Electronic Supplementary Information for

N-Heterocyclic Carbene-Mediated Hydrosilylation of Styryl Alcohols with Dihydrosilanes: A Mechanistic Investigation

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General Remarks

Reactions were carried out under argon, with magnetic stirring and distilled solvents. THF and Et_2O were distilled from Na / benzophenone. Toluene, CH_2Cl_2, DMF and DMSO were distilled from CaH_2.Thin layer chromatography (TLC) was performed on Merck 60 F254 silica gel Merck Geduran SI 60 A silica gel (35−70 mm) was used for column chromatography. IR spectra were recorded with a Bruker Tensor 27 ATR diamant PIKE spectrometer. ^{1}H- and ^{13}C- NMR spectra were recorded with Bruker Avance 300 or 400 spectrometer. Chemical shifts are given in ppm and they are reported as values relative to the internal chloroform (7.27 ppm for ^{1}H and 77.23 ppm for ^{13}C) or benzene (7.16 ppm for ^{1}H and 128.39 ppm for ^{13}C). Coupling constants (*J*) are given in Hertz (Hz). The following abbreviations are used to describe coupling: s = singlet; d = doublet; t = triplet; q = quartet; quint = quintuplet; sext = sextuplet; sept = septuplet; oct = octuplet; m = multiplet; br = broad. HRMS were performed at the Institut de Parisien de Chimie Moléculaire on a Bruker MicrOTOF with a ESI source and a TOF analyzer. NaH and Ph_2SiH_2 obtained from commercial sources were used as received. IPr (1,3-Bis(2,6-di-*iso*-propylphenyl)imidazol-2-ylidene) was purchased from Strem Chemicals Inc., stored in a glove box and used as received. Ph_2SiD_2 and Ph_2SiClH were prepared following the procedure described by Bosnich et al.[1] *trans*-3-Phenyl-cyclohex-2-en-1-ol **10** were prepared following the procedure described by Schurig et al[2] from *trans*-4-Phenyl-3-butene-2-one[3]

General protocols:

Pathway A:

A solution of Ph_2SiH_2 (1.1 mmol, 203 mg, 1.1 equiv) and the substrate **1**, **3**, **5**, **6** or **7** (1 mmol, 1 equiv) in dry DMF (1 mL) was added to the free carbene (or base) solution in DMF (1 mL). The reaction was monitored by TLC until no substrate was left. TBAF (1 mmol, 1 mL, 1.0 M in THF, 1 equiv) was then added to the resulting mixture, which was stirred for a further 30 min and quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3×10 mL) and the combined organic layers were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered, and the solution was concentrated under vacuum. The crude product was purified by flash column chromatography over silica gel.

[1] S. H. Bergens, P. Noheda, J. Whelan and B. Bosnich, *J. Am. Chem. Soc.* 1992, **114**, 2128
[2] A. Ghanem, V. Schurig, *Tetrahedron: Asymmetry* 2003, **14**, 57
[3] S. Kehrli, D. Martin, D. Rix, M. Mauduit and A. Alexakis, *Chem. Eur. J.* 2010, **16**, 9890

Pathway B:

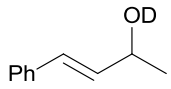
Substrate **1**, **3**, **5**, **6** or **7** (1 mmol, 1 equiv) was added to a solution of the free carbene (or base) (0.1 mmol, 0.1 equiv) in DMF (2 mL). The reaction was stirred at room temperature for 30 min and diphenylsilane (1.1 mmol, 203 mg, 1.1 equiv) was then added. The substrate **1**, **3**, **5**, **6** or **7** (1 mmol, 1 equiv) was added to a solution of base (0.1 mmol, 0.1 equiv) in DMF (2 mL). The reaction was stirred at room temperature for 30 min and diphenylsilane (1.1 mmol, 203 mg, 1.1 equiv) was then added. The reaction was monitored by TLC until complete reaction. TBAF (1 mmol, 1 mL, 1.0m in THF, 1 equiv) was then added to the resulting mixture, which was stirred for a further 30 min and quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3×10 mL) and the combined organic layers were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered, and the solution was concentrated under vacuum. The crude product was purified by flash column chromatography over silica gel.

Pathway C:

Diphenylsilane (1.1 mmol, 203 mg, 1.1 equiv) was added to a solution of the free carbene or base (0.1 mmol, 0.1 equiv) in DMF (2 mL). The reaction was stirred at room temperature for 30 min and the substrate (**1**, **3**, **5**, **6** or **7**) (1 mmol, 1 equiv) was then added. The reaction was monitored by TLC until no substrate was left. TBAF (1 mmol, 1 mL, 1.0m in THF, 1 equiv) was then added to the resulting mixture, which was stirred for a further 30 min and quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3×10 mL) and the combined organic layers were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered, and the solution was concentrated under vacuum. The crude product was purified by flash column chromatography over silica gel.

Characterizations of products 1-D, 2a, 2c, 5, 6, 8, 9, 10.

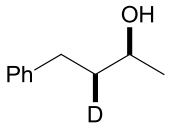
(*E*)-4-phenylbut-3-en-2-ol-^{2}*H* 1-D



Alcohol **1** (1.48 g, 10 mmol) was introduced in a round bottom flask of 25 mL in the presence of 5 mL of D_2O under an atmosphere of argon. The biphasic mixture was stirred at room temperature for 6 h and after this mixing time, deuterated alcohol **1**-D was extracted with ethylacetate (3×15 mL) dried over Na_2SO_4 and concentrated under vacuum. **1**-D was obtained in 98% yield (1.46 g, 9.8 mmol). Colorless oil. IR (neat): ν (cm^{-1}) 2970, 2505, 1493, 1448, 1371,

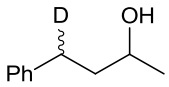
1066, 965, 940, 746, 692. ^{1}H NMR (300 MHz, C_6D_6) δ 7.27–7.20 (m, 2H), 7.15–7.09 (m, 2H), 7.06 (m, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.07 (dd, *J* = 15.9, 6.1 Hz, 1H), 4.13 (quint, *J* = 6.6 Hz, 1H), 1.15 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 137.1, 134.1, 128.8, 128.5 (2C), 127.3, 126.5 (2C), 68.2, 23.2. HRMS calcd for C10H11DONa ($[M + Na]^+$): 172.0843. Found: 172.0851.

3-deuterio-4-phenylbutan-2-ol 2a[4]



Colorless oil. ^{1}H NMR (300MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 3H), 3.83 (sext, *J* = 5.1 Hz, 1H), 2.76 (dd, *J* = 13.5, 9.9 Hz, 1H), 2.68 (dd, *J* = 13.5, 7.8 Hz, 1H), 1.82-1.69 (m, 1H), 1.32 (d, *J* = 5.2 Hz, 1H), 1.23 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 128.4 (4C), 125.8, 67.5, 40.4 (t, *J* = 19.3 Hz), 32.1, 23.6.

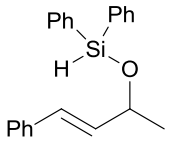
4-deuterio-4-phenylbutan-2-ol 2c



Colorless oil**,** diastereomeric mixture: 1/1. IR (neat): ν (cm^{-1}) 3329, 3026, 2964, 2923, 1450, 1372, 1124, 1075, 950, 739, 696. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.29 (m, 3H), 7.27–7.19 (m, 2H), 3.86 (sext, J = 6.1 Hz, 1H), 2.85–2.66 (m, 1H), 1.90–1.70 (m, 2H), 1.60–1.45 (br, 1H), 1.26 (dd, J = 6.2, 1.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 128.5 (4C), 125.9, 67.6, 40.9, 32.2 (from **2b**), 31.9 (t, *J* = 19.4 Hz), 31.80 (t, *J* = 19.4 Hz), 23.7. HRMS calcd for $C_{10}H_{13}DONa$ ($[M + Na]^+$): 174.1005. Found: 174.0999.

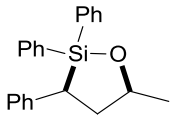
[4] Q. Zhao, D. P. Curran, M. Malacria, L. Fensterbank, J.-P. Goddard, E. Lacôte, *Chem. Eur. J.* 2011, **17**, 9911

Allylic Silyl Ethers 5[5]



This entire procedure was carried out under an atmosphere of dried argon. A solution of the allylic alcohol 1 (2.22 g, 15 mmol, 1 equiv) and triethylamine (2.10 g, 15.1 mmol, 1.01 equiv) in Et_20 (15 mL) was added dropwise over 20 min to a rapidly stirred solution of the chlorodialkylsilane (3.30g, 15.1 mmol) in Et_20 (50 mL) that was cooled to 0 °C with an ice bath. Large quantities of a fluffy white precipitate (Et_3NHCl) was formed. The mixture was stirred at 0 °C for 20 min after the addition was complete, the cooling bath was removed, and stirring was continued for 18 h further at room temperature. The solution was filtered through a Celite plug, the solvent was removed, and the residue was distilled under reduce pressure using a Kugelrohr distillation apparatus (0.5 mbar, 180 °C) to give the product in 25% yield (1.24g, 3.75 mmol) with contaminant. Colorless oil. IR (neat): ν (cm^{-1}) 3069, 3025, 2973, 2122, 1590, 1493, 1429, 1113, 1059, 965, 813, 732, 695. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.76 (m, 4H), 7.58–7.46 (m, 6H), 7.46–7.37 (m, 4H), 7.35–7.30 (m, 1H), 6.60 (dd, *J* = 15.9, 0.9 Hz, 1H), 6.35 (dd, *J* = 15.9, 6.3 Hz, 1H), 5.63 (s, 1H), 4.75 (quintd, *J* = 6.3, 1.1 Hz, 1H), 1.53 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 134.8 (4C), 134.4 (2C), 133.1, 130.4 (2C), 129.4, 128.6 (2C), 128.1 (4C), 127.6, 126.6 (2C), 71.6, 24.2. ^{13}C NMR Characteristics signals of the contaminant 134.8, 134.39, 130.36, 128.1. HRMS calcd for $C_{22}H_{22}OSiNa$ ($[M + Na]^+$): 353.1332. Found: 353.1365.

Cyclic siloxane 6[6]



The silane **5** (1 g, 3.0 mmol) was dissolved in THF (3 mL) and added, dropwise, to a solution of activated 4 Å molecular sieves (8.0 g) in THF (6 mL). After stirring for 5 min, Wilkinson's catalyst (8.0 mg, 0.002 equiv.) was added and the heterogeneous reaction mixture was heated to reflux for 4 h. After cooling to rt, the contents of the flask were concentrated and passed through

[5] S. H. Bergens, P. Noheda, J. Whelan and B. Bosnich, *J. Am. Chem. Soc.* 1992, **114**, 2123
[6] A. B. Smith III, R. Tong, W.-S. Kim and W. A. Maio, *Angew. Chem. Int. Ed.* 2011, **50**, 8904

a plug of celite. Distillation of the crude black material under vacuum using a Kugelrohr distillation apparatus (0.5 mbar, 170 °C) provided a colorless oil in 75% yield (0.75 g, 2,25 mmol), which existed as a ca. *syn*;*anti* 8:1 mixture of diastereomers. IR (neat): ν (cm^{-1}) 3068, 2966, 2926, 2858, 1591, 1493, 1429, 1377, 1118, 1016, 905, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.71 (m, 3H), 7.52–7.22 (m, 10H), 7.09–6.96 (m, 2H), 4.91–4.81 (m, 0.16H, minor), 4.44 (dqd, *J* = 11.9, 6.0, 3.8 Hz, 1H), 3.26 (dd, *J* = 13.9, 6.8 Hz, 1H), 2.59 (ddd, J = 13.4, 9.4, 6.3 Hz, 0.17H, minor), 2.51 (ddd, *J* = 12.7, 6.7, 3.7 Hz, 1H), 2.23 (ddd, J = 13.3, 7.7, 4.4 Hz, 0.17H, minor), 2.06 (ddd, *J* = 13.8, 12.8, 10.9 Hz, 1H), 1.58 (d, *J* = 6.0 Hz, 3H), 1.48 (d, J = 6.3 Hz, 0.52H, minor). ^{13}C NMR (101 MHz, CDCl3) δ 140.7, 135.0 (2C), 134.8 (2C), 134.3, 132.5, 130.4, 130.0, 128.2 (2C), 128.1 (2C), 127.5 (2C), 127.1 (2C), 124.7, 74.5, 40.7, 35.2, 23.3. HRMS calcd for $C_{22}H_{22}OSiNa$ ($[M + Na]^+$): 353.1332. Found: 353.1345.

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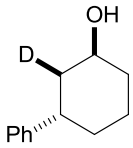
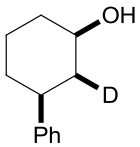
(±)(1*R*,2*S*,3*R*)-2-deuterio-3-phenylcyclohexanol 8



White solid; Mp 68°C. IR (neat): ν (cm^{-1}) 3267, 3025, 2924, 2851, 1592, 1491, 1428, 1127, 717, 696; ^{1}H NMR (600 MHz, C_6D_6) *δ* 7.22–7.17 (m, 2H), 7.14–7.11 (m, 2H), 7.11–7.06 (m, 1H), 3.85 (brd, *J* = 2.6 Hz, 1H), 3.04 (td, *J* = 12.3, 3.2 Hz, 1H), 1.84 (tt, *J* = 13.2, 3.7 Hz, 1H), 1.83–1.78 (m, 1H), 1.61–1.56 (m, 1H), 1.46–1.39 (m, 2H), 1.33 – 1.26 (m, 1H), 1.22 (tdd, *J* = 13.5, 4.3, 2.8 Hz, 1H), 0.98 (s, 1H). ^{13}C NMR (151 MHz, C_6D_6) *δ* 147.3, 128.3 (2C), 126.9 (2C), 125.9, 66.0, 40.2 (t, *J* = 20.2 Hz), 37.4, 33.8, 32.3, 20.4. HRMS calcd for $C_{12}H_{15}DONa$ ($[M + Na]^+$): 200.1156. Found: 200.1160.

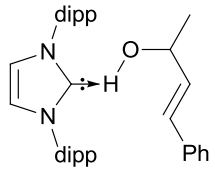
(±)(1*R*,2*S*,3*S*)-2-deuterio-3-phenylcyclohexanol 9



Colorless oil. IR (neat): ν (cm^{-1}) 3275, 2924, 2853, 1493, 1428, 1226, 717, 696; ^{1}H NMR (600 MHz, C_6D_6) δ 7.22–7.13 (m, 3H), 7.12–7.01 (m, 2H), 3.39 – 3.33 (m, 1H), 2.31 – 2.25 (m, 1H),

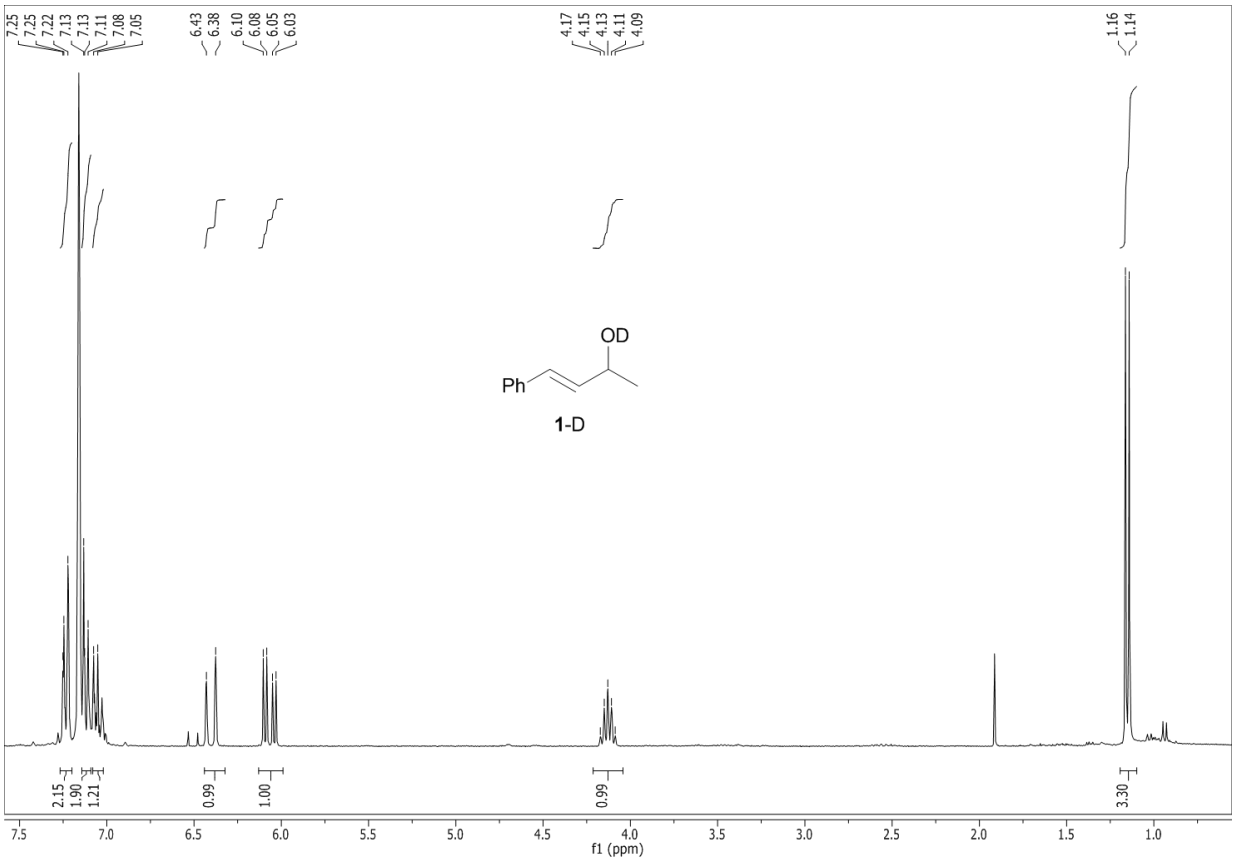
1.94 (s, 2H), 1.86 – 1.80 (m, 1H), 1.63–1.56 (m, 2H), 1.14 – 1.05 (m, 3H); ^{13}C NMR (151 MHz, C_6D_6) δ 146.3, 128.3 (2C), 126.8 (2C), 126.0, 70.4, 42.9 (t, *J* = 19.2 Hz), 42.7, 35.2, 33.4, 24.4. HRMS calcd for $C_{12}H_{15}DONa$ ($[M + Na]^+$): 200.1156. Found: 200.1150.

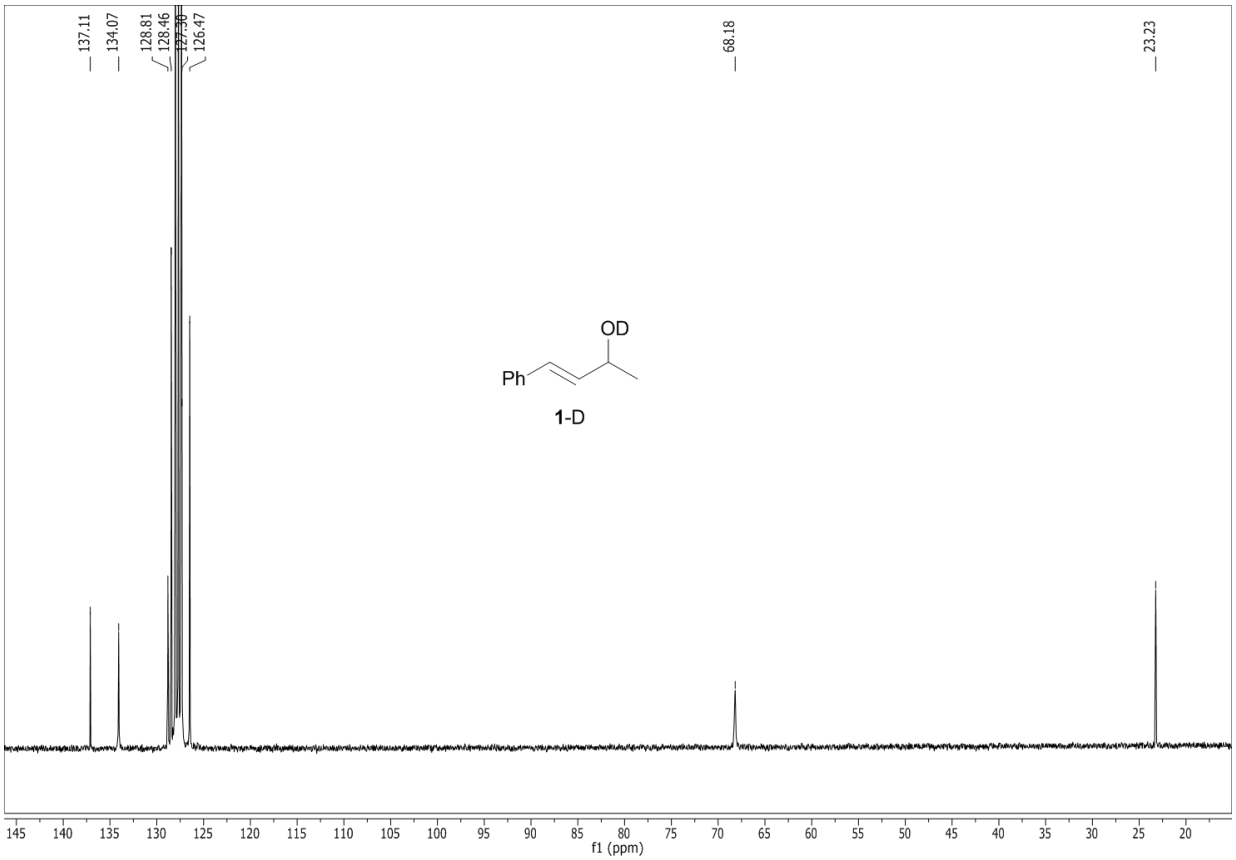
Alcohol carbene complex 10

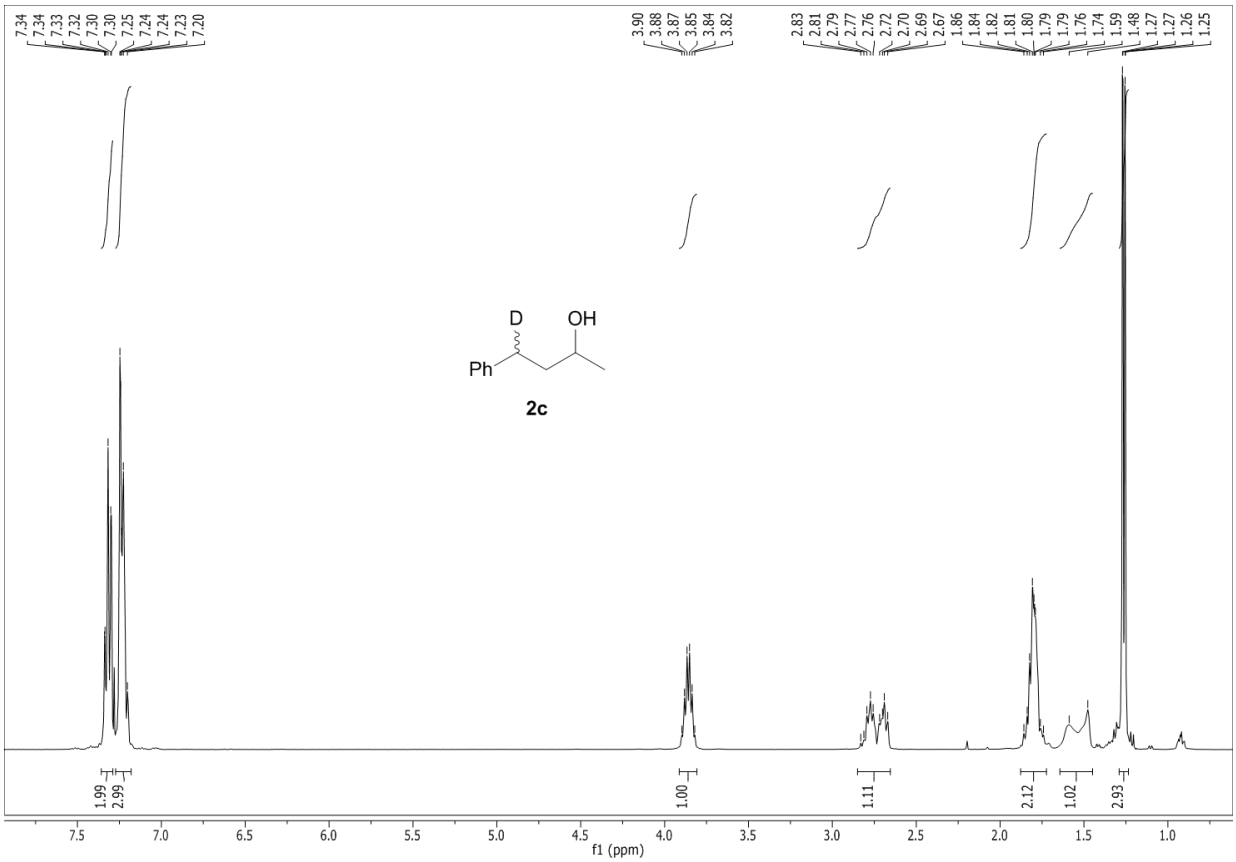


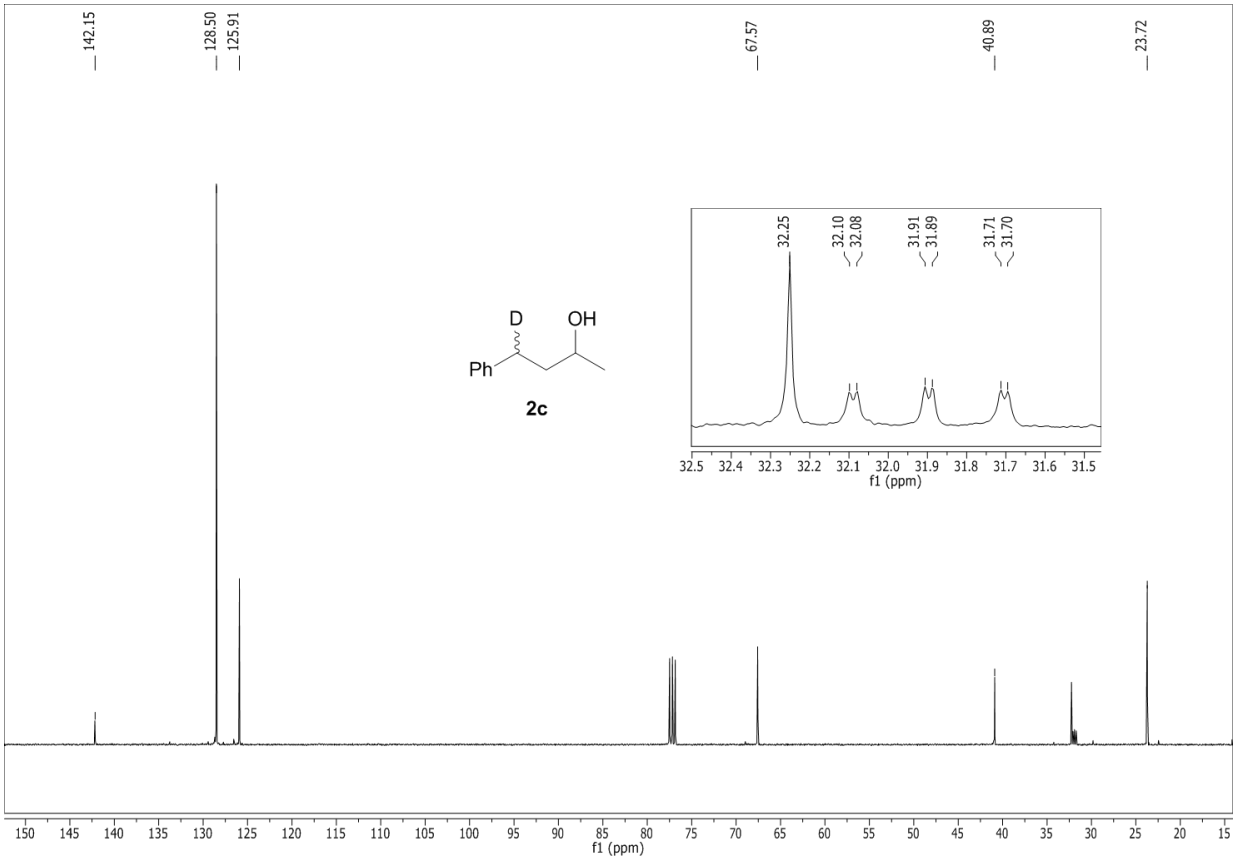
Free carbene (0.1 mmol, 38.8 mg, 1 equiv) was introduced in a schlenk tube under argon atmosphere and dissolved in DMF-d^7 or C_6D_6 (1 mL). The alcohol **1** (0.1 mmol, 1 equiv) was added to the solution and after 15 minutes, 0.5 mL of the solution was introduced in a dry NMR tube under argon atmosphere. ^{1}H NMR (400 MHz, C_6D_6) δ 7.26 (dd, *J* = 8.3, 7.1 Hz, 2H), 7.22–7.18 (m, 2H), 7.17–7.08 (m, 6H), 7.06–7.00 (m, 1H), 6.53 (s, 2H), 6.38 (dd, *J* = 15.9, 1.0 Hz, 1H), 6.11 (dd, *J* = 15.9, 5.5 Hz, 1H), 4.55 (s, 1H), 4.11 – 4.00 (quintd, *J* = 6.3, 1.3 Hz, 1H), 2.86 (hept, *J* = 6.9 Hz, 4H), 1.32 (d, *J* = 6.9 Hz, 12H), 1.15 (d, *J* = 6.9 Hz, 12H), 1.11 (d, *J* = 6.5 Hz, 3H).

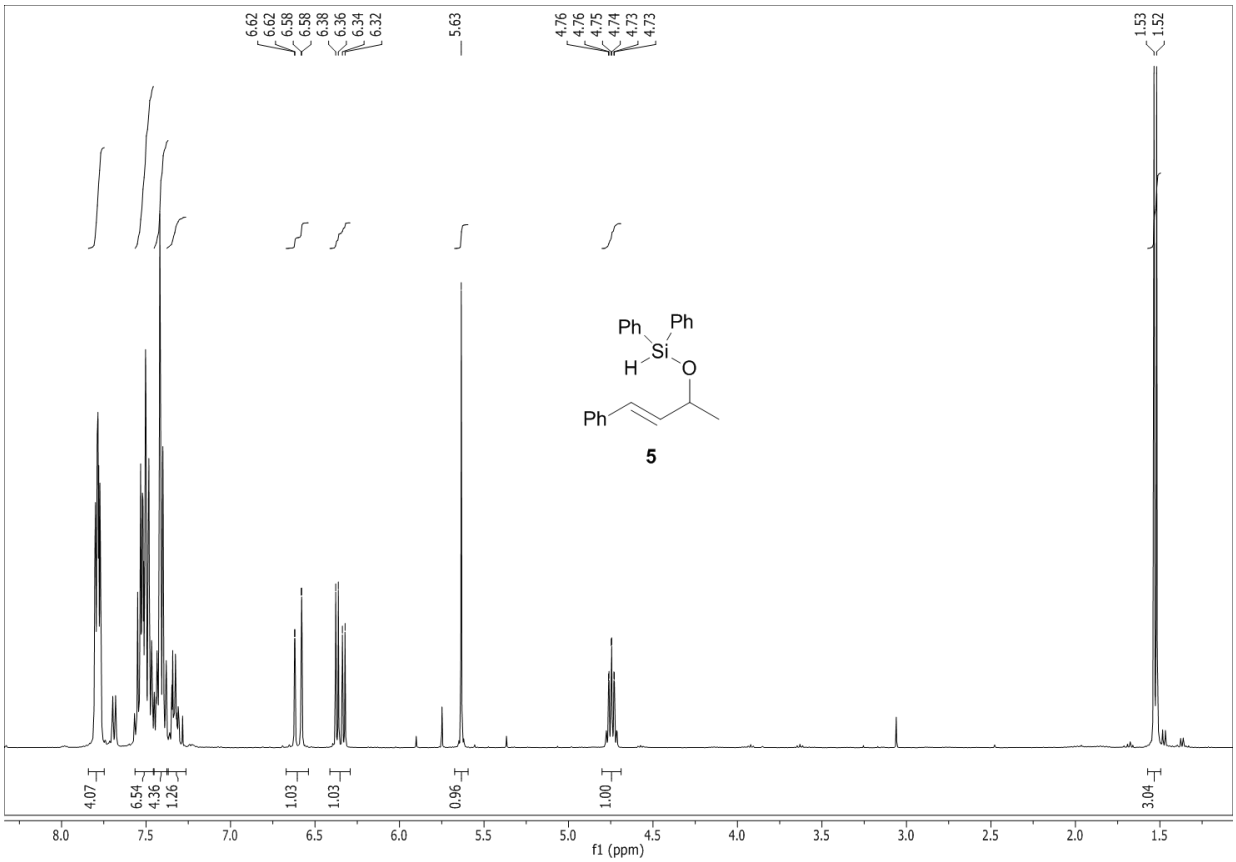
^{1}H NMR and ^{13}C NMR spectra of products 1-D, 2c, 5, 5-D, 2a + 1 from 5-D, 6, 8, 9, 1, 10

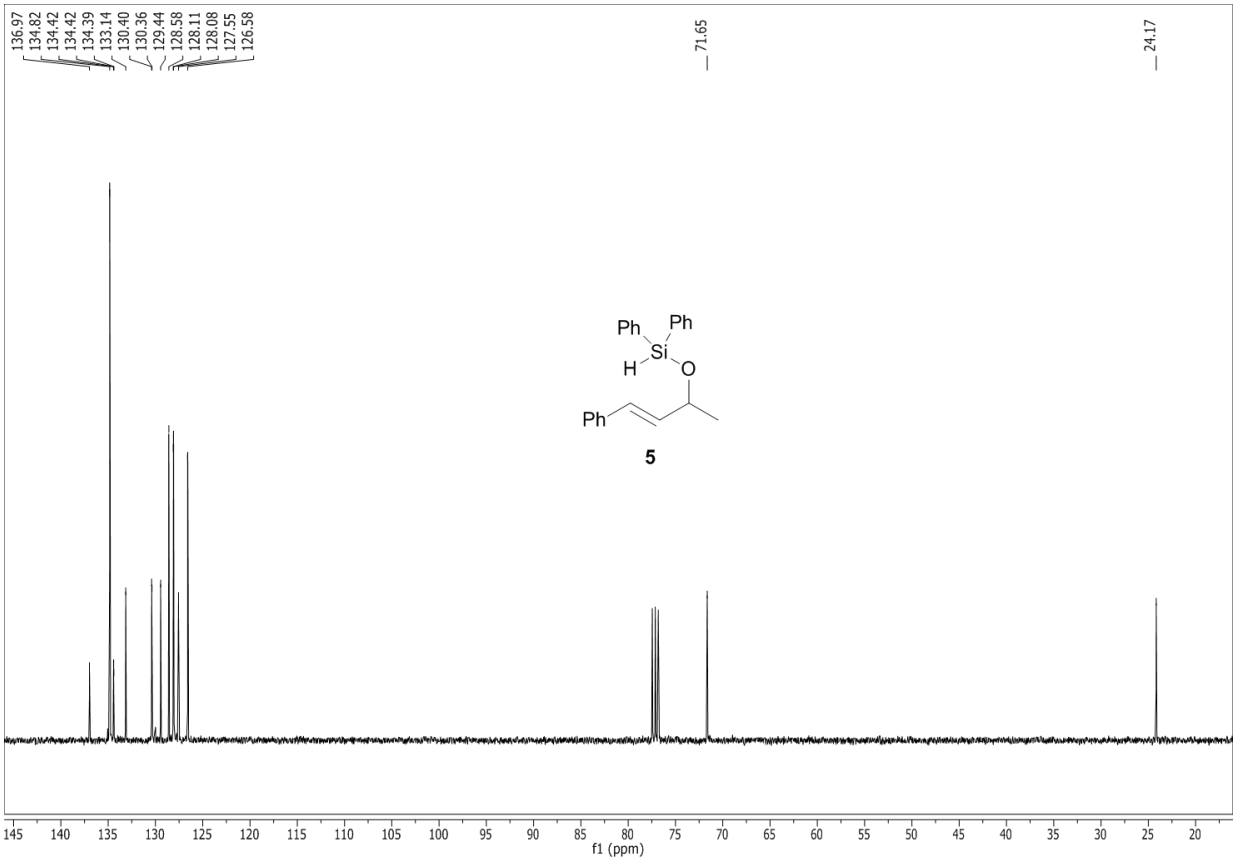


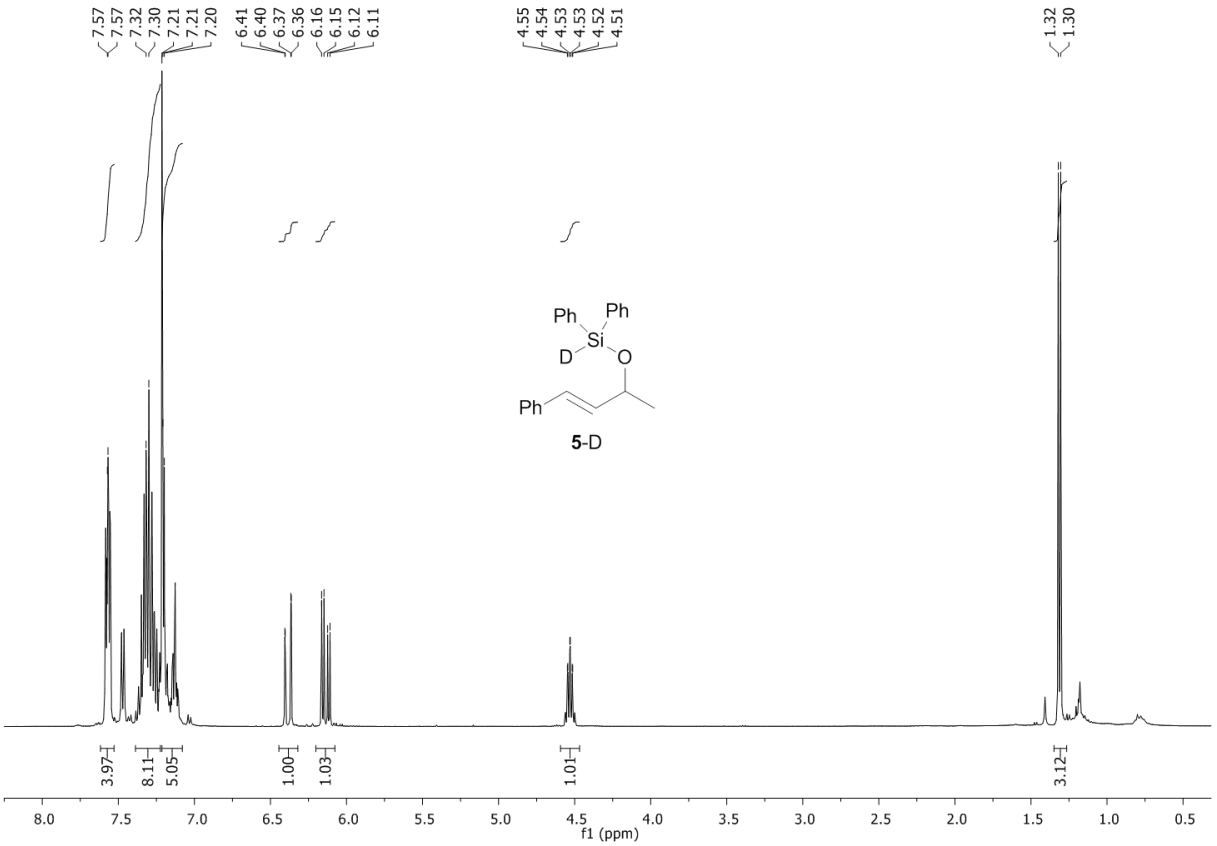


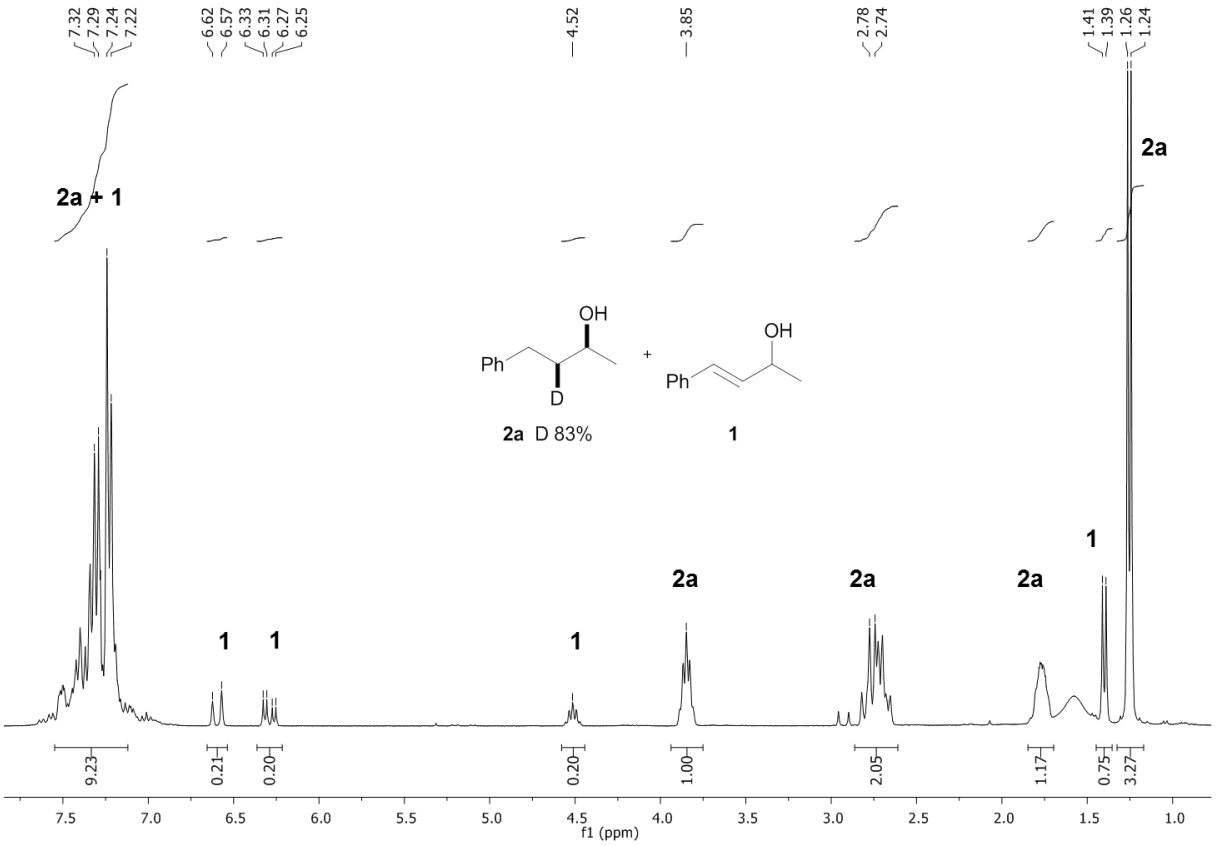


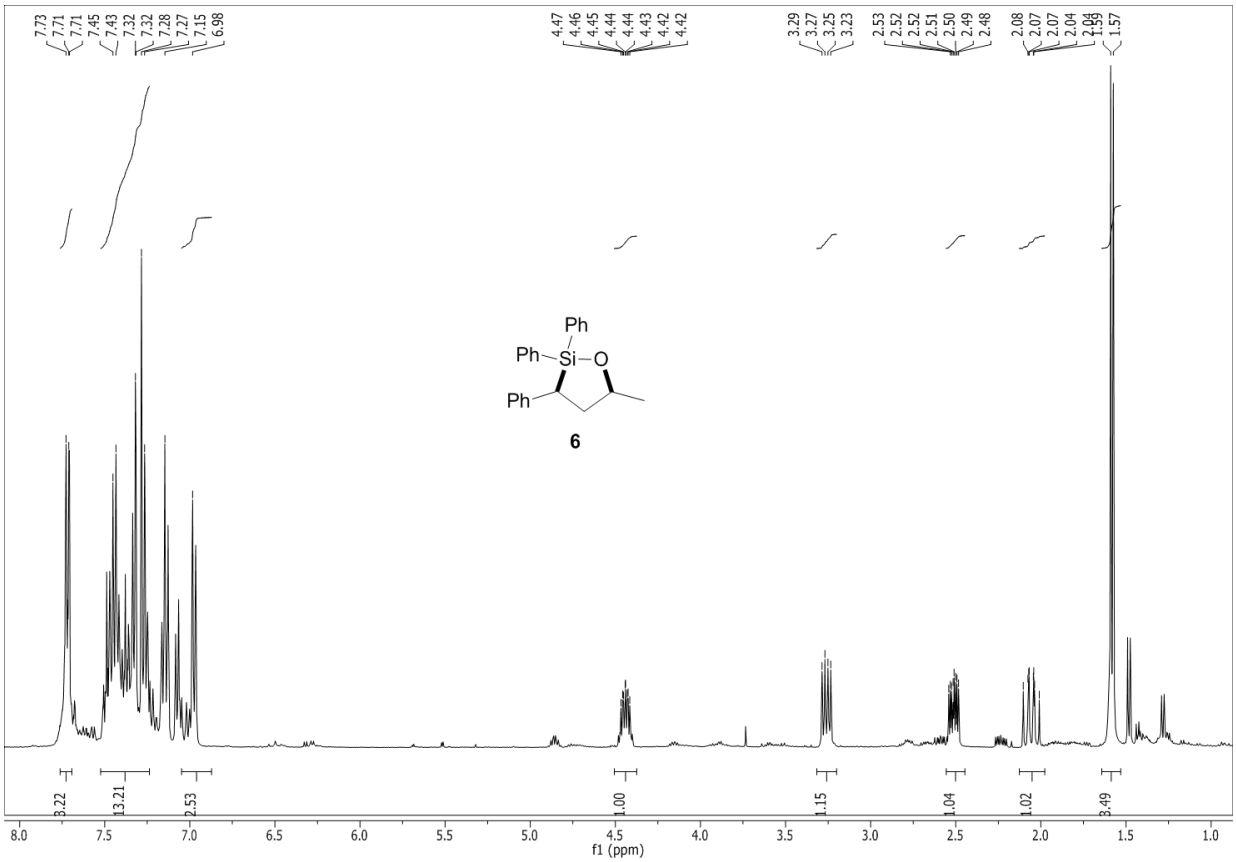








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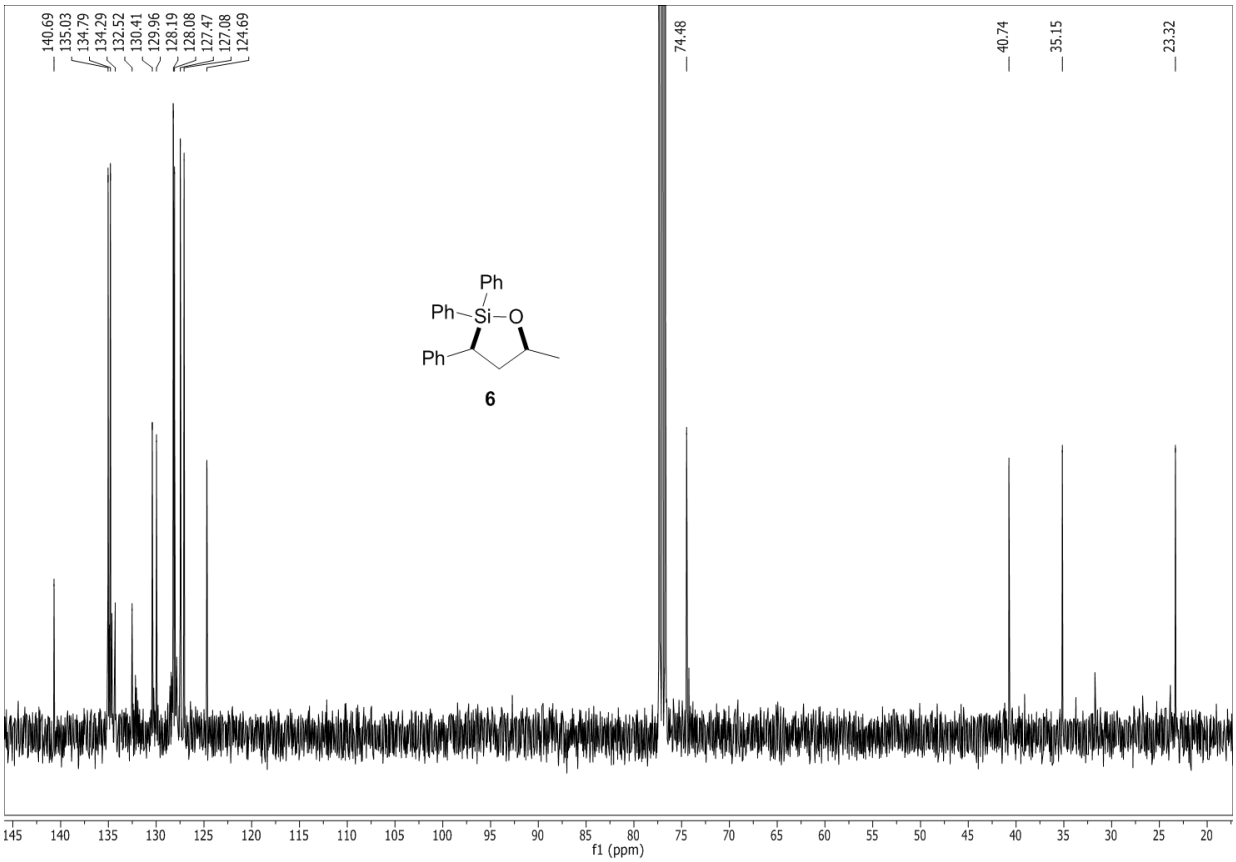
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Si
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Ph
6
f1 (ppm)