

Supporting Information

for

Direct synthesis of alkylsilanes by platinum-catalyzed coupling of hydrosilanes and iodoalkanes

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1. Spectroscopic characterization of products

dimethyl(*n*-butyl)phenylsilane (1**):**¹ Condition A. Yield: 60%. Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.52–7.50 (m, 2H), 7.36–7.34 (m, 3H), 1.35–1.27 (m, 4H), 0.87 (t, 3H, J = 7.0 Hz), 0.76–0.73 (m, 2H), 0.26 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 139.7 (C_q), 133.5 (CH), 128.7 (CH), 127.7 (CH), 26.6 (CH₂), 26.1 (CH₂), 15.4 (CH₂), 13.8 (CH₃), -3.1 (CH₃). EI-MS m/z 192 (M⁺).

(*n*-butyl)ethylmethylphenylsilane (2**):** Condition B. Yield: 45%. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.51–7.47 (m, 2H), 7.36–7.32 (m, 3H), 1.33–1.24 (m, 4H), 0.94 (t, 3H, J = 7.6 Hz), 0.86 (t, 3H, J = 7.1 Hz), 0.78–0.72 (m, 4H), 0.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 138.7 (C_q), 133.8 (CH), 128.7 (CH), 127.6 (CH), 26.7 (CH₂), 26.0 (CH₂), 13.8 (CH₃), 13.4 (CH₂), 7.4 (CH₃), 5.8 (CH₂), -5.6 (CH₃). EI-MS m/z 206 (M⁺). Anal. Calcd for C₁₃H₂₂Si: C, 75.65; H, 10.74. Found: C, 75.38; H, 10.88.

diphenyl(*n*-butyl)methylsilane (3**):**² Condition B. Yield: 55%. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.52–7.49 (m, 4H), 7.35–7.30 (m, 6H), 1.38–1.33 (m, 4H), 1.09–1.04 (m, 2H), 0.88–0.84 (m, 3H), 0.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 137.5 (C_q), 134.4 (CH), 129.0 (CH), 127.8 (CH), 26.6 (CH₂), 26.0 (CH₂), 13.9 (CH₂), 13.7 (CH₃), -4.5 (CH₃). EI-MS m/z 254 (M⁺).

dimethyl(*n*-butyl)(4-methoxyphenyl)silane (4**):** Condition B. Yield: 45%. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, 2H, J = 8.8 Hz), 6.89 (d, 2H, J = 8.8 Hz), 3.79 (s, 3H), 1.30–1.24 (m, 4H), 0.84 (t, 3H, J = 6.8 Hz), 0.72–0.67 (m, 2H), 0.21 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 160.2 (C_q), 134.9 (CH), 130.6 (C_q), 113.4 (CH), 55.0 (CH₃), 26.6 (CH₂), 26.1 (CH₂), 15.6 (CH₂), 13.8 (CH₃), -2.8 (CH₃). FAB-MS m/z 222 (M⁺). FAB-HRMS Calcd for C₁₃H₂₂OSi: 222.1440. Found: 222.1448 (M⁺).

butyldimethyl(4-trifluoromethylphenyl)silane (5**):** Condition C. Yield: 79%. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.63–7.57 (m, 4H), 1.35–1.26 (m, 4H), 0.88–0.85 (t, 3H, J = 6.9 Hz), 0.78–0.74 (m, 2H), 0.28 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 144.8 (C_q), 133.8 (CH), 130.7 (CF₃-C_q, q, J = 32.0 Hz), 124.3 (CF₃, q, J = 272.1 Hz), 124.2 (CF₃-C_q-CH, q, J = 3.7 Hz), 26.5 (CH₂), 26.0 (CH₂), 15.2 (CH₂), 13.7 (CH₃), -3.2 (CH₃). EI-MS m/z 260 (M⁺). Anal. Calcd for C₁₃H₁₉F₃Si: C, 59.97; H, 7.36. Found: C, 59.68; H, 7.40.

butyldimethyl(2-thiophenyl)silane (6**):** Condition D. Yield: 71%. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (dd, 1H, J = 2.3 Hz, 0.5 Hz), 7.25 (dd, 1H, J = 1.6 Hz, 0.4 Hz), 7.19 (dd, 2H, J = 2.3 Hz, 1.6 Hz), 1.36–1.31 (m, 4H), 0.87 (d, 3H, J = 7.1 Hz), 0.79–0.75 (m, 2H), 0.30 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 139.2 (C_q), 134.1 (CH), 130.3 (CH), 128.0 (CH), 26.4 (CH₂), 26.0 (CH₂), 16.3 (CH₂), 13.7 (CH₃), 1.8 (CH₃). EI-MS m/z 198 (M⁺). Anal. Calcd for C₁₀H₁₈SSi: C, 60.54; H, 9.14. Found: C, 60.28; H, 9.05.

dimethyl(*n*-octyl)phenylsilane (7):³ Condition E. Yield: 83% (alkylated product: reduced product = 90: 10). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.62–7.58 (m, 2H), 7.45–7.42 (m, 3H), 1.42–1.34 (m, 12H), 0.98 (t, 3H, *J* = 7.0 Hz), 0.85 (t, 2H, *J* = 7.8 Hz), 0.35 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 139.7 (C_q), 133.6 (CH), 128.7 (CH), 127.7 (CH), 33.7 (CH₂), 32.0 (CH₂), 29.3 (CH₂), 29.3 (CH₂), 23.9 (CH₂), 22.7 (CH₂), 15.7 (CH₂), 14.1 (CH₃), -3.0 (CH₃). EI-MS *m/z* 248 (M⁺).

dimethylphenyl(3-phenylpropyl)silane (8):⁴ Condition E. Yield: 50% (alkylated product: reduced product = 63: 37). Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.49–7.47 (m, 2H), 7.35–7.32 (m, 3H), 7.27–7.24 (m, 2H), 7.17–7.12 (m, 3H), 2.61 (t, 2H, *J* = 7.6 Hz), 1.67–1.60 (m, 2H), 0.81–0.77 (m, 2H), 0.25 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 142.5 (C_q), 139.4 (C_q), 133.5 (CH), 128.7 (CH), 128.4 (CH), 128.2 (CH), 127.7 (CH), 125.6 (CH), 39.7 (CH₂), 25.9 (CH₂), 15.5 (CH₂), -3.1 (CH₃). EI-MS *m/z* 254 (M⁺).

trimethylphenylsilane (9):⁵ Condition F. Yield (GC): 83%. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.55–7.52 (m, 2H), 7.38–7.35 (m, 3H), 0.28 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 140.5 (C_q), 133.3 (CH), 128.8 (CH), 127.7 (CH), -1.1 (CH₃). EI-MS *m/z* 150 (M⁺).

1,4-bis(butyldimethylsilyl)benzene (10):⁶ Condition G. Yield: 14%. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (s, 2H), 2.09–2.01 (m, 3H), 1.35–1.31 (m, 4H), 0.87 (t, 3H), 0.76–0.72 (m, 2H), 0.24 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 140.2 (C_q), 132.6 (CH), 26.6 (CH₂), 26.1 (CH₂), 15.3 (CH₂), 13.8 (CH₃), -3.1 (CH₃). EI-MS *m/z* 312 (M⁺).

dimethylphenyl(4,4,4-trifluorobutyl)silane (11): Condition B. Yield: 58%. Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.50–7.49 (m, 2H), 7.36–7.35 (m, 3H), 2.10–2.01 (m, 3H), 1.60–1.54 (m, 2H), 0.81–0.78 (m, 2H), 0.28 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 138.5 (C_q), 133.5 (CH), 129.1 (CH), 127.9 (CH), 127.0 (CF₃, q, *J* = 276.9 Hz), 37.2 (CH₂-CF₃, q, *J* = 27.7 Hz), 16.7 (CH₂-CH₂-CF₃, q, *J* = 2.4 Hz), 15.3 (CH₂), -3.3 (CH₃). EI-MS *m/z* 246 (M⁺). Anal. Calcd for C₁₂H₁₇F₃Si: C, 58.51; H, 6.96. Found: C, 58.21; H, 7.10.

methyl 4-(dimethylphenylsilyl)butanoate (12): Condition E. Yield: 71%. Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.51–7.49 (m, 2H), 7.36–7.34 (m, 3H), 3.65 (s, 3H), 2.32 (t, 2H, *J* = 7.4 Hz), 1.69–1.61 (m, 2H), 0.79–0.75 (m, 2H), 0.27 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 174.0 (C_q), 138.9 (C_q), 133.5 (CH), 128.9 (CH), 127.7 (CH), 51.4 (CH₃), 37.6 (CH₂), 19.7 (CH₂), 15.5 (CH₂), -3.2 (CH₃). EI-MS *m/z* 236 (M⁺); Anal. Calcd for C₁₃H₂₀O₂Si: C, 66.05; H, 8.53. Found: C, 65.80; H, 8.51.

4-(dimethyl(phenyl)silyl)butyronitrile (13): Condition B. Yield: 68%. Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.50–7.48 (m, 2H), 7.37–7.36 (m, 3H), 2.31 (t, 3H, *J* = 7.0 Hz), 1.68–1.61 (m, 2H), 0.91–0.88 (m, 2H), 0.30 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 138.0 (C_q), 133.4 (CH), 129.1 (CH), 127.9 (CH), 119.7 (C_q), 20.7 (CH₂), 20.5 (CH₂), -3.3 (CH₃). FAB-MS *m/z* 202 ([M-H]⁺); HRMS Calcd for C₁₂H₁₆NSi: 202.1052. Found: 202.1064 ([M-H]⁺).

(3-chloropropyl)dimethylphenylsilane (14):⁷ Condition B. Yield: 58%. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.52–7.48 (m, 2H), 7.36–7.33 (m, 3H), 3.57 (t, 2H, *J* = 7.0 Hz), 1.80–1.72 (m, 2H), 0.86–0.82 (m, 2H), 0.28 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 138.6 (C_q), 133.5 (CH), 129.0 (CH), 127.8 (CH), 47.9 (CH₂), 27.8 (CH₂), 13.4 (CH₂), -3.2 (CH₂). EI-MS *m/z* 212 (M⁺).

benzyldimethyl(*n*-butyl)silane (15):⁸ Condition B. Yield: 55%. Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.38 (m, 2H), 7.26 (t, 1H, *J* = 7.3 Hz), 7.19 (d, 2H, *J* = 6.8 Hz), 2.27 (s, 2H), 1.52–1.44 (m, 4H), 1.07 (t, 3H, *J* = 7.0 Hz), 0.72–0.68 (m, 2H), 0.15 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 140.5 (C_q), 128.1 (CH), 128.1 (CH), 123.8 (CH), 26.6 (CH₂), 26.0 (CH₂), 25.6 (CH₂), 14.4 (CH₂), 13.8 (CH₃), -3.6 (CH₃). EI-MS *m/z* 206 (M⁺).

(4-ethoxyphenyl)[3-(4-fluoro-3-phenoxyphenyl)propyl]dimethylsilane (16):⁵ Condition B. Yield: 42% (alkylated product: reduced product = 55: 45). Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.37 (d, 2H, *J* = 8.7 Hz), 7.30 (dd, 2H, *J* = 7.6 Hz, 8.1 Hz), 7.08–7.03 (m, 2H), 6.96 (d, 2H, *J* = 7.8 Hz), 6.88–6.82 (m, 4H), 4.03 (q, 2H, *J* = 7.0 Hz), 2.52 (t, 2H, *J* = 7.6 Hz), 1.59–1.53 (m, 2H), 1.40 (t, 3H, *J* = 7.0 Hz), 0.72–0.69 (m, 2H), 2.07 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 159.6 (C_q), 157.6 (C_q), 152.6 (C_q, d, *J* = 246.5 Hz), 142.9 (C_q, d, *J* = 11.7 Hz), 139.4 (C_q, d, *J* = 3.7 Hz), 134.9 (CH), 129.7 (C_q), 129.6 (CH), 124.7 (CH, d, *J* = 7.0 Hz), 122.8 (CH), 121.9 (CH), 117.0 (C_q), 116.5 (CH, d, *J* = 8.1 Hz), 114.0 (CH), 63.1 (CH₂), 38.8 (CH₂), 25.9 (CH₂), 15.5 (CH₂), 14.8 (CH₃), -2.9 (CH₃). EI-MS *m/z* 408 (M⁺).

Conditions

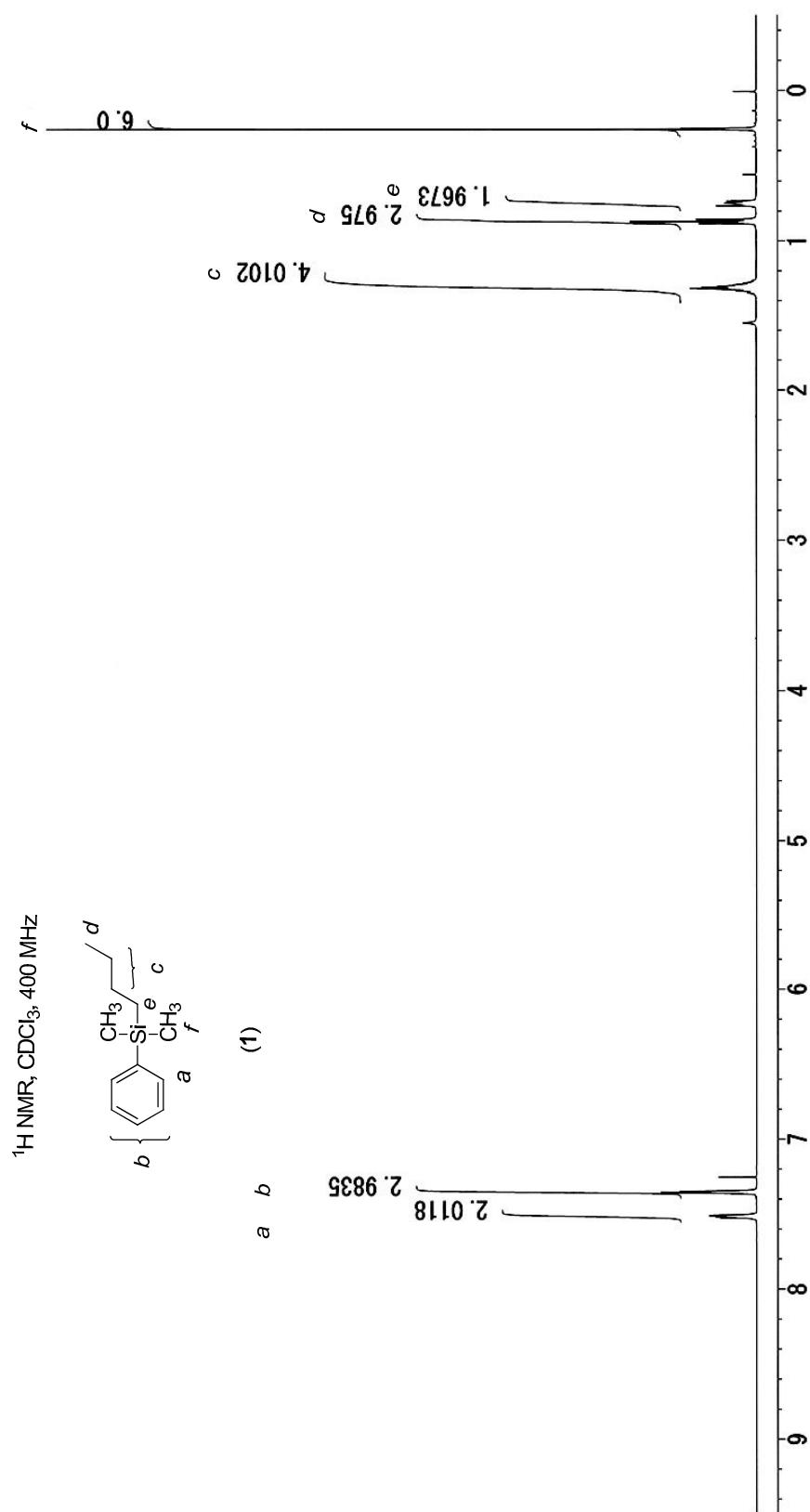
- A: 1-iodobutane (1.0 mmol), dimethylphenylsilane (3.0 mmol), (iPr)₂EtN (1.0 mmol), Pt(P(tBu)₃)₂ (0.05 mmol), CH₃CN (2.0 mL)
- B: iodoalkane (0.5 mmol), hydrosilane (1.0 mmol), (iPr)₂EtN (1.0 mmol), Pt(P(tBu)₃)₂ (0.025 mmol), CH₃CN (1.0 mL).
- C: iodoalkane (0.5 mmol), hydrosilane (1.25 mmol), (iPr)₂EtN (1.0 mmol), Pt(P(tBu)₃)₂ (0.025 mmol), CH₃CN (1.0 mL).
- D: iodoalkane (0.5 mmol), hydrosilane (1.5 mmol), (iPr)₂EtN (1.5 mmol), Pt(P(tBu)₃)₂ (0.025 mmol), CH₃CN (1.0 mL).
- E: iodoalkane (0.5 mmol), hydrosilane (2.0 mmol), (iPr)₂EtN (2.0 mmol), Pt(P(tBu)₃)₂ (0.025 mmol), CH₃CN (1.0 mL).
- F: iodoalkane (0.5 mmol), hydrosilane (2.5 mmol), (iPr)₂EtN (2.5 mmol), Pt(P(tBu)₃)₂ (0.025 mmol), CH₃CN (1.0 mL).

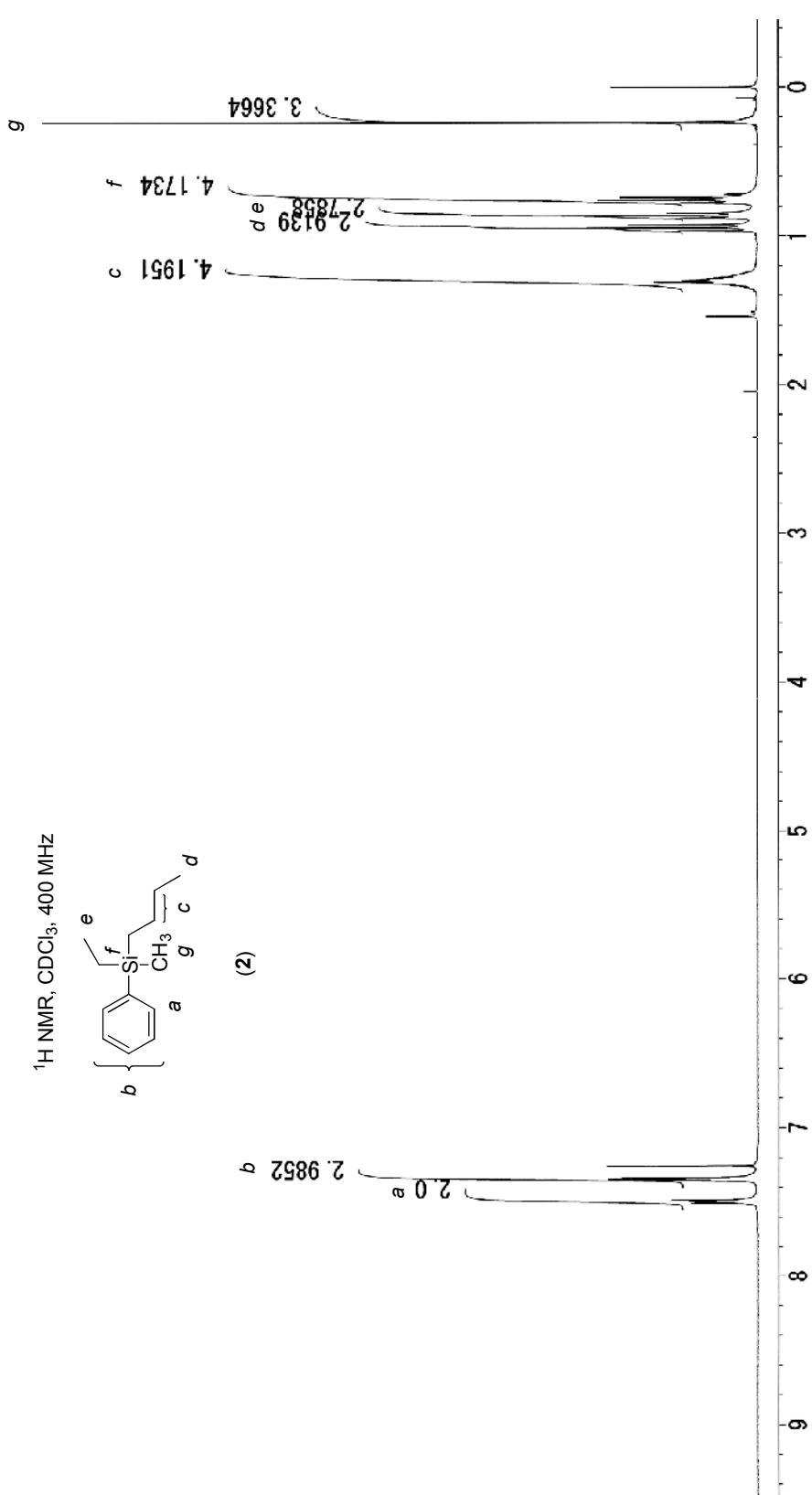
2. References

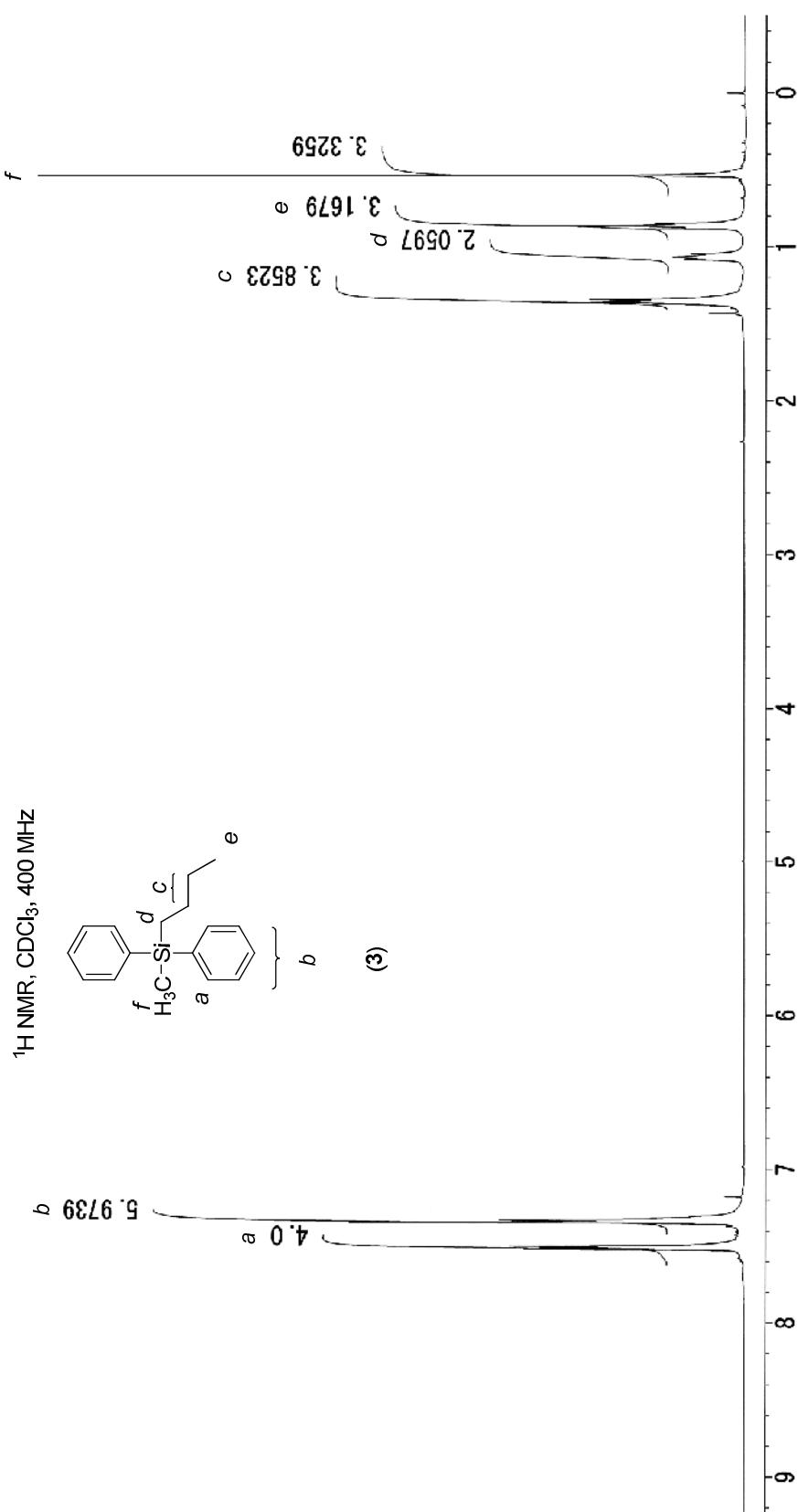
1. J. W. Wilt, W. K. Chwang, C. F. Dockus, N. M. Tomiuk, *J. Am. Chem. Soc.* **1978**, *100*, 5534.

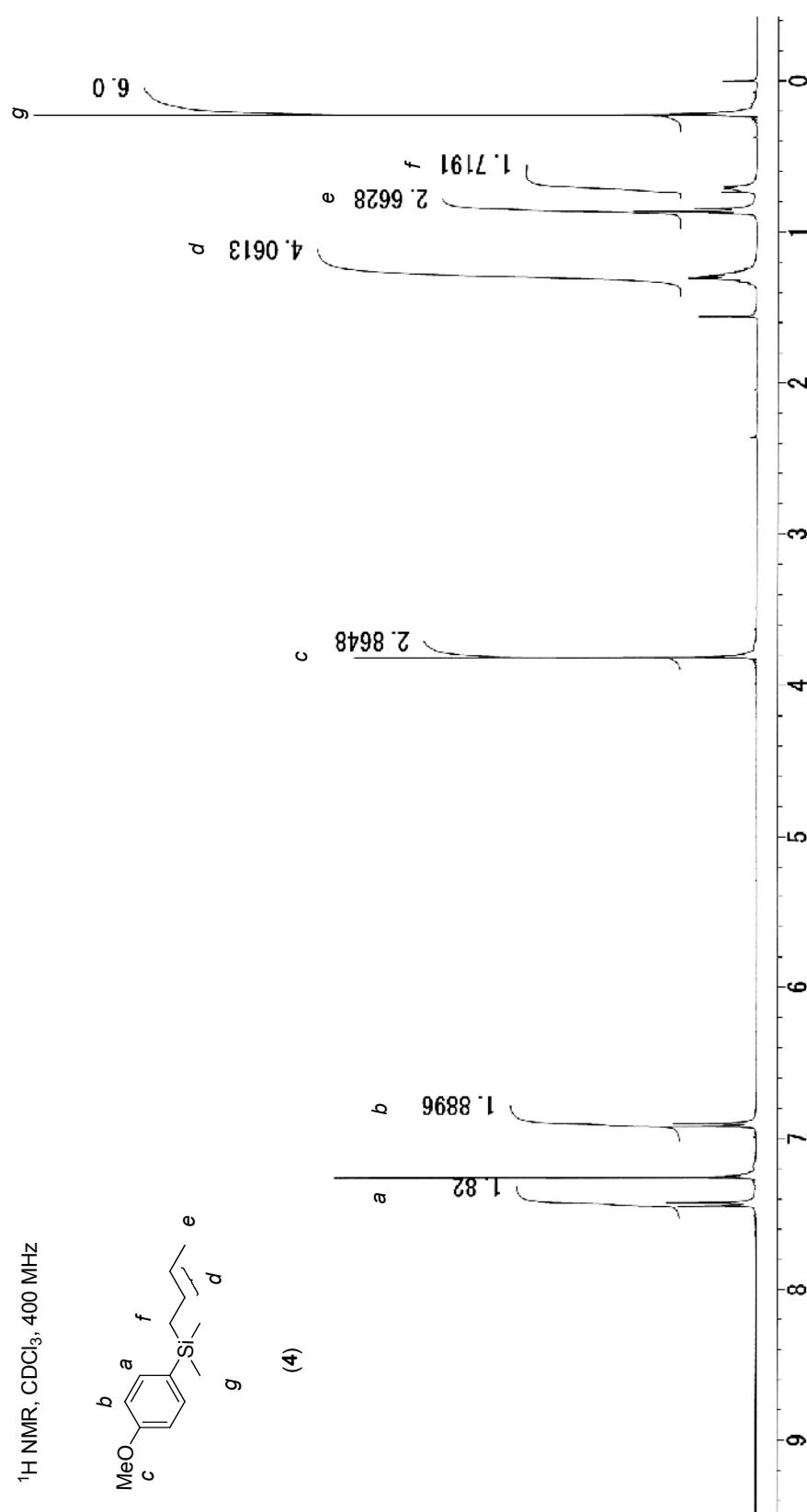
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3. M. Rubin, T. Schwier, V. Gevorgyan, *J. Org. Chem.* 2002, **67**, 1936.
4. T. Takeda, N. Nozaki, T. Fujiwara, *Tetrahedron Lett.* 1998, **39**, 3533.
5. This compound is commercially available.
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7. I. Fleming, R. Henning, D. C. Parker, H. E. Pault, P. E. J. Sanderson, *J. Chem. Soc. Perkin Trans. 1* 1995, **4**, 317.
8. A. Maercker, R. Stoetzel, *Chem. Ber.* 1987, **120**, 1965.

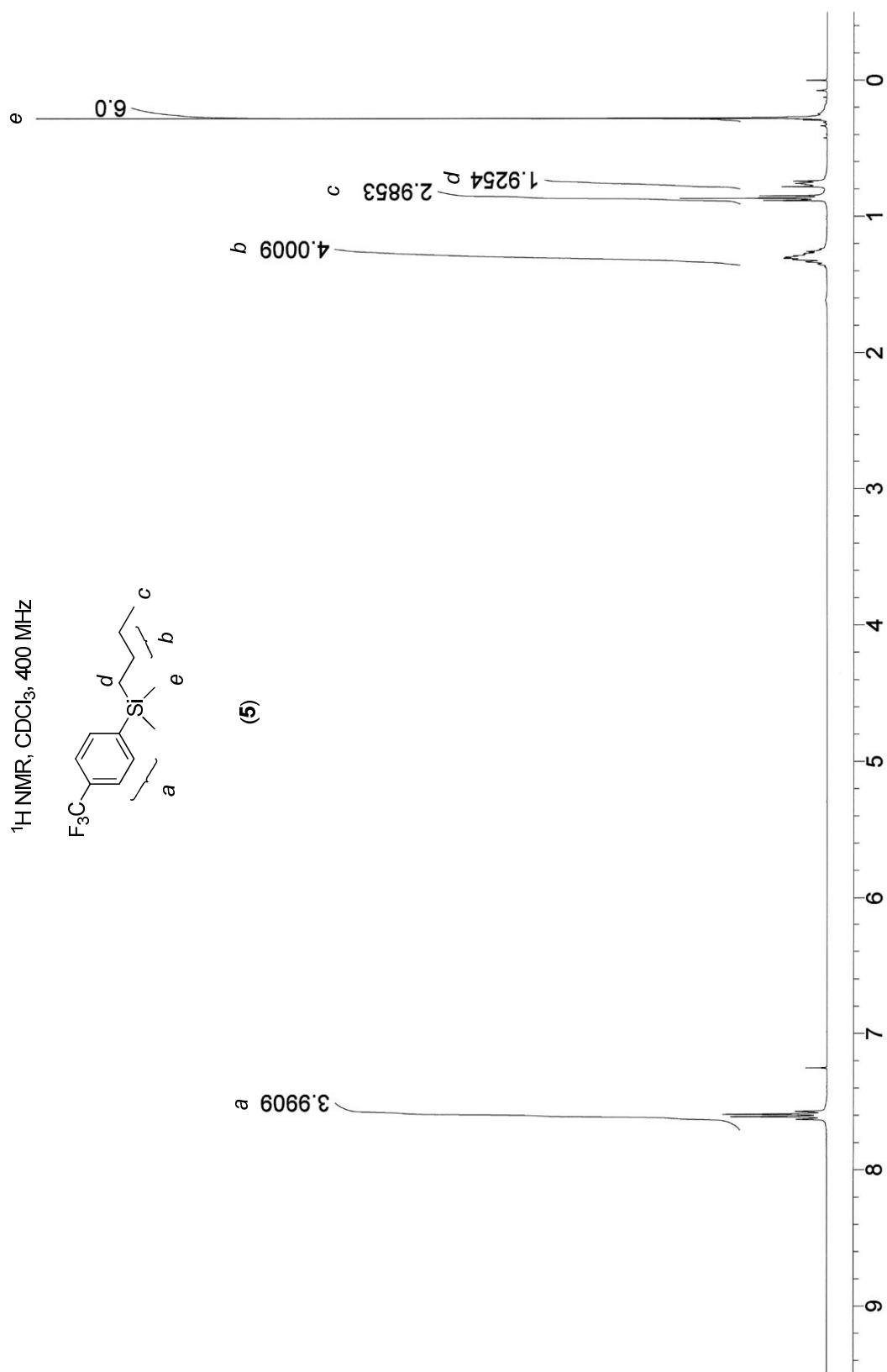
3. ^1H NMR spectra of products

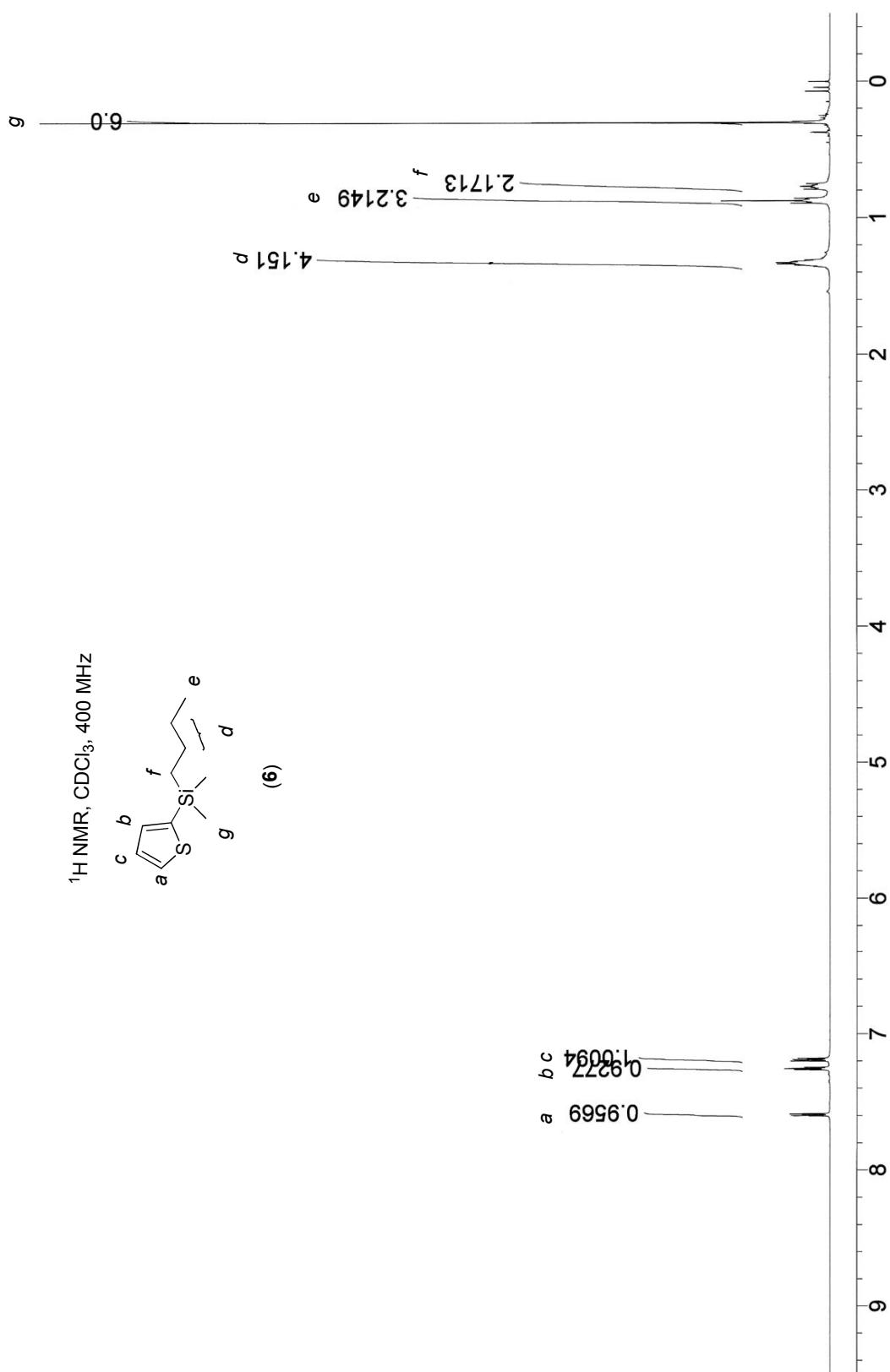


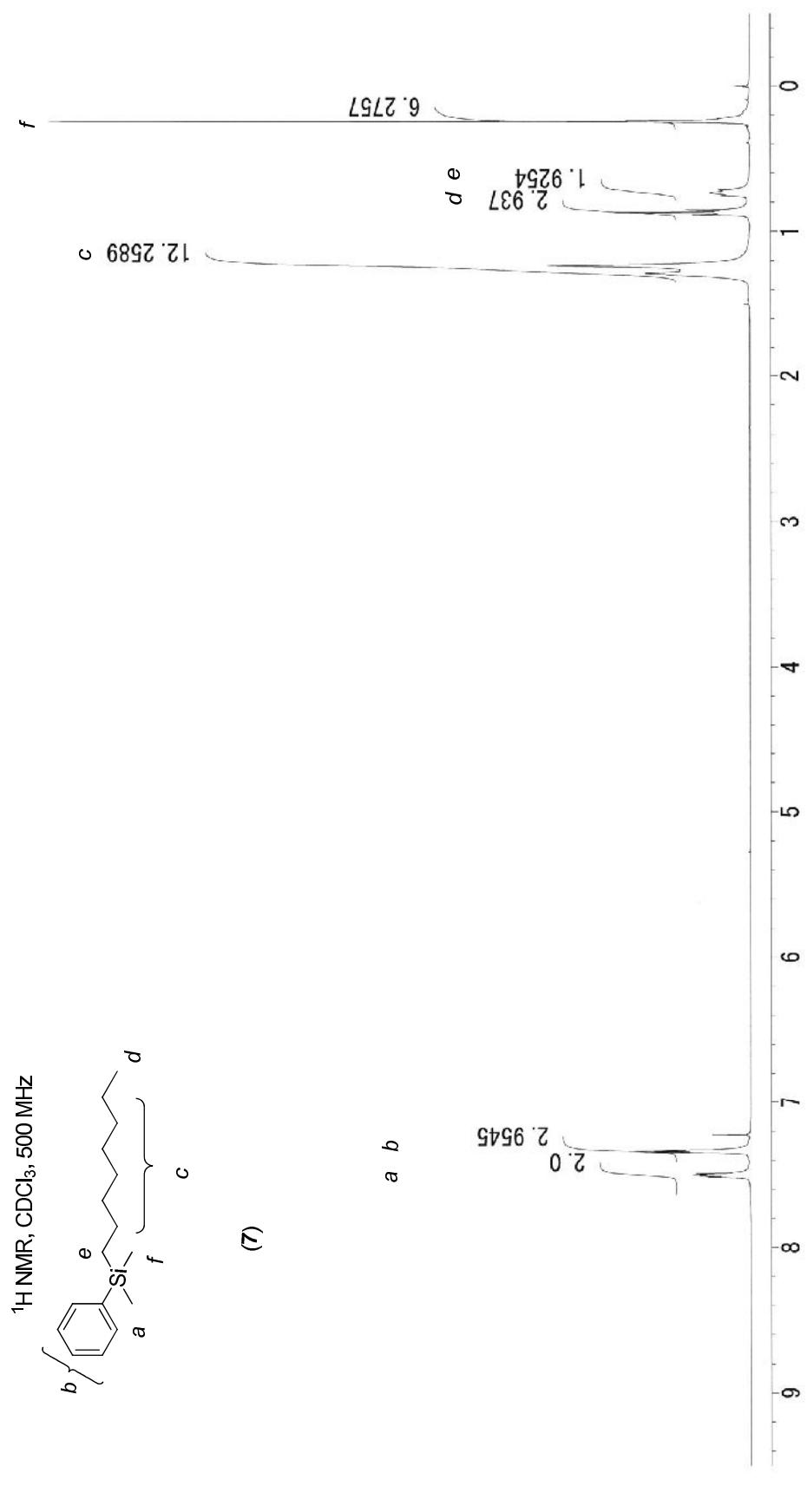


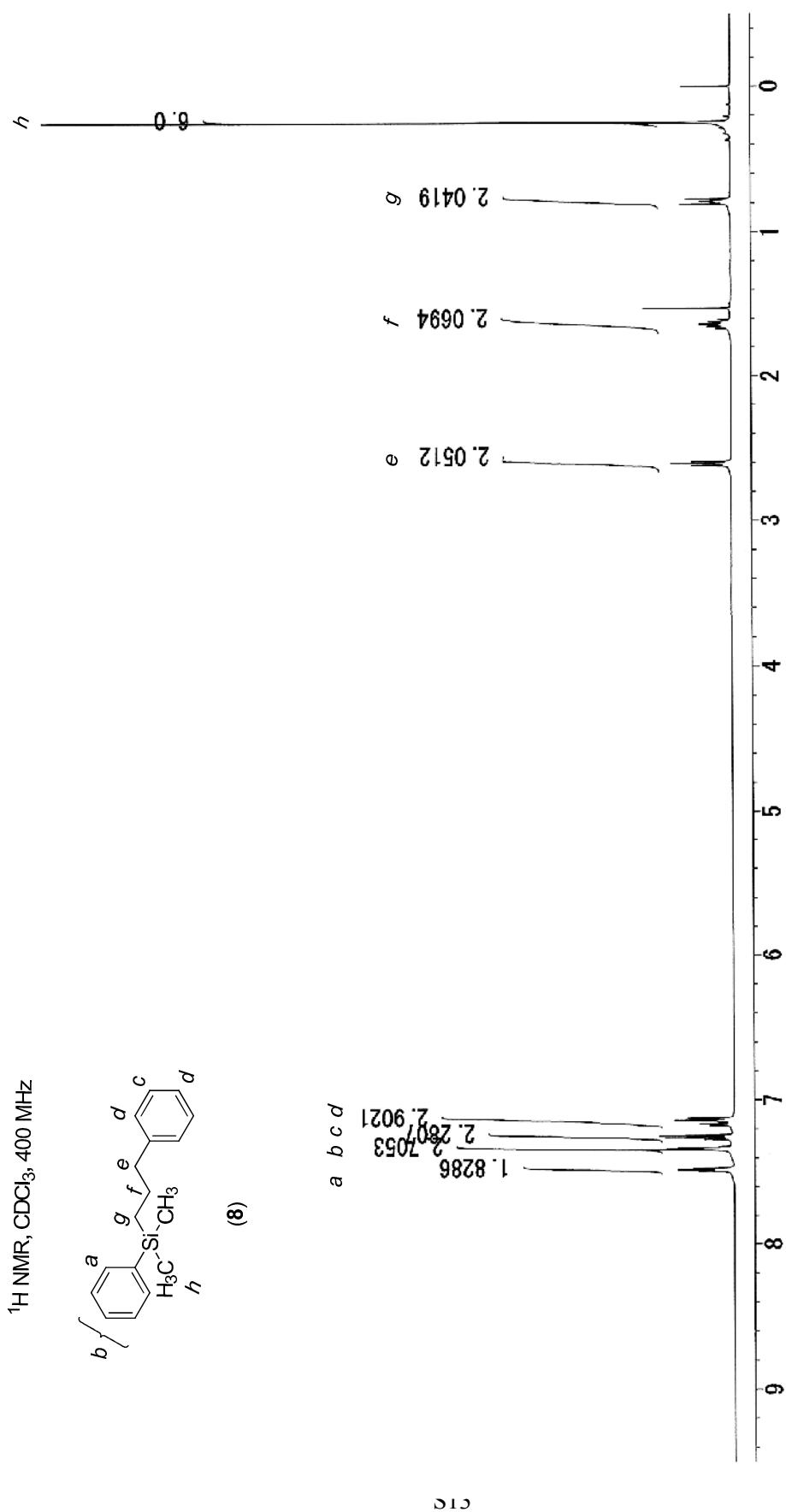


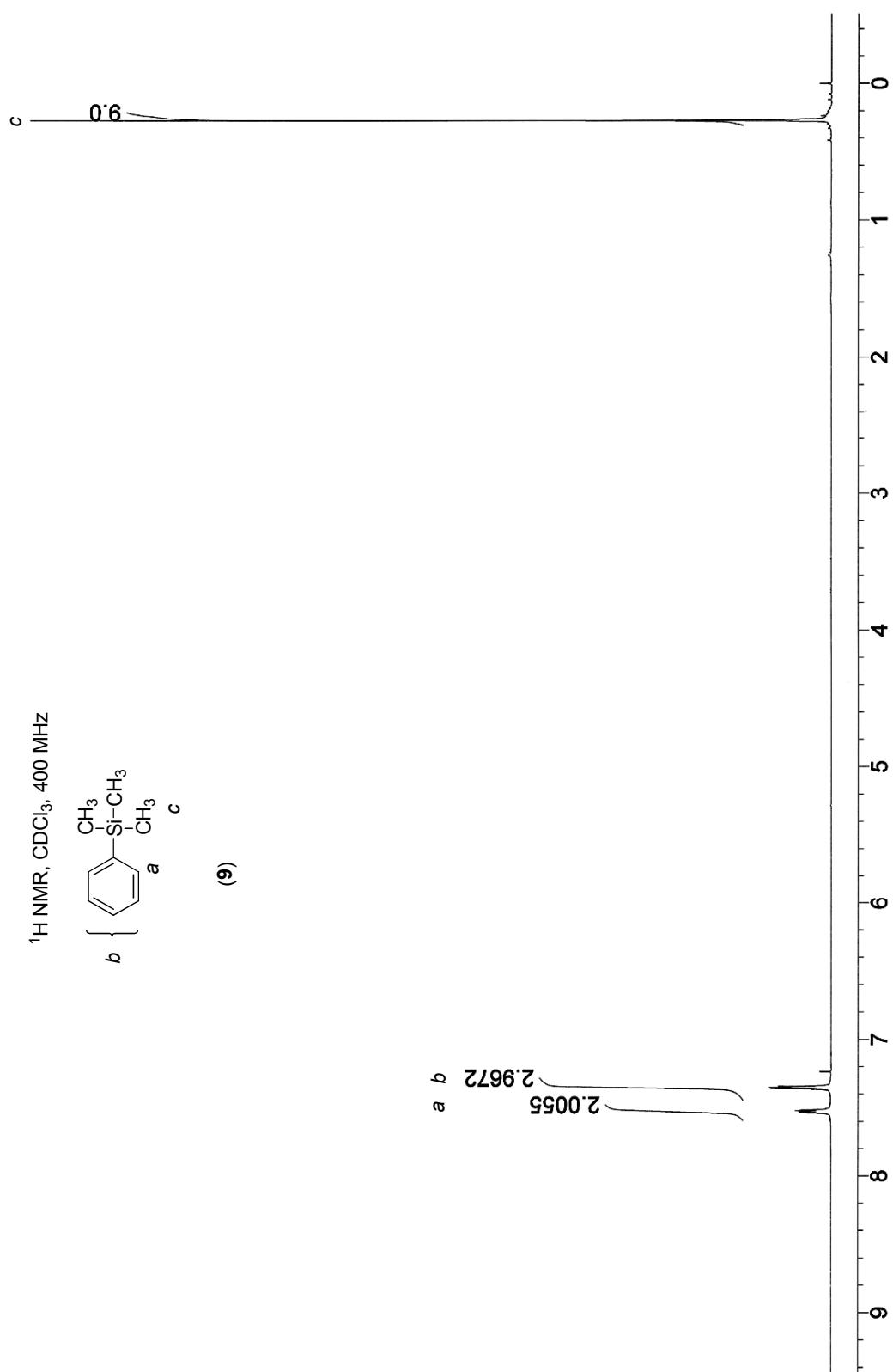


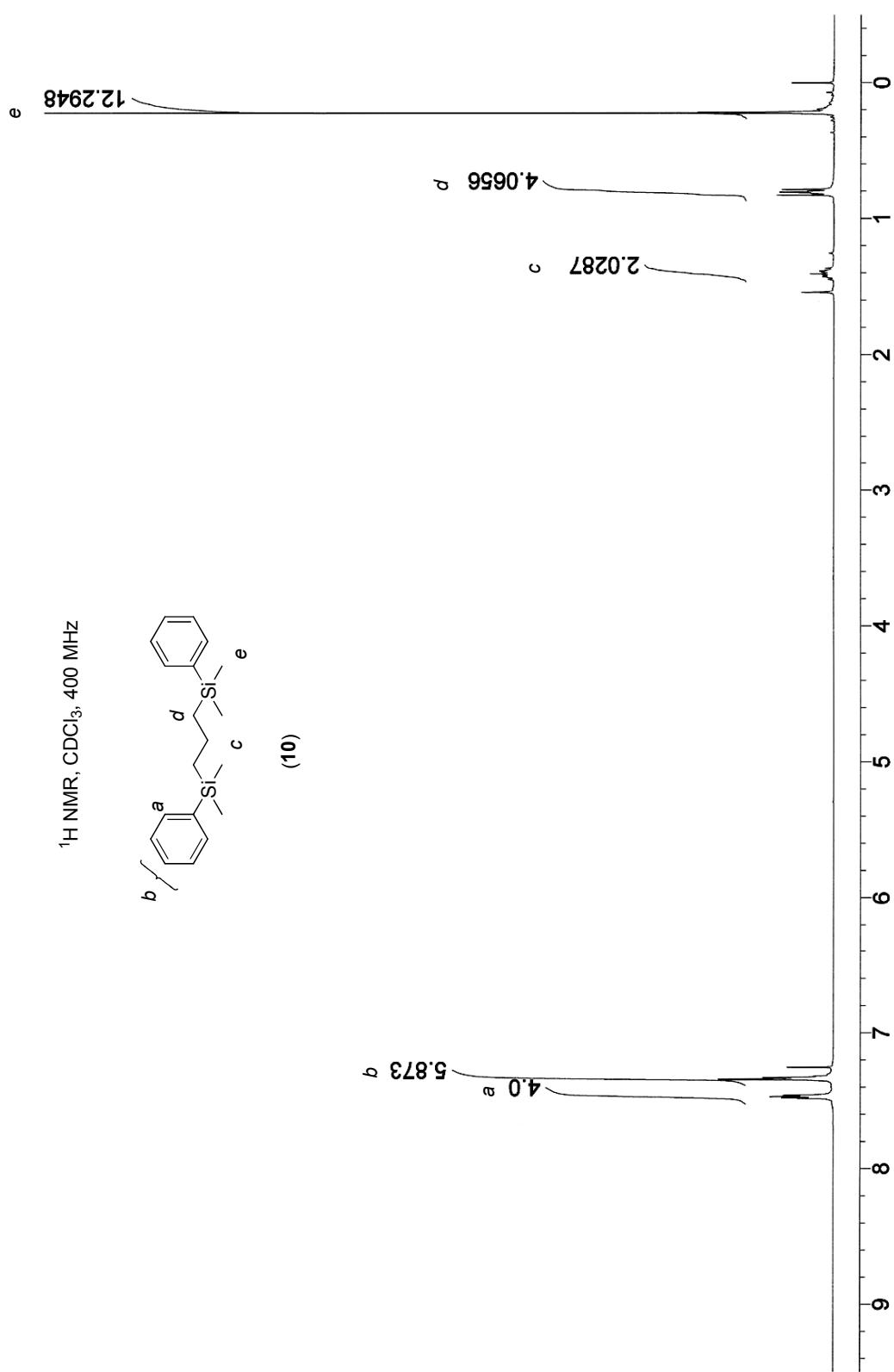


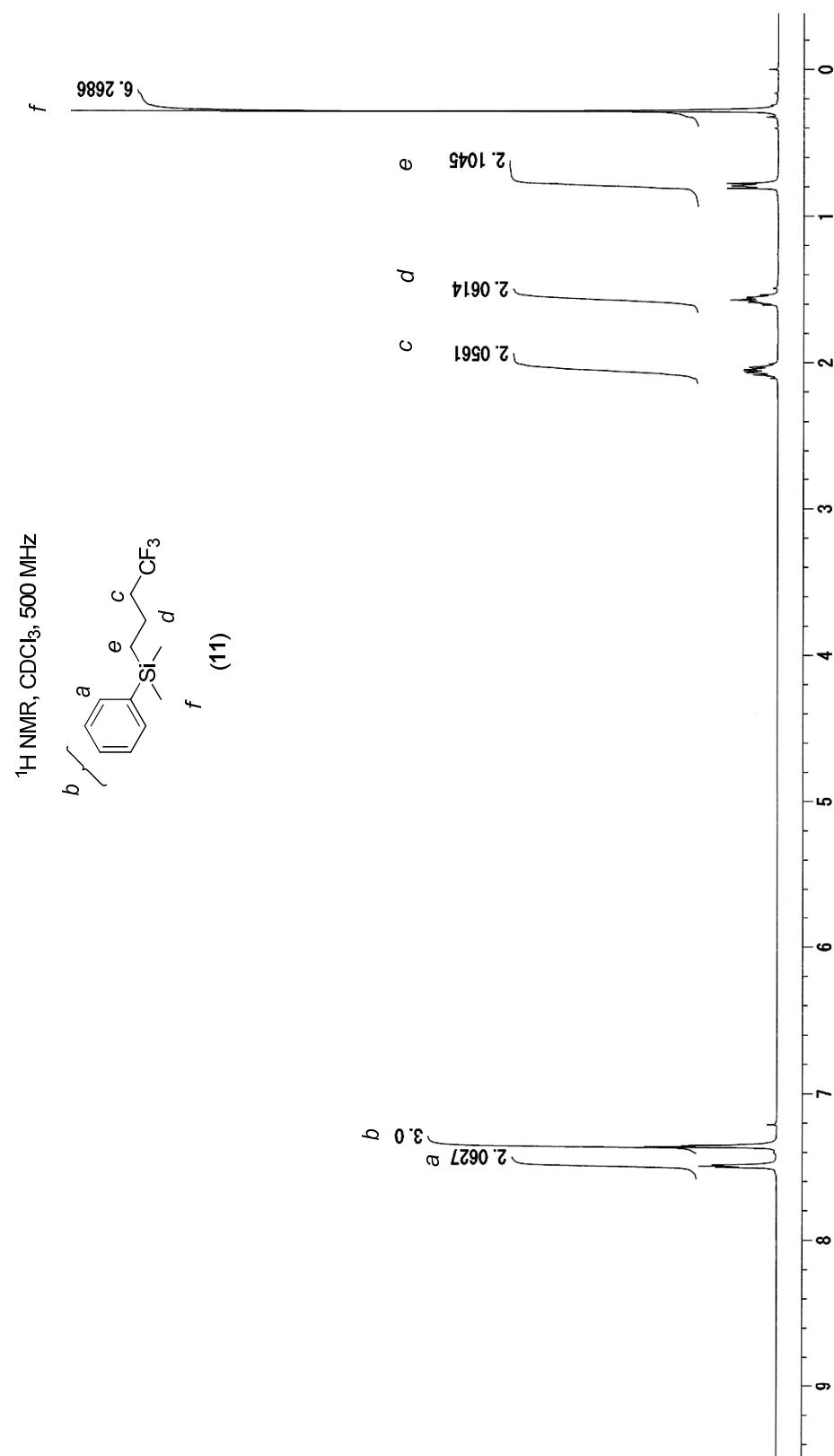


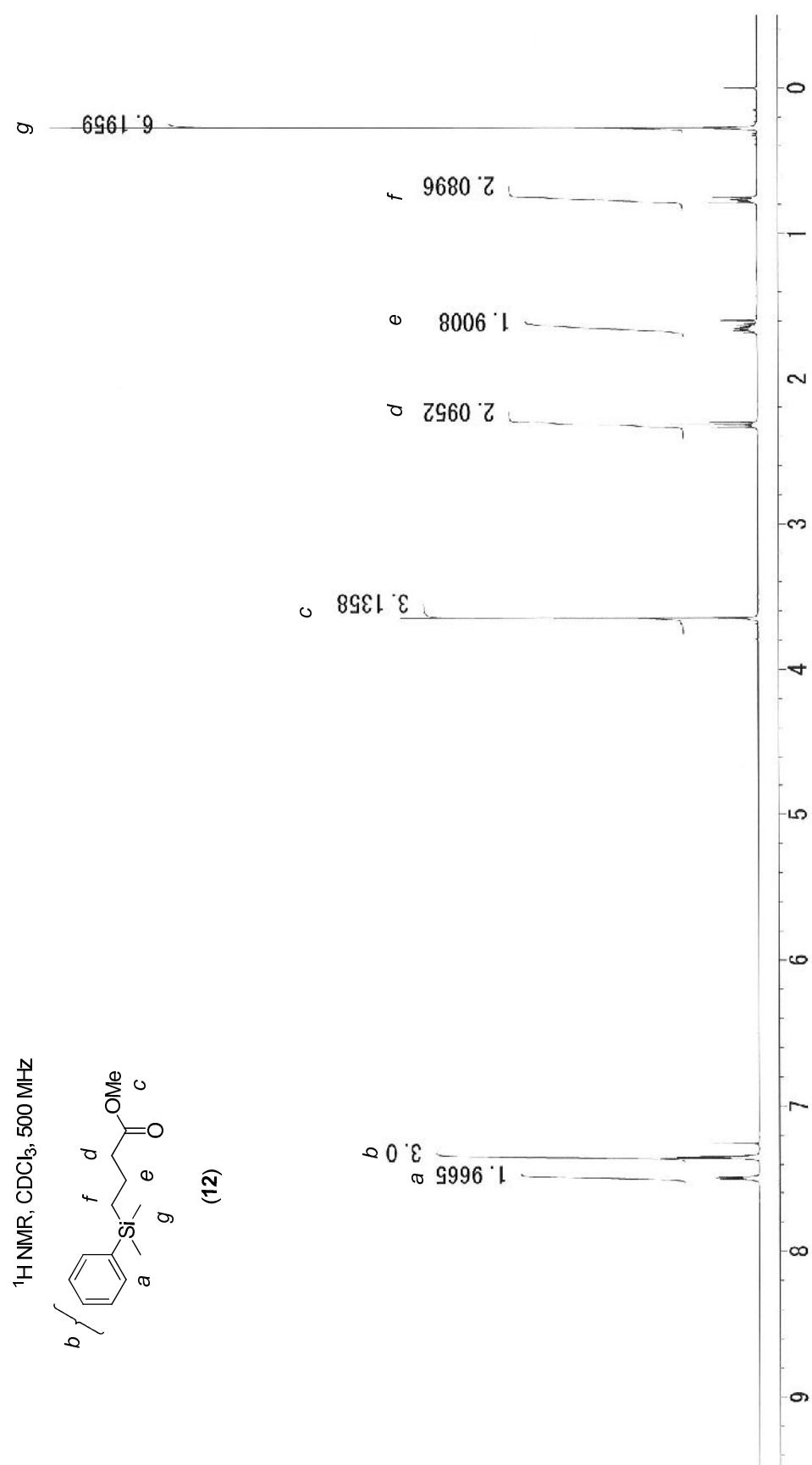


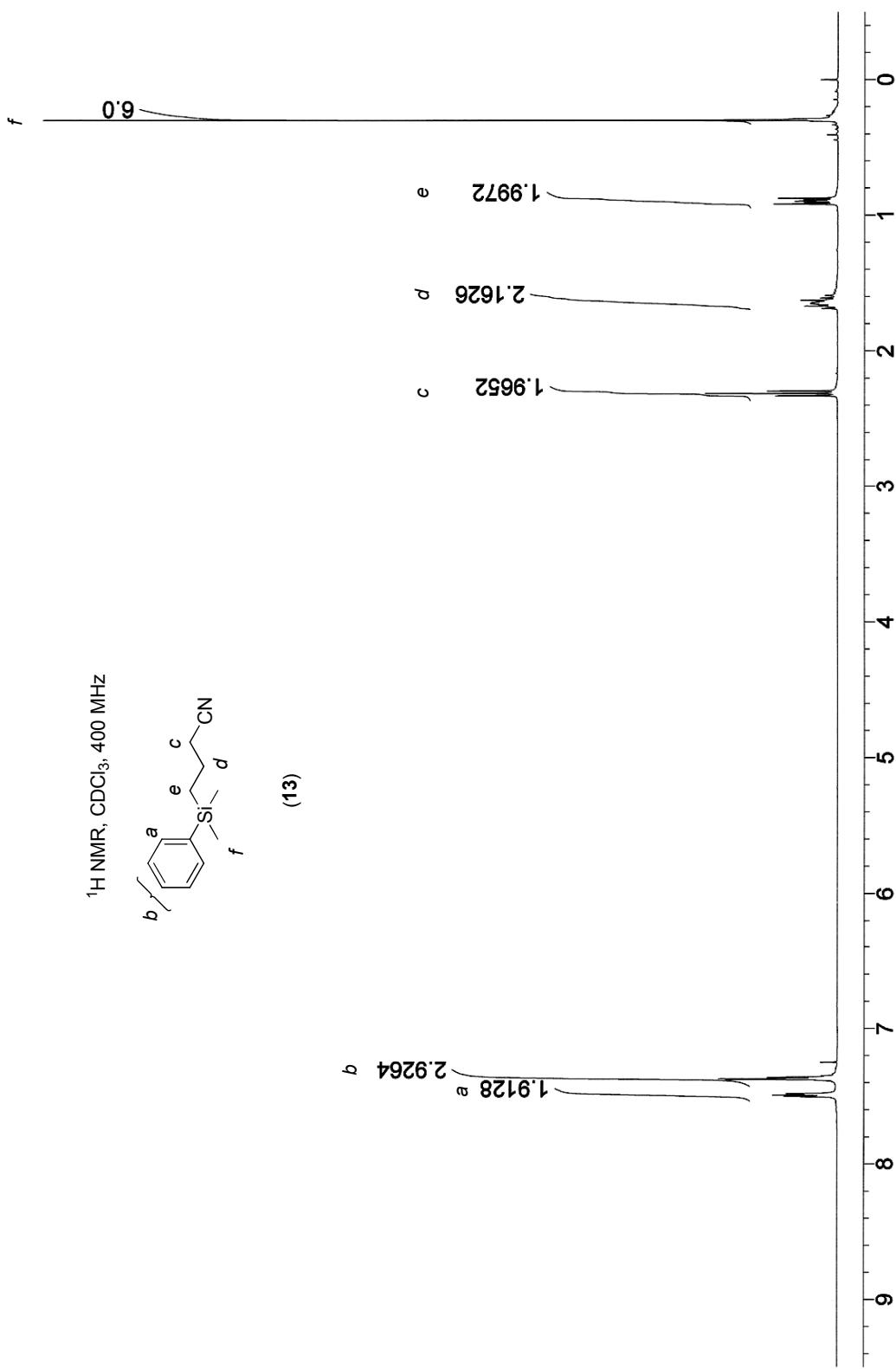


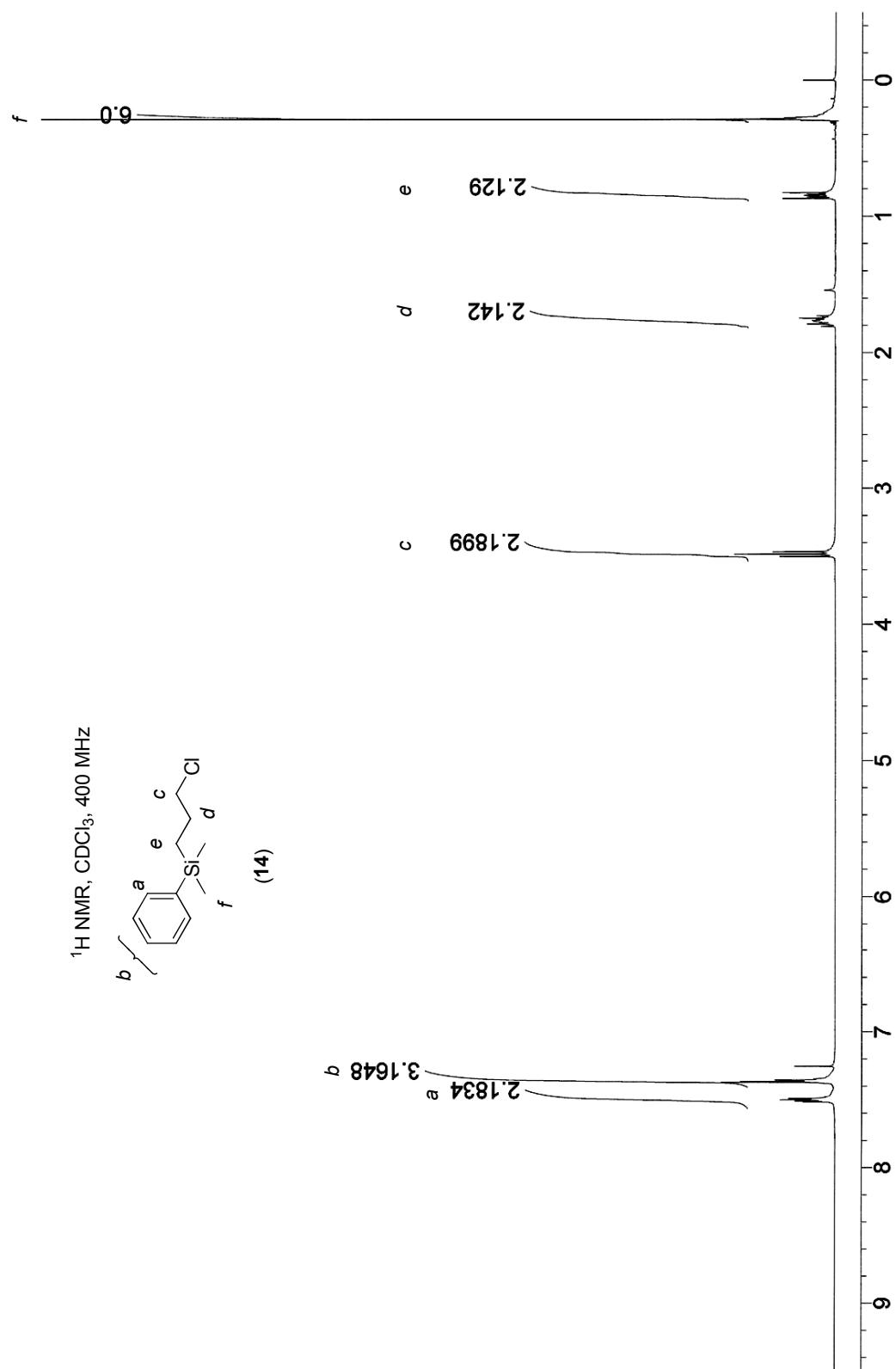


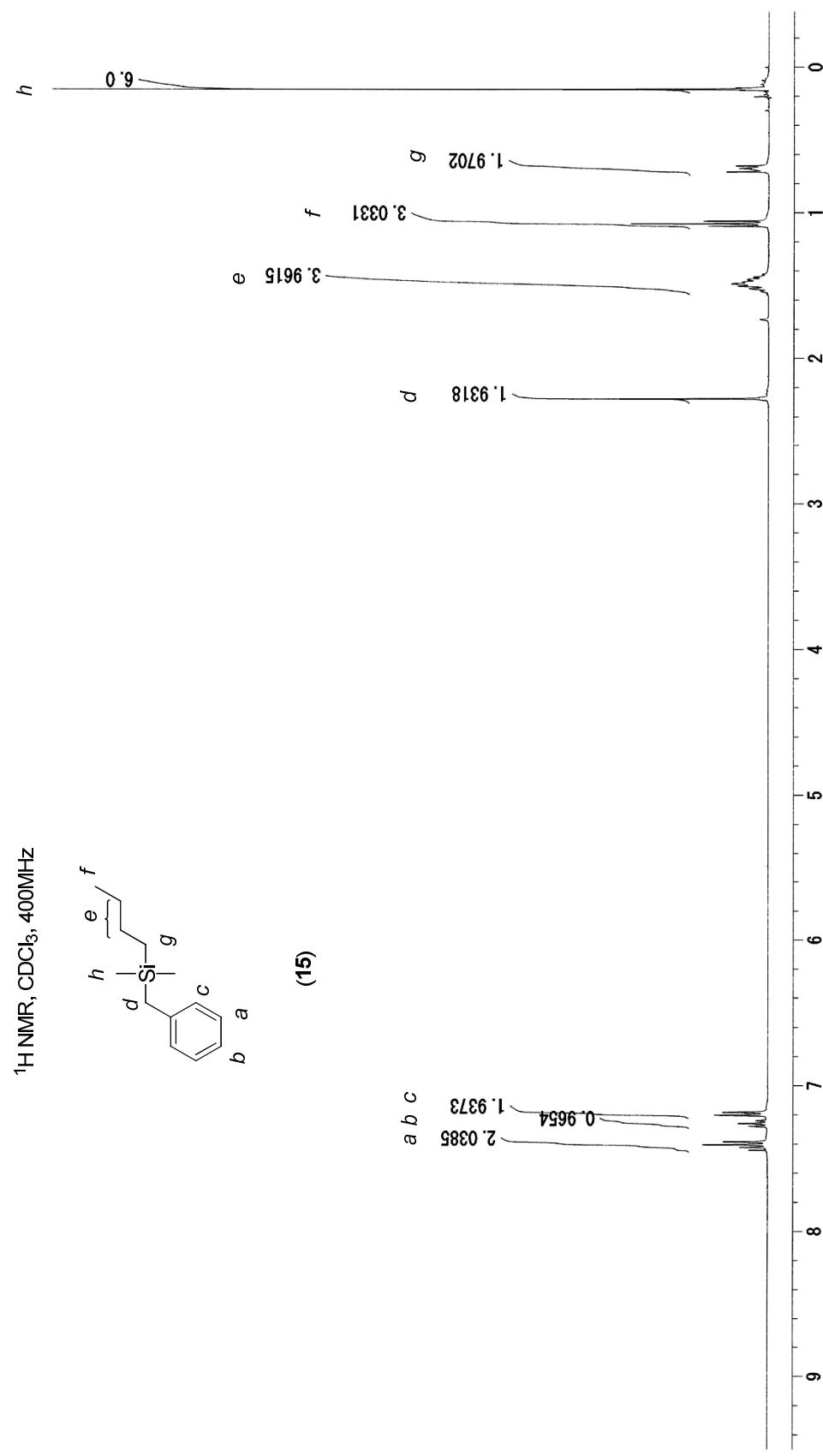


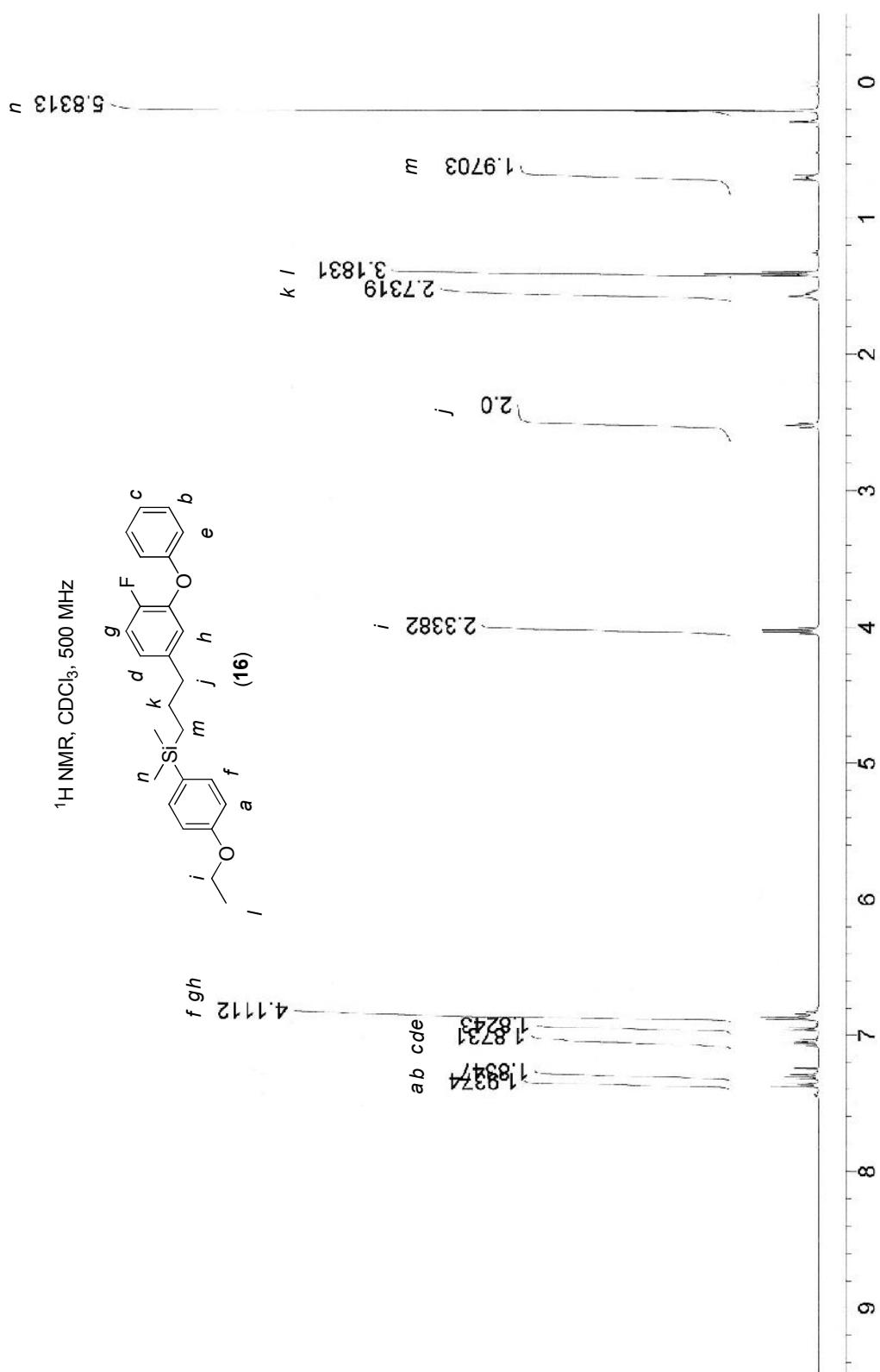




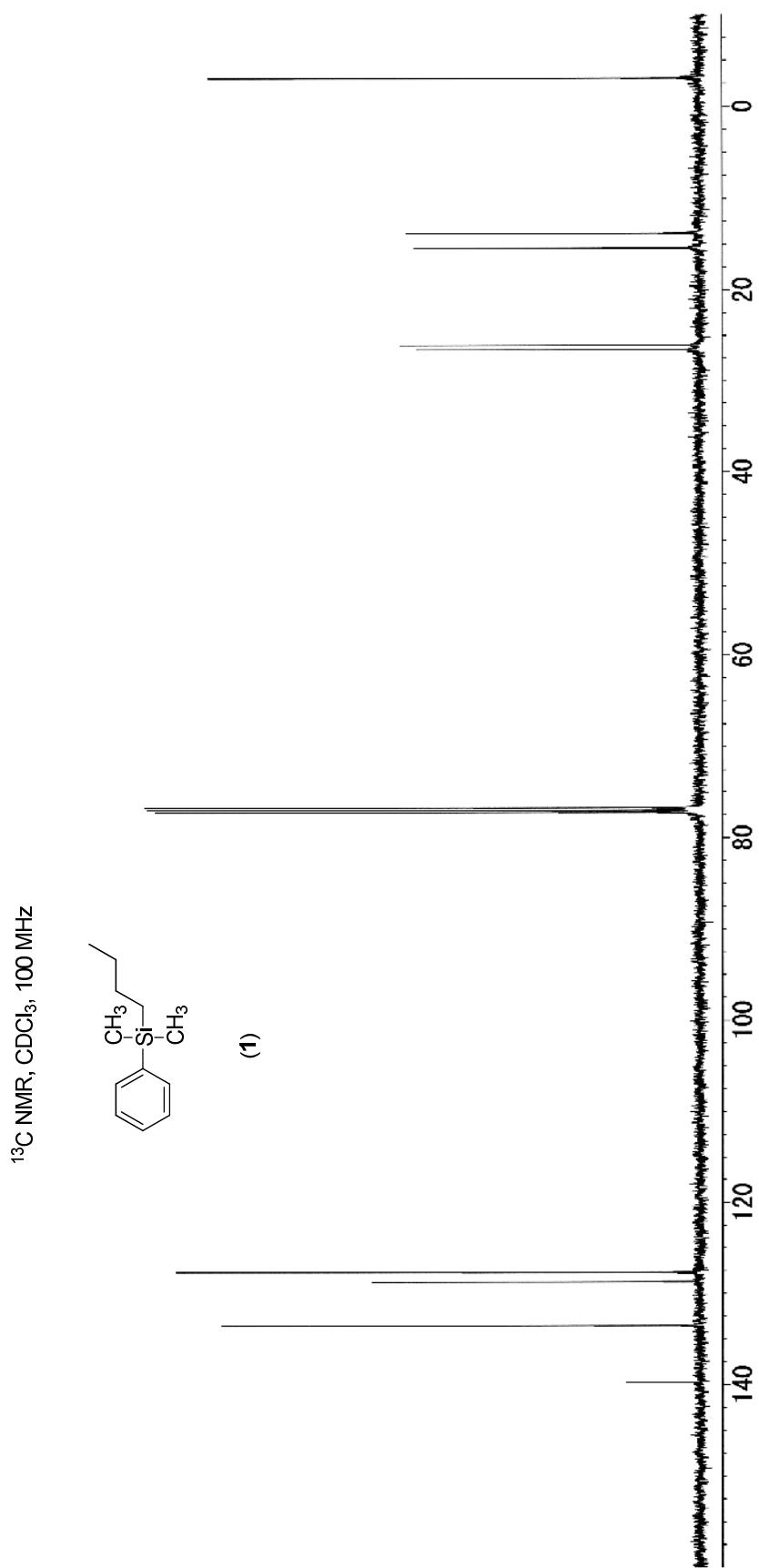




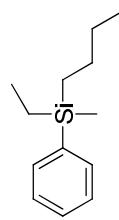




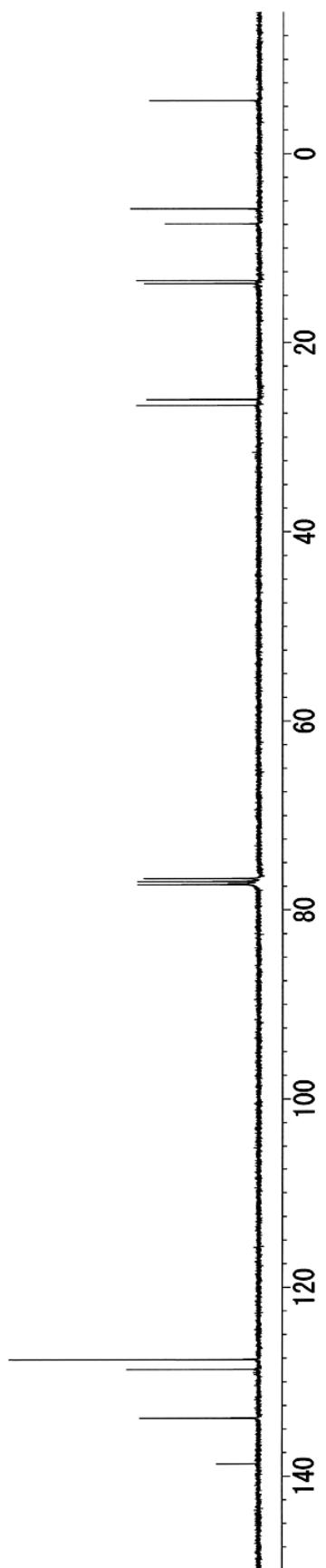
4. ^{13}C NMR spectra of products



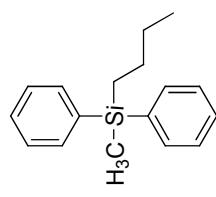
^{13}C NMR, CDCl_3 , 100 MHz



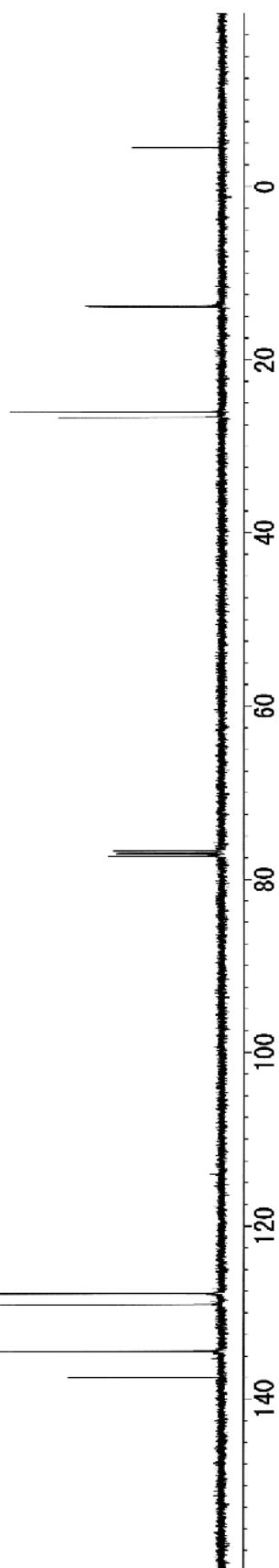
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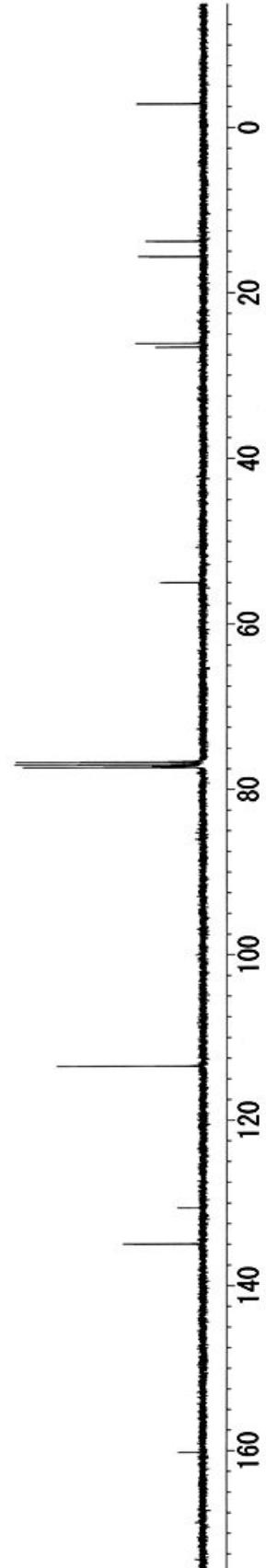
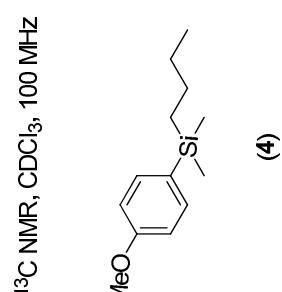


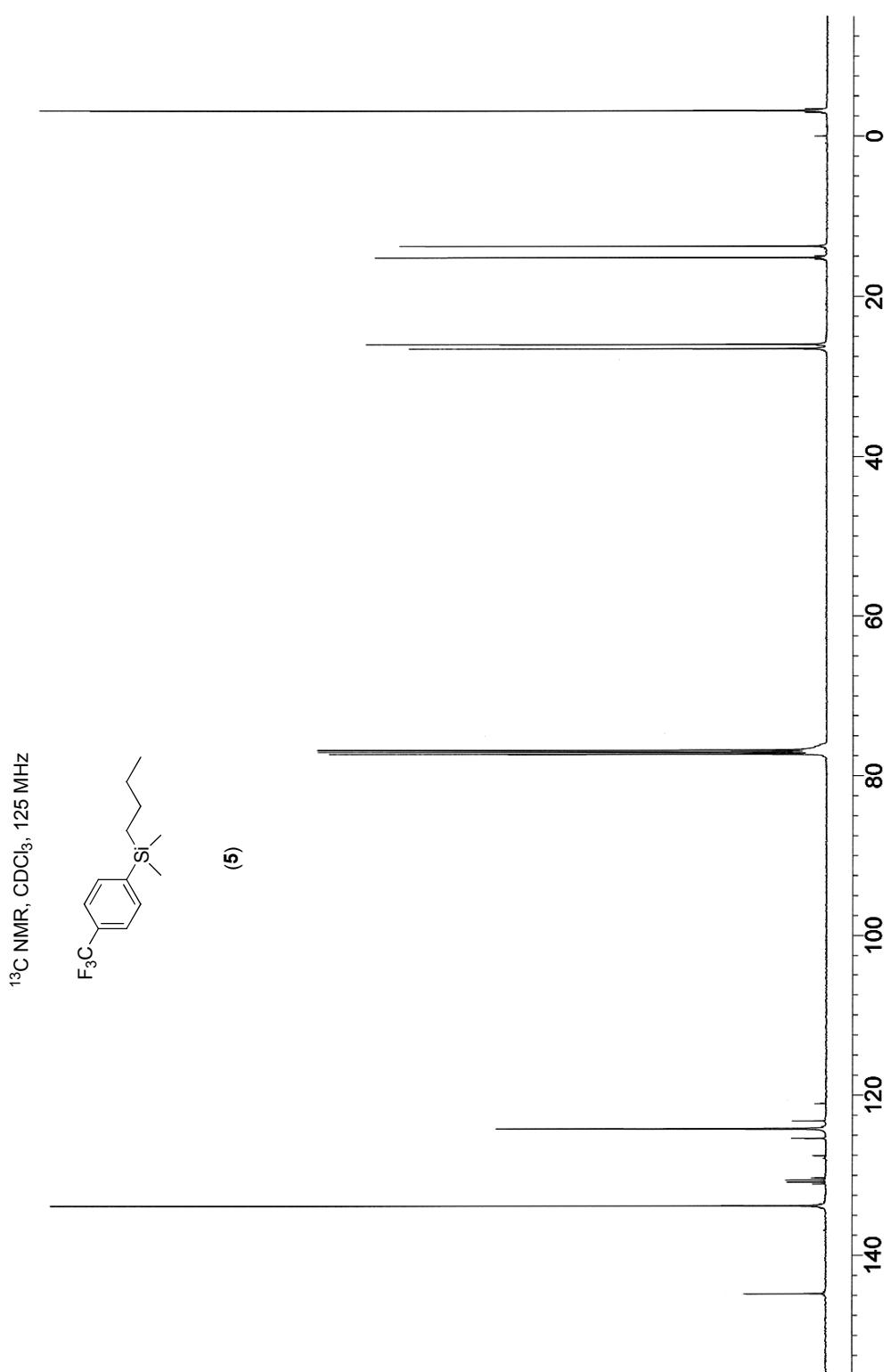
^{13}C NMR, CDCl_3 , 100 MHz



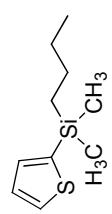
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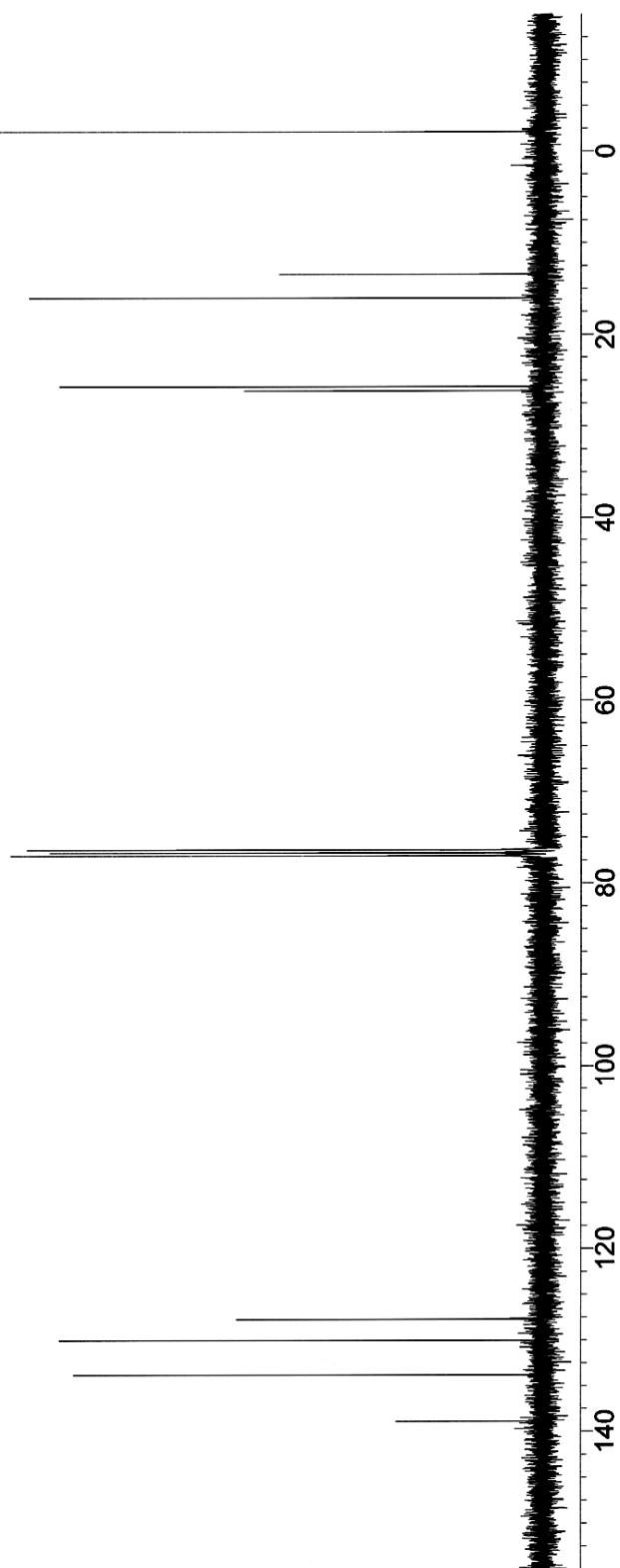


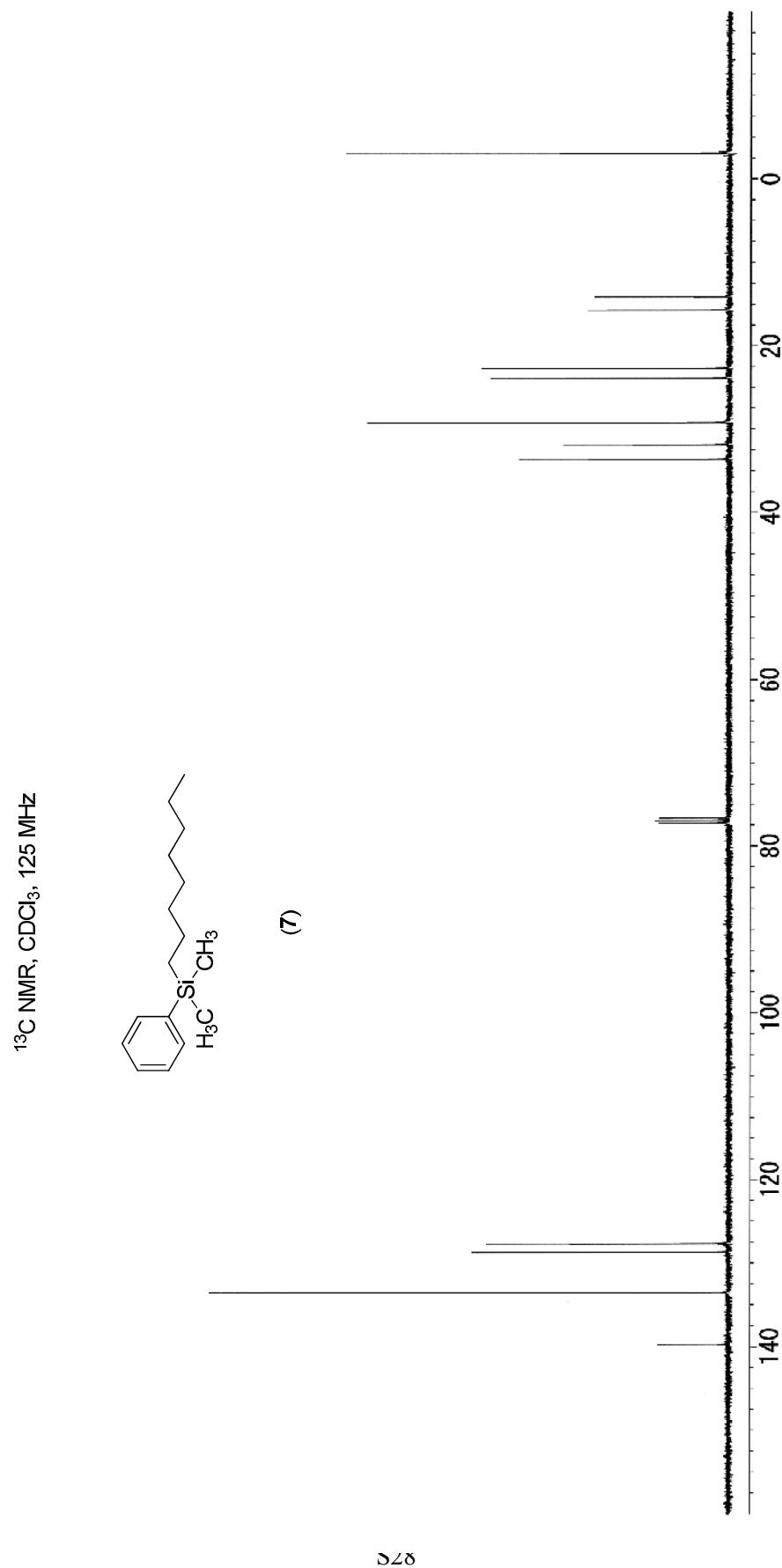


¹³C NMR, CDCl₃, 100 MHz

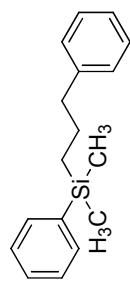


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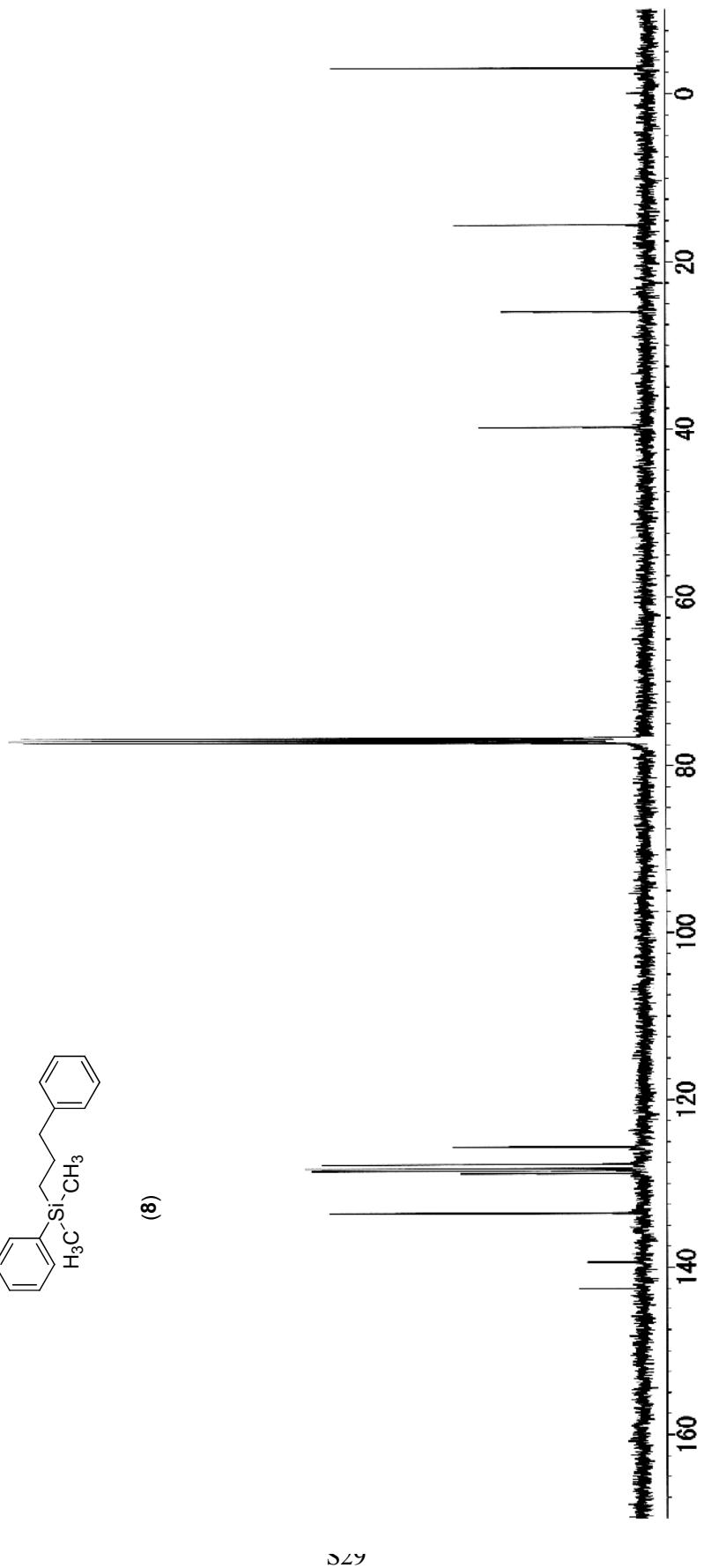


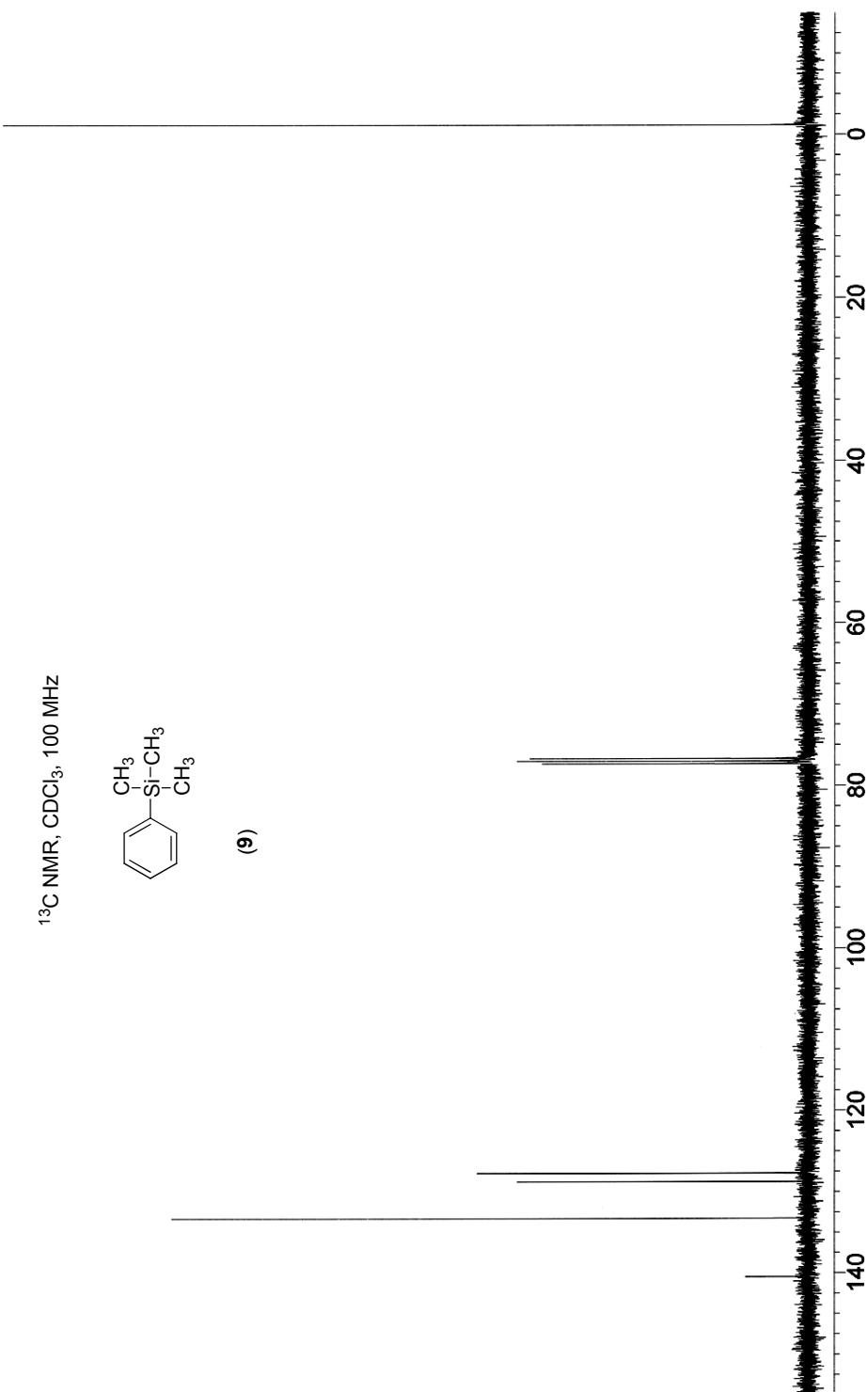


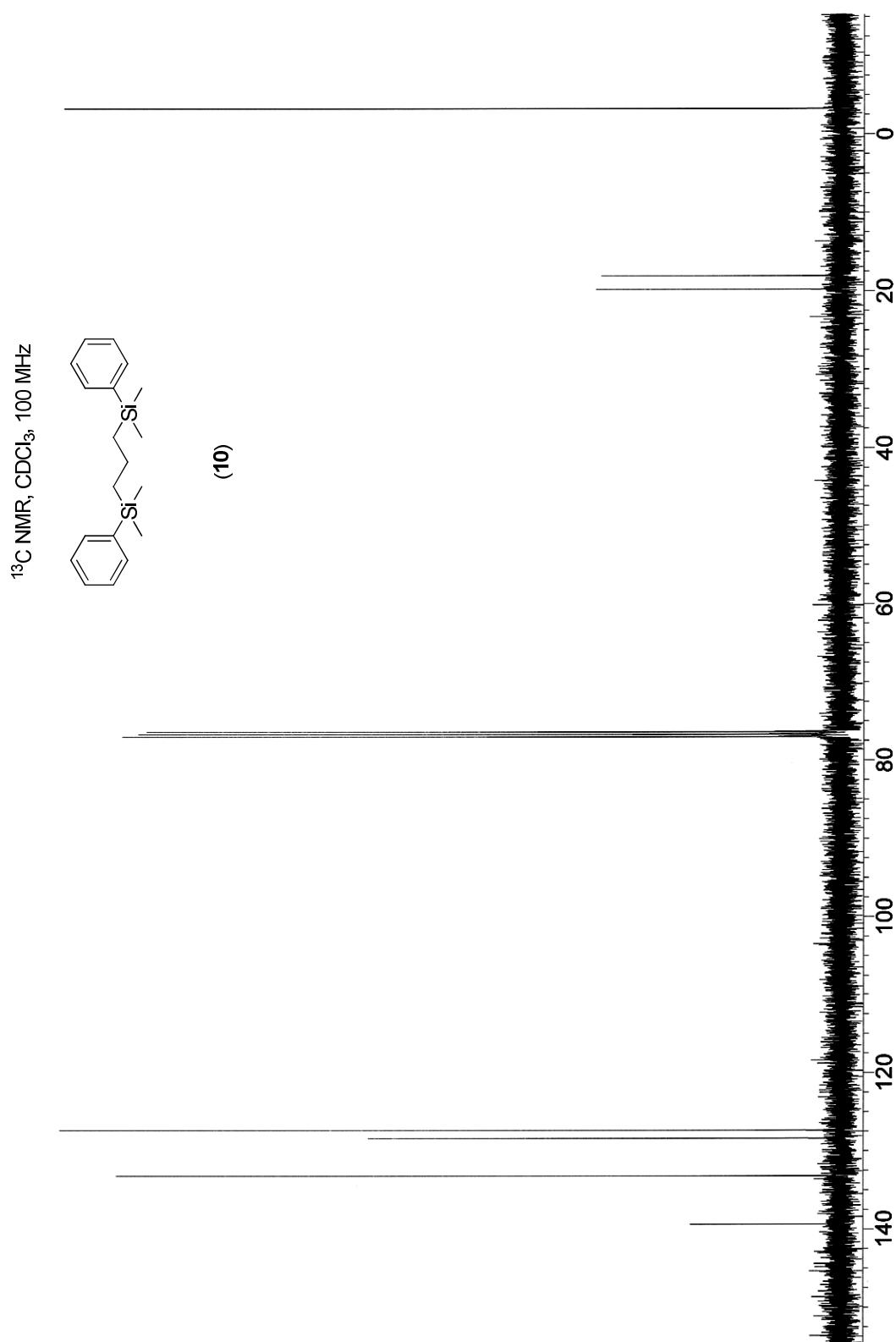
^{13}C NMR, CDCl_3 , 100 MHz

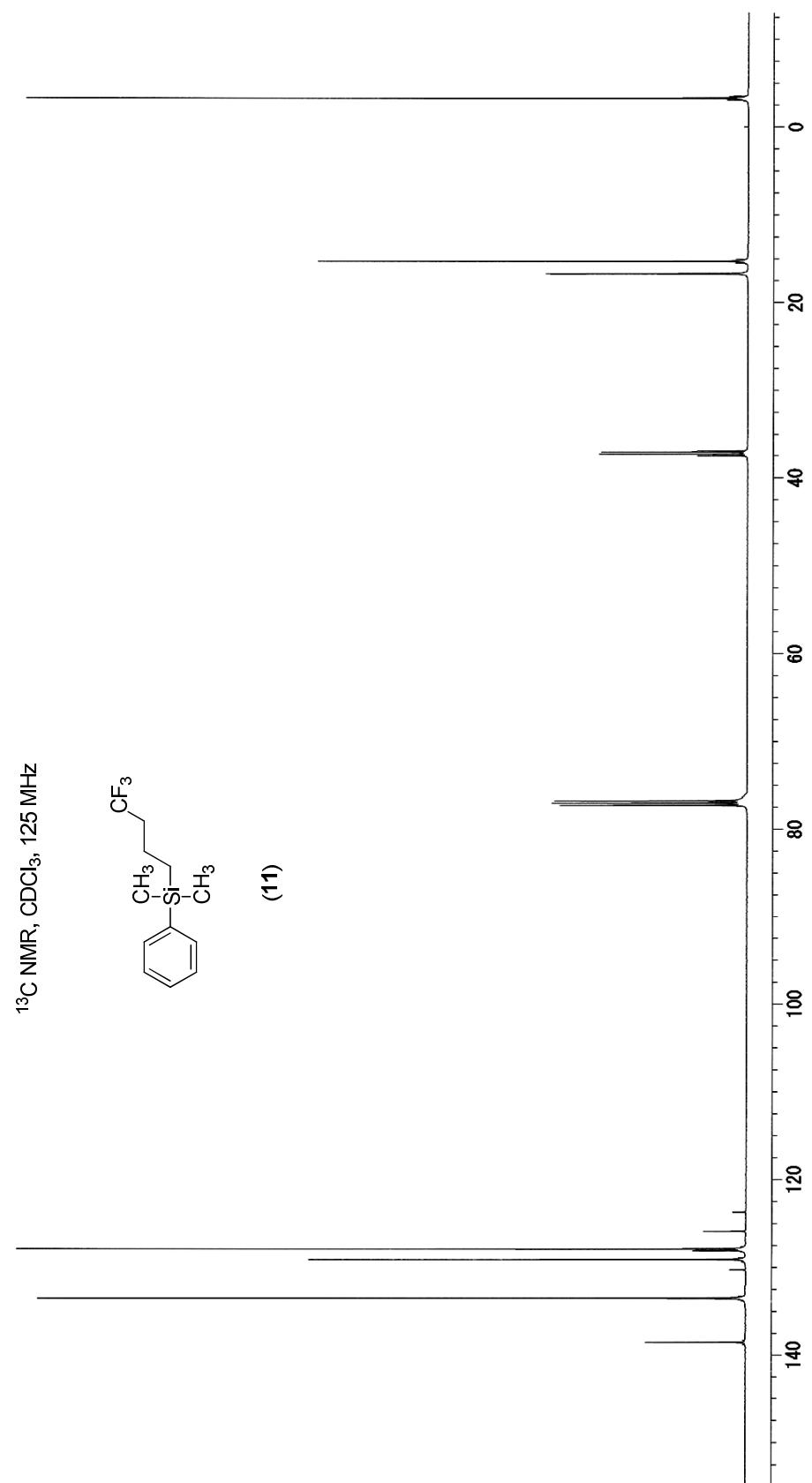


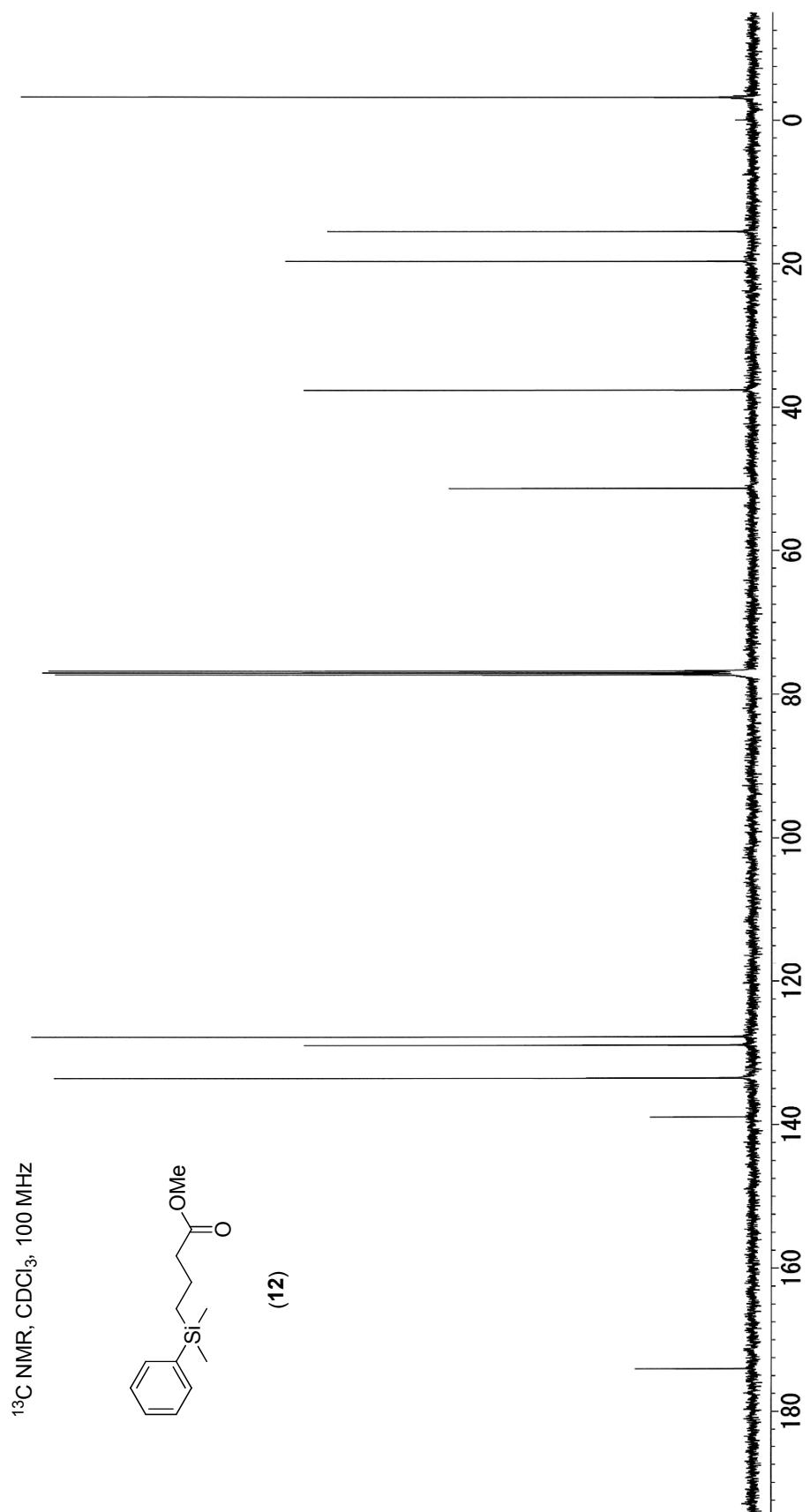
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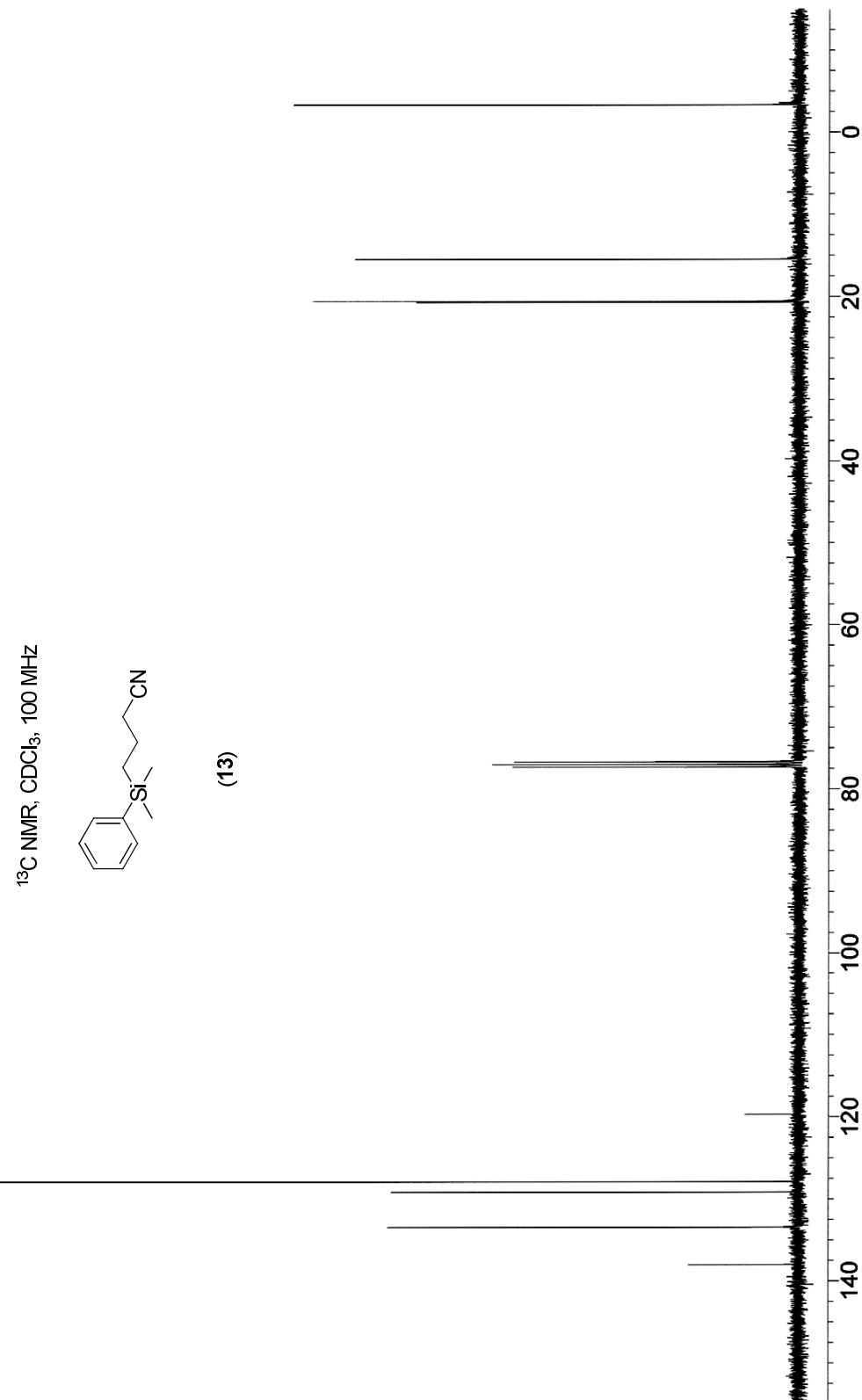


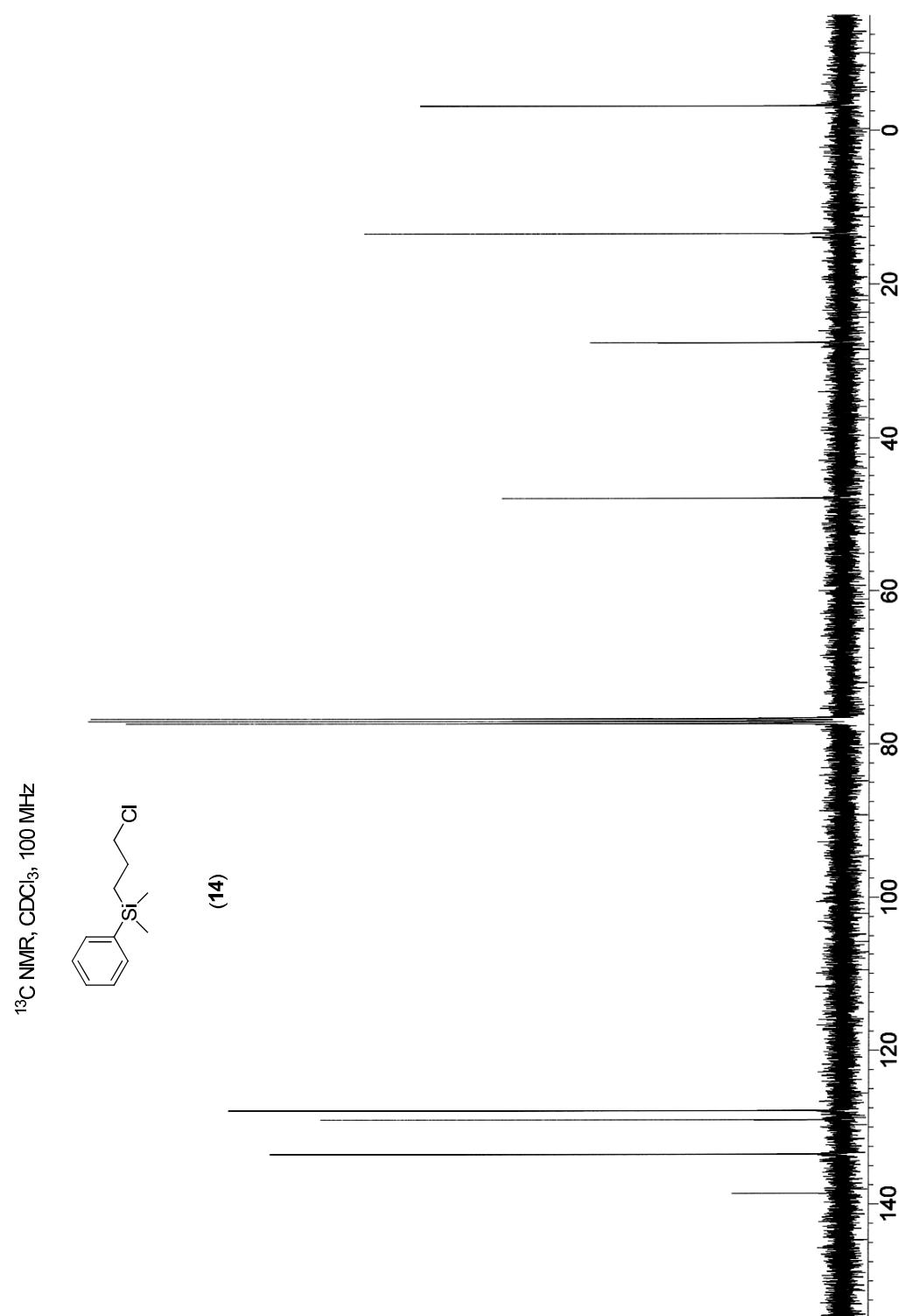


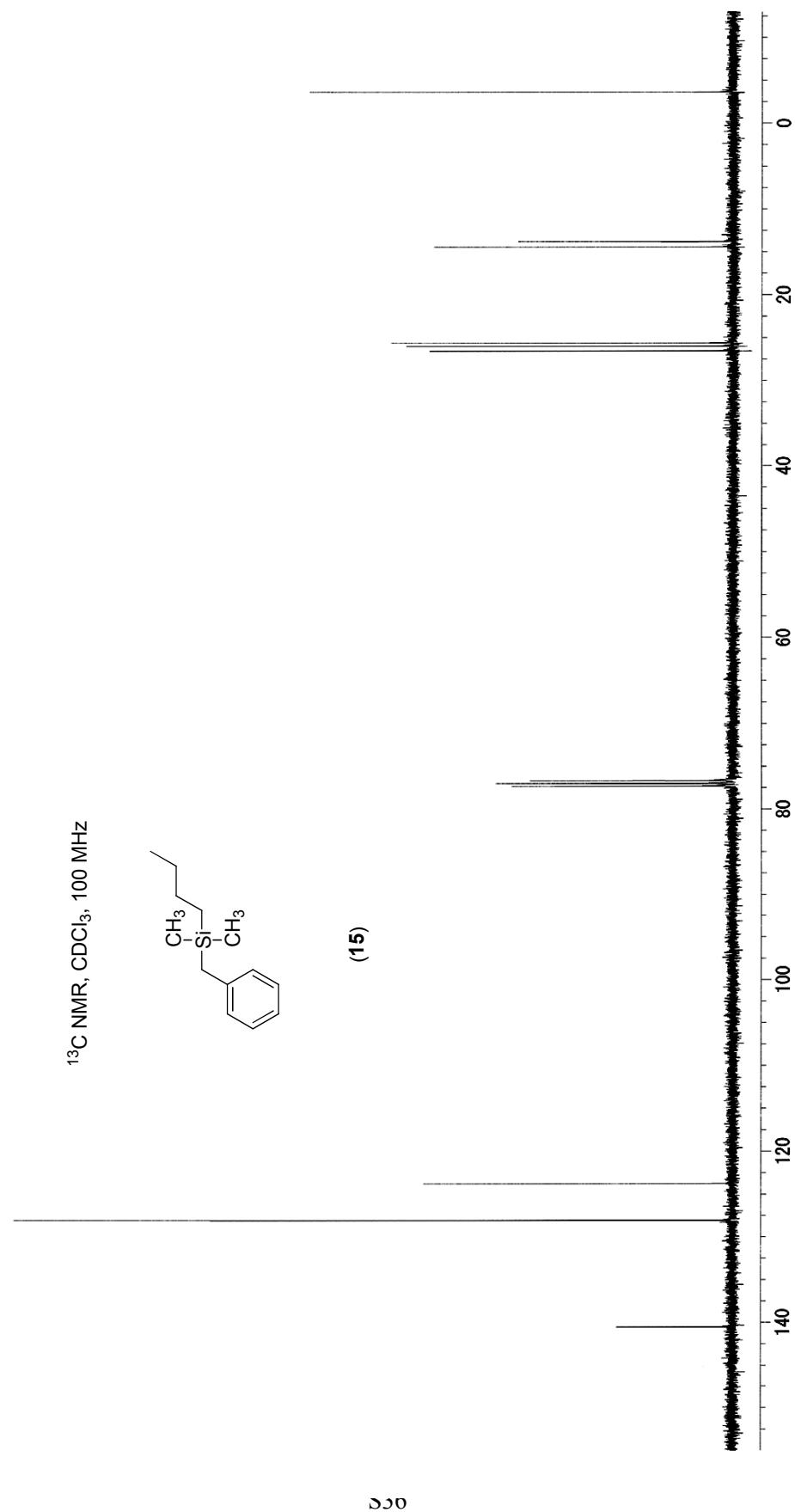


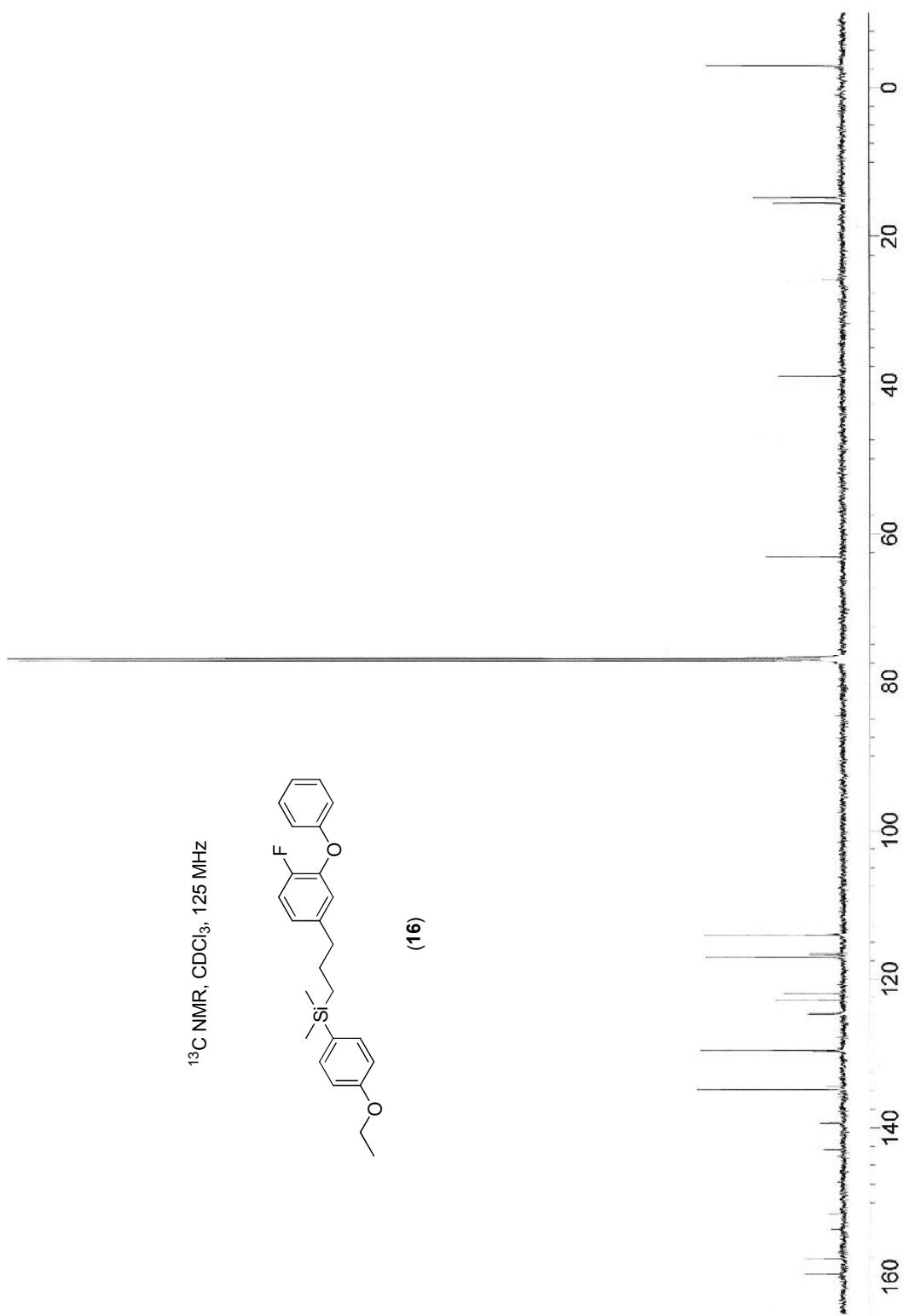












5. ^1H NMR study of the reaction mechanism

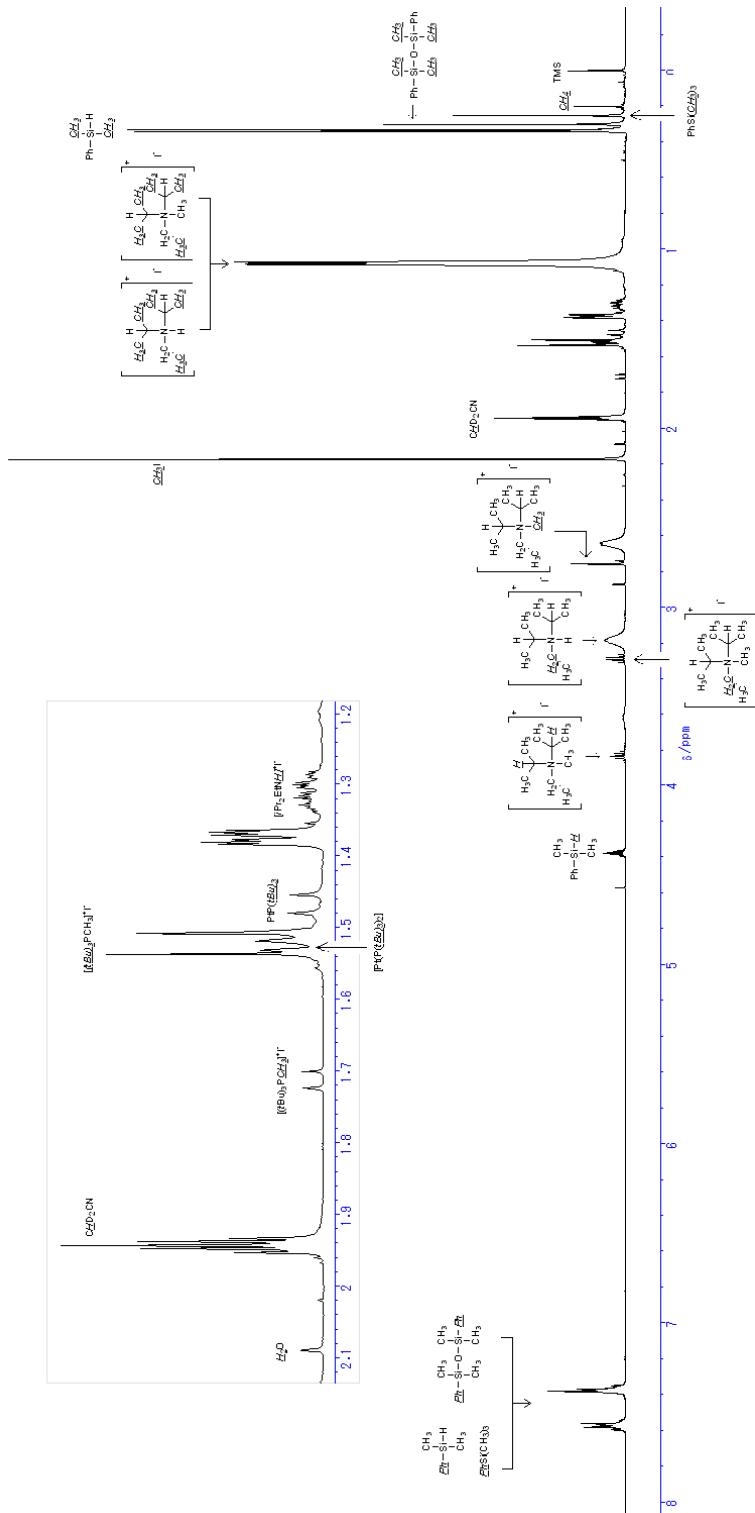


Fig. S1 ^1H NMR study of the reaction of dimethylphenylsilane with iodomethane in CD_3CN in the presence of $(i\text{Pr})_2\text{NEt}$ and $\text{Pt}(\text{P}(t\text{Bu})_3)_2$ at 25 °C. $\text{Pt}(\text{P}(t\text{Bu})_3)_2:\text{PhMe}_2\text{SiH}:(i\text{Pr})_2\text{NEt}:\text{CH}_3\text{I} = 1:2:2:2$, 3 h.

6. Plausible reaction mechanism

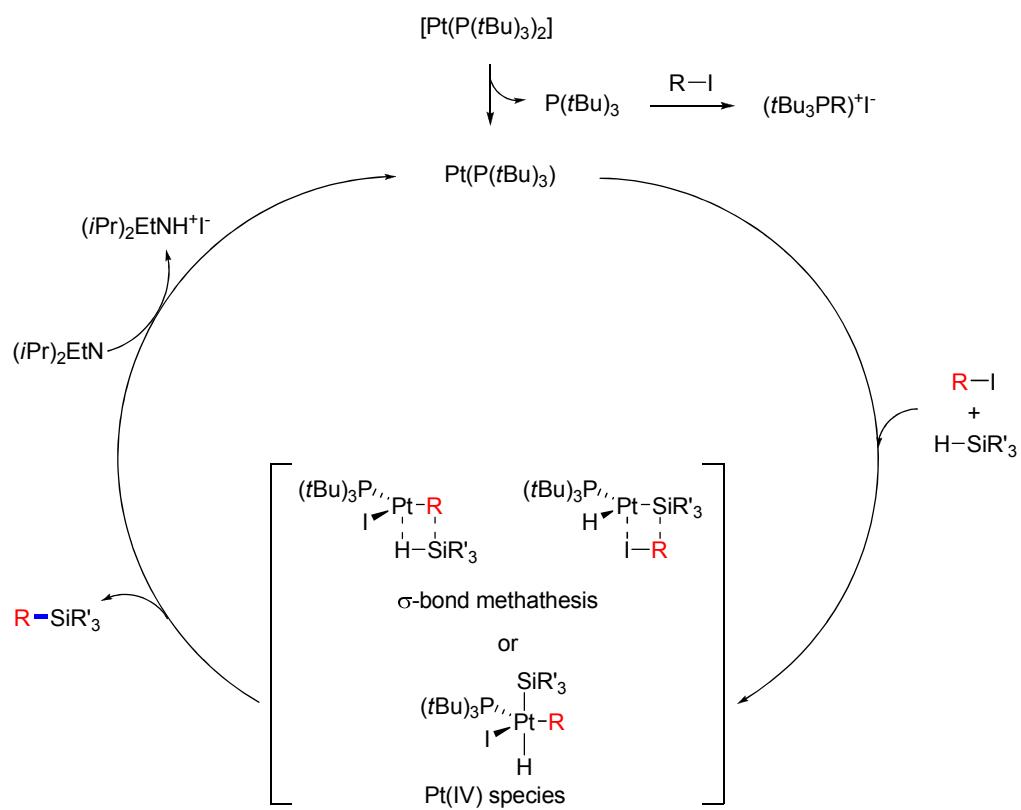


Fig. S2 Plausible reaction mechanism.