Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Bifunctional catalyst for carbon dioxide fixation: cooperative double activation of epoxides for the synthesis of cyclic carbonates

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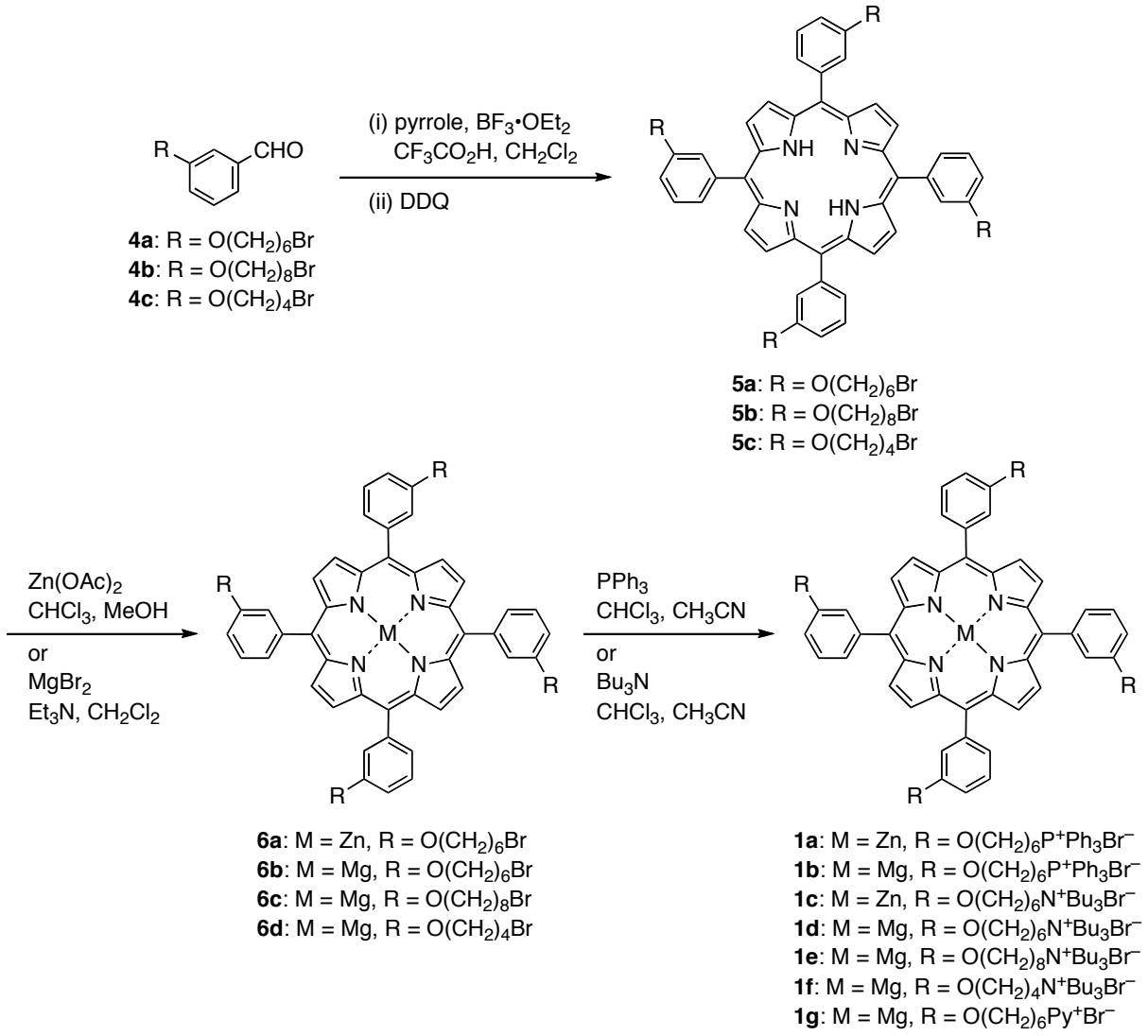
[1] Synthesis of Bifunctional Catalysts 1.



4a: R = $O(CH_2)_6Br$
4b: R = $O(CH_2)_8Br$
4c: R = $O(CH_2)_4Br$

5a: R = $O(CH_2)_6Br$
5b: R = $O(CH_2)_8Br$
5c: R = $O(CH_2)_4Br$

6a: M = Zn, R = $O(CH_2)_6Br$
6b: M = Mg, R = $O(CH_2)_6Br$
6c: M = Mg, R = $O(CH_2)_8Br$
6d: M = Mg, R = $O(CH_2)_4Br$

1a: M = Zn, R = $O(CH_2)_6P^+Ph_3Br^-$
1b: M = Mg, R = $O(CH_2)_6P^+Ph_3Br^-$
1c: M = Zn, R = $O(CH_2)_6N^+Bu_3Br^-$
1d: M = Mg, R = $O(CH_2)_6N^+Bu_3Br^-$
1e: M = Mg, R = $O(CH_2)_8N^+Bu_3Br^-$
1f: M = Mg, R = $O(CH_2)_4N^+Bu_3Br^-$
1g: M = Mg, R = $O(CH_2)_6Py^+Br^-$

5,10,15,20-Tetrakis[3-(6-bromohexyloxy)phenyl]porphyrin (5a).

A solution of pyrrole (695 μL, 10.0 mmol) and 3-(6-bromohexyloxy)benzaldehyde (**4a**)[1,2] (2.86 g, 10.0 mmol) in dry CH_2Cl_2 (1.0 L) was bubbled with Ar, and then $BF_3{\cdot}OEt_2$ (12 μL, 0.097 mmol) and CF_3CO_2H (670 μL, 9.02 mmol) were added. The mixture was stirred at room temperature for 4 h in the dark. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2.27 g, 10.0 mmol) was added, and the mixture was stirred at room temperature for 9 h. Et_3N (1.0 mL, 7.2 mmol) was added, and the mixture was concentrated. Purification by silica gel column chromatography ($CHCl_3$/hexane (2:1)) gave **5a** as a purple solid (1.73 g, 52%): ^1H NMR ($CDCl_3$, 600 MHz) δ –2.80 (s, 2H), 1.55 (br s, 16H), 1.89–1.92 (m, 16H), 3.41 (t, J = 6.8 Hz, 8H), 4.15 (t, J = 6.4 Hz, 8H), 7.32 (dd, J = 2.3, 8.5 Hz, 4H), 7.63 (t, J = 7.9 Hz, 4H), 7.77 (s, 4H), 7.81 (d, J = 7.1 Hz, 4H), 8.90 (s, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz, 50 °C) δ 25.4, 28.0, 29.2, 32.7, 33.5, 68.2, 114.3, 120.0, 121.4, 127.5, 127.6, 131.1, 143.6, 146.7, 157.6; IR (KBr) 3317, 3063, 2932, 2862, 1589, 1466, 1435, 1342, 1281, 1173, 1042, 972, 926, 795, 733, 648 cm^{-1}; Anal. Calcd for $C_{68}H_{74}Br_4N_4O_4$: C, 61.36; H, 5.60; N, 4.21. Found: C,

60.99; H, 5.76; N, 4.11; MS (FAB) calcd for $C_{68}H_{75}{}^{79}Br_2{}^{81}Br_2N_4O_4$ 1331.2, found 1331.3 ([M + H]$^+$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(8-bromooctyloxy)phenyl]porphyrin (5b).
A solution of pyrrole (0.81 mL, 12 mmol) and 3-(8-bromooctyloxy)benzaldehyde (**4b**)[1,2] (3.66 g, 11.7 mmol) in dry CH_2Cl_2 (1.2 L) was bubbled with Ar, and then $BF_3{\cdot}OEt_2$ (15 μL, 0.12 mmol) and CF_3CO_2H (0.78 mL, 11 mmol) were added. The mixture was stirred at room temperature for 4 h in the dark. DDQ (2.66 g, 11.7 mmol) was added, and the mixture was stirred at room temperature for 13 h. Et_3N (1.2 mL, 8.6 mmol) was added, and the mixture was concentrated. Purification by silica gel column chromatography ($CHCl_3$/hexane (4:3)) gave **5b** as a purple highly viscous solid (2.24 g, 53%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ –2.79 (s, 2H), 1.35–1.46 (m, 24H), 1.50–1.54 (m, 8H), 1.82–1.90 (m, 16H), 3.38 (t, J = 6.8 Hz, 8H), 4.15 (t, J = 6.5 Hz, 8H), 7.33 (dd, J = 2.0, 8.4 Hz, 4H), 7.64 (t, J = 7.9 Hz, 4H), 7.78 (s, 4H), 7.81 (d, J = 7.3 Hz, 4H), 8.91 (s, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz, 50 °C) δ 26.0, 28.1, 28.6, 29.2, 29.4, 32.8, 33.6, 68.3, 114.3, 120.0, 121.4, 127.4, 127.6, 131.1, 143.5, 146.8, 157.6; IR (CH_2Cl_2) 3317, 3031, 2932, 2862, 1597, 1466, 1435, 1396, 1350, 1281, 1180, 1042, 995, 980, 918, 872, 802, 748, 702, 640 cm^{-1}; Anal. Calcd for $C_{76}H_{90}Br_4N_4O_4$: C, 63.25; H, 6.29; N, 3.88. Found: C, 63.64; H, 6.38; N, 3.49; MS (FAB) calcd for $C_{76}H_{91}{}^{79}Br_2{}^{81}Br_2N_4O_4$ 1443.4, found 1443.4 ([M + H]$^+$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(4-bromobutoxy)phenyl]porphyrin (5c).
A solution of pyrrole (140 μL, 2.02 mmol) and 3-(4-bromobutoxy)benzaldehyde (**4c**)[1,2] (521 mg, 2.03 mmol) in dry CH_2Cl_2 (200 mL) was bubbled with Ar, and then $BF_3{\cdot}OEt_2$ (3 μL, 20 μmol) and CF_3CO_2H (135 μL, 1.82 mmol) were added. The mixture was stirred at room temperature for 4 h in the dark. DDQ (455 mg, 2.00 mmol) was added, and the mixture was stirred at room temperature for 12 h. Et_3N (0.28 mL, 2.0 mmol) was added, and the mixture was concentrated. Purification by silica gel column chromatography ($CHCl_3$/hexane (2:1)) gave **5c** as a purple solid (349 mg, 57%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ –2.82 (s, 2H), 2.04 (quint, J = 6.6 Hz, 8H), 2.14 (quint, J = 6.6 Hz, 8H), 3.52 (t, J = 6.6 Hz, 8H), 4.19 (t, J = 6.0 Hz, 8H), 7.32 (dd, J = 2.5, 8.5 Hz, 4H), 7.64 (t, J = 7.9 Hz, 4H), 7.76 (s, 4H), 7.81 (d, J = 7.3 Hz, 4H), 8.88 (s, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz, 50 °C) δ 28.1, 29.6, 33.2, 67.3, 114.3, 119.9, 121.3, 127.5, 127.8, 131.1, 143.6, 157.4; IR (KBr) 3314, 3063, 2936, 2870, 1597, 1574, 1470, 1431, 1396, 1346, 1285, 1261, 1165, 1045, 976, 949, 918, 880, 802, 775, 733, 698, 660 cm^{-1}; HRMS (FAB) calcd for $C_{60}H_{59}{}^{79}Br_2{}^{81}Br_2N_4O_4$ 1219.1229, found 1219.1172 ([M + H]$^+$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(6-bromohexyloxy)phenyl]porphyrin zinc(II) (6a).
A solution of porphyrin **5a** (266 mg, 0.200 mmol) in dry $CHCl_3$ (28 mL) under N_2 was heated at 70 °C for 45 min. A solution of $Zn(OAc)_2{\cdot}2H_2O$ (439 mg, 2.00 mmol) in dry MeOH (4 mL) was added, and the mixture was heated at 70 °C for 4 h. The mixture was cooled to room

temperature, concentrated, and washed with water. The mixture was dried over Na_2SO_4, and concentrated. Purification by silica gel column chromatography (CH_2Cl_2/hexane (2:1)) gave **6a** as a reddish purple solid (272 mg, 98%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.53–1.55 (m, 16H), 1.88–1.90 (m, 16H), 3.40 (t, J = 6.8 Hz, 8H), 4.11–4.15 (m, 8H), 7.30–7.32 (m, 4H), 7.63 (t, J = 7.9 Hz, 4H), 7.76–7.77 (m, 4H), 7.81 (d, J = 7.3 Hz, 4H), 9.00 (s, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 25.3, 27.9, 29.1, 32.6, 33.7, 67.9, 114.0, 120.9, 121.0, 127.3, 127.5, 132.0, 144.0, 150.1, 157.1; IR (KBr) 3062, 2936, 2858, 1597, 1578, 1477, 1435, 1339, 1285, 1258, 1184, 1049, 999, 937, 799, 721, 702, 648 cm^{-1}; Anal. Calcd for $C_{68}H_{72}Br_4N_4O_4Zn$: C, 58.57; H, 5.20; N, 4.02. Found: C, 58.65; H, 5.25; N, 3.70; MS (FAB) calcd for $C_{68}H_{73}{}^{79}Br_2{}^{81}Br_2N_4O_4{}^{64}Zn$ 1393.2, found 1393.2 ([M + H]$^+$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(6-bromohexyloxy)phenyl]porphyrin magnesium(II) (6b).
A mixture of porphyrin **5a** (266 mg, 0.200 mmol) and $MgBr_2$ (368 mg, 2.00 mmol) in dry CH_2Cl_2 (17 mL) under N_2 was stirred at room temperature for 5 min, and Et_3N (1.7 mL, 12 mmol) was added. The mixture was stirred at room temperature for 30 min. The mixture was washed with 0.5% HCl and then water. The mixture was dried over Na_2SO_4, and concentrated. Recrystallization from CH_2Cl_2/hexane gave **6b** as a purple solid (261 mg, 96%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.53–1.54 (m, 16H), 1.86–1.91 (m, 16H), 3.40 (t, J = 6.8 Hz, 8H), 4.14 (t, J = 6.4 Hz, 8H), 7.29 (dd, J = 2.0, 8.4 Hz, 4H), 7.60 (t, J = 7.9 Hz, 4H), 7.78 (br s, 4H), 7.81 (d, J = 7.6 Hz, 4H), 8.91 (s, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz, 50 °C) δ 25.3, 27.9, 29.1, 32.7, 33.5, 68.3, 113.9, 121.3, 121.7, 126.9, 128.0, 131.8, 145.1, 149.9, 156.9; IR (KBr) 3055, 2932, 2862, 1666, 1597, 1474, 1427, 1389, 1335, 1281, 1180, 1049, 995, 941, 880, 795, 725, 640 cm^{-1}; Anal. Calcd for $C_{68}H_{72}Br_4MgN_4O_4$: C, 60.35; H, 5.36; N, 4.14. Found: C, 60.12; H, 5.48; N, 3.76; MS (FAB) calcd for $C_{68}H_{73}{}^{79}Br_2{}^{81}Br_2MgN_4O_4$ 1353.2, found 1353.2 ([M + H]$^+$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(8-bromooctyloxy)phenyl]porphyrin magnesium (6c).
A mixture of porphyrin **5b** (588 mg, 0.407 mmol) and $MgBr_2$ (752 mg, 4.09 mmol) in dry CH_2Cl_2 (34 mL) under N_2 was stirred at room temperature for 5 min, and Et_3N (3.4 mL, 24 mmol) was added. The mixture was stirred at room temperature for 30 min. The mixture was washed with 0.5% HCl and then water. The mixture was dried over Na_2SO_4, and concentrated. Recrystallization from CH_2Cl_2/hexane gave **6c** as a purple highly viscous solid (547 mg, 92%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.33–1.52 (m, 32H), 1.80–1.85 (m, 16H), 3.36 (t, J = 6.8 Hz, 8H), 4.03–4.09 (m, 8H), 7.24–7.25 (m, 4H), 7.59 (t, J = 7.9 Hz, 4H), 7.73 (br s, 4H), 7.80 (d, J = 7.2 Hz, 4H), 8.91 (s, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 25.7, 25.76, 25.80, 25.83, 28.0, 28.59, 28.60, 28.9, 28.96, 29.04, 29.07, 29.10, 32.7, 33.9, 68.3, 113.76, 113.84, 121.3, 121.4, 126.9, 127.8, 131.9, 144.8, 149.7, 156.5, 156.6 (signals for the atropisomers were observed); IR (CH_2Cl_2) 3047, 2936, 2858, 1597, 1576, 1518, 1472, 1431, 1391, 1333, 1285, 1265, 1207, 1184, 1165, 1067, 999, 937, 870, 800, 785, 756, 708, 644 cm^{-1}; Anal. Calcd for

$C_{76}H_{88}Br_4MgN_4O_4$: C, 62.29; H, 6.05; N, 3.82. Found: C, 62.24; H, 5.97; N, 3.57; MS (FAB) calcd for $C_{76}H_{89}{}^{79}Br_2{}^{81}Br_2MgN_4O_4$ 1465.3, found 1465.4 ($[M + H]^+$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(4-bromobutoxy)phenyl]porphyrin magnesium(II) (6d).

A mixture of porphyrin **5c** (515 mg, 0.423 mmol) and $MgBr_2$ (779 mg, 4.23 mmol) in dry CH_2Cl_2 (35 mL) under N_2 was stirred at room temperature for 5 min, and Et_3N (3.5 mL, 25 mmol) was added. The mixture was stirred at room temperature for 30 min. The mixture was washed with 0.5% HCl and then water. The mixture was dried over Na_2SO_4, and concentrated. Recrystallization from CH_2Cl_2/hexane gave **6d** as a purple solid (474 mg, 90%): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.97–2.00 (m, 8H), 2.08–2.12 (m, 8H), 3.50 (t, J = 6.6 Hz, 8H), 4.13 (t, J = 4.7 Hz, 8H), 7.26 (d, J = 7.9 Hz, 4H), 7.60 (t, J = 7.9 Hz, 4H), 7.74 (s, 4H), 7.82 (d, J = 7.0 Hz, 4H), 8.91 (s, 8H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 27.7, 29.3, 33.5, 67.1, 113.7, 121.3, 127.0, 127.9, 131.9, 144.9, 149.7, 156.5; IR (KBr) 3063, 2943, 2870, 1597, 1574, 1474, 1431, 1389, 1330, 1285, 1254, 1184, 1065, 1045, 1022, 999, 961, 883, 799, 725, 698 cm^{-1}; Anal. Calcd for $C_{60}H_{56}Br_4MgN_4O_4$: C, 58.07; H, 4.55; N, 4.51. Found: C, 57.86; H, 4.81; N, 4.12; HRMS (FAB) calcd for $C_{60}H_{57}{}^{79}Br_3{}^{81}BrMgN_4O_4$ 1239.0943, found 1239.0964 ($[M + H]^+$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(6-triphenylphosphoniohexyloxy)phenyl]porphyrin zinc(II) tetrabromide (1a).

A solution of Zn^{II} porphyrin **6a** (139 mg, 0.100 mmol) and PPh_3 (315 mg, 1.20 mmol) in dry $CHCl_3$ (1 mL) and dry CH_3CN (1 mL) under Ar was heated at 70 °C for 48 h in the dark. The mixture was cooled to room temperature, and concentrated. The crude product was washed with Et_2O, and filtered. Recrystallization from CH_2Cl_2/Et_2O gave **1a** as a purple solid (207 mg, 85%): ^{1}H NMR (d_6-DMSO, 600 MHz) δ 1.50–1.55 (m, 24H), 1.74–1.81 (m, 8H), 3.59 (br s, 8H), 4.13 (br s, 8H), 7.35–7.36 (m, 4H), 7.66–7.83 (m, 72H), 8.78 (s, 8H); ^{13}C NMR (CD_3OD, 150 MHz) δ 22.4 (d, J_{CP} = 51.6 Hz), 23.3, 26.3, 29.8, 30.9 (d, J_{CP} = 15.6 Hz), 68.8, 114.2, 119.7 (d, J_{CP} = 85.7 Hz), 121.6, 122.8, 128.4, 128.6, 131.4 (d, J_{CP} = 12.6 Hz), 132.6, 134.6 (d, J_{CP} = 9.7 Hz), 136.0, 145.8, 151.2, 158.5; ^{31}P NMR (CD_3OD, 243 MHz) δ 24.2; IR (KBr) 3055, 2932, 2862, 1582, 1474, 1435, 1327, 1281, 1173, 1111, 1057, 995, 934, 787, 725, 687 cm^{-1}; HRMS (ESI) calcd for $C_{140}H_{132}{}^{81}Br_3N_4O_4P_4{}^{64}Zn$ 2363.5979, found 2363.5986 ($[M – Br]^+$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(6-triphenylphosphoniohexyloxy)phenyl]porphyrin magnesium(II) tetrabromide (1b).

A solution of Mg^{II} porphyrin **6b** (271 mg, 0.200 mmol) and PPh_3 (630 mg, 2.40 mmol) in dry $CHCl_3$ (2 mL) and dry CH_3CN (2 mL) under Ar was heated at 70 °C for 48 h in the dark. The mixture was cooled to room temperature, and concentrated. The crude product was washed with Et_2O, and filtered. Recrystallization from CH_2Cl_2/Et_2O gave **1b** as a purple solid (337 mg,

70%): ^{1}H NMR (CD_3OD, 600 MHz) δ 1.58–1.69 (m, 24H), 1.82 (br s, 8H), 3.35–3.38 (m, 8H), 4.15 (br s, 8H), 7.31 (d, J = 8.4 Hz, 4H), 7.62–7.74 (m, 72H), 8.77–8.78 (m, 8H); ^{13}C NMR (CD_3OD, 150 MHz) δ 22.4 (d, J_{CP} = 49.9 Hz), 23.3, 26.3, 29.8, 31.0 (d, J_{CP} = 15.9 Hz), 68.8, 114.0, 119.7 (d, J_{CP} = 85.1 Hz), 122.6, 122.9, 128.3, 128.8, 131.4 (d, J_{CP} = 12.3 Hz), 132.7, 134.6 (d, J_{CP} = 9.2 Hz), 136.1, 146.3, 151.1, 158.5; ^{31}P NMR (CD_3OD, 243 MHz) δ 28.2; IR (KBr) 3055, 2939, 2862, 1593, 1516, 1477, 1435, 1331, 1285, 1254, 1180, 1111, 1061, 995, 934, 883, 795, 721, 691 cm^{-1}; HRMS (ESI) calcd for $C_{140}H_{132}{}^{81}BrMgN_4O_4P_4$ 720.6071, found 720.5831 ($[M - 3Br]^{3+}$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(6-tributylammoniohexyloxy)phenyl]porphyrin zinc(II) tetrabromide (1c).

A solution of Zn^{II} porphyrin **6a** (110 mg, 0.0788 mmol) and Bu_3N (0.45 mL, 1.9 mmol) in dry $CHCl_3$ (0.79 mL) and dry CH_3CN (0.79 mL) under N_2 was heated at 70 °C for 90 h in the dark. The mixture was cooled to room temperature, and concentrated. A layer of Bu_3N was removed with a pipette. CH_2Cl_2 was added, and the mixture was washed with 0.5% HBr and then water containing NaBr. The mixture was dried over Na_2SO_4, and concentrated. Recrystallization from CH_2Cl_2/Et_2O gave **1c** as a purple solid (123 mg, 73%): ^{1}H NMR (CD_3OD, 600 MHz) δ 0.92–0.97 (m, 36H), 1.31–1.64 (m, 72H), 1.89 (br s, 8H), 3.11–3.20 (m, 32H), 4.19–4.20 (m, 8H), 7.34–7.35 (m, 4H), 7.62–7.65 (m, 4H), 7.73–7.77 (m, 8H), 8.85 (s, 8H); ^{13}C NMR (CD_3OD, 150 MHz) δ 14.0, 20.5, 22.58, 22.62, 24.6, 26.6, 26.9, 30.1, 59.3, 68.9, 114.3, 121.6, 122.7, 128.4, 128.6, 132.7, 145.9, 151.3, 158.7; IR (KBr) 3063, 2936, 2870, 1597, 1574, 1474, 1431, 1385, 1335, 1285, 1258, 1180, 1049, 995, 937, 880, 791, 718, 702 cm^{-1}; HRMS (ESI) calcd for $C_{116}H_{180}{}^{81}BrN_8O_4{}^{64}Zn$ 631.4194, found 631.3962 ($[M - 3Br]^{3+}$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(6-tributylammoniohexyloxy)phenyl]porphyrin magnesium(II) tetrabromide (1d).

A solution of Mg^{II} porphyrin **6b** (135 mg, 0.100 mmol) and Bu_3N (0.57 mL, 2.4 mmol) in dry $CHCl_3$ (1 mL) and dry CH_3CN (1 mL) under Ar was heated at 70 °C for 90 h in the dark. The mixture was cooled to room temperature, and concentrated. A layer of Bu_3N was removed with a pipette. CH_2Cl_2 was added, and the mixture was washed with 0.5% HBr and then water containing NaBr. The mixture was dried over Na_2SO_4, and concentrated. Recrystallization from CH_2Cl_2/Et_2O gave **1d** as a purple solid (157 mg, 75%): ^{1}H NMR (CD_3OD, 600 MHz) δ 0.93–1.01 (m, 36H), 1.32–1.36 (m, 24H), 1.45–1.50 (m, 8H), 1.57–1.71 (m, 40H), 1.89–1.95 (m, 8H), 3.14–3.24 (m, 32H), 4.21 (br s, 8H), 7.34 (dd, J = 1.8, 8.6 Hz, 4H), 7.63 (t, J = 7.9 Hz, 4H), 7.74–7.75 (m, 4H), 7.78 (d, J = 6.5 Hz, 4H), 8.81–8.82 (m, 8H); ^{13}C NMR (CD_3OD, 150 MHz) δ 14.0, 20.6, 22.6, 22.7, 24.7, 26.6, 26.9, 30.1, 59.3, 68.9, 114.2, 122.6, 122.8, 128.3, 128.8, 132.7, 146.4, 151.2, 158.6; IR (KBr) 3038, 2963, 2876, 1597, 1578, 1474, 1431, 1383, 1333, 1279, 1184, 1165, 997, 937, 880, 799, 727, 710, 694 cm^{-1}; HRMS (ESI) calcd for $C_{116}H_{180}{}^{79}Br^{81}Br_2MgN_8O_4$ 2014.1487, found 2014.1243 ($[M - Br]^{+}$) (cluster peaks based on

isotope abundance).

5,10,15,20-Tetrakis[3-(8-tributylammoniooctyloxy)phenyl]porphyrin magnesium(II) tetrabromide (1e).

A solution of Mg^{II} porphyrin **6c** (147 mg, 0.100 mmol) and Bu_3N (0.57 mL, 2.4 mmol) in dry $CHCl_3$ (1 mL) and dry CH_3CN (1 mL) under Ar was heated at 70 °C for 92 h in the dark. The mixture was cooled to room temperature, and concentrated. A layer of Bu_3N was removed with a pipette. CH_2Cl_2 was added, and the mixture was washed with 0.5% HBr and then water containing NaBr. The mixture was dried over Na_2SO_4, and concentrated. Recrystallization from CH_2Cl_2/Et_2O gave **1e** as a purple solid (187 mg, 85%): ^{1}H NMR (CD_3OD, 600 MHz) δ 0.90–0.99 (m, 36H), 1.21–1.52 (m, 88H), 1.84–1.87 (m, 8H), 2.98–3.00 (m, 32H), 4.16 (br s, 8H), 7.31 (d, J = 8.3 Hz, 4H), 7.62 (t, J = 7.8 Hz, 4H), 7.73 (br s, 4H), 7.77 (br s, 4H), 8.85 (s, 8H); ^{13}C NMR (CD_3OD, 150 MHz) δ 14.0, 20.5, 22.6, 24.6, 27.0, 27.1, 29.9, 30.1, 30.4, 59.2, 59.4, 69.2, 114.2, 122.6, 122.8, 128.3, 128.8, 132.8, 146.4, 151.2, 158.7; IR (KBr) 3038, 2939, 2876, 1597, 1578, 1474, 1433, 1383, 1333, 1281, 1207, 1184, 1165, 997, 937, 880, 799, 712, 696 cm^{-1}; HRMS (ESI) calcd for $C_{124}H_{196}{}^{79}Br^{81}Br_2MgN_8O_4$ 2126.2739, found 2126.2368 ([M – Br]$^+$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(4-tributylammoniobutoxy)phenyl]porphyrin magnesium(II) tetrabromide (1f).

A solution of Mg^{II} porphyrin **6d** (124 mg, 0.100 mmol) and Bu_3N (0.57 mL, 2.4 mmol) in dry $CHCl_3$ (1 mL) and dry CH_3CN (1 mL) under Ar was heated at 70 °C for 90 h in the dark. The mixture was cooled to room temperature, and concentrated. A layer of Bu_3N was removed with a pipette. CH_2Cl_2 was added, and the mixture was washed with 0.5% HBr and then water containing NaBr. The mixture was dried over Na_2SO_4, and concentrated. Recrystallization from CH_2Cl_2/Et_2O gave **1f** as a purple solid (192 mg, 97%): ^{1}H NMR (CD_3OD, 600 MHz) δ 0.89–1.00 (m, 36H), 1.32–1.42 (m, 24H), 1.65–1.67 (m, 24H), 1.98 (br s, 16H), 3.23–3.28 (m, 24H), 3.40 (br s, 8H), 4.30 (br s, 8H), 7.38 (d, J = 8.2 Hz, 4H), 7.66 (t, J = 8.0 Hz, 4H), 7.79–7.81 (m, 8H), 8.79–8.80 (m, 8H); ^{13}C NMR (CD_3OD, 150 MHz) δ 14.0, 19.7, 20.6, 24.7, 26.8, 59.0, 59.4, 67.8, 114.1, 122.4, 122.7, 128.3, 129.1, 132.6, 146.7, 151.1, 158.3; IR (KBr) 3063, 2959, 2874, 1597, 1574, 1474, 1435, 1381, 1331, 1285, 1257, 1180, 1065, 995, 934, 880, 799, 721, 702 cm^{-1}; HRMS (ESI) calcd for $C_{108}H_{164}{}^{81}BrMgN_8O_4$ 580.7296, found 580.7075 ([M – 3Br]$^{3+}$) (cluster peaks based on isotope abundance).

5,10,15,20-Tetrakis[3-(6-pyridiniohexyloxy)phenyl]porphyrin magnesium(II) tetrabromide (1g).

A solution of Mg^{II} porphyrin **6b** (136 mg, 0.100 mmol) in pyridine (2 mL) was heated under N_2 at 115 °C for 14 h. The mixture was cooled to room temperature, and concentrated. Recrystallization from MeOH/EtOAc gave **1g** as a purple solid (162 mg, 97%): ^{1}H NMR (CD_3OD, 600 MHz) δ 1.32–1.38 (m, 8H), 1.52–1.53 (m, 8H), 1.78–1.81 (m, 8H), 1.85–1.93

(m, 8H), 4.10–4.12 (m, 8H), 4.34–4.42 (m, 8H), 7.26 (d, J = 7.9 Hz, 4H), 7.59 (t, J = 7.8 Hz, 4H), 7.70 (s, 4H), 7.76 (d, J = 7.8 Hz, 4H), 7.81–7.87 (m, 8H), 8.27–8.33 (m, 4H), 8.70–8.78 (m, 8H), 8.82 (s, 8H); ^{13}C NMR (CD_3OD, 150 MHz) δ 26.5, 26.7, 30.0, 32.1, 62.6, 68.9, 114.2, 122.6, 122.8, 128.3, 128.8, 129.1, 132.8, 145.5, 146.3, 146.5, 151.1, 158.6; IR (KBr) 3051, 2936, 2862, 1632, 1597, 1574, 1485, 1431, 1331, 1285, 1254, 1180, 1053, 995, 941, 795, 775, 683 cm^{-1}; HRMS (ESI) calcd for $C_{88}H_{92}{}^{81}BrMgN_8O_4$ 476.5418, found 476.5147 ([M – 3Br]$^{3+}$) (cluster peaks based on isotope abundance).

[2] Coupling Reaction of CO_2 with Epoxide.

General Procedure. A 30-mL stainless autoclave was charged with epoxide (10.0 mmol), catalyst (amount indicated in the text), and then CO_2 (initial pressure indicated in the text). The mixture was heated with stirring at a constant temperature for a reaction time. The reactor was then cooled in an ice bath for 30 min, and excess CO_2 was released carefully. The NMR yield was determined by using 2-methoxynaphthalene as an internal standard, or the product was purified by silica gel column chromatography.

4-*n*-Butyl-1,3-dioxolan-2-one (3a).[3] 99% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.93 (t, J = 7.1 Hz, 3H), 1.33–1.49 (m, 4H), 1.66–1.72 (m, 1H), 1.79–1.85 (m, 1H), 4.07 (dd, J = 7.6, 8.4 Hz, 1H), 4.52 (dd, J = 7.6, 8.4 Hz, 1H), 4.70 (dq, J = 5.5, 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 13.6, 22.1, 26.2, 33.3, 69.3, 77.0, 155.0; IR (neat) 2959, 2936, 2870, 1798, 1466, 1385, 1173, 1123, 1065, 775, 717 cm^{-1}.

4-Methyl-1,3-dioxolan-2-one (3b).[3] 99% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.50 (d, J = 6.6 Hz, 3H), 4.03 (dd, J = 7.5, 8.3 Hz, 1H), 4.55 (dd, J = 7.5, 8.3 Hz, 1H), 4.83–4.88 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 19.3, 70.6, 73.5, 155.0; IR (neat) 2990, 2936, 1790, 1558, 1485, 1454, 1389, 1354, 1180, 1119, 1049, 775, 710 cm^{-1}.

4-*n*-Octyl-1,3-dioxolan-2-one (3c).[3] 93% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.88 (t, J = 7.0 Hz, 3H), 1.28–1.51 (m, 12H), 1.65–1.70 (m, 1H), 1.78–1.84 (m, 1H), 4.07 (dd, J = 7.7, 8.2 Hz, 1H), 4.52 (dd, J = 7.7, 8.2 Hz, 1H), 4.70 (dq, J = 5.7, 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 13.9, 22.5, 24.2, 28.96, 28.99, 29.2, 31.6, 33.7, 69.3, 77.0, 155.0; IR (neat) 2928, 2858, 1798, 1458, 1385, 1169, 1065, 775, 721 cm^{-1}.

(*R*)-4-Phenyl-1,3-dioxolan-2-one ((*R*)-3d).[3] 93% yield; white solid; mp 68–69 °C (lit.[4] 49–52 °C); >99% ee; $[\alpha]^{28}_D$ = –48.5 (*c* 1.00, $CHCl_3$), lit.[5] $[\alpha]^{20}_D$ = –51.8 (*c* 1.0, $CHCl_3$) for (*R*)-**3d** with 99% ee; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.35 (dd, J = 8.2, 8.4 Hz, 1H), 4.80 (dd, J = 8.2, 8.4 Hz, 1H), 5.68 (t, J = 8.2 Hz, 1H), 7.36–7.37 (m, 2H), 7.43–7.47 (m, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 71.1, 78.0, 125.8, 129.2, 129.7, 135.7, 154.8; IR (KBr) 2978, 2932, 1778, 1481, 1458, 1396, 1358, 1323, 1177, 1053, 961, 907, 764, 702 cm^{-1}; HPLC: Chiralcel OD-H, hexane/*i*-PrOH = 9:1, flow rate 1.0 mL/min, detection 254 nm, (*R*) 21.5 min, (*S*) 25.4 min.

4-Chloromethyl-1,3-dioxolan-2-one (3e).[3] 95% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.72–3.78 (m, 2H), 4.42 (dd, J = 5.8, 8.8 Hz, 1H), 4.59 (dd, J = 8.3, 8.8 Hz, 1H), 4.94–4.97 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 43.9, 66.8, 74.3, 154.3; IR (neat) 2986, 2924, 1794, 1543, 1477, 1396, 1358, 1335, 1165, 1072, 768, 718, 667 cm^{-1}.

4-Methoxymethyl-1,3-dioxolan-2-one (3f).[3] 95% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.43 (s, 3H), 3.58 (dd, J = 3.9, 10.9 Hz, 1H), 3.64 (dd, J = 3.9, 10.9 Hz, 1H), 4.38 (dd, J = 7.3, 8.4 Hz, 1H), 4.49 (t, J = 8.4 Hz, 1H), 4.78–4.82 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 59.6, 66.1, 71.4, 74.9, 154.9; IR (neat) 2993, 2939, 2897, 2824, 1794, 1543, 1474, 1396, 1362, 1339, 1173, 1134, 1076, 1049, 957, 775, 714 cm^{-1}.

4-Phenoxymethyl-1,3-dioxolan-2-one (3g).[6] 98% yield; white solid; mp 99–100 °C (lit.[4] 98–100 °C); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.16 (dd, J = 4.0, 10.5 Hz, 1H), 4.24 (dd, J = 4.0, 10.5 Hz, 1H), 4.55 (dd, J = 5.9, 8.5 Hz, 1H), 4.62 (t, J = 8.5 Hz, 1H), 5.02–5.05 (m, 1H), 6.91 (d, J = 7.8 Hz, 2H), 7.02 (t, J = 7.8 Hz, 1H), 7.31 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 66.2, 66.8, 74.1, 114.5, 121.9, 129.7, 154.6, 157.7; IR (KBr) 2928, 1805, 1601, 1493, 1458, 1396, 1312, 1250, 1169, 1092, 1057, 1015, 760, 694 cm^{-1}.

4-Hydroxymethyl-1,3-Dioxolan-2-one (3h).[7] 87% yield; colorless oil; ^{1}H NMR (d_6-acetone, 600 MHz) δ 3.68–3.72 (m, 1H), 3.85–3.89 (m, 1H), 4.39–4.42 (m, 2H), 4.56 (t, J = 8.4 Hz, 1H), 4.84–4.87 (m, 1H); ^{13}C NMR (d_6-acetone, 150 MHz) δ 62.0, 66.6, 77.8, 156.2; IR (neat) 3418, 2932, 2882, 1790, 1636, 1481, 1404, 1373, 1339, 1310, 1182, 1086, 1055, 984, 841, 775, 718 cm^{-1}.

4-Vinyl-1,3-dioxolan-2-one (3i).[8] 81% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.16 (dd, J = 7.6, 8.4 Hz, 1H), 4.60 (t, J = 8.4 Hz, 1H), 5.12 (q, J = 7.6 Hz, 1H), 5.45 (d, J = 10.4 Hz, 1H), 5.52 (d, J = 17.1 Hz, 1H), 5.90 (ddd, J = 7.6, 10.4, 17.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 68.9, 77.1, 120.8, 132.0, 154.7; IR (neat) 3094, 2993, 2932, 1794, 1543, 1485, 1435, 1385, 1327, 1169, 1065, 991, 949, 772, 725 cm^{-1}.

***trans*-4-*n*-Butyl-5-deuterio-1,3-dioxolan-2-one (3j).**[9] 72% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.93 (t, J = 7.2 Hz, 3H), 1.32–1.49 (m, 4H), 1.66–1.72 (m, 1H), 1.79–1.85 (m, 1H), 4.06 (d, J = 7.0 Hz, 1H), 4.70 (q, J = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 13.5, 22.0, 26.2, 33.2, 68.9 (t, J_{CD} = 23.7 Hz), 76.9, 155.0; IR (neat) 2962, 2936, 2870, 1794, 1543, 1466, 1366, 1304, 1177, 1061, 775, 714 cm^{-1}.

References

1 Y. Zhao, Y. Zhou, K. M. O'Boyle and P. V. Murphy, *Bioorg. Med. Chem.*, 2008, **16**, 6333–6337.

2 A. H. Éll, G. Csjernyik, V. F. Slagt, J.-E. Bäckvall, S. Berner, C. Puglia, G. Ledung and S. Oscarsson, *Eur. J. Org. Chem.*, 2006, 1193–1199.

3 Y. Tsutsumi, K. Yamakawa, M. Yoshida, T. Ema and T. Sakai, *Org. Lett.*, 2010, **12**, 5728–5731.

4 W. Clegg, R. W. Harrington, M. North and R. Pasquale, *Chem. Eur. J.*, 2010, **16**, 6828–6843.

5 Y. Du, J.-Q. Wang, J.-Y. Chen, F. Cai, J.-S. Tian, D.-L. Kong and L.-N. He, *Tetrahedron Lett.*, 2006, **47**, 1271–1275.

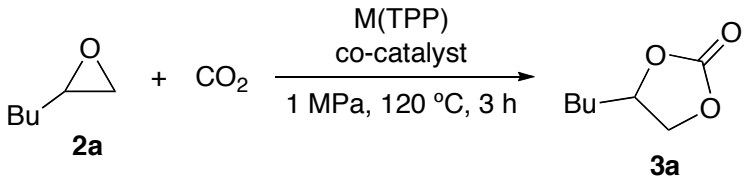
6 X.-Y. Dou, J.-Q. Wang, Y. Du, E. Wang and L.-N. He, *Synlett*, 2007, 3058–3062.

7 G. Rokicki, P. Rakoczy, P. Parzuchowski and M. Sobiecki, *Green Chem.*, 2005, **7**, 529–539.

8 T. Fujinami, T. Suzuki, M. Kamiya, S. Fukuzawa and S. Sakai, *Chem. Lett.*, 1985, 199–200.

9 Y.-M. Shen, W.-L. Duan and M. Shi, *Eur. J. Org. Chem.*, 2004, 3080–3089.

[3] Screening of Two-component Catalytic Systems.



2a **3a**

Table S1. Screening of Two-component Catalytic Systems (Data for Fig. 4).[a]

entry	M(TPP)	co-catalyst	yield (%)[b]
1	Mg(TPP)	TPPB	94
2	Mg(TPP)	TBAB	93
3	Mg(TPP)	DMAP	85
4	Mg(TPP)	PTAT	6
5	Co(TPP)	TPPB	7
6	Co(TPP)	TBAB	20
7	Co(TPP)	DMAP	5
8	Co(TPP)	PTAT	1
9	Ni(TPP)	TPPB	33
10	Ni(TPP)	TBAB	13
11	Ni(TPP)	DMAP	6
12	Ni(TPP)	PTAT	0.4
13	Cu(TPP)	TPPB	34
14	Cu(TPP)	TBAB	14
15	Cu(TPP)	DMAP	5
16	Cu(TPP)	PTAT	0.1
17	Zn(TPP)	TPPB	93
18	Zn(TPP)	TBAB	93
19	Zn(TPP)	DMAP	54
20	Zn(TPP)	PTAT	1
21	–	TPPB	6
22	–	TBAB	13
23	–	DMAP	5
24	–	PTAT	0.3
25	Mg(TPP)	–	0.4
26	Co(TPP)	–	0.1
27	Ni(TPP)	–	0
28	Cu(TPP)	–	0.1
29	Zn(TPP)	–	0.5

[a] Conditions: **2a** (1.00 g, 10.0 mmol), M(TPP) (0.010 mmol, 0.1 mol %), co-catalyst (0.010 mmol, 0.1 mol %), CO_2 (1.0 MPa), 120 °C, 3 h, in a 30-mL autoclave. [b] Determined by ^{1}H NMR using 2-methoxynaphthalene as an internal standard.

[4] Summary of Reported Porphyrin Catalysts.

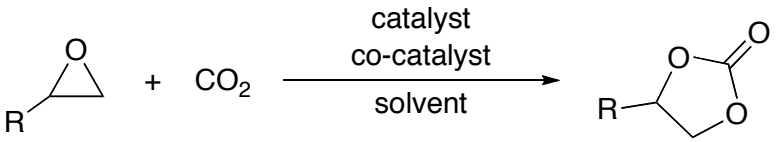


Table S2. Two-component Catalytic Systems with Metalloporphyrins.

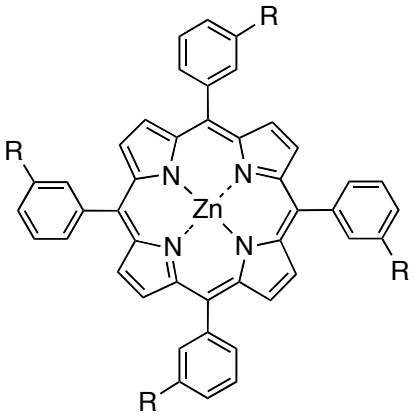
catalyst	co-catalyst (equiv)[a]	R	CO_2 (MPa)	solvent	temp. (°C)	time (h)	yield (%)	TON	ref.
Cr(TPP)(O)	*N*-MeIm[b] (8)	Me	5.2	–	80	48	95	7,300	1
Co(TPP)(Cl)	DMAP (2)	Me	1.7	CH_2Cl_2	120	1	42	1,100	2
Cu(TPP)	DMAP (1)	CH_2Cl	0.69	CH_2Cl_2	120	4	75	2,000	3
Co(TPP)(OAc)	PTAT (2)	Me	0.69	–	25	3	90	900	4
Sn(TPP)$(OTf)_2$	TBPB[c] (50)	Hex	0.1	DMF	50	3	100	50	5
Mg(TPP)	Et_3N (1.25)	CH_2Cl	1.5	–	140	8	92	9,200	6

[a] Amount relative to catalyst. [b] *N*-MeIm: *N*-methylimidazole. [c] TBPB: tetrabutylphosphonium bromide.

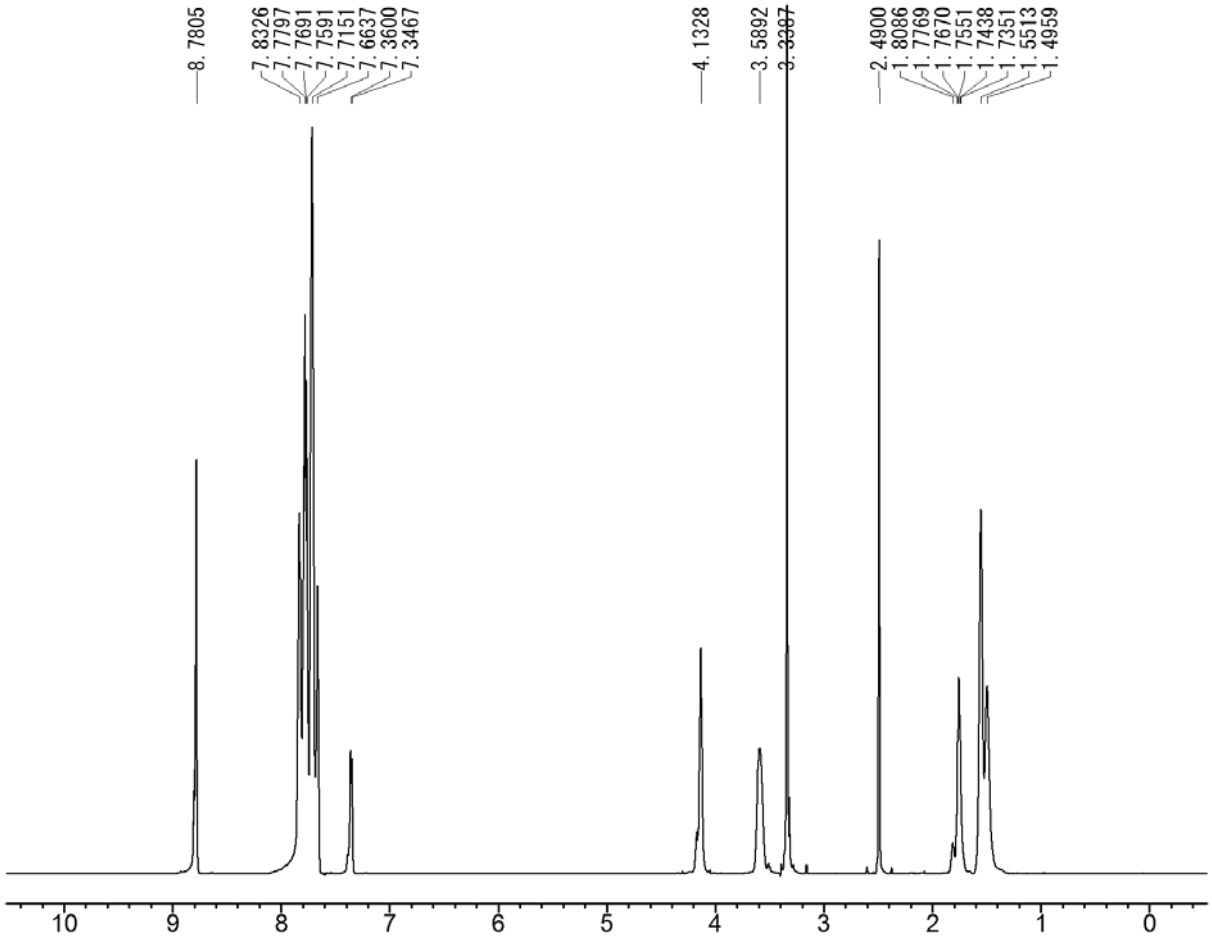
References

1 W. J. Kruper and D. V. Dellar, *J. Org. Chem.*, 1995, **60**, 725–727.
2 R. L. Paddock, Y. Hiyama, J. M. McKay and S. T. Nguyen, *Tetrahedron Lett.*, 2004, **45**, 2023–2026.
3 R. Srivastava, T. H. Bennur and D. Srinivas, *J. Mol. Catal. A: Chem.*, 2005, **226**, 199–205.
4 L. Jin, H. Jing, T. Chang, X. Bu, L. Wang and Z. Liu, *J. Mol. Catal. A: Chem.*, 2007, **261**, 262–266.
5 F. Ahmadi, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork and A. R. Khosropour, *Inorg. Chem. Commun.*, 2011, **14**, 1489–1493.
6 M. Wang, Y. She, X. Zhou and H. Ji, *Chin. J. Chem. Eng.*, 2011, **19**, 446–451.

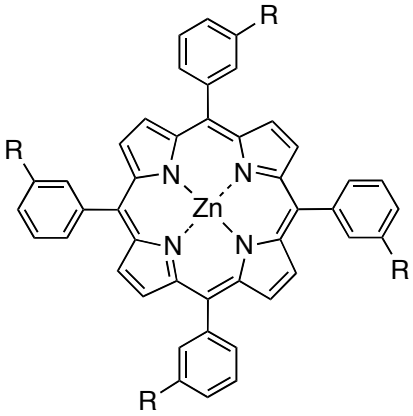
[5] ^{1}H and ^{13}C NMR Spectra.



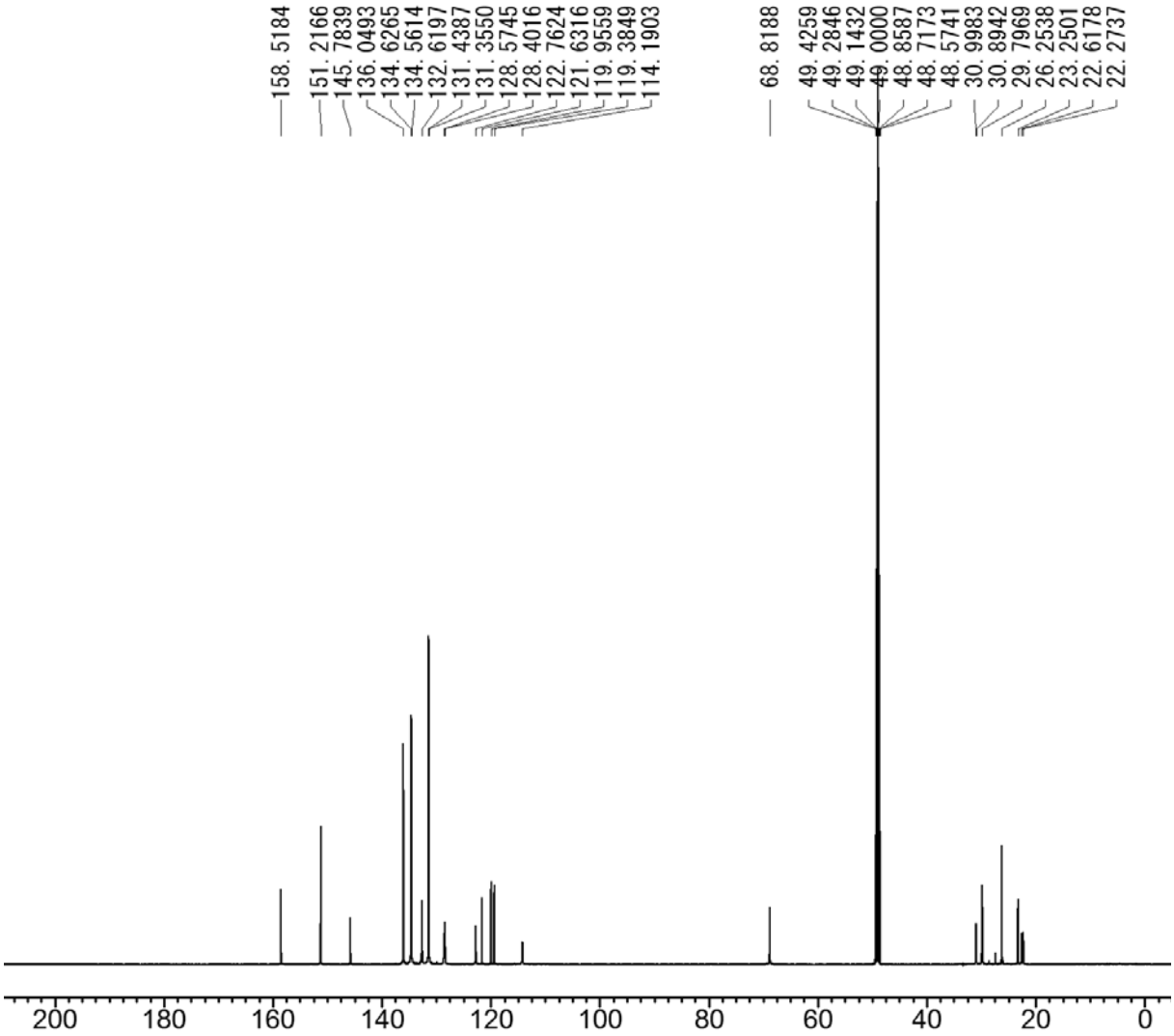
1a: R = $O(CH_2)_6P^+Ph_3Br^-$



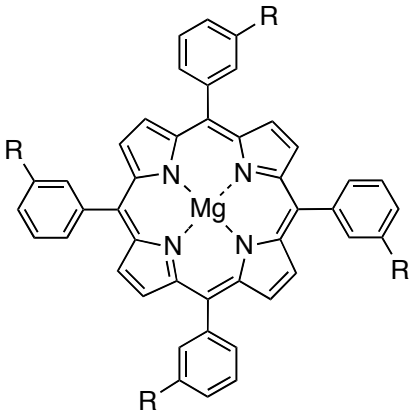
600 MHz ^{1}H NMR spectrum of **1a** in d_6-DMSO.



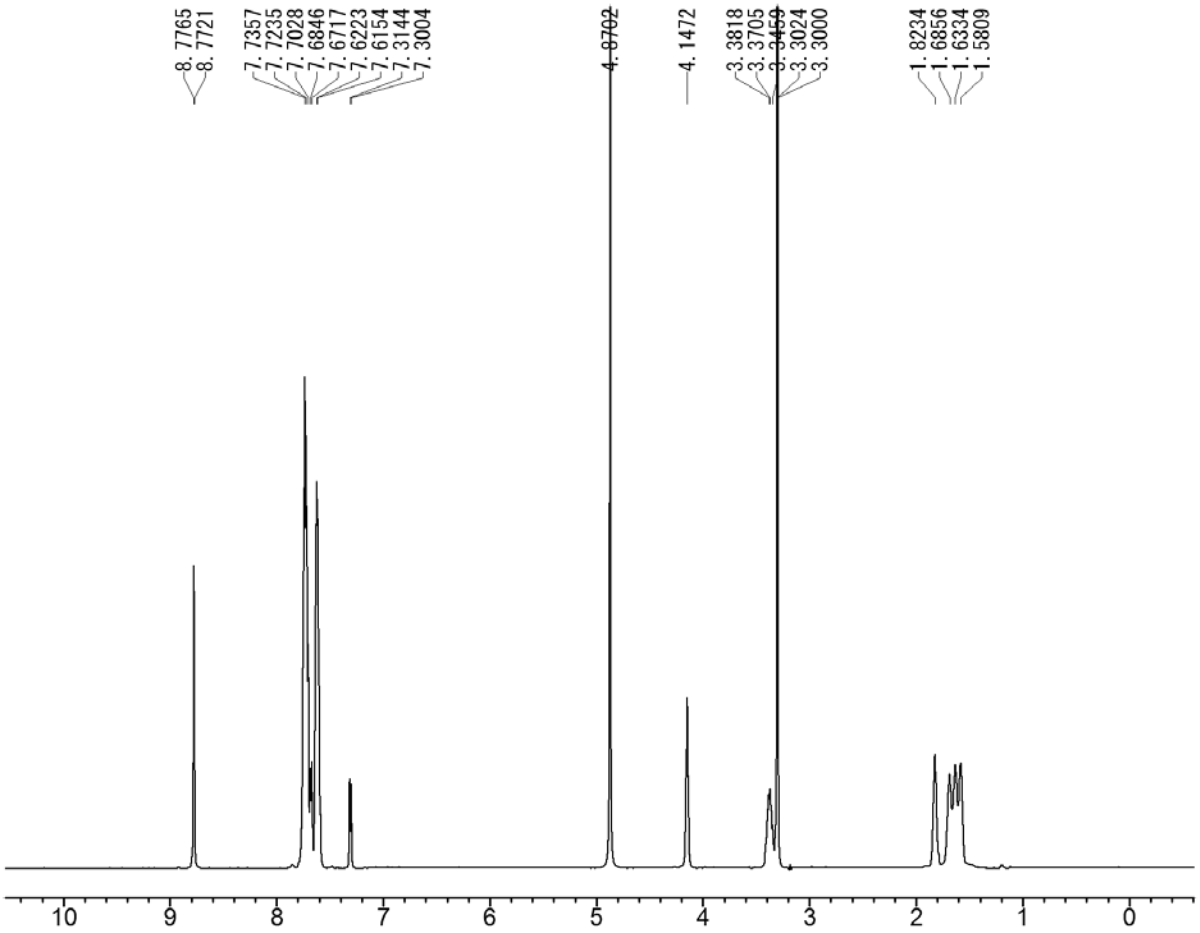
1a: R = $O(CH_2)_6P^+Ph_3Br^-$



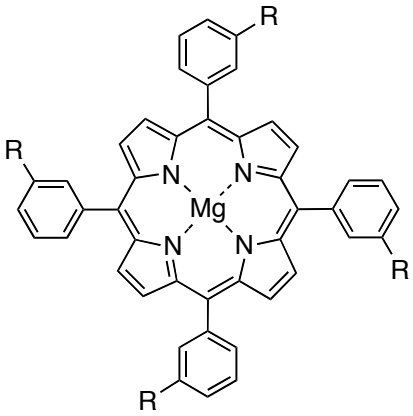
150 MHz ^{13}C NMR spectrum of **1a** in CD_3OD.



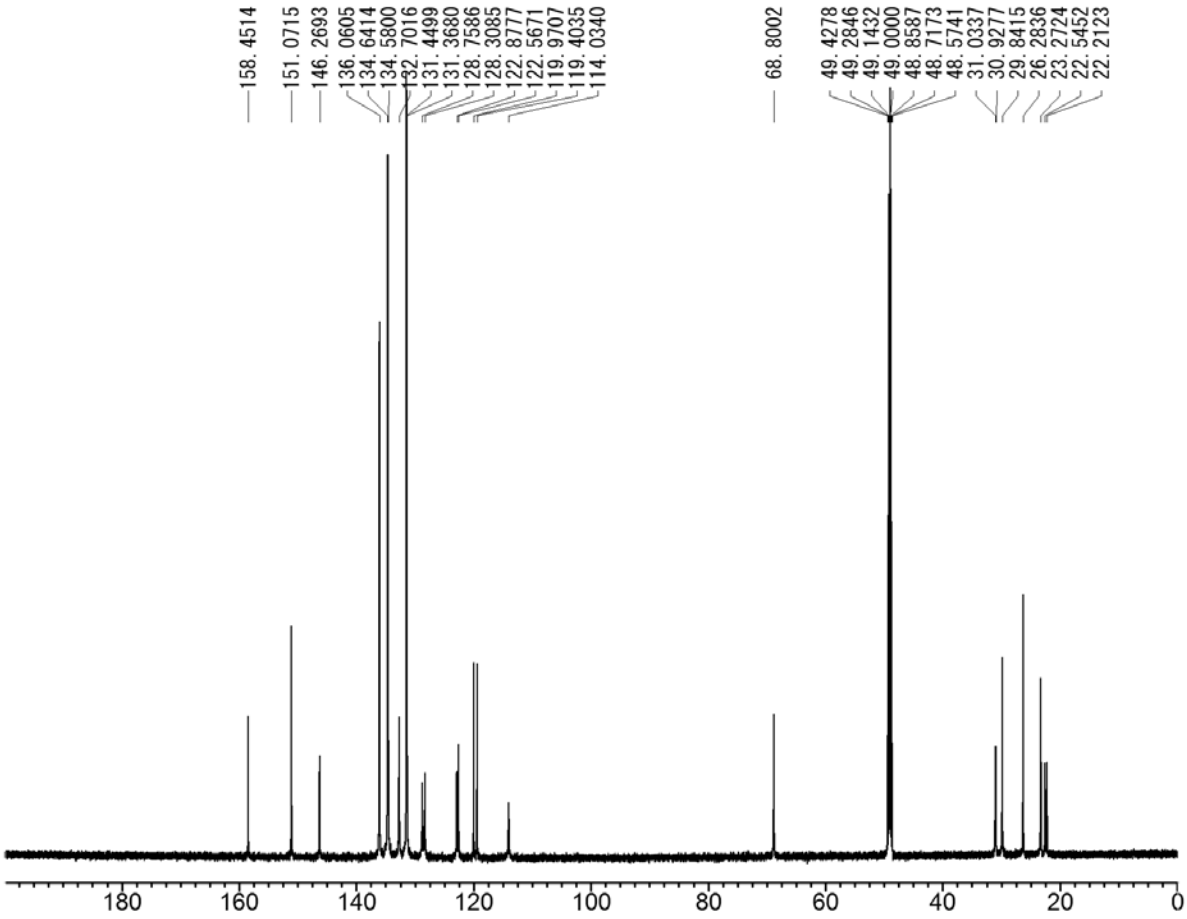
1b: R = $O(CH_2)_6P^+Ph_3Br^-$



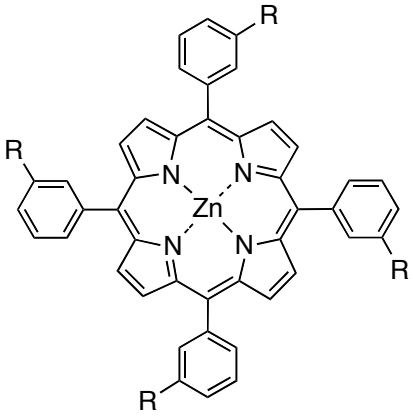
600 MHz ^{1}H NMR spectrum of **1b** in CD_3OD.



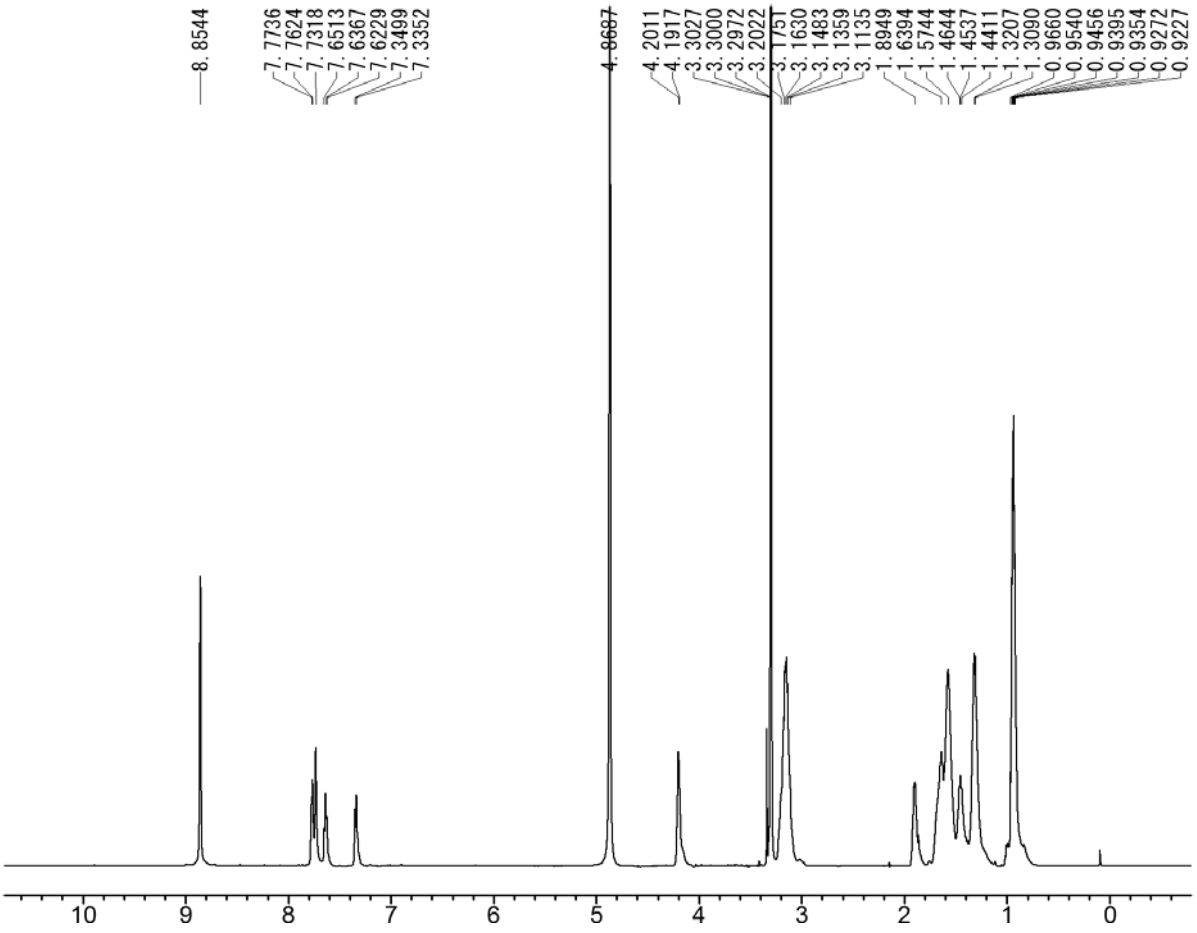
1b: R = $O(CH_2)_6P^+Ph_3Br^-$



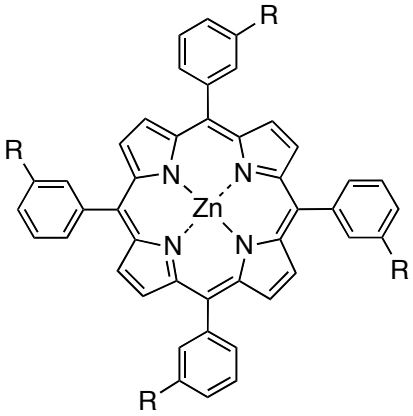
150 MHz ^{13}C NMR spectrum of **1b** in CD_3OD.



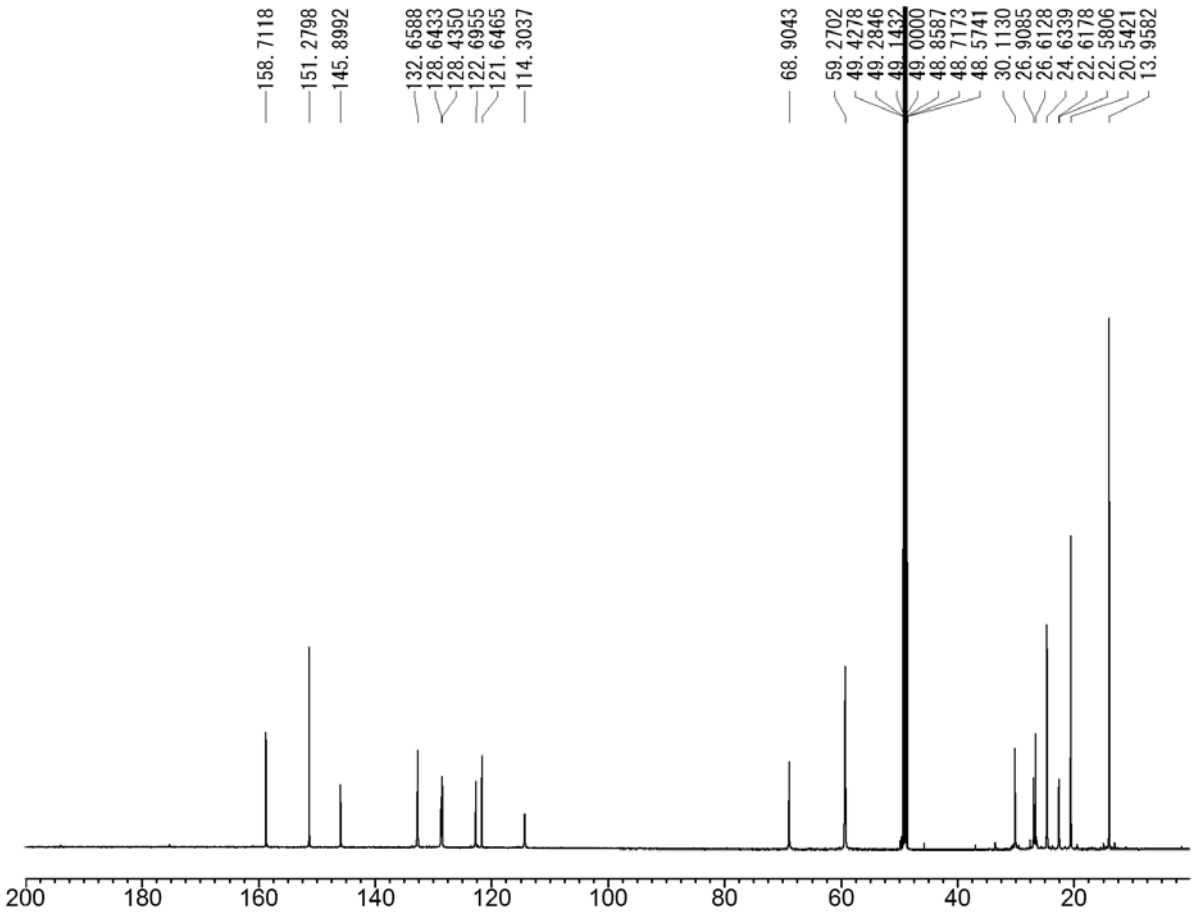
1c: R = $O(CH_2)_6N^+Bu_3Br^-$



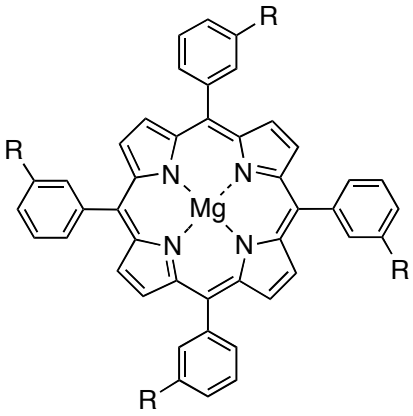
600 MHz ^{1}H NMR spectrum of **1c** in CD_3OD.



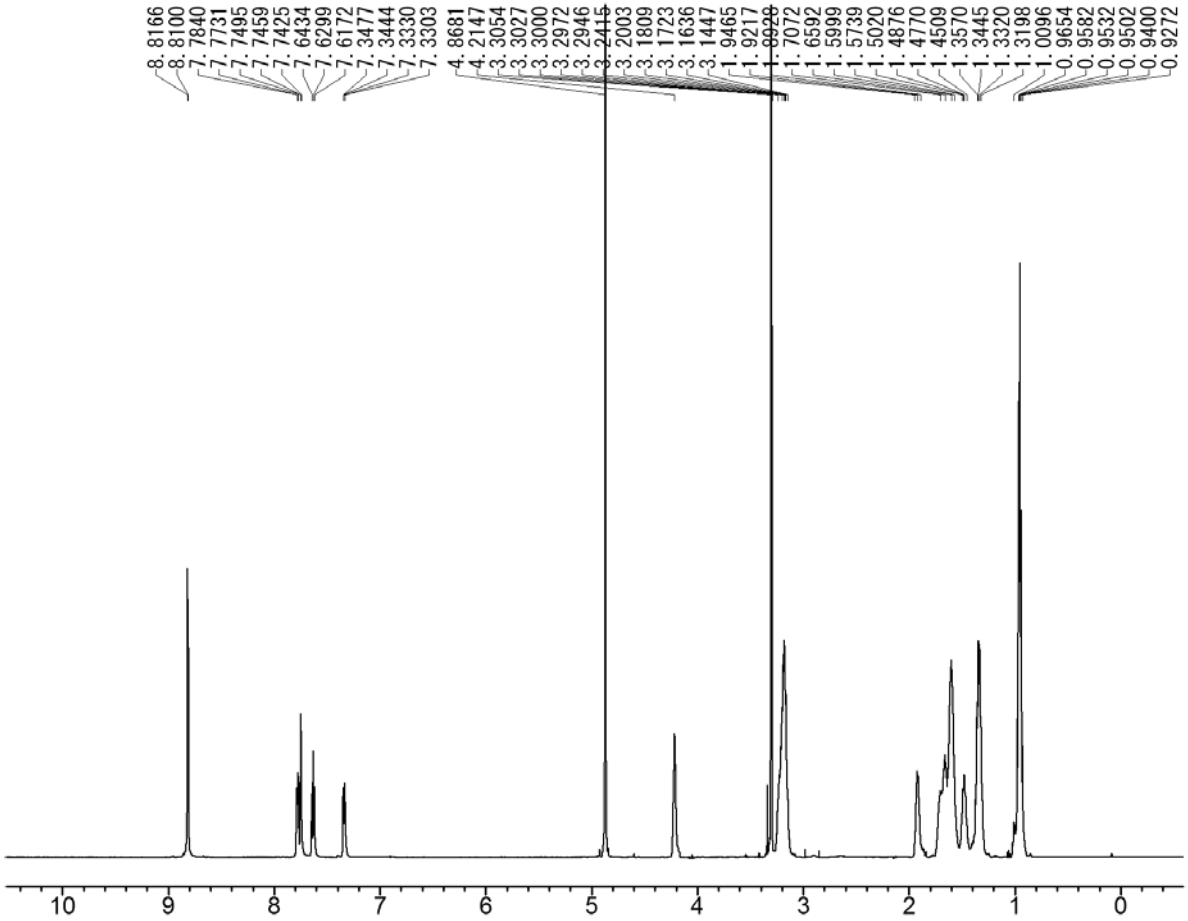
1c: R = $O(CH_2)_6N^+Bu_3Br^-$



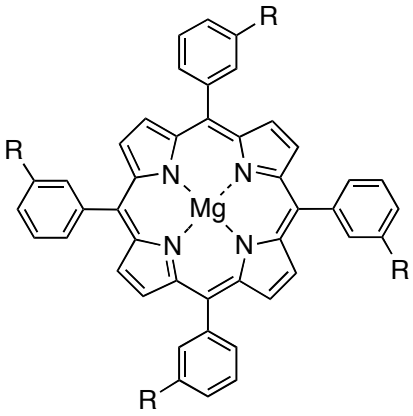
150 MHz ^{13}C NMR spectrum of **1c** in CD_3OD.



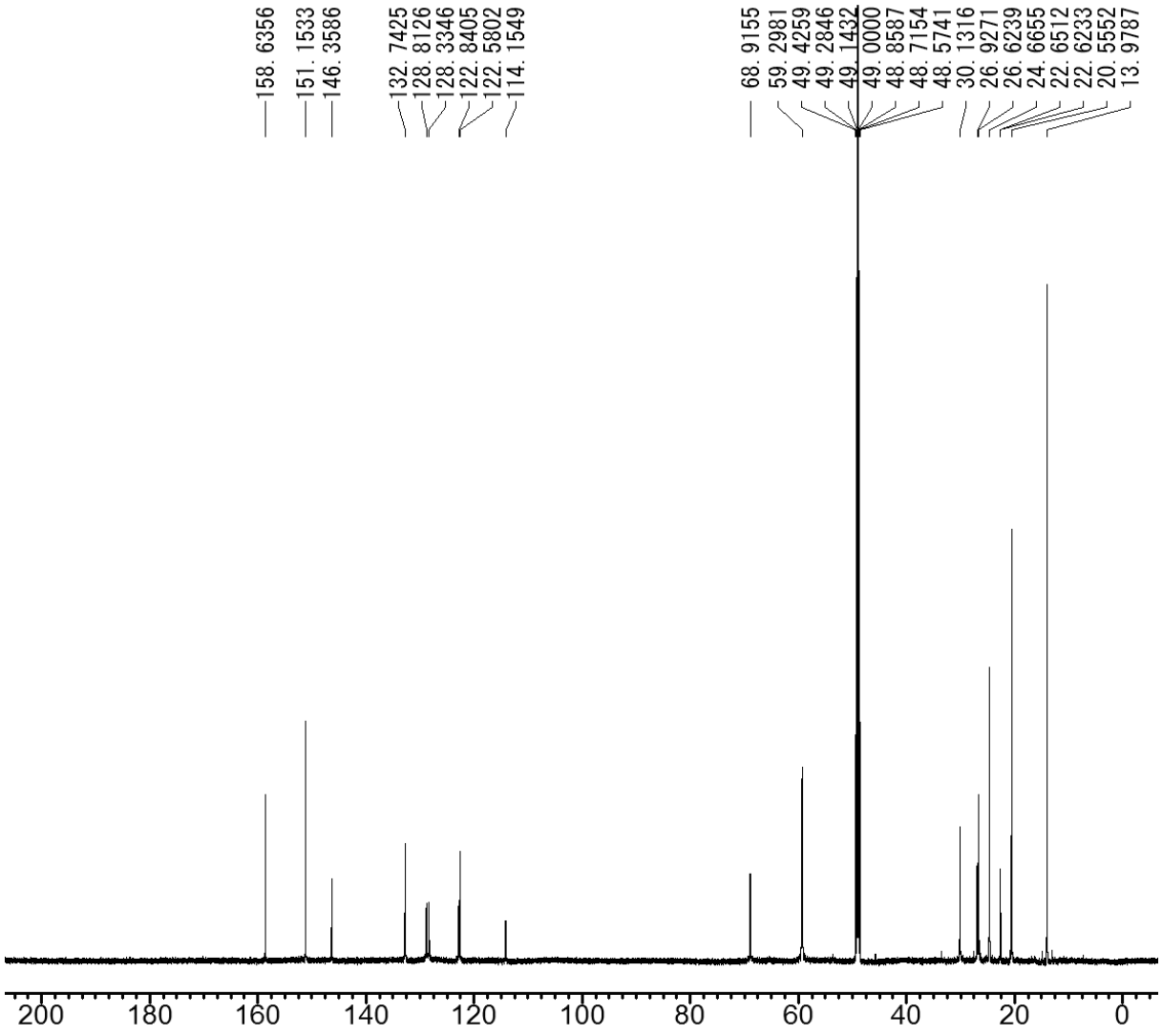
1d: R = $O(CH_2)_6N^+Bu_3Br^-$



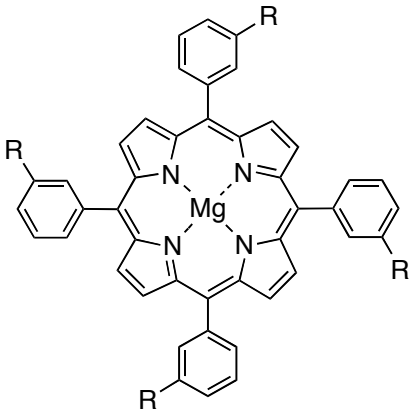
600 MHz ^{1}H NMR spectrum of **1d** in CD_3OD.



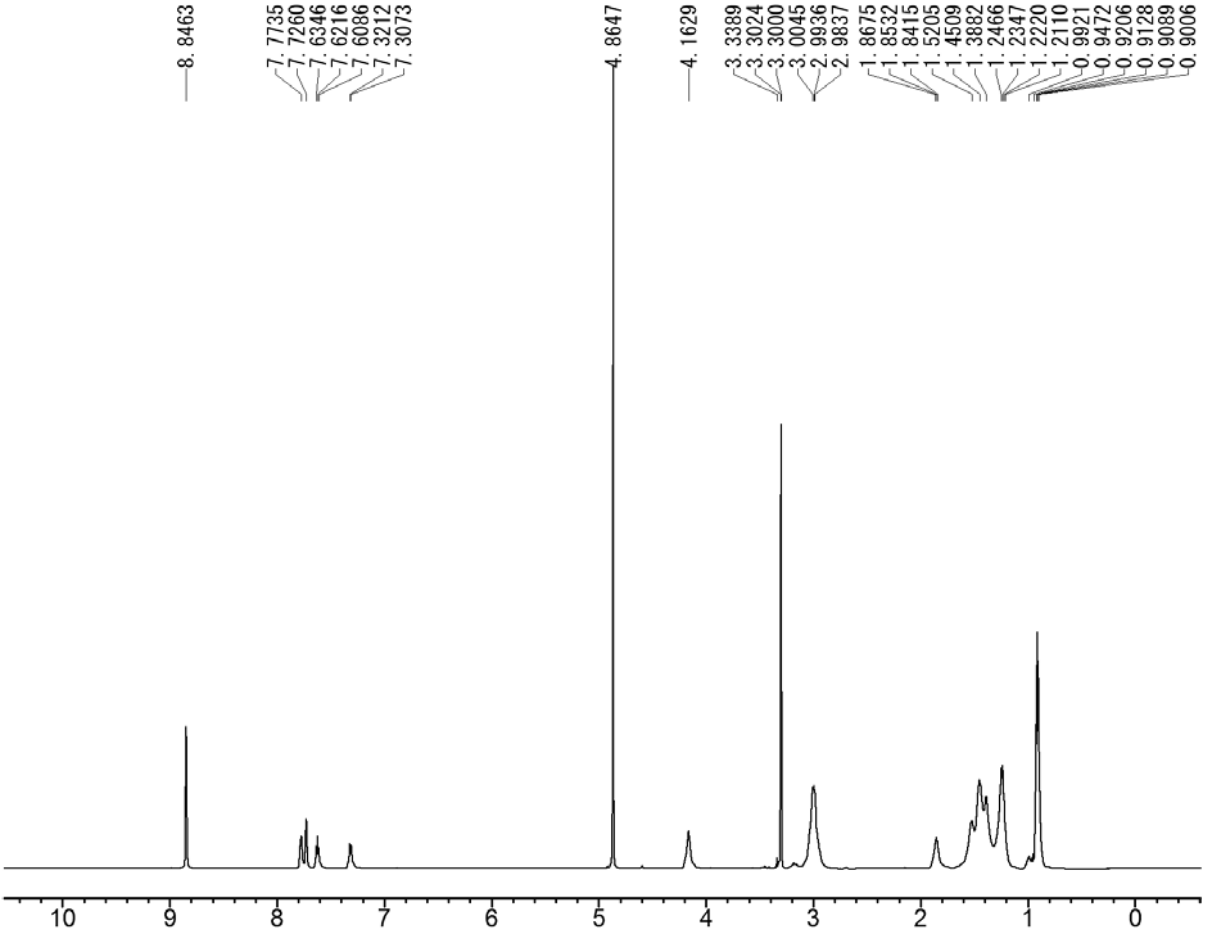
1d: R = $O(CH_2)_6N^+Bu_3Br^-$



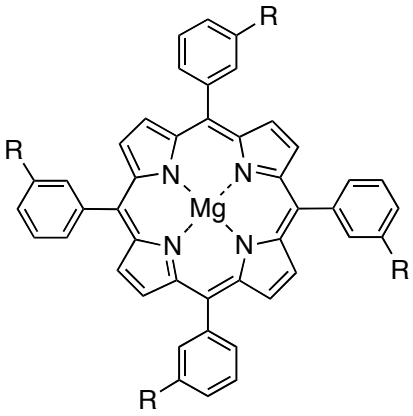
150 MHz ^{13}C NMR spectrum of **1d** in CD_3OD.



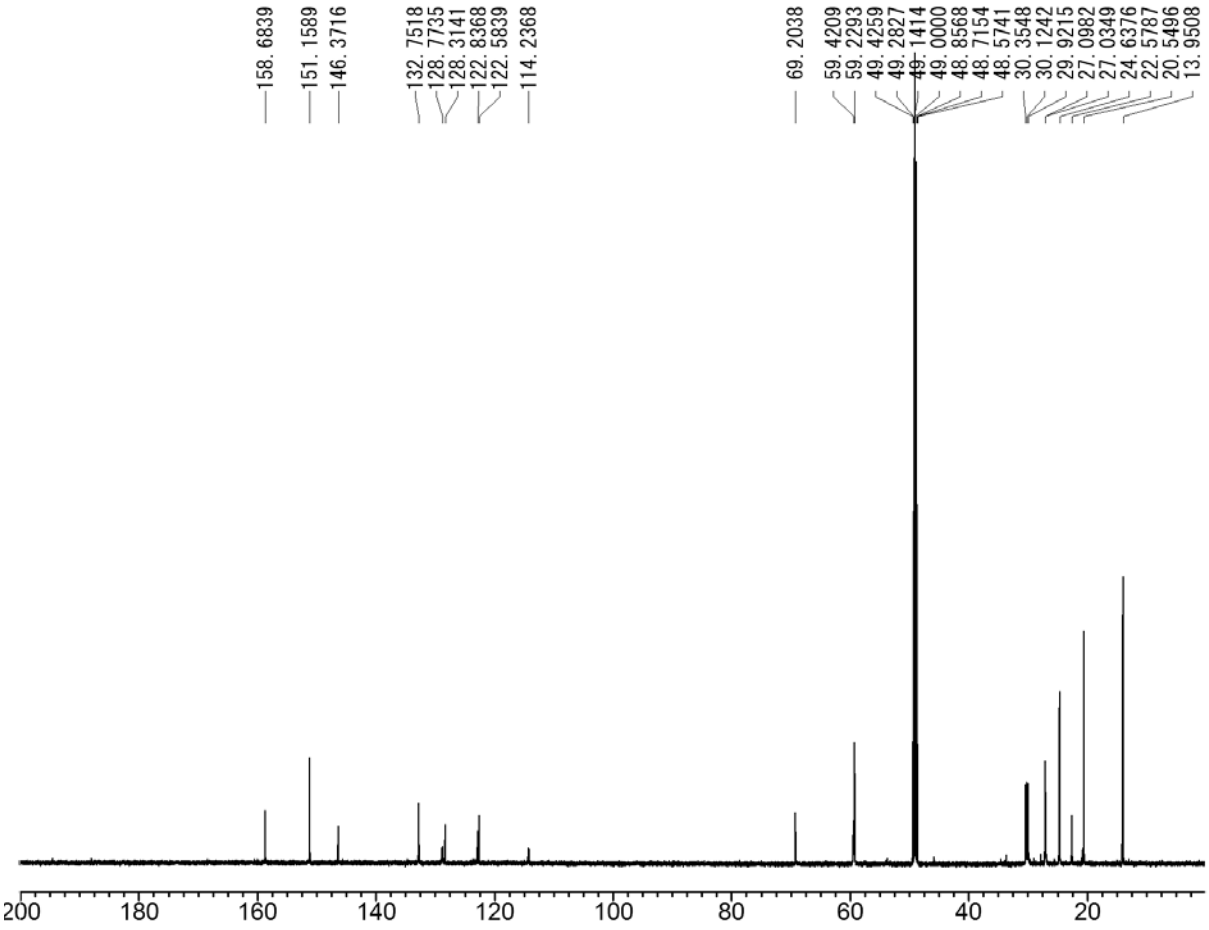
1e: R = $O(CH_2)_8N^+Bu_3Br^-$



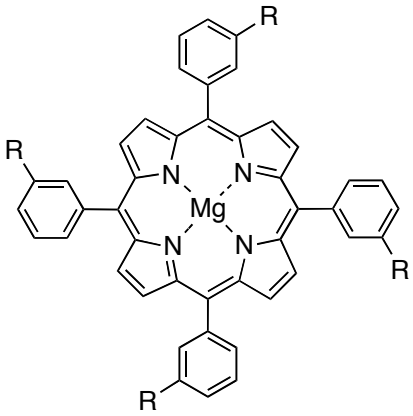
600 MHz ^{1}H NMR spectrum of **1e** in CD_3OD.



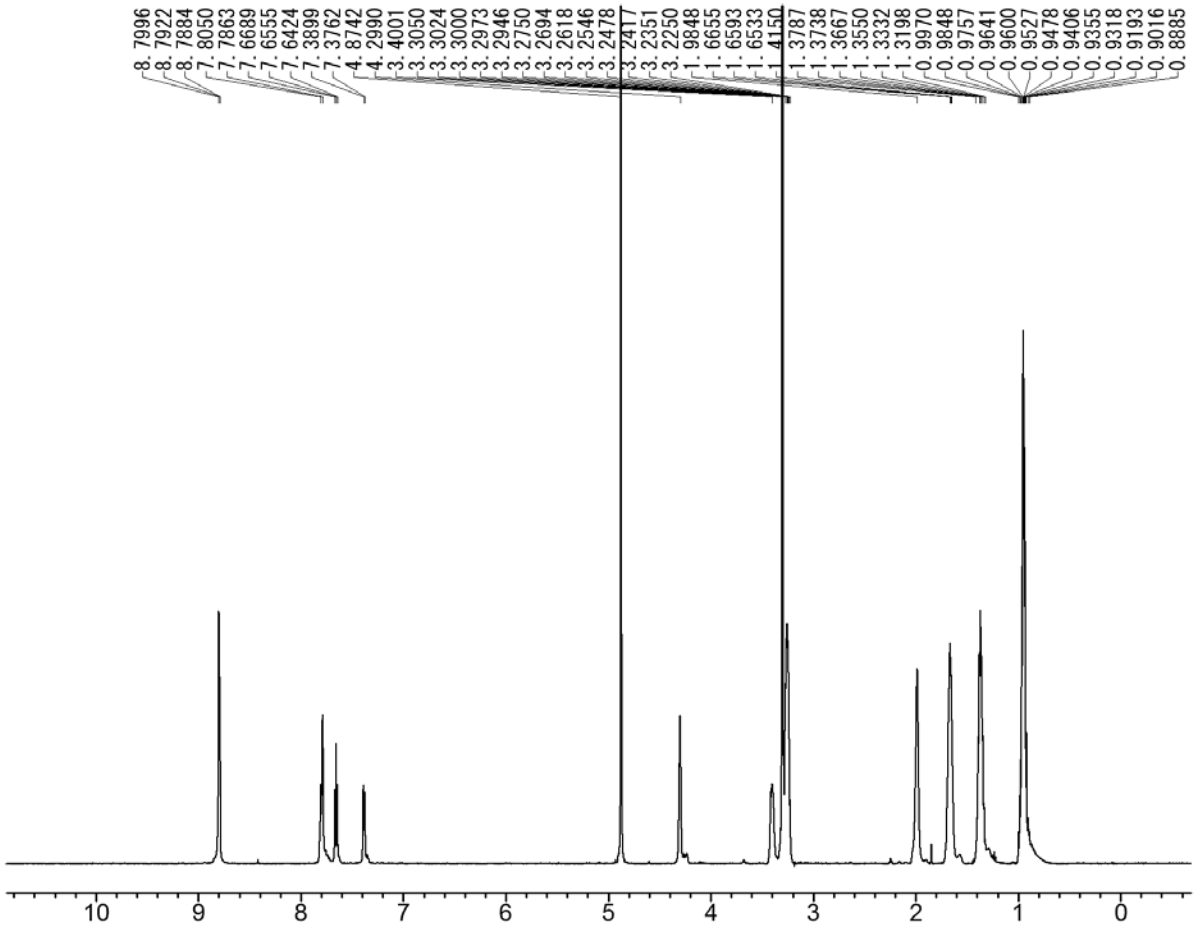
1e: R = $O(CH_2)_8N^+Bu_3Br^-$



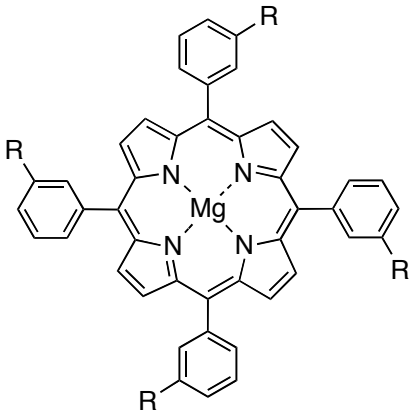
150 MHz ^{13}C NMR spectrum of **1e** in CD_3OD.



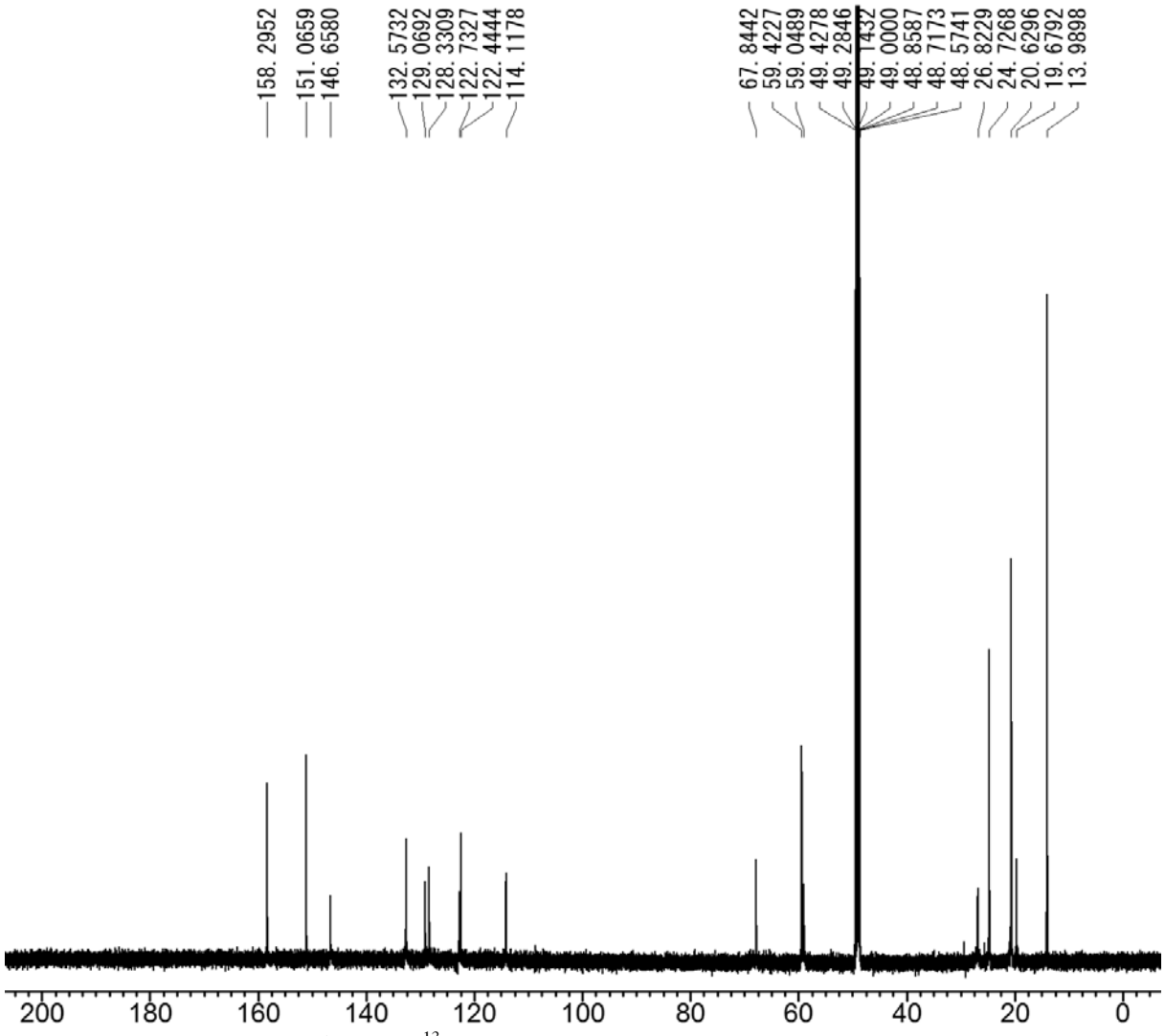
1f: R = $O(CH_2)_4N^+Bu_3Br^-$



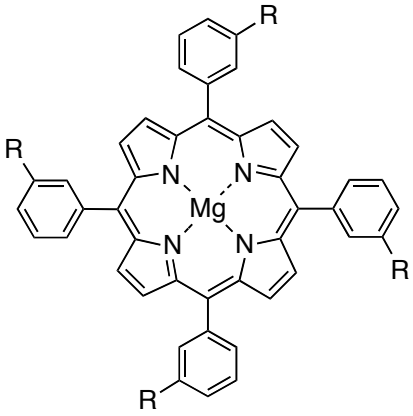
600 MHz ^{1}H NMR spectrum of **1f** in CD_3OD.



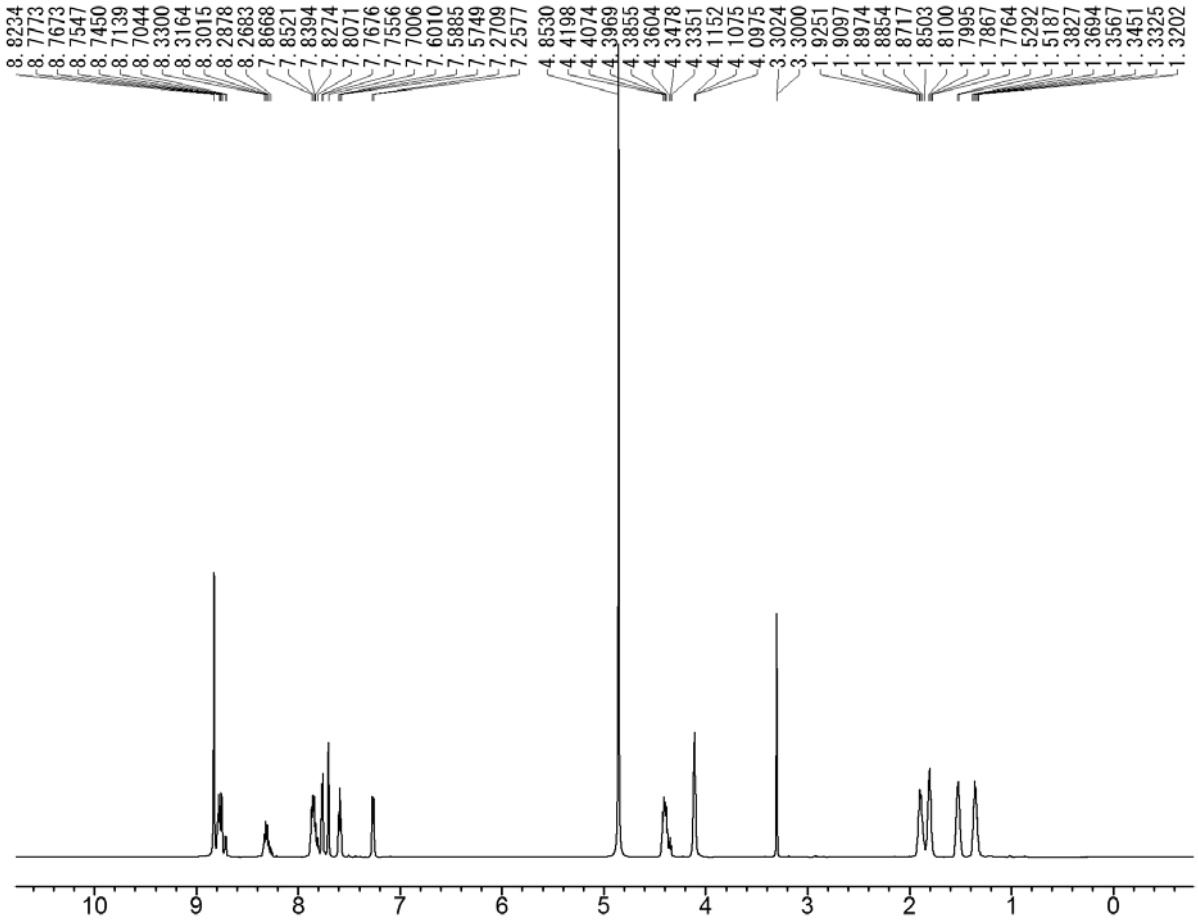
1f: R = $O(CH_2)_4N^+Bu_3Br^-$



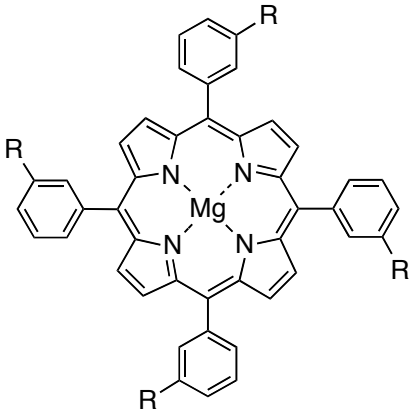
150 MHz ^{13}C NMR spectrum of **1f** in CD_3OD.



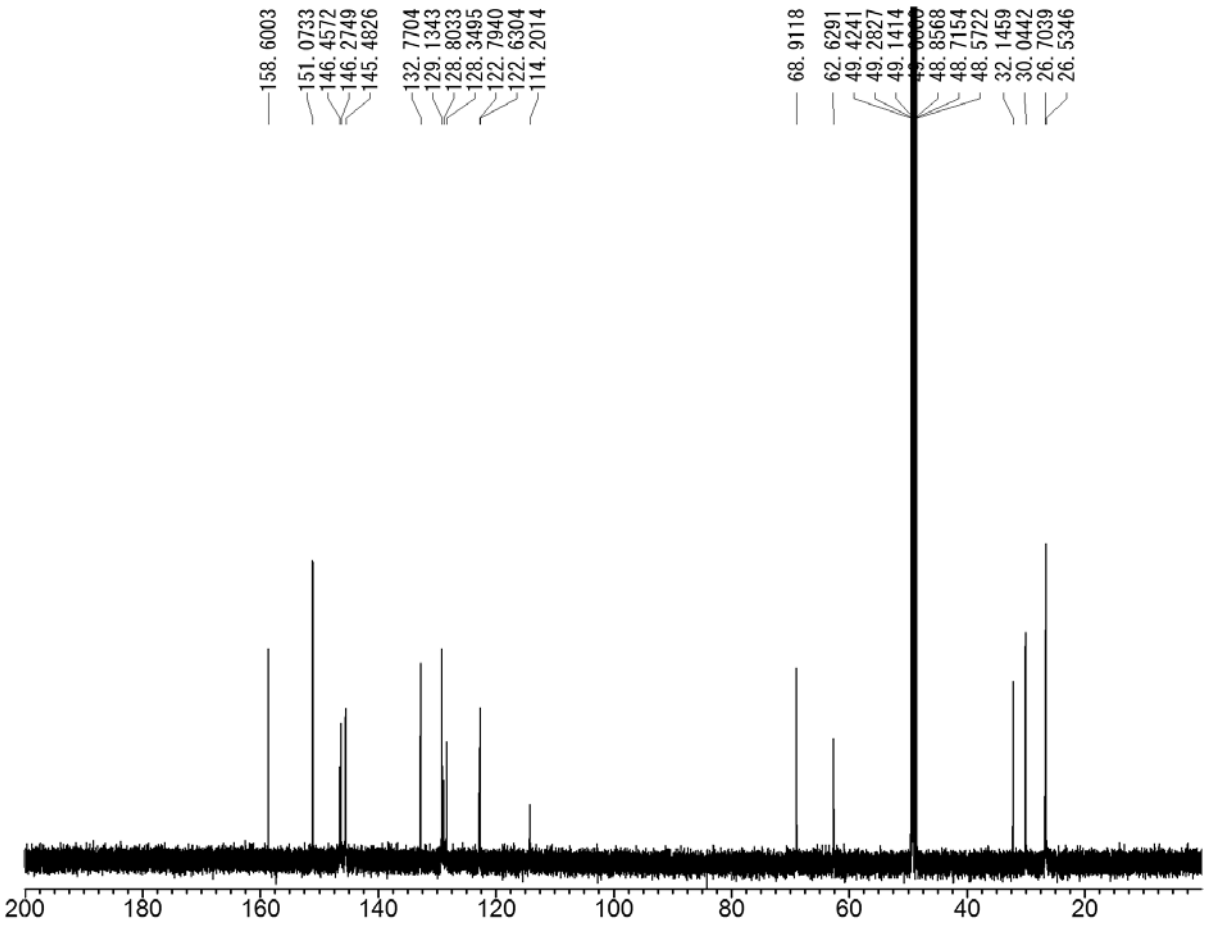
1g: R = $O(CH_2)_6Py^+Br^-$



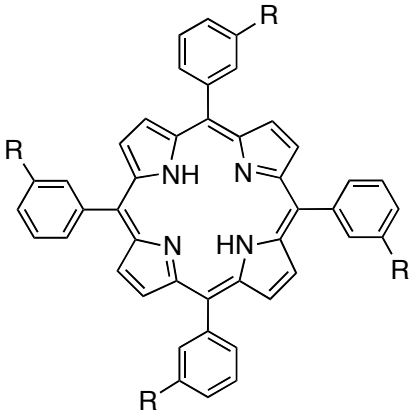
600 MHz ^{1}H NMR spectrum of **1g** in CD_3OD.



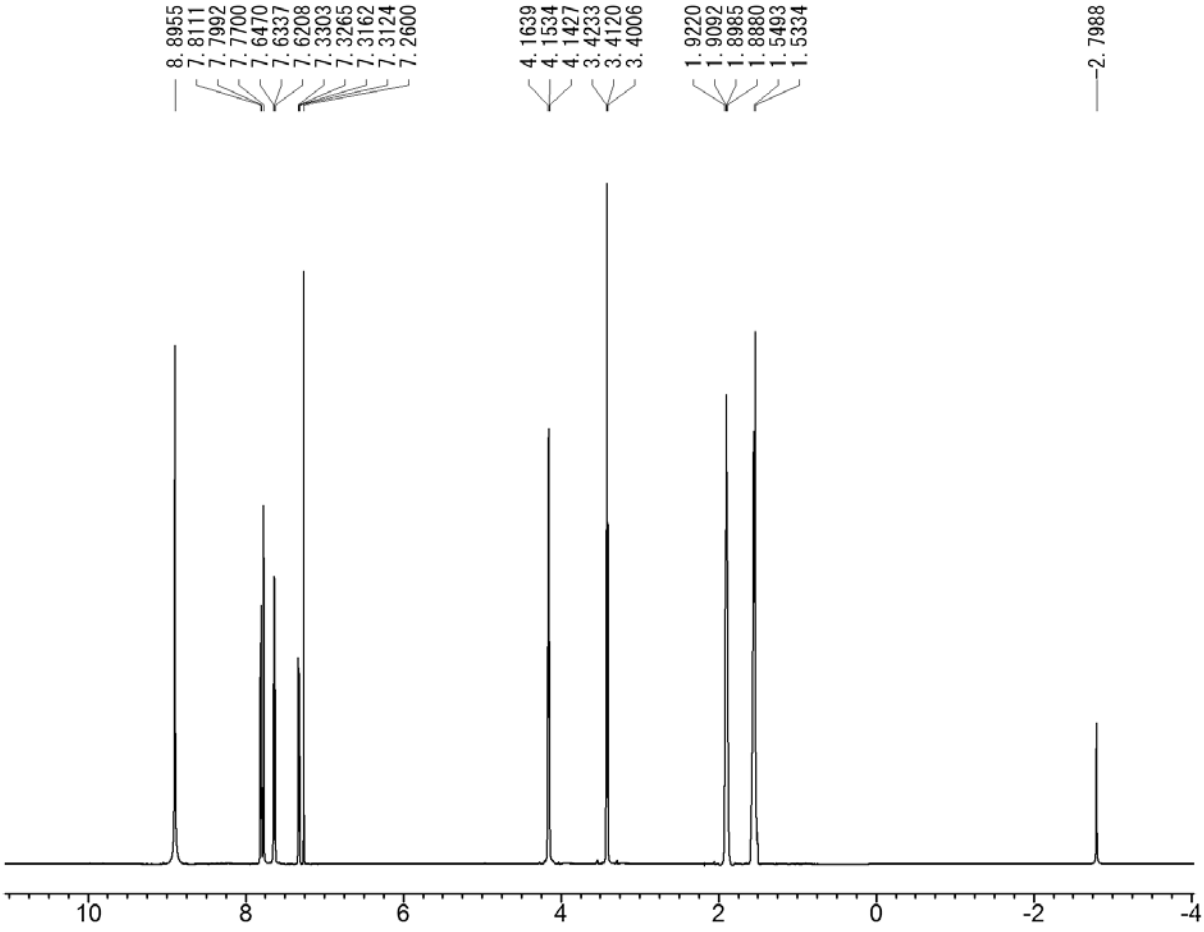
1g: R = $O(CH_2)_6Py^+Br^-$



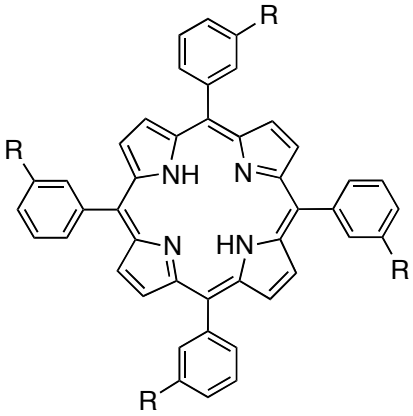
150 MHz ^{13}C NMR spectrum of **1g** in CD_3OD.



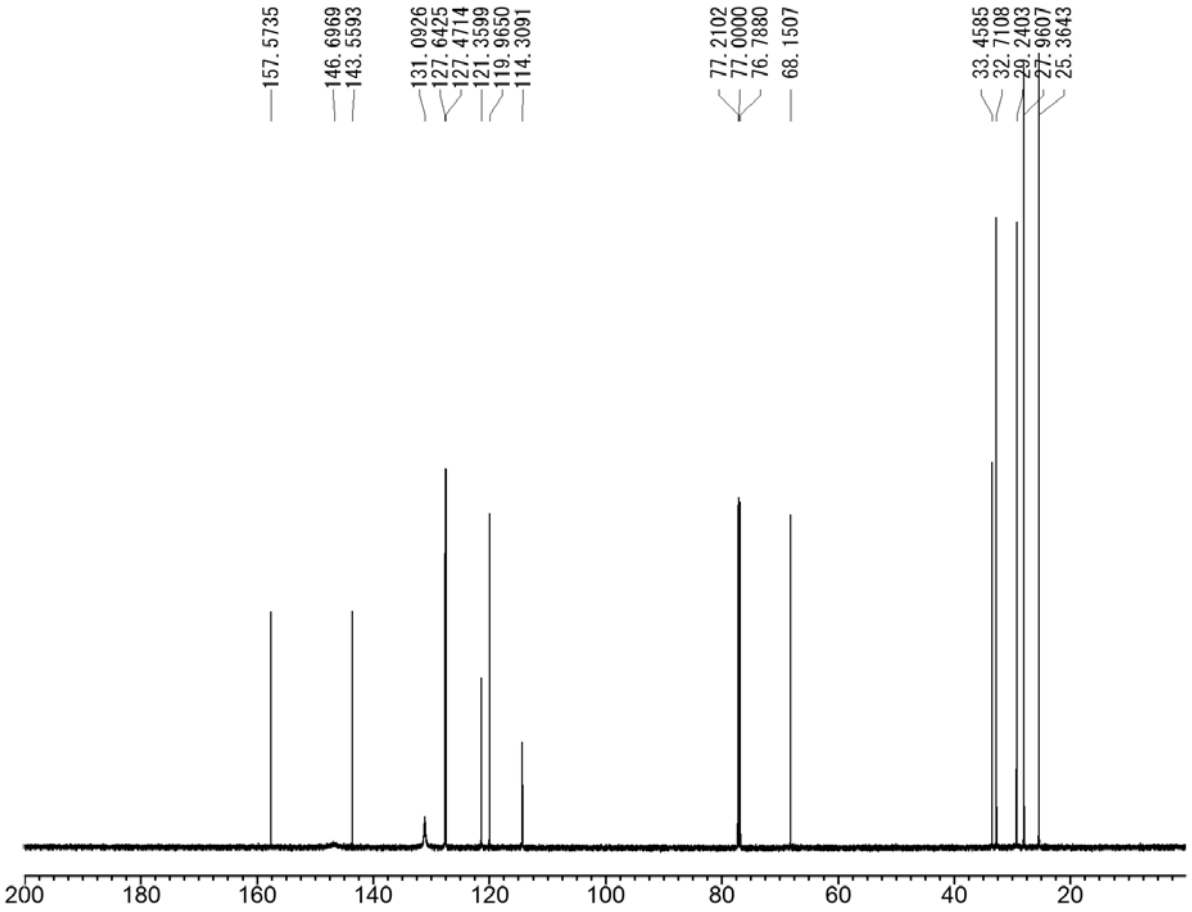
5a: R = $O(CH_2)_6Br$



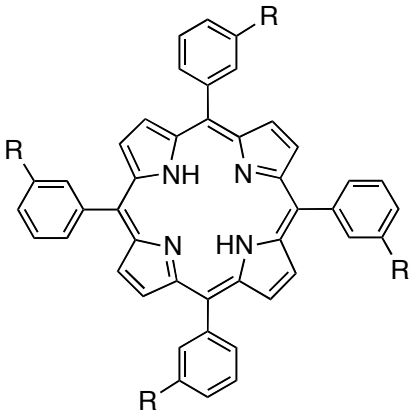
600 MHz ^{1}H NMR spectrum of **5a** in $CDCl_3$.



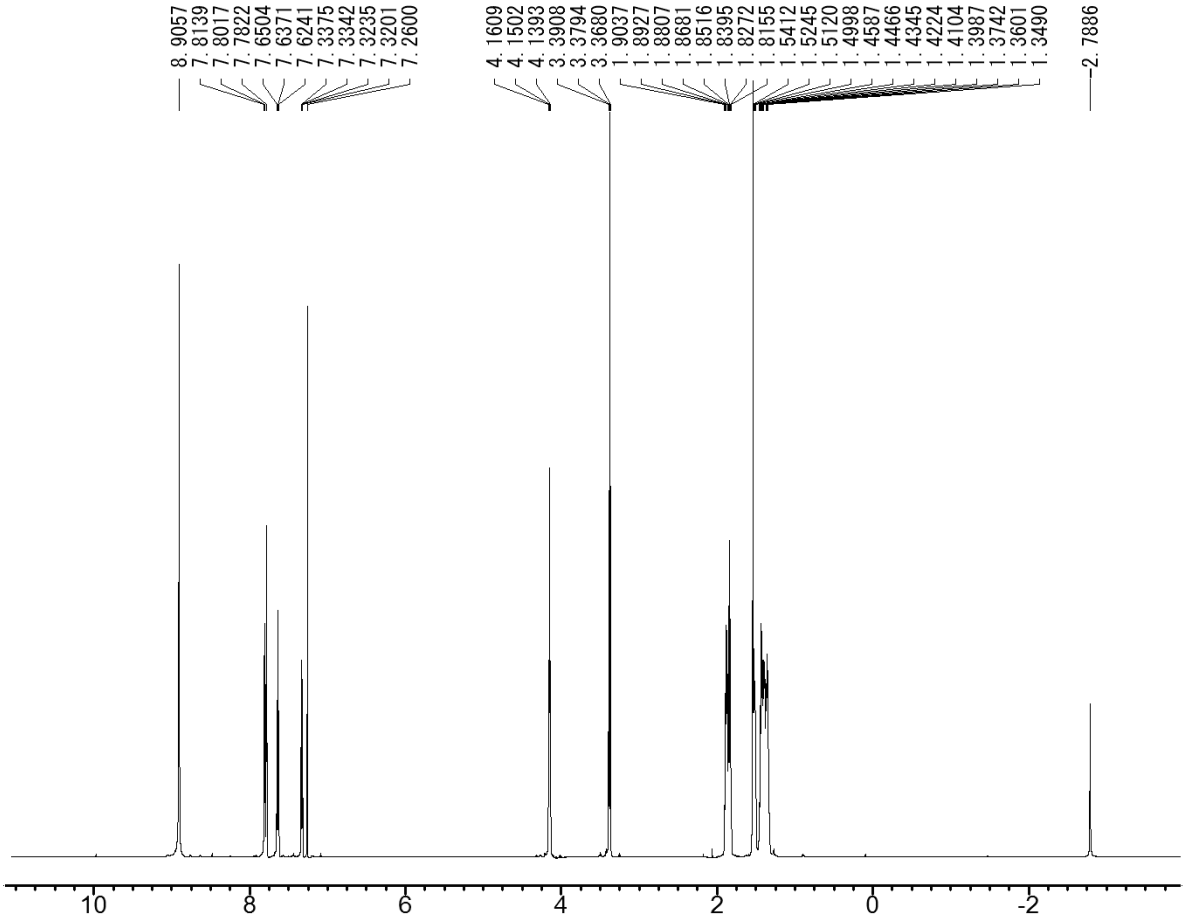
5a: R = $O(CH_2)_6Br$



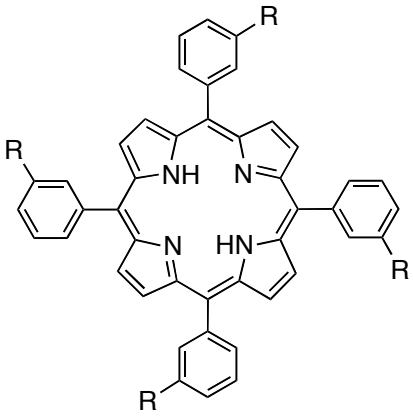
150 MHz ^{13}C NMR spectrum of **5a** in $CDCl_3$ at 50 °C.



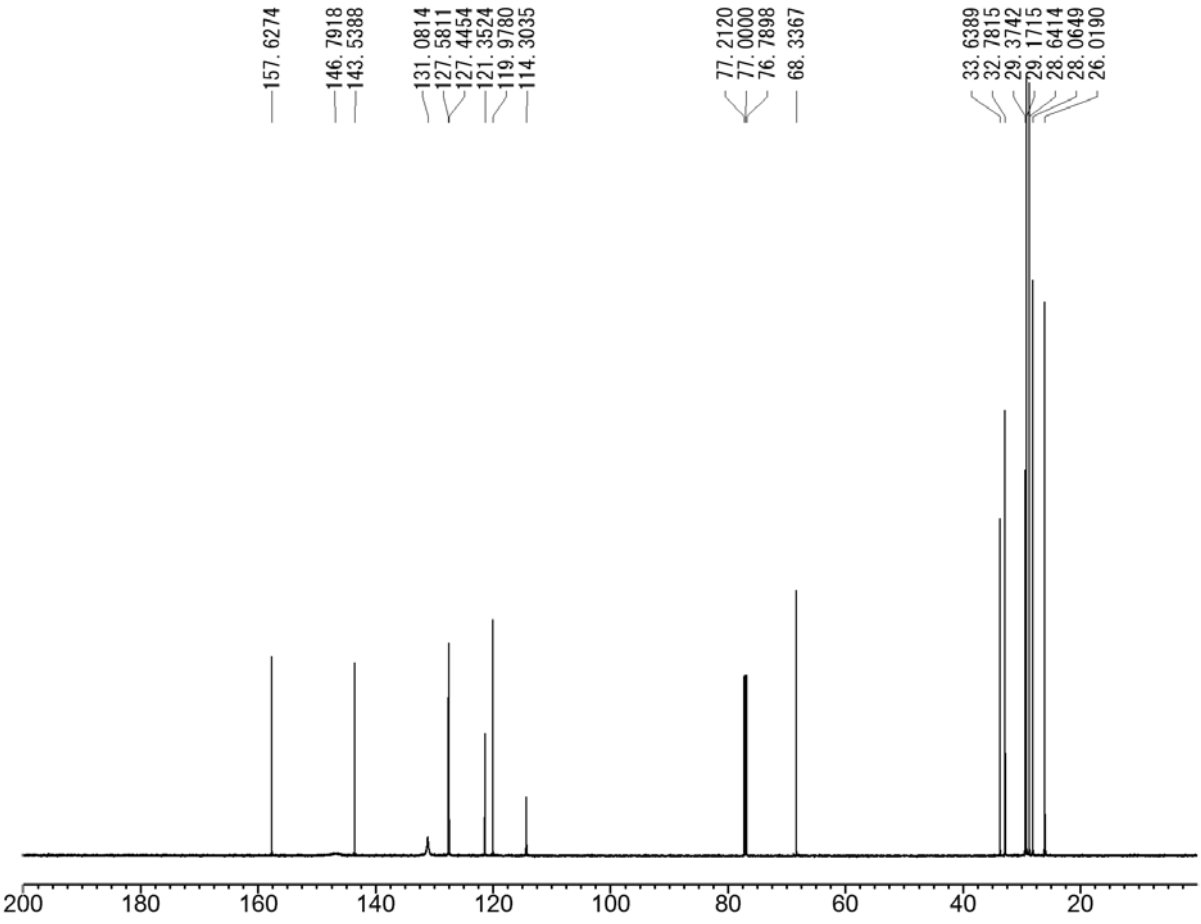
5b: R = $O(CH_2)_8Br$



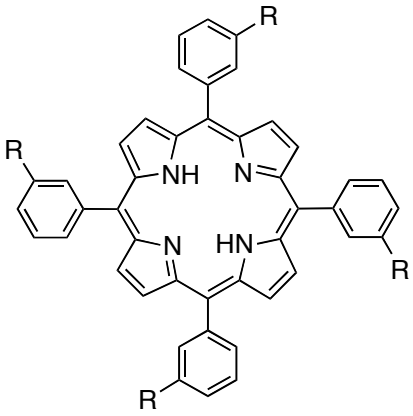
600 MHz ^{1}H NMR spectrum of **5b** in $CDCl_3$.



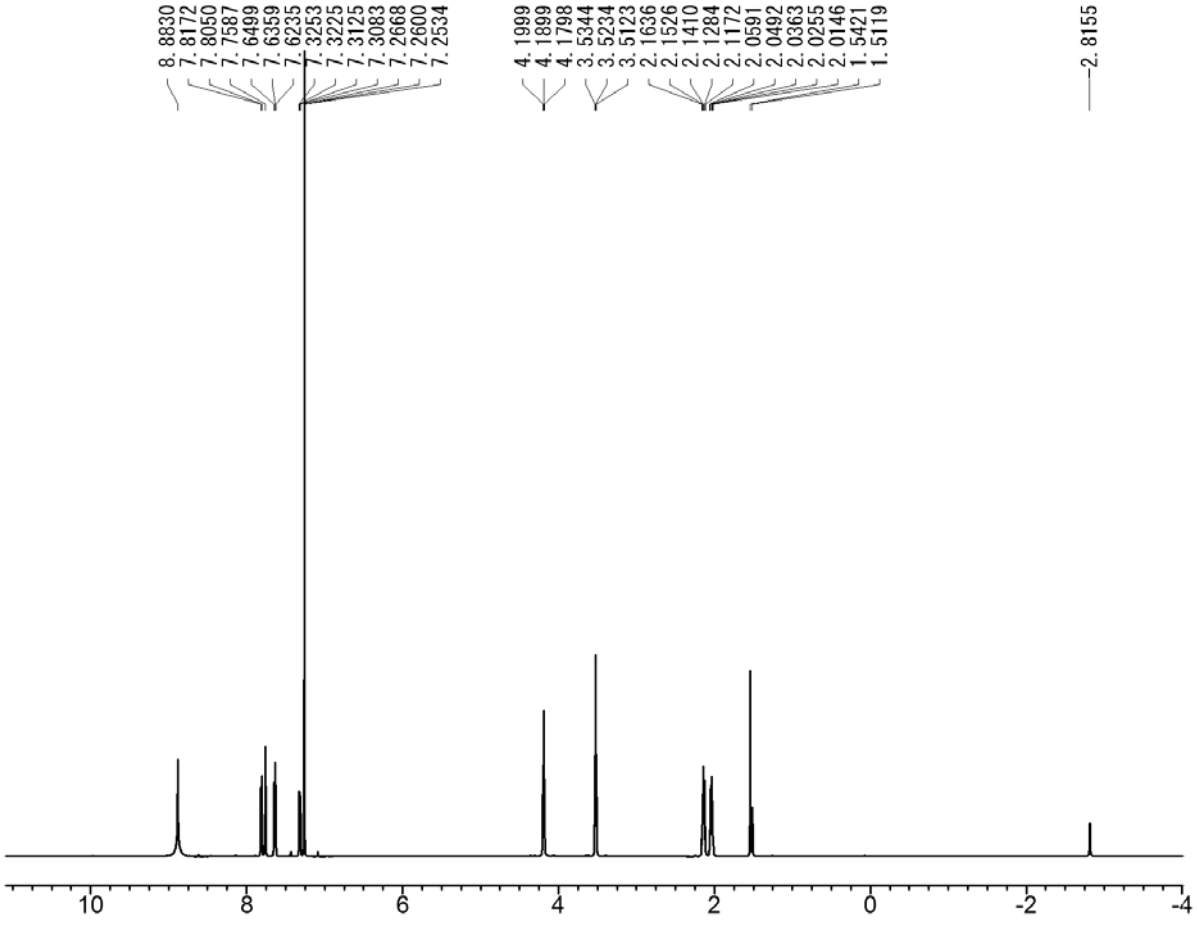
5b: R = $O(CH_2)_8Br$



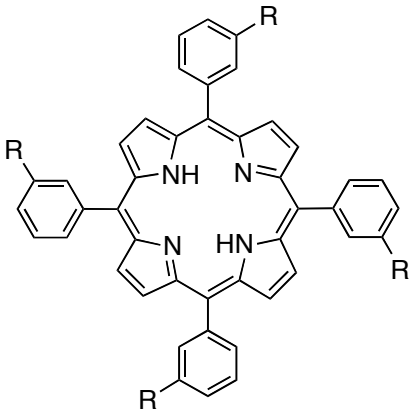
150 MHz ^{13}C NMR spectrum of **5b** in $CDCl_3$ at 50 °C.



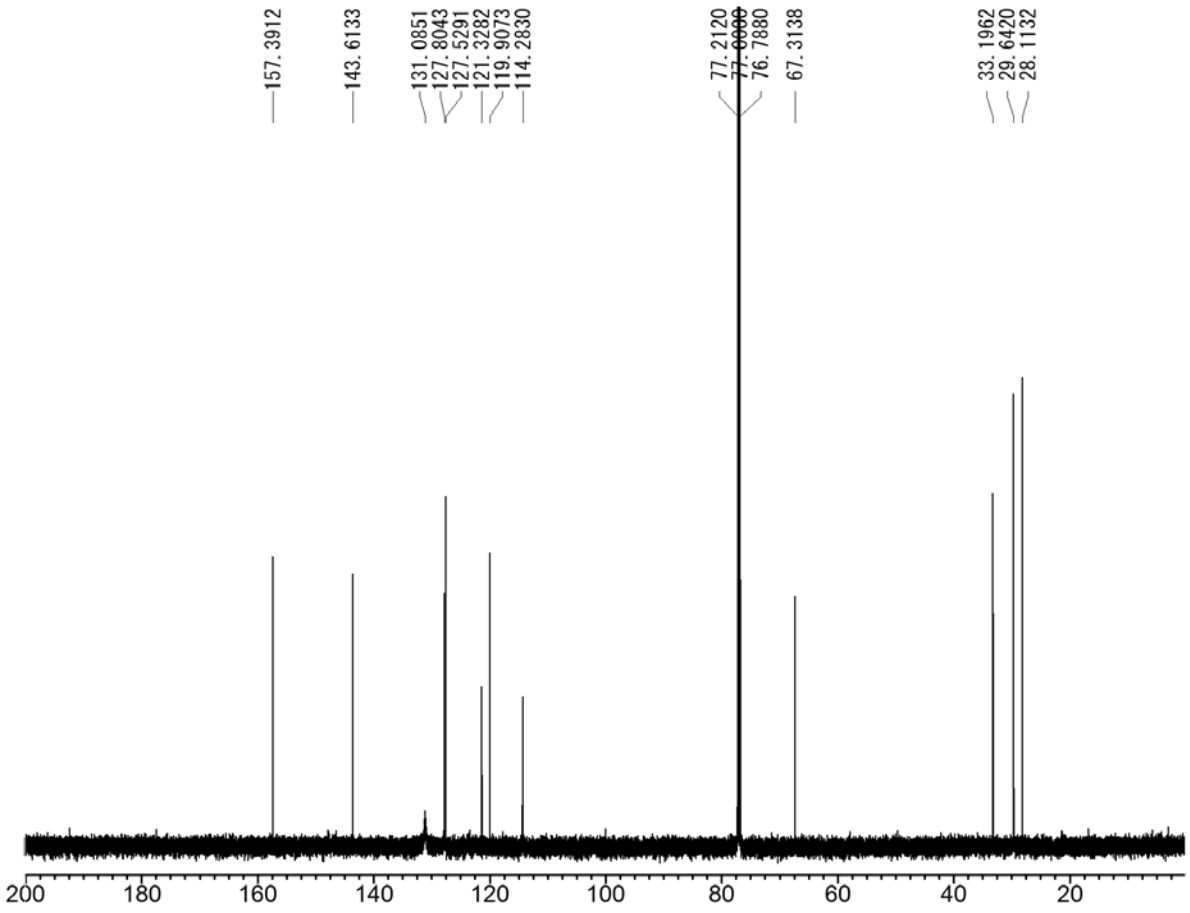
5c: R = $O(CH_2)_4Br$



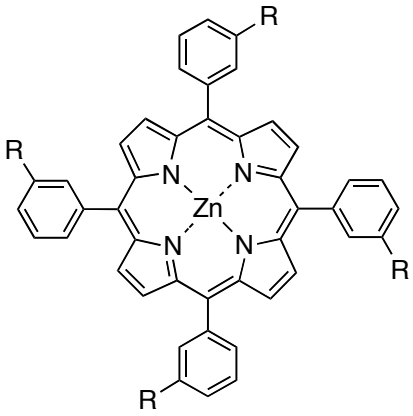
600 MHz ^{1}H NMR spectrum of **5c** in $CDCl_3$.



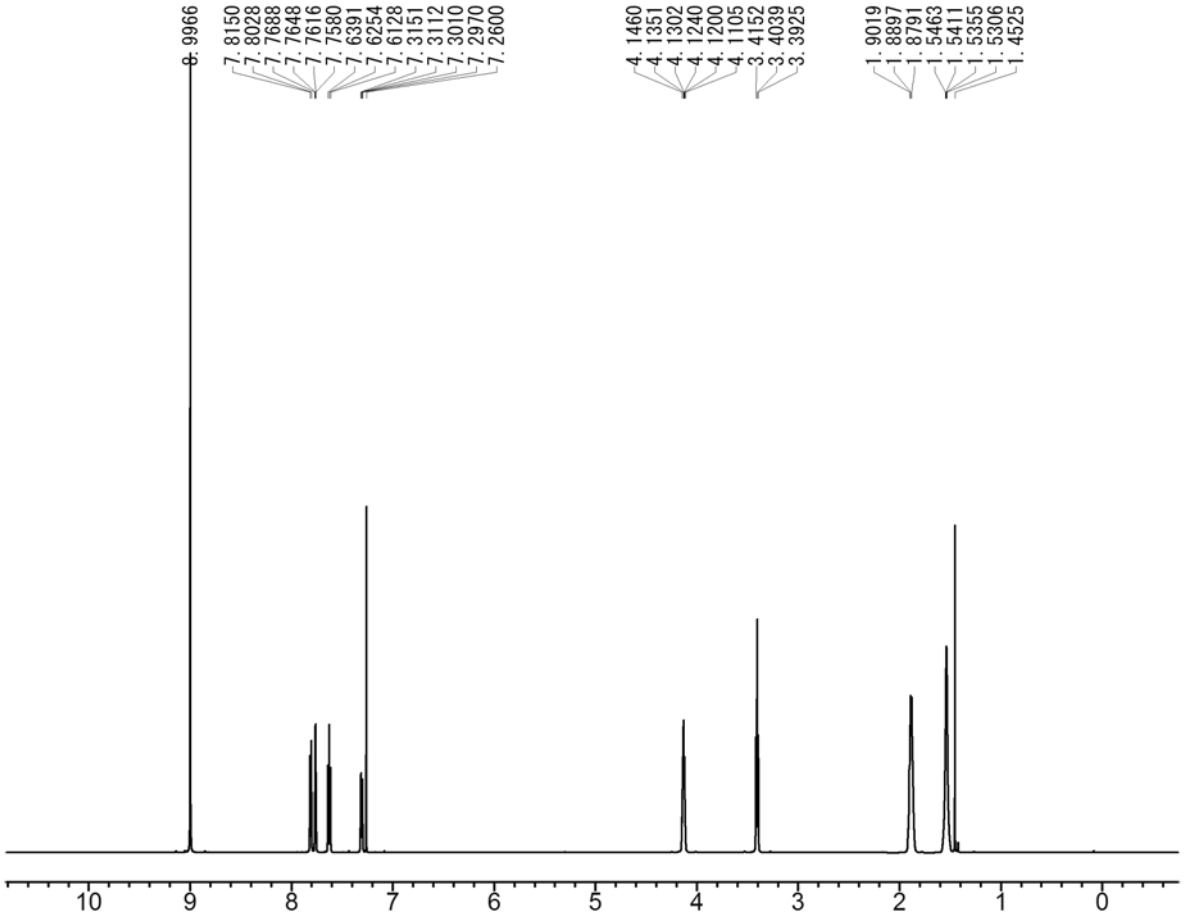
5c: R = $O(CH_2)_4Br$



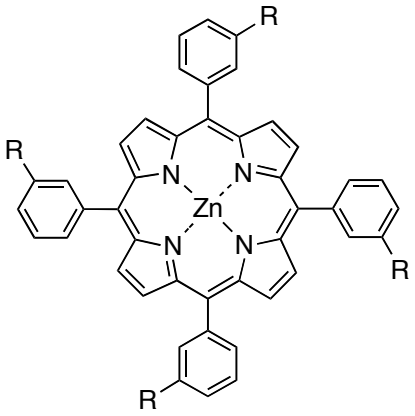
150 MHz ^{13}C NMR spectrum of **5c** in $CDCl_3$ at 50 °C.



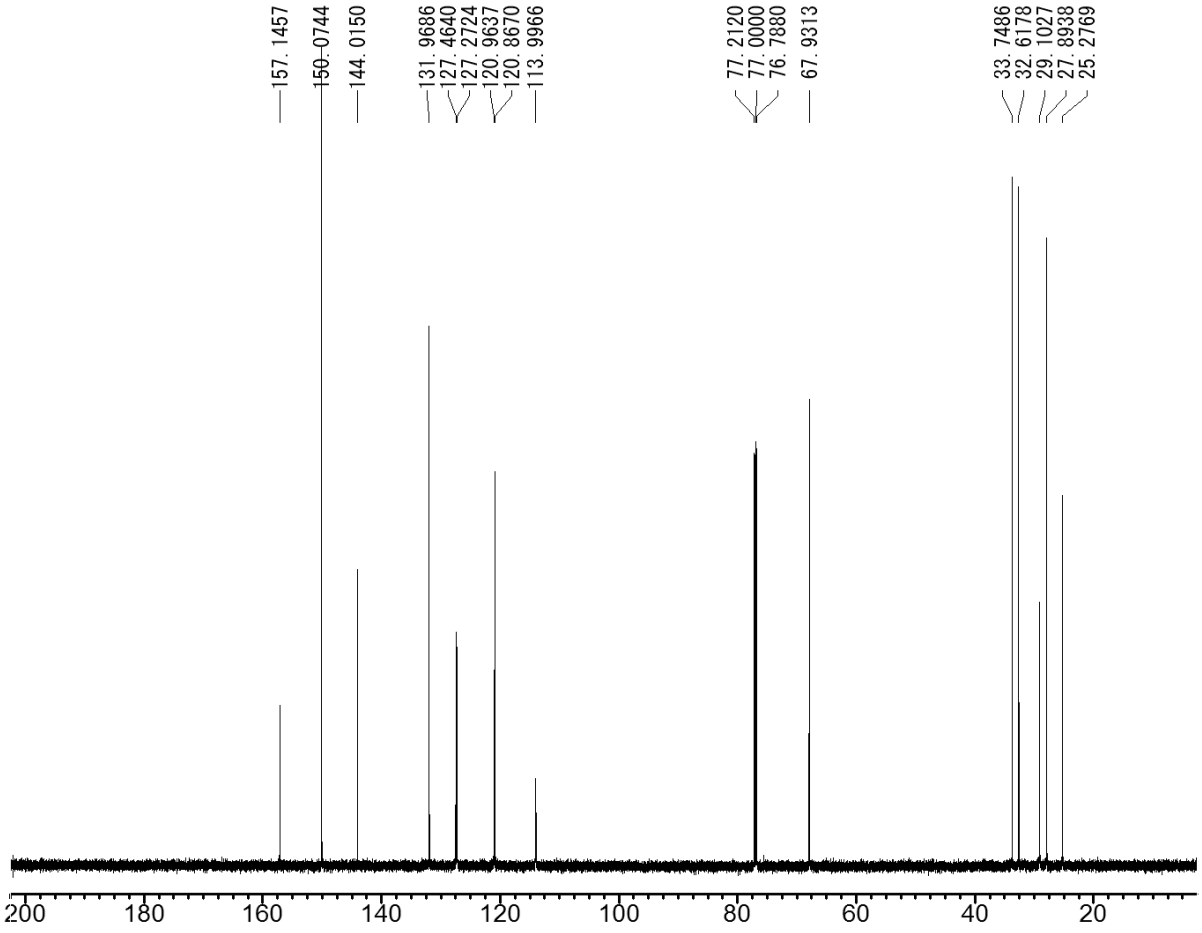
6a: R = $O(CH_2)_6Br$



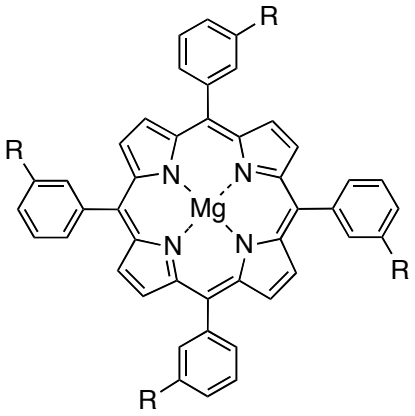
600 MHz ^{1}H NMR spectrum of **6a** in $CDCl_3$.



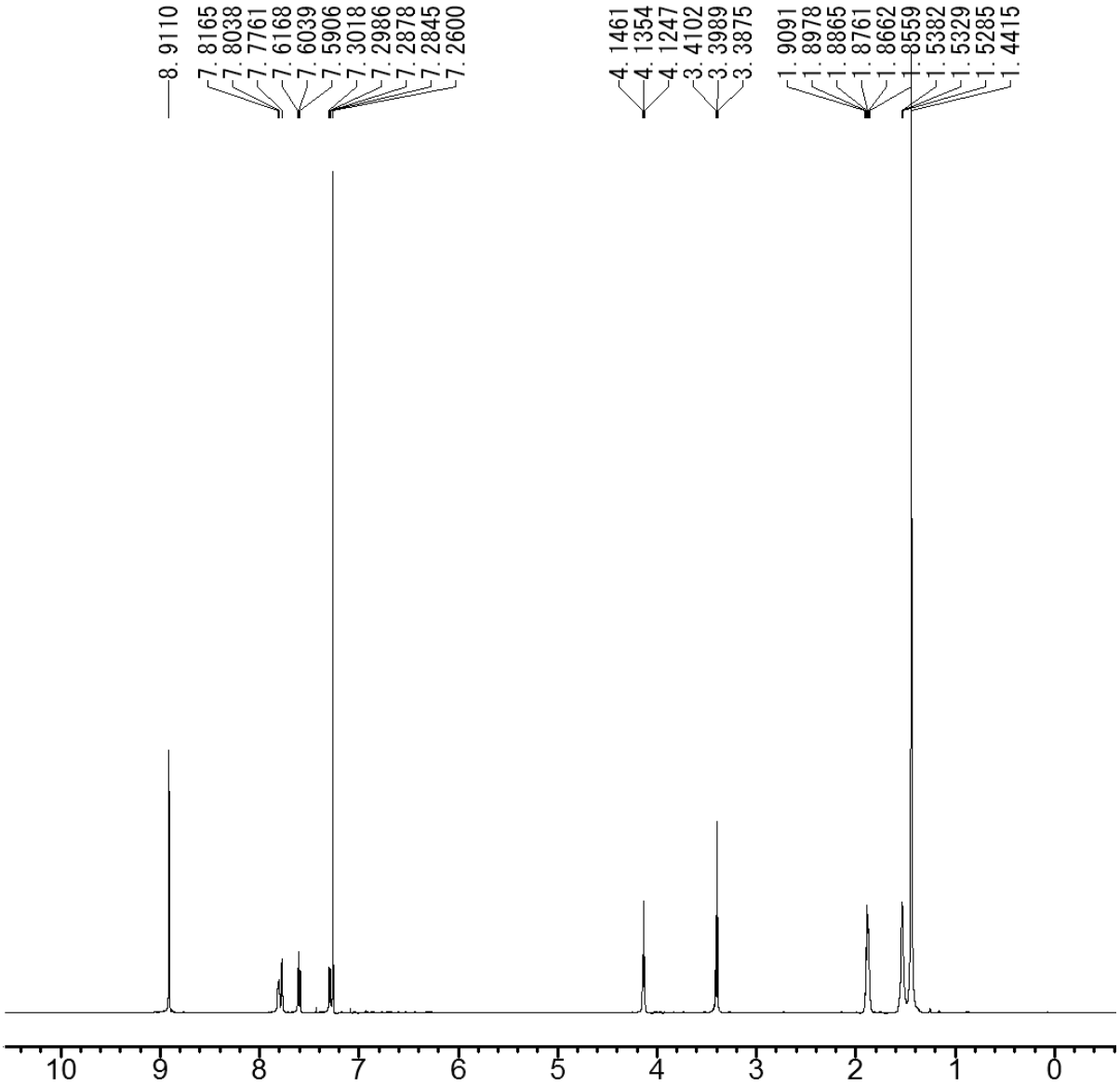
6a: R = $O(CH_2)_6Br$



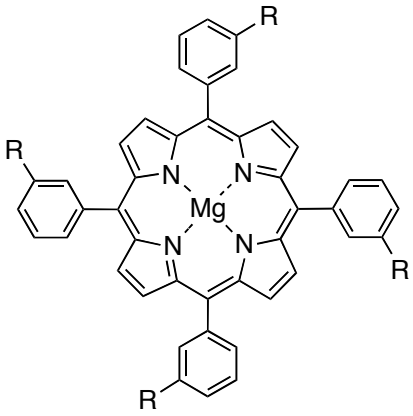
150 MHz ^{13}C NMR spectrum of **6a** in $CDCl_3$.



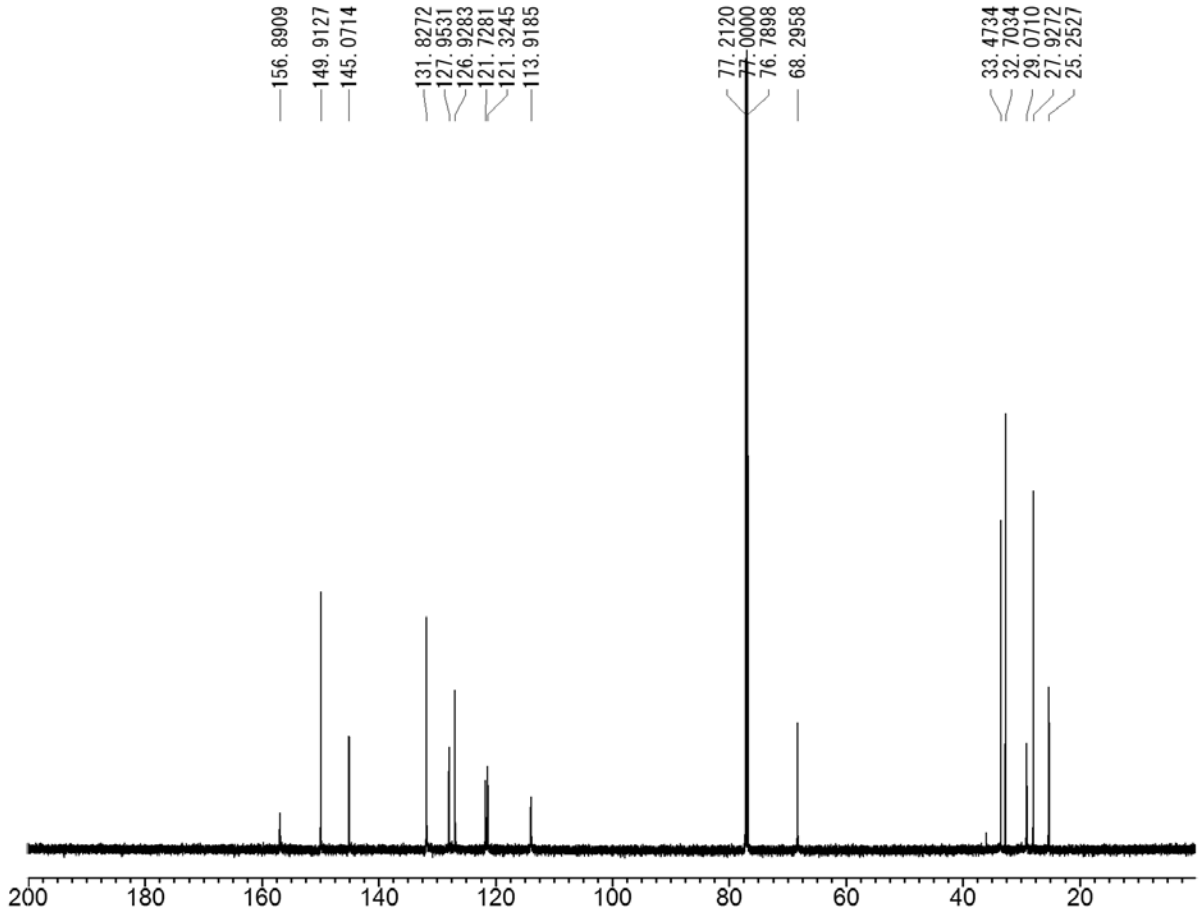
6b: R = $O(CH_2)_6Br$



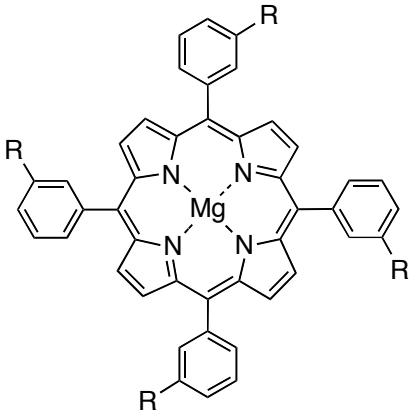
600 MHz ^{1}H NMR spectrum of **6b** in $CDCl_3$.



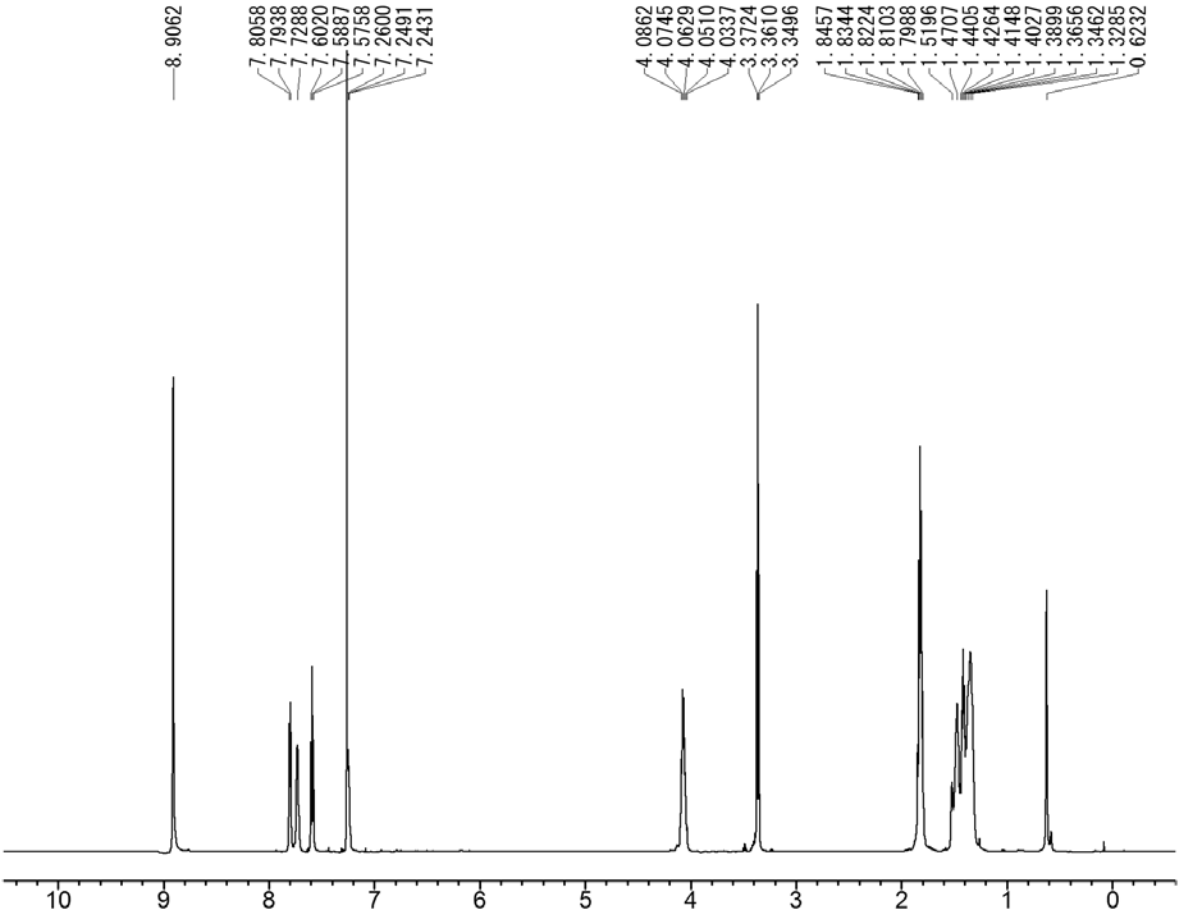
6b: R = $O(CH_2)_6Br$



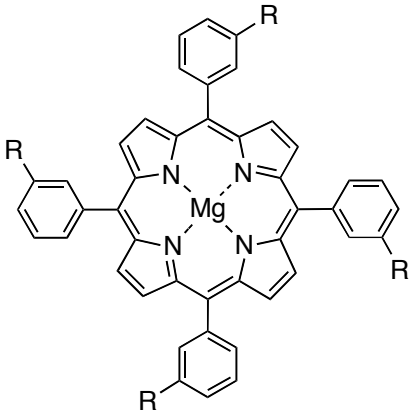
150 MHz ^{13}C NMR spectrum of **6b** in $CDCl_3$ at 50 °C.



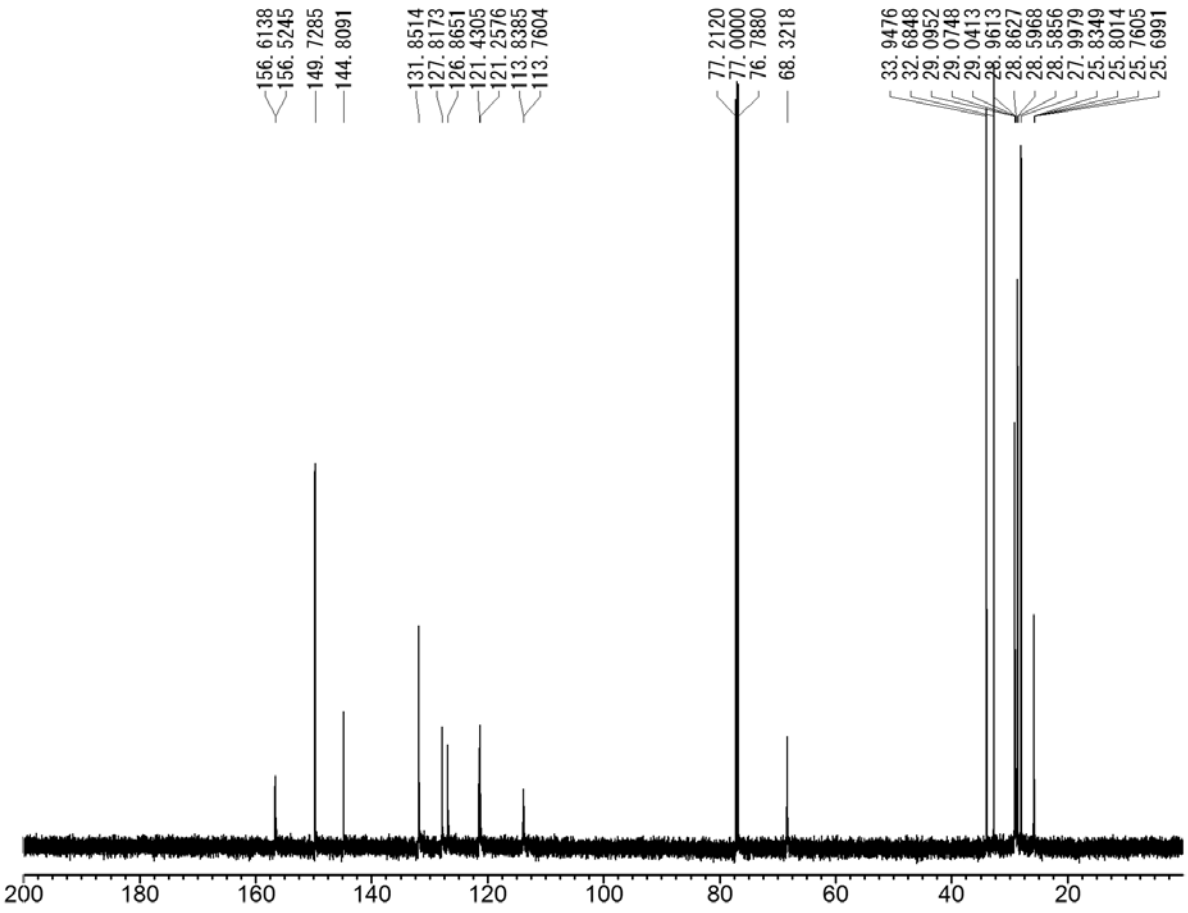
6c: R = $O(CH_2)_8Br$



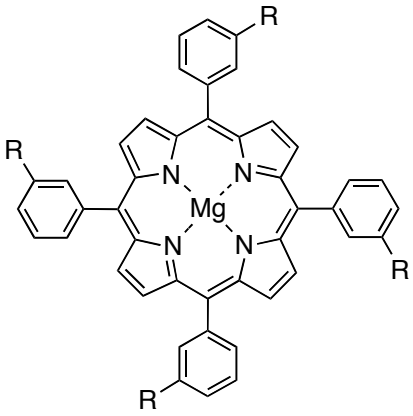
600 MHz ^{1}H NMR spectrum of **6c** in $CDCl_3$.



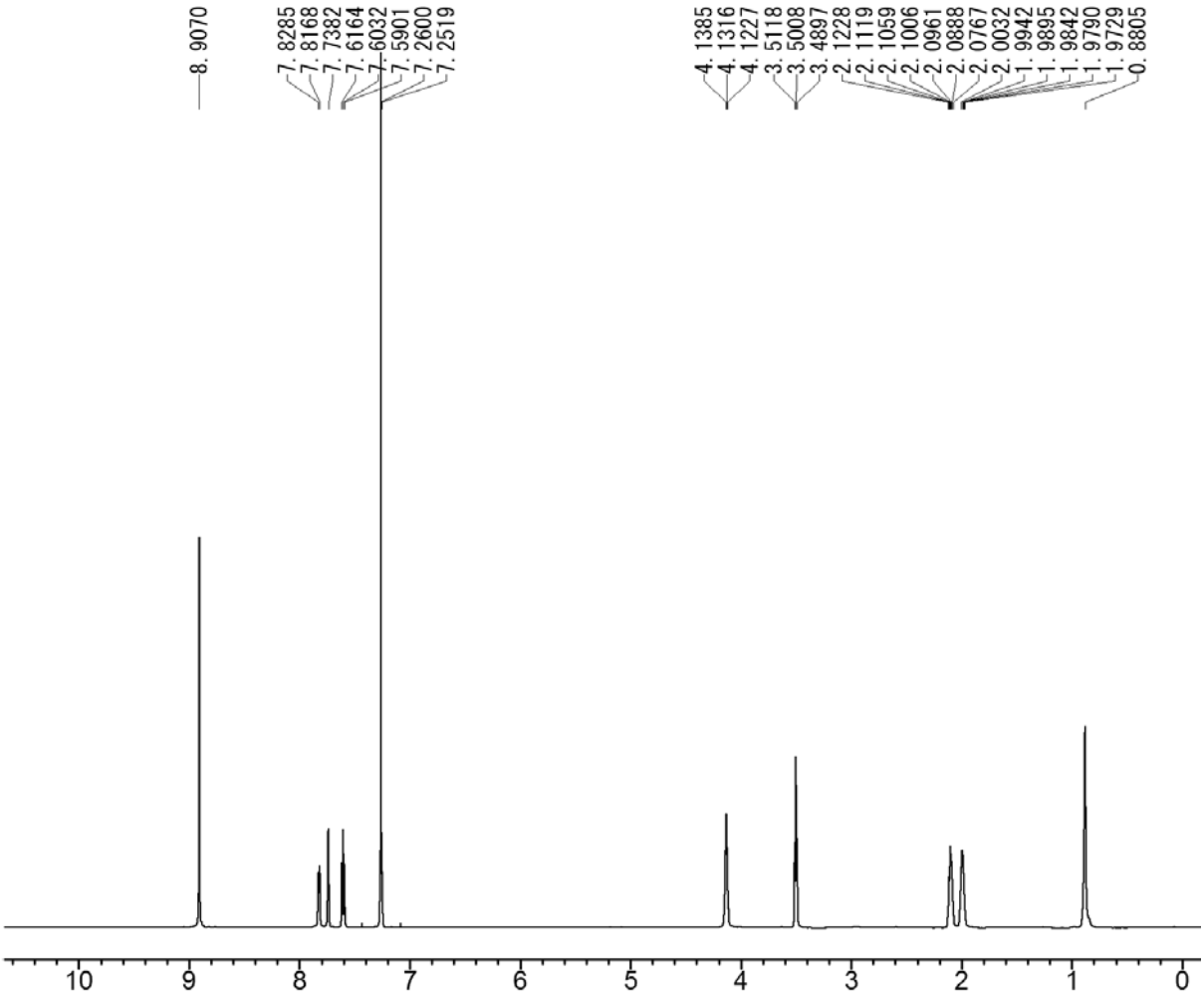
6c: R = $O(CH_2)_8Br$



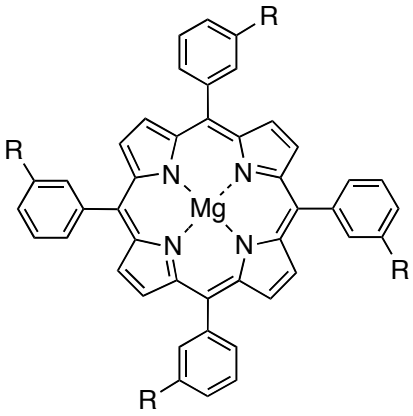
150 MHz ^{13}C NMR spectrum of **6c** in $CDCl_3$.



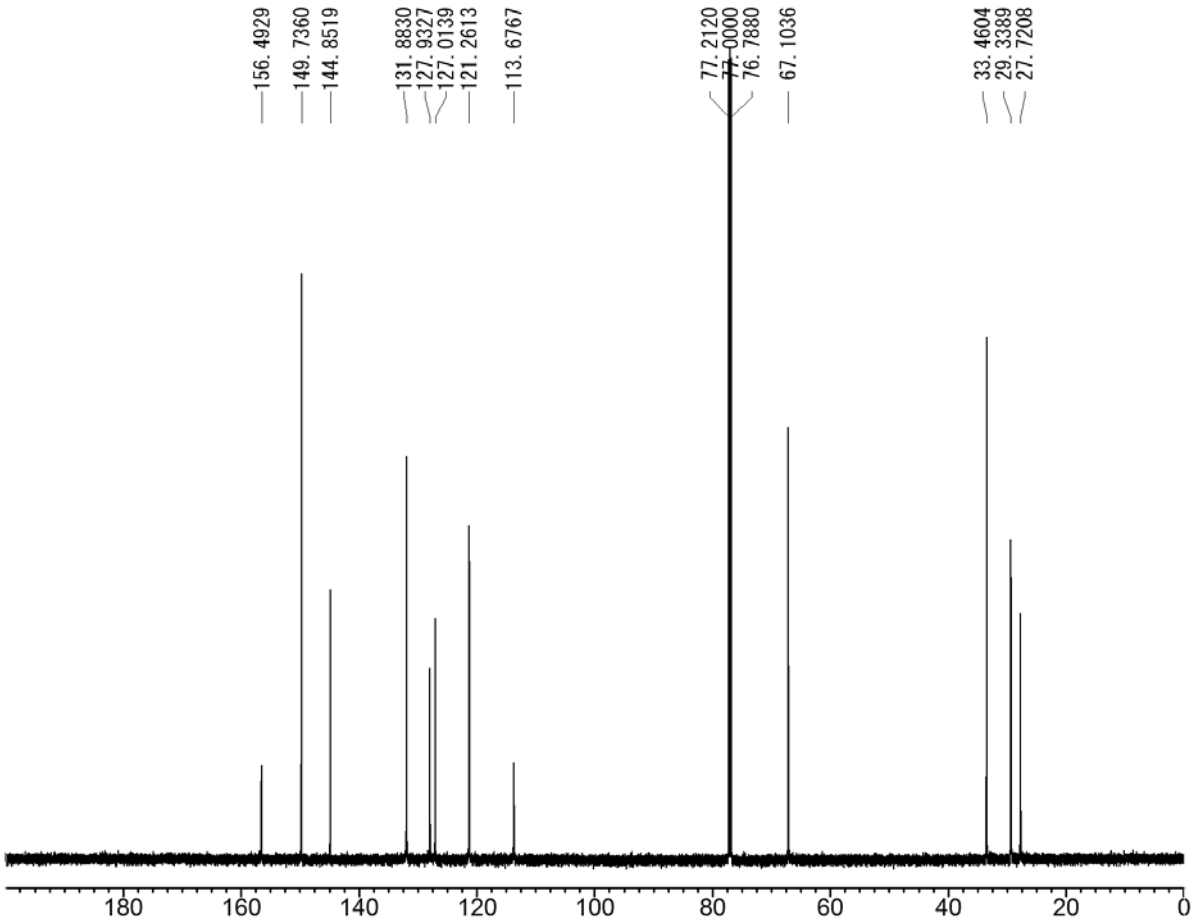
6d: R = $O(CH_2)_4Br$



600 MHz ^{1}H NMR spectrum of **6d** in $CDCl_3$.



6d: R = $O(CH_2)_4Br$



150 MHz ^{13}C NMR spectrum of **6d** in $CDCl_3$.