Electronic Supplementary Information

Intense blue circularly polarized luminescence from helical aromatic esters

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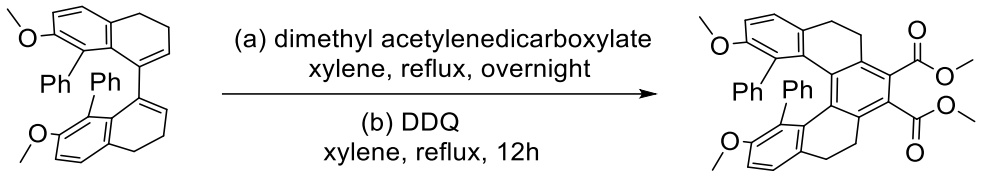
1. General information

All the reagents and solvents were commercially available and used without further purification. Reactions were carried out under inert and anhydrous conditions unless otherwise noted. ^{1}H, ^{13}C NMR spectra were recorded on Brucker® Avance III 400 MHz and Brucker® AVIII 500 MHz NMR spectrometers in $CDCl_3$ solutions at 298 K. All the melting points were not calibrated and determined on YuHua X-5 digital melting point apparatus. High resolution mass spectra were obtained on the Thermo Fisher® Exactive high-resolution LC-MS spectrometer. The X-ray crystallographic data were collected by Rigaku® X-ray diffraction apparatus RAPID IP, MM007HF Saturn 724+, ST Saturn 724+. Optical resolutions were carried out on Semi-preparative chromatography using the column (Chiralpak® IE, 0.46 cm I.D. × 15 cm L) and the mobile phase of Hexane/DCM (40:60, *v*/*v*). HPLC analysis were performed on Agilent 1260 Infinity. Analytical injections were performed on chiral stationary phase using the column (Chiralpak® IE, 5 μm, 4.6 mm × 250 mm) and the mobile phase of hexane and dichloromethane (60:40, 50:50 and 74:26, *v*/*v*). The UV-vis spectra were recorded on PerkinElmer® UV/Vis/NIR spectrometer (Lambda 950), and the fluorescence spectra were recorded on HITACHI® F-7000 Fluorescence Spectrometer at room temperature. Absolute fluorescence quantum yield, measured by Hamamatsu Absolute PL Quantum Yield Spectrometer C11347. Fluorescence lifetimes were measured by Quantaurus Tau C11367–11. CD spectra were recorded on a JASCO J810 spectropolarimeter, and CPL spectra were performed with a JASCO CPL-200 spectrometer at room temperature. The optical rotation was determined by Rudolph Autopol VI Automatic polarimeter. The starting diene **2** was synthesized by reported method.[1]

2. Synthetic procedures and characterized data

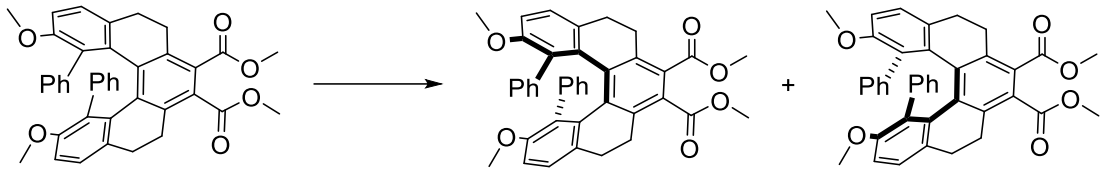
Synthesized of racemic compound 3



2 **3**

Compound 3. A solution of diene **2** (5 g, 10.6 mmol) and acetylenedicarboxylic acid dimethyl ester (15.1 g, 106 mmol) in xylene (300 mL) was refluxed overnight. After cooling, the reaction mixture was concentrated under reduced pressure, and subjected to flash column chromatography with ethyl acetate, dichloromethane and petroleum ether (1:3:15, v/v/v) as eluent. After rotatory evaporation, the rude product was dissolved in anhydrous xylene (300 mL), and DDQ (22.7 g, 100 mmol) was added to the solution. The mixture was refluxed for 12 h. After cooling, the solution was subjected to column chromatography with ethyl acetate, dichloromethane and petroleum ether (1:3:15, v/v/v) as eluent to give pure product **3** (5.5 g, 86%) as pale-white powder. R_f = 0.39 (EtOAc : PE, v/v ~ 1 : 4). M. p.: 262-264° C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03 (tt, *J* = 7.3, 1.4 Hz, 2H), 6.97 (td, *J* = 7.6, 1.6 Hz, 2H), 6.85 (dt, *J* = 7.7, 1.4 Hz, 4H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.56 (dt, *J* = 7.8, 1.6 Hz, 2H), 6.12 (dt, *J* = 7.8, 1.5 Hz, 2H), 3.88 (s, 6H), 3.57 (s, 6H), 2.64 (ddd, *J* = 15.4, 4.0, 2.4 Hz, 2H), 2.35 (td, *J* = 15.0, 4.2 Hz, 2H), 2.14 (ddd, *J* = 14.1, 4.1, 2.4 Hz, 2H), 1.35–1.27 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.0, 155.5, 138.3, 137.3, 136.4, 136.0, 134.1, 130.9, 130.7, 129.9, 128.5, 127.2, 127.0, 126.8, 125.7, 111.2, 56.3, 52.4, 29.4, 28.1. HRMS (APCI): *m/z* calcd for $C_{40}H_{35}O_6$ $[M + H]^+$ 611.2389, found 611.2328.

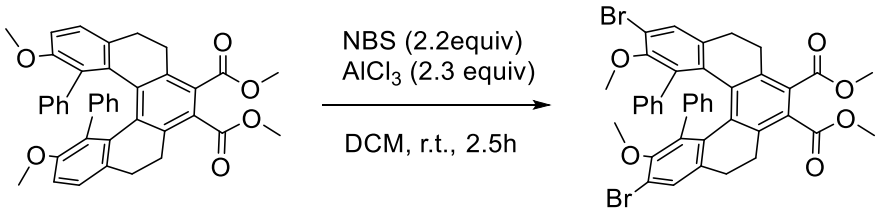
Optical resolution



3 (-)-*P*-**3** (+)-*M*-**3**

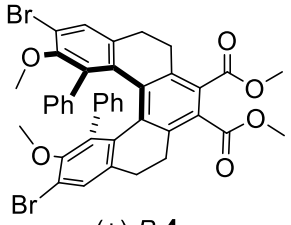
Efficiently semi-preparative optical resolution of *rac*-**3** was performed by semi-preparative chromatography, which provided the pair of enantiomers *P*-**3** and *M*-**3** (ee > 99%) in gram scale (for detail, see ***HPLC charts***)

Synthesis of enantiomers 4



(+)-*P*-**3** or (-)-*M*-**3** (+)-*P*-**4** or (-)-*M*-**4**

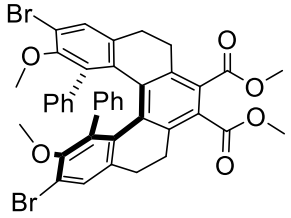
A mixture of compound *P*-**3** or *M*-**3** (1.5g, 2.46 mmol), *N*-bromosuccinimide (0.96 g, 5.4 mmol), and anhydrous aluminum chloride (0.75g, 5.66 mmol) in dry dichloromethane (100 mL) was stirred at room temperature for 3 h. The organic layer was washed with saturated brine (3×150 mL), dried over anhydrous $MgSO_4$, and then concentrated in *vacuo*. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether (1:5, *v*/*v*) as eluent to afford pure product **4** (1.8g, 95%) as white powder.



(+)-*P*-**4**

Compound (+)-*P*-**4.** R_f = 0.40 (EtOAc : PE, *v*/*v* ~ 1 : 4). M. p.: >300 °C. $[\alpha]^{25}D$ = 593 °. ^1H NMR (500 MHz, $CDCl_3$): δ 7.11 (s, 2H), 7.09 (d, *J* = 6.0 Hz, 4H), 6.86 (s, 2H), 6.77

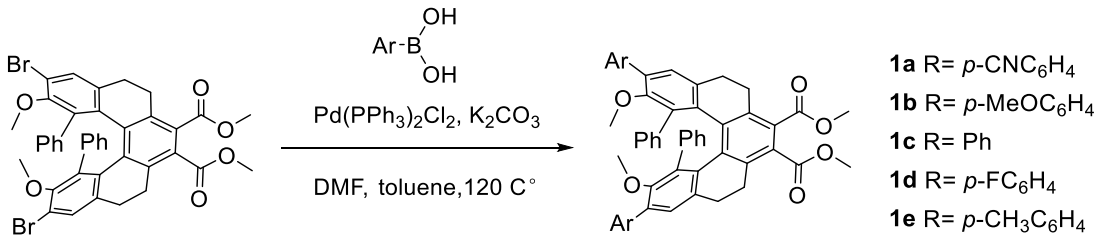
(s, 2H), 6.14 (d, *J* = 7.6 Hz, 2H), 3.89 (s, 6H), 2.97 (s, 6H), 2.69–2.61 (m, 2H), 2.36 (td, *J* = 15.4, 3.9 Hz, 2H), 2.14 (dt, *J* = 14.2, 3.1 Hz, 2H), 1.34 (td, *J* = 14.7, 4.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.6, 153.4, 140.2, 138.0, 136.1, 135.6, 135.5, 133.3, 131.3, 130.3, 130.0, 129.0, 128.0, 126.9, 126.6, 117.3, 59.4, 52.5, 29.3, 27.5. HRMS (APCI): *m/z* calcd for $C_{40}H_{33}Br_2O_6$ $[M + H]^+$ 769.0545, found, 766.0603.



(-)-*M*-**4**

Compound (–)-*M*-**4.** R_f = 0.40 (EtOAc : PE, *v*/*v* ~ 1 : 4). M. p.: >300 °C. $[\alpha]^{25}D$ = -631°. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (s, 2H), 7.11–7.04 (m, 4H), 6.86 (s, 2H), 6.76 (s, 2H), 6.14 (d, *J* = 7.6 Hz, 2H), 3.89 (s, 6H), 2.97 (s, 6H), 2.65 (dt, *J* = 15.1, 3.3 Hz, 2H), 2.36 (td, *J* = 15.3, 3.9 Hz, 2H), 2.14 (dt, *J* = 14.3, 3.2 Hz, 2H), 1.34 (td, *J* = 14.8, 4.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.6, 153.4, 140.2, 138.0, 136.1, 135.7, 135.5, 133.3, 131.3, 130.2, 130.0, 128.9, 128.0, 126.9, 126.5, 117.3, 59.4, 52.5, 29.3, 27.5. HRMS (APCI): *m/z* calcd for $C_{40}H_{33}Br_2O_6$ $[M + H]^+$ 769.0545, found 766.0593.

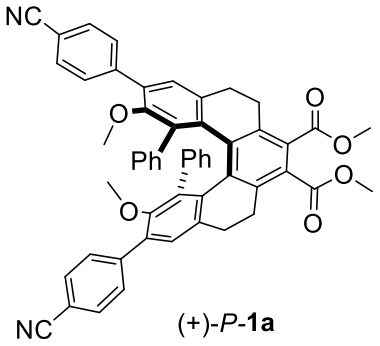
General procedure for the synthesis of enantiomers 1a-e by suzuki-miyaura cross coupling reactions



(+)-*P*-**4** or (-)-*M*-**4** (+)-*P*-**1a-e** or (-)-*M*-**1a-e**

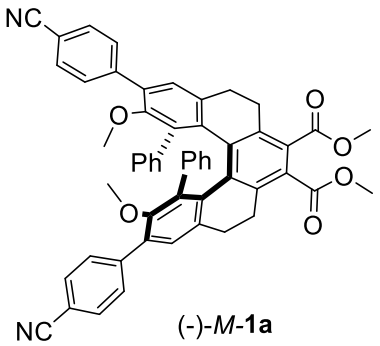
To a mixture of compound (+)-*P*-**3** or (–)-*M*-**3** (320 mg, 0.42 mmol), K_2CO_3 (583 mg, 4.2 mmol), and arylboronic acid (2.8 mmol) in DMF (60mL) and toluene (40 mL) under argon atmosphere was added catalytic amount of $[PdCl_2(PPh_3)_2]$ (5 mol %), followed

by stirring at 120 °C for 12h under argon atmosphere. After cooling, the reaction mixture was poured into ethyl acetate (50 mL). The organic layer was washed with saturated brine (3×50 mL), dried over anhydrous $MgSO_4$, and then concentrated in *vacuo*. The residue was purified by flash column chromatography with ethyl acetate, dichloromethane and petroleum ether (1:3:15, *v*/*v*/*v*) as eluent to afford pure product (+)-*P*-**1a-e** or (–)-*M*-**1a-e**.



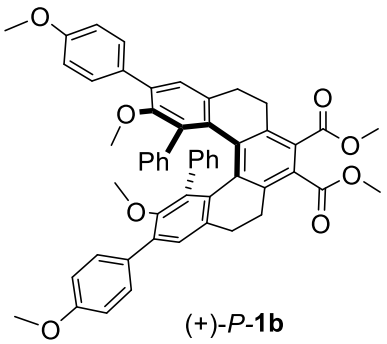
(+)-*P*-**1a**

Compound (+)-*P*-**1a.** According to the general method, (+)-*P*-**1a** (271 mg, 80%) was obtained as white powder. R_f = 0.21 (EtOAc : PE, *v*/*v* ~ 1 : 4). M. p.: >300 °C. $[\alpha]^{25}_D$ = 589°. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.4 Hz, 4H), 7.76 (d, *J* = 8.4 Hz, 4H), 7.06 – 6.98 (m, 2H), 6.94 (s, 2H), 6.88 (td, *J* = 7.3, 1.3 Hz, 4H), 6.82 (d, *J* = 7.9 Hz, 2H), 6.23 (d, *J* = 7.5 Hz, 2H), 3.92 (s, 6H), 2.73 (ddd, *J* = 15.6, 4.1, 2.2 Hz, 2H), 2.62 (s, 6H), 2.46 (td, *J* = 15.4, 3.9 Hz, 2H), 2.26 (ddd, *J* = 14.4, 4.0, 2.2 Hz, 2H), 1.45 (td, *J* = 14.7, 4.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.7, 153.9, 143.3, 139.2, 138.3, 136.3, 136.0, 134.7, 134.5, 132.9, 132.1, 130.4, 129.9, 129.8, 129.1, 128.8, 127.6, 127.1, 126.3, 119.0, 111.9, 59.7, 52.5, 29.6, 27.7. HRMS (APCI): *m/z* calcd for $C_{54}H_{41}N_2O_6$ $[M + H]^+$ 813.2920, found 813.2933.



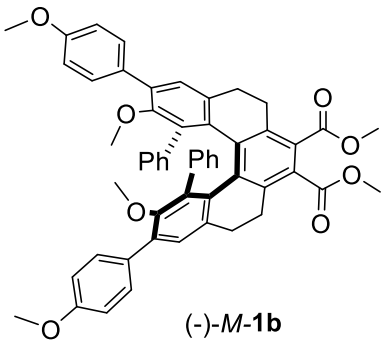
(-)-*M*-**1a**

Compound (–)-*M*-**1a**. According to the general method, (–)-*M*-**1a** (264 mg, 78%) was obtained as white powder. R_f = 0.21 (EtOAc : PE, v/v ~ 1 : 4). M. p.: >300 °C. $[\alpha]^{25}_D$ = -593°. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.9 Hz, 4H), 7.77 (d, *J* = 8.0 Hz, 4H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.95 (s, 2H), 6.89 (t, *J* = 7.6 Hz, 4H), 6.83 (d, *J* = 7.9 Hz, 2H), 6.23 (d, *J* = 7.8 Hz, 2H), 3.93 (s, 6H), 2.79 – 2.70 (m, 2H), 2.63 (s, 6H), 2.47 (td, *J* = 15.5, 3.9 Hz, 2H), 2.31 – 2.23 (m, 2H), 1.46 (td, *J* = 14.7, 4.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.7, 153.9, 143.2, 139.2, 138.3, 136.3, 136.0, 134.7, 134.5, 132.9, 132.1, 130.4, 129.9, 129.8, 129.1, 128.8, 127.6, 127.0, 126.3, 119.0, 110.9, 59.7, 52.5, 29.6, 27.7. HRMS (APCI): *m/z* calcd for $C_{54}H_{41}N_2O_6$ $[M + H]^+$ 813.2920, found 813.2959.



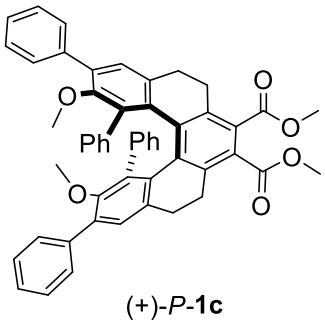
(+)-*P*-**1b**

Compound (+)-*P*-**1b.** According to the general method, (+)-*P*-**1b** (251mg, 75%) was obtained as white powder. R_f = 0.30 (EtOAc : PE, *v*/*v* ~ 1 : 4). M. p.: 162-164 °C. $[\alpha]^{25}_D$ = 654°. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (s, 2H), 7.62 (s, 2H), 7.02–6.98 (m, 6H), 6.93 (d, *J* = 4.9 Hz, 4H), 6.89–6.81 (m, 4H), 6.23 (d, *J* = 7.6 Hz, 2H), 3.91 (s, 6H), 3.88 (s, 6H), 2.71 (s, 6H), 2.68 (d, *J* = 3.4 Hz, 2H), 2.46 (td, *J* = 15.4, 4.0 Hz, 2H), 2.22 (dt, *J* = 13.9, 3.1 Hz, 2H), 1.42 (td, *J* = 14.7, 4.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.9, 158.9, 153.8, 138.7, 138.2, 136.7, 136.6, 134.5, 134.2, 132.9, 131.0, 130.4, 130.2, 128.9, 128.5, 127.5, 126.7, 125.9, 113.7, 59.4, 55.3, 52.4, 29.6, 27.8. HRMS (APCI): *m/z* calcd for $C_{54}H_{47}O_8$ $[M + H]^+$ 823.3226, found 823.3265.



(-)-*M*-**1b**

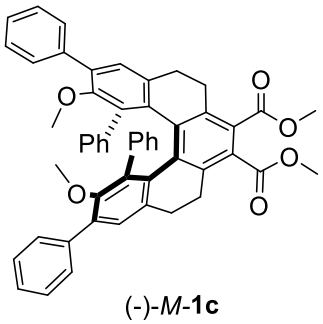
Compound (–)-*M*-**1b.** According to the general method, (–)-*M*-**1b** (271mg, 84%) was obtained as white powder. R_f = 0.30 (EtOAc : PE, *v*/*v* ~ 1 : 4). M. p.: 162-164 °C. $[\alpha]^{25}_D$ = -646°. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 2.2 Hz, 2H), 7.63 (d, *J* = 2.1 Hz, 2H), 7.02–6.98 (m, 6H), 6.93 (d, *J* = 4.6 Hz, 4H), 6.84 (t, *J* = 6.0 Hz, 4H), 6.23 (d, *J* = 7.6 Hz, 2H), 3.91 (s, 6H), 3.88 (s, 6H), 2.71 (s, 6H), 2.71–2.66 (m, 2H), 2.47 (td, *J* = 15.3, 4.0 Hz, 2H), 2.22 (dt, *J* = 12.0, 2.4 Hz, 2H), 1.42 (td, *J* = 14.7, 4.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.0, 158.9, 153.8, 138.8, 138.2, 136.7, 136.6, 134.5, 134.2, 132.9, 131.0, 130.5, 130.2, 129.0, 128.6, 127.5, 126.7, 125.9, 113.7, 59.4, 55.3, 52.4, 29.6, 27.8. HRMS (APCI): *m/z* calcd for $C_{54}H_{47}O_8$ $[M + H]^+$ 823.3226, found 823.3245.



(+)-*P*-**1c**

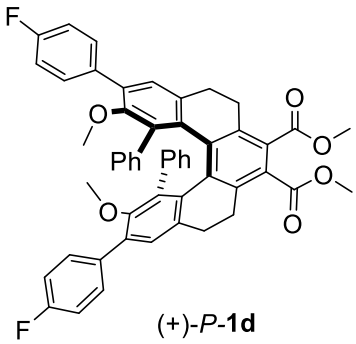
Compound (+)-*P*-**1c.** According to the general method, (+)-*P*-**1c** (221 mg, 70%) was obtained as white powder. R_f = 0.42 (EtOAc : PE, *v*/*v* ~ 1 : 4). M. p.: 162-164 °C. $[\alpha]^{25}_D$ = 627°. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 1.4 Hz, 2H), 7.68 (t, *J* = 1.2 Hz, 2H), 7.49–7.43 (m, 4H), 7.40–7.34 (m, 2H), 7.00 (tt, *J* = 7.3, 1.4 Hz, 2H), 6.97–6.91 (m, 4H), 6.90–6.83 (m, 4H), 6.24 (d, *J* = 7.6 Hz, 2H), 3.92 (s, 6H), 2.71 (s, 6H), 2.70–2.66 (m, 2H), 2.48 (td, *J* = 15.2, 3.8 Hz, 2H), 2.23 (ddd, *J* = 14.3, 4.0, 2.3 Hz, 2H), 1.45 (dd, *J* = 15.2, 4.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.9, 153.9, 138.8, 138.7, 138.2, 136.7, 136.5, 134.7, 134.5, 133.3, 130.5, 130.2, 129.2, 129.1, 128.7, 128.2, 127.5,

127.1, 126.8, 126.0, 59.6, 52.4, 29.6, 27.8. HRMS (APCI): *m/z* calcd for $C_{52}H_{43}O_6$ [M + H]$^+$ 763.3015, found 763.3028.



(-)-*M*-**1c**

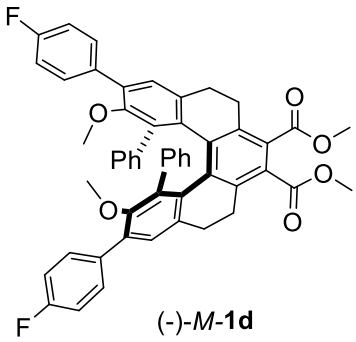
Compound (–)-*M*-**1c.** According to the general method, (–)-*M*-**1c** (232 mg, 73%) was obtained as white powder. R_f = 0.42 (EtOAc : PE, *v*/*v* ~ 1 : 4). M. p.: 162-164 °C. $[\alpha]^{25}_D$ = -642°. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (s, 2H), 7.69 (s, 2H), 7.47 (t, *J* = 7.5 Hz, 4H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 2H), 6.96 (s, 4H), 6.88 (d, *J* = 8.1 Hz, 4H), 6.25 (d, *J* = 7.6 Hz, 2H), 3.92 (s, 6H), 2.78–2.72 (m, 2H), 2.72 (s, 6H), 2.49 (td, *J* = 15.4, 4.0 Hz, 2H), 2.25 (dt, *J* = 13.8, 3.2 Hz, 2H), 1.45 (td, *J* = 14.7, 4.0 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3): δ 168.9, 153.9, 138.8, 138.7, 138.2, 136.6, 136.5, 134.7, 134.5, 133.3, 130.4, 130.2, 129.2, 129.1, 128.7, 128.2, 127.5, 127.1, 126.7, 125.9, 59.5, 52.4, 29.6, 27.8. HRMS (APCI): *m/z* calcd for $C_{52}H_{43}O_6$ [M + H]$^+$ 763.3015, found 763.3031.



(+)-*P*-**1d**

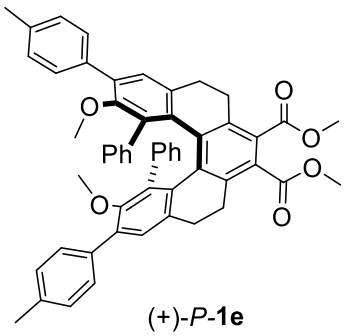
Compound (+)-*P*-**1d.** According to the general method, (+)-*P*-**1d** (253 mg, 76%) was obtained as white powder. R_f = 0.44 (EtOAc : PE, *v*/*v* ~ 1 : 4). M. p.: 170-172 °C. [α]25$_D$ = 685°. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.64 (m, 4H), 7.15 (t, *J* = 8.7 Hz, 4H), 7.01 (tt, *J* = 7.4, 1.4 Hz, 2H), 6.95–6.82 (m, 8H), 6.23 (d, *J* = 7.6 Hz, 2H), 3.92 (s, 6H), 2.75–2.69 (m, 2H), 2.68 (s, 6H), 2.47 (td, *J* = 15.3, 4.1 Hz, 2H), 2.23 (ddd, *J* = 14.3,

4.1, 2.3 Hz, 2H), 1.49–1.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.9, 163.5, 161.0, 153.8, 138.9, 138.2, 136.5, 136.4, 134.6, 134.5, 134.5, 133.7, 133.4, 130.7, 130.6, 130.4, 130.1, 129.0, 128.8, 127.5, 126.8, 126.0, 59.4, 52.4, 29.6, 27.8. HRMS (APCI): *m/z* calcd for $C_{52}H_{41}F_2O_6$ $[M + H]^+$ 799.2827, found 799.2831.



(-)-*M*-**1d**

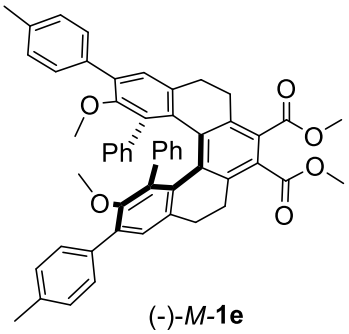
Compound (–)-*M*-**1d.** According to the general method, (–)-*M*-**1d** (236 mg, 71%) was obtained as white powder. R_f = 0.44 (EtOAc : PE, v/v ~ 1 : 4). M. p.: 170-172 °C. $[\alpha]^{25}_D$ = -663°. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 8.5, 5.5 Hz, 4H), 7.15 (t, *J* = 8.6 Hz, 4H), 7.01 (t, *J* = 7.3 Hz, 2H), 6.95–6.82 (m, 8H), 6.23 (d, *J* = 7.7 Hz, 2H), 3.92 (s, 6H), 2.75–2.70 (m, 2H), 2.68 (s, 6H), 2.47 (td, *J* = 15.4, 4.0 Hz, 2H), 2.23 (dt, *J* = 13.7, 3.2 Hz, 2H), 1.44 (td, *J* = 14.7, 4.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.9, 163.2, 161.2, 153.8, 138.9, 138.2, 136.5, 136.4, 134.6, 134.5, 134.5, 133.7, 133.4, 130.7, 130.7, 130.4, 130.1, 129.0, 128.8, 127.5, 126.8, 126.0, 115.2, 115.1, 76.8, 59.4, 52.5, 29.6, 27.8. HRMS (APCI): *m/z* calcd for $C_{52}H_{41}F_2O_6$ $[M + H]^+$ 799.2827, found 799.2865.



(+)-*P*-**1e**

Compound (+)-*P*-**1e**. According to the general method, (+)-*P*-**1e** (244 mg, 74%) was obtained as white powder. R_f = 0.46 (EtOAc : PE, *v*/*v* ~ 1 : 4). M. p.: 202-204 °C. $[\alpha]^{25}_D$

= 385°. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.8 Hz, 4H), 7.28 (s, 4H), 6.99 (t, *J* = 7.3 Hz, 2H), 6.93 (s, 4H), 6.86 (s, 4H), 6.23 (d, *J* = 7.6 Hz, 2H), 3.91 (s, 6H), 2.71 (s, 6H), 2.70–2.65 (m, 2H), 2.49 (dd, *J* = 15.6, 4.0 Hz, 2H), 2.43 (s, 6H), 2.22 (dt, *J* = 13.8, 3.1 Hz, 2H), 1.43 (td, *J* = 14.7, 4.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.0, 153.9, 138.7, 138.2, 136.8, 136.7, 136.5, 135.7, 134.6, 134.5, 133.1, 130.4, 130.2, 129.1, 129.0, 128.6, 127.5, 126.7, 125.9, 59.5, 52.4, 29.6, 27.8, 21.3. HRMS (APCI): *m/z* calcd for $C_{54}H_{47}O_6$ $[M + H]^+$ 791.3328, found 791.3345.



(-)-*M*-**1e**

Compound (–)-*M*-**1e.** According to the general method, (–)-*M*-**1e** (208 mg, 63%) was obtained as white powder. R_f = 0.46 (EtOAc : PE, *v*/*v* ~ 1 : 4). M. p.: 202-204 °C. $[\alpha]^{25}_{D}$ = -391°. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.7 Hz, 4H), 7.27–7.24 (m, 4H), 6.99 (t, *J* = 7.4 Hz, 2H), 6.93 (s, 4H), 6.85 (d, *J* = 6.3 Hz, 4H), 6.23 (d, *J* = 7.6 Hz, 2H), 3.91 (s, 6H), 2.71 (s, 6H), 2.70–2.65 (m, 2H), 2.48 (dd, *J* = 15.3, 4.0 Hz, 2H), 2.43 (s, 6H), 2.22 (dd, *J* = 13.7, 3.2 Hz, 2H), 1.42 (td, *J* = 14.8, 4.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.9, 153.8, 138.7, 138.2, 136.8, 136.7, 136.5, 134.6, 134.5, 133.1, 130.4, 130.2, 129.1, 129.0, 128.6, 127.5, 126.7, 125.9, 59.5, 52.4, 29.6, 27.8, 21.3. HRMS (APCI): *m/z* calcd for $C_{54}H_{47}O_6$ $[M + H]^+$ 791.3328, found 791.3367.

3. Crystal structure and crystal data of (+)-*P*-4

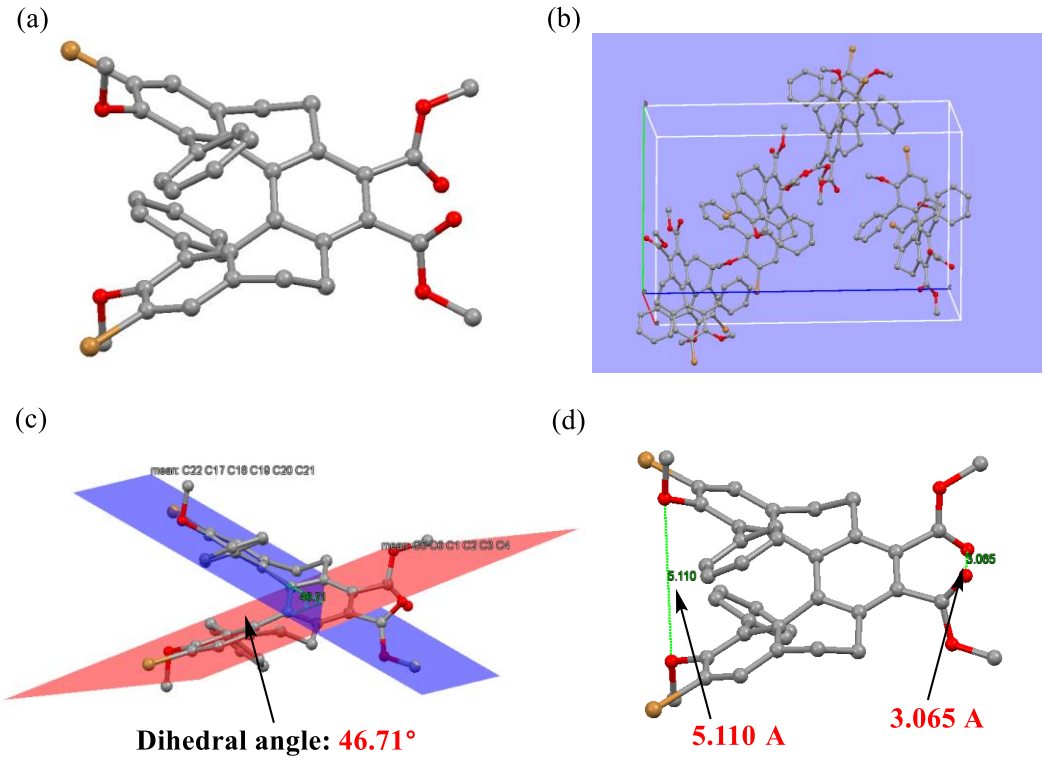


Fig. S1. (a) X-ray crystal structure, (b) crystal packing, (c) dihedral angle of terminal rings, and (d) distance of methoxyl groups and methyl groups, carbonyl group and carbonyl group of (+)-*P*-**4.**

Table S1. Crystal data and structure refinement for (+)-*P*-**4** (CCDC 1536347)

Empirical formula	$C_{40}H_{32}Br_2O_6$	
Formula weight	768.47	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.3148(18) Å	= 90°.
	b = 14.552(3) Å	= 90°.
	c = 23.285(4) Å	= 90°.
Volume	3495.1(10) $Å^3$	
Z	4	
Density (calculated)	1.460 Mg/m^3	

Absorption coefficient	2.366 mm^{-1}
F(000)	1560
Crystal size	0.164 x 0.067 x 0.033 mm^3
Theta range for data collection	1.650 to 27.486°.
Index ranges	-13<=h<=13, -18<=k<=18, -30<=l<=28
Reflections collected	27947
Independent reflections	7931 [R(int) = 0.0630]
Completeness to theta = 26.000°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.56274
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7931 / 0 / 437
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)]	R_1 = 0.0634, wR_2 = 0.1573
R indices (all data)	R_1 = 0.0699, wR_2 = 0.1624
Absolute structure parameter	0.016(6)
Extinction coefficient	n/a
Largest diff. peak and hole	1.710 and -0.728 e.$Å^{-3}$

4. HPLC charts

Optical resolution conditions

Table S2. Semi-preparative chromatography conditions

Column	:	CHIRALPAK IE
Column size	:	0.46 cm I.D. × 15 cm L
Injection	:	0.2 ul
Mobile phase	:	Hexane/DCM=40/60(V/V)
Flow rate	:	1.0 ml/min
Wave length	:	UV 254 nm
Temperature	:	35 °C

Analysis of the enantiomer excess of 3

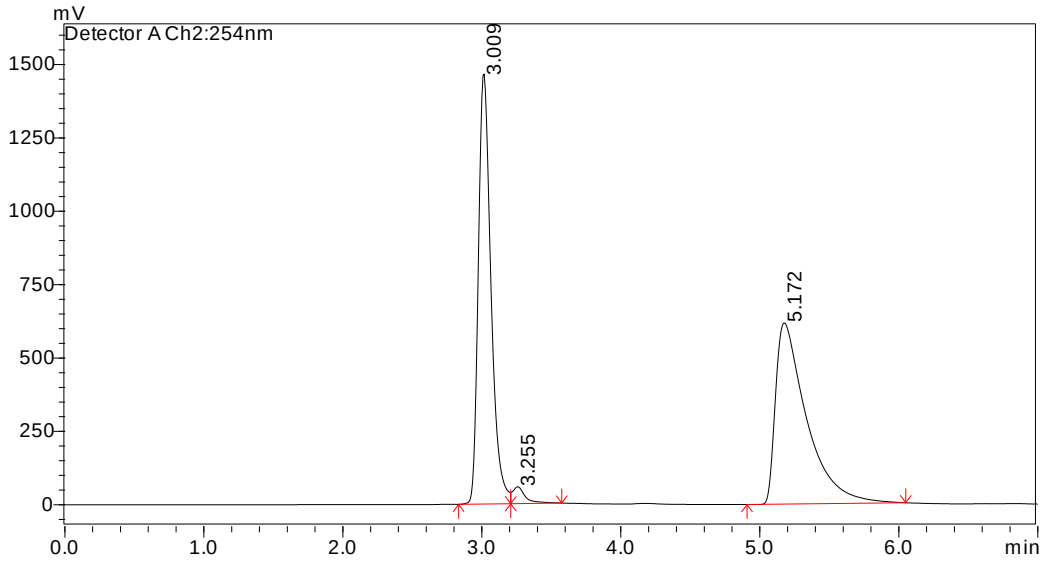


Fig. S2. HPLC profile of *rac*-**3**.

Table S3. The summary of HPLC profiles of *rac*-**3**.

Peak	Ret. Time	Area	Area%	T. Plate	Tailing F.	Resolution
1	3.009	9301533	48.3282	4720.025	1.466	--
2	3.255	359835	1.8696	3338.207	--	1.226
3	5.172	9585228	49.8022	2835.433	2.582	6.245

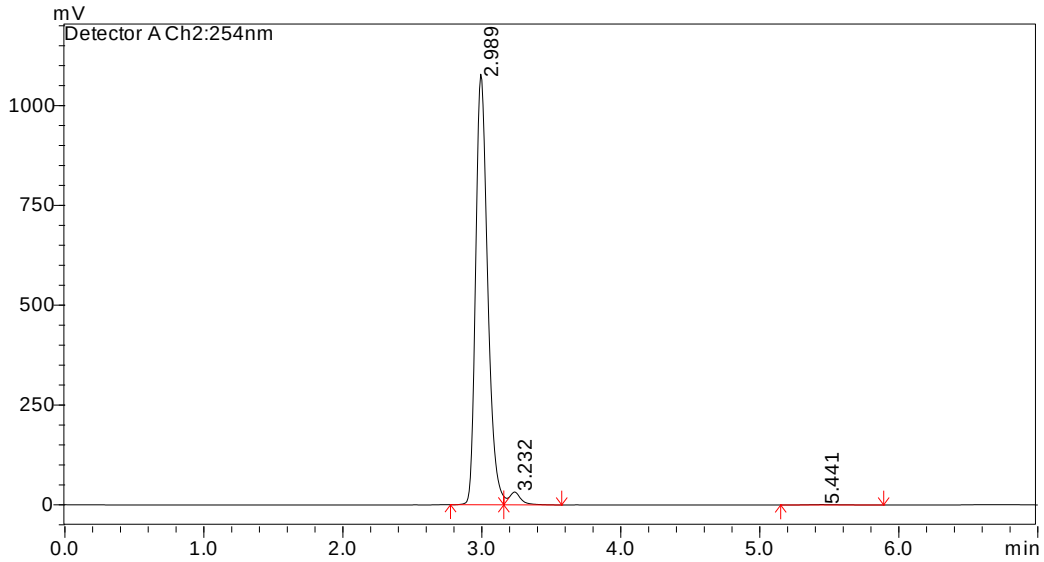


Fig. S3. HPLC profile of (+)-*P*-**3**.

Table S4. The summary of HPLC profiles of (+)-*P*-**3**.

Peak	Ret. Time	Area	Area%	T. Plate	Tailing F.	Resolution
1	2.989	6487488	96.7323	4948.355	1.374	--
2	3.232	203521	3.0346	5161.724	--	1.388
3	5.441	15630	0.2330	2654.274	1.295	7.334
***ee* value of (+)-*P*-3: > 99%**						

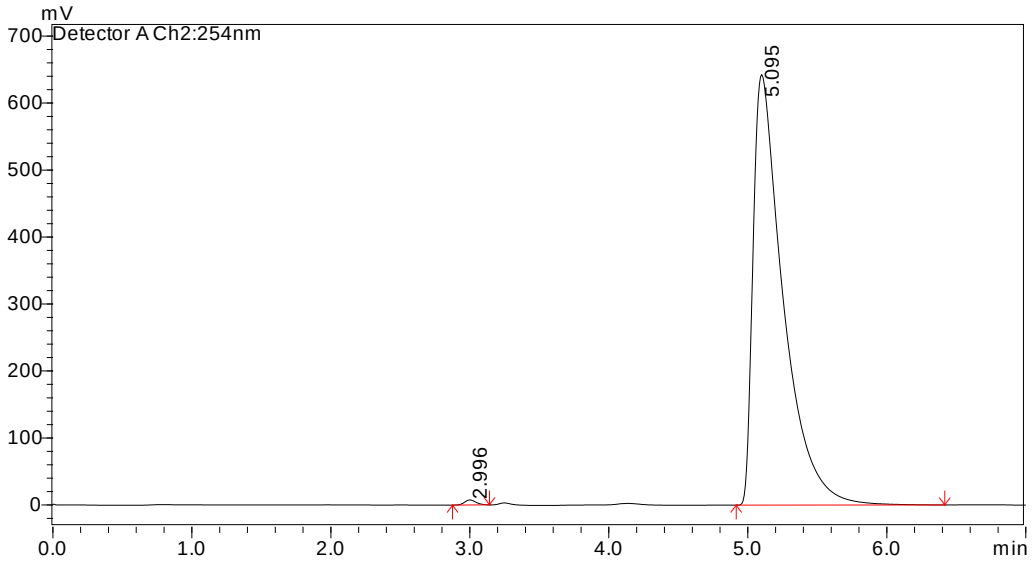


Fig. S4. HPLC profile of (–)-*M*-**3**.

Table S5. The summary of HPLC profiles of (–)-*M*-**3**.

Peak	Ret. Time	Area	Area%	T. Plate	Tailing F.	Resolution
1	2.996	42712	0.4393	5287.737	1.227	--
2	5.095	9680321	99.5607	2882.498	2.516	7.712
***ee* value of (–)*M*-3: > 99%**						

Analysis of the enantiomer excess of (+)-*P*-1a-e and (–)-*M*-1a-e

HPLC Analysis Conditions:

Column: Chiralpak® IE 5 μm, 4.6 mm × 250 mm

Mobile phase: hexane: dichloromethane = 40:60 for (+)-*P*-**1a** and (–)-*M*-**1a**

hexane: dichloromethane = 60:40 for (+)-*P*-**1b** and (–)-*M*-**1b**

hexane: dichloromethane = 74:26 for (+)-*P*-**1c-e** and (–)-*M*-**1c-e**

Flow rate: 1.0 mL/min

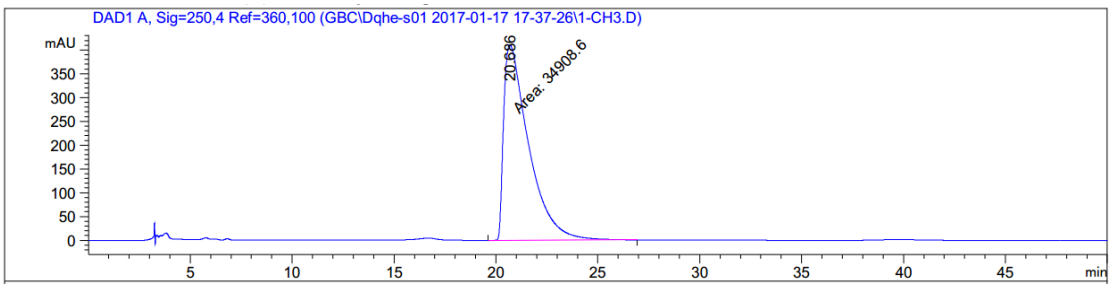


Fig. S5. HPLC profile of (+)-*P*-**1a**.

Table S6. The summary of HPLC profiles of (+)-*P*-**1a**.

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(+)-*P*-**1a**	1	20.69	3.49×10^4	100%	> 99.9 %

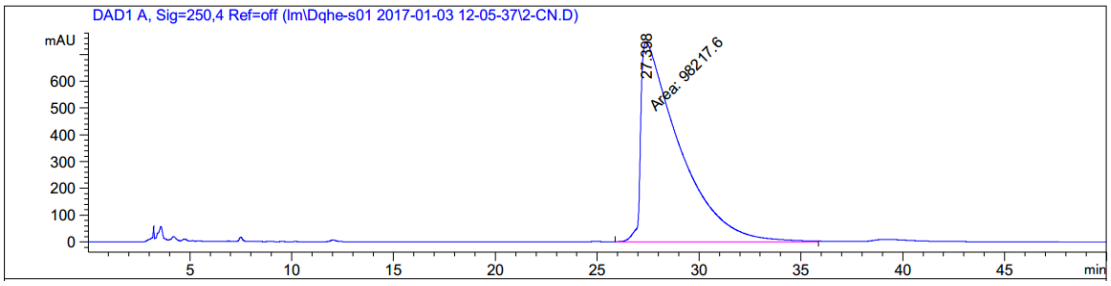


Fig. S6. HPLC profile of (–)-*M*-**1a**.

Table S7. The summary of HPLC profiles of (–)-*M*-**1a**.

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(–)-*M*-**1a**	1	27.40	9.82×10^4	100%	> 99.9 %

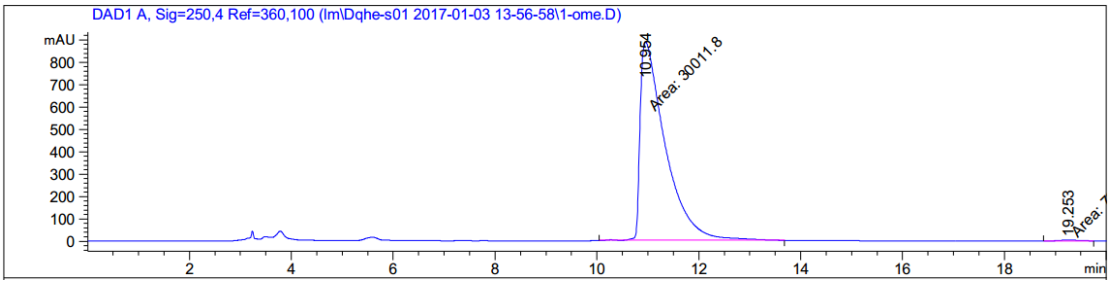


Fig. S7. HPLC profile of (+)-*P*-**1b**.

Table S8. The summary of HPLC profiles of (+)-*P*-**1b**.

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(+)-*P*-**1b**	1	10.95	3.00×10^4	99.76	99.52 %

	2	19.25	3.17	0.24	

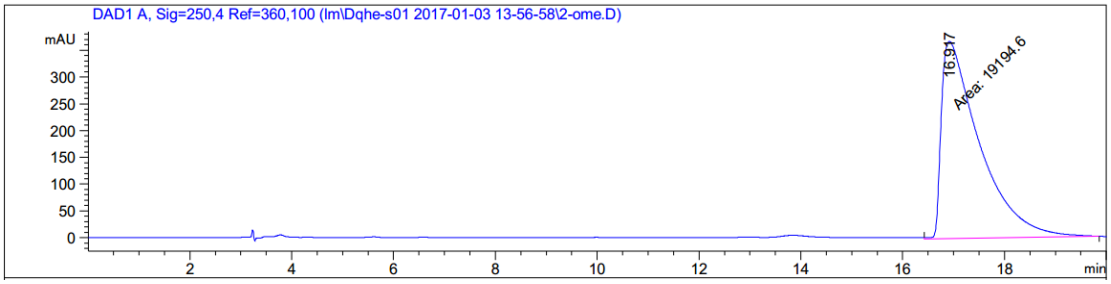


Fig. S8. HPLC profile of (–)-*M*-**1b**.

Table S9. The summary of HPLC profiles of (–)-*M*-**1b**.

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(–)-*M*-**1b**	1	16.92	1.92×10^4	100	>99.9 %

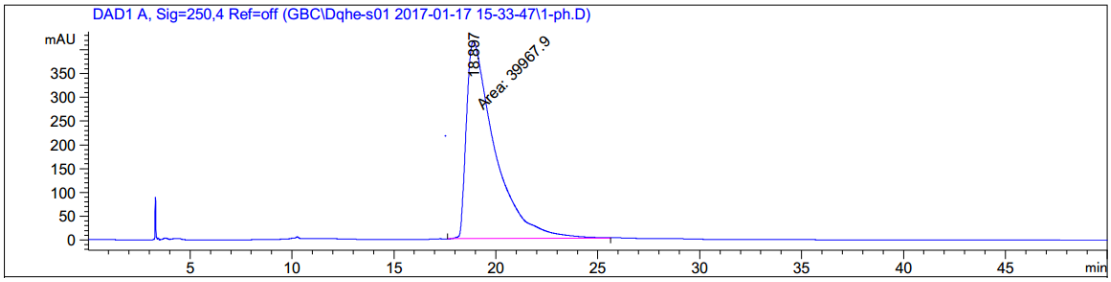


Fig. S9. HPLC profile of (+)-*P*-**1c**.

Table S10. The summary of HPLC profiles of (+)-*P*-**1c**.

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(+)-*P*-**1c**	1	18.90	4.00×10^4	100	>99.9 %

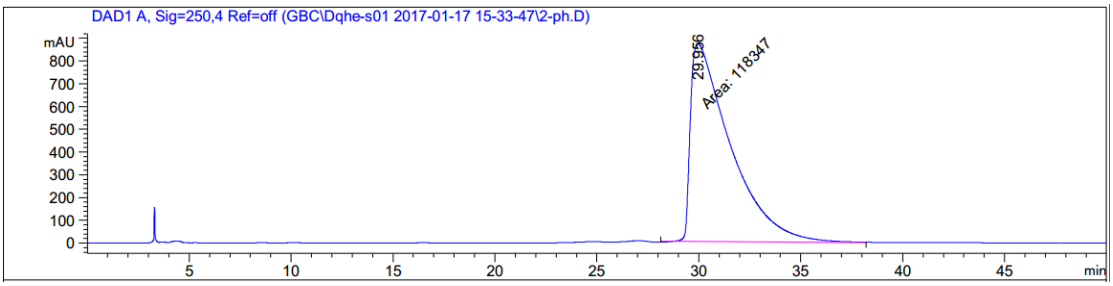


Fig. S10. HPLC profile of (–)-*M*-**1c**.

Table S11. The summary of HPLC profiles of (–)-*M*-**1c**.

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(–)-*M*-**1c**	1	29..96	1.18×10^5	100	>99.9 %

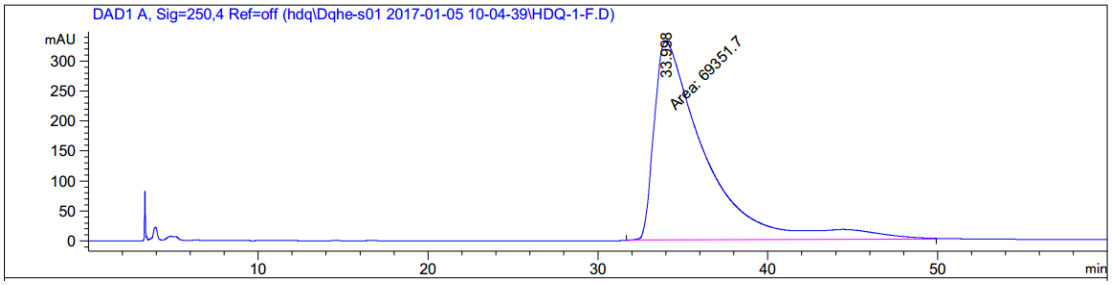


Fig. S11. HPLC profile of (+)-*P*-**1d**.

Table S12. The summary of HPLC profiles of (+)-*P*-**1d**.

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(+)-*P*-**1d**	1	34.00	6.94×10^4	100	>99.9 %

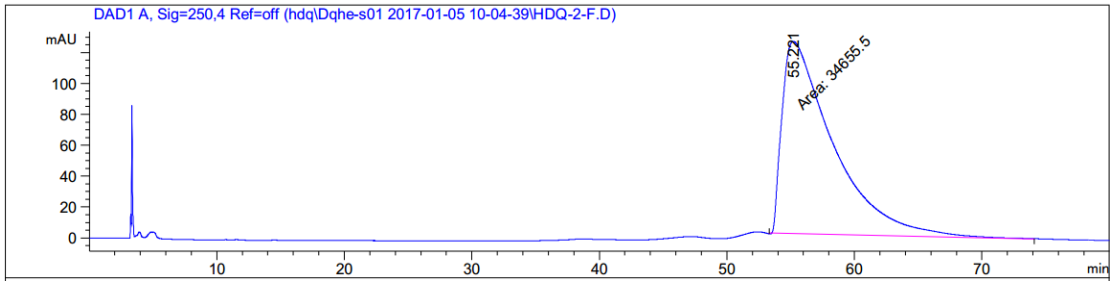


Fig. S12. HPLC profile of (–)-*M*-**1d**.

Table S13. The summary of HPLC profiles of (–)-*M*-**1d**.

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(–)-*M*-**1d**	1	55.22	3.47×10^4	100	>99.9 %

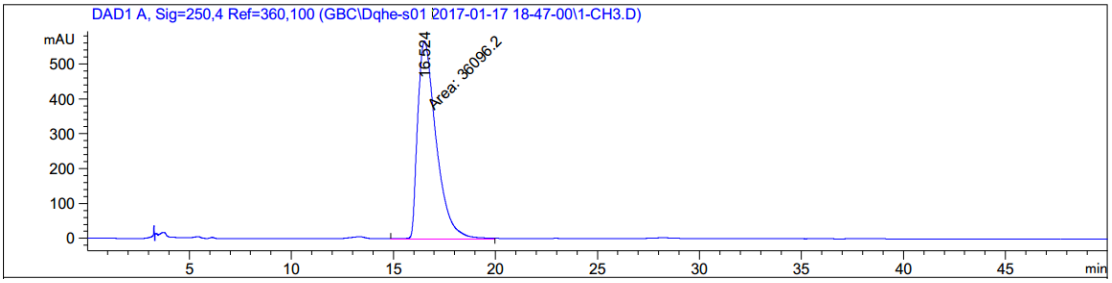


Fig. S13. HPLC profile of (+)-*P*-**1e**.

Table S14. The summary of HPLC profiles of (+)-*P*-**1e**.

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(+)-*P*-**1e**	1	16.52	3..61 × 10^4	100	>99.9 %

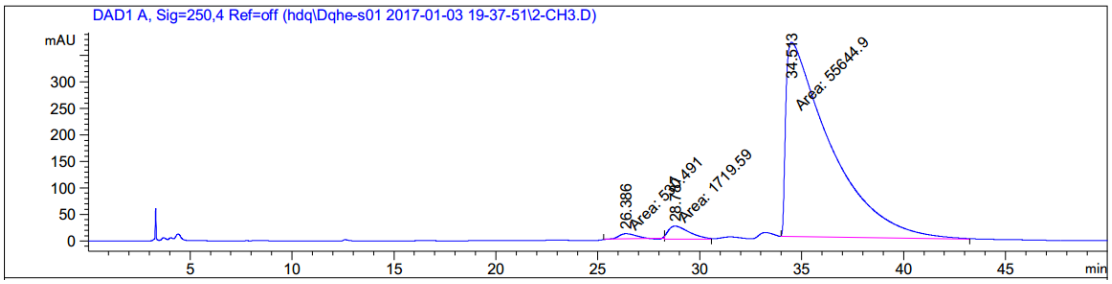


Fig. S14. HPLC profile of (–)-*M*-**1e**.

Table S15. The summary of HPLC profiles of (–)-*M*-**1e**.

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(–)-*M*-**1e**	3	55.22	5.56 × 10^4	96.1	>99.9 %

Optical stability analysis of the enantiomers

Time-dependent HPLC measurements were performed to determine the optical stability of the enantiomers. (+)-*P*-**1c** (5 mg) was dissolved in diethylene glycol dibutyl ether (6 mL). The solution was heated at 453 K continuously, and 0.2 mL of this solution was sampled for different time intervals to analyze immediately by HPLC to determine the initial enantiomeric excess depending on time. The HPLC measurements were performed keeping the column at 4 °C.

HPLC Analysis Conditions:

Column: Chiralpak® IE 5 μm, 4.6 mm × 250 mm

Mobile phase: hexane: dichloromethane = 75:25

Flow rate: 1.0 mL/min

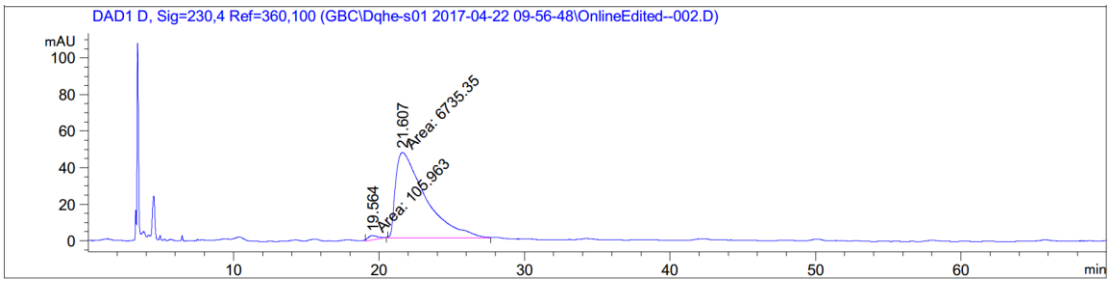


Fig. S15. HPLC profile of (+)-*P*-**1c** (heated for 0 h at 453 K).

Table S16. The summary of HPLC profiles of (+)-*P*-**1c** (heated 0 h at 453 K).

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(+)-*P*-**1c**	1	19.56	105.96	1.55	>99.9 %
	2	21.607	6.74×10^3	98.45	

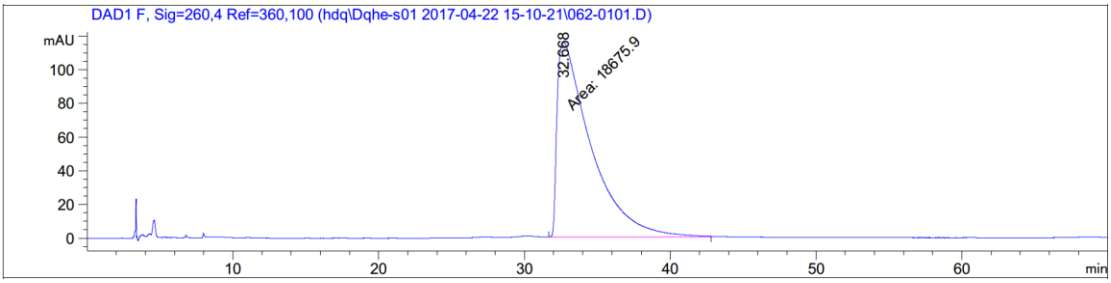


Fig. S16. HPLC profile of (–)-*M*-**1c** (heated for 0 h at 453 K).

Table S17. The summary of HPLC profiles of (–)-*M*-**1c** (heated 0 h at 453 K).

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(–)-*M*-**1c**	1	32.67	1.86×10^4	100	>99.9 %

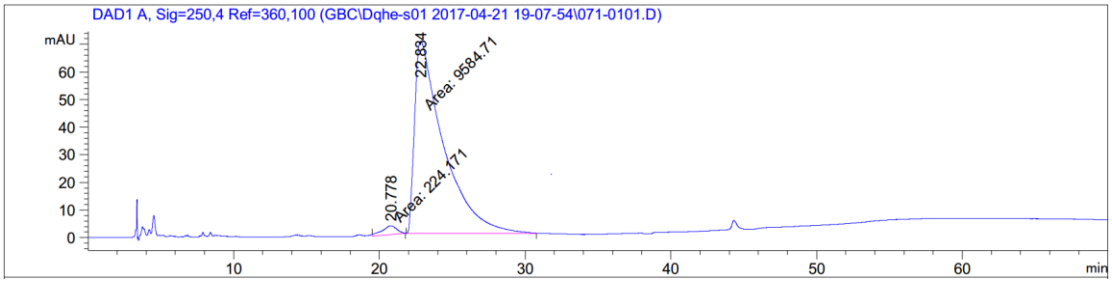


Fig. S17. HPLC profile of (+)-*P*-**1c** (heated for 1 h at 453 K).

Table S18. The summary of HPLC profiles of (+)-*P*-**1c** (heated for 1 h at 453 K).

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(+)-*P*-**1c**	1	20.77	224.17	2.29	>99.9 %
	2	22.83	9.58×10^3	97.71	

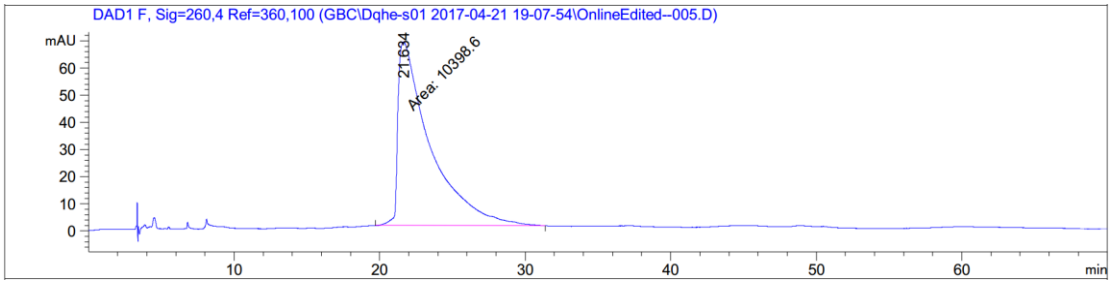


Fig. S18. HPLC profile of (+)-*P*-**1c** (heated for 4 h at 453 K).

Table S19. The summary of HPLC profiles of (+)-*P*-**1c** (heated for 4 h at 453 K).

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(+)-*P*-**1c**	1	21.63	1.04×10^4	100	>99.9 %

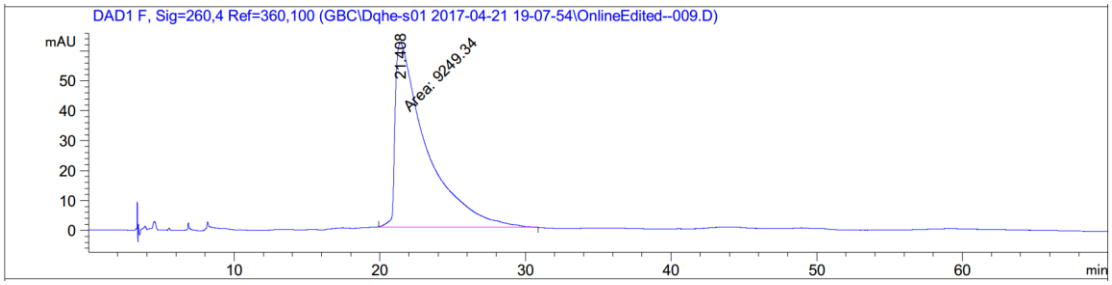


Fig. S19. HPLC profile of (+)-*P*-**1c** (heated for 8 h at 453 K).

Table S20. The summary of HPLC profiles of (+)-*P*-**1c** (heated for 8 h at 453 K).

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(+)-*P*-**1c**	1	21.41	9.25×10^3	100	>99.9 %

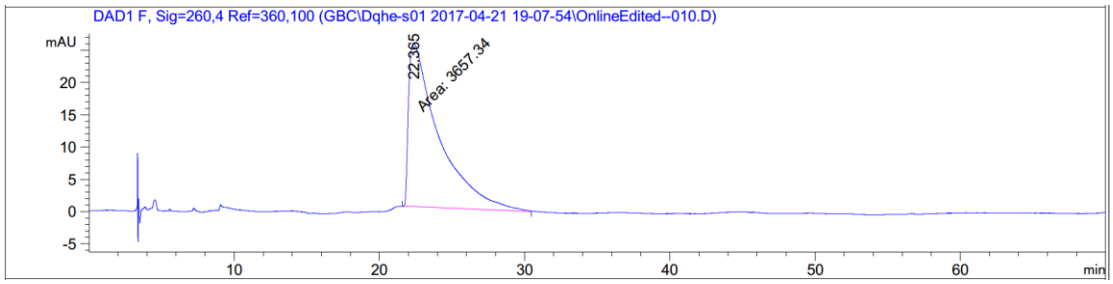


Fig. S20. HPLC profile of (+)-*P*-**1c** (heated 10 h at 453 K).

Table S21. The summary of HPLC profiles of (+)-*P*-**1c** (heated for 10 h at 453 K).

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(+)-*P*-**1c**	1	22.36	3.66×10^3	100	>99.9 %

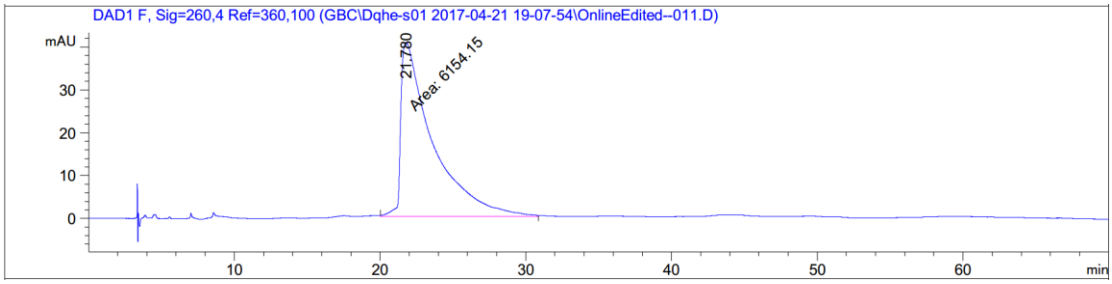


Fig. S21. HPLC profile of (+)-*P*-**1c** (heated for12 h at 453 K).

Table S22. The summary of HPLC profiles of (+)-*P*-**1c** (heated for 12 h at 453 K).

Compound	Peak	Ret Time (min)	Area (mAU·s)	Area %	ee value
(+)-*P*-**1c**	1	21.78	6.15×10^3	100	>99.9 %

5. Photophysical properties of enantiomers (+)-*P*-1a-e and (+)-*P*-3

UV-vis absorption and fluorescence spectra

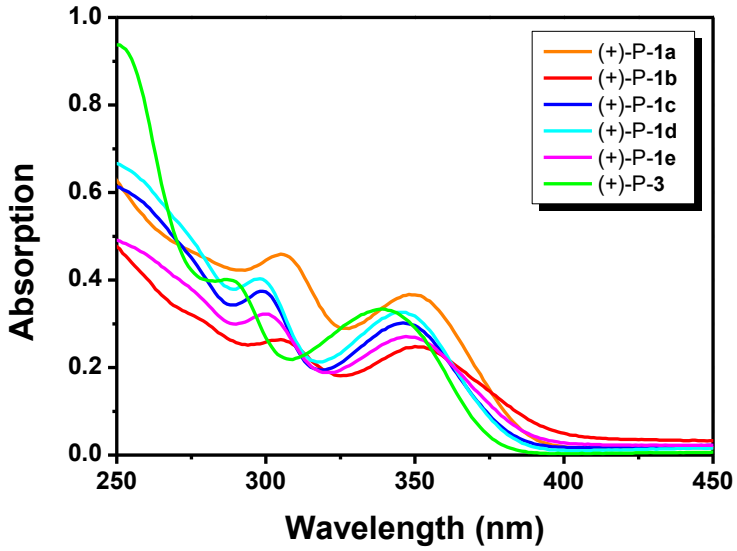


Fig. S22. UV/Vis spectra of (+)-*P*-**1a-e** and (+)-*P*-**3** at room temperature (neat film).

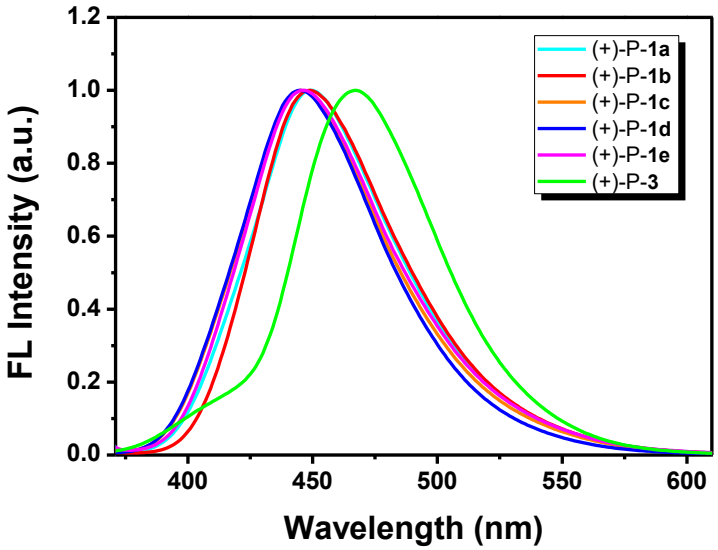


Fig. S23. Emission spectra of (+)-*P*-**1a-e** and (+)-*P*-**3** at room temperature (neat film).

Table S23. Photophysical properties of enantiomers (+)-*P*-**1a-e** and (+)-*P*-**3** in solution

Enantiomers	λ_{abs} (nm)	log ε	λ_{em} (nm)	Φ_{PL}	τ (ns)	SS (cm^{-1})
(+)-*P*-**1a**	299, 347	4.71, 4.51	440	0.48	4.00	6091
(+)-*P*-**1b**	300, 349	4.52, 4.41	442	0.59	4.02	6029
(+)-*P*-**1c**	295, 344	4.58, 4.41	439	0.40	4.09	6291
(+)-*P*-**1d**	293, 344	4.60, 4.39	438	0.41	4.19	6239
(+)-*P*-**1e**	298, 345	4.54, 4.44	440	0.42	4.53	6258
(+)-*P*-**3**	286, 338	4.94, 4.85	465	0.03	2.53	8080

Table S24. Photophysical properties of enantiomers (+)-*P*-**1a-e** and (+)-*P*-**3** (neat film)

Enantiomers	λ_{abs} (nm)	log ε	λ_{em} (nm)	Φ_{PL}	τ (ns)	SS (cm^{-1})
(+)-*P*-**1a**	305, 348	4.66, 4.56	449	0.22	3.54	6464
(+)-*P*-**1b**	305, 350	4.42, 4.39	449	0.26	3.40	6300
(+)-*P*-**1c**	299, 346	4.57, 4.48	445	0.20	3.67	6430
(+)-*P*-**1d**	298, 346	4.61, 4.51	445	0.21	3.50	6430
(+)-*P*-**1e**	300, 347	4.51, 4.43	446	0.21	3.36	6397
(+)-*P*-**3**	287, 339	4.60, 4.52	467	0.12	5.11	8085

CD and CPL spectra

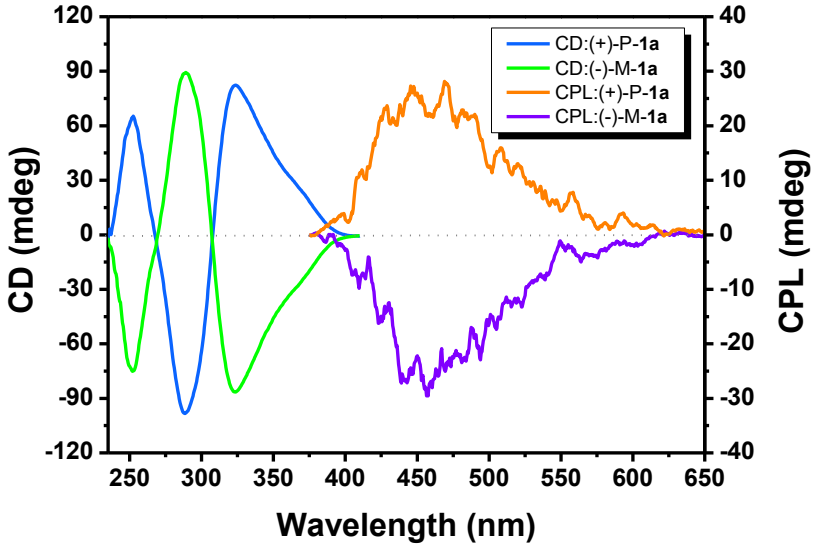


Fig. S24. Mirror image CD and CPL spectra of (+)-*P*-**1a** and (–)-*M*-**1a** in THF at room temperature (c = 5.0 × 10^{-5} M).

Absorption dissymmetry factors (g_{abs}) and luminescence dissymmetry factors (g_{lum}) of the enantiomers 1a-e and 3

Table S25. Absorption dissymmetry factor (g_{abs}) of enantiomers **1a-e** and **3**

Enantiomers	g_{abs} (×10^{-3})	Enantiomers	g_{abs} (×10^{-3})
(+)-*P*-**1a**	2.63 (324nm)	(–)-*M*-**1a**	-2.73 (324nm)
(+)-*P*-**1b**	3.55 (323nm)	(–)-*M*-**1b**	-3.66 (323nm)
(+)-*P*-**1c**	4.34 (318nm)	(–)-*M*-**1c**	-4.77 (318nm)
(+)-*P*-**1d**	3.82 (318nm)	(–)-*M*-**1d**	-4.01 (318nm)
(+)-*P*-**1e**	3.21 (320nm)	(–)-*M*-**1e**	-3.42 (320nm)
(+)-*P*-**3**	7.87 (316nm)	(–)-*M*-**3**	-7.73 (316nm)

Table S26. Luminescence dissymmetry factors (g_{lum}) of enantiomers **1a-e** and **3**

Enantiomers	g_{lum} (×10^{-3})	Enantiomers	g_{lum} (×10^{-3})
(+)-*P*-**1a**	5.63 (459nm)	(–)-*M*-**1a**	-5.04 (457nm)
(+)-*P*-**1b**	3.66 (453nm)	(–)-*M*-**1b**	-3.40 (463nm)
(+)-*P*-**1c**	6.32 (453nm)	(–)-*M*-**1c**	-5.84 (449nm)
(+)-*P*-**1d**	6.41 (459nm)	(–)-*M*-**1d**	-6.59 (439nm)

(+)-*P*-**1e**	4.58 (453nm)	(–)-*M*-**1e**	-4.68 (455nm)
(+)-*P*-**3**	28.2 (455nm)	(–)-*M*-**3**	-31.2 (463nm)

Reference

1. W.-B. Lin, M. Li, L. Fang, Y. Shen and C.-F. Chen, *Chem. Asian J.* **2017**, *12*, 86-94.

6. Copies of ^{1}H NMR and ^{13}C NMR spectra of new compounds

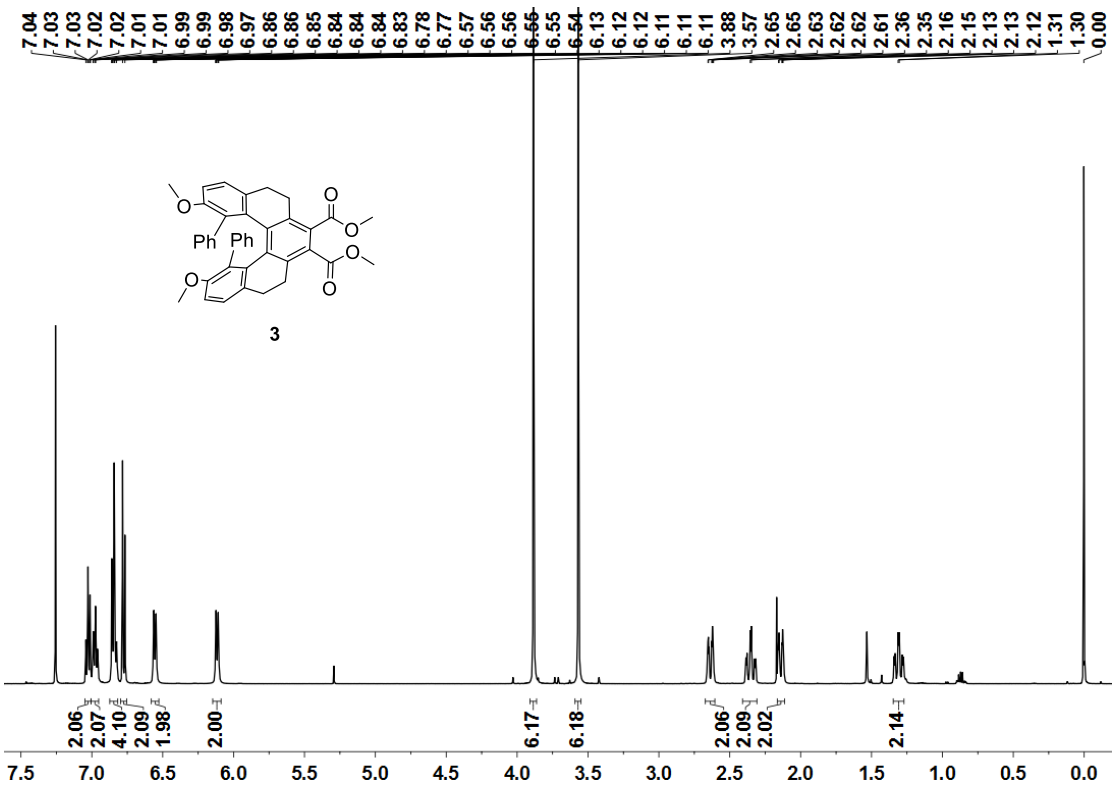


Fig. S25. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3**.

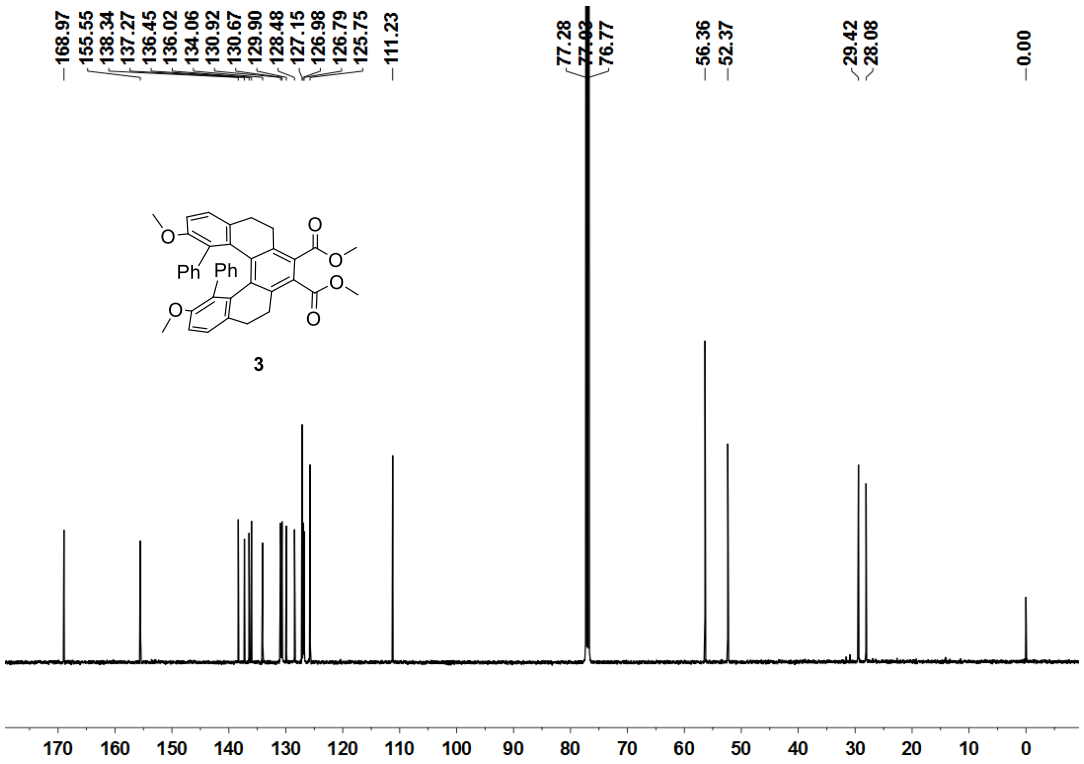


Fig. S26. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **3**.

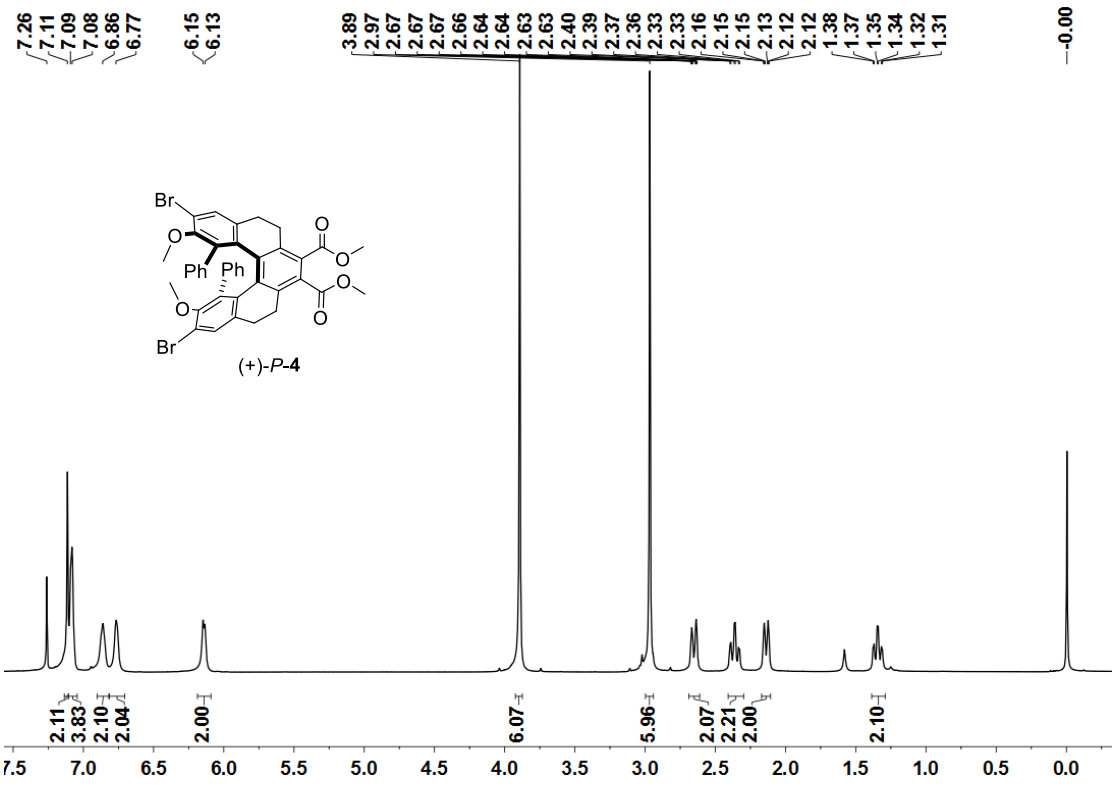


Fig. S27. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (+)-*P*-**4**.

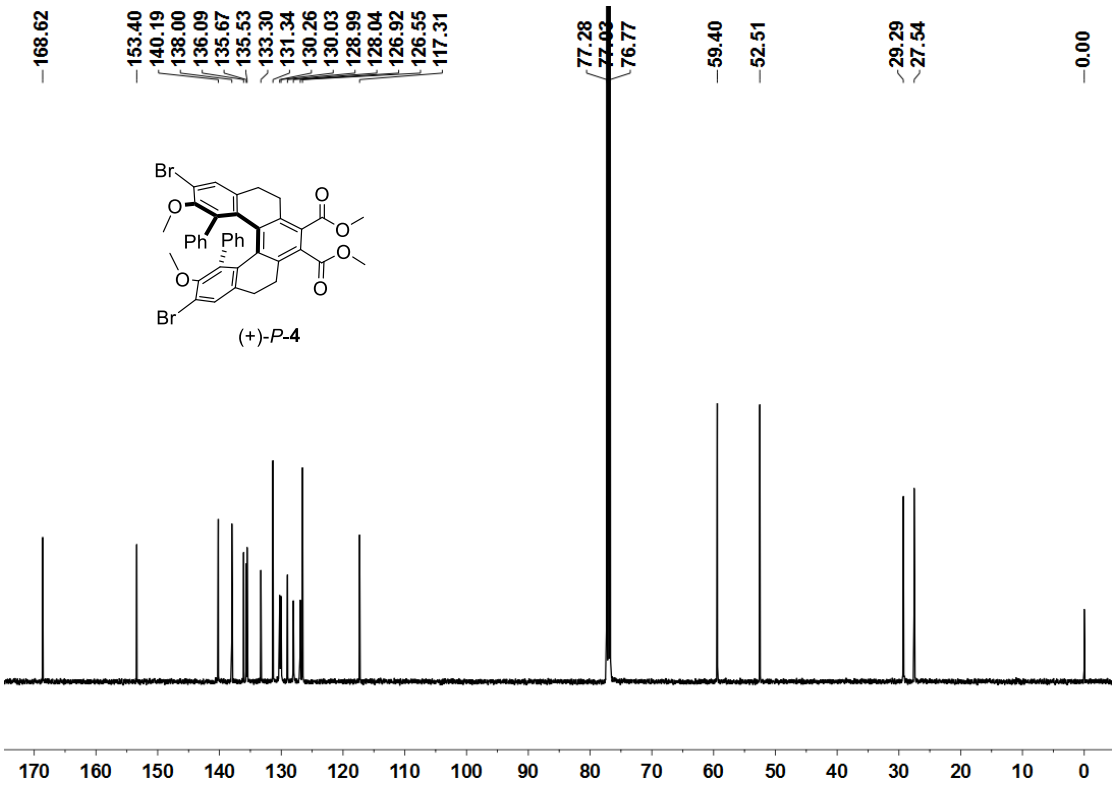


Fig. S28. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of (+)-*P*-**4**.

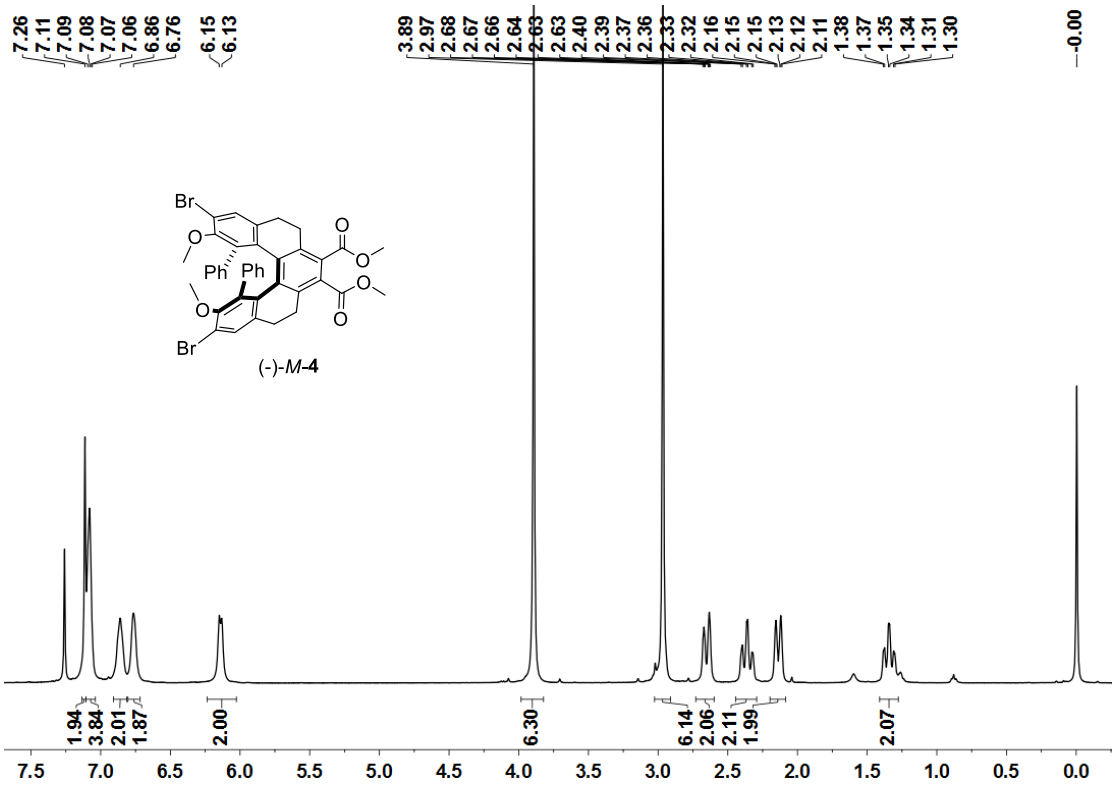


Fig. S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (–)-*M*-**4**.

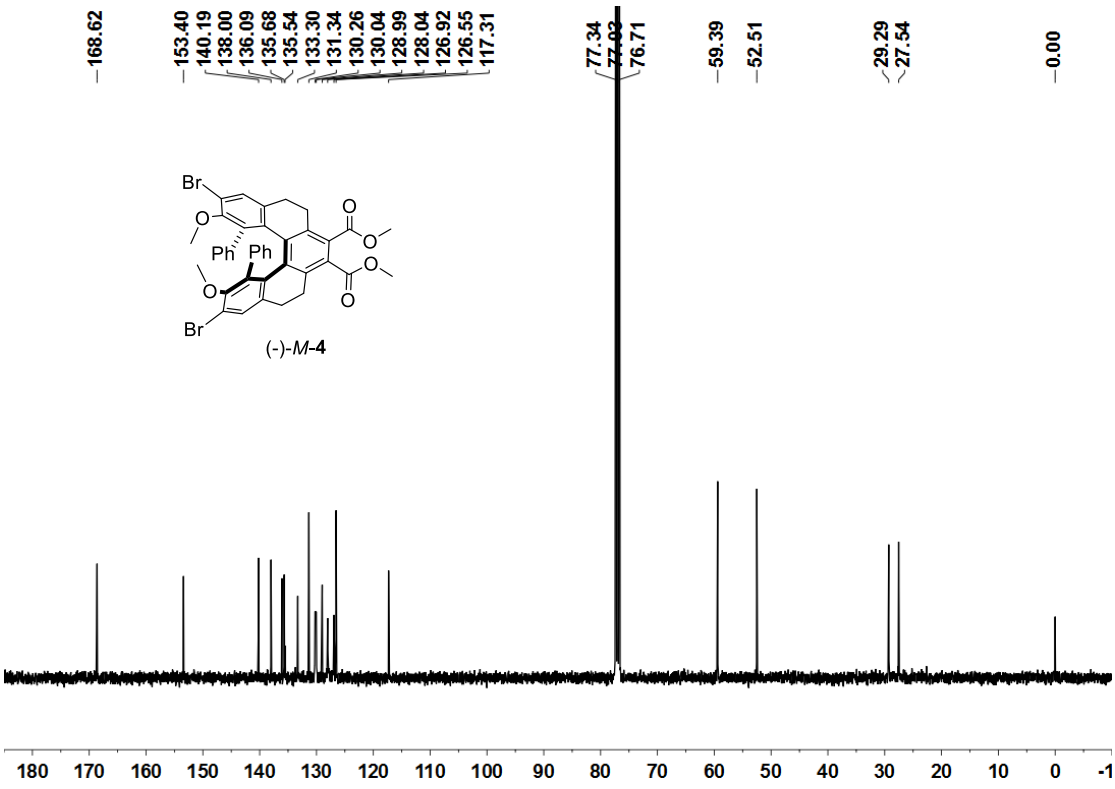


Fig. S30. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of (–)-*M*-**4**.

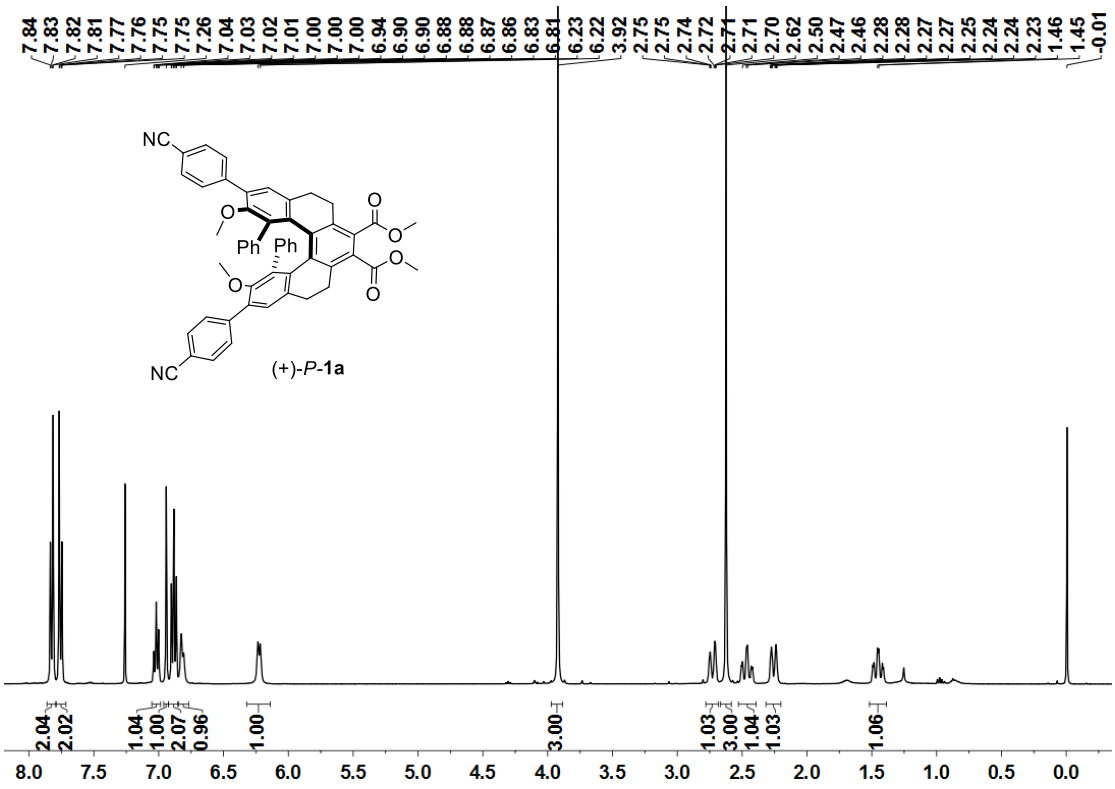


Fig. S31. ^{1}H NMR spectrum (400 MHz, CDCl3) of (+)-*P*-**1a**.

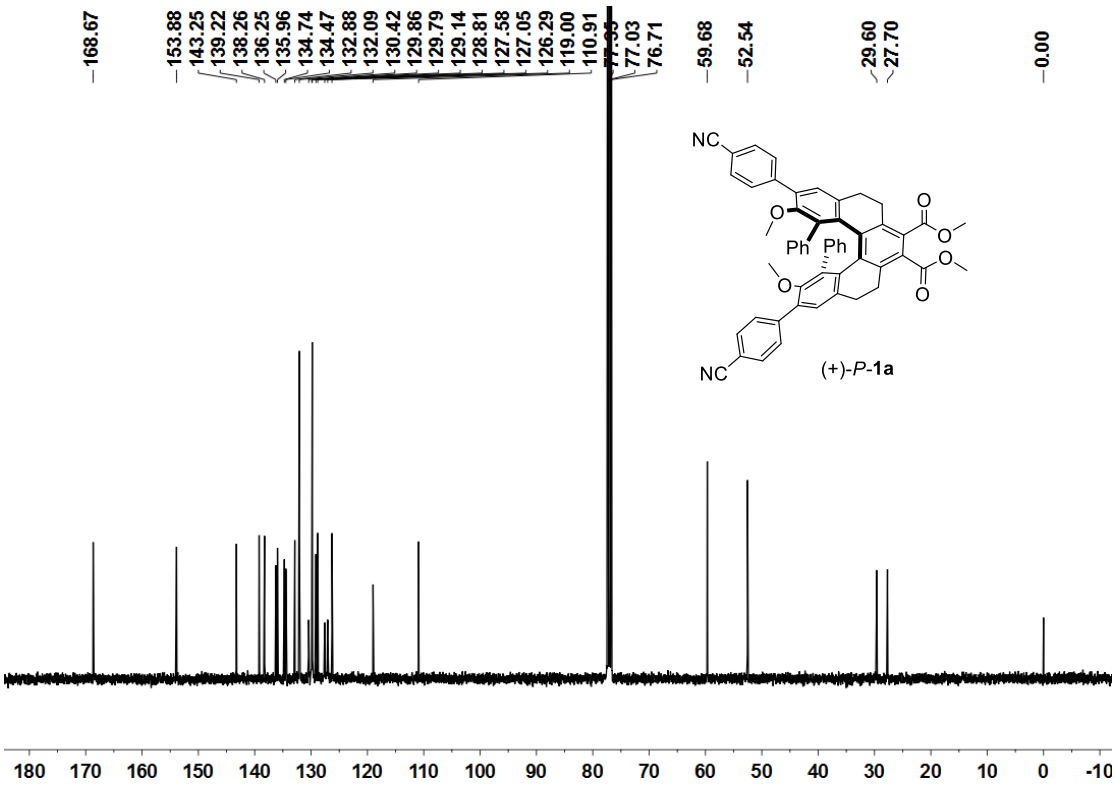


Fig. S32. ^{13}C NMR spectrum (101 MHz, CDCl3) of (+)-*P*-**1a**.

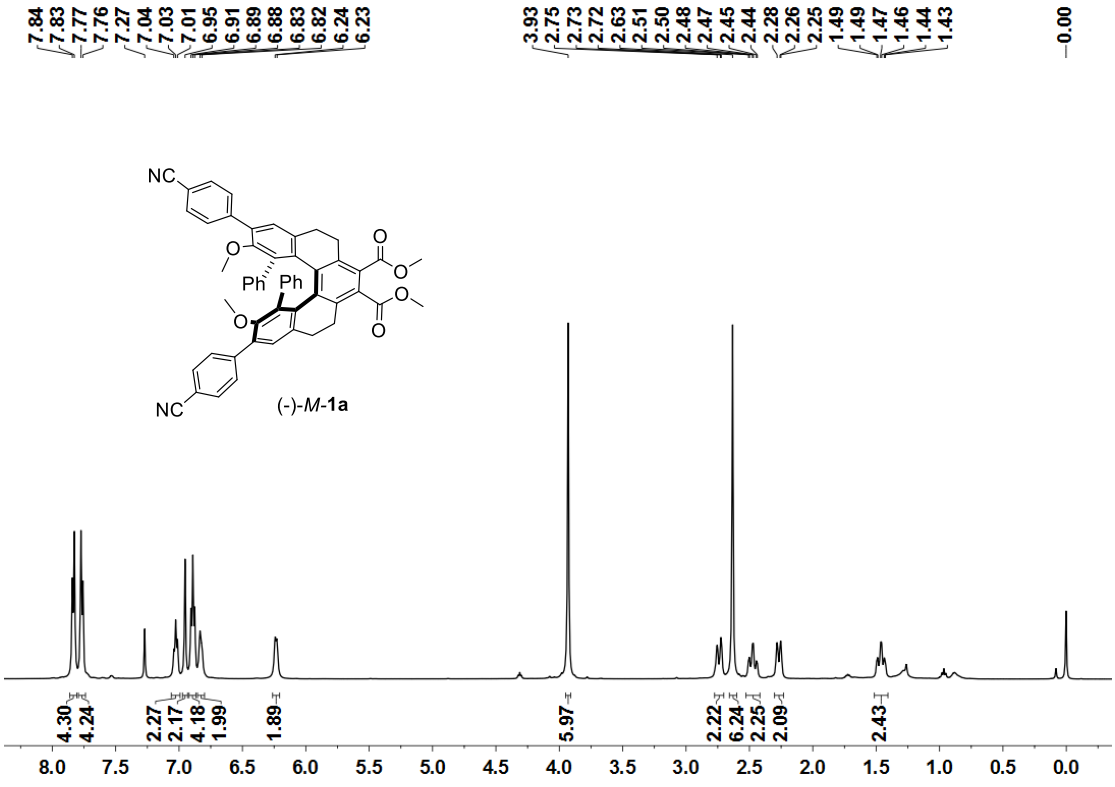


Fig. S33. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (–)-*M*-**1a**.

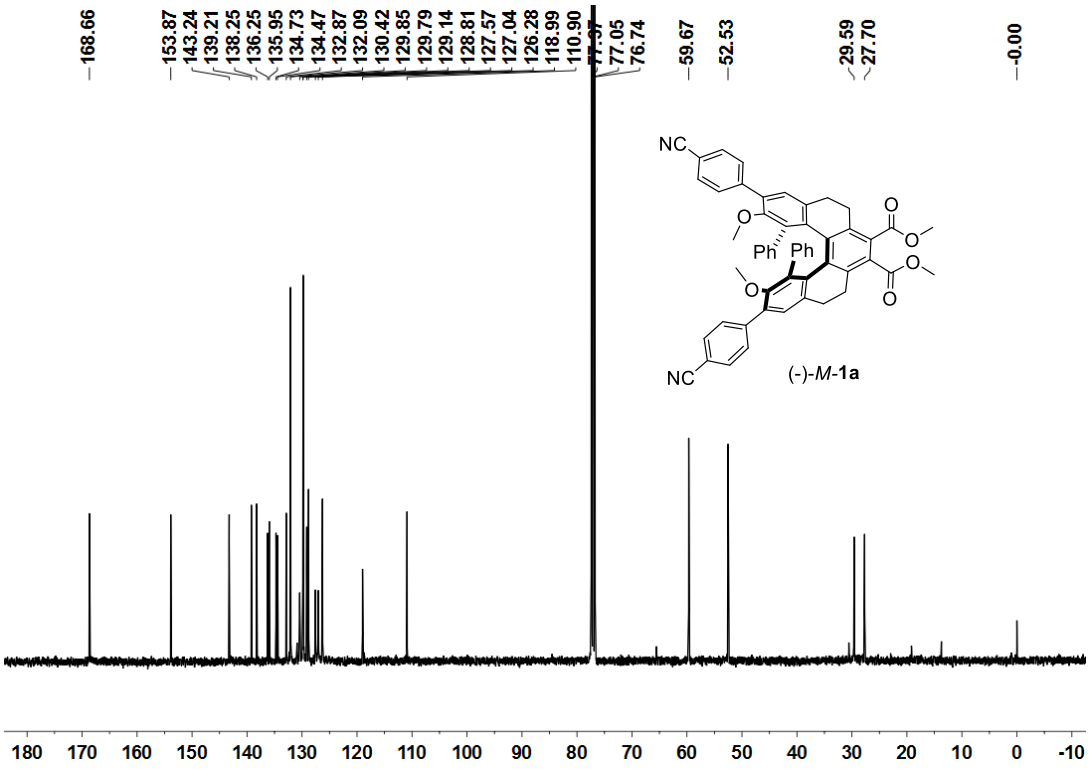


Fig. S34. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of (–)-*M*-**1a**.

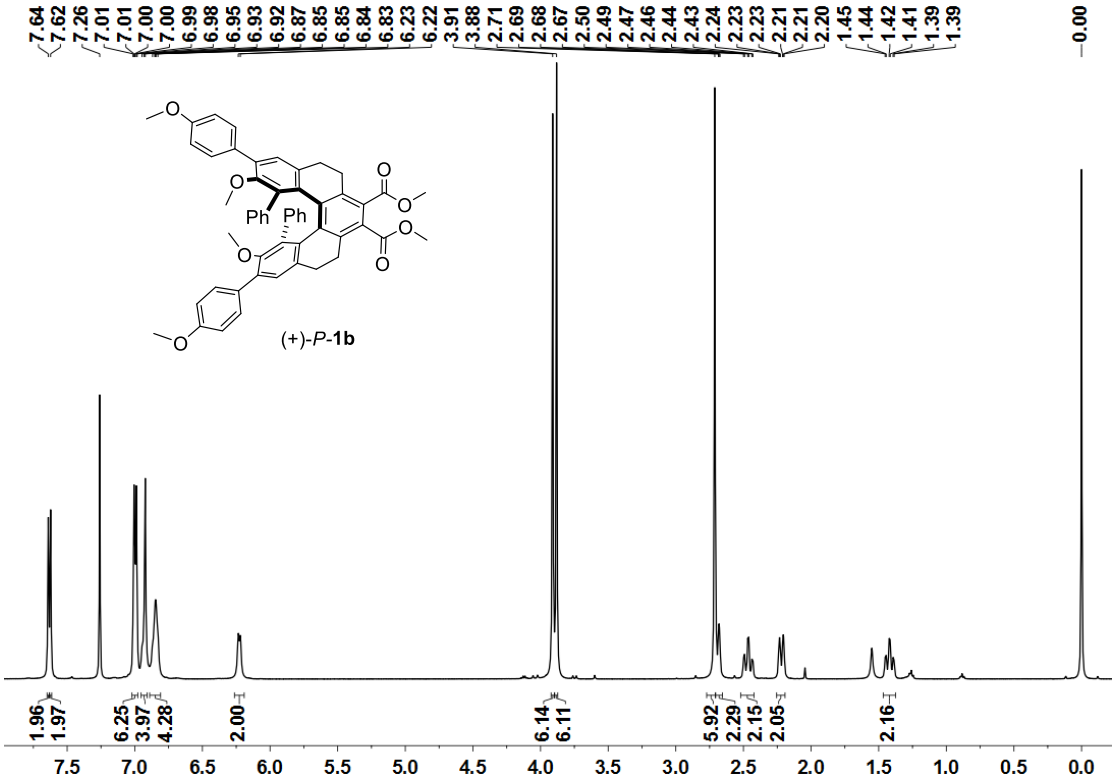


Fig. S35. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (+)-*P*-**1b**.

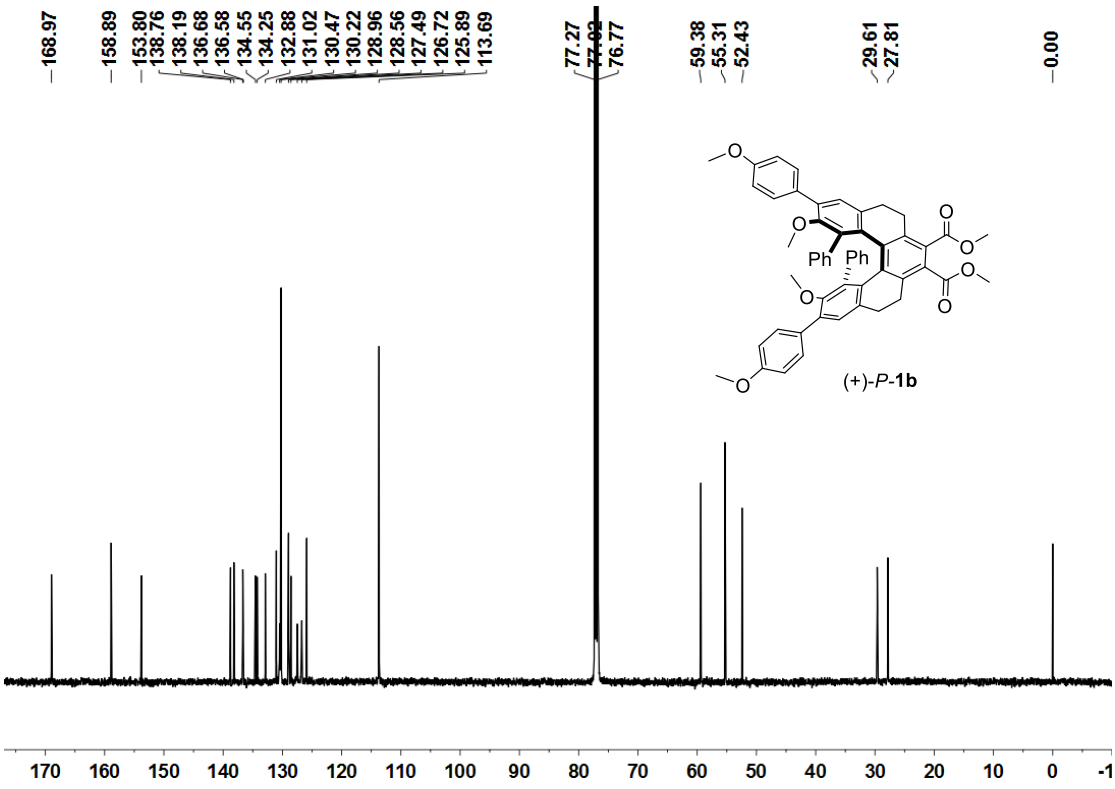


Fig. S36. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of (+)-*P*-**1b**.

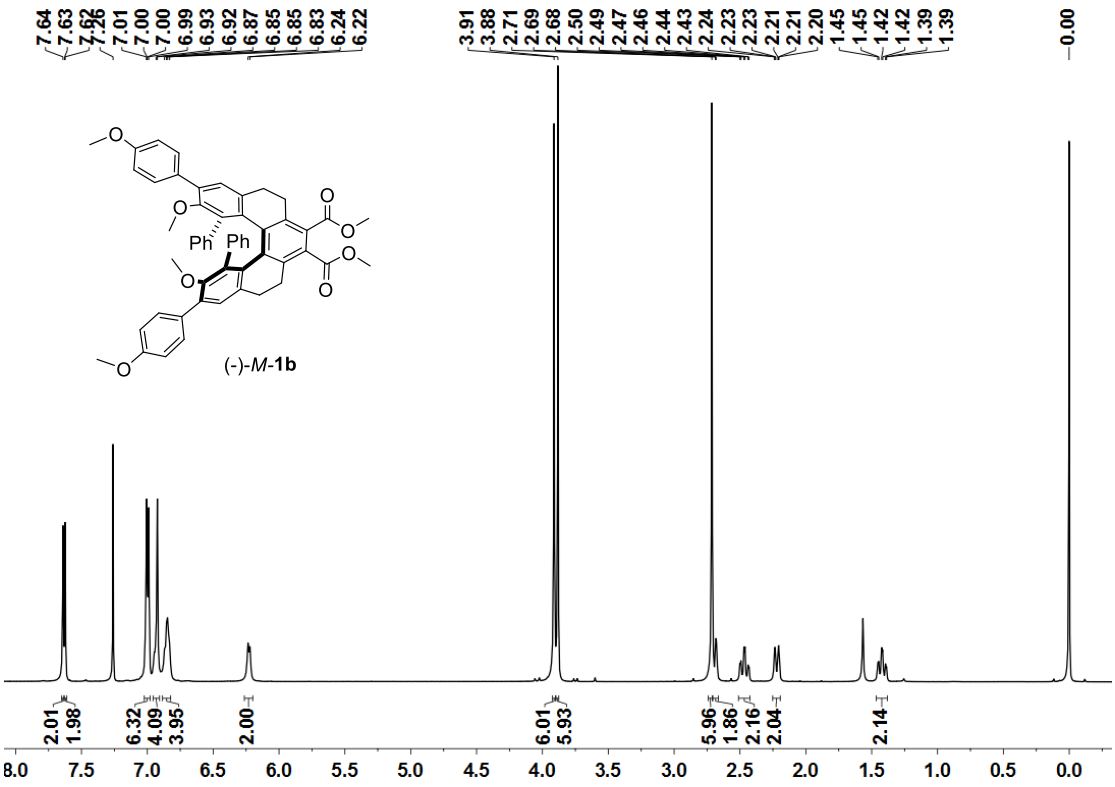


Fig. S37. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (–)-*M*-**1b**.

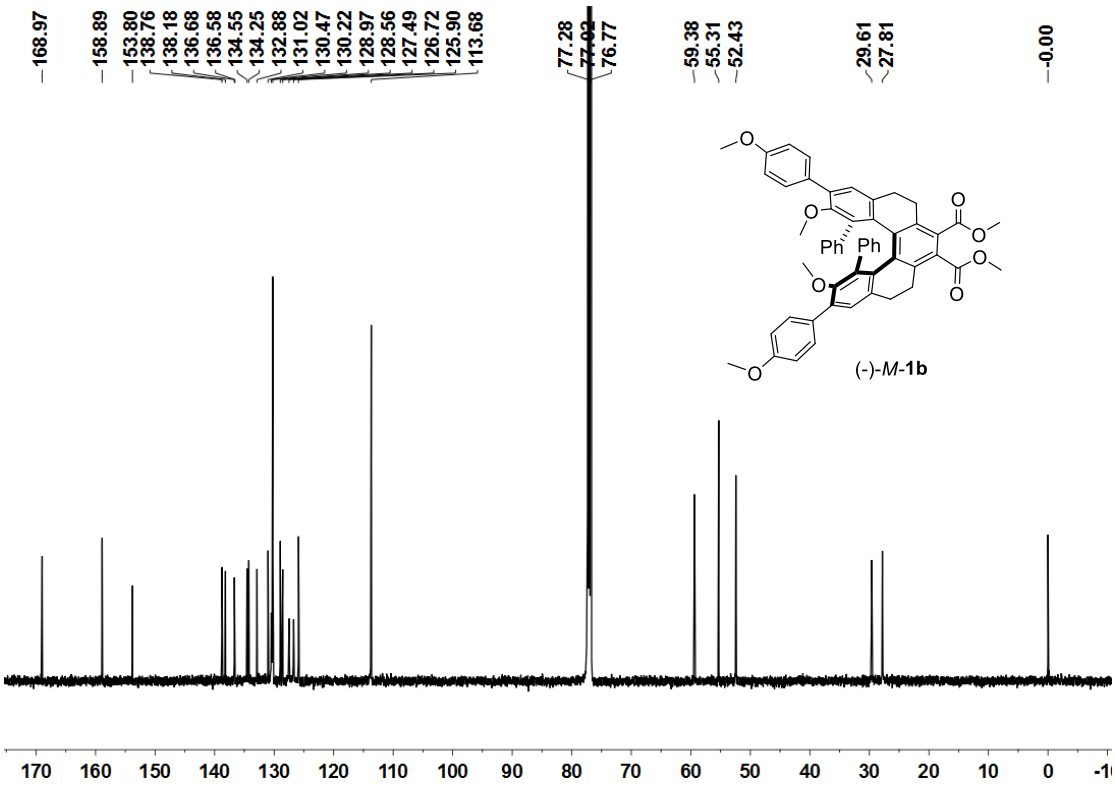


Fig. S38. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of (–)-*M*-**1b**.

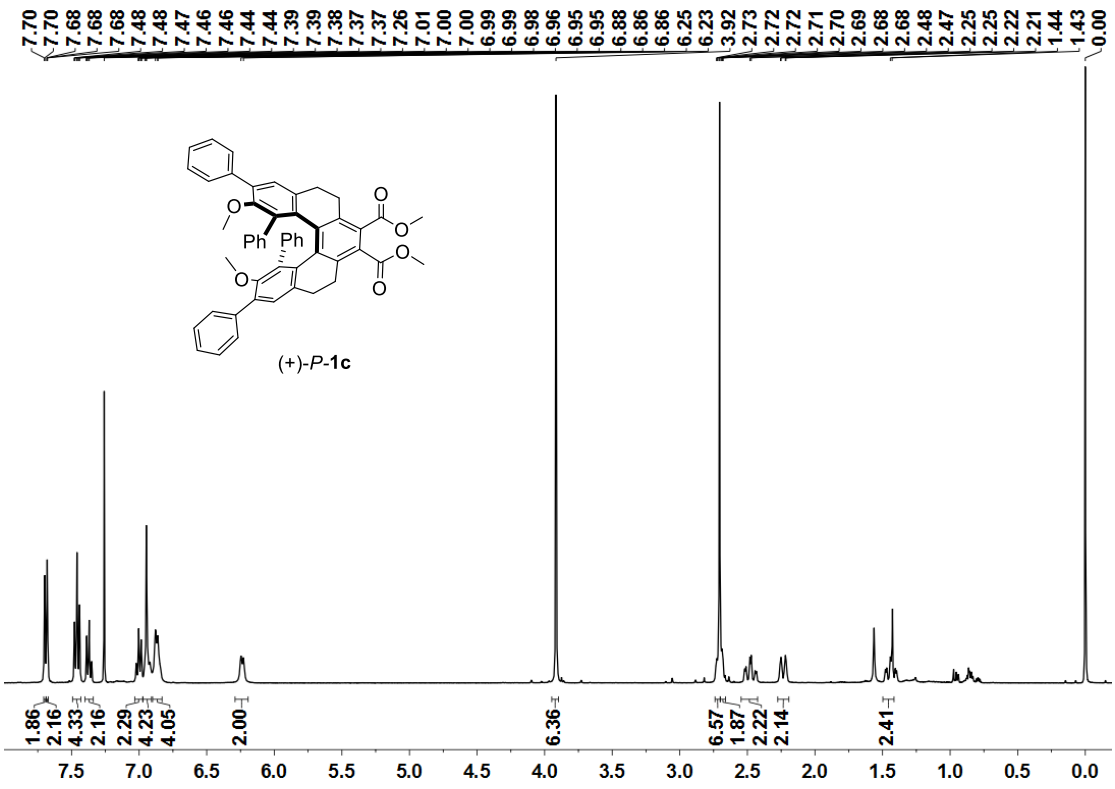


Fig. S39. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (+)-*P*-**1c**.

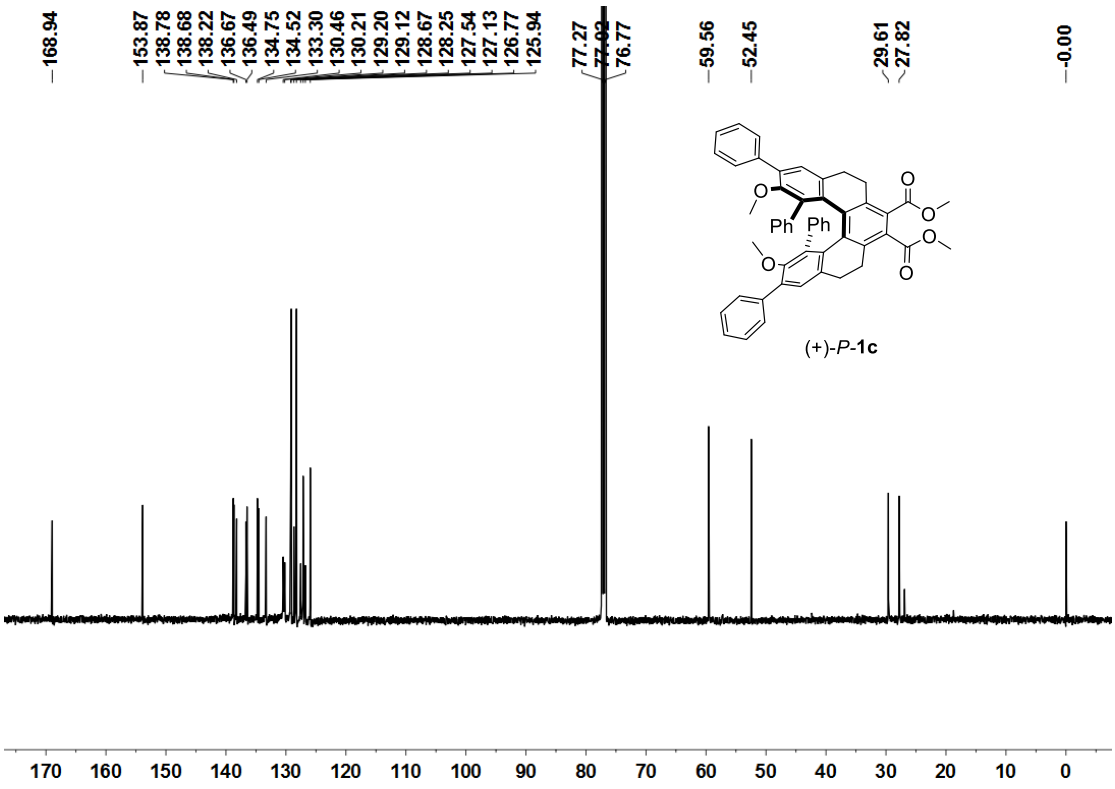


Fig. S40. ^{13}C NMR spectrum (126 MHz, CDCl3) of (+)-*P*-**1c**.

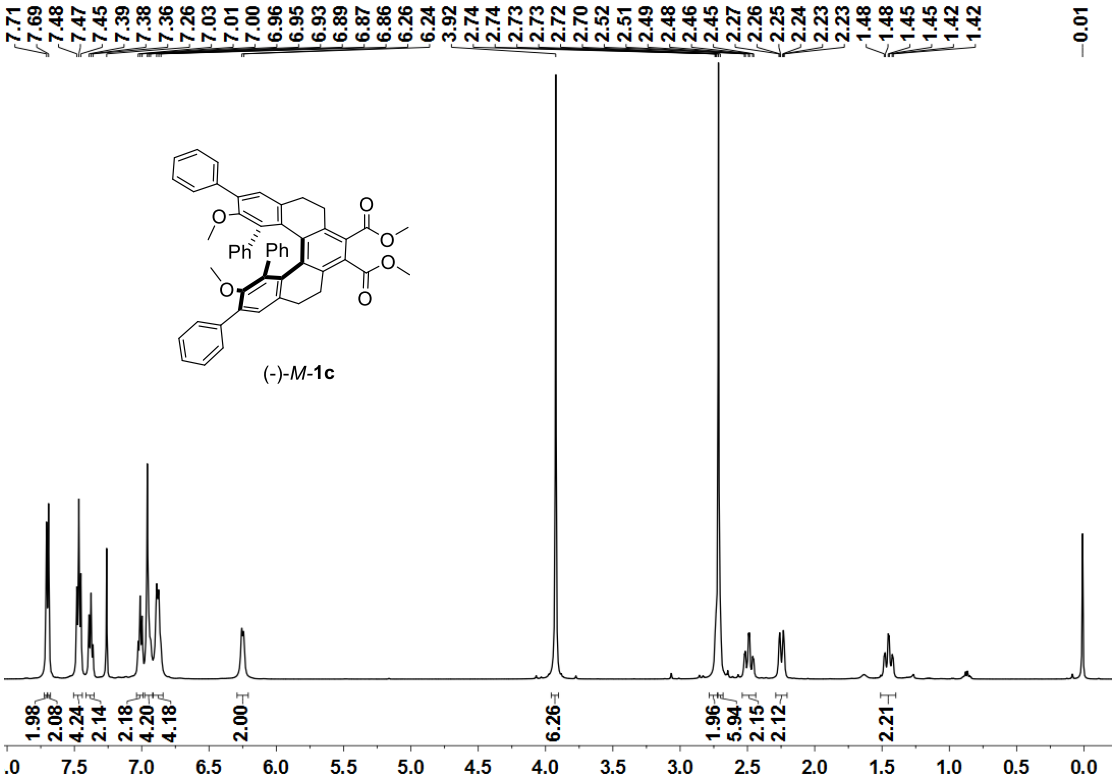


Fig. S41. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (–)-*M*-**1c**.

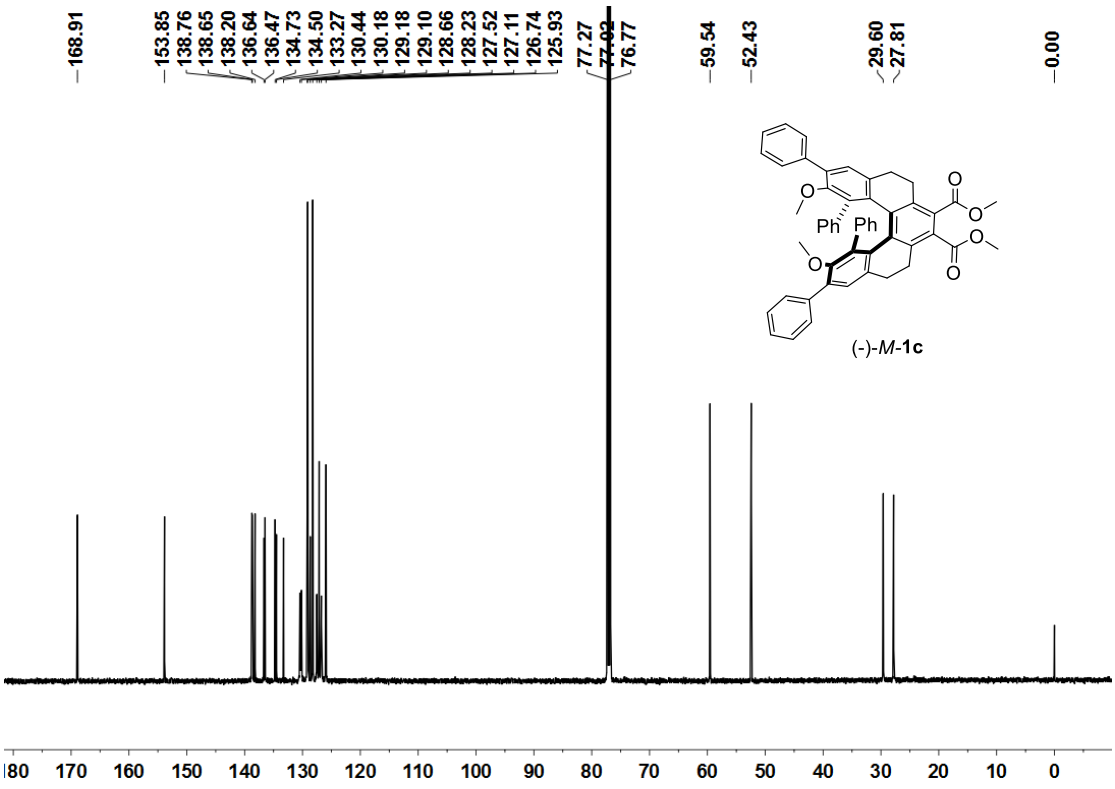


Fig. S42. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of (–)-*M*-**1c**.

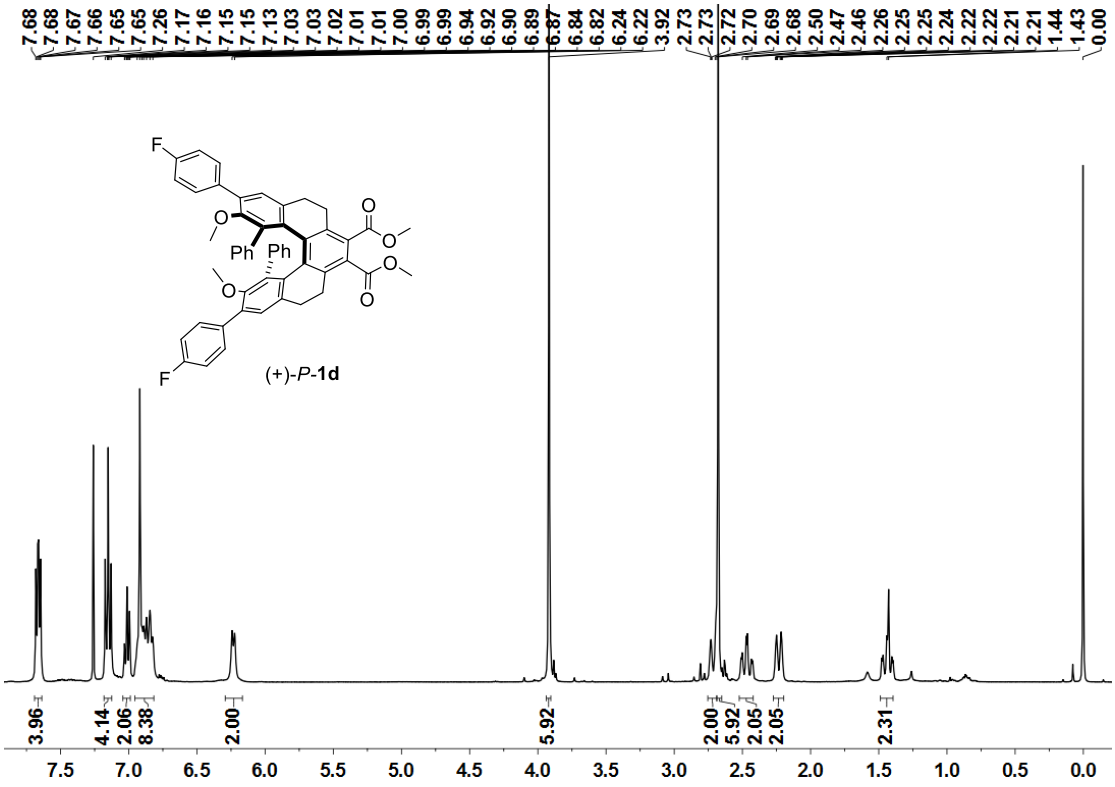


Fig. S43. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (+)-*P*-**1d**.

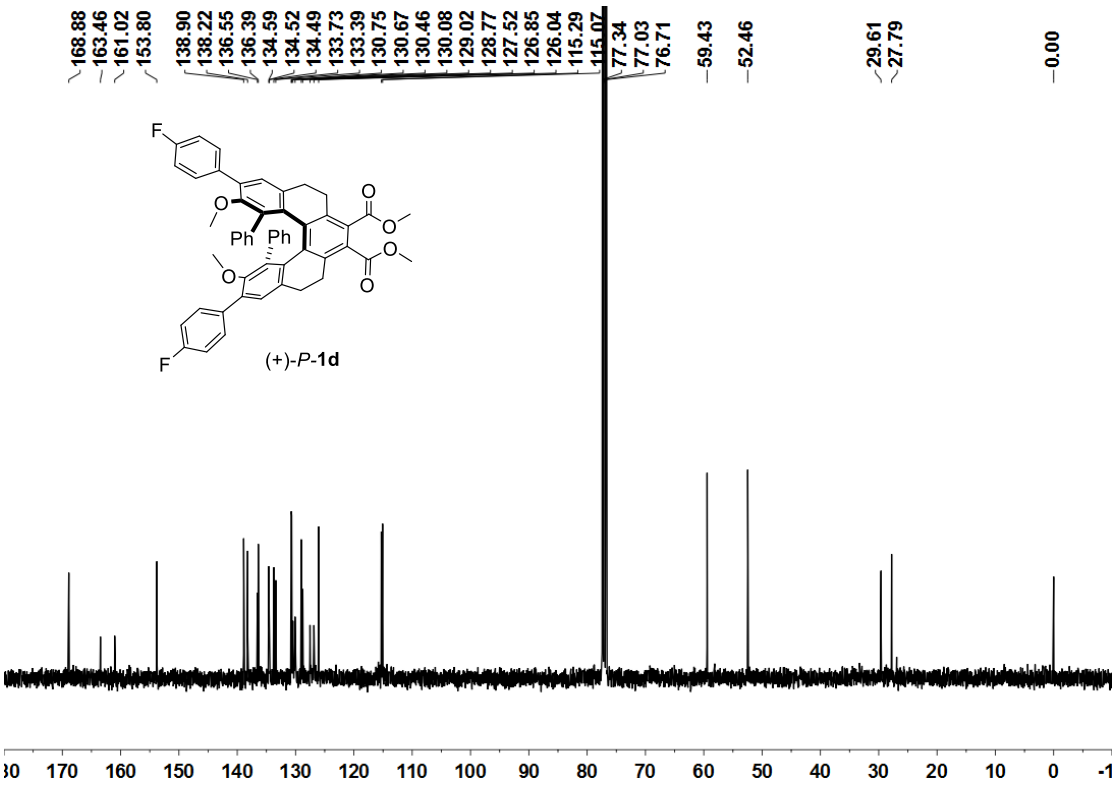


Fig. S44 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of (+)-*P*-**1d**

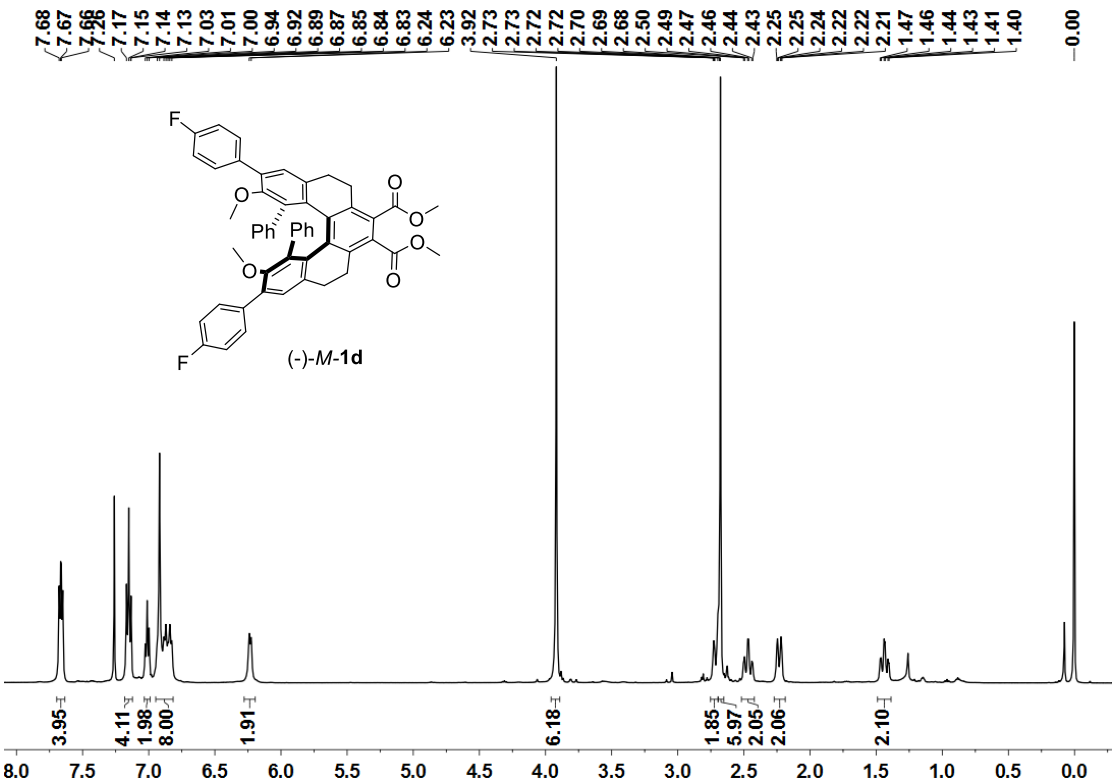


Fig. S45. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (–)-*M*-**1d**.

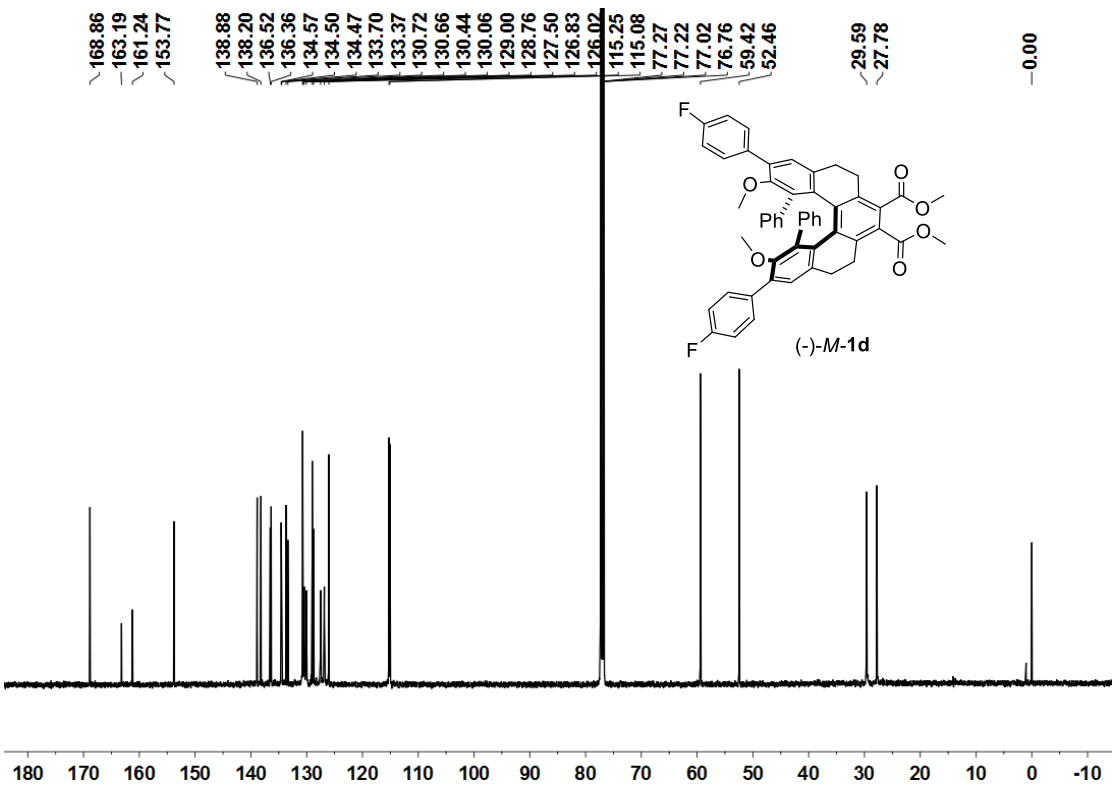


Fig. S46. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of (–)-*M*-**1d**.

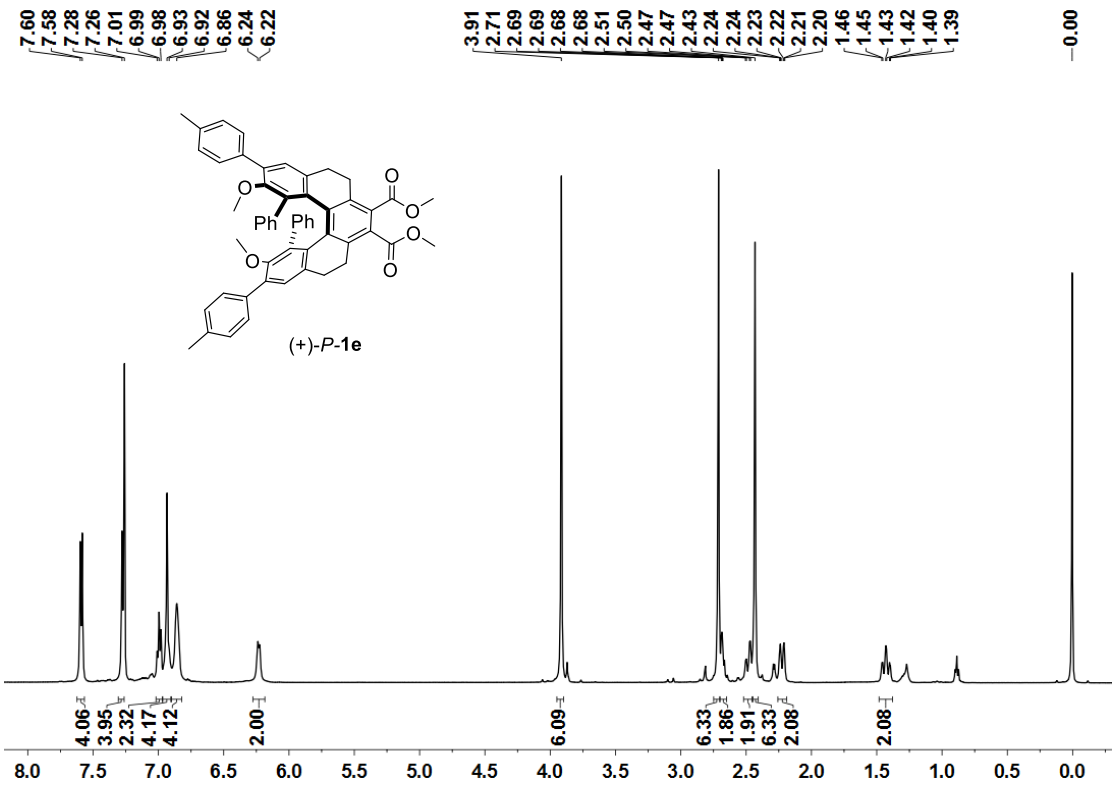


Fig. S47. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (+)-*P*-**1e**.

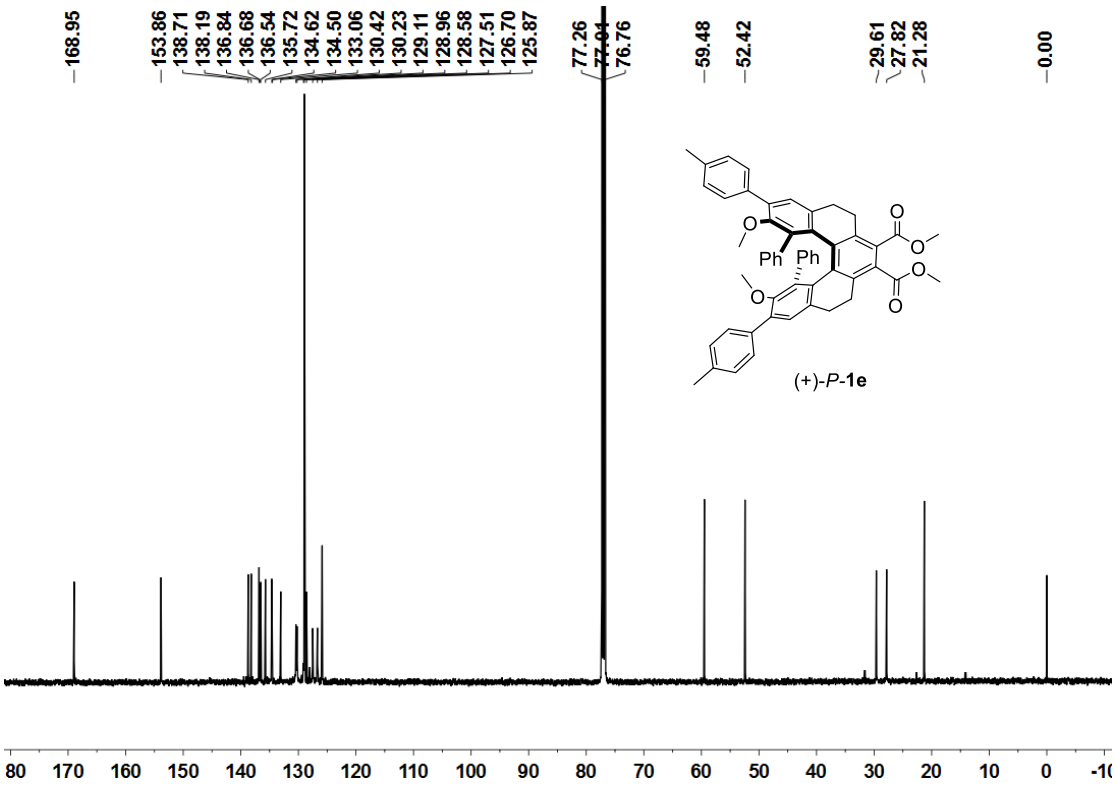


Fig. S48. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of (+)-*P*-**1e**.

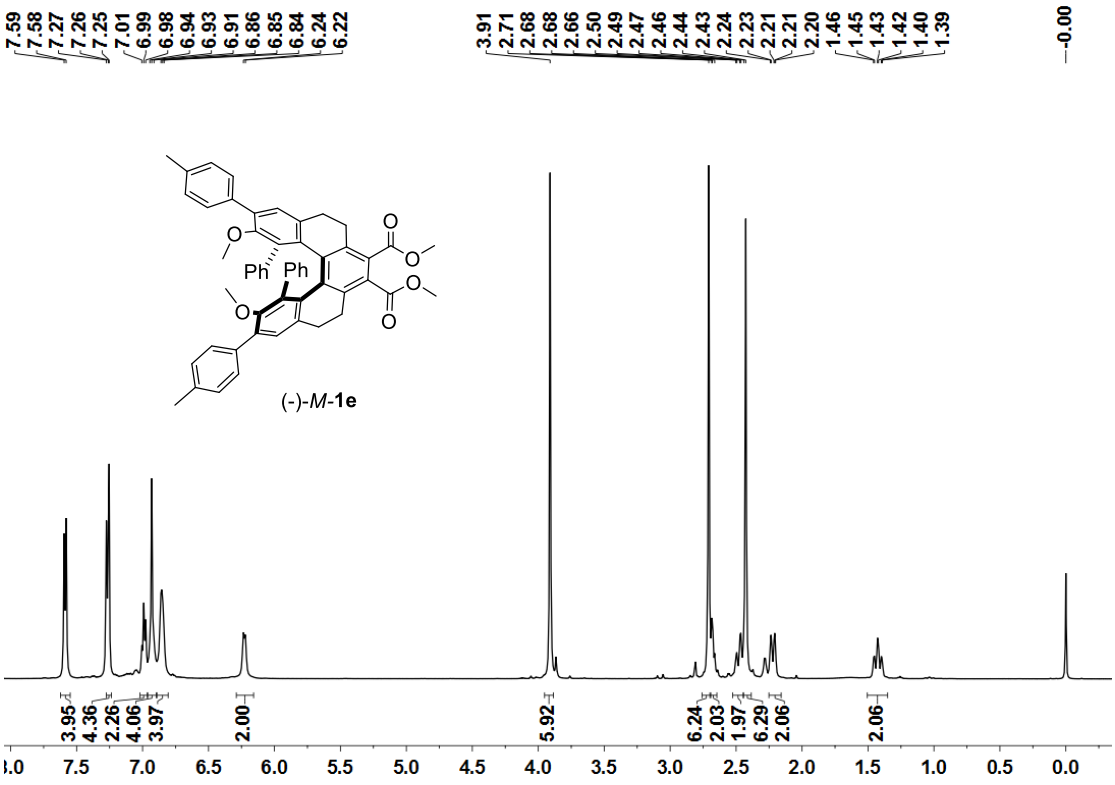


Fig. S49. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (–)-*M*-**1e**.

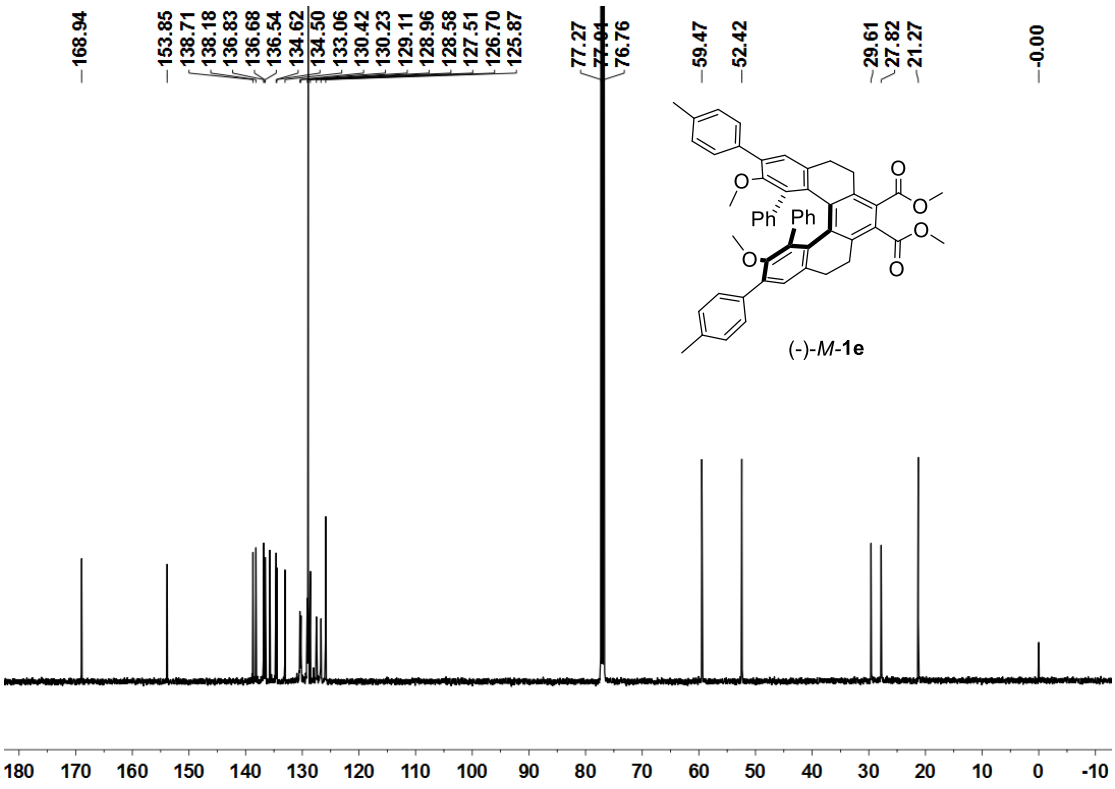


Fig. S50. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of (–)-*M*-**1e**.