# Supporting Information

## Evaluation of Tuned Phosphorus Cavitands

## on Catalytic Cross-dimerization of Terminal Alkynes

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### Contents

**1.** General Information.

All reactions sensitive to air or moisture 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 (MADI-TOF or LCMS-IT-TOF; Shimadzu), and DART (Direct Analysis in Real Time)-MS. $^1$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 in delta (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), $CD_2Cl_2$ (54.0), $C_6D_6$ (128.0), $C_7D_8$ (20.4)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

**2.** Synthesis of the **2** and **4** (Scheme 3).

For **2**: To the two-necked flask charged with a solution of the tetra-hydroxy cavitand platform (548 mg, 0.4 mmol) in dry toluene (4 mL) under an argon atmosphere at 75 ºC, $Et_3N$ (0.29 mL, 1.92 mmol) and $P[N(CH_2CH_3)_2]_3$ (0.26 mL, 0.96 mmol) were added. After stirred for 1 h, the mixture was allowed to cool to room temperature and followed by filtration through a pad of Celite. The residue was evaporated off to give 713 mg of crude products as yellow solid materials. Purification by short-plug silica-gel column chromatography (eluent; $CH_2Cl_2$) and consecutive reprecipitation from $CH_2Cl_2$/$CH_3OH$ afforded 399 mg of **2** as white solid materials (64% yield). Data for **2**: $^1$H NMR (400 MHz, $CDCl_3$) 7.81 (dd, $J$ = 6.3, 3.4 Hz, 4H*)*, 7.53 (dd, $J$ = 6.3, 3.4 Hz, 4H), 7.29 (s,4H), 7.20 (s, 4H), 5.68 (t, $J$ = 8.2 Hz, 2H), 4.60 (t, $J$ = 7.6 Hz, 2H), 3.30 (dq, $^3J_{PH}$ = 10.8 Hz, $J$ = 7.0 Hz,

8H), 2.28-2.21 (m, 8H), 1.44-1.22 (m, 84H), 0.91-0.87 (m, 12H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) 153.4, 152.4, 150.1 (d, $J_{CP}$ = 5.7 Hz), 140.1, 137.4 (d, $J_{CP}$ = 2.4 Hz), 134.7, 129.5, 128.2, 122.8, 117.6, 39.3 (d, $J_{CP}$ = 19.3 Hz), 36.0, 34.3, 32.3, 32.2, 31.9, 30.1, 29.78, 29.76, 28.4, 23.06, 23.05, 15.4 (d, $J_{CP}$ = 4.2 Hz), 14.5 ppm. $^{31}$P NMR (162 MHz, $CDCl_3$) 143.0 ppm. MS (MALDI-TOF) *m/z*: 1560 ($[MH]^+$). IR (neat): 2921, 2850, 1605, 1577, 1482, 1401, 1329, 1159 cm$^{-1}$. HRMS (MALDI-TOF) calcd for $C_{96}H_{133}N_6O_8P_2$: 1559.9655 $[MH]^+$, found: 1559.9566.

For **4**: To the two-necked flask charged with a solution of the tetra-hydroxy cavitand platform (2.5 g, 1.8 mmol) in dry toluene (19 mL) under an argon atmosphere at 85 ºC, $Et_3N$ (1.2 mL, 8.8 mmol) and $PhP[N(CH_2CH_3)_2]_2$ (1.9 mL, 7.4 mmol) were added. After stirred for 26 h, the mixture was allowed to cool to room temperature and followed by concentration to give 5.18 g of crude products as yellow solid materials. Purification by silica-gel column chromatography (eluent; hexane/$CH_2Cl_2$=2/1) afforded 1.11 g of **4** as white solid materials (38% yield). Data for **4**: $^1$H NMR (400 MHz, $CDCl_3$) 7.93-7.90 (m, 4H), 7.84 (dd, *J* = 6.4, 3.5 Hz, 4H), 7.60-7.58 (m, 6H), 7.52 (dd, *J* = 6.4, 3.5 Hz, 4H), 7.42 (s, 4H), 7.32 (s, 4H), 5.77 (t, *J* = 8.1 Hz, 2H), 4.68 (t, *J* = 8.2 Hz, 2H), 2.34-2.32 (m, 4H), 2.27-2.25 (m, 4H), 1.47-1.28 (m, 72H), 0.91-0.86 (m, 12H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) 153.2, 152.7, 152.6, 140.1, 137.1 (d, $J_{CP}$ = 3.3 Hz), 135.5, 131.6, 130.1, 129.9, 129.6, 128.9 (d, $J_{CP}$ = 6.0 Hz), 128.3, 123.4, 117.1 (d, $J_{CP}$ = 3.1 Hz), 36.4, 34.4, 32.6, 32.3 (many peaks are overlapped), 32.23, 32.20, 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. $^{31}$P NMR (162 MHz, $CDCl_3$) 166.0 ppm. MS (MALDI-TOF) *m/z*: 1571 ($[M + H_2]^+$). IR (neat): 2921, 2851, 1609, 1576, 1481, 1401, 1329, 1158, 1068, 902 cm$^{-1}$. HRMS (MALDI-TOF) calcd for $C_{100}H_{122}N_4O_8P_2H$: 1569.8811 $[M + H]^+$, found 1569.8741.

**3.** Synthesis of **3** (Scheme 4).

To the two-necked flask charged with a solution of the phosphorus trichloride (0.08 mL, 0.96 mmol) in dry $CH_2Cl_2$ (10 mL) under $N_2$ atmosphere at 0 °C, *N*-metylbenzylamine (0.45 mL, 3.5 mmol) was added, and the mixture was stirred for 10 min. A solution of tetra-hydroxy cavitand platform (136 mg, 0.1 mmol) and $Et_3N$ (0.67 mL, 4.8 mmol) in dry $CH_2Cl_2$ (2 mL) was added dropwise over 2 min, and the reaction was stirred for 10 min. The mixture was warmed to room temperature with additional 2 h reaction time. Then, all the volatiles were evaporated off to give the crude products, and the following purification by short-plugged silica-gel column chromatography (eluent: hexane/$CH_2Cl_2$, 1:1) to afford 41 mg of **3** as white solid materials (25% yield). For Data of **3**: $^1$H NMR (400 MHz, $CDCl_3$) 7.83 (dd, $J$ = 6.4, 3.6 Hz, 4H), 7.51 (dd, $J$ = 6.4, 3.6 Hz, 4H), 7.49-7.43 (m, 4H), 7.38 (s, 4H), 7.37-7.33 (m, 1H), 7.23 (s, 4H), 5.72 (t, $J$ = 8.2 Hz, 2H), 4.61 (t, $J$ = 7.8 Hz, 2H), 4.35 (d, $^3J_{PH}$ = 11.4 Hz, 4H), 2.75 (d, $^3J_{PH}$ = 8.5 Hz, 6H), 2.30-2.22 (m, 8H), 1.45-1.27 (m, 72H), 0.91-0.86 (m, 12H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) 153.4, 152.5, 149.9 (d, $J_{CP}$ = 5.7 Hz), 140.2, 138.6 (d, $J_{CP}$ = 3.8 Hz), 137.4 (d, $J_{CP}$ = 2.6 Hz), 135.0, 129.6, 128.9, 128.8, 128.3, 127.7, 122.9, 117.6 (d, $J_{CP}$ = 2.6 Hz), 53.3 (d, $J_{CP}$ = 25.5 Hz), 36.1 34.3, 32.3 (many peaks are overlapped), 32.1, 31.92 (d, $J_{CP}$ = 13.4 Hz), 31.91, 30.1 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.40, 28.36, 23.1 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm. $^{31}$P NMR (162 MHz, $CDCl_3$) 139.9 ppm; MS (MALDI-TOF) *m/z*: 1656 $[MH]^+$. IR (neat): 2920, 2846, 1577, 1481, 1402, 1329, 1159, 898 $cm^{-1}$. HRMS (MALDI-TOF) calcd for $C_{104}H_{133}N_6O_8P_2$: 1655.9655 $[MH]^+$, found : 1656.1453.

**4.** Synthesis of **5** and **7** (Scheme 5).

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(*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 **5** (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 **5**: $^1$H NMR (400 MHz, $CDCl_3$) 7.84 (dd, $J$ = 6.4, 3.4 Hz, 4H), 7.54 (dd, $J$ = 6.4, 3.4 Hz, 4H), 7.41 (s, 4H), 7.25 (s, 4H), 5.74 (t, $J$ = 8.2 Hz, 2H), 4.58 (t, $J$ = 7.6 Hz,2H), 3.97 (d, $^3J_{PH}$ = 8.7 Hz, 6H), 2.31-2.24 (m, 8H), 1.46-1.30 (m, 72H), 0.93-0.88 (m, 12H) 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.

**5.** Complexation of AuCl•$S(CH_3)_2$ with **2**-**5**, and **7**. (Scheme 6 and Scheme 8).

Under $N_2$, a solution of the phosphorus cavitand (0.01 mmol) in toluene (2 mL) underwent addition of AuCl•$S(CH_3)_2$ (7.1 mg, 0.024 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, 2:1 or 4:1) to afford the corresponding bis-Au complex as white powders in appropriate yields described in Scheme 6. For the complex of **5**•2AuCl, all data were prepared in the section below: additionally, $^1$H and $^{31}$P NMR data for **2**•2AuCl and **7**•2AuCl, and $^1$H, $^{13}$C and $^{31}$P NMR and IR data for **3**•2AuCl, and $^1$H, $^{13}$C and $^{31}$P NMR data for **4**•2AuCl are listed in the section below.

For data of **5**•2AuCl: $^1$H NMR (400 MHz, $CDCl_3$) 7.89 (dd, $J$ = 6.2, 3.4 Hz, 4H), 7.59 (dd, $J$ = 6.2, 3.4 Hz, 4H), 7.46 (s,4H), 7.26 (s, 4H), 5.75 (t, $J$ = 8.2 Hz, 2H), 4.52 (t, $J$ = 7.4 Hz, 2H), 4.12 (d, $^3J_{PH}$ = 13.8 Hz, 6H), 2.32-2.21 (m, 8H), 1.41-1.24 (m, 72H), 0.91-0.86 (m, 12H) 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 $[M\text{-}Cl]^+$. 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 $[M\text{-}Cl]^+$, Found : 1905.7333.

For data of **2**•2AuCl: $^1$H NMR (400 MHz, toluene-$d_8$) 8.10 (dd, $J$ = 6.2, 3.2 Hz, 4H), 7.87 (s, 4H), 7.47 (s, 4H), 7.24 (dd, $J$ = 6.2, 3.2 Hz, 4H), 6.07 (t, $J$ = 7.9 Hz, 2H), 4.77 (t, $J$ = 7.7 Hz, 2H), 3.25-3.20 (m, 8H), 2.37-2.31 (m, 8H), 1.41-1.30 (m, 72 H), 0.98-0.92 (m, 24H) ppm ppm. $^{31}$P NMR (162 MHz, toluene-$d_8$) 117.1 ppm.

For data of **3**•2AuCl: $^{1}$H NMR (400 MHz, $CDCl_3$) 7.93 (dd, $J$ = 6.4, 3.4 Hz, 4H), 7.59 (dd, $J$ = 6.4, 3.4 Hz, 4H), 7.49-7.36 (m, 14H), 7.26 (s, 4H), 5.76 (t, $J$ = 8.2 Hz, 2H), 4.70 (d, $^{3}J_{PH}$ = 12.5 Hz, 4H), 4.61 (t, $J$ = 7.8 Hz, 2H), 2.97 (d, $^{3}J_{PH}$ = 12.2 Hz, 6H), 2.35-2.33 (m, 4H), 2.23-2.21 (m, 4H), 1.54-1.26 (m, 72H), 0.91-0.86 (m, 12H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) 153.1, 152.0, 146.3 (d, $J_{CP}$ = 5.7 Hz), 140.2, 136.8, 136.4 (d, $J_{CP}$ = 5.3 Hz), 136.0 (d, $J_{CP}$ = 2.4 Hz), 130.4, 129.2, 128.7, 128.4, 128.3, 122.9, 118.0, 53.9 (d, $J_{CP}$ = 14.3 Hz), 35.9, 34.3, 33.7, 33.6, 32.7, 32.3 (many peaks are overlapped), 30.5, 30.0 (many peaks are overlapped), 29.7 (many peaks are overlapped), 28.2, 28.1, 23.0 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm. $^{31}$P NMR (162 MHz, $CDCl_3$) 112.0 ppm. IR (neat): 2922, 2851, 1608, 1564, 1481, 1455, 1402, 1272, 1154 cm$^{-1}$.

For data of **4**•2AuCl: $^{1}$H NMR (400 MHz, $CDCl_3$) 8.17 (d, $J$ = 7.1 Hz, 2H), 8.14 (d, $J$ = 7.1 Hz, 2H), 7.91 (dd, $J$ = 6.3, 3.4 Hz, 4H), 7.73 (t, $J$ = 7.5 Hz, 2H), 7.65 (dd, $J$ = 7.5, 7.5 Hz, 4H), 7.59 (dd, $J$ = 6.3, 3.4 Hz, 4H), 7.51 (s, 4H), 7.34 (s, 4H), 5.77 (t, $J$ = 8.1 Hz, 2H), 4.69 (t, $J$ = 7.9 Hz, 2H), 2.37-2.26 (m, 8H), 1.49-1.27 (m, 72H), 0.91-0.86 (m, 12H) ppm. $^{31}$P NMR (162 MHz, $CDCl_3$) 133.6 ppm. $^{13}$C NMR (100 MHz, $CDCl_3$) 153.3 (d, $J_{CP}$ = 1.9 Hz), 151.9, 148.4 (d, $J_{CP}$ = 7.9 Hz), 140.2, 137.0, 136.0 (d, $J_{CP}$ = 2.9 Hz), 134.4, 133.3, 131.5 (d, $J_{CP}$ = 19.1 Hz), 130.3, 129.4 (d, $J_{CP}$ = 14.3 Hz), 128.7, 123.2, 117.7 (d, $J_{CP}$ = 4.3 Hz), 36.1, 34.4, 32.7, 32.2 (many peaks are overlapped), 31.2, 30.0 (many peaks are overlapped), 29.7, 28.2, 23.0 (many peaks are overlapped), 14.4 (many peaks are overlapped) ppm.

For data of **7**•2AuCl: $^{1}$H NMR (400 MHz, $CDCl_3$) 7.91 (dd, $J$ = 6.6, 2.2 Hz, 2H), 7.75 (dd, $J$ = 6.6, 2.2 Hz, 2H), 7.61-7.55 (m, 4H), 7.50 (s, 2H), 7.35 (s, 2H), 7.27 (s, 2H), 7.23 (s, 2H), 5.75 (t, $J$ = 8.2 Hz, 2H), 4.52 (t, $J$ = 8.0 Hz, 1H), 4.47 (t, $J$ = 7.8 Hz), 4.16 (d, $^{3}J_{PH}$ = 13.6 Hz, 3H), 3.36 (d, $^{3}J_{PH}$ = 15.5 Hz), 2.36-2.23 (m, 8H), 1.55-1.27 (m, 72H), 0.91-0.86 (m, 12H); $^{1}$P NMR (162 MHz, $CDCl_3$) 109.7, 101.6 ppm.

**6.** Procedure for cross-dimerization of terminal alkynes in Scheme 7.

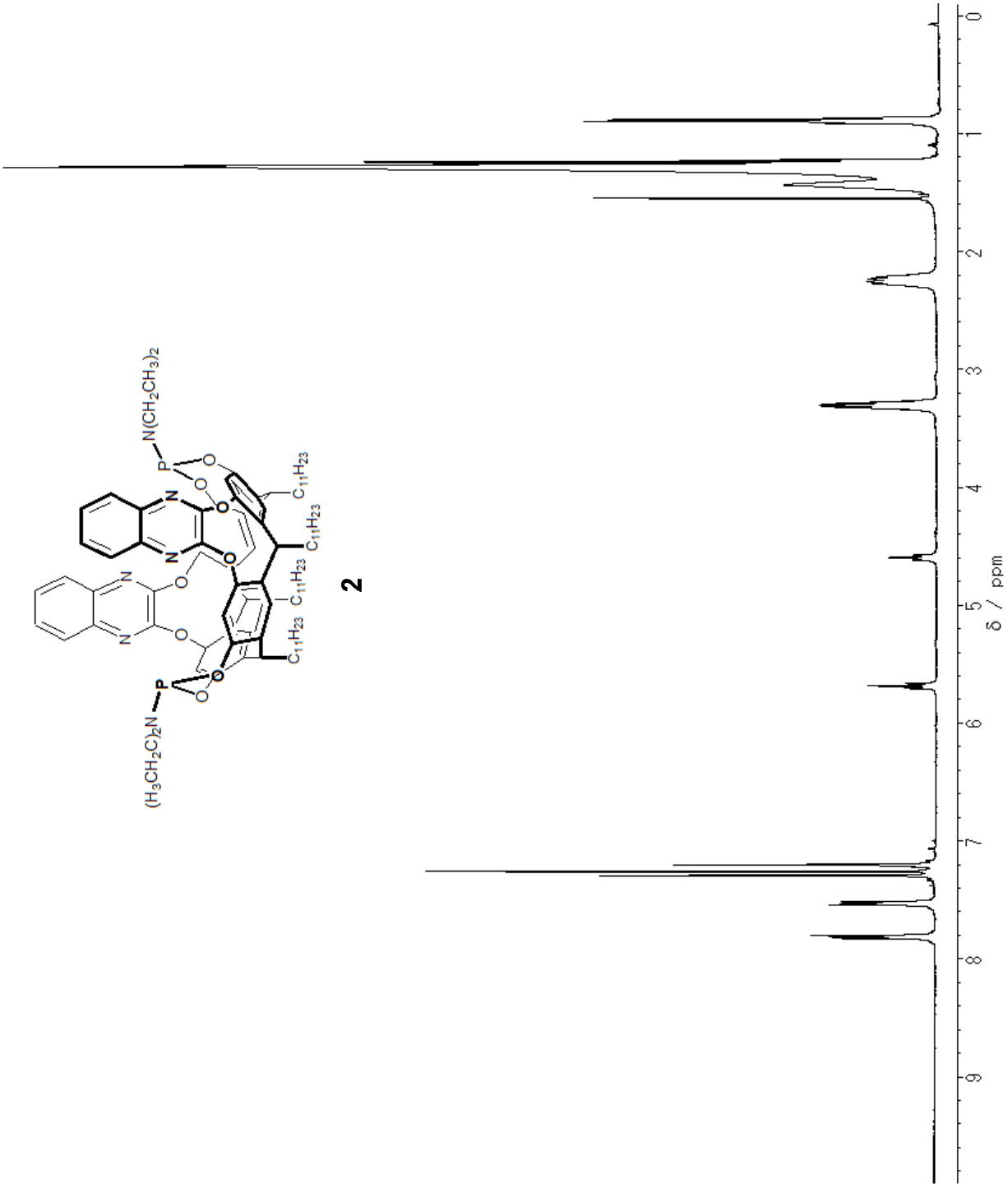
Under $N_2$, the appropriate cavitand catalyst (0.01 mmol) in a vessel was dissolved in dry toluene (5 mL), and the starting alkynes of ethynylbenzene (102 mg, 1 mmol) and the other partner 1.5 mmol (165 mg of 1-octyne or 195 mg of 4-phenyl-1-butyne) were added. After addition of AgOTf (5.0 mg, 0.02 mmol) at room temperature, the reaction was conducted for the appropriate hours. The solvent was evaporated 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]

**7.** The $^{1}H$ and $^{13}C$ NMR spectra of all new compounds **2**-**5** and **7**.

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

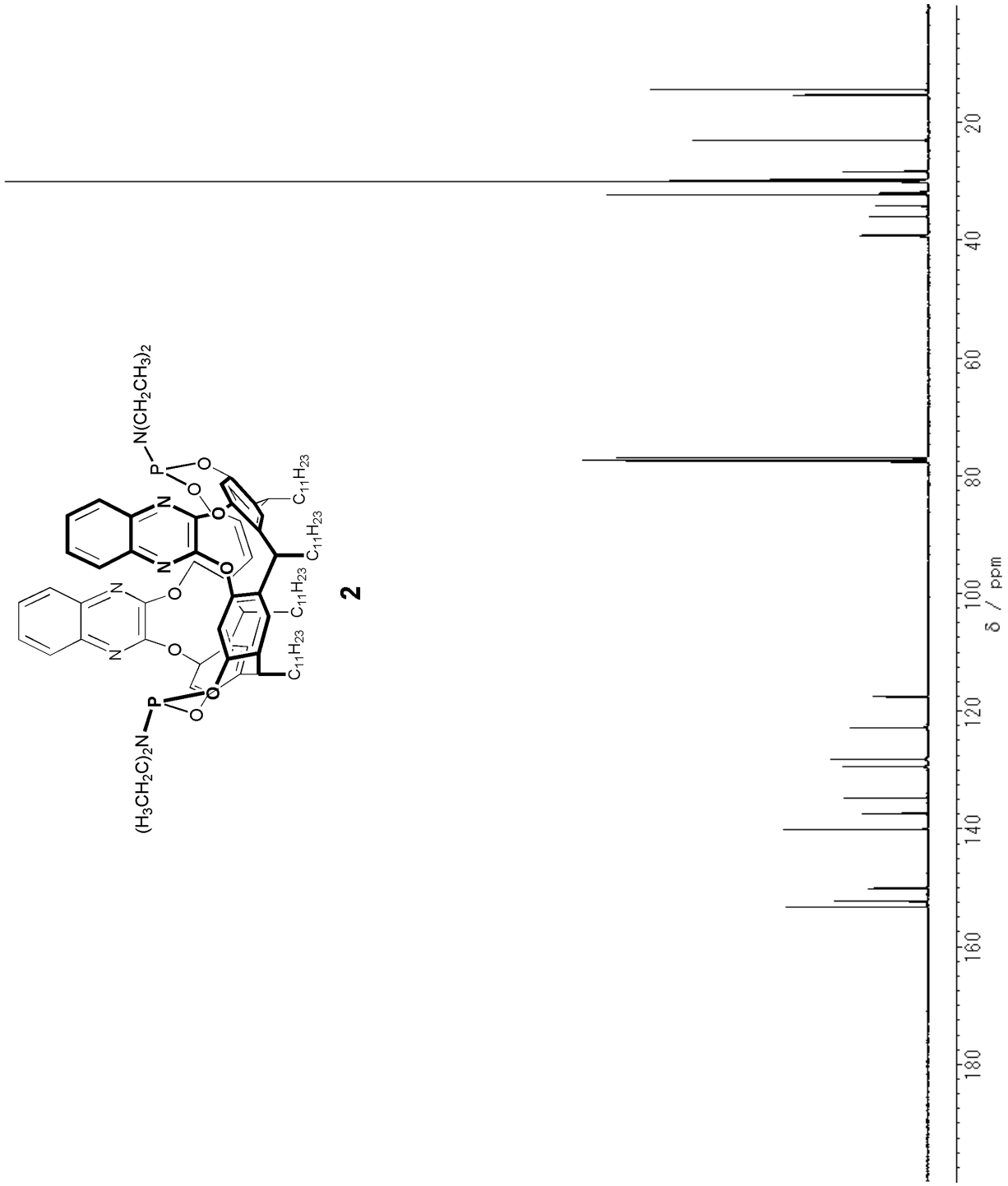
**Compound 2**

$^{1}H$ NMR spectrum in $CDCl_3$



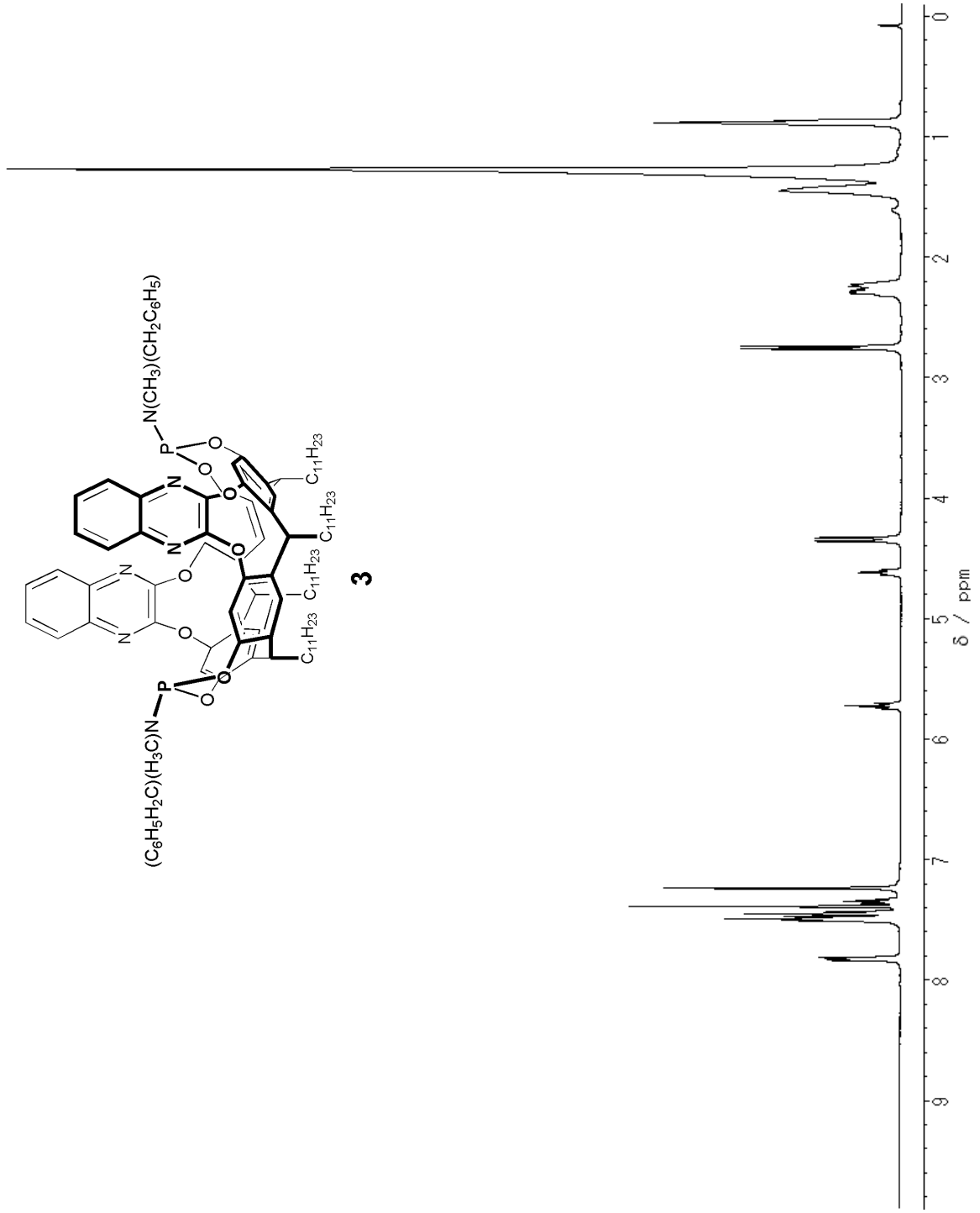
**Compound 2**

$^{13}C$ NMR spectrum in $CDCl_3$



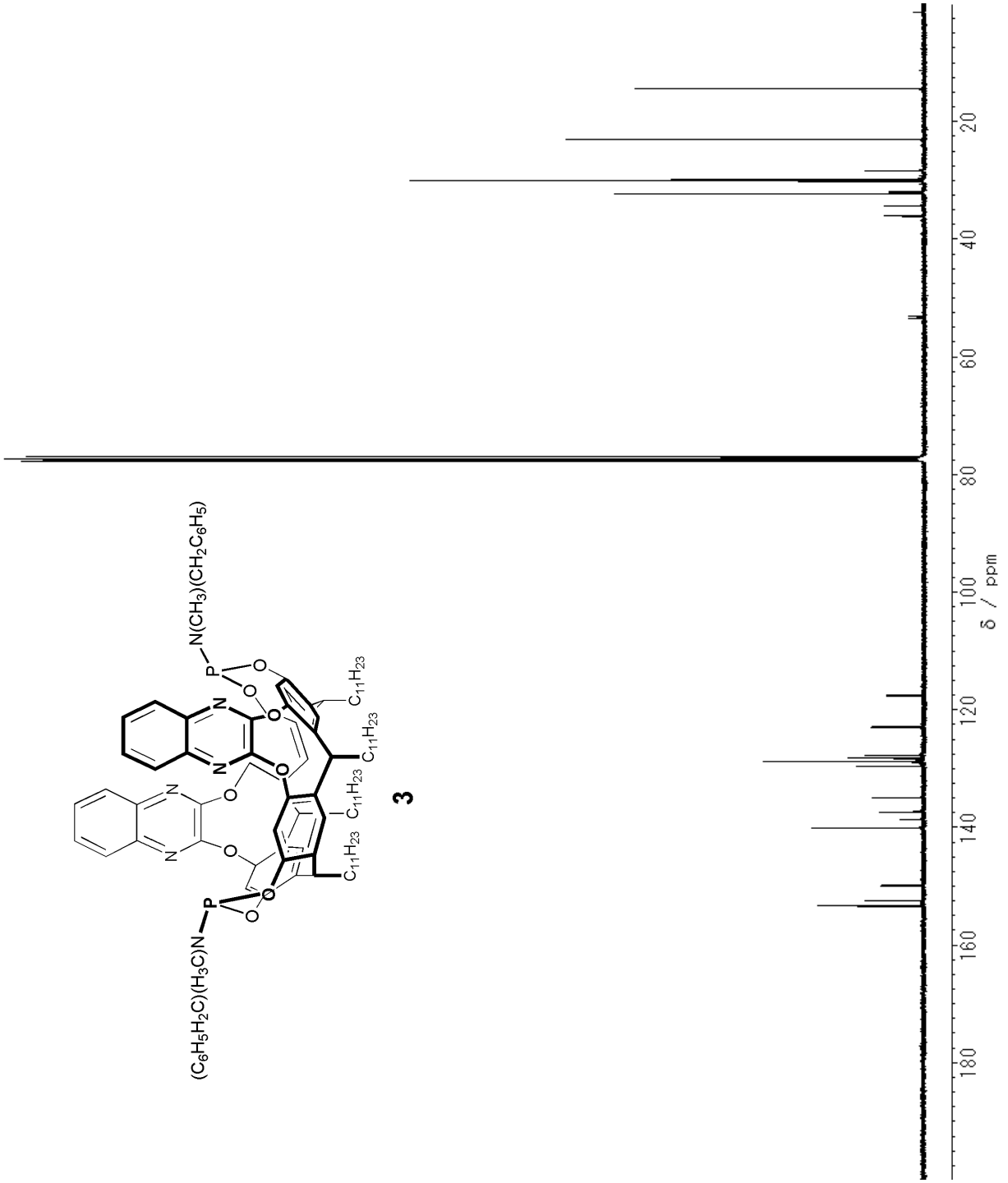
**Compound 3**

$^{1}H$ NMR spectrum in $CDCl_3$



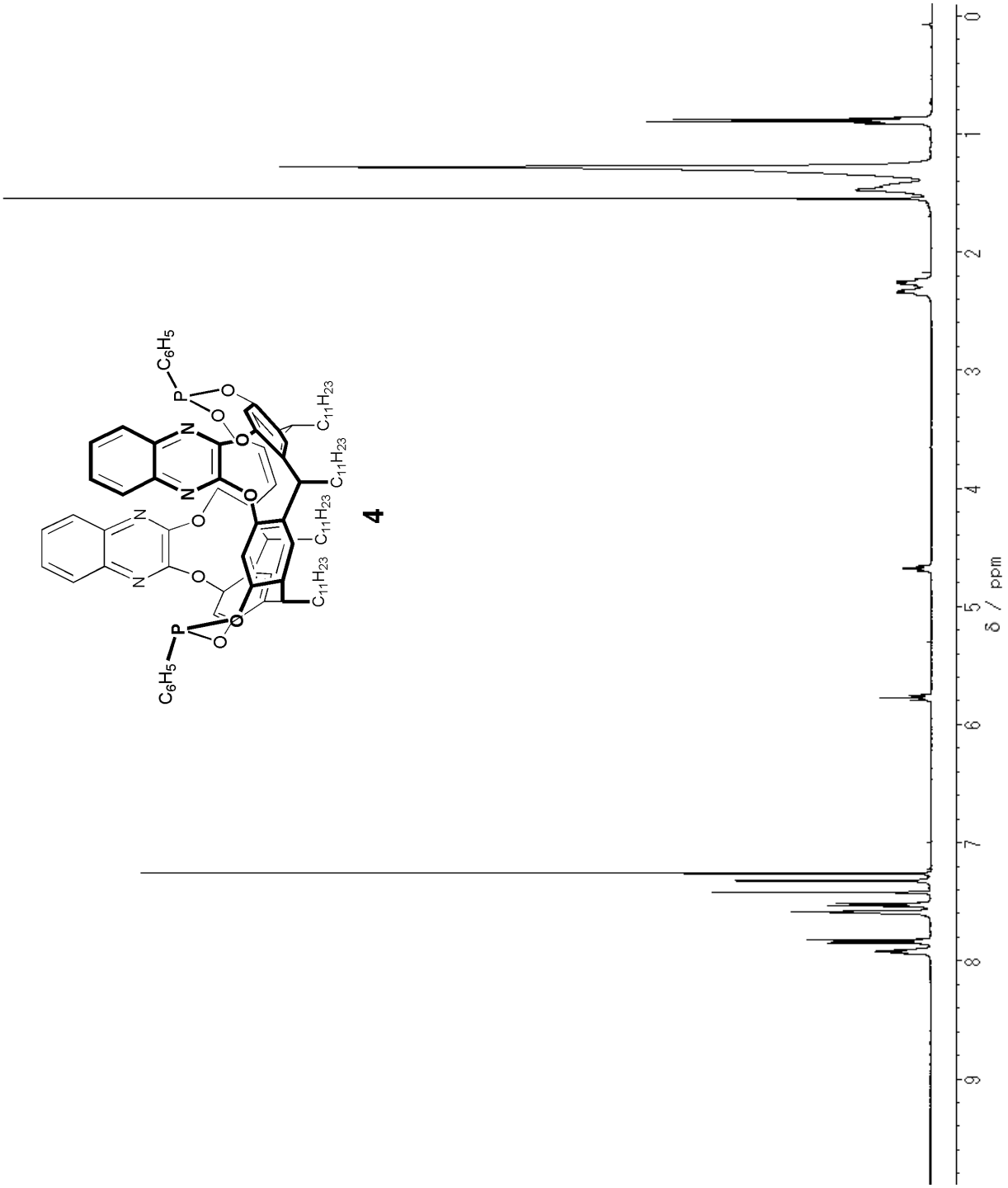
**Compound 3**

$^{13}C$ NMR spectrum in $CDCl_3$



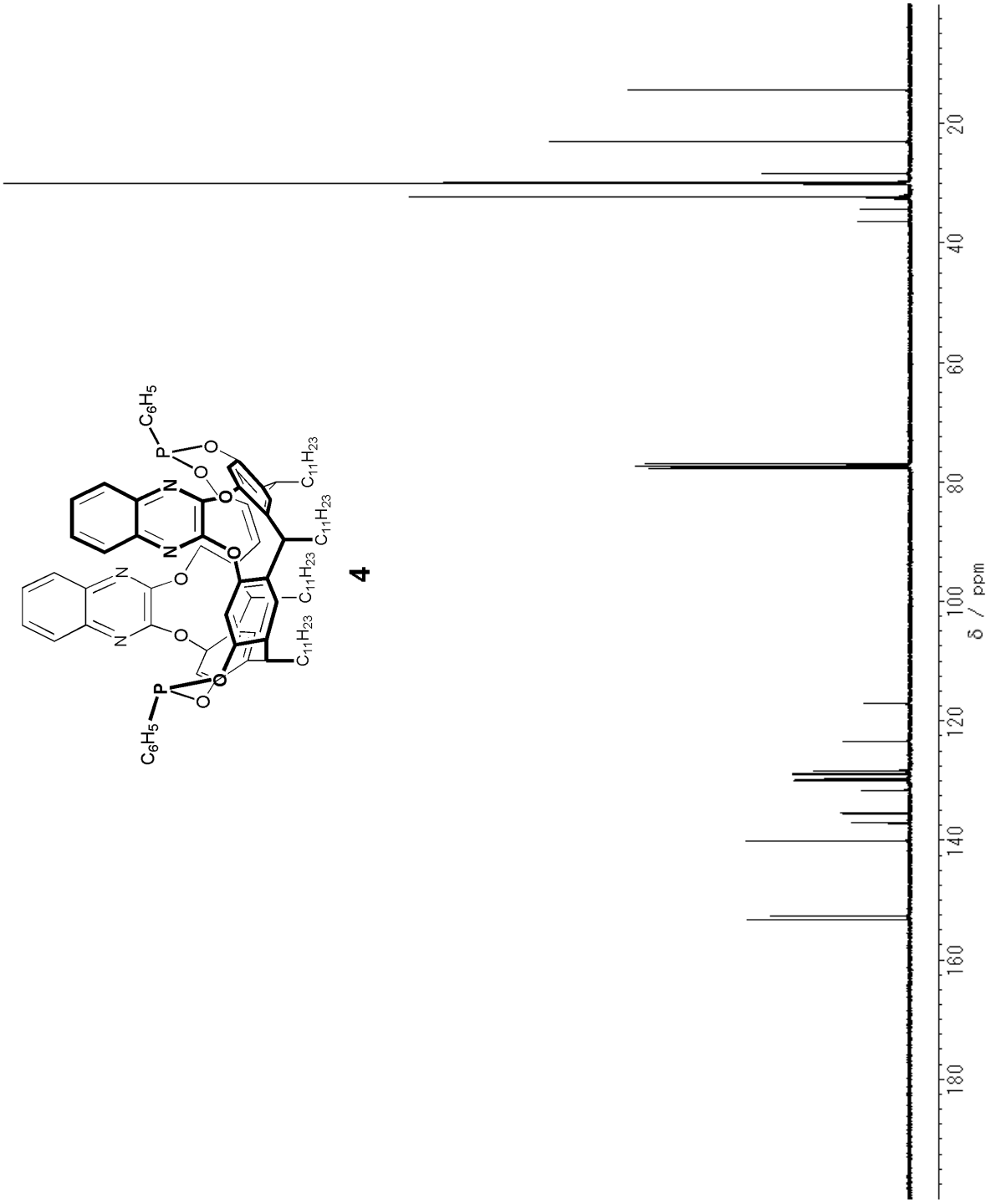
**Compound 4**

$^{1}H$ NMR spectrum in $CDCl_3$



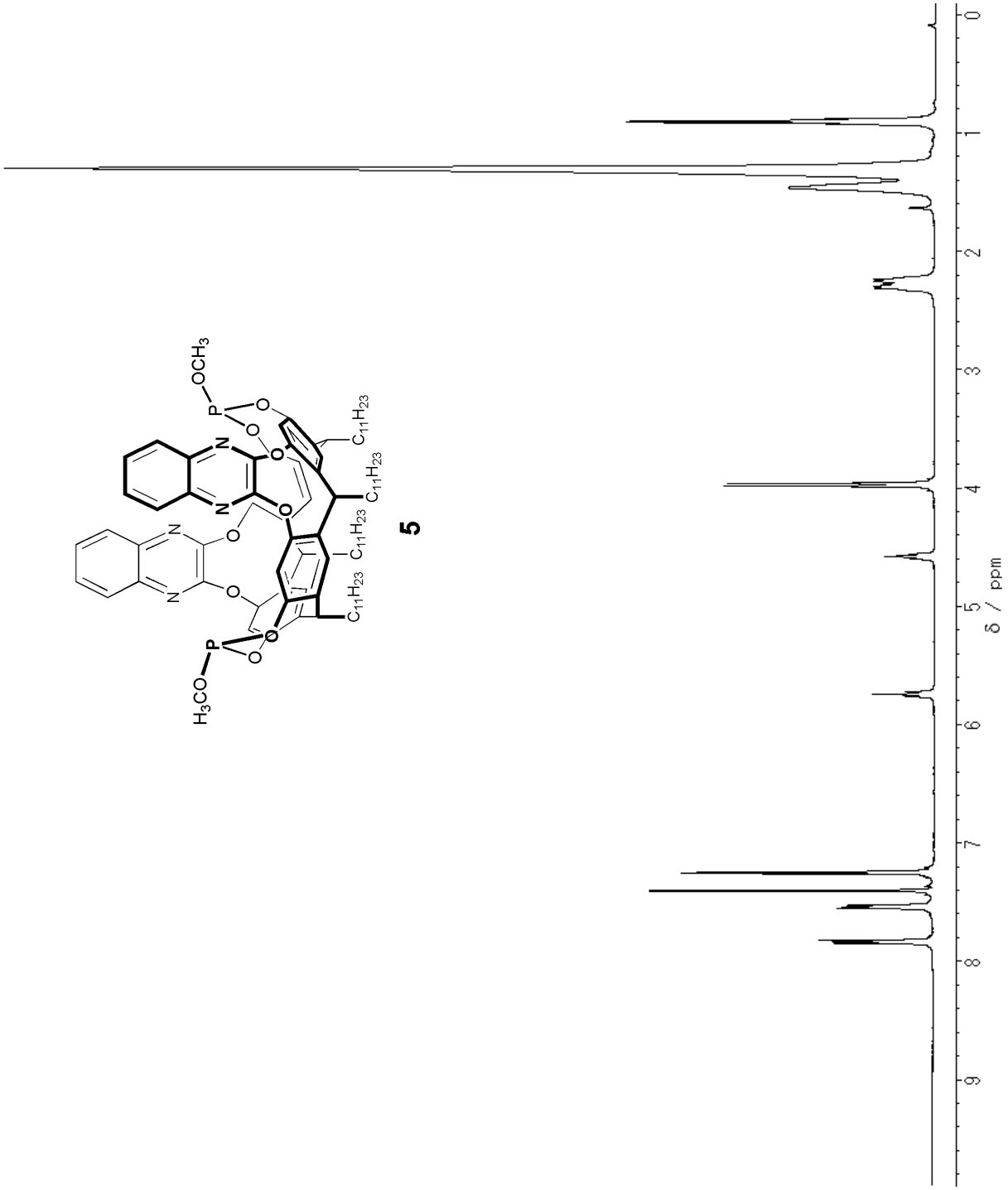
**Compound 4**

$^{13}C$ NMR spectrum in $CDCl_3$



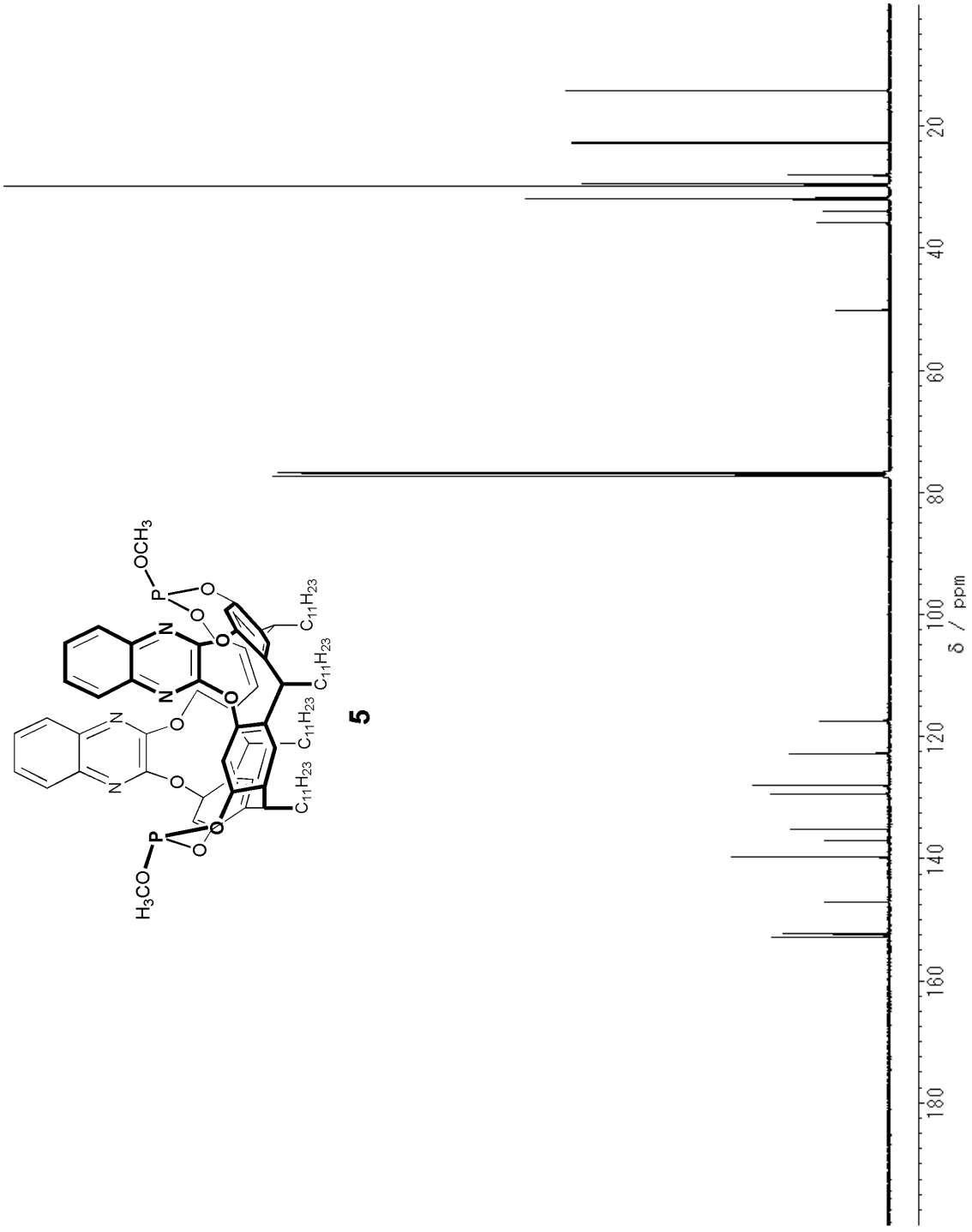
**Compound 5**

$^{1}H$ NMR spectrum in $CDCl_3$



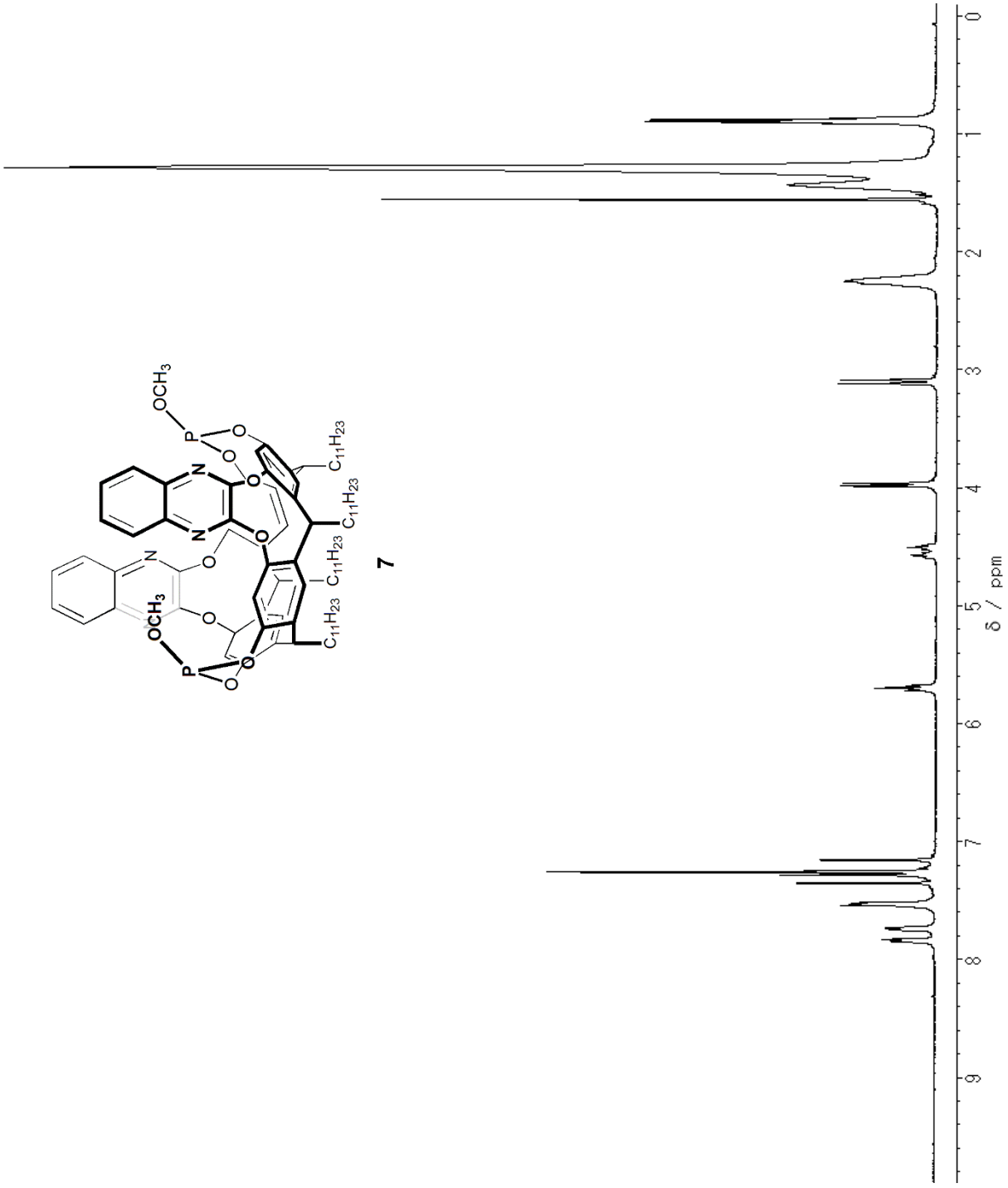
**Compound 5**

$^{13}C$ NMR spectrum in $CDCl_3$



**Compound 7**

$^{1}H$ NMR spectrum in $CDCl_3$



**Compound 7**

$^{13}C$ NMR spectrum in $CDCl_3$