Electronic Supplementary Information

Catalytic synthesis and physical properties of CO_2-based cross-linked poly(cyclohexene carbonate)s

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[A] Instrumentation and Materials

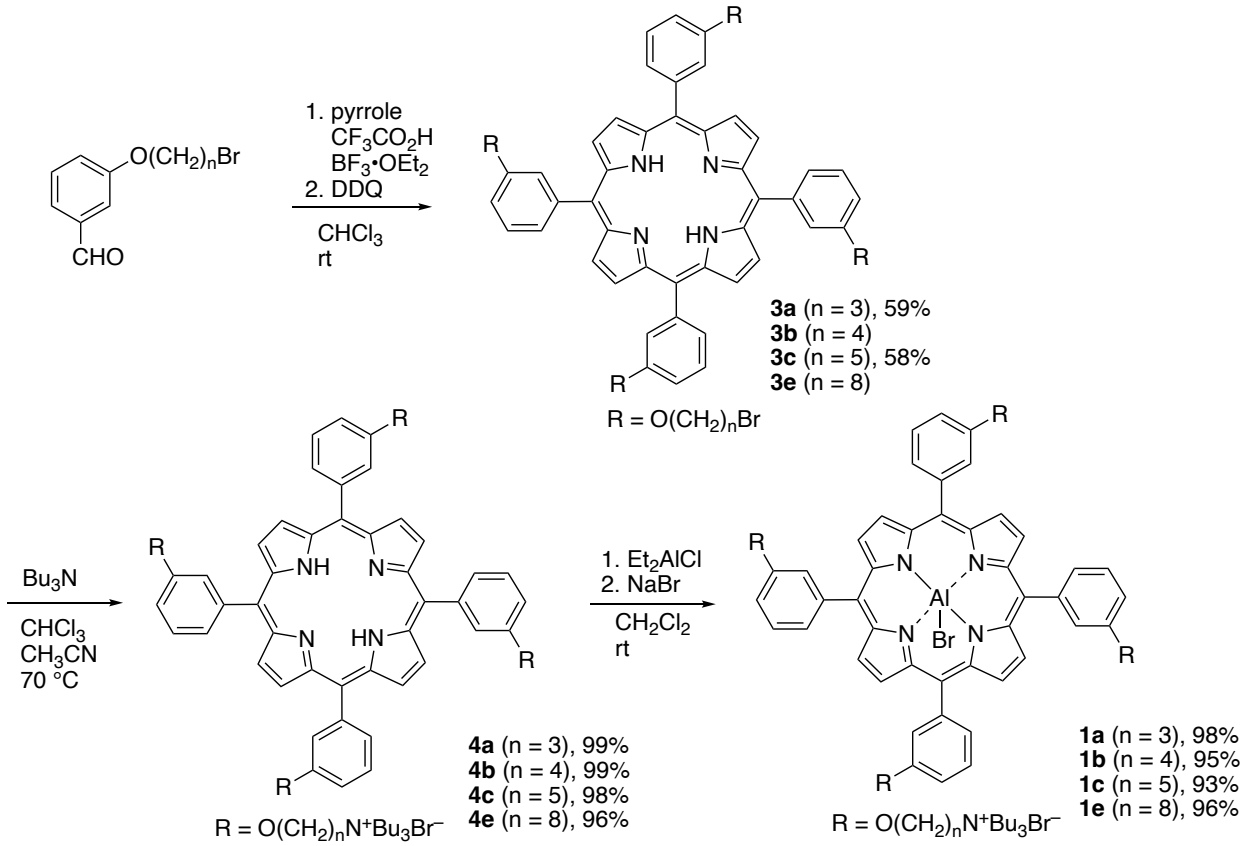
NMR spectra were recorded on a JEOL ECS400 spectrometer (^{1}H: 400 MHz and ^{13}C: 100 MHz) or a JEOL ECZ 600 spectrometer (^{1}H: 600 MHz and ^{13}C: 150 MHz), and chemical shifts are reported as the delta scale in ppm using an internal reference of deuterated solvents (δ = 7.26 ($CDCl_3$) for ^{1}H NMR, δ = 77.16 ($CDCl_3$) for ^{13}C NMR, δ = 3.31 (CD_3OD) for ^{1}H NMR, and δ = 49.00 (CD_3OD) for ^{13}C NMR). Size-exclusion chromatography (SEC) was carried out with two columns (Shodex KF-804L) using THF as an eluent at 1 mL/min at 40 °C, where molar masses were calibrated by using polystyrene standard samples. Electrospray ionization (ESI) mass spectra were recorded on a Bruker micrOTOF. IR spectra were recorded on a PerkinElmer Spectrum One or a Shimadzu IRAffinity-1. Thermogravimetric analysis (TGA) was performed on a HITACHI STA7200RV. Samples were heated from 30 °C to 500 °C at a rate of 10 °C min^{-1} under N_2 flow (200 mL/min). Differential scanning calorimetry (DSC) analysis was performed on a TA Instruments DSC Q200 V24.4 Build 116 analyzer. Samples were heated from 0 °C to 200 °C at a rate of 20 °C min^{-1} under N_2 flow (50 mL/min). Glass-transition temperature (T_g) was reported as the midpoint of a transition from the second heating run. Mechanical properties of the film state of polymers were recorded on a Shimadzu Autograph AG-Xplus universal testing machine. Intrinsic viscosity was measured by an Ostwald viscometer in $CHCl_3$ at 30 °C. Most reagents for the synthesis of the catalysts were purchased and used without further purification unless otherwise specified. Dry solvents were purchased or distilled over an appropriate drying agent and stored over molecular sieves 3A or 4A. Cyclohexene oxide (CHO) was freshly distilled from CaH_2. 3,4-Epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate (**2a**) was purchased from FUJIFILM Wako Pure Chemical and purified by silica gel column chromatography (EtOAc/hexane = 1/1). **1d**,[S1] **3b**,[S2] **3e**,[S2] 3-(3-bromopropoxy)benzaldehyde,[S3] and 3-(5-bromopentoxy)benzaldehyde[S3] were prepared and characterized according to the previously reported methods.

(S1) J. Deng, M. Ratanasak, Y. Sako, H. Tokuda, C. Maeda, J. Hasegawa, K. Nozaki and T. Ema, *Chem. Sci.*, 2020, **11**, 5669–5675.

(S2) T. Ema, Y. Miyazaki, S. Koyama, Y. Yano and T. Sakai, *Chem. Commun.*, 2012, **48**, 4489–4491.

(S3) S. Muthusamy, K. Selvaraj and E. Suresh, *Eur. J. Org. Chem.,* 2016, 1849–1859.

[B] Experimental Procedures and Compound Data



Synthesis of 3a

A solution of pyrrole (0.35 mL, 5.1 mmol) and 3-(3-bromopropoxy)benzaldehyde (1.22 g, 5.02 mmol) in dry $CHCl_3$ (500 mL) was bubbled with Ar, and $BF_3{\cdot}OEt_2$ (6.3 μL, 50 μmol) and CF_3CO_2H (0.35 mL, 4.6 mmol) were added. The mixture was stirred at room temperature for 7 h in the dark. DDQ (1.14 g, 5.02 mmol) was added, and the mixture was stirred at room temperature for 16 h. Et_3N (0.70 mL, 5.1 mmol) was added, and the mixture was concentrated. Purification by silica gel column chromatography ($CHCl_3$) gave **3a** (857 mg, 59%) as a purple solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ –2.81 (s, 2H), 2.41 (m, 8H), 3.68 (t, J = 6.4 Hz, 8H), 4.30 (t, J = 5.8 Hz, 8H), 7.34 (dd, J = 1.5, 8.2 Hz, 4H), 7.65 (t, J = 7.9 Hz, 4H), 7.79 (s, 4H), 7.83 (d, J = 7.3 Hz, 4H), 8.90 ppm (s, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.2, 32.6, 65.7, 114.2, 119.9, 121.3, 127.7, 128.0, 131.5, 143.6, 157.2 ppm; IR (KBr) 3318, 3059, 2924, 2874, 1597, 1574, 1470, 1431, 1400, 1385, 1350, 1315, 1285, 1258, 1204, 1180, 1165, 1084, 1042, 1011, 995, 976, 941, 891, 802, 775, 733, 698 cm^{-1}; HR-MS (ESI) *m/z* = 1163.0630, calcd for $C_{56}H_{51}N_4O_4Br_4$: 1163.0608 $[M+H]^+$.

Synthesis of 3c

A solution of pyrrole (0.35 mL, 5.1 mmol) and 3-(5-bromopentoxy)benzaldehyde (1.36 g, 5.02 mmol) in dry $CHCl_3$ (500 mL) was bubbled with Ar, and $BF_3{\cdot}OEt_2$ (6.3 μL, 50 μmol) and CF_3CO_2H (0.35 mL, 4.6 mmol) were added. The mixture was stirred at room temperature for 9 h in the dark. DDQ (1.14 g, 5.02 mmol) was added, and the mixture was stirred at room temperature for 14 h. Et_3N (0.70 mL, 5.1 mmol) was added, and the mixture was concentrated. Purification by silica gel column chromatography ($CHCl_3$) gave **3c** (928 mg, 58%) as a purple solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ –2.80 (s, 2H), 1.68 (m, 8H), 1.87–2.00 (m, 16H), 3.44 (t, J = 6.7 Hz, 8H), 4.16 (t, J = 6.1 Hz, 8H), 7.32 (dd, J = 1.8, 8.5 Hz, 4H), 7.64 (t, J = 7.9 Hz, 4H), 7.77−7.82 (m, 8H), 8.90 ppm (s, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.1, 28.7, 32.7, 33.8, 67.9, 114.2, 120.0, 121.2, 127.7, 127.8, 131.2, 143.6, 157.5 ppm; IR (KBr) 3318, 3059, 2940, 2866, 1597, 1574, 1470, 1431, 1396, 1350, 1315, 1285, 1265, 1204, 1180, 1165, 1045, 995, 976, 918, 876, 802, 775, 733, 698 cm^{-1}; HR-MS (ESI) *m/z* = 1275.1817, calcd for $C_{64}H_{67}N_4O_4Br_4$: 1275.1862 $[M+H]^+$.

Synthesis of 4a

A screw cap test tube containing **3a** (115 mg, 98.9 μmol) and Bu_3N (1.0 mL, 4.2 mmol) in dry $CHCl_3$ (1.0 mL) and dry CH_3CN (1.0 mL) was heated at 70 °C for 1 week. After the solvents were evaporated, excess Bu_3N was removed with a pipette, and the residue was precipitated with CH_2Cl_2/Et_2O to give **4a** (187 mg, 99%) as a purple solid.
^{1}H NMR (CD_3OD, 400 MHz, 60 °C) δ 0.92 (t, J = 7.1 Hz, 36H), 1.35 (m, 24H), 1.58–1.73 (m, 24H), 2.10–2.27 (m, 8H), 3.18–3.31 (m, 24H), 3.52 (s, 8H), 4.28 (s, 8H), 7.38 (d, J = 7.8 Hz, 4H), 7.65 (s, 4H), 7.77 (s, 8H), 8.84 ppm (s, 8H); ^{13}C NMR (CD_3OD, 100 MHz, 60 °C) δ 13.8, 20.7, 23.6, 24.9, 57.4, 60.0, 66.1, 115.6, 121.2, 122.5, 129.0, 129.2, 132.0, 144.7, 158.5 ppm; IR (KBr) 3318, 3059, 2959, 2874, 1597, 1574, 1470, 1431, 1381, 1350, 1315, 1288, 1265, 1204, 1180, 1165, 1092, 1057, 995, 976, 937, 914, 876, 802, 779, 737, 698 cm^{-1}; HR-MS (ESI) *m/z* = 871.5404, calcd for $C_{104}H_{158}N_8O_4Br_2$: 871.5373 $[M–2Br]^{2+}$.

Synthesis of 4b

A screw cap test tube containing **3b** (118 mg, 96.8 μmol) and Bu_3N (1.0 mL, 4.2 mmol) in dry $CHCl_3$ (1.0 mL) and dry CH_3CN (1.0 mL) was heated at 70 °C for 1 week. After the solvents were evaporated, excess Bu_3N was removed with a pipette, and the residue was precipitated with CH_2Cl_2/Et_2O to give **4b** (189 mg, 99%) as a purple solid.
^{1}H NMR (CD_3OD, 400 MHz, 60 °C) δ 0.93 (t, J = 6.7 Hz, 36H), 1.37–1.40 (m, 24H), 1.57–1.77 (m, 24H), 1.88–2.08 (m, 16H), 3.24–3.31 (m, 24H), 3.40 (s, 8H), 4.32 (s, 8H), 7.44 (dd, J = 2.1, 8.2 Hz, 4H), 7.71 (t, J = 7.9 Hz, 4H), 7.76–7.84 (m, 8H), 8.88 ppm (s, 8H); ^{13}C NMR (CD_3OD, 100 MHz, 60 °C) δ 13.8, 20.0, 20.7, 24.9, 27.1, 59.6, 59.9, 68.4, 115.4, 121.2, 122.7, 129.0, 132.3, 144.7, 158.8 ppm; IR (KBr) 3319, 3059, 2959, 2874, 1601, 1576, 1470, 1435, 1381, 1348, 1315, 1285, 1263, 1204, 1182, 1165, 1055, 1032, 997, 974, 920, 880, 804, 777, 737, 700 cm^{-1}; HR-MS (ESI) *m/z* = 899.5719, calcd for $C_{108}H_{166}N_8O_4Br_2$: 899.5686 $[M–2Br]^{2+}$.

Synthesis of 4c

A screw cap test tube containing **3c** (113 mg, 88.6 μmol) and Bu_3N (1.0 mL, 4.2 mmol) in dry $CHCl_3$ (1.0 mL) and dry CH_3CN (1.0 mL) was heated at 70 °C for 1 week. After the solvents were evaporated, excess Bu_3N was removed with a pipette, and the residue was precipitated with CH_2Cl_2/Et_2O to give **4c** (176 mg, 99%) as a purple solid.
^{1}H NMR (CD_3OD, 400 MHz, 60 °C) δ 0.84–1.00 (m, 36H), 1.26–2.00 (m, 72H), 3.08–3.31 (m, 32H), 4.24 (t, J = 6.1 Hz, 8H), 7.39 (dd, J = 1.6, 8.0 Hz, 4H), 7.67 (t, J = 7.6 Hz, 4H), 7.73–7.82 (m, 8H), 8.87 ppm (s, 8H); ^{13}C NMR (CD_3OD, 100 MHz, 60 °C) δ 13.8, 20.6, 22.7, 24.3, 24.9, 29.7, 59.9, 69.2, 115.4, 121.3, 122.7, 128.7, 128.9, 131.9, 144.5, 159.1 ppm; IR (KBr) 3325, 2959, 2874, 1597, 1574, 1470, 1431, 1381, 1350, 1315, 1285, 1265, 1204, 1180, 1165, 1069, 1034, 995, 976, 926, 883, 802, 779, 737, 702 cm^{-1}; HR-MS (ESI) *m/z* = 928.0986, calcd for $C_{112}H_{174}N_8O_4Br_2$: 928.1018 $[M–2Br]^{2+}$.

Synthesis of 4e

A screw cap test tube containing **3e** (81.7 mg, 56.6 μmol) and Bu_3N (1.0 mL, 4.2 mmol) in dry $CHCl_3$ (1.0 mL) and dry CH_3CN (1.0 mL) was heated at 70 °C for 1 week. After the solvents were evaporated, excess Bu_3N was removed with a pipette, and the residue was precipitated with CH_2Cl_2/Et_2O to give **4e** (119 mg, 96%) as a purple solid. ^{1}H NMR (CD_3OD, 400 MHz, 60 °C) δ 0.93 (t, J = 7.0 Hz, 36H), 1.30–1.71 (m, 88H), 1.86–1.95 (m, 8H), 2.97–3.01 (m, 32H), 4.22 (t, J = 6.4 Hz, 8H), 7.29 (dd, J = 2.0, 8.4 Hz, 4H), 7.68 (t, J = 7.6 Hz, 4H), 7.74–7.79 (m, 8H), 8.89 ppm (s, 8H); ^{13}C NMR (CD_3OD, 100 MHz, 60 °C) δ 12.4, 19.2, 21.4, 23.5, 25.7, 28.7, 58.5, 68.2, 114.0, 120.0, 121.5, 127.2, 127.5, 131.0, 143.1, 157.8 ppm; IR (KBr) 3419, 2958, 2933, 2872, 1595, 1575, 1469, 1431, 1381, 1348, 1315, 1286, 1263, 1203, 1182, 1165, 1037, 995, 975, 921, 879, 802, 777, 736, 700 cm^{-1}; HR-MS (ESI) *m/z* = 1012.1911, calcd for $C_{124}H_{198}N_8O_4Br_2$: 1012.1958 $[M–2Br]^{2+}$.

Synthesis of 1a

Et_2AlCl (0.87 M in hexane, 0.92 mL, 0.54 mmol) was slowly added to a solution of **4a** (68.2 mg, 35.8 μmol) in dry CH_2Cl_2 (3.0 mL), and the mixture was stirred at rt for 16 h. The mixture was diluted with CH_2Cl_2, washed with 3% HBr aq. and then 1 M NaBr aq., dried over Na_2SO_4, and evaporated to give **1a** (70.4 mg, 98%) as a purple solid. ^{1}H NMR (CD_3OD, 400 MHz, 60 °C) δ 0.95 (t, J = 7.4 Hz, 36H), 1.40 (m, 24H), 1.71 (m, 24H), 2.28 (m, 8H), 3.27 (m, 24H), 3.58 (t, J = 8.2 Hz, 8H), 4.34 (t, J = 5.5 Hz, 8H), 7.44 (d, J = 7.3 Hz, 4H), 7.71 (t, J = 8.2 Hz, 4H), 7.76–7.84 (m, 8H), 9.09 ppm (s, 8H); ^{13}C NMR (CD_3OD, 100 MHz, 60 °C) δ 13.9, 20.7, 23.7, 25.0, 57.5, 60.1, 66.2, 115.8, 121.8, 122.6, 129.1, 129.2, 133.3, 144.2, 149.2, 158.7 ppm; IR (KBr) 2959, 2874, 1597, 1578, 1508, 1474, 1427, 1381, 1350, 1315, 1285, 1258, 1207, 1184, 1057, 1015, 976, 941, 880, 802, 741, 721, 702 cm^{-1}; HR-MS (ESI) *m/z* = 924.4771, calcd for $C_{104}H_{156}N_8O_4AlBr_3$: 924.4785 $[M–2Br]^{2+}$.

Synthesis of 1b

Et_2AlCl (0.87 M in hexane, 0.96 mL, 0.84 mmol) was slowly added to a solution of **4b** (109 mg, 55.6 μmol) in dry CH_2Cl_2 (3.0 mL), and the mixture was stirred at rt for 15 h. The mixture was diluted with CH_2Cl_2, washed with 3% HBr aq. and then 1 M NaBr aq., dried over Na_2SO_4, and evaporated to give **1b** (109 mg, 95%) as a purple solid. ^{1}H NMR (CD_3OD, 400 MHz, 60 °C) δ 0.98 (t, J = 7.3 Hz, 36H), 1.42 (m, 24H), 1.71 (m, 24H), 1.94–2.07 (m, 16H), 3.20–3.31 (m, 24H), 3.43 (t, J = 7.4 Hz, 8H), 4.33 (t, J = 5.4 Hz, 8H), 7.47 (d, J = 8.5 Hz, 4H), 7.73 (t, J = 7.9 Hz, 4H), 7.78–7.84 (m, 8H), 9.13 ppm (s, 8H); ^{13}C NMR (CD_3OD, 100 MHz, 60 °C) δ 13.9, 20.0, 20.7, 25.0, 27.2, 59.7, 60.0, 68.4, 115.6, 121.9, 122.5, 128.8, 129.1, 133.2, 144.2, 149.2, 159.0 ppm; IR (KBr) 2959, 2874, 1597, 1578, 1508, 1474, 1431, 1385, 1350, 1315, 1285, 1261, 1211, 1184, 1069, 1011, 945, 883, 849, 802, 741, 721, 702 cm^{-1}; HR-MS (ESI) *m/z* = 952.5081, calcd for $C_{108}H_{164}N_8O_4AlBr_3$: 952.5114 $[M–2Br]^{2+}$.

Synthesis of 1c

Et_2AlCl (0.87 M in hexane, 0.52 mL, 0.45 mmol) was slowly added to a solution of **4c** (60.5 mg, 30.0 μmol) in dry CH_2Cl_2 (2.5 mL), and the mixture was stirred at rt for 15 h. The mixture was diluted with CH_2Cl_2, washed with 3% HBr aq. and then 1 M NaBr aq., dried over Na_2SO_4, and evaporated to give **1c** (59.3 mg, 93%) as a purple solid.

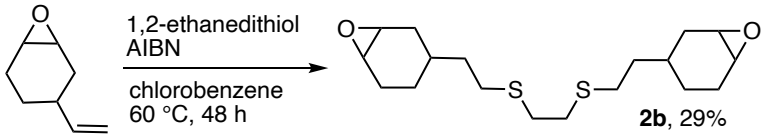
^{1}H NMR (CD_3OD, 400 MHz, 60 ℃) δ 1.00 (t, J = 7.3 Hz, 36H), 1.42 (m, 24H), 1.65–2.04 (m, 48H), 3.18–3.31 (m, 32H), 4.28 (t, J = 6.1 Hz, 8H), 7.45 (dd, J = 1.2, 7.3 Hz, 4H), 7.71 (t, J = 7.9 Hz, 4H), 7.75–7.84 (m, 8H), 9.15 ppm (s, 8H); ^{13}C NMR (CD_3OD, 150 MHz, 60 ℃) δ 13.8, 20.7, 22.9, 24.3, 25.0, 29.9, 59.9, 60.0, 69.3, 115.5, 122.0, 122.5, 128.5, 129.1, 133.2, 144.0, 149.2, 159.1 ppm; IR (KBr) 2959, 2870, 1597, 1574, 1508, 1474, 1427, 1385, 1350, 1315, 1285, 1261, 1211, 1184, 1072, 1015, 945, 891, 802, 741, 721, 702 cm^{-1}; HR-MS (ESI) *m/z* = 980.5388, calcd for $C_{112}H_{172}N_8O_4AlBr_3$: 980.5411 $[M–2Br]^{2+}$.

Synthesis of 1e

Et_2AlCl (0.87 M in hexane, 0.17 mL, 0.15 mmol) was slowly added to a solution of **4e** (21.0 mg, 9.64 μmol) in dry CH_2Cl_2 (1.0 mL), and the mixture was stirred at rt for 18 h. The mixture was diluted with CH_2Cl_2, washed with 3% HBr aq. and then 1 M NaBr aq., dried over Na_2SO_4, and evaporated to give **1e** (21.2 mg, 96%) as a purple solid.

^{1}H NMR (CD_3OD, 400 MHz, 60 ℃) δ 1.00 (t, J = 7.3 Hz, 36H), 1.37−1.94 (m, 96H), 3.23 (t, J = 7.9 Hz, 32H), 4.22 (t, J = 6.4 Hz, 8H), 7.39 (d, J = 7.9 Hz, 4H), 7.65−7.79 (m, 12H), 9.04 ppm (m, 8H); ^{13}C NMR (CD_3OD, 100 MHz, 60 ℃) δ 13.8, 20.7, 22.9, 24.9, 27.1, 27.3, 30.0, 30.2, 30.5, 59.9, 60.1, 69.6, 115.3, 121.6, 122.6, 128.6, 128.7, 132.6, 149.1, 159.2 ppm; IR (KBr) 3061, 2959, 2934, 2872, 1595, 1576, 1512, 1472, 1427, 1383, 1350, 1314, 1287, 1261, 1209, 1186, 1070, 1011, 941, 881, 800, 721, 702 cm^{-1}; HR-MS (ESI) *m/z* = 1064.6401, calcd for $C_{124}H_{196}N_8O_4AlBr_3$: 1064.6370 $[M–2Br]^{2+}$.

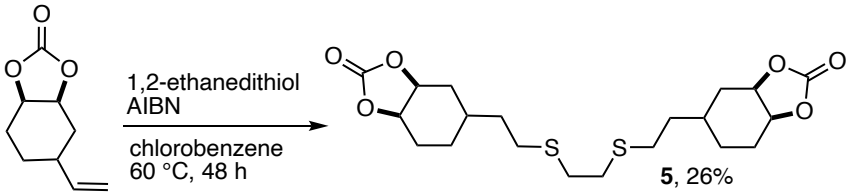
Synthesis of 2b



To a stirred solution of AIBN (164 mg, 1.00 mmol) in chlorobenzene (20 mL) was added dropwise a solution of 1,2-epoxy-4-vinylcyclohexane (3.3 mL, 25 mmol) and 1,2-ethanedithiol (0.80 mL, 10 mmol) in chlorobenzene (2 mL) over 1 h at 60 °C, and the mixture was stirred at 60 °C for 48 h under N_2. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography ($CHCl_3$/MeOH = 30/1) to give **2b** (996 mg, 2.91 mmol, 29%) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86–1.20 (m, 2H), 1.31–1.88 (m, 12H) 1.95–2.07 (m, 2H), 2.12–2.19 (m, 2H), 2.50–2.55 (m, 4H), 2.69–2.70 (m, 4H), 3.12–3.17 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 23.3, 24.1, 25.0, 26.8, 29.0, 29.4, 29.5, 30.2, 31.5, 32.0, 36.1, 36.3, 51.5, 51.7, 52.4, 52.8; IR (KBr) 2990, 2924, 2870, 2853, 1429, 1375, 1341, 1256, 1204, 1136, 970, 924, 907, 849, 822, 810, 793, 739, 694, 542 cm^{-1}; HR-MS (ESI) *m/z* = 365.1579, calcd for $C_{18}H_{30}O_2S_2Na$: 365.1579 $[M+Na]^+$.

Synthesis of model compound 5 for photodegradation



To a stirred solution of AIBN (28.7 mg, 175 μmol) in chlorobenzene (3.0 mL) was added dropwise a solution of cyclic 4-vinylcyclohexene carbonate (670 mg, 3.99 mmol) and 1,2-ethanedithiol (0.14 mL, 1.7 mmol) in chlorobenzene (0.5 mL) over 30 min at 60 °C, and the mixture was stirred at 60 °C for 48 h under N_2. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography ($CHCl_3$/MeOH = 30/1) to give **5** (222 mg, 518 μmol, 26%) as a white solid.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.92–1.37 (m, 4H), 1.43–1.83 (m, 10H), 2.06–2.27 (m, 4H), 2.51–2.55 (m, 4H), 2.66 (s, 4H), 4.61–4.75 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 24.9, 25.56, 25.59, 26.6, 28.9, 29.0, 29.1, 29.3, 31.2, 31.3, 31.9, 31.95, 31.98, 33.7, 35.5, 35.5, 38.3, 75.1, 75.5, 75.7, 76.0, 154.9, 155.0; IR (KBr) 2924, 2864, 1795, 1450, 1429, 1373, 1354, 1209, 1193, 1147, 1028, 779, 732, 694 cm^{-1}; HR-MS (ESI) *m/z* = 453.1379, calcd for $C_{20}H_{30}O_6S_2Na$: 453.1376 $[M+Na]^+$.

General procedure for the terpolymerization reactions

CHO (2.9 mL, 2.9 mmol) was added to a test tube containing catalyst **1** (0.29 μmol), **2** (0–0.87 mmol) and a Teflon stirring bar in an autoclave (preheated at 150 °C for 1 h and cooled down in vacuo) in a glove box (purge type) under N_2. The autoclave was closed, and the sealed autoclave was taken out from the glovebox and pressurized with 2.0 MPa of CO_2. The reaction mixture was stirred at 130 °C for 24 h. The reactor was cooled down to ambient temperature and vented in a fume hood. The crude mixture was dissolved in $CHCl_3$, and 0.5 M HCl in MeOH (0.1 mL) was added. Mesitylene (70 μL, 0.50 mmol) was added as an internal standard, and the conversion was calculated by ^{1}H NMR spectroscopy. The solution was then evaporated to dryness with heating. A small portion of the mixture was used for SEC analysis. Reprecipitation from CH_2Cl_2/MeOH (a CH_2Cl_2 (10 mL) solution of the crude product was added dropwise to MeOH (300 mL)) followed by filtration and vacuum drying gave a white powdered sample; 1.38 g, 33% (Table 2, entry 1, 58% conv.), 1.70 g, 41% (entry 2, 66% conv.), 1.51 g, 36% (entry 3, 52% conv.), 1.49 g, 36% (entry 4, 52% conv.), 1.41 g, 34% (entry 5, 44% conv.), 1.63 g, 39% (entry 6, 55% conv.), and 1.33 g, 32% (entry 7, 48% conv.).

General procedure for the terpolymerization reactions for the preparation of insoluble polymers

CHO (1.5 mL, 1.5 mmol) was added to a test tube containing catalyst **1b** (0.15 μmol), **2a** (0.15–0.60 mmol) and a Teflon stirring bar in an autoclave (preheated at 150 °C for 1 h and cooled down in vacuo) in a glove box (purge type) under N_2. The autoclave was closed, and the sealed autoclave was taken out from the glovebox and pressurized with 4.0 MPa of CO_2. The reaction mixture was stirred at 130 °C for 48 h. The reactor was cooled down to ambient temperature and vented in a fume hood. Because the insoluble polymer products were usually stuck tightly to the test tube, the test tube was cooled in liquid N_2, and it was quickly put in a plastic bag and broken with a hammer to take out the product. The rigid product was ground by using a mill (Waring bottle blender 7011HBC), washed with MeOH, dried under reduced pressure, and analyzed by IR, TGA, and DSC (262 mg, 10% from 10 mol% of **2a**; 493 mg, 16% from 20 mol% of **2a**; 1.29 g, 35% from 30 mol% of **2a**; and 1.21 g, 29% from 40 mol% of **2a**).

[C] Characterization of Polymers

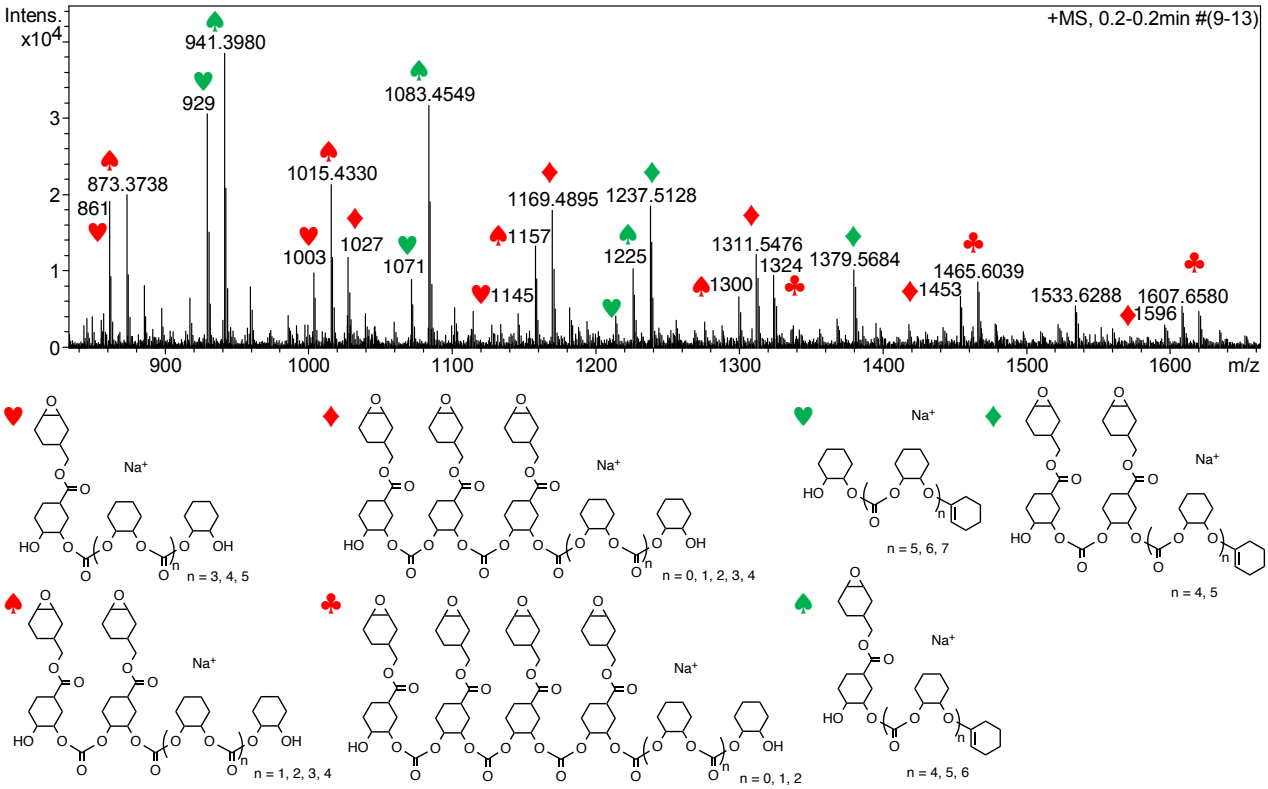


Fig. S1 ESI-MS spectrum of polymers. Reaction conditions: CHO (3.0 mmol), **2a** (0.33 mmol), **1b** (0.30 μmol), CO_2 (2 MPa), 130 °C, 5 min. Only one regioisomer is shown as a typical example.

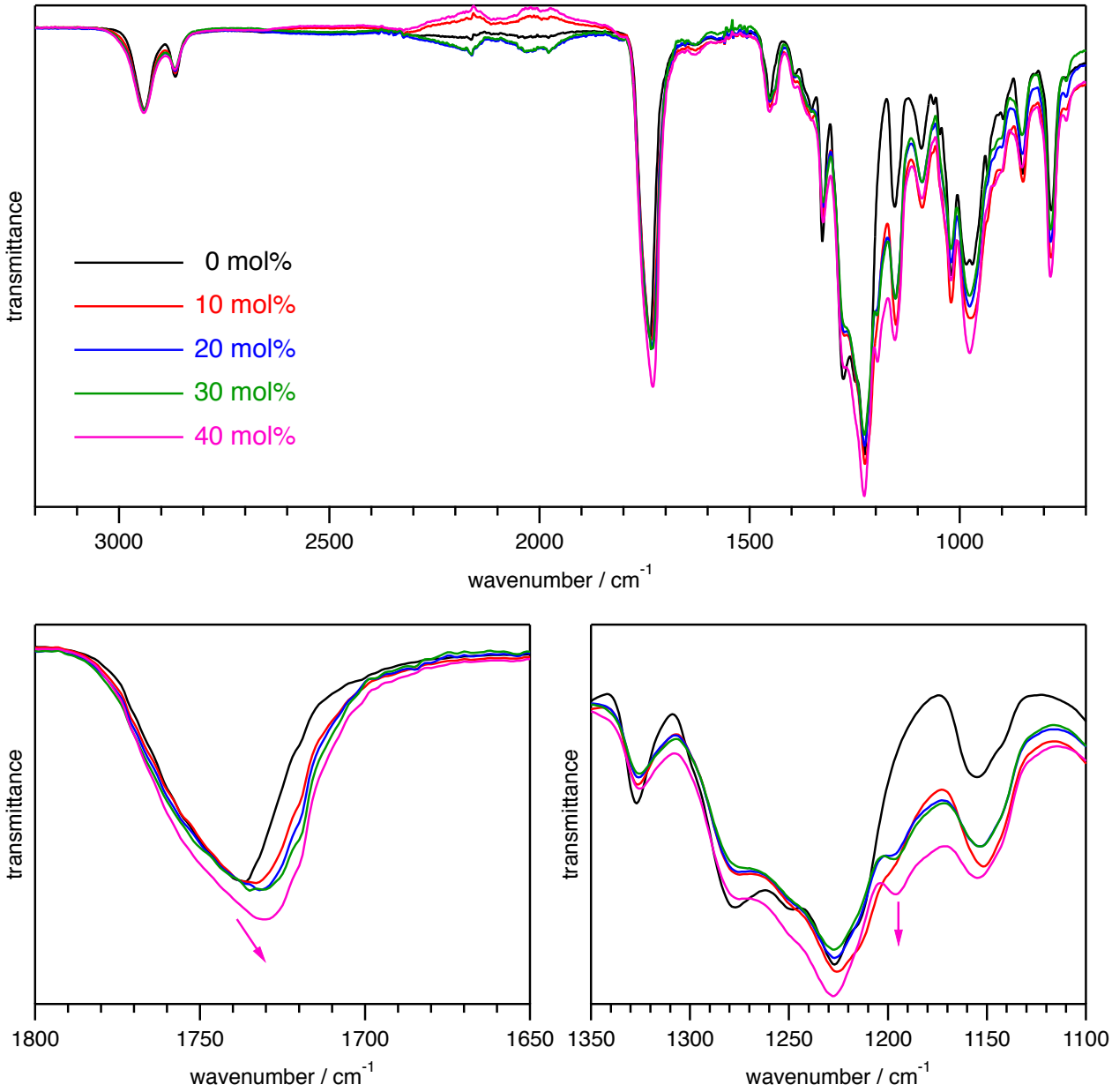


Fig. S2 IR (ATR) spectra of polycarbonates prepared from CHO, **2a**, and CO_2 with catalyst **1b**. **1b**:**2a**:CHO = 1:x:100000 (x = 0, 10000, 20000, 30000, or 40000).

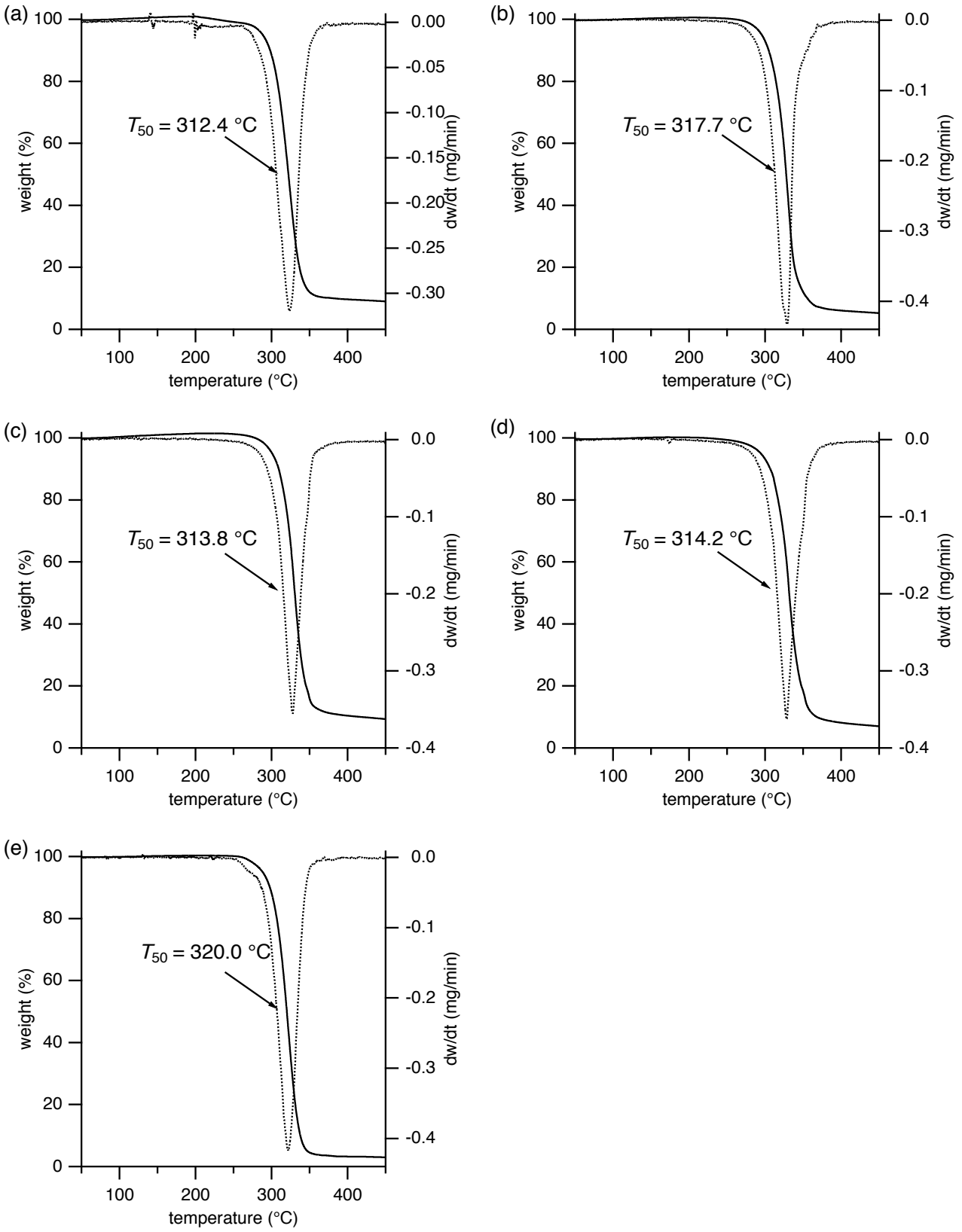


Fig. S3 TGA profiles of polycarbonates prepared from CHO, **2a**, and CO_2 with catalyst **1b**. (a) **1b**:**2a**:CHO = 1:0:100,000 (Table 2, entry 1). (b) **1b**:**2a**:CHO = 1:100:100,000 (entry 2). (c) **1b**:**2a**:CHO = 1:200:100,000 (entry 3). (d) **1b**:**2a**:CHO = 1:300:100,000 (entry 4). (e) **1b**:**2a**:CHO = 1:3,000:100,000. Heating rate was 10 °C/min.

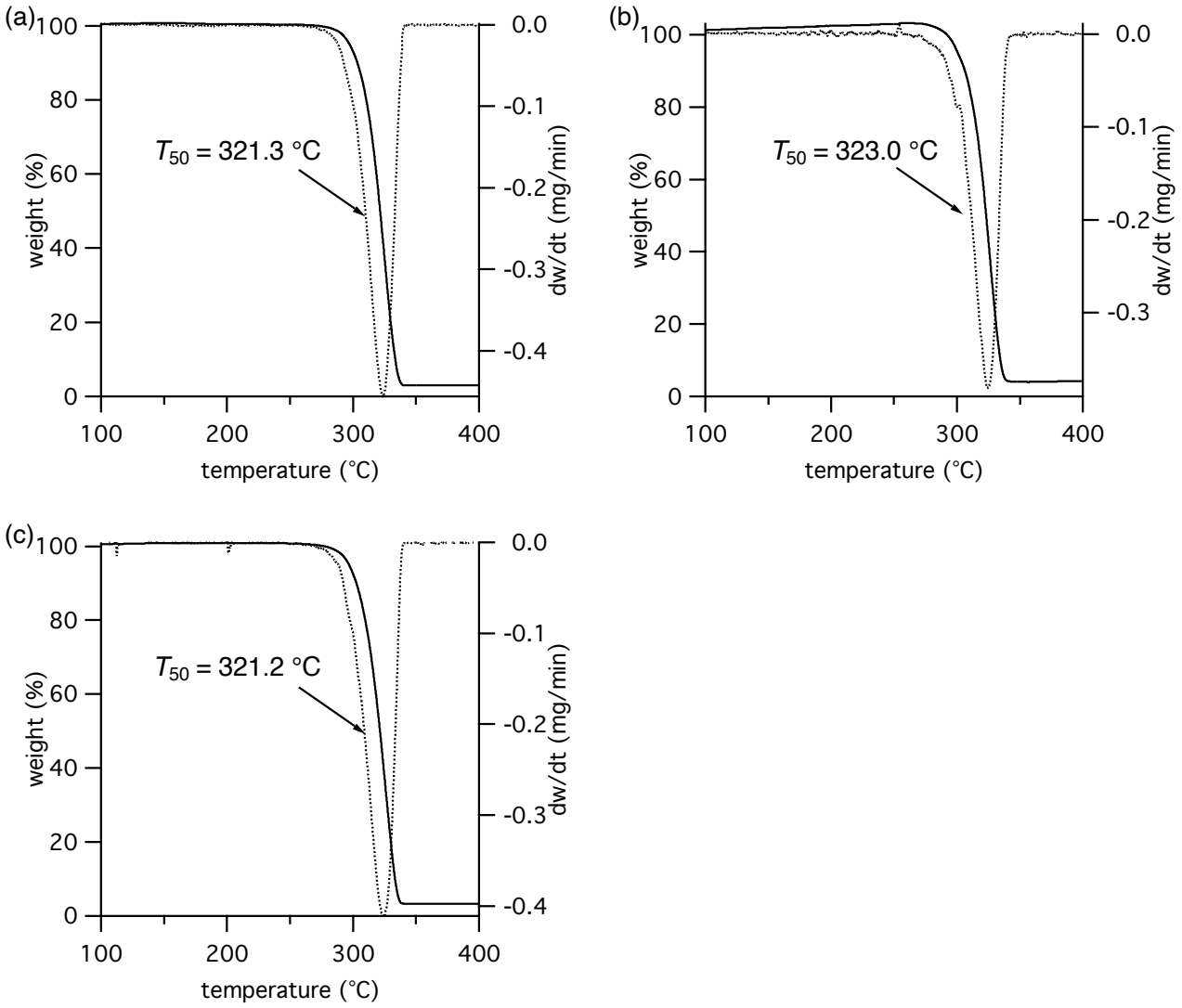


Fig. S4 TGA profiles of polycarbonates prepared from CHO, **2b**, and CO_2 with catalyst **1b**. (a) **1b**:**2b**:CHO = 1:100:100,000 (Table 2, entry 5). (b) **1b**:**2b**:CHO = 1:200:100,000 (entry 6). (c) **1b**:**2b**:CHO = 1:300:100,000 (entry 7). Heating rate was 10 °C/min.

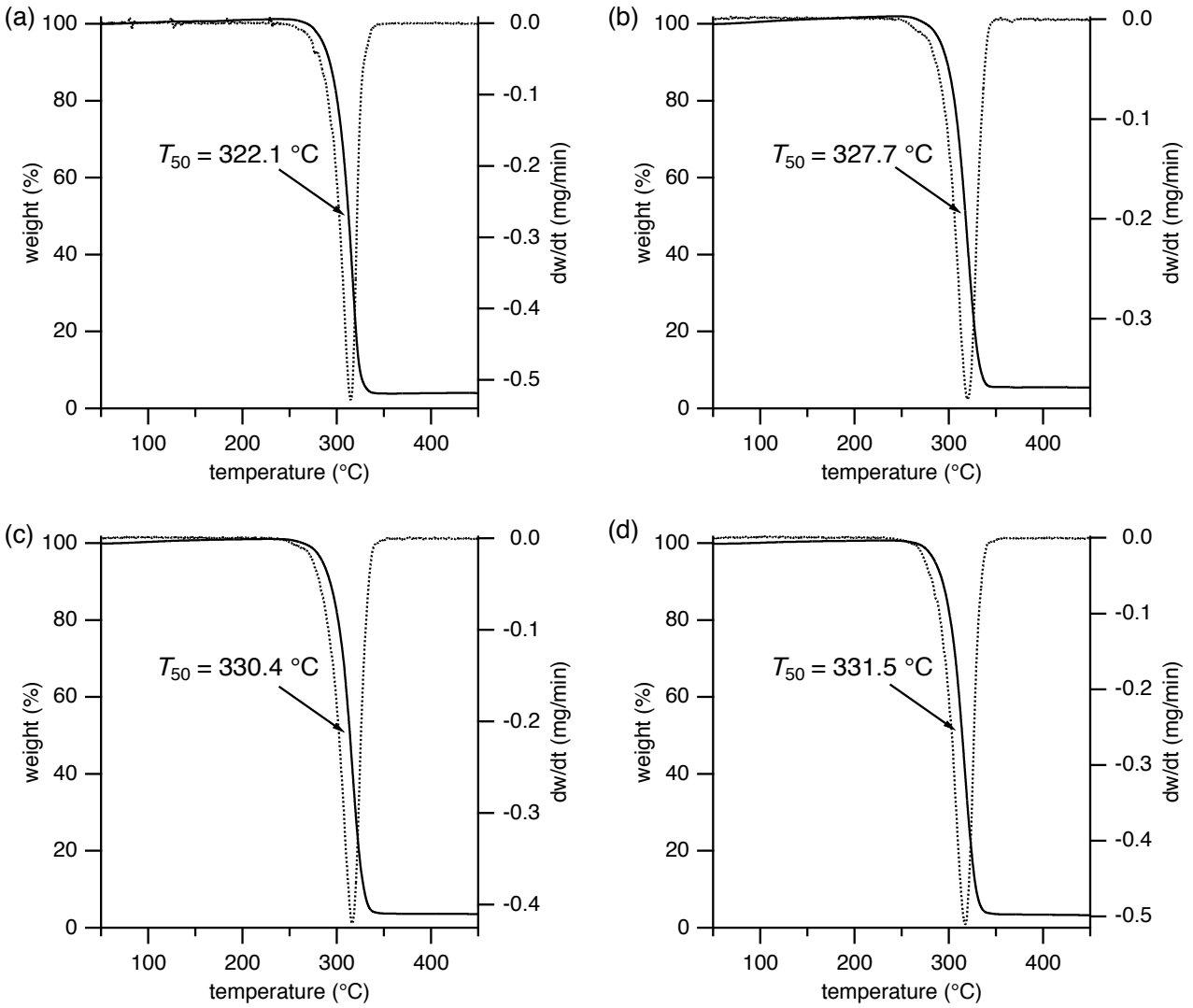


Fig. S5 TGA profiles of polycarbonates prepared from CHO, **2a**, and CO_2 with catalyst **1b**. (a) **1b**:**2a**:CHO = 1:10,000:100,000. (b) **1b**:**2a**:CHO = 1:20,000:100,000. (c) **1b**:**2a**:CHO = 1:30,000:100,000. (d) **1b**:**2a**:CHO = 1:40,000:100,000. Heating rate was 10 °C/min.

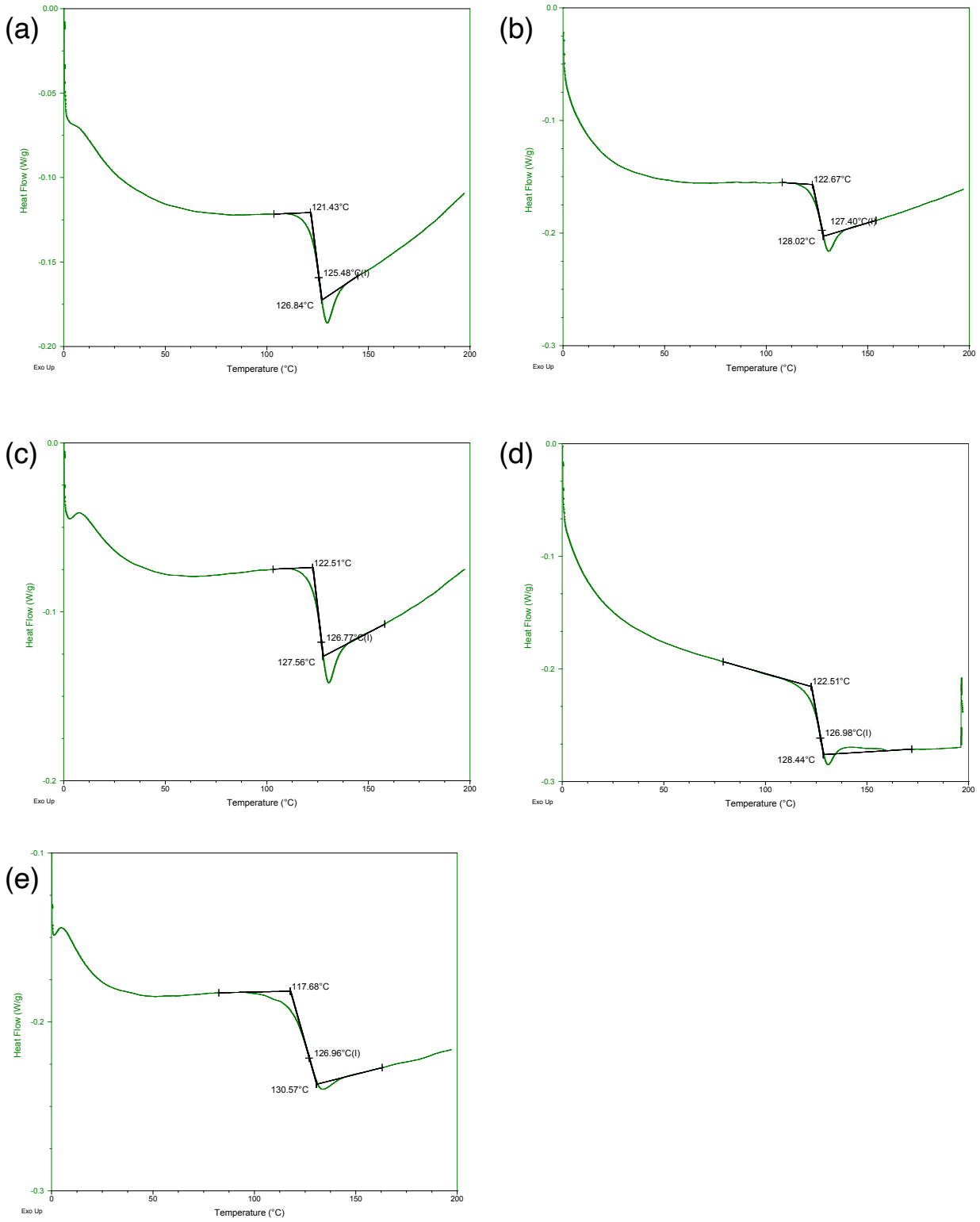


Fig. S6 DSC profiles of polycarbonates prepared from CHO, **2a**, and CO_2 with catalyst **1b**. (a) **1b**:**2a**:CHO = 1:0:100,000 (Table 2, entry 1). (b) **1b**:**2a**:CHO = 1:100:100,000 (entry 2). (c) **1b**:**2a**:CHO = 1:200:100,000 (entry 3). (d) **1b**:**2a**:CHO = 1:300:100,000 (entry 4). (e) **1b**:**2a**:CHO = 1:3,000:100,000. Heating rate was 20 °C/min.

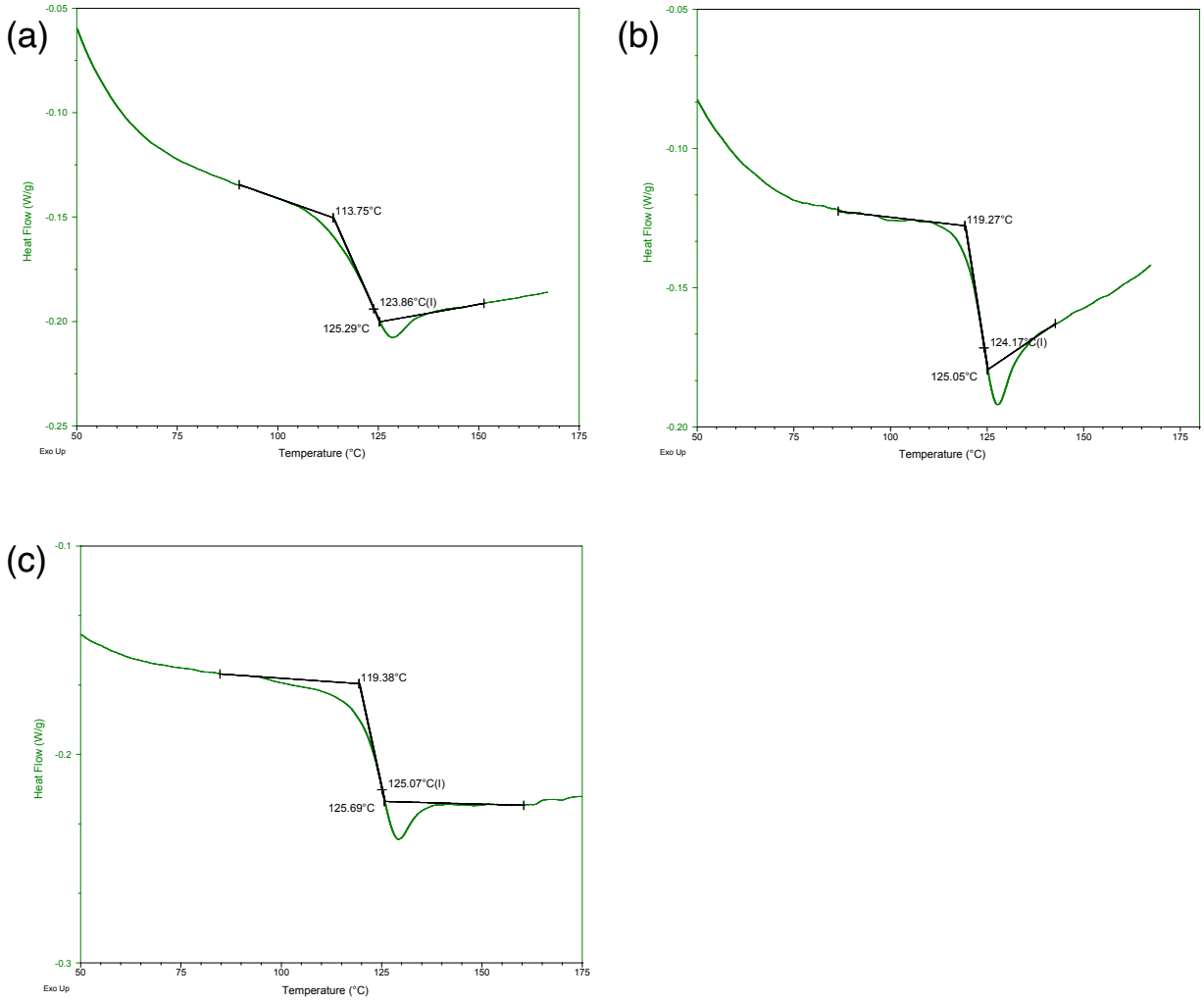


Fig. S7 DSC profiles of polycarbonates prepared from CHO, **2b**, and CO_2 with catalyst **1b**. (a) **1b**:**2b**:CHO = 1:100:100,000 (Table 2, entry 5). (b) **1b**:**2b**:CHO = 1:200:100,000 (entry 6). (c) **1b**:**2b**:CHO = 1:300:100,000 (entry 7). Heating rate was 20 °C/min.

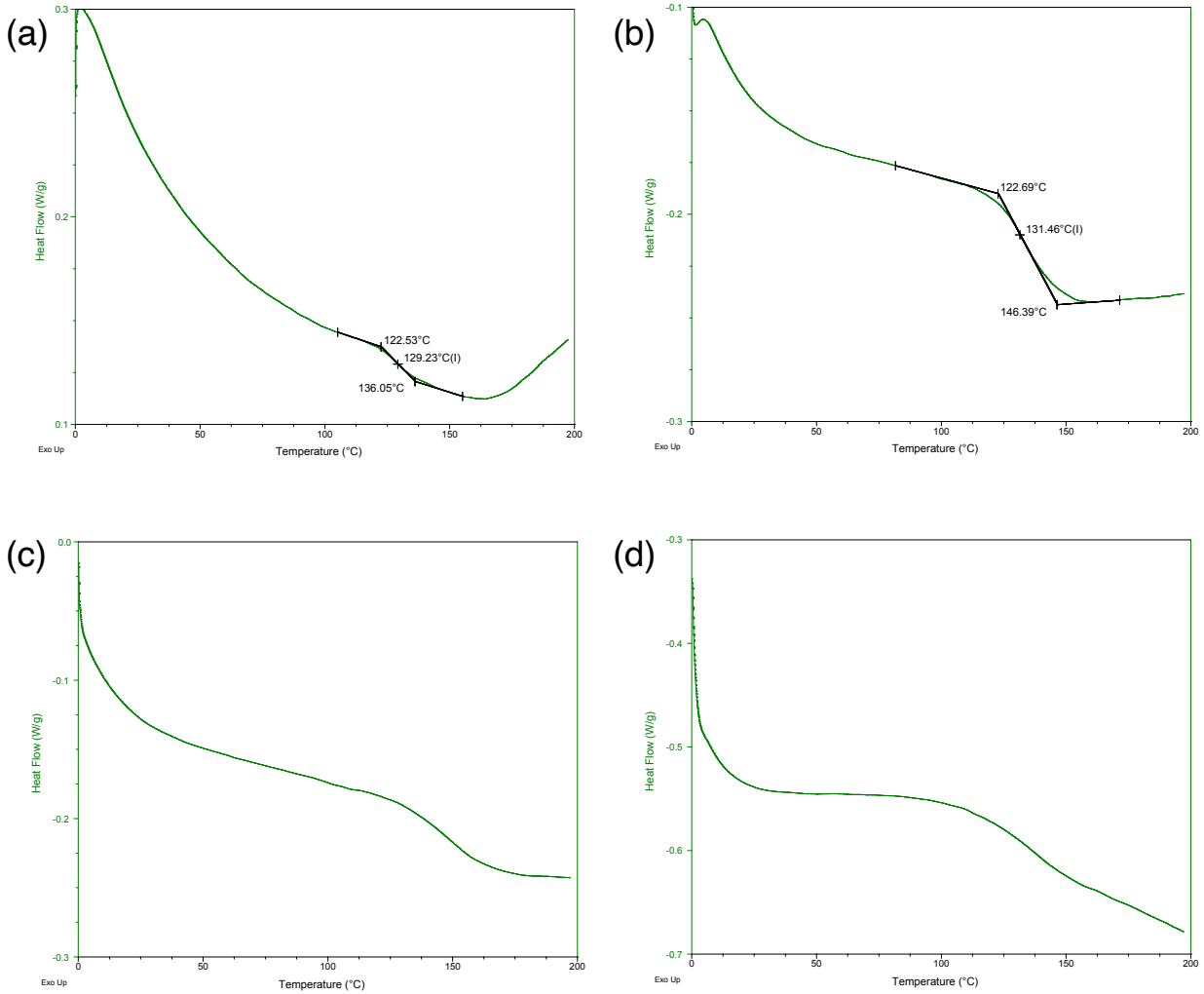


Fig. S8 DSC profiles of polycarbonates prepared from CHO, **2a**, and CO_2 with catalyst **1b**. (a) **1b**:**2a**:CHO = 1:10,000:100,000. (b) **1b**:**2a**:CHO = 1:20,000:100,000. (c) **1b**:**2a**:CHO = 1:30,000:100,000. (d) **1b**:**2a**:CHO = 1:40,000:100,000. Heating rate was 20 °C/min.

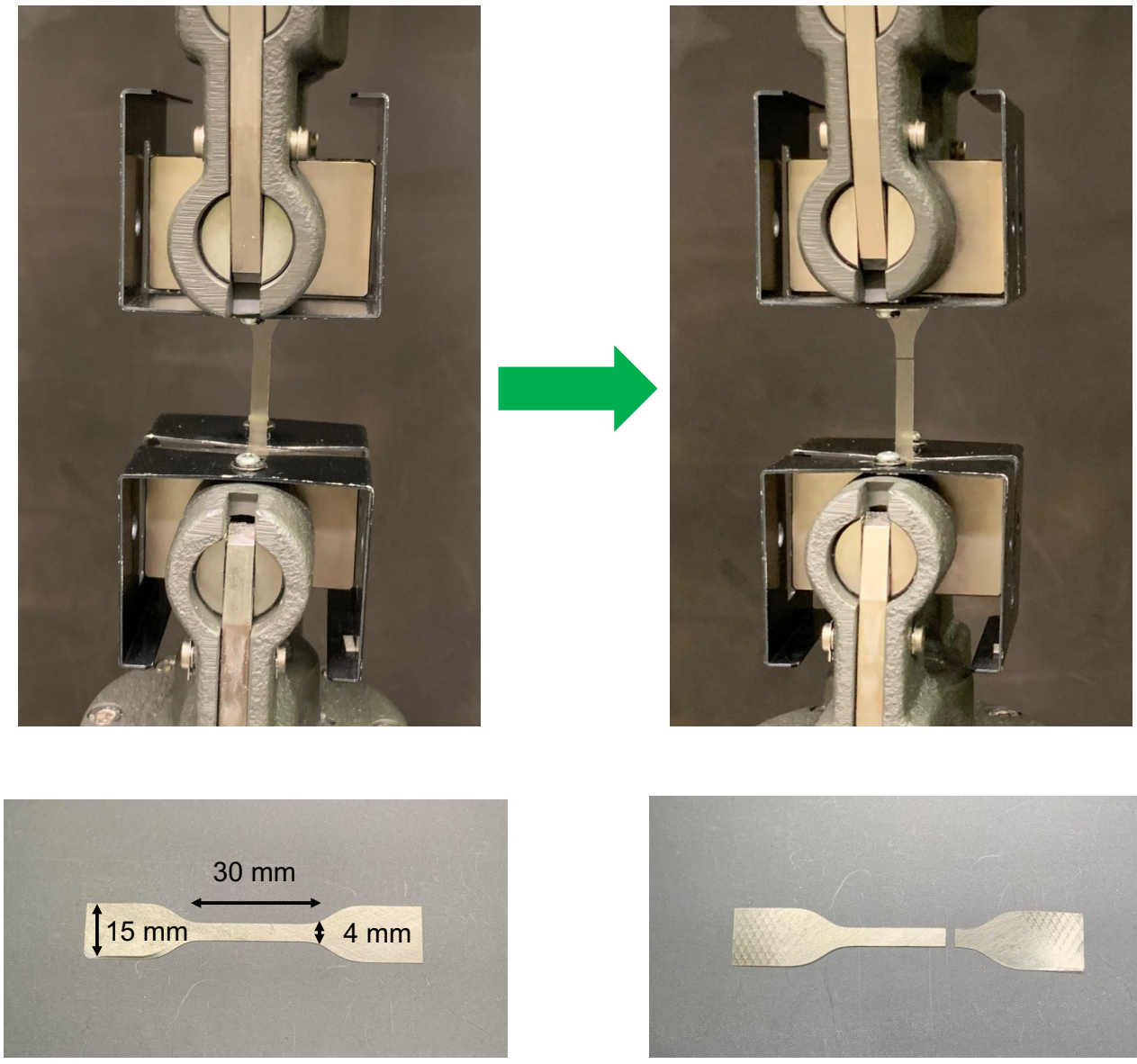


Fig. S9 Photographs of the films of CLPs (**1b**:**2a**:CHO = 1:200:100,000) in the tensile tests measured on a universal testing machine.

Polymer films were prepared by hot-pressing at 150 °C. The dog-bone-shaped specimens were obtained by die cutting. A dog-bone-shaped specimen (30 × 4 × 0.2–0.3 mm) was tested with a chuck distance of 40 mm and a strain rate of 5 mm/min at 23±1 °C. The films were confirmed to contain no solvents by measuring ^{1}H NMR spectra of the $CDCl_3$ solutions of the edges of the films.

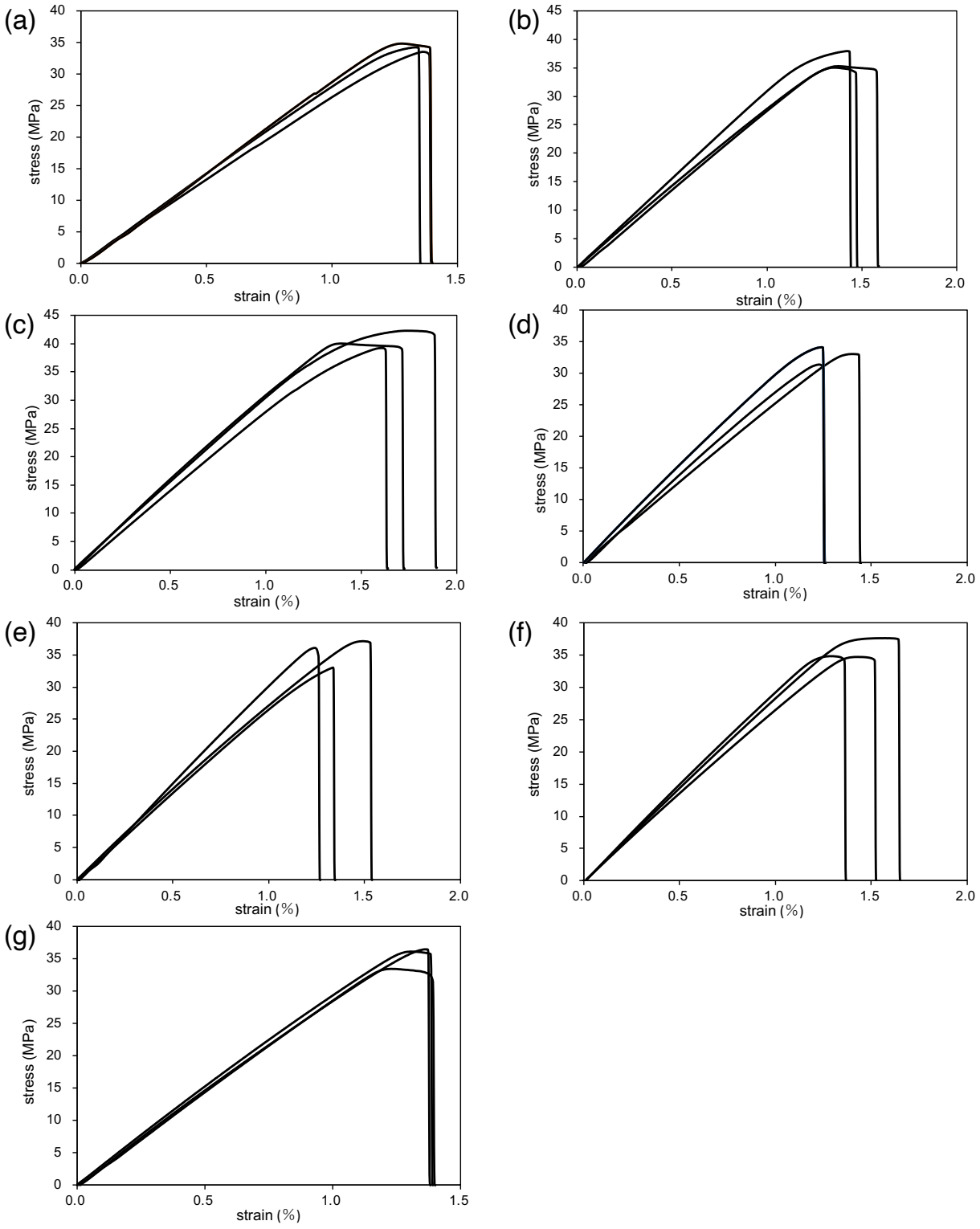
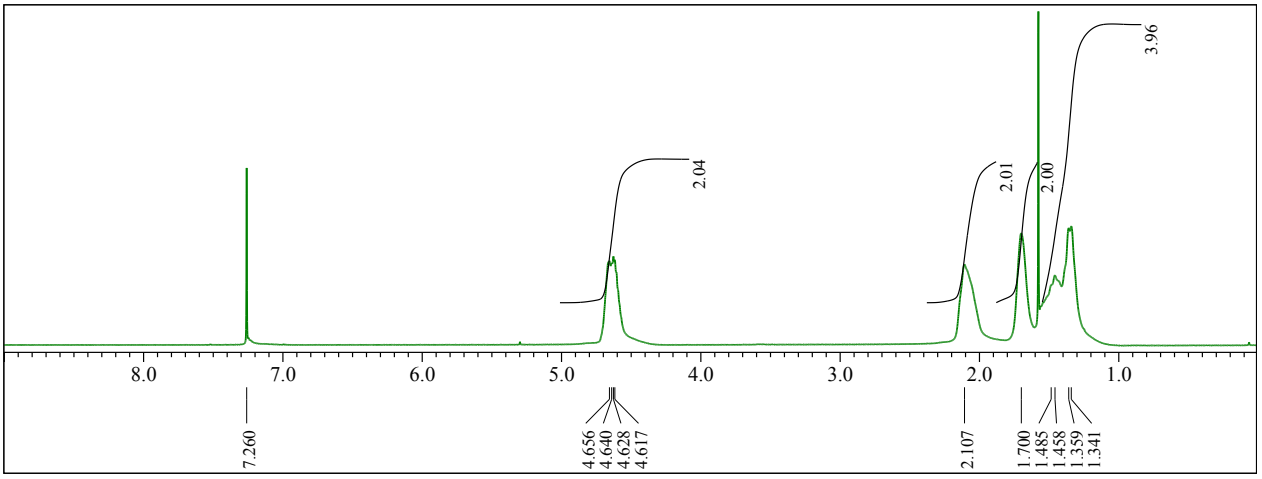
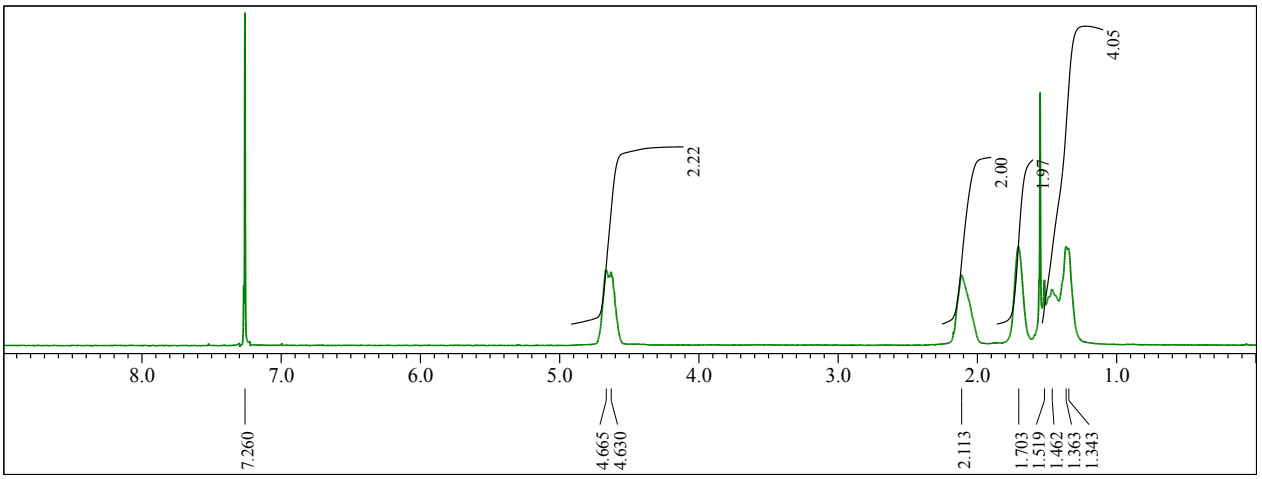


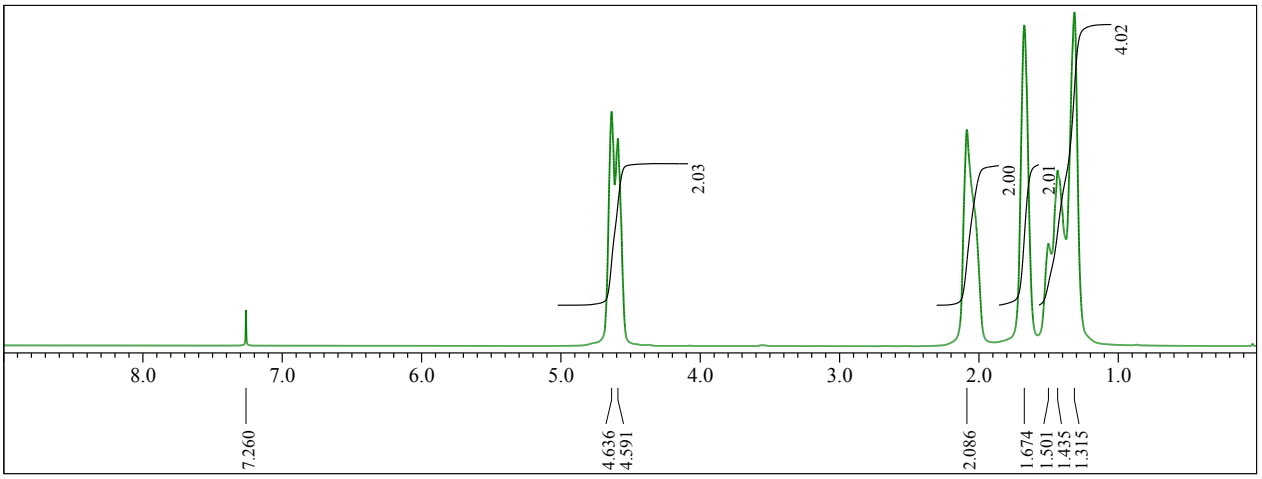
Fig. S10 Stress–strain curves for the films of the polycarbonates prepared from CHO, **2a** or **2b**, and CO_2 with catalyst **1b**. (a) **1b**:**2a**:CHO = 1:0:100,000 (Table 2, entry 1). (b) **1b**:**2a**:CHO = 1:100:100,000 (entry 2). (c) **1b**:**2a**:CHO = 1:200:100,000 (entry 3). (d) **1b**:**2a**:CHO = 1:300:100,000 (entry 4). (e) **1b**:**2b**:CHO = 1:100:100,000 (entry 5), (f) **1b**:**2b**:CHO = 1:200:100,000 (entry 6). (g) **1b**:**2b**:CHO = 1:300:100,000 (entry 7).



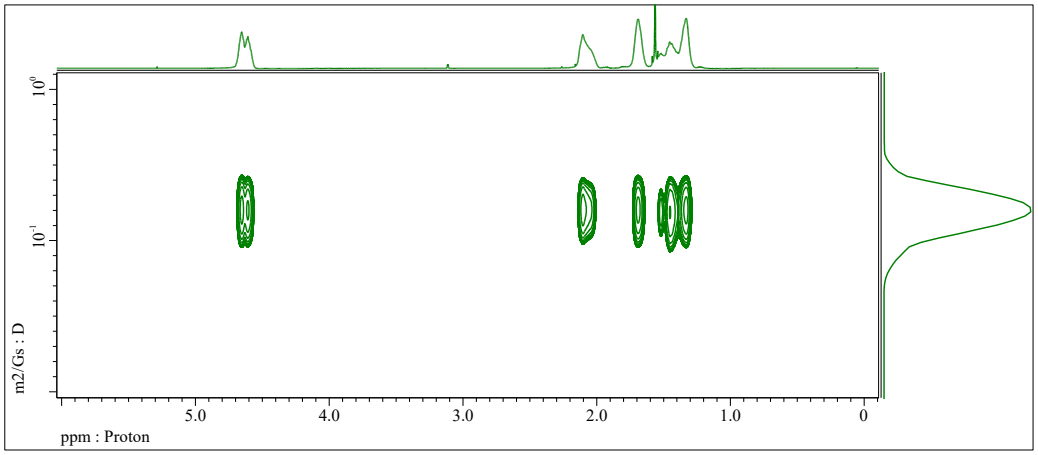
^{1}H NMR spectrum of PCHC (Table 2, entry 1) in $CDCl_3$



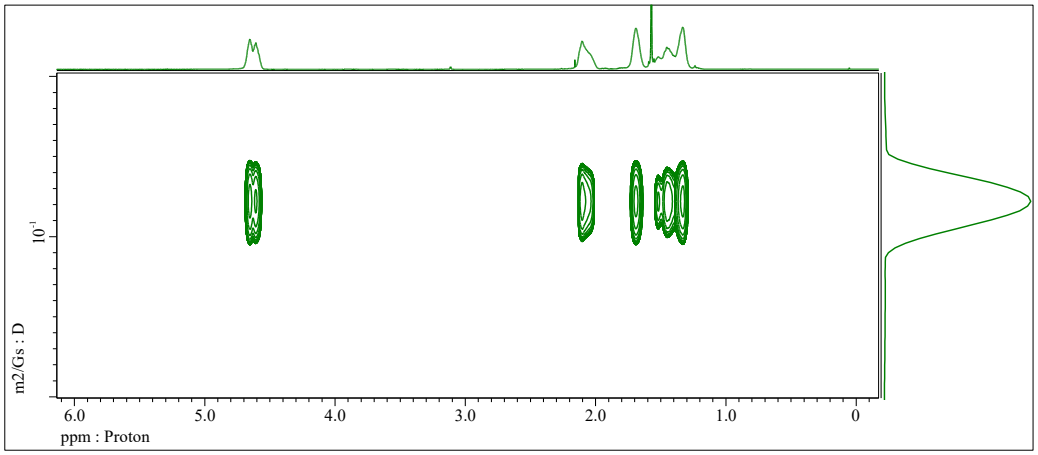
^{1}H NMR spectrum of CLP (Table 2, entry 3) in $CDCl_3$



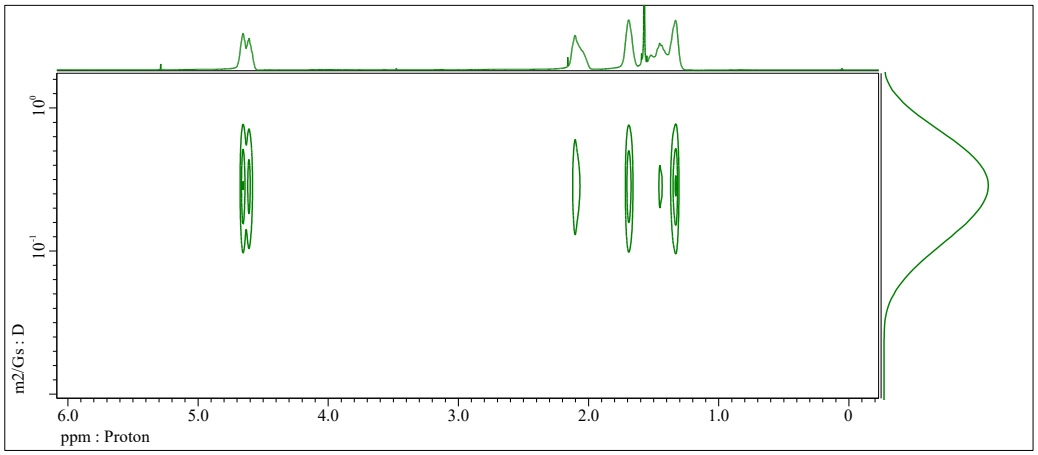
^{1}H NMR spectrum of CLP (Table 2, entry 6) in $CDCl_3$



DOSY spectrum of PCHC (Table 2, entry 1) in $CDCl_3$ ($D = 1.6 \times 10^{-6}$ [cm^2/s])



DOSY spectrum of CLP (Table 2, entry 3) in $CDCl_3$ ($D = 1.7 \times 10^{-6}$ [cm^2/s])



DOSY spectrum of CLP (Table 2, entry 6) in $CDCl_3$ ($D = 3.2 \times 10^{-6}$ [cm^2/s])

CLPs with flexible thioether links showed somewhat larger diffusion coefficient (D).

[D] Degradation of Polymers

Base-promoted hydrolysis: To a solution of polymer samples (15 mg) in THF (1 mL) was added aqueous 2 M KOH (0.2 mL), and the mixture was stirred at 50 °C for 24 h under N_2. The mixture was neutralized with aqueous 1 M HCl, and organic compounds were extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4, evaporated, and monitored by SEC.

Photodegradation: A solution of polymer samples (30 mg) in THF (1 mL) was irradiated by a high-pressure mercury lamp (ASAHI SPECTRA REX-250) in the range of λ = 248–436 nm at rt under N_2, and the reaction progress was monitored by SEC.

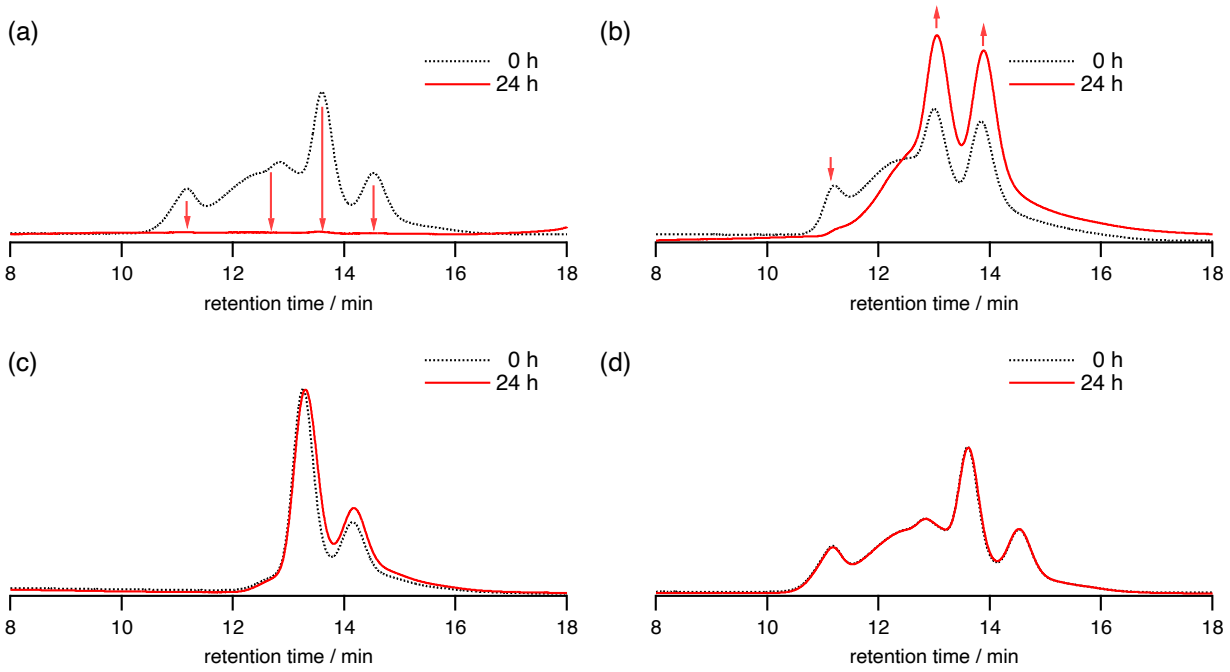
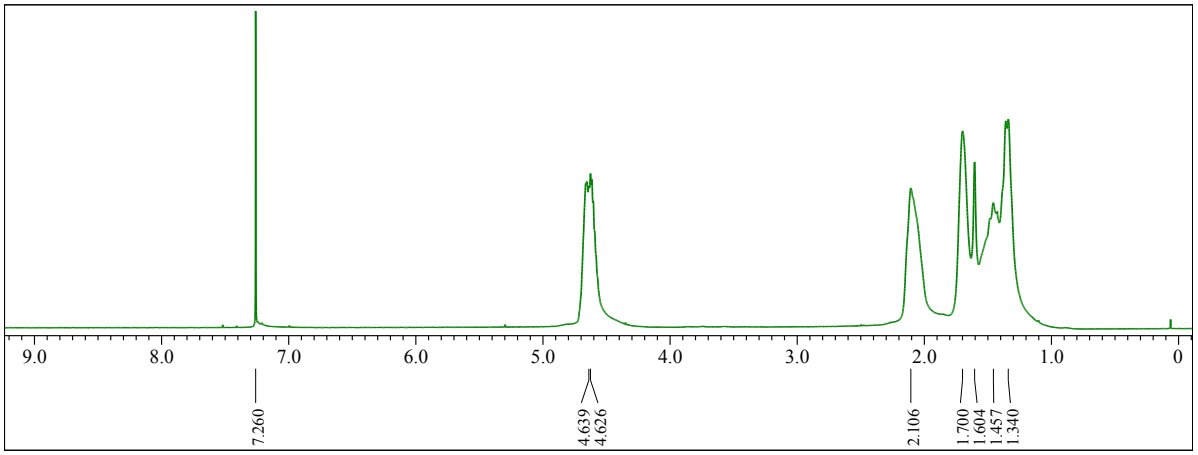
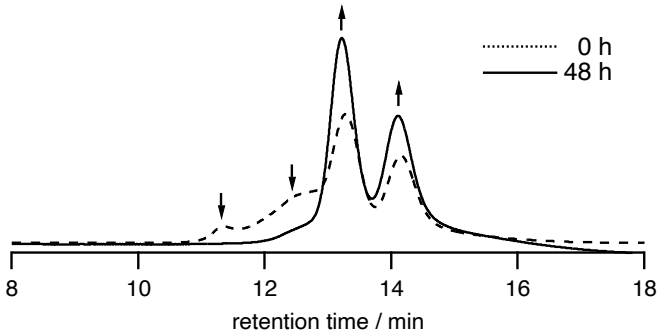


Fig. S11 (a) SEC chart of CLPs (Table 2, entry 3) after the base-promoted hydrolysis. (b) SEC chart of CLPs (Table 2, entry 6) after the photoirradiation. (c) SEC chart of PCHC (Table 2, entry 1) after the photoirradiation. (d) SEC chart of CLPs (Table 2, entry 3) after the photoirradiation.

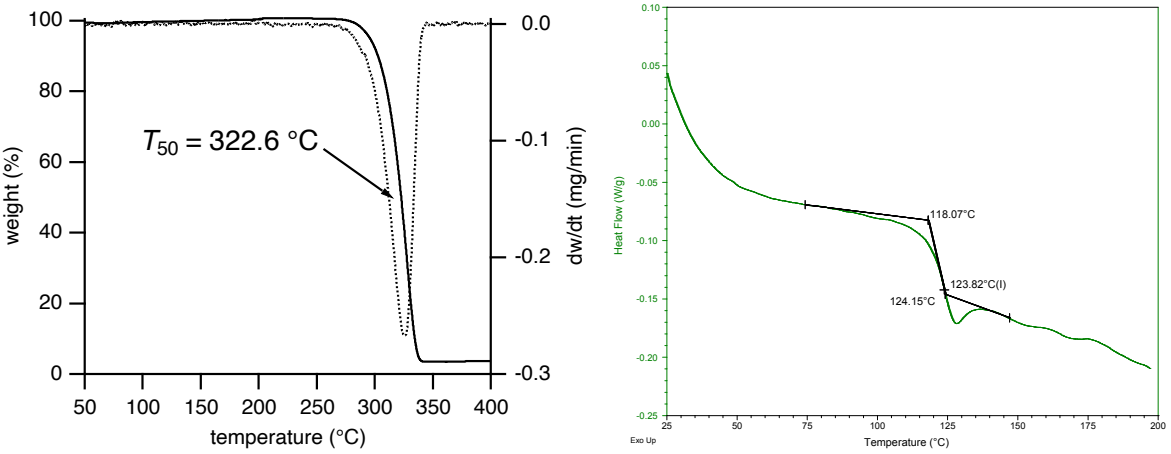
Photodegradation (batch scale): A solution of polymer samples (1.44 g) in THF (100 mL) was irradiated by a high-pressure mercury lamp (ASAHI SPECTRA REX-250) at rt for 48 h under N_2. After the solvent was evaporated, reprecipitation of the residue from CH_2Cl_2/MeOH gave linear PCHC (1.39 g) as confirmed by NMR and SEC analysis. The resultant polymers showed the T_{50} of 323 °C and T_g of 124 °C, which are typical values for linear PCHCs.



^{1}H NMR spectrum of CLPs (Table 2, entry 6) after the photoirradiation in $CDCl_3$



SEC chart of CLPs before and after the photoirradiation.



TGA (left) and DSC (right) profiles of CLPs (Table 2, entry 6) after the photoirradiation.

Photodegradation of model compound for the identification of the bond-cleavage site

We performed the UV irradiation of model compound **5**, and the reaction mixture was analyzed by ESI-MS spectrometry. As a result, peaks for alcohol and thiol compounds were detected as shown below. This model experiment strongly suggests that the photocleavage sites in the CLPs prepared from **2b** are the cross-linking C–S bonds. The alcohol and thiol compounds are considered to be produced via thiyl radicals and alkyl radicals generated by the homolytic cleavage of the C–S bonds as reported in the literature (S. M. Bonesi, M. Fagnoni, D. Dondi and A. Albini, *Inorg. Chim. Acta*, 2007, **360**, 1230–1234).

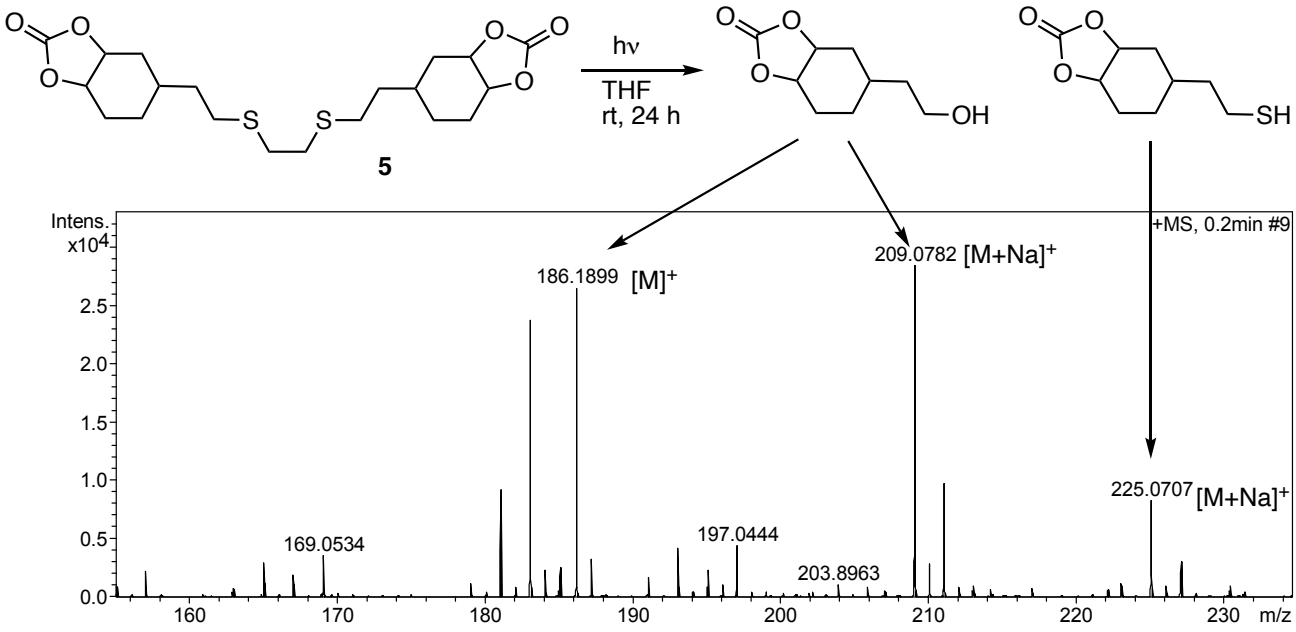
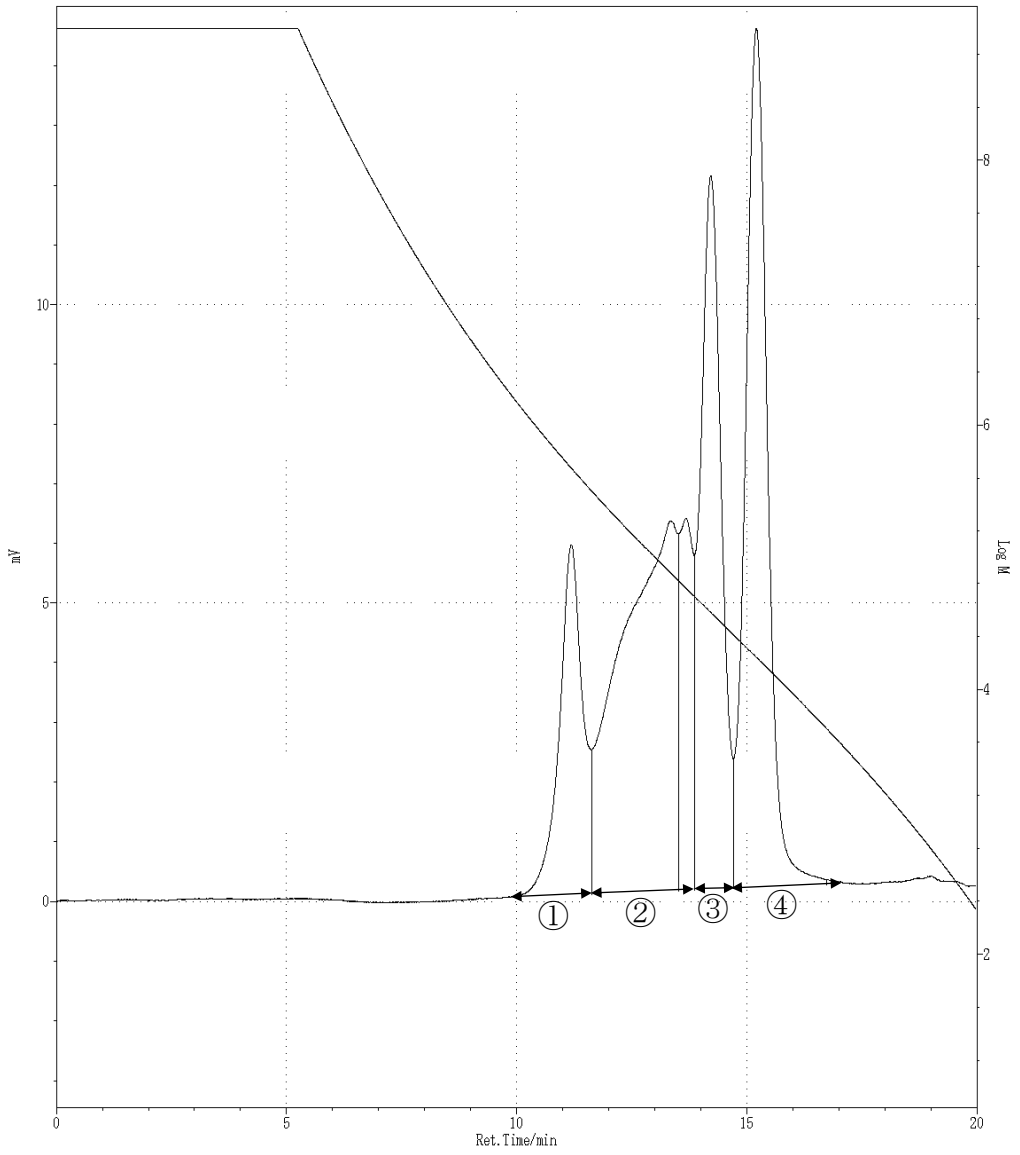


Fig. S12 ESI-MS spectrum of the reaction mixture

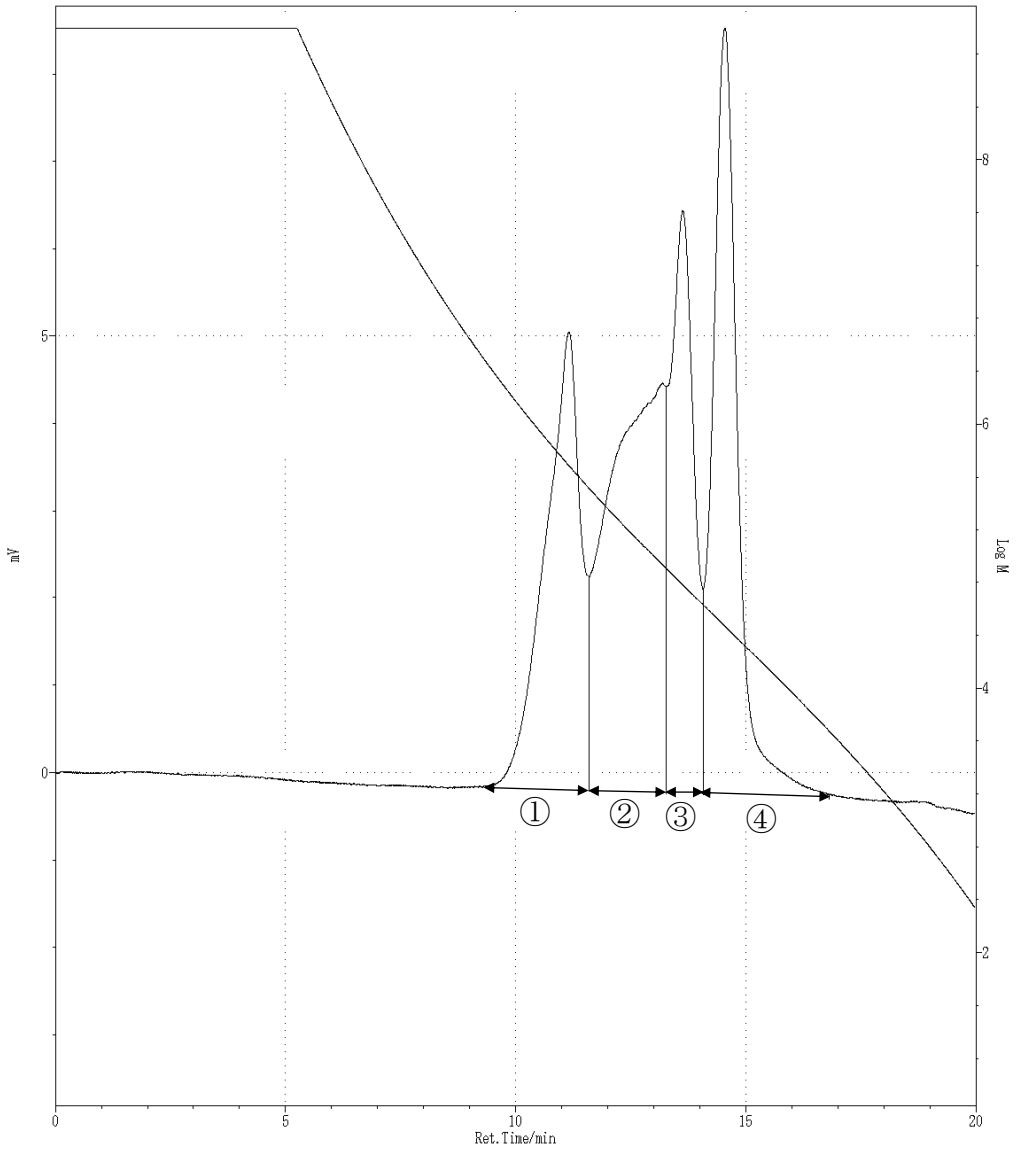
[E] SEC Charts

Table 1, entry 1 (**1a**:**2a**:CHO = 1:400:100,000)



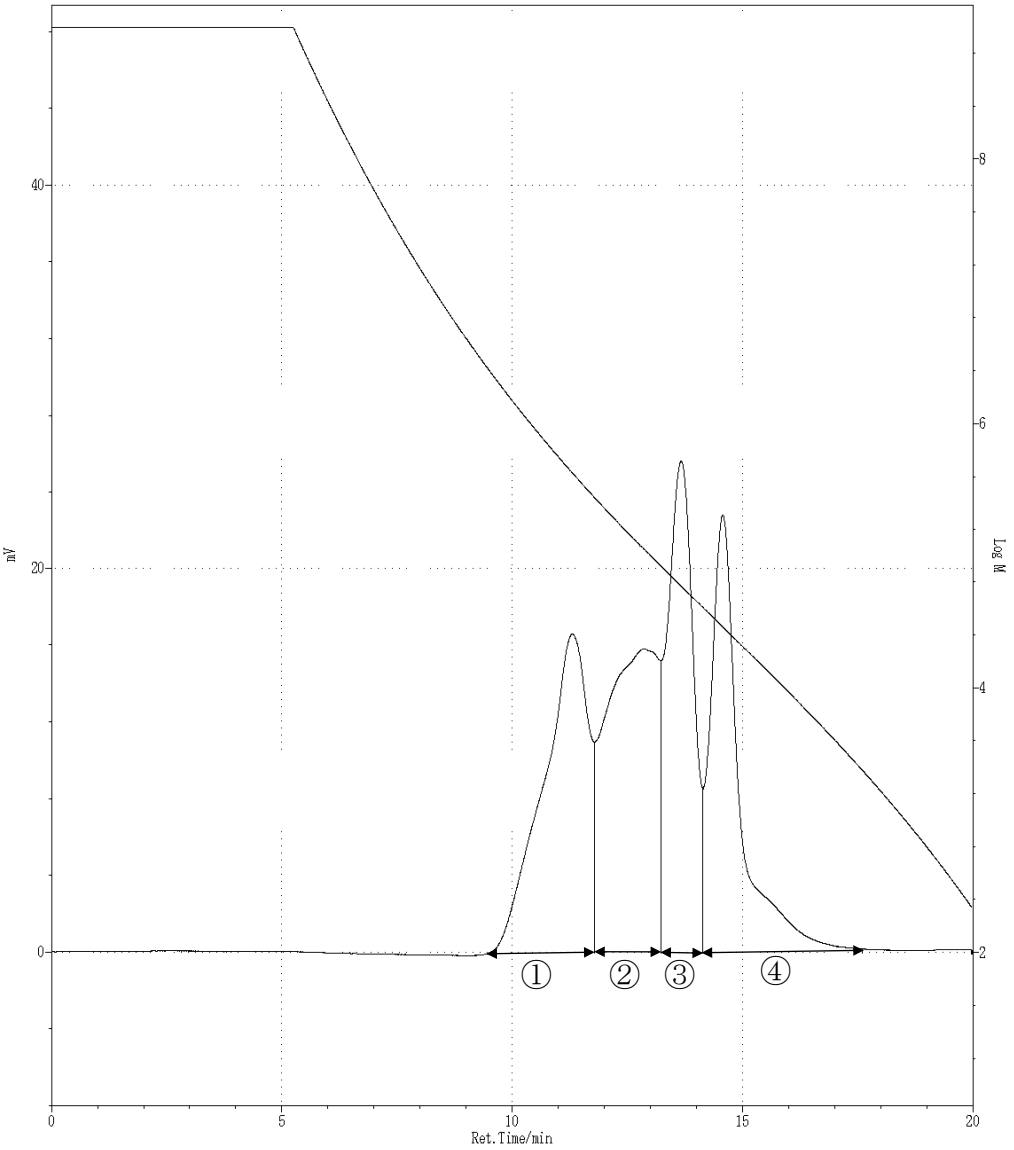
	M_n [kg/mol]	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	476	507	1.06
②	98	126	1.28
③	37	38	1.02
④	16	17	1.05
①+②+③+④	37	122	3.33

Table 1, entry 2 (**1b**:**2a**:CHO = 1:400:100,000)



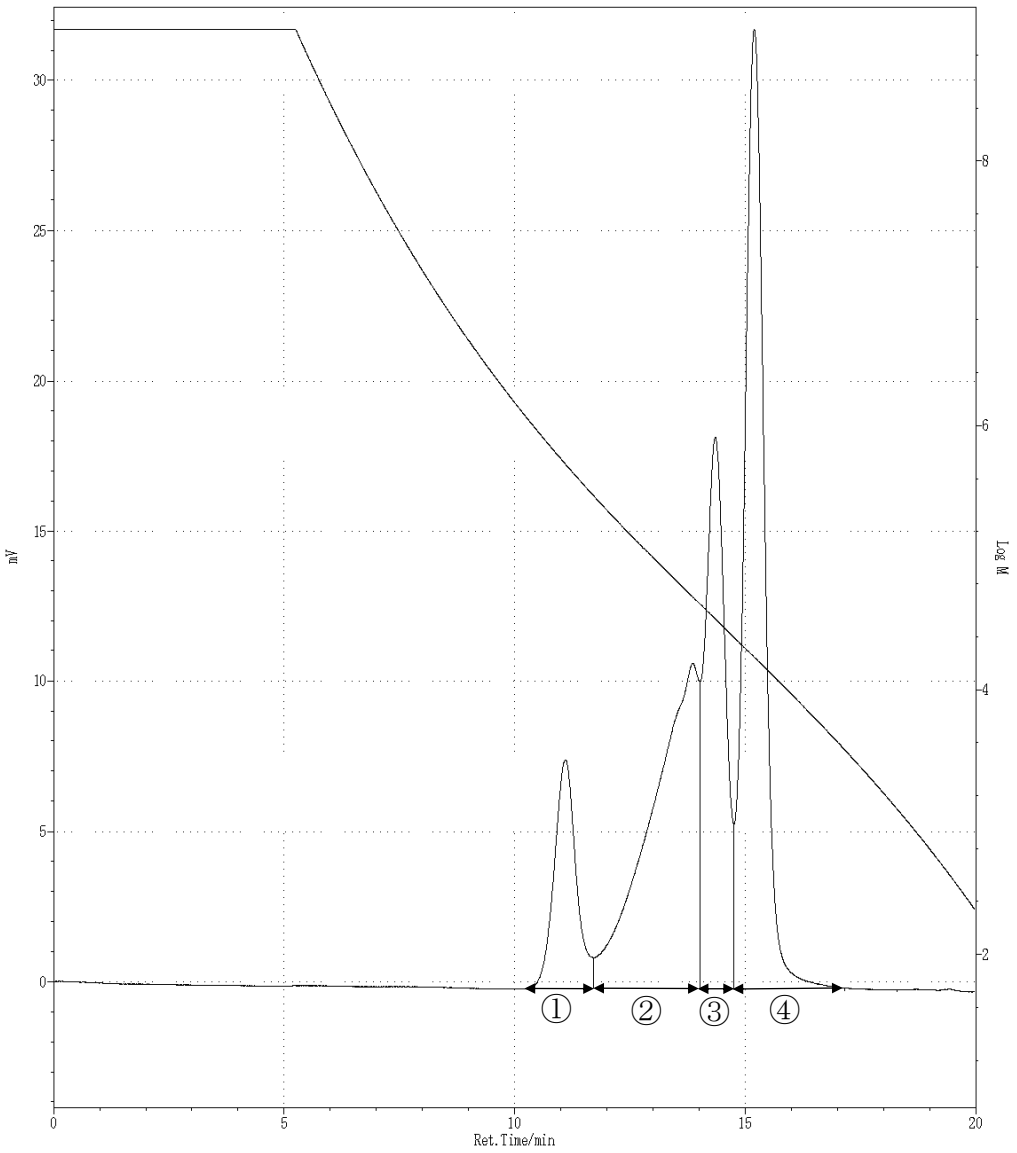
	M_n	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	558	647	1.16
②	138	158	1.16
③	58	59	1.03
④	25	28	1.12
①+②+③+④	61	219	3.62

Table 1, entry 3 (**1c**:**2a**:CHO = 1:400:100,000)



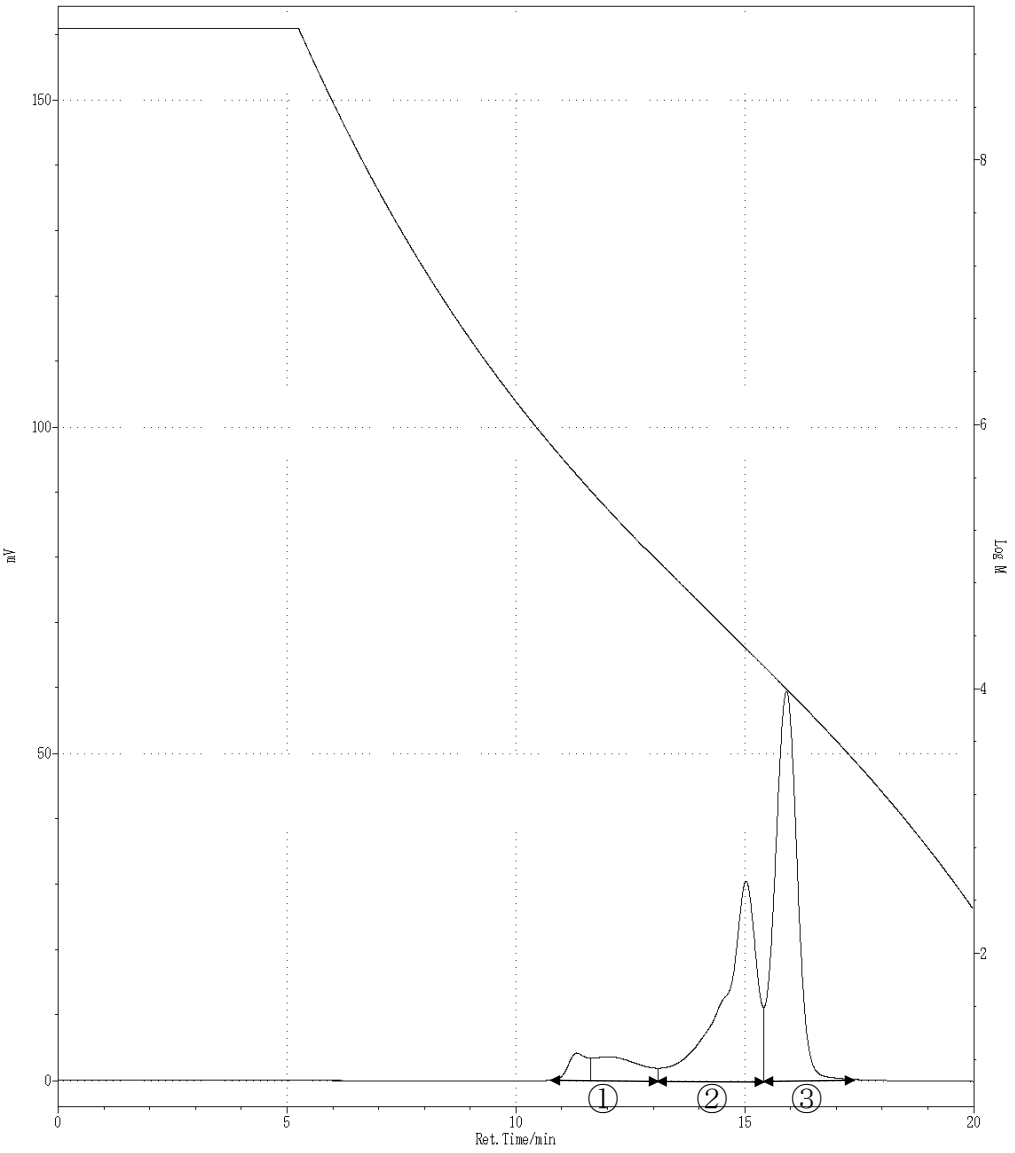
	M_n [kg/mol]	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	498	610	1.22
②	138	155	1.12
③	58	60	1.03
④	21	26	1.20
①+②+③+④	58	222	3.82

Table 1, entry 4 (**1d**:**2a**:CHO = 1:400:100,000)



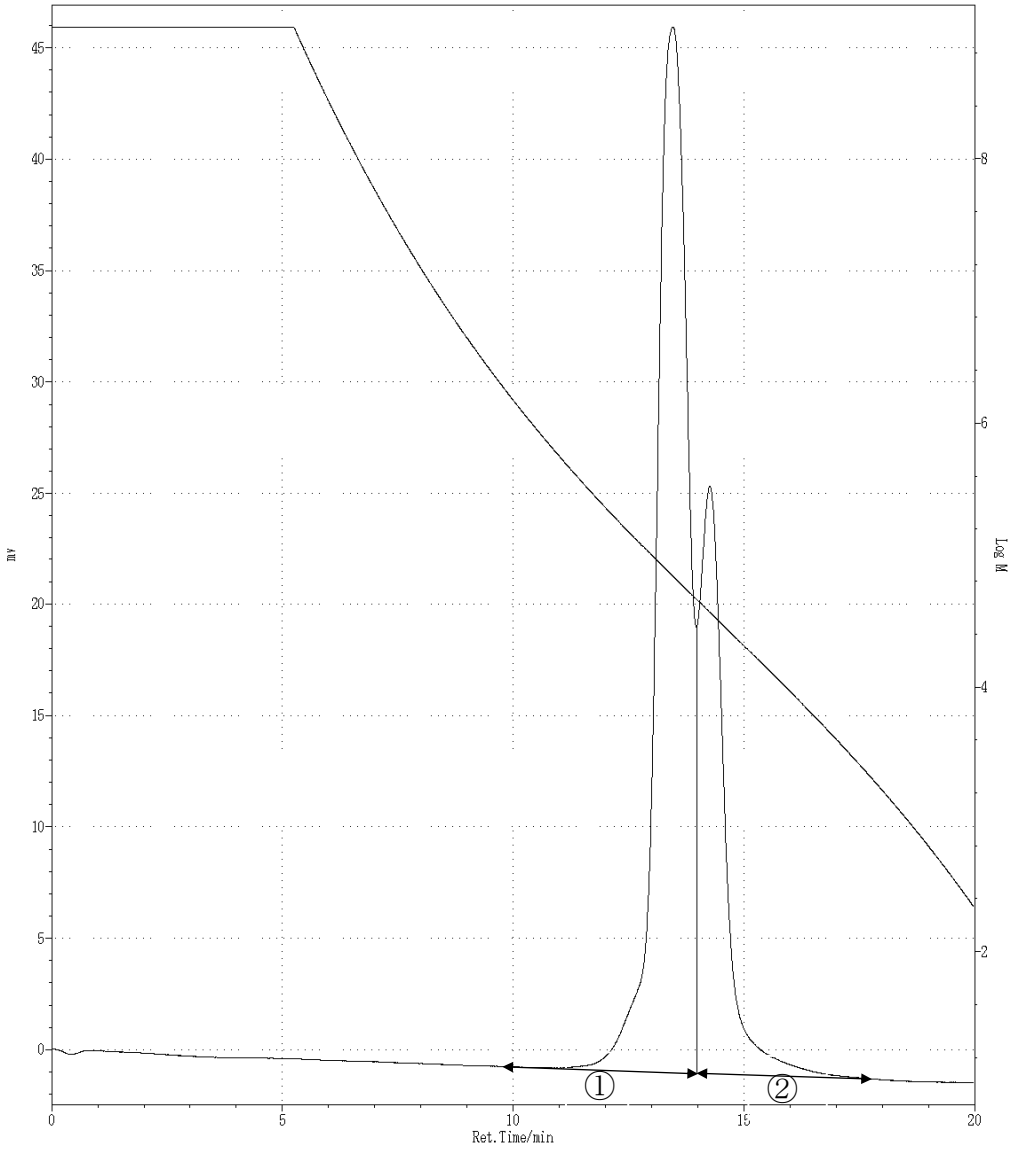
	M_n [kg/mol]	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	496	521	1.05
②	75	91	1.21
③	34	34	1.02
④	17	17	1.05
①+②+③+④	30	93	3.13

Table 1, entry 5 (**1e**:**2a**:CHO = 1:400:100,000)



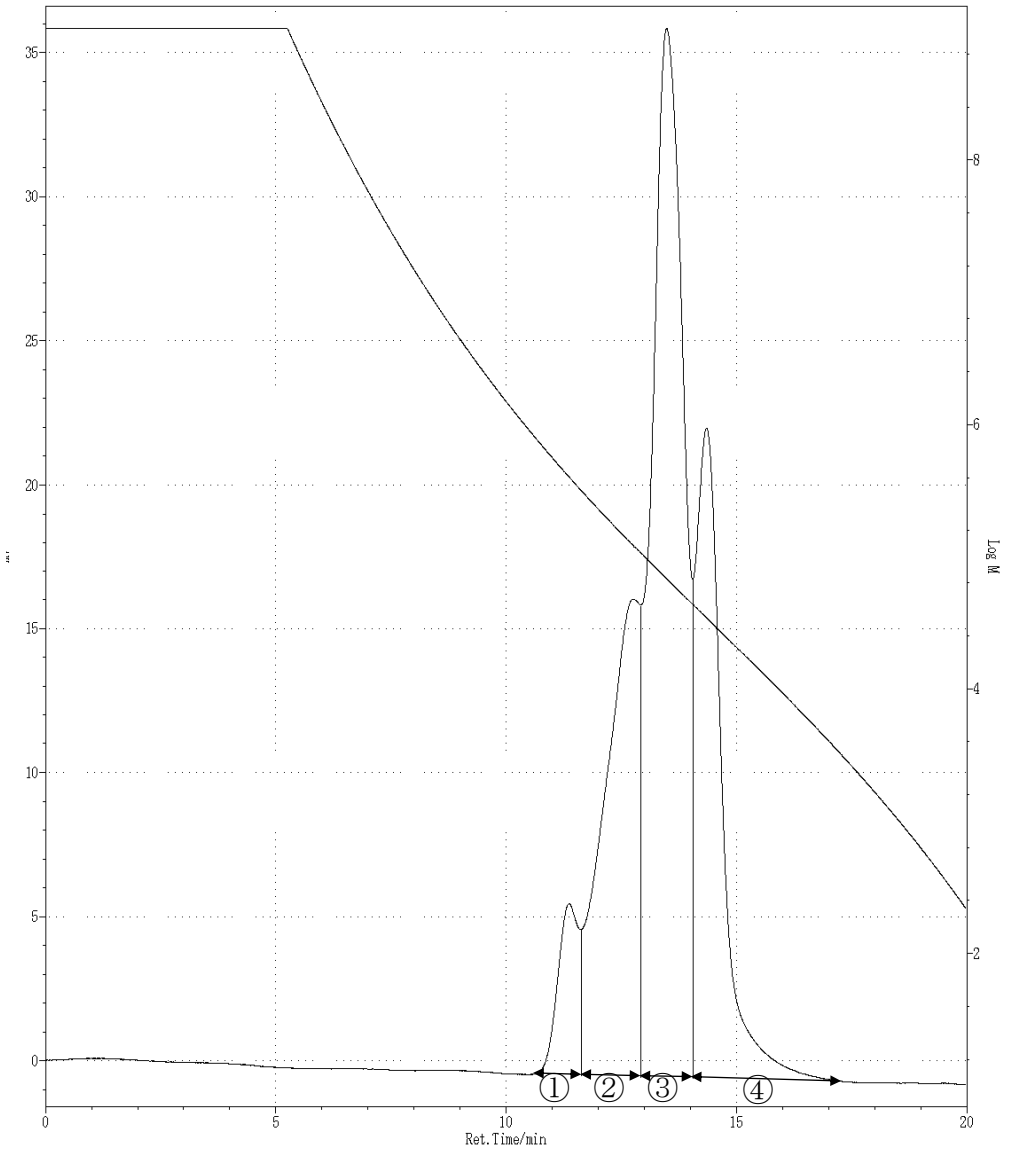
	M_n [kg/mol]	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	208	262	1.26
②	24	28	1.17
③	9.6	10	1.04
①+②+③	14	42	2.97

Table 2, entry 1 (**1b**:**2a**:CHO = 1:0:100,000)



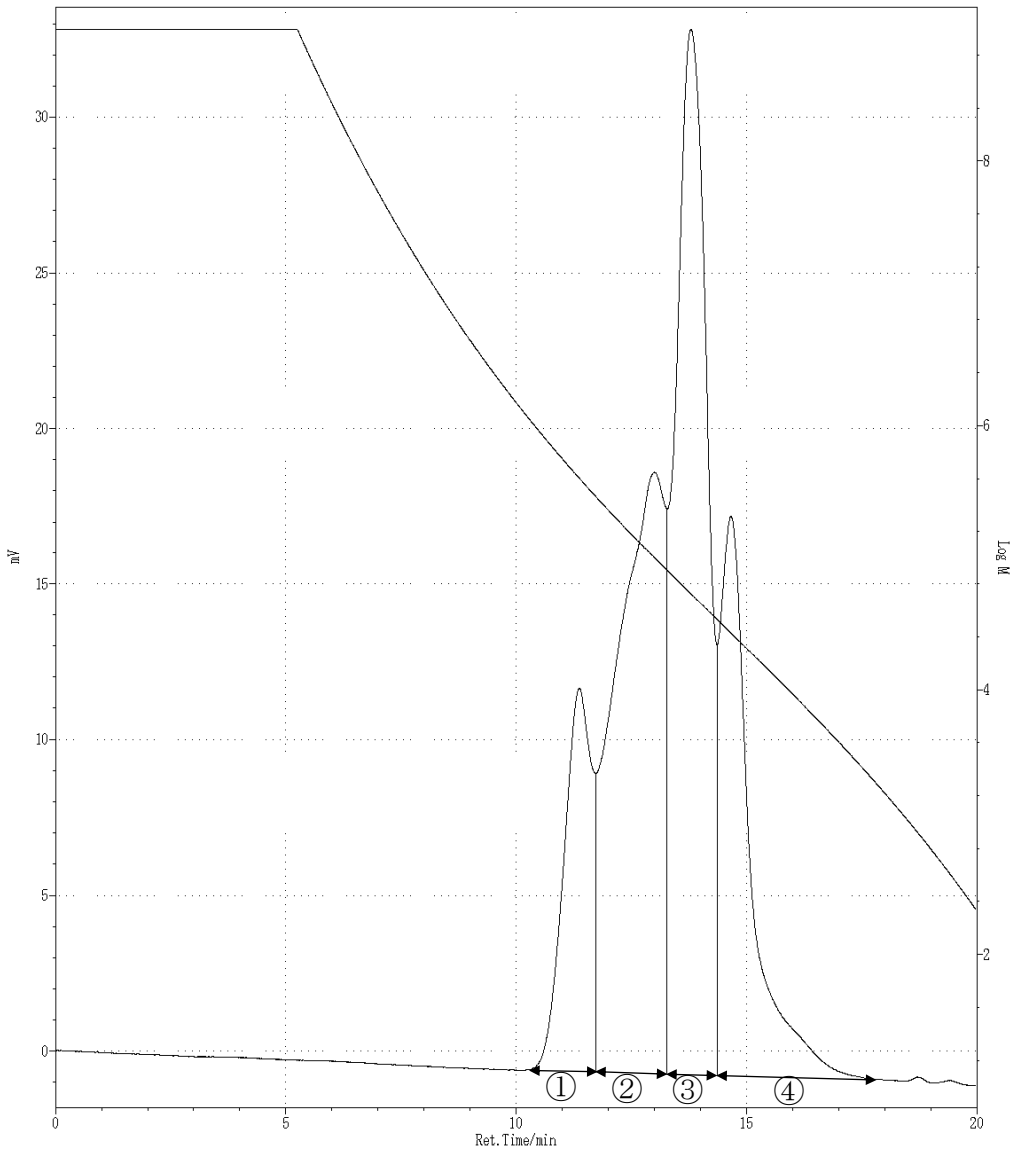
	M_n [kg/mol]	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	67	73	1.09
②	29	33	1.15
①+②	49	62	1.28

Table 2, entry 2 (**1b**:**2a**:CHO = 1:100:100,000)



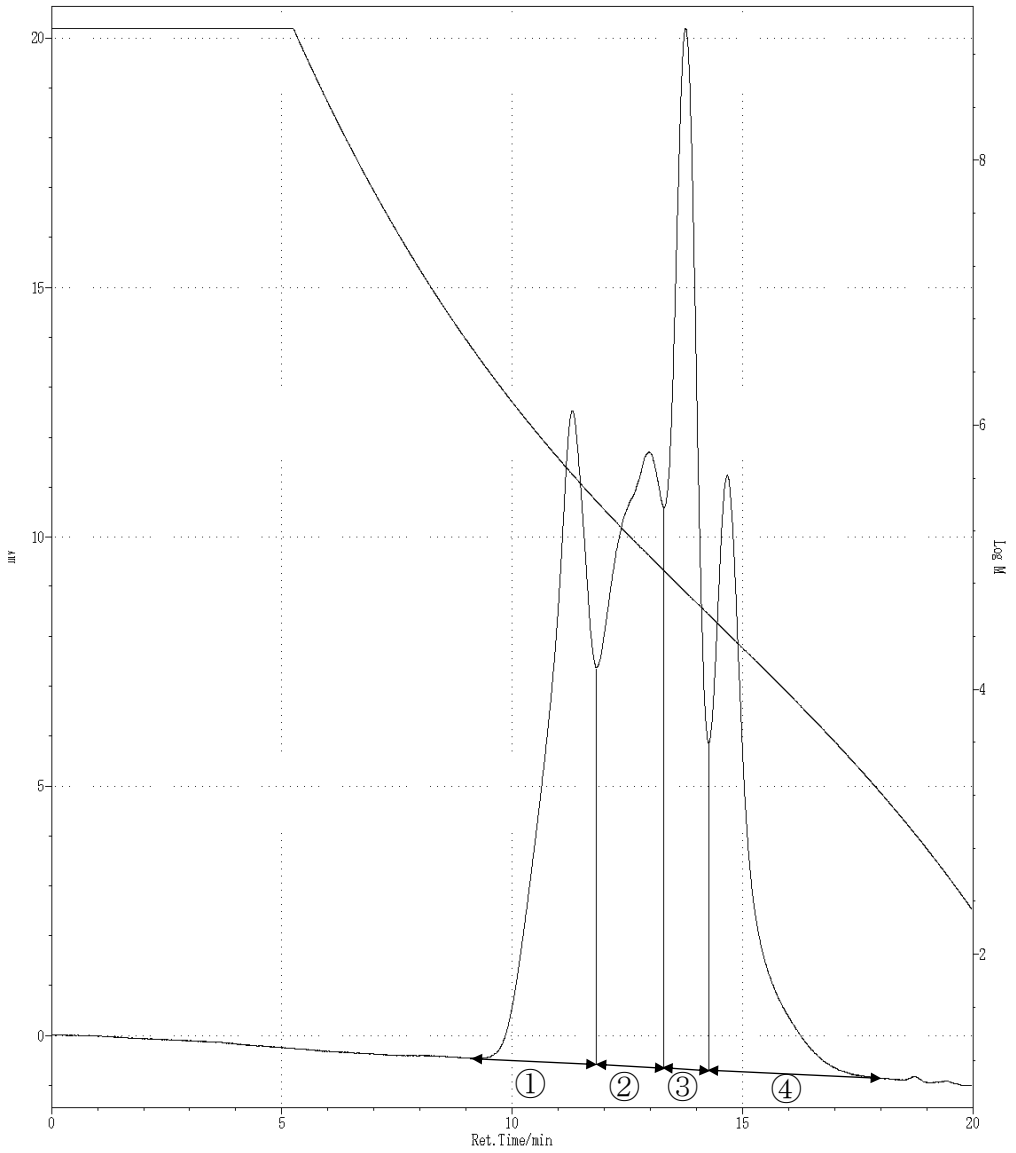
	M_n [kg/mol]	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	381	398	1.04
②	148	163	1.10
③	64	68	1.06
④	28	31	1.13
①+②+③+④	57	101	1.79

Table 2, entry 3 (**1b**:**2a**:CHO = 1:200:100,000)



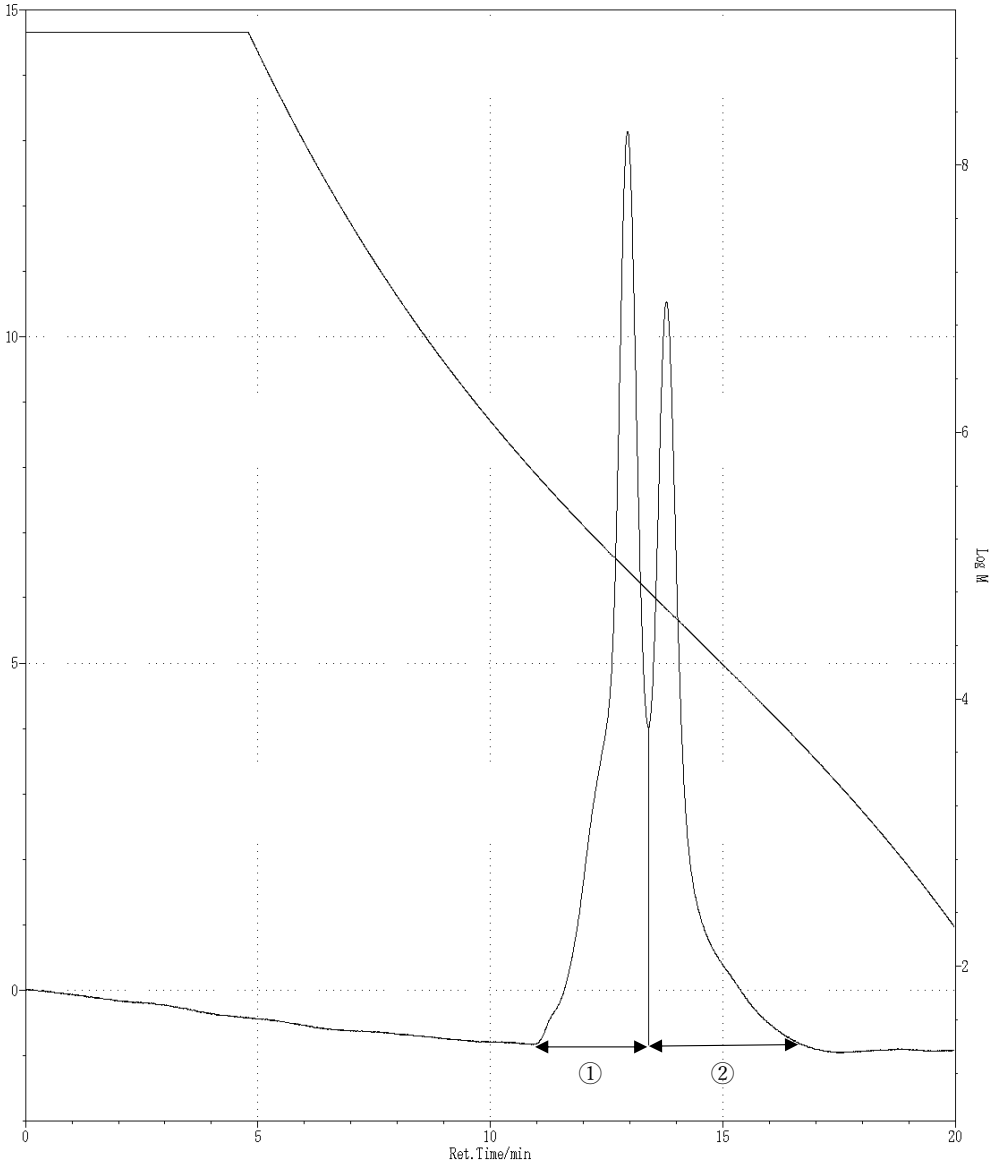
	M_n [kg/mol]	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	399	426	1.07
②	129	147	1.14
③	49	51	1.06
④	19	23	1.21
①+②+③+④	50	125	2.49

Table 2, entry 4 (**1b**:**2a**:CHO = 1:300:100,000)



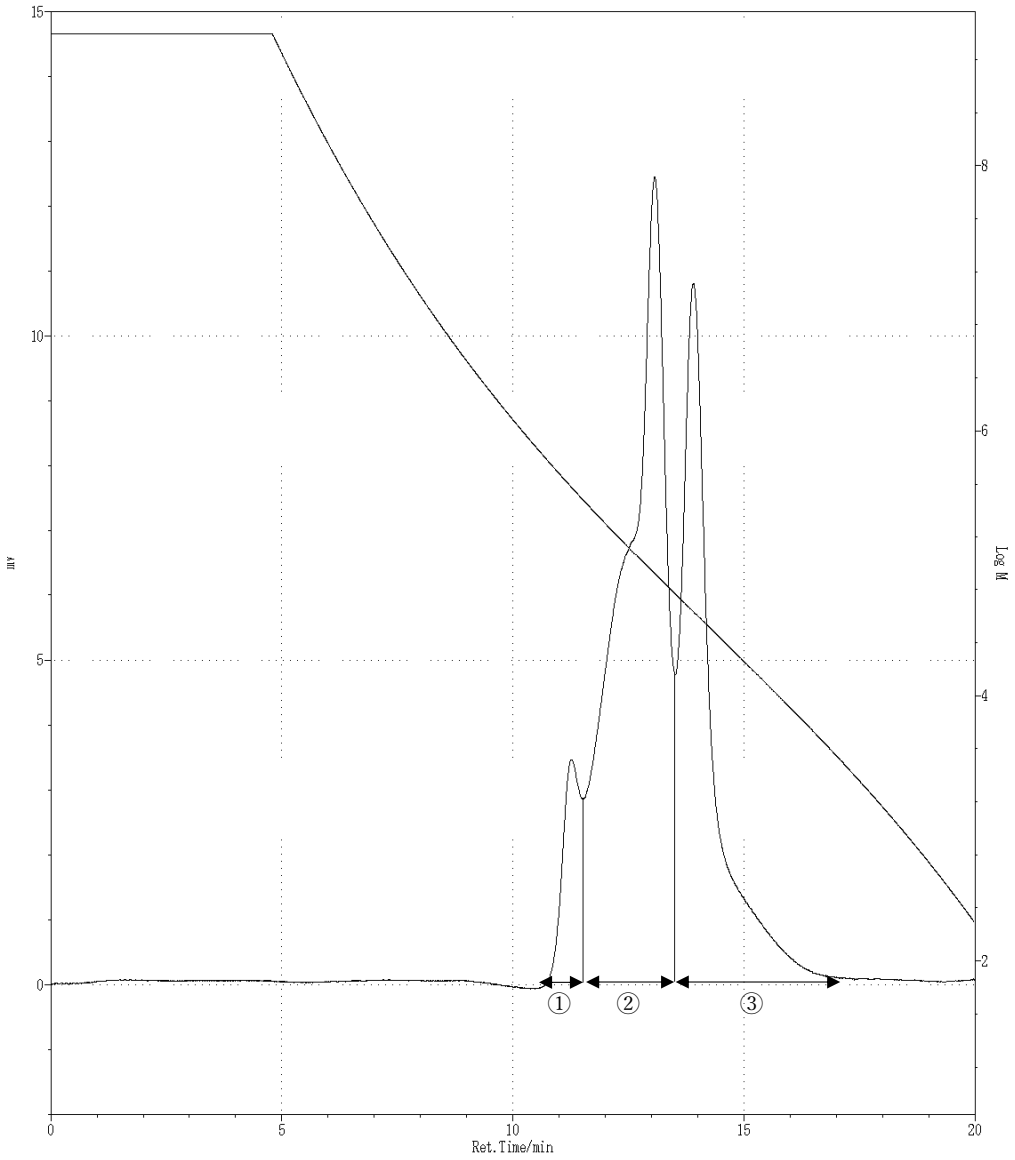
	M_n [kg/mol]	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	424	524	1.24
②	120	137	1.14
③	53	55	1.04
④	19	23	1.21
①+②+③+④	57	206	3.60

Table 2, entry 5 (**1b**:**2b**:CHO = 1:100:100,000)



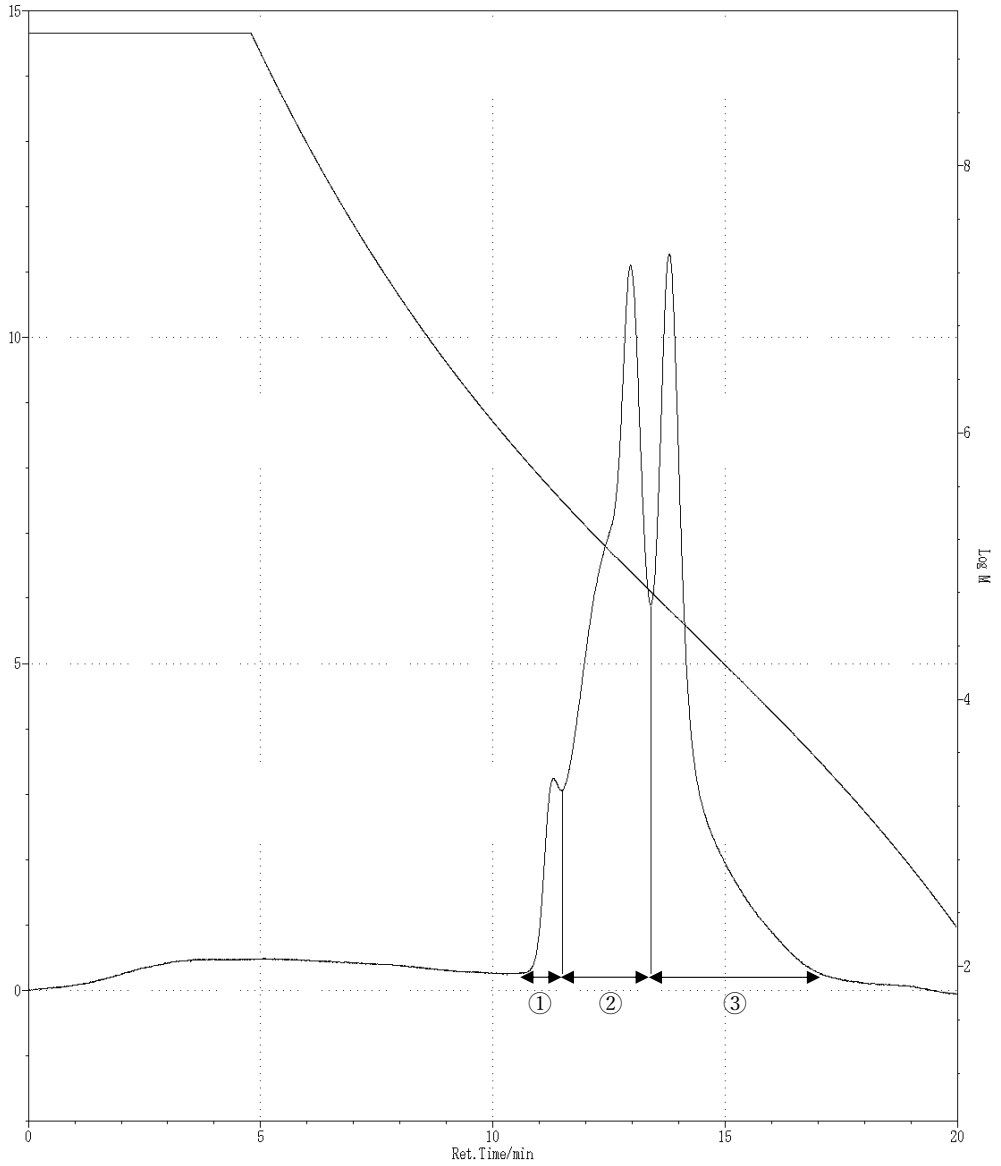
	M_n [kg/mol]	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	103.4	118.2	1.14
②	32.5	40.4	1.24
①+②	53.3	83.8	1.59

Table 2, entry 6 (**1b**:**2b**:CHO = 1:200:100,000)



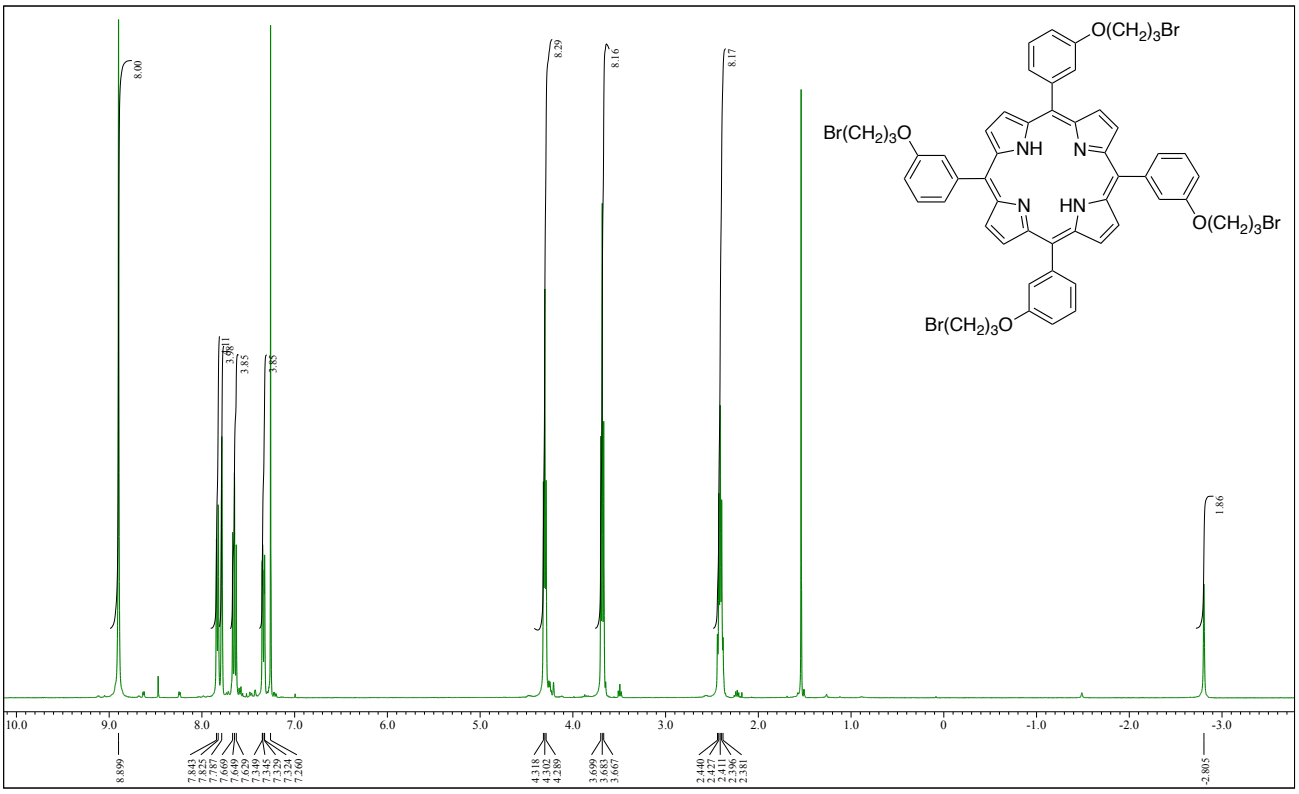
	M_n [kg/mol]	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	377.9	386.4	1.02
②	106.0	126.3	1.19
③	29.4	37.0	1.26
①+②+③	56.5	112.6	1.99

Table 2, entry 7 (**1b**:**2b**:CHO = 1:300:100,000)

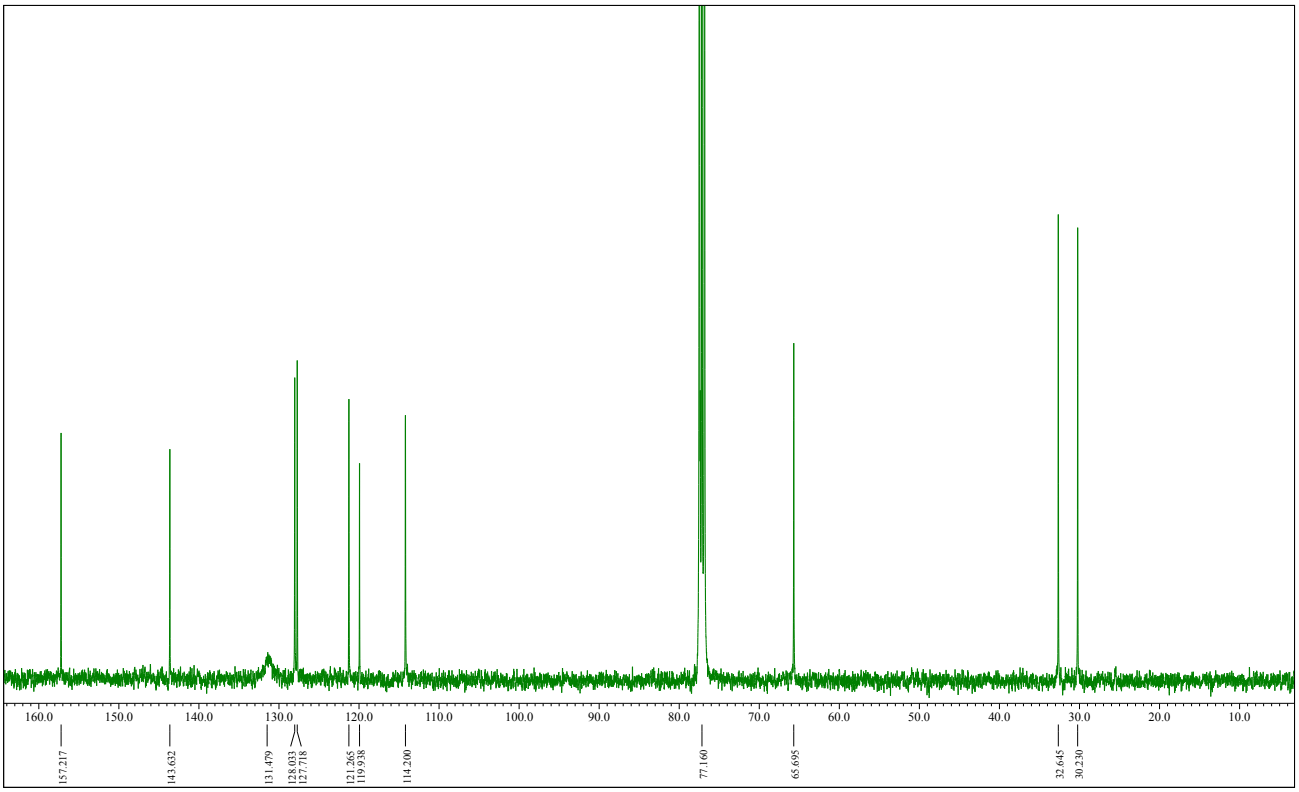


	M_n [kg/mol]	M_w [kg/mol]	$Đ$ (M_w/M_n)
①	364.5	371.8	1.02
②	112.3	131.4	1.17
③	28.1	38.2	1.36
①+②+③	50.7	106.3	2.10

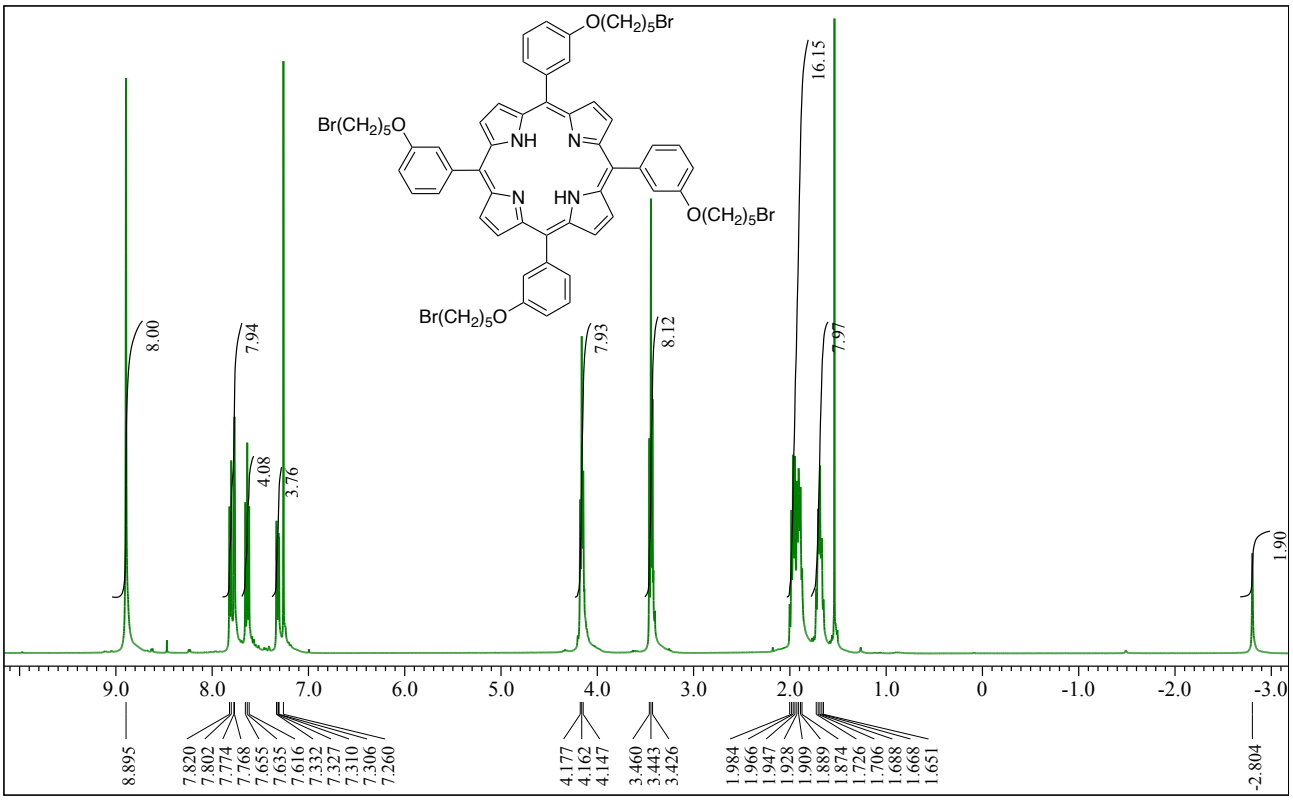
[F] NMR Spectra



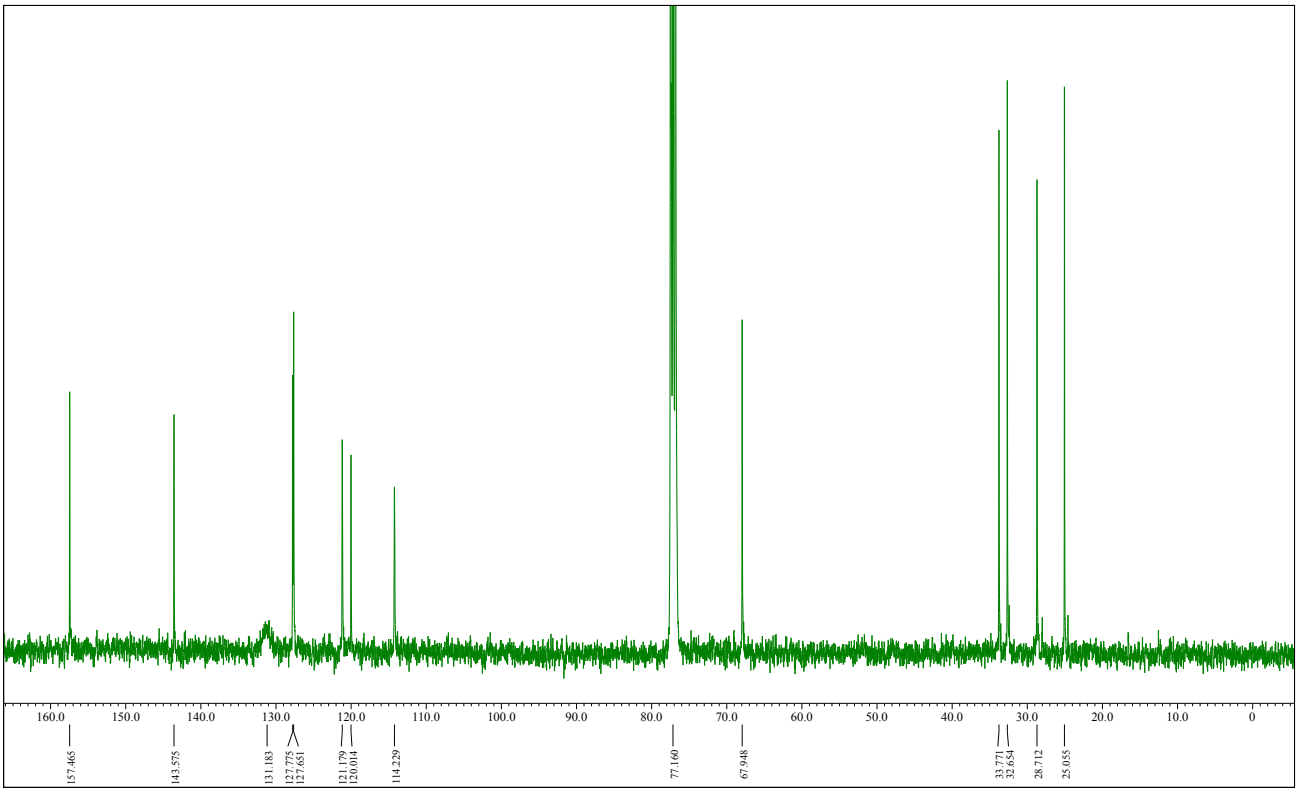
^{1}H NMR spectrum of **3a** in $CDCl_3$



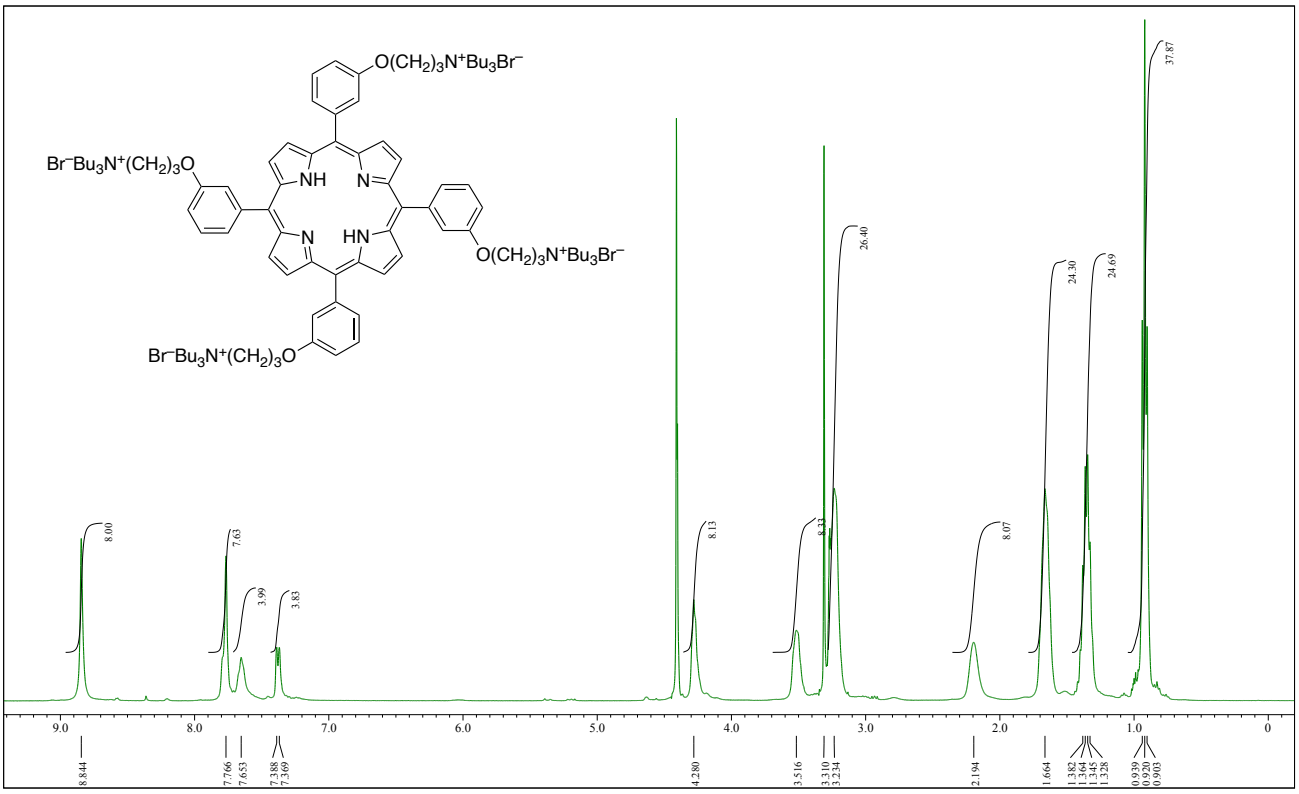
^{13}C NMR spectrum of **3a** in $CDCl_3$



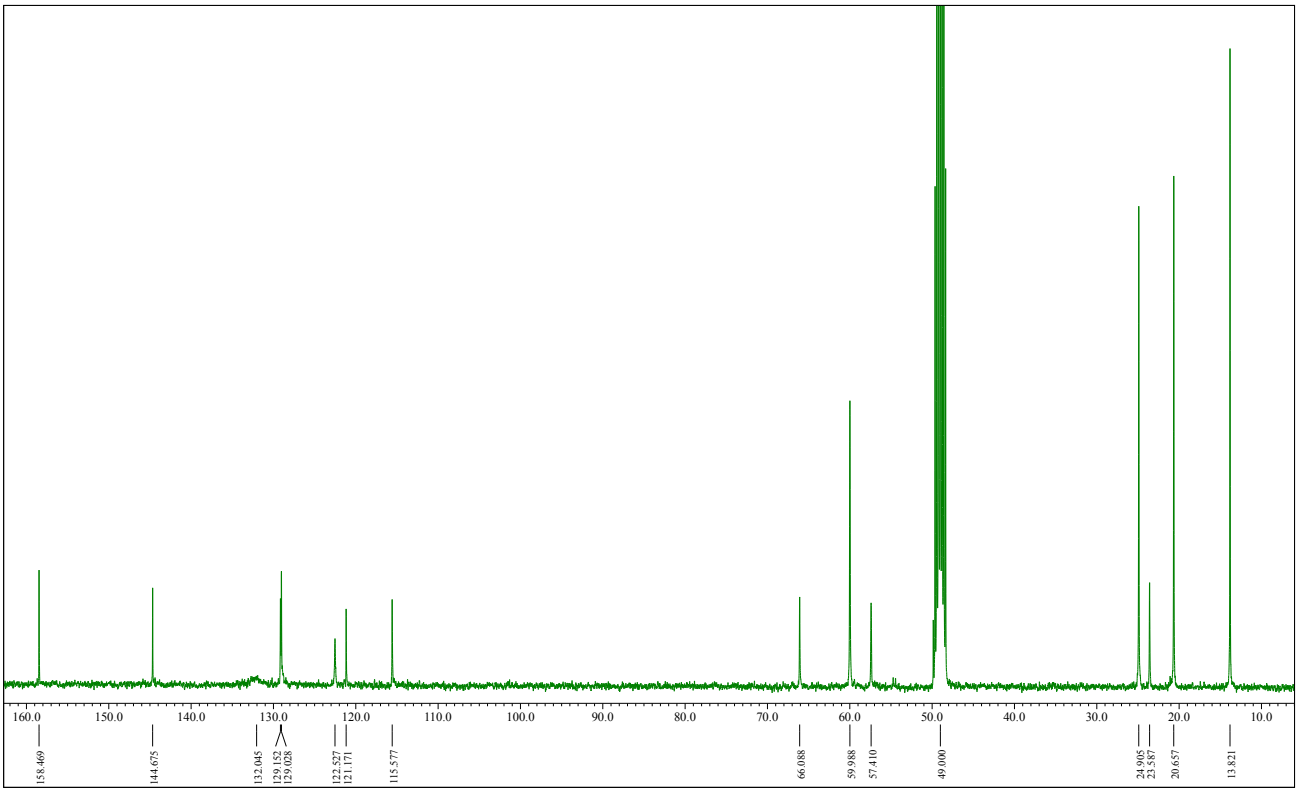
^{1}H NMR spectrum of **3c** in $CDCl_3$



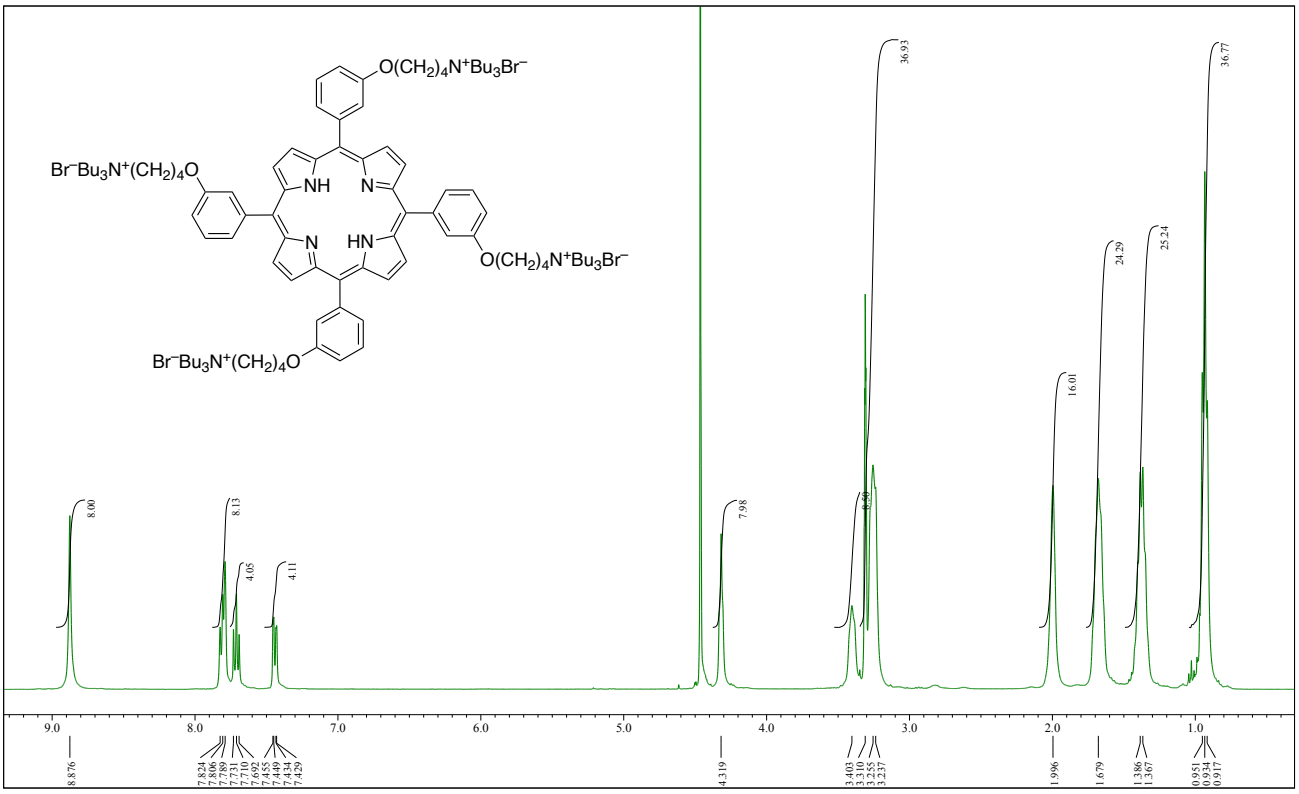
^{13}C NMR spectrum of **3c** in $CDCl_3$



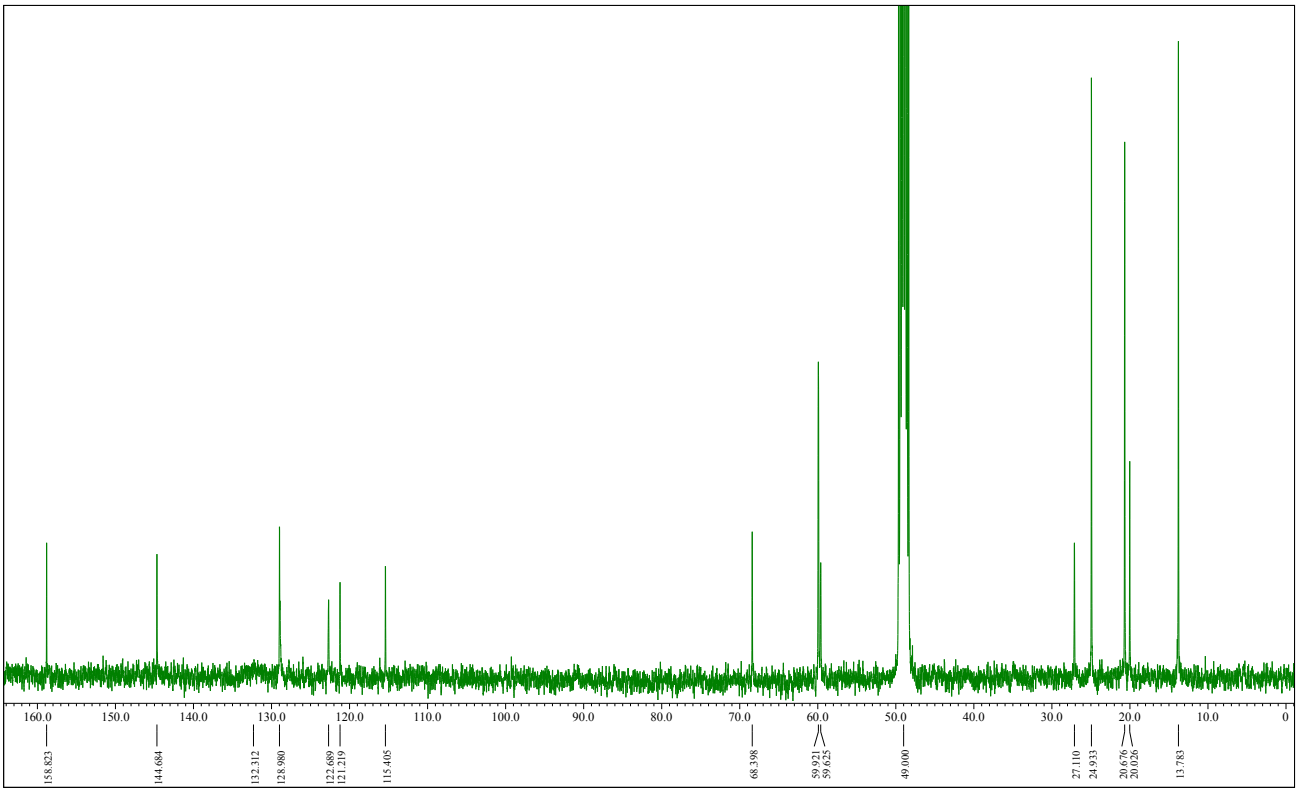
^{1}H NMR spectrum of **4a** in CD_3OD at 60 °C



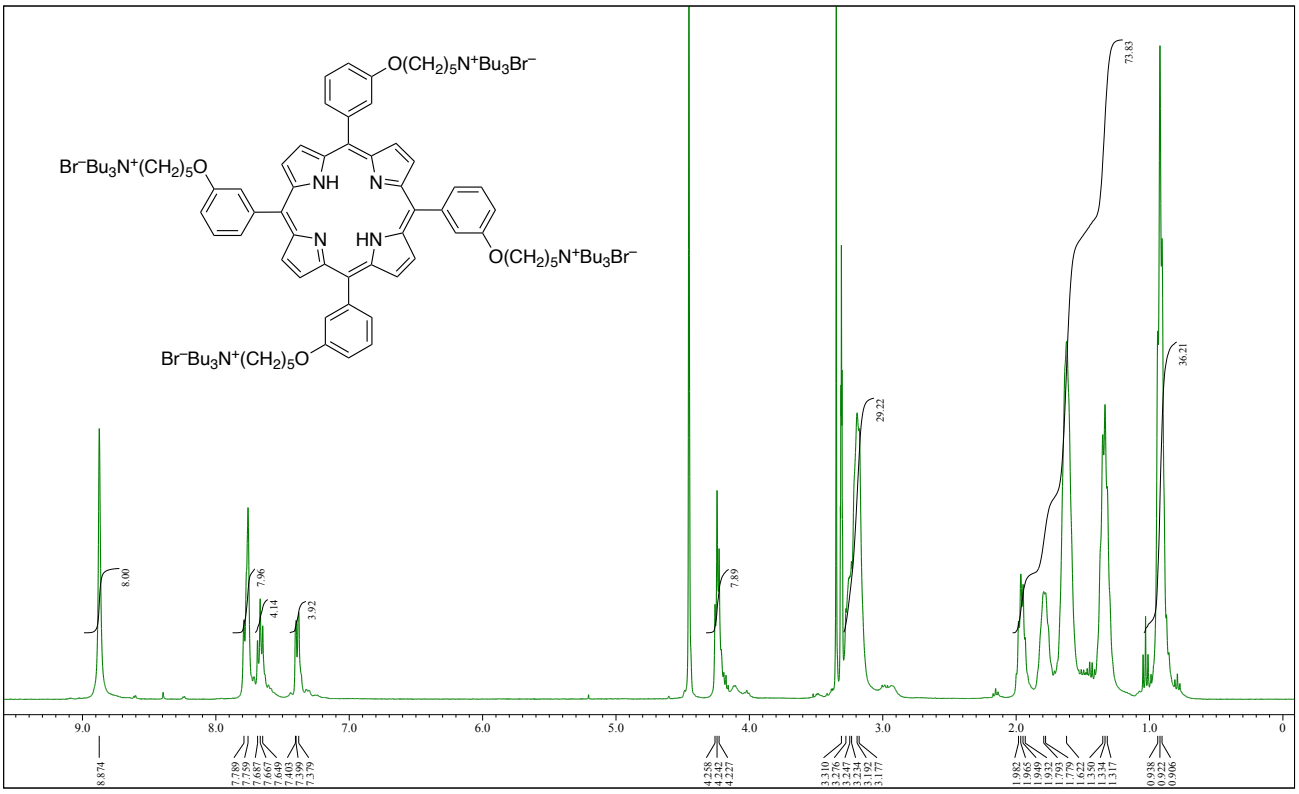
^{13}C NMR spectrum of **4a** in CD_3OD at 60 °C



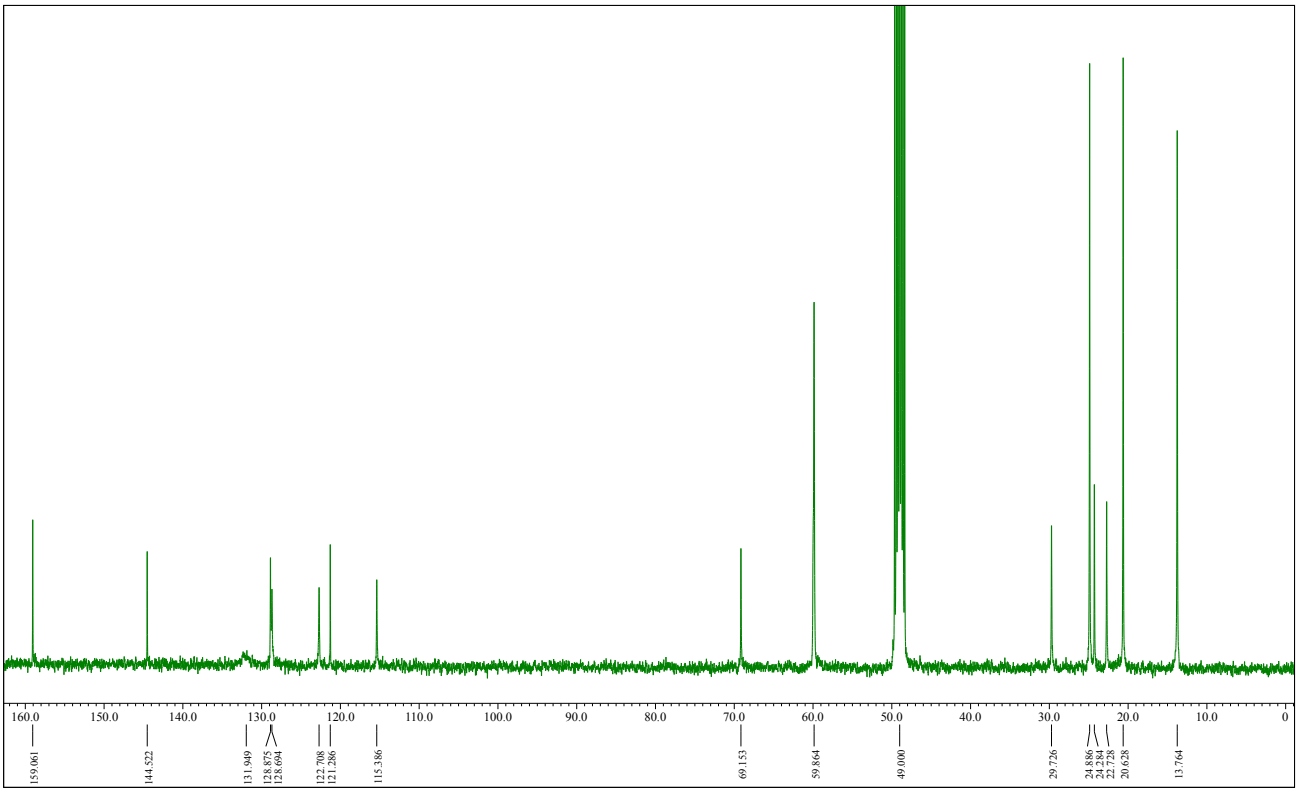
^{1}H NMR spectrum of **4b** in CD_3OD at 60 °C



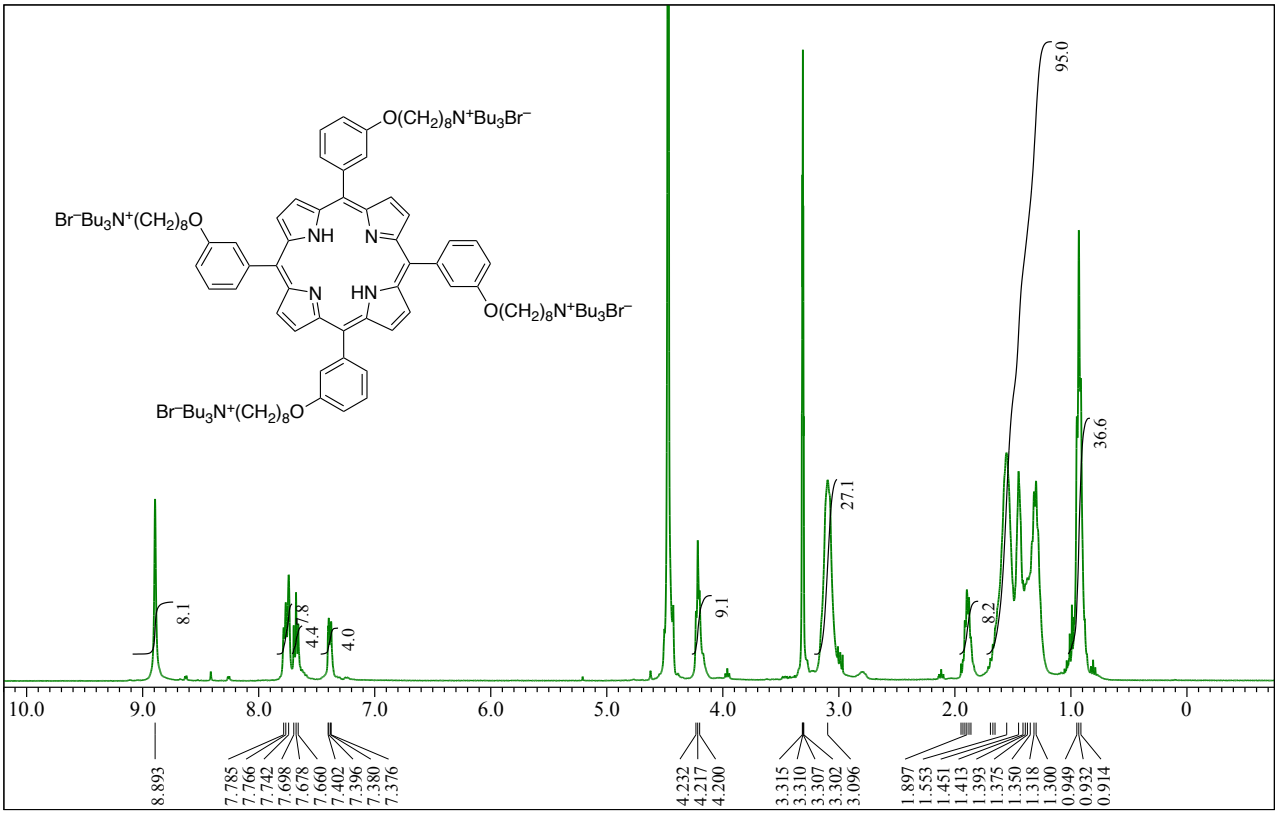
^{13}C NMR spectrum of **4b** in CD_3OD at 60 °C



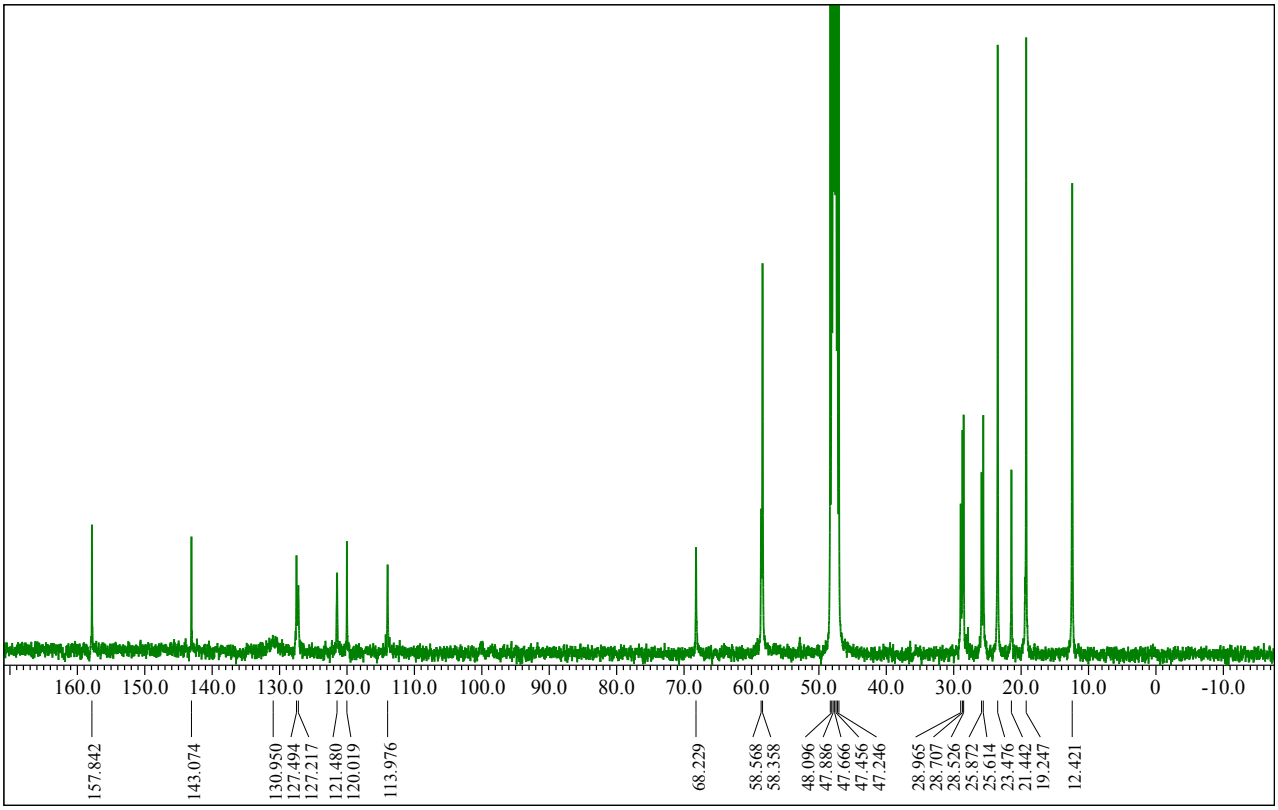
^{1}H NMR spectrum of **4c** in CD_3OD at 60 °C



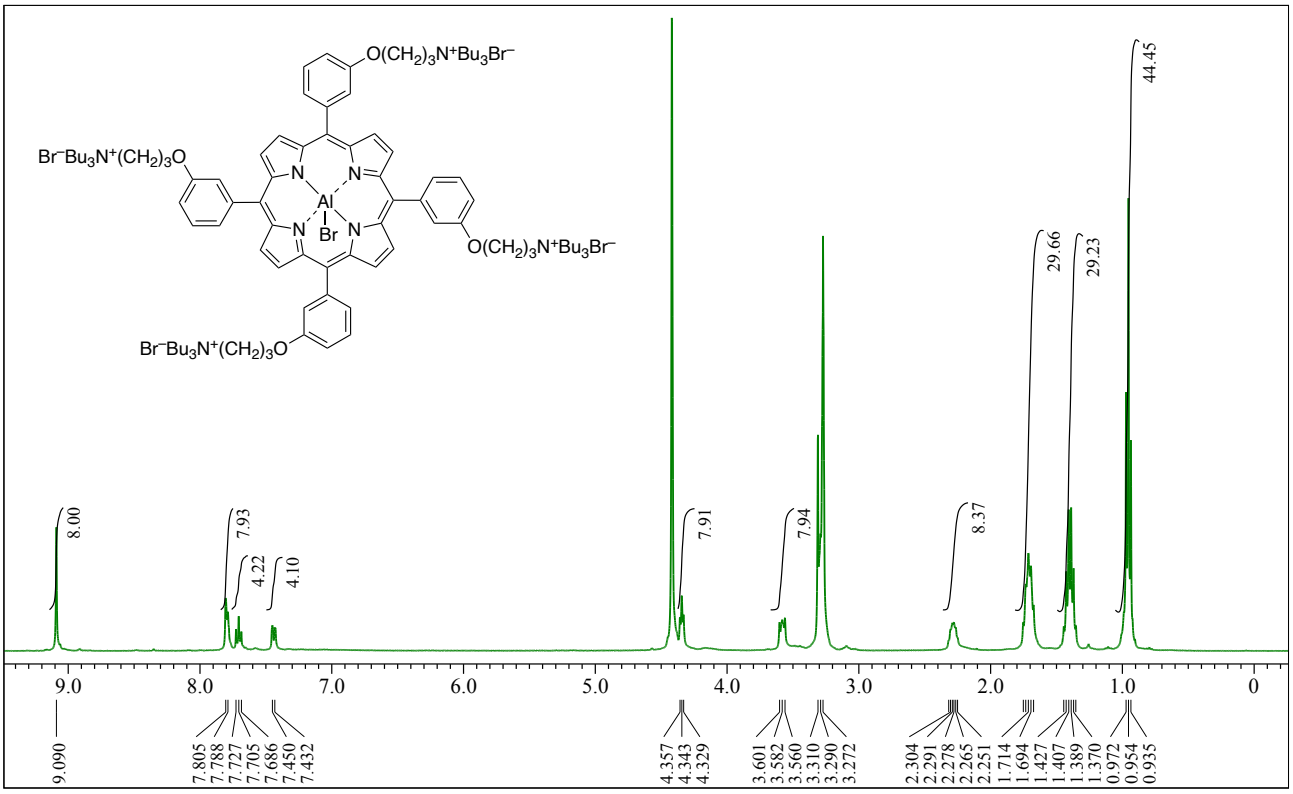
^{13}C NMR spectrum of **4c** in CD_3OD at 60 °C



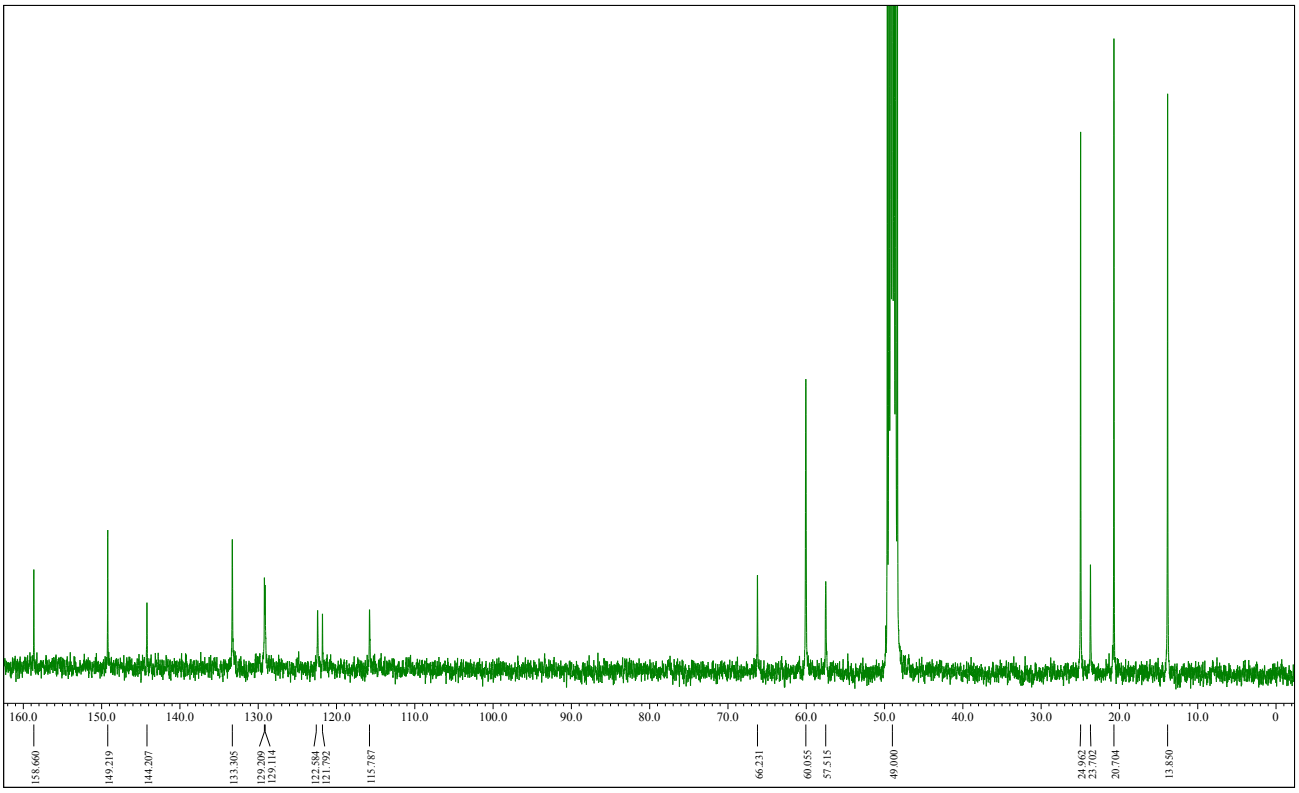
^{1}H NMR spectrum of **4e** in CD_3OD at 60 °C



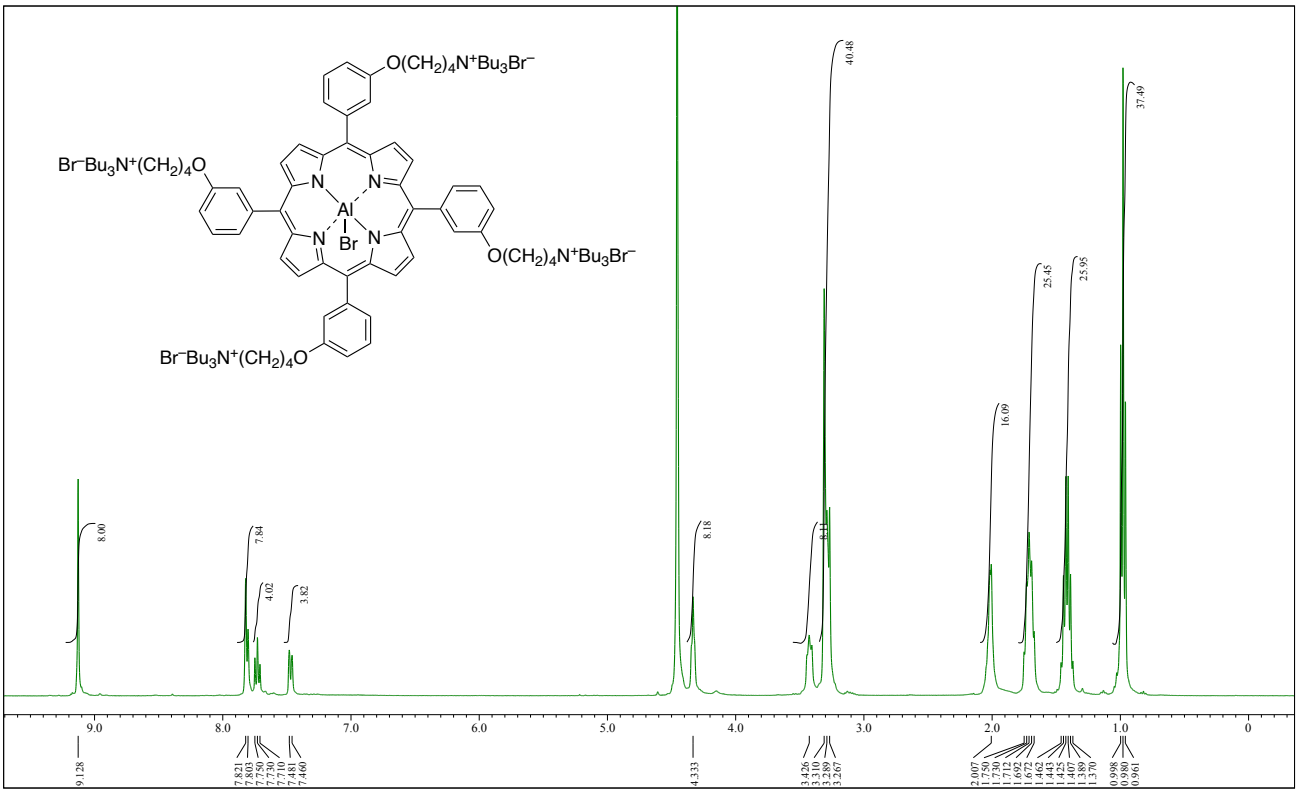
^{13}C NMR spectrum of **4e** in CD_3OD at 60 °C



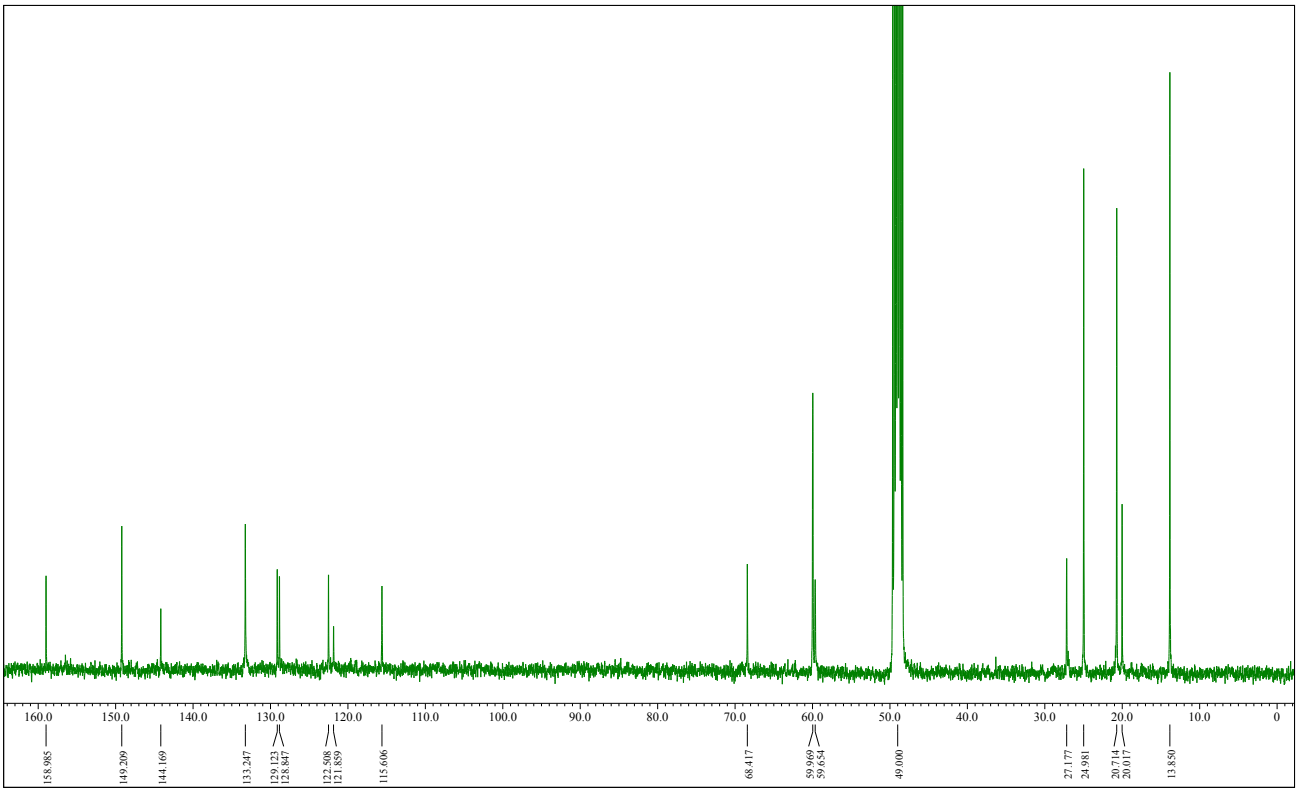
^{1}H NMR spectrum of **1a** in CD_3OD at 60 °C



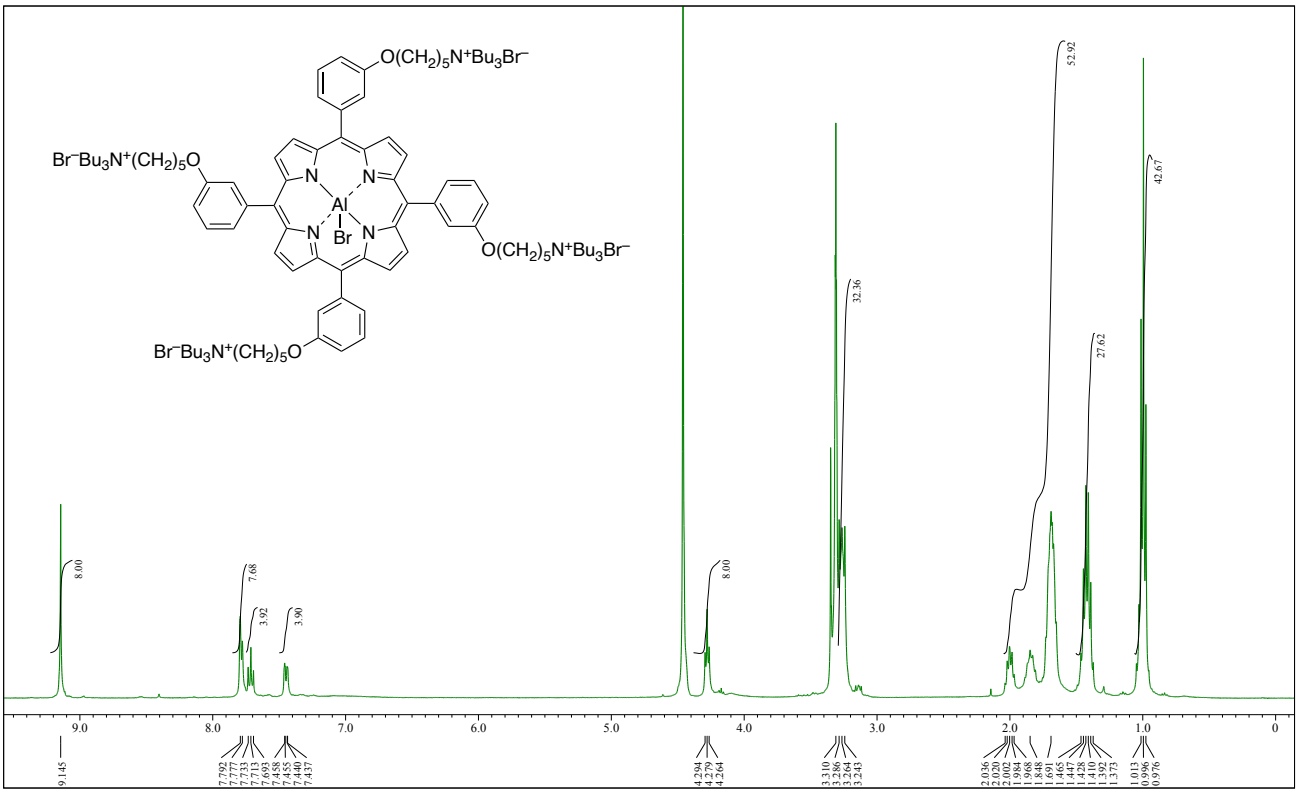
^{13}C NMR spectrum of **1a** in CD_3OD at 60 °C



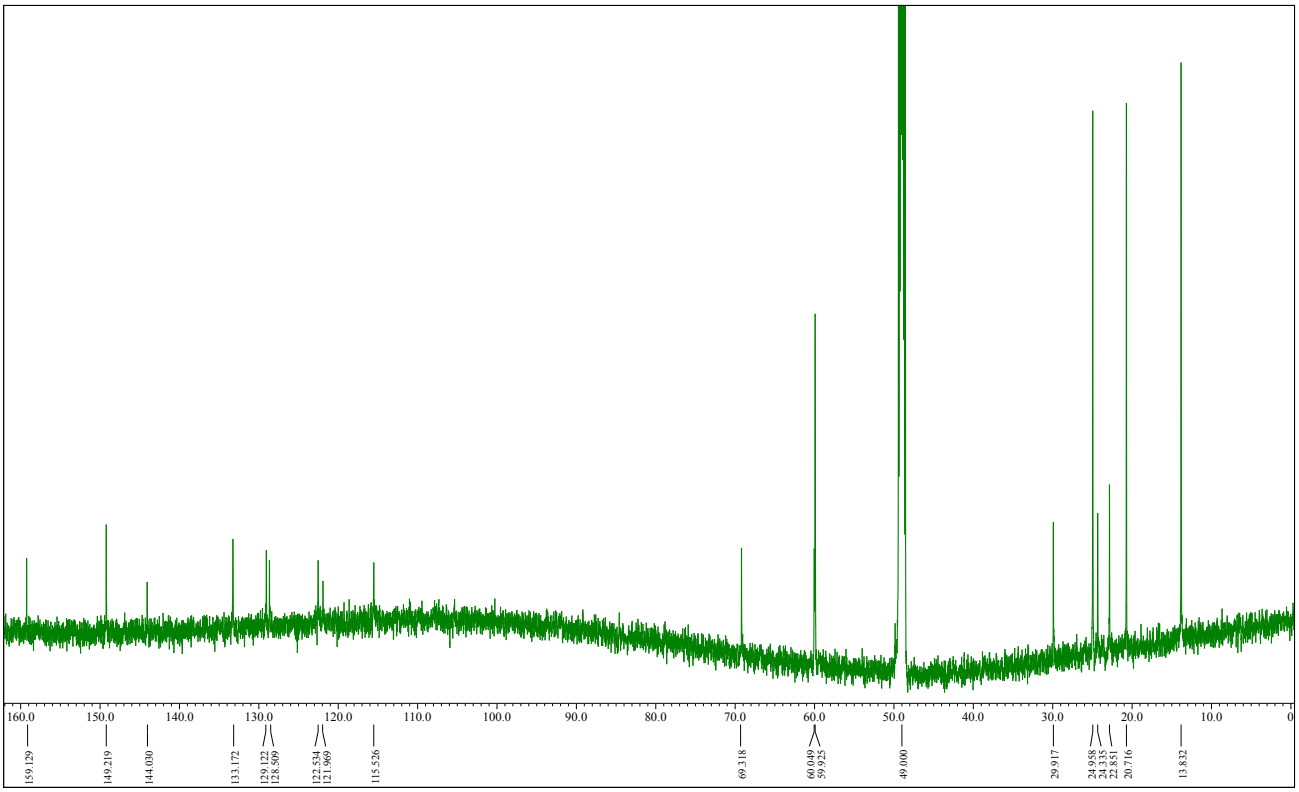
^{1}H NMR spectrum of **1b** in CD_3OD at 60 °C



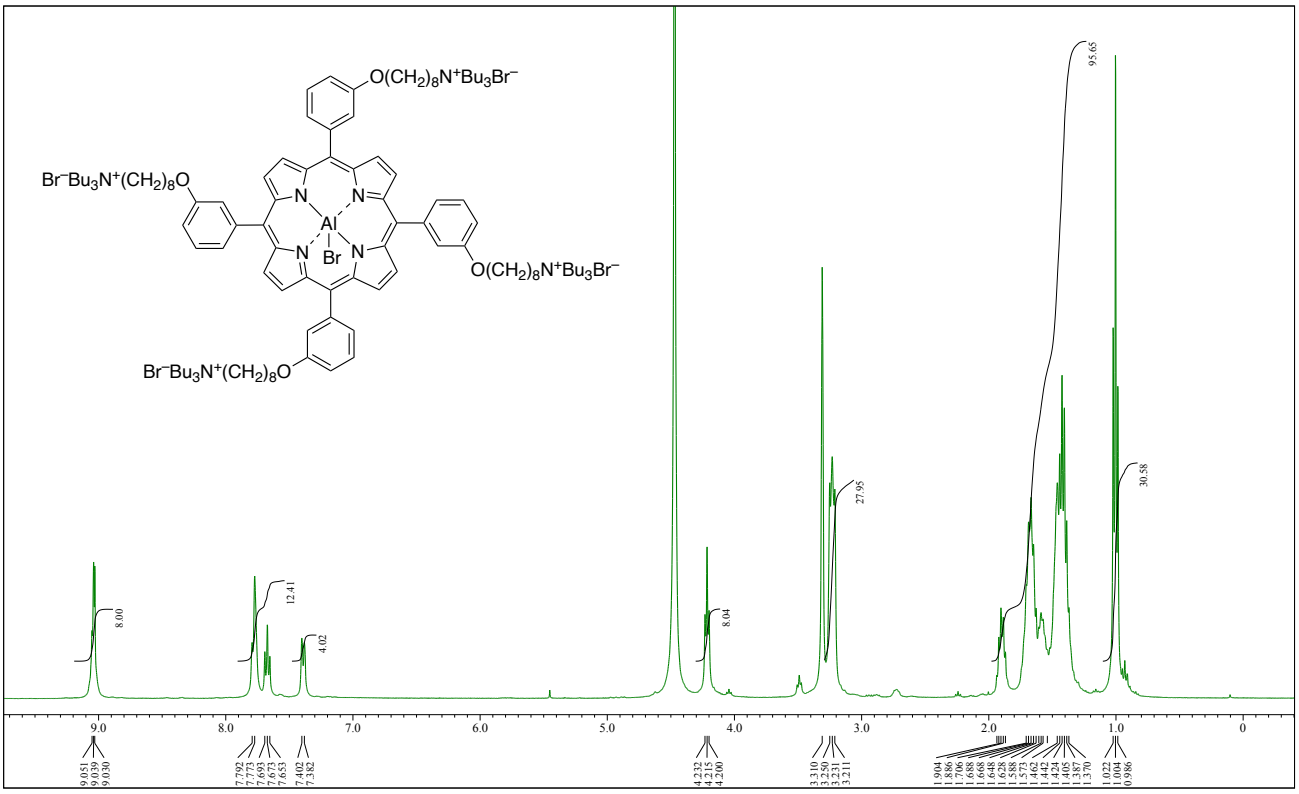
^{13}C NMR spectrum of **1b** in CD_3OD at 60 °C



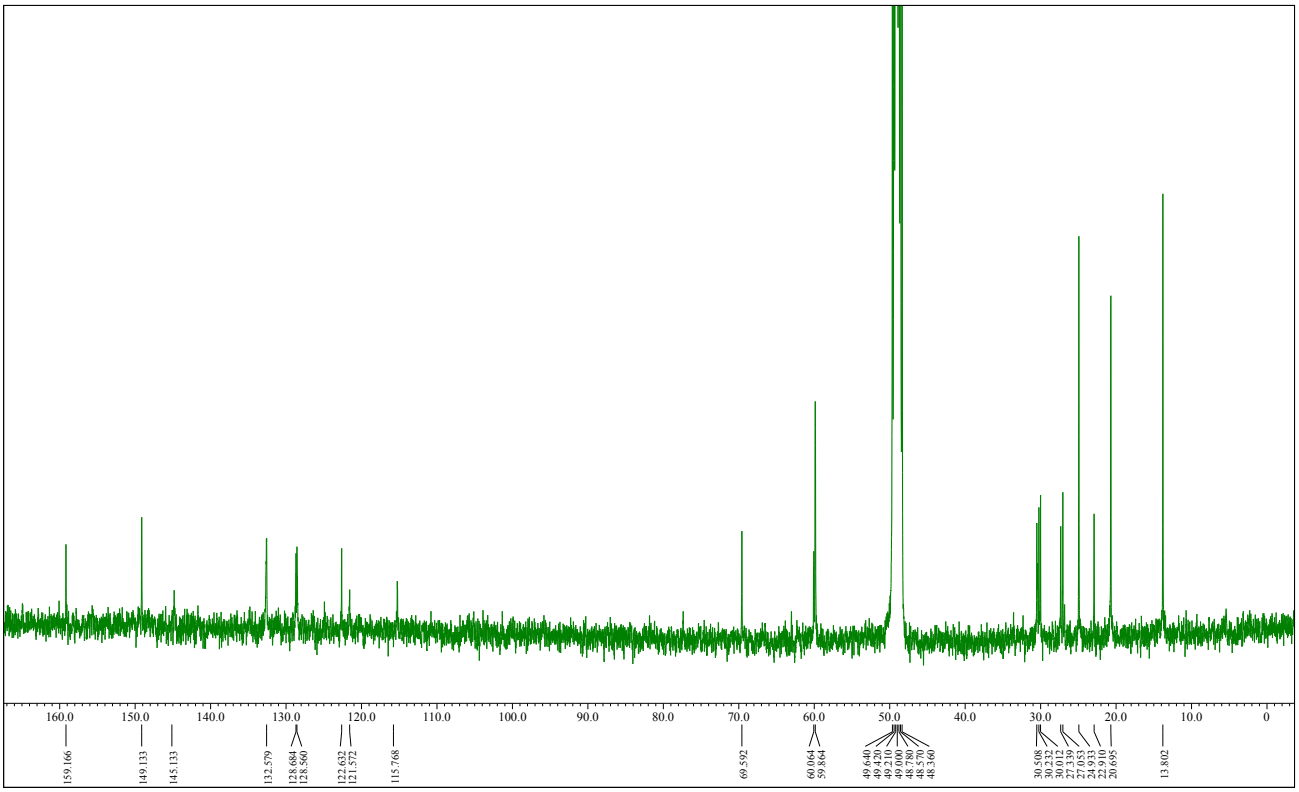
^{1}H NMR spectrum of **1c** in CD_3OD at 60 °C



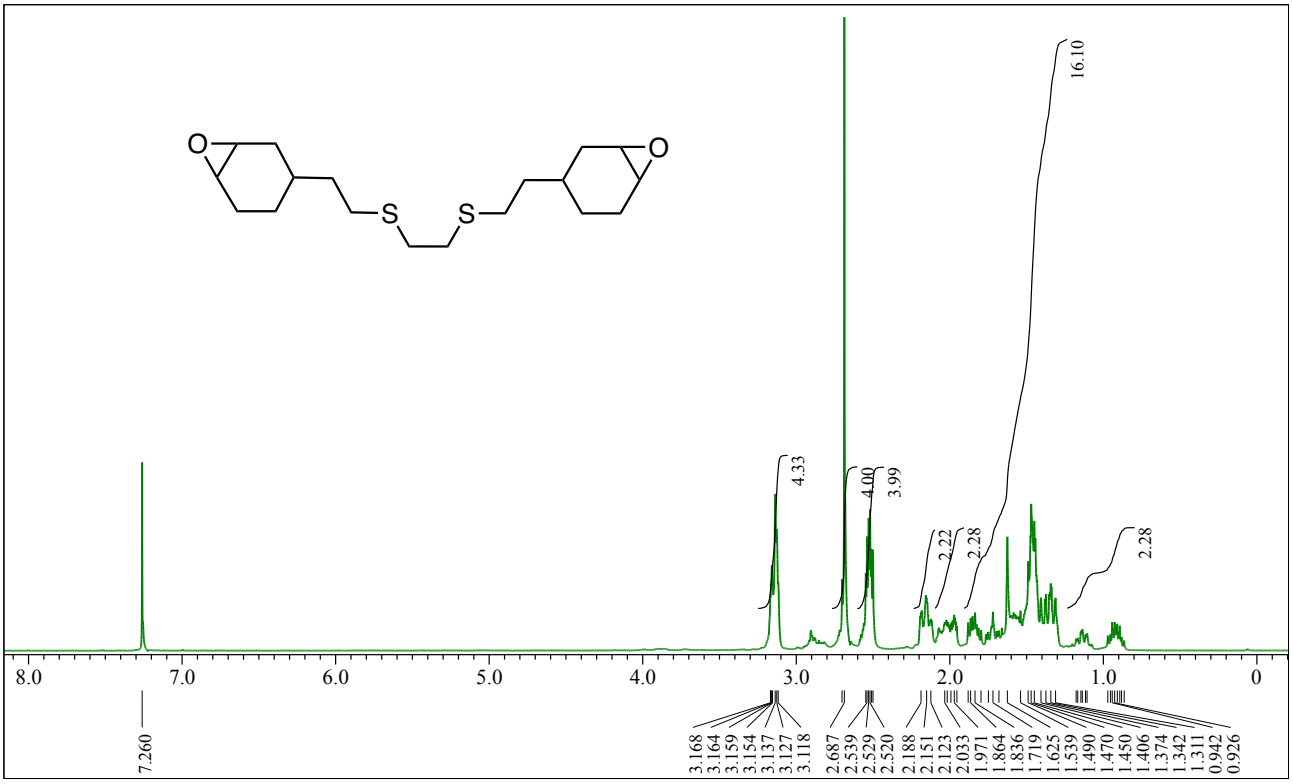
^{13}C NMR spectrum of **1c** in CD_3OD at 60 °C



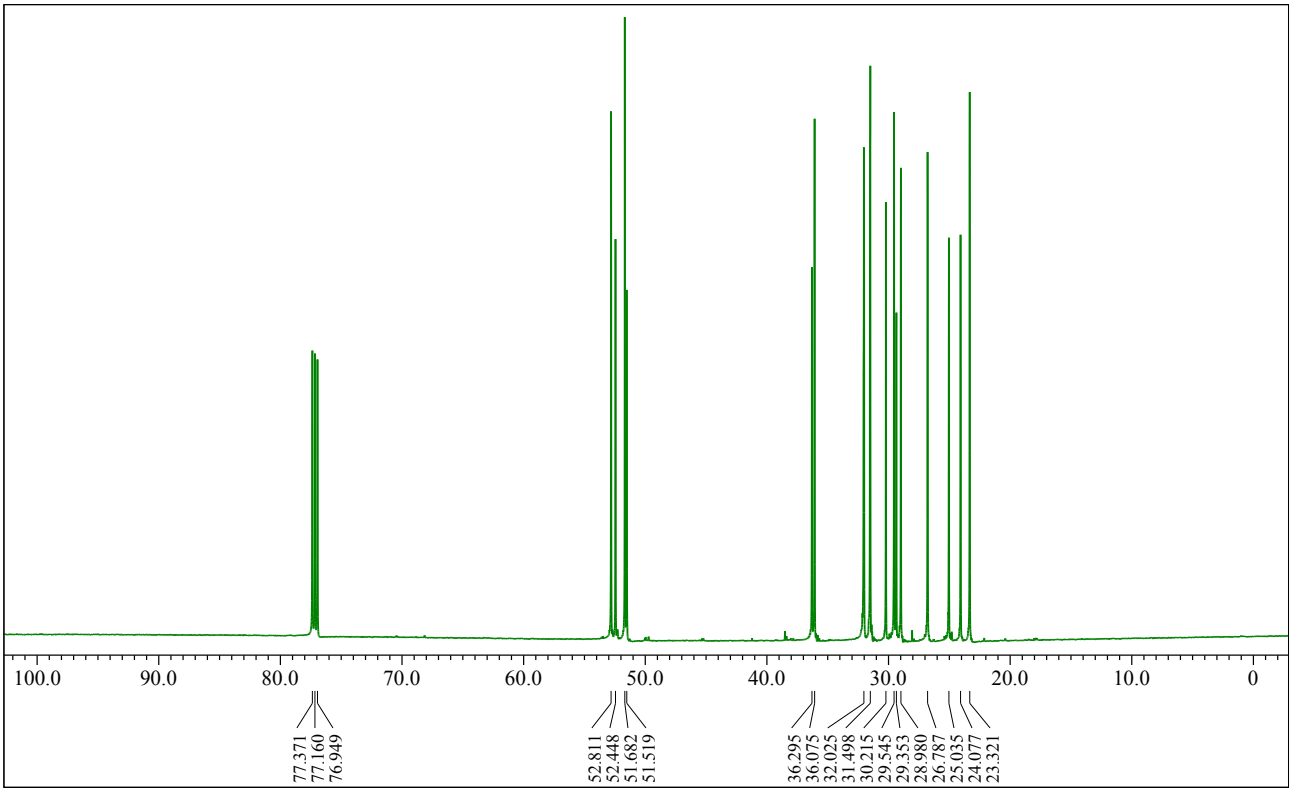
^{1}H NMR spectrum of **1e** in CD_3OD at 60 °C



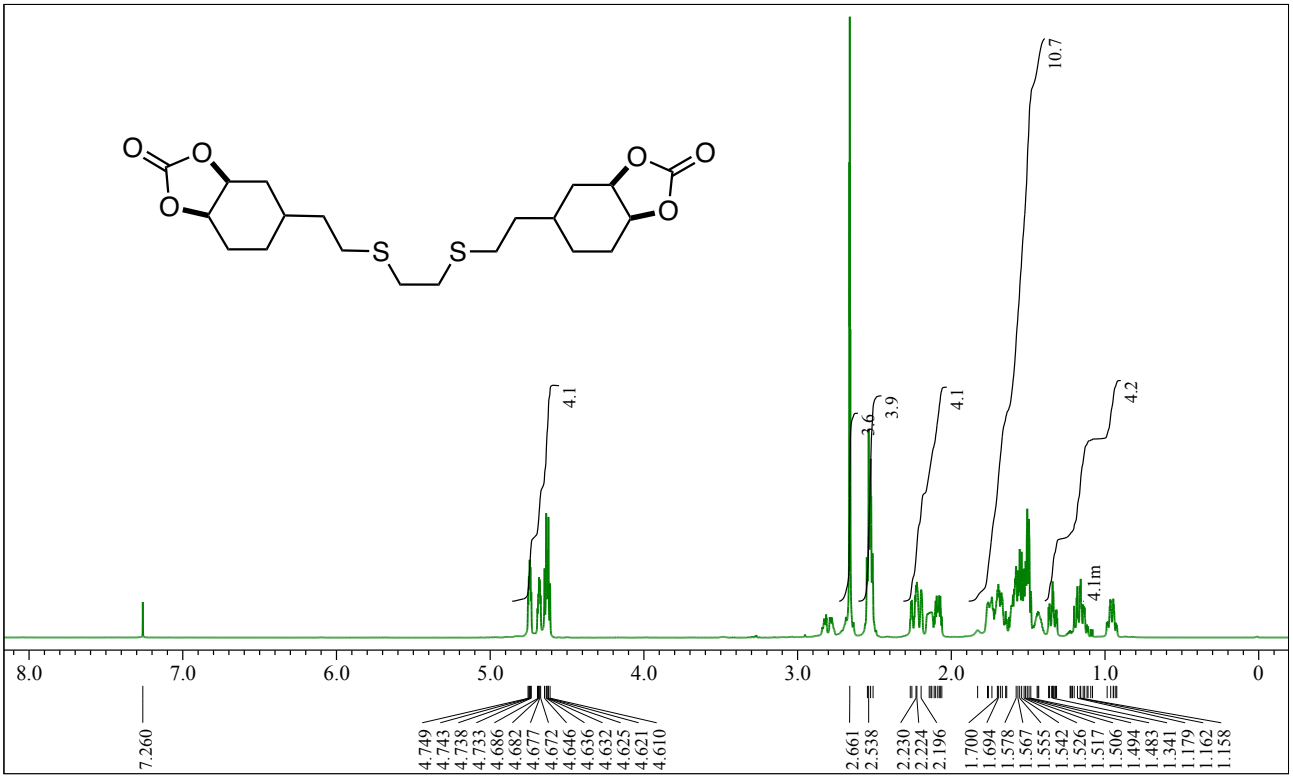
^{13}C NMR spectrum of **1e** in CD_3OD at 60 °C



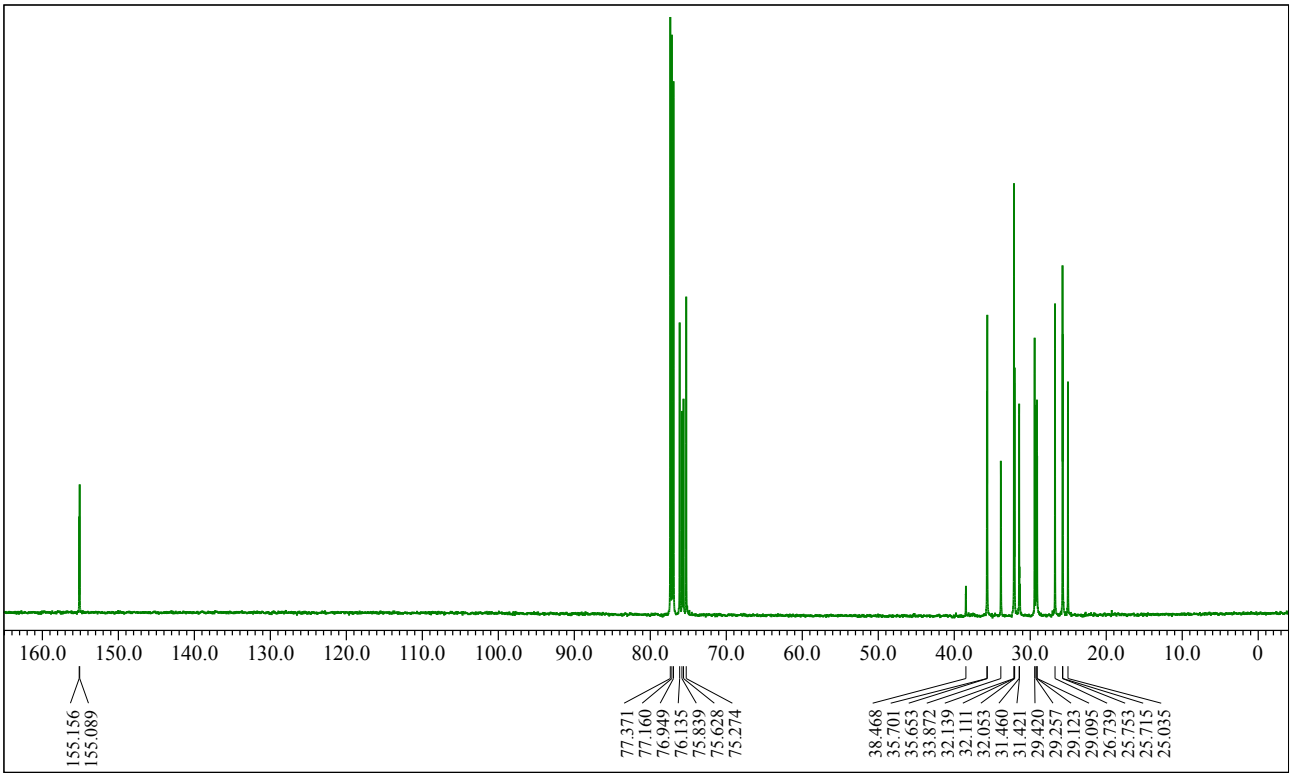
^{1}H NMR spectrum of **2b** in $CDCl_3$



^{13}C NMR spectrum of **2b** in $CDCl_3$



^{1}H NMR spectrum of **5** in $CDCl_3$



^{13}C NMR spectrum of **5** in $CDCl_3$