

Supporting Information

Circularly Polarized Luminescence Triggered by Self-Assembly of Tris(phenylisoxazolyl)benzene Possessing Perylenebisimide

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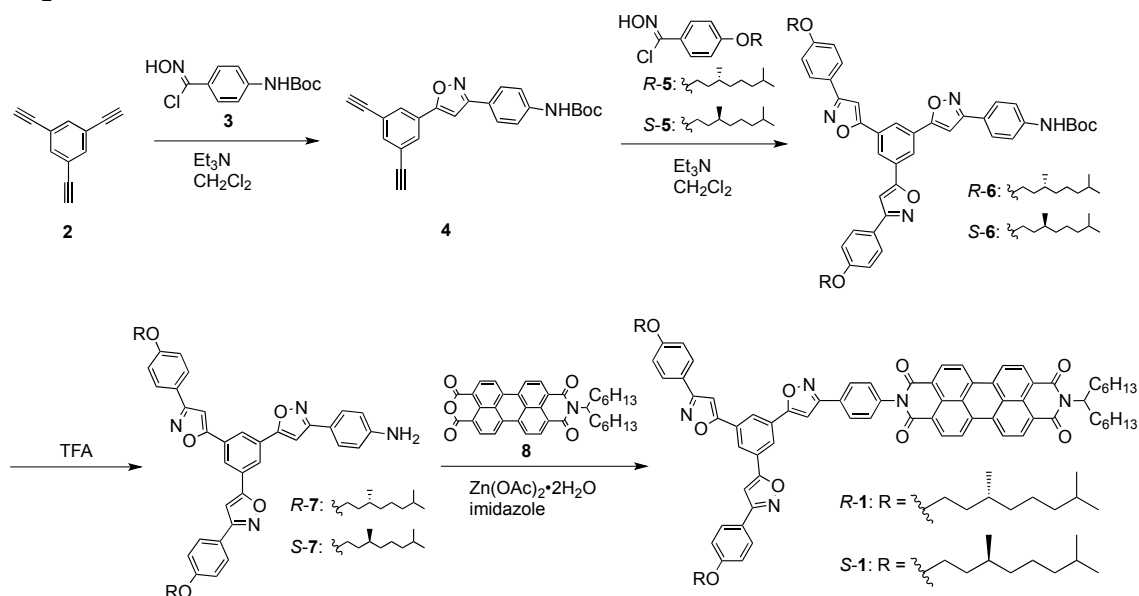
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Experimental Section



Scheme S1.

General: All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. Dry CH_2Cl_2 , DMF, and triethylamine were obtained by distillation over CaH_2 . Decahydronaphthalene (*cis* and *trans* mixture) was purchased from Kanto Chemical Co., Inc. ^1H and ^{13}C NMR spectra were recorded on a Varian mercury-300 spectrometer and JEOL JNM-ECA600 spectrometer at 25 °C in CDCl_3 and chemical shifts were reported as the delta scale in ppm relative to CHCl_3 ($\delta = 7.260$ for ^1H and 77.3 for ^{13}C). UV/vis absorption spectra were recorded on a JASCO V-560 spectrometer. Fluorescence spectra were recorded on a JASCO FP-6500 spectrofluorometer. Fluorescence quantum yields were recorded on a JASCO FP-6500 spectrofluorometer with an integrating sphere (JASCO, ILF-533, diameter 10 cm). CD spectra were recorded on a JASCO J-720W spectropolarimeter. IR spectra were recorded on JASCO FT/IR-420S spectrometer. ESI-Mass spectra were recorded on Thermo Scientific LTQ Orbitrap XL hybrid FTMS. Optical rotations were recorded on a JASCO DIP-370 polarimeter. UV/vis absorption, fluorescence, and CD spectra were measured using a conventional quartz cell (light path 1 cm) with temperature control. Elemental analyses were performed using CHN analyzer. Preparative separations were performed by silica gel gravity column chromatography (Silica Gel 60N (spherical, neutral)). Recycling preparative GPC-HPLC

separations were carried out on JAI LC-908s using preparative JAIGEL-2H, 2H, 1H columns in series. Compound **2**,¹ **3**,² *R*- and *S*-**5**,¹ and **8**³ were prepared according to the reported methods.

1-[3-[4-(*N*-tert-Butoxycarbonyl)aminophenyl]isoxazol-5-yl]-3,5-diethynylbenzene (4**):** To a solution of 1,3,5-triethynylbenzene (**2**) (12.1 g, 80.6 mmol) and triethylamine (3 mL, 21.5 mmol) in CH₂Cl₂ (40 mL) was added chlorooxime **3** (2.42 g, 7.76 mmol) in CH₂Cl₂ (30 mL). After being stirred at room temperature for 23 h under argon atmosphere, 1N HCl was added to the mixture. After extraction with EtOAc, the organic layer was washed with brine, dried over Na₂SO₄, and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (EtOAc/hexane) to give a desired product (2.39 g, 72%) as a yellow solid. M.p. 181 – 183 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.89 (d, *J* = 1.5 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.64 (t, *J* = 1.5 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 6.82 (s, 1H), 6.72 (s, 1H), 3.17 (s, 2H), and 1.53 (s, 9H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 168.2, 162.6, 152.4, 140.2, 136.6, 129.3, 128.0, 127.6, 123.5, 123.2, 118.4, 104.7, 98.3, 81.6, 81.0, 79.0, and 28.3 ppm; IR (KBr): ν 3392, 3288, 3112, 2979, 1709, 1614, 1594, 1568, 1536, 1510, 1457, 1442, 1423, 1387, 1367, 1316, 1229, 1162, 1053, 1024, 952, 924, 887, 835, 810, 771, 648, 522, and 459 cm⁻¹; HRMS (ESI⁺): calcd for C₂₄H₂₀N₂O₃Na *m/z* 407.1366 [M+Na]⁺, found *m/z* 407.1366; Anal. calcd for C₂₄H₂₀N₂O₃•0.5H₂O: C 73.27, H 5.38, N 7.11, found C 73.25, H 5.22, N 6.91%.

1-[3-[4-(*N*-tert-Butoxycarbonyl)aminophenyl]isoxazol-5-yl]-3,5-bis{3-[(*R*)-(-)-4-(3,7-dimethyloctyloxyphenyl)isoxazol-5-yl]benzene (R-6**):** To a solution of chlorooxime *R*-**5** (1.33 g, 4.28 mmol) in CH₂Cl₂ (7 mL) was added **4** (760.2 mg, 1.98 mmol) and triethylamine (0.8 mL, 5.8 mmol) in CH₂Cl₂ (18 mL). After being stirred at room temperature for 12 h under argon atmosphere, 1N HCl was added to the mixture. After extraction with EtOAc, the organic layer was washed with brine, dried over Na₂SO₄, and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (EtOAc/hexane) to give a desired product (1.11 g, 60%) as a white solid. M.p. 79 – 81 °C; [α]_D²⁵ = +6.1 cm³ g⁻¹ dm⁻¹ (c 0.11 g cm⁻³); ¹H NMR (300 MHz, CDCl₃): δ 8.22 (s, 1H), 8.22 (s, 2H), 7.78 (d, *J* = 8.9 Hz, 2H), 7.77 (d, *J* = 8.9 Hz, 4H), 7.47 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 4H), 6.94 (s, 1H), 6.92 (s, 2H), 6.66 (s, 1H), 4.01 (m, 4H), 1.84 (m, 2H), 1.67–1.10 (m, 27H), 0.94 (d, *J* = 6.3 Hz, 6H), and 0.86 (d, *J* = 6.3 Hz, 6H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 168.3, 168.2, 163.1, 162.9, 161.0, 152.7, 140.5, 129.4, 129.3, 128.4, 127.8, 124.0, 124.0, 123.3, 121.0, 118.7, 115.1, 99.0, 99.0, 81.2,

66.7, 39.5, 37.5, 36.4, 30.1, 28.6, 28.2, 24.9, 23.0, 22.9, and 19.9 ppm; IR (KBr): ν 3369, 2927, 1732, 1613, 1528, 1465, 1436, 1386, 1253, 1159, 1051, 950, 792, 655, 533, and 417 cm^{-1} ; HRMS (ESI⁺): calcd for $\text{C}_{58}\text{H}_{70}\text{N}_4\text{O}_7\text{Na}$ m/z 957.5137 [M+Na]⁺, found m/z 957.5114; Anal. calcd for $\text{C}_{58}\text{H}_{70}\text{N}_4\text{O}_7 \cdot \text{H}_2\text{O}$: C 73.08, H 7.61, N 5.88, found C 72.99, H 7.55, N 6.01%.

1-[3-[4-(*N*-tert-Butoxycarbonyl)aminophenyl]isoxazol-5-yl]-3,5-bis{3-[(*S*)-(+)-4-(3,7-dimethyl)octyloxyphenyl]isoxazol-5-yl}benzene (S-6): To a solution of chlorooxime S-5 (3.84 g, 12.3 mmol) in CH_2Cl_2 (10 mL) was added **4** (1.58 g, 4.1 mmol) and triethylamine (1.1 mL, 8 mmol) in CH_2Cl_2 (25 mL). After being stirred at room temperature for 13 h under argon atmosphere, 1N HCl was added to the mixture. After extraction with EtOAc, the organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (EtOAc/hexane) to give a desired product (2.65 g, 69%) as white solid. M.p. 79 – 81 °C; $[\alpha]^{25}_{\text{D}} = -6.2 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ (c 0.10 g cm^{-3}); ^1H NMR (300 MHz, CDCl_3): δ 8.25 (s, 1H), 8.24 (s, 2H), 7.80 (d, $J = 8.9 \text{ Hz}$, 2H), 7.79 (d, $J = 8.9 \text{ Hz}$, 4H), 7.49 (d, $J = 8.9 \text{ Hz}$, 2H), 6.98 (d, $J = 8.9 \text{ Hz}$, 4H), 6.96 (s, 1H), 6.94 (s, 2H), 6.68 (s, 1H), 4.03 (m, 4H), 1.85 (m, 2H), 1.68–1.13 (m, 27H), 0.96 (d, $J = 6.3 \text{ Hz}$, 6H), and 0.88 (d, $J = 6.3 \text{ Hz}$, 6H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 168.1, 167.9, 162.8, 162.7, 160.7, 152.4, 140.2, 129.1, 129.1, 128.2, 127.6, 123.8, 123.8, 123.0, 120.8, 118.4, 114.8, 98.7, 98.7, 80.9, 66.4, 39.2, 37.3, 36.1, 29.8, 28.3, 27.9, 24.6, 22.7, 22.6, and 19.6 ppm; IR (KBr): ν 3360, 2927, 1722, 1613, 1528, 1466, 1435, 1387, 1252, 1159, 1050, 950, 789, 649, 525, and 418 cm^{-1} ; HRMS (ESI⁺): calcd for $\text{C}_{58}\text{H}_{70}\text{N}_4\text{O}_7\text{Na}$ m/z 957.5137 [M+Na]⁺, found m/z 957.5117; Anal. calcd for $\text{C}_{58}\text{H}_{70}\text{N}_4\text{O}_7 \cdot 1.5\text{H}_2\text{O}$: C 72.40, H 7.65, N 5.82, found C 72.14, H 7.36, N 5.89%.

1-[3-(4-Aminophenyl)isoxazol-5-yl]-3,5-bis{3-[(*R*)-(-)-4-(3,7-dimethyl)octyloxyphenyl]isoxazol-5-yl}benzene (R-7): **R-6** (792.3 mg, 0.847 mmol) was dissolved in TFA (8 mL), and the solution was stirred for 1 h at room temperature under argon atmosphere. The reaction was quenched by addition of 10% NaOH aq. in ice bath, and the precipitate was filtered to give a desired product (686.0 mg, 97%) as a white solid. M.p. 95 – 97 °C; $[\alpha]^{25}_{\text{D}} = +68.0 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ (c 0.086 g cm^{-3}); ^1H NMR (300 MHz, CDCl_3): δ 8.29 (s, 2H), 8.27 (s, 1H), 7.82 (d, $J = 8.9 \text{ Hz}$, 4H), 7.69 (d, $J = 8.9 \text{ Hz}$, 2H), 7.00 (d, $J = 8.9 \text{ Hz}$, 4H), 6.95 (s, 2H), 6.94 (s, 1H), 6.76 (d, $J = 8.9 \text{ Hz}$, 2H), 4.05 (m, 4H), 3.93 (s, 2H), 1.85 (m, 2H), 1.73–1.50 (m, 8H), 1.39–1.13 (m, 10H), 0.96 (d, $J = 6.3 \text{ Hz}$, 6H), and 0.88 (d, $J = 6.3 \text{ Hz}$, 6H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 168.3,

168.0, 163.4, 163.1, 161.0, 148.6, 129.4, 129.4, 128.5, 128.4, 124.1, 124.0, 121.1, 118.8, 115.2, 115.2, 99.0, 98.9, 66.7, 39.5, 37.5, 36.4, 30.1, 28.2, 24.9, 23.0, 22.9, and 19.9 ppm; IR (KBr): ν 3388, 2954, 2926, 1612, 1563, 1528, 1466, 1439, 1386, 1295, 1253, 1177, 1016, 950, 835, 793, 762, 651, and 529 cm^{-1} ; HRMS (ESI⁺): calcd for $\text{C}_{53}\text{H}_{63}\text{N}_4\text{O}_5$ m/z 835.4793 [M+H]⁺, found m/z 835.4796; Anal. calcd for $\text{C}_{53}\text{H}_{62}\text{N}_4\text{O}_5 \cdot 1.5\text{H}_2\text{O}$: C 73.84, H 7.60, N 6.50, found C 73.87, H 7.71, N 6.14%.

1-[3-(4-Aminophenyl)isoxazol-5-yl]-3,5-bis{3-[(S)-(+)-4-(3,7-dimethyl)octyloxyphenyl]isoxazol-5-yl}benzene (S-7): S-6 (968.0 mg, 1.04 mmol) was dissolved in TFA (10 mL), and the solution was stirred for 1 h at room temperature under argon atmosphere. The reaction was quenched by addition of 10% NaOH aq. in ice bath, and the precipitate was filtered to give a desired product (820.1 mg, 95%) as a white solid. M.p. 95 – 97 °C; $[\alpha]_{\text{D}}^{25} = -67.9 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ (c 0.099 g cm^{-3}); ¹H NMR (300 MHz, CDCl_3): δ 8.23 (s, 1H), 8.22 (s, 2H), 7.79 (d, $J = 8.9 \text{ Hz}$, 4H), 7.66 (d, $J = 8.9 \text{ Hz}$, 2H), 6.98 (d, $J = 8.9 \text{ Hz}$, 4H), 6.93 (s, 2H), 6.89 (s, 1H), 6.74 (d, $J = 8.9 \text{ Hz}$, 2H), 4.03 (m, 4H), 3.92 (s, 2H), 1.84 (m, 2H), 1.73–1.50 (m, 8H), 1.39–1.13 (m, 10H), 0.96 (d, $J = 6.3 \text{ Hz}$, 6H), and 0.88 (d, $J = 6.3 \text{ Hz}$, 6H) ppm; ¹³C NMR (75 MHz, CDCl_3): δ 168.3, 168.0, 163.3, 163.1, 161.0, 148.6, 129.5, 129.4, 128.4, 128.4, 124.0, 123.9, 121.1, 118.8, 115.2, 115.1, 99.0, 98.8, 66.7, 39.5, 37.5, 36.4, 30.1, 28.2, 24.9, 23.0, 22.9, and 19.9 ppm; IR (KBr): ν 3364, 2953, 2925, 1612, 1561, 1527, 1466, 1437, 1387, 1295, 1252, 1177, 1017, 950, 835, 791, 762, 650, and 527 cm^{-1} ; HRMS (ESI⁺): calcd for $\text{C}_{53}\text{H}_{63}\text{N}_4\text{O}_5$ m/z 835.4793 [M+H]⁺, found m/z 835.4796; Anal. calcd for $\text{C}_{53}\text{H}_{62}\text{N}_4\text{O}_5 \cdot 2\text{H}_2\text{O}$: C 73.08, H 7.64, N 6.43, found C 73.34, H 7.30, N 6.25%.

N-{4-[5-{3,5-Bis{3-[(R)-(-)-4-(3,7-dimethyl)octyloxyphenyl]isoxazol-5-yl}phenyl]isoxazol-3-yl}phenyl]-N'-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic acid bisimide (R-1): R-7 (156.3 mg, 0.187 mmol), perylene monoimide monoanhydride **8** (107.0 mg, 0.186 mmol), zinc(II)acetate dihydrate (61.5 mg, 0.280 mmol), and imidazole (1.96 g) were added to a schlenk flask. After being stirred for 3 h at 160 °C under argon atmosphere, the reaction was quenched by addition of 6N HCl (100 mL). After standing overnight, the precipitate was filtered, and the crude product was further purified by column chromatography on silica gel (EtOAc/hexane) and by GPC. Reprecipitation from chloroform/MeOH gave a desired product (144.9 mg, 56%) as a dark red solid. M.p. >300 °C (decomp.); $[\alpha]_{\text{D}}^{25} = +12.1 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ (c 0.041 g cm^{-3}); ¹H NMR (600 MHz, CDCl_3): δ 8.78 (d, $J = 8.0 \text{ Hz}$, 2H), 8.73–8.67

(m, 6H), 8.38 (s, 2H), 8.37 (s, 1H), 8.13 (d, $J = 8.3$ Hz, 2H), 7.84 (d, $J = 8.3$ Hz, 4H), 7.53 (d, $J = 8.3$ Hz, 2H), 7.13 (s, 1H), 7.02 (d, $J = 8.3$ Hz, 4H), 7.02 (s, 2H), 5.19 (m, 1H), 4.06 (m, 4H), 2.26 (m, 4H), 1.88 (m, 4H), 1.78–1.14 (m, 40H), 0.98 (d, $J = 6.0$ Hz, 6H), 0.88 (d, $J = 6.0$ Hz, 12H), and 0.83 (t, $J = 6.6$ Hz, 6H) ppm; ^{13}C NMR (150 MHz, CDCl_3 , 323 K): δ 168.8, 168.1, 168.1, 163.5, 163.0, 162.7, 161.0, 161.0, 137.0, 135.4, 134.3, 132.0, 130.0, 129.7, 129.5, 129.4, 129.3, 128.3, 128.3, 128.0, 127.0, 126.5, 124.2, 124.1, 123.4, 123.3, 123.1, 121.1, 115.1, 115.1, 99.2, 98.9, 66.7, 55.0, 39.3, 37.4, 36.3, 32.5, 31.9, 30.0, 29.7, 29.4, 28.0, 27.0, 24.7, 22.7, 22.6, 19.7, and 14.0 ppm; IR (KBr): ν 2926, 2859, 1698, 1660, 1594, 1526, 1437, 1343, 1257, 1176, 1101, 1032, and 810 cm^{-1} ; HRMS (ESI $^{+}$): calcd for $\text{C}_{90}\text{H}_{96}\text{N}_5\text{O}_9$ m/z 1390.7203 $[\text{M}+\text{H}]^{+}$, found m/z 1390.7193; Anal. calcd for $\text{C}_{90}\text{H}_{95}\text{N}_5\text{O}_9 \cdot 3.5\text{H}_2\text{O}$: C 74.35, H 7.07, N 4.82, found C 74.28, H 7.21, N 4.50%.

***N*-[4-[5-[3,5-Bis{3-[(*S*)-(+)-4-(3,7-dimethyl)octyloxyphenyl]isoxazol-5-yl]phenyl]isoxazol-3-yl]phenyl]-*N'*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic acid bisimide (*S*-1):** *S*-7 (911.7 mg, 1.09 mmol), perylene monoimide monoanhydride **8** (576.8 mg, 1.01 mmol), zinc(II)acetate dihydrate (251.2 mg, 1.14 mmol), and imidazole (6.59 g) were added to a schlenk flask. After being stirred for 3 h at 160 °C under argon atmosphere, the reaction was quenched by addition of 6N HCl (300 mL). After standing overnight, the precipitate was filtered, and the crude product was further purified by column chromatography on silica gel (EtOAc/hexane) and by GPC. Reprecipitation from chloroform/MeOH gave a desired product (763.8 mg, 55%) as a dark red solid. M.p. >300 °C (decomp.); $[\alpha]_D^{25} = -11.7$ $\text{cm}^3 \text{g}^{-1} \text{dm}^{-1}$ (c 0.047 g cm^{-3}); ^1H NMR (600 MHz, CDCl_3): δ 8.77 (d, $J = 7.9$ Hz, 2H), 8.73–8.67 (m, 6H), 8.37 (s, 2H), 8.36 (s, 1H), 8.13 (d, $J = 7.9$ Hz, 2H), 7.84 (d, $J = 7.9$ Hz, 4H), 7.53 (d, $J = 7.9$ Hz, 2H), 7.12 (s, 1H), 7.02 (d, $J = 7.9$ Hz, 4H), 7.02 (s, 2H), 5.19 (m, 1H), 4.06 (m, 4H), 2.24 (m, 4H), 1.86 (m, 4H), 1.69 (m, 2H), 1.62 (m, 2H), 1.51 (m, 4H), 1.38–1.13 (m, 32H), 0.96 (d, $J = 6.6$ Hz, 6H), 0.87 (d, $J = 6.6$ Hz, 12H), and 0.82 (t, $J = 6.6$ Hz, 6H) ppm; ^{13}C NMR (150 MHz, CDCl_3 , 323 K): δ 168.8, 168.1, 168.1, 163.5, 163.0, 162.7, 161.0, 161.0, 137.0, 135.4, 134.3, 132.0, 130.0, 129.6, 129.5, 129.4, 129.3, 128.3, 128.3, 128.0, 126.9, 126.6, 124.2, 124.1, 123.4, 123.3, 123.1, 121.1, 115.1, 115.1, 99.2, 98.9, 66.7, 55.0, 39.3, 37.4, 36.3, 32.5, 31.8, 30.0, 29.7, 29.2, 28.0, 27.0, 24.7, 22.7, 22.6, 19.7, and 14.0 ppm; IR (KBr): ν 2925, 2854, 1698, 1660, 1594, 1527, 1437, 1343, 1259, 1176, 1095, 1021, and 809 cm^{-1} ; HRMS (ESI $^{+}$): calcd for $\text{C}_{90}\text{H}_{96}\text{N}_5\text{O}_9$ m/z 1390.7203 $[\text{M}+\text{H}]^{+}$, found m/z 1390.7216; Anal. calcd for $\text{C}_{90}\text{H}_{95}\text{N}_5\text{O}_9 \cdot 7.5\text{CH}_3\text{OH}$: C 71.80, H 7.72, N 4.29, found C 71.73, H 7.38, N 4.05%.

Analysis of self-association by ^1H NMR and UV/vis experiments: Hyperbolic curves were obtained by plotting of compound concentrations vs ^1H NMR chemical shifts (δ) of the aromatic protons or ε . The curve-fitting analysis of the plots was carried out on the basis of an isodesmic association model, which is a type of unlimited self-association where the addition of each successive monomer to polymer involves an equal association constant ($K_2 = K_3 = \dots = K_i = K_E$). The fitting functions are given by equations 1 and 2 for NMR and UV/vis experiments. ε denotes the apparent extinction coefficient obtained from the spectra; ε_m and ε_a are the extinction coefficients for the monomer and the self-assembled species, respectively; K_E is the association constant; and c is the total concentration of a compound. δ denotes apparent chemical shifts obtained from spectra; δ_m and δ_a are chemical shifts for a monomer and self-assembled species, respectively. The complexation-induced shift $\Delta\delta$ displays the difference between δ_m and δ_a .

$$\delta(c) = \delta_m + (\delta_a - \delta_m) \left(1 + \frac{1 - \sqrt{4K_E c + 1}}{2K_E c} \right) \quad (1)$$

$$\varepsilon(c) = \varepsilon_a + (\varepsilon_m - \varepsilon_a) \frac{2K_E c + 1 - \sqrt{4K_E c + 1}}{2K_E^2 c^2} \quad (2)$$

Correction of CPL signals by means of compensation for linearly polarized luminescence: In the CPL measurement system, the light from the sample was collimated with a lens, modulated with a photo-elastic modulator, PEM, and a cubic polarizer, LP, and was detected with a photomultiplier sensor. The Stokes vector which is obtained from Mueller matrix calculation for the measurement system, eq. 3, represents nature of light after the polarizer,

$$\begin{pmatrix} I \\ LPL'_+ \\ LPL'_x \\ -CPL' \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 0 & \pm 1 & 0 \\ 0 & 0 & 0 & 0 \\ \pm 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos(\delta \sin 2\pi\omega t) & -\sin(\delta \sin 2\pi\omega t) \\ 0 & 0 & \sin(\delta \sin 2\pi\omega t) & \cos(\delta \sin 2\pi\omega t) \end{pmatrix} \begin{pmatrix} I_0 \\ LPL_+ \\ LPL_x \\ -CPL \end{pmatrix} \quad (3)$$

where I, LPL and CPL are total light intensity, linearly polarized component, ΔI_{LPL} , and circularly polarized component, ΔI_{CPL} , respectively. LPL_+ and LPL_x are intensity of linearly polarized components perpendicularly each other. The first and the second terms in the right side of eq. 3 correspond respectively to LP and PEM in which retardation is modulated with $\omega = 50$ kHz in the present measurement system.

$$I = \frac{1}{2} \left(I_0 \pm LPL_x \cos\left(\frac{\pi}{2} \sin 2\pi\omega t\right) \pm (CPL) \sin\left(\frac{\pi}{2} \sin 2\pi\omega t\right) \right) \quad (4)$$

Equation 4 presents contribution of LPL and CPL components on the total light intensity, I. The second and the third terms in the right side of eq. 4 indicate contribution of CPL and LPL, respectively, for the signal intensity, which is modulated with both 2ω and ω because of the second and the third terms, respectively.

$$\cos\left(\frac{\pi}{2} \sin 2\pi\omega t\right) = 0.472 + 2 \sum_{k=1}^{\infty} (-1)^k J_{2k}(\pi/2) \sin(2k\omega t) \quad (5)$$

Equation 5 is derived for understanding the LPL component in eq. 4. The mean intensity of total signal in eq. 2 corresponds to $(I_0 \pm 0.472LPL)$ but not I_0 . In usual solution measurements, sample is isotropic and zero-LPL assumption is applicable. Meanwhile, molecular assembly has potential anisotropy and non-zero LPL must be corrected. In our system, therefore, the LPL component was derived from the amplitude of 2ω component

of signal simultaneously with the CPL signal of ω component with a lock-in amplifier, and the mean component (i.e. DC component) of light signal was corrected. This procedure corresponds to that in the solid-state CD spectroscopy reported by Kuroda et al. (R. Kuroda, T. Harada, and Y. Shindo, *Rev. Sci. Instru.*, **2001**, 72, 3802-3810. & T. Harada, H. Hayakawa, and R. Kuroda, *Rev. Sci. Instru.*, **2008**, 79, 073103.).

Determination of the CD dissymmetry factor g_{abs} and the CPL dissymmetry factor g_{lum} :

The CD dissymmetry factors g_{abs} were defined as $\Delta\epsilon/\epsilon$ at the wavelength of the first Cotton effect (545 nm). $\Delta\epsilon$ and ϵ are the molar circular dichroism and the molar extinction coefficient, respectively.

The CPL dissymmetry factors g_{lum} were defined as $\Delta I/I$ at the wavelength of the strongest CPL (650 nm). ΔI and I are the CPL and fluorescence intensities, respectively.

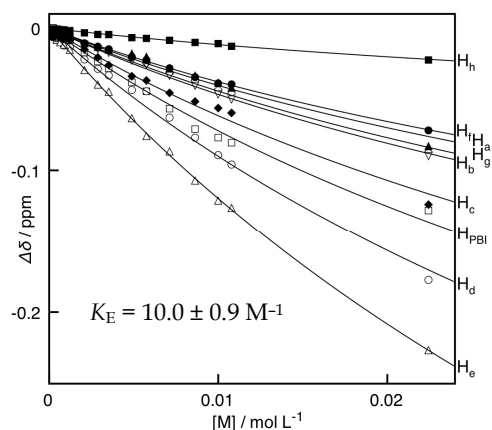


Fig. S1. Non-linear curve fitting of **S-1** using ¹H NMR in chloroform-*d*₁ at 298 K. The solid curves were obtained by the fitting analysis.

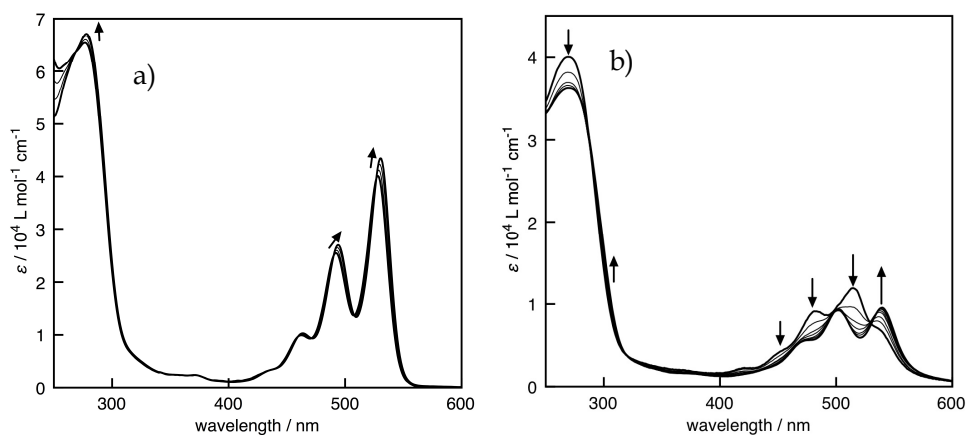


Fig. S2. Temperature-dependent UV/vis absorption spectra of **S-1** in (a) chloroform and (b) methylcyclohexane. $[S-1] = 1.0 \times 10^{-5} \text{ mol L}^{-1}$. The temperature of the solution of **S-1** are (a): 323, 313, 303, and 293 K and (b): 363, 353, 343, 333, 323, 313, 303, and 293 K. Arrows indicate changes upon decreasing temperature.

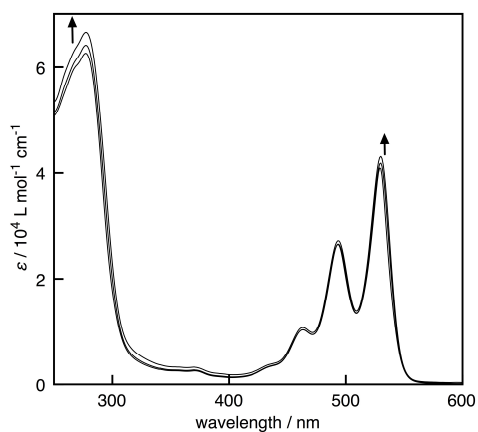


Fig. S3. Concentration-dependent UV/vis absorption spectra of *S*-1 in chloroform at 298 K. [*S*-1] = 1.0, 2.5, and 5.0 × 10⁻⁵ mol L⁻¹. Arrows indicate changes upon increasing concentration.

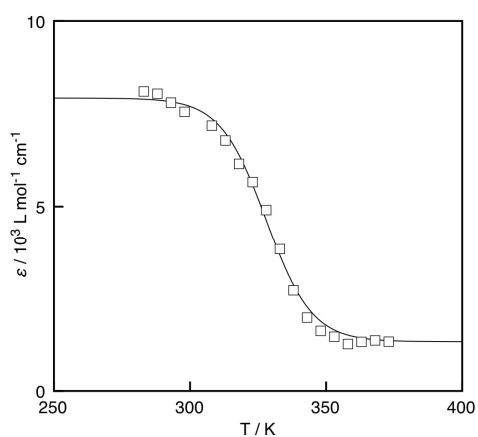
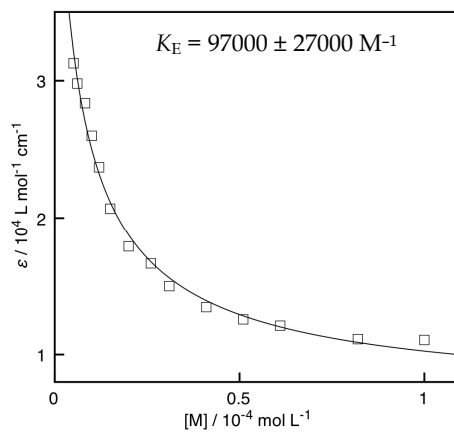
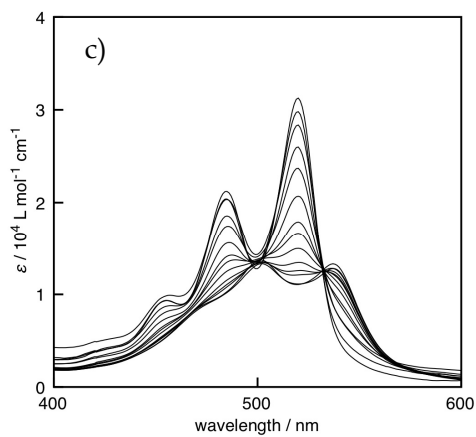
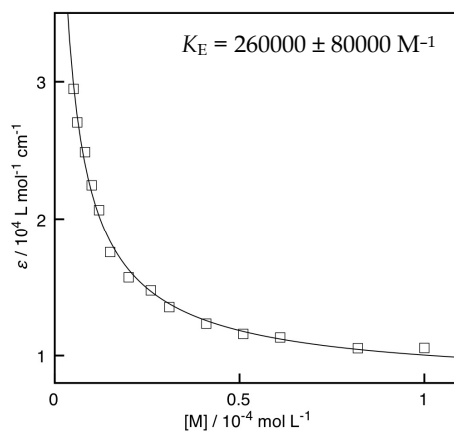
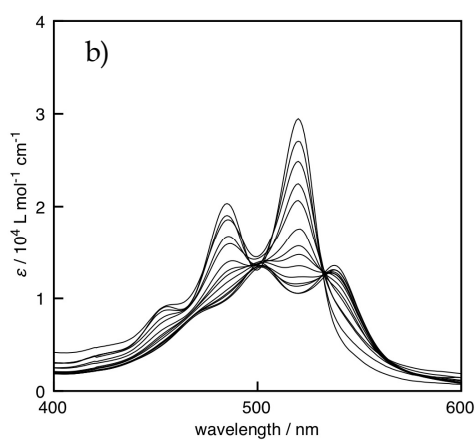
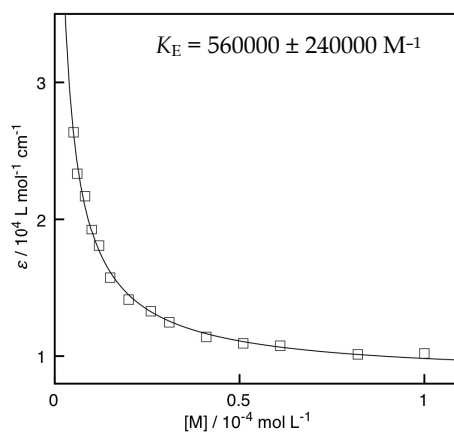
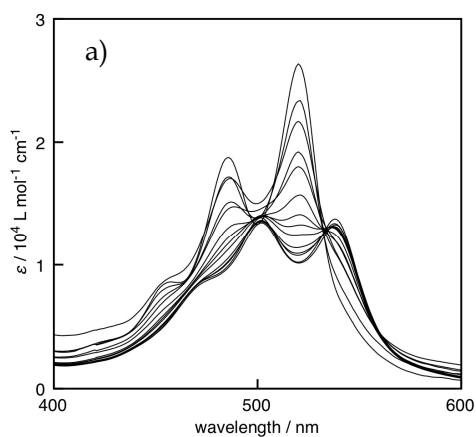


Fig. S4. A plot of ϵ of *S*-1 at 540 nm vs temperature in decalin.



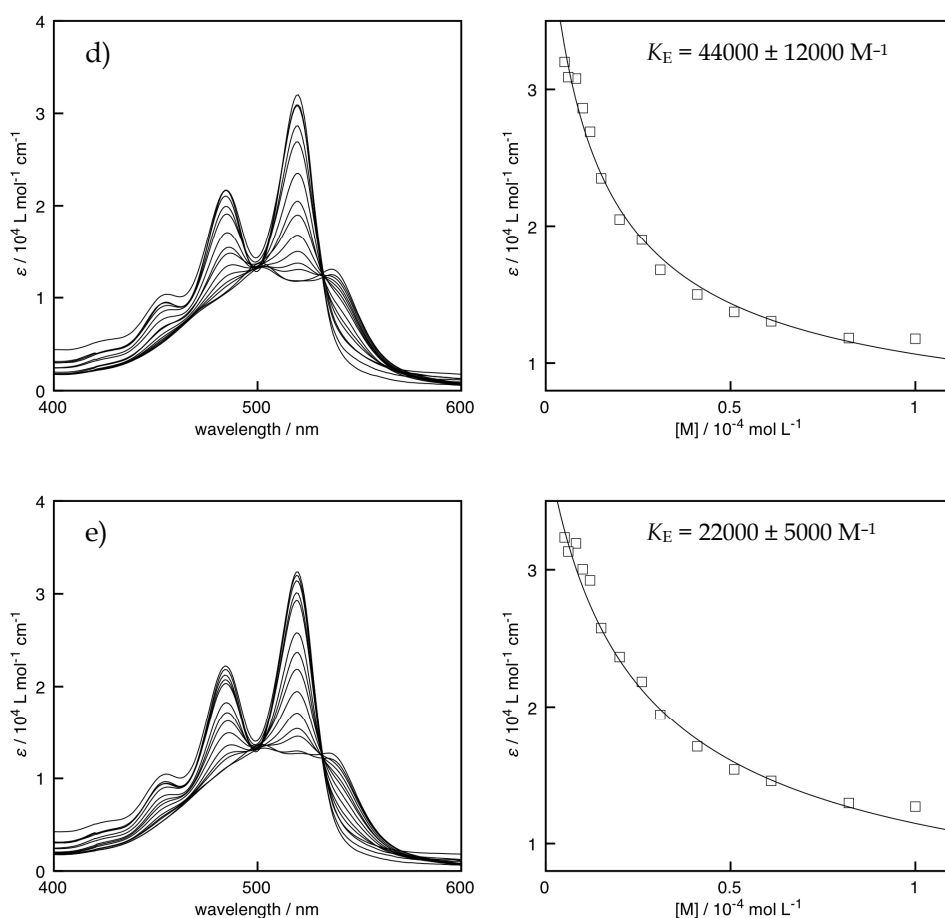


Fig. S5. Concentration-dependent UV/vis absorption spectra (left) and non-linear curve fitting (right) of S-1 in decalin. [S-1] = 10.0, 8.2, 6.1, 5.1, 4.1, 3.1, 2.6, 2.0, 1.5, 1.2, 1.0, 0.8, 0.6, and 0.5×10^{-5} mol L⁻¹. The temperatures are (a) 333, (b) 338, (c) 343, (d) 348, and (e) 353 K. The solid curves were obtained by the fitting analysis.

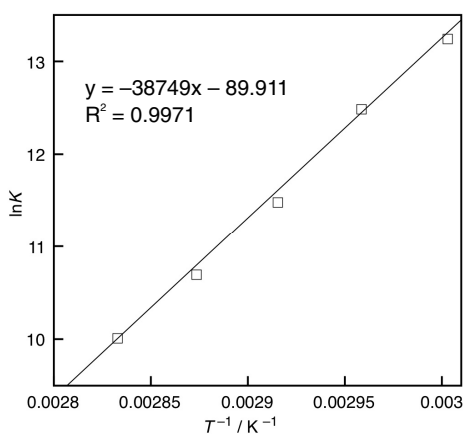


Fig. S6. van't Hoff plot of S-1 in decalin.

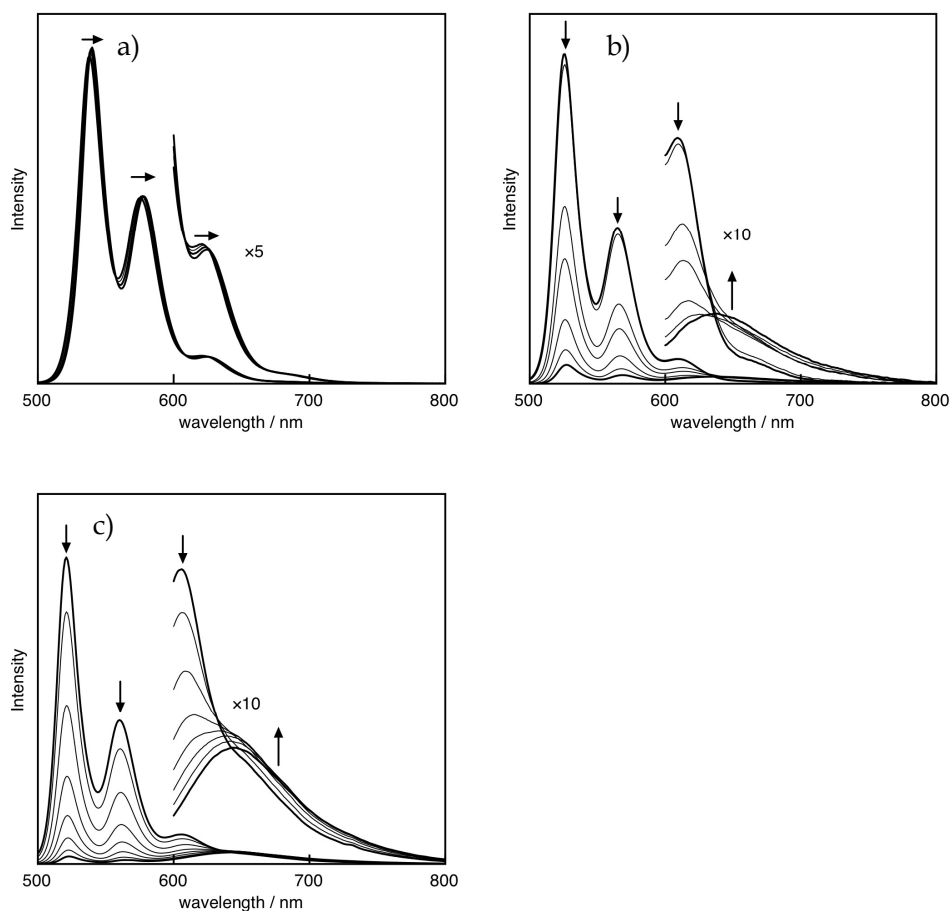


Fig. S7. Temperature-dependent fluorescence spectra of *S-1* in (a) chloroform, (b) decalin, and (c) methylcyclohexane. $[S-1] = 1.0 \times 10^{-5} \text{ mol L}^{-1}$. $\lambda_{\text{ex}} = 488 \text{ nm}$. The temperature of the solution of *S-1* are (a): 323, 313, 303, and 293 K, (b): 353, 343, 333, 323, 313, 303, and 293 K, and (c): 363, 353, 343, 333, 323, 313, 303, and 293 K. Arrows indicate changes upon decreasing temperature.

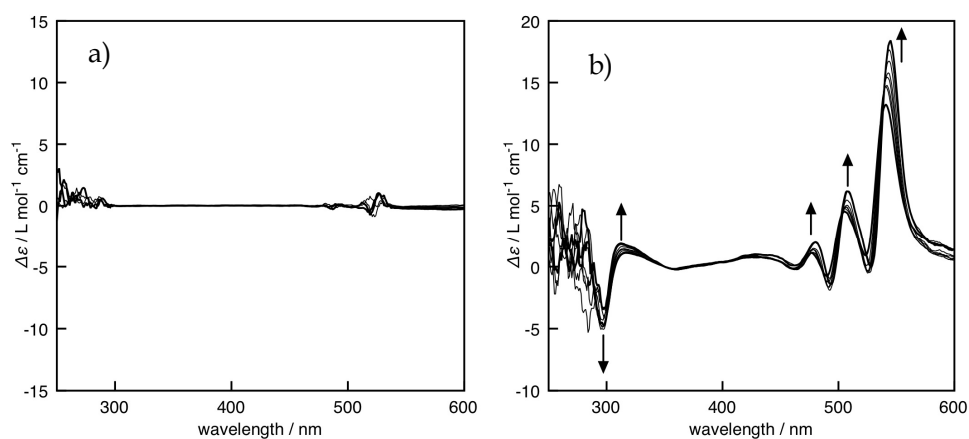


Fig. S8. Temperature-dependent CD spectra of *S-1* in (a) chloroform and (b) methylcyclohexane. [*S-1*] = 1.0×10^{-5} mol L⁻¹. The temperature of the solution of *S-1* are (a): 323, 313, 303, and 293 K and (b): 363, 353, 343, 333, 323, 313, 303, and 293 K. Arrows indicate changes upon decreasing temperature.

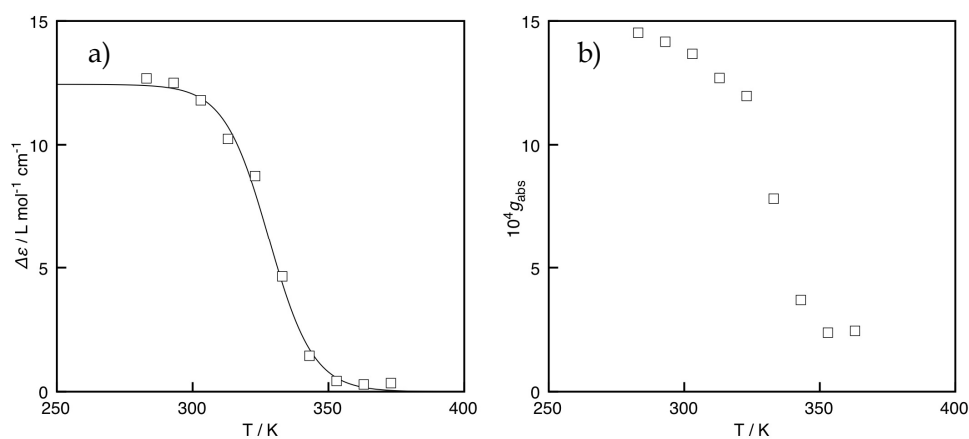


Fig. S9. Plots of (a) $\Delta\epsilon$ and (b) $10^4 g_{\text{abs}}$ of *S-1* in decalin at 545 nm vs temperature.

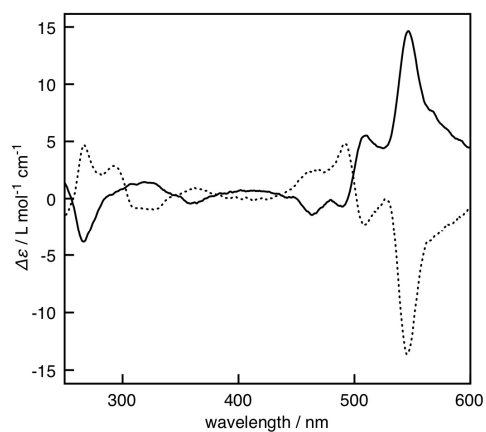
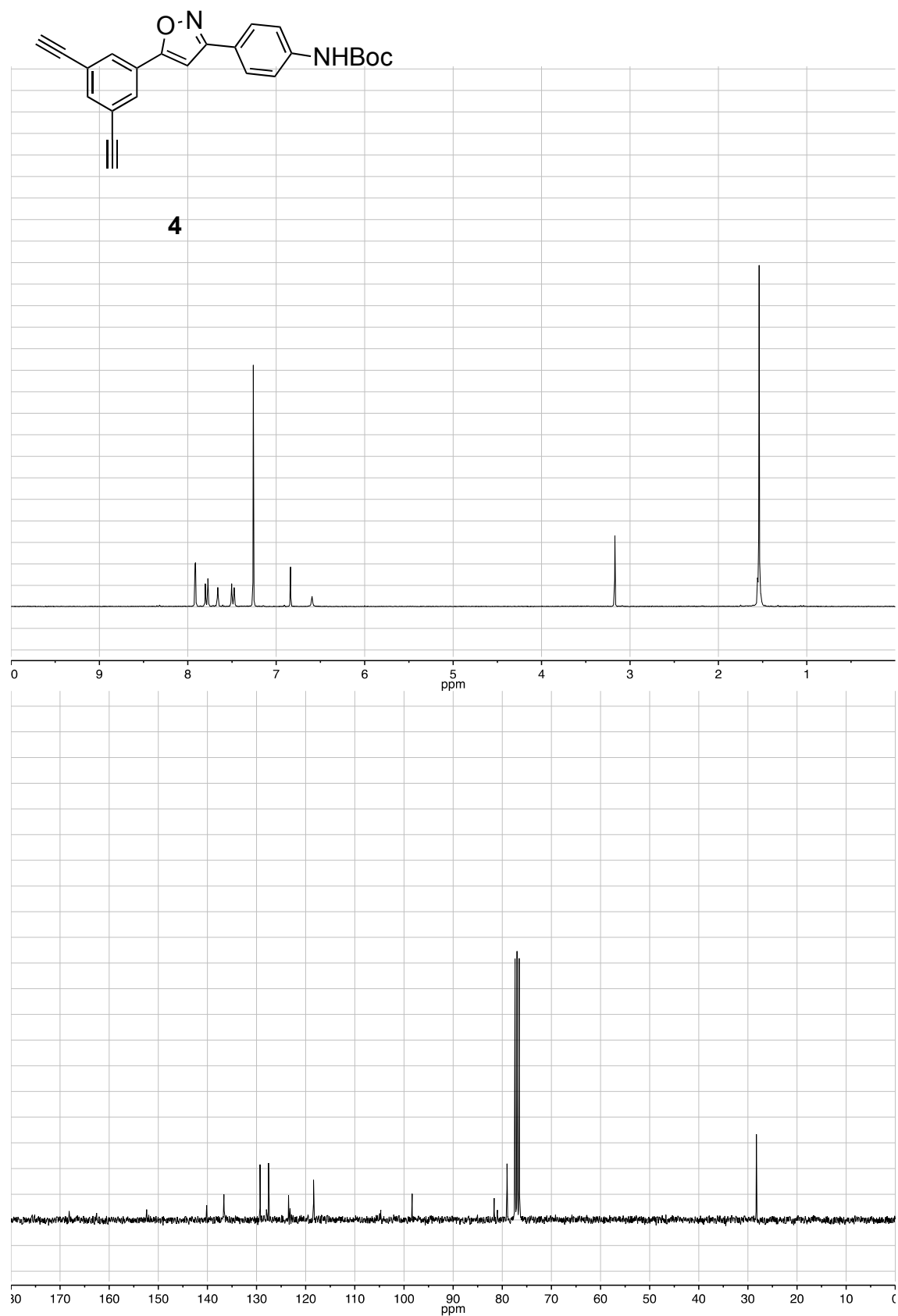
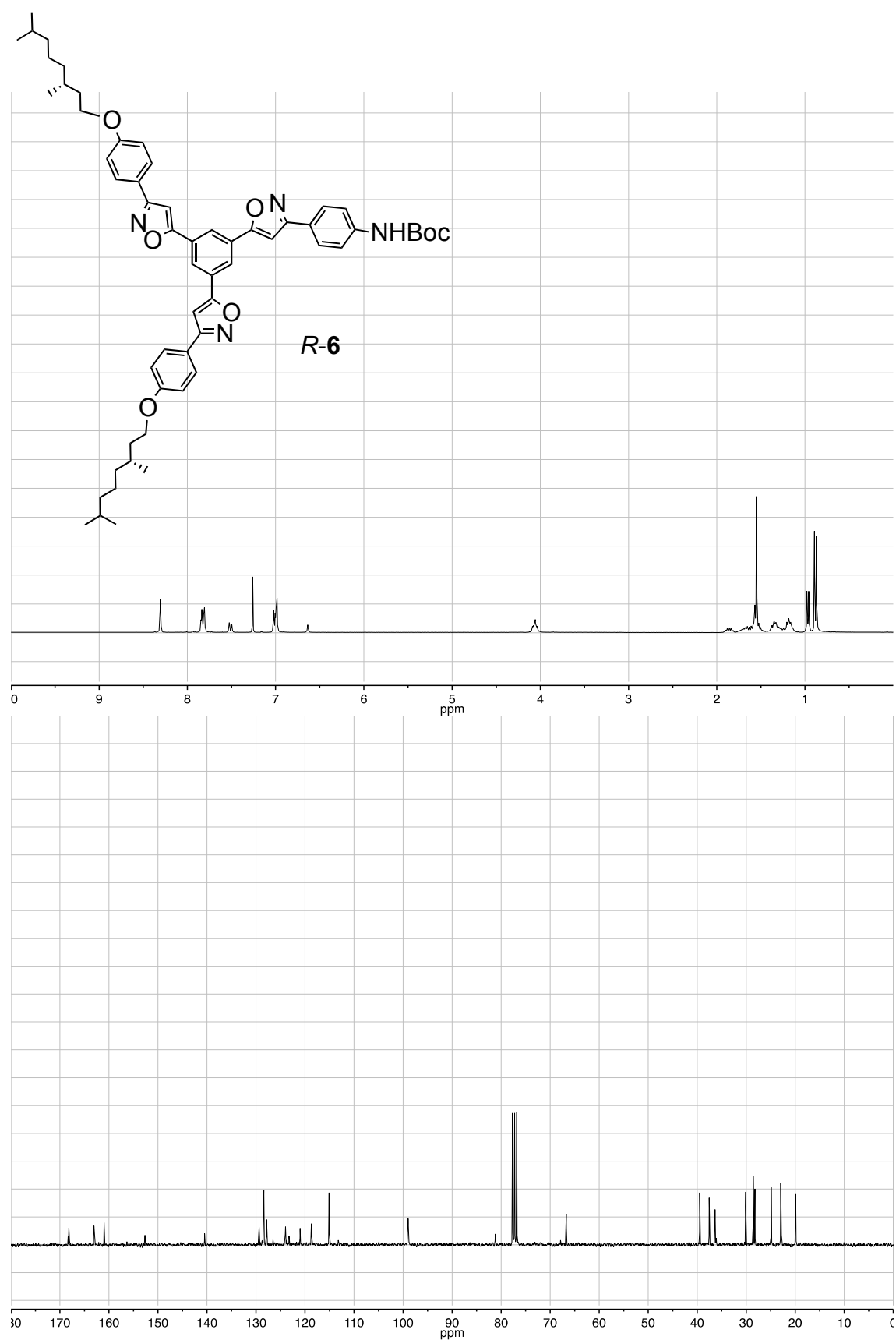


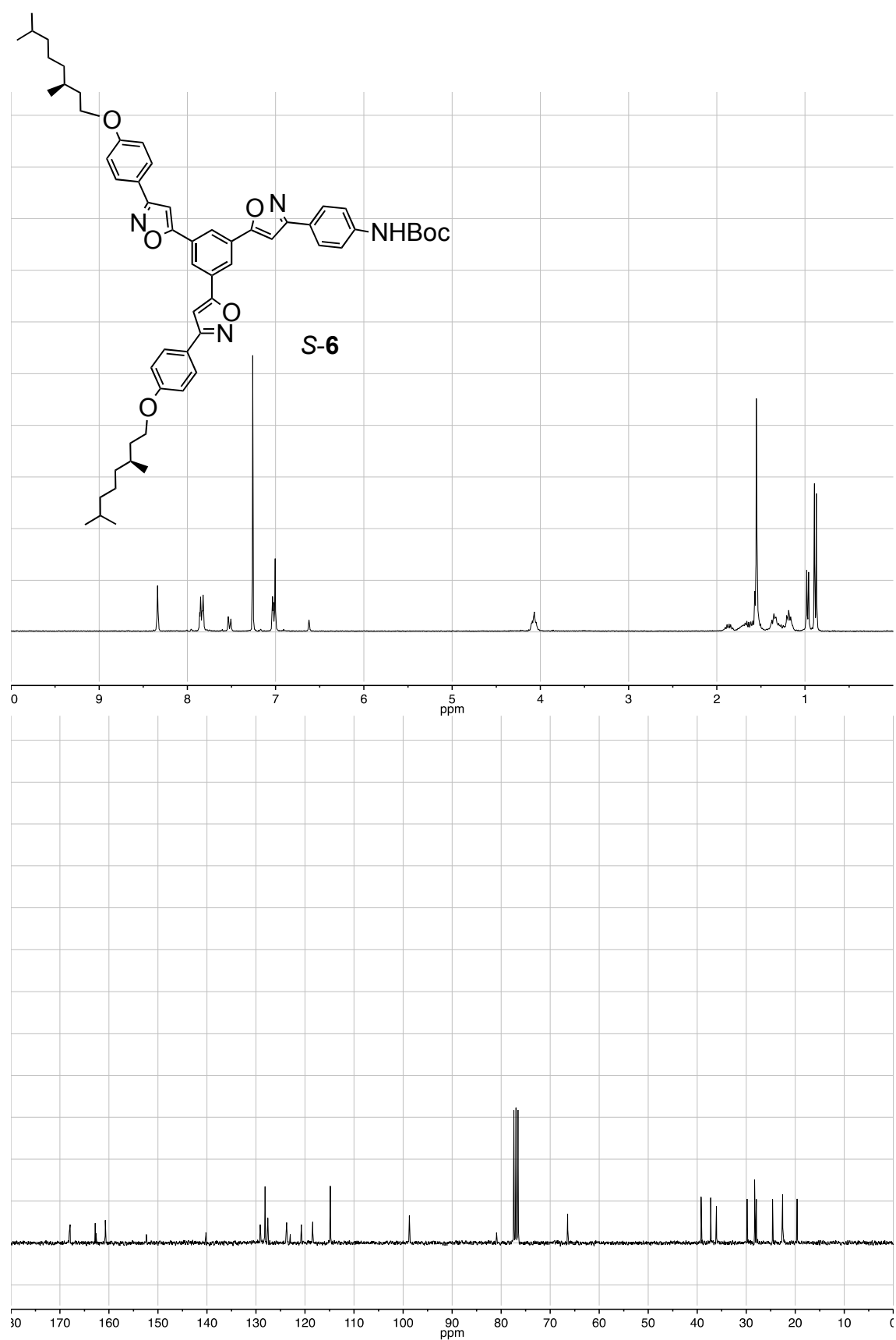
Fig. S10. CD spectra of S-1 (solid line) and R-1 (dashed line) in decalin at 293 K. $[S-1] = [R-1] = 1.0 \times 10^{-5} \text{ mol L}^{-1}$.

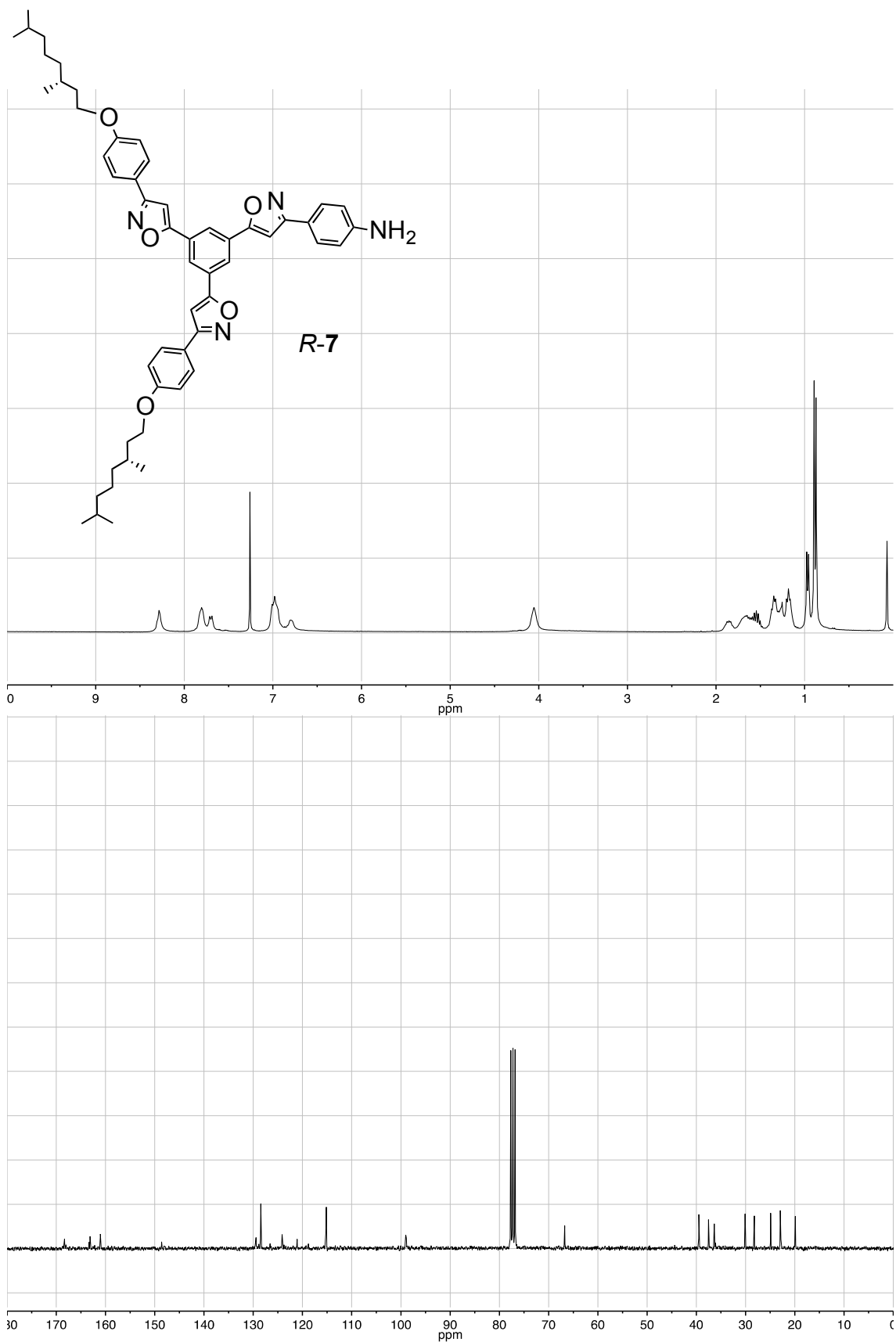
References

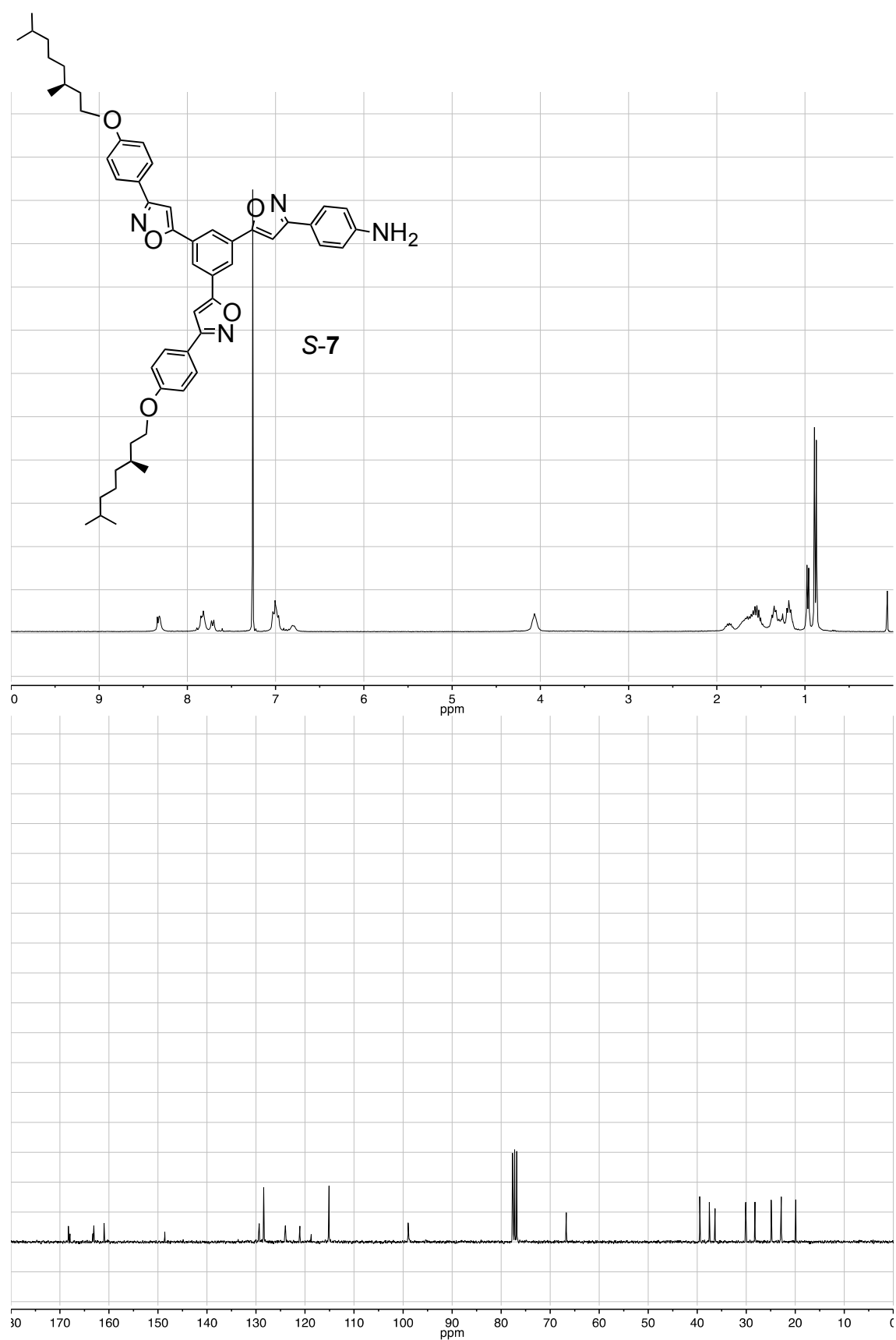
- 1) M. Tanaka, T. Ikeda, J. Mack, N. Kobayashi and T. Haino, *J. Org. Chem.*, 2011, **76**, 5082.
- 2) T. Haino and H. Saito, *Aust. J. Chem.*, 2010, **63**, 640
- 3) N. Soh, T. Ariyoshi, T. Fukaminato, H. Nakajima, K. Nakano and T. Imato, *Org. Biomol. Chem.*, 2007, **5**, 3762.

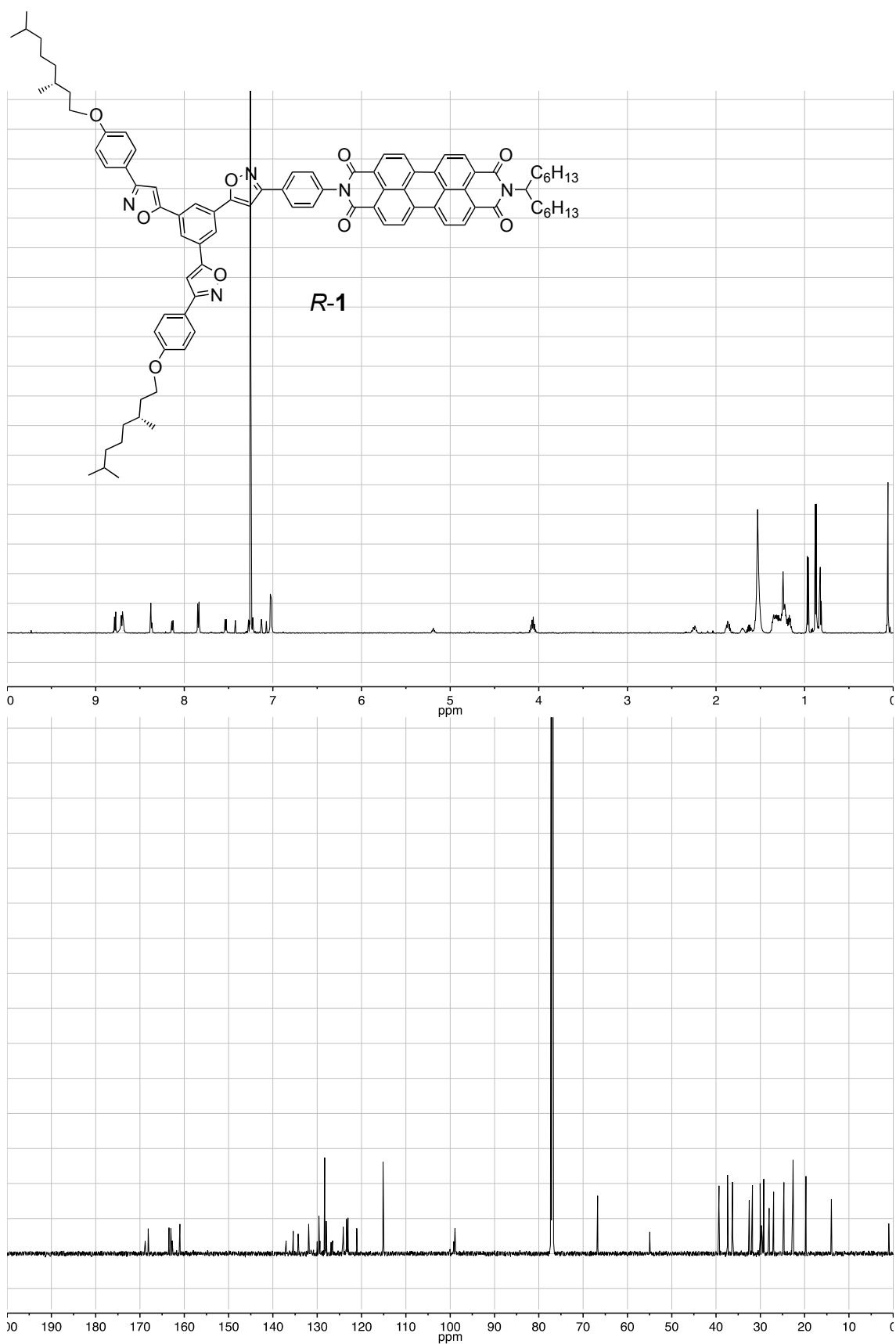




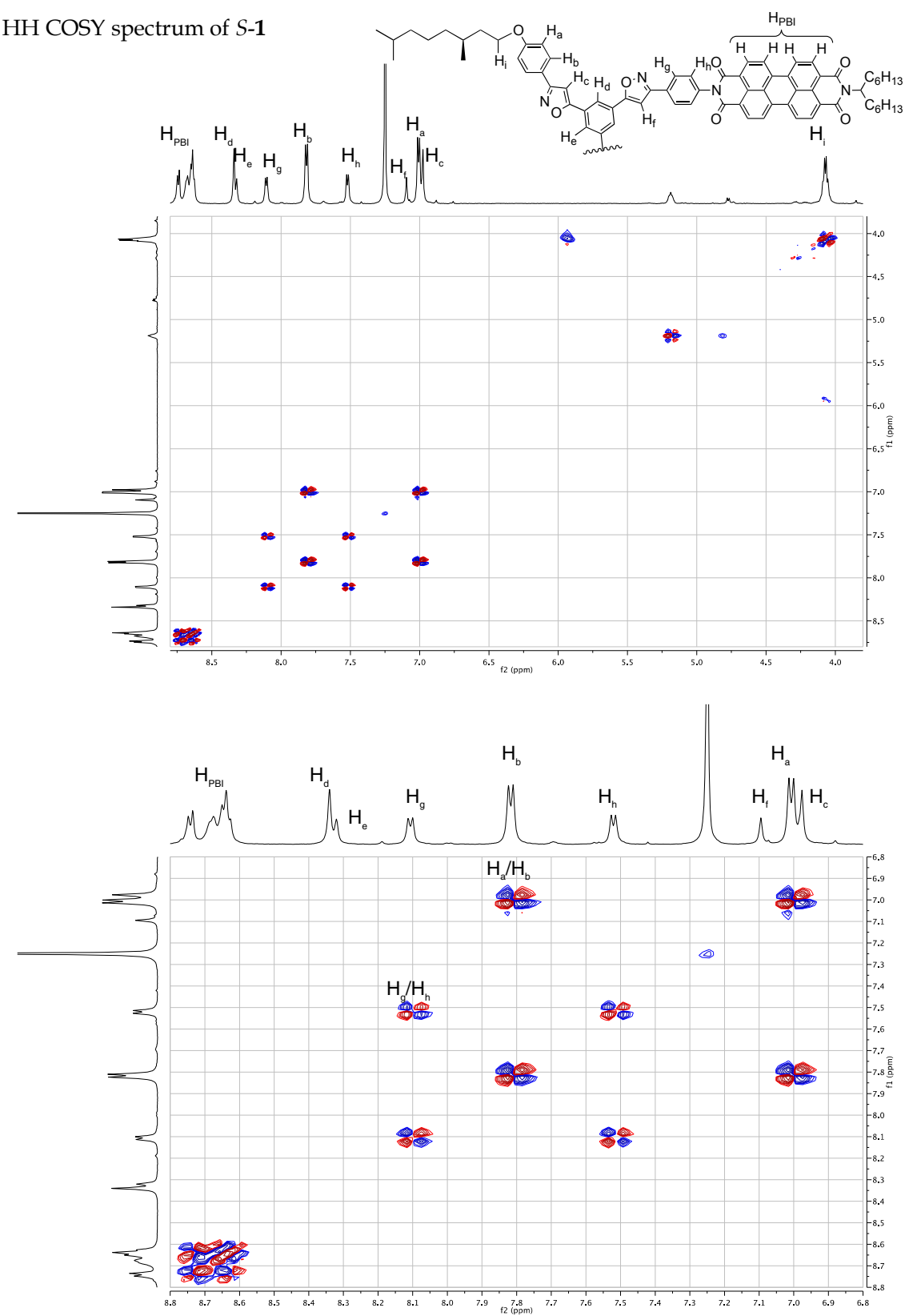








HH COSY spectrum of S-1



NOESY spectrum of S-1

