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SUPPORTING INFORMATION

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Title: Self-Folded Silyl Cavitands with In- and Outwardly Directed Allyl Groups

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Contents

a) **General Information**: All reactions sensitive to air or moisture were carried out under argon atmosphere and anhydrous conditions unless otherwise noted. All reagents were purchased and used without further purification. Column chromatography was carried out with silica gel. HRMS were reported on the basis of TOF (time of flight)-MS, and EB (double-focusing)-MS. Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in δ (ppm) with reference to residual solvent signals [^{1}H NMR: $CHCl_3$ (7.26), C_7D_8 (2.08); ^{13}C NMR: $CDCl_3$ (77.36)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

b) **Synthesis of Cavitand 4 and 5, for Scheme 3**: Under an argon atmosphere, to a Schlenk tube charged with **2** (or **3**) (125 mg, 0.08 mmol) and anhydrous toluene (1 mL) was added mCPBA (20 mg, 0.08 mmol). After overnight stirring, the reaction was quenched at 0 ºC with satd. aq. $Na_2S_2O_3$ (3 mL), and followed by dilution with each 10 mL of toluene and water. The aqueous phases were extracted with toluene, and the combined organic phases were washed with brine, and concentrated *in vacuo* to give crude products. Purification by silica gel column chromatography (hexane/ethyl acetate = 4/1) afforded **4** of 69 mg in 54% yield as white solid materials (in the case of **5**, 59 mg in 46% yield as white solid materials). **Compound 4:** 54% yield (69 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) 8.28 (s, 1H), 8.27 (s, 1H), 7.92-7.85 (m, 4H), 7.64-7.62 (m, 2H), 7.56-7.52 (m, 4H), 7.49-7.45 (m, 2H), 7.33 (s, 2H), 7.18-7.16 (m, 4H), 5.76 (t, *J* = 8.1 Hz, 1H), 5.68 (t, *J* = 8.3 Hz, 2H), 4.54 (t, *J* = 7.9 Hz, 1H), 2.61 (dddd, *J* = 6.6, 6.2, 4.6, 4.6 Hz, 1H, $SiCH_2CHOCH_2$), 2.46 (dd, *J* = 4.6, 4.6 Hz, 1H, SiCH2CHOCH_2), 2.36-2.18 (m, 8H), 1.93 (dd, *J* = 4.6, 4.6 Hz, 1H, $SiCH_2CHOCH_2$), 1.47-1.30 (m, 72H), 0.92-0.89 (m, 12H), 0.56 (s, 3H, $SiCH_3$), 0.30 (dd, *J* = 15.0, 6.6 Hz, 1H, $SiCH_2CHOCH_2$), 0.14 (dd, *J* = 15.0, 6.2 Hz, 1H, $SiCH_2CHOCH_2$) ppm; ^{1}H NMR (400 MHz, toluene-d_8) 8.69 (s, 1H), 8.66 (s, 1H), 8.01-7.99 (m, 2H), 7.73 (s, 2H), 7.65-7.52 (m, 6H), 7.47 (s, 1H), 7.45 (s, 1H), 7.28-7.23 (m, 2H), 7.14-7.04 (m, 4H), 6.15-6.13 (m, 2H), 6.03 (t, *J* = 8.2 Hz, 1H), 4.74 (t, *J* = 8.0 Hz, 1H), 2.47-2.32 (m, 8H), 1.90-1.83 (m, 2H, $SiCH_2CHOCH_2$, $SiCH_2CHOCH_2$), 1.54-1.32 (m, 72H), 1.12 (dd, *J* = 5.3, 5.3 Hz, 1H, $SiCH_2CHOCH_2$), 0.96-0.93 (m, 12H), 0.40 (s, 3H, $SiCH_3$), -0.69 (dd, *J* = 15.4, 7.0 Hz, 1H, $SiCH_2CHOCH_2$), -0.80 (dd, *J* = 15.4, 5.4 Hz, 1H, $SiCH_2CHOCH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 153.3, 153.2, 153.13, 153.09, 152.94, 152.87, 152.72, 152.70, 152.6, 150.2, 150.1, 140.13, 140.12, 140.10, 140.09, 140.06, 140.0, 136.86, 136.8, 136.3, 134.6, 134.5, 133.2, 133.1, 129.71, 129.66, 129.4, 128.1, 128.0, 127.8, 124.20, 124.16, 123.2, 123.1, 119.0, 116.1, 115.9, 48.7, 48.2, 35.4, 34.6, 34.3, 32.9, 32.8, 32.72, 32.70, 32.3 (many peaks are overlapped), 30.1 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.4, 23.1 (many peaks are overlapped), 16.8, 14.5 (many peaks are overlapped), -2.7 ppm; MS (MALDI-TOF) *m/z*: 1581 ($[MH]^+$); IR (neat): 2922, 2852, 1482, 1413, 1331, 1162 cm^{-1};

HRMS (MALDI-TOF) calcd for $C_{100}H_{124}N_6O_9Si$ (M^+): 1580.9199, found 1580.9226. **Compound 5:** 46% yield (59 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) 8.27 (s, 2H), 7.91-7.86 (m, 4H), 7.68 (dd, *J* = 8.2, 5.4 Hz, 2H), 7.56-7.51 (m, 4H), 7.46 (dd, *J* = 8.3, 8.3 Hz, 2H), 7.32 (s, 2H), 7.16-7.14 (m, 4H), 5.75 (t, *J* = 8.2 Hz, 1H), 5.67 (t, *J* = 8.2 Hz, 2H), 4.55 (t, *J* = 8.0 Hz, 1H), 3.29-3.24 (m, 1H, $SiCH_2C\underline{H}OCH_2$), 2.90 (dd, *J* = 4.6, 4.6 Hz, 1H, $SiCH_2CHOC\underline{H_2}$), 2.64 (dd, *J* = 4.6, 4.6 Hz, 1H, $SiCH_2CHOC\underline{H_2}$), 2.36-2.19 (m, 8H), 1.55-1.50 (m, 1H, $SiC\underline{H_2}CHOCH_2$), 1.46-1.30 (m, 72H), 1.15 (dd, *J* = 14.8, 7.3 Hz, 1H, $SiC\underline{H_2}CHOCH_2$), 0.92-0.88 (m, 12H), -0.47 (s, 3H, $SiC\underline{H_3}$) ppm; ^{1}H NMR (400 MHz, toluene-d_8) 8.70 (s, 2H), 7.98 (d, *J* = 7.0 Hz, 2H), 7.74 (s, 2H), 7.62-7.56 (m, 6H), 7.44 (s, 1H), 7.43 (s, 1H), 7.25 (dd, *J* = 7.0, 7.0 Hz, 2H), 7.10-7.06 (m, 4H), 6.14 (t, *J* = 8.1 Hz, 2H), 6.05 (t, *J* = 8.1 Hz, 1H), 4.76 (t, *J* = 7.9 Hz, 1H), 2.90-2.85 (m, 1H, $SiCH_2C\underline{H}OCH_2$), 2.48-2.34 (m, 9H, $C\underline{H_2}(CH_2)_9CH_3$, $SiCH_2CHOC\underline{H_2}$), 2.17 (dd, *J* = 5.4, 5.4 Hz, 1H, $SiCH_2CHOC\underline{H_2}$), 1.54-1.29 (m, 72H), 1.07 (dd, *J* = 14.8, 5.4 Hz, 1H, $SiC\underline{H_2}CHOCH_2$), 0.96-0.93 (m, 12H), 0.78 (dd, *J* = 14.8, 7.0 Hz, 1H, $SiC\underline{H_2}CHOCH_2$), -1.30 (s, 3H, $SiC\underline{H_3}$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 153.2, 153.1, 153.0, 152.9, 152.7, 152.6, 150.1, 140.13, 140.10, 140.06, 136.8, 136.3, 134.62, 134.60, 133.1, 129.65, 129.57, 129.3, 128.2, 128.0, 124.2, 123.1, 119.0, 116.1, 48.9, 48.7, 35.3, 34.6, 34.3, 32.9, 32.8 (two peaks are overlapped), 32.6, 32.3 (many peaks are overlapped), 30.1 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.4, 23.1 (many peaks are overlapped), 19.1, 14.5 (many peaks are overlapped), -4.7 ppm; MS (MALDI-TOF) *m/z*: 1581 ($[MH]^+$); IR (neat): 2922, 2851, 1482, 1414, 1331, 1159 cm^{-1}; HRMS (MALDI-TOF) calcd for $C_{100}H_{124}N_6O_9Si$ (M^+): 1580.9199, found 1580.9175.

c) **Synthesis of 6, for Scheme 3:** Under an argon atmosphere, to the two-necked flask charged with *p*-cresol (4.0 mmol, 433 mg) and triethylamine (4.0 mmol, 0.56 mL) in anhydrous toluene (4 mL) was added allyl(dichloro)methylsilane (2.0 mmol, 0.29 mL) at 0 ºC. After stirring for 10 min, the cooling-bath was removed to warm to room temperature, and the overnight reaction was performed. The reaction mixture was diluted with toluene 10 mL) and washed with 1 N aqueous NaOH (10 mL x 3). The organic phase was washed with water (10 mL x 2) and brine (10 mL). The mixture was dried over sodium sulfate, and filtered, and concentrated *in vacuo* to give 448 mg of desired **6** (79%) as a yellow oil in pure form. ^{1}H NMR (400 MHz, $CDCl_3$) 7.04 (d, *J* = 8.1 Hz, 4H), 6.85 (d, *J* = 8.1 Hz, 4H), 5.80 (ddt, *J* = 17.0, 10.2, 8.0 Hz, 1H), 5.00-4.94 (m, 2H), 2.29 (s, 6H), 1.85 (d, *J* = 8.0 Hz, 2H), 0.33 (s, 3H) ppm; ^{1}H NMR (400 MHz, toluene-d_8) 6.93 (d, *J* = 8.1 Hz, 4H), 6.84 (d, *J* = 8.1 Hz, 4H), 5.80 (ddt, *J* = 17.5, 9.6, 7.9 Hz, 1H), 4.96-4.91 (m, 2H), 2.06 (s, 6H), 1.81 (d, *J* = 7.9 Hz, 2H), 0.28 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 152.1, 132.2, 131.7, 130.4, 119.9, 115.9, 22.0, 20.9, -4.4 ppm; MS (DI) *m/z*: 298 (M^+); IR (neat): 3031, 2974, 2923, 1878, 1611, 1505, 1234, 917, 818 cm^{-1}; HRMS (DI) calcd for $C_{18}H_{22}O_2Si$ (M^+): 298.1389, found 298.1405.

d) **Synthesis of 7, for Scheme 3:** To a flask charged with **6** (149 mg, 0.5 mmol) and dry dichloromethan (2 mL) was added mCPBA (125 mg, 0.5 mmol). After stirring for 24 h, the reaction was quenched with saturated aqueous $Na_2S_2O_3$ (10 mL). The mixture was washed with satd. aq. $NaHCO_3$ (10 mL x 3), and the aqueous layer was extracted with toluene (10 mL x 3). Combined organic phases were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give crude products of 149 mg. Purification by silica gel column chromatography (eluent; hexane/EtOAc = 19/1) afforded 47 mg of **7** in 30% yield as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) 7.04 (d, *J* = 8.6 Hz, 4H), 6.86-6.83 (m, 4H), 3.06 (dddd, *J* = 7.8, 5.1, 4.9, 4.9 Hz, 1H), 2.72 (dd, *J* = 4.9, 4.9 Hz, 1H), 2.39 (dd, *J* = 4.9, 4.9 Hz, 1H), 2.28 (s, 6H), 1.46 (dd, *J* = 14.8, 5.1 Hz, 1H), 0.99 (dd, *J* = 14.8, 7.8 Hz, 1H), 0.41 (s, 3H) ppm; ^{1}H NMR (400 MHz, toluene-d_8) 6.92-6.89 (m, 4H), 6.84 (d, *J* = 7.4 Hz, 4H), 2.86-2.82 (m, 1H), 2.35 (dd, *J* = 5.2,

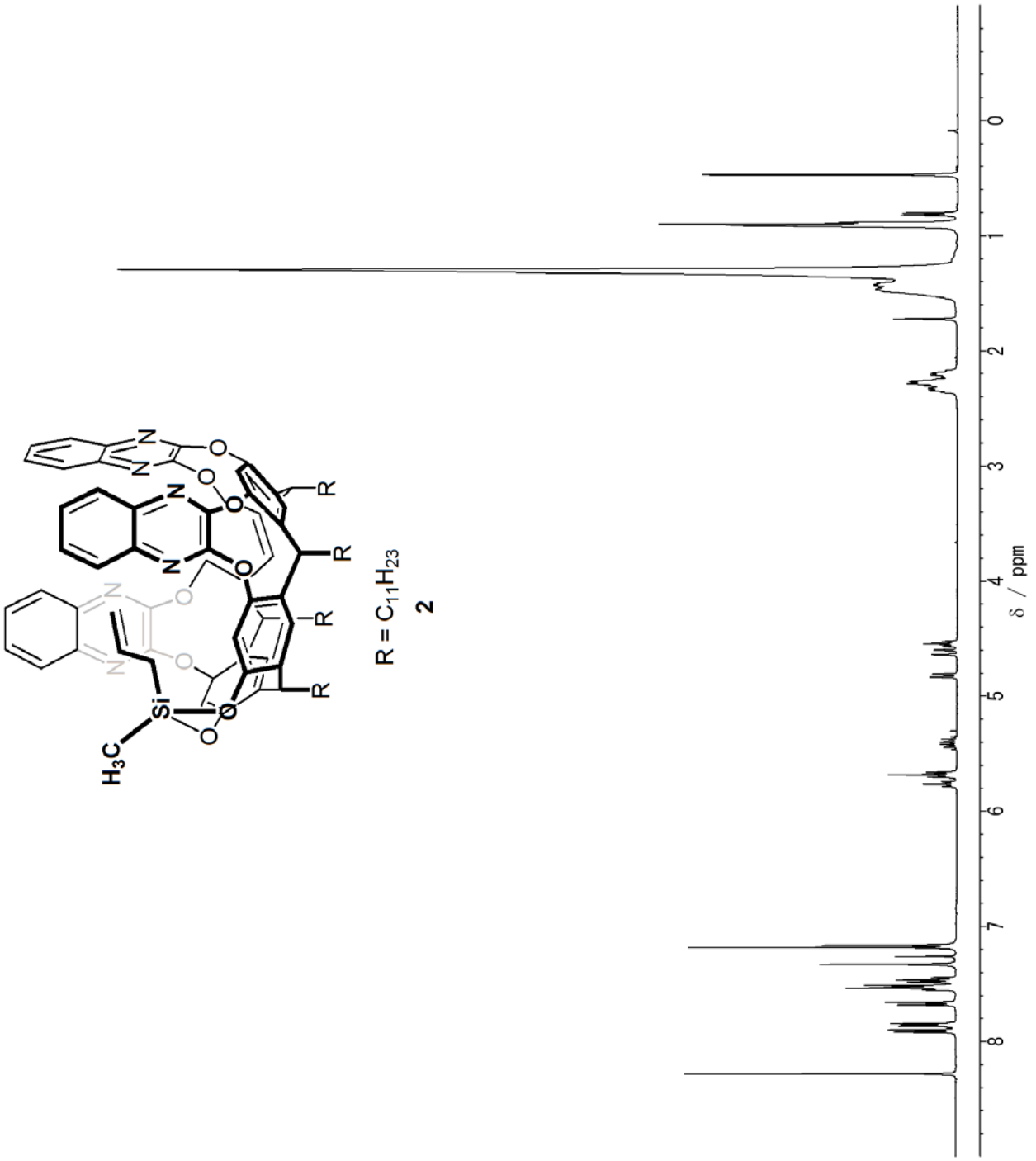
5.2 Hz, 1H), 2.07-2.06 (m, 7H), 1.21 (dd, J = 14.9, 5.7 Hz, 1H), 0.93 (dd, J = 14.9, 7.0 Hz, 1H), 0.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 151.90, 151.87, 131.9, 130.47, 130.46, 119.77, 119.76, 49.0, 48.8, 20.9, 19.3, -2.7 ppm; MS (DI) *m/z*: 314 (M^+); IR (neat): 3030, 2922, 1611, 1505, 1232, 917, 818 cm^{-1}; HRMS (DI) calcd for $C_{18}H_{22}O_3Si$ (M^+): 314.1338, found 314.1337.

e) **General Procedure of Competitive Epoxidation Experiments for Table 1 and 2:** To the NMR tube charged with **2** (0.02 mmol, 31 mg) and **3** (0.02 mmol, 31 mg) under an argon atmosphere was added 0.5 mL of anhydrous toluene-d_8, and followed by addition of mCPBA (5.0 mg, 0.02 mmol). After 20 h, the reaction proceeded with the ratio of **4**/**5**/**2**/**3**=32/23/19/26. The ratios of **4**/**5**/**2**/**3** in C_6D_6, and in *p*-xylene-d_{10} were 27/17/24/32, and 31/18/19/32, respectively.

^{1}H NMR and ^{13}C NMR spectra for compounds 2 - 7:

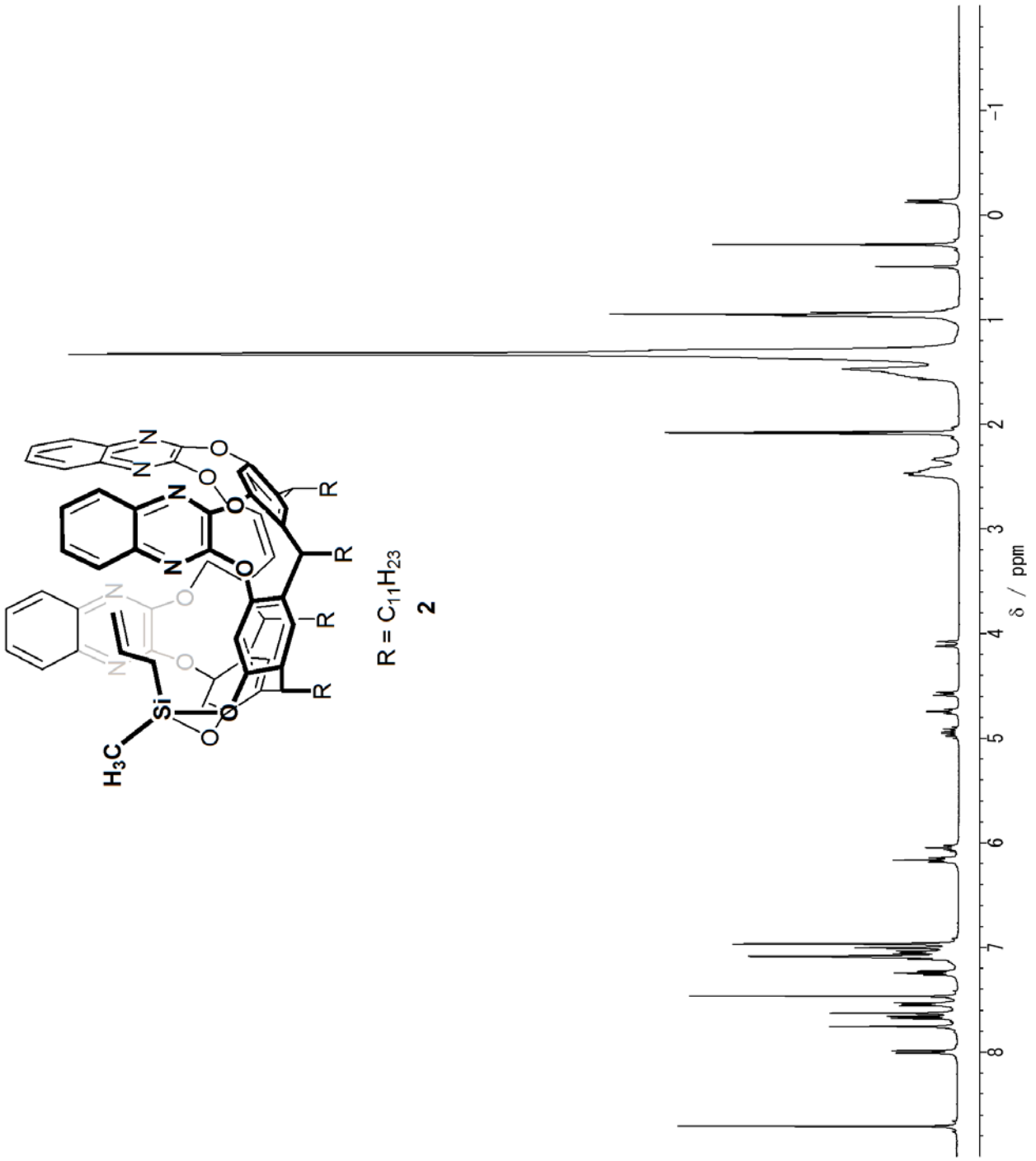
Compound 2

^{1}H NMR spectrum in $CDCl_3$



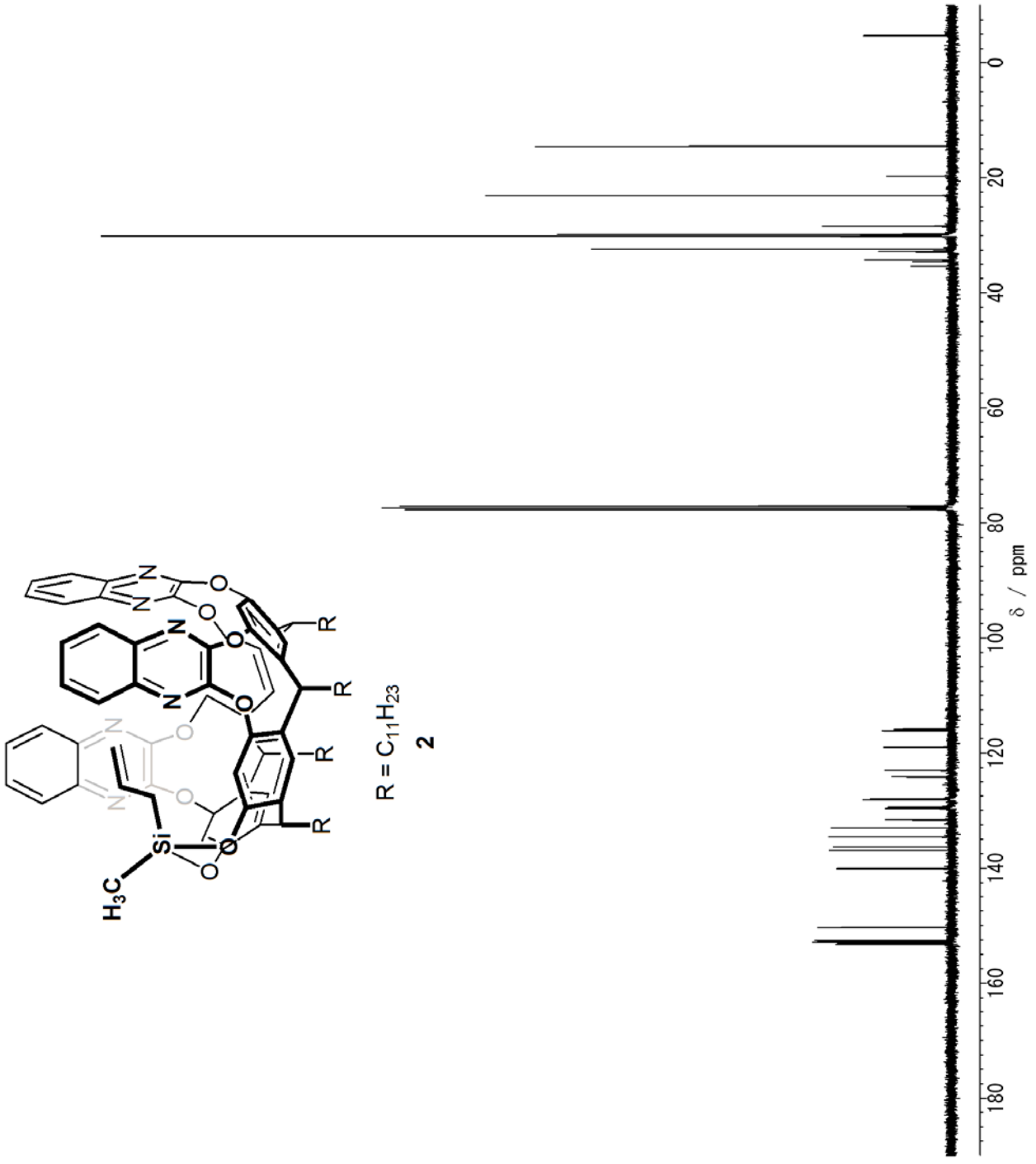
Compound 2

^{1}H NMR spectrum in toluene-d_8



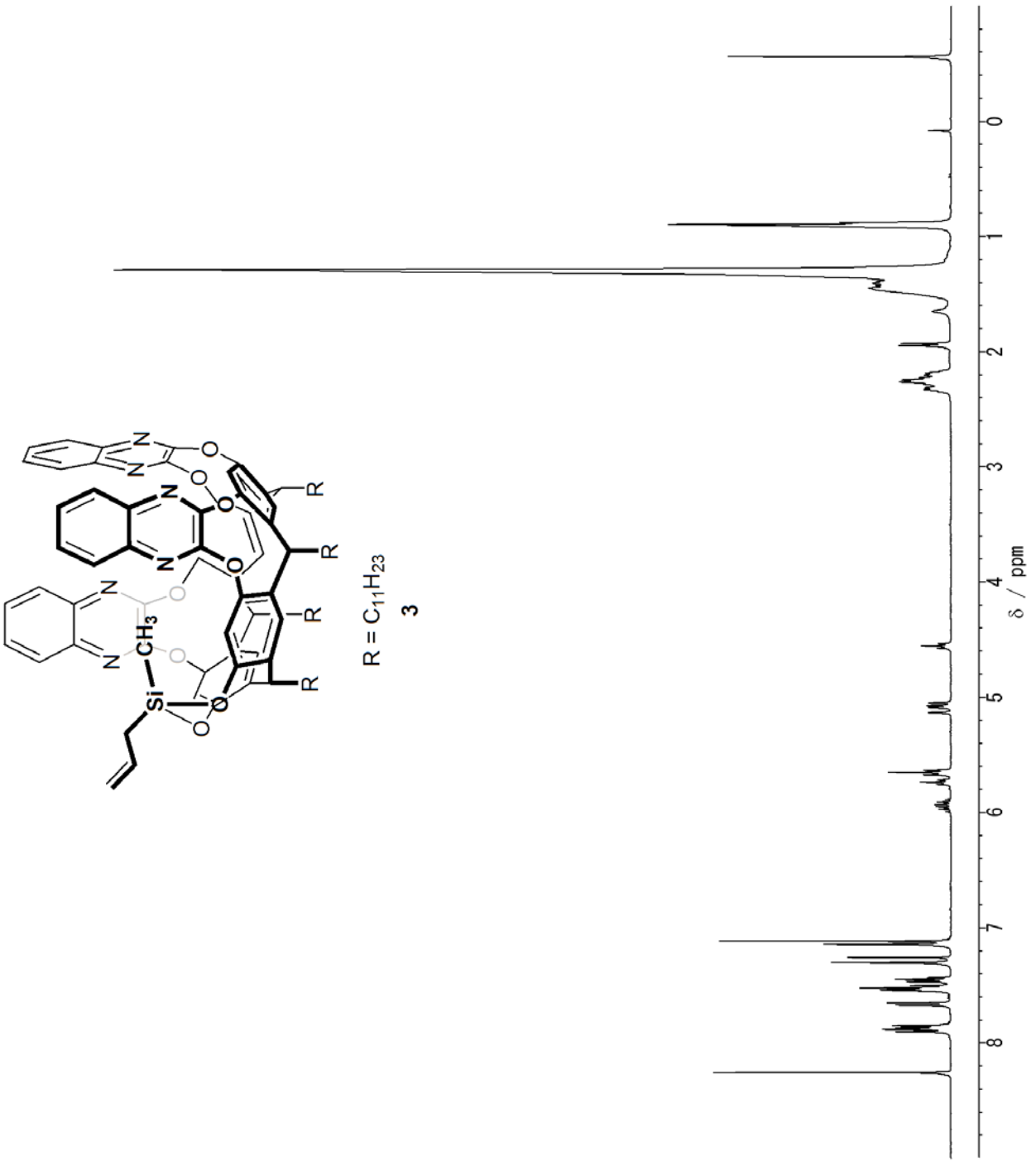
Compound 2

^{13}C NMR spectrum in $CDCl_3$



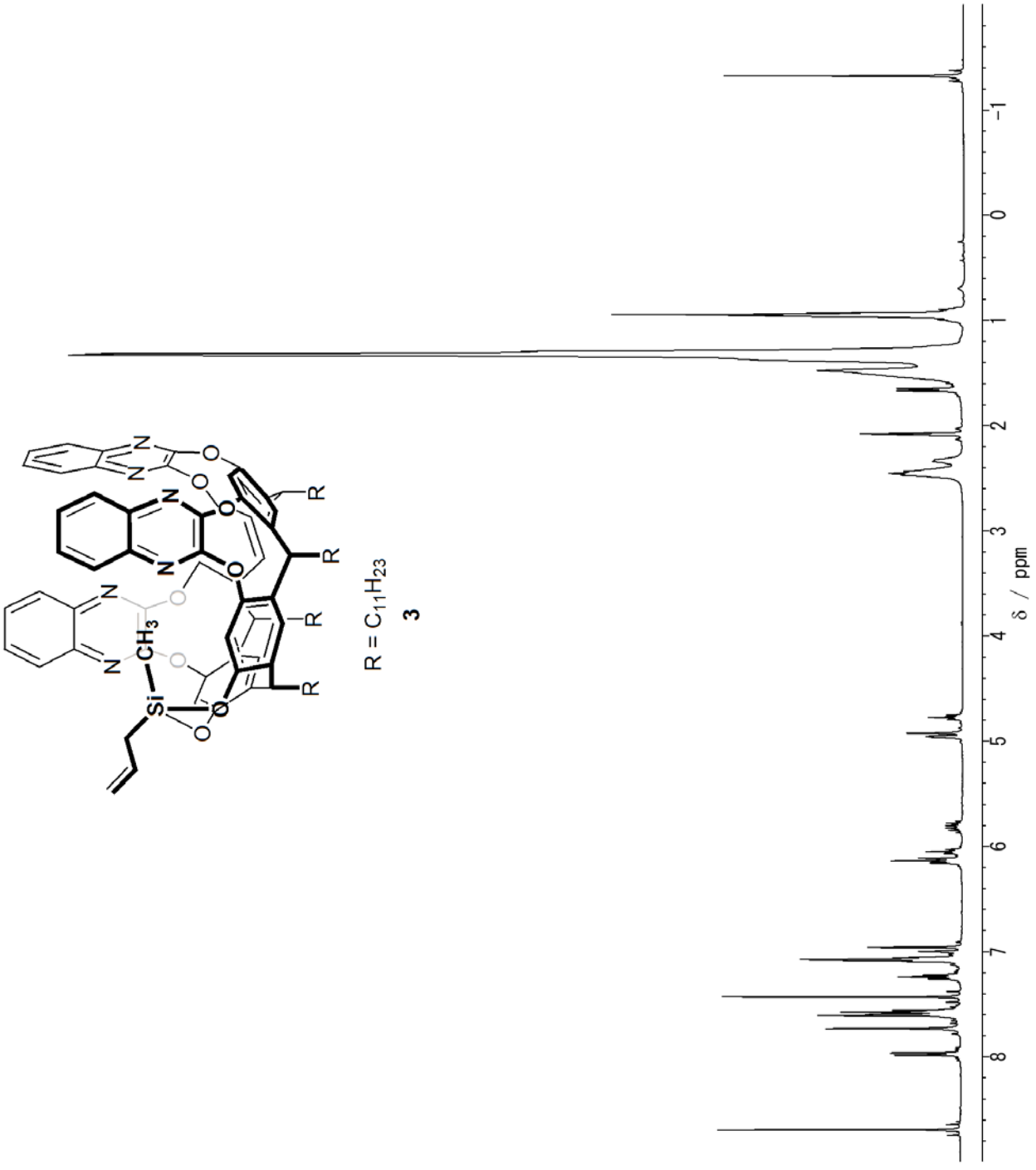
Compound 3

^{1}H NMR spectrum in $CDCl_3$



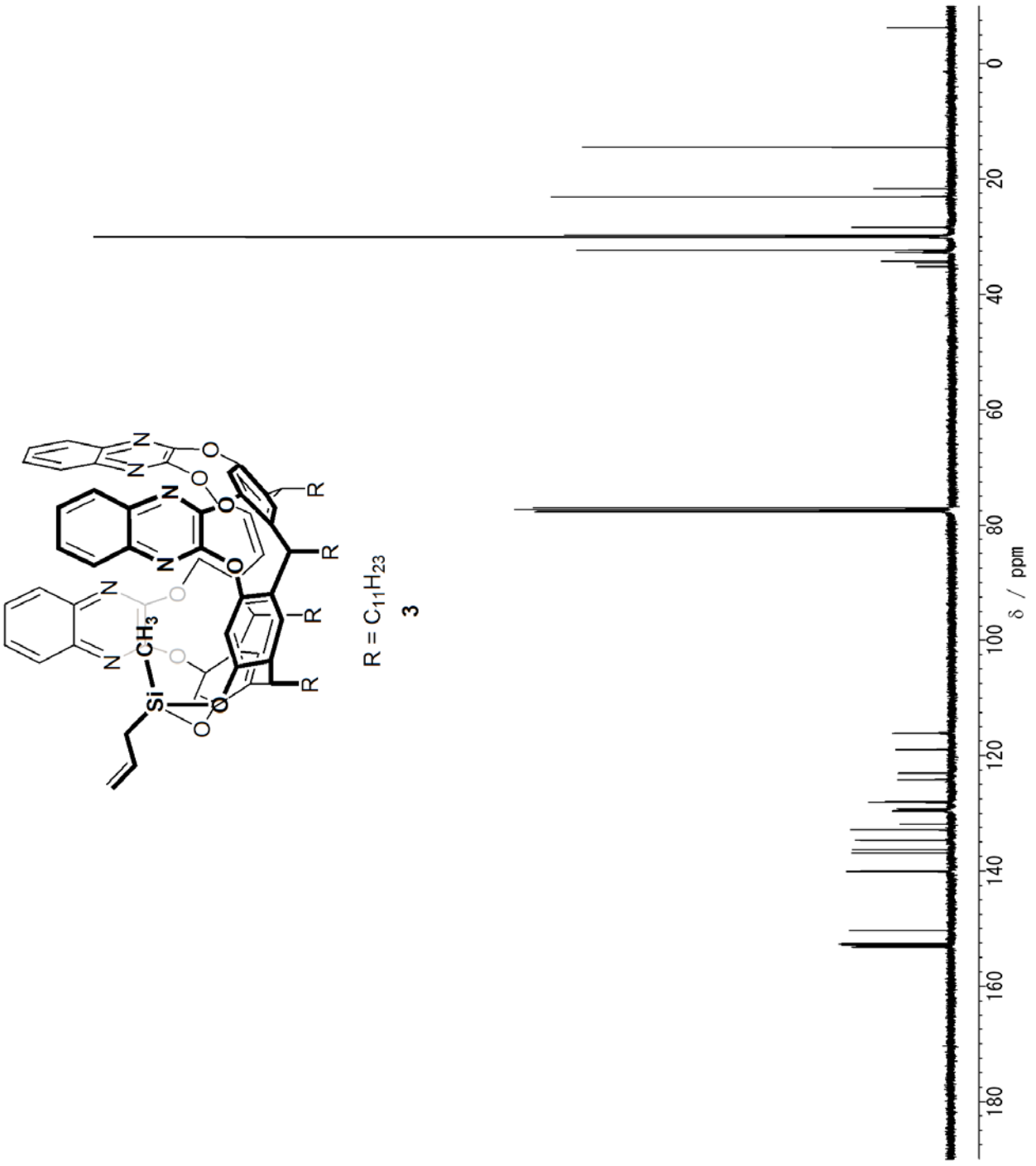
Compound 3

^{1}H NMR spectrum in toluene-d_8



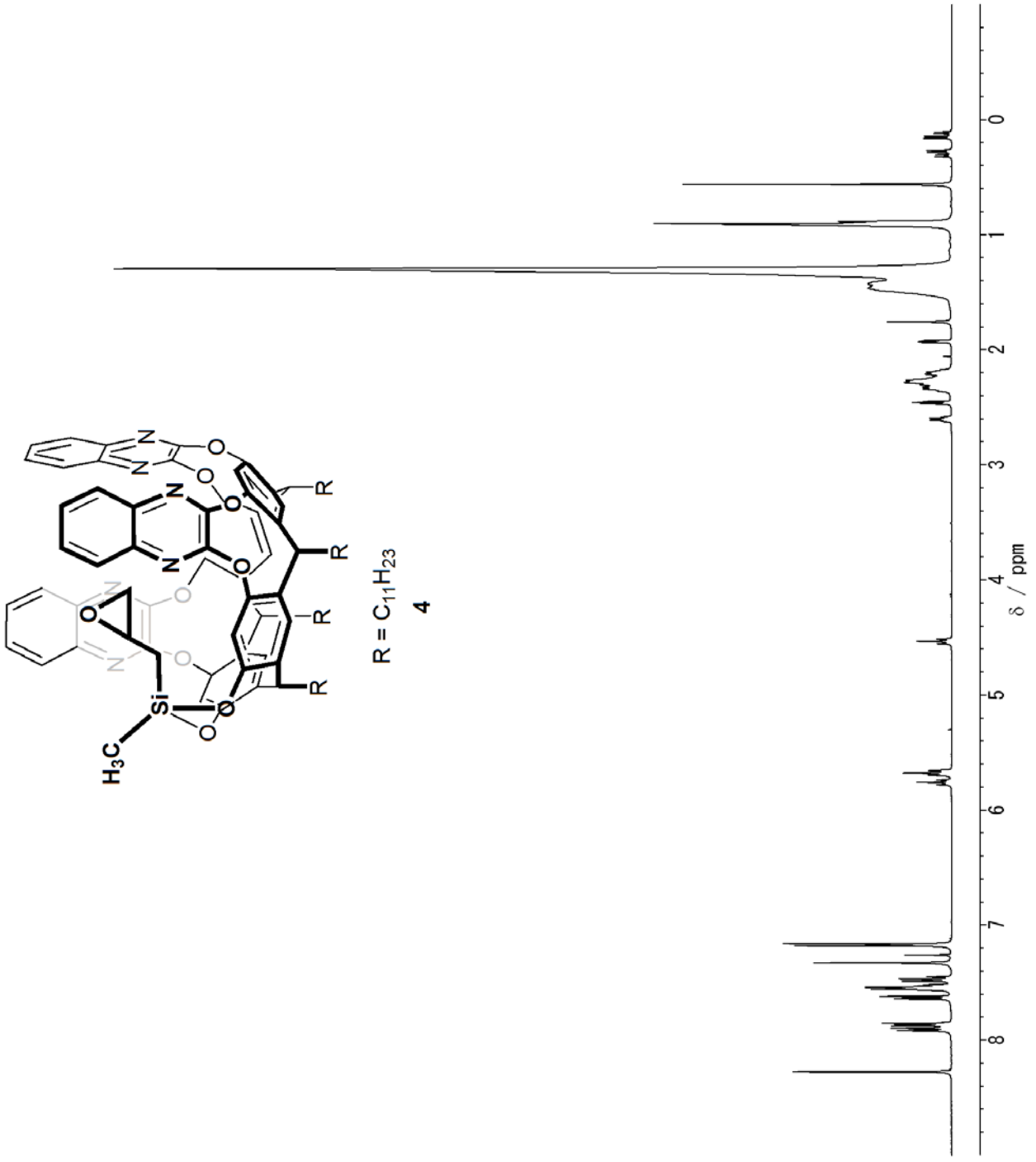
Compound 3

^{13}C NMR spectrum in $CDCl_3$



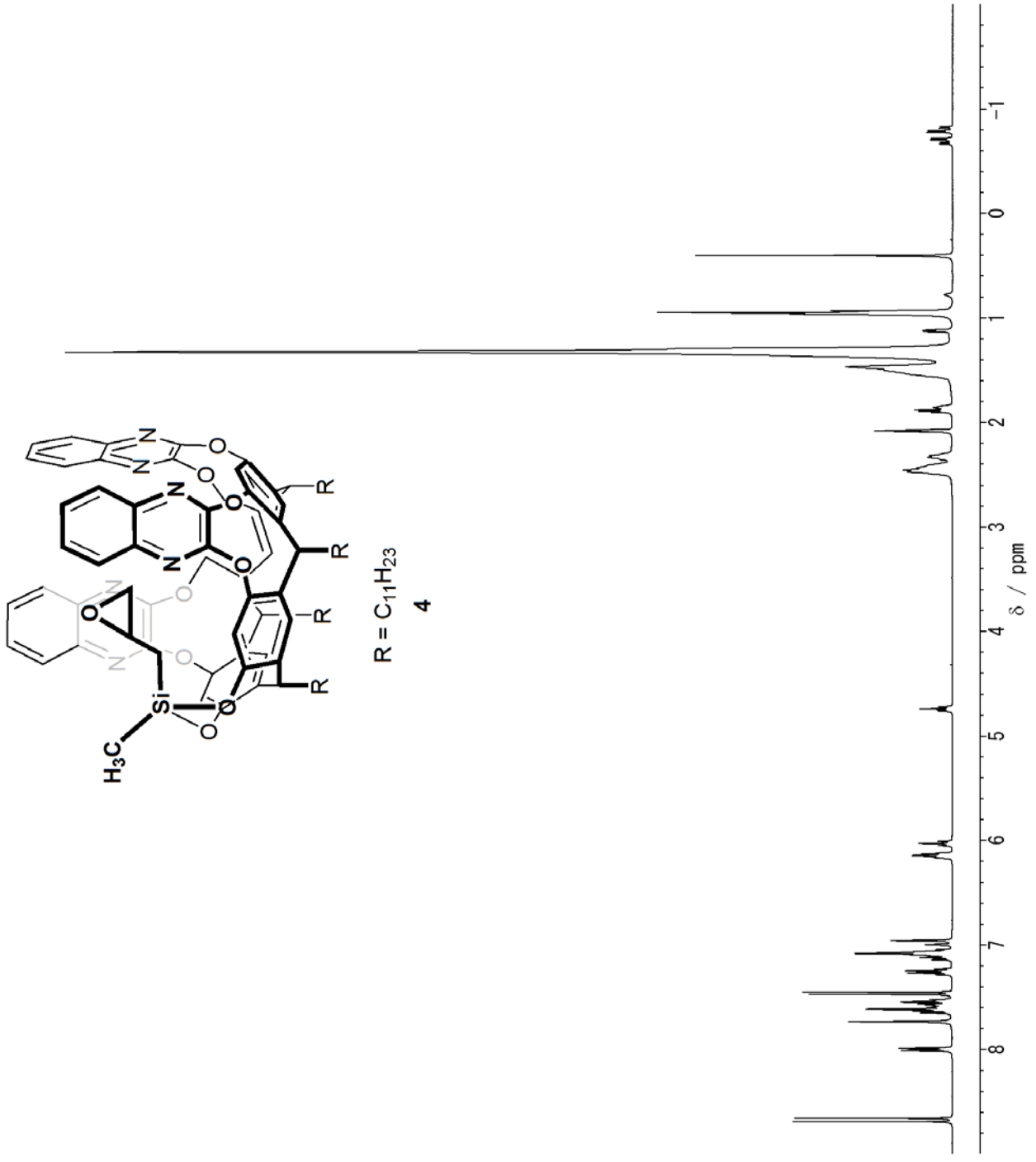
Compound 4

^{1}H NMR spectrum in $CDCl_3$



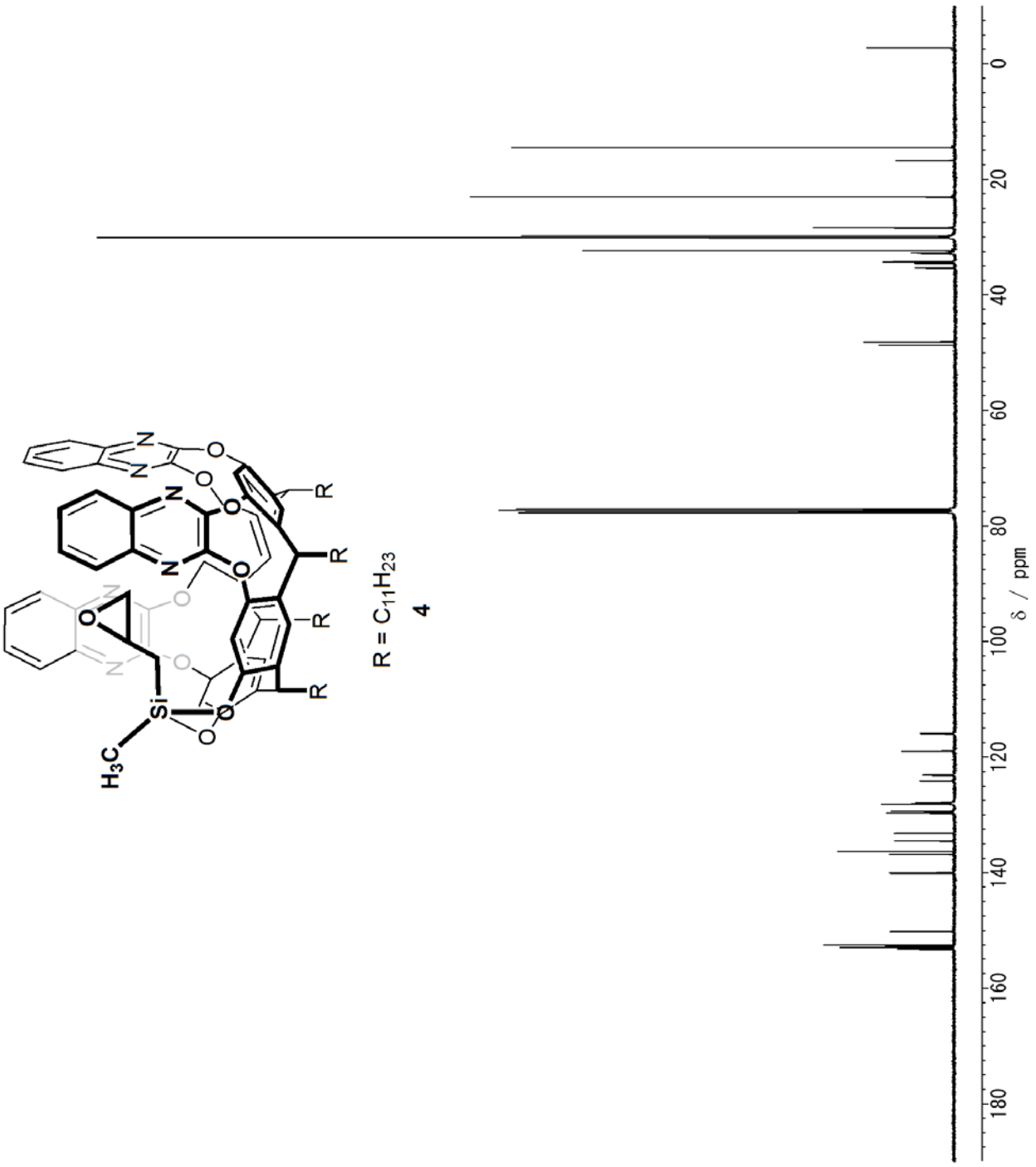
Compound 4

^{1}H NMR spectrum in toluene-d_8



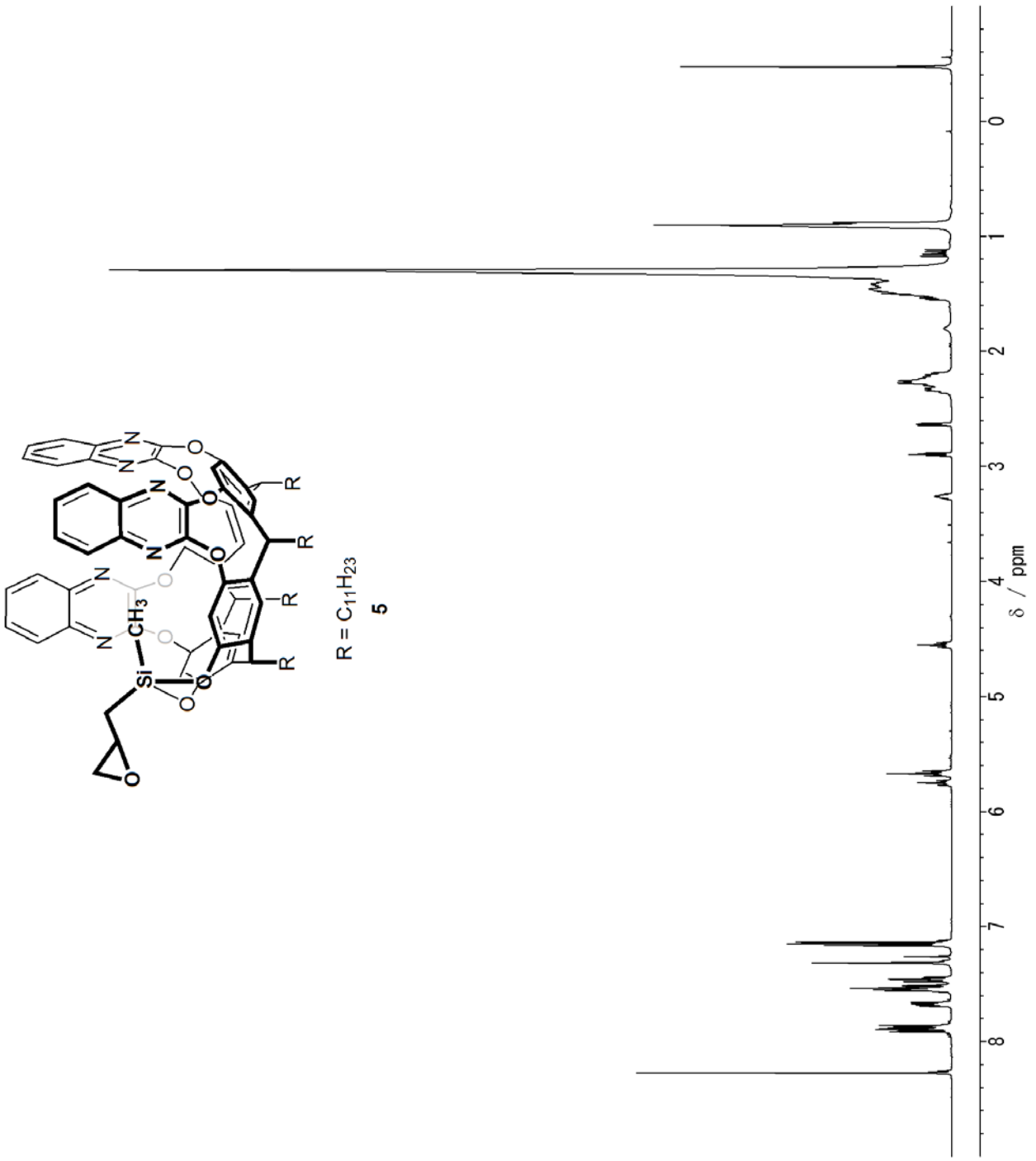
Compound 4

^{13}C NMR spectrum in $CDCl_3$



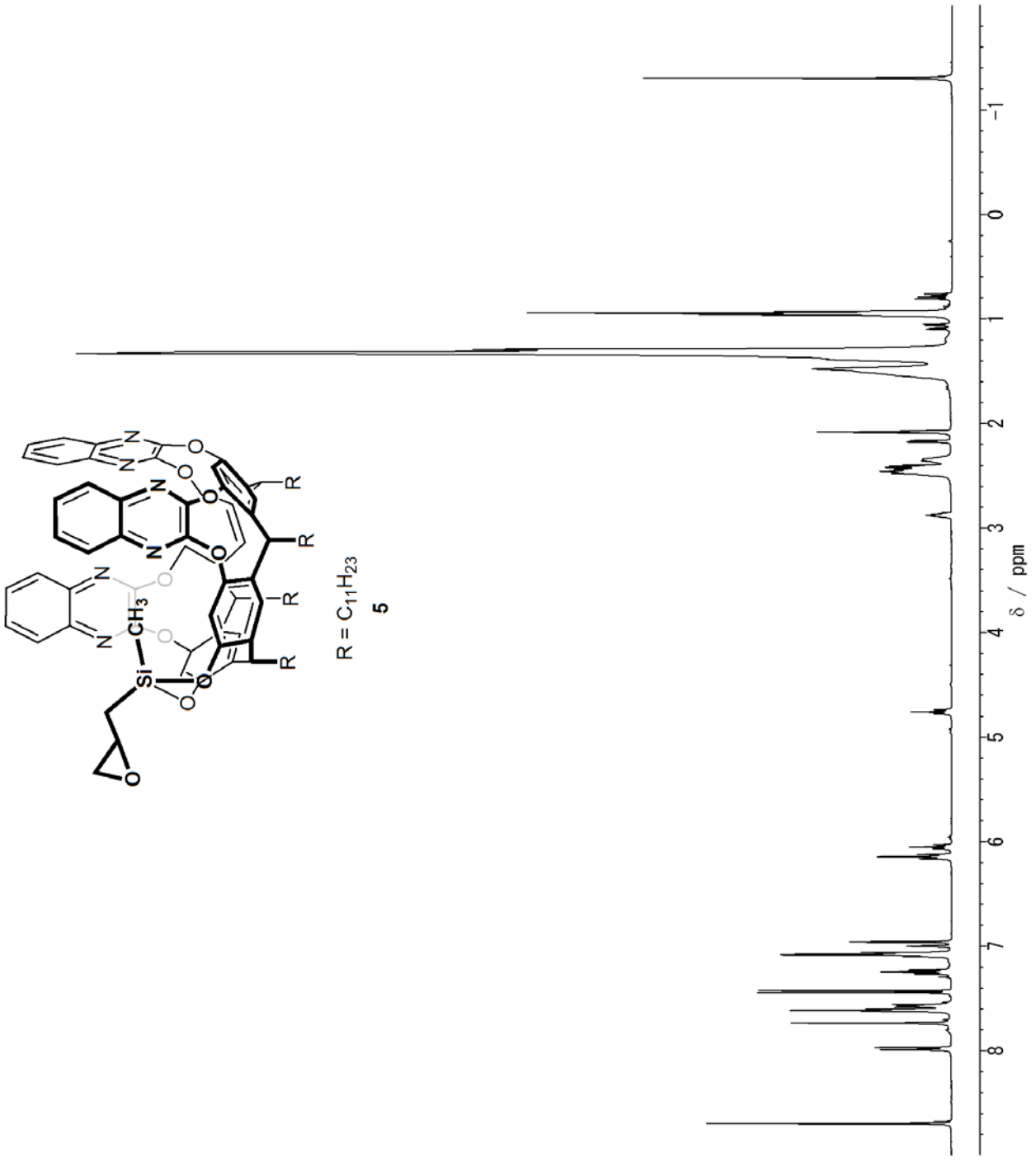
Compound 5

^{1}H NMR spectrum in $CDCl_3$



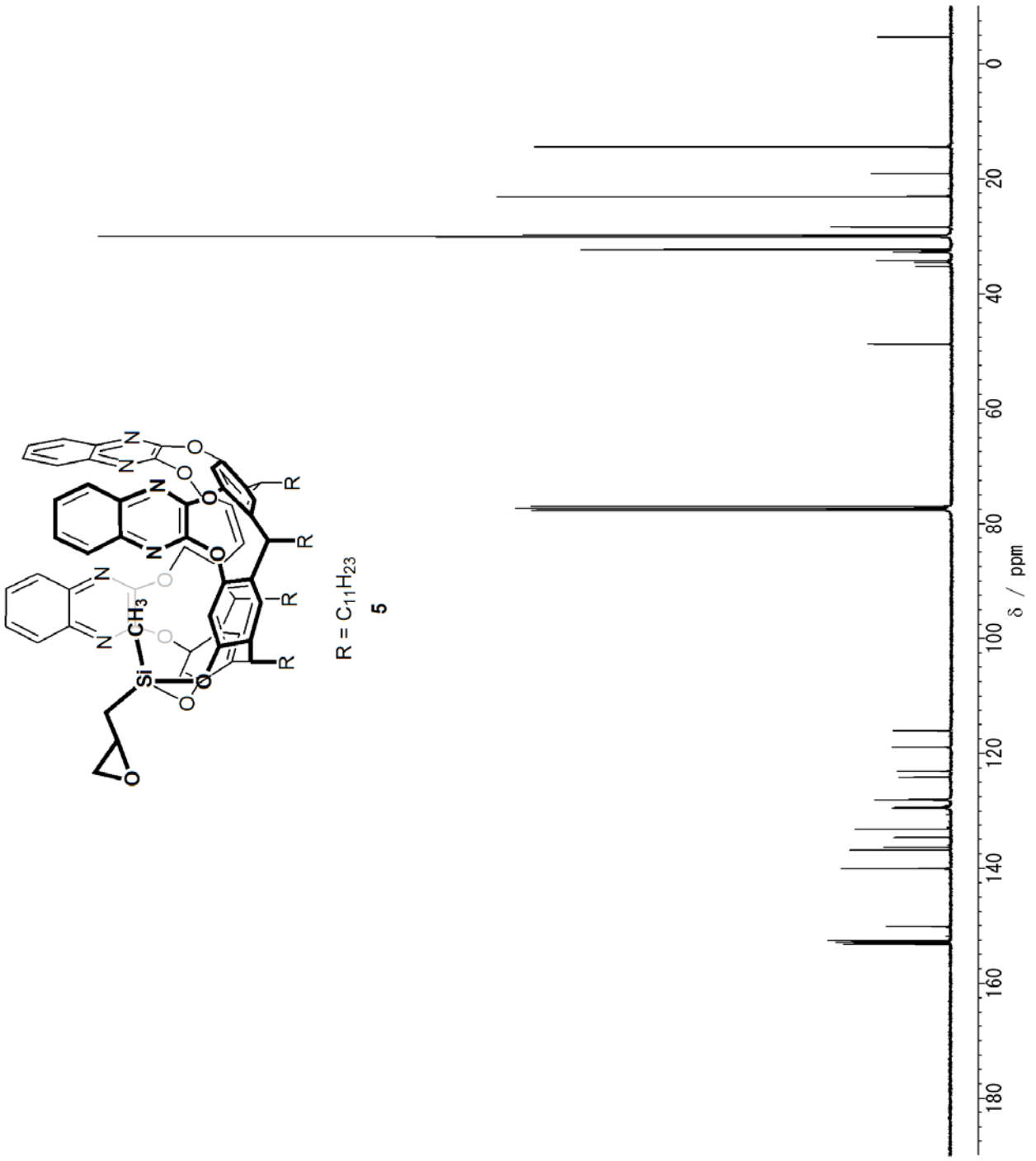
Compound 5

^{1}H NMR spectrum in toluene-d_8



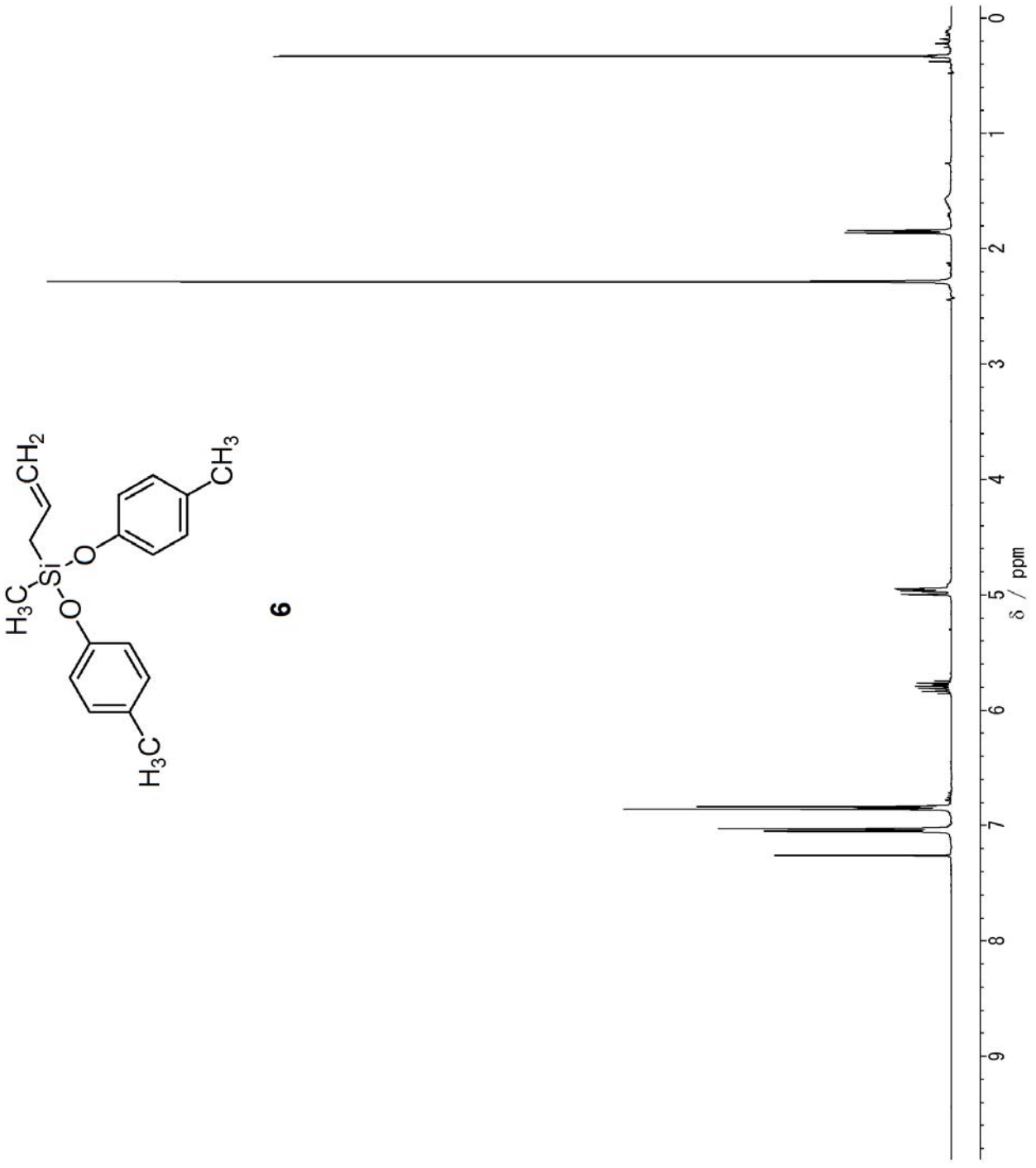
Compound 5

^{13}C NMR spectrum in $CDCl_3$



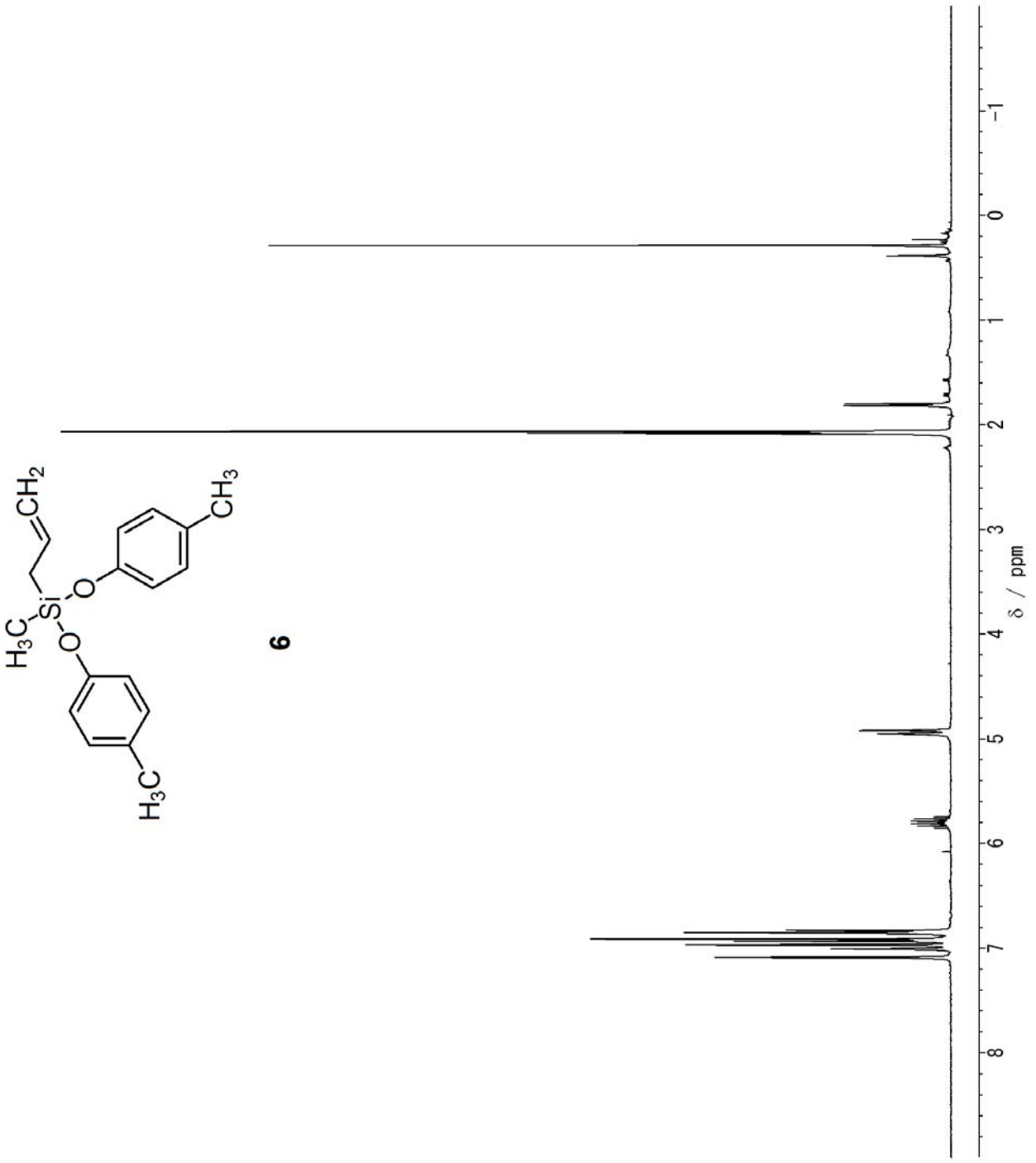
Compound 6

^{1}H NMR spectrum in $CDCl_3$



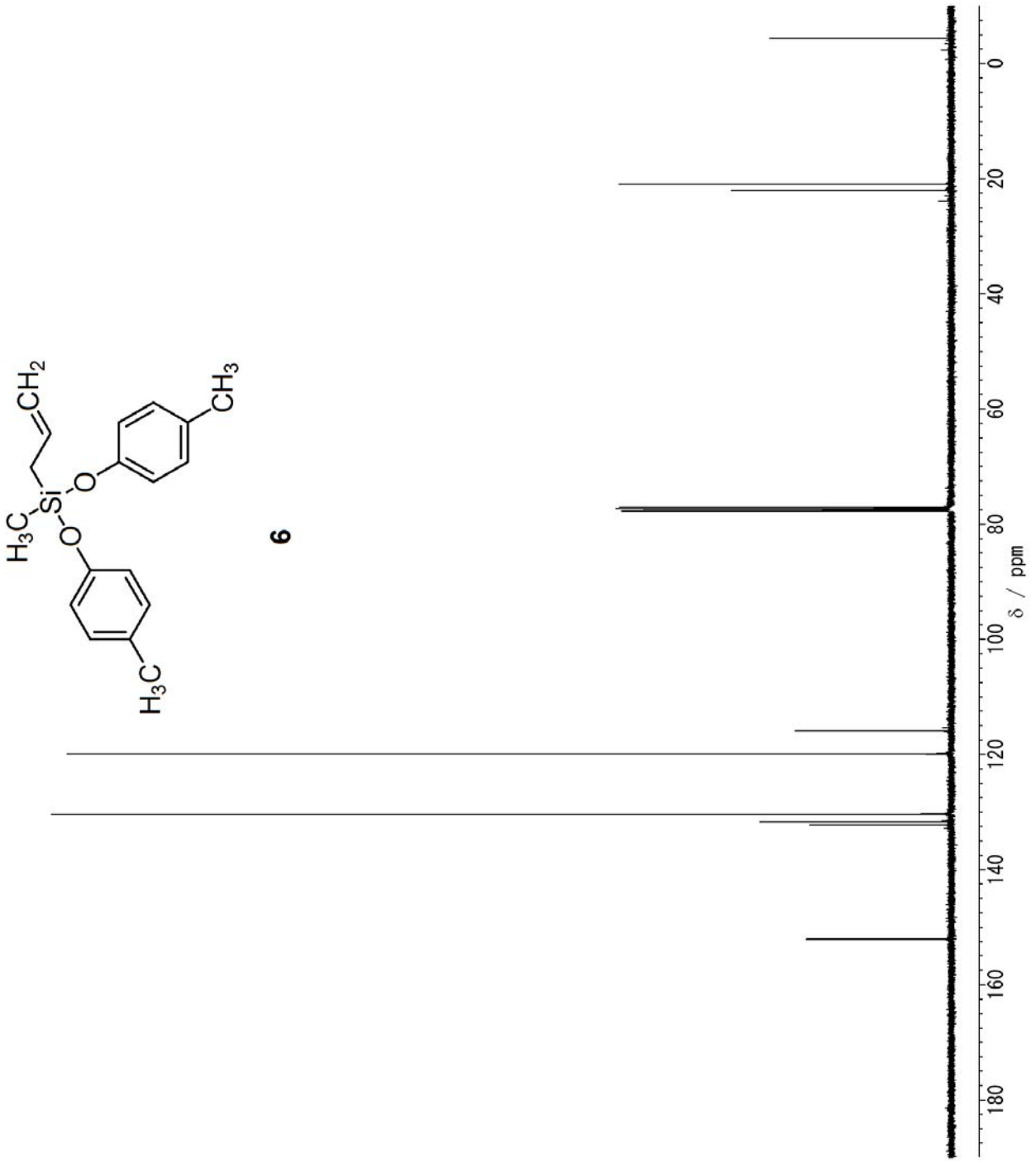
Compound 6

^{1}H NMR spectrum in toluene-d_8



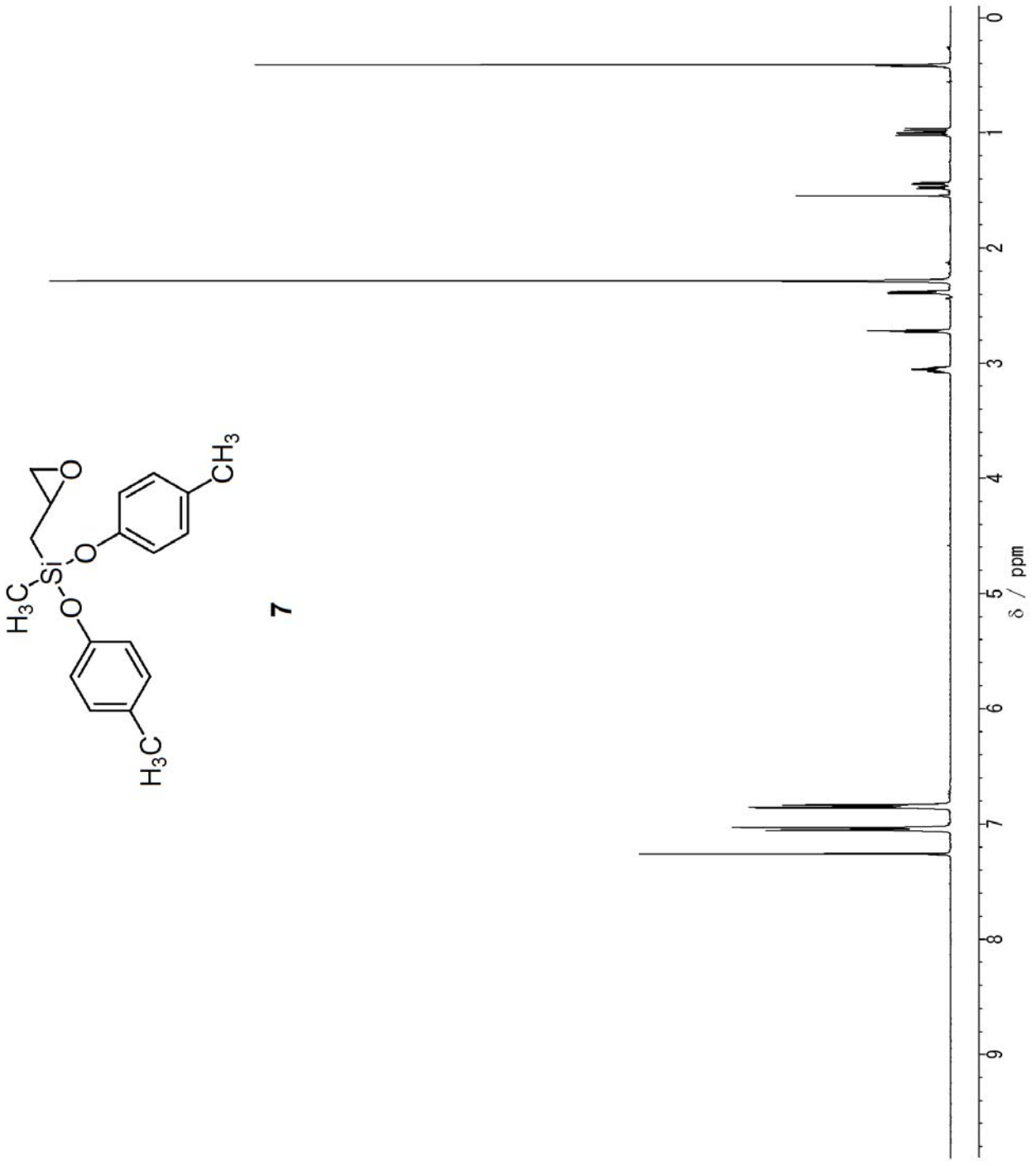
Compound 6

^{13}C NMR spectrum in $CDCl_3$



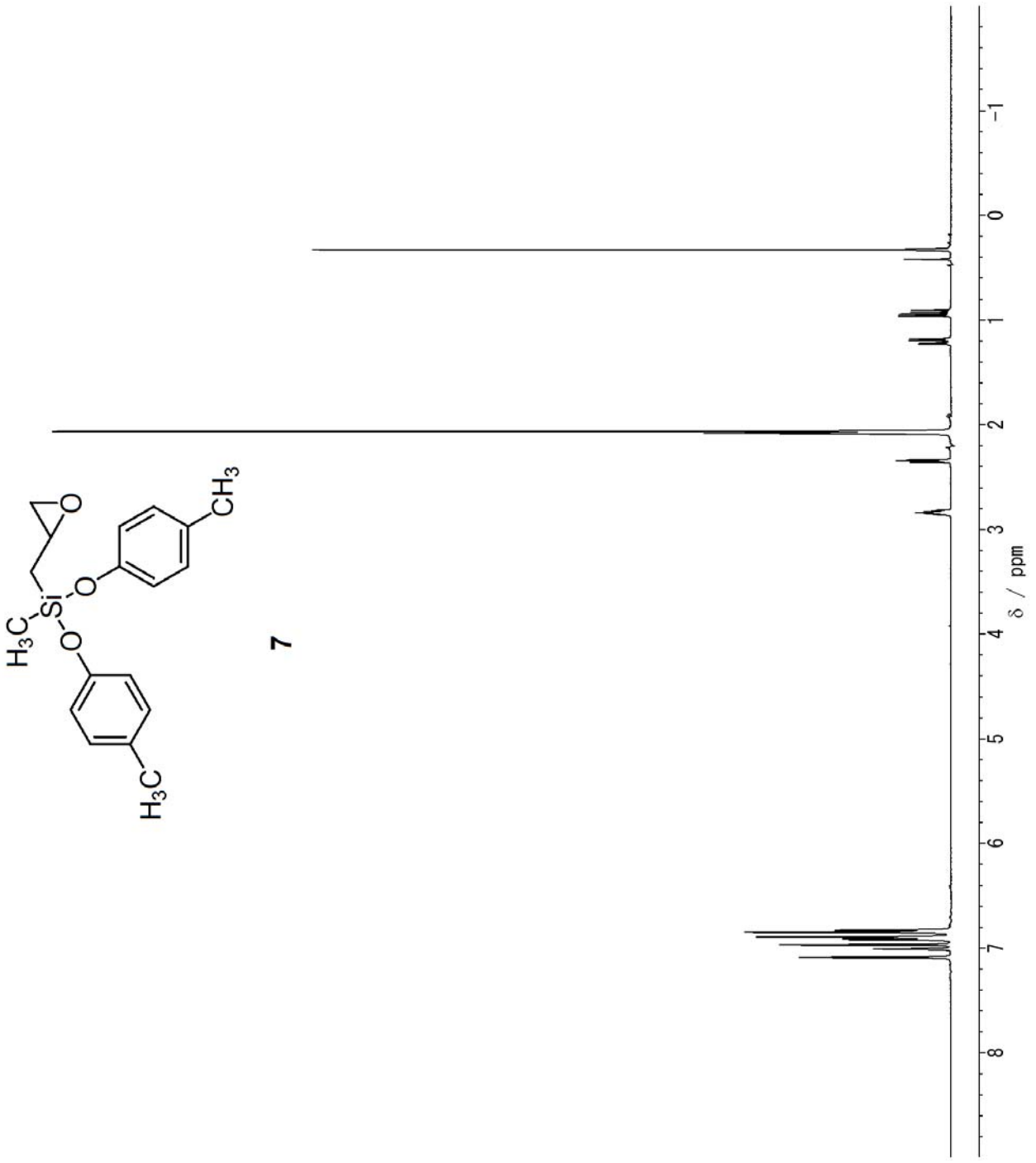
Compound 7

^{1}H NMR spectrum in $CDCl_3$



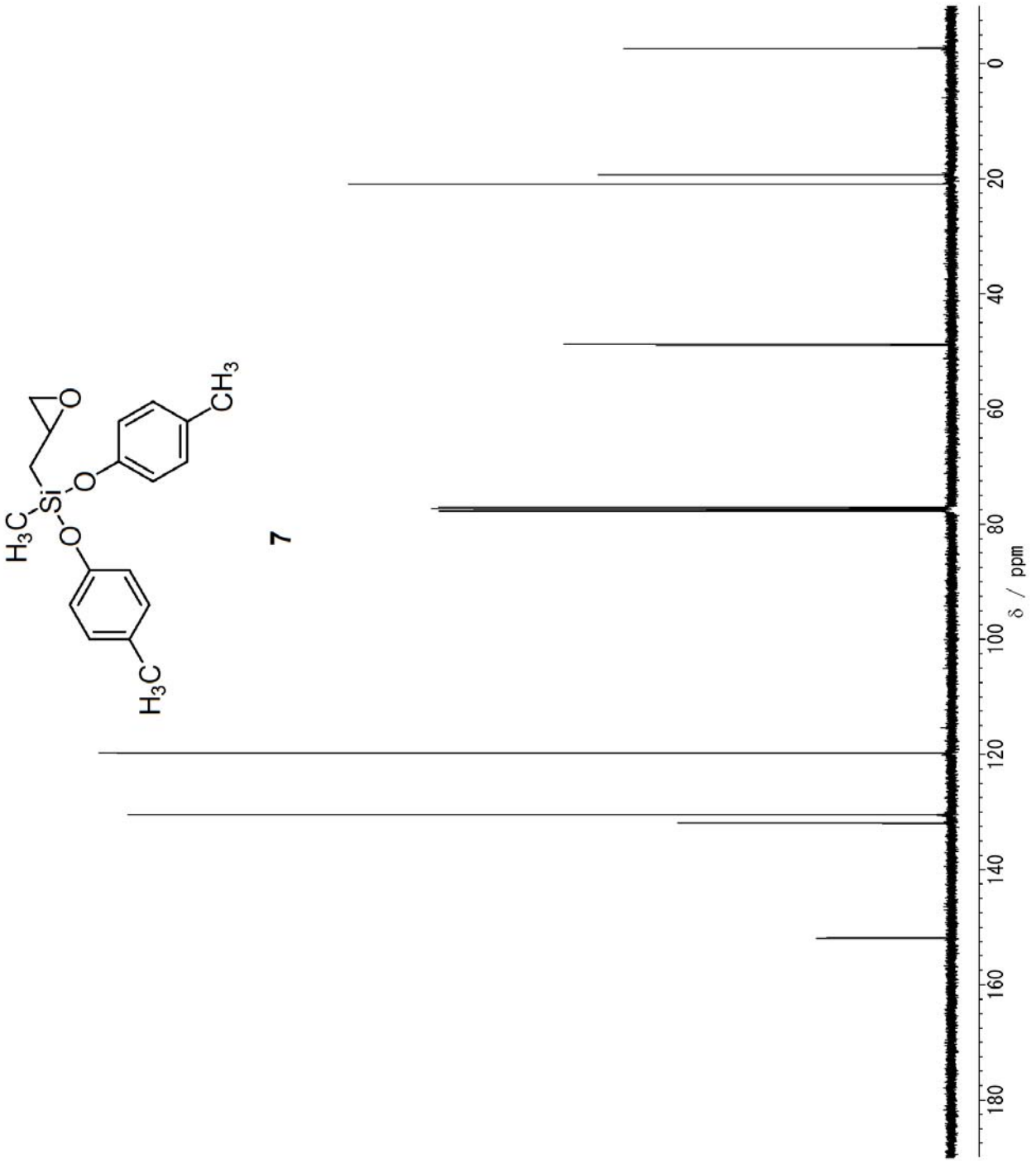
Compound 7

^{1}H NMR spectrum in toluene-d_8

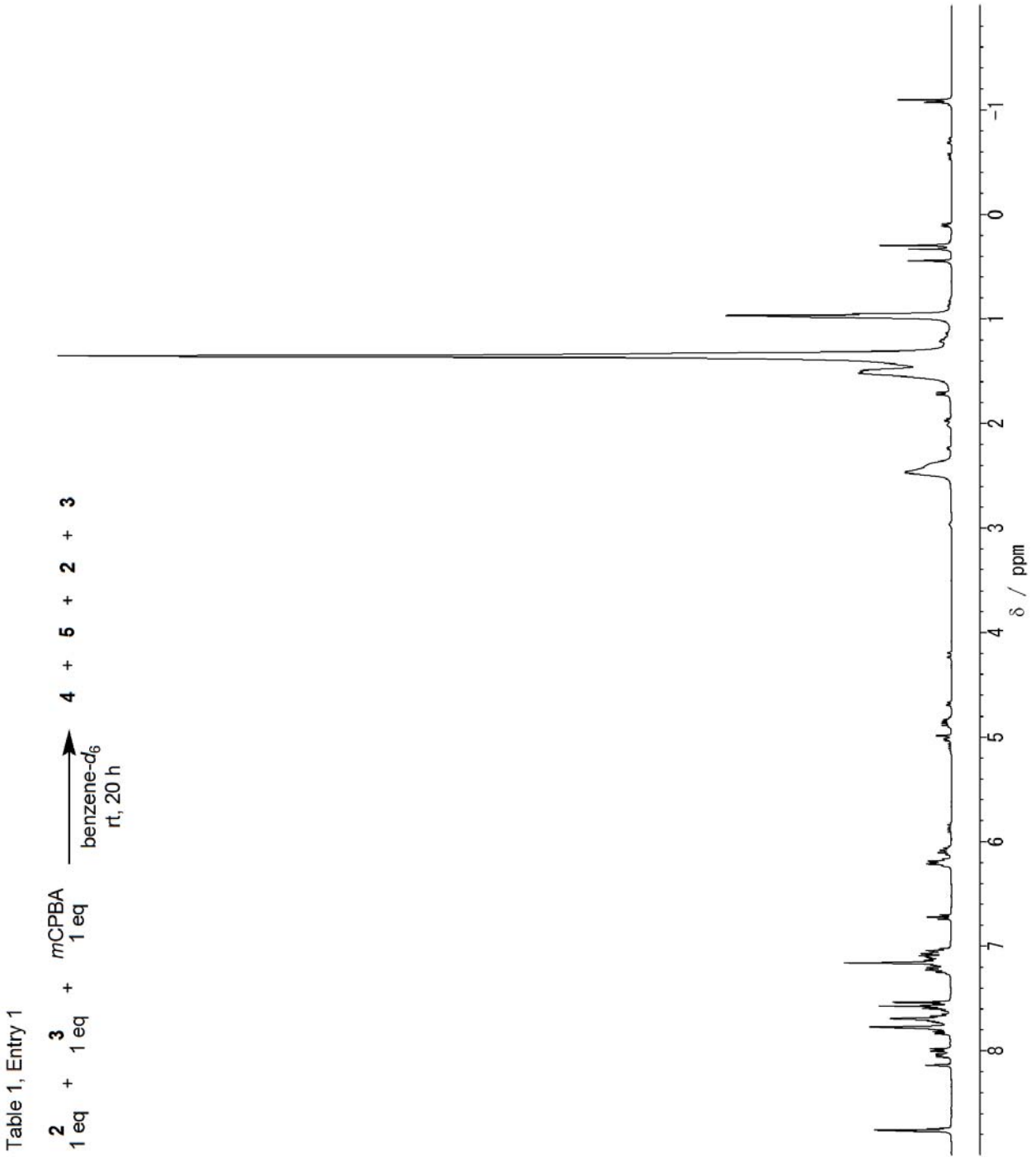


Compound 7

^{13}C NMR spectrum in $CDCl_3$



^{1}H NMR spectrum (Table 1, Entry 1)



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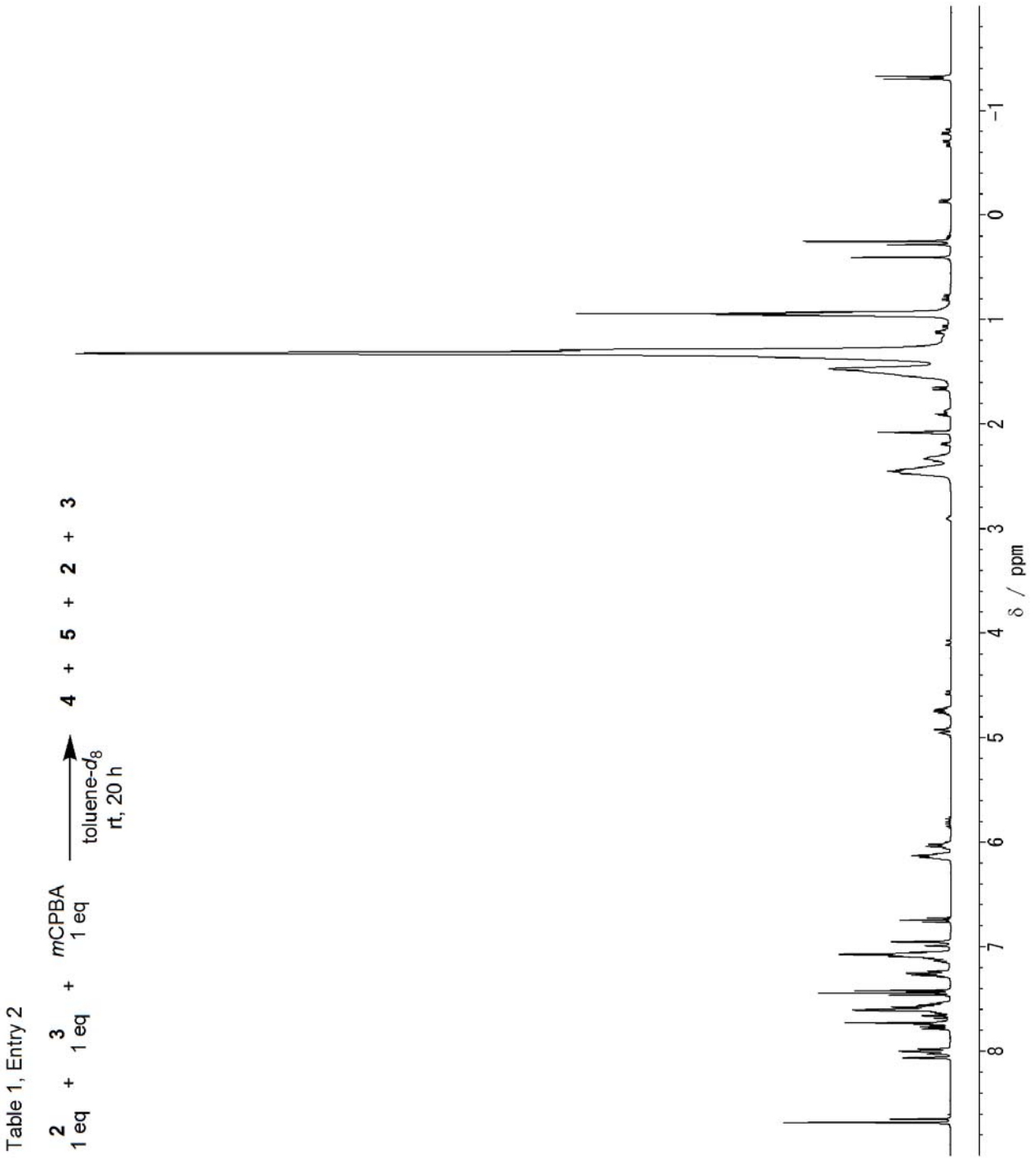

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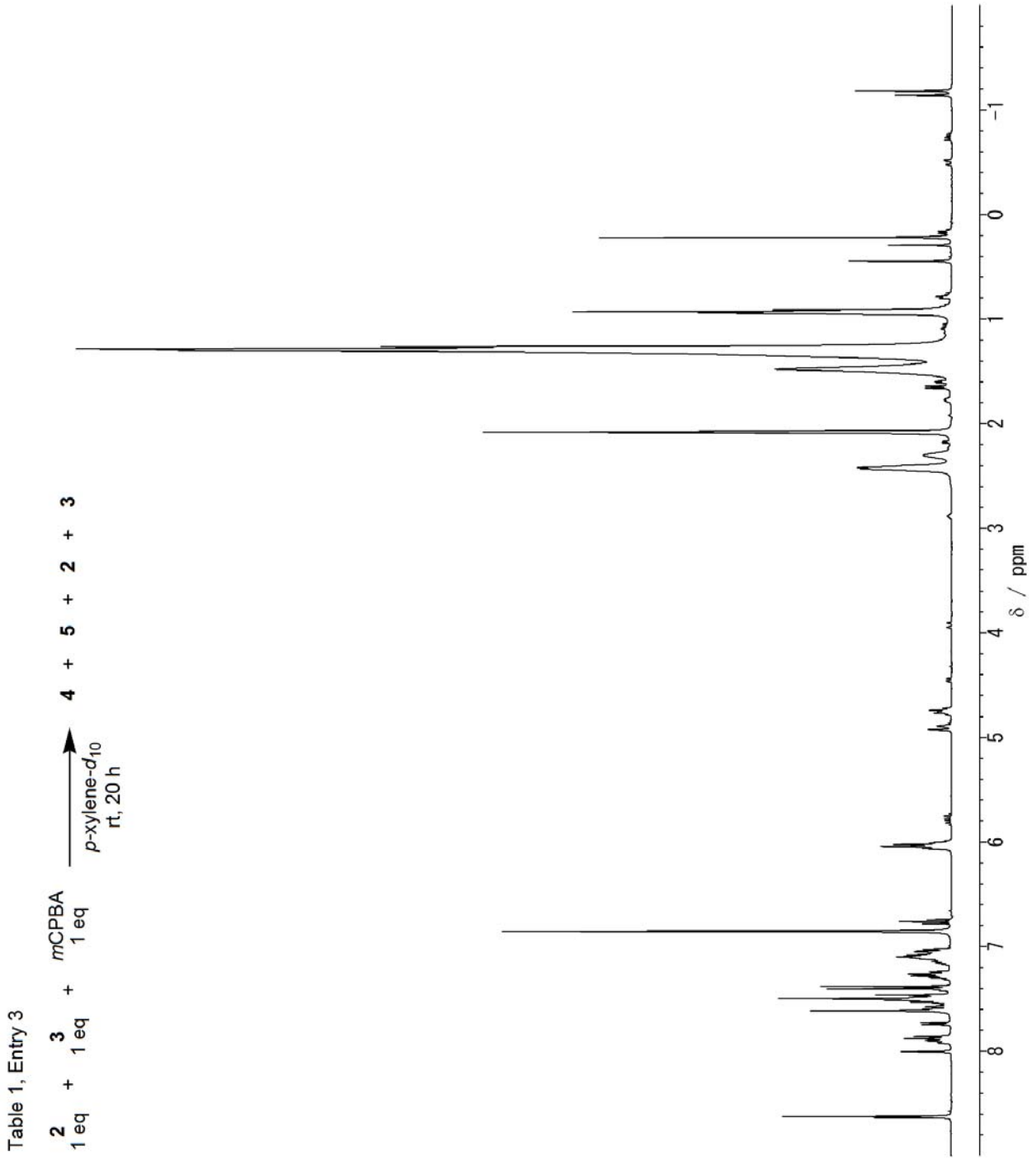

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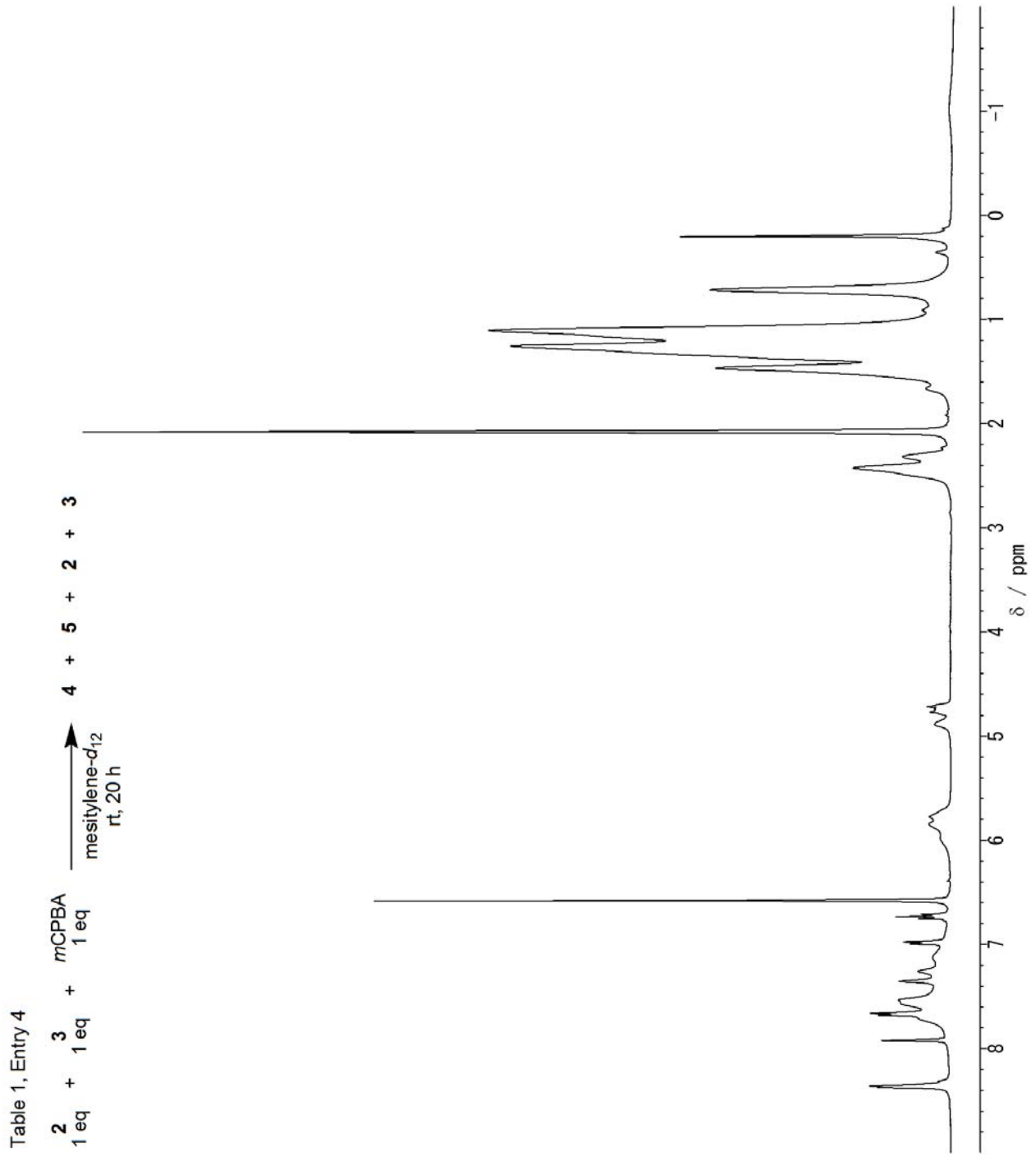

^{1}H NMR spectrum (Table 2)