

Supporting Information For:

Helicity of a polyacetylene directed by molecular recognition of biscalixarene and fullerene

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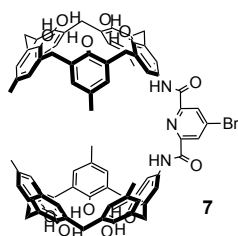
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General: All reagents and solvents were commercial reagent grade and were used without further purification unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded on a Varian mercury-300 spectrometer and JEOL JNM-ECA600 spectrometer, and chemical shifts were reported on the delta scale in ppm relative to residual chloroform ($\delta = 7.26$ and 77.0 for ^1H and ^{13}C , respectively). UV/vis absorption spectra were recorded on a JASCO V-560 spectrometer. High resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL hybrid FTMS by electron spray ionization (ESI) methods. Melting points (M.p.) were measured with a Yanagimoto micro melting point apparatus. Infrared (IR) spectra were recorded on a JASCO FT/IR-4600 spectrometer with ZeSe ATR accessory. Preparative separations were performed by silica gel gravity column chromatography (Silica Gel 60 N (spherical, neutral)). Recycling preparative GPC-HPLC separations were carried out on JAI LC-908s using preparative JAIGEL-2H, 2H, 1H columns in series. Size exclusion chromatogram was recorded on Shimadzu LC-20AC with CTO-20AC accessory and TOSOH UV-8011 detector using preparative Shodex GPC-K-804, K-803, K-802.5 columns in series. The number-average molecular weights (M_n) of the poly-**1** were determined by the size exclusion chromatography (SEC) based on polystyrene standards in chloroform. **4**^[1], **5**^[2], **6**^[3], and (*R*)-, (*S*)-**11**^[4] were synthesized according to reported methods.

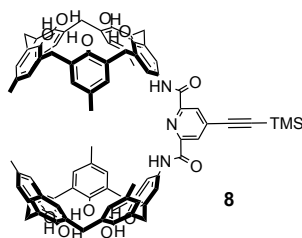


Synthesis of bis(calix[5]arene) monobromide **7**:

To a solution of 4-bromo-2,6-pyridinedicarbonyl dichloride **5** (138 mg, 0.488 mmol) in dry THF (4.9 mL) was added amino calix[5]arene **6** (701 mg, 1.17 mmol) in dry THF (4.9 mL). After being stirred for 22 h at room temperature under an argon atmosphere, the reaction mixture was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (0%–5% THF in benzene, eluent) to afford desired product **7** (498 mg, 71%) as a white solid.

Compound data for **7**:

M.p. >280 °C (decomp.); ^1H NMR (600 MHz, CDCl_3): δ 9.28 (s, 2H), 9.09 (s, 2H), 8.78 (s, 4H), 8.76 (s, 4H), 8.60 (s, 2H), 7.60 (s, 4H), 6.95–7.00 (m, 16H), 3.80 (br, 20H), 2.23 (s, 12H), 2.14 (s, 12H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ 160.3, 150.3, 148.0, 147.8, 147.8, 130.8, 130.7, 130.2, 129.9, 129.7, 129.7, 129.6, 128.9, 127.6, 126.6, 126.5, 126.4, 125.8, 122.2, 31.5, 31.3, 20.4 ppm; FTIR-ATR (neat): ν 3290, 3009, 2919, 2867, 1677, 1542, 1480, 1453, 1380, 1290, 1222, 1167, 1143, 1037, 910 cm^{-1} ; HRMS (ESI^+): calcd for $\text{C}_{85}\text{H}_{78}\text{O}_{12}\text{N}_3\text{BrNa}$ m/z 1434.46611 $[\text{M}+\text{Na}]^+$, found m/z 1434.46727.

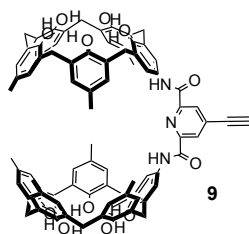


Synthesis of TMSacetyl biscalic[5]arene **8**:

To a solution of **7** (140 mg, 98 μmol) and CuI (1.9 mg, 1.0 μmol) in dry DMF (1.0 mL) was added dry (*i*-Pr)₂NH (1.0 mL, 7.2 mmol). After being stirred for 15 min at room temperature under an argon atmosphere, TMSA (0.30 mL, 1.2 mmol) was added to the solution. The resulting mixture was further stirred for 15 min, and then Pd(PPh₃)₂Cl₂ (14 mg, 20 μmol) was added in the dark. After being stirred for 1.5 h at room temperature under an argon atmosphere in the dark, the reaction mixture was diluted with CH₂Cl₂. The organic layer was passed through florisil, washed with saturated aqueous NH₄Cl and saturated aqueous NaCl, dried over Na₂SO₄, and then concentrated *in vacuo*. The crude product was purified by GPC to give desired product **8** (124 mg, 87 %) as a yellow solid.

Compound data for **8**:

M.p. >270 °C (decomp.); ¹H NMR (300 MHz, CDCl₃): δ 9.27 (s, 2H), 9.08 (s, 2H), 8.79 (s, 4H), 8.76 (s, 4H), 8.38 (s, 2H), 7.59 (s, 4H), 6.99 (s, 4H), 6.97 (s, 4H), 6.93 (s, 4H), 6.91 (s, 4H), 3.79 (br, 20H), 2.23 (s, 12H), 2.10 (s, 12H), 0.29 (s, 9H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 161.0, 149.6, 147.8, 147.7, 135.0, 130.8, 130.6, 130.4, 129.8, 128.6, 129.6, 127.6, 127.3, 126.5, 126.4, 125.7, 121.7, 103.9, 100.7, 31.5, 31.3, 20.4, 20.3, -0.5 ppm; FTIR-ATR (neat): ν 3290, 3011, 2920, 2868, 1677, 1600, 1542, 1480, 1453, 1380, 1290, 1222, 1167, 1143, 1037, 999, 961 cm⁻¹; HRMS (ESI⁺) calcd for C₉₀H₈₈O₁₂N₃Si m/z 1430.61313 [M+H]⁺, found m/z 1430.61511.

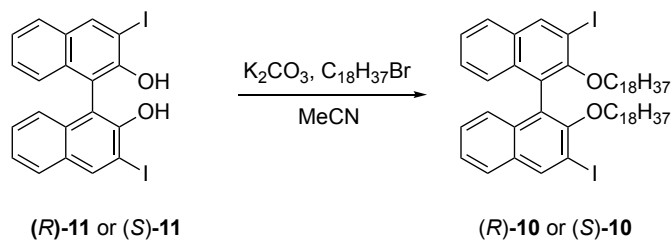


Synthesis of ethynyl biscalix[5]arene **9**:

TBAF (1.0 mL, 1.0 mol L⁻¹ THF solution) was added to a solution of **8** (563 mg, 0.409 mmol) in DMF (4 mL). After being stirred for 15 min at room temperature under an open-air atmosphere, the resulting mixture was diluted with CH₂Cl₂. The organic layer was washed with saturated aqueous NaCl, dried over Na₂SO₄, and then concentrated in vacuo to yield desired product **9** (523 mg, 98%) as a yellow solid without further purification.

Compound data for **9**:

M.p. >260 °C (decomp.); ¹H NMR (300 MHz, CDCl₃): δ 9.24 (s, 2H), 9.09 (s, 2H), 8.79 (s, 4H), 8.76 (s, 4H), 8.44 (s, 2H), 7.58 (s, 4H), 6.98 (s, 4H), 6.97 (s, 4H), 6.95 (s, 4H), 6.93 (s, 4H), 3.79 (br, 20H), 3.48 (s, 1H), 2.22 (s, 12H), 2.11 (s, 12H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 160.8, 149.7, 147.9, 147.8, 147.7, 134.2, 130.8, 130.6, 130.3, 129.8, 129.7, 127.6, 126.5, 126.5, 126.4, 125.7, 121.8, 84.9, 79.8, 31.5, 31.3, 20.4, 20.4 ppm; FTIR-ATR (neat): ν 3287, 3009, 2917, 2865, 1680, 1601, 1540, 1480, 1454, 1379, 1288, 1222, 1034, 995, 909 cm⁻¹; HRMS (ESI⁺) calcd for C₈₇H₇₉O₁₂N₃Na *m/z* 1380.55560 [M+Na]⁺, found *m/z* 1380.55614.



Scheme S2. Synthesis of (*R*)- and (*S*)-**10**.

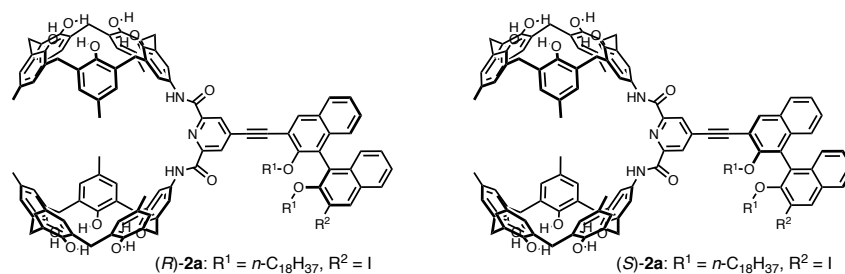


(S)-10

Compound data for (*R*)-**10**:

Compound data for (S)-2,2'-Dioctadetoxy-3,3'-diiodo-1,1'-binaphthalene ((S)-**10**):

$[\alpha]^{25}_{\text{D}} = +43 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ (c 0.10 g dL⁻¹); ¹H NMR (300 MHz, CDCl₃): δ 8.49 (s, 2H), 7.77 (d, 2H, $J = 8.1$ Hz), 7.39 (t, 2H, $J = 8.1$ Hz), 7.26 (t, 2H, $J = 8.1$ Hz), 7.11 (d, 2H, $J = 8.1$ Hz), 3.82 (m, 2H), 3.30 (m, 2H), 0.80–1.33 (m, 64H), 0.88 (t, 6H, $J = 7.2$ Hz) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 154.1, 139.5, 133.9, 132.0, 126.8, 125.9, 125.7, 125.4, 93.0, 73.6, 31.9, 29.7, 29.7, 29.7, 29.7, 29.5, 29.5, 29.4, 29.0, 25.4, 22.7, 14.1 ppm; FTIR-ATR (neat): ν 2920, 2851, 1562, 1496, 1462, 1414, 1374, 1343, 1226, 1039, 1012, 967 cm⁻¹; HRMS (ESI⁺) calcd for C₅₆H₈₄I₂O₂Na m/z 1065.44529 [M+Na]⁺, found m/z 1065.44676.



Synthesis of calix[5]arene mono iodide (**S**)-**2a**:

To a solution of (**S**)-**10** (52 mg, 50 μ mol) in DMF (0.5 ml) was added CuI (1.0 mg, 5.3 μ mol) and dry diisopropylamine (0.50 ml, 3.6 mmol). After being stirred for 15 min at room temperature under an argon atmosphere, **9** (100 mg, 75 μ mol) was added. After being stirred for 15 min at room temperature under argon atmosphere, Pd(dppf)Cl₂ (7.3 mg, 10 μ mol) was added to the resultant solution. After being stirred at 60 °C for 3 h under an argon atmosphere in the dark, the reaction mixture was passed through celite and diluted with dichloromethane. The organic layer was washed with saturated aqueous NH₄Cl and saturated aqueous NaCl, dried over Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by GPC and column chromatography on silica gel (3% THF in toluene, eluent) to give a desired product **2a** (18 mg, 15%) as a yellow solid.

(**R**)-**2a** (a yellow solid, 10 % yield) was synthesized by the same procedure as that used for synthesis of (**R**)-**2a**.

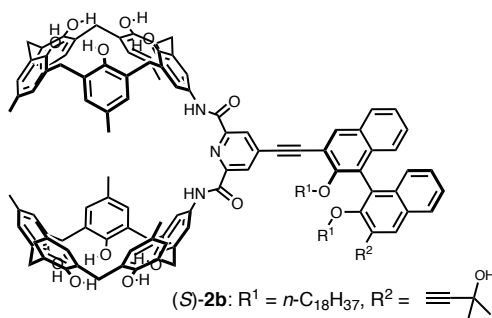
Compound data for (**S**)-**2a**:

M.p. >240 °C (decomp.); [α]_D²⁵ = +42 cm³ g⁻¹ dm⁻¹ (c 0.10 g dL⁻¹); ¹H NMR (600 MHz, CDCl₃): δ 9.22 (s, 2H), 9.10 (s, 2H), 8.79 (s, 4H), 8.78 (s, 4H), 8.54 (s, 2H), 8.51 (s, 1H), 8.28 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.59 (s, 4H), 7.45 (t, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 8.2 Hz, 1H), 7.27 (m, 1H), 7.16 (m, 2H), 6.91–7.03 (m, 16H), 4.10 (m, 1H), 3.81 (m, 1H), 3.78 (br, 20H), 3.75 (m, 1H), 3.40 (m, 1H), 2.23 (s, 12H), 2.14 (s, 12H), 0.91–1.41 (m, 64 H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (150 MHz, CDCl₃): δ 160.9, 155.2, 154.1, 149.6, 147.9, 147.8, 147.8, 139.5, 135.6, 134.6, 134.0, 132.2, 130.8, 130.6, 130.4, 129.9, 129.7, 128.1, 128.1, 127.6, 127.1, 126.9, 126.8, 126.6, 126.5, 126.4, 125.8, 125.8, 125.7, 125.5, 125.4, 122.1, 116.1, 94.7, 93.0, 89.7, 74.3, 73.7, 31.9, 31.9, 31.6, 31.4, 30.0, 29.8, 29.7, 29.7, 29.5, 29.5, 29.5, 29.4, 29.3, 29.1, 29.0, 25.5, 25.4, 22.7, 22.7, 20.4, 14.1, 14.1 ppm; FTIR-ATR (neat): ν 3255, 2917, 2850, 2210, 1678, 1599, 1536, 1480, 1453, 1374, 1288, 1220 cm⁻¹; HRMS (ESI⁺) calcd for C₁₄₃H₁₆₃N₃O₁₄I m/z 2273.11743 [M+H]⁺, found m/z 2273.11877.

Compound data for (**R**)-**2a**:

M.p. >240 °C (decomp.); [α]_D²⁵ = -42 cm³ g⁻¹ dm⁻¹ (c 0.10 g dL⁻¹); ¹H NMR (600 MHz, CDCl₃): δ 9.22 (s, 2H), 9.10 (s, 2H), 8.79 (s, 4H), 8.78 (s, 4H), 8.54 (s, 2H), 8.51 (s, 1H), 8.27 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H),

7.59 (s, 4H), 7.44 (t, $J = 8.2$ Hz, 1H), 7.40 (t, $J = 8.2$ Hz, 1H), 7.32 (t, $J = 8.2$ Hz, 1H), 7.27 (m, 1H), 7.16 (m, 2H), 6.95–7.01 (m, 16H), 4.10 (m, 1H), 3.82 (m, 1H), 3.78 (br, 20H), 3.75 (m, 1H), 3.40 (m, 1H), 2.23 (s, 12H), 2.14 (s, 12H), 0.91–1.40 (m, 64 H), 0.87 (t, $J = 7.1$ Hz, 3H), 0.84 (t, $J = 7.1$ Hz, 3H) ppm; FTIR-ATR (neat): ν 3252, 2917, 2849, 2210, 1679, 1599, 1536, 1480, 1453, 1375, 1288, 1221 cm^{-1} ; HRMS (ESI⁺) calcd for C₁₄₃H₁₆₃N₃O₁₄I m/z 2273.11743 [M+H]⁺, found m/z 2273.12009.



Synthesis of calix[5]arene mono alcohol (S)-**2b**:

To solution of **2a** (18 mg, 8.1 μmol) in DMF (0.1 ml) was added CuI (0.20 mg, 1.1 μmol) and dry diisopropylamine (0.10 ml, 0.71 mmol). After being stirred for 15 min at room temperature under an argon atmosphere, 2-methyl-3-butyn-2-ol (1.4 μl , 24 μmol) was added. After being stirred for 15 min at room temperature under argon atmosphere, Pd(dppf)Cl₂ (1.2 mg, 1.6 μmol) was added to the resultant solution. After being stirred for 1 h at 60 °C under an argon atmosphere in the dark, the reaction mixture was passed through celite (dichloromethane, eluent) and diluted with dichloromethane. The organic layer was washed with saturated aqueous NH₄Cl and saturated aqueous NaCl, dried over Na₂SO₄, and concentrated *in vacuo*. The crude product was purified by GPC and column chromatography on silica gel (5% THF in toluene, eluent) to yield desired product **2b** (5.6 mg, 33 %) as a yellow solid.

Compound data for (S)-**2b**:

$[\alpha]_D^{25} = +43 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ (c 0.10 g dL⁻¹); ¹H NMR (600 MHz, CDCl₃): δ 9.23 (s, 2H), 9.10 (s, 2H), 8.80 (s, 4H), 8.79 (s, 4H), 8.55 (s, 2H), 8.26 (s, 1H), 8.09 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.60 (s, 4H), 7.43 (t, *J* = 8.2 Hz, 1H), 7.39 (t, *J* = 8.2 Hz, 1H), 7.30 (t, *J* = 8.2 Hz, 1H), 7.27 (m, 1H), 7.17 (m, 2H), 6.92–7.03 (m, 16H), 4.05 (m, 1H), 4.01 (m, 1H), 3.78 (br, 20H), 3.73 (m, 1H), 3.69 (m, 1H), 2.23 (s, 12H), 2.14 (s, 12H), 0.90–1.33 (m, 64 H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (150 MHz, CDCl₃): δ 160.9, 155.2, 155.1, 149.6, 147.9, 147.8, 147.8, 139.5, 135.6, 135.3, 134.8, 134.2, 133.8, 130.8, 130.6, 130.4, 130.0, 130.0, 129.9, 129.7, 128.1, 127.6, 127.1, 126.6, 126.5, 126.4, 125.8, 125.7, 125.4, 125.1, 124.8, 122.1, 117.2, 116.0, 97.7, 94.9, 89.5, 79.4, 74.3, 73.6, 65.8, 31.9, 31.9, 31.6, 31.4, 31.4, 31.3, 30.0, 30.0, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.5, 29.4, 29.3, 29.1, 29.0, 25.5, 25.5, 22.7, 22.6, 20.4, 14.1, 14.1 ppm; HRMS (ESI⁺) calcd for C₁₄₈H₁₇₀N₃O₁₅ *m/z* 2229.26265 [M+H]⁺, found *m/z* 2229.26357.

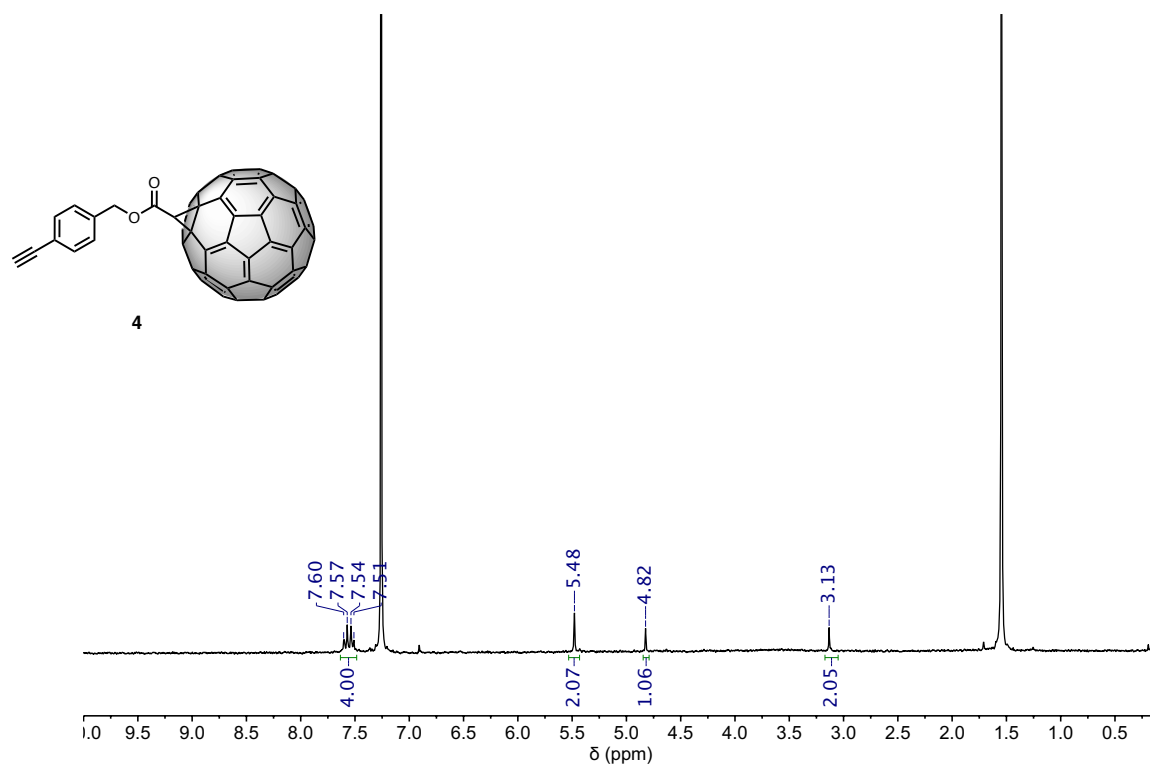


Figure S1. ¹H spectrum of **4** in chloroform-*d*.

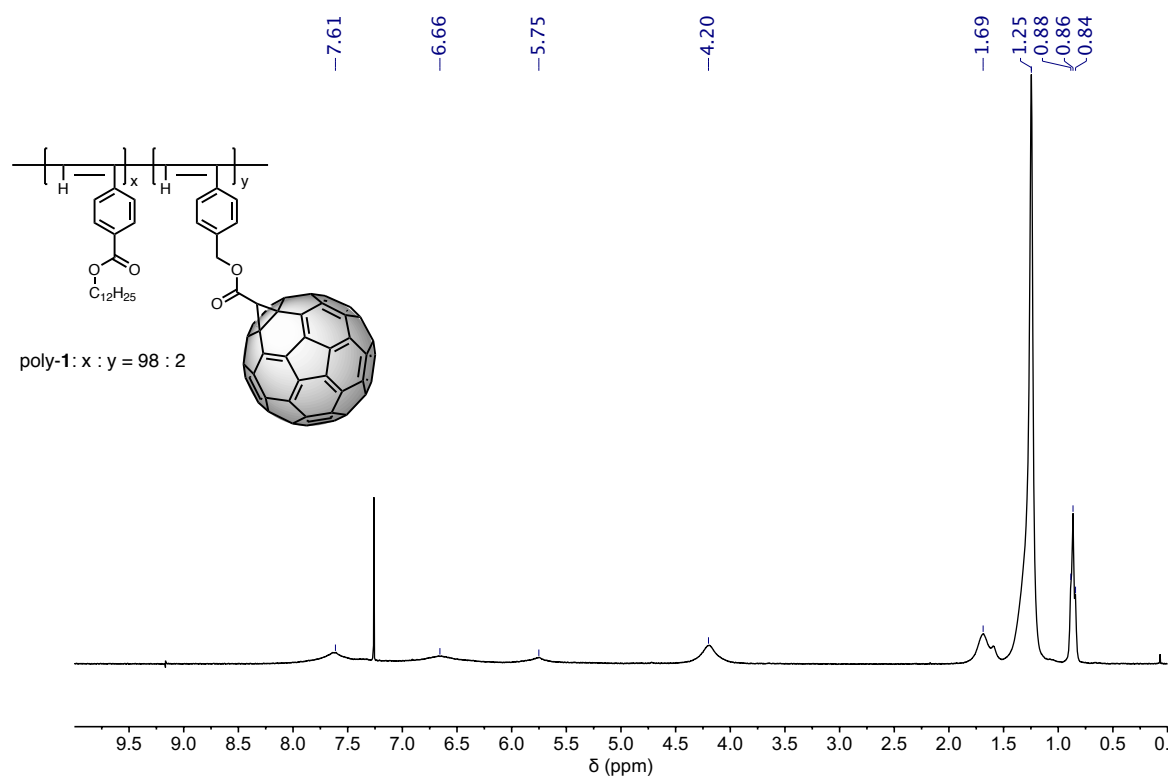


Figure S2. ¹H spectrum of **poly-1** in chloroform-*d*.

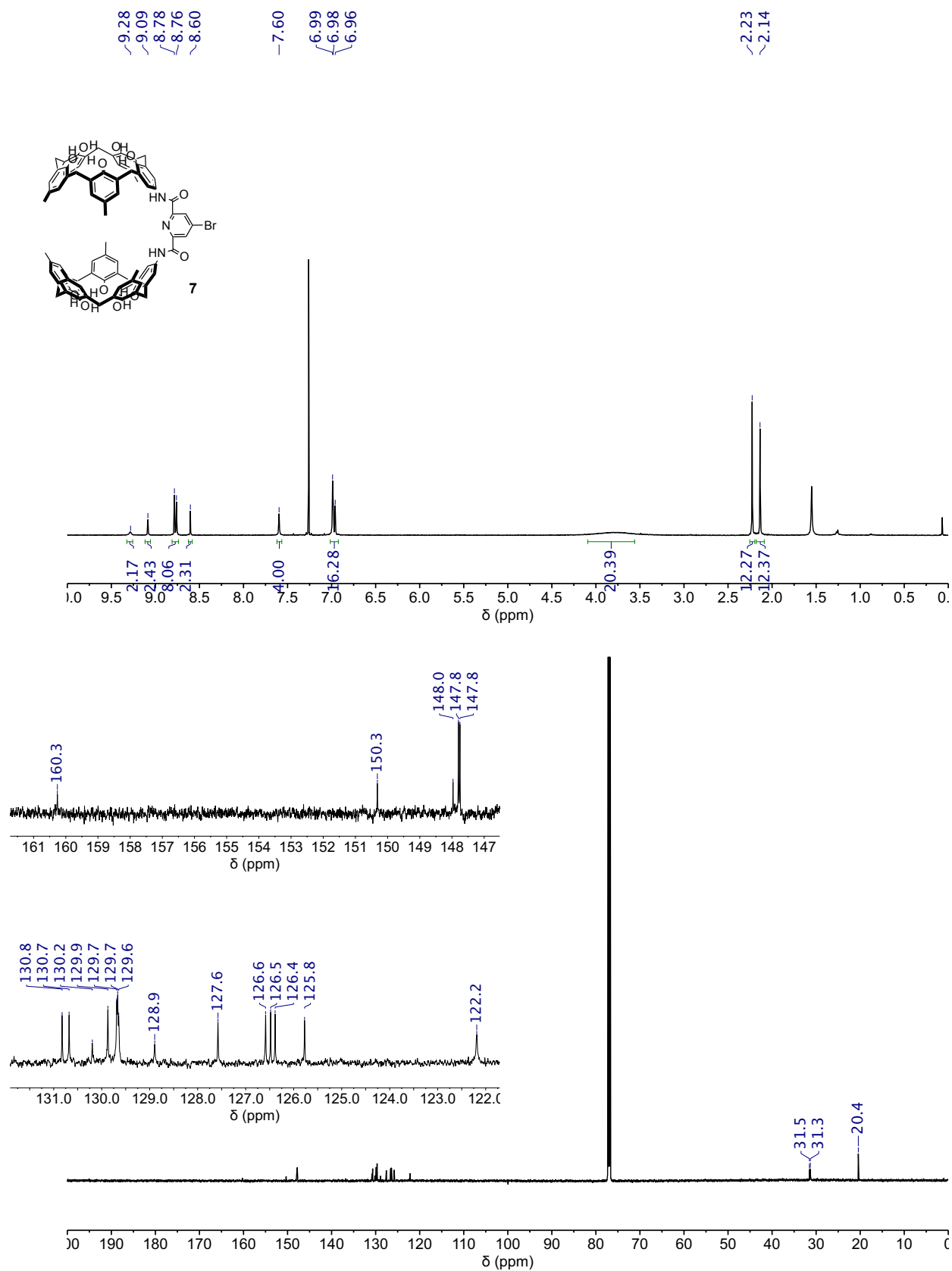


Figure S3. ¹H and ¹³C NMR spectra of **7** in chloroform-*d*.

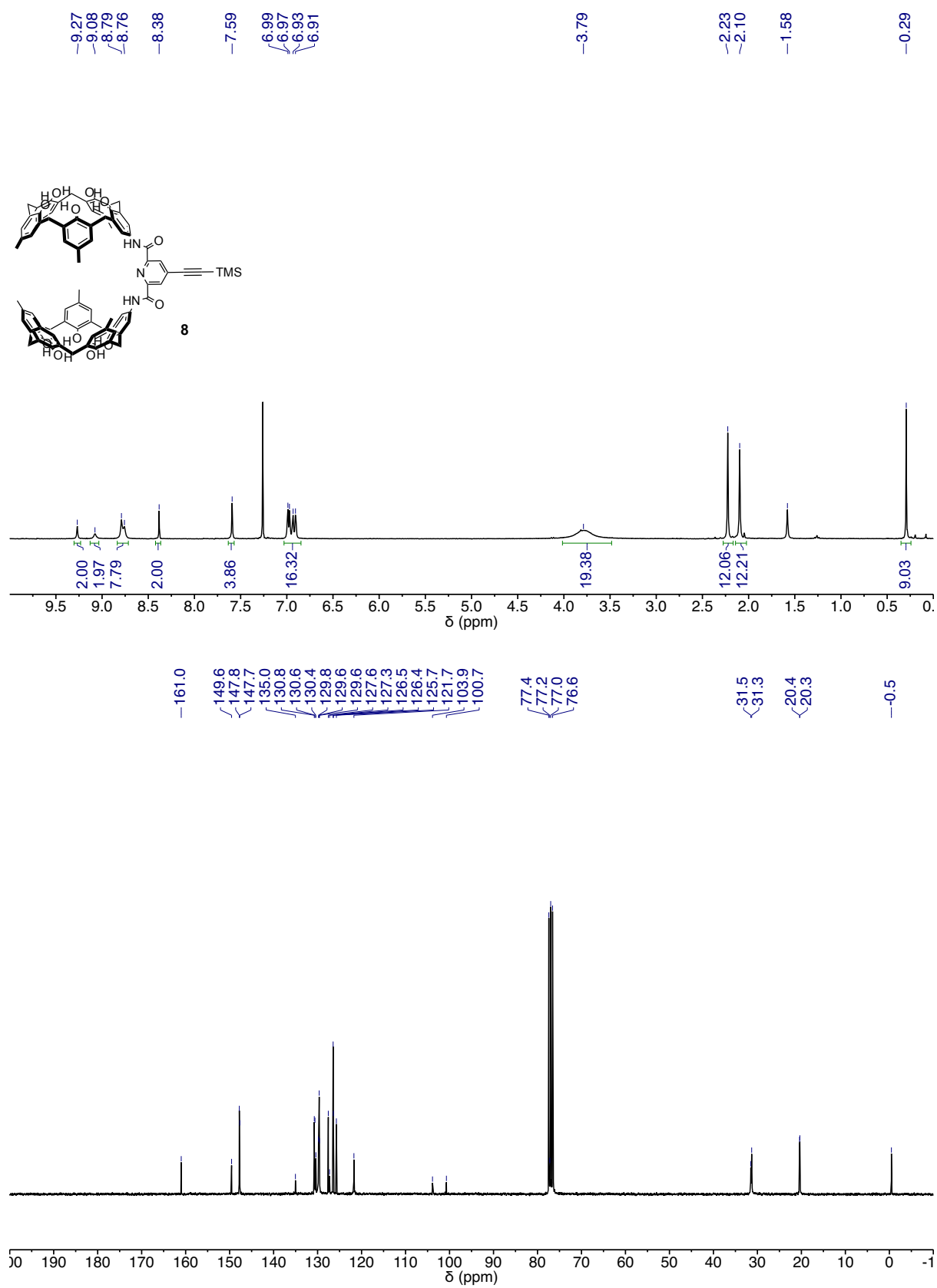


Figure S4. ¹H and ¹³C NMR spectra of **8** in chloroform-*d*.

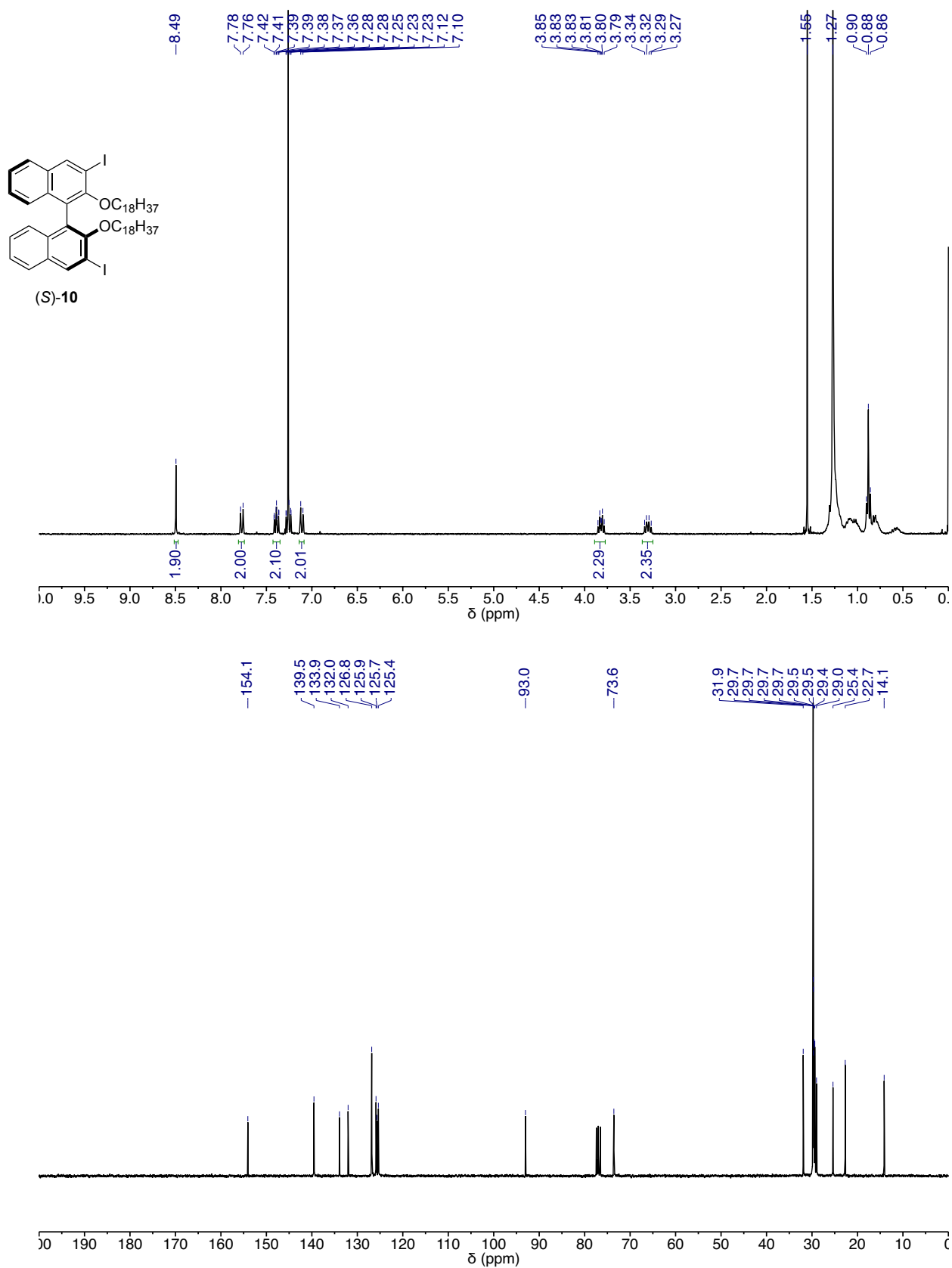


Figure S6. ^1H and ^{13}C NMR spectra of (S)-**10** in chloroform-*d*.

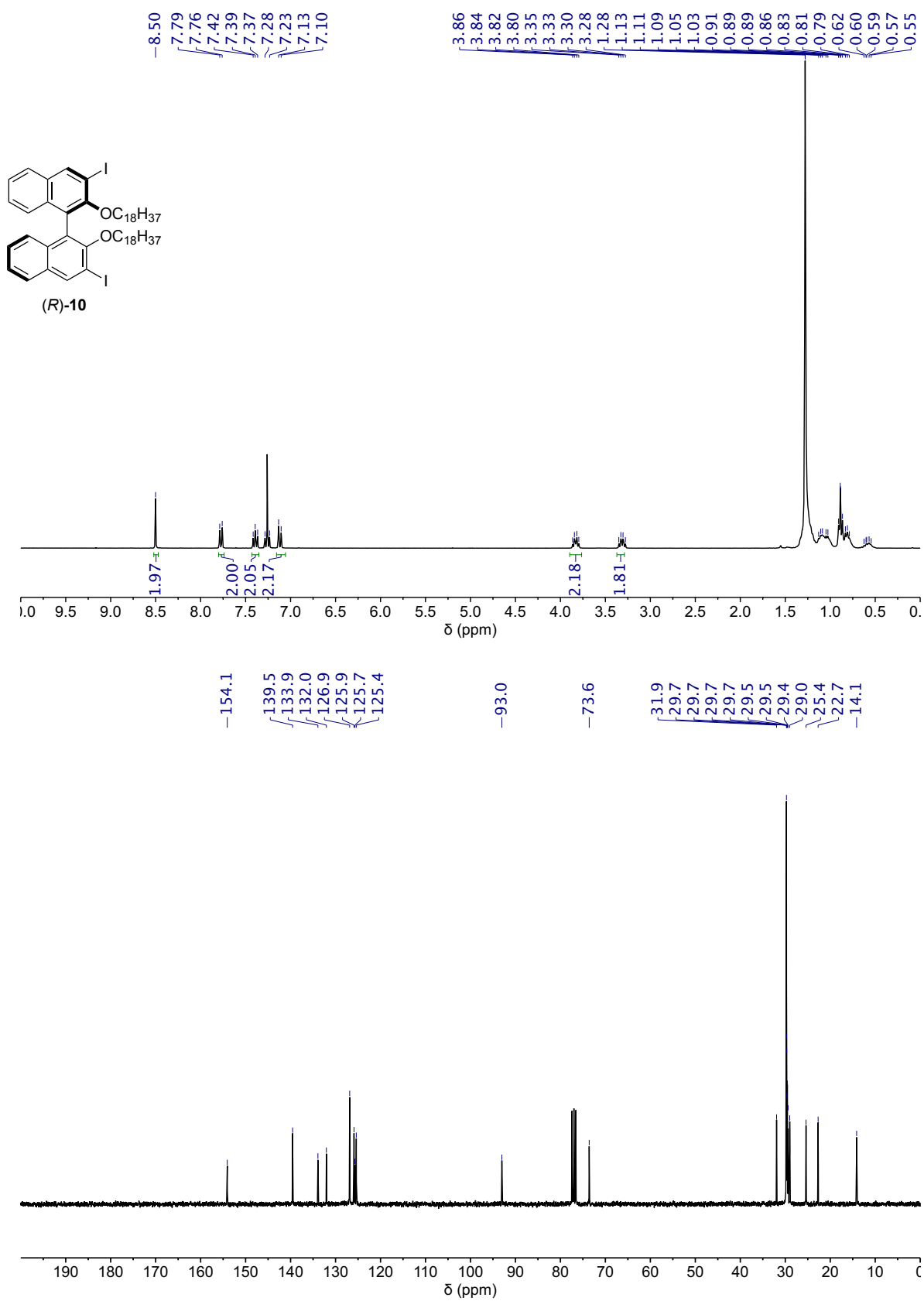


Figure S7. ^1H and ^{13}C NMR spectra of (R)-**10** in chloroform-*d*.

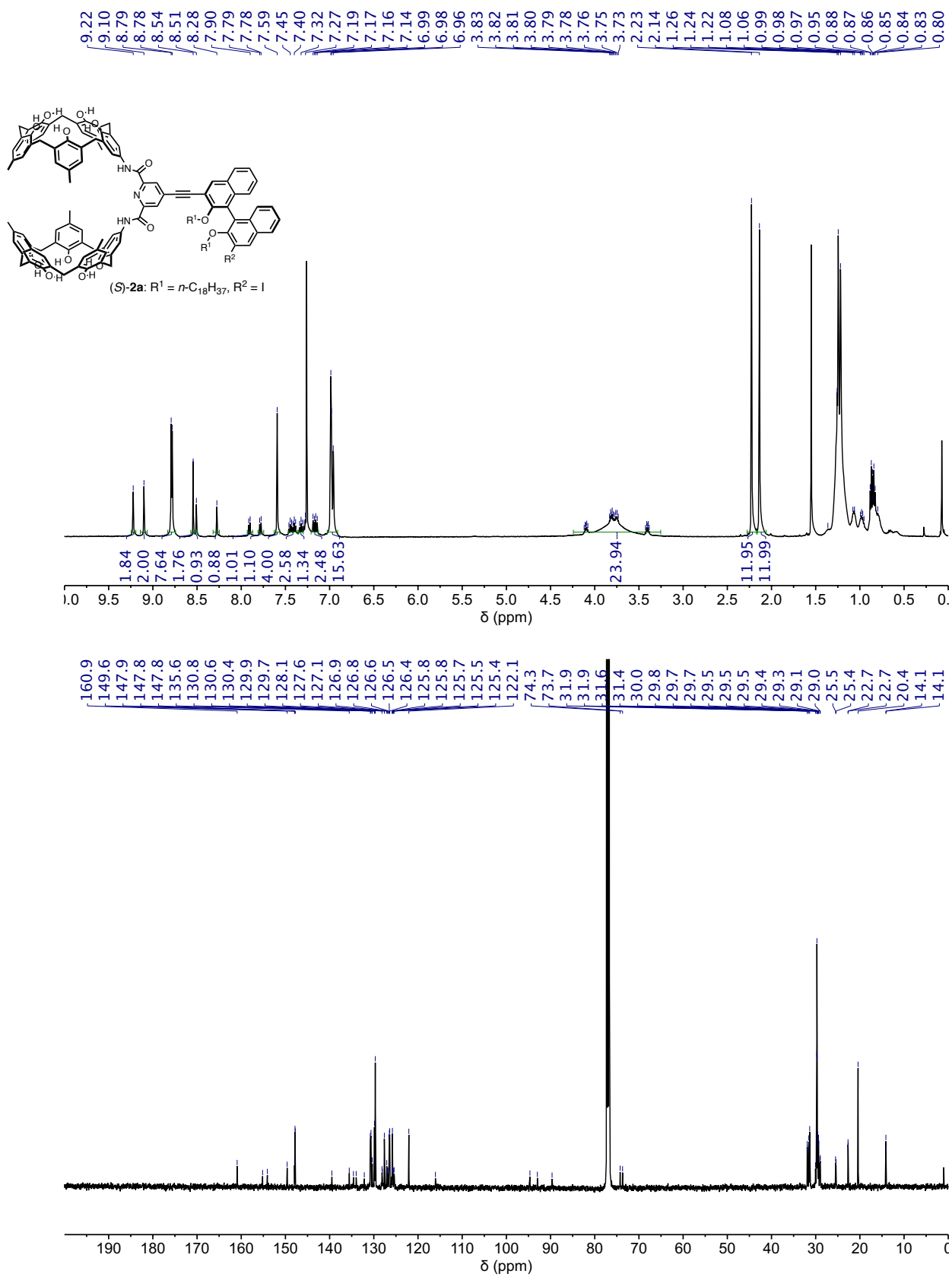


Figure S8. ^1H and ^{13}C NMR spectra of (S)-2a in chloroform-*d*.

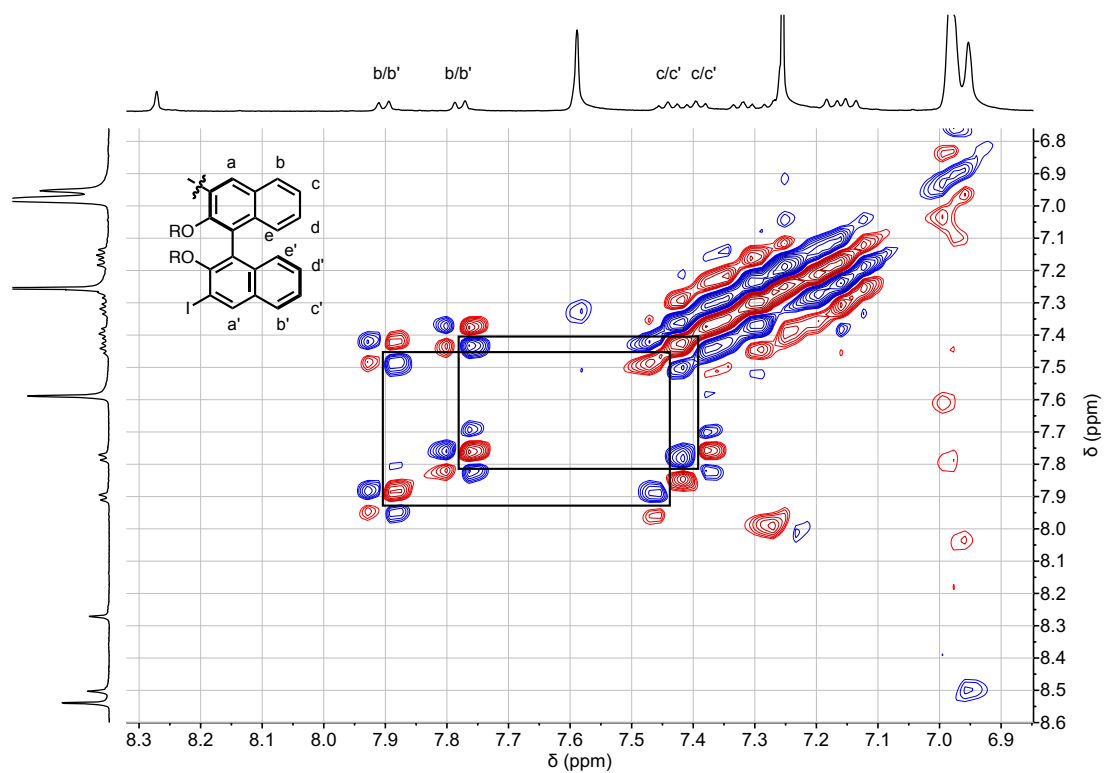


Figure S9. DQF-COSY spectrum of (*S*)-**2a** in chloroform-*d*.

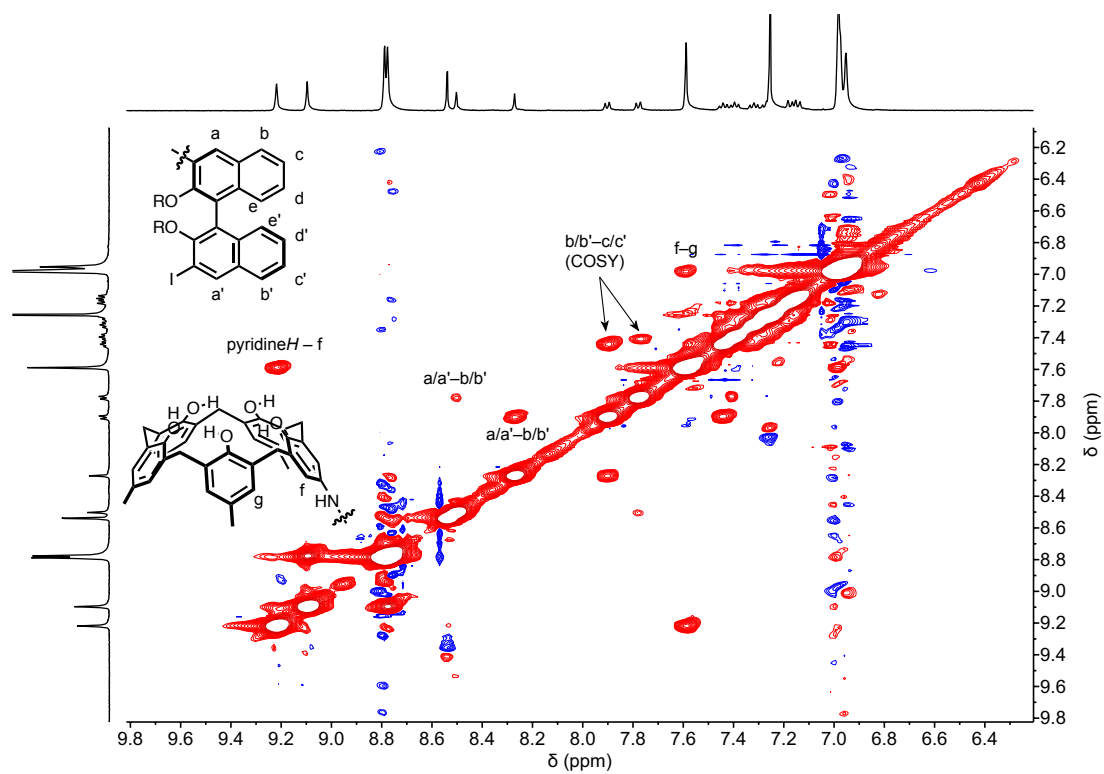


Figure S10. NOESY spectrum of (*S*)-**2a** in chloroform-*d*.

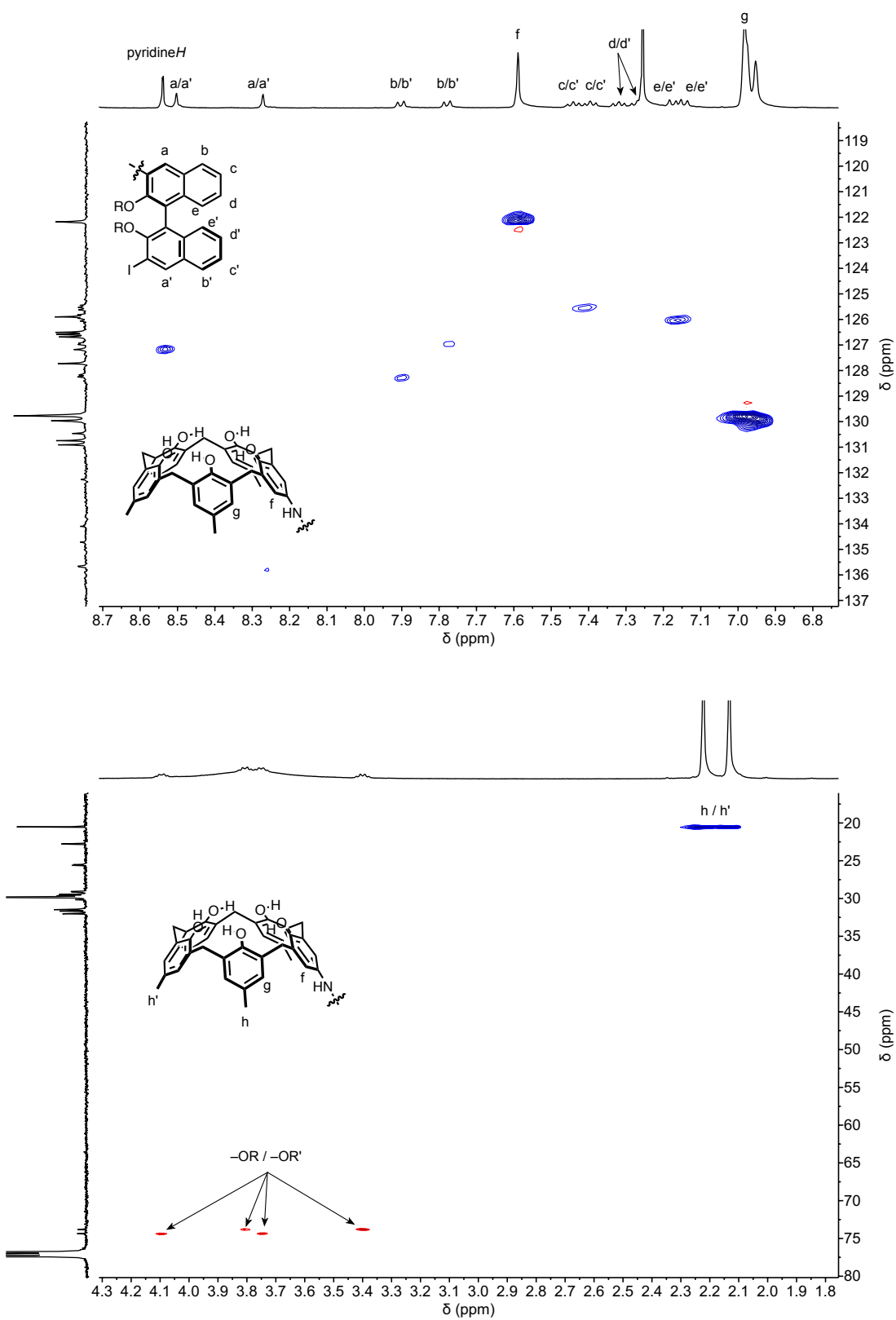


Figure S11. HSQC spectrum of *(S)*-**2a** in *chloroform-d*. CH_3 and CH carbons are phased down (blue), and CH_2 carbons are phased up (red).

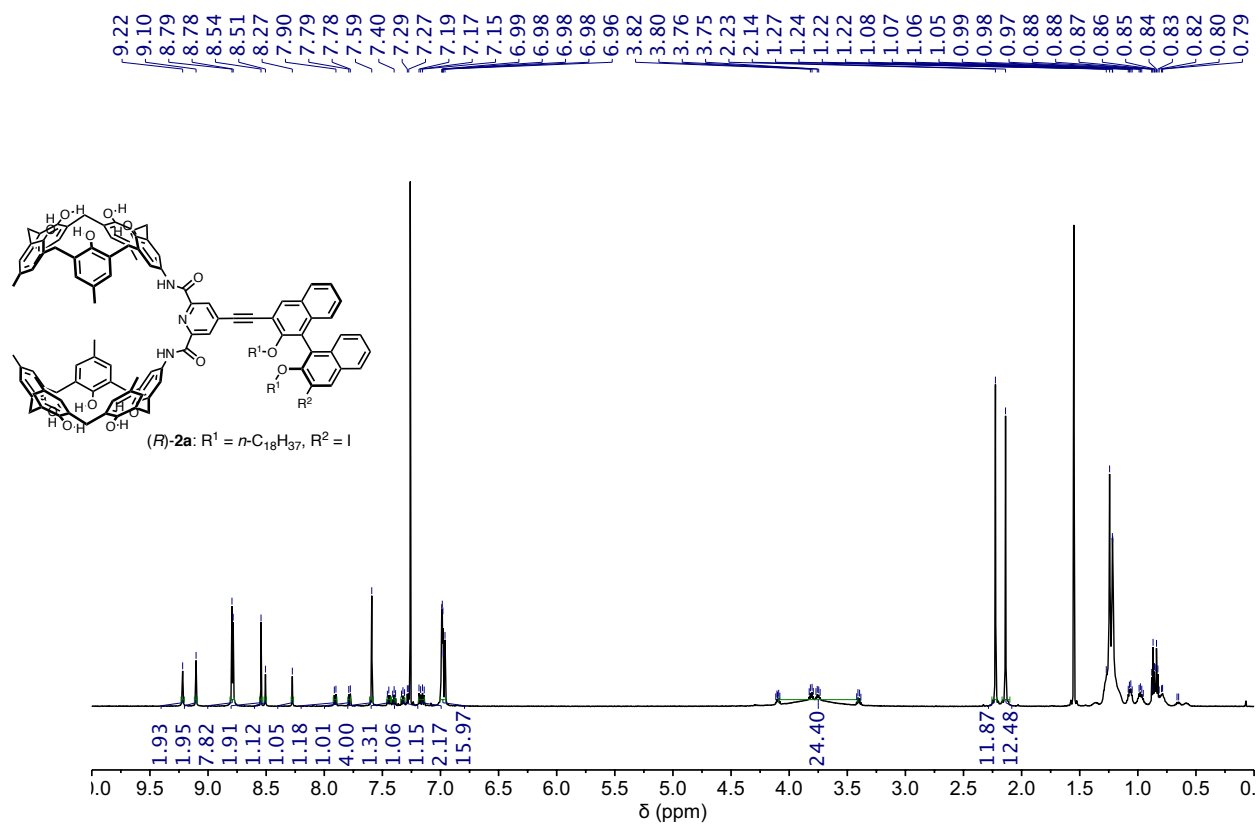


Figure S12. ¹H NMR spectrum of *(R)*-**2a** in chloroform-*d*.

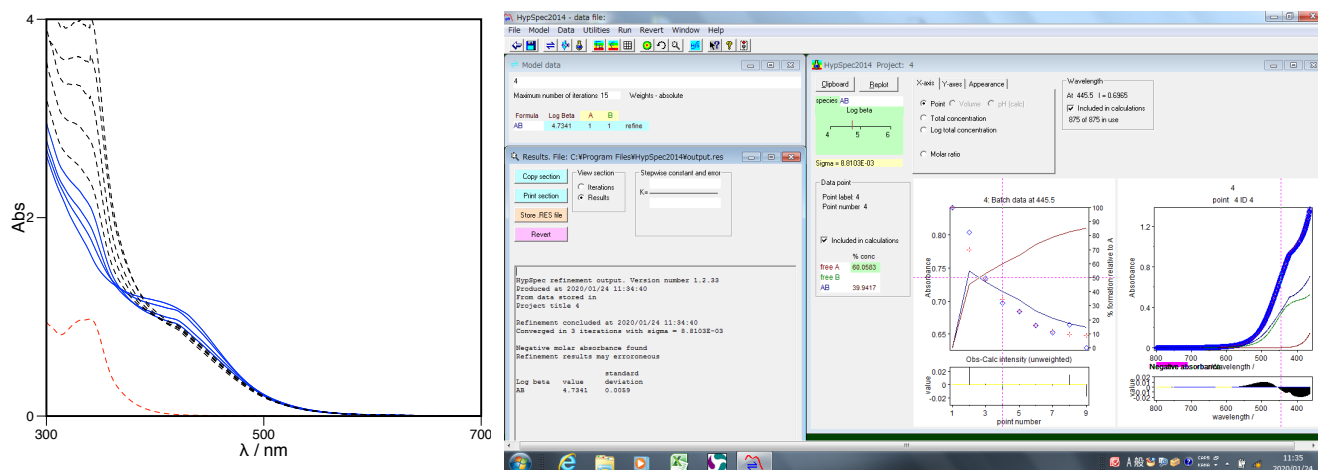


Figure S14. (left) UV/vis spectra of poly-1 (1.76×10^{-5} mol L $^{-1}$) with **2a** (from bottom: 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0 eq.) and **2a** (6.19×10^{-5} mol L $^{-1}$) (dashed red curve) at 293 K in toluene. (b) Screen capture of the global analysis of the titration data using Hypspec.

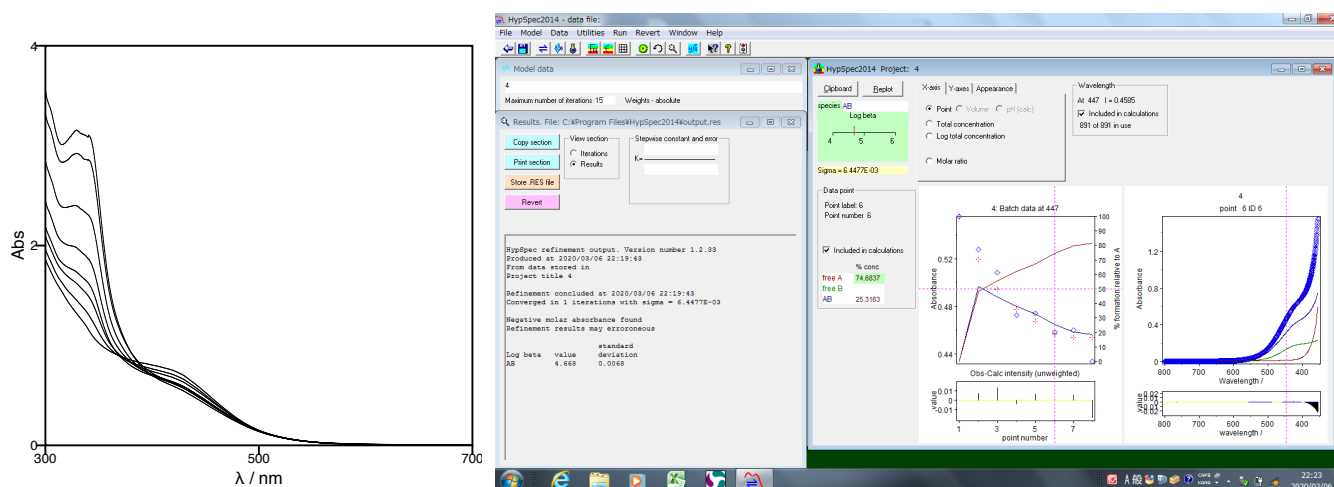


Figure S15. (left) UV/vis spectra of poly-1 (3.08×10^{-5} mol L $^{-1}$) with **2b** (from bottom: 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 4.5 eq.) and **2a** (6.19×10^{-5} mol L $^{-1}$) (dashed red curve) at 293 K in toluene. (b) Screen capture of the global analysis of the titration data using Hypspec.

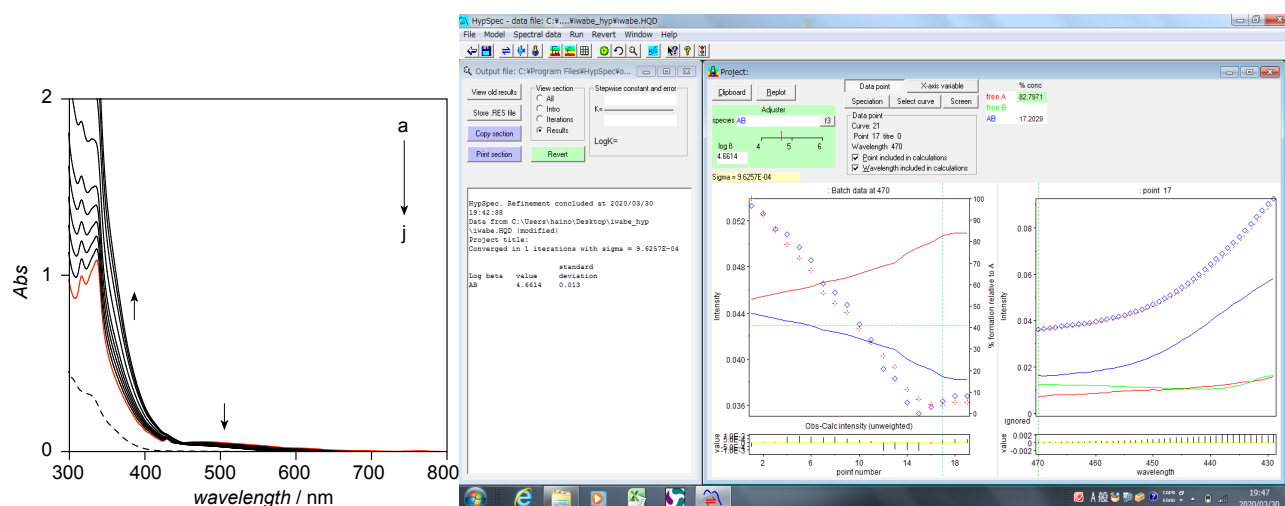


Figure S16. UV/vis spectra of **4** ($2.01 \times 10^{-5} \text{ mol L}^{-1}$) with **9** (a-j: 0.00, 0.812, 1.61, 2.40, 3.22, 4.08, 6.02, 8.06, 10.1, $12.1 \times 10^{-5} \text{ mol L}^{-1}$) and **9** (dashed curve) at 293 K in toluene.

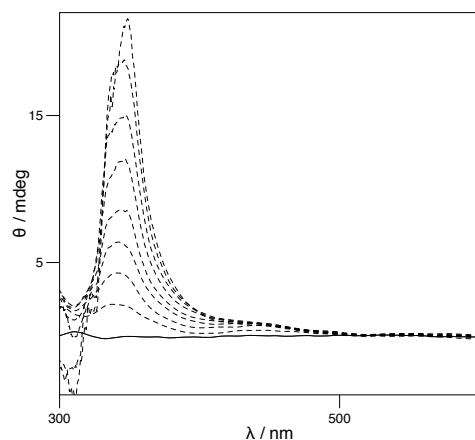


Figure S17. CD changes of poly-**1** ($1.76 \times 10^{-5} \text{ mol L}^{-1}$) upon the addition of (*S*)-**2a** (from bottom: 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0 eq) at 273 K in toluene. An optical path length of 1 mm was used for measurements.

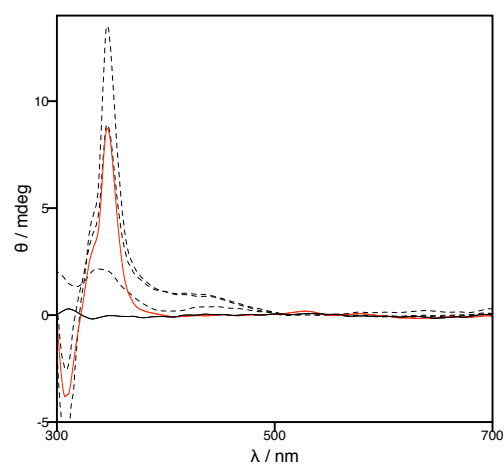


Figure S18. CD changes of poly-**1** ($1.76 \times 10^{-5} \text{ mol L}^{-1}$) upon the addition of (*S*)-**2b** (from bottom: 0.0, 2.0, 3.0 eq), and CD spectra of (*S*)-**2b** ($6.19 \times 10^{-5} \text{ mol L}^{-1}$) (solid red curve) and at 273 K in toluene. An optical path length of 1 mm was used for measurements.

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