Asymmetric Synthesis of Heteroaryl Atropisomers via a Chiral Gold-Catalyzed Cycloisomerization/Amination Cascade

Rui Guo, a Kang-Nan Li, a Bin Liu, a Hua-Jie Zhu*, b Yu-Meng Fan, a Liu-Zhu Gong* a

a Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China.
b Chinese Centre for Chirality, Key Laboratory of Medicinal Chemistry and Molecular Diagnostics of Education Administration of China Department of Chemistry and Environmental Engineering, Hebei University, Baoding, Hebei 071002, China.

Supporting Information

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**General method.** NMR spectra were recorded on a Brucker-400 MHz spectrometer. ESIMS spectra were recorded on BioTOF Q. Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-343 polarimeter. HPLC analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254 nm) and Agilent 1200 series. All chiral columns were purchased from Daicel Chemical Industries, LTD. Toluene, diethyl ether and tetrahydrofuran were dried over Na and distilled prior to use. Dichloromethane and dichloroethane were dried over CaH₂ and distilled prior to use. All starting materials were purchased from Alfa and Aldrich and used directly.

**Part I Experimental Part**

**Synthesis of 1a-1m**

Compounds 1a and 1j have been reported,¹ and the analytical data of which was matched with those reported in the literatures. Compounds 1b-1i and 1k-1m were prepared following the known procedure.¹,²

**(2-(pent-1-yn-1-yl)phenyl)boronic acid (1b).** Yield: 75% (0.32 g, two steps). Rᵥ = 0.6 (Petroleum ether: EtOAc = 5:1). Light yellow solid. ¹H NMR (400 MHz, acetone-d₆) δ 7.91 (dd, J = 7.4, 0.8 Hz, 1H), 7.38-7.45 (m, 2H), 7.34 (td, J = 7.3, 1.7 Hz, 1H), 7.12 (s, 2H), 2.48 (t, J = 7.0 Hz, 2H), 1.70-1.56 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H).

**(13C NMR (101 MHz, acetone-d₆) δ 135.91, 133.22, 131.02, 94.88, 82.62, 22.80, 21.73, 13.80.**

**(2-(hept-1-yn-1-yl)phenyl)boronic acid (1c).** Yield: 63% (0.46 g, two steps). Rᵥ = 0.6 (Petroleum ether: EtOAc = 5:1). Light yellow solid. ¹H NMR (400 MHz, CD₃OD) δ 7.40-7.17 (m, 4H), 2.40 (t, J = 6.8 Hz, 2H), 1.67-1.54 (m, 2H), 1.53-1.43 (m, 2H), 1.41-1.36 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H).

**(13C NMR (101 MHz, CD₃OD) δ 132.12, 132.06, 129.57, 128.09, 127.41, 91.85, 82.17, 32.11, 29.62, 23.34, 19.94, 14.36.**

**(2-(oct-1-yn-1-yl)phenyl)boronic acid (1d).** Yield: 67% (0.28 g, two steps). Rᵥ = 0.6 (Petroleum ether: EtOAc = 5:1). Colorless oil. ¹H NMR (400 MHz, CD₃OD) δ 7.37-7.22 (m, 4H), 2.41 (t, J = 6.8 Hz, 2H), 1.66-1.54 (m, 2H), 1.54-1.43 (m, 2H), 1.41-1.26 (m, 4H), 0.93 (t, J = 7.0 Hz, 3H).

**(13C NMR (101 MHz, CD₃OD) δ 132.13, 132.07, 129.57, 128.09, 127.42, 91.85, 82.17, 32.62, 29.90, 29.59, 23.69, 19.98, 14.43.**

**(2-(5-chloropent-1-yn-1-yl)phenyl)boronic acid (1e).** Yield: 63% (0.81 g, two steps). Rᵥ = 0.6 (Petroleum ether: EtOAc = 5:1). White solid. ¹H NMR (400 MHz, acetone-d₆) δ 7.85 (d, J = 7.3 Hz, 1H), 7.47-7.31 (m, 3H), 7.09 (s, 2H), 3.81 (t, J = 6.4 Hz, 2H), 2.70 (t, J = 6.9 Hz, 2H), 2.13-2.06 (m,
(2-(4-phenylbut-1-yn-1-yl)phenyl)boronic acid (1f). Yield: 72% (1.33 g, two steps). \(R_f = 0.5\) (Petroleum ether: EtOAc = 5:1). White solid. \(^1\)H NMR (400 MHz, acetone-\(d_6\)) \(\delta\) 7.88 (d, \(J = 7.3\) Hz, 1H), 7.47-7.26 (m, 7H), 7.26-7.14 (m, 1H), 7.05 (s, 2H), 2.95 (t, \(J = 7.3\) Hz, 2H). \(^13\)C NMR (101 MHz, acetone-\(d_6\)) \(\delta\) 141.45, 135.85, 133.23, 130.96, 129.39, 129.25, 128.26, 128.08, 127.18, 94.29, 83.02, 35.48, 22.03.

(2-(5-methylhex-1-yn-1-yl)phenyl)boronic acid (1g). Yield: 68% (0.95 g, two steps). \(R_f = 0.4\) (Petroleum ether: EtOAc = 5:1). Colorless oil. \(^1\)H NMR (400 MHz, CD3OD) \(\delta\) 7.42-7.17 (m, 4H), 2.42 (t, \(J = 7.2\) Hz, 2H), 1.85-1.76 (m, 1H), 1.50-1.45 (m, 2H), 0.95 (d, \(J = 6.6\) Hz, 6H).

(2-(pent-4-en-1-yn-1-yl)phenyl)boronic acid (1h). Yield: 23% (120 mg, four steps). \(R_f = 0.6\) (Petroleum ether: EtOAc = 5:1). Colorless oil. \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 7.96 (dd, \(J = 7.4, 1.1\) Hz, 1H), 7.48 (dd, \(J = 7.7, 1.0\) Hz, 1H), 7.41 (td, \(J = 7.5, 1.6\) Hz, 1H), 7.36 (td, \(J = 7.4, 1.5\) Hz, 1H), 5.96-5.86 (m, 1H), 5.63 (br, 2H), 5.41 (ddd, \(J = 17.0, 3.1, 1.7\) Hz, 1H), 5.22 (ddd, \(J = 10.0, 2.9, 1.6\) Hz, 1H), 3.28 (dt, \(J = 5.4, 1.7\) Hz, 2H).

(2-(4-(1,3-dioxolan-2-yl)but-1-yn-1-yl)phenyl)boronic acid (1i). Yield: 48% (1.58 g, three steps). \(R_f = 0.3\) (Petroleum ether: EtOAc = 3:1). Colorless oil. \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 7.95 (dd, \(J = 7.4, 0.9\) Hz, 1H), 7.45 (d, \(J = 7.4\) Hz, 1H), 7.39 (td, \(J = 7.5, 1.5\) Hz, 1H), 7.34 (td, \(J = 7.3, 1.3\) Hz, 1H), 6.01 (brs, 2H), 5.04 (t, \(J = 4.3\) Hz, 1H), 4.06-3.99 (m, 2H), 3.93-3.86 (m,
2H), 2.65 (t, J = 7.1 Hz, 2H), 2.03 (td, J = 7.1, 4.4 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 135.47, 132.68, 130.67, 127.68, 127.37, 103.18, 93.82, 81.64, 65.09, 32.31.

(2-(hex-1-yn-1-yl)-5-methylphenyl)boronic acid (1k). Yield: 46% (0.33 g, two steps). R$_f$ = 0.6 (Petroleum ether: EtOAc = 5:1). Colorless oil. $^1$H NMR (400 MHz, acetone-d$_6$) δ 7.71 (s, 1H), 7.32 (d, J = 7.8 Hz, 1H), 7.22 (dd, J = 7.8, 1.3 Hz, 1H), 7.12 (brs, 2H), 2.50 (t, J = 7.0 Hz, 2H), 2.33 (s, 3H), 1.64-1.56 (m, 2H), 1.54-1.42 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, acetone-d$_6$) δ 137.05, 135.71, 132.28, 130.85, 124.37, 93.33, 81.57, 30.61, 21.76, 20.45, 18.52, 12.98.

(2-(hex-1-yn-1-yl)-5-isopropylphenyl)boronic acid (1l).

Synthesis of azodicarboxylate esters 2a-2g

Compounds 2f$^3$ and 2g$^4$ were synthesized according to the literature procedure and the analytical data were matched with the reported data. Compounds 2d and 2e were synthesized following the known literature procedures via the scheme bellow.$^4$

(E)-dicyclopentyl diazene-1,2-dicarboxylate (2d). Yield: 89% (0.70 g, two steps). Yellow oil. $^1$H

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NMR (400 MHz, CDCl$_3$) $\delta$ 5.59-5.22 (m, 2H), 2.03-1.62 (m, 16H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.22, 83.29, 32.67, 23.58.

(E)-dineopentyl diazene-1,2-dicarboxylate (2e). Yield: 85% (0.65 g, two steps). Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.08 (s, 4H), 0.95 (s, 18H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.61, 77.27, 30.76, 25.13.

Ligands and solvents screen

Table S1 Ligands and solvents effect on the asymmetric gold-catalyzed cycloaddition/amination of 1a with 2a$^a$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>L*(AuCl)$_2$</th>
<th>Solvent</th>
<th>Yield (%)$^b$</th>
<th>Ee (%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(R)-BINAP(AuCl)$_2$</td>
<td>DCM</td>
<td>83</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>(S)-(8$H$)-BINAP(AuCl)$_2$</td>
<td>DCM</td>
<td>68</td>
<td>-75</td>
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<tr>
<td>3</td>
<td>(S)-Tol-BINAP(AuCl)$_2$</td>
<td>DCM</td>
<td>58</td>
<td>-76</td>
</tr>
<tr>
<td>4</td>
<td>(R)-DTBM-SEGPHOS (AuCl)$_2$</td>
<td>DCM</td>
<td>31</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>(R)-BINAP(AuCl)$_2$</td>
<td>Toluene</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>(R)-BINAP(AuCl)$_2$</td>
<td>DCE</td>
<td>61</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>(R)-BINAP(AuCl)$_2$</td>
<td>THF</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ 0.4 mmol 2a, catalysts and additives were added 1 mL DCM followed by 0.2 mmol 1a in 1 mL of DCM and the reaction was run for 12 h.$^b$ Isolated yields after flash chromatography. $^c$ Determined by HPLC.

Synthesis of 4a-4t

General procedure: A solution of 2 (2 equiv.), (R)-BINAP(AuCl)$_2$ (0.11 equiv.), AgNTf$_2$ (0.1 equiv.) and 4Å MS (100 mg) in DCM (1 mL) was stirred at room temperature for 10 min. Then the reaction mixture was cooled to 0 °C, added boronic acid 1 (0.025 M) in DCM (1 mL) and stirred for 24 h (TLC monitored) at that temperature. The resulting mixture was directly purified by flash column chromatography on silica gel to give the product 4 as yellow oil or a white solid and the enantiomeric excesses were determined by HPLC analysis. 4a-4f and 4t were obtained from 0.2 mmol of 1 and 4g-4s were obtained from 0.05 mmol of 1 at the standard conditions. The racemic 4a-4t were synthesized by using (±)-BINAP(AuCl)$_2$ instead.

Diisopropyl 1-(3-butyl-1-hydroxy-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4a). Yield: 83% (66.8 mg). $R_f = 0.3$ (Petroleum ether: EtOAc = 5:1). Colorless oil. Doubled signals in NMR spectra were observed when 4a was dissolved in deuterium acetone due to the presence of several rotamers. The same situation was to 4b-4t. The spectra got “clean” when 4a was dissolved in deuterium dimethyl sulfoxide at 70 °C (where the barrier of rotation was damaged).

$^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 8.65 (two singlets, 1H), 8.11 (two singlets, 1H), 8.03 (m, 1H), 7.80
7.67 (m, 1H), 7.63-7.57 (m, 1H), 7.35 (q, J = 7.2 Hz, 1H), 5.02-4.78 (m, 2H), 2.89-2.82 (m, 2H), 1.71-1.63 (m, 2H), 1.46-1.38 (m, 2H), 1.31-0.99 (m, 12H), 0.96-0.91 (m, 3H). 13C NMR (101 MHz, acetone-d6) δ 157.02, 156.90, 156.42, 155.69, 142.28, 133.66, 132.83, 126.40, 126.32, 123.06, 122.88, 121.25, 70.73, 70.61, 69.48, 31.61, 23.38, 22.29, 22.28, 22.25, 22.01, 14.37, 14.34.

1H NMR (400 MHz, DMSO-d6) δ 9.45 (s, 1H), 9.08 (s, 1H), 8.04 (dd, J = 6.8, 0.5 Hz, 1H), 7.73 (s, 1H), 7.65-7.56 (m, 1H), 7.36 (td, J = 7.3, 0.7 Hz, 1H), 4.99-4.74 (m, 2H), 2.84-2.76 (m, 1H), 2.68-2.62 (m, 1H), 1.74-1.58 (m, 2H), 1.45-1.36 (m, 2H), 1.35-0.99 (m, 12H), 0.96 (t, J = 7.3 Hz, 3H).

13C NMR (101 MHz, DMSO-d6) δ 155.75, 155.39, 154.94, 140.70, 132.55, 131.51, 125.13, 123.04, 121.92, 119.69, 69.41, 68.18, 30.27, 28.30, 21.88, 21.65, 21.61, 21.44 (brs, 2C), 13.50.

IR (neat) γ 3401, 3274, 2958, 1710, 1397, 1303, 1244, 1058 cm⁻¹. HRMS (ESI): m/z Calcd for C20H30BN2O6 [M + H]+ 405.21969, found 405.21872. [α]D²⁰ = +14° (c 0.97, CHCl₃). Enantiomeric excess: 82%, determined by chiral HPLC analysis [Daicel Chiralpak AS, n-Hexane: 2-propanol = 97:3, flow rate 0.5 ml/min, T = 30 °C, λ = 254 nm. tR (S) = 11.64 min; tR (R) = 20.27 min].

Diethyl 1-(3-butyl-1-hydroxy-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4b).

Yield: 92% (69.2 mg). Rf = 0.3 (Petroleum ether: EtOAc = 5:1). Colorless oil. 1H NMR (400 MHz, acetone-d6) δ 8.83 (two singlets, 1H), 8.17 (two singlets, 1H), 8.08 (d, J = 7.3 Hz, 1H), 7.78 (d, J = 7.4 Hz, 1H), 7.67-7.60 (m, 1H), 7.42-7.36 (m, 1H), 4.44-3.99 (m, 4H), 2.95-2.80 (m, 2H), 1.77-1.60 (m, 2H), 1.48-1.43 (m, 2H), 1.34-1.10 (m, 6H), 0.97 (t, J = 7.3 Hz, 3H).

13C NMR (101 MHz, acetone-d6) δ 157.35, 157.07, 156.96, 156.84, 156.14, 142.19, 133.72, 132.95, 132.83, 126.47, 126.36, 122.90, 122.82, 121.14, 63.06, 61.94, 31.70, 31.59, 23.34, 14.91, 14.84, 14.34. IR (neat) γ 3412, 3285, 2956, 1710, 1397, 1303, 1244, 1070 cm⁻¹. HRMS (ESI): m/z Calcd for C18H26BN2O6 [M + H]+ 377.18839, found 377.18768. [α]D²⁰ = +16° (c 1.09, CHCl₃). Enantiomeric excess: 62%, determined by chiral HPLC analysis [Daicel Chiralpak AS, n-Hexane: 2-propanol = 90:10, flow rate 1.0 ml/min, T = 30 °C, λ = 254 nm. tR (S) = 4.50 min; tR (R) = 7.25 min].

Dibenzyl 1-(3-butyl-1-hydroxy-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4c).

Yield: 60% (60.0 mg). Rf = 0.3 (Petroleum ether: EtOAc = 3:1). Colorless oil. 1H NMR (400 MHz, acetone-d6) δ 9.34-8.88 (m, 1H), 8.20 (s, 1H), 8.08 (d, J = 7.4 Hz, 1H), 7.84-7.73 (m, 1H), 7.61 (s, 1H), 7.55-7.00 (m, 11H), 5.34-2.87 (m, 1H), 2.81-2.78 (m, 1H), 1.69-1.60 (m, 2H), 1.43-1.33 (m, 2H), 0.96-0.88 (m, 3H). 13C NMR (101 MHz, acetone-d6) δ 157.82, 157.28, 157.17, 156.90, 156.07, 142.06, 137.47, 137.33, 133.77, 133.00, 132.89, 129.28, 129.13, 128.90, 128.88, 128.84, 128.65, 128.41, 126.53, 126.44, 122.83, 121.06, 68.60, 67.62, 31.77, 31.63, 31.15, 31.08, 23.29, 14.34. IR (neat) γ 3412, 3289, 2956, 1709, 1389, 1298, 1253, 1054, 690 cm⁻¹. HRMS (ESI): m/z Calcd for C28H30BN2O6 [M + H]+ 501.21969, found 501.21875. [α]D²⁰ = -9° (c 1.89, CHCl₃). Enantiomeric
excess: 59%, determined by chiral HPLC analysis [Daicel Chiralpak AS, n-Hexane:2-propanol = 90:10, flow rate 0.5 ml/min, T = 30 °C, λ = 254 nm. t_R(S) = 12.08 min; t_R(R) = 19.44 min].

**Dicyclopentyl 1-(3-butyl-1-hydroxy-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4d).** Yield: 61% (55.8 mg). R_f = 0.5 (Petroleum ether: EtOAc = 4:1). Colorless oil. ¹H NMR (400 MHz, acetone-d₆) δ 8.68 (two singlets, 1H), 8.11 (two singlets, 1H), 8.04 (d, J = 7.0 Hz, 1H), 7.86-7.66 (m, 1H), 7.63-7.56 (m, 1H), 7.37-7.32 (m, 1H), 5.16-5.08 (m, 2H), 2.93-2.88 (m, 1H), 2.83-2.77 (m, 1H), 1.97-1.52 (m, 16H), 1.44-1.29 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H). ¹³C NMR (101 MHz, acetone-d₆) δ 157.60, 157.24, 157.17, 156.92, 156.59, 155.83, 142.32, 133.68, 132.81, 126.39, 122.74, 121.39, 80.01, 78.89, 33.57, 33.34, 33.30, 33.11, 31.52, 24.22, 23.98, 23.77, 23.32, 14.40. IR (neat) γ 3412, 3289, 2956, 1709, 1389, 1298, 1253, 1054, 690 cm⁻¹. HRMS (ESI): m/z Calcd for C₂₄H₃₄BN₂O₆ [M + H]⁺ 457.25099, found 457.25024. [α]D₂₀ = -16° (c 1.08, CHCl₃). Enantiomeric excess: 77%, determined by chiral HPLC analysis [Daicel Chiralpak IC, n-Hexane:2-propanol = 95:5, flow rate 1.0 ml/min, T = 30 °C, λ = 254 nm. t_R(S) = 7.77 min; t_R(R) = 10.87 min].

**Dineopentyl 1-(3-butyl-1-hydroxy-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4e).** Yield: 79% (72.9 mg). R_f = 0.6 (Petroleum ether: EtOAc = 4:1). Colorless oil. ¹H NMR (400 MHz, acetone-d₆) δ 8.93 (two singlets, 1H), 8.12 (two singlets, 1H), 8.05 (d, J = 6.8 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.62-7.55 (m, 1H), 7.37-7.32 (m, 1H), 3.97-3.64 (m, 4H), 2.84-2.76 (m, 2H), 1.74-1.54 (m, 2H), 1.45-1.40 (m, 2H), 1.03-0.61 (m, 21H). ¹³C NMR (101 MHz, acetone-d₆) δ 156.74, 155.98, 155.31, 141.40, 141.24, 132.85, 131.98, 125.55, 121.94, 120.52, 75.35, 74.10, 31.46, 31.35, 31.13, 30.99, 30.79, 25.69, 25.43, 22.44, 22.40, 13.48, 13.45. IR (neat) γ 3396, 3290, 2956, 2864, 1693, 1389, 1298, 1237, 1070, 765 cm⁻¹. HRMS (ESI): m/z Calcd for C₂₄H₃₈BN₂O₆ [M + H]⁺ 461.28229, found 461.28079. [α]D₂₀ = +16° (c 1.08, CHCl₃). Enantiomeric excess: 81%, determined by chiral HPLC analysis [Daicel Chiralpak IC, n-Hexane:2-propanol = 95:5, flow rate 1.0 ml/min, T = 30 °C, λ = 254 nm. t_R(S) = 4.36 min; t_R(R) = 6.50 min].

**Bis(2,2,2-trichloroethyl) 1-(3-butyl-1-hydroxy-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4f).** Yield: 82% (95.3 mg). R_f = 0.6 (Petroleum ether: EtOAc = 4:1). Colorless oil. ¹H NMR (400 MHz, acetone-d₆) δ 9.79 (two singlets, 1H), 8.21 (two singlets, 1H), 8.05 (d, J = 7.3 Hz, 1H), 7.81-7.73 (m, 1H), 7.63-7.59 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 5.01-4.77 (m, 4H), 3.00-2.92 (m, 1H), 2.86-2.75 (m, 1H), 1.80-1.55 (m, 2H), 1.43-1.39 (m, 2H), 0.95-0.90 (m, 3H). ¹³C NMR (101 MHz, acetone-d₆) δ 158.27, 157.87, 155.53, 155.27, 155.22, 154.51, 141.58, 141.33, 133.82, 133.05, 126.71, 122.69, 120.39, 109.70, 96.34, 96.29, 96.26, 95.99, 76.90, 76.29, 75.46, 31.83, 31.75, 23.36, 14.39. IR (neat) γ 3304, 2956, 1739, 1404, 1222, 1115,720 cm⁻¹. HRMS (ESI): m/z Calcd for C₁₈H₂₀BCl₆N₂O₆ [M + H]⁺ 580.95456, found 580.95401. [α]D²₀ = +17° (c 1.82, CHCl₃). Enantiomeric excess: 80%. Enantiomeric excess: 77%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%. Enantiomeric excess: 81%.
excess: 80%, determined by chiral HPLC analysis [Daicel Chiralpak IC, n-Hexane:2-propanol = 90:10, flow rate 0.5 ml/min, T = 30 °C, λ = 254 nm. t_R(S) = 6.96 min; t_R(R) = 8.81 min].

**Di-tert-butyl 1-(3-butyl-1-hydroxy-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4g).** Yield: 70% (15.1 mg). R_f = 0.5 (Petroleum ether: EtOAc = 5:1). Colorless oil. ¹H NMR (400 MHz, acetone-d_6) δ 8.39 (two singlets, 1H), 8.05 (two singlets, 1H), 8.02-8.01 (m, 1H), 7.81-7.70 (m, 1H), 7.63-7.56 (m, 1H), 7.37-7.31 (m, 1H), 2.87-2.79 (m, 2H), 1.72-1.61 (m, 2H), 1.53-1.27 (m, 20H), 1.01-0.90 (m, 3H). ¹³C NMR (101 MHz, acetone-d_6) δ 157.43, 156.60, 156.45, 156.29, 155.68, 142.48, 133.64, 132.75, 126.27, 123.05, 122.88, 121.76, 121.24, 81.42, 80.61, 31.72, 31.57, 28.54, 28.51, 28.40, 28.26, 23.36, 14.44. IR (neat) γ 3396, 2986, 1709, 1374, 1161 cm⁻¹. HRMS (ESI): m/z Calcd for C_{22}H_{34}BN_2O_6 [M + H]^+ 433.25099, found 433.24982. [α]_D²⁰ = +24° (c 0.19, CHCl₃). Enantiomeric excess: 89%, determined by chiral HPLC analysis [Daicel Chiralpak IC, n-Hexane:2-propanol = 95:5, flow rate 1.0 ml/min, T = 30 °C, λ = 254 nm. t_R(S) = 4.16 min; t_R(R) = 4.46 min].

**Di-tert-butyl 1-(1-hydroxy-3-propyl-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4h).** Yield: 88% (18.4 mg). R_f = 0.5 (Petroleum ether: EtOAc = 5:1). Colorless oil. ¹H NMR (400 MHz, acetone-d_6) δ 8.39 (two singlets, 1H), 8.07 (two singlets, 1H), 8.04-7.98 (m, 1H), 7.82-7.71 (m, 1H), 7.64-7.56 (m, 1H), 7.37-7.32 (m, 1H), 2.81-2.67 (m, 2H), 1.75-1.68 (m, 2H), 1.53-1.29 (m, 20H), 1.01-0.95 (m, 3H). ¹³C NMR (101 MHz, acetone-d_6) δ 156.50, 156.32, 155.64, 142.20, 133.62, 132.75, 126.30, 123.10, 122.93, 81.29, 80.50, 33.49, 28.48, 28.36, 28.22, 20.85, 14.22. IR (neat) γ 3365, 2986, 1709, 1374, 1161 cm⁻¹. HRMS (ESI): m/z Calcd for C_{21}H_{32}BN_2O_6 [M + H]^+ 419.23534, found 419.23418. [α]_D²⁰ = +12° (c 0.34, CHCl₃). Enantiomeric excess: 84%, determined by chiral HPLC analysis [Daicel Chiralpak IC, n-Hexane:2-propanol = 97:3, flow rate 0.5 ml/min, T = 30 °C, λ = 254 nm. t_R(S) = 11.47 min; t_R(R) = 12.83 min].

**Di-tert-butyl 1-(1-hydroxy-3-pentyl-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4i).** Yield: 78% (17.4 mg). R_f = 0.6 (Petroleum ether: EtOAc = 5:1). Colorless oil. ¹H NMR (400 MHz, acetone-d_6) δ 8.39 (two singlets, 1H), 8.07 (two singlets, 1H), 8.04-7.98 (m, 1H), 7.82-7.71 (m, 1H), 7.64-7.56 (m, 1H), 7.37-7.32 (m, 1H), 2.81-2.67 (m, 2H), 1.75-1.68 (m, 2H), 1.53-1.29 (m, 20H), 1.01-0.95 (m, 3H). ¹³C NMR (101 MHz, acetone-d_6) δ 157.43, 156.46, 156.30, 155.67, 142.47, 133.65, 132.76, 126.28, 123.06, 122.89, 121.73, 121.25, 81.41, 80.55, 32.71, 31.93, 31.79, 28.56, 28.52, 28.41, 28.27, 27.39, 23.43, 14.42. IR (neat) γ 3365, 2986, 1709, 1374, 1161, 765 cm⁻¹. HRMS (ESI): m/z Calcd for C_{23}H_{36}BN_2O_6 [M + H]^+ 447.26664, found 447.26526. [α]_D²⁰ = +13° (c 0.32, CHCl₃). Enantiomeric excess: 89%, determined by chiral HPLC analysis [Daicel Chiralpak IC, n-Hexane:2-
propanol = 98:2, flow rate 1.0 ml/min, T = 30 °C, $\lambda = 254$ nm. $t_R (R) = 5.27$ min; $t_R (S) = 6.13$ min.

**Di-tert-butyl 1-(3-hexyl-1-hydroxy-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4j).** Yield: 81% (18.7 mg). $R_f = 0.6$ (Petroleum ether: EtOAc = 5:1). Colorless oil. $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 8.38 (two singlets, 1H), 8.07 (two singlets, 1H), 8.08-8.01 (m, 1H), 7.81-7.70 (m, 1H), 7.66-7.51 (m, 1H), 7.39-7.28 (m, 1H), 2.85-2.79 (m, 2H), 1.71-1.66 (m, 2H), 1.53-1.30 (m, 24H), 0.94-0.77 (m, 3H). $^{13}$C NMR (101 MHz, acetone-$d_6$) $\delta$ 157.44, 156.62, 156.46, 156.30, 155.67, 155.10, 142.48, 133.65, 132.75, 126.28, 123.06, 122.88, 121.71, 121.24, 81.33, 80.52, 32.71, 32.61, 31.86, 28.56, 28.52, 28.41, 28.27, 27.68, 23.29, 14.41. IR (neat) $\gamma$ 3396, 2940, 1693, 1374, 1161, 765 cm$^{-1}$. HRMS (ESI): $m/z$ Calcd for C$_{24}$H$_{38}$BN$_2$O$_6$ [M + H]$^+$ 461.28229, found 461.28098. $[\alpha]_{D}^{20} = +16^\circ$ (c 0.37, CHCl$_3$). Enantiomeric excess: 89%, determined by chiral HPLC analysis [Daicel Chiralpak IC, n-Hexane:2-propanol = 98:2, flow rate 1.0 ml/min, $T = 30$ °C, $\lambda = 254$ nm. $t_R (R) = 5.21$ min; $t_R (S) = 6.00$ min].

**Di-tert-butyl 1-(3-(3-chloropropyl)-1-hydroxy-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4k).** Yield: 78% (17.7 mg). $R_f = 0.5$ (Petroleum ether: EtOAc = 5:1). Colorless oil. $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 8.46 (two singlets, 1H), 8.17 (two singlets, 1H), 8.06-8.03 (m, 1H), 7.78-7.68 (m, 1H), 7.66-7.53 (m, 1H), 7.40-7.33 (m, 1H), 3.81-3.64 (m, 2H), 2.31-2.08 (m, 2H), 1.61-1.15 (m, 20H). $^{13}$C NMR (101 MHz, acetone-$d_6$) $\delta$ 156.60, 155.55, 155.11, 142.16, 133.76, 132.88, 126.58, 126.52, 123.05, 122.87, 81.69, 45.40, 31.23, 29.40, 28.52, 28.42, 28.27, 15.65. IR (neat) $\gamma$ 3335, 2986, 1709, 1374, 1253, 1161, 751 cm$^{-1}$. HRMS (ESI): $m/z$ Calcd for C$_{21}$H$_{31}$BClN$_2$O$_6$ [M + H]$^+$ 453.19637, found 453.19495. $[\alpha]_{D}^{20} = +18^\circ$ (c 0.18, CHCl$_3$). Enantiomeric excess: 87%, determined by chiral HPLC analysis [Daicel Chiralpak AD, n-Hexane:2-propanol = 98:2, flow rate 1.0 ml/min, $T = 30$ °C, $\lambda = 254$ nm. $t_R (S) = 12.29$ min; $t_R (R) = 17.31$ min].

**Di-tert-butyl 1-(1-hydroxy-3-phenethyl-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4l).** Yield: 65% (15.6 mg). $R_f = 0.4$ (Petroleum ether: EtOAc = 5:1). Colorless oil. $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 8.37 (two singlets, 1H), 8.18 (two singlets, 1H), 8.10-8.00 (m, 1H), 7.83-7.70 (m, 1H), 7.63-7.58 (m, 1H), 7.46-7.23 (m, 5H), 7.22-7.13 (m, 1H), 3.35-2.88 (m, 4H), 1.52-1.31 (m, 18H). $^{13}$C NMR (101 MHz, acetone-$d_6$) $\delta$ 156.50, 155.60, 155.16, 143.05, 142.88, 142.32, 133.74, 132.88, 129.36, 129.21, 129.16, 126.76, 126.50, 123.06, 122.88, 81.45, 34.38, 33.81, 28.51, 28.42, 28.28. IR (neat) $\gamma$ 3365, 2970, 1709, 1374, 1253, 1161, 751 cm$^{-1}$. HRMS (ESI): $m/z$ Calcd for C$_{26}$H$_{34}$BN$_2$O$_6$ [M + H]$^+$ 481.25099, found 481.24985. $[\alpha]_{D}^{20} = -10^\circ$ (c 0.37, CHCl$_3$). Enantiomeric excess: 88%, determined by chiral HPLC analysis [Daicel Chiralpak IC, n-Hexane:2-propanol = 97:3, flow rate 1.0 ml/min, $T = 30$ °C, $\lambda = 254$ nm. $t_R (R) = 5.06$ min; $t_R (S) = 5.88$ min].
dicarboxylate (4m). Yield: 66% (14.7 mg). R\textsubscript{f} = 0.4 (Petroleum ether: EtOAc = 5:1). Colorless oil. \textsuperscript{1}H NMR (400 MHz, acetone-\textit{d}_6) δ 8.40 (m, 1H), 8.08 (m, 1H), 8.05-7.99 (m, 1H), 7.83-7.66 (m, 1H), 7.65-7.51 (m, 1H), 7.40-7.29 (m, 1H), 3.02-2.84 (m, 1H), 1.73-1.66 (m, 1H), 1.62-1.59 (m, 1H), 1.54-1.29 (m, 20H), 0.98-0.93 (m, 6H). \textsuperscript{13}C NMR (101 MHz, acetone-\textit{d}_6) δ 156.43, 156.28, 155.67, 142.49, 133.64, 132.76, 126.27, 126.20, 123.04, 122.86, 81.34, 80.53, 36.70, 36.64, 28.98, 28.51, 28.42, 28.28, 23.06, 22.91. IR (neat) γ 3365, 2970, 1709, 1253, 1100, 1024, 796 cm\textsuperscript{-1}. HRMS (ESI): m/z Calcd for C\textsubscript{23}H\textsubscript{36}BN\textsubscript{2}O\textsubscript{6} [M + H]\textsuperscript{+} 447.26664, found 447.26511. [α]\textsubscript{D}\textsuperscript{20} = +22° (c 0.30, CHCl\textsubscript{3}). Enantiomeric excess: 86%, determined by chiral HPLC analysis [Daicel Chiralpak IC, n-Hexane: 2-propanol = 98:2, flow rate 1.0 ml/min, T = 30 °C, λ = 254 nm. t\textsubscript{R} (R) = 4.82 min; t\textsubscript{R} (S) = 5.36 min].

Di-tert-butyl 1-(3-allyl-1-hydroxy-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4n). Yield: 48% (10.0 mg). R\textsubscript{f} = 0.5 (Petroleum ether: EtOAc = 5:1). Colorless oil. \textsuperscript{1}H NMR (400 MHz, acetone-\textit{d}_6) δ 8.47 (two singlets, 1H), 8.21 (two singlets, 1H), 8.06-8.02 (m, 1H), 7.85-7.52 (m, 2H), 7.43-7.29 (m, 1H), 6.10-5.89 (m, 1H), 5.32-5.16 (m, 1H), 5.11-5.04 (m, 1H), 3.80-3.47 (m, 2H), 1.52-1.31 (m, 18H). \textsuperscript{13}C NMR (101 MHz, acetone-\textit{d}_6) δ 156.56, 155.58, 154.23, 142.37, 135.10, 133.75, 132.86, 126.56, 122.83, 117.29, 81.50, 80.70, 79.68, 79.56, 64.66, 64.56, 27.60, 27.51, 27.35, 25.97. IR (neat) γ 3389, 2984, 1706, 1375, 1149 cm\textsuperscript{-1}. HRMS (ESI): m/z Calcd for C\textsubscript{21}H\textsubscript{30}BN\textsubscript{2}O\textsubscript{6} [M + H]\textsuperscript{+} 417.21969, found 417.21881. [α]\textsubscript{D}\textsuperscript{20} = +31° (c 0.10, CHCl\textsubscript{3}). Enantiomeric excess: 91%, determined by chiral HPLC analysis [Daicel Chiralpak AD, n-Hexane: 2-propanol = 97:3, flow rate 0.5 ml/min, T = 30 °C, λ = 254 nm. t\textsubscript{R} (S) = 18.58 min; t\textsubscript{R} (R) = 21.85 min].

Di-tert-butyl 1-(3-(2-(1,3-dioxolan-2-yl)ethyl)-1-hydroxy-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4o). Yield: 62% (14.8 mg). R\textsubscript{f} = 0.5 (Petroleum ether: EtOAc = 5:1). Colorless oil. \textsuperscript{1}H NMR (400 MHz, acetone-\textit{d}_6) δ 8.31 (two singlets, 1H), 8.10 (two singlets, 1H), 7.92-7.85 (m, 1H), 7.85-7.66 (m, 1H), 7.55-7.39 (m, 1H), 7.25-7.19 (m, 1H), 4.84-4.70 (m, 1H), 3.84-3.80 (m, 2H), 2.81-2.56 (m, 2H), 1.87-1.76 (m, 2H), 1.41-1.16 (m, 18H). \textsuperscript{13}C NMR (101 MHz, acetone-\textit{d}_6) δ 155.37, 155.21, 154.64, 141.37, 132.75, 131.95, 125.62, 122.24, 103.48, 80.59, 79.68, 64.66, 64.56, 27.60, 27.51, 27.35, 25.97. IR (neat) γ 3374, 2968, 1720, 1375, 1254, 1164, 774 cm\textsuperscript{-1}. HRMS (ESI): m/z Calcd for C\textsubscript{23}H\textsubscript{34}BN\textsubscript{2}O\textsubscript{8} [M + H]\textsuperscript{+} 477.24082, found 477.24082. [α]\textsubscript{D}\textsuperscript{20} = -17° (c 0.08, CHCl\textsubscript{3}). Enantiomeric excess: 90%, determined by chiral HPLC analysis [Daicel Chiralpak AD, n-Hexane: 2-propanol = 97:3, flow rate 0.5 ml/min, T = 30 °C, λ = 254 nm. t\textsubscript{R} (S) = 18.93 min; t\textsubscript{R} (R) = 21.85 min].

Di-tert-butyl 1-(1-hydroxy-3-phenyl-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4p). Yield: 35% (7.9 mg). R\textsubscript{f} = 0.4 (Petroleum ether: EtOAc = 5:1). Colorless oil. \textsuperscript{1}H NMR (400 MHz, acetone-\textit{d}_6) δ 8.34 (s, 1H), 8.27 (m, 1H), 8.13-8.04 (m, 1H), 7.75-7.58 (m, 3H), 7.52-
7.21 (m, 5H), 1.50-1.27 (m, 18H). $^1$H NMR (101 MHz, acetone-$d_6$) $\delta$ 155.87, 155.37, 154.96, 142.51, 136.33, 133.33, 132.58, 129.90, 129.54, 128.78, 128.57, 127.17, 125.17, 123.38, 82.17, 80.22, 28.48, 28.42, 28.38, 28.35. IR (neat) $\gamma$ 2922, 2848, 1720, 1359, 1149 cm$^{-1}$. HRMS (ESI): $m/z$ Calcd for C$_{24}$H$_{30}$BN$_2$O$_6$ [M + H]$^+$ 453.21699, found 453.21866. $[\alpha]_{D20}^{20} = +16^\circ$ (c 0.09, CHCl$_3$). Enantiomeric excess: 77%, determined by chiral HPLC analysis [Daicel Chiralpak AD, $n$-Hexane: 2-propanol = 97:3, flow rate 1.0 ml/min, T = 30 °C, $\lambda$ = 254 nm., $t_R (S) = 5.94$ min; $t_R (R) = 11.14$ min].

**Di-tert-butyl 1-(3-butyl-1-hydroxy-7-methyl-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4q).** Yield: 73% (16.3 mg). $R_f = 0.4$ (Petroleum ether: EtOAc = 5:1). Colorless oil. $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 8.36 (two singlets, 1H), 7.96 (two singlets, 1H), 7.83-7.82 (m, 1H), 7.71-7.59 (m, 1H), 2.92-2.74 (m, 2H), 2.39 (d, $J = 6.3$ Hz, 3H), 1.69-1.63 (m, 2H), 1.51-1.31 (m, 20H), 0.97-0.91 (m, 3H). $^{13}$C NMR (101 MHz, acetone-$d_6$) $\delta$ 156.38, 155.65, 155.01, 140.04, 135.67, 133.80, 130.53, 122.95, 81.31, 80.51, 32.62, 31.46, 28.52, 28.48, 28.37, 28.24, 23.35, 21.22, 14.42. IR (neat) $\gamma$ 3335, 2970, 1709, 1496, 1374, 1161 cm$^{-1}$. HRMS (ESI): $m/z$ Calcd for C$_{23}$H$_{36}$BN$_2$O$_6$ [M + H]$^+$ 447.26664, found 447.26526. $[\alpha]_{D20}^{20} = +19^\circ$ (c 0.33, CHCl$_3$). Enantiomeric excess: 88%, determined by chiral HPLC analysis [Daicel Chiralpak AD, $n$-Hexane: 2-propanol = 98:2, flow rate 1.0 ml/min, T = 30 °C, $\lambda$ = 254 nm. $t_R (S) = 10.89$ min; $t_R (R) = 14.85$ min].

**Di-tert-butyl 1-(3-butyl-1-hydroxy-7-isopropyl-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4r).** Yield: 72% (17.1 mg). $R_f = 0.6$ (Petroleum ether: EtOAc = 5:1). Colorless oil. $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 8.35 (two singlets, 1H), 8.01 (two singlets, 1H), 7.92-7.91 (m, 1H), 7.74-7.62 (m, 1H), 3.03-2.94 (m, 1H), 2.88-2.74 (m, 2H), 1.70-1.65 (m, 2H), 1.54-1.31 (m, 20H), 1.29-1.26 (m, 6H), 0.97-0.91 (m, 3H). $^{13}$C NMR (101 MHz, acetone-$d_6$) $\delta$ 156.41, 155.70, 155.09, 146.68, 140.45, 131.39, 131.00, 123.25, 123.02, 121.70, 81.27, 80.46, 34.66, 31.49, 28.53, 28.49, 28.39, 28.27, 24.41, 24.32, 23.36, 14.43. IR (neat) $\gamma$ 3381, 2970, 1709, 1496, 1374, 1161 cm$^{-1}$. HRMS (ESI): $m/z$ Calcd for C$_{25}$H$_{40}$BN$_2$O$_6$ [M + H]$^+$ 475.29794, found 475.29684. $[\alpha]_{D20}^{20} = +19^\circ$ (c 0.33, CHCl$_3$). Enantiomeric excess: 88%, determined by chiral HPLC analysis [Daicel Chiralpak AD, $n$-Hexane: 2-propanol = 98:2, flow rate 1.0 ml/min, T = 30 °C, $\lambda$ = 254 nm. $t_R (S) = 19.56$ min; $t_R (R) = 24.40$ min].

**Di-tert-butyl 1-(3-butyl-1-hydroxy-7-fluoro-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4s).** Yield: 81% (18.3 mg). $R_f = 0.5$ (Petroleum ether: EtOAc = 5:1). Colorless oil. $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 8.45 (two singlets, 1H), 8.24 (two singlets, 1H), 7.90 (d, 1H), 7.75-7.59 (m, 1H), 7.42-7.32 (m, 1H), 2.80-2.66 (m, 2H), 1.71-1.61 (m, 2H), 1.53-1.30 (m, 20H), 0.97-0.91 (m, 3H). $^{13}$C NMR (101 MHz, acetone-$d_6$) $\delta$ 162.95, 160.51, 156.57, 155.41, 155.01, 139.07, 130.56, 126.11, 125.92, 121.26, 120.13, 118.25, 81.48, 80.68, 31.56, 31.42, 28.50, 28.47, 28.35, 28.21, 23.31,
14.33. IR (neat) ν 3396, 2940, 1709, 1496, 1374, 1161 cm⁻¹. HRMS (ESI): m/z Calcd for C_{22}H_{33}BFN_{2}O_{6} [M + H]^+ 451.24157, found 451.24014. [α]_D^{20} = +13° (c 0.29, CHCl₃). Enantiomeric excess: 74%, determined by chiral HPLC analysis [Daicel Chiralpak IC, n-Hexane: 2-propanol = 97:3, flow rate 1.0 ml/min, T = 30 °C, λ = 254 nm. tᵣ (R) = 4.52 min; tᵣ (S) = 5.56 min].

**Diisopropyl 1-(1-hydroxy-3-propyl-1H-benzo[c][1,2]oxaborinin-4-yl)hydrazine-1,2-dicarboxylate (4t).** Yield: 89% (69.1 mg). R_<sub>f</sub> = 0.5 (Petroleum ether: EtOAc = 3:1). Colorless oil. ^1H NMR (400 MHz, acetone-d₆) δ 8.65 (two singlets, 1H), 8.11 (two singlets, 1H), 8.05-8.02 (m, 1H), 7.89-7.67 (m, 1H), 7.64-7.57 (m, 1H), 7.38-7.33 (m, 1H), 5.02-4.76 (m, 2H), 2.85-2.63 (m, 2H), 1.75-1.69 (m, 2H), 1.33-0.97 (m, 15H). ^13C NMR (101 MHz, acetone-d₆) δ 157.86, 156.41, 142.26, 133.66, 132.84, 126.35, 122.90, 121.39, 70.73, 69.51, 33.60, 22.29, 22.26, 22.15, 22.02, 20.82, 14.27. HRMS (ESI): m/z Calcd for C_{19}H_{28}BN_{2}O_{6} [M + H]^+ 391.20404, found 391.20377. [α]_D^{20} = +9° (c 1.4, CHCl₃). Enantiomeric excess: 80%, determined by chiral HPLC analysis [Daicel Chiralpak IC, n-Hexane: 2-propanol = 97:3, flow rate 1.0 ml/min, T = 30 °C, λ = 254 nm. tᵣ (S) = 5.68 min; tᵣ (R) = 8.89 min].
Part II Copies of NMR Spectra of compounds
\[ \text{S} \text{19} \]
Part III Copies of HPLC Spectra of compounds

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Part IV Barriers to racemization of 4g

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Exponential decay:

\[ y = -4.33762 + 1.16616E-06x \]

\[ R^2 = 0.99396 \]

Half-life at 40 °C = 163.8 h
Fractions collected and racemised by incubation at 60 °C in 5:1 PE:EtOAc

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Exponential decay:

\[ y = -4.45926 + 1.10783 \times 10^{-5} x \]

\[ R^2 = 0.99842 \]

Half-life at 60 °C = 17.3 h
Fractions collected and racemized by incubation at 80 °C in 5:1 PE:EtOAc

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Exponential decay:

\[ y = -4.42931 + 3.84089 \times 10^{-5}x \]

\[ R^2 = 0.99803 \]

Half-life at 60 °C = 5.0 h
Identification code gr130224
Empirical formula C19H27BN2O6
Formula weight 390.24
Temperature/K 290(2)
Crystal system triclinic
Space group         P-1
a/Å                 9.8024(4)
b/Å                10.2502(3)
c/Å                11.0769(3)
α/°                 91.745(2)
β/°               108.985(3)
γ/°                92.310(3)
Volume/Å3           1050.45(6)
Z                     2
ρcalc/mg/mm³        1.234
m/mm 1             0.750
F(000)             416.0
Crystal size/mm³    0.36 × 0.32 × 0.27
2Θ range for data collection           9.56 to 139.68°
Index ranges        -10 ≤ h ≤ 11, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected             17227
Independent reflections            3896[R(int) = 0.0233]
Data/restraints/parameters            3896/1/258
Goodness-of-fit on F²             1.045
Final R indexes[I>=2σ(I)]            R1 = 0.0448, wR2 = 0.1269
Final R indexes [all data]          R1 = 0.0469, wR2 = 0.1295
Largest diff. peak/hole / e Å⁻³    0.41/-0.26
Part VI VCD for the absolute configuration determination of 4t

Fig. S1 The 3D structure (left) and its most stable conformation (right) at the B3LYP/6-31G(d) level in the gas phase (H atoms are hidden for clarity).

Fig. S2 The predicted VCD and IR curves and the experimental VCD and IR.
The conformational search using MMFF94F force field was performed for it and totally 184 geometries were found. Further optimization was carried out for the geometries with the same absolute configurations at the B3LYP/6-31G (d) level in the gas phase. Then the B3LYP/6-31G (d)-optimized conformations were used for VCD calculations at the same level. The lowest energy conformer is illustrated in Fig. S2 (for clarity, the H atoms are hidden). The simulated VCD and experimental VCD are illustrated in Fig. S3. It is found that the two VCD curves matched well and therefore, the absolute configuration of 4t should be S (Fig. S2). A hydrogen bond between the hydroxyl and the carbonyl groups somehow contributed to the chirality of 4t.

Part VII References