

# Supporting Information

for

## **One-pot tandem cyclization of enantiopure asymmetric *cis*-2,5-disubstituted pyrrolidines: Facile access to chiral 10-heteroazatriquinanes**

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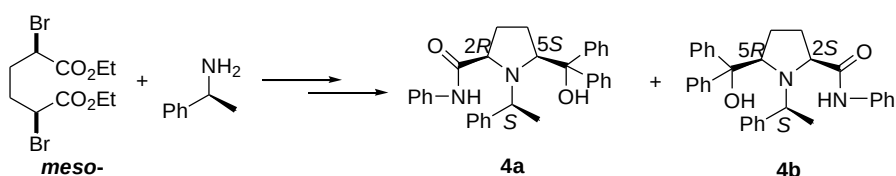
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**Full experimental details, analytical data and crystallographic information.**

## A. General

Melting points are uncorrected and expressed in °C.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured in  $\text{CDCl}_3$  or MeOD solution on a Bruker AV-500 spectrometer using TMS as an internal reference. Coupling constant ( $J$ ) values are given in Hz. Multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, multiplet. Optical rotations analyses were performed on a Perkin-Elmer Model 343 Polarimeter. Low- and high-resolution mass spectra were performed on a VG Micromass 7070F Mass Spectrometer with ES ionization (ESI). All commercially available reagents were used as received. Products were purified by flash column chromatography on silica gel purchased from Qingdao Haiyang Chemical Co., Ltd. All reactions involving air- or moisture-sensitive species were performed in oven-dried glassware under inert atmosphere.



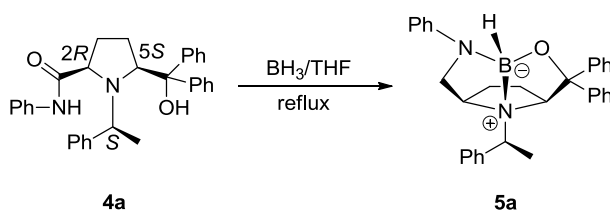
Compounds **4a** and **4b** were synthesized from commercially available starting materials diethyl *meso*-2,5-dibromoadipate and (S)-(-)-1-phenylethylamine according to our previous literature procedure [1]. Crystallographic data of **4b** have been deposited with the Cambridge Crystallographic Data Centre (CCDC# 633772). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Chemical names were generated using ChemDraw Ultra 12.0 (CambridgeSoft).

## B. General Procedures

### General procedure for reduction of the highly hindered amides **4** by $\text{BH}_3$ in THF

As described in [1], to a solution of compound **4a** or **4b** (7.2 g, 15 mmol) in absolute THF (120 mL) was added dropwise  $\text{BH}_3\cdot\text{THF}$  (30.0 mL, 60 mmol) at rt under an inert atmosphere, and the reaction mixture was stirred for 1.0 h. Then, the reaction mixture was heated under reflux and stirred for 24 h. The reaction was examined by TLC. The mixture was cooled to  $0^\circ\text{C}$  and carefully quenched by the addition of methanol (10.0 mL) and water (10.0 mL). The mixture was evaporated under reduced pressure and the residue was dissolved in EtOAc (180 mL). After removal of solid by filtration, the cake was washed with EtOAc ( $2 \times 50$  mL). The combined filtrate was washed with water and brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated to give a crude product as a white foam. The pure product **5a** or **5b** was obtained by flash column chromatography on silica gel (eluant: hexane/EtOAc). The single crystals of **5a** were obtained by slow evaporation from the mixed solvents of  $\text{CH}_2\text{Cl}_2$ /hexane.



**5a** (2aS,2a<sup>1</sup>R,4aR,6aS)-2,2,6-Triphenyl-2a<sup>1</sup>-((S)-1-phenylethyl)octahydro-2H-1-oxa-2a<sup>1</sup>,6-diaza-6a-boracyclopenta[cd]pentalen-2a<sup>1</sup>-ium-7-uide

$R_f$  (hexane/EtOAc = 4:1): 0.40; Yield: 87%; white powder; m.p.  $214\text{--}216^\circ\text{C}$ ;  $[\alpha]_D^{20} = +165.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ );

IR (neat): 3431, 2934, 1366, 1047, 991, 880, 839, 748, 707  $\text{cm}^{-1}$ ;

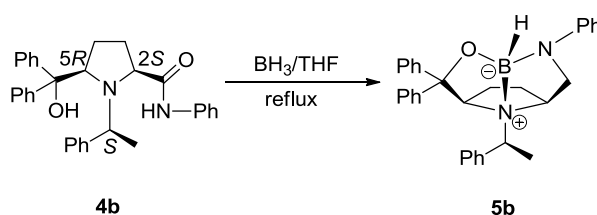
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.90–7.88 (m, 2H), 7.56–6.95 (m, 17H), 6.68 (m, 1H), 4.65–4.63 (t,  $J = 7.0$  Hz, 1H), 4.40–4.36 (m, 1H), 4.03–3.98 (q,  $J = 7.0$  Hz, 1H), 3.86–

3.82 (t,  $J$  = 8.5 Hz, 1H), 3.32–3.29 (dd,  $J$  = 6.0, 4.0 Hz, 1H), 1.80–1.76 (m, 1H), 1.63–1.50 (m, 5H), 1.46–1.41 (m, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  149.6, 146.6, 146.3, 138.7, 129.4, 129.2, 129.1, 128.9, 128.1, 127.8, 126.8, 126.6, 126.1, 125.7, 114.8, 113.6, 84.5, 74.5, 65.6, 64.0, 52.4, 30.6, 29.5, 18.7;

LRMS (ESI)  $m/z$  (%) = 472.28 (25.6)  $[\text{M} (^{10}\text{B}) + \text{H}]^+$ , 473.28 (100)  $[\text{M} (^{11}\text{B}) + \text{H}]^+$ ;

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{34}\text{BN}_2\text{O}$  ( $[\text{M} + \text{H}]^+$ ) 473.2764, found 473.2756.



**5b** (2a*R*,2a<sup>1</sup>*S*,4a*S*,6a*R*)-2,2,6-Triphenyl-2a<sup>1</sup>-((*S*)-1-phenylethyl)octahydro-2*H*-1-oxa-2a<sup>1</sup>,6-diaza-6a-boracyclopenta[*cd*]pentalen-2a<sup>1</sup>-ium-7-uide

$R_f$  (hexane/EtOAc = 3:1): 0.45; Yield: 91%; white powder; m.p. 188–190°C;  $[\alpha]_D^{20} = -210.5$  ( $c$  = 1.0,  $\text{CHCl}_3$ );

IR (neat): 3435, 2939, 1366, 1179, 1062, 986, 753, 693  $\text{cm}^{-1}$ ;

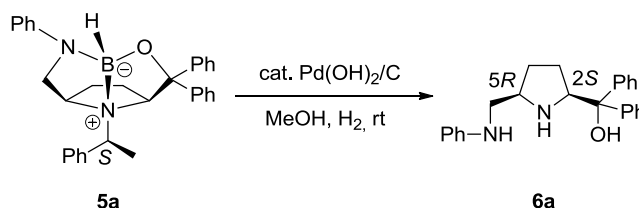
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.83–7.81 (m, 2H), 7.66–7.65 (m, 2H), 7.41–7.13 (m, 13H), 6.84–6.82 (m, 2H), 6.69–6.66 (m, 1H), 4.97–4.95 (m, 1H), 4.15–4.11 (m, 1H), 3.80–3.78 (m, 1H), 3.44–3.39 (m, 1H), 3.32–3.29 (dd,  $J$  = 7.5, 2.5 Hz, 1H), 2.09–2.02 (m, 1H), 1.74–1.69 (m, 2H), 1.60–1.57 (m, 1H), 1.38–1.36 (d,  $J$  = 7.0 Hz, 3H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  149.8, 147.5, 146.1, 138.5, 129.2, 128.9, 128.8, 128.7, 128.1, 127.8, 126.4, 126.3, 126.2, 126.1, 114.8, 113.3, 86.1, 71.3, 66.7, 64.7, 49.7, 31.2, 30.6, 19.3;

LRMS (ESI)  $m/z$  (%) = 472.29 (24.4)  $[\text{M} (^{10}\text{B}) + \text{H}]^+$ , 473.29 (100)  $[\text{M} (^{11}\text{B}) + \text{H}]^+$ ;

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{34}\text{BN}_2\text{O}$  ( $[\text{M} + \text{H}]^+$ ) 473.2764, found 473.2757.

## General procedure for tandem debenzoylation-ring opening of 5



As described in [1], a solution of compound **5a** or **5b** (5 mmol) in MeOH (50 mL) was hydrogenated (1.0 atm H<sub>2</sub>) over 20% Pd(OH)<sub>2</sub>/C (700 mg, 1.0 mmol) for 24 h. The air was removed gently by vacuum before introduction of H<sub>2</sub>. The catalyst was removed by filtration through Celite and the cake was washed with MeOH (2 × 10 mL). The combined filtrate was evaporated to give crude product as a white foam, which was recrystallized from MeOH–Et<sub>2</sub>O (v/v = 1:10). After recrystallization, the pure product **6a** or **6b** was obtained as a white needle crystal.

### **6a** Diphenyl((2*S*,5*R*)-5-((phenylamino)methyl)pyrrolidin-2-yl)methanol

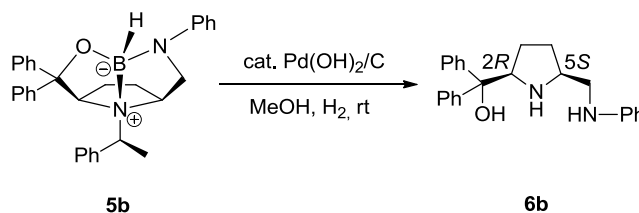
Yield: 81%; white needle crystal; m.p. 199–201°C (dec.);  $[\alpha]_{\text{D}}^{20} = -39.1$  (*c* = 1.0, MeOH);

IR (neat): 3405, 3030, 2942, 1320, 1260, 1067, 756, 699 cm<sup>-1</sup>;

<sup>1</sup>H NMR (MeOD, 500 MHz):  $\delta$  7.59–7.15 (m, 12H), 6.74–6.71 (m, 3H), 5.00–4.98 (m, 1H), 3.89–3.88 (m, 1H), 3.54–3.44 (m, 2H), 2.28–1.97 (m, 4H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  147.8, 144.0, 143.8, 128.9, 128.5, 128.2, 127.4, 127.3, 125.5, 125.4, 117.8, 112.9, 77.2, 67.2, 60.6, 43.4, 27.6, 25.1;

HRMS (ESI) *m/z* calcd for C<sub>24</sub>H<sub>27</sub>N<sub>2</sub>O ([*M* + H]<sup>+</sup>) 359.2123, found 359.2103.



### **6b** Diphenyl((2*R*,5*S*)-5-((phenylamino)methyl)pyrrolidin-2-yl)methanol

Yield: 78%; white needle crystal; m.p. 236–238°C (dec.);  $[\alpha]_{\text{D}}^{20} = +38.8$  ( $c = 1.0$ , MeOH);

IR (neat): 3385, 3028, 2933, 1315, 1260, 1086, 758, 707  $\text{cm}^{-1}$ ;

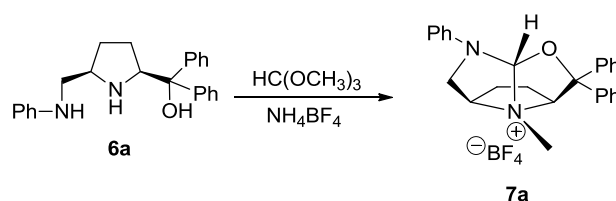
$^1\text{H}$  NMR (MeOD, 500 MHz):  $\delta$  7.58–7.15 (m, 12H), 6.74–6.70 (m, 3H), 4.97–4.95 (m, 1H), 3.87–3.86 (m, 1H), 3.53–3.44 (m, 2H), 2.28–1.96 (m, 4H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  147.8, 144.1, 143.8, 128.9, 128.5, 128.2, 127.3, 127.2, 125.5, 125.4, 117.7, 112.7, 77.2, 67.1, 60.5, 43.3, 27.7, 25.0;

HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}$  ( $[\text{M} + \text{H}]^+$ ) 359.2123, found 359.2144.

### General procedure for tandem cyclization-methylation of **6**

A mixture of **6a** or **6b** (0.72 g, 2.0 mmol) and  $\text{NH}_4\text{BF}_4$  (0.43 g, 4.0 mmol) in 7.0 mL of trimethyl orthoformate (65 mmol) was heated under reflux for 8 h under an Ar atmosphere. The reaction was examined by TLC. After the starting material disappeared, the remaining trimethyl orthoformate was evaporated under reduced pressure to give a brown oily residue, which was washed with *n*-hexane ( $2 \times 3.0$  mL) and recrystallized from *n*-hexane and  $\text{CH}_2\text{Cl}_2$  ( $v/v = 10:1$ ) to give **7a** or **7b** as light yellow crystals. The single crystals of **7b** were obtained by slow evaporation from the mixed solvents of  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ .



**7a** (2a*S*,2a<sup>1</sup>*S*,4a*R*,6a*S*)-2a<sup>1</sup>-Methyl-2,2,6-triphenyloctahydro-2*H*-1-oxa-2a<sup>1</sup>,6-diazacyclopenta[*cd*]pentalen-2a<sup>1</sup>-ium tetrafluoroborate

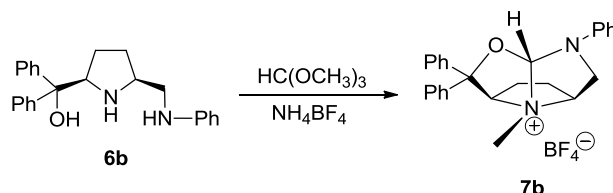
Yield: 82%; light yellow crystal; m.p. 212–214°C (dec.);  $[\alpha]_{\text{D}}^{20} = +23.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ );

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.88–7.86 (m, 2H), 7.56–6.99 (m, 13H), 6.14 (s, 1H), 5.83–5.80 (t,  $J = 8.0$  Hz, 1H), 4.69–4.66 (t,  $J = 8.0$  Hz, 1H), 4.42–4.38 (t,  $J = 8.0$  Hz,

1H), 3.64–3.60 (t,  $J = 9.0$  Hz, 1H), 3.32 (s, 3H, CH<sub>3</sub>), 2.83–2.74 (m, 1H), 2.55–2.53 (m, 1H), 2.12–2.11 (m, 1H), 1.91–1.83 (m, 1H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  147.4, 139.6, 139.1, 130.1, 130.0, 129.3, 128.9, 128.1, 125.2, 124.4, 122.6, 116.1, 108.5, 89.9, 79.6, 79.3, 51.1, 49.7, 30.6, 27.4;

HRMS (ESI)  $m/z$  calcd for C<sub>26</sub>H<sub>27</sub>N<sub>2</sub>O ([M – BF<sub>4</sub>]<sup>+</sup>) 383.2123, found 383.2119.



**7b** (2a*R*,2a<sup>1</sup>*R*,4a*S*,6a*R*)-2a<sup>1</sup>-Methyl-2,2,6-triphenyloctahydro-2*H*-1-oxa-2a<sup>1</sup>,6-diazacyclopenta[*cd*]pentalen-2a<sup>1</sup>-ium

Yield: 85%; light yellow crystal; m.p. 211–213°C (dec.); [ $\alpha$ ]<sub>D</sub><sup>20</sup> = –24.3 ( $c = 1.0$ , CHCl<sub>3</sub>);

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.87–7.86 (m, 2H), 7.55–7.00 (m, 13H), 6.14 (s, 1H), 5.80–5.77 (t,  $J = 8.5$  Hz, 1H), 4.72–4.68 (t,  $J = 7.5$  Hz, 1H), 4.44–4.40 (m, 1H), 3.62–3.58 (m, 1H), 3.29 (s, 3H, CH<sub>3</sub>), 2.75–2.70 (m, 1H), 2.52–2.49 (m, 1H), 2.15–2.10 (m, 1H), 1.92–1.85 (m, 1H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  147.4, 139.6, 139.0, 130.1, 130.0, 129.9, 129.2, 128.9, 128.1, 125.2, 124.4, 122.6, 116.1, 108.5, 89.9, 79.6, 79.3, 51.1, 49.7, 30.6, 27.4;

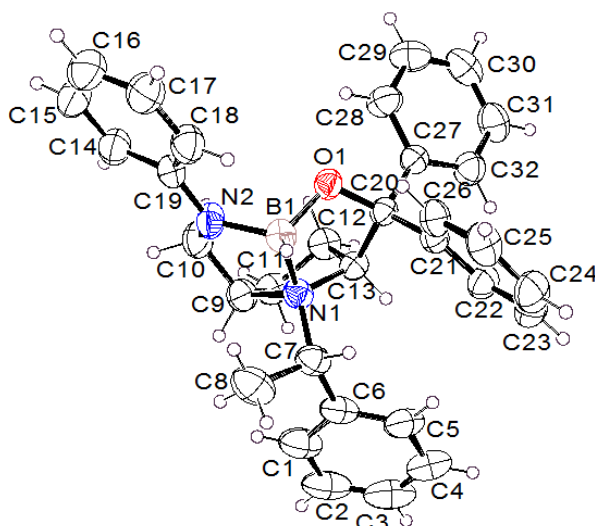
HRMS (ESI)  $m/z$  calcd for C<sub>26</sub>H<sub>27</sub>N<sub>2</sub>O ([M – BF<sub>4</sub>]<sup>+</sup>) 383.2123, found 383.2117.

## X-ray crystal structure data for compounds 5a and 7b

### 1. X-ray crystallographic data for compound 5a

Crystals of compound **5a** suitable for X-ray analysis were obtained by slow evaporation from the mixed solvents of CH<sub>2</sub>Cl<sub>2</sub>/hexane. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC# 891107). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail:

[deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).



**Table S1:** Crystal data and structure refinement for compound **5a**.

|                     |                                                    |
|---------------------|----------------------------------------------------|
| Identification code | compound 5a                                        |
| Empirical formula   | C <sub>32</sub> H <sub>33</sub> B N <sub>2</sub> O |
| Formula weight      | 472.41                                             |
| Temperature         | 296(2) K                                           |
| Wavelength          | 0.71073 Å                                          |
| Crystal colour      | colourless                                         |
| Crystal description | block                                              |



|                                      |                                                                                                                                                             |
|--------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Crystal system                       | Orthorhombic                                                                                                                                                |
| Space group                          | P2(1)2(1)2(1)                                                                                                                                               |
| Unit cell dimensions                 | $a = 9.0271(16) \text{ \AA}$ $\alpha = 90^\circ$ .<br>$b = 14.669(3) \text{ \AA}$ $\beta = 90^\circ$ .<br>$c = 19.643(3) \text{ \AA}$ $\gamma = 90^\circ$ . |
| Volume                               | $2601.0(8) \text{ \AA}^3$                                                                                                                                   |
| Z                                    | 4                                                                                                                                                           |
| Calculated density                   | $1.206 \text{ Mg/m}^3$                                                                                                                                      |
| Absorption coefficient               | $0.072 \text{ mm}^{-1}$                                                                                                                                     |
| F(000)                               | 1008                                                                                                                                                        |
| Crystal size                         | $0.38 \times 0.29 \times 0.17 \text{ mm}$                                                                                                                   |
| Theta range for data collection      | $1.73$ to $25.10^\circ$                                                                                                                                     |
| Limiting indices                     | $-10 \leq h \leq 10$ , $-17 \leq k \leq 12$ , $-22 \leq l \leq 23$                                                                                          |
| Reflections collected                | 13137                                                                                                                                                       |
| Independent reflections              | 4635 [R(int) = 0.0317]                                                                                                                                      |
| Completeness to theta = $25.10$      | 99.8 %                                                                                                                                                      |
| Absorption correction                | constr                                                                                                                                                      |
| Max. and min. transmission           | 0.9880 and 0.9735                                                                                                                                           |
| Refinement method                    | Full-matrix least-squares on $F^2$                                                                                                                          |
| Data / restraints / parameters       | 4635 / 0 / 327                                                                                                                                              |
| Goodness-of-fit on $F^2$             | 0.990                                                                                                                                                       |
| Final R indices [ $I > 2\sigma(I)$ ] | R1 = 0.0363, wR2 = 0.0793                                                                                                                                   |
| R indices (all data)                 | R1 = 0.0641, wR2 = 0.0855                                                                                                                                   |
| Absolute structure parameter         | 0.0(14)                                                                                                                                                     |
| Extinction coefficient               | 0.0085(8)                                                                                                                                                   |
| Largest diff. peak and hole          | 0.117 and $-0.120 \text{ e.\AA}^{-3}$                                                                                                                       |

**Table 2:** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for compound **5a**. U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

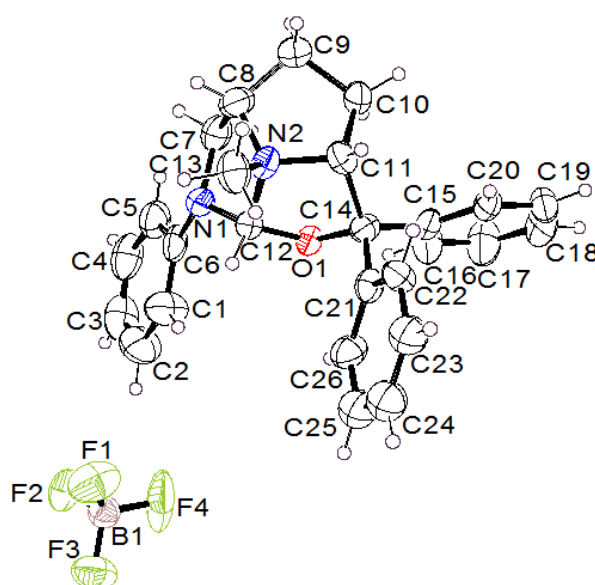
|       | x        | y       | z       | U(eq)  |
|-------|----------|---------|---------|--------|
| N(1)  | 7081(2)  | 5374(1) | 2386(1) | 58(1)  |
| N(2)  | 5005(2)  | 6240(1) | 1929(1) | 68(1)  |
| O(1)  | 6271(1)  | 5057(1) | 1231(1) | 56(1)  |
| B(1)  | 6435(3)  | 5843(2) | 1685(1) | 60(1)  |
| C(1)  | 8905(3)  | 5397(2) | 3877(1) | 97(1)  |
| C(2)  | 9676(4)  | 4923(2) | 4382(1) | 106(1) |
| C(3)  | 10849(4) | 4382(2) | 4204(2) | 113(1) |
| C(4)  | 11292(3) | 4317(2) | 3551(2) | 101(1) |
| C(5)  | 10528(3) | 4801(2) | 3052(1) | 85(1)  |
| C(6)  | 9318(3)  | 5330(2) | 3196(1) | 73(1)  |
| C(7)  | 8526(2)  | 5828(2) | 2622(1) | 67(1)  |
| C(8)  | 8276(3)  | 6836(2) | 2769(1) | 102(1) |
| C(9)  | 5831(2)  | 5419(2) | 2906(1) | 67(1)  |
| C(10) | 4474(2)  | 5778(2) | 2533(1) | 76(1)  |
| C(11) | 5664(2)  | 4453(2) | 3160(1) | 73(1)  |
| C(12) | 5931(2)  | 3902(1) | 2524(1) | 66(1)  |
| C(13) | 7241(2)  | 4366(1) | 2198(1) | 54(1)  |
| C(14) | 2535(3)  | 6845(2) | 1707(1) | 79(1)  |
| C(15) | 1600(3)  | 7339(2) | 1292(2) | 96(1)  |
| C(16) | 2064(4)  | 7698(2) | 693(2)  | 100(1) |

|       |          |         |         |       |
|-------|----------|---------|---------|-------|
| C(17) | 3506(3)  | 7548(2) | 496(1)  | 91(1) |
| C(18) | 4474(3)  | 7060(2) | 902(1)  | 79(1) |
| C(19) | 4008(2)  | 6700(1) | 1523(1) | 64(1) |
| C(20) | 7270(2)  | 4354(1) | 1404(1) | 51(1) |
| C(21) | 8822(2)  | 4547(1) | 1120(1) | 53(1) |
| C(22) | 10066(2) | 4099(1) | 1374(1) | 67(1) |
| C(23) | 11464(2) | 4278(2) | 1131(1) | 80(1) |
| C(24) | 11650(3) | 4913(2) | 627(1)  | 86(1) |
| C(25) | 10438(3) | 5344(2) | 353(1)  | 79(1) |
| C(26) | 9036(2)  | 5162(1) | 602(1)  | 64(1) |
| C(27) | 6670(2)  | 3455(1) | 1118(1) | 54(1) |
| C(28) | 5292(3)  | 3432(2) | 816(1)  | 77(1) |
| C(29) | 4721(3)  | 2633(2) | 549(1)  | 94(1) |
| C(30) | 5509(4)  | 1849(2) | 578(1)  | 91(1) |
| C(31) | 6866(3)  | 1844(2) | 878(1)  | 86(1) |
| C(32) | 7442(2)  | 2648(1) | 1149(1) | 74(1) |

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## 2. X-ray crystallographic data for compound **7b**

Crystals of compound **7b** suitable for X-ray analysis were obtained by slow evaporation from the mixed solvents of CH<sub>2</sub>Cl<sub>2</sub>/MeOH. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC# 891108). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).



**Table S2:** Crystal data and structure refinement for compound **7b**.

|                     |                                                                   |
|---------------------|-------------------------------------------------------------------|
| Identification code | compound <b>7b</b>                                                |
| Empirical formula   | C <sub>26</sub> H <sub>27</sub> B F <sub>4</sub> N <sub>2</sub> O |
| Formula weight      | 470.31                                                            |
| Temperature         | 296(2) K                                                          |
| Wavelength          | 0.71073 Å                                                         |
| Crystal colour      | colourless                                                        |
| Crystal description | block                                                             |
| Crystal system      | Monoclinic                                                        |

|                                      |                                                                                                                                                                   |
|--------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Space group                          | P2(1)                                                                                                                                                             |
| Unit cell dimensions                 | $a = 8.887(4) \text{ \AA}$ $\alpha = 90^\circ$ .<br>$b = 10.259(4) \text{ \AA}$ $\beta = 101.714(7)^\circ$ .<br>$c = 13.390(6) \text{ \AA}$ $\gamma = 90^\circ$ . |
| Volume                               | $1195.4(9) \text{ \AA}^3$                                                                                                                                         |
| Z                                    | 2                                                                                                                                                                 |
| Calculated density                   | $1.307 \text{ Mg/m}^3$                                                                                                                                            |
| Absorption coefficient               | $0.100 \text{ mm}^{-1}$                                                                                                                                           |
| F(000)                               | 492                                                                                                                                                               |
| Crystal size                         | $0.33 \times 0.18 \times 0.11 \text{ mm}$                                                                                                                         |
| Theta range for data collection      | $1.55$ to $25.10 \text{ deg.}$                                                                                                                                    |
| Limiting indices                     | $-10 \leq h \leq 10$ , $-6 \leq k \leq 12$ , $-15 \leq l \leq 15$                                                                                                 |
| Reflections collected                | 6121                                                                                                                                                              |
| Independent reflections              | 3281 [ $R(\text{int}) = 0.0691$ ]                                                                                                                                 |
| Completeness to $\theta = 25.10$     | 100.0 %                                                                                                                                                           |
| Absorption correction                | constr                                                                                                                                                            |
| Max. and min. transmission           | 0.9891 and 0.9679                                                                                                                                                 |
| Refinement method                    | Full-matrix least-squares on $F^2$                                                                                                                                |
| Data / restraints / parameters       | 3281 / 1 / 288                                                                                                                                                    |
| Goodness-of-fit on $F^2$             | 0.960                                                                                                                                                             |
| Final R indices [ $I > 2\sigma(I)$ ] | $R1 = 0.0617$ , $wR2 = 0.1234$                                                                                                                                    |
| R indices (all data)                 | $R1 = 0.1550$ , $wR2 = 0.1654$                                                                                                                                    |
| Absolute structure parameter         | 2(2)                                                                                                                                                              |
| Largest diff. peak and hole          | $0.239$ and $-0.240 \text{ e.\AA}^{-3}$                                                                                                                           |

**Table 2:** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for compound **7b**. U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

|       | x        | y         | z        | U(eq)  |
|-------|----------|-----------|----------|--------|
| N(1)  | 4373(7)  | 9436(7)   | 3062(5)  | 64(2)  |
| O(1)  | 1863(5)  | 10141(5)  | 3066(3)  | 48(1)  |
| C(1)  | 4814(11) | 9020(12)  | 4865(8)  | 95(4)  |
| C(2)  | 5656(13) | 9245(14)  | 5821(8)  | 113(5) |
| C(3)  | 6889(13) | 10073(14) | 5980(9)  | 103(4) |
| C(4)  | 7305(12) | 10693(12) | 5197(11) | 99(4)  |
| C(5)  | 6419(11) | 10508(11) | 4236(8)  | 85(3)  |
| C(6)  | 5202(10) | 9719(11)  | 4070(7)  | 71(3)  |
| C(7)  | 4645(8)  | 10232(10) | 2197(7)  | 71(3)  |
| C(8)  | 3661(10) | 9532(10)  | 1282(7)  | 72(3)  |
| C(9)  | 2826(9)  | 10383(10) | 415(6)   | 80(3)  |
| C(10) | 1426(8)  | 10897(9)  | 816(6)   | 61(2)  |
| C(11) | 930(9)   | 9703(9)   | 1363(6)  | 58(2)  |
| N(2)  | 2370(7)  | 8927(7)   | 1716(5)  | 56(2)  |
| C(12) | 2810(8)  | 9138(8)   | 2881(6)  | 51(2)  |
| C(13) | 2153(10) | 7474(9)   | 1479(7)  | 75(3)  |
| C(14) | 382(8)   | 10029(10) | 2372(5)  | 54(2)  |
| C(15) | -463(9)  | 11327(9)  | 2344(7)  | 52(2)  |
| C(16) | 43(11)   | 12266(11) | 3022(7)  | 81(3)  |
| C(17) | -795(12) | 13434(13) | 3039(8)  | 108(4) |

|       |           |           |          |        |
|-------|-----------|-----------|----------|--------|
| C(18) | -2158(12) | 13560(10) | 2352(9)  | 80(3)  |
| C(19) | -2622(10) | 12612(11) | 1655(7)  | 75(3)  |
| C(20) | -1812(9)  | 11466(9)  | 1645(6)  | 55(2)  |
| C(21) | -535(8)   | 8934(9)   | 2729(6)  | 53(2)  |
| C(22) | -1641(10) | 8233(9)   | 2052(7)  | 67(3)  |
| C(23) | -2557(11) | 7296(10)  | 2405(7)  | 80(3)  |
| C(24) | -2351(11) | 7064(10)  | 3415(7)  | 86(3)  |
| C(25) | -1296(11) | 7706(11)  | 4091(7)  | 83(3)  |
| C(26) | -358(9)   | 8659(10)  | 3764(6)  | 74(3)  |
| B(1)  | 6500(14)  | 9336(14)  | 9140(10) | 74(3)  |
| F(1)  | 6276(7)   | 8613(8)   | 8276(4)  | 139(3) |
| F(2)  | 8024(5)   | 9688(6)   | 9398(4)  | 92(2)  |
| F(3)  | 6105(6)   | 8590(7)   | 9869(4)  | 121(2) |
| F(4)  | 5630(6)   | 10379(7)  | 8963(8)  | 204(5) |

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## References:

- [1] Wang, P.-A.; Xu, Z.-S.; Chen, C.-F.; Gao, X.-G.; Sun, X.-L.; Zhang, S.-Y. *Chirality* **2007**, *19*, 581–588. doi:10.1002/chir.20424

