Ruthenium-Catalyzed Silyl Ether Formation and Enyne Metathesis Sequence: Synthesis of Siloxacycles from Terminal Alkenyl Alcohols and Alkynylsilanes

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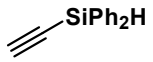
Supporting Information

Materials and Methods. All reagents were purchased from Aldrich except $[RhCl(cod)_2]_2$ which was purchased from Strem. Reactions were monitored by thin layer chromatography (TLC) using Fisher Silica Gel 60 F_{254} precoated plates. Proton and carbon-13 NMR spectra were recorded on Bruker AC-300 spectrometers. Chemical shifts are reported in δ values relative to the internal standard, tetramethylsilane (TMS). High resolution mass spectra were obtained using Leu5-enkephalin or erythromycin as a lock mass on a Micromass LCT ESI-TOF spectrometer equipped with Z-spray™ and a reflectron.

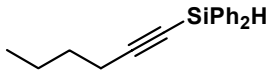
A. Experimental Section

(3-Methoxy-prop-1-ynyl)-diphenyl silane. To a stirred solution of methyl propargyl ether (0.43 mL, 5.11mmol) in 12 mL of dry THF at –78 °C was added *n*-BuLi (2.15 mL of a 2.5 M solution in hexanes, 5.37 mmol). After stirring for 15 minutes, chlorodiphenyl silane (1.0 mL, 5.11 mmol) was added. Reaction was stirred for 30 minutes at –78 °C, then allowed to warm to ambient temperature and stir for an additional three hours.

Reaction was then diluted with diethyl ether and quenched with saturated NH_4Cl solution. Ethereal layer was washed with brine, dried over $MgSO_4$ and concentrated to give 1.36 g of turbid light yellow oil. Filtration through a silica plug with hexanes and concentration gives 1.24 g of clear light yellow oil (97 % yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66 (m, 4H), 7.39 (m, 6H), 5.19 (s, 1H), 4.21 (s, 2H), 3.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.0, 131.6, 130.0, 128.0, 105.9, 84.7, 60.3, 57.6; HRMS (ESI) calcd for $C_{16}H_{16}OSi$ (MNa^+) 275.0868, found 275.0876.



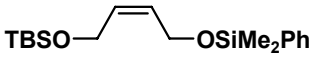
Ethynyl-diphenyl silane. Acetylene gas was bubbled through a stirred solution of *n*-BuLi (1.23 mL of a 2.5 M solution in hexanes, 3.09 mmol) in 10 mL of dry THF at –78 °C under nitrogen atmosphere. After stirring for 15 minutes, chlorodiphenyl silane (0.5 mL, 2.06 mmol) was added. Reaction was stirred for one hour at –78 °C, then allowed to warm to ambient temperature and stir for an additional two hours. Reaction was then diluted with diethyl ether and quenched with saturated NH_4Cl solution. Ethereal layer was washed with saturated $NaHCO_{3\,(aq)}$, dried over $MgSO_4$ and concentrated to give 0.38 g of light yellow oil. Flash column chromatography with hexanes and Et_2O gives 0.21 g of clear colorless oil (50 % yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.67 (m, 4H), 7.42 (m, 6H), 5.12 (s, 1H), 2.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.0, 131.1, 130.1, 128.0, 97.6, 83.3; HRMS (EI) calcd for $C_{14}H_{12}Si$ ($M^{\bullet+}$) 208.0708, found 208.0700.



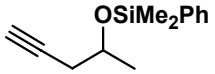
Hex-1-ynyl-diphenyl silane. To a stirred solution of 1-hexyne (0.24 mL, 2.06mmol) in 10 mL of dry THF at –78 °C was added *n*-BuLi (0.86 mL of a 2.5 M solution in hexanes, 2.16 mmol). After stirring for 15 minutes, chlorodiphenyl silane (0.5 mL, 2.06 mmol) was added. Reaction was stirred for 30 minutes at –78 °C, then allowed to warm to ambient temperature and stir for an additional three hours. Reaction was then diluted

with diethyl ether and quenched with saturated NH_4Cl solution. Ethereal layer was washed with saturated $NaHCO_{3\,(aq)}$, dried over $MgSO_4$ and concentrated to give 0.584 g of light yellow oil. Flash column chromatography with hexanes and Et_2O gives 0.53 g of clear colorless oil (98.5 % yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65 (m, 4H), 7.40 (m, 6H), 5.14 (s, 1H), 2.35 (t, J = 7.0 Hz, 2H), 1.59 (m, 2H), 1.47 (m, 2H), 0.93 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.9, 132.7, 129.7, 127.8, 117.8, 112.7, 30.3, 21.8, 19.7, 13.4; HRMS (EI) calcd for $C_{18}H_{20}Si$ ($M^{\bullet+}$) 264.1334, found 264.1339.

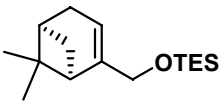
General reaction procedure for silyl ether formation. $[RuCl_2(p\text{-cymene})]_2$ (0.050 g, 0.082 mmol) was slowly added to a stirring mixture of (*R*)-myrtenol (5.00 g, 0.0328 mol), and triethyl silane (3.84 g, 0.033 mol). Reaction was heated to 50 °C for 6 hours and then flushed through a silica plug using ether/hexanes (1:3) to remove the catalyst. After concentration, 8.16 g (0.031 mol, 94 % yield) of the silyl ether was isolated.



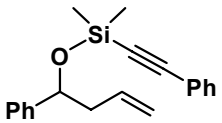
{[4-(*tert*-butyl-dimethyl-silanyloxy)-*cis*-but-2-enyloxy]-dimethyl-silanyl}-benzene. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62 (m,2H), 7.4 (m, 3H), 5.56 (m, 2H), 4.17 (m,4H), 1.8 (s, 9H), 0.4 (s, 6H), 0.08 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.6, 133.5, 130.8, 129.7, 127.9, 59.5, 59.3, 25.9, 18.3, -1.71, -5.23; HRMS (ESI) calcd for $C_{18}H_{32}O_2Si_2$ (MNa^+) 359.1839, found 359.1833.



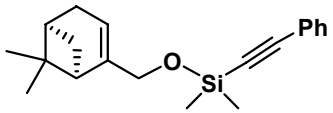
Dimethyl-(1-methyl-but-3-ynyloxy)-phenyl silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.6 (m, 2H), 7.35 (m, 3H), 3.99 (sext, J = 6.3 Hz, 1H), 2.38 (ddd, J = 16.5, 5.5, 2.8 Hz, 1H), 2.28 (ddd, J = 16.5, 7, 2.7 Hz, 1H), 1.96 (t, J = 2.3 Hz, 1H), 1.24 (d, J = 6.1 Hz, 3H), 0.40 (d, J = 1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.8, 133.3, 129.4, 127.6, 81.4, 69.7, 67.4, 29.0, 22.8, –1.34, –1.42; HRMS (ESI) calcd for $C_{13}H_{18}OSi$ (MNa^+) 241.1025, found 241.1025.



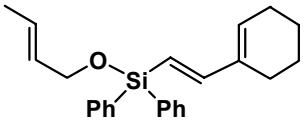
(*R*)-(-)-Myrtenoxy-triethyl silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.44 (m, 1H), 3.99 (m, 2H), 2.36 (m, 1H), 2.25 (m, 2H), 2.09 (m, 1H), 2.0 (td, *J* = 5.7, 1.3 Hz. 1H), 1.27 (s, 3H), 1.19 (d, *J* = 8.4 Hz, 1H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.83 (s, 3H), 0.61 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.2, 115.6, 65.1, 42.8, 41.0, 37.8, 26.0, 20.7, 6.59, 4.32; MS (ESI) calcd for $C_{163}H_{30}OSi$ (MNa^+) 289.1964, found 189.1976.



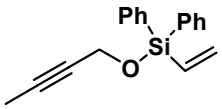
Dimethyl-(1-phenyl-but-3-enyloxy)-phenylethynyl silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35 (m, 10H), 5.82 (m, 1H), 5.03 (m, 3H), 2.55 (m, 2H), 0.4 (s, 3H), 0.2 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.9, 134.9, 131.8, 128.0, 127.9, 127.0, 126.0, 122.5, 116.8, 105.2, 91.7, 75.5, 44.4, 2.02, 0.48; HRMS (ESI) calcd for $C_{20}H_{22}OSi$ (MNa^+) 329.1338, found 329.1353.



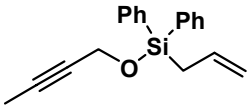
Dimethyl-((*R*)-(-)-myrtenoxy)-phenylethynyl silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35 (m, 2H), 7.2 (m, 3H), 5.35 (m, 1H), 3.9 (m, 2H), 2.25 (m, 1H), 2.09 (m, 1H), 2.0 (d, *J* = 5.5 Hz, 1H), 1.27 (s, 3H), 1.10 (d, *J* = 8.4 Hz, 1H), 0.83 (s, 3H), 0.2 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.8, 131.9, 128.5, 128.0, 122.4, 116.7, 104.8, 91.5, 65.7, 42.8, 40.8, 37.6, 31.2, 30.6, 25.7, 20.5, 1.7, –0.35; HRMS (ESI) calcd for $C_{20}H_{26}OSi$ (MNa^+) 333.1651, found 333.1653.



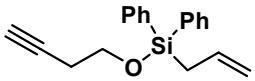
But-2-enyloxy-(2-cyclohex-1-enyl-vinyl)-dimethyl silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62 (m, 4H), 7.37 (m, 3H), 6.7 (d, *J* = 19 Hz, 1H), 5.95 (d, *J* = 19 Hz, 1H), 5.83 (t, *J* = 3.8 Hz, 1H), 5.63 (m, 2H), 4.21 (m, 2H), 2.19 (m, 4H), 1.65 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.6, 137.1, 134.9, 133.1, 129.7, 129.6, 127.6, 126.8, 116.9, 64.3, 25.9, 23.8, 22.3, 22.2, 17.5; HRMS (ESI) calcd for $C_{23}H_{26}OSi$ (MNa^+) 383.1807, found 383.1816.



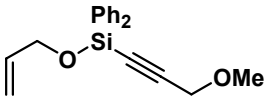
But-2-ynyloxy-diphenyl-vinyl silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65 – 7.62 (m, 4H), 7.45 – 7.34 (m, 6H), 6.52 (dd, *J* = 15, 20, 1H), 6.42 (dd, *J* = 15, 3.6, 1H), 5.93 (dd, *J* = 20, 3.5, 1H), 4.37 (m, 2H), 1.77 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.269, 135.055, 134.775, 133.637, 133.066, 130.035, 127.795, 82.022, 52.527, 3.675; HRMS (EI) calcd for $C_{18}H_{18}OSi$ ($M^{\bullet+}$) 278.1127, found 278.1117.



Allyl-but-2-ynyloxy-diphenyl silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64 – 7.61 (m, 4H), 7.46 – 7.35 (m, 6H), 5.85 (m, 1H), 5.00 – 4.867 (m, 2H), 4.34 (q, *J* = 2.4, 2H), 2.24 (dt, *J* = 7.5, 1.5, 2H), 1.79 (t, *J* = 2.1, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.869, 133.883, 132.810, 130.046, 127.799, 115.258, 81.842, 77.206, 52.530, 21.929, 3.607; HRMS (EI) calcd for $C_{19}H_{20}OSi$ (M -C_3H_5) $^{\bullet+}$, 251.0892, found 251.0884.

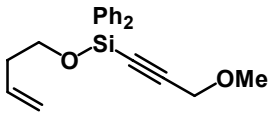


Allyl-but-3-ynyloxy-diphenyl silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64 – 7.59 (m, 4H), 7.46 – 7.34 (m, 6H), 5.83 (m, 1H), 5.00 – 4.89 (m, 2H), 2.46 (dt, *J* = 6.9, 2.3, 2H), 2.21 (dt, *J* = 7.5, 1.5, 2H), 1.95 (t, *J* = 2.7, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.453, 133.827, 132.503, 129.775, 127.581, 114.953, 81.324, 69.196, 61.773, 22.257, 21.448; HRMS (EI) calcd for $C_{19}H_{20}OSi$ (M -C_3H_5) $^{\bullet+}$, 251.0892, found 251.0890.

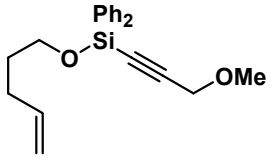


Allyloxy-(3-methoxy-prop-1-ynyl)-diphenyl-silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (m, 4H), 7.41 (m, 6H), 5.97 (ddt, *J* = 17, 10.4, 4.9 Hz, 1H), 5.32 (dq, *J* = 17, 1.9 Hz, 1H), 5.12 (dq, *J* = 10.4, 1.7 Hz, 1H), 4.36 (dt, *J* = 5, 1.7 Hz, 2H), 4.24 (s, 2H), 3.44 (s,

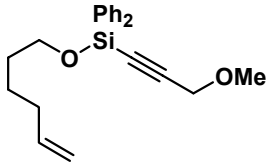
3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.1, 134.5, 133.1, 130.3, 127.8, 114.9, 104.8, 86.1, 64.8, 60.2, 57.6; HRMS (ESI) calcd for $C_{19}H_{20}O_2Si$ (MNa^+) 331.1130, found 331.1143.



But-3-enyloxy-(3-methoxy-prop-1-ynyl)-diphenyl silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71 (m, 4H), 7.41 (m, 6H), 5.83 (ddt, *J* = 17.2, 10.3, 6.8 Hz, 1H), 5.04 (m, 2H), 4.24 (s, 2H), 3.87 (t, *J* = 6.8 Hz, 2H), 3.44 (s, 3H), 2.39 (ABq, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.8, 134.5, 133.3, 130.2, 127.7, 116.4, 104.7, 86.1, 63.4, 60.2, 57.6, 36.6; HRMS (ESI) calcd for $C_{20}H_{22}O_2Si$ (MNa^+) 345.1287, found 345.1279.

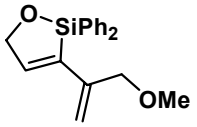


(3-Methoxy-prop-1-ynyl)-pent-4-enyloxy-diphenyl silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71 (m, 4H), 7.41 (m, 6H), 5.80 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 4.95 (m, 2H), 4.24 (s, 2H), 3.83 (t, *J* = 6.4 Hz, 2H), 3.44 (s, 3H), 2.15 (ABq, *J* = 7 Hz, 2H), 1.72 (pent, *J* = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.1, 134.4, 133.4, 130.2, 127.7, 114.4, 104.6, 86.1, 63.4, 60.2, 57.6, 31.3, 29.8; HRMS (ESI) calcd for $C_{21}H_{24}O_2Si$ (MNa^+) 359.1443, found 359.1450.

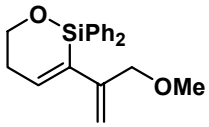


Hex-5-enyloxy-(3-methoxy-prop-1-ynyl)-diphenyl silane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71 (m, 4H), 7.41 (m, 6H), 5.79 (ddt, *J* = 16.9, 10, 6.6 Hz, 1H), 4.95 (m, 2H), 4.24 (s, 2H), 3.82 (t, *J* = 6.5 Hz, 2H), 3.44 (s, 3H), 2.04 (m, 2H), 1.64 (m, 2H), 1.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.0, 135.8, 134.8, 131.6, 129.1, 115.6, 105.7, 87.6, 65.2, 61.6, 58.9, 34.6, 32.9, 26.3; HRMS (EI) calcd for $C_{22}H_{26}O_2Si$ $(M - C_4H_5O)^{\bullet+}$ 281.1362, found 281.1370.

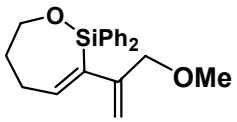
Procedure for silyl ether formation and ring closing enyne metathesis. In a vial, 0.063g (0.30 mmol) of diphenylethynyl silane and 0.026 g (0.30 mmol) of 4-penten-1-ol were mixed followed by 0.001 g (0.500 mol %) of $[RuCl_2(p\text{-cymene})]_2$. Immediate hydrogen evolution occurs. After reacting six hours, the resulting oil was flushed over a small plug of silica gel with hexanes and diethyl ether (1:1) and then concentrated to give 88 mg of light yellow oil. A portion of this silyl ether (0.42 g, 0.145 mmol) was placed in a 100 mL roundbottom flask and diluted with 35 mL of dry dichloromethane (0.003 M with respect to the silyl ether), followed by addition of 9 mg (7.5 mol %) of Grubbs' second generation catalyst. After refluxing for one hour, the mixture was concentrated after being allowed to cool. Flash column chromatography using hexanes and diethyl ether gave 34 mg of clear oil (81 % yield over two steps).



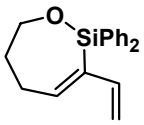
3-(1-Methoxymethyl-vinyl)-2,2-diphenyl-2,5-dihydro-[1,2]oxasilole. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65 (m, 4H), 7.40 (m, 6H), 7.09 (t, J = 2.0 Hz, 1H), 5.21 (bs, 1H), 5.13 (bs, 1H), 4.88 (bs, 2H), 4.13 (bs, 2H), 3.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.9, 141.3, 136.5, 135, 133.6, 130.2, 127.8, 117.7, 74.1, 72.6, 57.7; HRMS (ESI) calcd for $C_{19}H_{20}O_2Si$ (MNa^+) 331.1130, found 331.1127.



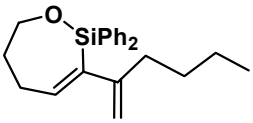
3-(1-Methoxymethyl-vinyl)-2,2-diphenyl-5,6-dihydro-2*H*-[1,2]oxasiline. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70 (m, 4H), 7.40 (m, 6H), 7.06 (t, J = 4.7 Hz, 1H), 5.09 (bs, 1H), 4.99 (bs, 1H), 4.06 (t, J = 5.5 Hz, 2H), 4.02 (bs, 2H), 3.20 (s, 3H), 2.56 (ABq, J = 5.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.9, 144.5, 135.3, 134.6,134.1, 130.2, 127.7, 116.4, 74.3, 61.3, 57.4, 30.6; HRMS (ESI) calcd for $C_{20}H_{22}O_2Si$ (MNa^+) 345.1287, found 345.1293.



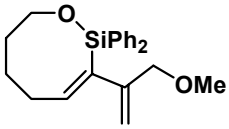
3-(1-Methoxymethyl-vinyl)-2,2-diphenyl-2,5,6,7-tetrahydro-[1,2]oxasilepine. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68 (m, 4H), 7.41 (m, 6H), 6.89 (t, *J* = 6.0 Hz, 1H), 4.93 (bs, 1H), 4.88 (bs, 1H), 4.01 (t, *J* = 5.7 Hz, 2H), 3.74 (bs, 2H), 3.10 (s, 3H), 2.56 (ABq, *J* = 5.8 Hz, 2H), 1.87 (pent, *J* = 5.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.6, 139.0, 135.0, 129.7, 127.6, 113.6, 75.0, 64.9, 57.4, 29.9, 29.0; HRMS (ESI) calcd for $C_{21}H_{24}O_2Si$ (MNa^+) 359.1443, found 359.1460.



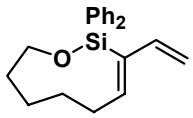
2,2-Diphenyl-3-vinyl-2,5,6,7-tetrahydro-[1,2]oxasilepine. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64 (m, 4H), 7.40 (m, 6H), 6.91 (t, *J* = 5.7 Hz, 1H), 6.44 (dd, *J* = 17.6, 10.9 Hz, 1H), 4.85 (d, *J* = 7.7 Hz, 1H), 4.80 (bs, 1H), 3.99 (t, *J* = 5.8 Hz, 2H), 2.56 (ABq, *J* = 5.7 Hz, 2H), 1.85 (m, 2H) ; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.8, 142.0, 137.7, 135.1, 134.8, 129.8, 127.7, 115.1, 65.2, 30.6, 29.3; HRMS (EI) calcd for $C_{19}H_{20}OSi$ ($M^{\bullet+}$) 292.1283, found 292.1281. Small amount of hydrogenated alkyne present.



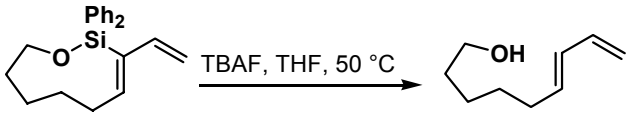
3-(1-Methylene-pentyl)-2,2-diphenyl-2,5,6,7-tetrahydro-[1,2]oxasilepine. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63 (m, 4H), 7.37 (m, 6H), 6.75 (t, *J* = 6.1 Hz, 1H), 4.66 (m, 2H), 3.99 (t, *J* = 5.8 Hz, 2H), 2.52 (m, 2H), 1.94 (m, 2H), 1.85 (m, 2H), 1.21 (m, 4H), 1.09 (m, 2H), 0.89 (m, 2H), 0.77 (t, *J* = 7.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.8, 145.6, 141.6, 135.0, 134.9, 129.6, 127.6, 111.9, 64.4, 35.6, 29.5, 28.4, 21.8, 13.6; HRMS (ESI) calcd for $C_{21}H_{26}OSi$ (MNa^+) 371.1807, found 371.1825. Small amount of hydrogenated alkyne present.



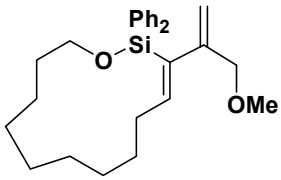
3-(1-Methoxymethyl-vinyl)-2,2-diphenyl-5,6,7,8-tetrahydro-2H-[1,2]oxasilocine. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.67 (m, 4H), 7.39 (m, 6H), 6.68 (t, *J* = 8.7 Hz, 1H), 4.95 (m, 1H), 4.90 (bs, 1H), 4.06 (m, 2H), 3.76 (bs, 2H), 3.11 (s, 3H), 2.65 (m, 2H), 1.81 (m, 2H), 1.69 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.6, 146.5, 140.0, 135.2, 134.9, 129.5, 127.6, 113.0, 75.0, 66.0, 57.6, 28.8, 27.7, 25.8; HRMS (ESI) calcd for $C_{22}H_{26}O_2Si$ (MNa^+) 373.1600, found 373.1595.



2,2-Diphenyl-3-vinyl-2,5,6,7,8,9-hexahydro-[1,2]oxasilonine. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.64 (m, 4H), 7.39 (m, 6H), 6.56 (t, *J* = 9 Hz, 1H), 6.40 (ddd, *J* = 17.5, 11, 0.8 Hz, 1H), 4.86 (dd, *J* = 17.5, 1.2 Hz, 1H), 4.79 (dd, *J* = 11, 1.4 Hz, 1H), 3.75 (m, 2H), 2.54 (m, 2H), 1.63 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.8, 142.4, 137.4, 135.0, 134.9, 129.6, 127.6, 114.1, 65.2, 30.9, 29.2, 27.9, 22.6; HRMS (EI) calcd for $C_{21}H_{24}OSi$ ($M^{\bullet+}$) 320.1596, found 320.1604. Small amount of hydrogenated alkyne present. To fully characterize and determine stereochemistry of internal double bond, proteodesilylation was performed.

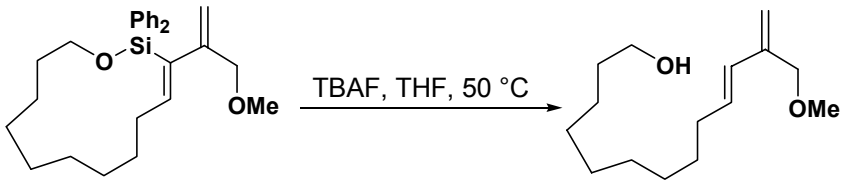


Nona-(*E*)6, 8-dienol. See Wulff, W. D.; Powers, T. S. *J. Org. Chem.* **1993**, *58*, 2381.

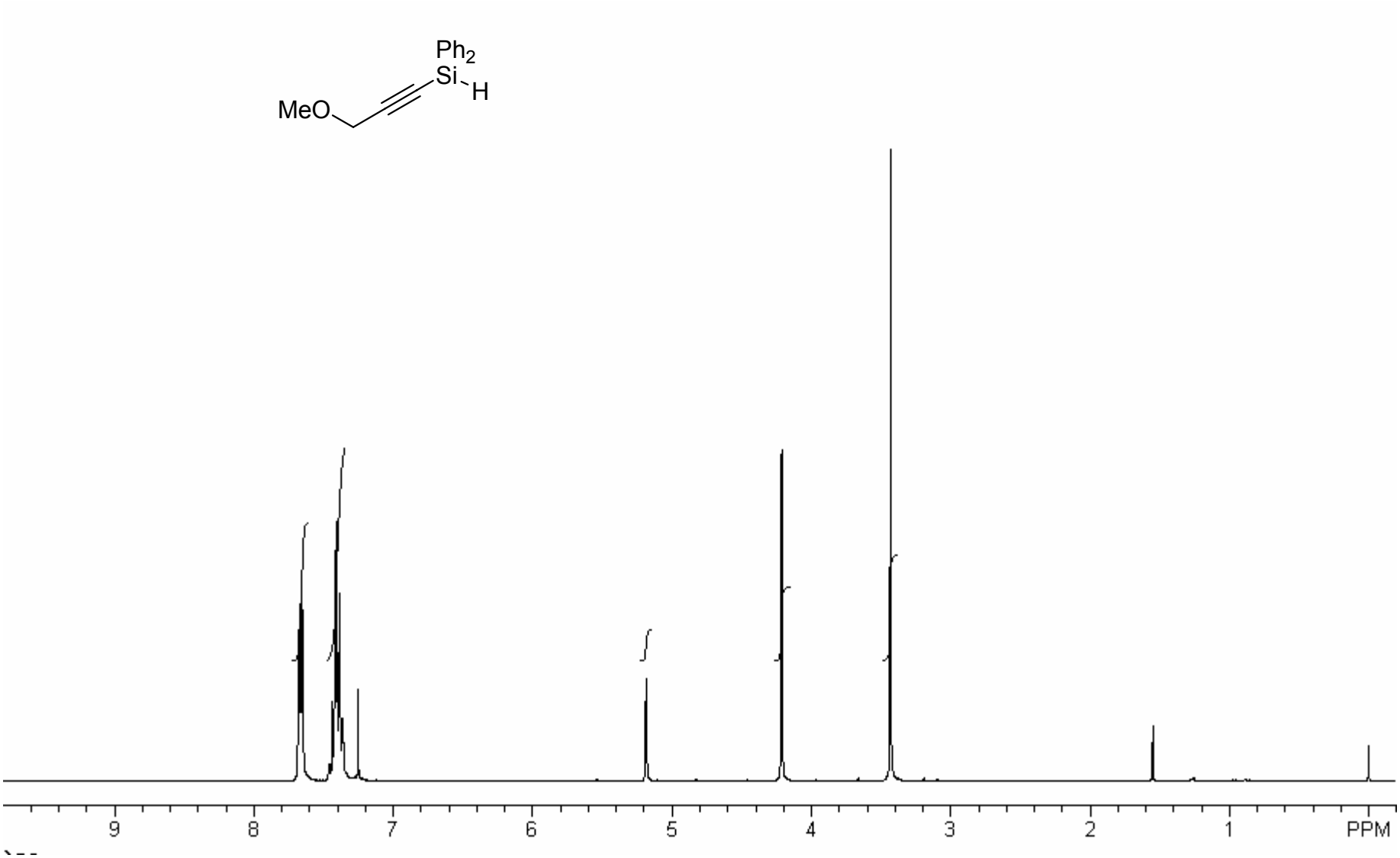


3-(1-Methoxymethyl-vinyl)-2,2-diphenyl-1-oxa-2-sila-cyclotridec-3-ene. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63 (m, 4H), 7.37 (m, 6H), 6.38 (t, *J* = 7.5 Hz, 1H), 4.83 (m, 2H),

3.81 (m, 2H), 3.47 (bs, 2H), 2.99 (s, 3H), 2.22 (m, 2H), 1.55 (m, 2H), 1.35 (m, 8H), 1.25 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.7, 150.7, 135.1, 134.3, 129.5, 127.7, 111.1, 75.2, 63.1, 57.6, 31.0, 30.6, 27.3, 26.8, 26.3, 25.2, 24.2, 22.7; HRMS (EI) calcd for $C_{27}H_{36}O_2Si$ ($M^{\bullet+}$) 420.2485, found 420.2488. To fully characterize and determine stereochemistry of internal double bond, proteodesilylation was performed.



12-Methoxymethyl-trideca-(*E*)10,12-dien-1-ol. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.05 (d, *J* = 15.8 Hz, 1H), 5.78 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.09 (s, (ABq, *J* = 7.4 Hz, 2H), 1.57 (m, 4H), 1.29 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 145.0, 134.3, 132.3, 117.4, 75.6, 65.8, 60.7, 35.7, 35.5, 32.2, 32.1, 31.9; HRMS (ESI) calcd for $C_{15}H_{28}O_2$ (MNa^+) 263.1987, found 263.1990.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8
7
6
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4
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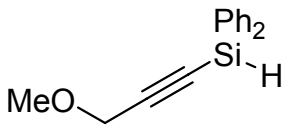
2
1
PPM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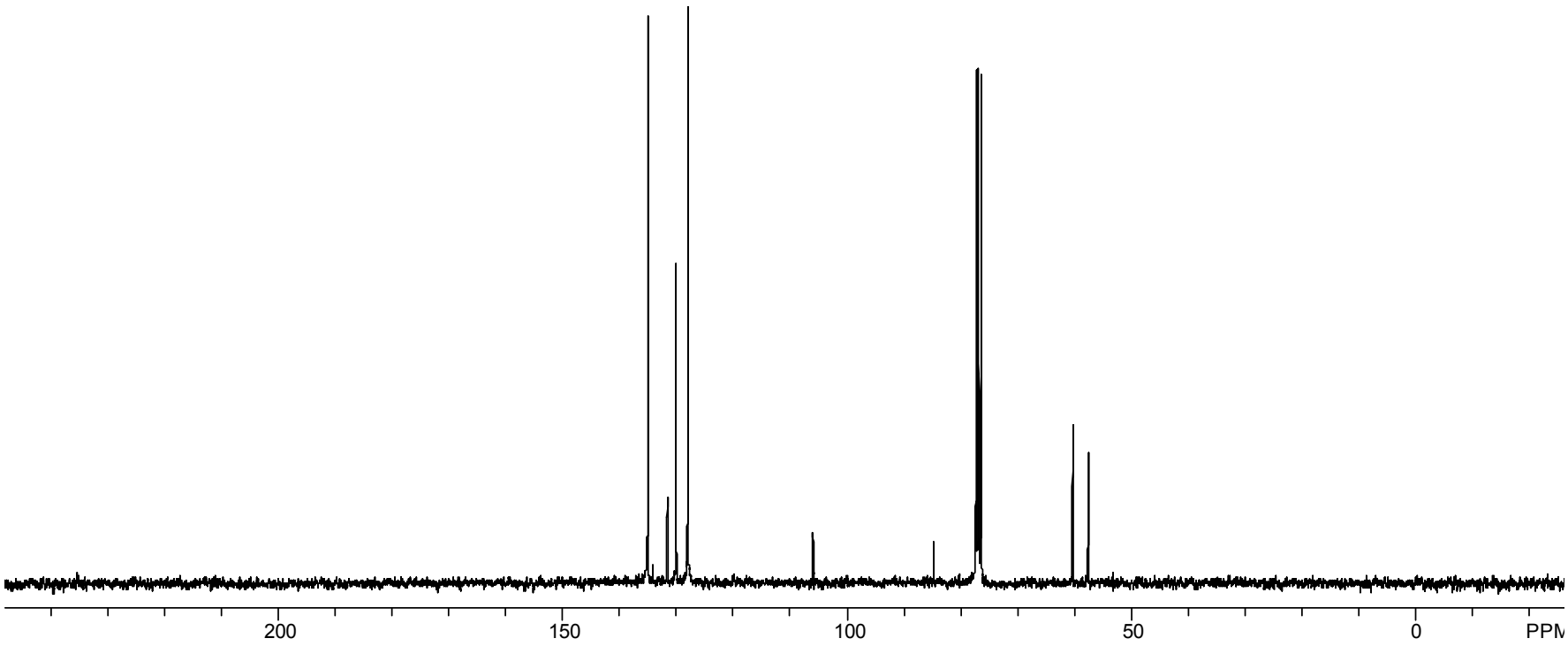
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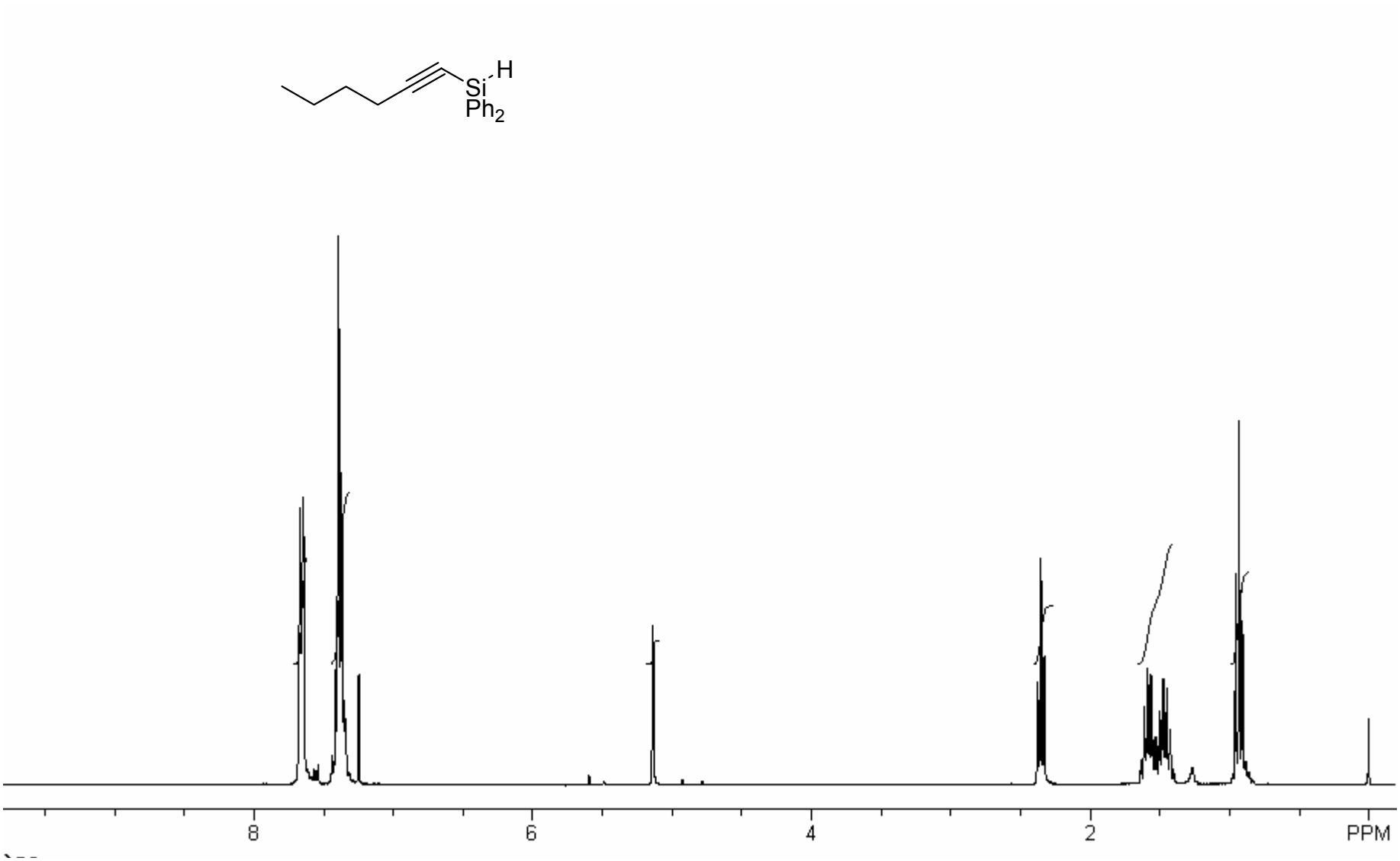
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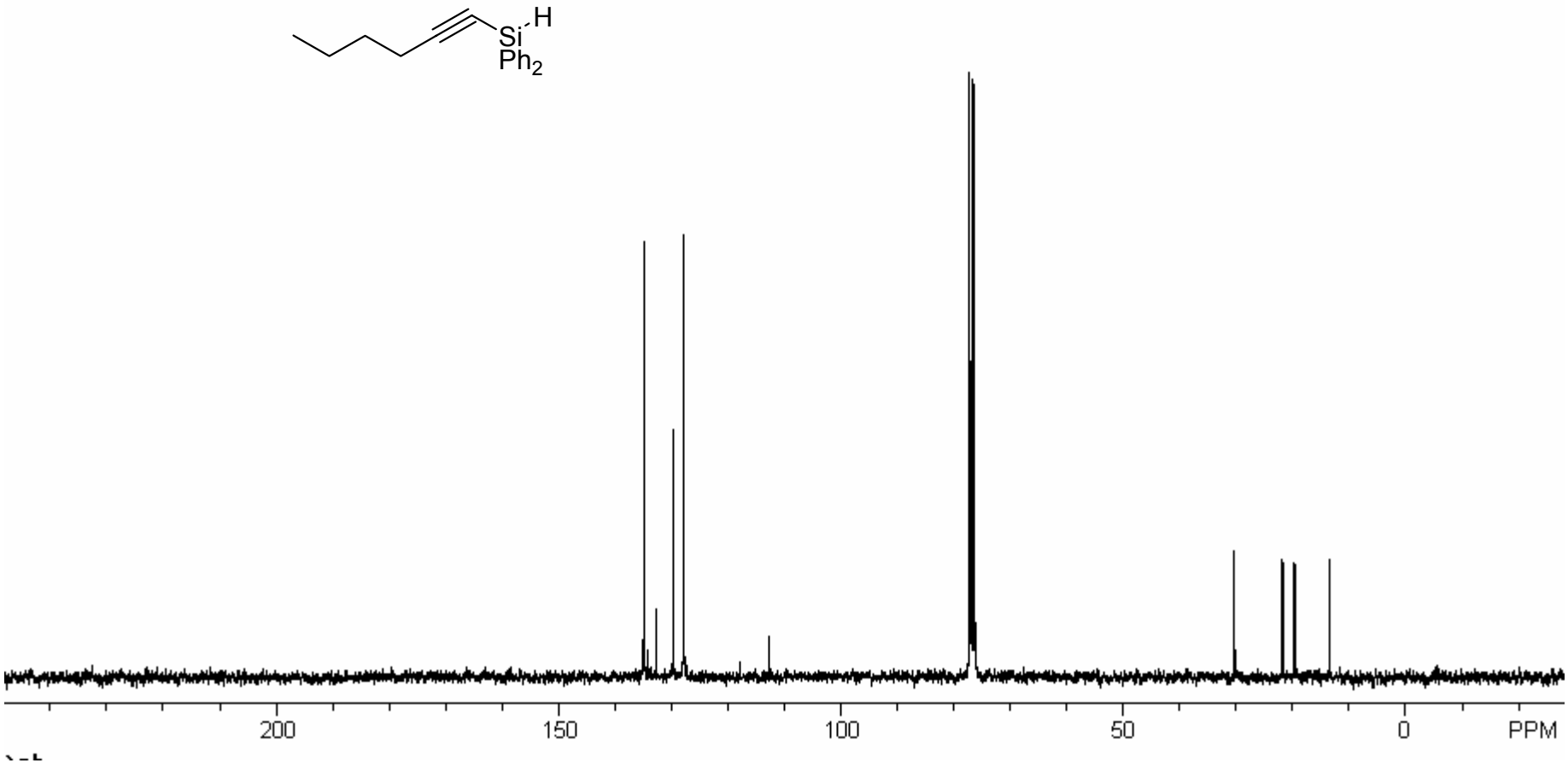
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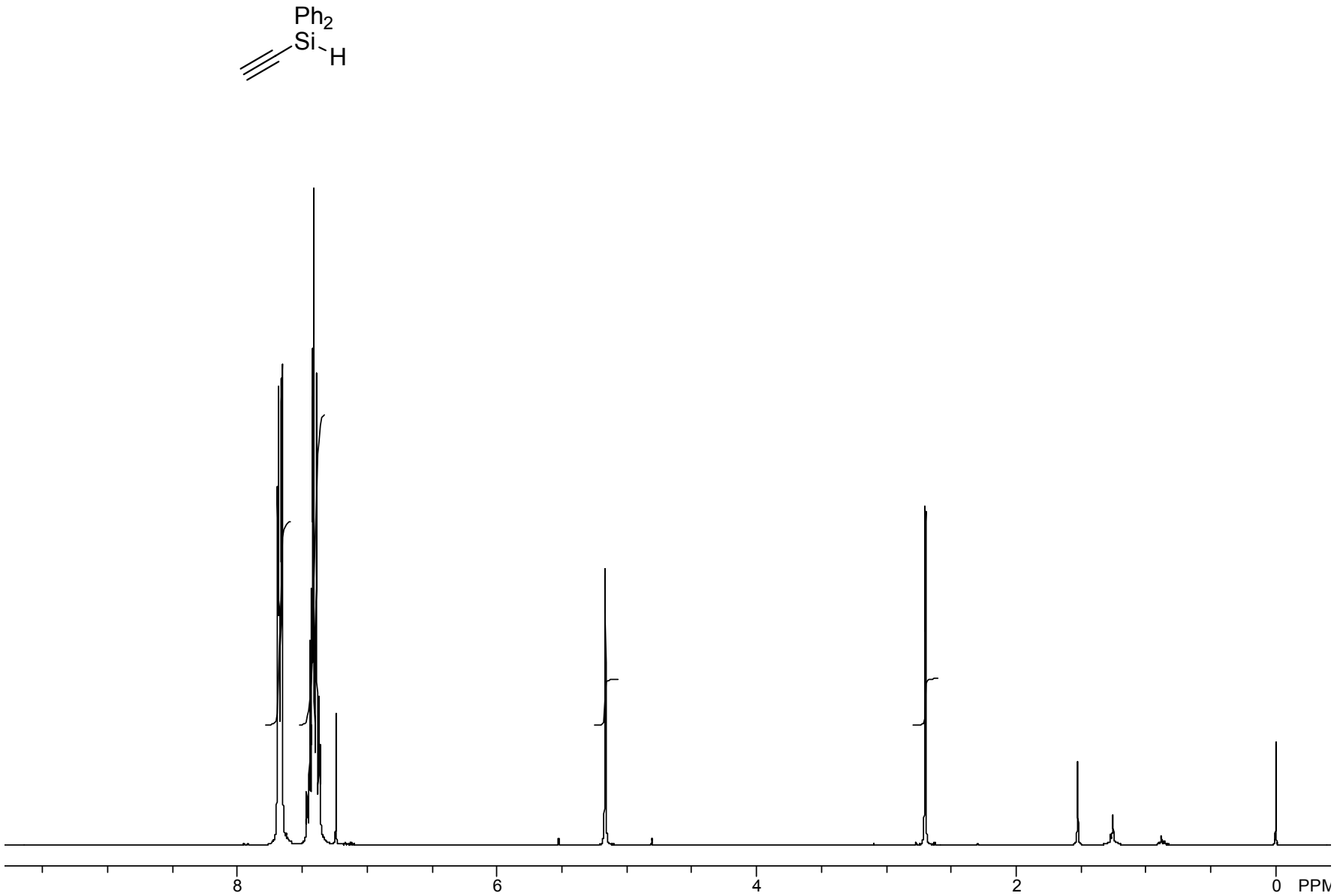
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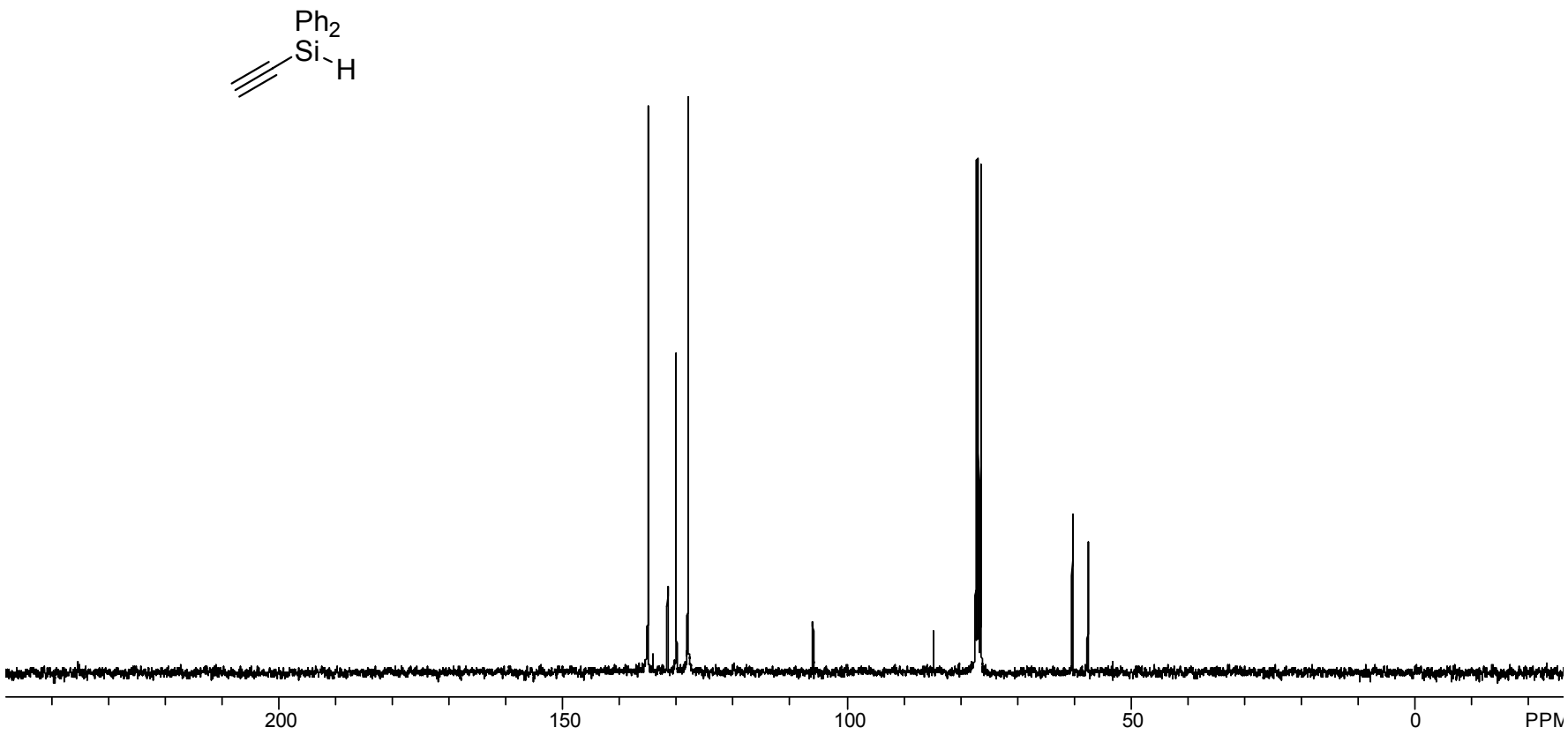
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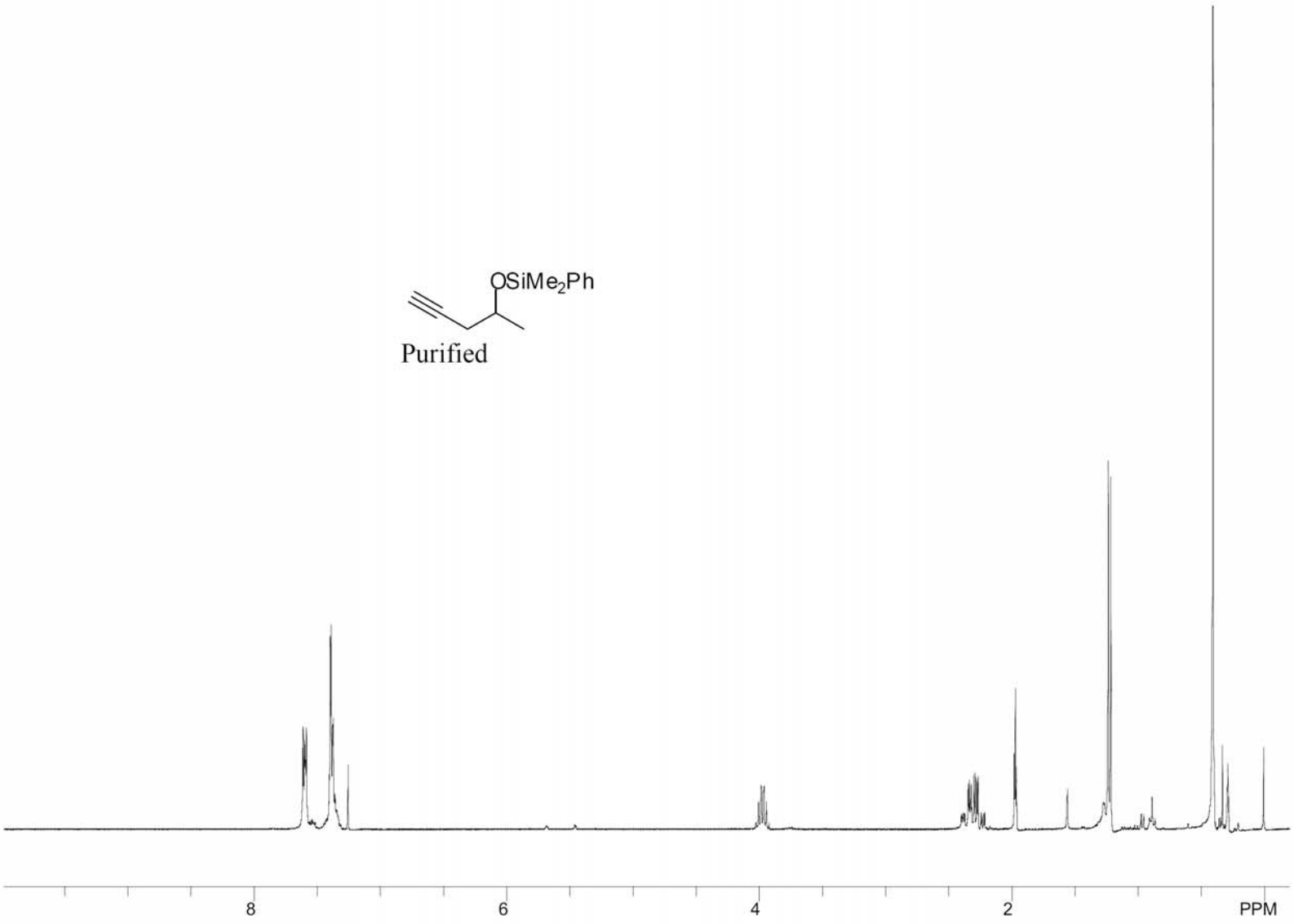
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Purified
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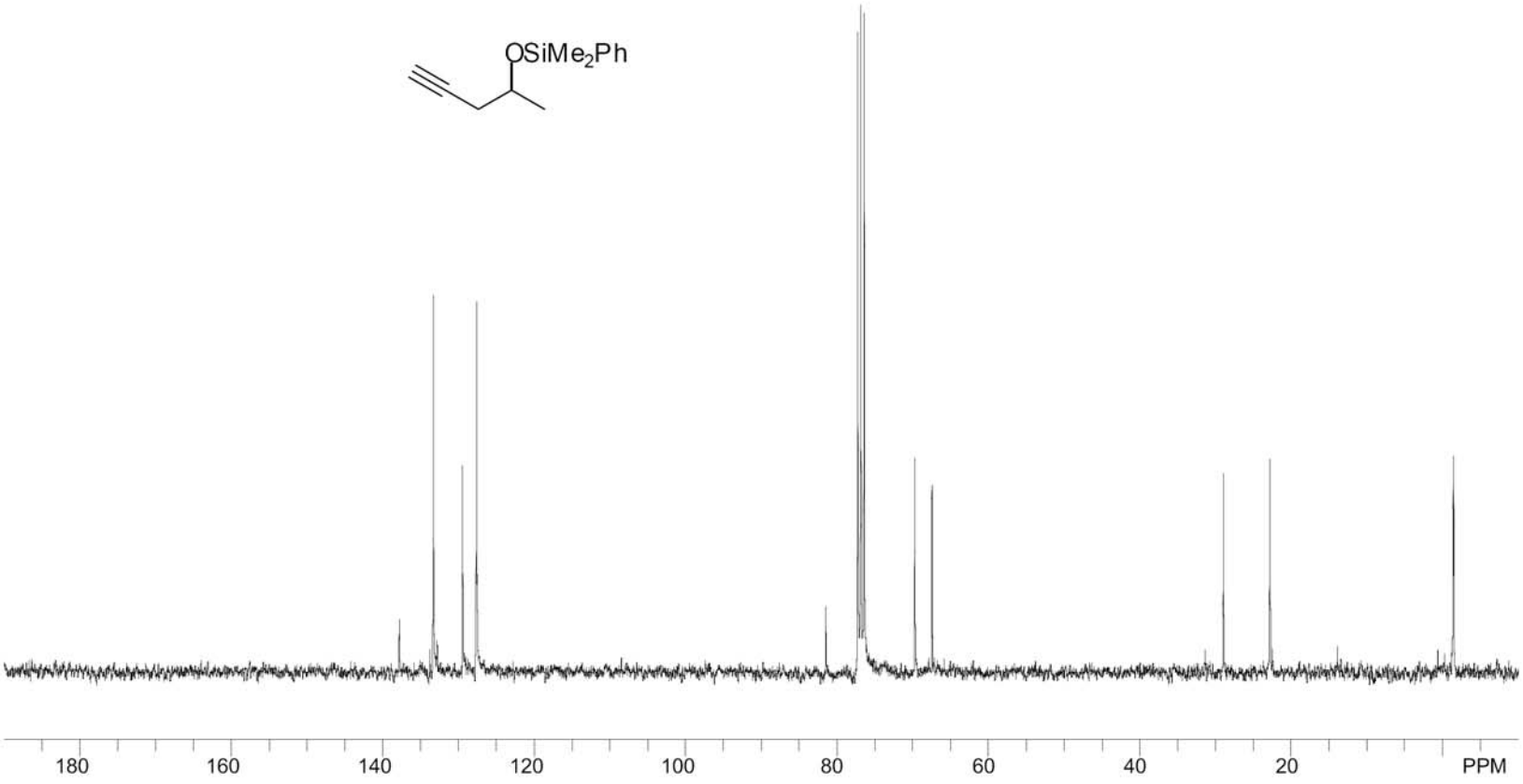
6
4
2
PPM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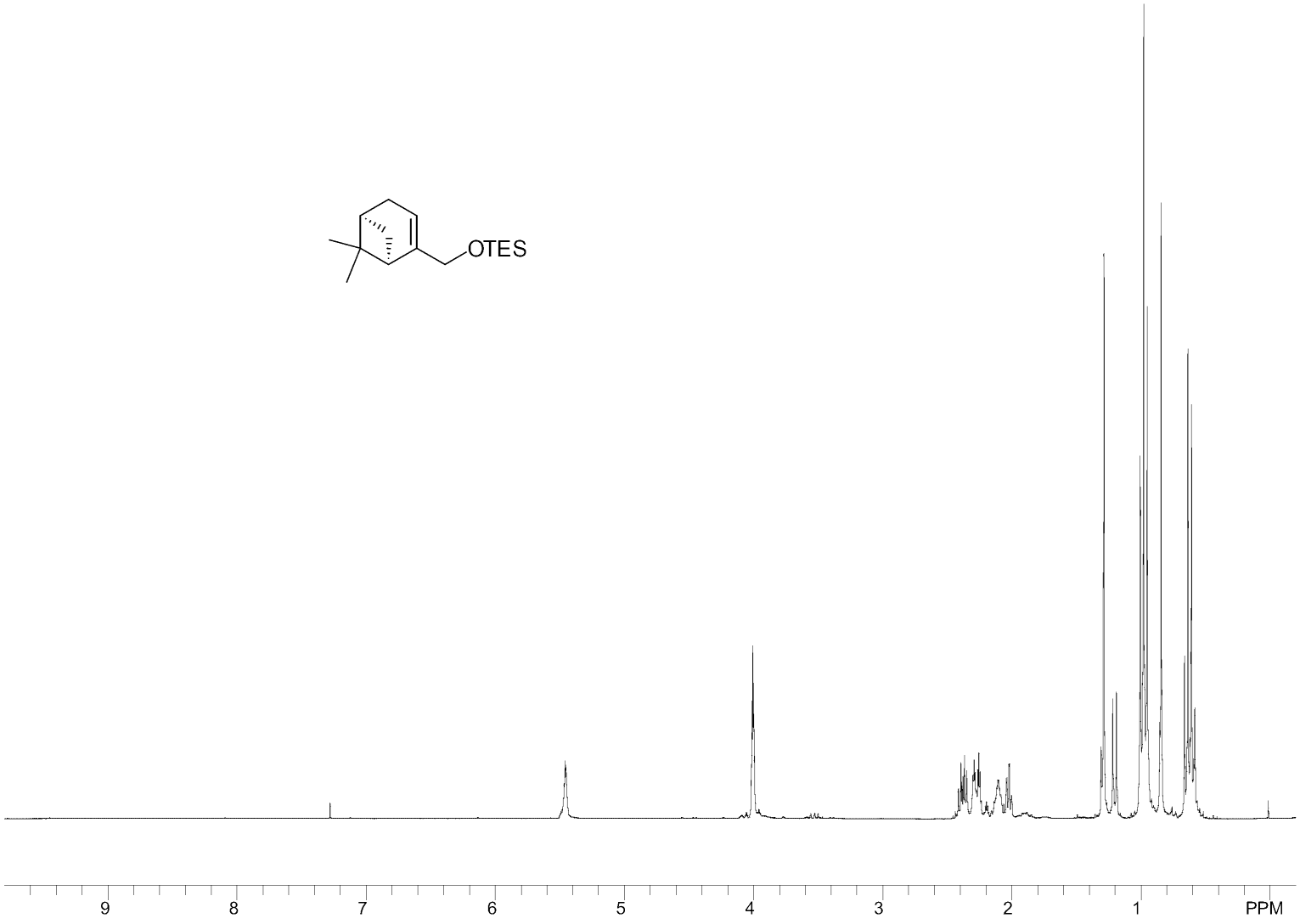
PPM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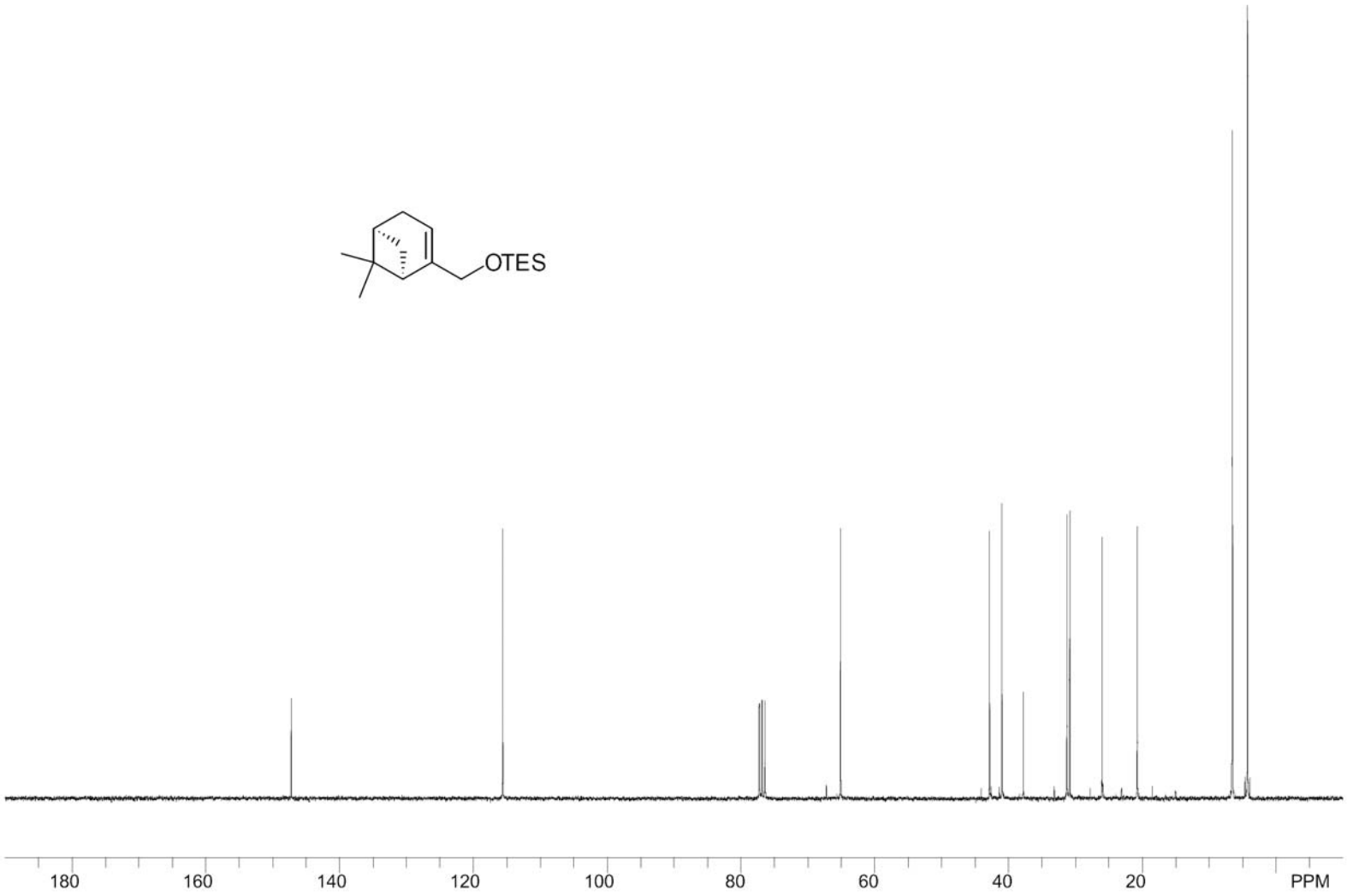
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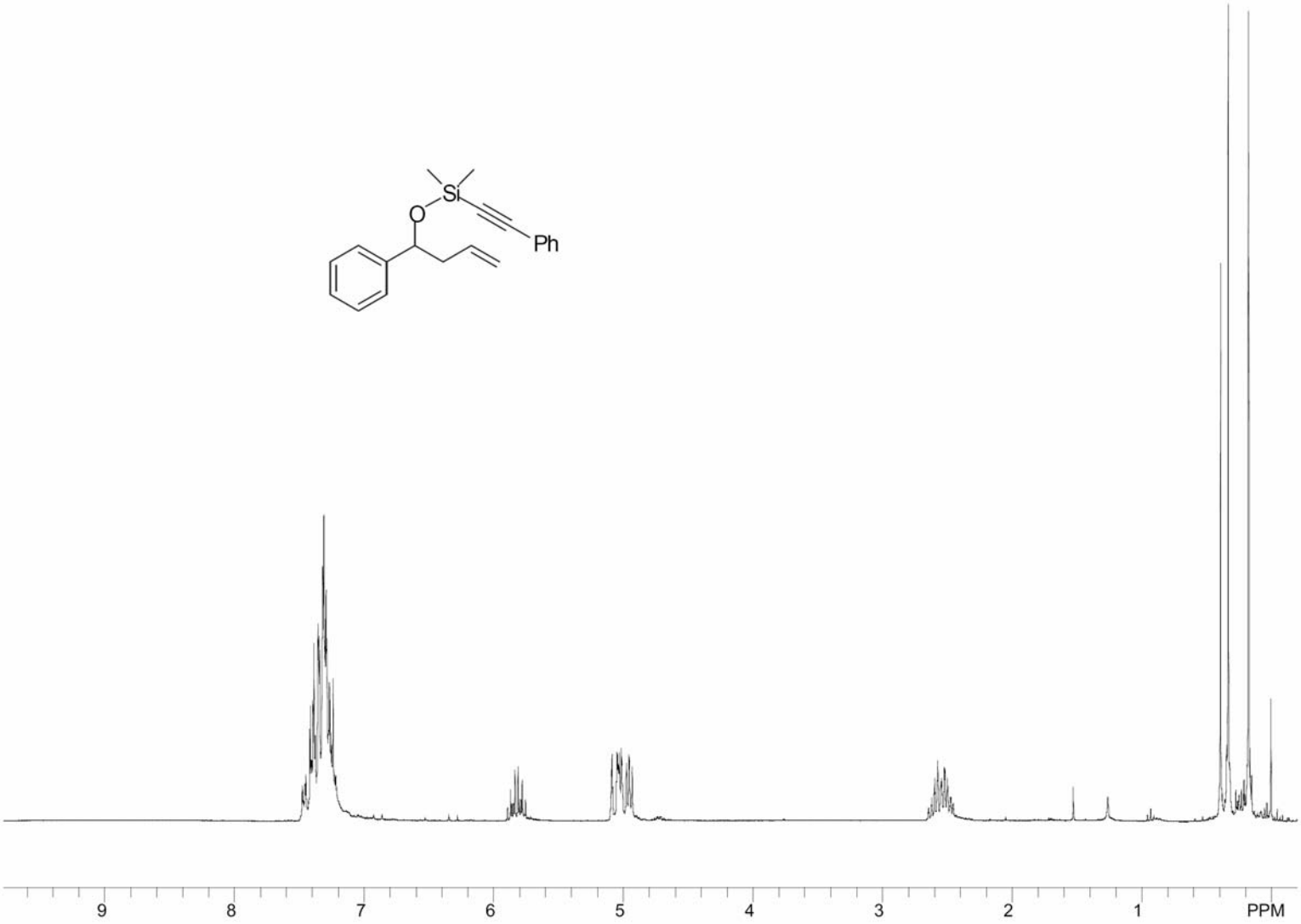
Si
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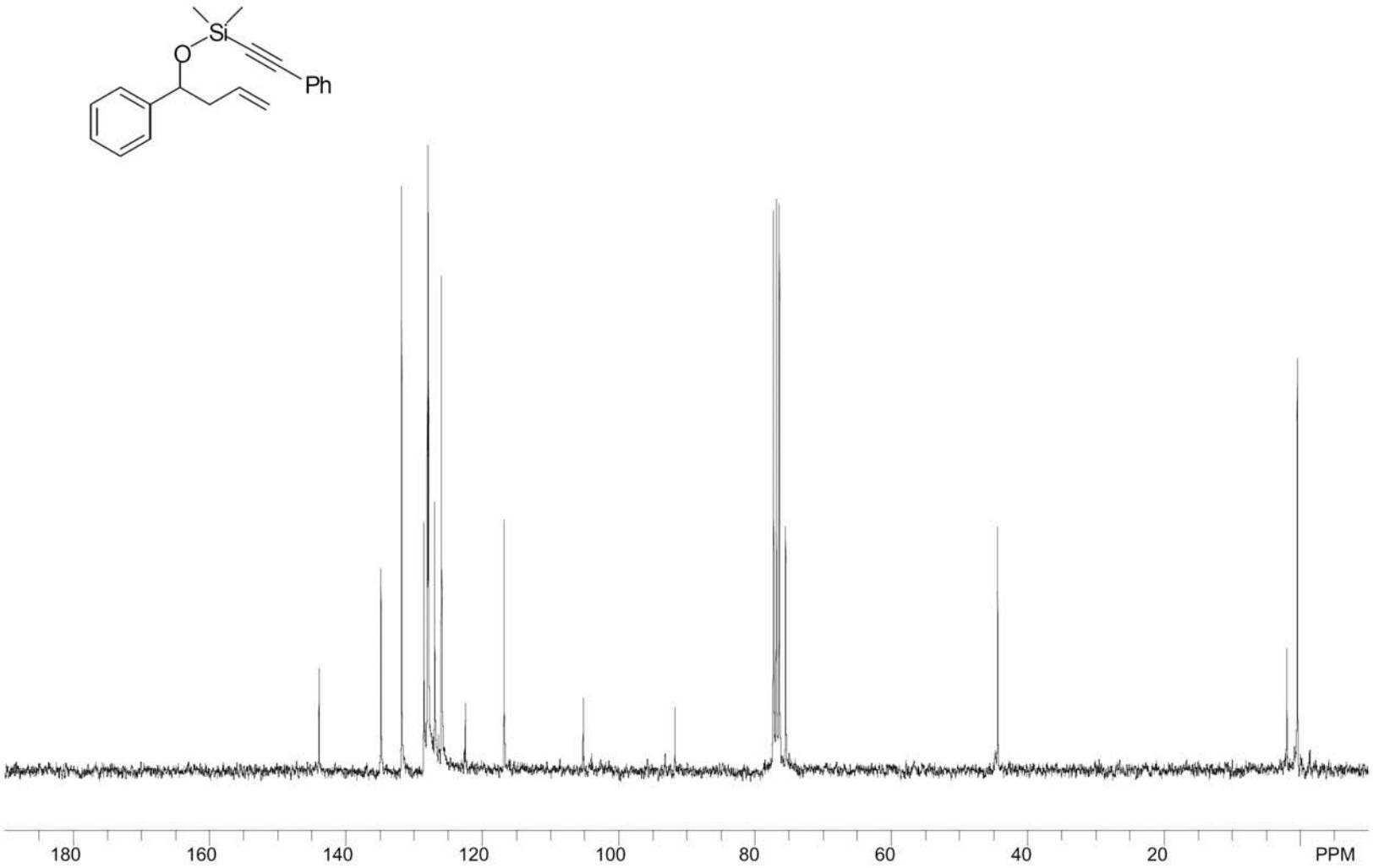
PPM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PPM