Electronic Supplementary Information

Circularly Polarized Luminescence of AIE-active Chiral *O*-BODIPYs Induced from Intramolecular Energy Transfer

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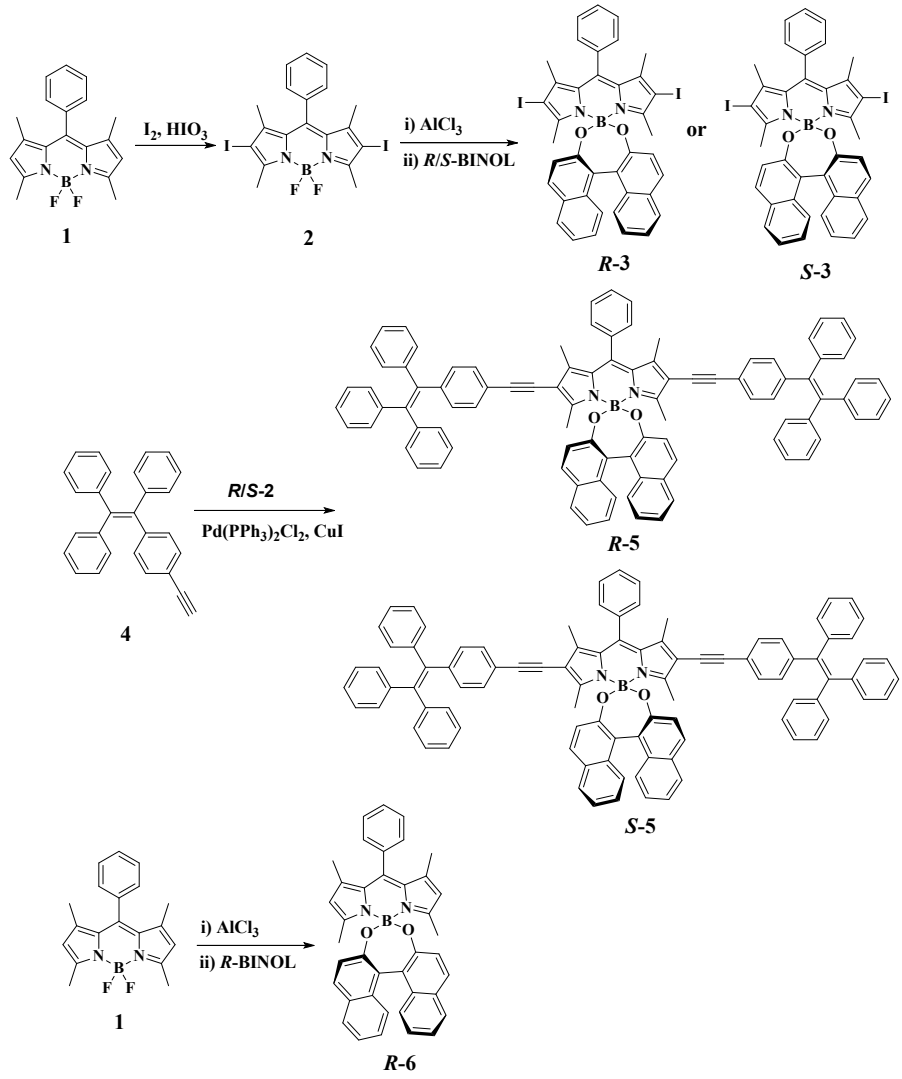
ESI 1. Instrumentations and materials.

All solvents and reagents were commercially available and analytical reagent grade. THF was distilled from sodium in the presence of benzophenone. NMR spectra were obtained from Bruker Avance 300 spectrometer with 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR and reported as parts per million (ppm) from the internal standard TMS. Mass spectrometry was performed on a SHIMADZU LCMS-2020 Instrument. UV-vis spectra were obtained from a Perkin-Elmer Lambda 25 spectrometer. Fluorescence spectra were obtained from an RF-5301PC spectrometer. Circular dichroism (CD) spectra were recorded on a JASCO J-810 spectropolarimeter. Circularly polarized luminescence (CPL) spectra were performed on a JASCO CPL-200 spectrofluoropolarimeter. Elemental analysis was performed on an Elementar Vario MICRO analyzer.

ESI 2. Synthesis procedures of the molecules



Synthesis of *R*/*S*-**3**

A mixture of compound **2** (0.50 g, 0.87 mmol) and aluminum chloride (0.29 g, 2.17 mmol) in dry CH_2Cl_2 (30 mL) was stirred for 5 min at 40 °C under nitrogen atmosphere. Then the mixture was cooled down to room temperature, and a solution of the enantiopure *R*-BINOL or *S*-BINOL (1.24 g, 4.34 mmol) in anhydrous acetonitrile (15 mL) was added. The resulting mixture was stirred for

15 min at r.t. Then the solvent was removed, and the residue was extracted with CH_2Cl_2 and and dried over anhydrous Na_2SO_4. After removal of solvent under reduced pressure, the crude product was purified by column chromatography deactivated basic alumina (petroleum ether/ dichloromethane, 2/1) to afford *R*/*S*-**2** as a red solid.

R-**3**: (0.63 g, 88.3%). $[\alpha]_D^{20}$ -4986 (c 0.10, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.89-7.81 (m, 4H), 7.57-7.55 (m, 3H), 7.39-7.34 (m, 4H), 7.30-7.27 (m, 2H), 7.22-7.17 (m, 4H), 1.79 (s, 6H), 1.41 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.3, 154.0, 145.0, 135.4, 133.7, 131.3, 130.0, 129.5, 129.3, 128.3, 128.1, 127.9, 127.4, 127.1, 125.3, 124.0, 123.5, 123.4, 121.4, 117.7, 17.5, 17.4. Anal. calcd for $C_{39}H_{29}BI_2N_2O_2$: C, 56.97; H, 3.55. Found: C, 56.96; H, 3.55. MS (ESI, m/z): 822.90 (M^++1).

S-**3**: (0.58 g, 81.3%). $[\alpha]_D^{20}$ 5202 (c 0.12, $CHCl_3$). Anal. calcd for $C_{36}H_{48}B_2O_6$: C, 56.97; H, 3.55. Found: C, 56.96; H, 3.56. MS (ESI, m/z): 822.95 (M^++1).

Synthesis of *R*/*S*-**5**

A mixture of compound *R*/*S*-**3** (0.50 mg, 0.61 mmol), **4** (0.46 mg, 1.28 mmol), $Pd(PPh_3)_2Cl_2$ (5% mmol), CuI (5% mmol) were added to THF (20 mL) and Et_3N (10 mL) under nitrogen atmosphere. The reaction mixture was stirred at 70 °C for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography deactivated basic alumina (petroleum ether/ dichloromethane, 4/1) to afford *R*/*S*-**5** as a brown red solid.

R-**5**: (0.56 g, 72.0%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.90-7.82 (m, 4H), 7.57-7.55 (m, 3H), 7.41-7.31 (m, 5H), 7.26-7.17 (m, 5H), 7.13-7.07 (m, 22H), 7.05-6.98 (m, 12H), 6.94-6.92 (m, 4H), 1.80 (s, 6H), 1.51 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.5, 154.3, 143.6, 143.4, 143.3, 143.3, 141.8, 141.5, 140.2, 135.1, 133.7, 131.9, 131.3, 131.2, 130.4, 130.0, 129.5, 129.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.1, 126.6, 126.5, 125.3, 123.4, 121.5, 121.1, 117.0, 96.6, 82.3, 14.8, 13.6. Anal. calcd for $C_{95}H_{67}BN_2O_2$: C, 89.19; H, 5.28. Found: C, 89.21; H, 5.28. MS (ESI, m/z): 1279.85 (M^++1).

S-**5**: (0.52 g, 66.8%). Anal. calcd for $C_{95}H_{67}BN_2O_2$: C, 89.19; H, 5.28. Found: C, 89.23; H, 5.27. MS (ESI, m/z): 1279.50 (M^++1).

Synthesis of *R*-**6**

A mixture of compound **1** (0.20 g, 0.62 mmol) and aluminum chloride (0.21 g, 1.54 mmol) in dry CH_2Cl_2 (20 mL) was stirred for 5 min at 40 °C under nitrogen atmosphere. Then the mixture was cooled down to room temperature, and a solution of the enantiopure *R*-BINOL (0.88 g, 3.08 mmol) in anhydrous acetonitrile (10 mL) was added. The resulting mixture was stirred for 15 min at r.t. Then the solvent was removed, and the residue was extracted with CH_2Cl_2 and and dried over anhydrous Na_2SO_4. After removal of solvent under reduced pressure, the crude product was purified by column chromatography deactivated basic alumina (petroleum ether/ dichloromethane, 2/1) to afford *R*-**6** as a red solid (0.25 g, 71.6%). $[\alpha]_D^{20}$ -4825 (c 0.10, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, J = 6.0 Hz, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.53-7.48 (m, 3H), 7.38-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.26-7.21 (m, 4H), 7.17-7.12 (m, 2H), 5.79 (s, 2H), 1.65 (s, 6H), 1.36 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.6, 154.7, 142.8, 141.4, 135.7, 133.8, 132.2, 129.9, 129.2, 129.1, 128.9, 128.4, 127.9, 127.2, 125.2, 123.9, 123.3, 122.5, 121.5, 16.0, 14.7. Anal. calcd for $C_{39}H_{29}BI_2N_2O_2$: C, 82.11; H, 5.48. Found: C, 82.09; H, 5.49. MS (ESI, m/z): 571.25 (M^++1).

ESI 3. Optical data

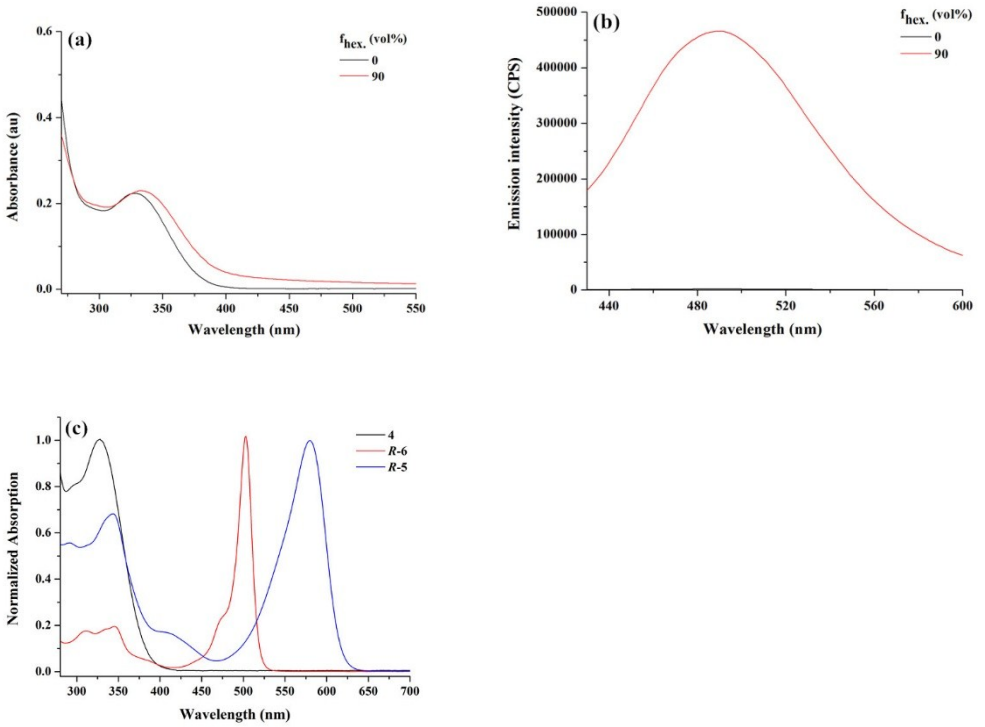


Figure S1. (a) UV-vis spectra of **4**; (b) Fluorescence spectra of **4** in dichloromethane/ hexane mixed solvents; (c) Normalized UV-vis spectra of **4**, *R*-**5** and *R*-**6** in dichloromethane. Solution concentration: 1.0×10^{-5} mol L^{-1}.

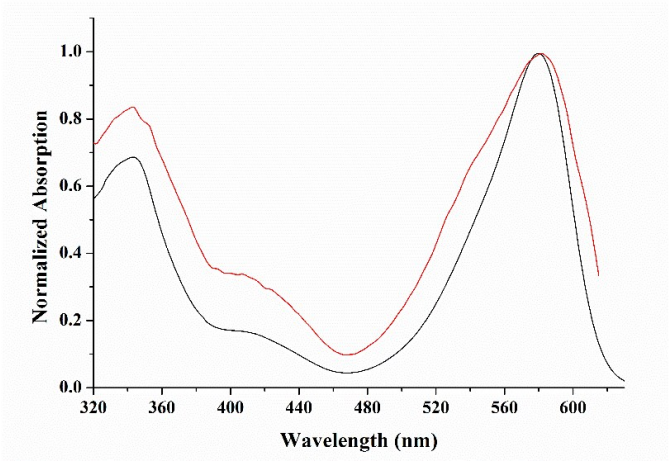


Figure S2. Comparison of absorption (black) and excitation (red) spectra recorded for *R*-**5** in dichloromethane solution. Solution concentration: 1.0×10^{-5} mol L^{-1}.

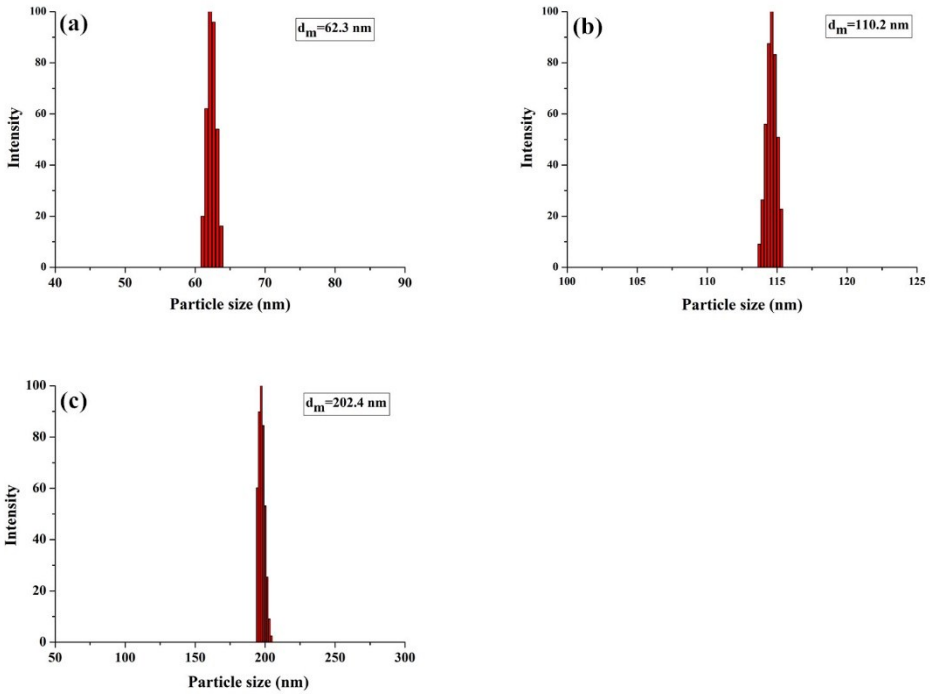


Figure S3. DLS data of *R*-**5** in dichloromethane/hexane mixed solvents (a) 70/30 v/v; (b) 40/60 v/v; (c) 10/90 v/v, where d_m is the mean diameter. Solution concentration: 1.0×10^{-5} mol L^{-1}.

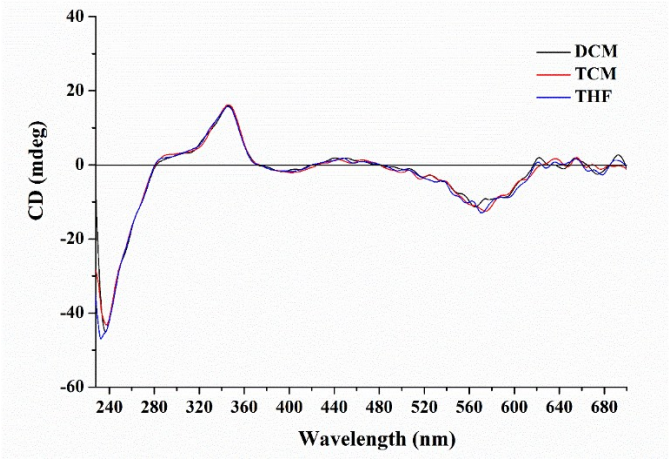


Figure S4. CD spectra of *R*-**5** in different solvents. Dichloromethane (DCM); Chloroform (TCM); Tetrahydrofuran (THF). Solution concentration: 1.0×10^{-5} mol L^{-1}.

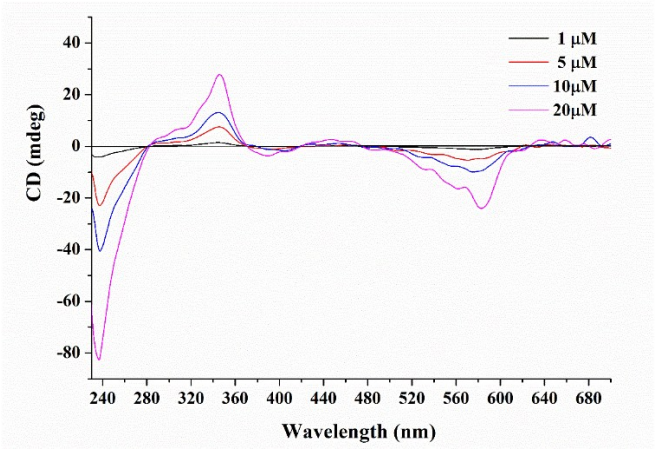


Figure S5. CD spectra of *R*-**5** with different concentration in dichloromethane. Solution concentration: 1.0×10^{-5} mol L^{-1}.

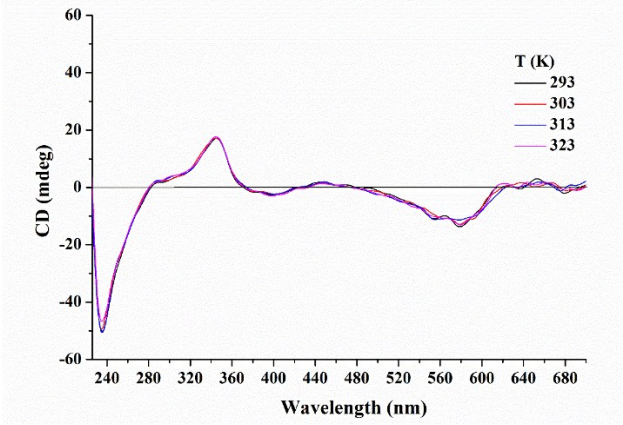
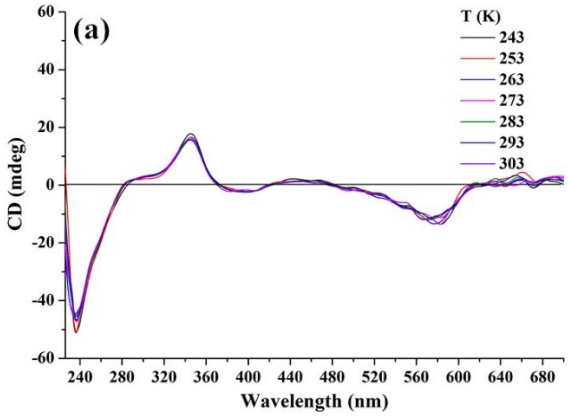


Figure S6. CD spectra of *R*-**5** with variable temperature in chloroform. Solution concentration: 1.0×10^{-5} mol L^{-1}.



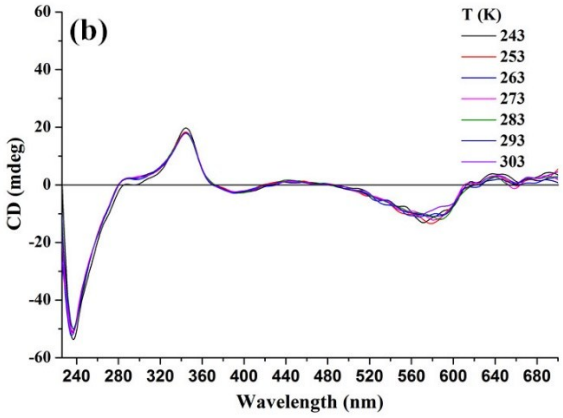


Figure S7. Variable temperature CD spectra of *R*-**5** in dichloromethane/hexane mixed solvents (a) 70/30 v/v and (b) 40/60 v/v. Solution concentration: 1.0×10^{-5} mol L^{-1}.

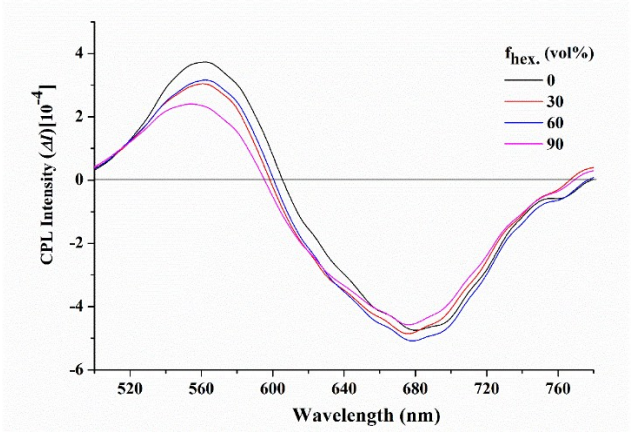


Figure S8. CPL spectra of *R*-**5** in dichloromethane/hexane mixed solvents. (Excitation Wavelength: 580 nm). Solution concentration: 1.0×10^{-5} mol L^{-1}.

ESI 4. NMR spectra

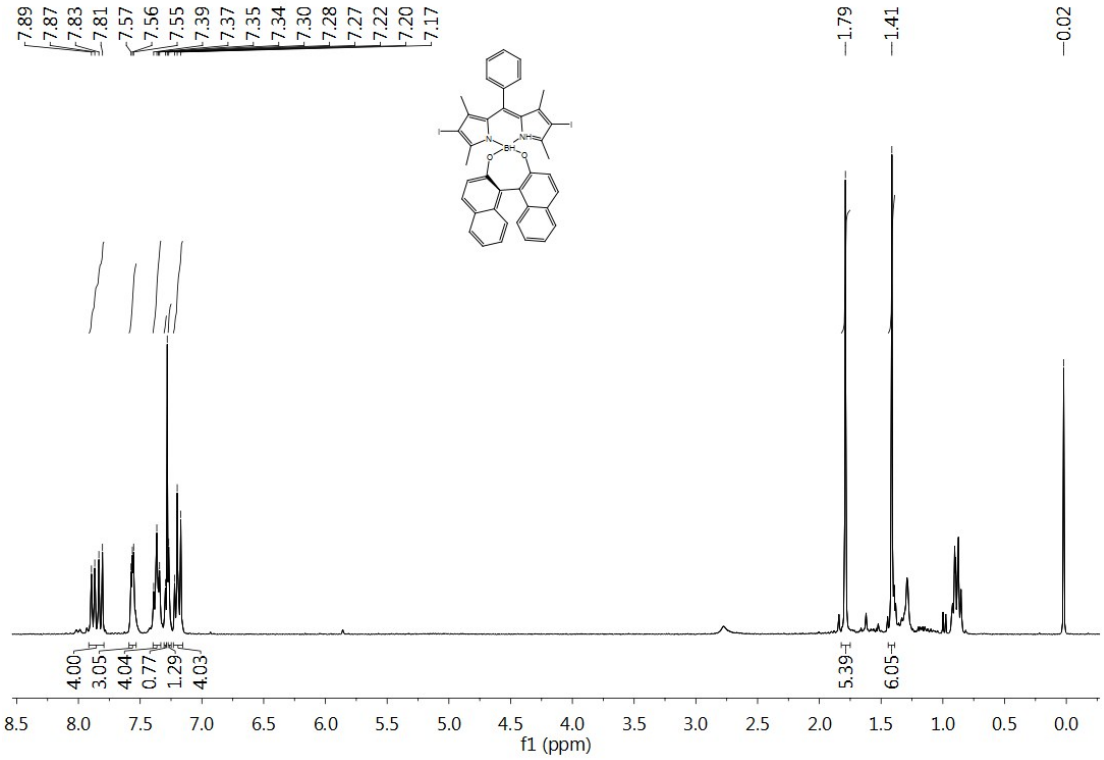


Figure S9. ^{1}H NMR of *R*-**3** in $CDCl_3$.

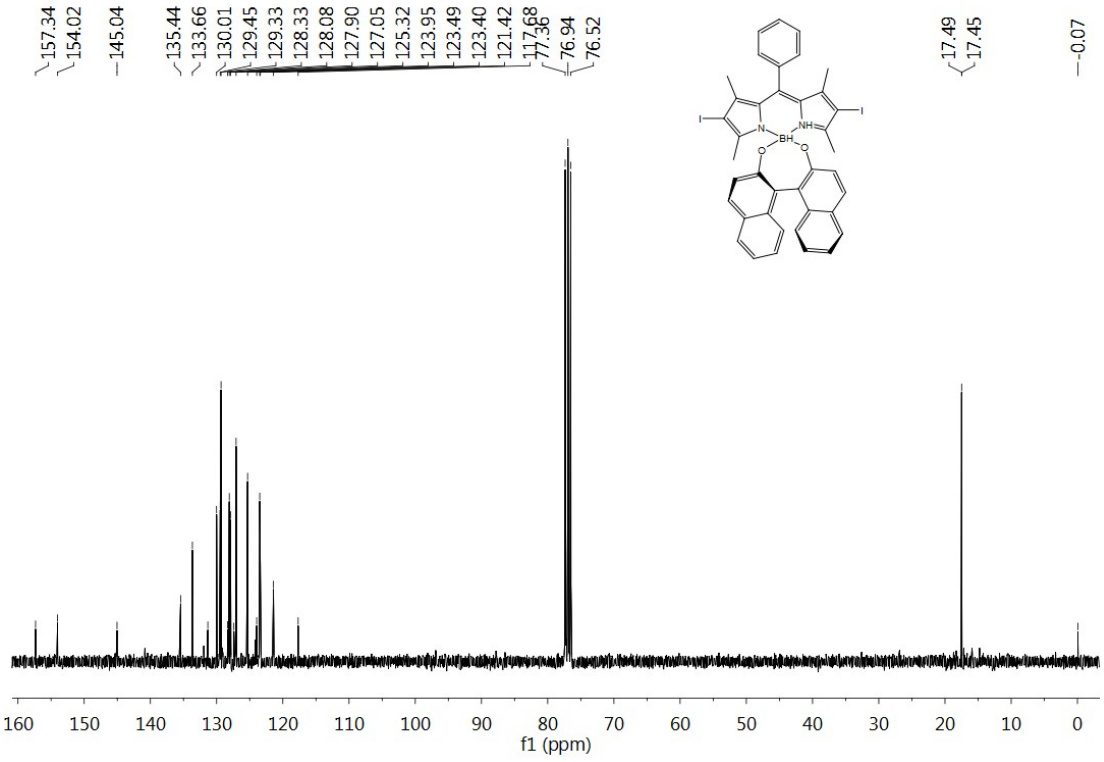


Figure S10. ^{13}C NMR of *R*-**3** in $CDCl_3$.

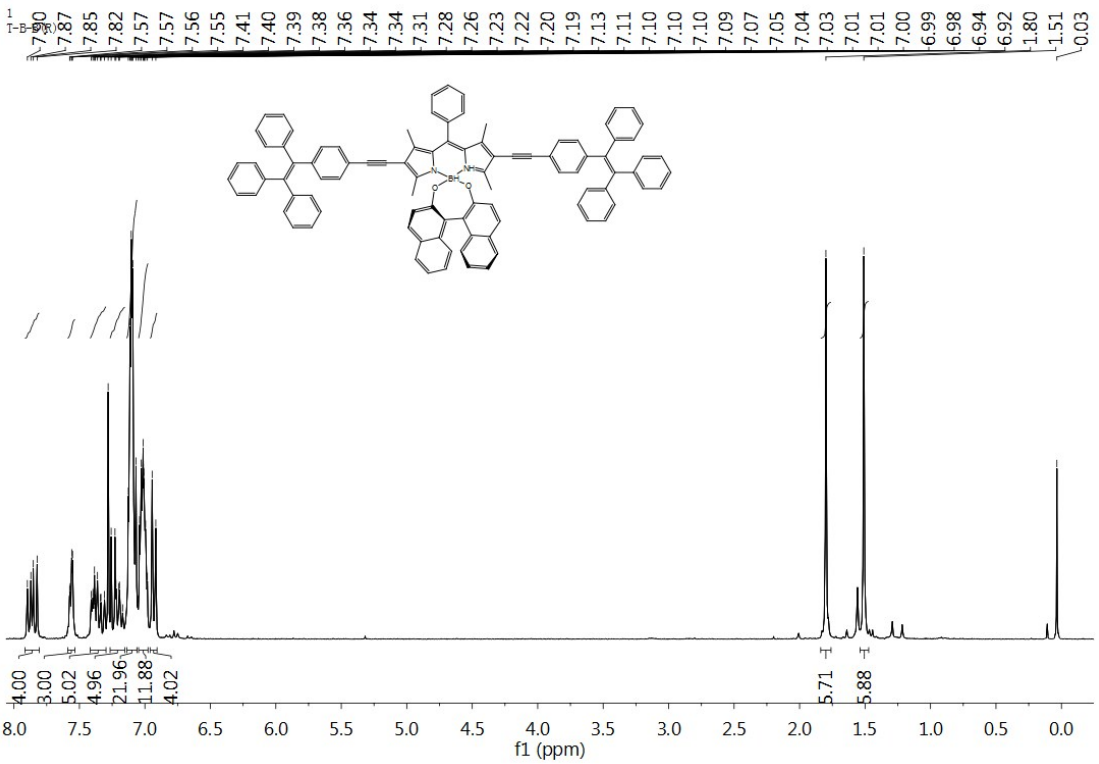


Figure S11. ^{1}H NMR of *R*-**5** in $CDCl_3$.

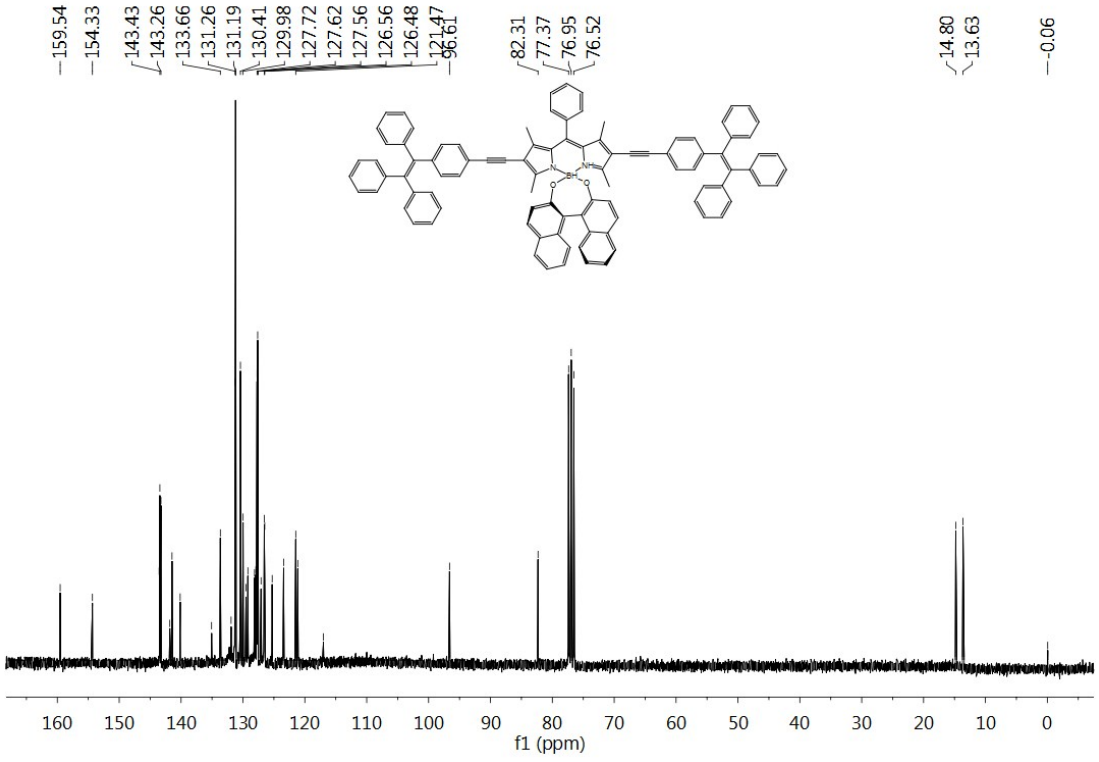


Figure S12. ^{13}C NMR of *R*-**5** in $CDCl_3$.

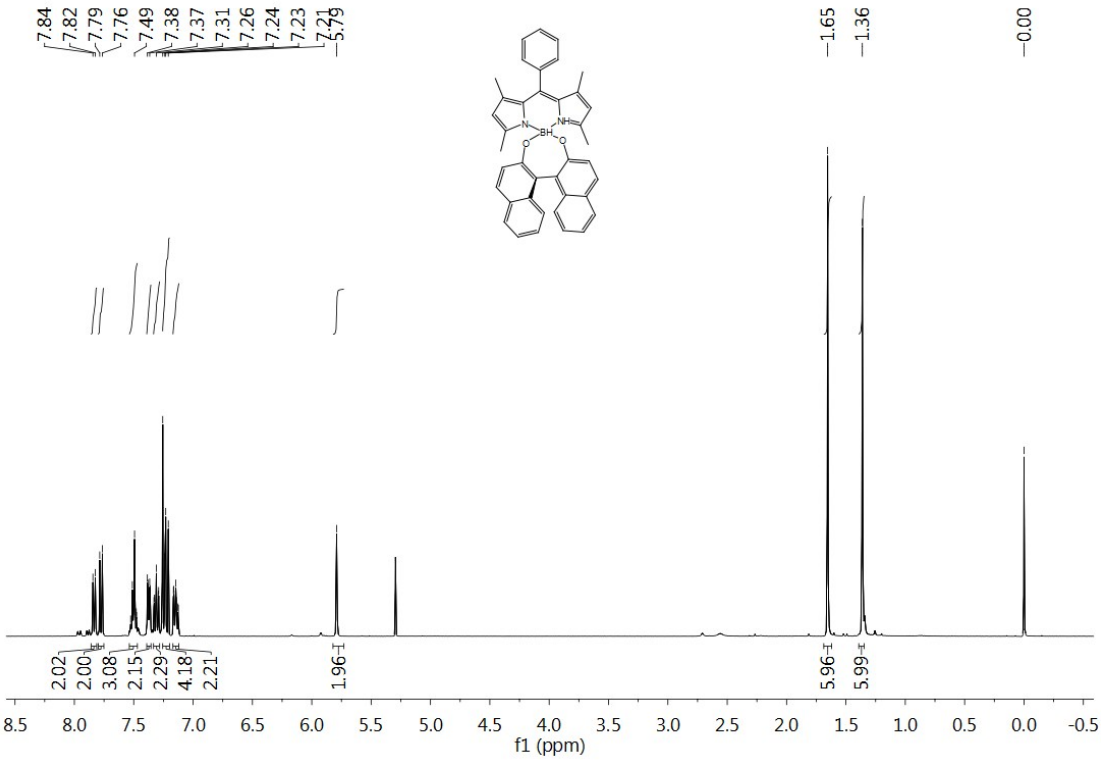


Figure S13. ^{1}H NMR of *R*-**6** in $CDCl_3$.

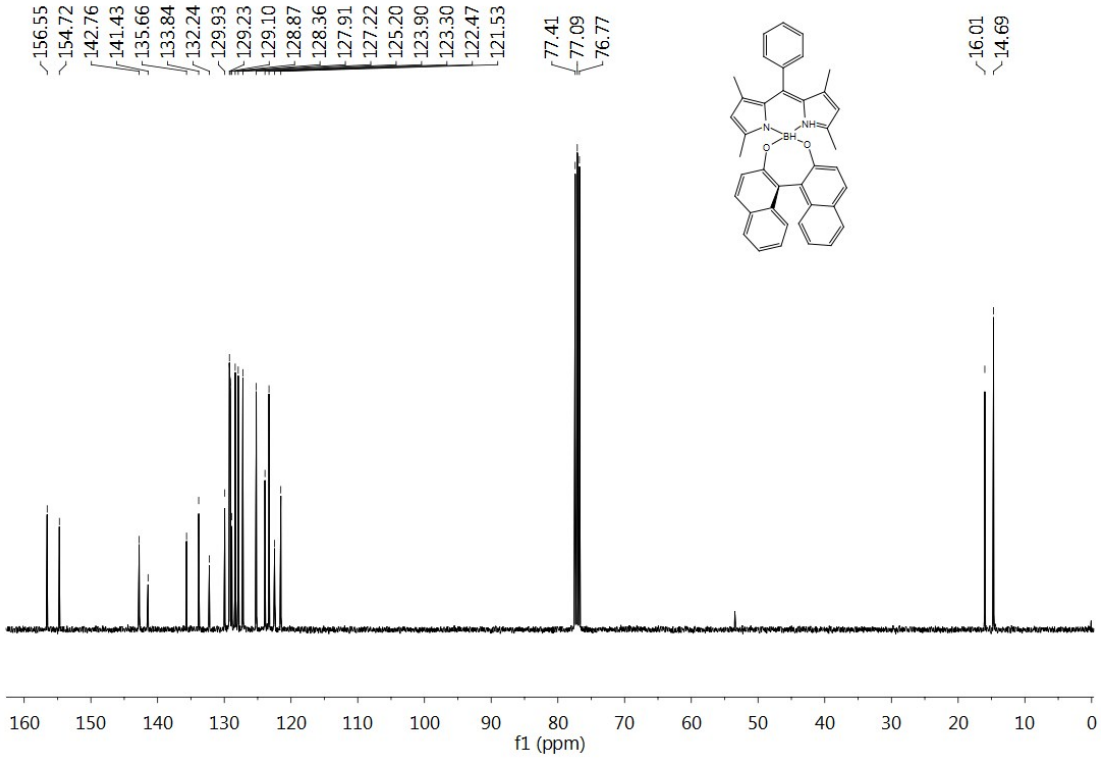


Figure S14. ^{13}C NMR of *R*-**6** in $CDCl_3$.