

# Chiral metal organic cages decorated with binaphthalene moieties

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## 1. General Information

All the reagents and solvents were purchased from commercial sources and used as received.

**NMR:** The chemical structures of the synthesized compounds were confirmed by nuclear magnetic resonance (NMR) spectra in a Bruker Avance 500 (500 MHz) instrument using an internal deuterium lock for the residual protons in  $\text{CDCl}_3$  at ambient probe temperature.

**Mass spectra:** The precise molecular weights of the synthesized compounds were recorded through mass spectra. Fourier transform ion cyclotron resonance (FT-ICR) mass spectra were performed on SolariX 7.0T (USA). Matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectra were performed on a Bruker Speed MALDI-TOF 7090 (Bruker, Germany).

**FT-IR:** Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 FT-IR using ATR measurements for solids as neat samples.

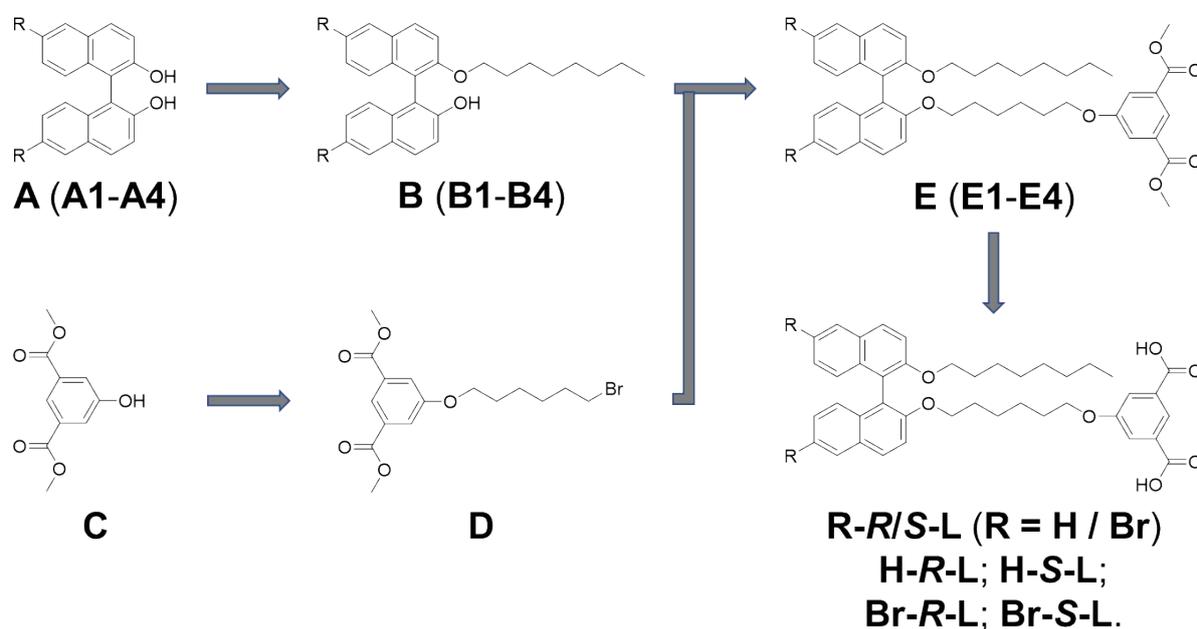
**SEC:** The molecular weights and polydispersity indexes (PDI) of the chiral ligands and related MOCs were accessed by size exclusion chromatography (SEC) on a Malver GPC using polymethymethacrylate as standard. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min at 35 °C.

**DLS:** The sizes of the chiral MOCs were recorded through dynamic light scattering (DLS) performed with a size and zeta potential analyzer (Malvern, UK).

**TGA:** Thermal gravimetric analysis (TGA) was performed using a TG 209 F1 Libra thermos gravimetric analyzer in flowing nitrogen atmosphere.

## 2. Synthetic Details of Chiral Ligands and MOCs

The chiral ligands were synthesized according to the synthetic route as shown **Scheme S1**.



**Scheme S1** The synthetic route of the chiral ligands.

Compound **B1~B4**: Compound **A** (17.46 mmol) and NaOH (838 mg, 20.95 mmol, 1.2 eq.) were dissolved in DMF (50 mL). 1-bromooctane (3.391 g, 17.46 mmol, 1eq.) dissolved in DMF (30 mL) was added dropwise to the above solution. The mixture was stirred for about 5 hours at room temperature. After removing the solvent under reduced pressure, the residue was extracted with dichloromethane and H<sub>2</sub>O (30 mL x 3). The combined organic layers were dried with MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. Afterwards, the crude product was purified by column chromatography on silica gel with PE: EtOAc (80:1, v/v) as eluent to afford compound **B1~B4**.

**B1 (R)** (yield 46%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*, ppm) δ 8.02 (d, *J* = 9.0 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 9.1 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.20 (dd, *J* = 6.4, 4.9 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 1H), 4.96 (s, 1H), 3.98 (ddt, *J* = 31.1, 9.3, 6.3 Hz, 2H), 1.45 (pd, *J* = 6.5, 2.4 Hz, 2H), 1.23 (dt, *J* = 14.7, 7.2 Hz, 2H), 1.14 – 1.07 (m, 2H), 1.07 – 0.91 (m, 6H), 0.86 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*, ppm) δ 155.69, 151.39, 134.22, 133.99, 130.94, 129.74, 129.63, 129.22, 128.24, 128.14, 127.30, 126.35, 125.16, 125.08, 124.29, 123.22, 117.56, 116.47, 115.77,

115.37, 69.88, 31.78, 29.32, 29.19, 29.15, 25.64, 22.77, 14.24. MS (ESI): Calculated for  $C_{28}H_{30}O_2$ ,  $[M+Na]^+$  421.2138, found 421.2141.

**B2 (S)** (yield 50%).  $^1H$  NMR (500 MHz, Chloroform-*d*, ppm)  $\delta$  8.02 (d,  $J = 9.0$  Hz, 1H), 7.89 (dd,  $J = 8.4, 3.2$  Hz, 2H), 7.85 (d,  $J = 6.7$  Hz, 1H), 7.46 (d,  $J = 9.1$  Hz, 1H), 7.36 (dd,  $J = 18.4, 8.5$  Hz, 2H), 7.30 (t,  $J = 7.5$  Hz, 2H), 7.21 (dd,  $J = 7.6, 5.3$  Hz, 2H), 7.05 (d,  $J = 9.6$  Hz, 1H), 4.95 (s, 1H), 4.05 – 3.92 (m, 2H), 1.44 (pd,  $J = 6.5, 2.5$  Hz, 2H), 1.23 (dt,  $J = 14.7, 6.9$  Hz, 2H), 1.10 (ddd,  $J = 13.0, 6.6, 1.9$  Hz, 2H), 1.05 – 0.93 (m, 6H), 0.85 (t,  $J = 7.3$  Hz, 3H).  $^{13}C$  NMR (126 MHz, Chloroform-*d*, ppm)  $\delta$  155.68, 151.40, 134.22, 133.98, 130.91, 129.73, 129.61, 129.21, 128.23, 128.13, 127.29, 126.34, 125.16, 125.07, 124.27, 123.21, 117.57, 116.48, 115.75, 115.35, 69.86, 31.78, 29.31, 29.18, 29.14, 25.63, 22.77, 14.24. MS (ESI): Calculated for  $C_{28}H_{30}O_2$ ,  $[M+Na]^+$  421.2138, found 421.2131.

**B3 (R)** (yield 43%).  $^1H$  NMR (500 MHz, Chloroform-*d*, ppm)  $\delta$  8.05 (d,  $J = 2.0$  Hz, 1H), 8.00 (d,  $J = 2.0$  Hz, 1H), 7.93 (d,  $J = 9.1$  Hz, 1H), 7.79 (d,  $J = 8.9$  Hz, 1H), 7.46 (d,  $J = 9.1$  Hz, 1H), 7.36 – 7.34 (m, 1H), 7.34 – 7.32 (m, 1H), 7.27 (d,  $J = 2.1$  Hz, 1H), 7.01 (d,  $J = 9.0$  Hz, 1H), 6.86 (d,  $J = 9.0$  Hz, 1H), 4.94 (s, 1H), 3.99 (ddt,  $J = 35.6, 9.3, 6.3$  Hz, 2H), 1.23 (ddd,  $J = 12.2, 7.4, 4.0$  Hz, 6H), 1.13 – 1.06 (m, 2H), 1.02 (t,  $J = 5.6$  Hz, 4H), 0.86 (t,  $J = 7.3$  Hz, 3H).  $^{13}C$  NMR (126 MHz, Chloroform-*d*, ppm)  $\delta$  155.82, 151.81, 132.60, 132.38, 130.68, 130.54, 130.33, 130.23, 130.17, 130.13, 129.71, 129.02, 126.76, 126.71, 118.83, 118.13, 117.09, 116.39, 116.04, 115.07, 69.73, 31.78, 29.21, 29.20, 29.11, 25.66, 22.75, 14.31. MS (ESI): Calculated for  $C_{28}H_{28}Br_2O_2$ ,  $[M+Na]^+$  577.0348, found 577.0354.

**B4 (S)** (yield 41%).  $^1H$  NMR (500 MHz, Chloroform-*d*, ppm)  $\delta$  8.04 (d,  $J = 2.0$  Hz, 1H), 8.00 (d,  $J = 2.1$  Hz, 1H), 7.92 (d,  $J = 9.1$  Hz, 1H), 7.79 (d,  $J = 8.9$  Hz, 1H), 7.46 (d,  $J = 9.2$  Hz, 1H), 7.36 – 7.34 (m, 1H), 7.34 – 7.32 (m, 1H), 7.28 – 7.25 (m, 1H), 7.02 (d,  $J = 9.0$  Hz, 1H), 6.87 (d,  $J = 9.0$  Hz, 1H), 4.94 (s, 1H), 4.07 – 3.91 (m, 2H), 1.45 (ddt,  $J = 13.3, 6.8, 5.2$  Hz, 2H), 1.27 – 1.19 (m, 2H), 1.12 – 0.96 (m, 6H), 0.86 (t,  $J = 7.3$  Hz, 3H).  $^{13}C$  NMR (126 MHz, Chloroform-*d*)  $\delta$  155.84, 151.78, 132.60, 132.37, 130.72, 130.55, 130.36, 130.25, 130.23, 130.15, 129.73, 129.05, 126.76, 126.72, 118.82, 118.17, 117.13, 116.39, 115.95, 115.07, 69.74, 31.79, 29.22, 29.12, 25.68, 22.77, 14.24. MS (ESI): Calculated for  $C_{28}H_{28}Br_2O_2$ ,  $[M+Na]^+$  577.0348, found 577.0340.

Compound **D**: Compound **C** (5.00 g, 23.79 mmol, 1 eq.) dissolved in CH<sub>3</sub>CN (150 mL) and DMF (10 mL) was added 1,6-dibromohexane (11.61 g, 47.58 mmol, 2 eq.) and K<sub>2</sub>CO<sub>3</sub> (3.29 g, 23.79 mmol, 1.2 eq.). The mixture was refluxed for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was extracted with dichloromethane and H<sub>2</sub>O (30 mL x 3). The combined organic layers were dried with MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. Afterwards, the crude product was purified by column chromatography on silica gel with PE: EtOAc (50:1, v/v) as eluent to afford compound **C** (yield 72%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*, ppm) δ 8.26 (s, 1H), 7.74 (s, 2H), 4.04 (t, *J* = 6.4 Hz, 2H), 3.94 (d, *J* = 1.6 Hz, 6H), 3.43 (td, *J* = 6.8, 1.5 Hz, 2H), 1.90 (t, *J* = 7.0 Hz, 2H), 1.83 (t, *J* = 6.7 Hz, 2H), 1.58 (d, *J* = 1.6 Hz, 2H), 1.52 (s, 2H).

Compound **E1~E4**: Compound **B** (2.51 mmol, 1.2 eq.) and Compound **D** (2.09 mmol, 1 eq.) and Cs<sub>2</sub>CO<sub>3</sub> (818 mg, 2.51 mmol, 1.2 eq.) were dissolved in DMF (30 mL). The mixture was stirred for about 5 h at room temperature. The solvent was removed under reduced pressure and the residue partitioned was extracted with dichloromethane and H<sub>2</sub>O (30 mL x 3). The combined organic layers were dried with MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. Afterwards, the crude product was purified by column chromatography on silica gel with PE: EtOAc (50:1, v/v) as eluent to afford compound **E1~E4**.

**E1 (R)** (yield 83%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*, ppm) δ 8.28 (s, 1H), 7.91 (dd, *J* = 10.5, 9.0 Hz, 2H), 7.83 (dd, *J* = 12.8, 8.2 Hz, 2H), 7.72 (d, *J* = 1.5 Hz, 2H), 7.40 (dd, *J* = 9.0, 2.9 Hz, 2H), 7.30 (dd, *J* = 12.7, 6.3 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.03 – 3.96 (m, 2H), 3.95 (s, 6H), 3.93 – 3.86 (m, 2H), 3.79 (t, *J* = 6.6 Hz, 2H), 1.42 (dq, *J* = 40.8, 6.7, 6.1 Hz, 6H), 1.23 – 1.18 (m, 2H), 1.09 (dt, *J* = 15.4, 7.7 Hz, 4H), 1.02 – 0.95 (m, 4H), 0.90 (q, *J* = 8.8 Hz, 4H), 0.85 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*, ppm) δ 166.22, 159.28, 154.64, 154.53, 134.30, 134.26, 131.75, 129.39, 129.31, 129.14, 129.08, 127.84, 126.08, 125.55, 123.50, 123.46, 122.78, 120.87, 120.78, 119.85, 115.93, 69.80, 69.71, 68.36, 52.40, 31.73, 29.45, 29.34, 29.16, 29.14, 28.88, 25.66, 25.48, 25.34, 22.70, 14.16. MS (ESI): Calculated for C<sub>44</sub>H<sub>50</sub>O<sub>7</sub>, [M+Na]<sup>+</sup> 713.3449, found 713.3455.

**E2 (S)** (yield 87%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*, ppm) δ 8.28 (s, 1H), 7.95 – 7.88 (m, 2H), 7.84 (dd, *J* = 12.0, 7.6 Hz, 2H), 7.72 (d, *J* = 1.5 Hz, 2H), 7.41 (dd, *J* = 9.0, 2.7 Hz, 2H),

7.33 – 7.26 (m, 2H), 7.22 – 7.18 (m, 2H), 7.16 (d,  $J = 8.4$  Hz, 2H), 4.03 – 3.97 (m, 2H), 3.95 (s, 6H), 3.92 – 3.86 (m, 2H), 3.80 (t,  $J = 6.6$  Hz, 2H), 1.51 – 1.34 (m, 6H), 1.25 – 1.18 (m, 2H), 1.09 (q,  $J = 7.6$  Hz, 4H), 1.03 – 0.94 (m, 4H), 0.94 – 0.87 (m, 4H), 0.85 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*, ppm)  $\delta$  166.22, 159.27, 154.63, 154.53, 134.30, 134.26, 131.75, 129.38, 129.31, 129.14, 129.08, 127.84, 126.08, 125.55, 123.50, 123.46, 122.78, 120.86, 120.77, 119.84, 115.92, 69.79, 69.71, 68.36, 52.40, 31.74, 29.45, 29.34, 29.16, 29.14, 28.88, 25.66, 25.48, 25.34, 22.70, 14.16. MS (ESI): Calculated for  $\text{C}_{44}\text{H}_{50}\text{O}_7$ ,  $[\text{M}+\text{Na}]^+$  713.3449, found 713.3445.

**E3 (R)** (yield 83%).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*, ppm)  $\delta$  8.28 (s, 1H), 8.00 (d,  $J = 2.1$  Hz, 1H), 7.97 (d,  $J = 2.0$  Hz, 1H), 7.82 (t,  $J = 9.3$  Hz, 2H), 7.72 (d,  $J = 1.5$  Hz, 2H), 7.41 (d,  $J = 2.6$  Hz, 1H), 7.39 (d,  $J = 2.6$  Hz, 1H), 7.27 (d,  $J = 2.0$  Hz, 1H), 7.25 (d,  $J = 2.1$  Hz, 1H), 6.99 (d,  $J = 9.0$  Hz, 2H), 4.02 – 3.96 (m, 2H), 3.94 (s, 6H), 3.90 (d,  $J = 6.7$  Hz, 2H), 3.85 (t,  $J = 6.5$  Hz, 2H), 1.55 – 1.34 (m, 6H), 1.31 – 1.18 (m, 4H), 1.16 (d,  $J = 8.0$  Hz, 2H), 1.09 (t,  $J = 7.4$  Hz, 2H), 0.96 (ddd,  $J = 33.6, 16.0, 9.8$  Hz, 6H), 0.86 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*, ppm)  $\delta$  166.33, 159.32, 154.92, 154.82, 132.71, 132.67, 131.84, 130.38, 130.31, 129.90, 129.87, 129.60, 129.57, 128.57, 128.52, 127.26, 127.25, 122.89, 120.24, 120.17, 119.94, 117.43, 117.36, 116.58, 116.54, 69.68, 69.54, 68.40, 52.50, 31.82, 29.41, 29.32, 29.25, 29.18, 29.00, 25.77, 25.57, 25.46, 22.76, 14.22. MS (ESI): Calculated for  $\text{C}_{44}\text{H}_{48}\text{Br}_2\text{O}_7$ ,  $[\text{M}+\text{Na}]^+$  869.1659, found 869.1684.

**E4 (S)** (yield 82%).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*, ppm)  $\delta$  8.27 (s, 1H), 8.00 (d,  $J = 2.0$  Hz, 1H), 7.97 (d,  $J = 2.1$  Hz, 1H), 7.86 – 7.80 (m, 2H), 7.72 (d,  $J = 1.5$  Hz, 2H), 7.40 (dd,  $J = 9.0, 3.4$  Hz, 2H), 7.27 (d,  $J = 2.1$  Hz, 1H), 7.25 (d,  $J = 2.1$  Hz, 1H), 6.98 (d,  $J = 9.0$  Hz, 2H), 4.02 – 3.96 (m, 2H), 3.95 (s, 6H), 3.92 – 3.87 (m, 2H), 3.84 (t,  $J = 6.5$  Hz, 2H), 1.51 – 1.36 (m, 6H), 1.28 – 1.18 (m, 4H), 1.14 (d,  $J = 7.7$  Hz, 2H), 1.08 (d,  $J = 7.8$  Hz, 2H), 1.02 – 0.90 (m, 6H), 0.85 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*, ppm)  $\delta$  166.21, 159.25, 154.85, 154.75, 132.64, 132.60, 131.77, 130.30, 130.24, 129.83, 129.81, 129.52, 129.50, 128.51, 128.47, 127.20, 127.19, 122.82, 120.13, 120.06, 119.86, 117.36, 117.29, 116.47, 116.43, 69.56, 69.43, 68.32, 52.41, 31.75, 29.35, 29.25, 29.19, 29.12, 28.94, 25.71, 25.51, 25.40, 22.70, 14.18. MS (ESI): Calculated for  $\text{C}_{44}\text{H}_{48}\text{Br}_2\text{O}_7$ ,  $[\text{M}+\text{Na}]^+$  869.1659, found

869.1657.

Compound **R-R/S-L**: Compound **E** (0.76 mmol) dissolved in THF (20 ml) was added NaOH aqueous solution (1 M, 20 mL). Then the mixture was refluxed at 70 °C for 3 h. The solution was cooled to room temperature, added hydrochloric acid to adjust the pH to 1. The solvent was removed under reduced pressure and the residue partitioned was extracted with ethyl acetate and H<sub>2</sub>O (30 mL × 3). Then the combined organic layers were dried with MgSO<sub>4</sub>, filtered, and concentrated under pressure to afford chiral ligands **R-R/S-L**.

**H-R-L** (yield 88%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*, ppm) δ 8.37 (s, 1H), 7.91 (d, *J* = 9.0 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.65 (s, 2H), 7.39 (d, *J* = 9.4 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.17 (p, *J* = 8.2 Hz, 4H), 3.95 (dd, *J* = 17.2, 8.6 Hz, 2H), 3.91 – 3.84 (m, 2H), 3.70 (s, 2H), 1.52 – 1.28 (m, 8H), 1.20 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.5 Hz, 4H), 0.96 (s, 2H), 0.89 (dt, *J* = 14.6, 7.8 Hz, 4H), 0.84 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*, ppm) δ 171.59, 154.75, 154.64, 134.40, 134.37, 130.83, 129.49, 129.43, 129.26, 129.21, 127.98, 127.94, 126.19, 125.67, 123.61, 120.94, 120.89, 120.45, 116.05, 116.01, 69.93, 69.87, 68.35, 31.82, 29.56, 29.45, 29.24, 29.09, 25.76, 25.43, 22.79, 14.25. MS (ESI): Calculated for C<sub>42</sub>H<sub>46</sub>O<sub>7</sub>, [M+Na]<sup>+</sup> 685.3136, found 685.3134.

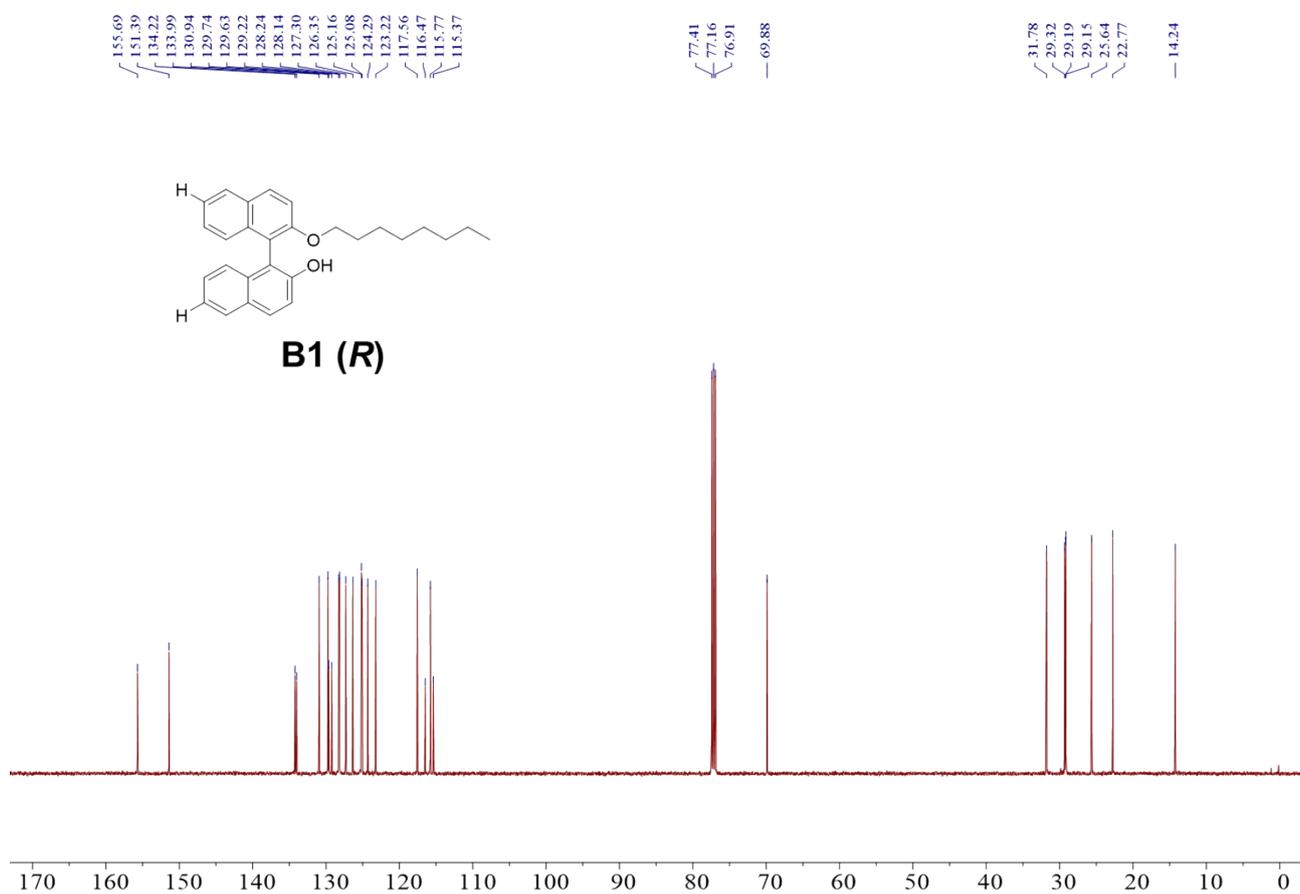
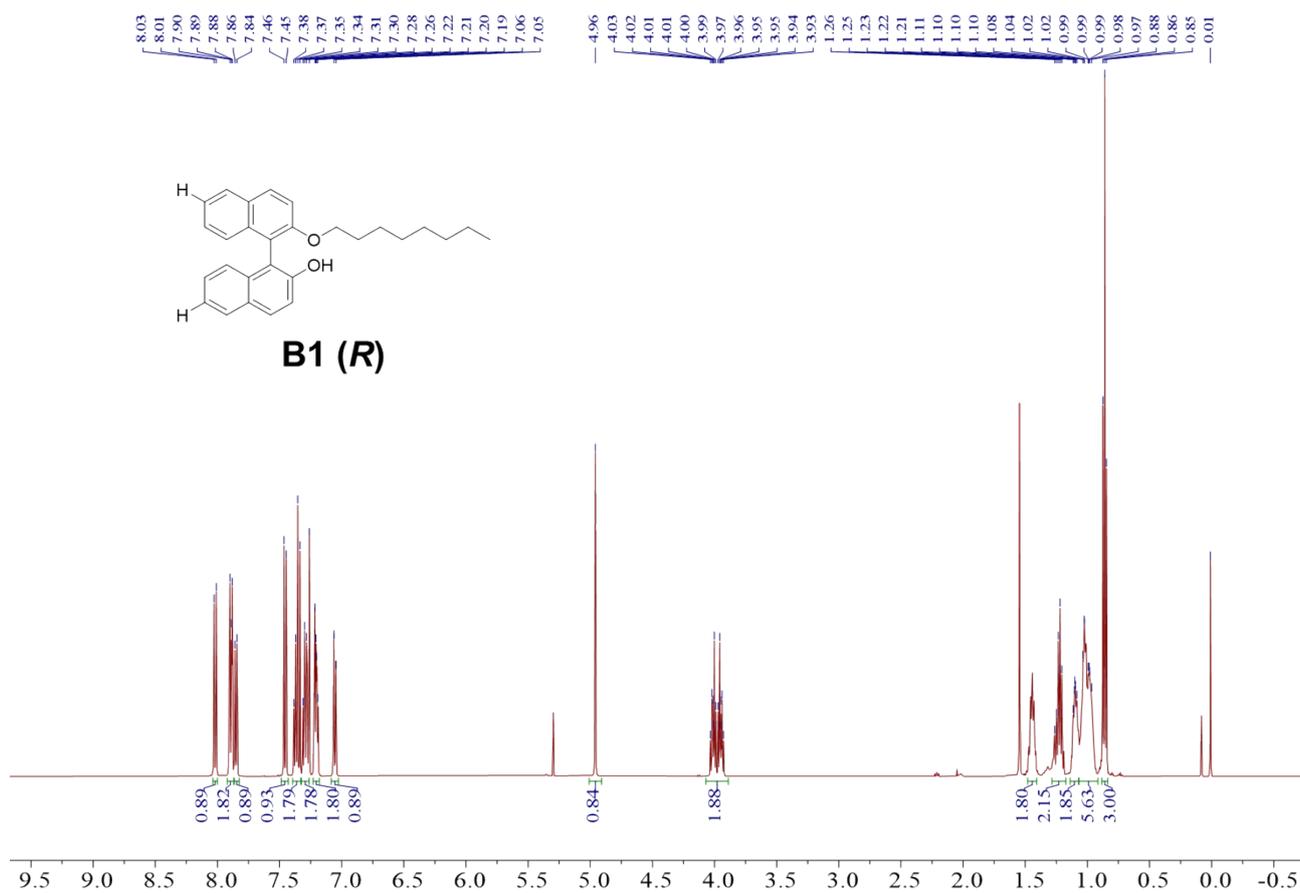
**H-S-L** (yield 90%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*, ppm) δ 8.39 (s, 1H), 7.91 (dd, *J* = 9.0, 4.0 Hz, 2H), 7.83 (dd, *J* = 8.3, 3.3 Hz, 2H), 7.70 (s, 2H), 7.40 (d, *J* = 9.0 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.22 – 7.13 (m, 4H), 3.96 (dt, *J* = 15.6, 5.8 Hz, 2H), 3.88 (p, *J* = 6.8 Hz, 2H), 3.72 (d, *J* = 15.0 Hz, 2H), 1.47 – 1.33 (m, 6H), 1.20 (q, *J* = 7.4 Hz, 2H), 1.07 (t, *J* = 7.7 Hz, 4H), 0.97 (t, *J* = 6.2 Hz, 4H), 0.89 (dt, *J* = 13.9, 7.6 Hz, 4H), 0.84 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*, ppm) δ 171.60, 154.72, 154.61, 134.34, 130.78, 129.46, 129.40, 129.25, 129.21, 127.94, 126.19, 125.64, 124.51, 123.60, 120.88, 120.84, 116.01, 115.96, 69.89, 69.84, 68.30, 31.82, 29.54, 29.43, 29.23, 29.08, 25.75, 25.41, 22.79, 14.25. MS (ESI): Calculated for C<sub>42</sub>H<sub>46</sub>O<sub>7</sub>, [M+Na]<sup>+</sup> 685.3136, found 685.3146.

**Br-R-L** (yield 85%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*, ppm) δ 8.27 (s, 1H), 7.98 (s, 2H), 7.80 (d, *J* = 9.1 Hz, 2H), 7.49 (s, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 10.8 Hz, 2H), 3.99 – 3.90 (m, 2H), 3.88 – 3.77 (m, 2H), 3.67 (s, 2H), 1.48 – 1.32 (m, 6H), 1.30 – 1.13 (m, 4H), 1.06 (t, *J* = 7.8 Hz, 4H), 1.01 – 0.88 (m, 6H), 0.85 – 0.81 (m, 3H).

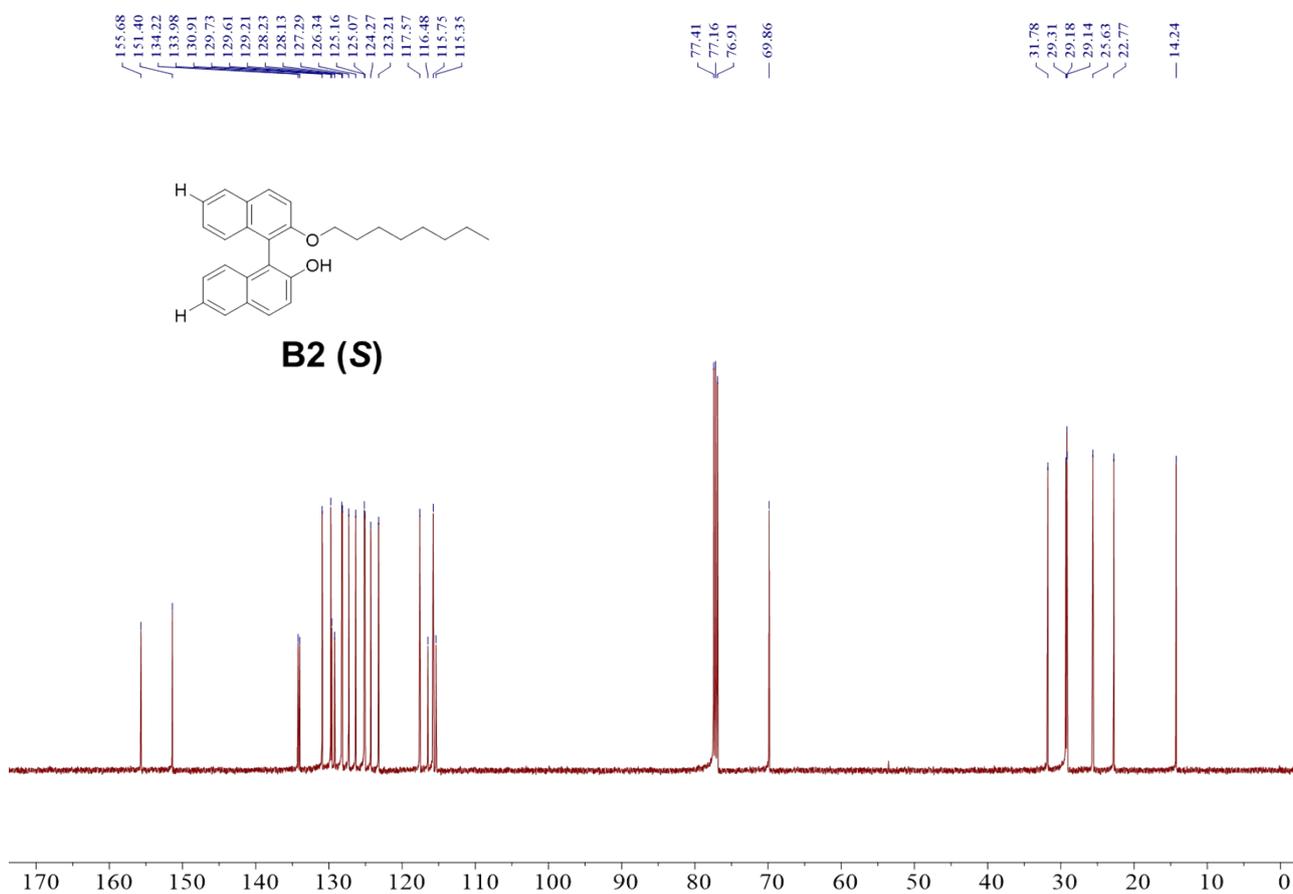
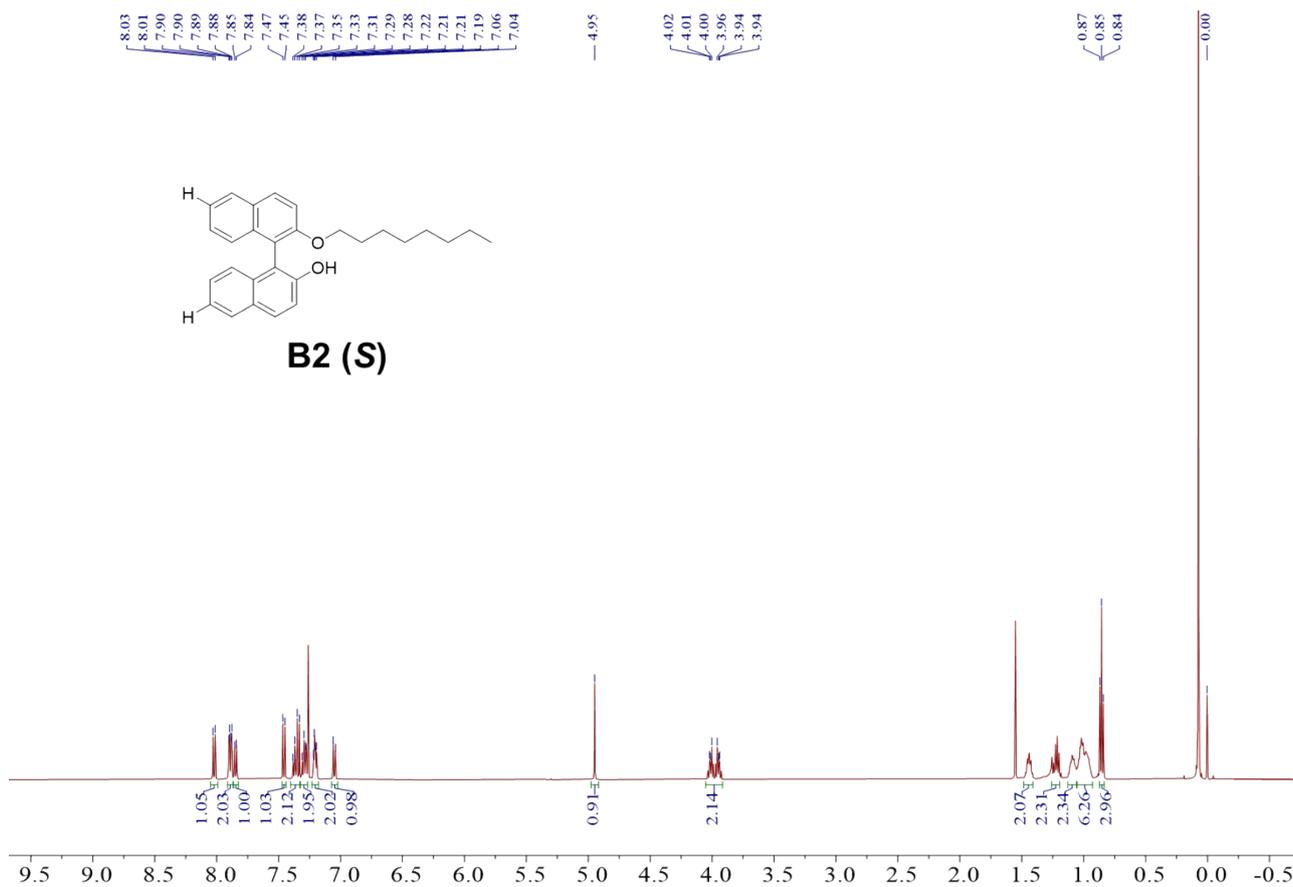
$^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*, ppm)  $\delta$  171.50, 158.88, 154.94, 154.80, 132.70, 132.67, 130.91, 130.39, 130.32, 129.92, 129.63, 129.57, 128.64, 128.60, 127.28, 120.45, 120.15, 120.11, 117.47, 117.37, 116.53, 116.45, 69.64, 69.54, 68.30, 31.85, 29.44, 29.36, 29.29, 29.23, 29.12, 25.82, 25.50, 22.79, 14.27. MS (ESI): Calculated for  $\text{C}_{42}\text{H}_{44}\text{Br}_2\text{O}_7$ ,  $[\text{M}+\text{Na}]^+$  841.1346, found 841.1333.

**Br-S-L** (yield 87%).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*, ppm)  $\delta$  8.28 (s, 1H), 7.99 (d,  $J = 2.0$  Hz, 2H), 7.81 (d,  $J = 9.0$  Hz, 2H), 7.49 (s, 2H), 7.38 (t,  $J = 9.6$  Hz, 2H), 7.26 – 7.18 (m, 2H), 6.99 (dd,  $J = 13.3, 9.1$  Hz, 2H), 3.99 – 3.91 (m, 2H), 3.91 – 3.82 (m, 2H), 3.68 (s, 2H), 1.50 – 1.32 (m, 6H), 1.22 – 1.15 (m, 2H), 1.08 (d,  $J = 7.7$  Hz, 4H), 1.03 – 0.86 (m, 8H), 0.83 (d,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*, ppm)  $\delta$  171.58, 158.86, 154.95, 154.80, 132.71, 132.67, 130.84, 130.40, 130.33, 129.93, 129.63, 129.57, 128.64, 128.61, 127.32, 127.27, 124.56, 120.47, 120.15, 120.12, 117.47, 117.38, 116.54, 116.45, 69.65, 69.55, 68.30, 60.56, 31.85, 29.45, 29.37, 29.29, 29.23, 29.13, 25.82, 25.50, 22.79, 14.27. MS (ESI): Calculated for  $\text{C}_{42}\text{H}_{44}\text{Br}_2\text{O}_7$ ,  $[\text{M}+\text{Na}]^+$  841.1346, found 841.1342.

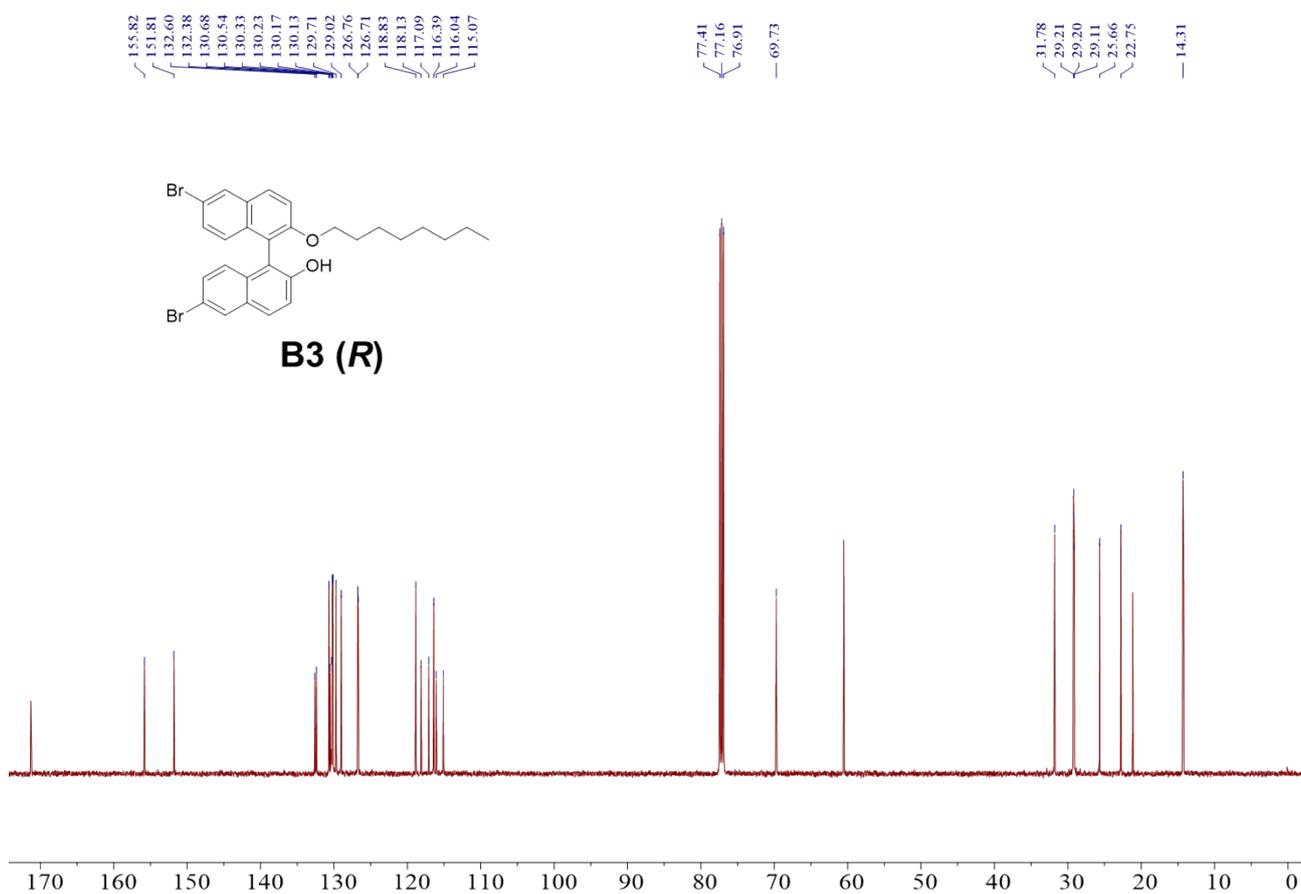
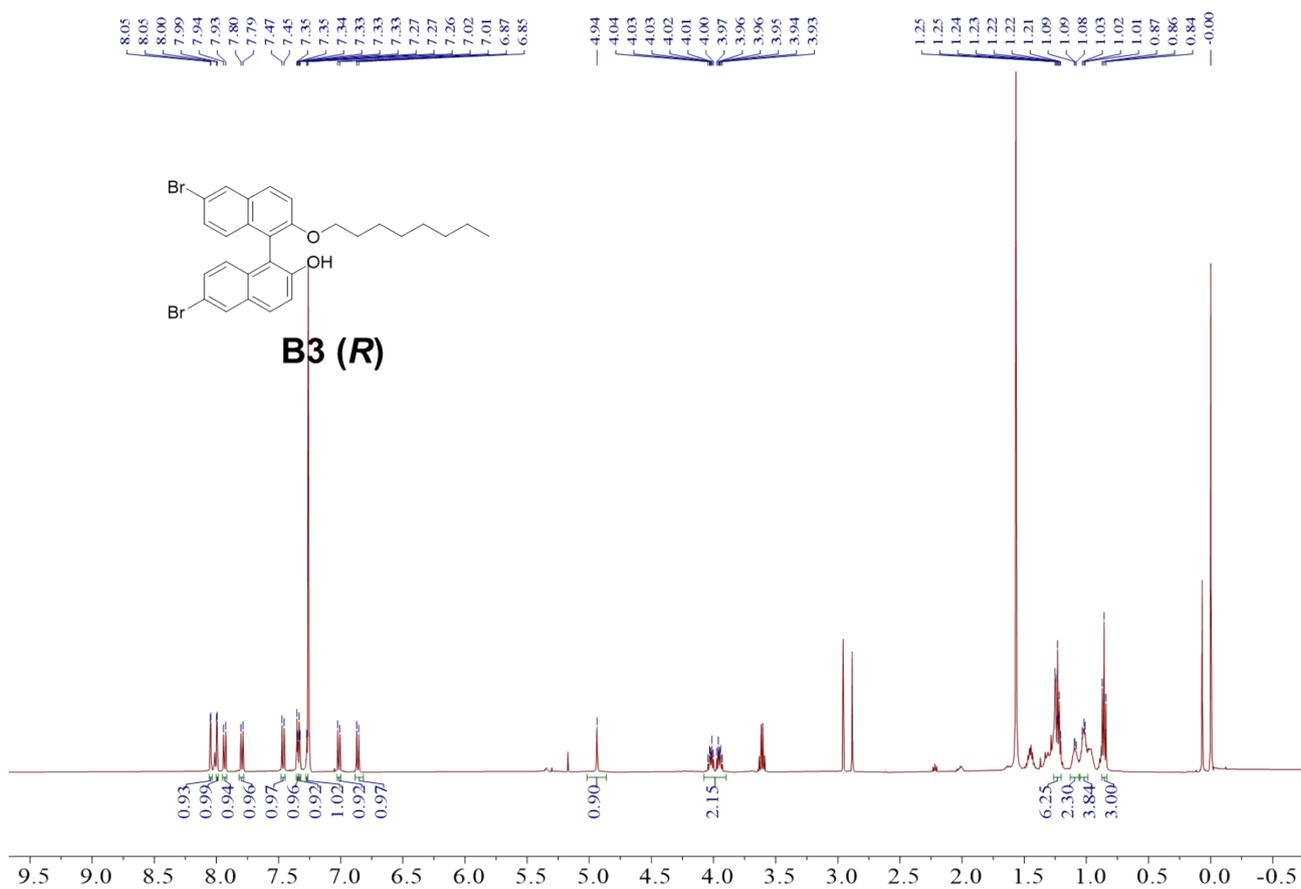
**R-R/S-MOC**: The chiral ligand, **R-R/S-L**, (0.20 mmol, 1.0 eq.) and copper (II) acetate monohydrate (0.04 g, 0.20 mmol, 1.0 eq.) was dissolved in THF (15 mL and 8 mL) separately. The two solutions were mixed and stirred for 3 hours at room temperature. The reaction mixture was concentrated and added dropwise to methanol (30 mL). The precipitate was collected by centrifugation (10000 rpm, 10 min) and dried under reduced pressure at 40 °C for 3 h to afford the chiral cages, **R-R/S-MOC**. **H-R-MOC** (86%), **H-S-MOC** (83%), **Br-R-MOC** (82%), **Br-S-MOC** (80%).



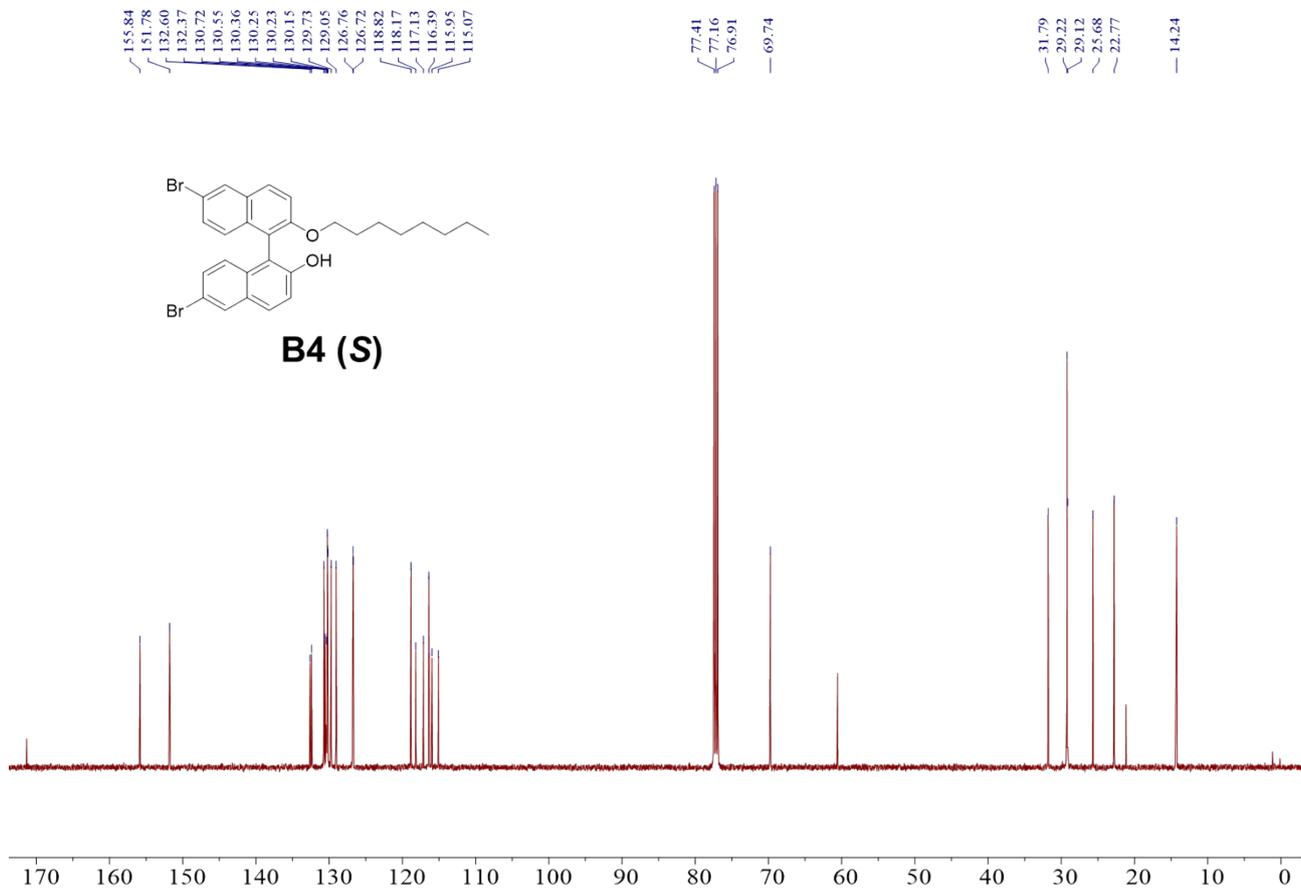
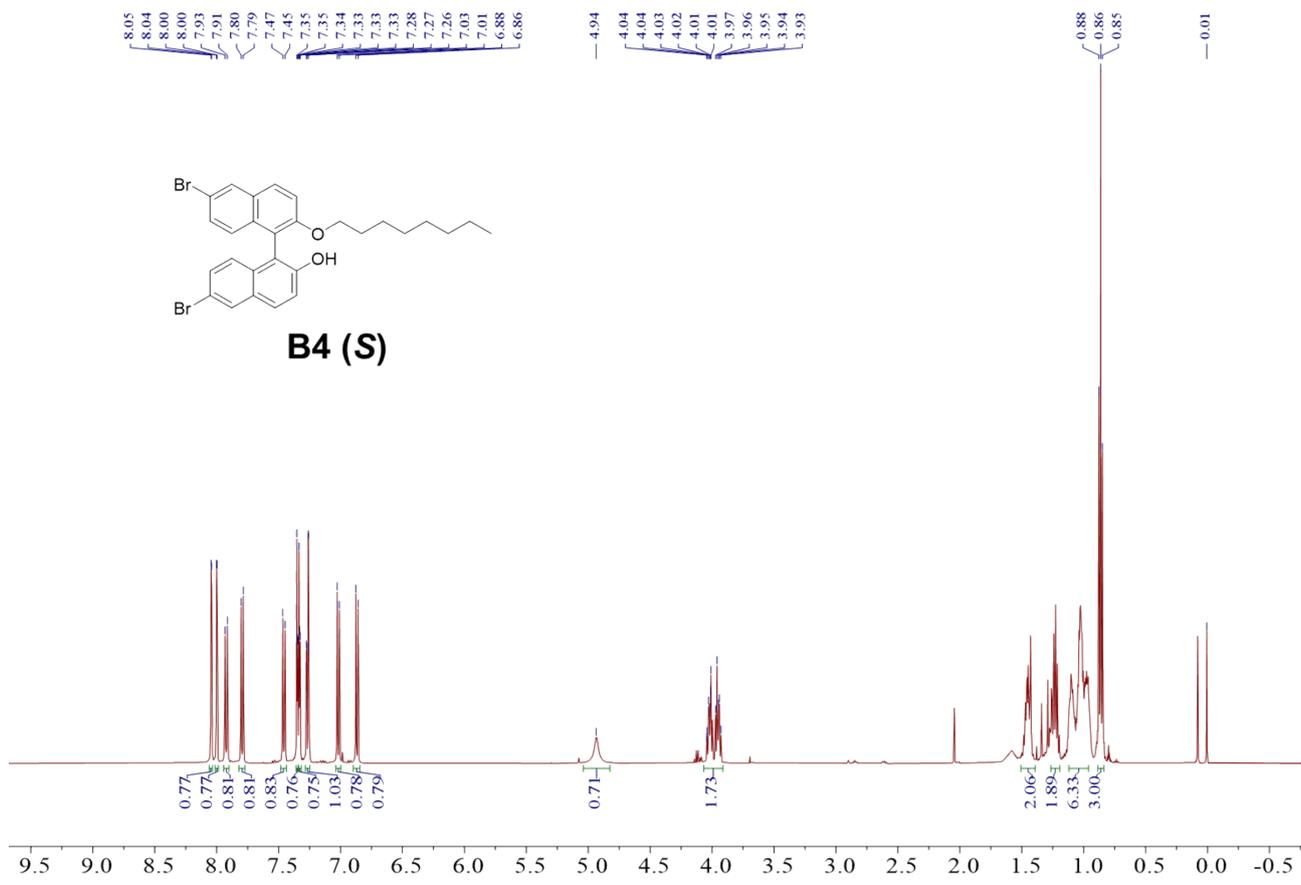
**Fig. S1** The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of compound **B1** in CDCl<sub>3</sub>.



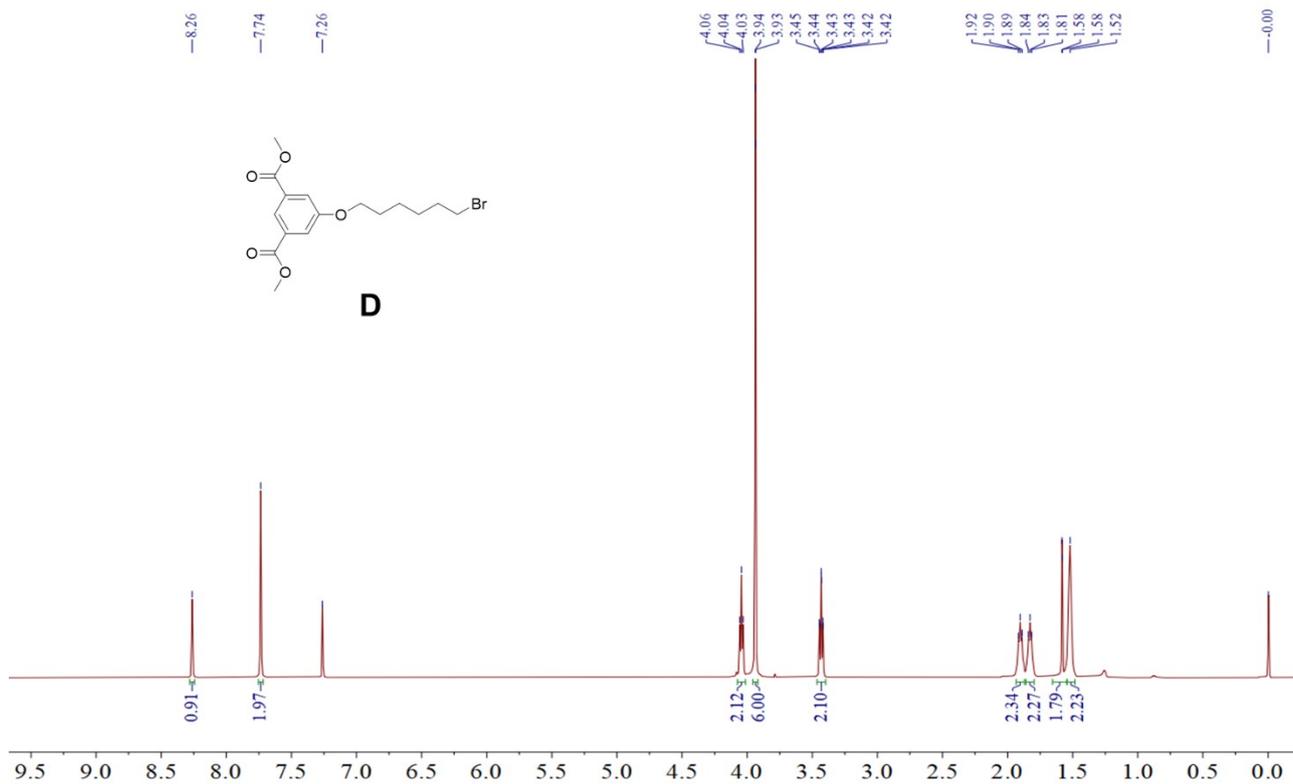
**Fig. S2** The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of compound **B2** in CDCl<sub>3</sub>.



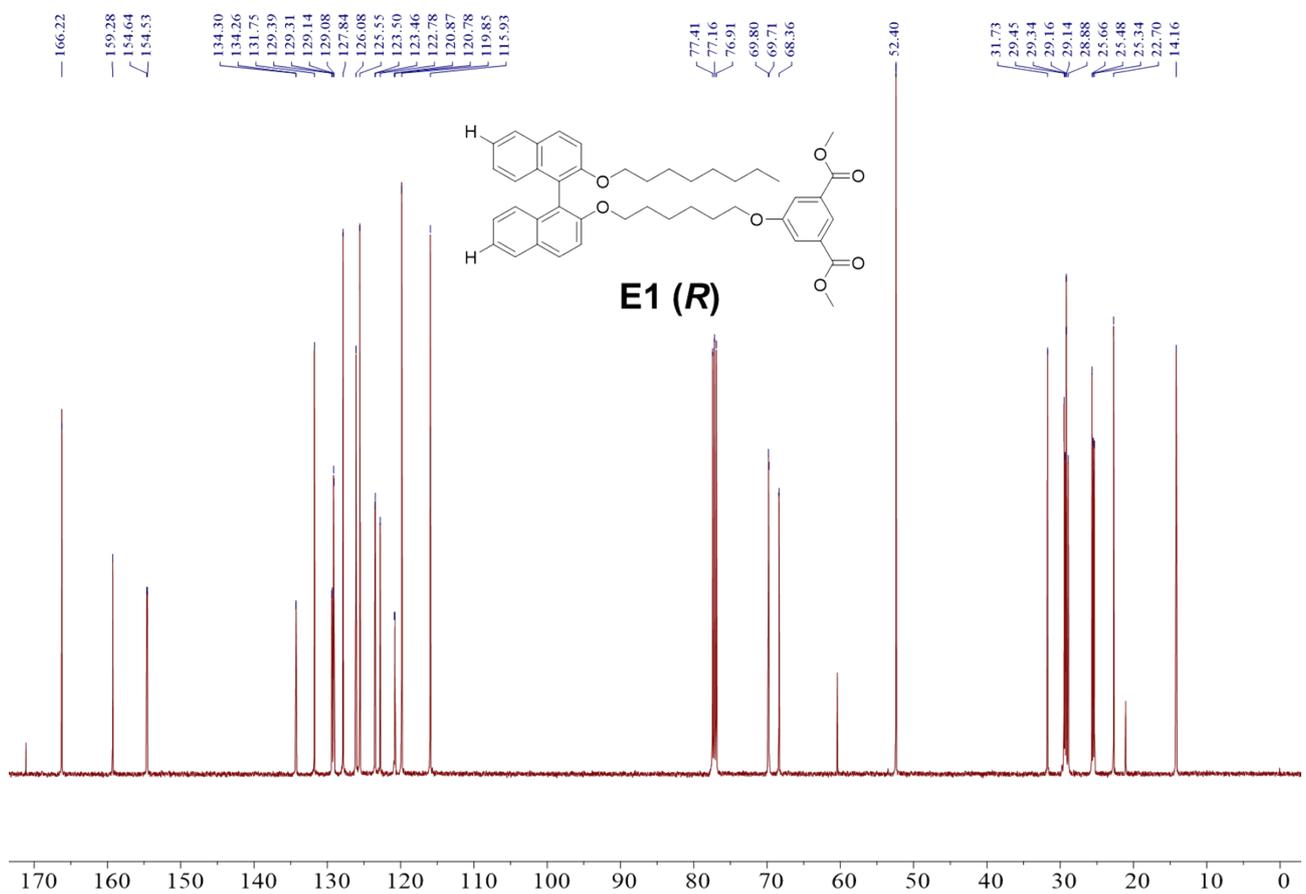
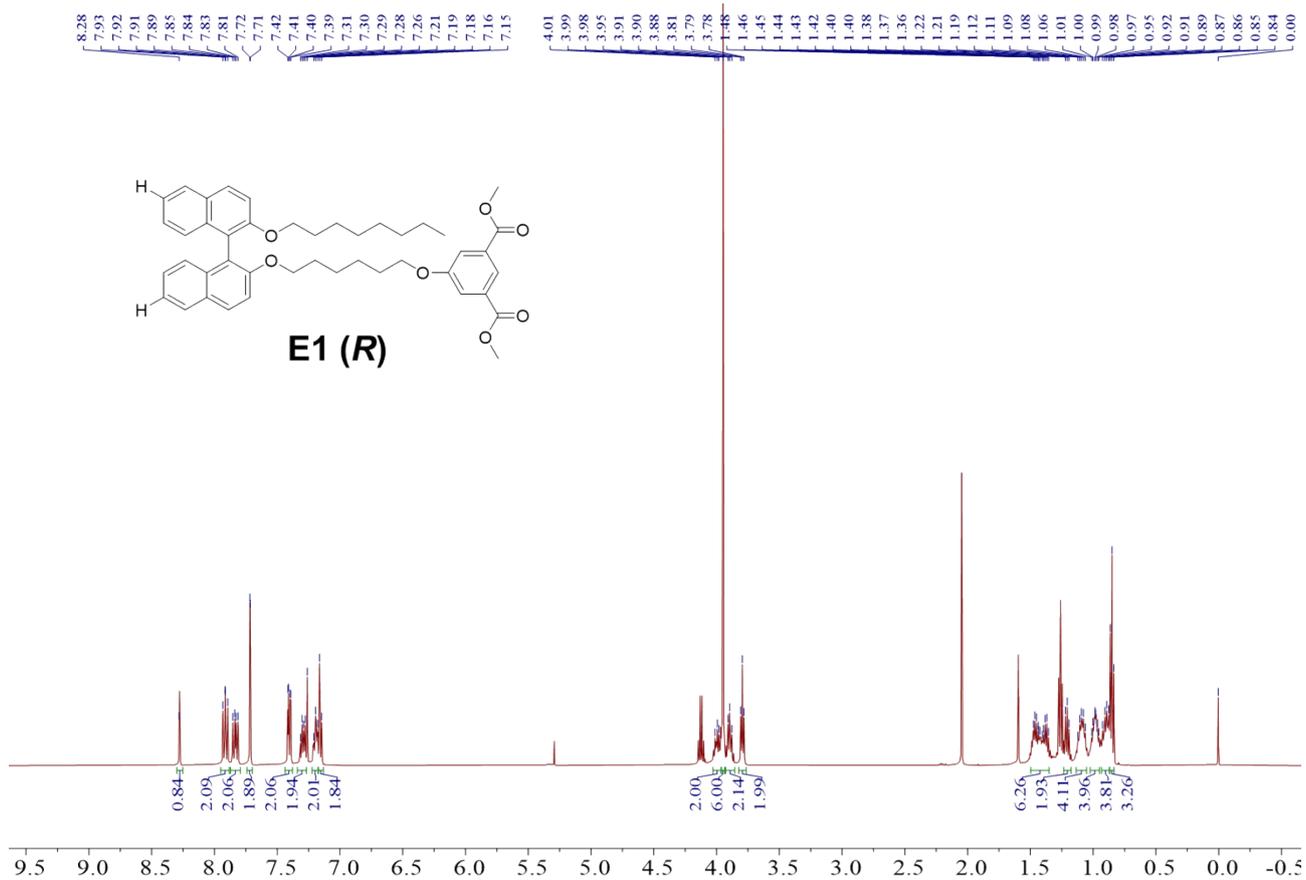
**Fig. S3** The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of compound **B3** in CDCl<sub>3</sub>.



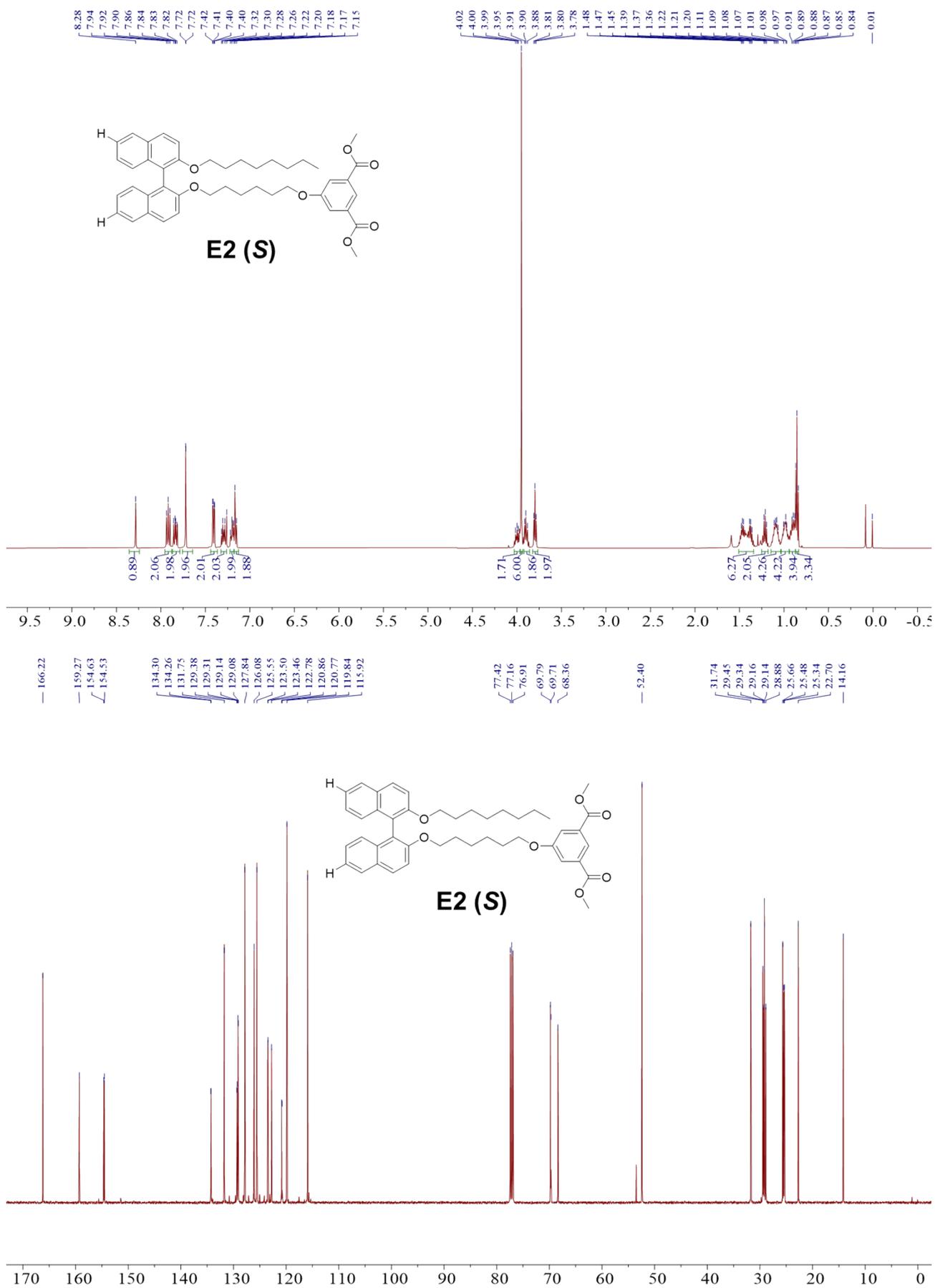
**Fig. S4** The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of compound **B4** in CDCl<sub>3</sub>.



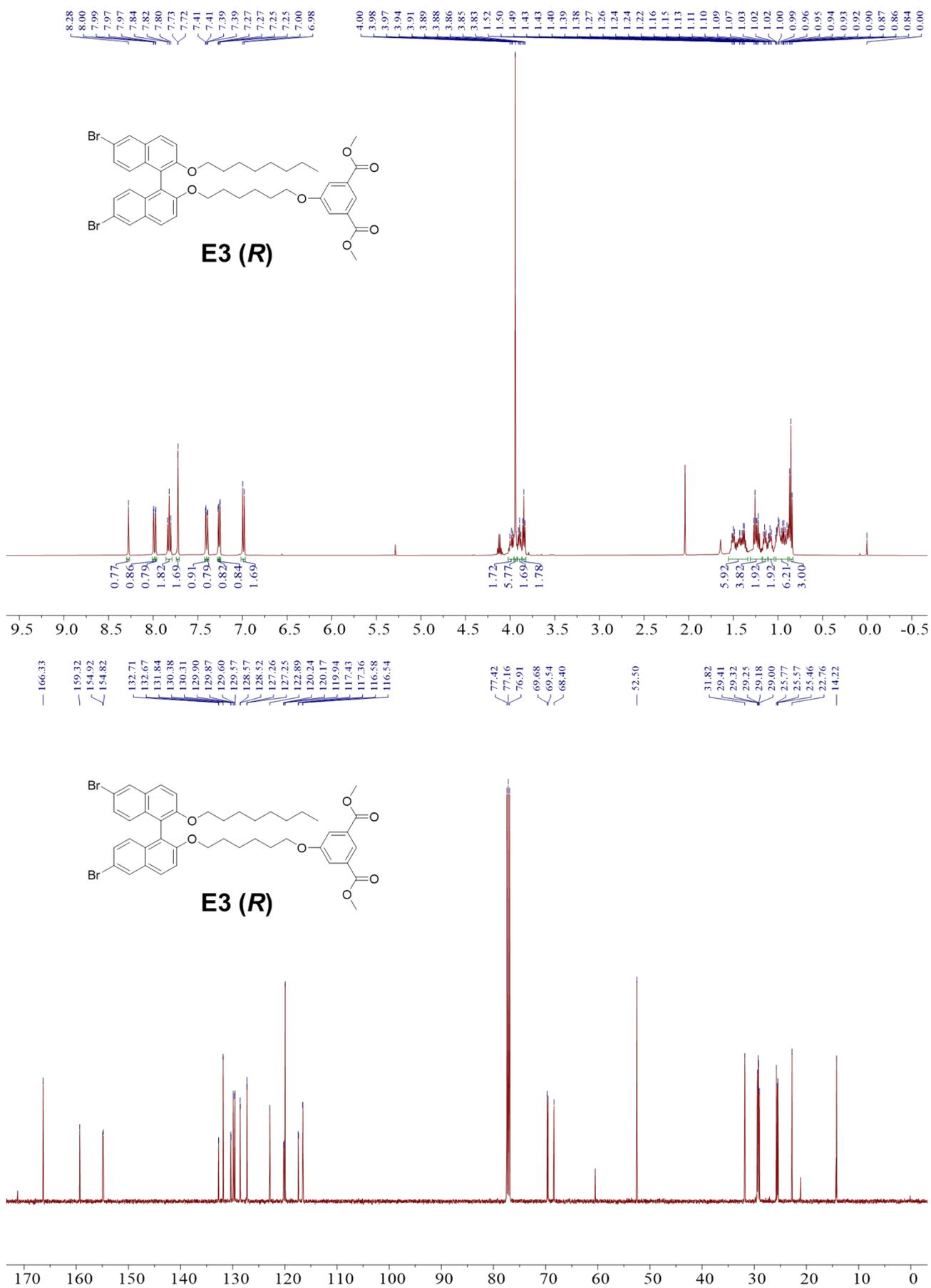
**Fig. S5** The <sup>1</sup>H-NMR spectrum of compound **D** in CDCl<sub>3</sub>.



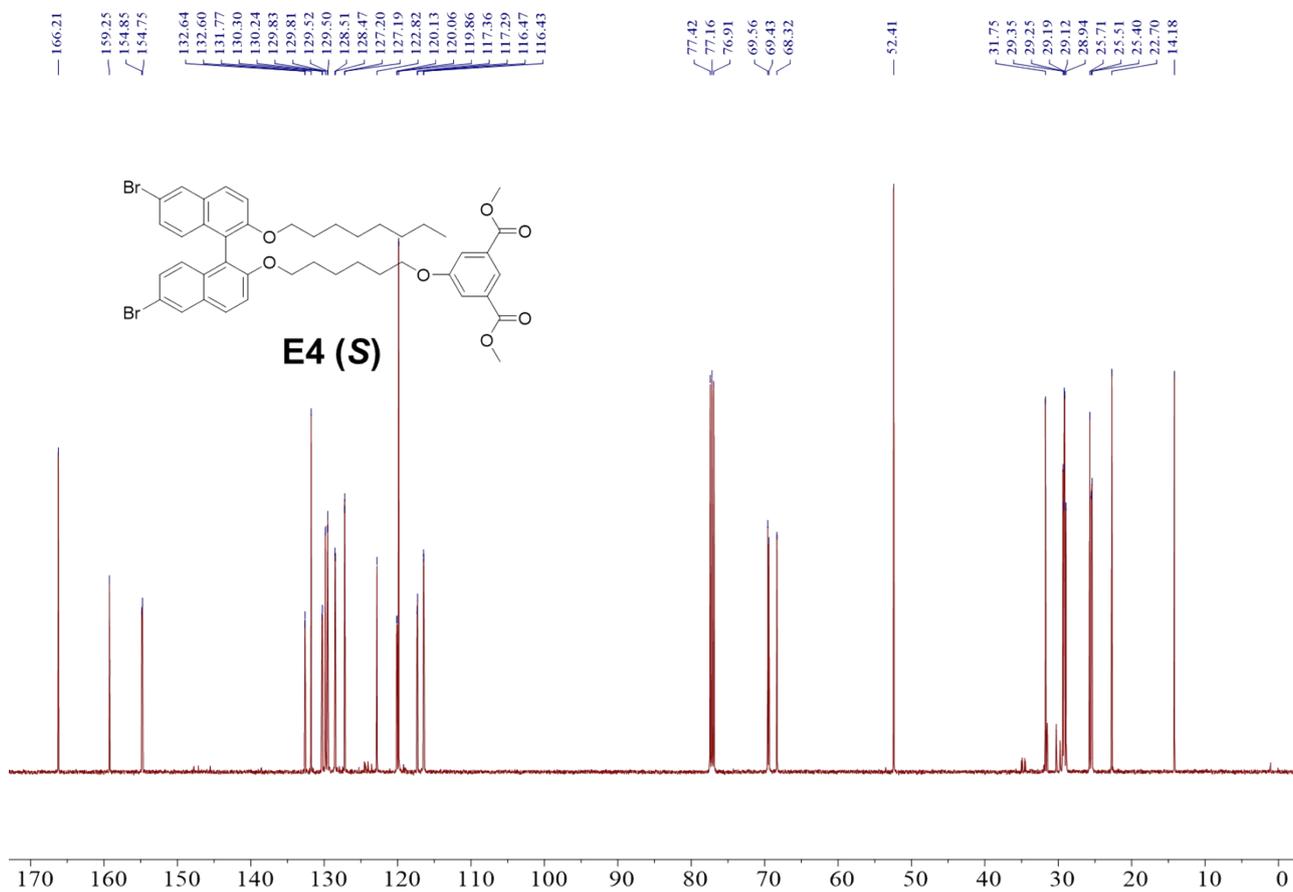
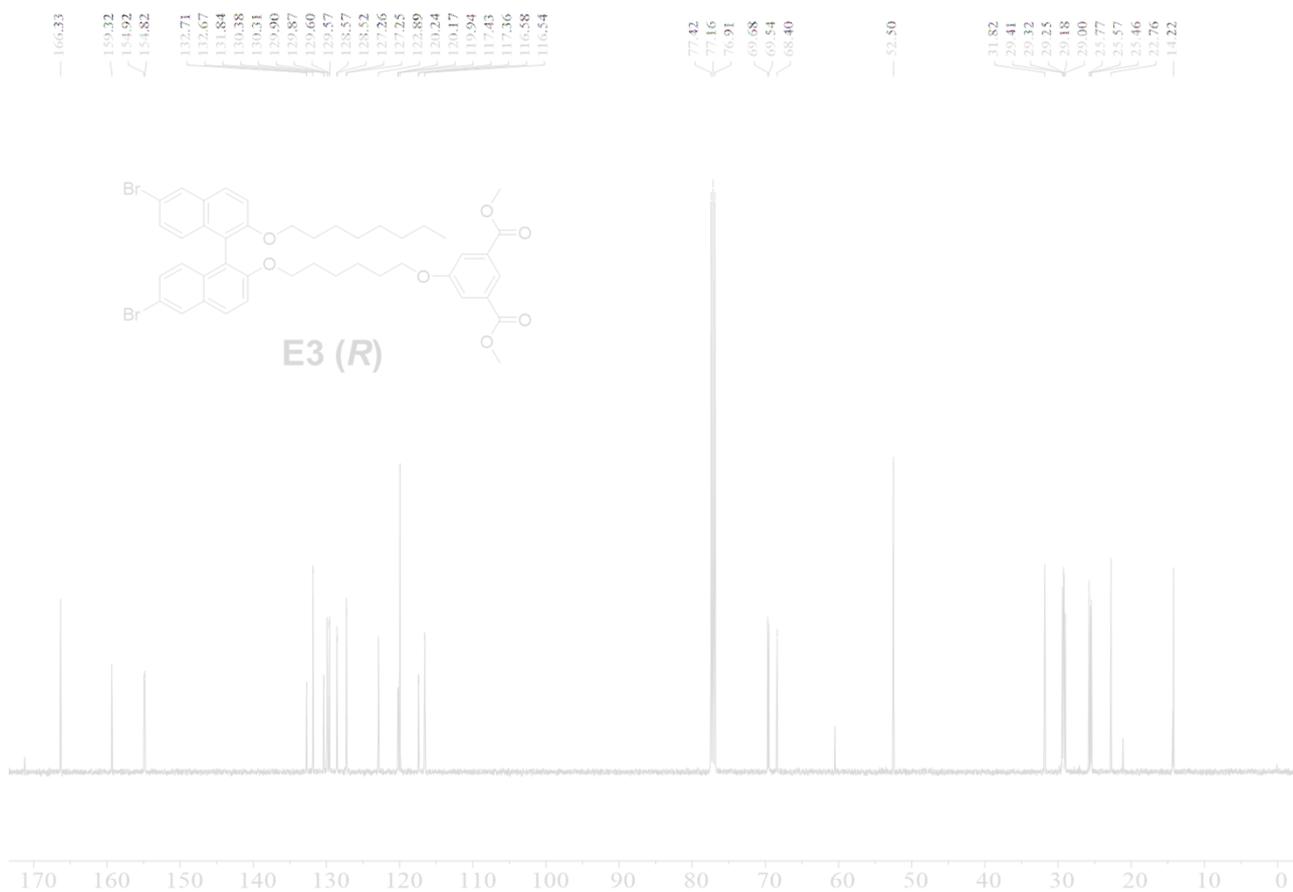
**Fig. S6** The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of compound **E1** in CDCl<sub>3</sub>.



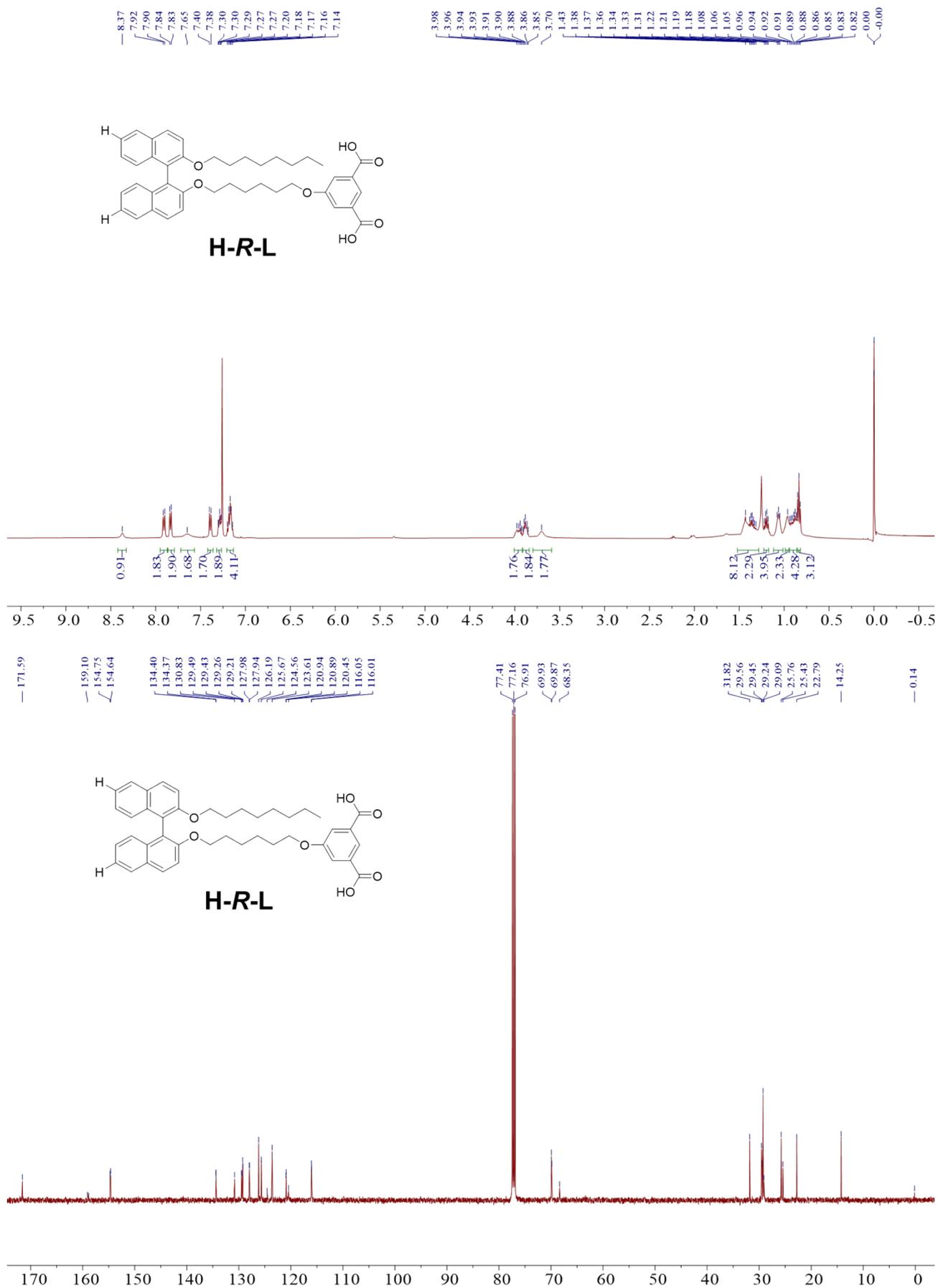
**Fig. S7** The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of compound **E2** in CDCl<sub>3</sub>.



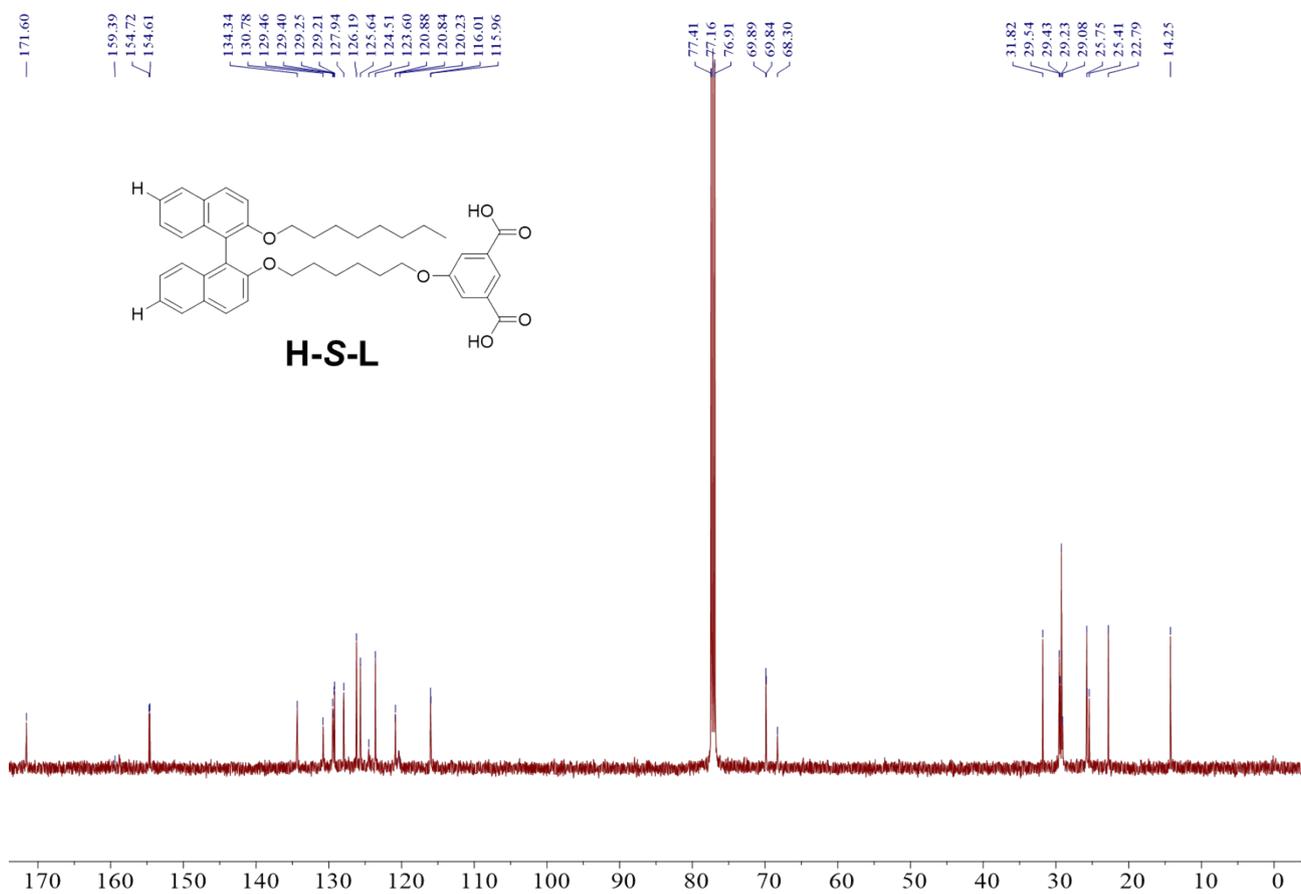
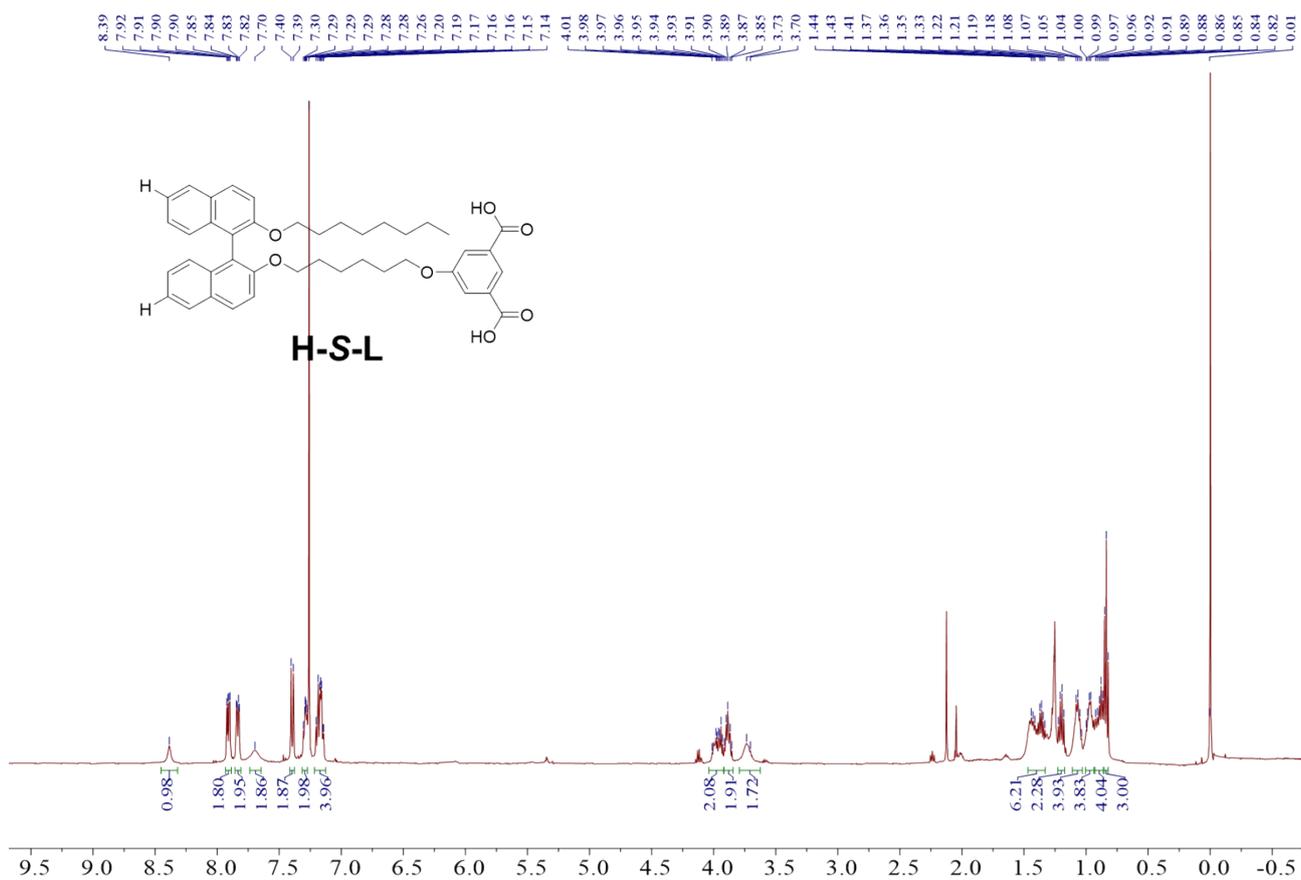
**Fig. S8** The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of compound **E3** in  $\text{CDCl}_3$ .



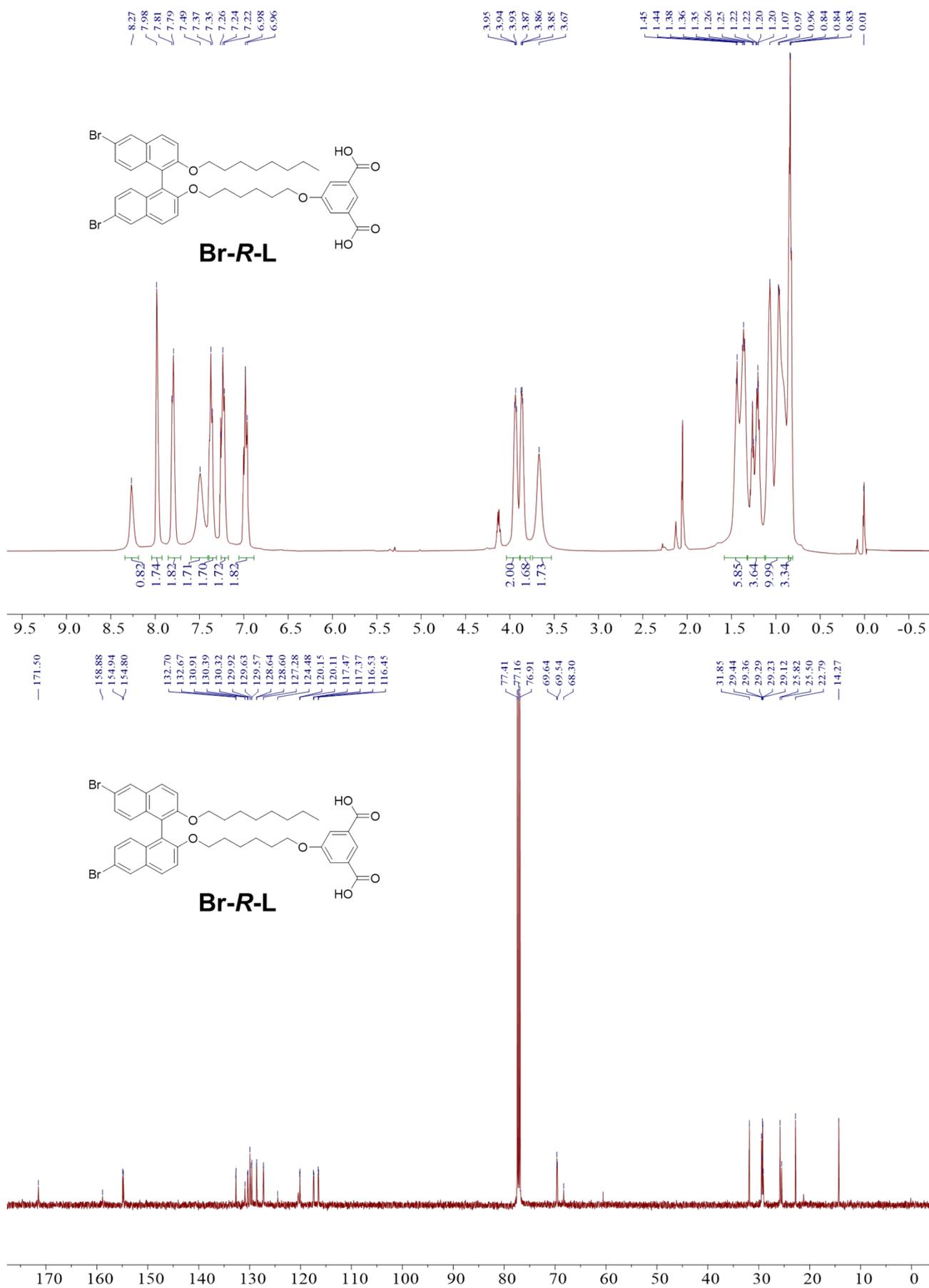
**Fig. S9** The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of compound **E4** in CDCl<sub>3</sub>.



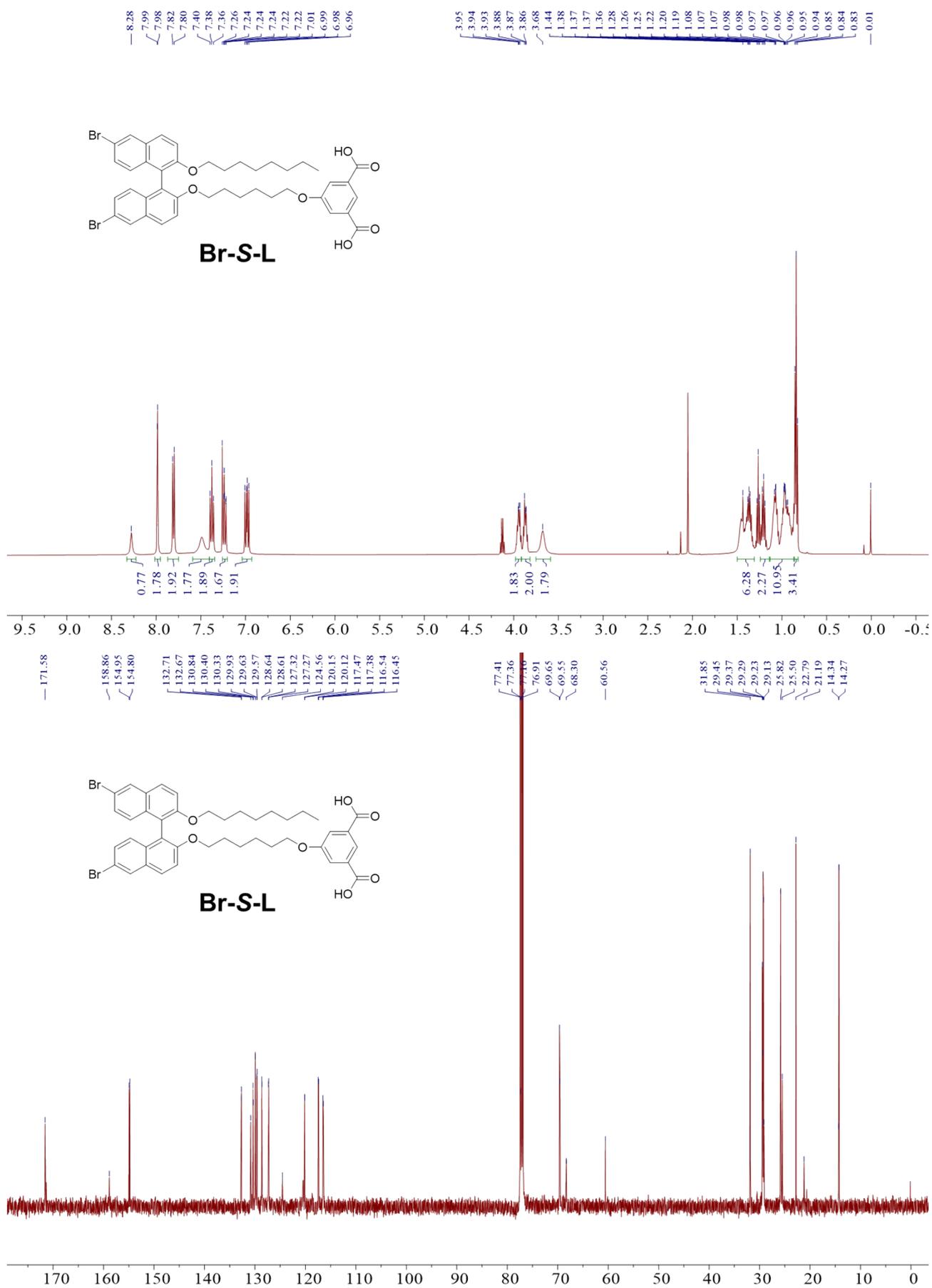
**Fig. S10** The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of ligand **H-R-L** in CDCl<sub>3</sub>.



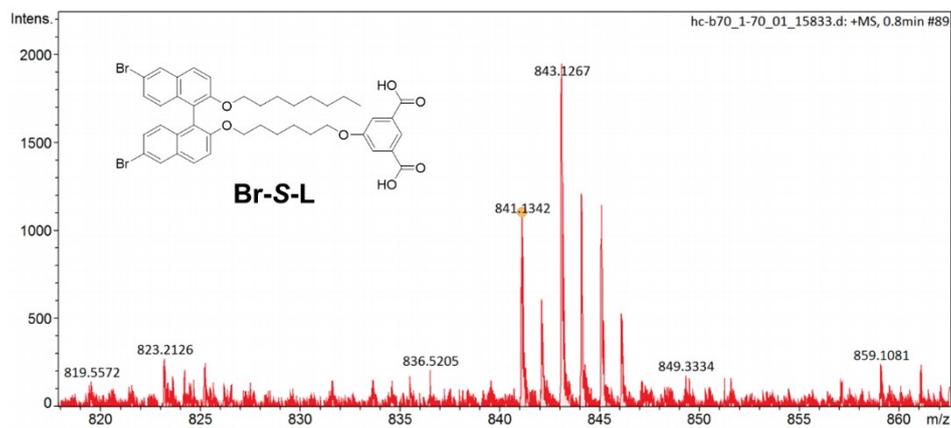
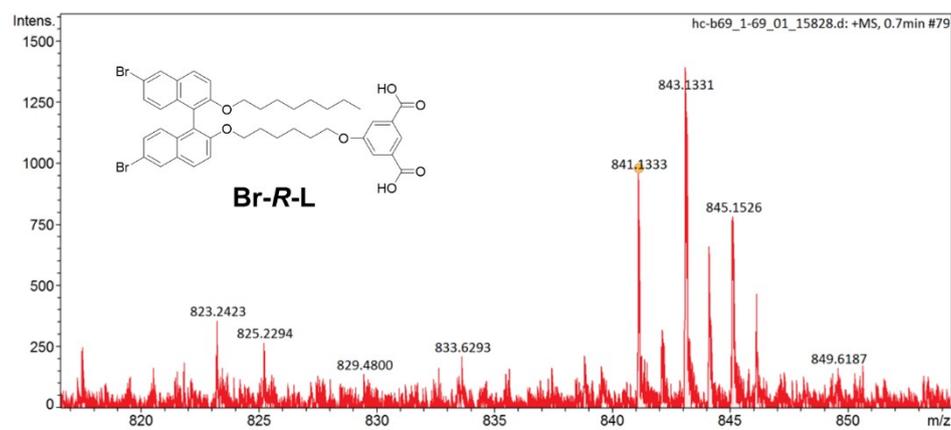
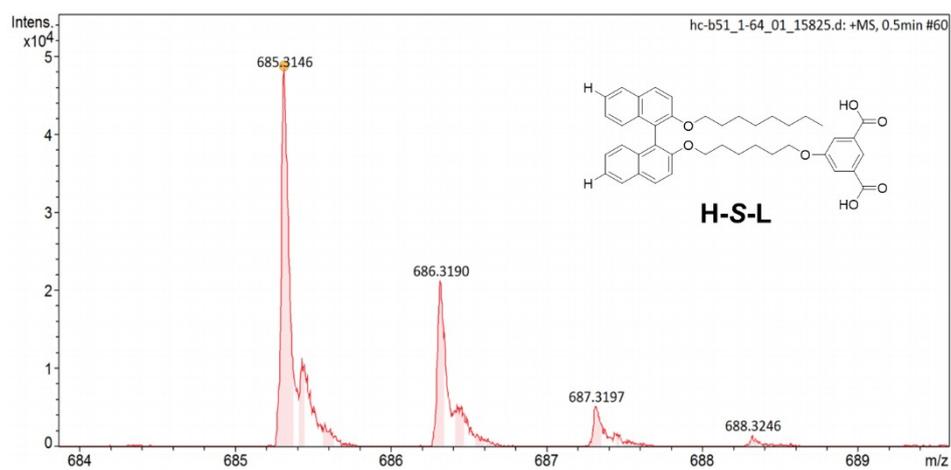
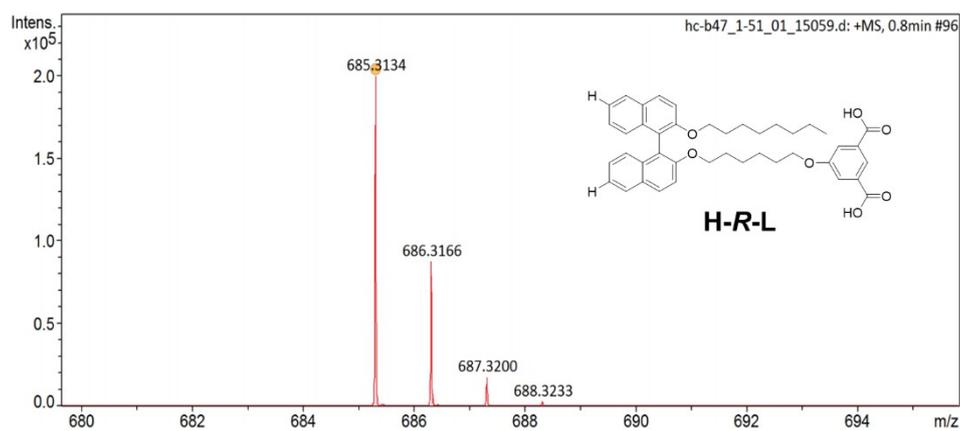
**Fig. S11** The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of ligand H-S-L in CDCl<sub>3</sub>.



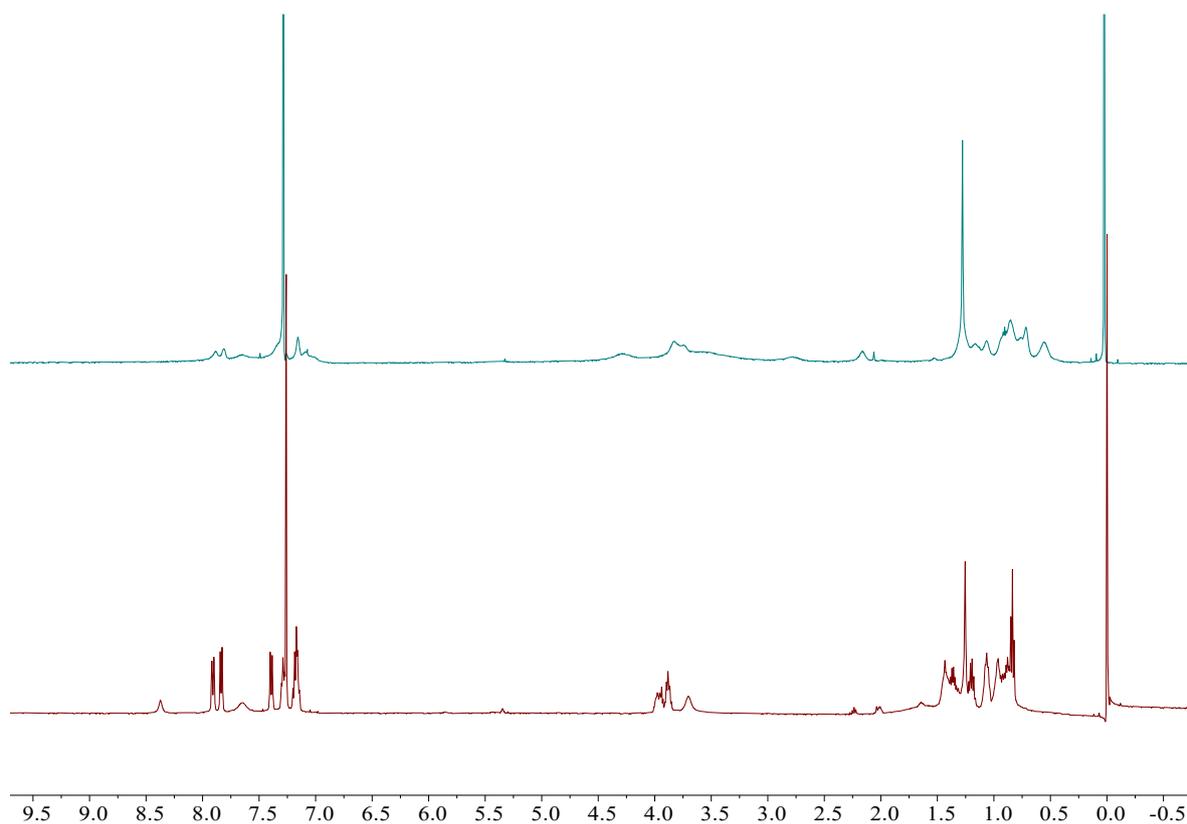
**Fig. S12** The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of ligand **Br-R-L** in CDCl<sub>3</sub>.



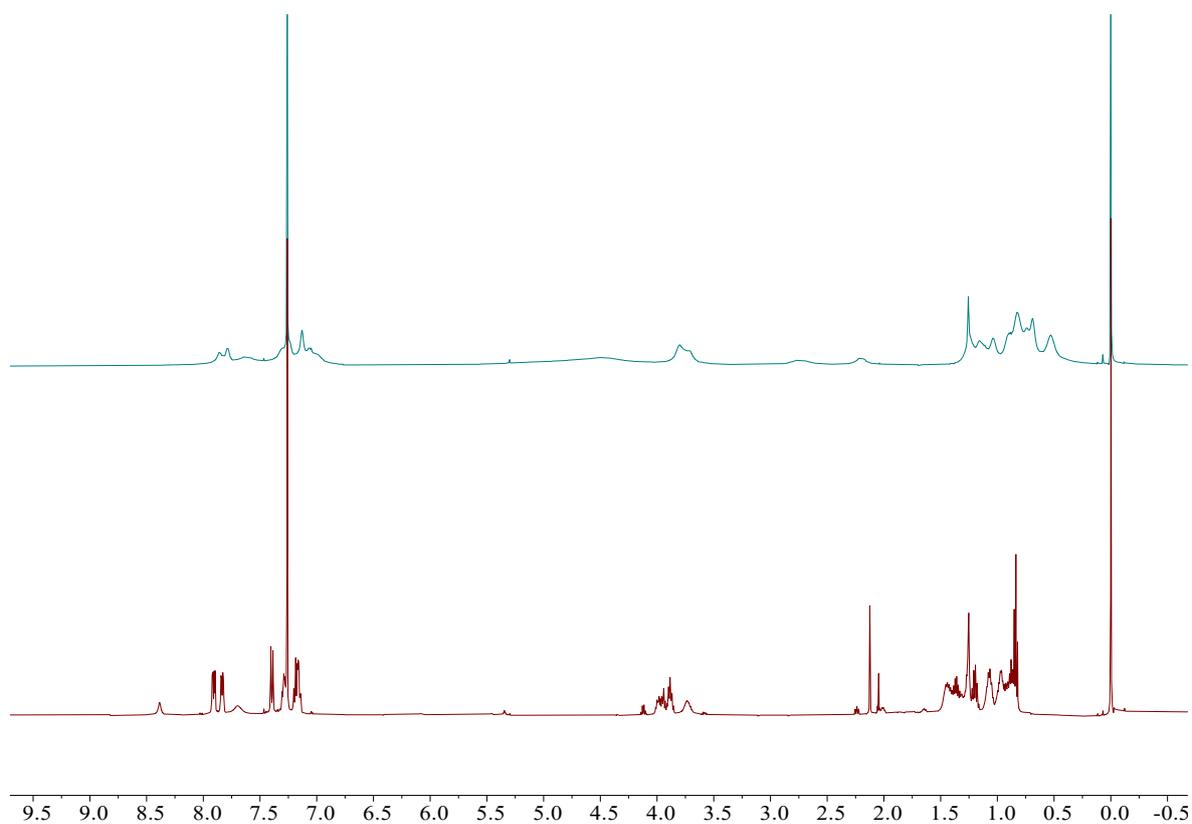
**Fig. S13** The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of ligand **Br-S-L** in CDCl<sub>3</sub>.



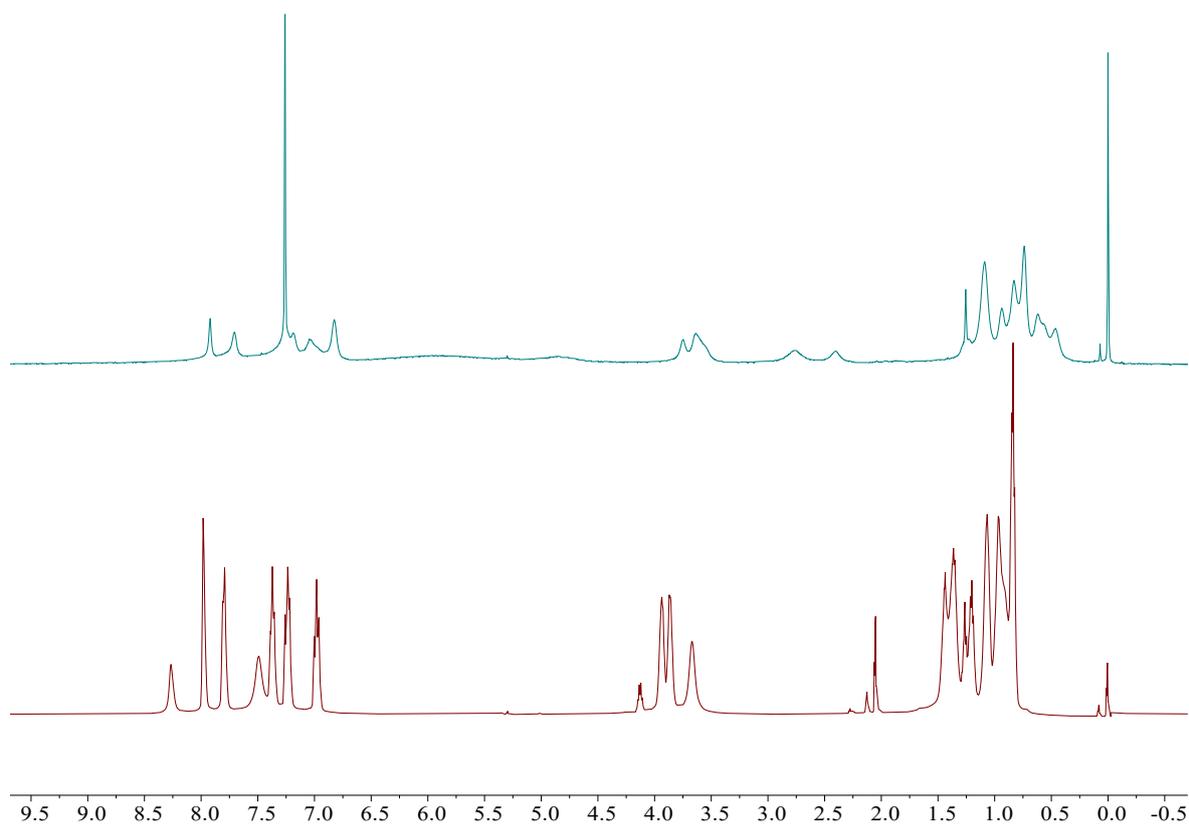
**Fig. S14** The ESI mass spectra of four chiral ligands.



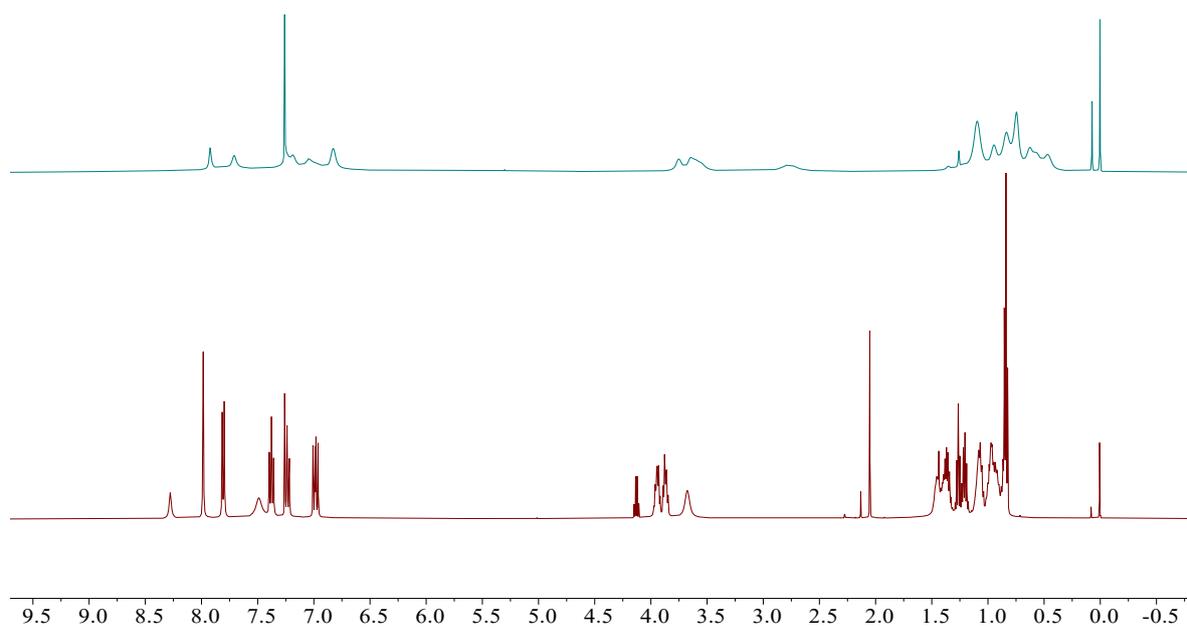
**Fig. S15** The <sup>1</sup>H-NMR spectra of **H-R-L** and **H-R-MOC** in CDCl<sub>3</sub>.



**Fig. S16** The <sup>1</sup>H-NMR spectra of **H-S-L** and **H-S-MOC** in CDCl<sub>3</sub>.



**Fig. S17** The <sup>1</sup>H-NMR spectra of **Br-R-L** and **Br-R-MOC** in CDCl<sub>3</sub>.



**Fig. S18** The <sup>1</sup>H-NMR spectra of **Br-S-L** and **Br-S-MOC** in CDCl<sub>3</sub>.

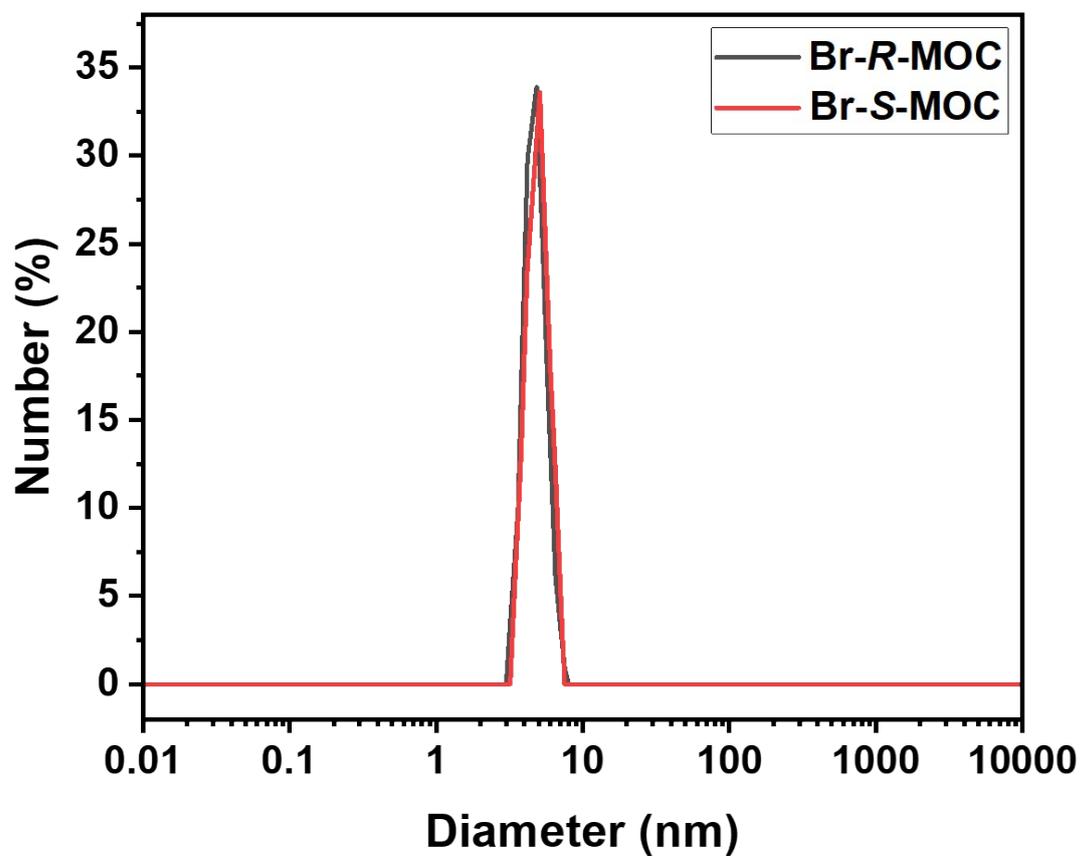
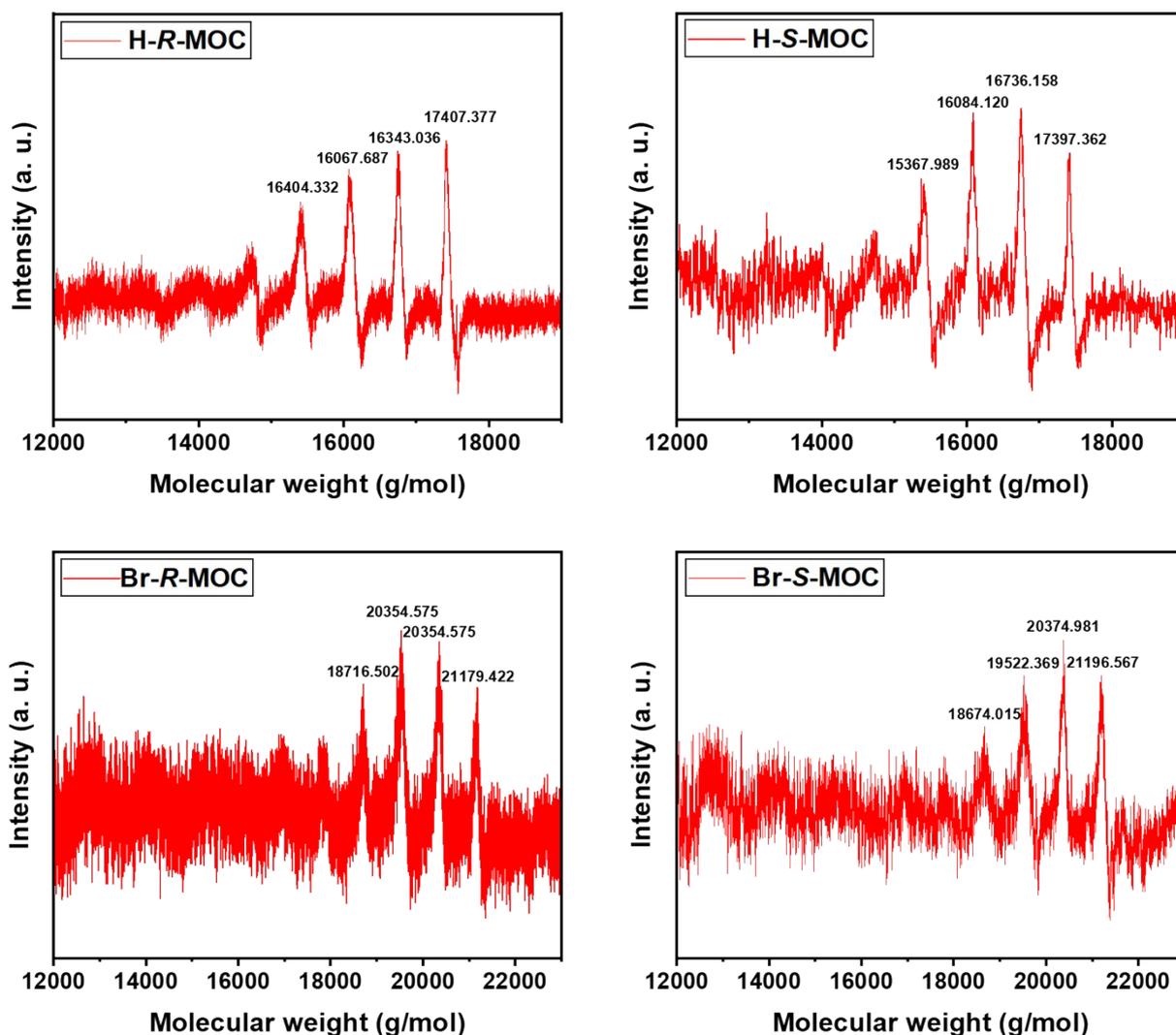


Fig. S19 The DLS plots of **Br-R-MOC** and **Br-S-MOC** in THF.



**Fig. S20** The Maldi-TOF mass spectra of four chiral MOCs.

**Table S1** The SEC and Maldi results of the chiral MOCs.

Entry	$M_{n, theoretical}$ (g/mol)	$M_{n, SEC}$ (g/mol)	$\mathcal{D}_{SEC}$	$M_{n, Maldi}$ (Dalton)
H-R-MOC	17384	--	--	17407
H-S-MOC	17384	--	--	17384
Br-R-MOC	21171	18695	1.04	21179
Br-S-MOC	21171	18708	1.05	21196

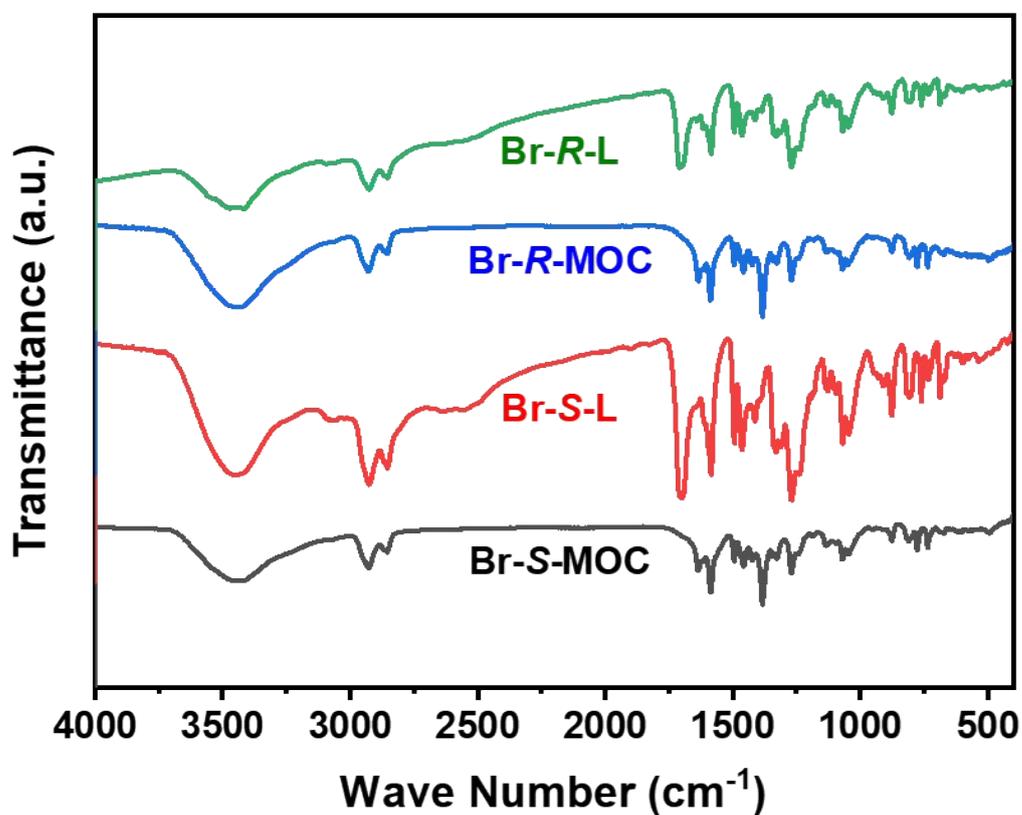
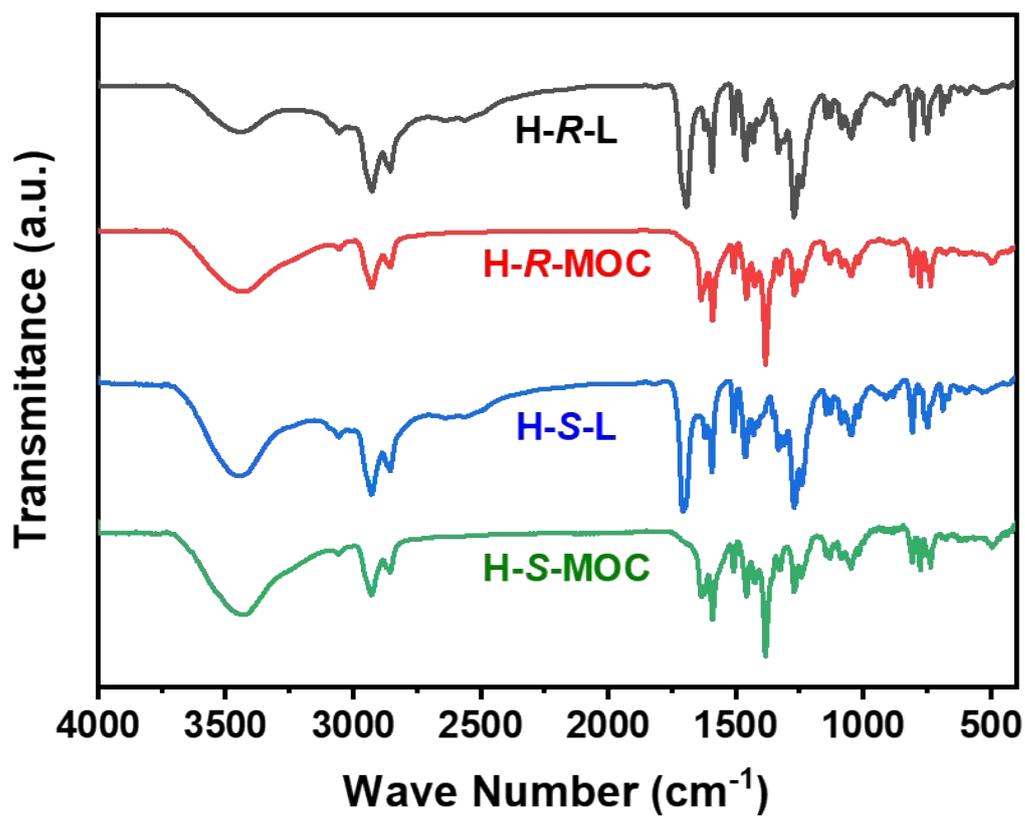
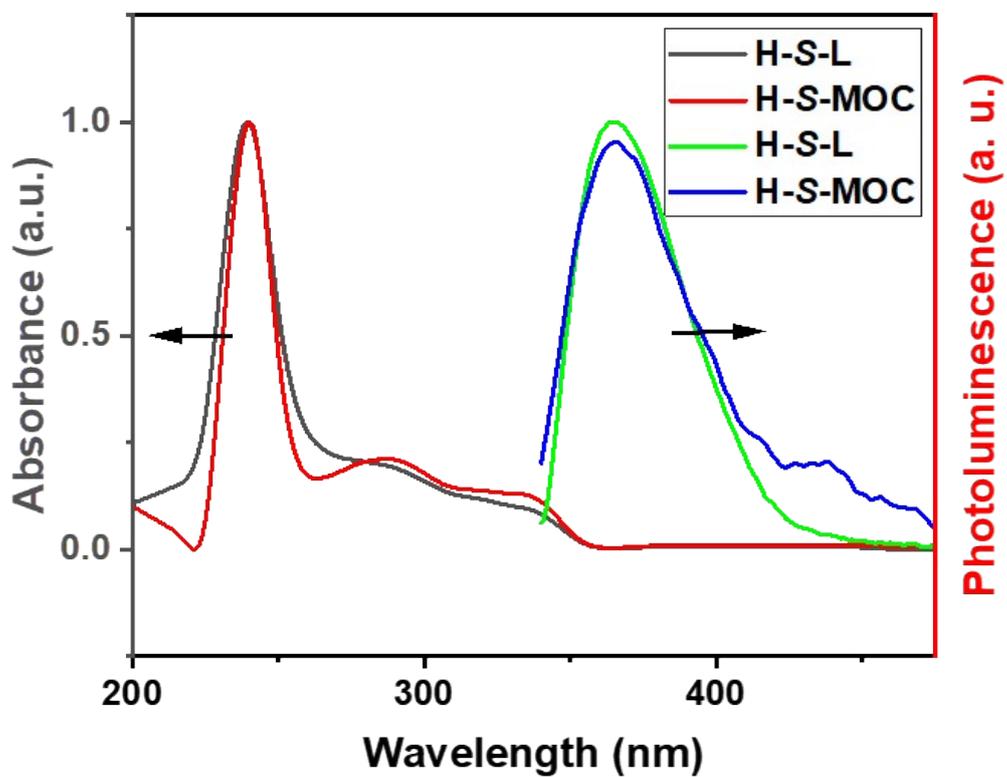
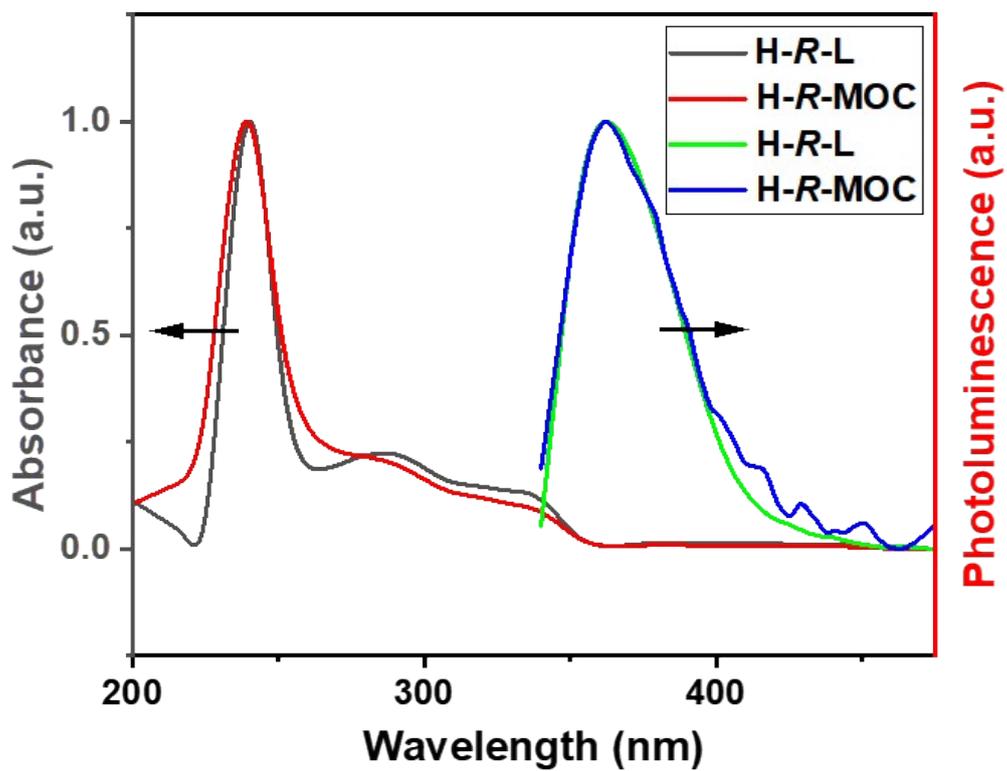


Fig. S21 The FT-IR spectra of the chiral ligands and MOCs.



**Fig. S22** The UV-vis absorption and PL spectra of H-R/S-L and H-R/S-MOC.

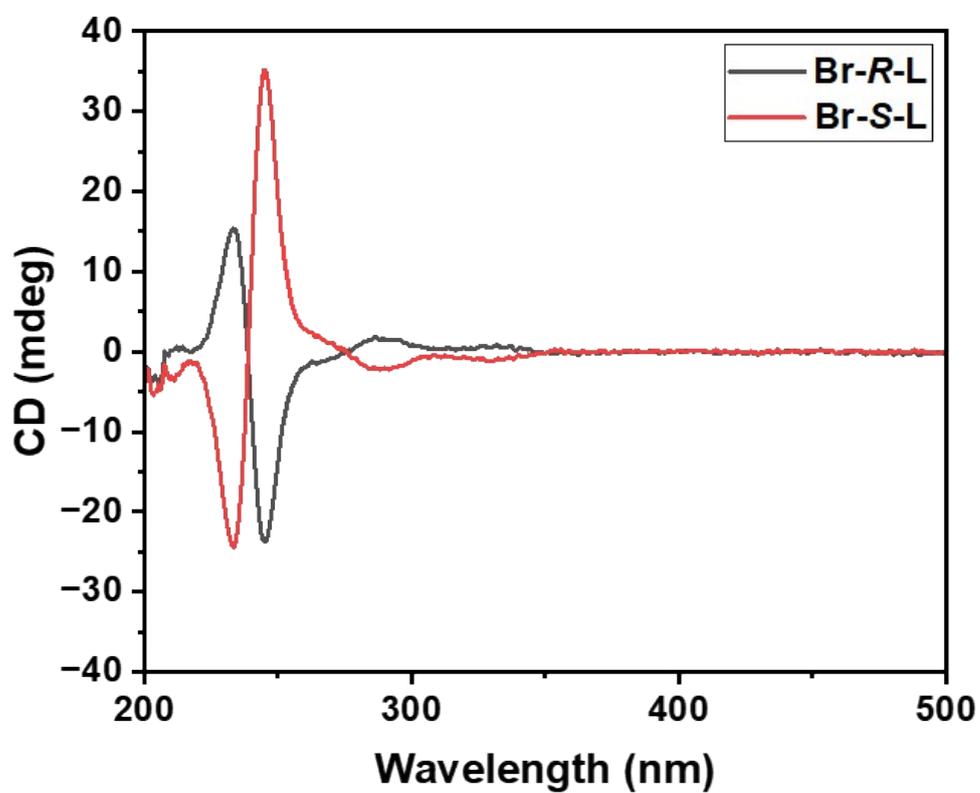
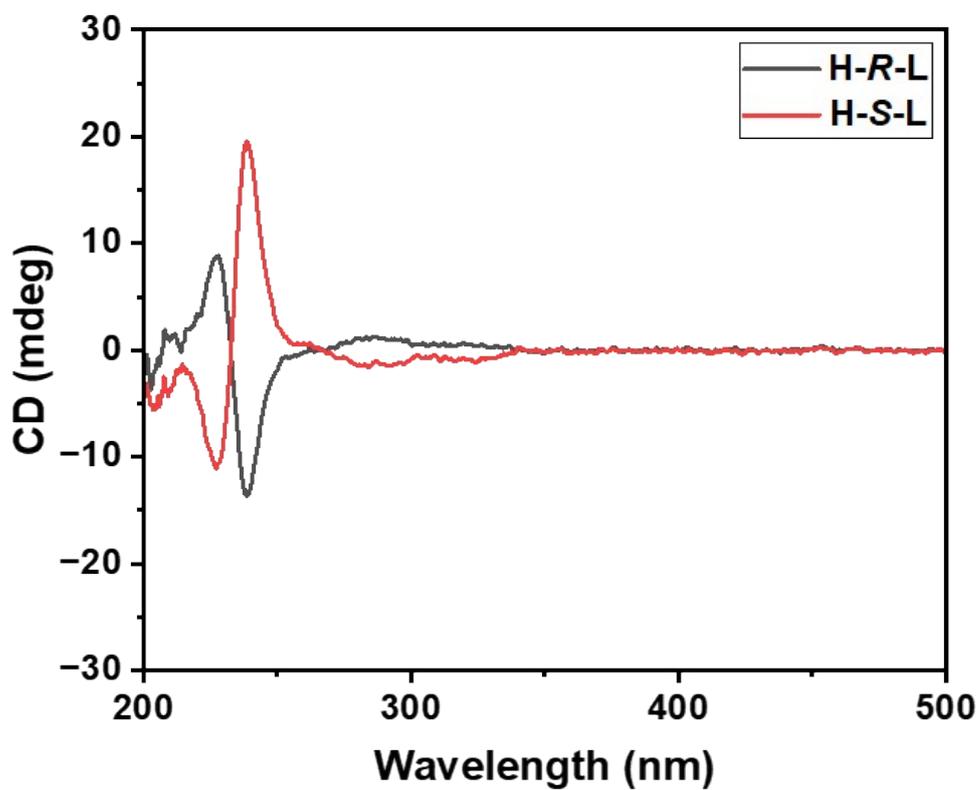
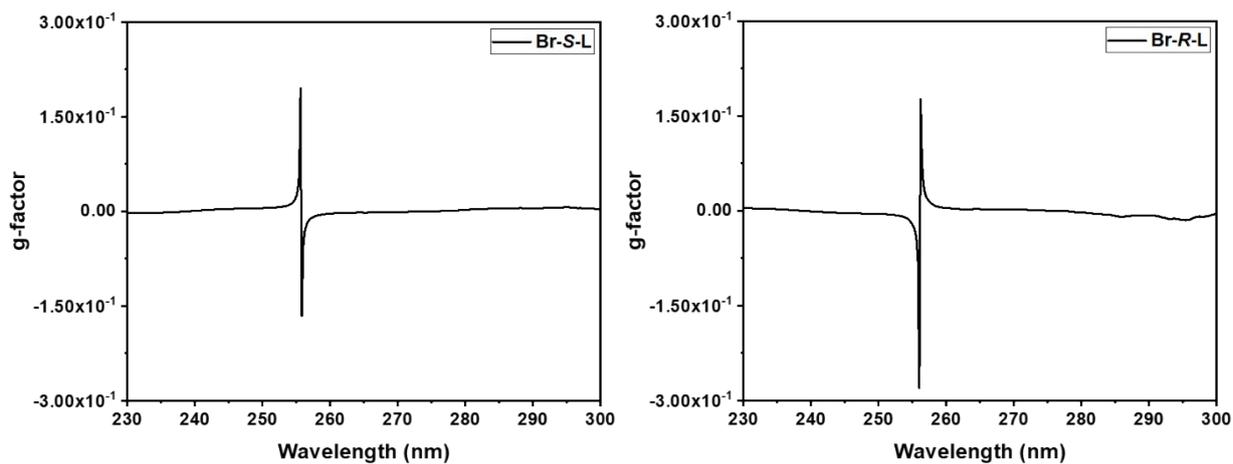
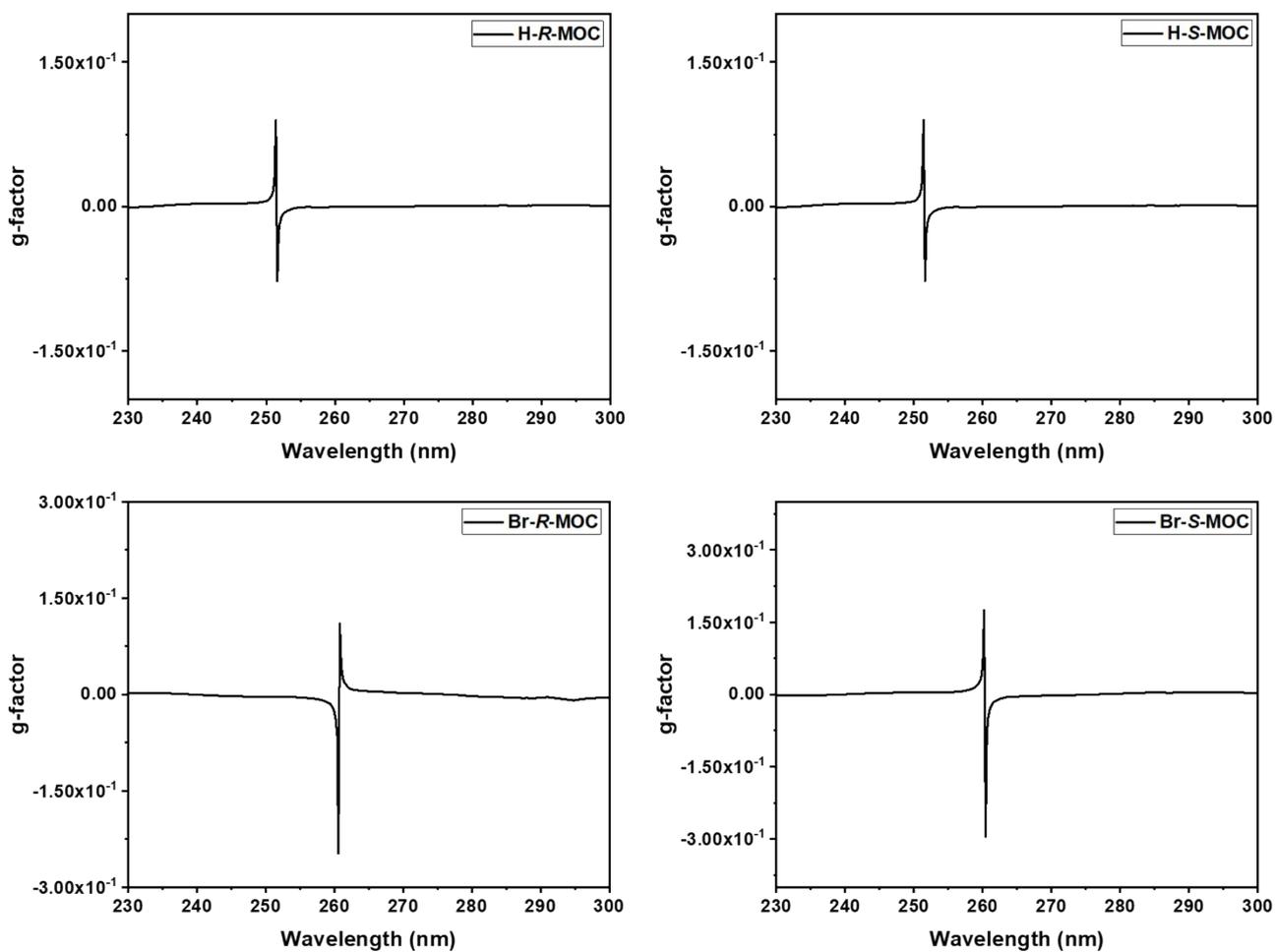


Fig. S23 The CD curves of the chiral ligands in THF.



**Fig. S24** The g-factor curves of the chiral ligands in THF.



**Fig. S25** The g-factor curves of the chiral MOCs in THF.

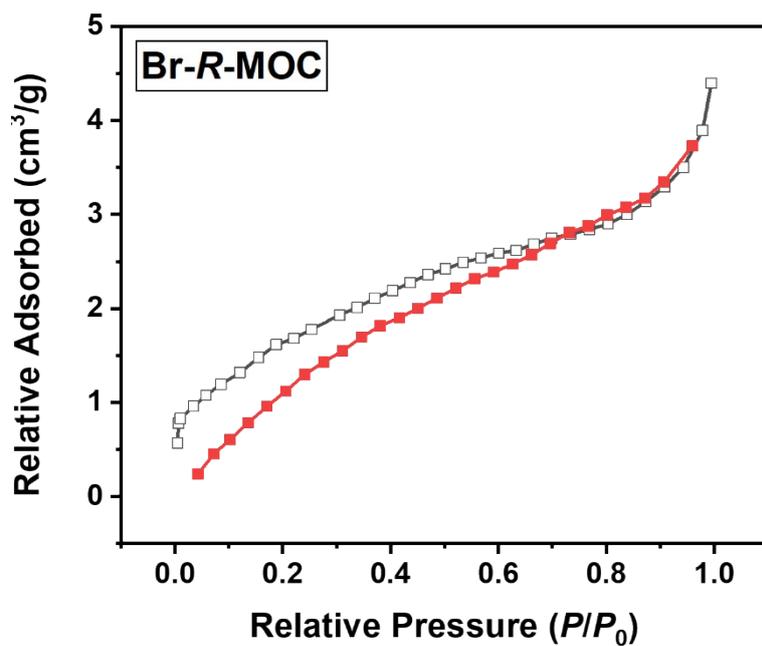


Fig. S26 The  $N_2$  adsorption-desorption isotherms of **Br-R-MOC**.

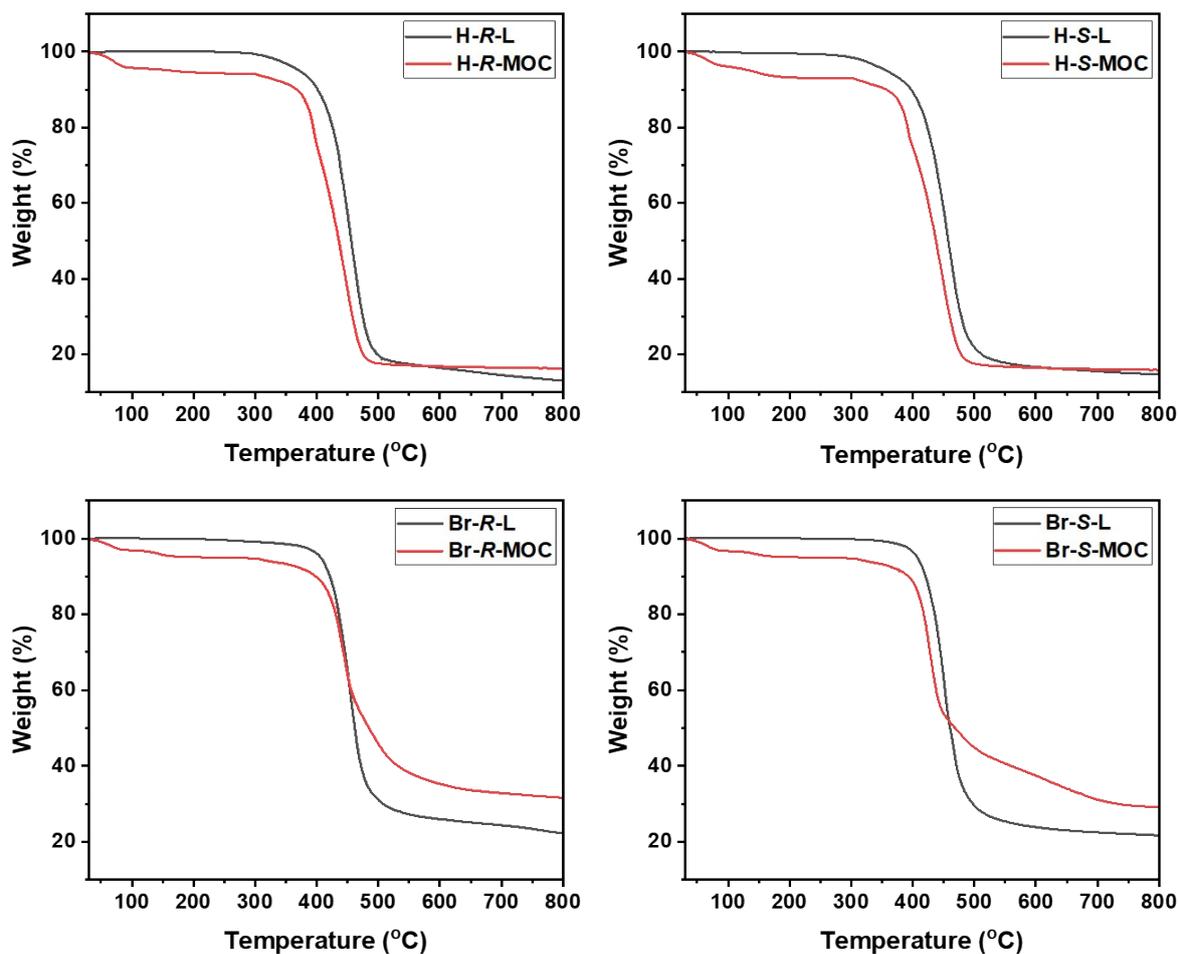


Fig. S27 The TGA plots of the chiral ligands and related MOCs.