

Development of Enantiospecific Coupling of Secondary and Tertiary Boronic Esters with Aromatic Compounds

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Supporting Material I

Experimental procedures, React-IR experiments and plots, DFT calculations

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1. General Information

All required fine chemicals were used directly without purification unless otherwise noted. All air- and water-sensitive reactions were carried out in flame-dried glassware under nitrogen atmosphere by using standard Schlenk manifold techniques. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired at various field strengths as indicated, and were referenced to CHCl_3 (7.27 and 77.00 ppm for ^1H and ^{13}C , respectively) or DMSO (2.54 and 40.45 ppm for ^1H and ^{13}C , respectively). ^1H NMR coupling constants are reported in Hertz. Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, qi = quintet, sx = sextet, sp = septet, m = multiplet, dd = doublet of doublets) and integration. ^{11}B NMR spectra were recorded with

complete proton decoupling by using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.0 ppm) as an external standard. High resolution mass spectra were recorded using electronic ionization (EI), electron spray ionization (ESI) or chemical ionization (CI). For CI, methane or $\text{NH}_4\text{OAc}/\text{MeOH}$ were used as reagent gases. All IR data was obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer. Optical rotations were obtained on a Perkin-Elmer 241MC polarimeter. Analytical TLC: aluminium-backed plates precoated (0.25 mm) with Merck Silica Gel 60 F254. Compounds were visualized by exposure to UV light or by dipping the plates in permanganate (KMnO_4) stain followed by heating. Flash column chromatography was performed using Merck Silica Gel 60 (40–63 μm). All mixed solvent eluents are reported as v/v solutions. Chiral HPLC was performed using Diacel Chiralpak IA, IB and IC columns (4.6 \times 250 mm \times 5 μm) fitted with the respective guards (4 \times 10 mm) and monitored by DAD (diode array detector). Chiral GC was performed on an Agilent Technologies 6890N Network GC system by using a Supelco DM column (30 m \times 2.5 mm). Solvents were purified by standard methods. TMEDA was distilled over CaH_2 . (–)-Sparteine was obtained from the commercially available sulfate pentahydrate salt (99%, Acros) and isolated according to literature procedure.¹ The (–)-sparteine free base readily absorbs atmospheric carbon dioxide (CO_2) and should be stored under argon/nitrogen at $-20\text{ }^\circ\text{C}$ in a Schlenk flask. *sec*-BuLi (1.3 M sol. in cyclohexane/hexane (92/8)) was purchased from Acros. *n*-BuLi (1.6 M sol. in hexanes) and *t*-BuLi (1.7 M sol. in pentane) were purchased from Sigma-Aldrich. Abbreviations: PMP = *para*-methoxyphenyl; DDQ = 2,3-dichloro-4,5-dicyano-1,4-benzoquinone; NBS = *N*-bromosuccinimide; NIBS = *N*-iodosuccinimide; DBDMH = 1,3-dibromo-5,5-dimethylhydantoin.

¹ Nikolic, N. A.; Beak, P.; *Org. Synth.*, **1997**, 74, 23.

2. General Procedures

Hydroborations with $\text{HBBr}_2 \cdot \text{SMe}_2$ and BBr_3 – General Procedure 1

A solution of the alkene (1.1 eq.) in CH_2Cl_2 (0.5 M) was cooled to 0 °C and dibromoborane dimethylsulfide complex (1.0 eq., 1 M in CH_2Cl_2) and boron tribromide (1.0 eq.) were added dropwise. The cooling bath was removed and the mixture was stirred for 2 h at room temperature. ^{11}B NMR spectroscopy revealed the complete formation of the hydroborated product [^{11}B NMR (96 MHz, CH_2Cl_2) $\delta_{\text{B}} \sim 63$ ppm]. In a second flask, pinacol (3.0 eq.) was dissolved in CH_2Cl_2 (0.5 M), Et_3N (8.0 eq.) was added and the resulting solution was cooled to 0 °C. The crude hydroborated product was slowly added dropwise. The mixture was allowed to warm to room temperature and stirred for 2 h. ^{11}B NMR spectroscopy revealed complete formation of the pinacol boronic ester [^{11}B NMR (96 MHz, CH_2Cl_2) $\delta_{\text{B}} \sim 32$ ppm]. The mixture was diluted with CH_2Cl_2 (50 mL) and washed with water (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were concentrated under vacuum. The crude material was dissolved in MeOH and water was added until the mixture turned turbid. The solvents were evaporated to dryness under vacuum. The cycle of dissolution/concentration was repeated (x 6) until TLC analysis showed almost complete removal of pinacol. The crude product was dissolved in CH_2Cl_2 , dried over MgSO_4 , filtered and concentrated. Purification by column chromatography on silica gel, gave the desired boronic ester.

$\text{C}(\text{sp}^3)\text{-C}(\text{sp}^2)$ coupling of boronic esters with furan by using NBS – General Procedure 2

A solution of furan (1.2 eq.) in THF (0.3 M) was cooled to -78 °C and treated with *n*-BuLi (1.2 eq., 1.6 M in hexanes). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to -78 °C and the boronic ester (1.0 eq.) was added dropwise as a solution in THF (0.5 M). The mixture was stirred at -78 °C for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR (96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. A solution of *N*-bromosuccinimide (NBS, 1.2 eq.) in THF (0.3 M) was added dropwise. After 1 h at -78 °C, a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et_2O and water. The layers were separated and the aqueous layer was extracted with Et_2O . The combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by column chromatography on silica gel, gave

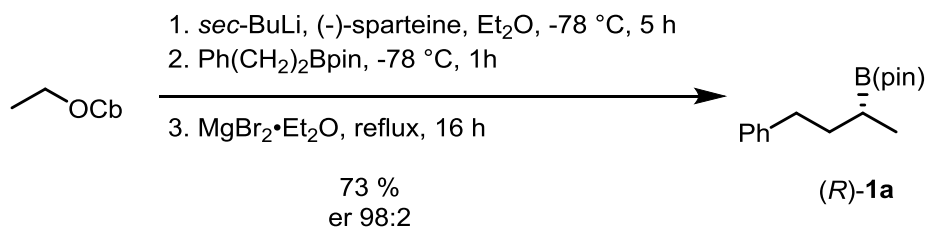
the desired product. *NOTE: NBS must be dissolved and added to the 'ate' complex solution before it turns orange. This applies particularly to examples where NBS (or other electrophile) is added in MeOH.*

C(sp³)-C(sp²) coupling of boronic esters with furan by using DDQ—General Procedure 3

A solution of furan (1.2 eq.) in THF (0.3 M) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated with *n*-BuLi (1.2 eq., 1.6 M in hexanes). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and the boronic ester (1.0 eq.) was added dropwise as a solution in THF (0.5 M). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the 'ate' complex [¹¹B NMR (96 MHz, THF) $\delta_{\text{B}} \sim 8\text{ ppm}$]. A solution of DDQ (1.5 eq.) in THF (0.3 M) was added dropwise. After 1 h at $-78\text{ }^{\circ}\text{C}$, a saturated aqueous solution of Na₂S₂O₃ was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et₂O and water. The layers were separated and the aqueous layer was extracted with Et₂O. The combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by column chromatography on silica gel, gave the desired product. *NOTE: NBS must be dissolved and added to the 'ate' complex solution before it turns orange. This applies particularly to examples where NBS (or other electrophile) is added in MeOH.*

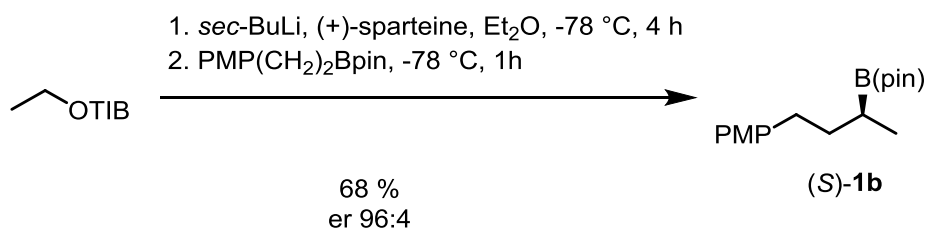
3. Synthesis of the starting materials

(*R*)-4,4,5,5-Tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane [(*R*)-1a]



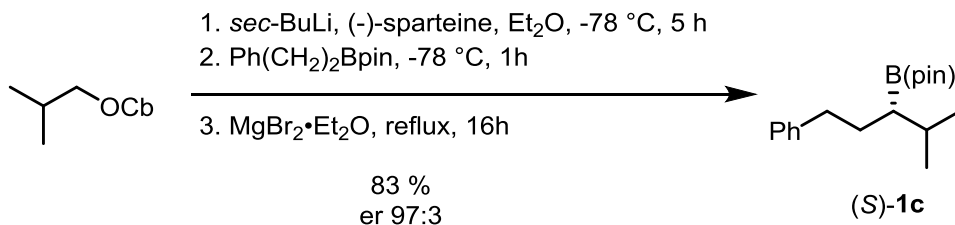
Prepared according to a literature known procedure.²

(*S*)-2-(4-(4-methoxyphenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-1b]



Prepared according to a literature known procedure.³

(*S*)-4,4,5,5-Tetramethyl-2-(4-methyl-1-phenylpentan-3-yl)-1,3,2-dioxaborolane [(*S*)-1c]



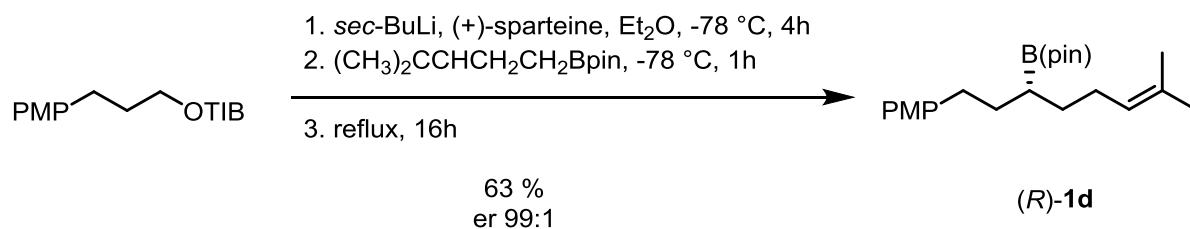
Prepared using the same procedure as reported for [(*R*)-1a]. Data in accordance with the literature.⁴

² Hesse, M. J.; Butts, C. P.; Willis, C. L.; Aggarwal, V. K.; *Angew. Chem. Int. Ed.*, **2012**, *51*, 12444.

³ Larouche-Gauthier, R.; Elford, T. G.; Aggarwal, V. K.; *J. Am. Chem. Soc.*, **2011**, *133*, 16794.

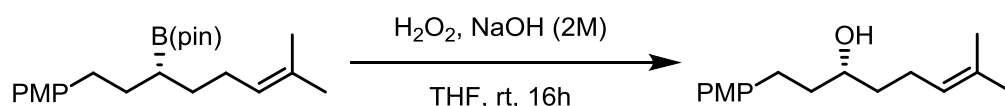
⁴ Bagutski, V.; Ros, A.; Aggarwal, V. K.; *Tetrahedron*, **2009**, *65*, 9956.

(R)-2-(1-(4-methoxyphenyl)-7-methyloct-6-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(R)-1d]



A solution of the (3-(4-methoxyphenyl)propyl 2,4,6-triisopropylbenzoate (345 mg, 0.87 mmol, 1.0 eq.) and (+)-sparteine (245mg, 1.04 mmol, 1.2 eq.) in Et₂O (4.5 ml) was cooled to -78 °C. The solution was treated with *sec*-BuLi (0.82 mL, 1.042 mmol, 1.15 eq., 1.4 M in cyclohexane). The mixture was stirred for 4h at -78 °C and then a solution of 2-(3-methylbut-2-en-1-yl)-B(pin) (219 mg, 1.04 mmol, 1.2 eq.) in Et₂O (5.0 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 1 h and at refluxing conditions for 16h. Water (10 mL) was added and the layers were separated. The aqueous layer was extracted with Et₂O (3 x 10 ml). The combined organic layers were washed with brine (30 ml), dried over MgSO₄ and concentrated under vacuum. The crude material was purified by column chromatography on silica gel, eluting with petrol:Et₂O (99:1) to give (R)-1d (196 mg, 63%), which was obtained as an oil; er (*R*:*S*) 96:4; *R*_f 0.51 (pentane:Et₂O 95:5); [α]_D²⁴ -2 (*c* 1.0, CHCl₃); IR (film): ν (cm⁻¹) 2977, 2923, 2855, 1511, 1379, 1314, 1244, 1143; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.14–7.09 (m, 2H), 6.86–6.80 (m, 2H), 5.14 (br t, *J* = 7.1 Hz, 1H), 3.79 (s, 3H), 2.64–2.49 (m, 2H), 2.09–1.91 (m, 2H), 1.80–1.60 (m, 2H), 1.71 (s, 3H), 1.61 (s, 3H), 1.52 (m, 1H), 1.42 (m, 1H), 1.28 (s, 12H), 1.08 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 157.6, 135.2, 131.1, 129.2, 124.9, 113.6, 82.9, 55.2, 34.6, 33.6, 31.4, 27.7, 25.7, 24.8, 17.6; ¹¹B NMR (96 MHz, NONE) δ ppm 34.1; HRMS (ESI) calcd. for C₂₂H₃₅BNaO₃ [*M*+Na]⁺ 381.2571, found 381.2586.

1d was converted into the corresponding alcohol through oxidation to achieve resolution of the enantiomers in chiral HPLC analysis (see below):

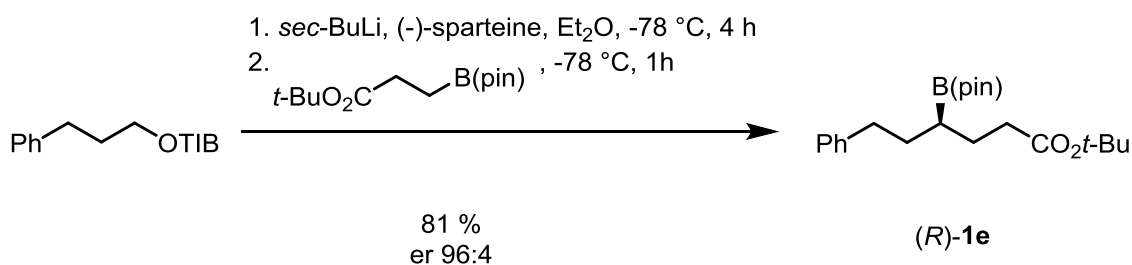


Boronic ester **1d** was treated with a solution of 2 N NaOH/30% H₂O₂ (2:1 v/v) in THF/Et₂O (1:1 v/v) to give, after purification by column chromatography (SiO₂, 85:15 petrol/EtOAc), the desired secondary alcohol (20 mg, 95%) as an oil. *R*_f 0.42 (petrol: Et₂O 85:15); [α]_D²⁴ -20 (*c* 0.6, CHCl₃); IR (film): ν (cm⁻¹) 3371, 2924, 2855, 1612, 1511, 1243, 1037, 820; ¹H

NMR (400 MHz, CDCl₃) δ ppm 7.16–7.10 (m, 2H), 6.87–6.81 (m, 2H), 5.14 (br t, $J = 7.1$ Hz, 1H), 3.80 (s, 3H), 3.64 (m, 1H), 2.75 (m, 1H), 2.63 (m, 1H), 2.20–2.00 (m, 2H), 1.82–1.71 (m, 2H), 1.70 (s, 3H), 1.63 (s, 3H), 1.52–1.45 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 157.8, 134.2, 132.2, 129.3, 124.0, 113.8, 71.2, 55.2, 39.4, 37.4, 31.1, 25.7, 24.4, 17.7; HRMS (ESI) calcd. for C₁₆H₂₄NaO₂ [$M+Na$]⁺ 271.1669, found 271.1668.

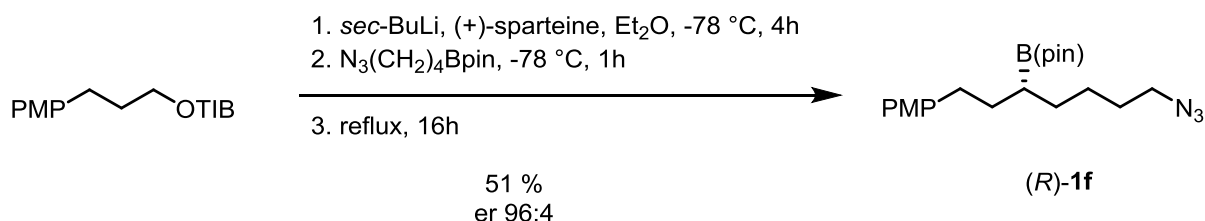
Resolution of the enantiomers of the alcohol was achieved by using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO₂:[*n*-hexane:*i*-PrOH (9:1 v:v)] as the mobile phase at a flow rate of 4.0 mL min⁻¹ ($P = 125$ bar). Injection volume: 20 μ L of a 2 g L⁻¹ solution of the compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) eluted at 11.5 and 13.4 min., respectively, with a total analysis time of 18 min.

(*R*)-*tert*-Butyl 6-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate [(*R*)-1e]



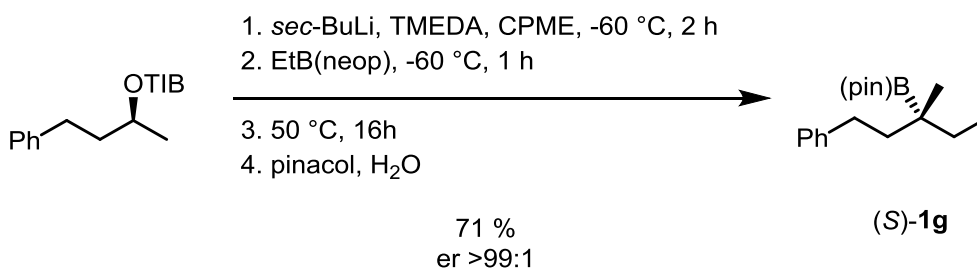
Prepared according to a literature known procedure.³

(*R*)-2-(7-azido-1-(4-methoxyphenyl)heptan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*R*)-1f]



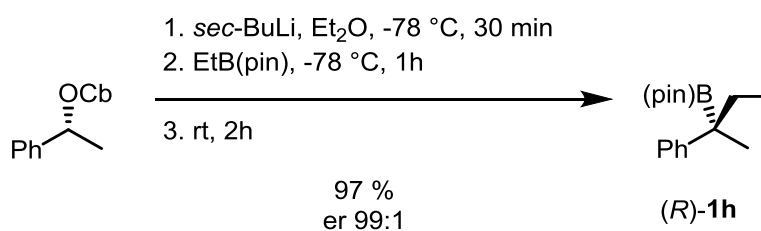
Prepared according to a literature known procedure.³

(S)-4,4,5,5-Tetramethyl-2-(3-methyl-1-phenylpentan-3-yl)-1,3,2-dioxaborolane [(S)-1g]



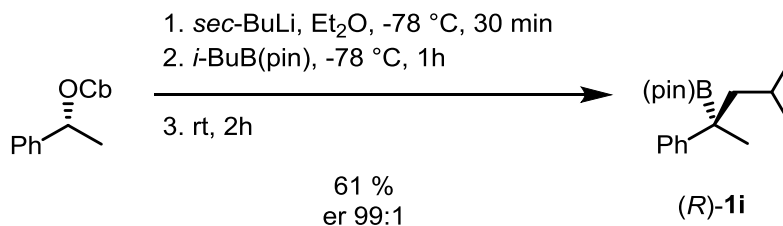
Prepared according to a literature known procedure.⁵

(R)-4,4,5,5-Tetramethyl-2-(2-phenylbutan-2-yl)-1,3,2-dioxaborolane [(R)-1h]



Prepared according to a literature known procedure.⁶

(R)-4,4,5,5-Tetramethyl-2-(4-methyl-2-phenylpentan-2-yl)-1,3,2-dioxaborolane [(R)-1i]



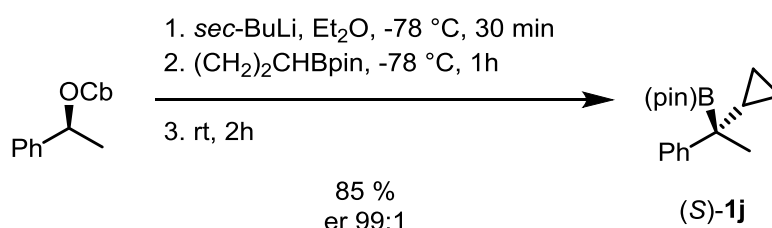
Prepared according to a literature known procedure.⁷

⁵ Pulis, A. P.; Blair, D. J.; Torres, E.; Aggarwal, V. K.; *J. Am. Chem. Soc.*, **2013**, *135*, 16054.

⁶ Bagutski, V.; French, R. M.; Aggarwal, V. K.; *Angew. Chem. Int. Ed.*, **2010**, *49*, 5142.

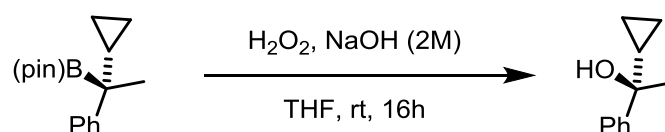
⁷ Nave, S.; Sonawane, R. P.; Elford, T. G.; Aggarwal V. K.; *J. Am. Chem. Soc.* **2010**, *132*, 17096.

(S)-2-(1-cyclopropyl-1-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(S)-1j]



A solution of the (*S*)-1-phenylethyl diisopropylcarbamate (1.5 g, 6.02 mmol, 1.15 eq.) in Et₂O (15.0 ml) was cooled to -78 °C and treated with *sec*-BuLi (4.3 mL, 6.02 mmol, 1.15 eq., 1.4 M in cyclohexane). The mixture was stirred for 30 min -78 °C and then a solution of cyclopropyl-B(pin) (955 μL, 5.24 mmol, 1.0 eq.) in Et₂O (5.0 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 1 h and at room temperature for 2 h. Water (15 mL) was added and the layers were separated. The aqueous layer was extracted with Et₂O (3 x 15 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄ and concentrated under vacuum. Purification by column chromatography on silica gel, eluting with petrol:Et₂O (99:1) gave **1j** (1.2 g, 81%), which was obtained as an oil; er (*S*:*R*) 99:1; *R*_f 0.33 (pentane:Et₂O 95:5); [α]_D²¹ 25 (*c* 1.0, CHCl₃); IR (film): ν (cm⁻¹) 3058, 2977, 1380, 1371, 1306, 849, 698; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.45–7.41 (m, 2H), 7.32–7.27 (m, 2H), 7.15 (m, 1H), 1.23 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 1.13 (m, 1H), 0.52–0.47 (m, 3H), 0.33 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 148.4, 128.0, 127.2, 125.2, 83.3, 24.7, 24.6, 21.8, 18.6, 2.1, 1.6; ¹¹B NMR (96 MHz, NONE) δ ppm 32.9; HRMS (EI) calcd. for C₁₇H₂₅BO₂ [*M*]⁺ 272.1948, found 272.1954.

1j was oxidised to the corresponding alcohol to determine enantiopurity:

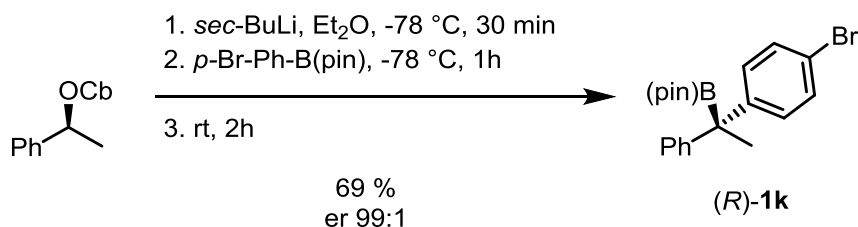


Resolution of the enantiomers of the alcohol was achieved by using a chiral SFC system fitted with a Chiracel IA column as the stationary phase with CO₂: [*n*-hexane:*i*-PrOH (9:1 v:v)] as the mobile phase at a flow rate of 4.0 mL min⁻¹ (*P* = 125 bar). Injection volume: 20 μL of a 2 g L⁻¹ solution of the compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 5.3 and 5.9 min., respectively, with a total analysis time of 15 min. [α]_D²⁴ 28 (*c* 0.5, CHCl₃) in accordance with literature precedent ([α]_D²⁴ 28.5 (*c* 0.49, CHCl₃)⁸).

⁸ Stymiest, J. L.; Bagutski, V.; French, R. M.; Aggarwal, V. K.; *Nature*, **2008**, 456, 778.

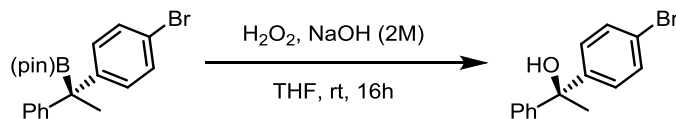
Data in accordance with literature precedent.⁸

(R)-2-(1-(4-Bromophenyl)-1-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(R)-1k]



A solution of the (*S*)-1-phenylethyl diisopropylcarbamate (300 mg, 1.20 mmol, 1.2 eq.) in Et₂O (5.0 ml) was cooled to -78 °C and treated with *sec*-BuLi (1.0 mL, 1.25 mmol, 1.25 eq., 1.4 M in cyclohexane). The mixture was stirred for 20 min at -78 °C and then a solution of *p*-Br-Ph-B(pin) (283 mg, 1.00 mmol, 1 eq.) in Et₂O (1.0 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 30 min and at room temperature for 2 h. Water (5 mL) was added and the layers were separated. The aqueous layer was extracted with Et₂O (3 x 10 ml). The combined organic layers were washed with brine (30 ml), dried over MgSO₄ and concentrated under vacuum. Purification by column chromatography on silica gel, eluting with petrol:Et₂O (99:1→95:5), gave (*R*)-1k (265 mg, 69%) as an amorphous solid; er (*R*:*S*) 99:1; *R*_f 0.43 (petrol:Et₂O 20:1); [α]_D²² +8.6 (*c* 0.5, CHCl₃); IR (film): ν (cm⁻¹) 2929, 2854, 1464, 1378, 1318, 1252, 1142, 1078, 1063, 836, 770; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.39–7.33 (m, 2H), 7.29–7.22 (m, 2H), 7.21–7.13 (m, 3H), 7.12–7.06 (m, 2H), 1.65 (s, 3H), 1.20 (s, 6H), 1.19 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 147.1, 146.8, 131.0, 130.4, 128.4, 128.1, 125.6, 119.3, 83.9, 25.7, 24.5; ¹¹B NMR (96 MHz, CDCl₃) δ 32.9 ppm; HRMS (EI) calcd. for C₂₀H₂₄BBro₂ [*M*]⁺ 386.1053, found 386.1048.

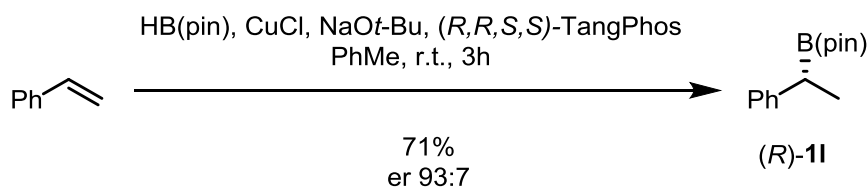
1s was oxidised to the corresponding alcohol to aid in determining enantiopurity (see below):



Resolution of the enantiomers of the alcohol was achieved by using a chiral SFC system fitted with a Chiralcel IB column as the stationary phase with CO₂: [*n*-hexane:*i*-PrOH (1:1 v:v)] (95:5 v:v) as the mobile phase at a flow rate of 4.0 mL min⁻¹ (*P* = 125 bar). Injection volume: 20 μ L of a 2 g L⁻¹ solution of the compound in the eluent. Under these conditions,

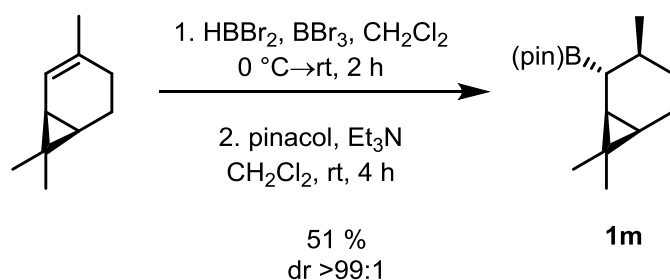
the faster running component (*R*) and the slower running component (*S*) were eluted at 11.5 and 12.2 min., respectively, with a total analysis time of 15 min.

(*R*)-4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane [(*R*)-11]



Prepared according to a literature known procedure.⁹

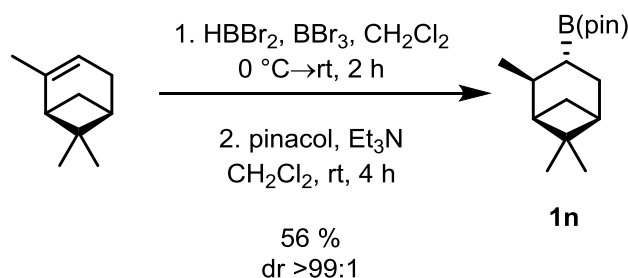
4,4,5,5-Tetramethyl-2-((1*S*,2*R*,3*S*,6*R*)-3,7,7-trimethylbicyclo[4.1.0]heptan-2-yl)-1,3,2-dioxaborolane (1m**)**



Following **GP1** (3.35 mmol scale), **1m** (448 mg, 51%) was obtained as an oil; R_f -0.27 (petrol: Et₂O 98:2); $[\alpha]_D^{20}$ -3.0 (c 1.0, CHCl₃); IR (film): ν (cm⁻¹) 2978, 2921, 2864, 1368, 1314, 1142; ¹H NMR (400 MHz, CDCl₃) δ ppm 1.86–1.76 (m, 1H), 1.71 (dd, J = 14.4, 6.7 Hz, 1H), 1.35 (dddd, J = 13.0, 7.7, 3.2, 1.8 Hz, 1H), 1.27 (s, 6H), 1.26 (s, 6H), 1.22 (m, 1H), 0.95 (s, 3H), 0.92 (s, 3H), 0.80 (d, J = 6.6 Hz, 3H), 0.65 (m, 1H), 0.57 (dd, J = 9.1, 5.0 Hz, 1H), 0.42 (t, J = 9.1 Hz, 1H), 0.35 (dd, J = 11.8, 5.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, CH-B not observed) δ ppm 82.8, 31.7, 29.6, 24.7, 24.6, 22.5, 22.2, 19.6, 18.5, 17.9, 15.5; ¹¹B NMR (96 MHz, CDCl₃) δ ppm 32.0; LRMS 264 (GC-MS); HRMS (EI) calcd. for C₁₆H₂₉BO₂ [M]⁺ 264.2261, found 264.2266.

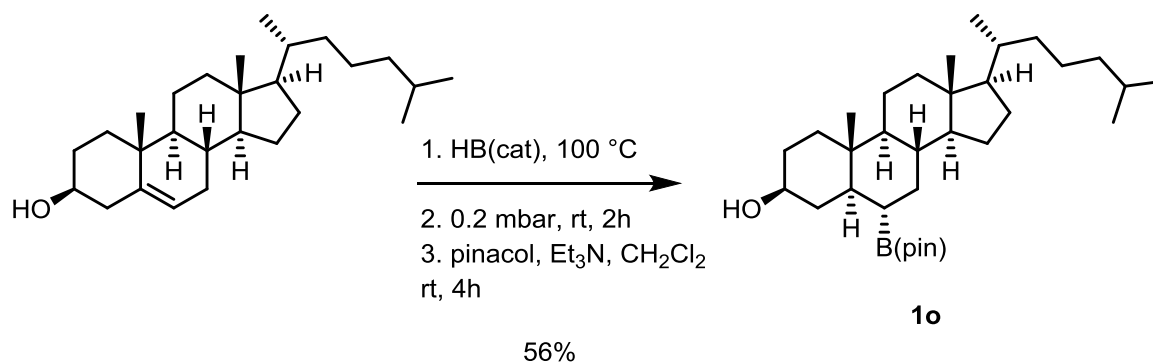
⁹ Noh, D.; Chea, H.; Ju, J.; Yun, J.; *Angew. Chem. Int. Ed.*, **2009**, *48*, 6062.

4,4,5,5-Tetramethyl-2-((1*R*,2*S*,3*R*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)-1,3,2-dioxaborolane (1n)



Following **GPI** (3.35 mmol scale), **1n** (490 mg, 56%) was obtained as an oil; R_f 0.51 (petrol: Et₂O 95:5); $[\alpha]_D^{20}$ -10.0 (c 1.0, CHCl₃); IR (film): ν (cm⁻¹) 2978, 2897, 2870, 1369, 1346, 1311, 1144; ¹H NMR (400 MHz, CDCl₃) δ ppm 2.29 (ddd, J = 9.3, 6.3, 2.0 Hz, 1H), 2.14 (dq, J = 8.3, 7.4, 2.0 Hz, 1H), 2.04 (ddd, J = 12.0, 3.1, 2.0 Hz, 1H), 1.92–1.81 (m, 2H), 1.76 (td, J = 5.5, 2.0 Hz, 1H), 1.25 (s, 12H), 1.17 (s, 3H), 1.04 (s, 3H), 1.02 (s, 3H), 0.87–0.80 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, CH–B not observed) δ ppm 82.7, 47.9, 41.2, 38.5, 38.2, 34.1, 28.6, 28.4, 24.7, 24.6, 23.1, 22.7; ¹¹B NMR (96 MHz, CDCl₃) δ ppm 33.0; LRMS 264 (GC-MS); HRMS (ESI) calcd. for C₁₆H₃₀BO₂ [$M+H$]⁺ 265.2339, found 265.2336.

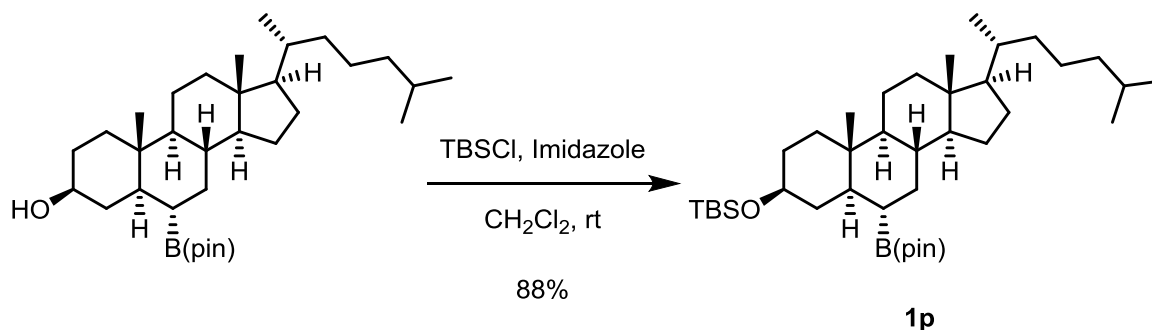
(3*S*,5*R*,6*S*,8*R*,10*S*,13*R*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexadecahydro-1*H*-cyclopenta[α]phenanthren-3-ol (1o)



Freshly distilled catecholborane (1.4 mL, 13.36 mmol, 6.0 eq.) was added to a Schlenk flask containing cholesterol (2.2 g, 5.69 mmol, 1.0 eq.). The resulting mixture was heated to 100 °C at which point a solution formed. After 16 h at the same temperature, the mixture was cooled to room temperature and TLC analysis (petrol:EtOAc 7:3) revealed complete consumption of cholesterol. Excess catecholborane was removed under high vacuum (0.2 mbar, 2 h, r.t.). The crude material was diluted with CH₂Cl₂ (15 mL) and Et₃N (2.5 mL, 17.82 mmol, 8.0 eq.) and pinacol (788 mg, 6.68 mmol, 3.0 eq.) were added. After 1 h the mixture

was diluted with CH₂Cl₂ (20 mL) and water (20 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 20 mL). The combined organics layers were dried over MgSO₄, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel, eluting with *n*-hexane:EtOAc (95:5→75:25) gave **1o** (592 mg, 52%) as an amorphous solid; *R*_f 0.41 (petrol:EtOAc 7:3); mp 196–199 °C; [α]_D²³ +32.4 (*c* 1.0, CHCl₃); IR (film): ν (cm⁻¹) 3229, 2929, 2865, 1371, 1315, 1143, 1043, 850; ¹H NMR (400 MHz, CDCl₃) δ ppm. 3.62 (tt, *J* = 10.5, 4.4 Hz, 1H), 1.95 (br d, *J* = 12.5 Hz, 1H), 1.85–1.75 (m, 2H), 1.71 (m, 1H), 1.64–1.44 (m, 5H), 1.32–1.29 (m, 5H), 1.24 (s, 16H), 1.15–0.95 (m, 10H), 0.94–0.84 (m, 11H) 0.80 (s, 3H), 0.68 (m, 1H), 0.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 82.9, 71.2, 56.2, 53.9, 45.3, 42.6, 40.0, 39.5, 37.7, 36.7, 36.2, 35.8, 35.6, 35.2, 33.5, 31.5, 28.2, 28.0, 24.8, 24.7, 24.2, 23.8, 22.8, 22.5, 21.2, 18.6, 12.4, 12.0; ¹¹B NMR (96 MHz, CDCl₃) δ ppm 32.1; LRMS 514 (GC-MS); HRMS (ESI) calcd. for C₃₃H₅₉BNaO₃ [*M*+Na]⁺ 537.4455, found 537.4451.

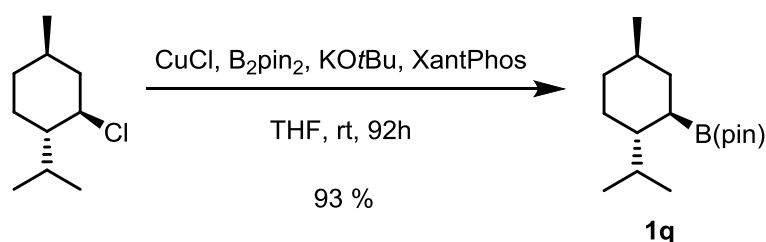
***tert*-Butyl(((3*S*,5*R*,6*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexadecahydro-1H-cyclopenta[α]phenanthren-3-yl)oxy)dimethylsilane (**1p**)**



A solution of **1o** (150 mg, 0.29 mmol, 1.0 eq.) in CH₂Cl₂ (3 mL) was cooled to 0 °C and imidazole (60 mg, 0.87 mmol, 3.0 eq.) and *tert*-butyldimethylsilyl chloride (132 mg, 0.87 mmol, 3.0 eq.) were added. The reaction mixture was allowed to warm to room temperature overnight and was quenched with water (3 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 10 mL). The combined organics layers were dried over MgSO₄, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel, eluting with *n*-hexane:EtOAc (99:1→97:3) gave **1p** (161 mg, 88%) as an amorphous solid; *R*_f 0.55 (petrol:EtOAc 95:5); mp 180–182 °C; [α]_D²² +8.6 (*c* 0.5, CHCl₃); IR (film): ν (cm⁻¹) 2929, 2854, 1464, 1378, 1318, 1252, 1142, 1078, 1063, 836, 770; ¹H NMR (400 MHz, CDCl₃) δ ppm 3.57 (tt, *J* = 10.8, 4.5 Hz, 1H), 1.95 (dt, *J* = 12.5, 3.3 Hz,

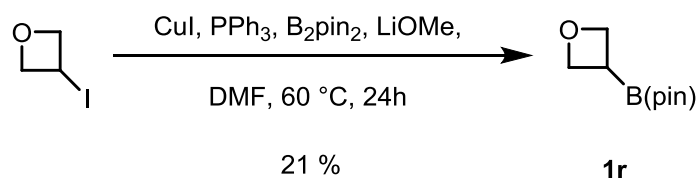
1H), 1.79 (m, 1H), 1.70–1.60 (m, 3H), 1.60–1.40 (m, 5H), 1.40–1.27 (m, 5H), 1.24 (m, 14H), 1.06 (m, 11H), 0.91–0.78 (m, 19H), 0.78 (s, 3H), 0.72–0.61 (m, 1H), 0.56 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 82.6, 71.9, 56.1, 56.0, 53.8, 45.3, 42.4, 39.9, 39.4, 37.9, 36.7, 36.0, 35.6, 35.4, 35.1, 33.4, 31.7, 28.1, 27.8, 25.8, 24.7, 24.6, 24.0, 23.7, 22.7, 22.4, 21.0, 18.5, 18.2, 12.3, 11.9, –4.7, –4.8; ¹¹B NMR (96 MHz, CDCl₃) δ ppm 32.0; HRMS (ESI) calcd. for C₃₉H₇₃BNaO₃Si [M+Na]⁺ 651.5320, found 651.5321.

2-((1*R*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1q)



Prepared according to literature known procedure.¹⁰

4,4,5,5-tetramethyl-2-(oxetan-3-yl)-1,3,2-dioxaborolane (1r)



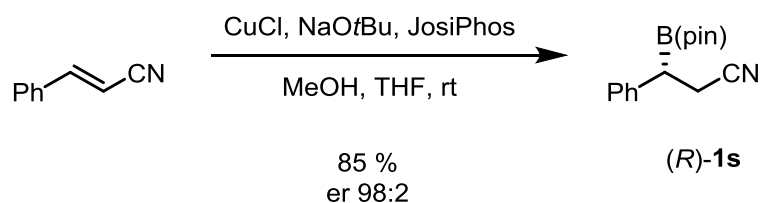
In air, CuI (9.5 mg, 0.05 mmol, 0.01 eq.), PPh₃ (183 mg, 0.07 mmol, 0.14 eq.), LiOMe (418 mg, 10.9 mmol, 2.0 eq.), and bis(pinacolato)diboron (2.1 g, 8.3 mmol, 1.5 eq.) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with nitrogen (three cycles). DMF (10.5 mL), 3-iodooxetane (920 mg, 0.5 mmol, 1.0 eq.) were added in turn by syringe under a nitrogen atmosphere. The resulting reaction mixture was stirred at 60 °C for 24 h. The reaction mixture was then diluted with Et₂O (30 mL), filtered through silica gel with copious amount of Et₂O. Evaporation of solvent under vacuum and purification by column chromatography eluting with *n*-hexane:EtOAc (75:25) gave **1r** (186 mg, 21%) as a solid; *R*_f 0.12 (pentane:Et₂O 85:15); mp. 24–26 °C; IR (film): ν (cm⁻¹) 2977, 2871, 1385,

¹⁰ Ito H.; Kubota, K.; *Org. Lett.*, **2012**, *14*, 890.

1320, 1216, 1141, 857; ¹H NMR (400 MHz, CDCl₃) δ ppm 4.70–4.55 (m, 4H), 2.59 (m, 1H), 1.13 (s, 12H); ¹³C NMR (100 MHz, CDCl₃, CH–B not observed) δ ppm 83.2, 73.0, 24.3; HRMS (CI) calcd. for C₉H₁₈BO₃ [M+H]⁺ 185.1349, found 185.1342.

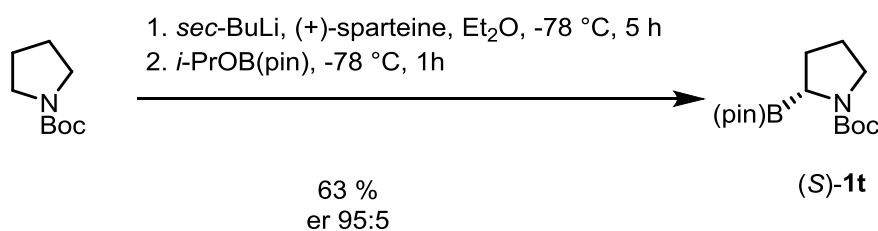
Prepared using a modification of a literature known procedure.¹¹

(R)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanenitrile [(R)-1s]



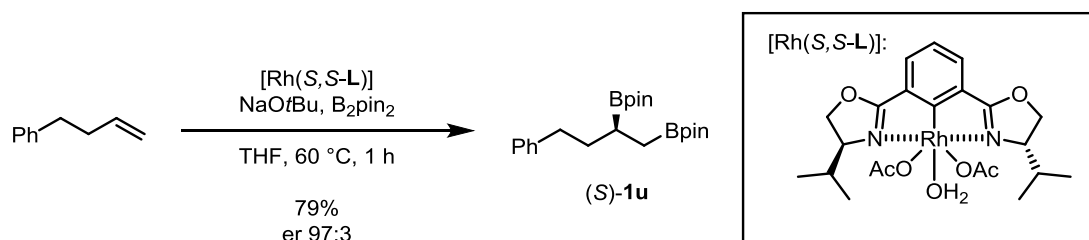
Prepared according to a literature known procedure.¹²

(S)-tert-Butyl 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate [(S)-1t]



Prepared according to a literature known procedure.¹³

(S)-2,2'-(4-phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) [(S)-1u]



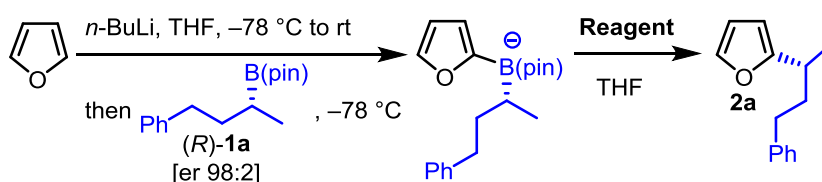
Prepared according to a literature known procedure.¹⁴

¹¹ Yang, C.-T.; Zhang, Z.-Q.; Tajuddin, H.; Wu, C.-C.; Liang, J.; Liu, J.-H.; Fu, Y.; Czyzewska, M.; Steel, P. G.; Marder, T. B.; Liu, L.; *Angew. Chem. Int. Ed.*, **2012**, *51*, 528.

¹² Lee, J.-E.; Yun, J.; *Angew. Chem. Int. Ed.*, **2008**, *47*, 145.

¹³ Batsanov, A. S.; Grosjean, C.; Schutz, T.; Whiting, A.; *J. Org. Chem.*, **2007**, *72*, 6276.

4. Oxidant/Electrophile Screening



General Procedure for the Screening:

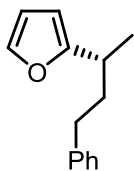
A solution of furan (44 μL , 0.6 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to $-78\text{ }^\circ\text{C}$ and treated with *n*-BuLi (0.37 mL, 0.6 mmol, 1.2 eq., 1.6 M in hexanes). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to $-78\text{ }^\circ\text{C}$ and (*R*)-**1a** (66 mg, 0.5 mmol, 1.0 eq.) was added dropwise as a solution in THF (1.0 mL). The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR (96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. A solution of an oxidant/electrophile (0.6 mmol, 1.2 eq.) in THF (2.0 mL) was added dropwise. After 1 h at $-78\text{ }^\circ\text{C}$, a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et_2O (15 mL) and water (15 mL). The layers were separated and the aqueous layer was extracted with Et_2O . The combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane to give (*R*)-**2a**.

Entry	Reagent	T ($^\circ\text{C}$)	time	Yield (%)	es (%)
1	DDQ	-78	5 min \rightarrow 1 h	82	100
2	DDQ	0	5 min	20	100
3	chloranil	$-78 \rightarrow \text{rt}$	5 min \rightarrow 16 h	0	–
4	$\text{Mn}(\text{OAc})_3$	$-78 \rightarrow \text{rt}$	5 min \rightarrow 16 h	0	–
5	$\text{Cu}(\text{OAc})_2$	$-78 \rightarrow \text{rt}$	5 min \rightarrow 16 h	0	–
6	CAN	$-78 \rightarrow \text{rt}$	5 min \rightarrow 16 h	0	–
7	WCl_6	$-78 \rightarrow \text{rt}$	5 min \rightarrow 16 h	0	–
8	$(p\text{-Br-Ph})_3\text{N}^{++}$	$-78 \rightarrow \text{rt}$	5 min \rightarrow 16 h	0	–
9	I_2	-78	5 min \rightarrow 1 h	39	–
10	NIS	-78	5 min \rightarrow 1 h	42	–
11	NBS	-78	5 min \rightarrow 1 h	91	100
12	NBS	0	5 min \rightarrow 1 h	92	100
13	NCS	-78	5 min \rightarrow 1 h	61	–
14	TCCA	-78	5 min \rightarrow 1 h	<5	–

¹⁴ Toribatake, K.; Nishiyama, H.; *Angew. Chem. Int. Ed.*, **2013**, 52, 11011.

5. Reaction Products – Coupling to heterocycles

(*R*)-2-(4-Phenylbutan-2-yl)furan [(*R*)-**2a**]

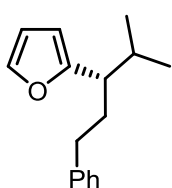


Following **GP2** (0.50 mmol scale), (*R*)-**2a** (91 mg, 91%) was obtained as an oil; er (*R*:*S*) 98:2; R_f 0.82 (petrol:Et₂O 95:5); $[\alpha]_D^{23}$ -28.3 (*c* 0.5, CHCl₃); IR (film): ν (cm⁻¹) 3114, 3085, 3063, 3027, 2966, 2927, 2858, 1454, 1008, 727, 697; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.38 (br s, 1H), 7.36–7.31 (m, 2H), 7.26–7.21 (m, 3H), 6.35 (dd, $J = 3.1, 1.9$ Hz, 1H), 6.07 (d, $J = 3.1$ Hz, 1H), 2.92 (sx, $J = 6.9$ Hz, 1H), 2.66 (t, $J = 8.1$ Hz, 2H), 2.08 (m, 1H), 1.89 (m, 1H), 1.33 (d, $J = 7.0$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 160.3, 142.4, 140.7, 128.4, 128.3, 125.8, 109.9, 103.8, 37.6, 33.5, 32.8, 19.3; HRMS (CI) calcd. for C₁₄H₁₆O [*M*]⁺ 200.1201, found 200.1210.

Resolution of the enantiomers of **2a** was achieved by using a chiral HPLC system fitted with a Chiralpak AD-H column with guard as the stationary phase with *n*-hexanes the mobile phase at a flow rate of 0.2 mL min⁻¹ ($T = 0$ °C). Injection volume: 20 μ L of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 51.1 and 56.1 min., respectively, with a total analysis time of 75 min.

Coupling in the presence of DDQ was performed following **GP3** and resulted in 82% yield and 100% e.s.

(*S*)-2-(4-Methyl-1-phenylpentan-3-yl)furan [(*S*)-**2c**]



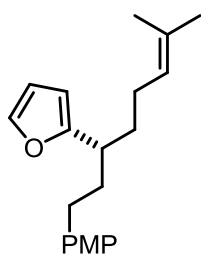
Following **GP2** (0.50 mmol scale), (*S*)-**2c** (105 mg, 92%) was obtained as an oil; er (*S*:*R*) 97:3; R_f 0.90 (petrol:Et₂O 95:5); $[\alpha]_D^{25}$ -9.0 (*c* 1.0, CHCl₃); IR (film): ν (cm⁻¹) 3112, 3085, 3063, 3027, 2957, 2929, 2870, 1454, 1009, 727, 697; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.40 (br s, 1H), 7.35–7.27 (m, 2H), 7.25–7.16 (m, 3H), 6.35 (dd, $J = 3.0, 1.9$ Hz, 1H), 6.07 (d, $J = 3.0$ Hz, 1H), 2.63–2.53 (m, 2H), 2.47 (m, 1H), 2.08–1.96 (m, 2H), 1.92 (app. oct, $J = 6.8$ Hz, 1H), 0.95 (d, $J = 6.8$ Hz, 3H), 0.85 (d, $J = 6.8$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 157.7, 142.6, 140.7, 128.4, 128.3, 125.7, 109.8, 106.2, 45.4, 34.1, 33.1, 32.2, 20.8, 19.8; HRMS (EI) calcd. for C₁₆H₂₀O [*M*+H]⁺ 228.1514, found 228.1516.

Resolution of the enantiomers of **2c** was achieved using a chiral GC system fitted with a Supelco DM column. Injector $T = 250$ °C, detector $T = 300$ °C. Oven conditions: $T = 70$ °C for 3 min then ramp (1 °C min⁻¹) until 180 °C, H₂ carrier gas at 14 psi. Under these

conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 64.6 and 64.7 min respectively with a total analysis time of 75 min.

Coupling in the presence of DDQ was performed following **GP3** and resulted in 67% yield and 100% e.s.

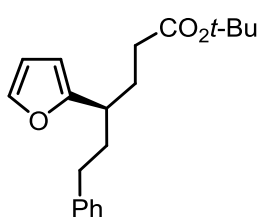
(*R*)-2-(1-(4-methoxyphenyl)-7-methyloct-6-en-3-yl)furan [(*R*)-**2d**]



Following **GP2** (0.28 mmol scale), (*R*)-**2d** (78 mg, 94%) was obtained as an oil; er (*R*:*S*) 92:8; R_f 0.63 (petrol:Et₂O 95:5); $[\alpha]_D^{22}$ -8.7 (*c* 1.3, CHCl₃); IR (film): ν (cm⁻¹) 2928, 2857, 1511, 1244, 1176, 1037, 728; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.35 (br s, 1H), 7.11–7.04 (m, 2H), 6.86–6.80 (m, 2H), 6.32 (dd, J = 3.1, 1.9 Hz, 1H), 6.03 (br d, J = 3.1 Hz, 1H), 5.08 (m, 1H), 3.80 (s, 3H), 2.72 (m, 1H), 2.55–2.39 (m, 2H), 1.99–1.81 (m, 4H), 1.78–1.56 (m, 2H), 1.68 (s, 3H), 1.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 158.6, 157.7, 140.7, 134.5, 131.6, 129.2, 124.2, 113.7, 109.8, 105.2, 55.2, 38.1, 36.2, 34.3, 32.6, 25.7, 25.7, 17.6; HRMS (EI) calcd. for C₂₀H₂₆O₂ [M]⁺ 298.1933, found 298.1935.

Resolution of the enantiomers of **2d** was achieved using a chiral HPLC system fitted with a Chiralpak IB column with guard as the stationary phase with 99:1 [*n*-hexanes:(10 % *i*-PrOH in *n*-hexanes)] the mobile phase at a flow rate of 0.5 mL min⁻¹ (T = 0 °C). Injection volume: 5 μ L of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 16.4 and 17.5 min., respectively, with a total analysis time of 35 min.

(*R*)-*tert*-Butyl 4-(furan-2-yl)-6-phenylhexanoate [(*R*)-**2e**]



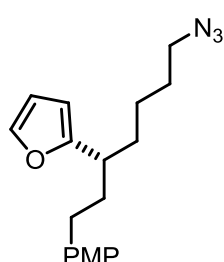
Following **GP2** (0.50 mmol scale), (*R*)-**2e** (142 mg, 90%) was obtained as an oil; er (*R*:*S*) 96:4; R_f 0.72 (petrol:Et₂O 95:5); $[\alpha]_D^{21}$ +8.0 (*c* 1.0, CHCl₃); IR (film): ν (cm⁻¹) 3063, 3027, 2977, 2931, 2862, 1726, 1366, 1146, 729, 698; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.37 (dd, J = 1.8, 0.7 Hz, 1H), 7.31–7.26 (m, 2H), 7.22–7.14 (m, 3H), 6.33 (dd, J = 3.2, 1.8 Hz, 1H), 6.07 (d, J = 3.2 Hz, 1H), 2.80–2.72 (m, 1H), 2.62–2.48 (m, 2H), 2.22–2.10 (m, 2H), 2.08–1.86 (m, 4H), 1.44 (s, 9H); ¹³C NMR (400 MHz, CDCl₃) δ ppm 172.8, 157.4, 142.1, 141.1, 128.4, 128.3, 125.8, 109.9, 105.9, 80.1, 38.0, 35.9, 33.5, 33.3, 29.5, 28.1; HRMS (EI) calcd. for C₂₀H₂₆O₃ [M]⁺ 314.1882, found 314.1870.

Resolution of the enantiomers of **2e** was achieved using a chiral HPLC system fitted with a Chiralpak IB column with guard as the stationary phase with *n*-hexane:*i*-PrOH (99:1 v:v) as

the mobile phase at a flow rate of 0.5 mL min⁻¹ (*T* = 20 °C). Injection volume: 20 μL of a 2 g L⁻¹ solution of the compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 9.5 and 10.3 min., respectively, with a total analysis time of 30 min.

Coupling in the presence of DDQ was performed following **GP3** and resulted in 71% yield and 100% e.s.

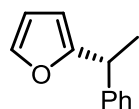
(*R*)-2-(7-azido-1-(4-methoxyphenyl)heptan-3-yl)furan [(*R*)-**2f**]



Following **GP2** (0.23 mmol scale), (*R*)-**2f** (52 mg, 71%) was obtained as an oil; er (*R*:*S*) 96:4; *R*_f 0.32 (petrol:Et₂O 95:5); [*α*]_D²⁴ - 11 (*c* 0.6, CHCl₃); IR (film): *ν* (cm⁻¹) 2935, 2860, 2091, 1510, 1243, 1036, 730; ¹H NMR (400 MHz, CDCl₃) *δ* ppm 7.36 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.10–7.05 (m, 2H), 6.86–6.81 (m, 2H), 6.33 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.05 (br d, *J* = 3.1 Hz, 1H), 3.60 (s, 3H), 3.26–3.18 (m, 2H), 2.70 (m, 1H), 2.56–2.39 (m, 2H), 2.01–1.80 (m, 2H), 1.73–1.47 (m, 4H), 1.36–1.22 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) *δ* ppm 158.2, 157.7, 140.8, 134.2, 129.2, 113.7, 109.8, 105.4, 55.2, 51.3, 38.4, 36.2, 33.8, 32.6, 28.8, 24.4; HRMS (EI) calcd. for C₁₈H₂₃N₃O₂ [*M*]⁺ 313.1790, found 313.1786.

Resolution of the enantiomers of **2f** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO₂:*n*-hexane as the mobile phase at a flow rate of 4.0 mL min⁻¹ (*P* = 125 bar). Injection volume: 10 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 8.8 and 10.0 min., respectively, with a total analysis time of 15 min.

(*R*)-2-(1-Phenylethyl)furan [(*R*)-**2l**]



Following **GP2** (0.5 mmol scale), (*R*)-**2l** (80 mg, 93%) was obtained as an oil; er (*R*:*S*) 93:7; *R*_f 0.90 (petrol:Et₂O 95:5); [*α*]_D²³ -24.3 (*c* 1, CHCl₃) [Lit. for (*R*)-**2l** [*α*]_D²⁰ -40.9 (*c* 0.88, CHCl₃), er (*R*:*S*) 98:2]¹³; ¹H NMR (CDCl₃, 400 MHz) *δ* ppm 7.36–7.16 (m, 6H), 6.29 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.05 (dt, *J* = 3.2, 0.9 Hz, 1H), 4.12 (q, *J* = 7.2, 1H), 1.60 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) *δ* ppm 159.0, 144.1, 141.3, 128.5, 127.3, 126.5, 109.9, 104.9, 39.2, 20.5.

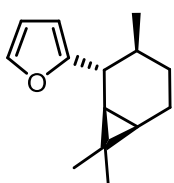
Resolution of the enantiomers of **2l** was achieved using a chiral HPLC system fitted with a Chiralpak IB column with guard as the stationary phase with *n*-hexane as the mobile phase at a flow rate of 0.3 mL min⁻¹ (*T* = 5 °C). Injection volume: 20 μL of a 2 g L⁻¹ solution of the

compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 39.6 and 41.7 min., respectively, with a total analysis time of 60 min.

Data in accordance with the literature.¹⁵

The stereospecificity of the process has been determined to be retentive by comparing the chiral HPLC traces and the optical rotation of this compound with the literature.¹⁵

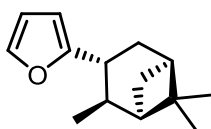
2-((1*R*,2*R*,3*S*,6*R*)-3,7,7-Trimethylbicyclo[4.1.0]heptan-2-yl)furan (**2m**)



Following **GP2** (0.5 mmol scale), **2m** (69 mg, 68%) was obtained as an oil; R_f 0.77 (petrol: Et₂O 95:5); $[\alpha]_D^{22}$ -34.0 (*c* 1.0, CHCl₃); IR (film): ν (cm⁻¹) 2922, 2864, 1458, 1375, 1148, 1009, 792, 724; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.35 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.32 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.04 (dd, *J* = 3.1, 0.6 Hz, 1H), 2.08 (dd, *J* = 11.5, 4.7 Hz, 1H), 1.90 (ddt, *J* = 14.5, 11.5, 7.9 Hz, 1H), 1.76 (ddt, *J* = 14.0, 6.8, 1.3 Hz, 1H), 1.55 (dddd, *J* = 14.0, 7.9, 3.6, 1.8 Hz, 1H), 1.47 (m, 1H), 1.05 (s, 3H), 1.00 (s, 3H), 0.92–0.81 (m, 2H), 0.71 (d, *J* = 6.5 Hz, 3H), 0.65 (td, *J* = 8.0, 1.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 160.5, 140.5, 109.8, 104.6, 39.2, 33.2, 31.6, 29.4, 26.7, 20.2, 19.6, 19.3, 17.6, 15.6; HRMS (EI) calcd. for C₁₄H₂₀O [*M*]⁺ 204.1516, found 204.1514.

Coupling in the presence of DDQ was performed following **GP3** and resulted in 58% yield and 100% e.s.

2-((1*R*,2*R*,3*R*,5*S*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl)furan (**2n**)

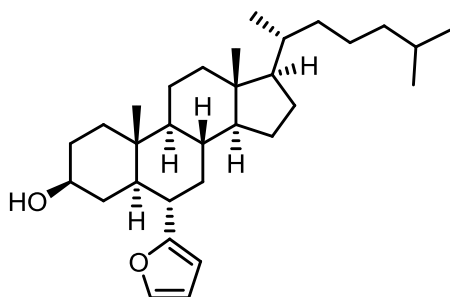


Following **GP2** (0.50 mmol scale), **2n** (84 mg, 82%) was obtained as an oil; R_f 0.84 (petrol:Et₂O 95:5); $[\alpha]_D^{21}$ -34.0 (*c* 0.5, CHCl₃); IR (film): ν (cm⁻¹) 2924, 2902, 2870, 1507, 1454, 1150, 1008, 796, 784, 691; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.35 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.32 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.04 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.07 (dt, *J* = 10.5, 7.3 Hz, 1H), 2.44–2.30 (m, 2H), 2.21 (pd, *J* = 7.3, 2.0, 1H), 2.06–1.98 (m, 2H), 1.88 (td, *J* = 6.2, 2.0 Hz, 1H), 1.26 (s, 3H), 1.13–1.05 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 161.4, 141.0, 109.8, 103.4, 47.6, 42.3, 41.4, 38.6, 36.5, 34.1, 33.5, 28.3, 23.0, 21.6; HRMS (CI) calcd. for C₁₄H₂₁O [*M*+H]⁺ 205.1592, found 205.1607.

¹⁵ Fessard, T. C.; Andrews S. P.; Motoyoshi, H.; Carreira, E. M.; *Angew. Chem. Int. Ed.*, **2007**, 46, 9331.

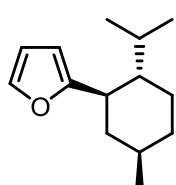
Coupling in the presence of DDQ was performed following **GP3** and resulted in 62% yield and 100% e.s.

(3*S*,5*R*,6*S*,8*S*,10*R*,13*R*,17*R*)-6-(Furan-2-yl)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[α]phenanthren-3-ol (2o**)**



A solution of furan (31 μ L, 0.43 mmol, 2.2 eq.) in THF (2.0 mL) was cooled to -78 $^{\circ}$ C and treated with *n*-BuLi (0.3 mL, 0.43 mmol, 2.2 eq., 1.6 M in hexanes). The mixture was stirred at -78 $^{\circ}$ C for 30 min. and at r.t. for 30 min. The mixture was cooled to -78 $^{\circ}$ C and a solution of **1o** (100 mg, 0.19 mmol, 1.0 eq.) in THF (2.0 mL) was added dropwise. The mixture was stirred at -78 $^{\circ}$ C for 1 h at which point 11 B NMR spectroscopy showed complete formation of the boron-ate complex [11 B NMR (96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. A solution of NBS (62 mg, 0.23 mmol, 1.2 eq.) in THF (2.0 mL) was added dropwise. The mixture was stirred at -78 $^{\circ}$ C for 16 h at which point saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (1 mL) was added. The reaction mixture was diluted with Et_2O (10 mL) and washed with water (15 mL). The aqueous layer was extracted with Et_2O (2 x 15 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography on silica gel, eluting with petrol:EtOAc (95:55 \rightarrow 85:15) gave **2o** (69 mg, 78 %) as a solid; R_f 0.77 (petrol:EtOAc 7:3); mp. 126-130 $^{\circ}$ C; $[\alpha]_{\text{D}}^{22} + 21.9$ (*c* 0.73, CHCl_3); IR (film): ν (cm^{-1}) 3256, 2931, 2855, 1467, 1381, 1073, 1049, 1009, 796, 724; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.28 (dd, $J = 1.8, 0.6$ Hz, 1H), 6.26 (dd, $J = 3.1, 1.8$ Hz, 1H), 5.95 (dd, $J = 3.1, 0.6$ Hz, 1H), 3.49 (tt, $J = 11.0, 4.8$ Hz, 1H), 2.60 (td, $J = 12.0, 3.6$ Hz, 1H), 1.83–1.73 (m, 4H), 1.58–1.45 (m, 5H), 1.39–1.22 (m, 7H), 1.20–0.97 (m, 12H), 0.92–0.84 (m, 13H), 0.77 (m, 1H) 0.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 159.1, 140.5, 109.8, 104.6, 71.3, 56.2, 56.2, 53.9, 48.6, 42.6, 40.0, 39.5, 38.1, 38.0, 37.0, 36.1, 35.9, 35.8, 35.1, 34.9, 31.1, 28.2, 28.0, 24.1, 23.8, 22.8, 22.5, 21.3, 18.7, 12.9, 12.1, 1.0; HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{51}\text{O}_2$ [$M+\text{H}$] $^+$ 455.3884, found 455.3865.

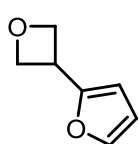
2-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)furan (2q**)**



Following **GP2** (0.45 mmol scale), **2q** (63 mg, 80%) was obtained as an oil; R_f 0.91 (pentane:Et $_2$ O 99:1); $[\alpha]_{\text{D}}^{23} - 45$ (*c* 1, CHCl_3); IR (film): ν (cm^{-1}) 3675, 2954, 2918, 1594, 1505, 1455, 1385, 1368, 1347, 1321, 1238, 1222,

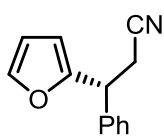
1171, 1148, 1073, 1056, 1009, 977, 949, 938, 914, 885, 874, 794, 725, 691, 599, 526; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.28 (dd, $J = 1.8, 0.8$ Hz, 1H), 6.27 (dd, $J = 3.1, 1.8$ Hz, 1H), 5.95 (dd, $J = 3.1, 0.8$ Hz, 1H), 2.57 (td, $J = 11.8, 3.4$ Hz, 1H), 1.86–1.75 (m, 2H), 1.71 (dq, $J = 12.8, 3.1$ Hz, 1H), 1.52–1.37 (m, 3H), 1.27 (m, 1H), 1.10 (m, 1H), 0.99 (m, 1H), 0.91 (d, $J = 6.5$ Hz, 3H), 0.84 (d, $J = 6.8$ Hz, 3H), 0.72 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 159.7, 140.2, 109.8, 104.1, 46.8, 42.0, 40.9, 35.0, 32.9, 28.3, 24.8, 22.4, 21.2, 15.7; HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{22}\text{O}$ [M] $^+$ 206.1671, found 206.1673.

2-(oxetan-3-yl)furan (2r)



Following **GP2** (0.22 mmol scale), **2r** (10 mg, 38%) was obtained as an oil; R_f 0.41 (pentane:Et₂O 85:15); IR (film): ν (cm^{-1}) 2958, 2881, 1148, 979, 931, 734; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.40 (br s, 1H), 6.35 (m, 1H), 6.20 (d, $J = 3.2$ Hz, 1H), 4.94 (dd, $J = 8.3, 5.8$ Hz, 2H), 4.90–4.84 (m, 2H), 4.32 (qi, $J = 8.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 154.1, 141.9, 110.4, 105.7, 76.5, 33.9; HRMS (EI) calcd. for $\text{C}_7\text{H}_8\text{O}_2$ [M] $^+$ 124.0524, found 124.0529.

(R)-3-(furan-2-yl)-3-phenylpropanenitrile [(R)-2s]



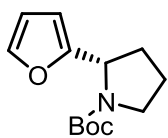
A solution of furan (36 μL , 0.48 mmol) in THF (2.0 mL) was cooled to -78 $^\circ\text{C}$ and treated with *n*-BuLi (0.2 mL, 0.32 mmol, 1.6 M in hexanes). The mixture was stirred at room temperature for 1 h. The mixture was cooled to -98 $^\circ\text{C}$ (MeOH/ liquid N₂) and a solution of boronic ester (**R**)-**1s** (84.8 mg, 0.33 mmol, 1.0 eq.) in THF (1.0 mL) was added dropwise. The reaction was stirred at -98 $^\circ\text{C}$ during 1 h at which time possible excess of organolithium was quench adding 200 μL of EtOH to the reaction mixture. ^{11}B NMR spectroscopy showed complete formation of the boron-ate complex [^{11}B NMR (96 MHz, THF) $\delta_B \sim 8$ ppm]. The mixture was kept at -98 $^\circ\text{C}$ and a solution of NBS (69 mg, 0.38 mmol, 1.15 eq.) in THF (2.0 mL) was added dropwise and allowed to warm to r.t. for 1h. At this point saturated aqueous solution of Na₂S₂O₃ (1 mL) was added. The reaction mixture was diluted with Et₂O (10 mL) and washed with water (15 mL). The aqueous layer was extracted with Et₂O (2 x 15 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by column chromatography on silica gel, eluting with petrol:Et₂O (95:5→7:3) gave (**R**)-**2s** (mg, 90 %) as an oil; er (**R**:**S**) 98:2; R_f 0.25 (petrol:Et₂O 8:2) [α]_D²² 33; ^1H NMR (400 MHz, CDCl_3) δ ppm; 7.41–7.35 (m, 3H), 7.34–7.26 (m, 3H) 6.34 (dd, $J = 3.2, 1.9$ Hz, 1H), 6.17 (d, 1H, $J = 3.2$ Hz, 1H), 4.39 (t, $J =$

7.3 Hz, 1H), 3.09 (dd, $J = 16.7, 7.3$ Hz, 1H), 2.96 (dd, $J = 16.7, 7.3$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 153.6, 142.4, 139.0, 129.0, 127.9, 127.5, 117.8, 110.4, 107.1, 41.7, 23.5.

Data in accordance with literature.¹⁶

Resolution of the enantiomers of **2s** was achieved using a chiral SFC system fitted with a Chiralcel Whelk-01 column as the stationary phase with CO_2 : [*n*-hexane:*i*-PrOH (1:1 v:v)] as the mobile phase at a flow rate of a 2.0 mL min^{-1} ($P = 125$ bar). Injection volume: $10 \mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 11.6 and 12.5 min., respectively, with a total analysis time of 20 min.

(*R*)-tert-butyl 2-(furan-2-yl)pyrrolidine-1-carboxylate [(*R*)-2t]

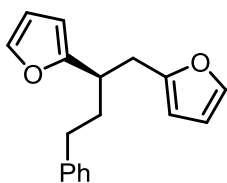


Following **GP2**, (0.25 mmol scale), (*R*)-**2t** (56 mg, 74%) was obtained as an oil; er (*R*:*S*) 93:7; R_f 0.24 (petrol:EtOAc 95:5); $[\alpha]_D^{22} -90.6$ (c 1.0, CHCl_3); IR (film): ν (cm^{-1}) 2974, 2929, 2879, 1693, 1387, 1365, 1159, 1111, 1007, 729; ^1H NMR (400 MHz, CDCl_3 , broad signals due to rotamers) δ 7.29 (dd, $J = 1.8, 0.9$ Hz, 1H), 6.28 (dd, $J = 3.2, 1.8$ Hz, 1H), 6.17-5.99 (br m, 1H), 4.97 & 4.84 (br s, 1H), 3.54 (br s, 1H), 3.45 (br s, 1H), 2.13 (br s, 1H), 2.08–1.97 (m, 2H), 1.89 (m, 1H), 1.45 & 1.35 (br s, 9H); ^{13}C NMR (100 MHz, CDCl_3 , broad signals due to rotamers) δ 154.4, 141.0, 110.0, 105.2, 79.3, 54.7 & 54.5, 46.3 & 46.0, 32.2 & 31.9, 28.3, 24.2 & 23.6; HRMS (CI) calcd. for $\text{C}_{13}\text{H}_{20}\text{NO}_3$ $[M+H]^+$ 238.1443, found 238.1443.

Resolution of the enantiomers of **2t** was achieved using a chiral SFC system fitted with a Chiralcel Whelk-01 column as the stationary phase with CO_2 : [*n*-hexane:*i*-PrOH (1:1 v:v)] (9:1 v:v) as the mobile phase at a flow rate of 4.0 mL min^{-1} ($P = 125$ bar). Injection volume: $20 \mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 4.7 and 6.7 min., respectively, with a total analysis time of 15 min.

¹⁶ Arutyunyan, N. S.; Akopyan, L. A.; Gevorgyan, G. A.; Snkhchyan, G. M.; Panosyan, G. A.; *Chem. Heterocyclic Compounds*, **2005**, *41*, 437.

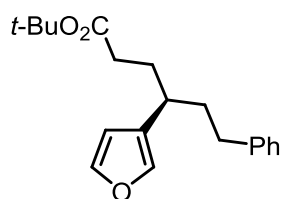
(*R*)-2,2'-(4-phenylbutane-1,2-diyl)difuran [(*R*)-2u]



(*R*)-2u was synthesised through a modification of the **GP2** procedure. A solution of furan (21 μ L, 0.28 mmol, 2.2 eq.) in THF (0.3 M) was cooled to 0 $^{\circ}$ C and treated with *n*-BuLi (0.2 mL, 0.28 mmol, 2.2 eq., 1.6 M in hexanes). The mixture was stirred at this temperature for 1 h and the boronic ester (***R*-1u**) (50 mg, 0.13 mmol, 1.0 eq.) was added dropwise as a solution in THF (0.5 M). The mixture was stirred at 0 $^{\circ}$ C for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the 'ate' complex [^{11}B NMR (96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. A solution of *N*-bromosuccinimide (NBS, 57.4 mg, 0.32 mmol, 2.5 eq.) in anhydrous MeOH (0.2 M) was added dropwise. A suspension of NaOMe (17 mg, 0.32 mmol, 2.65 eq.) in anhydrous MeOH (0.2 M) was added 1 min. after NBS addition. After 1 h at 0 $^{\circ}$ C, a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et_2O (15 mL) and water (15 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 15 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-pentane to give (***R*-2u**) (20 mg, 58%) as an oil; er (*R*:*S*) 97.3; R_f 0.89 (pentane: Et_2O : 95:5); $[\alpha]_{\text{D}}^{23} +13.0$ (*c* 0.6, CHCl_3); IR (film): ν (cm^{-1}) 3027, 2926, 1506, 1147, 1008, 725. ^1H NMR (400 MHz, CDCl_3) δ ppm; 7.36 (dd, $J = 1.8, 0.8$ Hz, 1H), 7.28 (dd, $J = 1.8, 0.8$ Hz, 1H), 7.28–7.24 (m, 2H), 7.18 (m, 1H), 7.15–7.11 (m, 2H), 6.30 (dd, $J = 3.2, 1.8$ Hz, 1H), 6.24 (dd, $J = 3.1, 1.8$ Hz, 1H), 6.02 (br d, $J = 3.2$ Hz, 1H), 5.88 (dd, $J = 3.1, 0.8$ Hz, 1H), 3.13 (m, 1H), 3.02 (dd, $J = 14.9, 7.2$ Hz, 1H), 2.93 (dd, $J = 14.9, 7.2$ Hz, 1H), 2.59 (dq, $J = 9.4, 5.9$ Hz, 1H), 2.51 (dq, $J = 9.4, 5.9$ Hz, 1H), 2.07–1.89 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 157.4, 153.8, 142.0, 141.0, 140.9, 128.4, 128.3, 125.7, 110.1, 109.9, 106.2, 105.5, 37.9, 35.0, 33.3, 32.8; HRMS (EI) calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_2$ [M] $^+$ 266.1307, found 266.1303.

Resolution of the enantiomers of **2u** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO_2 : $[n$ -hexane] as the mobile phase at a flow rate of 4.0 mL min^{-1} ($P = 125$ bar). Injection volume: 20 μ L of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 2.6 and 3.0 min., respectively, with a total analysis time of 15 min.

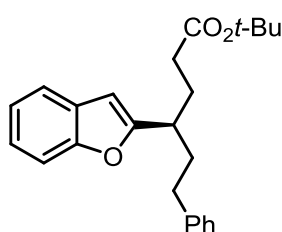
(*R*)-tert-Butyl 4-(furan-3-yl)-6-phenylhexanoate [(*R*)-3e]



A solution of 3-bromofuran (29 μL , 0.32 mmol, 1.2 eq.) in THF (1.0 mL) was cooled to $-78\text{ }^\circ\text{C}$ and treated with *n*-BuLi (0.2 mL, 0.32 mmol, 1.2 eq., 1.6 M in hexanes). The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h. (*R*)-**1e** (90 mg, 0.25 mmol, 1.0 eq.) was added as a solution in THF (0.5 mL) and the reaction was stirred at the same temperature for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the boron-ate complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. A solution of NBS (53 mg, 0.32 mmol, 1.2 eq.) in THF (1.0 mL) was added dropwise. After 1 h at $-78\text{ }^\circ\text{C}$, saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added and the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with Et_2O (5 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 5 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane to give (*R*)-**3e** (65 mg, 85%) as an oil; er (*R*:*S*) 96:4; R_f 0.44 (*n*-hexane: Et_2O 95:5); $[\alpha]_{\text{D}}^{24} +0.1$ (*c* 0.5, CHCl_3); IR (film): ν (cm^{-1}) 2923, 2855, 1728, 1454, 1367, 1146, 1028, 874, 699; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.41 (t, $J = 1.7$ Hz, 1H), 7.30–7.23 (m, 3H), 7.21–7.10 (m, 3H), 6.29 (s, 1H), 2.66–2.42 (m, 3H), 2.22–2.02 (m, 2H), 1.98–1.63 (m, 4H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 173.0, 143.12, 142.2, 139.4, 128.4, 128.3, 127.4, 125.7, 108.9, 80, 37.6, 34.8, 33.5, 33.4, 31.2, 29.6, 28.0; HRMS (EI) $\text{C}_{20}\text{H}_{26}\text{O}_3$ [M] $^+$ calcd. 314.1882, found 314.1875

Resolution of the enantiomers of **3e** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO_2 :*n*-hexane (4:1, v:v) as the mobile phase at a flow rate of 4.0 mL min^{-1} ($P = 125$ bar). Injection volume: $20\mu\text{L}$ of 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 3.9 and 4.6 min., respectively, with a total analysis time of 15 min.

(*R*)-tert-Butyl 4-(benzofuran-2-yl)-6-phenylhexanoate [(*R*)-4e]

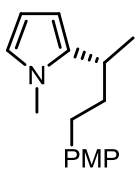


A solution of benzofuran (35 μL , 0.32 mmol, 1.2 eq.) in THF (1.0 mL) was cooled to $-78\text{ }^\circ\text{C}$ and treated with *n*-BuLi (0.2 mL, 0.32 mmol, 1.2 eq., 1.6 M in hexanes). The mixture was warmed to r.t. and stirred for 1 h. The mixture was cooled to $-78\text{ }^\circ\text{C}$ and (*R*)-**1e** (90 mg,

0.25 mmol, 1.0 eq.) was added as a solution in THF (0.5 mL) and the reaction was stirred at the same temperature for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the 'ate' complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. A solution of NBS (53 mg, 0.32 mmol, 1.2 eq.) in THF (1.0 mL) was added dropwise. After 1 h at -78 °C, saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added and the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with Et_2O (5 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 5 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane to give (*R*)-**4e** (65 mg, 66%) as an oil; er (*R*:*S*) 96:4; R_{f} 0.29 (*n*-hexane: Et_2O 95:5); $[\alpha]_{\text{D}}^{23} +13.4$ (*c* 1.0, CHCl_3); IR (film): ν (cm^{-1}) 2979, 2952, 2933, 1727, 1452, 1248, 1142, 849, 745; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.52 (br d, $J = 7.3$ Hz, 1H), 7.45 (dt, $J = 3.3$ Hz, 1H), 7.31–7.12 (m, 7H), 6.45 (m, 1H), 2.87 (m, 1H), 2.69–2.49 (m, 2H), 2.25–1.90 (m, 6H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 172.7, 160.4, 154.7, 141.8, 128.4, 128.3, 125.8, 123.2, 122.4, 120.3, 110.9, 103.2, 80.2, 38.4, 35.5, 33.5, 33.2, 29.2, 28.0; HRMS (EI) $\text{C}_{24}\text{H}_{28}\text{O}_3$ [M] $^+$ calcd. 364.2038, found 364.2040.

Resolution of the enantiomers of **4e** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO_2 : [*n*-hexane:*i*-PrOH (1:1 v:v)] (4:1 v:v) as the mobile phase at a flow rate of 4.0 mL min^{-1} ($P = 125$ bar). Injection volume: $20 \mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 4.5 and 5.3 min., respectively, with a total analysis time of 15 min.

(*R*)-2-(4-(4-methoxyphenyl)butan-2-yl)-1-methyl-1H-pyrrole [(*R*)-**5b**]

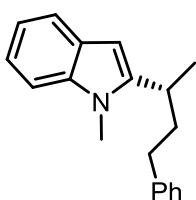


A solution of 1-methylpyrrole ($23 \mu\text{L}$, 0.26 mmol, 1.5 eq.) in THF (2.0 mL) was cooled to -78 °C and treated with *s*-BuLi (0.2 mL, 0.26 mmol, 1.5 eq., 1.3 M in cyclohexane/hexane (92/8)). The mixture was stirred at -78 °C for 5 min. and then it was allowed to warm to r.t. After 40 min. a solution of (*R*)-**1b** (50 mg, 0.17 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the 'ate' complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. A solution of NIS (46 mg, 0.21 mmol, 1.2 eq.) in THF (2.0 mL) was added dropwise. After 1 h at -78 °C, saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added and the reaction mixture was allowed to warm to room temperature. The

reaction mixture was diluted with EtOAc (10 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane to give (*R*)-**5b** (20 mg, 47%) as an oil; er (*R*:*S*) 95:5; *R*_f 0.25 (petrol:Et₂O 95:5); [α]_D²¹ 2.7 (*c* 0.37, CHCl₃); IR (film): ν (cm⁻¹) 2957, 2930, 1698, 1511, 1298, 1242, 1034, 700; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.11–7.05 (m, 2H), 6.85–6.81 (m, 2H), 6.52 (m, 1H), 6.10 (m, 1H), 5.93 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.80 (s, 3H), 3.48 (s, 3H), 2.75 (sx, *J* = 6.9 Hz, 1H), 2.67–2.53 (m, 2H), 1.95 (qid, *J* = 8.8, 6.9 Hz, 1H), 1.81 (qid, *J* = 8.8, 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 157.7, 138.5, 134.4, 129.2, 120.8, 113.7, 106.5, 103.5, 55.2, 39.0, 33.5, 32.6, 30.0, 21.0; HRMS (EI) calcd. for C₁₆H₂₁NO [*M*]⁺ 243.1623, found 243.1619.

Resolution of the enantiomers of **5b** was achieved using a chiral HPLC system fitted with a Chiralpak IB column with guard as the stationary phase with *n*-hexane as the mobile phase at a flow rate of 0.5 mL min⁻¹ (*T* = 0 °C). Injection volume: 5 μ L of the sample prepared in a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 41.5 and 48.5 min., respectively, with a total analysis time of 60 min.

(*R*)-1-Methyl-2-(4-phenylbutan-2-yl)-1H-indole [(*R*)-**6a**]

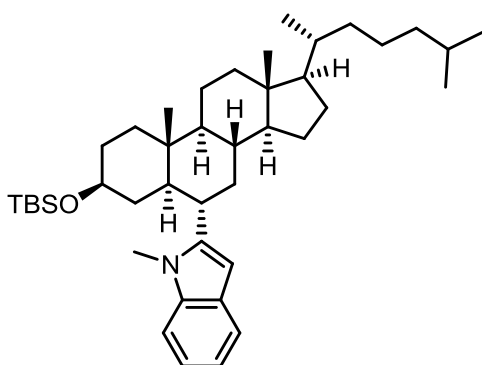


A solution of *N*-methylindole (50 μ L, 0.40 mmol, 1.6 eq.) in THF (1.0 mL) was treated with BuLi (0.3 mL, 0.40 mmol, 1.6 eq., 1.6 M in hexanes) at r.t. The mixture was heated under refluxing conditions for 3 h. The mixture was gradually cooled to -78 °C and (*R*)-**1a** (65 mg, 0.25 mmol, 1.0 eq.) was added dropwise as a solution in THF (1.0 mL). The mixture was stirred at -78 °C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the 'ate' complex [¹¹B NMR, 96 MHz, THF) δ_B ~ 8 ppm]. A solution of NIS (68 mg, 0.30 mmol, 1.2 eq.) in THF (1.0 mL) was added dropwise. After 1 h saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (99:1) gave (*R*)-**6a** (57 mg, 86%) as an oil; er (*R*:*S*) 98:2; *R*_f 0.82 (petrol:EtOAc 95:5); [α]_D²² - 54.3 (*c* 1.0, CHCl₃); IR (film): ν (cm⁻¹) 3056, 3025, 2962,

2926, 2859, 1539, 1466, 1454, 1309, 1011, 774, 746, 730, 698; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.63 (br d, $J = 7.73$ Hz, 1H), 7.38–7.31 (m, 3H), 7.28–7.19 (m, 4H), 7.15 (td, $J = 7.3$, 1.1 Hz, 1H), 6.38 (s, 1H), 3.65 (s, 3H), 3.01 (app. sx, $J = 6.9$ Hz, 1H), 2.76 (t, $J = 7.9$ Hz, 2H), 2.18 (dq, $J = 13.7$, 7.5 Hz, 1H), 2.00 (dq, $J = 14.2$, 7.9 Hz, 1H), 1.42 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 146.2, 142.1, 137.3, 128.5, 128.4, 128.0, 125.9, 120.6, 119.9, 119.3, 108.9, 97.0, 38.5, 33.5, 30.4, 29.4, 21.0; HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{21}\text{N}$ $[M]^+$ 263.1674, found 263.1674.

Resolution of the enantiomers of **6a** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO_2 : $[n$ -hexane: i -PrOH (1:1 v:v)] (9:1 v:v) as the mobile phase at a flow rate of 4.0 mL min^{-1} ($P = 125$ bar). Injection volume: $20 \mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (S) and the slower running component (R) were eluted at 6.9 and 7.5 min., respectively, with a total analysis time of 15 min.

2-((3*S*,5*R*,6*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-((*tert*-Butyldimethylsilyl)oxy)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[α]phenanthren-6-yl)-1-methyl-1*H*-indole (6p**)**

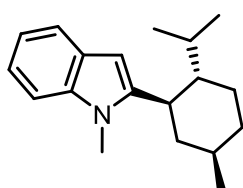


n -BuLi (0.3 mL, 0.48 mmol, 3.0 eq., 1.6 M in hexanes) was added at r.t. to a stirred solution of N -methylindole (60 μL , 0.48 mmol, 3.0 eq.) in THF (1.0 mL). The mixture was heated under refluxing conditions for 3 h. The reaction mixture was cooled to -78 $^\circ\text{C}$ and **1p** (100 mg, 0.16 mmol, 1.0 eq.) was added dropwise as a solution in THF (1.0 mL). The

mixture was stirred at -78 $^\circ\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the boron-ate complex [^{11}B NMR, 96 MHz) $\delta_{\text{B}} \sim 8$ ppm]. MeOH (0.5 mL) was added at -78 $^\circ\text{C}$ to quench the excess organolithium. A solution of NIS (43 mg, 0.19 mmol, 1.2 eq.) in THF (1.0 mL) was added dropwise. After 18 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm up to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried (MgSO_4), filtered and concentrated under vacuum. Purification by flash column chromatography eluting with n -hexane:Et $_2$ O (99.5:0.5) gave **6p** (75 mg, 75%) as a

solid; R_f 0.30 (petrol:Et₂O 99:1); mp 194–196 °C; $[\alpha]_D^{22} + 30.4$ (c 0.9, CHCl₃); IR (film): ν (cm⁻¹) 2927, 2851, 1467, 1444, 1248, 1099, 1084, 867, 834, 768, 749, 728; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.53 (br d, $J = 7.8$ Hz, 1H), 7.27 (m, 1H), 7.14 (m, 1H), 7.04 (m, 1H), 6.20 (s, 1H), 3.67 (s, 3H), 3.44 (m, 1H), 2.74 (td, $J = 11.6, 3.6$ Hz, 1H), 2.06–1.99 (dt, $J = 12.6, 3.2$ Hz, 1H), 1.93–1.86 (dt, $J = 13.2, 3.9$ Hz, 1H), 1.84–1.74 (m, 2H), 1.72–1.67 (m, 1H), 1.60–1.54 (m, 2H), 1.54–1.50 (m, 2H), 1.49–1.47 (m, 1H), 1.46–1.43 (m, 1H), 1.39–1.32 (m, 4H), 1.27 (s, 3H), 1.19–1.16 (m, 1H), 1.15–1.09 (m, 4H), 1.07–1.02 (m, 3H), 1.0–0.99 (m, 4H), 0.92 (d, $J = 6.5$ Hz, 3H), 0.87 (dd, $J = 6.6, 1.8$ Hz, 8H), 0.74 (s, 9H), 0.70 (s, 3H), –0.09 (s, 3H), –0.13 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 145.7, 136.6, 128.2, 120.2, 119.6, 119.1, 108.8, 96.8, 72.3, 56.2, 54.2, 50.9, 42.6, 40.7, 40.0, 39.5, 37.3, 36.2, 36.2, 35.8, 35.4, 35.1, 34.8, 31.8, 29.7, 29.5, 28.2, 28.0, 25.8, 24.1, 23.8, 22.8, 22.6, 21.3, 18.7, 18.2, 13.2, 12.1, –4.7; HRMS (ESI) calcd. for C₄₂H₇₀NOSi $[M+H]^+$ 632.5221, found 632.5227.

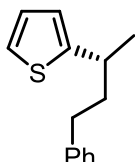
2-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)-1-methyl-1*H*-indole (**6q**)



A solution of *N*-methylindole (75 μ L, 0.60 mmol, 1.6 eq.) in THF (1.0 mL) was treated with *n*-BuLi (0.4 mL, 0.60 mmol, 1.6 eq., 1.6 M in hexanes) at r.t. The mixture was heated under refluxing conditions for 3 h. The mixture was cooled to –78 °C and **1q** (100 mg, 0.38 mmol, 1.0 eq.) was added dropwise as a solution in THF (2.0 mL). The mixture was stirred at –78 °C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [¹¹B NMR, 96 MHz, THF) $\delta_B \sim 8$ ppm]. A solution of NIS (135 mg, 0.60 mmol, 1.2 eq.) in THF (2.0 mL) was added dropwise. After 1 h saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (99:1) gave **6q** (66 mg, 65%) as an oil; R_f 0.40 (pentane:Et₂O 99:1); $[\alpha]_D^{23} - 105$ (c 1, CHCl₃); IR (film): ν (cm⁻¹) 3677, 3056, 2951, 2918, 2867, 1543, 1466, 1409, 1384, 1367, 1342, 1308, 1265, 1226, 1170, 1143, 1129, 1114, 1097, 1081, 1054, 1013, 977, 939, 916, 904, 870, 833, 775, 746, 729, 688, 672, 589, 569, 535, 525; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.61 (d, $J = 7.7$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.22 (t, $J = 7.7$ Hz, 1H), 7.14 (t, $J = 7.7$ Hz, 1H), 6.30 (s, 1H), 3.77 (s, 3H), 2.75 (br t, $J = 11.5$ Hz,

1H), 1.99–1.83 (m, 4H), 1.68 (d, $J = 11.9$ Hz, 1H), 1.56 (m, 1H), 1.32–1.04 (m, 3H) 0.95 (d, $J = 6.5$ Hz, 3H), 0.89 (d, $J = 7.0$ Hz, 3H), 0.72 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 146.0, 136.6, 128.2, 120.1, 119.6, 119.2, 108.8, 96.8, 47.3, 45.0, 38.4, 35.0, 33.1, 29.3, 27.3, 24.6, 22.4, 21.7, 15.8; HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{28}\text{N}$ $[M+\text{H}]^+$ 270.2216, found 270.2215.

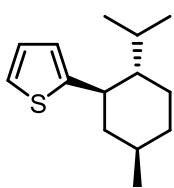
(*R*)-2-(4-Phenylbutan-2-yl)thiophene [(*R*)-7a]



A solution of thiophene (48 μL , 0.60 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to -78 $^\circ\text{C}$ and treated with *n*-BuLi (0.4 mL, 0.60 mmol, 1.2 eq., 1.6 M in hexanes). The mixture was warmed to 0 $^\circ\text{C}$ and stirred for 30 min. The mixture was cooled to -78 $^\circ\text{C}$ and the (*R*)-**1a** (130 mg, 0.50 mmol, 1.0 eq.) was added dropwise as a solution in THF (1.0 mL). The mixture was stirred at -78 $^\circ\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR (96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. A solution of NBS (107 mg, 0.60 mmol, 1.2 eq.) in THF (2.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with EtOAc (10 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane to give (*R*)-**7a** (100 mg, 92 %) as an oil; er (*R*:*S*) 98:2; R_f 0.47 (*n*-hexane); $[\alpha]_{\text{D}}^{24} - 25.0$ (c 1.0, CHCl_3); IR (film): ν (cm^{-1}) 3062, 3026, 2958, 2923, 2856, 1603, 1496, 1453, 1030, 849, 746; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.38–7.32 (m, 2H), 7.29–7.23 (m, 3H), 7.22 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.02 (dd, $J = 5.1, 3.5$ Hz, 1H), 6.92–6.89 (br d, $J = 3.5$ Hz, 1H), 3.15 (app. sx, $J = 6.9$ Hz, 1H), 2.68 (t, $J = 8.3$ Hz, 2H), 2.12–1.96 (m, 2H), 1.44 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 151.6, 142.3, 128.5, 128.4, 126.5, 125.8, 122.8, 122.5, 41.0, 34.9, 33.7, 23.5; HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{16}\text{S}$ $[M]^+$ 216.0973, found 216.0972.

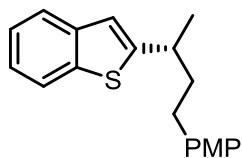
Resolution of the enantiomers of **7a** was achieved using a chiral HPLC system fitted with a Chiracel OD column with guard as the stationary phase with *n*-hexane as the mobile phase at a flow rate of 0.3 mL min^{-1} ($T = 0$ $^\circ\text{C}$). Injection volume: $20\mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 76.8 and 85.8 min., respectively, with a total analysis time of 100 min.

2-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)thiophene (**7q**)



A solution of thiophene (36 μL , 0.45 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to $-78\text{ }^\circ\text{C}$ and treated with *n*-BuLi (0.3 mL, 0.45 mmol, 1.2 eq., 1.6 M in hexanes). The mixture was warmed to $0\text{ }^\circ\text{C}$ and stirred for 30 min. The mixture was cooled to $-78\text{ }^\circ\text{C}$ and the **1q** (100 mg, 0.38 mmol, 1.0 eq.) was added dropwise as a solution in THF (1.0 mL). The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the 'ate' complex [^{11}B NMR (96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. A solution of NBS (81 mg, 0.45 mmol, 1.2 eq.) in THF (2.0 mL) was added dropwise. After 1 h at $-78\text{ }^\circ\text{C}$, saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added and the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane to give **7q** (54 mg, 65%) as an oil; R_f 0.87 (pentane:Et₂O 99:1); $[\alpha]_{\text{D}}^{23} - 38$ (*c* 1, CHCl_3); IR (film): ν (cm^{-1}) 3677, 3069, 2953, 2917, 2869, 2846, 1455, 1444, 1385, 1368, 1347, 1312, 1277, 1266, 1239, 1224, 1187, 1131, 1075, 1054, 1038, 997, 975, 929, 861, 845, 819, 772, 750, 688, 607, 586, 532; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.12 (br d, $J = 5.1$ Hz, 1H), 6.91 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.77 (br d, $J = 3.4$ Hz, 1H), 2.80 (td, $J = 11.6, 3.6$ Hz, 1H), 1.95 (dq, $J = 12.9, 2.8$ Hz, 1H), 1.82 (m, 1H), 1.74 (dq, $J = 12.8, 3.2$ Hz, 1H), 1.59 (qid, $J = 6.9, 2.8$ Hz, 1H), 1.48 (m, 1H), 1.34 (tt, $J = 11.6, 2.8$ Hz, 1H), 1.23 (m, 1H), 1.13 (m, 1H), 1.02 (m, 1H), 0.91 (d, $J = 6.6$ Hz, 3H), 0.83 (d, $J = 6.9$ Hz, 3H), 0.72 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 150.8, 126.2, 123.0, 122.2, 49.6, 46.5, 43.0, 35.0, 33.9, 27.4, 24.6, 22.4, 21.5, 15.3; HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{22}\text{S}$ [M]⁺ 222.1443, found 222.1441.

(*R*)-2-(4-(4-methoxyphenyl)butan-2-yl)benzo[*b*]thiophene [(*R*)-**8b**]



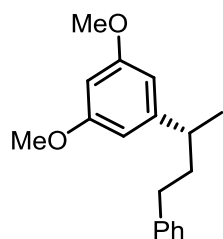
A solution of benzo[*b*]thiophene (35 μL , 0.30 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to $-78\text{ }^\circ\text{C}$ and treated with *t*-BuLi (0.2 mL, 0.30 mmol, 1.2 eq., 1.6 M in hexane). The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h and then a solution of (*R*)-**1b** (72 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the 'ate' complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. A solution of NBS (53 mg, 0.30 mmol, 1.2 eq.) in THF (2.0 mL) was added dropwise. After 1 h

at $-78\text{ }^{\circ}\text{C}$, saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added and the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane to give (*R*)-**8b** (58 mg, 78%) as an oil; er (*R*:*S*) 96.4; R_f 0.36 (pentane:Et₂O: 95:5); $[\alpha]_{\text{D}}^{23}$ 38 (*c* 1.0, CHCl_3); mp. 56-58 $^{\circ}\text{C}$; IR (film): ν (cm^{-1}) 2971, 2927, 1610, 1511, 1431, 1241, 1175, 1035, 819, 743, 726. ^1H NMR (400 MHz, CDCl_3) δ ppm; 7.81 (d, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.32 (t, $J = 7.7$ Hz, 1H), 7.27 (t, $J = 7.7$ Hz, 1H), 7.09 (d, $J = 7.7$ Hz, 2H), 7.05 (s, 1H), 6.83 (d, $J = 7.8$ Hz, 2H), 3.80 (s, 3H), 3.12 (sx, $J = 6.8$ Hz, 1H), 2.59 (m, 2H), 2.00 (m, 2H), 1.42 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 157.7, 152.5, 140.0, 138.9, 134.1, 129.3, 124.0, 123.4, 122.8, 122.3, 119.4, 113.8, 55.3, 40.7, 35.6, 32.6, 23.1; HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{20}\text{OS}$ [M]⁺ 296.1235, found 296.1238.

Resolution of the enantiomers of **8b** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO_2 : [*n*-hexane:*i*-PrOH (9:1 v:v)] as the mobile phase at a flow rate of 4.0 mL min^{-1} ($P = 125$ bar). Injection volume: $20\text{ }\mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 15.0 and 17.0 min., respectively, with a total analysis time of 15 min.

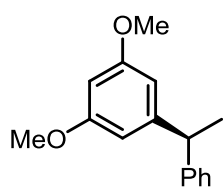
6. Reaction Products – Coupling of secondary boronic esters to 6-membered aromatics

(*R*)-1,3-Dimethoxy-5-(4-phenylbutan-2-yl)benzene [(*R*)-**9a**]



A solution of 3,5-(dimethoxy)bromobenzene (50 mg, 0.23 mmol, 1.2 eq.) in THF (2.5 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated with *t*-BuLi (0.27 mL, 0.46 mmol, 2.4 eq., 1.7 M in pentane). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. and then a solution of (*R*)-**1a** (50 mg, 0.19 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2 mL) and the mixture was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of NBS (41 mg, 0.23 mmol, 1.2 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm up to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (98:2) gave (*R*)-**9a** (43 mg, 83%) as an oil, er (*R*:*S*) 98:2; R_f 0.49 (*n*-hexane:Et₂O 95:5); $[\alpha]_{\text{D}}^{22} -19.7$ (*c* 1.0, CHCl_3); IR (film): ν (cm^{-1}) 2926, 2837, 1593, 1454, 1427, 1203, 1150, 1056, 831, 696; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.31–7.25 (m, 2H), 7.22–7.14 (m, 3H), 6.38 (d, $J = 2.3$ Hz, 2H), 6.32 (t, $J = 2.3$ Hz, 1H), 3.80 (s, 6H), 2.66 (app. sx, $J = 6.9$ Hz, 1H), 2.53 (t, $J = 8.0$, 2H), 2.00–1.84 (m, 2H), 1.26 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 160.8, 149.9, 142.5, 128.4, 128.3, 125.6, 105.3, 97.6, 55.2, 39.9, 39.8, 33.9, 22.4; HRMS (EI) calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_2$ [M]⁺ 270.1620, found 270.1625. Resolution of the enantiomers of **9a** was achieved using a chiral SFC system fitted with a Chiracel IA column as the stationary phase with CO_2 :*n*-hexane (95:5, v:v) as the mobile phase at a flow rate of 4.0 mL min^{-1} ($P = 125$ bar). Injection volume: $20\text{ }\mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 7.3 and 8.0 min., respectively, with a total analysis time of 15 min.

(S)-1,3-dimethoxy-5-(1-phenylethyl)benzene [(S)-9I]

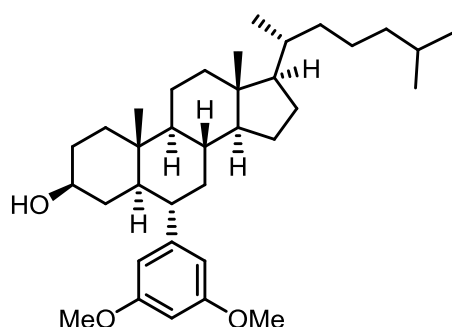


A solution of 3,5-(dimethoxy)bromobenzene (70.5 mg, 0.325 mmol, 1.2 eq.) in THF (2.5 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated with *t*-BuLi (0.38 mL, 0.65 mmol, 2.4 eq., 1.7 M in pentane). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. and then a solution of (S)-**11** (58 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2 mL) and the mixture was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of NBS (45 mg, 0.25 mmol, 1.0 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (98:2) gave (S)-**9I** (39 mg, 64%) as an oil; er (S:R) 97:3; R_f 0.26 (petrol:Et₂O 95:5); $[\alpha]_{\text{D}}^{21}$ 0.3 (*c* 0.7, CHCl_3) (lit. $[\alpha]_{\text{D}}^{20}$ -2.5 (*c* 0.4, CHCl_3) for (R)-enantiomer); ^1H NMR (400 MHz, CDCl_3) δ ppm; 7.32–7.20 (m, 4H), 7.18 (tt, $J = 7.0, 1.5$ Hz, 1H), 6.39 (d, $J = 2.3$ Hz, 2H), 6.30 (t, $J = 2.3$ Hz, 1H), 4.08 (q, $J = 7.2$ Hz, 1H), 3.75 (s, 6H), 1.61 (d, $J = 7.2$ Hz, 3H) ^{13}C NMR (100 MHz, CDCl_3) δ ppm 160.7, 148.8, 146.0, 128.3, 127.5, 126.1, 106.0, 97.6, 55.2, 55.2, 45.0, 21.7. Data in accordance with literature.¹⁷

Resolution of the enantiomers of **9I** was achieved using a chiral HPLC system fitted with a Chiralpak IA column with guard as the stationary phase with *n*-hexanes as the mobile phase at a flow rate of 1.0 mL min^{-1} . Injection volume: $2\text{ }\mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (R) and the slower running component (S) were eluted at 18.5 and 20.3 min., respectively, with a total analysis time of 40 min.

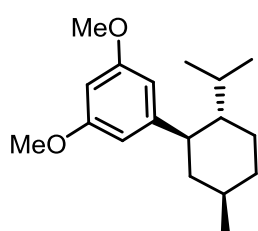
¹⁷ Bess, E. N.; Sigman, M. S.; *Org. Lett.*, **2013**, *15*, 646.

(3*S*,5*R*,6*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-6-(3,5-Dimethoxyphenyl)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol (9o**)**



A solution of 3,5-(dimethoxy)bromobenzene (126 mg, 0.58 mmol, 3.0 eq.) in THF (4.0 mL) was cooled to -78 °C and treated with *t*-BuLi (0.5 mL, 0.71 mmol, 2.6 eq., 1.4 M in pentane). The mixture was stirred at -78 °C for 30 min and then a solution of **1o** (100 mg, 0.19 mmol, 1.0 eq.) in THF (2.0 mL) was added. The mixture was stirred at -78 °C for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the boron-ate complex [^{11}B NMR, 96 MHz) $\delta_{\text{B}} \sim 8$ ppm]. A solution of NBS (104 mg, 0.58 mmol, 3.0 eq.) in MeOH (3.0 mL) was added dropwise. The mixture was allowed to warm to room temperature overnight and saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography (*n*-hexane:EtOAc 9:1 \rightarrow 7:3) gave **9o** (93 mg, 91%) as an amorphous solid; R_f 0.50 (*n*-hexane:EtOAc 7:3); mp. 96–98 °C; $[\alpha]_{\text{D}}^{22} + 66.9$ (*c* 3.0, CHCl_3); IR (film): ν (cm^{-1}) 3364, 2929, 2866, 1594, 1460, 1428, 1204, 1152, 1061, 756, 698. ^1H NMR (400 MHz, CDCl_3) δ ppm 6.29 (br s, 3H), 3.78 (s, 6H), 3.44 (tt, $J = 11.0, 4.8$ Hz, 1H), 2.38 (td, $J = 12.0, 3.1$ Hz, 1H), 2.01 (br d, $J = 12.5$ Hz, 1H), 1.86–1.72 (m, 4H), 1.61–1.47 (m, 4H), 1.40–1.29 (m, 6H), 1.28–1.23 (m, 3H), 1.18–1.10 (m, 6H), 1.06–0.99 (m, 5H), 0.94–0.90 (m, 6H), 0.89–0.85 (m, 6H), 0.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 148.5, 97.6, 71.5, 56.3, 56.2, 55.2, 54.2, 49.4, 45.1, 42.6, 41.0, 40.0, 39.5, 37.1, 36.2, 36.0, 35.8, 35.3, 34.5, 31.0, 29.7, 28.2, 28.0, 24.1, 23.8, 22.8, 22.6, 21.3, 20.8, 18.7, 17.5, 17.3, 14.6, 13.2, 12.1, 7.9; HRMS (ESI) calcd. for $\text{C}_{35}\text{H}_{56}\text{NaO}_3$ [$M+\text{Na}$] $^+$ 547.4127, found 547.4122.

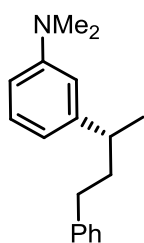
1-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)-3,5-dimethoxybenzene (9q**)**



A solution of 3,5-(dimethoxy)bromobenzene (70.5 mg, 0.325 mmol, 1.2 eq.) in THF (2.5 mL) was cooled to -78 °C and treated with *t*-BuLi (0.38 mL, 0.65 mmol, 2.4 eq., 1.7 M in pentane). The mixture was stirred at -78 °C for 30 min. and then a solution of **1q** (67mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’

complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2 mL) and the mixture was cooled to -78 °C. A solution of NBS (45 mg, 0.25 mmol, 1.0 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm up to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane: Et_2O (98:2) gave **9q** (58 mg, 84%) as an oil; R_f 0.27 (pentane: Et_2O 99:1); $[\alpha]_{\text{D}}^{23} - 40$ (c 1, CHCl_3); IR (film): ν (cm^{-1}) 3675, 2951, 2914, 2869, 2843, 1593, 1457, 1427, 1384, 1367, 1342, 1311, 1292, 1248, 1220, 1203, 1149, 1060, 993, 981, 954, 940, 930, 913, 877, 828, 698, 604, 570, 539; ^1H NMR (400 MHz, CDCl_3) δ ppm; 6.34 (d, $J = 2.3$ Hz, 2H), 6.29 (t, $J = 2.3$ Hz, 1H), 3.80 (s, 6H), 2.38 (td, $J = 11.6, 3.2$ Hz, 1H), 1.85–1.70 (m, 3H), 1.58–1.38 (m, 3H), 1.18–1.07 (dq, $J = 11.6, 2.5$ Hz, 2H), 1.12 (m, 1H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.81 (d, $J = 6.9$ Hz, 3H), 0.70 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 160.7, 149.3, 105.6, 97.3, 55.2, 48.4, 47.3, 45.1, 35.3, 33.2, 27.4, 24.5, 22.5, 21.6, 15.5.; HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{29}\text{O}_2$ $[M+\text{H}]^+$ 277.2168, found 277.2164.

(*R*)-*N,N*-Dimethyl-3-(4-phenylbutan-2-yl)aniline [(*R*)-10a]

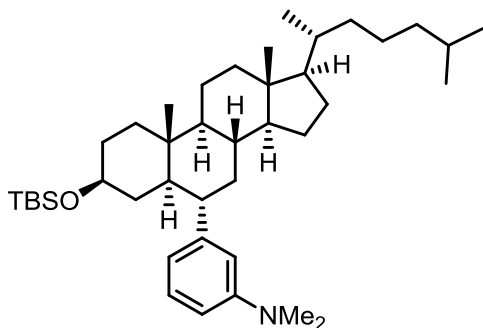


A solution of 3-*N,N*-dimethylaminobromobenzene (43 μL , 0.30 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to -78 °C and treated with *n*-BuLi (0.2 mL, 0.30 mmol, 1.2 eq., 1.6 M in hexanes). The mixture was stirred at -78 °C for 1 h and then a solution of (*R*)-**1a** (65 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to -78 °C. A solution of NIS (68 mg, 0.30 mmol, 1.2 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane: Et_2O (99:1) gave (*R*)-**10a**

(41 mg, 65 %) as an oil; er (*R:S*) 98:2; R_f 0.60 (petrol:Et₂O 95:5); $[\alpha]_D^{20} + 2.0$ (c 1.0, CHCl₃); IR (film): ν (cm⁻¹) 3025, 2954, 2922, 2854, 2801, 1601, 1495, 1348, 1348, 994, 773, 746, 696; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.31–7.14 (m, 6H), 6.66–6.61 (m, 3H), 2.97 (s, 6H), 2.70 (app. sx, $J = 6.9$ Hz, 1H), 2.56 (t, $J = 8.0$ Hz, 2H), 2.02–1.85 (m, 2H), 1.26 (d, $J = 6.9$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 150.6, 148.3, 142.7, 129.1, 128.4, 128.2, 125.6, 115.7, 111.9, 110.6, 40.9, 40.0, 39.9, 34.0, 22.6; HRMS (EI) calcd. for C₁₈H₂₃N $[M]^+$ 253.1830, found 253.1825.

Resolution of the enantiomers of **10a** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO₂:*n*-hexane (9:1 v:v) as the mobile phase at a flow rate of 4.0 mL min⁻¹ ($P = 125$ bar). Injection volume: 20 μ L of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 6.5 and 7.2 min., respectively, with a total analysis time of 15 min.

3-((3*S*,5*R*,6*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-((*tert*-Butyldimethylsilyl)oxy)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[α]phenanthren-6-yl)-*N,N*-dimethylaniline (10p**)**

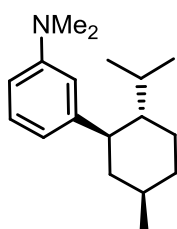


A solution of 3-*N,N*-dimethylaminobromobenzene (27 μ L, 0.19 mmol, 1.2 eq.) in THF (1.0 mL) was cooled to -78 °C and treated with *n*-BuLi (0.1 mL, 0.19 mmol, 1.2 eq., 1.6 M in hexanes). The mixture was stirred at -78 °C for 1 h and then a solution of **1p** (100 mg, 0.16 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 1 h at

which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [¹¹B NMR, 96 MHz, THF) $\delta_B \sim 8$ ppm]. A solution of NIS (43 mg, 0.19 mmol, 1.2 eq.) in MeOH (1.0 mL) was added dropwise. The mixture was allowed to warm to room temperature overnight and saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (98:2) gave **10p** (67 mg, 68%) as an amorphous solid; R_f 0.26 (petrol:Et₂O 99:1); mp 53–56 °C; $[\alpha]_D^{22} + 54.3$ (c 2.0, CHCl₃); IR (film): ν (cm⁻¹) 2929,

2852, 1601, 1467, 1440, 1250, 1096, 1081, 872, 834, 772, 700; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.16 (br s, 1H), 6.60 (br d, $J = 7.7$ Hz, 1H), 6.52 (br s, 2H), 3.42 (m, 1H, H), 2.94 (s, 6H), 2.38 (br t, $J = 11.0$ Hz, 1H), 2.02 (br d, $J = 12.4$ Hz, 1H), 1.87–1.73 (m, 3H), 1.72–1.65 (m, 1H), 1.61–1.46 (m, 4H), 1.42–1.25 (m, 8H), 1.24–1.08 (m, 6H), 1.08–0.98 (m, 6H), 0.98–0.92 (m, 6H), 0.88 (dd, $J = 6.6, 1.6$ Hz, 7H), 0.79 (s, 9H), 0.70 (s, 3H), –0.08 (s, 3H), –0.10 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 147.0, 128.9, 114.1, 110.2, 72.7, 54.4, 49.5, 45.2, 42.6, 41.6, 41.0, 40.1, 39.5, 37.6, 36.2, 36.0, 35.8, 35.4, 34.8, 31.8, 29.7, 28.3, 28.0, 26.0, 24.2, 23.8, 22.8, 22.6, 21.3, 18.7, 18.3, 13.3, 12.1, –4.6, –4.8; HRMS (ESI) calcd. for $\text{C}_{41}\text{H}_{72}\text{NOSi}$ $[M+\text{H}]^+$ 622.5305, found 622.5386.

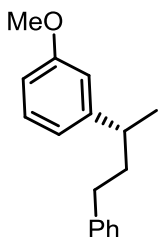
3-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)-*N,N*-dimethylaniline (**10q**)



A solution of 3-*N,N*-dimethylaminobromobenzene (43 μL , 0.30 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to -78 $^\circ\text{C}$ and treated with *n*-BuLi (0.2 mL, 0.30 mmol, 1.2 eq., 1.6 M in hexanes). The mixture was stirred at -78 $^\circ\text{C}$ for 1 h and then a solution of **1q** (67 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 $^\circ\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2 mL) and the mixture was cooled to -78 $^\circ\text{C}$. A solution of NIS (68 mg, 0.30 mmol, 1.2 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (99:1) gave **10q** (54 mg, 70%) as an oil; R_f 0.18 (pentane:Et₂O 99:1); $[\alpha]_{\text{D}}^{23} - 45$ (c 1, CHCl_3); IR (film): ν (cm^{-1}) 2951, 2914, 2869, 2845, 2801, 1684, 1600, 1579, 1500, 1454, 1437, 1383, 1347, 1230, 1177, 1150, 1135, 1098, 1060, 995, 972, 934, 847, 835, 772, 733, 723, 699, 640, 589, 535, 525; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.17 (t, $J = 8.0$ Hz, 1H), 6.63–6.55 (m, 3H), 2.96 (s, 6H), 2.40 (td, $J = 11.6, 3.4$ Hz, 1H), 1.86–1.78 (m, 2H), 1.78–1.71 (m, 1H), 1.58–1.42 (m, 3H), 1.23–1.09 (m, 2H), 1.02 (m, 1H), 0.91 (d, $J = 6.5$ Hz, 3H), 0.81 (d, $J = 6.9$ Hz, 3H), 0.71 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 150.7, 147.6, 128.8, 110.2, 48.6,

47.3, 45.4, 40.7, 35.4, 33.3, 27.4, 24.6, 22.6, 21.6, 15.5; HRMS (ESI) calcd. for C₁₈H₃₀N [M+H]⁺ 260.2373, found 260.2383.

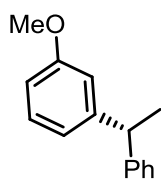
(R)-1-methoxy-3-(4-phenylbutan-2-yl)benzene [(R)-11a]



A solution of 3-methoxybromobenzene (29 μ L, 0.23 mmol, 1.2 eq.) in THF (1.0 mL) was cooled to -78 $^{\circ}$ C and treated with *n*-BuLi (0.15 mL, 0.23 mmol, 1.2 eq., 1.6 M in hexanes). The mixture was stirred at -78 $^{\circ}$ C for 1 h and then a solution of (*R*)-**1a** (50 mg, 0.19 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 $^{\circ}$ C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [(¹¹B NMR, 96 MHz, THF) δ_B \sim 8 ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to -78 $^{\circ}$ C. A solution of NBS (62 mg, 0.35 mmol, 1.8 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography (*n*-hexane:Et₂O 98:2) gave (*R*)-**11a** (33 mg, 72 %) as an oil; er (*R*:*S*) 98:2; *R*_f 0.56 (petrol:Et₂O 95:5); [α]_D²⁰ -11.2 (*c* 0.67, CHCl₃); IR (film): ν (cm⁻¹) 3026, 2956, 2926, 2834, 1600, 1583, 1485, 1453, 1259, 1157, 1045, 871, 777, 747; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.31–7.23 (m, 3H), 7.21–7.13 (m, 3H), 6.83 (br d, *J* = 7.5 Hz, 1H), 6.79–6.74 (m, 2H), 3.83 (s, 3H), 2.72 (sx, *J* = 6.9 Hz, 1H), 2.60–2.49 (m, 2H), 2.01–1.85 (m, 2H), 1.29 (d, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 159.7, 149.0, 142.5, 129.3, 128.4, 128.2, 125.6, 119.5, 113.1, 110.9, 55.1, 39.9, 39.6, 33.9, 22.5; HRMS (CI) calcd. For C₁₇H₂₁O [M+H]⁺ 241.1592, found 241.1590.

Resolution of the enantiomers of **11a** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO₂:[*n*-hexane:*i*-PrOH (9:1 v:v)] as the mobile phase at a flow rate of 4.0 mL min⁻¹ (*P* = 125 bar). Injection volume: 20 μ L of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 3.8 and 4.2 min., respectively, with a total analysis time of 15 min.

(R)-1-methoxy-3-(1-phenylethyl)benzene [(R)-11I]



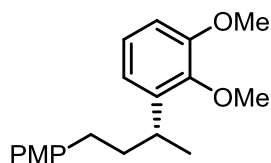
A solution of 3-methoxybromobenzene (40 μ L, 0.32 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to -78 $^{\circ}$ C and treated with *n*-BuLi (0.2 mL, 0.32 mmol, 1.2 eq., 1.6 M in hexanes). The mixture was stirred at -78 $^{\circ}$ C for 1 h and then a solution of (R)-**11** (58 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 $^{\circ}$ C for 1 h at which point 11 B NMR spectroscopy showed complete formation of the 'ate' complex [(11 B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to -78 $^{\circ}$ C. A solution of NBS (62 mg, 0.35 mmol, 1.8 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography (*n*-hexane:Et₂O 98:2) gave (R)-**11I** (25 mg, 43%) as an oil; er (*R*:*S*) 97:3; R_f 0.49 (petrol:Et₂O 95:5); $[\alpha]_{\text{D}}^{23} 2$ (*c* 1, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.31–7.15 (m, 6H), 6.83 (br d, $J = 7.5$ Hz, 1H), 6.78 (m, 1H), 6.73 (ddd, $J = 8.2, 2.6, 0.8$ Hz, 1H), 4.12 (q, $J = 7.2$ Hz, 1H), 3.77 (s, 3H), 1.63 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 159.6, 148.0, 146.2, 129.3, 128.3, 127.6, 126.0, 120.1, 113.8, 110.9, 55.1, 44.8, 21.8.

Data in accordance with literature.¹⁸

Resolution of the enantiomers of **11I** was achieved using a chiral SFC system fitted with a Chiracel IA column as the stationary phase with CO_2 :*n*-hexane as the mobile phase at a flow rate of 4.0 mL min^{-1} ($P = 125$ bar). Injection volume: 20 μ L of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 10.5 and 13.2 min., respectively, with a total analysis time of 20 min.

¹⁸ Lopez-Perez, A.; Adrio, J.; Carretero, J. C.; *Org. Lett.*, **2009**, *11*, 5514.

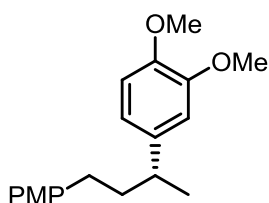
(R)-1,2-dimethoxy-3-(4-(4-methoxyphenyl)butan-2-yl)benzene [(R)-12b]



A solution of 3,4-dimethoxybromobenzene (29 μL , 0.19 mmol, 1.1 eq.) in THF (1.0 mL) was cooled to $-78\text{ }^\circ\text{C}$ and treated with *t*-BuLi (0.2 mL, 0.38 mmol, 2.2 eq., 1.7 M in hexanes). The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h and then a solution of (*R*)-**1b** (50 mg, 0.17 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the 'ate' complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to $-78\text{ }^\circ\text{C}$. A solution of NBS (46 mg, 0.26 mmol, 1.5 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography (*n*-hexane:Et₂O 98:2) gave (*R*)-**12b** (24 mg, 46%) as an oil; er (*R*:*S*) 95:5; R_f 0.23 (pentane:Et₂O 85:15); $[\alpha]_{\text{D}}^{22}$ 33 (*c* 0.48, CHCl_3); IR (film): ν (cm^{-1}) 2956, 2931, 2833, 1611, 1582, 1510, 1475, 1243, 1036, 1008, 745; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.11–7.03 (m, 3H), 6.88–6.76 (m, 4H), 3.88 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.26 (app. sx, $J = 7.0$ Hz, 1H), 2.55 (m, 1H), 2.45 (m, 1H), 1.96–1.79 (m, 2H), 1.27 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 157.6, 152.7, 146.7, 141.1, 134.8, 129.2, 124.0, 118.7, 113.6, 109.6, 60.8, 55.6, 55.2, 39.6, 33.2, 31.7, 22.0; HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{24}\text{O}_3$ [M]⁺ 300.1725, found 300.1717.

Resolution of the enantiomers of **12b** was achieved using a chiral HPLC system fitted with a Chiralcel IB column as the stationary phase with hexane:MTBE (95:5) as the mobile phase at a flow rate of 0.7 mL min^{-1} . Injection volume: 2 μL of a 2 g L^{-1} solution of the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 34.3 and 38.7 min., respectively, with an analysis time of 40 min.

(R)-1,2-dimethoxy-4-(4-(4-methoxyphenyl)butan-2-yl)benzene [(R)-13b]

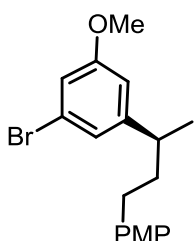


A solution of 3,4-dimethoxybromobenzene (29 μL , 0.19 mmol, 1.1 eq.) in THF (1.0 mL) was cooled to $-78\text{ }^\circ\text{C}$ and treated with *t*-BuLi (0.2 mL, 0.38 mmol, 2.2 eq., 1.7 M in hexanes). The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h and then a solution of (*R*)-**1b** (50 mg, 0.17 mmol, 1.0

eq.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of NBS (46 mg, 0.26 mmol, 1.5 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography (*n*-hexane:Et₂O 98:2) gave (*R*)-**13b** (26 mg, 51%) as an oil; er (*R*:*S*) 95:5; R_f 0.16 (pentane:Et₂O 85:15); $[\alpha]_{\text{D}}^{22} - 20$ (*c* 0.73, CHCl_3); IR (film): ν (cm^{-1}) 2954, 2931, 2833, 1591, 1511, 1441, 1243, 1030, 830; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.08–7.04 (m, 2H), 6.85–6.81 (m, 3H), 6.76 (dd, $J = 8.0, 1.9$ Hz, 1H), 6.72 (d, $J = 1.9$ Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.80 (s, 3H), 2.67 (app. sx, $J = 7.0$ Hz, 1H), 2.51–2.44 (m, 2H), 1.91–1.83 (m, 2H), 1.27 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 157.6, 148.8, 147.1, 140.0, 134.6, 129.2, 118.8, 113.7, 111.2, 110.3, 55.9, 55.8, 55.2, 40.3, 39.0, 33.0, 22.7; HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{24}\text{O}_3$ [M]⁺ 300.1725, found 300.1721.

Resolution of the enantiomers of **13b** was achieved using a chiral HPLC system fitted with a Chiracel IC column as the stationary phase with hexane:*i*-PrOH as the mobile phase at a flow rate of 0.7 mL min^{-1} . Injection volume: 2 μL of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 24.3 and 26.3 min., respectively, with a total analysis time of 40 min.

(*S*)-1-bromo-3-methoxy-5-(4-(4-methoxyphenyl)butan-2-yl)benzene [(*S*)-**14b**]

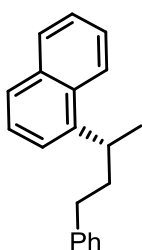


A solution of 3,5-dibromoanisole (85 mg, 0.32 mmol, 1.2 eq.) in THF (1.0 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated with *t*-BuLi (0.4 mL, 0.64 mmol, 2.4 eq., 1.7 M in hexanes). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h and then a solution of (*S*)-**1b** (72 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to $-78\text{ }^{\circ}\text{C}$. A

solution of NBS (108 mg, 0.61 mmol, 2.4 eq.) in MeOH (5.0 mL) was added dropwise. After 1 h saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography (*n*-hexane:Et₂O 98:2) gave (*S*)-**14b** (70 mg, 81%) as an oil; er (*S*:*R*) 95:5; *R*_f 0.40 (petrol:Et₂O 9:1); [α]_D²² -1 (*c* 1, CHCl₃); IR (film): ν (cm⁻¹) 2957, 2926, 2848, 2350, 1595, 1567, 1512, 1457, 1267, 1244, 1037, 820, 693 ¹H NMR (400 MHz, CDCl₃) δ ppm 7.04 (d, *J* = 8.9 Hz, 2H), 6.94 (m, 1H), 6.89 (m, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.66 (m, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 2.63 (app. sx, *J* = 7.0 Hz, 1H), 2.45 (t, *J* = 8.0 Hz, 2H), 1.92–1.78 (m, 2H), 1.23 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 160.4, 157.7, 150.7, 134.2, 129.2, 122.7, 122.6, 114.2, 113.7, 112.4, 55.4, 55.2, 39.8, 39.4, 32.8, 22.2; HRMS (EI) calcd. for C₁₈H₂₁BrO₂ [*M*]⁺ 348.0725, found 348.0718.

Resolution of the enantiomers of **14b** was achieved using a chiral HPLC system fitted with a Chiralpak IA column with guard as the stationary phase with *n*-hexanes as the mobile phase at a flow rate of 0.8 mL min⁻¹ (*T* = 0 °C). Injection volume: 5 μ L of a 2 g L⁻¹ solution of the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 44.2 and 56.3 min., respectively, with a total analysis time of 70 min.

(*R*)-1-(4-Phenylbutan-2-yl)naphthalene [(*R*)-**15a**]

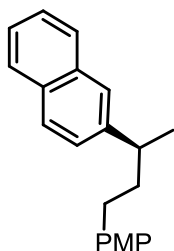


A solution of 1-bromonaphthalene (28 μ L, 0.16 mmol, 1.2 eq.) in Et₂O (1.0 mL) was cooled to 0 °C and *n*-BuLi (0.1 mL, 0.16 mmol, 1.2 eq., 1.6 M in hexanes) was added dropwise. The mixture was stirred at 0 °C for 1 h. (*R*)-**1a** (36 mg, 0.125 mmol, 1.0 eq.) was added as a solution in Et₂O (0.5 mL) and the reaction was stirred at the same temperature for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the boron-ate complex [(¹¹B NMR, 96 MHz) δ_B ~ 8 ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2 mL) and the mixture was cooled to -78 °C. A solution of NBS (53 mg, 0.32 mmol, 2.4 eq.) in MeOH (3.0 mL) was added dropwise and the reaction mixture was warmed to r.t. After 1 h saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers

were dried over MgSO_4 , filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane to give (*R*)-**15a** (23 mg, 89%) as an oil; er (*R*:*S*) 98:2; R_f 0.47 (petrol); $[\alpha]_D^{22}$ 40 (*c* 1.0, CHCl_3); IR (film): ν (cm^{-1}) 3026, 2959, 2926, 2858, 1596, 1509, 1496, 1453, 1395, 1375, 1256, 1168, 797, 777, 747; ^1H NMR (400 MHz, CDCl_3) δ ppm 8.00 (m, 1H), 7.88 (m, 1H), 7.73 (dd, $J = 7.4, 1.7$ Hz, 1H), 7.50–7.43 (m, 3H), 7.30–7.25 (m, 3H), 7.21–7.13 (m, 3H), 3.64 (app. sx, $J = 6.9$ Hz, 1H), 2.73–2.59 (m, 2H), 2.14 (m, 1H), 2.08 (m, 1H), 1.44 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 143.3, 142.4, 133.9, 131.6, 128.9, 128.4, 128.3, 126.3, 125.7, 125.6, 125.6, 125.2, 123.1, 122.5, 39.5, 33.9, 31.5, 21.77; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{20}$ [M] 260.1565, found 260.1570.

Resolution of the enantiomers of **15a** was achieved using chiral HPLC system fitted with a Chiracel OJ-H column with guard as the stationary phase and *n*-hexane:*i*-PrOH (99:1) as the mobile phase at a flow rate of 0.5 mL min^{-1} ($T = 5 \text{ }^\circ\text{C}$). Injection volume: $20 \mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) major were eluted at 50.7 min and 60.7 min., respectively, with an analysis time of 85 min.

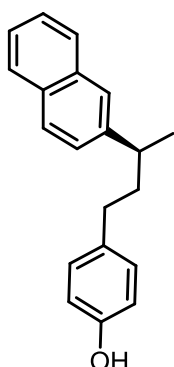
(*S*)-2-(4-(4-methoxyphenyl)butan-2-yl)naphthalene [(*S*)-**16b**]



A solution of 2-bromonaphthalene (43 mg, 0.21 mmol, 1.2 eq.) in Et_2O (1.0 mL) was cooled to $-15 \text{ }^\circ\text{C}$ and treated with *n*-BuLi (0.13 mL, 0.21 mmol, 1.2 eq., 1.7 M in hexanes). The mixture was stirred at $-15 \text{ }^\circ\text{C}$ for 30 min. and then a solution of (*S*)-**1b** (50 mg, 0.17 mmol, 1.0 eq.) in Et_2O (1.0 mL) was added. The mixture was stirred at $-15 \text{ }^\circ\text{C}$ for 30 min. at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_B \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to $-15 \text{ }^\circ\text{C}$. A solution of NBS (74 mg, 0.41 mmol, 2.0 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography (*n*-hexane: Et_2O 98:2) gave (*S*)-**16b** (31 mg, 62%) as an oil; er (*S*:*R*) 96:4; R_f 0.72 (petrol: Et_2O 95:5); IR (film): ν (cm^{-1}) 2955, 2924,

1510, 1243, 1037, 817, 745; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.87–7.80 (m, 3H), 7.65 (s, 1H), 7.52–7.42 (m, 2H), 7.38 (dd, $J = 8.5, 1.3$ Hz, 1H), 7.11–7.05 (m, 2H), 6.89–6.83 (m, 2H), 3.80 (s, 3H), 2.90 (app. sx, $J = 6.9$ Hz, 1H), 2.58–2.44 (m, 2H), 2.10–1.91 (m, 2H), 1.39 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 157.6, 144.8, 134.5, 133.6, 132.2, 129.2, 128.0, 127.6, 127.5, 125.8, 125.8, 125.3, 125.1, 113.7, 55.2, 40.0, 39.5, 33.0, 22.5; HRMS (EI) calcd. for $\text{C}_{21}\text{H}_{22}\text{O}$ [M] $^+$ 290.1671, found 290.1668.

(S)-4-(3-(naphthalen-2-yl)butyl)phenol {(S)-16b[OH]}



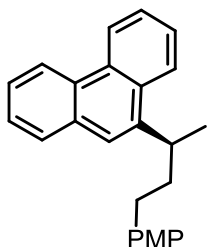
The enantioenriched material **16b** could not be purified on several attempts. The impure product was therefore derivatised by subjecting it to demethylation conditions.¹⁹ A round bottom flask was charged with **16b** (71 mg, 0.26 mmol). Anhydrous CH_2Cl_2 ([0.025]) was added and the solution cooled to 0 °C. BBr_3 (1 M in CH_2Cl_2 , 0.2 mL, 0.2 mmol, 2.0 eq.) was added. After 1 h at 0 °C, H_2O was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et_2O (10 mL) and water (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O . The combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane: EtOAc (95:5) to give (S)-**16b**-[OH] (22 mg, 30%) as a solid; er (*S*:*R*) 96:4; R_f 0.29 (petrol:EtOAc 9:1); $[\alpha]_D^{24}$ 18 (*c* 0.6, CHCl_3); mp. 111–114 °C; IR (film): ν (cm^{-1}) 3490, 2920, 2857, 1509, 1227, 816, 718; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.85–7.79 (m, 3H), 7.63 (s, 1H), 7.50–7.41 (m, 2H), 7.38 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.07–7.01 (m, 2H), 6.78–6.72 (m, 2H), 4.55 (s, 1H), 2.90 (app. sx, $J = 6.9$ Hz, 1H), 2.56–2.42 (m, 2H), 2.07–1.90 (m, 2H), 1.37 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 153.4, 144.7, 134.7, 133.6, 132.2, 129.4, 128.0, 127.6, 127.5, 125.8, 125.7, 125.3, 125.1, 115.1, 40.0, 39.5, 33.0, 22.4; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{20}\text{O}$ [M] $^+$ 276.1514, found 276.1526.

Resolution of the enantiomers of **16b**-[OH] was achieved using a chiral SFC system fitted with a Chiracel IA column as the stationary phase with CO_2 : [*n*-hexane:*i*-PrOH (1:1 v:v)] as the mobile phase at a flow rate of 4.0 mL min^{-1} ($P = 125$ bar). Injection volume: 20 μL of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running

¹⁹ McOmie, J. F. W.; Watts, M. L.; West, D. E.; *Tetrahedron*, **1968**, *24*, 2289.

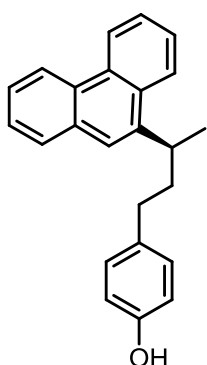
component (*S*) and the slower running component (*R*) were eluted at 26.1 and 29.3 min., respectively, with an analysis time of 40 min.

(*S*)-9-(4-(4-methoxyphenyl)butan-2-yl)phenanthrene [(*S*)-17b]



A solution of 9-bromoanthracene (53 mg, 0.21 mmol, 1.2 eq.) in THF (1.0 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated with *t*-BuLi (0.26 mL, 0.41 mmol, 2.4 eq., 1.7 M in hexanes). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h and then a solution of (*S*)-1b (50 mg, 0.17 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of NBS (74 mg, 0.41 mmol, 2.4 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography (*n*-hexane:Et₂O 98:2) gave (*S*)-17b (27 mg, 47%) as an oil; er (*S*:*R*) 96:4; R_{f} 0.55 (pentane:Et₂O 95:5); $[\alpha]_{\text{D}}^{20} -12.1$ (*c* 0.4, CHCl_3); IR (film): ν (cm^{-1}) 2958, 2930, 1610, 1510, 1450, 1243, 1035, 745, 724; ^1H NMR (400 MHz, CDCl_3) δ ppm 8.78 (d, $J = 8.2$ Hz, 1H), 8.68 (d, $J = 7.2$ Hz, 1H), 8.06 (d, $J = 8.2$ Hz, 1H), 7.87 (d, $J = 6.8$ Hz, 1H), 7.70–7.56 (m, 5H), 7.12–7.07 (m, 2H), 6.86–6.81 (m, 2H), 3.80 (s, 3H), 3.63 (app. sx, $J = 6.8$ Hz, 1H), 2.76–2.63 (m, 2H), 2.26 (m, 1H), 2.04 (m, 1H), 1.53 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 157.7, 141.4, 134.5, 131.9, 131.1, 130.8, 129.4, 129.4, 128.3, 126.6, 126.4, 126.0, 125.9, 123.8, 123.3, 122.4, 113.7, 55.3, 39.4, 33.0, 29.7, 21.4; HRMS (EI) calcd. for $\text{C}_{25}\text{H}_{24}\text{O}$ [M]⁺ 340.1827, found 340.1823.

(*S*)-4-(3-(phenanthren-9-yl)butyl)phenol {(*S*)-17b[OH]}

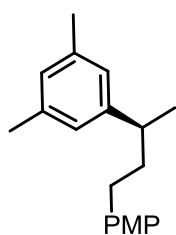


The enantioenriched material (*S*)-17b could not be purified on several attempts. The impure product was therefore derivatised by subjecting it to demethylation conditions.¹⁹ A round bottom flask was charged with (*S*)-17b (31 mg, 0.09 mmol). Anhydrous CH_2Cl_2 [0.025] was added and the solution cooled to $0\text{ }^{\circ}\text{C}$. BBr_3 (1M in CH_2Cl_2 , 0.2 mL, 0.2 mmol, 2.0 eq)

was added. After 1 h at 0 °C, water (1 mL) was added and the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with Et₂O (10 mL) and water (10 mL). The layers were separated and the aqueous layer was extracted with Et₂O (3 x 10 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane: EtOAc (95:5) to give (*S*)-**17b**-[OH] (19 mg, 66%) as an oil; er (*S*:*R*) 96:4; *R*_f 0.30 (petrol:EtOAc 90:10); [α]_D²⁴ 13 (*c* 0.63, CHCl₃) IR (film): ν (cm⁻¹) 3330, 3021, 2960, 2925, 2856, 1512, 1449, 1224, 746, 725; ¹H NMR (400 MHz, CDCl₃) δ ppm 8.78 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.1 Hz, 1H), 7.71–7.58 (m, 5H), 7.07–7.01 (m, 2H), 6.79–6.72 (m, 2H), 4.74 (s, 1H), 3.63 (app. sx, *J* = 6.8 Hz, 1H), 2.68 (m, 2H), 2.25 (m, 1H), 2.05 (m, 1H), 1.51 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 153.5, 141.4, 134.6, 131.9, 131.0, 130.7, 129.5, 129.3, 128.2, 126.5, 126.4, 126.0, 125.9, 123.7, 123.3, 123.0, 122.4, 115.1, 39.4, 33.0, 21.4; HRMS (EI) calcd. for C₂₄H₂₂O [*M*]⁺ 326.1671, found 326.1674.

Resolution of the enantiomers of **17b**-[OH] was achieved using a chiral HPLC system fitted with a Chiralpak IB column with guard as the stationary phase with *n*-hexane:*i*-PrOH (97:3) as the mobile phase at a flow rate of 0.3 mL min⁻¹. Injection volume: 5 μ L of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 94.0 and 104.5 min., respectively, with a total analysis time of 130 min.

(*S*)-1-(4-(4-methoxyphenyl)butan-2-yl)-3,5-dimethylbenzene [(*S*)-**18b**]

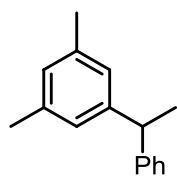


A solution of 3,5-dimethylbromobenzene (70 μ L, 0.52 mmol, 1.5 eq.) in THF (3.0 mL) was cooled to -78 °C and treated with *t*-BuLi (0.5 mL, 1.03 mmol, 3.0 eq., 1.9 M in pentane). The mixture was stirred at -78 °C for 1 h and then a solution of (*S*)-**1b** (100 mg, 0.34 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [¹¹B NMR, 96 MHz, THF) δ_B ~ 8 ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to -78 °C. A solution of NBS (122 mg, 0.69 mmol, 2.0 eq.) in MeOH (5.0 mL) was added dropwise. After 1 h the reaction mixture was diluted with pentane (15 mL) and washed with water (15 mL). The aqueous layer was extracted with pentane (2 x 15 mL) and the combined organic layers

were dried over MgSO₄, filtered and concentrated under vacuum. The residue was dissolved in 2,2,2-trifluoroethanol (5.0 mL) and *p*-toluenesulfonic acid (327 mg, 1.72 mmol, 5.0 eq.) was added. The reaction mixture was heated under reflux for 3 h. The reaction was cooled to r.t. and saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. The reaction mixture was diluted with EtOAc (15 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography on silica gel eluting with pentane:Et₂O (95:5), gave (*S*)-**18b** (78 mg, 83%) as an oil; er (*S*:*R*) 96:4; *R*_f 0.70 (pentane:Et₂O 95:5); [α]_D²¹ 23 (*c* 2.6, CHCl₃); IR (film): ν (cm⁻¹) 2954, 2920, 2855, 1607, 1511, 1242, 1176, 1037, 826, 705; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.10–7.05 (m, 2H), 6.88–6.81 (m, 5H), 3.80 (s, 3H), 2.65 (app. sx, *J* = 7.0 Hz, 1H), 2.52–2.45 (m, 2H), 2.32 (s, 6H), 1.96–1.79 (m, 2H), 1.75 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 157.7, 147.5, 137.8, 134.8, 129.3, 127.7, 124.9, 113.7, 55.3, 40.2, 39.4, 33.2, 22.6, 21.5.; HRMS (EI) calcd. for C₁₉H₂₄O [*M*]⁺ 268.1827, found 268.1827.

Resolution of the enantiomers of **18b** was achieved using a chiral SFC system fitted with a Chiracel IA column as the stationary phase with CO₂:*n*-hexane as the mobile phase at a flow rate of 2.0 mL min⁻¹ (*P* = 125 bar). Injection volume: 20 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 14.3 and 15.3 min., respectively, with a total analysis time of 20 min.

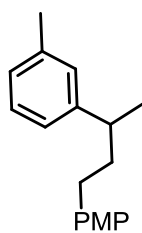
1,3-dimethyl-5-(1-phenylethyl)benzene (**18l**)



A solution of 3,5-dimethylbromobenzene (64 μL, 0.47 mmol, 1.1 eq.) in THF (3.0 mL) was cooled to -78 °C and treated with *t*-BuLi (0.61 mL, 1.04 mmol, 2.2 eq., 1.7 M in pentane). The mixture was stirred at -78 °C for 1 h and then a solution of **11** (100 mg, 0.43 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the 'ate' complex [(¹¹B NMR, 96 MHz, THF) δ_B ~ 8 ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to -78 °C. A solution of NBS (153 mg, 0.86 mmol, 2.0 eq.) in MeOH (5.0 mL) was added dropwise. After 1 h the reaction mixture was diluted with pentane (15 mL) and washed with water (15 mL). The aqueous layer was extracted with pentane (2 x 15 mL) and the combined organic layers were

dried over MgSO₄, filtered and concentrated under vacuum. The residue was dissolved in 2,2,2-trifluoroethanol (5.0 mL) and *p*-toluenesulfonic acid (327 mg, 1.72 mmol, 5.0 eq.) was added. The reaction mixture was heated under reflux for 3 h. The reaction was cooled to r.t. and saturated aqueous solution of NaHCO₃ (2 mL) was added. The reaction mixture was diluted with EtOAc (15 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography on silica gel eluting with pentane:Et₂O (95:5), gave **18l** (19 mg, 21%) as an oil; *R*_f 0.47 (pentane:Et₂O 97.5:2.5); ¹H NMR (300 MHz, CDCl₃) δ ppm 7.09–6.89 (m, 5H), 6.62–6.57 (m, 3H), 3.83 (q, *J* = 7.2 Hz, 1H), 2.03 (s, 6H), 1.38 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (76 MHz, CDCl₃) δ ppm 146.6, 146.3, 137.7, 128.3, 127.7, 127.6, 125.9, 125.4, 44.7, 21.9, 21.4. Data in accordance with literature precedent.²⁰

1-(4-(4-methoxyphenyl)butan-2-yl)-3-methylbenzene (**19b**)

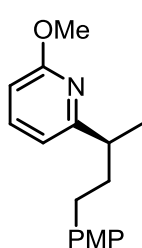


A solution of 3-bromotoluene (40 μL, 0.33 mmol, 1.2 eq.) in THF (1.0 mL) was cooled to –78 °C and treated with *t*-BuLi (0.42 mL, 0.66 mmol, 2.4 eq., 1.6 M in pentane). The mixture was stirred at –78 °C for 1 h and then a solution of **1b** (80 mg, 0.28 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at –78 °C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [(¹¹B NMR, 96 MHz, THF) δ_B ~ 8 ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to –78 °C. A solution of NBS (118 mg, 0.66 mmol, 2.4 eq.) in MeOH (4.0 mL) was added dropwise. After 1 h the reaction mixture was diluted with pentane (15 mL) and washed with water (15 mL). The aqueous layer was extracted with pentane (2 x 15 mL) and the combined organic layers were dried (MgSO₄), filtered and concentrated under vacuum. The residue was dissolved in 2,2,2-trifluoroethanol (4.0 mL) and *p*-toluenesulfonic acid (238 mg, 0.69 mmol, 5.0 eq.) was added. The reaction mixture was heated under reflux for 3 h. The reaction was cooled to r.t. and NaHCO₃ (2 mL) was added. The reaction mixture was diluted with EtOAc (15 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum.

²⁰ Imao, D.; Glasspoole, B. W.; Laberge, V. S; Crudden, C. M.; *J. Am. Chem. Soc.*, **2009**, *131*, 5024.

Purification by flash column chromatography on silica gel eluting with pentane:Et₂O (95:5), gave a mixture of **19b** and 1-(3-bromobutyl)-4-methoxybenzene in a ¹H NMR ratio of 28:72 in favour of 1-(3-bromobutyl)-4-methoxybenzene. Compound **19b** was isolated in 17 % yield (12 mg). **19b**: *R*_f 0.77 (pentane:Et₂O 95:5); diagnostic peaks from ¹H NMR analysis (400 MHz, CDCl₃) δ ppm 3.79 (s, 3H), 2.36 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 3H); GC-MS: *R*_t 7.37 min., *m/z*: 254, 161, 147, 135, 121, 105, 91, 77. 1-(3-bromobutyl)-4-methoxybenzene: *R*_f 0.80 (pentane:Et₂O 95:5); diagnostic peaks from ¹H NMR analysis (400 MHz, CDCl₃) δ ppm 4.08 (m, 1H), 3.80 (s, 3H), 1.72 (d, *J* = 6.7 Hz, 3H); GC-MS: *R*_t 5.39 min., *m/z*: 242/244, 162, 147, 121, 105, 121, 105, 91, 77.

(*S*)-2-methoxy-6-(4-(4-methoxyphenyl)butan-2-yl)pyridine [(*S*)-20b**]**

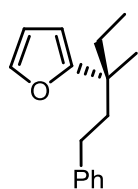


A solution of 2-bromo-6-methoxypyridine (36 μL, 0.29 mmol, 1.7 eq.) in THF:Et₂O:pentane (4:1:1, 0.3 M) was cooled to -78 °C and treated with *n*-BuLi (0.2 mL, 0.29 mmol, 1.7 eq., 1.6 M in hexanes) and the mixture was stirred at this temperature for 30 min. (*S*)-**1b** (50 mg, 0.17 mmol, 1.0 eq.) was added dropwise as a solution in THF (0.5 mL). The mixture was stirred at -78 °C for 30 min. at which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [¹¹B NMR (96 MHz, THF) δ_B ~ 8 ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. A solution of DBDMH (1,3-dibromo-5,5-dimethylhydantoin) (197 mg, 0.69 mmol, 2.0 eq.) in MeOH (5.0 mL) was added dropwise. After 1 h at 0 °C saturated aqueous solution of Na₂S₂O₃ was added and the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (15 mL) and water (15 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 15mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane to give (*S*)-**20b** (27 mg, 58%) was obtained as an oil; er (*S*:*R*) 95:5; *R*_f 0.40 (petrol:Et₂O 95:5); [α]_D²³ 27 (*c* 0.15, CHCl₃); IR (film): ν (cm⁻¹) 2935, 2855, 1577, 1510, 1463, 1413, 1288, 1242, 1175, 1029, 801, 743; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.49 (t, *J* = 7.3 Hz, 1H), 7.10–7.02 (d, *J* = 8.5 Hz, 2H), 6.89–6.81 (m, 2H), 6.70 (d, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.3 Hz, 1H), 3.94 (s, 3H), 3.79 (s, 3H), 2.80 (app. sx, *J* = 6.8 Hz, 1H), 2.54–2.42 (m, 2H), 2.13 (m, 1H), 1.85 (m, 1H), 1.29 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 164.0, 163.6, 157.6, 138.6, 134.8, 129.2, 114.3, 113.6, 107.4, 55.2, 53.1, 40.9, 38.6, 32.9, 20.9; HRMS (EI) calcd. for C₁₇H₂₁NO₂ [*M*]⁺ 271.1572, found 271.1570.

Resolution of the enantiomers of **20b** was achieved using a chiral HPLC system fitted with a Chiralpak AD-H column with guard as the stationary phase with [*n*-hexane:(10 % *i*-PrOH in *n*-hexanes) (99:1, v:v)] as the mobile phase at a flow rate of 0.5 mL min⁻¹ (*T* = 0 °C). Injection volume: 5 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 24.6 and 26.6 min., respectively, with a total analysis time of 35 min.

7. Reaction Products – Coupling of tertiary boronic esters to 6-membered aromatics

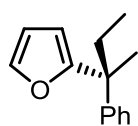
(*S*)-2-(3-Methyl-1-phenylpentan-3-yl)furan [(*S*)-**2g**]



Following **GP2** (0.25 mmol scale), (*S*)-**2g** (51 mg, 89%) was obtained as an oil; er (*S*:*R*) >99:1; *R*_f 0.30 (*n*-hexane); [*α*]_D²⁴ -22.0 (*c* 1, CHCl₃); IR (film): *ν* (cm⁻¹) 2966, 2929, 2877, 1506, 1497, 1455, 1156, 1011, 729, 680; ¹H NMR (400 MHz, CDCl₃) *δ* ppm 7.36 (m, 1H), 7.28–7.13 (m, 5H), 6.29 (m, 1H), 6.04 (m, 1H), 2.48 (td, *J* = 13.0, 5.1 Hz, 1H), 2.32 (td, *J* = 13.1, 4.6 Hz, 1H), 1.98 (td, *J* = 13.0, 4.5 Hz, 1H), 1.85–1.7 (m, 2H), 1.67–1.55 (m, 1H), 1.29 (s, 3H), 0.77 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) *δ* ppm 161.4, 143.1, 140.7, 128.3, 128.2, 109.6, 104.9, 42.3, 39.5, 32.9, 31.0, 22.3, 8.6; HRMS (EI) calcd. for C₁₆H₂₀O [*M*]⁺ 228.1514, found 228.1508.

Resolution of the enantiomers of **2g** was achieved using a chiral HPLC system fitted with a Chiralpak OD column with guard as the stationary phase with *n*-hexanes as the mobile phase at a flow rate of 0.5 mL min⁻¹ (*T* = 0 °C). Injection volume: 20 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 29.9 and 34.3 min., respectively, with a total analysis time of 60 min.

(*S*)-2-(2-Phenylbutan-2-yl)furan [(*S*)-**2h**]

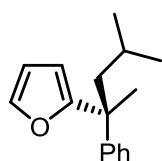


Following **GP2** (0.25 mmol scale), (*S*)-**2h** (82 mg, 83%) was obtained as an oil; er (*S*:*R*) >99:1; *R*_f 0.5 (*n*-hexane); [*α*]_D²³ -2.3 (*c* 0.5, CHCl₃); IR (film): *ν* (cm⁻¹) 2970, 2929, 2879, 1599, 1504, 1494, 1456, 1380, 1159, 1014, 923, 730, 699, 598; ¹H NMR (400 MHz, CDCl₃) *δ* ppm 7.32 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.30–7.26 (m, 2H), 7.22–7.15 (m, 3H), 6.31 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.16–6.13 (m, 1H), 2.14 (dq, *J* = 13.3, 7.4 Hz, 1H), 2.09–1.98 (m, 1H), 1.6 (s, 3H), 0.78 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (MHz, CDCl₃) *δ*

ppm 161.4, 147.0, 141.1, 128.0, 126.4, 125.9, 109.6, 105.5, 44.0, 33.0, 24.5, 9.0; HRMS (EI) calcd. for C₁₄H₁₆O [M]⁺ 200.1201, found 200.1203

Resolution of the enantiomers of **2h** was achieved using a chiral HPLC system fitted with a Chiracel OJ-RH column with guard as the stationary phase with MeCN:water (4:1, v:v) as the mobile phase at a flow rate of 1.0 mL min⁻¹ (*T* = 20 °C). Injection volume: 20 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 21.0 and 27.3 min., respectively, with a total analysis time of 60 min.

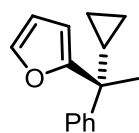
(*S*)-2-(4-Methyl-2-phenylpentan-2-yl)furan [(*S*)-**2i**]



Following **GP2** (0.5 mmol scale), (*S*)-**2i** (82 mg, 76%) was obtained as an oil; er (*S*:*R*) 99:1; *R*_f 0.29 (*n*-hexane); [α]_D²³ -15.4 (*c* 1.0, CHCl₃); IR (film): ν (cm⁻¹) 2954, 2927, 1495, 1445, 1158, 1011, 729, 697, 598; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.34–7.30 (m, 1H), 7.30–7.25 (m, 2H), 7.23–7.15 (m, 3H), 6.32 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.16–6.12 (m, 1H), 2.08 (dd, *J* = 13.8, 5.8 Hz, 1H), 1.94 (dd, *J* = 13.8, 5.1 Hz, 1H), 1.66 (s, 3H), 1.65–1.60 (m, 1H), 0.79 (br d, *J* = 6.7 Hz, 3H), 0.72 (br d, *J* = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 161.5, 147.7, 140.8, 128.0, 126.3, 125.9, 109.8, 105.4, 49.0, 43.8, 25.6, 25.0, 24.7, 24.0; HRMS (EI) calcd. for C₁₆H₂₀O [M]⁺ 228.1514, found 228.1522.

Resolution of the enantiomers of **2i** was achieved using a chiral GC system fitted with a Supelco β -DM column. Injector *T* = 250 °C, detector *T* = 300 °C. Oven conditions: *T* = 70 °C for 3 min., then ramp (0.5 °C min⁻¹) until 180 °C, H₂ carrier gas at 14 psi. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 64.6 and 64.7 min., respectively, with a total analysis time of 75 min.

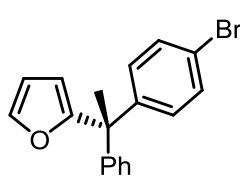
(*R*)-2-(1-cyclopropyl-1-phenylethyl)furan [(*R*)-**2j**]



Following **GP2** (0.29 mmol scale), (*R*)-**2j** (58 mg, 94%) was obtained as an oil; er (*R*:*S*) 98:2; *R*_f 0.83 (pentane:Et₂O 95:5); [α]_D²² 22.7 (*c* 1.5, CHCl₃); IR (film): ν (cm⁻¹) 3059, 2981, 1502, 1494, 1010, 730, 698; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.30 (br s, 1H), 7.29–7.24 (m, 4H), 7.20 (m, 1H), 6.31 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.20 (d, *J* = 3.1 Hz, 1H), 1.53 (s, 3H), 1.43 (m, 1H), 0.58–0.44 (m, 2H), 0.30–0.18 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 161.0, 146.4, 141.3, 127.9, 127.1, 126.2, 109.5, 106.0, 43.8, 24.4, 20.5, 1.8, 1.5; HRMS (EI) calcd. for C₁₅H₁₆O [M]⁺ 212.1201, found 212.1200.

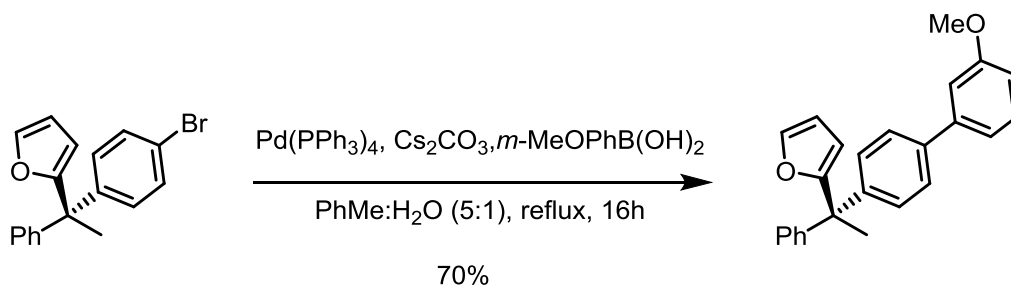
Resolution of the enantiomers of **2j** was achieved using a chiral HPLC system fitted with a Chiralpak OJ-RH column with guard as the stationary phase with MeCN:water (85:15, v:v) as the mobile phase at a flow rate of 1.0 mL min⁻¹. Injection volume: 2 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 3.3 and 3.9 min., respectively, with a total analysis time of 15 min.

(*S*)-2-(1-(4-Bromophenyl)-1-phenylethyl)furan [(*S*)-2k]



Following **GP2** (0.25 mmol scale), (*S*)-**2k** (43 mg, 53%) was obtained as an amorphous solid; er (*S*:*R*) 98:2; *R*_f 0.37 (*n*-hexane); [α]_D²¹ -7.6 (*c* 0.5, CHCl₃); IR (film): ν (cm⁻¹) 3058, 2980, 1589, 1489, 1395, 1373, 1359, 1260, 1209, 1148, 1075, 1026, 1008, 923, 884, 829, 803, 789, 750, 734; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.42–7.36 (m, 3H), 7.31–7.19 (m, 3H), 7.08 (dt, *J* = 6.4, 1.9 Hz, 2H), 6.99 (dt, *J* = 9.0, 2.1 Hz, 2H), 6.30 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.93 (d, *J* = 3.3 Hz, 1H), 2.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 159.7, 146.6, 146.3, 141.9, 131.0, 129.8, 128.0, 127.8, 126.5, 120.4, 109.9, 107.8, 49.2, 27.7; HRMS (EI) calcd. for C₁₈H₁₅BrO [*M*]⁺ 326.0306, found 326.0304.

The enantiomers of **2k** could not be separated by chiral GC, HPLC or SFC. In order to evaluate the enantiomeric ratio of the reaction product it was further functionalized using Suzuki cross-coupling.

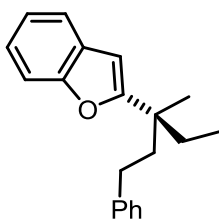


A flask was charged with Pd(PPh₃)₄ (12 mg, 0.01 mmol, 10 mol%), Cs₂CO₃ (4 mg, 0.01 mmol, 10 mol%) and *m*-methoxyphenyl boronic acid (31 mg, 0.20 mmol, 2.0 eq.). The flask was evacuated and refilled with nitrogen (x 3). Degassed toluene (1.0 mL) and water (0.2 mL) were added. A solution of (*S*)-**2s** (33 mg, 0.10 mmol, 1.0 eq.) in degassed toluene (1.0 mL) was added and the mixture was heated under refluxing conditions for 16 h. The reaction was cooled to room temperature and water (5 mL) was added. The layers were separated and the aqueous layer was extracted with Et₂O (3 x 5 mL). The combined organic layers were

dried over MgSO₄, filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting *n*-hexane:Et₂O (99:1→99:5) to give the desired product (24 mg, 70%) as an oil; er (*S*:*R*) 98:2; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.65–6.80 (m, 13H), 6.33 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.98 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.80 (s, 3H), 2.11 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 160.3, 159.9, 147.1, 146.4, 142.3, 141.8, 139.0, 129.7, 128.7, 128.4, 128.0, 126.7, 126.4, 119.6, 112.7, 112.6, 109.9, 107.7, 55.3, 49.3, 27.8; HRMS (EI) calcd. for C₂₅H₂₂O₂ [*M*]⁺ 354.1620, found 354.1627.

Resolution of the enantiomers of the cross-coupling product was achieved using a chiral HPLC system fitted with a Chiracel OD + OD-H column as the stationary phase with *n*-hexane:*i*-Pr (99.8:0.2, v:v) as the mobile phase at a flow rate of 0.7 mL min⁻¹ (*T* = 0 °C). Injection volume: 20 μL of 2 g L⁻¹ solution of compound in the eluent. Under these conditions the faster running component (*R*) and the slower running component (*S*) were eluted at 96.0 and 102.3 min., respectively, with a total analysis time of 120 min.

(*S*)-2-(3-methyl-1-phenylpentan-3-yl)benzofuran [(*S*)-**4g**]

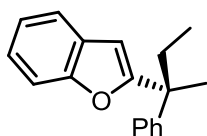


A solution of benzofuran (14 μL, 0.12 mmol, 1.2 eq.) in THF (2.5 mL) was cooled to 0 °C and treated with *n*-BuLi (0.1 mL, 0.12 mmol, 1.2 eq., 1.6 M in hexane). The mixture was stirred at 0 °C for 1 h and then a solution of (*R*)-**1g** (30 mg, 0.10 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at 0 °C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [(¹¹B NMR, 96 MHz, THF) δ_B ~ 8 ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to 0 °C. A solution of NBS (22 mg, 0.12 mmol, 1.2 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (98:2) gave (*S*)-**4g** (20 mg, 69%) was obtained as an oil; er (*S*:*R*) 99:1; *R*_f 0.75 (pentane:Et₂O 95:5); [α]_D²³ -25 (*c* 0.6, CHCl₃); R (film): ν (cm⁻¹) 2966, 2933, 1453, 1252, 1167, 884, 750, 738; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.53(m, 1H), 7.47 (m, 1H), 7.30–7.25 (m, 3H), 7.22 (m, 1H), 7.20–7.14

(m, 3H), 6.47 (d, $J = 1$ Hz, 1H), 2.56 (dt, $J = 13.1, 4.8$ Hz, 1H), 2.41 (dt, $J = 13.1, 4.8$ Hz, 1H), 2.14 (dt, $J = 13.1, 4.8$ Hz, 1H), 1.98–1.87 (m, 2H), 1.72 (dq, $J = 13.1, 7.5$, 1H), 1.41 (s, 3H), 0.84 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 164.6, 154.7, 142.8, 128.7, 128.3, 125.6, 123.1, 122.3, 120.3, 110.8, 102.2, 42.0, 40.0, 32.7, 30.9, 22.2, 8.6; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{22}\text{O}$ $[M]^+$ 278.1671 found 278.1675.

Resolution of the enantiomers of **4g** was achieved using a chiral HPLC system fitted with a Chiralpak OJ-RH column as the stationary phase with MeCN:water (7:3, v:v) as the mobile phase at a flow rate of 0.5 mL min^{-1} ($T = 20 \text{ }^\circ\text{C}$). Injection volume: $5 \text{ } \mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 23.3 and 30.2 min., respectively, with a total analysis time of 35 min.

(*R*)-2-(2-phenylbutan-2-yl)benzofuran [(*R*)-**4h**]

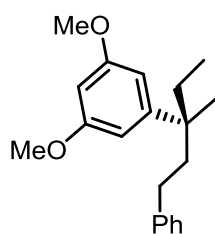


A solution of benzofuran ($14 \text{ } \mu\text{L}$, 0.12 mmol , 1.2 eq.) in THF (1.0 mL) was cooled to $0 \text{ }^\circ\text{C}$ and treated with *n*-BuLi (0.1 mL , 0.12 mmol , 1.2 eq. , 1.6 M in hexane). The mixture was stirred at $0 \text{ }^\circ\text{C}$ for 1 h and then a solution of (*R*)-**1h** (26 mg , 0.10 mmol , 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at $0 \text{ }^\circ\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz , THF) $\delta_{\text{B}} \sim 8 \text{ ppm}$]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2 mL) and the mixture was cooled to $0 \text{ }^\circ\text{C}$. A solution of NBS (22 mg , 0.12 mmol , 1.2 eq.) in MeOH (2.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc ($2 \times 15 \text{ mL}$), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (98:2) gave (*R*)-**4h** (16 mg , 64%) as an oil; er (*R*:*S*) 99:1; R_{f} 0.27 (pentane); $[\alpha]_{\text{D}}^{23} 12$ ($c 0.5$, CHCl_3); IR (film): ν (cm^{-1}) 2970, 2950, 1578, 1498, 1453, 1301, 1250, 1168, 1028, 1006, 937, 798, 750, 738; ^1H NMR (400 MHz , CDCl_3) δ ppm 7.54 (m, 1H), 7.40 (m, 1H), 7.34–7.26 (m, 4H), 7.25–7.18 (m, 3H), 6.57 (d, $J = 0.9$ Hz, 1H), 2.29 (dq, $J = 13.7, 7.4$ Hz, 1H), 2.17 (dq, $J = 13.7, 7.4$ Hz, 1H), 1.72 (s, 3H), 0.85 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 164.6, 154.7, 146.2, 128.5, 128.2, 126.6, 126.2, 123.3,

122.4, 120.4, 111.1, 102.7, 44.6, 32.8, 24.4, 9.0; HRMS (CI) calcd. for C₁₈H₁₉O [M+H]⁺ 251.1436, found 251.1437.

Resolution of the enantiomers of **4h** was achieved using a chiral HPLC system fitted with a Chiracel OD-H column as the stationary phase with heptane:MTBE (95:5, v:v) as the mobile phase at a flow rate of 0.5 mL min⁻¹. Injection volume: 2 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 16.7 and 20.8 min., respectively, with a total analysis time of 30 min.

(*S*)-1,3-dimethoxy-5-(3-methyl-1-phenylpentan-3-yl)benzene [(*S*)-**9g**]

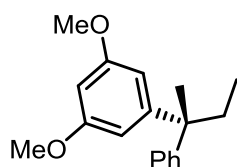


A solution of 3,5-(dimethoxy)bromobenzene (35 mg, 0.16 mmol, 1.3 eq.) in THF (2.5 mL) was cooled to -78 °C and treated with *t*-BuLi (0.17 mL, 0.32 mmol, 2.6 eq., 1.4 M in pentane). The mixture was stirred at -78 °C for 30 min. and then a solution of (*R*)-**1g** (36 mg, 0.125 mmol, 1.0 eq.) in THF (0.5 mL) was added. The mixture was stirred at -78 °C for 1 h and then warm to r.t. at which point ¹¹B NMR spectroscopy showed complete formation of the 'ate' complex [(¹¹B NMR, 96 MHz, THF) δ_B ~ 8 ppm]. The reaction mixture was stirred at -78 °C and a solution of NBS (27 mg, 0.15 mmol, 1.2 eq.) in MeOH (3.0 mL) was added dropwise and the mixture was warmed to r.t. After 1 h saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-pentane:Et₂O (98:2) gave (*S*)-**9g** (28 mg, 78%) as an oil, er (*S*:*R*) 99:1; *R*_f 0.38 (*n*-pentane:Et₂O 95:5); [α]_D²⁰ -14 (*c* 0.5, CHCl₃); IR (film): ν (cm⁻¹) 2962, 2933, 1593, 1454, 1421, 1298, 1260, 1203, 1153, 1124, 1060, 925, 801, 746, 699; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.28–7.21 (m, 2H), 7.15 (tt, *J* = 7.4, 2.3 Hz, 1H), 7.12–7.08 (m, 2H), 6.51 (d, *J* = 2.2 Hz, 2H), 6.33 (t, *J* = 2.2 Hz, 1H), 3.81 (s, 6H), 2.46 (td, *J* = 13.1, 5.1 Hz, 1H), 2.27 (td, *J* = 13.0, 4.4 Hz, 1H), 1.97 (td, *J* = 13.1, 4.4 Hz, 1H), 1.87–1.68 (m, 2H), 1.67–1.55 (m, 1H), 1.33 (s, 3H), 0.72 (t, *J* = 7.4 Hz, 3H), ¹³C NMR (100 MHz, CDCl₃) δ ppm 160.5, 150.1, 143.2, 128.2, 125.5, 105.3, 96.7, 55.2, 45.2, 41.6, 35.7, 30.8, 23.2, 8.65.

Resolution of the enantiomers of **9g** was achieved using a chiral HPLC system fitted with a Chiracel IB column with guard as the stationary phase, *n*-hexane:*i*-PrOH (99.9:0.1 v:v) as the

mobile phase at a flow rate of 0.6 mL min⁻¹. Injection volume: 2 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 22.3 and 25.0 min., respectively, with a total analysis time of 30 min.

(*R*)-1,3-dimethoxy-5-(2-phenylbutan-2-yl)benzene [(*R*)-9h**]**

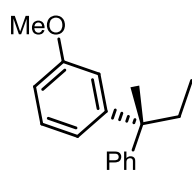


A solution of 3,5-(dimethoxy)bromobenzene (117 mg, 0.54 mmol, 1.3 eq.) in THF (5.0 mL) was cooled to -78 °C and treated with *t*-BuLi (0.5 mL, 1.08 mmol, 2.6 eq., 1.9 M in pentane). The mixture was stirred at -78 °C for 30 min. and then a solution of (*S*)-**1h** (70 mg, 0.27 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [(¹¹B NMR, 96 MHz, THF) δ_B ~ 8 ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to -78 °C. A solution of DBDMH (1,3-dibromo-5,5-dimethylhydantoin) (176 mg, 0.61 mmol, 2.0 eq.) in MeOH (5.0 mL) was added dropwise. After 1 h reaction mixture was warmed to 70 °C and heated at this temperature for 3 h. The reaction mixture was cooled to r.t. and saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (98:2) gave (*R*)-**9h** (73 mg, 63%) as an oil, er (*R*:*S*) >99:1; *R*_f 0.51 (*n*-hexane:Et₂O 95:5); [α]_D²⁰ -22.0 (*c* 1.0, CHCl₃); IR (film): ν (cm⁻¹) 2959, 2933, 2836, 1592, 1454, 1203, 1057, 831; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.27–7.13 (m, 5H), 6.35 (d, *J* = 2.2 Hz, 2H), 6.28 (t, *J* = 2.2 Hz, 1H), 3.72 (s, 6H), 2.10 (q, *J* = 7.4 Hz, 1H), 1.56 (s, 3H) 0.72 (t, *J* = 7.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 160.2, 152.2, 149.3, 127.8, 127.2, 125.5, 106.3, 96.8, 55.1, 46.7, 33.9, 26.8, 9.1; HRMS (ESI) calcd. for C₁₈H₂₃O₂ [*M*+H]⁺ 271.1694, found 271.1693.

Resolution of the enantiomers of **9h** was achieved using a chiral HPLC system fitted with a Chiracel OD-H column as the stationary phase with *n*-hexane:*i*-Pr (99.5:0.5 v:v) as the mobile phase at a flow rate of 0.5 mL min⁻¹. Injection volume: 20 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the

slower running component (*S*) were eluted at 9.4 and 10.9 min., respectively, with a total analysis time of 30 min.

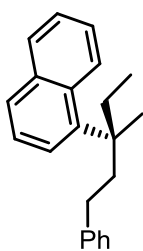
(*R*)-1-methoxy-3-(2-phenylbutan-2-yl)benzene [(*R*)-11h**]**



A solution of 3-methoxybromobenzene (43 μ L, 0.34 mmol, 1.1 eq.) in THF (2.0 mL) was cooled to -78 $^{\circ}$ C and treated with *t*-BuLi (0.42 mL, 0.68 mmol, 2.2 eq., 1.7 M in hexanes). The mixture was stirred at -78 $^{\circ}$ C for 1 h and then a solution of (*S*)-**1h** (80 mg, 0.31 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 $^{\circ}$ C for 1 h at which point 11 B NMR spectroscopy showed complete formation of the ‘ate’ complex [11 B NMR, 96 MHz, THF) $\delta_B \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to -78 $^{\circ}$ C. A solution of DBDMH (176 mg, 0.61 mmol, 2.0 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography (*n*-hexane:Et₂O 98:2) gave (*R*)-**11h** (34 mg, 47%) as an oil; er (*R*:*S*) 99:1; R_f 0.50 (pentane:Et₂O 95:5); $[\alpha]_D^{21}$ 43 (*c* 0.1, CHCl_3); IR (film): ν (cm^{-1}) 2968, 2936, 1598, 1580, 1253, 774, 762, 698; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.30-7.24 (m, 2H), 7.22-7.14 (m, 4H), 6.80-6.76 (m, 2H), 6.73 (ddd, $J = 8.1, 2.4, 0.9$ Hz, 1H), 3.77 (s, 3H), 2.13 (q, $J = 7.4$ Hz, 2H), 1.61 (s, 3H), 0.75 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 159.2, 151.4, 149.5, 128.7, 127.8, 127.3, 125.5, 120.2, 114.1, 110.0, 55.1, 46.5, 34.0, 26.8, 9.2; HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{20}\text{O}$ [M]⁺ 240.1514, found 240.1516.

Resolution of the enantiomers of **11h** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO_2 :*n*-hexane as the mobile phase at a flow rate of 4.0 mL min⁻¹ ($P = 125$ bar). Injection volume: 10 μ L of a 2 g L⁻¹ solution of the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 3.7 and 4.3 min., respectively, with a total analysis time of 10 min.

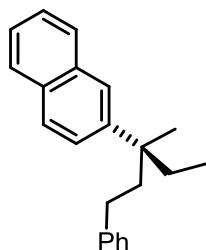
(S)-1-(3-Methyl-1-phenylpentan-3-yl)naphthalene [(S)-**15g**]



A solution of 1-bromonaphthalene (28 μL , 0.16 mmol, 1.2 eq.) in Et_2O (1.0 mL) was cooled to 0 $^\circ\text{C}$ and *n*-BuLi (0.1 mL, 0.16 mmol, 1.2 eq., 1.6 M in hexanes) was added dropwise. The mixture was stirred at 0 $^\circ\text{C}$ for 1 h. (*R*)-**1g** (36 mg, 0.125 mmol, 1.0 eq.) was added as a solution in Et_2O (0.5 mL) and the reaction was stirred at the same temperature for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the boron-ate complex [^{11}B NMR, 96 MHz) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2 mL) and the mixture was cooled to -78 $^\circ\text{C}$. A solution of NBS (53 mg, 0.32 mmol, 2.4 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h the reaction mixture was diluted with pentane (15 mL) and washed with water (15 mL). The aqueous layer was extracted with pentane (2 x 15 mL) and the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. The residue was dissolved in 2,2,2-trifluoroethanol (3.0 mL) and *p*-toluenesulfonic acid (49 mg, 0.26 mmol, 2.5 eq.) was added. The reaction mixture was heated under reflux for 3 h. The reaction was cooled to r.t. and saturated aqueous solution of NaHCO_3 (2 mL) was added. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography eluting with pentane gave (*S*)-**15g** (27 mg, 75%) as an oil; er (*S*:*R*) 99:1; R_f 0.17 (pentane); $[\alpha]_{\text{D}}^{21} +1$ (*c* 0.5, CHCl_3); IR (film): ν (cm^{-1}); 3048, 3025, 2966, 2932, 2876, 1601, 1510, 1496, 1454, 1397, 1380, 1279, 1030, 800, 777, 748, 698, 573, 497; ^1H NMR (400 MHz, CDCl_3) δ ppm 8.50 (m, 1H), 7.89 (m, 1H), 7.75 (d, $J = 7.7$ Hz, 1H), 7.54–7.34 (m, 4H), 7.19 (tt, $J = 7.5$, 1.5 Hz, 2H), 7.11 (tt, $J = 7.3$, 2.1, 1H), 7.02–6.92 (m, 2H), 2.75–2.62 (m, 1H), 2.49–2.34 (m, 2H), 2.10–1.96 (m, 2H), 1.88 (dq, $J = 13.8$, 7.4 Hz, 1H), 1.63 (s, 3H), 0.65 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 143.2, 142.0, 134.9, 132.2, 129.7, 128.2, 128.1, 127.6, 126.5, 125.8, 125.5, 125.0, 124.9, 44.4, 43.7, 34.5, 31.4, 27.1, 9.0.

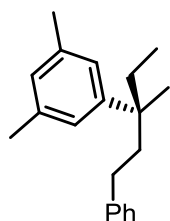
Resolution of the enantiomers of **15g** was achieved using chiral HPLC system fitted with a Chiracel IB column with guard as the stationary phase with *n*-hexane:*i*-PrOH (99.9:0.1, v:v) as the mobile phase at a flow rate of 0.5 mL min^{-1} ($T = 0$ $^\circ\text{C}$). Injection volume: 2 μL of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) major were eluted at 16.1 min and 17.0 min., respectively, with a total analysis time of 30 min.

(S)-2-(3-methyl-1-phenylpentan-3-yl)naphthalene [(S)-16g]



A solution of 1-bromonaphthalene (32 mg, 0.16 mmol, 1.5 eq.) in Et₂O (1.0 mL) was cooled to -15 °C and *n*-BuLi (0.1 mL, 0.16 mmol, 1.5 eq., 1.6 M in hexanes) was added dropwise. The mixture was stirred at -15 °C for 30 min. (*R*)-**1g** (30 mg, 0.1 mmol, 1.0 eq.) was added as a solution in Et₂O (0.5 mL) and the reaction was stirred at the same temperature for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the boron-ate complex [¹¹B NMR, 96 MHz) δ_B ~ 8 ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2 mL) and the mixture was cooled to -15 °C. A solution of NBS (37 mg, 0.21 mmol, 2.0 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h the reaction mixture was diluted with pentane (15 mL) and washed with water (15 mL). The aqueous layer was extracted with pentane (2 x 15 mL) and the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. The residue was dissolved in 2,2,2-trifluoroethanol (3.0 mL) and *p*-toluenesulfonic acid (49 mg, 0.26 mmol, 2.5 eq.) was added. The reaction mixture was heated under reflux for 3 h. The reaction was cooled to r.t. and saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography eluting with pentane gave (*S*)-**16g** (14 mg, 49%) as an oil; er (*S*:*R*) 95:5; *R*_f 0.87 (petrol:Et₂O 95:5); [α]_D²³ - 2 (c 0.4, CHCl₃) IR (film): ν (cm⁻¹) 2963, 2925, 1454, 1380, 816, 744, 699; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.87–7.80 (m, 3H), 7.73 (br d, *J* = 2.0 Hz, 1H), 7.53 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.50–7.41 (m, 2H), 7.26–7.20 (m, 2H), 7.14 (m, 1H), 7.10–7.05 (m, 2H), 2.47 (dt, *J* = 13.0, 4.5 Hz, 1H), 2.22 (dt, *J* = 13.0, 4.5 Hz, 1H), 2.12 (dt, *J* = 13.0, 4.5 Hz, 1H), 1.98–1.84 (m, 2H), 1.71 (dq, *J* = 13.0, 7.4 Hz, 1H), 1.47 (s, 3H), 0.72 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 144.8, 143.2, 133.4, 131.7, 128.2, 128.2, 127.9, 127.7, 127.3, 125.7, 125.5, 125.3, 125.2, 125.0, 45.1, 41.5, 35.5, 31.0, 23.2, 8.7; HRMS (EI) calcd. for C₂₂H₂₄ [*M*] 288.1878, found 288.1883.

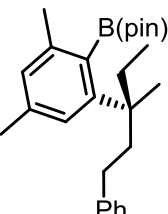
(S)-1,3-dimethyl-5-(3-methyl-1-phenylpentan-3-yl)benzene [(S)-18g]



A solution of 3,5-dimethylbromobenzene (22 μL, 0.16 mmol, 1.2 eq.) in THF (1.0 mL) was cooled to -78 °C and treated with *t*-BuLi (0.19 mL, 0.32 mmol, 2.4 eq., 1.6 M in hexanes). The mixture was stirred at -78 °C for 1 h and then

a solution of (*R*)-**1g** (36 mg, 0.125 mmol, 1.0 eq.) in THF (0.5 mL) was added. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [$(^{11}\text{B}$ NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was redissolved in MeOH (2.0 mL) and the mixture was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of NBS (53 mg, 0.32 mmol, 2.4 eq.) in MeOH (3.0 mL) was added dropwise and the reaction mixture was warmed to r.t. After 1 h $\text{Na}_2\text{S}_2\text{O}_3\text{sat}$ (2 mL) was added. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried (MgSO_4), filtered and concentrated under vacuum. Purification by flash column chromatography eluting with pentane gave (*S*)-**18g** (22 mg, 66%) as an oil; er (*S*:*R*) 99:1; R_{f} 0.32 (pentane); $[\alpha]_{\text{D}}^{21} -11$ (c 0.65, CHCl_3) IR (film): ν (cm^{-1}) 3026, 2965, 2920, 2877, 1603, 1496, 1454, 1377, 1031, 847, 707, 698, 502; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.30–7.22 (m, 2H), 7.21–7.08 (m, 3H), 6.97–6.92 (m, 2H), 6.84 (m, 1H), 2.52–2.22 (m, 2H), 2.32 (s, 6H), 1.99 (td, $J = 13.1, 4.4$ Hz, 1H), 1.88–1.70 (m, 2H), 1.61 (m, 1H), 1.33 (s, 3H), 0.72 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 147.4, 143.4, 137.2, 128.4, 128.2, 127.0, 125.5, 124.3, 44.9, 40.9, 35.5, 30.9, 23.5, 21.6; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{26}$ $[M]^+$ 266.2035, found 266.2027.

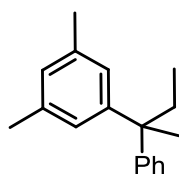
The enantiomers of **18g** could not be separated by either chiral GC, HPLC and SFC. In order to evaluate the enantiomeric ratio of the reaction product we separated the enantiomers of the B(pin)-incorporated reaction by-product **18ga** (< 10%). This compound is formed due to preferential B(pin) migration over elimination after the key 1,2-metalate rearrangement. Thus its enantioerichment reflects the one of **18g**.

 (*S*)-**18ga**: R_{f} 0.3 (pentane:Et₂O 95:5); IR (film): ν (cm^{-1}) 2975, 2927, 1607, 1453, 1372, 1324, 1295, 1141, 1059, 855, 699, 684, 745; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.24–7.14 (m, 4H), 7.11 (tt, $J = 7.1, 1.6$, 1H), 6.97–6.91 (m, 1H), 6.80 (dt, $J = 1.4, 0.7$ Hz, 1H), 2.45–2.08 (m, 3H), 2.39 (s, 3H), 2.28 (s, 3H), 1.91 (dq, $J = 14.6, 7.4$ Hz, 1H), 1.83–1.70 (m, 1H), 1.63 (dq, $J = 13.5, 7.3$ Hz, 1H), 1.41 (s, 3H), 1.38 (s, 6H), 1.36 (s, 6H), 0.70 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 147.4, 143.4, 137.2, 128.4, 128.2, 127.0, 125.5, 124.3, 44.9, 40.9, 35.5, 30.9, 23.5, 21.6; ^{11}B NMR (96 MHz, CDCl_3) δ 31.2 ppm; HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{37}\text{BO}_2$ $[M+\text{H}]^+$ 393.2964, found 393.2949, $[M+\text{Na}]^+$ 415.2783, found 415.2766.

Resolution of the enantiomers of **18ga** was achieved using a chiral SFC system fitted with a Chiralcel Whelk-01 column as the stationary phase with CO_2 :n-hexane as the mobile phase at

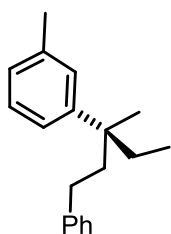
a flow rate of 2.0 mL min⁻¹ ($P = 125$ bar). Injection volume: 20 μ L of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 18.0 and 19.0 min., respectively, with an analysis time of 25 min.

1,3-dimethyl-5-(2-phenylbutan-2-yl)benzene (**18h**)



A solution of 3,5-dimethylbromobenzene (115 μ L, 0.85 mmol, 1.1 eq.) in THF (3.0 mL) was cooled to -78 °C and treated with *t*-BuLi (1.0 mL, 1.69 mmol, 2.2 eq., 1.7 M in hexanes). The mixture was stirred at -78 °C for 1 h and then a solution of **1h** (200 mg, 1.54 mmol, 1.0 eq.) in THF (2.0 mL) was added. The mixture was stirred at -78 °C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [(¹¹B NMR, 96 MHz, THF) $\delta_B \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (5.0 mL) and the mixture was cooled to -78 °C. A solution of NBS (274 mg, 1.92 mmol, 2.0 eq.) in MeOH (5.0 mL) was added dropwise and the reaction mixture was warmed to r.t. After 1 h the reaction mixture was diluted with pentane (15 mL) and washed with water (15 mL). The aqueous layer was extracted with pentane (2 x 15 mL) and the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. The residue was dissolved in 2,2,2-trifluoroethanol (5.0 mL) and *p*-toluenesulfonic acid (366 mg, 1.92 mmol, 2.5 eq.) was added. The reaction mixture was heated under reflux for 3 h. The reaction was cooled to r.t. and saturated aqueous solution of NaHCO₃ (2 mL) was added. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (5 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography eluting with pentane gave **18h** (43 mg, 24%) as an oil; R_f 0.17 (pentane); IR (film): ν (cm⁻¹) 2967, 2922, 2877, 1599, 1494, 1445, 765, 698; ¹H NMR (300 MHz, CDCl₃) δ ppm 7.34–7.13 (m, 5H), 6.83 (s, 3H), 2.28 (s, 6H), 2.14 (q, $J = 7.3$ Hz, 2H), 1.60 (s, 3H), 0.75 (d, $J = 7.3$ Hz, 3H); ¹³C NMR (76 MHz, CDCl₃) δ ppm 149.8, 149.6, 137.0, 127.8, 127.4, 127.2, 125.3, 125.3, 46.3, 34.0, 26.9, 21.5, 9.2; HRMS (EI) calcd. for C₁₈H₂₂ [M]⁺ 238.1722, found 238.1714.

(S)-1-methyl-3-(3-methyl-1-phenylpentan-3-yl)benzene [(S)-19g]

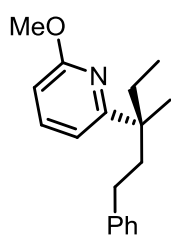


A solution of 3-bromotoluene (14 μL , 0.12 mmol, 1.1 eq.) in THF (0.5 mL) was cooled to $-78\text{ }^\circ\text{C}$ and treated with *t*-BuLi (0.13 mL, 0.23 mmol, 2.2 eq., 1.7 M in pentane). The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h and then a solution of (*R*)-**1g** (30 mg, 0.1 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the mixture was cooled to $-78\text{ }^\circ\text{C}$. A solution of NBS (44 mg, 0.25 mmol, 2.4 eq.) in MeOH (2.0 mL) was added dropwise. After 1 h the reaction mixture was diluted with pentane (15 mL) and washed with water (15 mL). The aqueous layer was extracted with pentane (2 x 15 mL) and the combined organic layers were dried (MgSO_4), filtered and concentrated under vacuum. The residue was dissolved in 2,2,2-trifluoroethanol (3.0 mL) and *p*-toluenesulfonic acid (49 mg, 0.26 mmol, 2.5 eq.) was added. The reaction mixture was heated under reflux for 3 h. The reaction was cooled to r.t. and saturated aqueous solution of NaHCO_3 (2 mL) was added. The reaction mixture was diluted with EtOAc (15 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography on silica gel eluting with pentane:Et₂O (95:5), gave (0.10 mmol scale), (*S*)-**19g** (12 mg, 46%) as an oil; er (*S*:*R*) 99:1; R_{f} 0.86 (petrol:Et₂O 97.5:2.5); $[\alpha]_{\text{D}}^{23} - 1$ (*c* 0.3, CHCl_3); IR (film): ν (cm^{-1}) 3026, 2964, 2926, 1604, 1496, 1454, 705, 699; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.27–7.19 (m, 3H), 7.18–7.07 (m, 5H), 7.01 (d, $J = 7.3$ Hz, 1H), 2.44 (dt, $J = 13.1$ Hz, 1H), 2.37 (s, 3H), 2.26 (dt, $J = 12.9, 4.3$ Hz, 1H), 2.01 (dt, $J = 13.1, 4.3$ Hz, 1H), 1.83 (dt, $J = 12.9, 5.0$ Hz, 1H), 1.77 (dq, $J = 14.7, 7.3$ Hz, 1H), 1.61 (dq, $J = 14.7, 7.3$ Hz, 1H), 1.35 (s, 3H), 0.71 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 147.3, 143.3, 137.4, 128.2, 127.9, 127.2, 126.1, 125.5, 123.5, 45.1, 41.1, 35.6, 30.9, 23.4, 21.8, 8.7; HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{24}$ [M]⁺ 252.1878, found 252.1876.

Resolution of the enantiomers of **19g** was achieved using a chiral HPLC system fitted with a Chirapak IB column as the stationary phase with *n*-heptane as the mobile phase at a flow rate of 0.5 mL min^{-1} . Injection volume: 2 μL of a 2 g L^{-1} solution of the eluent. Under these

conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 12.4 and 12.8 min., respectively, with a total analysis time of 20 min.

(*S*)-2-methoxy-6-(3-methyl-1-phenylpentan-3-yl)pyridine [(*S*)-20g**]**



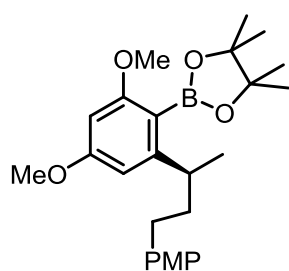
A solution of 2-bromo-6-methoxypyridine (0.17 μL , 0.14 mmol, 1.3 eq.) in THF:Et₂O:pentane (4:1:1, 0.3 M) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated with *n*-BuLi (0.2 mL, 0.14 mmol, 1.3 eq., 1.6 M in hexanes) and the mixture was stirred at this temperature for 30 min. (*R*)-**1g** (30 mg, 0.1 mmol, 1.0 eq.) was added dropwise as a solution in THF (0.5 mL). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min at which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [¹¹B NMR (96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeOH (2 mL) and the mixture was cooled to $0\text{ }^{\circ}\text{C}$. A solution of DBDMH (74 mg, 0.26 mmol, 2.0 eq.) in MeOH (3.0 mL) was added dropwise. After 1 h at $0\text{ }^{\circ}\text{C}$ saturated aqueous solution of Na₂S₂O₃ was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with EtOAc (15 mL) and water (15 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 15 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography on silica gel eluting with *n*-hexane to give (0.10 mmol scale), (*S*)-**20g** (17 mg, 60%) as an oil; er (*S*:*R*) 99:1; *R*_f 0.59 (pentane:Et₂O 97.5:2.5); [α]_D²³ -1 (*c* 1.5, CHCl₃); IR (film): ν (cm⁻¹) 2964, 2926, 1580, 1461, 1408, 1256, 1029, 801, 742, 698; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.52 (t, *J* = 7.7 Hz, 1H), 7.28–7.22 (m, 2H), 7.19–7.10 (m, 3H), 6.86 (d, *J* = 7.7 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 1H), 3.94 (s, 3H), 2.47 (dt, *J* = 12.8, 3.8 Hz, 1H), 2.30–2.18 (m, 2H), 1.92 (m, 1H), 1.85 (dt, *J* = 12.8, 3.8 Hz, 1H), 1.65 (m, 1H), 1.37 (s, 3H) 0.73 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 164.6, 162.9, 143.5, 138.3, 128.2, 128.2, 125.4, 113.5, 107.1, 53.0, 43.8, 43.6, 34.4, 31.0, 22.4, 8.7; HRMS (ESI) calcd. for C₁₈H₂₄NO [*M*+H]⁺ 270.1852, found 270.1842.

Resolution of the enantiomers of **20g** was achieved using a chiral HPLC system fitted with a Chiralpak IB column with guard as the stationary phase with [*n*-heptane:MTBE (98:2, v:v)] as the mobile phase at a flow rate of 0.5 mL min⁻¹ (*T* = $0\text{ }^{\circ}\text{C}$). Injection volume: 2 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component

(*S*) and the slower running component (*R*) were eluted at 11.3 and 11.8 min., respectively, with a total analysis time of 30 min.

8. Reaction products – B(pin) incorporation

(*S*)-2-(2,4-dimethoxy-6-(4-(4-methoxyphenyl)butan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-**9ba**]

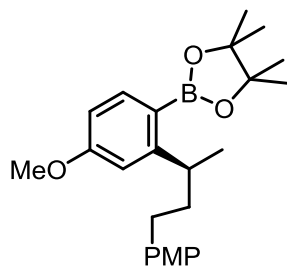


A solution of 3,5-(dimethoxy)bromobenzene (65 mg, 0.30 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated with *t*-BuLi (0.35 mL, 0.60 mmol, 2.4 eq., 1.7 M in pentane). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and then a solution of (*S*)-**1b** (72 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeCN:*i*-PrOH (1:1, 2 mL) and the mixture was cooled to $0\text{ }^{\circ}\text{C}$. A solution of NBS (45 mg, 0.25 mmol, 1.0 eq.) in MeCN (1.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm up to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:EtOAc (95:5) gave (*S*)-**9ba** (41 mg, 38%) as an oil; er (*S*:*R*) 95:5; R_f 0.22 (petrol:Et₂O 90:10); $[\alpha]_{\text{D}}^{25} - 25$ (*c* 0.8, CHCl_3); IR (film): ν (cm^{-1}) 2961, 2928, 2852, 1601, 1511, 1330, 1243, 1199, 1142, 1034, 857, 829, 698; ^1H NMR (400 MHz, CDCl_3) δ ppm; 7.10–7.05 (m, 2H), 6.83–6.78 (m, 2H), 6.39 (d, $J = 2.0$ Hz, 1H), 6.25 (d, $J = 2.0$ Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 2.76 (sx, $J = 6.9$ Hz, 1H), 2.60–2.40 (m, 2H), 1.96 (m, 1H), 1.87 (m, 1H), 1.35 (s, 6H), 1.34 (s, 6H), 1.26 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.9, 162.1, 157.5, 153.6, 134.9, 129.2, 113.6, 102.2, 95.0, 83.53, 55.4, 55.2, 55.1, 39.8, 39.7, 33.1, 29.7, 24.8, 24.6, 22.6; ^{11}B NMR (96 MHz, NONE) δ ppm 31.7; HRMS (EI) calcd. for $\text{C}_{25}\text{H}_{33}\text{BO}_5$ [M]⁺ 426.2578, found 426.2563.

Resolution of the enantiomers of **9ba** was achieved using a chiral SFC system fitted with a Chiralcel IA column as the stationary phase with CO_2 : [*n*-hexane:*i*-PrOH (9:1, v:v)] as the

mobile phase at a flow rate of 4.0 mL min⁻¹ ($P = 125$ bar). Injection volume: 20 μ L of a 2 g L⁻¹ solution of the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 5.2 and 7.8 min., respectively, with a total analysis time of 15 min.

(*S*)-2-(4-methoxy-2-(4-(4-methoxyphenyl)butan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-11ba-major]

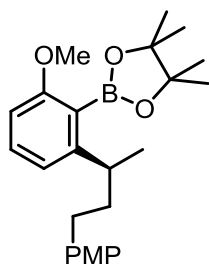


A solution of 3-bromoanisole (56 mg, 0.30 mmol, 1.2 eq.) in THF (2.5 mL) was cooled to -78 °C and treated with *t*-BuLi (0.35 mL, 0.60 mmol, 2.4 eq., 1.7 M in pentane). The mixture was stirred at -78 °C for 1 h and then a solution of (*S*)-**1b** (72 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [¹¹B NMR, 96 MHz, THF) $\delta_B \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeCN:*i*-PrOH (1:1, 2 mL) and the mixture was cooled to 0 °C. A solution of NBS (45 mg, 0.25 mmol, 1.0 eq.) in MeCN (1.0 mL) was added dropwise. After 1 h saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:EtOAc (95:5) gave (*S*)-**11ba-major** (40 mg, 40%) as an oil; er (*S*:*R*) 96:4; R_f 0.21 (petrol:Et₂O 95:5); $[\alpha]_D^{23} - 20$ (c 1, CHCl₃); IR (film): ν (cm⁻¹) 2974, 2931, 2837, 1600, 1511, 1347, 1243, 1144, 1029, 859, 817, 659; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.75 (d, $J = 8.3$ Hz, 1H), 7.08–7.03 (m, 2H), 6.87 (d, $J = 2.4$ Hz, 1H), 6.83–6.77 (m, 2H), 6.73 (dd, $J = 8.3, 2.4$ Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.65 (sx, $J = 7.0$ Hz, 1H), 2.56 (m, 1H), 2.47 (m, 1H), 1.91 (m, 1H), 1.81 (m, 1H), 1.32 (s, 6H), 1.31 (s, 6H), 1.27 (d, $J = 7.0$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm 162.0, 157.5, 156.7, 137.8, 135.2, 129.1, 113.6, 111.4, 109.8, 83.1, 55.2, 55.0, 40.8, 36.4, 33.2, 30.9, 24.9, 24.8, 22.4; ¹¹B NMR (96 MHz, NONE) δ ppm 30.4; HRMS (ESI) calcd. for C₂₄H₃₄BO₄ [$M+H$]⁺ 397.2549, found 397.2537.

Resolution between the enantiomers of **11ba-major** was achieved using a chiral SFC system fitted with a Chiralcel Whelk-01 column as the stationary phase with CO₂:*n*-hexane:*i*-PrOH

(9:1 v:v)] as the mobile phase at a flow rate of 4.0 mL min⁻¹ (*P* = 125 bar). Injection volume: 10 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 33.5 and 35.0 min., respectively, with a total analysis time of 45 min.

(*S*)-2-(2-methoxy-6-(4-(4-methoxyphenyl)butan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-11ba-minor]

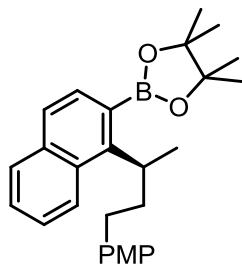


A solution of 3-bromoanisole (56 mg, 0.30 mmol, 1.2 eq.) in THF (2.5 mL) was cooled to -78 °C and treated with *t*-BuLi (0.35 mL, 0.60 mmol, 2.4 eq., 1.7 M in pentane). The mixture was stirred at -78 °C for 1 h and then a solution of (*S*)-**1b** (50 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the 'ate' complex [¹¹B NMR, 96 MHz, THF) δ_B ~ 8 ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeCN:*i*-PrOH (1:1, 2 mL) and the mixture was cooled to 0 °C. A solution of NBS (45 mg, 0.25 mmol, 1.0 eq.) in MeCN (1.0 mL) was added dropwise. After 1 h saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. After 2 min the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:EtOAc (95:5) gave (*S*)-**11ba-minor** (15 mg, 15%) was obtained as an oil; er (*S*:*R*) 96:4; *R*_f 0.15 (petrol:Et₂O 9:1); [α]_D²³ - 58 (*c* 0.5, CHCl₃); IR (film): ν (cm⁻¹) 2987, 2972, 2901, 1511, 1372, 1248, 1074, 855; ¹H NMR (400 MHz, CDCl₃) δ ppm 7.28 (t, *J* = 7.9 Hz, 1H), 7.10–7.03 (m, 2H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.83–6.87 (m, 2H), 6.66 (d, *J* = 7.9 Hz, 1H), 3.78 (s, 6H), 2.72 (sx, *J* = 7.0 Hz, 1H), 2.59–2.40 (m, 2H), 1.98 (m, 1H), 1.83 (m, 1H), 1.37 (s, 6H), 1.36 (s, 6H), 1.27 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ ppm; 162.4, 157.5, 152.2, 134.9, 130.5, 129.2, 117.5, 113.6, 107.1, 83.8, 55.4, 55.2, 39.8, 39.7, 33.1, 24.8, 24.7, 22.7; ¹¹B NMR (96 MHz, NONE) δ ppm 32.8; HRMS (ESI) calcd. for C₂₄H₃₄BO₄ [*M*+H]⁺ 397.2549, found 397.2541.

Resolution of the enantiomers of **11ba-minor** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO₂:*n*-hexane:*i*-PrOH (1:1, v:v)] as the mobile phase at a flow rate of 4.0 mL min⁻¹ (*P* = 125 bar). Injection volume: 20 μL of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running

component (*S*) and the slower running component (*R*) were eluted at 5.7 and 7.3 min., respectively, with a total analysis time of 15 min.

(*S*)-2-(1-(4-(4-methoxyphenyl)butan-2-yl)naphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-15ba]

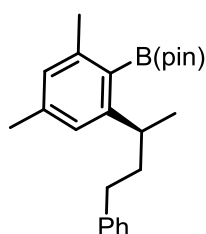


A solution of 1-bromonaphthalene (42 μ L, 0.30 mmol, 1.2 eq.) in Et₂O (1.0 mL) was cooled to 0 °C and *n*-BuLi (0.19 mL, 0.30 mmol, 1.2 eq., 1.6 M in hexanes) was added dropwise. The mixture was stirred at 0 °C for 1 h. (*S*)-**1b** (72 mg, 0.25 mmol, 1.0 eq.) was added and the mixture was stirred at 0 °C for 1 h at which point ¹¹B NMR spectroscopy showed complete formation of the ‘ate’ complex [¹¹B NMR, 96 MHz, THF) δ_B ~ 8 ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude residue was re-dissolved in MeCN:*i*-PrOH (1:1, 2 mL) and the mixture was cooled to 0 °C. A solution of NBS (128 mg, 0.72 mmol, 2.4 eq.) in MeCN (2.0 mL) was added dropwise. After 1 h saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (95:5) gave (*S*)-**15ba** (75 mg, 72%) as an oil; er (*S*:*R*) 95:5; *R*_f 0.23 (petrol:Et₂O 95:5); [α]_D²⁴ – 25 (*c* 0.3, CHCl₃) IR (film): ν (cm⁻¹) 2987, 2972, 2901, 1393, 1249, 1075, 1066, 878; ¹H NMR (500 MHz, DMSO, 90 °C) δ ppm 8.28 (m, 1H), 7.92 (m, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.56–7.50 (m, 2H), 7.07–7.02 (m, 2H), 6.85–6.80 (m, 2H), 3.95 (sx., *J* = 7.2 Hz, 1H), 3.75 (s, 3H), 2.63 (dt, *J* = 13.9, 7.8 Hz, 1H), 2.40 (dt, *J* = 13.9, 7.8 Hz, 1H), 2.26 (q, *J* = 7.8 Hz, 2H), 1.57 (d, *J* = 7.2 Hz, 3H), 1.40 (s, 6H), 1.39 (s, 6H); ¹³C NMR (126 MHz, DMSO, 90 °C) δ ppm 158.0, 149.8, 135.4, 134.6, 131.5, 130.7, 129.4, 129.3, 126.3, 125.9, 125.7, 114.4, 84.2, 55.6, 55.6, 39.6, 34.0, 25.1, 21.6; ¹¹B NMR (96 MHz, NONE) δ ppm 30.7; HRMS (ESI) calcd. for C₂₇H₃₃BNaO₃ [*M*+Na]⁺ 439.2415, found 439.2406.

Resolution of the enantiomers of **15ba** was achieved using a chiral SFC system fitted with a Chiracel IA column as the stationary phase with CO₂: [*n*-hexane:*i*-PrOH (1:1, v:v)] as the mobile phase at a flow rate of 4.0 mL min⁻¹ (*P* = 125 bar). Injection volume: 20 μ L of a 2 g L⁻¹ solution of compound in the eluent. Under these conditions, the faster running component

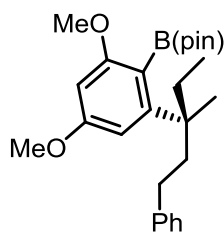
(*R*) and the slower running component (*S*) were eluted at 10.3 and 11.5 min., respectively, with a total analysis time of 15 min.

(*S*)-2-(2,4-dimethyl-6-(4-phenylbutan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-18aa]



A solution of 3,5-(dimethyl)bromobenzene (41 mg, 0.30 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated with *t*-BuLi (0.35 mL, 0.60 mmol, 2.4 eq., 1.7 M in pentane). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min and then a solution of (*S*)-**1a** (72 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeCN:*i*-PrOH (1:1, 2 mL) and the mixture was cooled to $0\text{ }^{\circ}\text{C}$. A solution of NBS (107 mg, 0.6 mmol, 2.4 eq.) in MeCN (2.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (9:1) gave (*S*)-**18aa** (82 mg, 90%) as an oil; er (*R*:*S*) 95:5; R_f 0.38 (petrol:Et₂O 9:1); $[\alpha]_{\text{D}}^{21} -36$ (*c* 1, CHCl_3); IR (film): ν (cm^{-1}) 2981, 2931, 2850, 1327, 1296, 1141, 1060, 855, 697, 685.; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.29–7.22 (m, 2H), 7.20–7.12 (m, 3H), 6.89 (s, 1H), 6.81 (s, 1H) 2.88 (sx, $J = 7.1$ Hz, 1H), 2.63 (m, 1H), 2.51(m, 1H), 2.37 (s, 3H), 2.29 (s, 3H), 2.08–1.95 (m, 1H), 1.92–1.79 (m, 1H), 1.36 (s, 12H), 1.28 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm; 151.3, 142.9, 141.1, 138.9, 128.3, 128.2, 127.8, 125.5, 122.5, 83.6, 39.8, 39.3, 34.2, 25.1, 25.0, 22.9, 22.1, 21.5; ^{11}B NMR (96 MHz, NONE) δ ppm 31.6; HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{33}\text{BO}_2$ [$M+\text{H}$]⁺ 365.2651, found 365.2642. Resolution of the enantiomers of **18aa** was achieved using a chiral HPLC system fitted with a Chiralpak IB column with guard as the stationary phase with *n*-hexanes the mobile phase at a flow rate of 1.0 mL min^{-1} ($T = 0\text{ }^{\circ}\text{C}$). Injection volume: $2\text{ }\mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 38.4 and 48.8 min., respectively, with a total analysis time of 70 min.

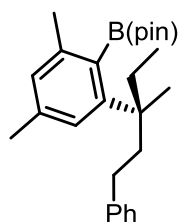
(S)-2-(2,4-dimethoxy-6-(3-methyl-1-phenylpentan-3-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(S)-9ga]



A solution of 3,5-(dimethoxy)bromobenzene (65 mg, 0.30 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to -78 °C and treated with *t*-BuLi (0.35 mL, 0.60 mmol, 2.4 eq., 1.7 M in pentane). The mixture was stirred at -78 °C for 30 min. and then a solution of (*R*)-**1g** (72 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeCN:*i*-PrOH (1:1, 2 mL) and the mixture was cooled to 0 °C. A solution of NBS (45 mg, 0.25 mmol, 1.0 eq.) in MeCN (1.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:EtOAc (95:5) gave (*S*)-**9ga** (48 mg, 46%) as an oil; er (*S*:*R*) 99:1; R_{f} 0.32 (petrol:Et₂O 65:35); $[\alpha]_{\text{D}}^{23} - 3$ (*c* 0.1, CHCl_3); IR (film): ν (cm^{-1}) 2973, 2931, 1599, 1569, 1453, 1325, 1293, 1141, 1041, 856, 698 ^1H NMR (400 MHz, CDCl_3) δ ppm; 7.25–7.18 (m, 4H), 7.16–7.10 (m, 1H), 6.52 (d, $J = 2.0$ Hz, 1H), 6.30 (d, $J = 2.06$ Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.42 (dt, $J = 13.1, 4.6$ Hz, 1H), 2.29 (dt, $J = 13.1, 4.6$ Hz, 1H), 2.16 (dt, $J = 13.1, 4.6$ Hz, 1H), 1.90 (m, 1H), 1.74 (dt, $J = 13.1, 4.6$ Hz, 1H), 1.59 (m, 1H), 1.40 (s, 3H), 1.37 (s, 6H), 1.36 (s, 6H), 0.71 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 164.5, 161.0, 153.3, 143.5, 128.6, 128.0, 125.3, 106.1, 94.2, 83.6, 55.4, 55.1, 45.6, 43.2, 36.0, 31.1, 25.1, 24.9, 24.2, 8.7; ^{11}B NMR (96 MHz, NONE) δ ppm 30.4; HRMS (EI) calcd. for $\text{C}_{26}\text{H}_{37}\text{BO}_4$ [M]⁺ 424.2421, found 424.2427.

Resolution of the enantiomers of **9ga** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO_2 : [*n*-hexane:*i*-PrOH (9:1 v:v)] as the mobile phase at a flow rate of 4.0 mL min^{-1} ($P = 125$ bar). Injection volume: 20 μL of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 5.8 and 6.8 min., respectively, with a total analysis time of 15 min.

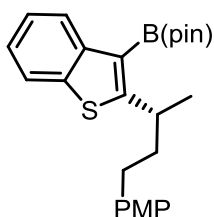
(S)-2-(2,4-dimethyl-6-(3-methyl-1-phenylpentan-3-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(S)-18ga]



A solution of 3,5-(dimethyl)bromobenzene (41 mg, 0.30 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and treated with *t*-BuLi (0.35 mL, 0.60 mmol, 2.4 eq., 1.7 M in pentane). The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h and then a solution of (*R*)-**1g** (72 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h at which point ^{11}B NMR spectroscopy showed complete formation of the ‘ate’ complex [^{11}B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeCN:*i*-PrOH (1:1, 2 mL) and the mixture was cooled to $0\text{ }^{\circ}\text{C}$. A solution of NBS (107 mg, 0.6 mmol, 2.4 eq.) in MeCN (2.0 mL) was added dropwise. After 1 h saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried over MgSO_4 , filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (9:1) gave (*S*)-**18ga** (81 mg, 83%) as an oil R_f 0.3 (pentane:Et₂O 95:5); IR (film): ν (cm^{-1}) 2975, 2927, 1607, 1453, 1372, 1324, 1295, 1141, 1059, 855, 699, 684, 745; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.25–7.21 (m, 2H), 7.20–7.17 (m, 2H), 7.13 (m, 1H) 7.11 (tt, $J = 7.2, 1.5$ Hz, 1H), 6.96 (m, 1H), 6.82 (br s, 1H), 2.41 (dt, $J = 13.0, 4.5$ Hz, 1H), 2.41 (s, 3H), 2.30 (s, 3H), 2.26 (dt, $J = 13.0, 4.5$ Hz, 1H), 2.20 (dt, $J = 13.0, 4.5$ Hz, 1H), 1.93 (dq, $J = 14.4, 7.4$ Hz, 1H), 1.78 (dt, $J = 13.5, 4.5$ Hz, 1H), 1.65 (dq, $J = 14.4, 7.4$ Hz, 1H), 1.43 (s, 3H), 1.40 (s, 6H), 1.38 (s, 6H), 0.72 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 150.5, 143.7, 140.8, 137.4, 128.6, 128.0, 127.5, 125.3, 125.2, 83.7, 45.4, 42.9, 35.8, 31.2, 25.8, 25.6, 24.8, 22.50 21.6, 8.8.; ^{11}B NMR (96 MHz, CDCl_3) δ ppm 31.2; HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{37}\text{BO}_2$ [$M+\text{H}$]⁺ 393.2964, found 393.2949.

Resolution of the enantiomers of **18ga** was achieved using a chiral SFC system fitted with a Chiralcel Whelk-01 column as the stationary phase with CO_2 :*n*-hexane as the mobile phase at a flow rate of 2.0 mL min^{-1} ($P = 125$ bar). Injection volume: $20\text{ }\mu\text{L}$ of a 2 g L^{-1} solution of compound in the eluent. Under these conditions, the faster running component (*S*) and the slower running component (*R*) were eluted at 18.0 and 19.0 min., respectively, with a total analysis time of 25 min.

(R)-2-(2-(4-(4-methoxyphenyl)butan-2-yl)benzo[b]thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(R)-8ba]

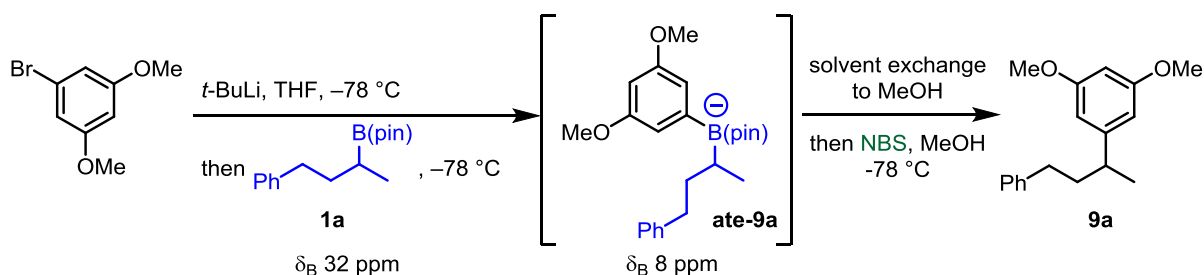


A solution of benzothiophene (35 μ L, 0.30 mmol, 1.2 eq.) in THF (2.0 mL) was cooled to -78 $^{\circ}$ C and treated with *t*-BuLi (0.2 mL, 0.30 mmol, 1.2 eq., 1.6 M in hexane). The mixture was stirred at -78 $^{\circ}$ C for 1 h and then a solution of (*R*)-**1b** (72 mg, 0.25 mmol, 1.0 eq.) in THF (1.0 mL) was added. The mixture was stirred at -78 $^{\circ}$ C for 1 h at which point 11 B NMR spectroscopy showed complete formation of the ‘ate’ complex [11 B NMR, 96 MHz, THF) $\delta_{\text{B}} \sim 8$ ppm]. The mixture was warmed to r.t. and the solvents were removed under high vacuum. The crude was re-dissolved in MeCN:*i*-PrOH (1:1, 2 mL) and the mixture was cooled to 0 $^{\circ}$ C. A solution of NBS (53 mg, 0.3 mmol, 1.2 eq.) in MeCN (1.0 mL) was added dropwise. After 1 h saturated aqueous solution of Na₂S₂O₃ (2 mL) was added. After 2 min. the reaction mixture was allowed to warm to r.t. The reaction mixture was diluted with EtOAc (10 mL) and washed with water (15 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL), the combined organic layers were dried (MgSO₄), filtered and concentrated under vacuum. Purification by flash column chromatography eluting with *n*-hexane:Et₂O (9:1) gave (*R*)-**8ba** (48 mg, 46%) was obtained as an oil; er (*R*:*S*) 96:4; *R*_f 0.21 (petrol:Et₂O 95:5); $[\alpha]_{\text{D}}^{23} - 39$ (*c* 1, CHCl₃); IR (film): ν (cm⁻¹) 2973, 2921, 1511, 1456, 1370, 1234, 1142, 762; ^1H NMR (400 MHz, CDCl₃) δ ppm: 8.33 (br d, *J* = 8.0 Hz, 1H), 7.77 (br d, *J* = 8.0 Hz, 1H), 7.34 (m, 1H), 7.27 (m, 1H), 7.10–7.04 (m, 2H), 6.83–6.76 (m, 2H), 4.01 (sx, *J* = 7.0 Hz, 1H), 3.77 (s, 3H), 2.66–2.45 (m, 2H), 2.01–1.90 (m, 2H), 1.39 (d, *J* = 7.0 Hz, 3H), 1.37 (s, 6 H), 1.36 (s, 6H); ^{13}C NMR (100 MHz, CDCl₃) δ ppm: 167.51, 157.73, 144.27, 139.10, 134.72, 129.32, 125.12, 124.16, 123.43, 121.78, 113.78, 83.17, 55.33, 41.96, 35.50, 33.23, 25.08, 24.99, 24.17; HRMS (ESI) calcd. for C₂₅H₃₂BO₃S [*M*+*H*]⁺ 423.2165, found 423.2186.

Resolution of the enantiomers of **8ba** was achieved using a chiral SFC system fitted with a Chiracel IB column as the stationary phase with CO₂:*n*-hexane:*i*-PrOH (9:1, v:v) as the mobile phase at a flow rate of 4.0 mL min⁻¹ (*P* = 125 bar). Injection volume: 10 μ L of a 2 g L⁻¹ solution of the eluent. Under these conditions, the faster running component (*R*) and the slower running component (*S*) were eluted at 14.3 and 19.0 min., respectively, with a total analysis time of 25 min.

9. React-IR studies

The following reaction was studied with use of React-IR:



Experimental procedure:

A three-neck round bottom flask equipped with a stirring bar was connected to the React-IR probe, evacuated and refilled with N₂ (x 3). The flask was charged with 3,5-(dimethoxy)-bromobenzene (50 mg, 0.23 mmol, 1.2 eq.) and evacuation/refilling procedure was repeated (x3). THF (2.0 mL) was added and the solution was cooled to -78 °C. The background spectrum was acquired. *t*-BuLi (0.27 mL, 0.46 mmol, 2.4 eq., 1.7M in pentane) was added dropwise and the reaction mixture was stirred for 30 min. *The peak at 1379 cm⁻¹ was selected to follow organolithium species.* The solution of boronic ester **1a** (50 mg, 0.19 mmol, 1.0 eq.) in THF (1.0 mL) was added (*slow addition is necessary to avoid signal fluctuation*) and the reaction mixture was stirred for 30 min. At this point, the development of new species was observed immediately. The new peak at 1512 cm⁻¹ was attributed to the 'ate' complex **xx** and its presence was confirmed by ¹¹B-NMR analysis of a reaction aliquot (δ_B ~ 8 ppm). React-IR instrument was switched off. The reaction mixture was allowed to warm to r.t and the solvent was removed under high vacuum. The crude was re-dissolved in MeOH (2.0 mL) and the resulting solution was cooled to -78 °C. The React-IR instrument was switched on and the spectrum of 'ate' complex in MeOH -78 °C recorded. *The peak at 1583 cm⁻¹ was selected to follow the 'ate' complex ate-9a.* The solution of NBS (34 mg, 0.19 mmol, 1.0 eq.) in MeOH (3.0 mL) was added slowly. *Two peaks: 1712 cm⁻¹ and 1570 cm⁻¹ appeared rapidly and were attributed to succinimide and the product 9a, respectively.* The diagnostic peak for **9a** was confirmed by preparing the compound separately and recording a React-IR spectrum in MeOH. Et₂O and water were added to the reaction mixture at -78°C and warmed to ambient temperature. The layers were separated and the aqueous phase was extracted with Et₂O (x 2). The combined organic layers were dried over MgSO₄ and the solvent was removed under vacuum. ¹H NMR spectroscopy analysis of the crude revealed complete formation of **9a**.

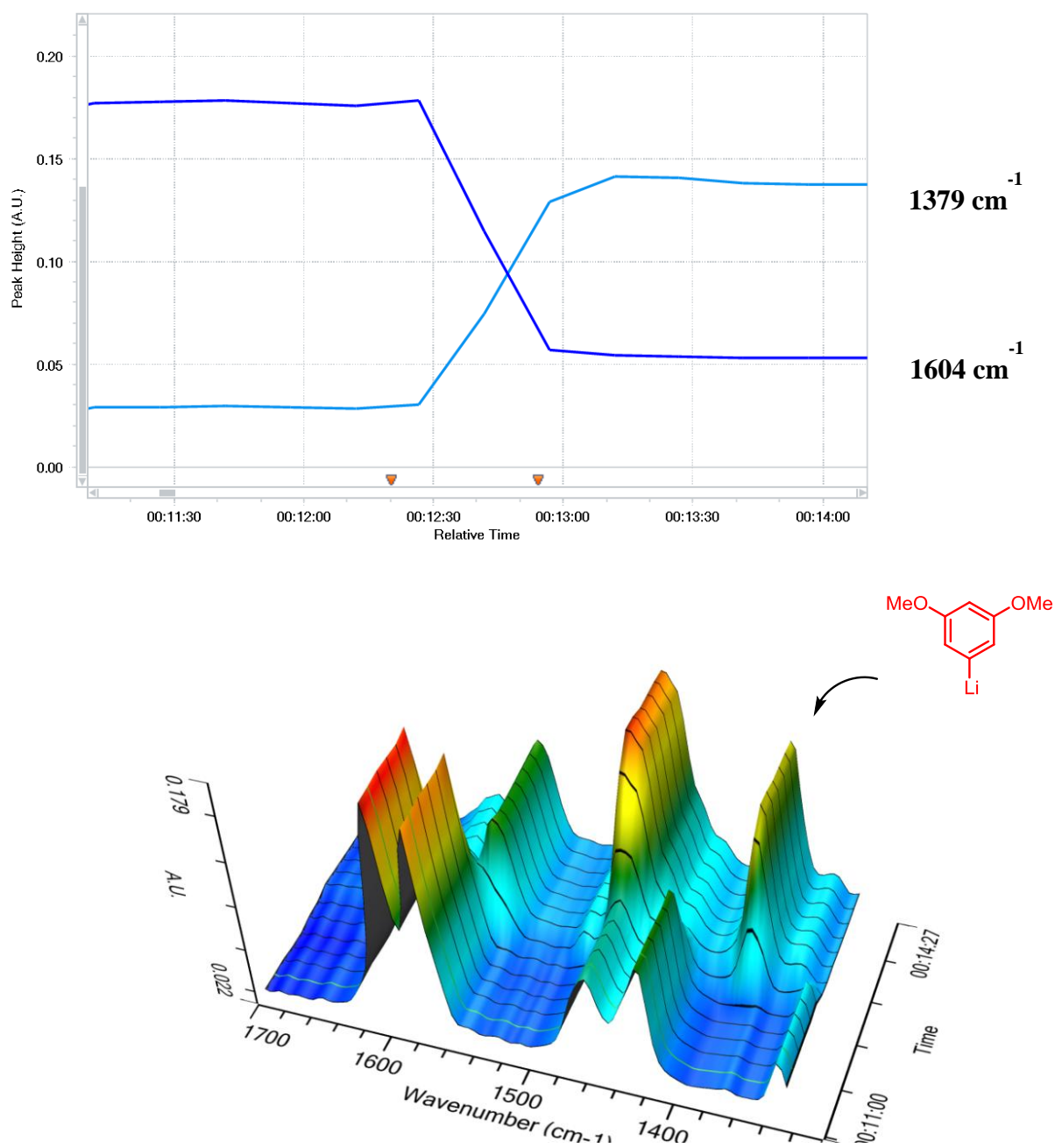


Figure 1. Formation of 3,5-dimethoxyaryllithium.

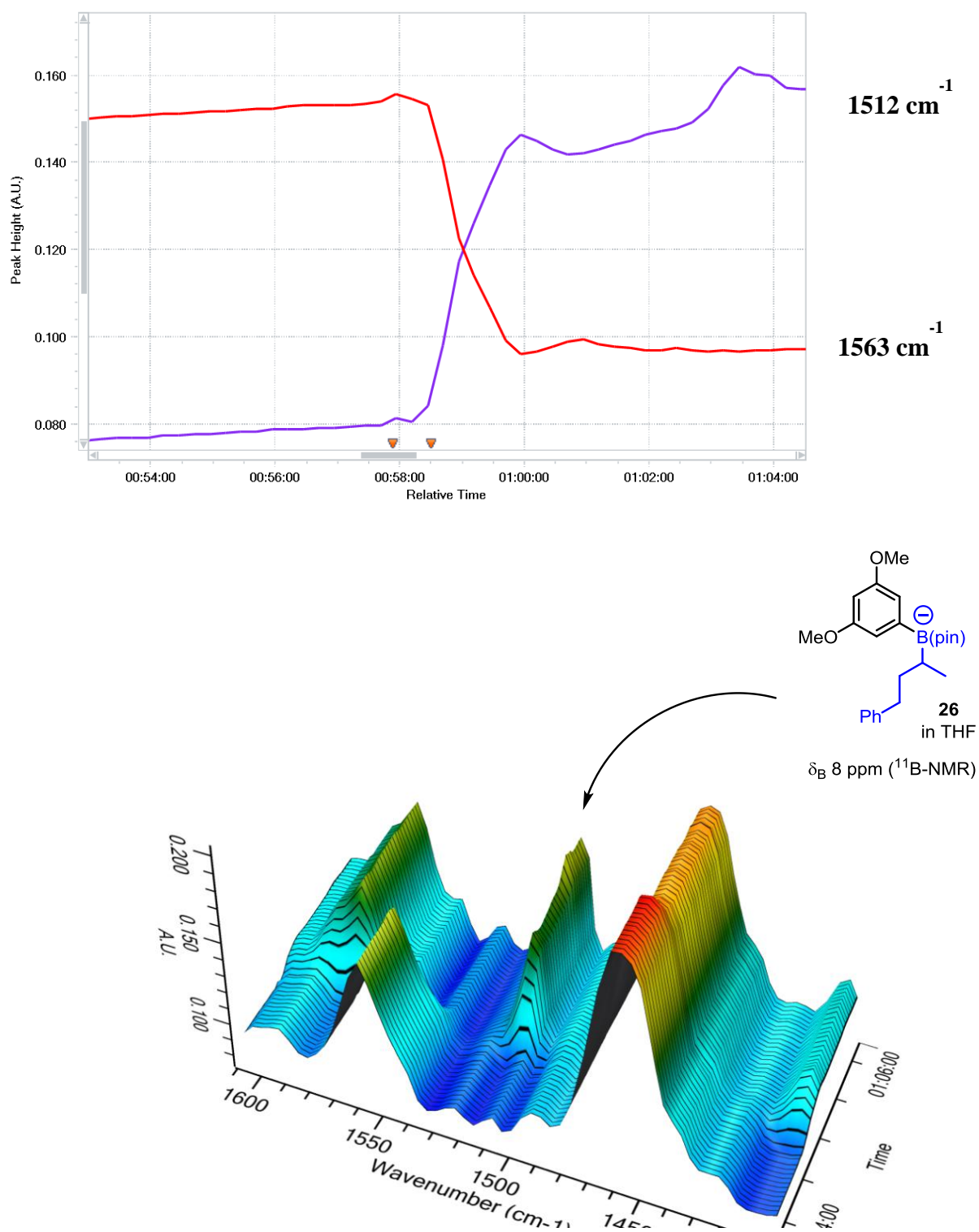


Figure 2. Formation of 'ate' complex **26**.

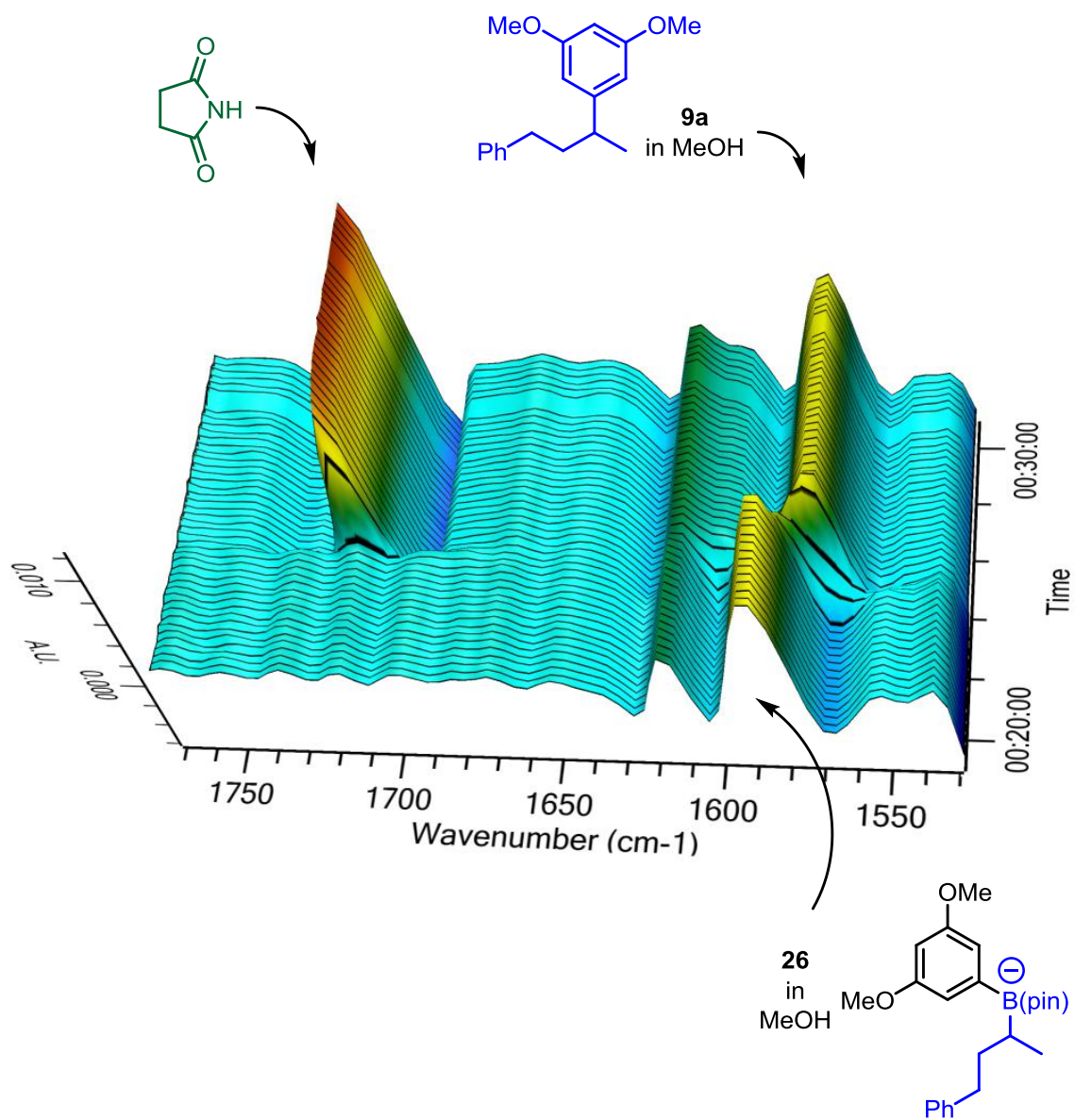
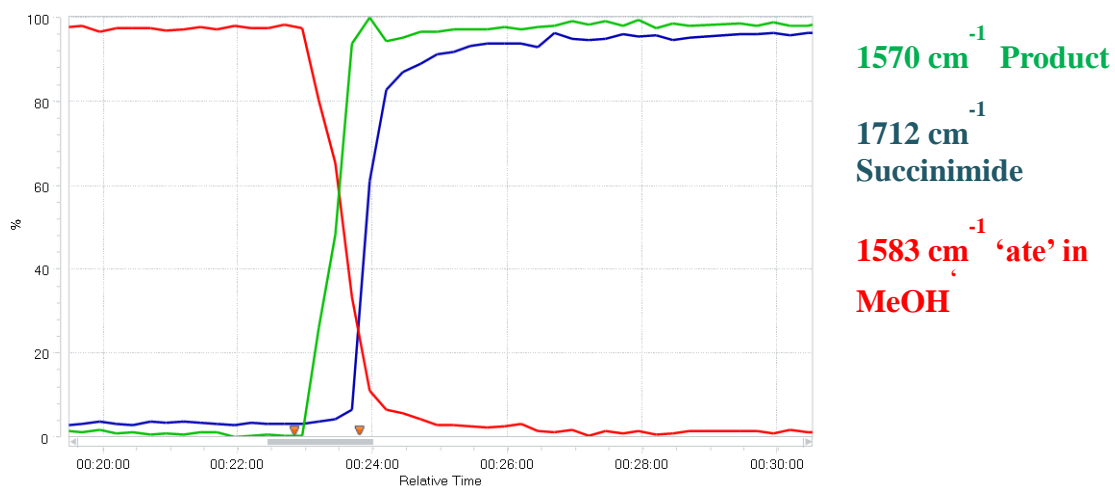


Figure 3. Product formation upon addition of *N*-Bromosuccinimide.

10. DFT calculations

General. Calculations were performed with the GAUSSIAN 09 suite of programs.²¹ Density Functional Theory (DFT) was applied by the means of the B3LYP hybrid functional²² corrected for dispersion as proposed by Grimme (D2 correction).²³ The 6-31+G(d) basis set was used for all atoms. Geometry optimizations were performed without any symmetry constraints. The stationary points were characterized by full vibration frequencies calculations. Gibbs free energies at 195 K were obtained from the standard enthalpies and entropies computed at 298 K in Gaussian based on the rigid rotor harmonic oscillator approach to statistical mechanics. Also, Gibbs energies were corrected to take into account a standard state corresponding to species in solution at a concentration of 1 M. To do this, we used the correction: $G^{1M} = G^{1atm} + RT \ln(C^{1M}/C^{1atm})$ where G^{1atm} is the Gibbs free energy at 195 K, C^{1M} is the assumed concentration in solution and C^{1atm} is the gas phase concentration ($C^{1atm} = 1/V_m = P/RT = 0.0409 \text{ mol.L}^{-1}$ for an ideal gas at 195.15 K and 1 atm). Solvent effects (thf or MeOH) were included by means of SMD single point calculations on the gas-phase optimized structures.²⁴ Gibbs free energies in solution were estimated as: $G^{thf} = G^{1M} + E^{thf} - E^{gas\ phase}$. The counter-cation was not explicitly included in the calculations as it is not expected to actively participate in the reaction.

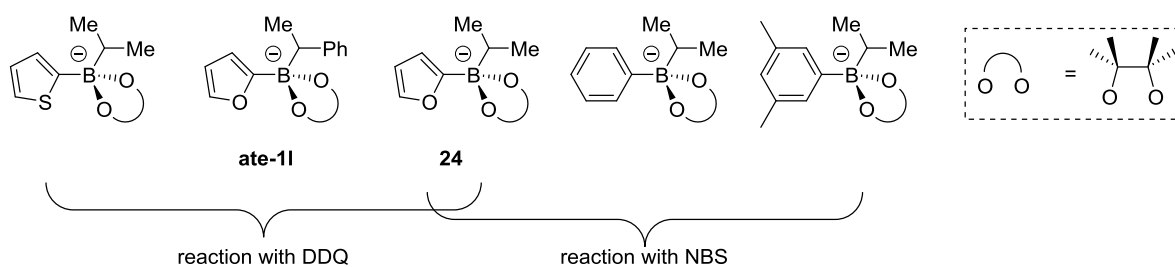
Results. We chose to focus our computational work on the reactivity of furan-, thiophene- and phenyl-substituted boronate complexes. In order to avoid unnecessary conformational issues, we considered model complexes (Scheme 1).

²¹ Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

²² (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch M. J. *J. Phys. Chem.* **1994**, *98*, 11623-11627.

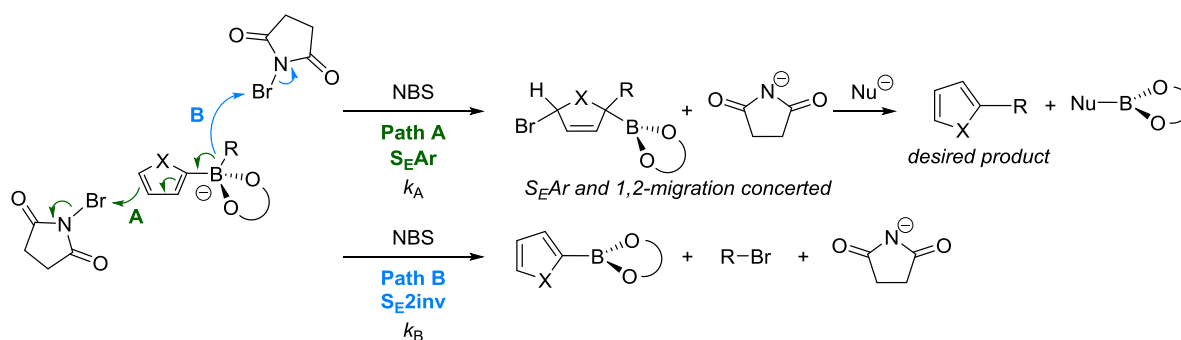
²³ Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787-1799.

²⁴ Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B*, **2009**, *113*, 6378-96.

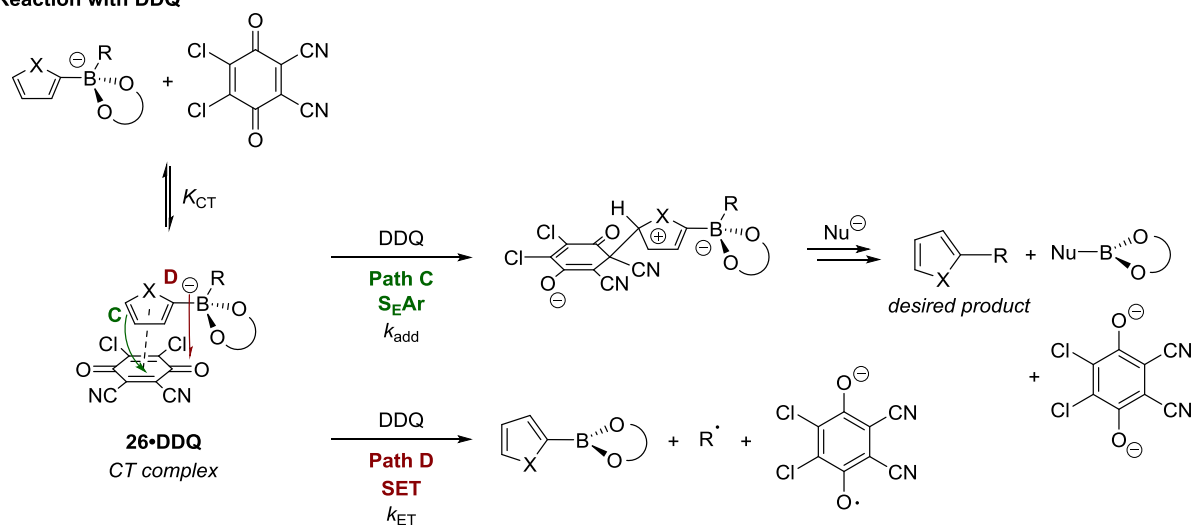


Scheme 1. Complexes under study.

Reaction with NBS



Reaction with DDQ



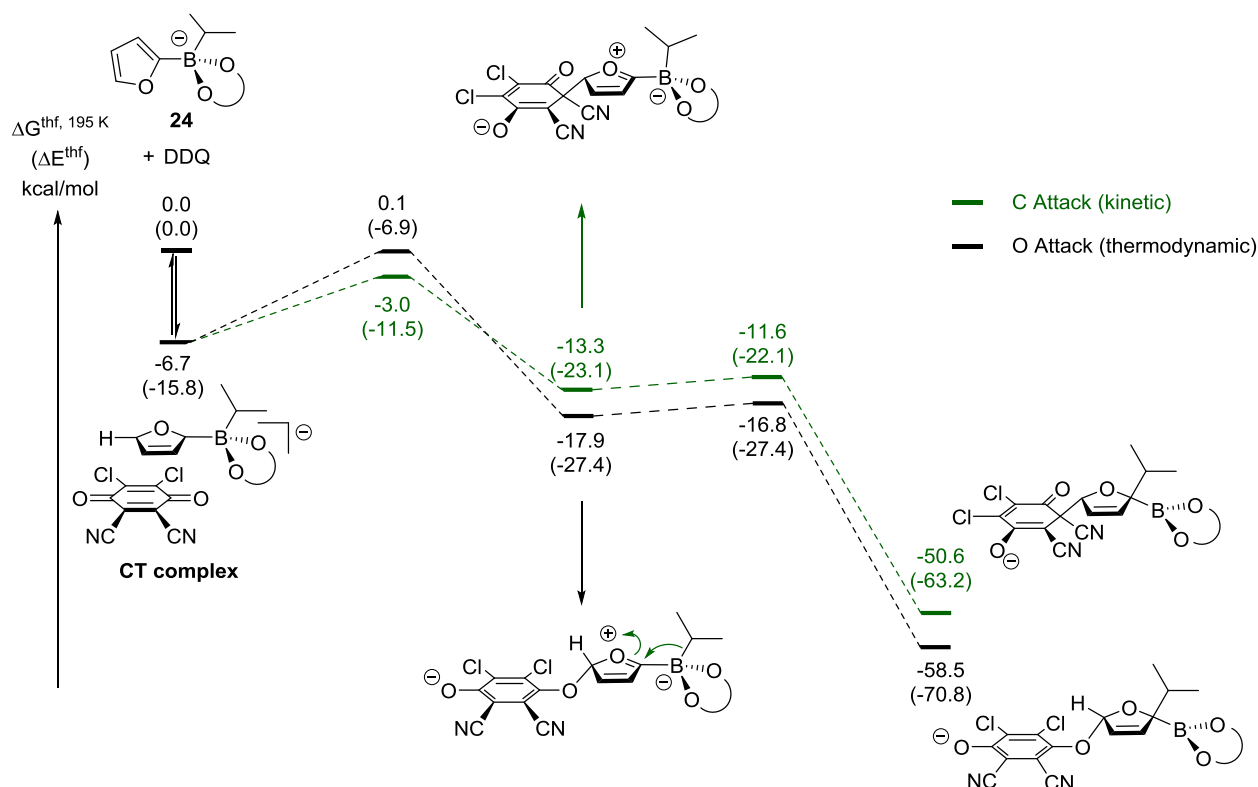
Scheme 2. Proposed mechanistic scheme based on DFT calculations.

Reaction with DDQ. The calculated potential energy surface for Path C (Scheme 3) involves initial formation of a strongly bound encounter complex - or “charge-transfer” complex. It then involves nucleophilic addition of the boronate to DDQ followed by migration of the alkyl group from boron to carbon. The resulting species can undergo facile elimination of the DDQ and boronate moieties. The migration step is computed to be highly exothermic (ΔG_{mig}^0 ranges from -39.0 to -40.6 kcal.mol⁻¹ depending on the position of the attack), so that the backward reaction is not expected to compete with the subsequent elimination step. Mayr recently showed that addition of a π -nucleophile to DDQ can occur either through C or O

attack.²⁵ Based on our calculations, we predict that both of these processes should be very fast at -78 °C ($\Delta G_{add}^\ddagger = 3.7$ kcal.mol⁻¹ for C attack and $\Delta G_{add}^\ddagger = 6.8$ kcal.mol⁻¹ for O attack). C attack appears to be kinetically favored but thermodynamically disfavored, in agreement with Mayr's experimental observations. The apparent second-order rate constant for aromatic electrophilic substitution (k_C) is given by

$$\frac{1}{k_C} = \frac{1}{k_{diff}} + \frac{1}{K_{CT}k_{add}}$$

where k_{diff} is the rate constant for diffusion under the experimental conditions ($k_{diff} \cong (8RT)/(3\eta) = 2 \cdot 10^9$ M⁻¹.s⁻¹ in THF at -78 °C),²⁶ K_{CT} is the equilibrium constant for formation of the encounter complex and k_{add} is the first-order rate constant for electrophilic addition within the charge-transfer complex.



Scheme 3. Computed free energy surfaces for Path C (B3LYP-D2) for **24**.

Computed first- and second-order rate constants for nucleophilic addition of selected boronate complexes to DDQ are summarized below.

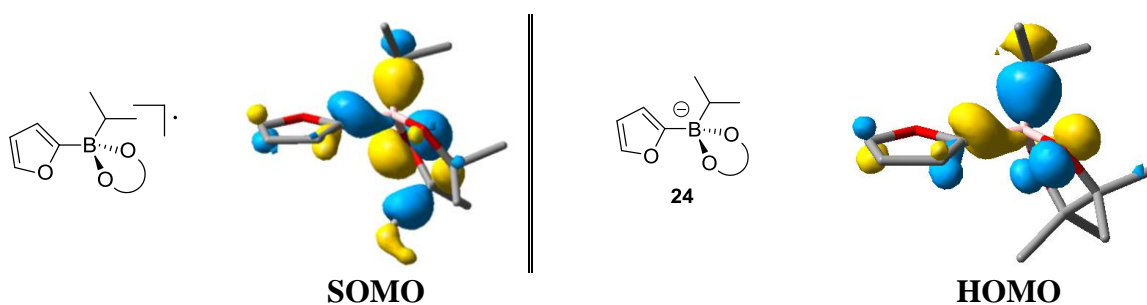
²⁵ Guo, X.; Mayr, H. *J. Am. Chem. Soc.* **2013**, *135*, 12377-12387.

²⁶ <http://ddbonline.ddbst.de/VogelCalculation/VogelCalculationCGI.exe> (accessed the 24/06/2016).

		K_{CT} (M^{-1})	ΔG_{add}^\ddagger ($kcal.mol^{-1}$)	k_{add} (s^{-1})	k_C ($M^{-1}.s^{-1}$)	ΔG_C^\ddagger ($kcal.mol^{-1}$)
Ia	C attack	$3.4 \cdot 10^7$	3.7	$3 \cdot 10^8$	$2 \cdot 10^9$	2.9
	O attack		6.8	$1 \cdot 10^5$	$2 \cdot 10^9$	2.9
Ic	C attack	$6.4 \cdot 10^5$	6.9	$8 \cdot 10^4$	$2 \cdot 10^9$	2.9
	O attack		11.8	$2 \cdot 10^{-1}$	$2 \cdot 10^5$	6.6

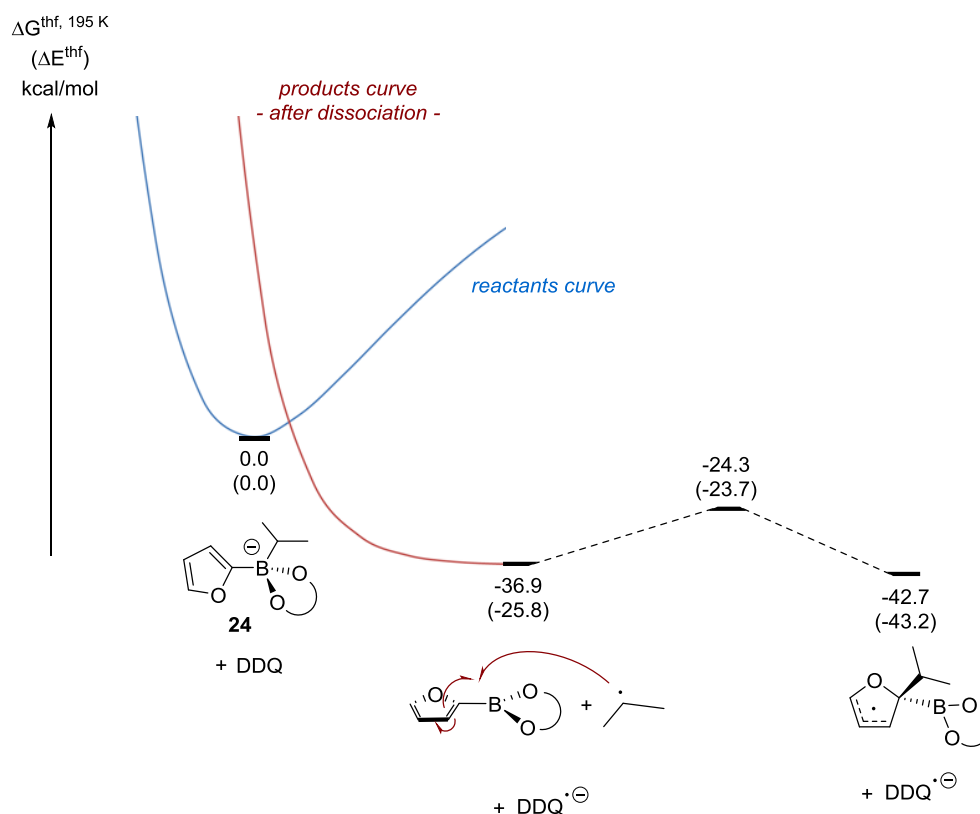
In both cases, the second order rate constant for C attack is found to be equal to k_{diff} , owing to the exothermicity of the formation of the encounter complex ($K_{CT} = 10^5$ - $10^7 M^{-1}$). On another hand, the first-order rate constant is computed to be significantly slower in the case of the less nucleophilic thiophene-substituted boronate complex.

The calculated potential energy surface for Path D first involves the formation of the encounter complex. This initial step is followed by single electron transfer from the boronate moiety to the DDQ moiety of the complex, which occurs with a rate constant k_{ET} . DFT calculations have revealed that single-electron oxidation of **24** occurs by removing an electron from the σ C–B bond. The SOMO of the resulting neutral radical complex (single point calculation at the optimized geometry of **24**) is indeed predominantly localized on the boronate moiety, with only very small coefficients on the furan ring (below, left). As one might expect, this molecular orbital corresponds to the HOMO of **24** (below, right). Geometry optimization of the neutral radical complex accordingly led to C–B bond breaking and generated a carbon-centred radical intermediate and the corresponding boronic ester. A relaxed scan along the C-B distance showed that this process is barrierless.



It is possible to connect path D to path C, by locating a transition state associated with addition of the radical formed upon single electron transfer to the boronic ester, as shown in Scheme 4. This transition state lies $12.6 kcal.mol^{-1}$ above the separated radical and boronic

ester in solvated free energy. This suggests that addition of the radical would be relatively slow, so that this intermediate would be long-lived enough to racemize. Hence this mechanism is inconsistent with (i) the observed stereospecific coupling and (ii) the retention of the cyclopropane unit in some cases.



Scheme 4. Computed free energy surface for Path D (B3LYP-D2) for **24**.

The rate constant k_{ET} was calculated using Marcus-Savéant theory.²⁷ In this theory, the free energy of activation (ΔG^*) for a concerted dissociative electron transfer is given by

$$\Delta G^* = \frac{\lambda_o + BDE}{4} \left(1 + \frac{\Delta G^0}{\lambda_o + BDE} \right)^2$$

where λ_o is the solvent reorganization energy, BDE is the dissociation energy of the C-B bond and ΔG^0 is the standard free energy of the reaction. The solvent reorganization energy was estimated using Marcus' equation²⁸

$$\lambda_o = \Delta e^2 \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_s} \right) \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right)$$

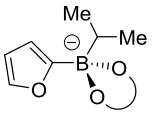
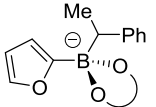
²⁷ Saveant, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 6788–6795.

²⁸ Marcus, R. A. *Angew. Chem. Int. Ed.* **1993**, *32*, 1111–1121.

where ϵ_{opt} and ϵ_s are the optical and static dielectric constants of the solvent ($\epsilon_{opt} = 1.97$ and $\epsilon_s = 7.52$ for THF),²⁹ Δe is the amount of charge transferred (here, 1 atomic unit of charge), a_1 is the radius of the donor (boronate complex) a_2 is the radius of the acceptor (DDQ) and R is the radius of the charge transfer complex. The radii were obtained based on single-point B3LYP calculations as implemented in Gaussian (using the keyword “volume”, which requests that the molecular volume, *i.e.* the volume enclosed by an electron isodensity surface with the value 0.001 electrons/Bohr³, be computed, derives the corresponding radius assuming that the species is a sphere and adds 0.5 Å). The bond dissociation energy was calculated as the difference, in solvated energy, between the boronate complex and the two fragments resulting from the homolytic cleavage of the C-B bond in their relaxed geometries ([furane-B(pin)]^{•-} and [R][•]).

$$BDE = E^{thf}([B]^{•-}) + E^{thf}([R]^{•}) - E^{thf}([B-R]^{-})$$

Finally, the standard free energy of the reaction was calculated as the difference, in solvated free energy, between the initial diabatic state (boronate complex + DDQ) and the final diabatic state ([furane-B(pin)] + [R][•] + [DDQ]^{•-}).

	a_1 (Å)	a_2 (Å)	R (Å)	λ_o (kcal.mol ⁻¹)	BDE (kcal.mol ⁻¹)	ΔG^0 (kcal.mol ⁻¹)	ΔG^* (kcal.mol ⁻¹)
	4.7	5.1	6.2	5.3	69.1	-36.9	4.7
	4.7	5.9	7.0	5.9	62.5	-42.5	2.5

In the adiabatic limit, the first-order (intra-complex) rate constant for the electron transfer is given by

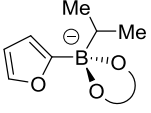
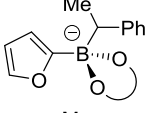
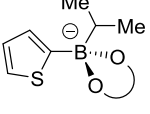
$$k_{ET} = \kappa_{el} \nu_n \exp\left(\frac{-\Delta G^*}{RT}\right)$$

where κ_{el} is the electronic transmission coefficient and ν_n is the nuclear vibration frequency related to electron transfer ($\kappa_{el} \nu_n$ was approximated to 10¹² M⁻¹.s⁻¹). The apparent second-order rate constant for electron transfer (k_D) is given by

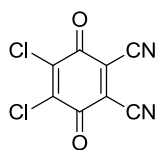
²⁹ Lide, D. R. CRC Handbook of Chemistry and Physics Boca Raton, FL, CRC Press, 2008.

$$\frac{1}{k_D} = \frac{1}{k_{diff}} + \frac{1}{K_{CT}k_{ET}}$$

The table below summarizes the results as far as the reactivity towards DDQ is concerned.

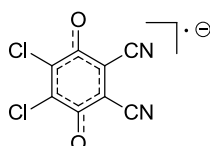
	K_{CT} (M^{-1})	k_{add} (s^{-1})	k_C ($M^{-1}.s^{-1}$)	k_{ET} (s^{-1})	k_D ($M^{-1}.s^{-1}$)	Favored Pathway
	3×10^7	3×10^8	k_{diff}	3×10^6	k_{diff}	C > D
	1×10^7	8×10^7	k_{diff}	2×10^9	k_{diff}	D > C
	6×10^5	5×10^6	k_{diff}	2×10^8	k_{diff}	D > C

Cartesian Coordinates.



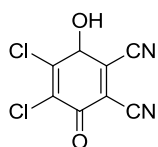
E = -1485.112755 Hartree

C	-0.309151	0.089515	-0.012886
C	1.050908	0.089592	0.012753
C	1.830628	1.377696	0.027006
C	1.050015	2.656965	0.011899
C	-0.308520	2.656888	-0.013711
C	-1.089001	1.377530	-0.028029
O	-2.303501	1.357221	-0.050898
O	3.045128	1.357525	0.049977
Cl	-1.248087	4.095242	-0.031876
Cl	1.989436	4.095427	0.029157
C	-1.073560	-1.116519	-0.026889
C	1.815439	-1.116355	0.027574
N	-1.691113	-2.101590	-0.038198
N	2.433092	-2.101355	0.039551



E = -1485.255263 Hartree

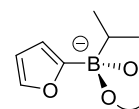
C	-0.330629	0.128508	-0.013367
C	1.072385	0.128588	0.013084
C	1.851727	1.361148	0.027219
C	1.054942	2.607522	0.012061
C	-0.313443	2.607444	-0.013738
C	-1.110092	1.360979	-0.028620
O	-2.356044	1.370436	-0.052435
O	3.097691	1.370747	0.050403
Cl	-1.237423	4.087511	-0.031291
Cl	1.978758	4.087694	0.029346
C	-1.064352	-1.095229	-0.026609
C	1.806224	-1.095065	0.027511
N	-1.653333	-2.101366	-0.037233
N	2.395302	-2.101135	0.039098



E = -1485.859260 Hartree

C	1.357354	-0.749170	-0.001199
C	1.337865	0.674816	-0.004273
C	0.132601	1.381263	-0.005960
C	-1.071357	0.642225	-0.004764
C	-1.084535	-0.745438	-0.001918
C	0.143784	-1.551681	0.000164
O	0.130010	-2.801140	0.002840

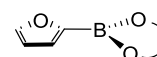
O	0.172238	2.755317	-0.008525
Cl	-2.588406	-1.629949	-0.000686
Cl	-2.576497	1.582442	-0.007288
C	2.600051	-1.441624	0.000636
C	2.557228	1.424520	-0.005800
N	3.626518	-1.998145	0.002542
N	3.544113	2.043699	-0.007217
H	-0.738833	3.092492	-0.010754



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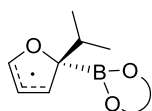
E = -759.353569 Hartree

C	1.513237	-0.892359	-0.730242
C	1.785884	-0.363759	0.731669
C	0.851684	-2.287791	-0.732288
H	0.521667	-2.507890	-1.755819
H	1.557035	-3.068006	-0.409544
H	-0.024507	-2.302606	-0.078400
C	2.763828	-0.954710	-1.615808
H	3.525211	-1.614096	-1.172864
H	2.489569	-1.352362	-2.602410
H	3.193299	0.043075	-1.754004
C	2.932930	0.666334	0.762583
H	2.939036	1.146816	1.749866
H	3.911768	0.194050	0.590457
H	2.769898	1.436049	0.003511
C	2.100507	-1.471533	1.746515
H	2.990213	-2.044115	1.443064
H	2.295209	-1.019671	2.728963
H	1.252945	-2.157709	1.843925
C	-1.632618	-0.267795	0.020669
C	-2.183501	-1.004287	1.042186
O	-2.559855	-0.234671	-1.011894
C	-3.486117	-1.446843	0.625523
H	-1.688696	-1.193190	1.986534
C	-3.659849	-0.947665	-0.634640
H	-4.197087	-2.049946	1.180161
H	-4.461089	-1.010099	-1.359176
C	-0.581115	2.161451	-0.348262
H	-1.210882	2.232441	-1.252860
C	0.668681	3.023657	-0.576417
H	1.286585	3.041744	0.333335
H	1.280775	2.614705	-1.391456
H	0.408866	4.070007	-0.820844
C	-1.383588	2.727453	0.835159
H	-1.622894	3.798433	0.701927
H	-2.324971	2.179232	0.979329
H	-0.797853	2.624730	1.761482
B	-0.231773	0.568741	-0.135696
O	0.624816	0.069515	-1.255862
O	0.580491	0.275835	1.095710



E = -640.770657 Hartree

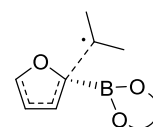
C	2.076643	-0.235233	-0.758780
C	2.069251	-0.297003	0.810809
C	2.633289	-1.508270	-1.404481
H	2.434738	-1.474556	-2.481282
H	3.715112	-1.587335	-1.244710
H	2.150255	-2.399344	-0.987467
C	2.756131	0.995461	-1.346473
H	3.812954	1.019645	-1.050892
H	2.701622	0.955195	-2.440329
H	2.272613	1.916182	-1.008239
C	2.012089	1.088152	1.463130
H	1.820952	0.967013	2.535124
H	2.959769	1.623189	1.330103
H	1.205244	1.689639	1.029067
C	3.194055	-1.122696	1.423030
H	4.166915	-0.691172	1.154630
H	3.100467	-1.115525	2.515071
H	3.159574	-2.159743	1.077663
C	-1.511065	-1.065066	0.015765
C	-2.336753	-1.535039	1.009738
O	-2.259824	-0.898531	-1.134042
C	-3.646203	-1.664234	0.451927
H	-2.025810	-1.758203	2.022259
C	-3.532495	-1.262362	-0.851136
H	-4.546870	-2.006139	0.944981
H	-4.238391	-1.182719	-1.665836
B	-0.009182	-0.728221	-0.004335
O	0.655232	-0.185319	-1.075376
O	0.797403	-0.950953	1.088845



E = -59.287188 Hartree

C	1.853078	-1.237411	-0.380394
C	2.031675	-0.259922	0.834383
C	1.515977	-2.669161	0.046664
H	1.224422	-3.242227	-0.840200
H	2.381572	-3.153397	0.513955
H	0.681175	-2.677449	0.756825
C	3.007090	-1.238470	-1.374786
H	3.931549	-1.563250	-0.880060
H	2.785150	-1.936478	-2.189892
H	3.164427	-0.244402	-1.802765
C	2.842127	0.992007	0.483861
H	2.763922	1.707367	1.310100
H	3.898837	0.744936	0.328822
H	2.455275	1.465049	-0.425874
C	2.576559	-0.905505	2.101918
H	3.578033	-1.314596	1.916394
H	2.650923	-0.151333	2.893764
H	1.923919	-1.711526	2.448882
C	-1.523970	0.517323	-0.279628
C	-2.420892	-0.305473	0.614417
O	-1.979047	0.155768	-1.636019
C	-3.275080	-1.047689	-0.194286

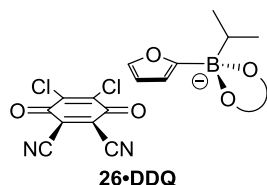
H	-2.347992	-0.311868	1.693341
C	-2.988468	-0.748317	-1.517805
H	-4.040780	-1.742013	0.132776
H	-3.419544	-1.102037	-2.444675
C	-1.692044	2.056233	-0.140254
H	-2.731635	2.263188	-0.430681
C	-0.748203	2.792963	-1.100815
H	0.298746	2.635439	-0.802110
H	-0.872233	2.433925	-2.128598
H	-0.942784	3.873138	-1.077934
C	-1.481353	2.532336	1.303243
H	-1.634653	3.617980	1.358507
H	-2.189049	2.051410	1.989135
H	-0.464431	2.307748	1.644306
B	-0.031334	-0.000158	-0.094257
O	0.665433	-0.704326	-1.036968
O	0.662992	0.179903	1.079042



E = -759.256113 Hartree

C	2.180590	-0.499182	-0.839860
C	2.191411	0.181678	0.575188
C	2.619370	-1.966403	-0.799366
H	2.404402	-2.425575	-1.770403
H	3.693562	-2.049800	-0.596255
H	2.070792	-2.513988	-0.024523
C	2.952706	0.254768	-1.915746
H	4.011658	0.330804	-1.637197
H	2.880497	-0.287973	-2.865077
H	2.551777	1.262066	-2.060315
C	2.258445	1.710958	0.501824
H	2.079676	2.122355	1.501249
H	3.243478	2.043325	0.153958
H	1.494464	2.103769	-0.178079
C	3.253746	-0.347891	1.529906
H	4.254364	-0.174747	1.113446
H	3.180955	0.178120	2.488834
H	3.126207	-1.418952	1.710191
C	-1.461192	-0.534090	0.124808
C	-2.244321	-0.804230	1.270520
O	-2.156020	-1.039450	-0.979656
C	-3.462028	-1.370726	0.826721
H	-1.948321	-0.579139	2.285975
C	-3.363339	-1.489872	-0.538985
H	-4.309174	-1.669673	1.431409
H	-4.035062	-1.862034	-1.299281
C	-1.580439	1.646463	-0.190319
H	-0.761614	1.789610	-0.898404
C	-1.375258	2.254047	1.169641
H	-2.168156	1.924773	1.855463
H	-0.407618	1.975476	1.600971
H	-1.423189	3.356134	1.117930
C	-2.952113	1.786286	-0.786469
H	-3.207556	2.852164	-0.927136
H	-3.025289	1.288792	-1.759367
H	-3.707503	1.354236	-0.116107

B	0.071310	-0.408336	0.002255
O	0.765658	-0.487553	-1.180360
O	0.874613	-0.163701	1.093879

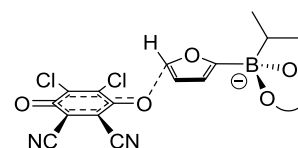


26-DDQ

E = -2244.514690 Hartree

C	3.261186	0.361359	-1.406204
C	4.156899	-0.701465	-0.675927
C	2.250001	-0.304112	-2.353042
H	1.517409	0.443701	-2.674452
H	2.749431	-0.718947	-3.239969
H	1.707153	-1.102132	-1.841478
C	4.048744	1.424708	-2.175273
H	4.682420	0.956586	-2.942424
H	3.349148	2.108741	-2.673404
H	4.680500	2.008736	-1.498283
C	5.448237	-0.075013	-0.114614
H	5.912663	-0.791211	0.574809
H	6.162100	0.161373	-0.916446
H	5.219876	0.843577	0.434978
C	4.526144	-1.912952	-1.536160
H	5.069422	-1.596852	-2.438359
H	5.171574	-2.589112	-0.959676
H	3.628926	-2.462716	-1.837115
C	0.936726	-0.682000	0.929268
C	0.560337	-2.031082	1.020665
O	-0.123363	0.062295	1.392247
C	-0.740886	-2.095721	1.549078
H	1.206618	-2.847099	0.729670
C	-1.140068	-0.783442	1.722218
H	-1.346400	-2.973303	1.732421
H	-2.033392	-0.326163	2.122361
C	2.804869	0.678822	2.220122
H	3.881643	0.880303	2.106743
C	2.631081	-0.268119	3.415220
H	1.565614	-0.473338	3.600961
H	3.128903	-1.228961	3.226290
H	3.047211	0.163680	4.341675
C	2.095220	2.015860	2.467844
H	2.489420	2.516323	3.370245
H	2.226513	2.687514	1.610054
H	1.017369	1.868626	2.617571
B	2.415503	-0.010707	0.748082
O	2.575059	0.987071	-0.327530
O	3.334473	-1.126355	0.400432
O	-0.750241	-0.973019	-1.384373
C	-1.777264	-0.485765	-0.916903
C	-2.939176	-1.328337	-0.544481
C	-1.958139	0.988593	-0.761597
C	-4.150208	-0.780438	-0.177496
C	-3.149605	1.523390	-0.368483
C	-4.331914	0.685135	-0.047306
O	-5.406727	1.165762	0.309053
Cl	-0.582903	1.937510	-1.156181

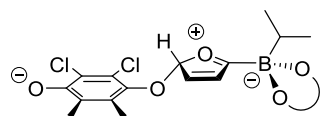
Cl	-3.386744	3.235931	-0.210279
C	-5.279555	-1.597812	0.129768
C	-2.786775	-2.741290	-0.707508
N	-2.692657	-3.892768	-0.843051
N	-6.195099	-2.272236	0.380606



E = -2244.498072 Hartree

C	-3.640199	-1.292992	-1.259307
C	-4.602572	-0.080645	-1.529195
C	-2.283666	-1.119252	-1.967011
H	-1.580644	-1.857132	-1.563787
H	-2.374969	-1.265929	-3.051842
H	-1.871854	-0.120599	-1.786869
C	-4.227603	-2.658065	-1.618385
H	-4.498825	-2.694528	-2.683027
H	-3.483542	-3.440472	-1.421349
H	-5.117481	-2.866480	-1.015886
C	-6.063359	-0.428984	-1.189138
H	-6.652166	0.496889	-1.191765
H	-6.496094	-1.127352	-1.919121
H	-6.118001	-0.878799	-0.191871
C	-4.530137	0.475281	-2.952348
H	-4.795452	-0.299776	-3.685693
H	-5.236958	1.308953	-3.056742
H	-3.524170	0.844948	-3.174397
C	-1.986868	0.844588	0.672724
C	-1.524031	2.164716	0.452783
O	-0.987117	0.148993	1.287387
C	-0.218917	2.245638	0.905940
H	-2.118541	2.929682	-0.027245
C	0.119018	0.939846	1.351491
H	0.470700	3.076468	0.835028
H	0.889041	0.607366	2.032172
C	-4.232869	0.430319	1.963347
H	-5.221789	-0.002602	1.739936
C	-4.425256	1.905428	2.332995
H	-3.464402	2.372196	2.598439
H	-4.848711	2.463986	1.487693
H	-5.097412	2.021382	3.199812
C	-3.601942	-0.360648	3.113169
H	-4.225356	-0.318120	4.022736
H	-3.464260	-1.412361	2.831793
H	-2.613912	0.046779	3.374080
B	-3.457758	0.200651	0.500087
O	-3.454495	-1.225037	0.150461
O	-4.143004	0.905629	-0.612321
O	1.118765	0.352509	-0.291394
C	2.379795	0.167493	-0.172858
C	3.318572	1.188813	-0.559909
C	2.927361	-1.060086	0.382958
C	4.695164	0.982952	-0.506320
C	4.280494	-1.281936	0.449180
C	5.268331	-0.278915	-0.006575
O	6.487731	-0.476611	0.036299

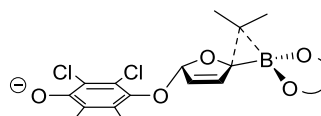
Cl	1.762045	-2.223557	0.941838
Cl	4.943029	-2.762746	1.070427
C	5.610845	1.991677	-0.926794
C	2.766793	2.441210	-0.977911
N	2.305251	3.467972	-1.273799
N	6.349449	2.824420	-1.271379



E = -2244.523986 Hartree

C	3.233788	0.530424	-1.079528
C	4.137194	-0.741711	-0.894789
C	1.989783	0.230993	-1.935131
H	1.280960	1.059633	-1.827978
H	2.250275	0.114203	-2.995113
H	1.497011	-0.691099	-1.604412
C	3.960509	1.746860	-1.650457
H	4.381644	1.516232	-2.638899
H	3.253753	2.579166	-1.758224
H	4.768196	2.063915	-0.983249
C	5.547942	-0.369860	-0.406477
H	6.062652	-1.286722	-0.093979
H	6.134986	0.115201	-1.197972
H	5.481464	0.307452	0.451728
C	4.241993	-1.625671	-2.137739
H	4.671353	-1.061632	-2.977665
H	4.893960	-2.483058	-1.925955
H	3.258005	-2.004291	-2.432535
C	1.173505	-1.036665	0.986870
C	0.808703	-2.452421	1.072501
O	0.118115	-0.292794	1.172187
C	-0.503773	-2.535028	1.341347
H	1.536692	-3.239368	0.929032
C	-1.064870	-1.148681	1.458991
H	-1.138337	-3.402810	1.479979
H	-1.354616	-0.885180	2.482916
C	3.144488	-0.377283	2.523603
H	4.186859	-0.041402	2.396338
C	3.166356	-1.719030	3.267647
H	2.145999	-2.076870	3.475887
H	3.679354	-2.486560	2.672790
H	3.679676	-1.632230	4.238336
C	2.380293	0.692319	3.310866
H	2.826166	0.856247	4.305255
H	2.373442	1.645351	2.768077
H	1.333118	0.393880	3.470415
B	2.685464	-0.471653	0.926716
O	2.833629	0.815960	0.258571
O	3.471260	-1.458799	0.143121
O	-2.072577	-0.904875	0.550077
C	-3.140066	-0.115374	0.980261
C	-4.108822	-0.675306	1.817856
C	-3.294390	1.206662	0.512579
C	-5.239555	0.069692	2.228393
C	-4.401795	1.954605	0.888399
C	-5.458935	1.442084	1.779945
O	-6.444960	2.122139	2.115321

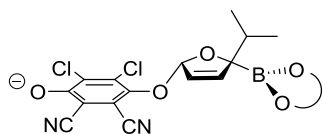
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Cl	-4.615345	3.586464	0.321194
C	-6.203893	-0.518231	3.092748
C	-3.889335	-2.024133	2.245646
N	-3.615905	-3.112440	2.559434
N	-6.979963	-1.023780	3.802894



E = -2244.522441 Hartree

C	4.239309	1.658088	-0.353173
C	5.193338	0.437394	-0.606998
C	3.596801	2.169497	-1.652355
H	2.806358	2.883376	-1.395035
H	4.334234	2.666666	-2.295701
H	3.147112	1.339479	-2.209136
C	4.880966	2.821338	0.398700
H	5.731495	3.224503	-0.168243
H	4.141602	3.620174	0.532426
H	5.229764	2.504633	1.386544
C	6.162867	0.201423	0.562669
H	6.638879	-0.777872	0.432529
H	6.943127	0.973128	0.595360
H	5.627656	0.208070	1.517830
C	5.981585	0.511189	-1.913551
H	6.612386	1.410436	-1.929708
H	6.629407	-0.370022	-2.003575
H	5.307531	0.535267	-2.775010
C	1.757917	-0.903231	-0.359184
C	1.532241	-2.241348	-0.906303
O	0.588017	-0.376344	-0.002375
C	0.220891	-2.514922	-0.840695
H	2.335343	-2.860466	-1.283488
C	-0.489335	-1.338305	-0.232056
H	-0.324290	-3.395562	-1.158322
H	-0.943352	-1.546994	0.742669
C	2.975481	-1.345649	1.591319
H	3.769288	-0.716258	2.011525
C	3.490206	-2.770362	1.427908
H	2.688632	-3.451170	1.111427
H	4.301066	-2.810827	0.690561
H	3.876108	-3.149262	2.388351
C	1.749299	-1.249500	2.485985
H	1.995143	-1.571891	3.510267
H	1.363723	-0.224489	2.528492
H	0.944035	-1.905815	2.127103
B	3.104181	-0.289517	0.067645
O	3.212773	1.082555	0.463903
O	4.277491	-0.664282	-0.679843
O	-1.428447	-0.796283	-1.109903
C	-2.610817	-0.325743	-0.550174
C	-3.592887	-1.236387	-0.148757
C	-2.864372	1.059755	-0.447978
C	-4.831272	-0.797706	0.380411
C	-4.075697	1.516694	0.053745
C	-5.151211	0.619903	0.512699
O	-6.231008	1.040026	0.968751

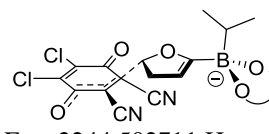
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C	-5.806344	-1.746972	0.793625
C	-3.280991	-2.627419	-0.286478
N	-2.945487	-3.736289	-0.411031
N	-6.590274	-2.544990	1.127290



E = -2244.586571 Hartree

C	3.398484	1.638719	-0.559289
C	4.616703	0.720214	-0.924852
C	2.416754	1.826850	-1.720801
H	1.504664	2.293212	-1.336939
H	2.853411	2.462481	-2.501066
H	2.141714	0.860463	-2.157670
C	3.767907	2.986383	0.047292
H	4.353079	3.576474	-0.670581
H	2.851219	3.536793	0.286392
H	4.350649	2.863360	0.965051
C	5.808867	0.902464	0.020171
H	6.537054	0.105174	-0.168443
H	6.293525	1.872898	-0.141822
H	5.484936	0.842533	1.065638
C	5.069877	0.807435	-2.376763
H	5.404451	1.827744	-2.606293
H	5.908243	0.120099	-2.542438
H	4.258099	0.540511	-3.059073
C	2.271047	-1.716023	0.817635
C	2.000834	-2.711219	-0.287607
O	0.937886	-1.348470	1.264579
C	0.695991	-2.757877	-0.555490
H	2.799457	-3.243073	-0.794369
C	-0.013561	-1.749246	0.308243
H	0.173168	-3.325235	-1.316310
H	-0.909204	-2.102180	0.830973
C	3.046679	-2.314738	2.020443
H	4.029720	-2.613751	1.625729
C	2.344472	-3.551988	2.595603
H	1.347477	-3.277001	2.959305
H	2.225260	-4.336500	1.838848
H	2.923227	-3.958804	3.435881
C	3.255749	-1.259818	3.118362
H	3.807950	-1.691483	3.964080
H	3.815313	-0.391465	2.746248
H	2.284593	-0.900598	3.478674
B	3.023564	-0.461757	0.195757
O	2.713336	0.842904	0.446084
O	4.080638	-0.612268	-0.677618
O	-0.403834	-0.647571	-0.544589
C	-1.658859	-0.113684	-0.345849
C	-2.791917	-0.779320	-0.827915
C	-1.830886	1.139105	0.291098
C	-4.095158	-0.236758	-0.680264
C	-3.092475	1.701283	0.432561
C	-4.325469	1.050768	-0.038267
O	-5.455474	1.560512	0.101892

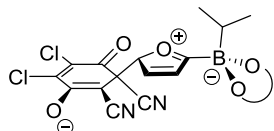
Cl	-0.390276	1.941076	0.884471
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C	-5.224797	-0.946964	-1.172421
C	-2.585123	-2.039015	-1.477329
N	-2.369445	-3.063922	-1.988069
N	-6.139533	-1.546078	-1.582261



E = -2244.502711 Hartree

C	-3.689603	-0.655040	-1.110060
C	-4.650917	0.281707	-0.292694
C	-2.700499	0.151297	-1.967116
H	-1.902196	-0.513800	-2.314021
H	-3.200672	0.599993	-2.836049
H	-2.242431	0.958989	-1.388742
C	-4.401994	-1.685334	-1.986547
H	-5.046498	-1.185598	-2.723630
H	-3.654974	-2.282131	-2.525279
H	-5.012131	-2.360358	-1.377120
C	-5.884073	-0.480644	0.225171
H	-6.403772	0.151201	0.956450
H	-6.579904	-0.729194	-0.588473
H	-5.569600	-1.406226	0.719464
C	-5.102810	1.532667	-1.047977
H	-5.646328	1.257338	-1.963273
H	-5.773263	2.124375	-0.410361
H	-4.243793	2.153981	-1.319158
C	-1.371264	0.325948	1.089439
C	-0.987486	1.576139	1.645147
O	-0.244139	-0.364991	0.804910
C	0.390345	1.632543	1.668514
H	-1.697253	2.331637	1.952168
C	0.859603	0.425729	1.073544
H	1.027050	2.456589	1.967720
H	1.750884	-0.133854	1.327385
C	-2.989249	-1.165255	2.488701
H	-3.993785	-1.604158	2.372568
C	-3.014966	-0.221826	3.696810
H	-2.018790	0.209664	3.879385
H	-3.714825	0.606934	3.525240
H	-3.316708	-0.748680	4.617735
C	-1.982435	-2.302744	2.687073
H	-2.223530	-2.907015	3.578318
H	-1.963531	-2.962573	1.810447
H	-0.965441	-1.906326	2.827818
B	-2.826107	-0.383848	1.019758
O	-2.983430	-1.338884	-0.077973
O	-3.853092	0.666527	0.822839
O	0.858590	-0.603666	-2.140449
C	1.737420	-0.240680	-1.381779
C	1.739815	1.131045	-0.751348
C	2.880632	-1.116829	-0.995421
C	2.984504	1.708278	-0.364268
C	4.001314	-0.587004	-0.443100
C	4.155877	0.891708	-0.141581
O	5.235259	1.321368	0.274949

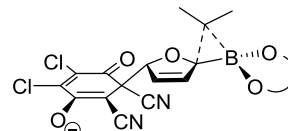
Cl	2.711440	-2.793825	-1.403416
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C	3.040399	3.071662	0.024170
C	0.689077	1.985709	-1.241648
N	-0.168058	2.674307	-1.616761
N	3.040932	4.188517	0.364230



E = -2244.516369 Hartree

C	-2.835259	1.586385	-0.222646
C	-3.954456	0.822185	0.573165
C	-1.674971	2.015980	0.690713
H	-0.823556	2.317036	0.070448
H	-1.964806	2.856177	1.334944
H	-1.349968	1.197179	1.341033
C	-3.333612	2.795262	-1.012918
H	-3.807169	3.525094	-0.341385
H	-2.485432	3.280437	-1.512104
H	-4.056875	2.490065	-1.775995
C	-5.272013	0.757262	-0.219399
H	-5.945789	0.048928	0.278582
H	-5.763134	1.738768	-0.270842
H	-5.077996	0.403523	-1.237920
C	-4.223163	1.379352	1.971151
H	-4.544177	2.429159	1.912637
H	-5.020951	0.798293	2.452262
H	-3.325658	1.319279	2.594469
C	-1.064299	-1.167004	0.226587
C	-0.891548	-2.062950	1.351153
O	0.103116	-0.952406	-0.340554
C	0.418509	-2.374591	1.455313
H	-1.715128	-2.373440	1.979414
C	1.153527	-1.671187	0.368533
H	0.913893	-2.977037	2.207878
H	1.620405	-2.339768	-0.360746
C	-2.874975	-1.918072	-1.463860
H	-3.831944	-1.531315	-1.851379
C	-3.148761	-3.260416	-0.773771
H	-2.213926	-3.722651	-0.420187
H	-3.807370	-3.122689	0.094106
H	-3.623748	-3.979365	-1.460798
C	-1.905063	-2.076825	-2.640168
H	-2.300368	-2.770957	-3.400019
H	-1.709622	-1.108269	-3.116830
H	-0.938481	-2.482385	-2.303243
B	-2.462293	-0.680653	-0.428826
O	-2.383210	0.589749	-1.138794
O	-3.427821	-0.499737	0.680989
O	2.342340	1.204657	-0.637045
C	2.761476	0.094364	-0.387733
C	2.299918	-0.692841	0.870388
C	3.682860	-0.649273	-1.280208
C	3.394592	-1.554866	1.473534
C	4.447125	-1.657874	-0.788199
C	4.427365	-2.110710	0.675986
O	5.296315	-2.913118	1.052756

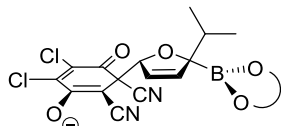
Cl	3.795500	-0.051117	-2.913237
Cl	5.583714	-2.489617	-1.791749
C	3.219505	-2.014564	2.793010
C	1.724643	0.260289	1.832631
N	1.244454	0.983087	2.601880
N	2.990009	-2.393105	3.877769



E = -2244.511986 Hartree

C	-4.054640	-0.565457	-1.487748
C	-4.857728	0.300883	-0.453325
C	-3.505143	0.275707	-2.650038
H	-2.795211	-0.334759	-3.218833
H	-4.309190	0.609084	-3.319089
H	-2.973561	1.155657	-2.271042
C	-4.816658	-1.770646	-2.032130
H	-5.723722	-1.444246	-2.559353
H	-4.179305	-2.314875	-2.739401
H	-5.100562	-2.453741	-1.225298
C	-5.773606	-0.550793	0.439862
H	-6.130215	0.070029	1.270442
H	-6.640065	-0.925159	-0.120887
H	-5.228933	-1.407261	0.850367
C	-5.664360	1.439334	-1.074044
H	-6.400434	1.042360	-1.786643
H	-6.200691	1.983268	-0.286146
H	-5.007553	2.141708	-1.595295
C	-1.292487	0.525433	0.553569
C	-0.897985	1.620707	1.422800
O	-0.183990	-0.118868	0.147119
C	0.441227	1.615194	1.551133
H	-1.606269	2.309438	1.862917
C	0.990322	0.487075	0.735926
H	1.068591	2.320465	2.082100
H	1.514847	-0.271673	1.325336
C	-2.423697	-0.866003	1.971878
H	-3.262454	-1.496462	1.656503
C	-2.831934	-0.012609	3.163041
H	-1.975526	0.547259	3.562026
H	-3.620641	0.696985	2.885327
H	-3.211817	-0.650104	3.978884
C	-1.216600	-1.746795	2.244799
H	-1.441310	-2.467459	3.048102
H	-0.916894	-2.307389	1.352027
H	-0.358751	-1.146421	2.579012
B	-2.690500	-0.017381	0.265701
O	-2.943108	-1.027970	-0.706143
O	-3.814898	0.861961	0.358712
O	1.695317	-0.525118	-2.297964
C	2.275953	-0.326024	-1.250492
C	2.018886	0.936505	-0.388618
C	3.222216	-1.299088	-0.652369
C	3.268227	1.443148	0.320040
C	4.150497	-0.887085	0.247975
C	4.303672	0.562983	0.719384
O	5.302404	0.854491	1.400231

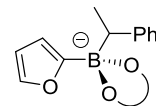
Cl	3.134464	-2.924120	-1.284154
Cl	5.314233	-1.991356	0.901109
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C	1.388441	1.958724	-1.238469
N	0.871467	2.774462	-1.881031
N	3.198235	3.859445	1.219213



E = -2244.574206 Hartree

C	-3.788417	-0.534186	-1.479253
C	-4.281962	0.804786	-0.809777
C	-2.827099	-0.310376	-2.648922
H	-2.387565	-1.272487	-2.932820
H	-3.360870	0.111062	-3.510286
H	-2.011639	0.361604	-2.371614
C	-4.905745	-1.488105	-1.888769
H	-5.548652	-1.012664	-2.641241
H	-4.465695	-2.390998	-2.327960
H	-5.520706	-1.780180	-1.031819
C	-5.626343	0.660649	-0.089614
H	-5.812733	1.570167	0.493048
H	-6.445042	0.524710	-0.807060
H	-5.611615	-0.196388	0.594208
C	-4.294346	2.009822	-1.743207
H	-4.958118	1.819332	-2.597501
H	-4.665575	2.887595	-1.200295
H	-3.285725	2.228386	-2.102496
C	-1.488474	-0.340662	1.529215
C	-1.091372	0.940530	2.213667
O	-0.271707	-0.718787	0.806715
C	0.166854	1.271611	1.923995
H	-1.777439	1.512376	2.828864
C	0.747024	0.253095	0.982368
H	0.707901	2.156937	2.237128
H	1.655504	-0.230724	1.366910
C	-1.847085	-1.496276	2.499440
H	-1.984175	-2.383650	1.867330
C	-3.170192	-1.205550	3.224700
H	-3.079579	-0.306283	3.849488
H	-3.996261	-1.046089	2.518206
H	-3.439927	-2.045402	3.878727
C	-0.723449	-1.776575	3.503666
H	-0.952167	-2.678025	4.088774
H	0.228380	-1.929009	2.982999
H	-0.604192	-0.934876	4.198547
B	-2.620067	-0.142541	0.427279
O	-3.018339	-1.153299	-0.407663
O	-3.283434	1.034607	0.222895
O	0.613910	-0.708434	-2.123160
C	1.461886	-0.310167	-1.344815
C	1.223122	0.894540	-0.414229
C	2.761025	-0.991140	-1.148874
C	2.473064	1.720717	-0.140548
C	3.808939	-0.326187	-0.596766
C	3.761220	1.135206	-0.141759
O	4.831480	1.684924	0.180425

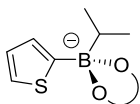
Cl	2.869417	-2.616406	-1.785555
Cl	5.357015	-1.089801	-0.424845
C	2.316417	3.029069	0.356951
C	0.134539	1.692837	-0.993502
N	-0.732126	2.313473	-1.451995
N	2.135701	4.105092	0.785408



ate-11

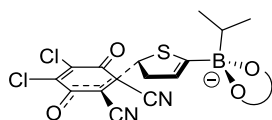
E = -951.115505 Hartree

C	-3.836840	-0.651511	-0.152571
O	-2.766861	0.075984	-0.584464
C	-1.689411	-0.182078	0.251612
C	-2.114266	-1.071094	1.208493
C	-3.494676	-1.379434	0.951758
B	-0.278707	0.598718	-0.011308
O	0.675434	0.160648	1.043536
C	1.814843	-0.429969	0.441912
C	2.237866	-1.651465	1.269378
C	1.329190	-0.784874	-1.017239
O	0.369665	0.216800	-1.292055
C	0.658362	-2.172089	-1.092891
C	2.436262	-0.714857	-2.074770
C	2.974947	0.582407	0.439186
C	-0.593692	2.245901	-0.000102
C	-1.303033	2.644108	1.304099
C	0.651128	3.031362	-0.273386
H	0.196484	-2.274962	-2.083410
H	1.386832	-2.984216	-0.953571
H	-0.127886	-2.258548	-0.337306
H	3.252931	-1.410752	-1.832091
H	2.021148	-0.992024	-3.053421
H	2.840169	0.300043	-2.143159
H	3.124951	0.938971	1.465812
H	3.907811	0.120610	0.082999
H	2.742242	1.443988	-0.189507
H	3.069343	-2.185624	0.785496
H	2.569763	-1.317943	2.262041
H	1.399352	-2.343335	1.399705
H	-1.487084	-1.447960	2.006382
H	-4.145079	-2.046413	1.507114
H	-4.747799	-0.548966	-0.727159
H	-1.438652	3.735328	1.393011
H	-2.287576	2.164116	1.355185
H	-0.730019	2.299557	2.176358
H	-1.286109	2.404072	-0.841679
C	1.170304	3.089293	-1.584465
C	2.370762	3.741859	-1.867315
C	3.099055	4.365768	-0.842944
C	2.597883	4.324112	0.462040
C	1.393132	3.667339	0.739151
H	0.629697	2.570130	-2.370338
H	2.748739	3.755769	-2.889047
H	4.039311	4.869996	-1.059939
H	3.152266	4.794946	1.273218
H	1.032803	3.626410	1.762916



E = -1082.334803 Hartree

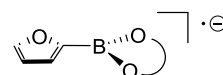
C	-3.886744	-1.281340	-0.577874
S	-2.690091	-0.387574	-1.477912
C	-1.619152	-0.220821	-0.101251
C	-2.205230	-0.840225	0.981752
C	-3.480314	-1.442457	0.724474
B	-0.194112	0.615012	-0.177479
O	0.578982	0.291280	1.067039
C	1.780059	-0.370455	0.722847
C	2.041529	-1.504189	1.723701
C	1.534440	-0.865190	-0.755541
O	0.683731	0.130807	-1.284494
C	0.837922	-2.242297	-0.799490
C	2.805305	-0.940624	-1.610290
C	2.947282	0.633091	0.804214
C	-0.517381	2.217212	-0.355522
C	-1.365050	2.757191	0.808194
C	0.754635	3.065192	-0.499093
H	0.523140	-2.435768	-1.832831
H	1.516445	-3.045271	-0.475736
H	-0.051327	-2.245437	-0.163747
H	3.540839	-1.623850	-1.159960
H	2.547400	-1.315589	-2.609975
H	3.259659	0.049442	-1.719960
H	2.933590	1.098645	1.798450
H	3.919711	0.140387	0.655469
H	2.826054	1.417865	0.052621
H	2.924985	-2.091926	1.431483
H	2.221694	-1.075772	2.719312
H	1.175850	-2.171363	1.786157
H	-1.702751	-0.857117	1.945223
H	-4.067050	-1.973477	1.472209
H	-4.797081	-1.640209	-1.045701
H	-1.104549	2.330873	-1.285074
H	1.336667	3.030611	0.433257
H	1.390542	2.681164	-1.308087
H	0.521907	4.125436	-0.707115
H	-1.584477	3.834644	0.697397
H	-2.317259	2.216216	0.891732
H	-0.822062	2.619047	1.755691



E = -2567.477796 Hartree

C	4.342023	1.145482	0.069750
C	3.099330	1.628375	-0.478596
C	2.041670	0.731631	-0.844289
C	2.419696	-0.701228	-1.164724
C	3.611130	-1.220111	-0.434266
C	4.503446	-0.364957	0.123150
O	1.780472	-1.385408	-1.940980
C	0.974836	1.235027	-1.677838
N	0.104098	1.644826	-2.327774

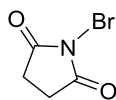
Cl	3.814639	-2.945046	-0.455936
C	2.864811	3.026602	-0.450474
N	2.633554	4.170458	-0.413507
Cl	5.936365	-0.926177	0.913373
O	5.253327	1.866246	0.486732
C	1.009453	0.280260	0.900751
S	-0.299656	-0.907471	0.667921
C	-1.537943	0.266364	0.851094
C	-0.968381	1.533490	1.159017
C	0.405926	1.546917	1.226496
B	-3.122401	-0.113237	0.842130
O	-3.875574	0.991721	0.205292
C	-4.679912	0.431613	-0.826462
C	-4.803589	1.436978	-1.972778
C	-3.912541	-0.886663	-1.205139
O	-3.413111	-1.324090	0.056410
C	-2.740153	-0.611025	-2.161535
C	-4.798633	-1.984715	-1.794471
C	-6.077265	0.132107	-0.252523
C	-3.560363	-0.348408	2.431730
C	-2.875079	-1.547457	3.095758
C	-3.440439	0.910460	3.298911
H	-2.106689	-1.504810	-2.210152
H	-3.097493	-0.374190	-3.172521
H	-2.127424	0.225900	-1.815147
H	-5.293149	-1.630914	-2.710156
H	-4.180738	-2.855911	-2.047821
H	-5.561874	-2.298719	-1.074881
H	-6.476549	1.053652	0.189130
H	-6.769910	-0.219224	-1.030175
H	-6.006003	-0.630830	0.530104
H	-5.342874	0.992397	-2.821696
H	-5.362213	2.317464	-1.628691
H	-3.815488	1.763805	-2.310370
H	-1.603981	2.401639	1.292228
H	1.008050	2.431358	1.411466
H	1.907853	-0.068021	1.402841
H	-4.631001	-0.585381	2.318281
H	-2.384657	1.159250	3.484407
H	-3.908174	1.770240	2.800779
H	-3.921102	0.773964	4.282260
H	-3.329336	-1.786040	4.072401
H	-2.941379	-2.437262	2.455714
H	-1.809023	-1.341040	3.276137



E = -640.745554 Hartree

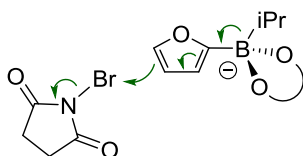
C	1.113219	-0.394698	-0.730562
O	1.932406	-0.581839	0.355031
C	1.340793	-1.564307	1.170115
C	0.170449	-1.996295	0.527441
C	0.031308	-1.248083	-0.667881
B	1.996858	-1.983258	2.464167
O	1.493304	-3.033441	3.253141
C	2.244631	-3.033608	4.481372
C	2.360641	-4.466150	4.997551
C	3.607039	-2.386554	4.040190
O	3.206042	-1.496114	2.982371

C	4.573572	-3.422849	3.448049
C	4.310927	-1.581916	5.128653
C	1.481335	-2.169316	5.493828
H	5.413208	-2.893957	2.981681
H	4.963594	-4.094570	4.226302
H	4.068902	-4.025096	2.682954
H	4.546268	-2.223513	5.989576
H	5.248853	-1.172704	4.732135
H	3.685900	-0.748600	5.467490
H	0.473825	-2.585098	5.621276
H	1.983519	-2.151806	6.469531
H	1.387442	-1.140802	5.120615
H	3.021697	-4.506549	5.875570
H	1.368814	-4.831134	5.293936
H	2.757865	-5.133819	4.225041
H	-0.501100	-2.753335	0.913537
H	-0.765226	-1.320438	-1.400977
H	1.441528	0.340261	-1.452235



E = -373.2200217 Hartree

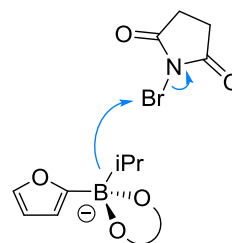
N	-0.079896	-0.013390	-0.173785
C	-0.079052	-0.032485	1.234395
C	1.383503	-0.041692	1.668300
C	2.209629	-0.026260	0.367513
C	1.194955	-0.008508	-0.771598
O	1.414723	0.006908	-1.959586
H	1.558882	0.832738	2.303969
O	-1.061078	-0.039813	1.938192
H	2.845839	-0.909564	0.247211
H	2.850198	0.856796	0.270874
H	1.554705	-0.933636	2.280339
Br	-1.657227	0.003614	-1.175413



E = -1132.5768145 Hartree

C	-3.161304	2.467787	0.039247
C	-3.959207	1.711979	1.160940
C	-1.931101	3.203201	0.591835
H	-1.312036	3.530682	-0.250620
H	-2.220042	4.079493	1.186486
H	-1.333028	2.532064	1.218305
C	-3.999083	3.422355	-0.807384
H	-4.436189	4.209571	-0.177907
H	-3.359554	3.894571	-1.562768
H	-4.804810	2.888915	-1.320845
C	-5.401715	1.395646	0.738954
H	-5.841288	0.705740	1.469060
H	-6.011188	2.307905	0.702048
H	-5.422003	0.920645	-0.246737
C	-3.969104	2.417589	2.515597
H	-4.433722	3.409367	2.428290

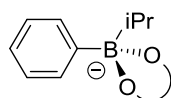
H	-4.548261	1.823818	3.234016
H	-2.952689	2.534411	2.902440
C	-1.355292	-0.681811	0.018211
C	-1.019237	-1.735536	0.964776
O	-0.467957	-0.714934	-1.000528
C	0.034865	-2.417129	0.474537
H	-1.549680	-1.888039	1.895761
C	0.463651	-1.796256	-0.803054
H	0.572579	-3.239290	0.931306
C	-3.228821	-1.408612	-0.871993
H	-2.518879	-2.192996	-1.142420
C	-3.789546	-0.816306	-2.159228
H	-4.534775	-0.038193	-1.959490
H	-2.995009	-0.363015	-2.762636
H	-4.270752	-1.612853	-2.753739
C	-4.275875	-1.987207	0.067725
H	-4.824849	-2.804315	-0.432630
H	-3.814968	-2.395786	0.975748
H	-5.000668	-1.228499	0.377339
B	-2.537477	0.268984	0.058297
O	-2.697926	1.391961	-0.789403
O	-3.227676	0.482547	1.287256
H	0.443045	-2.444916	-1.683143
Br	2.371212	-1.117109	-0.676164
N	4.857364	-0.356710	-0.483673
C	5.508833	0.523375	-1.299314
C	5.677967	-0.806457	0.509234
C	6.971748	0.737972	-0.828527
C	7.086322	-0.165747	0.401128
H	7.652110	0.467729	-1.646124
H	7.833831	-0.963113	0.301452
O	5.047230	1.097242	-2.289193
O	5.391287	-1.614519	1.398242
H	7.123330	1.803680	-0.614948
H	7.303948	0.372854	1.332261



E = -1132.5702497 Hartree

C	-6.492228	0.629746	0.346511
C	-5.011835	1.007786	0.126162
N	-4.254415	-0.140962	0.079306
C	-5.003149	-1.285987	0.228405
C	-6.486244	-0.902114	0.415301
Br	-2.053238	-0.159599	-0.232042
C	0.376263	-0.359729	-0.886742
C	0.450506	-1.871834	-0.945910
O	-4.594771	-2.439786	0.218810
O	-4.612925	2.158991	0.014652
B	2.149617	0.202679	-0.184734
O	2.222761	-0.324919	1.154004
C	3.569254	-0.756036	1.346246
C	3.596745	-1.856831	2.406507

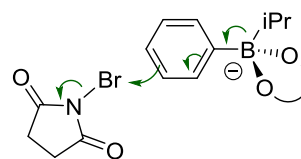
C	2.095003	1.778944	-0.392658
C	1.191927	3.795605	-0.160439
C	2.261099	3.957560	-0.995303
C	2.840047	2.651302	-1.145007
H	2.586356	4.886255	-1.449019
O	3.190365	-0.413413	-0.958926
C	3.996493	-1.227837	-0.097257
C	3.697229	-2.712199	-0.350855
C	5.467875	-0.963903	-0.434226
C	4.397679	0.443720	1.842598
C	0.265985	0.341985	-2.229902
H	0.447208	4.468117	0.241275
H	3.941624	0.817947	2.766866
H	5.438211	0.157908	2.047343
H	4.385548	1.251121	1.103253
H	4.611803	-2.265081	2.511487
H	3.287197	-1.437001	3.371596
H	2.911057	-2.669593	2.149182
H	3.798903	-2.913019	-1.424497
H	4.405631	-3.348480	0.197023
H	2.682736	-2.972911	-0.044845
H	6.126985	-1.494181	0.267587
H	5.677164	-1.325491	-1.449129
H	5.694279	0.105963	-0.394686
H	0.140221	0.156003	0.051297
H	1.327690	-2.160622	-1.539672
H	0.548762	-2.301056	0.056923
H	-0.439767	-2.305636	-1.423035
H	-0.535647	-0.099107	-2.840465
H	0.057893	1.409517	-2.108342
H	1.213109	0.237814	-2.781209
H	3.694616	2.368872	-1.746377
H	-6.832786	-1.303047	1.375223
H	-6.842962	1.112330	1.266462
H	-7.074625	-1.383250	-0.375002
H	-7.083579	1.033224	-0.483993
O	1.080023	2.492008	0.212945



E = -761.5789701 Hartree

C	-3.757469	-0.485058	0.043502
C	-3.168403	-0.057569	-1.155154
C	-1.816859	0.308404	-1.180282
C	-1.003893	0.258106	-0.031593
C	-1.622283	-0.172738	1.156958
C	-2.974037	-0.540099	1.204197
B	0.572087	0.722138	-0.092812
O	1.314549	0.159506	1.091659
C	2.316005	-0.731664	0.647333
C	2.370841	-1.947492	1.582849
H	-4.808391	-0.771792	0.071041
C	1.885381	-1.079492	-0.829975
O	1.277274	0.115610	-1.270595
C	0.874625	-2.246364	-0.876563
C	3.055986	-1.420884	-1.759979
C	3.683611	-0.021525	0.687400
C	0.633412	2.366872	-0.170581

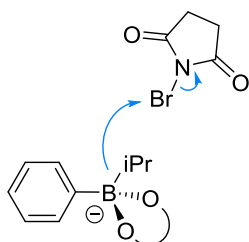
C	-0.006106	3.011092	1.070838
C	2.060292	2.905615	-0.345133
H	0.458503	-2.301982	-1.890541
H	1.357588	-3.204538	-0.634599
H	0.050406	-2.076525	-0.178896
H	3.625245	-2.279163	-1.372882
H	2.666774	-1.680406	-2.753974
H	3.730783	-0.565095	-1.866222
H	3.829057	0.392852	1.693679
H	4.509332	-0.713795	0.464388
H	3.702590	0.800271	-0.033096
H	3.079469	-2.701230	1.207070
H	2.701568	-1.624958	2.579848
H	1.381331	-2.405756	1.678796
H	0.044322	2.673547	-1.054387
H	2.659093	2.669523	0.546032
H	2.550086	2.442288	-1.212222
H	2.075407	4.003294	-0.476369
H	0.034459	4.115131	1.035162
H	-1.056154	2.708445	1.182717
H	0.531044	2.683458	1.974088
H	-1.363880	0.626464	-2.119098
H	-1.010228	-0.231098	2.055848
H	-3.418558	-0.872578	2.143190
H	-3.764826	-0.015177	-2.067417



E = -1134.7813526 Hartree

C	0.314747	-1.709379	-1.397409
C	1.032271	-2.136325	-0.191855
C	0.308102	-1.945862	1.068674
C	-0.891007	-1.306481	1.122658
C	-1.549204	-0.825233	-0.072897
C	-0.884210	-1.071849	-1.335110
Br	2.837240	-0.905885	-0.071610
H	0.802961	-2.265878	1.982944
B	-2.911414	-0.141621	-0.018524
O	-3.420609	0.419235	1.190507
C	-4.404541	1.401620	0.846005
C	-5.799777	0.762934	0.916772
H	0.814893	-1.850038	-2.353006
O	-3.469937	0.560778	-1.131006
C	-4.000235	1.788920	-0.621182
C	-5.162482	2.238840	-1.504129
C	-2.881941	2.842842	-0.656054
C	-4.323728	2.551620	1.849034
C	-3.413691	-2.107763	-0.180077
C	-4.334825	-2.122618	-1.391097
C	-4.095001	-2.422294	1.142122
N	4.900746	0.391628	0.041678
C	5.493557	0.978442	-1.042782
C	6.780506	1.724853	-0.612112
C	6.858032	1.475690	0.897262
C	5.607283	0.611109	1.192329
O	5.102377	0.945618	-2.208857

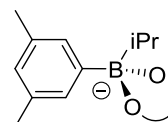
O	5.332408	0.202007	2.319816
H	1.542900	-3.097048	-0.281906
H	-2.515813	2.931609	-1.685358
H	-3.242538	3.823671	-0.319762
H	-2.046747	2.534500	-0.017312
H	-5.646277	3.128446	-1.077670
H	-4.785151	2.492747	-2.502399
H	-5.908269	1.444420	-1.608099
H	-5.943317	0.336891	1.916846
H	-6.585707	1.507120	0.732531
H	-5.896229	-0.039450	0.179134
H	-4.994176	3.369532	1.550670
H	-4.629251	2.194780	2.840622
H	-3.302226	2.936460	1.920204
H	-2.603690	-2.818527	-0.343570
H	-5.157733	-1.406887	-1.286085
H	-3.791424	-1.863686	-2.307468
H	-4.766893	-3.131768	-1.517798
H	-4.509781	-3.446069	1.116653
H	-3.384141	-2.366852	1.975359
H	-4.911293	-1.725506	1.353574
H	-1.366779	-0.708857	-2.239068
H	-1.373025	-1.117159	2.078072
H	6.682234	2.783176	-0.883776
H	6.806390	2.389410	1.502209
H	7.752174	0.923299	1.211826
H	7.630305	1.318825	-1.174718



E = -1134.7970374 Hartree

C	-6.378164	0.305134	1.130154
C	-4.847216	0.490662	1.192394
N	-4.265729	-0.212175	0.161154
C	-5.180938	-0.873707	-0.625103
C	-6.601083	-0.604447	-0.084554
Br	-2.074771	-0.282033	-0.198493
C	0.355757	-0.515915	-0.914859
C	0.372711	-2.019371	-1.093502
O	-4.943870	-1.571422	-1.602394
O	-4.275423	1.163053	2.039415
B	2.124578	-0.033111	-0.159790
O	2.176620	-0.664943	1.139146
C	3.511736	-1.139153	1.301059
C	3.514626	-2.302773	2.292076
C	2.082559	1.569046	-0.200062
C	1.225049	2.292873	0.648491
C	1.168775	3.689698	0.615513
C	1.979997	4.402743	-0.277607
C	2.842599	3.703339	-1.130445
C	2.887211	2.304258	-1.087544
H	0.488837	4.221321	1.278884
H	3.476137	4.248059	-1.829740

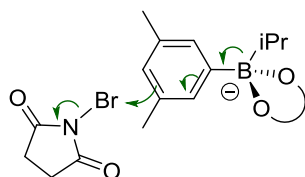
O	3.145998	-0.635743	-0.973996
C	3.923734	-1.530512	-0.169874
C	3.575146	-2.985182	-0.516597
C	5.403483	-1.295935	-0.490932
C	4.372350	0.007409	1.866287
C	0.253086	0.289037	-2.198195
H	1.936308	5.490143	-0.310322
H	3.928646	0.337865	2.812868
H	5.405226	-0.317880	2.049638
H	4.381833	0.858691	1.177781
H	4.518693	-2.743364	2.367368
H	3.219790	-1.934877	3.282652
H	2.806797	-3.079977	1.988694
H	3.667332	-3.119200	-1.601424
H	4.263733	-3.678608	-0.014590
H	2.553480	-3.230279	-0.222150
H	6.043482	-1.889918	0.176870
H	5.602571	-1.601364	-1.526216
H	5.664589	-0.238764	-0.385695
H	0.113913	-0.080232	0.060433
H	1.245817	-2.293983	-1.699782
H	0.443208	-2.530164	-0.127064
H	-0.527687	-2.377182	-1.613187
H	-0.569616	-0.076251	-2.830023
H	0.091964	1.351530	-1.994513
H	1.191382	0.190375	-2.766056
H	0.585031	1.750819	1.342602
H	3.556256	1.759762	-1.750920
H	-7.069823	-1.564614	0.161592
H	-6.716090	-0.131512	2.077433
H	-7.196146	-0.141203	-0.880496
H	-6.846577	1.291950	1.035881



E = -840.2217759 Hartree

C	1.527033	-0.921371	-0.691972
C	1.788822	-0.365455	0.571767
C	1.467322	-1.109279	1.712683
C	0.906931	-2.399497	1.646118
C	0.666446	-2.915481	0.363401
C	0.961632	-2.197286	-0.806791
B	0.517323	-3.216506	3.017983
O	0.366080	-4.684562	2.712916
C	1.340336	-5.421073	3.421470
C	1.885671	-6.541284	2.525036
H	1.767597	-0.354364	-1.593482
C	2.415554	-4.339195	3.822588
O	1.636207	-3.178795	4.017655
C	3.449511	-4.110947	2.697799
C	3.174718	-4.657643	5.116127
C	0.689908	-6.063145	4.663252
C	-0.846232	-2.544931	3.654274
C	-2.032789	-2.662991	2.683321
C	-1.236832	-3.146193	5.011912
H	4.037532	-3.217978	2.945544
H	4.128366	-4.970677	2.597118

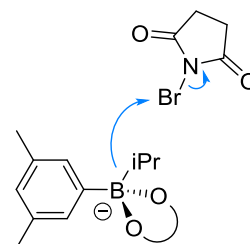
H	2.950500	-3.936384	1.740957
H	3.702107	-5.619731	5.033862
H	3.915722	-3.869012	5.305344
H	2.489083	-4.698794	5.968822
H	-0.190388	-6.632226	4.336820
H	1.382572	-6.744307	5.180091
H	0.363624	-5.288267	5.361888
H	2.712477	-7.074020	3.019065
H	1.083560	-7.262196	2.314326
H	2.242401	-6.134958	1.573031
H	-0.638645	-1.470032	3.808208
H	-1.516282	-4.202429	4.888191
H	-0.394949	-3.101000	5.715893
H	-2.101148	-2.623952	5.462099
H	-2.957592	-2.222877	3.099134
H	-1.815760	-2.169401	1.726211
H	-2.229966	-3.724901	2.470946
H	1.673847	-0.684698	2.695839
H	0.243217	-3.917144	0.285961
C	0.654206	-2.786402	-2.168142
C	2.437108	0.998682	0.686864
H	1.138698	-2.212641	-2.970850
H	0.996817	-3.828651	-2.236319
H	-0.428659	-2.790835	-2.366989
H	2.014461	1.708873	-0.039169
H	2.297986	1.413774	1.693796
H	3.521165	0.947675	0.497533



E = -1213.4336166 Hartree

C	-5.402509	1.159036	1.031107
N	-4.807987	0.605410	-0.067699
C	-5.486384	0.902765	-1.215903
C	-6.717235	1.790494	-0.902671
C	-6.657053	1.968776	0.617506
Br	-2.739998	-0.757864	0.038310
O	-5.202749	0.539628	-2.358353
O	-5.033897	1.057034	2.202102
C	-0.972924	-1.998906	0.165786
C	-0.239048	-1.842601	-1.108229
C	0.960953	-1.201961	-1.136814
C	1.603409	-0.707929	0.058720
C	0.943466	-0.965742	1.318399
C	-0.257060	-1.599747	1.396688
C	-0.897855	-2.347899	-2.363127
C	-0.934868	-1.854594	2.715852
B	2.959298	-0.012914	0.009393
O	3.509905	0.692321	1.123675
C	4.038746	1.921478	0.614999
C	2.916392	2.971352	0.641358
C	3.469852	-1.982230	0.177419
C	4.167453	-2.292702	-1.137200
O	3.474224	0.546560	-1.197386
C	4.452889	1.532918	-0.848986

C	4.374183	2.680697	-1.854688
C	4.378405	-1.989922	1.397757
C	5.850732	0.898976	-0.909744
C	5.193957	2.377420	1.504087
H	-1.471233	-2.968172	0.255840
H	2.544154	3.061037	1.668378
H	3.275240	3.952730	0.304764
H	2.085911	2.658380	-0.001243
H	5.677048	3.267954	1.078751
H	4.809489	2.632062	2.499451
H	5.942161	1.586136	1.614566
H	6.001985	0.470940	-1.907831
H	6.632795	1.646499	-0.722513
H	5.945395	0.098849	-0.169373
H	5.040028	3.501451	-1.553788
H	4.686879	2.323100	-2.843774
H	3.351835	3.061936	-1.932718
H	2.662293	-2.697502	0.332441
H	5.196800	-1.267806	1.300991
H	3.823274	-1.734739	2.308178
H	4.817184	-2.995565	1.529724
H	4.586778	-3.314628	-1.107783
H	3.465757	-2.239620	-1.978184
H	4.983227	-1.592568	-1.339203
H	1.437547	-0.626005	2.225881
H	1.461933	-1.036268	-2.087519
H	-1.169083	-3.409106	-2.255853
H	-1.828156	-1.798409	-2.558328
H	-0.230781	-2.240725	-3.227107
H	-1.218774	-2.914098	2.805660
H	-0.274967	-1.594645	3.552471
H	-1.859491	-1.267594	2.793499
H	-6.527130	3.009983	0.938129
H	-6.630096	2.728381	-1.465185
H	-7.621849	1.279193	-1.254920
H	-7.529647	1.568331	1.148491



E = -1213.4412676 Hartree

C	1.065869	3.937210	-0.102555
C	0.324147	3.060941	0.700309
C	0.686125	1.706514	0.717328
C	1.738787	1.202146	-0.060861
C	2.459018	2.114995	-0.851299
C	2.143812	3.478828	-0.877110
B	2.042798	-0.372434	-0.097862
O	3.176047	-0.767825	-0.894318
C	4.035272	-1.600764	-0.108564
C	5.482501	-1.162411	-0.351060
H	0.790835	4.992481	-0.135093
C	3.523499	-1.351298	1.361736
O	2.139775	-1.069964	1.167091

C	4.187440	-0.122130	2.011018	H	3.273155	1.739274	-1.469492
C	3.667519	-2.552949	2.295055	C	2.944889	4.447705	-1.720762
C	3.880882	-3.063859	-0.545978	C	-0.856733	3.541214	1.514864
C	0.412759	-1.070423	-0.959613	H	3.595925	5.080638	-1.097988
C	0.318826	-0.295281	-2.260883	H	3.585223	3.910808	-2.432625
C	0.522945	-2.571268	-1.103122	H	2.288403	5.120834	-2.290648
H	3.664605	0.097423	2.949435	H	-1.095899	4.588391	1.284552
H	5.248963	-0.304726	2.226104	H	-1.747290	2.928540	1.320196
H	4.098545	0.752475	1.358416	H	-0.645507	3.473602	2.592738
H	4.722901	-2.846302	2.386185	Br	-2.044732	-0.782464	-0.307888
H	3.292089	-2.285765	3.290816	N	-4.223000	-0.482111	0.062149
H	3.091593	-3.407754	1.927560	C	-5.219625	-1.355638	-0.305915
H	4.019851	-3.122338	-1.632688	C	-4.697707	0.643309	0.694524
H	4.632341	-3.699530	-0.057770	C	-6.584056	-0.777737	0.127491
H	2.887204	-3.442750	-0.301032	C	-6.235265	0.560373	0.791797
H	6.167439	-1.704967	0.315929	H	-7.067982	-1.493143	0.802969
H	5.760837	-1.382063	-1.389975	H	-6.523566	0.618983	1.848013
H	5.598158	-0.087850	-0.181259	O	-5.083817	-2.425961	-0.884004
H	0.072603	-0.660529	-0.003007	O	-4.035766	1.580221	1.123627
H	1.398279	-2.802586	-1.725379	H	-7.220766	-0.678754	-0.759597
H	0.652042	-3.051399	-0.126742	H	-6.665459	1.431471	0.283520
H	-0.360804	-3.002964	-1.595148				
H	-0.439601	-0.730320	-2.928647				
H	0.069171	0.754555	-2.085431				
H	1.292485	-0.335100	-2.773558				
H	0.101503	1.023923	1.332408				