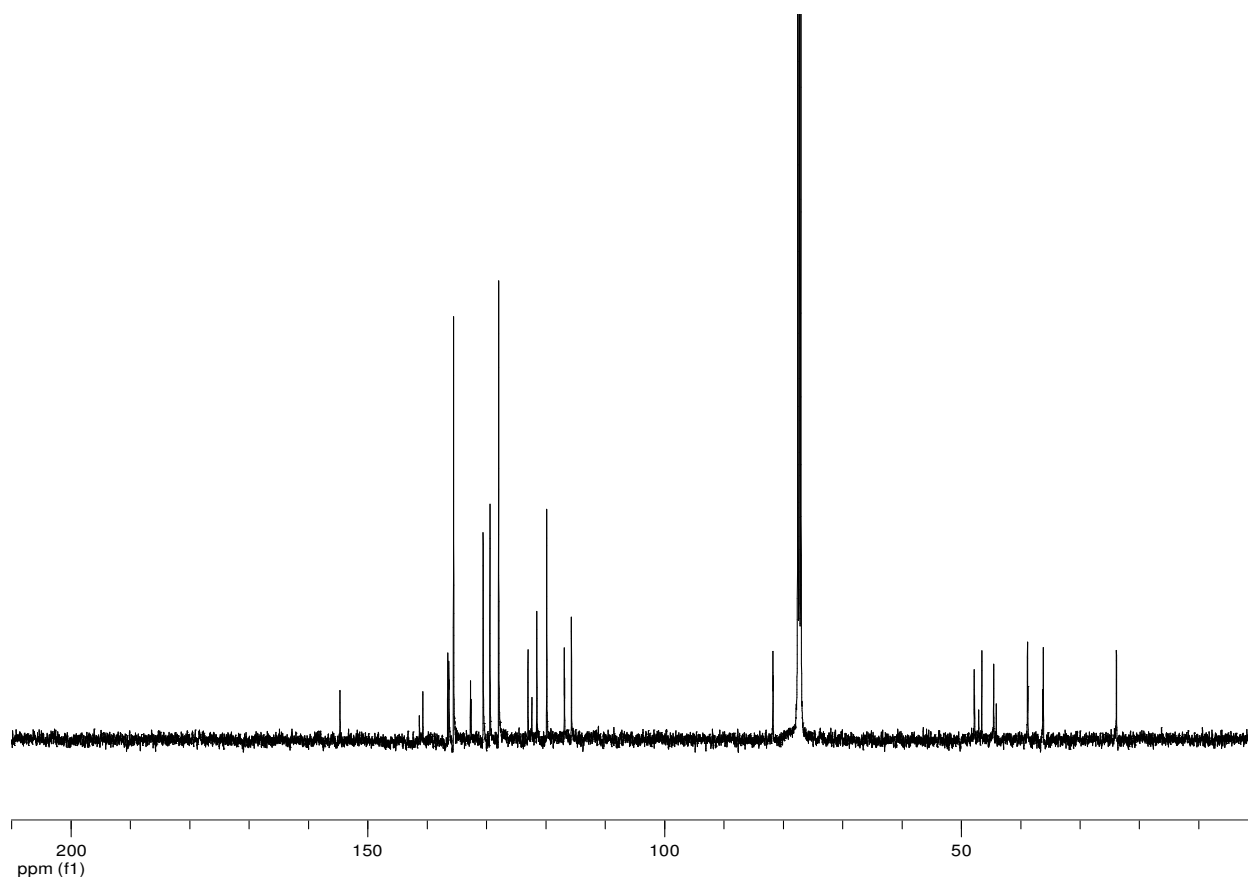
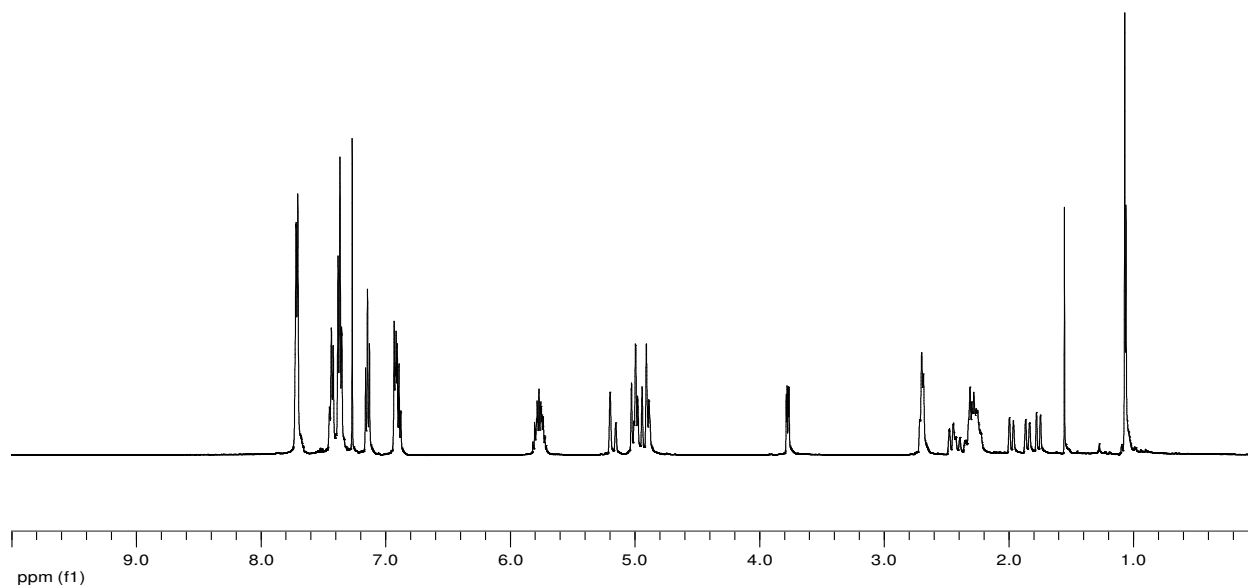
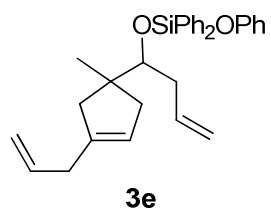


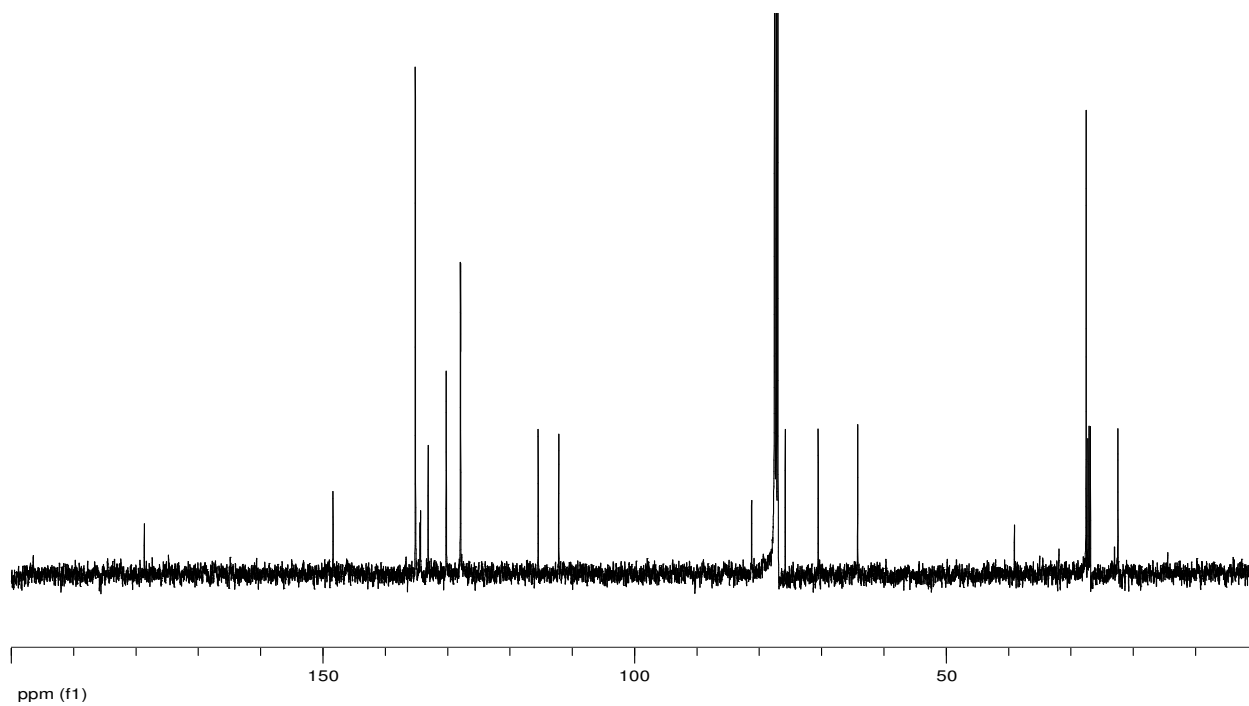
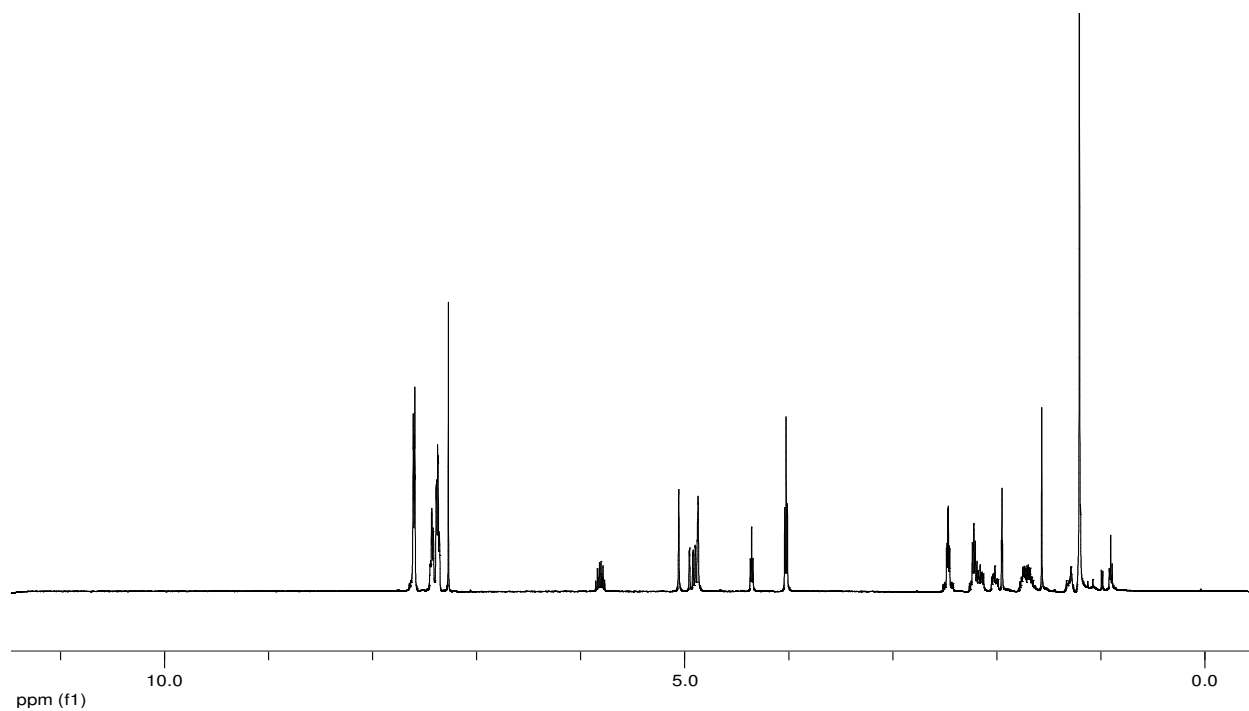
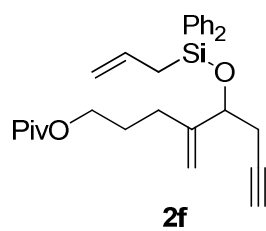


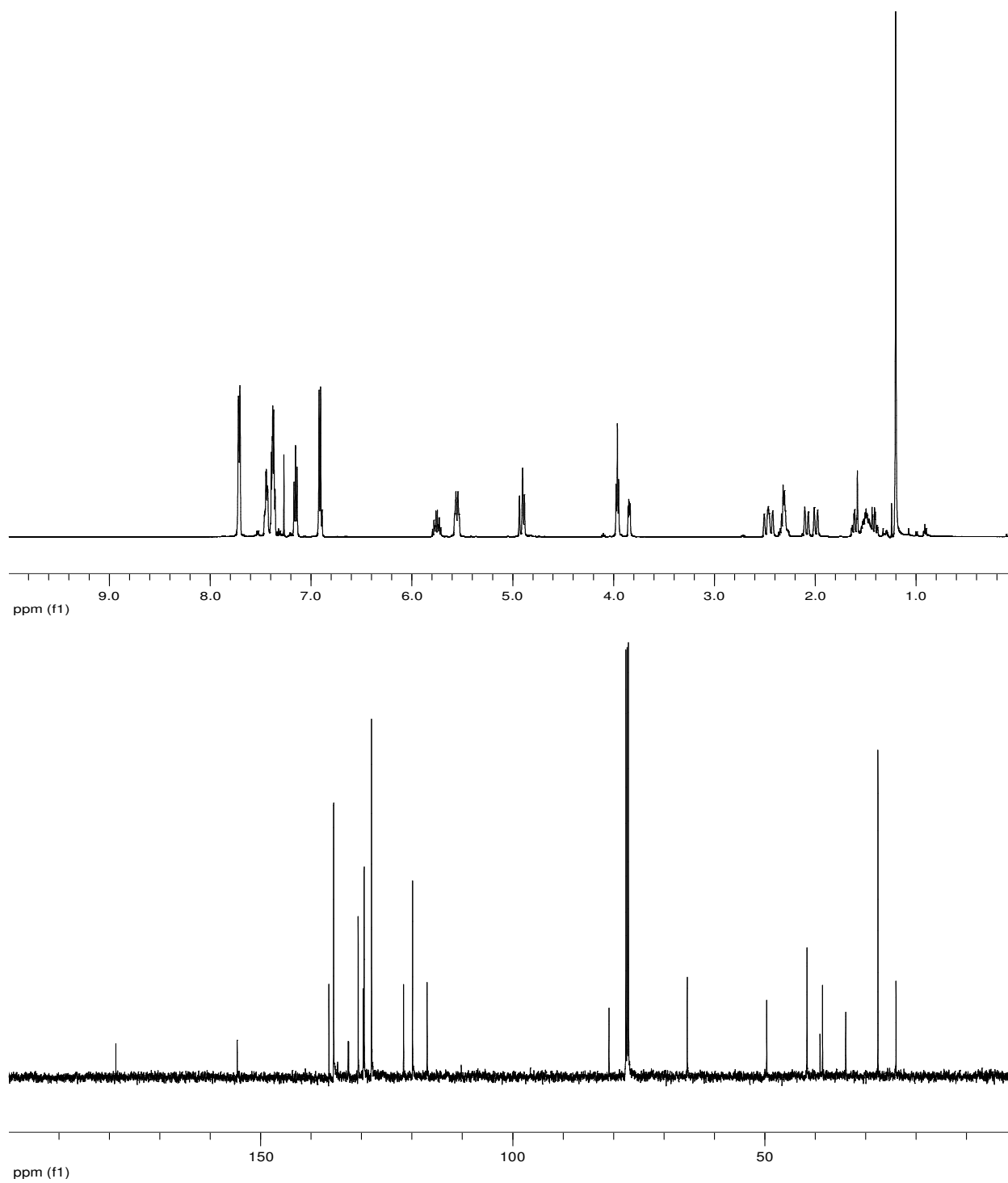


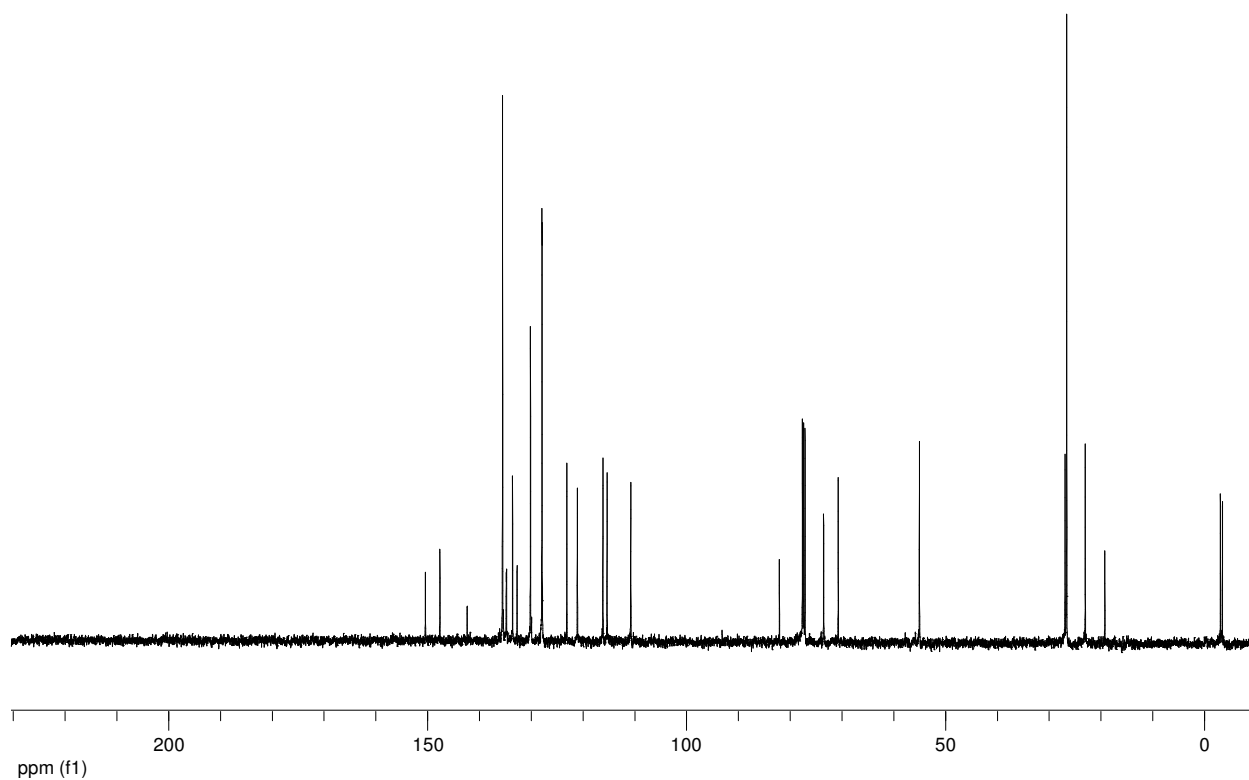
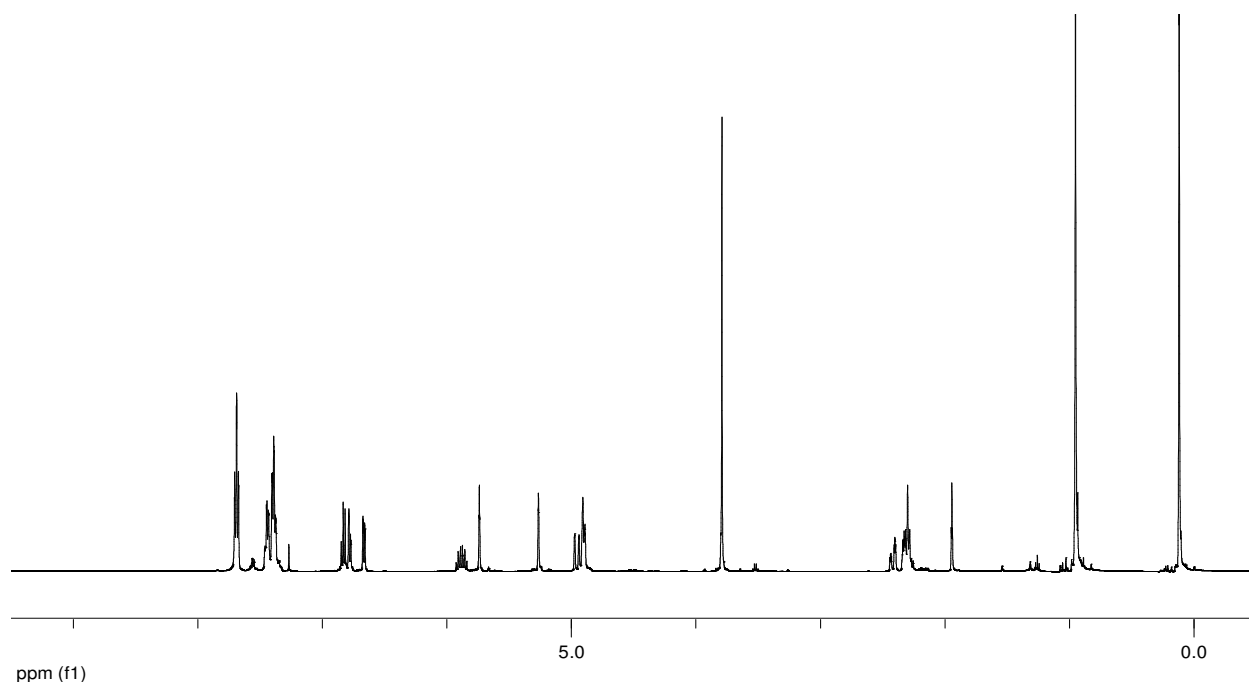
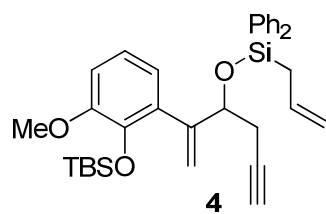


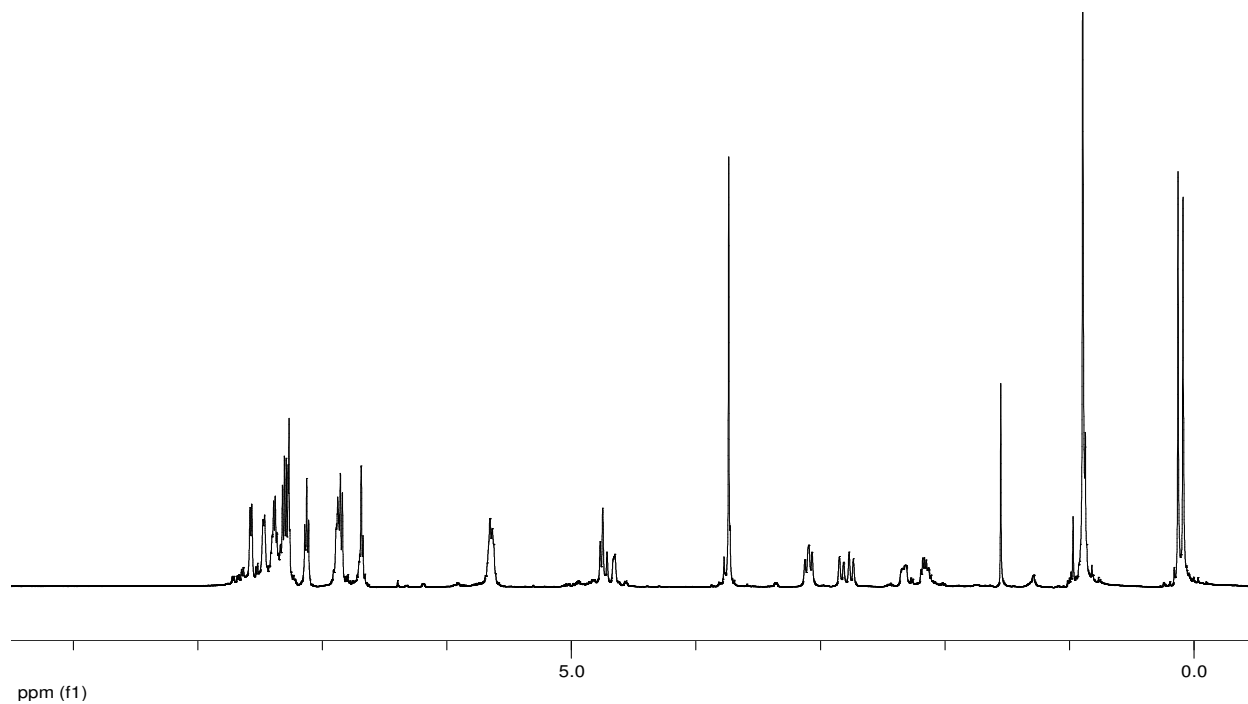


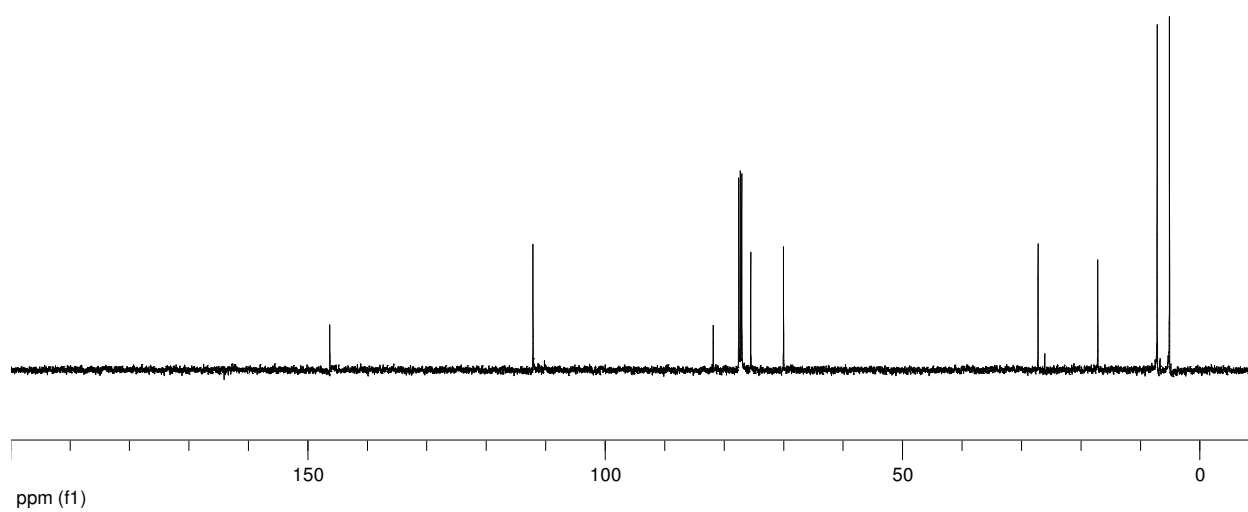
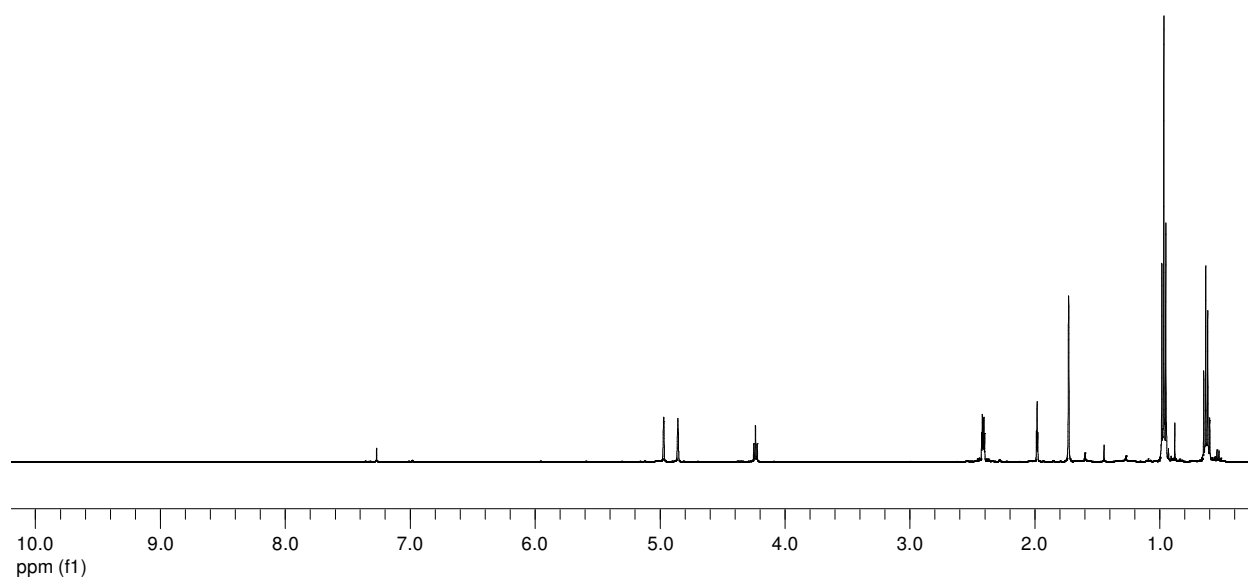
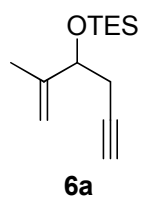


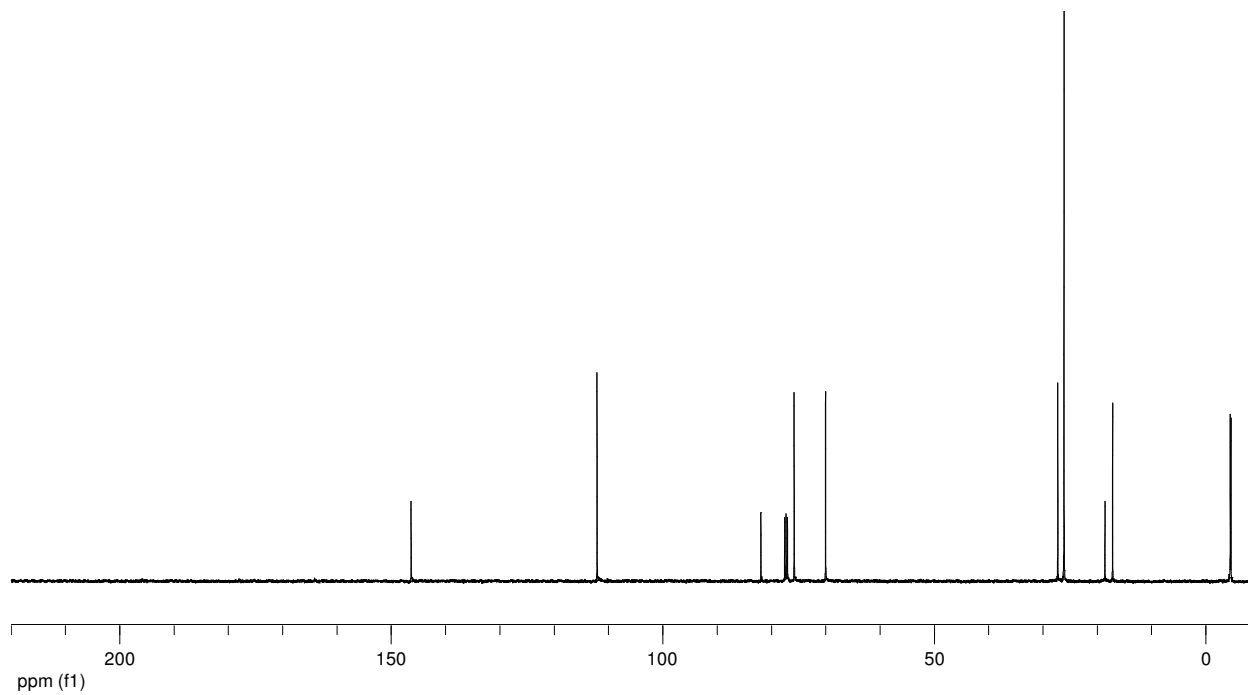
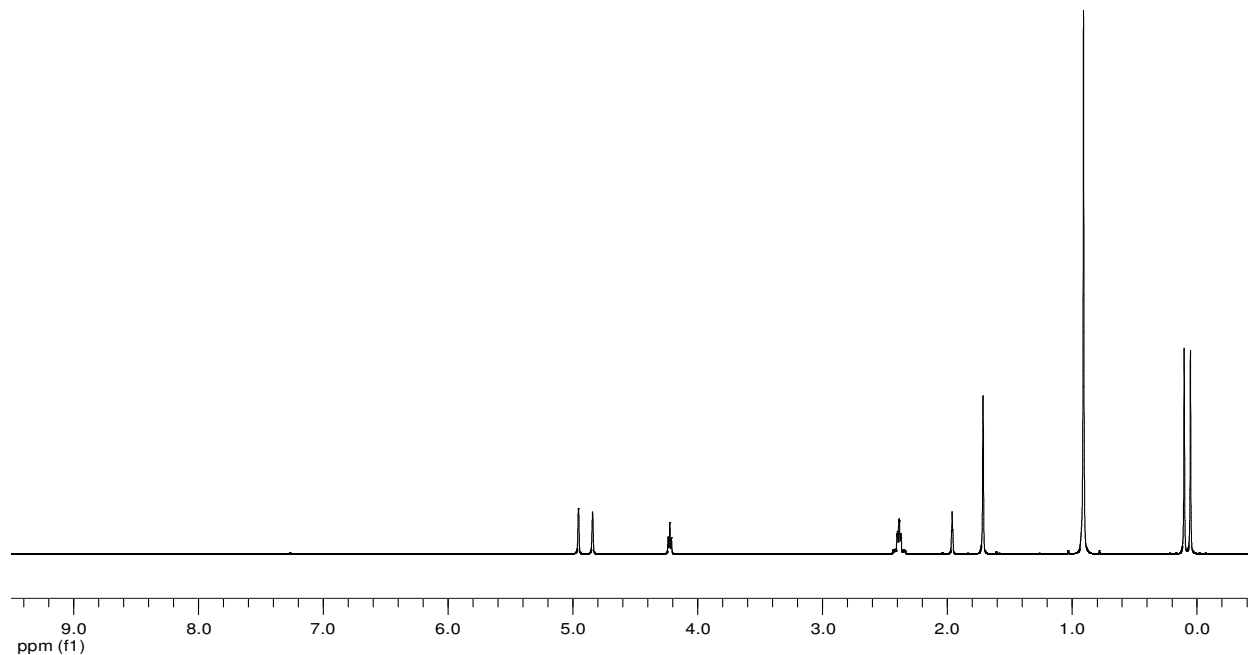
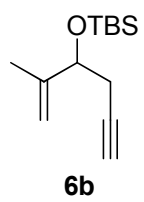


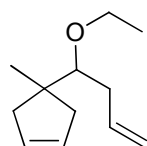




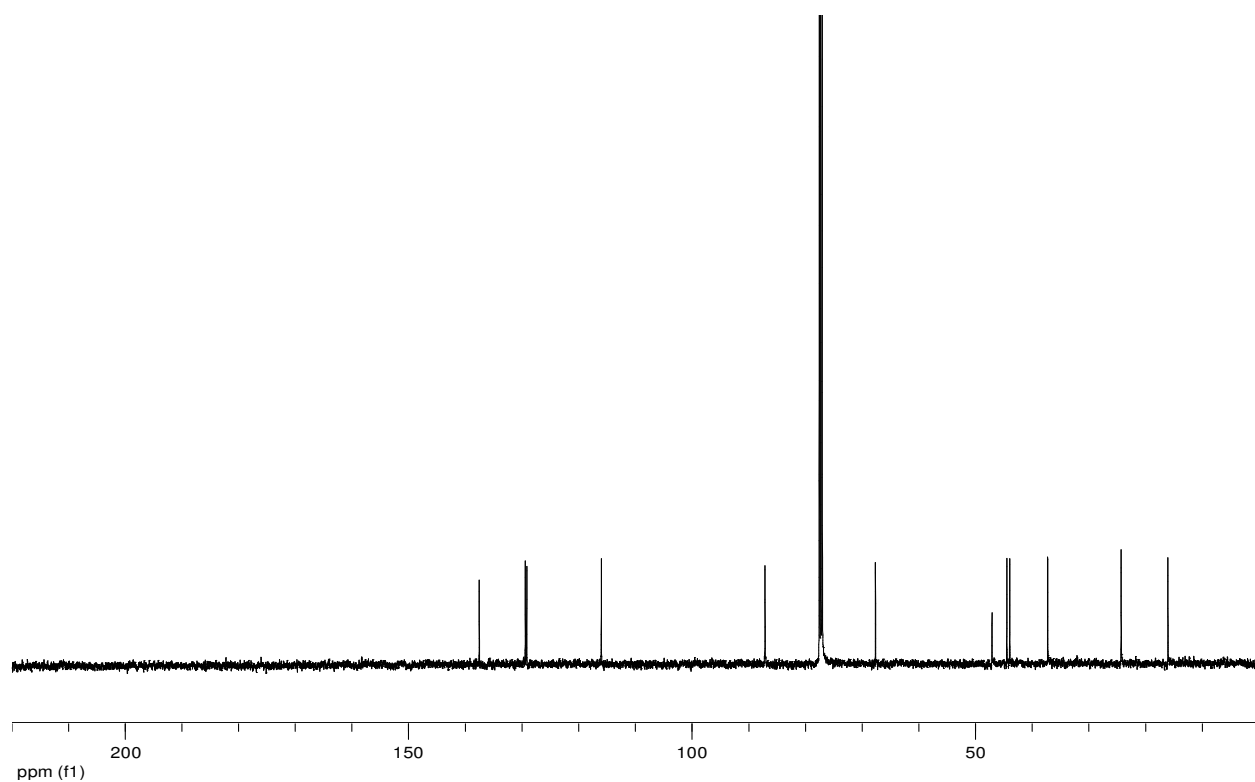
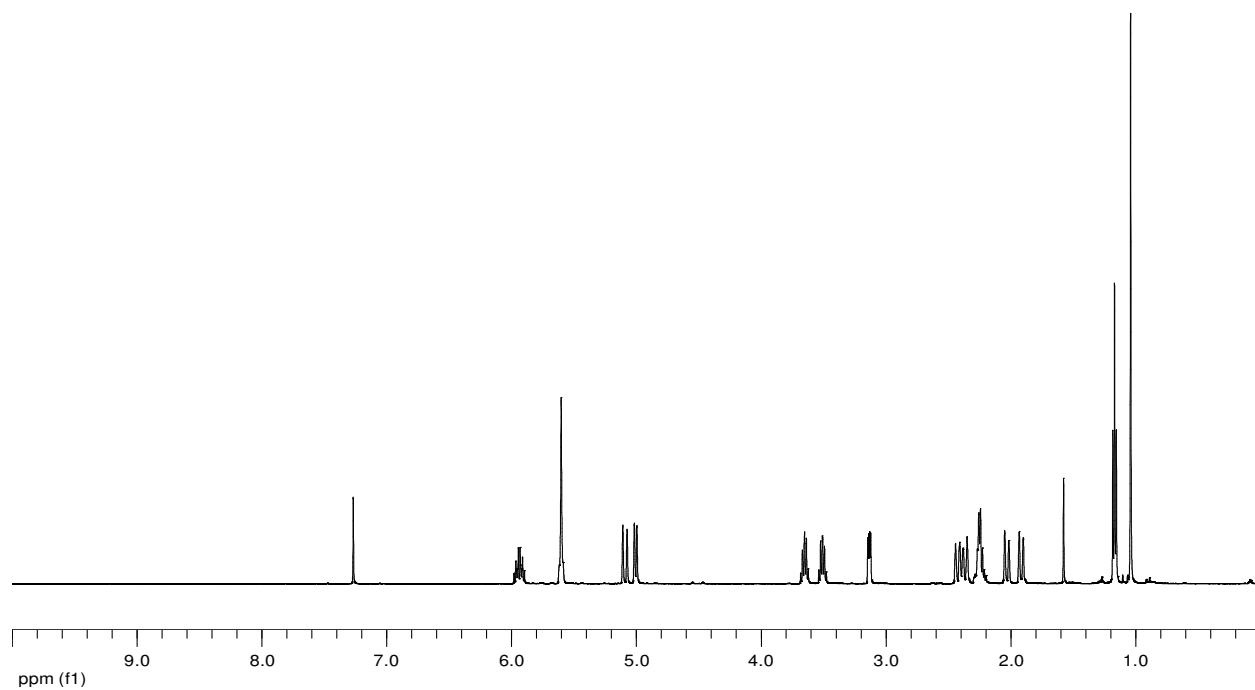


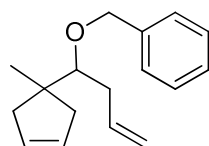




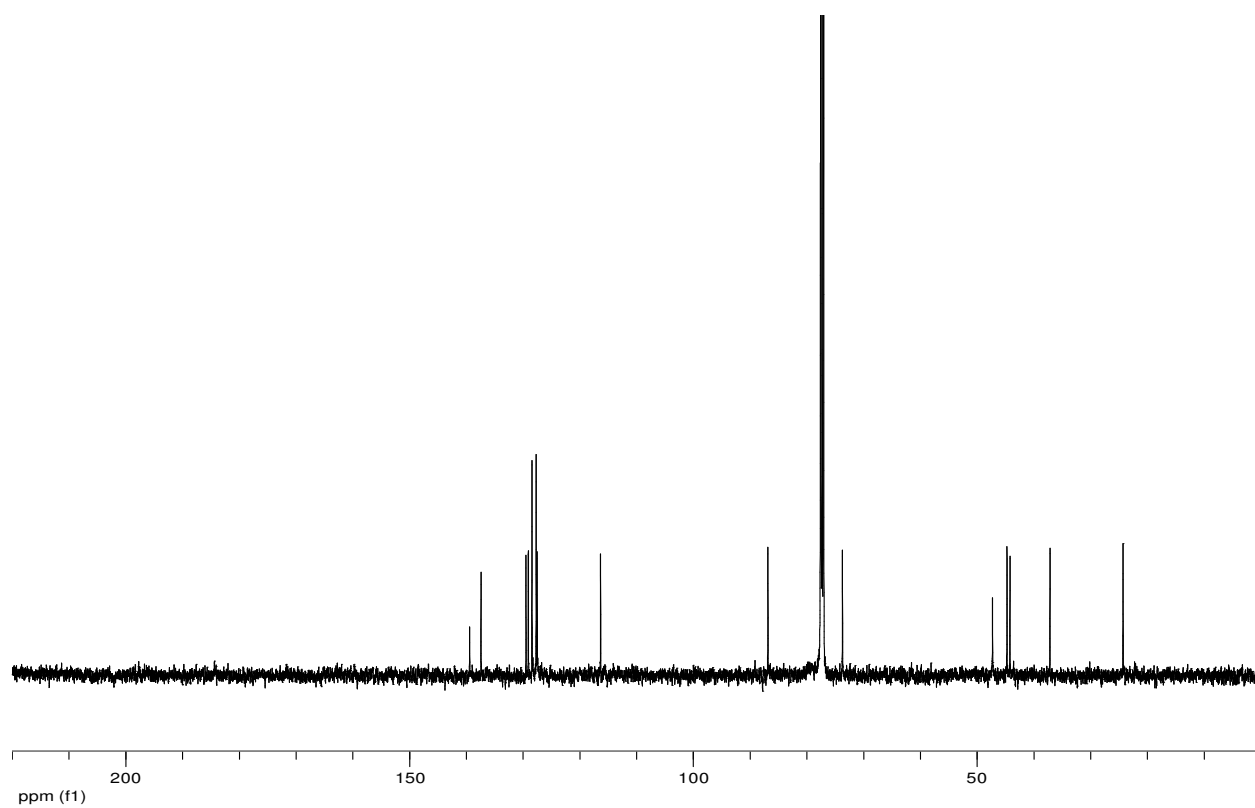
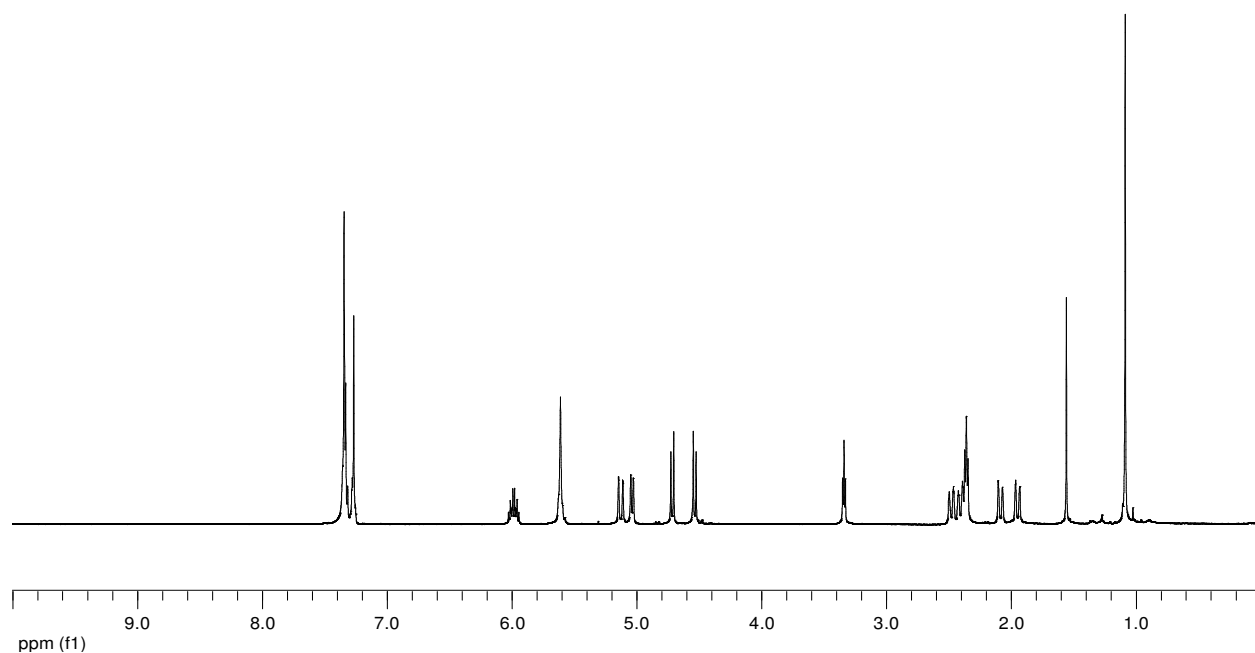


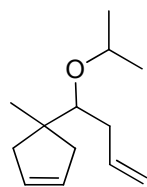
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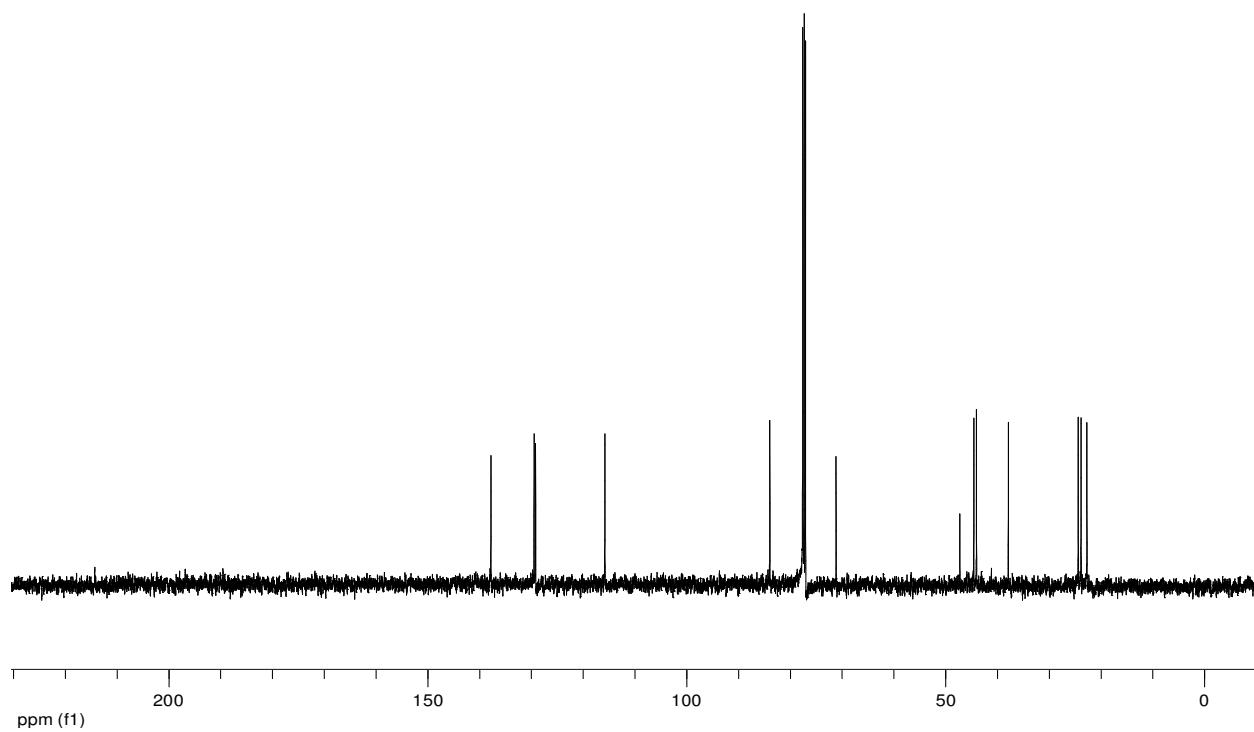
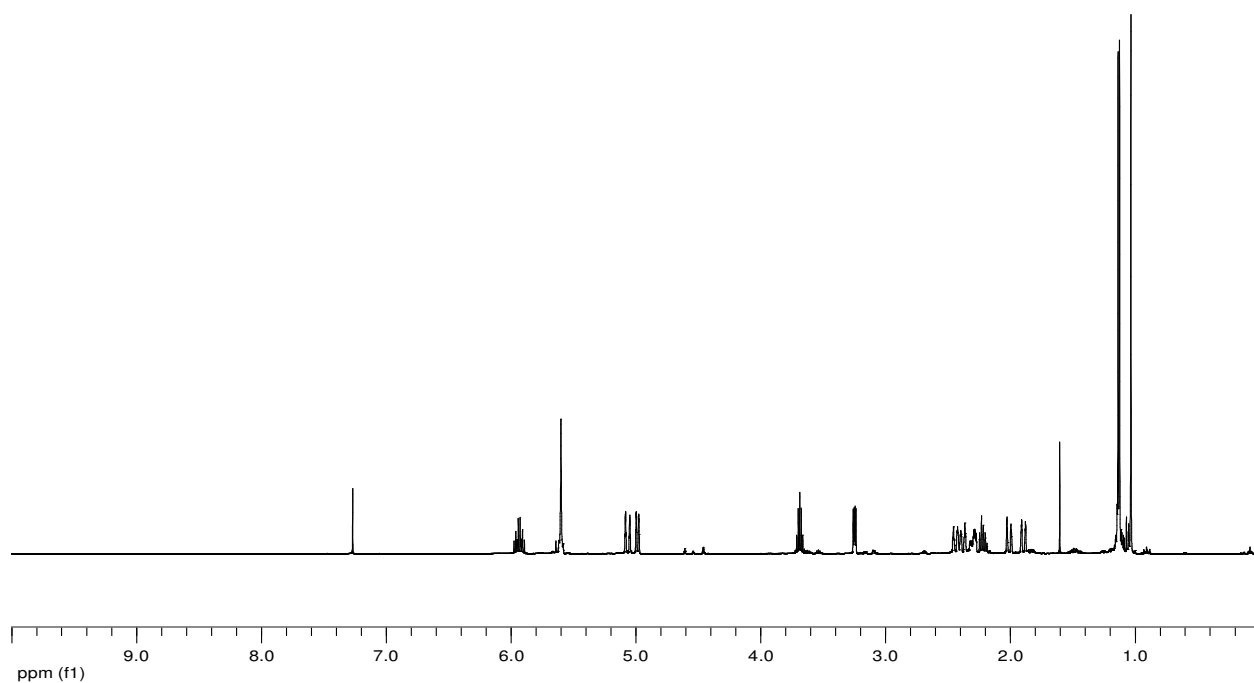


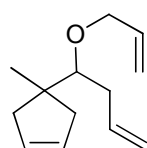
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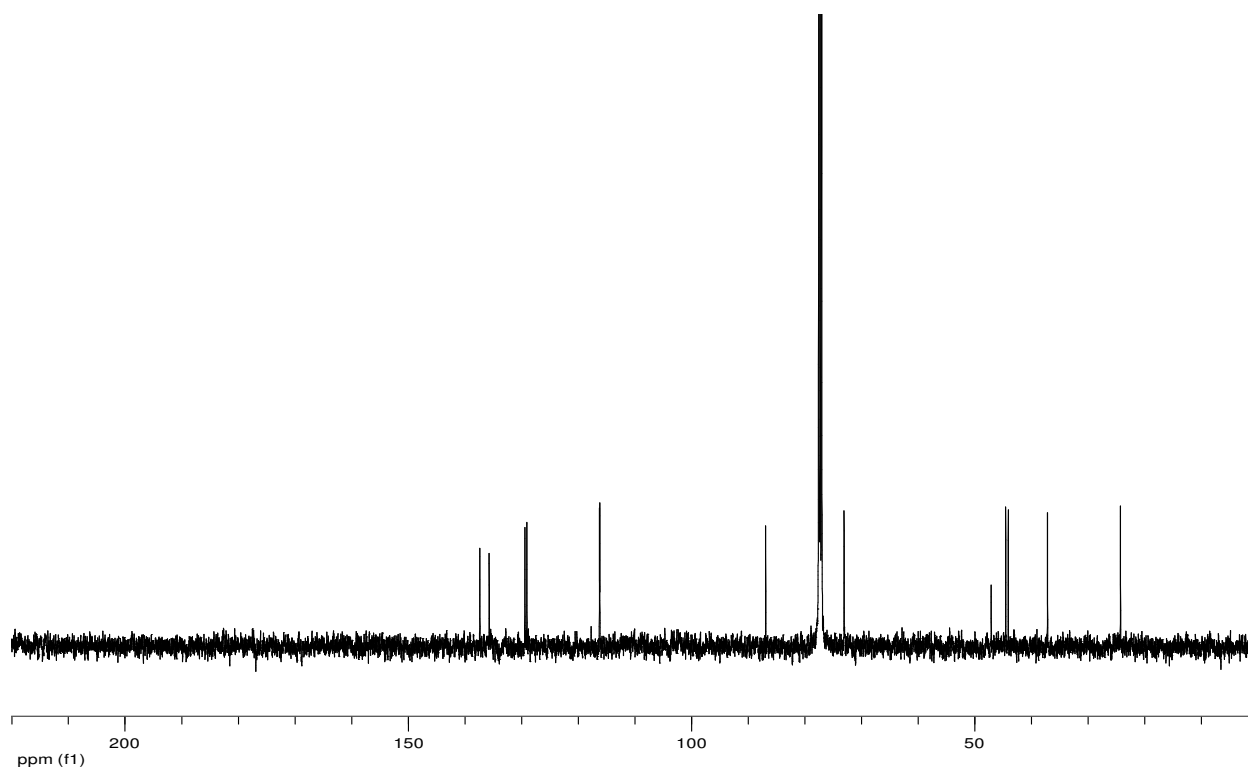
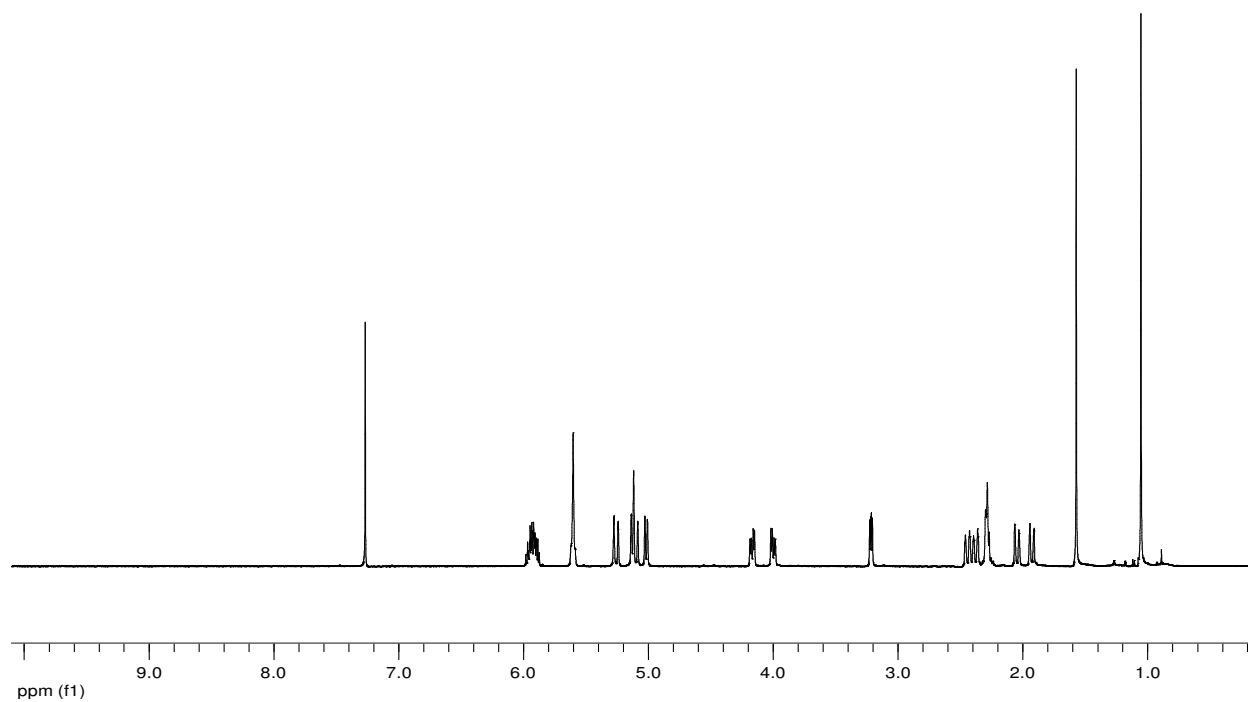


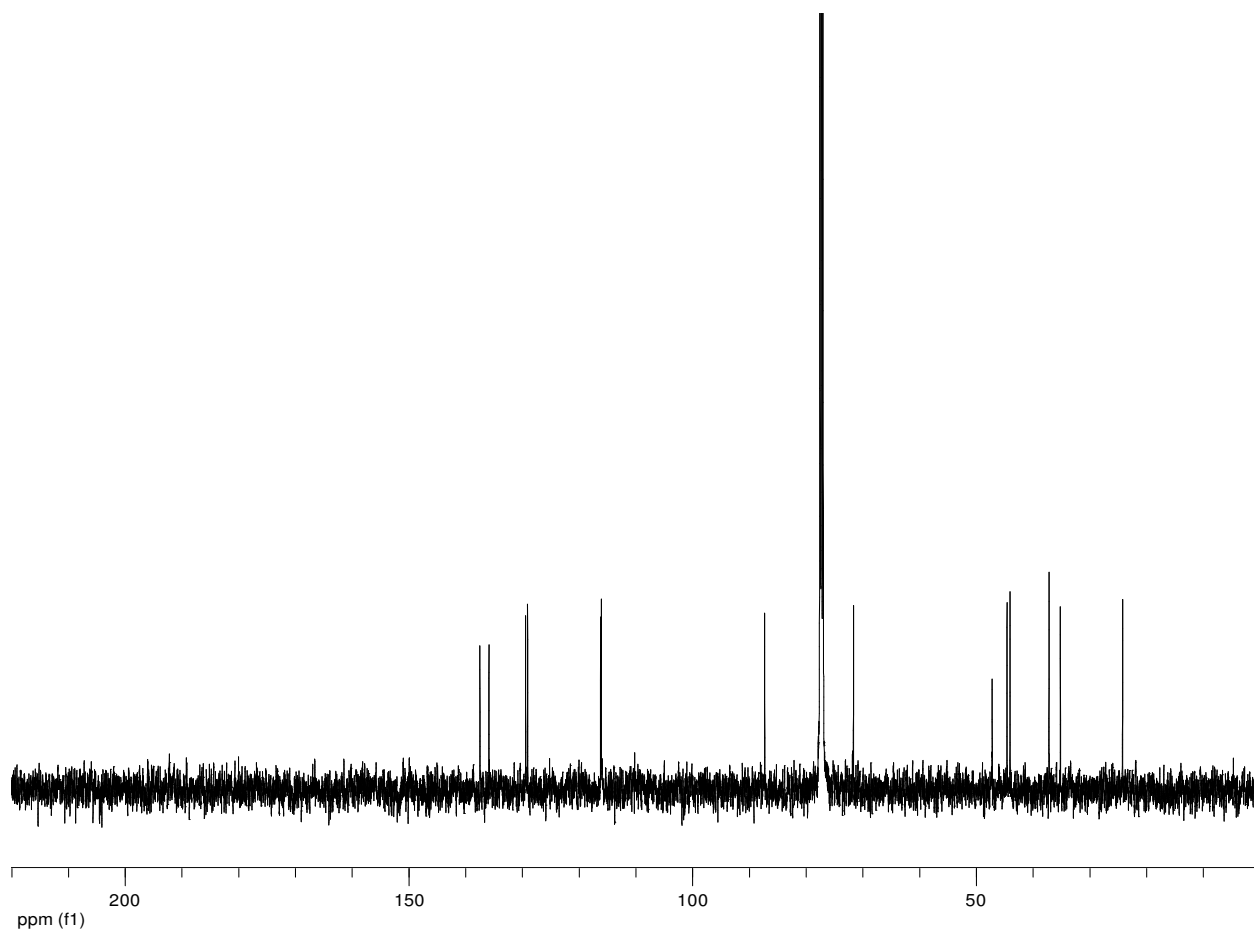
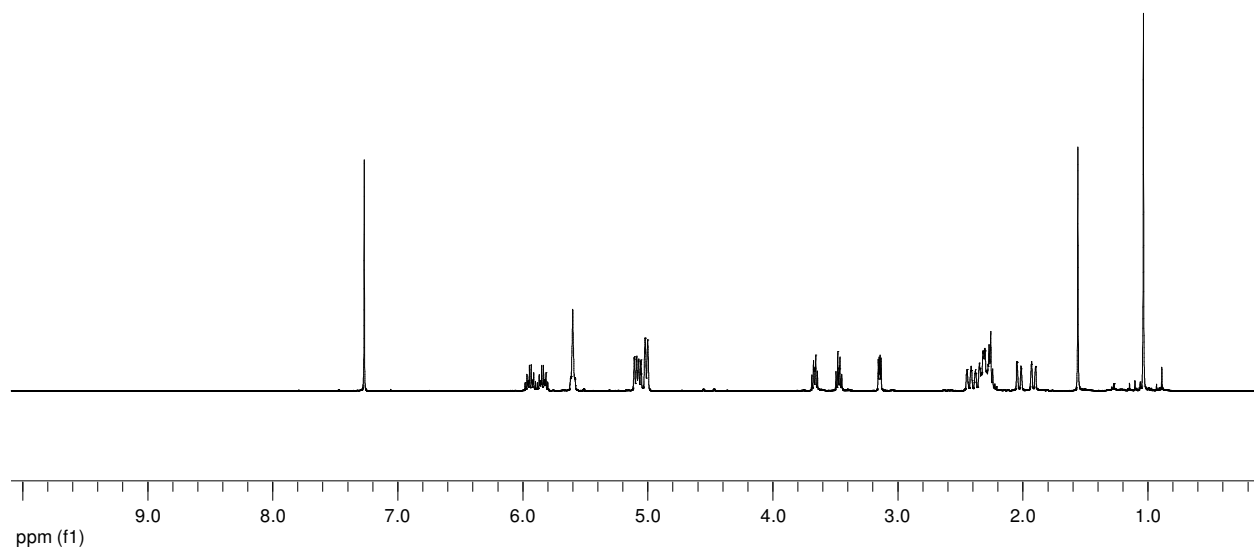
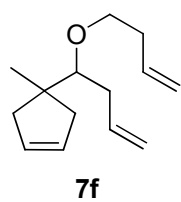
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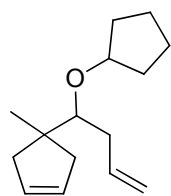




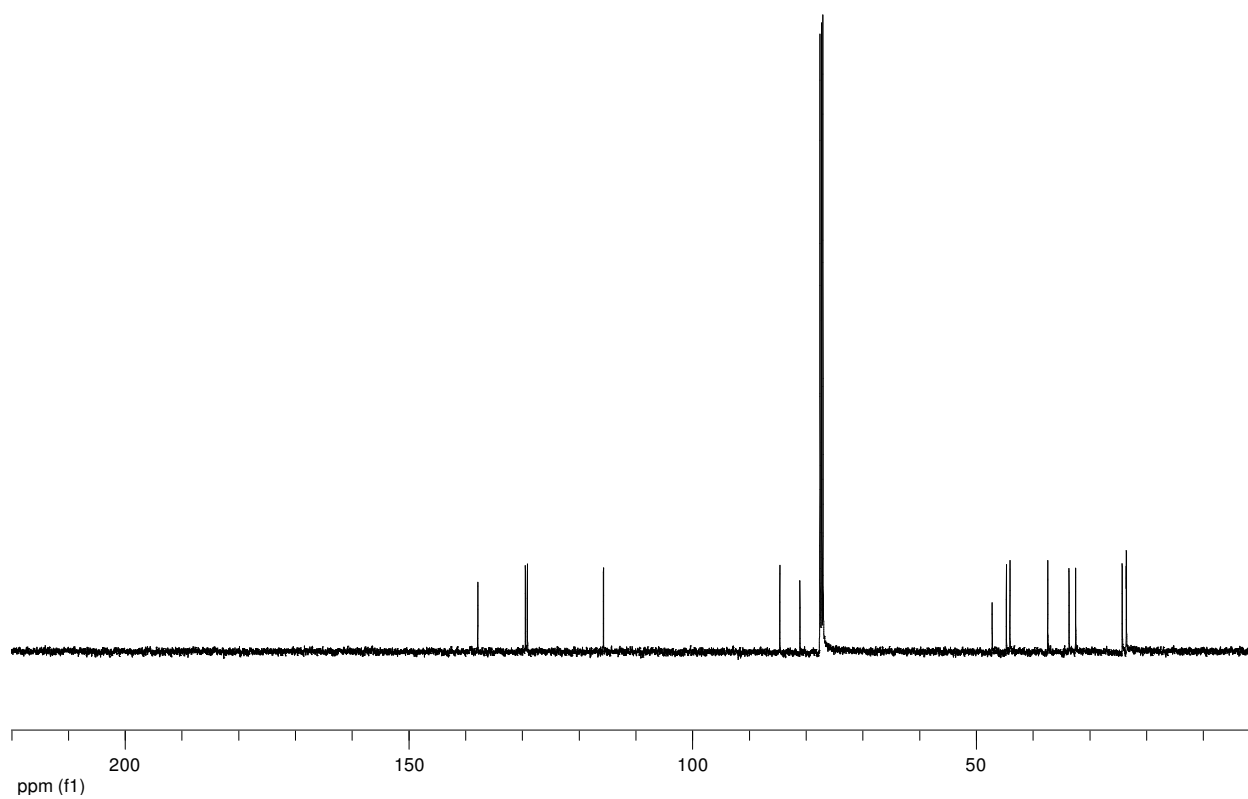
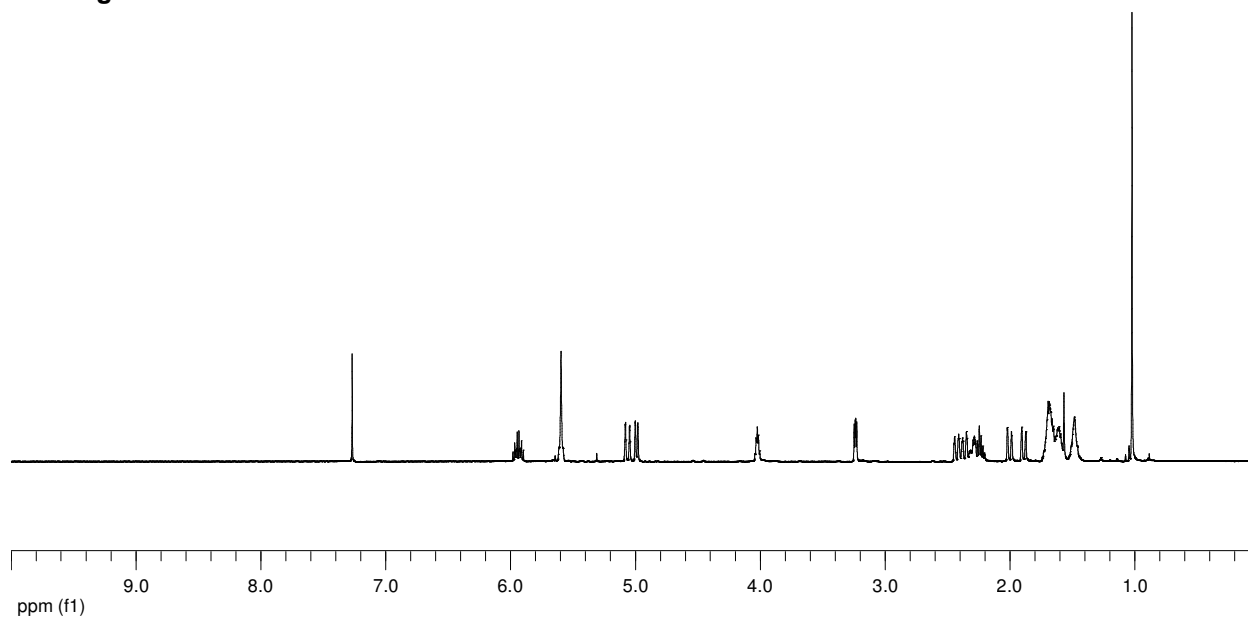
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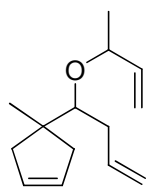




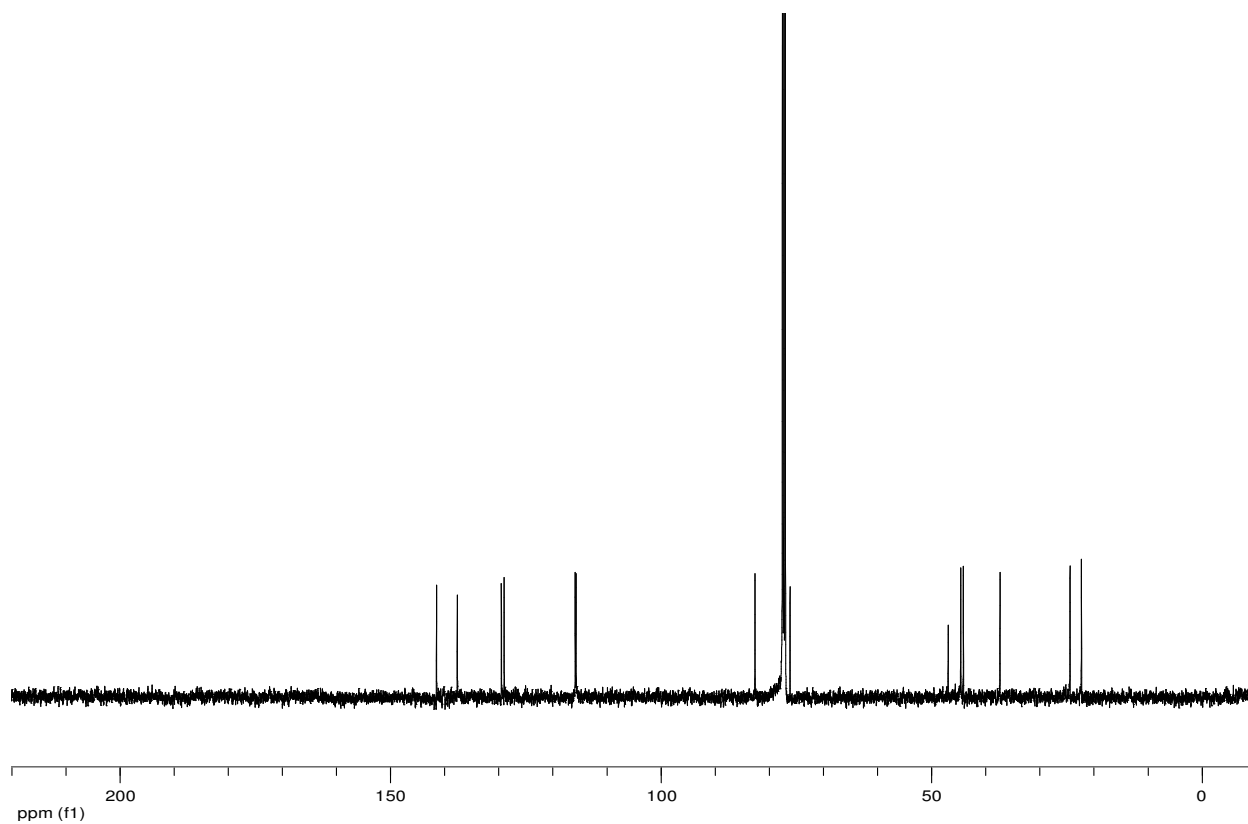
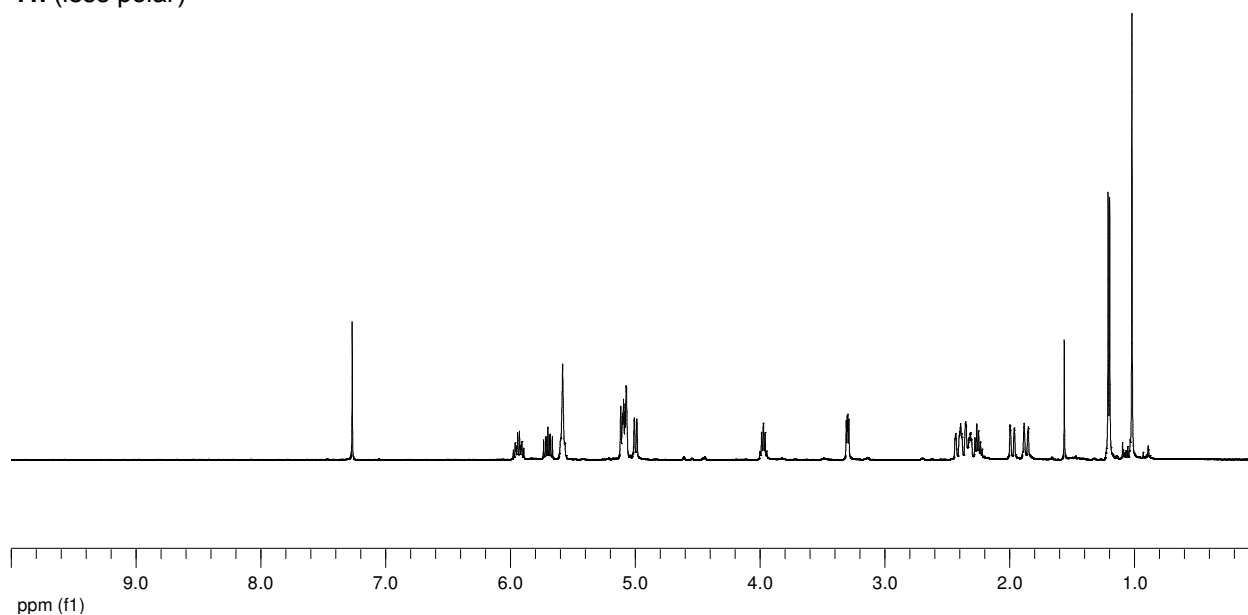


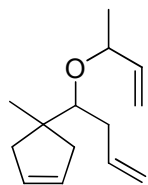
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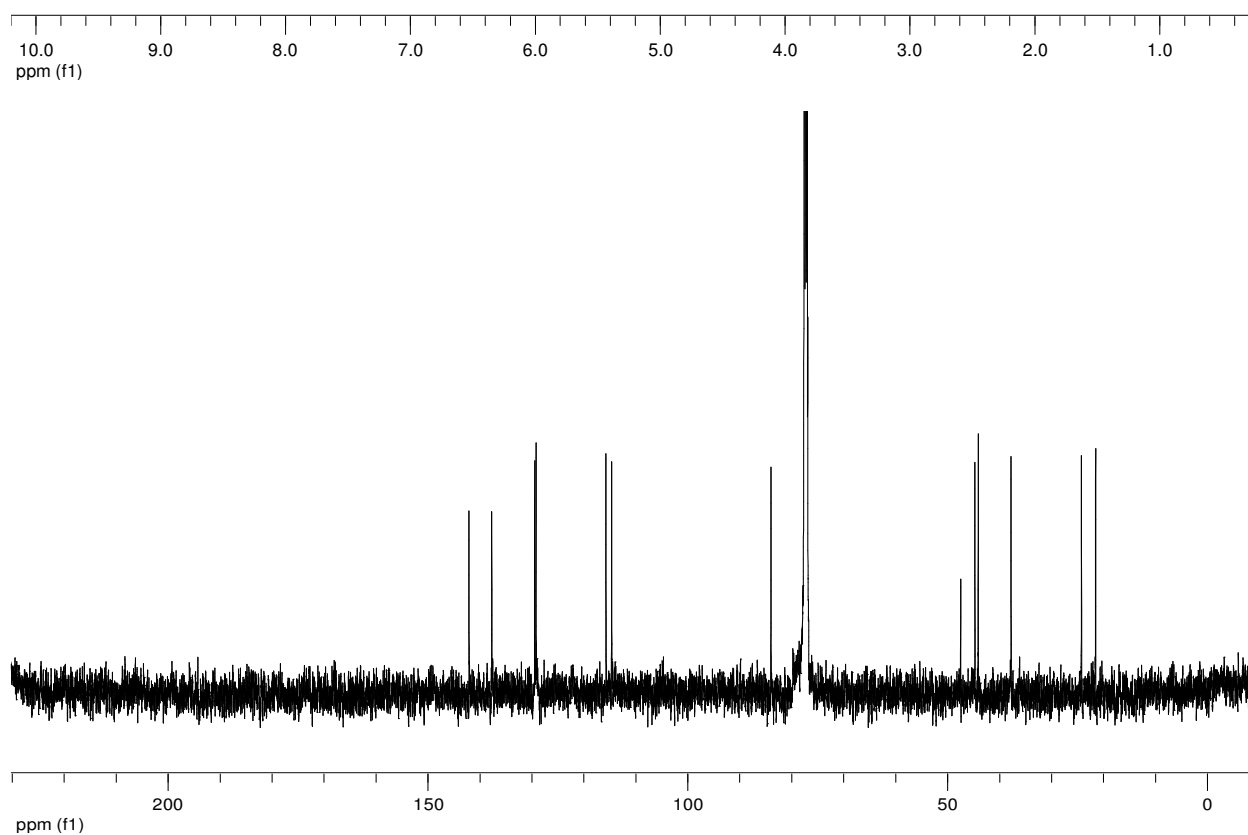
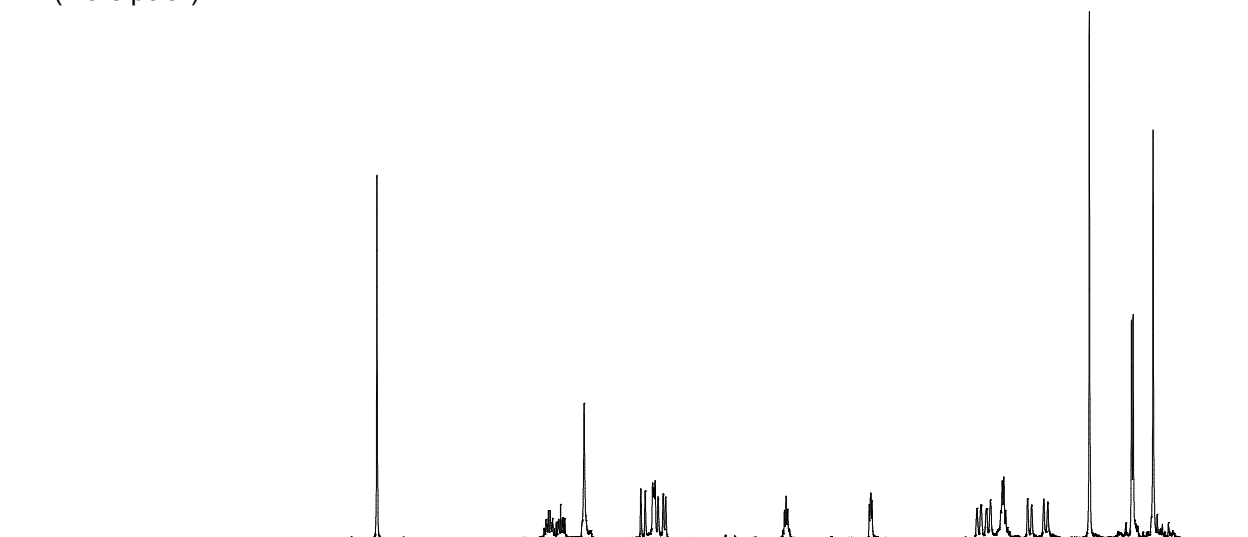


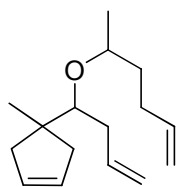
7h (less polar)



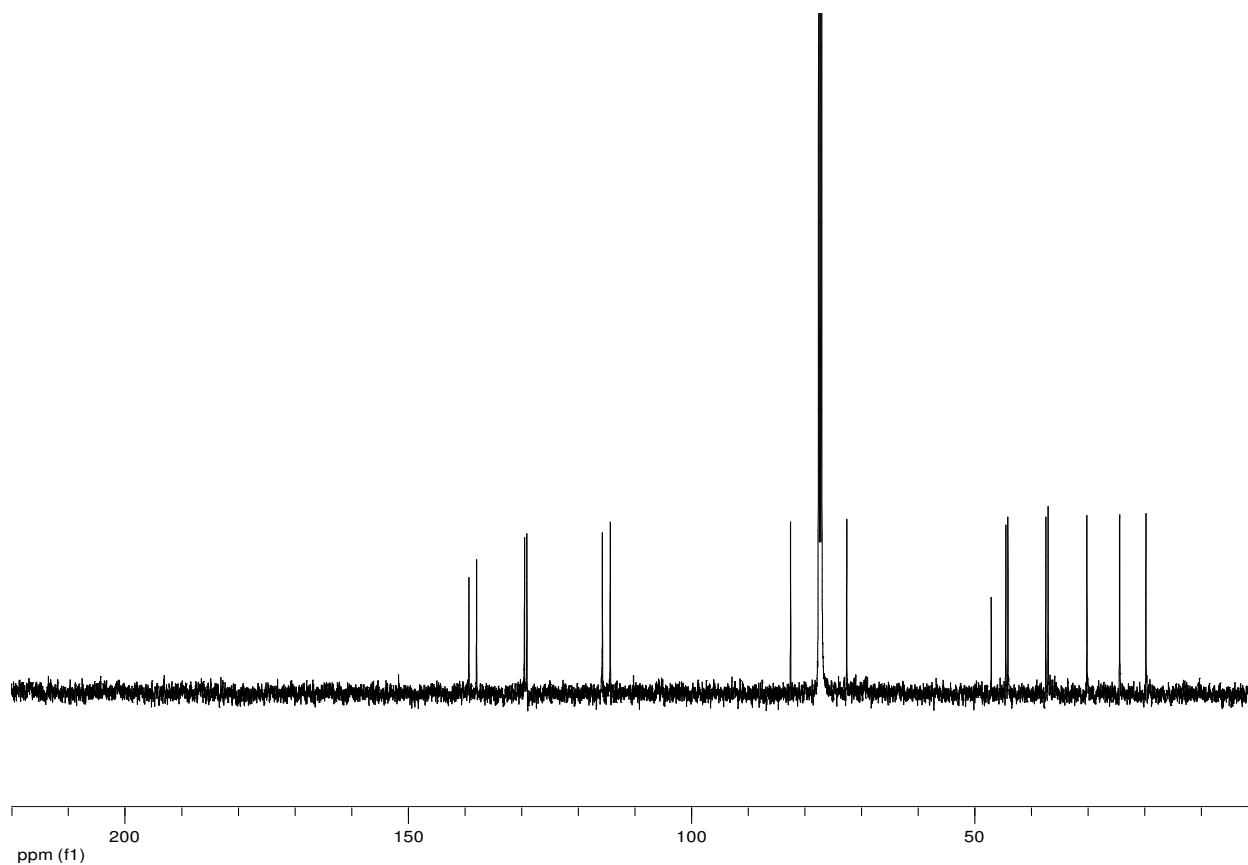
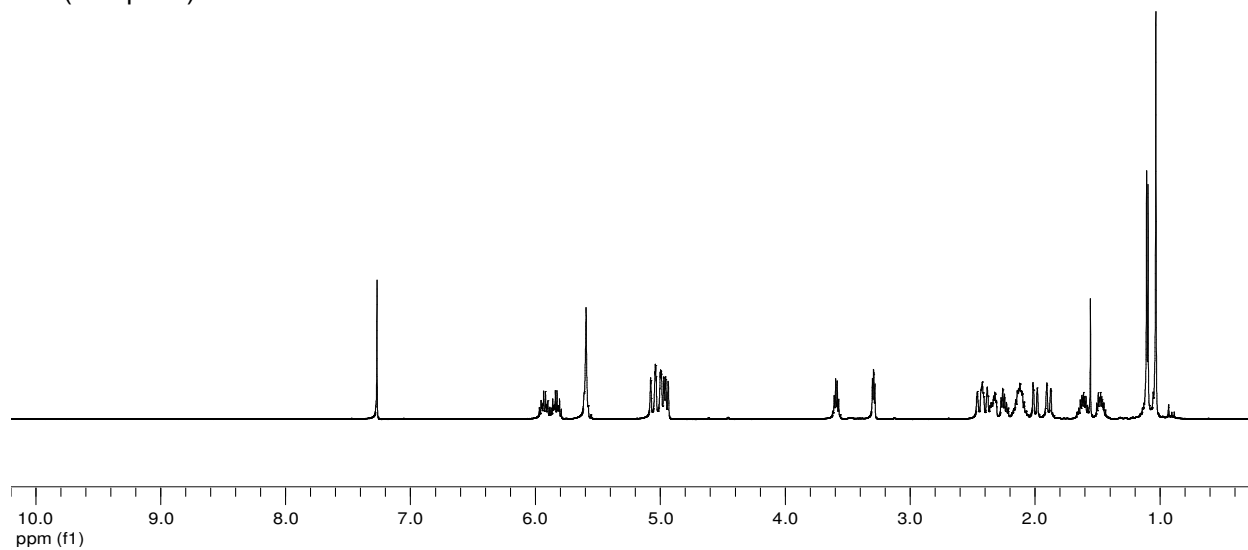


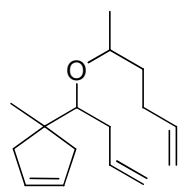
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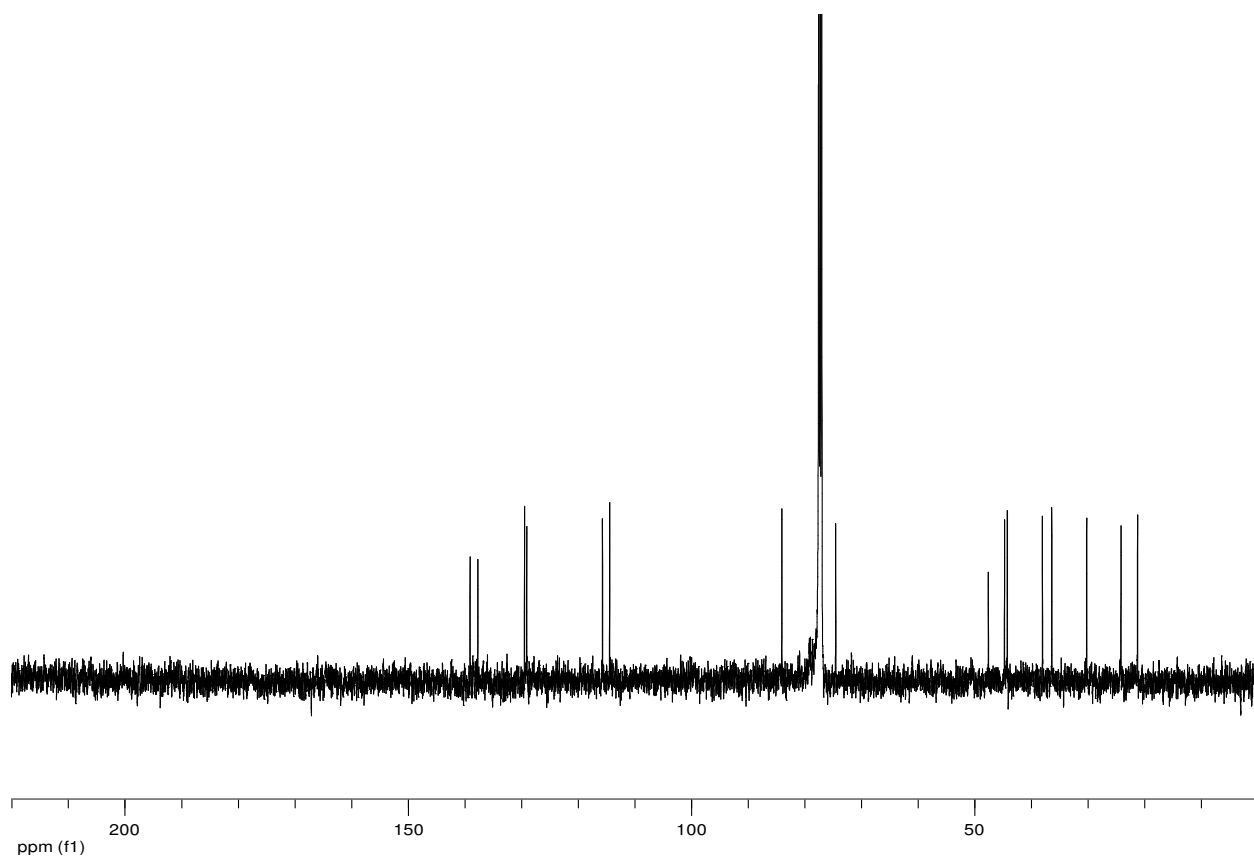
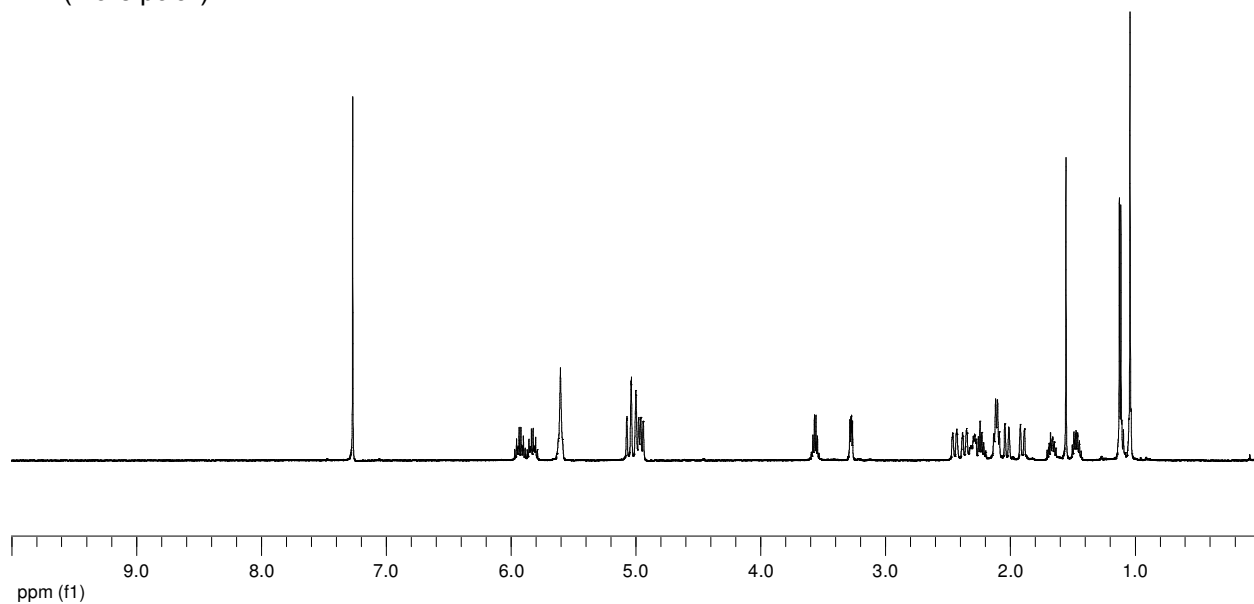


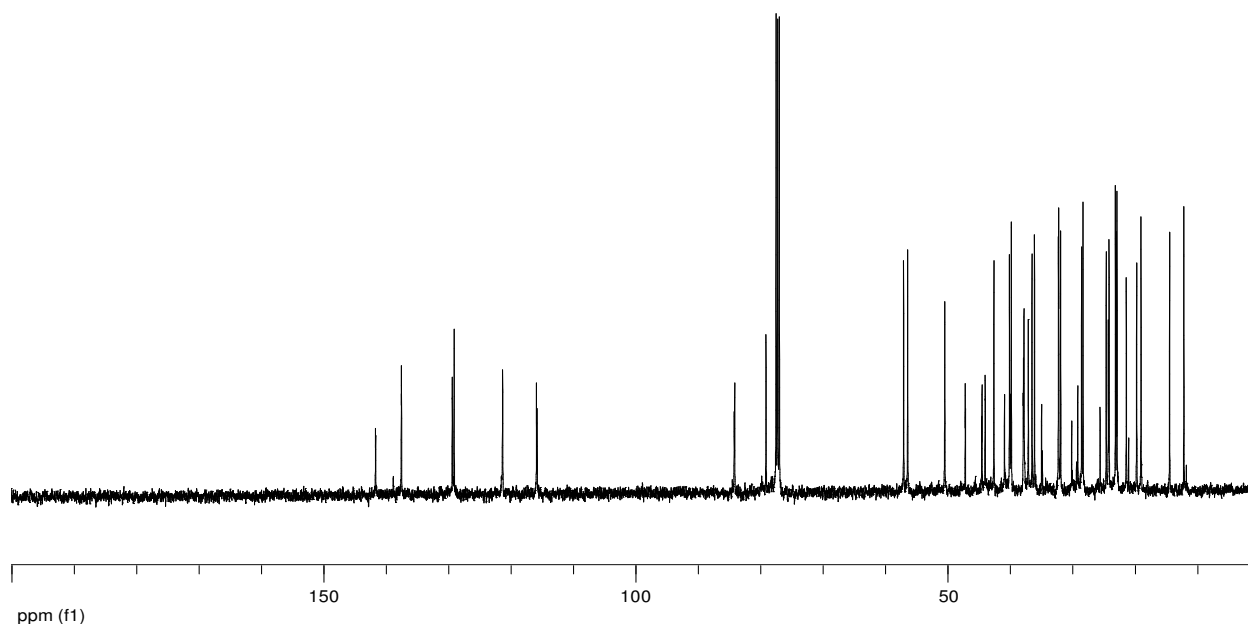
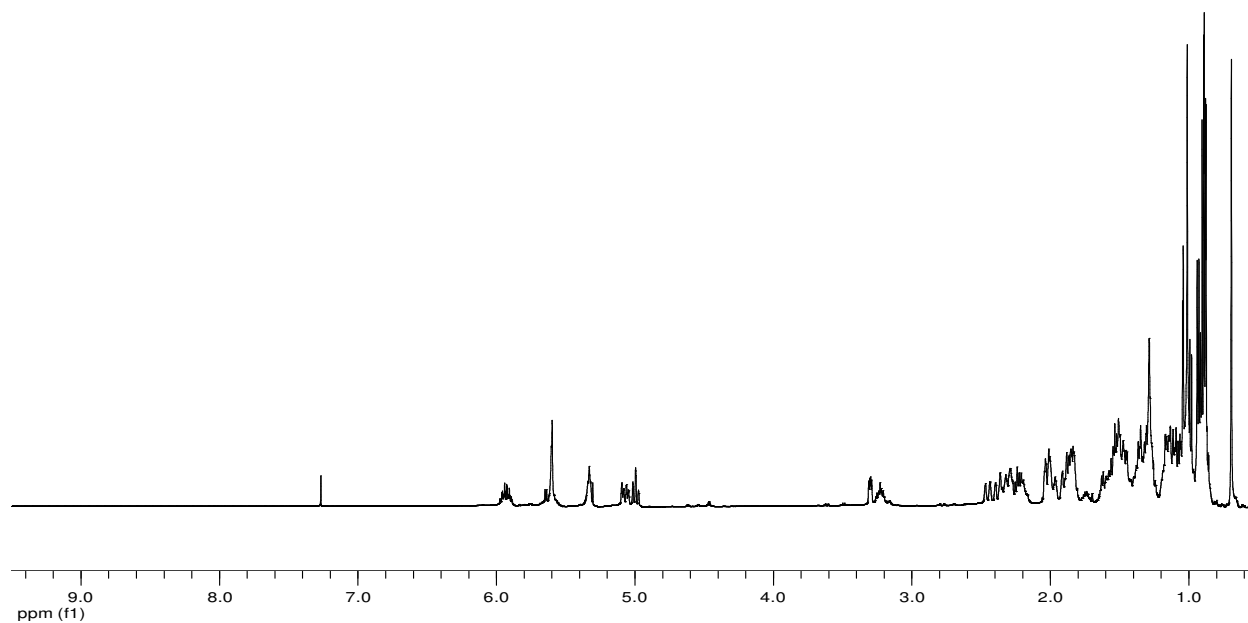
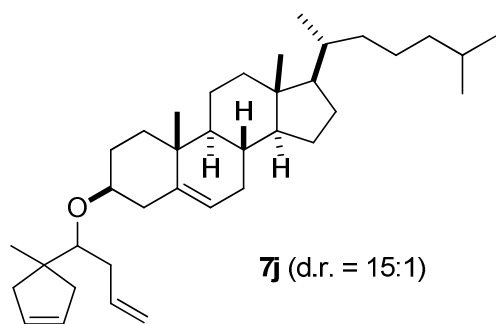
7i (less polar)

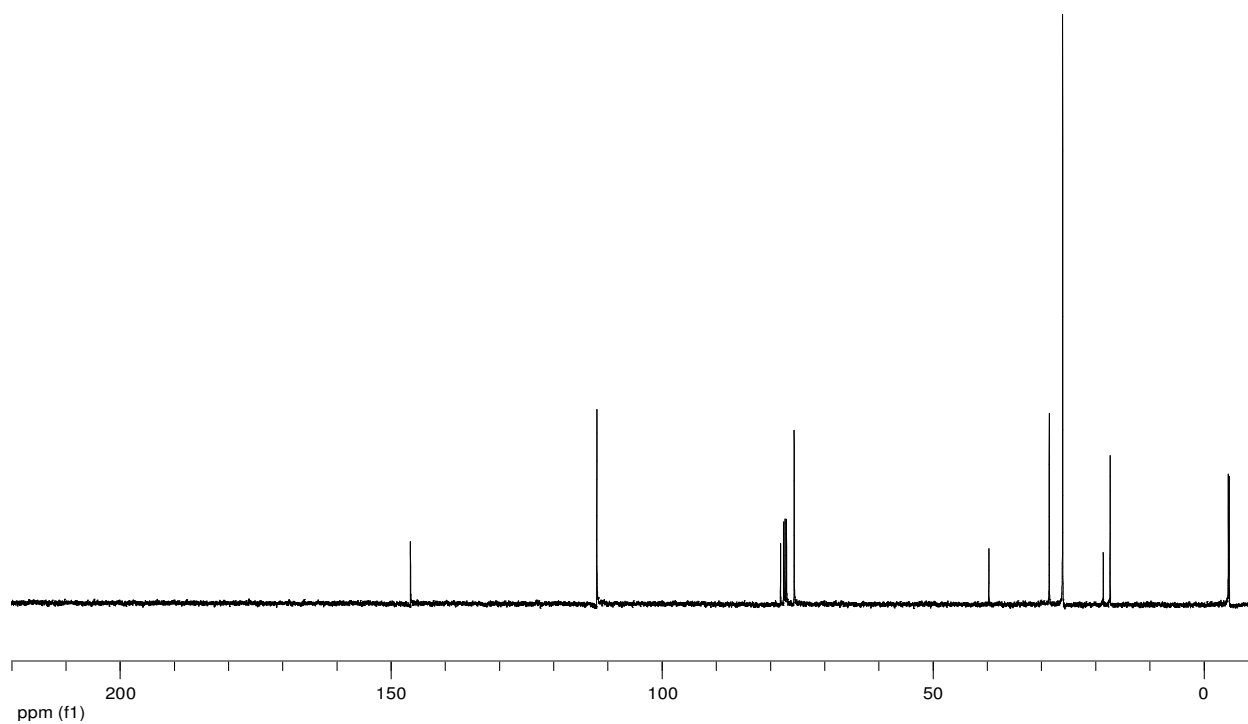
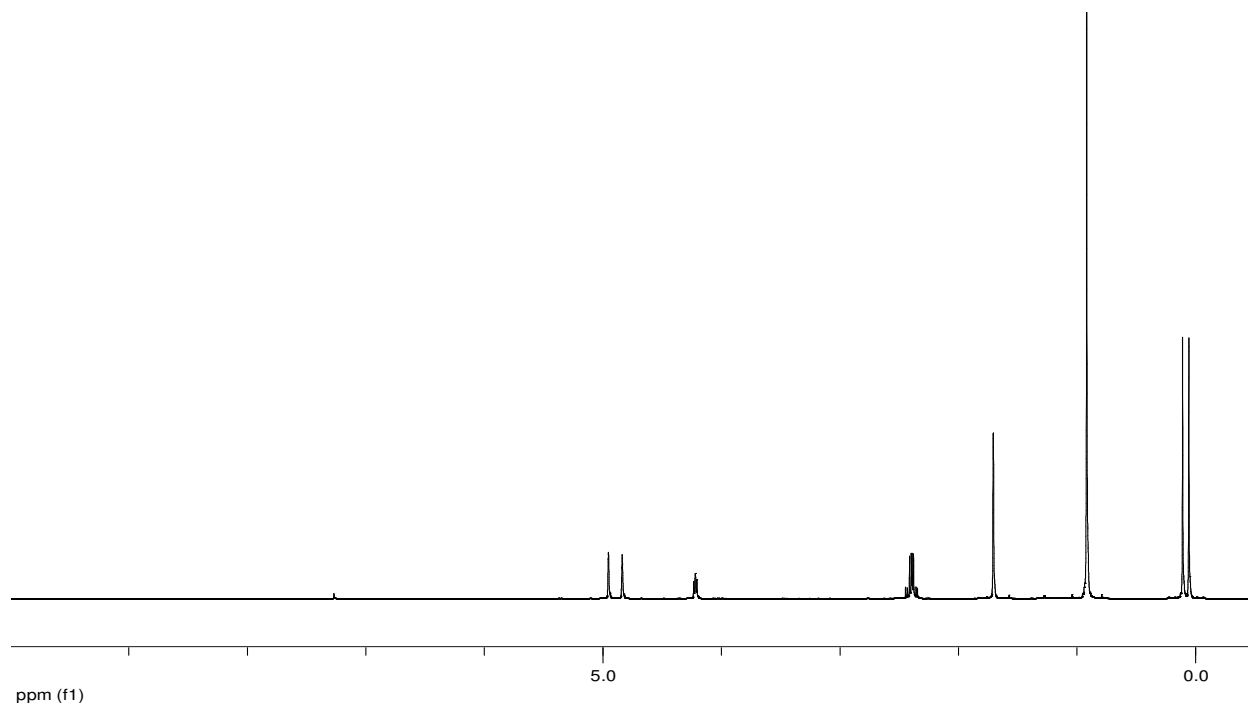
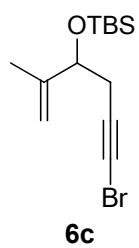




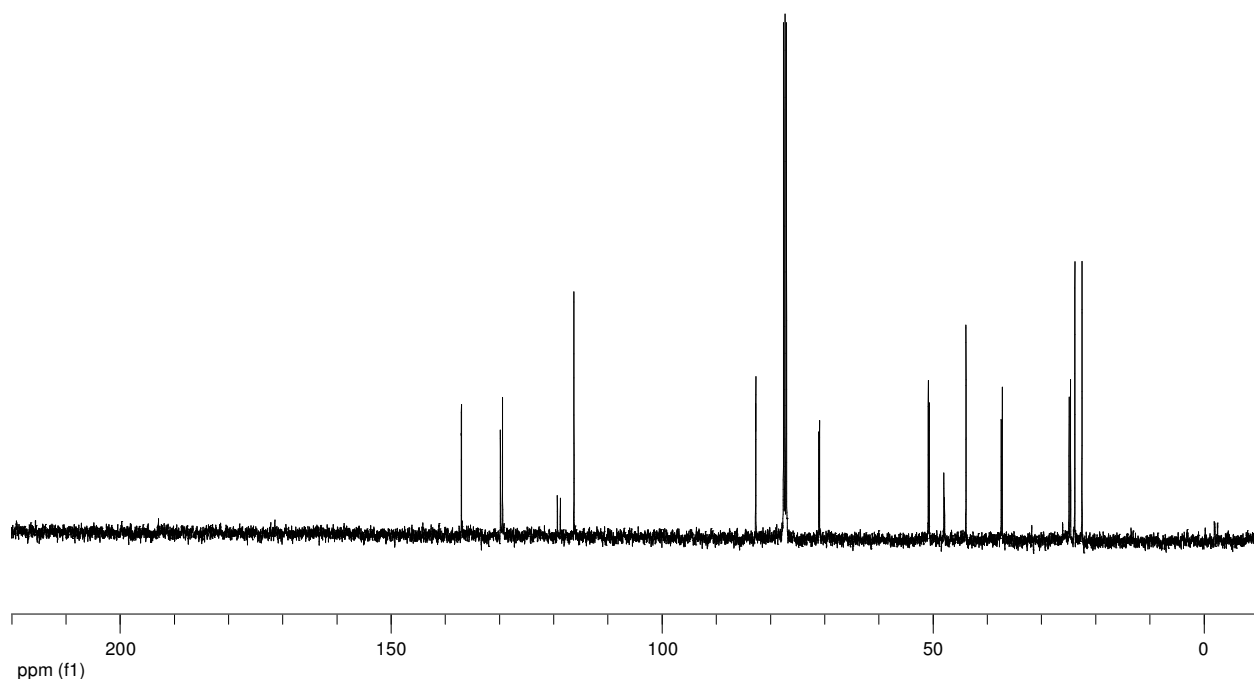
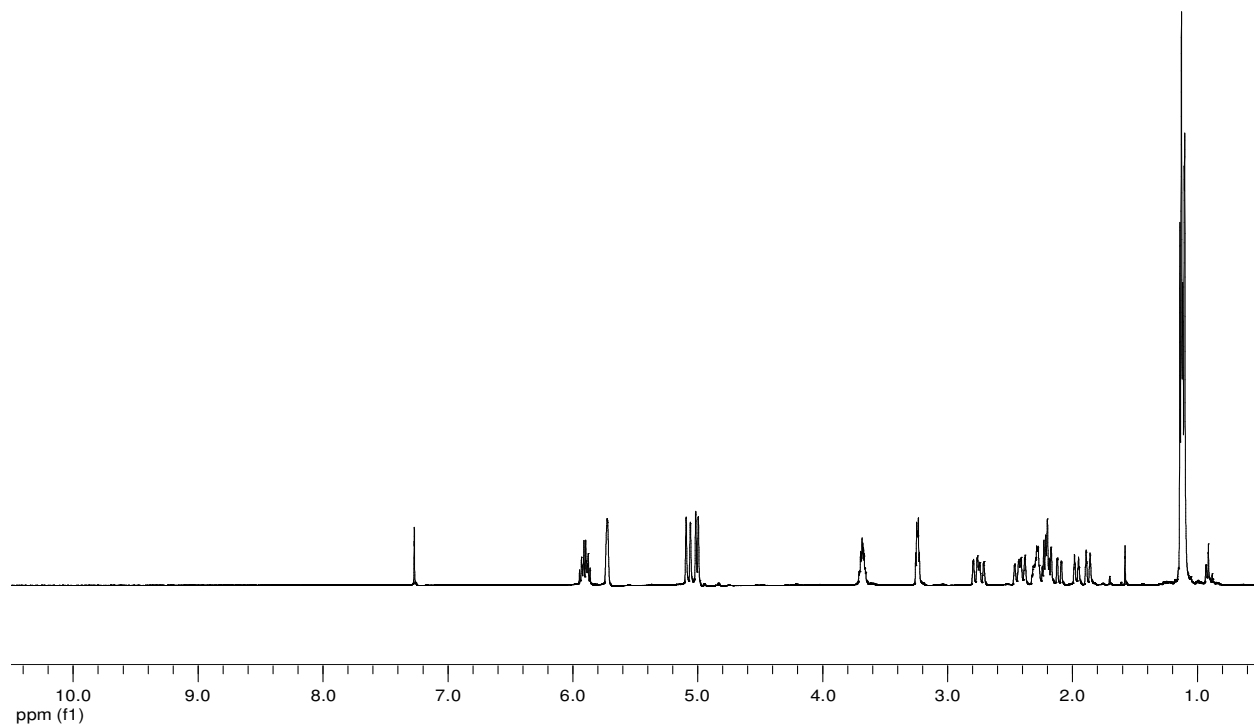
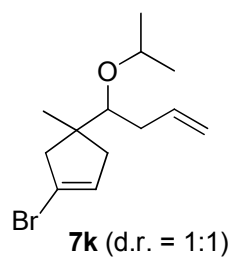
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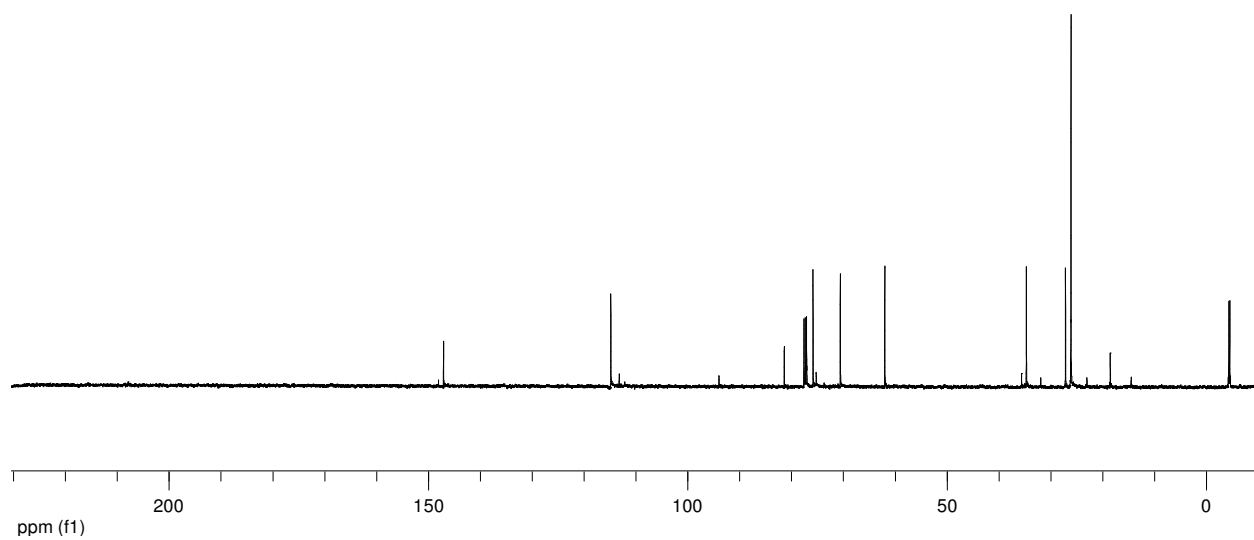
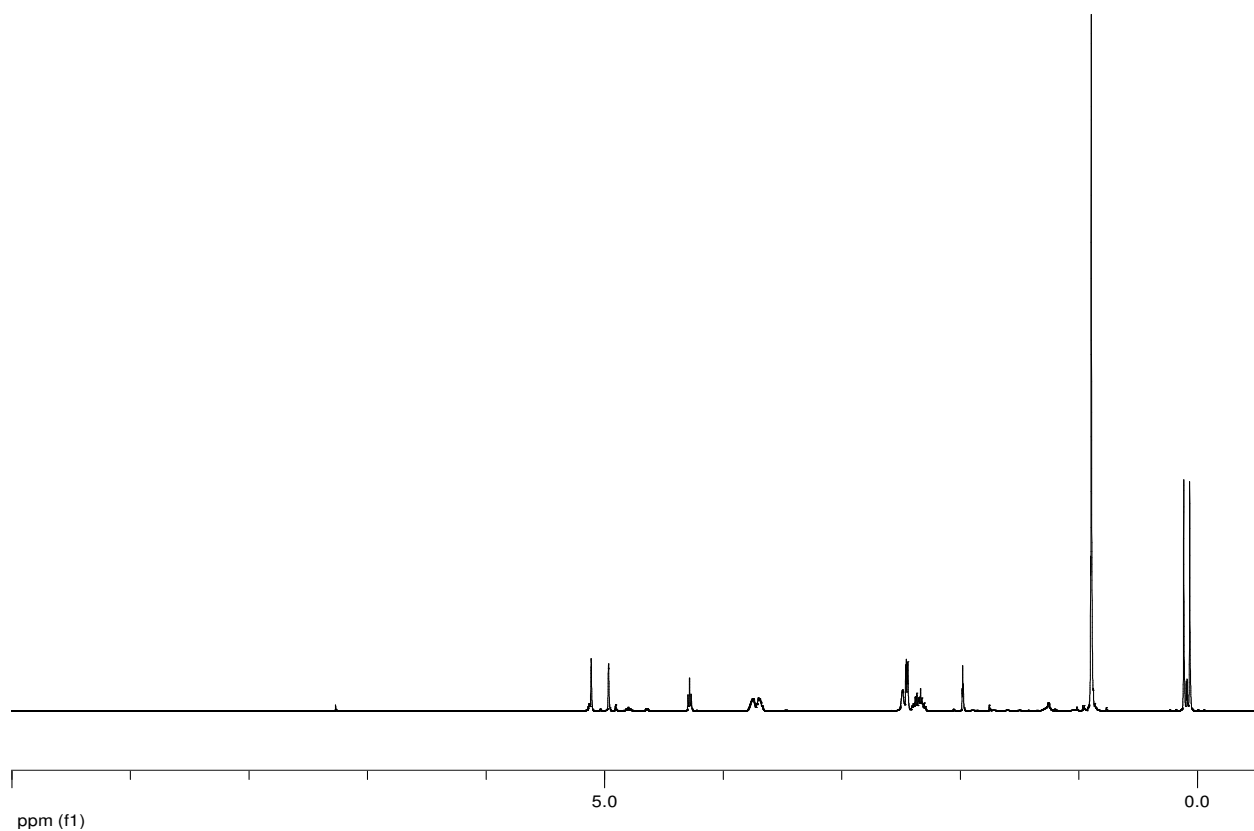
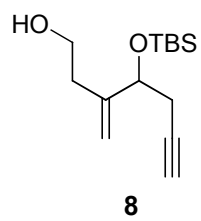




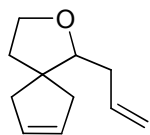


S-43

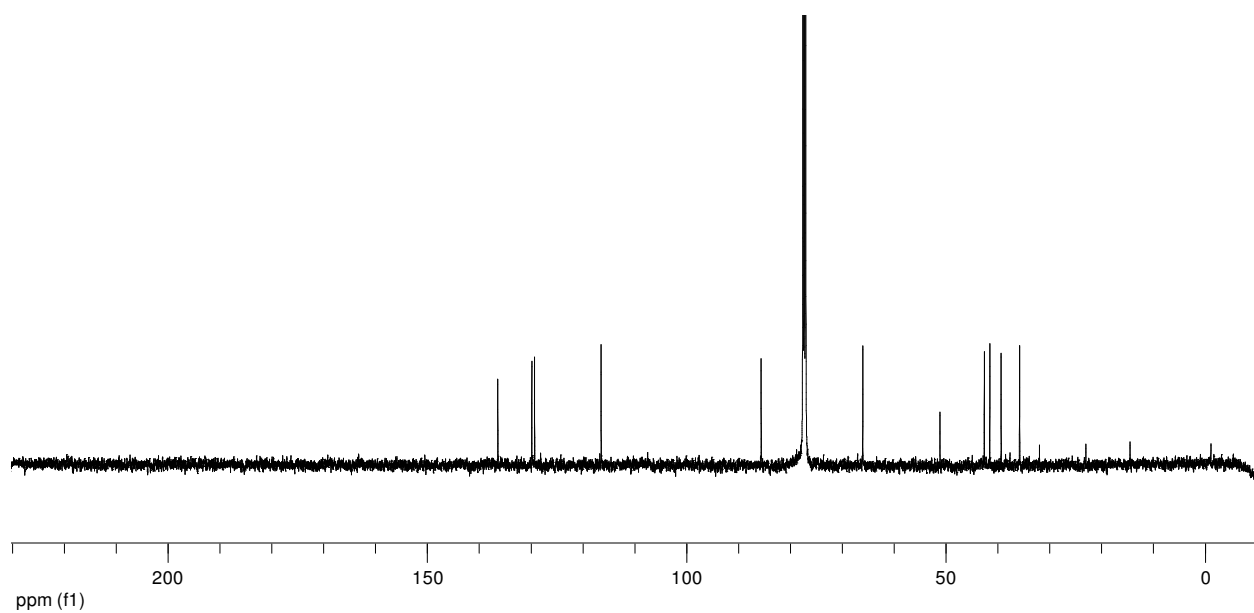
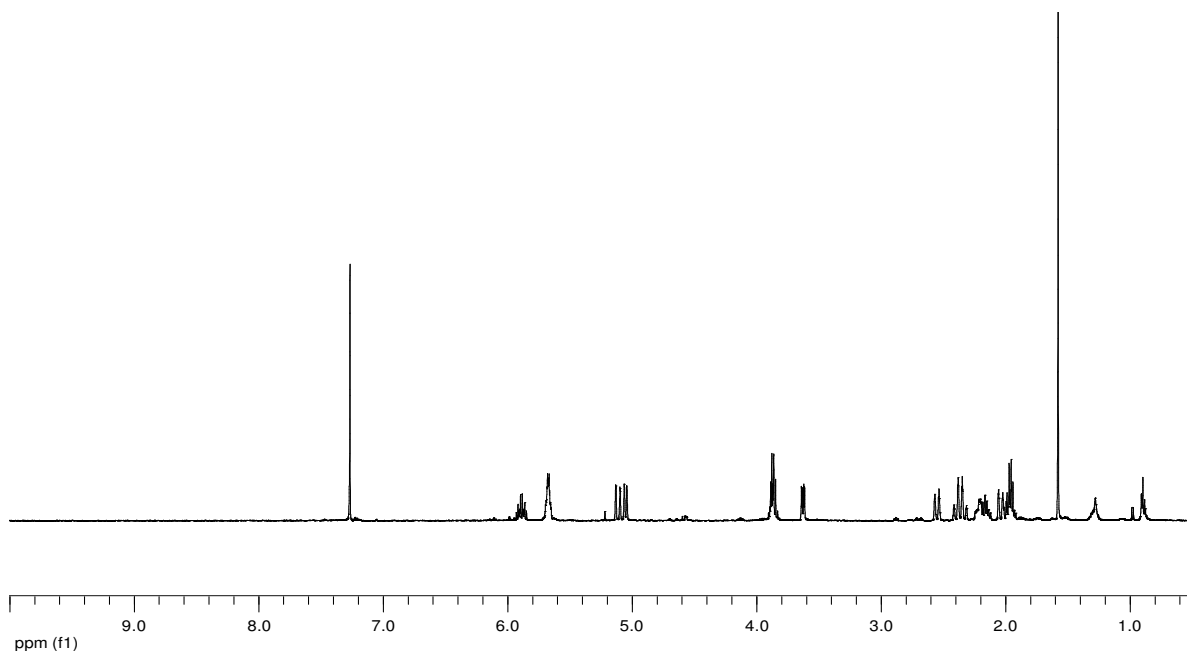




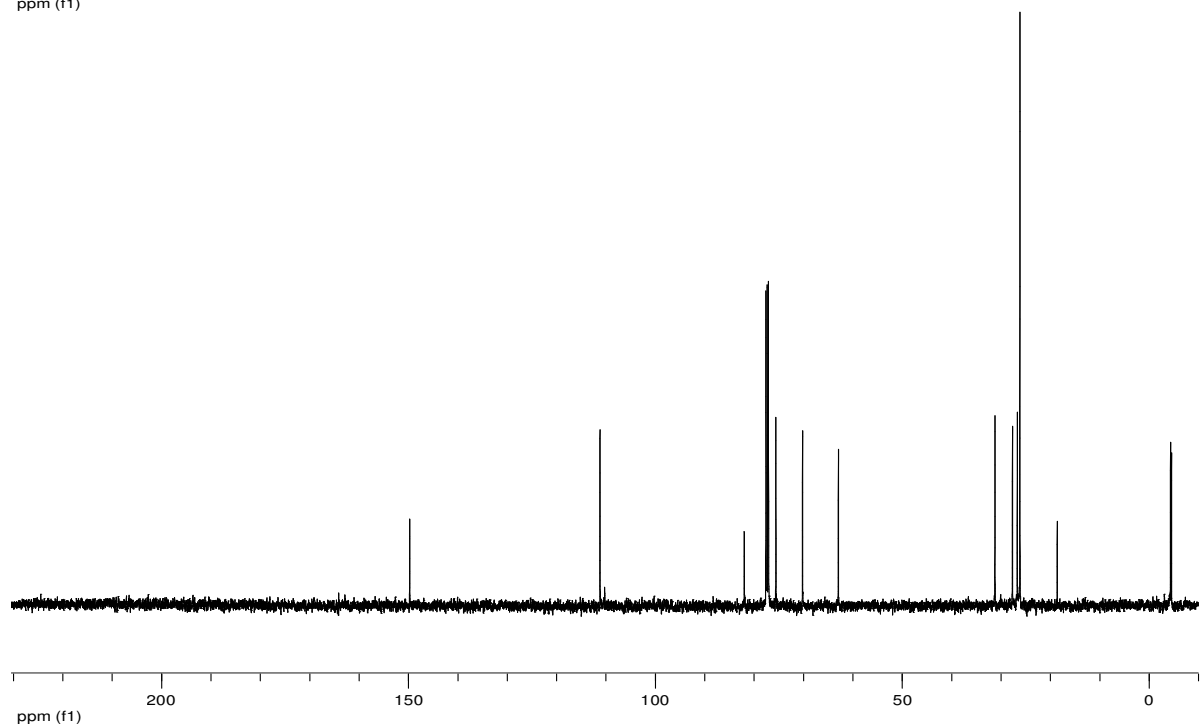
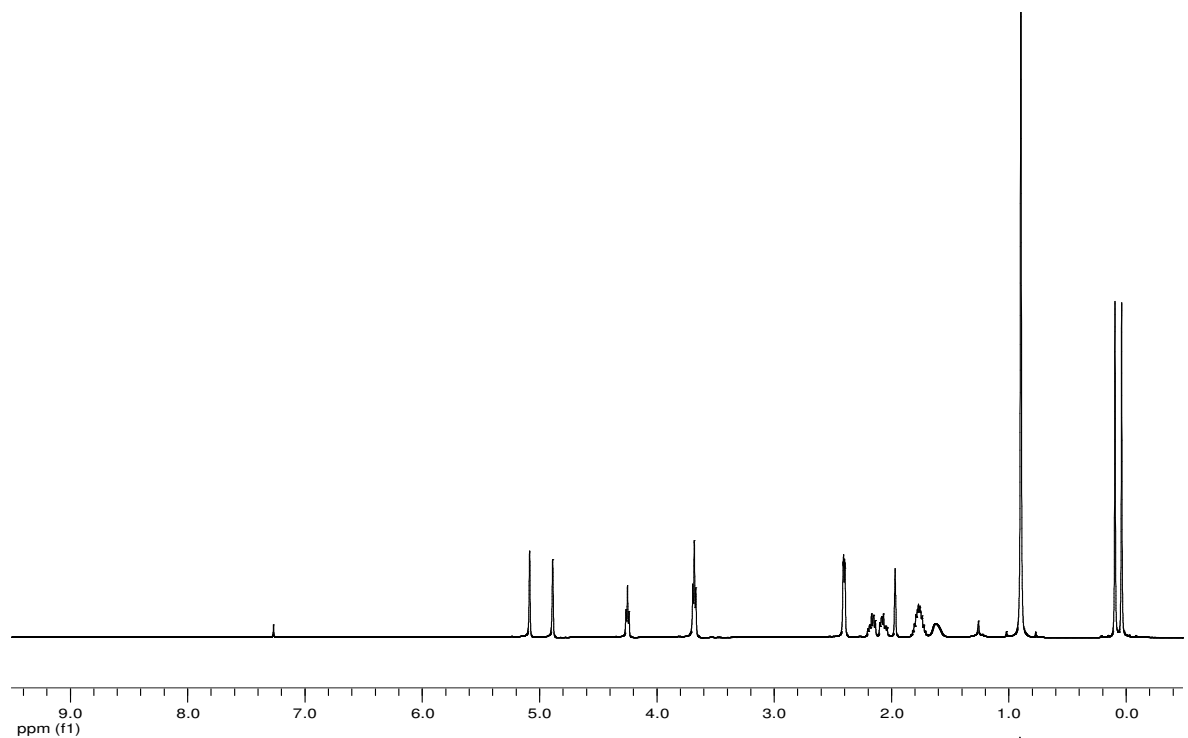
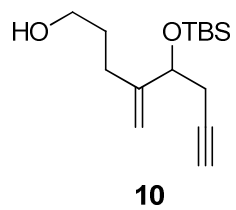
S-45

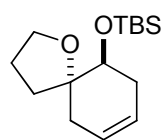


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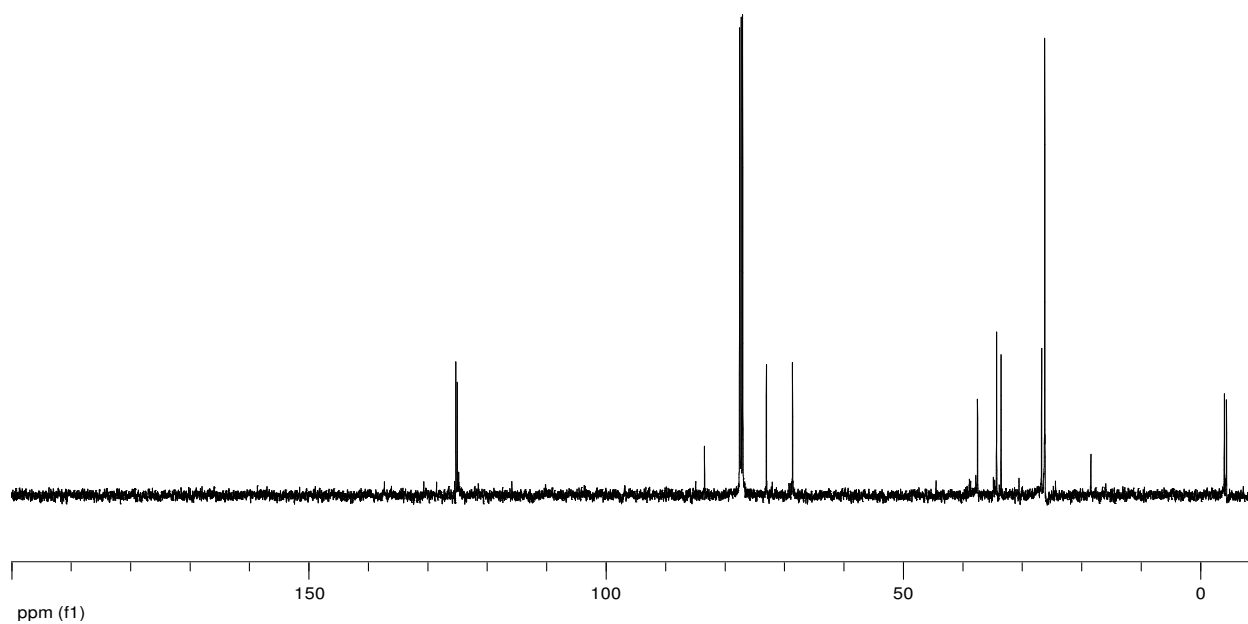
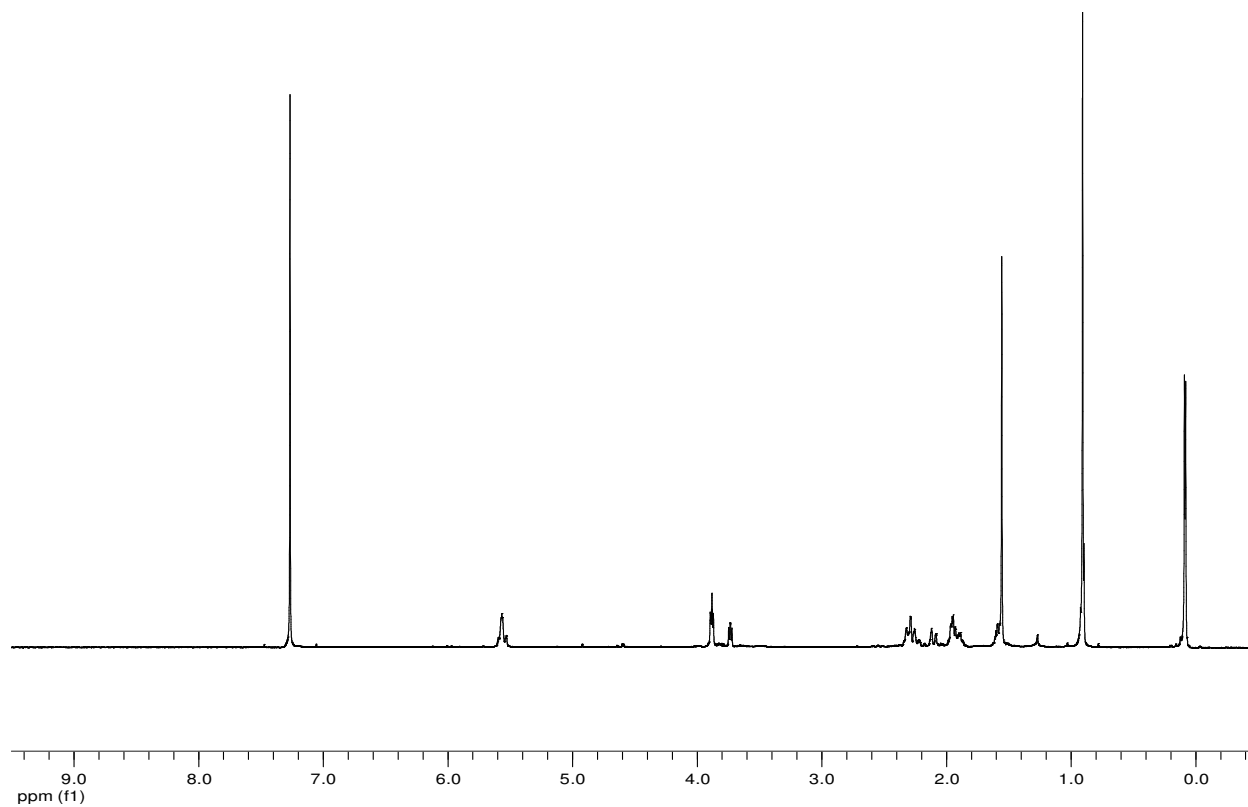


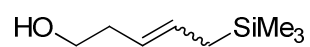
S-46



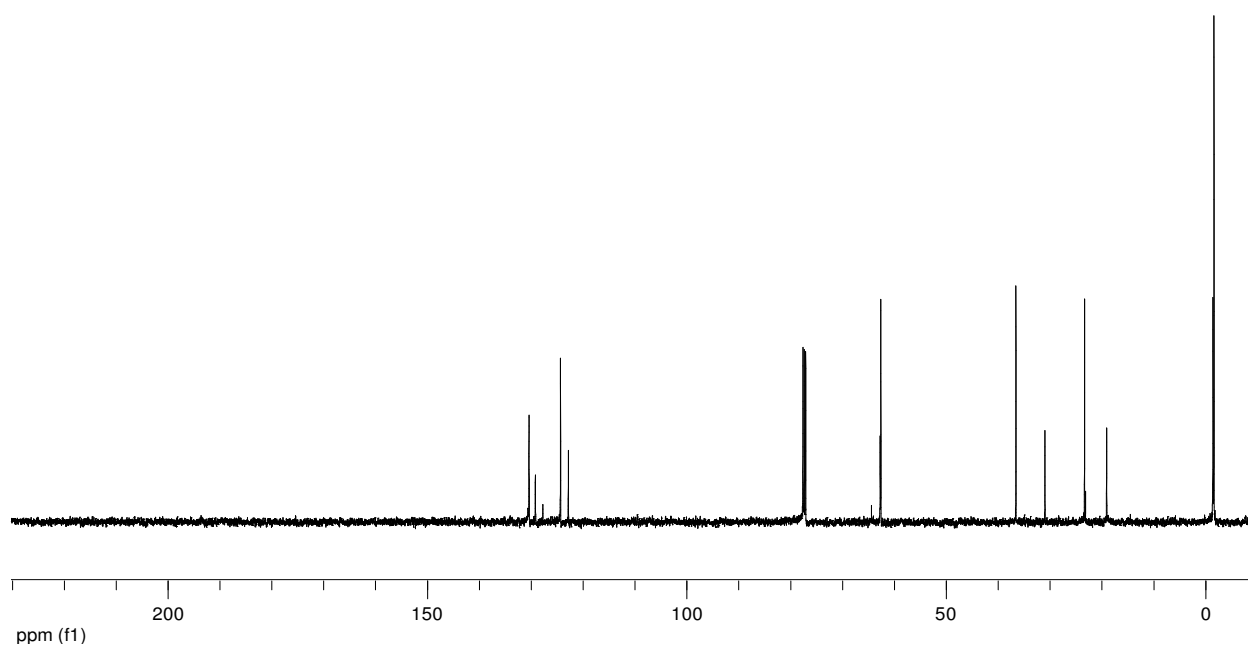
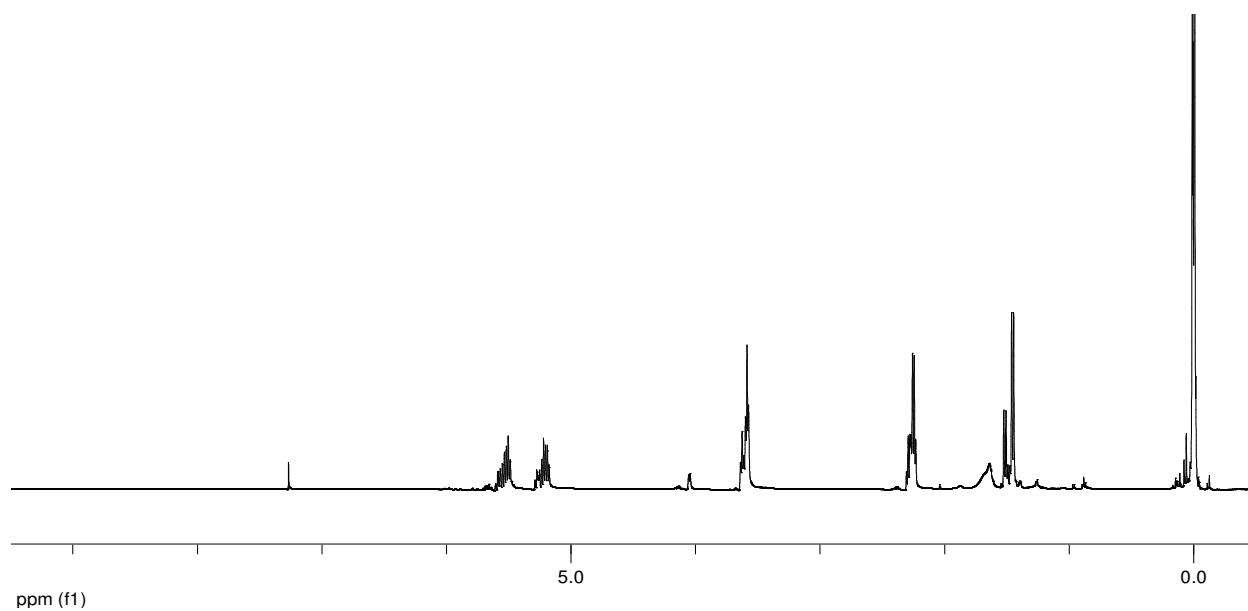


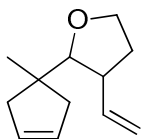
11



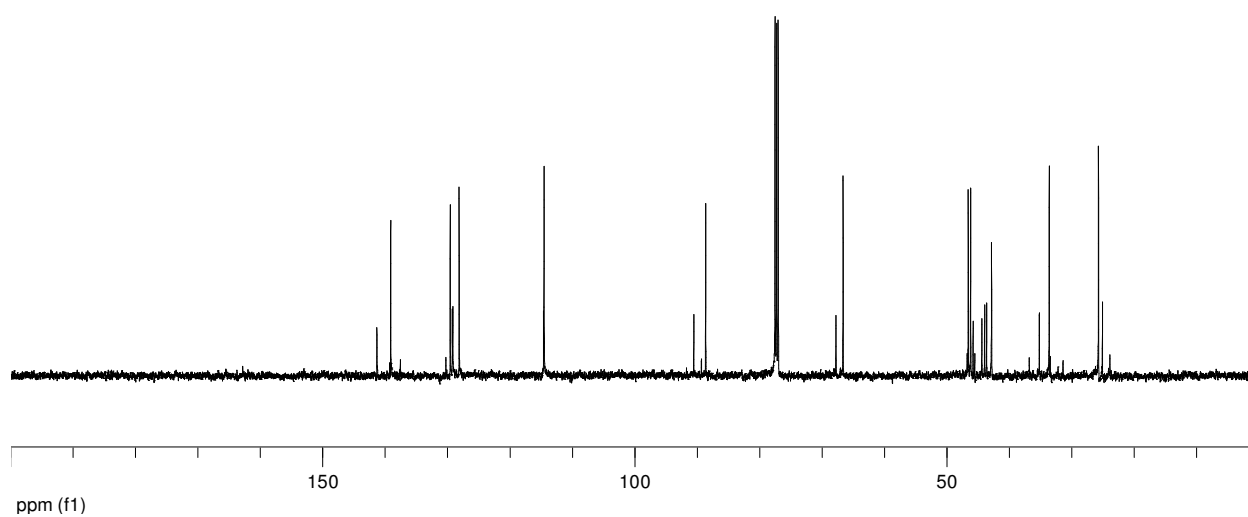
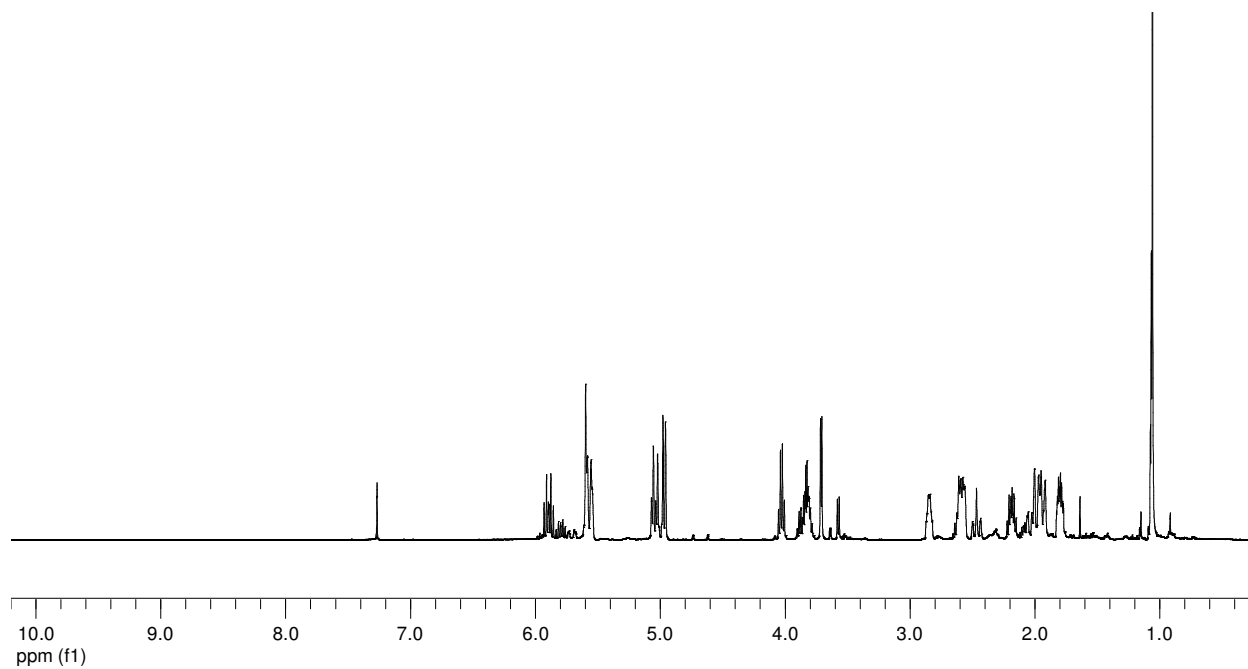


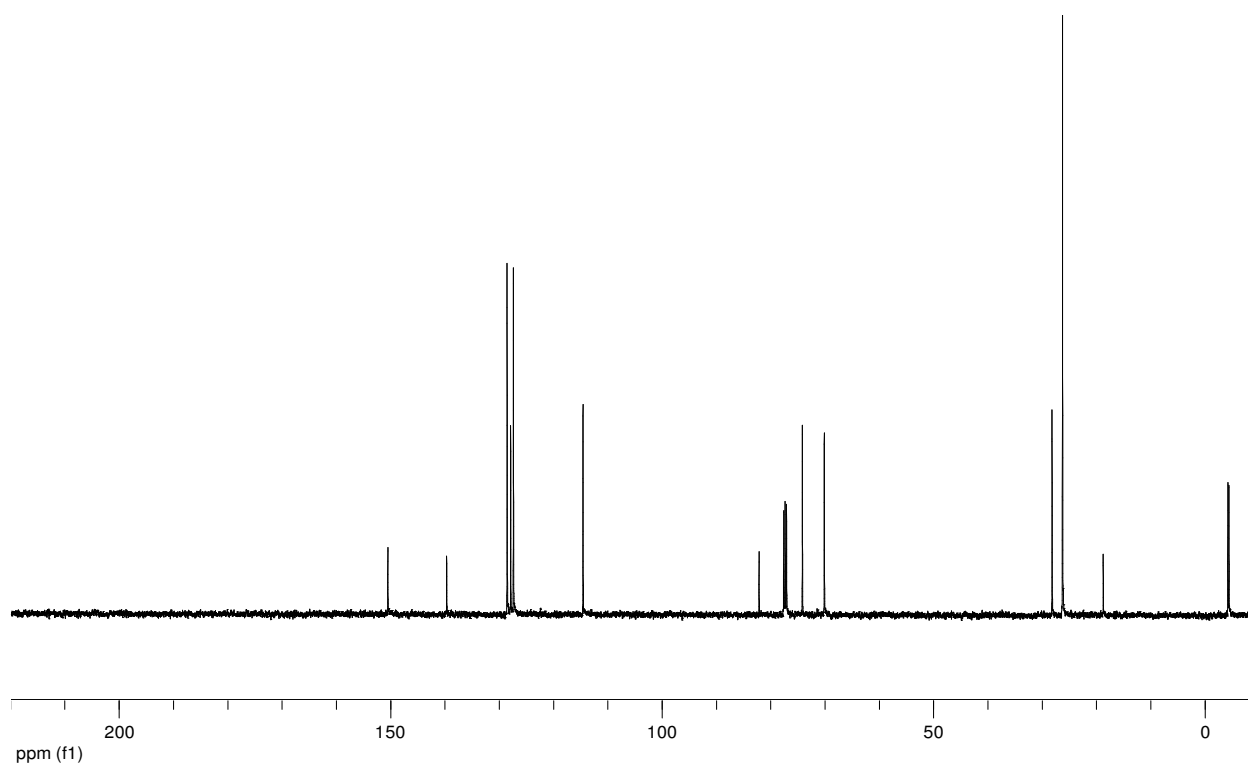
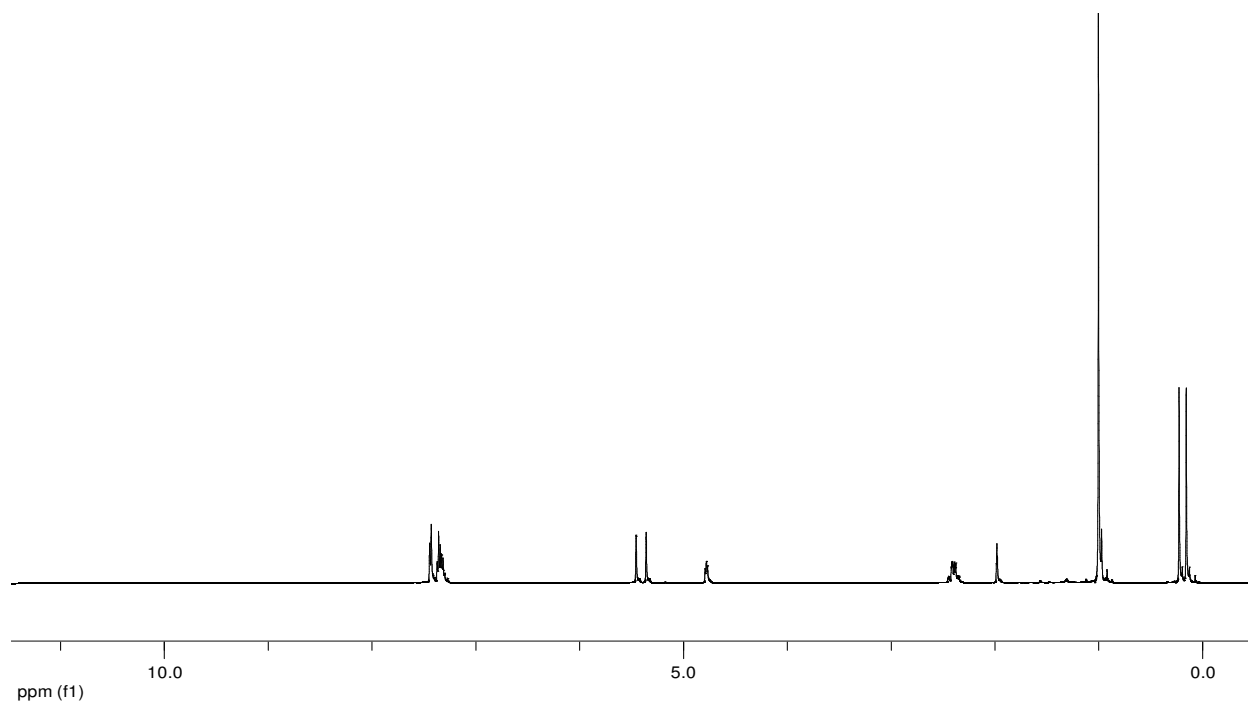
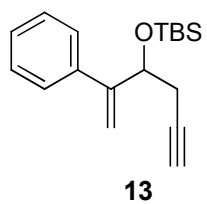
SI-1



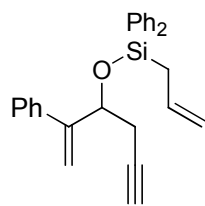


12 (d.r. = 2.5:1)

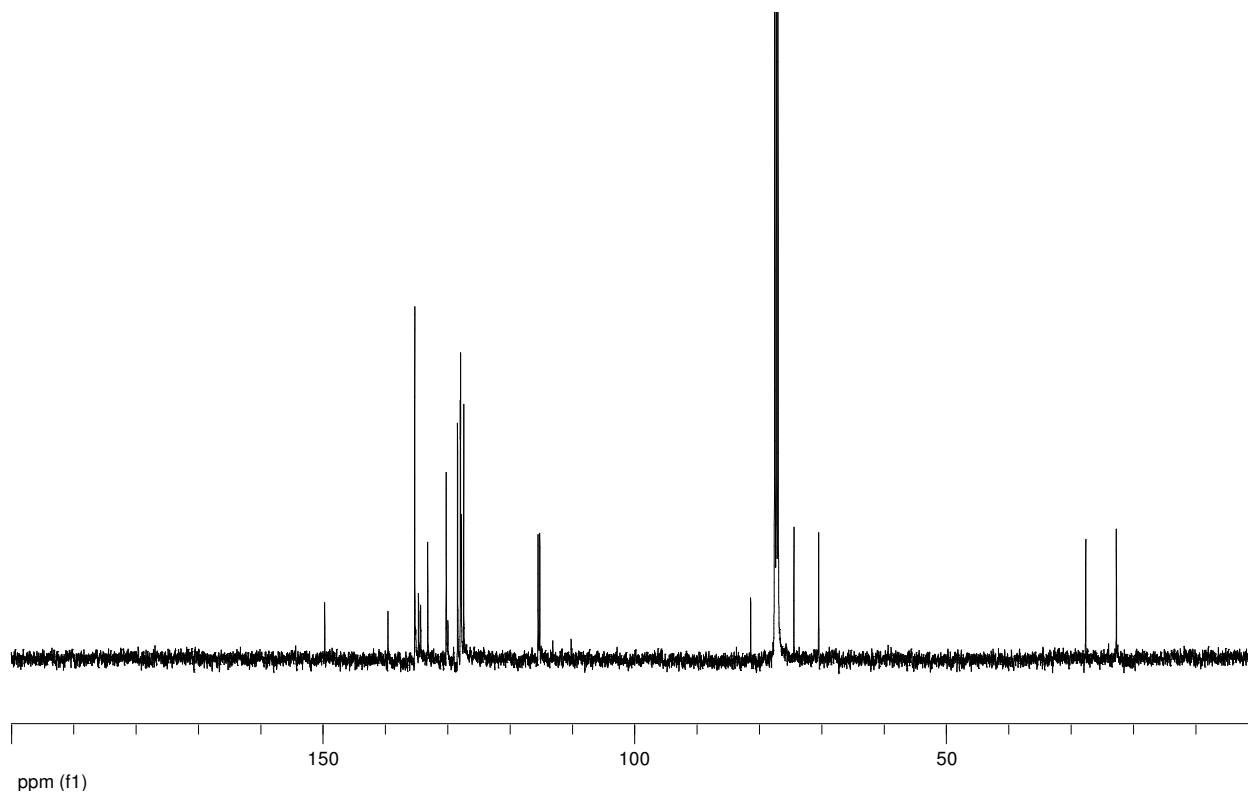
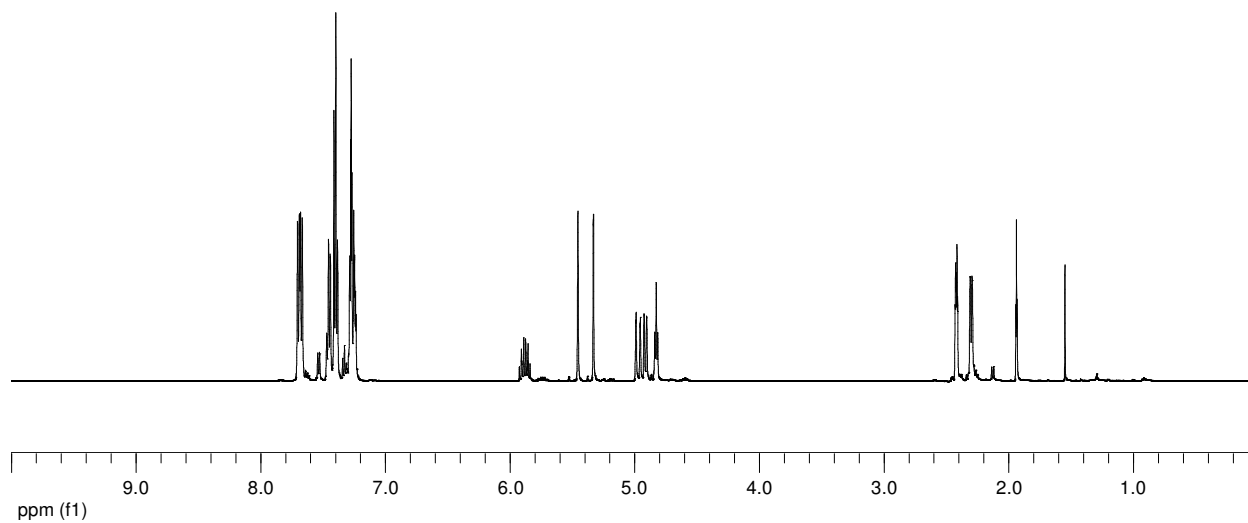


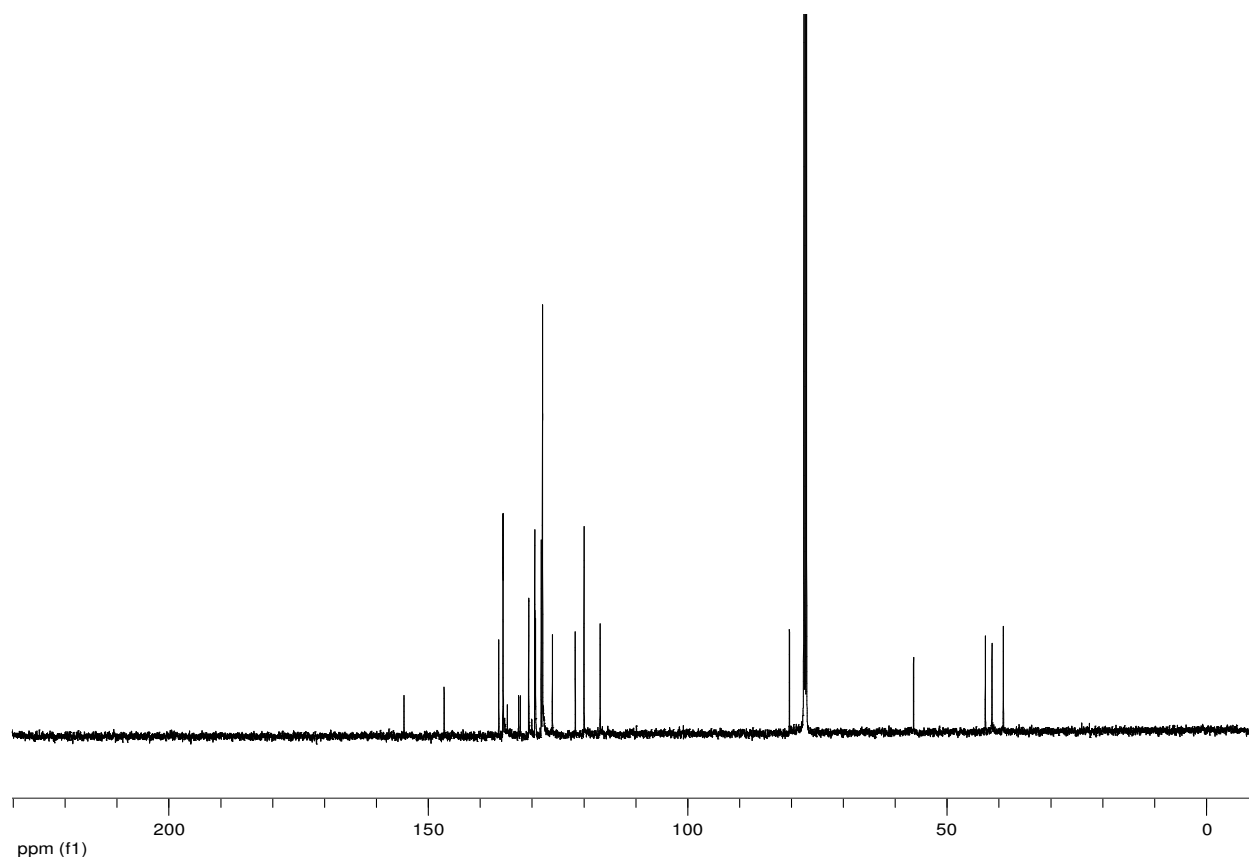
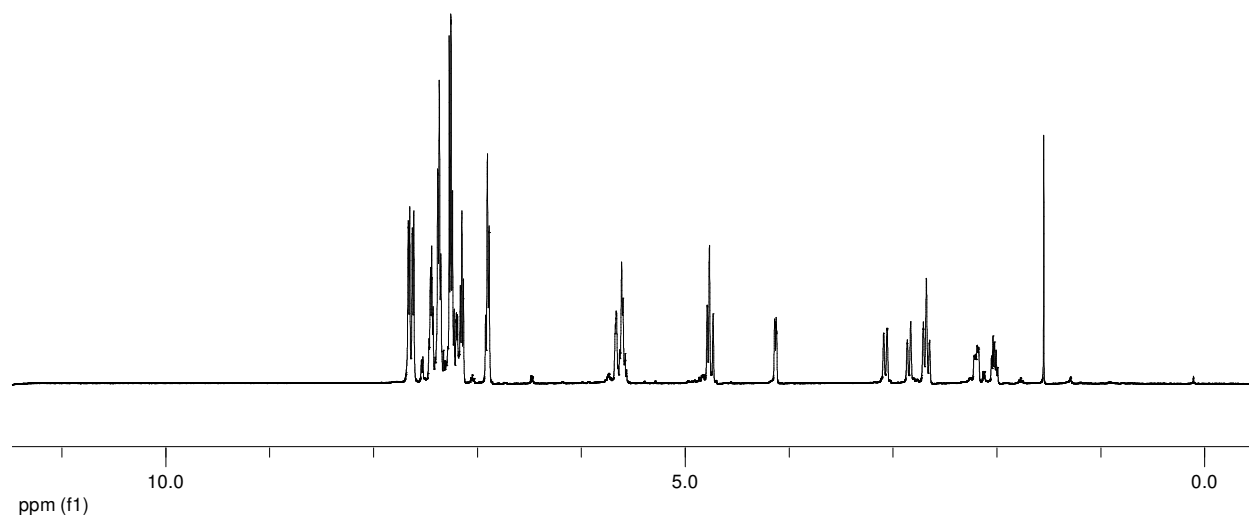
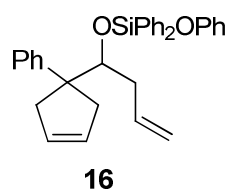


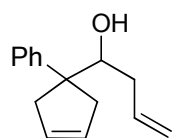
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SI-2

