Supporting Information

# Catalyst- and Additive-free Synthesis of Alkoxyhydrosiloxanes from Silanols and Alkoxyhydrosilanes

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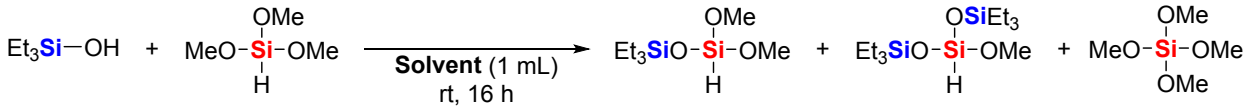
## 1. General Information

$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} ($^{1}$H: 600 MHz; $^{13}$C: 150 MHz; $^{29}$Si: 119 MHz) were recorded on a BRUKER Biospin AVANCE III HD 600 NMR spectrometer. Chemical shifts are reported in δ (ppm) and are referenced to the residual solvent signal of benzene-$d_6$ ($^{1}$H: $\delta$ = 7.16 ppm), to the central line of benzene-$d_6$ ($^{13}$C: $\delta$ = 128.39 ppm), or to phenyltrimethylsilane ($^{29}$Si: $\delta$ = –4.71 ppm). GC-MS (EI) spectra were measured on a SHIMADZU GCMS-QP2010 Plus. NMR yields of the products were determined based on the $^{29}$Si{$^{1}$H} NMR spectra using an inverse-gated decoupling pulse sequence in order to suppress the nuclear Overhauser effect. To ensure quantitative analysis by $^{29}$Si{$^{1}$H} NMR spectroscopy, samples were dissolved in benzene-$d_6$ with a trace amount of $Cr(acac)_3$ as a relaxation agent, and a delay time of 10 s was applied. Thermogravimetric analysis (TGA) was conducted with Seiko Instruments STA7000RV for the cross-linked siloxanes polymers (**7daa**, **7dab**, and **7dac**).

Unless otherwise noted, all manipulations were performed under an argon atmosphere using either Schlenk-line or glove-box techniques. Benzene-$d_6$ was dried over sodium benzophenone ketyl and distilled prior to use. All reagents except for **1e**,[1] **1g**,[2] **1h**,[3] and **1i**[4] were purchased from common commercial sources and used without further purification.

**Table S1. Solvent effect for the reaction between triethylsilanol and trimethoxysilane**

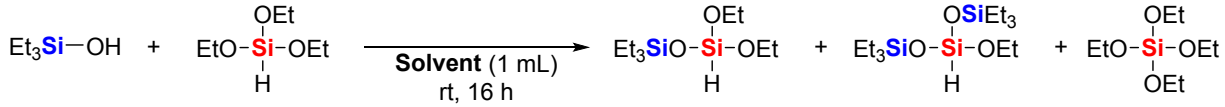



0.5 mmol **1a** | 1 mmol **2a** | **3aa** | **4aa** | **TMOS**

| Entry | Solvent | $^{29}$Si NMR Yield (%) | | |
|---|---|---|---|---|
| | | **3aa**[a] | **4aa**[a] | **TMOS**[b] |
| 1 | Benzene | 90 | trace | 2 |
| 2 | Toluene | 82 | trace | 1 |
| 3 | $CH_2Cl_2$ | 94 | 3 | 4 |
| 4 | $Et_2O$ | 79 | trace | 3 |
| 5 | THF | 91 | trace | 3 |
| 6 | Dioxane | 84 | trace | 2 |
| 7 | $CH_3CN$ | 94 | 2 | 4 |
| 8 | DMF | 97 | trace | 7 |
| 9 | DMAc | 90 | trace | 9 |
| 10 | DMSO | 91 | trace | 5 |

a) Based on **1a**
b) Based on **2a**

**Table S2. Solvent effect for the reaction between triethylsilanol and triethoxysilane**




0.5 mmol **1a** | 1 mmol **2b** | **3ab** | **4ab** | **TEOS**

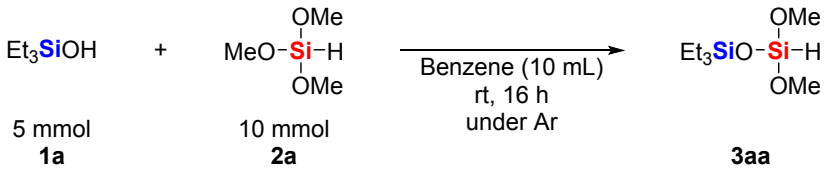
| Entry | Solvent | $^{29}$Si NMR Yield (%) | | |
|---|---|---|---|---|
| | | **3ab**[a] | **4ab**[a] | **TEOS**[b] |
| 1 | Benzene | 63 | trace | 2 |
| 2 | Toluene | 46 | trace | 1 |
| 3 | $CH_2Cl_2$ | 45 | trace | trace |
| 4 | $Et_2O$ | 41 | trace | 3 |
| 5 | $CH_3CN$ | 12 | trace | 2 |
| 6 | DMAc | 45 | 4 | 4 |

a) Based on **1a**
b) Based on **2b**

## 2. Experimental Details

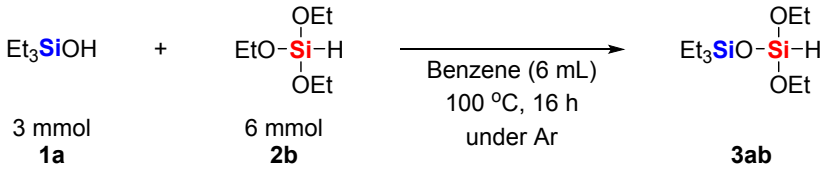
### 2-1. Synthesis of alkoxyhydrosiloxanes 3aa-3ia

**Synthesis of 3aa**



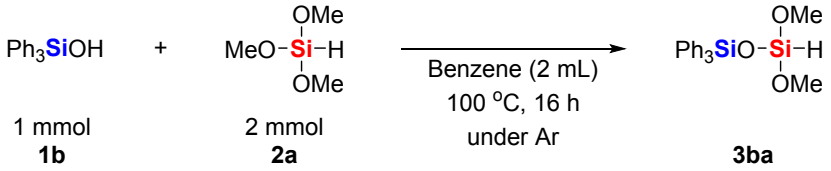

A mixture of triethylsilanol (**1a**) (661 mg, 5.0 mmol), trimethoxysilane (**2a**) (1.2 g, 10.0 mmol), and benzene (10 mL) was stirred for 16 h at room temperature under Ar. Then, the solvent was removed under reduced pressure and the residue was purified by Kugelrohr distillation (8 Torr, oven temperature: 70-80 °C) to give **3aa** as a colorless liquid (834 mg, 75% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 4.59 (s, 1H, Si*H*, $^{1}J$(Si,H) = 289.7 Hz), 3.40 (s, 6H), 1.02(t, 9H, $J$ = 8.0 Hz ), 0.61 (q, 6H, $J$ = 8.0 Hz); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 49.9, 7.2, 6.8; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ 13.9, –63.7 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 222 (1) [M] $^{+}$, 193 (100), 191 (5), 131 (1), 107 (12), 31 (2), 29 (9); HRMS (EI) calcd for $C_6H_{17}O_3Si_2$ 193.0711 [M-Et]$^{+}$, found 193.0710.

**Synthesis of 3ab**



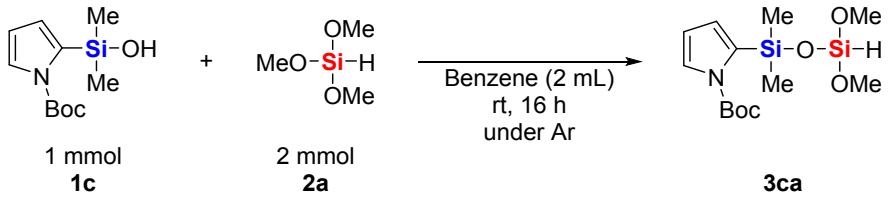

Compound **3ab** was synthesized as described for **3aa** from triethylsilanol (**1a**) (397 mg, 3.0 mmol), triethoxysilane (**2b**) (986 mg, 6.0 mmol), and benzene (6 mL) in a pressure tube. Kugelrohr distillation (8 Torr, oven temperature: 75-85 °C) of the crude mixture afforded **3ab** as a colorless liquid (600 mg, 80% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 4.68 (s, 1H, Si*H*, $^{1}J$(Si,H) = 287.5 Hz), 3.79 (q, 4H, $J$ = 7.0 Hz), 1.15 (t, 6H, $J$ = 7.0 Hz ), 1.04 (t, 9H, $J$ = 8.0 Hz ), 0.63 (q, 6H, $J$ = 8.0 Hz); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 58.4, 18.8, 7.2, 6.8; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ 13.6, –66.5 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 250 (0) [M] $^{+}$, 235 (3), 221 (100), 205 (4), 135 (13), 119 (16), 45 (3), 29 (24); HRMS (EI) calcd for $C_8H_{21}O_3Si_2$ 221.1024 [M-Et]$^{+}$, found 221.1026.

**Synthesis of 3ba**



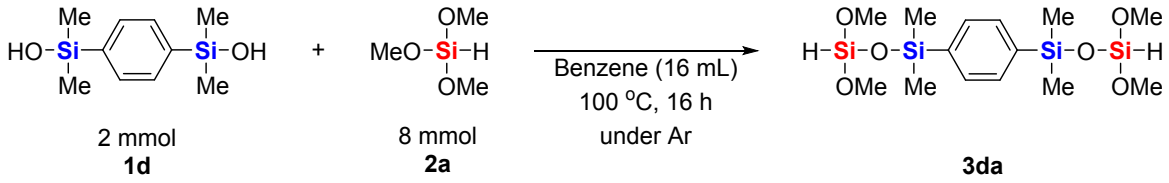

Compound **3ba** was synthesized as described for **3aa** from triphenylsilanol (**1b**) (276 mg, 1.0 mmol), trimethoxysilane (**2a**) (244 mg, 2.0 mmol), and benzene (2 mL) in a pressure tube. Then, the solvent and **2a** were removed under reduced pressure to afford **3ba** as a colorless liquid (341 mg, 93% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.77-7.78 (m, 6H), 7.17-7.19 (m, 9H), 4.74 (s, 1H, Si*H*, $^{1}J$(Si,H) = 295.7 Hz), 3.30 (s, 6H); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 136.0, 135.8, 130.7, 128.6, 50.1; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ –17.8, –63.5 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 366 (40) $[M]^+$, 335 (2), 289 (100), 259 (27), 107 (12), 91 (84), 77 (15), 31 (1); HRMS (ESI): *m*/*z* calcd for $C_{20}H_{22}O_3Si_2K$ 405.0739 $[M+K]^+$, found: 405.0745.

**Synthesis of 3ca**



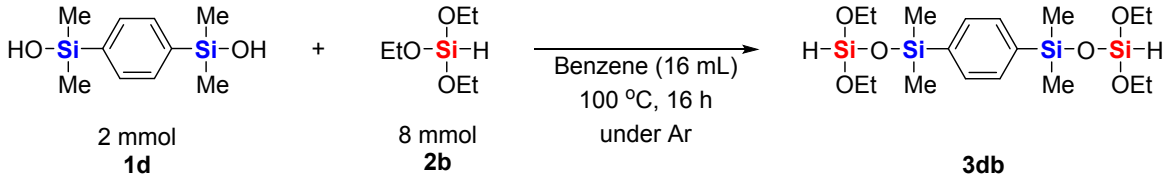

Compound **3ca** was synthesized as described for **3aa** from (*N*-Boc-2-pyrrolyl)dimethylsilanol (**1d**) (241 mg, 1.0 mmol), trimethoxysilane (**2a**) (244 mg, 2.0 mmol), and benzene (2 mL). Then, the solvent and **2a** were removed under reduced pressure to afford **3ca** as a colorless liquid (298 mg, 90% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.34 (dd, 1H, $J$ = 3.1, 1.5 Hz), 6.94-6.95 (m, 1H), 6.22 (t, 1H, $J$ = 3.1 Hz), 4.69 (s, 1H, Si*H*, $^{1}J$(Si,H) = 292.3 Hz), 3.44 (s, 6H), 1.25 (s, 9H), 0.65 (s, 6H); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 150.7, 134.2, 125.5, 124.8, 113.2, 83.8, 49.9, 28.0, 2.1; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ –7.1, –63.8 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 331 (11) $[M]^+$, 274 (4), 258 (12), 230 (16), 166 (7), 165 (22), 56 (100), 31 (2); HRMS (ESI): *m*/*z* calcd for $C_{13}H_{25}NO_5Si_2K$ 370.0903 $[M+K]^+$, found 370.0909.

**Synthesis of 3da**



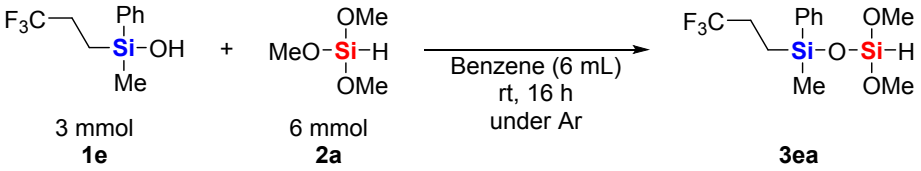

Compound **3da** was synthesized as described for **3aa** from 1, 4-bis(hydroxydimethylsilyl)benzene (**1d**) (453 mg, 2.0 mmol), trimethoxysilane (**2a**) (978 mg, 8.0 mmol), and benzene (16 mL) in a pressure tube. Then, the solvent and **2a** were removed under reduced pressure to afford **3da** as a colorless liquid (691 mg, 85% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.68 (s, 4H), 4.58 (s, 2H, Si*H*, $^{1}J$(Si,H) = 292.0 Hz), 3.35 (s, 12H), 0.39 (s, 12H); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 140.8, 133.1, 49.9, 0.9; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ 0.9, –63.8 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 406 (6) $[M]^+$, 391 (100), 315 (4), 299 (5), 165 (39), 91 (5), 76 (1); HRMS (ESI): *m*/*z* calcd for $C_{14}H_{30}O_6Si_4Na$ 429.1012 $[M+Na]^+$, found 429.1003.

**Synthesis of 3db**



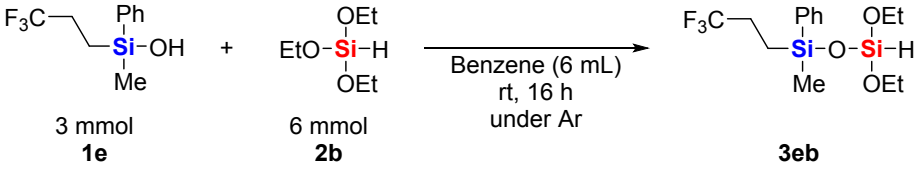

Compound **3db** was synthesized as described for **3aa** from 1, 4-bis(hydroxydimethylsilyl)benzene (**1d**) (453 mg, 2.0 mmol), triethoxysilane (**2b**) (1.3 g, 8.0 mmol), and benzene (16 mL) in a pressure tube. Then, the solvent and **2b** were removed under reduced pressure to afford **3db** as a colorless liquid (722 mg, 78% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.72 (s, 4H), 4.70 (s, 2H, Si*H*, $^{1}J$(Si,H) = 289.2 Hz), 3.74 (q, 8H, $J$ = 7.0 Hz), 1.11 (t, 12H, $J$ = 7.0 Hz), 0.42 (s, 12H); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 141.0, 133.2, 58.6, 18.8, 1.0; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ 0.5, –66.6 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 462 (5) $[M]^+$, 447 (26), 343 (3), 239 (100), 192 (30), 135 (23), 76 (1), 29 (67); HRMS (ESI): *m*/*z* calcd for $C_{18}H_{38}O_6Si_4Na$ 485.1638 $[M+Na]^+$, found 485.1630.

**Synthesis of 3ea**



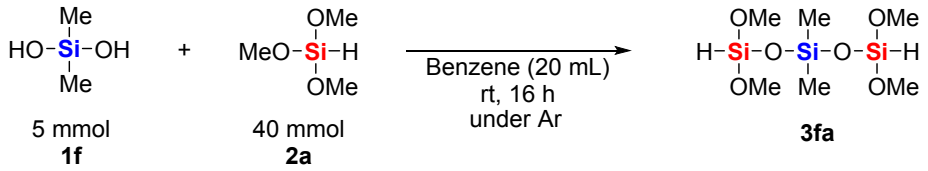

Compound **3ea** was synthesized as described for **3aa** from methyl(phenyl)(3,3,3-trifluoropropyl)silanol (**1e**) (703 mg, 3.0 mmol), trimethoxysilane (**2a**) (733 mg, 6.0 mmol), and benzene (6 mL). Then, the solvent and **2a** were removed under reduced pressure to afford **3ea** as a colorless liquid (837 mg, 86% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.45-7.47 (m, 2H), 7.18-7.19 (m, 3H), 4.51 (s, 1H, Si*H*, $^{1}J$(Si,H) = 293.9 Hz), 3.29 (s, 6H), 1.97-2.06 (m, 2H), 0.93-1.02 (m, 2H), 0.23 (s, 3H); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 136.8, 133.7, 130.7, 128.727 ($CH_2CF_3$, q, $^{1}J_{C\text{-}F}$ = 274.7 Hz), 128.725, 49.9, 28.6 ($CH_2CF_3$, q, $^{2}J_{C\text{-}F}$ = 29.9 Hz), 9.6, –1.3; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ 0.4, – 63.2 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 323 (0) $[M]^+$, 247 (1), 245 (4), 227(100), 107 (7), 77 (9), 31 (1); HRMS (ESI): *m*/*z* calcd for $C_{12}H_{19}F_3O_3Si_2Na$ 347.0717 $[M+Na]^+$, found 347.0724.

**Synthesis of 3eb**



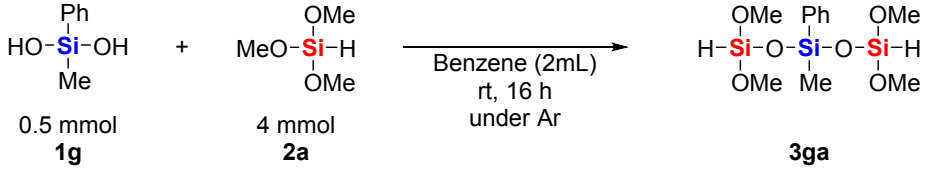

Compound **3eb** was synthesized as described for **3aa** from methyl(phenyl)(3,3,3-trifluoropropyl)silanol (**1e**) (703 mg, 3.0 mmol), triethoxysilane (**2b**) (986 mg, 6.0 mmol), and benzene (6 mL). Then, the solvent and **2b** were removed under reduced pressure to afford **3eb** as a colorless liquid (941 mg, 89% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.48-7.50 (m, 2H), 7.18-7.19 (m, 3H), 4.62 (s, 1H, Si*H*, $^{1}J$(Si,H) = 290.7 Hz), 3.68 (q, 4H, $J$ = 7.0 Hz), 2.04-2.09 (m, 2H), 1.07 (t, 6H, $J$ = 7.0 Hz), 0.99- 1.03 (m, 2H), 0.26 (s, 3H); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 136.9, 133.8, 131.5, 128.8 ($CH_2CF_3$, q, $^{1}J_{C\text{-}F}$ = 274.0 Hz), 128.7, 58.6, 28.7 ($CH_2CF_3$, q, $^{2}J_{C\text{-}F}$ = 29.7 Hz), 18.7, 9.7, –1.2; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ 0.1, –65.9 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 352 (0) $[M]^+$, 255 (100), 135 (2), 77 (15), 45 (6), 29 (28); HRMS (ESI): *m*/*z* calcd for $C_{14}H_{23}F_3O_3Si_2Na$ 375.1030 $[M+Na]^+$, found 375.1038.

**Synthesis of 3fa**



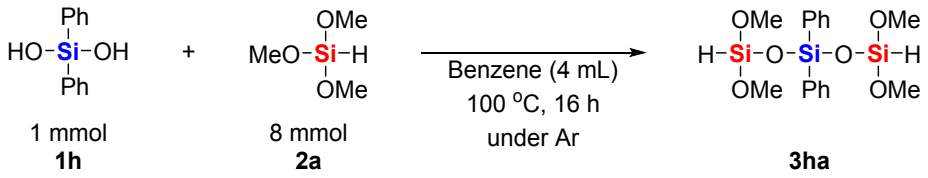

Compound **3fa** was synthesized as described for **3aa** from dimethylsilanediol (**1f**) (461 mg, 5.0 mmol), trimethoxysilane (**2a**) (4.9 g, 40.0 mmol), and benzene (20 mL). Then, the solvent and **2a** were removed under reduced pressure to afford **3fa** as a colorless liquid (1.1 g, 80% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 4.55 (s, 2H, Si*H*, $^{1}J$(Si,H) = 293.9 Hz), 3.40 (s, 12H), 0.22 (s, 6H); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene- $d_6$): $\delta$ 49.9, 1.0; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ –17.1, –64.4 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 272(5) $[M]^+$, 271 (22), 257 (100), 241 (26), 107 (3), 91 (7), 90 (2), 31 (3); HRMS (EI) *m*/*z* calcd for $C_5H_{17}O_5Si_3$ 241.0378 $[M\text{-}OMe]^+$, found 241.0384.

**Synthesis of 3ga**



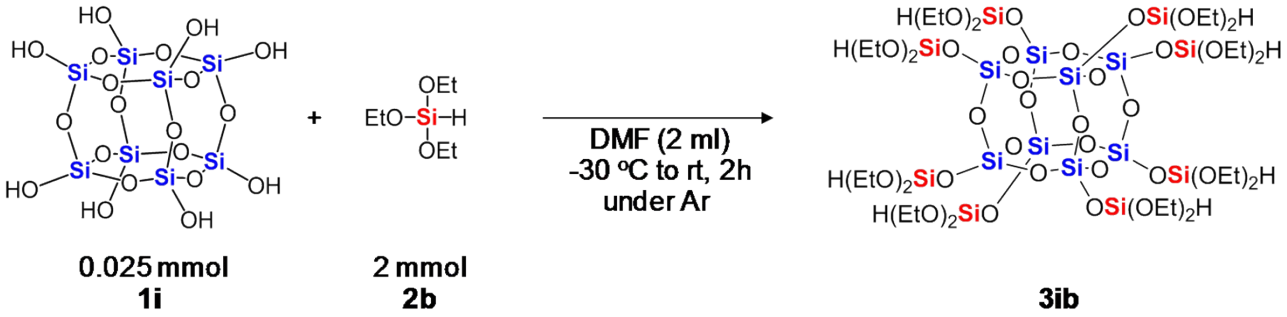

Compound **3ga** was synthesized as described for **3aa** from methylphenylsilanediol (**1g**) (77 mg, 0.5 mmol), trimethoxysilane (**2a**) (489 mg, 4.0 mmol), and benzene (2 mL). Then, the solvent and **2a** were removed under reduced pressure to afford **3ga** as a colorless liquid (162 mg, 97% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.76-7.79 (m, 2H), 7.18-7.22 (m, 3H), 4.62 (s, 2H, Si*H*, $^{1}J$(Si,H) = 295.7 Hz), 3.37 (d, 12H), 0.47 (s, 3H); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 136.8, 134.0, 130.8, 128.6, 50.0, –0.1; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ –30.7, –64.3; GC-MS (EI) *m*/*z* (relative intensity) 334 (22) $[M]^+$, 332 (64), 319 (100), 227 (13), 107 (6), 91 (90), 77 (6), 31 (2); HRMS (ESI): *m*/*z* calcd for $C_{11}H_{22}O_6Si_3Na$ 357.0616 $[M+Na]^+$, found 357.0618.

**Synthesis of 3ha**




Compound **3ha** was synthesized as described for **3aa** from diphenylsilanediol (**1h**) (216 mg, 1.0 mmol), trimethoxysilane (**2a**) (978 mg, 8.0 mmol), and benzene (4 mL) in a pressure tube. Then, the solvent and **2a** were removed under reduced pressure to afford **3ha** as a colorless liquid (385 mg, 97% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.87-7.89 (m, 4H), 7.18-7.19 (m, 6H), 4.70 (s, 2H, Si*H*, $^{1}J$(Si,H) = 276.2 Hz), 3.36 (s, 12H); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 135.1, 134.9, 131.1, 128.6, 50.1; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ –44.4, –64.3 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 396 (25) $[M]^+$, 395 (68), 319 (37), 107 (5), 91 (100), 77 (2); HRMS (ESI): *m*/*z* calcd for $C_{16}H_{24}O_6Si_3Na$ 419.0773 $[M+Na]^+$, found 419.0783.

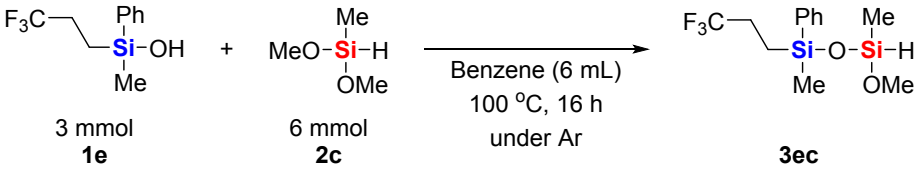
**Synthesis of $[Si_8O_{12}][OSi(OEt)_2H]_8$ (3ib).**




In a vial equipped with a magnetic stirring bar, $[Si_8O_{12}][OH]_8 \cdot 10.92$DMAc (37.6 mg, 0.0250 mmol) was dissolved in *N*,*N*-dimethylformamide (DMF) (1 mL) and cooled to –30 °C. To the cooled solution, a solution of $(EtO)_3HSi$ (329 mg, 2.00 mmol) in DMF (1 mL) was added dropwise. Then, the reaction mixture was allowed to warm to ambient temperature, where stirring was continued for 2 h, before the weight of the resulting mixture was moderately reduced to 1.02 g weight under reduced pressure in order to remove any unreacted $(EtO)_3HSi$ while concomitantly suppressing the condensation of generated $[Si_8O_{12}][OSi(OEt)_2H]_8$. Thus, a DMF solution (3.1wt%) of $[Si_8O_{12}][OSi(OEt)_2H]_8$ (0.0208 mmol, 83.2% yield; based on the $^{29}$Si NMR spectrum) was obtained. $^{1}$H NMR (600 MHz, DMF-$d_7$): 4.46 (s, 8H, Si*H*), 4.07 (m, 32H, $CH_2CH_3$), 1.42 (m, 48H, $CH_2CH_3$); $^{13}$C{$^{1}$H}NMR (150 MHz, DMF-$d_7$): 59.1, 18.6; $^{29}$Si{$^{1}$H} NMR (119 MHz, DMF-$d_7$): −67.9 (SiO*Si*H),

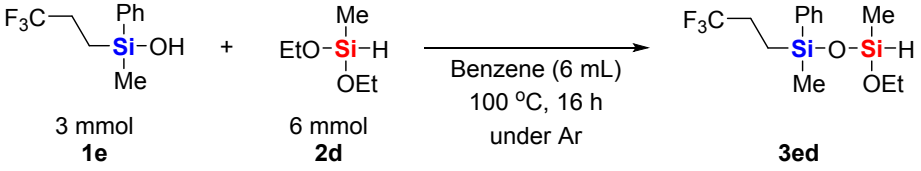
−110.2 (*Si*OSiH); HRMS (ESI): *m/z* calcd for $C_{32}H_{92}NO_{36}Si_{16}$ 1514.1702 $[M+NH_4]^+$, found 1514.1705.

**Synthesis of 3ec**




Compound **3ec** was synthesized as described for **3aa** from methyl(phenyl)(3,3,3-trifluoropropyl)silanol (**1e**) (703 mg, 3.0 mmol), dimethoxymethylsilane (**2c**) (637mg, 6.0 mmol), and benzene (6 mL) in a pressure tube. Then, the solvent and **2b** were removed under reduced pressure to afford **3eb** as a colorless liquid (805 mg, 87% yield). $^1$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.42-7.43 (m, 2H), 7.18- 7.19 (m, 3H), 4.83 (q, 1H, Si*H*, $J$ = 2.9 Hz, $^1J$(Si,H) = 233.8 Hz), 3.27 (s, 3H), 1.94-1.99 (m, 2H), 0.93-0.97 (m, 2H), 0.19 (s, 3H), 0.06 (d, 3H); $^{13}$C{$^1$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 137.0, 133.7, 130.6, 128.712 ($CH_2CF_3$, q, $^1J_{C\text{-}F}$ = 275.3 Hz), 128.710, 50.9, 28.7 ($CH_2CF_3$, q, $^2J_{C\text{-}F}$ = 29.8 Hz), 9.6, –0.8, –1.3; $^{29}$Si{$^1$H} NMR (119 MHz, benzene-$d_6$): $\delta$ –0.7, –22.5 (SiH); GC-MS (EI) *m/z* (relative intensity) 308 (0) $[M]^+$, 211 (100), 91 (72), 77 (12), 69 (1), 31 (1); HRMS (ESI): *m/z* calcd for $C_{12}H_{19}F_3O_2Si_2Na$ 331.0768 $[M+Na]^+$, found 331.0772.

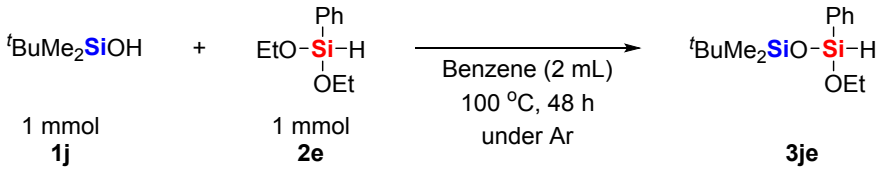
**Synthesis of 3ed**




Compound **3ed** was synthesized as described for **3aa** from methyl(phenyl)(3,3,3-trifluoropropyl)silanol (**1e**) (703 mg, 3.0 mmol), diethoxymethylsilane (**2d**) (806 mg, 6.0 mmol), and benzene (6 mL) in a pressure tube. Then, the solvent and **2b** were removed under reduced pressure to afford **3eb** as a colorless liquid (888 mg, 89% yield). $^1$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.43-7.44 (m, 2H), 7.18- 7.19 (m, 3H), 4.89 (q, 1H, Si*H*, $J$ = 2.9 Hz, $^1J$(Si,H) = 234.7 Hz), 3.59(m, 2H), 1.96-2.01 (m, 2H), 1.06 (t, 3H), 0.94-0.98 (m, 2H), 0.21 (d, 3H), 0.09 (t, 3H); $^{13}$C{$^1$H} NMR (150 MHz,

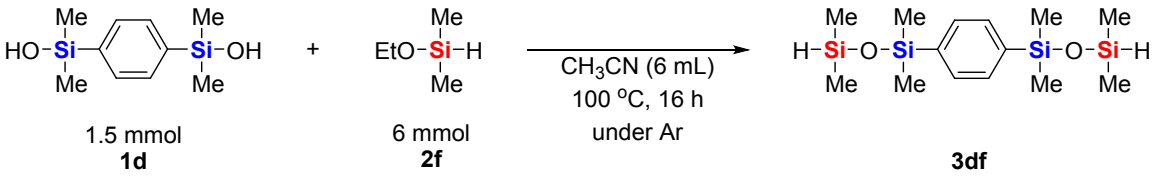
benzene-$d_6$): $\delta$ 137.1, 133.7, 130.6, 128.73 ($CH_2CF_3$, q, $^1J_{C\text{-}F}$ = 275.3 Hz), 128.69, 59.5, 28.7 ($CH_2CF_3$, q, $^2J_{C\text{-}F}$ = 29.8 Hz), 18.7, 9.6, –0.4, –1.29; $^{29}$Si{$^1$H} NMR (119 MHz, benzene-$d_6$): $\delta$ –0.9, –25.0 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 322 (0) $[M]^+$, 225 (100), 217 (2), 105 (27), 89 (6), 77 (19), 45 (5), 29 (19); HRMS (ESI): *m*/*z* calcd for $C_{13}H_{21}F_3O_2Si_2Na$ 345.0924 $[M+Na]^+$, found 345.0921.

**Synthesis of 3je**




Compound **3je** was synthesized as described for **3aa** from *tert*-butyldimethylsilanol (**1j**) (132 mg, 1.0 mmol), diethoxyphenylsilane (**2e**) (196 mg, 1.0 mmol), and benzene (2 mL) in a pressure tube. Then, the solvent was removed under reduced pressure to afford **3je** as a colorless liquid (223 mg, 79% yield). $^1$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.73-7.75 (m, 2H), 7.19-7.22 (m, 3H), 5.31 (s, 1H, Si*H*, $^1J$(Si,H) = 242.6 Hz), 3.77 (qd, 2H, $J$ = 7.0, 2.0 Hz), 1.14 (t, 3H, $J$ = 7.0 Hz), 0.96 (s, 9H), 0.12 (d, 3H, $J$ = 4.8 Hz); $^{13}$C{$^1$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 135.9, 134.3, 131.0, 128.6, 59.5, 26.2, 18.82, 18.76, –2.6; $^{29}$Si{$^1$H} NMR (119 MHz, benzene-$d_6$): $\delta$ 14.3, –39.1 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 282(0) $[M]^+$, 267 (2), 225 (100), 167 (2), 119 (74), 77 (2), 57 (2), 45 (3); HRMS (ESI): *m*/*z* calcd for $C_{14}H_{26}O_2Si_2Na$ 305.1364 $[M+Na]^+$, found 305.1355.

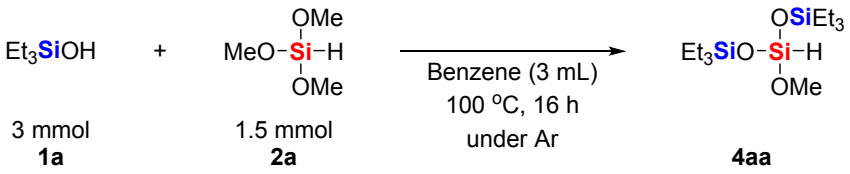
**Synthesis of 3df**




Compound **3df** was synthesized as described for **3aa** from 1, 4-bis(hydroxydimethylsilyl)benzene (**1d**) (340 mg, 1.5 mmol), ethoxy(dimethyl)silane (**2f**) (625 mg, 6.0 mmol), and $CH_3CN$ (6 mL) in a pressure tube. After the reaction, the mixture was cooled to room temperature, and the organic phase was extracted with hexane. The hexane phase was isolated and all volatiles were removed under reduced pressure before the thus obtained residue was purified by flash column chromatography on silica gel (eluent: hexane) to give the desired product as a colorless liquid (283 mg, 55% yield). $^1$H

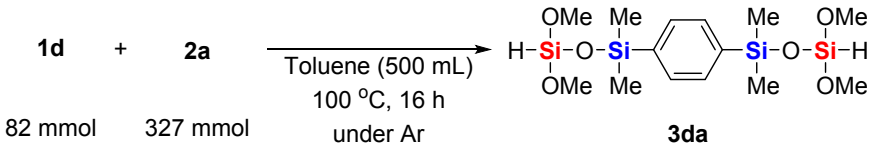
NMR (600 MHz, benzene-$d_6$): $\delta$ 7.66 (s, 4H), 5.05 (sept, 2H, Si*H*, $^1J$(Si,H) = 204.2 Hz), 0.36 (s, 12H), 0.15 (d, 12H, $J$ = 2.8 Hz); $^{13}$C{$^1$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 141.3, 133.1, 1.3, 1.0; $^{29}$Si{$^1$H} NMR (119 MHz, benzene- $d_6$): $\delta$ 0.1, –5.0 (SiH); HRMS (ESI): *m*/*z* calcd for $C_{14}H_{31}O_2Si_4$ 343.1396 $[M+H]^+$, found 343.1387.

### 2-5. Synthesis of 4aa



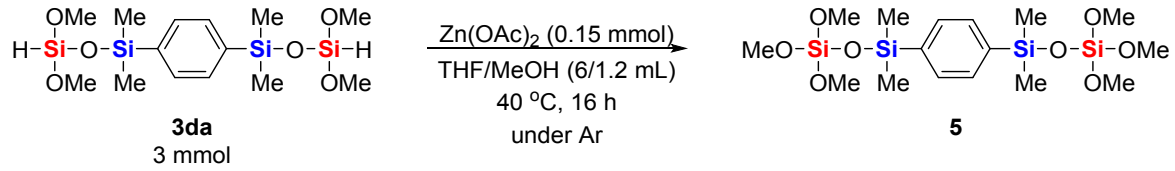

A mixture of triethylsilanol (**1a**) (397 mg, 3.0 mmol), trimethoxysilane (**2a**) (183 mg, 1.5 mmol), and benzene (3 mL) was stirred for 16 h at 100 °C under Ar in a pressure tube. Then, the solvent was evaporated and the residue was purified by Kugelrohr distillation (8 Torr, oven temperature 120-130 °C) to give 4**aa** as a colorless liquid (295 mg, 61% yield). $^1$H NMR (600 MHz, benzene-$d_6$): $\delta$ 4.67 (s, 1H, Si*H*, $^1J$(Si,H) = 290.0 Hz), 3.42 (s, 3H), 1.04 (t, 18H, $J$ = 8.0 Hz ), 0.63 (q, 12H, $J$ = 8.0 Hz); $^{13}$C{$^1$H} NMR (150 MHz, , benzene-$d_6$): $\delta$ 49.6, 7.2, 6.8; $^{29}$Si{$^1$H} NMR (119 MHz, benzene-$d_6$): $\delta$ 13.2, –73.2 (SiH); GC-MS (EI) *m*/*z* (relative intensity) 322 (0) $[M]^+$, 321 (1), 293 (100), 132 (4), 115 (3), 90 (2), 60 (1); HRMS (ESI): *m*/*z* calcd for $C_{13}H_{34}O_3Si_3K$ 361.1447 $[M+K]^+$, found 361.1452.

### 2-6. Large-scale synthesis of 3da




A mixture of 1,4-bis(hydroxydimethylsilyl)benzene (**1d**) (18.6 g, 82 mmol), trimethoxysilane (**2a**) (40.0 g, 327 mmol), and toluene (500 mL) was stirred for 16 h at 100 °C under ambient atmosphere. Then, the solvent and **2a** were removed under reduced pressure to afford **3da** as a colorless liquid (33.2 g, 99% yield).

## 2-7. Synthesis 5 from methoxylation of 3da



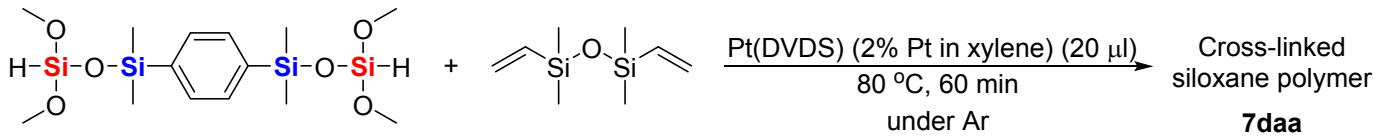

**3da**
3 mmol

**5**

A mixture of **3da** (1.2 g, 3.0 mmol), $Zn(OAc)_2$ (28 mg, 0.15 mmol), and THF/MeOH (6/1.2 mL) was stirred for 16 h at 40 °C under Ar in a pressure tube. After the reaction, the mixture was diluted with hexane (6 mL) and filtered through a filter paper. The filtrate was concentrated under reduced pressure to afford **5** as a colorless liquid (1.17 g, 81% yield). $^{1}$H NMR (600 MHz, benzene-$d_6$): $\delta$ 7.74 (s, 4H), 3.45 (s, 18H), 0.44 (s, 12H); $^{13}$C{$^{1}$H} NMR (150 MHz, benzene-$d_6$): $\delta$ 141.0, 133.2, 51.3, 0.9; $^{29}$Si{$^{1}$H} NMR (119 MHz, benzene-$d_6$): $\delta$ 1.1, –83.6; GC-MS (EI) *m*/*z* (relative intensity) 466 (0) $[M]^+$, 451 (100), 435 (1), 271 (2), 195 (93), 77 (1), 31 (2); HRMS (ESI): *m*/*z* calcd for $C_{16}H_{34}O_8Si_4Na$ 489.1223 $[M+Na]^+$, found 489.1210.

## 2-8. Synthesis of 7daa-7dfa

### Synthesis of 7daa



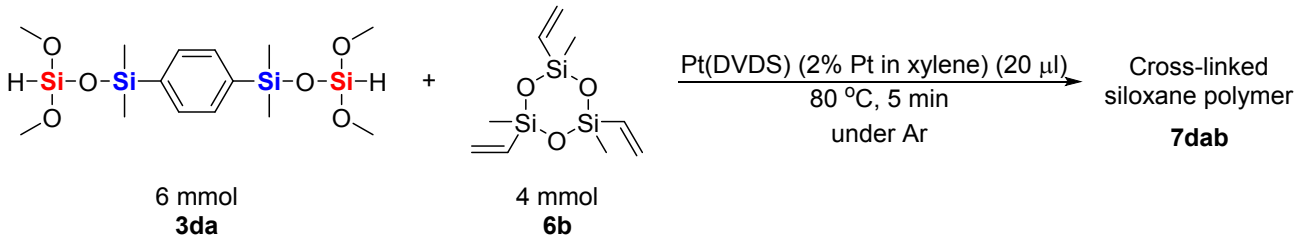

5 mmol
**3da**

5 mmol
**6a**

**7daa**

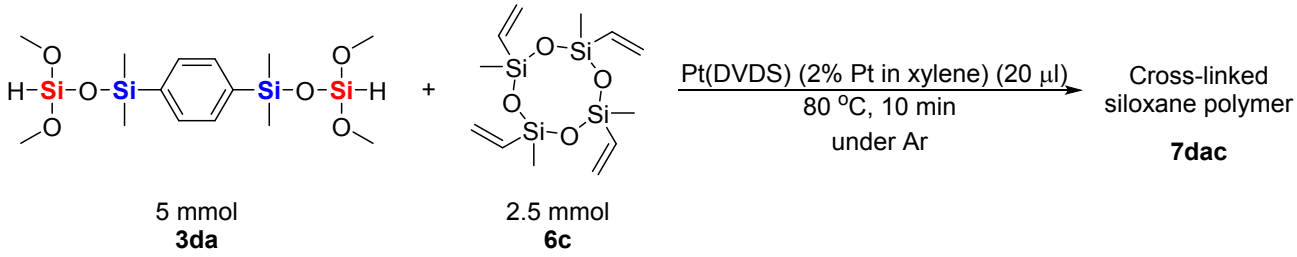
A mixture of **3da** (2.0 g, 5 mmol), **6a** (932 mg, 5 mmol), and Pt(DVDS) (20 $\mu$L, 2% Pt in xylene, Gelest) was stirred for 60 min at 80 °C under Ar to afford **7daa** as a colorless elastomer that is insoluble in common solvents.

### Synthesis of 7dab



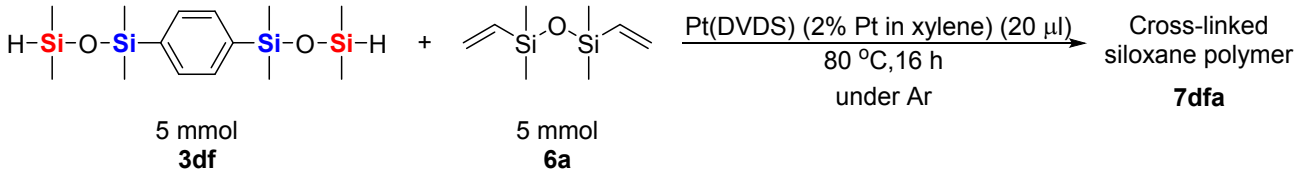

A mixture of **3da** (2.4 g, 6 mmol), **6b** (1.0 g, 4 mmol), and Pt(DVDS) (20 $\mu$L, 2% Pt in xylene, Gelest) was stirred for 5 min at 80 °C under Ar to afford **7dab** as a colorless elastomer that is insoluble in common solvents.

**Synthesis of 7dac**




A mixture of **3da** (2.0 g, 5 mmol), **6c** (862 mg, 2.5 mmol), and Pt(DVDS) (20 $\mu$L, 2% Pt in xylene, Gelest) was stirred for 10 min at 80 °C under Ar to afford **7dac** as a colorless elastomer that is insoluble in common solvents.

**Synthesis of 7dfa**

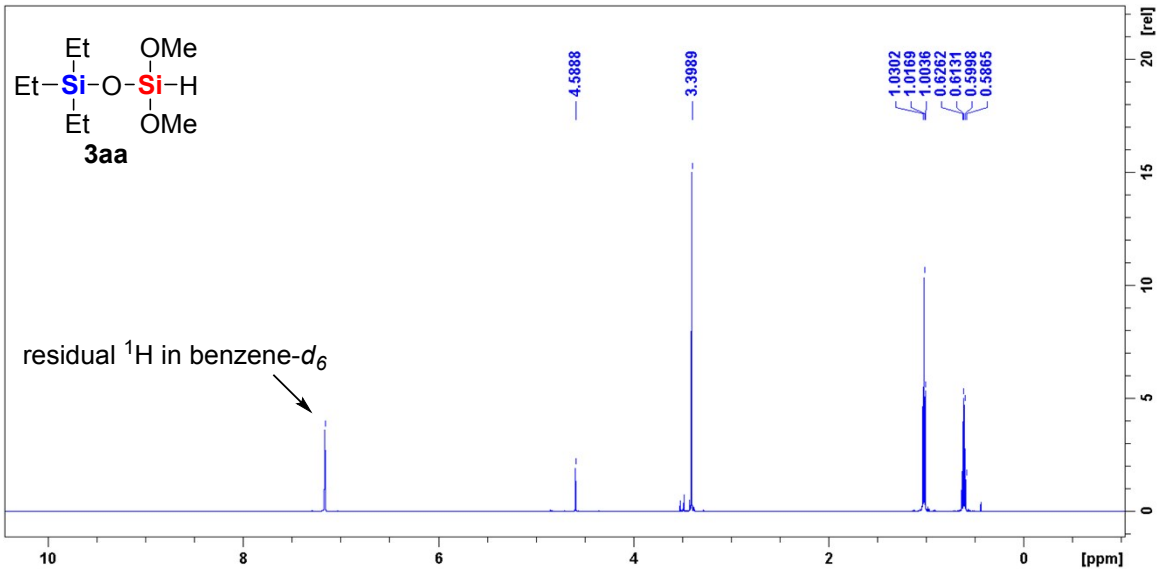



A mixture of **3dfa** (1.7 g, 5 mmol), **6a** (932 mg, 5 mmol), and Pt(DVDS) (20 $\mu$L, 2% Pt in xylene, Gelest) was stirred for 16 h at 80 °C under Ar to afford **7dfa** as a brown sticky gum-like elastomer that is insoluble in common solvents.

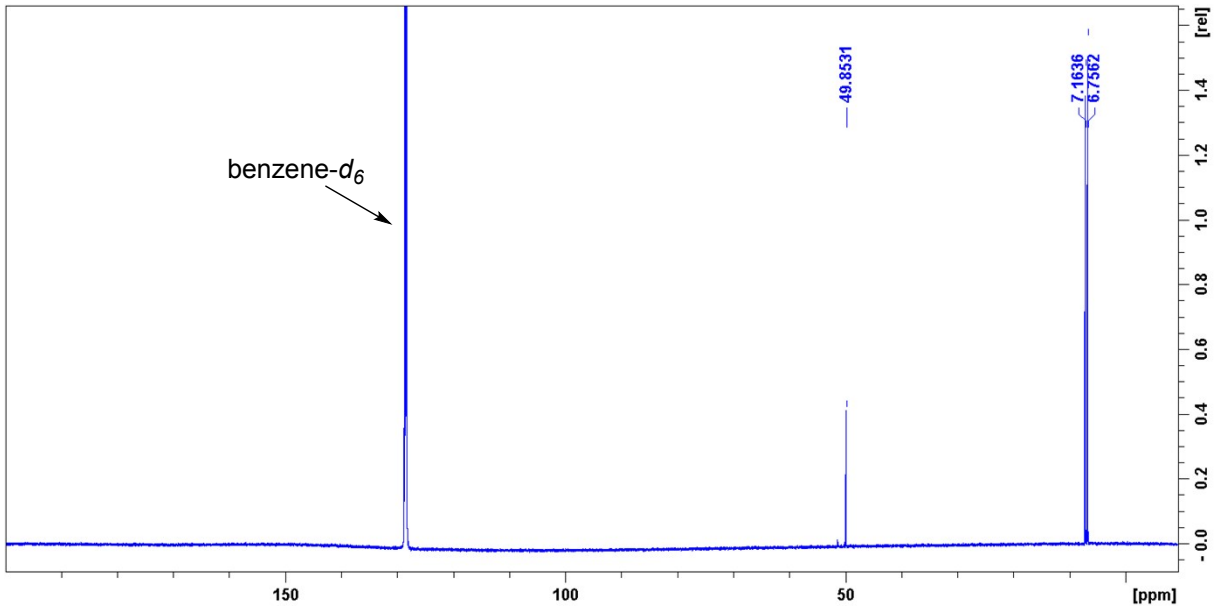
## 3. NMR Spectra

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

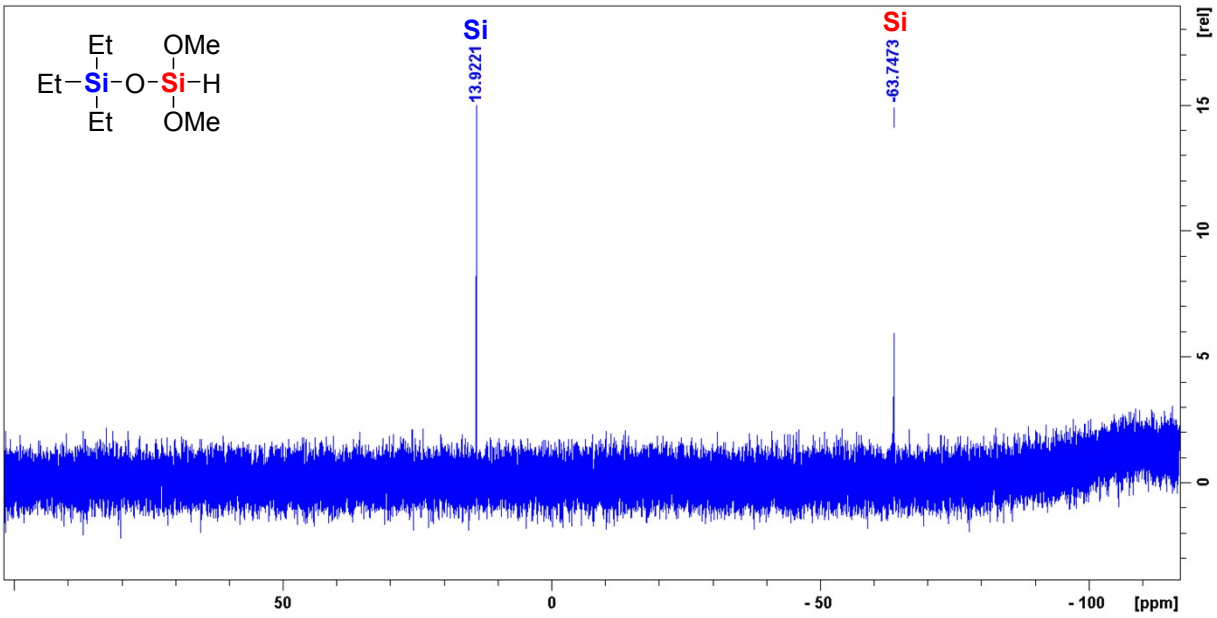
$^{1}$H NMR (benzene-$d_6$)




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

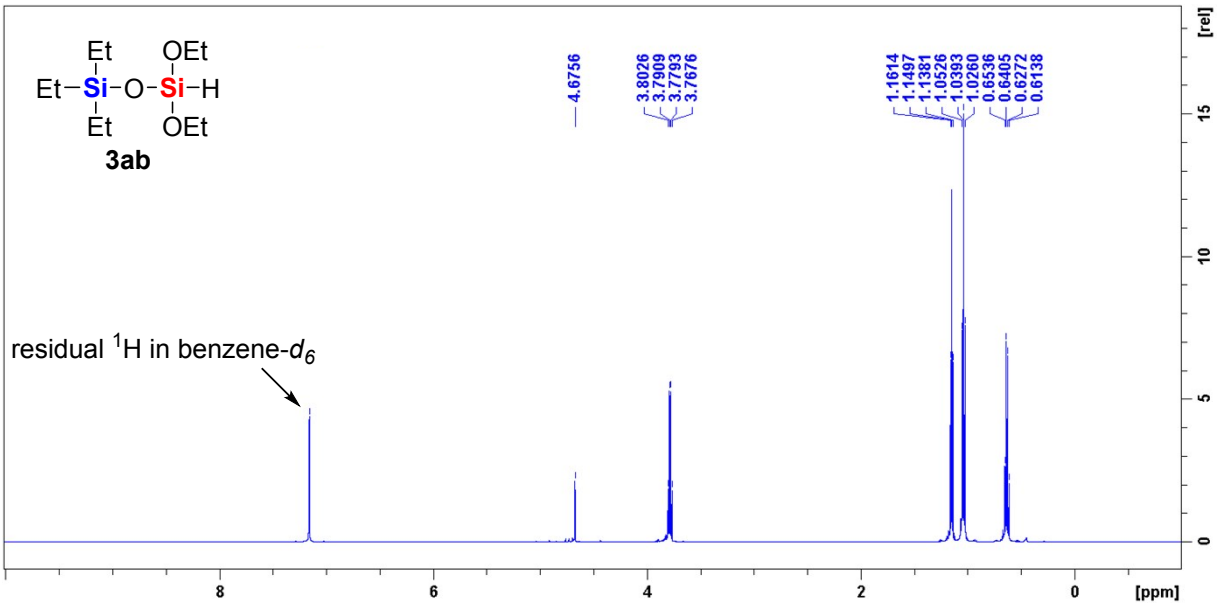


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

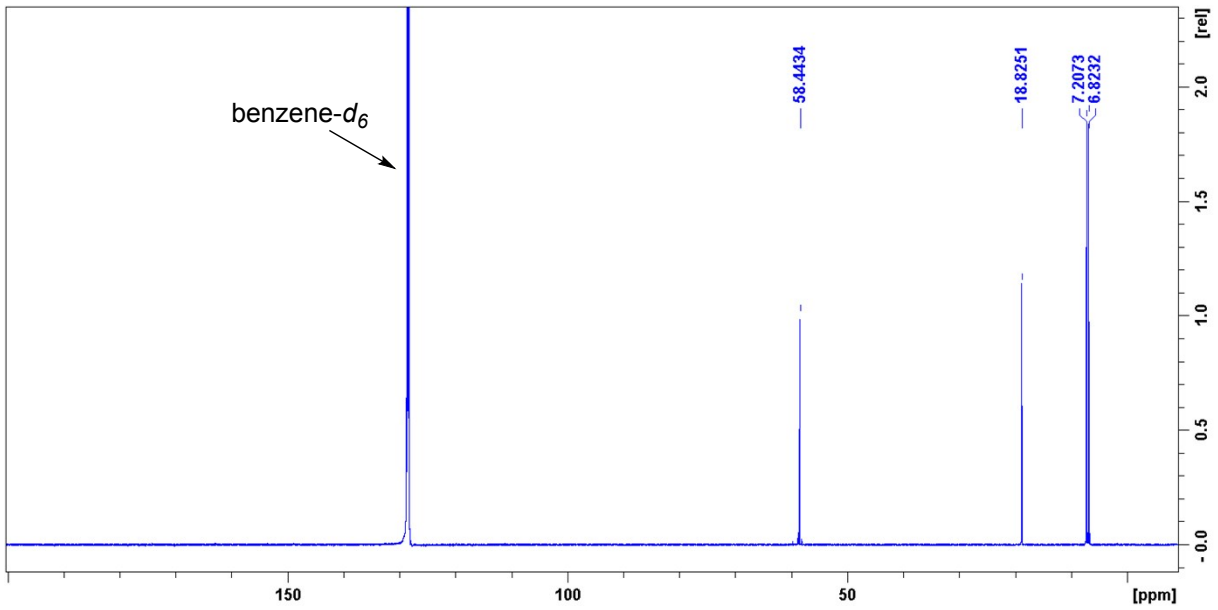


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3ab.**

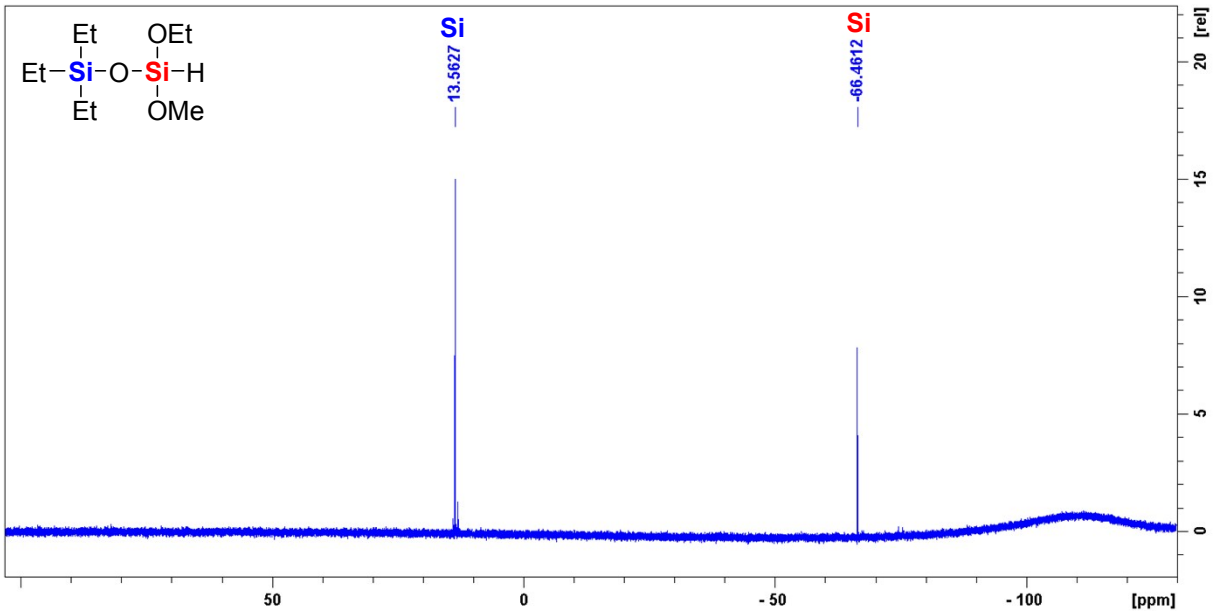
$^{1}$H NMR (benzene-$d_6$)




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

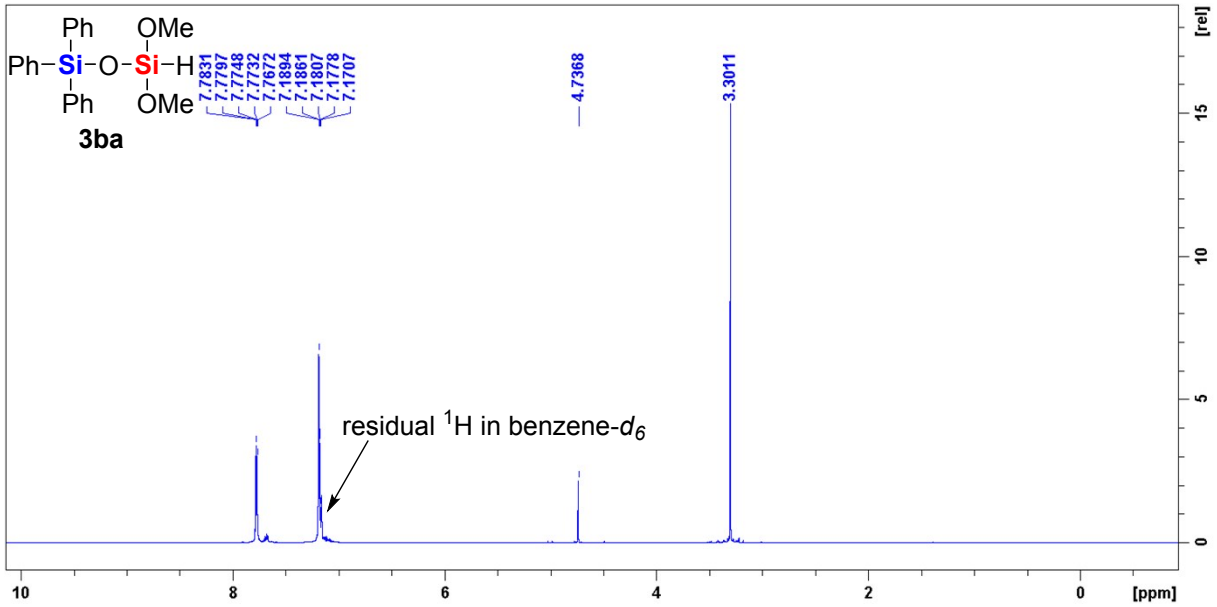


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

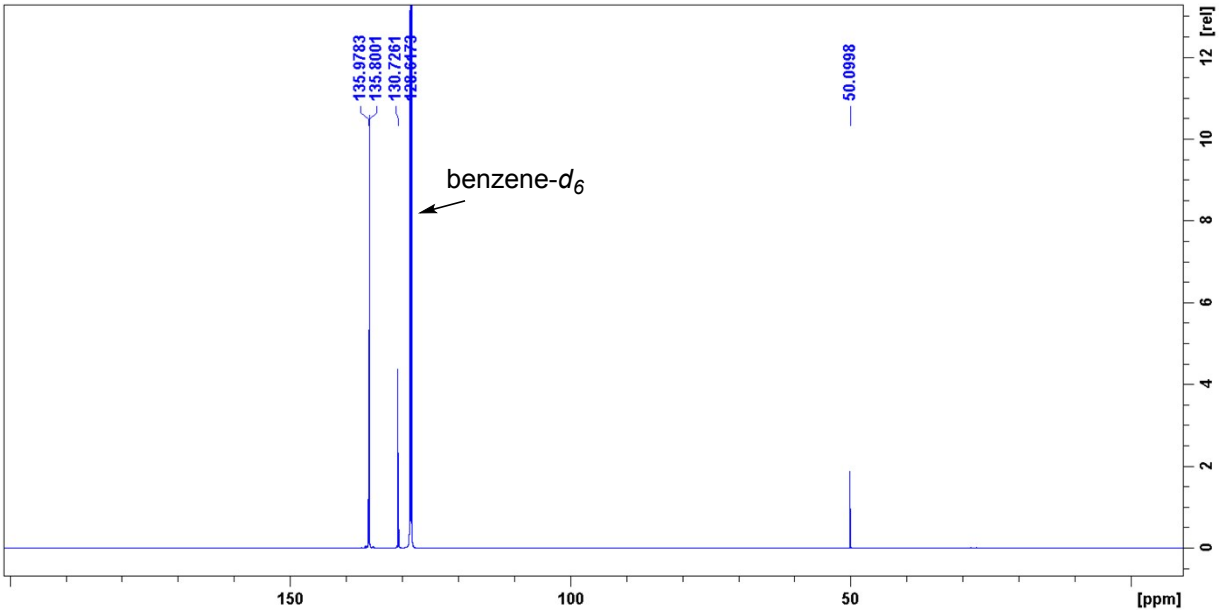


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3ba.**

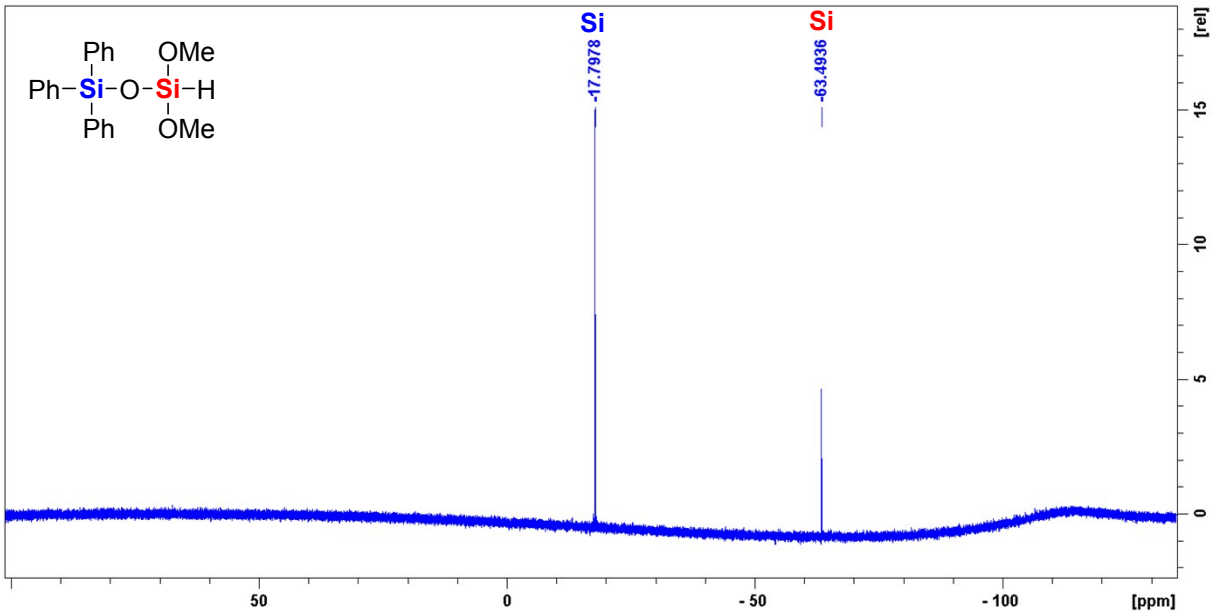
$^{1}$H NMR (benzene-$d_6$)




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

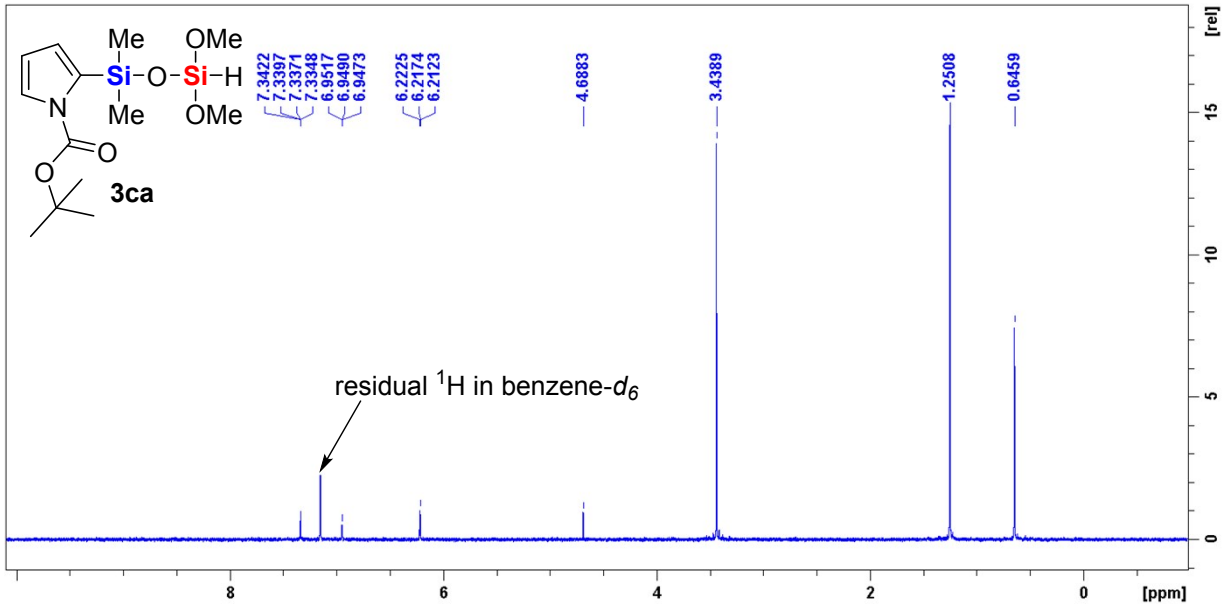


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

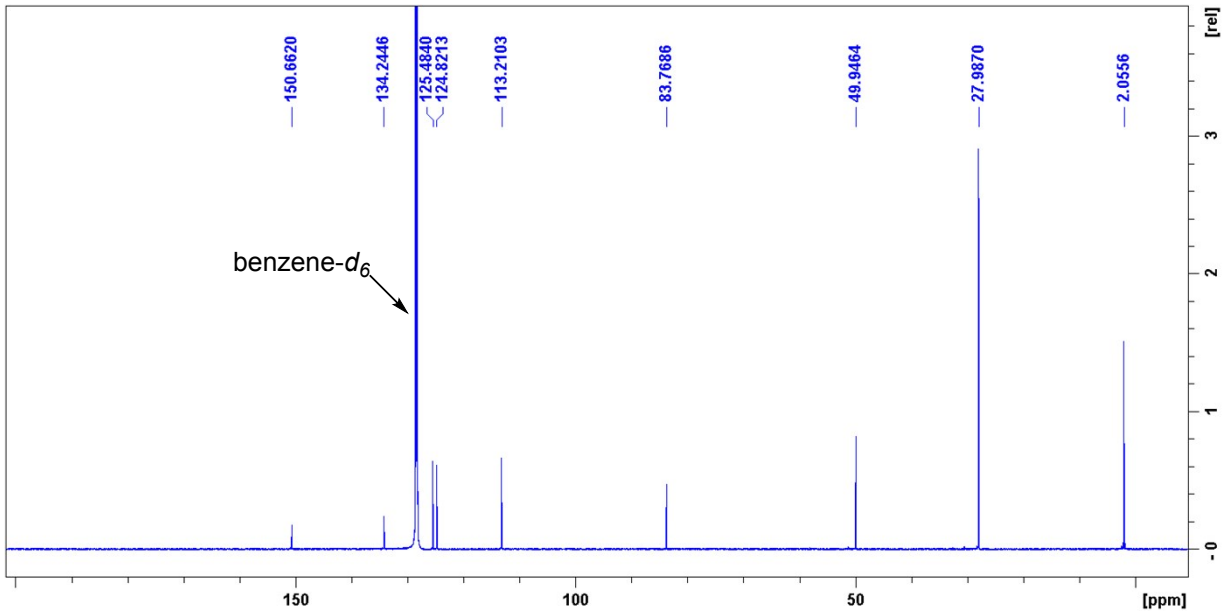


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3ca.**

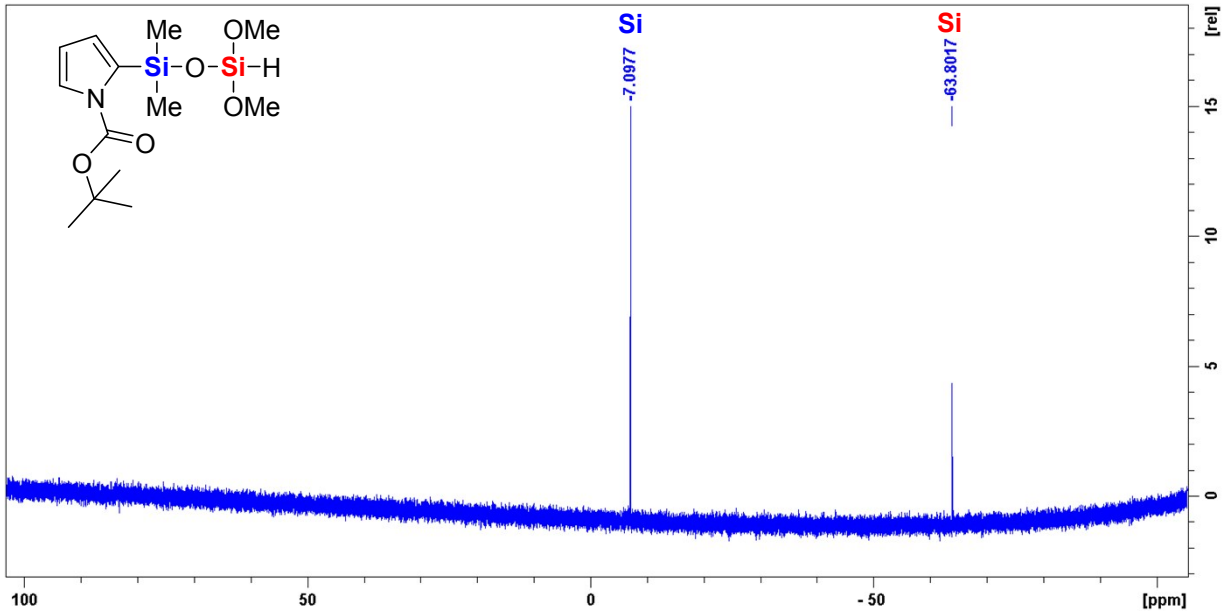
$^{1}$H NMR (benzene-$d_6$)




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

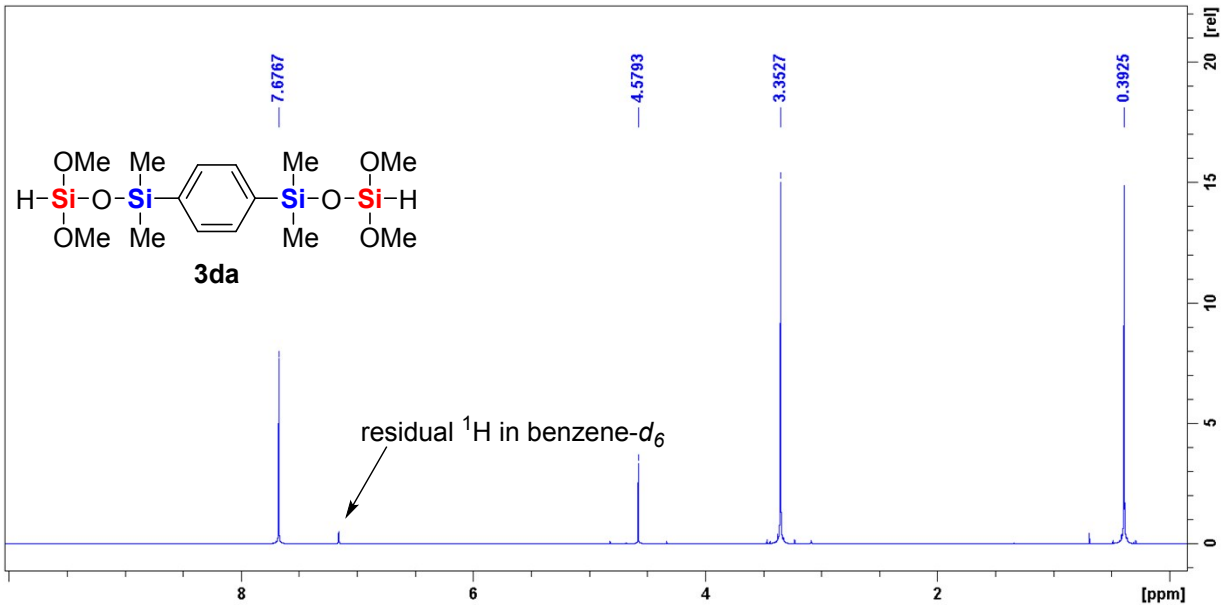


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

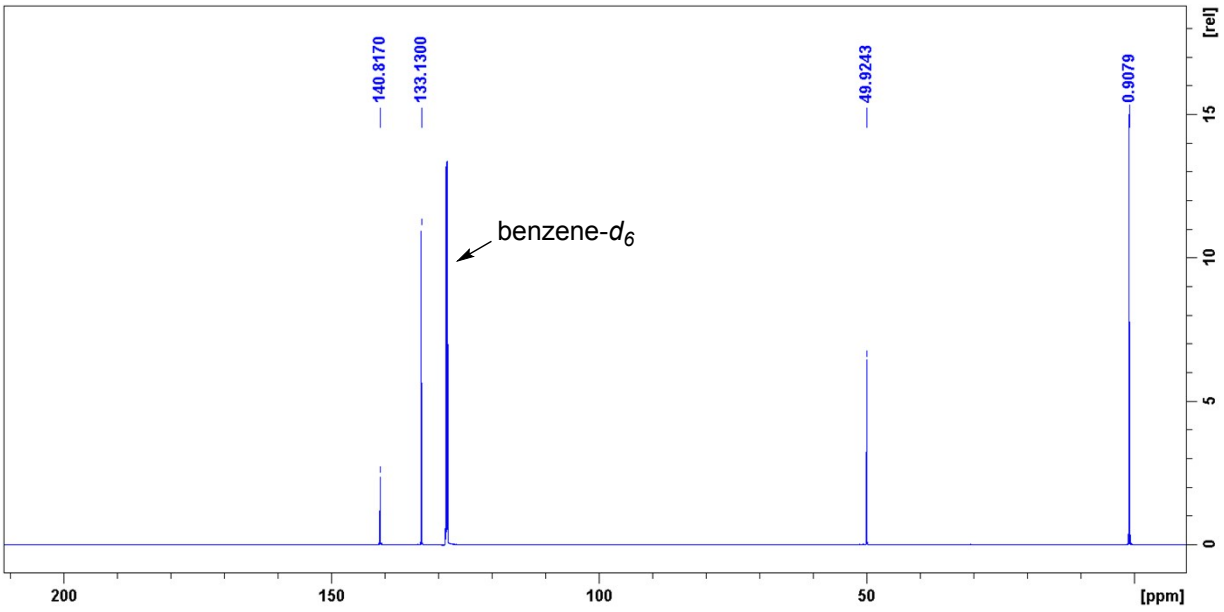


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3da.**

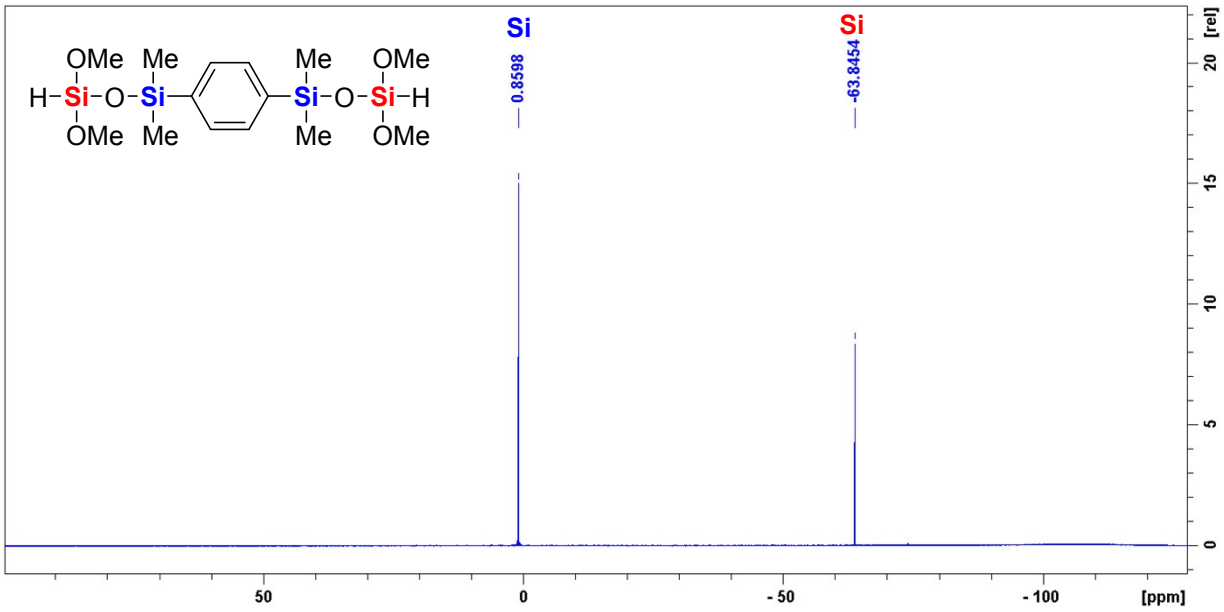
$^{1}$H NMR (benzene-$d_6$)




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

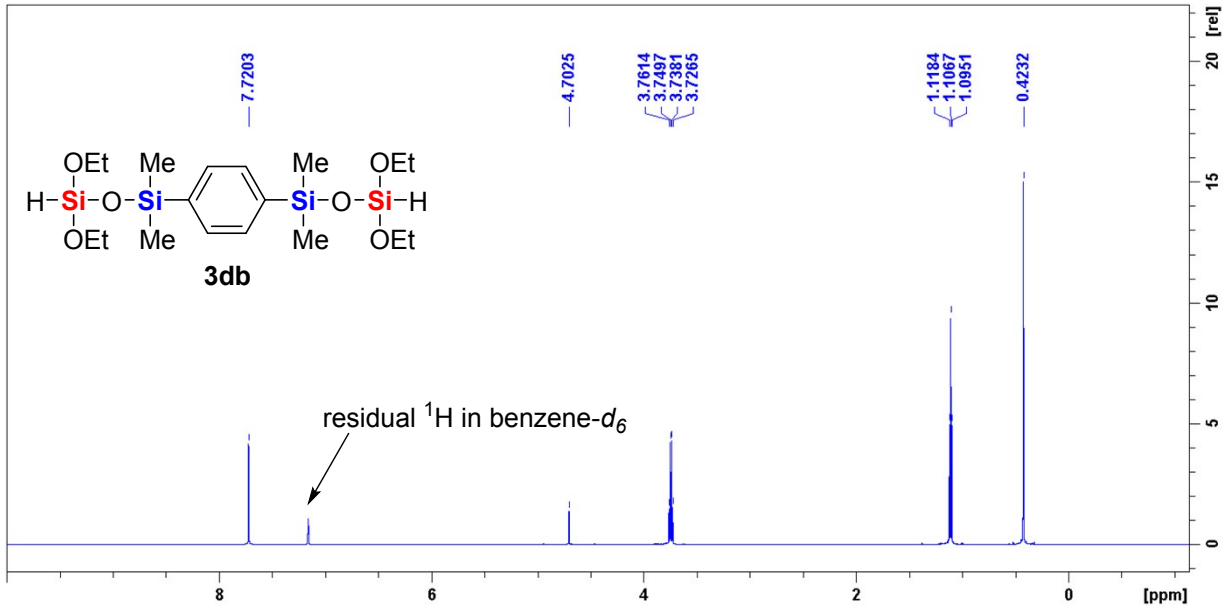


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

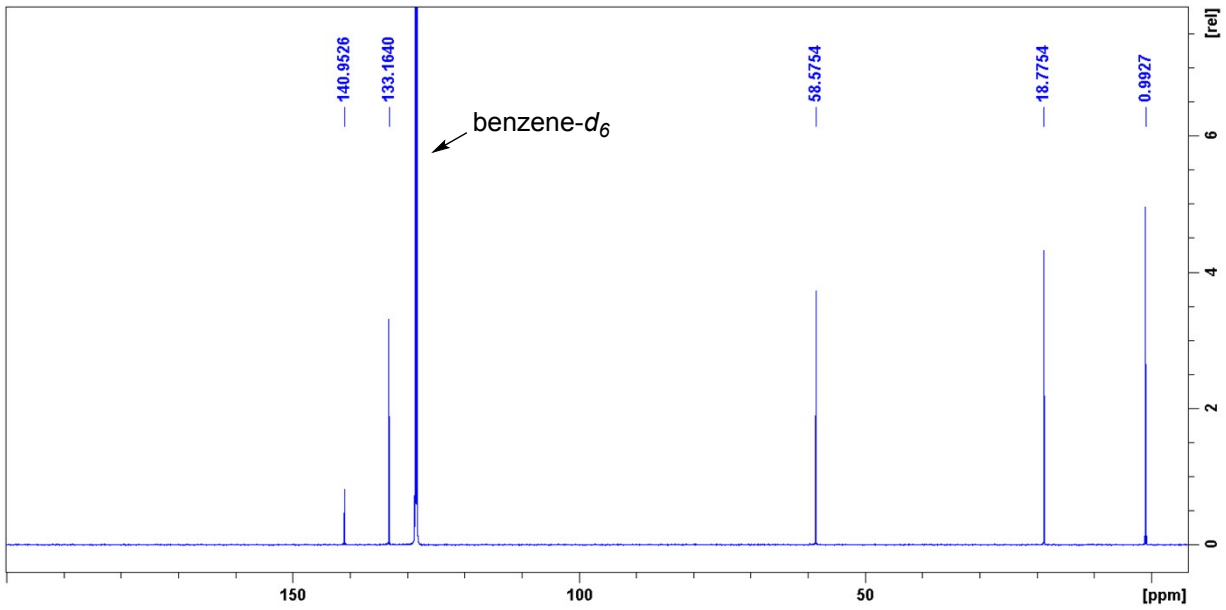


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3db.**

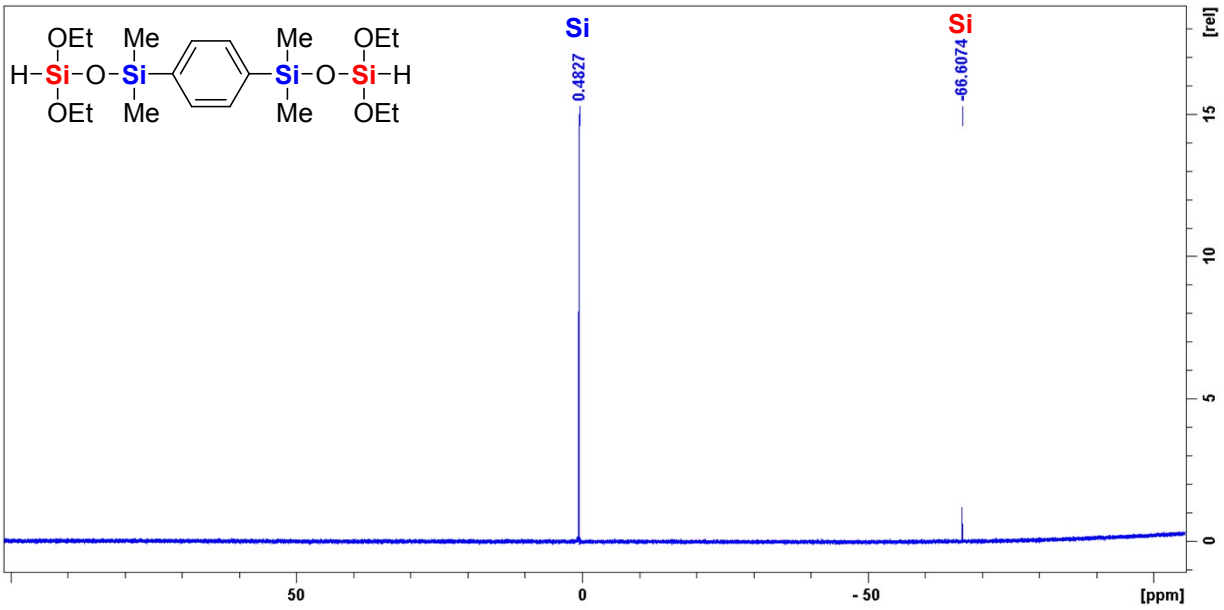
$^{1}$H NMR (benzene-$d_6$)




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

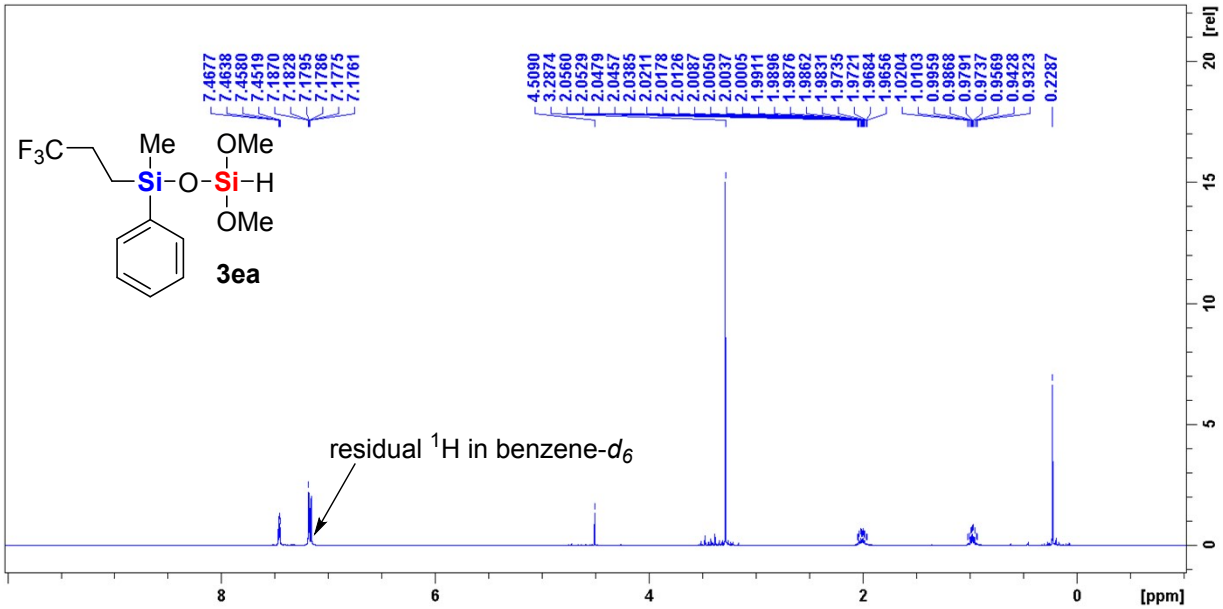


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

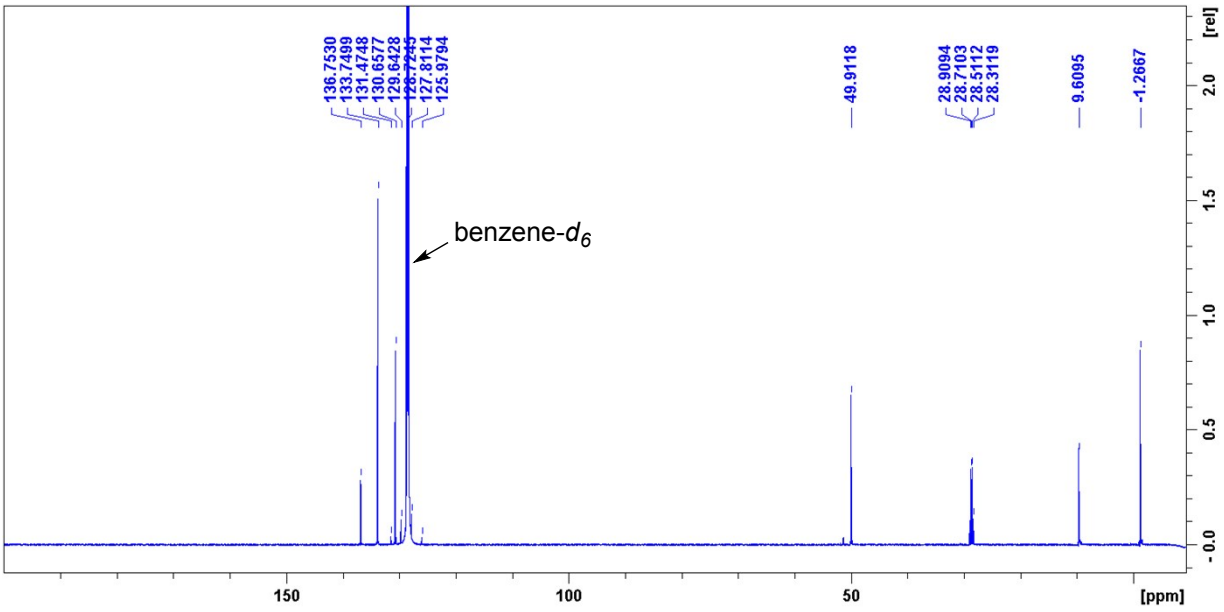


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3ea.**

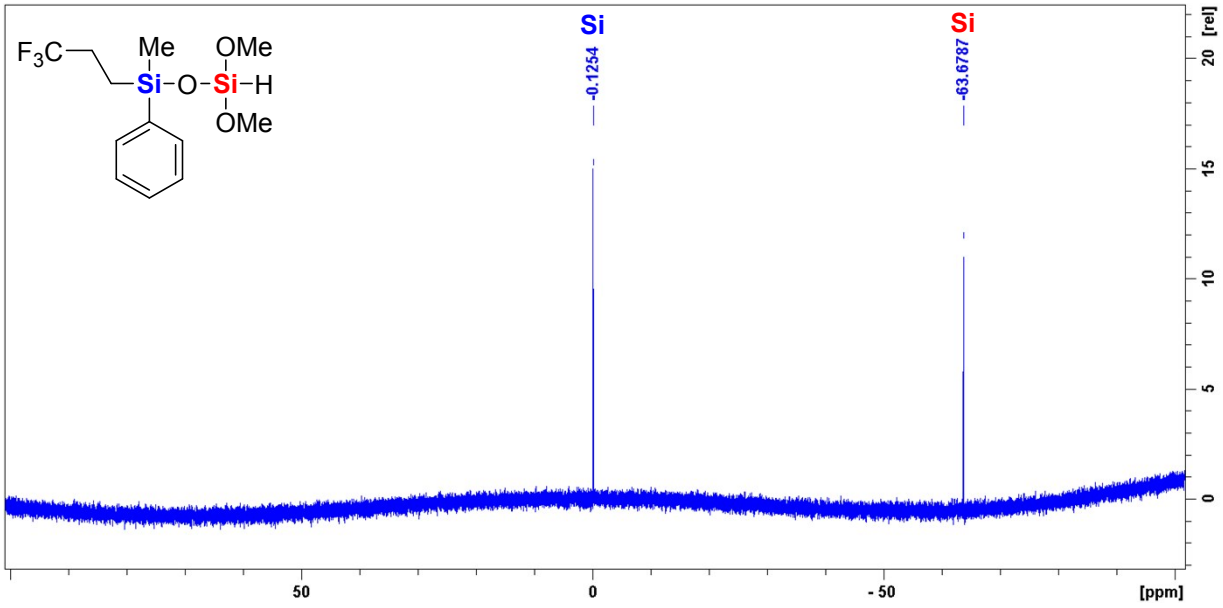
$^{1}$H NMR (benzene-$d_6$)




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

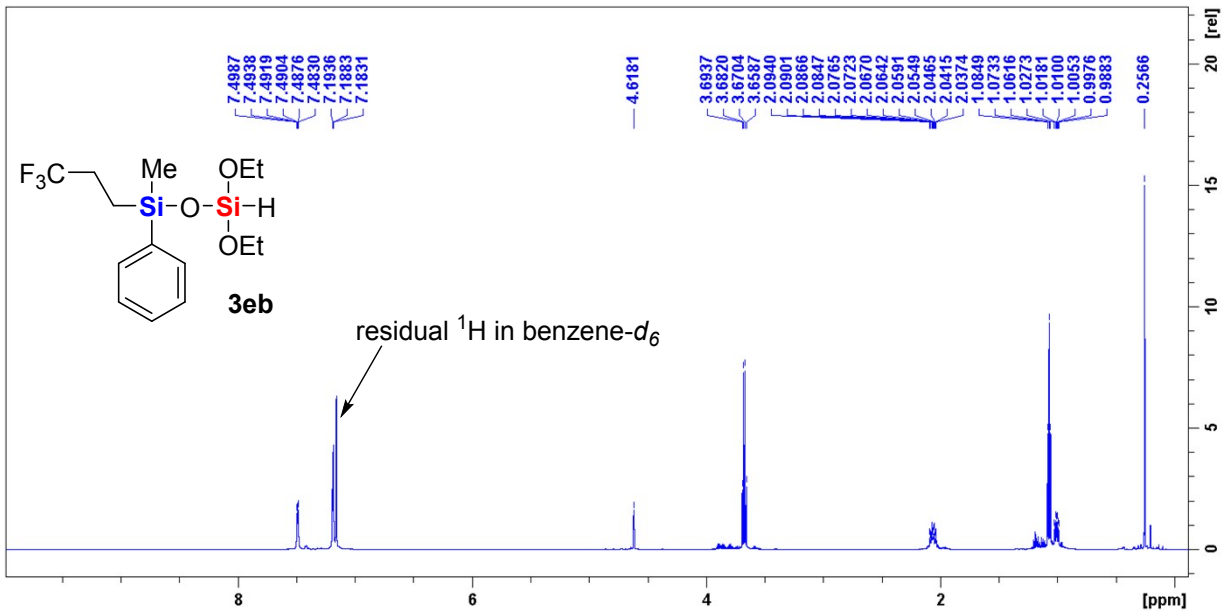


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

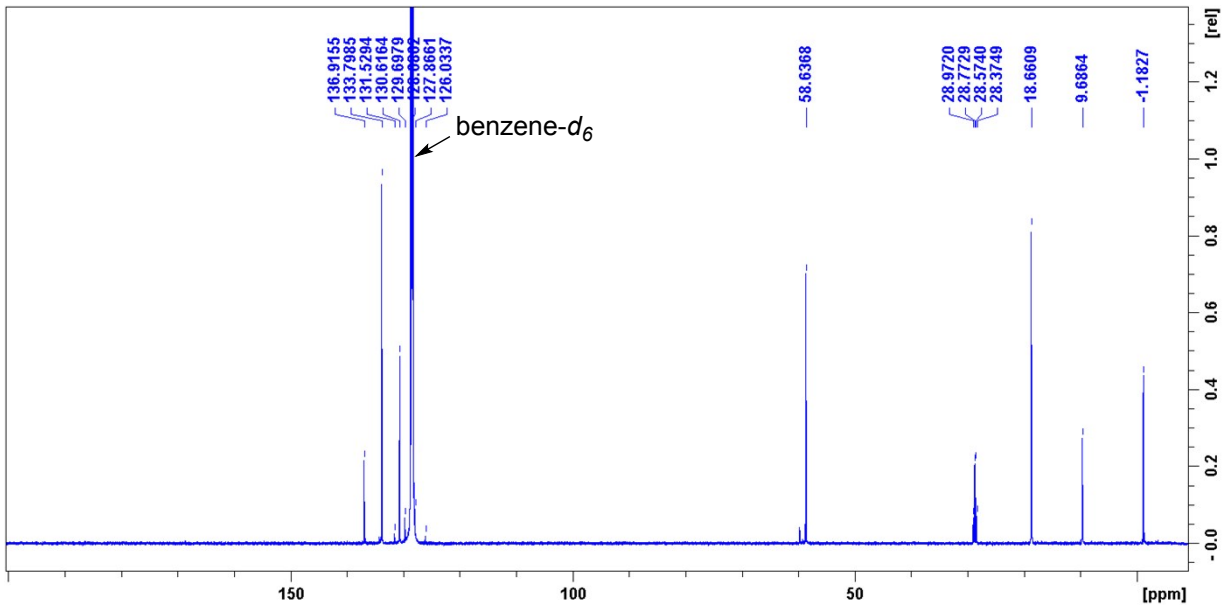


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3eb.**

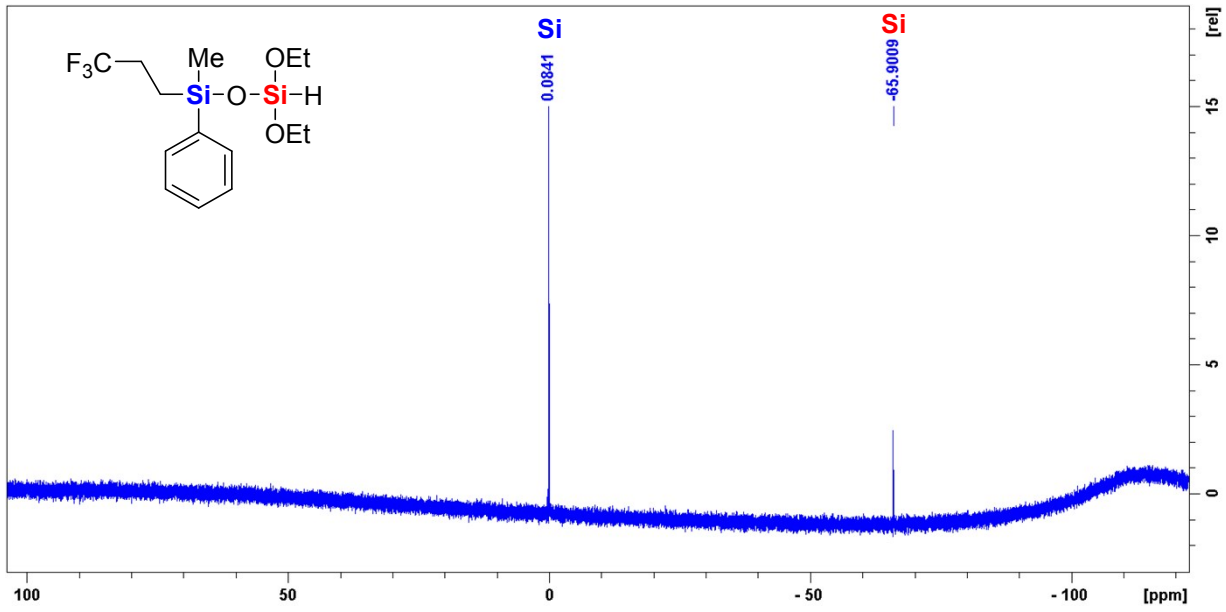
$^{1}$H NMR (benzene-$d_6$)




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

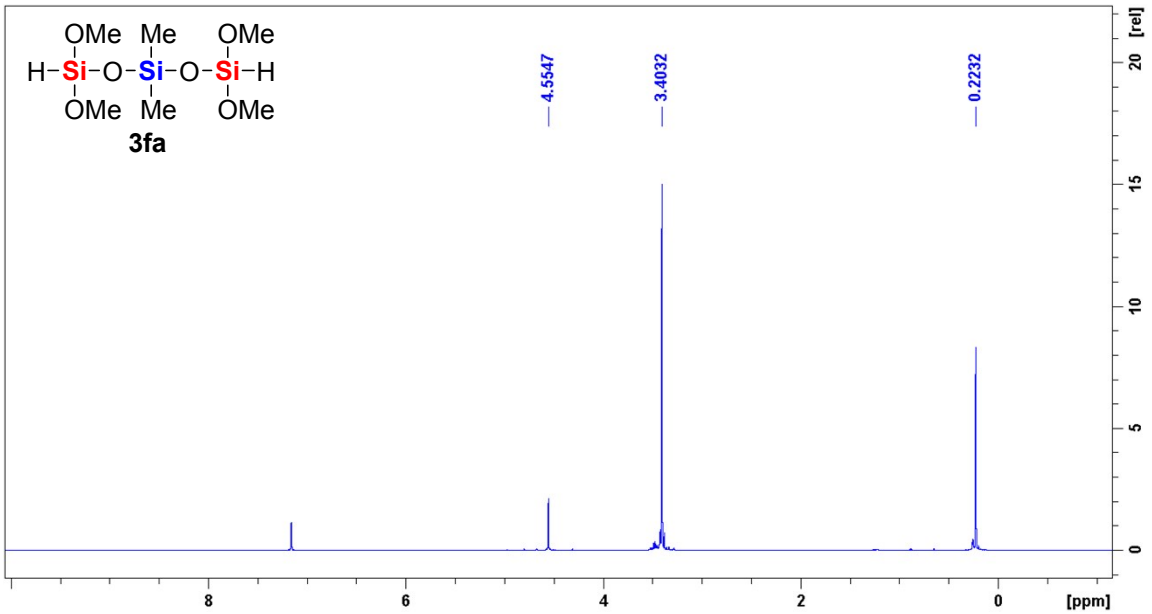


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

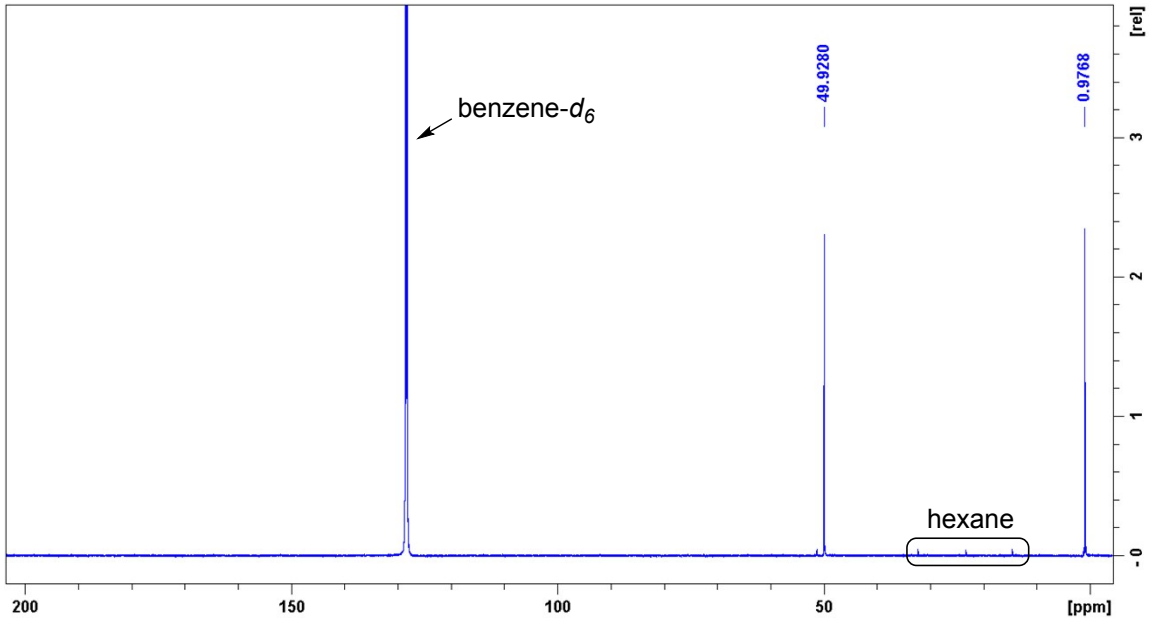


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3fa.**

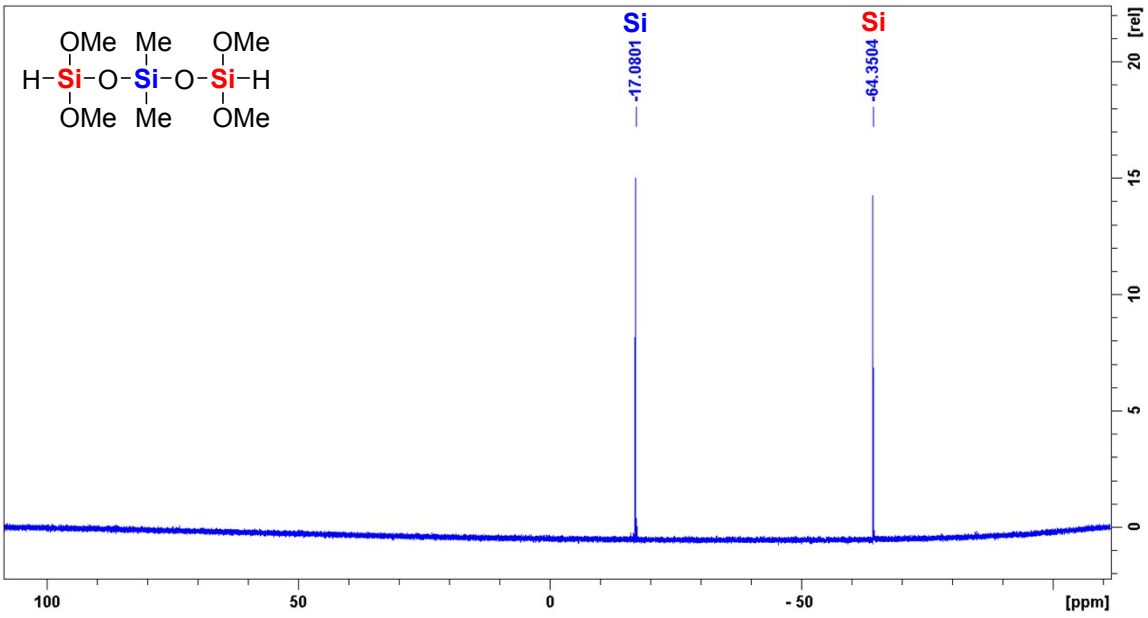
$^{1}$H NMR (benzene-$d_6$)




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

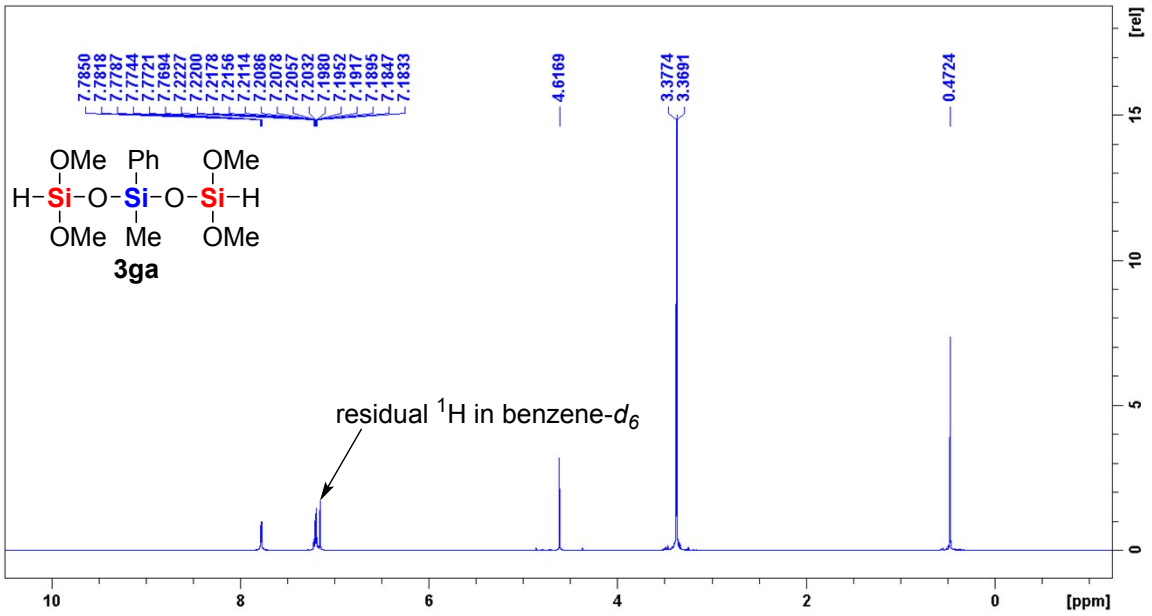


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

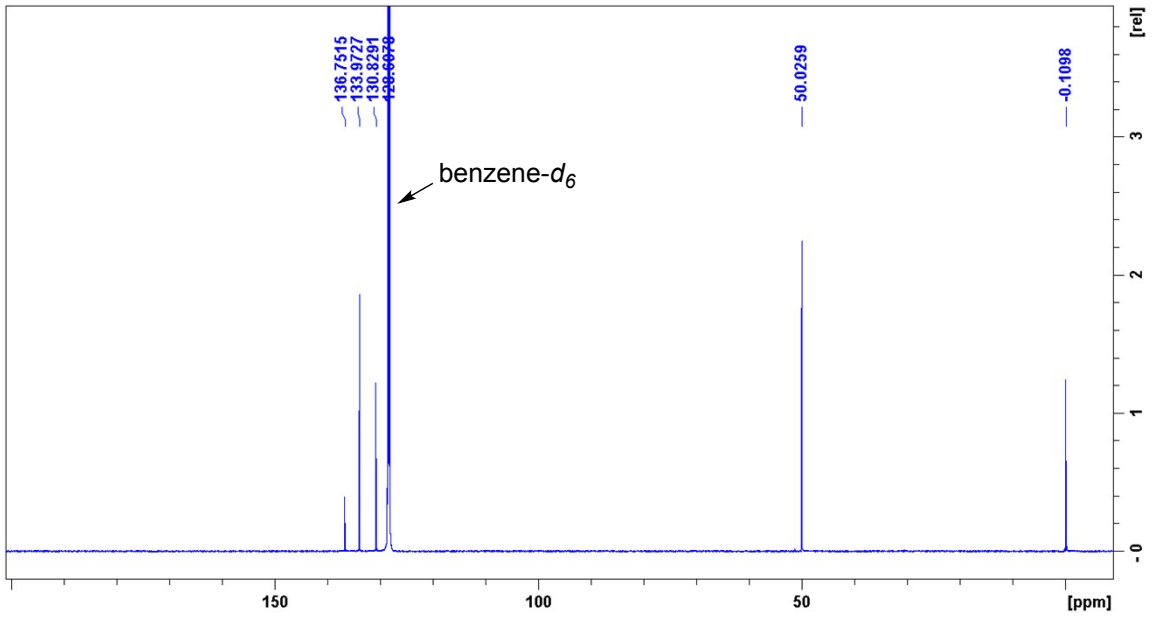


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3ga.**

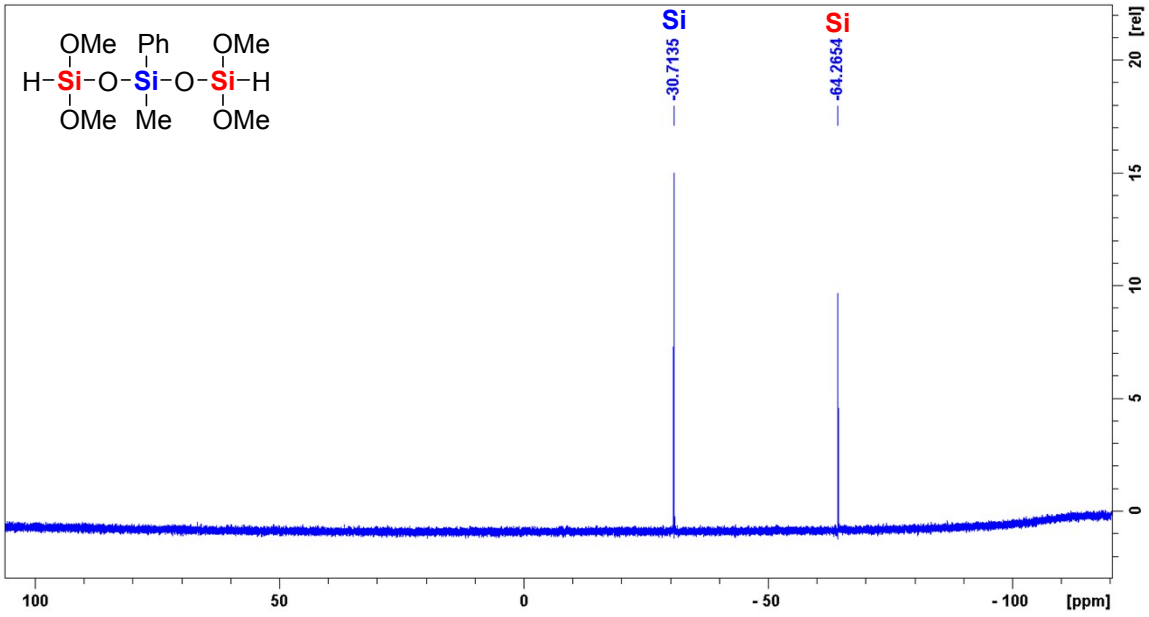
$^{1}$H NMR (benzene-$d_6$)




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

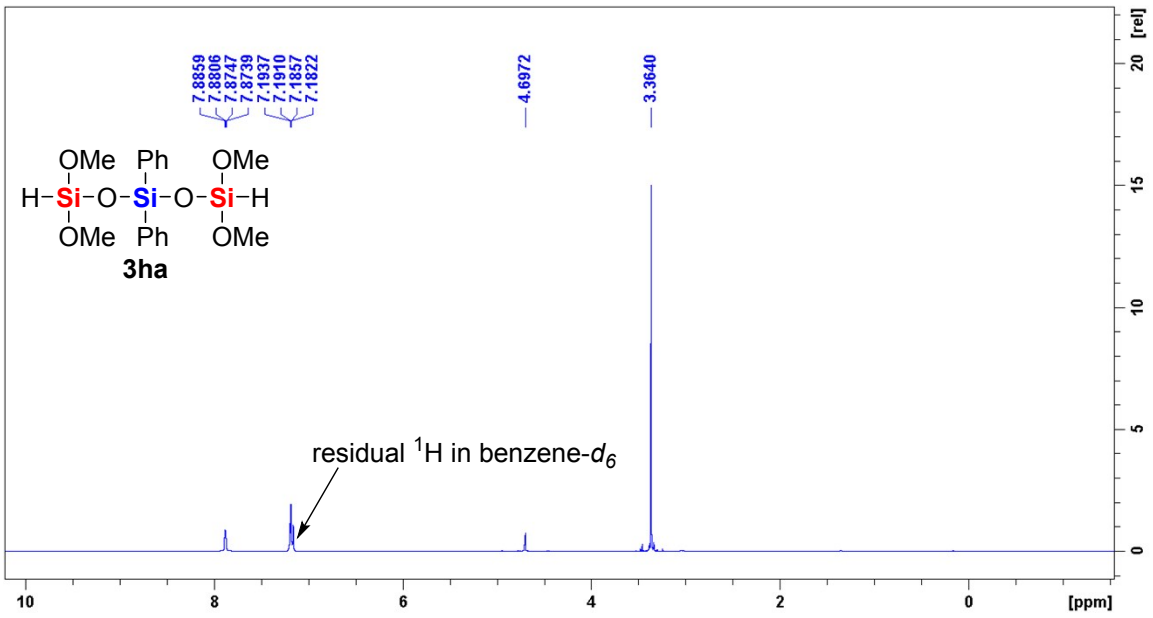


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

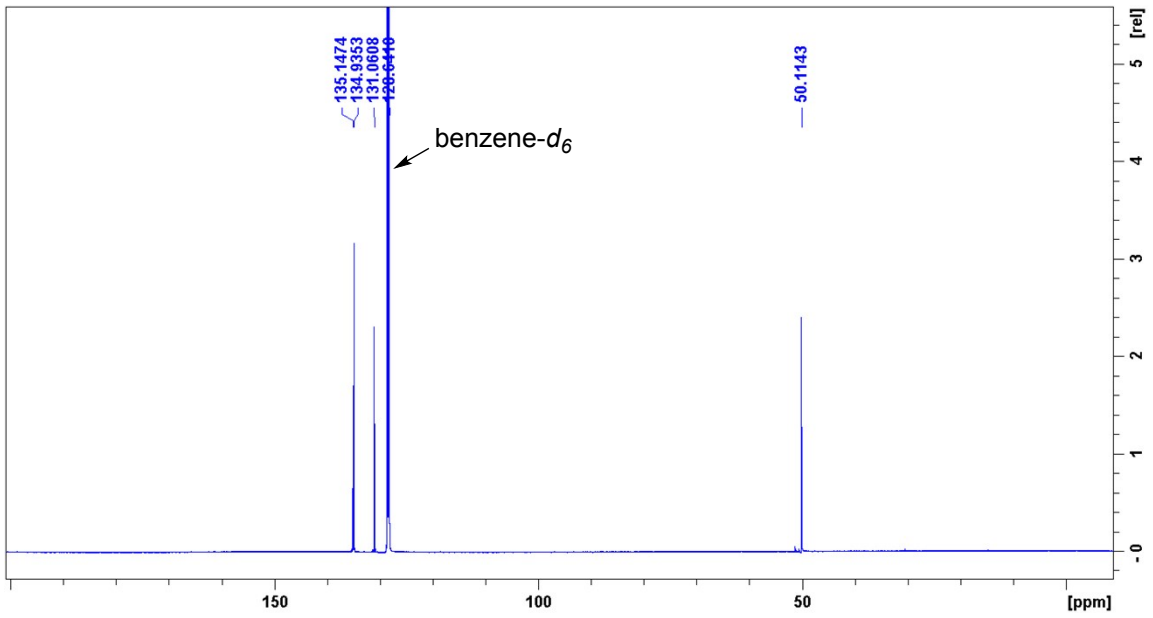


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3ha.**

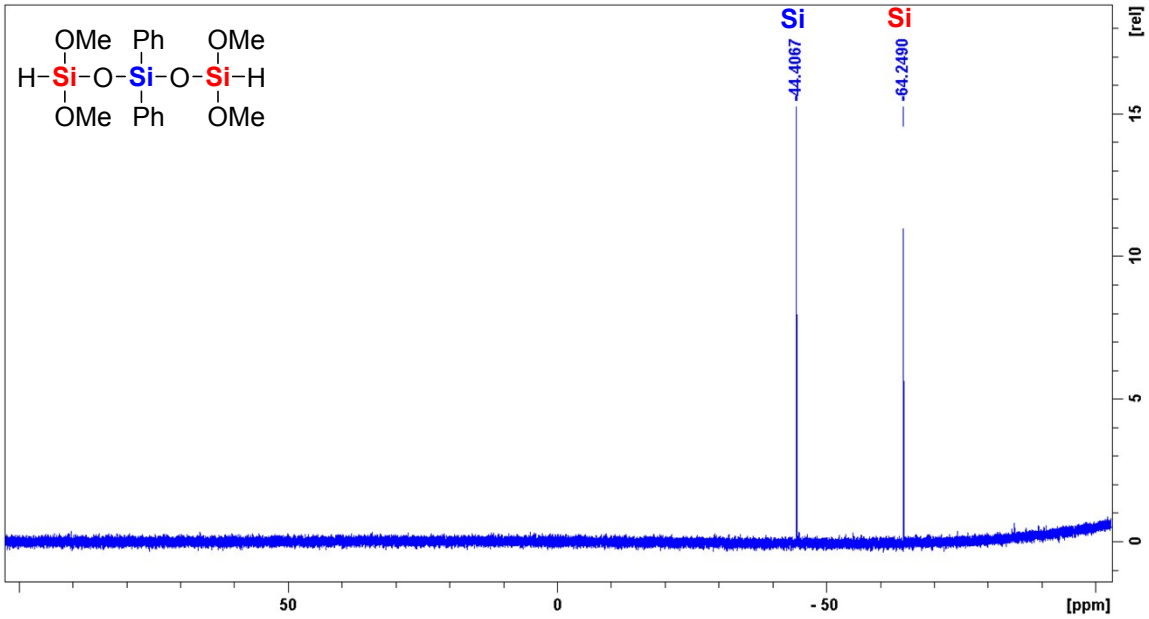
$^{1}$H NMR (benzene-$d_6$)




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

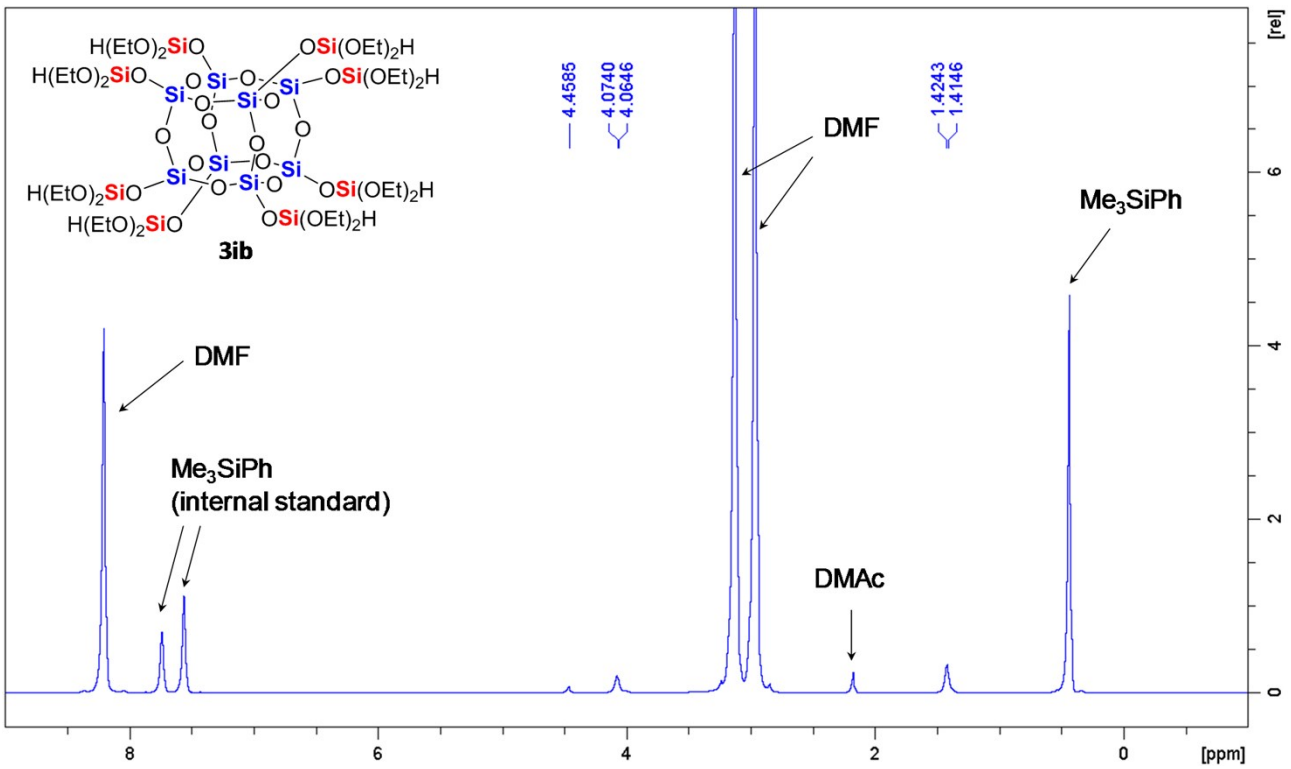


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

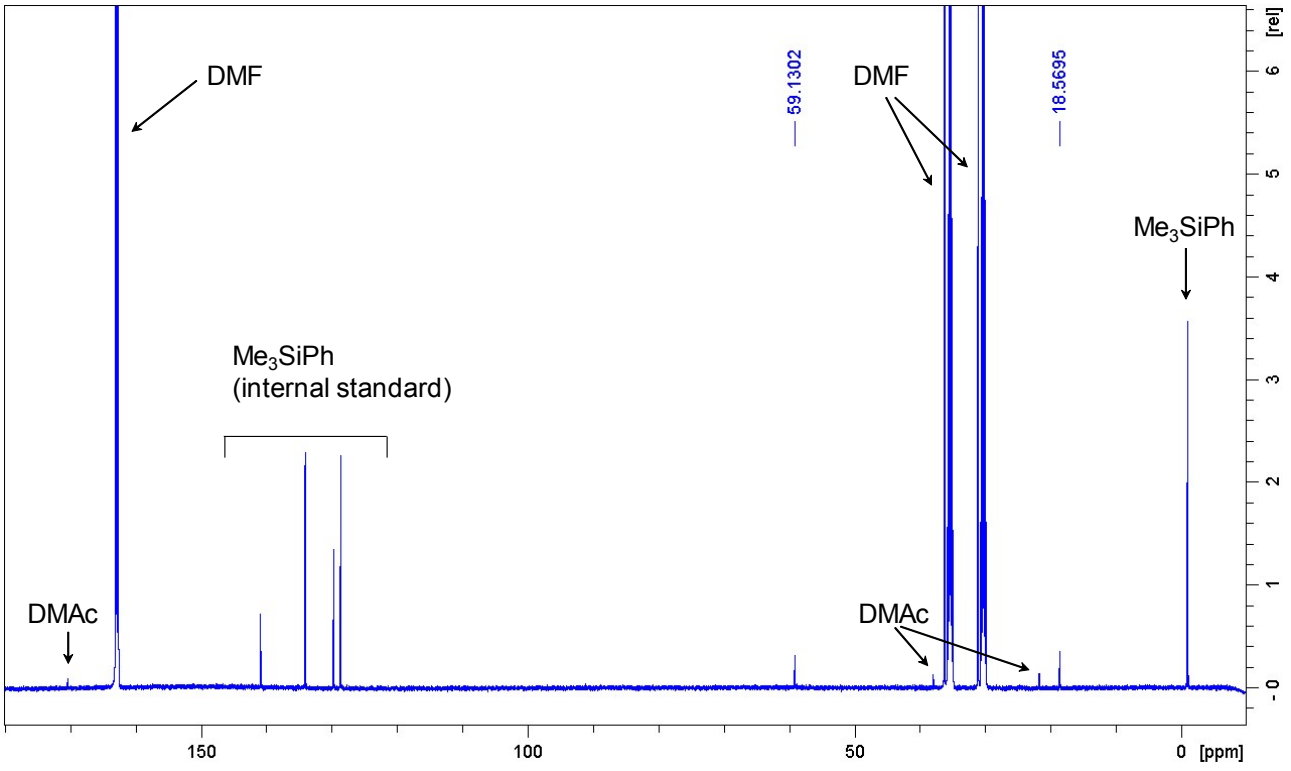


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{1H} NMR spectra of compound 3ib.**

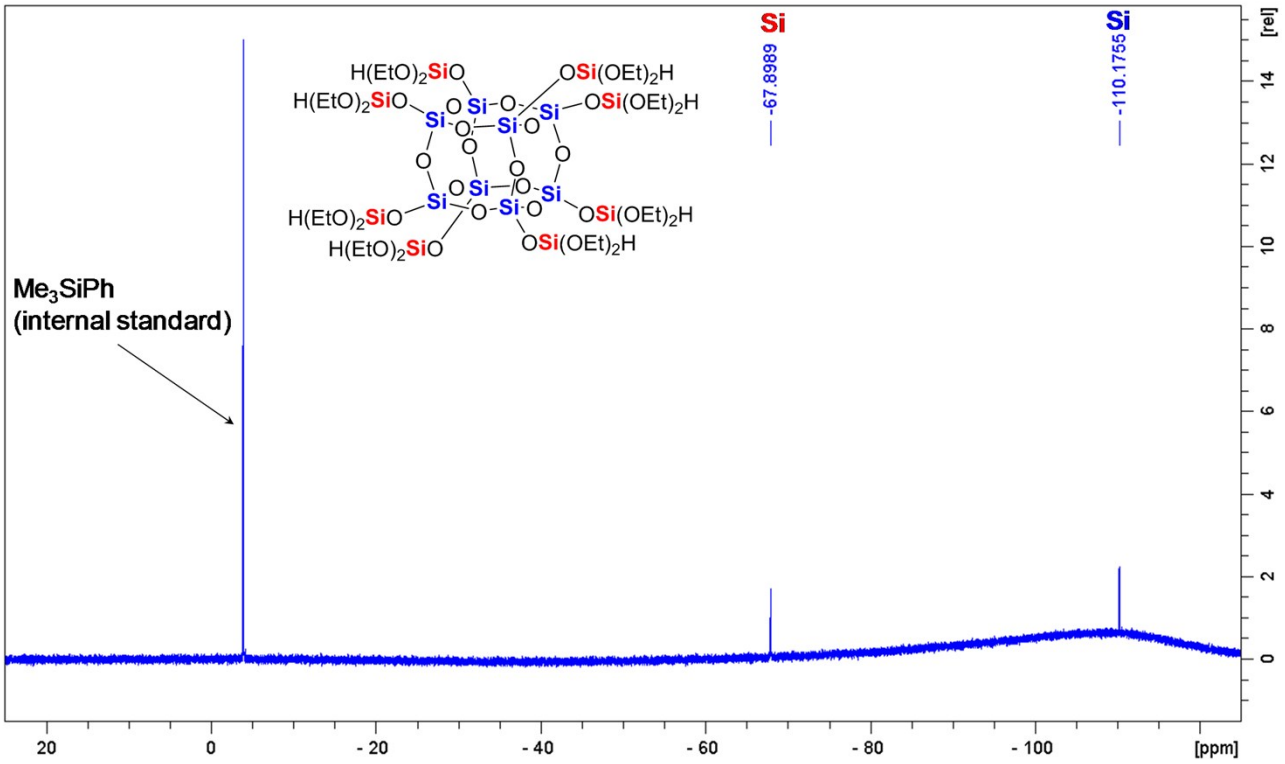
$^{1}$H NMR (DMF-$d_7$)




$^{13}$C{$^{1}$H} NMR (DMF-$d_7$)

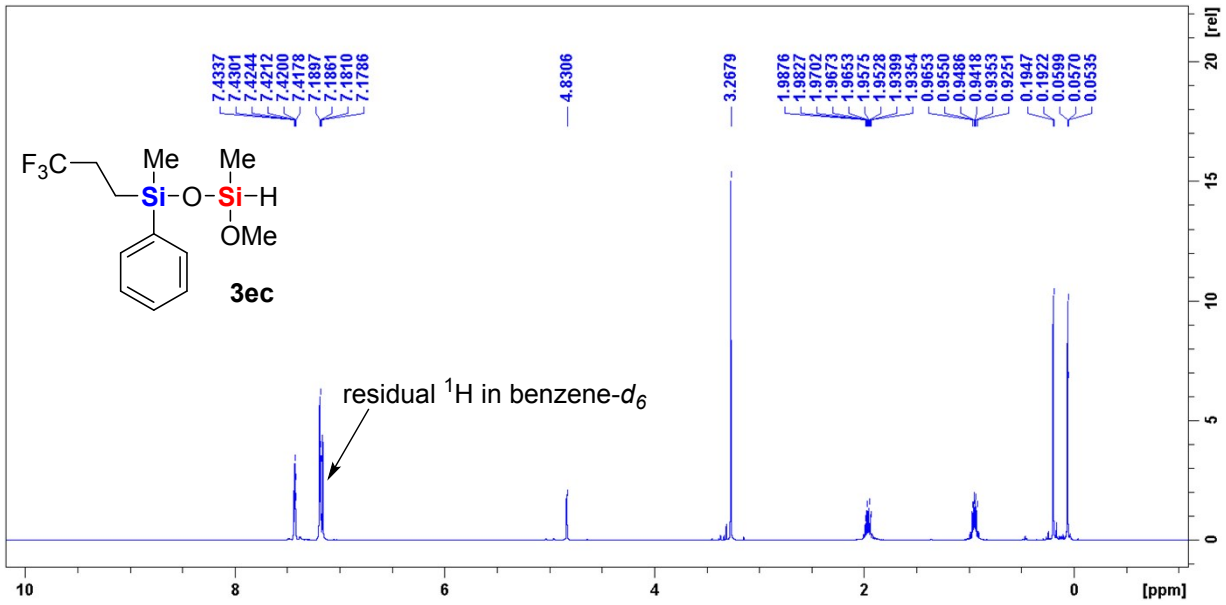


$^{29}Si\{^{1}H\}$ NMR (DMF-$d_7$)

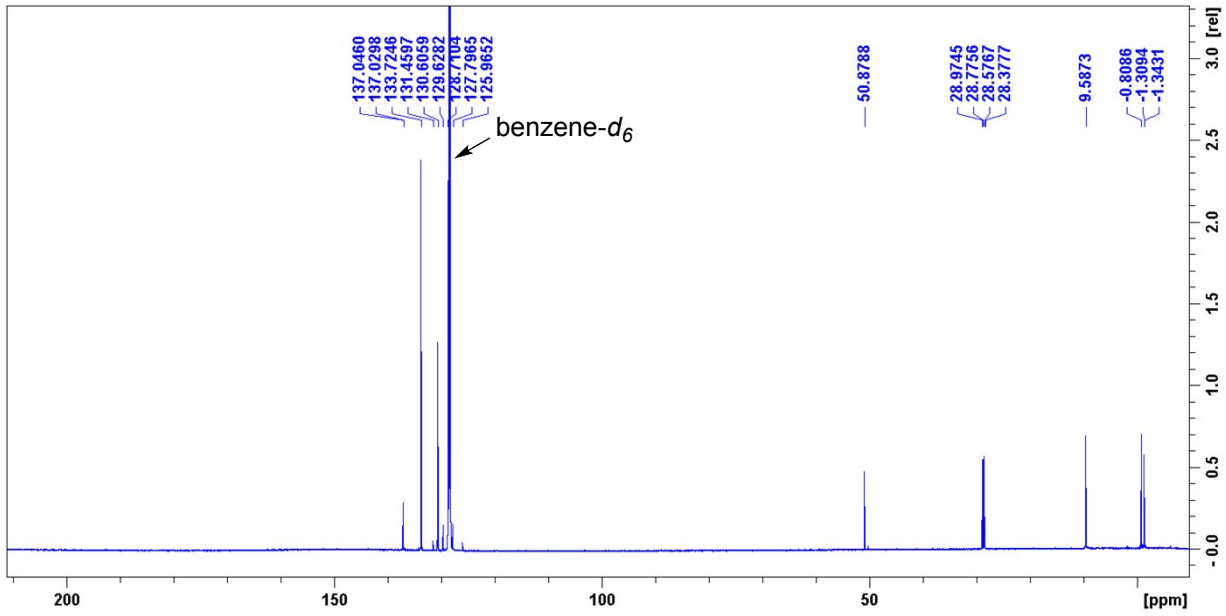


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3ec.**

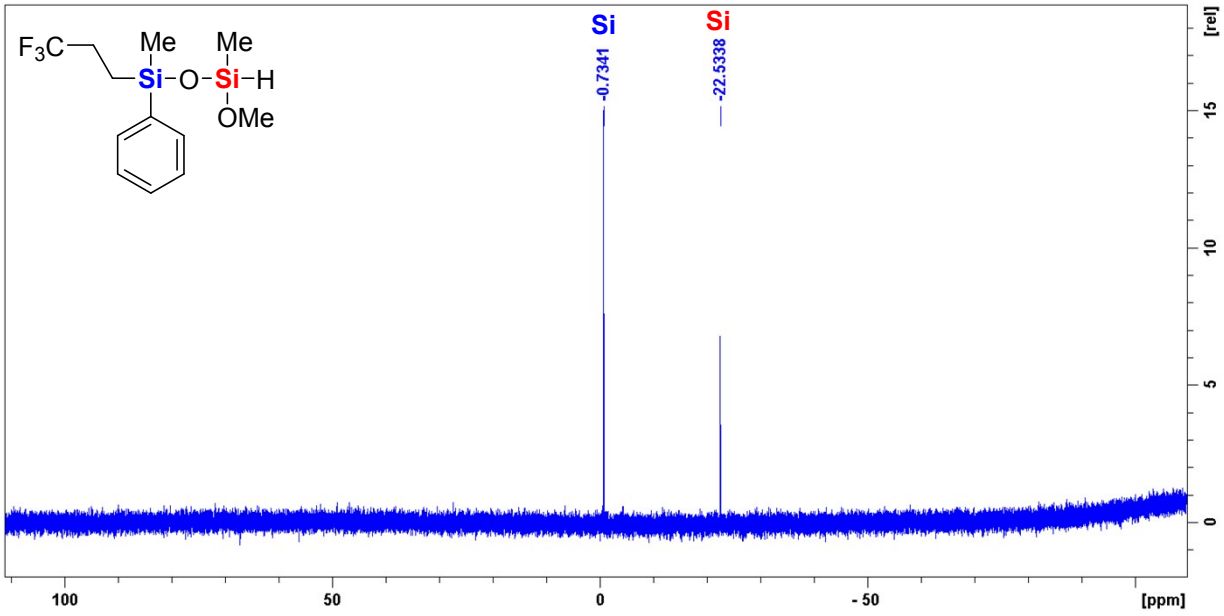
$^{1}$H NMR (benzene-$d_6$)




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

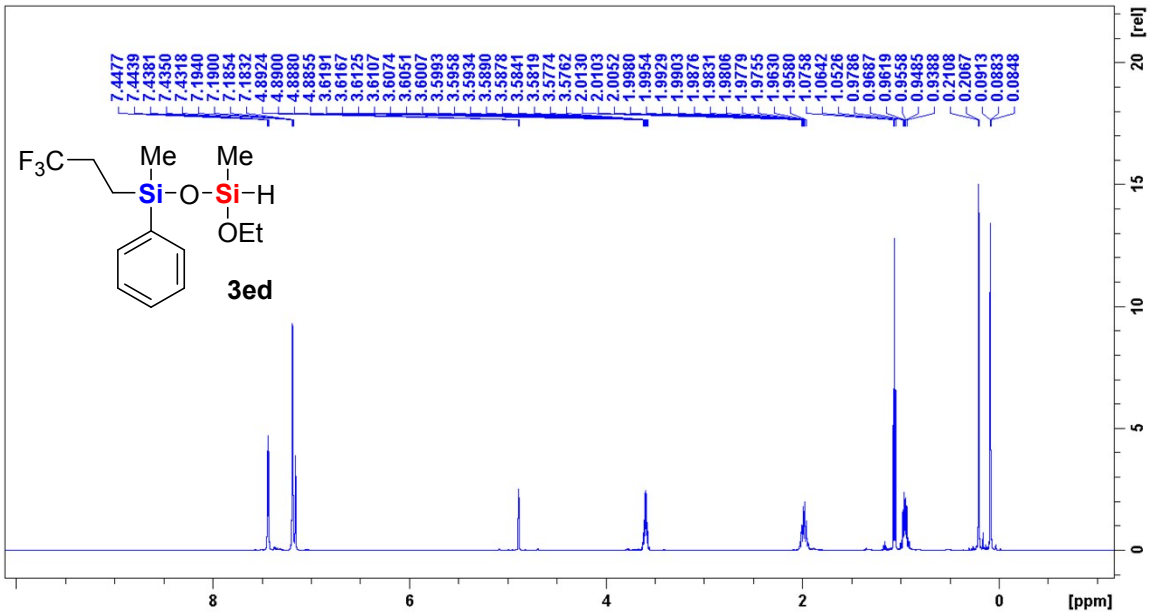


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

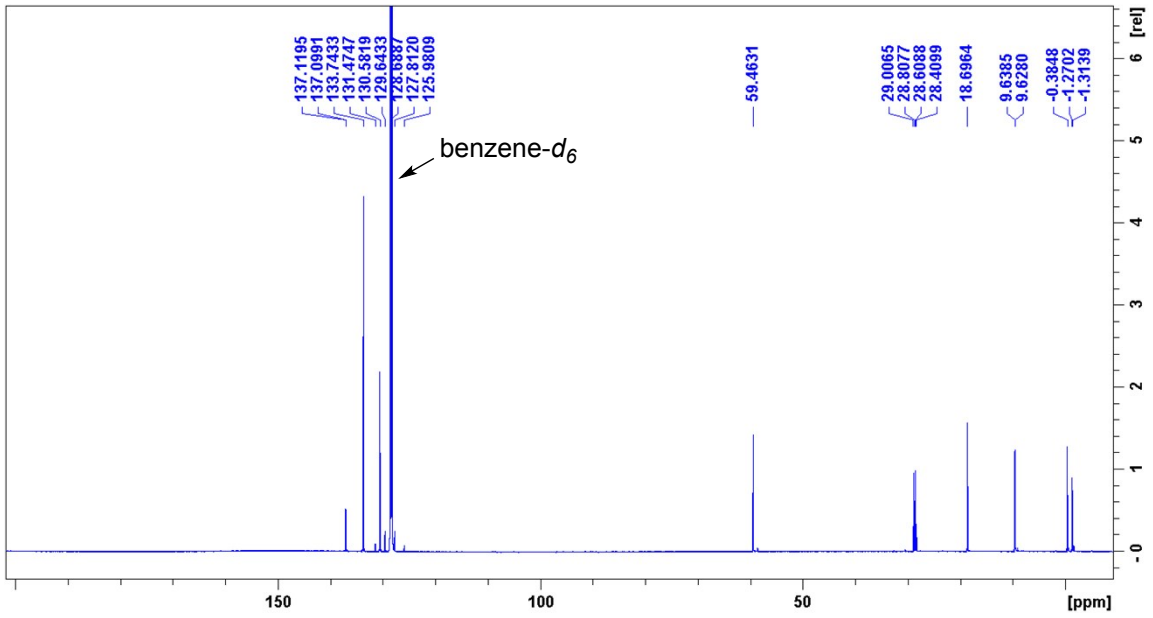


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3ed.**

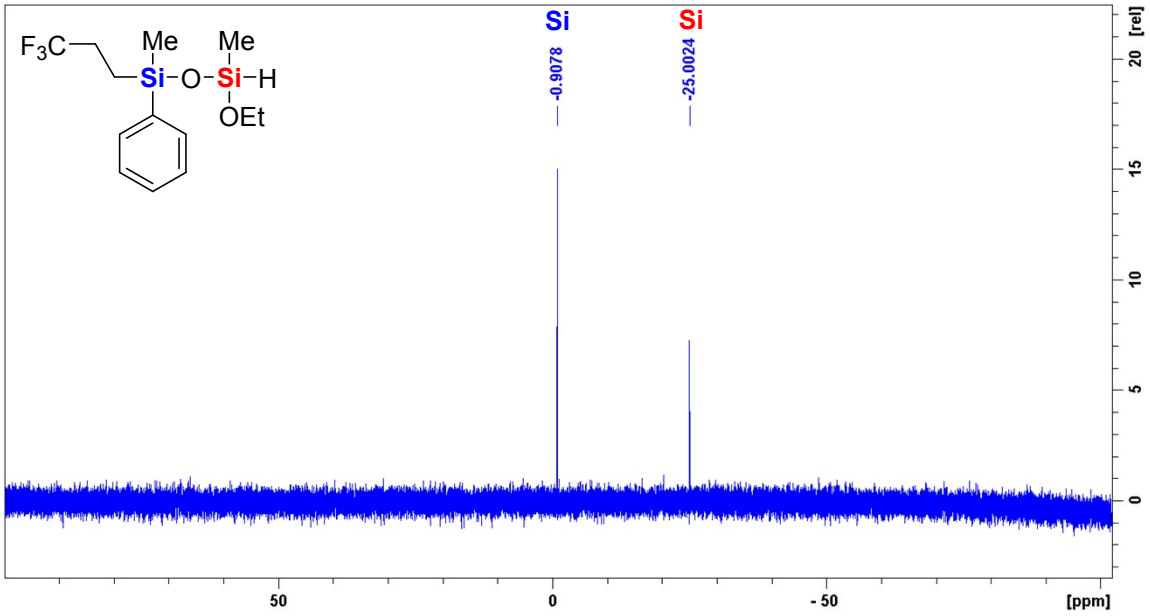
$^{1}$H NMR (benzene-$d_6$)




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

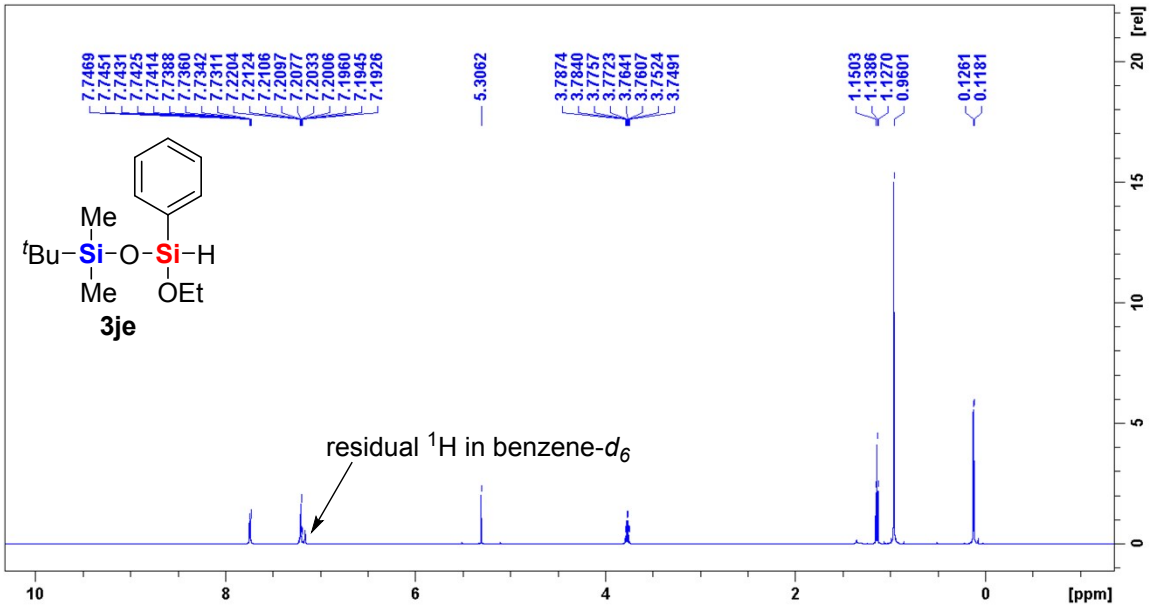


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

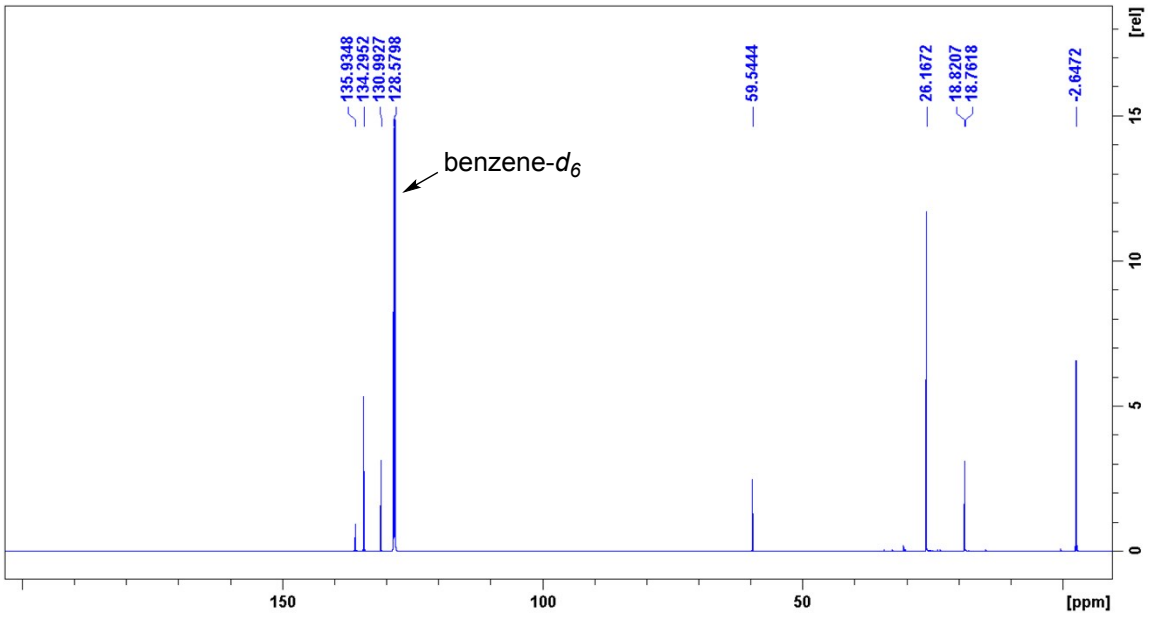


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3je.**

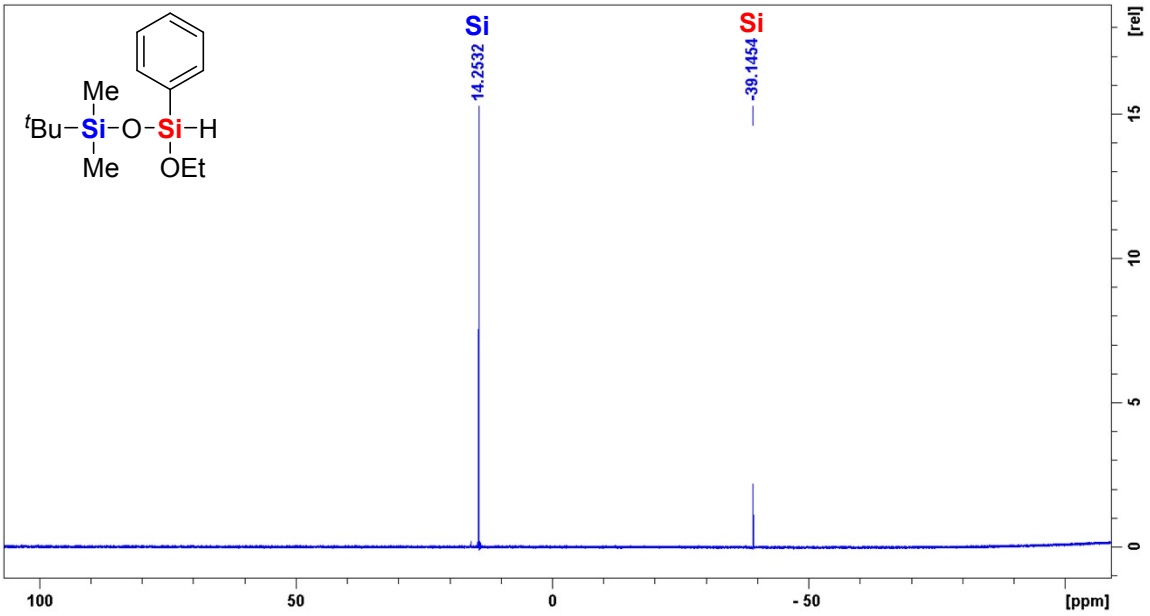
$^{1}$H NMR (benzene-$d_6$)




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

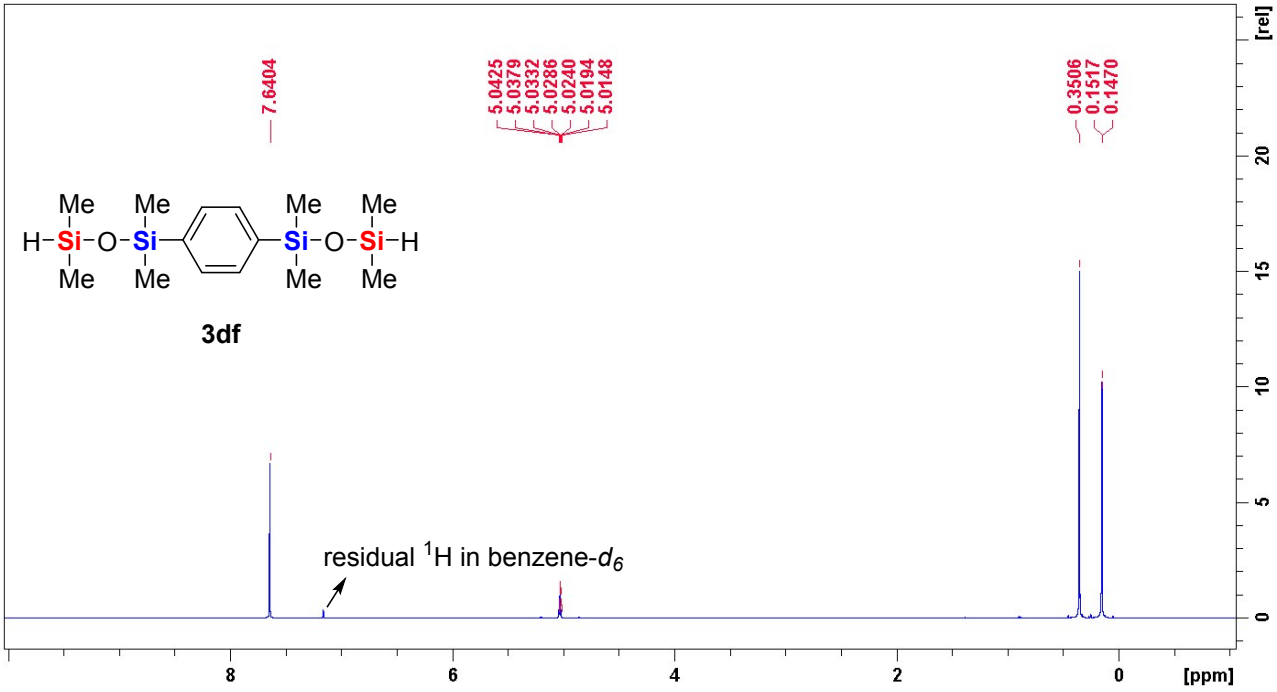


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

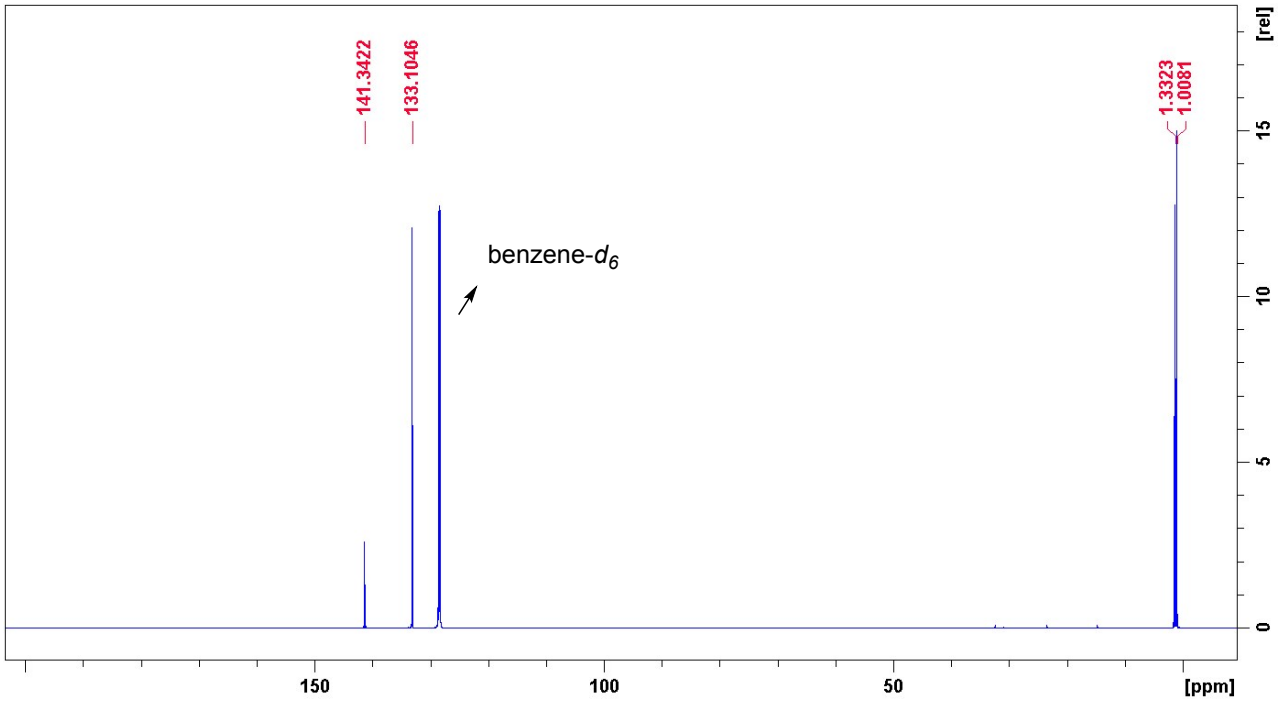


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 3df.**

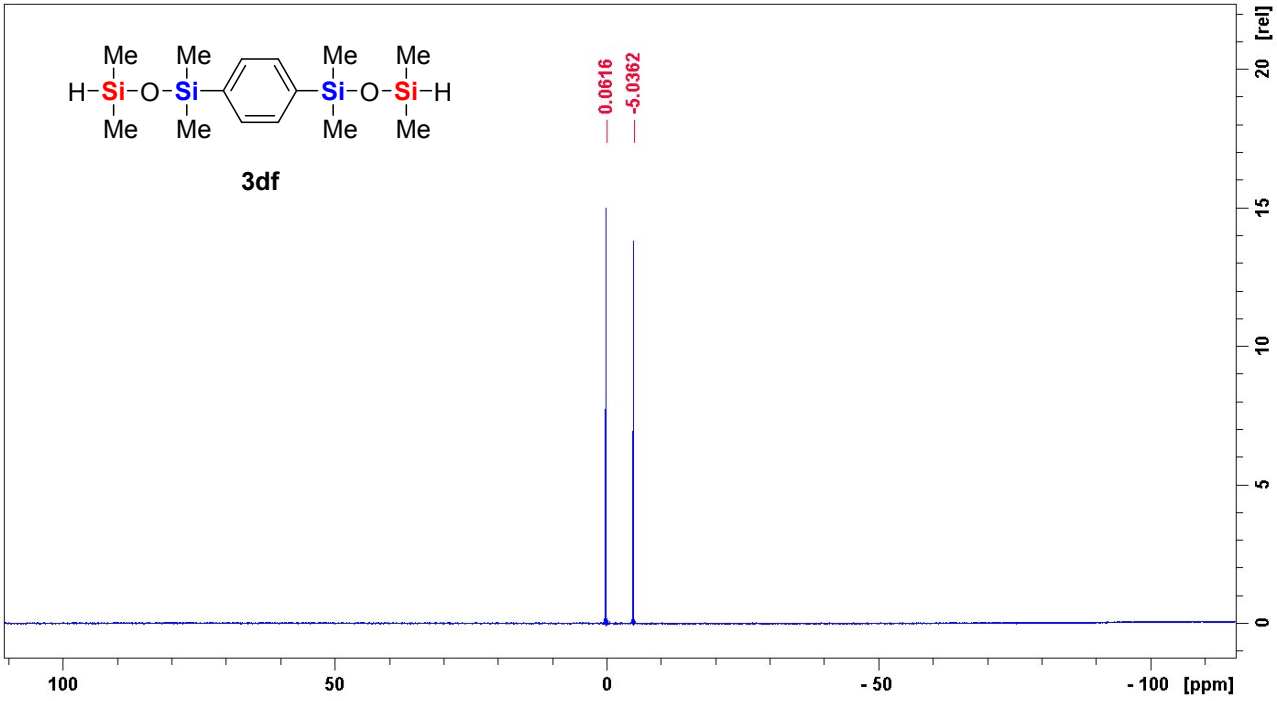
$^{1}$H NMR (benzene-$d_6$)




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

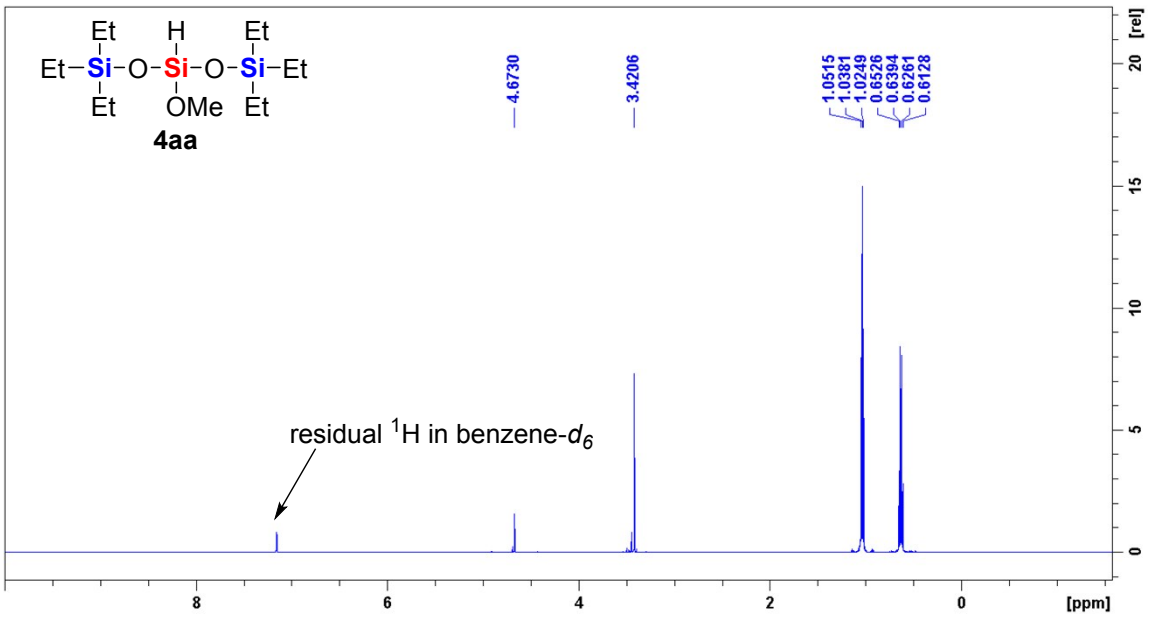


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

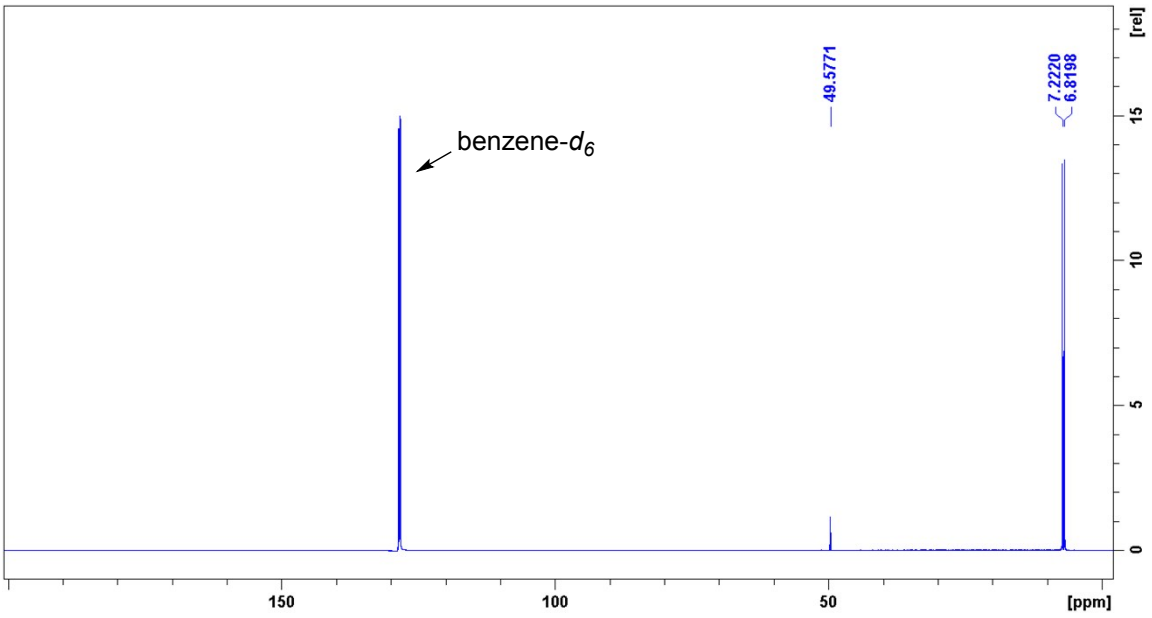


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 4aa.**

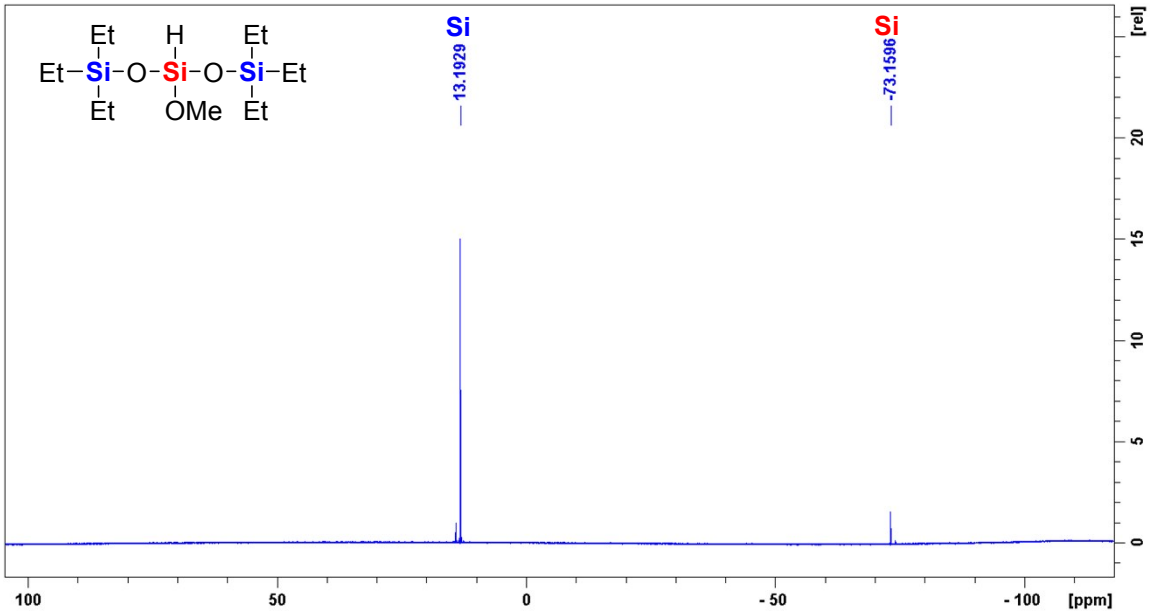
$^{1}$H NMR (benzene-$d_6$)




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

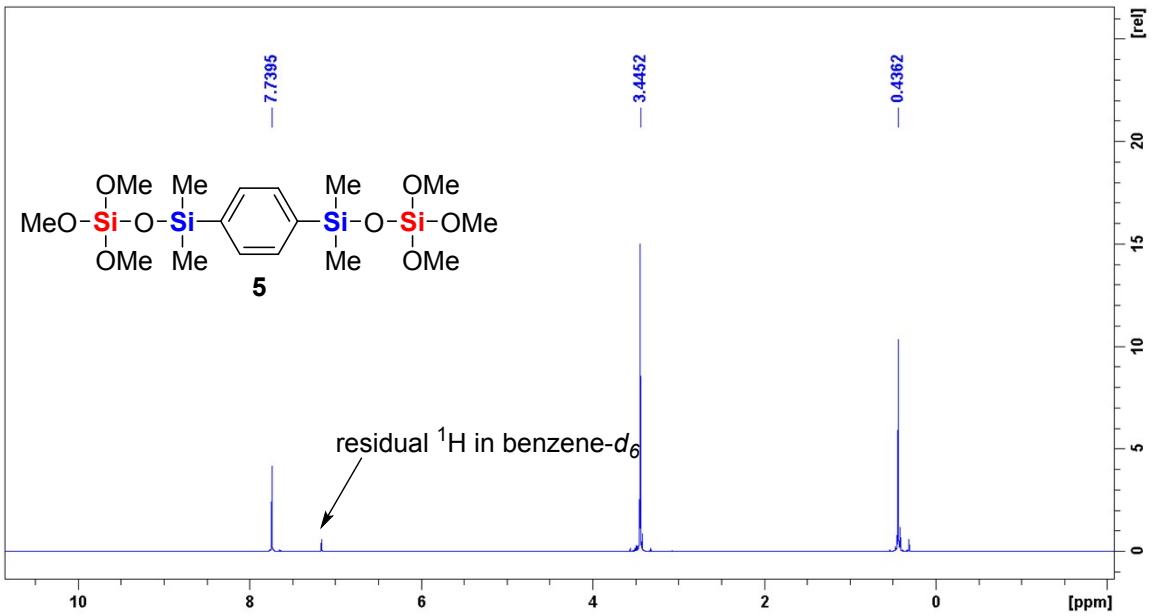


$^{29}Si\{^{1}H\}$ NMR (benzene-$d_6$)

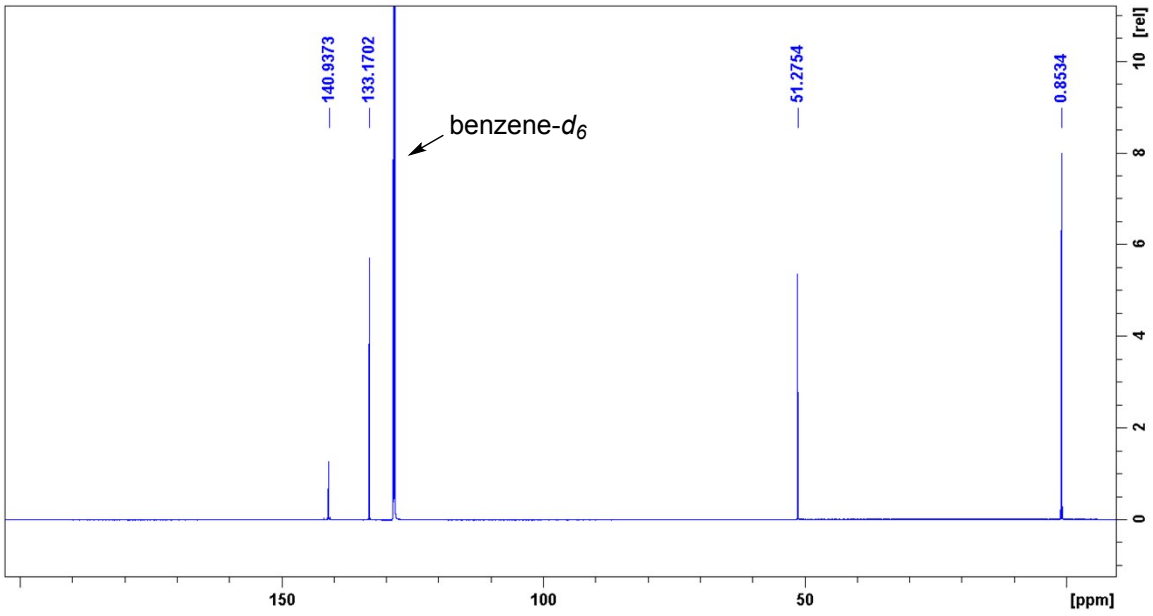


**$^{1}$H, $^{13}$C{$^{1}$H}, and $^{29}$Si{$^{1}$H} NMR spectra of compound 5.**

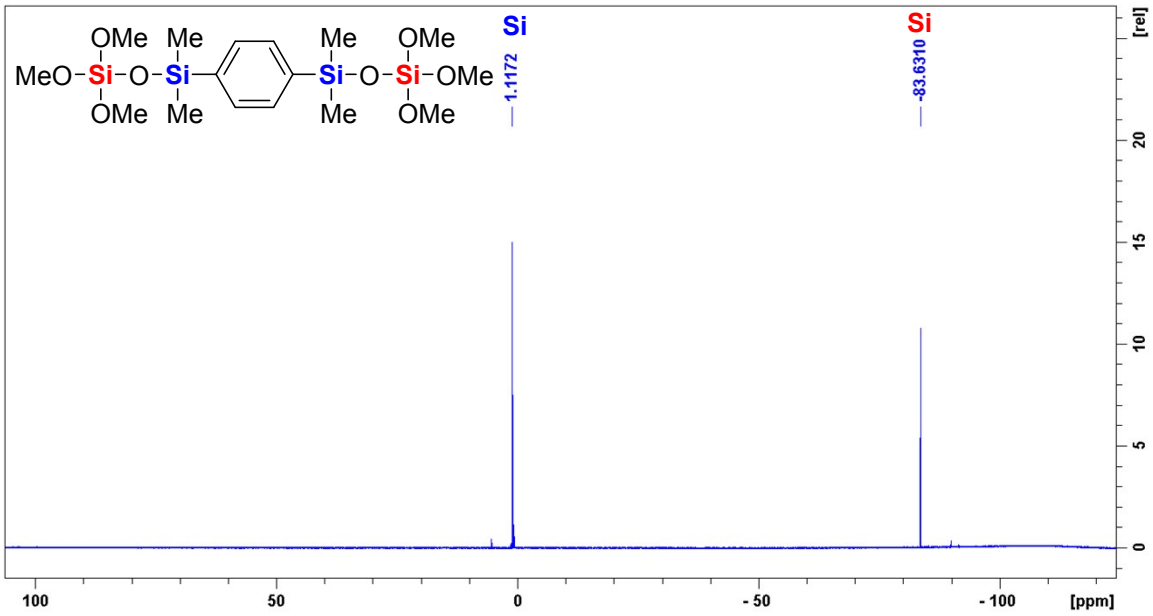
$^{1}$H NMR (benzene-$d_6$)




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



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



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3. K. Hirabayashi, A. Mori, J. Kawashima, M. Suguro, Y. Nishihara and T. Hiyama, *J. Org. Chem.,* 2000, **65**, 5342.

4. T. Nozawa, T. Matsumoto, F. Yagihashi, T. Beppu, K. Sato, and M. Igarashi, *Chem. Lett.*, 2018, **47**, 1530.