Supporting Information for

(Salicylaldiminato)Ni(II)-Catalysts for Hydrosilylation of Olefins

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General considerations.

Unless otherwise noted, all manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glove box. Toluene, benzene, hexane, and CH_2Cl_2 were purified by a solvent purification system (MBraun SPS-800). Other solvents (THF, benzene-d_6, toluene-d_8, and THF-d_8) were dried over sodium benzophenone ketyl and distilled. CD_3CN was dried over CaH_2 and distilled prior to use. All reagents, unless otherwise stated, were purchased from commercial suppliers and used without further purification. ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra (^1H, 600 MHz; ^{13}C, 150 MHz; ^{29}Si, 119 MHz) were recorded using a Bruker AVANCE 600 spectrometer. Chemical shifts are reported in δ (ppm) and are referenced to the residual solvent signals for ^1H or to tetramethysilane (0.0 ppm) for ^{13}C and ^{29}Si. GLC analysis was performed on a Shimadzu GC-14B instrument (FID; CBP-1, 25 m × 0.25 mm). Elemental analyses were carried out on a Thermo Scientific FLASH2000 CHNS analyzer. $[Ni(CH_3)_2(tmeda)]$[1] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and a series of salicylaldimine ligands[2] were prepared according to the literature procedures.

Synthesis of 1a. To a stirred solution of $[Ni(CH_3)_2(tmeda)]$ (0.100 g, 0.49 mmol) in ether (10 mL) was added a solution of (*E*)-2-(((2,6-diisopropylphenyl)imino)methyl)phenol (137 mg, 0.49 mmol) and pyridine (394 μL, 4.9 mmol) in ether (10 mL) slowly at –50 °C. The resulting yellow-green solution was slowly warmed to 0 °C over a period of 3-4 h to give a red-colored solution. The solvent was removed under vacuum at 25 °C and the resulting solid was dissolved in ether (5 mL). The solution was filtered with a Celite pad and dried under vacuum to yield **1a** as a red solid (0.211 g, 0.47 mmol, 95%). Complex **1a** was identified by comparing its ^1H and $^{13}C\{^1H\}$ NMR data with those previously reported.[4]

Synthesis of 1b. Complex **1b** (0.150 g, 0.22 mmol, 86%) was prepared according to the above mentioned procedure using (*E*)-2-((phenylimino)methyl)phenol (0.25 mmol) and [Ni(CH$_3$)$_2$(tmeda)] (0.25 mmol). ^{1}H NMR (C$_6$D$_6$, 25 °C) δ −0.62 (s, 3H), 6.23 (br, 2H), 6.49 (t, J = 7.2 Hz, 1H), 6.59 (br, 2H), 6.93 (d, J = 6.6 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 7.08-7.22 (m, 5H), 7.60 (s, 1H), 8.67 (d, J = 1.0 Hz, 2H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ −6.7, 113.8, 120.4, 122.9, 123.2, 124.7, 125.4, 128.6, 134.4x2, 135.6, 151.9, 155.9, 166.2, 168.1; Anal. Calcd. for $C_{19}H_{18}N_2NiO$: C, 65.38; H, 5.20; N, 8.03. Found: C, 65.31; H, 5.35; N, 7.93.

Synthesis of 1c. Complex **1c** (0.152 g, 0.21 mmol, 91%) was prepared according to the above mentioned procedure using (*E*)-2-(((3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-2'-yl)imino)methyl)phenol (0.23 mmol) and [Ni(CH$_3$)$_2$(tmeda)] (0.23 mmol). ^{1}H NMR (C$_6$D$_6$, 25 °C) δ –0.93 (s, 3H), 6.17 (br, 2H), 6.24 (t, J = 6.9 Hz, 1H), 6.46 (t, J = 6.6 Hz, 1H), 6.55 (d, J = 7.2, 2.1 Hz, 1H), 6.63 (d, J = 8.4 Hz, 1H), 6.85 (s, 1H), 6.92-6.94 (m, 5H), 7.77 (s, 1H), 8.22-8.27 (m, 6H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ –7.0, 113.4, 120.1, 122.5, 122.8, 124.4, 125.0, 127.5, 127.7, 127.9, 128.0, 128.2, 134.0, 134.1, 135.2, 151.6, 155.5, 165.8, 167.8; Anal. Calcd. for $C_{35}H_{22}F_{12}N_2NiO$: C, 54.37; H, 2.87; N, 3.62. Found: C, 53.68; H, 2.88; N, 3.64.

Synthesis of 1d. Complex **1d** (0.106 g, 0.23 mmol, 92%) was prepared according to the above mentioned procedure using (*E*)-2-(((2,6-diisopropylphenyl)imino)methyl)phenol (0.25 mmol), DMAP (0.25 mmol) and [Ni(CH$_3$)$_2$(tmeda)] (0.25 mmol). ^{1}H NMR (C$_6$D$_6$, 25 °C) δ –0.57 (s, 3H), 1.09 (d, J = 6.6 Hz, 6H), 1.57 (d, J = 6.6 Hz, 6H), 1.96 (s, 6H), 4.34 (septet, J = 6.9 Hz, 2H), 5.63 (t, J = 6.0 Hz, 2H), 6.49 (t, J = 7.2 Hz, 1H), 6.99 (t, J = 7.8 Hz, 1H), 7.10-7.24 (m, 5H), 7.62 (s, 1H), 8.45 (d, J = 6.6 Hz, 2H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C) δ –8.2, 23.3, 25.0, 28.6, 38.1, 106.5, 113.5, 120.4, 122.9, 123.6, 126.3, 134.0, 134.1, 141.3, 150.8, 150.9, 153.7, 166.0, 168.5; Anal. Calcd. for $C_{27}H_{35}N_3NiO.C_6H_6$: C, 71.48; H, 7.45; N, 7.58. Found: C, 71.83; H, 7.17; N, 7.36.

Synthesis of 1e. Complex **1e** (0.081 g, 0.11 mmol, 94%) was prepared by using (*E*)-2-(((2,6-diisopropylphenyl)imino)methyl)-4,6-diiodophenol (0.12 mmol) and [Ni(CH_3)$_2$(tmeda)] (0.12 mmol)]. The ^{1}H and ^{13}C{^{1}H} NMR data are in agreement with the reported one.[3]

Catalytic hydrosilylations. A typical procedure (enrty 1 in Table 1) is as follows. To a stirred solution of precatalyst **1a** (1.0 mg, 0.0025 mmol) in CH_3CN (2 mL) was added Et_2SiH_2 (64 μL, 0.5 mmol) and 1-octene (94 μL, 0.6 mmol) at room temperature. The solution was stirred at room temperature, and the progress of the reaction was monitored by GLC. After completion of the reaction, mesitylene (60 mg, 0.50 mmol) was added as an internal standard to the reaction mixture. The GLC analysis of the resulting solution revealed the formation of Et_2(*n*Oct)SiH (**2**, 0.47 mmol, 93%) and Et_2(*n*Oct)$_2$Si (**3**, 0.02 mmol, 4%). The solution was concentrated under vacuum, and the residue was purified by gel permeation chromatography (GPC) using toluene as an eluent to give **2** (88 mg, 0.44 mmol, 88%) and **3** (0.5 mg, 0.015 mmol, 3%). The final products were characterized by ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR.

Et$_2$(*n*Oct)SiH (**2**): ^{1}H NMR (C_6D_6, 25 °C) δ 0.60 (m, 6H), 0.92 (t, J = 6.0 Hz, 3H), 1.02 (t, J = 8.0 Hz, 6H), 1.29-1.41 (12H), 3.97 (m, 1H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 3.2, 8.5, 11.0, 14.3, 23.0, 25.1, 29.7, 31.9, 32.3, 33.7; ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ –1.63; Anal. Calcd. for $C_{12}H_{28}Si$: C, 71.91; H, 14.08. Found: C, 71.76; H, 14.03.

Et$_2$(*n*Oct)$_2$Si (**3**): ^{1}H NMR (C_6D_6, 25 °C) δ 0.57-0.62 (m, 8H), 0.92 (t, J = 7.2 Hz, 6H), 1.04 (t, J = 8.1 Hz, 6H), 1.23-1.40 (24H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 4.2, 7.9, 12.2, 14.4, 23.1, 24.4, 29.7, 29.8, 32.3, 34.4; ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ 5.82; Anal. Calcd. for $C_{20}H_{44}Si$: C, 76.83; H, 14.19. Found: C, 76.97; H, 14.49.

Ph_2(*n*Oct)SiH (**4**): Compound **4** was identified by comparison of the ^{1}H and ^{13}C{^{1}H} NMR data with those previously reported.[5] ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ –13.14.

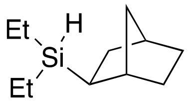
Ph_2(*n*Oct)$_2$Si (**5**): ^{1}H NMR (C_6D_6, 25 °C) δ 0.88 (t, J = 7.2 Hz, 6H), 1.13-1.16 (m, 4H), 1.22-1.28 (m, 16H), 1.33-1.36 (m, 4H), 1.45-1.50 (m, 4H), 7.19-7.23 (m, 6H), 7.58-7.59 (m, 4H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 12.7, 14.0, 22.7, 23.9, 29.2, 29.3, 31.9, 33.8, 127.8, 129.1, 135.0, 136.7; ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ –6.09; Anal. Calcd. for $C_{28}H_{44}Si$: C, 82.28; H, 10.85. Found: C, 82.10; H, 11.15.

(*n*Hex)$_2$(*n*Oct)SiH (6): ^{1}H NMR (C_6D_6, 25 °C) δ 0.66-0.70 (m, 6H), 0.89-0.92 (m, 9H), 1.27-1.46 (m, 28H), 4.05-4.08 (m, 1H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 11.5, 14.0 x 2, 22.7, 22.8, 24.8, 24.9, 29.4 x 2 , 31.6, 32.0, 33.2, 33.5; ^{29}Si{1H} NMR (C_6D_6, 25 °C) δ –6.07; Anal. Calcd. for $C_{20}H_{44}Si$: C, 76.83; H, 14.19. Found: C, 77.34; H, 14.52;

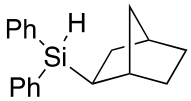
(*n*Hex)$_2$(*n*Oct)$_2$Si (7): ^{1}H NMR (C_6D_6, 25 °C) δ 0.65-0.69 (m, 8H), 0.90-0.93 (m, 12H), 1.29-1.46 (m, 40H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 12.7×2, 14.0, 14.0, 22.7, 22.8, 24.1, 24.2, 29.4, 31.7, 32.0, 33.8, 34.1; ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ 3.40; Anal. Calcd. for $C_{28}H_{60}Si$: C, 79.16; H, 14.23. Found: C, 79.77; H, 14.51.

Ph(*n*Oct)SiH$_2$ (**8**): Compound **8** was identified by comparison of the ^{1}H and ^{13}C{^{1}H} NMR data with those previously reported.[6] ^{29}Si{1H} NMR (C_6D_6, 25 °C) δ –30.50.

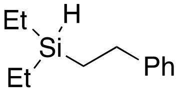
(*n*Oct)$_2$SiH$_2$ (**9**): Compound **9** was identified by comparison of the partial ^{1}H and ^{13}C{^{1}H} NMR data with those previously reported.[7] Full ^{1}H and ^{13}C NMR spectral data have been collected in this study. ^{1}H NMR (C_6D_6, 25 °C) δ 0.65-0.68 (m, 4H), 0.90 (t, J = 7.2 Hz, 6H), 1.26-1.34 (m, 20H), 1.40-1.44 (m, 4H), 3.98 (quintet, J = 3.6 Hz, 2H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 9.2, 14.0, 22.7, 25.6, 29.3, 29.4, 32.0, 33.0; ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ –28.17.



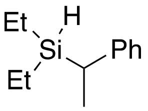
10: Compound **10** was identified by comparison of the ^{1}H and ^{13}C{^{1}H} NMR data with those previously reported.[8] ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ 1.25.



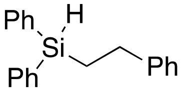
11: Compound **11** was identified by comparison of the ^{1}H and ^{13}C{^{1}H} NMR data with those previously reported.[8] ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ −10.28.



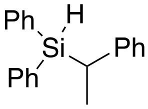
12a: Compound **12a** was identified by comparison of the ^{1}H and ^{13}C{^{1}H} NMR data with those previously reported.[9] ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ –1.90.



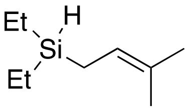
12b: ^{1}H NMR (C_6D_6, 25 °C) δ 0.40-0.56 (m, 4H), 0.85 (t, J = 7.8 Hz, 3H), 0.91 (t, J = 7.8 Hz, 3H), 1.33 (d, J = 7.8 Hz, 3H), 2.19-2.23 (m, 1H), 3.85-3.88 (m, 1H), 7.01-7.06 (m, 3H), 7.16-7.18 (m, 2H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 1.9, 2.0, 8.4 x 2, 16.3, 26.1, 125.0, 127.4, 128.3, 128.6, 145.9; ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ 5.13; Anal. Calcd. for $C_{12}H_{20}Si$: C, 74.92; H, 10.48. Found: C, 74.68; H, 10.52.



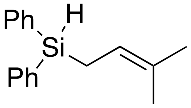
13a: Compound **13a** was identified by comparison of the ^{1}H and ^{13}C{^{1}H} NMR data with those previously reported.[9] ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ –13.56.



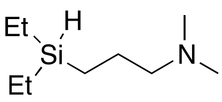
13b: Compound **13b** was identified by comparison of the ^{1}H and ^{13}C{^{1}H} NMR data with those previously reported.[10] ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ –7.71.



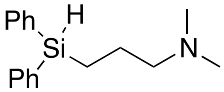
14: ^{1}H NMR (C_6D_6, 25 °C) δ 0.53-0.58 (m, 4H), 0.97 (t, J = 7.8 Hz, 6H), 1.54-1.56 (m, 5H), 1.73 (quintet, J = 1.2 Hz, 3H), 3.96 (septet, J = 3.0 Hz, 1H), 5.14-5.19 (m, 1H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 3.2, 8.0, 13.6, 16.8, 25.6, 116.4, 128.0, 128.9, 133.1; ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ –3.58; Anal. Calcd. for $C_9H_{20}Si$: C, 69.14; H, 12.89. Found: C, 68.99; H, 12.83.



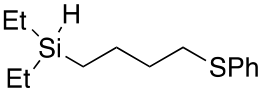
15: Compound **15** was identified by comparison of the ^{1}H and ^{13}C{^{1}H} NMR data with those previously reported.[11] ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ –17.32.



16: ^{1}H NMR ($CDCl_3$, 25 °C) δ 0.52-0.61 (m, 6H), 0.97 (t, J = 7.8 Hz, 6H), 1.50 (quintet, J = 7.8 Hz, 2H), 2.21 (s, 6H), 2.25 (t, J = 7.2 Hz, 2H), 3.62-3.66 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) δ 2.9, 8.3, 8.4, 22.9, 45.6, 63.3; ^{29}Si{^{1}H} NMR ($CDCl_3$, 25 °C) δ –1.38. Elemental analysis was not successful due to high unstabiliy of **16** under air. Full ^{1}H and ^{13}C NMR spectra were shown on page S8.



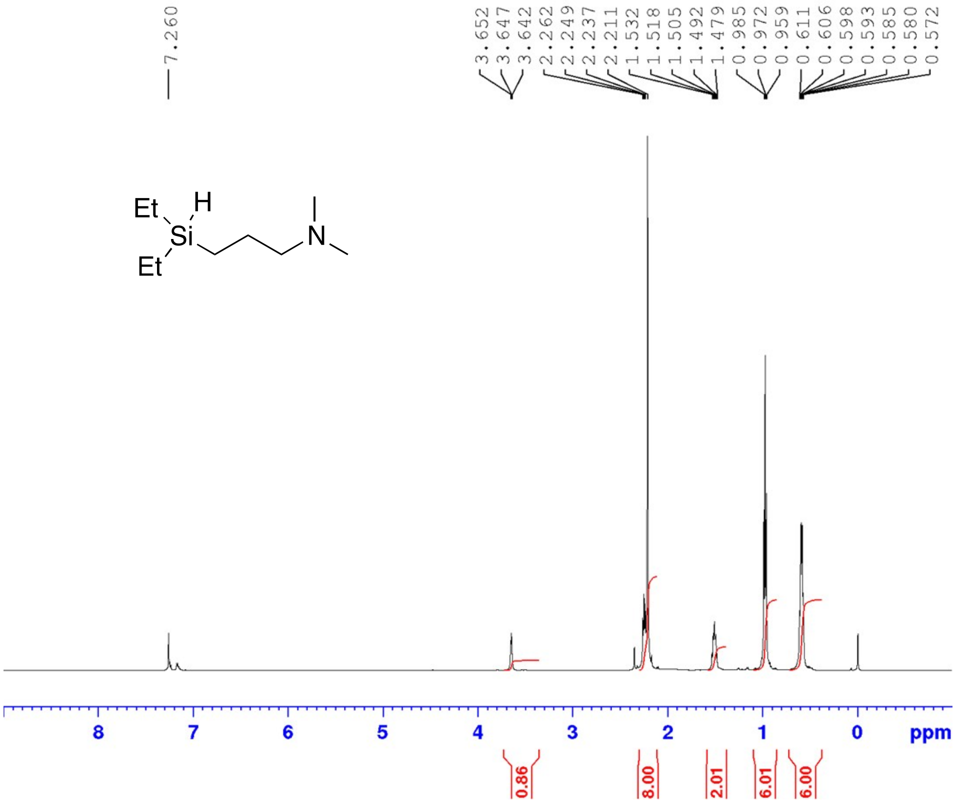
17: ^{1}H NMR (C_6D_6, 25 °C) δ 1.11-1.16 (m, 2H), 1.61 (quintet, J = 7.6 Hz, 2H), 2.16 (s, 6H), 2.28 (t, J = 7.3 Hz, 2H), 4.86 (t, J = 3.7 Hz, 1H), 7.32-7.38 (m, 6H), 7.53-7.55 (m, 4H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 9.7, 22.6, 45.1, 62.1, 128.0, 129.4, 134.8, 135.1; ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ –13.00. Elemental analysis was not successful due to high unstabiliy of **17** under air. Full ^{1}H and ^{13}C NMR spectra were shown on page S9.

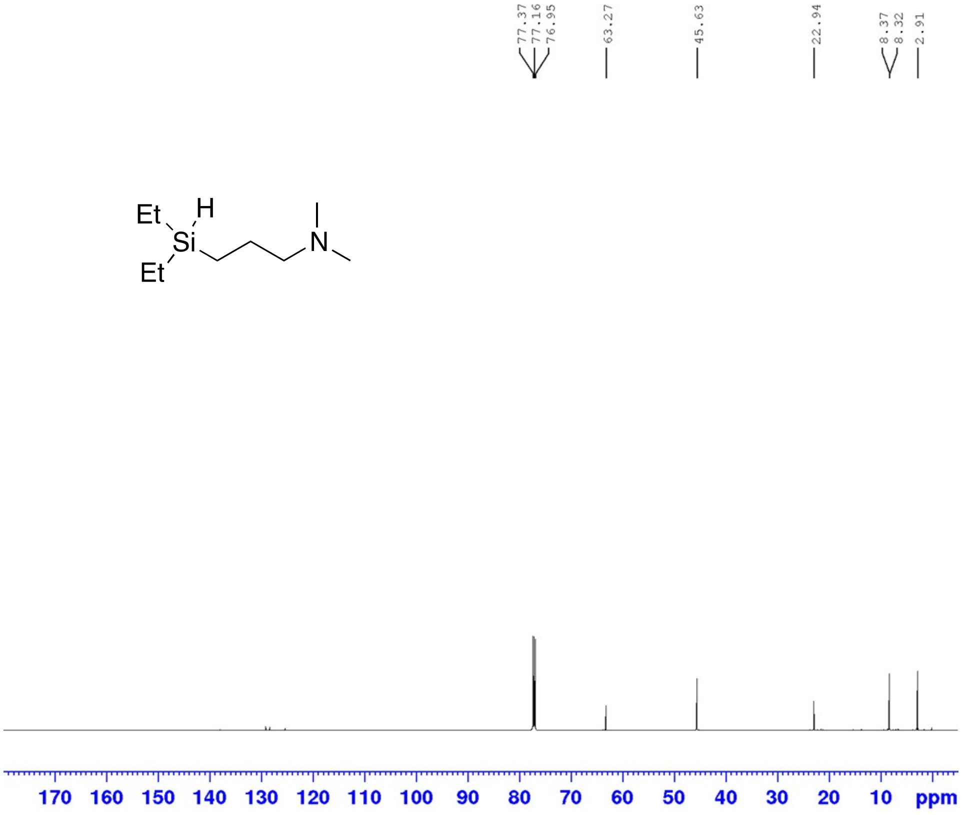


18: ^{1}H NMR (C_6D_6, 25 °C) δ 0.42-0.46 (m, 2H), 0.50-0.54 (m, 4H), 0.96 (t, J = 7.8 Hz, 6H), 1.33-1.38 (m, 2H), 1.54-1.59 (m, 2H), 2.69 (t, J = 7.2 Hz, 2H), 3.86-3.87 (m, 1H), 6.93 (td, J = 7.2, 1.2 Hz, 1H), 7.03 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 0.6 Hz, 1H), 7.31 (d, J = 1.2 Hz, 1H); ^{13}C{^{1}H} NMR (C_6D_6, 25 °C) δ 2.7, 8.1, 10.1, 23.7, 32.6, 32.9, 125.4, 128.7, 128.9, 137.5; ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C) δ –1.75; Anal. Calcd. for $C_{14}H_{24}SSi$: C, 66.60; H, 9.58; S, 12.70. Found: C, 66.85; H, 9.73; S, 12.71.

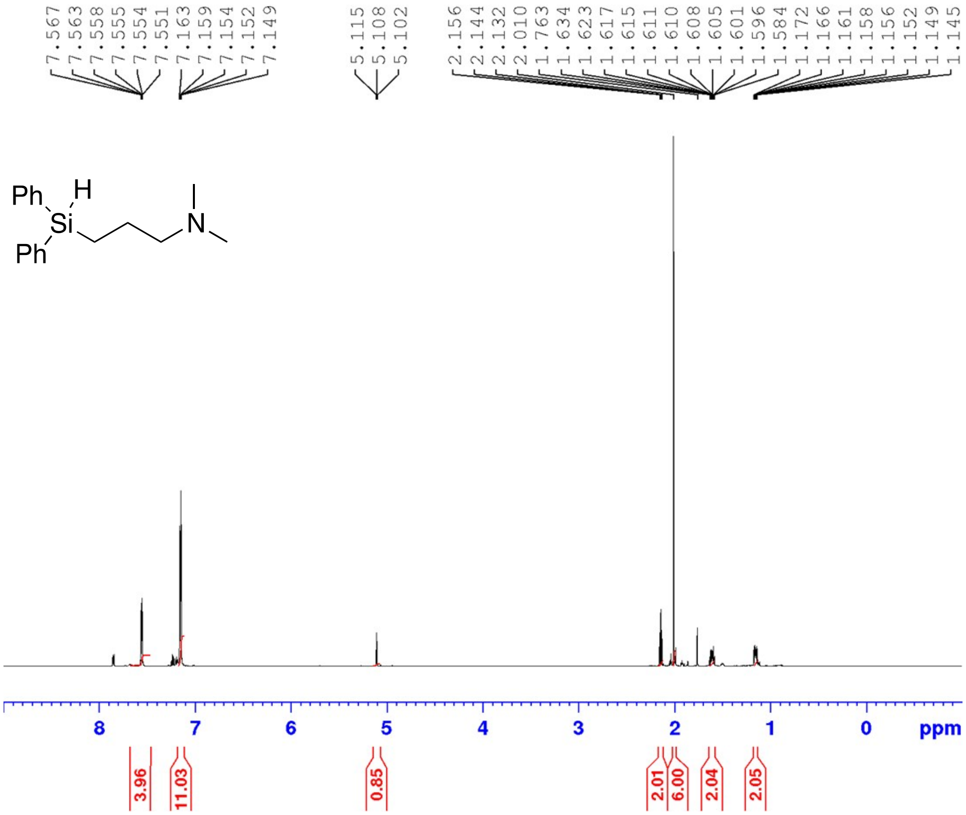
Formation of 3 via octyl group redistribution in 2. To a toluene solution (2 mL) of **1a (**0.5 mg, 0.001 mmol) were successively added Et_2SiH_2 (1.0 mg, 0.01 mmol) and Et_2(*n*Oct)SiH (**2**, 46.7 mg, 0.23 mmol). After the mixture was stirred at 25 °C for 24 h, formation of Et_2(*n*Oct)$_2$Si (**3**, 0.02 mmol, 15%) was confirmed by GLC analysis. It was also confirmed that the reactions of **1a** with Et_2(*n*Oct)SiH (**2**) and/or 1-octene resulted in the full recovery of the starting materials.

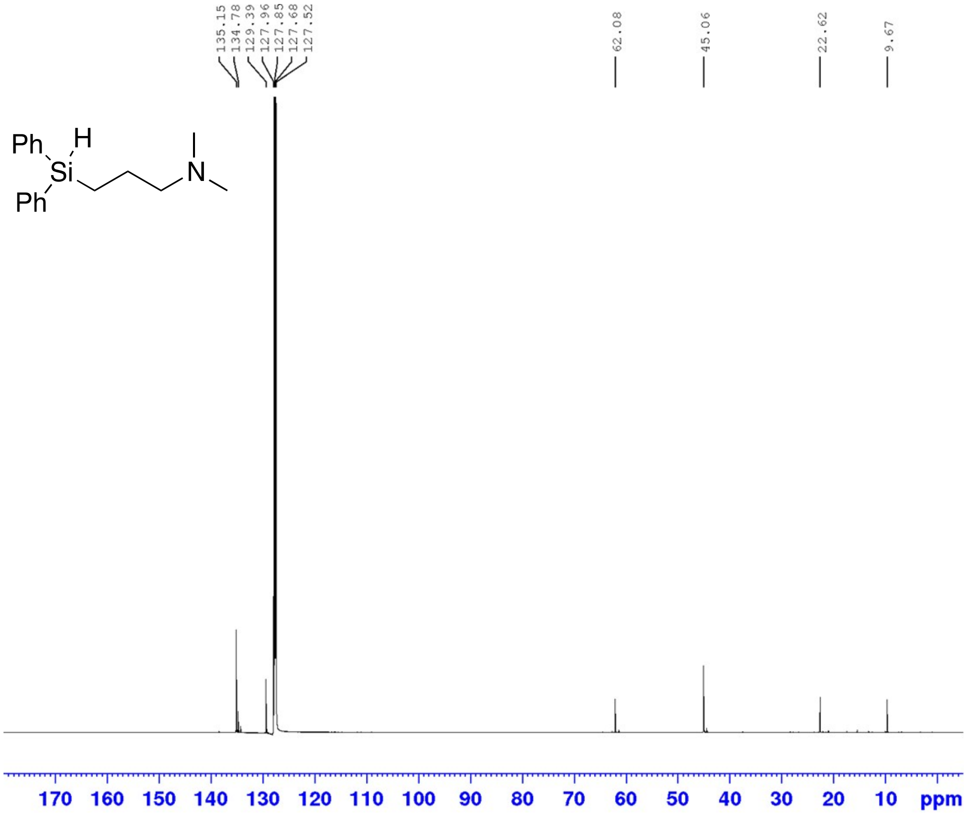
^{1}H and ^{13}C NMR spectra of 16 (in $CDCl_3$ at room temperature)





^{1}H and ^{13}C NMR spectra of 17 (in C_6D_6 at room temperature)





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