Supporting Information

(*Tetrahedron. Lett.*)

Cavitands with Inwardly and Outwardly Directed Functional Groups

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Contents

a) **General Information**: All reactions sensitive to air or moisture were carried out under an argon atmosphere and anhydrous conditions unless otherwise noted. Dry solvents were purchased and used without further purification and dehydration. All reagents were purchased and used without further purification. Analytical thin layer chromatography was carried out on Merck silica $60F_{254}$. Column chromatography was carried out with silica gel 60 $_{N}$ (Kanto Chemical Co.). HRMS were reported on the basis of TOF (time of flight), and EB

(double-focusing) techniques. ^{1}H and ^{13}C NMR spectra were recorded with a 5 mm QNP probe at 400 MHz and 100 MHz, respectively. Chemical shifts are reported on the basis of residual protonated-solvent signals [^{1}H NMR: $CHCl_3$ (7.26), C_7H_8 (2.08), C_6H_6 (7.16); ^{13}C NMR: $CDCl_3$ (77.0)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br., broad.

b) **Synthesis of pyridine 2, for Scheme 2.** Under N_2 atmosphere, to the two-necked flask charged with 2-(dibromomethyl)pyridine[1] (474 mg, 1.9 mmol) and *N*,*N*-Dimethylacetamide was added **1** (2.67 g, 1.8 mmol) and K_2CO_3 (995 mg, 7.2 mmol). Immediately, the flask was soaked into pre-heated oil bath (80 °C). After overnight stirring, the reaction mixture was allowed to cool to room temperature, and filtered through a pad of celite, and washed with toluene. The organic phases were washed with water and brine, and concentrated in *vacuo* to give crude products. Purification by silica gel column chromatography two times (first, CH_2Cl_2/toluene = 4/1; second, hexane/EtOAc = 4/1) afforded the target **2** of 877 mg in 31% yield as yellowish white solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) 8.67 (d, *J* = 4.2 Hz, 1H), 8.28 (s, 2H), 7.91 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.85 (dd, *J* = 6.4, 3.4 Hz, 2H), 7.82-7.80 (m, 1H), 7.66 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.65-7.63 (m, 1H), 7.54-7.51 (m, 4H), 7.44 (dd, *J* = 8.2, 7.1 Hz, 2H), 7.35 (s, 2H), 7.36-7.33 (m, 1H), 7.25 (s, 2H), 7.23 (s, 2H), 5.71-5.67 (m, 3H), 5.03 (s, 1H), 4.90 (t, *J* = 8.0 Hz, 1H), 2.28 (m, 8H), 1.46-1.29 (m, 72H), 0.91-0.88 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 157.1, 155.0, 153.2, 153.0, 152.95, 152.89, 152.85, 152.4, 149.6, 140.1, 140.05, 140.00, 139.0, 137.2, 136.5, 136.2, 135.9, 129.6, 129.4, 129.3, 128.13, 128.10, 124.1, 121.9, 120.8, 119.1, 117.9, 107.3, 36.8, 34.6, 34.5, 32.7, 32.5, 32.32, 32.30, 30.7, 30.3, 30.18, 30.16, 30.10 (many peaks are overlapped), 28.38, 28.32, 23.05 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm. MS (MALDI-TOF) *m/z*: 1573 ($[MH]^+$). IR (neat): 2931, 2852, 1577, 1481, 1414, 1329, 1159 cm^{-1}. Anal. Calcd for $C_{102}H_{121}N_7O_8$: C, 77.88; H, 7.75; N, 6.23. Found: C, 77.75; H, 7.69; N, 6.15.

c) **Synthesis of pyridine *N*-oxide 3, for Scheme 2.** Under N_2 atmosphere, to the solution of **2** (315 mg, 0.2 mmol) in anhydrous CH_2Cl_2 (2 mL) at 0 °C was added mCPBA (55 mg, 0.22 mmol), and the mixture at 0 °C was stirred for 1 h. After additional stirring at room temperature for 4 h, the reaction was quenched at 0 °C with saturated aqueous sodium thiosulfate (2 mL), and stirred for 10 min, and warmed to ambient temperature. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were washed with brine, and concentrated in *vacuo* to give crude products. Purification by silica gel column chromatography (toluene/EtOAc = 4/1) and the following reprecipitation ($CHCl_3$/CH_3OH = 1/8) afforded the target **3** of 241 mg in 76% yield as yellowish white solid materials.

^{1}H NMR (400 MHz, $CDCl_3$) 8.28 (s, 2H), 8.22 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.92 (dd, *J* = 7.6, 2.2 Hz, 1H), 7.91 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.81 (dd, *J* = 6.4, 3.4 Hz, 2H), 7.73 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.53-7.42 (m, 8H), 7.35 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.30 (ddd, *J* = 7.6, 6.4, 2.2 Hz, 1H), 7.24 (s, 2H), 7.20 (s, 2H), 5.70 (t, *J* = 8.0 Hz, 3H), 5.32 (s, 1H), 4.81 (t, *J* = 8.0 Hz, 1H), 2.36-2.26 (m, 8H), 1.45-1.29 (m, 72H), 0.91-0.87 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 154.6, 153.2, 153.03, 152.97, 152.9, 152.3, 148.2, 140.2, 140.1, 140.0, 138.4, 136.4, 136.2, 136.1, 129.7, 129.3, 129.22, 129.15, 128.3, 128.2, 128.1, 125.9, 125.0, 123.9, 121.8, 119.3, 118.2, 100.9, 36.8, 34.54, 34.50, 32.8, 32.5, 32.3 (many peaks are overlapped), 30.7, 30.3, 30.2, 30.12, 30.06 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.42, 28.38, 28.3, 23.0 (many peaks are overlapped), 14.4 (many peaks are overlapped) ppm. MS (MALDI-TOF) *m/z*: 1589 ($[MH]^+$). IR (neat): 2922, 2851, 1571, 1481, 1159, 756, 603 cm^{-1}. HRMS (MALDI-TOF, *m/z*, $[MH]^+$), Calcd for $C_{102}H_{122}N_7O_9$: 1588.9304. Found: 1588.9254.

d) **Synthesis of pyridine 4, for Figure 1.** Under N_2 atmosphere, to the flask charged with 2-(dibromomethyl)pyridine (376 mg, 1.5 mmol) and *N*,*N*-Dimethylacetamide was added phenol (423 mg, 4.5 mmol) and K_2CO_3 (746 mg, 5.4 mmol). After overnight stirring at 80 °C, the reaction mixture was filtered through a pad of celite, and washed with toluene. The organic phase was washed with water and 0.5 N aqueous NaOH, and brine. The mixture was dried over Na_2SO_4, and filtered, and concentrated in *vacuo* to give crude products. Purification by silica gel column chromatography (CH_2Cl_2/ hexane = 2/1) afforded **4** of 341 mg in 61% yield as yellow viscous materials. ^{1}H NMR (400 MHz, $CDCl_3$) 8.66 (d, *J* = 4.8 Hz, 1H), 7.79-7.77 (m, 2H), 7.32 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.27-7.24 (m, 4H) 7.04-7.00 (m, 6H), 6.74 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 156.8, 156.4, 149.3, 137.4, 129.8, 124.4, 122.8, 121.7, 117.4, 101.1 ppm. MS (FAB) *m/z*: 278 ($[MH]^+$). IR (neat): 3060, 2931, 1584, 1493, 1201, 1032, 983, 679 cm^{-1}. Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.03; H, 5.44; N, 4.88.

e) **Synthesis of pyridine *N*-oxide 5, for Figure 1.** Under N_2 atmosphere, to the solution of **4** (139 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (1 mL) at 0 °C was added mCPBA (138 mg, 0.55 mmol), and the mixture at 0 ºC was stirred for 1 h. After additional stirring at room temperature for 4 h, the reaction was quenched with saturated aqueous $Na_2S_2O_3$ (1.5 mL) at 0 °C. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo* to give crude products. Purification by silica gel column chromatography (toluene/EtOAc = 4/1) afforded

5 of 62 mg in 42% yield as yellowish white viscous materials. ^{1}H NMR (400 MHz, $CDCl_3$) 8.31-8.29 (m, 1H), 7.80-7.77 (m, 1H), 7.39 (s, 1H), 7.35-7.22 (m, 6H), 7.09-7.00 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 156.2, 147.5, 139.9, 129.9, 126.5, 126.1, 125.2, 123.4, 117.6, 94.7 ppm. IR (neat): 3053, 2925, 1590, 1498, 1432, 1201, 1013, 746 cm^{-1}. Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.67; H, 5.25; N, 4.90.

f) **Synthesis of 6, for Scheme 3.** Under an argon atmosphere, to the diol **1** (148 mg, 0.1 mmol) in a 20 mL Schlenk flask were added toluene (2 mL), and Et_3N (24 mg, 0.24 mmol). After stirring for 10 min, Ph_2SiCl_2 (51 mg, 0.11 mmol) was added, and the reaction was conducted for 2 h. The mixture was filtered, and washed with toluene, and then the filtrate was concentrated *in vacuo* to give crude products. Purification by short-plug column chromatography (CH_2Cl_2) and *N*,*N*-Dimethylacetamide was added phenol (423 mg, 4.5 mmol) and K_2CO_3 (746 mg, afforded white solid materials, which were reprecipitated from CH_3OH to give **6** as white powders of 147 mg in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) 8.25 (s, 2H), 7.91-7.86 (m, 5H), 7.82-7.80 (m, 2H), 7.75 (d, *J* = 6.4 Hz, 2H), 7.60-7.39 (m, 14H), 7.16 (s, 2H), 6.66-6.64 (m, 3H), 5.72 (t, *J* = 8.2 Hz, 1H), 5.65 (t, *J* = 8.2 Hz, 2H), 4.69 (t, *J* = 8.2 Hz, 1H), 2.32-2.18 (m, 8H), 1.51-1.23 (m, 72H), 0.92-0.88 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 153.2, 153.0, 152.7, 152.6, 152.4, 152.3, 150.0, 140.1, 140.0, 139.9, 136.5, 136.2, 134.7, 134.4 (2 peaks are overlapped), 133.6, 132.8, 132.2, 131.2, 130.5, 130.1, 129.2 (2 peaks are overlapped), 129.0, 128.2 (2 peaks are overlapped), 128.1-127.9 (many peaks are overlapped), 123.4, 123.1, 118.8, 116.0, 35.2, 34.3, 34.1, 32.9, 32.8, 32.4, 32.2 (many peaks are overlapped), 30.0 (many peaks are overlapped), 29.6 (many peaks are overlapped), 28.3, 23.0, 14.4 ppm. ESI-MS *m/z*: 1663 ([MH]$^+$). Anal. Calcd for $C_{108}H_{126}N_6O_8Si$: C, 77.94; H, 7.63; N, 5.05. Found: C, 77.82; H, 7.78; N, 4.91.

g) **Synthesis of 7a-e and 8a-e, for Table 2.** Under an argon atmosphere, a two-necked flask was charged with **1** (148 mg, 1 mmol), Et_3N (2.4 equiv), and anhydrous toluene. The appropriate reagents of $Cl_2Si(CH_3)R$ (3 equiv) was then added. After stirring at ambient temperature for 2 h, the reaction mixture was filtered through a pad of cotton and concentrated *in vacuo* to give the crude products as white solid materials. Purification by silica gel column chromatography (hexane/EtOAc) yielded **7** and **8** as a white solid material, respectively. The isomers **7a** and **8a** were not isolated while ^{1}H NMR spectrum indicates 48% yield for **7a** and 52% yield for **8a**. For **7b** and **8b**, the data are reported previously.[2]

Data for 7c: 32% yield, white solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) 8.25 (s, 2H), 7.89-7.85 (m, 4H), 7.68 (dd, *J* = 8.3Hz, 1.4 Hz, 2H), 7.58-7.44 (m, 6H), 7.31 (s, 2H), 7.14 (s, 4H), 5.75 (t, *J* = 8.1 Hz, 1H), 5.66 (t, *J* = 8.2 Hz, 2H), 4.51 (t, *J* = 8.0 Hz, 1H), 2.71 (t, *J* = 7.0 Hz, 2H), 2.33-2.18 (m, 8H), 1.55-1.28 (m, 74H), 0.91-0.87 (m, 12H), 0.48 (s, 3H), 0.02 (t, *J* = 8.4 Hz, 2H) ppm; ^{1}H NMR (400 MHz, toluene–d_8) 8.66 (s, 2H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.74-7.72 (m, 4H), 7.65-7.62 (m, 4H), 7.43 (s, 2H), 7.24 (ddd, *J* = 7.7 Hz, 7.7 Hz, 1.4 Hz, 2H, H_2 or *H*), 7.17-7.12 (m, 4H), 6.15 (t, *J* = 8.2 Hz, 2H), 6.04 (t, *J* = 8.2 Hz, 1H), 4.77 (t, *J* = 7.8 Hz, 1H), 2.47-2.36 (m, 8H,), 1.93 (t, *J* = 7.2 Hz, 2H), 1.51-1.34 (m, 72H), 1.07-0.94 (m, 14H), 0.25 (s, 3H), -0.84 (t, *J* = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 153.3, 153.2, 153.0, 152.9, 152.7, 152.5, 150.3, 140.11, 140.07 (two peaks are overlapped), 136.9, 136.3, 134.6, 132.9, 129.73, 129.68, 129.4, 128.2, 128.1, 128.0, 124.3, 123.1, 119.0, 115.9, 46.9, 35.4, 34.6, 34.3, 32.9, 32.8, 32.7, 32.3 (many peaks are overlapped), 30.19 (many peaks are overlapped), 30.16 (many peaks are overlapped), 30.1 (many peaks are overlapped), 29.82 (many peaks are overlapped), 29.80 (many peaks are overlapped), 28.4, 26.2, 23.1, 14.5, 9.8, -4.0. MS (MALDI-TOF) *m/z*: 1602 ($[MH]^+$). IR (neat) 2920, 2850, 1570, 1481, 1404, 1331, 1153 cm^{-1}. Anal. Calcd for $C_{18}H_{15}NO_2$: $C_{100}H_{125}ClN_6O_8Si$: C, 74.94; H, 7.86; N, 5.24. Found: C, 74.97; H, 7.71; N, 5.20.

Data for 8c: 34% yield, white solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) 8.25 (s, 2H), 7.90-7.84 (m, 4H), 7.66 (dd, *J* = 7.5 Hz), 7.54-7.43 (m, 6H), 7.30 (s, 2H), 7.14 (s, 2H), 7.10 (s, 2H), 5.73 (t, *J* = 8.2 Hz, 1H), 5.65 (t, *J* = 8.2 Hz, 2H), 4.52 (t, *J* = 7.9 Hz, 1H), 3.64 (t, *J* = 6.7 Hz, 2H), 2.32-2.18 (m, 8H), 2.08 (tt, *J* = 8.2 Hz, 6.7 Hz, 2H), 1.44-1.28 (m, 72H), 1.05 (t, *J* = 8.2 Hz, 2H), 0.91-0.87 (m, 12H), -0.57 (s, 3H) ppm; ^{1}H NMR (400 MHz, toluene–d_8) 8.73 (s, 3H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.75 (s, 2H), 7.65-7.63 (m, 4H), 7.59-7.56 (m, 2H), 7.44 (s, 2H), 7.25 (ddd, *J* = 8.4 Hz, 8.4 Hz, 1.4 Hz, 2H), 7.09-7.02 (m, 4H), 6.17 (t, *J* = 8.1 Hz, 2H), 6.07 (t, *J* = 8.3 Hz, 1H), 4.75 (t, *J* = 7.7 Hz, 1H), 3.12 (t, *J* = 6.8 Hz, 2H), 2.49-2.37 (m, 8H), 1.69 (tt, *J* = 8.4 Hz, 6.8 Hz, 2H), 1.49-1.31 (m, 72H), 0.97-0.94 (m, 12H), 0.59 (t, *J* = 8.4 Hz, 2H), -1.41 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 153.3, 153.2, 153.0, 152.9, 152.7, 152.6, 150.3, 140.13, 140.11, 140.1, 136.9, 136.3, 134.7, 133.0, 129.6, 129.5, 129.3, 128.2 (two peaks are overlapped), 127.9, 124.2, 123.1, 119.0, 116.1, 47.6, 35.3, 34.6, 34.3, 32.9, 32.8, 32.6, 32.3 (many peaks are overlapped), 30.2 (many peaks are overlapped), 30.12 (many peaks are overlapped), 30.11 (many peaks are overlapped), 29.80 (many peaks are overlapped), 29.79 (many peaks are overlapped), 28.4, 26.3, 23.1 (many peaks are overlapped), 14.5 (many peaks are overlapped), 12.0, -5.5 ppm. MS (MALDI-TOF) *m/z*: 1602 ($[MH]^+$). IR (neat) 2920, 2850, 1481, 1408, 1331, 1153 cm^{-1}. Anal. Calcd for $C_{100}H_{125}ClN_6O_8Si$: C, 74.94; H, 7.86; N, 5.24. Found: C, 74.79; H, 7.93; N, 5.15.

Data for 7d: 34% yield, white solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) 8.25 (s, 2H), 7.88 (dd, *J* = 7.7, 1.0 Hz, 2H), 7.85 (dd, *J* = 6.4, 3.4 Hz, 2H), 7.65 (dd, *J* = 7.7, 1.0 Hz, 2H), 7.55 (dd, *J* = 6.4, 3.4 Hz, 2H), 7.52 (ddd, *J* = 7.7, 7.7, 1.0 Hz, 2H), 7.44 (ddd, *J* = 7.7, 7.7, 1.0 Hz, 2H), 7.30 (s, 2H), 7.14 (s, 2H), 7.13 (s, 2H), 5.74 (t, *J* = 8.1 Hz, 1H), 5.65 (t, *J* = 8.1 Hz, 2H), 4.51 (t, *J* = 8.1 Hz, 1H), 3.42 (t, *J* = 6.8 Hz, 2H), 2.32-2.18 (m, 8H), 1.90 (s, 3H), 1.56-1.28 (m, 74H), 0.91-0.87 (m, 12H), 0.48 (s, 3H), -0.05 (t, *J* = 8.4 Hz, 2H); ^{1}H NMR (400 MHz, toluene–d_8) 8.67 (s, 2H), 7.97 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.73 (s, 2H, *H*), 7.70 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.63 (s, 2H), 7.63-7.61 (m, 2H), 7.44 (s, 2H), 7.24 (ddd, *J* = 7.7, 7.7, 1.3 Hz, 2H), 7.15 (ddd, *J* = 7.7, 7.7, 1.3 Hz, 2H), 7.12-7.09 (m, 2H), 6.15 (t, *J* = 8.3 Hz, 2H), 6.04 (t, *J* = 7.8 Hz, 1H), 4.79 (t, *J* = 7.8 Hz, 1H), 2.84 (t, *J* = 7.0 Hz, 2H), 2.45-2.36 (m, 8H), 1.65 (s, 3H), 1.47-1.33 (m, 72H), 0.96-0.93 (m, 12H), 0.90 (tt, *J* = 8.3, 7.0 Hz, 2H), 0.29 (s, 3H), -0.88 (t, *J* = 8.3 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 171.0, 153.3, 153.2, 152.94, 152.92, 152.7, 152.5, 150.3, 140.11, 140.06 (two peaks are overlapped), 136.9, 136.3, 134.5, 132.9, 129.69, 129.66, 129.4, 128.1 (two peaks are overlapped), 127.8, 124.2, 123.1, 119.0, 115.9, 66.2, 35.3, 34.6, 34.3, 32.9, 32.8, 32.6, 32.3 (many peaks are overlapped), 30.2 (many peaks are overlapped), 30.1 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.41 (many peaks are overlapped), 28.38 (many peaks are overlapped), 23.1 (many peaks are overlapped), 21.7, 21.2, 14.5 (many peaks are overlapped), 8.3, -3.7 ppm. MS (MALDI-TOF) *m/z*: 1626 ($[MH]^+$). IR (neat) 2922, 2851, 1742, 1482, 1402, 1331, 1559 cm^{-1}. Anal. Calcd for $C_{102}H_{128}N_6O_{10}Si$: C, 75.33; H, 7.93; N, 5.17. Found: C, 75.14; H, 7.80; N, 5.28.

Data for 8d: 33% yield, white solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) 8.25 (s, 2H), 7.89 (dd, *J* = 7.6, 1.0 Hz, 2H), 7.85 (dd, *J* = 6.3, 3.4 Hz, 2H), 7.66 (dd, *J* = 7.6, 1.0 Hz, 2H), 7.54-7.50 (m, 4H), 7.45 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 2H), 7.30 (s, 2H), 7.14 (s, 2H), 7.10 (s, 2H), 5.73 (t, *J* = 8.1 Hz, 1H), 5.65 (t, *J* = 8.1 Hz, 2H), 4.53 (t, *J* = 8.0 Hz, 1H), 4.14 (t, *J* = 6.8 Hz, 2H), 2.32-2.18 (m, 8H), 2.10 (s, 3H), 1.92 (tt, *J* = 8.0, 6.8 Hz, 2H), 1.57-1.28 (m, 72H), 0.94 (t, *J* = 8.0 Hz, 2H), 0.91-0.87 (m, 12H), -0.58 (s, 3H); ^{1}H NMR (400 MHz, toluene–d_8) 8.72 (s, 2H), 7.98 (dd, *J* = 7.7, 0.9 Hz, 2H), 7.75 (s, 2H), 7.64-7.62 (m, 2H), 7.62 (s, 2H), 7.56 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.44 (s, 2H), 7.23 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 2H), 7.09-7.05 (m, 4H), 6.16 (t, *J* = 8.2 Hz, 2H), 6.06 (t, *J* = 8.2 Hz, 1H), 4.77 (t, *J* = 8.0 Hz, 1H), 3.92 (t, *J* = 6.9 Hz, 2H), 2.48-2.36 (m, 8H), 1.67 (s, 3H), 1.66 (tt, *J* = 8.2, 6.9 Hz, 2H), 1.56-1.30 (m, 72H), 0.96-0.93 (m, 12H), 0.57 (t, *J* = 8.2 Hz) , -1.41 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 171.5, 153.3, 153.2, 153.0, 152.9, 152.7, 152.6, 150.3, 140.12, 140.10 , 140.0, 136.9, 136.3, 134.7, 132.9, 129.6, 129.5, 129.3, 128.2, 128.1, 127.9, 124.2, 123.1, 119.0, 116.0, 66.7, 35.3, 34.6, 34.3, 32.9, 32.8, 32.6, 32.3 (many peaks are overlapped), 30.1 (many peaks are

overlapped), 29.77, 29.76 (many peaks are overlapped), 28.41 (many peaks are overlapped), 28.38 (many peaks are overlapped), 23.0 (many peaks are overlapped), 22.1, 21.4, 14.5 (many peaks are overlapped), 10.5, -5.5 ppm. MS (MALDI-TOF) *m/z*: 1626 ($[MH]^+$). IR (neat) 2921, 2850, 1740, 1483, 1414, 1332, 1158 cm^{-1}. Anal. Calcd for $C_{102}H_{128}N_6O_{10}Si$: C, 75.33; H, 7.93; N, 5.17. Found: C, 75.36; H, 7.94; N, 5.34.

Data for 7e: 22% yield, white solid materials. ^1H NMR (400 MHz, $CDCl_3$) 8.27 (s, 2H), 7.90 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.87 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.70 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.58 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.55 (ddd, *J* = 8.1, 8.1, 1.4 Hz, 2H), 7.55 (ddd, *J* = 8.1, 8.1, 1.4 Hz, 2H), 7.32 (s, 2H), 7.15 (s, 2H), 7.13 (s, 2H), 5.76 (t, *J* = 8.1 Hz, 1H), 5.67 (t, *J* = 8.2 Hz, 2H), 4.50 (t, *J* = 8.0 Hz, 1H), 2.34-2.18 (m, 8H), 1.44-1.29 (m, 76H), 0.91-0.88 (m, 12H), 0.50 (s, 3H), 0.05 (t, *J* = 8.5 Hz, 2H); ^1H NMR (400 MHz, toluene–d_8) 8.66 (s, 2H), 8.00-7.98 (m, 2H), 7.79-7.76 (m, 2H), 7.71 (s, 2H), 7.63 (dd, *J* = 6.3, 3.5 Hz, 2H), 7.61 (s, 2H), 7.40 (s, 2H), 7.29-7.23 (m, 4H), 7.14 (dd, *J* = 6.3, 3.5 Hz, 2H), 6.15 (t, *J* = 8.2 Hz, 2H), 6.03 (t, *J* = 8.1, 1H), 4.76 (t, *J* = 8.0 Hz, 1H), 2.47-2.35 (m, 8H), 1.50-1.33 (m, 72H), 0.98-0.94 (m, 12H), 0.70 (tt, *J* = 8.6, 7.5 Hz, 2H), 0.20 (t, *J* = 7.5 Hz, 2H), 0.19 (s, 3H), -0.92 (t, *J* = 8.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 153.3, 153.1, 152.9, 152.8, 152.7, 152.4, 150.1, 140.01, 139.97, 139.9, 136.9, 136.3, 164.4, 133.0, 129.9, 129.8, 129.5, 128.1 (two peaks are overlapped), 127.9, 124.3, 123.1, 119.2, 119.0, 115.7, 35.3, 34.5, 34.2, 32.8, 32.64, 32.60, 32.2 (many peaks are overlapped), 31.9, 30.0 (many peaks are overlapped), 29.7 (many peaks are overlapped), 28.3 (many peaks are overlapped), 23.0 (many peaks are overlapped), 22.9, 20.1, 19.2, 14.4 (many peaks are overlapped), 12.0, -4.0 ppm. MS (MALDI-TOF) *m/z*: 1593 ($[MH]^+$). IR (neat) 2922, 2850, 2175, 1572, 1483, 1414, 1400, 1331, 1159 cm^{-1}. Anal. Calcd for $C_{101}H_{125}N_7O_8Si$: C, 76.14; H, 7.91; N, 6.15. Found: C, 76.14; H, 7.87; N, 6.02.

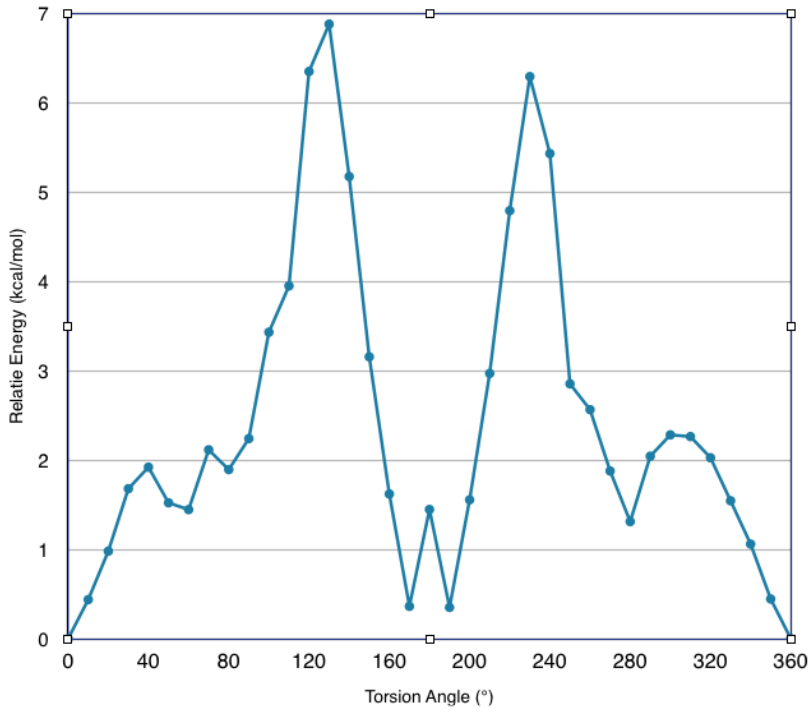
Data for 8e: 20% yield, white solid materials. ^1H NMR (400 MHz, $CDCl_3$) 8.25 (s, 2H), 7.90 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.85 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.67 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.55-7.50 (m, 4H), 7.46 (dd, *J* = 6.4, 3.5 Hz, 2H), 7.30 (s, 2H), 7.14 (s, 2H), 7.11 (s, 2H), 5.73 (t, *J* = 8.1 Hz, 1H), 5.65 (t, *J* = 8.2 Hz, 2H), 4.51 (t, *J* = 7.9 Hz, 1H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.32-2.19 (m, 8H), 2.00 (tt, *J* = 8.0, 7.0 Hz, 2H), 1.45-1.28 (m, 72H), 1.08 (t, *J* = 8.0 Hz, 2H), 0.91-0.87 (m, 12H), -0.57 (s, 3H) ppm; ^1H NMR (400 MHz, toluene–d_8) 8.73 (s, 2H), 8.00 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.75 (s, 2H), 7.67 (dd, *J* = 7.7 Hz, 1.4 Hz, 2H), 7.63 (s, 2H) 7.58 (dd, *J* = 6.3, 3.4 Hz, 2H)7.43 (s, 2H), 7.25 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 2H), 7.12-7.06 (m, 4H), 6.17 (t, *J* = 8.2 Hz, 2H), 6.07 (t, *J* = 8.2 Hz, 1H), 4.71 (t, *J* = 8.0 Hz, 1H), 2.49-2.38 (m, 8H), 1.50 (t, *J* = 7.2 Hz, 2H) 1.51-1.24 (m, 72H), 1.27 (tt, *J* = 8.4, 7.2 Hz, 2H), 0.97-0.94 (m, 12H), 0.45 (t, *J* = 8.4 Hz, 2H), -1.46 (s, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) 153.2, 153.1, 153.0, 152.9, 152.7, 152.6, 150.1, 140.12, 140.10, 140.06, 136.8, 136.3, 134.6, 133.1, 129.7, 129.6, 129.3, 128.2, 128.1, 127.9, 124.2, 123.1, 119.8 ($SiCH_2CH_2CH_2\underline{C}N$), 119.0, 116.0, 35.3, 34.6, 34.3, 32.9, 32.8, 32.6, 32.5, 32.3 (many peaks are overlapped), 30.1 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.4, 23.07 (many peaks are overlapped), 23.06 (many peaks are overlapped), 20.5, 19.5, 14.5 (many peaks are overlapped), 13.8, -5.4 ppm. MS (MALDI-TOF) *m/z*: 1593 ($[MH]^+$). IR (neat) 2922, 2851, 2152, 1483, 1414, 1331, 1156 cm^{-1}. Anal. Calcd for $C_{101}H_{125}N_7O_8Si$: C, 76.14; H, 7.91; N, 6.15. Found: C, 76.11; H, 7.84; N, 5.79.

h) **Synthesis of the aldehyde 9, for Scheme 4.** Under an argon atmosphere, to the flask charged with **7e** (350 mg, 0.22 mmol) in toluene (15 mL) at -20 ºC was added DIBAL-H (0.26 mL, 1 M hexane solution) over 3 min. After stirring at -20 °C for 30 min, the mixture was allowed to warm to ambient temperature. The reaction was quenched with saturated aqueous NH_4Cl at 0 ºC, and then warmed to room temperature. The aqueous layer was extracted with toluene, and combined organic phases were washed with water, brine, and dried over Na_2SO_4, and concentrated *in vacuo* to give crude products. Purification by silica gel column chromatography (hexane/EtOAc/CH_2Cl_2 = 15/3/2) afforded **9** of 250 mg in 71% yield as pale yellow solid materials. ^{1}H NMR (400 MHz, $CDCl_3$) 9.38 (t, *J* = 1.4 Hz, 1H), 8.26 (s, 2H), 7.90-7.86 (m, 4H), 7.62 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.57 (dd, *J* = 6.3, 3.4 Hz, 2H), 7.52 (ddd, *J* = 8.2, 8.2, 1.1 Hz, 2H), 7.46 (ddd, *J* = 8.2, 8.2, 1.1 Hz, 2H), 7.32 (s, 2H), 7.14 (s, 2H), 7.12 (s, 2H), 5.75 (t, *J* = 8.0 Hz, 1H), 5.66 (t, *J* = 8.2 Hz, 2H), 4.51 (t, *J* = 8.0 Hz, 1H), 2.35-2.15 (m, 8H), 1.71 (td, *J* = 7.4, 1.4 Hz, 2H), 1.44-1.28 (m, 74H), 0.92-0.87 (m, 12H), 0.48 (s, 3H), -0.07 (t, *J* = 8.5 Hz, 2H) ppm; ^{1}H NMR (400 MHz, toluene-d_8) 8.87 (t, *J* = 1.3 Hz, 1H), 8.65 (s, 2H), 7.98 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.72 (s, 2H), 7.67-7.61 (m, 6H), 7.43 (s, 2H), 7.23 (ddd, *J* = 8.3, 8.3, 1.0 Hz, 2H), 7.17-7.11 (m, 4H), 6.14 (t, *J* = 8.2 Hz, 2H), 6.03 (t, *J* = 8.2 Hz, 1H), 4.79 (t, *J* = 8.0 Hz, 1H), 2.47-2.34 (m, 8H), 1.50-1.33 (m, 72H), 0.97-0.93 (m, 12H), 0.83 (tt, *J* = 8.2, 7.3 Hz, 2H), 0.70 (t, *J* = 7.3 Hz, 2H), 0.29 (s, 3H), -0.90 (t, *J* = 8.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 202.1, 153.3, 153.2, 152.92, 152.90, 152.7, 152.5, 150.3, 140.12, 140.07, 140.0, 137.0, 136.3, 134.6, 132.8, 129.7, 129.6, 129.4, 128.2, 127.9, 124.3, 123.1, 118.9, 115.8, 46.4, 35.3, 34.6, 34.3, 32.9, 32.74, 32.67, 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), 15.3, 14.5 (many peaks are overlapped), 11.7, -3.8 ppm. MS (MALDI-TOF) *m/z*: 1596 ($[MH]^+$). IR (neat) 2922, 2850, 1711, 1571, 1482, 1331, 1159 cm^{-1}. Anal. Calcd for $C_{101}H_{126}N_6O_9Si_9$: C, 76.00; H, 7.96; N, 5.27. Found: C, 76.08; H, 7.71; N, 5.41.

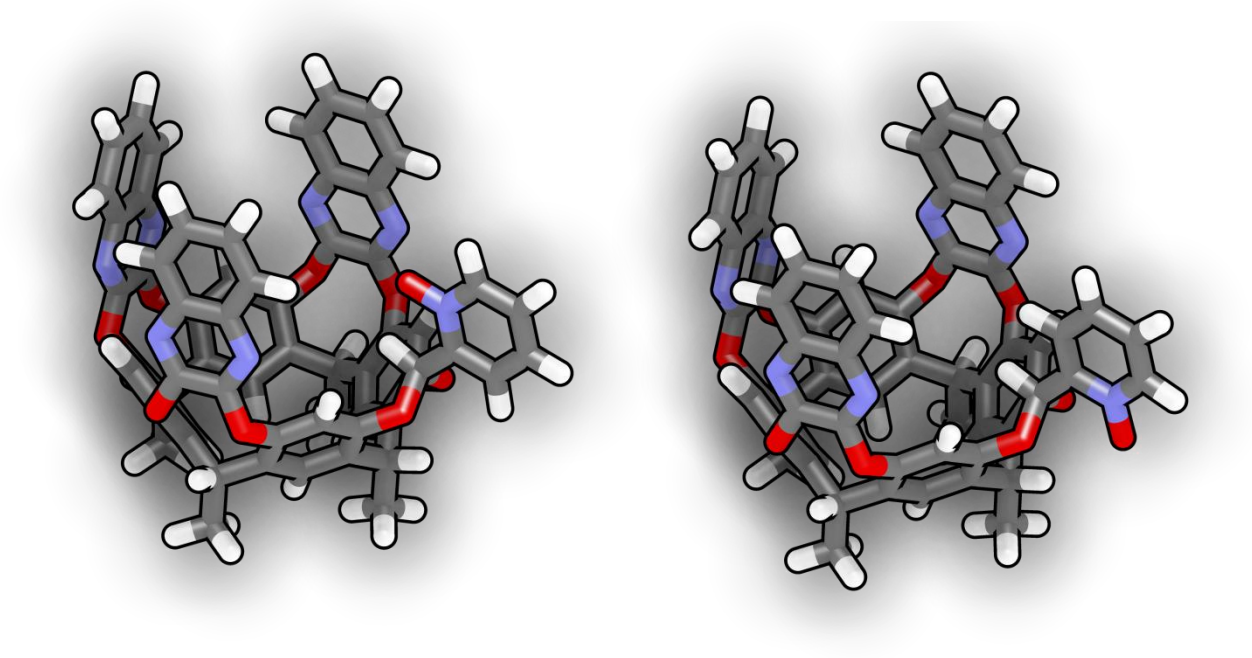
i) **MM+ torsion angle calculation of pyridine N-Oxide 3**

i) AM1 minimized structure was subjected to a torsion scan rotating about the methine-pyridyl bond using mm+ revealed a global minimum (0°) with oxygen inwardly directed.



ii) Global minima from 0 and 180 ° were then minimized at B3LYP/6-31G* followed by single point energy calculations using B3LYP/6-311G**

Inwardly directed oxygen is more stable than outwardly.



$\Delta E = 5.31$ kcal/mol $= \Delta H \approx \Delta G$

$\Delta G = -RT\ln K$

$K = e^{-\Delta G/RT}$ at 295 deg,

$K = e^{-5.31/(0.001987)(295)} = 0.0001172$ Thus

out/in = 0.0001172/1.0 and

% out = (0.0001172/1.0001172) x 100% = 0.012%

% in=99.988%

j) Portions of the ^{1}H NMR spectra of 2 and 3 in deuterated solvents

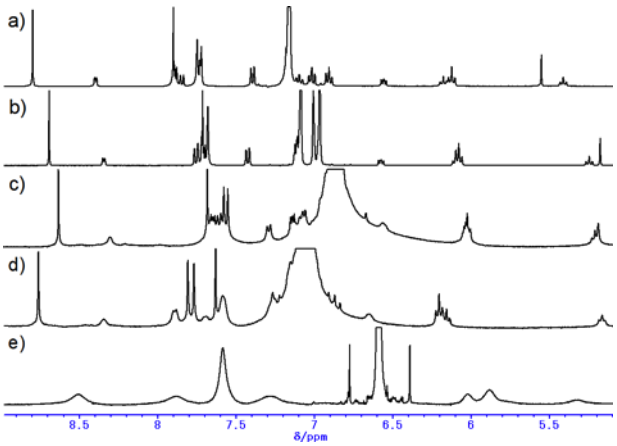


Figure 1S. Portions of the ^{1}H NMR spectra for **2** in a) [D6]benzene, b) [D8]toluene, c) [D9]-*p*-xylene, d) [D9]-*o*-xylene, and e) [D12]mesitylene.

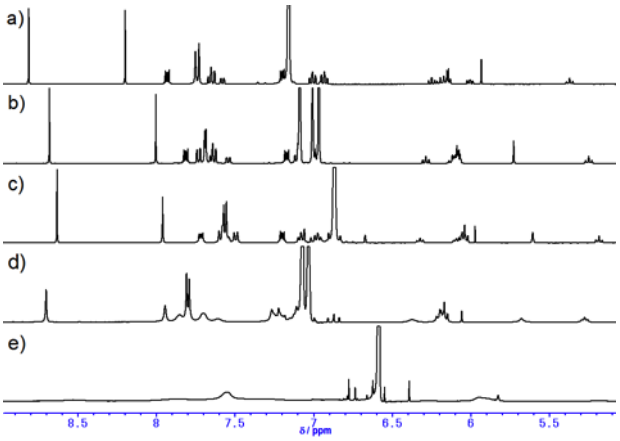
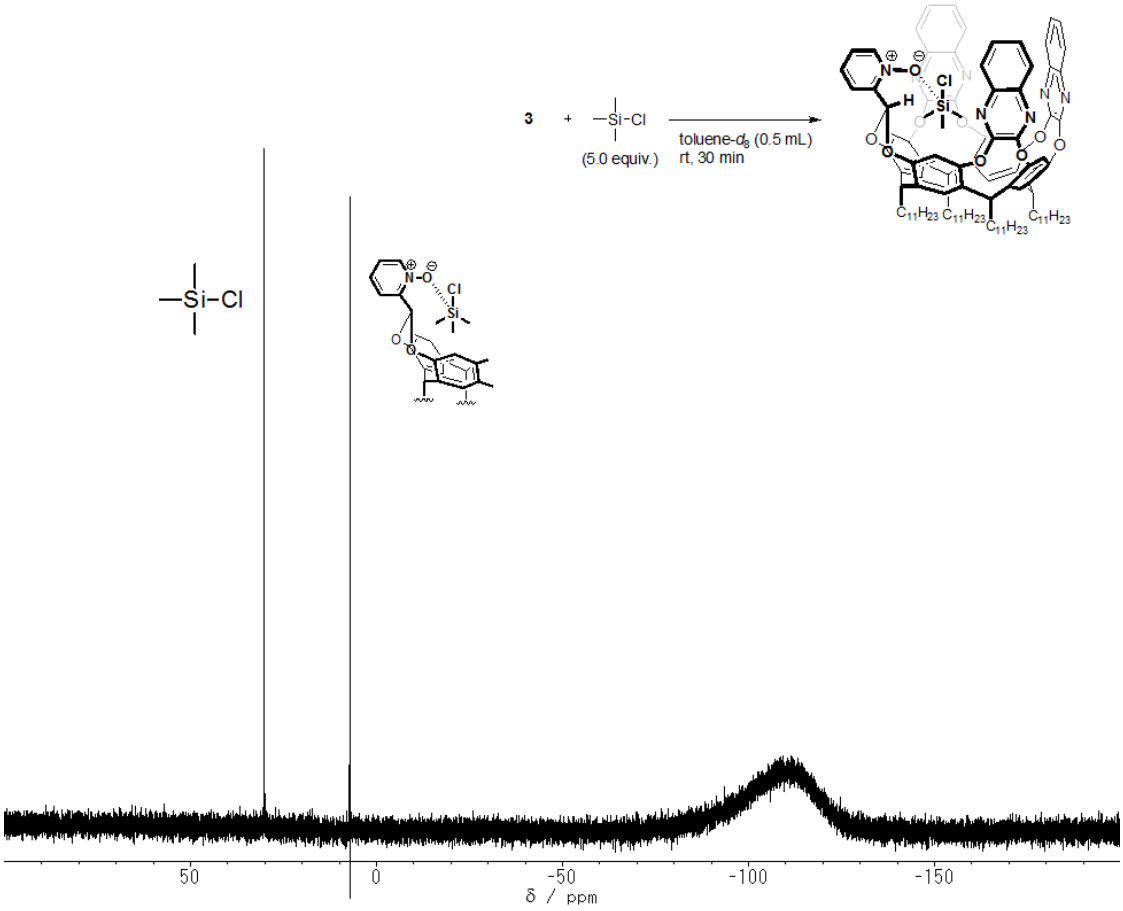


Figure 2S. Portions of the ^{1}H NMR spectra for **2** in a) [D6]benzene, b) [D8]toluene, c) [D9]-*p*-xylene, d) [D9]-*o*-xylene, and e) [D12]mesitylene.

k) ^{29}Si NMR data for host-guest complex obtained upon addition of TMSCl (5 equiv) to 3.



l) **References**

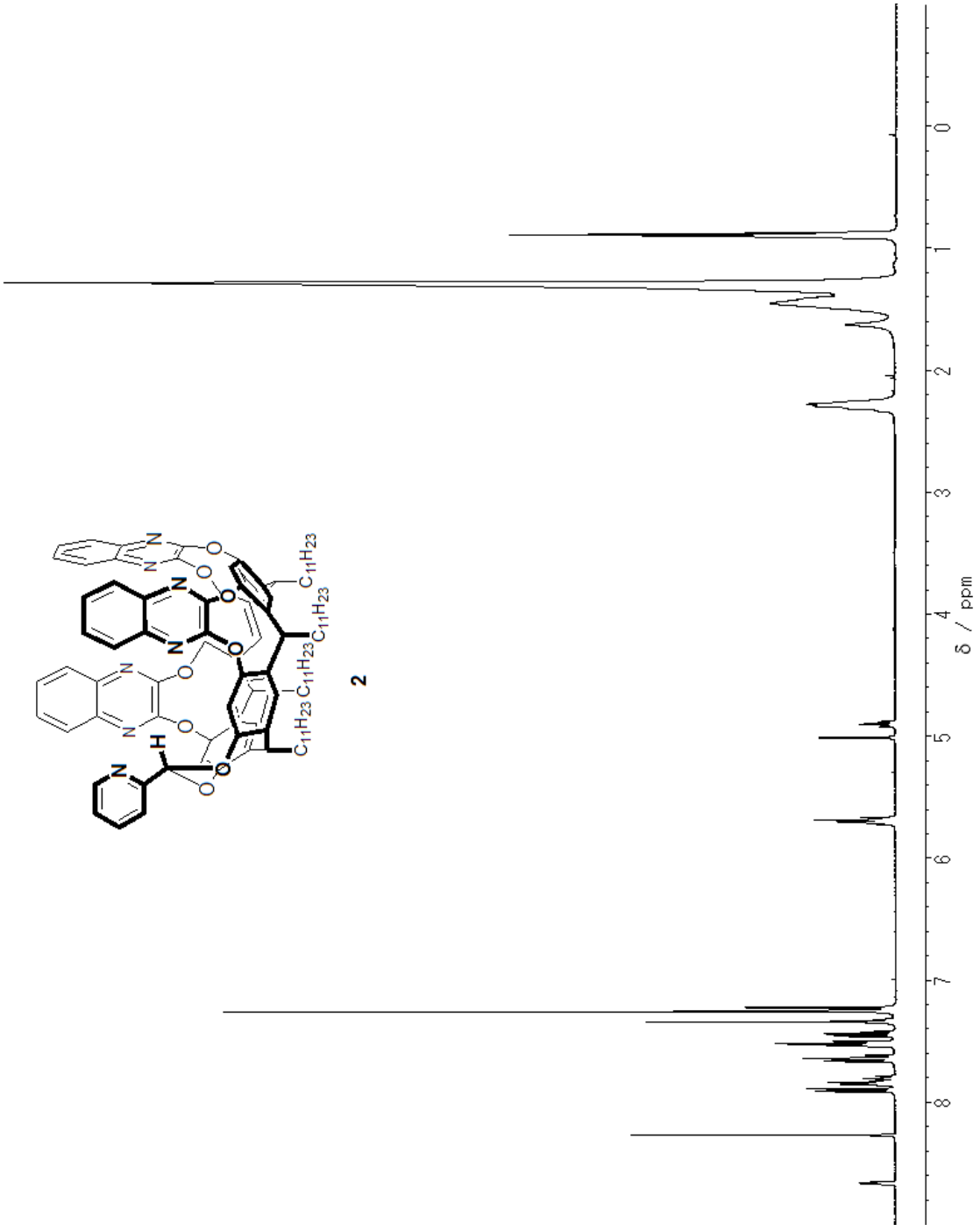
1) Spaggiari, A.; Vaccari, D.; Davoli, P.; Torre, G.; Prati, F. *J. Org. Chem.* **2007**, 72, 2216-2219.

2) K. Ohashi, K. Ito, T. Iwasawa, *Eur. J. Org. Chem.* **2014**, 1597-1561.

m) **^{1}H NMR and ^{13}C NMR spectra for compounds 2, 3, 4, 5, 6, 7c-e, 8c-e, 9.**

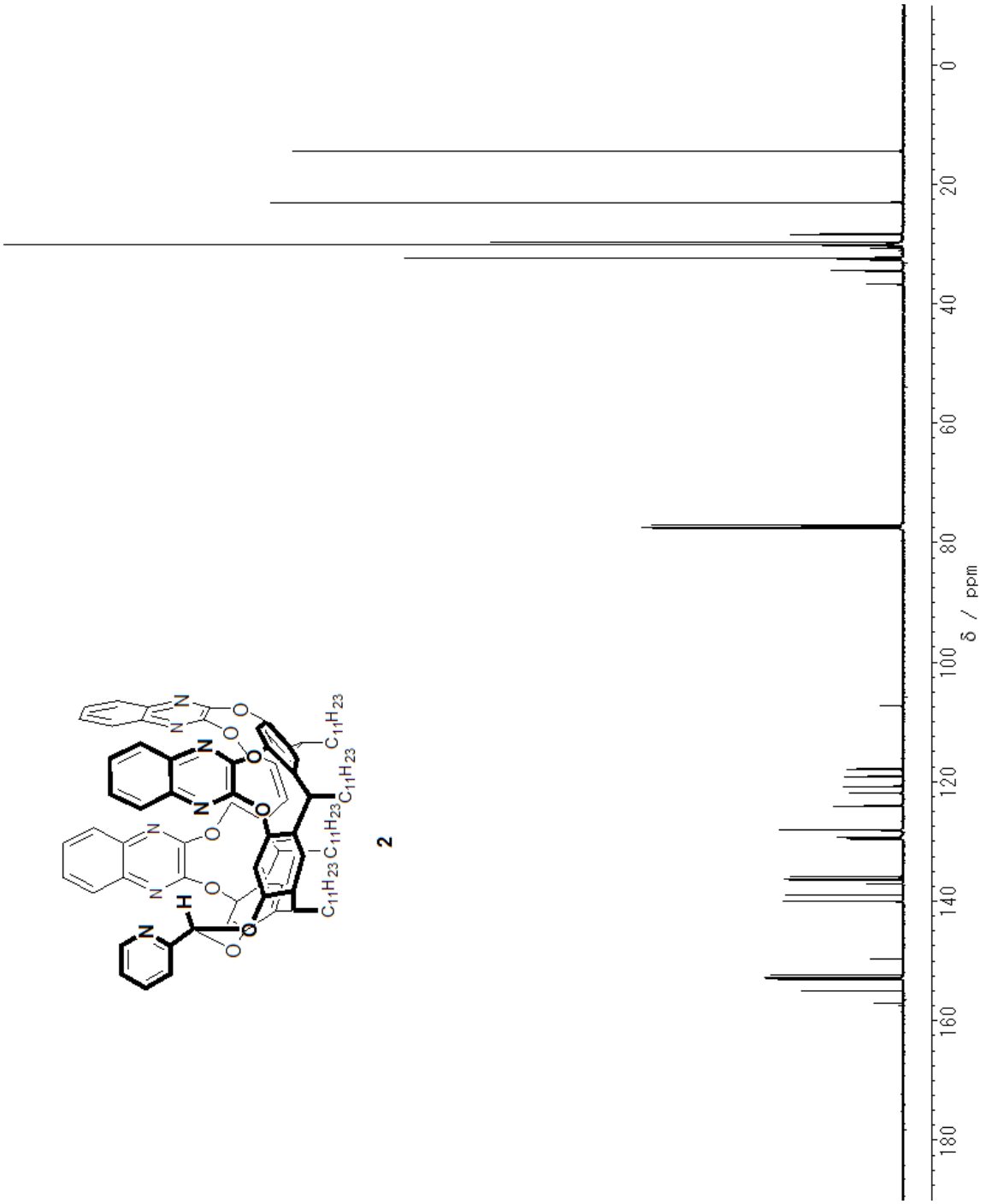
Compound 2

^{1}H NMR spectrum in $CDCl_3$



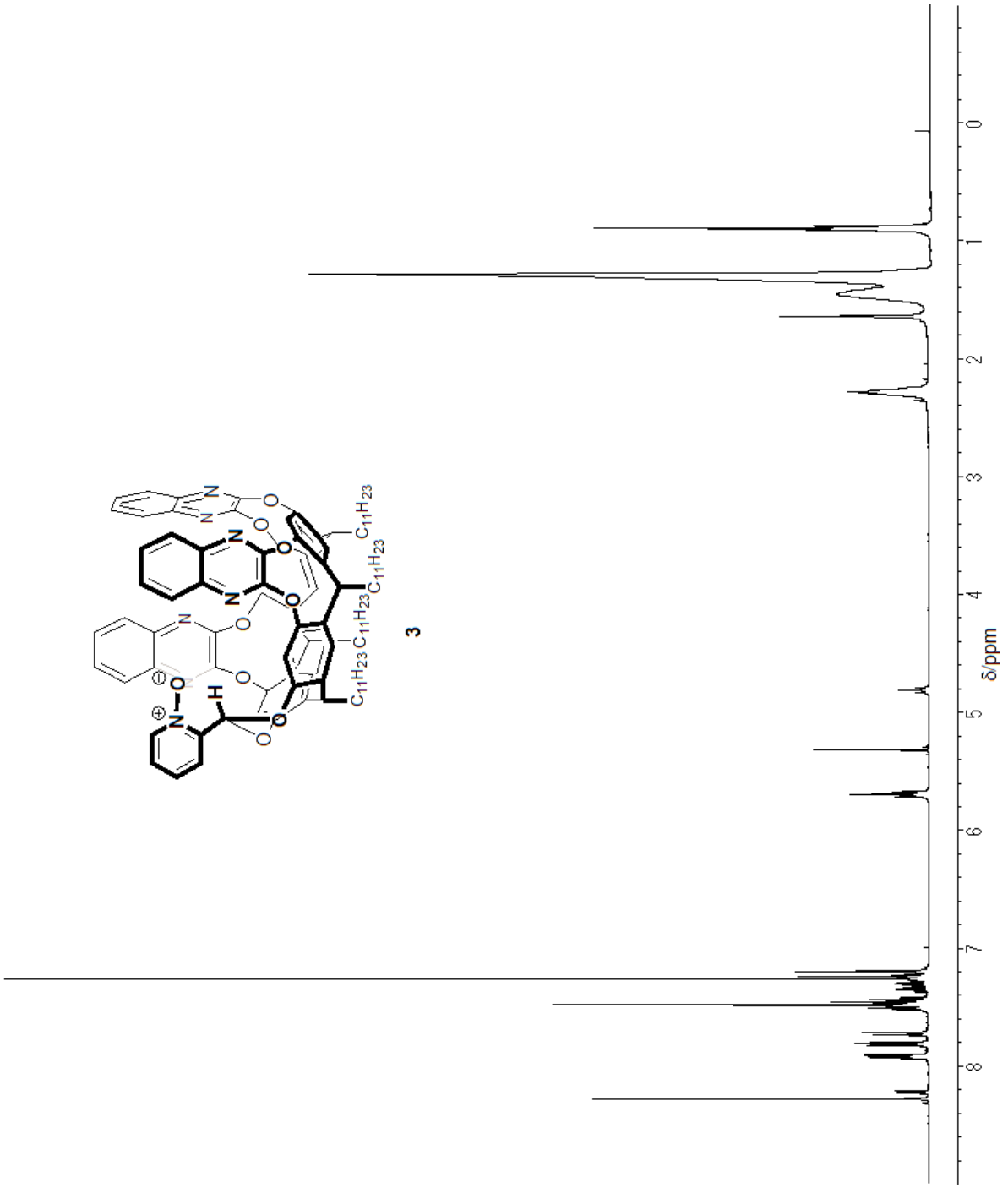
Compound 2

^{13}C NMR spectrum in $CDCl_3$



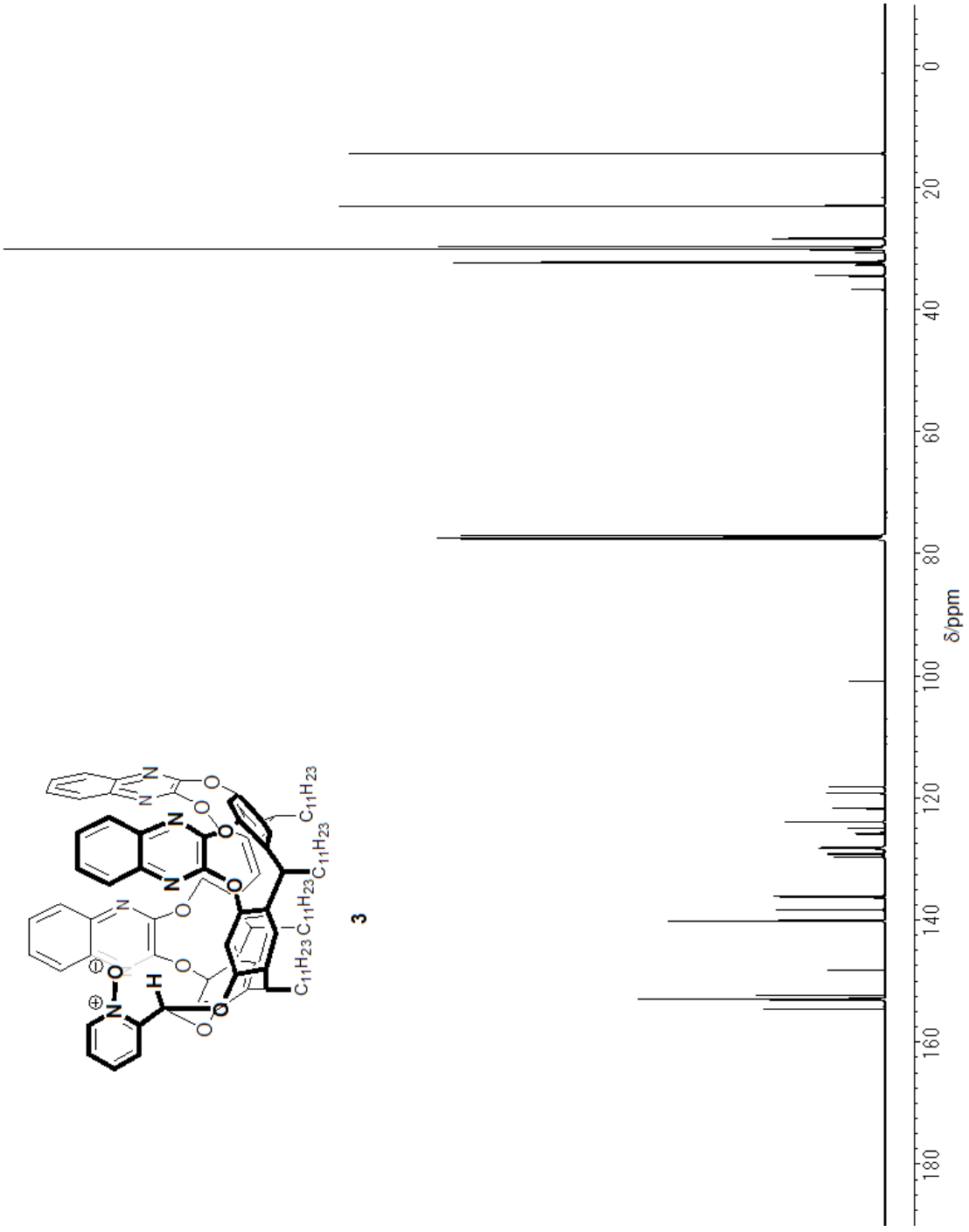
Compound 3

^{1}H NMR spectrum in $CDCl_3$



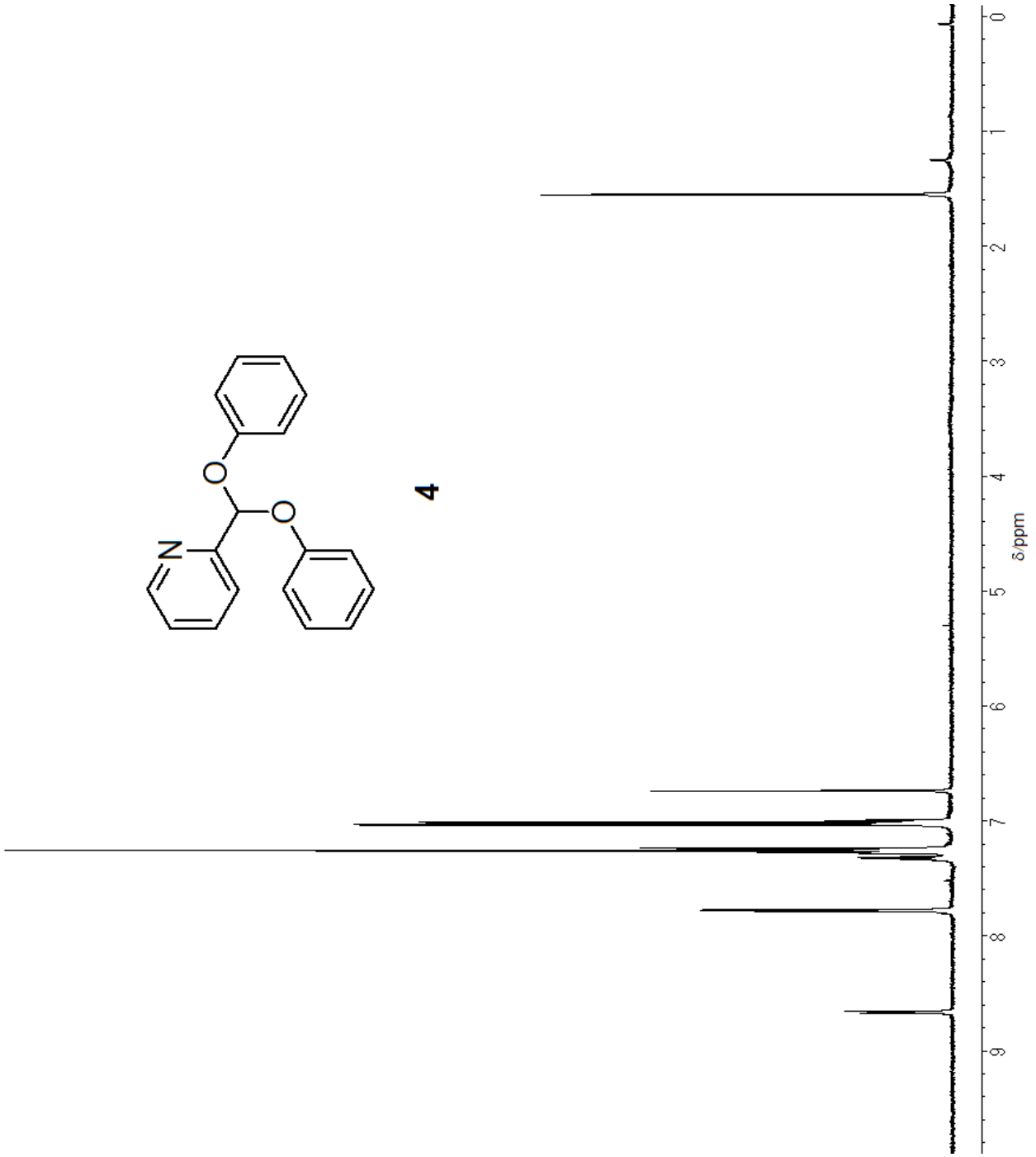
Compound 3

^{13}C NMR spectrum in $CDCl_3$



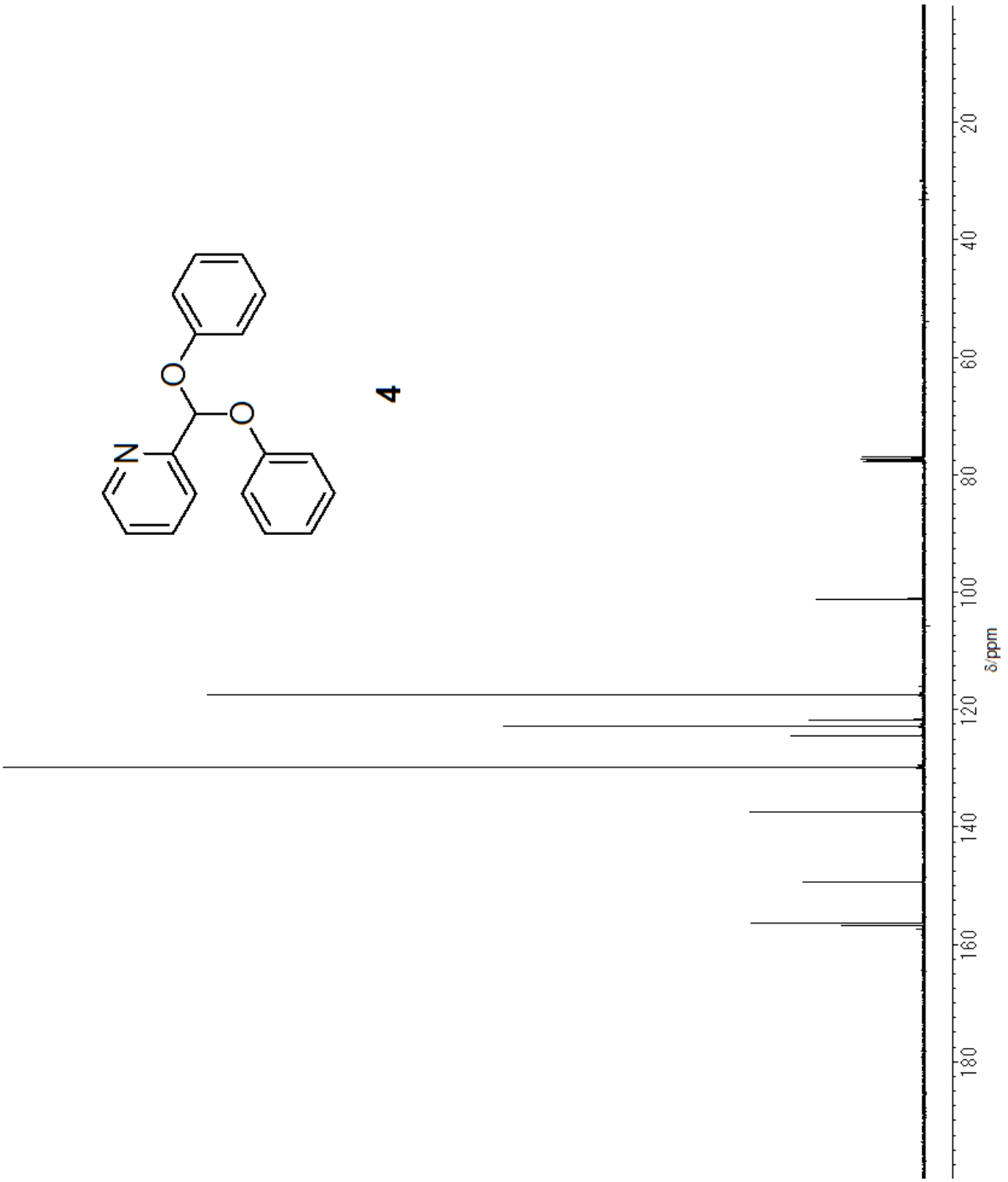
Compound 4

^{1}H NMR spectrum in $CDCl_3$



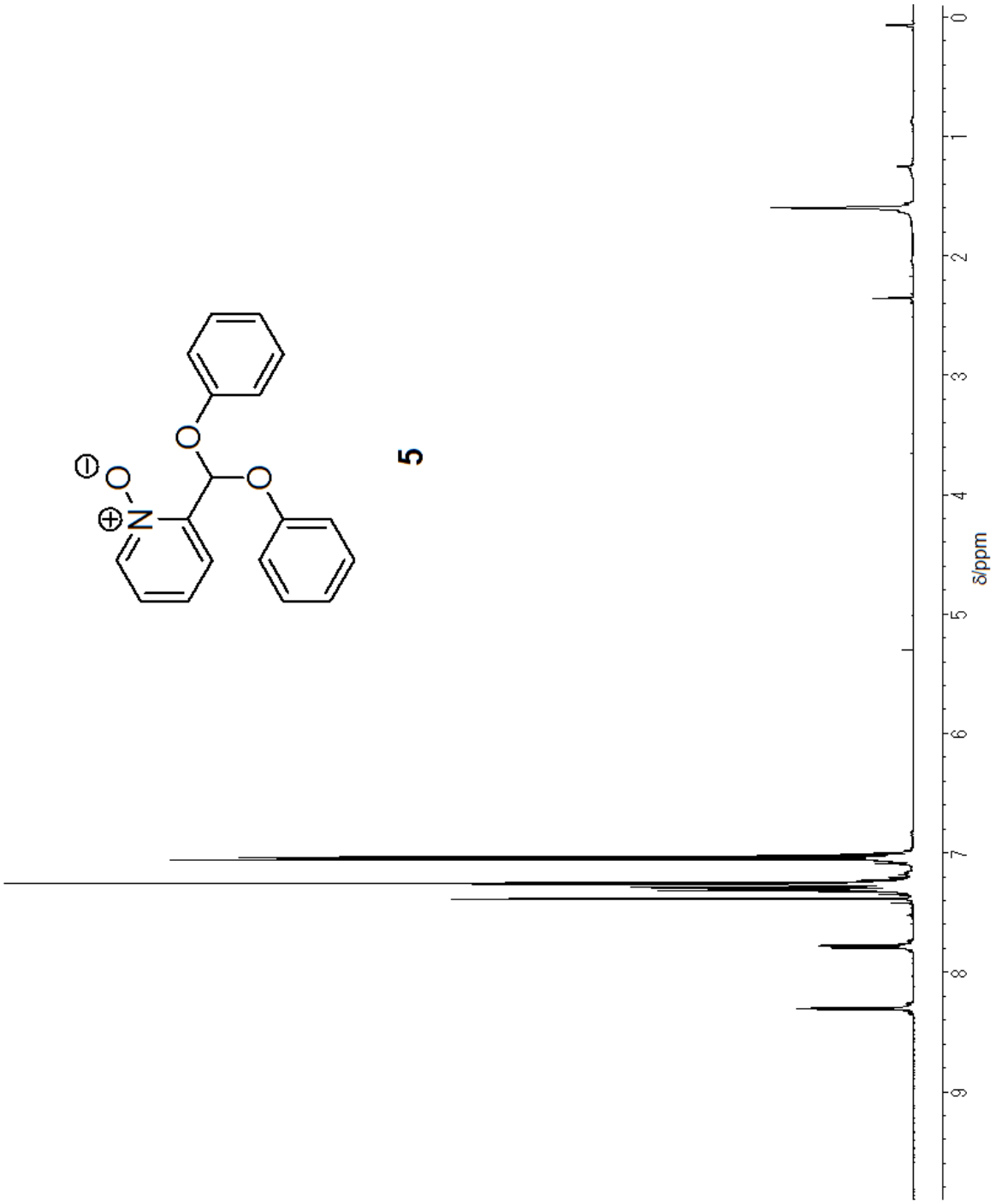
Compound 4

^{13}C NMR spectrum in $CDCl_3$



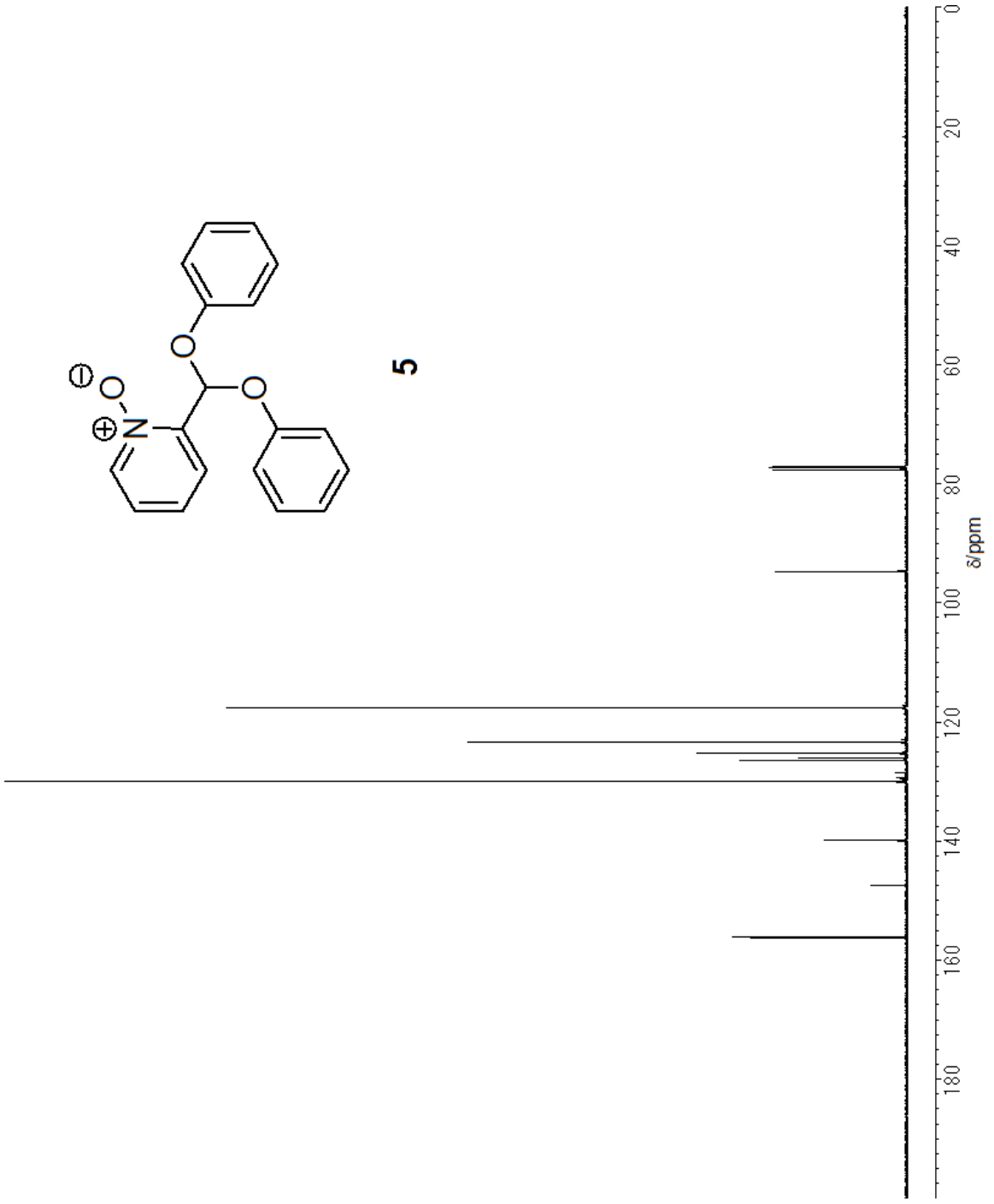
Compound 5

^{1}H NMR spectrum in $CDCl_3$



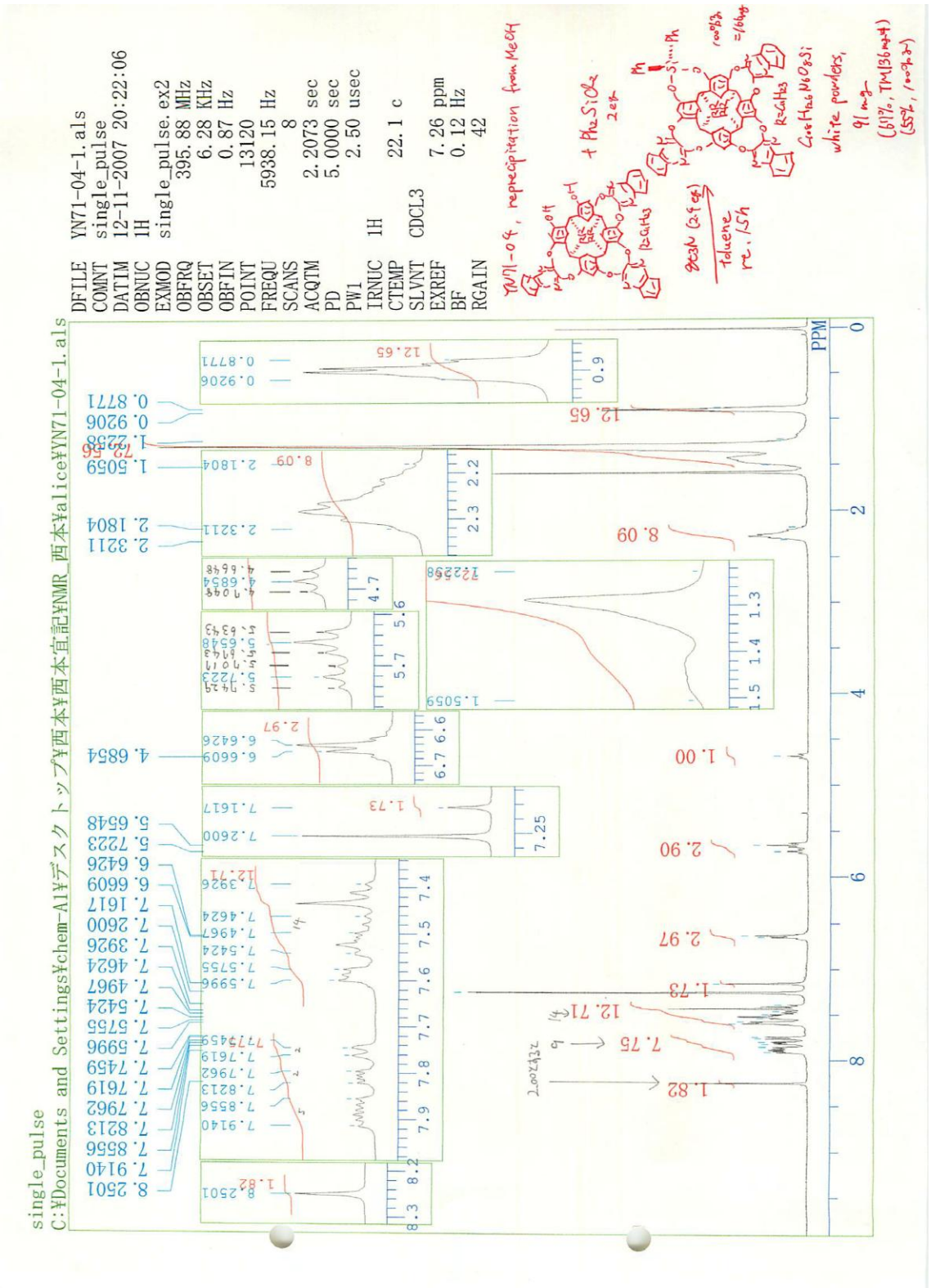
Compound 5

^{13}C NMR spectrum in $CDCl_3$



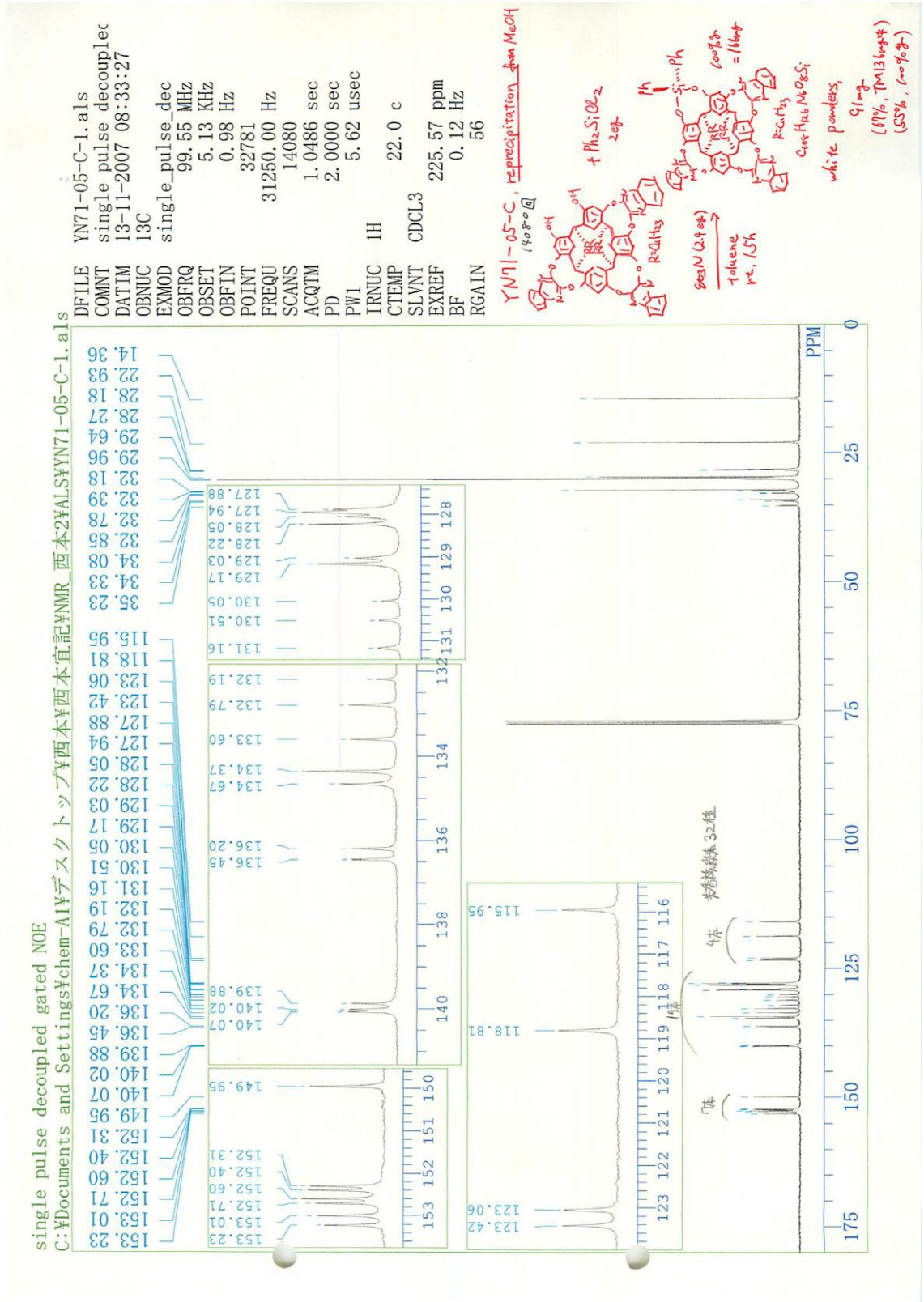
Compound 6

^{1}H NMR spectrum in $CDCl_3$



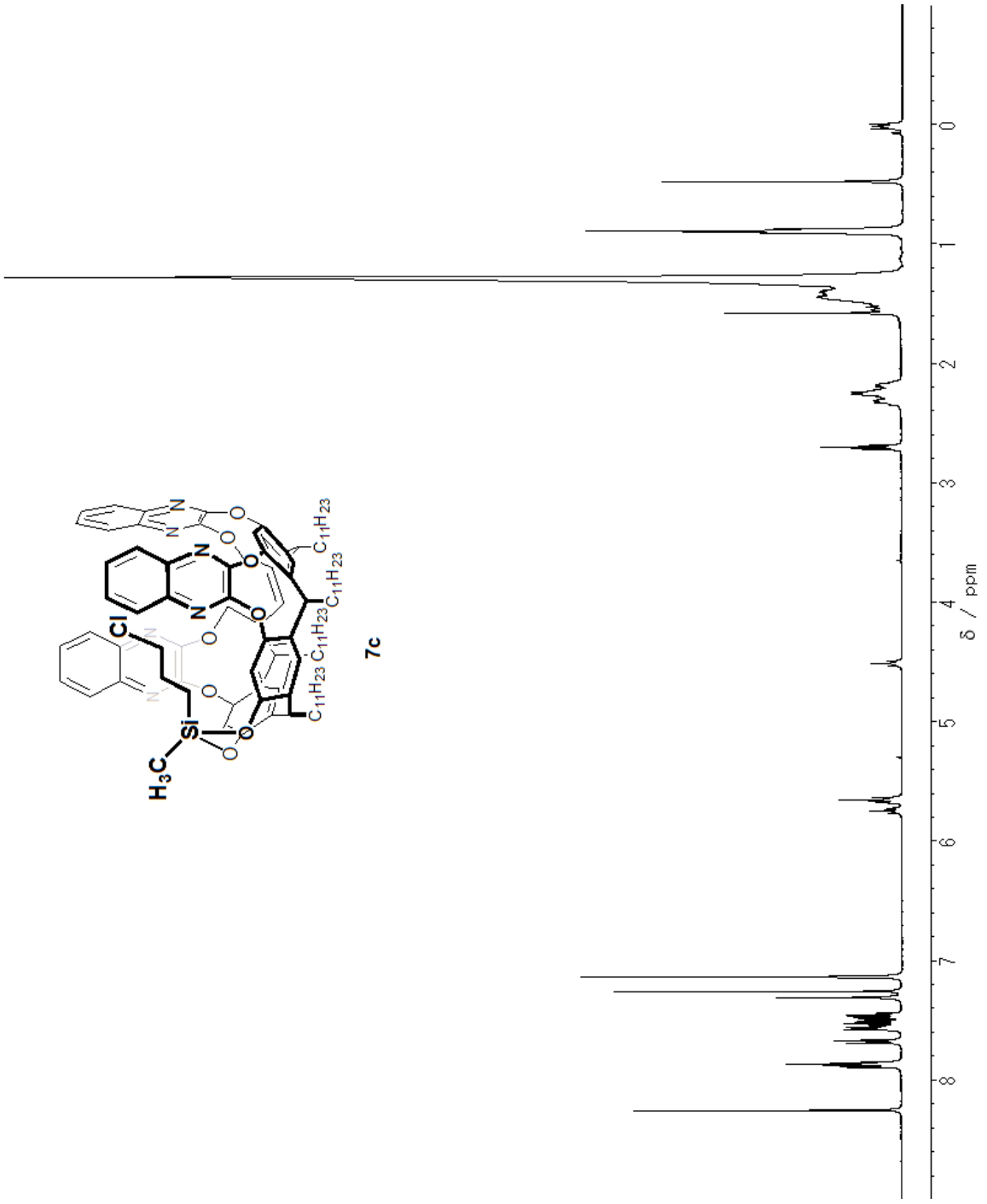
Compound 6

^{13}C NMR spectrum in $CDCl_3$



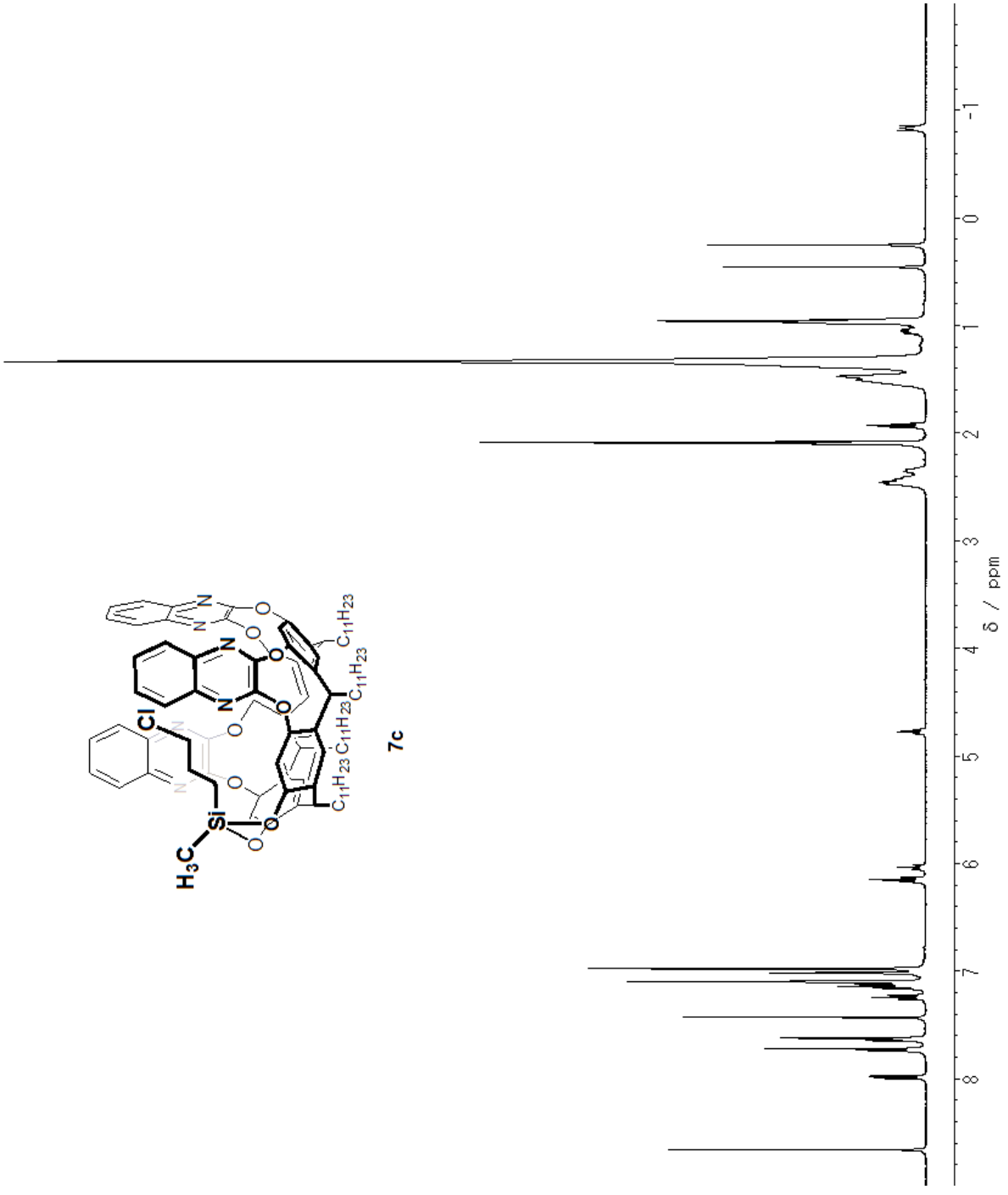
Compound 7c

^{1}H NMR spectrum in $CDCl_3$



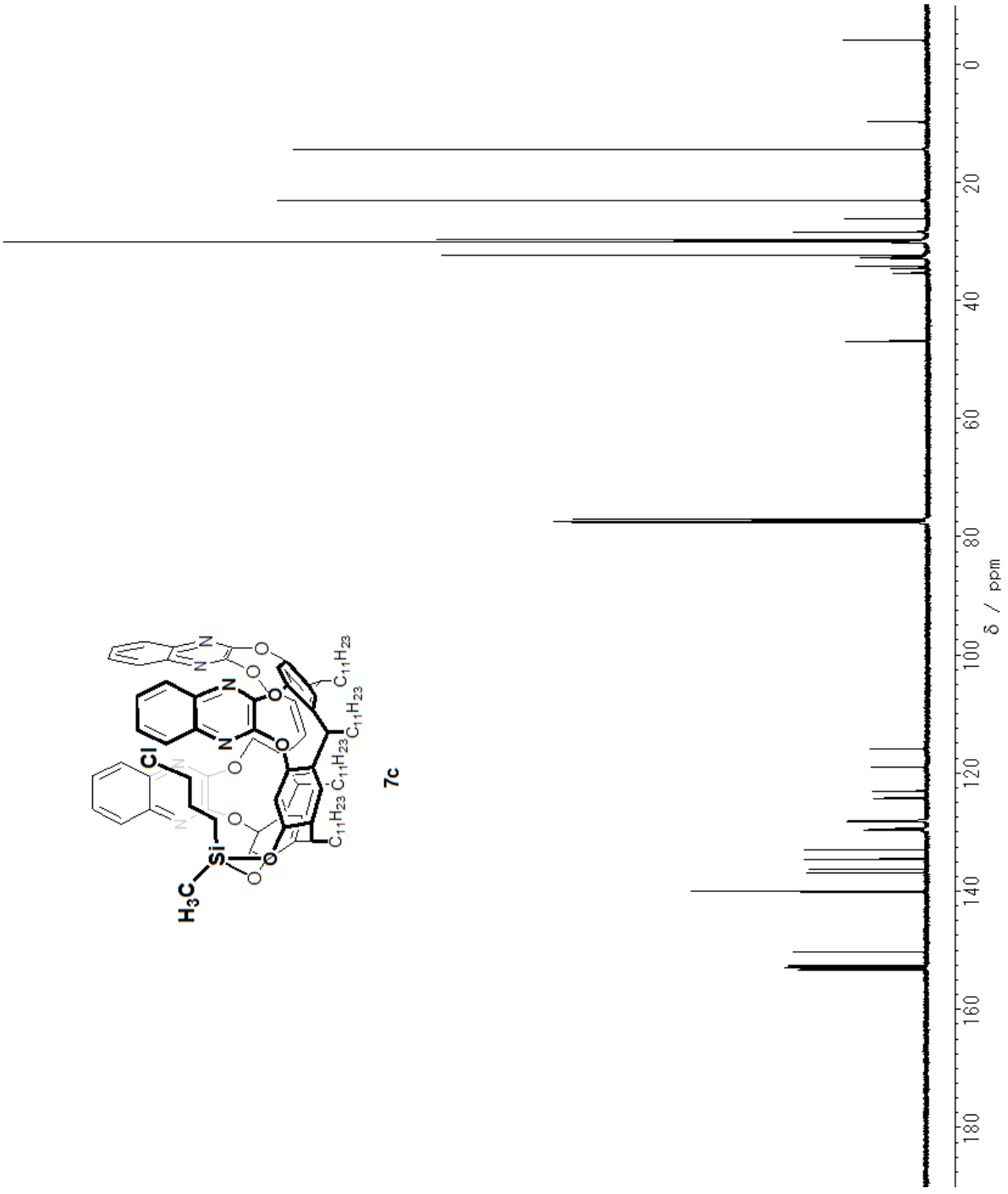
Compound 7c

^{1}H NMR spectrum in toluene-d_8



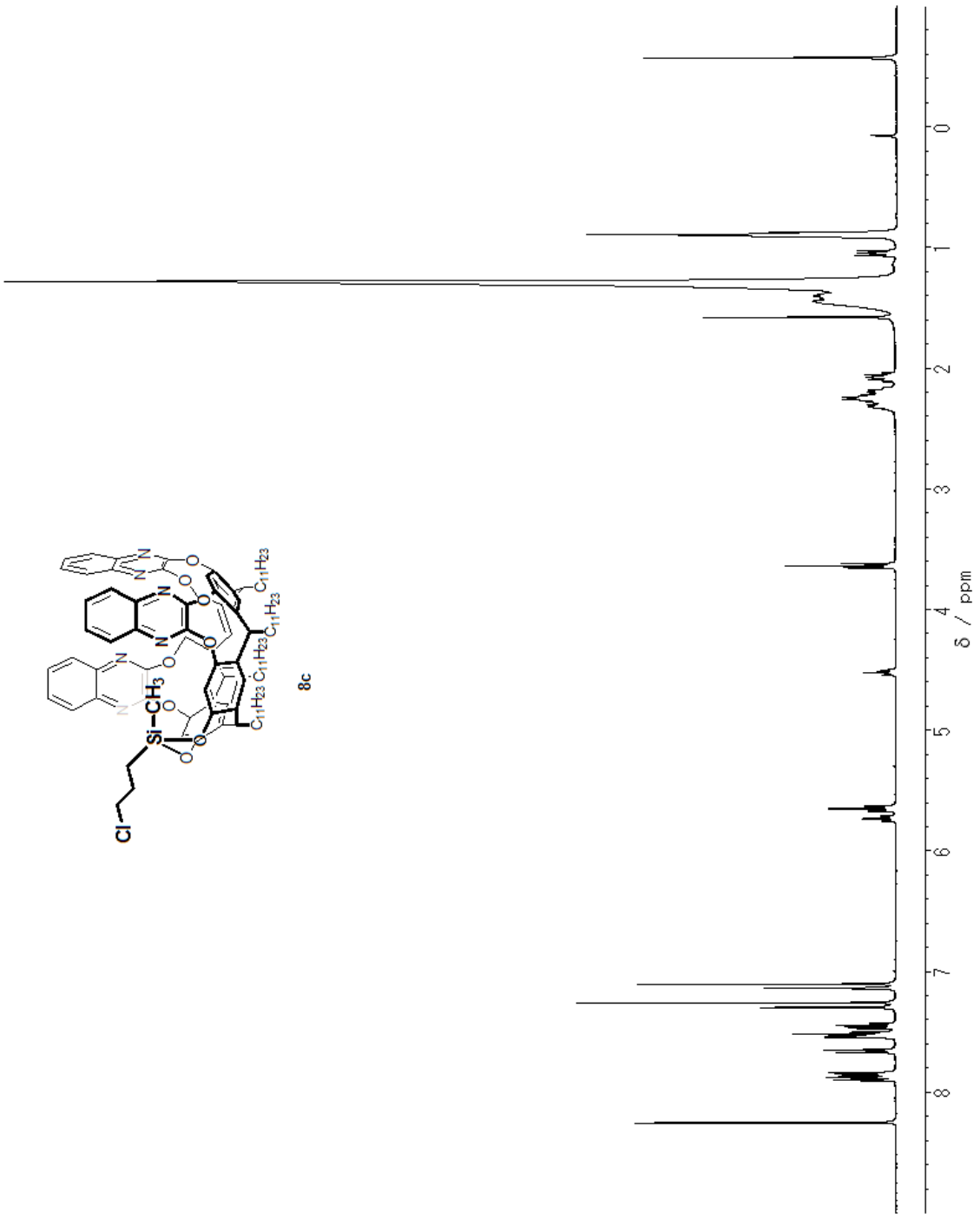
Compound 7c

^{13}C NMR spectrum in $CDCl_3$



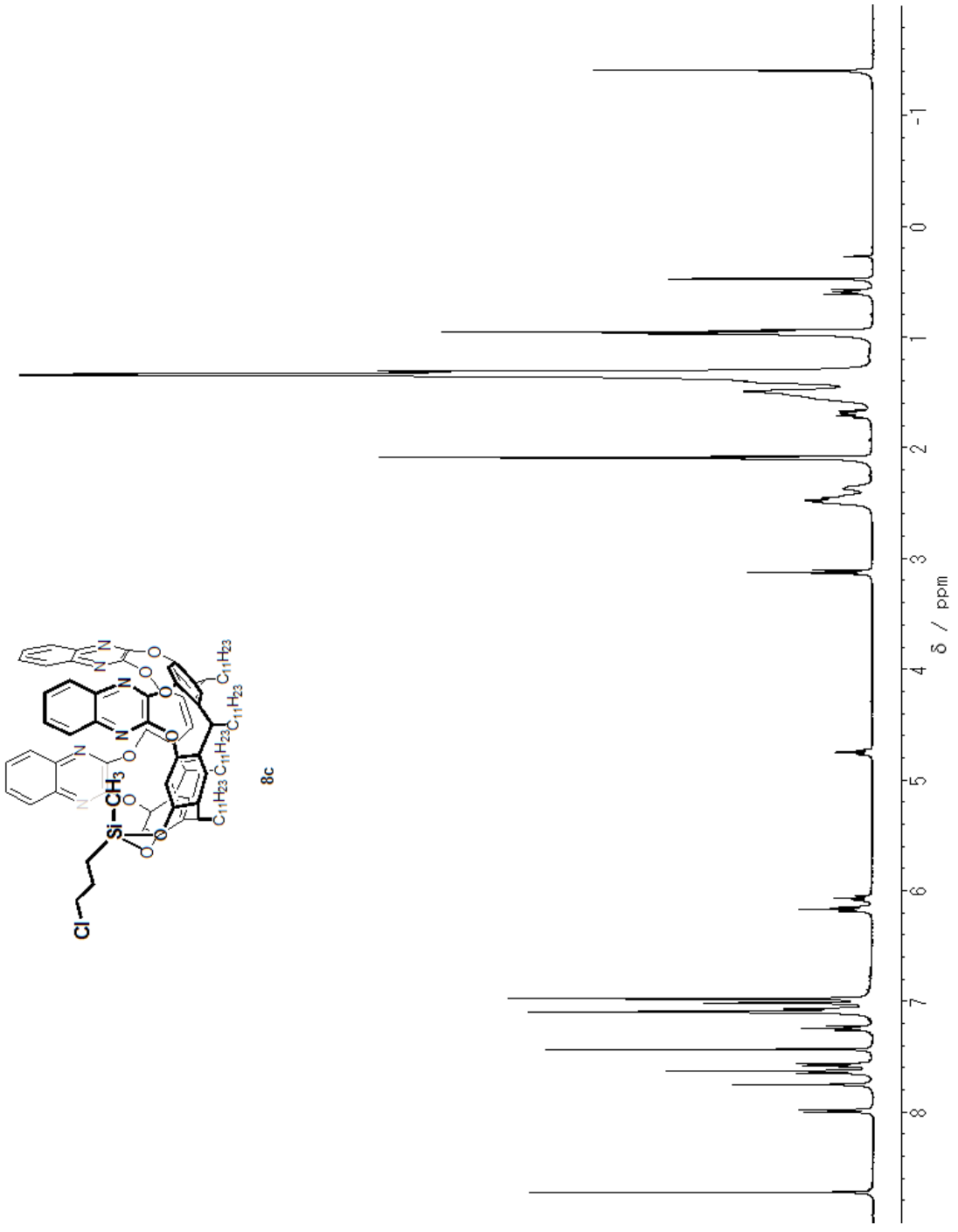
Compound 8c

^{1}H NMR spectrum in $CDCl_3$



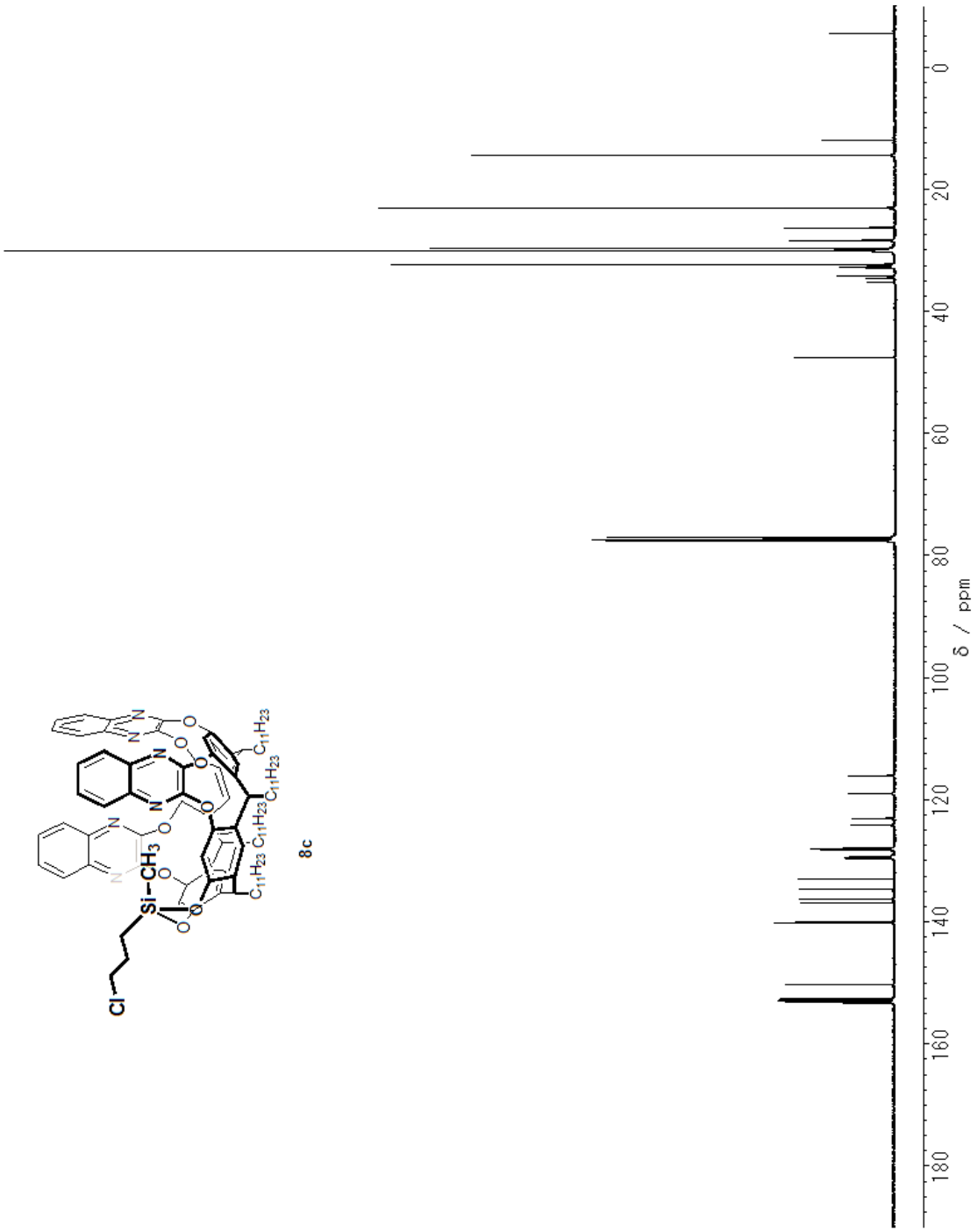
Compound 8c

^{1}H NMR spectrum in toluene-d_8



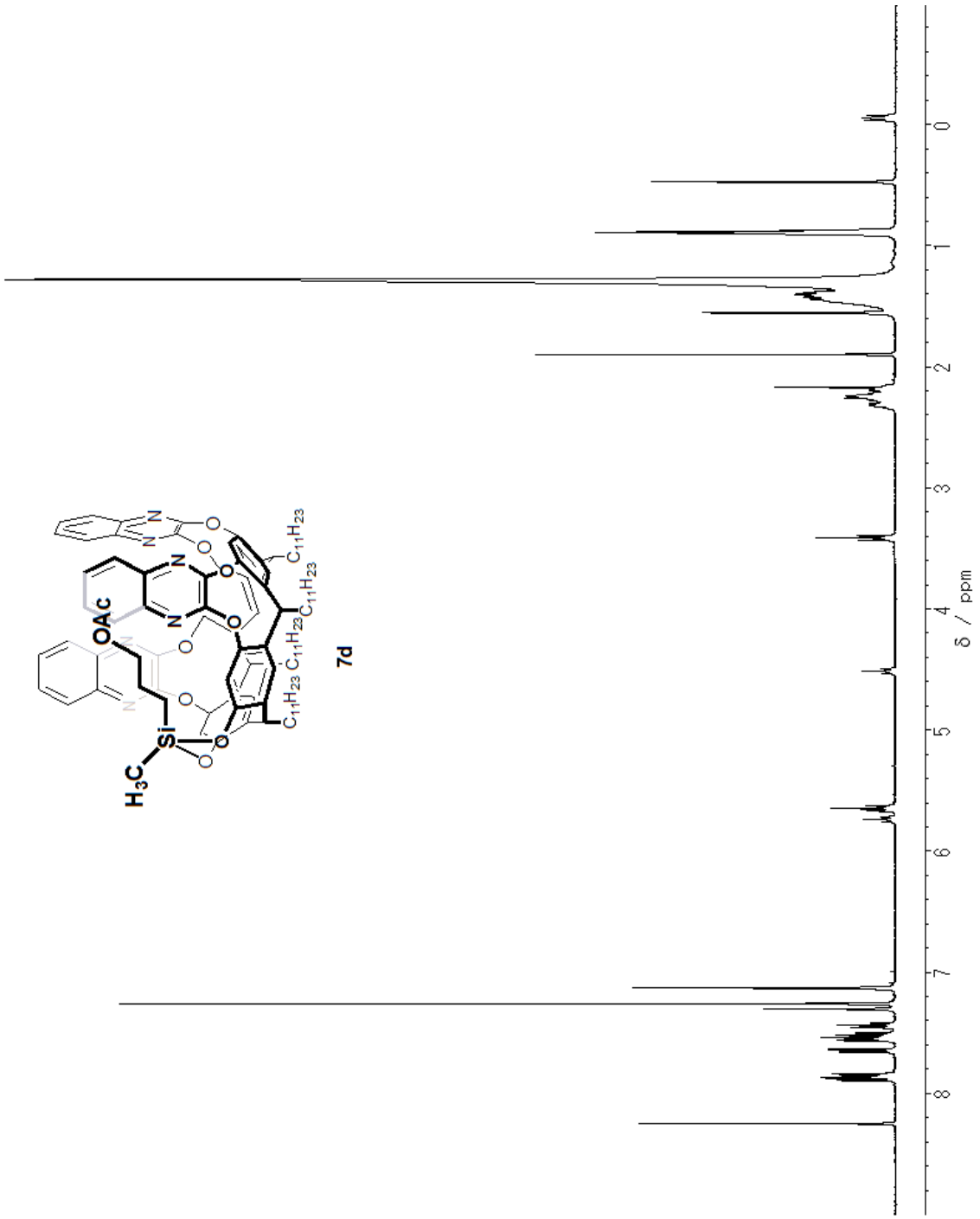
Compound 8c

^{13}C NMR spectrum in $CDCl_3$



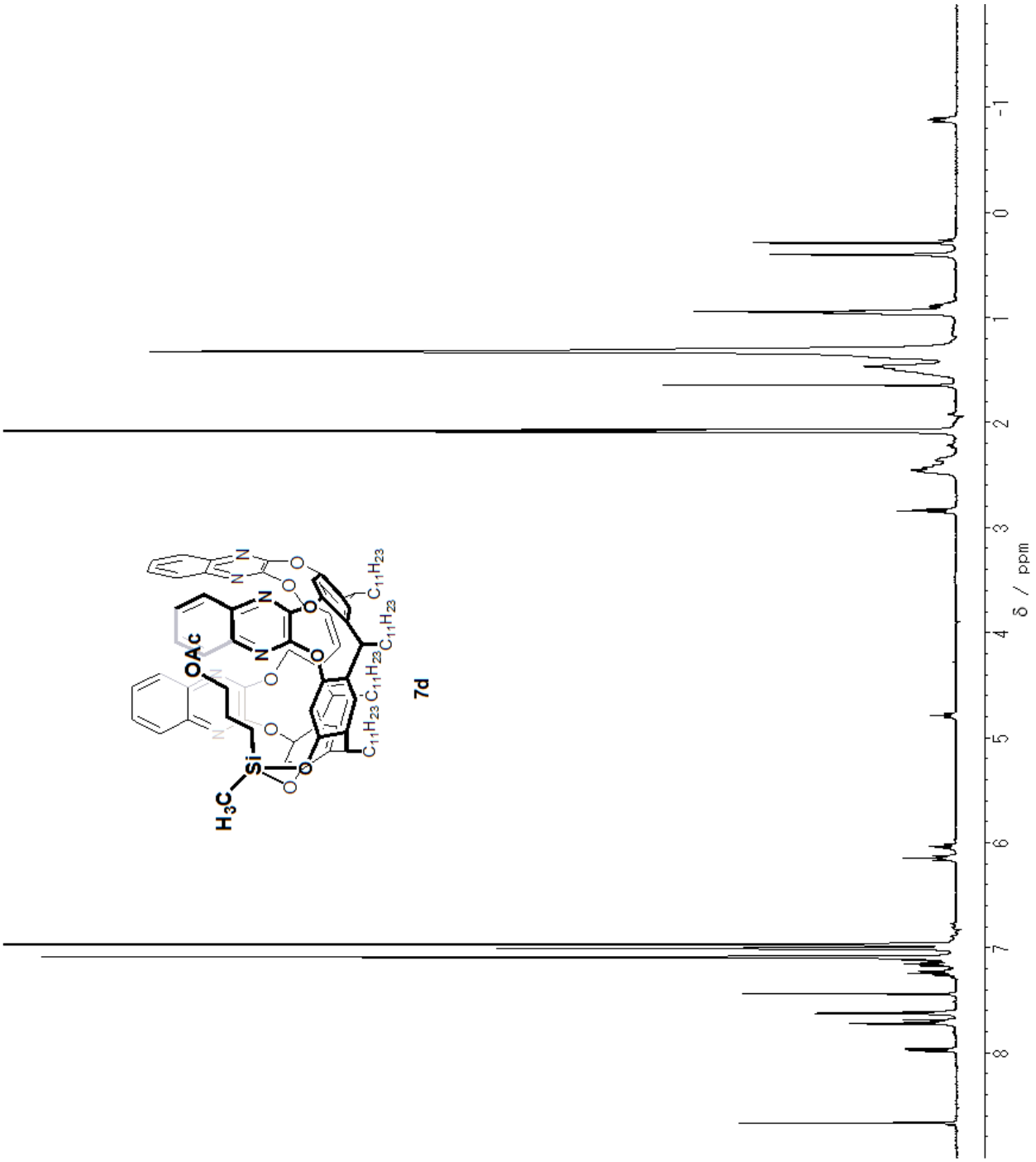
Compound 7d

^{1}H NMR spectrum in $CDCl_3$



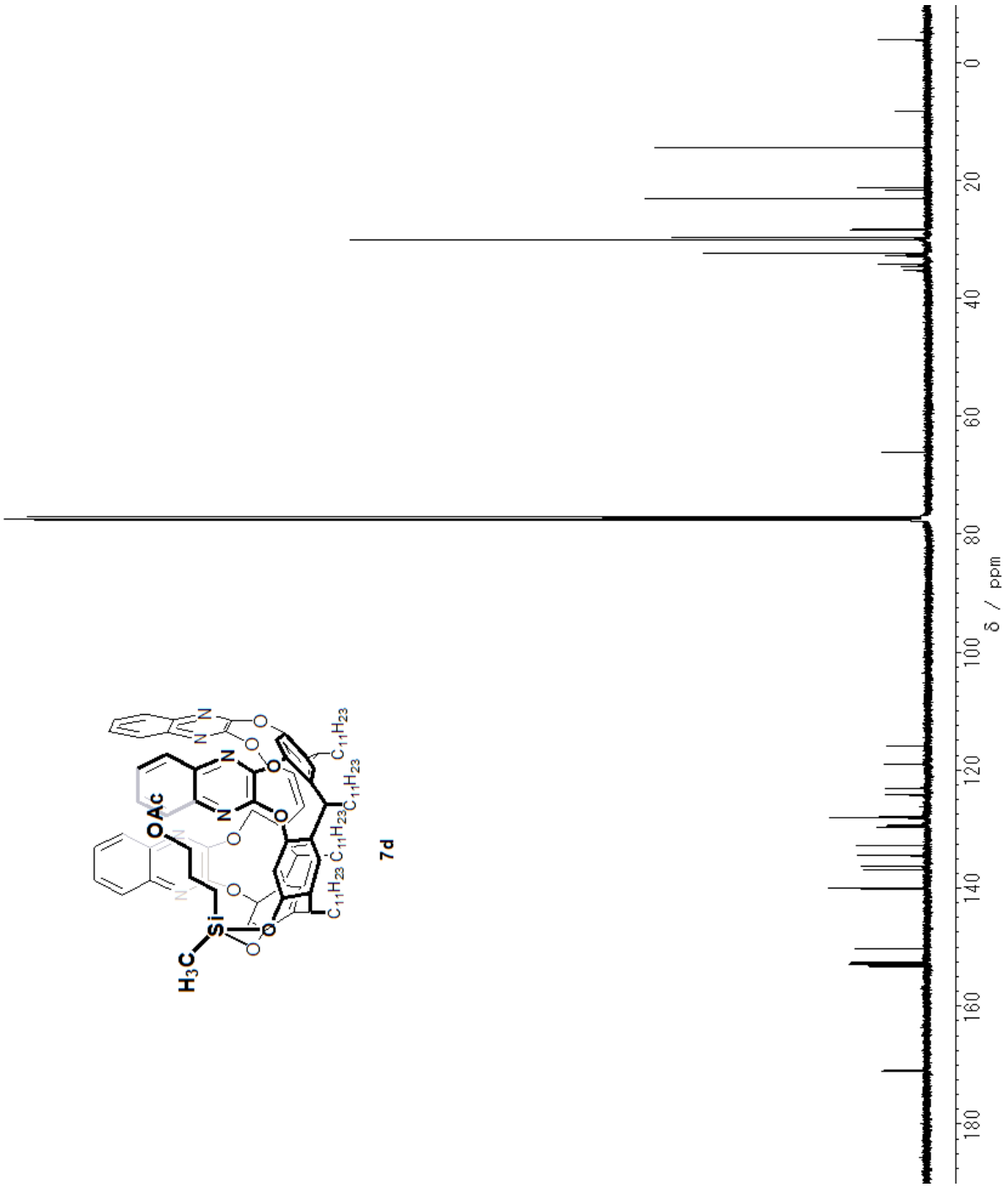
Compound 7d

^{1}H NMR spectrum in toluene-d_8



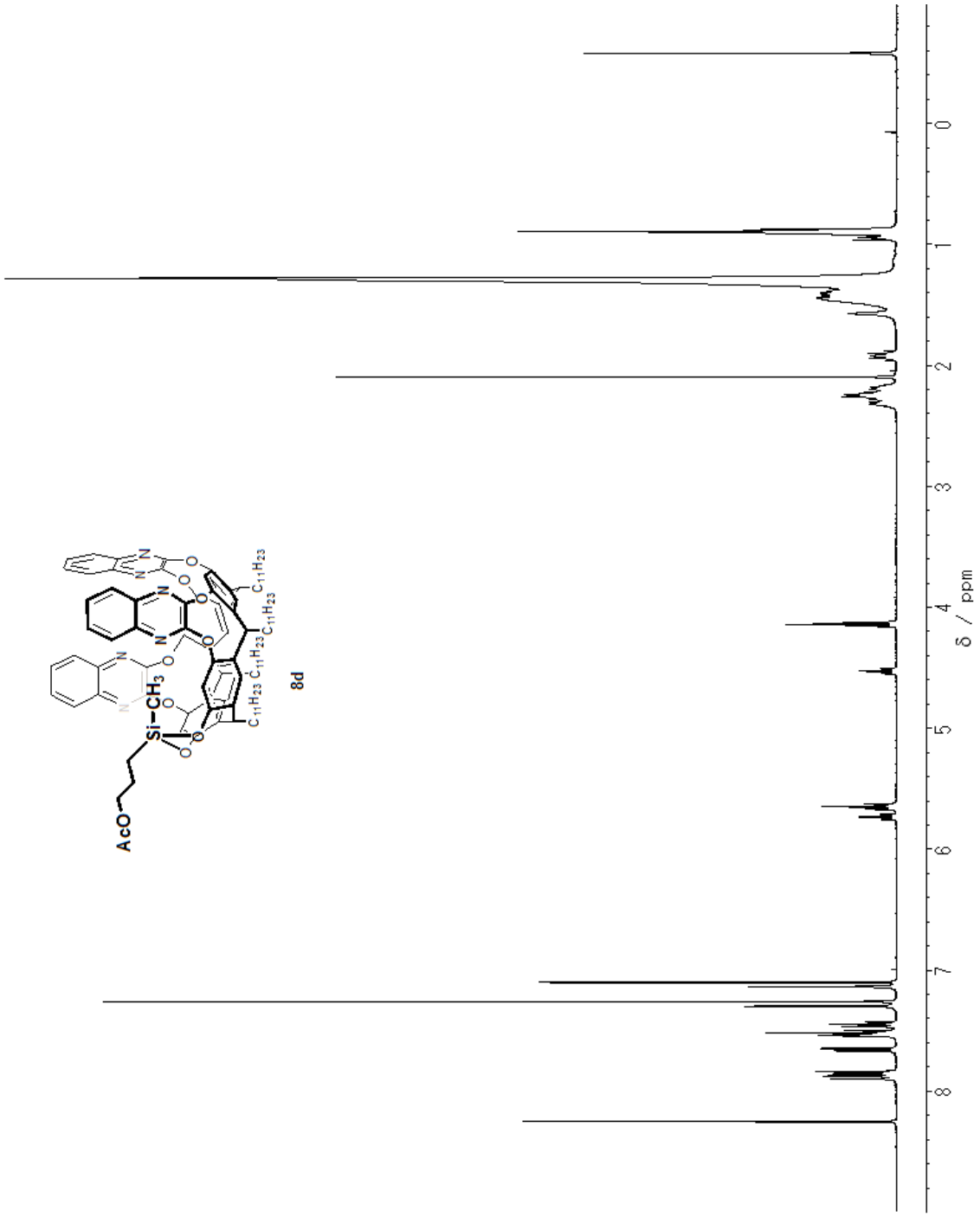
Compound 7d

^{13}C NMR spectrum in $CDCl_3$



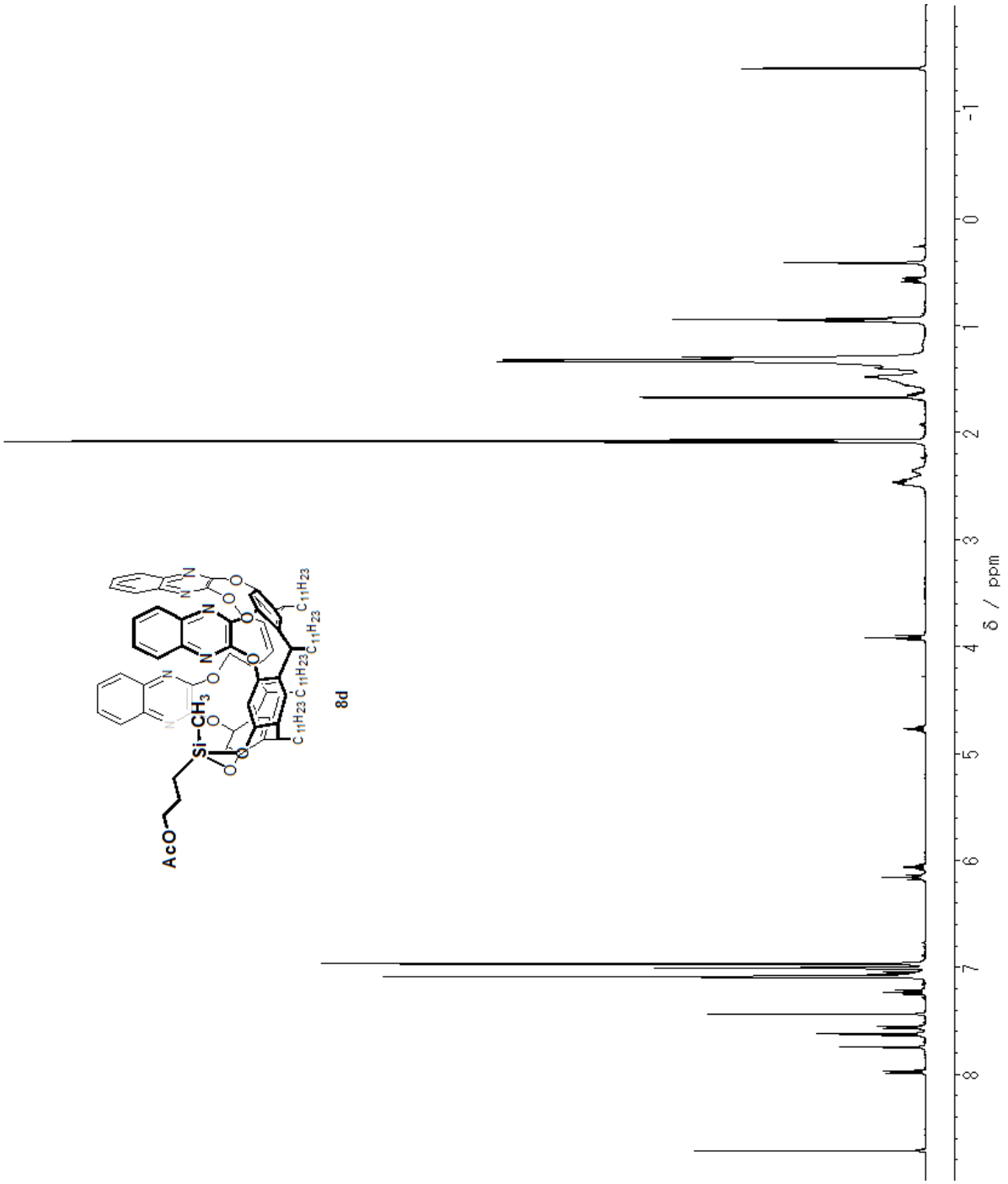
Compound 8d

^{1}H NMR spectrum in $CDCl_3$



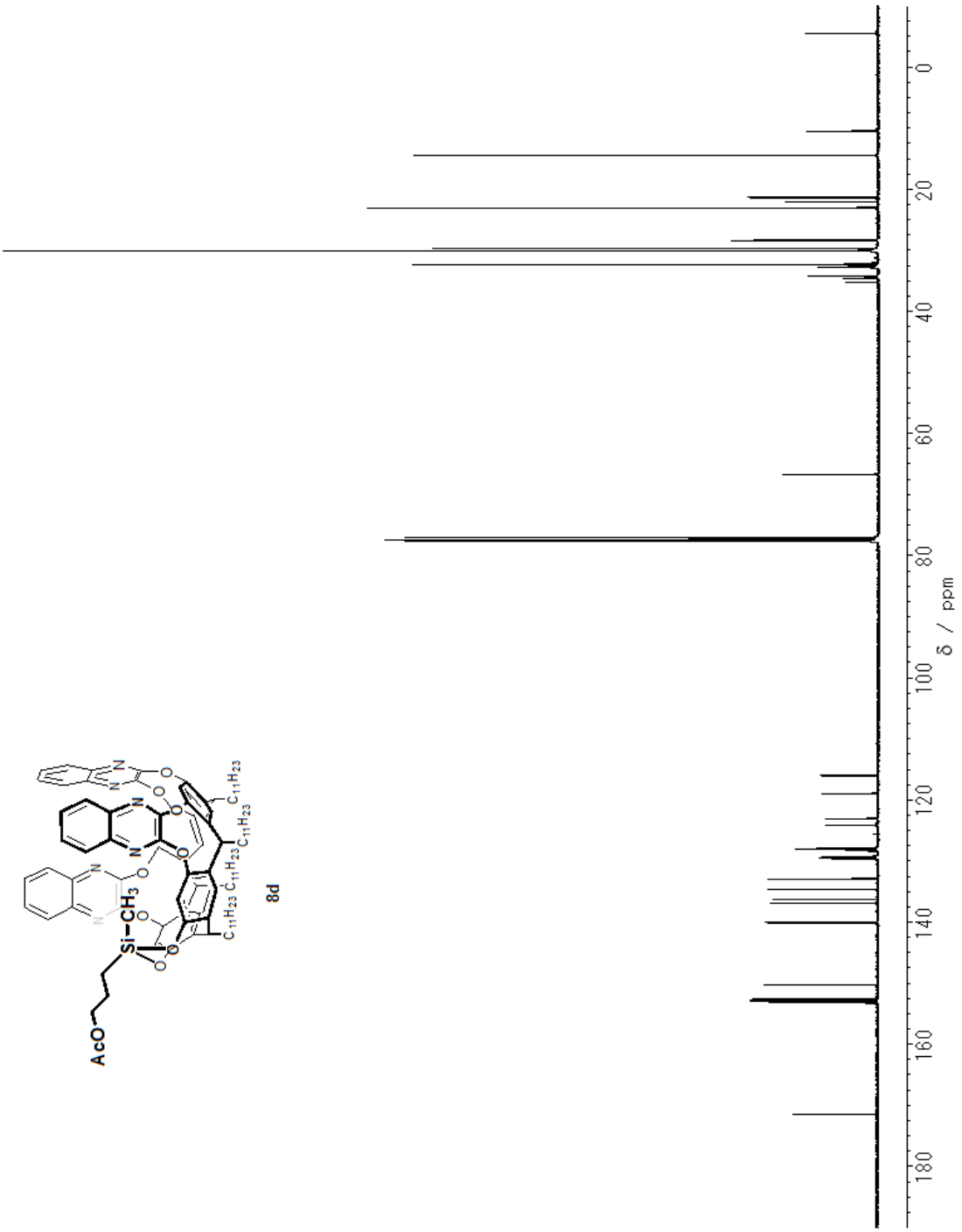
Compound 8d

^{1}H NMR spectrum in toluene-d_8



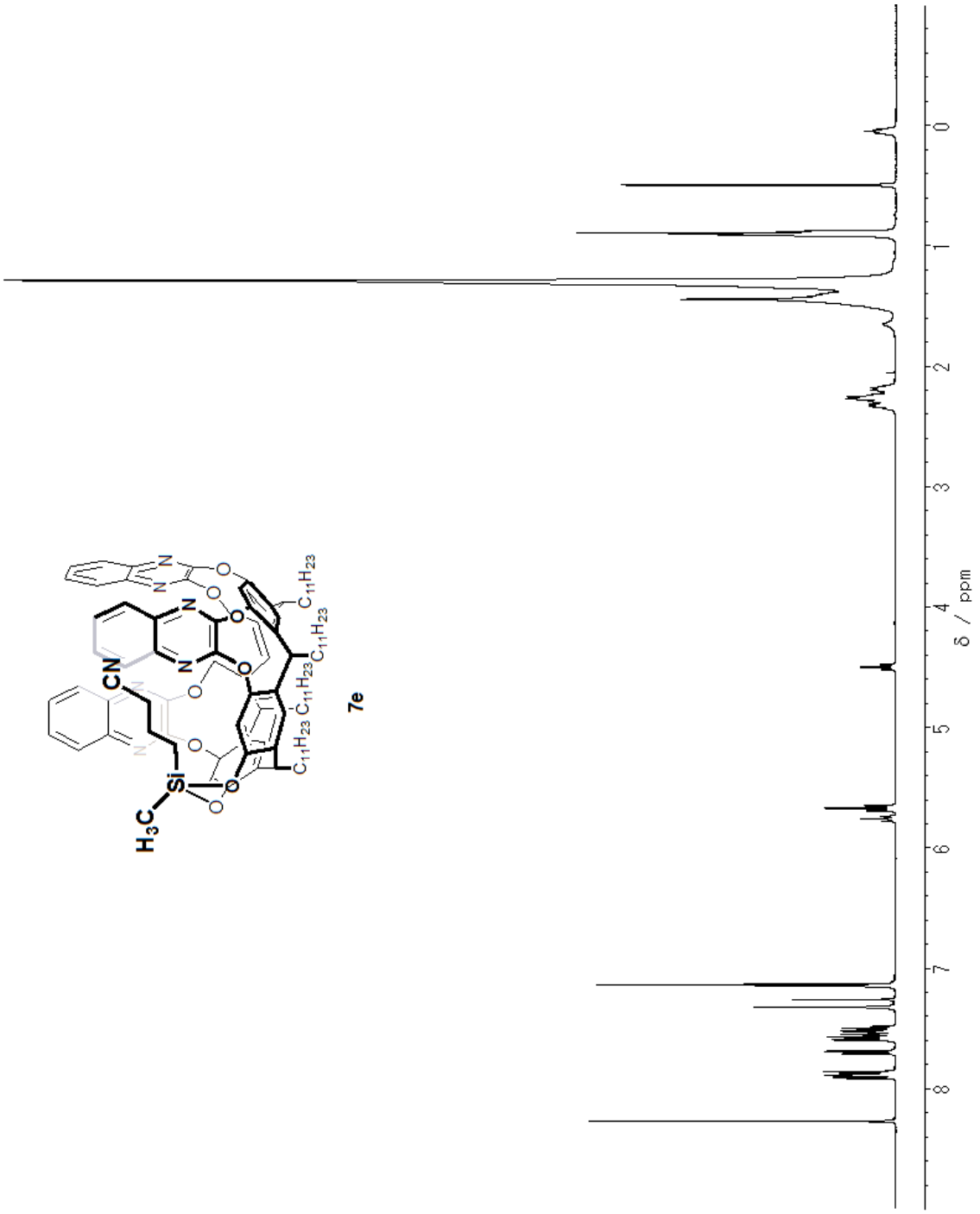
Compound 8d

^{13}C NMR spectrum in $CDCl_3$



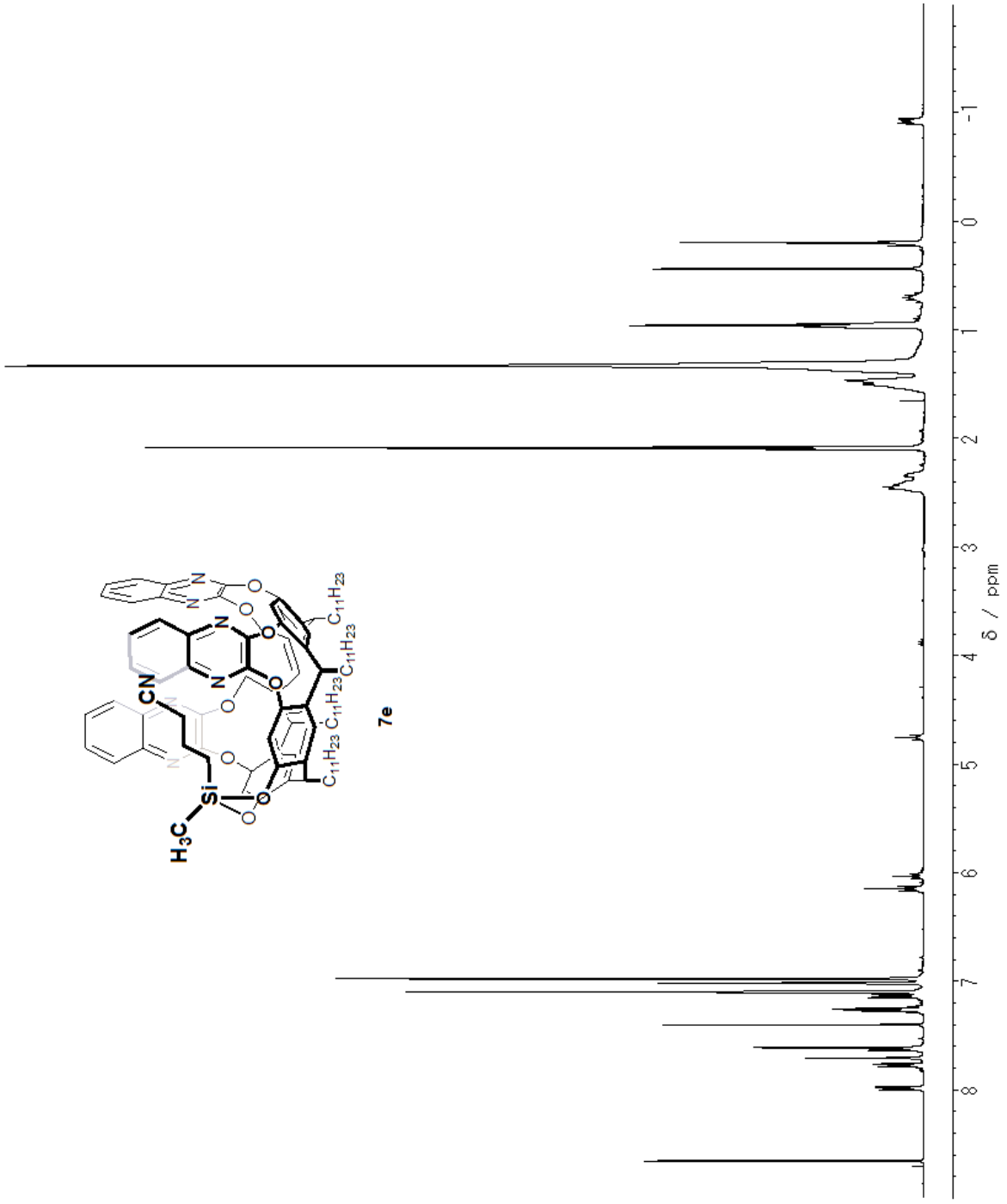
Compound 7e

^{1}H NMR spectrum in $CDCl_3$



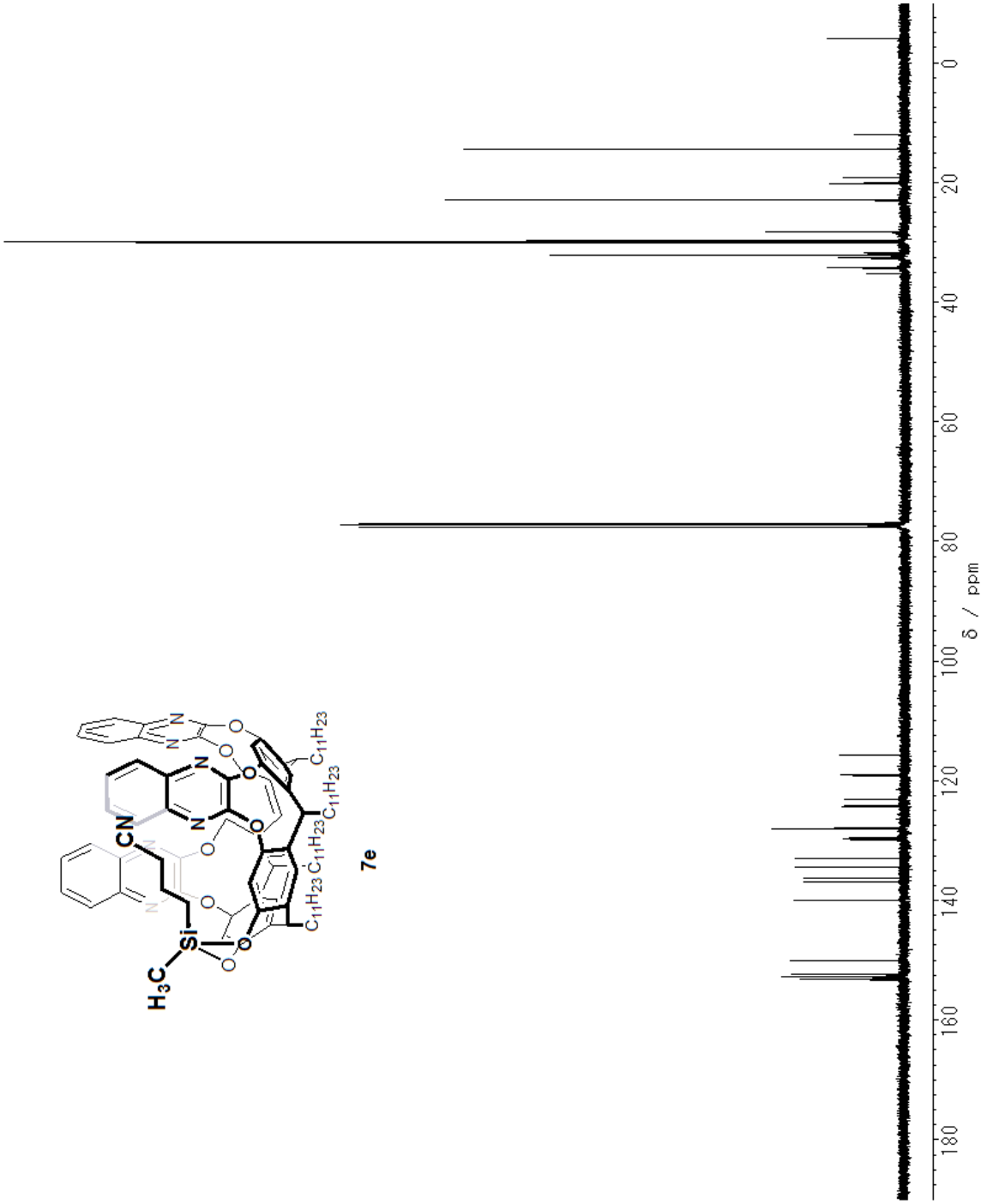
Compound 7e

^{1}H NMR spectrum in toluene-d_8



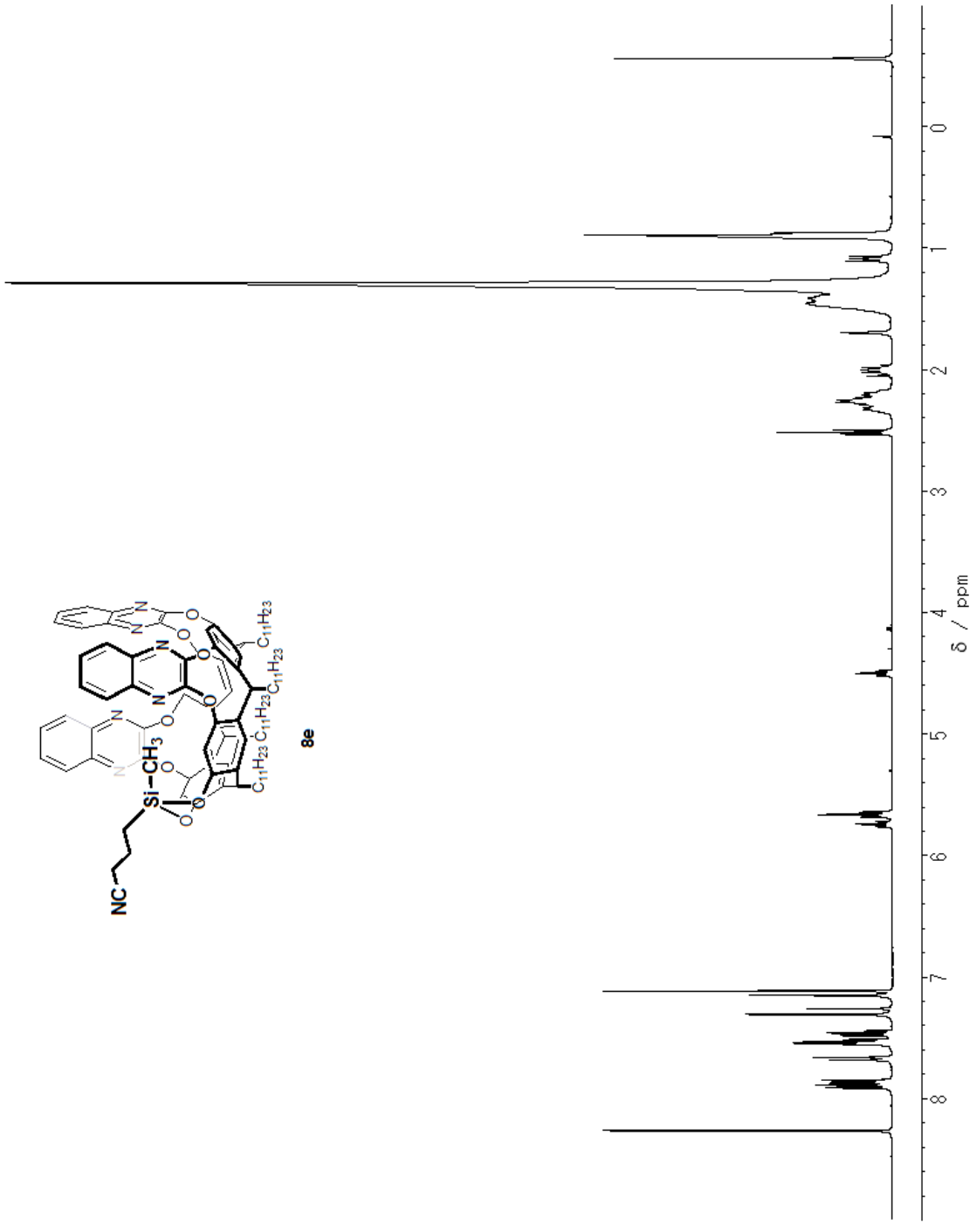
Compound 7e

^{13}C NMR spectrum in $CDCl_3$



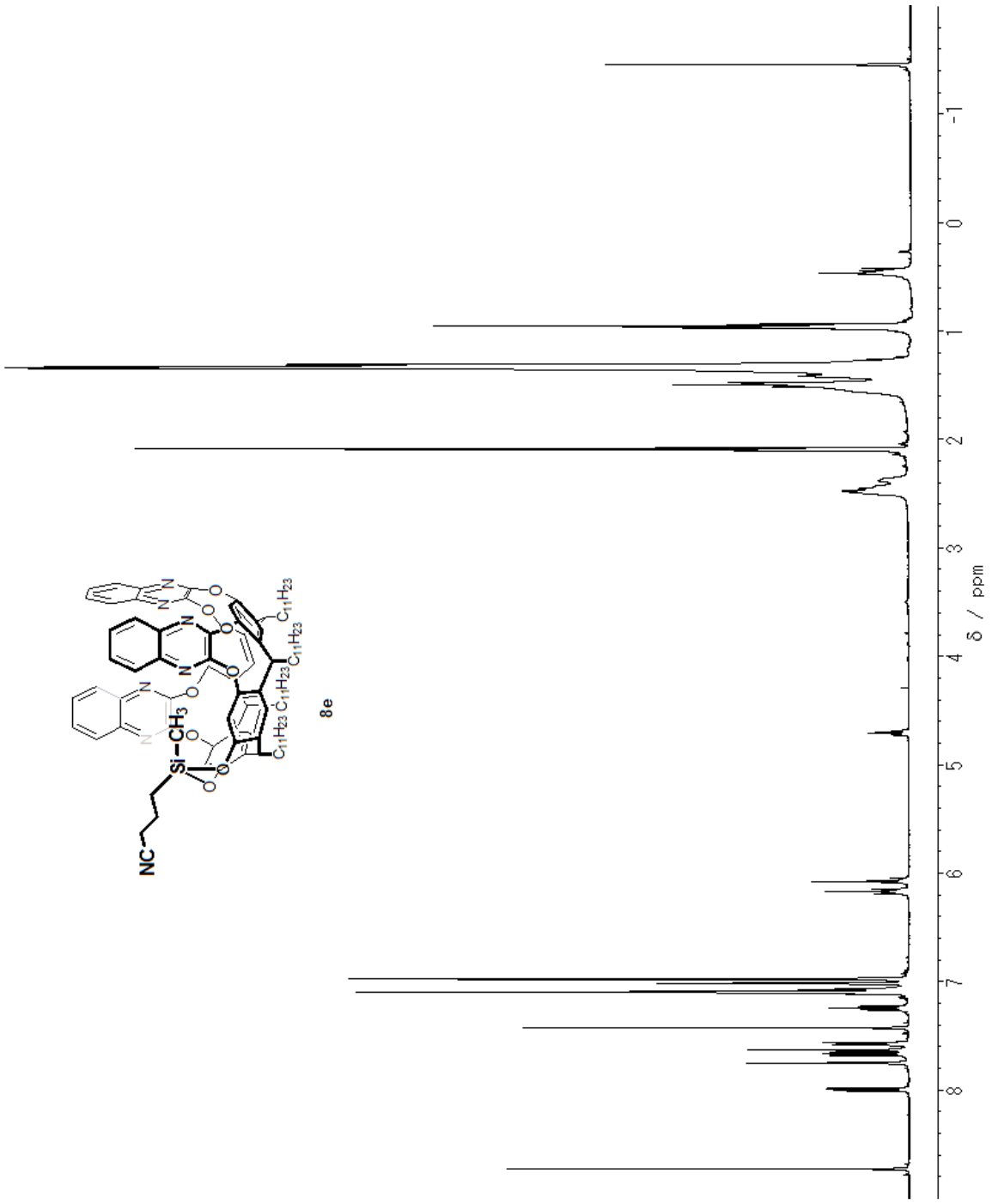
Compound 8e

^{1}H NMR spectrum in $CDCl_3$



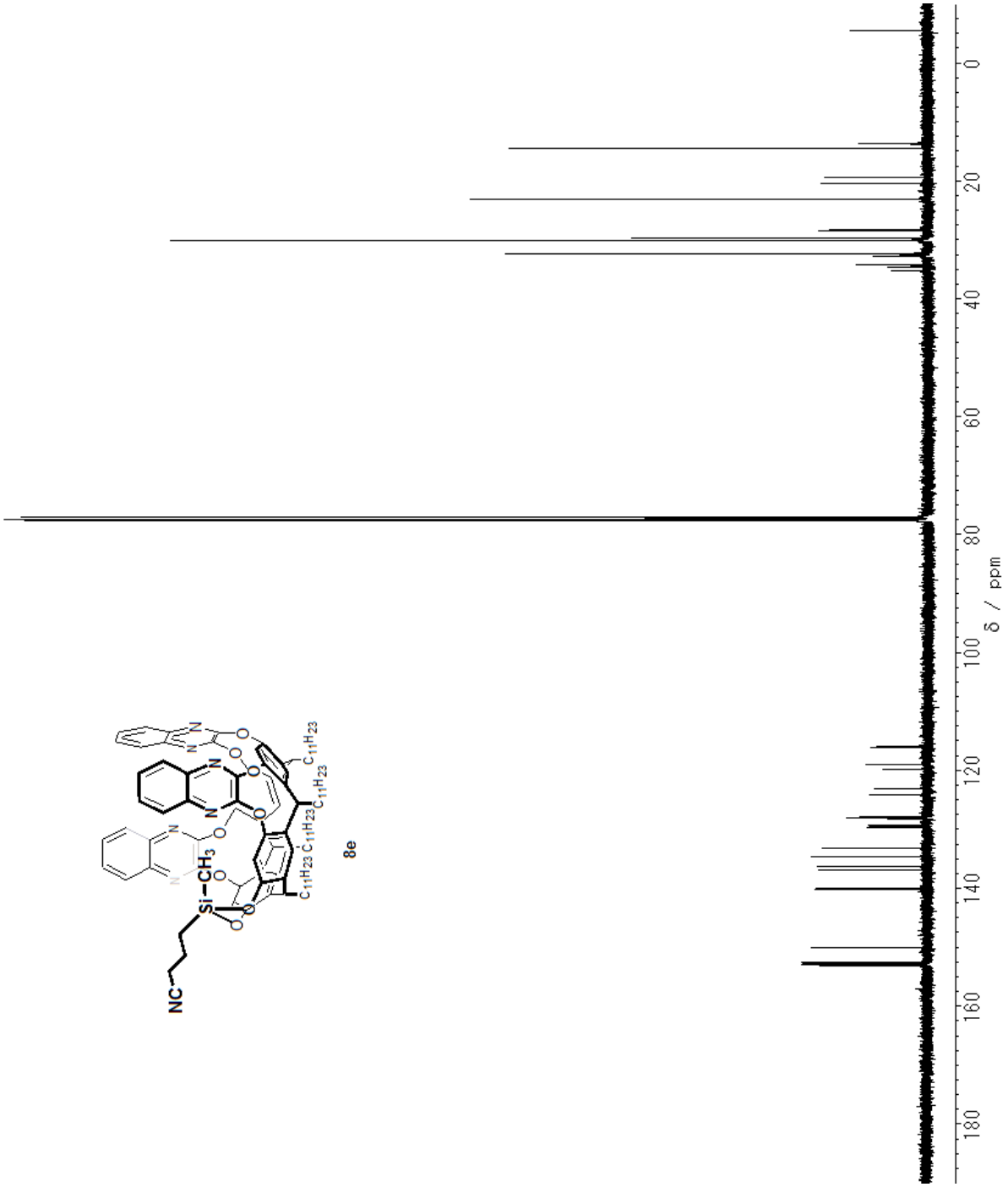
Compound 8e

^{1}H NMR spectrum in toluene-d_8



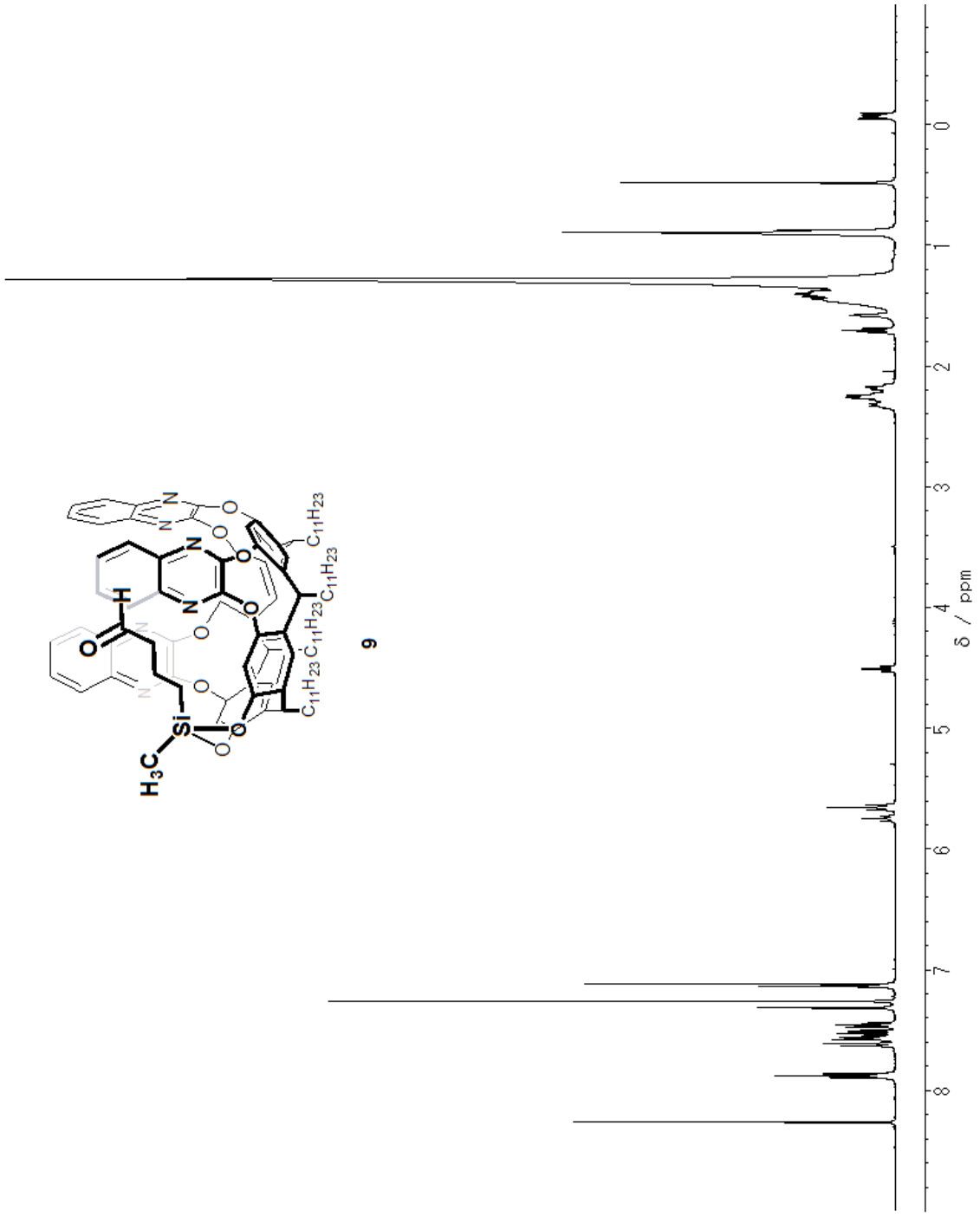
Compound 8e

^{13}C NMR spectrum in $CDCl_3$



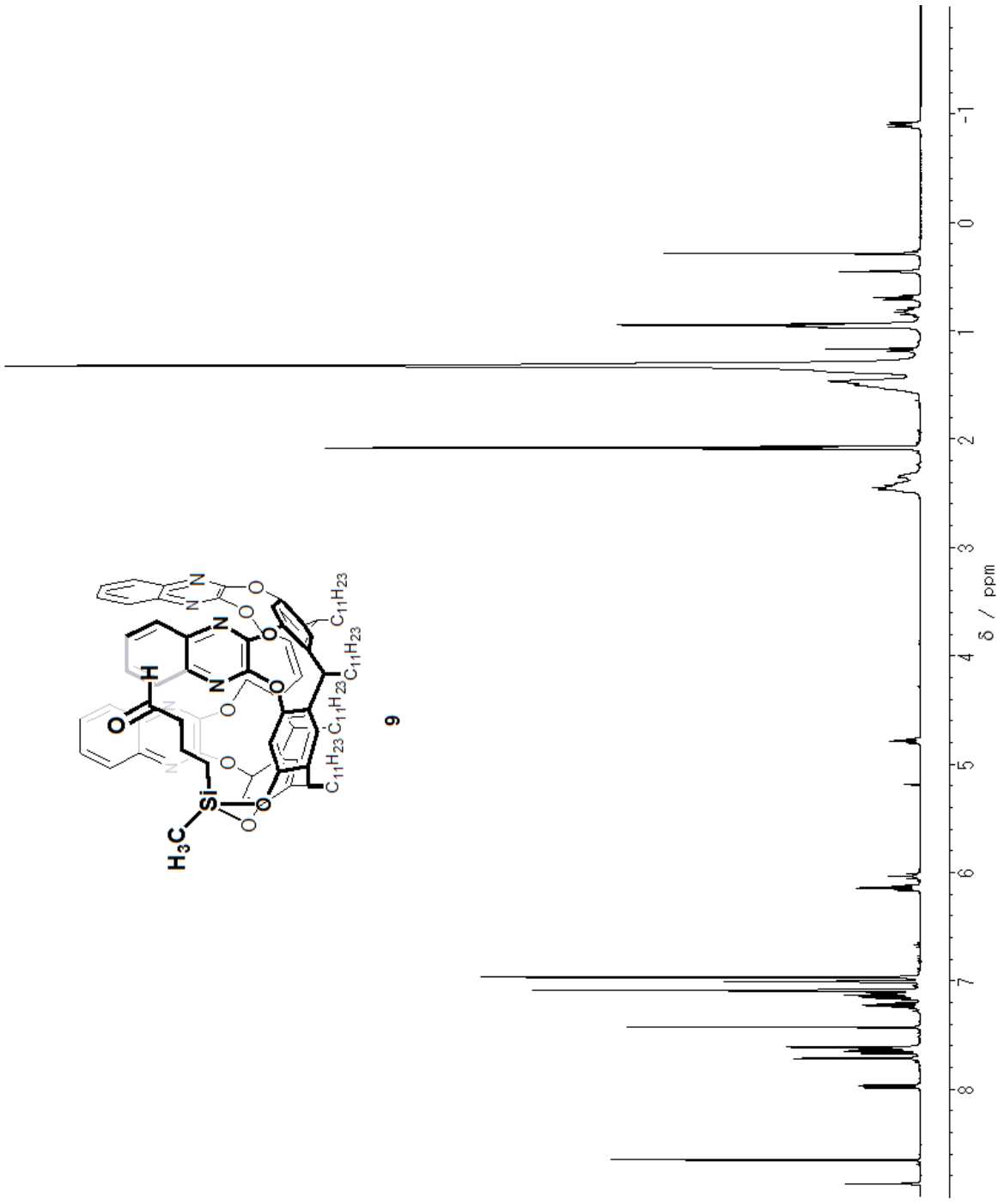
Compound 9

^{1}H NMR spectrum in $CDCl_3$



Compound 9

^{1}H NMR spectrum in toluene-d_8



Compound 9

^{13}C NMR spectrum in $CDCl_3$