*The Supporting Information for*

# Synthesis of Figure-of-Eight Helical BisBODIPY Macrocycles and Their Chiroptical Properties

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**Note added after first publication:** This Supplementary Information file replaces that originally published on 21st July 2016. Schemes S1 and S2, and the synthetic procedures for [H3**1**B] and [**1**B2], were incorrect in the original file and have been corrected here. For further details, please refer to the correction notice which was published for the original article (see DOI: 10.1039/C8CC90385A).

## Table of Contents

## Materials and methods

Unless otherwise noted, solvents and reagents were purchased from TCI Co., Ltd., Wako Pure Chemical Industries, Ltd., Kanto Chemical Co., Inc., Nacalai Tesque, Inc. or Sigma-Aldrich Co., and used without further purification. Silica gel for column chromatography was purchased from Kanto Chemical Co. Inc. (Silica Gel 60 N (spherical, neutral, 63–210 μm). Alumina for column chromatography was purchased from Wako Pure Chemical Industries, Ltd. (alumina, activated (about 75 μm)). GPC purification was performed on a JAI LC-9210 II NEXT system with JAIGEL-1HH/2HH columns using $CHCl_3$ as an eluent.

$^{1}H$, $^{13}C$, NMR, and other 2D NMR spectra were recorded on a Bruker AVANCE III-400, 600 spectrometers. Tetramethylsilane was used as an internal standard (δ 0.00 ppm) for $^{1}H$ and $^{13}C$ NMR measurements when $CDCl_3$ was used as a solvent. $BF_3 \cdot Et_2O$ in $CDCl_3$ (1 wt%) was used as an external standard (δ 0.0 ppm) for $^{11}B$ NMR measurements.

Single-crystal X-ray crystallographic measurements were performed using a Bruker APEX II ULTRA with Mo$K\alpha$ radiation. Obtained data were processed using a Bruker APEX2[S1] and Yadokari-XG[S2] crystallographic software package except for refinement, which was performed using SHELXL-2014[S3]. CCDC 1486268–1486272 contain the data for the structures. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

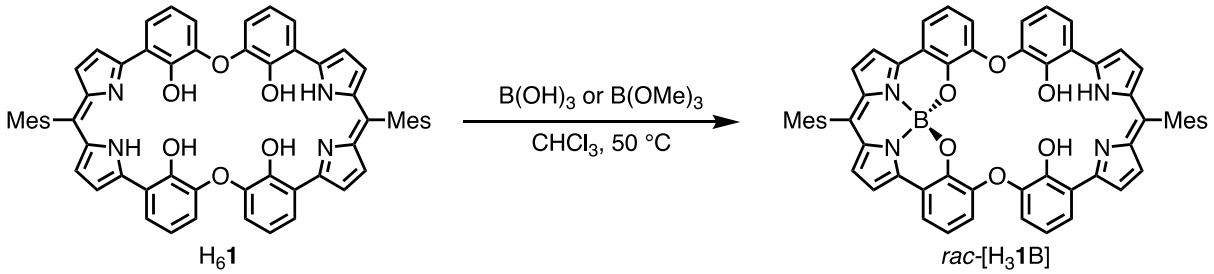
MALDI-TOF mass data were recorded on an AB SCIEX TOF/TOF 5800 system. ESI-TOF mass data were recorded on an AB SCIEX TripleTOF 4600 system.

UV-Vis spectra were recorded on a JASCO V-670 spectrophotometer. Emission spectra were recorded on a JASCO FP-8600 fluorescence spectrophotometer. Absolute fluorescence quantum yields were determined with a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-02. CD spectra were recorded on a JASCO J-720W spectrophotometer. CPL spectra were recorded on a JASCO CPL-200S spectrophotometer. Solvents used for measurements were air-saturated.

Elemental analysis was performed on a Yanaco MT-6 analyzer with tin boats purchased from Elementar. We appreciate Mr. Ikuo Iida for the measurements.

## Synthesis and characterization of the compounds

**Scheme S1.** Synthesis of [$H_3$**1**B]




Synthesis of [$H_3$**1**B] (method A, $B(OH)_3$)

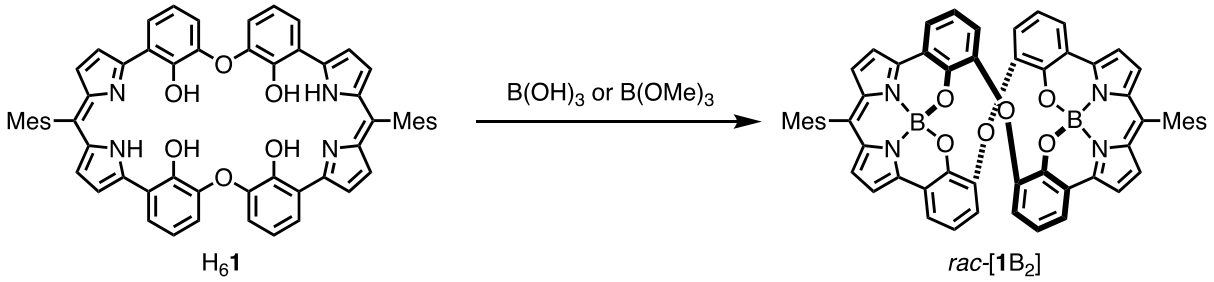
A 5 mL two-necked round-bottom flask was charged with $H_6$**1**[S4] (4.97 mg, 5.40 μmol) and boric acid (0.80 mg, 13 μmol). Chloroform (1.8 mL) was added to the flask. The mixture was stirred at 50 °C for 22.5 h. After cooling, the mixture was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/dichloromethane = 1/1) to give [$H_3$**1**B] (4.12 mg, 4.44 μmol, 82%).

Synthesis of [$H_3$**1**B] (method B, $B(OMe)_3$)

A 5 mL two-necked round-bottom flask was charged with $H_6$**1**[S4] (6.9 mg, 7.5 μmol) and trimethyl borate (2.50 μL, 22.5 μmol). Chloroform (2.0 mL) was added to the flask. The mixture was stirred at 50 °C for 66 h. After cooling, the mixture was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent: chloroform/*n*-hexane = 2/1) to give [$H_3$**1**B] (5.9 mg, 6.4 μmol, 84%).

[$H_3$**1**B]: dark purple solid.
m.p. >280 °C.
$^1$H NMR (400 MHz, $CDCl_3$) δ 12.70 (br, 1H), 7.56 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.46 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.03 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.00 (s, 2H), 6.96 (s, 2H), 6.90 (dd, *J* = 8.0, 8.0 Hz, 2H), 6.88–6.84 (m, 8H), 6.59 (dd, *J* = 8.0, 1.3 Hz, 2H), 6.46 (d, *J* = 4.4 Hz, 2H), 2.39 (s, 3H), 2.38 (s, 3H), 2.16 (s, 6H), 2.14 (s, 6H).
$^{11}$B NMR (128 MHz, $CDCl_3$) δ –0.3 (br).
$^{13}$C NMR (151 MHz, $CDCl_3$) δ 153.6, 150.5, 149.2, 149.1, 143.1, 141.3, 139.4, 138.6, 138.3, 137.9, 137.5, 137.2, 137.0, 135.2, 134.6, 129.4, 129.2, 128.3, 128.2, 127.8, 124.8, 124.8, 123.9, 120.6, 120.3, 120.0, 119.3, 119.0, 116.3, 115.8, 114.9, 21.18, 21.15, 20.3, 19.9.
Elemental analysis: calcd for $C_{60}H_{47}BN_4O_7$ ([$H_3$**1**B]·$H_2O$): C, 76.11; H, 5.00; N, 5.92. Found: C, 76.06; H, 5.16; N, 5.79.

**Scheme S2.** Synthesis of [**1**$B_2$]




Synthesis of [**1**$B_2$] (method A, $B(OH)_3$)

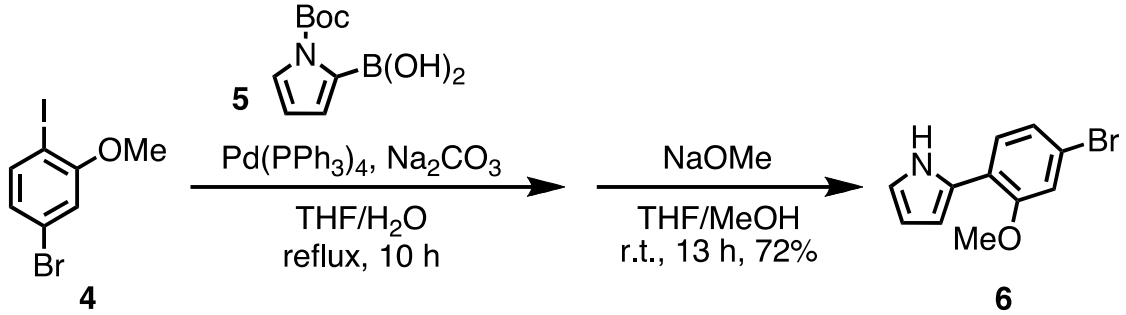
A 10 mL two-necked round-bottom flask was charged with $H_6$**1**[S4] (2.9 mg, 3.1 μmol) and boric acid (1.60 mg, 25.9 μmol). Chloroform (2.0 mL) was added to the flask. The mixture was refluxed for 66 h. After cooling, the mixture was concentrated in vacuo. The crude product was reprecipitated with chloroform (1.0 mL) and *n*-hexane (10 mL) to give [**1**$B_2$] (3.2 mg, quant.).

Synthesis of [**1**$B_2$] (method B, $B(OMe)_3$)

A 10 mL two-necked round-bottom flask was charged with $H_6$**1**[S4] (4.95 mg, 5.37 μmol) and trimethyl borate (18.0 μL, 162 μmol). 1,2-dichloroethane (3.0 mL) was added to the flask. The mixture was stirred at 67 °C for 66.5 h. After cooling, the mixture was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent: chloroform/*n*-hexane = 2/1). Reprecipitation with chloroform (1.0 mL) and *n*-hexane (20 mL) was performed to give [**1**$B_2$] (4.9 mg, 5.2 μmol, 92%).

[**1**$B_2$]: red solid.
m.p. >280 °C.
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, $J$ = 7.8, 1.6 Hz, 4H), 7.16 (dd, $J$ = 7.8, 1.6 Hz, 4H), 6.98 (s, 4H), 6.77 (d, $J$ = 4.2 Hz, 4H), 6.70 (d, $J$ = 4.2 Hz, 4H), 6.67 (dd, $J$ = 7.8, 7.8 Hz, 4H), 2.38 (s, 6H), 2.17 (s, 12H).
$^{13}$B NMR (128 MHz, $CDCl_3$) δ –1.1 (br).
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 149.5, 147.9, 146.5, 138.5, 138.0, 137.3, 134.2, 129.6, 128.3, 127.2, 125.7, 120.8, 120.6, 119.5, 115.9, 21.2, 20.5.
Elemental analysis: calcd for $C_{60}H_{47}B_2N_4O_{8.5}$ ([**1**$B_2$]·2.5$H_2O$): C, 73.41; H, 4.83; N, 5.71. Found: C, 73.14; H, 4.68; N, 5.40.

**Scheme S3.** Synthesis of **6**



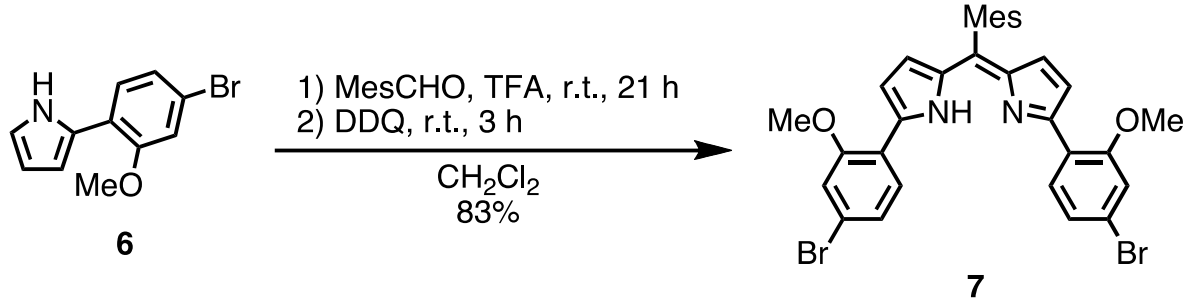

A 100 mL three-necked round-bottom flask was charged with **5**[S5] (2.25 g, 10.7 mmol), $Na_2CO_3$ (1.36 g, 12.8 mmol), and tetrakis(triphenylphosphine)palladium (0.218 g, 0.189 mmol). The flask was evacuated then refilled with argon. **4**[S6] (1.14 g, 3.63 mmol), dry THF (40 mL) and degassed water (13 mL) were added to the flask. The mixture was refluxed under argon for 10 h. After cooling, water (25 mL) was added, and the mixture was extracted with ethyl acetate (25 mL × 3). The combined organic layer was dried over $Na_2SO_4$, filtered, and concentrated in vacuo. The crude was purified by column chromatography on silica gel using dichloromethane / *n*-hexane (1:2) as the eluent. The obtained oil was dissolved in dry THF (35 mL) in a 100 mL round-bottom flask, and the mixture of 28% NaOMe in MeOH (3.25 g, 16.9 mmol) and dry THF (35 mL) was added. The mixture was stirred at room temperature for 13 h. Water (65 mL) was added, and the mixture was extracted with ethyl acetate (30 mL × 3). The combined organic layer was dried over $Na_2SO_4$, filtered, and concentrated in vacuo to give **6** (0.656 g, 2.60 mmol, 72%).

**6**: dark brown oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 9.70 (br, 1H), 7.50 (d, $J$ = 8.3 Hz, 1H), 7.11 (dd, $J$ = 8.3, 1.8 Hz, 1H), 7.08 (d, $J$ = 1.8 Hz, 1H), 6.88–6.86 (m, 1H), 6.61–6.59 (m, 1H), 6.29–6.27 (m, 1H), 3.95 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.1, 128.9, 127.6, 124.5, 120.3, 119.2, 118.2, 115.1, 109.0, 106.5, 56.0.

**Scheme S4.** Synthesis of **7**




A 200 mL three-necked round-bottom flask was charged with **6** (1.34 g, 5.30 mmol). The flask was evacuated then refilled with argon. Degassed dichloromethane solution (50 mL) of 2,4,6-trimethylbenzaldehyde (0.446 g, 3.01 mmol) and trifluoroacetic acid (0.080 mL, 1.04 mmol) was added, and the mixture was stirred under argon at room temperature in the dark for 21 h. DDQ (0.663 g, 2.92 mmol) was added and the mixture was stirred under argon at room temperature in the dark for another 3 h. Triethylamine (0.145 mL, 1.04 mmol) was added and the reaction mixture was loaded onto a short alumina-gel column and eluted with ethyl acetate / dichloromethane (1:1). Eluted bands were collected and concentrated in vacuo. The crude was purified reprecipitation from dichloromethane / *n*-hexane to yield **7**. The filtrate was further purified by column chromatography on silica gel using ethyl acetate / *n*-hexane (1:4) as the eluent to obtain **7** (total amount: 1.39 mg, 2.19 μmol, 83%).

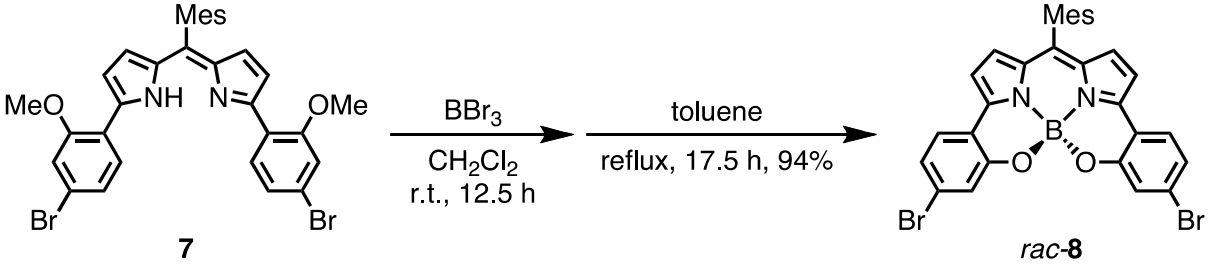
**7**: red solid.

$^1$H NMR (400 MHz, $CDCl_3$) δ 13.42 (br, 1H), 7.91 (d, $J$ = 8.3 Hz, 2H), 7.18 (dd, $J$ = 8.3, 1.7 Hz, 2H), 7.15 (d, $J$ = 1.7 Hz, 2H), 6.93 (s, 2H), 6.83 (d, $J$ = 4.3 Hz, 2H), 6.41 (d, $J$ = 4.3 Hz, 2H), 3.90 (s, 6H), 2.37 (s, 3H), 2.15 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.6, 151.0, 141.0, 138.5, 137.3, 137.0, 133.8, 129.9, 127.7, 127.4, 124.1, 122.9, 121.6, 118.4, 115.3, 56.3, 21.1, 20.1.

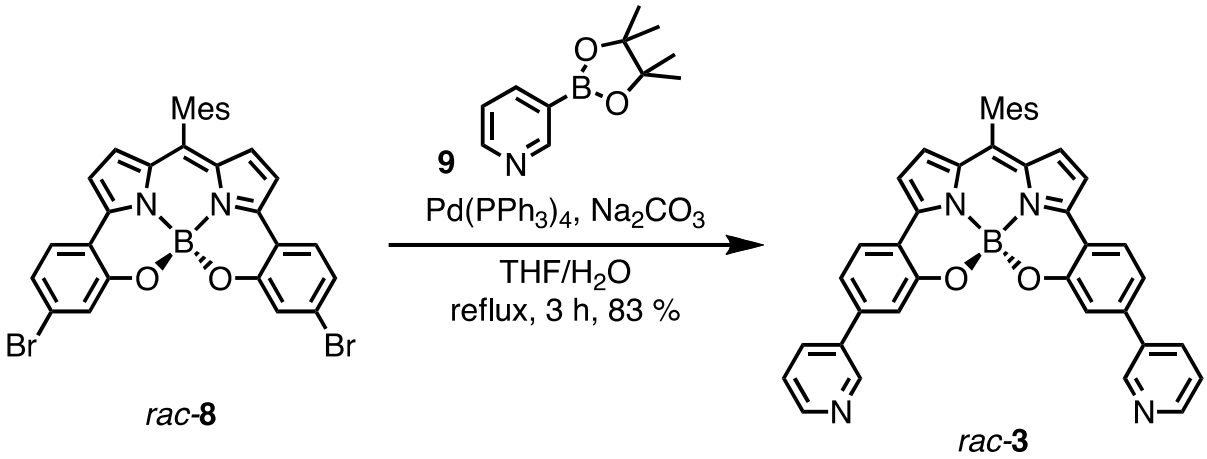
Elemental analysis: calcd for $C_{32}H_{28}Br_2N_2O_2$: C, 60.78; H, 4.46; N, 4.43. Found: C, 60.66; H, 4.46; N, 4.33.

**Scheme S5.** Synthesis of *rac*-**8**




**7** (0.326 g, 0.515 mmol) was placed in a 200 mL three-necked round-bottom flask. The flask was evacuated then refilled with argon. Dry $CH_2Cl_2$ was added to the flask, and stirred at 0 °C. Then, $BBr_3$ (0.732 mL, 7.72 mmol) was added, and the reaction mixture was stirred at room temperature for 12.5 h. The reaction was quenched with water (25 mL) and saturated $NaHCO_3$ aq (30 mL). The mixture was extracted with chloroform (50 mL × 3). The combined organic layer was dried over $Na_2SO_4$, filtered, and concentrated in vacuo. To the obtained residue was added toluene (150 mL), and refluxed for 17.5 h. After cooled, the reaction mixture was concentrated in vacuo., and the crude was purified by column chromatography on silica gel using ethyl acetate / *n*-hexane (1:8) as the eluent to obtain *rac*-**8** (0.297 g, 0.485 mmol, 94%).
*rac*-**8**: dark red solid;
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.63–7.61 (m, 2H), 7.21–7.19 (m, 4H), 6.97 (s, 2H), 6.84 (d, $J$ = 3.8 Hz, 2H), 6.82 (d, $J$ = 3.8 Hz, 2H), 2.37 (s, 3H), 2.10 (s, 6H).
$^{11}$B NMR (128 MHz, $CDCl_3$) δ –0.8 (br).
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.6, 149.5, 138.8, 138.5, 137.0, 135.1, 129.0, 128.6, 128.3, 126.6, 125.9, 124.0, 123.0, 118.7, 116.1, 21.2, 20.2.
Elemental analysis: calcd for $C_{30}H_{21}BBr_2N_2O_2$: C, 58.87; H, 3.46; N, 4.58. Found: C, 58.66; H, 3.59; N, 4.43.

**Scheme S6.** Synthesis of *rac*-**3**




A 100 mL three-necked round-bottom flask was charged with *rac*-**8** (124 mg, 0.203 mmol), **9**[S7] (111 mg, 0.542 mmol), $Na_2CO_3$ (95.5 mg, 0.901 mmol), and tetrakis(triphenylphosphine)palladium (18.3 mg, 0.0158 mmol). The flask was evacuated then refilled with argon. Dry THF (40 mL) and degassed water (14 mL) were added to the sflask. The mixture was refluxed under argon for 3 h. After cooling, THF was evaporated. Water (10 mL) was added, and the mixture was extracted with chloroform (20 mL × 3). The combined organic layer was dried over $Na_2SO_4$, filtered, and concentrated in vacuo. The crude was purified by column chromatography on silica gel using ethyl acetate as the eluent to give *rac*-**3** (102 mg, 0.168 mmol, 83%). Analytically pure sample was obtained by recrystallization from chlorohorm/*n*-hexane.

*rac*-**3**: dark purple solid.

m.p. > 280 °C.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, $J$ = 1.6 Hz, 2H), 8.56 (dd, $J$ = 4.7, 2.0 Hz, 2H), 7.90 (d, $J$ = 8.1 Hz, 2H), 7.87 (ddd, $J$ = 7.9, 2.0, 1.6 Hz, 2H), 7.34–7.31 (m, 4H), 7.26 (overlapped with $CHCl_3$), 6.99 (s, 2H), 6.91 (d, $J$ = 4.3 Hz, 2H), 6.87 (d, $J$ = 4.3 Hz, 2H), 2.38 (s, 3H), 2.14 (s, 6H).

$^{11}$B NMR (128 MHz, $CDCl_3$) δ –0.6 (br).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.6, 149.7, 148.9, 148.3, 141.7, 138.8, 138.1, 137.1, 135.9, 135.3, 134.3, 129.2, 128.46, 128.35, 126.5, 123.5, 119.4, 118.1, 116.3, 21.2, 20.3.

Elemental analysis: calcd for $C_{40}H_{29}BN_4O_2 \cdot 0.5H_2O \cdot CHCl_3$: C, 66.83; H, 4.24; N, 7.60. Found: C, 66.98; H, 4.28; N, 7.54.

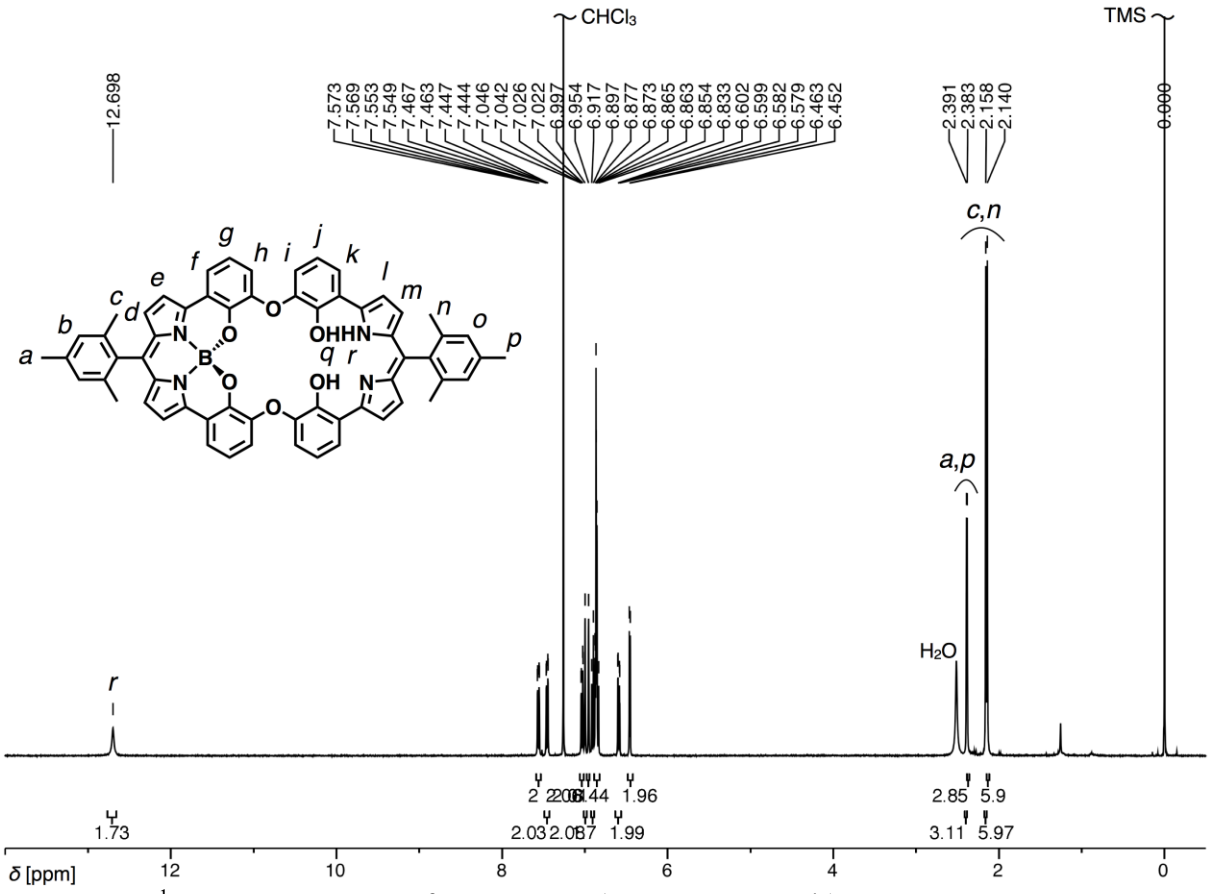



**Figure S1.** $^{1}$H NMR spectrum of *rac*-[$H_3$**1**B] (400 MHz, $CDCl_3$).

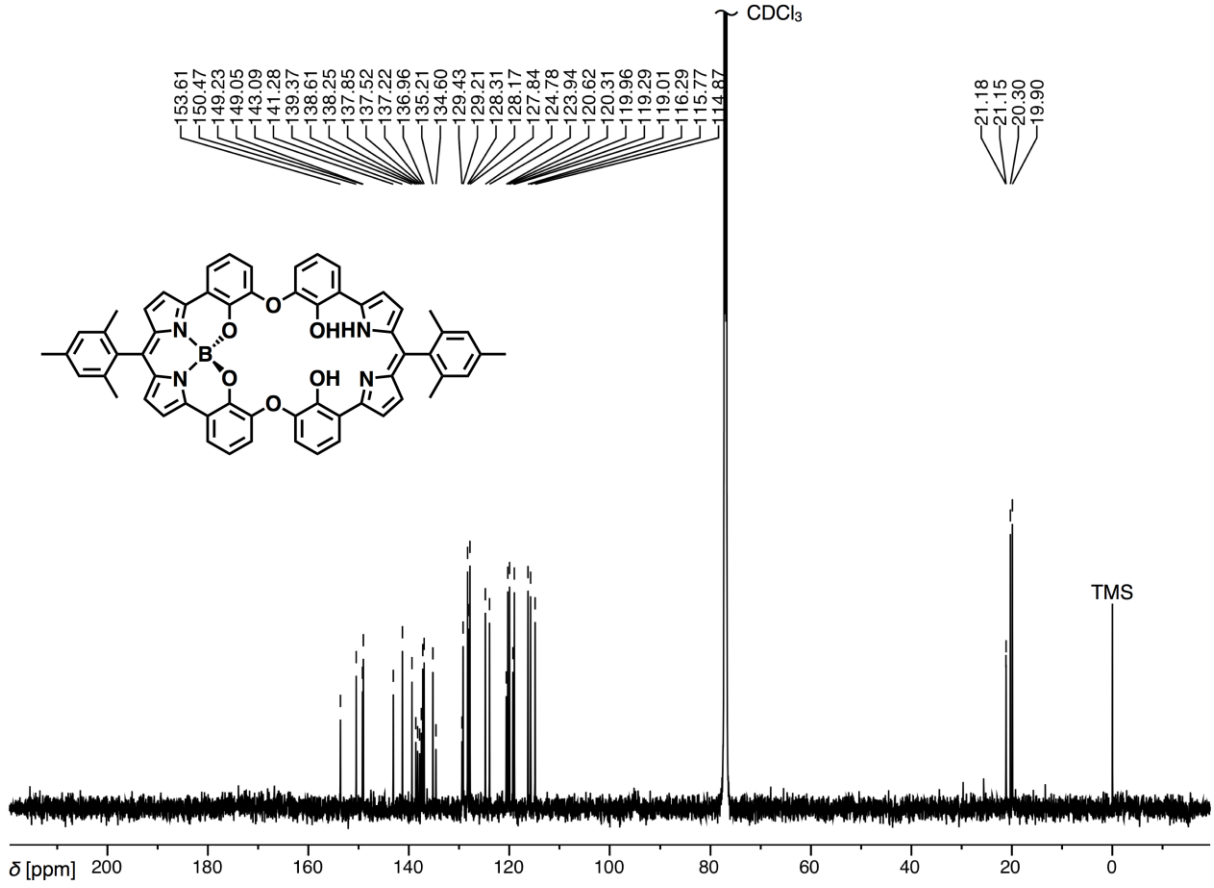



**Figure S2.** $^{13}$C NMR spectrum of *rac*-[$H_3$**1**B] (128 MHz, $CDCl_3$).

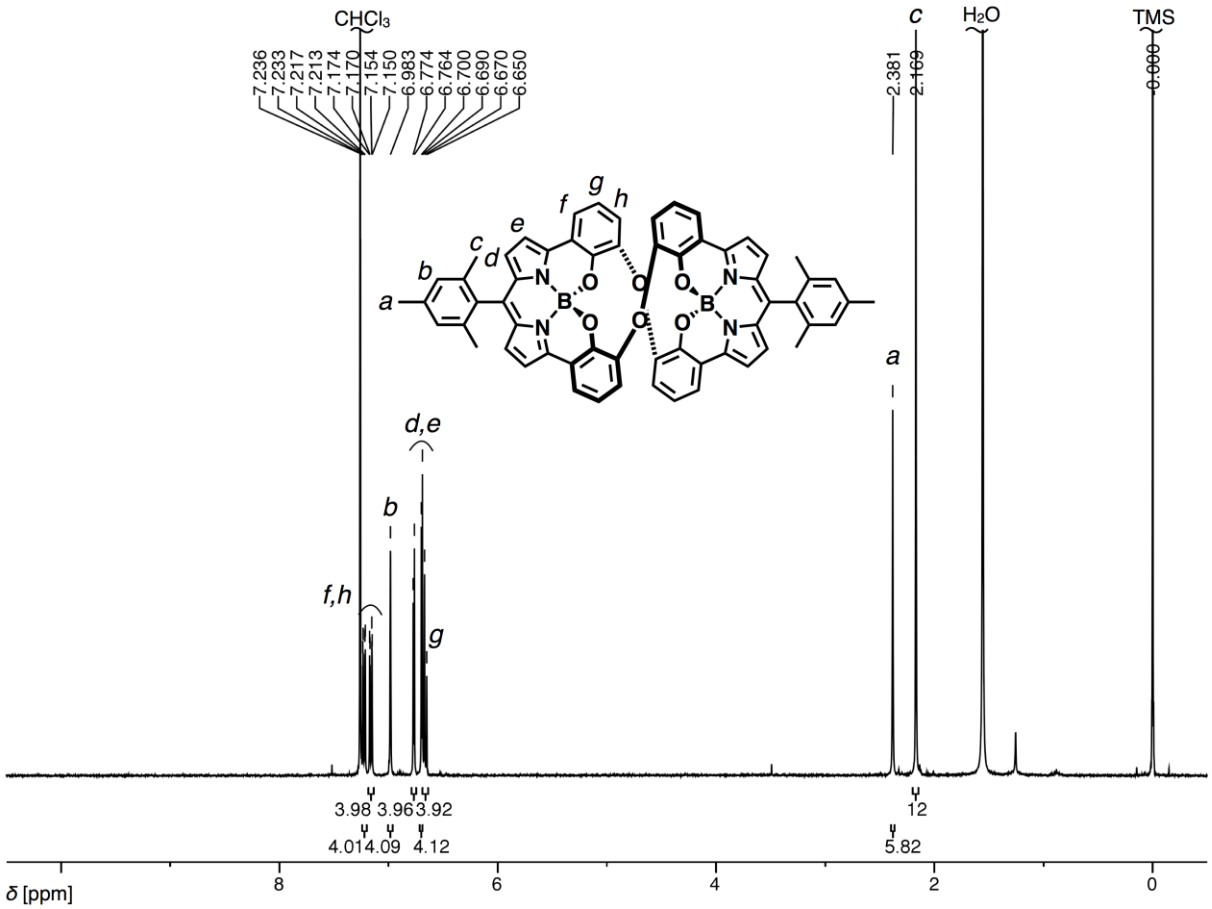



**Figure S3.** $^{1}$H NMR spectrum of *rac*-[**1**B$_2$] (400 MHz, CDCl$_3$).

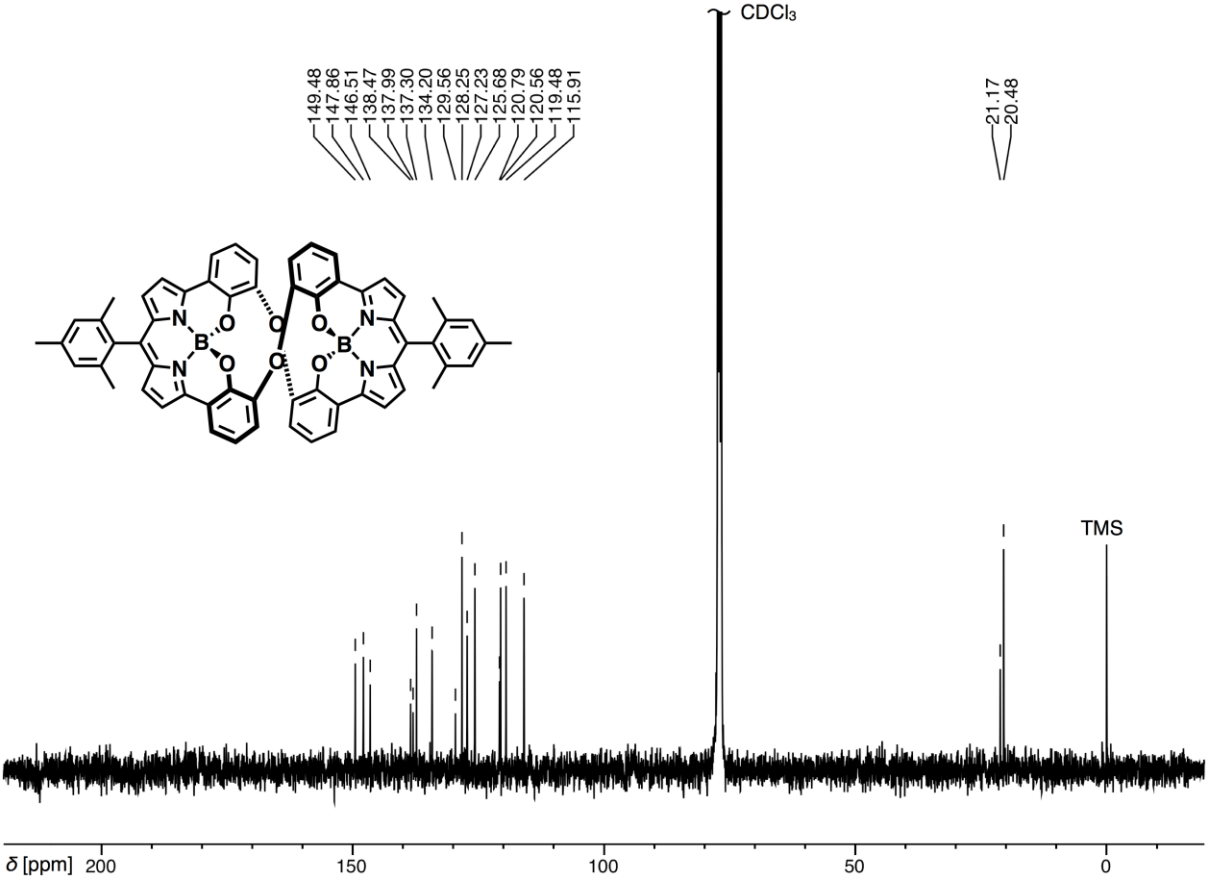



**Figure S4.** $^{13}$C NMR spectrum of *rac*-[**1**B$_2$] (128 MHz, CDCl$_3$).

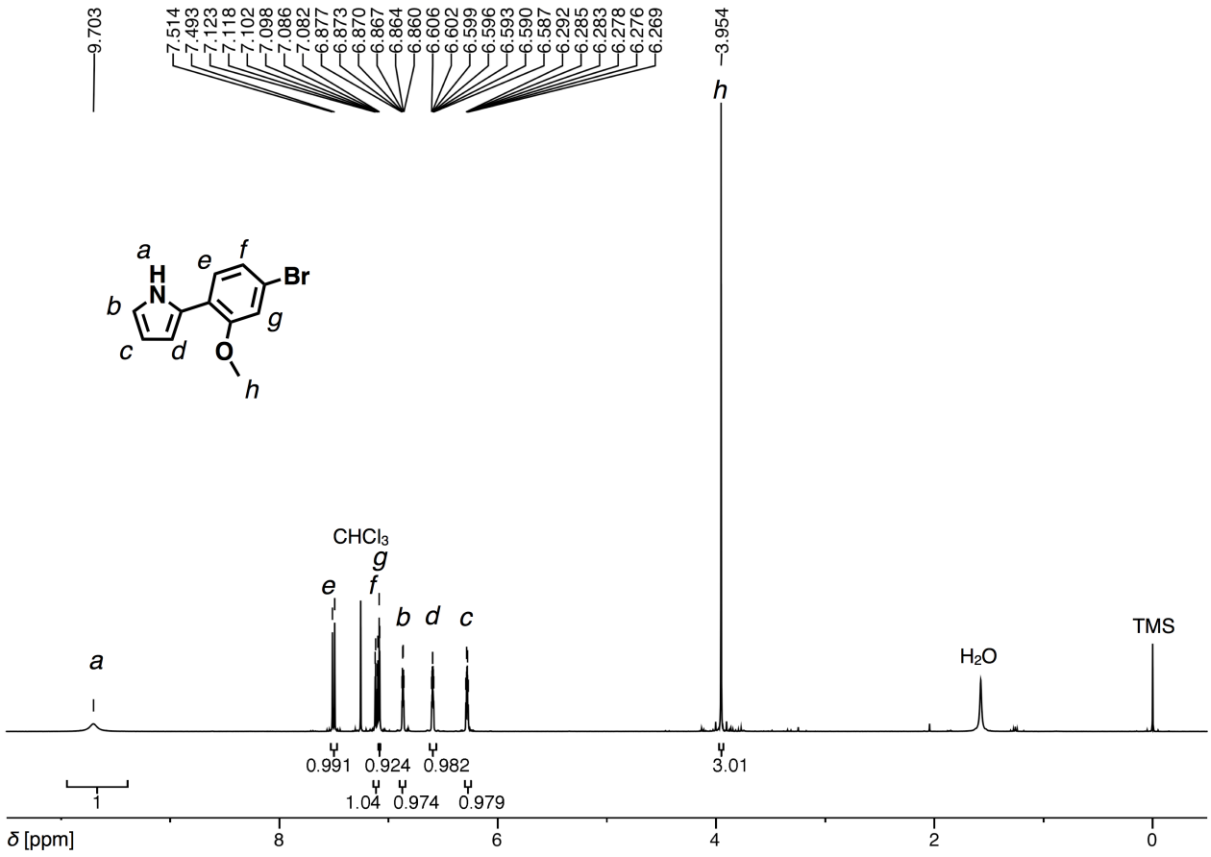



**Figure S5.** $^{1}$H NMR spectrum of **6** (400 MHz, $CDCl_3$).

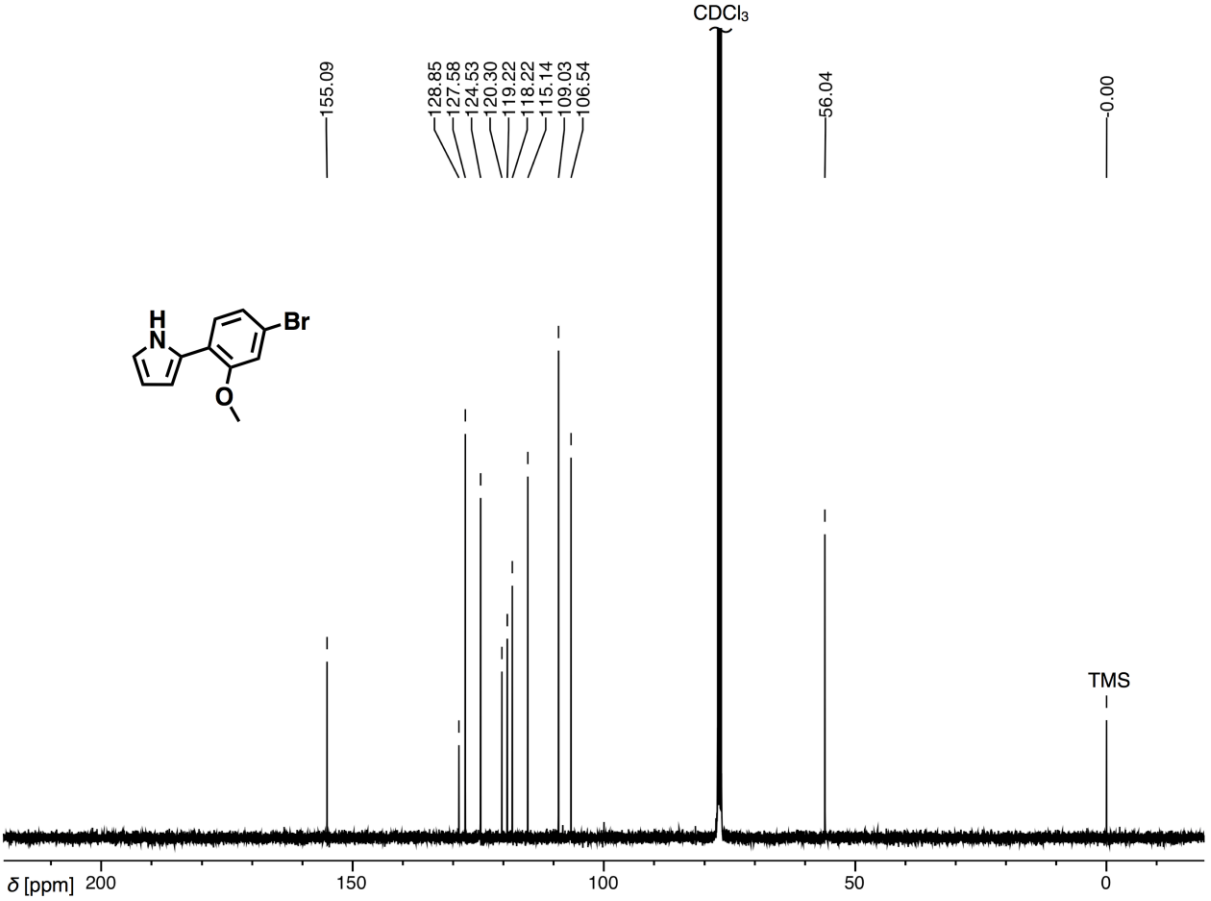



**Figure S6.** $^{13}$C NMR spectrum of **6** (101 MHz, $CDCl_3$).

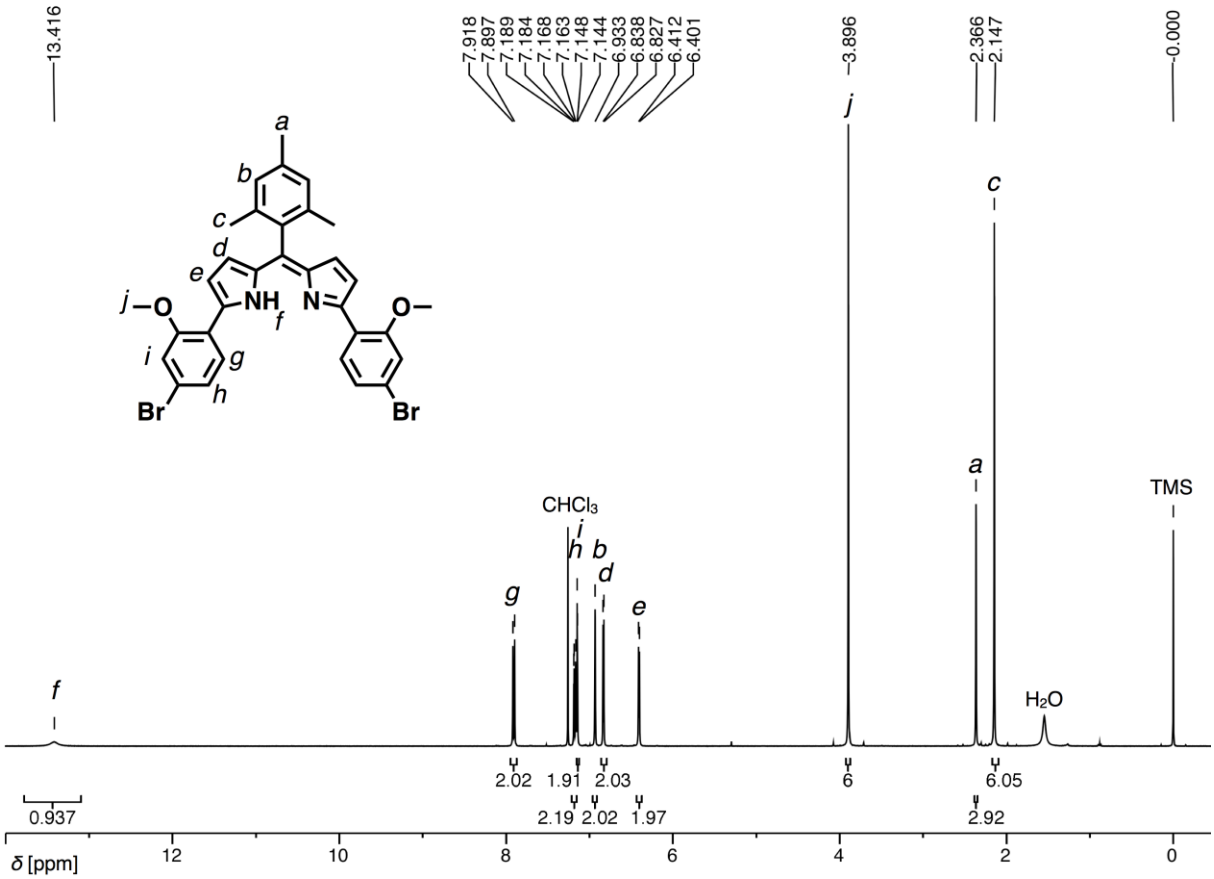



**Figure S7.** $^{1}$H NMR spectrum of **7** (400 MHz, $CDCl_3$).

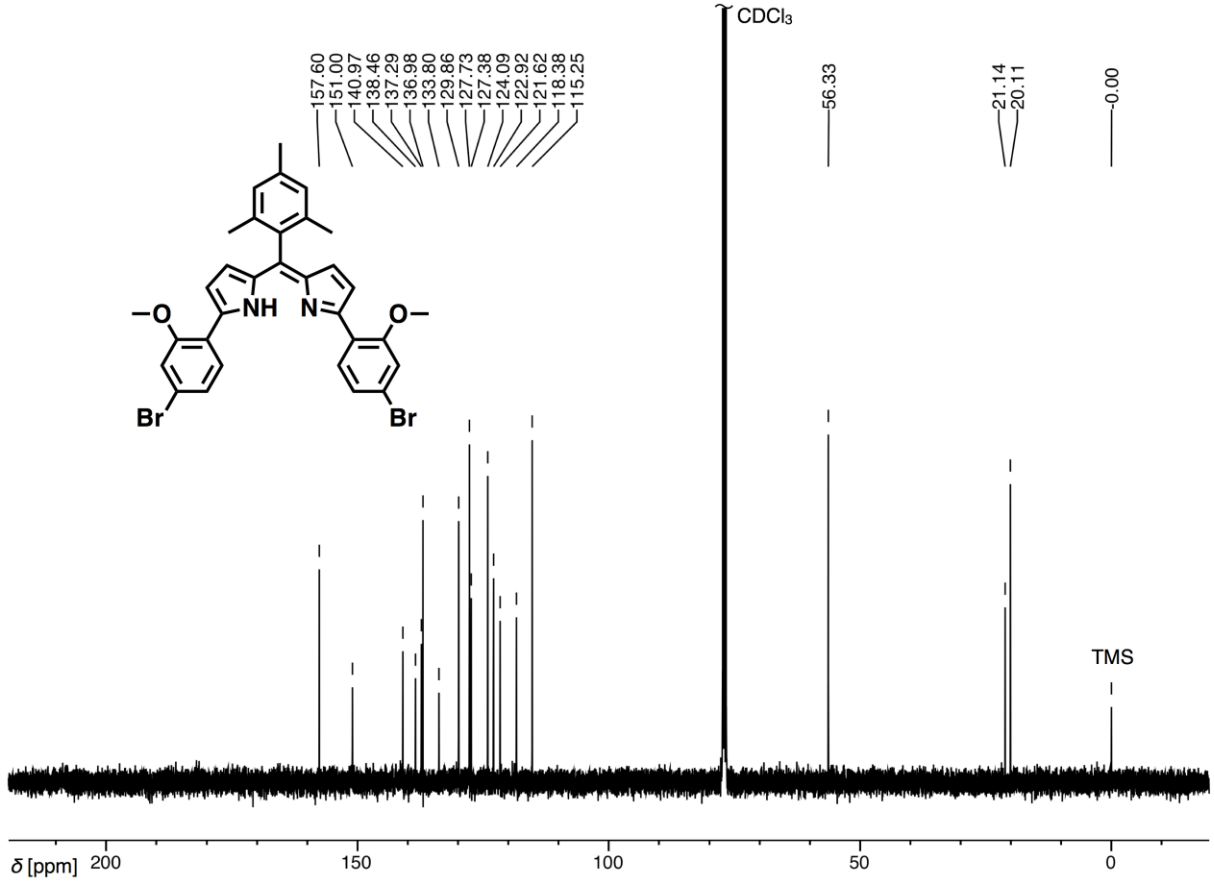



**Figure S8.** $^{13}$C NMR spectrum of **7** (101 MHz, $CDCl_3$).

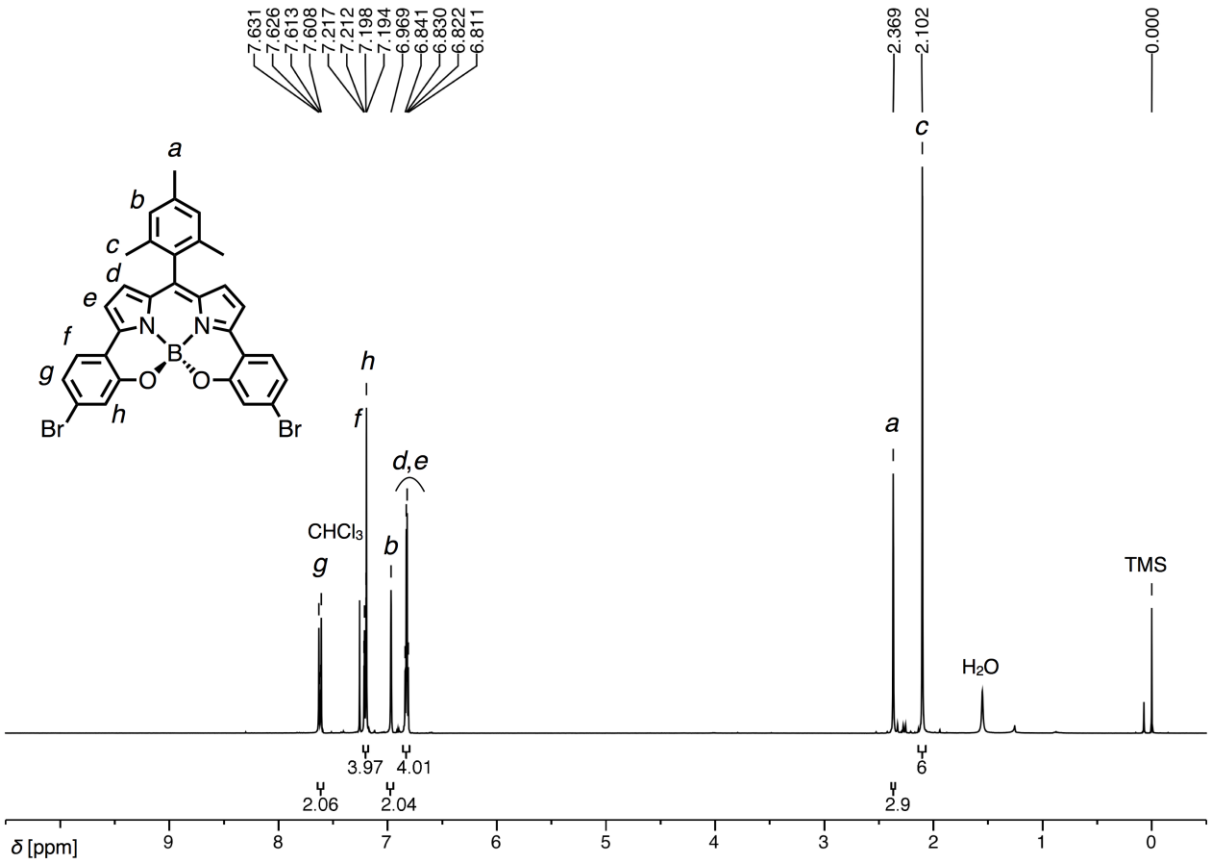



**Figure S9.** $^{1}$H NMR spectrum of *rac*-**8** (400 MHz, $CDCl_3$).

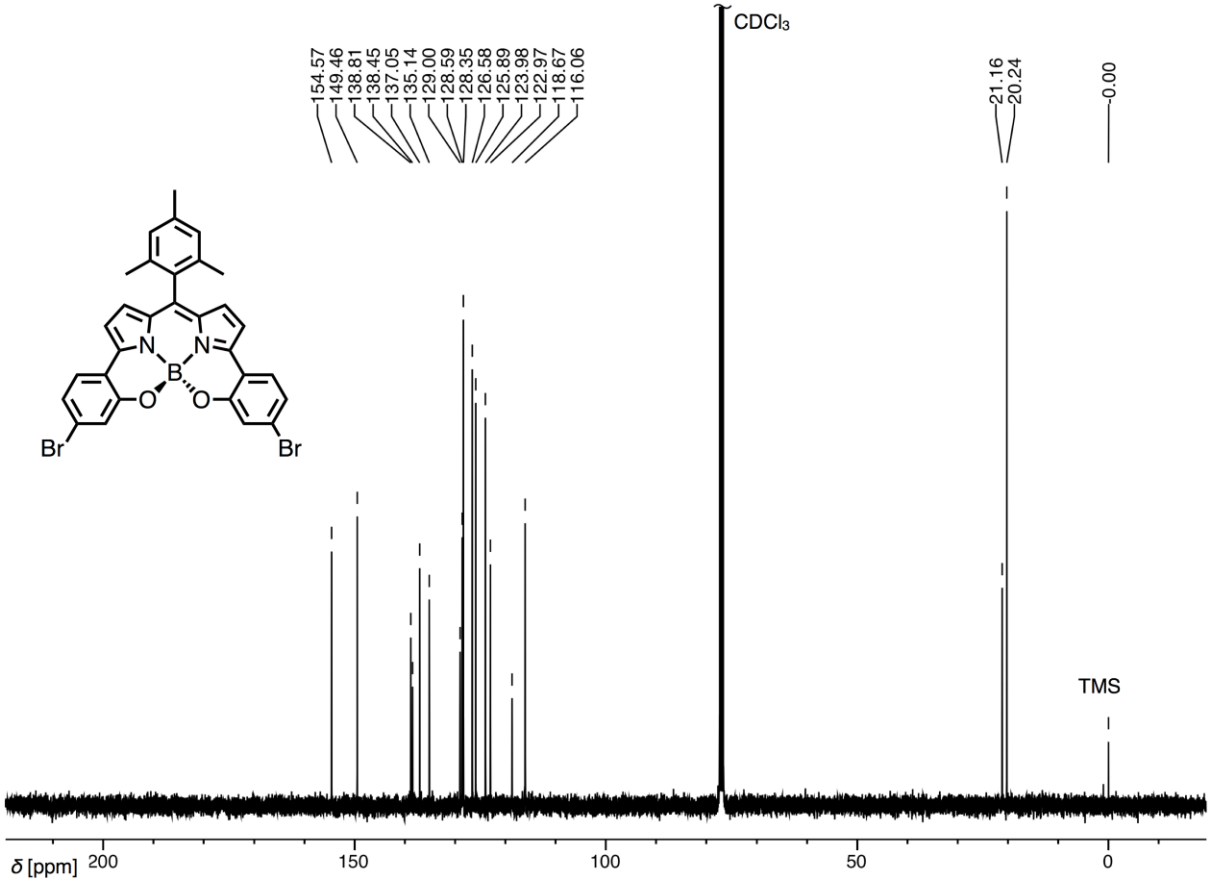



**Figure S10.** $^{13}$C NMR spectrum of *rac*-**8** (101 MHz, $CDCl_3$).

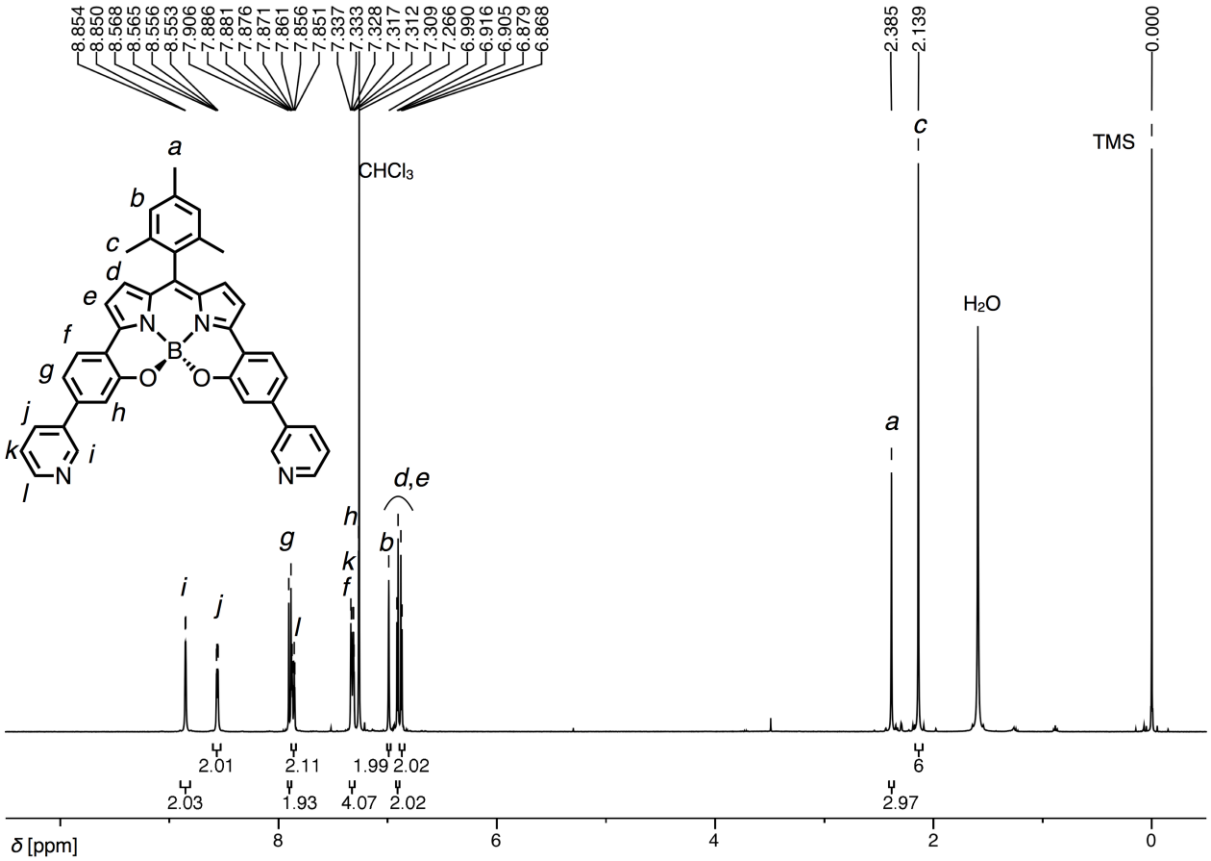



**Figure S11.** $^{1}$H NMR spectrum of *rac*-**3** (400 MHz, $CDCl_3$).

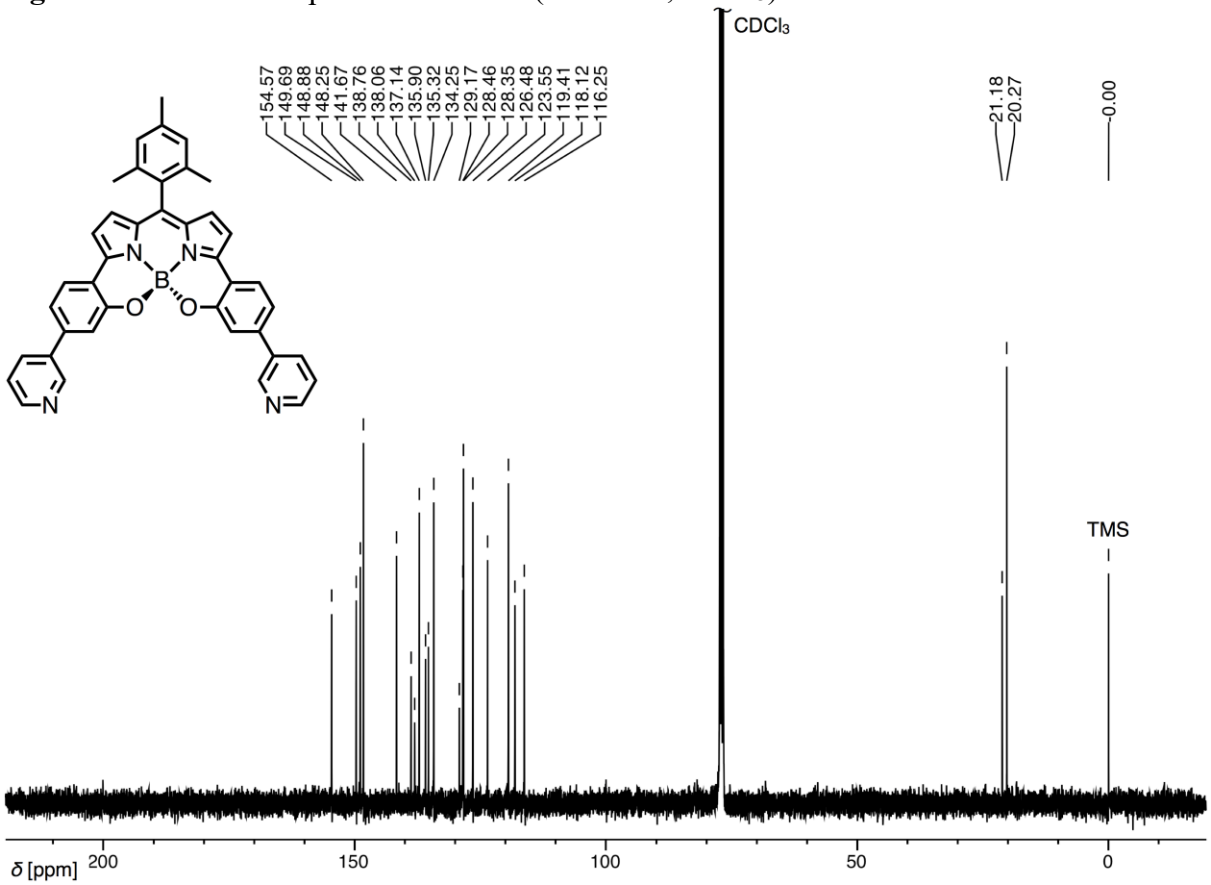



**Figure S12.** $^{13}$C NMR spectrum of *rac*-**3** (101 MHz, $CDCl_3$).

## Optical resolution by chiral HPLC

Optical resolution was performed by chiral HPLC on a JAI LC-9201 system (5.5 mL/min) with the Daicel CHIRALPAK IA column ($\phi$ 20 mm × 250 mm) or the Daicel CHIRALPAK IE column ($\phi$ 20 mm × 250 mm).

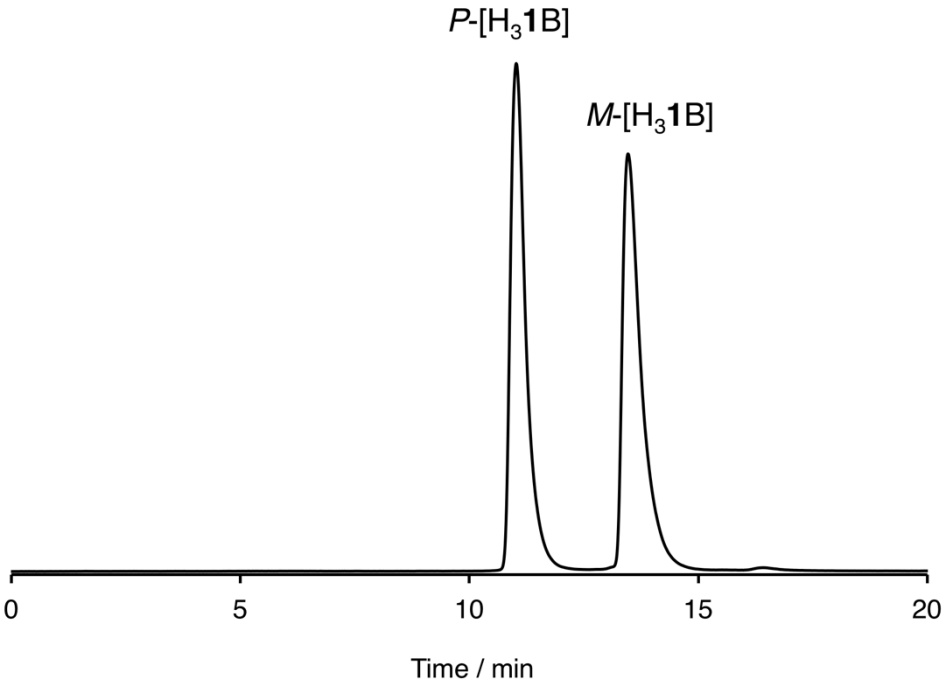



**Figure S13.** Chiral HPLC profile of for the separation of the enantiomers of [H$_3$**1**B] (column, CHIRALPAK IE; eluent, $CH_2Cl_2$).

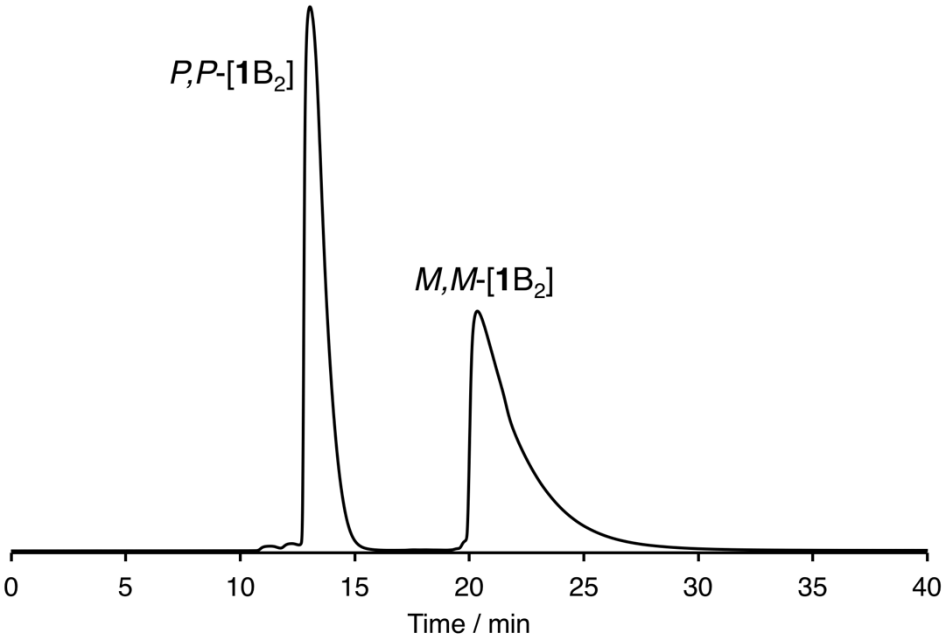



**Figure S14.** Chiral HPLC profile of for the separation of the enantiomers of [**1**B$_2$] (column, CHIRALPAK IE; eluent, $CH_2Cl_2$).

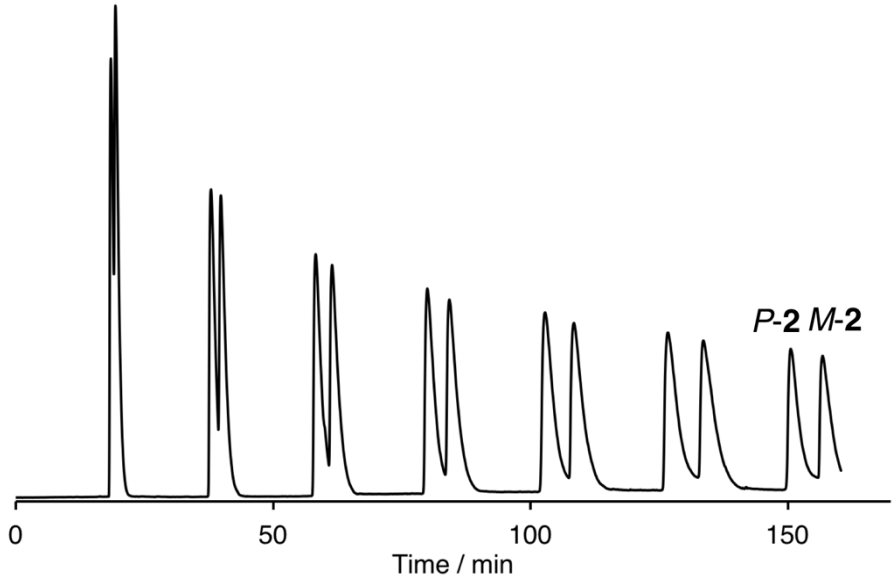



**Figure S15.** Chiral HPLC profile of for the separation of the enantiomers of **2**[S8] (column, CHIRALPAK IE; eluent, $CH_2Cl_2$:hexane = 1:1).

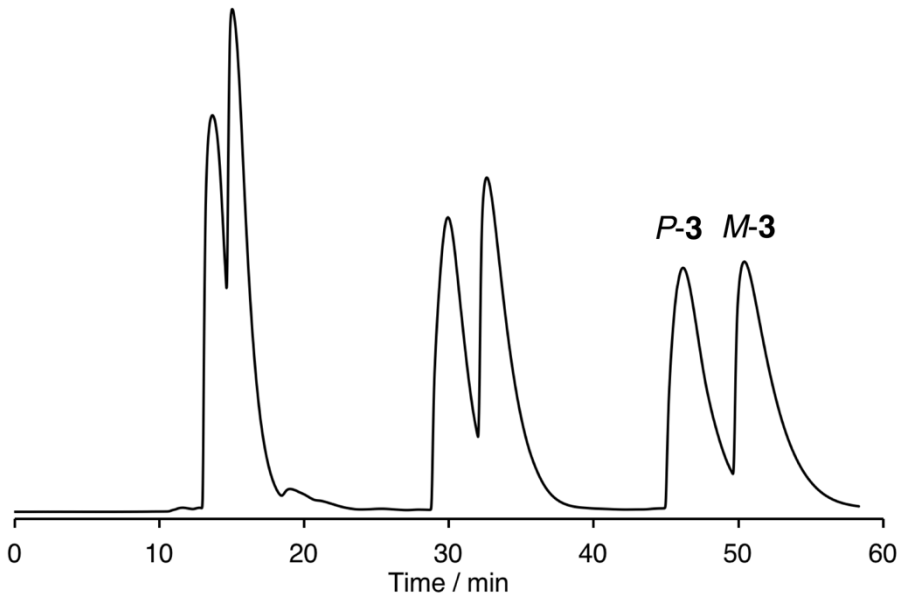



**Figure S16.** Chiral HPLC profile of for the separation of the enantiomers of **3** (column, CHIRALPAK IA; eluent, $CH_2Cl_2$:hexane = 1:1).

## UV-vis absorbance/fluorescence and CD measurements

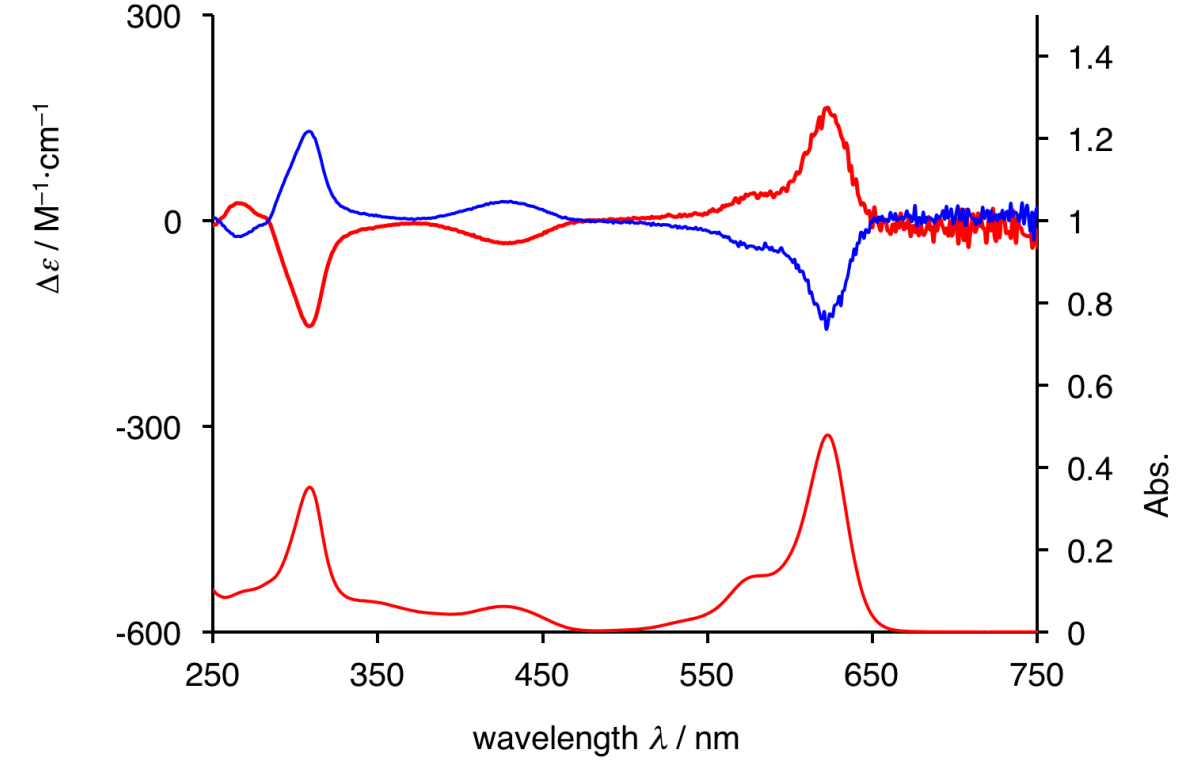



**Figure S17.** (top) CD spectra of *P*-**2** (red line) and *M*-**2** (blue line). (bottom) UV/vis absorption spectrum of *P*-**2**. Conditions: $CHCl_3$, 10 μM, 298 K, $l$ = 1 cm.

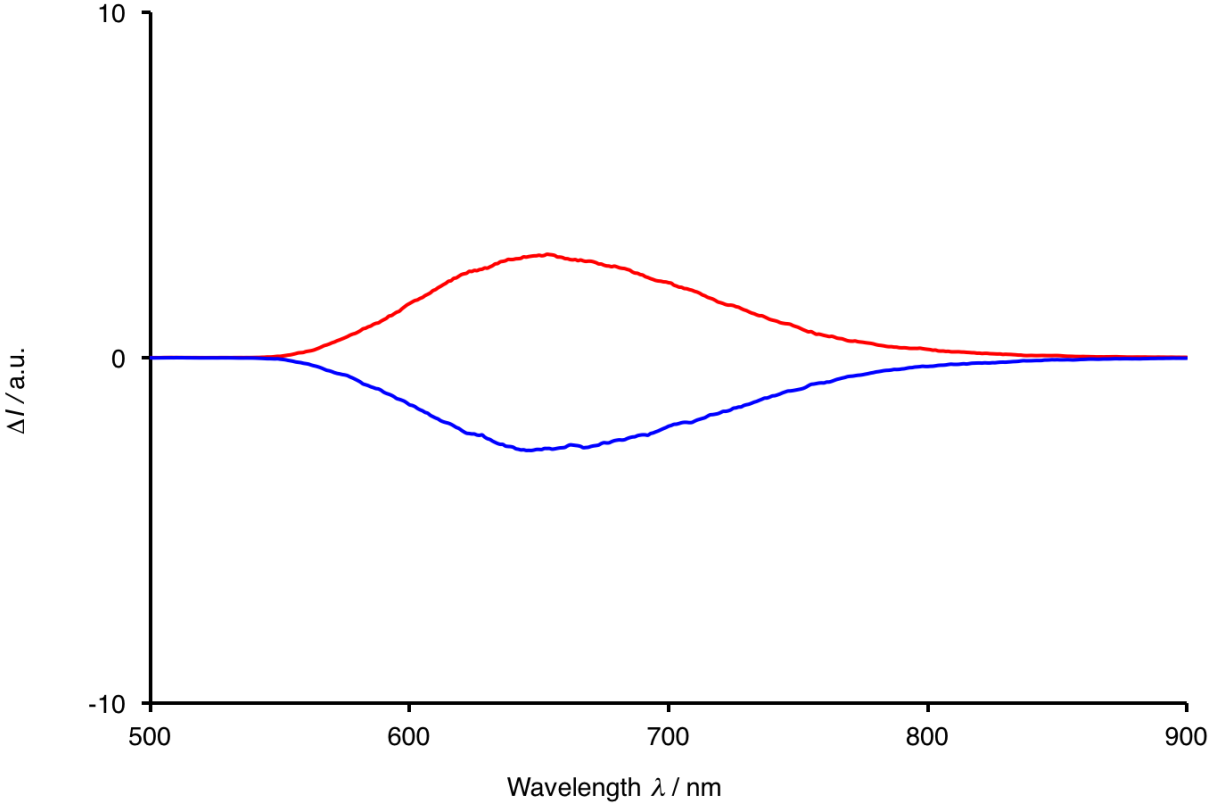



**Figure S18.** CPL spectra of *P*-**2** (red line) and *M*-**2** (blue line) (excited at 400 nm, $CHCl_3$, 10 μM, 298 K).

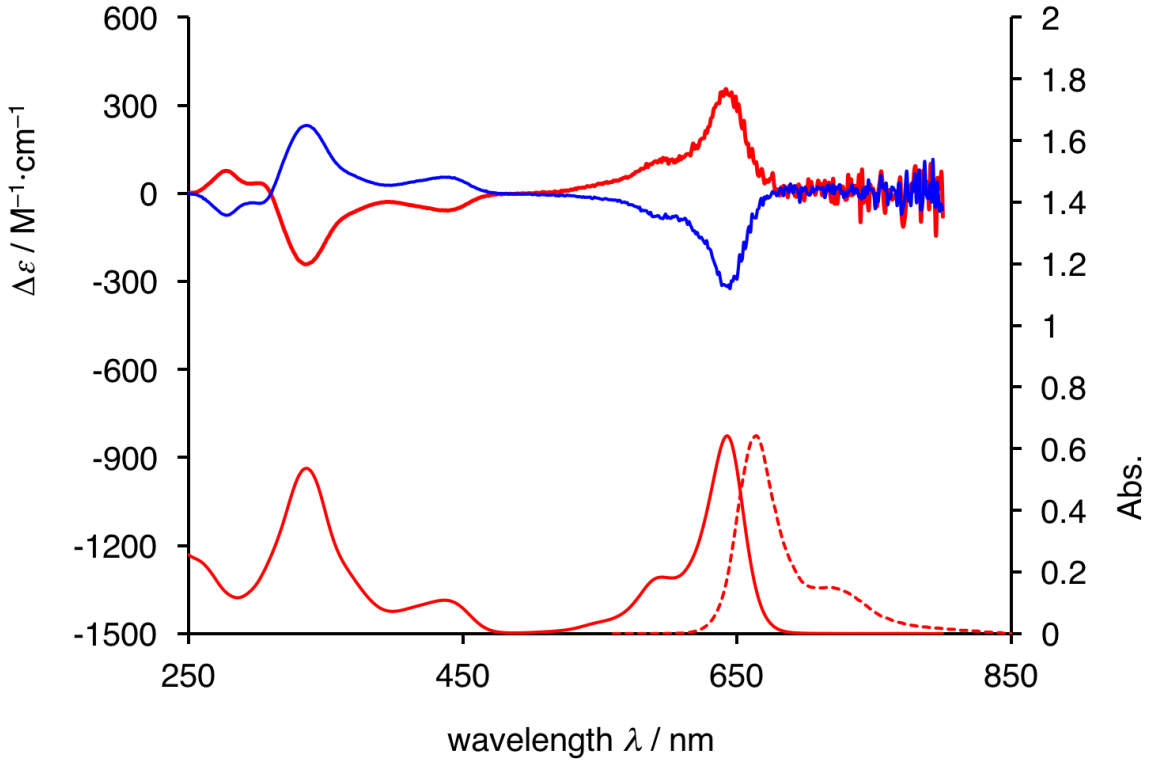



**Figure S19.** (top) CD spectra of *P*-**3** (red line) and *M*-**3** (blue line). (bottom) UV/vis absorption (solid line), and normalized fluorescence (dashed line, excited at 550 nm) spectra of *P*-**3**. Conditions: $CHCl_3$, 10 μM, 298 K, $l$ = 1 cm.

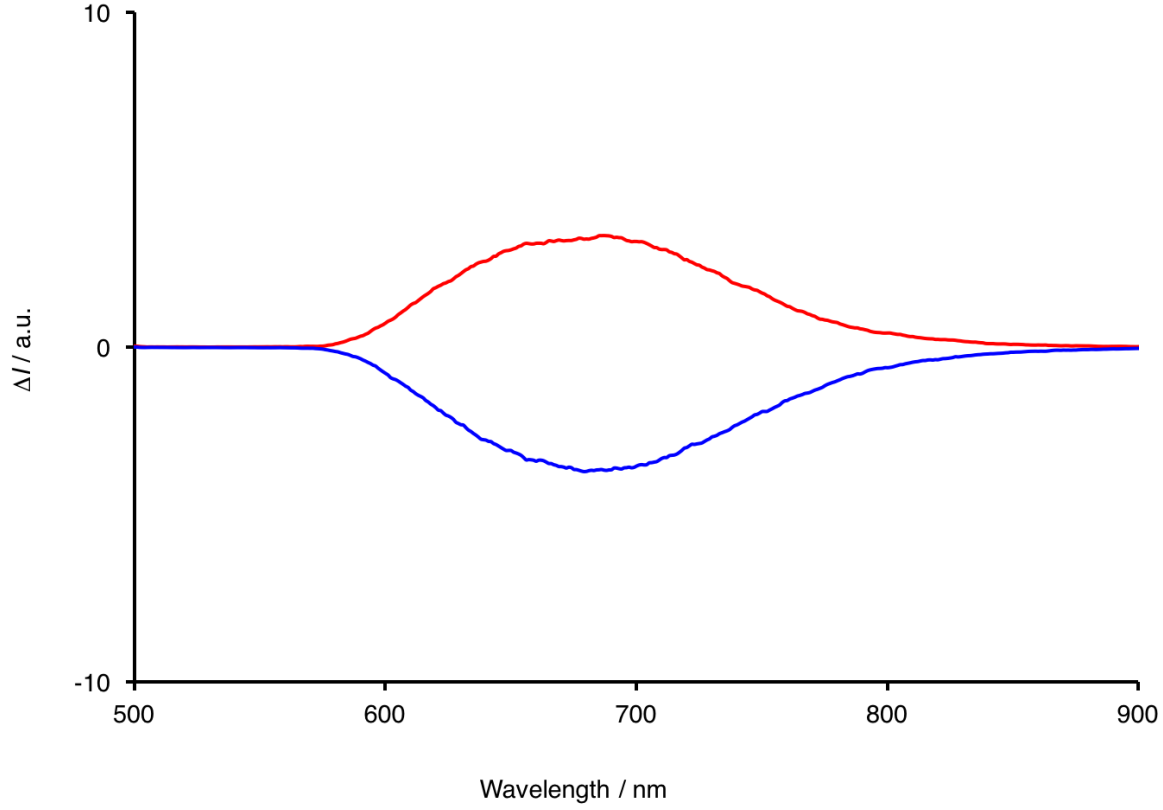



**Figure S20.** CPL spectra of *P*-**3** (red line) and *M*-**3** (blue line) (excited at 400 nm, $CHCl_3$, 10 μM, 298 K).

## X-ray crystallographic analysis

***rac*-[H$_3$1B]**

Single crystal of *rac*-[H$_3$**1**B] suitable for X-ray diffraction analysis was obtained by slow diffusion of *n*-hexane vapor in to chloroform solution of *rac*-[H$_3$**1**B].

Crystal data for 2(H$_3$**1**B)·3($CHCl_3$): $C_{123}H_{93}B_2Cl_9N_2O_4$, $Fw$ = 2215.72, purple block, 0.20 × 0.05 × 0.02 mm$^3$, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 13.411(3) Å, $b$ = 20.416(5) Å, $c$ = 21.320(5) Å, $\alpha$ = 75.181(3)°, $\beta$ = 83.052(4)°, $\gamma$ = 88.030(3)°, $V$ = 5602(2) Å$^3$, $Z$ = 2, $T$ = 120(2) K, $\lambda$(Mo$K\alpha$) = 0.71073 Å, $\theta_{max}$ = 21.984°, $R_1$ = 0.0912, $wR_2$ = 0.2635, GOF = 0.998. CCDC No. 1486269.

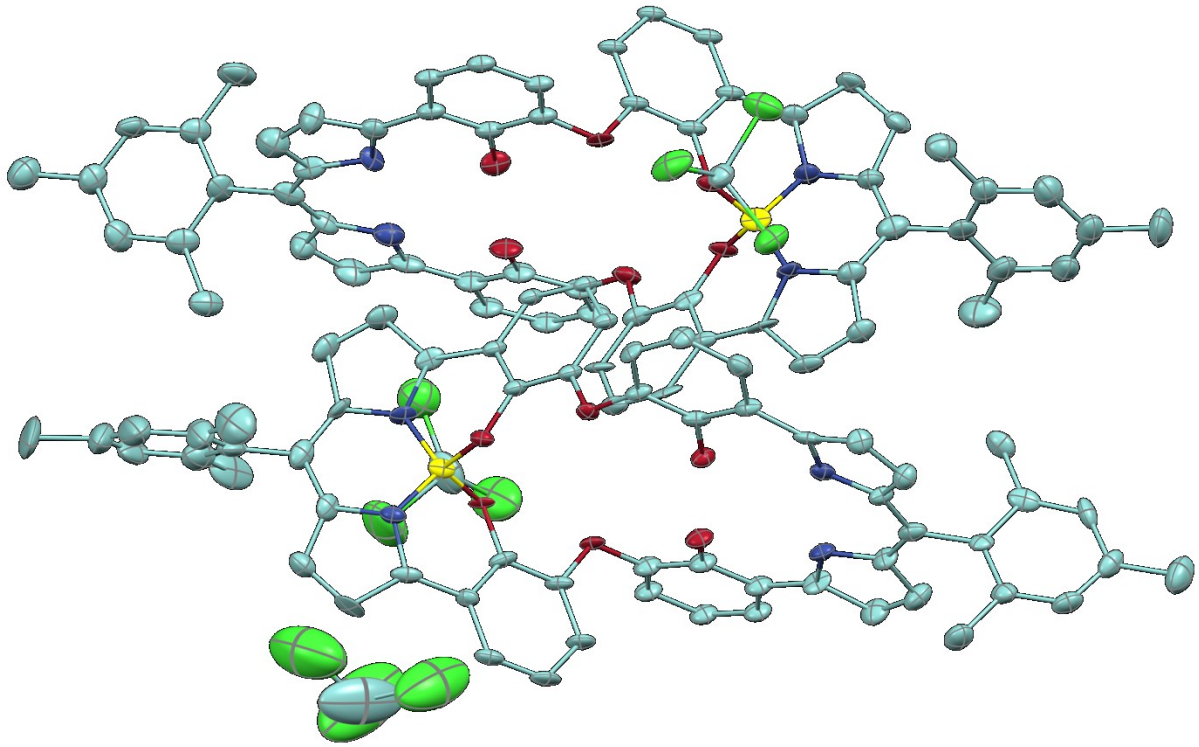


**Figure S21.** The molecular structure of (*P*-[H$_3$**1**B])·(*M*-[H$_3$**1**B])·3($CHCl_3$) determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light green; N, blue; O, red; B, yellow; Cl, green.

***rac*-[1B$_2$]**

Single crystal of *rac*-[**1**B$_2$] suitable for X-ray diffraction analysis was obtained by slow diffusion of *n*-hexane vapor in to chloroform solution of *rac*-[**1**B$_2$].

Crystal data for (**1**B$_2$)·2(CHCl$_3$): $C_{62}H_{42}B_2Cl_6N_4O_6$, *Fw* = 1175.33, purple plate, 0.24 × 0.12 × 0.03 mm$^3$, monoclinic, space group *P* 2$_1$/*c* (No. 14), *a* = 27.3653(13) Å, *b* = 13.7830(7) Å, *c* = 31.7984(14) Å, $\beta$ = 114.516(3)°, *V* = 10912.3(9) Å$^3$, *Z* = 8, *T* = 120(2) K, $\lambda$(Mo*K*$\alpha$) = 0.71073 Å, $\theta_{max}$ = 23.255°, $R_1$ = 0.0847, $wR_2$ = 0.2564, GOF = 1.522. CCDC No. 1486272.

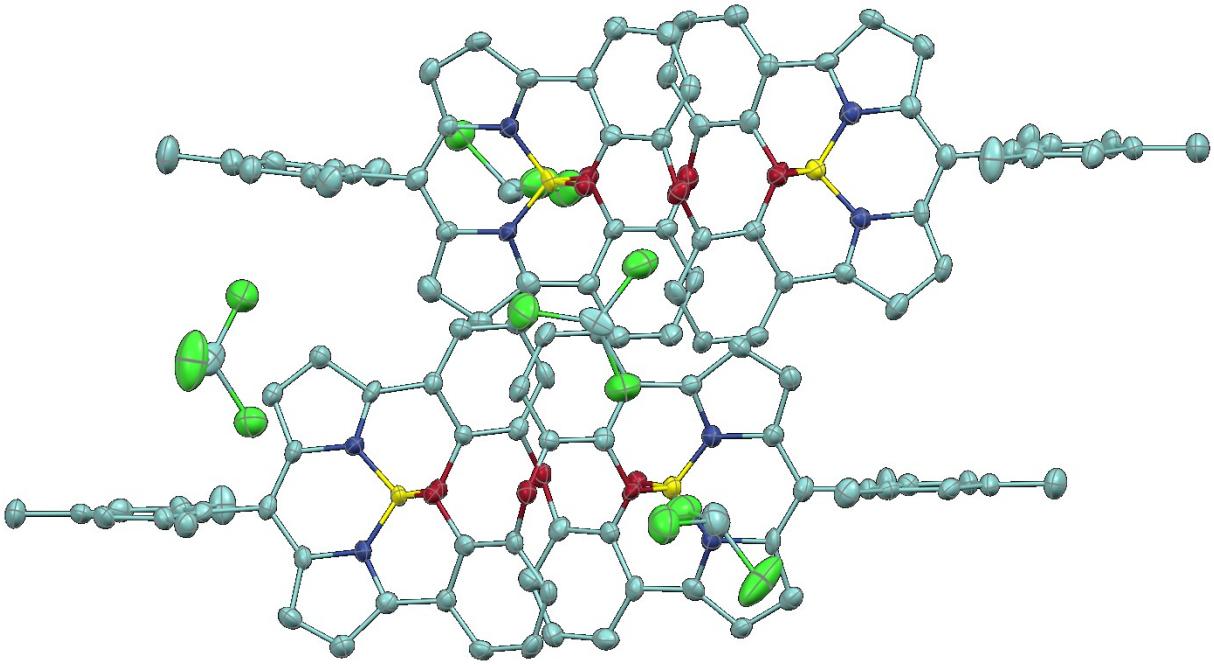


**Figure S22.** The molecular structure of (*P*-[**1**B$_2$])·(*M*-[**1**B$_2$])·4(CHCl$_3$) determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light green; N, blue; O, red; B, yellow; Cl, green.

***P,P*-[1B$_2$]**

Single crystal of *P*,*P*-[**1**B$_2$] suitable for X-ray diffraction analysis was obtained by slow diffusion of *n*-hexane vapor in to dichloromethane solution of *P,P*-[**1**B$_2$].

Crystal data for (**1**B$_2$): $C_{60}H_{42}B_2N_4O_6$, *Fw* = 936.59, purple prism, 0.15 × 0.10 × 0.10 mm$^3$, monoclinic, space group *P* 2$_1$ (No. 4), *a* = 11.4322(4) Å, *b* = 16.3704(5) Å, *c* = 12.5755(4) Å, $\beta$ = 100.994(2)°, *V* = 2310.31(13) Å$^3$, *Z* = 2, *T* = 120(2) K, $\lambda$(Mo*K*$\alpha$) = 0.71073 Å, $\theta_{max}$ = 30.606°, $R_1$ = 0.0443, $wR_2$ = 0.1431, GOF = 1.045. Flack *x* = –0.1(3). CCDC No. 1486271.

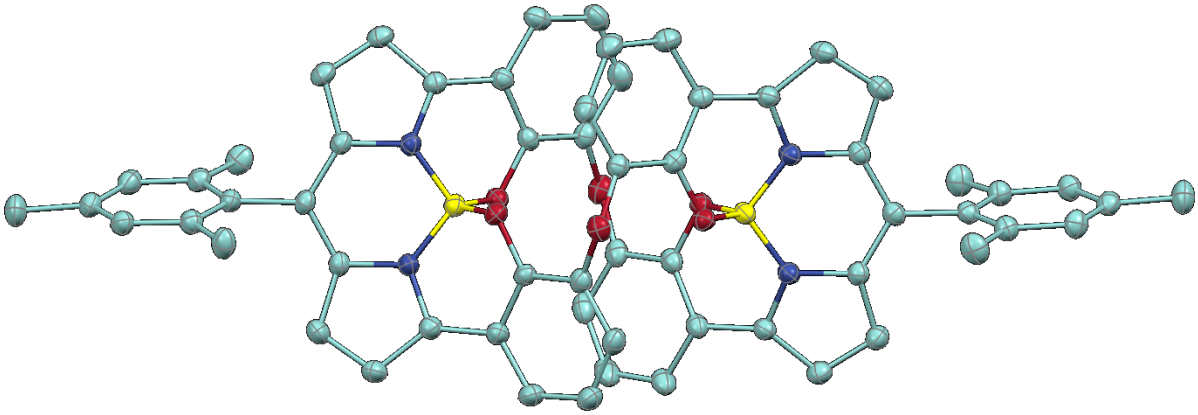


**Figure S23.** The molecular structure of *P*-[**1**B$_2$] determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light green; N, blue; O, red; B, yellow.

***rac*-3**

Single crystal of *rac*-**3** suitable for X-ray diffraction analysis was obtained by slow diffusion of *n*-hexane layer on chloroform solution of *rac*-**3**.

Crystal data for **3**·($CHCl_3$): $C_{41}H_{30}BCl_3N_4O_2$, $Fw$ = 727.85, purple prism, 0.10 × 0.04 × 0.02 mm$^3$, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 9.821(3) Å, $b$ = 12.383(3) Å, $c$ = 15.111(4) Å, $\alpha$ = 79.156(3)°, $\beta$ = 84.922(4)°, $\gamma$ = 73.193(3)°, $V$ = 1726.7(8) Å$^3$, $Z$ = 2, $T$ = 120(2) K, $\lambda$(Mo$K\alpha$) = 0.71073 Å, $\theta_{max}$ = 27.463°, $R_1$ = 0.0648, $wR_2$ = 0.2214, GOF = 1.746. CCDC No. 1486268.

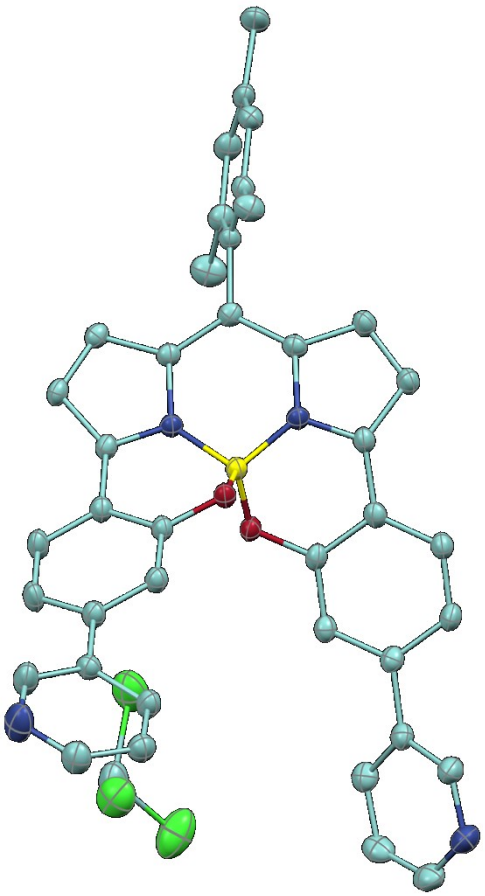


**Figure S24.** The molecular structure of **3**·($CHCl_3$) determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). A *P*-**3** isomer in the crystal of *rac*-**3** is shown. Hydrogen atoms were omitted for clarity. C, light green; N, blue; O, red; B, yellow; Cl, green.

***P*-3**

Single crystal of *P*-**3** suitable for X-ray diffraction analysis was obtained by slow diffusion of *n*-hexane layer on dichloromethane solution of *P*-**3**.

Crystal data for 2(**3**)·($CH_2Cl_2$): $C_{81}H_{60}B_2Cl_2N_8O_4$, *Fw* = 1301.89, deep green prism, 0.40 × 0.20 × 0.10 $mm^3$, triclinic, space group *P* 1 (No. 1), *a* = 9.887(3) Å, *b* = 11.839(4) Å, *c* = 15.495(5) Å, $\alpha$ = 77.762(3)°, $\beta$ = 80.071(3)°, $\gamma$ = 66.473(3)°, *V* = 1617.3(9) $Å^3$, *Z* = 1, *T* = 120(2) K, $\lambda$(Mo*K*$\alpha$) = 0.71073 Å, $\theta_{max}$ = 27.948°, $R_1$ = 0.0789, $wR_2$ = 0.1712, GOF = 1.185. Flack *x* = –0.03(9). CCDC No. 1486270.

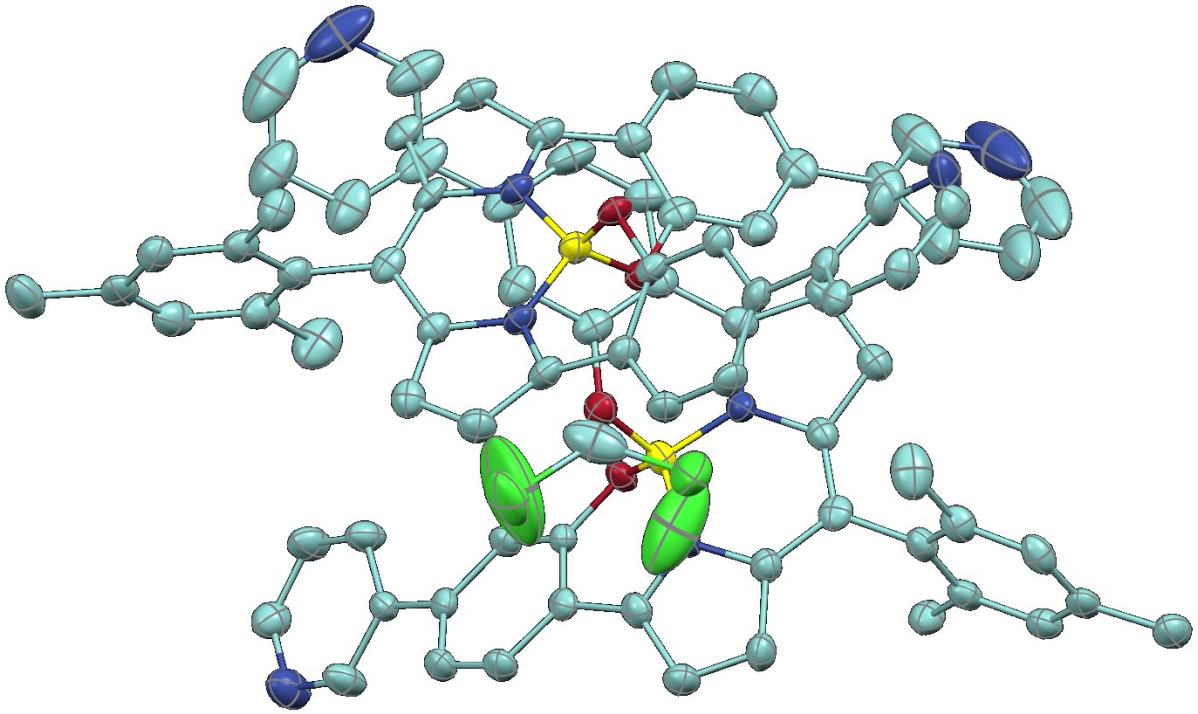


**Figure S25.** The molecular structure of 2(*P*-**3**)·($CH_2Cl_2$) determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light green; N, blue; O, red; B, yellow; Cl, green.

## References for the Supporting Information


1. Bruker, *APEX2*, 2014.
2. (a) K. Wakita, *Yadokari-XG, Software for Crystal Structure Analyses*, 2001; (b) C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218.
3. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
4. M. Saikawa, M. Daicho, T. Nakamura, J. Uchida, M. Yamamura and T. Nabeshima, *Chem. Commun.*, 2016, **52**, 4014.
5. D. M. Knapp, E. P. Gillis and M. D. Burke, *J. Am. Chem. Soc.*, 2009, **131**, 6961.
6. D. W. Lin, T. Masuda, M. B. Biskup, J. D. Nelson and P. S. Baran, *J. Org. Chem.*, 2011, **76**, 1013.
7. W. Li, D. P. Nelson, M. S. Jensen, R. S. Hoerrner, D. Cai, R. D. Larsen and P. J. Reider, *J. Org. Chem.*, 2002, **67**, 5394.
8. C. Ikeda, S. Ueda and T. Nabeshima, *Chem. Commun.*, 2009, 2544.