Eur. J. Org. Chem. **2016** · ISSN 1099–0690

SUPPORTING INFORMATION

DOI: 10.1002/ejoc.201601070
Title: Evaluation of the Reactivity of Metallocatalytic Cavities in the Dimerization of Terminal Alkynes
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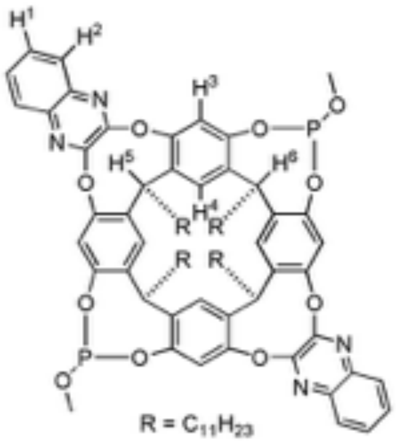
Contents

1. General Information.

All reactions were carried out under an argon or an nitrogen 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.). LRMS and HRMS were reported on the basis of TOF (time of flight)-MS (MALDI-TOF or LCMS-IT-TOF; Shimadzu), and DART (Direct Analysis in Real Time)-MS, and ESI (Thermo Fischer Scientific; Orbitrap FT-Mass). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a 5 mm QNP probe at 400 MHz, 100 MHz, and 162 MHz, respectively. Chemical shifts are reported in ppm with reference to residual solvent signals [^{1}H NMR: $CHCl_3$ (7.26), C_7H_8 (2.08), C_6H_6 (7.16), CH_2Cl_2 (5.32); ^{13}C NMR: $CDCl_3$ (77.0)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

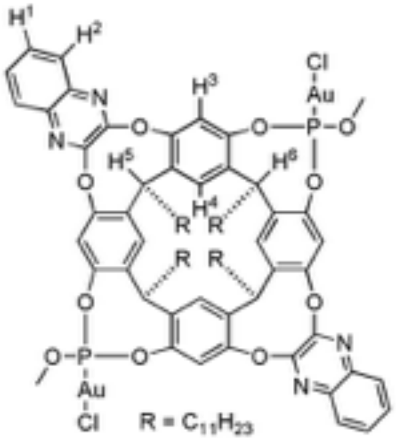
2. Synthesis of **2**, **6**, and **7** (Scheme 3).

For **6** and **7**: To the Schlenk tube charged with a solution of the tetra-hydroxy cavitand platform (136 mg, 0.1 mmol) in dry toluene (1 mL) under N_2 atmosphere at 135 °C, $EtN(\textit{i}Pr)_2$ (0.17 mL, 1 mmol) and $P(OCH_3)_3$ (0.09 mL, 0.8 mmol) were added. After stirred for 22 h, the mixture was allowed to cool to room temperature, and followed by concentration to give 156 mg of crude products as yellow viscous materials. Purification by silica-gel column chromatography (eluent: hexane/EtOAc, 9/1) afforded 54 mg of **6** (“out-out”) as colorless solid materials in 36% yield and 32 mg of **7** (“in-out”) as colorless solid materials in 22% yield. Data for **6**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.84 (dd, $J = 6.4, 3.4$ Hz, 4H, H^1 or H^2), 7.54 (dd, $J = 6.4, 3.4$ Hz, 4H, H^1or H^2), 7.41 (s, 4H, H^3), 7.25 (s, 4H, H^4), 5.74 (t, $J = 8.2$ Hz, 2H, H^5), 4.58 (t, $J = 7.6$ Hz, 2H, H^6), 3.97 (d, $^{3}J_{PH} = 8.7$ Hz, 6H,



$POC\underline{H}_3$), 2.31-2.24 (m, 8H, $C\underline{H}_2(CH_2)_9CH_3$), 1.46-1.30 (m, 72H, $CH_2(C\underline{H}_2)_9CH_3$), 0.93-0.88 (m, 12H, $CH_2(CH_2)_9C\underline{H}_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 152.8, 152.4, 147.1 (d, J_{CP} = 7.6 Hz), 139.8, 137.0 (d, J_{CP} = 2.1 Hz), 135.2, 129.4, 128.0, 122.8, 117.4 (d, J_{CP} = 2.6 Hz), 50.1 (d, J_{CP} = 3.6 Hz), 35.9, 34.0, 32.0 (many peaks are overlapped), 31.8, 29.8 (many peaks are overlapped), 29.5, 28.1, 28.0, 22.7 (many peaks are overlapped), 14.2 (many peaks are overlapped) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) 127.5 ppm; MS (MALDI-TOF) *m/z*: 1478 $[MH]^+$. IR (neat): 2925, 2852, 1572, 1487, 1395, 1335, 1159, 1032, 898 cm^{-1}. HRMS (ESI) calcd for $C_{90}H_{119}N_4O_{10}P_2$: 1477.8396 $[MH]^+$, found: 1477.8370. Data for **7**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.85-7.83 (m, 2H), 7.75-7.73 (m, 2H), 7.54-7.52 (m, 4H), 7.35 (s, 2H), 7.28 (s, 2H), 7.25 (s, 2H), 7.16 (s, 2H), 5.70 (t, *J* = 8.0Hz, 2H), 4.57 (t, *J* = 7.8 Hz, 1H), 4.51 (t, *J* = 8.0 Hz, 1H), 3.98 (d, $^3J_{PH}$ = 8.3 Hz, 3H), 3.10 (d, $^3J_{PH}$ = 12.4 Hz, 3H), 2.29-2.24 (m, 8H), 1.44-1.28 (m, 72H), 0.91-0.87 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 153.7, 153.6, 153.1, 152.5, 149.3 (d, J_{CP} = 15.0 Hz), 147.5 (d, J_{CP} = 5.5 Hz), 140.5, 140.4, 137.8 (d, J_{CP} = 2.4 Hz), 136.0, 135.8, 135.2, 130.1, 129.9, 128.8, 128.2, 123.9, 122.8, 118.0, 117.8, 52.1 (d, J_{CP} = 22.1 Hz), 50.9 (d, J_{CP} = 3.8 Hz), 37.1, 36.5, 34.6, 32.6 (many peaks are overlapped), 32.5, 32.4, 32.0, 30.4 (many peaks are overlapped), 30.1 (many peaks are overlapped), 28.7, 23.4 (many peaks are overlapped), 14.8 (many peaks are overlapped) ppm. ^{31}P (162 MHz, $CDCl_3$) 127.3, 111.6 ppm; MS (MALDI-TOF) *m/z*: 1479 $[MH_2]^+$. IR (neat): 2925, 2852, 1482, 1402, 1323, 1153, 1032, 898 cm^{-1}. Anal. Calcd for $C_{90}H_{118}N_4O_{10}P_2$: C, 73.14; H, 8.05; N, 3.79. Found: C, 73.14; H, 8.10; N, 3.88.

For **2**: Under N_2, a solution of "out-out" **6** (221 mg, 0.15 mmol) in toluene (3 mL) underwent addition of $AuCl \cdot S(CH_3)_2$ (106 mg, 0.36 mmol), and the mixture was stirred at room temperature for 30 min with confirmation that the appropriate cavitand had disappeared by TLC monitoring. After all the volatiles had been evaporated, the crude products were purified by short-plugged silica-gel column chromatography (eluent: hexane/EtOAc, 4:1) to afford the bis-Au **2** as white crystals in 62% yield. Data for **2**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.89 (dd, J = 6.2, 3.4 Hz, 4H, H^1 or H^2), 7.59 (dd, J = 6.2, 3.4 Hz, 4H, H^1 or H^2), 7.46 (s, 4H, H^3), 7.26 (s, 4H, H^4: this peak is overlapped with the peak of residual protons of $CDCl_3$), 5.75 (t, J = 8.2 Hz, 2H, H^5), 4.52 (t, J = 7.4 Hz, 2H, H^6), 4.12 (d, $^3J_{PH}$ = 13.8 Hz, 6H, POC$\underline{H}_3$), 2.32-2.21 (m, 8H, C$\underline{H}_2(CH_2)_9CH_3$), 1.41-1.24 (m, 72H, CH_2(C$\underline{H}_2$)$_9CH_3$), 0.91-0.86 (m, 12H, $CH_2(CH_2)_9$C$\underline{H}_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 152.9 (d, J_{CP} = 1.9 Hz), 151.5, 144.4 (d, J_{CP} = 4.8 Hz), 139.9, 136.9, 135.4 (d, J_{CP} = 2.6 Hz), 130.2, 128.3, 122.8, 117.6 (d, J_{CP} = 3.8 Hz), 54.6 (d, J_{CP} = 1.9 Hz), 35.7, 34.0, 32.3, 32.0 (many peaks are overlapped), 30.7, 29.7 (many peaks are overlapped), 29.4 (many peaks are overlapped), 27.9, 22.7 (many peaks are overlapped), 14.1 (many peaks are overlapped) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) 108.9 ppm. MS (ESI) *m/z*: 1906 $[M-Cl]^+$. IR (neat): 2921, 2851, 1608, 1581, 1482, 1401, 1329, 1271, 1154, 1037 cm^{-1}. HRMS (ESI) calcd for $C_{90}H_{118}Au_2ClN_4O_{10}P_2$: 1905.7337 $[M-Cl]^+$, found: 1905.7333.



3. Synthesis of **3**, **8-11** (Scheme 4).

For **8**: Under an argon atmosphere, a suspension of the platform **5** (1.9 g, 1.4 mmol) in *N*,*N*-dimethylacetamide that is namely DMA (14 mL) was heated in 80 °C for 5 min, and a base of K_2CO_3 (967 mg, 7.0 mmol) was added, and then 2,3-dibromopyrazine (809 mg, 3.4 mmol) was poured in one portion. After stirred for 14 h, the mixture was allowed to cool to ambient temperature, and the reaction was quenched with addition of water (25 mL) at 0 °C. The precipitation was filtered, and the solid materials was dissolved in CH_2Cl_2 (100 mL), and the resultant solution was transferred into a 300 mL separatory funnel. The organic phase was washed with brine (75 mL x 2), and dried over Na_2SO_4, and filtered, and concentrated *in vacuo* to give 2.07 g of whitish yellow solid materials as a crude. Purification by short-plugged silica-gel column chromatography (hexane/EtOAc 4/1) afforded **8** as white solid materials in 72% yield (1.52 g). Data for **8**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.88 (s, 4H), 7.85-7.82 (m, 8H), 7.57-7.55 (m, 4H),7.12 (s, 4H), 5.19 (brs, 4H), 2.20-2.18 (m, 8H), 1.38-1.26 (m, 72H), 0.90-0.87 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 154.0, 153.0 (two peaks are overlapped), 152.0, 139.7 (two peaks are overlapped), 135.8, 129.3, 127.8, 123.7 (two peaks are overlapped), 118.7, 34.6, 32.9, 32.3 (many peaks are overlapped), 30.0 (many peaks are overlapped), 29.7 (many peaks are overlapped), 28.2, 23.0 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm. MS (ESI) *m/z*: 1510 $[MH]^+$. IR (neat): 2922, 2851, 1605, 1576, 1479, 1415, 1397, 1328, 1281, 1145, 1116 cm^{-1}. HRMS (ESI) calcd for $C_{96}H_{117}N_8O_8$: 1509.8989 $[M]^+$, found : 1509.8975. Anal. Calcd for $C_{96}H_{116}N_8O_8$: C, 76.36; H, 7.74; N, 7.42. Found: C, 76.37; H, 7.75; N, 7.49.

For **9**: Under an argon atmosphere, to the suspension of **8** (1.36 g, 0.9 mmol) in DMF (9 mL) at 80 °C was added a base of CsF (2.73 g,18 mmol) in one portion, and then a stock solution of catechol (319 mg, 2.9 mmol) in DMF (4.5 mL) was slowly added over 1 min. After stirred at 80 °C for 30 min, the mixture was allowed to cool to ambient temperature, and the reaction was quenched with 1 M aq. HCl (25 mL) at 0 °C. The collected precipitation was dissolved in $CHCl_3$ (150 mL), and the resultant solution was transferred into a 300 mL separatory funnel. The organic phase was washed with brine (100 mL x 2), and dried over Na_2SO_4, and filleted, and concentrated *in vacuo* to give a crude of 1.54 g as a whitish yellow solid material. Purification with short-plugged silica gel column chromatography (CH_2Cl_2/EtOAc 19/1 ~ 4/1) afforded 1.05 g of **9** as a yellowish white solid material. Further reprecipitation from $CHCl_3/CH_3OH$ (1/8 v/v) yielded **9** of white solid materials in 82% (0.927 g). Data for **9**: ^{1}H NMR (400 MHz, $CDCl_3$) 8.28 (brs, 4H), 7.62 (brs, 4H), 7.23 (s, 4H), 6.99 (s, 4H), 5.40 (brs, 2H), 4.35 (t, *J* = 7.4 Hz, 2H), 2.22-2.18 (m, 8H), 1.38-1.28 (m, 72H), 0.89-0.87 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 153.5, 152.9, 151.8, 138.8, 131.5, 129.4, 123.7, 111.1, 34.3, 33.7, 33.0, 32.3 (many peaks are overlapped), 30.1 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.4, 23.0 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm. MS (ESI) *m/z*: 1258 [MH]$^+$. IR (neat): 3350, 3068, 2918, 2849, 1614, 1583, 1489, 1410, 1289, 1171, 1154 cm^{-1}. HRMS (ESI) calcd for $C_{80}H_{113}N_4O_8$: 1257.8553 [MH]$^+$, found : 1257.8540. Anal. Calcd for $C_{80}H_{112}N_4O_8$: C, 76.39; H, 8.98; N, 4.45. Found: C, 76.39; H, 9.16; N, 4.48.

For **10** and **11**: Under an argon atmosphere, to a colorless solution of **9** (252 mg, 0.2 mmol) in toluene (2 mL) under refluxing condition (oil bath temp. 135 °C) was added $P(OCH_3)_3$ (0.19 mL, 1.6 mmol). After stirred for 8 h, the mixture was allowed to cool to ambient temperature, and followed by evaporation of all the volatiles. The resultant yellow viscous materials was purified with silica gel column chromatography (hex/EtOAc 4/1), giving "*out-out*" **10** of white solid materials in 48% (132 mg) and "*in-out*" **11** of colorless solid materials in 19% (52 mg). Data for **10**: ^{1}H NMR (400 MHz, $CDCl_3$) 8.03 (s, 4H), 7.26 (s, 4H), 7.25 (s, 4H), 5.72 (t, *J* = 8.1 Hz, 2H), 4.57 (t, *J* = 7.5 Hz, 2H), 3.94 (d, $^3J_{PH}$ = 9.0 Hz, 6H), 2.30-2.23 (m, 8H), 1.44-1.29 (m, 72H), 0.93-0.88 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 154.7, 153.0, 147.5 (d, J_{CP} = 5.7 Hz), 140.2, 137.4 (d, J_{CP} = 2.9 Hz), 135.6, 123.3, 117.7 (d, J_{CP} = 2.6 Hz), 50.5 (d, J_{CP} = 2.9 Hz), 36.2, 34.1, 32.30, 30.28, 32.2, 30.1 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.34, 28.29, 23.05 (many peaks are overlapped) 14.5 (many peaks are overlapped) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) 127.7 ppm. MS (ESI) *m/z*: 1378 [MH]$^+$. IR (neat): 2918, 2849, 1605, 1572, 1483, 1399, 1278, 1156, 1140, 1023 cm^{-1}. HRMS (ESI) calcd for $C_{82}H_{115}N_4O_{10}P_2$: 1377.8083 [MH]$^+$, Found : 1377.8083. Anal. Calcd for $C_{82}H_{114}N_4O_{10}P_2$: C, 71.48; H, 8.34; N, 4.07. Found: C, 71.48; H, 8.41; N, 4.10. Data for **11**: ^{1}H NMR (400 MHz, $CDCl_3$) 8.01 (d, *J* = 2.8

Hz, 2H), 7.98 (d, *J* = 2.8 Hz, 2H), 7.26 (s, 2H), 7.23 (s, 2H), 7.16 (s, 2H), 7.11 (s, 2H), 5.68 (t, *J* = 8.2 Hz, 2H), 4.57 (t, *J* = 7.7 Hz, 1H), 4.49 (t, *J* = 7.9 Hz, 1H), 3.95 (d, $^3J_{PH}$ = 8.9 Hz, 3H), 3.27 (d, $^3J_{PH}$ = 12.4 Hz, 3H), 2.26-2.24 (m, 8H), 1.42-1.29 (m, 72H), 0.91-0.86 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.2, 155.1, 153.3, 152.7 (d, J_{CP} = 1.7 Hz), 149.3 (d, J_{CP} = 15.3 Hz), 147.5 (d, J_{CP} = 5.7 Hz), 140.4, 140.3, 137.8 (d, J_{CP} = 2.9 Hz), 136.1, 135.9, 135.3, 124.0, 123.0, 118.0 (d, J_{CP} = 2.6 Hz), 117.7, 52.3 (d, J_{CP} = 21.9 Hz), 51.0 (d, J_{CP} = 2.6 Hz), 37.1, 36.5, 34.3, 32.6 (many peaks are overlapped), 32.4, 32.0, 30.4, 30.1 (many peaks are overlapped), 28.6 (many peaks are overlapped), 23.4 (many peaks are overlapped), 14.8 (many peaks are overlapped) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) 127.8, 111.1 ppm. MS (ESI) *m/z*: 1378 $[MH]^+$; IR (neat): 2921, 2851, 1606, 1578, 1482, 1400, 1281, 1141, 1034 cm^{-1}. HRMS (ESI) calcd for $C_{82}H_{115}N_4O_{10}P_2$: 1377.8083 $[MH]^+$, found : 1377.8053. Anal. Calcd for $C_{82}H_{114}N_4O_{10}P_2$: C, 71.48; H, 8.34; N, 4.07. Found: C, 71.48; H, 8.35; N, 4.12.

For **3**: Under N_2, a solution of “out-out” **10** (197 mg, 0.14 mmol) in toluene (3 mL) underwent addition of $AuCl \cdot S(CH_3)_2$ (101 mg, 0.34 mmol), and the mixture was stirred at room temperature for 30 min with confirmation that the appropriate cavitand had disappeared by TLC monitoring. After all the volatiles had been evaporated, the crude products were purified by short-plugged silica-gel column chromatography (eluent: hexane/EtOAc, 4:1) to afford the bis-Au **3** as white solids in 84% yield (220 mg). Data for **3**: ^{1}H NMR (400 MHz, $CDCl_3$) 8.11 (s, 4H), 7.35 (s, 4H), 7.23 (s, 4H), 5.67 (t, *J* = 7.9 Hz, 2H), 4.53 (t, *J* = 7.8 Hz, 2H), 4.11 (d, $^3J_{PH}$ = 13.8 Hz, 6H), 2.31-2.14 (m, 8H), 1.45-1.25 (m, 72H), 0.90-0.85 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 154.0, 153.2, 144.6 (d, J_{CP} = 2.6 Hz), 141.7, 137.5, 136.2 (d, J_{CP} = 2.9 Hz), 123.4, 119.1 (d, J_{CP} = 4.3 Hz), 55.2 (d, J_{CP} = 1.7 Hz), 35.9, 34.0, 33.3, 32.3 (many peaks are overlapped), 30.8, 30.0 (many peaks are overlapped), 29.9 (many peaks are overlapped), 29.7 (many peaks are overlapped), 28.2 (many peaks are overlapped), 23.0 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) 112.7 ppm. MS (ESI) *m/z*: 1806 [M-Cl]$^+$. IR (neat): 2922, 2850, 1605, 1578, 1480, 1398, 1272, 1141, 1030 cm^{-1}. HRMS (ESI) calcd for $C_{82}H_{114}Au_2ClN_4O_{10}P_2$: 1805.7024 [M-Cl]$^+$, Found : 1805.7011.

4. Synthesis of **4**, **12-15** (Scheme 5).

For **12**: A solution of di-quinoxaline-spanned resorcin[4]arene (0.2 mmol, 272 mg) in toluene (1 mL) and DMSO (4 mL) was stirred at 55 °C for 5 min, and followed by addition of K_2CO_3 (0.8 mmol, 111 mg) and CH_2BrCl (4 mmol, 0.27 mL). After the mixture was stirred at 55 °C for 1 h, additional CH_2BrCl (4 mmol, 0.27 mL) was blended. The reaction was monitored for further 2.5 h, and allowed to cool to room temperature. The reaction mixture was poured into 10 mL of cold water, and the mixture was transferred into a 50 mL separatory funnel. The aqueous phase was extracted with CH_2Cl_2 (10 mL x 3), and the combined organic phases were washed with water (10 mL x 3) and brine (10 mL), and dried over Na_2SO_4, and filtered off, and concentrated to give a crude of 252 mg as a yellow solid material. After short-plugged column chromatography (SiO_2, hexane/EtOAc = 9/1), purification of reprecipitation from CH_2Cl_2 (0.5 mL)/CH_3OH (4 mL) gave 202 mg of **12** as a white solid material (73%). Data of **12**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.79 (dd, *J* = 6.2, 3.4 Hz, 4H), 7.54 (dd, *J* = 6.2, 3.4 Hz, 4H), 7.24 (s, 4H), 7.16 (s, 4H), 5.69 (d, *J* = 7.4 Hz, 2H), 5.66 (t, *J* = 8.2 Hz, 2H), 4.70 (t, *J* = 7.9 Hz, 2H), 4.10 (d, *J* = 7.4 Hz, 2H), 2.24-2.21 (m, 8H), 1.39-1.25 (m, 72H), 0.89-0.84 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.6, 153.2, 152.3, 140.1, 138.9, 136.1, 129.8, 128.3, 122.4, 117.5, 99.7, 36.7, 34.3, 32.3 (many peaks are overlapped), 32.1, 30.7, 30.2, 30.1 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.33, 28.26, 23.0 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm. MS (ESI) *m/z*: 1382 [MH]$^+$. IR (neat): 2920, 2841, 1487, 1414, 1341, 1165, 977 cm^{-1}. HRMS (ESI) calcd for $C_{90}H_{117}N_4O_8$: 1381.8866 [MH]$^+$, found : 1381.8849. Anal. Calcd for $C_{90}H_{116}N_4O_8$: C, 78.22; H, 8.46; N, 4.05. Found: C, 78.38; H, 8.45; N, 4.07.

For **13**: To a solution of **12** (1.3 mmol, 1.8 g) in DMF (13 mL) at 80 °C was added CsF (3.95 g, 26 mmol), and followed by addition of a solution of catechol (462 mg, 4.2 mmol) in DMF (6.5 mL). After the reaction mixture was stirred at 80 °C for 30 min, the mixture was allowed to cool to room temperature, and followed by quenching with slow addition of 1 M aqueous HCl (39 mL). The precipitates was filtered off, and washed thoroughly with water (350 mL), and dried up at ambient temperature. The filter cake was dissolved into CH_2Cl_2 (300 mL), and the solution was washed with brine (100 mL), and dried over Na_2SO_4, and filtered, and concentrated *in vacuo* to give a crude of 3.75 g as a whitish brown solid material. Purification by short-plugged column chromatography (SiO_2, CH_2Cl_2 only; then CH_2Cl_2/EtOAc = 4/1) was performed, and followed by recrystallization from CH_3OH (3.16 mL/g) to give 1.15 g of **13** (77%) as a yellowish white crystals. Data of **13**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.17 (s, 4H), 6.35 (s, 4H), 5.57 (d, *J* = 7.3 Hz, 2H), 4.67 (t, *J* = 8.0 Hz, 2H), 4.45 (d, *J* = 7.3 Hz, 2H), 4.27 (t, *J* = 7.7 Hz, 2H), 2.25-2.16 (m, 8H), 1.45-1.25 (m, 72H), 0.90-0.87 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 155.2, 151.0, 134.6, 128.8, 122.7, 110.4, 100.1, 36.1, 34.0, 33.8, 32.3 (many peaks are overlapped), 30.2 (many peaks are overlapped), 30.1 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.4, 23.0 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm; MS (ESI) *m/z*: 1128 $[M-H]^-$; IR (neat): 3272 (OH), 2920, 2846, 1584, 1493, 1286, 1165, 964 cm^{-1}; HRMS (ESI) calcd for $C_{74}H_{111}O_8$: 1127.8279 $[M-H]^-$, found : 1127.8256; Anal. Calcd for $C_{74}H_{112}O_8$: C, 78.68; H, 9.99. Found: C, 78.67; H, 9.95.

For **14** and **15**: To a solution of **13** (0.1 mmol, 113 mg) in toluene (1 mL) under refluxing condition (oil bath temp. 135 °C) was added $EtN(iPr)_2$ (0.17 mL, 1 mmol) and $P(OCH_3)_3$ (0.09 mL, 0.8 mmol). After overnight stirring, the mixture was allowed to cool to room temperature, and followed by concentration to give a crude of 168 mg as a yellowish white viscous material. Purification by silica-gel column chromatography (hexane/EtOAc = 9/1) afforded 52 mg of “out-out” **14** (41%) as a white solid material and 15 mg of “in-out” **15** (12%) as a white solid material. Data of **14**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.14 (s, 4H), 6.57 (s, 4H), 5.70 (d, J = 7.2 Hz, 2H), 4.74 (t, J = 7.2 Hz, 2H), 4.57 (t, J = 7.9 Hz, 2H), 4.55 (d, J = 7.2 Hz, 2H), 3.91 (d, $^{3}J_{PH}$ = 9.0 Hz, 6H), 2.24-2.18 (m, 8H), 1.39-1.27 (m, 72H), 0.90-0.87 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 155.5, 146.8 (d, J_{CP} = 4.1 Hz), 138.1, 137.2 (d, J_{CP} = 2.6 Hz), 121.6, 117.3 (d, J_{CP} = 2.4 Hz), 99.6, 50.3 (d, J_{CP} = 2.6 Hz), 36.5, 35.9, 32.3 (many peaks are overlapped), 31.4, 30.3, 30.0 (many peaks are overlapped), 29.7 (many peaks are overlapped), 28.2 (many peaks are overlapped), 23.0 (many peaks are overlapped), 14.4 (many peaks are overlapped) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) 127.7 ppm. MS (ESI) *m/z*: 1250 [MH]$^+$; IR (neat): 2921, 2851, 1606, 1577, 1488, 1285, 1152, 1090, 1022 cm^{-1}; HRMS (ESI) calcd for $C_{76}H_{115}O_{10}P_2$: 1249.7960 [MH]$^+$, Found : 1249.7951. Data of **15**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.17 (s, 2H), 7.07 (s, 2H), 6.57 (s, 2H), 6.42 (s, 2H), 5.67 (d, J = 7.2 Hz, 2H), 4.67 (t, J = 8.0 Hz, 1H), 4.56 (d, J = 7.2 Hz, 2H), 4.51 (t, J = 8.0 Hz, 1H), 3.94 (d, $^{3}J_{PH}$ = 8.9 Hz, 3H), 3.57 (d, $^{3}J_{PH}$ = 12.7 Hz, 3H), 2.22-2.20 (m, 8H), 1.41-1.27 (m, 72H), 0.90-0.87 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 156.0 (d, J_{CP} = 1.4 Hz), 155.3, 148.7 (d, J_{CP} = 15.3 Hz), 146.7 (d, J_{CP} = 4.1 Hz), 138.7, 137.7 (d, J_{CP} =2.9 Hz), 137.6, 135.7, 122.2, 121.5, 117.4 (d, J_{CP} = 3.1 Hz), 117.1, 100.0, 52.8 (d, J_{CP} = 21.9 Hz), 51.0 (d, J_{CP} = 3.6 Hz), 37.0, 36.9, 36.3, 32.6 (many peaks are overlapped), 31.5, 31.4, 30.9, 30.5, 30.45, 30.37 (many peaks are overlapped), 30.06 (many peaks are overlapped), 28.60, 28.55, 23.4 (many peaks are overlapped), 14.8 (many peaks are overlapped) ppm. ^{31}P NMR (162 MHz, $CDCl_3$) 127.0, 110.4 ppm. MS (ESI) *m/z*: 1250 [MH]$^+$. IR (neat): 2921, 2851, 1607, 1578, 1489, 1283, 1149, 1023, 969 cm^{-1}. HRMS (ESI) calcd for $C_{76}H_{115}O_{10}P_2$: 1249.7960 [MH]$^+$, Found : 1249.7952.

For **4**: Under N_2, a solution of "out-out" **14** (186 mg, 0.15 mmol) in toluene (2 mL) underwent addition of $AuCl\bullet S(CH_3)_2$ (106 mg, 0.36 mmol), and the mixture was stirred at room temperature for 30 min with confirmation that the **14** had disappeared by TLC monitoring. After all the volatiles had been evaporated, the crude products were purified by short-plugged silica-gel column chromatography (eluent: hexane/EtOAc, 4:1) to afford 187 mg of **4** as white solid materials in 73% yield. Data of **4**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.20 (s, 4H), 6.65 (s, 4H), 5.70 (d, J = 7.2 Hz, 2H), 4.76 (t, J = 7.8 Hz, 2H), 4.71 (d, J = 7.2 Hz, 2H), 4.43 (t, J = 7.9 Hz, 2H), 4.04 (d, $^3J_{PH}$ = 13.7 Hz, 6H), 2.24-2.22 (m, 8H), 1.49-1.26 (m, 72H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 156.2 (d, J_{CP} = 2.4 Hz), 144.8, 139.8, 135.6 (d, J_{CP} = 4.1 Hz), 122.1, 118.2 (d, J_{CP} = 4.8 Hz), 100.2, 55.1, 36.7, 36.0, 32.3 (many peaks are overlapped), 31.1, 30.5, 30.0 (many peaks are overlapped), 29.7 (many peaks are overlapped), 28.2, 23.0, 14.4 (many peaks are overlapped) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) 116.2 ppm. MS (ESI) *m/z*: 1678 [MH]$^+$. IR (neat): 2918, 2849, 1608, 1581, 1489, 1282, 1180, 1149, 957 cm^{-1}. HRMS (ESI) calcd for $C_{76}H_{114}Au_2ClO_{10}P_2$: 1677.6901 [M-Cl]$^+$, Found: 1677.6881.

5. Typical procedure for the cross-dimerization (Scheme 6 and Table 1).

Under N_2, the bis-Au catalyst (0.01 mmol) in a 25 mL of two-necked flask was dissolved in dry toluene (5 mL), and the starting alkynes of ethynylbenzene (102 mg, 1 mmol) and the other partner 1.5 mmol (165 mg of 1-octyne or 195 mg of 4-phenyl-1-butyne) were added. After addition of AgOTf (5.0 mg, 0.02 mmol) at room temperature, the reaction was conducted for the appropriate hours. The solvent was evaporated off, and filtered through a short-plugged column chromatography to give a crude product, and the following purification by silica-gel column chromatography (eluent: hexane only) afforded the corresponding cross-dimerized adduct in the appropriate yields described in Table 1. The molar ratios of cross-adduct to homo-adduct was determined in the crude state. All the dimerized adducts were identical to the authentic samples that we previously reported in the reference.[1]

6. Typical procedure for the homo-dimerization (Scheme 7 and Table 2).

Under N_2, the bis-Au catalyst (0.01 mmol) in a 25 mL of two-necked flask was dissolved in dry toluene (5 mL), and the starting alkynes of 1 mmol (115 mg of 1-octyne or 130 mg of 4-phenyl-1-butyne) was added. After addition of AgOTf (5.0 mg, 0.02 mmol) at room temperature, the reaction was conducted for the appropriate hours. The solvent was evaporated off, and filtered through a short-plugged column chromatography to give a crude product, and the following purification by silica-gel column chromatography (eluent: hexane only) afforded the corresponding homo-dimerized adduct in the appropriate yields and ratios described in Table 2 and 3. The molar ratios of isomers were determined in the purified state. The homo-dimerized adducts were identical to the authentic samples that we previously reported in the reference.[1]

7. The ^{1}H and ^{13}C NMR spectra of new 13 compound **2-4, 6-15**.

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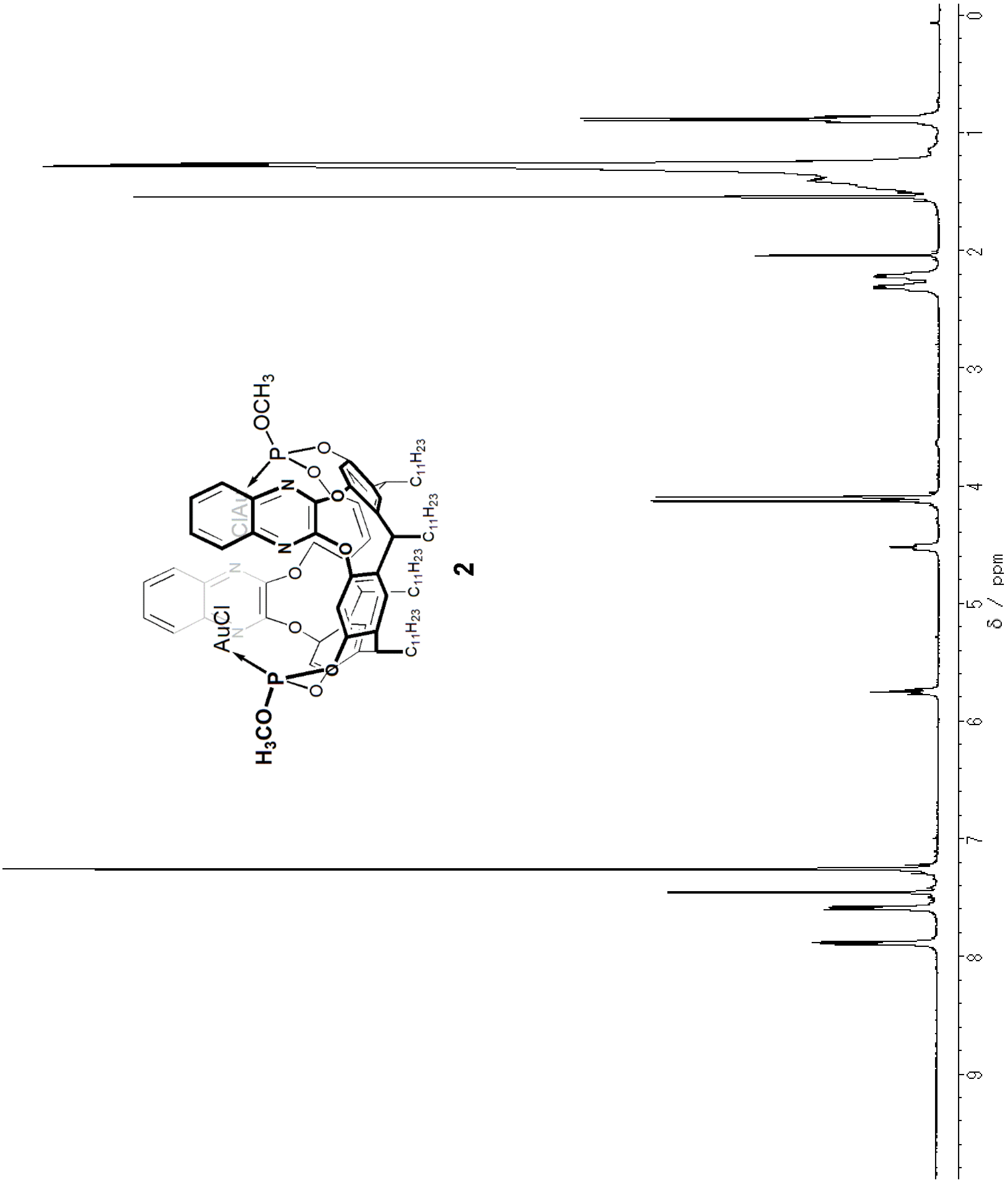
[1] N. Endo, M. Kanaura, M. P. Schramm, T. Iwasawa, *Eur. J. Org. Chem.* **2016**, 2514-2521.

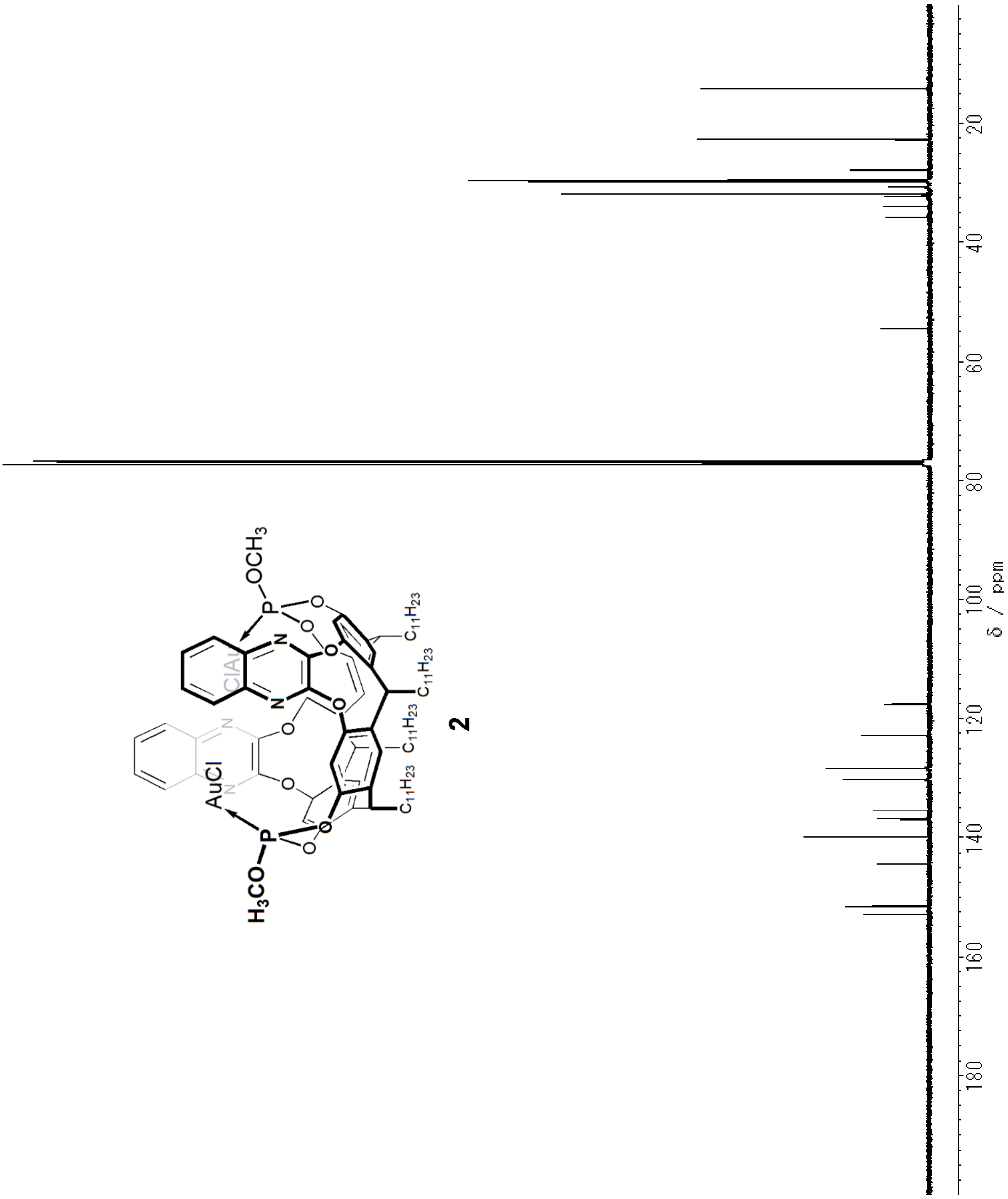
Compound 2

^{1}H NMR spectrum in $CDCl_3$



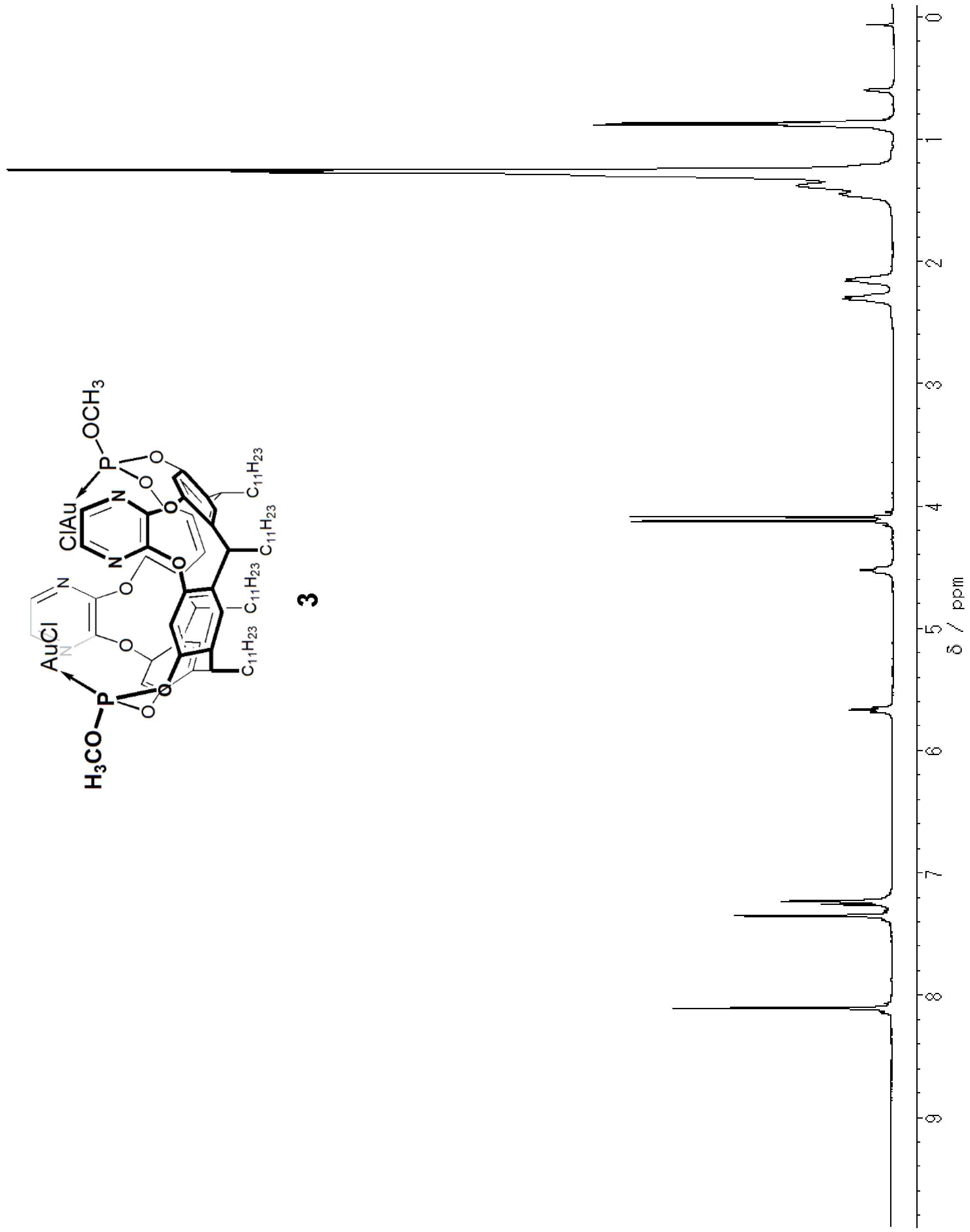
Compound 2

^{13}C NMR spectrum in $CDCl_3$



Compound 3

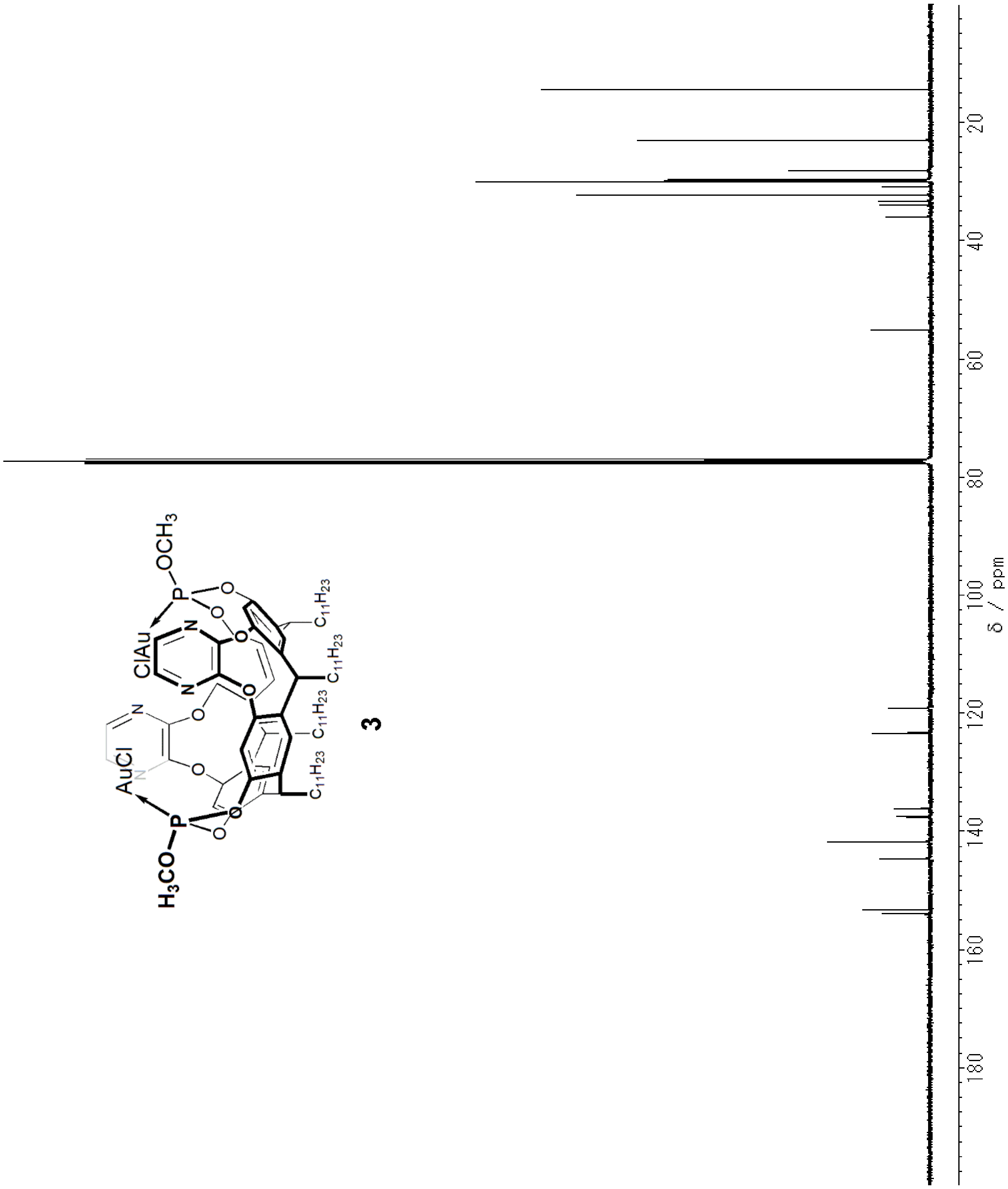
^{1}H NMR spectrum in CDCl$_3$



3

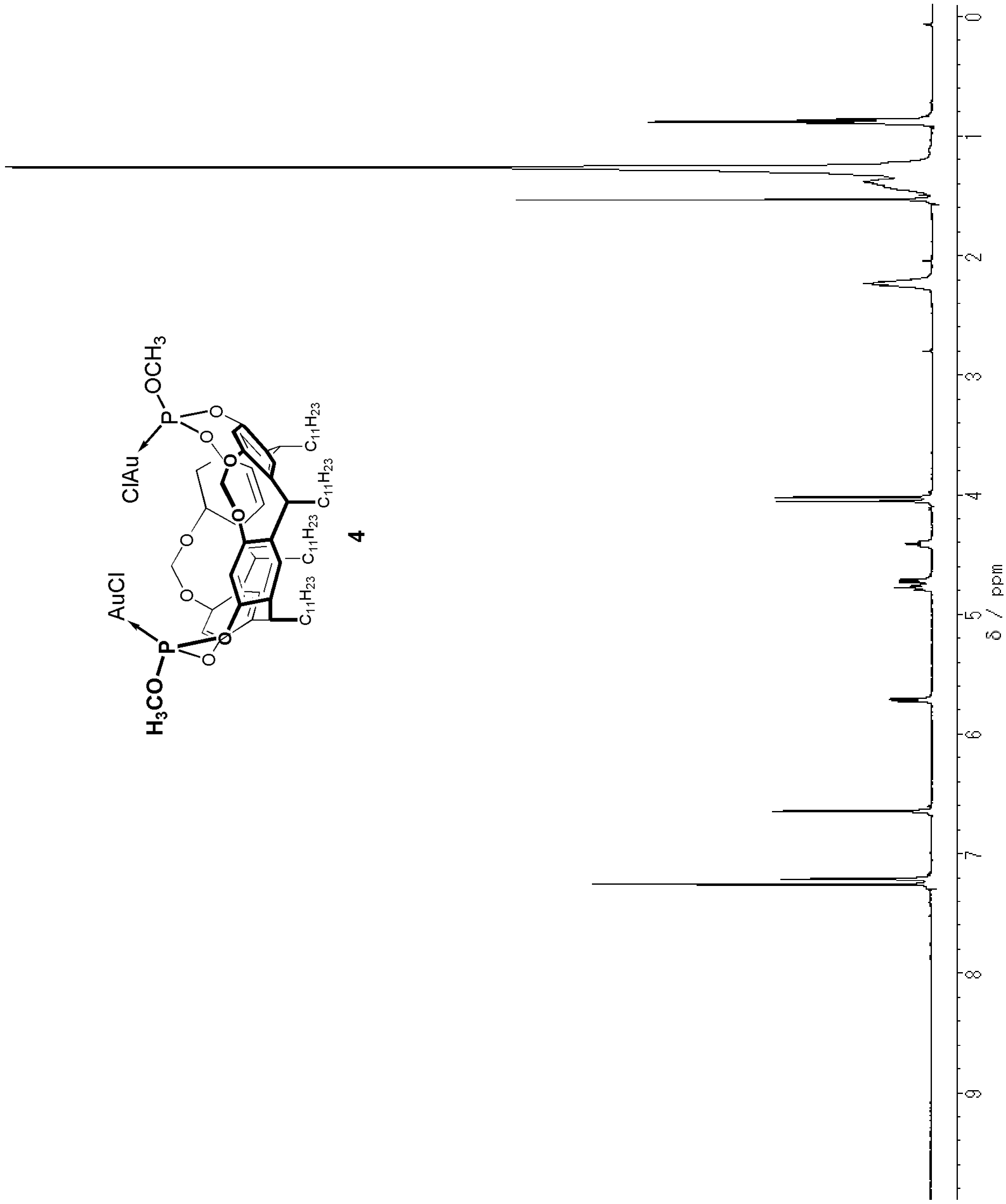
Compound 3

^{13}C NMR spectrum in $CDCl_3$



Compound 4

^{1}H NMR spectrum in $CDCl_3$



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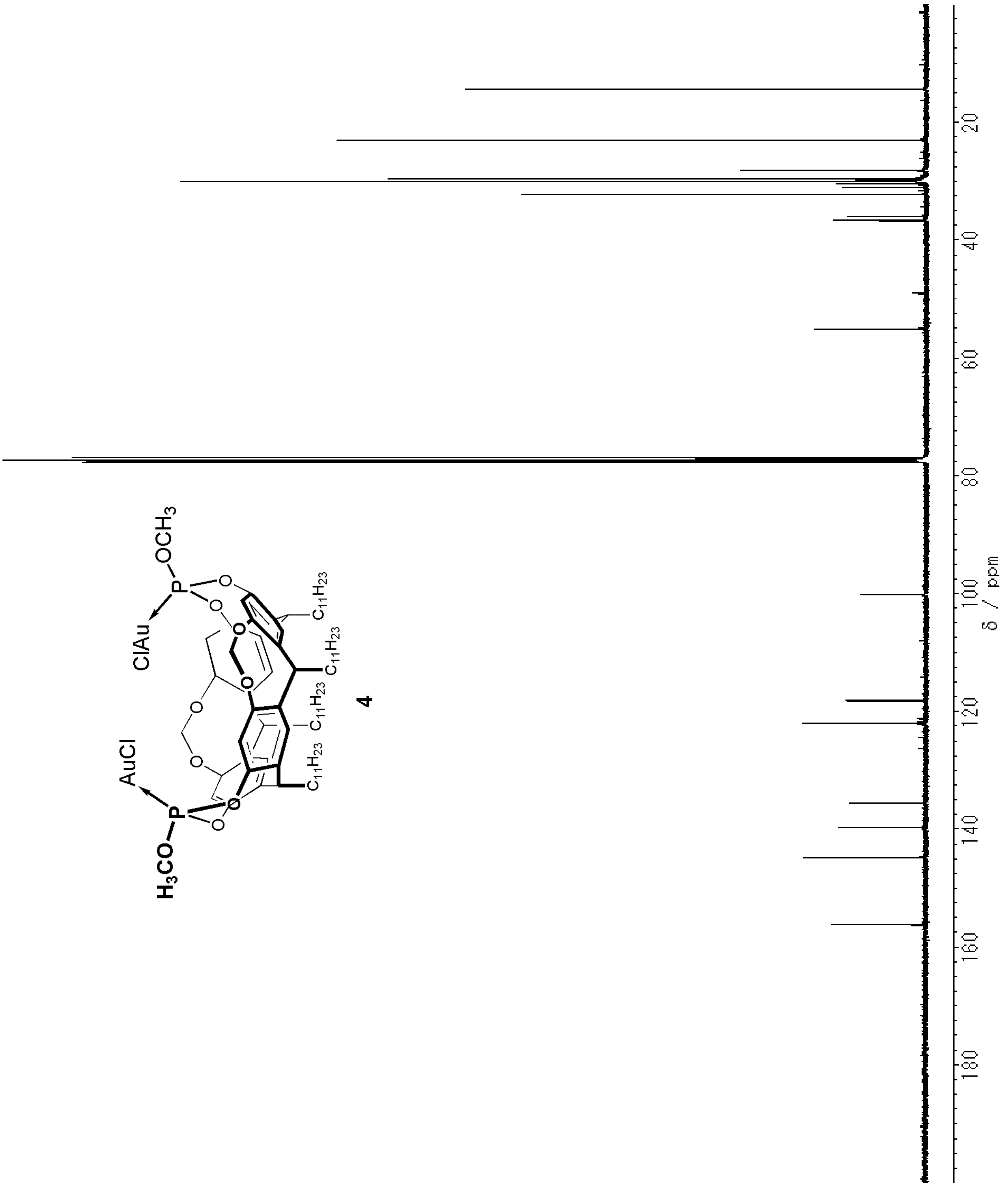
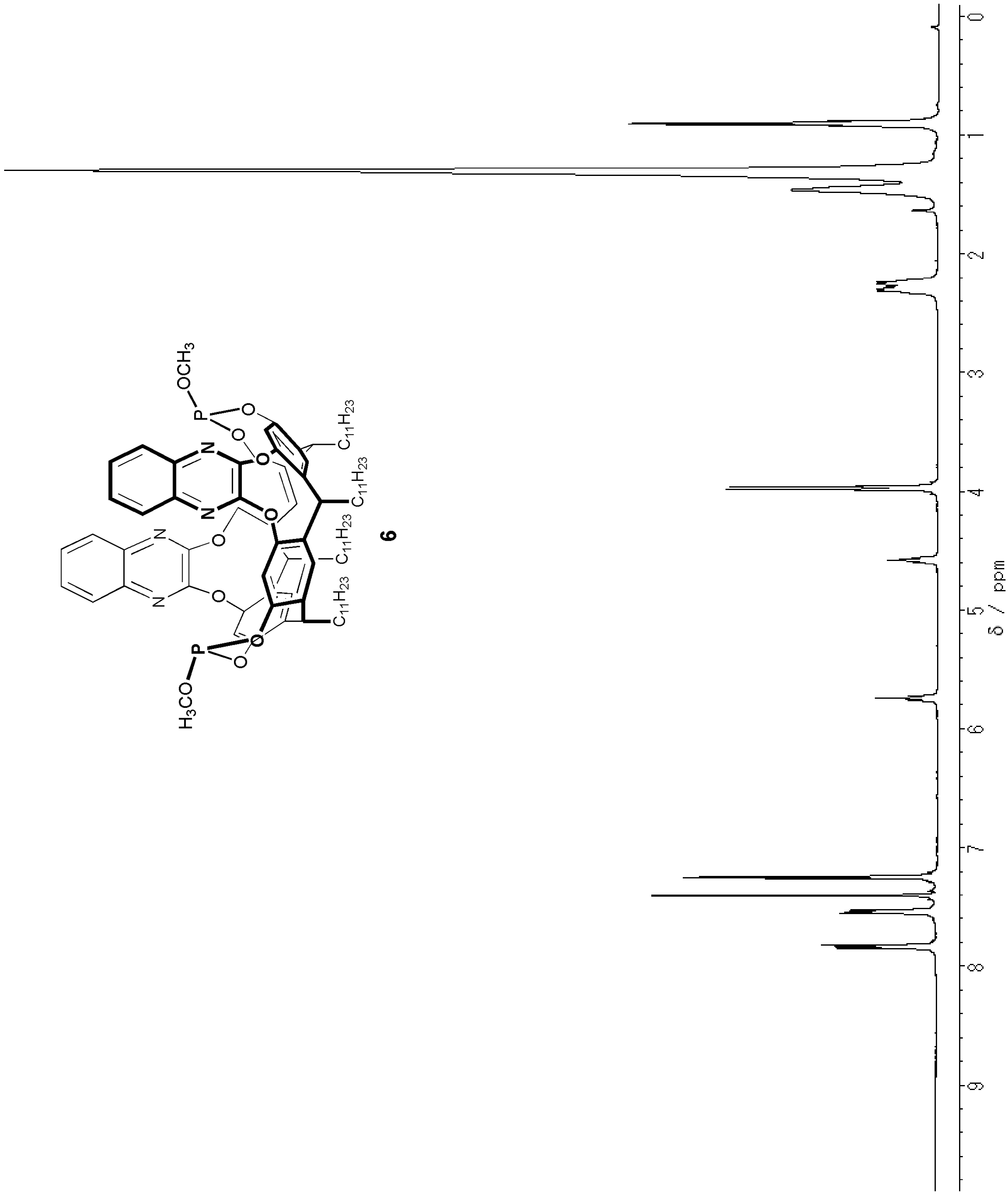
Compound 4

^{13}C NMR spectrum in CDCl$_3$



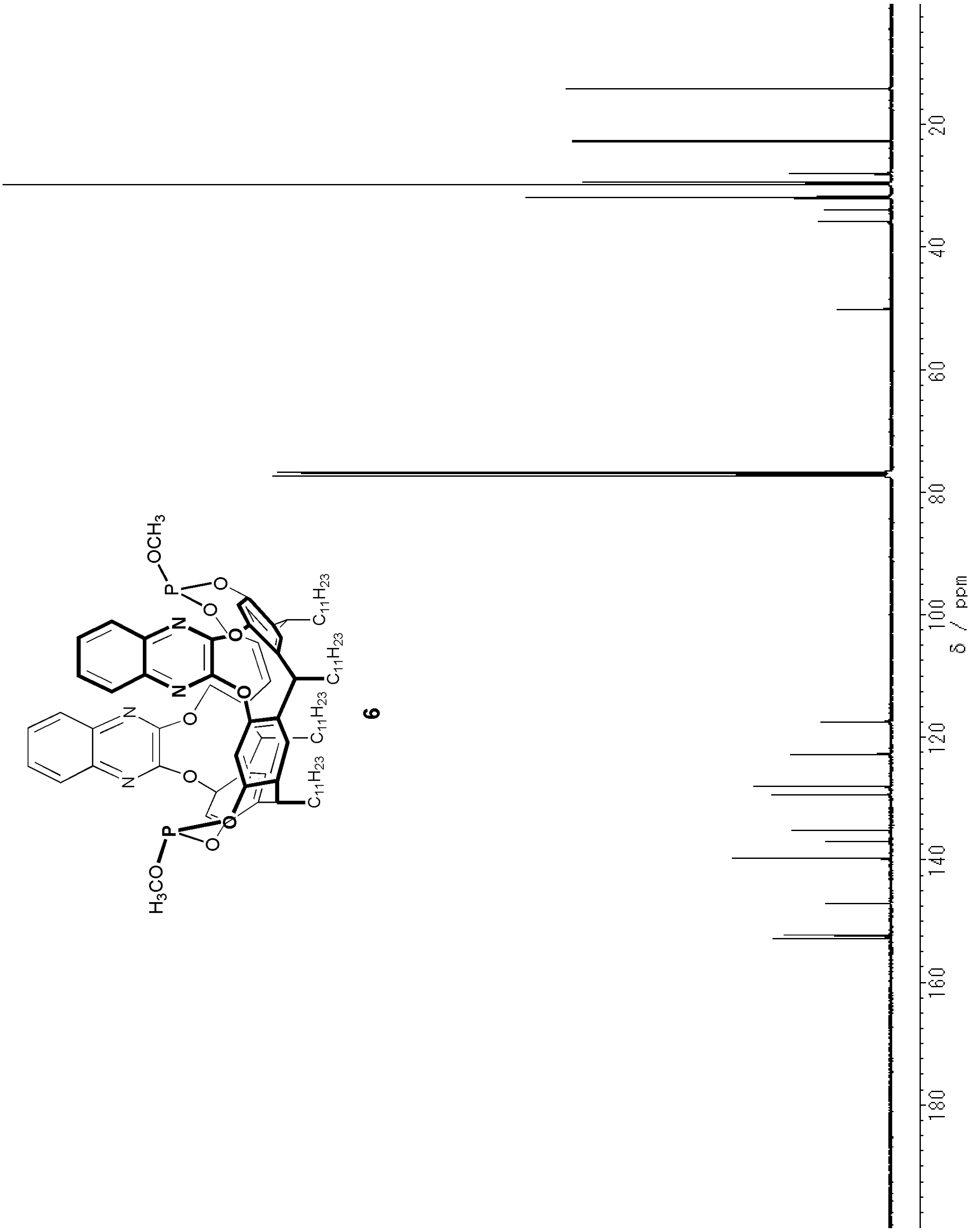
Compound 6

^{1}H NMR spectrum in $CDCl_3$



Compound 6

^{13}C NMR spectrum in $CDCl_3$



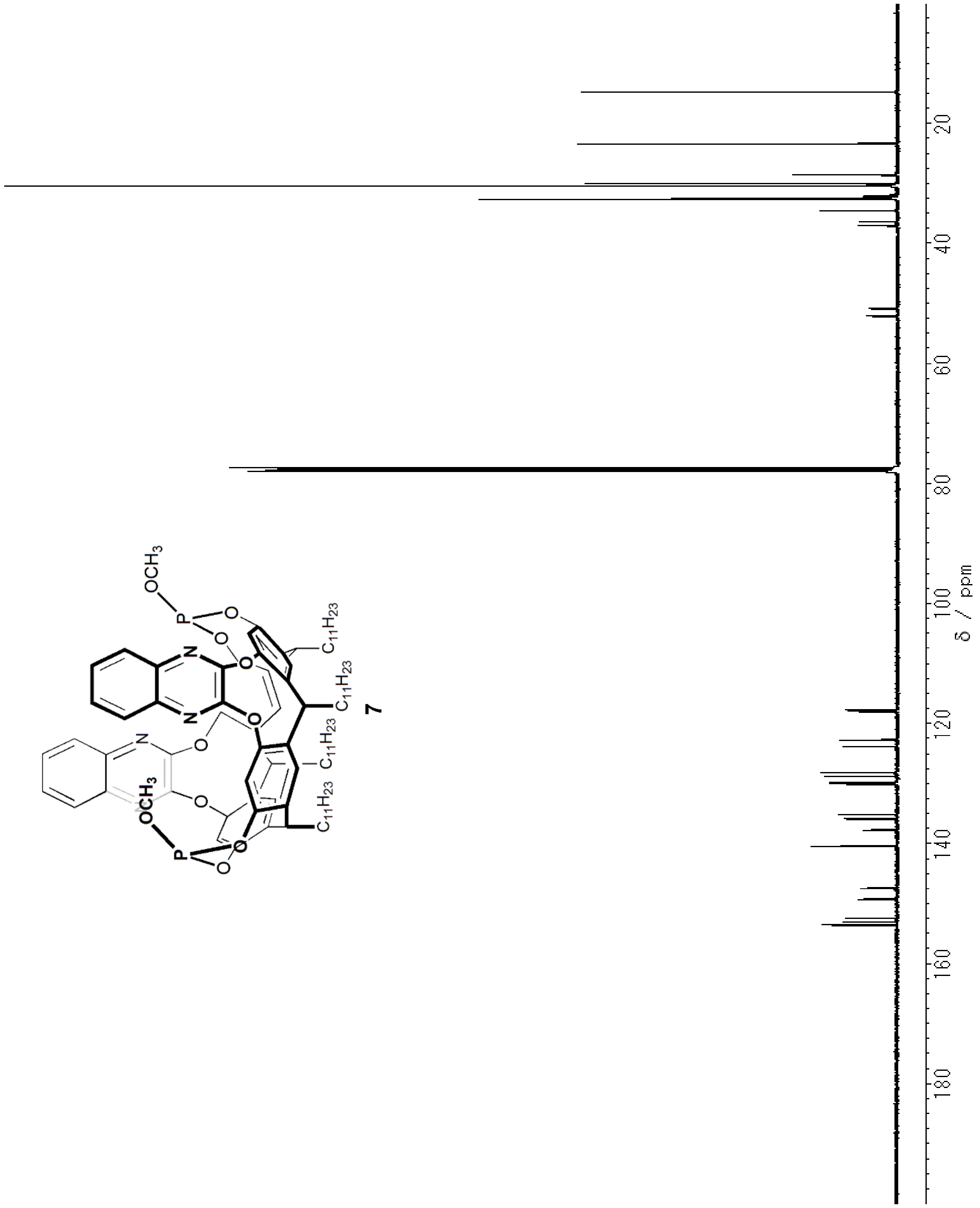
6

Compound 7

^{1}H NMR spectrum in $CDCl_3$

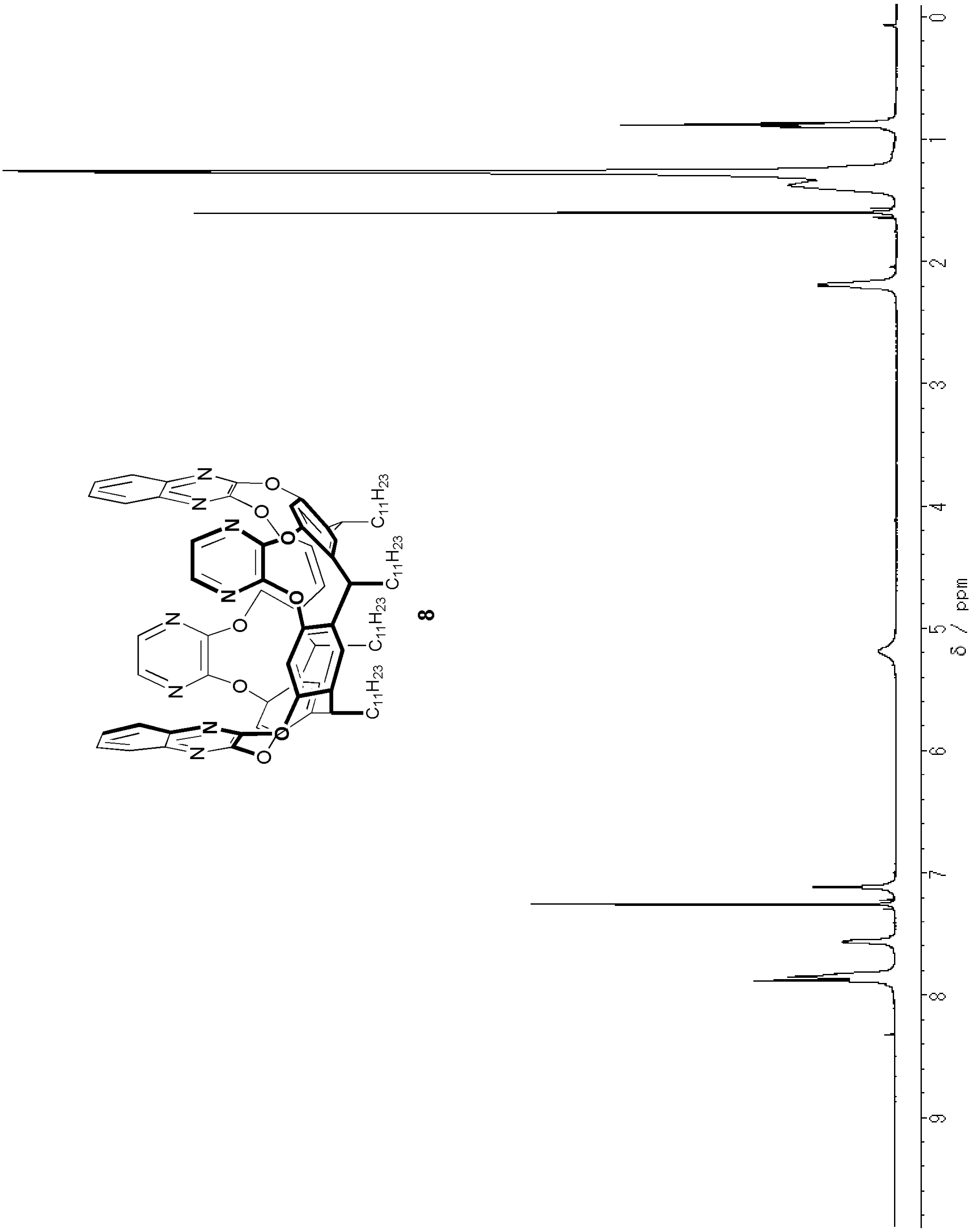
Compound 7

^{13}C NMR spectrum in $CDCl_3$



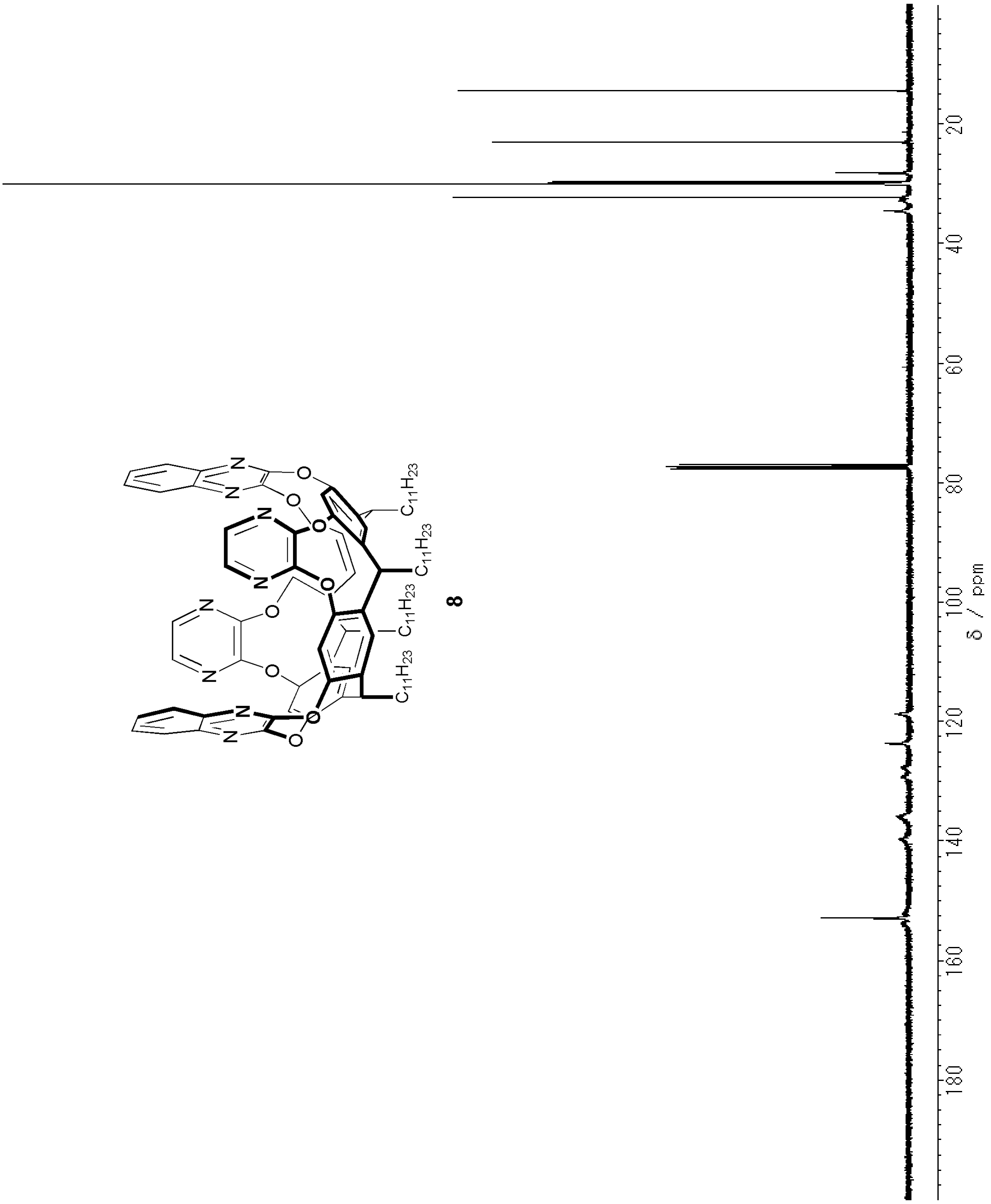
Compound 8

^1H NMR spectrum in $CDCl_3$



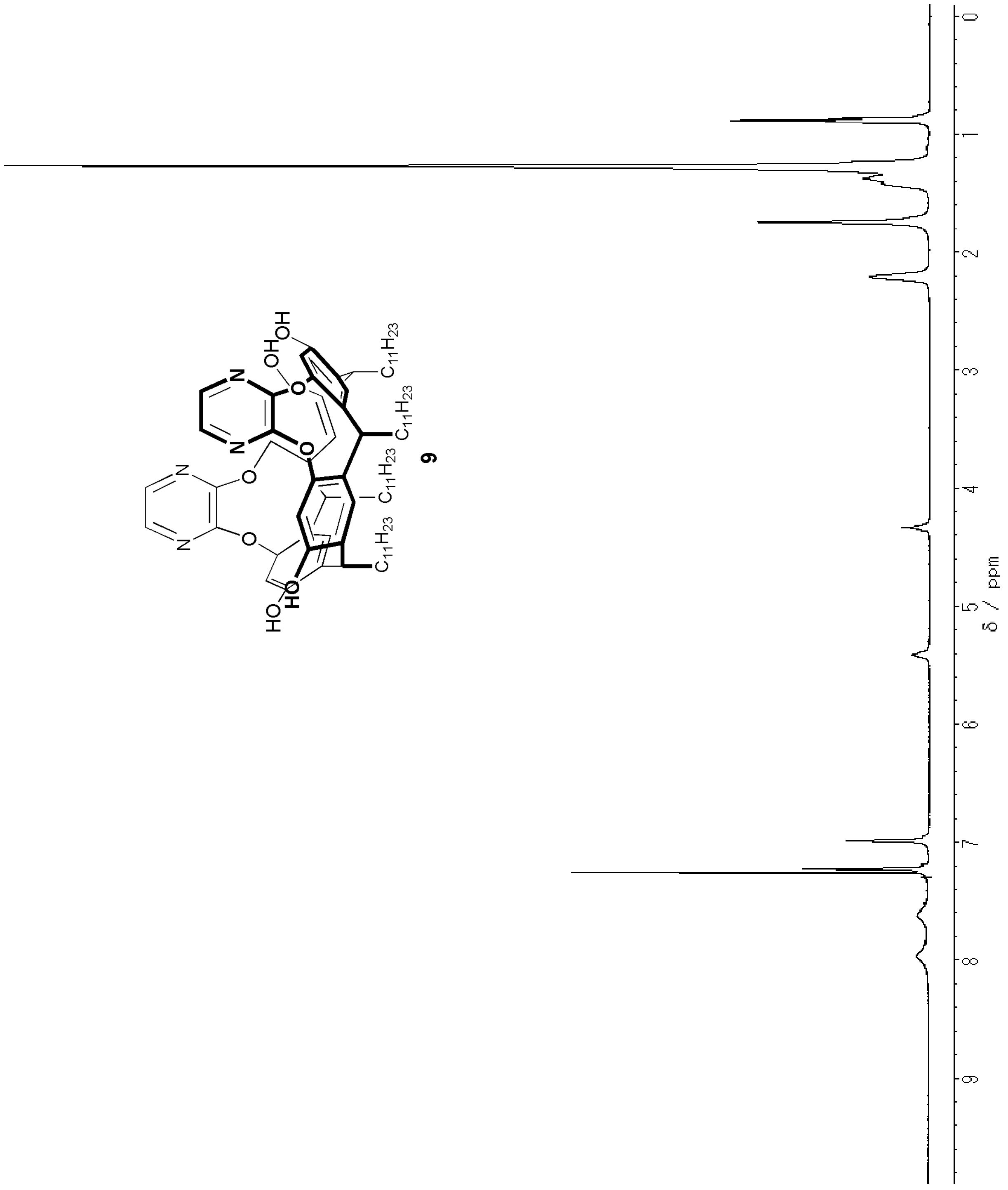
Compound 8

^{13}C NMR spectrum in $CDCl_3$


8

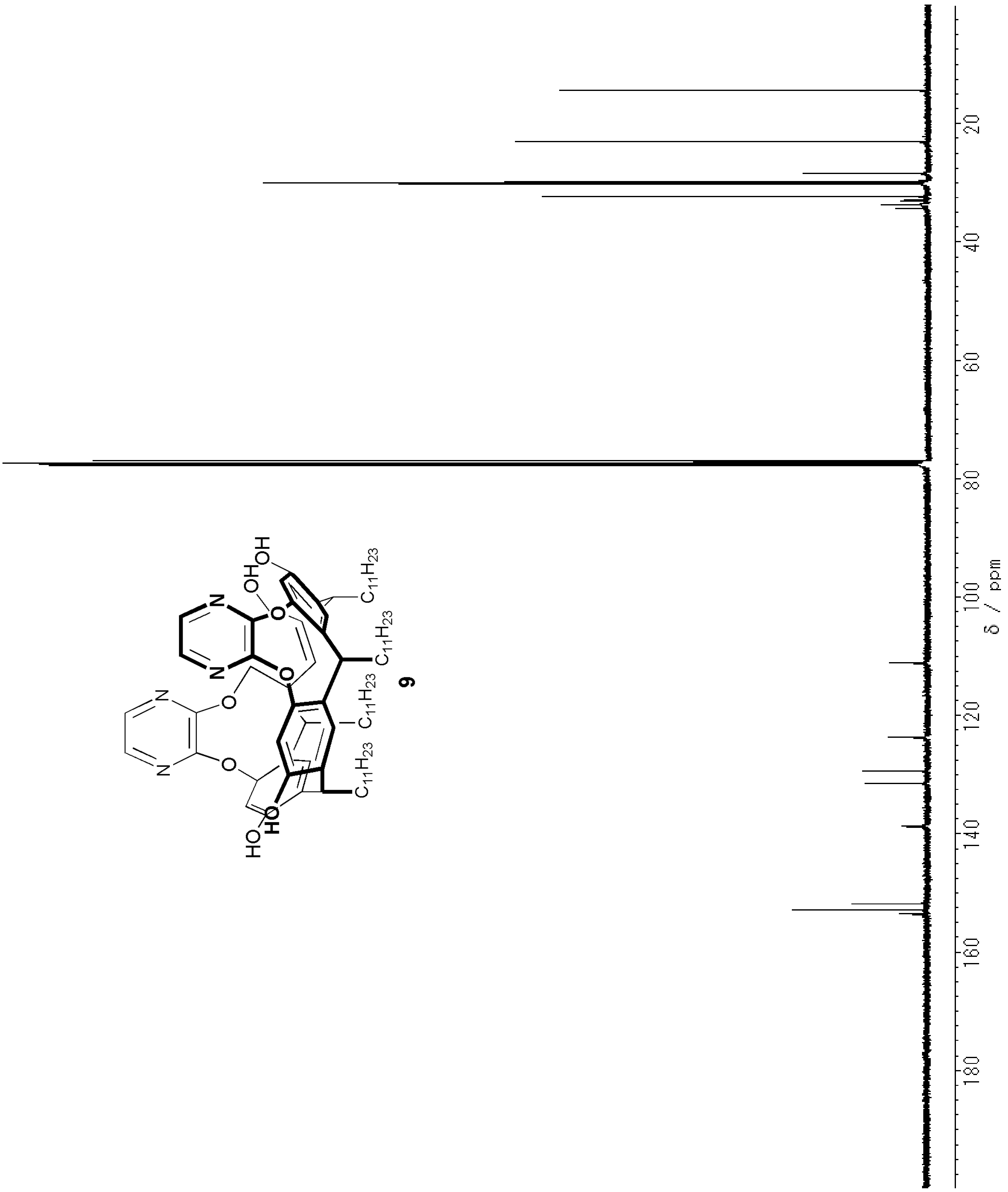
Compound 9

^{1}H NMR spectrum in CDCl$_3$



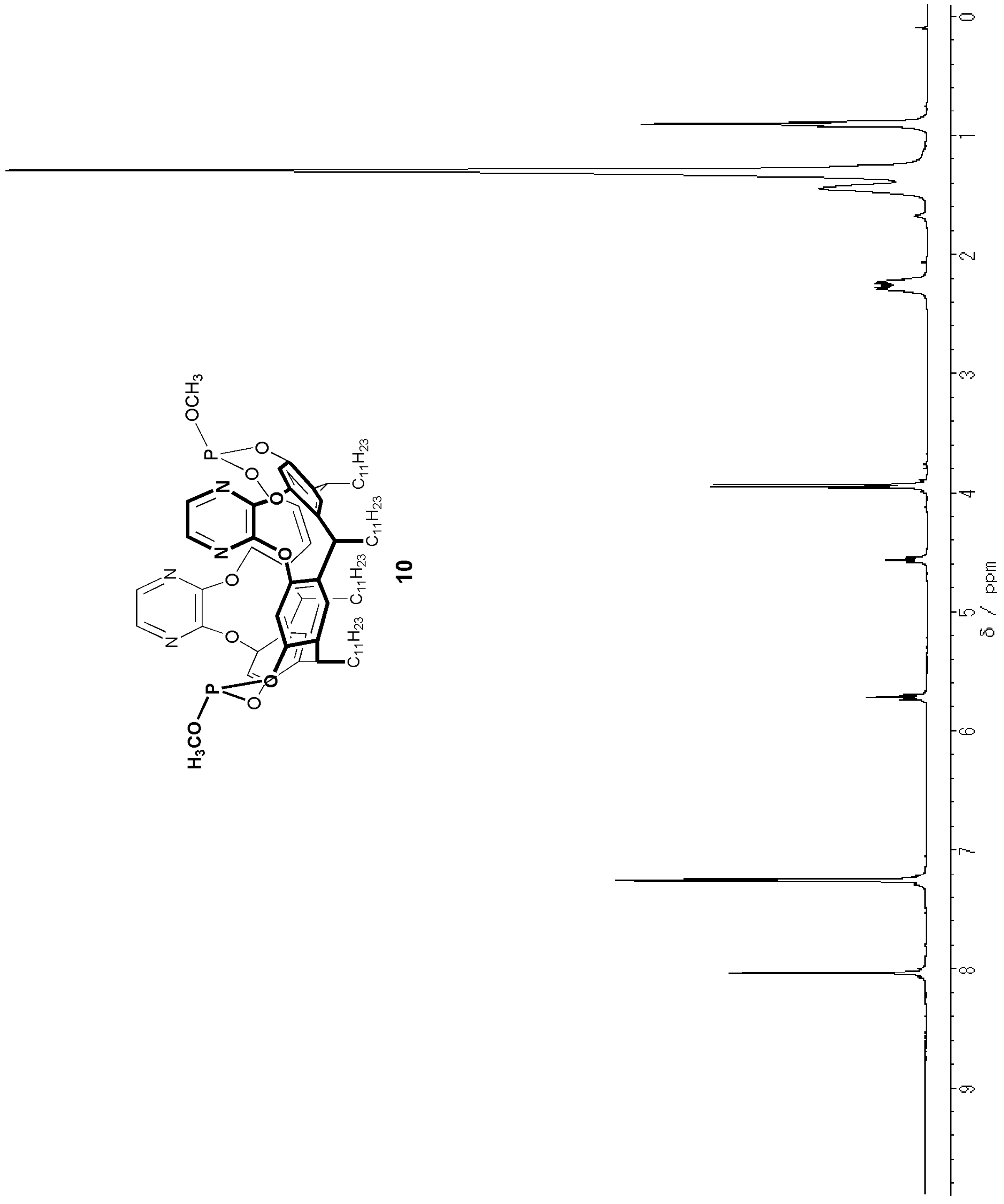
Compound 9

^{13}C NMR spectrum in $CDCl_3$



Compound 10

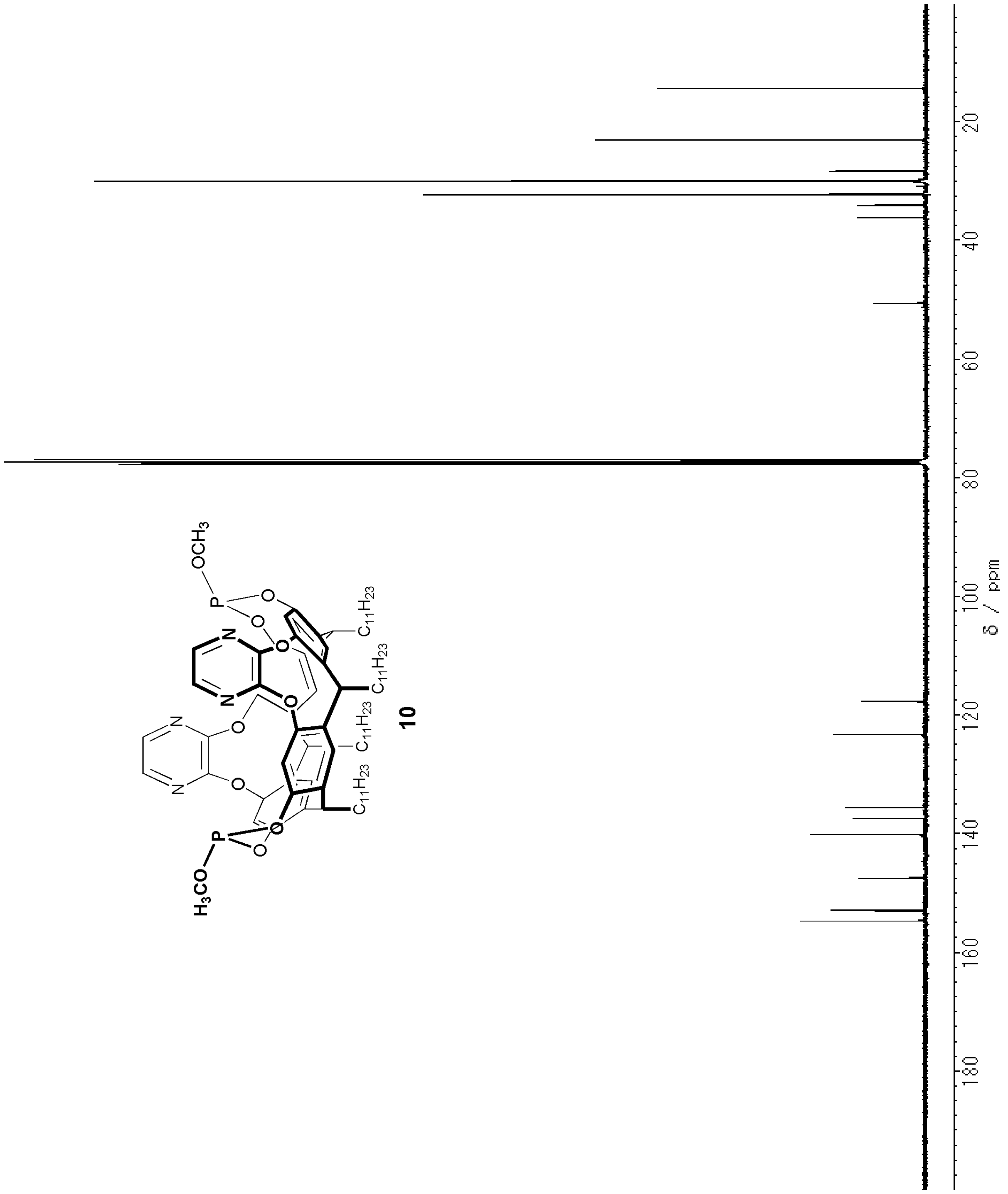
^{1}H NMR spectrum in $CDCl_3$



10

Compound 10

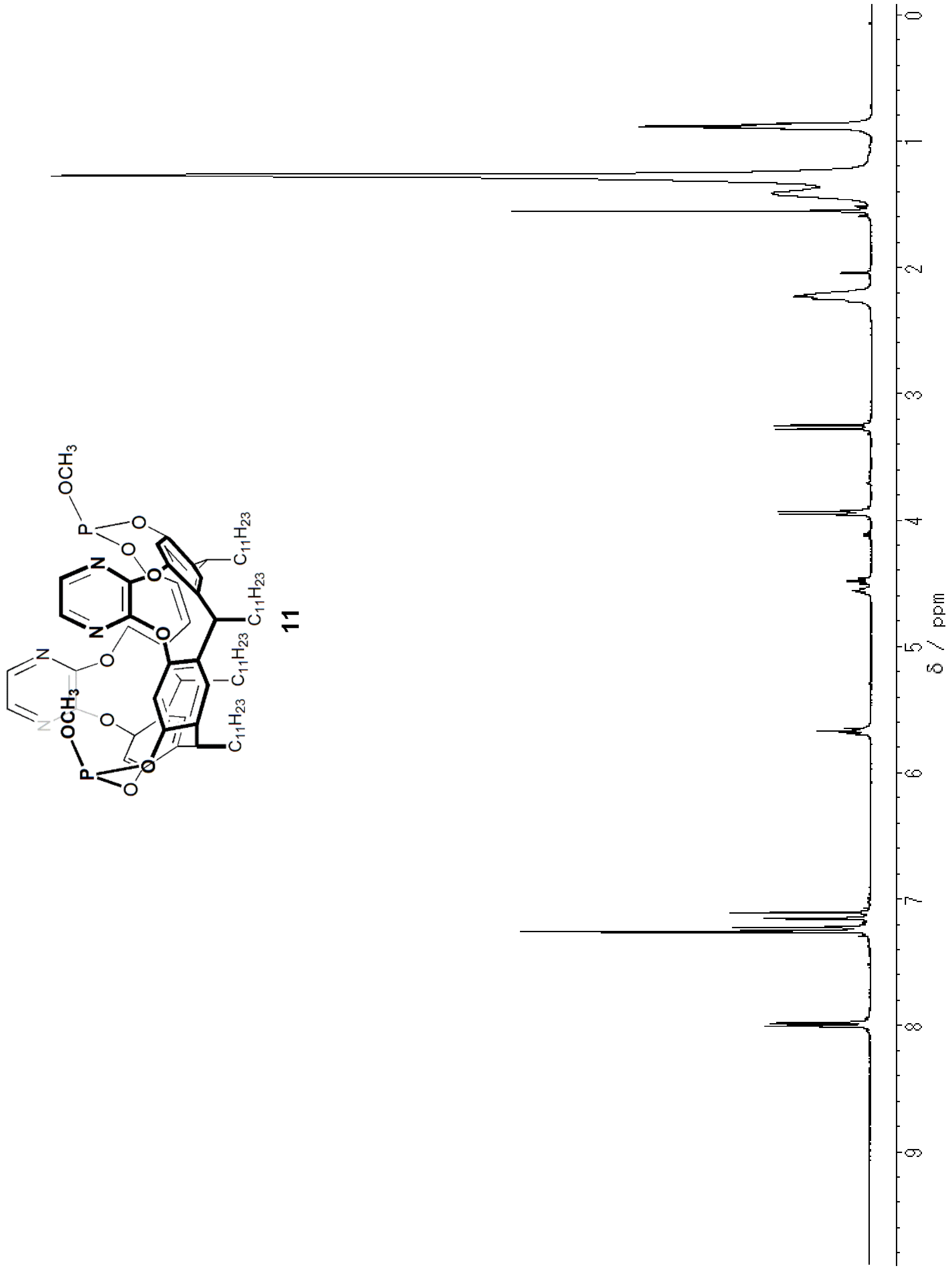
^{13}C NMR spectrum in $CDCl_3$



10

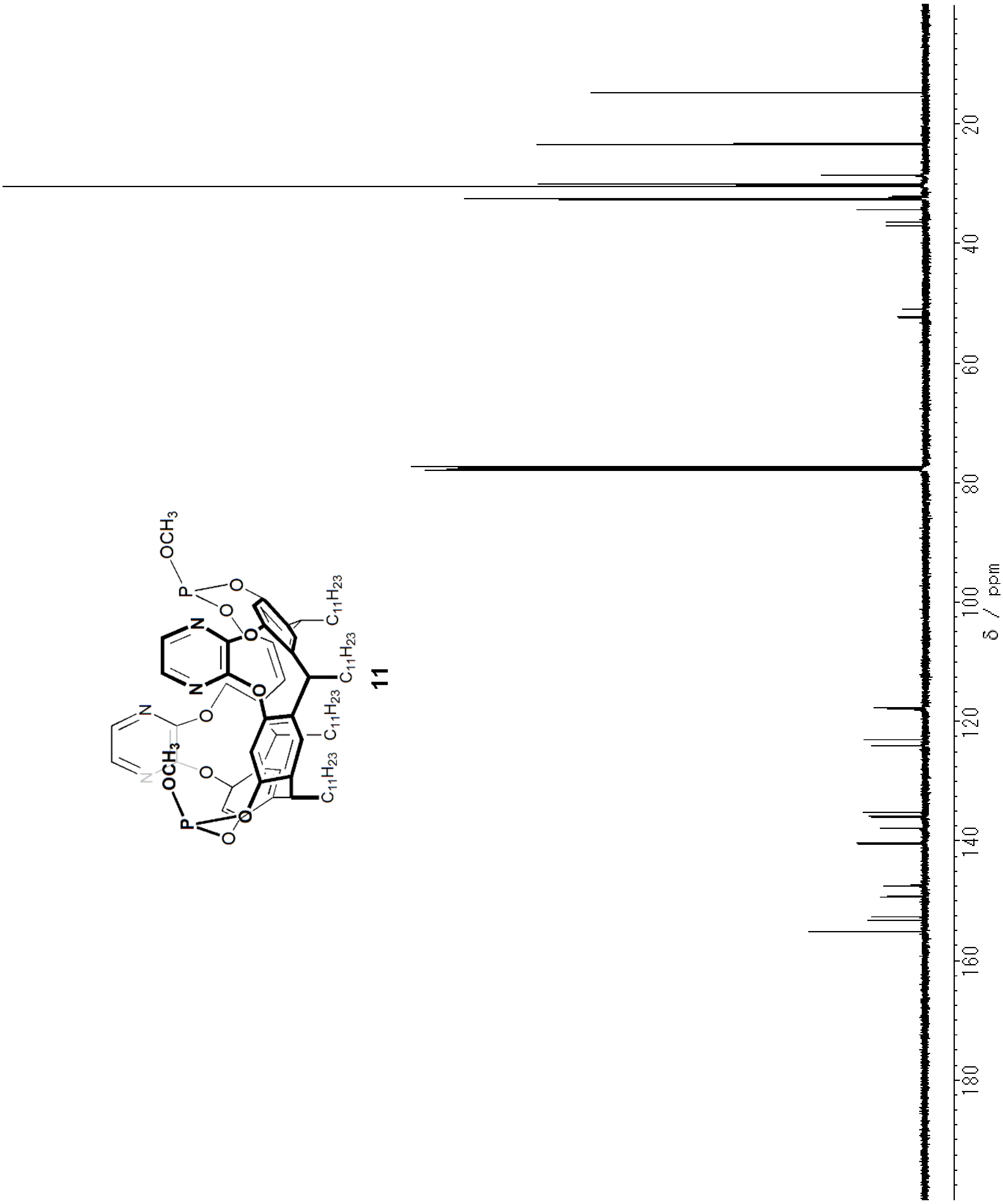
Compound 11

^{1}H NMR spectrum in $CDCl_3$



Compound 11

^{13}C NMR spectrum in $CDCl_3$



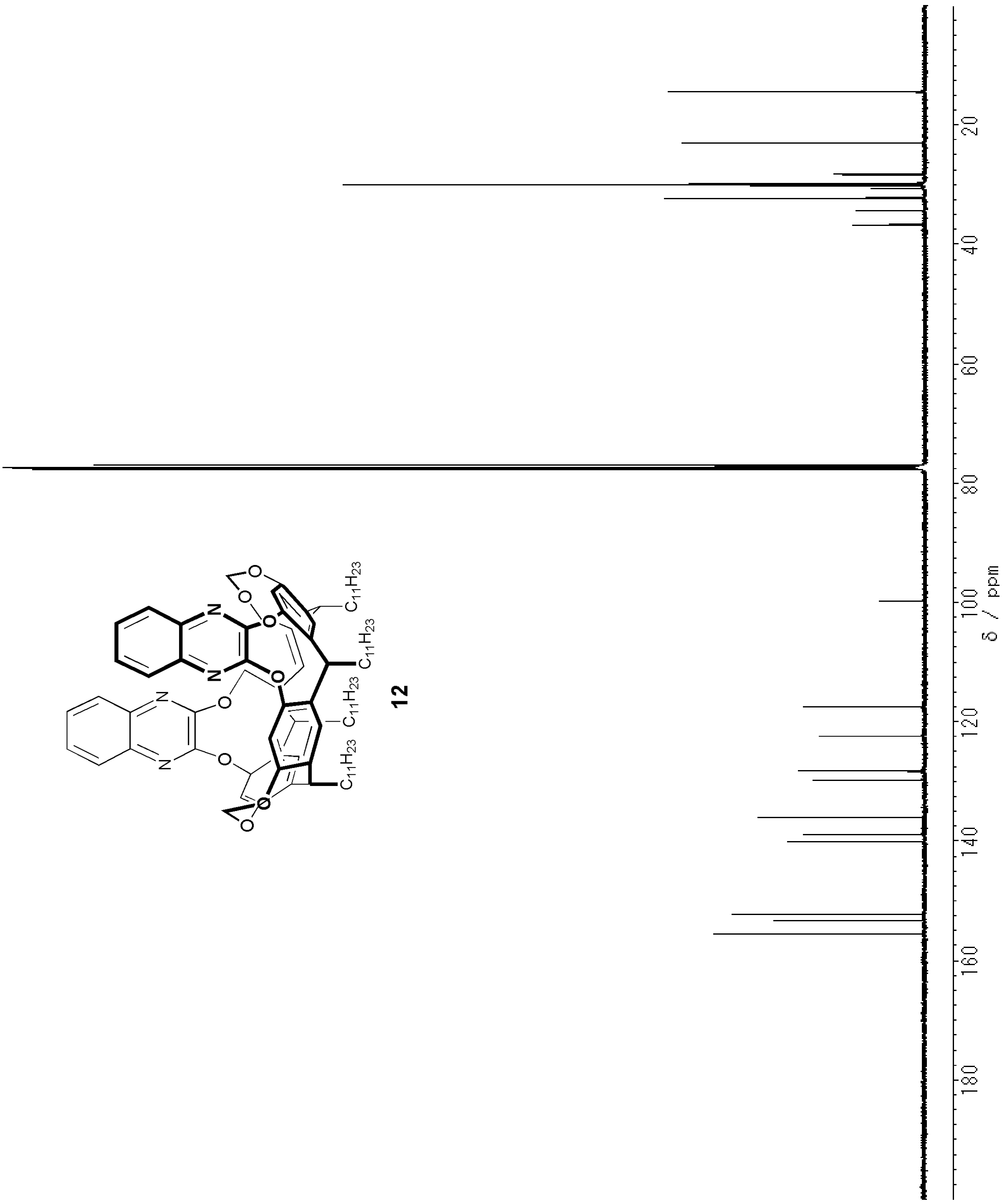
Compound 12

^{1}H NMR spectrum in $CDCl_3$


12

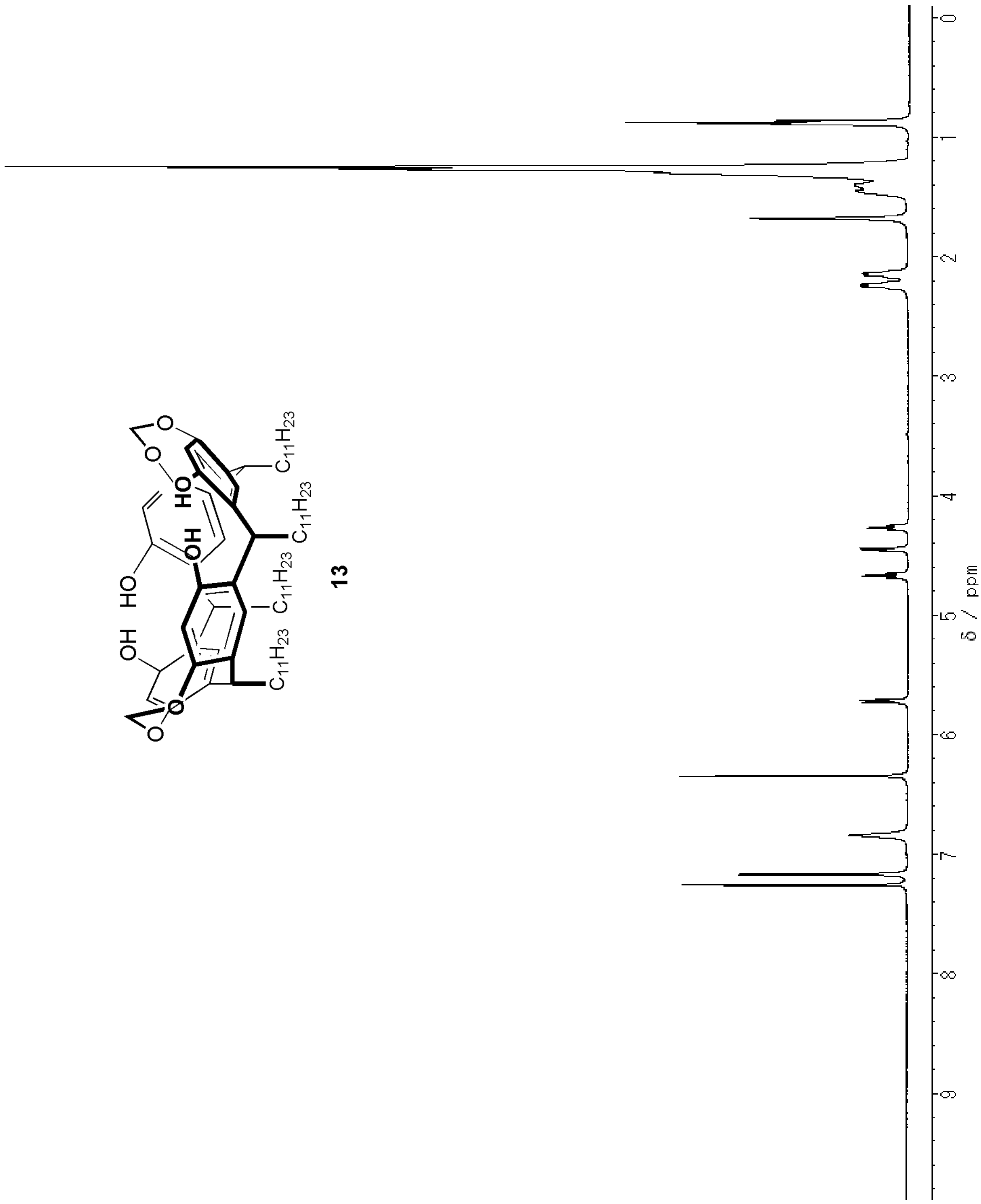
Compound 12

^{13}C NMR spectrum in $CDCl_3$



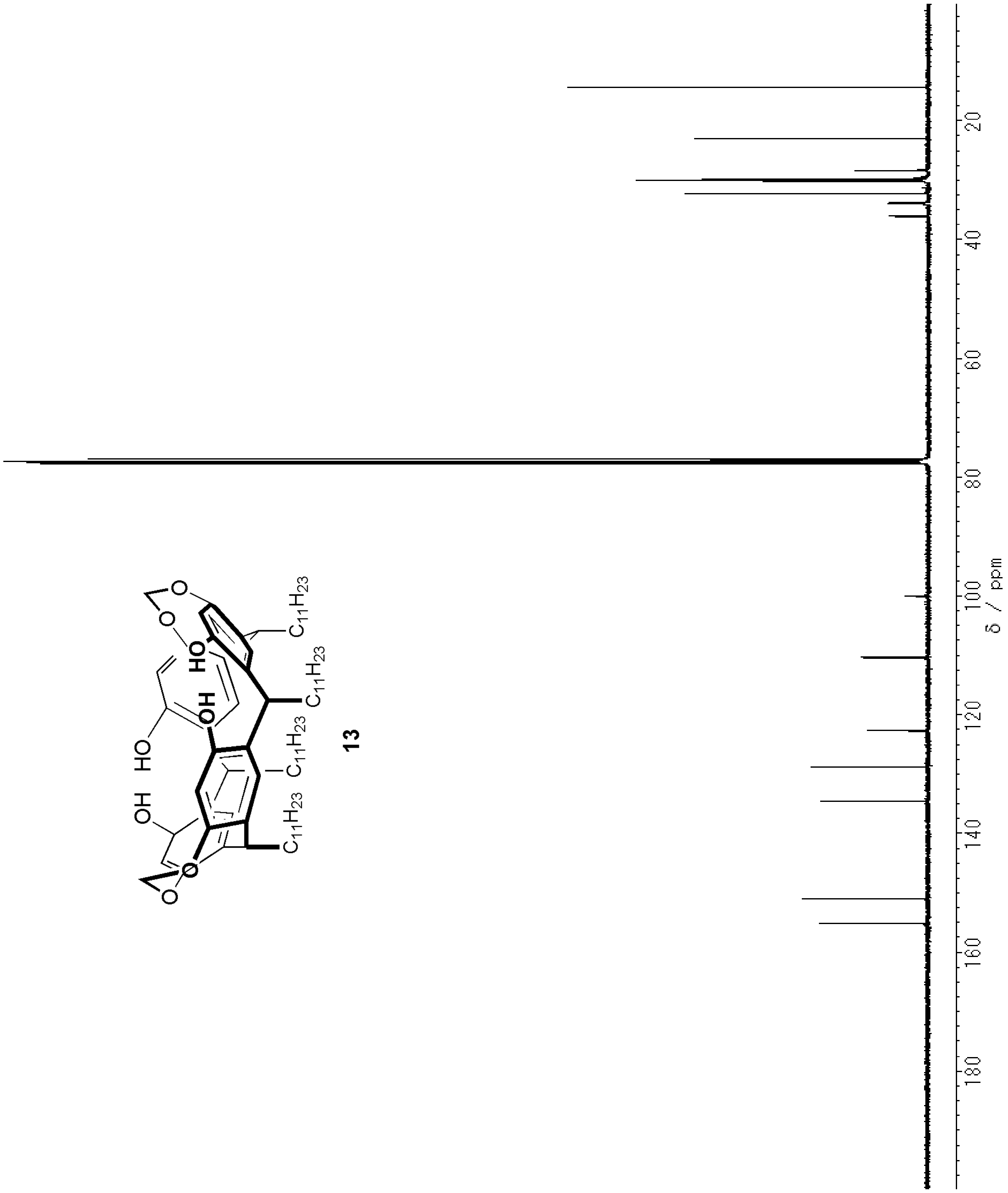
Compound 13

^{1}H NMR spectrum in $CDCl_3$


13

Compound 13

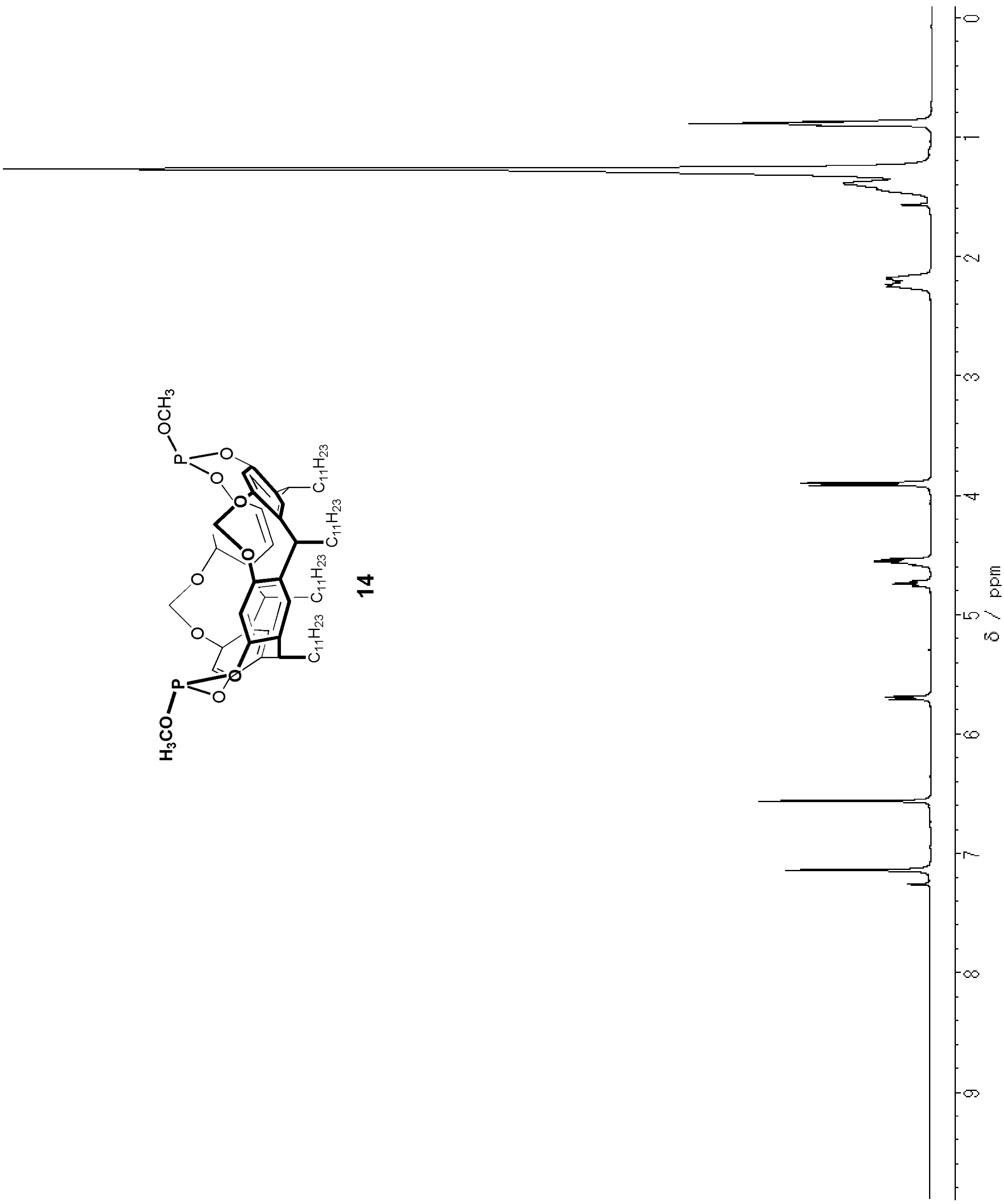
^{13}C NMR spectrum in $CDCl_3$



13

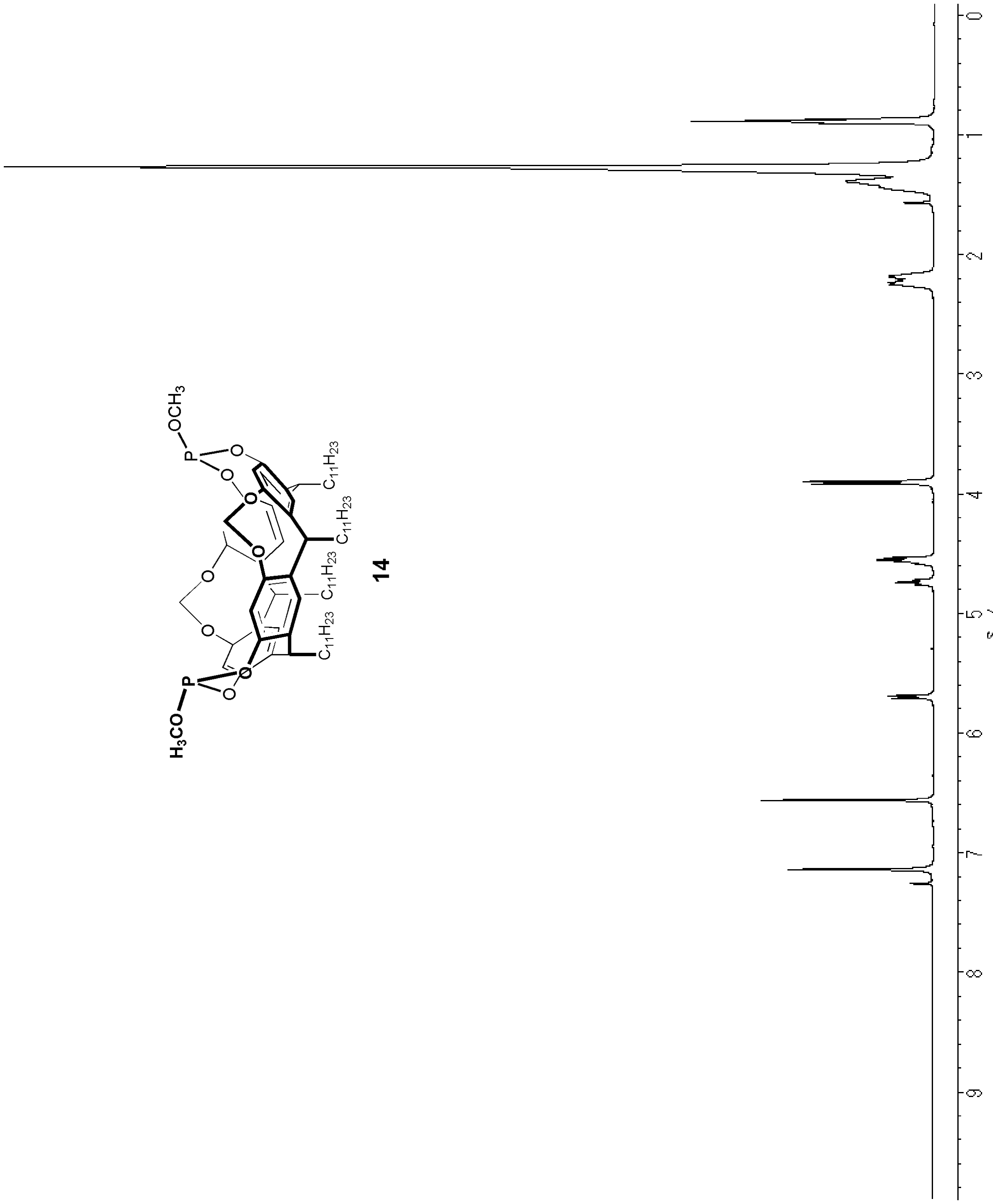
Compound 14

^{1}H NMR spectrum in $CDCl_3$



Compound 14

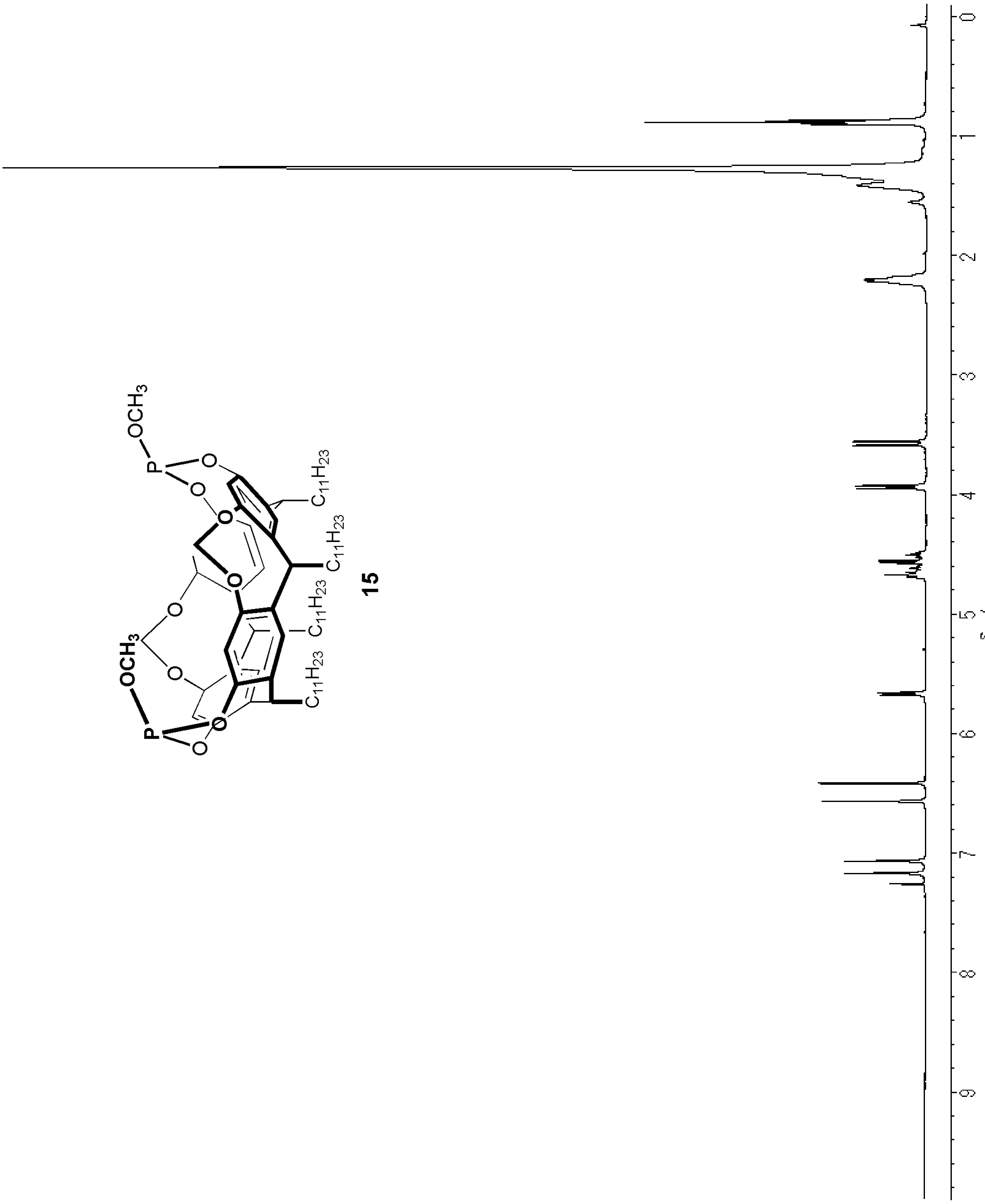
^{13}C NMR spectrum in $CDCl_3$



14

Compound 15

^1H NMR spectrum in $CDCl_3$



15

Compound 15

^{13}C NMR spectrum in $CDCl_3$