Supporting Information

Structural Elucidation of Partly-Folded Foldamers with No Long Range Conformational Order

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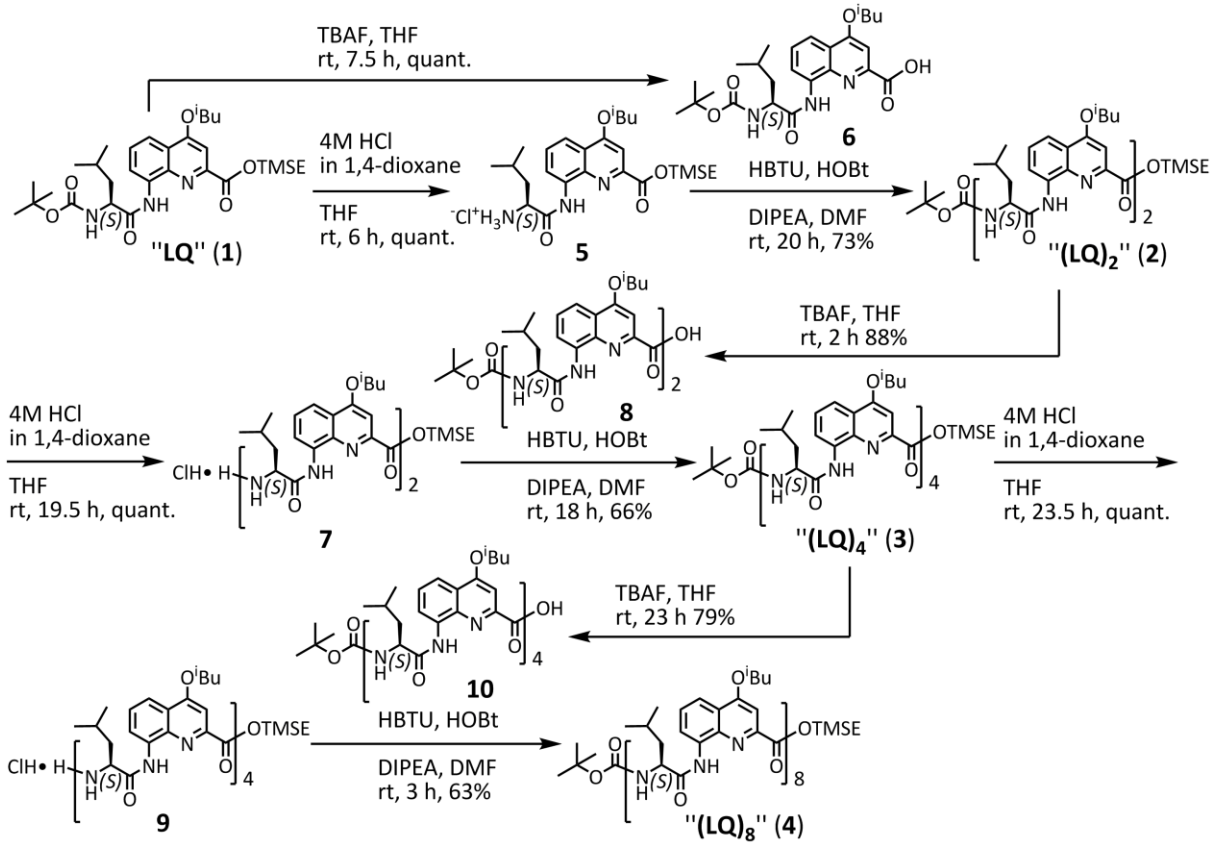
1. Synthetic Scheme



Scheme S1. Synthesis of *L*-**(LQ)$_n$** (**2**-**4**).

2. Experimental Section

General Methods and Materials

Unless otherwise noted, all reagents were purchased from Sigma-Aldrich Chemical Co., Tokyo Kasei Kogyo Co., Inc., Novabiochem, and Alfa Aesar. Open column chromatography was performed on Silica gel (40-60 μm; Merck). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 or Bruker Avance 400 or Bruker Avance 500 or Bruker Avance 600 spectrometer. Chemical shifts for ^{1}H NMR were reported in parts per million (ppm) relative to the centerline of a singlet at 7.26 ppm for chloroform in deuterochloroform or the centerline of a quintet at 3.31 ppm for methanol in deuteromethanol. Coupling constants are reported in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet. Chemical shifts for ^{13}C NMR were reported in ppm relative to the centerline of a triplet at 77.16 ppm for deuterochloroform.

Mass spectra were recorded on Bruker Daltonics microTOF-2focus spectrometer and Bruker Daltonics UltrafleXtreme in the positive or negative ion detection modes. UV/vis and CD spectra were recorded in a 0.2 mm quartz cell on a JASCO V-650 spectrometer and JASCO J-820 spectrometer.

Compound **1** was synthesized according to the previous report[1].

Synthesis

Synthesis of 5. A 4 M hydrogen chloride solution in 1,4-dioxane (8.0 mL, 32 mmol) was added to a solution of **1** (905 mg, 1.58 mmol) in dry tetrahydrofuran (8 mL) under N_2. The mixture was stirred for 6 h at 25°C. The reaction mixture was concentrated to give **5** (841 mg, 1.65 mmol, quant.) as a yellow solid; ^{1}H NMR (300 MHz, CD_3OD) δ 8.80 (dd, J = 7.8, 1.2 Hz, 1 H), 8.03 (dd, *J* = 8.5, 1.3 Hz, 1 H), 7.67 (s, 1 H), 7.66 (t, *J* = 8.4 Hz, 1 H), 4.66-4.61 (m, 2 H), 4.46 (t, *J* = 7.0 Hz, 1 H), 4.14 (d, *J* = 6.4 Hz, 2 H), 2.35-2.24 (m, 1 H), 1.99-1.78 (m, 3 H), 1.31-1.24 (m, 2 H), 1.17 (d, *J* = 6.7 Hz, 6 H), 1.08 (d, *J* = 6.2 Hz, 3 H), 1.06 (d, *J* = 6.3 Hz, 3 H), 0.15 (s, 9 H); ^{13}C NMR (75 MHz, CD_3OD) δ 169.5, 167.0, 164.5, 148.6, 140.4, 135.8, 129.2, 123.4, 120.3, 118.0, 102.5, 76.5, 66.2, 53.7, 41.9, 29.4, 25.7, 23.2, 22.7, 19.5, 18.3, -1.4; HRMS (ESI) calcd for $C_{25}H_{40}N_3O_4Si$ $(M+H)^+$: 474.2788, found: 474.2770.

Synthesis of 6. A 1 M tetra-*n*-butylammonium fluoride solution in tetrahydrofuran (3.5 mL, 3.5 mmol) was added to a solution of **1** (1.002 g, 1.75 mmol) in dry tetrahydrofuran (10 mL) under N_2. The mixture was stirred for 7.5 h at 25°C. The reaction mixture was quenched with a 5% aqueous citric acid solution and extracted with dichloromethane. The organic layer was washed with water and brine, dried over magnesium sulfate and filtered. The solvent was removed in vacuo to give **6** (856 mg, 1.81 mmol, quant.) as a yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.08 (br s, 1 H), 8.75 (dd, *J* = 7.7, 1.2 Hz, 1 H), 7.93 (dd, *J* = 8.5, 1.2 Hz, 1 H), 7.67 (s, 1H), 7.60 (t, *J* = 8.1 Hz, 1 H), 4.98 (dd, *J* = 7.7 Hz, 1 H), 4.45-4.37 (m, 1 H), 4.07 (d, *J* = 6.4 Hz, 2 H), 2.35-2.22 (m, 1 H), 1.99-1.56 (m, 3 H), 1.42 (s, 9 H), 1.28 (d, *J* = 6.7 Hz, 6 H), 1.01 (d, *J* = 6.7 Hz, 3 H), 0.99 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 165.6, 163.9, 157.1, 146.0, 137.7, 135.3, 128.7, 122.6, 117.9, 116.0, 99.9, 81.6, 75.6, 53.7, 38.4, 28.3, 28.2, 24.8, 23.0, 22.2, 19.3; HRMS (ESI) calcd for $C_{25}H_{34}N_3O_6$ $(M-H)^-$: 472.2448, found: 472.2447.

Synthesis of tetrapeptide 2. Dry *N,N*-diisopropylethylamine (1.4 mL, 8.23 mmol) was added to a solution of **6** (856 mg, 1.81 mmol), HBTU (1.29 g, 3.39 mmol) and HOBt (48 mg, 0.355 mmol) in dry dimethylformamide (4 mL) under N_2, and stirred for 5 min at 25°C. Then, **5** (841 mg, 1.65 mmol) in dry dimethylformamide (4 mL) was added to the reaction mixture, and stirred for 20 h at 25°C. The reaction mixture was quenched with 5% aqueous citric acid solution and extracted with ethyl acetate. The organic layer was washed with aqueous saturated sodium hydrogen carbonate, water and brine, dried over magnesium sulfate and filtered. After the solvent was removed in vacuo, the residue was purified by open column chromatography (silica gel, ethyl acetate/cyclohexane = 1:4 vol/vol) to give **2** (1.117 g, 1.20 mmol, 73%) as a yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.42 (br s, 1 H), 10.38 (br s, 1 H), 9.23 (br d, *J* = 6.8 Hz, 1 H), 8.82 (d, *J* = 7.4 Hz, 1 H), 8.72 (dd, *J* = 7.6, 1.1 Hz, 1 H), 7.96 (dd, *J* = 8.4, 1.0 Hz, 1 H), 7.91 (dd, *J* = 8.5, 1.2 Hz, 1 H), 7.67 (s, 1 H), 7.57 (t, *J* = 8.1 Hz, 1 H), 7.55 (t, *J* = 7.8 Hz, 1 H), 7.55 (s, 1 H), 6.15 (br s, 1 H), 5.13-5.06 (t, *J* = 8.2 Hz, 1 H), 7.26-7.10 (m, 3 H), 6.49 (br s, 1 H), 5.80 (br s, 1 H), 4.89-4.84 (m, 1 H), 4.47-4.40 (m, 1 H), 4.52-4.37 (m, 3 H), 4.07 (d, *J* = 6.4 Hz, 2 H), 4.05 (d, *J* = 6.3 Hz, 2 H), 2.34-2.24 (m, 2 H), 2.06-1.82 (m, 6 H), 1.21 (s, 9 H), 1.16-1.02 (m, 26 H), 0.12 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 170.8, 165.5, 164.4, 163.7, 163.1, 156.0, 149.5, 147.9, 138.9, 138.2, 134.5, 134.3, 128.0, 127.8, 122.1, 122.1, 118.0, 117.7, 116.5, 116.0, 101.5, 99.2, 79.9, 75.5, 75.4, 64.5, 55.5, 53.5, 43.3, 40.9, 28.3, 27.0, 25.4, 25.2, 23.2, 23.0, 22.8, 22.0, 19.3, 17.7, -1.3; HRMS (ESI) calcd for $C_{50}H_{73}N_6O_9Si$ $(M+H)^+$: 929.5208, found: 929.5215.

Synthesis of 7. A 4 M hydrogen chloride solution in 1,4-dioxane (3.2 mL, 12.8 mmol) was added to a solution of **2** (404 mg, 0.435 mmol) in dry tetrahydrofuran (3.2 mL) under N_2. The mixrure was stirred for 19.5 h

at 25°C. The reaction mixture was concentrated to give **7** (422 mg, 0.488 mmol, quant.) as a yellow solid; ^{1}H NMR (300 MHz, CD_3OD) δ 8.84-8.79 (m, 1 H), 7.77 (d, *J* = 7.2 Hz, 1 H), 8.06 (d, *J* = 8.4 Hz, 1 H), 7.99 (dd, *J* = 8.4, 1.1 Hz, 1 H), 7.76 (s, 1 H), 7.64 (t, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 8.3 Hz, 1 H), 7.55 (s, 1 H), 5.31-5.27 (m, 1 H), 4.51-4.45 (m, 1 H), 4.31-4.25 (m, 2 H), 4.15 (d, *J* = 6.3 Hz, 2 H), 4.10 (d, *J* = 6.4 Hz, 2 H), 2.35-2.21 (m, 2 H), 2.20 (t, *J* = 7.0 Hz, 2 H), 1.91-1.61 (m, 4 H), 1.17-1.06 (m, 20H), 0.93 (d, *J* = 6.4 Hz, 3 H), 0.89 (d, *J* = 6.4 Hz, 3 H), 0.08 (s, 9 H); HRMS (ESI) calcd for $C_{45}H_{65}N_6O_7Si$ $(M+H)^+$: 829.4684, found: 829.4672.

Synthesis of 8. A 1 M tetra-*n*-butylammonium fluoride solution in tetrahydrofuran (1.2 mL, 1.2 mmol) was added to a solution of **2** (506 mg, 0.544 mmol) in dry tetrahydrofuran (4 mL) under N_2. The mixture was stirred for 2 h at 25°C. The reaction mixture was quenched with a 5% aqueous citric acid solution and extracted with dichloromethane. The organic layer was washed with water and brine, dried over magnesium sulfate and filtered. The solvent was removed in vacuo to give **8** (397 mg, 0.479 mmol, 88%) as a yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.85 (br s, 1 H), 10.53 (br s, 1 H), 9.40 (br s, 1H), 8.84 (dd, *J* = 7.8, 1.1 Hz, 1 H), 8.72 (dd, *J* = 7.7, 1.0 Hz, 1 H), 8.00 (s, 1H), 7.92 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.91 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.67 (s, 1H), 7.58 (t, *J* = 8.1 Hz, 1 H), 7.54 (t, *J* = 8.1 Hz, 1 H), 4.99 (d, *J* = 8.1 Hz, 1 H), 4.86-4.78 (m, 1 H), 4.39-4.32 (m, 1 H), 4.23 (d, *J* = 5.8 Hz, 2 H), 4.06 (d, *J* = 6.5 Hz, 2 H), 2.42-2.13 (m, 4 H), 1.94-1.60 (m, 4 H), 1.33 (bt s, 9 H), 1.18 (d, *J* = 6.7 Hz, 6 H), 1.12 (d, *J* = 6.7 Hz, 6 H), 1.07 (d, *J* = 6.5 Hz, 3 H), 1.06 (d, *J* = 6.6 Hz, 3 H), 1.02 (d, *J* =6.4 Hz, 3 H), 0.99 (d, *J* = 6.3 Hz, 3 H); HRMS (ESI) calcd for $C_{45}H_{59}N_6O_9$ $(M-H)^-$: 827.4344, found: 827.4332.

Synthesis of octapeptide 3. Dry *N,N*-diisopropylethylamine (0.4 mL, 2.35 mmol) was added to a solution of **8** (397 mg, 0.479 mmol), HBTU (361 mg, 0.952 mmol) and HOBt (15 mg, 0.111 mmol) in dry dimethylformamide (3 mL) under N_2. The mixture was stirred for 3 min at 25°C. Then, **7** (422 mg, 0.488 mmol) in dry dimethylformamide (2 mL) was added. The reaction mixture was stirred for 18 h at 25°C, quenched with a 5% aqueous citric acid solution and extracted with ethyl acetate. The organic layer was washed with saturated aqueous sodium hydrogen carbonate, water and brine, dried over magnesium sulfate and filtered. After the solvent was removed in vacuo, the residue was purified by open column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 4) to give **3** (517 mg, 0.315 mmol, 66%) as a yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.34 (br s, 1 H), 11.30 (br s, 1 H), 10.48 (s, 1 H), 10.42 (s, 1 H), 9.83 (d, *J* = 7.5 Hz, 1 H), 9.78 (d, *J* = 7.6 Hz, 1 H), 9.22 (br s, 1 H), 8.85 (dd, *J* = 7.7, 1.2 Hz, 1 H), 8.83 (dd, *J* = 7.6, 1.2 Hz, 1 H), 8.72 (dd, *J* = 7.8, 1.1 Hz, 1 H), 8.69 (dd, *J* = 7.8, 1.1 Hz, 1 H), 7.92 (dd, *J* = 8.4, 1.3 Hz, 1 H), 7.92 (dd, *J* = 8.5, 1.3 Hz, 1 H), 7.88 (dd, *J* = 8.5, 1.3 Hz, 1 H), 7.86 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.78 (s, 1 H), 7.76 (s, 1 H), 7.73 (s, 1 H), 7.56-7.49 (m, 4 H), 7.47 (s, 1 H), 5.20 (d, *J* = 8.6 Hz, 1 H), 3.14-3.05 (m, 1 H), 3.02-4.94 (m, 1 H), 4.90-4.82 (m, 1 H), 4.45-4.18 (m, 5 H), 4.06 (d, *J* = 6.3 Hz, 4 H), 4.01 (d, *J* = 6.5 Hz, 2 H), 2.38-1.79 (m, 16 H), 1.38 (s, 9 H), 1.16-0.98 (m, 50 H), 0.06 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 170.6, 170.4, 166.2, 166.0, 165.6, 165.5, 164.0, 163.6, 163.3, 162.9, 156.3, 149.6, 149.6, 149.4, 147.5, 138.9, 138.5, 138.4, 137.9, 135.4, 135.1, 134.5, 128.1, 127.6, 127.5, 127.3, 122.3, 122.2, 122.0, 118.2, 117.7, 117.6, 116.2, 116.1, 116.0, 115.8, 101.2, 99.7, 99.6, 80.7, 75.4, 75.3, 75.2, 64.2, 56.3, 56.1, 54.3, 41.4, 39.6, 39.1, 30.2, 28.4, 28.2, 28.2, 25.3, 25.2, 24.9, 23.4, 23.2, 23.0, 22.9, 22.3, 22.2, 22.0, 19.3, 19.2, 17.6, -1.4; HRMS (ESI) calcd for $C_{90}H_{123}N_{12}O_{15}Si$ $(M+H)^+$: 1639.9000, found: 1639.8965.

Synthesis of 9. A 4 M hydrogen chloride solution in 1,4-dioxane (0.8 mL, 3.2 mmol) was added to a solution of **3** (206 mg, 0.126 mmol) in dry tetrahydrofuran (1 mL) under N_2, and stirred for 23.5 h at 25°C. The reaction mixture was concentrated to give **9** (199 mg, 0.126 mmol, quant.) as a yellow solid; ^{1}H NMR (300 MHz, CD_3OD) δ 8.78 (dd, *J* = 7.7, 0.9 Hz, 1 H), 8.73 (d, *J* = 7.5 Hz, 1 H), 8.71 (dd, *J* = 7.7, 1.0 Hz, 1 H), 8.62 (d, *J* = 7.6 Hz, 1 H), 7.99 (dd, *J* = 8.6, 0.9 Hz, 1 H), 7.96 (dd, *J* = 8.6, 1.1 Hz, 1 H), 7.81 (d, *J* = 8.3 Hz, 1 H), 7.75 (s, 1 H), 7.67-7.53

(m, 6 H), 7.45 (t, *J* = 8.1 Hz, 1 H), 7.29 (s, 1 H), 4.46 (t, *J* = 6.8 Hz, 1 H), 4.42-4.37 (m, 1 H), 4.22-4.17 (m, 1 H), 4.11-4.02 (m, 3 H), 3.96-3.84 (m, 8 H), 2.36-1.61 (m, 16 H), 1.17 (d, *J* = 6.8 Hz, 3 H), 1.17 (d, *J* = 6.7 Hz, 3 H), 1.12-0.88 (m, 42 H), -0.23 (s, 9 H); HRMS (ESI) calcd for $C_{85}H_{116}N_{12}O_{13}Si$ $(M+H)^+$: 1539.8476, found: 1539.8458.

Synthesis of 10. A 1 M tetra-*n*-butylammonium fluoride solution in tetrahydrofuran (0.45 mL, 0.45 mmol) was added to a solution of **3** (204 mg, 0.124 mmol) in dry tetrahydrofuran (1.4 mL) under N_2, and stirred for 23 h at 25°C. The reaction mixture was quenched with a 5% aqueous citric acid solution and extracted with dichloromethane. The organic layer was washed with water and brine, dried over magnesium sulfate and filtered. The solvent was removed in vacuo to give **10** (151 mg, 0.0981 mmol, 79%) as a yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.99 (br s, 1 H), 11.64 (br s, 1 H), 11.41 (br s, 1H), 10.44 (s, 1 H), 10.32 (d, *J* = 7.1 Hz, 1 H), 10.01 (d, *J* = 7.9 Hz, 1 H), 9.24 (s, 1 H), 8.87 (dd, *J* = 7.7, 1.0 Hz, 1 H), 8.77 (dd, *J* = 7.7, 1.0 Hz, 1 H), 8.73 (dd, *J* = 7.8, 1.1 Hz, 1 H), 8.68 (dd, *J* = 7.7, 1.0 Hz, 1 H), 8.06 (s, 1H), 7.96-7.90 (m, 3 H), 7.88 (dd, *J* = 8.5, 1.2 Hz, 1 H), 7.73 (s, 1 H), 7.71 (s, 1 H), 7.60 (t, *J* = 8.1 Hz, 1 H), 7.56 (s, 1H), 7.54-7.48 (m, 3 H), 5.10 (d, *J* = 8.2 Hz, 1 H), 5.05-4.79 (m, 3 H), 4.48-4.35 (m, 2 H), 4.26-3.97 (m, 8 H), 2.41-1.80 (m, 16 H), 1.39 (s, 9 H), 1.20 (d, *J* = 6.7 Hz, 3 H), 1.19 (d, *J* = 6.7 Hz, 3 H), 1.15 (d, *J* = 6.7 Hz, 6 H), 1.12-1.00 (m, 30 H), 0.96 (d, *J* = 6.7 Hz, 3 H), 0.95 (d, *J* = 6.7 Hz, 3 H); HRMS (ESI) calcd for $C_{85}H_{109}N_{12}O_{15}$ $(M-H)^-$: 1537.8135, found: 1537.8127.

Synthesis of hexadecapeptide 4. Dry *N,N*-diisopropylethylamine (0.09 mL, 0.529 mmol) was added to a solution of **10** (151 mg, 0.0981 mmol), HBTU (74 mg, 0.195 mmol) and HOBt (5 mg, 0.0370 mmol) in dry dimethylformamide (1 mL) under N_2. The mixture was stirred for 3 min at 25°C. Then, **9** (158 mg, 0.100 mmol) in dry dimethylformamide (1.5mL) was added and the mixture was stirred for 3 h at 25°C. The reaction was quenched with a 5% aqueous citric acid solution and extracted with dichloromethane. The organic layer was washed with aqueous saturated sodium hydrogen carbonate, water and brine, dried over magnesium sulfate and filtered. After the solvent was removed in vacuo, the residue was precipitated in ethyl acetate to give **4** (188 mg, 0.0614 mmol, 63%) as a brown solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.76-11.45 (m, 6 H), 10.48 (s, 2 H), 10.28-10.19 (m, 4 H), 9.99-9.90 (m, 2 H), 9.33 (br s, 1 H), 8.88-8.75 (m, 6 H), 8.74 (dd, *J* = 7.8, 1.0 Hz, 1 H), 8.70 (dd, *J* = 7.7, 0.8 Hz, 1 H), 7.95-7.74 (m, 14 H), 7.61-7.46 (m, 8 H), 5.13-4.78 (m, 8 H), 4.46-4.01 (m, 19 H), 2.50-1.83 (m, 32 H), 1.40 (s, 9 H), 1.15-1.00 (m, 98 H), 0.07 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3, 171.1, 170.9, 170.5, 170.4, 170.2, 166.8, 166.6, 166.5, 166.2, 165.8, 165.6, 164.1, 164.1, 164.0, 164.0, 164.0, 163.8, 163.4, 163.0, 156.4, 149.7, 149.5, 149.4, 147.6, 139.0, 138.7, 138.5, 138.4, 138.3, 138.3, 138.0, 135.7, 135.6, 135.4, 135.3, 135.2, 128.1, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 122.5, 122.5, 122.5, 122.5, 122.3, 122.3, 122.2, 118.3, 117.9, 117.8, 117.7, 117.6, 117.5, 116.3, 116.3, 116.1, 116.0, 116.0, 115.8, 101.2, 99.8, 99.7, 81.0, 77.6, 75.5, 75.4, 75.3, 64.4, 54.4, 41.3, 39.1, 38.7, 38.5, 38.4, 29.8, 28.5, 28.5, 28.4, 28.4, 28.4, 28.3, 28.3, 25.4, 25.3, 25.3, 25.3, 25.2, 25.2, 25.0, 23.5, 23.3, 23.3, 23.1, 23.0, 22.4, 22.2, 22.2, 22.2, 22.1, 22.0, 19.4, 19.4, 19.4, 19.4, 19.3, 19.3, 17.7, -1.3; HRMS (MALDI-TOF) calcd for $C_{170}H_{222}N_{24}NaO_{27}Si$ $(M+Na)^+$: 3082.6403, found: 3082.6280.

X-ray Crystallography (rac-(LQ)$_4$)

Data collections were performed on a Bruker Apex II Ultra diffractometer equipped with CCD area detector and fine-focus rotating anode at the copper k_α wavelength (1.54178 Å) at 120 K. The crystal was mounted on MicroMounts™ after quick soaking on Paratone-N oil from Hampton research and flash-frozen for the structure at 120 K. The crystal structure of **rac-(LQ)$_4$** was solved by direct methods SHELXS-97 (G. M. Sheldrick, Acta Cryst. A64, 112–122, 2008). The structure was refined by SHELXL-2013 (G. M. Sheldrick, 2013). Full-matrix least-squares refinement was performed on F^2 for all unique reflections with anisotropic displacement parameters for non-hydrogen atoms. The positions of all hydrogen atoms were calculated based on geometrical adequacies. Data statistics are reported in Table S1 and in the cif files.

An iso-butyl group of the molecule is disordered into two positions (C56A–C59A and C56B–C59B). The occupancies of the disordered atoms were refined. The SQUEEZE (Spek, A. L. *J. Appl. Cryst*, 2003, 36, 7-13.) procedure was used to take into account the electron density in the potential solvent area for the crystal structure of **rac-(LQ)$_4$**, which resulted in an electrons count of 1024 within a volume of 4035 Å^3 in the unit cell; most probably the cavities are partly occupied by disordered solvent molecules.

Table S1. Crystallographic data for **(LQ)$_4$**.

Solvent/precipitant	$CHCl_3$ / *n*-hexane	T/K	120
Formula	$C_{90}H_{122}N_{12}O_{15}Si$	ρ/g cm^{-3}	0.892
M	1640.08	Shape and colour	Plate, colorless
Crystal system	monoclinic	size (mm)	0.20×0.10×0.03
Z	4	λ/Å	1.54178
Space group	$P2_1/n$	μ/mm^{-1}	0.582
a/Å	16.9924(7)	Absorption correction	empirical
b/Å	27.8784(11)	Collected reflections	56324
c/Å	26.0023(10)	unique data [*Fo*>2 σ*Fo*)]	20816
α/°	90.00	R_{int} %	0.0904
β/°	97.315(3)	parameters/restraints	1125/102
γ/°	90.00	R_1, wR_2 ($I > 2\sigma(I)$)	0.1210, 0.3059
U/Å^3	12217.6(8)	goodness of fit	0.845

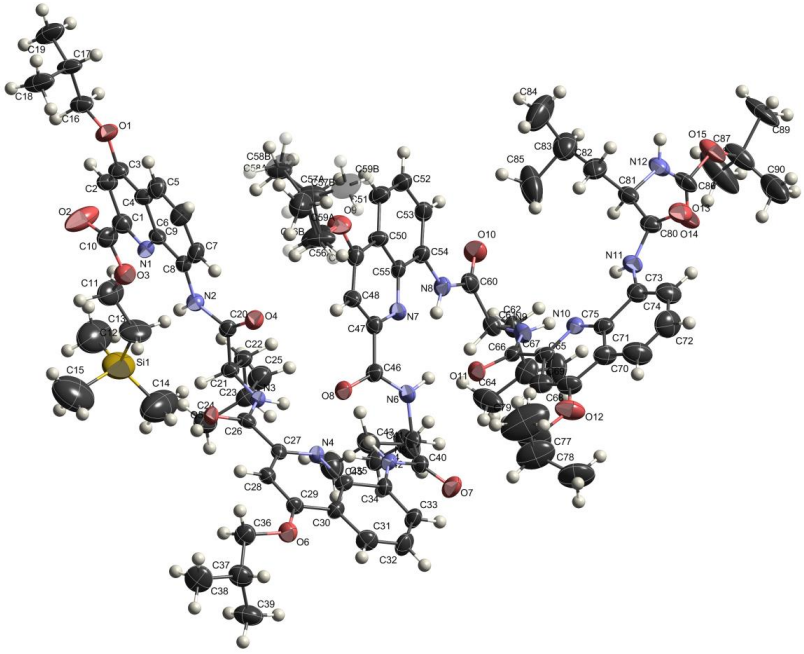


Figure S1. Thermal ellipsoid model of crystal **rac-(LQ)$_4$**. The ellipsoids of non-hydrogen atoms are drawn at the 30 % probability level while isotropic hydrogen atoms are represented by spheres of arbitrary size. The labels of hydrogen atoms are omitted for clarity. Disordered atoms are indicated and colored transparently.

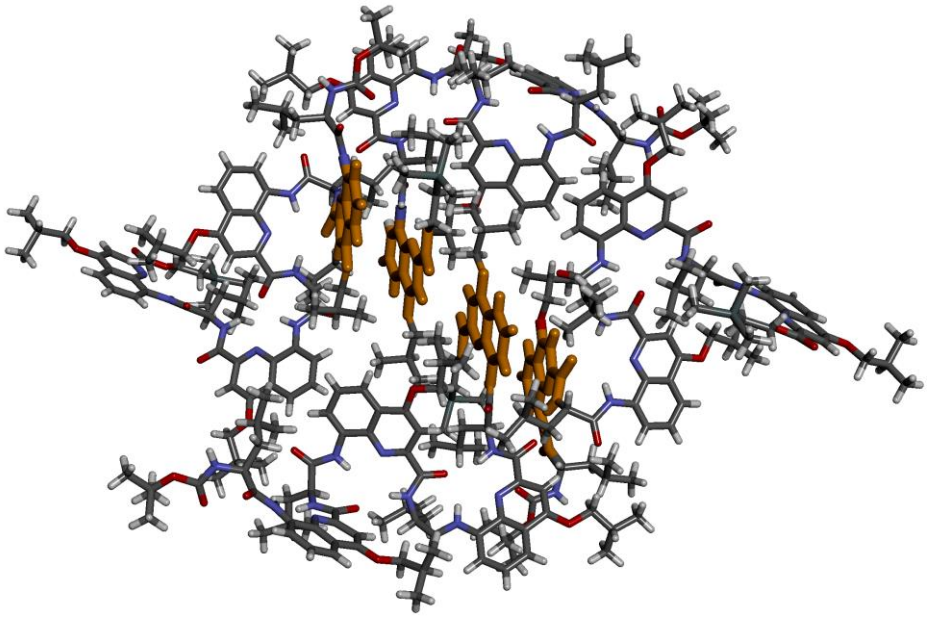


Figure S2. View down the *a* axis of an entire unit cell of the crystal structure of ***rac*-(LQ)$_4$**. A stack of four terminal quinolines, one from each of the molecules contained in the unit cell, is shown as thick sticks.

4. Variable temperature UV and CD spectra

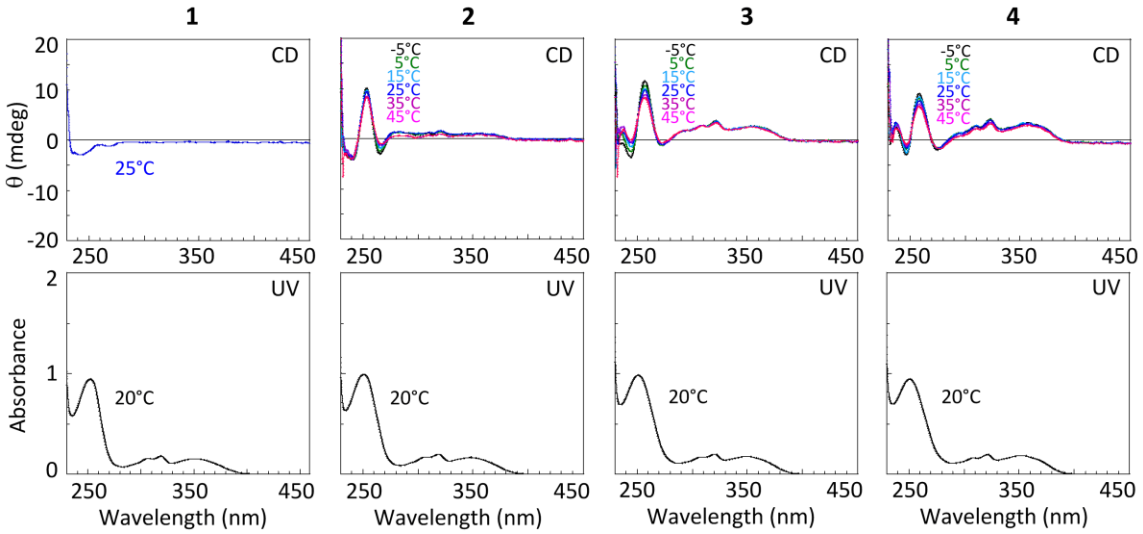


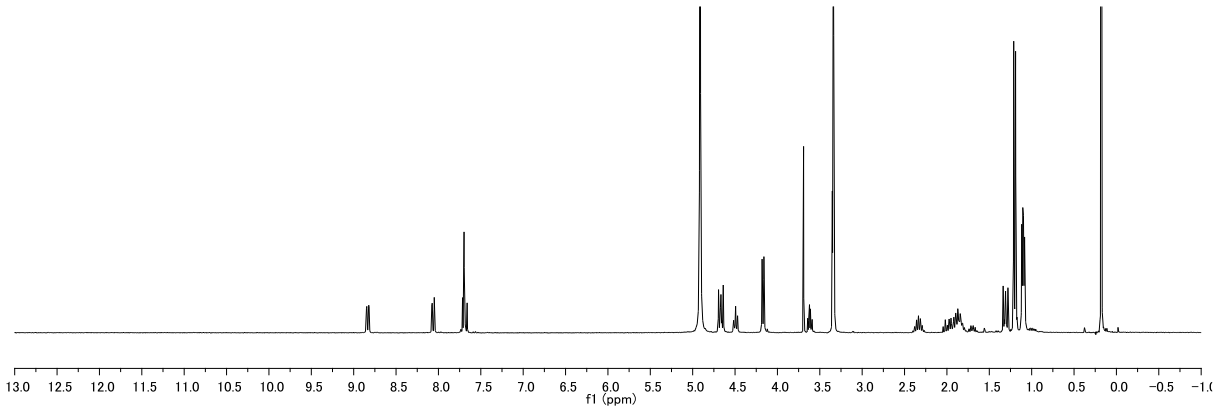
Figure S3. UV (20°C) and CD (-5-45°C) spectra of **1**-**4** in $CHCl_3$. (Concentrations: **1**: 1.2×10^{-4} M, **2**: 6.0×10^{-5} M, **3**: 3.0×10^{-5} M, **4**: 1.5×10^{-5} M).

5. References

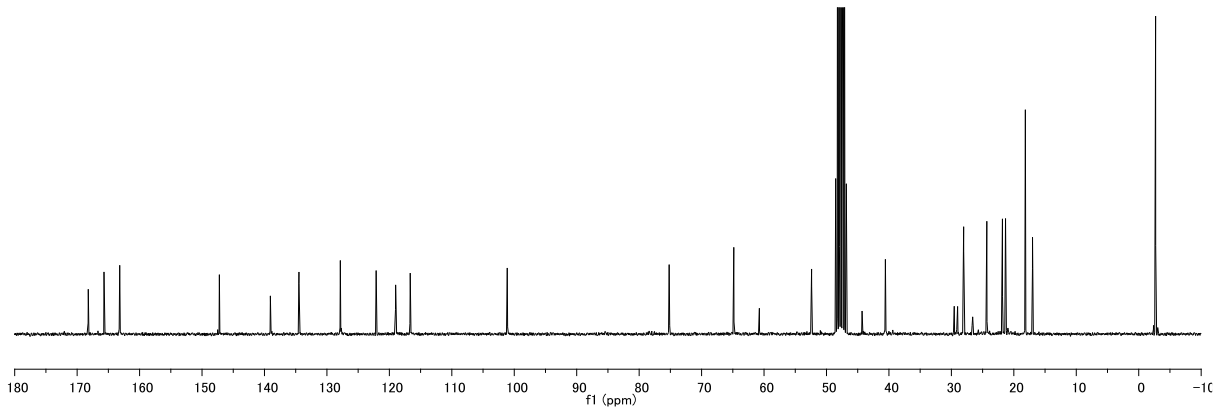
1. Kudo, M.; Maurizot, V.; Kauffmann, B.; Tanatani, A.; Huc, I. *J. Am. Chem.Soc.* **2013**, *135*, 9628-9631.

6. ^{1}H and ^{13}C NMR spectra

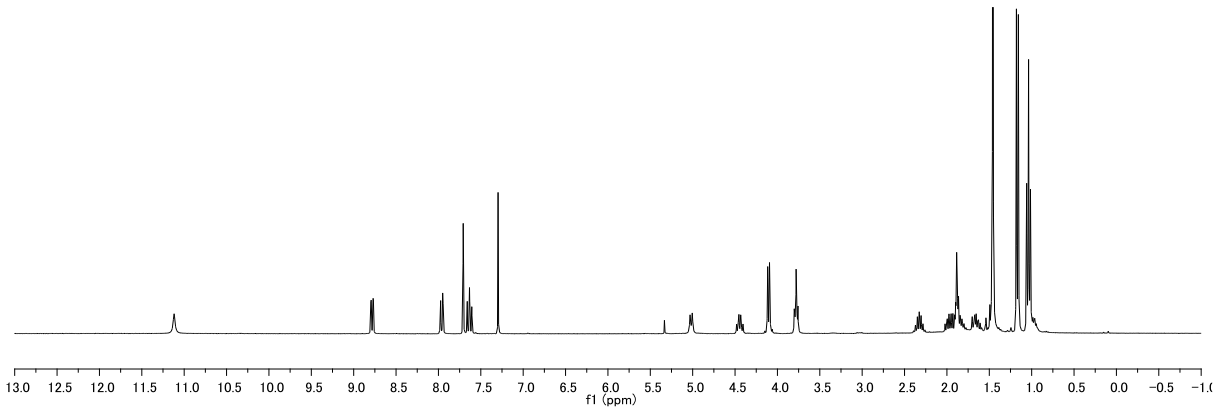
^{1}H NMR spectrum of **5** (300 MHz, CD_3OD)



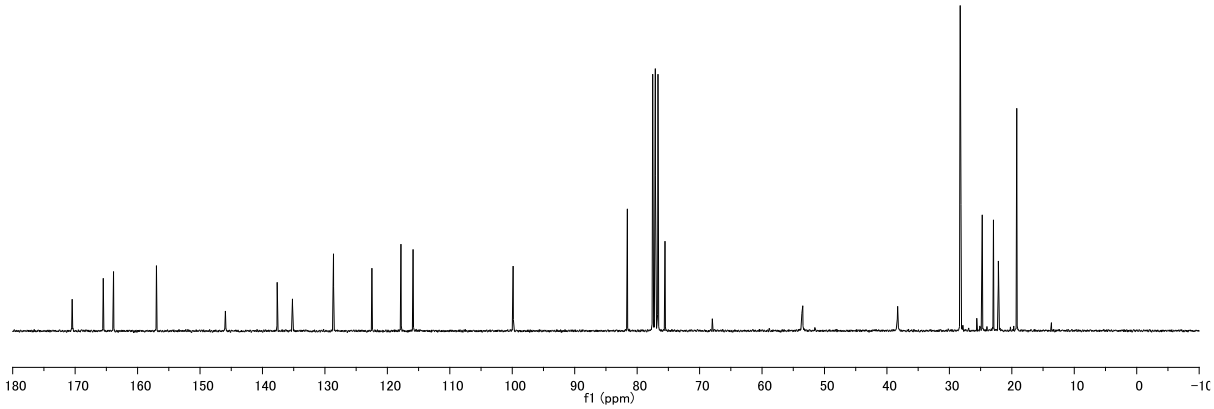
^{13}C NMR spectrum of **5** (75 MHz, $CDCl_3$)



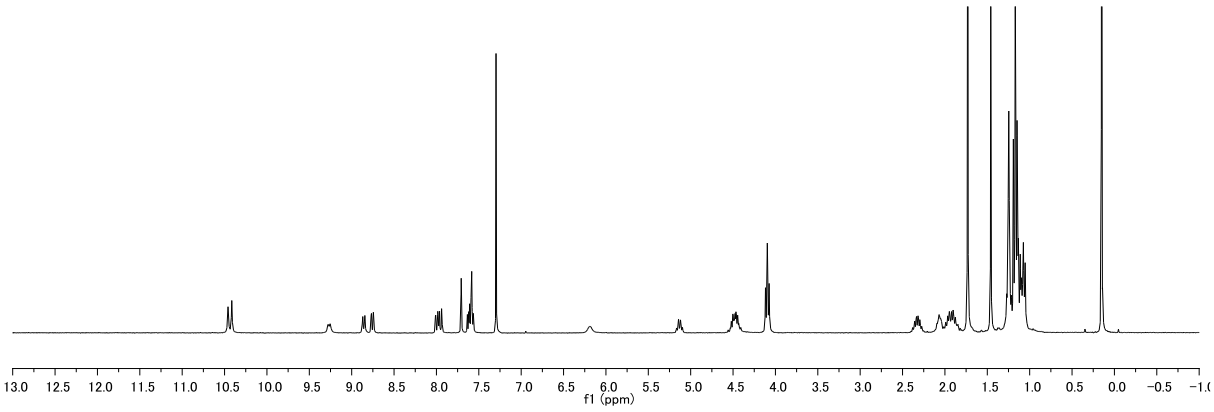
^{1}H NMR spectrum of **6** (300 MHz, $CDCl_3$)



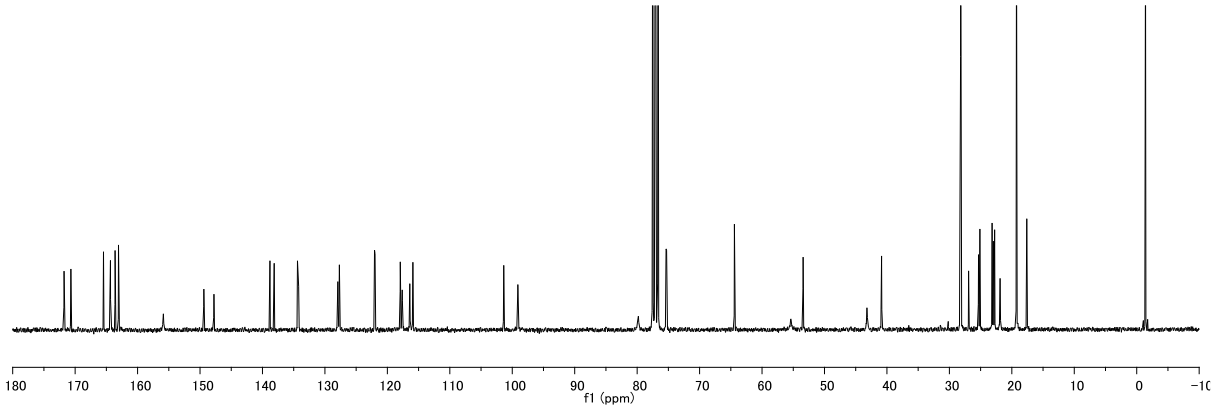
^{13}C NMR spectrum of **6** (75 MHz, $CDCl_3$)



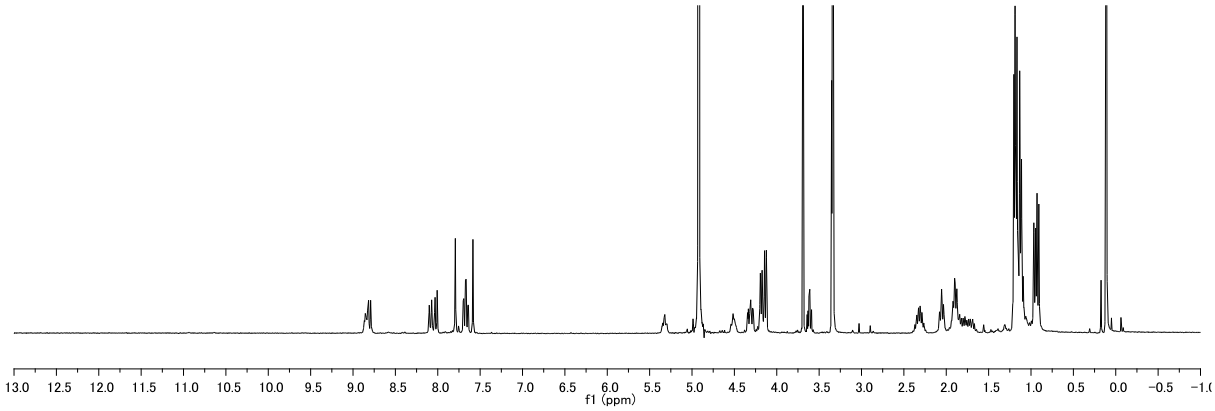
^{1}H NMR spectrum of **2** (300 MHz, $CDCl_3$)



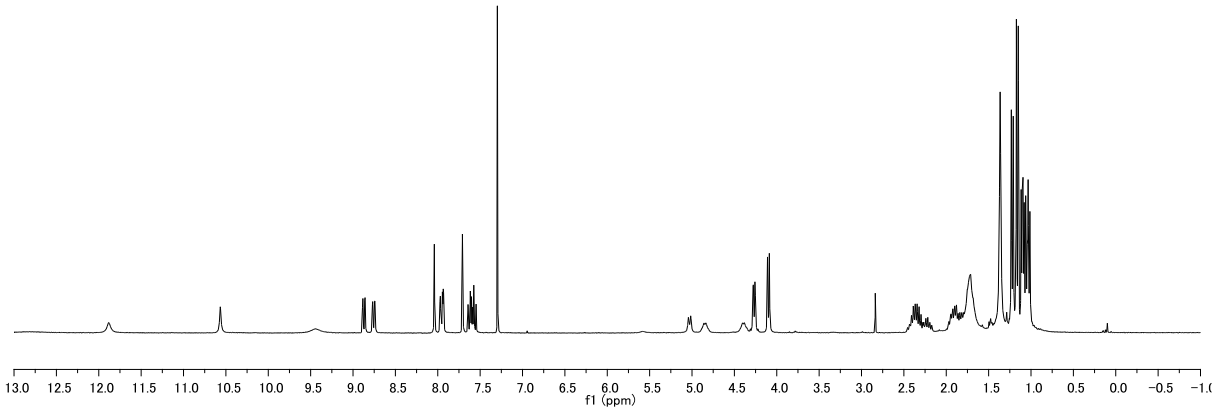
^{13}C NMR spectrum of **2** (75 MHz, $CDCl_3$)



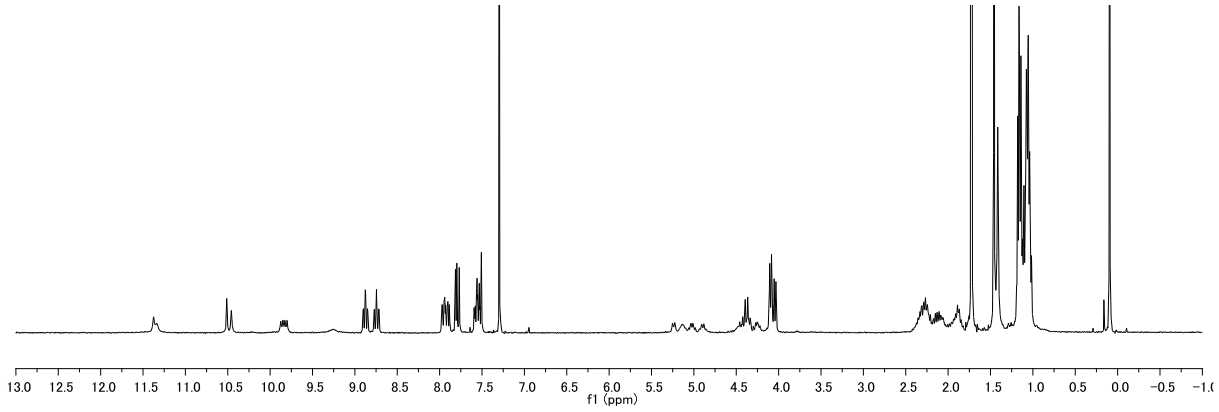
^{1}H NMR spectrum of **7** (300 MHz, CD_3OD)



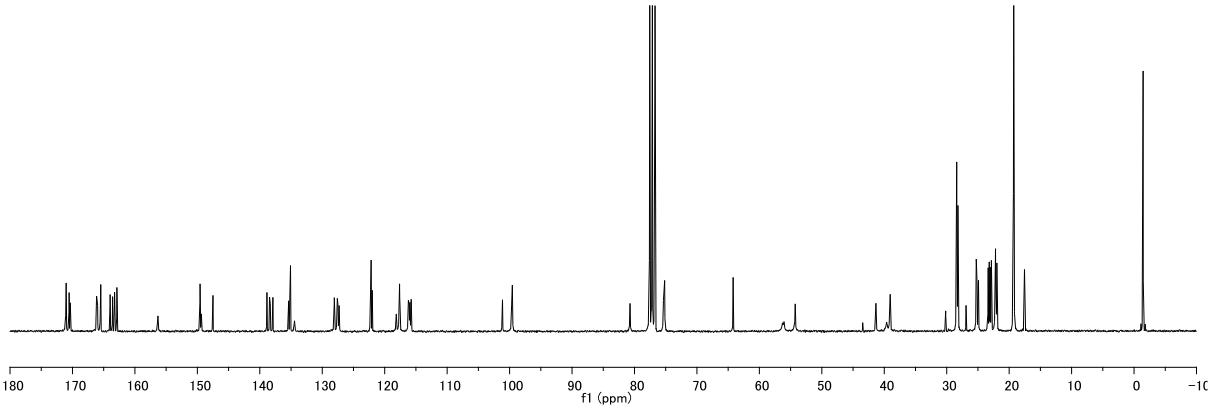
^{1}H NMR spectrum of **8** (300 MHz, $CDCl_3$)



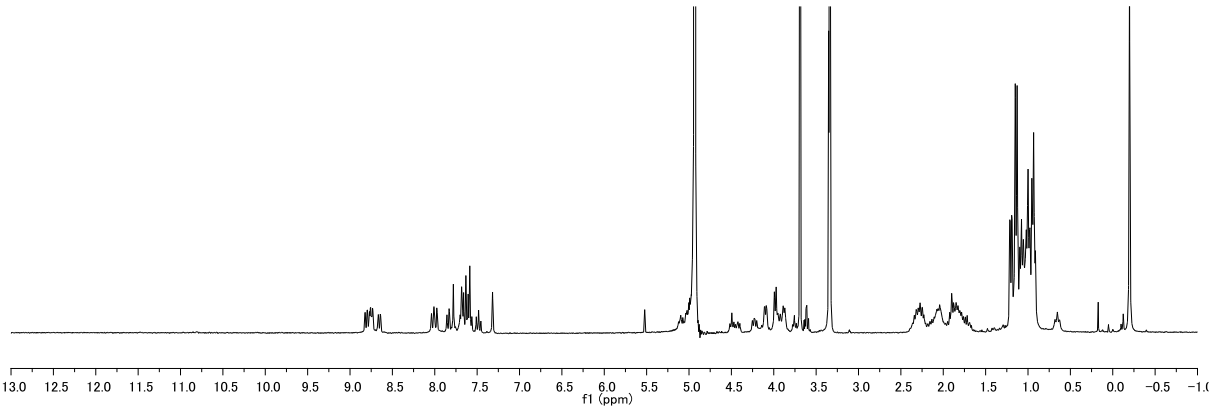
^{1}H NMR spectrum of **3** (300 MHz, $CDCl_3$)



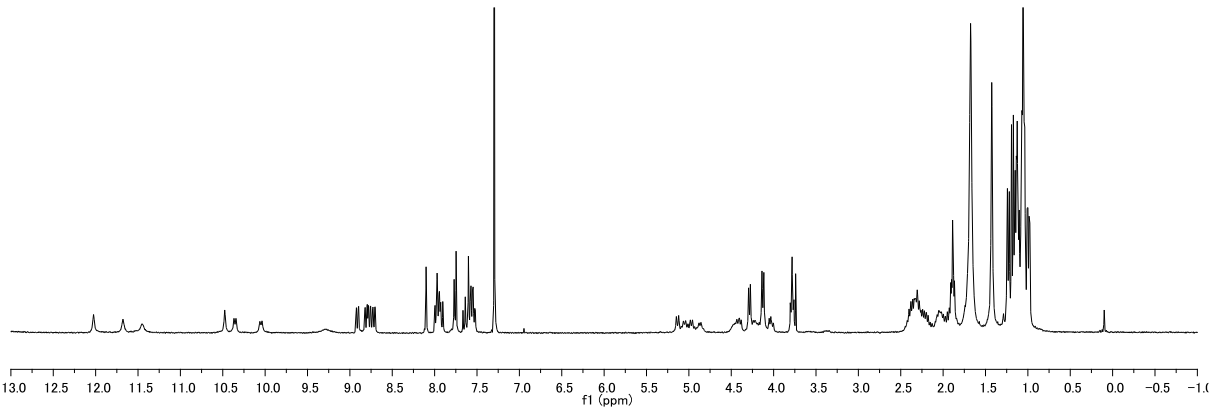
^{13}C NMR spectrum of **3** (75 MHz, $CDCl_3$)



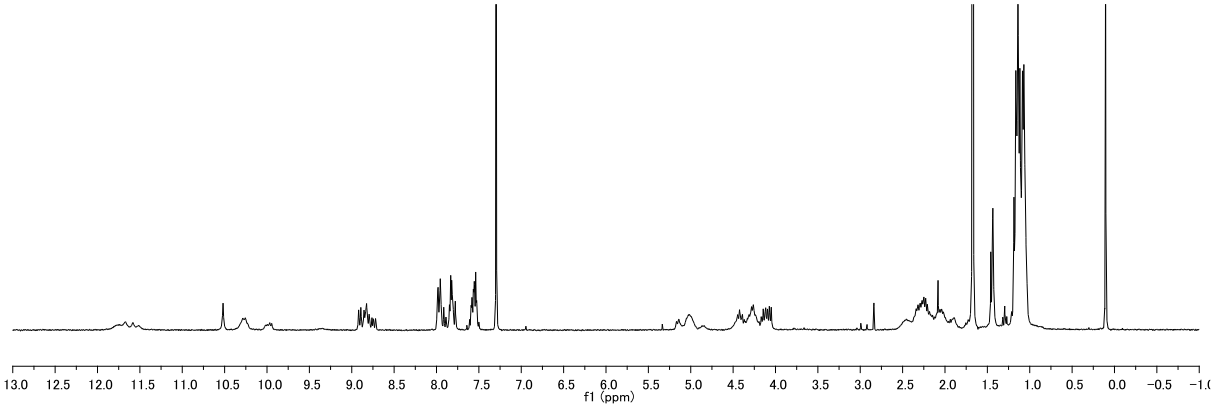
^{1}H NMR spectrum of **9** (300 MHz, $CDCl_3$)



^{1}H NMR spectrum of **10** (300 MHz, $CDCl_3$)



^{1}H NMR spectrum of **4** (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of **4** (150 MHz, $CDCl_3$)