Supporting Information

Efficient Synthesis of Alkynylsilyl Ethers and Silaketals via Base-Induced Alkynylsilane Alcoholysis

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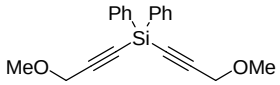
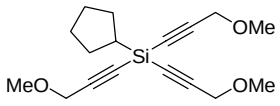
General Information: Hexanes, dichloromethane (CaH_2), and THF (sodium/benzophenone) were freshly distilled prior to use. Reactions were monitored by thin layer chromatography (TLC) on precoated TLC glass plates (silica gel 60 F_{254}, 250 μm thickness). Silica gel (60 Å porosity, 32–63 μm particle size) was used for flash chromatography. ^{1}H and ^{13}C NMR were obtained on 250 and 300 MHz spectrometers; chemical shifts (δ) are reported relative to an internal standard of tetramethylsilane (TMS). High resolution mass spectra were obtained using Leu5-enkephalin or erythromycin as a lock mass on an ESI-TOF spectrometer equipped with Z-spray and a reflectron.



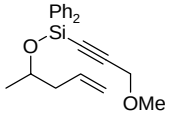
Dialkynylsilane 5: Methyl propargyl ether (2.07 g, 29.5 mmol) was dissolved in dry THF (20 mL) and cooled to −78 ºC. *n*-Butyllithium (2.5 M in hexanes, 11.8 mL, 29.5 mmol) was added dropwise, and the resulting solution was stirred at −78 ºC for 45 minutes. A solution of dichlorodiphenylsilane (3.00 g, 11.8 mmol) was then added slowly. After stirring for 15 minutes at −78 ºC, the reaction was allowed to warm to room temperature and stirred 2 hours. It was subsequently quenched by the slow addition of water and extracted with ether. The combined organic layers were washed with brine and dried over $MgSO_4$. Removal of the solvent gave a yellow oil that was chromatographed on silica gel with 20% to 30% ether/hexanes, affording 2.30 g (61%) of **5** as a white, flaky solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.79 – 7.71 (4H, m), 7.48 – 7.34 (6H, m), 4.22 (4H, s), 3.43 (6H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 134.9, 132.3, 130.5, 128.2, 105.7, 85.2, 60.6, 57.9; HRMS (ESI) calcd for $C_{20}H_{20}O_2Si$ $[M+Na]^+$ 343.1130, found 343.1121.



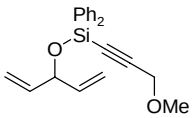
Trialkynylsilane 6: Methyl propargyl ether (4.64 g, 66.2 mmol) was dissolved in dry THF (50 mL) and cooled to −78 ºC. *n*-Butyllithium (2.5 M in hexanes, 26.5 mL, 66.2 mmol) was then added dropwise. The reaction was stirred at −78 ºC for 30 minutes. A solution of trichlorocyclopentylsilane (3.00 g, 14.7 mmol) in THF (20 mL) was then slowly added. After

stirring for 20 minutes at −78 ºC, the reaction was allowed to warm to room temperature and stirred 2 hours. Solid $NaHCO_3$ (~5 g) was added, and after stirring for an additional 30 minutes, the mixture was filtered through a short plug of silica. The solution was concentrated, taken up in 4:1 pentane:ether, filtered again, and evaporated to a yellow oil. Silica gel chromatography with an eluent of 20% to 30% ether/hexanes gave **6** (3.96 g, 88%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.14 (6H, s), 3.40 (9H, s), 1.96 – 1.78 (2H, m), 1.74 – 1.48 (6H, m), 1.30 – 1.17 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 103.4, 84.2, 60.4, 57.8, 27.7, 27.2, 25.1; HRMS (ESI) calcd for $C_{17}H_{24}O_3Si$ $[M+Na]^+$ 327.1392, found 327.1381.

General Procedure for Synthesis of Silyl Ethers 7a–7k from Primary and Secondary Alcohols: The following procedure for **7a** is representative. Silane **5** (400 mg, 1.25 mmol) and 4-penten-2-ol (54 mg, 0.63 mmol) were dissolved in hexanes (4 mL). Sodium hydride (60% dispersion in mineral oil, 3 mg, 0.06 mmol) was added, and the mixture was stirred at room temperature for 20 minutes. The solution was filtered through a small plug of Celite, and removal of the solvent gave a yellow residue. Flash chromatography of the crude on silica gel with 5% ether/hexanes afforded 210 mg (99%) of **7a** as a colorless oil.

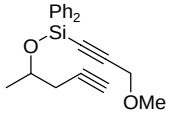


Silyl ether 7a: (99%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 – 7.68 (4H, m), 7.46 – 7.32 (6H, m), 5.82 (1H, ddt, J = 17.1, 9.9, 7.3 Hz), 5.08 – 4.98 (2H, m), 4.22 (2H, s), 4.17 (1H, sextet, J = 6.1 Hz), 3.43 (3H, s), 2.43 – 2.20 (2H, m), 1.22 (3H, d, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 135.2, 134.9, 134.8, 134.3, 134.1, 130.5, 128.1, 117.1, 104.9, 87.2, 70.2, 60.6, 57.8, 43.8, 23.0; HRMS (ESI) calcd for $C_{21}H_{24}O_2Si$ $[M+Na]^+$ 359.1443, found 359.1447.

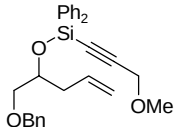


Silyl ether 7b: (97%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.77 – 7.69 (4H, m), 7.46 – 7.33 (6H, m), 5.88 (1H, ddd, J = 17.1, 10.3, 5.7 Hz), 5.23 (1H, dt, J = 17.1, 1.4 Hz), 5.09 (1H, dt, J = 10.3, 1.4 Hz), 4.88 (1H, t pentet, J = 5.7, 1.4 Hz), 4.21 (3H, s), 3.43 (3H, s); ^{13}C NMR

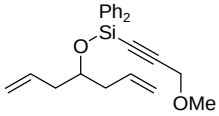
($CDCl_3$, 75.4 MHz) δ 139.0, 134.9, 133.8, 130.6, 128.0, 115.1, 105.2, 87.0, 76.1, 60.6, 57.9; HRMS (ESI) calcd for $C_{21}H_{22}OSi$ $[M+Na]^+$ 357.1287, found 357.1271.



Silyl ether 7c: (98%, colorless oil) ^1H NMR ($CDCl_3$, 300 MHz) δ 7.77 – 7.68 (4H, m), 7.47 – 7.33 (6H, m), 4.32 – 4.21 (1H, m), 4.23 (2H, s), 3.44 (3H, s), 2.52 (1H, ddd, J = 16.6, 5.1, 2.7 Hz), 2.37 (1H, ddd, J = 16.6, 7.5, 2.7 Hz), 1.96 (1H, t, J = 2.7 Hz), 1.34 (3H, d, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 134.85, 134.80, 133.9, 133.7, 130.6, 128.1, 105.3, 86.8, 81.4, 70.3, 69.0, 60.5, 57.9, 29.0, 22.7; HRMS (ESI) calcd for $C_{21}H_{22}O_2Si$ $[M+Na]^+$ 357.1287, found 357.1287.

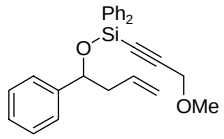


Silyl ether 7d: (77%, colorless oil, contaminated with ~5% of an unknown impurity – yield corrected for presence of this impurity) ^1H NMR ($CDCl_3$, 300 MHz) δ 7.76 – 7.60 (4H, m), 7.46 – 7.20 (11H, m), 5.83 (1H, ddt, J = 17.3, 10.1, 7.0 Hz), 5.11 – 4.98 (2H, m), 4.43 (2H, s), 4.29 – 4.20 (1H, m), 4.19 (2H, s), 3.50 (2H, AB of ABX, ν_A = 1056.5, J_{AX} = 5.5, ν_B = 1043.2, J_{BX} = 5.0, J_{AB} = 10.0 Hz), 3.41 (3H, s), 2.51 – 2.31 (2H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 138.6, 135.0, 134.6, 134.1, 134.0, 130.5, 128.4, 128.0, 127.7, 127.6, 117.5, 105.1, 87.1, 73.5, 73.3, 72.8, 60.5, 57.9, 38.8; HRMS (ESI) calcd for $C_{28}H_{30}O_3Si$ $[M+Na]^+$ 465.1862, found 465.1857.

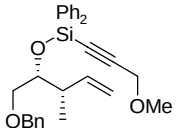


Silyl ether 7e: (97%, colorless oil) ^1H NMR ($CDCl_3$, 300 MHz) δ 7.76 – 7.69 (4H, m), 7.48 – 7.32 (6H, m), 5.89 – 5.73 (2H, m), 5.08 – 4.97 (4H, m), 4.22 (2H, s), 4.08 (1H, pentet, J = 5.8 Hz), 3.43 (3H, s), 2.36 – 2.29 (4H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 134.9, 134.1, 130.5,

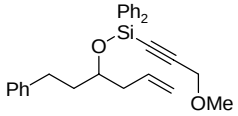
128.0, 117.3, 105.2, 87.1, 73.4, 60.6, 57.9, 40.9; HRMS (ESI) calcd for $C_{23}H_{26}O_2Si$ $[M+Na]^+$ 385.1600, found 385.1612.



Silyl ether 7f: (96%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 – 7.68 (2H, m), 7.63 – 7.55 (2H, m), 7.48 – 7.14 (11H, m), 5.83 – 5.65 (1H, m), 5.04 – 4.92 (3H, m), 4.11 (2H, s), 3.33 (3H, s), 2.71 – 2.47 (2H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 143.5, 134.9, 134.8, 134.7, 133.9, 133.6, 130.5, 130.4, 128.1, 128.0, 127.9, 127.3, 126.5, 117.4, 105.3, 86.9, 76.2, 60.4, 57.8, 44.5; HRMS (ESI) calcd for $C_{26}H_{26}O_2Si$ $[M+Na]^+$ 421.1600, found 421.1609.

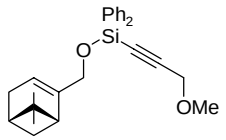


Silyl ether 7g: (88%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 – 7.67 (4H, m), 7.44 – 7.18 (11H, m), 5.81 (1H, ddd, J = 17.5, 10.3, 7.3 Hz), 5.07 – 4.92 (2H, m), 4.36 (2H, s), 4.17 (2H, s), 4.06 (1H, m), 3.56 - 3.45 (2H, AB of ABX, ν_A = 1053.0, J_{AX} = 4.1, ν_B = 1046.5, J_{BX} = 6.1, J_{AB} = 10.1 Hz), 3.39 (3H, s), 2.55 (1H, m), 1.06 (3H, d, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 141.1, 138.6, 135.0, 134.4, 134.3, 130.3, 128.3, 127.9, 127.7, 127.5, 114.7, 105.0, 87.3, 76.8, 73.1, 72.4, 60.5, 57.8, 41.1, 15.2; HRMS (ESI) calcd for $C_{29}H_{32}O_3Si$ $[M+Na]^+$ 479.2018, found 479.1998.

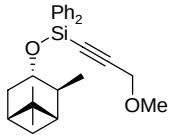


Silyl ether 7h: (89%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.78 – 7.70 (4H, m), 7.47 – 7.33 (6H, m), 7.26 – 7.04 (5H, m), 5.88 – 5.72 (1H, m), 5.06 – 4.97 (2H, m), 4.20 (2H, s), 4.10 (1H, pentet, J = 5.9 Hz), 3.40 (3H, s), 2.80 – 2.67 (1H, m), 2.65 – 2.52 (1H, m), 2.41 – 2.33 (2H, m), 1.92 – 1.78 (2H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.5, 134.9, 134.8, 134.1, 130.5,

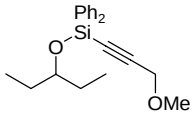
128.5, 128.4, 128.08, 128.05, 125.8, 117.4, 105.3, 87.2, 73.5, 60.6, 57.9, 41.5, 38.2, 31.8; HRMS (ESI) calcd for $C_{28}H_{30}O_2Si$ $[M+Na]^+$ 449.1913, found 449.1933.



Silyl ether 7i: (77%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 – 7.68 (4H, m), 7.46 – 7.33 (6H, m), 5.53 – 5.48 (1H, m), 4.22 (2H, s), 4.20 – 4.17 (2H, m), 3.43 (3H, s), 2.39 – 2.16 (3H, m), 2.11 – 2.05 (2H, m), 1.25 (3H, s), 1.15 (1H, d, J = 8.5 Hz), 0.81 (3H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 146.5, 134.8, 133.7, 130.5, 128.0, 117.6, 104.9, 86.7, 66.6, 60.6, 57.9, 43.2, 41.2, 38.2, 31.6, 31.3, 26.4, 21.2; HRMS (ESI) calcd for $C_{26}H_{30}O_2Si$ $[M+Na]^+$ 425.1913, found 425.1928.

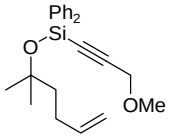


Silyl ether 7j: (98%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.78 – 7.69 (4H, m), 7.46 – 7.32 (6H, m), 4.33 (1H, dt, J = 9.2, 4.7 Hz), 4.23 (2H, s), 3.43 (3H, s), 2.44 – 2.27 (2H, m), 2.24 – 2.12 (1H, m), 1.99 – 1.84 (2H, m), 1.80 – 1.73 (1H, m), 1.20 – 1.15 (1H, m), 1.18 (3H, s), 1.01 (3H, d, J = 7.2 Hz), 0.83 (3H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 134.9, 134.5, 134.4, 130.4, 128.0, 104.9, 87.5, 73.9, 60.8, 57.8, 48.1, 47.2, 42.0, 39.2, 38.4, 34.1, 27.8, 24.0, 20.5; HRMS (ESI) calcd for $C_{26}H_{32}O_2Si$ $[M+Na]^+$ 427.2069, found 427.2068.

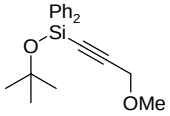


Silyl ether 7k: (99%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 – 7.69 (4H, m), 7.46 – 7.33 (6H, m), 4.23 (2H, s), 3.85 (1H, pentet, J = 5.9 Hz), 3.44 (3H, s), 1.55 (4H, qd, J = 7.4, 5.9 Hz), 0.87 (6H, t, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 134.9, 134.5, 130.4, 128.0, 104.8, 87.5, 76.9, 60.6, 57.8, 29.0, 9.9; HRMS (ESI) calcd for $C_{21}H_{26}O_2Si$ $[M+Na]^+$ 361.1600, found 361.1609.

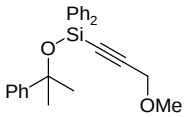
General Procedure for Synthesis of Silyl Ethers 7l–7o from Tertiary Alcohols: The following procedure for **7l** is representative. Silane **5** (100 mg, 0.31 mmol) and 2-methyl-5-hexen-2-ol (35 mg, 0.31 mmol) were dissolved in hexanes (2 mL). Sodium hydride (60% dispersion in mineral oil, 1 mg, 0.03 mmol) was added, and the reaction was stirred at 50 ºC until complete by TLC (approximately 2 hours). The solution was filtered through Celite, and removal of the solvent gave a yellow residue. Flash chromatography on silica gel with 5% ether/hexanes afforded 70 mg (62%) of **7l** as a colorless oil.



Silyl ether 7l: (62%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 – 7.65 (4H, m), 7.48 – 7.27 (6H, m), 5.81 (1H, ddt, *J* = 16.9, 10.2, 6.6), 5.00 (1H, ddt, *J* = 16.9, 2.0, 1.7 Hz), 4.93 (1H, ddt, *J* = 10.2, 2.0, 1.4 Hz), 4.23 (2H, s), 3.44 (3H, s), 2.25 – 2.14 (2H, m), 1.71 – 1.62 (2H, m), 1.33 (6H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 139.4, 136.0, 134.7, 130.1, 127.9, 114.1, 104.6, 88.9, 76.6, 60.7, 57.9, 43.7, 29.8, 29.0; HRMS (ESI) calcd for $C_{23}H_{28}O_2Si$ $[M+Na]^+$ 387.1756, found 387.1775.

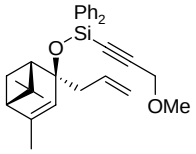


Silyl ether 7m: (89%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 – 7.68 (4H, m), 7.42 – 7.31 (6H, m), 4.22 (2H, s), 3.43 (3H, s), 1.37 (9H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 136.1, 134.7, 130.1, 127.9, 104.5, 89.0, 74.9, 60.7, 57.9, 31.9; HRMS (EI) calcd for $C_{20}H_{24}O_2Si$ $[M]^{\bullet+}$ 324.1546, found 324.1553.



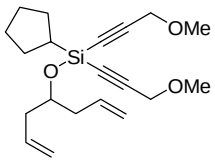
Silyl ether 7n: (87%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.78 – 7.69 (4H, m), 7.54 – 7.47 (2H, m), 7.44 – 7.17 (9H, m), 4.17 (2H, s), 3.37 (3H, s), 1.69 (6H, s); ^{13}C NMR ($CDCl_3$,

75.4 MHz) δ 149.5, 135.7, 134.7, 130.2, 128.1, 128.0, 126.6, 124.8, 105.0, 88.5, 77.9, 60.6, 57.8, 32.4; HRMS (ESI) calcd for $C_{26}H_{30}O_2Si$ $[M+Na]^+$ 409.1964, found 409.1982.

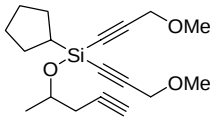


Silyl ether 7o: (47%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.78 – 7.68 (4H, m), 7.49 – 7.23 (6H, m), 5.90 (1H, dddd, *J* = 17.0, 10.4, 8.1, 6.1 Hz), 5.40 (1H, bs), 4.94 (1H, d, *J* = 10.4 Hz), 4.83 (1H, d, *J* = 17.0 Hz), 4.22 (2H, s), 3.44 (3H, s), 2.49 (1H, dd, *J* = 14.8, 6.2 Hz), 2.40 – 2.26 (3H, m), 1.88 (1H, t, *J* = 5.0 Hz), 1.65 (3H, d, *J* = 1.6 Hz), 1.34 (1H, d, *J* = 8.8 Hz), 1.27 (3H, s), 0.98 (3H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 146.0, 135.7, 135.6, 135.1, 134.5, 134.3, 130.2, 130.1, 127.9, 127.7, 122.5, 117.0, 104.8, 89.4, 82.5, 60.7, 57.9, 51.1, 47.7, 44.6, 42.9, 35.0, 27.5, 24.1, 22.8; HRMS (EI) calcd for $C_{29}H_{34}O_2Si$ $[M–C_3H_5]^{\bullet+}$ 401.1937, found 401.1924.

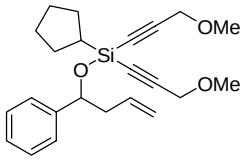
General Procedure for Synthesis of Silyl Ethers 8a–8e from Secondary Alcohols: The following procedure for **8a** is representative. Silane **6** (150 mg, 0.49 mmol) and 1,6-heptadien-4-ol (22 mg, 0.20 mmol) were dissolved in hexanes (1.5 mL). Sodium hydride (60% dispersion in mineral oil, 1 mg, 0.02 mmol) was added, and the reaction was stirred at room temperature for 10 minutes. The solution was filtered through a small plug of Celite, and evaporation of the solvent yielded a yellow residue. Flash chromatography of this residue on silica with 5% ether/hexanes gave **8a** (65 mg, 94%) as a colorless oil.



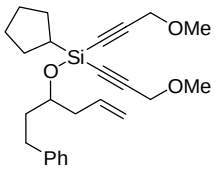
Silyl ether 8a: (94%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.86 (2H, ddt, *J* = 17.0, 10.2, 7.1 Hz), 5.11 – 5.02 (4H, m), 4.14 (4H, s), 4.07 (1H, pentet, *J* = 5.9 Hz), 3.39 (6H, s), 2.36 – 2.29 (4H, m), 1.89 – 1.73 (2H, m), 1.70 – 1.47 (6H, m), 1.23 – 1.09 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 134.9, 117.2, 102.6, 86.6, 73.7, 60.4, 57.8, 40.9, 27.2, 25.5; HRMS (ESI) calcd for $C_{20}H_{30}O_3Si$ $[M+Na]^+$ 369.1862, found 369.1862.



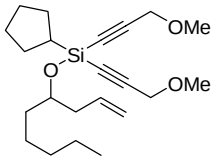
Silyl ether 8b: (63%, colorless oil) ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.32 – 4.19 (1H, m), 4.14 (4H, s), 3.40 (6H, s), 2.52 (1H, ddd, *J* = 16.5, 5.0, 2.7 Hz), 2.33 (1H, ddd, *J* = 16.5, 7.6, 2.7 Hz), 1.99 (1H, t, *J* = 2.7 Hz), 1.89 – 1.74 (2H, m), 1.70 – 1.45 (6H, m), 1.35 (3H, d, *J* = 6.1 Hz), 1.26 – 1.08 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 102.7, 102.6, 86.4, 86.2, 81.3, 70.2, 69.3, 60.4, 57.8, 28.8, 27.14, 27.11, 25.4, 22.5; HRMS (ESI) calcd for $C_{18}H_{26}O_3Si$ $[M+Na]^+$ 341.1549, found 341.1542.



Silyl ether 8c: (91%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.37 – 7.18 (5H, m), 5.79 (1H, ddt, *J* = 17.1, 10.3, 7.0 Hz), 5.08 – 4.97 (3H, m), 4.13 (2H, s), 4.00 (2H, s), 3.38 (3H, s), 3.24 (3H, s), 2.66 – 2.45 (2H, m), 1.83 – 1.68 (2H, m), 1.66 – 1.44 (6H, m), 1.19 – 1.04 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 143.5, 134.8, 128.1, 127.3, 126.3, 117.3, 102.8, 102.7, 86.4, 86.2, 76.2, 60.4, 60.3, 57.8, 57.6, 44.5, 27.2, 27.1, 25.4; HRMS (ESI) calcd for $C_{23}H_{30}O_3Si$ $[M+Na]^+$ 405.1862, found 405.1870.

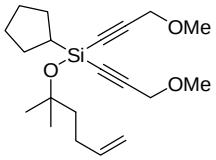


Silyl ether 8d: (83%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31 – 7.12 (5H, m), 5.85 (1H, ddt, *J* = 17.1, 10.1, 7.0 Hz), 5.12 – 5.01 (2H, m), 4.13 (2H, s), 4.12 (2H, s), 4.10 (1H, pentet, *J* = 5.9 Hz), 3.38 (3H, s), 3.36 (3H, s), 2.87 – 2.74 (1H, m), 2.71 – 2.58 (1H, m), 2.47 – 2.30 (2H, m), 1.93 – 1.75 (4H, m), 1.72 – 1.48 (6H, m), 1.27 – 1.11 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.7, 134.8, 128.6, 128.4, 125.8, 117.3, 102.7, 86.7, 73.8, 60.4, 57.7, 41.6, 38.2, 32.0, 27.2, 25.6; HRMS (ESI) calcd for $C_{25}H_{34}O_3Si$ $[M+Na]^+$ 433.2175, found 433.2167.

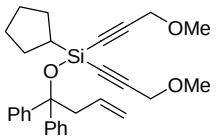


Silyl ether 8e: (93%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.85 (1H, ddt, *J* = 17.2, 10.2, 7.1), 5.11 – 4.99 (2H, m), 4.134 (2H, s), 4.131 (2H, s), 4.01 (1H, pentet, *J* = 5.9), 3.391 (3H, s), 3.390 (3H, s), 2.37 – 2.28 (2H, m), 1.89 – 1.74 (2H, m), 1.71 – 1.09 (15H, m), 0.94 – 0.83 (3H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 135.2, 116.9, 102.5, 102.4, 86.8, 74.3, 60.4, 57.7, 41.6, 36.3, 32.0, 27.2, 25.6, 25.2, 22.8, 14.2; HRMS (ESI) calcd for $C_{22}H_{36}O_3Si$ $[M+Na]^+$ 399.2331, found 399.2343.

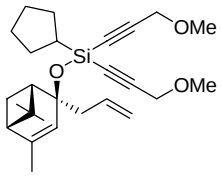
General Procedure for Synthesis of Silyl Ethers 8f–8h from Tertiary Alcohols: The following procedure for **8f** is representative. Silane **6** (200 mg, 0.66 mmol) and 2-methyl-5-hexen-2-ol (75 mg, 0.66 mmol) were combined in hexanes (3 mL), and sodium hydride (60% dispersion in mineral oil, 3 mg, 0.07 mmol) was added. The reaction was stirred at 50 ºC until complete by TLC (approximately 1 hour). The solution was then filtered through Celite. Evaporation of the solvent gave a yellow oil that was chromatographed on silica gel with 4% to 7% ether/hexanes to obtain 180 mg (78%) of a colorless oil.



Silyl ether 8f: (78%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.84 (1H, ddt, *J* = 16.9, 10.2, 6.6 Hz), 5.03 (1H, ddt, *J* = 16.9, 2.0, 1.7 Hz), 4.94 (1H, ddt, *J* = 10.2, 2.0, 1.1 Hz), 4.13 (4H, s), 3.39 (6H, s), 2.20 – 2.09 (2H, m), 1.87 – 1.72 (2H, m), 1.70 – 1.45 (8H, m), 1.38 (6H, s), 1.19 – 1.04 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 139.5, 114.1, 101.6, 88.6, 76.3, 60.5, 57.7, 43.4, 29.4, 28.8, 27.2, 26.5; HRMS (ESI) calcd for $C_{20}H_{32}O_3Si$ $[M+Na]^+$ 371.2018, found 371.2022.

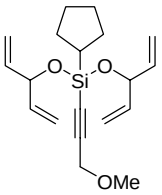


Silyl ether 8g: (87%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39 – 7.15 (10H, m), 5.72 (1H, ddt, *J* = 17.1, 10.3, 6.8 Hz), 5.03 – 4.89 (2H, m), 3.99 (4H, s), 3.35 (2H, d, *J* = 6.8 Hz), 3.31 (6H, s), 1.85 – 1.70 (2H, m), 1.67 – 1.45 (6H, m), 1.12 – 0.98 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 146.3, 134.0, 127.8, 127.4, 127.0, 118.0, 102.0, 87.3, 82.4, 60.3, 57.7, 45.2, 27.25, 27.22, 26.5; HRMS (ESI) calcd for $C_{29}H_{34}O_3Si$ $[M+Na]^+$ 481.2175, found 481.2186.

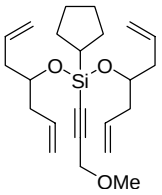


Silyl ether 8h: (92%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.99 (1H, dddd, *J* = 16.8, 10.4, 8.3, 6.0 Hz), 5.55 (1H, bs), 5.09 – 4.94 (2H, m), 4.14 (2H, s), 4.13 (2H, s), 3.40 (3H, s), 3.38 (3H, s), 2.82 (1H, dd, *J* = 14.5, 5.9 Hz), 2.48 – 2.32 (2H, m), 2.25 (1H, td, *J* = 5.9, 2.0 Hz), 1.92 (1H, t, *J* = 4.9 Hz), 1.86 – 1.75 (2H, m), 1.72 (3H, d, *J* = 1.5 Hz), 1.67 – 1.46 (6H, m), 1.36 (1H, d, *J* = 9.1 Hz), 1.32 (3H, s), 1.18 – 1.06 (1H, m), 1.07 (3H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 146.2, 134.4, 122.2, 117.1, 102.1, 88.8, 88.7, 82.3, 60.50, 60.46, 57.8, 57.7, 50.7, 47.8, 44.2, 42.8, 35.0, 27.5, 27.4, 27.2, 26.4, 23.8, 22.9; HRMS (EI) calcd for $C_{26}H_{38}O_3Si$ $[M - C_3H_5]^{\bullet+}$ 385.2199, found 385.2196.

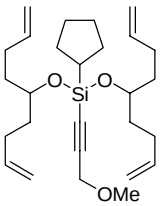
General Procedure for Synthesis of Symmetrical Silaketals 9a–9g: The following procedure for **9b** is representative. Silane **6** (100 mg, 0.33 mmol) and 1,6-heptadien-4-ol (74 mg, 0.66 mmol) were dissolved in hexanes (3 mL). Sodium hydride (60% dispersion in mineral oil, 3 mg, 0.07 mmol) was added, and the reaction was stirred at room temperature for 30 minutes. The solution was then filtered through a short plug of Celite, and evaporation of the solvent afforded a yellow residue. Flash chromatography of the crude product on silica gel with 1.5% ether/hexanes yielded 94 mg (73%) of **9b** as a colorless oil.



Silaketal 9a: The general procedure was followed, apart from the use of only 1.5 equivalents of alcohol (67%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.85 (4H, m), 5.25 (4H, dt, *J* = 17.2, 1.5 Hz), 5.10 (4H, dt, *J* = 10.3, 1.5 Hz), 4.95 – 4.88 (2H, m), 4.12 (2H, s), 3.38 (3H, s), 1.89 – 1.70 (2H, m), 1.69 – 1.44 (6H, m), 1.20 – 1.03 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 139.3, 114.8, 114.7, 101.9, 85.6, 75.3, 60.3, 57.6, 27.2, 27.1, 24.4; HRMS (ESI) calcd for $C_{19}H_{28}O_3Si$ $[M+Na]^+$ 355.1705, found 355.1706.

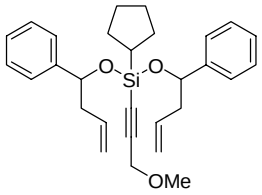


Silaketal 9b: (73%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.93 – 5.77 (4H, m), 5.11 – 5.00 (8H, m), 4.13 (2H, s), 4.08 (2H, pentet, *J* = 5.9 Hz), 3.39 (3H, s), 2.39 – 2.22 (8H, m), 1.85 – 1.69 (2H, m), 1.65 – 1.43 (6H, m), 1.11 – 0.97 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 135.0, 117.2, 101.7, 86.3, 72.6, 60.4, 57.7, 41.1, 41.0, 27.3, 27.1, 24.7; HRMS (EI) calcd for $C_{23}H_{36}O_3Si$ $[MH]^{\bullet+}$ 389.2512, found 389.2503.

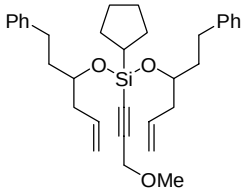


Silaketal 9c: (80%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.83 (4H, ddt, *J* = 17.0, 10.4, 6.7 Hz), 5.02 (4H, ddt, *J* = 17.0, 2.0, 1.7 Hz), 4.98 – 4.92 (4H, m), 4.12 (2H, s), 4.01 (2H, pentet, *J* = 5.8 Hz), 3.38 (3H, s), 2.24 – 2.02 (8H, m), 1.85 – 1.71 (2H, m), 1.69 – 1.45 (14H, m), 1.11 – 0.95 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 138.9, 114.5, 101.5, 86.8, 72.7, 60.4, 57.6, 36.1,

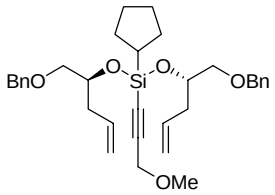
36.0, 29.73, 29.67, 27.4, 27.2, 24.9; HRMS (ESI) calcd for $C_{27}H_{44}O_3Si$ $[M+Na]^+$ 467.2957, found 467.2938.



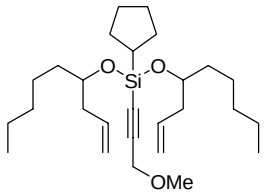
Silaketal 9d: (82%, colorless oil, diastereomeric mixture) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36 – 7.09 (10H, m), 5.85 – 5.46 (2H, m), 5.08 – 4.82 (4H, m), 4.80 (1H, t, *J* = 6.4), 4.72 (1H, t, *J* = 6.4), 4.12 (0.42H, s), 4.00 (1.02H, s), 3.93 (0.56H, s), 3.37 (0.63H, s), 3.25 (1.53H, s), 3.18 (0.84H, s), 2.65 – 2.20 (4H, m), 1.71 – 1.28 (8H, m), 1.04 – 0.83 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 144.0, 143.8, 134.9, 134.8, 134.7, 134.6, 128.2, 128.1, 128.0, 127.30, 127.25, 127.17, 127.11, 126.35, 126.32, 126.26, 126.21, 117.3, 117.2, 117.1, 102.1, 102.0, 101.9, 85.9, 85.8, 75.6, 75.33, 75.27, 60.4, 60.2, 60.1, 57.7, 57.5, 57.4, 44.8, 44.6, 27.2, 27.1, 26.9, 24.4; HRMS (ESI) calcd for $C_{29}H_{36}O_3Si$ $[M+Na]^+$ 483.2331, found 483.2313.



Silaketal 9e: (64%, colorless oil, diastereomeric mixture) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30 – 7.12 (10H, m), 5.94 – 5.77 (2H, m), 5.13 – 4.99 (4H, m), 4.16 – 4.07 (4H, m), 3.363 (0.75H, s), 3.356 (1.50H, s), 3.351 (0.75H, s), 2.85 – 2.57 (4H, m), 2.48 – 2.30 (4H, m), 1.92 – 1.73 (6H, m), 1.69 – 1.46 (6H, m), 1.15 – 1.00 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.7, 134.9, 128.6, 128.5, 125.8, 117.3, 101.8, 86.62, 86.56, 86.49, 72.7, 60.3, 57.7, 41.7, 41.6, 38.3, 31.9, 27.4, 27.2, 24.9; HRMS (ESI) calcd for $C_{33}H_{44}O_3Si$ $[M+Na]^+$ 539.2957, found 539.2983.

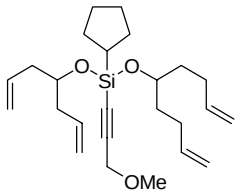


Silaketal 9f: The general procedure was followed, apart from the use of only 1.5 equivalents of alcohol (67%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.37 – 7.22 (10H, m), 5.93 – 5.75 (2H, m), 5.13 – 4.98 (4H, m), 4.53 – 4.49 (4H, m), 4.22 (2H, sextet, *J* = 5.6), 4.07 (2H, s), 3.55 – 3.39 (4H, m), 3.35 (3H, s), 2.51 – 2.23 (4H, m), 1.82 – 1.67 (2H, m), 1.65 – 1.39 (6H, m), 1.14 – 0.99 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 138.7, 134.8, 128.4, 127.7, 127.6, 117.31, 117.26, 101.7, 86.0, 73.6, 73.5, 73.4, 72.0, 71.9, 60.3, 57.6, 38.9, 27.3, 27.2, 27.1, 24.6; HRMS (ESI) calcd for $C_{33}H_{44}O_5Si$ $[M+Na]^+$ 571.2856, found 571.2866.

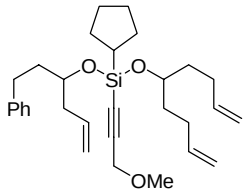


Silaketal 9g: (71%, colorless oil, diastereomeric mixture) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.85 (2H, ddt, *J* = 17.2, 10.4, 7.2 Hz), 5.10 – 4.98 (4H, m), 4.12 (2H, s), 4.01 (2H, pentet, *J* = 5.5 Hz), 3.39 (3H, s), 2.36 – 2.25 (4H, m), 1.84 – 1.69 (2H, m), 1.66 – 1.19 (22H, m), 1.10 – 0.97 (1H, m), 0.94 – 0.83 (6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 135.4, 116.81, 116.77, 101.3, 86.8, 73.1, 60.4, 57.6, 41.7, 41.6, 36.5, 36.4, 32.1, 27.4, 27.1, 25.13, 25.08, 24.9, 22.8, 14.2; HRMS (ESI) calcd for $C_{27}H_{48}O_3Si$ $[M+Na]^+$ 471.3270, found 471.3292.

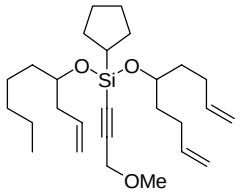
General Procedure for Synthesis of Unsymmetrical Silaketals 10a–10f: The following procedure for **10a** is representative. Silyl ether **8a** (60 mg, 0.17 mmol) and 1,8-nonadien-5-ol (24 mg, 0.17 mmol) were combined in hexanes (1 mL). Sodium hydride (60% dispersion in mineral oil, 1 mg, 0.02 mmol) was added. After stirring for 20 minutes at room temperature, the solution was filtered through Celite. Removal of the solvent gave a yellow residue. Chromatography on silica with 1.5% ether/hexanes afforded **10a** (55 mg, 77%) as a colorless oil.



Silaketal 10a: (77%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.94 – 5.75 (4H, m), 5.12 – 4.90 (8H, m), 4.13 (2H, s), 4.11 – 3.96 (2H, m), 3.39 (3H, s), 2.38 – 2.24 (4H, m), 2.21 – 2.04 (4H, m), 1.84 – 1.71 (2H, m), 1.69 – 1.44 (10H, m), 1.11 – 0.96 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 139.0, 135.0, 117.2, 114.5, 101.6, 86.5, 72.7, 72.6, 60.4, 57.7, 41.4, 41.0, 36.1, 36.0, 29.7, 27.3, 27.1, 24.8; HRMS (ESI) calcd for $C_{25}H_{40}O_3Si$ $[M+Na]^+$ 439.2644, found 439.2649.

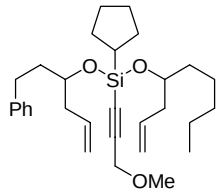


Silaketal 10b: (66%, colorless oil, diastereomeric mixture) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31 – 7.13 (5H, m), 5.93 – 5.74 (3H, m), 5.12 – 4.90 (6H, m), 4.14 – 3.98 (4H, m), 3.38 (1.5H, bs), 3.37 (1.5H, bs), 2.83 – 2.56 (2H, m), 2.46 – 2.29 (2H, m), 2.25 – 2.03 (4H, m), 1.88 – 1.72 (4H, m), 1.69 – 1.45 (10H, m), 1.13 – 0.99 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.7, 138.9, 134.9, 128.6, 128.5, 125.8, 117.2, 114.5, 101.7, 86.7, 86.6, 72.7, 60.4, 57.7, 41.7, 41.6, 38.3, 36.1, 36.0, 31.9, 29.8, 29.7, 27.4, 27.2, 24.9; HRMS (ESI) calcd for $C_{30}H_{44}O_3Si$ $[M+Na]^+$ 503.2957, found 503.2935.

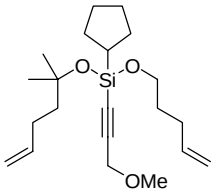


Silaketal 10c: (66%, colorless oil, diastereomeric mixture) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.92 – 5.75 (3H, m), 5.09 – 4.90 (6H, m), 4.12 (2H, s), 4.06 – 3.96 (2H, m), 3.39 (3H, s), 2.35 – 2.24 (2H, m), 2.22 – 2.03 (4H, m), 1.85 – 1.70 (2H, m), 1.68 – 1.20 (18H, m), 1.10 – 0.97 (1H, m), 0.93 – 0.84 (3H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 139.0, 135.3, 116.8, 114.4, 101.4, 86.8,

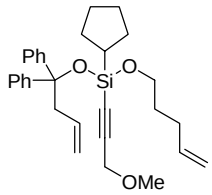
73.2, 72.7, 60.4, 57.6, 41.7, 41.6, 36.5, 36.4, 36.1, 36.0, 32.15, 32.12, 29.8, 29.7, 27.4, 27.2, 25.14, 25.06, 24.9, 22.9, 14.2; HRMS (ESI) calcd for $C_{27}H_{46}O_3Si$ $[M+Na]^+$ 469.3114, found 469.3091.



Silaketal 10d: (64%, colorless oil, diastereomeric mixture) ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.33 – 7.12 (5H, m), 5.85 (2H, ddt, *J* = 17.2, 10.2, 7.2 Hz), 5.13 – 4.98 (4H, m), 4.15 – 3.97 (4H, m), 3.40 – 3.36 (3H, m), 2.85 – 2.55 (2H, m), 2.43 – 2.25 (4H, m), 1.89 – 1.70 (4H, m), 1.68 – 1.19 (14H, m), 1.15 – 0.97 (1H, m), 0.94 – 0.81 (3H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.8, 135.3, 135.0, 128.6, 128.5, 125.8, 117.2, 117.1, 116.9, 101.6, 86.7, 86.6, 73.2, 72.6, 60.3, 57.6, 41.7, 41.6, 38.3, 38.2, 36.5, 36.4, 32.1, 31.9, 27.4, 27.2, 25.2, 25.1, 24.9, 22.8, 14.2; HRMS (ESI) calcd for $C_{30}H_{46}O_3Si$ $[M+Na]^+$ 505.3114, found 505.3093.

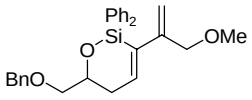


Silaketal 10e: (60%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.92 – 5.76 (2H, m), 5.08 – 4.89 (4H, m), 4.13 (2H, s), 3.83 – 3.76 (2H, m), 3.39 (3H, s), 2.20 – 2.08 (4H, m), 1.82 – 1.42 (12H, m), 1.34 (3H, s), 1.33 (3H, s), 1.07 – 0.94 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 139.5, 138.6, 114.7, 114.1, 100.7, 87.7, 75.3, 62.9, 60.4, 57.7, 43.7, 31.8, 30.2, 29.7, 29.6, 28.9, 27.4, 27.3, 27.1, 25.3; HRMS (ESI) calcd for $C_{21}H_{36}O_3Si$ $[M+Na]^+$ 387.2331, found 387.2348.

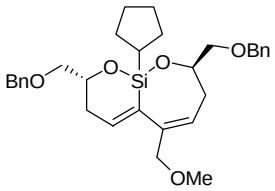


Silaketal 10f: (65%, colorless oil) ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.39 – 7.14 (10H, m), 5.86 – 5.60 (2H, m), 5.03 – 4.88 (4H, m), 4.01 (2H, s), 3.52 – 3.19 (4H, m), 3.33 (3H, s), 2.06 – 1.94 (2H, m), 1.80 – 1.40 (10H, m), 1.00 – 0.81 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 146.9, 146.7, 138.6, 134.2, 127.8, 127.3, 127.2, 126.93, 126.89, 117.8, 114.6, 101.1, 86.7, 81.7, 63.1, 60.3, 57.6, 45.6, 31.6, 30.1, 27.5, 27.20, 27.15, 25.4; HRMS (ESI) calcd for $C_{30}H_{38}O_3Si$ $[M+Na]^+$ 497.2488, found 497.2469.

General Procedure for Enyne Metathesis: The following procedure for the formation of **12** is representative. Silyl ether **7d** (100 mg, 0.230 mmol) was dissolved in dry CH_2Cl_2 (100 mL) in a 200 mL round bottom flask equipped with a reflux condenser. Nitrogen was bubbled through the solution for 20 minutes before adding catalyst **11** (15 mg, 0.018 mmol) in CH_2Cl_2 (5 mL). The reaction was then stirred at reflux until complete by TLC (approximately 4 hours). The solvent was removed to yield a brown residue that was flash chromatographed on silica with 5% to 15% ether/hexanes, affording 70 mg (70%) of **12** as a colorless, viscous oil.

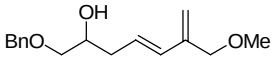


Siloxane 12: (70%, colorless oil) ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.77 – 7.62 (4H, m), 7.49 – 7.21 (11H, m), 7.01 (1H, t, *J* = 4.7 Hz), 5.08 (1H, bs), 4.98 (1H, bs), 4.53 (2H, s), 4.32 – 4.20 (1H, m), 4.01 (2H, s), 3.62 (1H, dd, *J* = 9.9, 5.0 Hz), 3.50 (1H, dd, *J* = 9.9, 5.9 Hz), 3.19 (3H, s), 2.58 – 2.49 (2H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 145.2, 143.7, 138.6, 135.5, 135.0, 134.7, 134.3, 130.4, 128.5, 128.1, 128.0, 127.8, 127.7, 116.6, 74.7, 74.5, 73.5, 70.4, 58.0, 33.3; HRMS (ESI) calcd for $C_{28}H_{30}O_3Si$ $[M+Na]^+$ 465.1862, found 465.1867.

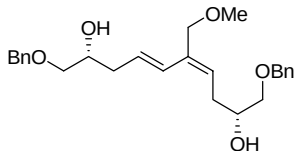


Siloxane 14: (83%, colorless oil, diastereomeric mixture) ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.37 – 7.22 (10H, m), 6.81 – 6.72 (1H, m), 5.68 (0.5H, t, *J* = 7.0 Hz), 5.59 – 5.52 (0.5H, m), 4.61 – 4.50 (4H, m), 4.37 – 4.25 (1H, m), 4.22 – 4.10 (1H, m), 4.08 – 3.90 (2H, m), 3.64 – 3.34 (4H, m), 3.320 (1.5H, s), 3.316 (1.5H, s), 2.67 – 2.15 (4H, m), 1.85 – 1.33 (8H, m), 1.14 – 0.96 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 143.0, 142.1, 140.8, 139.0, 138.62, 138.55, 136.9, 134.7, 134.4, 128.5, 127.9, 127.8, 127.7, 126.2, 124.7, 75.8, 74.6, 74.5, 74.3, 73.6, 73.5, 73.2, 72.8, 71.3, 70.7, 70.4, 58.0, 57.9, 37.0, 33.8, 33.6, 32.1, 27.5, 27.4, 27.2, 27.1, 27.0, 26.8, 24.6, 24.2; HRMS (ESI) calcd for $C_{31}H_{40}O_5Si$ $[M+Na]^+$ 543.2543, found 543.2558.

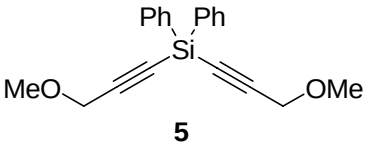
General Procedure for Protodesilylation: The following procedure for **13** is representative. Siloxane **12** (65 mg, 0.15 mmol) was taken up in dry THF (1 mL), and TBAF (1.0 M in THF, 0.45 mL, 0.45 mmol) was added. The solution was stirred at reflux for 45 minutes. It was then diluted with EtOAc and saturated NH_4Cl. The organic layer was removed, and the aqueous layer was extracted twice more with EtOAc. The combined organic layers were dried over $MgSO_4$ and evaporated to give a yellow oil. Flash chromatography of the crude product on silica with 20% to 40% EtOAc/hexanes yielded diene **13** (36 mg, 92%) as a thick, colorless oil.



Diene 13: (92%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40 – 7.26 (5H, m), 6.13 (1H, d, *J* = 15.9 Hz), 5.78 (1H, dt, *J* = 15.9, 7.3 Hz), 5.14 (1H, bs), 5.09 (1H, bs), 4.55 (2H, s), 4.07 (2H, s), 3.94 – 3.84 (1H, m), 3.51 (1H, dd, *J* = 9.5, 3.4 Hz), 3.38 (1H, dd, *J* = 9.5, 7.3 Hz), 3.33 (3H, s), 2.40 (1H, bs), 2.35 – 2.27 (2H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.1, 138.1, 132.7, 128.6, 128.0, 127.9, 126.3, 116.0, 74.0, 73.5, 73.0, 70.2, 58.2, 37.4; HRMS (ESI) calcd for $C_{16}H_{22}O_3$ $[M+Na]^+$ 285.1467, found 285.1469.



Diene 15: (68%, colorless oil) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40 – 7.27 (10H, m), 6.36 (1H, d, *J* = 15.8 Hz), 5.85 (1H, dt, *J* = 15.8, 7.6 Hz), 5.58 (1H, t, *J* = 7.5 Hz), 4.56 (2H, s), 4.55 (2H, s), 4.03 (2H, s), 3.95 – 3.84 (2H, m), 3.54 – 3.47 (2H, m), 3.38 (2H, dd, *J* = 9.5, 7.3 Hz), 3.28 (3H, s), 2.46 (2H, bs), 2.40 (2H, t, *J* = 7.1 Hz), 2.33 (2H, t, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 138.14, 138.07, 134.9, 128.6, 127.9, 127.4, 126.8, 75.0, 74.1, 74.0, 73.5, 70.4, 70.2, 57.8, 37.8, 31.6; HRMS (ESI) calcd for $C_{26}H_{34}O_5$ $[M+Na]^+$ 449.2304, found 449.2315.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Ph
Si
MeO
OMe

5

8
7
6
5
4
3
2
1
0


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105.690
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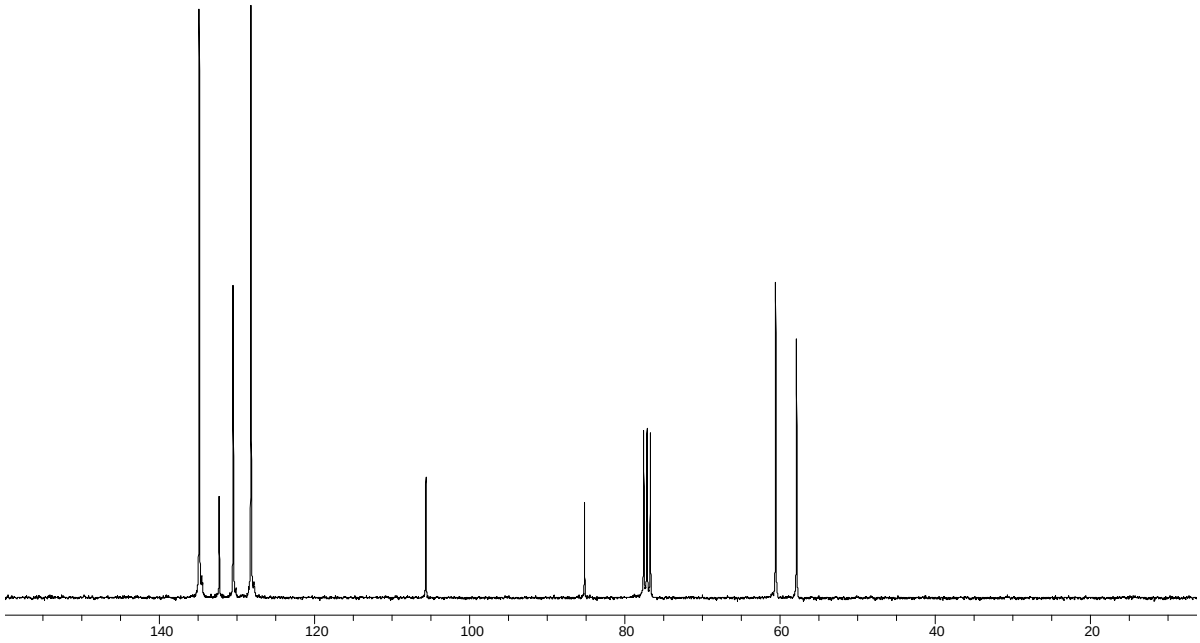
60.616
57.927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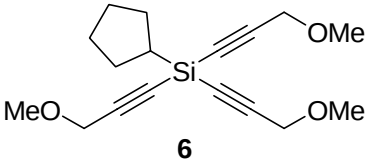
120
100
80
60
40
20


OMe
Si
MeO
OMe

6

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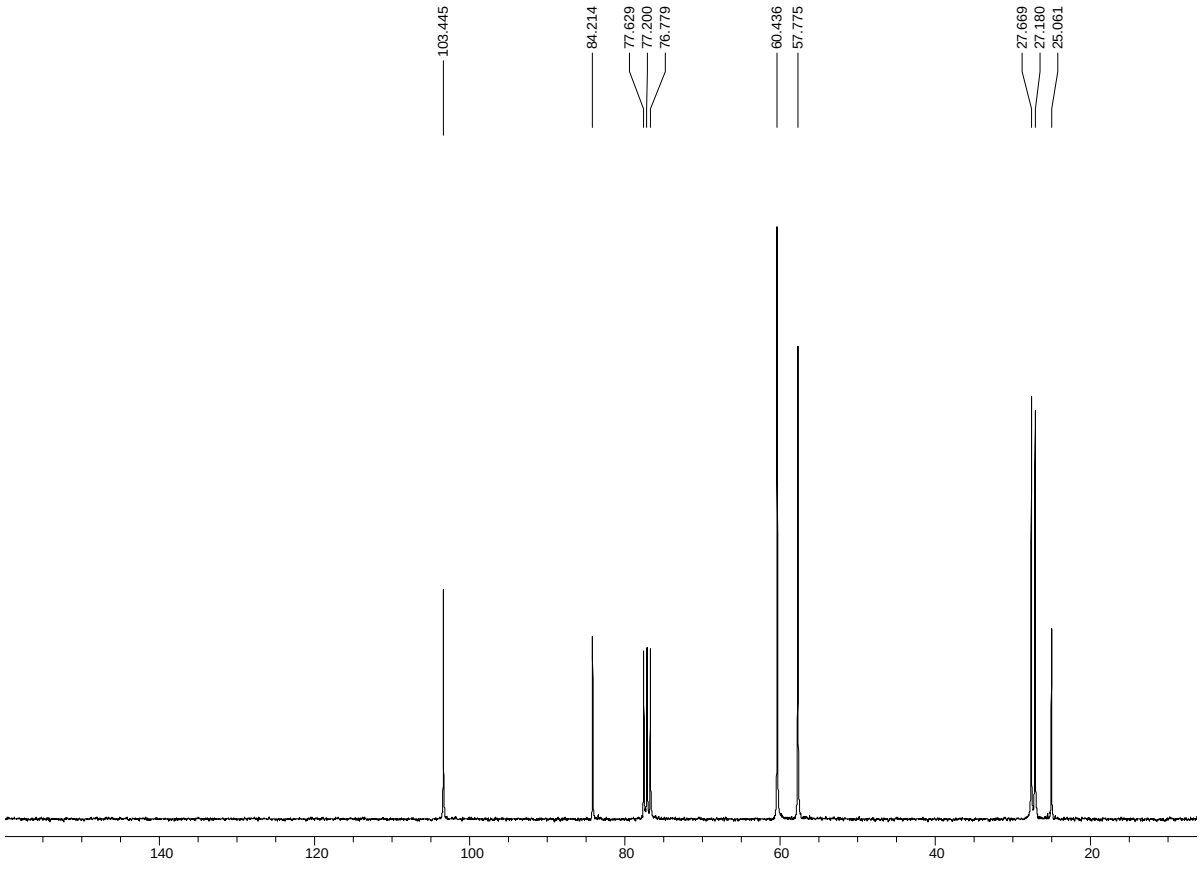
4
3
2
1
0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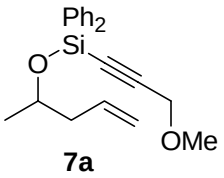
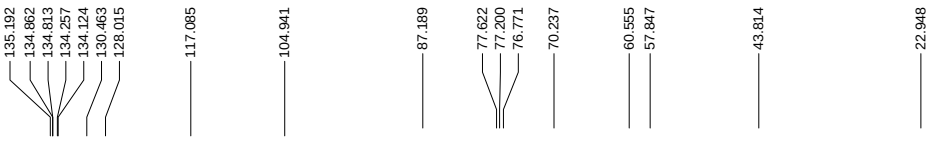
77.200
76.779
60.436
57.775
27.669
27.180
25.061
140
120
100
80
60
40
20


Ph2
Si
O
OMe

7a

8
7
6
5
4
3
2
1
0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130.463
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87.189
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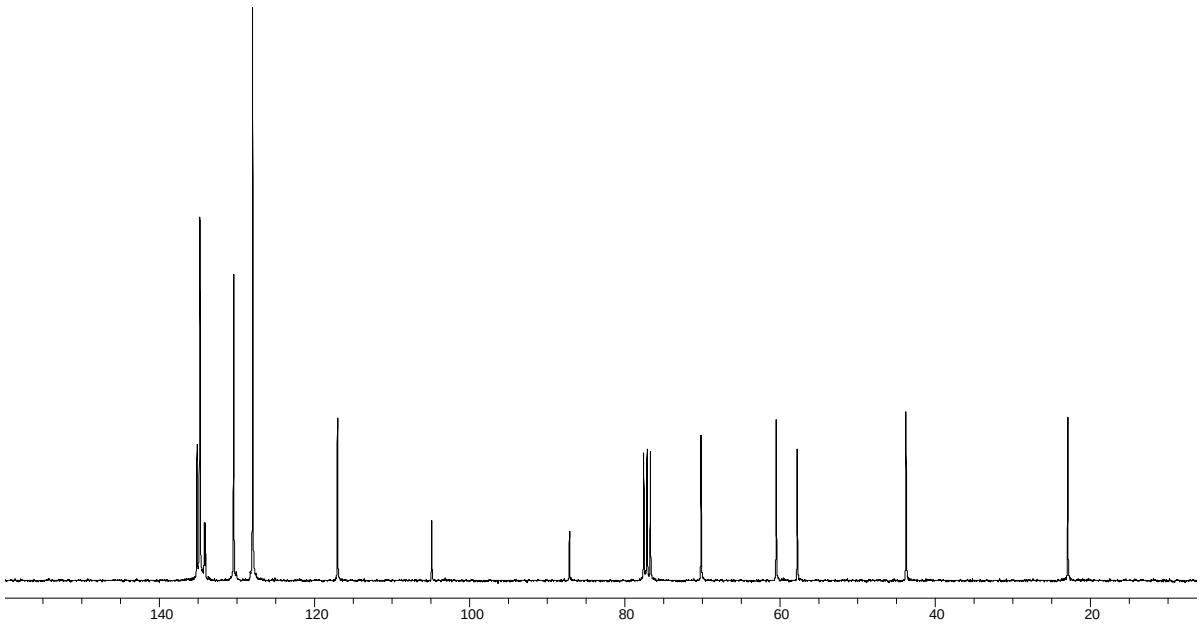
60.555
57.847
43.814
22.948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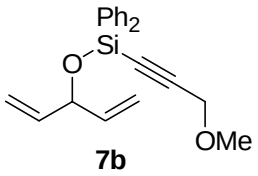
120
100
80
60
40
20


Ph2
Si
O
OMe

7b

8
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6
5
4
3
2
1
0


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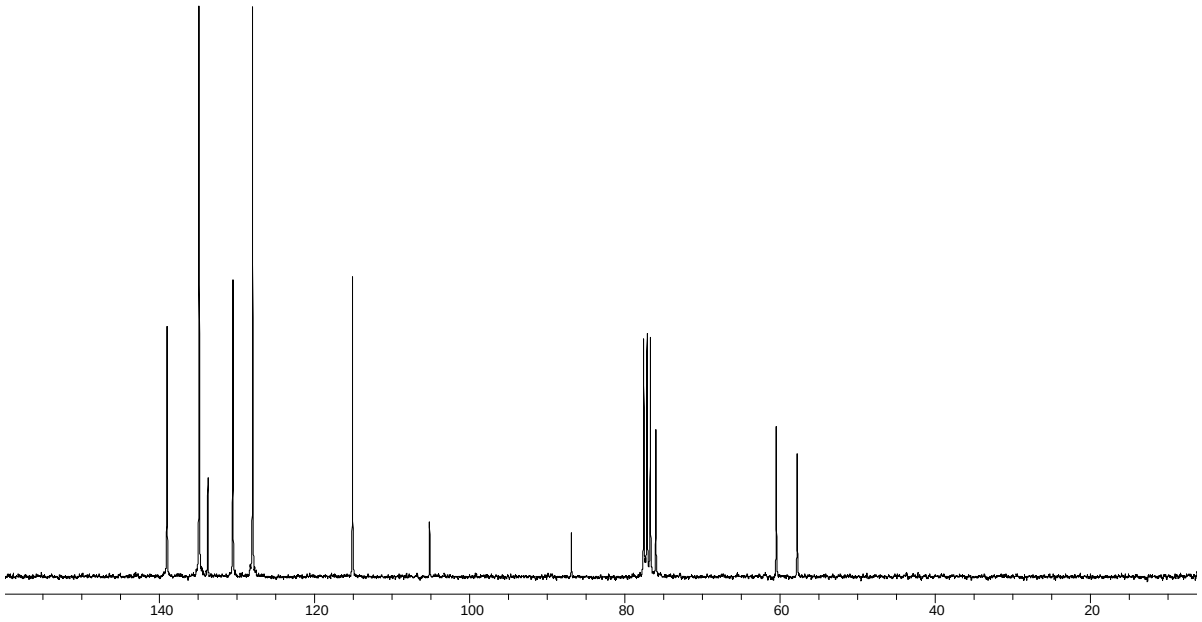
57.865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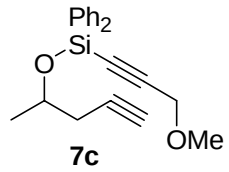
100
80
60
40
20


Ph2
Si
O
OMe

7c

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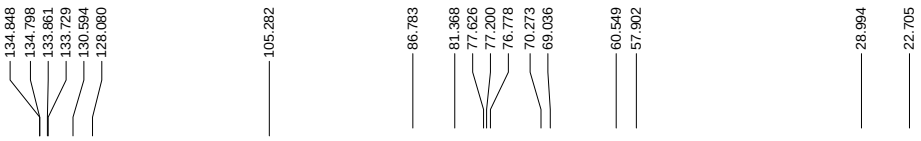
7
6
5
4
3
2
1
0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69.036
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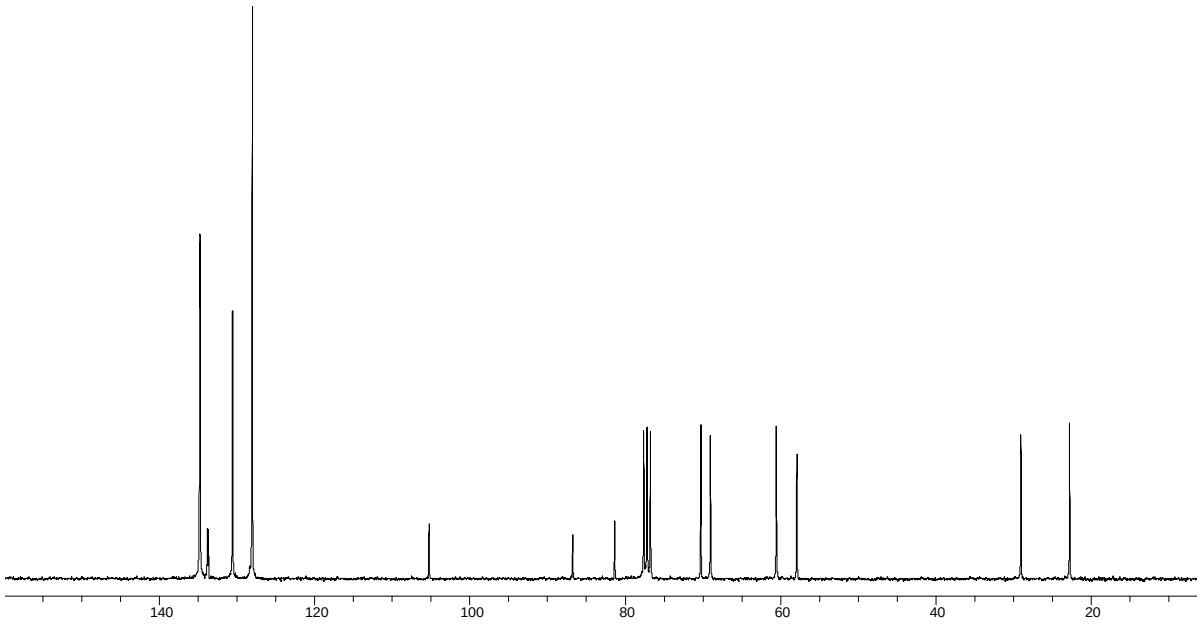
57.902
28.994
22.705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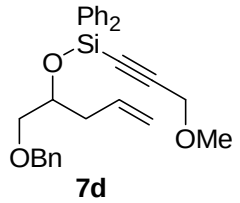
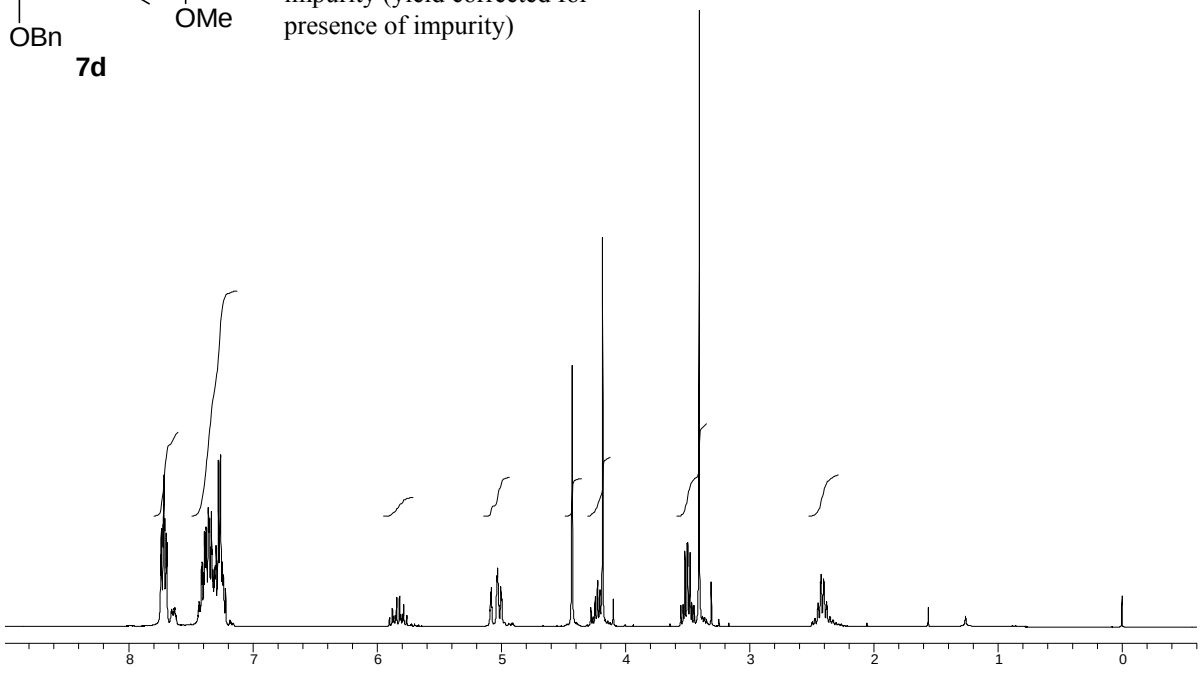
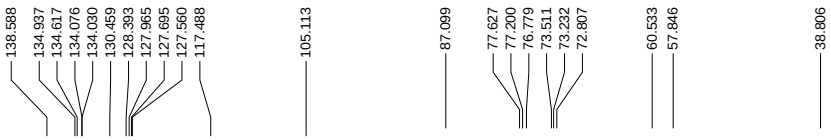
120
100
80
60
40
20

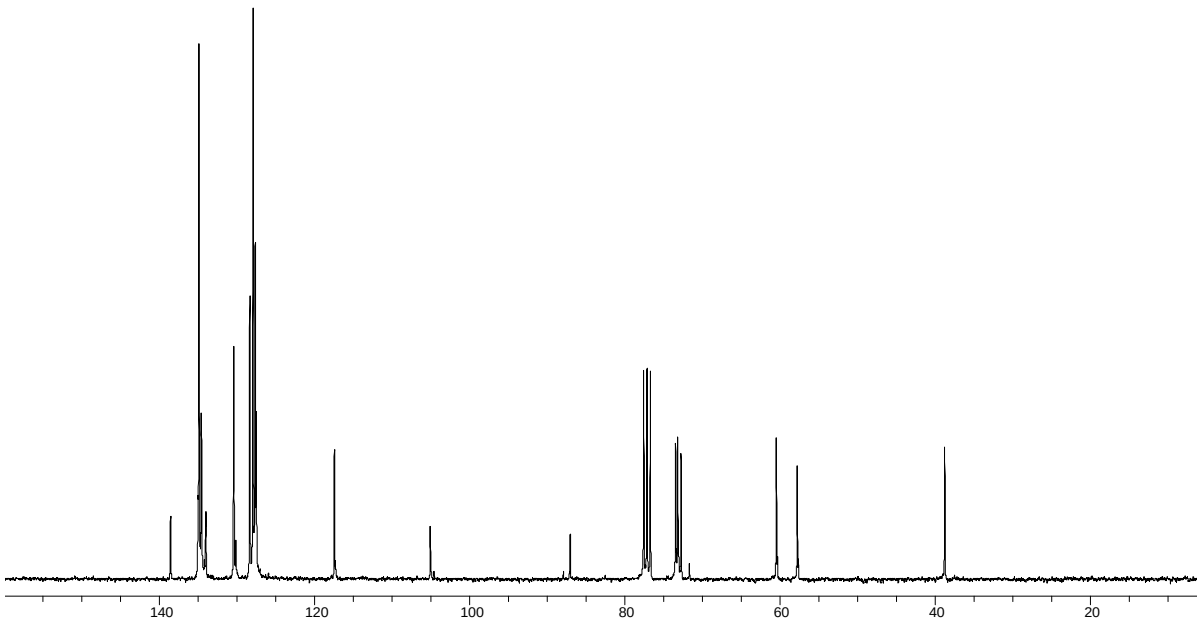


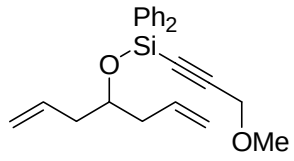
7d

Sample contaminated with ~5% of an inseparable, unknown impurity (yield corrected for presence of impurity)

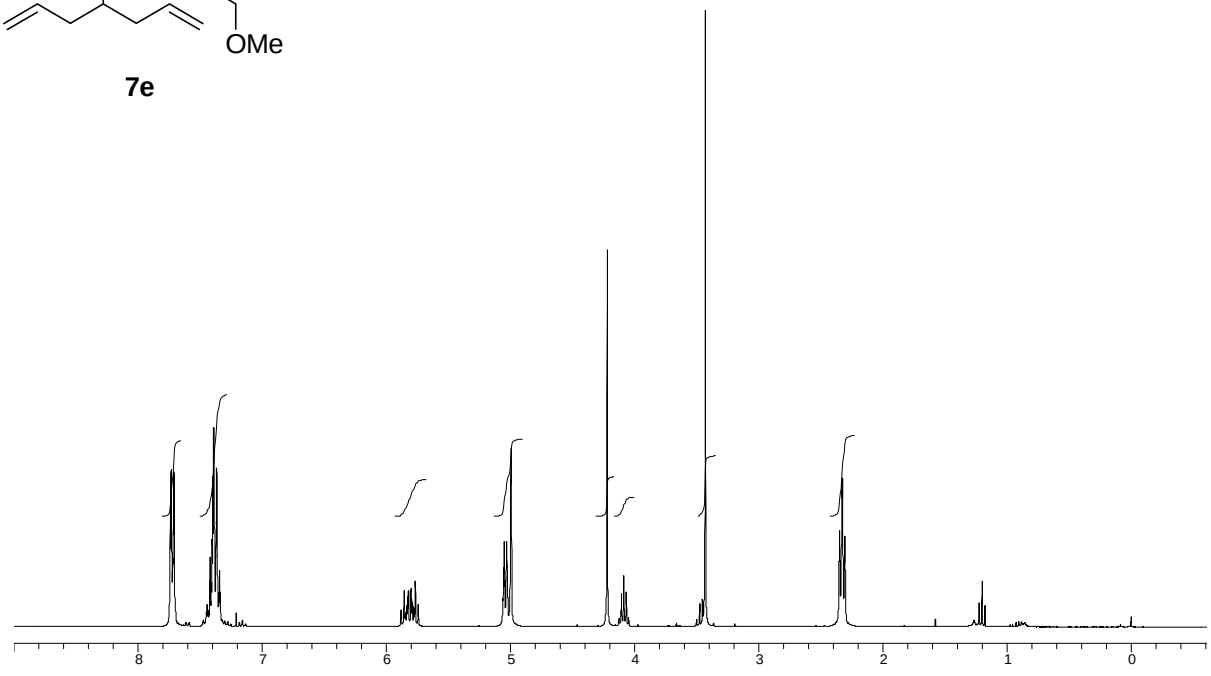







Ph2
Si
O
OMe

7e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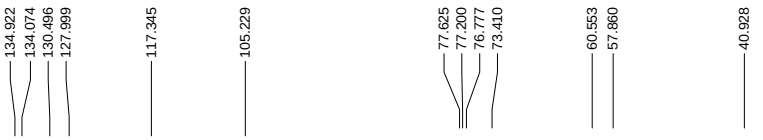
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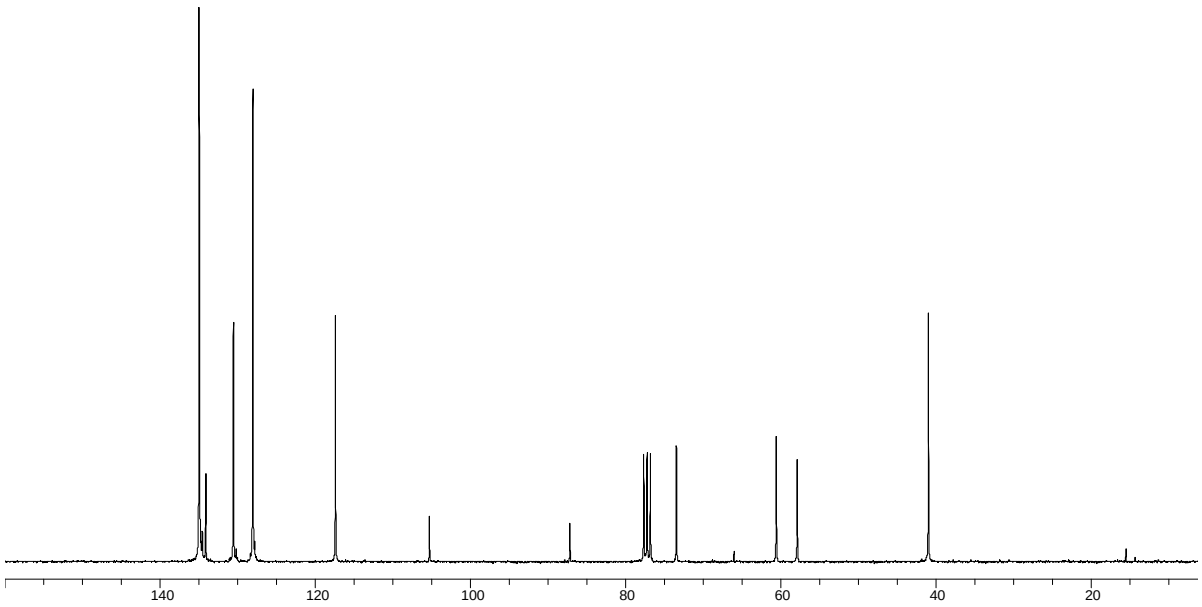
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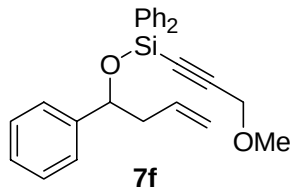
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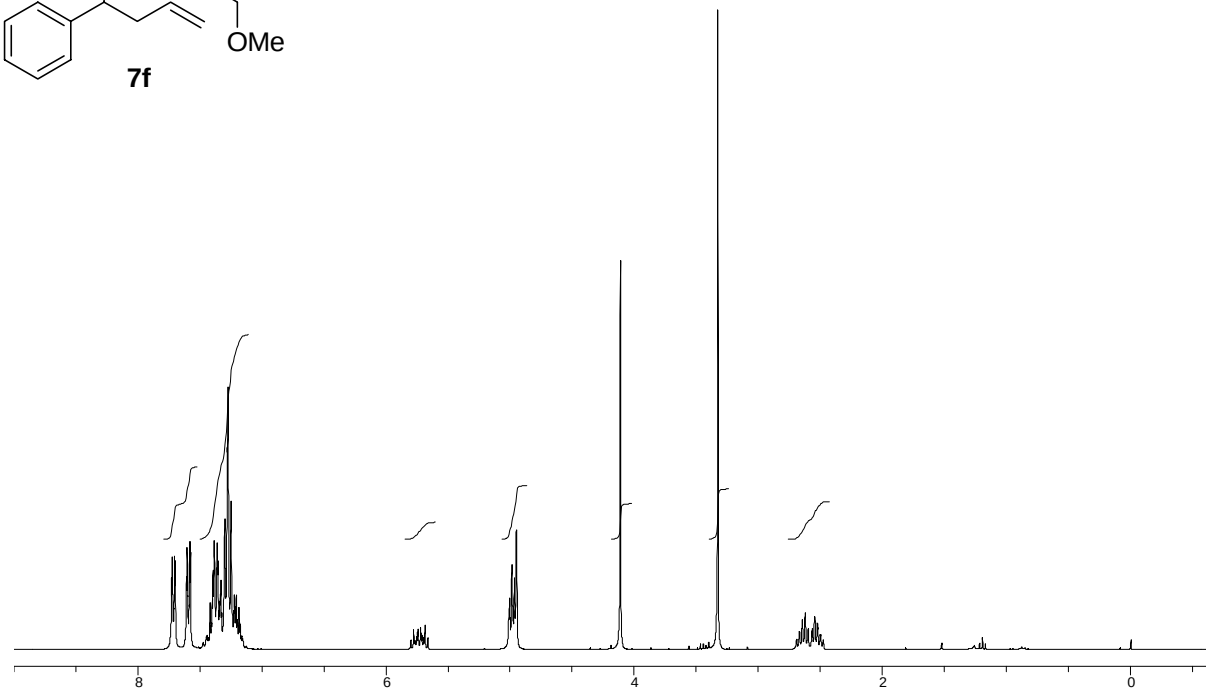
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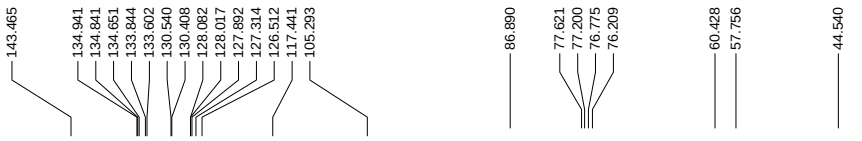
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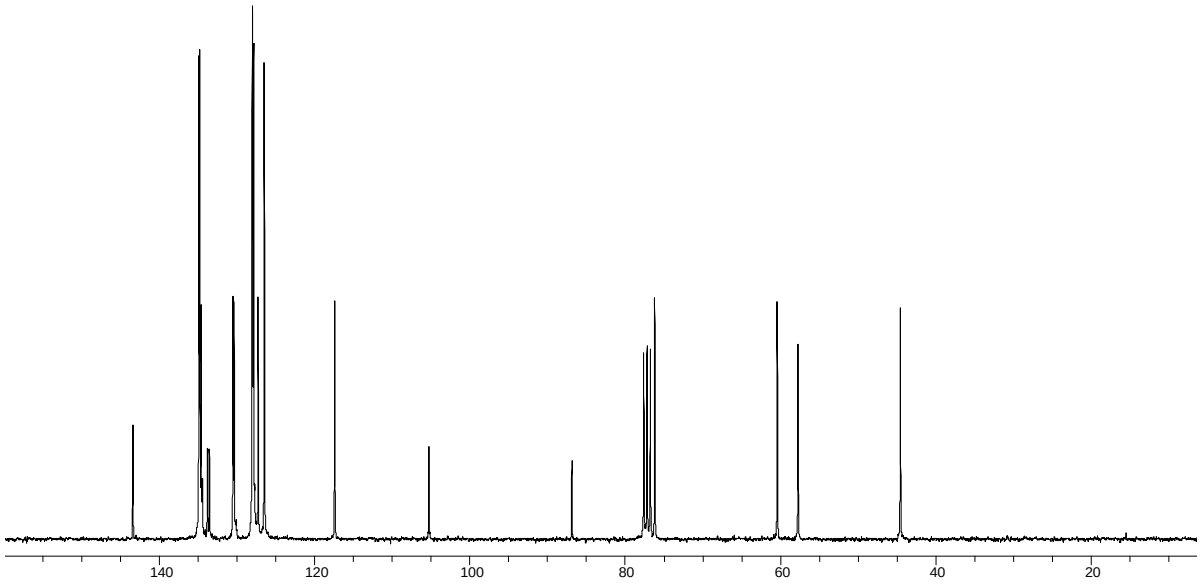
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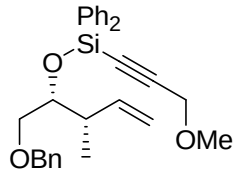
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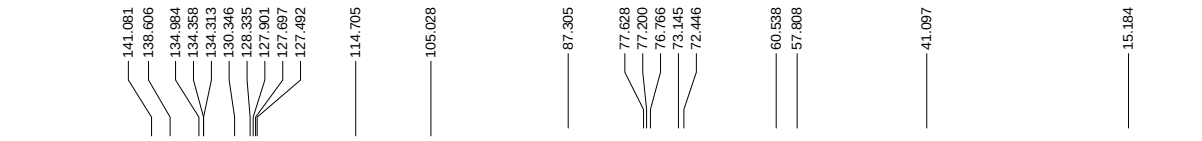
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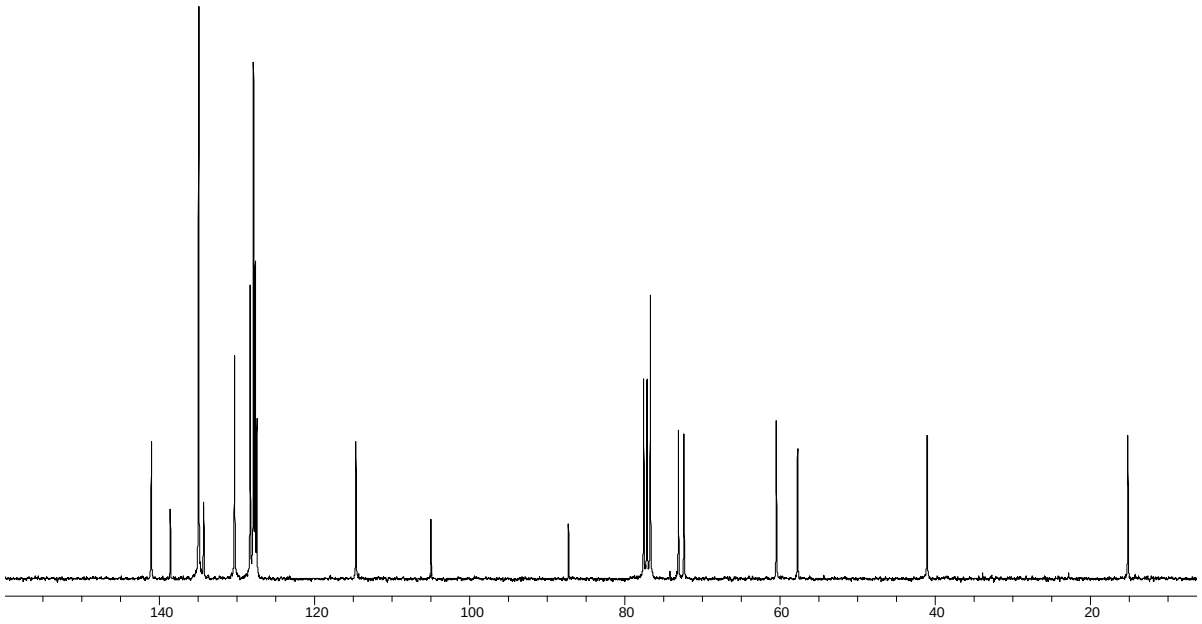
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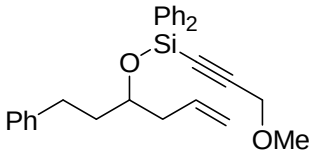
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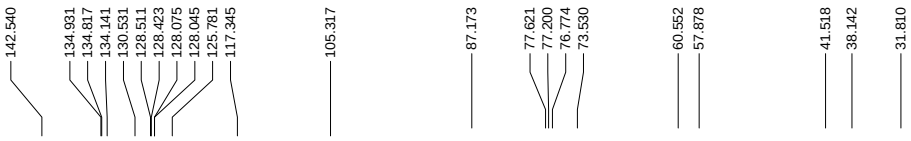
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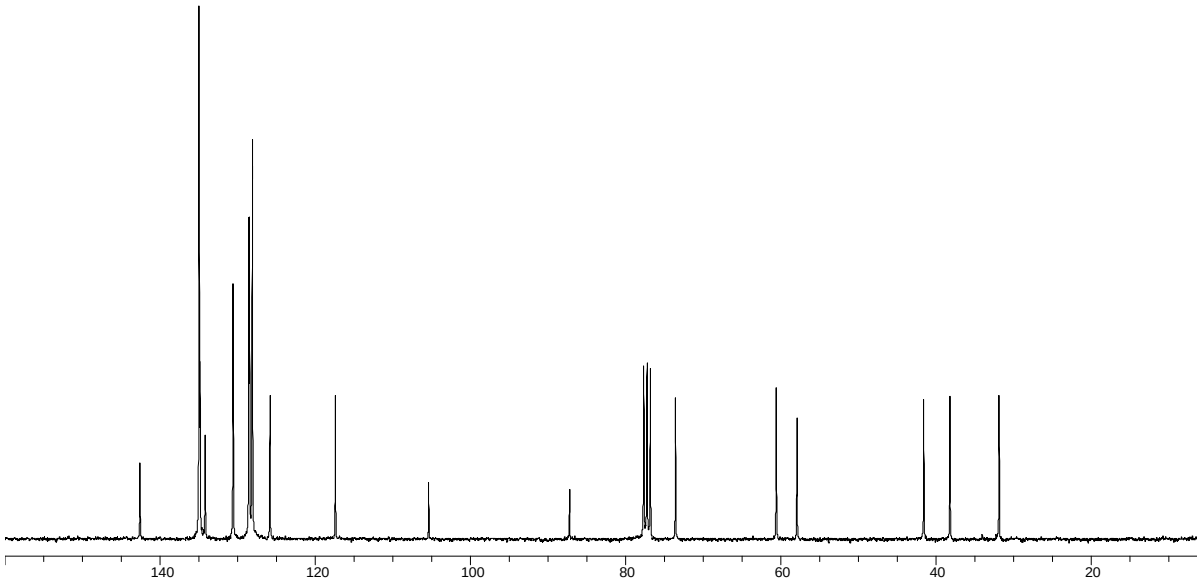
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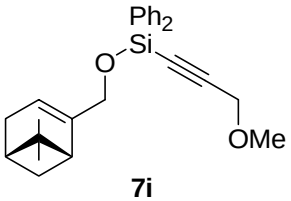
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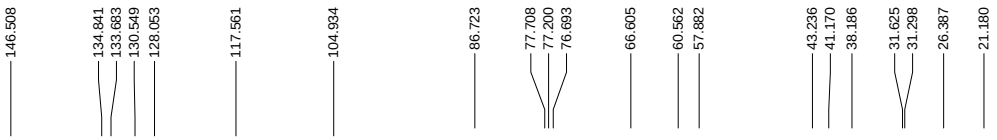
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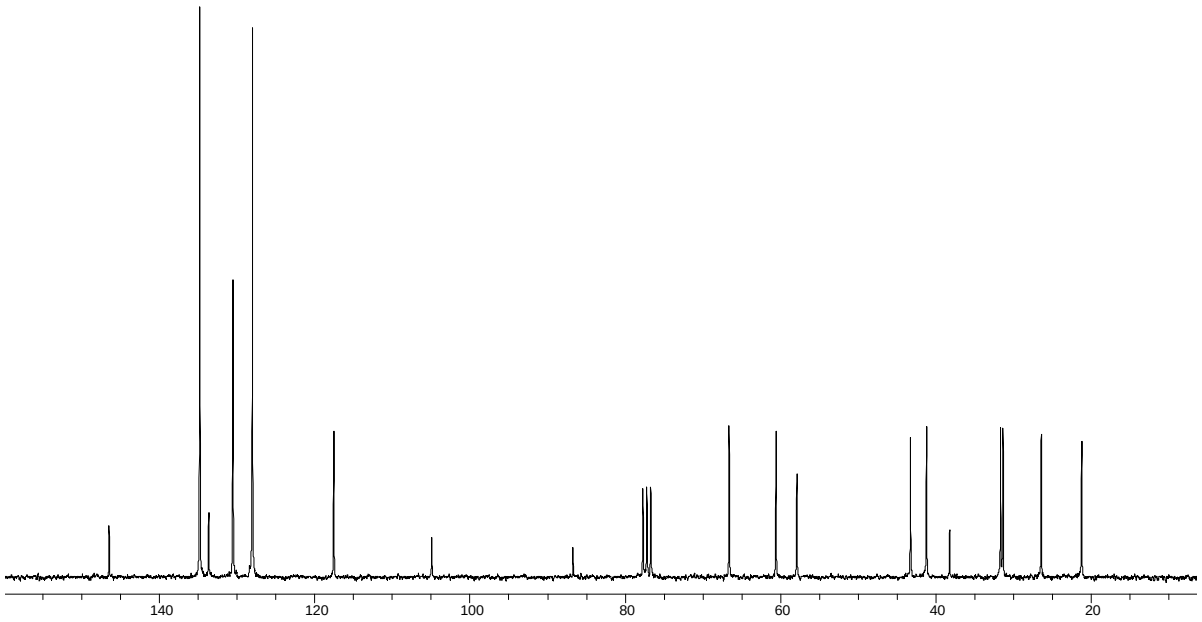
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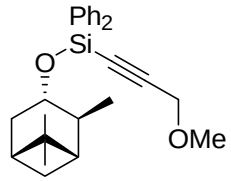
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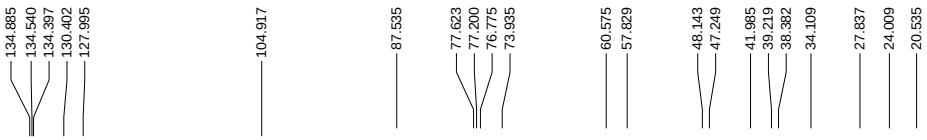
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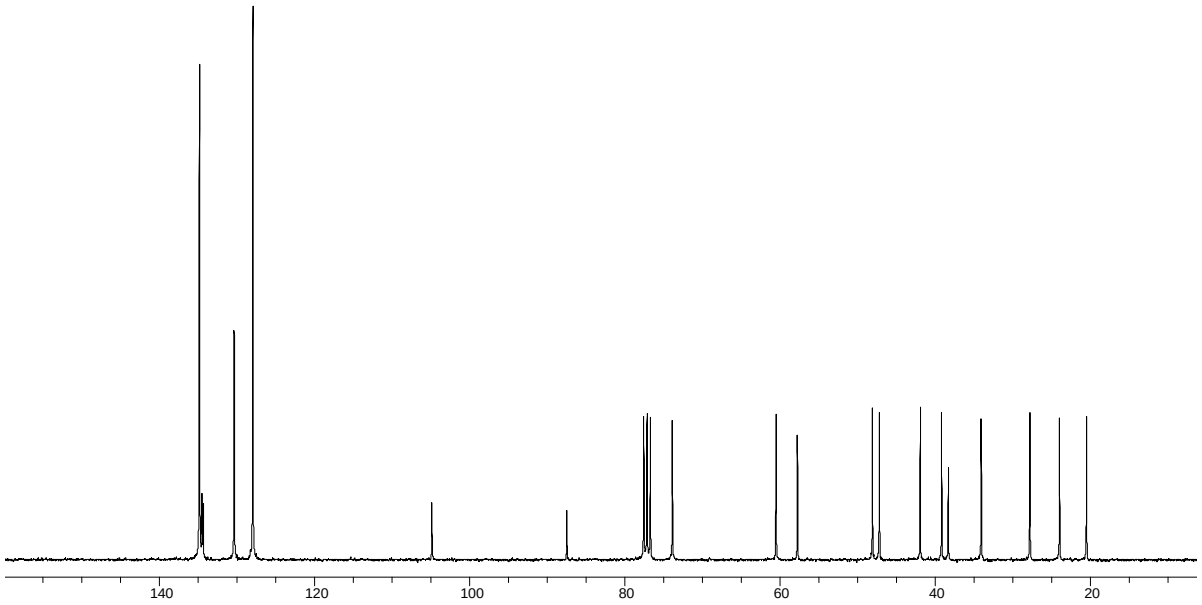
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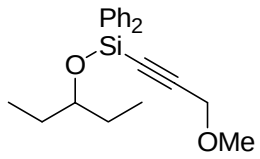
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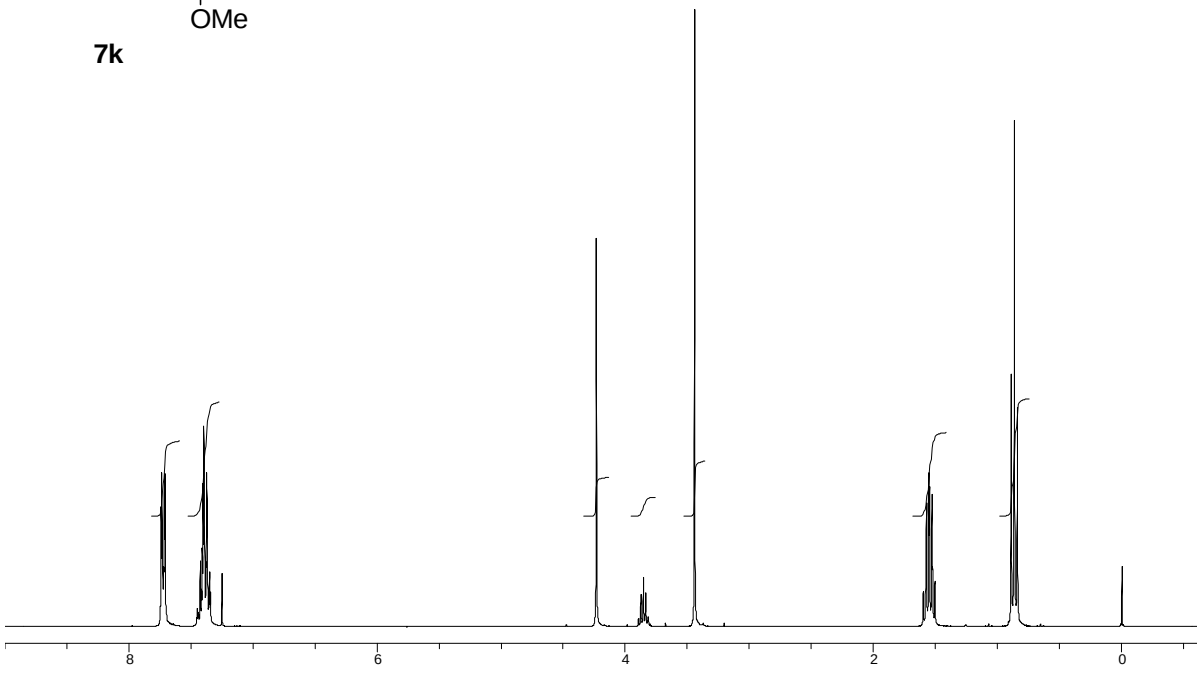
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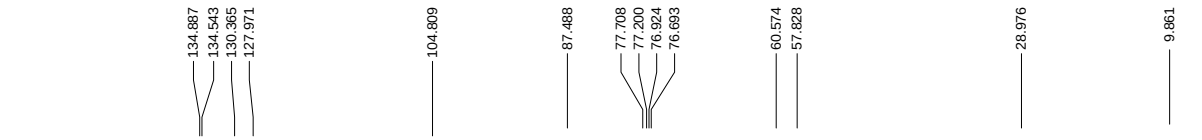
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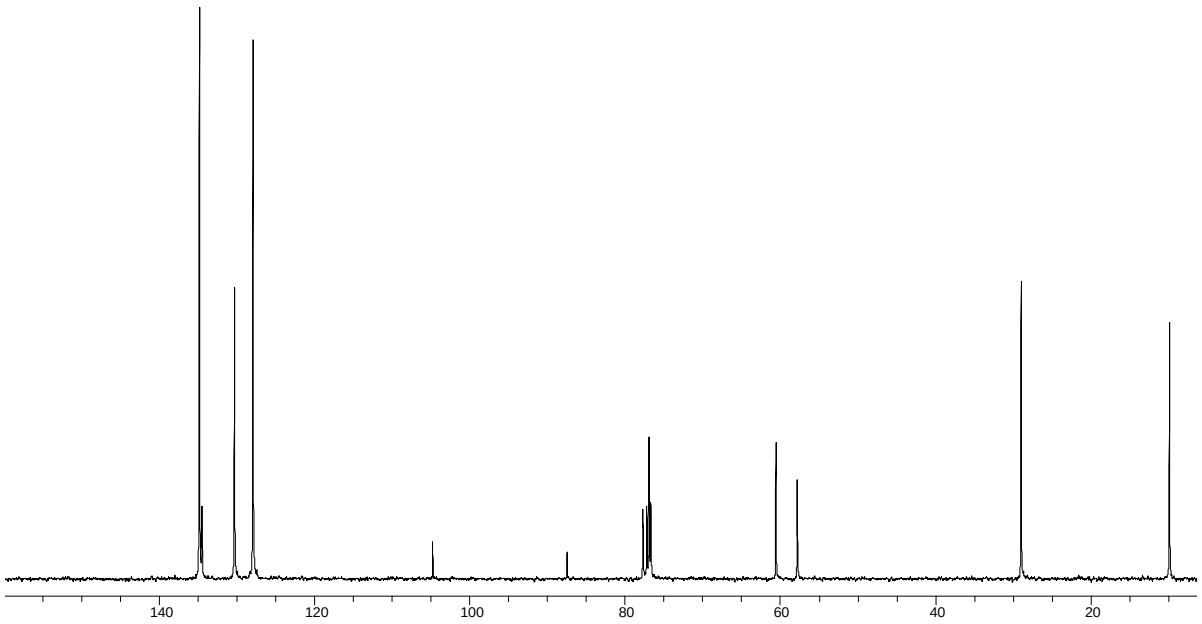
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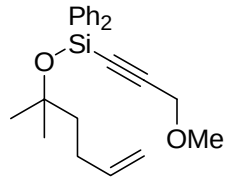
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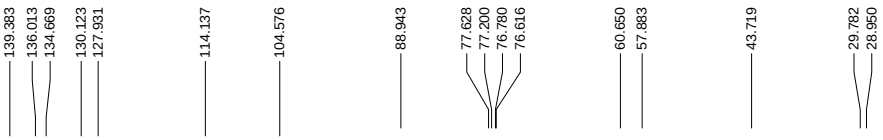
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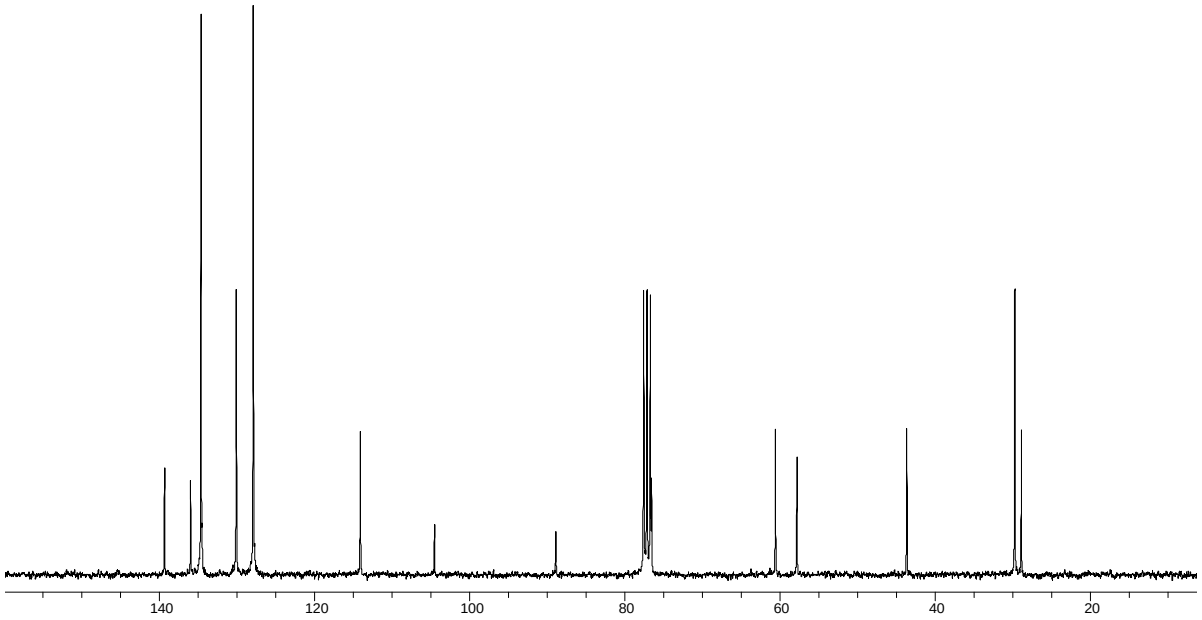
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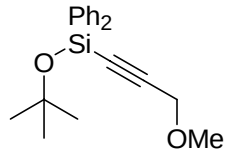
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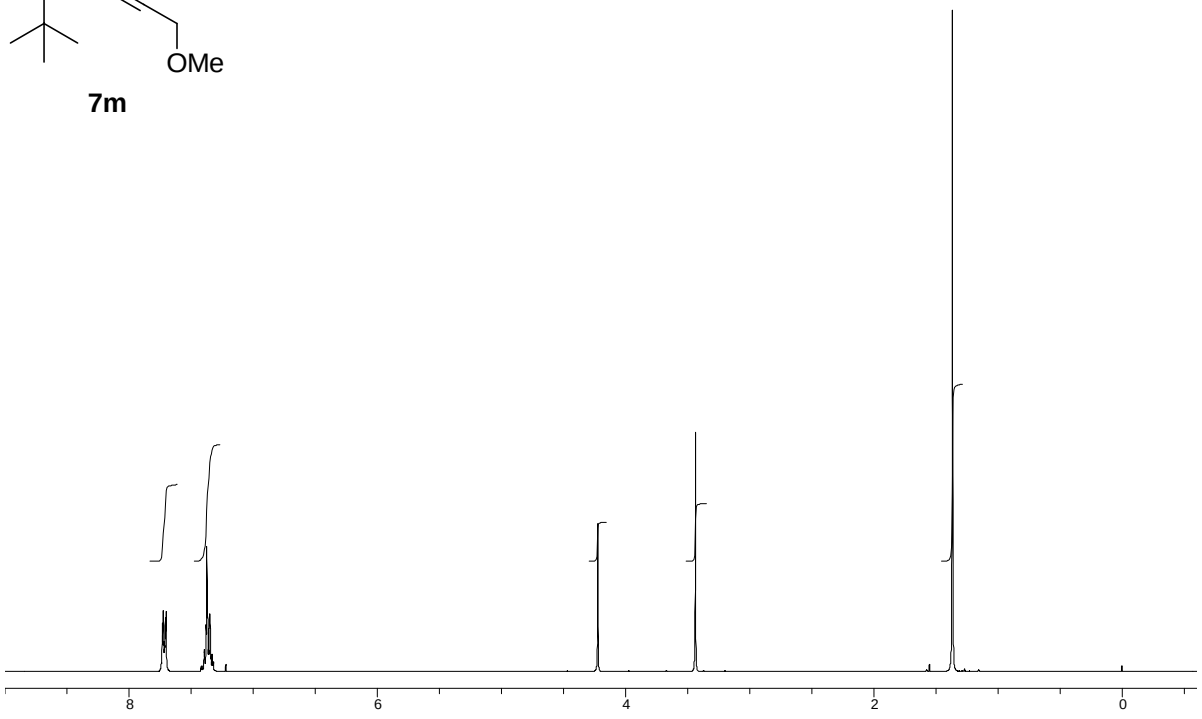
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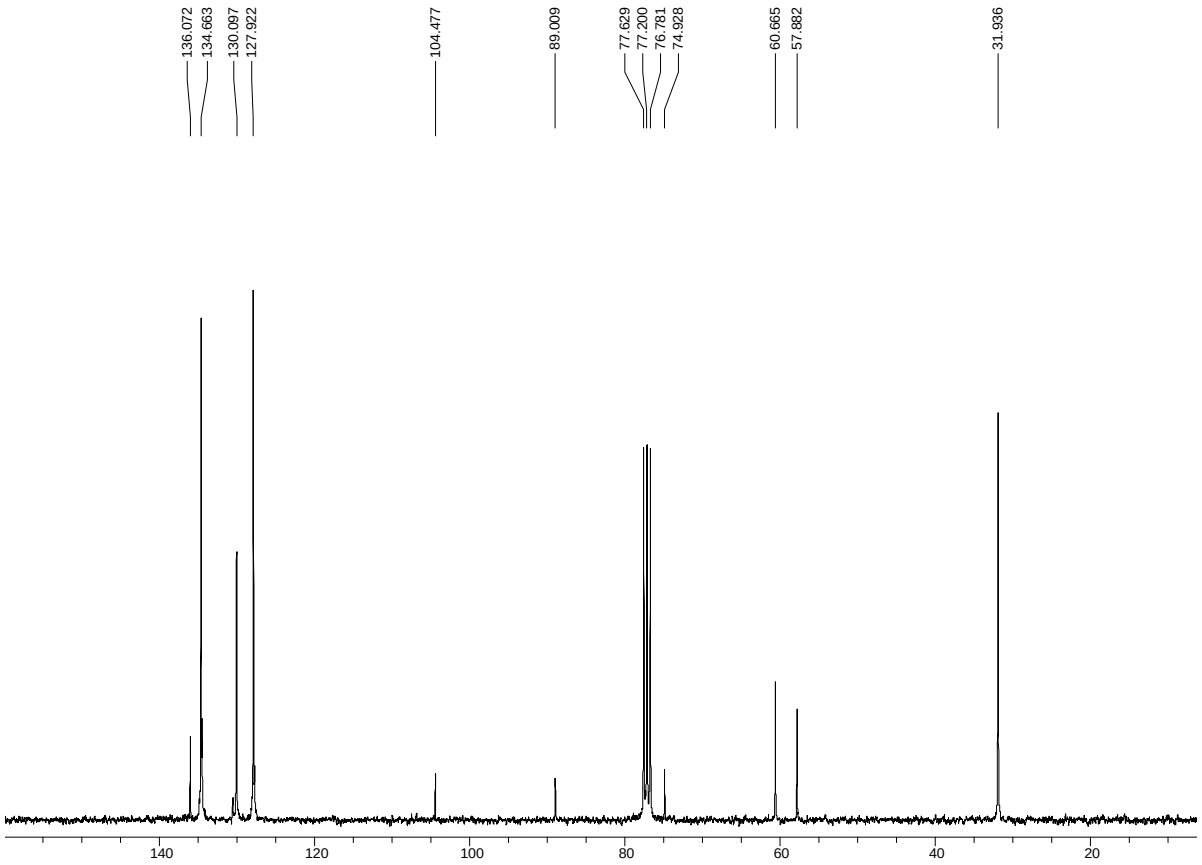
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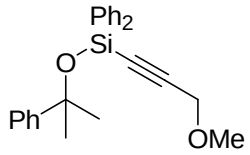
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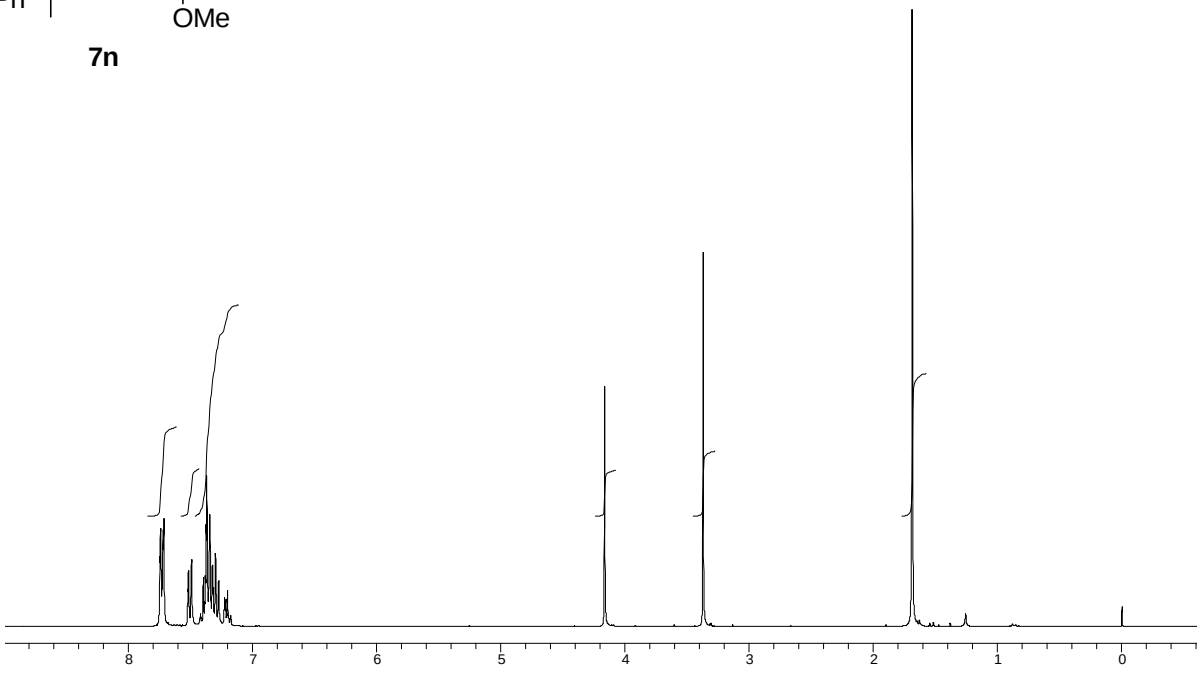
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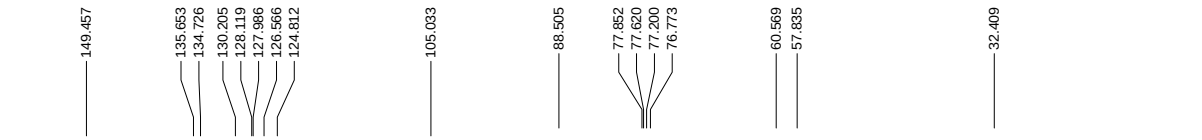
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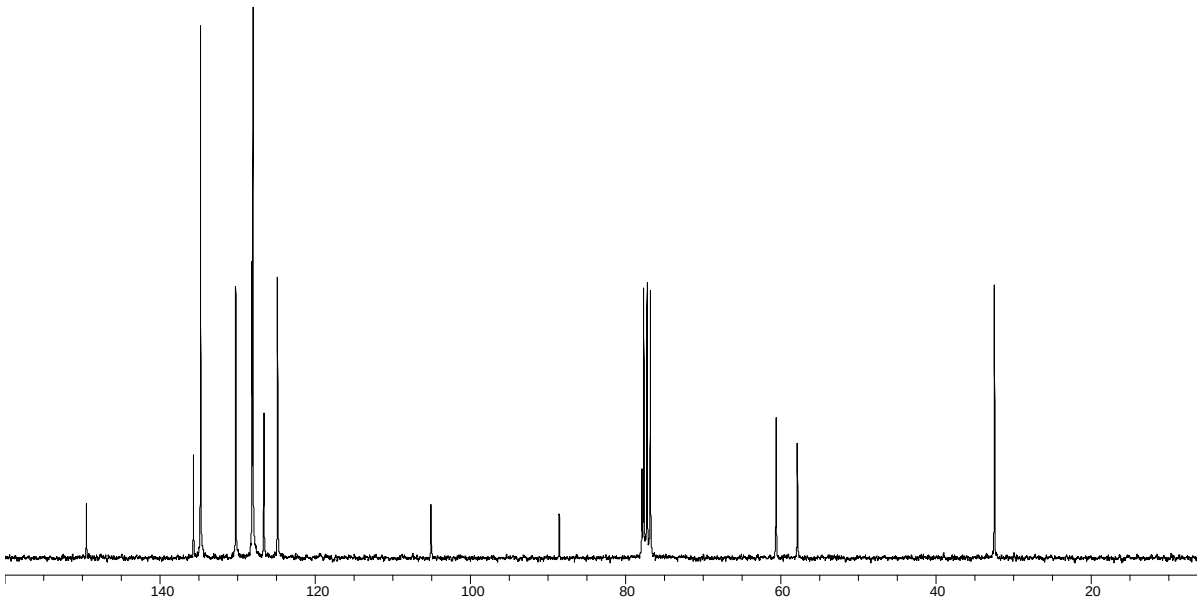
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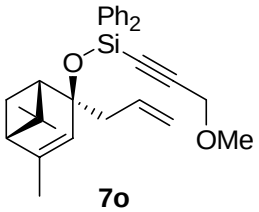
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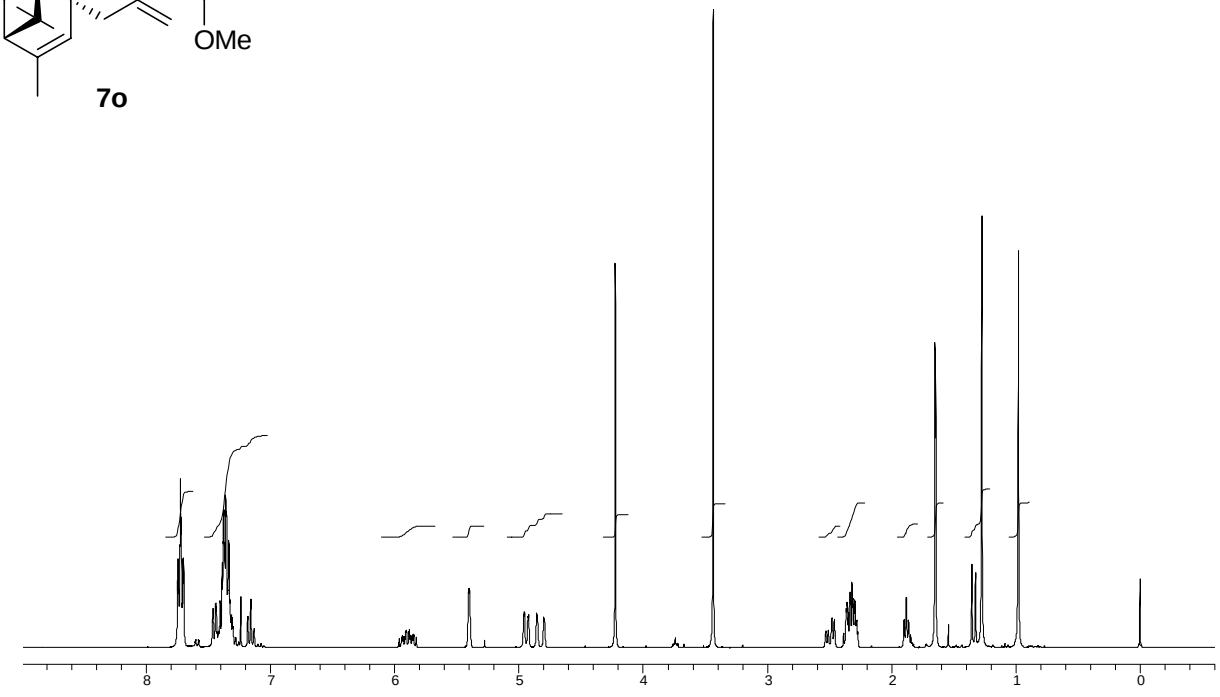
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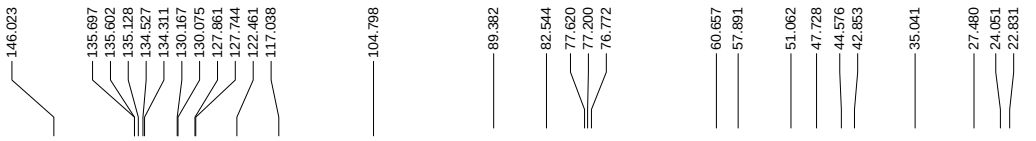
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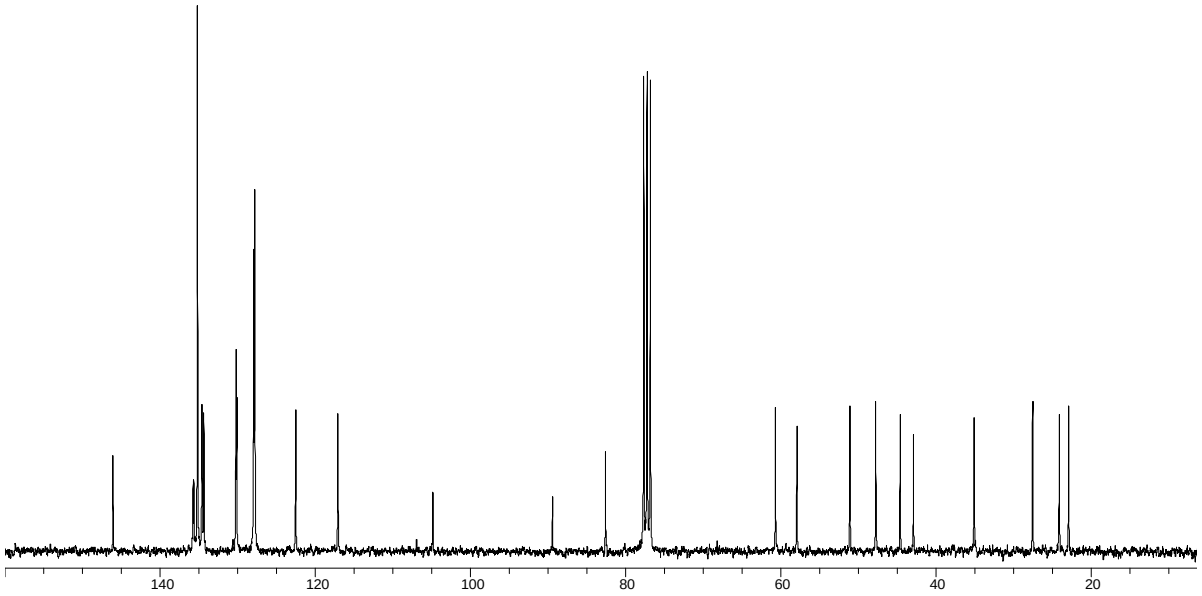
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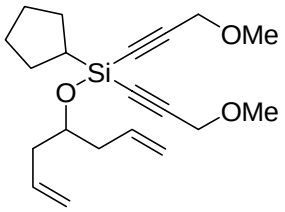
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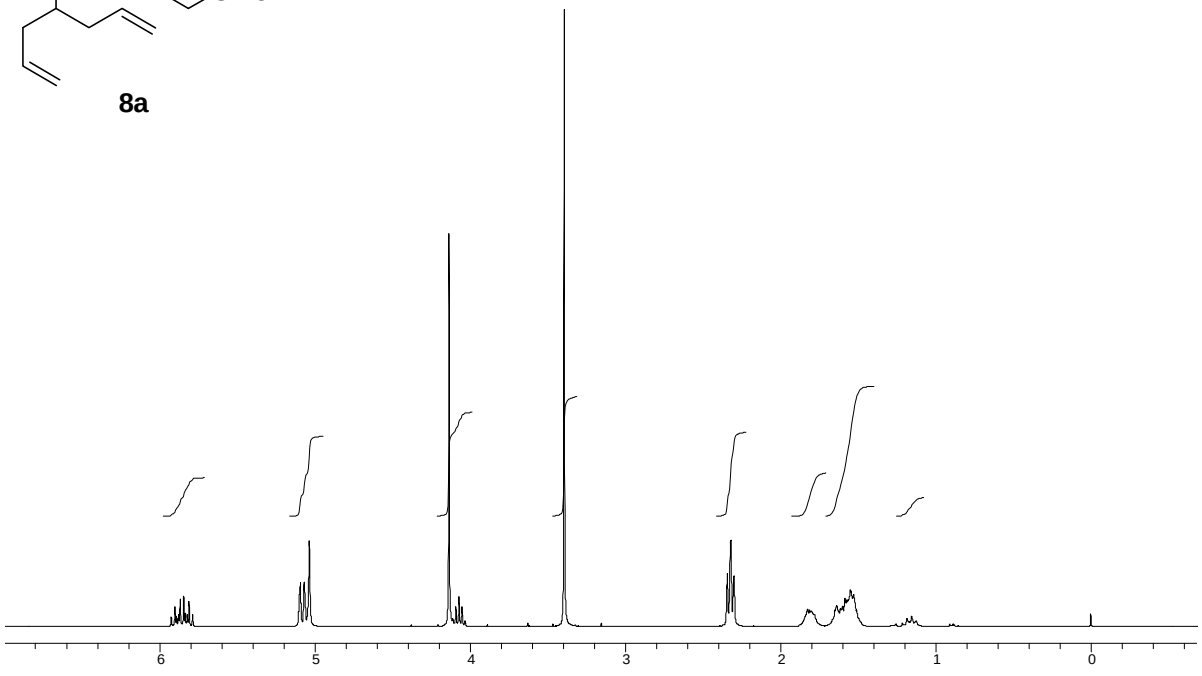
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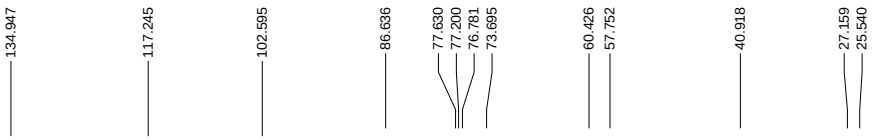
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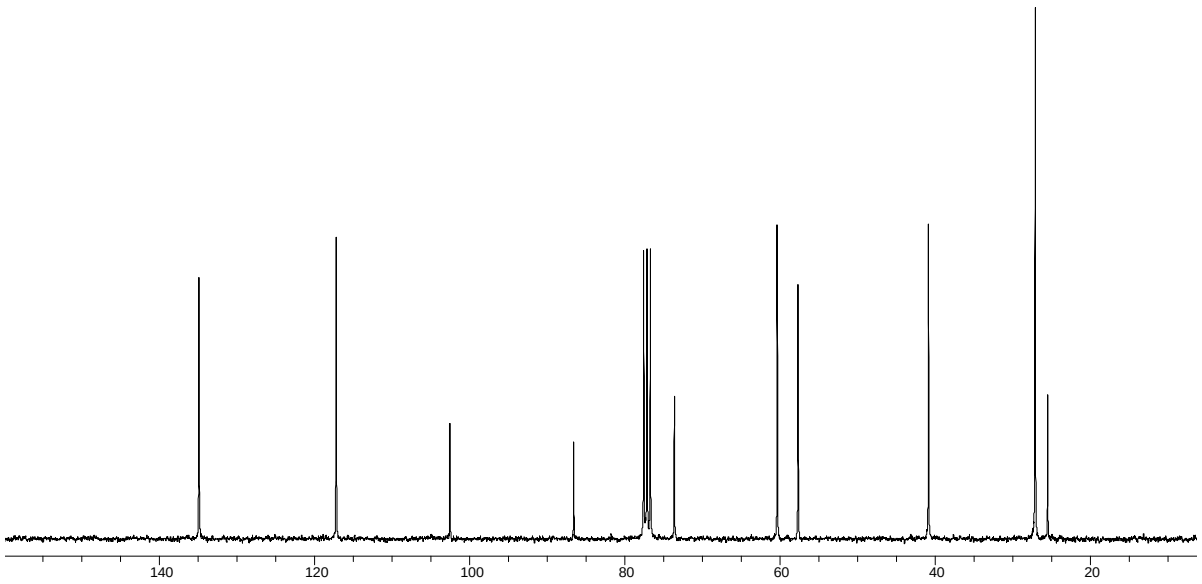
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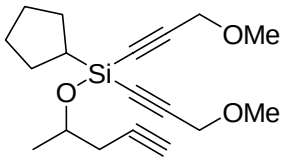
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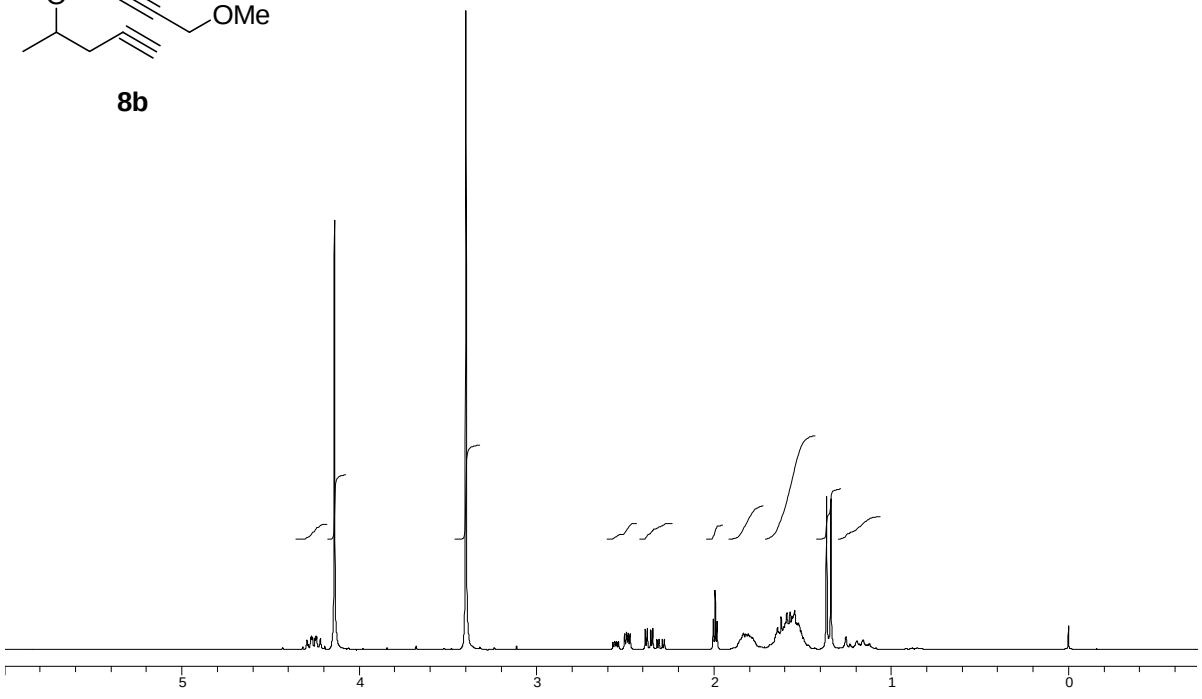
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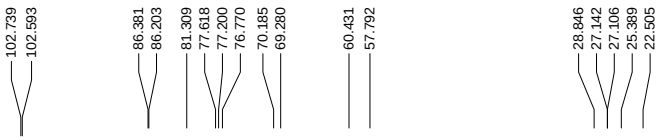
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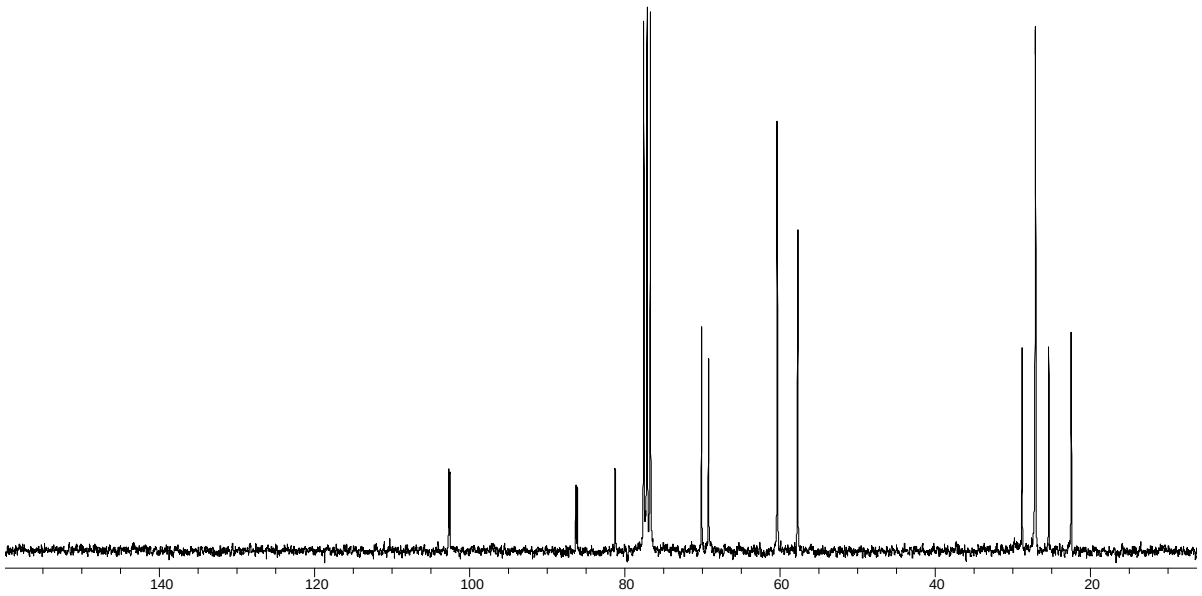
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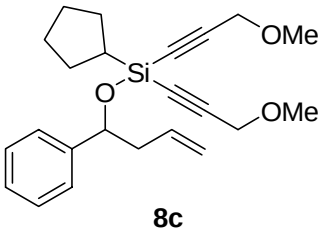
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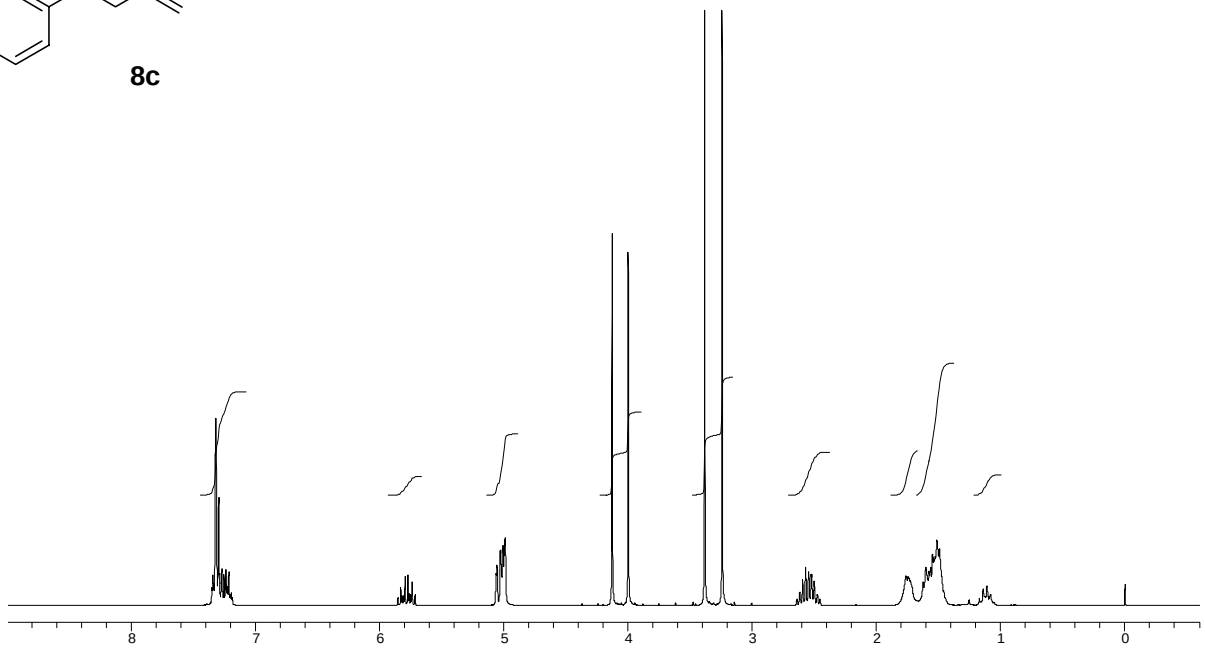
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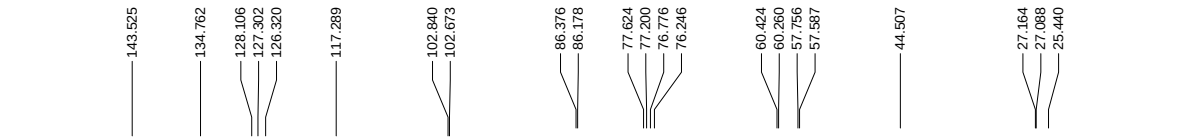
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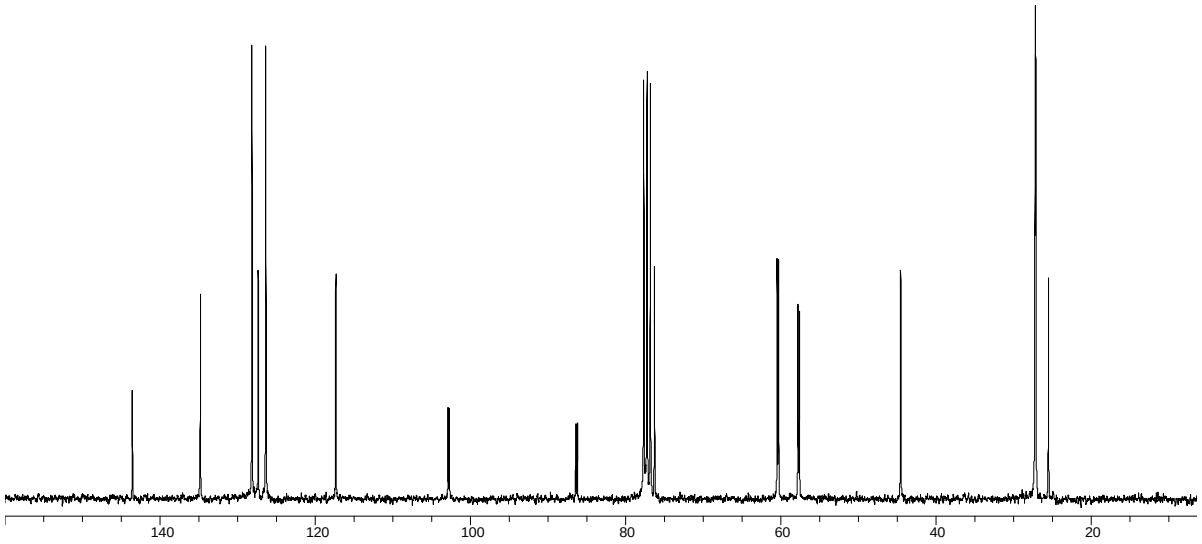
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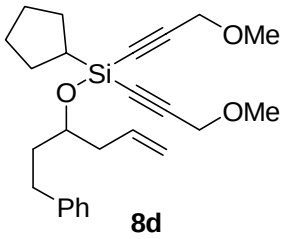
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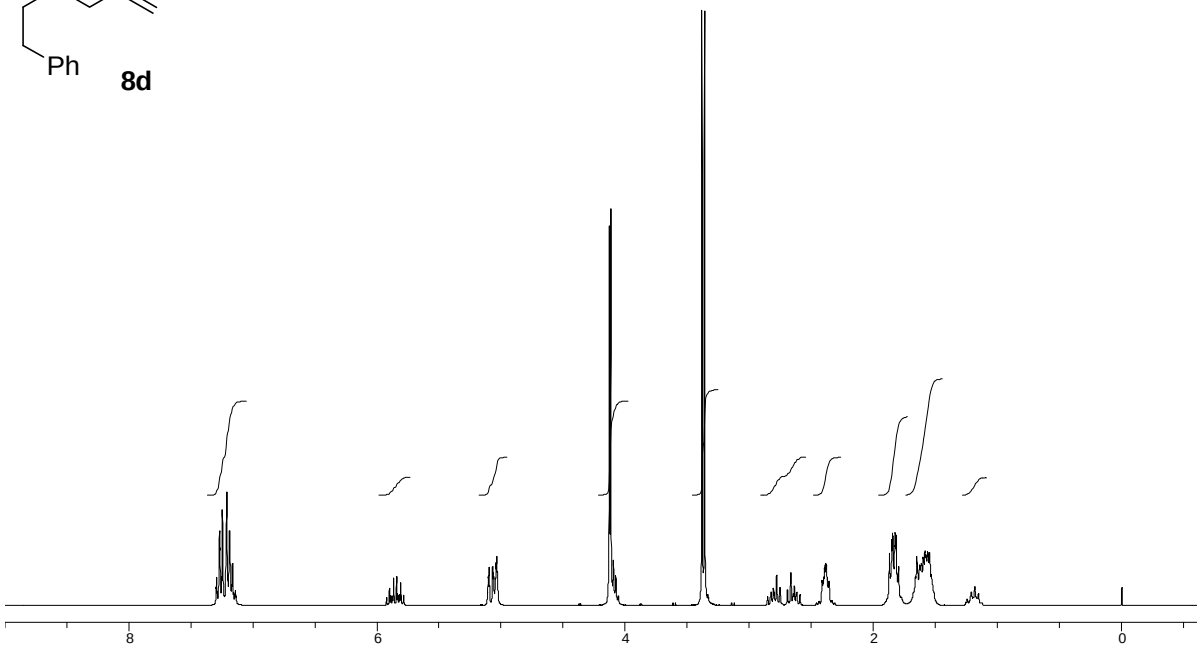
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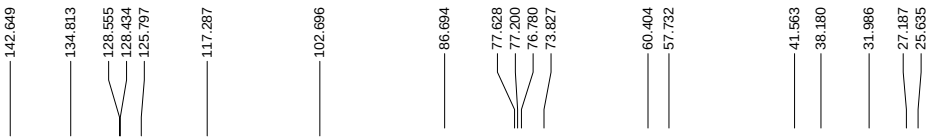
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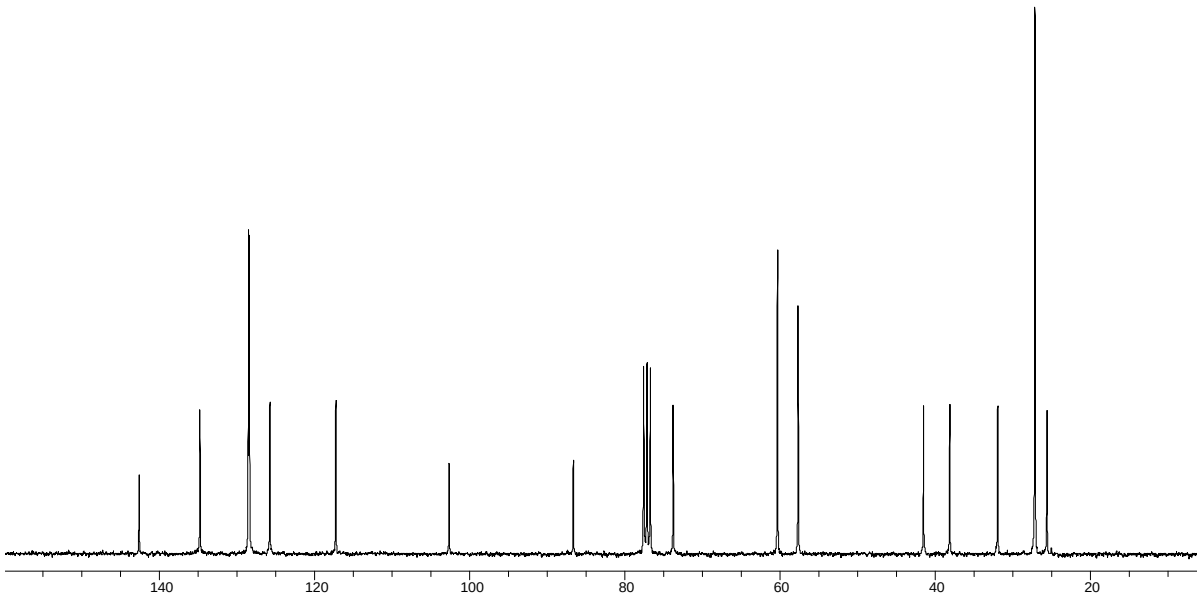
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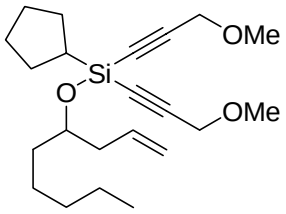
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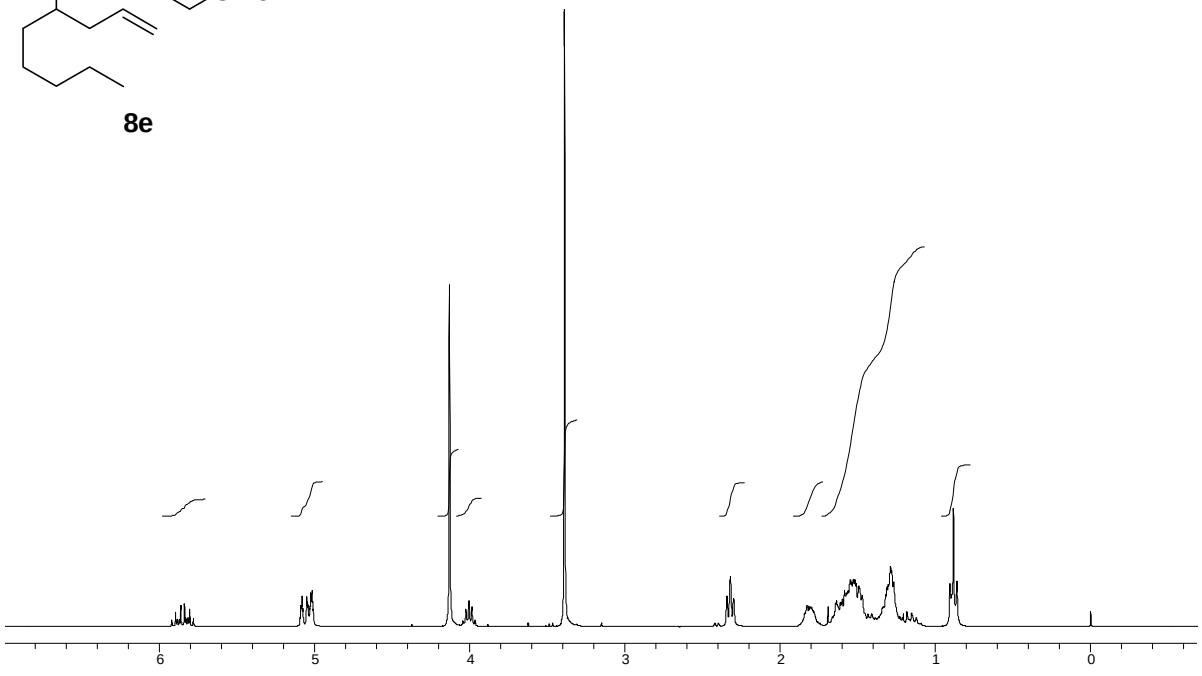
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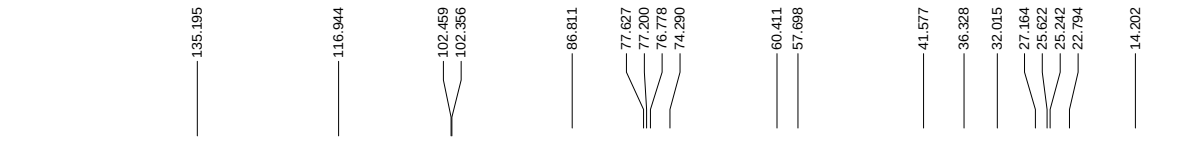
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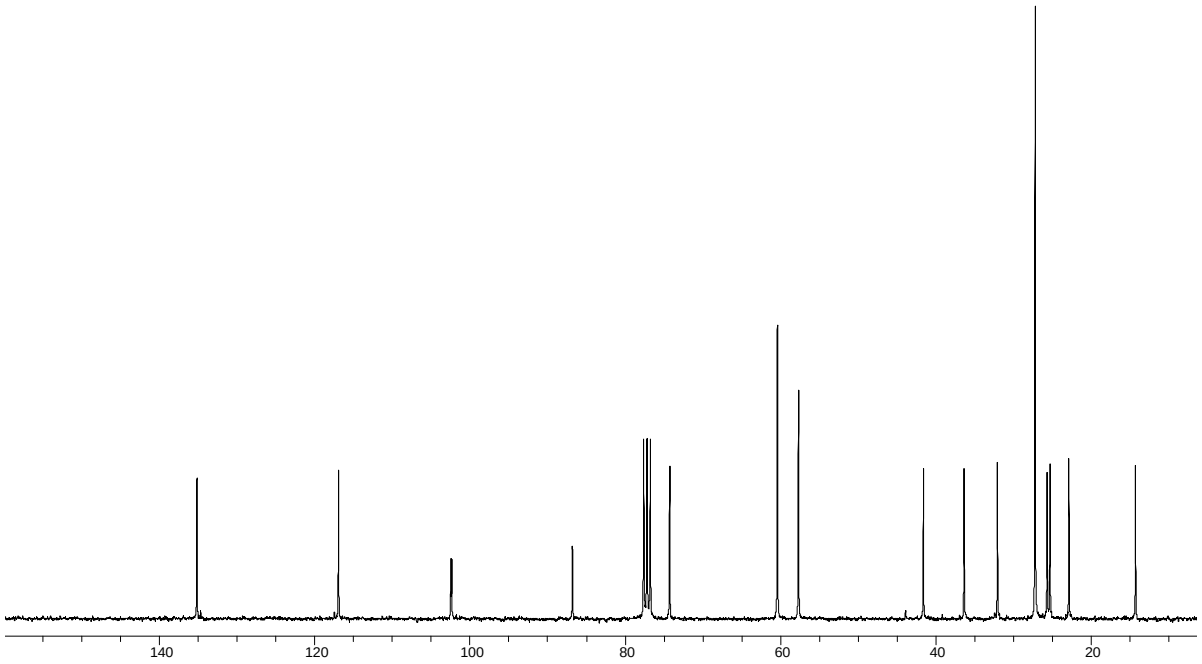
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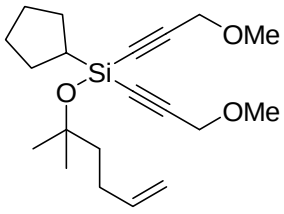
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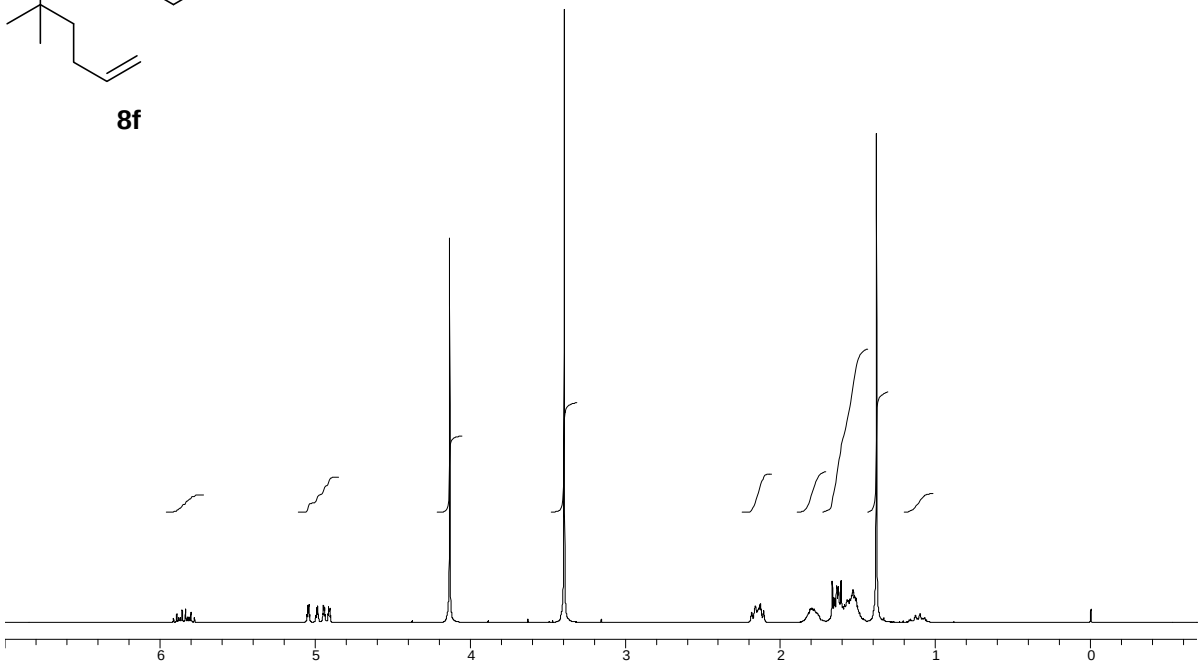
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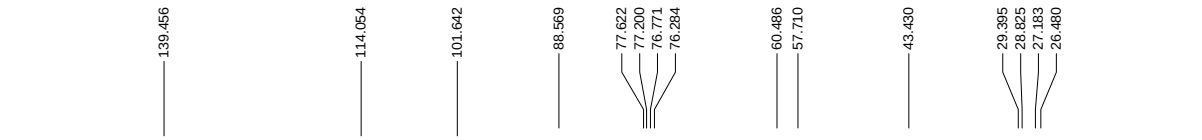
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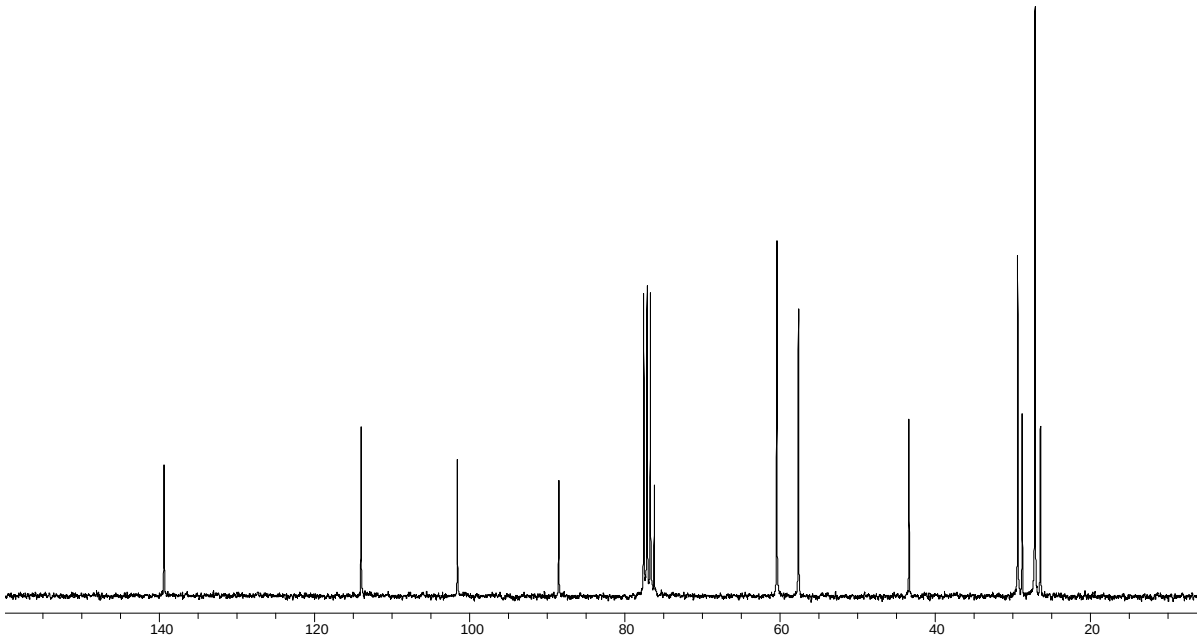
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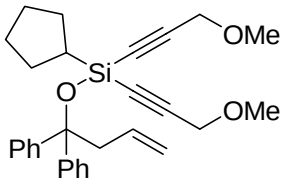
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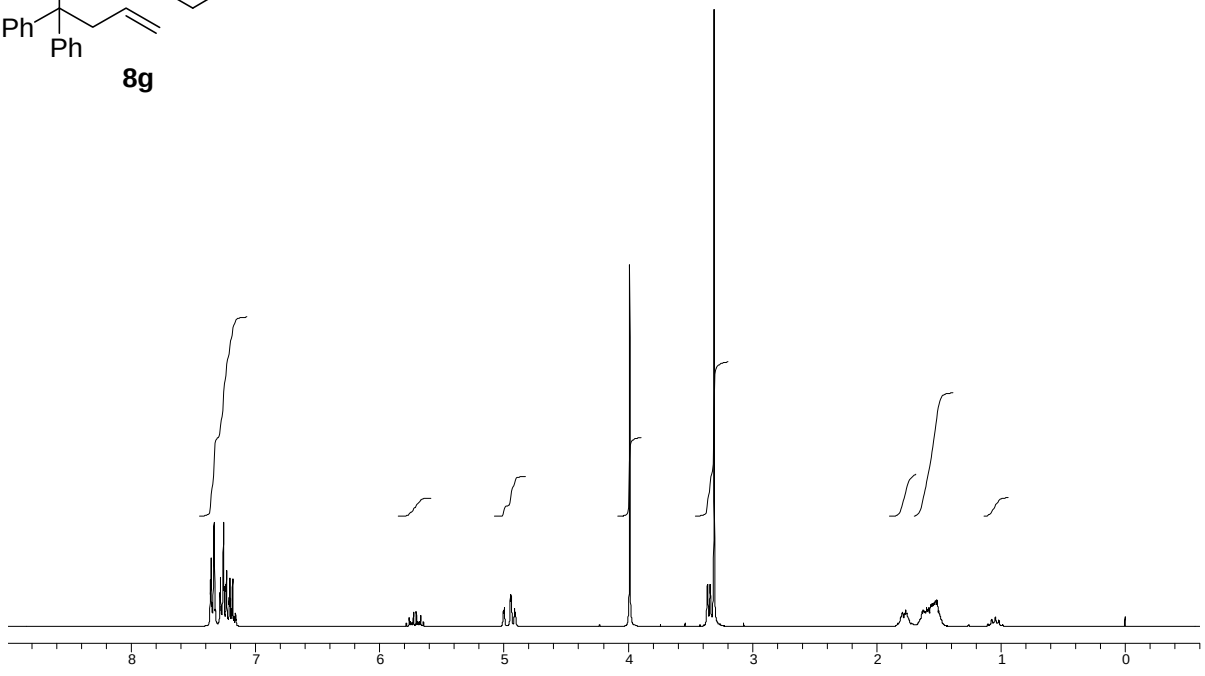
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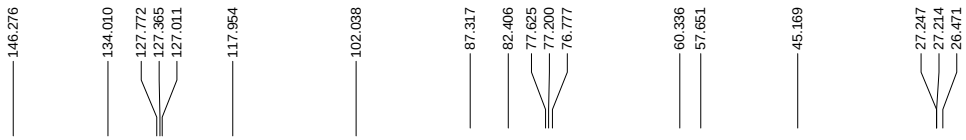
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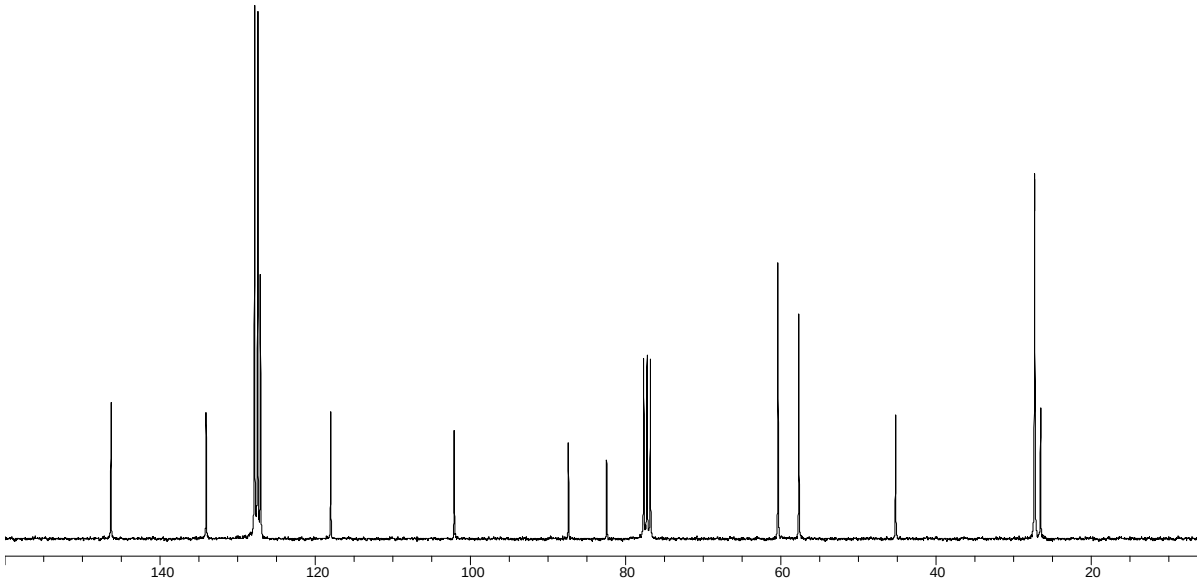
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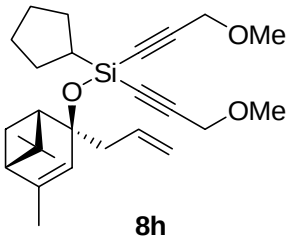
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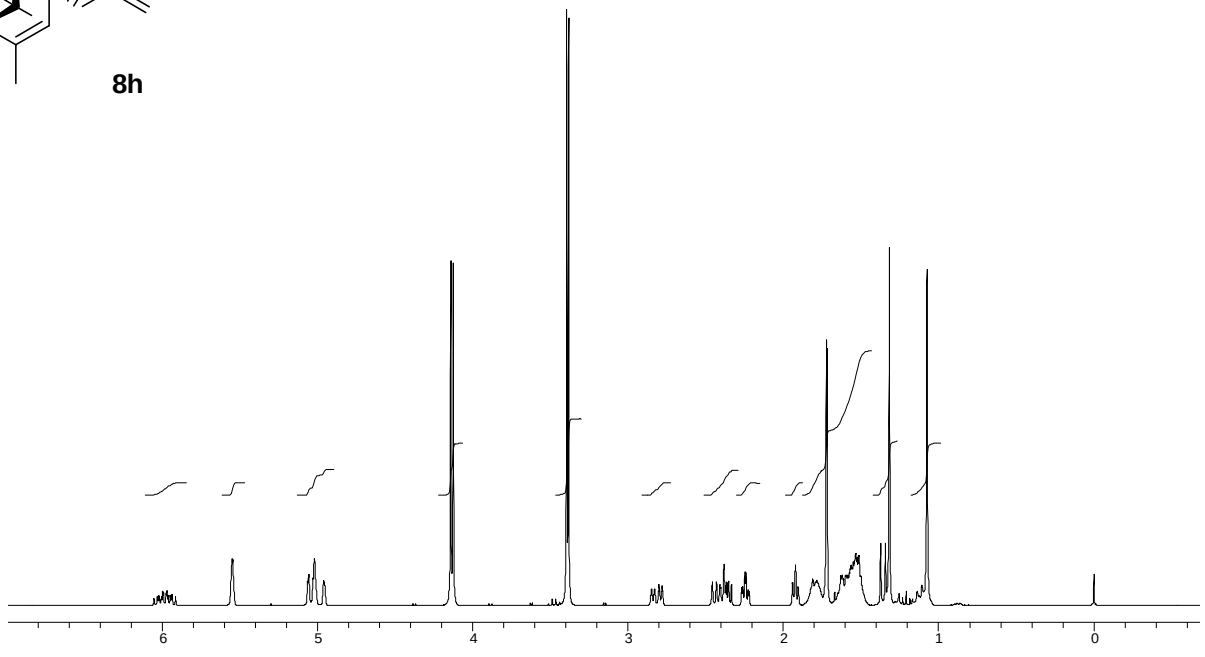
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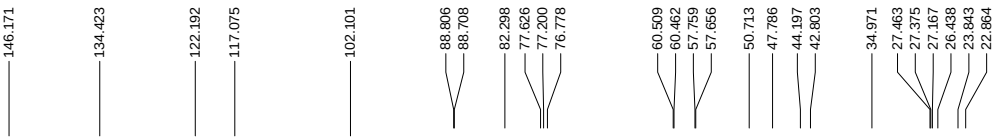
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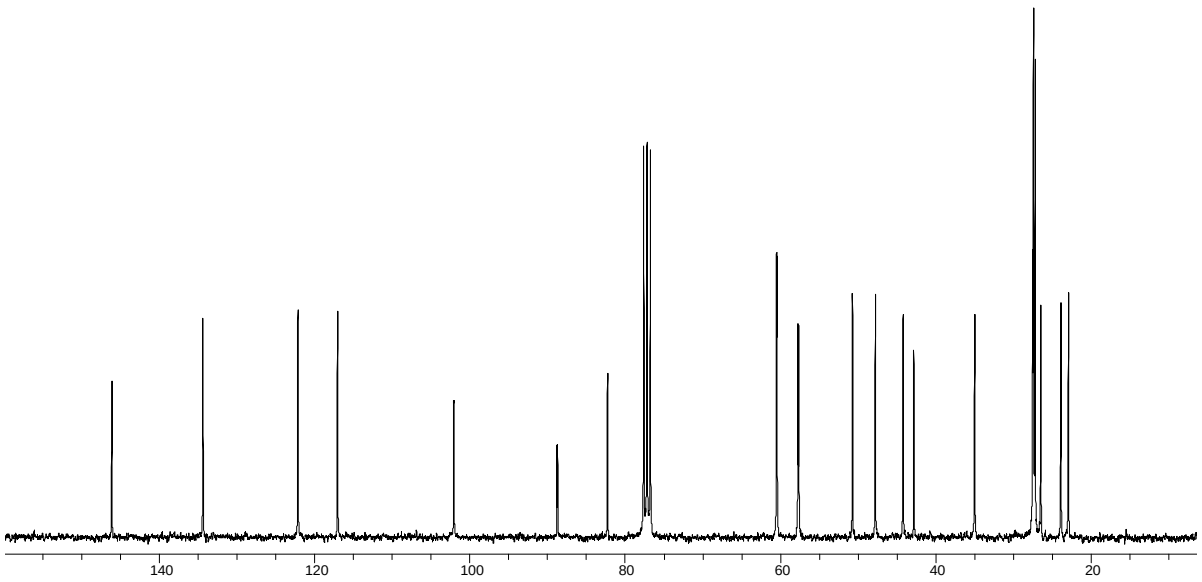
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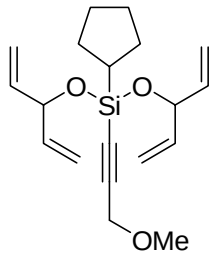
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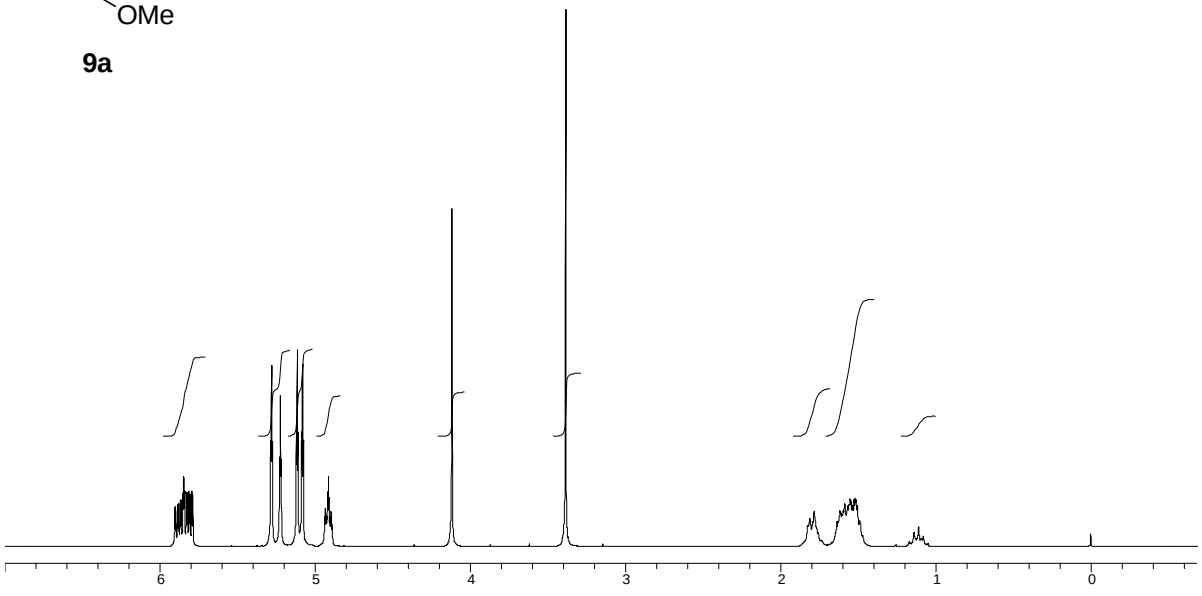
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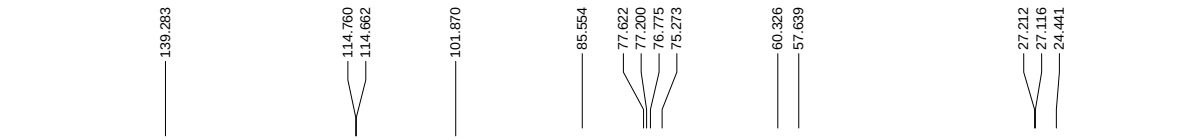
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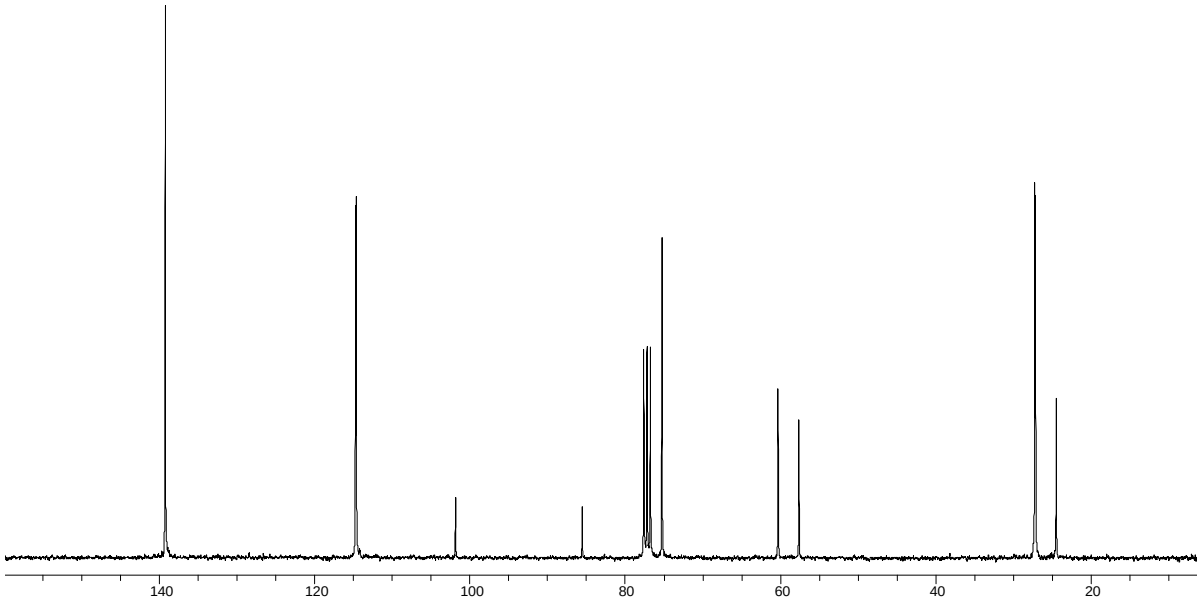
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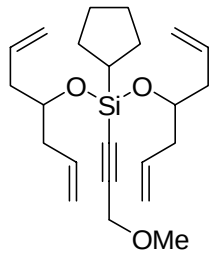
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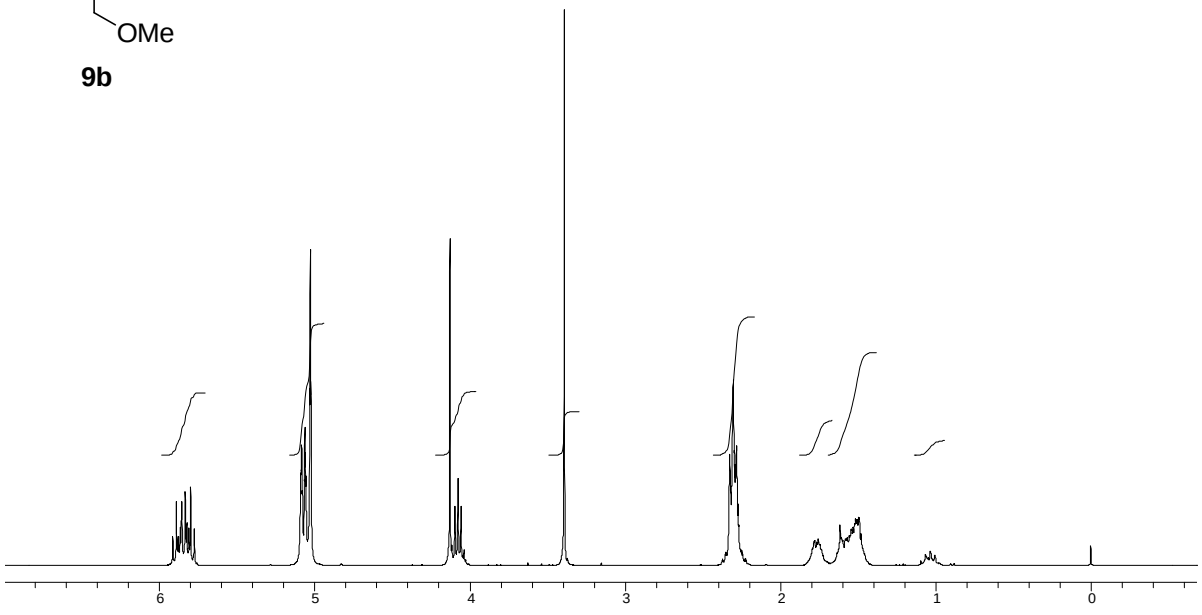
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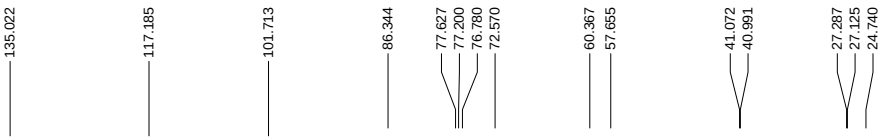
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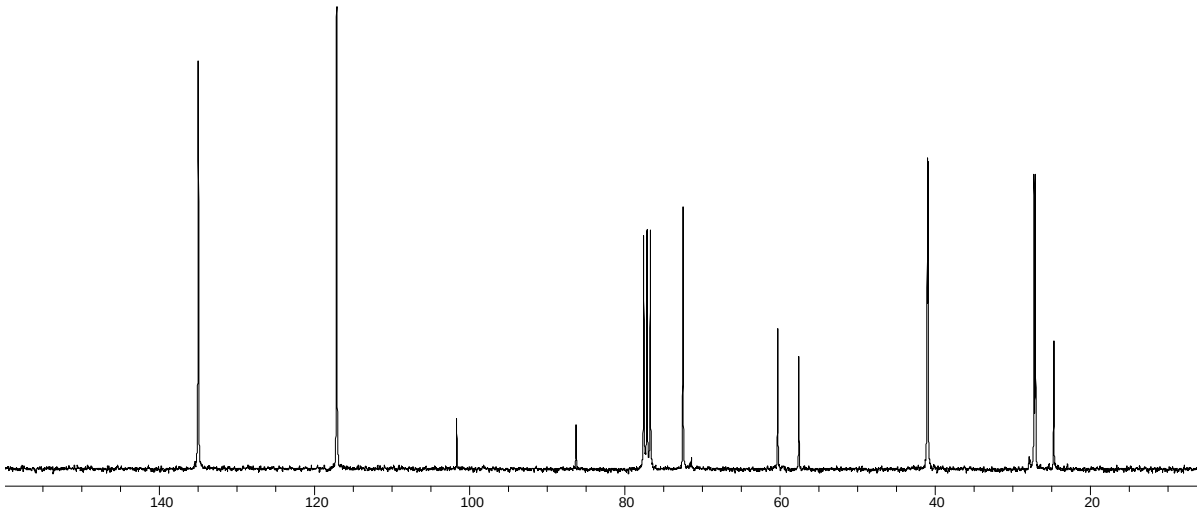
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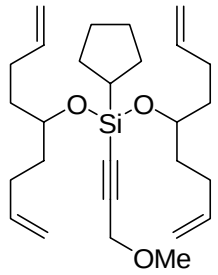
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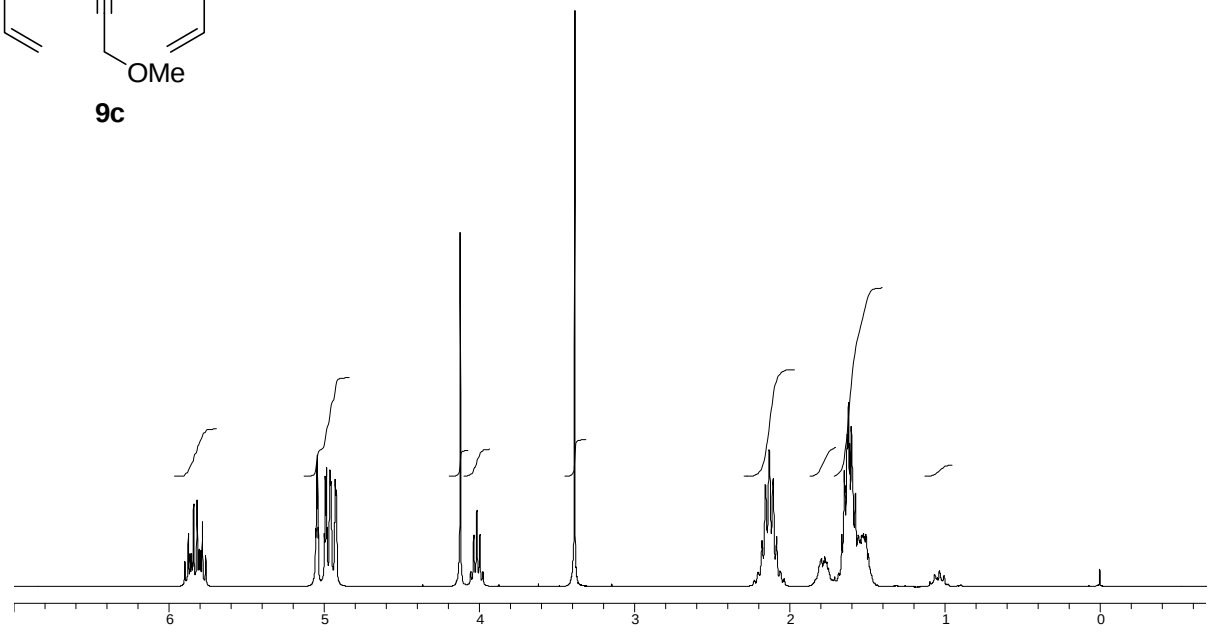
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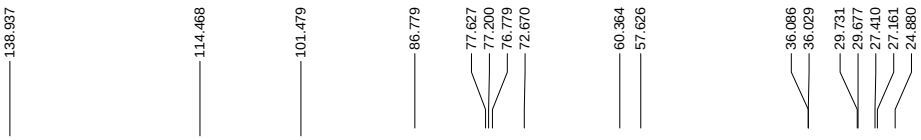
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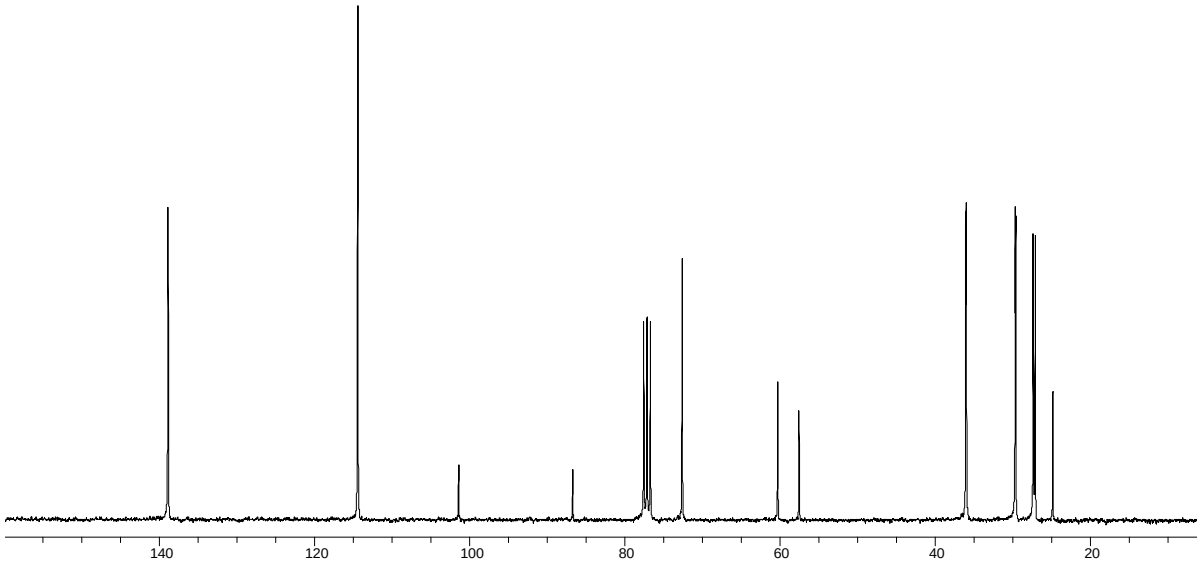
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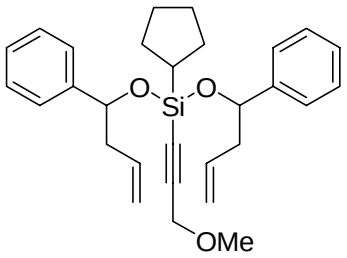
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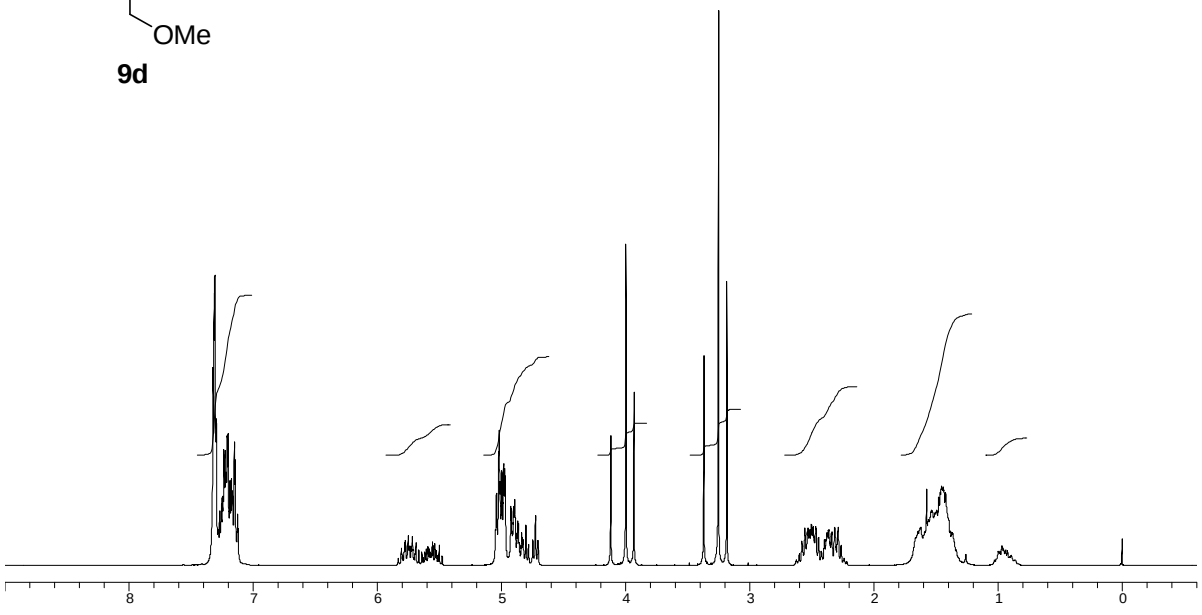
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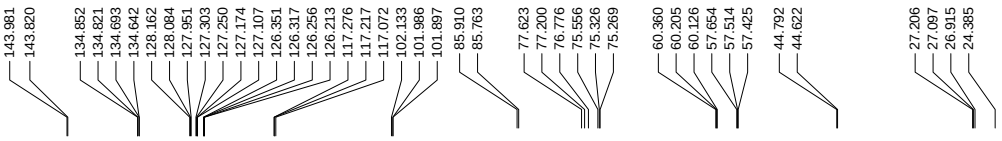
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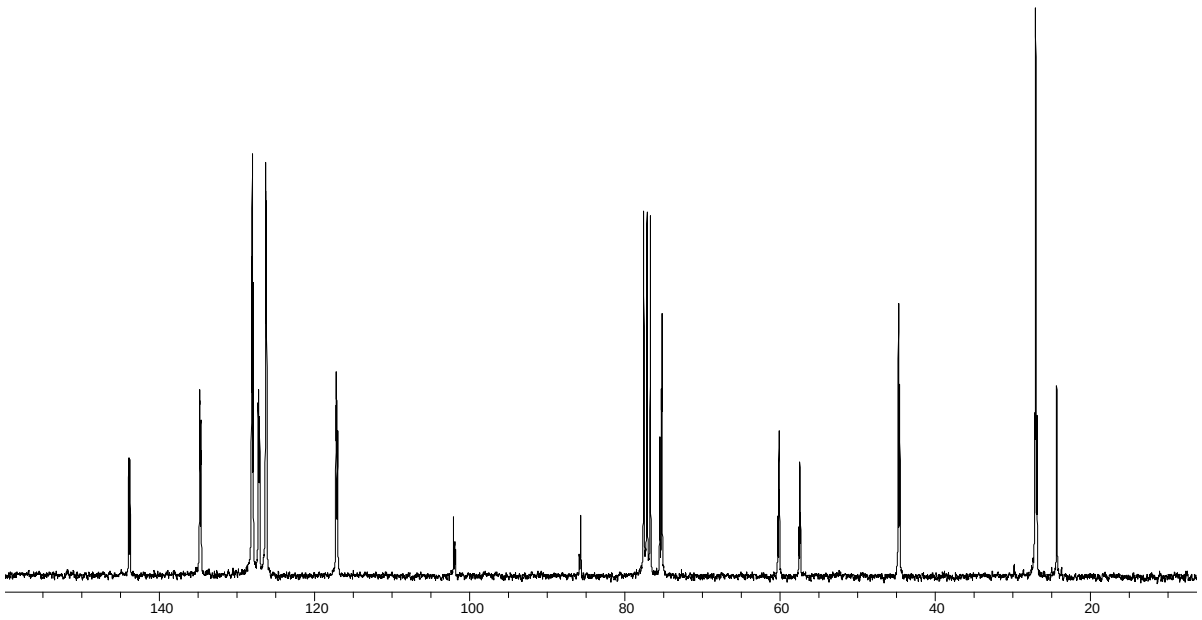
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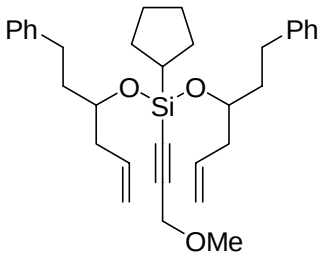
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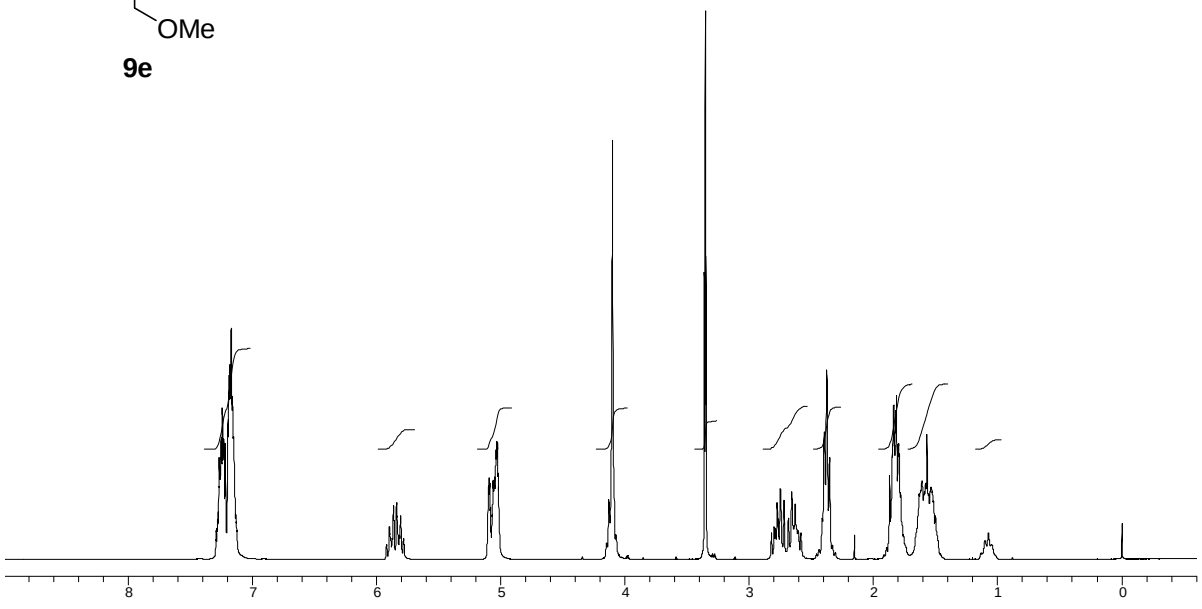
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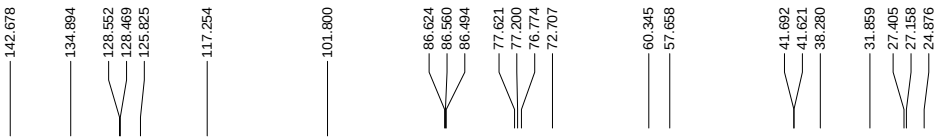
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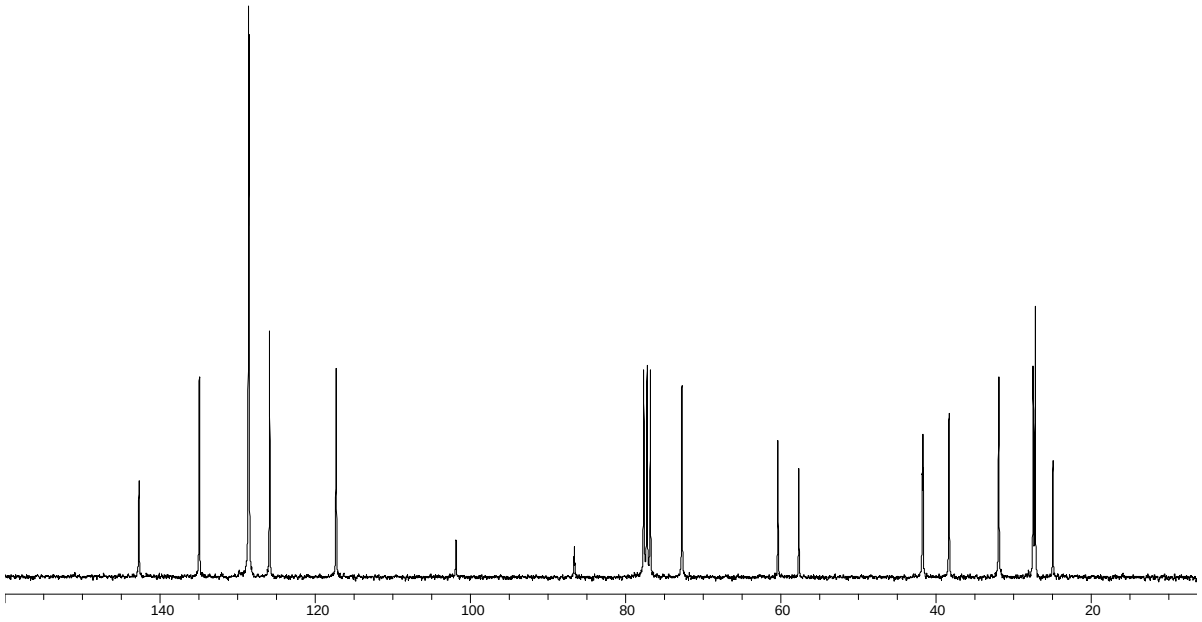
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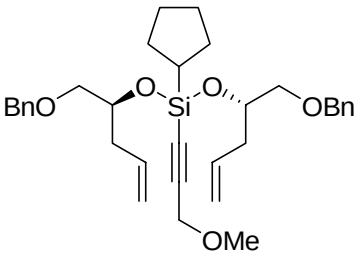
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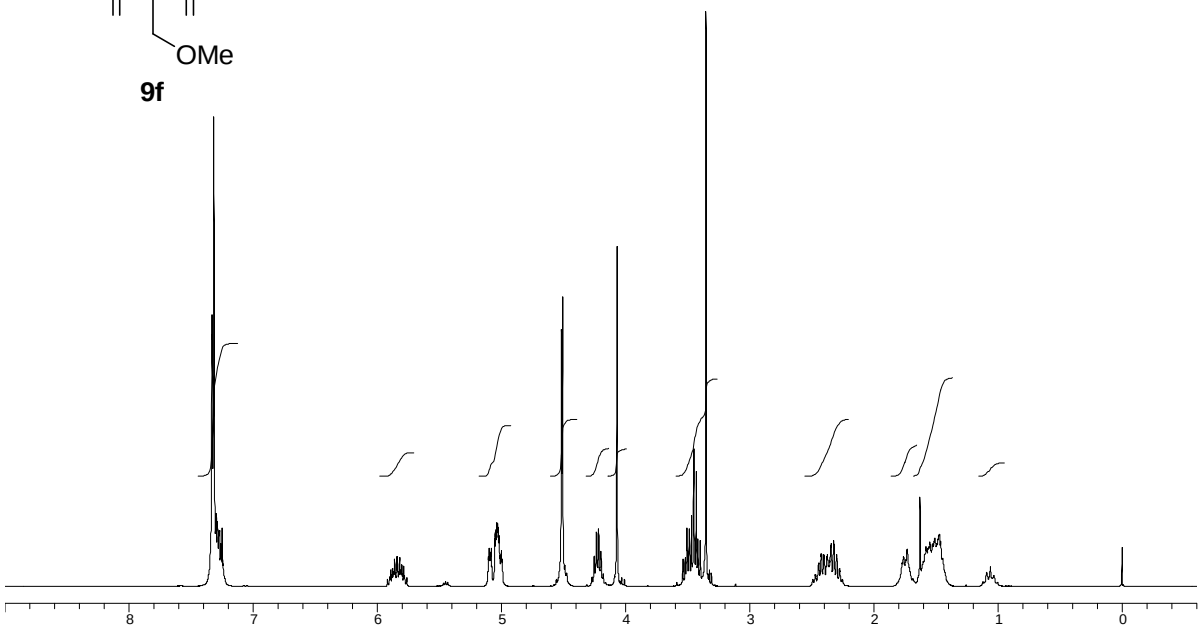
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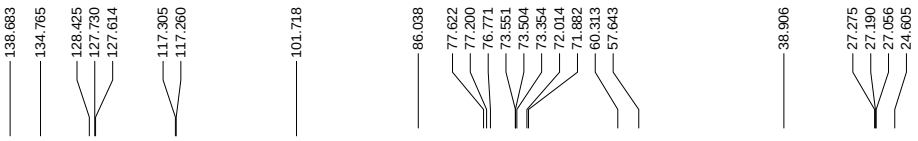
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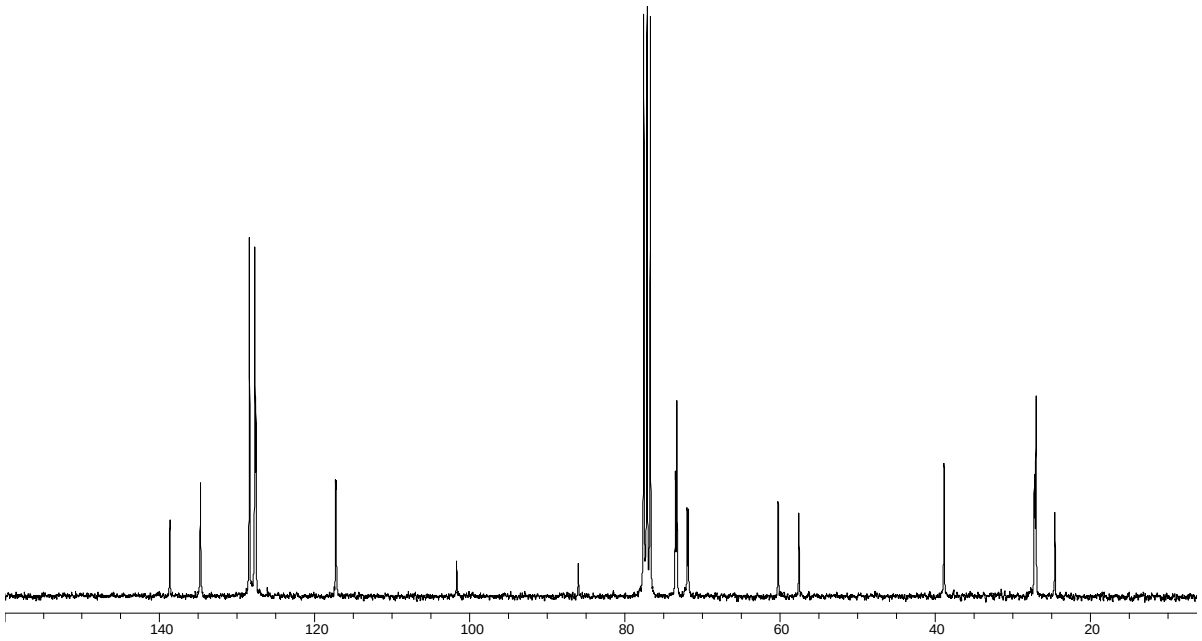
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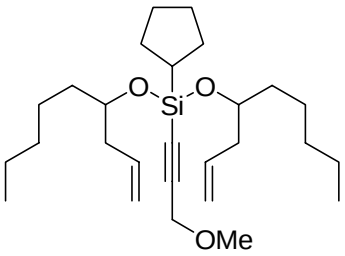
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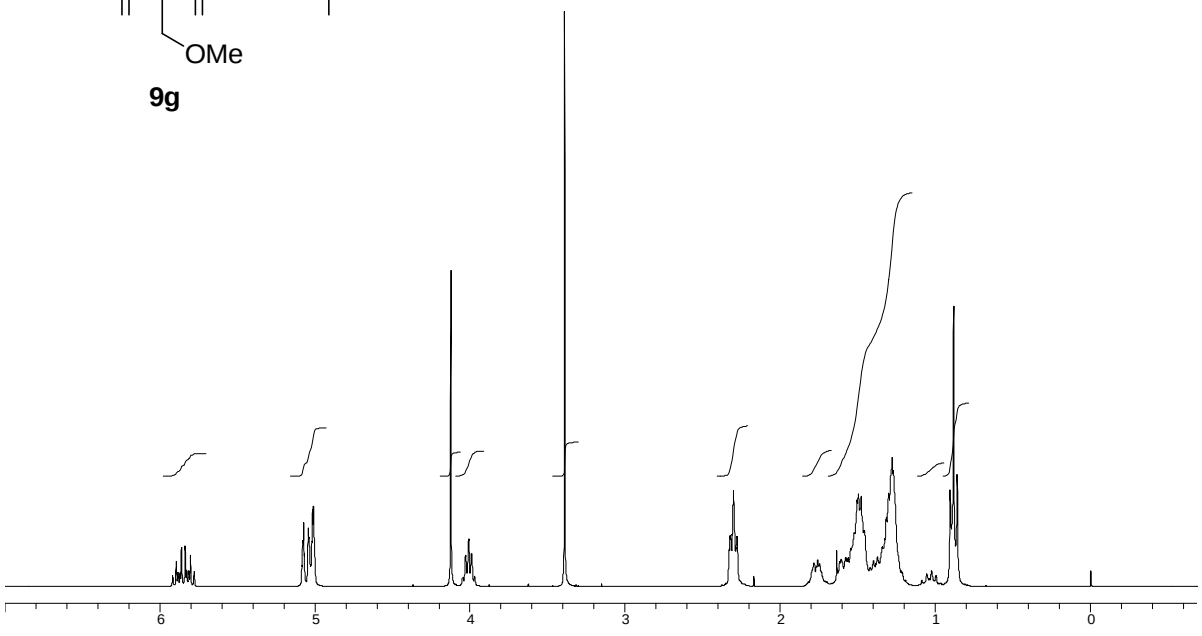
O
OMe

9g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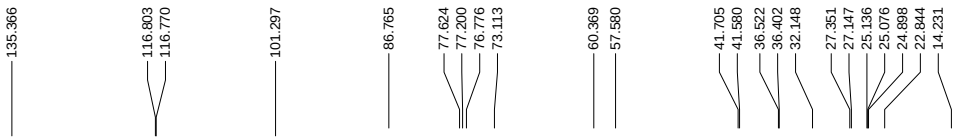
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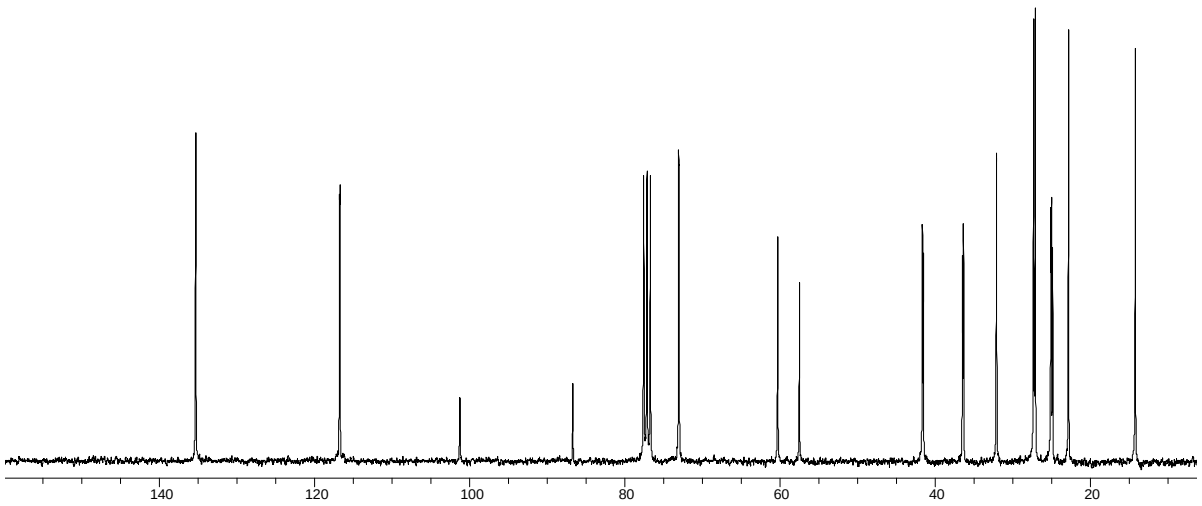
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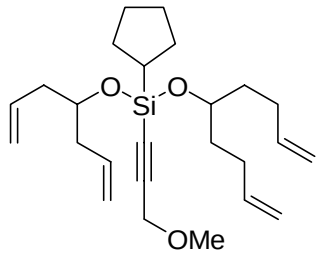
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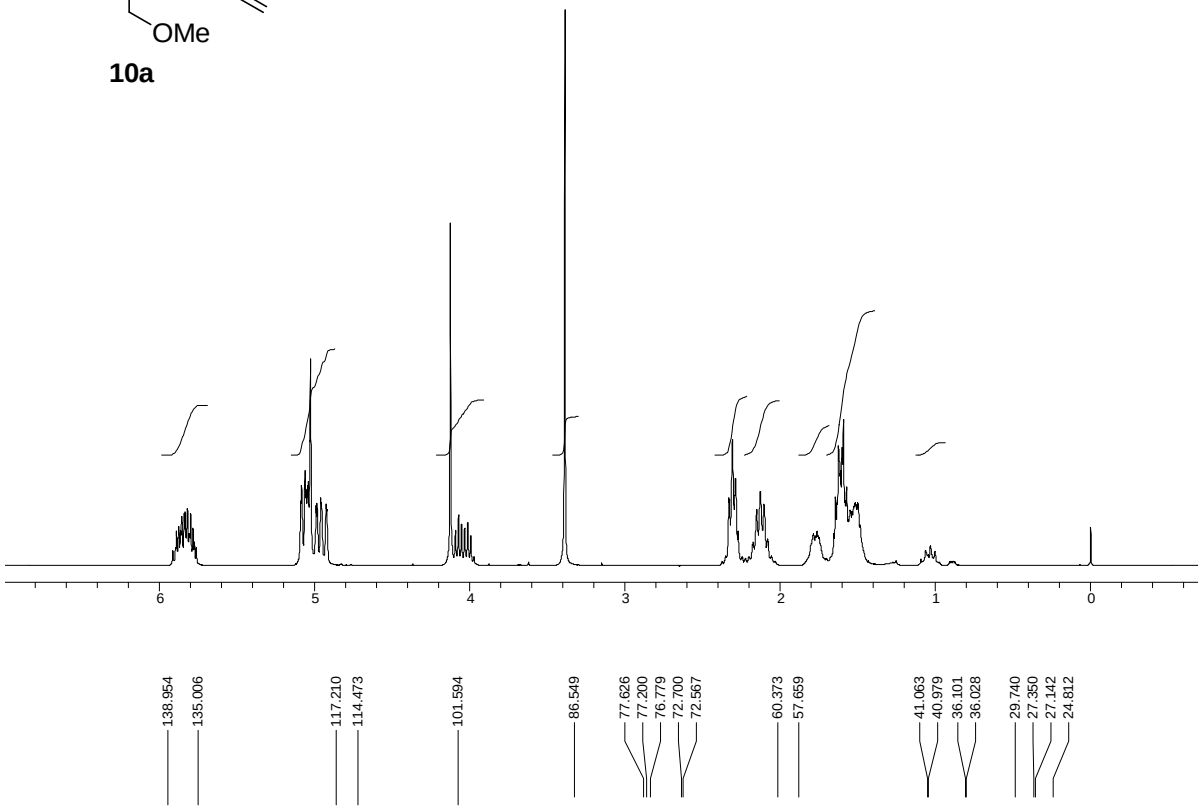
OMe

10a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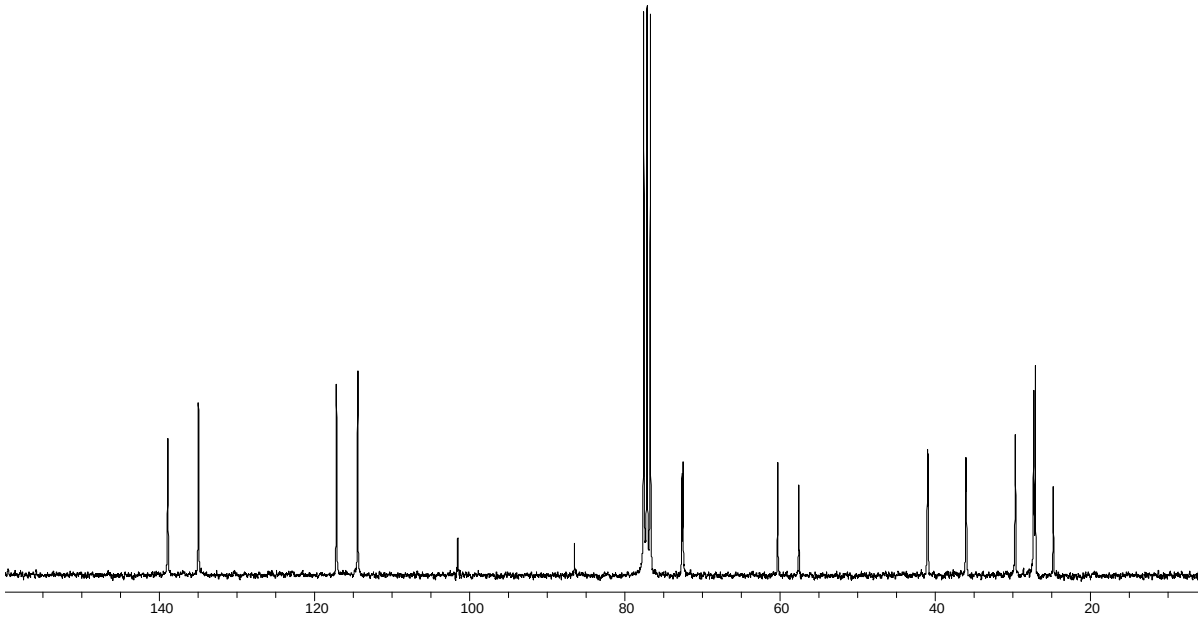
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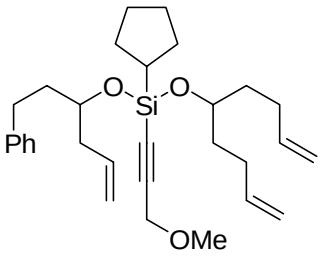
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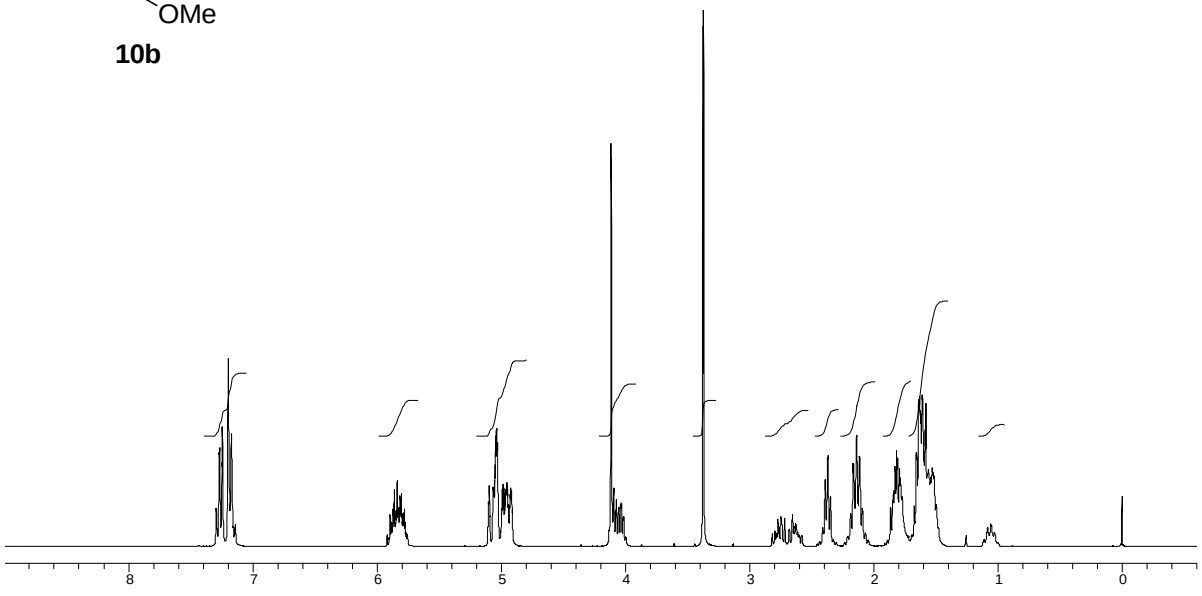
O
Ph
OMe

10b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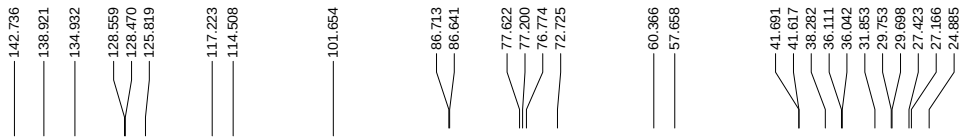
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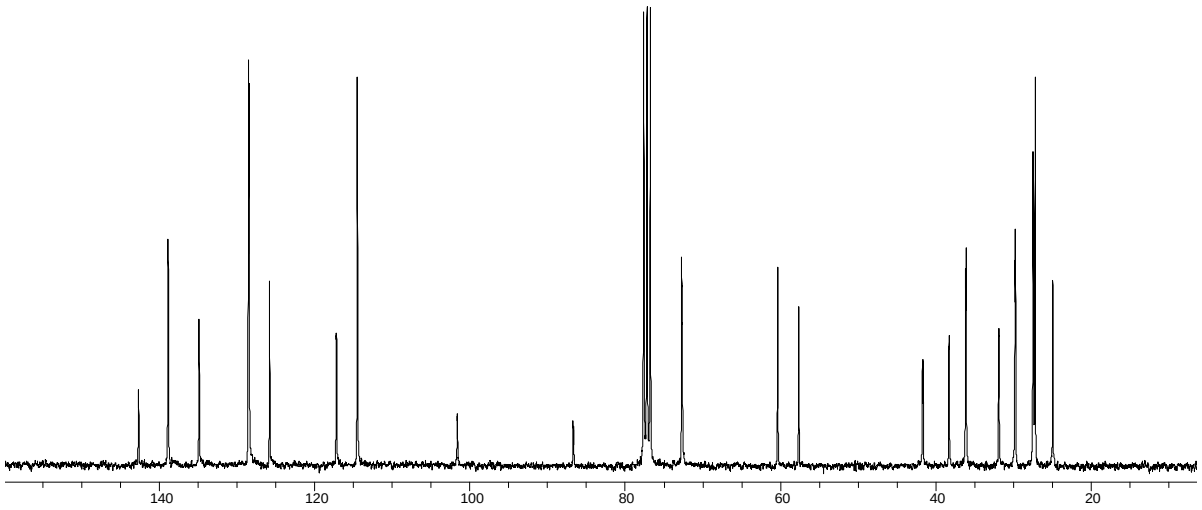
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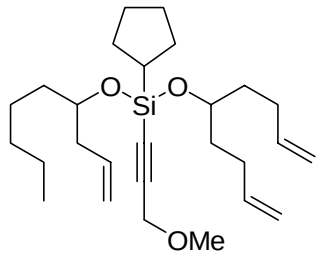
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O
OMe

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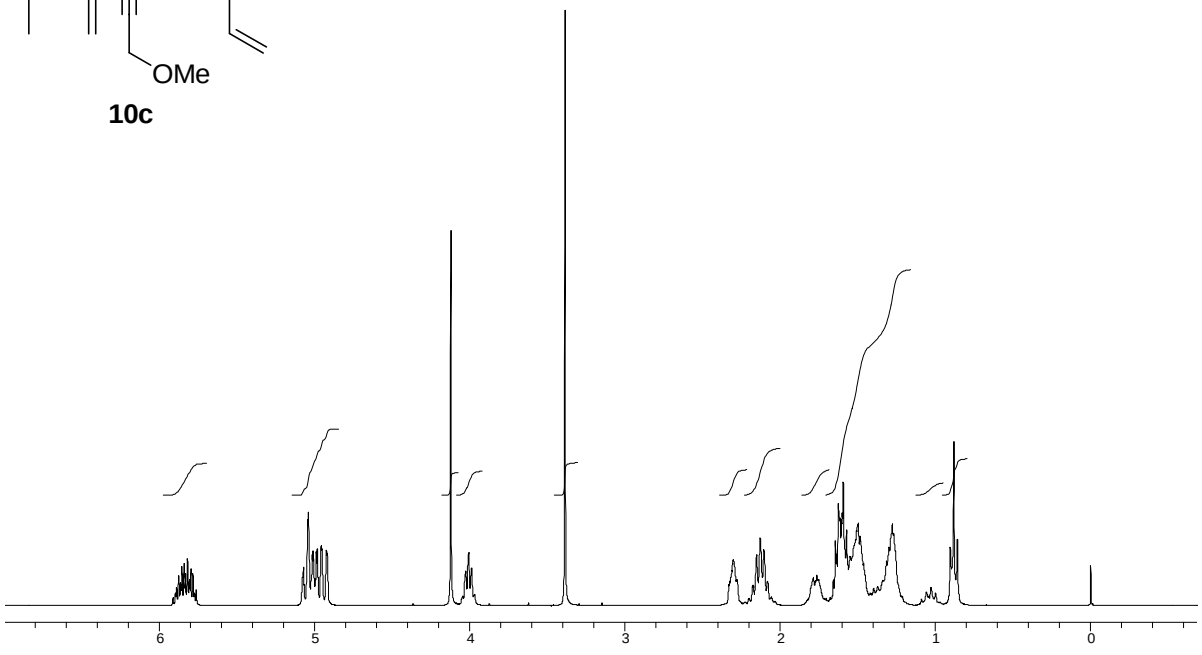
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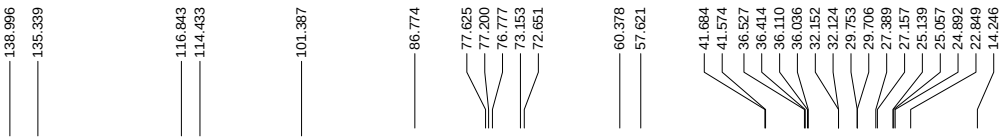
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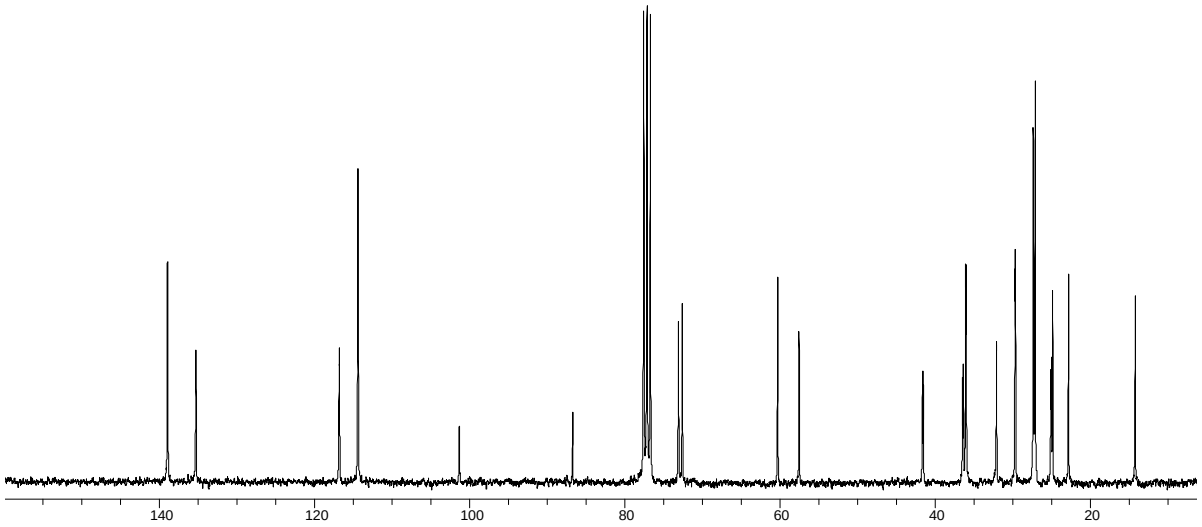
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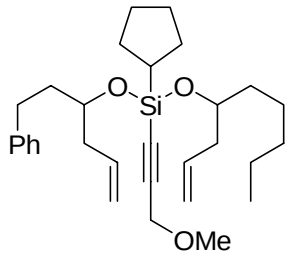
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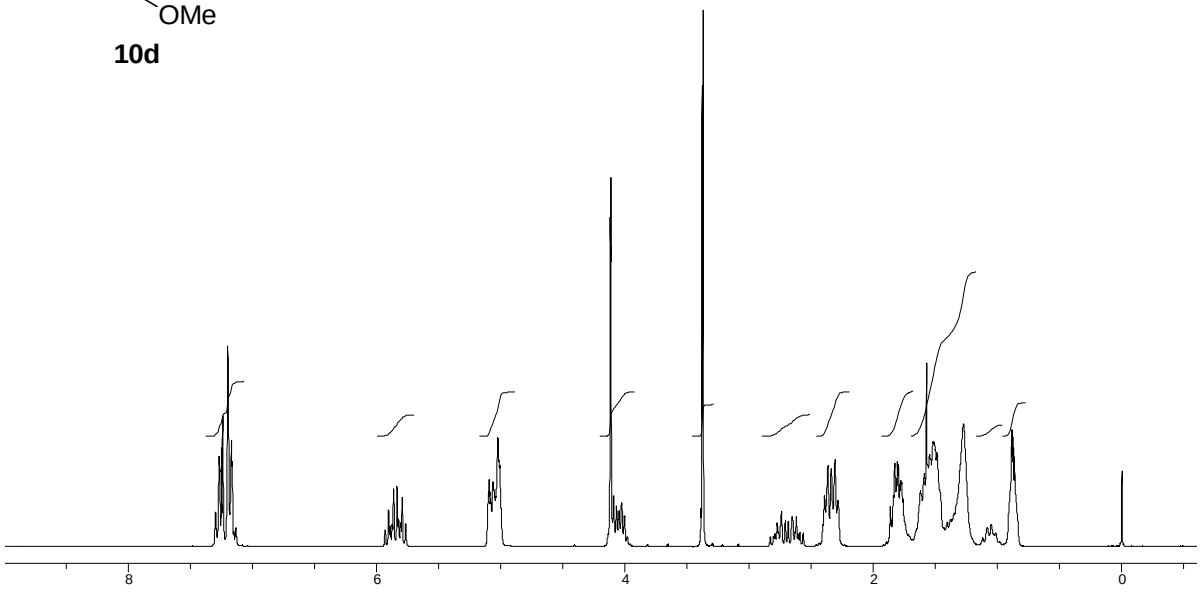
O
Ph
OMe

10d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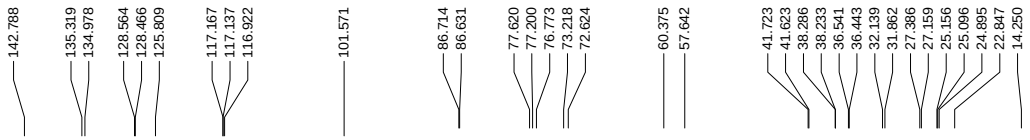
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77.200
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72.624
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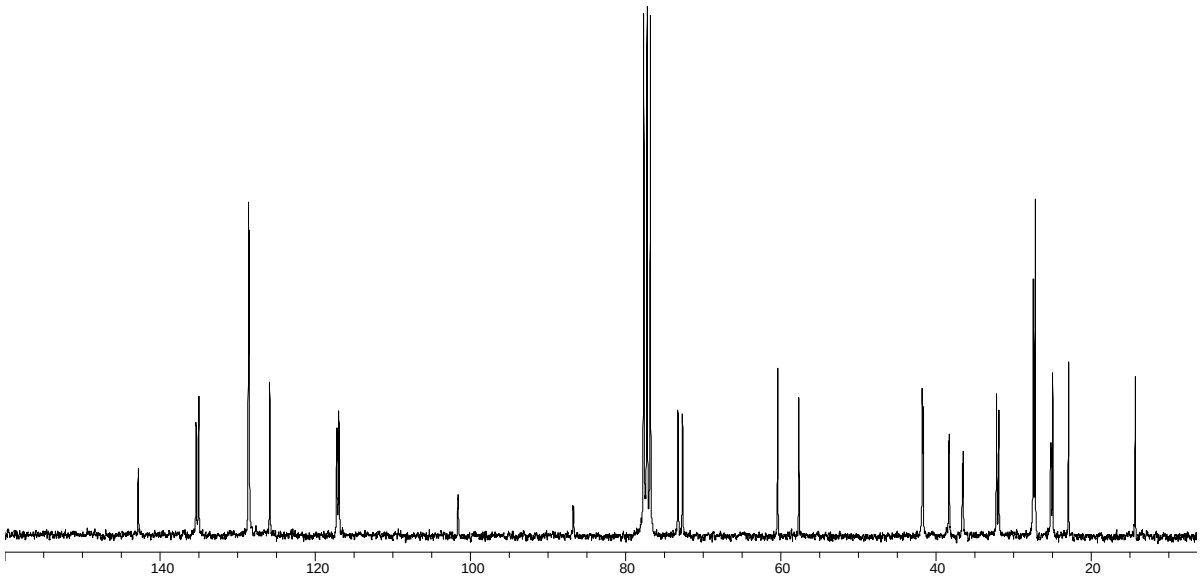
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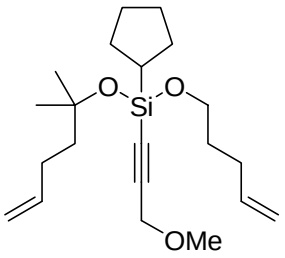
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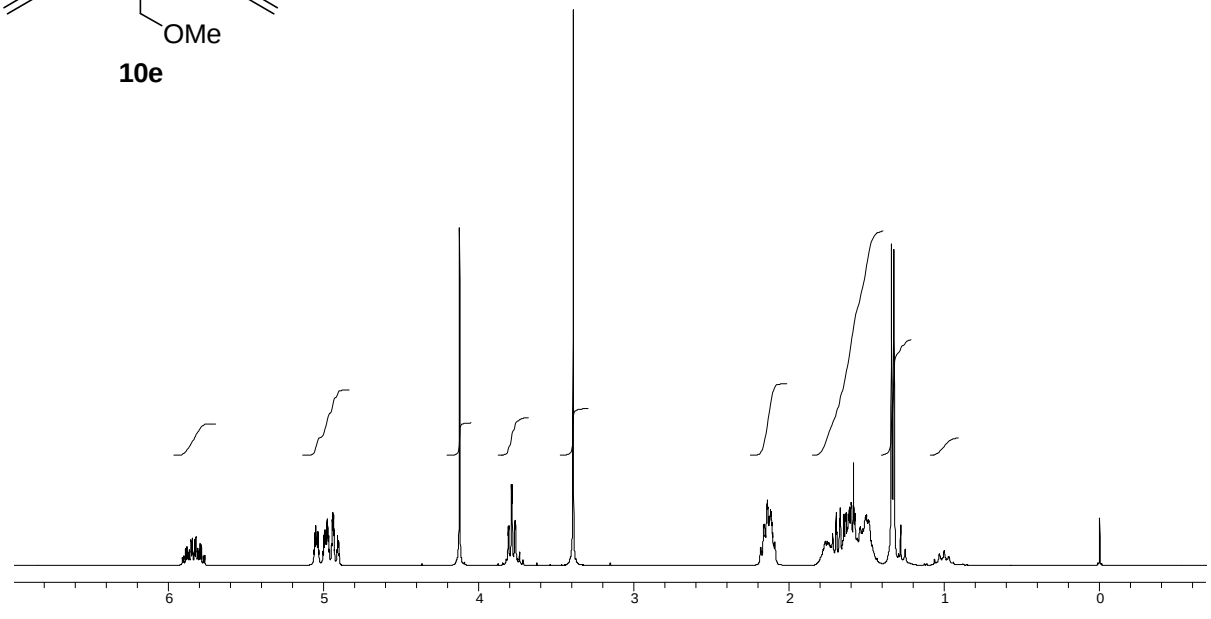
O
OMe

10e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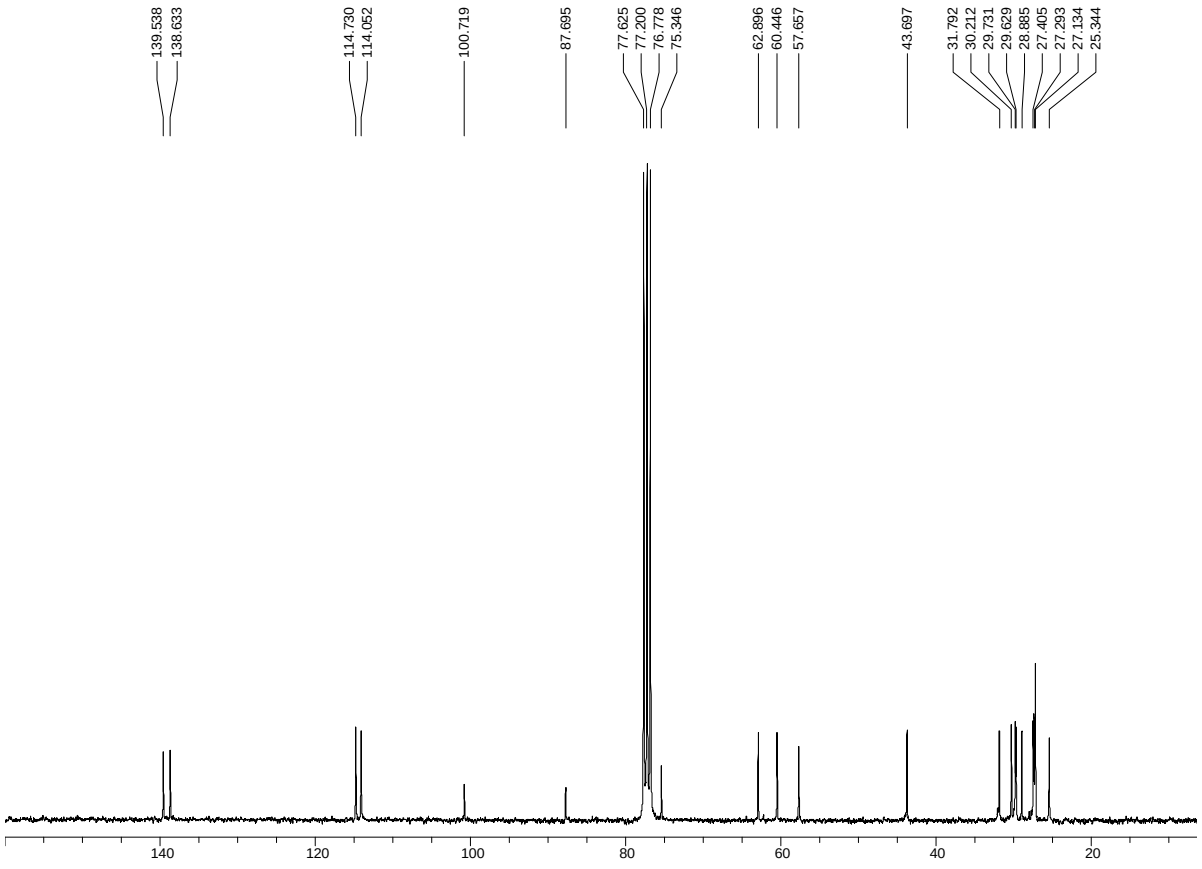
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57.657
43.697
31.792
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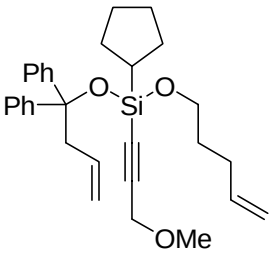
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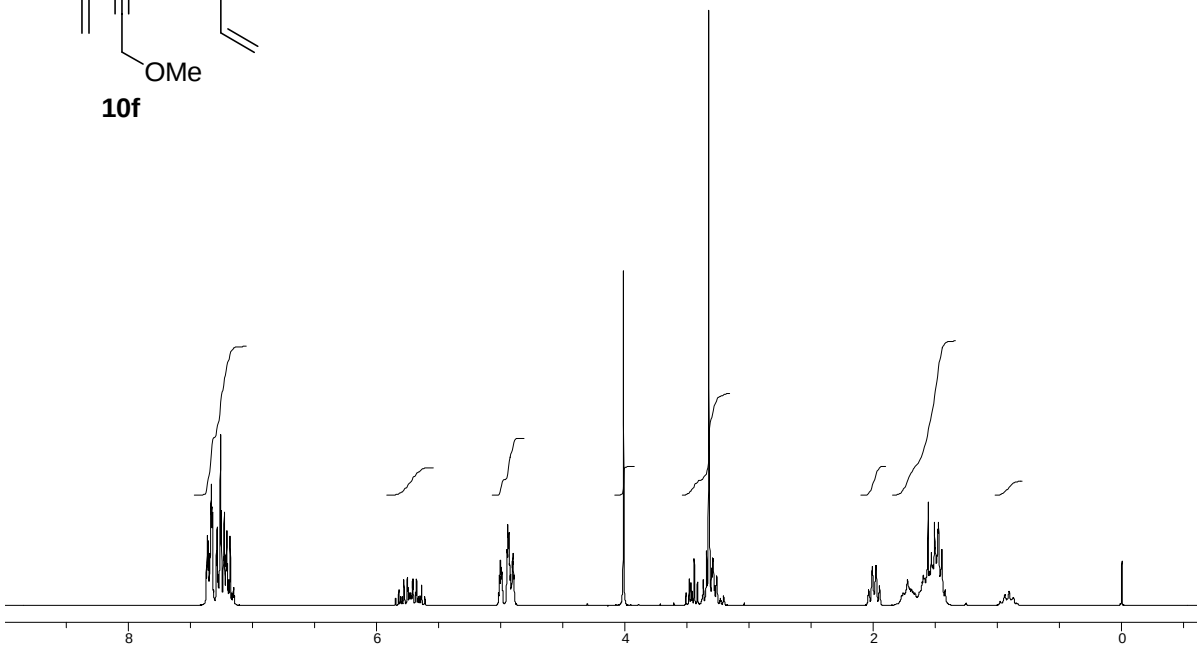
Ph
O
Si
O
OMe

10f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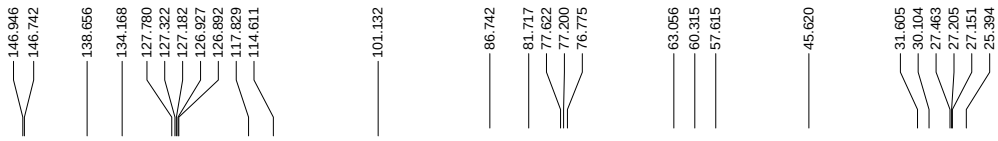
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77.622
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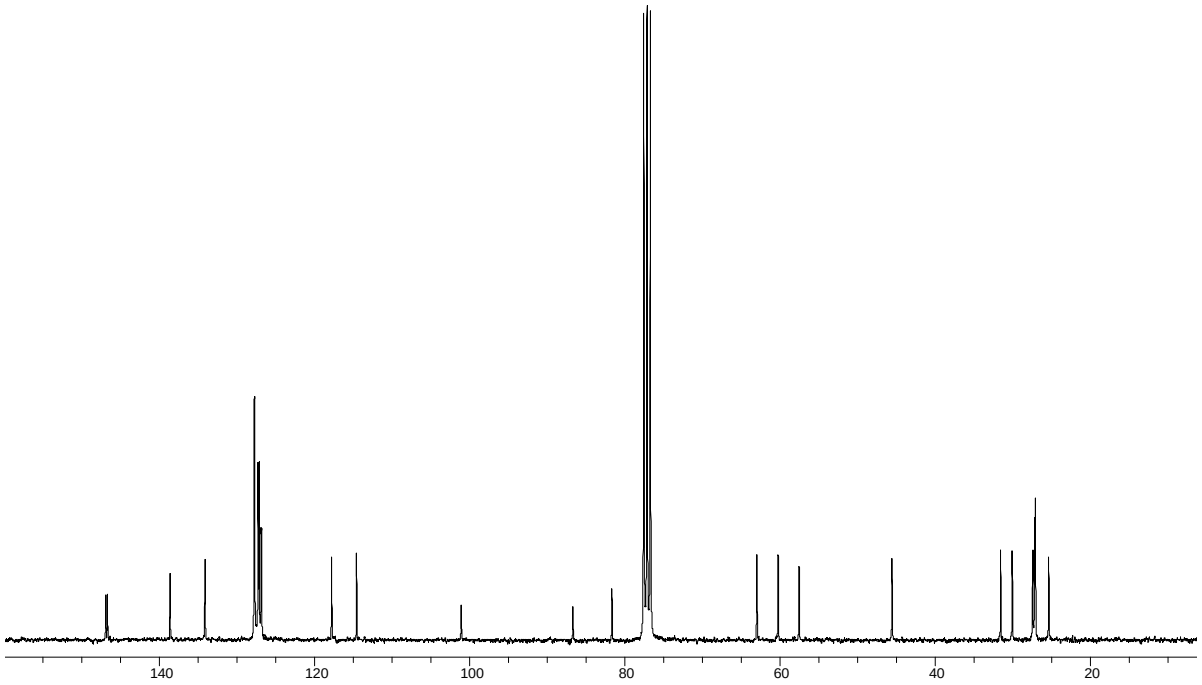
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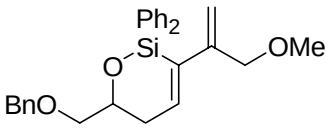
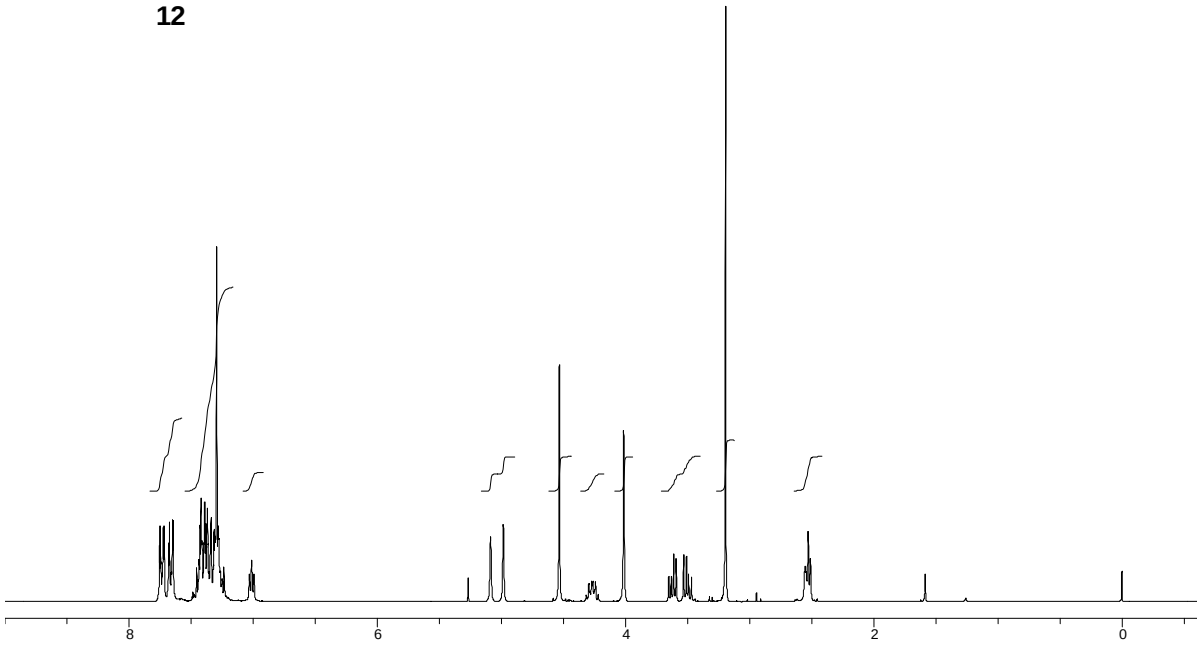

Ph2
Si
O
OMe
BnO

12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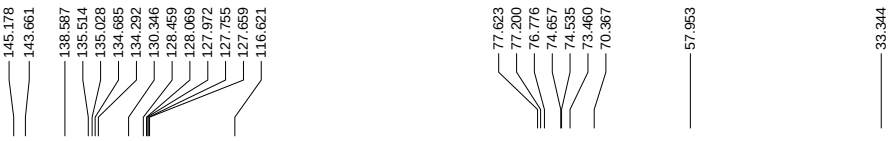
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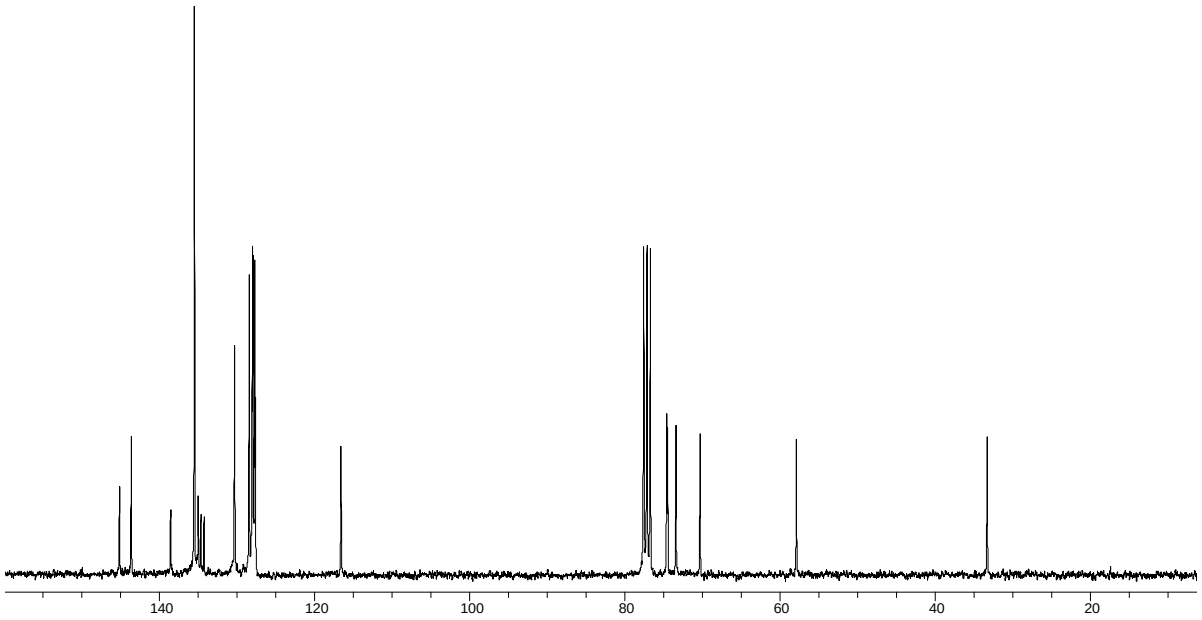
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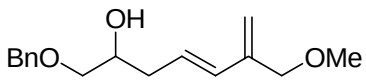
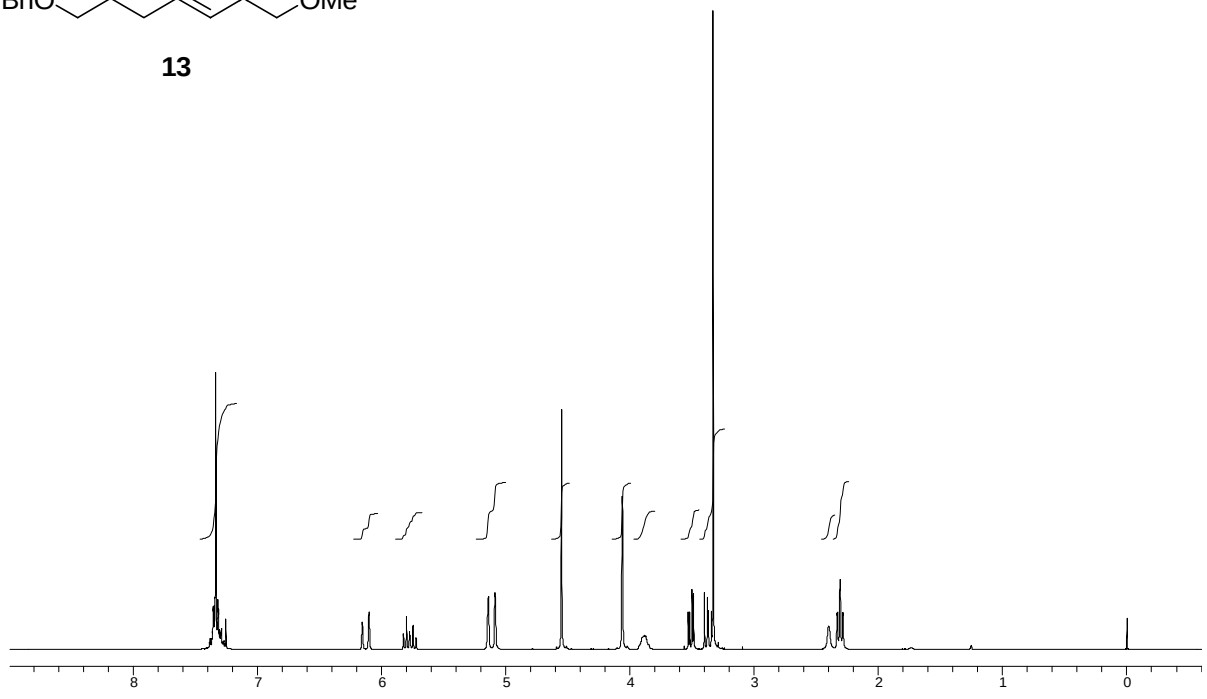

OH
BnO
OMe

13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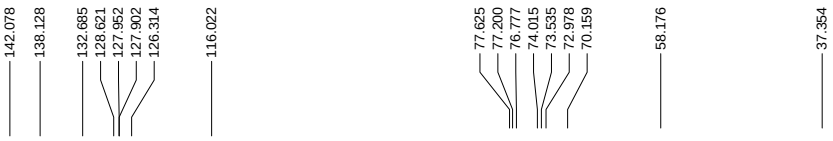
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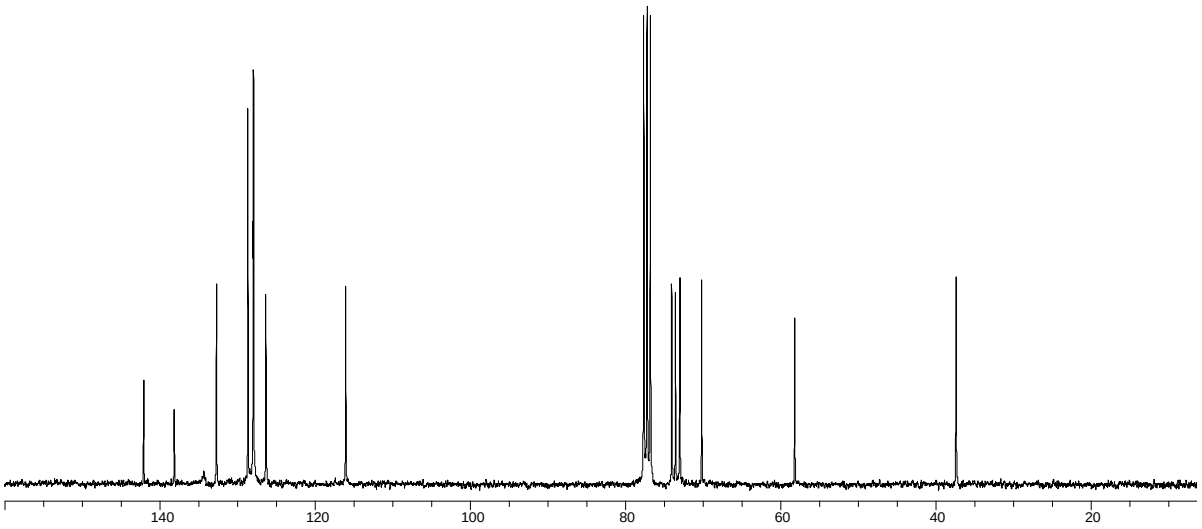
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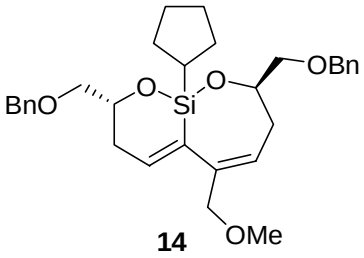
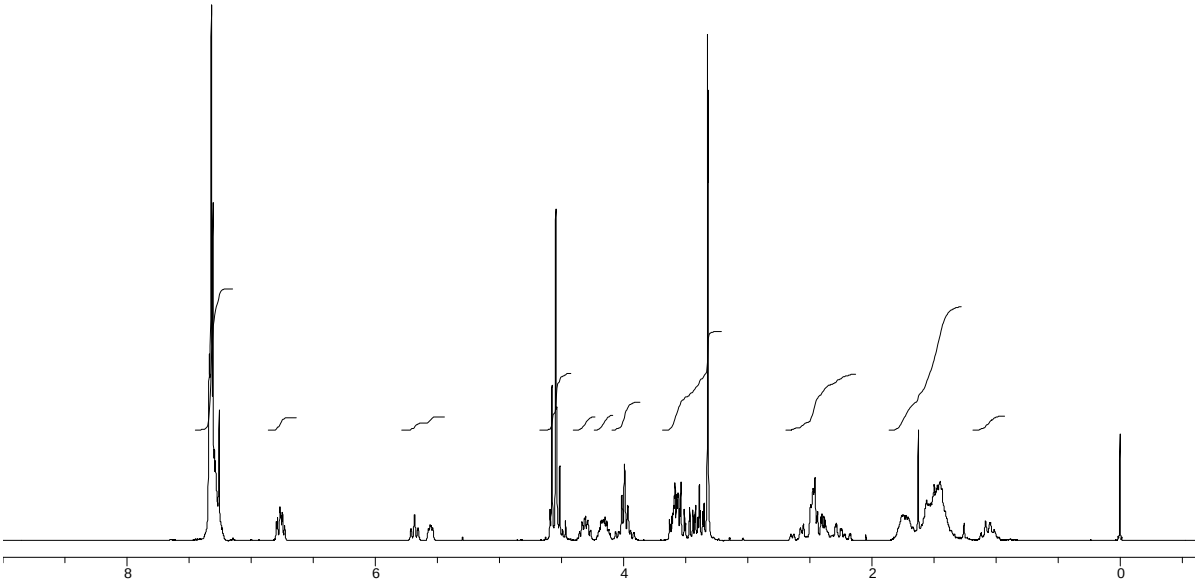

BnO
O
Si
O
OBn
OMe

14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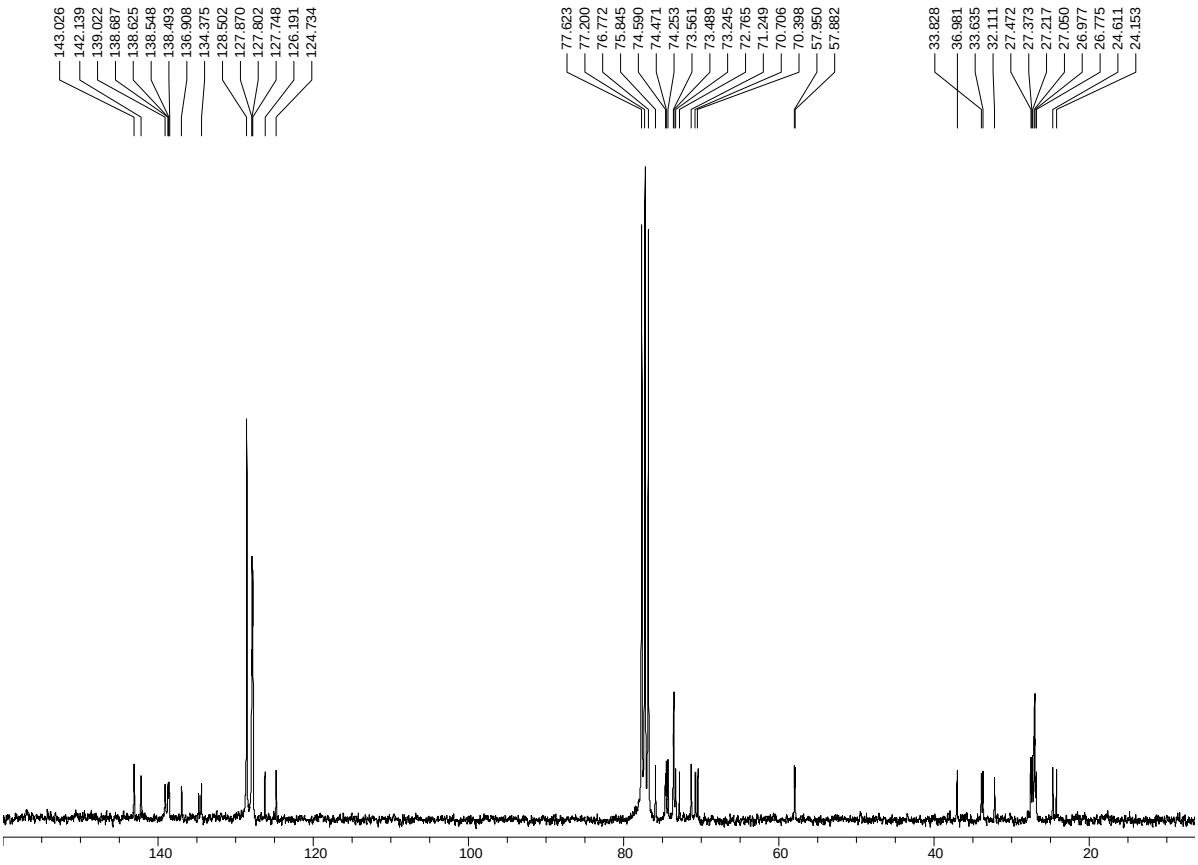
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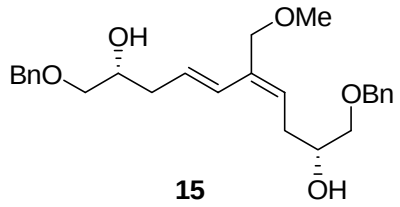
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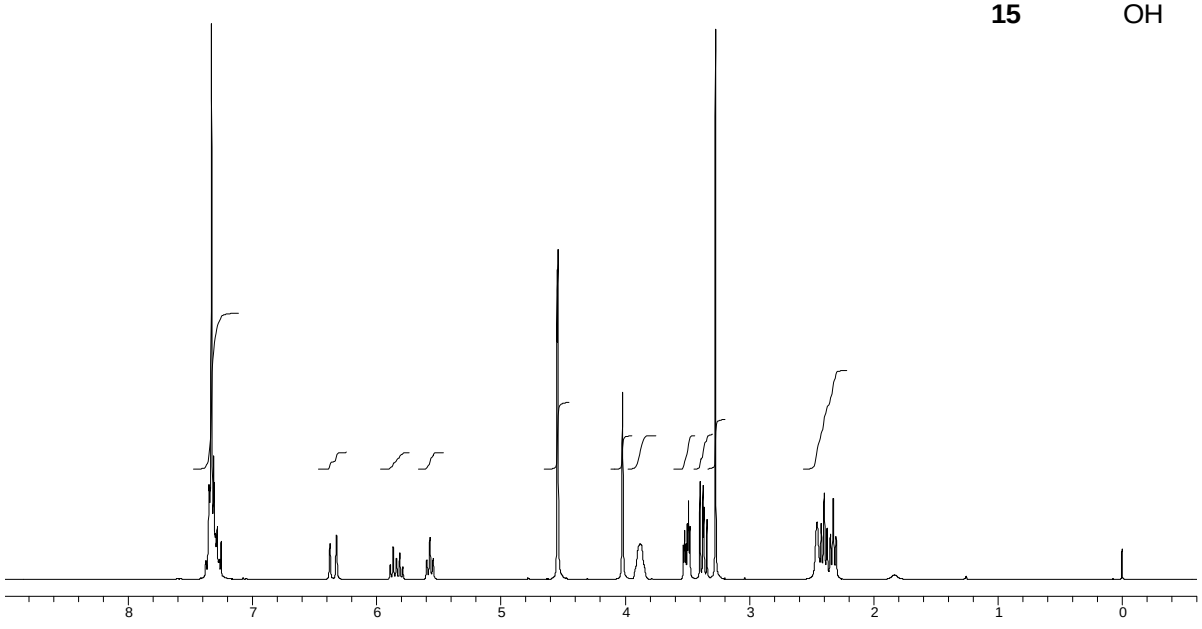
OH
BnO
OBn
OH

15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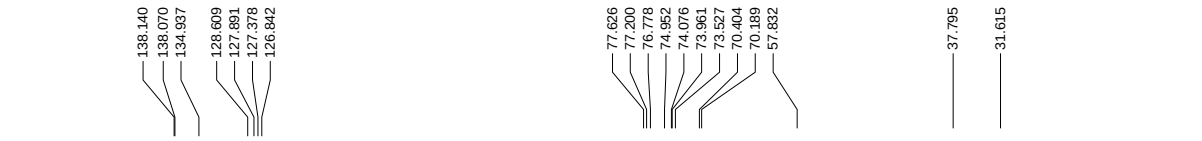
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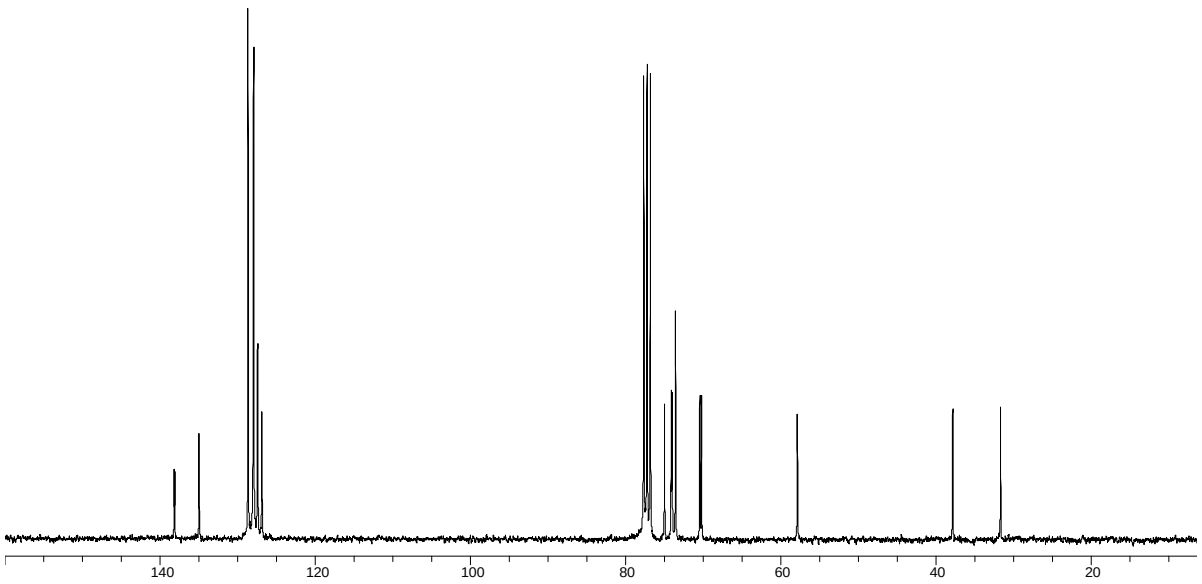
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