

Supplementary Information

Research on inorganic activators of dibromo Co-terpyridine complex precatalyst for hydrosilylation

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General information

All reactions were carried out under an N₂ atmosphere using the Schlenk technique. ¹H NMR and ¹³C{¹H} NMR spectra were recorded using a JEOL JNM-AL 400 spectrometer. The residual peaks of the solvent or TMS were used as internal standards. GC analyses were carried out using a Shimadzu GC-2014 equipped with a DB-1 (Agilent, 30 m, 0.25 mm ID, 0.25 μm) capillary column. The product yields were determined based on the calibration curve of each authentic sample.

Materials

[Co(tpy)Br₂] was synthesized according to a reported procedure.¹ Hydrosilylation products **11**,² **1b**,³ **2**,⁴ **3**,⁵ **4**,⁶ **5**,⁷ **7**,⁴ and **8**⁶ were synthesized as authentic samples according to the literature.

General procedure of hydrosilylation

[Co(tpy)Br₂] (2.4 mg, 5.4 μmol, 0.1 mol%) and the inorganic salt (0.108 mmol, 2.0 mol%) were placed in a Schlenk tube. The air in the Schlenk tube was then replaced with N₂. 1-Octene (0.85 mL, 5.4 mmol) and diphenylsilane (1.0 mL, 5.4 mmol) were added to the Schlenk tube under N₂. The solution was stirred at a controlled temperature (25 or 100 °C). After 24 h, the reaction was stopped by exposure to air. The product yields were determined using GC.

Investigation of solubility of additives

KOPv (76 mg, 0.54 mmol, 2 mol%) was suspended in a 1-octene/ Ph_2SiH_2 mixture (1-octene: 4.3 mL, 27 mmol, Ph_2SiH_2 : 5 mL, 27 mmol). The mixture was stirred at 25 °C for 2 h, then the insoluble solid was filtered off and washed with hexane. The filtered solid was collected completely by dissolving in MeOH. The MeOH was evaporated and the residue was dried in vacuo to obtain KOPv (42 mg, 55 %). The same operation was performed for KOAc (53 mg, 0.54 mmol). More than 99% of KOAc was recovered even by stirring at 100 °C for 2 h, indicating that KOAc was hardly soluble in a mixture of 1-octene and Ph_2SiH_2 .

For other inorganic salts (additives) listed in Table 1, an insoluble solid was collected by dissolving in H_2O . After removal of the H_2O , the residue was dried in vacuo. In all cases, more than 99% of the inorganic salts were recovered even by stirring at 100 °C for 2 h. Thus, these inorganic salts were found to be extremely sparingly soluble in a mixture of 1-octene and Ph_2SiH_2 .

Reaction of Ph_2SiH_2 with KO^tBu monitored by ^{29}Si NMR

KO^tBu was dispersed in $\text{THF-}d_8$ in a Schlenk tube at 0 °C. Then, Ph_2SiH_2 was added dropwise into the heterogeneous solution at 0 °C, which caused KO^tBu dissolution with small gas evolution. After the finish of gas evolution, the mixture was transferred to an NMR tube under N_2 . The ^{29}Si NMR spectra with and without ^1H irradiation were measured 3 h and 24 h after the

bubbling ceased. Comparison with ^{29}Si NMR spectra of authentic samples (Table S1) revealed that the reaction solution contained Ph_3SiH (at -17.9 ppm), $\text{Ph}_2\text{SiH}(\text{O}^t\text{Bu})$ (at -23.9 ppm), Ph_2SiH_2 (at -33.7 ppm) and unknown species at -47.5 ppm (s) and -68.5 ppm (s) (Figure S1).

Same experiments using KOPv and K_2CO_3 as additives were also conducted. (Figures S2 and S3)

Table S1 ^{29}Si NMR of $\text{Ph}_n\text{SiH}_{(4-n)}$ ($n = 1, 2, 3$) and $\text{Ph}_2\text{SiH}(\text{O}^t\text{Bu})$ in $\text{THF-}d_8$.

Hydrosilane	Chemical Shift ($J_{\text{Si-H}}$ coupling)
PhSiH_3	-60.6 ppm (q, $J_{\text{Si-H}} = 199.4$ Hz)
Ph_2SiH_2	-33.7 ppm (t, $J_{\text{Si-H}} = 197.6$ Hz)
Ph_3SiH	-17.9 ppm (d, $J_{\text{Si-H}} = 196.8$ Hz)
$\text{Ph}_2\text{SiH}(\text{O}^t\text{Bu})$	-23.9 ppm (d, $J_{\text{Si-H}} = 207.5$ Hz)

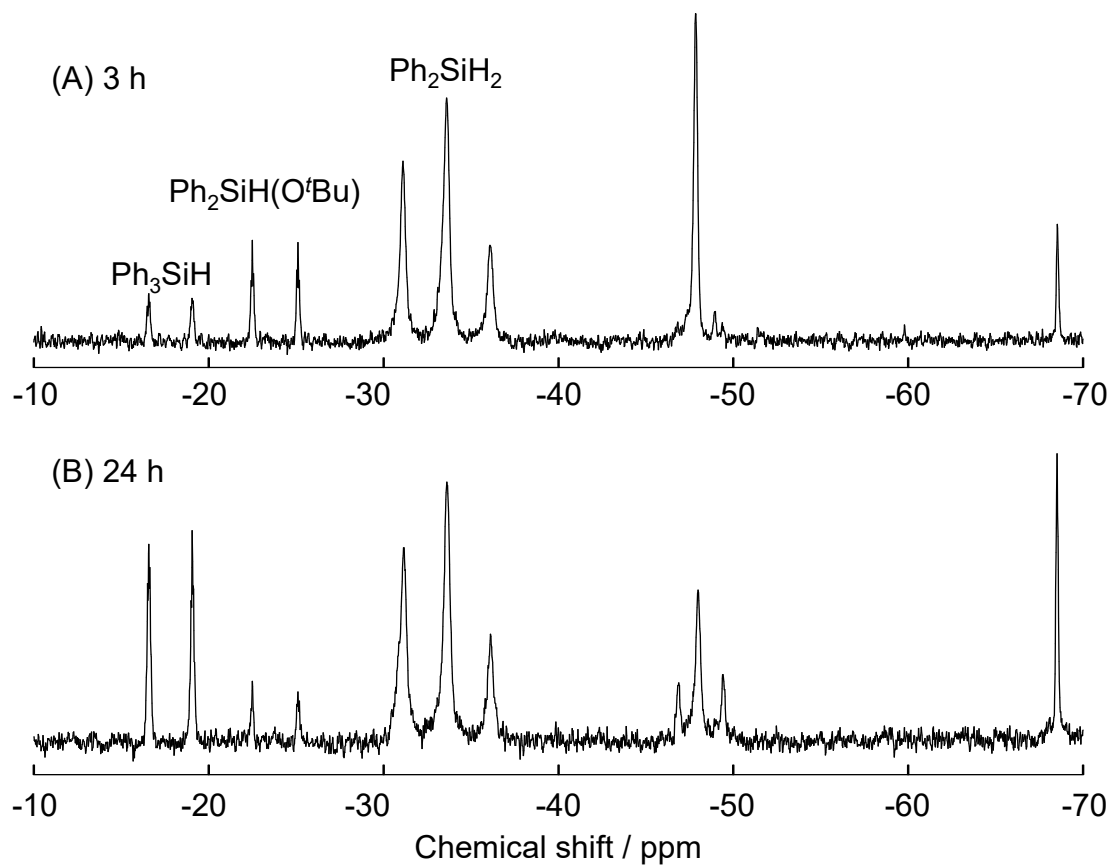


Figure S1. ²⁹Si NMR of the mixture of Ph₂SiH₂ and KO^tBu in THF-*d*₈.

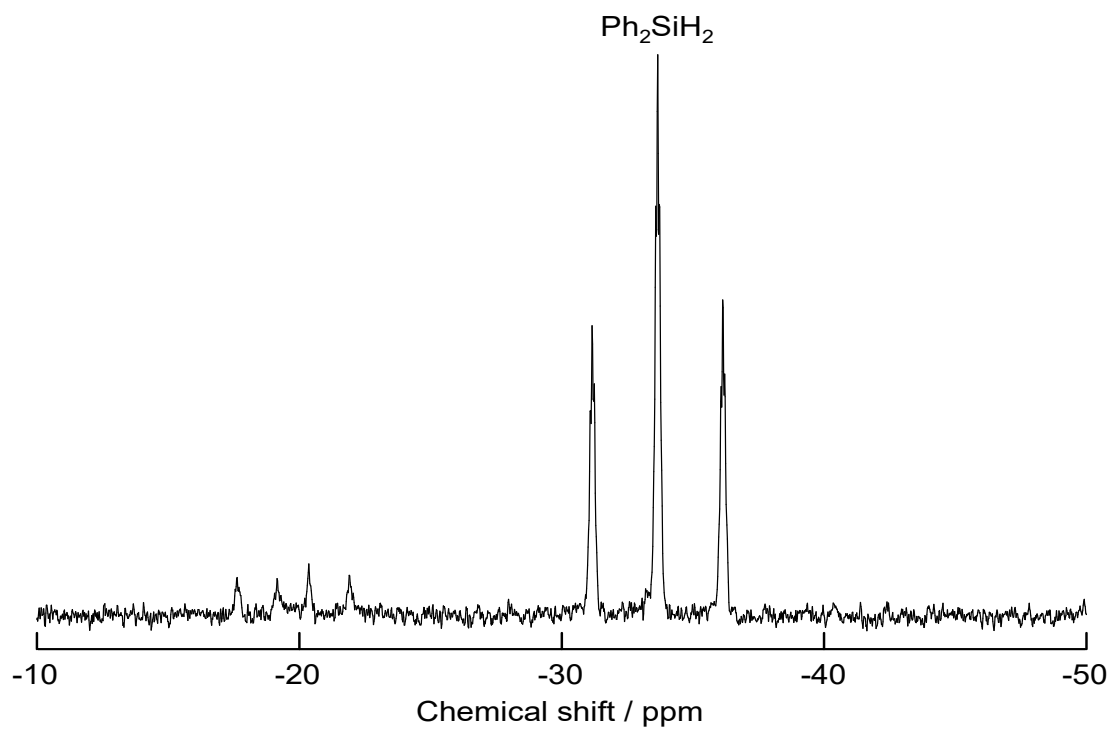


Figure S2. ^{29}Si NMR of the mixture of Ph_2SiH_2 and KOPv in $\text{THF-}d_8$ at 24 h.

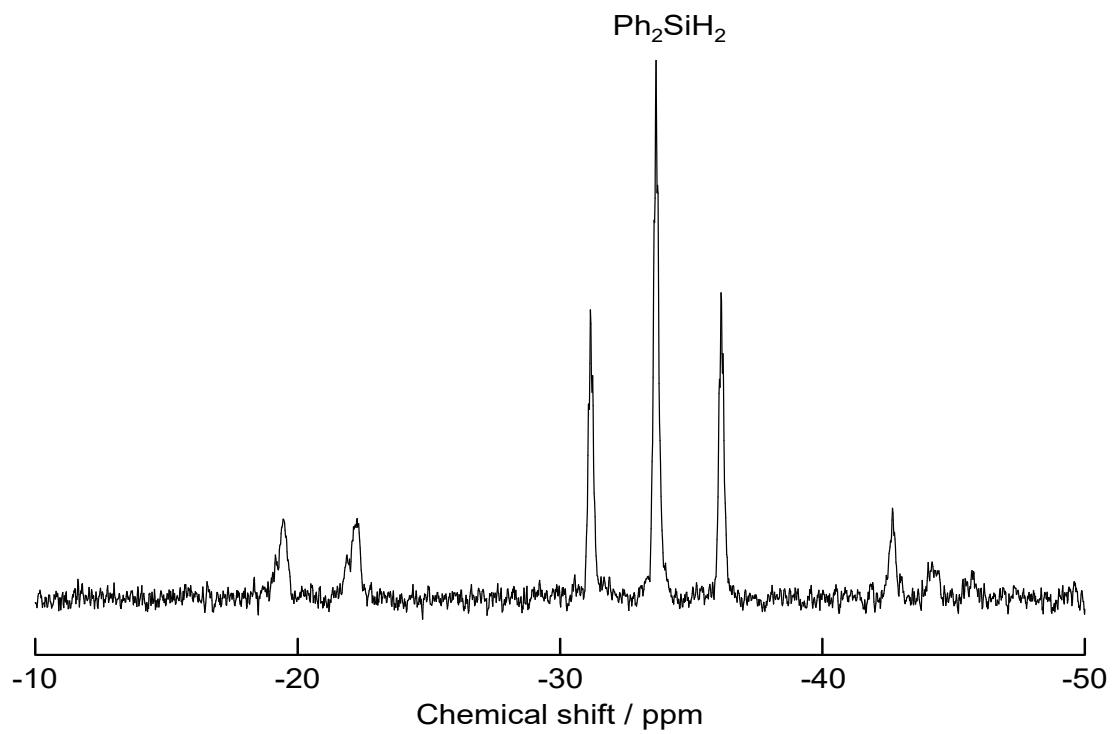


Figure S3. ^{29}Si NMR of the mixture of Ph_2SiH_2 and K_2CO_3 in $\text{THF-}d_8$ at 24 h.

Preparation of diphenyl-tert-butoxysilane (Ph₂SiH(O^tBu))

This compound was prepared with reference to the synthetic method of Ph₂SiH(O^tPr).⁸

Diphenylchlorosilane (Ph₂SiHCl) (169 μL, 1.0 mmol) was added slowly at 0 °C to the CH₂Cl₂ solution (5 mL) of ^tBuOH (114 μL, 1.2 mmol) and triethylamine (208 μL, 1.5 mmol). 3h stirring at 0 °C caused a white precipitate, which was removed by filtration and washed with 10 mL ether. The filtrate and the ether solution were put under reduced pressure to remove ether. The colorless oil thus obtained was purified by by Kugelrohr distillation (130 °C, 500 Pa), and the product was obtained as a colorless oil. (198 mg, 77%).

¹H NMR (400 MHz, THF-*d*₈): δ (ppm) 1.31 (s, 9H, O-^tBu), 5.55 (s, 1H, SiH), 7.28-7.38 (m, 3H, Ph), 7.58 (dd, 2H, *J* = 7.7, 1.7 Hz, Ph). ¹³C{¹H} NMR (100 MHz, THF-*d*₈): δ (ppm) 31.76, 74.12, 128.51, 130.57, 135.12, 136.92. ²⁹Si NMR (79.5 MHz, THF-*d*₈): δ (ppm) -23.9 (d, *J*_{Si-H} = 207.5 Hz). Anal. Calcd for C₁₆H₂₀OSi: C, 74.95; H, 7.86; N, 0.00. Found: C, 74.84; H, 7.83; N, 0.00. HRMS (EI): [M]⁺ Calcd. for C₁₆H₂₀OSi: 256.1283; Found: 256.1296.

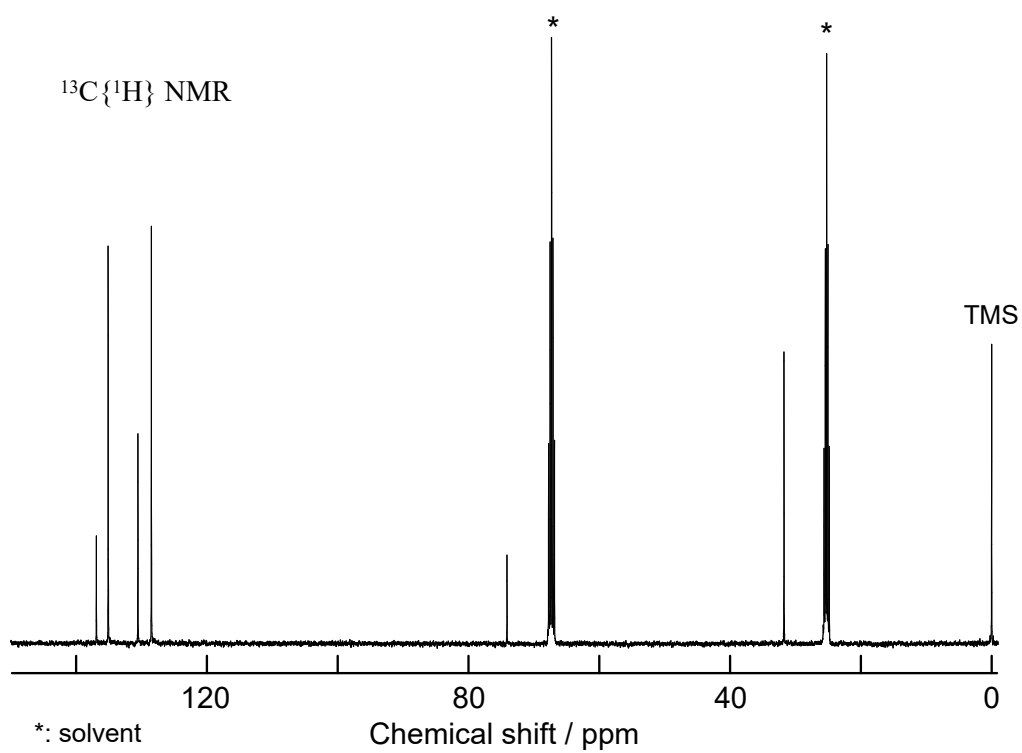
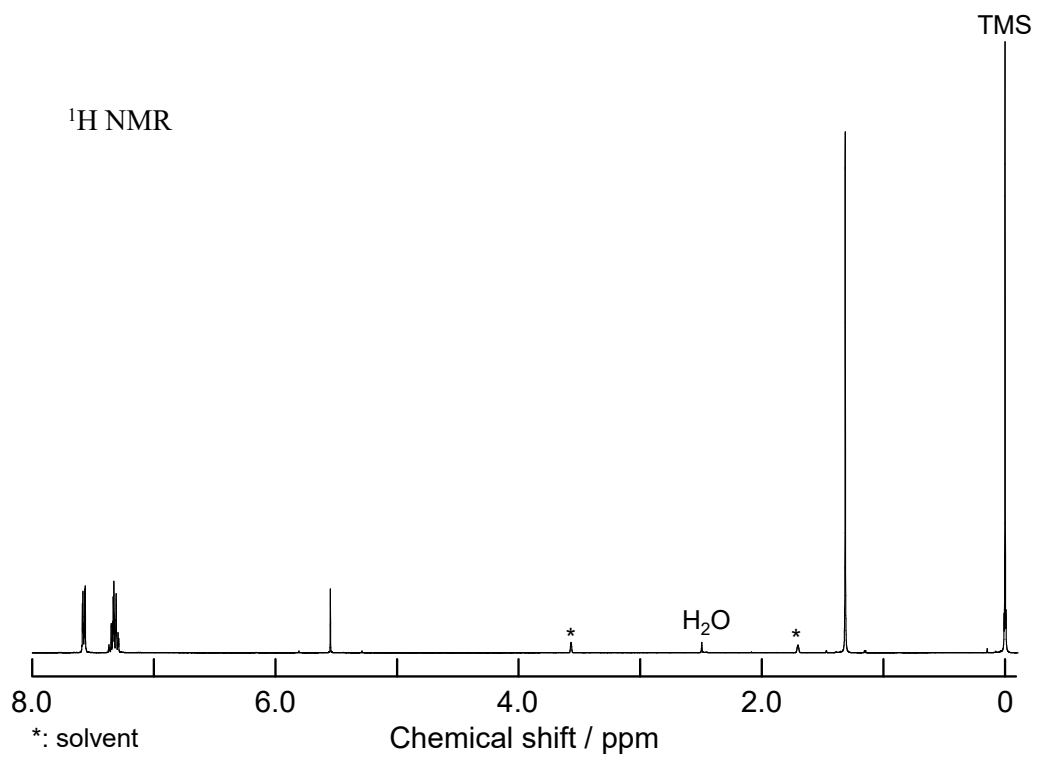


Figure S4. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of the mixture of $\text{Ph}_2\text{SiH}(\text{O}^t\text{Bu})$ in $\text{THF-}d_8$.

Optimization of hydrosilylation conditions catalyzed by K₂CO₃-activated [Co(tpy)Br₂]

Hydrosilylation of 1-octene with Ph₂SiH₂ catalyzed by [Co(tpy)Br₂] in the presence of various amounts of K₂CO₃ was conducted.

[Co(tpy)Br₂] (2.4 mg, 5.4 μmol, 0.1 mol%) and various amounts of K₂CO₃ (0.5, 1.0, 1.5, 2.0, and 2.5 mol%) were placed in a Schlenk tube. Then, the air in the Schlenk tube was replaced with N₂. 1-Octene (0.85 mL, 5.4 mmol) and diphenylsilane (1.0 mL, 5.4 mmol) were added to the Schlenk tube under N₂. The solution was stirred at a controlled temperature (25 °C). After 24 h, the reaction was stopped by exposure to air. The yield of the products was determined by GC.

Temperature dependence of the hydrosilylation catalyzed by [Co(tpy)Br₂] was also investigated. [Co(tpy)Br₂] (2.4 mg, 5.4 μmol, 0.1 mol%) and 2.0 mol% K₂CO₃ were placed in a Schlenk tube. Then, the air in the Schlenk tube was replaced with N₂. 1-Octene (0.85 mL, 5.4 mmol) and diphenylsilane (1.0 mL, 5.4 mmol) were added to the Schlenk tube under N₂. The mixture was stirred at various temperatures (25, 40, 60, 80 or 100 °C). After 24 h, the reaction was stopped by exposure to air. The yield of the products was determined by GC.

Preparation of hydrosilylated compounds

3-(Diphenylsilyl)-propionic acid methyl ester (6)

[Co(tpy)Br₂] (7.2 mg, 16.2 μmol, 0.1 mol%) and K₂CO₃ (45 mg, 0.324 mmol, 2.0 mol%) were

placed in a Schlenk tube. Then, the air in the Schlenk tube was replaced with N₂. Methyl acrylate (1.45 mL, 16.2 mmol) and diphenylsilane (3.0 mL, 16.2 mmol) were added to the Schlenk tube under N₂. The solution was stirred at 25 °C. After 24 h, the reaction was stopped by exposure to air. After removal of K₂CO₃ by filtration, the product was purified by Kugelrohr distillation (180 °C, 360 Pa). **6** was isolated as a colorless oil (4.38 g, 33%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.47 (dt, 2H, -CH₂-Si, *J* = 8.56, 3.42 Hz), 2.41 (t, 2H, CO-CH₂-, *J* = 8.56 Hz), 3.61 (s, 3H, -OMe), 4.87 (t, 1H, SiH, *J* = 3.42 Hz), 7.32-7.46 (m, 6H, *Ph*), 7.52-7.6 (m, 4H, *Ph*). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 7.53, 29.10, 51.78, 128.24, 129.97, 133.43, 135.26, 174.91. Anal. Calcd for C₁₆H₁₈O₂Si: C, 71.07; H, 6.71; N, 0.00. Found: C, 70.78; H, 6.76; N, 0.00. HRMS (EI): [M-H]⁺ Calcd. for C₁₆H₁₇O₂Si: 269.0998; Found: 269.0997.

(2-phenylethyl)diethoxymethylsilane (9)

[Co(tpy)Br₂] (4.8 mg, 10.8 μmol, 0.1 mol%) and K₂CO₃ (30 mg, 0.216 mmol, 2.0 mol%) were placed in a Schlenk tube. Then, the air in the Schlenk tube was replaced with N₂. Styrene (1.24 mL, 10.8 mmol) and diethoxymethylsilane (1.73 mL, 10.8 mmol) were added to the Schlenk tube under N₂. The solution was stirred at 25 °C. After 24 h, the reaction was halted by exposure to air. After removal of K₂CO₃ by filtration, the product was purified by Kugelrohr distillation (100 °C, 120 Pa). **9** was isolated as a colorless oil (2.10 g, 82%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.12

(s, 3H, Si-Me), 1.00 (m, 2H, Si-CH₂-), 1.23 (t, 6H, *J* = 6.99 Hz, -CH₂-Me), 2.71 (m, 2H, Ph-CH₂-), 3.78 (q, 4H, *J* = 6.99 Hz, -O-CH₂-Me), 7.12-7.24 (m, 3H, *Ph*), 7.25-7.31 (m, 2H, *Ph*).
¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) -4.68, 15.93, 18.55, 29.07, 58.30, 125.74, 127.93, 128.48, 144.79. Anal. Calcd for C₁₃H₂₂O₂Si: C, 65.50; H, 9.30; N, 0.00. Found: C, 65.16; H, 9.37; N, 0.00. HRMS (EI): [M]⁺ Calcd. for C₁₃H₂₂O₂Si: 238.1389; Found: 238.1404.

(2-phenylethyl)dimethylphenylsilane (10)

[Co(tpy)Br₂] (7.2 mg, 16.2 μmol, 0.1 mol%) and K₂CO₃ (45 mg, 0.324 mmol, 2.0 mol%) were placed in a Schlenk tube. Then, the air in the Schlenk tube was replaced with N₂. Styrene (1.87 mL, 16.2 mmol) and dimethylphenylsilane (2.48 mL, 16.2 mmol) were added to the Schlenk tube under N₂. The solution was stirred at 25 °C. After 24 h, the reaction was halted by exposure to air. After removal of K₂CO₃ by filtration, the product was purified by Kugelrohr distillation (175 °C, 300 Pa). **10** was isolated as a colorless oil (3.2 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.31 (s, 6H, Si-Me), 1.15 (m, 2H, Si-CH₂-), 2.66 (m, 2H, Ph-CH₂-), 7.14-7.22 (m, 3H, *Ph*), 7.24-7.31 (m, 2H, *Ph*), 7.36-7.42 (m, 3H, *Ph*), 7.52-7.59 (m, 2H, *Ph*). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) -2.97, 17.83, 30.07, 125.67, 127.89, 127.93, 128.42, 129.06, 133.72, 139.17, 145.13. Anal. Calcd for C₁₆H₂₀Si: C, 79.93; H, 8.38; N, 0.00. Found: C, 79.65; H, 8.38; N, 0.00. HRMS (EI): [M-H]⁺ Calcd. for C₁₆H₁₇O₂Si: 240.1334; Found: 240.1328.

1,1,1,3,3-pentamethyl-3-(2-phenylethyl)disiloxane (11)

[Co(tpy)Br₂] (4.8 mg, 10.8 μmol, 0.1 mol%) and K₂CO₃ (30 mg, 0.216 mmol, 2.0 mol%) were placed in a Schlenk tube. Then, the air in the Schlenk tube was replaced with N₂. Styrene (1.24 mL, 10.8 mmol) and 1,1,1,3,3-pentamethyldisiloxane (2.11 mL, 10.8 mmol) were added to the Schlenk tube under N₂. The solution was stirred at 25 °C. After 24 h, the reaction was halted by exposure to air. After removal of K₂CO₃ by filtration, the product was purified by Kugelrohr distillation (100 °C, 120 Pa). **11** was isolated as a colorless oil (2.0 g, 85%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.07 (s, 6H, Si-Me₂), 0.09 (s, 9H, Si-Me₃), 0.89 (m, 2H, Si-CH₂-), 2.65 (m, 2H, Ph-CH₂-), 7.13-7.23 (m, 3H, Ph), 7.24-7.31 (m, 2H, Ph). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 0.45, 2.14, 20.51, 29.55, 125.61, 127.93, 128.43, 145.35. Anal. Calcd for C₁₃H₂₄OSi₂: C, 61.84; H, 9.58; N, 0.00. Found: C, 61.75; H, 9.58; N, 0.00. HRMS (EI): [M]⁺ Calcd. for C₁₃H₂₄OSi₂: 252.1366; Found: 252.1372.

1,1,1,3,5,5,5-heptamethyl-3-(2-phenylethyl)trisiloxane (12)

[Co(tpy)Br₂] (4.8 mg, 10.8 μmol, 0.1 mol%) and K₂CO₃ (30 mg, 0.216 mmol, 2.0 mol%) were placed in a Schlenk tube. Then, the air in the Schlenk tube was replaced with N₂. Styrene (1.24 mL, 10.8 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (2.93 mL, 10.8 mmol) were added to the

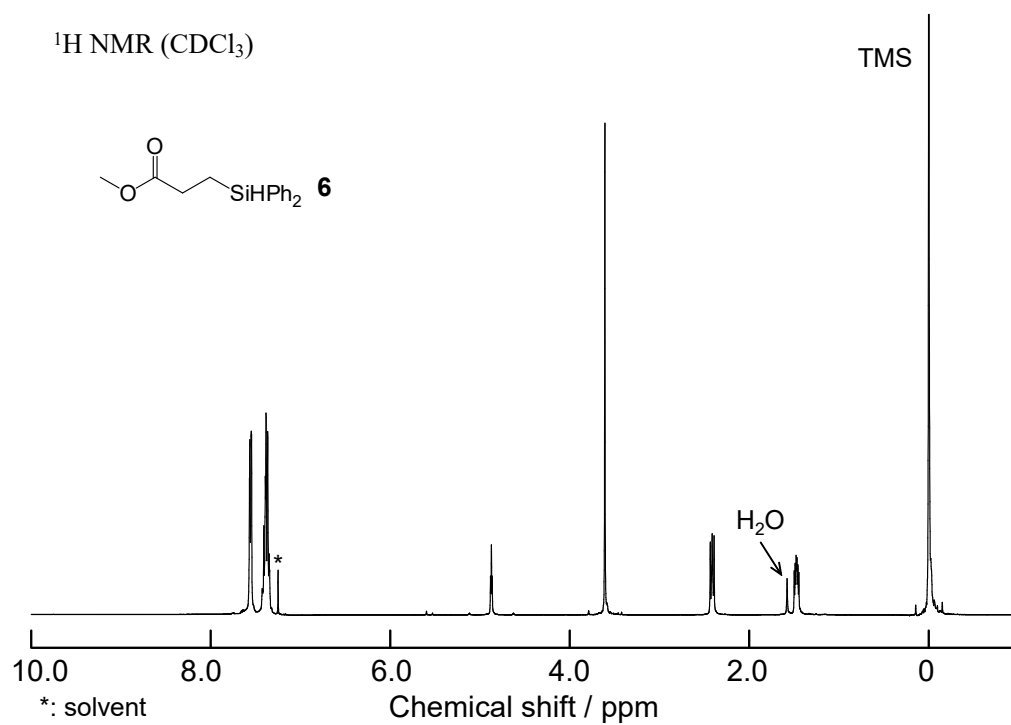
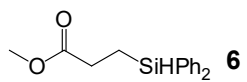
Schlenk tube under N₂. The solution was stirred 25 °C. After 24 h, the reaction was halted by exposure to air. After removal of K₂CO₃ by filtration, the product was purified by Kugelrohr distillation (150 °C, 190 Pa). **12** was isolated as a colorless oil (3.1 g, 87%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.03 (s, 3H, Si-Me), 0.11 (s, 18, Si-Me₃), 0.83 (m, 2H, Si-CH₂-), 2.64 (m, 2H, Ph-CH₂-), 7.12-7.22 (m, 3H, Ph), 7.23-7.3 (d, 2H, J = 7.3 Hz, Ph). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) -0.18, 2.03, 19.88, 29.41, 125.62, 127.93, 128.44, 145.30. Anal. Calcd for C₁₅H₃₀O₂Si₃: C, 55.15; H, 9.26; N, 0.00. Found: C, 54.89; H, 9.32; N, 0.00. HRMS (EI): [M]⁺ Calcd. for C₁₅H₃₀O₂Si₃: 326.1554; Found: 326.1552.

References.

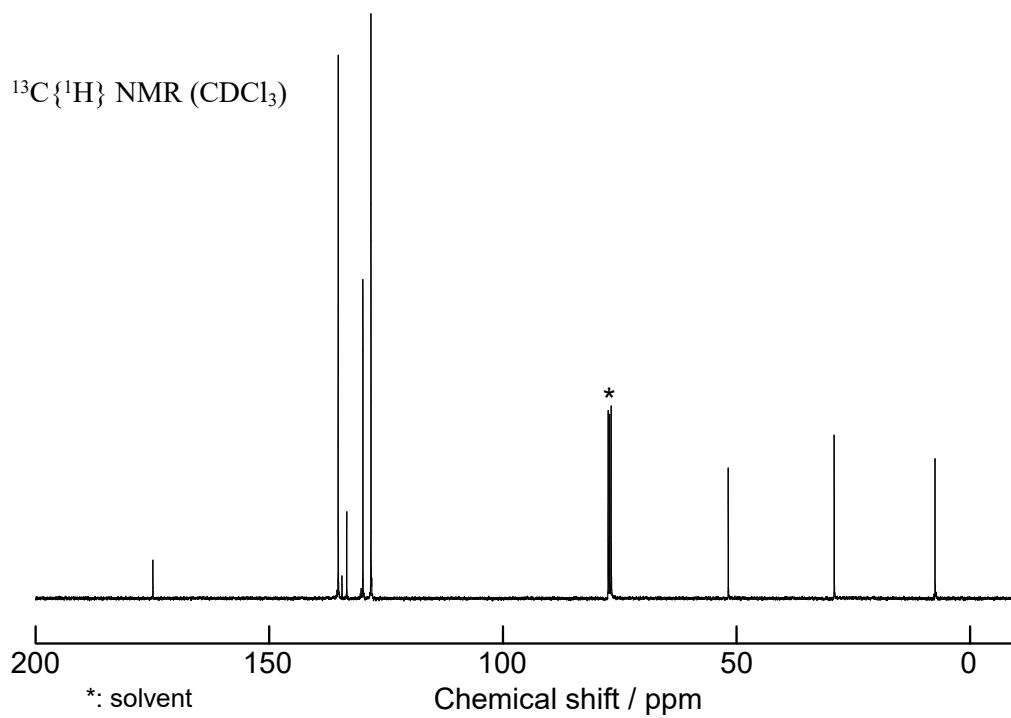
1. K. Kobayashi and H. Nakazawa, *Inorg. Chim. Acta*, 2021, **523**, 120403.
2. A. D. Ibrahim, S. W. Entsminger, L. Zhu and A. R. Fout, *ACS Catal.*, 2016, **6**, 3589-3593.
3. X. Du, Y. Zhang, D. Peng and Z. Huang, *Angew. Chem. Int. Ed.*, 2016, **55**, 6671-6675.
4. M. D. Greenhalgh, D. J. Frank and S. P. Thomas, *Adv. Synth. Catal.*, 2014, **356**, 584-590.
5. B. Raya, S. Jing, V. Balasanthiran and T. V. RajanBabu, *ACS Catal.*, 2017, **7**, 2275-2283.
6. S. Gutiérrez-Tarriño, P. Concepción and P. Oña-Burgos, *Eur. J. Inorg. Chem.*, 2018, 4867-4874.
7. D. Taguchi, K. Kobayashi, T. Moriuchi and H. Nakazawa, *Bull. Chem. Soc. Jpn.*, 2020, **93**, 1086-1094.
8. C. N. Foley and J. L. Leighton, *Org. Lett.*, 2014, **16**, 1180-1183.

NMR spectra of hydrosilylation products in CDCl₃

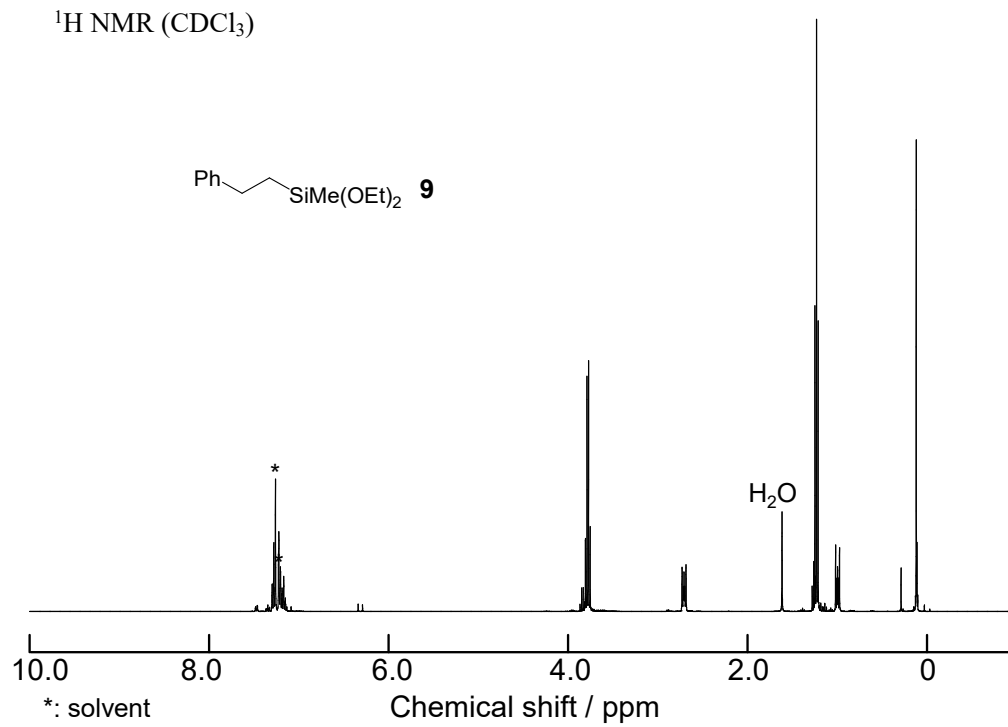
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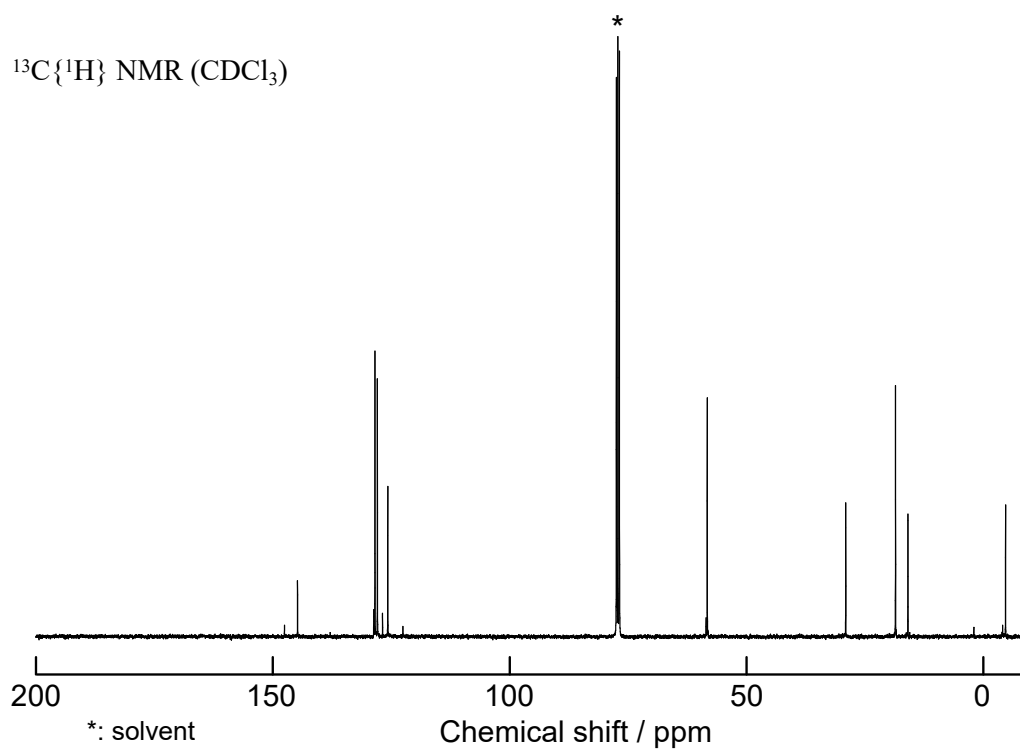
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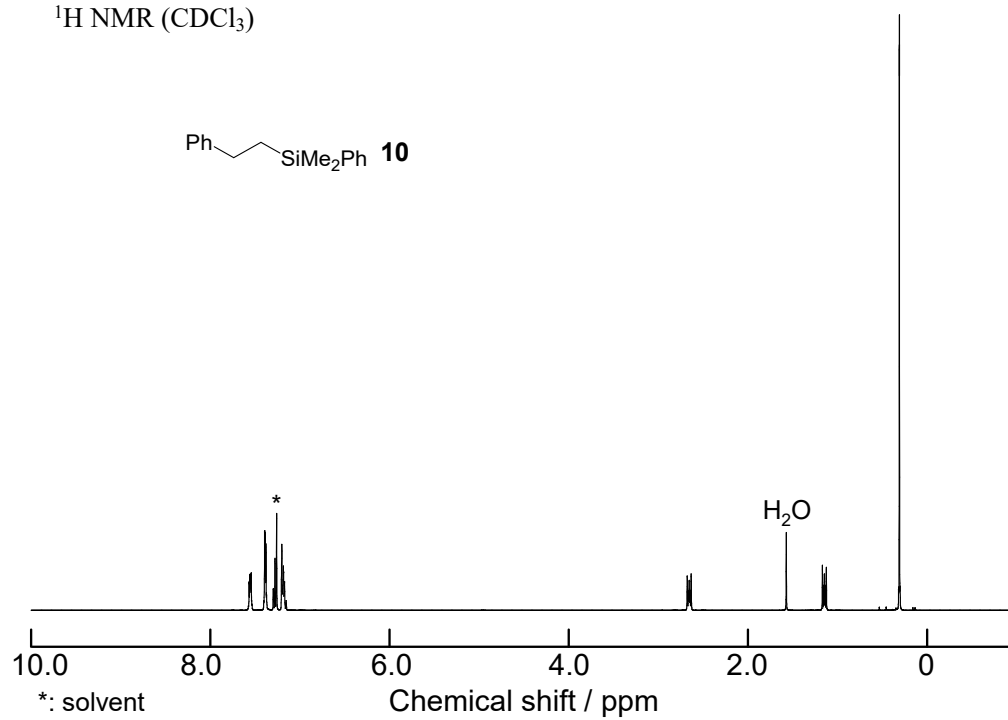
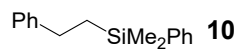
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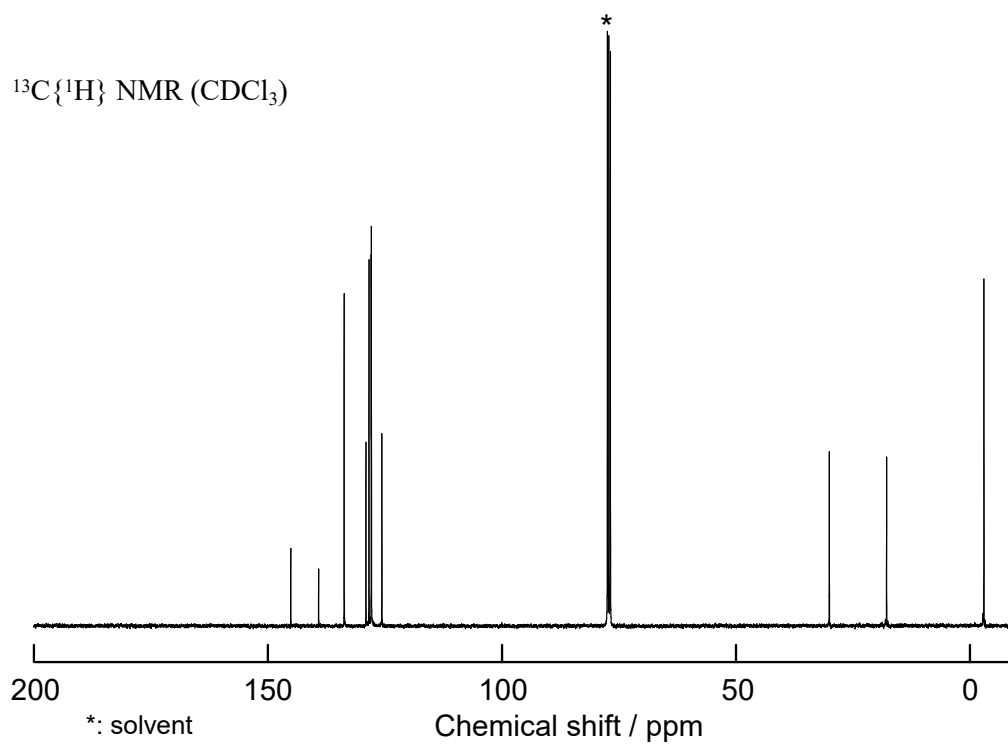
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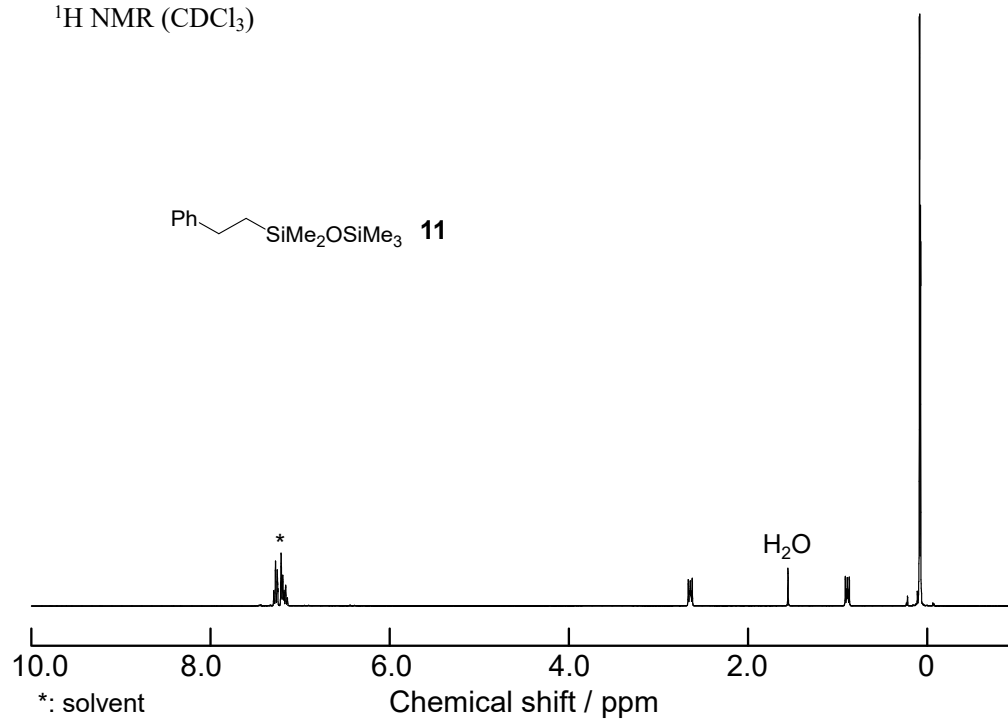
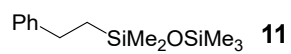
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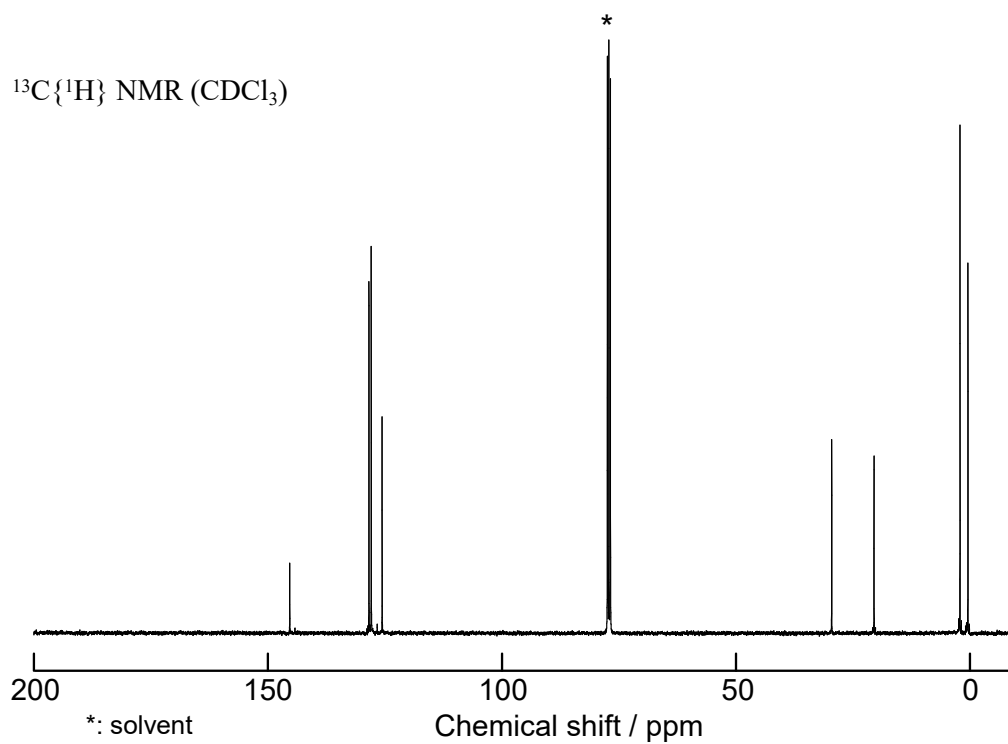
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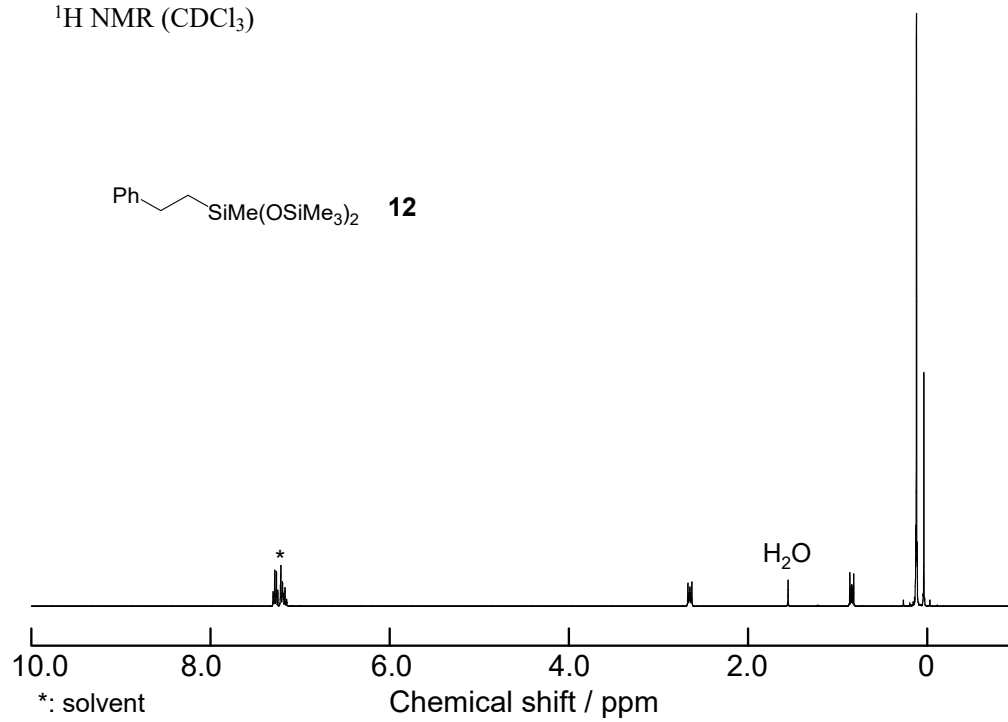
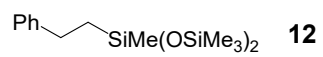
^1H NMR (CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3)



^1H NMR (CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3)

