

Supporting Information

Highly Selective Synthesis of Hydrosiloxanes by Au-Catalyzed Dehydrogenative Cross-Coupling Reaction of Silanols with Hydrosilanes

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1. General Information

^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra (^1H , 600 MHz; ^{13}C , 150 MHz; ^{29}Si , 119 MHz) were recorded on a BRUKER Biospin AVANCE III HD 600 NMR spectrometer. Chemical shifts were reported in δ (ppm) and were referenced to the residual solvent signal for ^1H (THF- d_8 = 3.58 ppm; benzene- d_6 = 7.16 ppm; toluene- d_8 = 2.09 ppm), to the central line of the solvent signal for ^{13}C (THF- d_8 = 67.57 ppm; benzene- d_6 128.39 ppm; toluene- d_8 = 20.4 ppm), and to phenyltrimethylsilane for ^{29}Si (THF- d_8 = -4.18. ppm; benzene- d_6 -4.71 ppm). GC-MS (EI) was measured on a SHIMADZU GCMS-QP2010 Plus. NMR yields of the products were determined by ^{29}Si NMR spectra using inverse-gated decoupling pulse sequence to suppress nuclear Overhauser effect. To ensure quantitative analysis by ^{29}Si NMR, samples were dissolved in a deuterated solvent (THF- d_8 or benzene- d_6) with a trace amount of $\text{Cr}(\text{acac})_3$ as a relaxation agent, and 10 sec delay time was applied.

Unless otherwise noted, all manipulations were performed under an argon atmosphere using Schlenk techniques or a glove box. Benzene- d_6 was dried over sodium benzophenone ketyl and distilled. All the reagents except **1i**¹ were purchased and used without further purification.

2. Experimental Details

2-1. Effect of PⁿBu₃ Amounts for the Reaction of Et₃SiOH with PhSiH₃ Catalyzed by AuCl(PPh₃)/ PⁿBu₃

A mixture of triethylsilanol (**1a**) (265 mg, 2.0 mmol), phenylsilane (**2a**) (216 mg, 2.0 mmol), AuCl(PPh₃) (0.040 M THF solution, 25 μL, 0.050 mol%), PⁿBu₃ (0.20 M THF solution, 0 - 100 μL, 0 - 1.0 mol%), and THF (0.5 mL) was stirred for 48 h at room temperature under Ar. After the reaction, trimethylphenylsilane (80 - 100 mg) was added to the reaction mixture as an internal standard for NMR analysis. Then, ca. 0.5 mL of the mixture was taken for NMR analysis, to which was added C₆D₆ (0.1 mL). Yields of **3aa** based on **1a** were determined by integral values of ¹H NMR signals. The results are summarized in Fig. S1.

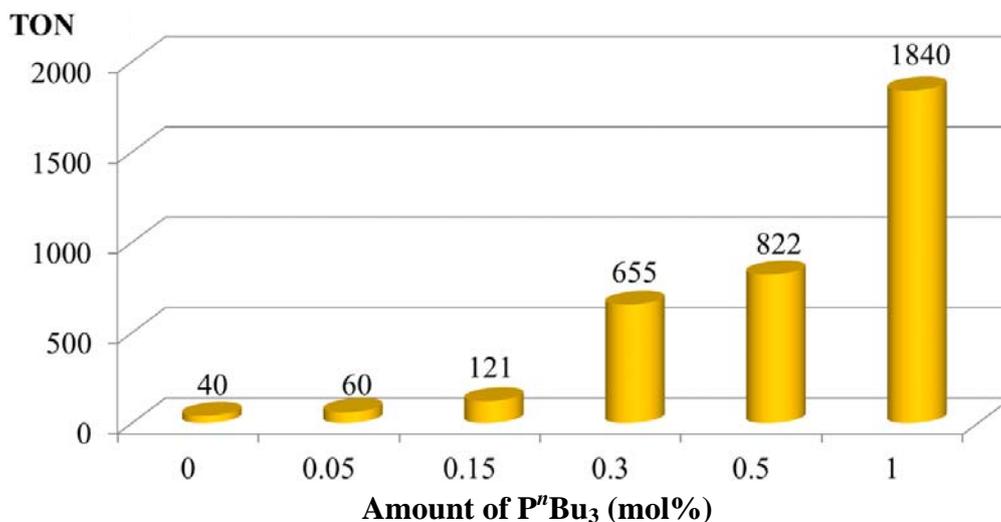
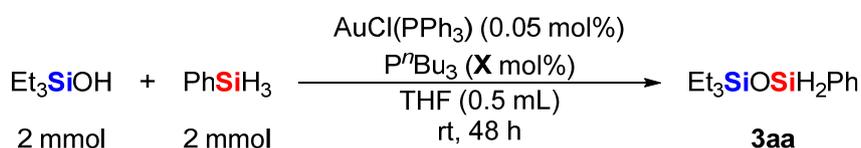
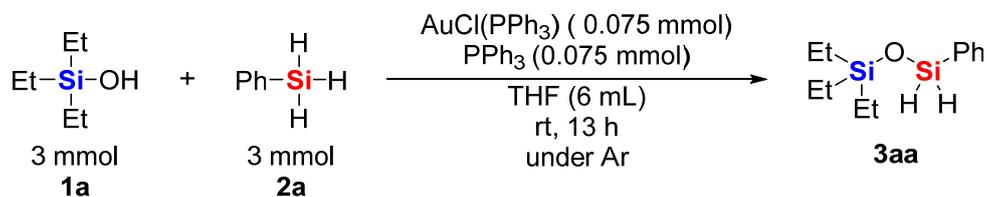


Figure S1. Effect of PⁿBu₃ amounts on the turnover number (TON)

When the same reaction was performed using 0.025 mol% of AuCl(PPh₃) (0.010 M THF solution, 50 μL) and 0.50 mol% of PⁿBu₃ (0.040 M THF solution, 250 μL), **3aa** was obtained in >99% NMR yield. TON of this reaction reached ca. 4000.

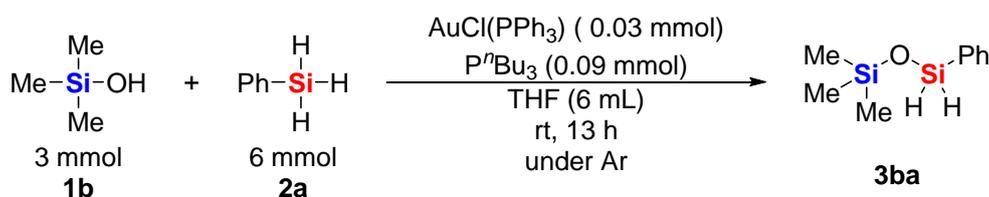
2-2. Synthesis of Dihydrosiloxanes

Synthesis of **3a**



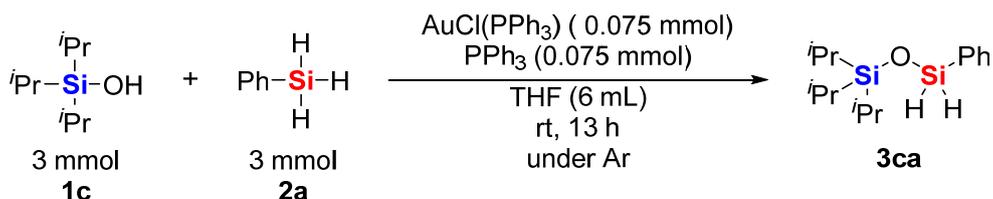
A mixture of triethylsilanol (**1a**) (397 mg, 3.0 mmol), phenylsilane (**2a**) (325 mg, 3.0 mmol), AuCl(PPh₃) (36 mg, 0.075 mmol), PPh₃ (20 mg, 0.075 mmol), and THF (6 mL) was stirred for 13 h at room temperature under Ar. Then, the solvent was evaporated and the residue was purified by Kugelrohr distillation (1 Torr, oven temperature 130 °C) to give **3a** as a colorless liquid (600 mg, 84% yield). ¹H NMR (600 MHz, THF-*d*₈): δ 7.60-7.61 (m, 2H, SiPh), 7.36-7.42 (m, 3H, SiPh), 5.12 (s, 2H, ¹J(Si,H) = 215.0 Hz, SiH₂), 0.95 (t, 9H, J = 8.0 Hz, SiCH₂CH₃), 0.60 (q, 6H, J = 8.0 Hz, SiCH₂CH₃); ¹³C{¹H} NMR (150 MHz, THF-*d*₈): δ 135.8, 134.6, 131.1, 128.8, 6.9, 6.6; ²⁹Si{¹H} NMR (119 MHz, THF-*d*₈): δ 12.9 (Et₃Si), -31.8 (SiH₂); GCMS (EI) m/z (relative intensity) 238 (1) [M]⁺, 209 (100), 181 (52), 151 (17), 131 (2), 107 (18), 77 (2), HRMS (EI) calcd for [C₁₀H₁₇OSi₂]⁺ [M-Et]⁺ 209.0812, found 209.0815.

Synthesis of **3ba**



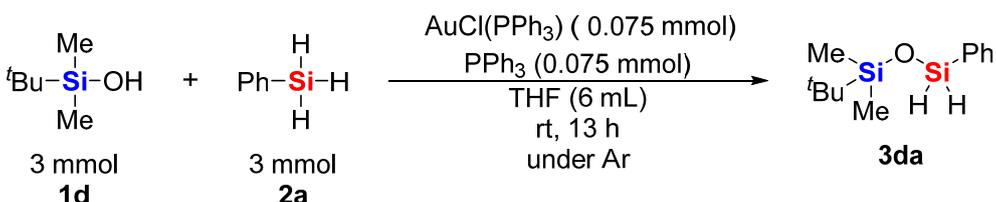
Compound **3ba** was synthesized as described for **3a** from trimethylsilanol (**1b**) (271 mg, 3.0 mmol), phenylsilane (**2a**) (649 mg, 6.0 mmol), AuCl(PPh₃) (15 mg, 0.03 mmol), and PⁿBu₃ (18 mg, 0.09 mmol). Kugelrohr distillation (1 Torr, oven temperature 100 °C) of the crude mixture afforded **3ba** as a colorless liquid (447 mg, 84% yield). ¹H NMR (600 MHz, THF-*d*₈): δ 7.59-7.60 (m, 2H, SiPh), 7.36-7.42 (m, 3H, SiPh), 5.05 (s, 2H, ¹J(Si,H) = 215.0 Hz, SiH₂), 0.12 (s, 9H, SiMe); ¹³C{¹H} NMR (150 MHz, THF-*d*₈): δ 135.8, 134.8, 131.3, 129.0, 1.5; ²⁹Si{¹H} NMR (119 MHz, THF-*d*₈): δ 12.9 (Me₃Si), -30.9 (SiH₂); GCMS (EI) m/z (relative intensity) 196 (16) [M]⁺, 181 (100), 118 (28), 107 (6), 77 (1), 73 (7), HRMS (EI) calcd for [C₈H₁₃OSi₂]⁺ [M-Me]⁺ 181.0499, found 181.0503.

Synthesis of 3ca



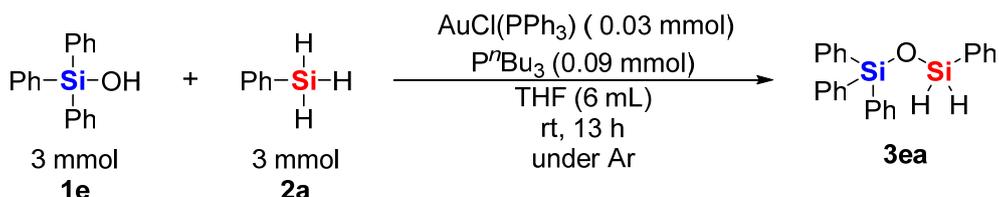
Compound **3ca** was synthesized as described for **3aa** from triisopropylsilanol (**1c**) (523 mg, 3.0 mmol), phenylsilane (**2a**) (325 mg, 3.0 mmol), AuCl(PPh₃) (36 mg, 0.075 mmol), and PPh₃ (20 mg, 0.075 mmol). Kugelrohr distillation (1 Torr, oven temperature 150 °C) of the crude mixture afforded **3ca** as a colorless liquid (639 mg, 76% yield). ¹H NMR (600 MHz, THF-*d*₈): δ 7.63-7.64 (m, 2H, SiPh), 7.38-7.39 (m, 3H, SiPh), 5.20 (s, 2H, ¹J(Si,H) = 214.6 Hz, SiH₂), 1.05-1.06 (m, 21H, SiⁱPr); ¹³C{¹H} NMR (150 MHz, THF-*d*₈): δ 136.0, 134.9, 131.3, 129.0, 18.3, 13.7; ²⁹Si{¹H} NMR (119 MHz, THF-*d*₈): δ 9.0 (ⁱPr₃Si), -31.6 (SiH₂); GCMS (EI) m/z (relative intensity) 280 (1) [M]⁺, 237 (100), 107 (12), 77 (1), 42 (2), HRMS calcd for [C₁₂H₂₁OSi₂]⁺ [M-ⁱPr]⁺ 237.1125, found 237.1125.

Synthesis of 3da



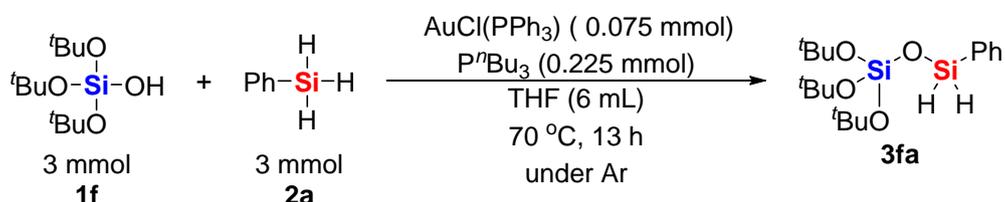
Compound **3da** was synthesized as described for **3aa** from *tert*-butyldimethylsilanol (**1d**) (397 mg, 3.0 mmol), phenylsilane (**2a**) (325 mg, 3.0 mmol), AuCl(PPh₃) (36 mg, 0.075 mmol), and PPh₃ (20 mg, 0.075 mmol). Kugelrohr distillation (1 Torr, oven temperature 100 °C) of the crude mixture afforded **3da** as a colorless liquid (607 mg, 85% yield). ¹H NMR (600 MHz, THF-*d*₈): δ 7.60-7.61 (m, 2H, SiPh), 7.36-7.41 (m, 3H, SiPh), 5.10 (s, 2H, ¹J(Si,H) = 215.0 Hz, SiH₂), 0.90 (s, 9H, Si^tBu), 0.08 (s, 6H, SiMe); ¹³C{¹H} NMR (150 MHz, THF-*d*₈): δ 135.8, 134.8, 131.13, 129.0, 26.1, 19.2, -3.2; ²⁹Si{¹H} NMR (119 MHz, THF-*d*₈): δ 13.6 (^tBuMe₂Si), -32.0 (SiH₂); GCMS(EI) m/z (relative intensity) 238 (1) [M]⁺, 223 (2), 181 (100), 107 (4), 57 (1), HRMS (EI) calcd for [C₈H₁₃OSi₂]⁺ [M-^tBu]⁺ 181.0499, found 181.0510.

Synthesis of 3ea



3ea was synthesized as described for **3aa** from triphenylsilanol (**1e**) (829 mg, 3.0 mmol), phenylsilane (**2a**) (325 mg, 3.0 mmol), AuCl(PPh₃) (15 mg, 0.03 mmol), and PⁿBu₃ (18 mg, 0.09 mmol). After the reaction, the solvent was removed by evaporation, and the remaining volatile compounds were removed by Kugelrohr distillation (1 Torr, oven temperature 170 °C). The residue was diluted with hexane (10 mL) and filtered through a filter paper to remove impure substances. The filtrate was concentrated under vacuum to yield **3ea** as a colorless liquid (1.02 g, 89% yield). ¹H NMR (600 MHz, THF-*d*₈): δ 7.54-7.56 (m, 8H, SiPh), 7.38-7.41 (m, 4H, SiPh), 7.30-7.34 (m, 8H, SiPh), 5.26 (s, 2H, ¹J(Si,H) = 218.2 Hz, SiH₂); ¹³C{¹H} NMR (150 MHz, THF-*d*₈): δ 136.2, 136.1, 136.0, 135.09, 131.4, 131.0, 129.0, 128.8; ²⁹Si{¹H} NMR (119 MHz, THF-*d*₈): δ -17.0 (Ph₃Si), -27.8 (SiH₂); GCMS (EI) m/z (relative intensity) 382 (7) [M]⁺, 305 (15), 259 (5), 226 (100), 107 (3), 77 (2), HRMS (EI) calcd for [C₁₈H₁₇OSi₂]⁺ [M-Ph]⁺ 305.0812, found 305.0816.

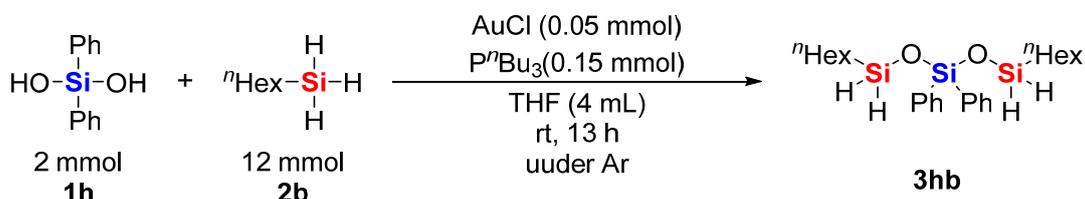
Synthesis of 3fa



Compound **3fa** was synthesized as described for **3aa** from tri(*tert*-butoxy)silanol (**1f**) (793 mg, 3.0 mmol), phenylsilane (**2a**) (325 mg, 3.0 mmol), AuCl(PPh₃) (36 mg, 0.075 mmol), and PⁿBu₃ (46 mg, 0.225 mmol). Kugelrohr distillation (1 Torr, oven temperature 150 °C) of the crude mixture afforded **3fa** as a colorless liquid (888 mg, 80% yield). ¹H NMR (600 MHz, benzene-*d*₆): δ 7.76-7.78 (m, 2H, SiPh), 7.18-7.22 (m, 3H, SiPh), 5.45 (s, 2H, ¹J(Si,H) = 217.5 Hz, SiH₂), 1.30 (s, 27H, ^tBu); ¹³C{¹H} NMR (150 MHz, benzene-*d*₆): δ 135.3, 135.1, 131.2, 128.8, 73.4, 31.9; ²⁹Si{¹H} NMR (119 MHz, benzene-*d*₆): δ -30.1 (SiH₂), -98.8 ((^tBuO)₃Si); GCMS (EI) m/z (relative intensity) 370 (0) [M]⁺, 355 (8), 313 (2), 297 (1), 293 (7), 200 (100), 122 (45), 107 (35), 77 (4), 57 (55); Anal. Calcd. for C₁₈H₃₄O₄Si₂: C, 58.33; H, 9.25; Found: C, 58.38; H, 9.33.

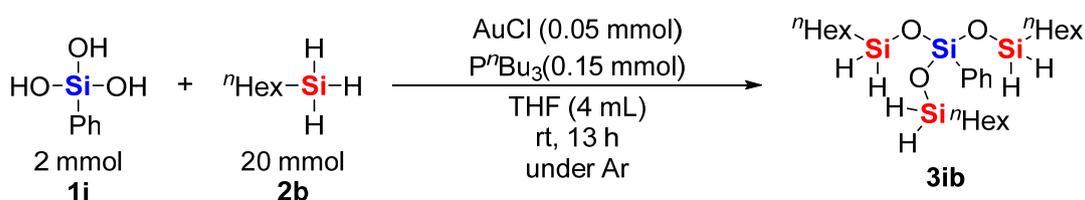
(100), 99 (2), 69 (6); HRMS (EI) calcd for $[C_{20}H_{38}O_2Si_4]^+ [M]^+$ 422.1943, found 422.1940.

Synthesis of 3hb



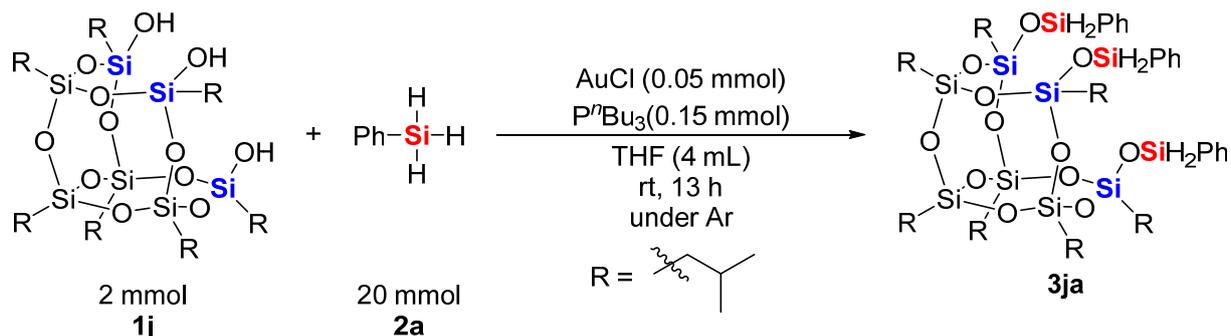
Compound **3hb** was synthesized as described for **3ea** from diphenylsilanediol (**1h**) (432 mg, 2.0 mmol), hexylsilane (**2b**) (1.39 g, 12 mmol), AuCl (12 mg, 0.05 mmol), and $P^n\text{Bu}_3$ (30 mg, 0.15 mmol). **3hb** was obtained as a colorless liquid (800 mg, 90% yield). ^1H NMR (600 MHz, THF- d_8): δ 7.57-7.58 (m, 4H, SiPh), 7.38-7.44 (m, 2H, SiPh), 7.29-7.36 (m, 4H, SiPh), 4.75 (s, 4H, $J = 2.6$ Hz, $^1J(\text{Si},\text{H}) = 210.2$ Hz, SiH₂), 1.38-1.44 (m, 4H, SiC₂H₂C₄H₈CH₃), 1.30-1.35 (m, 4H, SiC₂H₂C₄H₈CH₃), 1.21-1.29 (m, 8H, SiC₂H₂C₄H₈CH₃), 0.87 (t, 6H, $J = 6.9$ Hz, Me), 0.80-0.83 (m, 4H, SiCH₂); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, THF- d_8): δ 135.8, 135.0, 131.2, 128.8, 33.4, 32.6, 24.0, 23.6, 15.6, 14.6; $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, THF- d_8): δ -21.4 (SiH₂), -44.4; GCMS (EI) m/z (relative intensity) 444 (10) $[M]^+$, 366 (27), 359 (100), 182 (1), 85 (1), 77 (1), HRMS (EI) calcd for $[C_{24}H_{40}O_2Si_3]^+ [M]^+$ 444.2331, found 444.2331.

Synthesis of 3ib



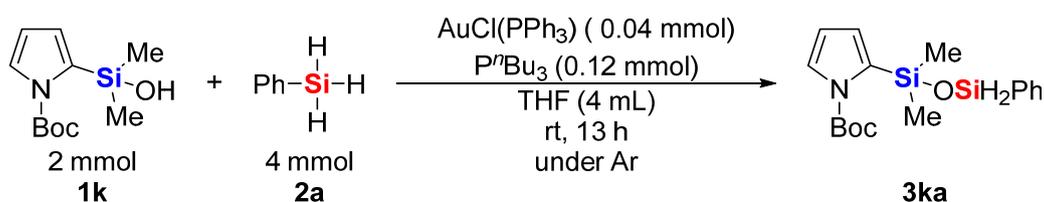
Compound **3ib** was synthesized as described for **3ea** from phenylsilanetriol (**1i**) (312 mg, 2.0 mmol), hexylsilane (**2b**) (2.3 g, 20 mmol), AuCl (12 mg, 0.05 mmol), and $P^n\text{Bu}_3$ (30 mg, 0.15 mmol). **3ib** was obtained as a colorless liquid (947 mg, 95% yield). ^1H NMR (600 MHz, THF- d_8): δ 7.55-7.56 (m, 2H, SiPh), 7.38-7.40 (m, 1H, SiPh), 7.32-7.35 (m, 2H, SiPh), 4.68 (t, 6H, $J = 2.6$ Hz, $^1J(\text{Si},\text{H}) = 210.4$ Hz, SiH₂), 1.41-1.45 (m, 6H, SiC₂H₂C₄H₈CH₃), 1.33-1.37 (m, 6H, SiC₂H₂C₄H₈CH₃), 1.26-1.29 (m, 12H, SiC₂H₂C₄H₈CH₃), 0.88 (t, 9H, $J = 6.8$ Hz, Me), 0.80-0.83 (m, 6H, SiCH₂); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, THF- d_8): δ 134.6, 133.3, 131.2, 128.7, 33.4, 32.5, 23.9, 23.5, 15.4, 14.5; $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, THF- d_8): δ -21.6 (SiH₂), -75.9 (SiPh); GCMS (EI) m/z (relative intensity) 498 (28) $[M]^+$, 421 (1), 413 (68), 383 (2), 213 (100), 131 (2), 115 (14), 85 (21), 77 (2), HRMS (EI) calcd for $[C_{24}H_{50}O_3Si_4]^+ [M]^+$ 498.2832, found 498.2825.

Synthesis of 3ja



Compound **3ja** was synthesized as described for **3ea** from 1,3,5,7,9,11,14-heptaisobutyltricyclo-[7.3.3.1^{5,11}]heptasiloxane-endo-3,7,14-triol (**1j**) (1.6 g, 2.0 mmol), phenylsilane (**2a**) (2.2 g, 20 mmol), AuCl (12 mg, 0.05 mmol), and PⁿBu₃ (30 mg, 0.15 mmol). **3ja** was obtained as a colorless liquid (2.4 g, 93% yield). ¹H NMR (600 MHz, *d*-benzene): δ 7.73-7.75 (m, 6H, SiPh), 7.16-7.20 (m, 9H, SiPh), 5.53 (s, 6H, ¹J(Si,H) = 220.7 Hz, SiH₂), 2.02-2.11 (m, 7H, CH₂CH(CH₃)₂), 1.09 (d, 18H, *J* = 6.6 Hz, CH₂CH(CH₃)₂), 1.06 (d, 6H, *J* = 6.7 Hz, CH₂CH(CH₃)₂), 1.05 (d, 18H, *J* = 6.6 Hz, CH₂CH(CH₃)₂), 0.80-0.84 (m, 14H, CH₂CH(CH₃)₂); ¹³C{¹H} NMR (150 MHz, benzene-*d*₆): δ 135.1, 130.9, 128.7, 128.6, 26.48, 26.46, 26.2, 25.1, 24.9, 24.8, 24.76, 24.3, 23.3; ²⁹Si{¹H} NMR (119 MHz, benzene-*d*₆): δ -28.2 (SiH₂), -65.9, -66.0, -67.0; HRMS (EI) calcd for [C₄₂H₇₃O₁₂Si₉]⁺ [M-SiH₂Ph]⁺ 1001.3389, found 1001.2924.

Synthesis of 3ka

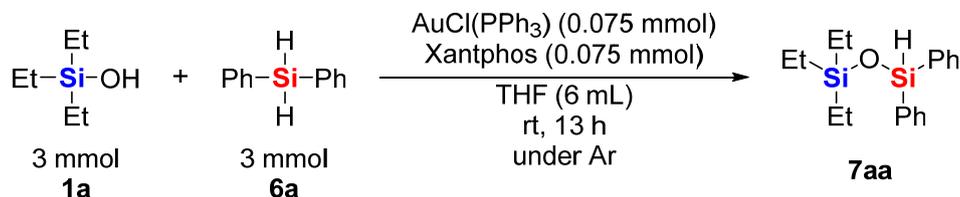


Compound **3ka** was synthesized as described for **3aa** from (*N*-Boc-2-pyrrolyl)dimethylsilanol (**1k**) (483 mg, 2.0 mmol), phenylsilane (**2a**) (433 mg, 4.0 mmol), AuCl(PPh₃) (20 mg, 0.04 mmol), and PⁿBu₃ (24 mg, 0.12 mmol). Kugelrohr distillation (1 Torr, oven temperature 170 °C) of the crude mixture afforded **3ka** as a colorless liquid (523 mg, 75% yield). ¹H NMR (600 MHz, benzene-*d*₆): δ 7.67-7.68 (m, 2H, SiPh), 7.32-7.33 (m, 1H, C₄H₃N), 7.16-7.17 (m, 3H, SiPh), 6.787-6.79 (m, 1H, C₄H₃N), 6.17 (t, 1H, *J* = 6.1 Hz, C₄H₃N), 5.47 (s, 2H, ¹J(Si,H) = 216.2 Hz, SiH₂), 1.23 (s, 9H, O^tBu), 0.58 (s, 6H, SiMe); ¹³C{¹H} NMR (150 MHz, benzene-*d*₆): δ 150.6, 135.9, 134.7, 134.2, 130.7, 128.6, 125.5, 124.9, 113.1, 83.8, 28.0, 1.7; ²⁹Si{¹H} NMR (119 MHz, benzene-*d*₆): δ -5.6 (SiMe₂), -30.2 (SiH₂); GCMS (EI) *m/z* (relative intensity) 347 (1) [M]⁺, 290 (1), 269 (2), 246 (1), 240 (1), 107 (2), 101 (9), 77 (5), 73 (100), 65 (5), 57 (9); HRMS (EI) calcd for

$[\text{C}_{13}\text{H}_{16}\text{NO}_3\text{Si}_2]^+ [\text{M}^t\text{Bu}]^+$ 290.0663, found 290.0664; Anal. Calcd. for $\text{C}_{17}\text{H}_{25}\text{NO}_3\text{Si}_2$: C, 58.75; H, 7.25; N, 4.03; Found: C, 58.49; H, 7.33; N, 3.73.

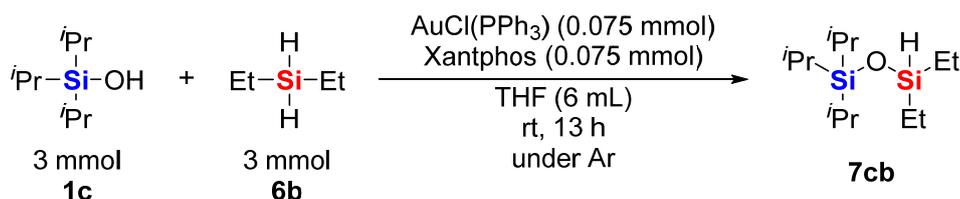
2-3. Synthesis of Monohydrosiloxanes

Synthesis of 7aa



A mixture of triethylsilanol (**1a**) (397 mg, 3.0 mmol), diphenylsilane (**6a**) (553 mg, 3.0 mmol), AuCl(PPh₃) (36 mg, 0.075 mmol), xantphos (43 mg, 0.075 mmol), and THF (6 mL) was stirred for 13 h at room temperature under Ar. Then, the solvent was evaporated and the residue was purified by Kugelrohr distillation (1 Torr, oven temperature 160 °C) to give **7aa** as a colorless liquid (773 mg, 82% yield). ¹H NMR (600 MHz, THF-*d*₈): δ 7.57-7.58 (m, 4H, SiPh), 7.33-7.40 (m, 6H, SiPh), 5.52 (s, 1H, ¹J(Si,H) = 213.7 Hz, SiH), 0.93 (t, 9H, *J* = 8.0 Hz, SiCH₂CH₃), 0.60 (q, 6H, *J* = 7.9 Hz, SiCH₂CH₃); ¹³C{¹H} NMR (150 MHz, THF-*d*₈): δ 137.1, 135.0, 131.0, 128.9, 7.2, 7.0; ²⁹Si{¹H} NMR (119 MHz, THF-*d*₈): δ 12.3 (SiEt₃), -24.1 (SiH); GCMS (EI) *m/z* (relative intensity) 314 (1) [M]⁺, 285 (100), 183 (9), 131 (1), 77 (1), HRMS (EI) calcd for [C₁₆H₂₁OSi₂]⁺ [M-Et]⁺ 285.1125, found 285.1137.

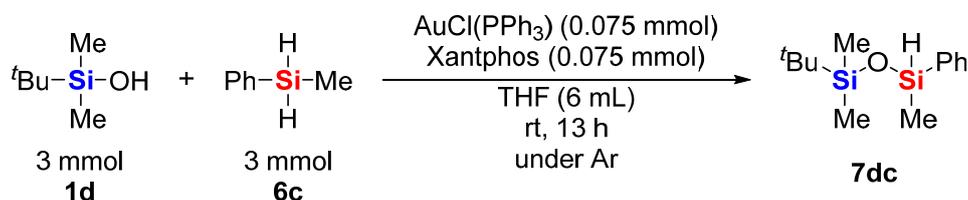
Synthesis of 7cb



Compound **7cb** was synthesized as described for **7aa** from triisopropylsilanol (**1c**) (523 mg, 3.0 mmol), diethylsilane (**6b**) (264 mg, 3.0 mmol), AuCl(PPh₃) (36 mg, 0.075 mmol), and xantphos (43 mg, 0.075 mmol). Kugelrohr distillation (1 Torr, oven temperature 140 °C) of the crude mixture afforded **7cb** as a colorless liquid (726 mg, 93% yield). ¹H NMR (600 MHz, THF-*d*₈): δ 4.63 (quint, 1H, *J* = 2.2 Hz, ¹J(Si,H) = 198.2 Hz, SiH), 1.05-1.06 (m, 21H, SiCH(CH₃)₂), 1.00 (t, 6H, *J* = 7.9 Hz, SiCH₂CH₃), 0.65-0.70 (m, 4H, SiCH₂CH₃); ¹³C{¹H} NMR (150 MHz, THF-*d*₈): δ 18.4, 13.9, 8.1, 7.1; ²⁹Si{¹H} NMR (119 MHz, THF-*d*₈): δ 7.8 (Si^{*i*}Pr₃), -0.9 (SiH); GCMS (EI) *m/z* (relative intensity) 260 (1) [M]⁺, 231 (3), 217 (100), 103 (8), 87 (3), 43 (2), HRMS (EI) calcd for

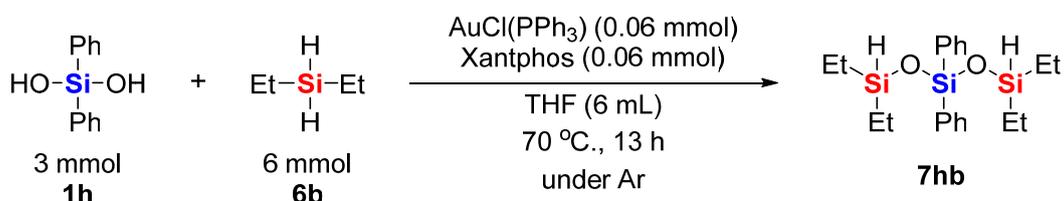
$[\text{C}_{10}\text{H}_{25}\text{OSi}_2]^+ [\text{M}^i\text{Pr}]^+$ 217.1438, found 217.1436.

Synthesis of **7dc**



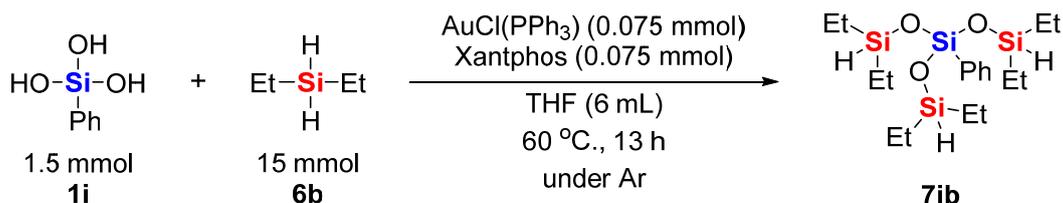
Compound **7dc** was synthesized as described for **7aa** from *tert*-butyldimethylsilanol (**1d**) (397 mg, 3.0 mmol), methylphenylsilane (**6c**) (367 mg, 3.0 mmol), AuCl(PPh₃) (36 mg, 0.075 mmol), and xantphos (43 mg, 0.075 mmol). Kugelrohr distillation (1 Torr, oven temperature 120 °C) of the crude mixture afforded **7dc** as a colorless liquid (719 mg, 95% yield). ¹H NMR (600 MHz, THF-*d*₈): δ 7.55-7.57 (m, 2H, SiPh), 7.33-7.37 (m, 3H, SiPh), 5.12 (q, 1H, *J* = 2.8 Hz, ¹*J*(Si,H) = 208.6 Hz, SiH), 0.90 (s, 9H, SiC(CH₃)₃), 0.40 (d, 3H, *J* = 2.8 Hz, Si(H)Me), 0.06 (s, 6H, SiMe₂); ¹³C{¹H} NMR (150 MHz, THF-*d*₈): δ 138.7, 134.2, 130.7, 128.8, 26.3, 19.0, 0.1, -2.88; ²⁹Si{¹H} NMR (119 MHz, THF-*d*₈): δ 13.4 (Si^tBu), -14.3 (SiH); GCMS (EI) *m/z* (relative intensity) 252 (1) [M]⁺, 237 (2), 195 (100), 137 (1), 131 (1), 121 (6), 57 (1); HRMS (EI) calcd for [C₉H₁₅OSi₂]⁺ [M-^tBu]⁺ 195.0656, found 195.0667.

Synthesis of **7hb**



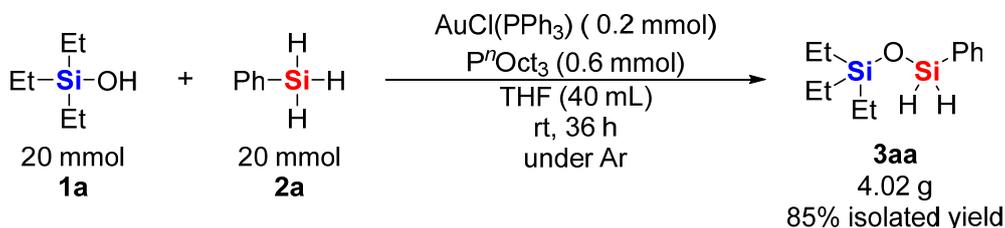
Compound **7hb** was synthesized as described for **7aa** from diphenylsilanediol (**1h**) (649 mg, 3.0 mmol), diethylsilane (**6b**) (529 mg, 6.0 mmol), AuCl(PPh₃) (30 mg, 0.06 mmol), and xantphos (35 mg, 0.06 mmol). Kugelrohr distillation (1 Torr, oven temperature 135 °C) of the crude mixture afforded **7hb** as a colorless liquid (1.02 g, 88% yield). ¹H NMR (600 MHz, TMS in benzene-*d*₆): δ 7.80-7.81 (m, 4H, SiPh), 7.19-7.22 (m, 6H, SiPh), 4.94 (quint, 2H, *J* = 2.3 Hz, ¹*J*(Si,H) = 201.6 Hz, SiH), 0.98 (t, 12H, *J* = 8.0 Hz, SiCH₂CH₃), 0.66 (qd, 8H, *J* = 7.2, 2.2 Hz, SiCH₂CH₃); ¹³C{¹H} NMR (150 MHz, TMS in benzene-*d*₆): δ 136.5, 135.0, 130.7, 128.5, 7.7, 7.1; ²⁹Si{¹H} NMR (119 MHz, TMS in benzene-*d*₆): δ 2.3 (SiH), -44.3 (SiPh₂); GCMS(EI) *m/z* (relative intensity) 388 (3) [M]⁺, 359 (100), 311 (5), 182 (2), 103 (2), 87 (2), 77 (1); HRMS (EI) calcd for [C₂₀H₃₂O₂Si₃]⁺ [M]⁺ 388.1705, found 388.1703.

Synthesis of **7ib**



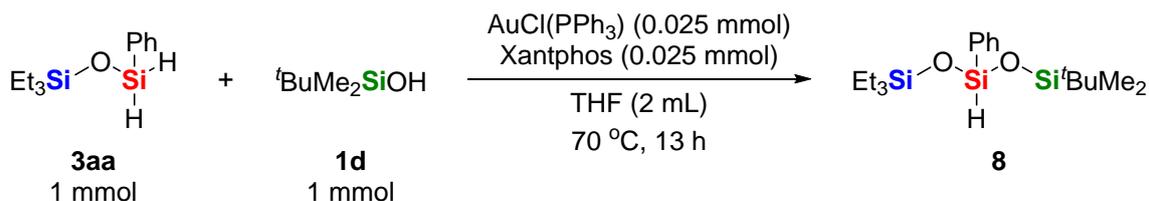
Compound **7ib** was synthesized as described for **7aa** from phenylsilanetriol (**1i**) (234 mg, 1.5 mmol), diethylsilane (**6b**) (1.32 g, 15 mmol), $\text{AuCl(PPh}_3\text{)}$ (30 mg, 0.06 mmol) and xantphos (35 mg, 0.06 mmol). Kugelrohr distillation (1 Torr, oven temperature 160 °C) of the crude mixture afforded **7ib** as a colorless liquid (522 mg, 84% yield). $^1\text{H NMR}$ (600 MHz, benzene- d_6): δ 7.85-7.86 (m, 2H, SiPh), 7.17-7.24 (m, 3H, SiPh), 4.90 (quint, 3H, $J = 2.3$ Hz, $^1J(\text{Si,H}) = 201.6$ Hz, SiH), 1.02 (t, 18H, $J = 8.0$ Hz, SiCH_2CH_3), 0.69 (qd, 12H, $J = 7.9, 2.4$ Hz, SiCH_2CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, benzene- d_6): δ 134.8, 134.6, 130.7, 128.5, 7.6, 7.1; $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, benzene- d_6): δ 1.1 (SiH), -76.1 (SiPh); GCMS (EI) m/z (relative intensity) 414 (11) $[\text{M}]^+$, 385 (63), 297 (100), 121 (6), 103 (2), 87 (26), 77 (2); HRMS (EI) calcd for $[\text{C}_{18}\text{H}_{38}\text{O}_3\text{Si}_4]^+$ $[\text{M}]^+$ 414.1893, found 414.1892.

2-4. Synthesis of **3aa** in a large scale



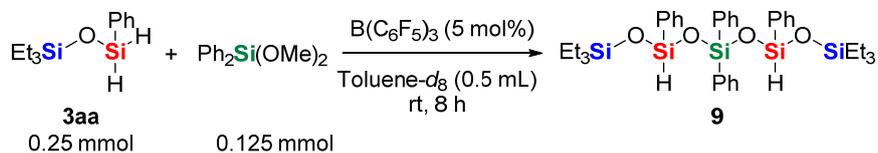
A mixture of triethylsilanol (**1a**) (2.65 g, 20.0 mmol), phenylsilane (**2a**) (2.16 g, 20.0 mmol), $\text{AuCl(PPh}_3\text{)}$ (99 mg, 0.2 mmol), P^nOct_3 (222 mg, 0.6 mmol), and THF (40 mL) was stirred for 36 h at room temperature under Ar. Then, the solvent was evaporated and the residue was purified by Kugelrohr distillation (1 Torr, oven temperature 130 °C) to give **3aa** as a colorless liquid (4.02 g, 85% yield).

2-5. Synthesis of Trisiloxane **8**



Compound **8** was synthesized as described for **7aa** from **3aa** (238 mg, 1.0 mmol), *tert*-butyldimethylsilanol (**1d**) (132 mg, 1.0 mmol), AuCl(PPh₃) (12 mg, 0.025 mmol) and xantphos (15 mg, 0.025 mmol). Kugelrohr distillation (1 Torr, oven temperature 190 °C) of the crude mixture afforded **8** as a colorless liquid (317 mg, 86% yield). ¹H NMR (600 MHz, benzene-*d*₆): δ 7.74-7.75 (m, 2H, SiPh), 7.19-7.24 (m, 3H, SiPh), 5.42 (s, 1H, ¹J(Si,H) = 243.4 Hz, SiH), 1.00 (t, 9H, *J* = 8.0 Hz, SiCH₂CH₃), 0.97 (s, 9H, SiC(CH₃)₃), 0.62 (q, 6H, *J* = 8.0 Hz, SiCH₂CH₃), 0.15 (s, 3H, SiMe), 0.13 (s, 3H, SiMe); ¹³C{¹H} NMR (150 MHz, benzene-*d*₆): δ 137.9, 133.7, 130.8, 128.7, 26.2, 18.8, 7.3, 6.9, -2.5; ²⁹Si{¹H} NMR (119 MHz, benzene-*d*₆): δ 13.8, 13.5, -48.2 (SiH); GCMS (EI) *m/z* (relative intensity) 368 (0) [M]⁺, 353 (2), 339 (14), 311 (100), 237 (2), 115 (1), 57 (1); HRMS (EI) calcd for [C₁₈H₃₆O₂Si₃]⁺ [M]⁺ 414.1893, found 414.1892.

2-6. Synthesis of Pentasiloxane **9**

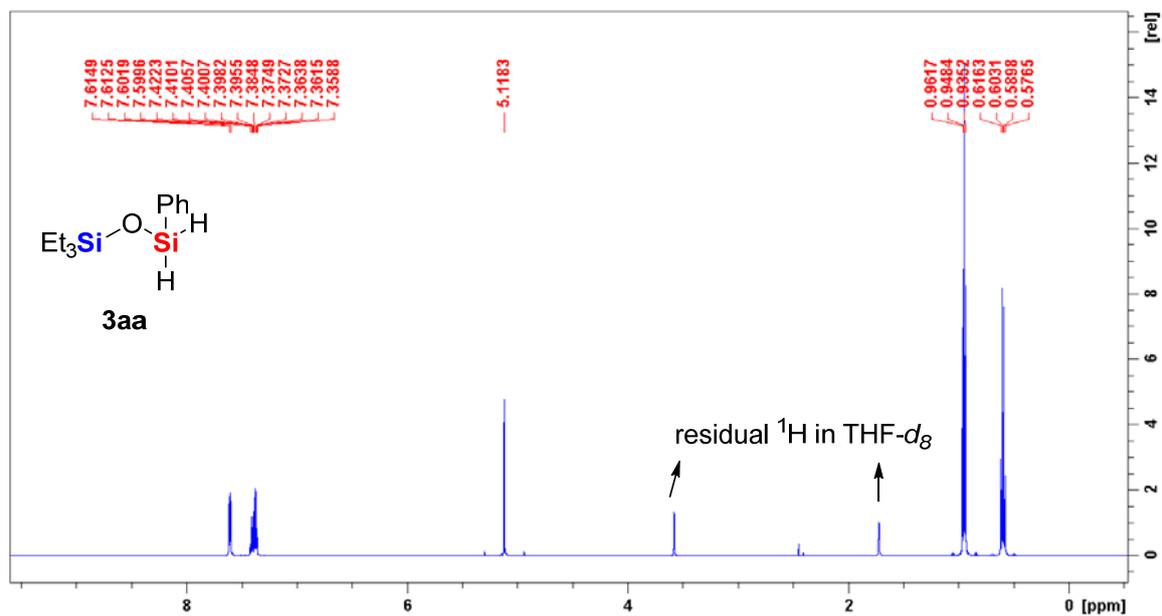


A mixture of dihydrosiloxane **3aa** (60 mg, 0.25 mmol), dimethoxydiphenylsilane (15 mg, 0.125 mmol), B(C₆F₅)₃ (6 mg, 0.0125 mmol), and toluene-*d*₈ (0.5 mL) was stirred for 8 h at room temperature under Ar. After the reaction, trimethylphenylsilane (35 mg) was added to the reaction mixture as an internal standard for NMR analysis. Yield of **9** (96%) was determined by integral values of ¹H NMR signals. ¹H NMR (600 MHz, toluene-*d*₈): δ 7.77-7.81 (m, 4H, SiPh), 7.64-7.66 (m, 4H, SiPh), 7.13-7.18 (m, 12H, SiPh), 5.48 (s, 2H, ¹J(Si,H) = 248 Hz, SiH), 0.91 (t, 18H, *J* = 8.0 HZ, SiCH₂CH₃), 0.53 (q, 12H, *J* = 8.0 HZ, SiCH₂CH₃); ¹³C{¹H} NMR (150 MHz, toluene-*d*₈): δ 137.4, 134.8, 134.7, 133.6, 130.5, 130.4, 128.1, 128.0, 6.9, 6.4; ²⁹Si{¹H} NMR (119 MHz, toluene-*d*₈): δ 14.0 (SiEt₃), -44.6, -48.1; GCMS (EI) *m/z* (relative intensity) 688 (4) [M]⁺, 659 (20), 611 (3), 435 (3), 237 (6), 182 (6), 107 (100), 77 (2); HRMS (EI) calcd for [C₃₄H₄₇O₄Si₅]⁺ [M-Et]⁺ 659.2315, found 659.2309. Attempted isolation of **9** by silica gel column chromatography was not successful due to the instability of **9** toward silica gel.

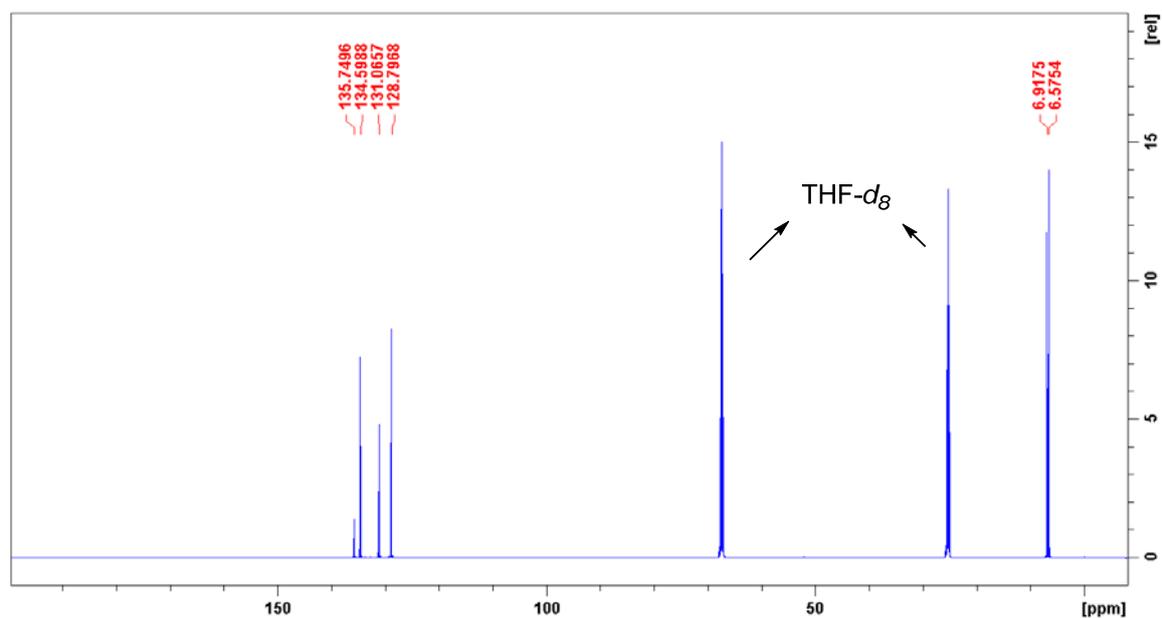
3. NMR Spectra

^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 3aa.

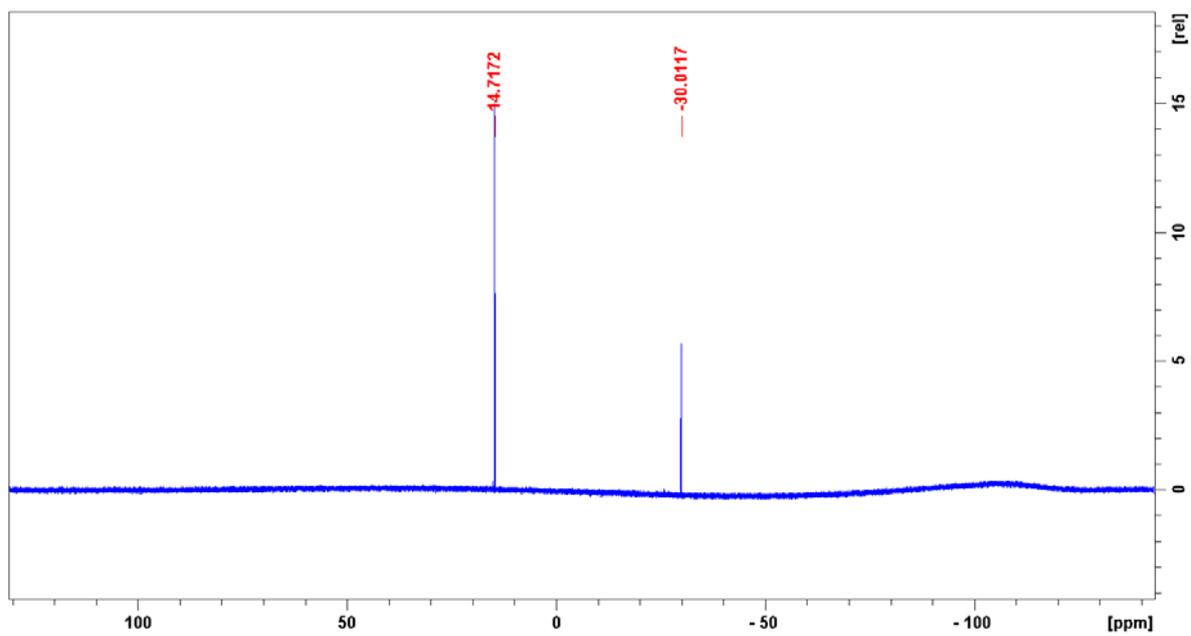
^1H NMR (THF- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8)

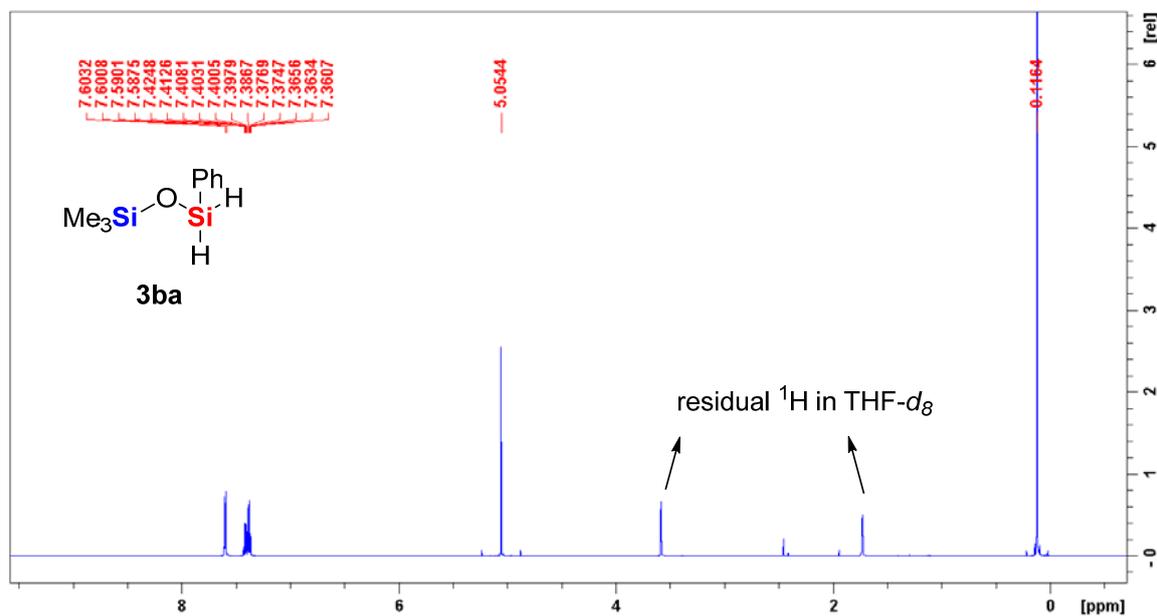


$^{29}\text{Si}\{^1\text{H}\}$ NMR (THF- d_8)

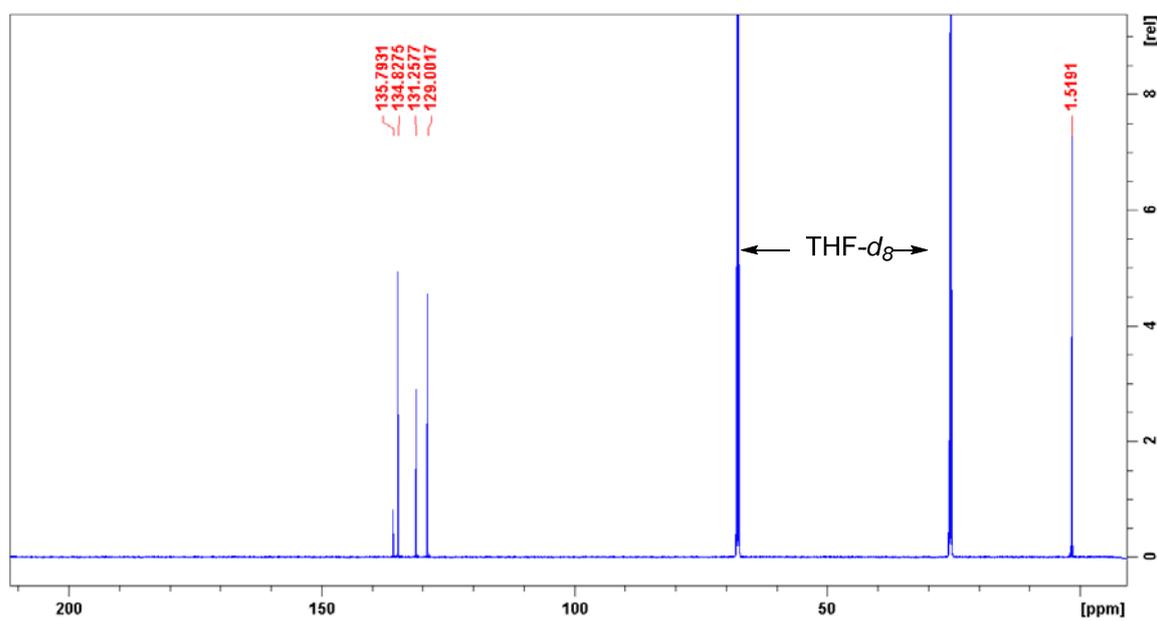


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 3ba.

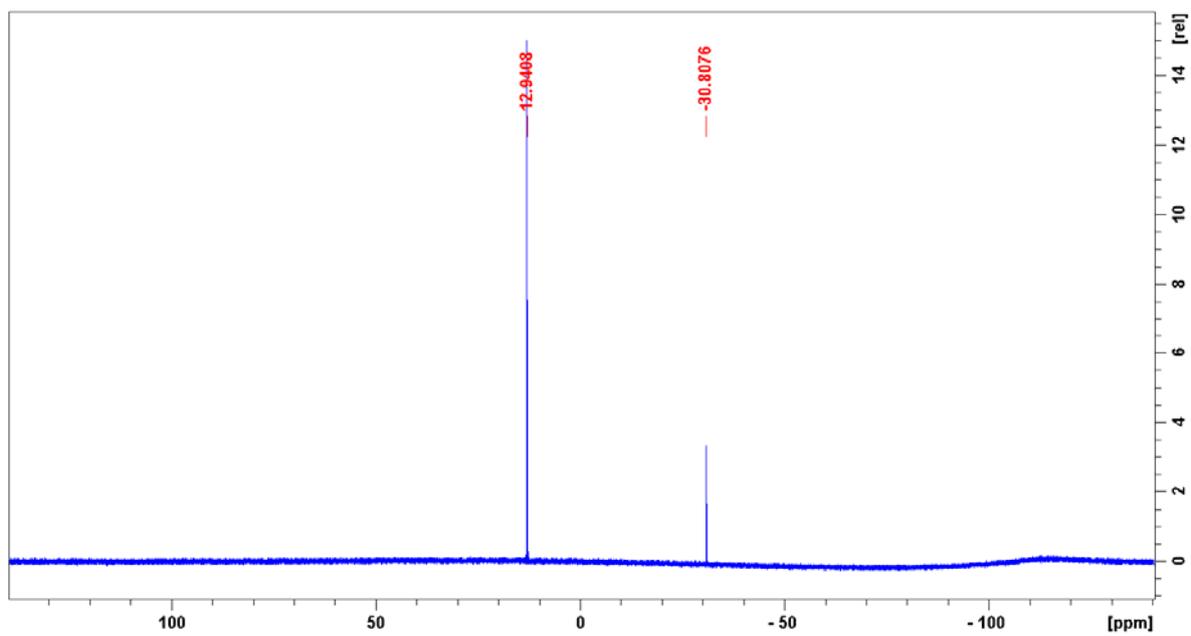
^1H NMR (THF- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8)

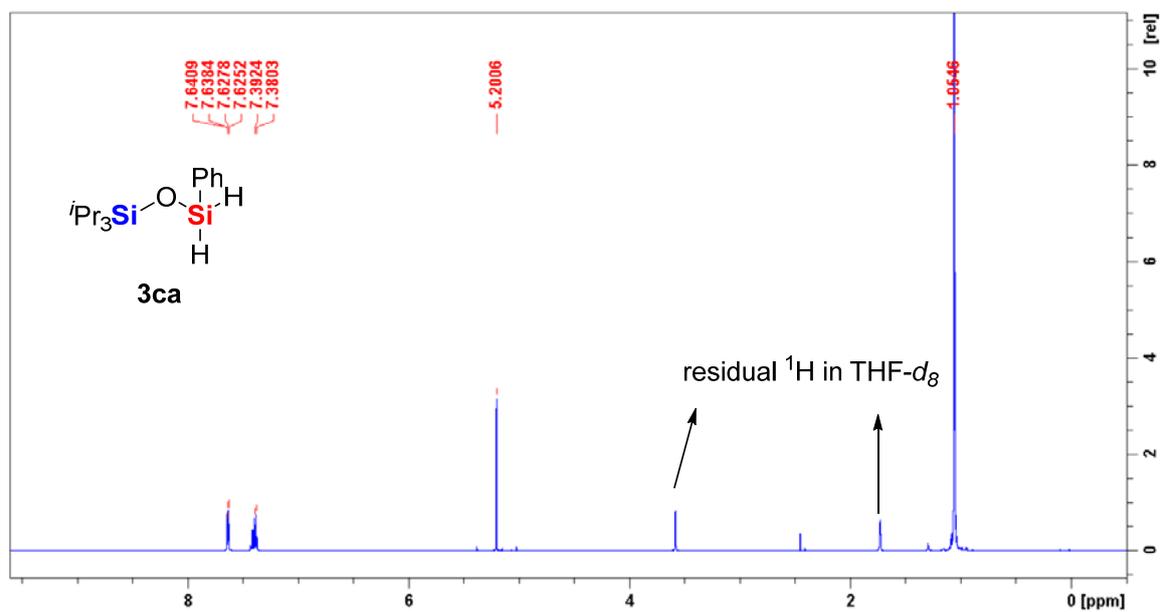


$^{29}\text{Si}\{^1\text{H}\}$ NMR (THF- d_8)

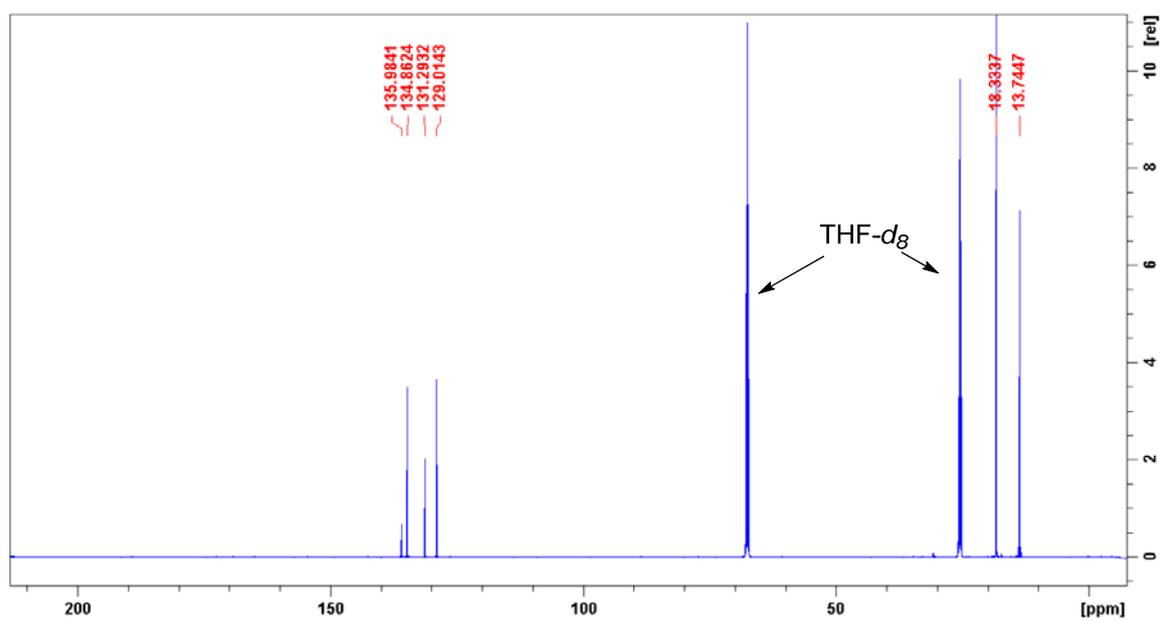


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 3ca.

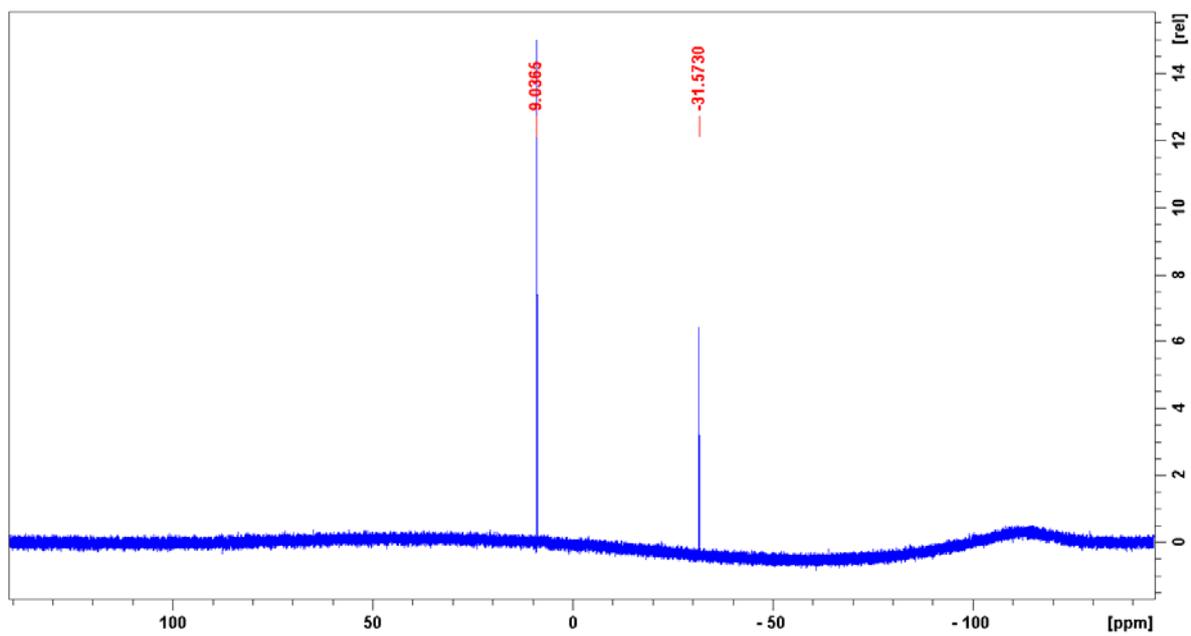
^1H NMR (THF- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8)

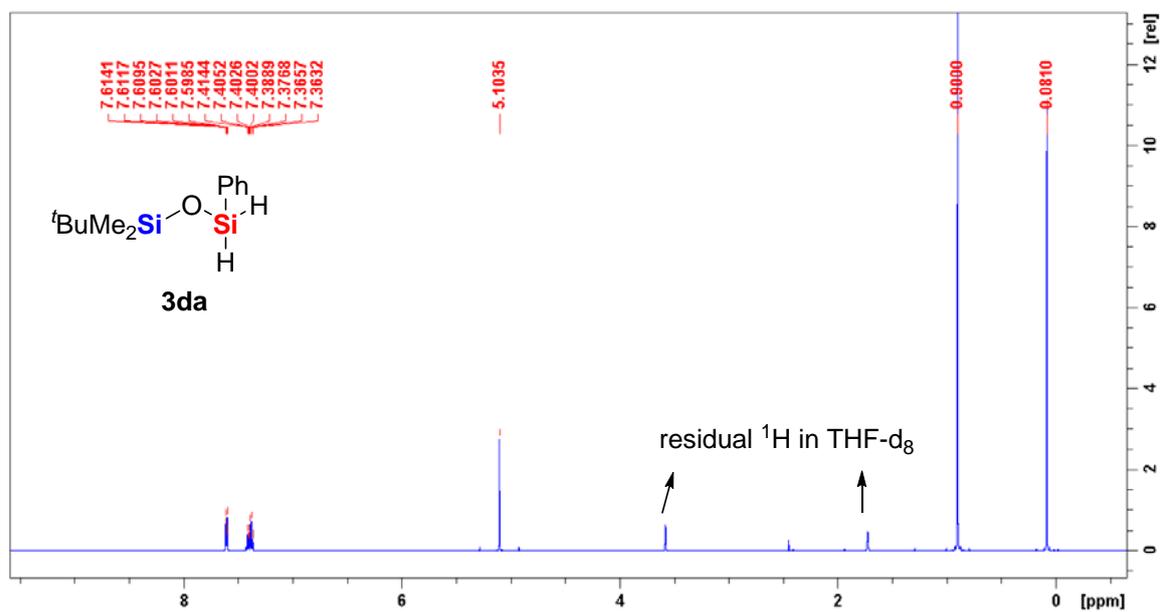


$^{29}\text{Si}\{^1\text{H}\}$ NMR (THF- d_8)

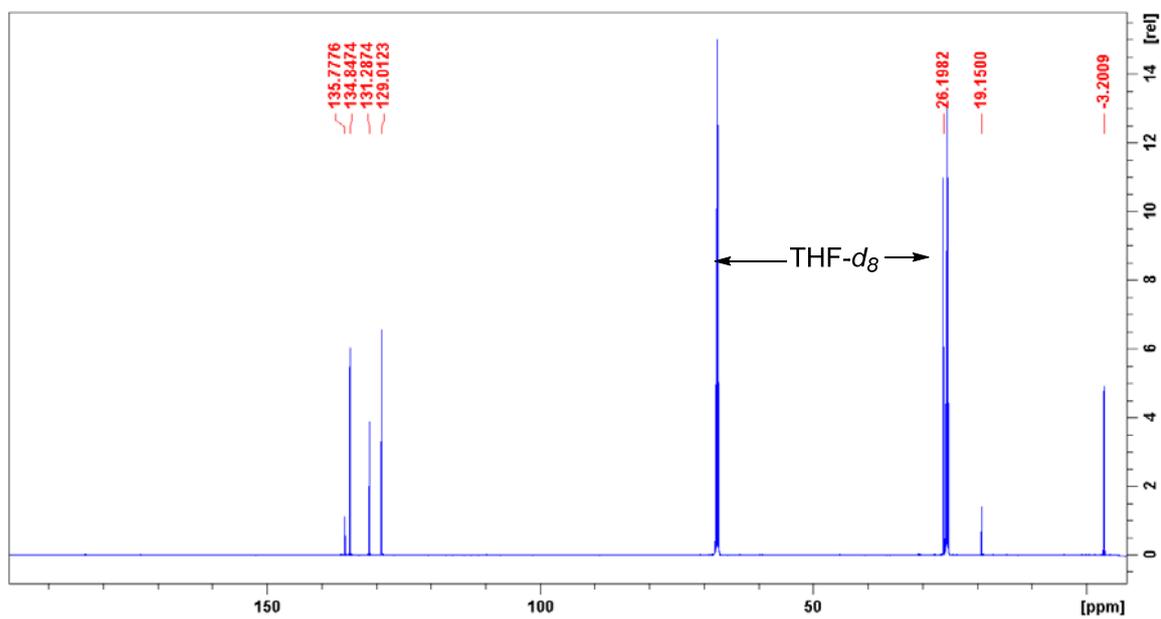


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 3da.

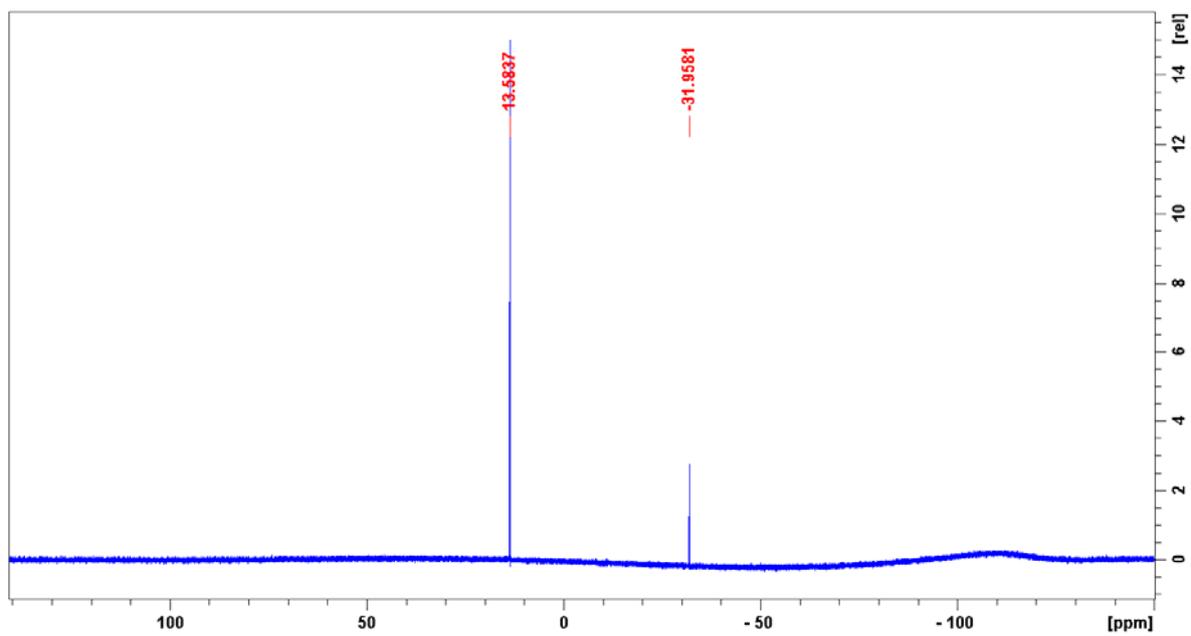
^1H NMR (THF- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8)

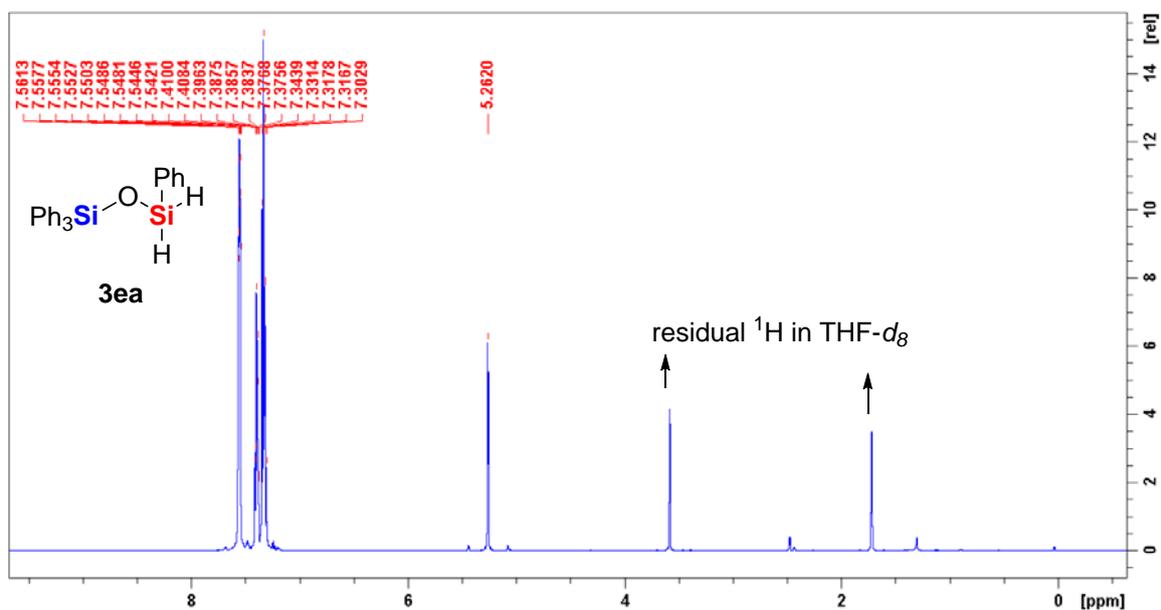


$^{29}\text{Si}\{^1\text{H}\}$ NMR (THF- d_8)

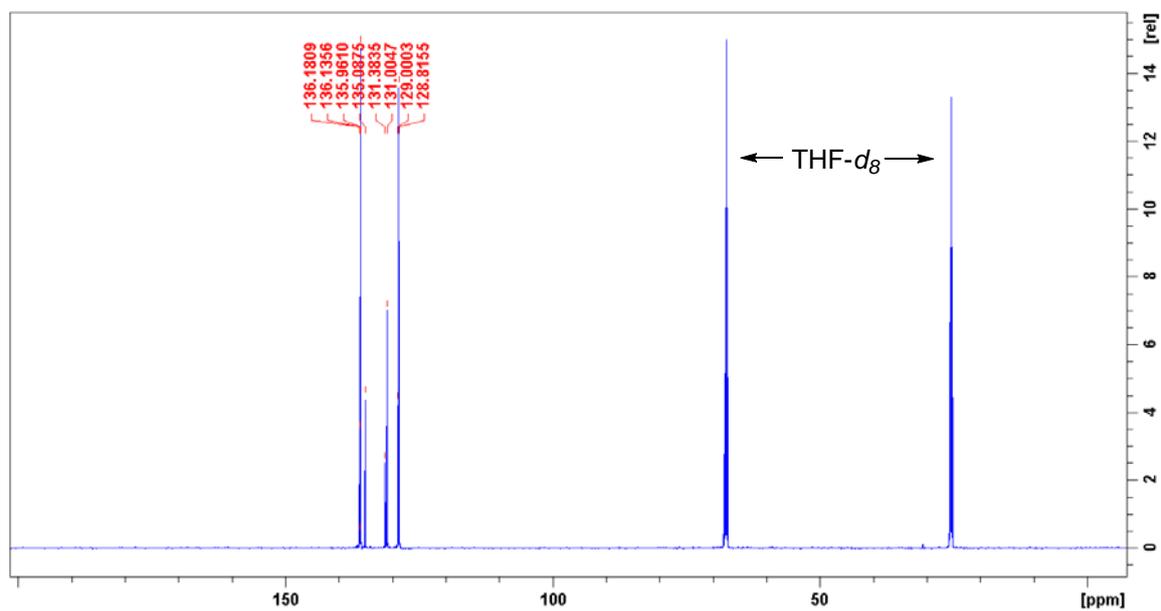


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 3ea.

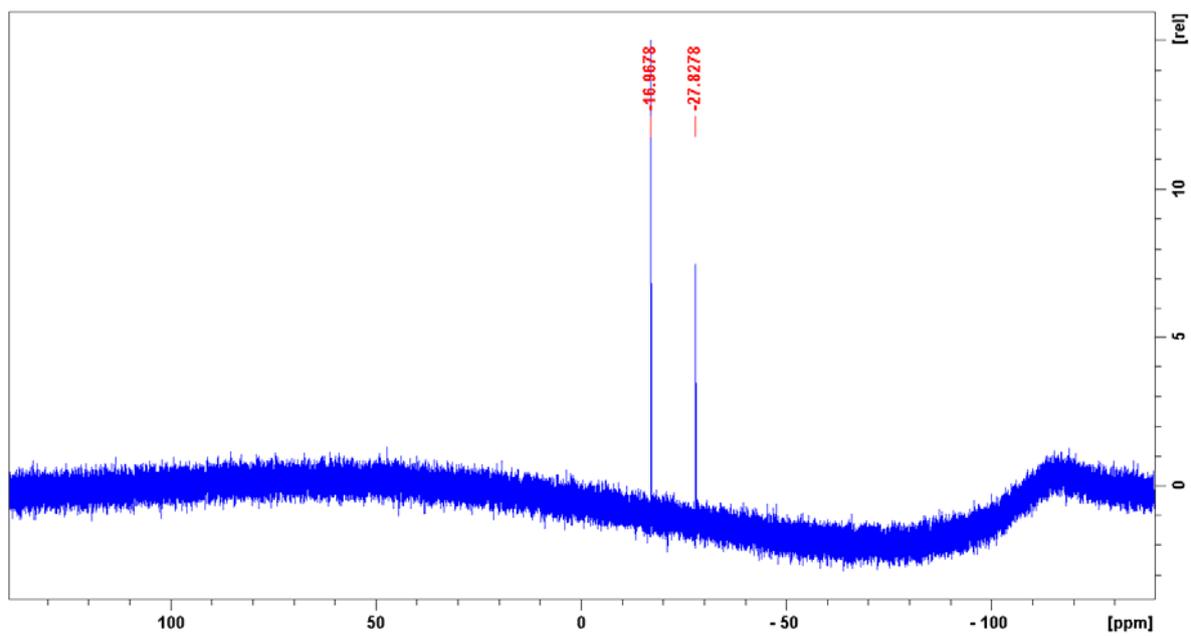
^1H NMR (THF- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8)

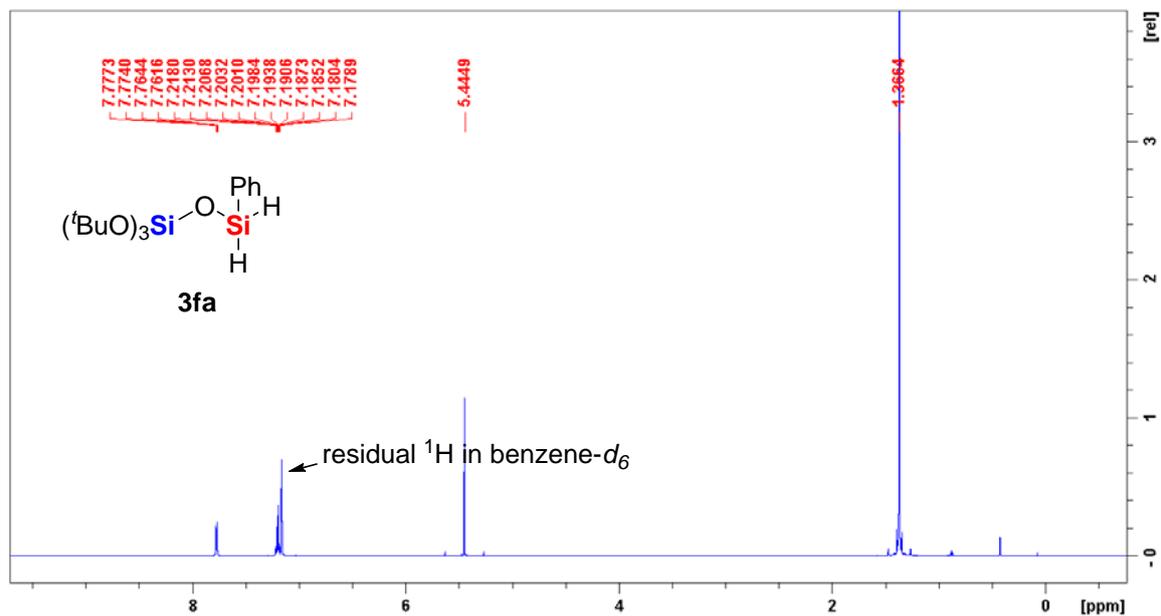


$^{29}\text{Si}\{^1\text{H}\}$ NMR (THF- d_8)

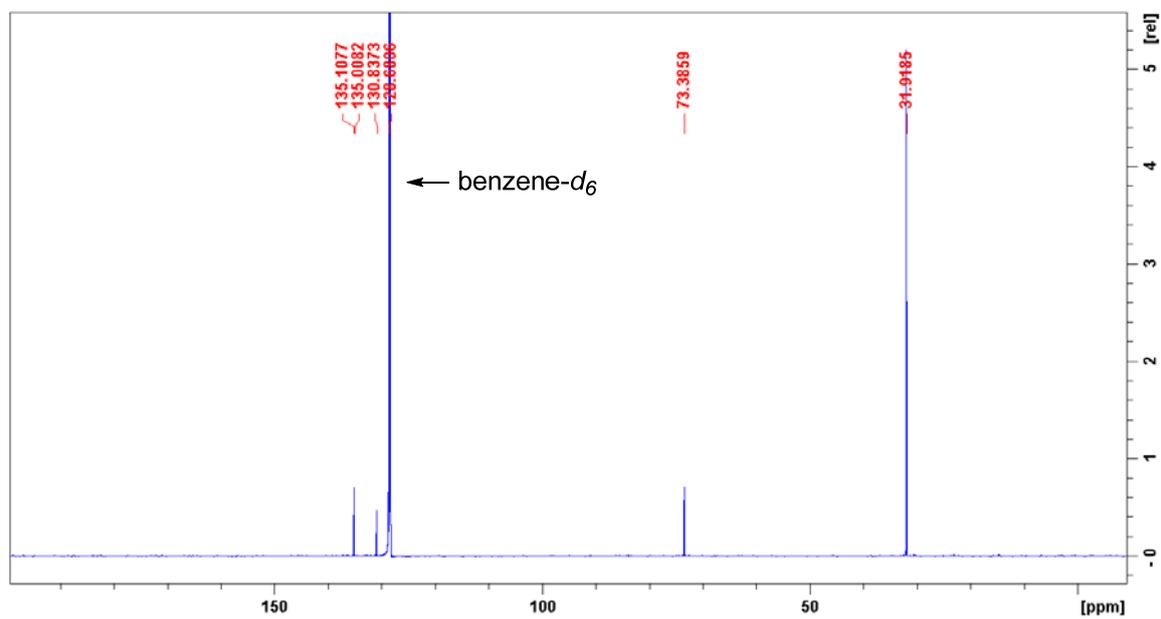


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 3fa.

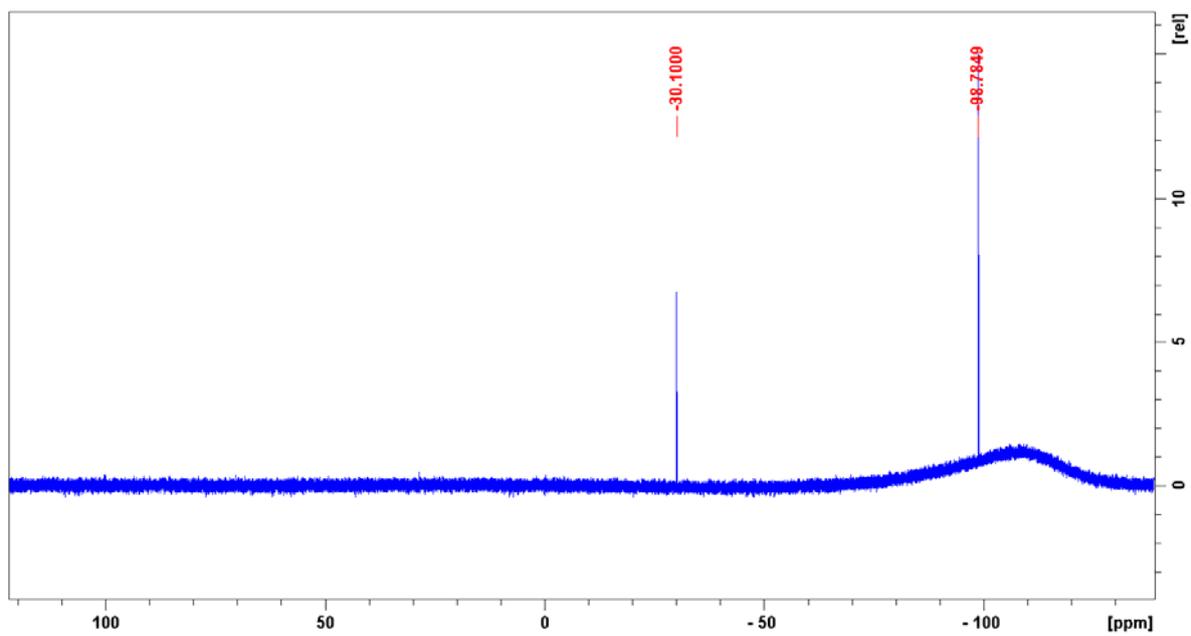
^1H NMR (benzene- d_6)



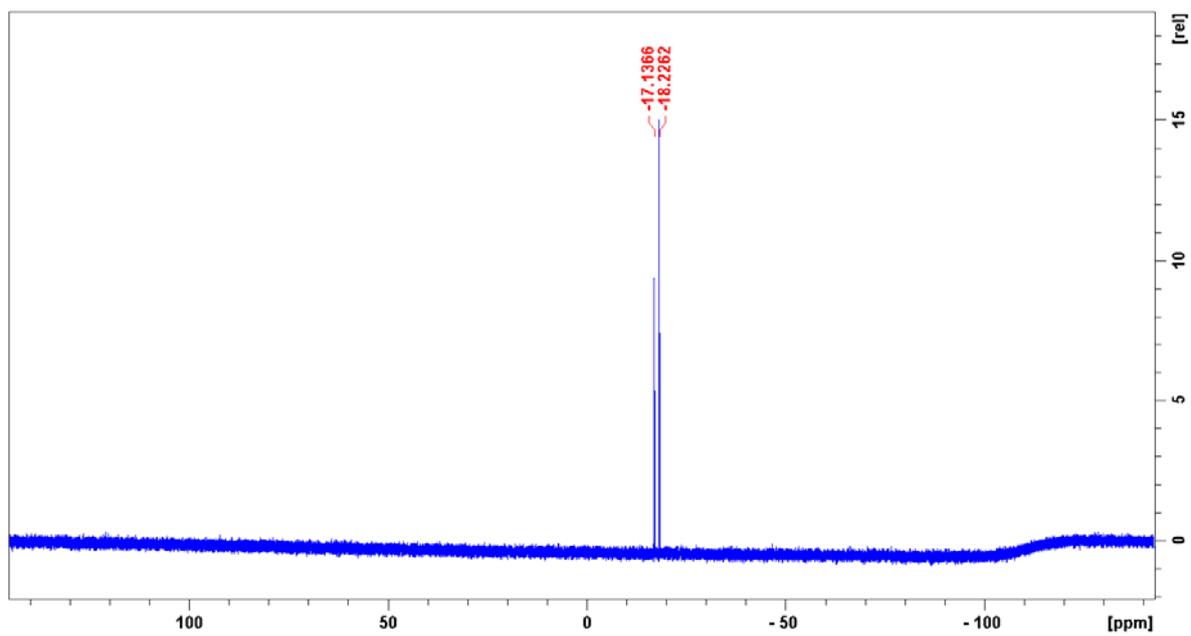
$^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6)



$^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6)

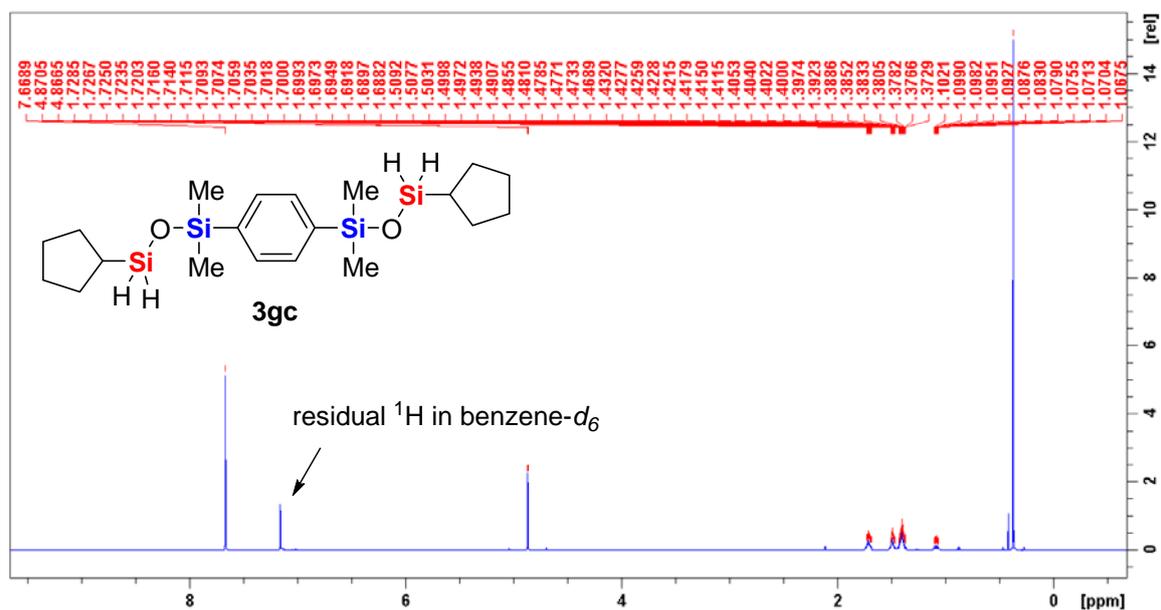


$^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6)

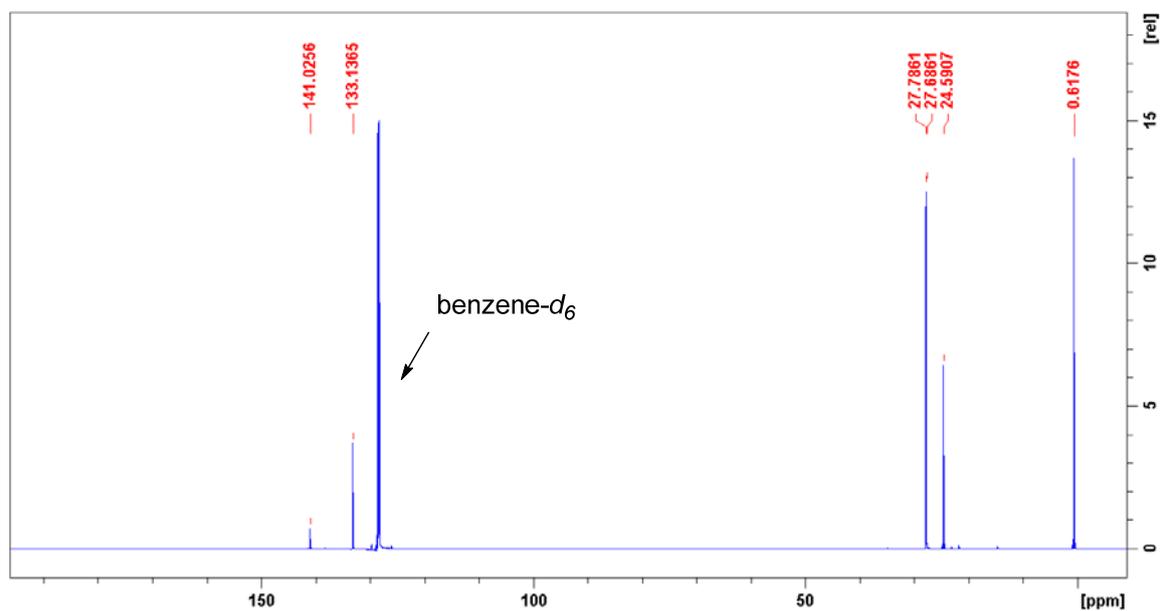


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound **3gc**.

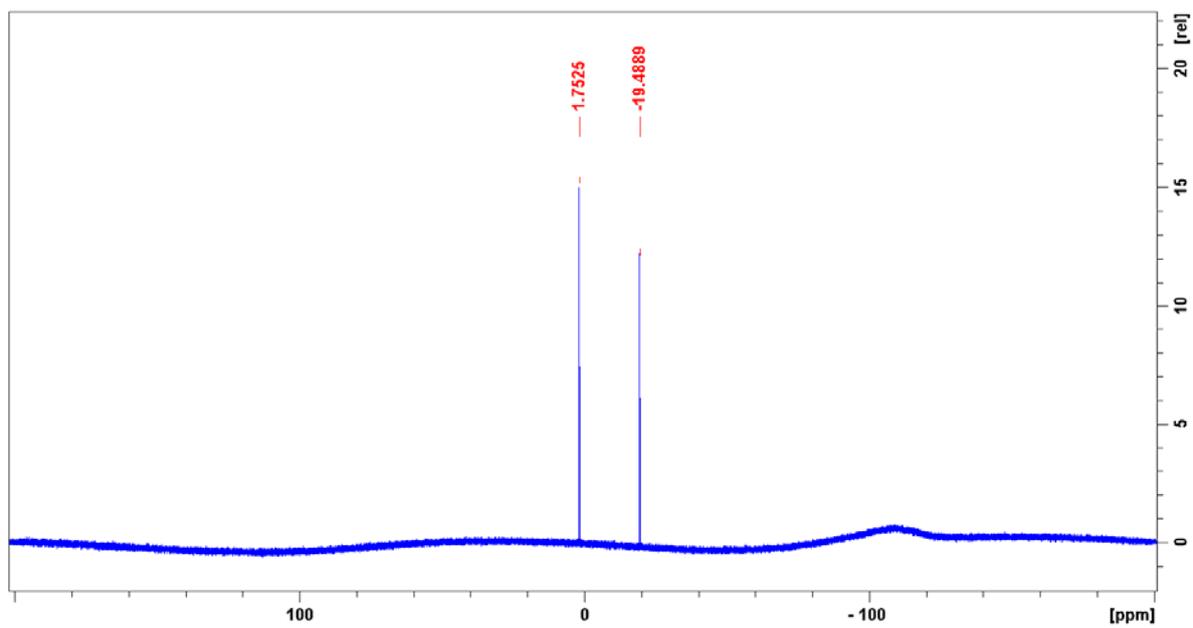
^1H NMR (benzene- d_6)



$^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6)

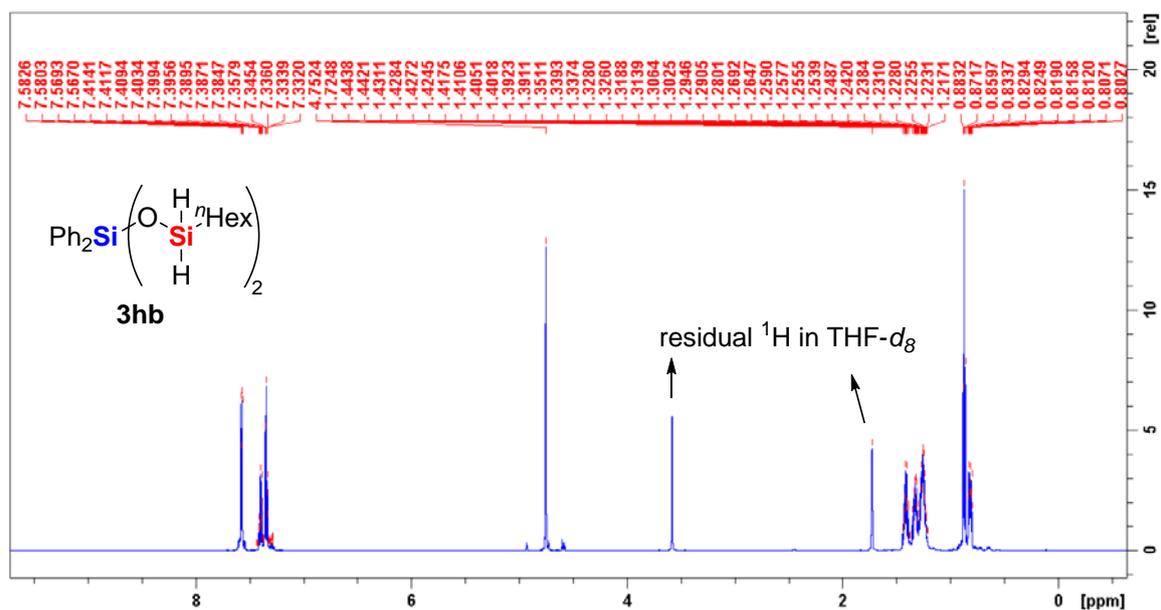


$^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6)

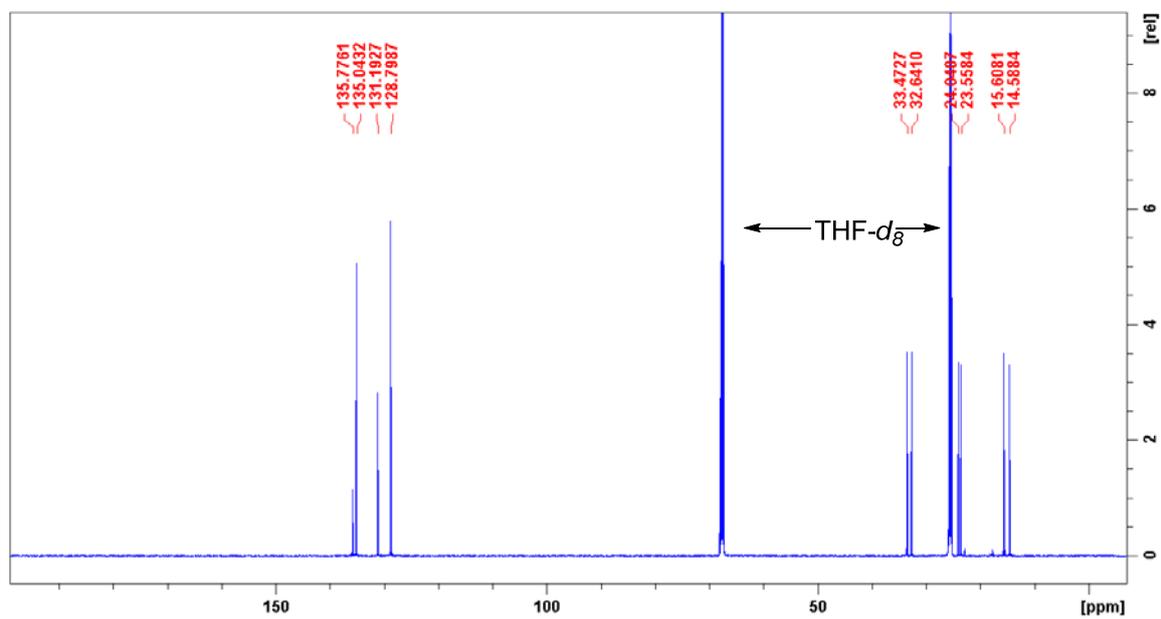


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 3hb.

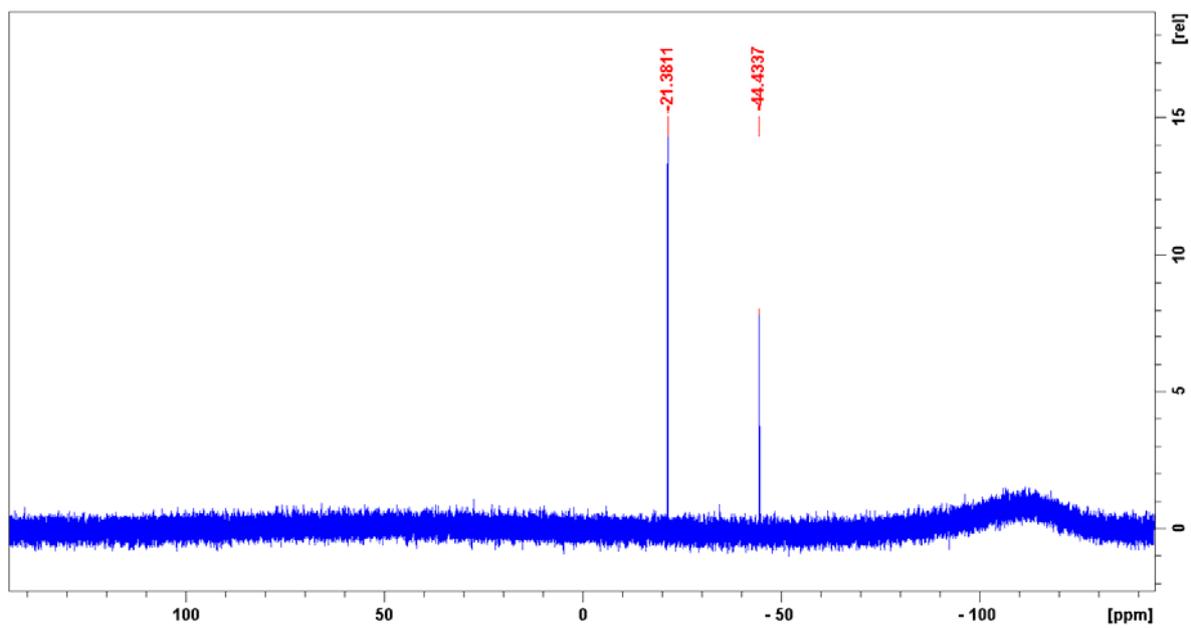
^1H NMR (THF- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8)

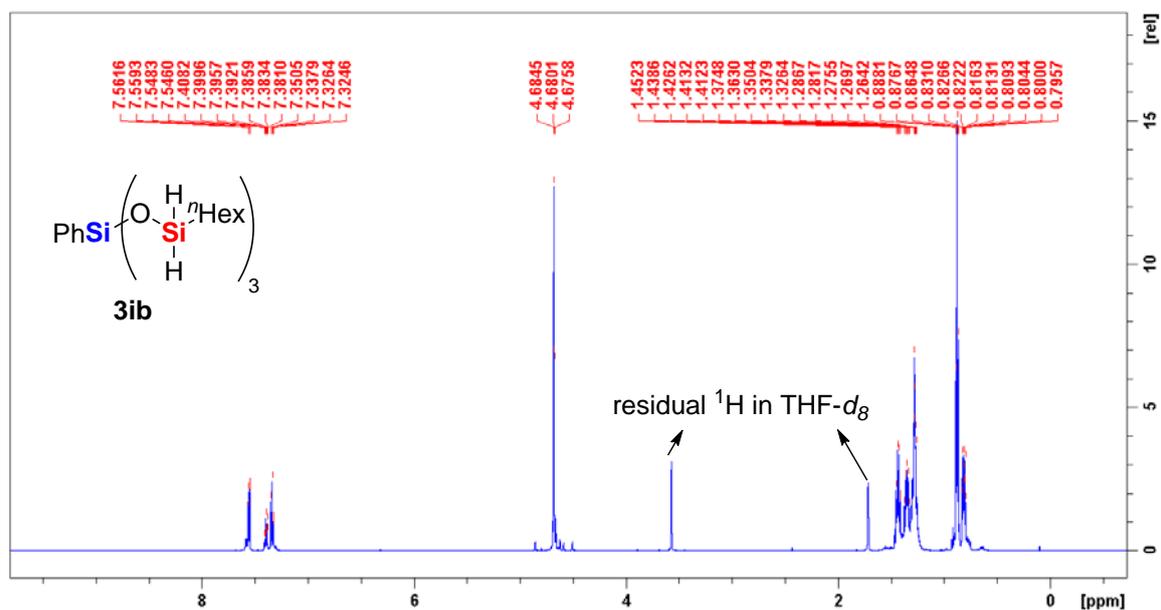


$^{29}\text{Si}\{^1\text{H}\}$ NMR (THF- d_8)

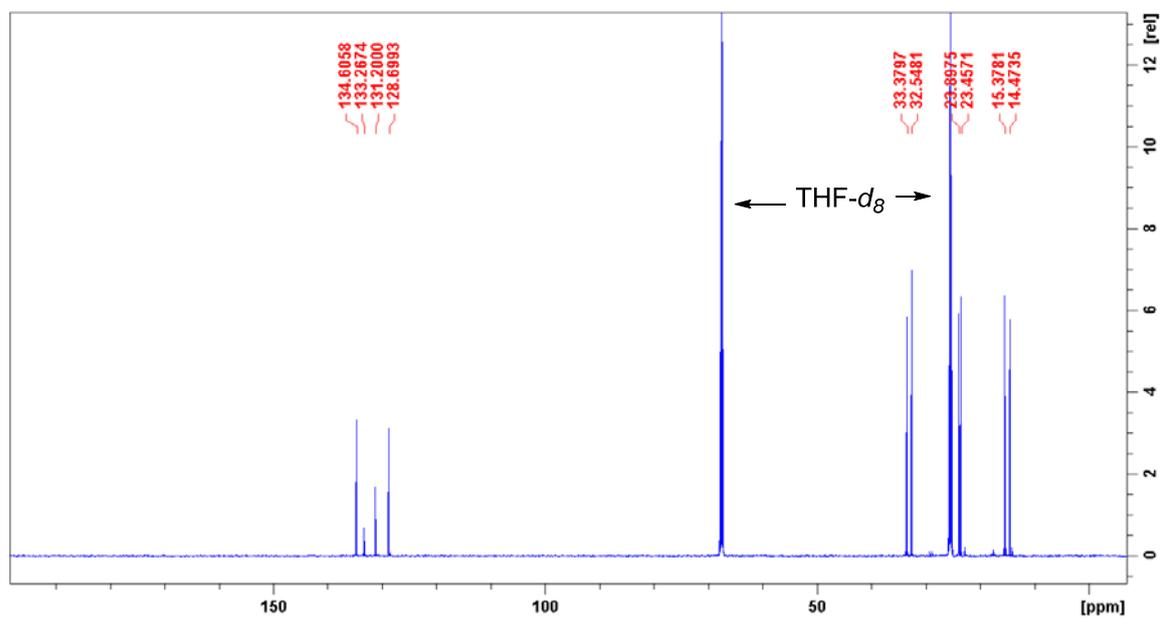


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 3ib.

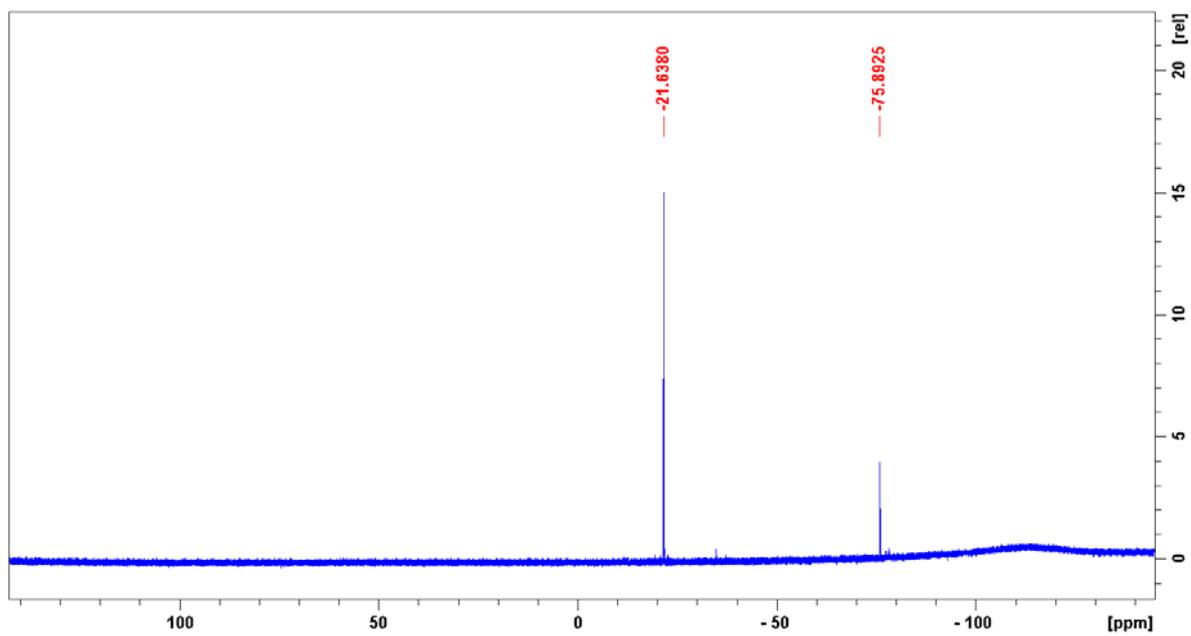
^1H NMR (THF- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8)

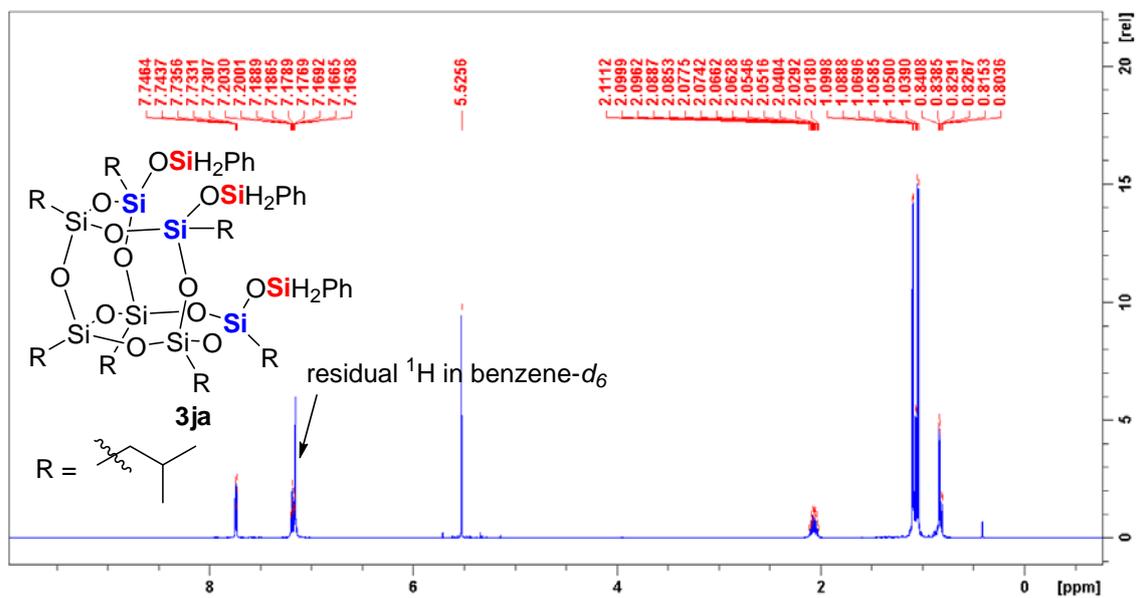


$^{29}\text{Si}\{^1\text{H}\}$ NMR (THF- d_8)

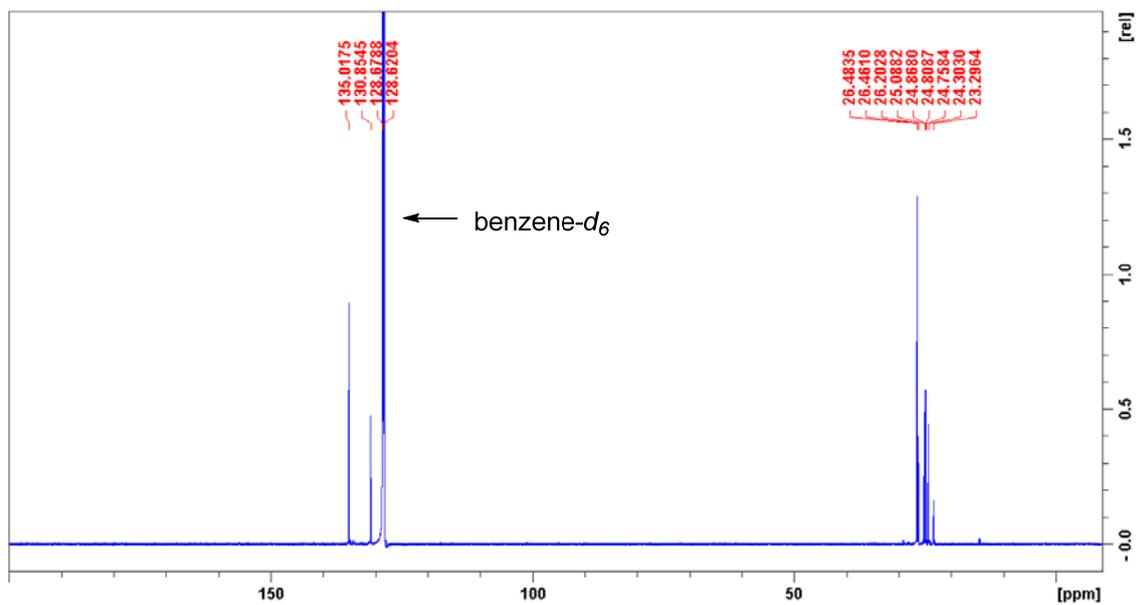


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 3ja.

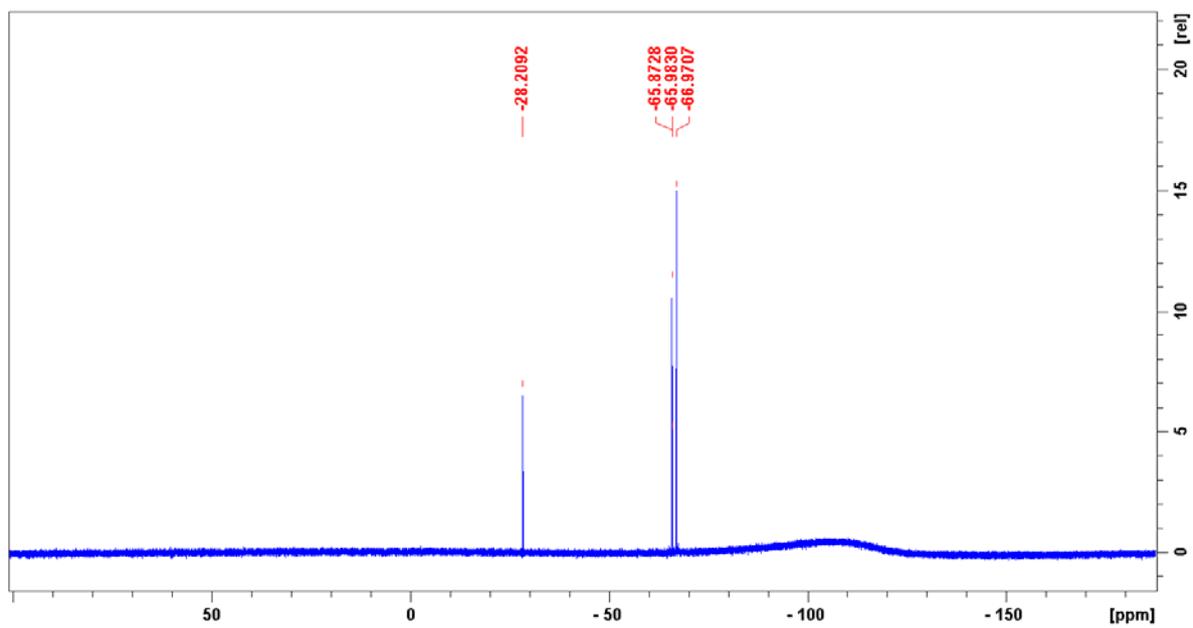
^1H NMR (benzene- d_6)



$^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6)

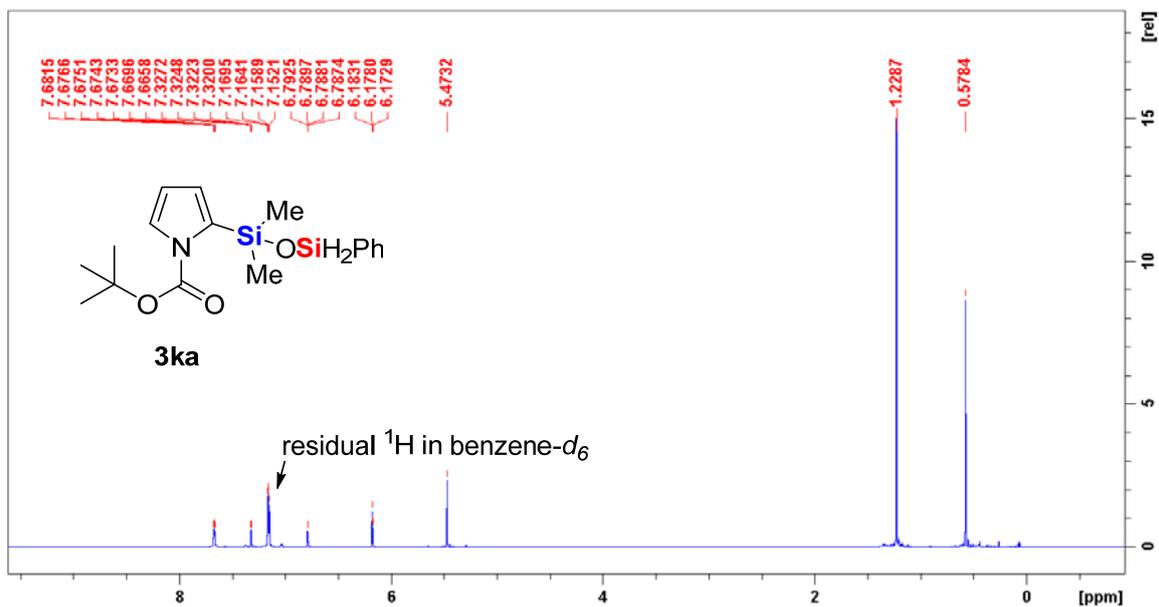


$^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6)

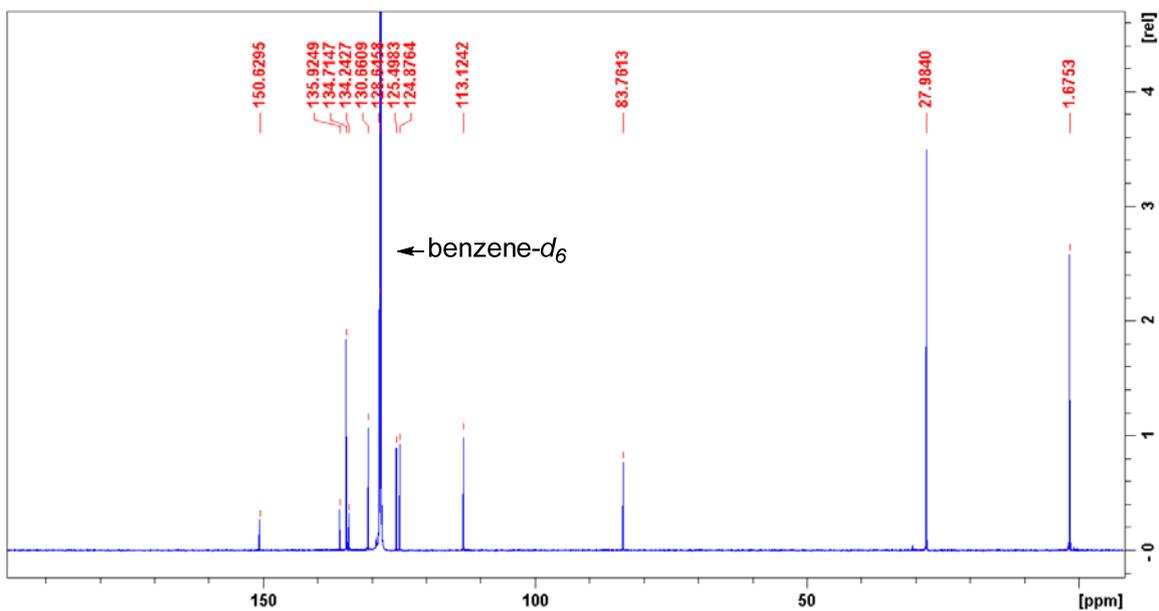


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 3ka.

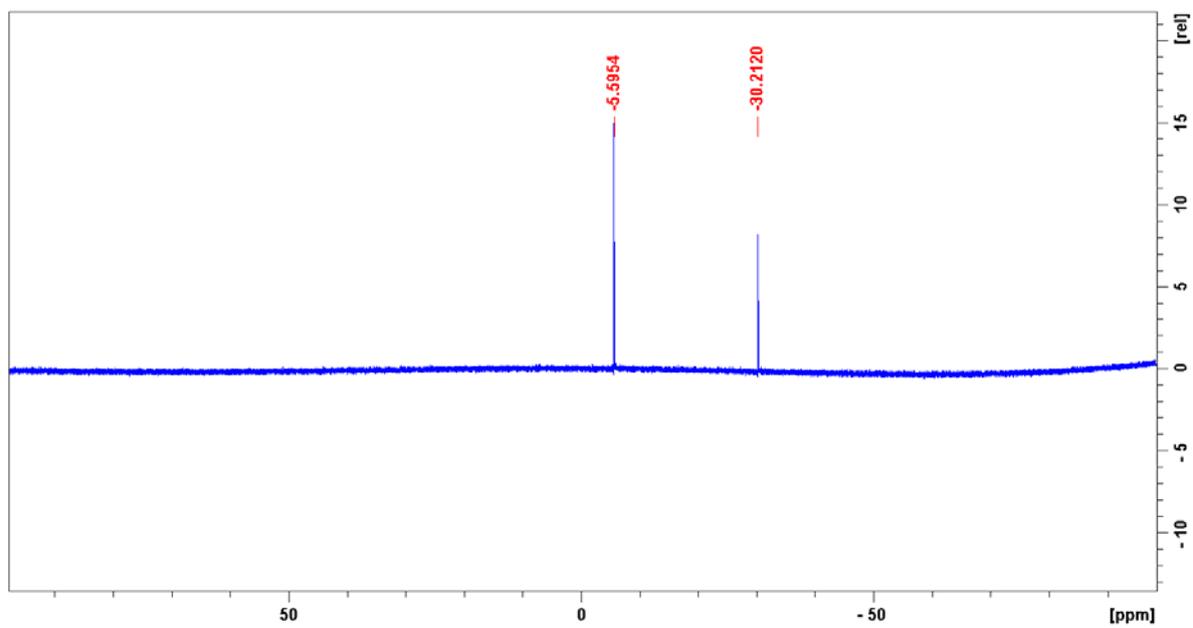
^1H NMR (benzene- d_6)



$^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6)

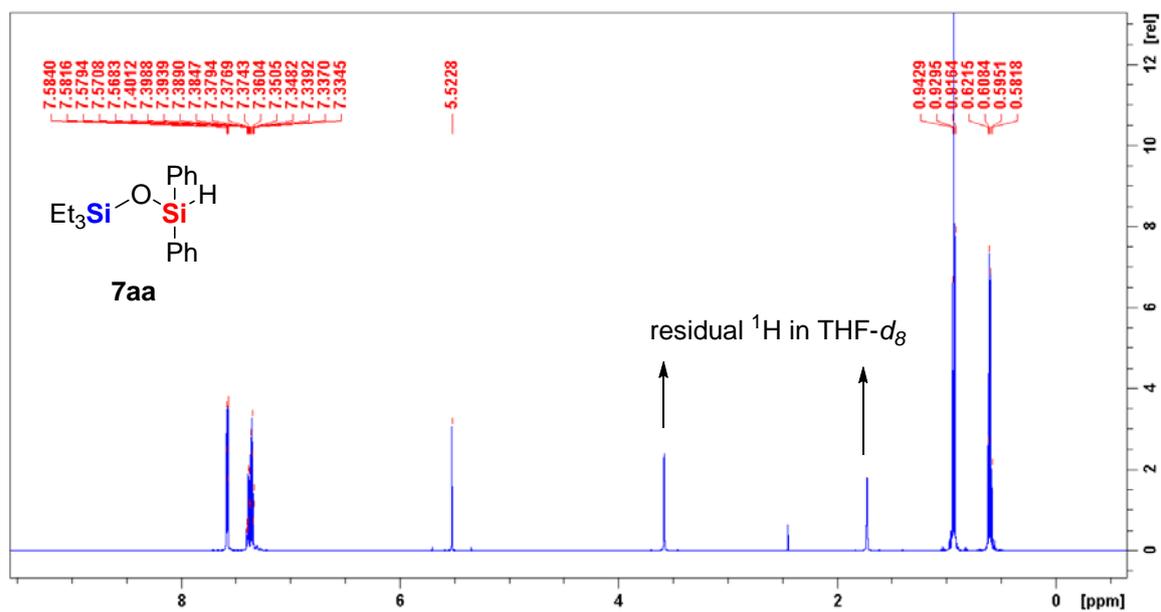


$^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6)

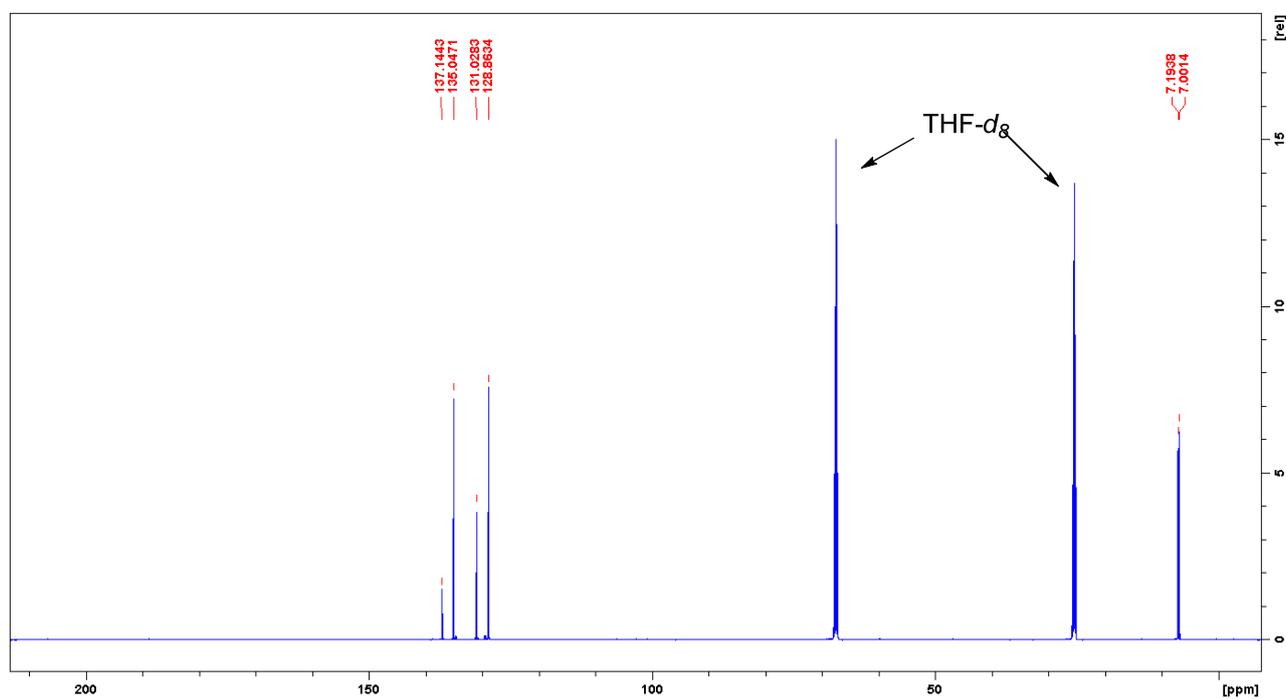


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 7aa.

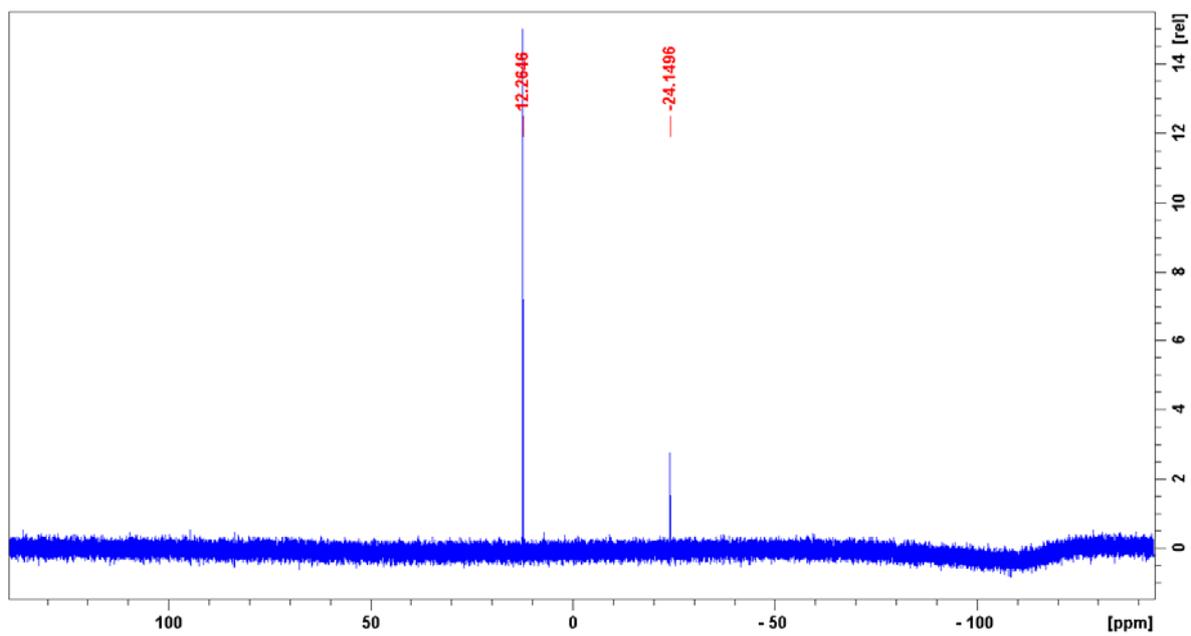
^1H NMR (THF- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8)

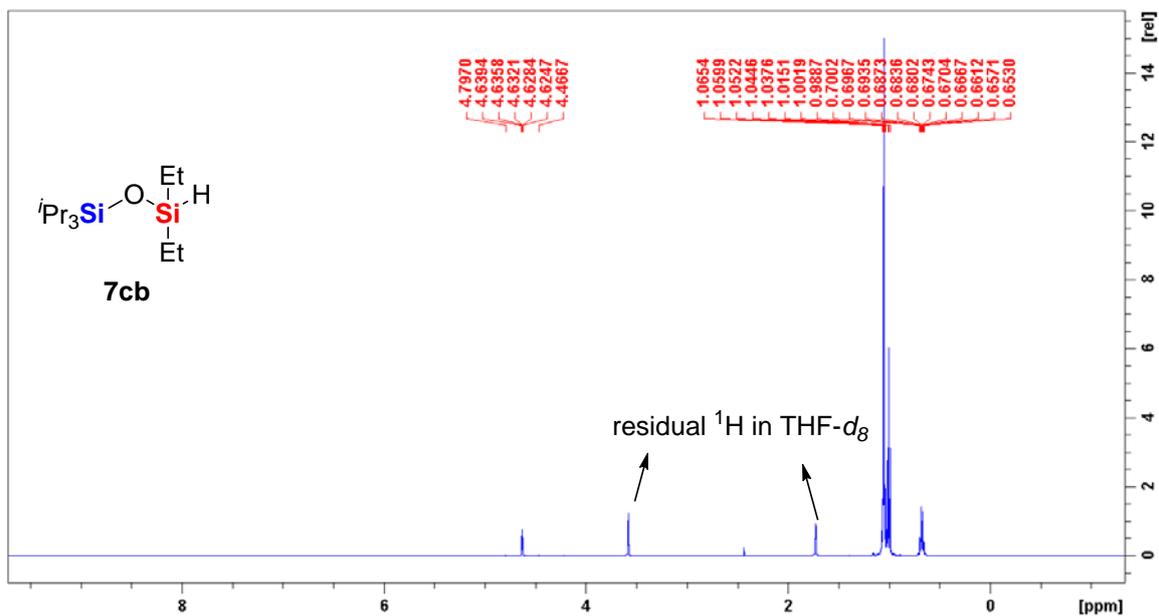


$^{29}\text{Si}\{^1\text{H}\}$ NMR (THF- d_8)

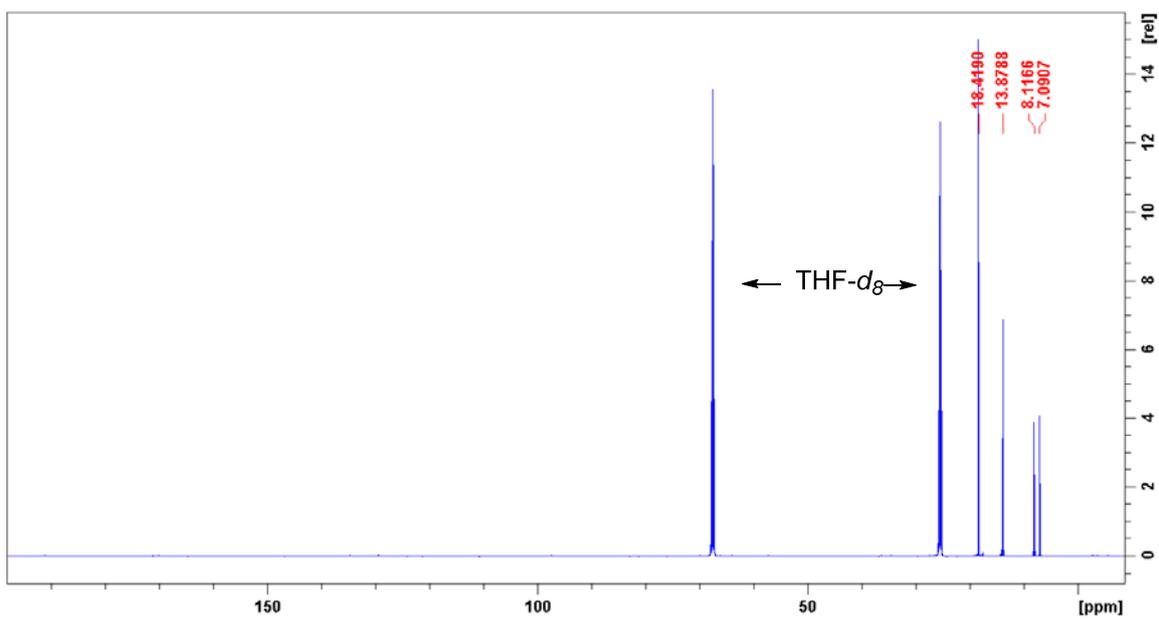


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 7cb.

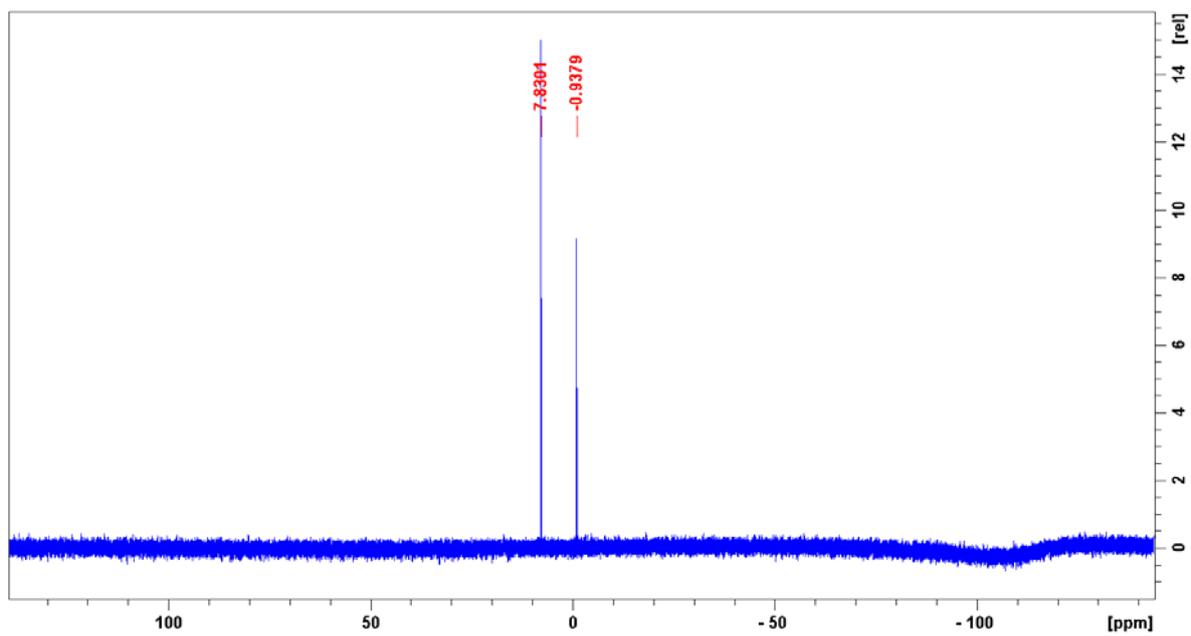
^1H NMR (THF- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8)

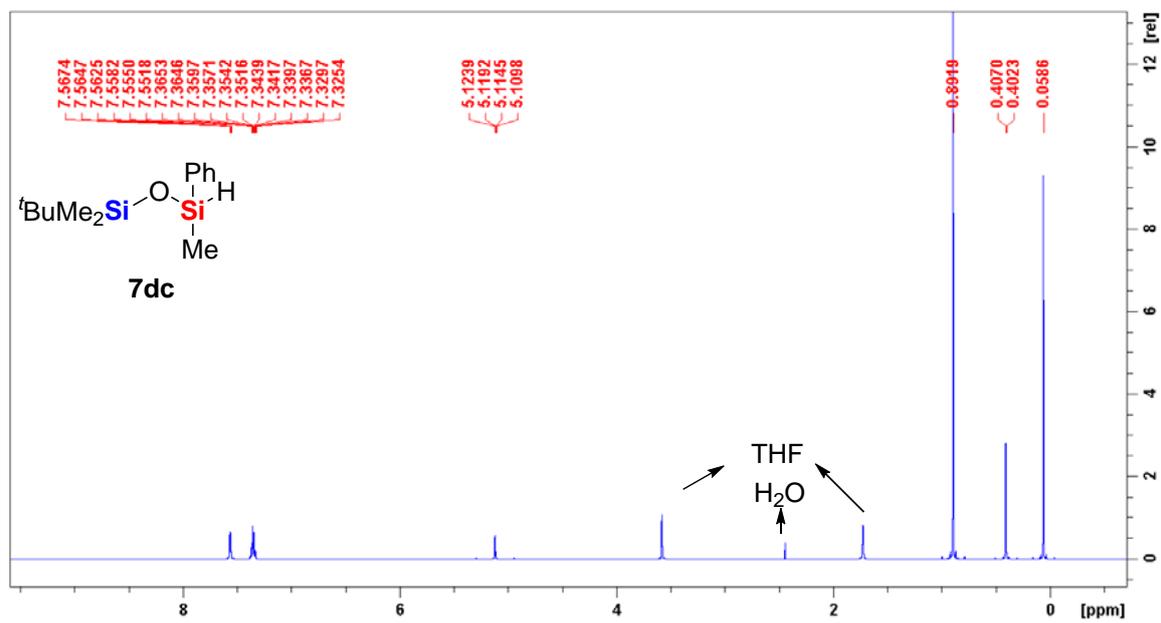


$^{29}\text{Si}\{^1\text{H}\}$ NMR (THF- d_8)

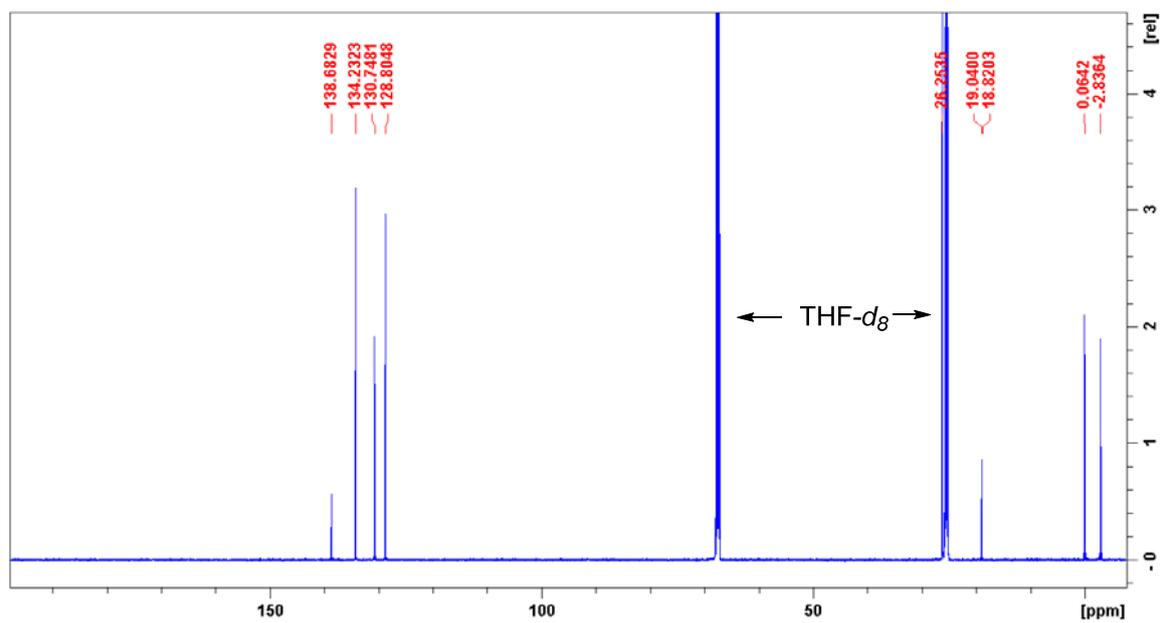


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 7dc.

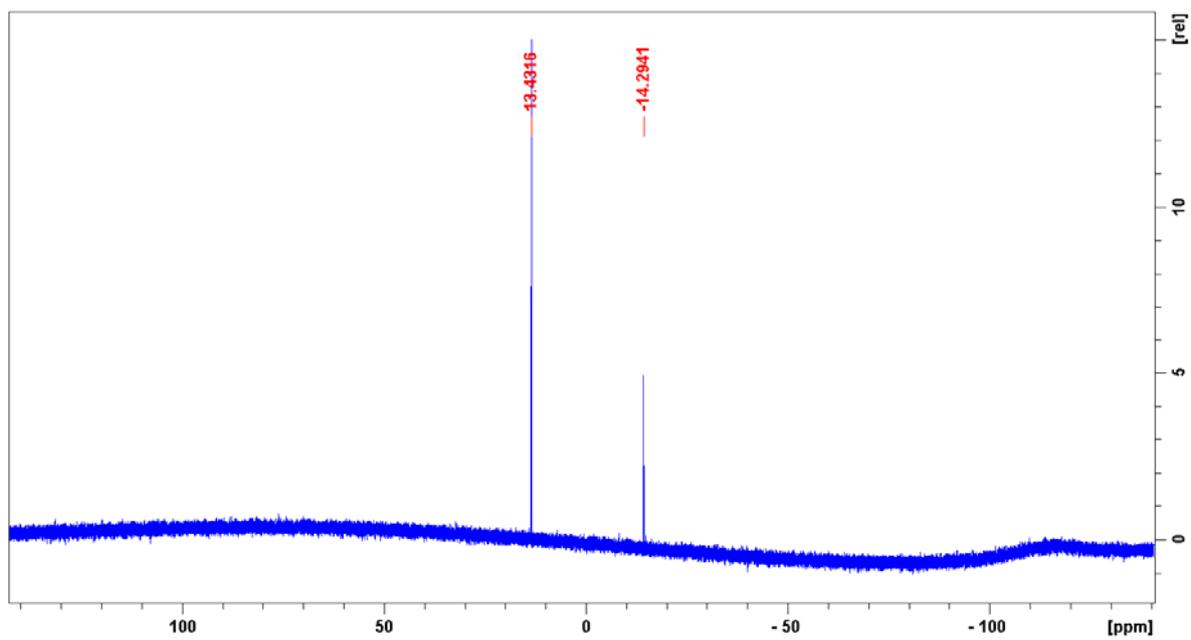
^1H NMR (THF- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8)

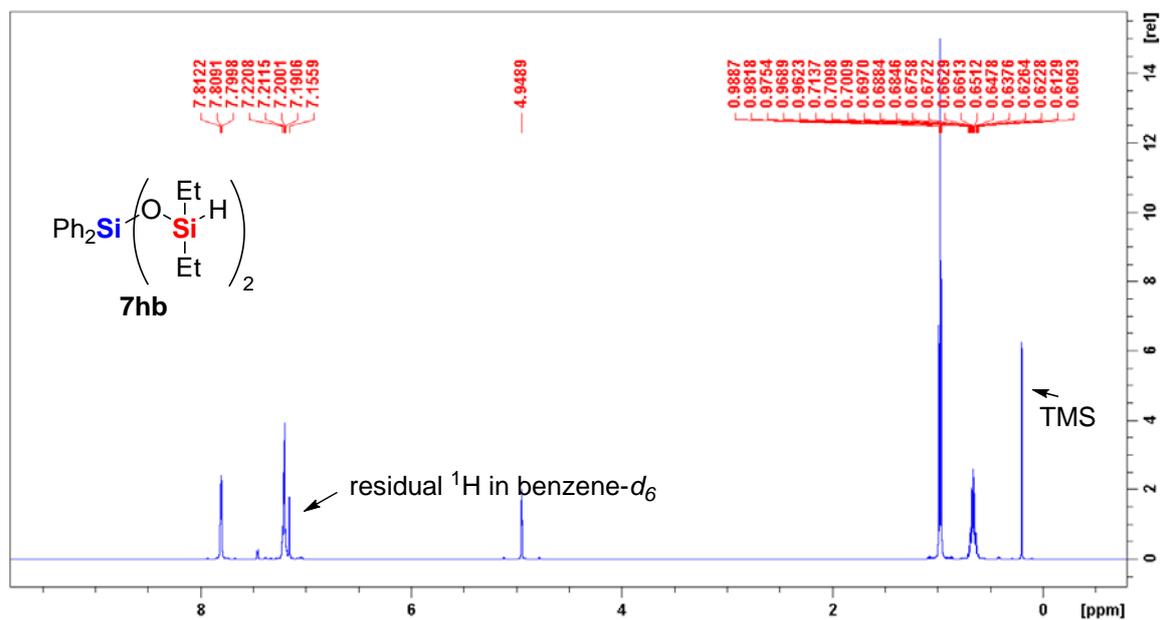


$^{29}\text{Si}\{^1\text{H}\}$ NMR (THF- d_8)

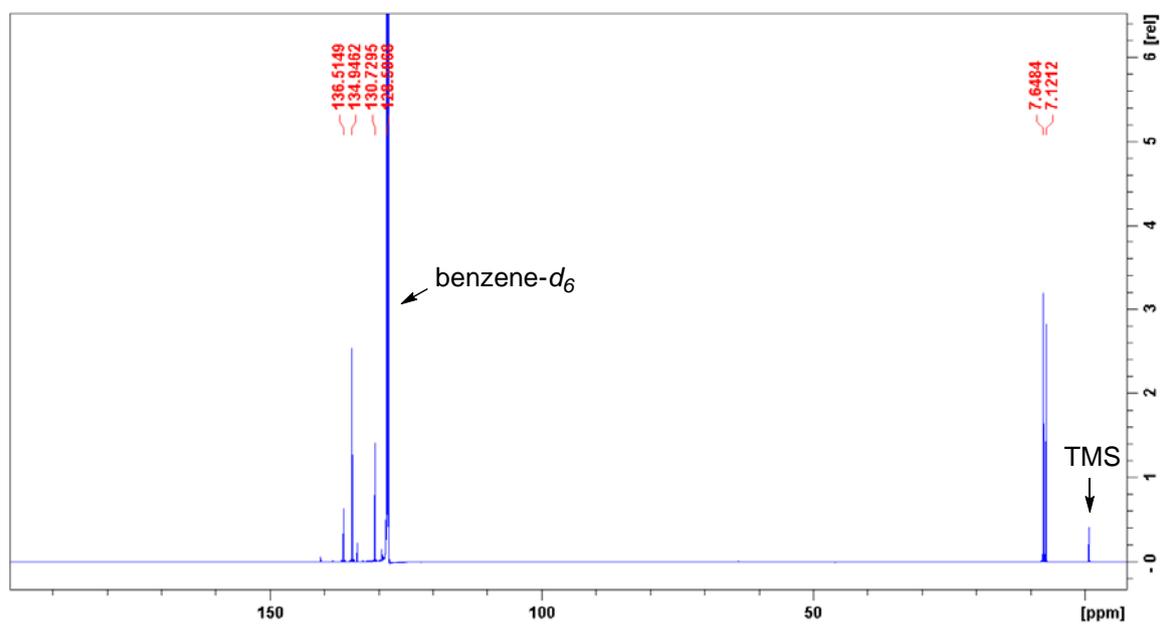


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 7hb.

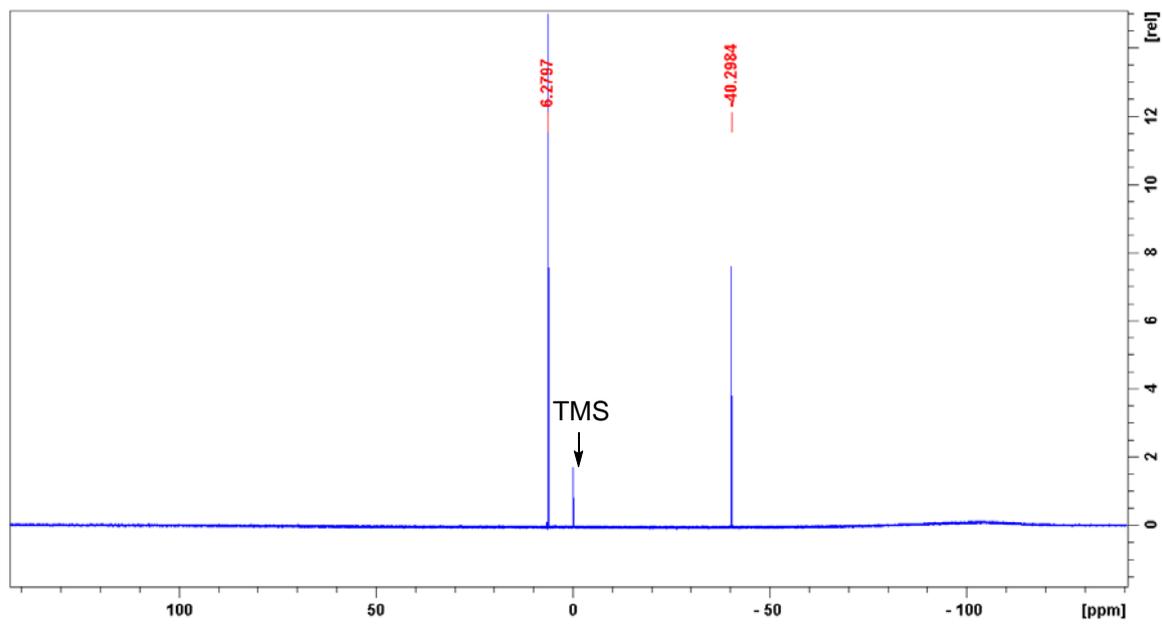
^1H NMR (with TMS in benzene- d_6)



$^{13}\text{C}\{^1\text{H}\}$ NMR (with TMS in benzene- d_6)

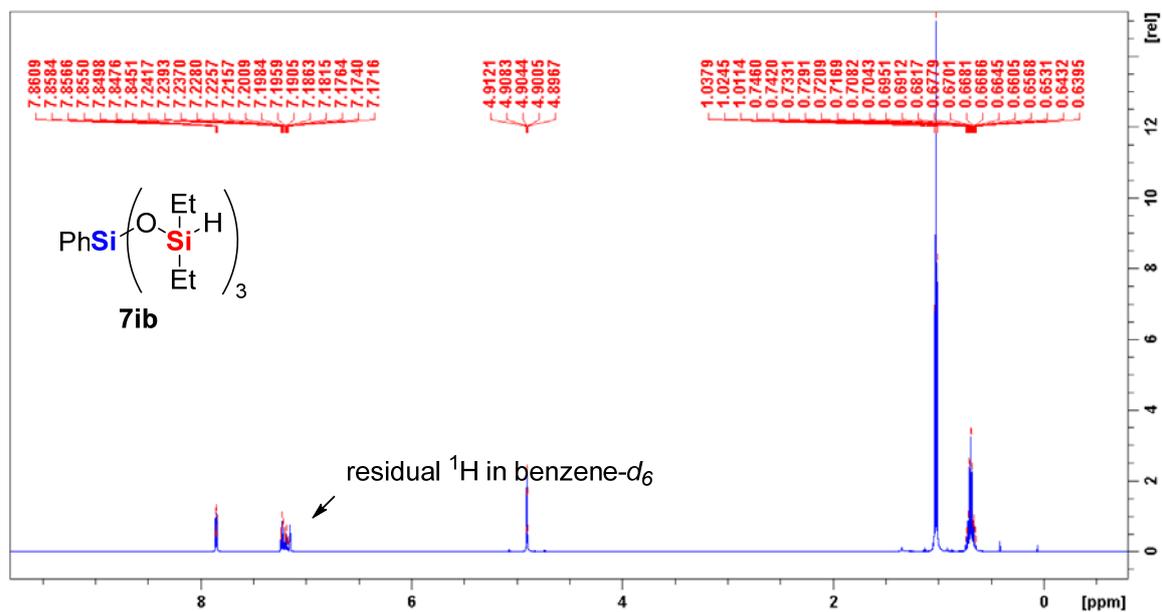


$^{29}\text{Si}\{^1\text{H}\}$ NMR (with TMS in *d*-benzene)

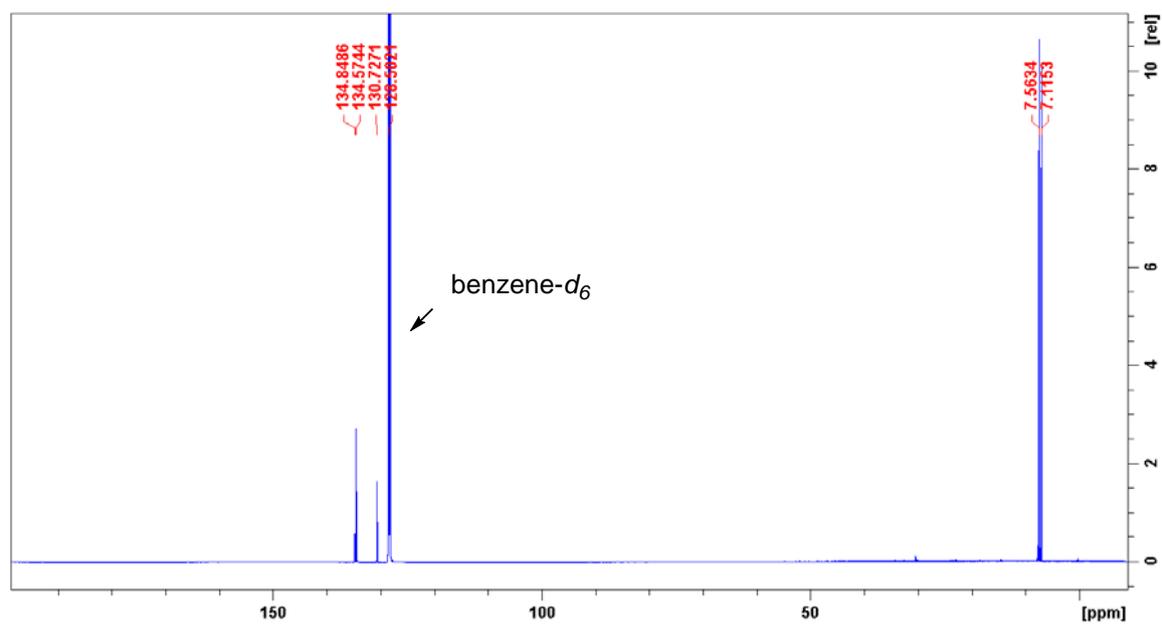


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound **7ib**.

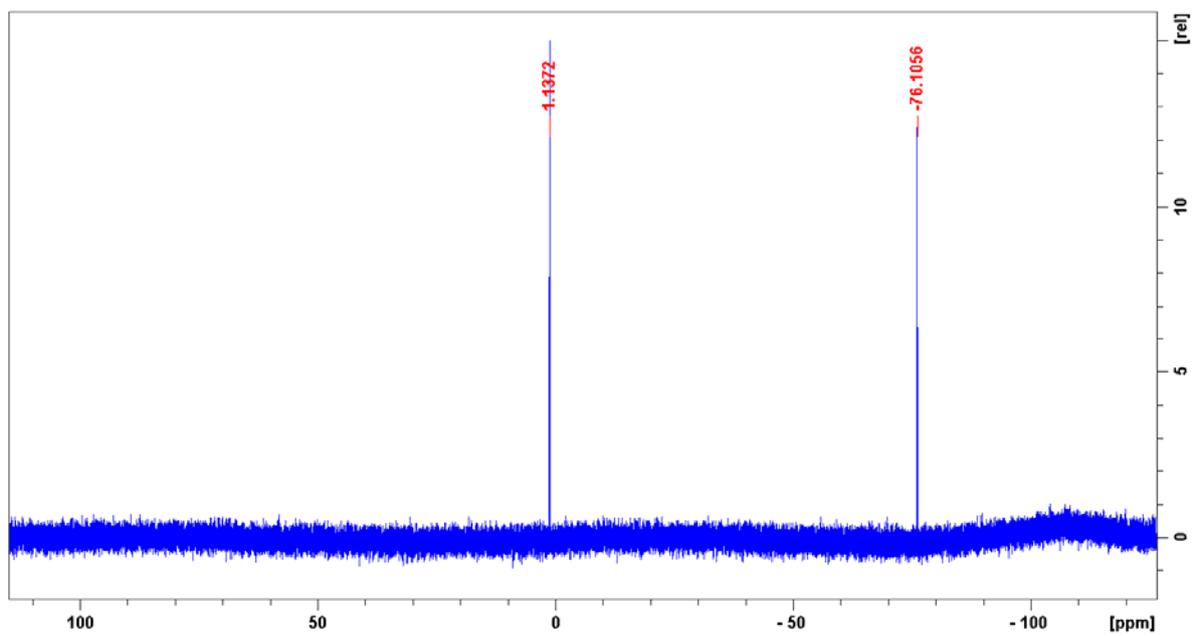
^1H NMR (benzene- d_6)



$^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6)

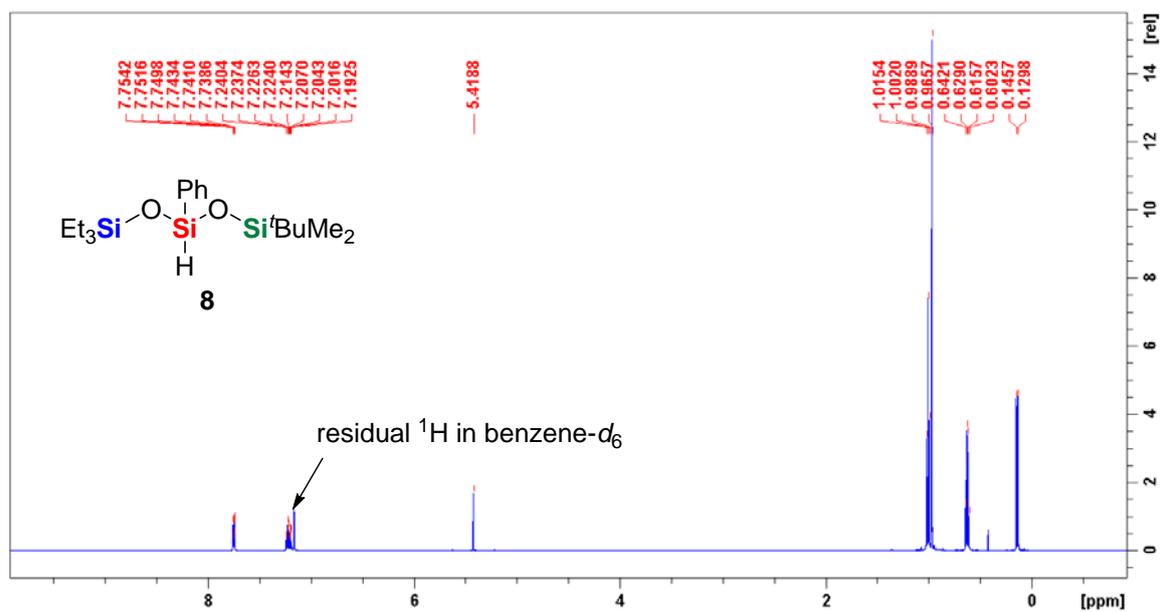


$^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6)

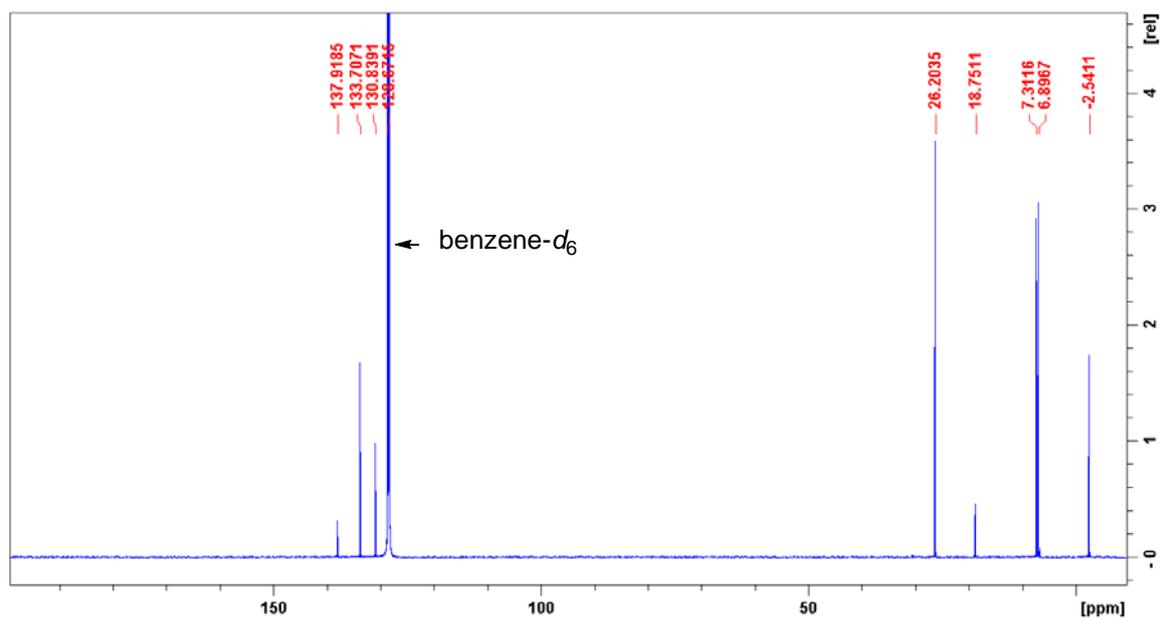


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound **8**.

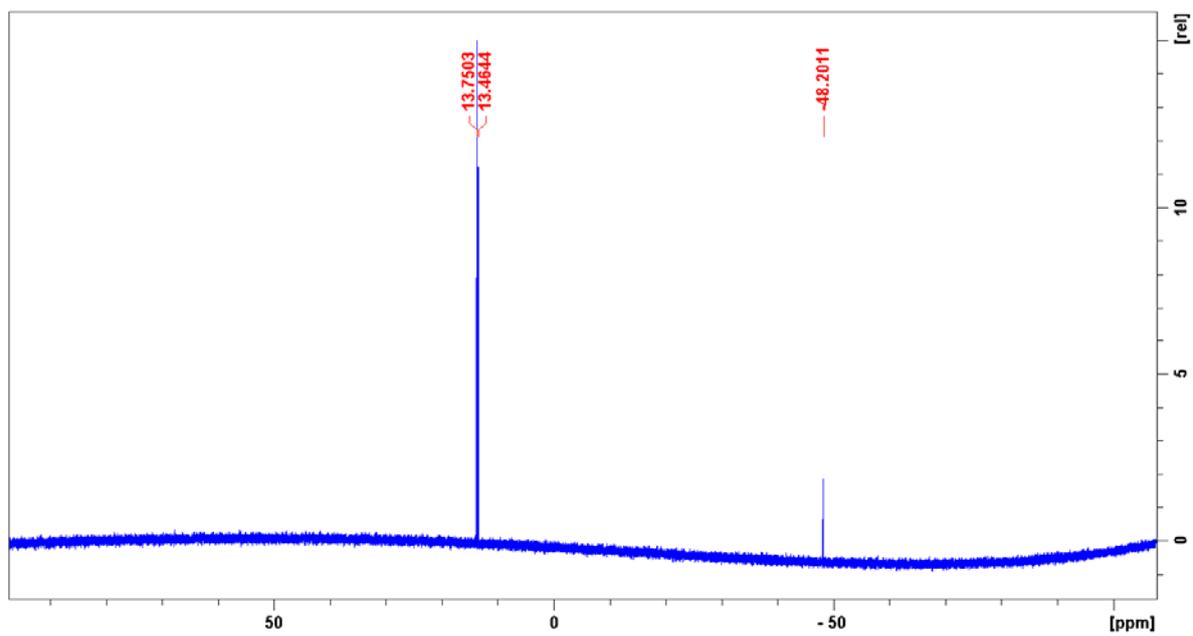
^1H NMR (benzene- d_6)



$^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6)

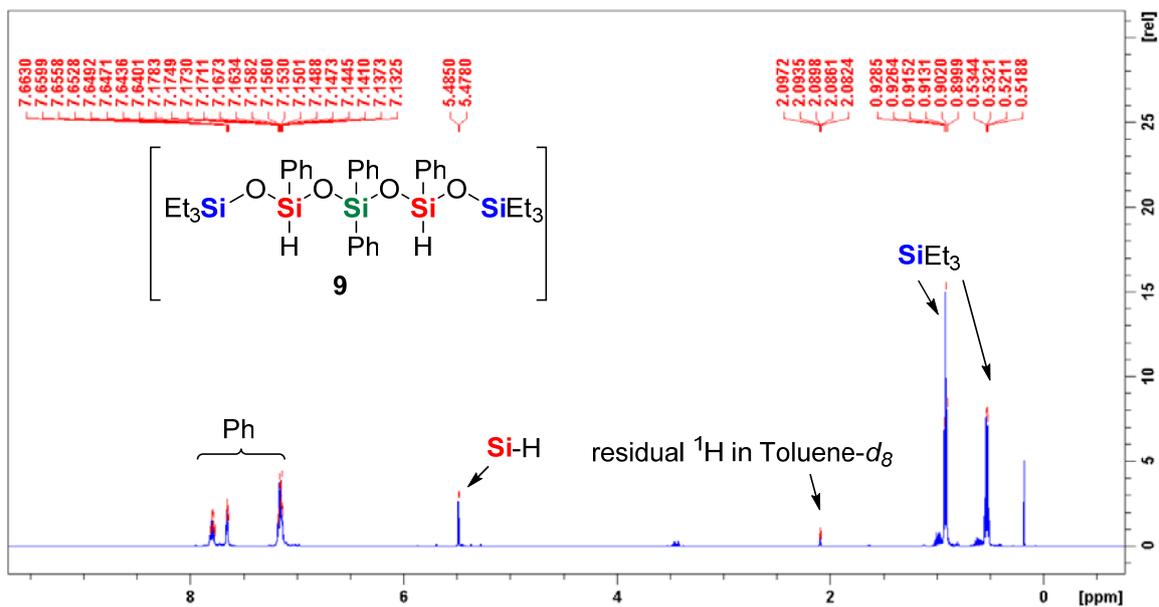


$^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6)

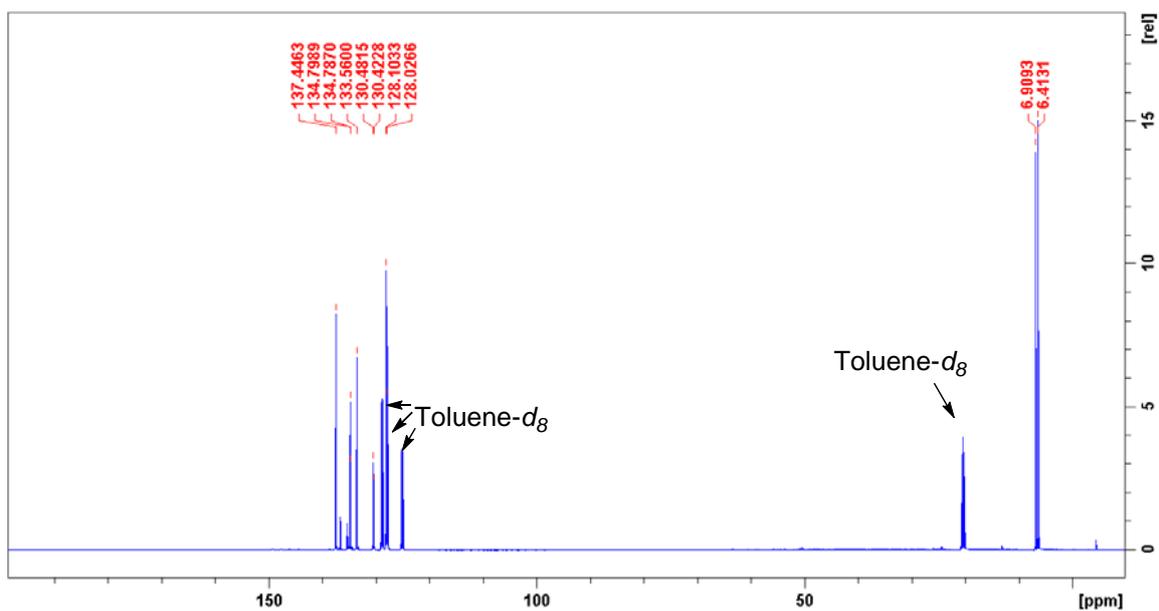


^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound 9.

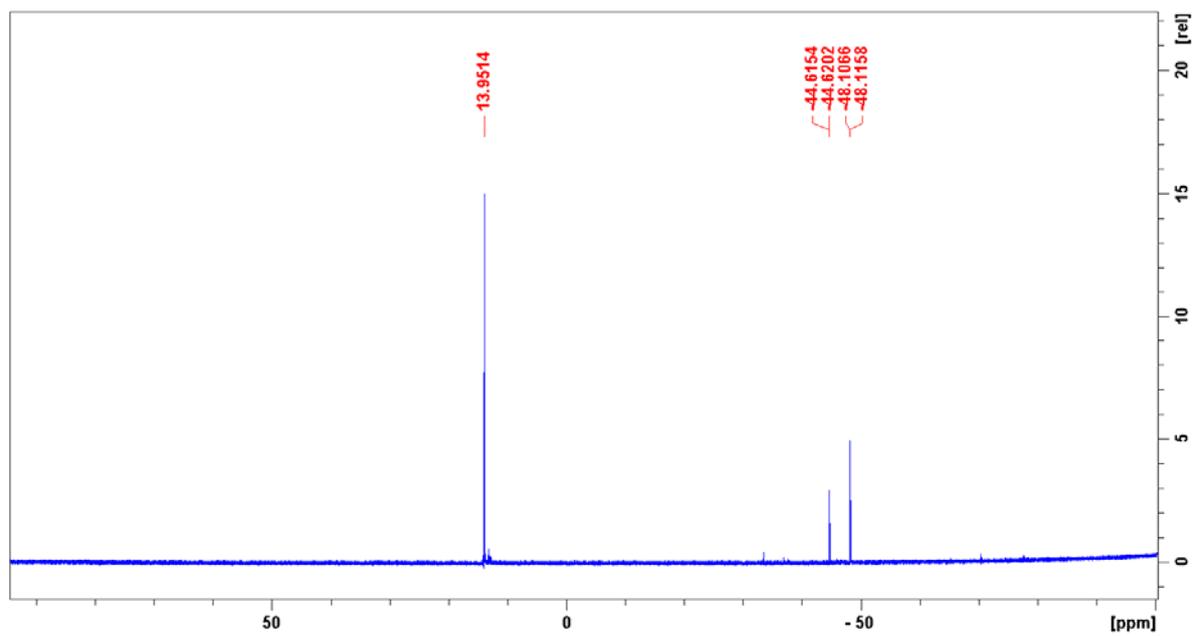
^1H NMR (toluene- d_8)



$^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8)



$^{29}\text{Si}\{^1\text{H}\}$ NMR (toluene- d_8)



4. References

- (1) Yagihashi, F.; Igarashi, M.; Nakajima, Y.; Ando, W.; Sato, K.; Yumoto, Y.; Matsui, C.; Shimada, S. *Organometallics* **2014**, *33*, 6278-6281.