

## Supporting Information

### Self-assembly of chiral BINOL cages via imine condensation

E. Ramakrishna,<sup>‡a</sup> Jia-Dong Tang,<sup>‡b</sup> Jia-Ju Tao,<sup>b</sup> Qiang Fang,<sup>a,b</sup> Zibin Zhang,<sup>b</sup>

Jiaying Huang\*<sup>a</sup> and Shijun Li\*<sup>b</sup>

<sup>a</sup> *School of Food Science and Biotechnology, Zhejiang Gongshang University,  
Hangzhou 310018, P. R. China*

<sup>b</sup> *College of Material, Chemistry and Chemical Engineering, Hangzhou Normal  
University, Hangzhou 311121, P. R. China*

**Email address:** huangjy@zjgsu.edu.cn, l\_shijun@hznu.edu.cn

<sup>‡</sup>These two authors contribute equally to this work.

1. Materials and Methods	S2
2. Synthesis of chiral BINOL cages 5	S3
3. Reduction of the [2+3] imine cages	S17
4. UV-vis and fluorescence spectra of the imine cages	S21
5. Fluorescence spectra for chiral recognition	S22
6. Single-crystal structure and X-ray analysis data of (R)-5	S24
7. Compared <sup>1</sup> H NMR spectra for chiral recognition	S26
8. References	S28

## 1. Materials and Methods

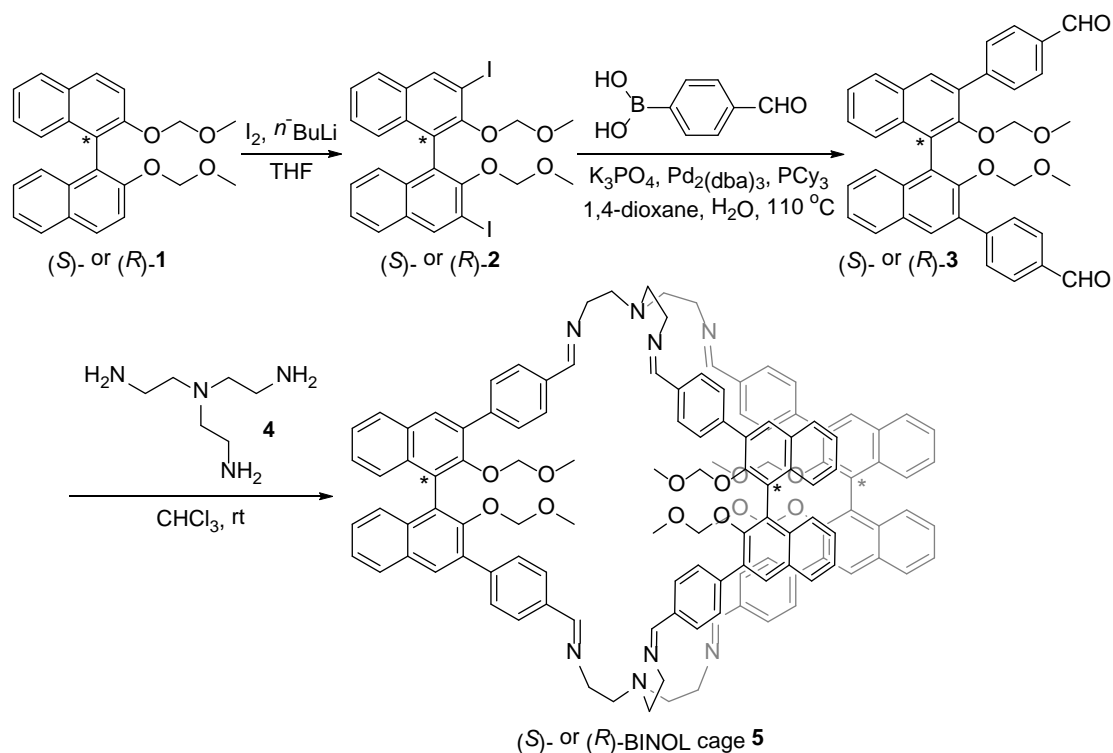
Tetrahydrofuran (THF) was dried over sodium metal and freshly distilled under nitrogen atmosphere prior to use. Other reactants are of reagent-grade quality and used as commercially purchased without further purification. 2,2'-Bis(methoxymethoxy)-1,1'-binaphthalene (**1**) was prepared according to the literature procedures.<sup>S1</sup> Column chromatography was performed by using silica gel (Yantai Institute of Chemical Industry) packed columns and with low pressure or atmospheric pressure operation.

NMR spectra were collected on a Bruker AVANCE DMX-500 spectrometer and chemical shifts were reported relative to internal standard tetramethylsilane (TMS) at 0.00 ppm or the residual solvent signals. Electrospray ionization mass spectra (ESI-MS) were obtained on an Agilent 1290-6530 UPLC-Q-TOF spectrometer using electrospray ionization. UV-vis spectra were measured with a Hitachi UH-5300 at room temperature. Fluorescence spectra were recorded on an F-7000 FL spectrophotometer at room temperature. Optical rotation analyses were performed on an MCP 500 optical instrument.

Circular dichroism (CD) spectra were recorded on a JASCO J-815 circular dichroism chiroptical spectrometer at room temperature. After adding a 0.3 mL solution of chiral cages in CHCl<sub>3</sub> (*c* = 0.13 mM) to the sample cell (*l* = 1 mm), the CD data were then recorded in a wavelength range of 230–500 nm with a scanning speed of 500 nm/min.

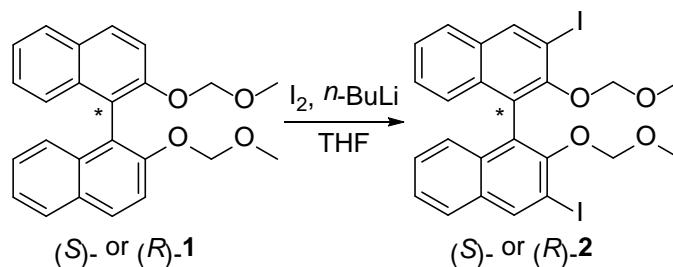
Single crystals of (*R*)-**5** were obtained by rapid addition of a chloroform solution of (*R*)-**5** into excess methanol and then standing the mixture for 3 days. A suitable crystal was selected and measured on a Bruker APEX-II CCD diffractometer. The crystal was kept at 170.0 K during data collection. The structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.

## 2. Synthesis of chiral BINOL cages 5



### 2.1 Synthesis of (*S*)- and (*R*)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene

**2<sup>SI</sup>**



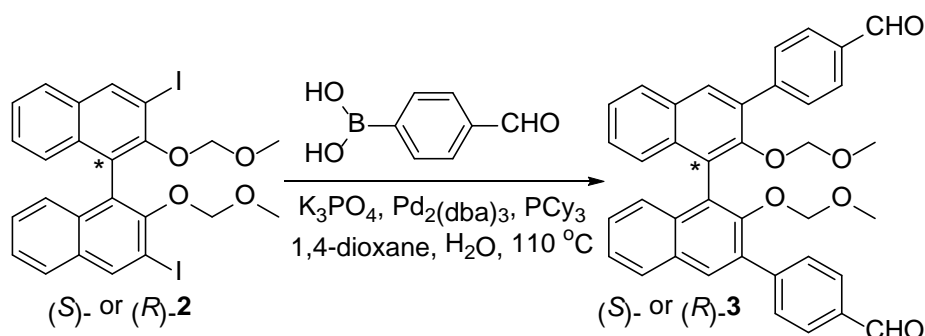
To a solution of (*S*)- or and (*R*)-**1** (6.5 g, 17.4 mmol) in 100 mL of dried THF, *n*-butyllithium (20.8 mL, 2.5 M in hexanes, 52.0 mmol) was added dropwise at  $-78$  °C. The reaction mixture was stirred at the same temperature for 30 min followed by 3 h at room temperature. After the solution was cooled to  $-78$  °C, a solution of iodine (13.0 g, 52.0 mmol) in 30 mL of THF was added dropwise. The mixture was slowly warmed up to room temperature and was further stirred at room temperature for 2 h. The reaction was then quenched with methanol and washed with saturated sodium thiosulfate solution to remove unreacted iodine. After the solution was extracted three times with ethyl acetate, the organic phases were combined, washed

with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The resulted residue was purified by column chromatography over silica gel (petroleum ether : ethyl acetate = 200 : 1) to afford product.

(*S*)-**2** (7.85 g, 72% yield): m.p. 115–116 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.55 (s, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.43 (ddd, *J* = 8.1, 6.9, 1.0 Hz, 2H), 7.30 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.82 (d, *J* = 5.7 Hz, 2H), 4.70 (d, *J* = 5.7 Hz, 2H), 2.61 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 152.2, 140.0, 133.8, 132.2, 127.1, 126.8, 126.5, 126.3, 125.9, 99.4, 92.5, 56.5. ESI-TOF-MS (*m/z*) Calcd. for C<sub>24</sub>H<sub>20</sub>I<sub>2</sub>NaO<sub>4</sub> [M + Na]<sup>+</sup>: 648.9343; Found: 648.9374, error: 4.7 ppm. Calcd. for C<sub>48</sub>H<sub>40</sub>I<sub>4</sub>NaO<sub>8</sub> [2M + Na]<sup>+</sup>: 1274.8794; Found: 1274.8821, error: 2.1 ppm.

(*R*)-**2** (7.72 g, 71% yield): m.p. 112–114 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.54 (s, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.43 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 2H), 7.30 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 4.81 (d, *J* = 5.7 Hz, 2H), 4.69 (d, *J* = 5.7 Hz, 2H), 2.60 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 152.2, 140.0, 133.8, 132.2, 127.1, 126.8, 126.5, 126.3, 125.9, 99.4, 92.5, 56.5. ESI-TOF-MS (*m/z*) Calcd. for C<sub>24</sub>H<sub>20</sub>I<sub>2</sub>NaO<sub>4</sub> [M + Na]<sup>+</sup>: 648.9343; Found: 648.9377, error: 5.2 ppm. Calcd. for C<sub>48</sub>H<sub>40</sub>I<sub>4</sub>NaO<sub>8</sub> [2M + Na]<sup>+</sup>: 1274.8794; Found: 1274.8823, error: 2.3 ppm.

## 2.2 Synthesis of (*S*)- and (*R*)-4,4'-(2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl)dibenzaldehyde **3**



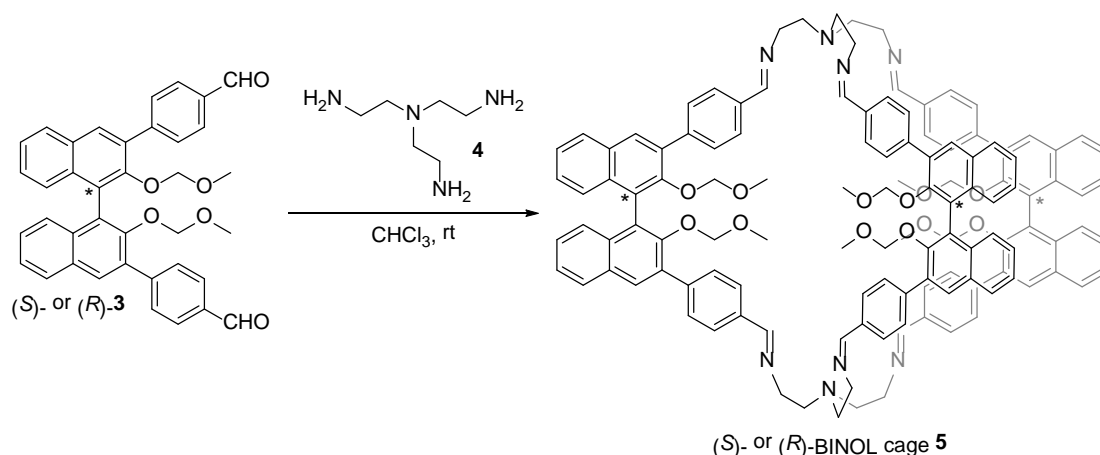
After (*S*)- or and (*R*)-**2** (2.00 g, 3.19 mmol), 4-formylphenylboronic acid (980.6 mg, 6.54 mmol), tripotassium phosphate (4.07 mg, 19.2 mmol), tris(dibenzylideneacetone)dipalladium (58.4 mg, 0.064 mmol), and

tricyclohexylphosphine (42.0 mg, 0.146 mmol) were added to a three-necked round bottom flask, a mixture of 1,4-dioxane and H<sub>2</sub>O (4:1, v/v, 50 mL) was added under nitrogen atmosphere. The reaction mixture was stirred at 110 °C for 18 h. After complete consumption of the starting material, the mixture was cooled down to room temperature and quenched with saturated ethylenediaminetetraacetic acid (EDTA) solution. The mixture was extracted three times with dichloromethane and the organic phases were combined, washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography over silica gel (petroleum ether : ethyl acetate = 10 : 1) to afford (*S*)- or (*R*)-**3** as a white solid.

(*S*)-**3** (1.23 g, 66% yield): m.p. 186–188 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.10 (s, 2H), 8.03–7.99 (m, 6H), 7.95 (dd, *J* = 14.9, 8.2 Hz, 6H), 7.46 (dd, *J* = 10.7, 3.9 Hz, 2H), 7.36–7.29 (m, 4H), 4.41 (d, *J* = 5.9 Hz, 2H), 4.37 (d, *J* = 5.9 Hz, 2H), 2.38 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 192.0, 151.1, 145.4, 135.2, 134.2, 134.0, 131.0, 130.8, 130.4, 129.8, 128.2, 127.0, 126.6, 126.4, 125.6, 98.9, 56.1. ESI-TOF-MS (*m/z*): Calcd. for C<sub>38</sub>H<sub>30</sub>NaO<sub>6</sub> [M + Na]<sup>+</sup>: 605.1935, Found: 605.1932, error: –0.5 ppm.

(*R*)-**3** (1.36 g, 68% yield): m.p. 185–187 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.10 (s, 2H), 8.07–7.99 (m, 6H), 7.95 (dd, *J* = 14.3, 8.2 Hz, 6H), 7.46 (dd, *J* = 10.7, 3.9 Hz, 2H), 7.37–7.28 (m, 4H), 4.41 (d, *J* = 5.9 Hz, 2H), 4.37 (d, *J* = 5.9 Hz, 2H), 2.38 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 192.0, 151.2, 145.4, 135.2, 134.3, 134.0, 131.0, 130.8, 130.4, 129.8, 128.2, 127.0, 126.6, 126.4, 125.6, 98.9, 56.1. ESI-TOF-MS (*m/z*): Calcd. for C<sub>38</sub>H<sub>30</sub>NaO<sub>6</sub> [M + Na]<sup>+</sup>: 605.1935, Found: 605.1940, error: 0.8 ppm.

### 2.3 Synthesis of (*S*)- and (*R*)-BINOL cages **5**



A solution of tris(2-aminoethyl)amine (0.2 M in chloroform, 308  $\mu$ L, 0.063 mmol) was added dropwise into a solution of (*S*)- or (*R*)-**3** (50 mg, 0.086 mmol) in 5 mL of chloroform or dichloromethane. After the reaction mixture was stirred at 25  $^{\circ}$ C for 24 h, the mixture was poured into 50 mL of methanol. The precipitate was filtered and dried under vacuum to afford (*S*)- or (*R*)-BINOL cage **5** as a white solid.

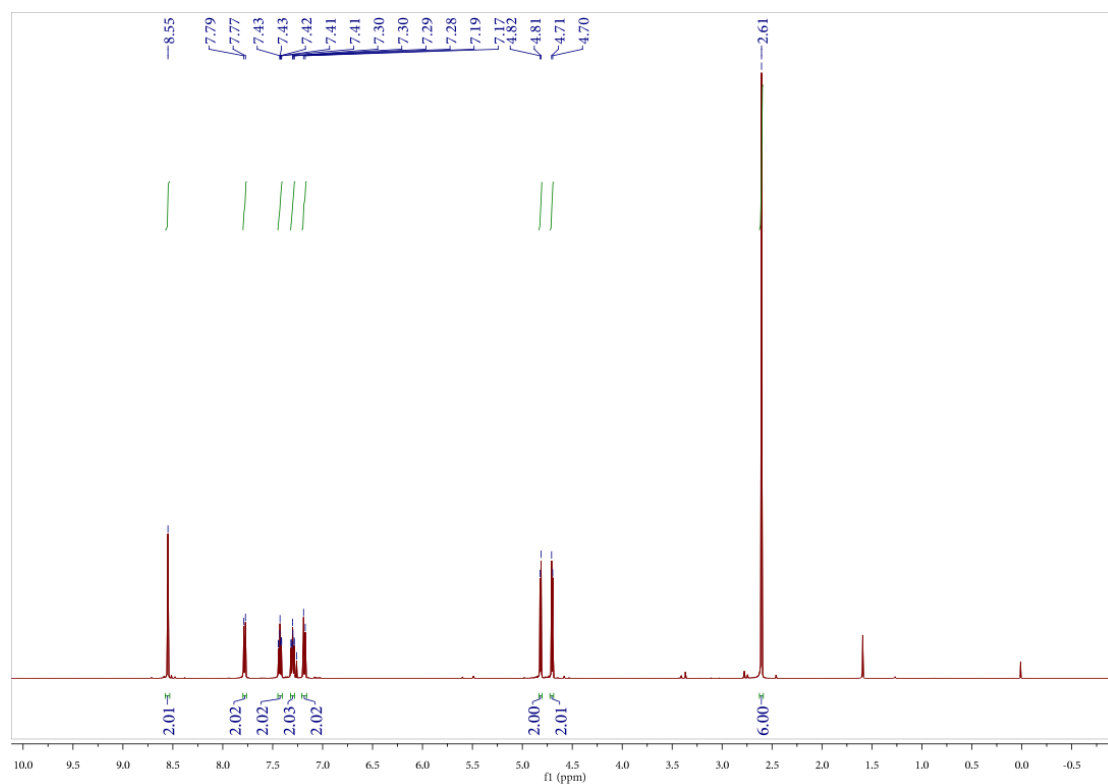
(*S*)-**5** (52 mg, 94% yield):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (s, 6H), 7.82–7.80 (m, 18H), 7.66 (s, 6H), 7.33–7.28 (m, 18H), 7.21–7.13 (m, 6H), 7.05 (d,  $J$  = 8.6 Hz, 6H), 4.48 (d,  $J$  = 5.1 Hz, 6H), 4.30 (d,  $J$  = 5.4 Hz, 6H), 3.59 (s, 12H), 3.15–3.02 (m, 6H), 3.01–2.93 (m, 6H), 2.33 (s, 18H). ESI-TOF-MS ( $m/z$ ): Calcd. for  $\text{C}_{126}\text{H}_{114}\text{N}_8\text{NaO}_{12}$  [ $\text{M} + \text{Na}$ ] $^+$ : 1954.8481, Found: 1954.8469, error:  $-0.6$  ppm. Calcd. for  $\text{C}_{126}\text{H}_{115}\text{N}_8\text{O}_{12}$  [ $\text{M} + \text{H}$ ] $^+$ : 1932.8662, Found: 1932.8644, error:  $-0.9$  ppm. Calcd. for  $\text{C}_{126}\text{H}_{116}\text{N}_8\text{O}_{12}$  [ $\text{M} + 2\text{H}$ ] $^{2+}$ : 966.9367, Found: 966.9350, error:  $-1.8$  ppm.  $[\alpha]_D^{20} = +98$  ( $c$  = 0.004 in  $\text{CHCl}_3$ ).

(*R*)-**5** (51 mg, 92% yield):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (s, 6H), 7.80 (d,  $J$  = 8.3 Hz, 18H), 7.66 (s, 6H), 7.37–7.28 (m, 18H), 7.19–7.13 (m, 6H), 7.05 (d,  $J$  = 8.6 Hz, 6H), 4.47 (d,  $J$  = 5.3 Hz, 6H), 4.30 (d,  $J$  = 5.5 Hz, 6H), 3.59 (s, 12H), 3.10–3.02 (m, 6H), 3.01–2.94 (m, 6H), 2.33 (s, 18H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.5, 150.8, 141.1, 135.5, 134.1, 131.0, 130.9, 130.0, 128.1, 127.7, 126.9, 126.5, 125.3, 100.0, 98.2, 60.4, 58.9, 55.4. ESI-TOF-MS ( $m/z$ ): Calcd. for  $\text{C}_{126}\text{H}_{114}\text{N}_8\text{NaO}_{12}$  [ $\text{M} + \text{Na}$ ] $^+$ : 1954.8481, Found: 1954.8451, error:  $-1.5$  ppm. Calcd. for  $\text{C}_{126}\text{H}_{115}\text{N}_8\text{O}_{12}$  [ $\text{M} + \text{H}$ ] $^+$ : 1932.8662, Found: 1932.8658, error:  $-0.2$  ppm. Calcd. for  $\text{C}_{126}\text{H}_{116}\text{N}_8\text{O}_{12}$  [ $\text{M} + 2\text{H}$ ] $^{2+}$ :

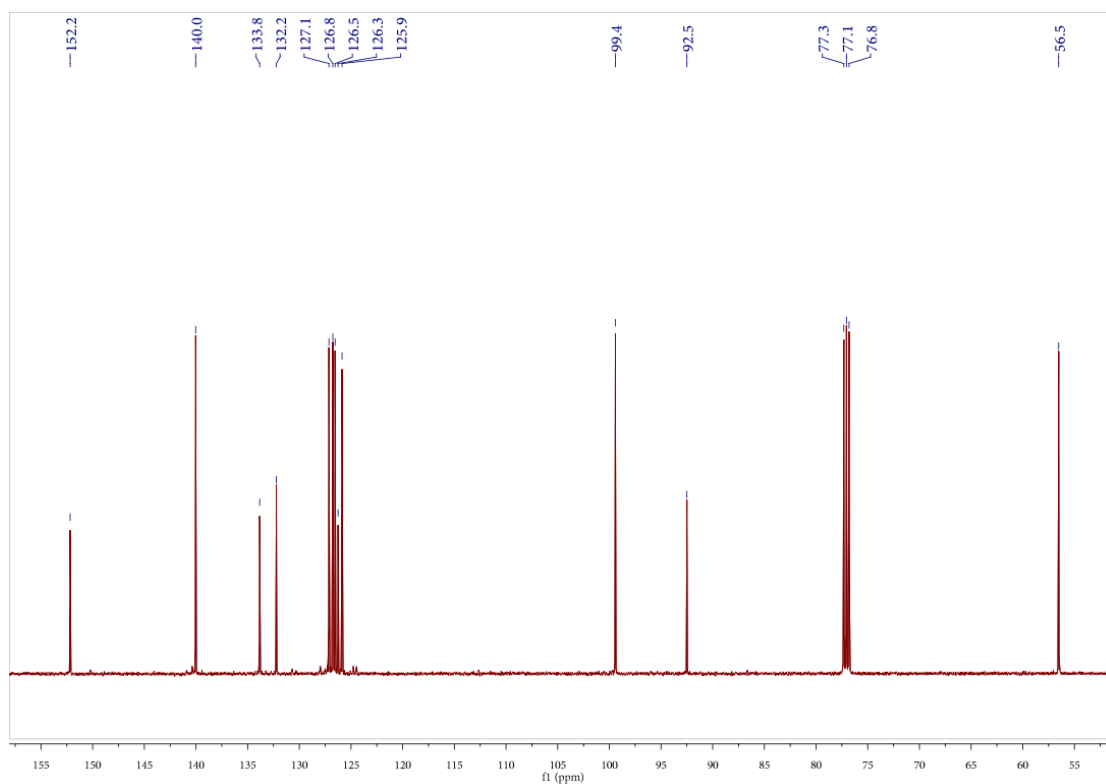
966.9367, Found: 966.9371, error: 0.4 ppm.  $[\alpha]_D^{20} = -96$  ( $c = 0.004$  in  $\text{CHCl}_3$ ).

(*R*)-**5**:  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.97 (s, 6H), 7.81 (d,  $J = 8.1$  Hz, 6H), 7.75 (d,  $J = 8.4$  Hz, 12H), 7.63 (s, 6H), 7.32–7.29 (m, 6H), 7.26 (d,  $J = 7.6$  Hz, 12H), 7.16–7.11 (m, 6H), 6.99 (d,  $J = 8.6$  Hz, 6H), 4.45 (d,  $J = 5.4$  Hz, 6H), 4.30 (d,  $J = 5.5$  Hz, 6H), 3.61–3.47 (m, 12H), 3.01 (dd,  $J = 10.3, 4.5$  Hz, 6H), 2.95–2.90 (m, 6H), 2.32 (s, 18H).

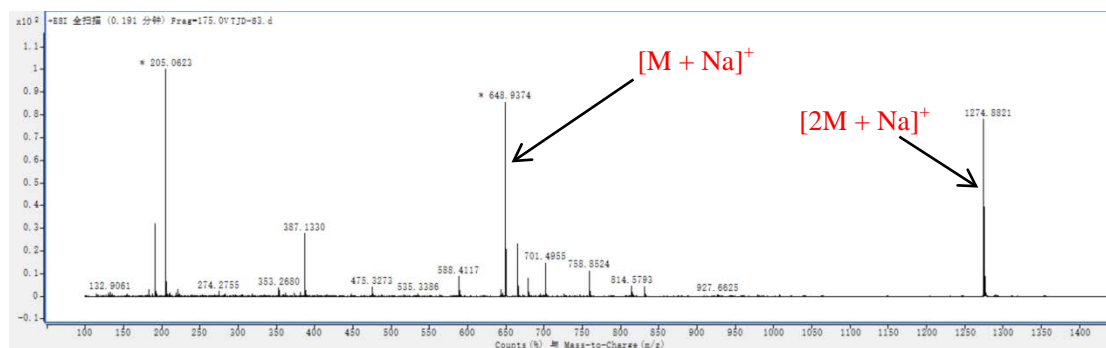
#### 2.4 $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and ESI-MS spectra of the compounds **2**, **3** and **5**



**Fig. S1**  $^1\text{H}$  NMR spectrum of (*S*)-**2** in  $\text{CDCl}_3$  at 22 °C.

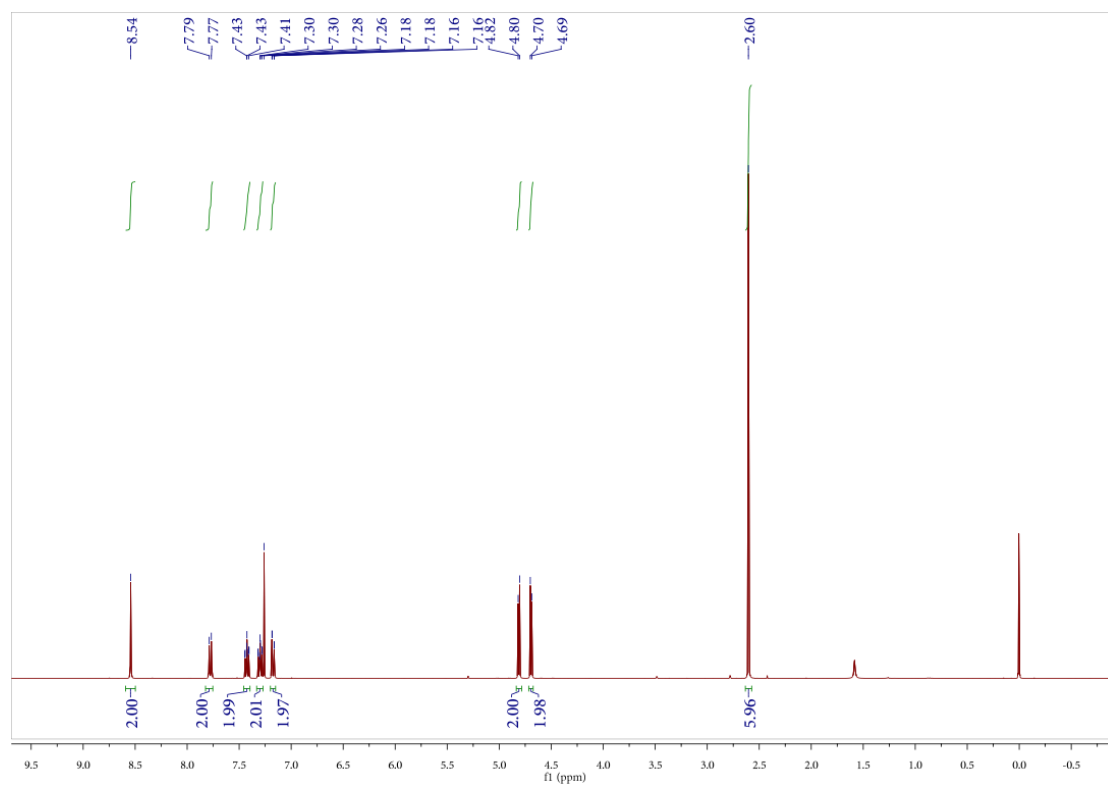


**Fig. S2**  $^{13}\text{C}$  NMR spectrum of (*S*)-**2** in  $\text{CDCl}_3$  at 22 °C.

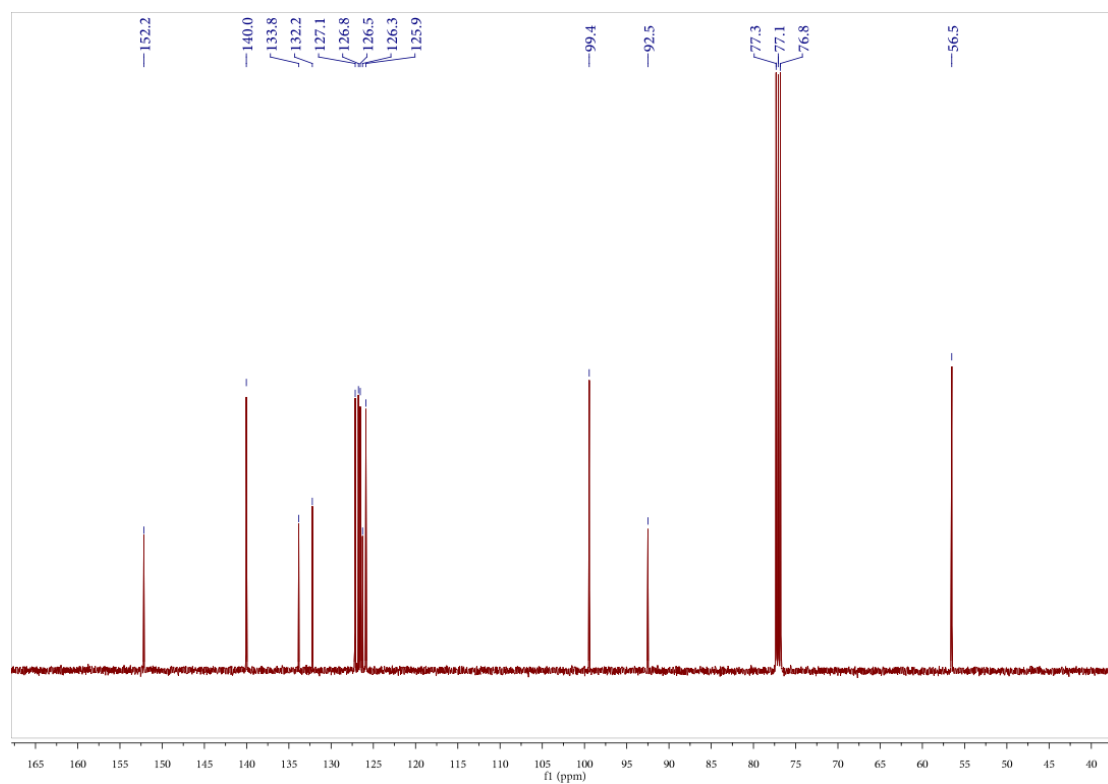


**Fig. S3** ESI-MS spectrum of (*S*)-**2**. ESI-TOF-MS ( $m/z$ ) Calcd. for  $\text{C}_{24}\text{H}_{20}\text{I}_2\text{NaO}_4$   $[\text{M} + \text{Na}]^+$ : 648.9343; Found: 648.9374, error: 4.7 ppm. Calcd. for  $\text{C}_{48}\text{H}_{40}\text{I}_4\text{NaO}_8$   $[2\text{M} + \text{Na}]^+$ : 1274.8794; Found: 1274.8821, error: 2.1 ppm.

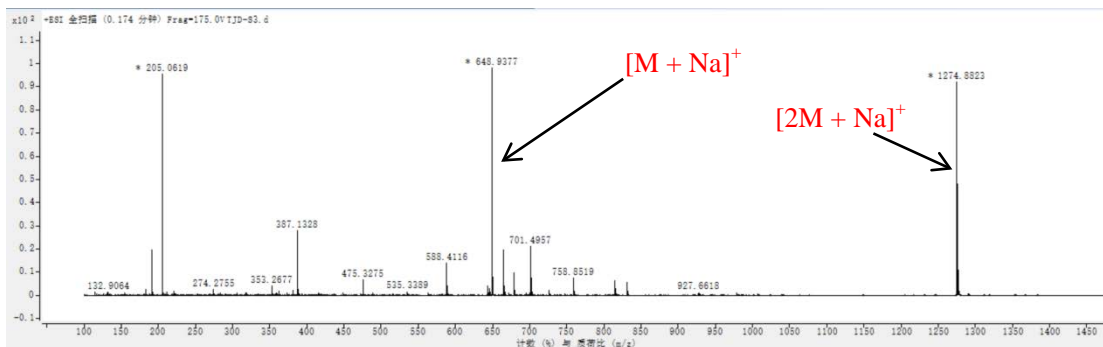




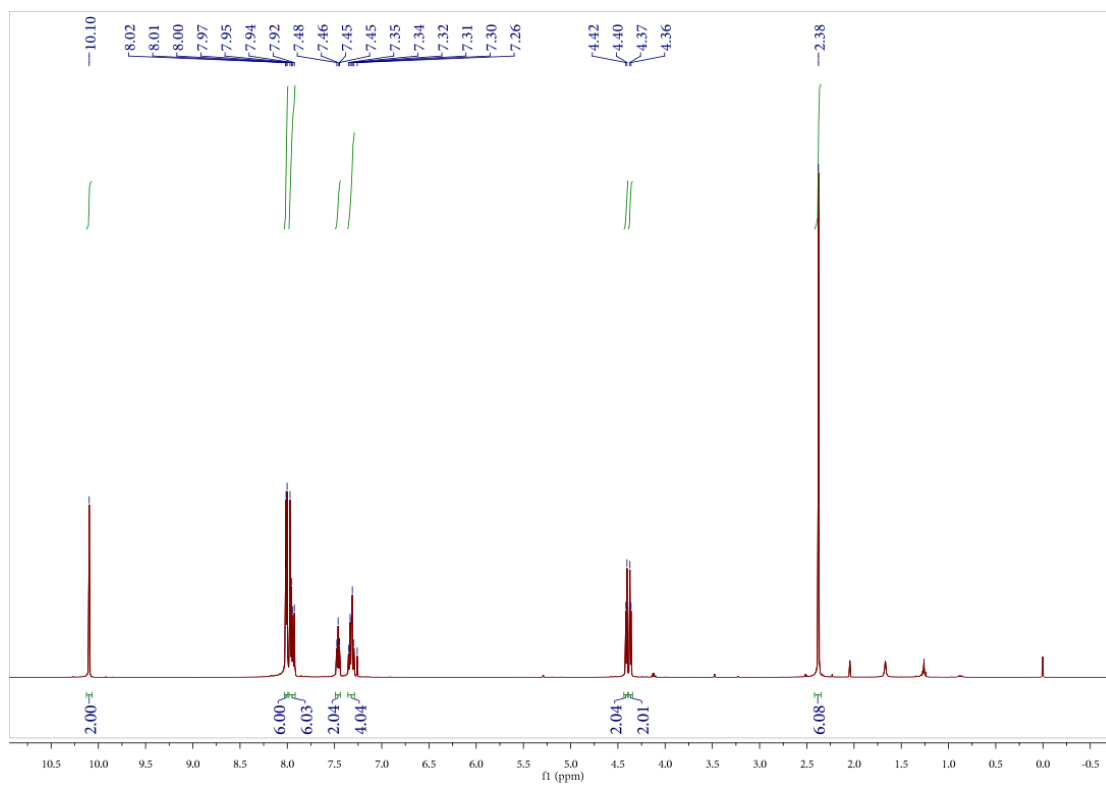
**Fig. S4**  $^1\text{H}$  NMR spectrum of (*R*)-**2** in  $\text{CDCl}_3$  at 22 °C.



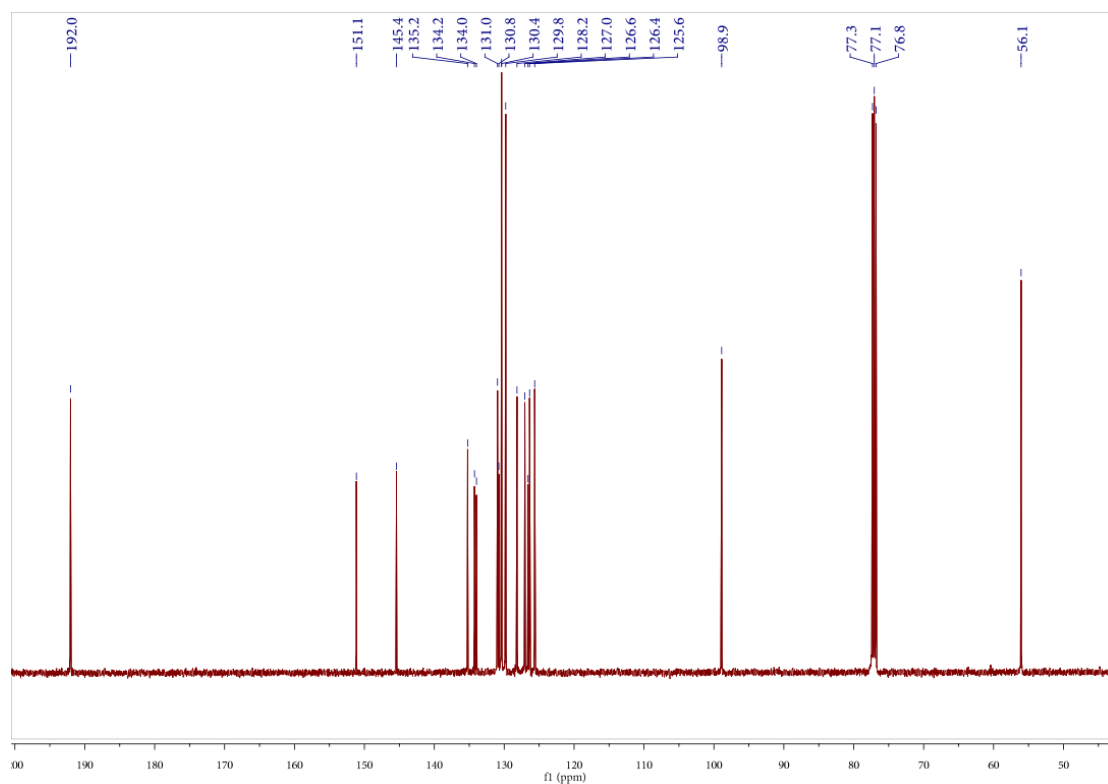
**Fig. S5**  $^{13}\text{C}$  NMR spectrum of (*R*)-**2** in  $\text{CDCl}_3$  at 22 °C.



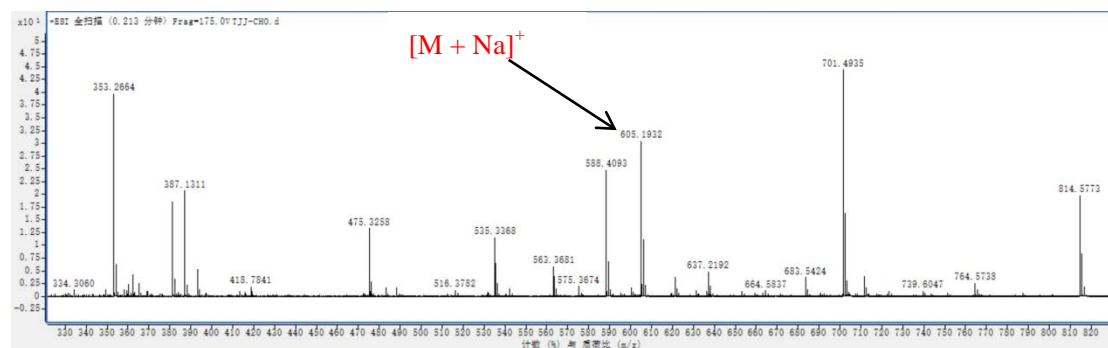
**Fig. S6** ESI-MS spectrum of (*R*)-**2**. ESI-TOF-MS ( $m/z$ ) Calcd. for  $C_{24}H_{20}I_2NaO_4$   $[M + Na]^+$ : 648.9343; Found: 648.9377, error: 5.2 ppm. Calcd. for  $C_{48}H_{40}I_4NaO_8$   $[2M + Na]^+$ : 1274.8794; Found: 1274.8823, error: 2.3 ppm.



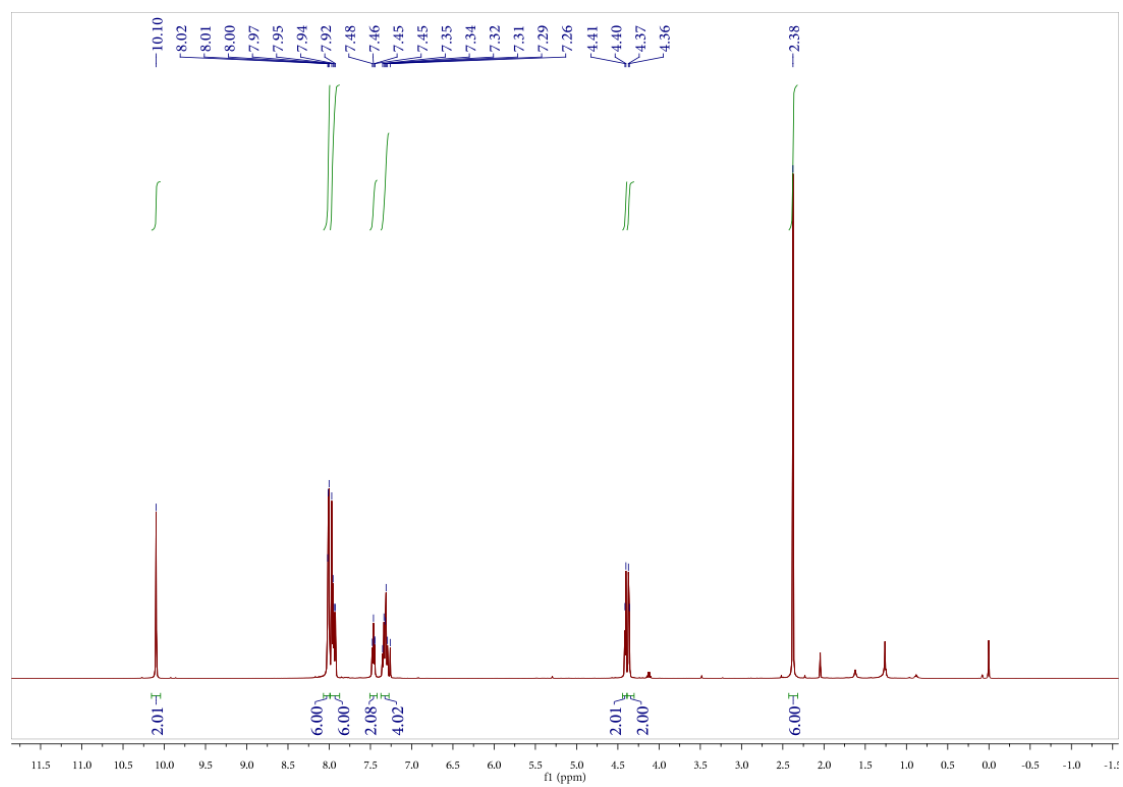
**Fig. S7**  $^1H$  NMR spectrum of (*S*)-**3** in  $CDCl_3$  at 22 °C.



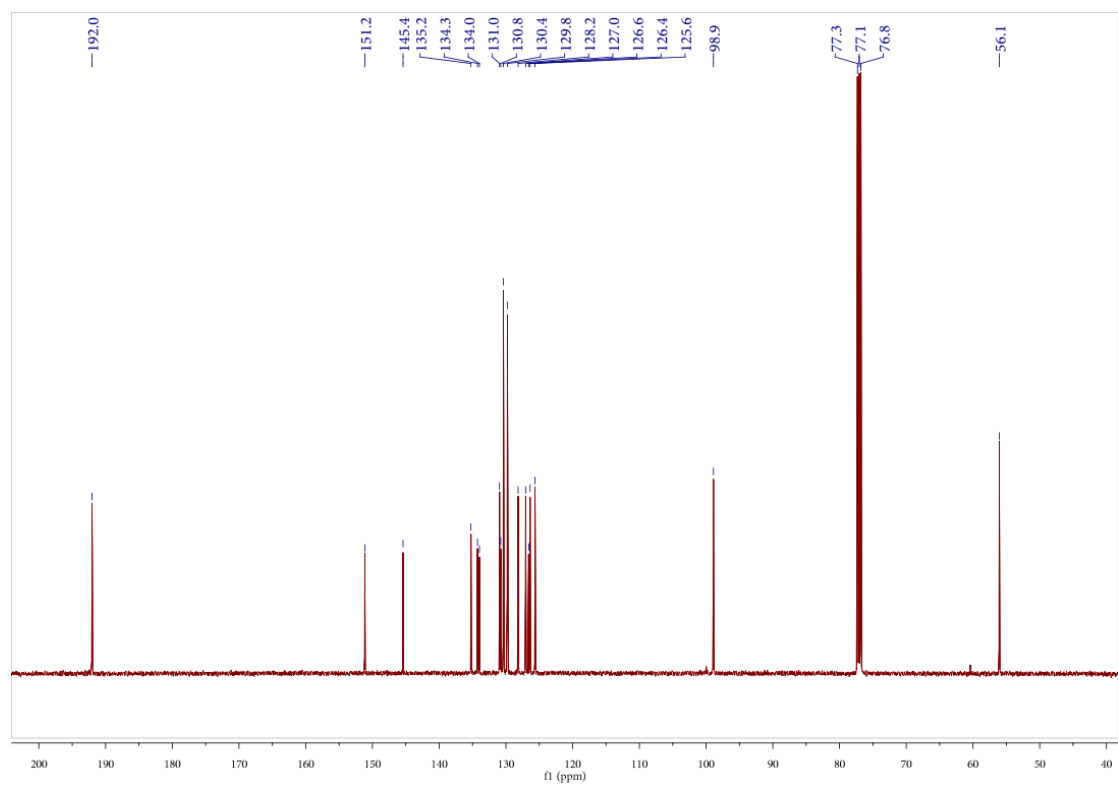
**Fig. S8**  $^{13}\text{C}$  NMR spectrum of (*S*)-**3** in  $\text{CDCl}_3$  at 22 °C.



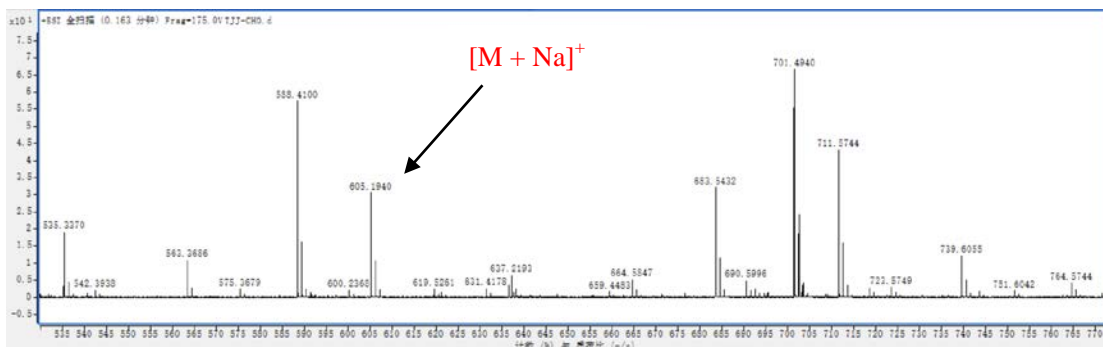
**Fig. S9** ESI-MS spectrum of (*S*)-**3**. ESI-TOF-MS ( $m/z$ ): Calcd. for  $\text{C}_{38}\text{H}_{30}\text{NaO}_6$   $[\text{M} + \text{Na}]^+$ : 605.1935, Found: 605.1932, error:  $-0.5$  ppm.



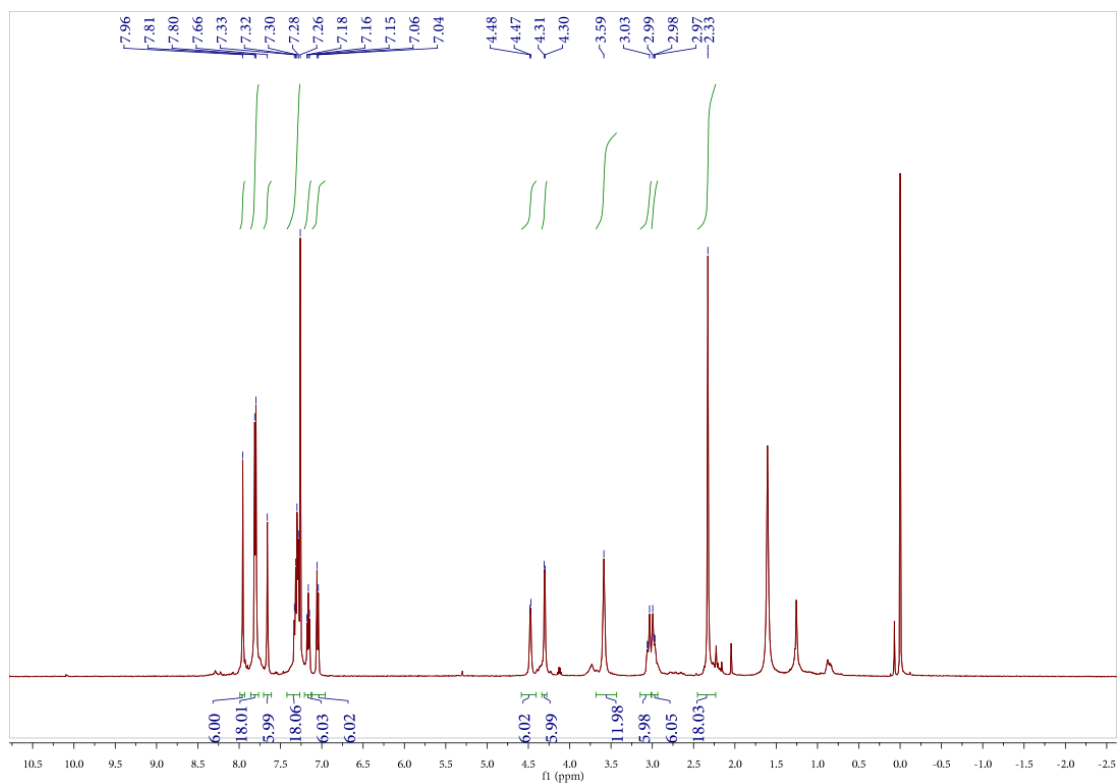
**Fig. S10**  $^1\text{H}$  NMR spectrum of (*R*)-**3** in  $\text{CDCl}_3$  at 22 °C.



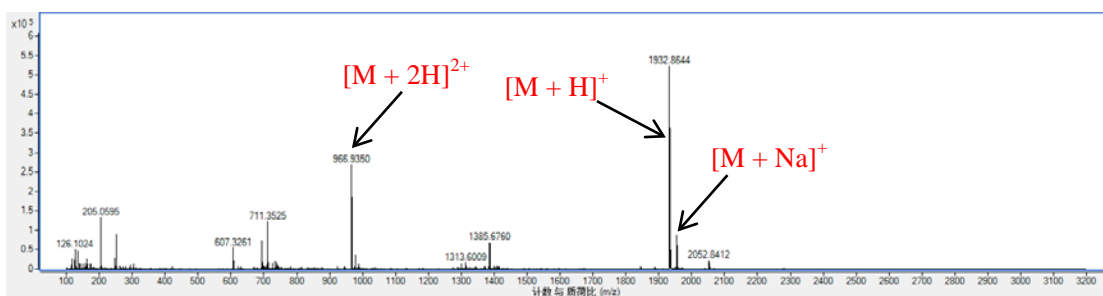
**Fig. S11**  $^{13}\text{C}$  NMR spectrum of (*R*)-**3** in  $\text{CDCl}_3$  at 22 °C.



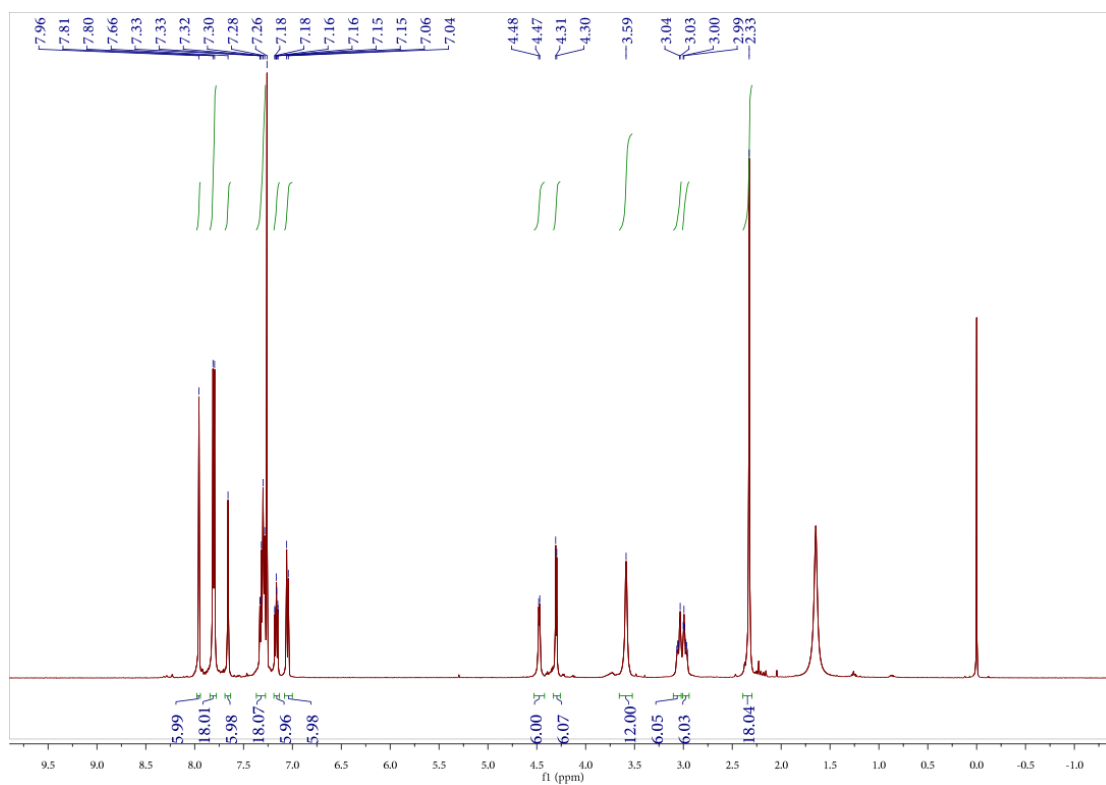
**Fig. S12** ESI-MS spectrum of (*R*)-**3**. ESI-TOF-MS ( $m/z$ ): Calcd. for  $C_{38}H_{30}NaO_6$   $[M + Na]^+$ : 605.1935, Found: 605.1940, error: 0.8 ppm.



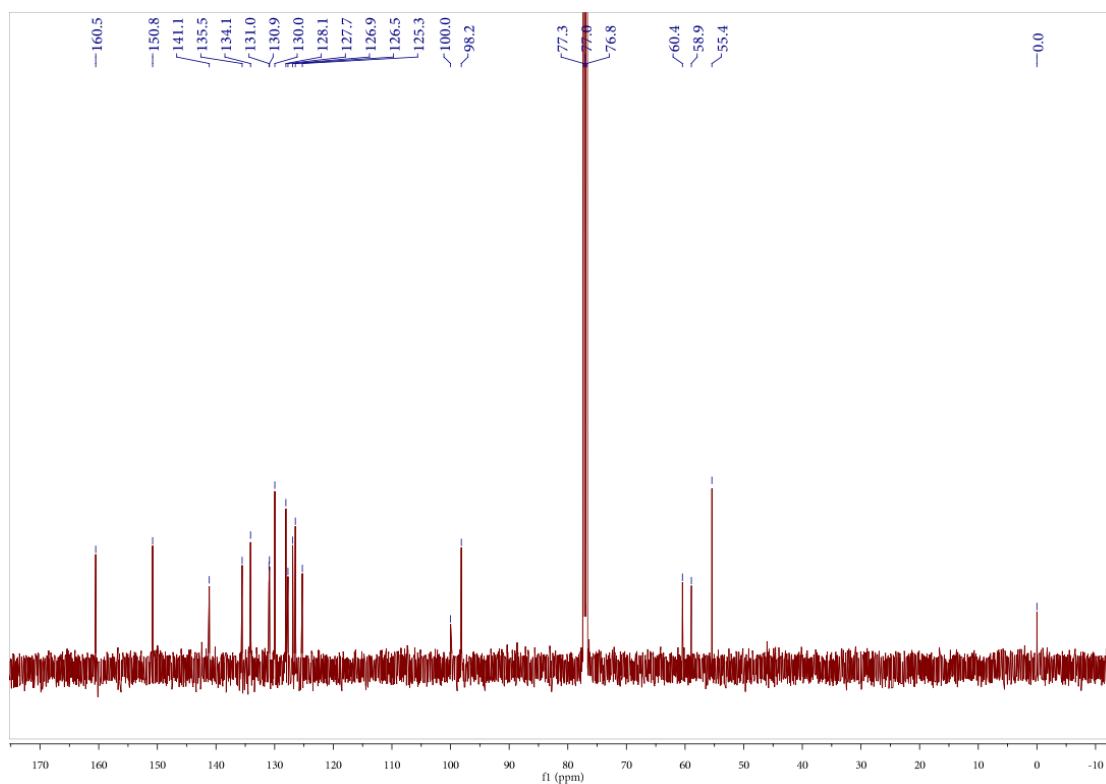
**Fig. S13**  $^1H$  NMR spectrum of (*S*)-**5** in  $CDCl_3$  at 22 °C.



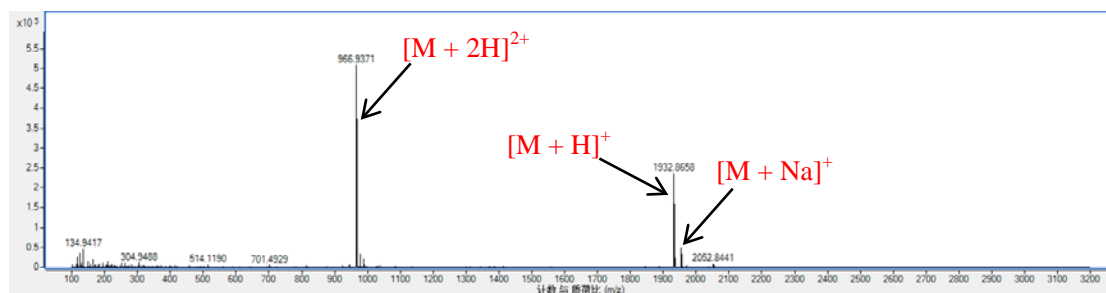
**Fig. S14** ESI-MS spectrum of (*S*)-**5**. ESI-TOF-MS ( $m/z$ ): Calcd. for  $C_{126}H_{114}N_8NaO_{12}$   $[M + Na]^+$ : 1954.8481, Found: 1954.8459, error:  $-1.1$  ppm. Calcd. for  $C_{126}H_{115}N_8O_{12}$   $[M + H]^+$ : 1932.8662, Found: 1932.8644, error:  $-0.9$  ppm. Calcd. for  $C_{126}H_{116}N_8O_{12}$   $[M + 2H]^{2+}$ : 966.9367, Found: 966.9350, error:  $-1.8$  ppm.



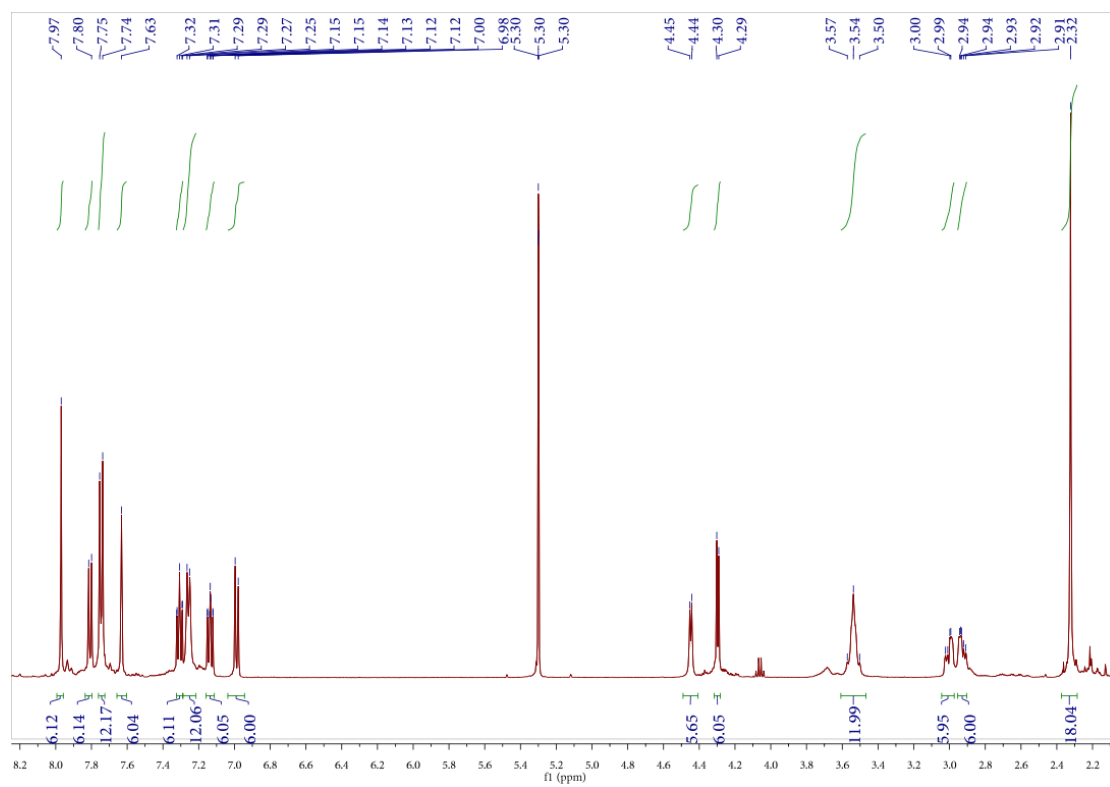
**Fig. S15**  $^1H$  NMR spectrum of (*R*)-**5** in  $CDCl_3$  at  $22$  °C.



**Fig. S16**  $^{13}\text{C}$  NMR spectrum of (*R*)-**5** in  $\text{CDCl}_3$  at 22 °C.



**Fig. S17** ESI-MS spectrum of (*R*)-**5**. ESI-TOF-MS ( $m/z$ ): Calcd. for  $\text{C}_{126}\text{H}_{114}\text{N}_8\text{NaO}_{12}$   $[\text{M} + \text{Na}]^+$ : 1954.8481, Found: 1954.8451, error:  $-1.5$  ppm. Calcd. for  $\text{C}_{126}\text{H}_{115}\text{N}_8\text{O}_{12}$   $[\text{M} + \text{H}]^+$ : 1932.8662, Found: 1932.8658, error:  $-0.2$  ppm. Calcd. for  $\text{C}_{126}\text{H}_{116}\text{N}_8\text{O}_{12}$   $[\text{M} + 2\text{H}]^{2+}$ : 966.9367, Found: 966.9371, error:  $0.4$  ppm.

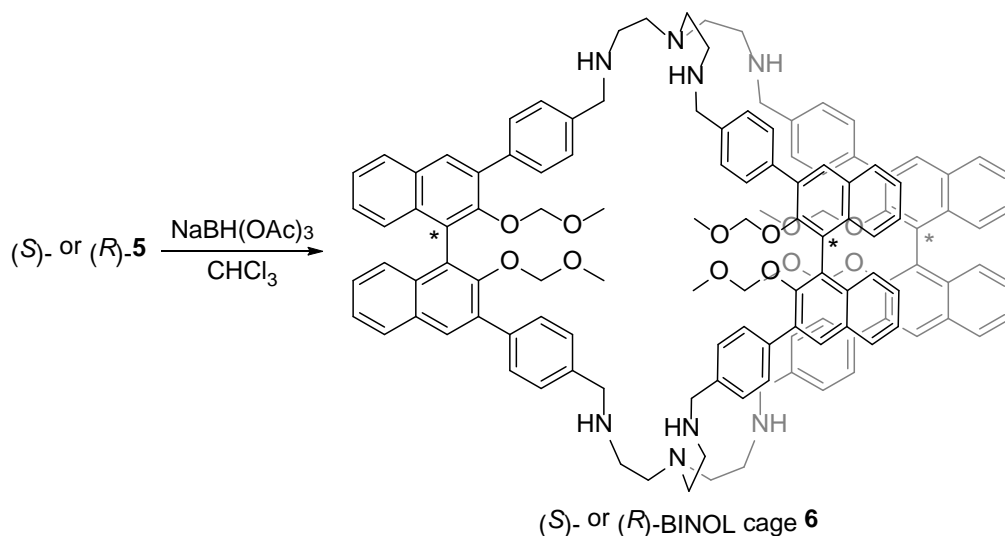


**Fig. S18**  $^1\text{H}$  NMR spectrum of (R)-5 in  $\text{CD}_2\text{Cl}_2$  at  $22\text{ }^\circ\text{C}$ .



### 3. Reduction of the [2+3] imine cages

#### 3.1 Synthesis of (*S*)- and (*R*)-BINOL cages **6**<sup>S2</sup>



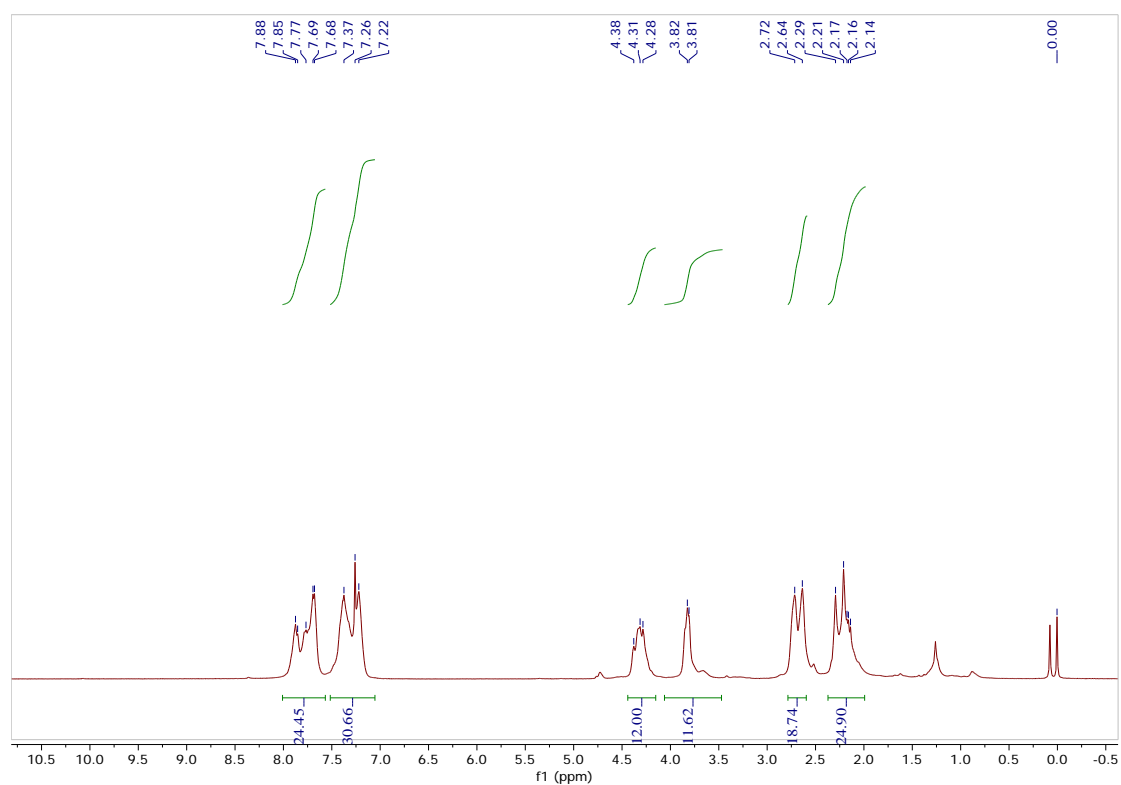
$\text{NaBH(OAc)}_3$  (200 mg, 0.944 mmol) was directly added into a reaction solution of **5** (from 0.086 mmol of **3**) at room temperature to selectively reduce the imine bonds. After the mixture was stirred for 8 h,  $\text{NaHCO}_3$  aqueous was added for neutralization. The organic phase was collected, dried by anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated to get the crude product. The crude product was then recrystallized in chloroform/hexane and chloroform/methanol, respectively, to afford the pure product.

(*S*)-**6** (53 mg, 95% yield); mp 314–315 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99–7.57 (m, 24H), 7.55–7.12 (m, 30H), 4.46–4.16 (m, 12H), 3.82 (t,  $J = 8.6$  Hz, 12H), 2.72–2.64 (m, 18H), 2.29–2.14 (m, 24H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  151.3, 139.4, 137.7, 135.1, 133.6, 130.8, 130.4, 129.6, 128.1, 127.8, 126.6, 126.4, 126.2, 125.1, 98.4, 55.7, 54.4, 53.7, 47.2. ESI-TOF-MS ( $m/z$ ): Calcd. for  $\text{C}_{126}\text{H}_{127}\text{N}_8\text{O}_{12}$  [ $\text{M} + \text{H}$ ] $^+$ : 1944.9602, Found: 1944.9540, error: –3.2 ppm. Calcd. for  $\text{C}_{126}\text{H}_{128}\text{N}_8\text{O}_{12}$  [ $\text{M} + 2\text{H}$ ] $^{2+}$ : 972.9837, Found: 972.9822, error: –1.5 ppm.  $[\alpha]_D^{20} = +82.5$  ( $c = 0.004$  in  $\text{CHCl}_3$ ).

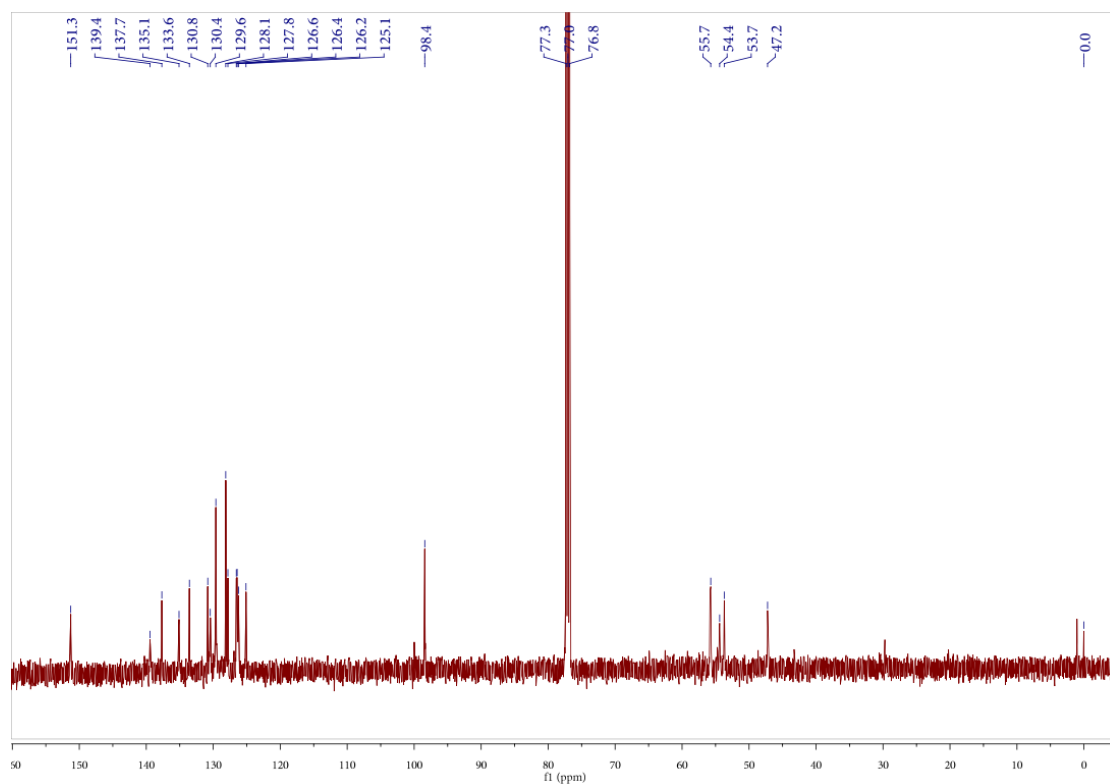
(*R*)-**6** (52 mg, 94% yield); mp 310–312 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87–7.68 (m, 24H), 7.39–7.22 (m, 30H), 4.47–4.16 (m, 12H), 3.82 (t,  $J = 12.4$  Hz, 4H), 2.71–2.63 (m, 18H), 2.29–1.99 (m, 24H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  151.3, 139.4, 137.7, 135.2, 133.6, 130.8, 130.5, 129.6, 128.2, 127.8, 126.6, 126.4, 126.2, 125.1, 98.4, 55.8, 54.4, 53.7, 47.2. ESI-TOF-MS ( $m/z$ ): Calcd. for  $\text{C}_{126}\text{H}_{127}\text{N}_8\text{O}_{12}$  [ $\text{M} + \text{H}$ ] $^+$ :

1944.9602, Found: 1944.9490, error:  $-5.8$  ppm. Calcd. for  $C_{126}H_{128}N_8O_{12}$   $[M + 2H]^{2+}$ :  
972.9837, Found: 972.9820, error:  $-1.7$  ppm.  $[\alpha]_D^{20} = -82.8$  ( $c = 0.004$  in  $CHCl_3$ ).

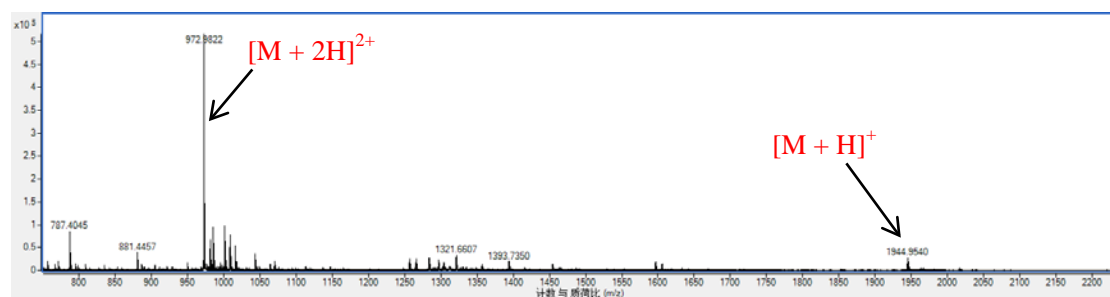
### 3.2 $^1H$ NMR, $^{13}C$ NMR and ESI-MS spectra of (*S*)- and (*R*)-BINOL cages **6**



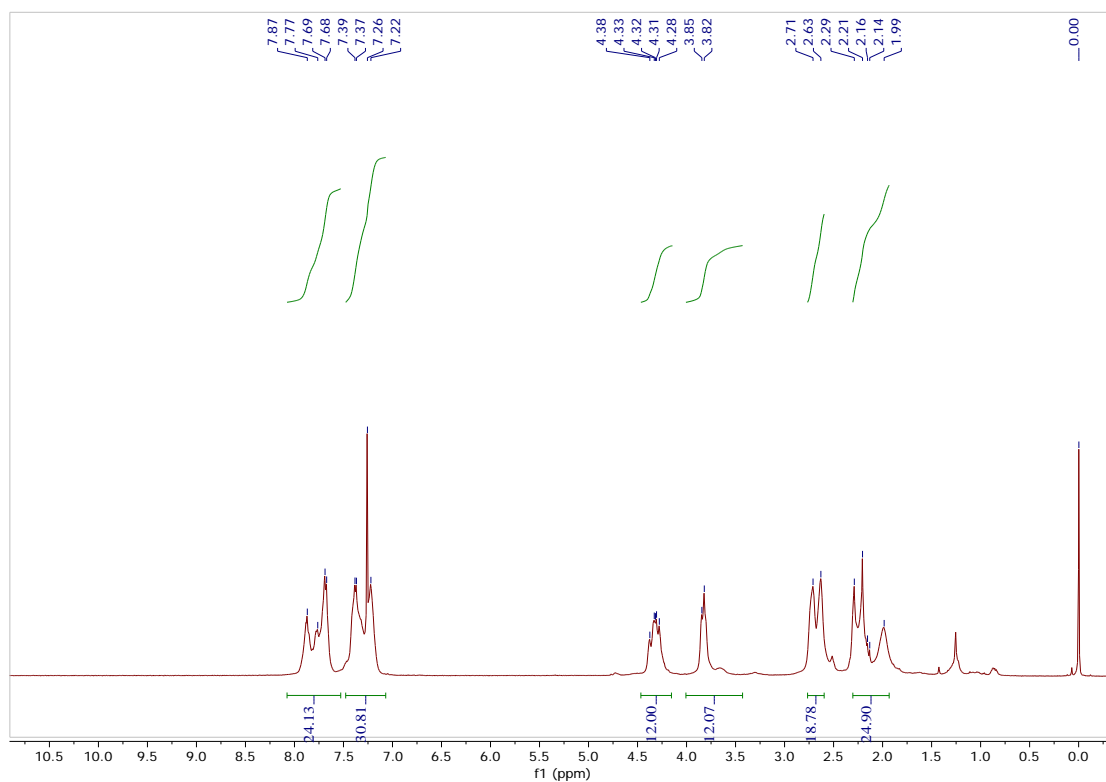
**Fig. S19**  $^1H$  NMR spectrum of (*S*)-**6** in  $CDCl_3$  at  $22$  °C.



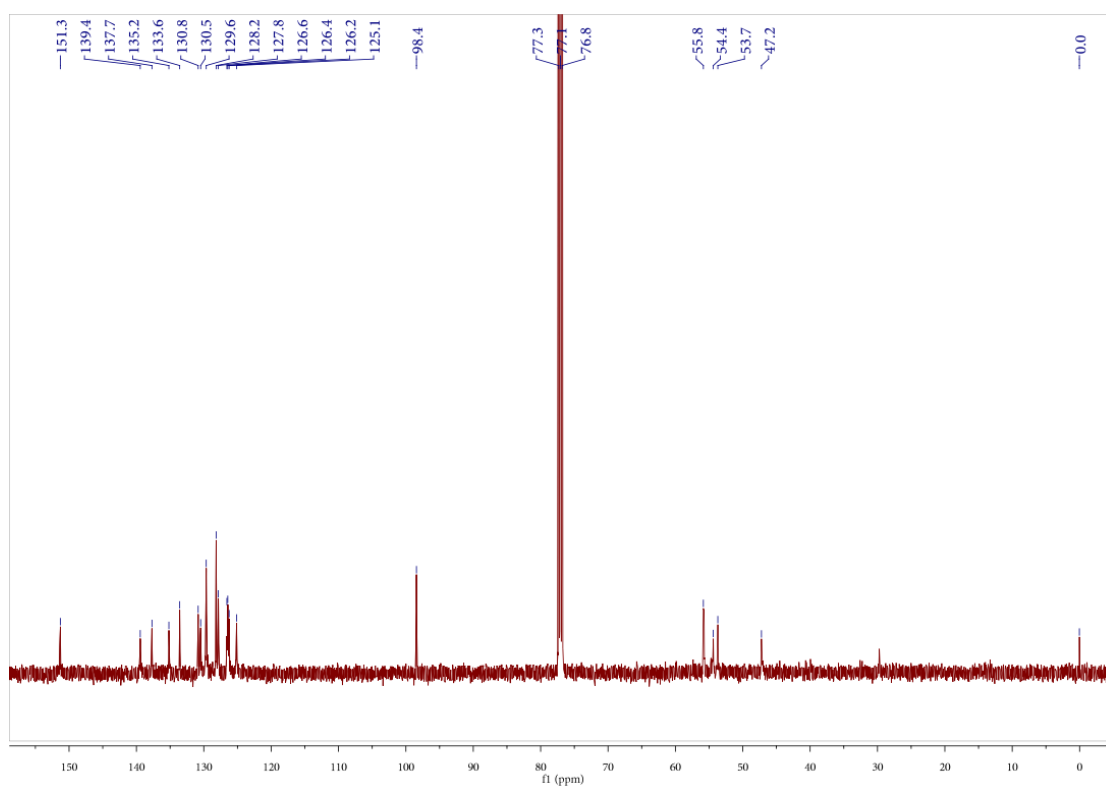
**Fig. S20**  $^{13}\text{C}$  NMR spectrum of (*S*)-**6** in  $\text{CDCl}_3$  at 22 °C.



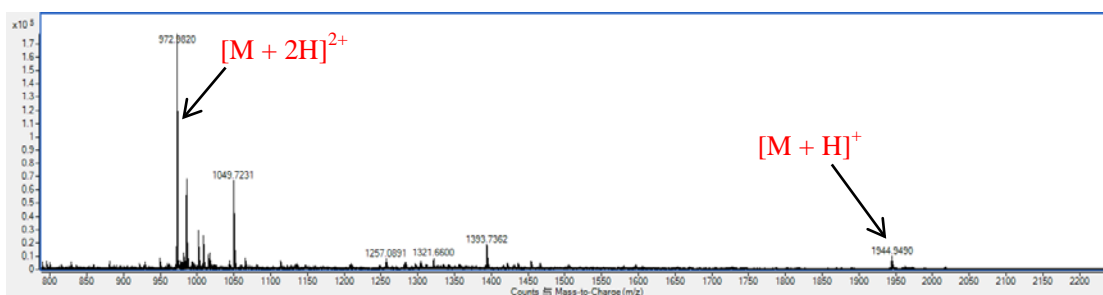
**Fig. S21** ESI-MS spectrum of (*S*)-**6**. ESI-TOF-MS ( $m/z$ ): Calcd. for  $\text{C}_{126}\text{H}_{127}\text{N}_8\text{O}_{12}$   $[\text{M} + \text{H}]^+$ : 1944.9602, Found: 1944.9540, error:  $-3.2$  ppm. Calcd. for  $\text{C}_{126}\text{H}_{128}\text{N}_8\text{O}_{12}$   $[\text{M} + 2\text{H}]^{2+}$ : 972.9837, Found: 972.9822, error:  $-1.5$  ppm.



**Fig. S22**  $^1\text{H}$  NMR spectrum of (*R*)-**6** in  $\text{CDCl}_3$  at 22 °C.

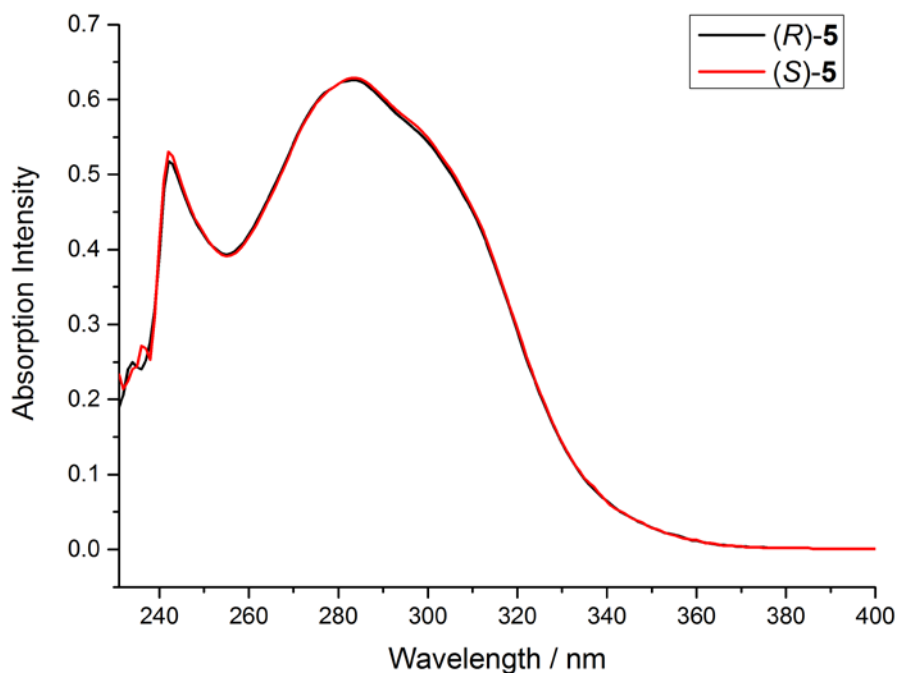


**Fig. S23**  $^{13}\text{C}$  NMR spectrum of (*R*)-**6** in  $\text{CDCl}_3$  at 22 °C.

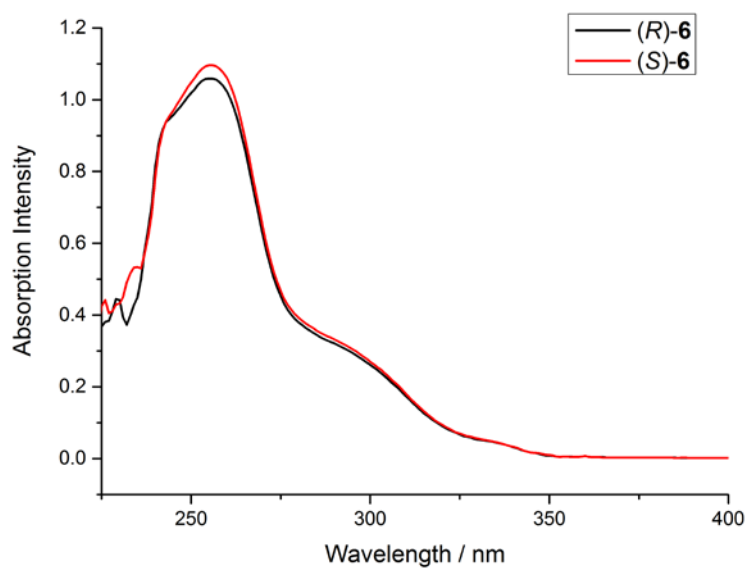


**Fig. S24** ESI-MS spectrum of (*R*)-**6**. ESI-TOF-MS (*m/z*): Calcd. for  $C_{126}H_{127}N_8O_{12}$   $[M + H]^+$ : 1944.9602, Found: 1944.9490, error:  $-5.8$  ppm. Calcd. for  $C_{126}H_{128}N_8O_{12}$   $[M + 2H]^{2+}$ : 972.9837, Found: 972.9820, error:  $-1.7$  ppm.

#### 4. UV-vis and fluorescence spectra of the imine cages

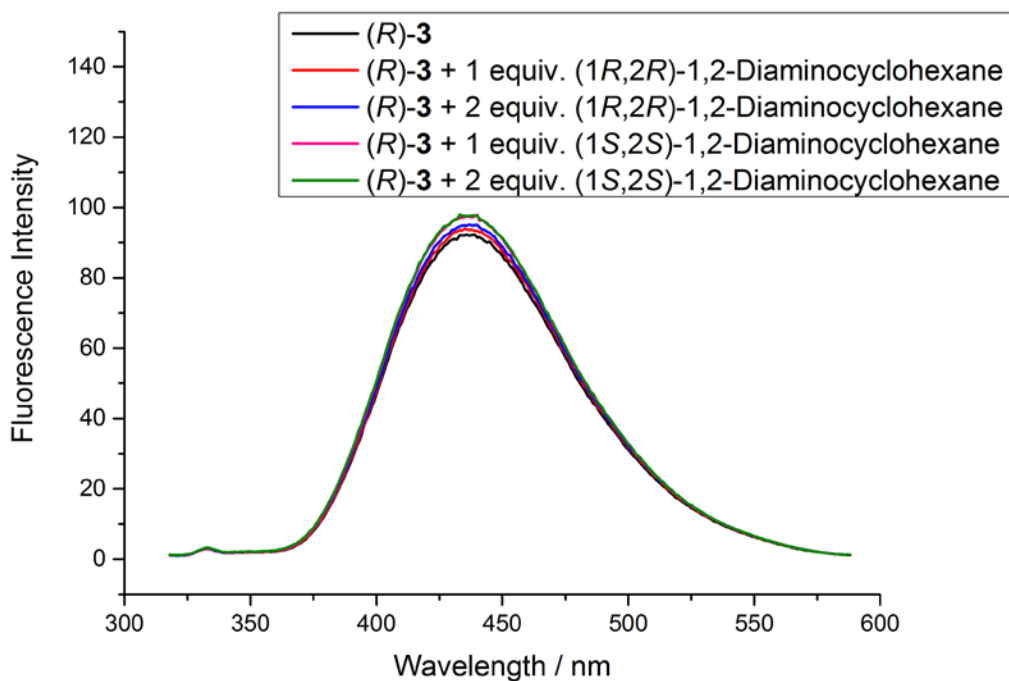


**Fig. S25** UV-vis spectra of (*R*)-**5** and (*S*)-**5** (0.07 mM in  $CHCl_3$ ).

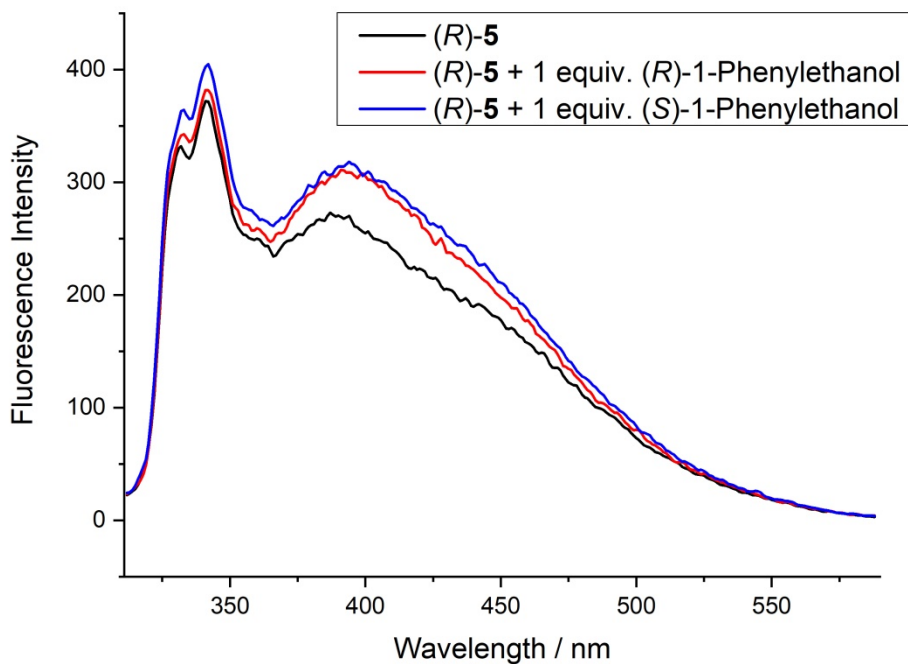


**Fig. S26** UV-vis spectra of (*R*)-**6** and (*S*)-**6** (0.07 mM in CHCl<sub>3</sub>).

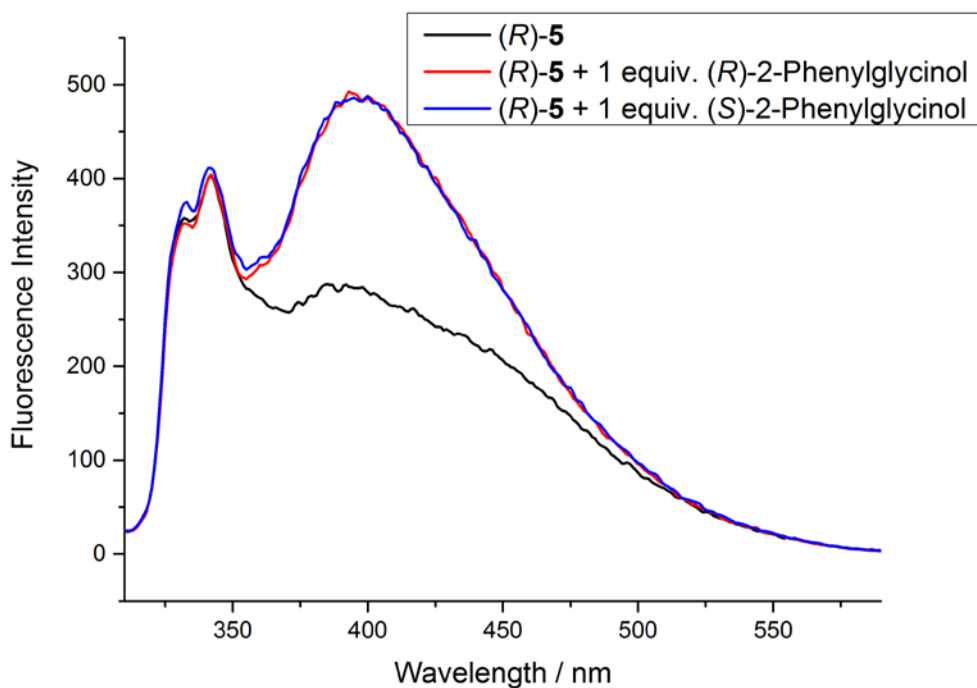
### 5. Fluorescence spectra for chiral recognition



**Fig. S27** Fluorescence spectral changes of (*R*)-**3** (0.03 mM in CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{\text{ex}} = 300$  nm) upon the addition of (*1R,2R*)-1,2-diaminocyclohexane and (*1S,2S*)-1,2-diaminocyclohexane.

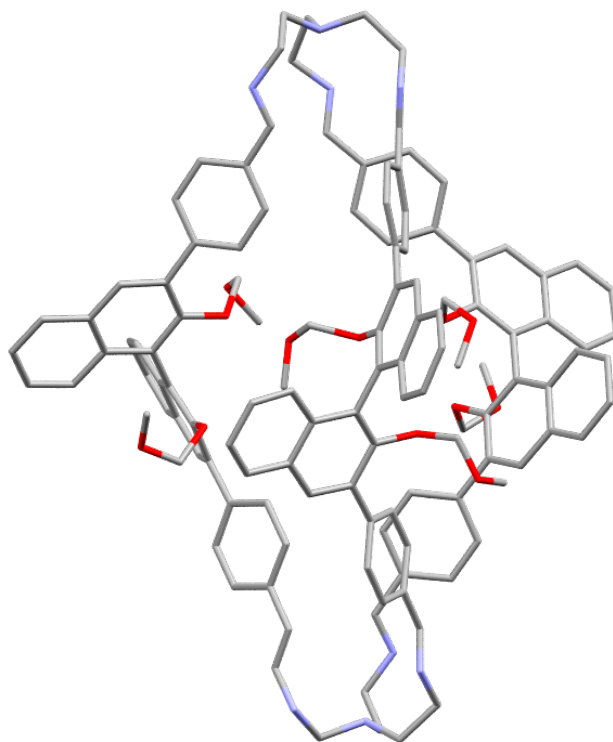


**Fig. S28** Fluorescence spectral changes of (*R*)-**5** (0.03 mM in CHCl<sub>3</sub>,  $\lambda_{\text{ex}} = 300$  nm) upon the addition of (*R*)-1-phenylethanol and (*S*)-1-phenylethanol.

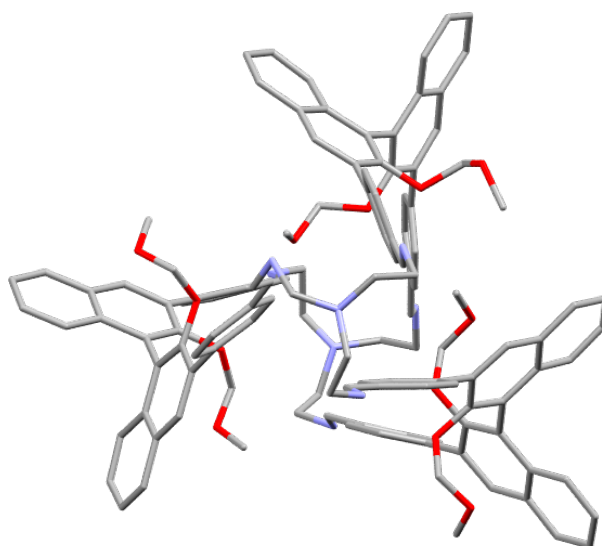


**Fig. S29** Fluorescence spectral changes of (*R*)-**5** (0.03 mM in CHCl<sub>3</sub>,  $\lambda_{\text{ex}} = 300$  nm) upon the addition of (*R*)-2-phenylglycinol and (*S*)-2-phenylglycinol.

6. Single-crystal structure and X-ray analysis data of (*R*)-5



**Fig. S30** Side view of (*R*)-5. The counterions have been omitted for clarity. Color code: gray = C; blue = N; red = O.



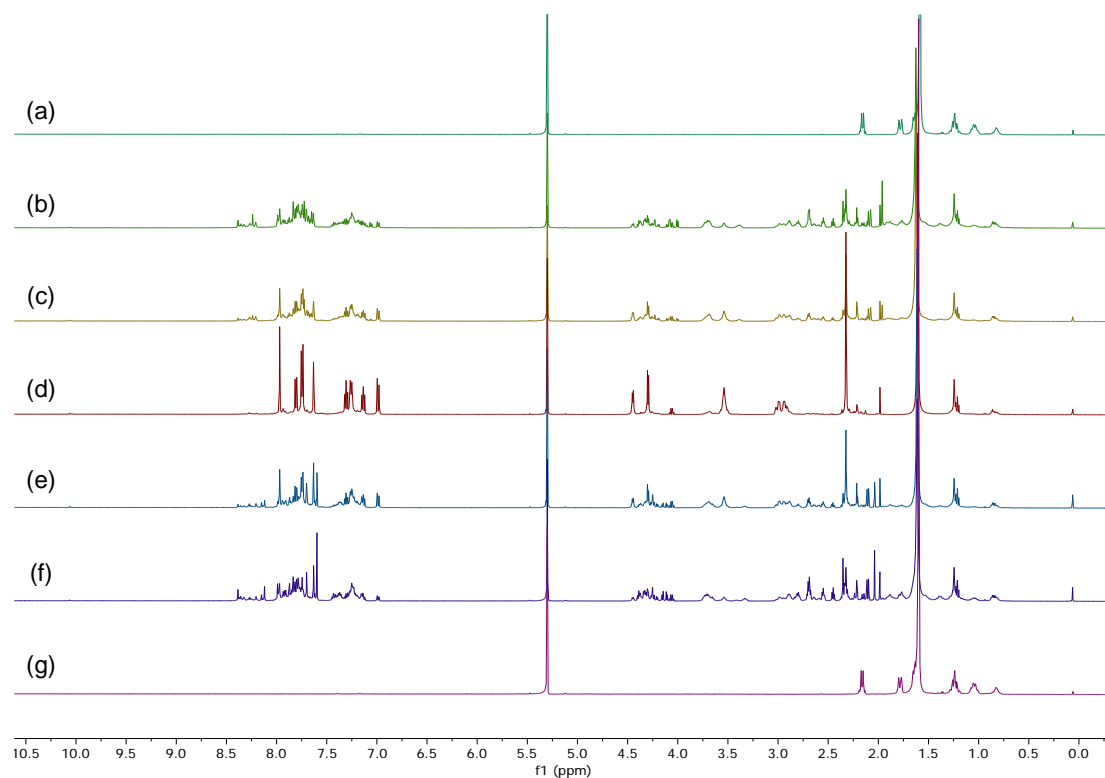
**Fig. S31** Top view of (*R*)-5. The counterions have been omitted for clarity. Color code: gray = C; blue = N; red = O.



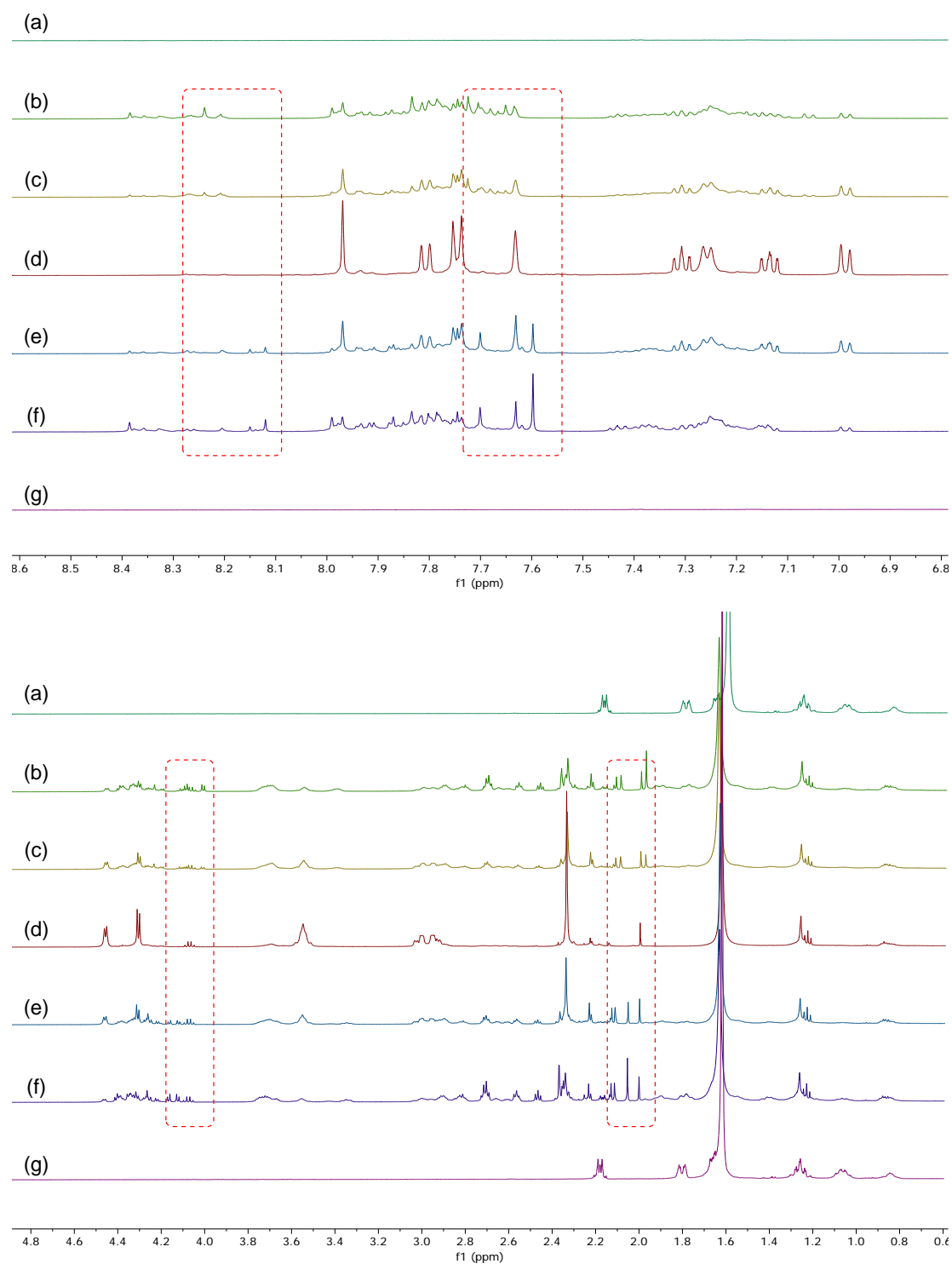
**Table S1** Crystal data of (R)-5.

<b>Deposition Number</b>	<b>2096620</b>
Empirical formula	C <sub>126</sub> H <sub>113</sub> N <sub>8</sub> O <sub>12</sub>
Formula weight	1931.24
Temperature/K	170.0
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub>
<i>a</i> /Å	16.0819(6)
<i>b</i> /Å	25.9667(8)
<i>c</i> /Å	17.0515(6)
$\alpha$ /°	90
$\beta$ /°	117.912(2)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	6292.2(4)
<i>Z</i>	2
$\rho_{\text{calc}}/\text{cm}^3$	1.019
$\mu/\text{mm}^{-1}$	0.522
<i>F</i> (000)	2042.0
Crystal size/mm <sup>3</sup>	0.49 × 0.35 × 0.29
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54178)
2 $\Theta$ range for data collection/°	5.866 to 133.854
Index ranges	-19 ≤ <i>h</i> ≤ 19, -30 ≤ <i>k</i> ≤ 31, -20 ≤ <i>l</i> ≤ 20
Reflections collected	84942
Independent reflections	22246 [ <i>R</i> <sub>int</sub> = 0.0524, <i>R</i> <sub>sigma</sub> = 0.0408]
Data/restraints/parameters	22246/62/1346
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.037
Final <i>R</i> indexes [ <i>I</i> >= 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0582, <i>wR</i> <sub>2</sub> = 0.1648
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0657, <i>wR</i> <sub>2</sub> = 0.1723
Largest diff. peak/hole / e Å <sup>-3</sup>	0.36/-0.23
Flack parameter	0.00(7)

7. Compared  $^1\text{H}$  NMR spectra for chiral recognition



**Fig. S32**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 22 °C) spectra of (1*R*,2*R*)-1,2-diaminocyclohexane (a), (R)-5 + 2 equiv (1*R*,2*R*)-1,2-diaminocyclohexane (b), (R)-5 + 1 equiv (1*R*,2*R*)-1,2-diaminocyclohexane (c), (R)-5 (d), (R)-5 + 1 equiv (1*S*,2*S*)-1,2-diaminocyclohexane (e), (R)-5 + 2 equiv (1*S*,2*S*)-1,2-diaminocyclohexane (f), and (1*S*,2*S*)-1,2-diaminocyclohexane (g).



**Fig. S33** Enlarged <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 22 °C) spectra of (1*R*,2*R*)-1,2-diaminocyclohexane (a), (*R*)-**5** + 2 equiv (1*R*,2*R*)-1,2-diaminocyclohexane (b), (*R*)-**5** + 1 equiv (1*R*,2*R*)-1,2-diaminocyclohexane (c), (*R*)-**5** (d), (*R*)-**5** + 1 equiv (1*S*,2*S*)-1,2-diaminocyclohexane (e), (*R*)-**5** + 2 equiv (1*S*,2*S*)-1,2-diaminocyclohexane (f), and (1*S*,2*S*)-1,2-diaminocyclohexane (g).

## 8. References

- S1. T. Hong, Z. Zhang, Y. Sun, J.-J. Tao, J.-D. Tang, C. Xie, M. Wang, F. Chen, S.-S. Xie, S. Li, and P. J. Stang, Chiral Metallacycles as Catalysts for Asymmetric Conjugate Addition of Styrylboronic Acids to  $\alpha,\beta$ -Enones. *J. Am. Chem. Soc.*, 2020, **142**, 10244–10249.
- S2. (a) Y. Jin, B. A. Voss, R. D. Noble and W. Zhang, *Angew. Chem., Int. Ed.*, 2010, **49**, 6348; (b) P. Li, S. Xu, C. Yu, Z.-Y. Li, J. Xu, Z.-M. Li, L. Zou, X. Leng, S. Gao, Z. Liu, X. Liu and S. Zhang, *Angew. Chem., Int. Ed.*, 2020, **59**, 7113.