Supporting Information

for

Synthesis of Optically Active Tertiary Silanes via Pd-catalyzed Enantioselective Arylation of Secondary Silanes

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1. Chemicals

(A) Asymmetric phosphoramidite ligands.

(*R,R*)-**1** was purchased from Sigma-Aldrich. (*R,R*)-**2**,[1] (*R,R*)-**3**,[1] (*R,R*)-**4**,[2] (*R,R*)-**5**,[3] and (*R,R*)-**8**[4] were prepared according to the literature protocols.

(*R,R*)-**6** and (*R,R*)-**7** were prepared by the following method. Dichloro(dimethylamino)phosphine (640 μL, 5.5 mmol) was added to a solution of TADDOL derivative (5.5 mmol) and triethylamine (1.9 mL, 13.8 mmol) in THF (38 mL) at 0 °C. After stirring for 1 hour at 0 °C, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was the quenched with water, extracted with dichloromethane three times, and dried over sodium sulfate. The solvent was evaporated under a reduced pressure and the resulting residue triturated with methanol. The pure compound was finally obtained by filtration.

(*1R,7R*)-2,2,6,6-tetra(3,5-diethylphenyl)-4-dimethylamino-9,9-dimethyl-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*R,R*)-6): Colorless powder. $[\alpha]_D^{24}$ = -75.0 (*c* 0.99, CH_2Cl_2). Mp: 93.0–96.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.27 (s, 2H), 7.12 (s, 2H), 7.05 (s, 2H), 6.91 (s, 1H), 6.90 (s, 2H), 6.85 (s, 1H), 5.18 (dd, 1H, *J* = 8.9, 2.9 Hz), 4.85 (d, 1H, *J* = 8.5 Hz), 2.75 (s, 3H), 2.72 (s, 3H), 2.62–2.52 (m, 16H), 1.32 (s, 3H), 1.21–1.17 (m, 24H), 0.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0 (C_q), 146.7 (C_q), 143.4 (CH), 143.0 (CH), 142.9 (CH), 142.5 (CH), 142.0 (C_q), 141.8 (C_q), 126.33 (C_q), 126.29 (C_q), 126.27 (C_q), 126.18 (C_q), 126.0 (CH), 125.9 (CH), 124.3 (CH), 124.1 (CH), 111.1 (C_q), 83.1 (CH), 82.8 (C_q), 81.7 (CH), 81.4 (C_q), 35.4 (CH_3), 35.2 (CH_3), 29.1 (CH_2), 28.94 (CH_2), 28.91 (CH_2), 27.6 (CH_3), 25.1 (CH_3), 15.9 (CH_3), 15.6 (CH_3), 15.5 (CH_3), 15.4 (CH_3). Anal: Calcd. for $C_{49}H_{66}NO_4P$: C, 77.03; H, 8.71; N, 1.83. Found: C, 76.81; H, 8.76; N, 1.70.

(*1R,7R*)-2,2,6,6-tetra(3,5-dimethoxyphenyl)-4-dimethylamino-9,9-dimethyl-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane ((*R,R*)-7): Colorless cube. $[\alpha]_D^{24}$ = -88.4 (*c* 1.01, CH_2Cl_2). Mp: 221.0–223.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, 2H, *J* = 2.2 Hz), 6.81 (d, 2H, *J* = 2.2 Hz), 6.70 (d, 2H, *J* = 2.0 Hz), 6.68 (d, 2H, *J* = 2.2 Hz), 6.35–6.30 (m, 4H), 5.13 (dd, 1H, *J* = 8.5, 3.4 Hz), 4.68 (d, 1H, *J* = 8.5 Hz), 3.74 (s, 6H), 3.73 (s, 12H), 3.72 (s, 6H), 2.81 (s, 3H), 2.79 (s, 3H), 1.42 (s, 3H), 0.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3 (CH), 160.0 (CH), 159.9 (CH), 159.6 (CH), 149.1 (C_q), 148.4 (C_q), 143.8 (C_q), 143.6 (C_q), 111.3 (C_q), 107.8 (CH), 107.1 (CH), 105.7 (CH), 105.6 (CH), 99.3 (C_q), 98.9 (C_q), 98.5 (C_q), 98.4 (C_q), 83.0 (CH), 82.6 (C_q), 81.1 (C_q), 81.0 (C_q), 55.3 (CH_3), 55.2 (CH_3), 55.1 (CH_3), 35.5 (CH_3), 35.3 (CH_3), 27.7 (CH_3), 25.3 (CH_3). Anal: Calcd. for $C_{41}H_{50}NO_{12}P$: C, 63.15; H, 6.46; N, 1.80. Found: C, 62.95; H, 6.58; N, 1.64.

(B) Dihydrosilanes.

Methylphenylsilane was purchased from Sigma-Aldrich. Phenylpropylsilane,[5] isopropylphenylsilane,[5] *t*-butylphenylsilane,[6] methyl(naphthalen-1-yl)silane,[6] (naphthalen-1-yl)phenylsilane,[5] and *t*-butylmethylsilane[7] was prepared by modified literature protocols.

(C) Enantioselective Arylation.

Typical experimental procedure for palladium-catalyzed asymmetric arylation reaction at -40 °C.

A mixture of $Pd_2(dba)_3$ (23 mg, 0.025 mmol) and phosphoramidite ligand (0.075 mmol) was stirred in THF (2 mL) for 2 hours at room temperature. The reaction mixture was cooled to -40 °C and stirred for an additional 10 minutes. To the reaction mixture were added triethylamine (418 µL, 3.0 mmol), aryl iodide (1.0 mmol) and secondary silane (1.5 mmol). After stirring for 3-10 days at -40 ^{o}C, the reaction mixture was quenched with water, extracted with dichloromethane three times, and the extracts dried over sodium sulfate. The solvent was then evaporated under a reduced pressure and crude product purified by preparative TLC (silica gel). Enantiomeric excess of the arylated product was determined by HPLC analysis employing a chiral stationary phase.

A typical experimental procedure for palladium-catalyzed asymmetric arylation reaction at room temperature.

A mixture of $Pd_2(dba)_3$ (23 mg, 0.025 mmol) and phosphoramidite ligand (0.075 mmol) was stirred in THF (2 mL) for 2 hours at room temperature. Triethylamine (418 µL, 3.0 mmol), aryl iodide (1.0 mmol) and secondary silane (1.5 mmol) were the added to the reaction mixture. After stirring for 2 days at room temperature, the reaction mixture was quenched with water, extracted with dichloromethane three times, and dried over sodium sulfate. The solvent was evaporated under a reduced pressure and purified by preparative TLC (silica gel). Enantiomeric excess of the product was determined by HPLC analysis employing a chiral stationary phase.

(2-methoxyphenyl)methylphenylsilane (9):[8] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.58 (m, 2H), 7.40–7.32 (m, 5H), 6.94 (td, 2H, *J* =7.3, 0.8 Hz), 6.84 (d, 1H, *J* = 8.1 Hz), 4.91 (q, 1H, *J* = 3.8 Hz), 3.78 (s, 3H), 0.61 (d, 3H, *J* = 3.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (C_q), 136.6 (CH), 135.9 (C_q), 134.8 (CH), 131.5 (CH), 129.1 (CH), 127.7 (CH), 123.7 (C_q), 120.6 (CH), 109.7 (CH), 55.2 (CH_3), -5.1 (CH_3). EI-MS *m/z* 228 (M^+). HPLC (OJ-H, methanol, 1.0 mL/min) t_1 = 7.7 min (*S*) and t_2 = 8.6 min (*R*).

(3-methoxyphenyl)methylphenylsilane (10):[9] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.55 (m, 2H), 7.39–7.34 (m, 3H), 7.31 (t, 1H, *J* = 7.7 Hz), 7.14 (d, 1H, *J* = 7.3 Hz), 7.09 (d, 1H, *J* = 2.7 Hz), 6.93 (dd, 1H, *J* = 2.7, 8.3 Hz), 4.92 (q, 1H, *J* = 3.8 Hz), 3.80 (s, 3H), 0.62 (d, 3H, *J* = 3.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0 (C_q), 136.9 (C_q), 135.2 (C_q), 134.8 (CH), 129.5 (CH), 129.2 (CH), 128.0 (CH), 127.1 (CH), 120.1 (CH), 114.9 (CH), 55.1 (CH_3), -5.0 (CH_3). EI-MS *m/z* 228 (M^+). HPLC (OJ-H, methanol, 1.0 mL/min) t_1 = 9.6 min (-) and t_2 = 11.0 min (+).

(4-methoxyphenyl)methylphenylsilane (11):[9] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H, *J* = 6.5 Hz), 7.48 (d, 2H, *J* = 8.6 Hz), 7.40–7.34 (m, 3H), 6.92 (d, 2H, *J* = 8.3 Hz), 4.92 (q, 1H, *J* = 3.7 Hz), 3.81 (s, 3H), 0.60 (d, 3H, *J* = 3.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (C_q), 136.3 (CH), 135.8 (C_q), 134.8 (CH), 129.4 (C_q), 127.9 (CH), 126.0 (C_q), 113.8 (CH), 55.0 (CH_3), -4.8 (CH_3). EI-MS *m/z* 228 (M^+). HPLC (OJ-H, methanol, 1.0 mL/min) t_1 = 9.3 min (-) and t_2 = 10.2 min (+).

methyl(2-methylphenyl)phenylsilane (12):[8] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (m, 2H), 7.48 (d, 1H, *J* = 7.3 Hz), 7.40–7.30 (m, 4H), 7.19 (t, 2H, *J* = 7.4 Hz), 5.03 (q, 1H, *J* = 3.8

Hz), 2.37 (s, 3H), 0.64 (d, 3H, *J* = 3.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2 (C_q), 135.7 (CH), 135.5 (C_q), 134.7 (CH), 133.9 (C_q), 129.9 (CH), 129.6 (CH), 129.3 (CH), 127.9 (CH), 125.1 (CH), 22.6 (CH_3), -4.8 (CH_3). EI-MS *m/z* 212 (M^+). HPLC (OJ-H, methanol, 1.0 mL/min) t_1 = 8.3 min (*S*) and t_2 = 8.8 min (*R*).

(2,3-dimethylphenyl)methylphenylsilane (13): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.51 (m, 2H), 7.40–7.32 (m, 4H), 7.22 (d, 1H, *J* = 7.3 Hz), 7.12 (t, 1H, *J* = 7.3 Hz), 5.05 (q, 1H, J = 3.8 Hz), 2.29 (s, 3H), 2.27 (s, 3H), 0.63 (d, 3H, *J* = 3.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6 (C_q), 136.4(C_q), 135.9 (C_q), 134.7 (CH), 134.0 (C_q), 133.7 (CH), 131.7 (CH), 129.3 (CH), 127.9 (CH), 125.3 (CH), 20.4 (CH_3), 19.7 (CH_3), -4.5 (CH_3). EI-MS *m/z* 226 (M^+). Anal: Calcd for $C_{15}H_{18}Si$: C, 79.58; H, 8.01. Found: C, 79.43; H, 8.15. HPLC (OJ-H, methanol, 1.0 mL/min) t_1 = 7.5 min (+) and t_2 = 9.0 min (-).

(2,4-dimethylphenyl)methylphenylsilane (14): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.48 (m, 2H), 7.39–7.31 (m, 4H), 7.01 (d, 2H, *J* = 5.4 Hz), 5.01 (q, 1H, *J* = 3.9 Hz), 2.33 (s, 3H), 2.32 (s, 3H), 0.62 (d, 3H, *J* = 3.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2 (C_q), 139.9 (C_q), 135.83 (CH), 135.79 (C_q), 134.7 (CH), 130.6 (CH), 130.3 (C_q), 129.3 (CH), 127.9 (CH), 125.9 (CH), 22.5 (CH_3), 21.3 (CH_3), -4.8 (CH_3). EI-MS *m/z* 226 (M^+). Anal: Calcd for $C_{15}H_{18}Si$: C, 79.58; H, 8.01. Found: C, 79.49; H, 8.18. HPLC (OJ-H, hexane, 0.5 mL/min) t_1 = 17.9 min (-) and t_2 = 20.0 min (+).

methylphenyl(5,6,7,8-tetrahydro-naphthalen-1-yl)silane (15): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (m, 2H), 7.37–7.31 (m, 4H), 7.14–7.08 (m, 2H), 5.01 (q, 1H, *J* = 3.9 Hz), 2.78–2.71 (m, 4H), 1.76–1.72 (m, 4H), 0.62 (d, 3H, *J* = 3.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2 (C_q), 136.7 (C_q), 135.8 (C_q), 134.7 (CH), 134.2 (Cq), 133.4 (CH), 131.3 (CH), 129.3 (CH), 127.9 (CH), 125.0 (CH), 30.1 (CH_2), 30.0 (CH_2), 23.4 (CH_2), 22.8 (CH_2), -4.6 (CH_3). EI-MS *m/z* 252 (M^+). Anal: Calcd for $C_{15}H_{18}Si$: C, 80.89; H, 7.99. Found: C, 80.92; H, 8.14. HPLC (OJ-H, methanol, 1.0 mL/min) t_1 = 7.7 min (+) and t_2 = 8.7 min (-).

methyl(naphthalen-1-yl)phenylsilane (16):[10] Colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, 1H, *J* = 8.4 Hz), 7.91 (d, 1H, *J* = 8.3 Hz), 7.87 (d, 1H, *J* = 8.5 Hz), 7.74 (dd, 1H, *J* = 6.8, 1.2 Hz), 7.49-7.42 (m, 3H), 7.40–7.32 (m, 3H), 5.35 (q, 1H, *J* = 3.8 Hz), 0.76 (d, 3H, *J* = 3.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1 (C_q), 135.3 (C_q), 135.2 (CH), 134.9 (CH), 133.3 (C_q), 133.2 (C_q), 130.5 (CH), 129.5 (CH), 128.9 (CH), 128.0 (CH), 127.9 (CH), 126.0 (CH), 125.6 (CH), 125.2 (CH), -4.5 (CH_3). EI-MS *m/z* 248 (M^+). HPLC (OJ-H, methanol, 1.0 mL/min) t_1 = 11.3 min (*R*) and t_2 = 12.1 min (*S*).

(2-methoxyphenyl)phenylpropylsilane (17): Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, 2H, *J* = 7.5, 1.9 Hz), 7.41–7.32 (m, 5H), 6.93 (t, 1H, *J* = 7.3 Hz), 6.84 (d, 1H, *J* = 8.4 Hz), 4.81 (t, 1H, *J* = 3.8 Hz), 3.78 (s, 3H), 1.49-1.43 (m, 2H), 1.20–1.13 (m, 2H), 0.98 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2 (C_q), 137.0 (CH), 135.4 (C_q), 135.1 (CH), 131.5 (CH), 129.1 (CH), 127.7 (CH), 123.1 (C_q), 120.6 (CH), 109.6 (CH), 55.1 (CH_3), 18.3 (CH_2), 17.8 (CH_2), 14.5 (CH_3). EI-MS *m/z* 256 (M^+). Anal: Calcd. for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86. Found: C, 74.74; H, 8.06. HPLC (OJ-H, methanol, 1.0 mL/min) t_1 = 5.6 min (+) and t_2 = 6.4 min (-).

isopropyl(2-methoxyphenyl)phenylsilane (18): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, 2H, *J* = 7.2, 1.7 Hz), 7.45 (dd, 1H, *J* = 7.1, 1.5 Hz), 7.39–7.31 (m, 4H), 6.94 (t, 1H, *J* = 7.3 Hz),

6.84 (d, 1H, *J* = 8.2 Hz), 4.60 (d, 1H, *J* = 4.2 Hz), 3.78 (s, 3H), 1.61–1.56 (m, 1H), 1.08 (d, 3H, *J* = 7.4 Hz), 1.04 (d, 3H, *J* = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1 (C_q), 137.5 (CH), 135.4 (CH), 134.9 (C_q), 131.4 (CH), 129.0 (CH), 127.6 (CH), 122.8 (C_q), 120.6 (CH), 109.6 (CH), 55.0 (CH_3), 18.8 (CH_3), 18.7 (CH_3), 11.6 (CH). EI-MS *m/z* 256 (M^+). Anal: Calcd. for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86. Found: C, 74.85; H, 8.02. HPLC (OZ-H, hexane, 1.0 mL/min) t_1 = 7.1 min (+) and t_2 = 8.2 min (-).

(2-methoxyphenyl)methyl(naphthalen-1-yl)silane (19): Colorless solid. Mp 108.0–109.0 °C (pure *S* form). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, 1H, *J* = 7.6 Hz), 7.90 (d, 1H, *J* = 8.3 Hz), 7.86 (d, 1H, *J* = 7.3 Hz), 7.76 (d, 1H, *J* = 6.6 Hz), 7.49–7.42 (m, 3H), 7.37 (td, 1H, *J* = 7.3, 2.0 Hz), 7.28 (dd, 1H, *J* = 7.2, 1.8 Hz), 6.88 (t, 1H, *J* = 7.2 Hz), 6.86 (d, 1H, *J* = 8.1 Hz), 5.36 (q, 1H, *J* = 3.9 Hz), 3.77 (s, 3H), 0.75 (d, 3H, *J* = 3.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (C_q), 137.2 (C_q), 136.8 (CH), 134.9 (CH), 133.9 (C_q), 133.1 (C_q), 131.5 (CH), 130.0 (CH), 128.7 (CH), 128.2 (CH), 125.8 (CH), 125.4 (CH), 125.2 (CH), 123.5 (C_q), 120.7 (CH), 109.7 (CH), 55.2 (CH_3), -4.6 (CH_3). EI-MS *m/z* 278 (M^+). Anal: Calcd. For $C_{18}H_{18}OSi$: C, 77.65; H, 6.52. Found: C, 77.42; H, 6.57. HPLC (OJ-H, methanol, 1.0 mL/min) t_1 = 7.1 min (*S*) and t_2 = 10.3 min (*R*).

(2-methoxyphenyl)naphthylphenylsilane (20):[8] Colorless solid. ^{1}H NMR (400 MHz, CDCl3): δ 8.05 (d, 1H, *J* = 8.3 Hz), 7.91 (d, 1H, *J* = 8.0 Hz), 7.86 (d, 1H, *J* = 8.0 Hz), 7.60–7.56 (m, 3H), 7.47–7.32 (m, 7H), 7.26–7.24 (m, 1H), 6.91 (t, 2H, *J* = 7.7 Hz), 5.91 (s, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5 (C_q), 137.9 (CH), 137.4 (C_q), 136.4 (CH), 135.8 (CH), 133.8 (C_q), 133.1 (Cq), 132.0 (CH), 131.8 (C_q), 130.3 (CH), 129.4 (CH), 128.7 (CH), 128.4 (CH), 127.8 (CH), 125.9 (CH), 125.5 (CH), 125.2 (CH), 121.6 (C_q), 120.8 (CH), 110.0 (CH), 55.3 (CH_3). EI-MS *m/z* 340 (M^+). HPLC (OD-H, methanol, 0.5 mL/min) t_1 = 11.7 min and t_2 = 12.7 min.

***t*-butylmethyl(2-methoxyphenyl)silane (21):** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, 1H, *J* = 1.7, 7.1 Hz), 7.37–7.33 (m, 1H), 6.94 (t, 1H, *J* = 7.2 Hz), 6.82 (d, 1H, *J* = 8.3 Hz), 4.13 (q, 1H, *J* = 3.7 Hz), 3.77 (s, 3H), 0.94 (s, 9H), 0.33 (d, 3H, *J* = 3.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1 (C_q), 137.3 (CH), 131.0 (CH), 123.8 (C_q), 120.3 (CH), 109.5 (CH), 54.8 (CH_3), 27.5 (CH_3), 17.1 (C_q), -7.7 (CH_3). EI-MS *m/z* 208 (M^+). Anal: Calcd. For $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 68.89; H, 9.70. HPLC (OJ-H, methanol, 0.3 mL/min) t_1 = 13.0(+) min and t_2 = 13.4 min(-).

2. References

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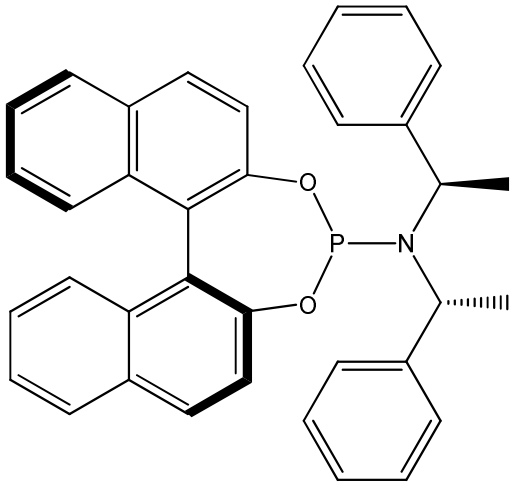
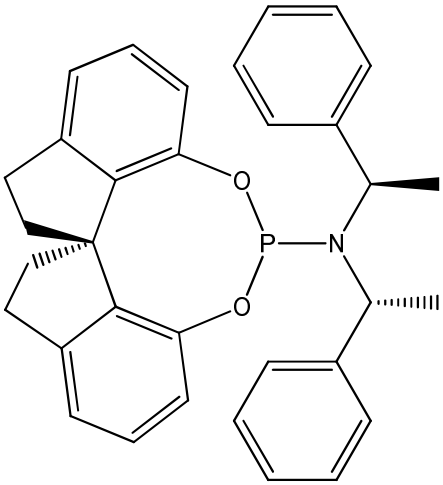
3. Structures of (*S,R,R*)-22 and (*R,R,R*)-23



(*S,R,R*)-**22**



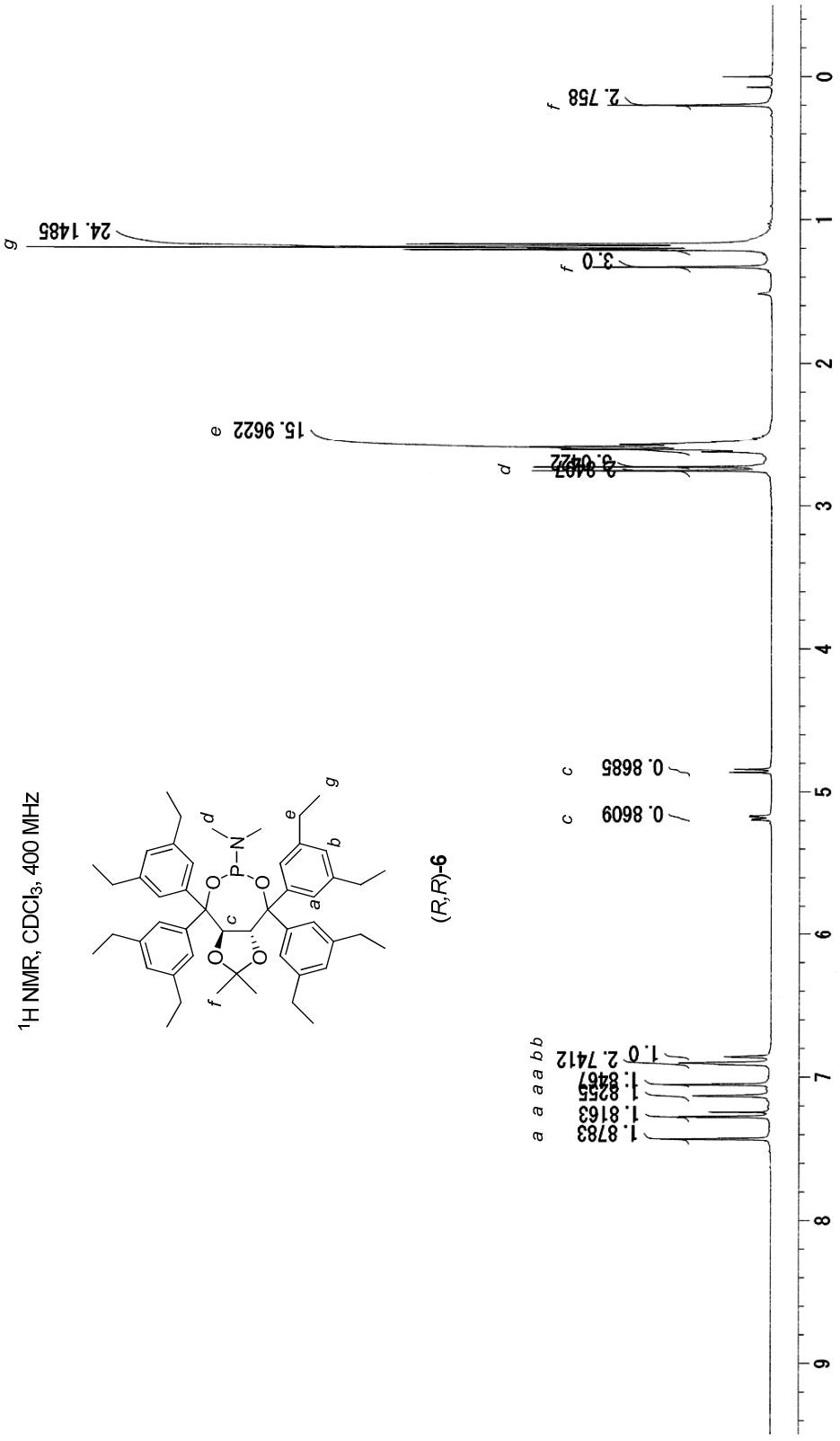
(*R,R,R*)-**23**

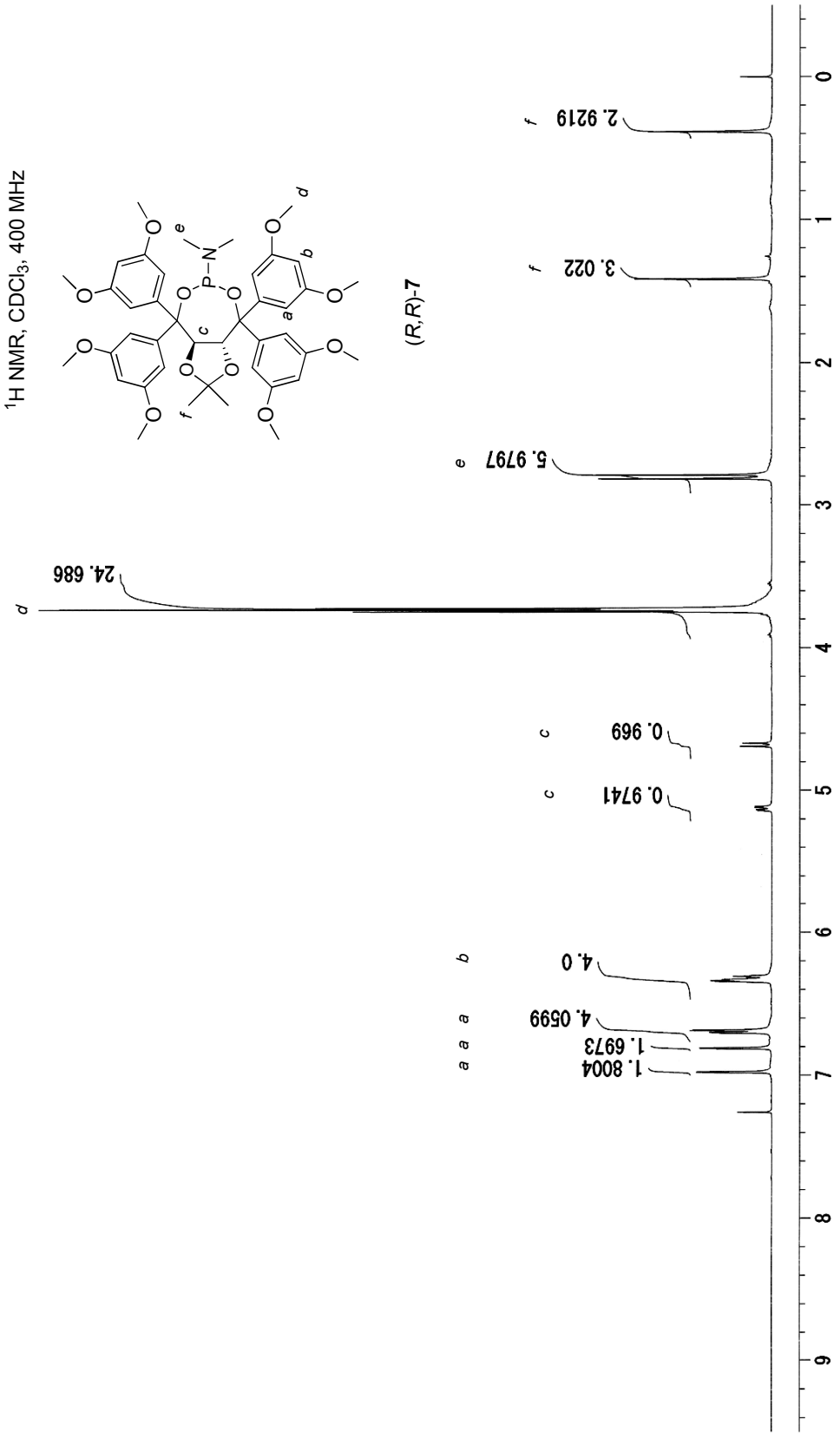
4. Crystallographic data of (*S*)-19

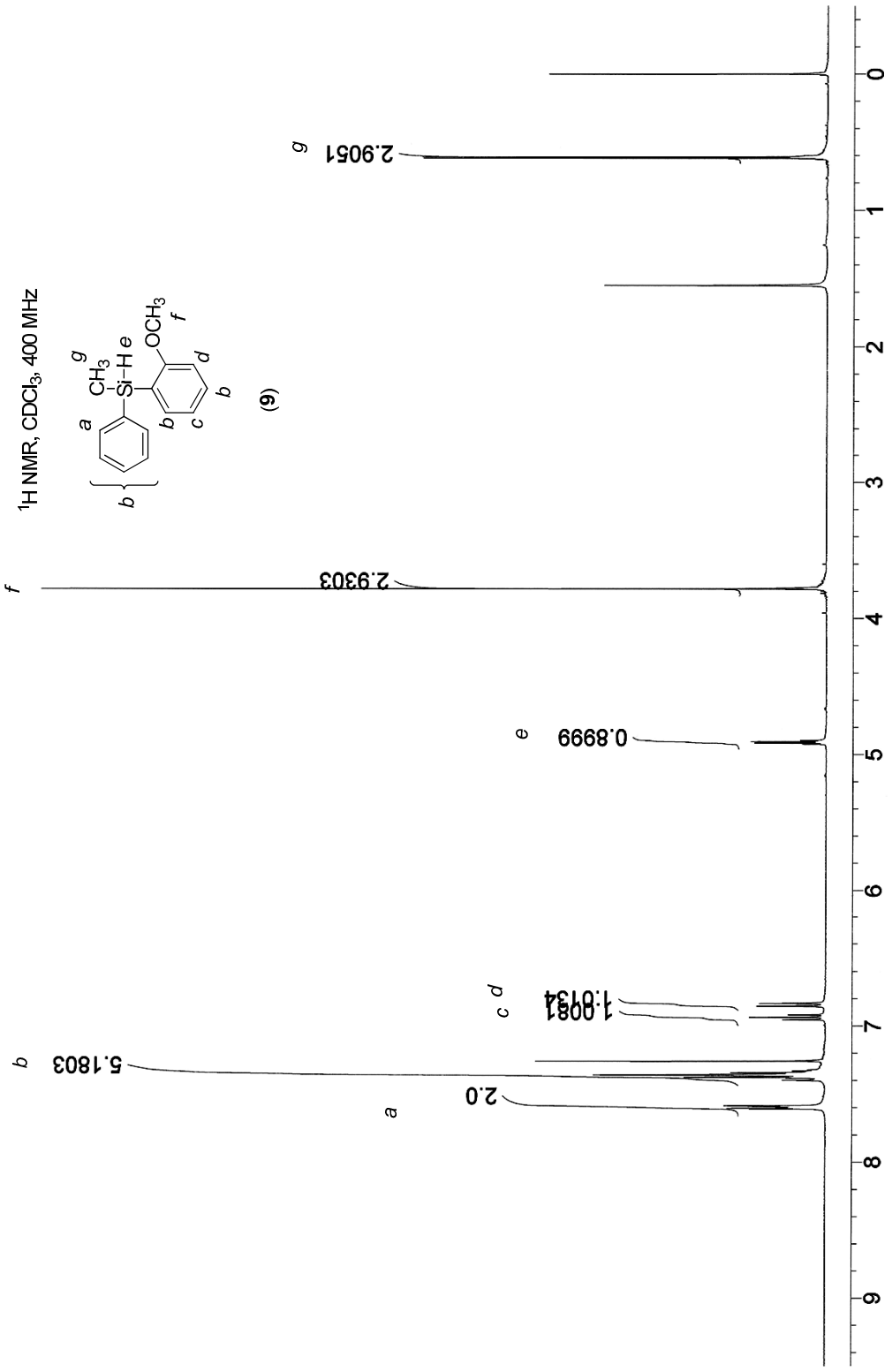
Molecular formula	$C_{18}H_{18}OSi$
Mw / g mol^{-1}	278.41
Crystal system	Monoclinic
Space group	$P2_1$
T / K	123
a / Å	7.975(3)
b / Å	8.530(3)
c / Å	11.592(5)
α / °	90
β / °	108.387(4)
γ / °	90
V / Å^3	748.3(5)
Z	2
Reflections collected	5332
Independent reflections	3186
R_{int}	0.021
ρ_{calcd} / g cm^{-3}	1.236
λ / Å	0.7107
μ /cm^{-1}	0.15
R_1[a]	0.0277
wR_2[b]	0.0719
GOF[c]	1.078
Flack parameter	0.05(8)

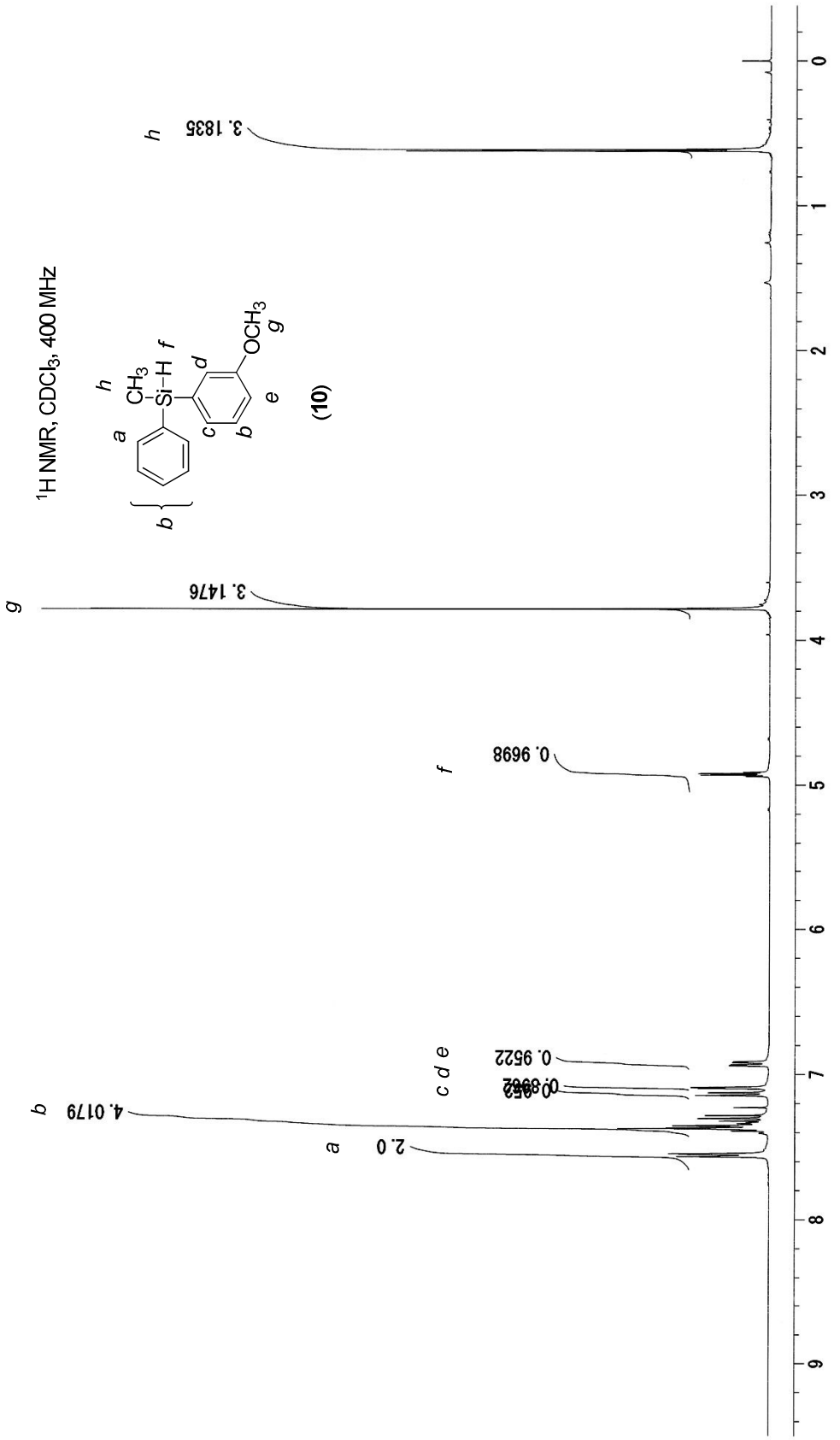
[a] $R_1 = \Sigma||F^o|-|F^c||/\Sigma|F^o|$ ($I>2\sigma(I)$). [b] $wR_2 = [\Sigma(w(F^{o2}-F^{c2})^2/\Sigma w(F^{o2})^2]^{1/2}$ ($I>2\sigma(I)$). [c] GOF = $[\Sigma(w(F^{o2}-F^{c2})^2/\Sigma(N^r-N^p)^2]$

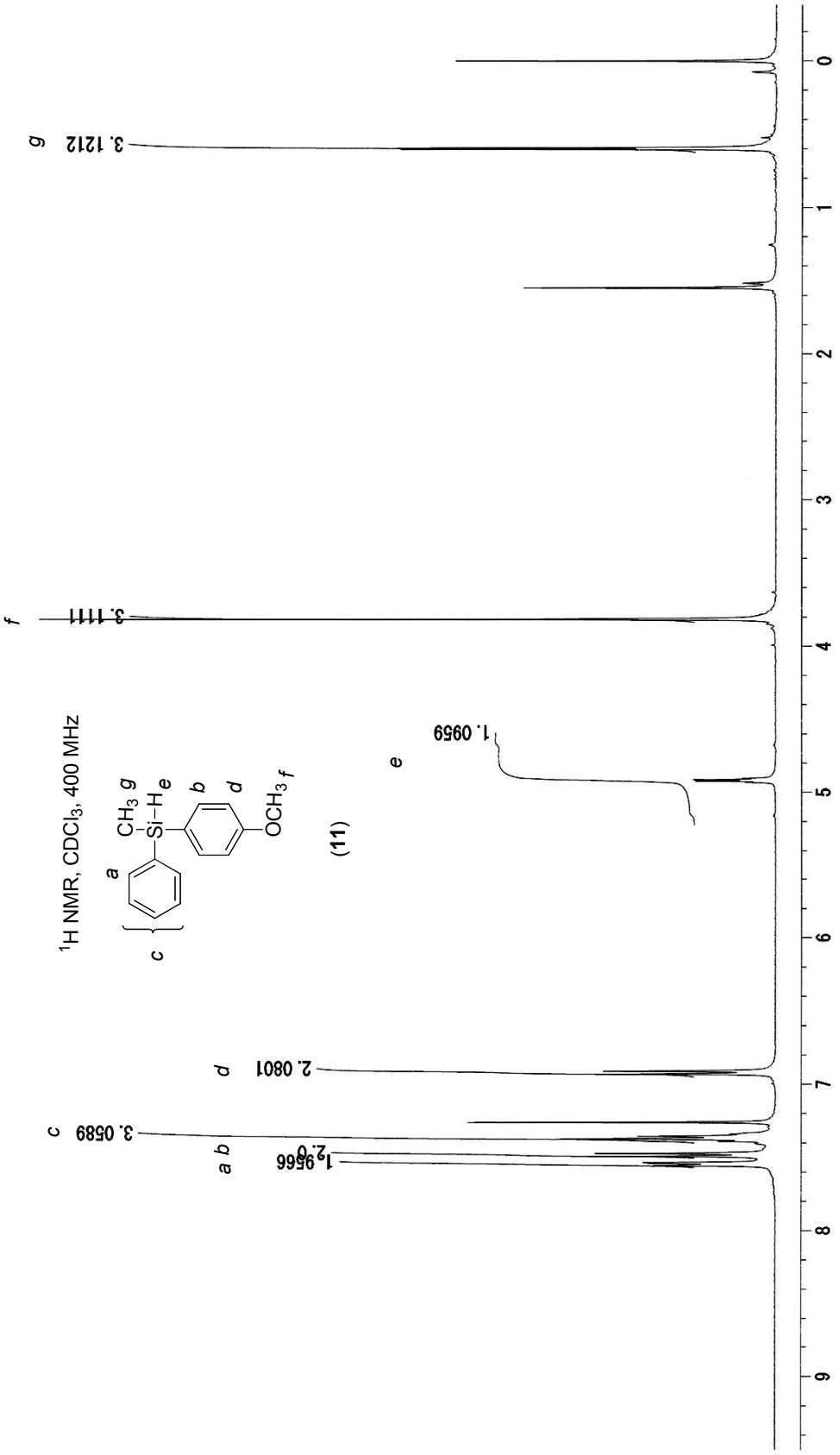
5. Copies of ^{1}H NMR spectra

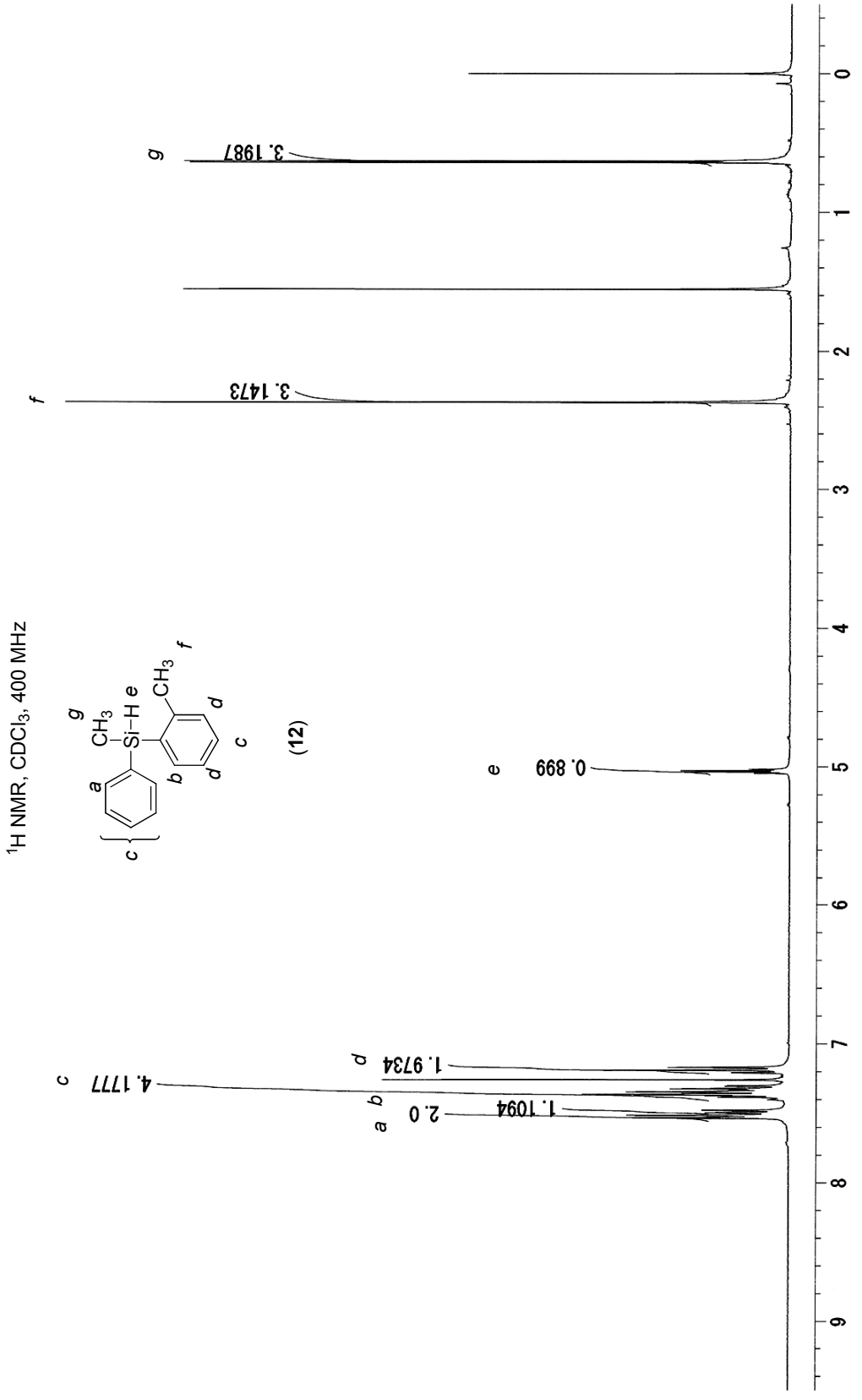


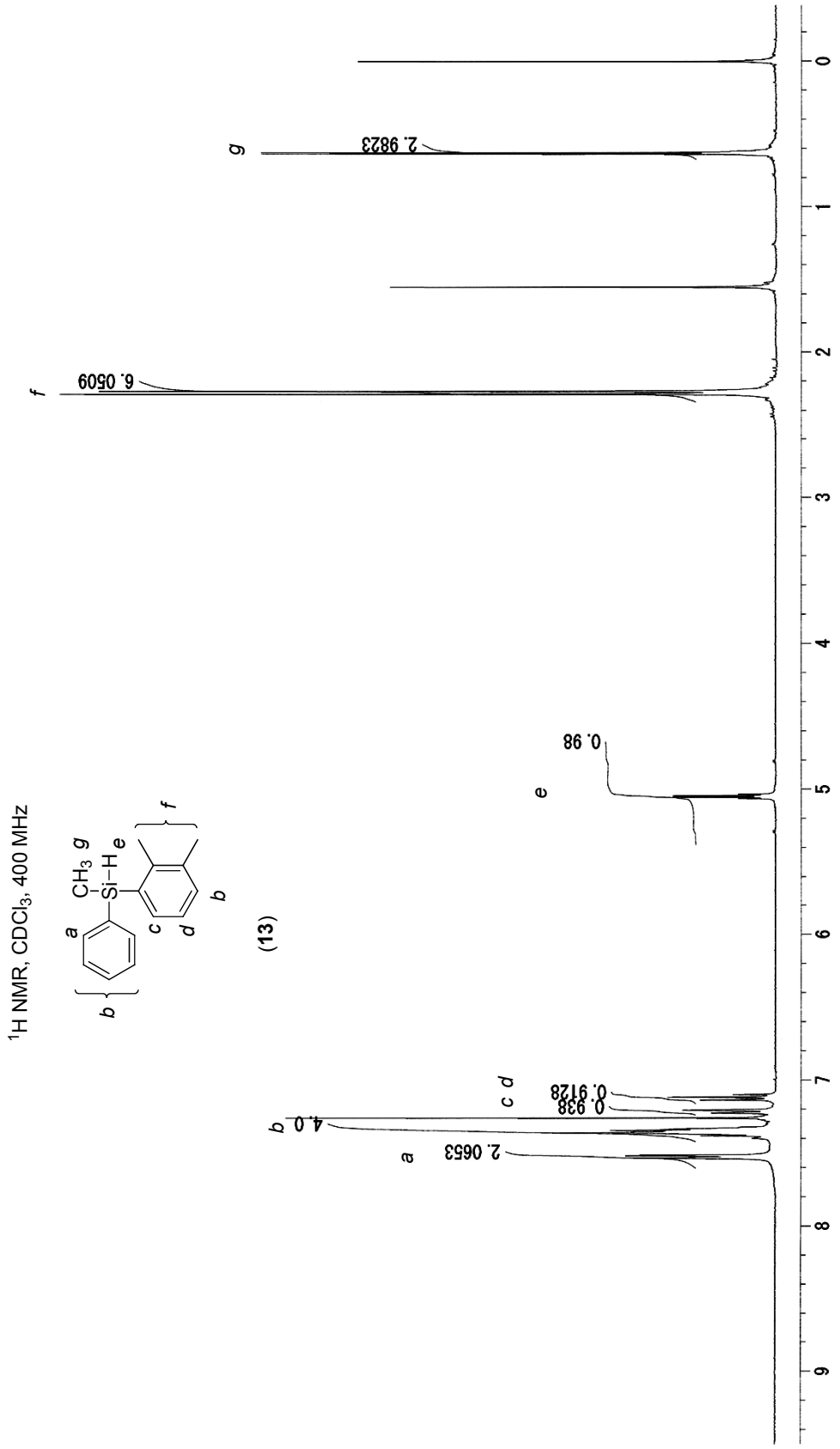

^{1}H NMR, $CDCl_3$, 400 MHz
(R,R)-7
d
24.686
e
5.9797
f
3.022
f
2.9219
c
0.969
c
0.9741
b
4.0
a a a
4.0599
1.6973
1.8004
0
1
2
3
4
5
6
7
8
9

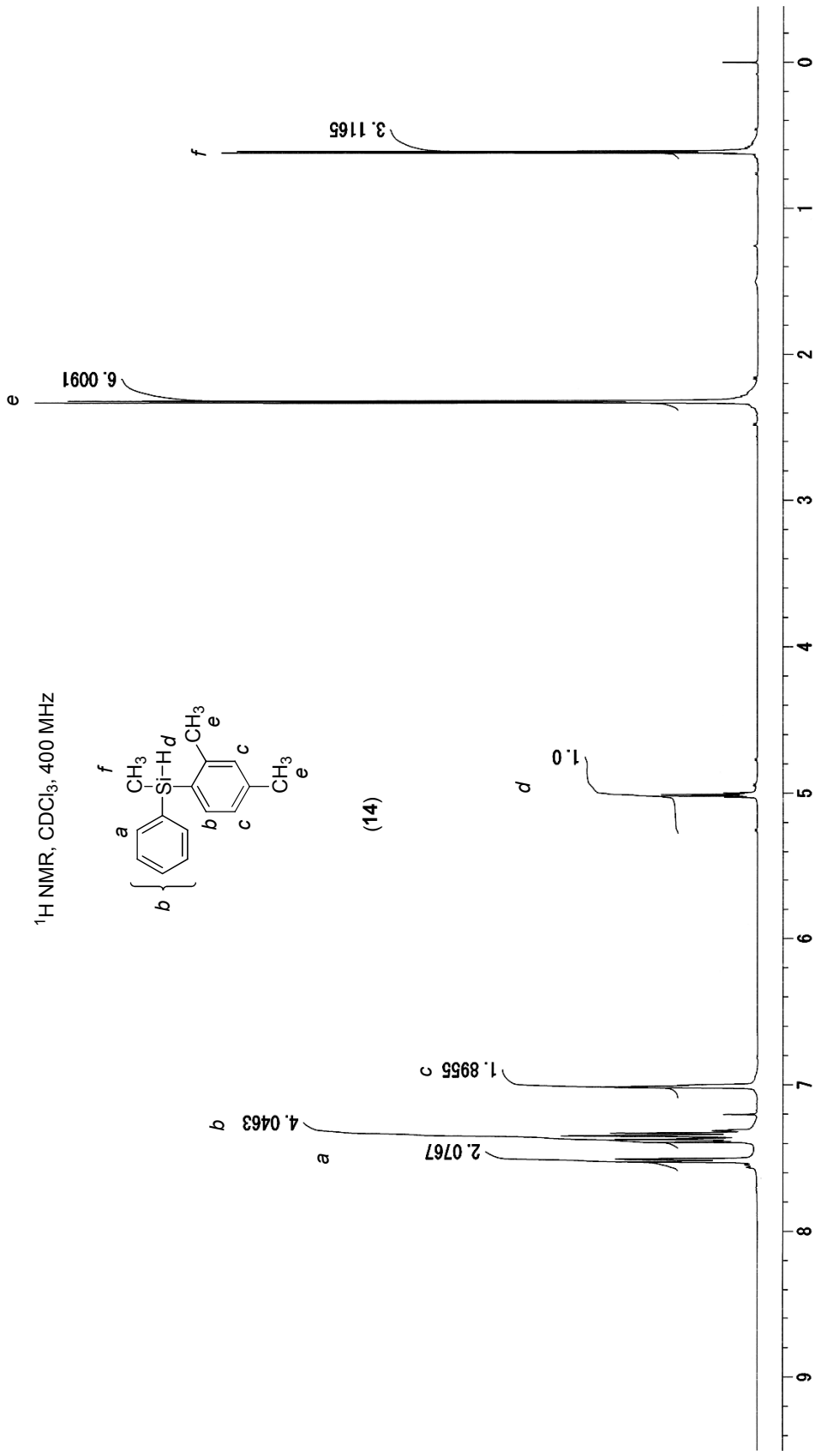

^{1}H NMR, $CDCl_3$, 400 MHz
(9)
2.9051
2.9303
0.8999
1.0081
1.0134
5.1803
2.0
0
1
2
3
4
5
6
7
8
9

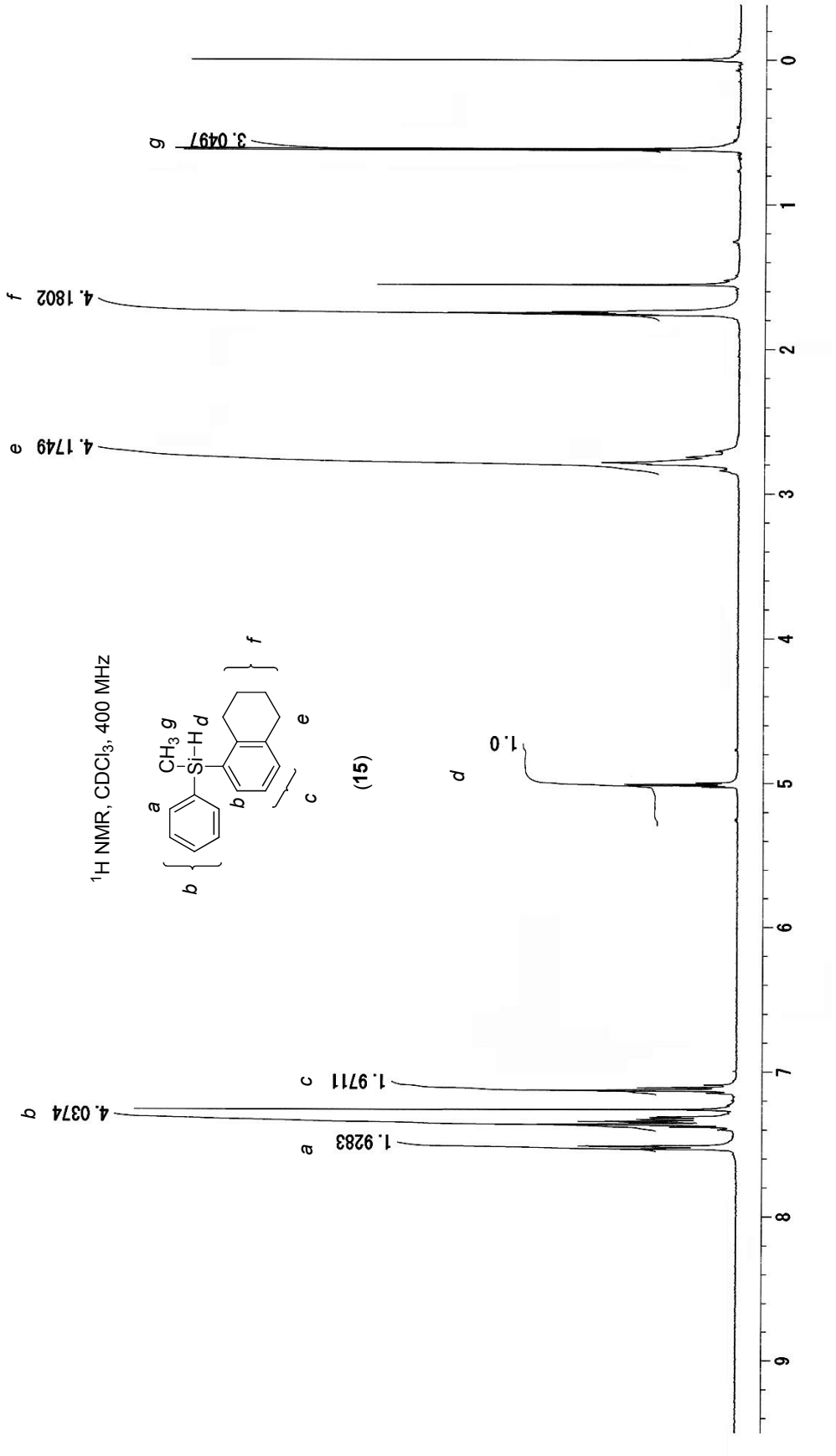

^{1}H NMR, $CDCl_3$, 400 MHz
(10)
3.1835
3.1476
0.9698
0.9522
4.0179
2.0
0
1
2
3
4
5
6
7
8
9

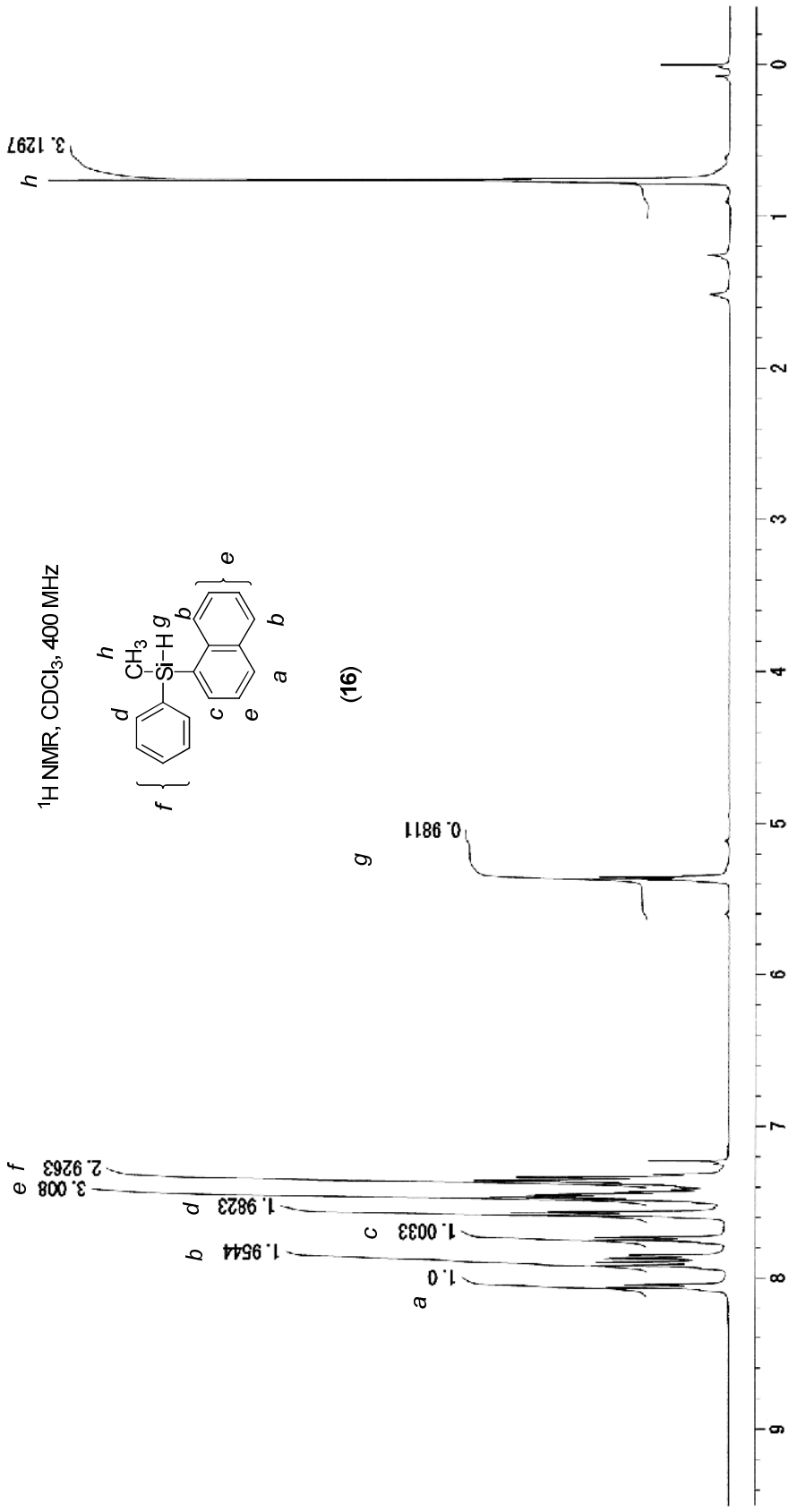

^{1}H NMR, $CDCl_3$, 400 MHz
(11)
3.1212
3.1111
1.0959
2.0801
3.0589
1.9566
2.0
0
1
2
3
4
5
6
7
8
9

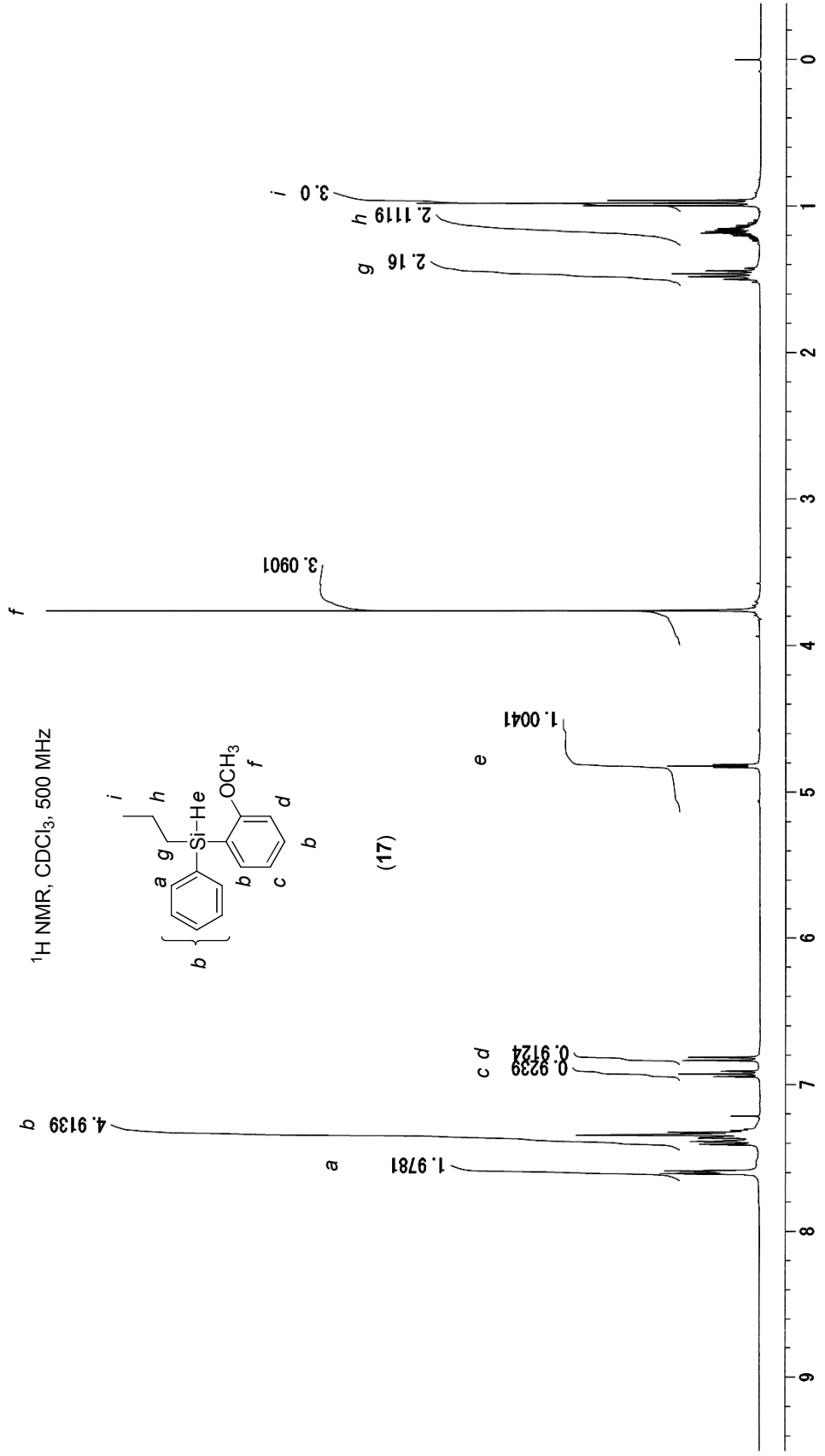

^{1}H NMR, CDCl$_3$, 400 MHz
(12)
CH$_3$
Si–H
CH$_3$
a
b
c
d
e
f
g
3.1987
3.1473
0.899
1.9734
4.1777
2.0
1.1094
0
1
2
3
4
5
6
7
8
9

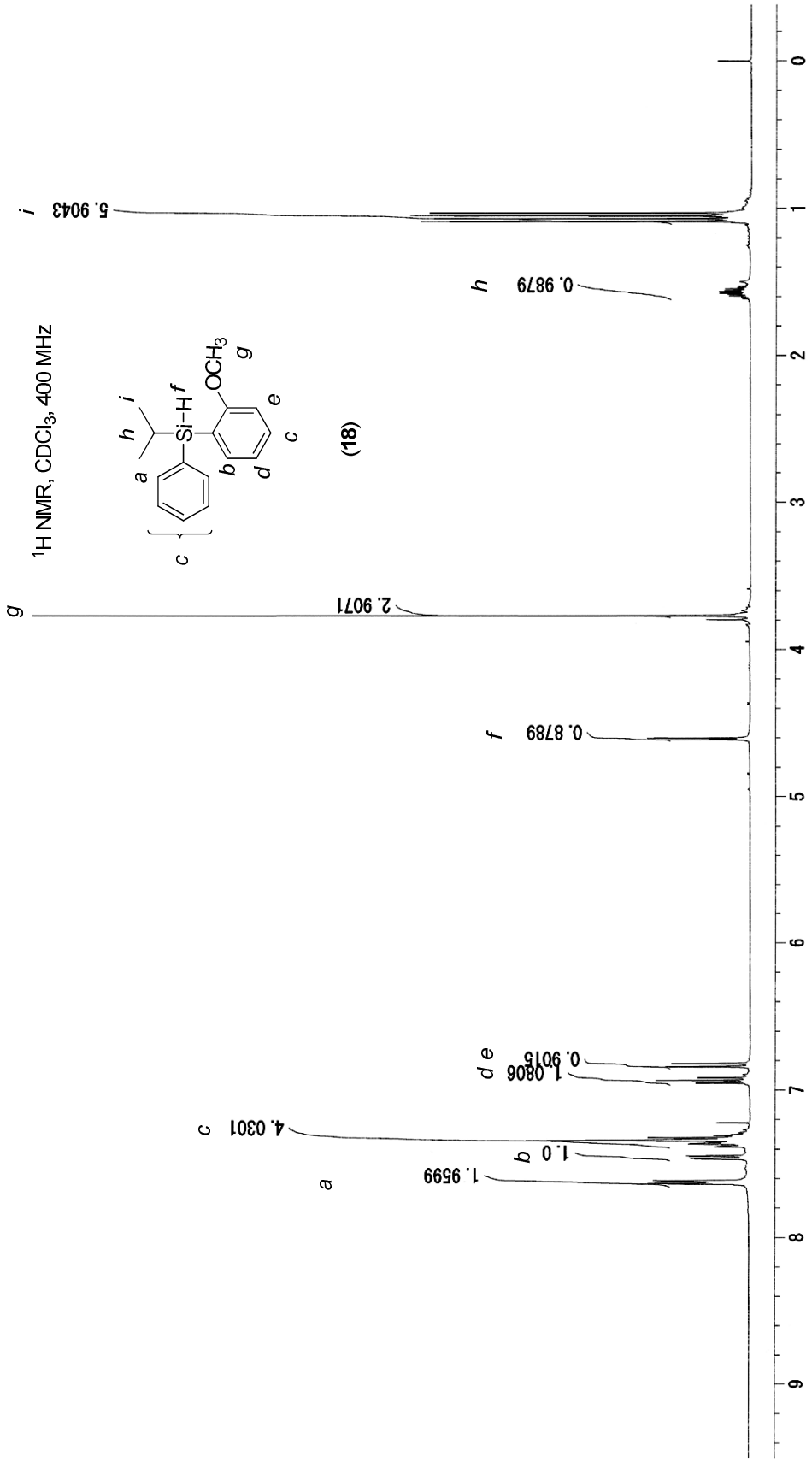

^{1}H NMR, $CDCl_3$, 400 MHz
(13)
a
b
c
d
e
f
g
2.0653
4.0
0.9128
0.938
0.98
6.0509
2.9823

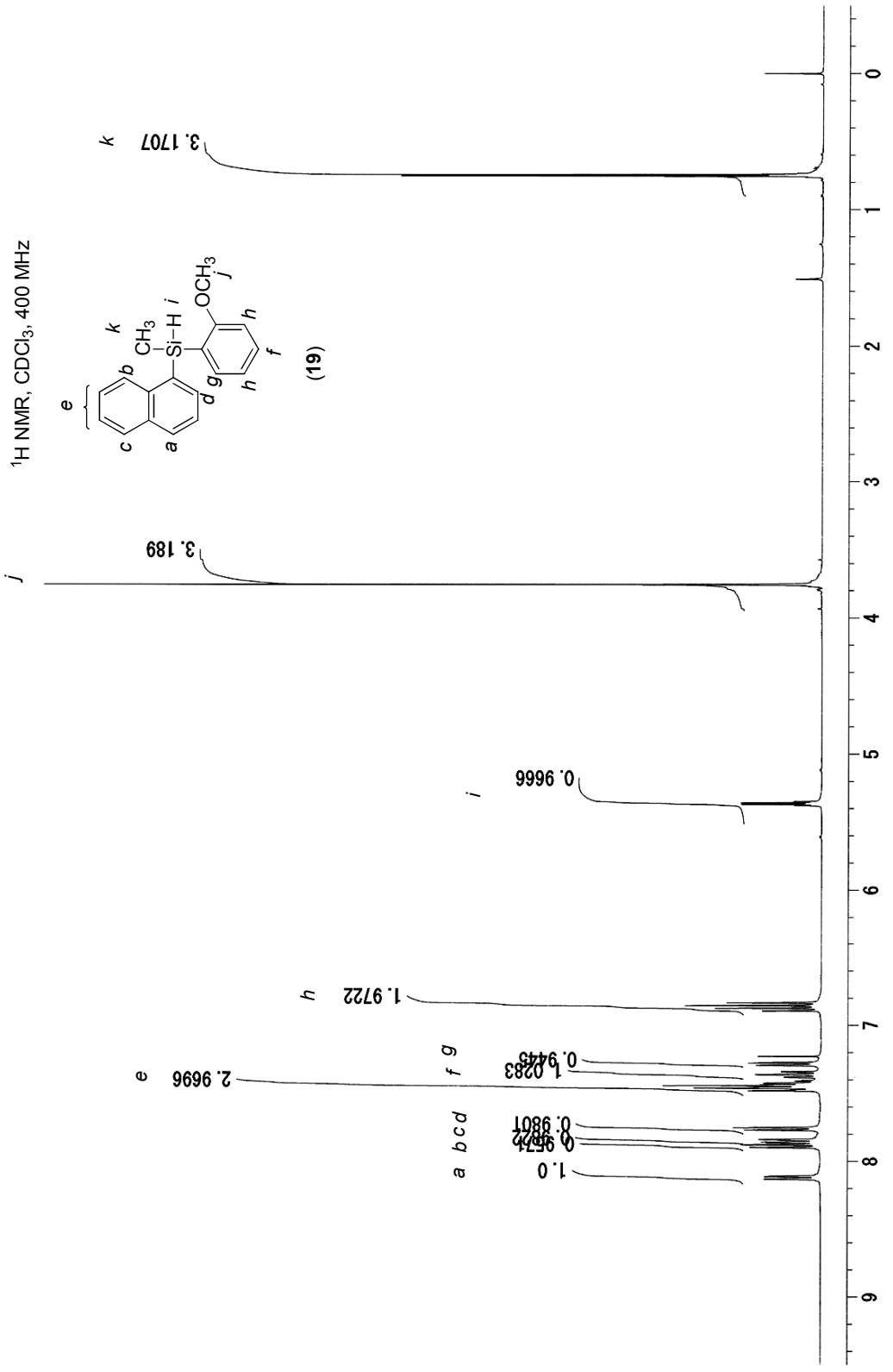

^{1}H NMR, $CDCl_3$, 400 MHz
(14)
3.1165
6.0091
1.0
1.8955
4.0463
2.0767
f
e
d
c
b
a

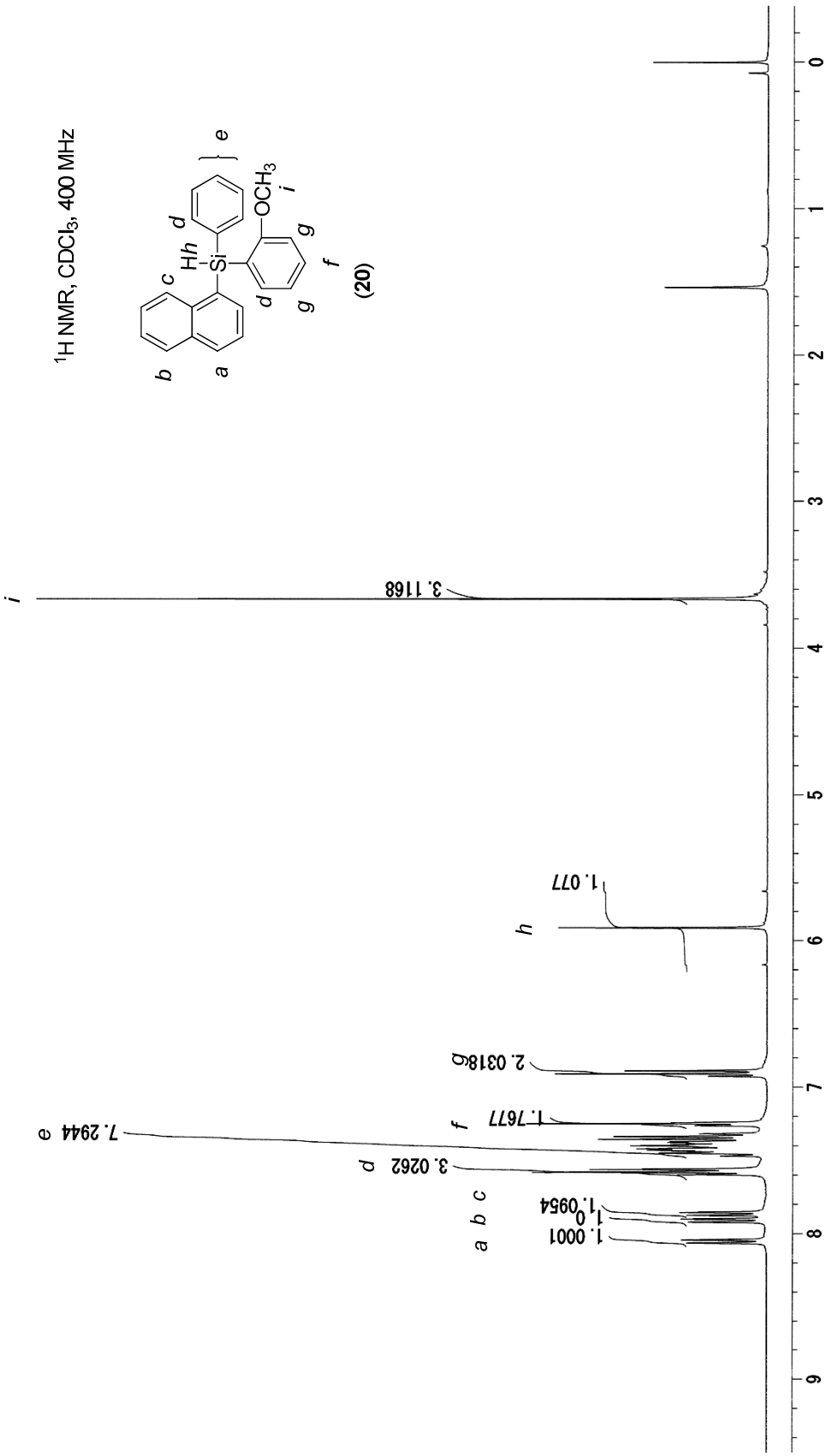

^{1}H NMR, $CDCl_3$, 400 MHz
(15)
CH_3 g
Si–H d
a
b
c
d
e
f
g
1.0
3.049
4.1802
4.1749
1.9711
4.0374
1.9283
0
1
2
3
4
5
6
7
8
9

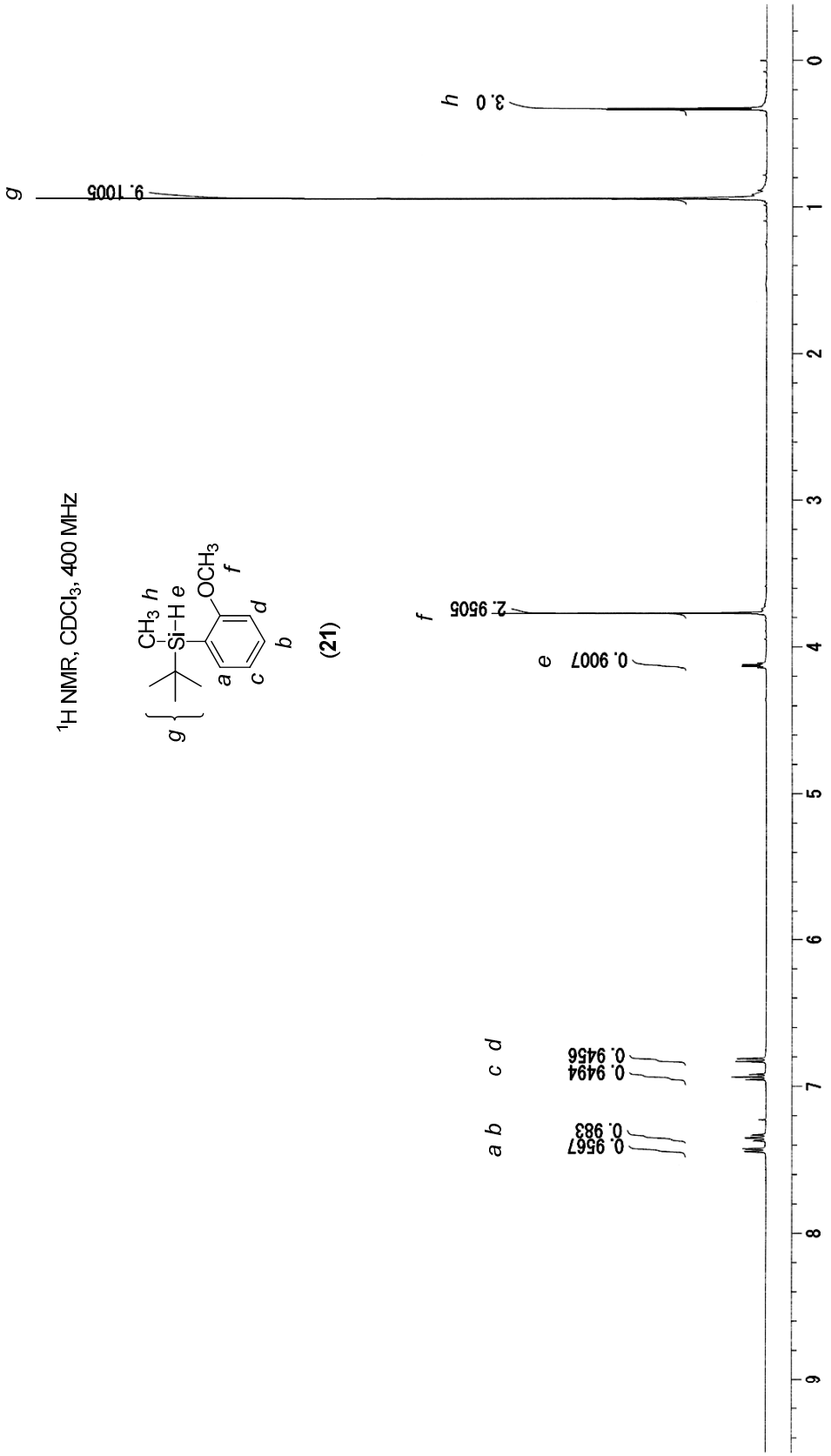



^{1}H NMR, $CDCl_3$, 500 MHz
(17)
OCH_3
Si–He
a
b
c
d
e
f
g
h
i
4.9139
1.9781
0.9239
0.9124
1.0041
3.0901
2.16
2.1119
3.0
0
1
2
3
4
5
6
7
8
9

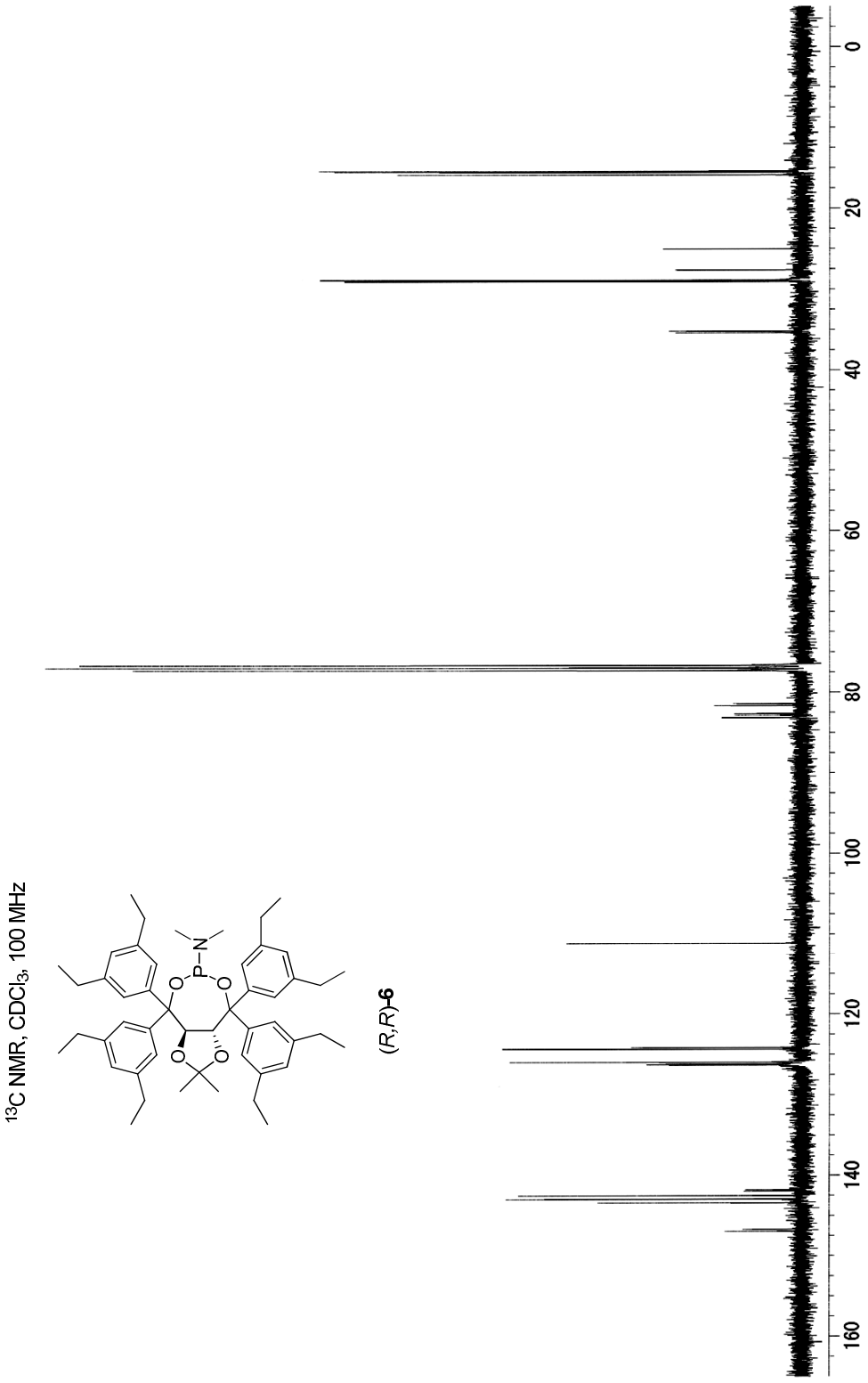

^{1}H NMR, $CDCl_3$, 400 MHz
(18)
OCH_3
Si–H
a
b
c
d
e
f
g
h
i
5.9043
0.9879
2.9071
0.8789
1.0806
0.9015
4.0301
1.0
1.9599
0
1
2
3
4
5
6
7
8
9

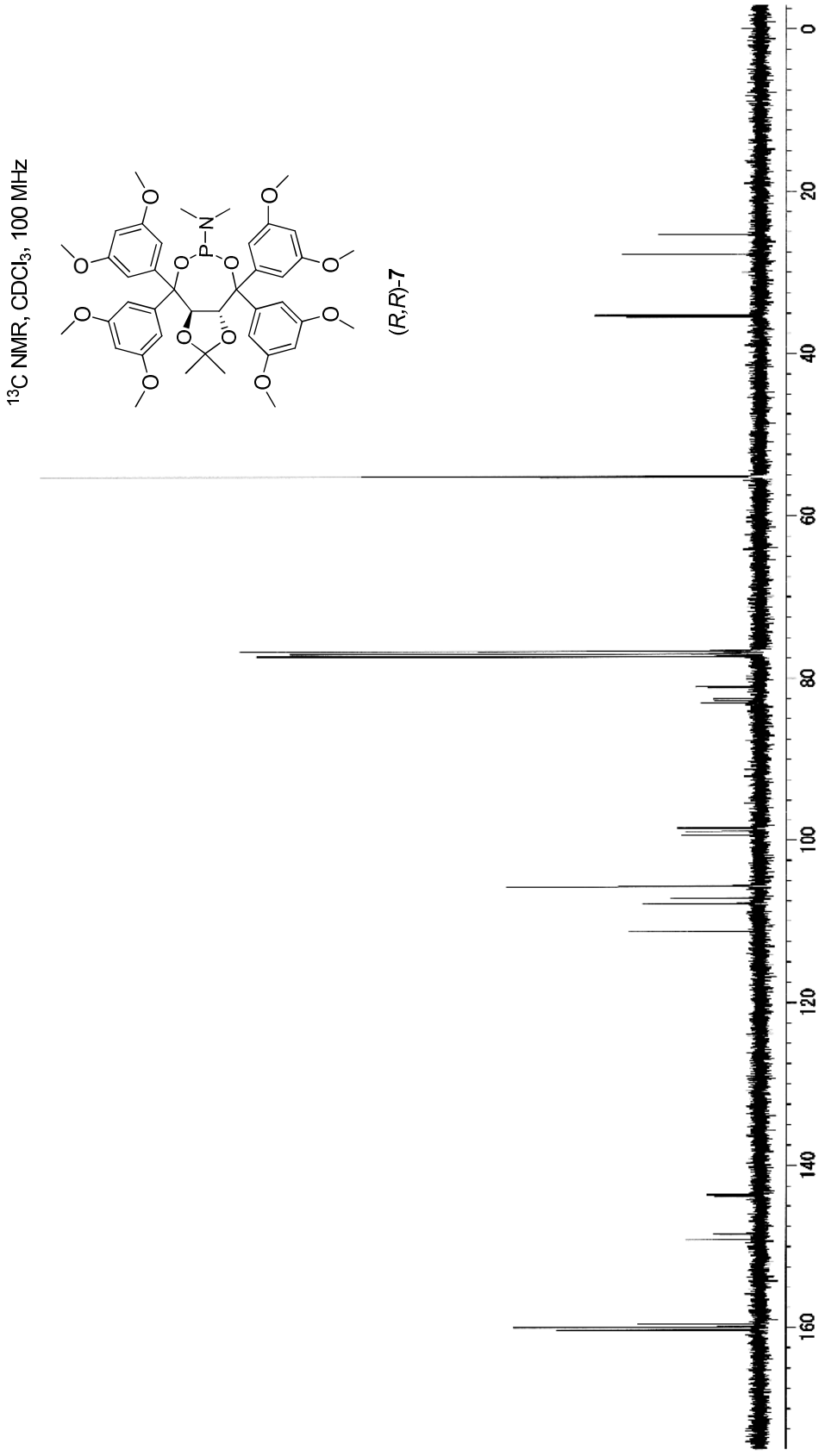

^{1}H NMR, CDCl$_3$, 400 MHz
(19)
3.1707
3.189
0.9666
1.9722
2.9696
1.0283
0.9445
1.0
0.9801

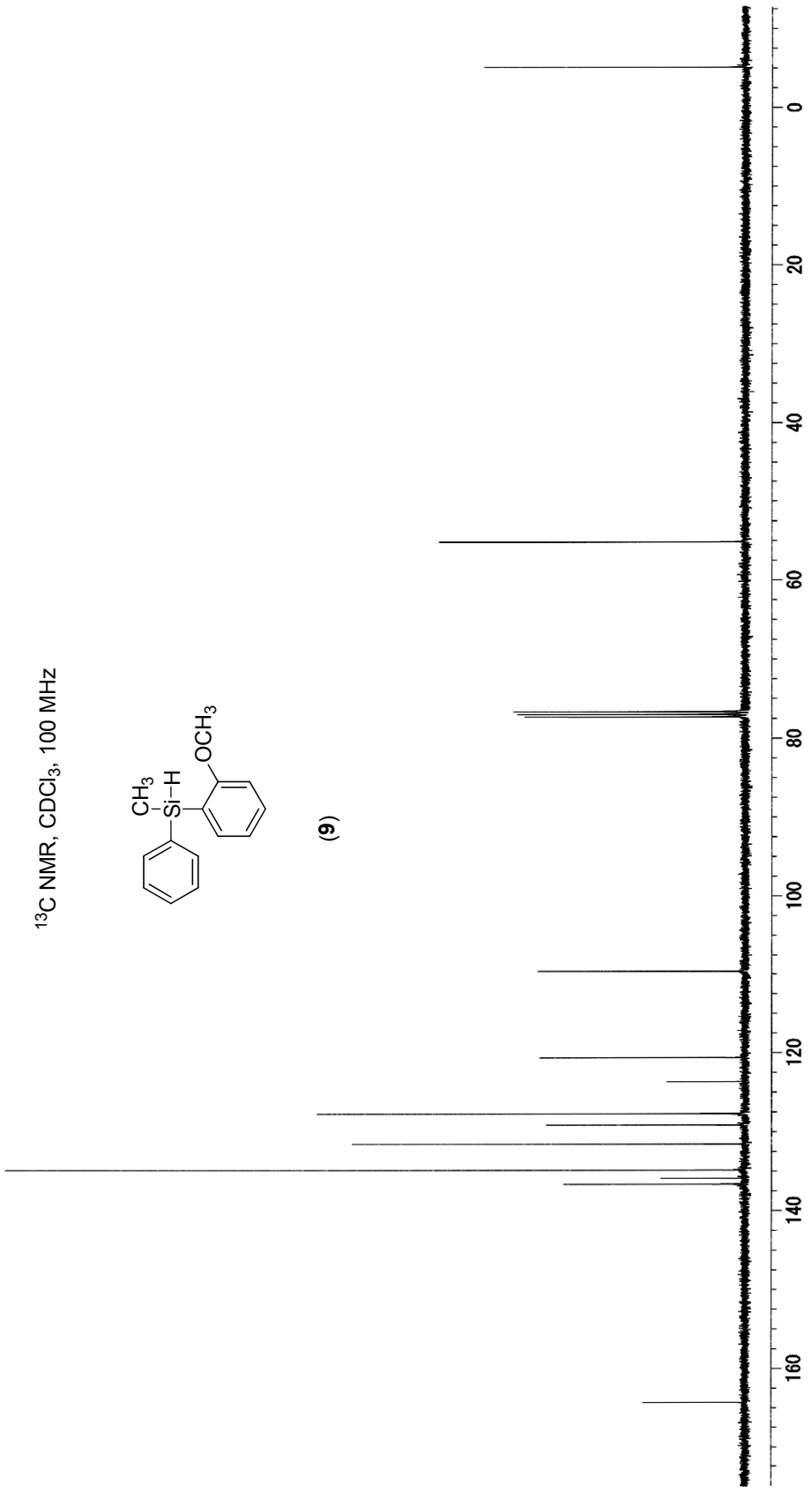

^{1}H NMR, $CDCl_3$, 400 MHz
(20)
3.1168
1.077
2.0318
1.7677
7.2944
3.0262
1.0954
1.0001

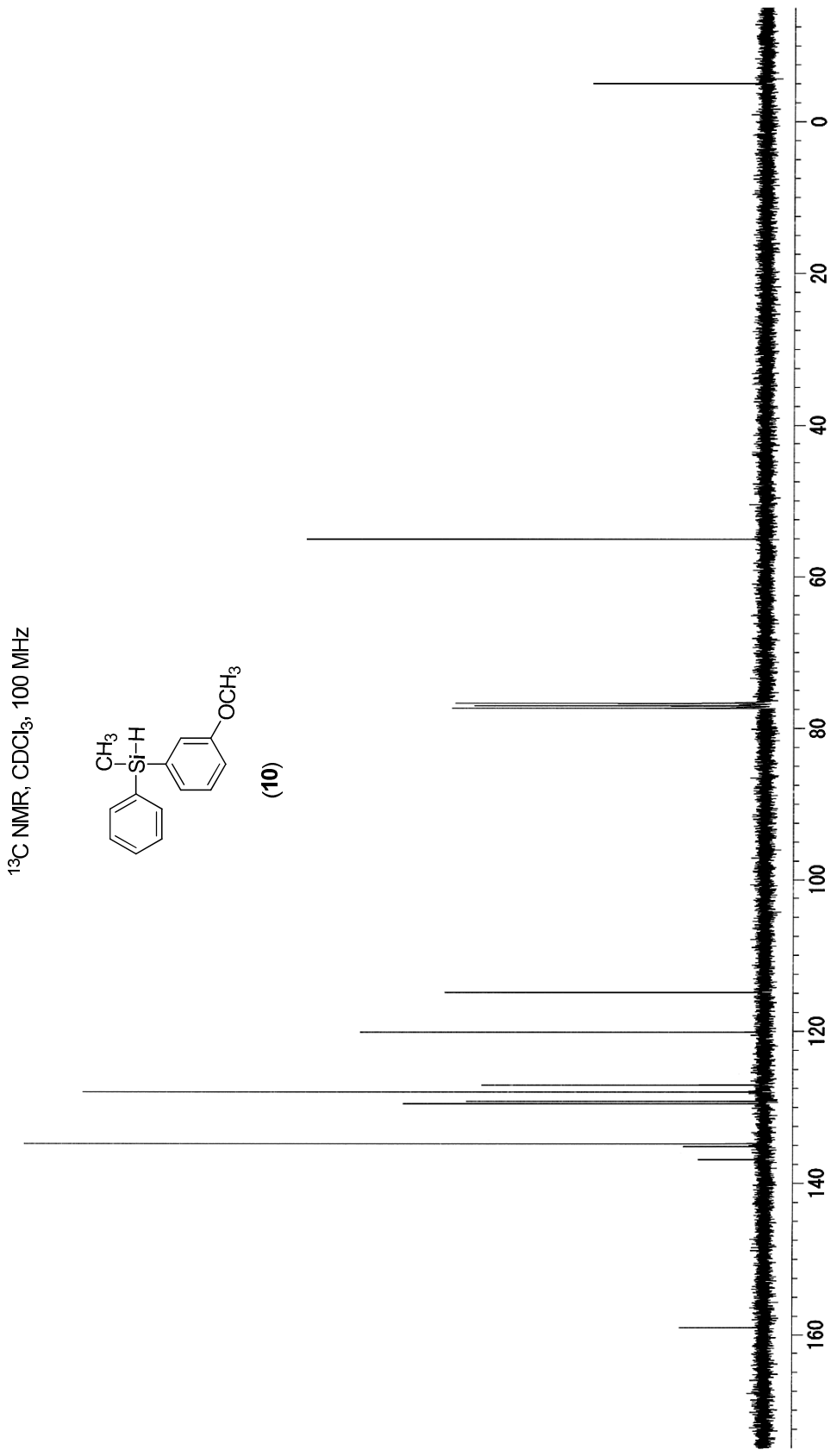

^{1}H NMR, CDCl$_3$, 400 MHz
CH$_3$ h
Si–H e
OCH$_3$ f
g
a
c
d
b
(21)
h
3.0
g
9.1005
f
2.9505
e
0.9007
a b
0.9567
0.983
c d
0.9494
0.9456
0
1
2
3
4
5
6
7
8
9

6. Copies of ^{13}C NMR spectra

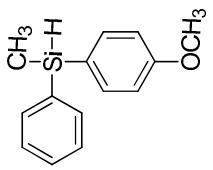





^{13}C NMR, $CDCl_3$, 100 MHz
CH_3
Si–H
OCH_3
(9)
0
20
40
60
80
100
120
140
160

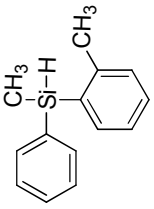

^{13}C NMR, $CDCl_3$, 100 MHz
CH_3
Si–H
OCH_3
(10)
0
20
40
60
80
100
120
140
160

^{13}C NMR, $CDCl_3$, 100 MHz



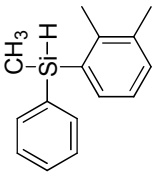
(**11**)

^{13}C NMR, $CDCl_3$, 100 MHz



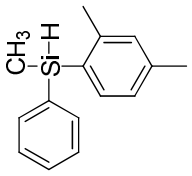
(**12**)

^{13}C NMR, $CDCl_3$, 100 MHz

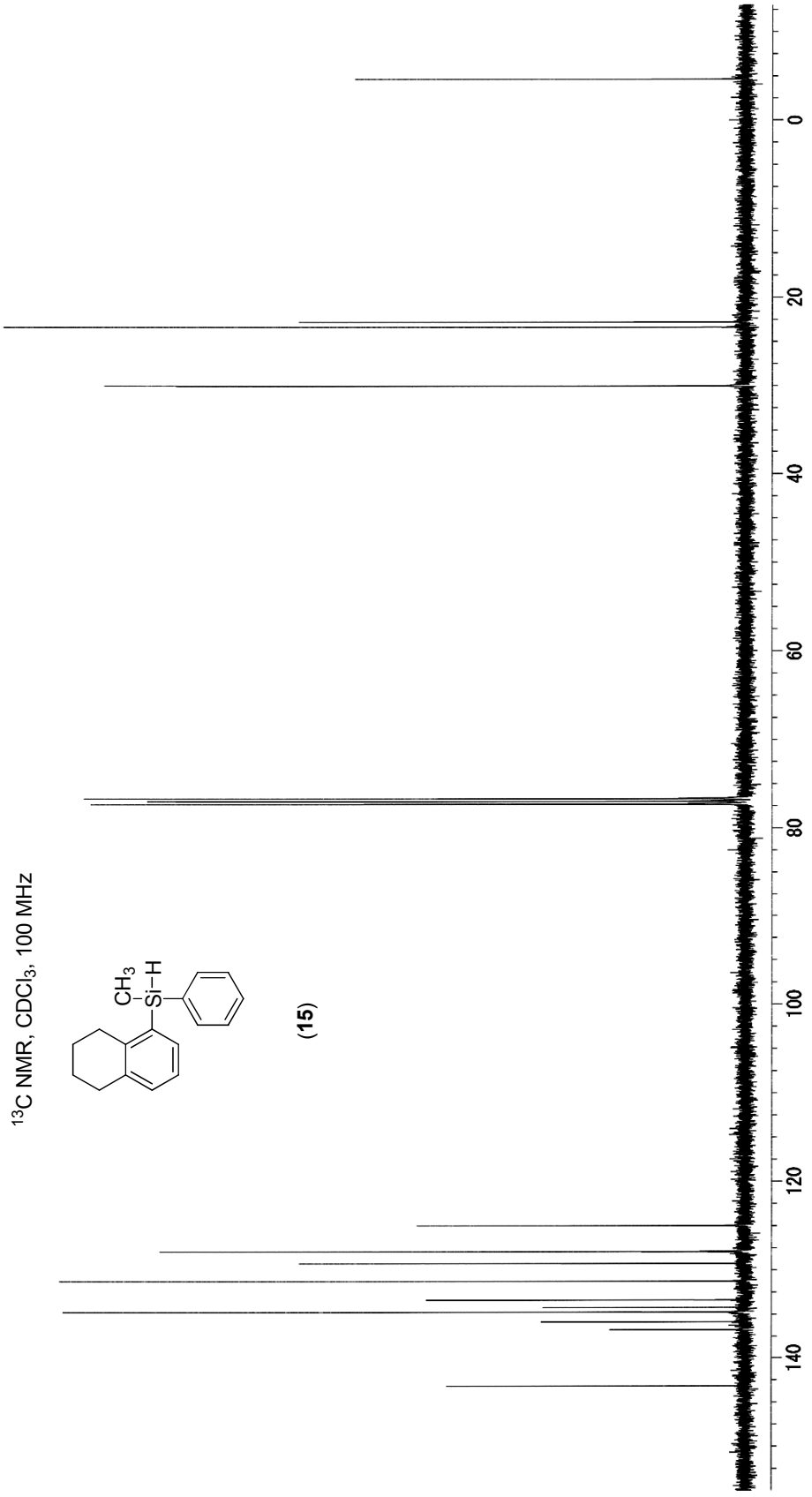


(13)

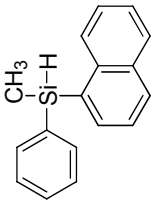
^{13}C NMR, $CDCl_3$, 100 MHz



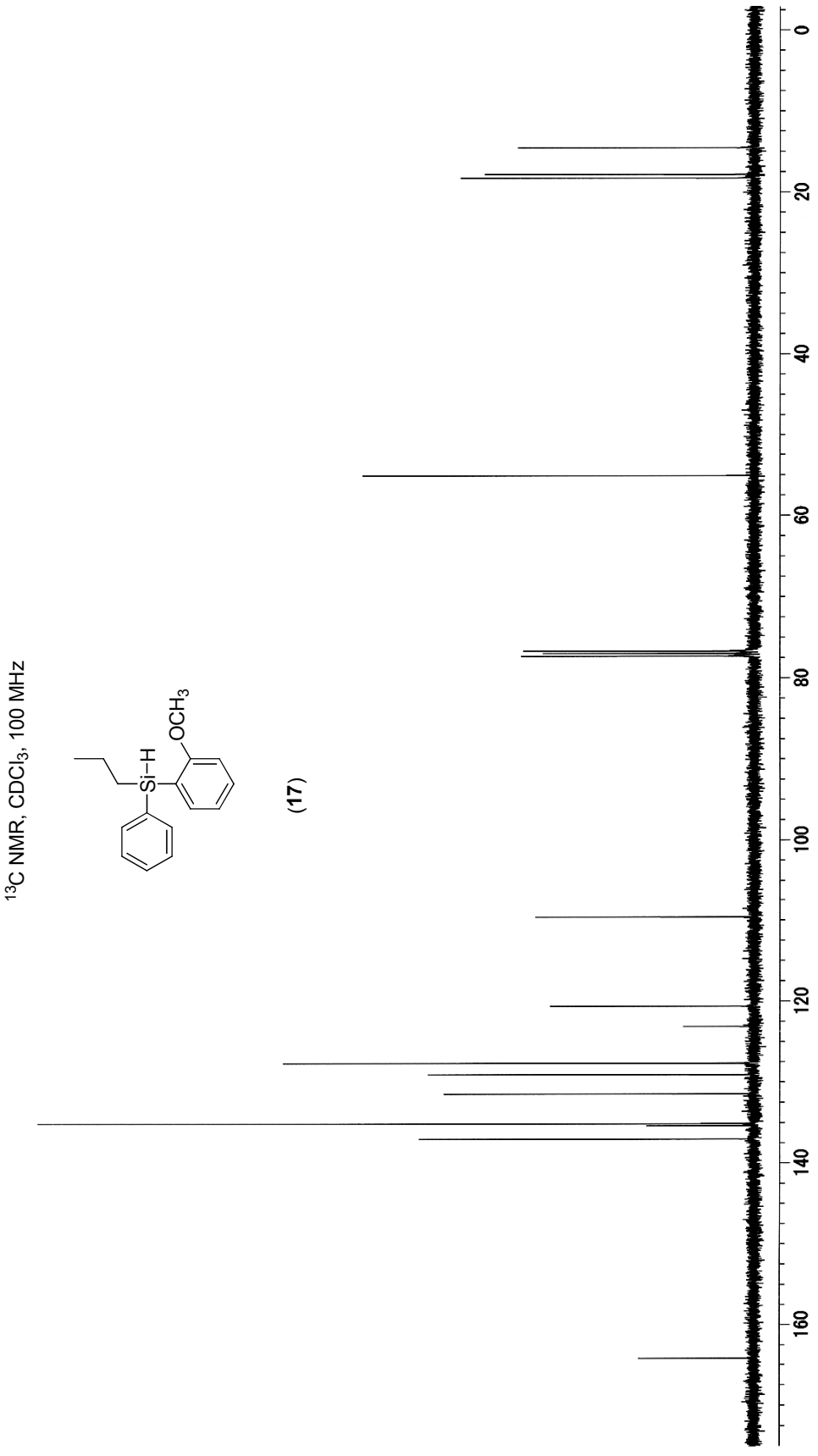
(**14**)


^{13}C NMR, $CDCl_3$, 100 MHz
CH_3
Si–H
(15)
0
20
40
60
80
100
120
140

^{13}C NMR, $CDCl_3$, 100 MHz

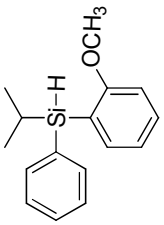


(**16**)



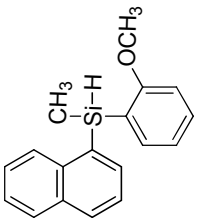
(17)

^{13}C NMR, $CDCl_3$, 100 MHz



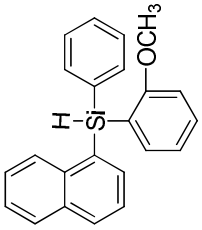
(**18**)

^{13}C NMR, $CDCl_3$, 100 MHz



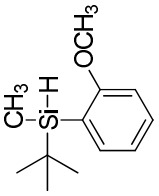
(**19**)

^{13}C NMR, $CDCl_3$, 100 MHz



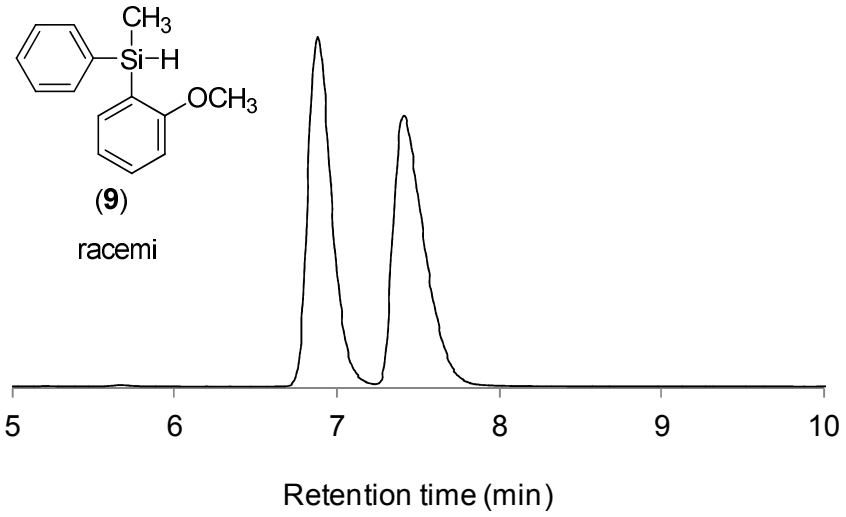
(20)

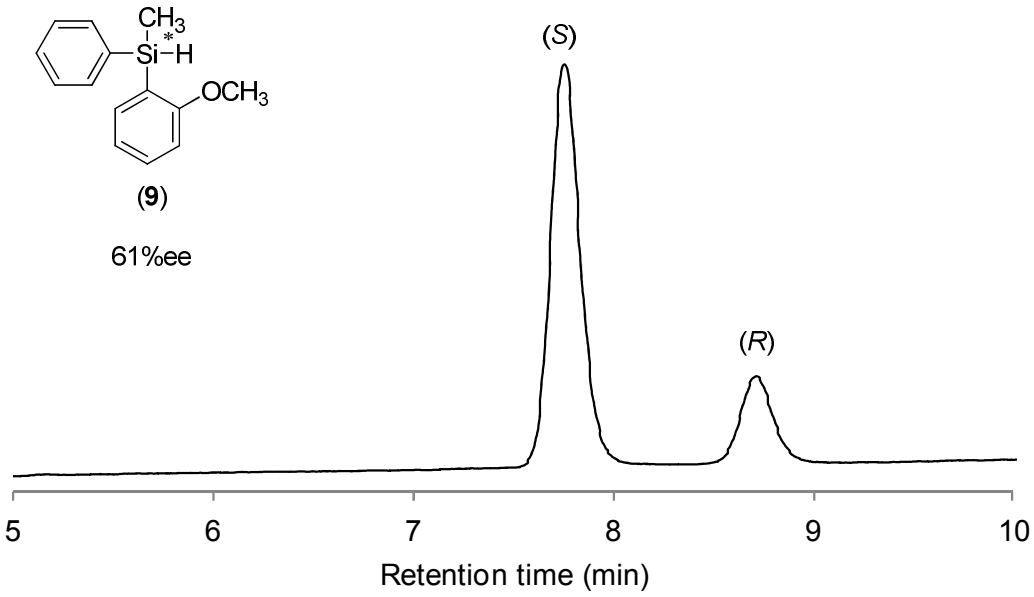
^{13}C NMR, $CDCl_3$, 100 MHz

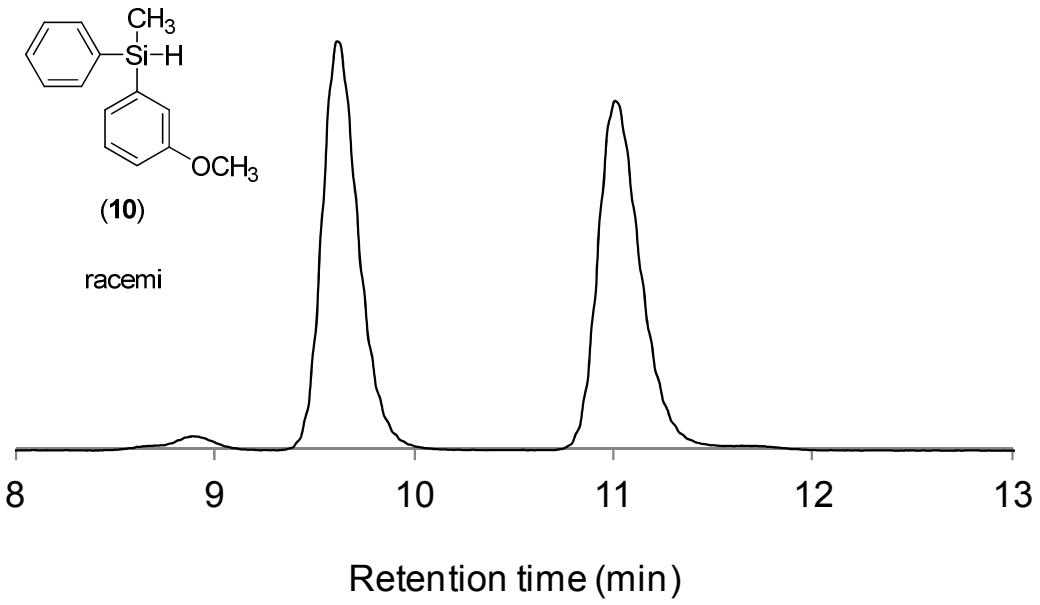


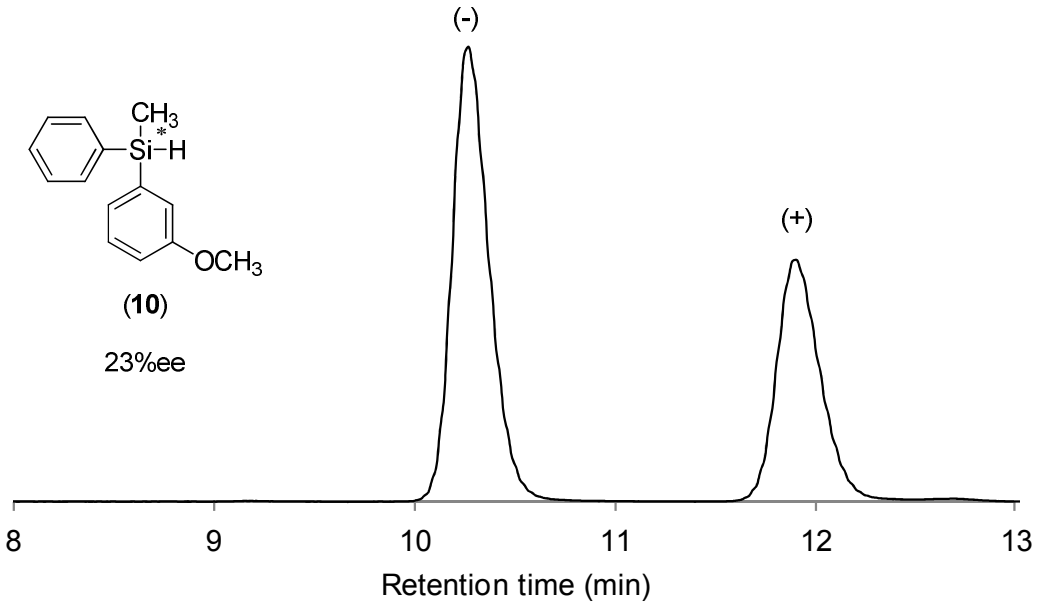
(21)

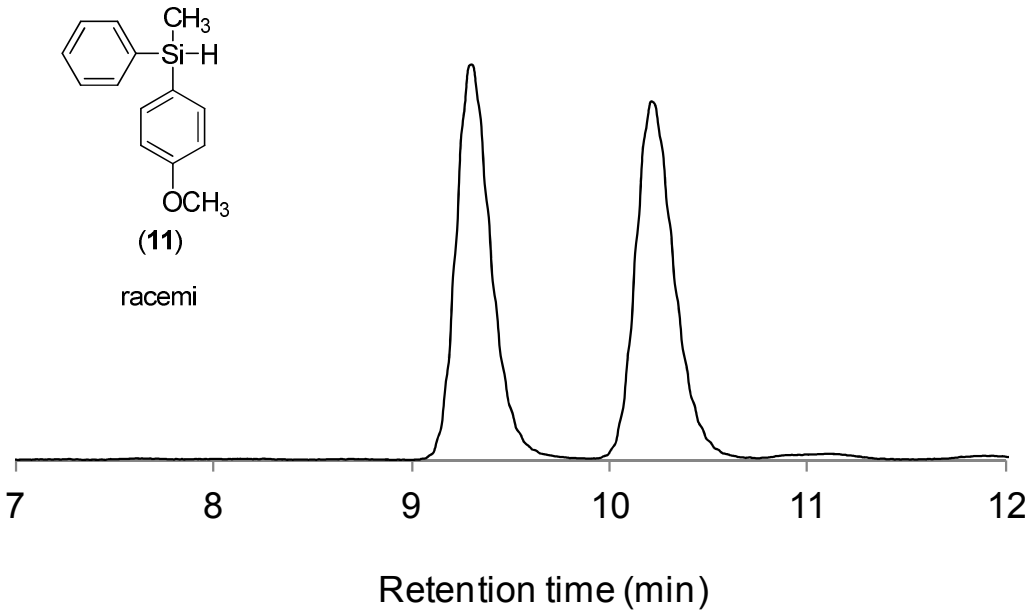
7. Copies of HPLC charts

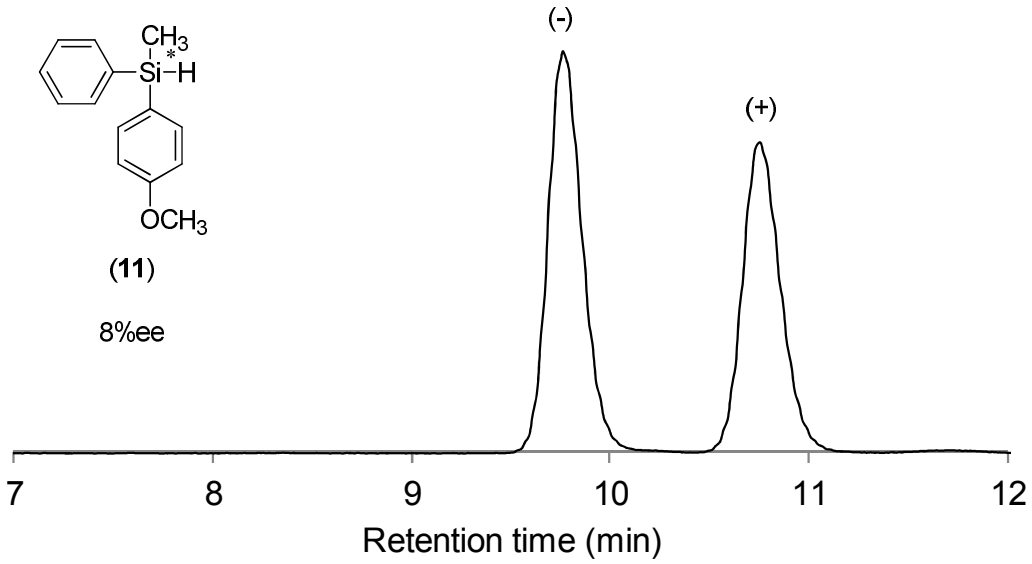


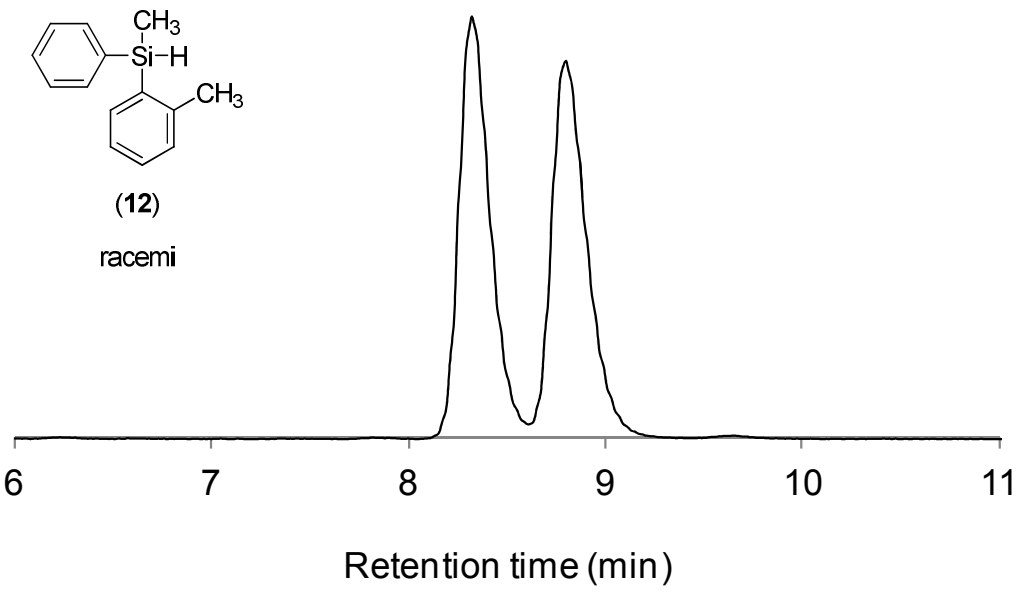


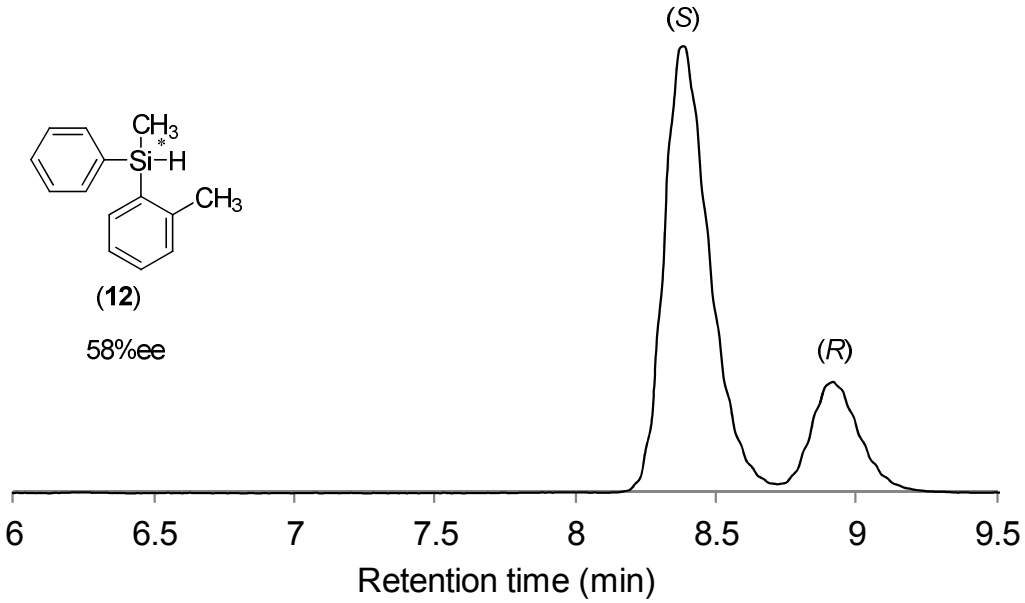

CH3
Si–H
OCH3
(10)
racemi
8
9
10
11
12
13
Retention time (min)

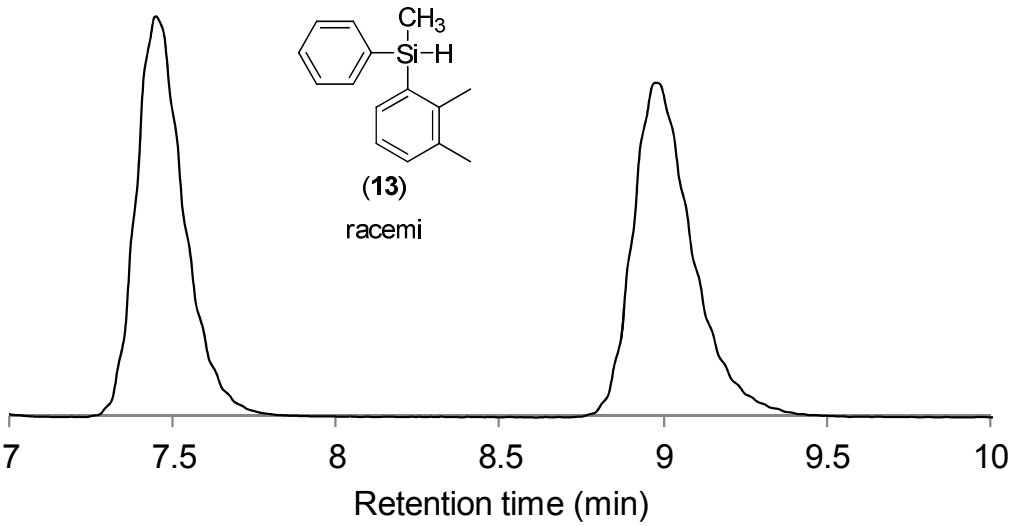

(-)
(+)
CH3
Si*–H
OCH3
(10)
23%ee
8
9
10
11
12
13
Retention time (min)

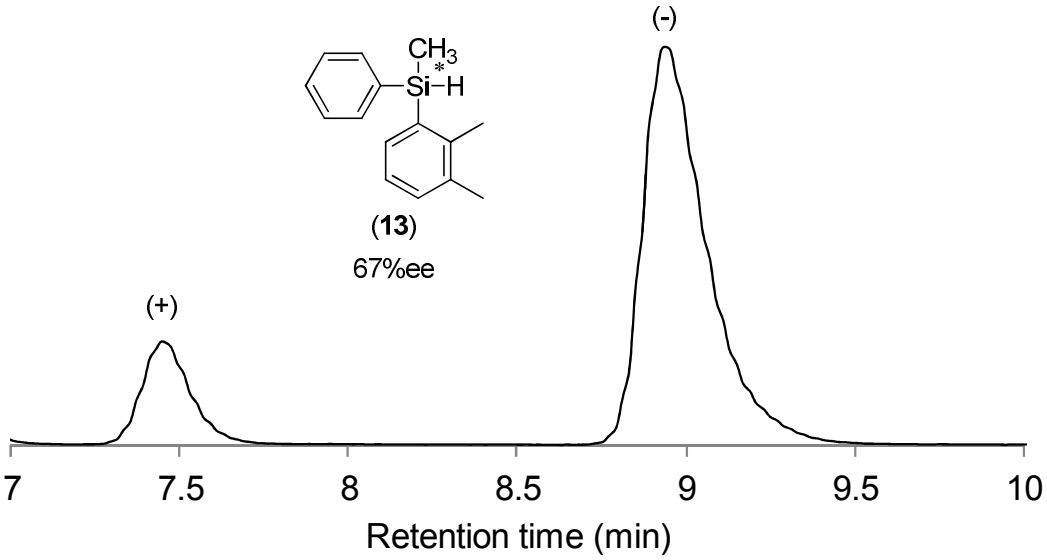


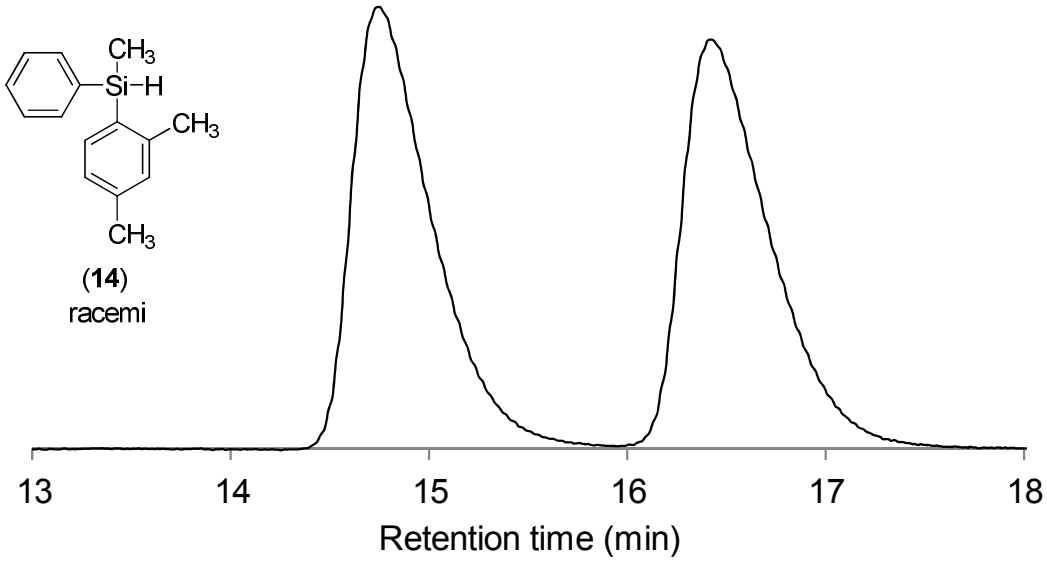


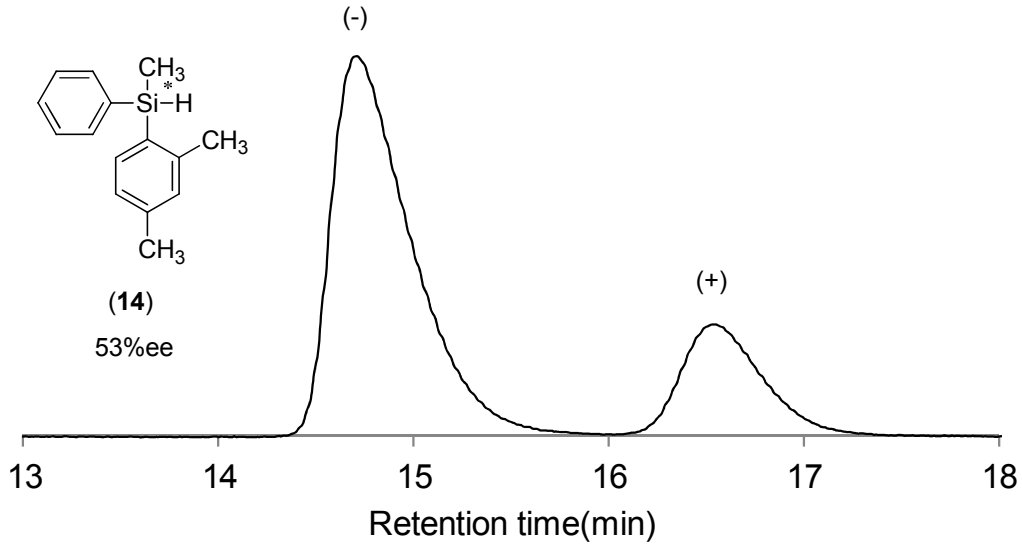

CH3
Si–H
CH3
(12)
racemi
6
7
8
9
10
11
Retention time (min)

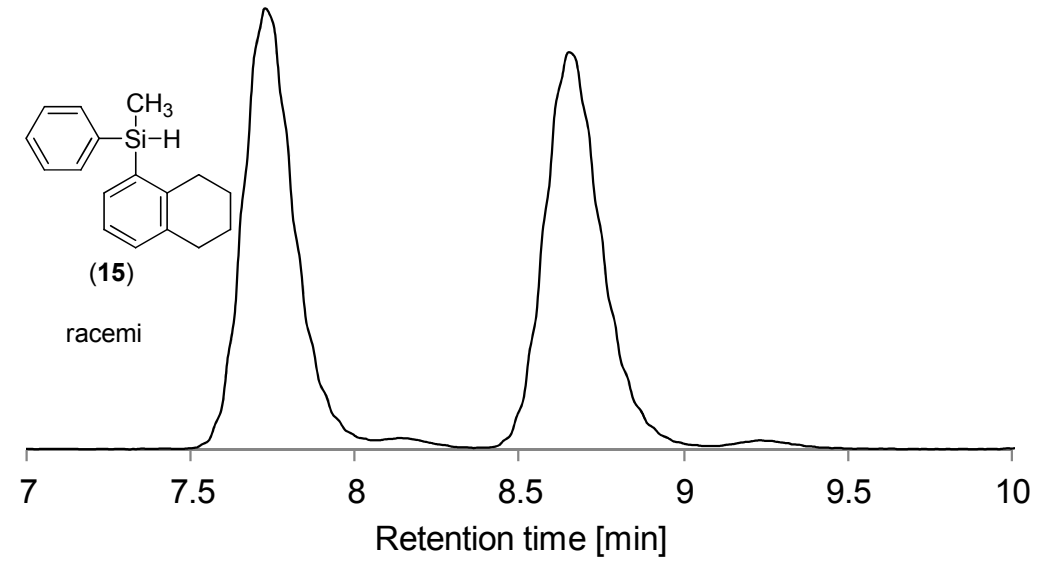

CH3
Si*–H
CH3
(12)
58%ee
(S)
(R)
6
6.5
7
7.5
8
8.5
9
9.5
Retention time (min)

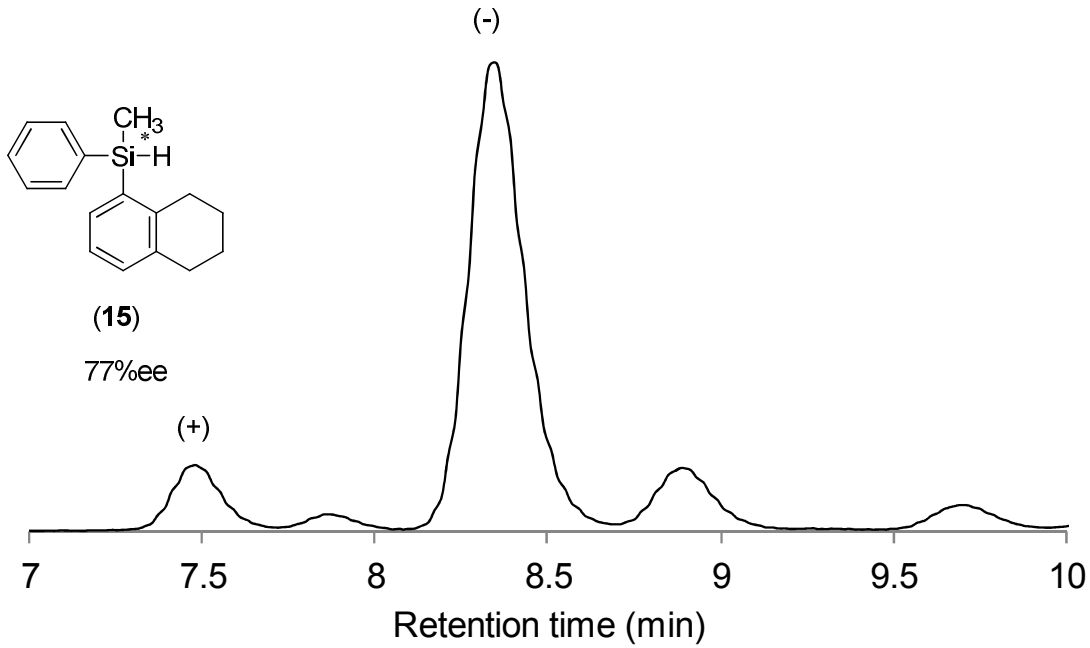


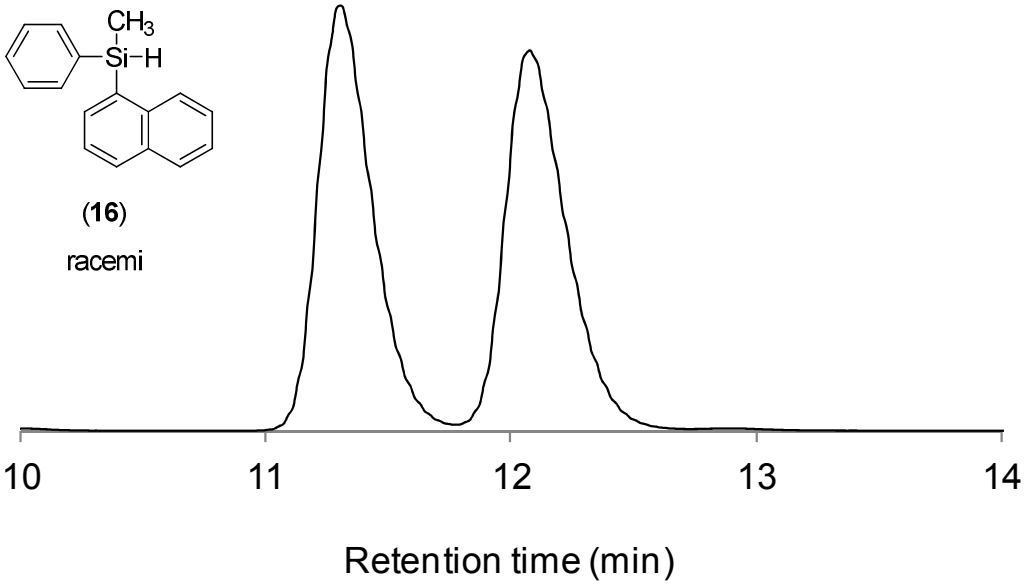


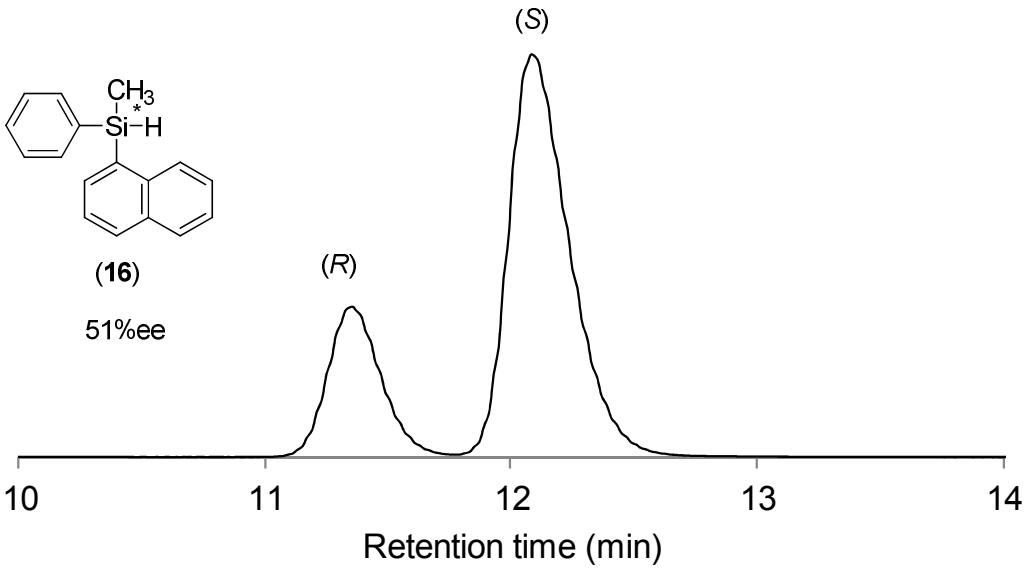

CH3
Si–H
CH3
CH3
(14)
racemi
13
14
15
16
17
18
Retention time (min)

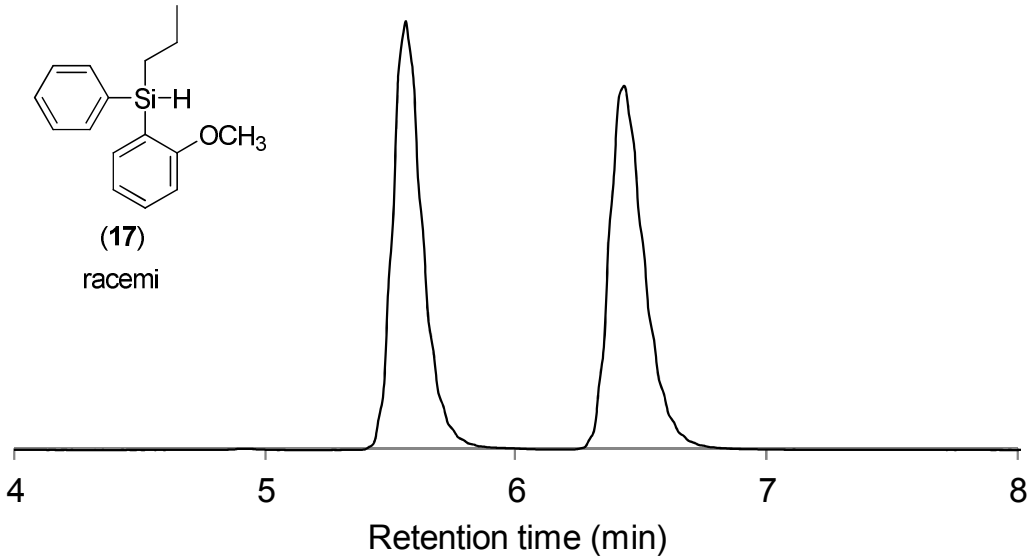

(-)
CH3
Si*–H
CH3
CH3
(14)
53%ee
(+)
13
14
15
16
17
18
Retention time(min)

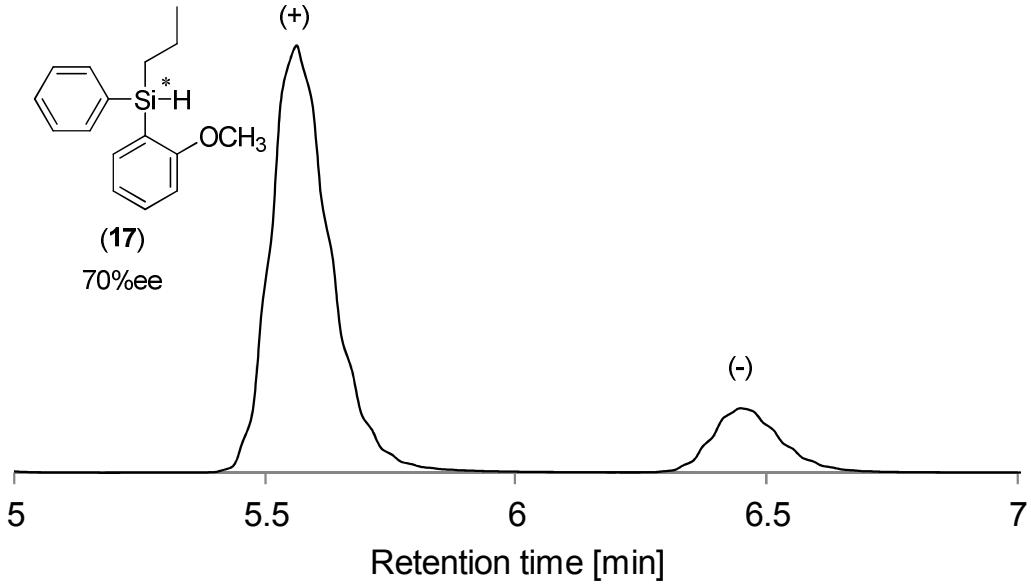

CH3
Si–H
(15)
racemi
7
7.5
8
8.5
9
9.5
10
Retention time [min]

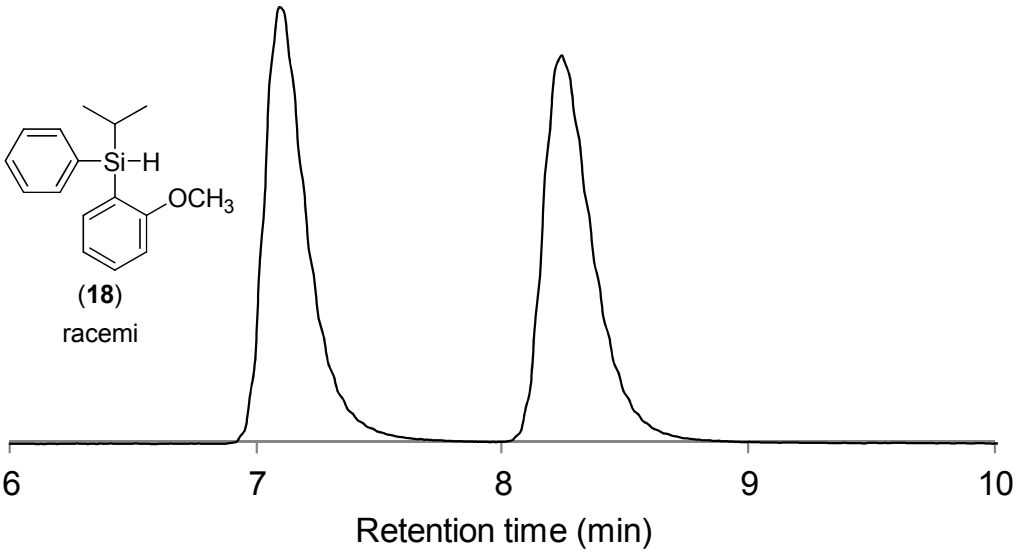

(-)
CH3
Si*–H
(15)
77%ee
(+)
7
7.5
8
8.5
9
9.5
10
Retention time (min)

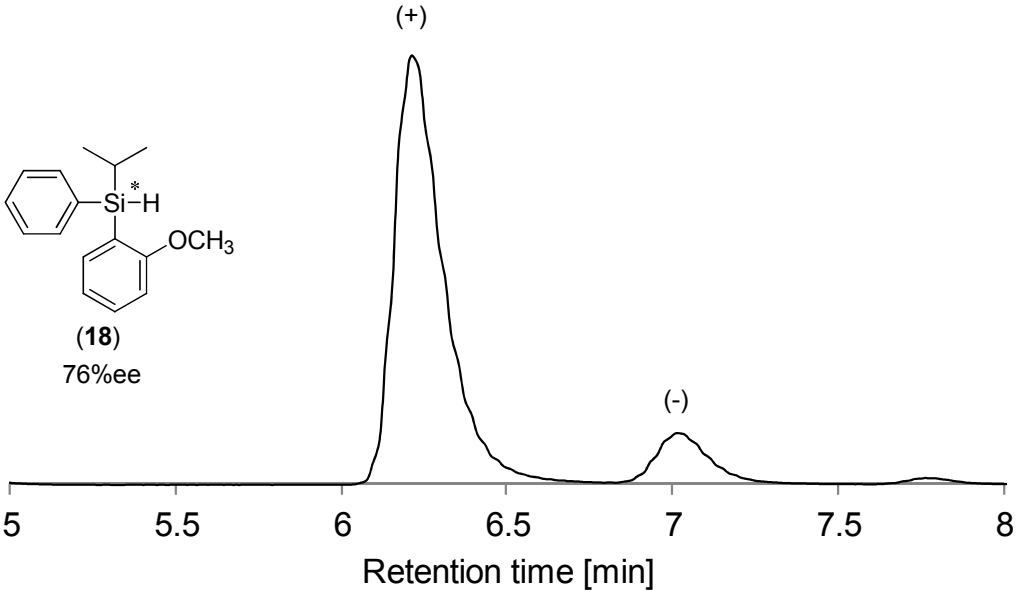

CH3
Si–H
(16)
racemi
10
11
12
13
14
Retention time (min)

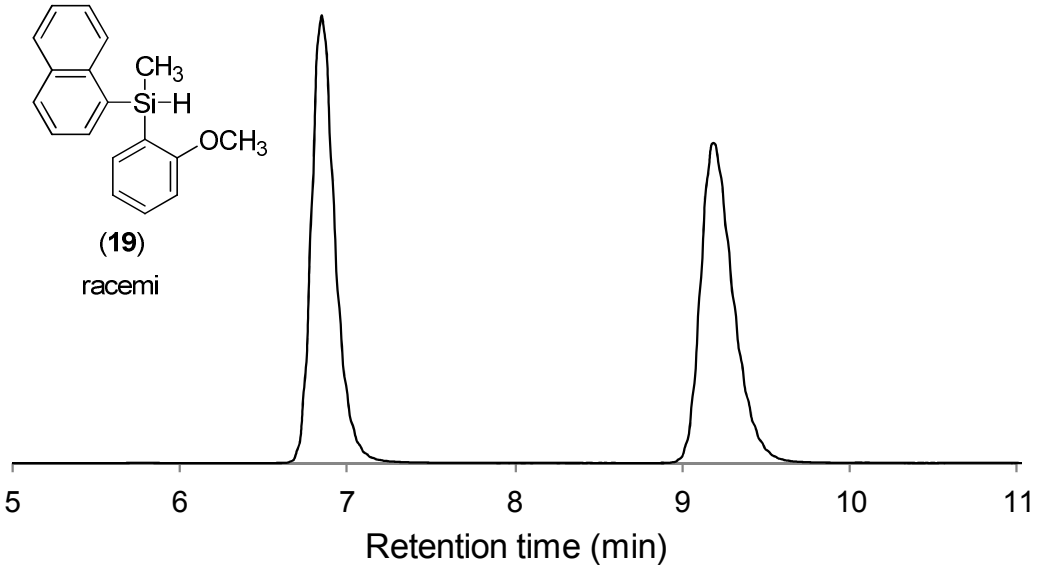

(S)
CH3
Si*–H
(16)
51%ee
(R)
10
11
12
13
14
Retention time (min)

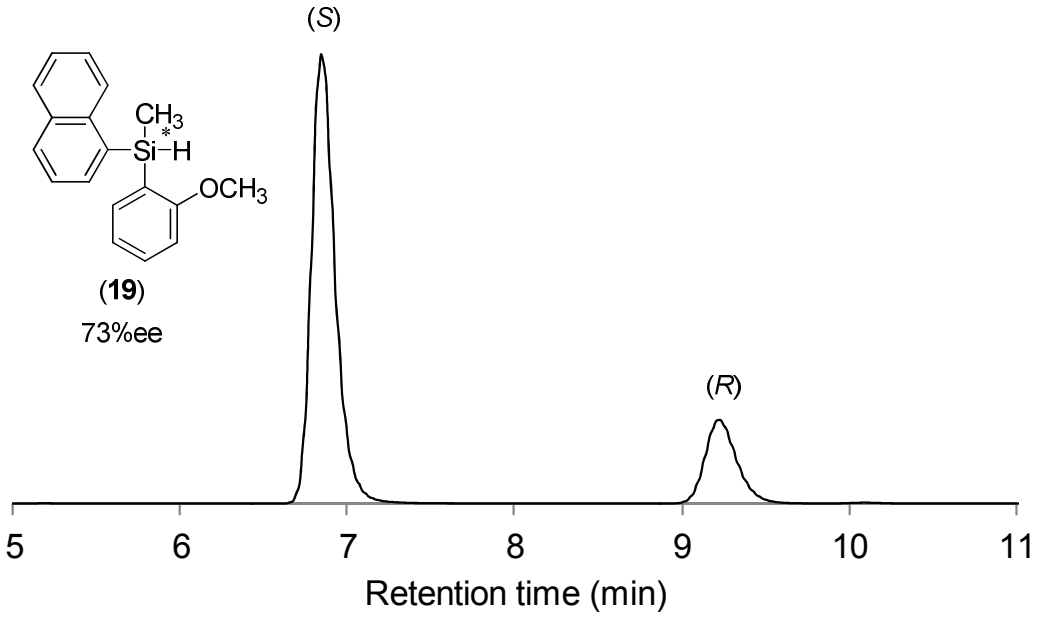

Si–H
OCH3
(17)
racemi
4
5
6
7
8
Retention time (min)

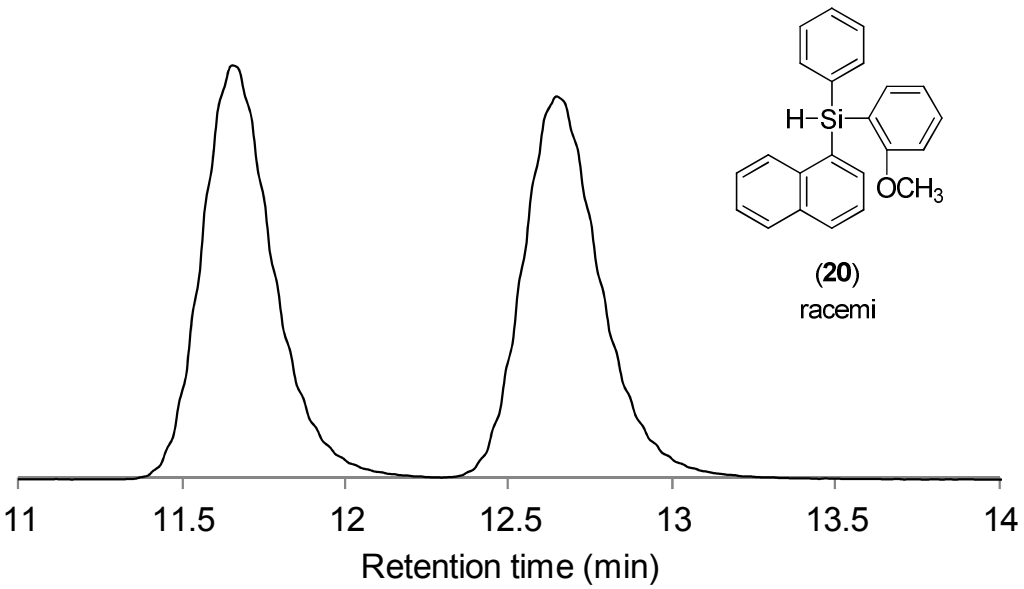

Si*–H
OCH3
(17)
70%ee
(+)
(-)
5
5.5
6
6.5
7
Retention time [min]

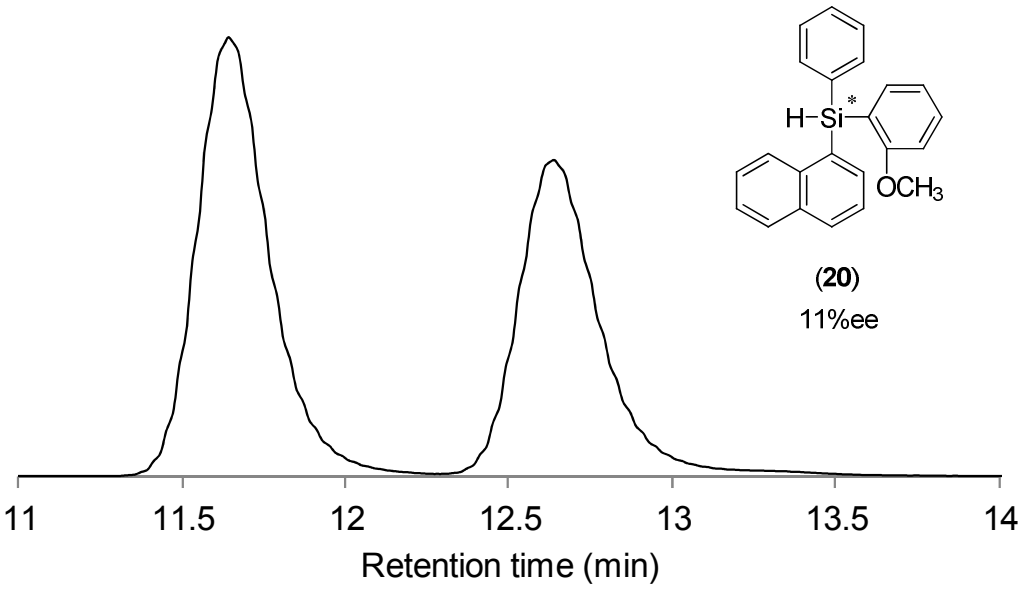


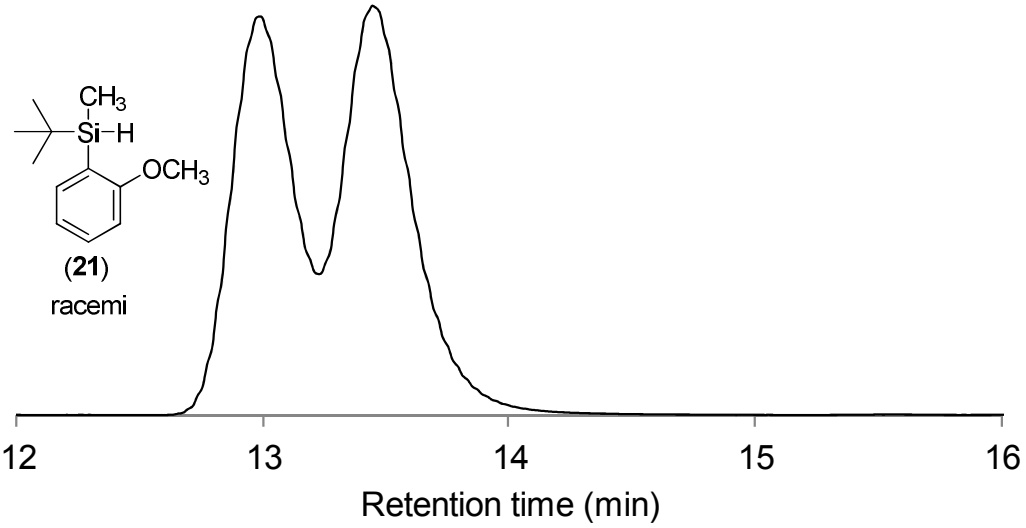


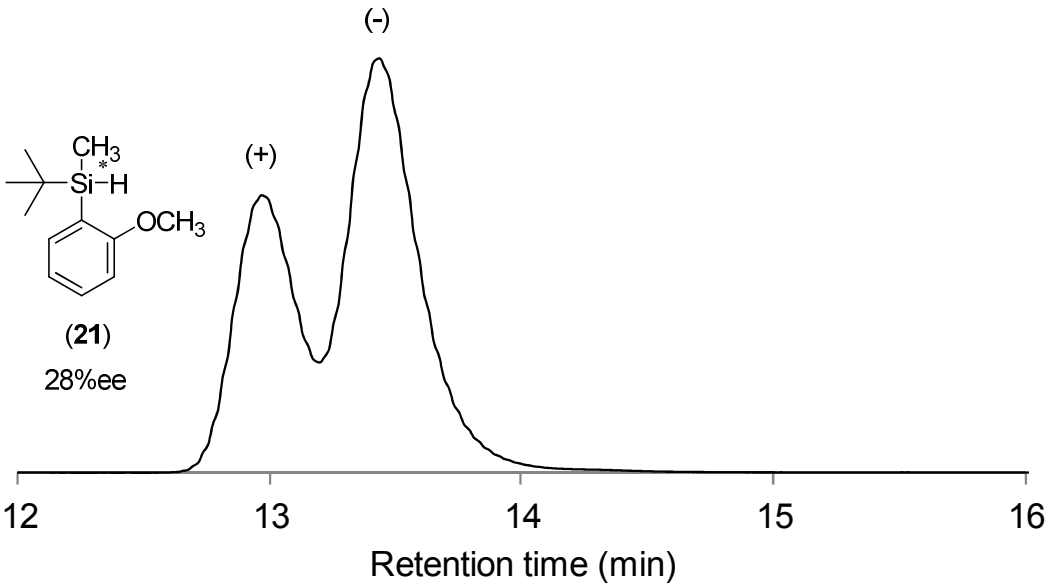

CH3
Si–H
OCH3
(19)
racemi
5
6
7
8
9
10
11
Retention time (min)


(S)
CH3
Si*–H
OCH3
(19)
73%ee
(R)
5
6
7
8
9
10
11
Retention time (min)


H–Si
OCH3
(20)
racemi
11
11.5
12
12.5
13
13.5
14
Retention time (min)


H–Si*
OCH3
(20)
11%ee
11
11.5
12
12.5
13
13.5
14
Retention time (min)


CH3
Si–H
OCH3
(21)
racemi
12
13
14
15
16
Retention time (min)


(-)
(+)
CH3
Si*–H
OCH3
(21)
28%ee
12
13
14
15
16
Retention time (min)