

Supplementary Materials
for

Hydrogen Atom Transfer Induced Boron Retaining Coupling of Organoboronic Esters and Organolithium Reagents

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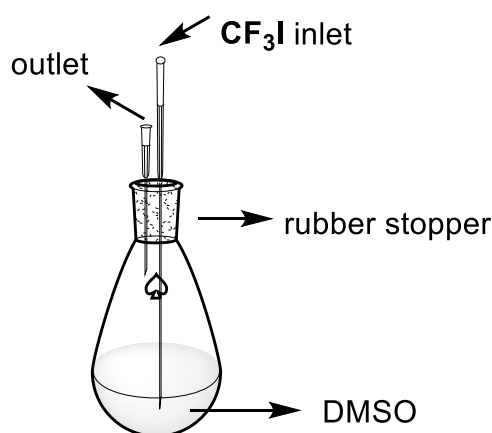
1. General Information

All reactions involving air or moisture sensitive reagents were carried out in flame-dried glassware under argon atmosphere using standard *Schlenk* techniques. Solvents used in reactions were either freshly distilled or obtained in extra-dry grade from commercial sources. Diethyl ether (Et₂O) was refluxed over K and freshly distilled from K-Na-alloy (4:1) afterwards. Tetrahydrofuran (THF) was refluxed over Na and distilled from K afterwards. Acetonitrile (MeCN, 99.9%, Extra Dry over Molecular Sieves) was purchased from *Acros Organics*. Dimethyl sulfoxide (DMSO, 99.9%, Extra Dry over Molecular Sieves) was purchased from *Acros Organics*. Solvents for extraction and for flash chromatography were distilled. Otherwise noticed, commercially available arylboronic acid pinacol esters were purchased from *ABCR*, *Acros Organics*, *Alfa Aesar*, *Fluka*, *Sigma Aldrich* and *TCI* and were used as received. *n*-Butyllithium was purchased from *Acros Organics*. *s*-Butyllithium, isopropyllithium, phenyllithium and lithium were purchased from *Sigma Aldrich*. Trifluoromethyl iodide was purchased from *ABCR* and dissolved in DMSO. All other chemicals were purchased from *ABCR*, *Acros Organics*, *Alfa Aesar*, *Fluka*, *Sigma Aldrich* and *TCI* and were used as received. Flash chromatography (**FC**) was performed on *Merck* silica gel 60 (40-63 μ m). *Merck* silica gel 60 F254 plates were used for thin layer chromatography (**TLC**) using UV light (254/366 nm) or oxidation with KMnO₄ (1.5 g in 200 mL H₂O, 5 g NaHCO₃) for detection. Melting points (**MP**) were determined with a *Stuart SMP10* and are uncorrected. Infrared spectra (**IR**) were measured on a *Digilab 3100 FT-IR Excalibur Series* spectrometer and the position of the absorption bands is given in wave numbers ν (cm⁻¹). **¹H NMR** (300 MHz, 400 MHz and 600 MHz), **¹³C NMR** (75 MHz, 100 MHz and 151 MHz), **¹⁹F NMR** (282 MHz and 564 MHz) and **¹¹B NMR** (96 MHz, 128 MHz and 192 MHz) spectra were measured on a *Bruker DPX 300*, *Bruker AV 300* or an *Agilent DD2 600* spectrometer. The multiplicity of all signals were described as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Chemical shifts (δ in ppm) were referenced on the residual peak of CDCl₃ (¹HNMR: δ = 7.26; ¹³C NMR: δ = 77.0) or on an external standard (CFCl₃: ¹⁹F NMR: δ = 0.0). **HRMS ESI** (m/z) measurements were performed on a *Bruker MicroTof* and **HRMS EI** (m/z) on a *Waters-Micromass QuattroMicro GC-MS*. **Chiral HPLC** analysis was performed on a *Hewlett Packard HP 1100 Series* HPLC System using AD-H (0.46*25 cm, 5 μ m silica-gel, *Daicel*TM) and IC (0.46*25 cm, 5 μ m silica-gel, *Daicel*TM) chiral columns eluting with a mixture of cyclohexane and isopropyl alcohol. Optical rotation ($[\alpha]_D^T$) was measured on a *Bellingham and Stanley Ltd. ADP220* polarimeter and is quoted in (° ml)(g dm)⁻¹. GCMS was performed on an *Agilent 6890+* with an *Agilent HP-5ms* column (15.0 m \times 250 μ m \times 0.30 μ m film thickness) and with an *Agilent 5973* mass detector operating at 70 eV. The method used for GCMS was: start at 50 °C and 1 ml/min, 1.85 psi, increase to 300 °C at 10 °C/min, hold for 15 min. Gas Chromatography (GC) was performed on an *Hewlett Packard HP 6890 series GC* system using an *Agilent HP-1* column (30 m \times 0.32 mm \times 0.25 μ m film thickness). The method used for GC was: start at 50 °C and 1.5 ml/min, 3.81 psi, increase to 300 °C at 10 °C/min, hold for 15 min.

Chiral GC analysis was performed on a *Hewlett Packard HP 6890 Series* GC System equipped with a *SUPELCO Beta DextTM 120* (30 m×0.25 mm×25 µL film thickness) column combined with a FID detector. The method used for chiral GC was: start at 50 °C and 1.5 ml/min, 8.86 psi, increase to 100 °C at 5 °C/min, hold for 0 min, then increase to 150 °C at 1 °C/min, hold for 0 min, then increase to 200 °C at 1 °C/min, hold for 20 min. Emission spectra were recorded using *Jasco FP-8300* spectrofluorometer, and UV/vis absorption spectra were recorded using *Jasco V-730* spectrophotometer.

2. General Procedures for Coupling of Organoboronic Esters and Organolithium Reagents

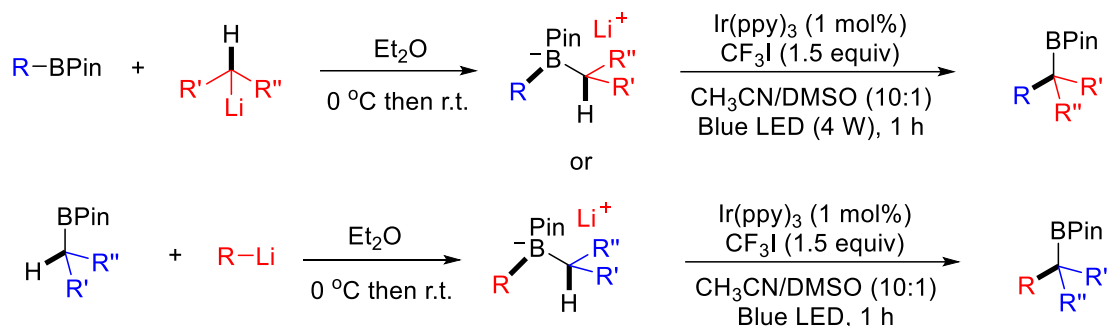
2.1 Preparation of CF₃I solution in DMSO



Apparatus for CF₃I solution preparation

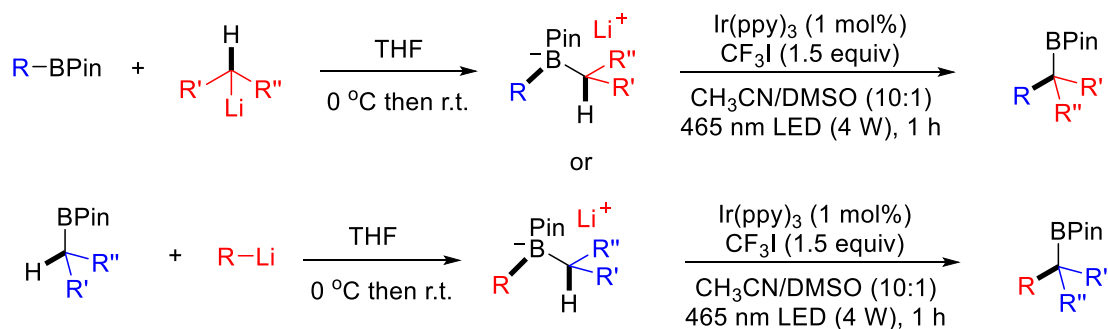
In a 10 mL flask was charged with 5 mL anhydrous DMSO under Argon flow. The flask was sealed with a rubber stopper and the mass of the flask was weighed to be m_1 . After bubbling CF₃I gas into the DMSO in the flask, the mass of the vial was weighed to be m_2 and the volume of the solution was determined to be V by a 10 mL syringe. The concentration of the prepared CF₃I solution was calculated to be $\frac{m_2 - m_1}{V \cdot M(\text{CF}_3\text{I})}$. ($M(\text{CF}_3\text{I})$ is the molecular weight of CF₃I)

2.2 General Procedure for coupling of organoboronic esters and organolithium reagents (GP1)



Organoboronic ester (0.20 mmol, 1.0 equiv) was dissolved in diethyl ether (2.0 mL). The alkyllithium solution (0.22 mmol, 1.1 equiv) was added dropwise over 5 min at 0 °C. The mixture was stirred at 0 °C for 30 min then room temperature for another 30 min. The solvent was carefully removed *in vacuo* and further dried for 30 min under high vacuum. After subsequent addition of Ir(ppy)₃ (1.3 mg, 0.002 mmol, 0.01 equiv), acetonitrile (2 mL), DMSO (0.1 mL) under argon, the mixture was stirred for 1 min until all solid was dissolved. Then CF₃I (3.0 M in DMSO, 0.1 mL, 0.3 mmol, 1.5 equiv) was added to the reaction mixture and the reaction mixture was immediately irradiated by a 4 W blue LED (465 nm) and stirred for 1 h. The reaction mixture was diluted with 20 mL CH₂Cl₂ and quenched with saturated NH₄Cl aqueous solution. The organic phase was separated and dried over MgSO₄ and concentrated under reduced pressure. Flash column chromatography eluting with pentane and CH₂Cl₂ afforded the desired product.

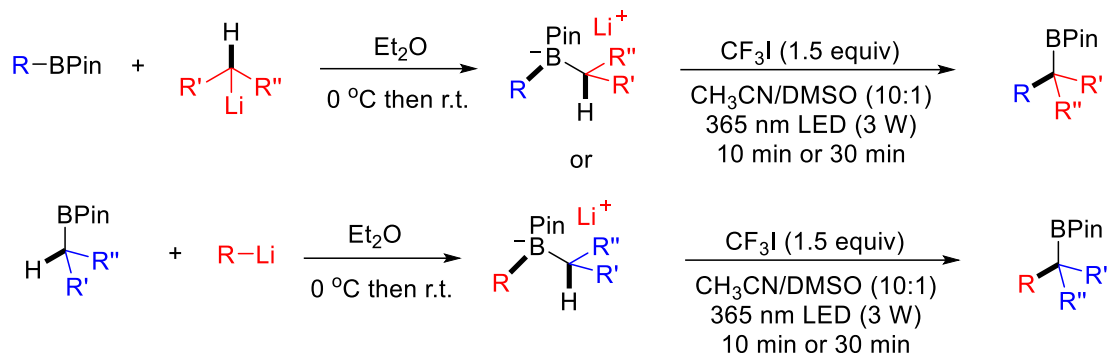
2.3 General Procedure for coupling of organoboronic esters and organolithium reagents (GP2)



Organoboronic ester (0.20 mmol, 1.0 equiv) was dissolved in tetrahydrofuran (2.0 mL). The alkyllithium solution (0.22 mmol, 1.1 equiv) was added dropwise over 5 min at 0 °C. The mixture was stirred at 0 °C for 30 min then room temperature for another 30 min. The solvent was carefully removed *in vacuo* and further dried for 30 min under high vacuum. After subsequent addition of Ir(ppy)₃ (1.3 mg, 0.002 mmol, 0.01 equiv), acetonitrile (2 mL), DMSO (0.1 mL) under argon, the mixture was stirred for 1 min until all solid was dissolved. Then CF₃I (3.0 M in DMSO, 0.1 mL, 0.3 mmol, 1.5 equiv) was added to the reaction mixture and the reaction mixture was immediately irradiated by a 4 W blue LED (465 nm) and stirred for 1 h. The reaction mixture was diluted with 20 mL CH₂Cl₂ and quenched with saturated NH₄Cl aqueous solution. The organic phase was separated and dried over MgSO₄ and concentrated

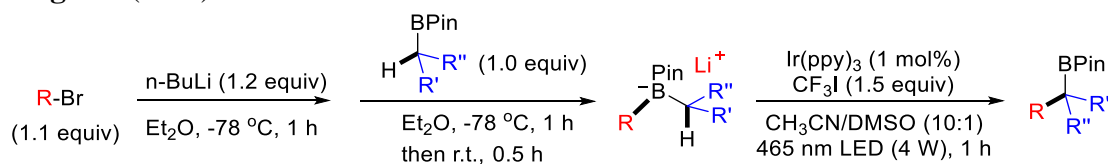
under reduced pressure. Flash column chromatography eluting with pentane and CH₂Cl₂ afforded the desired product.

2.4 General Procedure for coupling of organoboronic esters and organolithium reagents (GP3)



Organoboronic ester (0.20 mmol, 1.0 equiv) was dissolved in diethyl ether (2.0 mL). The alkyllithium solution (0.22 mmol, 1.1 equiv) was added dropwise over 5 min at 0 °C. The mixture was stirred at 0 °C for 30 min then room temperature for another 30 min. The solvent was carefully removed *in vacuo* and further dried for 30 min under high vacuum. After subsequent addition of acetonitrile (2 mL), DMSO (0.1 mL) under argon, the mixture was stirred for 1 min until all solid was dissolved. Then CF₃I (3.0 M in DMSO, 0.1 mL, 0.3 mmol, 1.5 equiv) was added to the reaction mixture and the reaction mixture was immediately irradiated by a 3 W LED (365 nm) and stirred for 10 or 30 min. (10 min for C(sp²)-C(sp³) coupling and 30 min for C(sp³)-C(sp³) coupling) The reaction mixture was diluted with 20 mL CH₂Cl₂ and quenched with saturated NH₄Cl aqueous solution. The organic phase was separated and dried over MgSO₄ and concentrated under reduced pressure. Flash column chromatography eluting with pentane and CH₂Cl₂ afforded the desired product.

2.5 General Procedure for coupling of organoboronic esters and organolithium reagents (GP4)



To a solution of arylbromide (0.22 mmol, 1.1 equiv) in diethyl ether (2 mL) was added a solution of *n*-butyllithium (1.6 M, 0.24 mmol, 1.2 equiv) under -78 °C over a period of 5 min. The mixture was stirred at that temperature for 1 h. Alkylboronic pinacol esters was added to the reaction mixture and stirred under -78 °C for 1 h. The mixture was then stirred at room temperature for another 30 min. The solvent was carefully removed *in vacuo* and further dried for 30 min under high vacuum. After subsequent addition of Ir(ppy)₃ (1.3 mg, 0.002 mmol, 0.01 equiv), acetonitrile (2 mL), DMSO (0.1 mL) under argon, the mixture was stirred for 5 min until all solid was

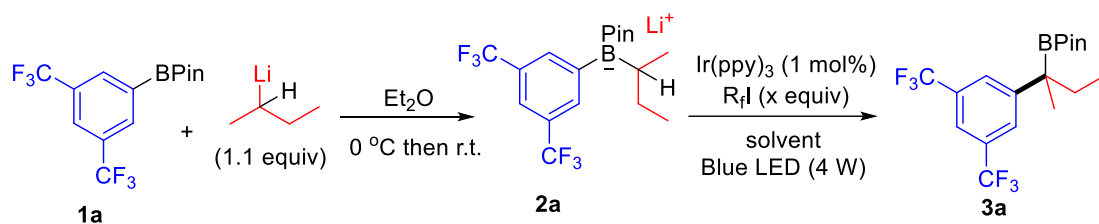
dissolved. Then CF₃I (3.0 M in DMSO, 0.1 mL, 0.3 mmol, 1.5 equiv) was added to the reaction mixture and the reaction mixture was immediately irradiated by a 4 W blue LED and stirred for 1 h. The reaction mixture was diluted with 20 mL CH₂Cl₂ and quenched with saturated NH₄Cl aqueous solution. The organic phase was separated and dried over MgSO₄ and concentrated under reduced pressure. Flash column chromatography eluting with pentane and CH₂Cl₂ afforded the desired product.

3. Reaction Screening

3.1 General Procedure for reaction condition optimization

3,5-Bis(trifluoromethyl)phenylboronic acid pinacol ester (68.0 mg, 0.20 mmol, 1.0 equiv) was dissolved in diethyl ether (2.0 mL). *s*-Butyllithium solution (1.4 M in cyclohexane, 0.16 mL, 0.22 mmol, 1.1 equiv) was added dropwise over 5 min at 0 °C. The mixture was stirred at 0 °C for 30 min then room temperature for another 30 min. The solvent was carefully removed *in vacuo* and further dried for 30 min under high vacuum. After subsequent addition of Ir(ppy)₃ (1.3 mg, 0.002 mmol, 0.01 equiv) and solvent under argon. The reaction mixture was stirred for 1 min until all solid was dissolved. Then perfluoroalkyl iodide was added to the reaction mixture and the reaction mixture was immediately irradiated by a 4 W blue LED and stirred for specified time. The reaction mixture was diluted with 20 mL CH₂Cl₂ and quenched with saturated NH₄Cl aqueous solution. The organic phase was separated and dried over MgSO₄ and concentrated under reduced pressure. The yields were determined by crude GC analysis with *n*-C₁₄H₃₀ as internal standard.

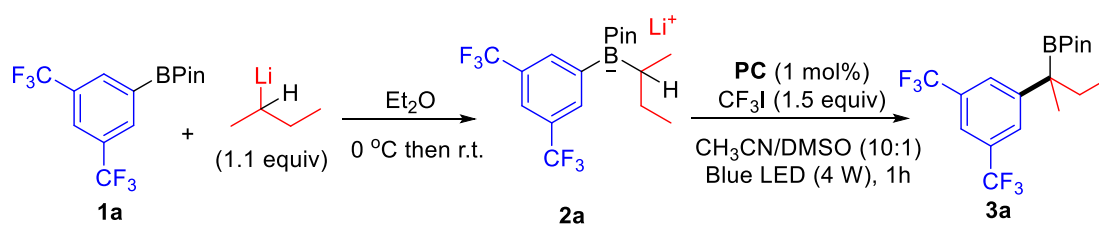
Table S1. Influence of solvents, time and oxidants.



Entry	solvent	R-I (x equiv)	time	Yield of 3a ^a
1	CH_3CN	CF_3I (1.5 equiv)	1 h	50%
2	DMSO	CF_3I (1.5 equiv)	1 h	62%
3	$\text{CH}_3\text{CN}/\text{DMSO}$ (10:1)	CF_3I (1.5 equiv)	1 h	72% (67% ^b)
4	$\text{CH}_3\text{CN}/\text{DMSO}$ (10:1)	CF_3I (5.0 equiv)	1 h	67%
5	$\text{CH}_3\text{CN}/\text{DMSO}$ (10:1)	CF_3I (1.5 equiv)	0.5 h	45%
6	$\text{CH}_3\text{CN}/\text{DMSO}$ (10:1)	CF_3I (1.5 equiv)	1.5 h	71%
7	$\text{CH}_3\text{CN}/\text{DMSO}$ (10:1)	$n\text{-C}_3\text{F}_7\text{I}$ (1.5 equiv)	1 h	21%
8	$\text{CH}_3\text{CN}/\text{DMSO}$ (10:1)	$n\text{-C}_4\text{F}_9\text{I}$ (1.5 equiv)	1 h	37%

^a 0.2 mmol scale reaction, yields determined by crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard. ^b Isolated yield.

Table S2. Influence of photo catalysts.

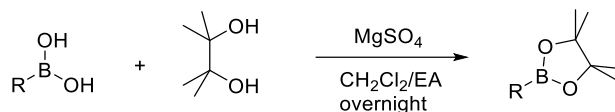


Entry	Photo Catalyst (PC)	Yield of 3a ^a
1	$\text{Ir}(\text{ppy})_3$	72%
2	$\text{Ru}(\text{bpy})_3\text{Cl}_2$	69%
3	Eosin Y	70%
4	Eosin B	17%
5	Rose Bengal	68%
6	Rhodamine B base	69%
7 ^b	$\text{Ir}(\text{ppy})_3$	0%
8	-	0%

^a 0.2 mmol scale reaction, yields determined by crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard. ^b No light.

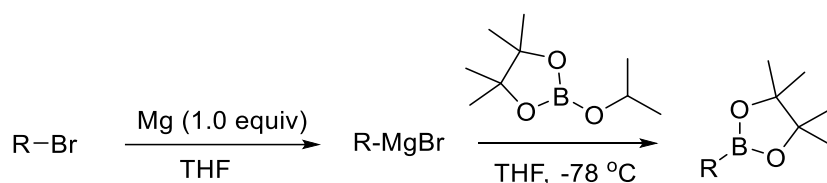
4. Preparation of Boronic Esters and Alkylolithium Reagents

4.1 General procedure for preparation of organoboronic acid pinacol esters (GP5)



A mixture of boronic acid (1.0 equiv), pinacol (1.1 equiv) and anhydrous MgSO_4 (4.0 equiv) in CH_2Cl_2 /Ethyl Acetate (5:1) was stirred at room temperature overnight. The reaction mixture was filtered and the solvent removed *in vacuo*. The crude material was purified by *Kugelrohr* distillation or flash column chromatography to give the pure boronic ester. *Attention: Sometimes a rapid Kugelrohr distillation could not afford a pure enough product, further purification by flash column chromatography was needed.*

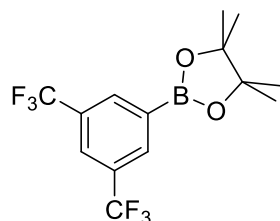
4.2 General procedure for preparation of organoboronic acid pinacol esters (GP6)



Magnesium shavings (1.0 equiv) were added to a dried flask under argon atmosphere and suspended with dry THF. A small amount of a solution of alkyl bromide (1.0 equiv) in dry THF was added to the magnesium and the activation of the Grignard formation was accelerated by addition of an iodine crystal and heating. Afterwards, the rest of the solution of alkyl bromide in THF was added dropwise. The reaction mixture was stirred until magnesium shavings disappeared. The reaction mixture was cooled to $-78\text{ }^\circ\text{C}$, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0 equiv) was added in one portion. The reaction mixture was stirred overnight, quenched with saturated NH_4Cl aqueous solution, and extracted with Et_2O . The combined organic layer was dried over MgSO_4 and filtered. The filtrate was concentrated under reduced pressure and purified by flash column chromatography to afford the pure alkylboronic ester. *Attention: Sometimes a rapid Kugelrohr distillation could not afford a pure enough product, further purification by flash column chromatography was needed.*

4.3 Preparation of organoboronic acid pinacol esters

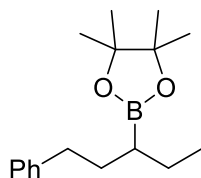
2-(3,5-Bis(trifluoromethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**)



Following **GP5**, using 3,5-bis(trifluoromethyl)phenylboronic acid (5.16 g, 20 mmol) and pinacol (2.6 g, 22 mmol), purifying the crude material by passing through a short

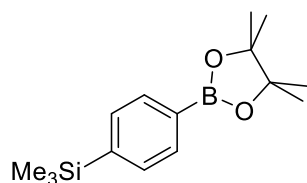
(~4 cm) silica plug eluting with CH₂Cl₂ and then Kugelrohr distillation (0.1 mbar, 150 °C, dry ice cooling) afforded **1a** as white solid (6.7 g, 98% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.24 (s, 2H), 7.94 (s, 1H), 1.37 (s, 12H). ¹¹B NMR (96 MHz, CDCl₃) δ 30.0. ¹⁹F NMR (282 MHz, CDCl₃) δ -62.9 (s). Spectral data were in accordance with the literature.^{S1}

4,4,5,5-Tetramethyl-2-(1-phenylpentan-3-yl)-1,3,2-dioxaborolane (**1e**)



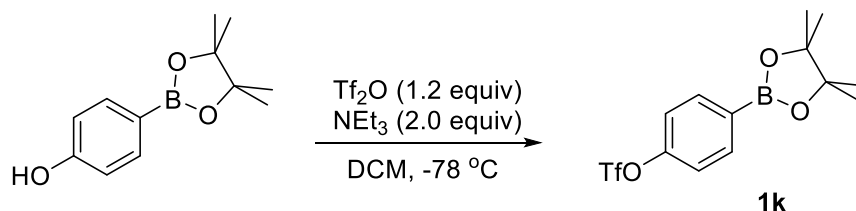
1e was prepared according to the reported procedure.^{S2}

Trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (**1f**)



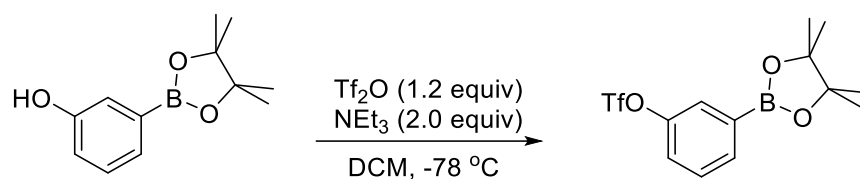
1f was prepared according to the reported procedure.^{S3}

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate (**1k**)



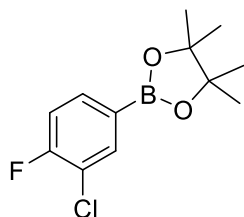
To a solution of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (1.0 g, 4.54 mmol) in CH₂Cl₂, was added triethylamine (0.92 g, 1.3 mL, 9.1 mmol, 2.0 equiv) at -78 °C. The mixture was allowed to stir at -78 °C for 5 min followed by dropwise addition of Tf₂O (1.54 g, 0.9 mL, 5.46 mmol, 1.2 equiv). The reaction mixture was allowed to stir over night. The resulting mixture was quenched with water (approx. 20 mL), and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layer was dried over MgSO₄ and filtered. The filtrate was concentrated under reduced pressure and purified by Kugelrohr distillation (0.1 mbar, 150 °C, dry ice cooling) to afford **1k** as white solid (1.3 g, 81% yield). **1k** was further purified by flash column chromatography (PENTANE/Et₂O = 10:1, R_f 0.4 (Pentane/Et₂O = 10:1). ¹H NMR (300 MHz, CDCl₃) δ 7.92-7.86 (m, 2H), 7.29-7.24 (m, 2H), 1.35 (s, 12H). ¹¹B NMR (96 MHz, CDCl₃) δ 29.8. ¹⁹F NMR (282 MHz, CDCl₃) δ -72.9 (s). Spectral data were in accordance with the literature.^{S4}

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate (**1s**)



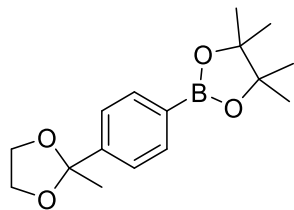
To a solution of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (2.2 g, 10 mmol) in CH_2Cl_2 , was added triethylamine (2.8 mL, 20 mmol, 2.0 equiv) at $-78\text{ }^\circ\text{C}$. The mixture was allowed to stir at $-78\text{ }^\circ\text{C}$ for 5 min followed by dropwise addition of Tf_2O (2.0 mL, 12 mmol, 1.2 equiv). The reaction mixture was allowed to stir overnight. The resulting mixture was quenched with water (approx. 40 mL), and extracted with CH_2Cl_2 ($3 \times 40\text{ mL}$). The combined organic layer was dried over MgSO_4 and filtered. The filtrate was concentrated under reduced pressure and purified by Kugelrohr distillation (0.1 mbar, $150\text{ }^\circ\text{C}$, dry ice cooling) to afford **1s** as sticky oil (2.0 g, 57% yield). **1s** was further purified by flash column chromatography (Pentane/ Et_2O = 10:1), R_f 0.4 (Pentane/ Et_2O = 10:1). ^1H NMR (300 MHz, CDCl_3) δ 7.81 (d, J = 7.3 Hz, 1H), 7.67 (d, J = 2.5 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.37 – 7.31 (m, 1H), 1.35 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 149.4, 134.6, 129.7, 127.0, 123.8, 118.8 (q, J = 320.5 Hz), 84.4, 24.9, carbon attached to boron not observed. ^{11}B NMR (96 MHz, CDCl_3) δ 30.2. ^{19}F NMR (282 MHz, CDCl_3) δ -73.0 (s). **HRMS** (ESI) m/z = 375.0656 calcd. for $\text{C}_{13}\text{H}_{16}\text{BF}_3\text{O}_5\text{SNa}^+$ [$\text{M}+\text{Na}$] $^+$, found: 375.0659. **FTIR** (neat): ν (cm^{-1}) 2984, 2936, 1572, 1490, 1422, 1354, 1331, 1247, 1205, 1167, 1136, 1095, 1071, 1004, 964, 911, 857, 830, 799, 748, 702, 670, 606.

2-(3-Chloro-4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1n**)



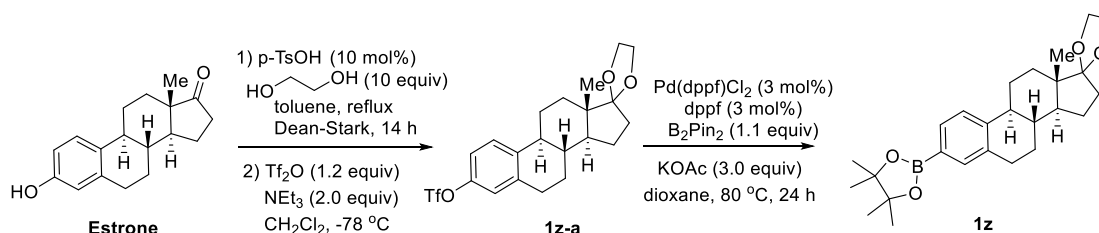
Following **GP5**, using (3-chloro-4-fluorophenyl)boronic acid (1.74 g, 10 mmol) and pinacol (1.30 g, 11 mmol, 1.1 equiv), purifying the crude material by passing through a short (~4 cm) silica plug eluting with CH_2Cl_2 and then Kugelrohr distillation (0.1 mbar, $150\text{ }^\circ\text{C}$, dry ice cooling) afforded **1n** as white solid (2.1 g, 82% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.84 (dd, J = 7.9, 1.3 Hz, 1H), 7.72 – 7.61 (m, 1H), 7.18 – 7.06 (m, 1H), 1.34 (s, 12H). ^{11}B NMR (96 MHz, CDCl_3) δ 30.2. ^{19}F NMR (282 MHz, CDCl_3) δ -111.2 (s). Spectral data were in accordance with the literature.^{S5}

4,4,5,5-Tetramethyl-2-(4-(2-methyl-1,3-dioxolan-2-yl)phenyl)-1,3,2-dioxaborolane (**1y**)



To a mixture of 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (1.0 g, 4.06 mmol) and ethylene glycol (2.54 g, 2.3 mL, 41 mmol, 10 equiv) in toluene (40 mL) was added *p*-tolylsulfonic acid trihydrate (38.0 mg, 0.2 mmol, 0.05 equiv). The mixture was refluxed for 16 hours over a Dean-Stark apparatus to remove generated water. Solvent was removed under reduced pressure. The residue was purified by silica chromatography eluting with (pentane/ethyl acetate = 4:1) to afford **1y** as white solid (1.0 g, 85% yield), *R*_f 0.4 (Pentane/ ethyl acetate = 3:1). ¹H NMR (300 MHz, CDCl₃) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 4.10 – 3.95 (m, 2H), 3.85 – 3.63 (m, 2H), 1.65 (s, 3H), 1.34 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 146.3, 134.7, 124.6, 108.8, 83.8, 64.4, 27.5, 24.9, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 30.8. Spectral data were in accordance with the literature.^{S6}

4,4,5,5-Tetramethyl-2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)-1,3,2-dioxaborolane (**1z**)

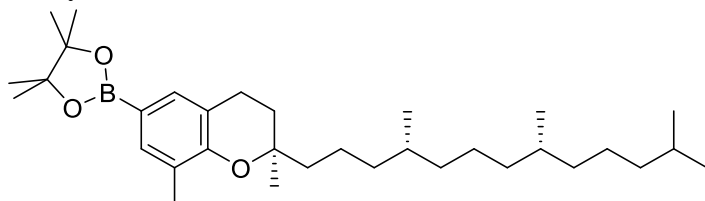


1z-a was synthesized from estrone according to the reported procedure.^{S7}

To a 50 mL Schlenk tube equipped with a stirring bar was added Pd(dppf)Cl₂ (124 mg, 0.17 mmol, 0.03 equiv), 1,1'-bis(diphenylphosphino)ferrocene (dppf, 98 mg, 0.17 mmol, 0.03 equiv), B₂Pin₂ (1.6 g, 6.3 mmol, 1.1 equiv), KOAc (1.67 g, 17 mmol, 3.0 equiv), **1z-a** (2.55 g, 5.7 mmol, 1.0 equiv) and then sealed. The Schlenk tube was evacuated and backfilled with Ar for 3 times. Dioxane (30 mL) was added under Ar atmosphere and the mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with Et₂O (200 mL). The organic layer was washed with water (3 × 100 mL) and dried over anhydrous MgSO₄. After filtration and concentration, the residue was purified by silica gel chromatography with pentane and ethyl acetate (Pentane/EA = 10:1) to afford **1z** as white solid (1.96 g, 81% yield). *R*_f 0.4 (pentane/EA = 20:3). M.p.: 179-181 °C. [α]_D²⁴ +20 (*c* 0.8, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.64 – 7.50 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 4.08 – 3.83 (m, 4H), 3.01 – 2.82 (m, 2H), 2.52 – 2.21 (m, 2H), 2.15 – 1.73 (m, 5H), 1.72 – 1.37 (m, 6H), 1.34 (s, 12H), 0.89 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 143.9,

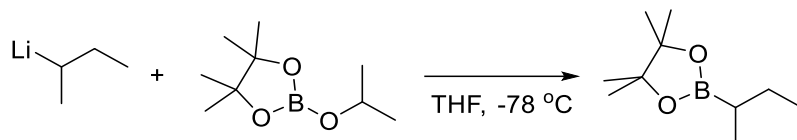
136.1, 135.5, 132.0, 124.7, 119.4, 83.6, 65.2, 64.5, 49.5, 46.1, 44.4, 38.7, 34.2, 30.7, 29.3, 26.9, 25.8, 24.8, 24.8, 22.4, 14.3, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 30.2. **HRMS** (ESI) m/z = 447.2677 calcd. for $\text{C}_{26}\text{H}_{37}\text{BO}_4\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 447.2678. **FTIR** (neat): ν (cm^{-1}) 2975, 2937, 2874, 1611, 1408, 1363, 1352, 1309, 1273, 1289, 1213, 1180, 1143, 1108, 1045, 964, 854, 725, 676.

2-((*R*)-2,8-Dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1aa**)



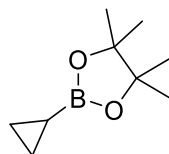
1aa was prepared according to the reported procedure.^{S8}

2-(Sec-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4c**)



To a solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.72 g, 4.1 mL, 20 mmol) in THF (50 mL) was added s-butyl lithium solution (1.4M in cyclohexane, 14.2 mL, 20 mmol) dropwise at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred overnight and quenched with saturated NH_4Cl aqueous solution. The mixture was extracted with Et_2O (50 mL \times 3). The organic phase was combined and dried over MgSO_4 . After filtration and evaporation of solvent, the residue was purified by Kugelrohr distillation (10 mbar, $100\text{ }^{\circ}\text{C}$, dry ice cooling) to afford **4c** as colorless liquid (2.0 g, 54% yield). **4c** was further purified by flash column chromatography (pentane/ Et_2O = 20:1), R_f 0.5 (pentane/ Et_2O = 20:1). ^1H NMR (300 MHz, CDCl_3) δ 1.55 – 1.40 (m, 1H), 1.40 – 1.29 (m, 1H), 1.24 (s, 12H), 0.99-0.92 (m, 4H), 0.90 (t, J = 7.4 Hz, 3H). The NMR spectra were in accordance with the literature.^{S9}

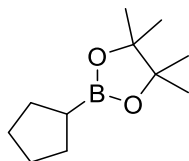
2-Cyclopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4d**)



Following **GP5**, using cyclopropylboronic acid (2.58 g, 30 mmol) and pinacol (3.54 g, 30 mmol), purifying the crude material by passing through a short (~4 cm) silica plug eluting with CH_2Cl_2 and then Kugelrohr distillation (10 mbar, $80\text{ }^{\circ}\text{C}$, dry ice cooling) afforded **4d** as colorless liquid (4.24 g, 84% yield). **4d** was further purified by flash column chromatography (Pentane/ Et_2O = 20:1), R_f 0.5 (pentane/ Et_2O = 20:1). ^1H NMR (300 MHz, CDCl_3) δ 1.22 (s, 12H), 0.65-0.57 (m, 2H), 0.55 – 0.44 (m, 2H),

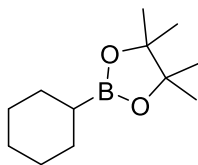
-0.20 (tt, $J = 9.2, 6.1$ Hz, 1H). ^{11}B NMR (96 MHz, CDCl_3) δ 33.5. The NMR spectra were in accordance with the literature.^{S9}

2-Cyclopentyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4e**)



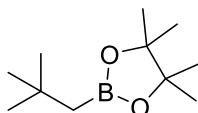
Following **GP6**, using cyclopentyl bromide (2.98 g, 2.14 mL, 20 mmol), magnesium (0.48 g, 20 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.7 g, 4.1 mL, 20 mmol), purifying the crude material by Kugelrohr distillation (10 mbar, 100 °C, dry ice cooling) afforded **4e** as colorless liquid (2.7 g, 69% yield). **4e** was further purified by flash column chromatography (Pentane/ Et_2O = 20:1), R_f 0.5 (pentane/ Et_2O = 20:1). ^1H NMR (300 MHz, CDCl_3) δ 1.82 – 1.66 (m, 2H), 1.66 – 1.35 (m, 6H), 1.23 (s, 12H), 1.21 – 1.05 (m, 1H). ^{11}B NMR (96 MHz, CDCl_3) δ 34.5. The NMR spectra were in accordance with the literature.^{S9}

2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4f**)



Following **GP6**, using cyclohexyl bromide (3.26 g, 2.46 mL, 20 mmol), magnesium (0.48 g, 20 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.7 g, 4.1 mL, 20 mmol), purifying the crude material by Kugelrohr distillation (10 mbar, 120°C, dry ice cooling) afforded **4f** as colorless liquid (2.45 g, 58% yield). **4f** was further purified by flash column chromatography (Pentane/ Et_2O = 20:1), R_f 0.5 (pentane/ Et_2O = 20:1). ^1H NMR (300 MHz, CDCl_3) δ 1.78 – 1.46 (m, 5H), 1.42 – 1.26 (m, 5H), 1.23 (s, 12H), 1.01 – 0.92 (m, 1H). ^{11}B NMR (96 MHz, CDCl_3) δ 33.8. The NMR spectra were in accordance with the literature.^{S9}

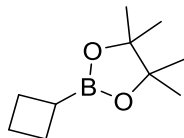
4,4,5,5-Tetramethyl-2-neopentyl-1,3,2-dioxaborolane (**4g**)



Following **GP6**, using neopentyl bromide (3.02 g, 2.5 mL, 20 mmol), magnesium (0.48 g, 20 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.7 g, 4.1 mL, 20 mmol), purifying the crude material by Kugelrohr distillation (10 mbar, 110°C, dry ice cooling) afforded **4g** as colorless liquid (2.13 g, 54% yield). ^1H NMR (300 MHz, CDCl_3) δ 1.24 (s, 12H), 0.99 (s, 9H), 0.80 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 32.0, 29.7, 24.9, carbon attached to boron not observed. ^{11}B NMR (96 MHz, CDCl_3) δ 33.6. **HRMS** (EI) m/z = 183.1551 calcd. for $\text{C}_{10}\text{H}_{20}\text{BO}_2^+$ [$\text{M}-\text{CH}_3$] $^+$, found: 183.1551. **FTIR** (neat): ν (cm^{-1}) 2979, 2952, 2870, 1466, 1354, 1318, 1269,

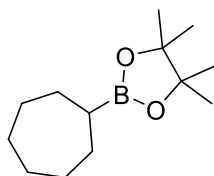
1247, 1214, 970, 877, 847.

2-Cyclobutyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4k**)



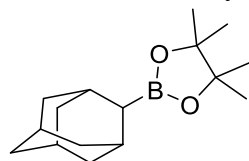
Following **GP6**, using cyclobutyl bromide (2.70 g, 20 mmol), magnesium (0.48 g, 20 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.7 g, 4.1 mL, 20 mmol), purifying the crude material by Kugelrohr distillation (10 mbar, 100°C, dry ice cooling) afforded **4k** as colorless liquid (1.2 g, 33% yield). **4k** was further purified by flash column chromatography (Pentane/Et₂O = 20:1), R_f 0.5 (pentane/Et₂O = 20:1). ¹H NMR (300 MHz, CDCl₃) δ 2.15 – 1.79 (m, 7H), 1.23 (s, 12H). ¹¹B NMR (96 MHz, CDCl₃) δ 33.8. The NMR spectra were in accordance with the literature^{S9}

2-Cycloheptyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4n**)



Following **GP6**, using cycloheptyl bromide (1.77 g, 10 mmol), magnesium (0.24 g, 10 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.85 g, 2.05 mL, 10 mmol), purifying the crude material by Kugelrohr distillation (1 mbar, 120°C, dry ice cooling) afforded **4n** as colorless liquid (1.0 g, 45% yield). **4n** was further purified by flash column chromatography (Pentane/Et₂O = 20:1), R_f 0.5 (pentane/Et₂O = 20:1). ¹H NMR (300 MHz, CDCl₃) δ 1.80 – 1.32 (m, 12H), 1.22 (s, 12H), 1.12-1.00 (m, 1H). ¹¹B NMR (96 MHz, CDCl₃) δ 34.3. The NMR spectra were in accordance with the literature.^{S9}

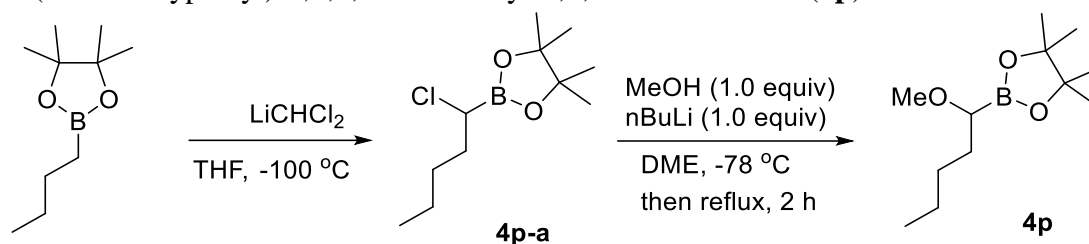
2-(Adamantan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4o**)



Following **GP6**, using 2-bromoadamantane (2.15g, 10 mmol), magnesium (0.24 g, 10 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.85 g, 2.05 mL, 10 mmol), purifying the crude material by flash chromatography (Pentane/Et₂O = 20:1) afforded **4o** as white solid (0.35 g, 13% yield), R_f 0.5 (pentane/Et₂O = 20:1). ¹H NMR (300 MHz, CDCl₃) δ 2.07-2.02 (br, 2H), 1.93 – 1.62 (m, 12H), 1.38 – 1.34 (br, 1H), 1.25 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 82.8, 39.4, 37.8, 36.3, 29.4, 28.3, 28.2, 24.8, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 33.6. **FTIR** (neat): ν (cm⁻¹) 2977, 2901, 2846, 1450, 1407, 1380, 1363, 1351, 1306, 1286, 1272, 1145, 1098, 1044, 980, 850, 737. The NMR spectra were in accordance with the

literature.^{S9}

2-(1-Methoxypentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4p**)

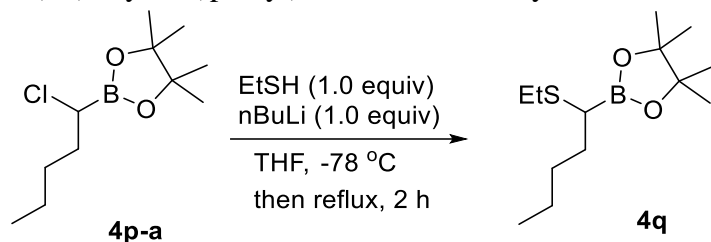


A solution of dichloromethane (2 mL, 31 mmol, 1.55 equiv) in 50 mL of THF was cooled to $-100\text{ }^\circ\text{C}$ in a 95% ethanol/liquid nitrogen slush bath and stirred magnetically during the dropwise addition of n -butyllithium (1.6 M in hexane, 13.1 mL, 21 mmol, 1.05 equiv) by a syringe over a period of 10 min. The butyllithium must be chilled before contacting the dichloromethane solution, by running the butyllithium solution down the cold wall of the reaction flask. After about half of the butyllithium had been added, a white precipitate of (dichloromethyl)lithium formed. The solution should remain colorless or pale yellow. Darkening is a sign of overheating and decomposition. After 30 min, a solution of n -butylboronic acid pinacol ester (3.68 g, 20 mmol, 1.0 equiv) in 10 mL of diethyl ether was injected in one portion, resulting in dissolution of the precipitate of (dichloromethyl)lithium. The solution was allowed to warm slowly to $20\text{--}25\text{ }^\circ\text{C}$ and was kept this temperature overnight. 100 mL of dichloromethane were added to precipitate the lithium chloride, the solution was filtered and concentrated under vacuum, and 2-(1-chloropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4p-a**) was purified by Kugelrohr distillation (10 mbar, 100°C , dry ice cooling) to afford a colorless liquid (3.56 g, 77% yield). ^1H NMR (300 MHz, CDCl_3) δ 3.46 – 3.32 (m, 1H), 1.90 – 1.70 (m, 2H), 1.52 – 1.29 (m, 4H), 1.27 (s, 12H), 0.89 (t, $J = 7.1\text{ Hz}$, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 84.3, 33.8, 29.5, 24.6, 24.6, 22.2, 13.9, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 31.5. **HRMS** (ESI) $m/z = 255.1294$ calcd. for $\text{C}_{11}\text{H}_{22}\text{BO}_2\text{ClNa}^+ [\text{M}+\text{Na}]^+$, found: 255.1294. **FTIR** (neat): ν (cm^{-1}) 2979, 2961, 2934, 2872, 1468, 1416, 1381, 1342, 1269, 1240, 1215, 1167, 1141, 1113, 967, 873, 846, 675, 652.

To anhydrous MeOH (64 mg, 2 mmol, 1.0 equiv) in DME (15 mL) was added n -butyllithium (1.6 M in hexane, 1.25 mL, 1.0 equiv) at $-78\text{ }^\circ\text{C}$. **4p-a** (0.46 g, 2 mmol, 1.0 equiv) was added from a syringe to the cold, stirred solution. When the mixture was warmed to room temperature, the mixture was refluxed 2 h. Filtration and evaporation of the solvent under reduced pressure gave the crude product. Kugelrohr distillation (1 mbar, 150°C , dry ice cooling) afforded **4p** as colorless liquid (0.2 g, 44% yield). ^1H NMR (300 MHz, CDCl_3) δ 3.32 (s, 3H), 3.16 (t, $J = 6.0\text{ Hz}$, 1H), 1.80 – 1.50 (m, 2H), 1.40 – 1.15 (m, 4H), 1.27 (s, 12H), 0.97 – 0.83 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 83.8, 57.8, 30.1, 28.3, 24.9, 24.7, 22.9, 14.0, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 32.5. **HRMS** (ESI) $m/z = 251.1789$ calcd. for $\text{C}_{12}\text{H}_{25}\text{BO}_3\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 251.1803. **FTIR** (neat): ν (cm^{-1}) 2979, 2958, 2930, 2814, 1467, 1407, 1380, 1372, 1332, 1255, 1215, 1144, 1110, 968, 855,

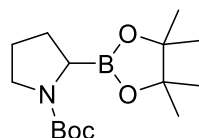
670.

2-(1-(Ethylthio)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4q**)



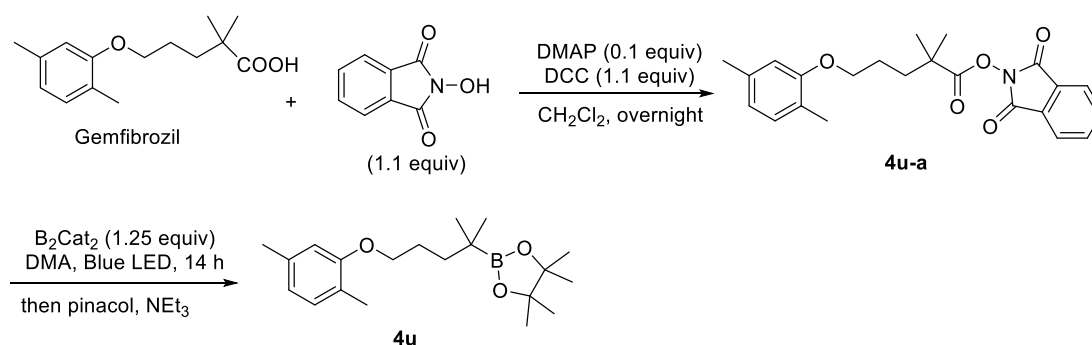
To ethanethiol (186 mg, 3 mmol, 1.0 equiv) in THF (15 mL) was added n-butyllithium (1.6 M in hexane, 2.0 mL, 1.05 equiv) at -78 °C. **4p-a** (0.70 g, 3 mmol, 1.0 equiv) was added by a syringe to the cold, stirred solution. The mixture was allowed to warm to room temperature, then the mixture was refluxed for 2 h. Filtration and evaporation of the solvent under reduced pressure gave the crude product. Flash chromatography (Pentane/Et₂O = 10:1) afforded **4q** as colorless liquid (0.55 g, 71% yield). *R*_f 0.3 (pentane/EtOAc = 20:1). ¹H NMR (300 MHz, CDCl₃) δ 2.68 – 2.49 (m, 2H), 2.10 (dd, *J* = 8.4, 6.9 Hz, 1H), 1.76 – 1.53 (m, 2H), 1.41 – 1.29 (m, 4H), 1.28 – 1.19 (m, 15H), 0.93 – 0.85 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 83.5, 31.1, 30.8, 25.5, 24.8, 24.6, 22.6, 14.8, 14.0, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 32.2. **HRMS** (ESI) *m/z* = 281.1717 calcd. for C₁₃H₂₇BO₂SN⁺ [*M*+Na]⁺, found: 281.1736. **FTIR** (neat): ν (cm⁻¹) 2976, 2960, 2930, 2863, 1457, 1402, 1370, 1324, 1264, 1141, 968, 875, 847.

Tert-butyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (**4r**)



4r was prepared according to the reported procedure.^{S10}

2-(5-(2,5-Dimethylphenoxy)-2-methylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4u**)

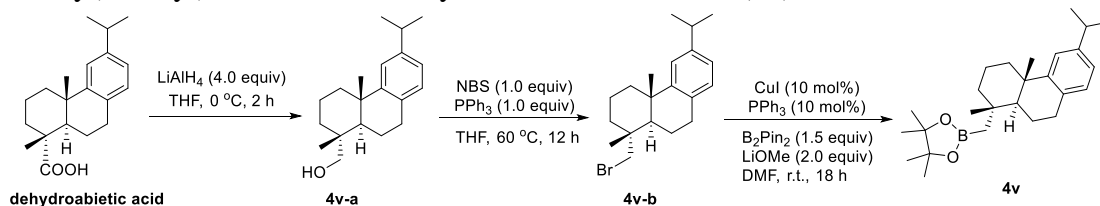


To a mixture of gemfibrozil (1.25 g, 5 mmol, 1.0 equiv), *N*-hydroxyphthalimide (0.89 g, 5.5 mmol, 1.1 equiv), 4-(*N,N*-dimethylamino)pyridine (61 mg, 0.5 mmol, 0.1 equiv)

in CH₂Cl₂ (40 mL) was added *N,N'*-dicyclohexylcarbodiimide (1.13 g, 5.5 mmol, 1.1 equiv). The reaction mixture was stirred overnight and filtered through a pad of silica gel, rinsed with CH₂Cl₂ (100 mL). Solvent amount was reduced under reduced pressure and the residue was purified by flash chromatography (PENTANE/EtOAc = 5:1) to afford **4u-a** as light yellow sticky oil (1.94 g, 98% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.92 – 7.84 (m, 2H), 7.83 – 7.74 (m, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.69-6.64 (m, 2H), 4.06-3.96 (m, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 1.99-1.93 (m, 4H), 1.46 (s, 6H). **FTIR** (neat): ν (cm⁻¹) 2975, 2930, 2871, 1807, 1783, 1743, 1615, 1585, 1509, 1468, 1371, 1265, 1187, 1157, 1131, 1044, 878, 696. The NMR spectra were identical to the literature.^{S11}

4u was synthesized in 4×0.5 mmol scale according to the method reported by Aggarwal's group.^{S12} To four Schlenk tubes were added **4u-a** (0.188 g, 0.5 mmol, 1 equiv), B₂cat₂ (149 mg, 0.625 mmol, 1.25 equiv), DMAc (5 mL, 0.1 M) and magnetic stirrer bar, respectively. The Schlenk tubes were tightly sealed and stirred under blue LED irradiation for 14 h. The reaction solution of the four Schlenk tubes was combined and pinacol (3.0 g, 16 mmol, 8 equiv) was added by NEt₃ (5 mL) at 0 °C. The mixture was stirred for 1 h, then quenched by water (40 mL). After extraction with EtOAc (30×4mL), the organic layers were combined and dried over MgSO₄. After filtration and evaporation of solvent under reduced pressure, the residue was purified by flash chromatography (Pentane/Et₂O = 10:1) to afford **4u** as white solid (0.49 g, 74% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.01 (d, *J* = 7.3 Hz, 1H), 6.69-6.62 (m, 2H), 3.93 (t, *J* = 6.6 Hz, 2H), 2.32 (s, 3H), 2.20 (s, 3H), 1.83 – 1.70 (m, 2H), 1.51 – 1.38 (m, 2H), 1.24 (s, 12H), 0.99 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 157.2, 136.3, 130.2, 123.7, 120.5, 112.1, 82.9, 68.7, 37.3, 26.5, 24.8, 24.7, 21.4, 15.8, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 35.2. **FTIR** (neat): ν (cm⁻¹) 2977, 2939, 2864, 1615, 1586, 1509, 1475, 1389, 1370, 1308, 1265, 1210, 1139, 1130, 1038, 967, 851, 802, 693. The NMR spectra were identical to the literature.^{S13}

2-(((1*R*,4*aS*,10*aS*)-6-Isopropyl-1,4*a*-dimethyl-1,2,3,4,4*a*,9,10,10*a*-octahydrophenanthren-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4v**)



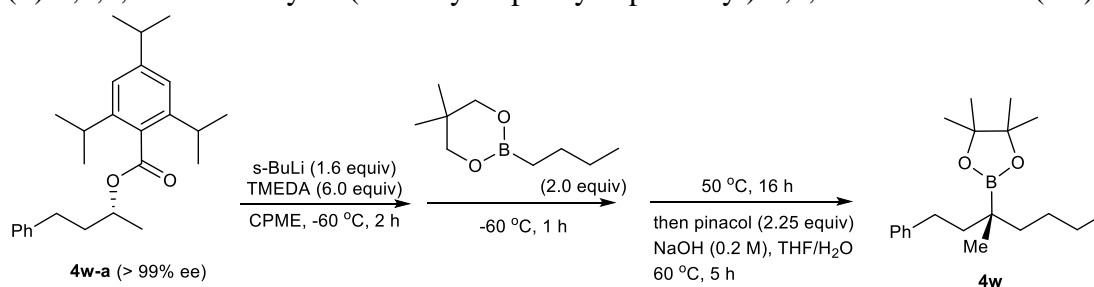
4v-a was synthesized according to a reported procedure.^{S14}

To a 50 mL sealed tube was added **4v-a** (0.57 g, 2.0 mmol, 1 equiv), N-bromosuccinimide (NBS, 0.36 g, 2.0 mmol, 1.0 equiv), triphenylphosphine (PPh₃, 0.52 g, 2.0 mmol, 1.0 equiv), dry THF (10 mL) and magnetic stir bar. The tube was sealed and stirred at 60 °C for 12 h. The reaction mixture was diluted with Et₂O (50 mL) and washed with water (30mL×4). The organic layer was dried over MgSO₄. After filtration and evaporation of solvent under reduced pressure, the residue was purified by flash chromatography (Pentane) to afford **4v-b** as colorless sticky liquid

(0.46 g, 65% yield). R_f 0.5 (pentane/DCM = 10:1). $[\alpha]_D^{24} +2$ (c 0.9, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.09 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.81 (s, 1H), 3.39 (d, J = 10.2 Hz, 1H), 3.20 (d, J = 10.2 Hz, 1H), 2.89 – 2.65 (m, 3H), 2.26 – 2.11 (m, 1H), 1.77 – 1.53 (m, 5H), 1.52 – 1.26 (m, 3H), 1.15 (s, 3H), 1.14 – 1.10 (m, 6H), 0.97 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 147.0, 145.6, 134.6, 126.8, 124.3, 123.9, 48.6, 45.5, 38.2, 37.5, 37.1, 36.4, 33.4, 30.0, 24.9, 24.0, 18.8, 18.7, 18.7. **HRMS** (EI) m/z = 348.1447 calcd. for $\text{C}_{20}\text{H}_{29}\text{Br}^+ [\text{M}]^+$, found: 348.1450. **FTIR** (neat): ν (cm^{-1}) 3001, 2958, 2931, 2868, 1497, 1458, 1381, 1363, 1345, 1248, 1172, 1074, 1058, 970, 1035, 909, 885, 821, 731, 665, 651, 627.

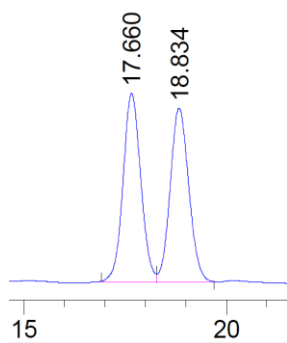
4v was synthesized according to Liu's procedure.^{S15} To a 10 mL Schlenk tube was added **4v-b** (0.19 g, 0.54 mmol, 1 equiv), CuI (10.3 mg, 0.054 mmol, 0.1 equiv), triphenylphosphine (PPh_3 , 14.1 mg, 0.054 mmol, 0.1 equiv), B_2Pin_2 (0.21 g, 0.81 mmol, 1.5 equiv), LiOMe (41.0 mg, 1.08 mmol, 2.0 equiv) and a magnetic stir bar. The Schlenk tube was evacuated and backfilled with Ar for 3 times. DMF (1.1 mL) was added under Ar flow. The reaction mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with Et_2O (50 mL) and washed with water (30 mL \times 4). The organic layer was dried over MgSO_4 . After filtration and evaporation of solvent under reduced pressure, the residue was purified by flash chromatography (Pentane/ Et_2O = 20:1) to afford **4v** as white solid (101 mg, 47% yield). R_f 0.3 (pentane/DCM = 2:1). M. p. = 133–134 °C. $[\alpha]_D^{24} +3$ (c 0.4, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.16 (d, J = 8.2 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 6.88 (s, 1H), 3.00 – 2.73 (m, 3H), 2.26 (d, J = 12.4 Hz, 1H), 2.00 – 1.86 (m, 1H), 1.84 – 1.51 (m, 4H), 1.49 – 1.31 (m, 3H), 1.25 – 1.20 (m, 18H), 1.19 (s, 3H), 1.10 (d, J = 14.3 Hz, 1H), 1.02 (s, 3H), 0.74 (d, J = 14.3 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 147.7, 145.2, 135.0, 126.8, 124.3, 123.7, 82.7, 51.6, 40.4, 38.8, 37.9, 35.9, 33.4, 30.6, 25.2, 25.0, 24.8, 24.0, 24.0, 21.8, 19.4, 19.1, carbon attached to boron not observed. ^{11}B NMR (96 MHz, CDCl_3) δ 32.3. **HRMS** (ESI) m/z = 419.3092 calcd. for $\text{C}_{26}\text{H}_{41}\text{BO}_2\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 419.3090. **FTIR** (neat): ν (cm^{-1}) 2958, 2926, 2869, 1498, 1458, 1419, 1378, 1351, 1319, 1213, 1146, 971, 882, 849, 821.

(S)-4,4,5,5-Tetramethyl-2-(3-methyl-1-phenylheptan-3-yl)-1,3,2-dioxaborolane (**4w**)

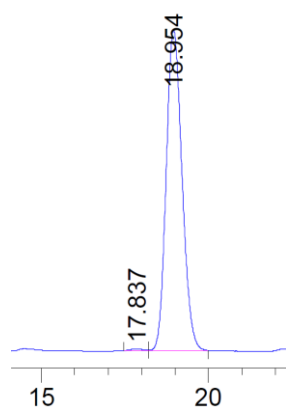


4w was synthesized according to Aggarwal's method.^{S16} To a vigorously stirred solution (without splashing) of benzoate **4w-a** (0.38 g, 1.0 mmol, 1.0 equiv, synthesized according to the reported procedure^{S16}) and TMEDA (0.92 mL, 6.0 mmol, 6.0 equiv) in anhydrous cyclopentyl methyl ether (CPME, 6 mL) at -60°C (internal temperature) under a argon atmosphere, was added $s\text{-BuLi}$ (1.4 M in cyclohexane, 1.14 mL, 1.6 mmol, 1.6 equiv) dropwise over 10 min. After 2 h, a solution of the

borylating agent (0.34 g, 2.0 mmol, 2.0 equiv) in CPME (2 ml) was added dropwise over 10 min. The reaction mixture was stirred at $-60\text{ }^{\circ}\text{C}$ for 1 h and then the cooling bath was removed and the reaction mixture was stirred at $50\text{ }^{\circ}\text{C}$ (migration temperature) overnight ($\sim 16\text{ h}$). The volatiles were removed from the reaction mixture *in vacuo* and the residue dissolved in THF (12 ml). To the stirred solution was added pinacol (0.26 g, 2.25 mmol, 2.25 equiv) and 0.2M NaOH (aq) (1 ml). The reaction mixture was stirred for 5 h at $60\text{ }^{\circ}\text{C}$ at which point GC/MS showed 95% conversion of the tertiary neopentyl boronic ester to the corresponding pinacol boronic ester. The reaction mixture was cooled to ambient temperature and Et₂O (20 ml) and water (5 ml) was added. The phases were separated and the aqueous phase extracted with Et₂O ($3 \times 20\text{ ml}$). The combined organic phases were washed with brine, dried over MgSO₄ and the solvent removed *in vacuo*. The crude material was purified by flash column chromatography eluting with pentane/DCM (4:1) to afford **4w** as colorless liquid (0.20 g, 63% yield, 99% ee). *R_f* 0.4 (pentane/DCM = 2:1). Ee value was determined by chiral HPLC after oxidation (NaOH/H₂O₂). ¹⁷ ¹H NMR (300 MHz, CDCl₃) δ 7.24 – 7.14 (m, 2H), 7.14 – 7.04 (m, 3H), 2.59 – 2.35 (m, 2H), 1.72 – 1.56 (m, 1H), 1.52 – 1.32 (m, 2H), 1.27 – 1.12 (m, 5H), 1.18 (s, 12H), 0.92 (s, 3H), 0.82 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 143.8, 128.3, 128.2, 125.4, 83.0, 41.6, 38.8, 32.4, 28.0, 24.9, 24.9, 23.6, 21.4, 14.1, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 34.6. **HRMS** (ESI) *m/z* = 339.2466 calcd. for C₂₀H₃₃BO₂Na⁺ [M+Na]⁺, found: 339.2466. **FTIR** (neat): ν (cm⁻¹) 2978, 2956, 2928, 2859, 1497, 1468, 1371, 1306, 1216, 1138, 967, 855, 746, 697. **Chiral HPLC** (IC, 0.5% *i*PrOH/cyclohexane, 1.0 ml/min) *T_R* 17.84 min (minor), 18.95 min (major). $[\alpha]_D^{26}$ -12 (*c* 0.46, CHCl₃).



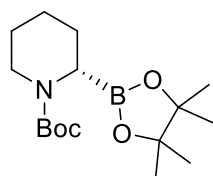
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.660	BV	0.4701	3140.21973	102.88875	50.8251
2	18.834	VB	0.5013	3038.26709	94.95518	49.1749



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.837	BV	0.3335	53.85359	1.95428	0.3875
2	18.954	VB	0.5147	1.38426e4	419.85208	99.6125

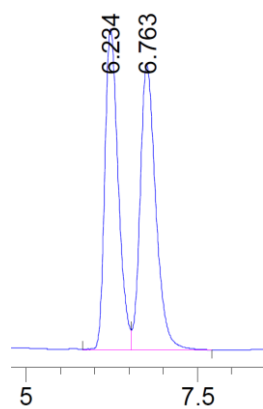
(*S*)-Tert-butyl

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate (**4x**)

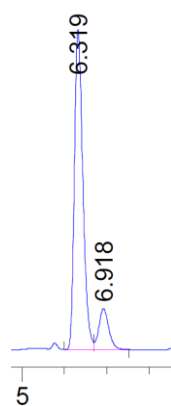


4x was prepared according to the reported procedure.^{S10}

N-Boc-piperidine (1.85 g, 10.0 mmol, 1.00 equiv) and (-)-sparteine (2.81 g, 2.75 mL, 12.0 mmol, 1.20 equiv) were dissolved in Et₂O (40 mL). The solution was cooled to -78 °C and *s*-BuLi (1.4 M in cyclohexane, 8.6 mL, 12.0 mmol, 1.20 equiv) was added dropwise. The solution was stirred for 3 h at -78 °C, then *i*-PrOB(pin) (2.42 g, 13.0 mmol, 1.30 equiv) was added dropwise. The solution was stirred for 1 h at -78 °C, then allowed to warm up to room temperature slowly. Aqueous 1 M HCl (150 mL) was added and the layers were separated. The organic layers were washed with brine (3 × 50 mL) and the combined aqueous layers were extracted with Et₂O (3 × 100 mL). The organic layers were combined, dried over MgSO₄ and concentrated under vacuum. The crude product was purified by fast column chromatography on silica gel, eluting with pentane:EA 4:1, to give (*S*)-**4x** as a colorless oil (0.1 g, 3% yield, 73% ee). *R*_f 0.3 (pentane/EA = 3:1). ¹H NMR (300 MHz, CDCl₃) δ 3.73 (d, *J* = 12.8 Hz, 1H), 2.81 – 2.60 (m, 1H), 2.34 (dd, *J* = 12.2, 3.3 Hz, 1H), 1.90 – 1.74 (m, 1H), 1.69 – 1.55 (m, 2H), 1.49 (s, 9H), 1.46 – 1.24 (m, 3H), 1.18 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 139.8, 85.6, 80.0, 42.5, 28.5, 26.5, 25.2, 25.1, 24.9, 24.5, carbon attached to boron not observed. ¹¹B NMR (96 MHz, CDCl₃) δ 14.9. The NMR spectra were identical to the literature.^{S10} **Chiral HPLC** (IC, 1.5% *i*PrOH/cyclohexane, 1.0 ml/min) *T*_R 6.32 min (major), 6.92 min (minor). [α]_D²⁴ +3 (*c* 0.7, CHCl₃).

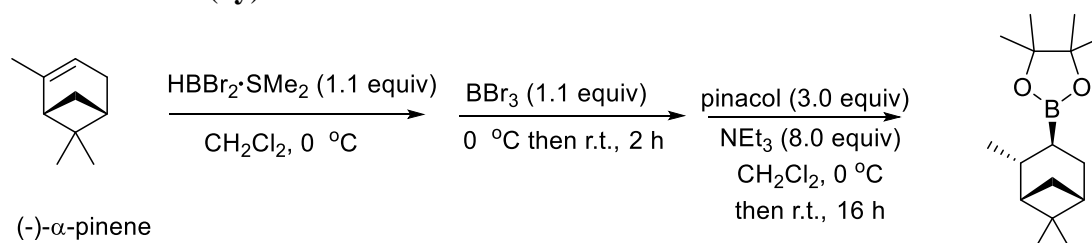


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.234	VV	0.2115	2851.35229	208.53979	49.0211
2	6.763	VB	0.2461	2965.23047	185.88123	50.9789



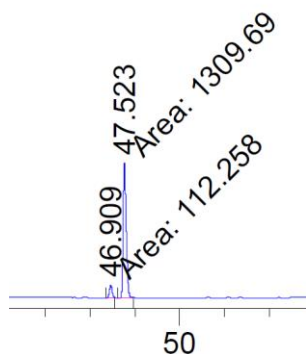
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.319	VV	0.2149	1825.63367	130.77518	86.6683
2	6.918	VB	0.2533	280.82797	16.94997	13.3317

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

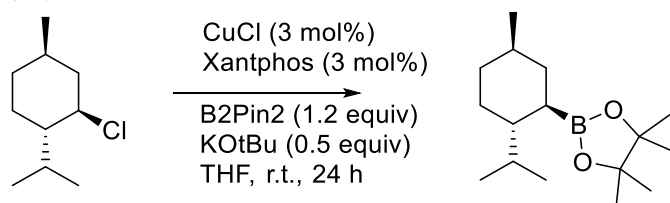


4y was synthesized according to the literature.^{S2} Dibromoborane dimethyl sulfide complex (1 M in CH_2Cl_2 , 11 mL, 11.0 mmol, 1.1 equiv) was added dropwise to a solution of (-)- α -pinene (1.36 g, 1.59 mL, 10.0 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) at 0 °C. After dropwise addition of tribromoborane (1M in CH_2Cl_2 , 11 mL, 11.0 mmol, 1.1 equiv), the mixture was allowed to warm up to room temperature and stirred for 2

h. This mixture was then added dropwise to a solution of pinacol (3.6 g, 30.0 mmol, 3.0 equiv) and triethylamine (11.2 mL, 80 mmol, 8.0 equiv) in CH₂Cl₂ (40 mL) at 0 °C. The mixture was then allowed to warm up to room temperature and stirred for 16 h. The mixture was diluted with CH₂Cl₂ (100 mL) and washed with H₂O (2 x 100 mL). The organic phase was dried over Na₂SO₄ and concentrated *in vacuo*. Flash column chromatography (pentane:DCM = 5:1) afforded compound **4y** (2.09 g, 79%) as a colorless oil. Diastereomeric ratio was determined to be 92:8 by chiral GC. R_f 0.3 (pentane/DCM = 4:1). $[\alpha]_D^{26} +12$ (c 1.0, CHCl₃). ($[\alpha]_D^{25} -10.5$ (c 1.0, CHCl₃) for product from (+)- α -pinene ^{S2}. ¹H NMR (300 MHz, CDCl₃) δ 2.36 – 2.23 (m, 1H), 2.20 – 1.96 (m, 2H), 1.94 – 1.79 (m, 2H), 1.79 – 1.71 (m, 1H), 1.30 – 1.20 (m, 13H), 1.17 (s, 3H), 1.07 – 0.99 (m, 6H), 0.82 (d, *J* = 9.4 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 82.8, 48.0, 41.3, 38.6, 38.2, 34.1, 28.6, 28.4, 24.7, 24.7, 23.2, 22.7, carbon attached to boron not observed. ¹¹B NMR (96 MHz, CDCl₃) δ 34.4. Spectroscopic data are in accordance with those described in the literature.^{S2}

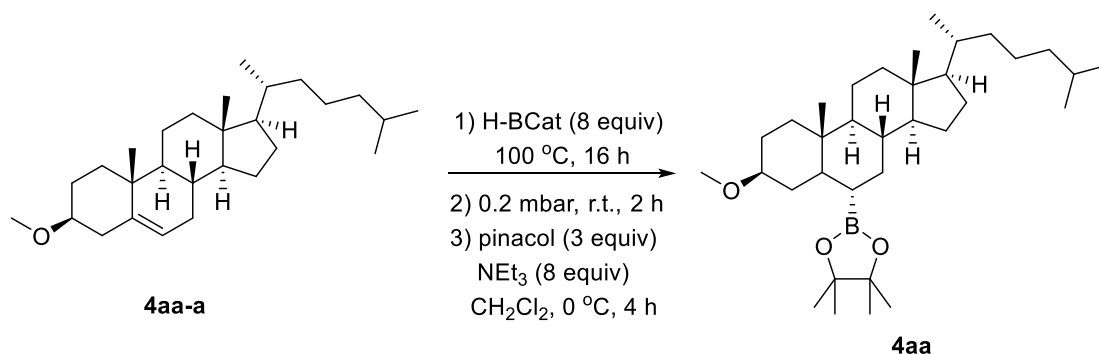


2-((1*R*,2*R*,5*R*)-2-Isopropyl-5-methylcyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4z**)



4z was synthesized according to a reported procedure.^{S2}

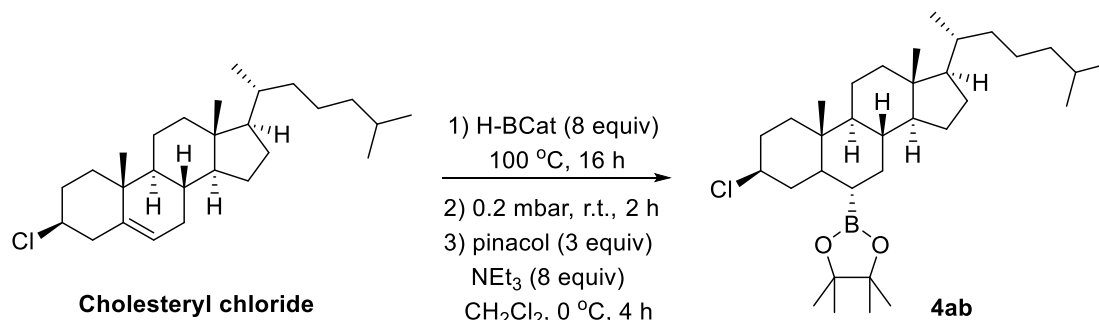
2-((3*S*,6*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-Methoxy-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4aa**)



4aa-a was synthesized from cholesterol by a reported procedure.^{S18}

4aa was synthesized according to Aggarwal's procedure.^{S19} Freshly distilled catecholborane (0.48 g, 4.0 mmol, 8.0 equiv) was added to a Schlenk flask containing **4aa-a** (0.4 g, 0.5 mmol, 1.0 equiv). The resulting mixture was heated to 100 °C at which point it turned into a solution. After 16 h at the same temperature, the mixture was cooled to room temperature and TLC analysis (pentane:EtOAc 3:1) revealed complete consumption of **4aa-a**. Excess catecholborane was removed under high vacuum (0.2 mbar, 2 h, room temperature). The crude material was diluted with CH₂Cl₂ (5 mL) and Et₃N (0.4 g, 0.56 mL, 8.0 equiv) and pinacol (177 mg, 1.5 mmol, 3.0 equiv) 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 × 20 mL). The combined organic layers were dried (MgSO₄), filtered, and concentrated under vacuum. Purification by column chromatography on silica gel, eluting with pentane:EtOAc (95:5 → 75:25) gave **4aa** as white solid (165 mg, 63% yield). M.p.: 138 – 140 °C. $[\alpha]_D^{24} +23$ (c 1.2, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 3.31 (s, 3H), 3.24 – 3.05 (m, 1H), 2.01 – 1.67 (m, 5H), 1.65 – 1.44 (m, 4H), 1.39 – 1.27 (m, 6H), 1.24 (s, 6H), 1.24 (s, 6H), 1.22 – 0.92 (m, 14H), 0.91 – 0.84 (m, 9H), 0.78 (s, 3H), 0.73 – 0.66 (m, 1H), 0.63 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 82.9, 79.8, 56.3, 55.4, 54.1, 45.3, 42.6, 40.1, 39.5, 36.7, 36.2, 35.8, 35.6, 35.6, 33.7, 33.5, 28.3, 28.0, 27.9, 24.9, 24.6, 24.2, 23.9, 22.8, 22.6, 21.2, 18.7, 12.4, 12.1, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 32.8. **HRMS** (ESI) *m/z* = 551.4606 calcd. for C₃₄H₆₁BO₃ Na⁺ [M+Na]⁺, found: 551.4625. **FTIR** (neat): ν (cm⁻¹) 2930, 2912, 2868, 2850, 1468, 1379, 1319, 1273, 1215, 1165, 1146, 1105, 972, 931, 851.

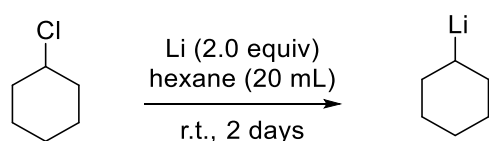
2-((3S,6S,8R,9S,10S,13R,14S,17R)-3-chloro-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4ab**)



4ab was synthesized according to Aggarwal's procedure.^{S19} Freshly distilled catecholborane (1.44 g, 12.0 mmol, 6.0 equiv) was added to a Schlenk flask containing cholesteryl chloride (0.81 g, 2.0 mmol, 1.0 equiv). The resulting mixture was heated to 100 °C at which point it turned into a solution. After 16 h at the same temperature, the mixture was cooled to room temperature and TLC analysis (pentane:DCM 2:1) revealed complete consumption of cholesteryl chloride. Excess catecholborane was removed under high vacuum (0.2 mbar, 2 h, room temperature). The crude material was diluted with CH₂Cl₂ (5 mL) and Et₃N (1.62 g, 2.2 mL, 16 mmol, 8.0 equiv) and pinacol (0.72 g, 6.0 mmol, 3.0 equiv) 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 × 20 mL). The combined organic layers were dried (MgSO₄), filtered, and concentrated under vacuum. Purification by column chromatography on silica gel, eluting with pentane:DCM (5:1→3:1) gave **4ab** as white solid (0.87 g, 86% yield). R_f 0.4 (pentane/DCM = 2:1). M.p.: 171-172 °C. [α]_D²⁴ +47 (c 0.8, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 4.04 – 3.75 (m, 1H), 2.09 – 1.90 (m, 2H), 1.88 – 1.69 (m, 4H), 1.67 – 1.41 (m, 6H), 1.39 – 1.27 (m, 6H), 1.24 (s, 12H), 1.15 – 0.95 (m, 10H), 0.93 – 0.80 (m, 13H), 0.74 – 0.67 (m, 1H), 0.63 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 83.0, 60.3, 56.3, 56.2, 53.8, 47.3, 42.6, 40.0, 39.5, 39.1, 38.5, 36.2, 35.8, 35.6, 35.1, 33.5, 33.1, 28.2, 28.0, 24.8, 24.7, 24.2, 23.9, 22.8, 22.6, 21.1, 18.7, 12.4, 12.1, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 34.4. **HRMS** (ESI) *m/z* = 555.4111 calcd. for C₃₃H₅₈BClO₂Na⁺ [M+Na]⁺, found: 555.4121. **FTIR** (neat): ν (cm⁻¹) 2937, 2868, 2848, 1468, 1444, 1378, 1320, 1273, 1229, 1214, 1167, 1145, 969, 850, 896, 850, 756.

4.4 Preparation of organolithium reagents

Cyclohexyllithium solution in hexane



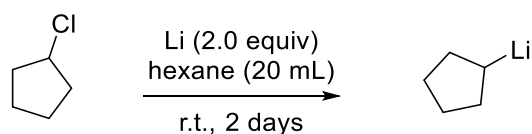
A Schlenk flask was flushed with dry Argon gas. After charging the flask with dry hexane (20 ml) and lithium sand (280 mg, 40 mmol, 2.0 equiv), cyclohexyl chloride (2.36 g, 20 mmol, 1.0 equiv) was added slowly. The reaction mixture was stirred at high speed (1000 rpm) for 2 days. The upper clear solution was transferred to a dry Schlenk tube flushed with Argon via syringe. The concentration of cyclohexyllithium was titrated to be 0.53 mol/L by menthol/2,2'-bipyridine.

Titration procedure: An oven dried 25 mL three neck flask equipped with an Argon inlet adapter, a stirring bar and two rubber septa, was cooled under a stream of Argon. Upon cooling the flask was charged with menthol (99.7 mg, 0.639 mmol), 3 mg of 2,2'-dipyridyl (as indicator) and 5 mL of dry Et₂O. To the resulting solution is added the organometallic reagent solution at 0 °C via a 1.0 mL syringe (graduated in 0.01 mL increments) in a dropwise fashion. 1.21 mL of the cyclohexyllithium solution was used.

The calculated concentration was $0.639 \text{ mmol}/1.21 \text{ mL} = 0.53 \text{ mol/L}$.

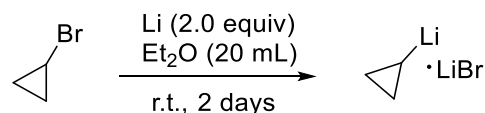
Caution: During addition, it will be observed that periodic quantities of a red colored substance will appear in solution. This is the charge transfer complex between the alkyl lithium and 2,2'-dipyridyl, and it will be noted that in the early stages of this titration this red color will disperse rapidly. As one nears the endpoint, the red coloration will require longer periods of time to disperse. At this point, it is necessary to slow the rate of addition of the alkyl lithium reagent as the endpoint is approaching. Eventually, the addition of a single drop of alkyl lithium will cause a persistent red coloration of the solution. This is the endpoint of the titration.

Cyclopentyllithium solution in hexane



A Schlenk flask was flushed with dry Argon gas. After charging the flask with dry hexane (20 ml) and lithium sand (280 mg, 40 mmol, 2.0 equiv), cyclopentyl chloride (2.08 g, 20 mmol, 1.0 equiv) was added slowly. The reaction mixture was stirred at high speed (1000 rpm) for 1 day. The upper clear solution was transferred to a dry Schlenk tube flushed with Argon. The concentration of cyclopentyllithium was determined to be 0.62 mol/L by menthol/2,2'-bipyridine with the titration procedure presented above.

Cyclopropanyllithium lithium bromide complex solution in Et₂O



A Schlenk flask was flushed with dry Argon gas. After charging the flask with dry Et₂O (20 ml) and lithium sand (280 mg, 40 mmol, 2.0 equiv), cyclopropyl bromide (2.42 g, 1.6 mL, 20 mmol, 1.0 equiv) was added slowly. The reaction mixture was stirred at high speed (1000 rpm) for 1 day. The upper clear solution was transferred to a dry Schlenk tube flushed with Argon. The concentration of cyclopropanyllithium lithium bromide complex solution was determined to be 1.17 mol/L by menthol/2,2'-bipyridine with the titration procedure presented above.

5. Mechanistic Studies

5.1 Stern-Volmer Fluorescence Quenching Experiments

All *fac*-Ir(ppy)₃ solutions were excited at 420 nm and the emission intensity was collected at 528 nm. In a typical experiment, the solution of *fac*-Ir(ppy)₃ in a mixture solvent of CH₃CN/DMSO (10:1) (178 μM) was added the appropriate amount of quencher (solution in CH₃CN/DMSO (10:1)) in a screw-top 1.0 cm quartz cuvette. After degassing with Argon for 3 min, the emission spectra of the samples were collected (**Figure S1**).

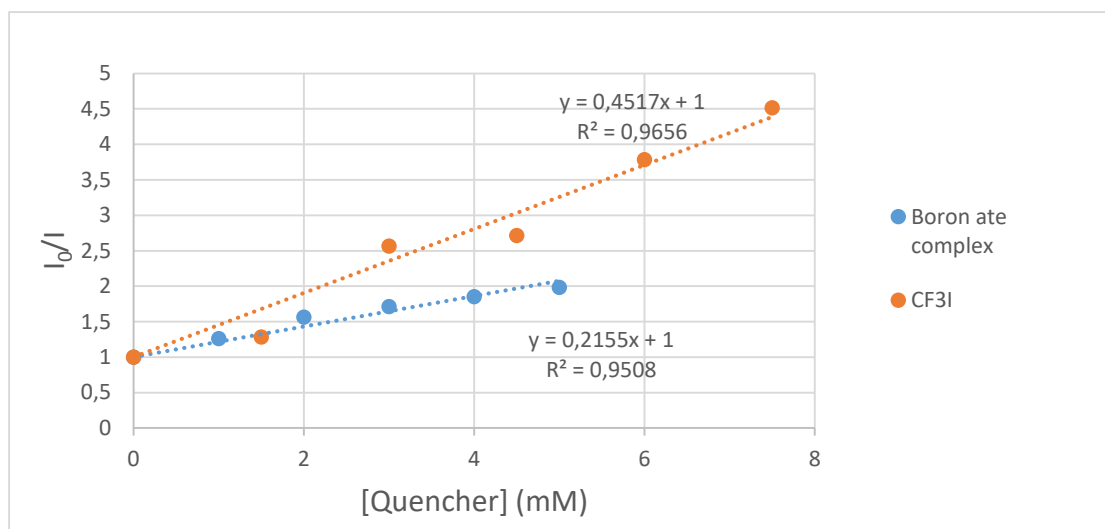


Figure S1. *Fac*-Ir(ppy)₃ Solutions Quenched by Boron Ate Complex and CF₃I.

5.2 Quantum Yield Analysis

The quantum yield of this reaction was determined by chemical actinometry. Following a similar procedure reported by Melchiorre^{S20} and Glorius^{S21}, an aqueous solution of potassium ferrioxalate was prepared and stored in the dark. This actinometer solution measures the photodecomposition of ferric oxalate anions to ferrous oxalate anions, which are then reacted with 1,10-phenanthroline to form [Fe(phen)₃]²⁺. The concentration of this complex is then estimated by UV/Vis absorbance at 510 nm. The number of moles of [Fe(phen)₃]²⁺ complex formed is related to the numbers of photons absorbed by the actinometer solution.

Preparation of the solutions used for the quantum yield measurements:

1. Potassium ferrioxalate solution: Potassium ferrioxalate trihydrate (294 mg) and 95-98% H₂SO₄ (140 μ L) were added to a 50 mL volumetric flask and filled to the mark with distilled water.
2. Buffer solution: Sodium acetate (4.94 g) and 95-98% H₂SO₄ (1.0 mL) were added to a 100 mL volumetric flask and filled to the mark with distilled water.

The actinometry measurements:

a) 1 mL of the actinometer solution was taken in a quartz cuvette ($l = 1$ cm). This solution was placed 5 cm away from a 4 W blue LED ($\lambda_{\text{max}} = 455$ nm) and irradiated for 15 s. The same process was repeated for different time intervals: 30, 45, 60 s.

b) After irradiation, the actinometer solution was transferred to a 10 mL volumetric flask containing 1.0 mg of 1,10-phenanthroline in 2 mL of buffer solution. The flask was filled to the mark with distilled water. In a similar manner, a blank solution was also prepared using the actinometer solution stored in dark.

c) The absorbance of the actinometer solution after complexation with 1,10-phenanthroline at $\lambda = 510$ nm was measured by UV/Vis spectrophotometry.

d) According to Beer's law, the number of moles of Fe²⁺ formed (x) for each sample was determined by:

$$Fe^{2+} = \frac{v_1 v_3 \Delta A(510 \text{ nm})}{10^3 v_2 l \varepsilon(510 \text{ nm})}$$

Where:

v_1 = Irradiated volume (1 mL).

v_2 = The aliquot of the irradiated solution taken for the estimation of Fe^{2+} ions (1 mL).

v_3 = Final volume of the solution after complexation with 1,10-phenanthroline (10 mL).

$\varepsilon(510 \text{ nm})$ = Molar extinction coefficient of $[Fe(Phen)_3]^{2+}$ complex ($11100 \text{ L mol}^{-1} \text{cm}^{-1}$).

l = Optical path-length of the cuvette (1 cm)

$\Delta A(510 \text{ nm})$ = Difference in absorbance between the irradiated solution and the solution stored in dark (blank)

e) The number of moles of Fe^{2+} formed (x) was plotted as a function of time (t) (**Figure S2**). The slope (dx/dt) of the line is equal to the number of moles of Fe^{2+} formed per unit time.

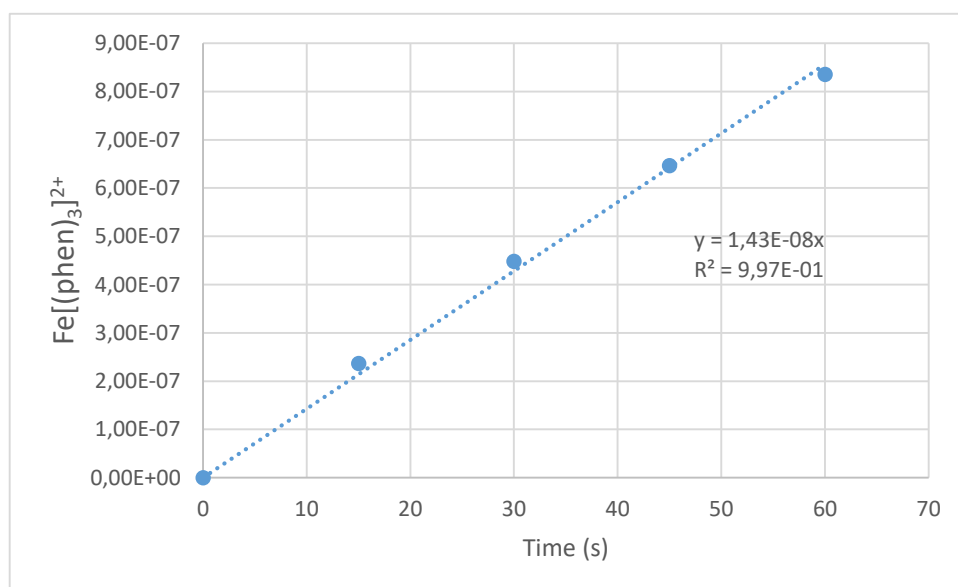


Figure S2. Moles of $[Fe(phen)_3]^{2+}$ per unit of time formed due to decomposition of the actinometer solution at 4 W blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) irradiation.

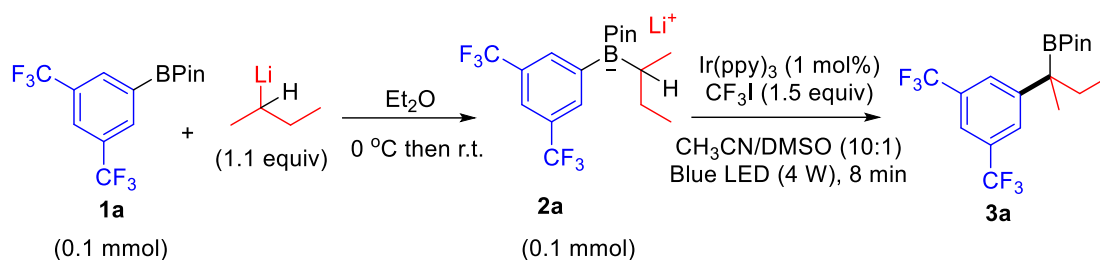
f) This slope (dx/dt) was correlated to the number of moles of incident photons per unit time (F = photon flux) by using following equation:

$$\Phi(\lambda) = \frac{dx/dt}{F(1 - 10^{-A(\lambda)})}$$

$\Phi(\lambda)$ = The quantum yield for Fe^{2+} formation at 450 nm is 0.9.^{S22}

g) $A(\lambda)$ = Absorbance of the ferrioxalate actinometer solution at a wavelength of 455 nm, which was measured placing 1 mL of the solution in a cuvette of pathlength 1 cm by UV/Vis spectrophotometry. We obtained an absorbance value of 0.246.

h) The determined incident photons per unit time (**F**) is 3.68×10^{-8} einsteins/s.



i) The number of moles of product formed upon irradiation of a reaction on 0.1 mmol scale of **2a** in 1 mL solvent (CH₃CN/DMSO 10:1) using the same reaction setup used before for the actinometer was determined by crude GC analysis using *n*-C₁₄H₃₀ as internal standard after 1 min of light irradiation. 19% of product was generated. Before irradiation, the measured absorbance of the reaction solution at 455 nm by UV/Vis spectrophotometry was 1.700. Using the following equation, the quantum yield of the reaction was determined to be 8.8:

$$\Phi(455 \text{ nm}) = \frac{\text{moles of product}}{F(1 - 10^{-A(\lambda)})t}$$

$$= \frac{0.1 \times 10^{-3} \times 0.19 \text{ mol}}{3.68 \times 10^{-8} \frac{\text{einsteins}}{\text{s}} (1 - 10^{-1.7}) \times 60\text{s}} = 8.8$$

5.3 Proposed Mechanisms

5.3.1 Smart initiation by oxidative quenching

According to the results of Stern-Volmer fluorescence quenching experiments, the excited photo catalyst (**PC***) was mainly quenched by CF₃I. A quantum yield of 8.8 indicated a radical chain process (**Figure S3**).

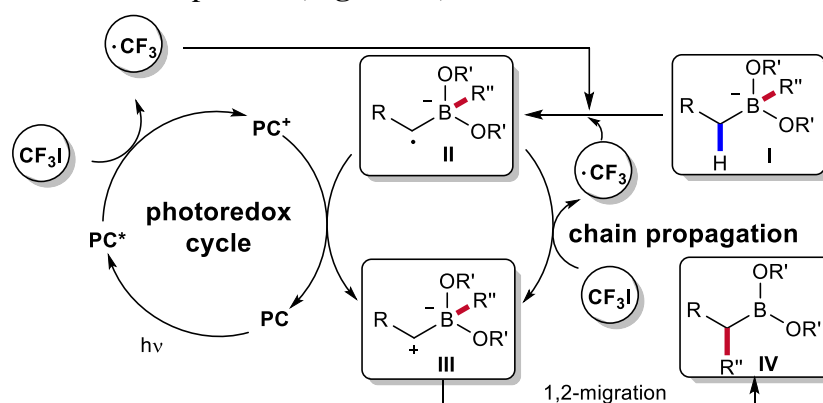


Figure S3. Possible reaction pathway initiated by oxidative quenching.

The radical chain process was initiated by a photoredox process. For the photoredox cycle, the photo catalyst Ir(ppy)₃ was excited by blue LED light to Ir(ppy)₃* {*E*_{1/2}^{red}[Ir^{IV}/Ir^{III}*] = -1.73 V vs SCE in MeCN}^{S23}, which would reduce CF₃I {*E*_p = -1.52 V vs SCE in DMF}^{S24} to release CF₃ radical. CF₃ radical would abstract the α-H of the boron ate complex **I** to afford the radical anion intermediate **II**. **II** could be further oxidized to zwitterion **III** by the oxidized photo catalyst Ir(ppy)₃⁺ {*E*_{1/2}^{red}[Ir^{IV}/Ir^{III}] = +0.77 V vs SCE in MeCN}^{S23}, regenerating Ir(ppy)₃. 1,2-Migration

of R'' group from **III** would give the final product **IV**.

For the radical chain propagation process, another equivalent of hydrogen atom abstractor, CF₃ radical, was released when radical anion **II** was oxidized to zwitterion **III** by CF₃I.^{S17,25,26}

5.3.2 Smart initiation by reductive quenching

According to the results of Stern-Volmer fluorescence quenching experiments, the excited photo catalyst (PC*) was also quenched by the boronate complex **I** (minor pathway). The possibility of smart initiation by reductive quenching could not be excluded (**Figure S4**). The excited photo catalyst Ir(ppy)₃* {E_{1/2}^{red}[Ir^{III}*/Ir^{II}] = +0.31 V vs SCE in MeCN}^{S23} could oxidize the boronate complex **I** (E_{p/2} = +0.31 V vs SCE in CH₃CN)^{S27}, releasing an alkyl radical ·R''. Then the reduced photo catalyst Ir(ppy)₃⁻ {E_{1/2}^{red}[Ir^{III}/Ir^{II}] = -2.19 V vs SCE in MeCN}^{S23} reduce CF₃I to CF₃ radical to initiate the chain reaction. CF₃ radical could also be generated by iodine atom transfer from CF₃I to radical ·R''.

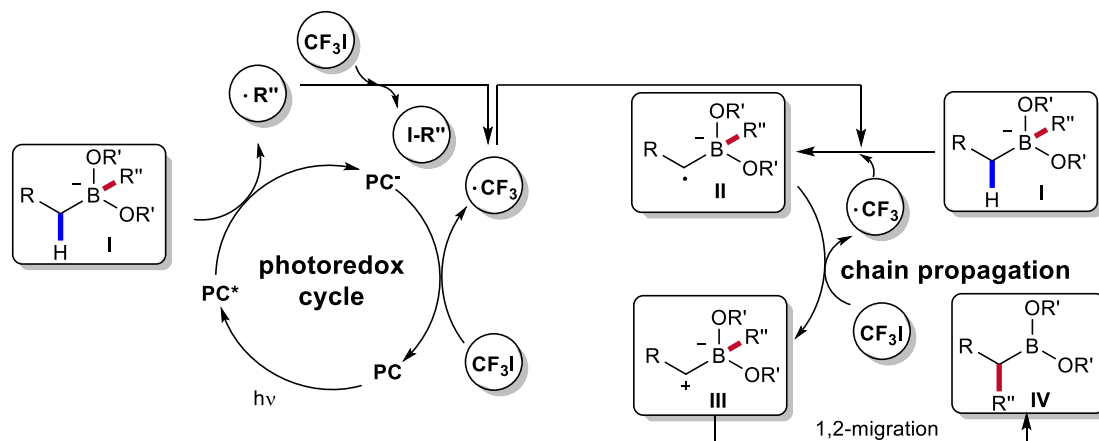
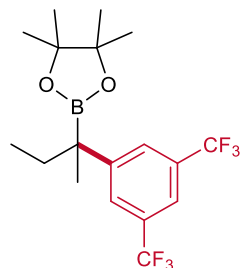


Figure S4. Possible reaction pathway initiated by reductive quenching.

6. Product Characterization

2-(2-(3,5-Bis(trifluoromethyl)phenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**)

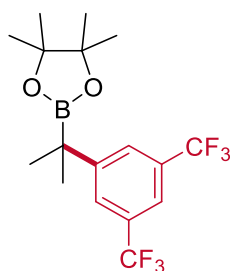


Following **GP1**, using **1a** (68.0 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in cyclohexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **3a** as colorless liquid (53.1 mg, 67% yield). R_f 0.5 (pentane/DCM = 4:1). ¹H NMR (300 MHz, CDCl₃) δ 7.78 (s, 2H), 7.66 (s, 1H), 1.96-1.84 (m, 1H), 1.79-1.67 (m, 1H), 1.37 (s, 3H), 1.22 (s, 12H), 0.84 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (75

MHz, CDCl₃) δ 150.3, 131.1 (q, J = 32.7 Hz), 127.5-127.2 (m), 123.7 (q, J = 272.5 Hz), 119.89 – 118.71 (m), 83.9, 32.0, 24.6, 24.5, 20.8, 9.9, *carbon attached to boron not observed*. ¹⁹F NMR (282 MHz, CDCl₃) δ -62.8. ¹¹B NMR (96 MHz, CDCl₃) δ 33.6. **HRMS** (EI) m/z = 396.1690 calcd. for C₁₈H₂₃BF₆O₂⁺ [M]⁺, found: 396.1688. **FTIR** (neat): ν (cm⁻¹) 2981, 1463, 1369, 1320, 1274, 1169, 1126, 965, 895, 851, 708, 682.

According to crude GC analysis with *n*-C₁₄H₃₀ as internal standard, GC yield of **3a** was 72% and recovered yield of **1a** was 18%.

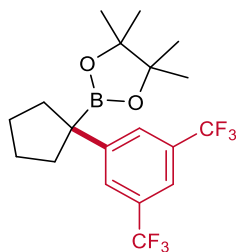
2-(2-(3,5-Bis(trifluoromethyl)phenyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**)



Following **GP1**, using **1a** (68.0 mg, 0.2 mmol) and isopropyllithium (0.7 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **3b** as colorless liquid (50.8 mg, 66% yield). R_f 0.6 (pentane/DCM = 4:1). ¹H NMR (300 MHz, CDCl₃) δ 7.76 (s, 2H), 7.66 (s, 1H), 1.39 (s, 6H), 1.21 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 151.5, 131.1 (q, J = 32.7 Hz), 126.9 – 126.5 (m), 123.7 (q, J = 272.6 Hz), 119.1 (dd, J = 7.7, 3.9 Hz), 83.9, 25.3, 24.4, *carbon attached to boron not observed*. ¹⁹F NMR (282 MHz, CDCl₃) δ -62.8. ¹¹B NMR (96 MHz, CDCl₃) δ 33.7. **HRMS** (EI) m/z = 382.1533 calcd. for C₁₇H₂₁BF₆O₂⁺ [M]⁺, found: 382.1538. **FTIR** (neat): ν (cm⁻¹) 2980, 2937, 2880, 1462, 1369, 1319, 1274, 1169, 1125, 965, 895, 878, 851, 708, 682. According to crude GC analysis with *n*-C₁₄H₃₀ as internal standard, GC yield of **3b** was 82% and recovered yield of **1a** was 8%.

Following **GP3**, using **1a** (68.0 mg, 0.2 mmol) and isopropyllithium (0.7 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **3b** as colorless liquid (42.0 mg, 55% yield). R_f 0.6 (pentane/DCM = 4:1). ¹H NMR (300 MHz, CDCl₃) δ 7.76 (s, 2H), 7.66 (s, 1H), 1.39 (s, 6H), 1.21 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 151.5, 131.1 (q, J = 32.7 Hz), 126.9 – 126.5 (m), 123.7 (q, J = 272.6 Hz), 119.1 (dd, J = 7.7, 3.9 Hz), 83.9, 25.3, 24.4, *carbon attached to boron not observed*. ¹⁹F NMR (282 MHz, CDCl₃) δ -62.8. ¹¹B NMR (96 MHz, CDCl₃) δ 33.7. **HRMS** (EI) m/z = 382.1533 calcd. for C₁₇H₂₁BF₆O₂⁺ [M]⁺, found: 382.1538. **FTIR** (neat): ν (cm⁻¹) 2980, 2937, 2880, 1462, 1369, 1319, 1274, 1169, 1125, 965, 895, 878, 851, 708, 682. According to crude GC analysis with *n*-C₁₄H₃₀ as internal standard, GC yield of **3b** was 76% and recovered yield of **1a** was 11%.

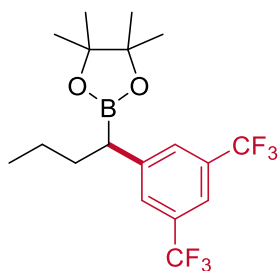
2-(1-(3,5-Bis(trifluoromethyl)phenyl)cyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**)



Following **GP1**, using **1a** (68.0 mg, 0.2 mmol) and cyclopentylolithium (0.62 M in hexane, 0.355 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **3c** as colorless sticky oil (51.7 mg, 63% yield). R_f 0.5 (pentane/DCM = 4:1). ^1H NMR (300 MHz, CDCl_3) δ 7.71 (s, 2H), 7.63 (s, 1H), 2.46 – 2.27 (m, 2H), 1.78-1.63 (m, 7H), 1.37 – 1.18 (m, 2H), 1.15 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 150.0, 130.7 (t, $J = 32.7$ Hz), 127.3-127.1 (m), 123.6 (q, $J = 272.6$ Hz), 119.5 – 118.4 (m), 83.9, 35.2, 24.4, 24.3, *carbon attached to boron not observed*. ^{19}F NMR (282 MHz, CDCl_3) δ -62.8. ^{11}B NMR (96 MHz, CDCl_3) δ 33.4. **HRMS** (ESI) m/z = 431.1588 calcd. for $\text{C}_{19}\text{H}_{23}\text{BF}_6\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$, found: 431.1583. **FTIR** (neat): ν (cm^{-1}) 2978, 2960, 2873, 1456, 1372, 1320, 1275, 1167, 1130, 982, 893, 854, 708, 682. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, GC yield of **3c** was 72% and recovered yield of **1a** was 18%.

Following **GP3**, using **1a** (68.0 mg, 0.2 mmol) and cyclopentylolithium (0.62 M in hexane, 0.355 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **3c** as colorless sticky oil (49.8 mg, 61% yield). R_f 0.5 (pentane/DCM = 4:1). ^1H NMR (300 MHz, CDCl_3) δ 7.71 (s, 2H), 7.63 (s, 1H), 2.46 – 2.27 (m, 2H), 1.78-1.63 (m, 7H), 1.37 – 1.18 (m, 2H), 1.15 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 150.0, 130.7 (t, $J = 32.7$ Hz), 127.3-127.1 (m), 123.6 (q, $J = 272.6$ Hz), 119.5 – 118.4 (m), 83.9, 35.2, 24.4, 24.3, *carbon attached to boron not observed*. ^{19}F NMR (282 MHz, CDCl_3) δ -62.8. ^{11}B NMR (96 MHz, CDCl_3) δ 33.4. **HRMS** (ESI) m/z = 431.1588 calcd. for $\text{C}_{19}\text{H}_{23}\text{BF}_6\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$, found: 431.1583. **FTIR** (neat): ν (cm^{-1}) 2978, 2960, 2873, 1456, 1372, 1320, 1275, 1167, 1130, 982, 893, 854, 708, 682. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, GC yield of **3c** was 66% and recovered yield of **1a** was 17%.

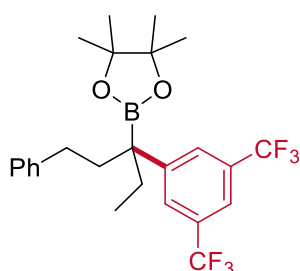
2-(1-(3,5-Bis(trifluoromethyl)phenyl)butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**)



Following **GP1**, using **1a** (68.0 mg, 0.2 mmol) and n -butyllithium (1.6 M in hexane, 0.14 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded

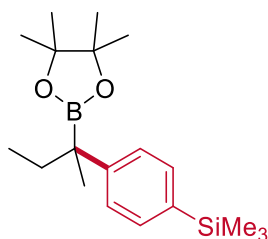
3d as colorless liquid (27.0 mg, 34% yield). R_f 0.6 (pentane/DCM = 4:1). ^1H NMR (300 MHz, CDCl_3) δ 7.69 – 7.60 (m, 3H), 2.46 (t, J = 7.9 Hz, 1H), 1.95 – 1.80 (m, 1H), 1.73 – 1.57 (m, 1H), 1.33 – 1.24 (m, 2H), 1.20 (s, 12H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 146.3, 131.3 (q, J = 32.8 Hz), 128.5, 123.6 (q, J = 272.6 Hz), 120.0 – 118.8 (m), 83.8, 34.7, 24.6, 24.5, 22.3, 14.0, *carbon attached to boron not observed*. ^{19}F NMR (282 MHz, CDCl_3) δ -62.9. ^{11}B NMR (96 MHz, CDCl_3) δ 33.5. **HRMS** (EI) m/z = 396.1690 calcd. for $\text{C}_{18}\text{H}_{23}\text{BF}_6\text{O}_2^+ [\text{M}]^+$, found: 396.1691. **FTIR** (neat): ν (cm^{-1}) 2979, 2935, 2875, 1467, 1433, 1373, 1332, 1276, 1167, 1128, 967, 896, 707, 682. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, GC yield of **3d** was 34% and recovered yield of **1a** was 39%.

2-(3-(3,5-Bis(trifluoromethyl)phenyl)-1-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**)



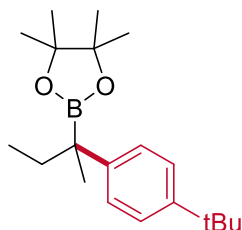
Following **GP4**, using **1e** (52.0 mg, 0.19 mmol), 1-bromo-3,5-bis(trifluoromethyl)benzene (64.5 mg, 0.22 mmol) and n -butyllithium (1.6 M in hexane, 0.15 mL, 0.24 mmol), flash chromatography eluting with pentane/DCM (1:1) afforded **3e** as light yellow oil (26.6 mg, 29% yield). R_f 0.4 (pentane/DCM = 1:1). ^1H NMR (300 MHz, CDCl_3) δ 7.74 (s, 2H), 7.61 (s, 1H), 7.23 – 7.01 (m, 5H), 2.39 – 2.22 (m, 2H), 2.12 – 2.00 (m, 2H), 1.90 (q, J = 7.4 Hz, 2H), 1.18 (s, 12H), 0.76 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 148.4, 142.5, 131.1 (q, J = 32.8 Hz), 128.4, 128.3, 128.0 – 127.8 (m), 125.9, 123.7 (q, J = 272.7 Hz), 119.3, 83.9, 37.1, 31.7, 27.7, 24.7, 9.4, *carbon attached to boron not observed*. ^{19}F NMR (282 MHz, CDCl_3) δ -62.8. ^{11}B NMR (96 MHz, CDCl_3) δ 33.2. **HRMS** (ESI) m/z = 509.2057 calcd. for $\text{C}_{25}\text{H}_{29}\text{BF}_6\text{NaO}_2^+ [\text{M}+\text{Na}]^+$, found: 509.2060. **FTIR** (neat): ν (cm^{-1}) 2981, 2936, 2879, 1455, 1371, 1323, 1274, 1167, 1126, 966, 889, 853, 798, 750, 724, 709, 699, 682. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, the crude yield of 3,5-bis(trifluoromethyl)phenylboronic acid pinacol ester was 35%.

Trimethyl(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)phenyl)silane (**3f**)



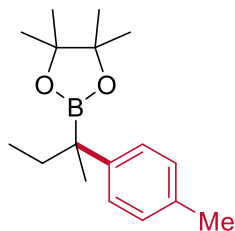
Following **GP1**, using **1f** (55.2 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **3f** as yellow oil (34.8 mg, 52% yield). R_f 0.4 (pentane/DCM = 4:1). ^1H NMR (300 MHz, CDCl_3) δ 7.48 – 7.39 (m, 2H), 7.34 – 7.27 (m, 2H), 1.94 – 1.82 (m, 1H), 1.76 – 1.66 (m, 1H), 1.33 (s, 1H), 1.23 (s, 6H), 1.23 (s, 6H), 0.85 (t, J = 7.4 Hz, 2H), 0.25 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 148.1, 136.1, 133.1, 126.3, 83.3, 32.0, 24.7, 24.6, 21.2, 10.2, -1.0, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 33.9. **HRMS** (ESI) m/z = 355.2235 calcd. for $\text{C}_{19}\text{H}_{33}\text{BO}_2\text{SiNa}^+$ $[\text{M}+\text{Na}]^+$, found: 355.2250. **FTIR** (neat): ν (cm^{-1}) 2978, 2958, 1598, 1458, 1372, 1345, 1315, 1248, 1139, 1087, 1043, 982, 835, 817, 753, 726, 691, 673.

2-(2-(4-(Tert-butyl)phenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**)



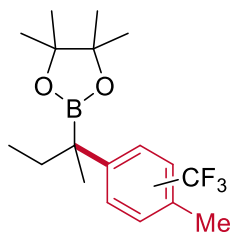
Following **GP1**, using **1g** (52.0 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **3g** as yellow oil (38.3 mg, 61% yield). R_f 0.5 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 7.24 – 7.09 (m, 4H), 1.76 – 1.72 (m, 1H), 1.64 – 1.52 (m, 1H), 1.23 – 1.21 (m, 12H), 1.14 (s, 6H), 1.14 (s, 6H), 0.76 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 147.5, 144.2, 126.4, 124.8, 83.2, 34.2, 32.1, 31.4, 24.6, 24.6, 21.4, 10.3, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 33.7. **HRMS** (ESI) m/z = 339.2466 calcd. for $\text{C}_{20}\text{H}_{33}\text{O}_2\text{BNa}^+$ $[\text{M}+\text{Na}]^+$, found: 339.2491. **FTIR** (neat): ν (cm^{-1}) 2965, 2939, 2871, 1512, 1461, 1380, 1364, 1351, 1308, 1269, 1140, 1114, 1017, 965, 851, 827, 794.

4,4,5,5-Tetramethyl-2-(2-(*p*-tolyl)butan-2-yl)-1,3,2-dioxaborolane (**3h**)



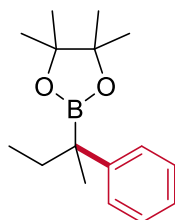
Following **GP2**, using **1h** (43.6 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **3h** as yellow oil (18.2 mg, 33% yield). R_f 0.4 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 7.21 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 2.31 (s, 3H), 1.92 – 1.80 (m, 1H), 1.74 – 1.60 (m, 1H), 1.31 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 0.83 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.3, 134.2, 128.7, 126.7, 83.2, 32.0, 24.6, 24.6, 21.1, 20.9, 10.1, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.4. **HRMS** (ESI) m/z = 297.1996 calcd. for $\text{C}_{17}\text{H}_{27}\text{BO}_2\text{Na}^+$

$[M+Na]^+$, found: 297.2009. **FTIR** (neat): ν (cm^{-1}) 2976, 2930, 2877, 1512, 1457, 1379, 1377, 1347, 1307, 1264, 1214, 1138, 1096, 1043, 1020, 965, 849, 815, 723, 673, 576. According to GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, GC yield of **3h** was 34% and recovered yield of **1h** was 33%.



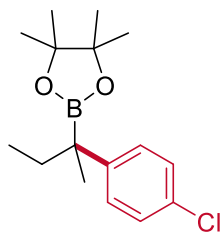
About 10% trifluoromethylated **3h** was also detected ($o/m = 1:1.2$) by crude GC and GC/MS.

4,4,5,5-Tetramethyl-2-(2-phenylbutan-2-yl)-1,3,2-dioxaborolane (**3i**)



Following **GP1**, using **1i** (40.8 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **3i** as yellow oil (31.1 mg, 60% yield). R_f 0.4 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 7.28 – 7.14 (m, 4H), 7.08 – 7.02 (m, 1H), 1.88 – 1.72 (m, 1H), 1.70 – 1.55 (m, 1H), 1.25 (s, 3H), 1.14 (s, 6H), 1.13 (s, 6H), 0.75 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 147.3, 128.0, 126.9, 124.9, 83.2, 31.9, 24.6, 21.0, 10.0, carbon attached to boron not observed. ^{11}B NMR (96 MHz, CDCl_3) δ 33.8. **HRMS** (ESI) $m/z = 283.1840$ calcd. for $\text{C}_{16}\text{H}_{25}\text{BO}_2\text{Na}^+$ $[M+Na]^+$, found: 283.1851. **FTIR** (neat): ν (cm^{-1}) 2976, 2931, 2876, 1600, 1495, 1458, 1371, 1348, 1309, 1264, 1215, 1139, 1099, 1031, 965, 856, 763, 699.

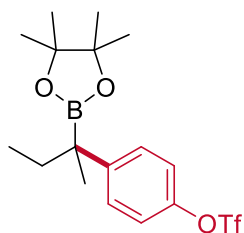
2-(2-(4-Chlorophenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3j**)



Following **GP1**, using **1j** (47.6 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **3j** as yellow sticky oil (34.5 mg, 59% yield). R_f 0.4 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 7.18-7.15 (m, 4H), 1.82 – 1.70 (m, 1H), 1.66 – 1.54 (m, 1H), 1.22 (s, 3H), 1.13 (s, 6H), 1.12 (s, 6H), 0.73 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz,

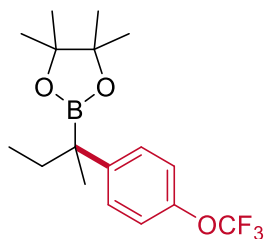
CDCl₃) δ 145.8, 130.7, 128.3, 128.0, 83.4, 31.9, 24.6, 24.7, 20.9, 9.8, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 34.2. **HRMS** (ESI) m/z = 317.1450 calcd. for C₁₆H₂₄BClO₂Na⁺ [M+Na]⁺, found: 317.1459. **FTIR** (neat): ν (cm⁻¹) 2976, 2936, 2877, 1491, 1460, 1372, 1346, 1313, 1264, 1214, 1166, 1138, 1098, 1043, 1013, 965, 858, 823, 757, 704, 672, 580.

4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)phenyl trifluoromethanesulfonate (**3k**)



Following **GP1**, using **1k** (70.4 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (3:1) afforded **3k** as yellow sticky oil (44.7 mg, 55% yield). R_f 0.4 (pentane/DCM = 5:2). ¹H NMR (300 MHz, CDCl₃) δ 7.43 – 7.34 (m, 2H), 7.22 – 7.12 (m, 2H), 1.92 – 1.77 (m, 1H), 1.77 – 1.63 (m, 1H), 1.32 (s, 3H), 1.20 (s, 12H), 0.81 (t, J = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 148.0, 147.2, 128.7, 120.6, 118.7 (q, J = 320.7 Hz), 83.5, 32.0, 24.5, 24.5, 21.0, 9.9, *carbon attached to boron not observed*. ¹⁹F NMR (282 MHz, CDCl₃) δ -73.0. ¹¹B NMR (96 MHz, CDCl₃) δ 34.3. **HRMS** (ESI) m/z = 431.1282 calcd. for C₁₇H₂₄O₅SBF₃Na⁺ [M+Na]⁺, found: 431.1291. **FTIR** (neat): ν (cm⁻¹) 2979, 2935, 1501, 1424, 1381, 1350, 1319, 1250, 1210, 1140, 1016, 889, 607. According to GC analysis with *n*-C₁₄H₃₀ as internal standard, GC yield of **3k** was 56% and recovered yield of **1k** was 24%.

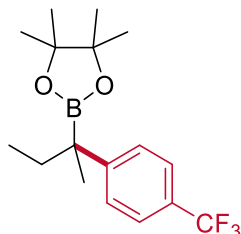
4,4,5,5-Tetramethyl-2-(2-(4-(trifluoromethoxy)phenyl)butan-2-yl)-1,3,2-dioxaborolane (**3l**)



Following **GP1**, using **1l** (57.6 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **3l** as yellow sticky oil (45.3 mg, 66% yield). R_f 0.4 (pentane/DCM = 3:1). ¹H NMR (300 MHz, CDCl₃) δ 7.37 – 7.29 (m, 2H), 7.16 – 7.06 (m, 2H), 1.94 – 1.77 (m, 1H), 1.77 – 1.61 (m, 1H), 1.32 (s, 3H), 1.21 (s, 6H), 1.21 (s, 6H), 0.82 (t, J = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 146.8 (q, J = 1.7 Hz), 146.1, 128.2, 120.6 (q, J = 256.3 Hz), 120.3, 83.5, 32.0, 24.6, 24.6, 21.1, 9.9, *carbon attached to boron not observed*. ¹⁹F NMR (282 MHz, CDCl₃) δ -57.9. ¹¹B NMR (96 MHz, CDCl₃) δ 34.3. **HRMS** (ESI) m/z = 367.1663 calcd. for C₁₇H₂₄BF₃O₃Na⁺ [M+Na]⁺, found: 367.1696. **FTIR**

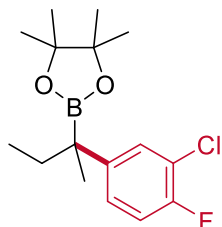
(neat): ν (cm^{-1}) 2979, 2937, 1510, 1350, 1318, 1260, 1222, 1168, 1142, 1020, 965, 860, 662.

4,4,5,5-Tetramethyl-2-(2-(4-(trifluoromethyl)phenyl)butan-2-yl)-1,3,2-dioxaborolane (**3m**)



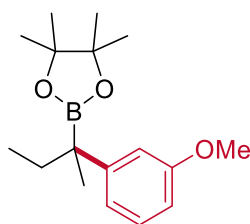
Following **GP1**, using **1m** (54.4 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **3m** as yellow sticky oil (43.2 mg, 66% yield). R_f 0.4 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 7.53 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 1.95 – 1.81 (m, 1H), 1.80 – 1.66 (m, 1H), 1.34 (s, 3H), 1.21 (s, 6H), 1.21 (s, 6H), 0.82 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 151.7, 127.3, 127.2 (q, J = 32.2 Hz), 124.8 (q, J = 3.8 Hz), 124.6 (q, J = 271.5 Hz), 83.5, 31.8, 24.6, 24.6, 20.8, 9.8, *carbon attached to boron not observed*. ^{19}F NMR (282 MHz, CDCl_3) δ -62.2. ^{11}B NMR (96 MHz, CDCl_3) δ 34.1. **HRMS** (ESI) m/z = 351.1714 calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_2\text{BF}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 351.1729. **FTIR** (neat): ν (cm^{-1}) 2978, 2938, 2878, 1618, 1460, 1373, 1349, 1324, 1265, 1164, 1139, 1121, 1099, 1069, 1016, 965, 860, 835, 687.

2-(2-(3-Chloro-4-fluorophenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3n**)



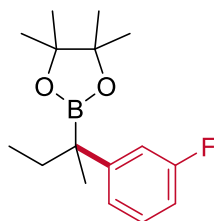
Following **GP1**, using **1n** (51.2 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **3n** as yellow sticky oil (35.6 mg, 57% yield). R_f 0.4 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 7.25 (dd, J = 7.2, 2.3 Hz, 1H), 7.13 – 7.05 (m, 1H), 6.96 (t, J = 8.8 Hz, 1H), 1.83 – 1.66 (m, 1H), 1.66 – 1.51 (m, 1H), 1.21 (s, 3H), 1.13 (s, 12H), 0.73 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 155.9 (d, J = 245.7 Hz), 144.4 (d, J = 3.7 Hz), 128.9, 126.7 (d, J = 6.7 Hz), 120.1 (d, J = 17.2 Hz), 115.8 (d, J = 20.5 Hz), 83.5, 32.0, 24.6, 24.5, 20.9, 9.8, *carbon attached to boron not observed*. ^{19}F NMR (282 MHz, CDCl_3) δ -121.4 (s). ^{11}B NMR (96 MHz, CDCl_3) δ 33.8. **HRMS** (ESI) m/z = 335.1356 calcd. for $\text{C}_{16}\text{H}_{23}\text{BClFO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 335.1353. **FTIR** (neat): ν (cm^{-1}) 2976, 2935, 2878, 1499, 1460, 1348, 1315, 1265, 1246, 1214, 1138, 1099, 1059, 965, 871, 852, 820, 743, 713, 674, 609, 580.

2-(2-(3-methoxyphenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3o**)



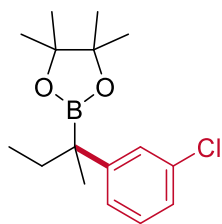
Following **GP1**, using **1o** (46.8 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (1:1) afforded **3o** as yellow sticky oil (27.6 mg, 48% yield). R_f 0.3 (pentane/DCM = 1:1). ^1H NMR (300 MHz, CDCl_3) δ 7.19 (t, $J = 7.9$ Hz, 1H), 6.94 – 6.86 (m, 2H), 6.68 (dd, $J = 7.9$, 2.0 Hz, 1H), 3.79 (s, 3H) 1.95 – 1.78 (m, 1H), 1.77 – 1.62 (m, 1H), 1.31 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 0.83 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 159.4, 149.2, 128.8, 119.5, 113.1, 110.1, 83.3, 55.0, 31.9, 24.6, 24.6, 21.0, 10.0, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.2. **HRMS** (ESI) m/z = 313.1945 calcd. for $\text{C}_{17}\text{H}_{27}\text{O}_3\text{BNa}^+$ $[\text{M}+\text{Na}]^+$, found: 313.1960. **FTIR** (neat): ν (cm^{-1}) 2977, 2935, 2877, 2836, 1599, 1581, 1486, 1461, 1372, 1347, 1311, 1289, 1253, 1215, 1166, 1139, 1041, 965, 852, 776, 704, 681.

2-(2-(3-Fluorophenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3p**)



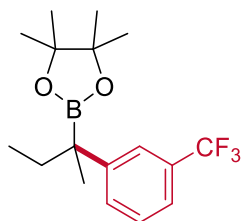
Following **GP1**, using **1p** (44.4 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **3p** as yellow sticky oil (25.5 mg, 46% yield). R_f 0.3 (pentane/DCM = 4:1). ^1H NMR (300 MHz, CDCl_3) δ 7.20 – 7.09 (m, 1H), 7.04 – 6.91 (m, 2H), 6.79 – 6.69 (m, 1H), 1.84 – 1.70 (m, 1H), 1.70 – 1.55 (m, 1H), 1.23 (s, 3H), 1.14 (s, 6H), 1.13 (s, 6H), 0.74 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 163.0 (d, $J = 243.7$ Hz), 150.3 (d, $J = 6.7$ Hz), 129.1 (d, $J = 8.4$ Hz), 122.7 (d, $J = 2.6$ Hz), 113.9 (d, $J = 21.5$ Hz), 111.7 (d, $J = 21.1$ Hz), 83.4, 31.8, 24.6, 24.6, 20.8, 9.8, *carbon attached to boron not observed*. ^{19}F NMR (282 MHz, CDCl_3) δ -114.1 (s). ^{11}B NMR (96 MHz, CDCl_3) δ 33.8. **HRMS** (ESI) m/z = 301.1746 calcd. for $\text{C}_{16}\text{H}_{24}\text{BF}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 301.1755. **FTIR** (neat): ν (cm^{-1}) 2978, 2933, 2878, 1612, 1583, 1486, 1460, 1372, 1349, 1314, 1266, 1242, 1215, 1164, 1139, 1120, 1100, 1042, 965, 914, 865, 851, 780, 702, 677, 586.

2-(2-(3-Chlorophenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3q**)



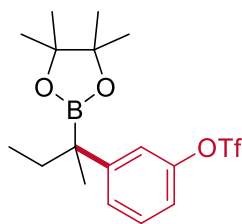
Following **GP1**, using **1q** (47.6 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **3q** as light yellow sticky oil (31.2 mg, 53% yield). R_f 0.4 (pentane/DCM = 4:1). ^1H NMR (300 MHz, CDCl_3) δ 7.25 – 7.20 (m, 1H), 7.15 – 7.09 (m, 2H), 7.07 – 6.99 (m, 1H), 1.84 – 1.69 (m, 1H), 1.69 – 1.54 (m, 1H), 1.23 (s, 3H), 1.14 (s, 6H), 1.14 (s, 6H), 0.74 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 149.6, 133.9, 129.1, 127.1, 125.3, 125.1, 83.4, 31.8, 24.6, 24.5, 20.8, 9.9, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 33.7. **HRMS** (ESI) m/z = 317.1450 calcd. for $\text{C}_{16}\text{H}_{24}\text{BClO}_2\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 317.1454. **FTIR** (neat): ν (cm^{-1}) 2976, 2935, 2876, 1593, 1567, 1460, 1372, 1348, 1314, 1263, 1214, 1167, 1138, 1107, 1043, 965, 874, 849, 781, 700, 668.

4,4,5,5-Tetramethyl-2-(2-(3-(trifluoromethyl)phenyl)butan-2-yl)-1,3,2-dioxaborolane (**3r**)



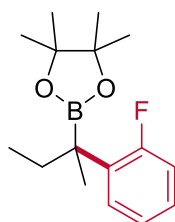
Following **GP1**, using **1r** (54.4 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **3r** as light yellow sticky oil (41.9 mg, 64% yield). R_f 0.5 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 7.59 (s, 1H), 7.54 – 7.46 (m, 1H), 7.43 – 7.35 (m, 2H), 1.96 – 1.81 (m, 1H), 1.80 – 1.64 (m, 1H), 1.35 (s, 3H), 1.22 (s, 12H), 0.83 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 148.4, 130.4 – 130.2 (m), 130.2 (q, J = 31.6 Hz), 128.3, 124.5 (d, J = 272.3 Hz), 123.9 (q, J = 3.8 Hz), 121.9 (q, J = 3.8 Hz), 83.5, 31.9, 24.6, 24.5, 20.9, 9.9, *carbon attached to boron not observed*. ^{19}F NMR (282 MHz, CDCl_3) δ -62.5 (s). ^{11}B NMR (96 MHz, CDCl_3) δ 34.1. **HRMS** (ESI) m/z = 351.1714 calcd. for $\text{C}_{17}\text{H}_{24}\text{BF}_3\text{O}_2\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 351.1727. **FTIR** (neat): ν (cm^{-1}) 2978, 2937, 2877, 1461, 1350, 1326, 1265, 1164, 1123, 1076, 965, 851, 803, 704.

3-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)phenyl trifluoromethanesulfonate (**3s**)



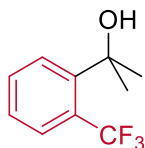
Following **GP1**, using **1s** (70.4 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (3:1) afforded **3s** as yellow sticky oil (48.1 mg, 59% yield). R_f 0.4 (pentane/DCM = 2:1). ^1H NMR (300 MHz, CDCl_3) δ 7.29 – 7.23 (m, 2H), 7.18 (s, 1H), 7.02 – 6.92 (m, 1H), 1.84 – 1.70 (m, 1H), 1.70 – 1.55 (m, 1H), 1.25 (s, 3H), 1.14 (s, 6H), 1.13 (s, 6H), 0.73 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 150.8, 149.7, 129.5, 126.8, 120.2, 118.8 (q, J = 320.8 Hz), 117.7, 83.6, 32.0, 24.6, 24.5, 20.8, 9.8, *carbon attached to boron not observed*. ^{19}F NMR (282 MHz, CDCl_3) δ -73.0 (s). ^{11}B NMR (96 MHz, CDCl_3) δ 33.8. **HRMS** (ESI) m/z = 431.1282 calcd. for $\text{C}_{17}\text{H}_{24}\text{BF}_3\text{O}_5\text{SNa}^+$ $[\text{M}+\text{Na}]^+$, found: 431.1299. **FTIR** (neat): ν (cm^{-1}) 2978, 2936, 2878, 1611, 1575, 1423, 1381, 1351, 1319, 1250, 1212, 1141, 926, 848, 799, 607. According to GC analysis with *n*- $\text{C}_{14}\text{H}_{30}$ as internal standard, GC yield of **3s** was 60% and recovered yield of **1s** was 24%.

2-(2-(2-Fluorophenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3t**)



Following **GP1**, using **1t** (44.4 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **3t** as yellow sticky oil (21.0 mg, 38% yield). R_f 0.3 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 7.22 – 7.12 (m, 1H), 7.11 – 6.96 (m, 2H), 6.94 – 6.84 (m, 1H), 1.84 – 1.57 (m, 2H), 1.21 (s, 3H), 1.18 (s, 12H), 0.70 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 161.1 (d, J = 242.9 Hz), 134.6 (d, J = 14.4 Hz), 127.5 (d, J = 5.5 Hz), 126.7 (d, J = 8.6 Hz), 123.9 (d, J = 3.2 Hz), 114.8 (d, J = 23.2 Hz), 83.3, 29.7, 24.6, 20.7, 9.2, *carbon attached to boron not observed*. ^{19}F NMR (282 MHz, CDCl_3) δ -112.4 (s). ^{11}B NMR (96 MHz, CDCl_3) δ 34.1. **HRMS** (ESI) m/z = 301.1746 calcd. for $\text{C}_{16}\text{H}_{24}\text{BFO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 301.1755. **FTIR** (neat): ν (cm^{-1}) 2977, 2929, 2876, 1487, 1462, 1447, 1380, 1351, 1317, 1266, 1218, 1198, 1142, 1114, 1101, 1032, 965, 870, 848, 808, 753, 684. According to GC analysis with *n*- $\text{C}_{14}\text{H}_{30}$ as internal standard, GC yield of **3t** was 39% and recovered yield of **1t** was 23%.

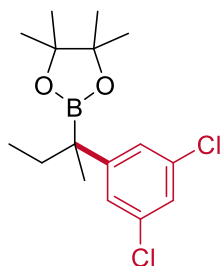
2-(2-(trifluoromethyl)phenyl)propan-2-ol (**3u-1**)



Following **GP1**, using **1u** (54.4 mg, 0.2 mmol) and isopropyllithium (0.7 M in hexane, 0.31 mL, 0.22 mmol) afford the crude alkylboronic ester **3u**. According to crude GC analysis with *n*-C₁₄H₃₀ as internal standard, recovered yield of **1u** was 12%. After oxidation workup with H₂O₂/NaOH,^{S17} flash chromatography eluting with pentane/diethylether (3:1) afforded **3u-1** as light yellow liquid (22.2 mg, 54% yield). R_f 0.4 (pentane/Et₂O = 3:1). ¹H NMR (300 MHz, CDCl₃) δ 7.68 (m, 1H), 7.59 – 7.51 (m, 1H), 7.47 – 7.37 (m, 1H), 7.27 (m, 1H), 1.87 (s, 1H), 1.62 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 148.1, 131.6, 128.0, 127.9 (q, *J* = 7.2 Hz), 127.0 (q, *J* = 30.8 Hz), 126.9, 124.9 (q, *J* = 271.4 Hz), 73.6, 32.5 (q, *J* = 2.4 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -54.2.

Following **GP3**, using **1u** (54.4 mg, 0.2 mmol) and isopropyllithium (0.7 M in hexane, 0.31 mL, 0.22 mmol) afford the crude alkylboronic ester **3u**. According to crude GC analysis with *n*-C₁₄H₃₀ as internal standard, recovered yield of **1u** was 8%. After oxidation workup with H₂O₂/NaOH,^{S17} flash chromatography eluting with pentane/diethylether (3:1) afforded **3u-1** as colorless liquid (20.5 mg, 50% yield). R_f 0.4 (pentane/Et₂O = 3:1). ¹H NMR (300 MHz, CDCl₃) δ 7.68 (m, 1H), 7.59 – 7.51 (m, 1H), 7.47 – 7.37 (m, 1H), 7.27 (m, 1H), 1.87 (s, 1H), 1.62 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 148.1, 131.6, 128.0, 127.9 (q, *J* = 7.2 Hz), 127.0 (q, *J* = 30.8 Hz), 126.9, 124.9 (q, *J* = 271.4 Hz), 73.6, 32.5 (q, *J* = 2.4 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -54.2.

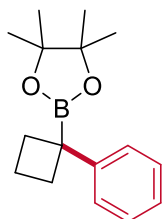
2-(2-(3,5-Dichlorophenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3v**)



Following **GP1**, using **1v** (54.6 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **3v** as light yellow sticky oil (31.8 mg, 48% yield). R_f 0.5 (pentane/DCM = 4:1). ¹H NMR (300 MHz, CDCl₃) δ 7.19 (d, *J* = 1.8 Hz, 2H), 7.13 (t, *J* = 1.8 Hz, 1H), 1.91 – 1.74 (m, 1H), 1.75 – 1.61 (m, 1H), 1.28 (s, 3H), 1.21 (s, 12H), 0.81 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 151.2, 134.5, 125.7, 125.2, 83.7, 31.7, 24.6, 24.5, 20.6, 9.8, carbon attached to boron not observed. ¹¹B NMR (96 MHz, CDCl₃) δ 33.5. **HRMS** (EI) *m/z* = 328.1163 calcd. for C₁₆H₂₃BCl₂O₂⁺ [M]⁺, found: 328.1162. **FTIR** (neat): ν (cm⁻¹) 2977, 2938, 2883, 1586, 1561, 1459, 1415, 1381, 1347, 1319, 1139, 852, 798, 692.

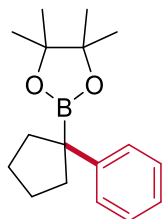
Following **GP3**, using **1v** (54.6 mg, 0.2 mmol) and *s*-butyllithium (1.4 M in hexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **3v** as colorless sticky oil (33.7 mg, 51% yield). R_f 0.5 (pentane/DCM = 4:1). ^1H NMR (300 MHz, CDCl_3) δ 7.19 (d, J = 1.8 Hz, 2H), 7.13 (t, J = 1.8 Hz, 1H), 1.91 – 1.74 (m, 1H), 1.75 – 1.61 (m, 1H), 1.28 (s, 3H), 1.21 (s, 12H), 0.81 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 151.2, 134.5, 125.7, 125.2, 83.7, 31.7, 24.6, 24.5, 20.6, 9.8, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 33.5. **HRMS** (EI) m/z = 328.1163 calcd. for $\text{C}_{16}\text{H}_{23}\text{BCl}_2\text{O}_2^+$ $[\text{M}]^+$, found: 328.1162. **FTIR** (neat): ν (cm^{-1}) 2977, 2938, 2883, 1586, 1561, 1459, 1415, 1381, 1347, 1319, 1139, 852, 798, 692. According to crude GC analysis with *n*- $\text{C}_{14}\text{H}_{30}$ as internal standard, crude yield of **3v** was 51% and recovered yield of **1v** was 16%.

4,4,5,5-Tetramethyl-2-(1-phenylcyclobutyl)-1,3,2-dioxaborolane (**3w**)



Following **GP1**, using cyclobutylboronic acid pinacol ester (36.4 mg, 0.2 mmol) and phenyllithium (1.9 M in dibutylether, 0.12 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **3w** as yellow sticky oil (22.0 mg, 43% yield). R_f 0.4 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 7.23 – 7.13 (m, 2H), 7.10 – 6.96 (m, 3H), 2.55 – 2.39 (m, 2H), 2.29 – 2.12 (m, 2H), 2.06 – 1.86 (m, 1H), 1.84 – 1.68 (m, 1H), 1.11 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 148.9, 127.9, 125.5, 124.4, 83.4, 32.0, 24.5, 18.8, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.1. **HRMS** (ESI) m/z = 281.1683 calcd. for $\text{C}_{16}\text{H}_{23}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 281.1680. **FTIR** (neat): ν (cm^{-1}) 2976, 2938, 2868, 1599, 1493, 1468, 1445, 1371, 1352, 1311, 1273, 1165, 1147, 1120, 965, 867, 842, 769, 736, 699.

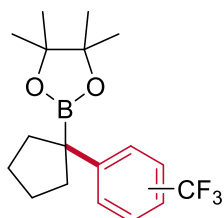
4,4,5,5-Tetramethyl-2-(1-phenylcyclopentyl)-1,3,2-dioxaborolane (**3x**)



Following **GP1**, using cyclopentylboronic acid pinacol ester (39.2 mg, 0.2 mmol) and phenyllithium (1.9 M in dibutylether, 0.12 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **3x** as yellow sticky oil (22.0 mg, 40% yield). R_f 0.3 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 7.25 – 7.11 (m, 4H), 7.10 – 6.97 (m, 1H), 2.38 – 2.06 (m, 2H), 1.75 – 1.42 (m, 6H), 1.06 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 147.2, 127.9, 127.0, 124.7, 83.3, 35.2, 24.6, 24.4, *carbon attached to*

boron not observed. ^{11}B NMR (96 MHz, CDCl_3) δ 34.2. **HRMS** (ESI) m/z = 295.1840 calcd. for $\text{C}_{17}\text{H}_{25}\text{BO}_2\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 295.1853. **FTIR** (neat): ν (cm^{-1}) 2979, 2960, 2870, 1351, 1309, 1265, 1141, 853, 735, 700, 617. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, crude yield of **3x** was 43% and recovered yield of phenylboronic acid pinacol ester was 16%.

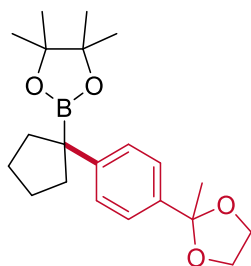
Following **GP3**, using cyclopentylboronic acid pinacol ester (39.2 mg, 0.2 mmol) and phenyllithium (1.9 M in dibutylether, 0.12 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **3x** as yellow sticky oil (25.0 mg, 46% yield). R_f 0.3 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 7.25 – 7.11 (m, 4H), 7.10 – 6.97 (m, 1H), 2.38 – 2.06 (m, 2H), 1.75 – 1.42 (m, 6H), 1.06 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 147.2, 127.9, 127.0, 124.7, 83.3, 35.2, 24.6, 24.4, carbon attached to boron not observed. ^{11}B NMR (96 MHz, CDCl_3) δ 34.2. **HRMS** (ESI) m/z = 295.1840 calcd. for $\text{C}_{17}\text{H}_{25}\text{BO}_2\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 295.1853. **FTIR** (neat): ν (cm^{-1}) 2979, 2960, 2870, 1351, 1309, 1265, 1141, 853, 735, 700, 617. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, crude yield of **3x** was 47% and recovered yield of phenylboronic acid pinacol ester was 10%.



trifluoromethylated **3x**

About 10% trifluoromethylated **3x** (o/p = 1:1.2) was also detected by crude GC and GC/MS.

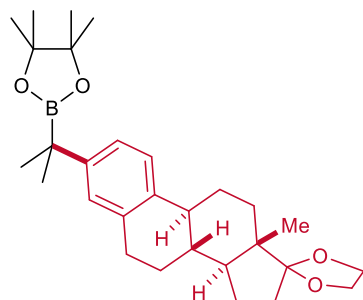
4,4,5,5-Tetramethyl-2-(1-(4-(2-methyl-1,3-dioxolan-2-yl)phenyl)cyclopentyl)-1,3,2-dioxaborolane (**3y**)



Following **GP1**, using **1y** (58.0 mg, 0.2 mmol) and cyclopentylolithium (0.55 M in hexane, 0.40 mL, 0.22 mmol), flash chromatography eluting with DCM (4:1) afforded **3y** as light yellow solid (30.0 mg, 42% yield). R_f 0.2 (DCM). m.p = 87-89 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.27 – 7.19 (m, 2H), 7.17 – 7.08 (m, 2H), 3.98 – 3.82 (m, 2H), 3.75 – 3.58 (m, 2H), 2.35 – 2.05 (m, 2H), 1.67 – 1.46 (m, 9H), 1.03 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 146.8, 139.5, 126.7, 124.8, 109.0, 83.3, 64.4, 35.3, 27.5, 24.6, 24.4, carbon attached to boron not observed. ^{11}B NMR (96 MHz, CDCl_3) δ 34.2. **HRMS** (ESI) m/z = 381.2208 calcd. for $\text{C}_{21}\text{H}_{31}\text{BO}_2\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 381.2217.

FTIR (neat): ν (cm⁻¹) 2978, 2952, 2868, 1610, 1508, 1372, 1353, 1314, 1258, 1198, 1167, 1142, 1041, 1019, 949, 870, 856, 833.

4,4,5,5-Tetramethyl-2-(2-((8R,9S,13S,14S)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)propan-2-yl)-1,3,2-dioxaborolane (**3z**)



Following **GP1**, using **1z** (84.8 mg, 0.2 mmol) and isopropyllithium (0.7 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with DCM afforded **3z** as light yellow solid (38.2 mg, 41% yield). R_f 0.1 (DCM). M.p.: 66-68 °C. $[\alpha]_D^{24} +27$ (c 0.5 CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.20 (d, J = 8.2 Hz, 1H), 7.07 (dd, J = 8.2, 1.8 Hz, 1H), 7.01 (s, 1H), 4.04 – 3.82 (m, 4H), 2.97 – 2.77 (m, 2H), 2.43 – 2.19 (m, 2H), 2.14 – 1.96 (m, 1H), 1.95 – 1.70 (m, 4H), 1.69 – 1.35 (m, 6H), 1.31 (s, 6H), 1.22 (s, 12H), 0.88 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 145.7, 136.9, 136.1, 126.6, 125.0, 123.8, 119.5, 83.2, 65.2, 64.6, 49.5, 46.2, 43.9, 38.9, 34.3, 30.8, 29.8, 27.1, 25.9, 25.8, 25.8, 24.5, 22.4, 14.4, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 34.2. **HRMS** (EI) m/z = 466.3249 calcd. for C₂₉H₄₃BO₄⁺ [M]⁺, found: 466.3250. **FTIR** (neat): ν (cm⁻¹) 2974, 2936, 2866, 1500, 1470, 1371, 1342, 1308, 1215, 1180, 1162, 1136, 1106, 1045, 965, 950, 885, 856, 835, 736.

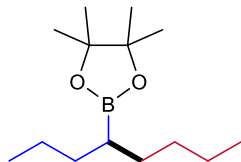
2-(2-((R)-2,8-Dimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3aa**)



Following **GP1**, using **1aa** (102.4 mg, 0.2 mmol) and isobutyllithium (0.7 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (3:1) afforded **3aa** as light yellow sticky oil (67.5 mg, 61% yield). R_f 0.4 (pentane/DCM = 2:1). $[\alpha]_D^{26} +10$ (c 0.46, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 6.88 (d, J = 1.8 Hz, 1H), 6.80 (d, J = 1.8 Hz, 1H), 2.82 – 2.63 (m, 2H), 2.14 (s, 3H), 1.87 – 1.64 (m, 2H), 1.63 – 1.32 (m, 9H), 1.32 – 1.26 (m, 11H), 1.25 (s, 3H), 1.22 (s, 12H), 1.20 – 0.99 (m, 7H), 0.93 – 0.83 (m, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 149.7, 138.5, 126.5, 125.4, 124.3, 119.7, 83.1, 40.4, 39.4, 37.5, 37.5, 37.3, 32.8, 32.7, 31.4, 28.0, 26.0, 24.8, 24.5,

24.5, 24.3, 22.7, 22.6, 22.6, 21.0, 19.8, 19.7, 16.2, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 33.6. **HRMS** (EI) m/z = 554.4865 calcd. for $\text{C}_{36}\text{H}_{63}\text{BO}_3^+ [\text{Ma}]^+$, found: 554.4878. **FTIR** (neat): ν (cm^{-1}) 2926, 2868, 1470, 1371, 1340, 1307, 1226, 1134, 1111, 966, 929, 856, 735, 697, 675.

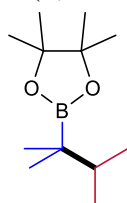
4,4,5,5-Tetramethyl-2-(octan-4-yl)-1,3,2-dioxaborolane (**6a**)



Following **GP1**, using *n*-butylboronic acid pinacol ester **4a** (36.8 mg, 0.2 mmol) and *n*-butyllithium (1.6 M in hexane, 0.14 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6a** as light yellow liquid (23.3 mg, 49% yield). R_f 0.4 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 1.46 – 1.26 (m, 10H), 1.23 (s, 12H), 1.01 – 0.91 (m, 1H), 0.91 – 0.81 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 33.8, 31.6, 31.1, 24.8, 23.0, 22.4, 14.4, 14.1, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.3. **HRMS** (ESI) m/z = 263.2153 calcd. for $\text{C}_{14}\text{H}_{29}\text{BO}_2\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 263.2161. **FTIR** (neat): ν (cm^{-1}) 2979, 2956, 2925, 2859, 1467, 1412, 1388, 1353, 1315, 1247, 1215, 1145, 967, 862, 687.

Following **GP3**, using *n*-butylboronic acid pinacol ester **4a** (36.8 mg, 0.2 mmol) and *n*-butyllithium (1.6 M in hexane, 0.14 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6a** as colorless liquid (20.9 mg, 44% yield). R_f 0.4 (pentane/DCM = 3:1). ^1H NMR (300 MHz, CDCl_3) δ 1.46 – 1.26 (m, 10H), 1.23 (s, 12H), 1.01 – 0.91 (m, 1H), 0.91 – 0.81 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 33.8, 31.6, 31.1, 24.8, 23.0, 22.4, 14.4, 14.1, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.3. **HRMS** (ESI) m/z = 263.2153 calcd. for $\text{C}_{14}\text{H}_{29}\text{BO}_2\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 263.2161. **FTIR** (neat): ν (cm^{-1}) 2979, 2956, 2925, 2859, 1467, 1412, 1388, 1353, 1315, 1247, 1215, 1145, 967, 862, 687. According to crude GC analysis with *n*- $\text{C}_{14}\text{H}_{30}$ as internal standard, crude yield of **6a** was 47% and recovered yield of *n*-butylboronic acid pinacol ester **4a** was 36%.

2-(2,3-Dimethylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6b**)

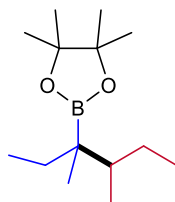


Following **GP1**, using isopropylboronic acid pinacol ester **4b** (34.0 mg, 0.2 mmol) and isopropyllithium (0.7 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6b** as light yellow liquid (30.5 mg, 72% yield). R_f 0.5 (pentane/DCM = 4:1). ^1H NMR (300 MHz, CDCl_3) δ 1.72 – 1.50 (m, 1H), 1.22 (s, 12H), 0.86 (s, 6H), 0.84 (d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 34.6, 24.7, 21.4, 18.4, *carbon attached to boron not observed*. ^{11}B NMR (96

MHz, CDCl₃) δ 34.8. **HRMS** (EI) m/z = 212.1942 calcd. for C₁₂H₂₅BO₂⁺ [M]⁺, found: 212.1944. **FTIR** (neat): ν (cm⁻¹) 2977, 2959, 2872, 1467, 1390, 1378, 1371, 1356, 1303, 1214, 1144, 1125, 1092, 1054, 967, 861, 838, 805, 689, 669. According to crude GC analysis with *n*-C₁₄H₃₀ as internal standard, recovered yield of isopropylboronic acid pinacol ester **4b** was 13%.

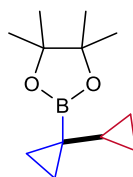
Following **GP3**, using isopropylboronic acid pinacol ester **4b** (34.0 mg, 0.2 mmol) and isopropyllithium (0.7 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6b** as light yellow liquid (32.7 mg, 77% yield). R_f 0.5 (pentane/DCM = 4:1). ¹H NMR (300 MHz, CDCl₃) δ 1.72 – 1.50 (m, 1H), 1.22 (s, 12H), 0.86 (s, 6H), 0.84 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 82.7, 34.6, 24.7, 21.4, 18.4, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 34.8. **HRMS** (EI) m/z = 212.1942 calcd. for C₁₂H₂₅BO₂⁺ [M]⁺, found: 212.1944. **FTIR** (neat): ν (cm⁻¹) 2977, 2959, 2872, 1467, 1390, 1378, 1371, 1356, 1303, 1214, 1144, 1125, 1092, 1054, 967, 861, 838, 805, 689, 669. According to crude GC analysis with *n*-C₁₄H₃₀ as internal standard, recovered yield of isopropylboronic acid pinacol ester **4b** was 15%.

2-(3,4-Dimethylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6c**)



Following **GP1**, using **4c** (36.8 mg, 0.2 mmol) and isobutyllithium (1.4 M in cyclohexane, 0.16 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (4:1) afforded **6c** as light yellow liquid (26.0 mg, 54% yield, *dr* = 1:1). R_f 0.4 (pentane/DCM = 3:1). *Dr* was determined by crude GCMS and GC. ¹H NMR (300 MHz, CDCl₃) δ 1.62 – 1.26 (m, 5H), 1.24 – 1.22 (m, 12H), 0.93 – 0.71 (m, 12). ¹³C NMR (75 MHz, CDCl₃) δ 82.8, 40.8, 40.6, 30.0, 29.1, 27.5, 25.0, 25.0, 24.9, 24.9, 23.7, 16.9, 16.1, 15.7, 13.1, 13.0, 12.5, 10.4, 10.4, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 34.8. **HRMS** (ESI) m/z = 263.2153 calcd. for C₁₄H₂₉BO₂Na⁺ [M+Na]⁺, found: 263.2155. **FTIR** (neat): ν (cm⁻¹) 2962, 2934, 2875, 1459, 1371, 1341, 1301, 1261, 1213, 1143, 1118, 966, 855, 684.

2-([1,1'-Bi(cyclopropan)]-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6d**)

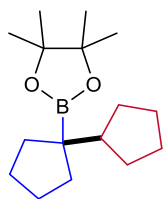


Following **GP1**, using **4d** (33.6 mg, 0.2 mmol) and cyclopropyllithium (0.85 M in Et₂O, 0.26 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (2:1) afforded **6d** as light yellow liquid (12.1 mg, 29% yield). R_f 0.5 (pentane/DCM = 10:7).

^1H NMR (300 MHz, CDCl_3) δ 1.21 (s, 12H), 1.10 – 0.96 (m, 1H), 0.56 – 0.47 (m, 2H), 0.33 – 0.18 (m, 4H), 0.02 – -0.09 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.9, 24.7, 13.0, 8.7, 1.9, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 33.8. **HRMS** (ESI) m/z = 231.1527 calcd. for $\text{C}_{12}\text{H}_{21}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 231.1540. **FTIR** (neat): ν (cm^{-1}) 3080, 2979, 1468, 1442, 1414, 1371, 1356, 1309, 1262, 1216, 1194, 1165, 1135, 1099, 1015, 967, 866, 845, 813, 706, 683, 667, 581.

Following **GP3**, using **4d** (33.6 mg, 0.2 mmol) and cyclopropyllithium (0.85 M in Et_2O , 0.26 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (2:1) afforded **6d** as light yellow liquid (14.8 mg, 35% yield). R_f 0.5 (pentane/DCM = 10:7). ^1H NMR (300 MHz, CDCl_3) δ 1.21 (s, 12H), 1.10 – 0.96 (m, 1H), 0.56 – 0.47 (m, 2H), 0.33 – 0.18 (m, 4H), 0.02 – -0.09 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.9, 24.7, 13.0, 8.7, 1.9, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 33.8. **HRMS** (ESI) m/z = 231.1527 calcd. for $\text{C}_{12}\text{H}_{21}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 231.1540. **FTIR** (neat): ν (cm^{-1}) 3080, 2979, 1468, 1442, 1414, 1371, 1356, 1309, 1262, 1216, 1194, 1165, 1135, 1099, 1015, 967, 866, 845, 813, 706, 683, 667, 581. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, recovered yield of cyclopropylboronic acid pinacol ester **4d** was 16%.

2-([1,1'-Bi(cyclopentan)]-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6e**)

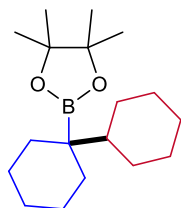


Following **GP1**, using cyclopentylboronic acid pinacol ester **4e** (39.2 mg, 0.2 mmol) and cyclopropyllithium (0.62 M in hexane, 0.355 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6e** as colorless liquid (37.1 mg, 70% yield). R_f 0.4 (pentane/DCM = 4:1). ^1H NMR (300 MHz, CDCl_3) δ 1.89 – 1.73 (m, 3H), 1.72 – 1.39 (m, 10H), 1.36 – 1.24 (m, 4H), 1.21 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 47.7, 33.9, 29.6, 25.7, 25.7, 24.7, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 35.1. **HRMS** (ESI) m/z = 287.2153 calcd. for $\text{C}_{16}\text{H}_{29}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 287.2163. **FTIR** (neat): ν (cm^{-1}) 2977, 2948, 2866, 1452, 1370, 1337, 1299, 1268, 1196, 1141, 984, 962, 859, 671. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, crude yield of **6e** was 76% and recovered yield of **4e** was 20%.

Following **GP1**, using cyclopentylboronic acid pinacol ester **4e** (39.2 mg, 0.2 mmol) and cyclopropyllithium (0.62 M in hexane, 0.355 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6e** as colorless liquid (34.4 mg, 65% yield). R_f 0.4 (pentane/DCM = 4:1). ^1H NMR (300 MHz, CDCl_3) δ 1.89 – 1.73 (m, 3H), 1.72 – 1.39 (m, 10H), 1.36 – 1.24 (m, 4H), 1.21 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 47.7, 33.9, 29.6, 25.7, 25.7, 24.7, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 35.1. **HRMS** (ESI) m/z = 287.2153 calcd. for

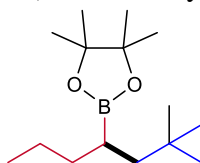
$\text{C}_{16}\text{H}_{29}\text{BO}_2\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 287.2163. **FTIR** (neat): ν (cm^{-1}) 2977, 2948, 2866, 1452, 1370, 1337, 1299, 1268, 1196, 1141, 984, 962, 859, 671. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, crude yield of **6e** was 72% and recovered yield of **4e** was 19%.

2-([1,1'-Bi(cyclohexan)]-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6f**)



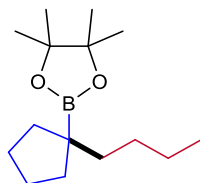
Following **GP1**, using **4f** (42.0 mg, 0.2 mmol) and cyclohexyllithium (0.53 M in hexane, 0.42 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6f** as light yellow solid (22.3 mg, 38% yield). R_f 0.5 (pentane/DCM = 3:1). M.p.: 72 – 73 °C. ^1H NMR (300 MHz, CDCl_3) δ 2.01 – 1.88 (m, 2H), 1.88 – 1.77 (m, 2H), 1.75 – 1.52 (m, 6H), 1.26 (s, 12H), 1.36 – 0.83 (m, 11H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.9, 47.5, 32.9, 29.0, 27.4, 27.1, 26.7, 25.7, 25.0, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.5. **HRMS** (ESI) m/z = 315.2466 calcd. for $\text{C}_{18}\text{H}_{33}\text{BO}_2\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 315.2470. **FTIR** (neat): ν (cm^{-1}) 2978, 2918, 2849, 1447, 1409, 1388, 1370, 1334, 1301, 1263, 1232, 1213, 1162, 1141, 1110, 969, 860, 832, 710, 671, 600. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, crude yield of **6e** was 40% and recovered yield of **4f** was 39%.

2-(2,2-Dimethylheptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6g**)



Following **GP1**, using **4g** (39.6 mg, 0.2 mmol) and n -butyllithium (1.6 M in hexane, 0.14 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6g** as light yellow liquid (24.8 mg, 49% yield, a mixture of two regioisomers). R_f 0.3 (pentane/DCM = 3:1). Regioisomeric ratio was determined to be 1.3:1 by crude GCMS and GC. ^1H NMR (300 MHz, CDCl_3) δ 1.58 – 1.07 (m, 44H), 0.92 (s, 9H), 0.90 – 0.75 (m, 7H), 0.86 (s, 11.6H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 82.7, 45.8, 35.9, 32.6, 32.0, 32.0, 31.0, 29.7, 29.6, 26.6, 25.0, 25.0, 24.9, 24.9, 23.0, 22.1, 14.4, 14.1, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.3. **HRMS** (ESI) m/z = 277.2309 calcd. for $\text{C}_{15}\text{H}_{31}\text{BO}_2\text{Na}^+ [\text{M}+\text{Na}]^+$, found: 277.2319. **FTIR** (neat): ν (cm^{-1}) 2955, 2928, 2869, 1467, 1371, 1314, 1235, 1143, 1113, 864,

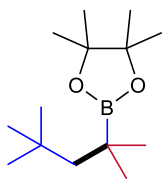
2-(1-Butylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6h**)



Following **GP1**, using cyclopentylboronic acid pinacol ester **4h** (39.2 mg, 0.2 mmol) and *n*-butyllithium (1.6 M in hexane, 0.14 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6h** as light yellow liquid (33.3 mg, 66% yield, a mixture of two regioisomers). R_f 0.5 (pentane/DCM = 3:1). Regioisomeric ratio was determined to be 9:1 by crude GCMS and GC. ^1H NMR (300 MHz, CDCl_3) δ 1.86 – 1.71 (m, 2.2H), 1.65 – 1.42 (m, 4.4H), 1.40 – 1.30 (m, 2.2H), 1.24 (s, 1.2H) (minor isomer), 1.30 – 1.14 (m, 6.6H), 1.22 (s, 12H), 0.92 – 0.82 (m, 3.3H). Major isomer: ^{13}C NMR (75 MHz, CDCl_3) δ 82.8, 38.7, 35.4, 30.3, 25.3, 24.7, 23.6, 14.1, *carbon attached to boron not observed*. Minor isomer: ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 42.0, 33.2, 32.6, 32.1, 24.9, 22.2, 14.5, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.9. **HRMS** (ESI) m/z = 275.2153 calcd. for $\text{C}_{15}\text{H}_{29}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 275.2160. **FTIR** (neat): ν (cm^{-1}) 2979, 2954, 2930, 2858, 1457, 1408, 1379, 1341, 1303, 1216, 1144, 979, 856.

Following **GP3**, using cyclopentylboronic acid pinacol ester **4h** (39.2 mg, 0.2 mmol) and *n*-butyllithium (1.6 M in hexane, 0.14 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6h** as colorless liquid (33.0 mg, 65% yield, a mixture of two regioisomers). R_f 0.5 (pentane/DCM = 3:1). Regioisomeric ratio was determined to be 7:1 by crude GC. According to crude GC analysis with *n*- $\text{C}_{14}\text{H}_{30}$ as internal standard, recovered yield of **4h** was 7% and the yield of *n*-butylboronic acid pinacol ester was 12%.

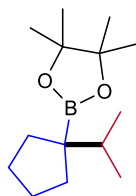
4,4,5,5-Tetramethyl-2-(2,4,4-trimethylpentan-2-yl)-1,3,2-dioxaborolane (**6i**)



Following **GP1**, using **4i** (39.6 mg, 0.2 mmol) and isopropyllithium (0.7 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6i** as light yellow liquid (35.5 mg, 74% yield, a mixture of two regioisomers). R_f 0.4 (pentane/DCM = 3:1). Regioisomeric ratio was determined to be 11.5:1 by crude GCMS and GC. ^1H NMR (300 MHz, CDCl_3) δ 1.35 (s, 2H), 1.25 (s, 1.1H) (minor), 1.22 (s, 12H), 1.02 – 0.89 (m, 16.6H). Major isomer: ^{13}C NMR (75 MHz, CDCl_3) δ 82.9, 54.5, 31.6, 31.3, 27.4, 24.8, *carbon attached to boron not observed*. Minor isomer: ^{13}C NMR (75 MHz, CDCl_3) δ 82.6, 30.1, 26.7, 26.4, 25.3, 25.0, 22.6, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.9. **HRMS** (ESI) m/z = 263.2153 calcd. for $\text{C}_{14}\text{H}_{29}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 263.2158. **FTIR** (neat): ν (cm^{-1}) 2979, 2953, 2905, 2869, 2837, 1480, 1388, 1369, 1339, 1305, 1271, 1197,

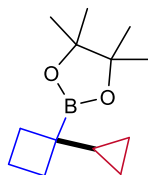
1146, 1130, 1102, 967, 867, 845, 714, 691, 669, 580.

2-(1-Isopropylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6j**)



Following **GP2**, using **4j** (39.2 mg, 0.2 mmol) and isopropyllithium (0.7 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6j** as light yellow liquid (29.7 mg, 62% yield, a mixture of two regioisomers). R_f 0.5 (pentane/DCM = 3:1). Regioisomeric ratio was determined to be 2.2:1 by crude GCMS and GC. ^1H NMR (300 MHz, CDCl_3) δ 1.95 – 1.37 (m, 7H), 1.32 – 1.11 (m, 14H), 0.94 – 0.86 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.8, 82.7, 48.5, 36.4, 34.0, 28.1, 25.9, 25.7, 24.8, 24.7, 22.9, 20.6, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.9. **HRMS** (ESI) m/z = 261.1996 calcd. for $\text{C}_{14}\text{H}_{27}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 261.1990. **FTIR** (neat): ν (cm^{-1}) 2977, 2951, 2867, 1473, 1371, 1338, 1302, 1271, 1214, 1196, 1141, 967, 863, 697, 670.

2-(1-Cyclopropylcyclobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6k**)

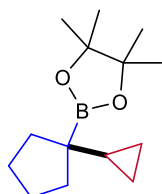


Following **GP1**, using cyclobutylboronic acid pinacol ester **4k** (36.4 mg, 0.2 mmol) and cyclopropyllithium (1.17 M in Et_2O , 0.19 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6k** as light yellow liquid (23.7 mg, 53% yield). R_f 0.5 (pentane/DCM = 3:1). Regioisomeric ratio was determined to be 11:1 by crude GCMS and GC. ^1H NMR (300 MHz, CDCl_3) δ 2.05 – 1.89 (m, 2H), 1.87 – 1.52 (m, 4H), 1.26 (s, 12H), 0.98 – 0.83 (m, 1H), 0.39 – 0.25 (m, 2H), 0.25 – 0.14 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 83.0, 27.6, 24.7, 18.1, 16.8, 1.0, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.5. **HRMS** (ESI) m/z = 245.1683 calcd. for $\text{C}_{13}\text{H}_{23}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 245.1697. **FTIR** (neat): ν (cm^{-1}) 3075, 2976, 2936, 2866, 1467, 1411, 1379, 1343, 1303, 1275, 1250, 1215, 1146, 1124, 1013, 967, 866, 840, 818, 684, 671, 579. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, recovered yield of **4k** was 3% and the yield of cyclopropylboronic acid pinacol ester was 17%.

Following **GP3**, using cyclobutylboronic acid pinacol ester **4k** (36.4 mg, 0.2 mmol) and cyclopropyllithium (1.17 M in Et_2O , 0.19 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6k** as light yellow liquid (21.6 mg, 49% yield). R_f 0.5 (pentane/DCM = 3:1). Regioisomeric ratio was determined to be 10:1 by crude GCMS and GC. ^1H NMR (300 MHz, CDCl_3) δ 2.05 – 1.89 (m, 2H), 1.87 –

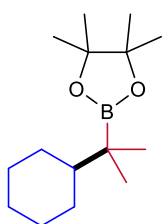
1.52 (m, 4H), 1.26 (s, 12H), 0.98 – 0.83 (m, 1H), 0.39 – 0.25 (m, 2H), 0.25 – 0.14 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 83.0, 27.6, 24.7, 18.1, 16.8, 1.0, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.5. **HRMS** (ESI) m/z = 245.1683 calcd. for $\text{C}_{13}\text{H}_{23}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 245.1697. **FTIR** (neat): ν (cm^{-1}) 3075, 2976, 2936, 2866, 1467, 1411, 1379, 1343, 1303, 1275, 1250, 1215, 1146, 1124, 1013, 967, 866, 840, 818, 684, 671, 579. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, recovered yield of **4k** was 3% and the yield of cyclopropylboronic acid pinacol ester was 14%.

2-(1-Cyclopropylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6l**)



Following **GP1**, using **4l** (39.2 mg, 0.2 mmol) and cyclopropyllithium (0.85 M in Et_2O , 0.26 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6l** as light yellow liquid (22.9 mg, 48% yield, single isomer). R_f 0.5 (pentane/DCM = 3:1). Regioisomeric ratio was determined to be 13:1 by crude GCMS and GC. The other isomer was not collected. ^1H NMR (300 MHz, CDCl_3) δ 1.82 – 1.66 (m, 2H), 1.66 – 1.40 (m, 4H), 1.32 – 1.14 (m, 14H), 0.82 – 0.67 (m, 1H), 0.34 – 0.23 (m, 2H), 0.23 – 0.14 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.9, 33.6, 25.4, 24.6, 17.3, 1.6, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.6. **HRMS** (ESI) m/z = 259.1840 calcd. for $\text{C}_{14}\text{H}_{25}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 259.1856. **FTIR** (neat): ν (cm^{-1}) 3079, 2978, 2952, 2867, 1454, 1371, 1346, 1303, 1273, 1214, 1197, 1143, 1112, 1013, 977, 863, 819, 670.

2-(2-Cyclohexylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6m**)

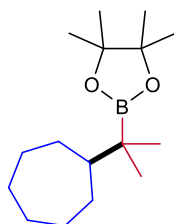


Following **GP1**, using **4m** (42.0 mg, 0.2 mmol) and isopropyllithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6m** as light yellow liquid (32.7 mg, 65% yield, a mixture of two isomers). R_f 0.3 (pentane/DCM = 5:1). Regioisomeric ratio was determined to be 29:1 by crude GCMS and GC. ^1H NMR (300 MHz, CDCl_3) δ 1.80 – 1.53 (m, 5H), 1.22 (s, 12H), 1.32 – 0.90 (m, 6H), 0.87 (s, 6H). Major isomer: ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 45.5, 28.7, 27.1, 27.0, 24.7, 21.7, *carbon attached to boron not observed*. Minor isomer: ^{13}C NMR (75 MHz, CDCl_3) δ 36.7, 32.9, 26.6, 25.6, 25.0, 18.9, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.8. **HRMS** (ESI) m/z = 275.2153 calcd. for $\text{C}_{15}\text{H}_{29}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 275.2146. **FTIR** (neat): ν (cm^{-1})

2978, 2925, 2853, 1472, 1449, 1388, 1371, 1354, 1302, 1145, 1134, 967, 855, 807. According to crude GC analysis with *n*-C₁₄H₃₀ as internal standard, recovered yield of **4m** was 9% and the yield of isopropylboronic acid pinacol ester was 5%.

Following **GP1**, using **4m** (42.0 mg, 0.2 mmol) and isopropylolithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6m** as light yellow liquid (26.7 mg, 53% yield, a mixture of two isomers). *R*_f 0.3 (pentane/DCM = 5:1). Regioisomeric ratio was determined to be 24:1 by crude GCMS and GC. ¹H NMR (300 MHz, CDCl₃) δ 1.80 – 1.53 (m, 5H), 1.22 (s, 12H), 1.32 – 0.90 (m, 6H), 0.87 (s, 6H). Major isomer: ¹³C NMR (75 MHz, CDCl₃) δ 82.7, 45.5, 28.7, 27.1, 27.0, 24.7, 21.7, *carbon attached to boron not observed*. Minor isomer: ¹³C NMR (75 MHz, CDCl₃) δ 36.7, 32.9, 26.6, 25.6, 25.0, 18.9, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 34.8. **HRMS** (ESI) *m/z* = 275.2153 calcd. for C₁₅H₂₉BO₂Na⁺ [M+Na]⁺, found: 275.2146. **FTIR** (neat): ν (cm⁻¹) 2978, 2925, 2853, 1472, 1449, 1388, 1371, 1354, 1302, 1145, 1134, 967, 855, 807. According to crude GC analysis with *n*-C₁₄H₃₀ as internal standard, recovered yield of **4m** was 18% and the yield of isopropylboronic acid pinacol ester was 7%.

2-(2-Cycloheptylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6n**)

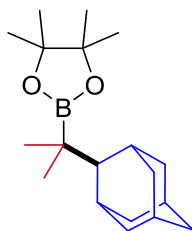


Following **GP1**, using cycloheptylboronic acid pinacol ester **4n** (44.8 mg, 0.2 mmol) and isopropylolithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6n** as light yellow liquid (37.1 mg, 70% yield, a mixture of two isomers). *R*_f 0.3 (pentane/DCM = 3:1). Regioisomeric ratio was determined to be 31:1 by crude GCMS and GC. ¹H NMR (300 MHz, CDCl₃) δ 1.77 – 1.31 (m, 11H), 1.22 (s, 12H), 1.29 – 1.12 (m, 2H), 0.86 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 82.7, 45.6, 30.3, 28.1, 28.1, 21.1, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 34.7. **HRMS** (ESI) *m/z* = 289.2309 calcd. for C₁₆H₃₁BO₂Na⁺ [M+Na]⁺, found: 289.2334. **FTIR** (neat): ν (cm⁻¹) 2979, 2924, 2857, 1471, 1387, 1371, 1355, 1303, 1270, 1214, 1142, 968, 858, 691, 671. According to crude GC analysis with *n*-C₁₄H₃₀ as internal standard, the yield of **6n** was 76%, recovered yield of **4n** was 7% and the yield of isopropylboronic acid pinacol ester was 13%.

Following **GP3**, using cycloheptylboronic acid pinacol ester **4n** (44.8 mg, 0.2 mmol) and isopropylolithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6n** as colorless liquid (34.0 mg, 64% yield, a mixture of two isomers). *R*_f 0.3 (pentane/DCM = 3:1). Regioisomeric ratio was

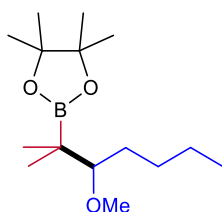
determined to be 31:1 by crude GCMS and GC. ^1H NMR (300 MHz, CDCl_3) δ 1.77 – 1.31 (m, 11H), 1.22 (s, 12H), 1.29 – 1.12 (m, 2H), 0.86 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 45.6, 30.3, 28.1, 28.1, 21.1, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.7. **HRMS** (ESI) m/z = 289.2309 calcd. for $\text{C}_{16}\text{H}_{31}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 289.2334. **FTIR** (neat): ν (cm^{-1}) 2979, 2924, 2857, 1471, 1387, 1371, 1355, 1303, 1270, 1214, 1142, 968, 858, 691, 671. According to crude GC analysis with $n\text{-C}_{14}\text{H}_{30}$ as internal standard, crude yield of **6n** was 69%, recovered yield of **4n** was 9% and the yield of isopropylboronic acid pinacol ester was 14%.

2-(2-Adamantan-2-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6o**)



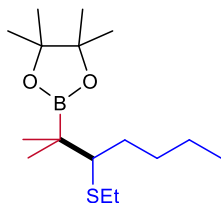
Following **GP1**, using **4o** (52.4 mg, 0.2 mmol) and isopropyllithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6o** as white solid (33.8 mg, 56% yield, a mixture of two isomers). R_f 0.4 (pentane/DCM = 5:1). M.p. = 61 – 62 °C. Regioisomeric ratio was determined to be 25:1 by crude GCMS and GC. ^1H NMR (300 MHz, CDCl_3) δ 2.16 – 1.94 (m, 4H), 1.90 – 1.64 (m, 8H), 1.57 – 1.43 (m, 3H), 1.23 (s, 12H), 0.99 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.8, 56.0, 41.0, 38.6, 32.9, 30.0, 28.7, 27.5, 26.3, 24.8, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 35.1. **HRMS** (ESI) m/z = 327.2466 calcd. for $\text{C}_{19}\text{H}_{33}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 327.2455. **FTIR** (neat): ν (cm^{-1}) 2976, 2903, 2850, 1476, 1455, 1389, 1371, 1315, 1296, 1257, 1137, 967, 859, 702.

2-(3-Methoxy-2-methylheptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6p**)



Following **GP1**, using **4p** (45.6 mg, 0.2 mmol) and isopropyllithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/ethyl acetate (15:1) afforded **6p** as light yellow liquid (39.0 mg, 72% yield). R_f 0.5 (pentane/ethyl acetate = 10:1). ^1H NMR (300 MHz, CDCl_3) δ 3.42 (s, 3H), 3.09 (dd, J = 8.2, 2.9 Hz, 1H), 1.56 – 1.26 (m, 6H), 1.22 (s, 6H), 1.21 (s, 6H), 1.00 – 0.82 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 87.7, 82.9, 60.4, 32.3, 29.8, 24.7, 24.5, 23.1, 20.7, 19.5, 14.1, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.2. **HRMS** (ESI) m/z = 293.2258 calcd. for $\text{C}_{19}\text{H}_{33}\text{BO}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 293.2275. **FTIR** (neat): ν (cm^{-1}) 2975, 2957, 2934, 2873, 2825, 1470, 1371, 1343, 1307, 1274, 1215, 1136, 1095, 967, 849, 691, 674, 579.

4,4,5,5-Tetramethyl-2-(2-methyl-3-(ethylthio)heptan-2-yl)-1,3,2-dioxaborolane (**6q**)



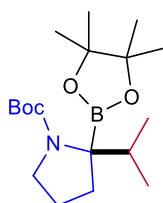
Following **GP1**, using **4q** (51.6 mg, 0.2 mmol) and isopropyllithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/ethyl acetate (20:1) afforded **6q** as light yellow liquid (37.7 mg, 63% yield). R_f 0.7 (pentane/ethyl acetate = 10:1). ^1H NMR (300 MHz, CDCl_3) δ 2.60 (q, $J = 7.4$ Hz, 2H), 2.49 (dd, $J = 10.4, 2.6$ Hz, 1H), 1.80 – 1.28 (m, 6H), 1.26 – 1.17 (m, 15H), 1.00 (s, 3H), 0.96 – 0.84 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 83.0, 56.3, 33.8, 30.6, 28.8, 24.8, 24.5, 22.8, 22.1, 20.8, 15.1, 14.1, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.4. **HRMS** (ESI) $m/z = 323.2187$ calcd. for $\text{C}_{16}\text{H}_{33}\text{BO}_2\text{SNa}^+$ $[\text{M}+\text{Na}]^+$, found: 323.2192. **FTIR** (neat): ν (cm^{-1}) 2958, 2928, 2869, 1468, 1371, 1343, 1307, 1138, 1118, 967, 850, 671.

Tert-butyl

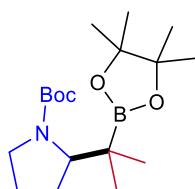
2-isopropyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (**6r-1**)

Tert-butyl

2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)pyrrolidine-1-carboxylate (**6r-2**)



6r-1



6r-2

Following **GP1**, using **4r** (59.4 mg, 0.2 mmol) and isopropyllithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/ethyl acetate (20:1) afforded **6r-1** as colorless sticky oil (40.5 mg, 60% yield), R_f 0.6 (pentane/ethyl acetate = 10:1); **6r-2** as colorless sticky oil (10.9 mg, 16% yield), R_f 0.5 (pentane/ethyl acetate = 10:1). Regioisomeric ratio was determined to be 4:1 by crude GCMS and GC.

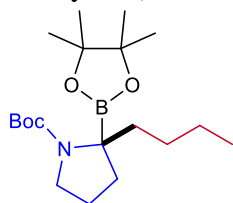
6r-1: ^1H NMR (600 MHz, DMSO-d_6 , 363 K) δ 3.58 – 3.47 (m, 1H), 3.20 – 3.08 (m, 1H), 2.35 – 2.18 (m, 1H), 1.94 – 1.63 (m, 4H), 1.45 (d, $J = 1.2$ Hz, 9H), 1.25 (s, 6H), 1.23 (s, 6H), 0.96 (d, $J = 6.9$ Hz, 3H), 0.80 (br, 3H). ^{13}C NMR (151 MHz, DMSO-d_6 , 363 K) δ 82.1, 77.7, 46.6, 30.1, 28.5, 27.8, 24.3, 24.0, 18.1, 16.5, *carbonyl and carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3 , 297 K) δ 32.5. **HRMS** (ESI) $m/z = 362.2473$ calcd. for $\text{C}_{18}\text{H}_{34}\text{BNO}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 362.2491. **FTIR** (neat): ν (cm^{-1}) 2975, 2934, 1681, 1479, 1403, 1366, 1311, 1243, 1215, 1167, 1143, 1097,

987, 972, 862, 771.

6r-2: ^1H NMR (600 MHz, DMSO- d_6 , 363 K) δ 3.88 – 3.82 (m, 1H), 3.61 – 3.51 (m, 1H), 3.16 – 3.09 (m, 1H), 1.92 – 1.80 (m, 2H), 1.74 – 1.61 (m, 2H), 1.45 (s, 9H), 1.23 (s, 12H), 0.85 (s, 3H), 0.82 (s, 3H). ^{13}C NMR (151 MHz, DMSO- d_6 , 363 K) δ 154.3, 81.7, 78.2, 62.5, 46.9, 27.8, 24.4, 24.3, 23.2, 20.9, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3 , 297 K) δ 26.5. **HRMS** (ESI) m/z = 362.2473 calcd. for $\text{C}_{18}\text{H}_{34}\text{BNO}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 362.2493. **FTIR** (neat): ν (cm^{-1}) 2974, 2871, 1685, 1473, 1419, 1385, 1366, 1324, 1308, 1167, 1143, 1124, 969, 861, 772.

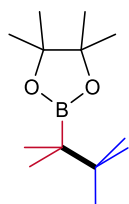
Tert-butyl

2-butyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrolidine-1-carboxylate (**6s**)



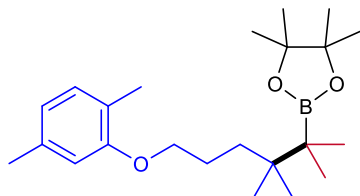
Following **GP1**, using **4s** (59.4 mg, 0.2 mmol) and isopropyllithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/ethyl acetate (10:1) afforded **6s** as colorless sticky oil (41.2 mg, 58% yield, single isomer), R_f 0.6 (pentane/ethyl acetate = 10:1). Regioisomeric ratio was determined to be 32:1 by crude GCMS and GC. The other isomer was not collected. ^1H NMR (300 MHz, CDCl_3) δ 3.67 – 3.34 (m, 1H), 3.35 – 3.13 (m, 1H), 2.01 – 1.47 (m, 7H), 1.43 (s, 9H), 1.38 – 1.26 (m, 3H), 1.24 (s, 6H), 1.21 (s, 6H), 0.88 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 83.1, 78.9, 46.7, 34.6, 32.8, 28.6, 26.7, 25.1, 24.5, 23.4, 14.3, *carbonyl and carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 32.1. **HRMS** (ESI) m/z = 376.2630 calcd. for $\text{C}_{19}\text{H}_{36}\text{BNO}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 376.2633. **FTIR** (neat): ν (cm^{-1}) 2978, 2934, 1677, 1402, 1380, 1367, 1166, 1143, 1052, 1025, 1006, 822, 760, 732, 700.

4,4,5,5-Tetramethyl-2-(2,3,3-trimethylbutan-2-yl)-1,3,2-dioxaborolane (**6t**)



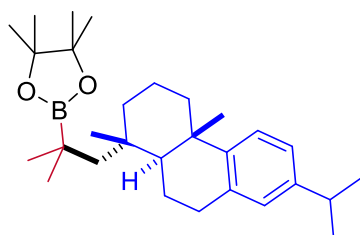
Following **GP1**, using **4t** (36.8 mg, 0.2 mmol) and isopropyllithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6t** as light yellow liquid (22.2 mg, 50% yield). R_f 0.5 (pentane/DCM = 5:1). ^1H NMR (300 MHz, CDCl_3) δ 1.22 (s, 12H), 0.90 (s, 9H), 0.88 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 33.9, 26.7, 24.7, 20.7, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.8. **HRMS** (ESI) m/z = 249.1996 calcd. for $\text{C}_{19}\text{H}_{33}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 249.2005. **FTIR** (neat): ν (cm^{-1}) 2971, 2872, 1464, 1401, 1379, 1371, 1339, 1298, 1261, 1214, 1150, 1121, 1022, 967, 877, 852, 805, 718, 682.

2-(6-(2,5-Dimethylphenoxy)-2,3,3-trimethylhexan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6u**)



Following **GP1**, using **4u** (66.4 mg, 0.2 mmol) and isopropyllithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (3:1) afforded **6u** as light yellow sticky oil (23.8 mg, 32% yield), R_f 0.6 (pentane/DCM = 2:1). ^1H NMR (300 MHz, CDCl_3) δ 7.00 (d, $J = 7.3$ Hz, 1H), 6.70 – 6.60 (m, 2H), 3.92 (t, $J = 6.6$ Hz, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 1.85 – 1.68 (m, 2H), 1.53 – 1.42 (m, 2H), 1.22 (s, 12H), 0.93 – 0.89 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 157.2, 136.4, 130.2, 123.6, 120.5, 112.0, 82.7, 69.0, 36.1, 34.5, 24.8, 24.7, 22.5, 21.4, 20.4, 15.8, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.8. **HRMS** (ESI) $m/z = 397.2884$ calcd. for $\text{C}_{23}\text{H}_{39}\text{BO}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 397.2897. **FTIR** (neat): ν (cm^{-1}) 2973, 2959, 2872, 1617, 1586, 1509, 1466, 1379, 1371, 1338, 1297, 1266, 1147, 1120, 1037, 967, 850, 802.

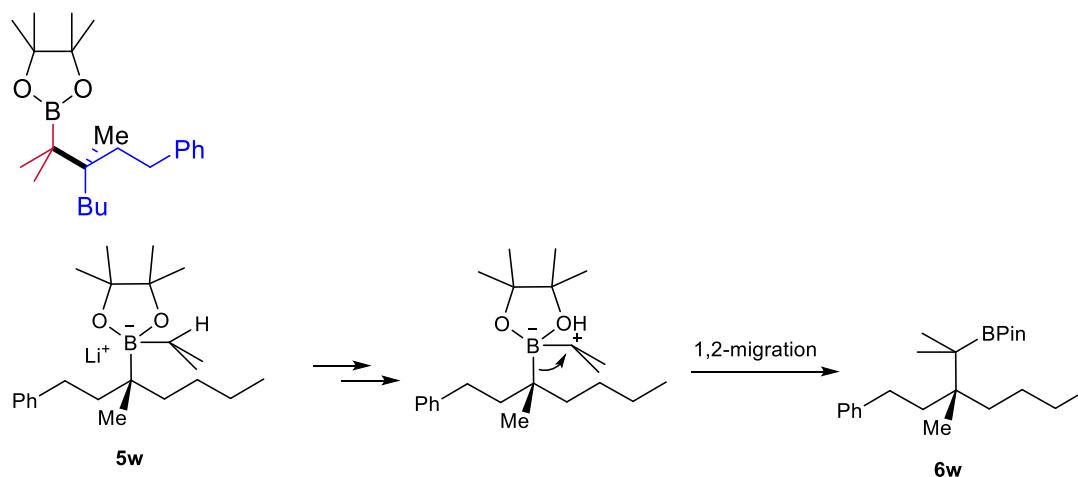
2-(1-((1S,4aS,10aS)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)-2-methylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6v**)



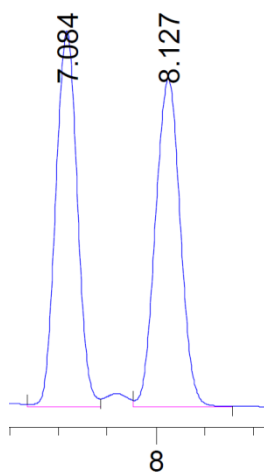
Following **GP1**, using **4v** (74.1 mg, 0.187 mmol) and isopropyllithium (0.70 M in pentane, 0.29 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (3:1) afforded **6v** as light yellow sticky oil (43.4 mg, 50% yield), R_f 0.5 (pentane/DCM = 2:1). $[\alpha]_D^{24} +4$ (c 0.4, CHCl_3). The other regioisomer was not detected by crude GCMS. ^1H NMR (300 MHz, CDCl_3) δ 7.16 (d, $J = 8.2$ Hz, 1H), 6.98 (dd, $J = 8.2, 1.6$ Hz, 1H), 6.90 (s, 1H), 3.00 – 2.72 (m, 3H), 2.33 – 2.19 (m, 1H), 2.10 – 1.89 (m, 1H), 1.80 – 1.52 (m, 5H), 1.51 – 1.29 (m, 4H), 1.25 (s, 3H), 1.24 – 1.19 (m, 18H), 0.99 (s, 6H), 0.96 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 148.1, 145.3, 135.0, 126.8, 124.0, 123.6, 82.9, 55.5, 51.0, 38.7, 37.9, 37.0, 33.5, 30.6, 28.1, 27.7, 25.5, 24.8, 24.7, 24.0, 20.1, 19.0, 1.0, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.7. **HRMS** (ESI) $m/z = 461.3561$ calcd. for $\text{C}_{29}\text{H}_{47}\text{BNaO}_2^+$ $[\text{M}+\text{Na}]^+$, found: 461.3553. **FTIR** (neat): ν (cm^{-1}) 2957, 2926, 2867, 1477, 1456, 1389, 1371, 1340, 1303, 1264, 1212, 1165, 1141, 1108, 1094, 1020, 967, 863, 847, 821, 802, 738, 704, 691, 670.

(*R*)-2-(2,3-Dimethyl-3-phenethylheptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

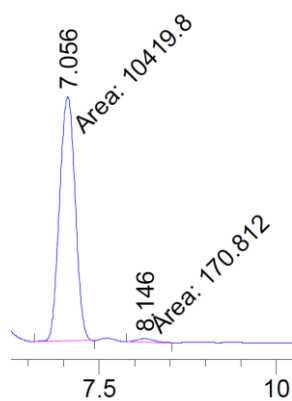
(6w)



Following **GP1**, using **4w** (73.2 mg, 0.2 mmol, 99% ee) and isopropyllithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6w** as colorless sticky oil (21.4 mg, 30% yield, 97% ee), R_f 0.5 (pentane/DCM = 3:1). Ee determined by chiral HPLC after oxidation (NaOH/H₂O₂). ¹⁷S¹⁷ ¹H NMR (300 MHz, CDCl₃) δ 7.23 – 7.15 (m, 2H), 7.15 – 7.04 (m, 3H), 2.62 – 2.33 (m, 2H), 1.74 – 1.17 (m, 8H), 1.14 (s, 12H), 0.94 – 0.75 (m, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 144.2, 128.3, 128.2, 125.4, 82.6, 39.3, 39.0, 36.7, 31.8, 27.4, 24.7, 24.1, 21.2, 21.1, 14.3, *carbon attached to boron not observed*. ¹¹B NMR (96 MHz, CDCl₃) δ 34.1. **HRMS** (ESI) m/z = 381.2935 calcd. for C₂₃H₃₉BO₂Na⁺ [M+Na]⁺, found: 381.2937. **FTIR** (neat): ν (cm⁻¹) 2956, 2933, 2870, 1603, 1497, 1468, 1389, 1371, 1331, 1295, 1214, 1143, 1118, 1031, 966, 855, 750, 720, 698, 687, 670, 583. **Chiral HPLC** (IC, 1% *i*PrOH/cyclohexane, 1.0 ml/min) T_R 7.06 min (major), 8.15 min (minor). $[\alpha]_D^{25}$ +2 (*c* 1.0, CHCl₃).



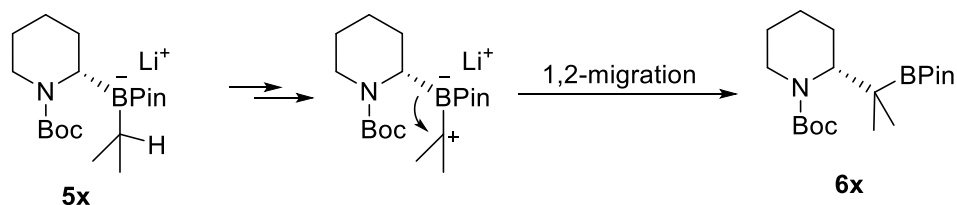
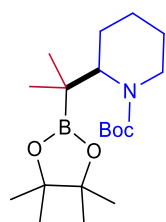
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1	7.084	VV	0.2440	4336.93262	281.06567	49.8763
2	8.127	VB	0.2835	4358.45215	245.08438	50.1237



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.056	MM	0.2563	1.04198e4	677.45465	98.3871
2	8.146	MM	0.2946	170.81223	9.66340	1.6129

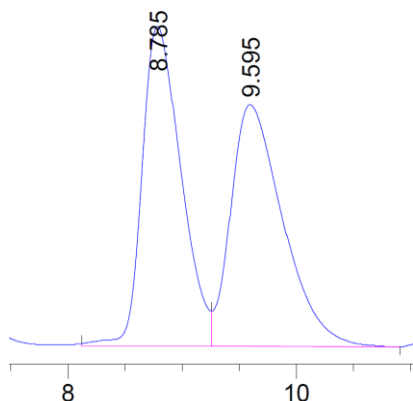
(*R*)-Tert-butyl

2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)piperidine-1-carboxylate (**6x**)

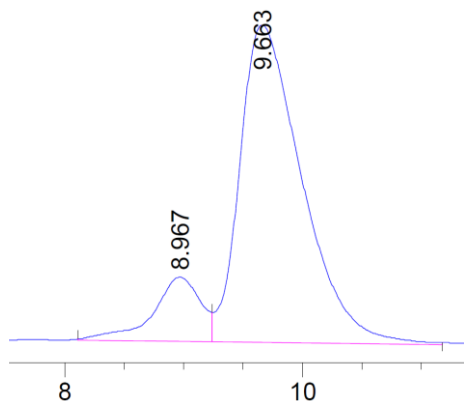


Following **GP1**, using *S*-**4x** (62.2 mg, 0.2 mmol, 73% ee) and isopropyllithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/ ethyl acetate (10:1) afforded *R*-**6u** as colorless sticky oil (31.4 mg, 44% yield, 73% ee). Regioisomeric ratio was determined to be 10:1 by crude GC and GCMS. The other regioisomer was not collected. R_f 0.6 (pentane/ethyl acetate = 20:3). ^1H NMR (600 MHz, DMSO- d_6 , 363 K) δ 3.79 – 3.57 (m, 2H), 3.29 – 3.10 (m, 1H), 1.83 – 1.72 (m, 1H), 1.71 – 1.59 (m, 2H), 1.52 – 1.47 (m, 2H), 1.46 (s, 9H), 1.43 – 1.36 (m, 1H), 1.24 (s, 12H), 0.94 (s, 6H). ^{13}C NMR (151 MHz, DMSO- d_6 , 363 K) δ 154.9, 81.8, 78.3, 27.7, 24.8, 24.3, 24.3, 23.6, 23.5, 22.6, 20.2, carbon attached to boron and two carbons attached to nitrogen not observed. ^{11}B NMR (192MHz, DMSO- d_6 , 363 K) δ 31.3. **HRMS** (ESI) m/z = 376.2630 calcd. for $\text{C}_{19}\text{H}_{36}\text{BNO}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 376.2643. **FTIR** (neat): ν (cm^{-1}) 2975, 2937, 1680, 1653, 1573, 1476, 1390, 1365, 1269, 1139, 1051, 1024, 1004, 822, 762, 733, 699, 632. **Chiral HPLC** (IC, 0.25%

*i*PrOH/cyclohexane, 1.0 ml/min) T_R 8.97min (minor), 9.66 min (major). $[\alpha]_D^{25} +27$ (*c* 0.5, CHCl₃).

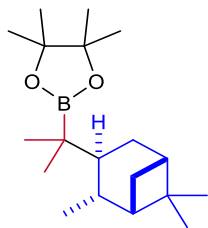


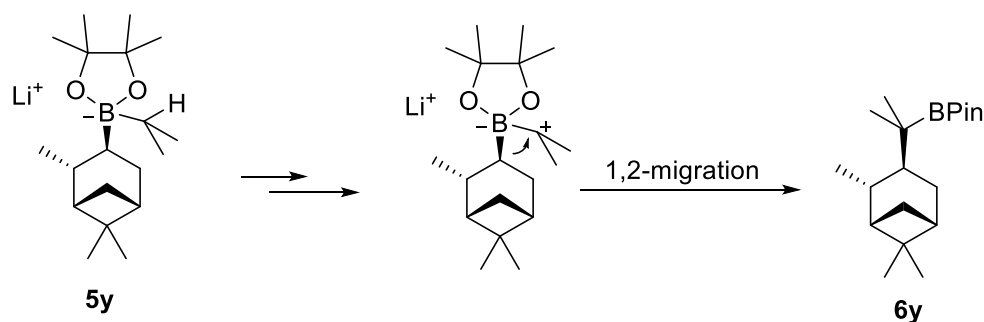
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.785	BV	0.3646	1592.75366	67.18864	49.6145
2	9.595	VB	0.4837	1617.50757	50.77238	50.3855



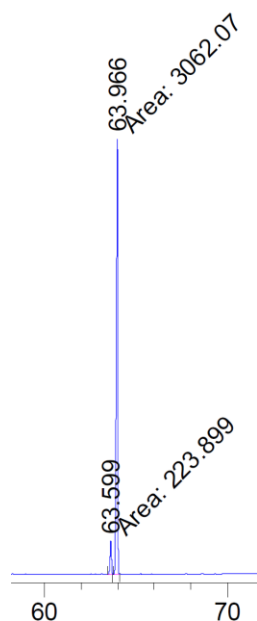
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.967	BV	0.4163	317.26120	11.27349	13.5692
2	9.663	VB	0.5521	2020.83142	55.58543	86.4308

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

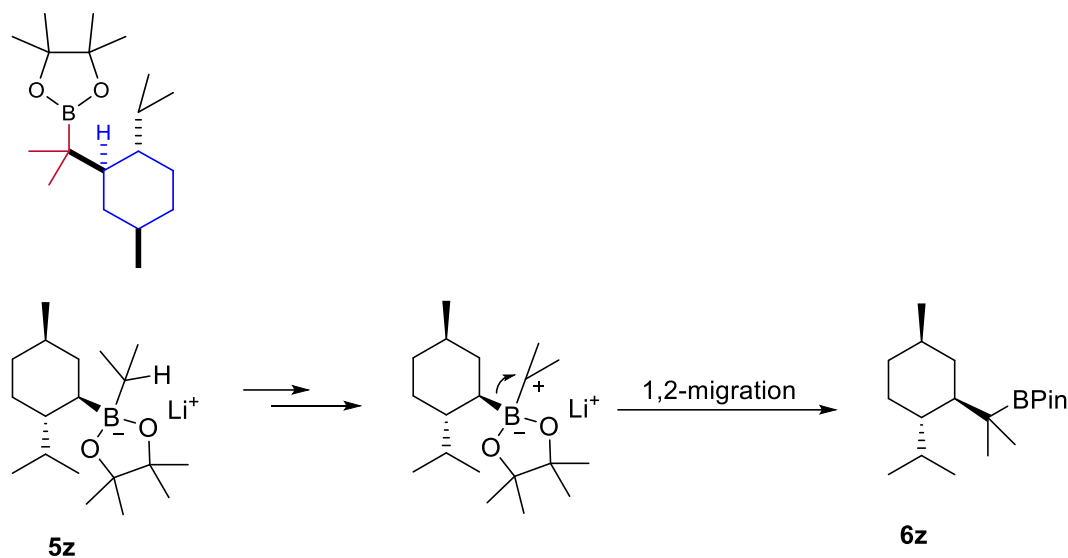




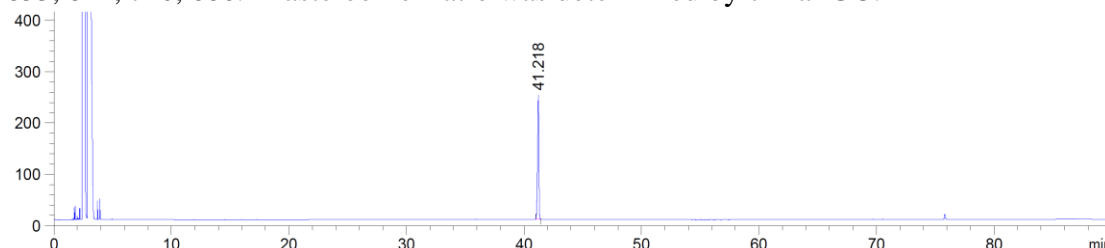
Following **GP1**, using **4y** (52.8 mg, 0.2 mmol, dr = 92:8) and isopropyllithium (0.70 M in pentane, 0.31 mL, 0.22 mmol), flash chromatography eluting with pentane/DCM (5:1) afforded **6y** as colorless sticky oil (42.6 mg, 70% yield, dr = 93:7), R_f 0.5 (pentane/DCM = 3:1). $[\alpha]_D^{26} +9$ (c 0.46, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 2.17 – 1.78 (m, 6H), 1.74 – 1.66 (m, 1H), 1.56 – 1.45 (m, 1H), 1.22 (s, 6H), 1.22 (s, 6H), 1.06 (d, J = 7.0 Hz, 3H), 1.03 (s, 3H), 0.98 (s, 3H), 0.95 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.8, 49.1, 43.0, 41.7, 39.0, 36.4, 32.0, 31.8, 31.2, 27.8, 24.9, 24.6, 24.2, 23.4, 21.0, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 33.7. **HRMS** (ESI) m/z = 329.2622 calcd. for $\text{C}_{19}\text{H}_{35}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 329.2629. **FTIR** (neat): ν (cm^{-1}) 2978, 2896, 2868, 1471, 1388, 1347, 1302, 1262, 1229, 1214, 1140, 1124, 1078, 1022, 967, 863, 839, 692, 672. Diastereomeric ratio was determined by chiral GC.



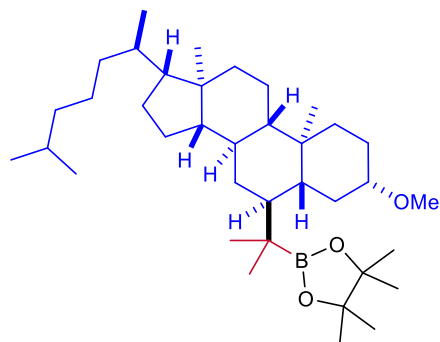
2-(2-((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6z**)

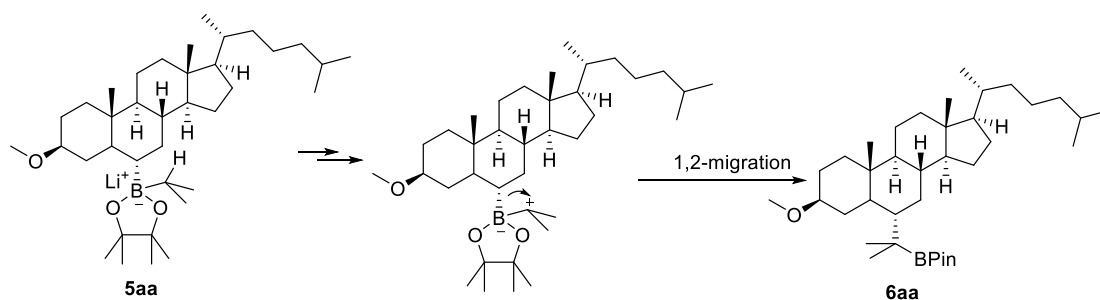


Following **GP1**, using **4z** (41.8 mg, 0.157 mmol, dr > 99:1) and isopropyllithium (0.70 M in pentane, 0.25 mL, 0.35 mmol, 1.1 equiv), flash chromatography eluting with pentane/DCM (5:1) afforded **6z** as colorless sticky oil (23.5 mg, 49% yield, dr > 99:1), R_f 0.5 (pentane/DCM = 3:1). $[\alpha]_D^{26}$ -65 (c 0.71, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 1.73 – 1.46 (m, 5H), 1.25 (s, 6H), 1.19 (s, 6H), 1.04 – 0.93 (m, 2H), 0.92 – 0.73 (m, 17H), 0.71 – 0.55 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.7, 45.4, 42.9, 35.3, 34.6, 33.0, 27.2, 25.4, 24.5, 24.0, 23.1, 22.4, 17.4, 16.8, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.2. **HRMS** (ESI) m/z = 331.2779 calcd. for $\text{C}_{19}\text{H}_{37}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 331.2788. **FTIR** (neat): ν (cm^{-1}) 2952, 2925, 2869, 1468, 1387, 1370, 1349, 1301, 1266, 1164, 1143, 1127, 1089, 966, 876, 853, 842, 710, 686. Diastereomer ratio was determined by chiral GC.



2-((3*S*,5*R*,6*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-Methoxy-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-6-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6aa**)

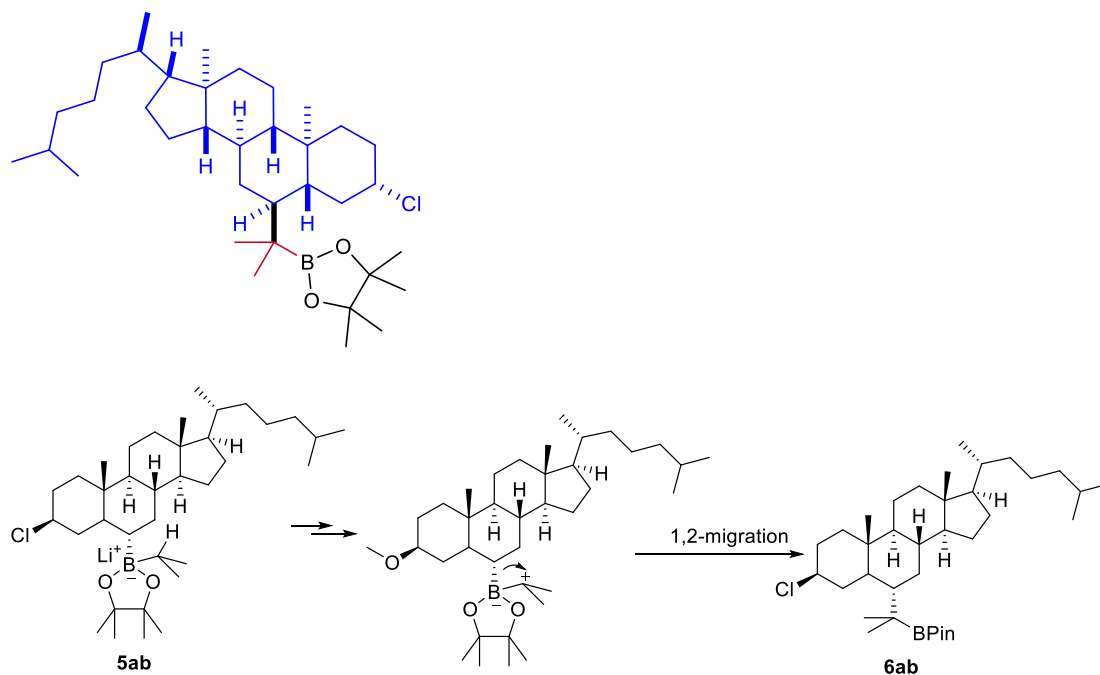




Following **GP1**, using **4aa** (62.6 mg, 0.119 mmol) and isopropylolithium (0.70 M in pentane, 0.19 mL, 0.13 mmol, 1.1 equiv), flash chromatography eluting with DCM afforded **6aa** as light yellow sticky oil (46.4 mg, 69% yield), R_f 0.2 (DCM). $[\alpha]_D^{26} +25$ (c 0.57, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 3.32 (s, 3H), 3.05 – 2.87 (m, 1H), 2.02 – 1.89 (m, 1H), 1.88 – 1.69 (m, 4H), 1.69 – 1.42 (m, 5H), 1.40 – 1.26 (m, 6H), 1.23 (s, 12H), 1.17 – 0.94 (m, 10H), 0.92 – 0.81 (m, 19H), 0.76 (s, 3H), 0.63 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 82.9, 81.1, 56.7, 56.4, 55.9, 54.5, 47.5, 42.7, 40.1, 40.0, 39.5, 37.6, 36.4, 36.2, 35.8, 35.1, 31.2, 30.6, 28.3, 28.0, 27.9, 24.8, 24.8, 24.4, 24.3, 23.9, 22.8, 22.6, 21.4, 18.7, 16.7, 13.7, 12.0, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 33.9. **HRMS** (ESI) m/z = 593.5075 calcd. for $\text{C}_{37}\text{H}_{67}\text{BO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 593.5082. **FTIR** (neat): ν (cm^{-1}) 2935, 2902, 2868, 2849, 1469, 1444, 1378, 1347, 1304, 1267, 1210, 1140, 1104, 966, 850, 710, 687, 577.

Dr and *rr* were determined by GCMS analysis after protondeboronation of **6aa**. The minor isomers were not detected by GCMS.

2-(2-((3*S*,5*R*,6*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-3-Chloro-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-6-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6ab**)



Following **GP1**, using **4ab** (106.6 mg, 0.2 mmol) and isopropylolithium (0.70 M in

pentane, 0.31 mL, 0.22 mmol, 1.1 equiv), flash chromatography eluting with pentane/DCM (4:1) afforded **6ab** as white solid (55.2 mg, 48% yield), R_f 0.4 (pentane/DCM = 3:1). M.p.: 71 – 73 °C. $[\alpha]_D^{25} +35$ (c 0.2, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 3.89 – 3.67 (m, 1H), 2.04 – 1.91 (m, 2H), 1.91 – 1.70 (m, 4H), 1.70 – 1.41 (m, 7H), 1.40 – 1.30 (m, 5H), 1.25 (s, 6H), 1.24 (s, 6H), 1.17 – 0.94 (m, 10H), 0.88 (t, J = 7.8 Hz, 16H), 0.76 (s, 3H), 0.63 (s, 3H), 0.60 – 0.44 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 83.0, 61.4, 56.6, 56.3, 54.2, 49.3, 42.6, 40.0, 39.9, 39.5, 39.3, 36.6, 36.2, 35.9, 35.8, 35.0, 33.0, 30.3, 28.3, 28.0, 25.0, 24.8, 24.5, 24.3, 23.9, 22.8, 22.7, 21.3, 18.7, 16.4, 13.7, 12.0, *carbon attached to boron not observed*. ^{11}B NMR (96 MHz, CDCl_3) δ 34.2. **HRMS** (ESI) m/z = 597.4580 calcd. for $\text{C}_{36}\text{H}_{64}\text{BClO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$, found: 597.4571. **FTIR** (neat): ν (cm^{-1}) 2948, 2869, 1468, 1444, 1372, 1347, 1306, 1167, 1139, 966, 908, 850, 732, 688.

Dr and *rr* were determined by GCMS analysis after protondeboronation of **6ab**. The minor isomers were not detected by GCMS.

7. DFT Calculations

7.1 General information for computation

All structures were optimized without geometry constraints using the BH-LYP hybrid functional^{S28-29} and an atom-pairwise dispersion correction (D3)^{S30-31}. A flexible triple zeta basis set (def2-TZVP)^{S32} and the COSMO implicit solvation model^{S33} with a dielectric constant of $\epsilon = 37.5$ (CH_3CN) were used in all calculations. For the calculation of zero point vibrational energies and free enthalpy contributions (G_{298}) with BH-LYP-D3, a rotor approximation was applied for the harmonic vibrational modes with wave numbers below 100 cm^{-1} .^{S34} Electronic energies were recalculated with the double hybrid functional PWPB95(-D3)^{S35} with the structures obtained with BH-LYP-D3, including a solvation energy obtained with the C-PCM^{S36} solvent model for acetonitrile. PWPB95 includes a component of the correlation energy which is computed by perturbation theory and performs more accurately in the determination of energies, even for open shell molecules.

All geometry optimizations and vibrational frequency calculations were performed with the TURBOMOLE program^{S37}. PWPB95-D3 calculations were performed with the ORCA program^{S38}.

7.2 Results

Transition Structures and HAT products

The electronic energies and thermodynamic corrections for the Gibbs free energy $G(298\text{K})$ are summarized in Table S3, the optimized structures are depicted in Figure S5 and S6.

Table S3: Electronic energies (E) and thermodynamic correction to the Gibbs Free Energy at $T = 298.15\text{ K}$ (G_{298}) for the structures involved in the reaction with CF_3 radical.

Structure	E(BH-LYP-D3) ^{[a][b]} [E _h]	G(298) ^{[a][b]} [kcal/mol]	E(PWPB95-D3) ^{[a][c]} ¹ [E _h]
$\cdot\text{CF}_3$	-337.5903708	-8.447	-337.5717281
CF ₃ H	-338.26902979	-0.001	-338.2508622
H ₃ CCH ₂ -Ph (EtPh)	-338.2508622	81.517	-310.7712210
[F ₃ C...H...CH(CH ₃)Ph] [‡] (EtPh-TS)	-648.3958687	83.228	-648.3316871
$\cdot\text{CH}(\text{CH}_3)\text{Ph}$ (EtPh-Rad)	-310.1760955	72.322	-310.1244915
[H(CH ₃) ₂ C(Ph)B(Pin)] [⊖] (Pinacolate)	-761.4423831	207.925	-761.3378077
[F ₃ C...H...C(CH ₃) ₂ CB(Ph)(P in)] ^{⊖‡} (Pinacolate-TS)	-1099.0253656	209.142	-1098.9038920
[$\cdot\text{C}(\text{CH}_3)_2\text{B}(\text{Ph})(\text{Pin})$] [⊖] (Pinacolate-Rad)	-760.7868038	197.751	-760.6802061
5j -Anion	-725.7302176	233.631	-725.6198361
5m -Anion	-765.0404387	252.563	-764.9204867
5j -TS _{iPr}	-1063.3154861	234.913	-1063.1881145
5j -TS _{cPent}	-1063.3164816	235.643	-1063.1897087
5m -TS _{iPr}	-1102.6292394	253.569	-1102.4924885
5m -TS _{cHex}	-1102.6257927	254.123	-1102.4886454

[a] All energies have been calculated with the def2-TZVP basis set

[b] using the COSMO solvation model, implemented in Turbomole ($\epsilon = 37.5$)

[c] Energy calculation for the structure optimized with BH-LYP-D3/def2-TZVP and with the C-PCM implicit solvation model (Solvent: acetonitrile).

We have performed a conformational search for all conformers of boron-ate complexes **5j** and **5m** (anion only). The conformers were subjected to reaction with a CF₃ radical in HAT reactions of the isopropyl and the cycloalkyl group. Only the most stable conformers of each anion and the two according transition structures with the lowest free energy are reported here (Figure S2). The relative barrier heights correctly predict the preferred products, namely **6j** with a ratio of 1.58:1 (exp: 2.2:1) and **6m** with a ratio of 150.6:1 (exp.: 29:1).

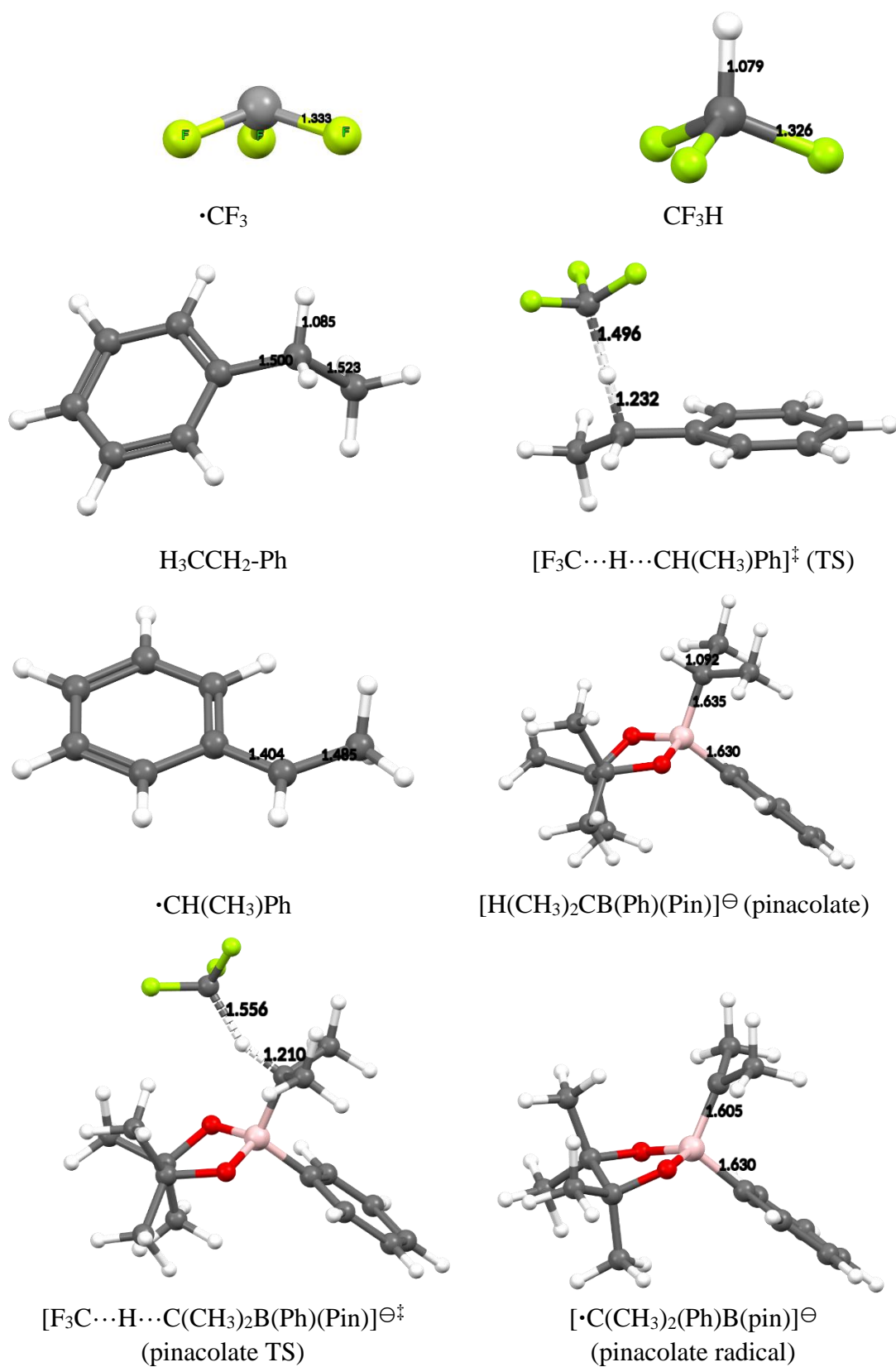


Figure S5. Optimized Structures in the reaction of radical $\cdot\text{CF}_3$ with ethyl benzene and the phenyl isopropyl boron-ate complex. (BH-LYP-D3/def2-TZVP +COSMO($\epsilon = 37.5$)). Distances are given in Å.

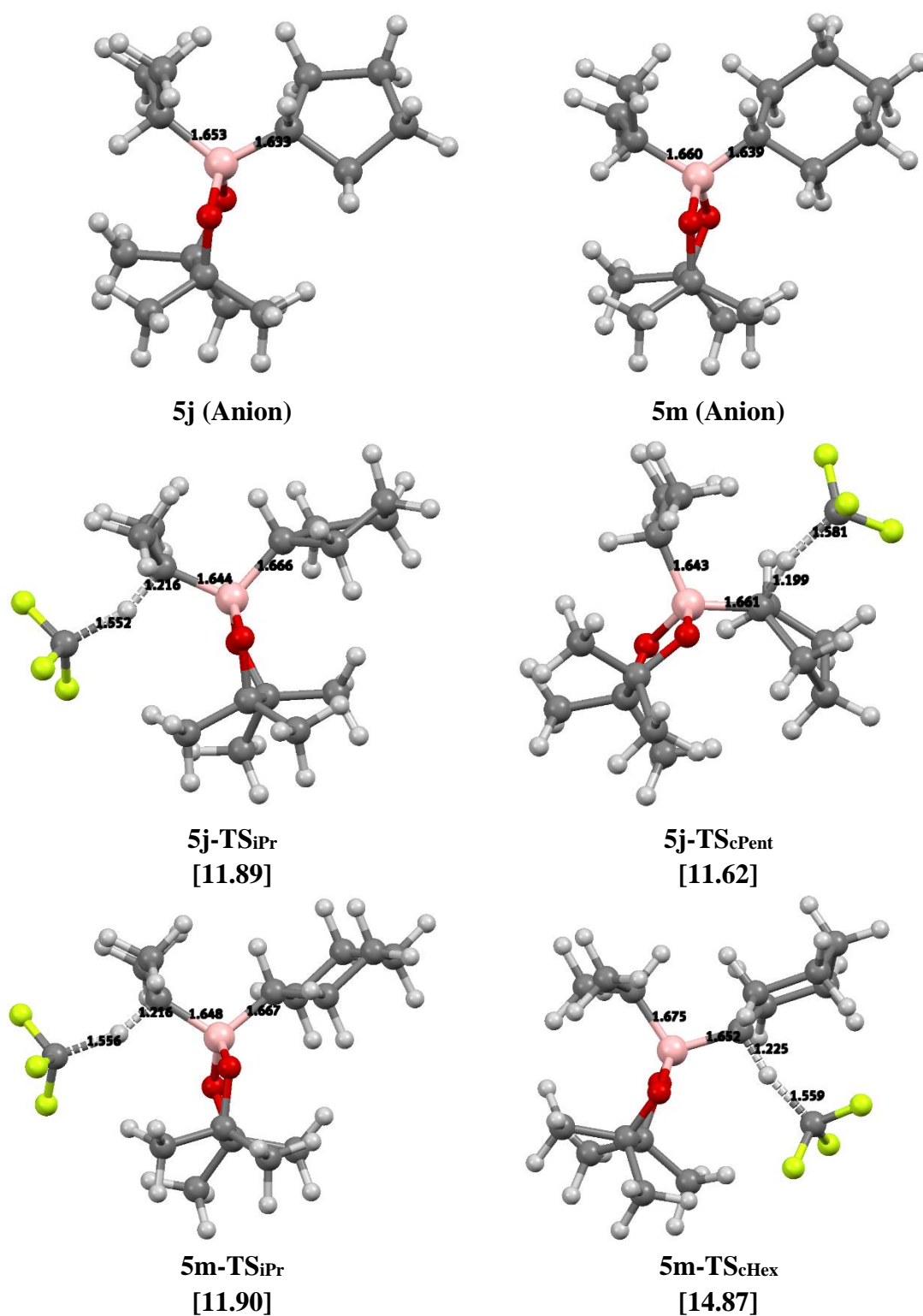


Figure S6. Optimized Structures of the most stable conformations of boron-ate complexes **5j** (*i*Pr/*cy*Pentyl) and **5m** (*i*Pr/*cy*Hexyl) and the favored transition structures in the HAT reaction with radical $\cdot\text{CF}_3$. (BH-LYP-D3/def2-TZVP +COSMO($\epsilon = 37.5$)). Distances are given in Å. Free energies (ΔG_{298}) relative to the boron-ate complex in kcal/mol are given in square brackets.

Cartesian Coordinates (in Å) of all optimized structures reported in Table S1.
 Lowest harmonic vibrational frequencies in cm⁻¹.

CF3 radical

E(BH-LYP-D3/def2-TZVP) = -337.5903707494 (conv)

Lowest Freq. = 529.07 cm⁻¹

4

CF3 (CF3/c1/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	1.1711941	0.0213555	0.0398263
F	1.5185977	0.0835525	1.2946534
F	1.6025755	-1.0749561	-0.5179996
F	1.5694598	1.0754761	-0.6154600

CF3H

E(BH-LYP-D3/def2-TZVP) = -338.2690297933 (conv)

Lowest Freq. = 527.12 cm⁻¹

5

CF3H (CF3H/c1/bhlyp-d3.def2-TZVP_COSMO_37.5)

H	0.0249365	0.0011027	0.0000588
C	1.1026042	0.0198655	0.0377755
F	1.5339586	0.0834396	1.2897903
F	1.6171219	-1.0699074	-0.5147688
F	1.5832061	1.0709276	-0.6118356

EtPh

E(BH-LYP-D3/def2-TZVP) = -310.8193020414 (conv)

Lowest Freq. = 32.89 cm⁻¹

18

EtPh (031/c1/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	-0.7791974	0.0606751	-0.0873873
C	-1.5273013	1.1458984	-0.5179717
C	-1.4511714	-1.0807023	0.3223917
C	-2.8319116	-1.1376789	0.3053681
C	-2.9080338	1.0949244	-0.5371538
C	-3.5662110	-0.0484144	-0.1242856
H	-0.8872496	-1.9346510	0.6558053
H	-1.0229309	2.0390262	-0.8441448
H	-3.3338227	-2.0335513	0.6242203
H	-3.4697714	1.9462124	-0.8776435
H	-4.6400939	-0.0913515	-0.1411353
C	0.7171980	0.1361423	-0.0245040
H	1.0801247	0.7718098	-0.8252722

H	1.1350905	-0.8513711	-0.1890938
C	1.2130100	0.6766010	1.3107675
H	0.8295645	1.6756038	1.4879830
H	2.2962755	0.7212381	1.3308437
H	0.8848724	0.0434457	2.1280079

EtPh-TS

E(BH-LYP-D3/def2-TZVP) = -310.1760954609 (conv)

Lowest Freq. = 60.45 cm⁻¹

17

EtPh-TS (032/c1/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	-0.8341424	0.0605821	0.2174012
C	-1.6027231	1.2046308	-0.0849443
C	-1.5105747	-1.1776416	0.2721073
C	-2.8605419	-1.2623802	0.0399584
C	-2.9548278	1.1077768	-0.3153025
C	-3.5967201	-0.1212122	-0.2558673
H	-0.9473158	-2.0653651	0.5002629
H	-1.1252400	2.1653928	-0.1362322
H	-3.3509551	-2.2181059	0.0873057
H	-3.5192653	1.9941429	-0.5435399
H	-4.6536363	-0.1897392	-0.4365607
C	0.5473842	0.1258728	0.4563611
H	1.0549071	-0.7954426	0.6813735
C	1.3428334	1.3791307	0.4198858
H	1.2789051	1.8688281	-0.5496138
H	2.3865997	1.1811250	0.6234276
H	0.9912496	2.1009972	1.1543843

EtPh-Rad

E(BH-LYP-D3/def2-TZVP) = -648.3958687174 (conv)

Lowest Freq. = -1562.98 cm⁻¹

22

EtPh-Rad (031TS/c1/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	-0.6399212	0.6680476	-0.4698628
C	-1.4438882	1.7928487	-0.3265682
C	-1.2436374	-0.5309542	-0.8332796
C	-2.6051221	-0.6074231	-1.0409691
C	-2.8067084	1.7182931	-0.5347967
C	-3.3936814	0.5190339	-0.8927157
H	-0.6360737	-1.4113051	-0.9484841
H	-1.0075856	2.7342223	-0.0491164
H	-3.0518662	-1.5457282	-1.3159903
H	-3.4118099	2.5989412	-0.4165435
H	-4.4549124	0.4622111	-1.0527269
C	0.8265199	0.7240694	-0.2952258
H	1.2830216	1.0412742	-1.3951342
H	1.2466957	-0.2644806	-0.1627840
C	1.4005993	1.7257868	0.6730040

H	1.1276304	2.7423308	0.4178595
H	2.4820011	1.6644723	0.6819897
H	1.0444730	1.5288917	1.6797275
C	1.8293786	1.5229362	-2.7021639
F	3.0794100	1.1365024	-2.8589836
F	1.7759832	2.8400858	-2.7359422
F	1.0982930	1.0357825	-3.6840613

Pinacolate

E(BH-LYP-D3/def2-TZVP) = -761.4423831268 (conv)

Lowest Freq. = 34.94 cm⁻¹

42

Pinacolate (022/c1/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	0.7714482	-2.8591935	-1.0231189
C	0.0894699	-2.2406647	0.1869886
C	0.8055470	-2.6555972	1.4634131
H	0.8411429	-3.7381919	1.5842570
H	0.3190026	-2.2392274	2.3402783
H	1.8317339	-2.2972019	1.4639879
H	-0.9244623	-2.6430362	0.2324241
B	-0.0927269	-0.6215695	0.0521016
O	-0.9089911	-0.2527778	-1.1395168
C	-2.1437330	0.2610953	-0.7248728
C	-3.1714527	-0.8657820	-0.6826717
H	-2.9053232	-1.6007770	0.0648833
H	-3.1850409	-1.3557429	-1.6499713
H	-4.1709194	-0.5004189	-0.4718995
C	-2.6114860	1.3102081	-1.7151552
H	-3.5176575	1.8006268	-1.3733851
H	-1.8497116	2.0612980	-1.8737335
H	-2.8260811	0.8402433	-2.6696222
C	-1.8332566	0.8129777	0.6945124
C	-1.1866294	2.1939357	0.6365110
H	-0.3636740	2.2053702	-0.0646964
H	-0.7939974	2.4332395	1.6185277
H	-1.8993480	2.9619557	0.3563076
C	-3.0301725	0.8724961	1.6227288
H	-3.4392394	-0.1135653	1.7976575
H	-2.7289679	1.2874988	2.5791576
H	-3.8129891	1.5048048	1.2160478
O	-0.9110094	-0.1198628	1.1876204
C	1.3517130	0.1283890	-0.0298844
C	1.9816210	0.3749830	-1.2453163
C	3.2171597	0.9931744	-1.3261158
C	3.8704465	1.3897346	-0.1727818
C	3.2686032	1.1587742	1.0515335
C	2.0338370	0.5374550	1.1112847
H	1.5745756	0.3776077	2.0715665
H	3.7625610	1.4673609	1.9574772
H	4.8299517	1.8733574	-0.2273052
H	3.6713678	1.1698344	-2.2865560
H	1.4803393	0.0851987	-2.1526225

H	0.2546061	-2.5913101	-1.9391982
H	1.7946581	-2.5033469	-1.1139225
H	0.8106405	-3.9467948	-0.9655449

Pinacolate-TS

E(BH-LYP-D3/def2-TZVP) = -1099.025365575 (conv)

Lowest Freq. = -896.03 cm⁻¹

46

Pinacolate-TS (022TS/c2/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	-0.6564785	-3.0005433	-0.8747872
C	-0.7794705	-2.2424978	0.4234856
C	0.2676163	-2.6818946	1.4230925
H	0.2293719	-3.7537263	1.6085124
H	0.1538775	-2.1712806	2.3729072
H	1.2617200	-2.4515226	1.0498467
H	-1.8215241	-2.5950082	0.9265420
B	-1.0046554	-0.6167409	0.2796865
O	-1.7671748	-0.2444239	-0.9322710
C	-3.0003646	0.3164247	-0.5728653
C	-4.0725036	-0.7633035	-0.6457595
H	-3.8771354	-1.5493886	0.0671373
H	-4.0576709	-1.1945223	-1.6407281
H	-5.0658644	-0.3681922	-0.4617781
C	-3.3561306	1.4183745	-1.5527225
H	-4.2609721	1.9369084	-1.2516255
H	-2.5551755	2.1399112	-1.6375385
H	-3.5286681	0.9889355	-2.5342455
C	-2.7539076	0.8131611	0.8829525
C	-2.1114378	2.1964234	0.9140146
H	-1.2451943	2.2350589	0.2676867
H	-1.7827110	2.4009765	1.9267918
H	-2.8072455	2.9731859	0.6166724
C	-3.9929413	0.8263567	1.7555572
H	-4.3956207	-0.1706094	1.8713854
H	-3.7399559	1.2052307	2.7403941
H	-4.7623756	1.4677723	1.3378373
O	-1.8488532	-0.1322561	1.3872946
C	0.4610969	0.0949521	0.2327009
C	1.1724515	0.2070172	-0.9568696
C	2.4347900	0.7720531	-1.0098887
C	3.0295593	1.2486680	0.1445627
C	2.3432378	1.1526387	1.3421648
C	1.0833302	0.5830531	1.3759857
H	0.5588946	0.5242894	2.3141780
H	2.7917728	1.5253975	2.2475068
H	4.0096719	1.6909393	0.1109766
H	2.9550157	0.8448794	-1.9499683
H	0.7202337	-0.1476899	-1.8673465

H	-1.4722926	-2.7625331	-1.5461320
H	0.2698198	-2.7272552	-1.3783222
H	-0.6315926	-4.0780032	-0.7221966
C	-2.7742676	-3.4386354	1.8222499
F	-2.5907931	-4.7193948	1.5144821
F	-2.4014337	-3.2683775	3.0828485
F	-4.0773051	-3.1912900	1.7490687

Pinacolate-Rad

E(BH-LYP-D3/def2-TZVP) = -760.7868038024 (conv)

Lowest Freq. = 10.05 cm⁻¹

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Pinacolate-Rad (023/c1/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	-1.1280064	1.7090216	2.1023087
C	-0.4187744	0.4089065	1.9599634
B	0.6467509	0.1929762	0.7790708
O	1.5003552	1.3962061	0.6060386
C	2.8343763	0.9865040	0.4957260
O	1.6257265	-0.8953427	1.0512418
C	2.8606408	-0.3074745	1.3535463
C	-0.1998303	-0.1570202	-0.5688200
C	-0.6339282	0.8405576	-1.4364517
C	-1.4182322	0.5654237	-2.5426441
C	-1.7998946	-0.7361165	-2.8174022
C	-1.3840944	-1.7491996	-1.9710762
C	-0.6012052	-1.4556410	-0.8685698
H	-2.0289493	1.7464928	1.4780052
H	-1.4627798	1.8932492	3.1242584
H	-0.4962301	2.5355210	1.7954967
H	-0.3369189	1.8568848	-1.2416014
H	-1.7308577	1.3635032	-3.1949573
H	-2.4086004	-0.9573298	-3.6764358
H	-1.6704113	-2.7674465	-2.1743105
H	-0.2841723	-2.2586723	-0.2245723
C	3.9773455	-1.2707789	1.0061273
H	3.8875158	-1.6193538	-0.0140266
H	3.9335220	-2.1337421	1.6628779
H	4.9508286	-0.8066930	1.1294424
C	2.9166731	0.0085850	2.8448225
H	2.1539720	0.7317759	3.1025513
H	3.8863386	0.3897162	3.1469988
H	2.7209212	-0.9031971	3.3984730
C	3.7429658	2.0910982	0.9965212
H	3.4486316	2.4154129	1.9854741
H	3.6820500	2.9450242	0.3293097
H	4.7783383	1.7667298	1.0297086
C	3.1553300	0.6983943	-0.9677328
H	2.9148422	1.5787266	-1.5535166
H	2.5537604	-0.1233796	-1.3333730
H	4.2036436	0.4636731	-1.1184582
C	-1.0932567	-0.7612945	2.5844997
H	-0.4490303	-1.6342118	2.5851137

H	-2.0050357	-1.0385470	2.0421770
H	-1.4024346	-0.5640896	3.6120305

5j-Anion

E(TPSS-D3/def2-TZVP) = -725.7302175552 (conv)

Lowest Freq. = 28.91 cm⁻¹

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5j-Anion (038/c4/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	-0.7185142	-3.0976769	-0.8140655
C	0.2625168	-1.9328765	-0.8002171
C	0.5818046	-1.5006019	-2.2244781
H	-0.3040223	-1.1449073	-2.7415003
H	0.9916994	-2.3179331	-2.8195639
H	1.3040407	-0.6915289	-2.2273272
B	-0.1986184	-0.7108200	0.2127656
O	0.6454443	0.5055044	0.0566667
C	1.6673142	0.5151415	1.0084764
C	2.9215709	-0.1355549	0.4256443
H	3.7673429	-0.0602757	1.1007147
H	2.7585898	-1.1772860	0.1927991
H	3.1760935	0.3782909	-0.4948839
C	2.0135957	1.9558311	1.3444675
H	2.4349050	2.4374500	0.4679386
H	2.7474696	2.0134819	2.1420597
H	1.1346257	2.5107381	1.6426363
C	1.0645665	-0.2921026	2.2081301
C	0.3652116	0.6065973	3.2239168
H	-0.1827543	-0.0227322	3.9171677
H	1.0701967	1.2034032	3.7931581
H	-0.3397222	1.2672401	2.7426097
O	0.1212805	-1.1361867	1.6143925
C	2.0857931	-1.1325881	2.9584005
H	1.5943248	-1.6467046	3.7782518
H	2.8787674	-0.5199907	3.3762886
H	2.5280880	-1.8784682	2.3121722
C	-1.7746176	-0.3143581	0.0521876
C	-2.3068392	0.7610845	0.9927995
H	-1.6400433	1.6205357	0.9679510
H	-2.3664727	0.4296231	2.0227145
C	-3.6642548	1.1399617	0.4147241
H	-4.3994983	0.3964521	0.7114777
H	-4.0306966	2.1040190	0.7550638
C	-3.4553213	1.0919631	-1.1046866
H	-3.3157030	2.0921808	-1.5027921
H	-4.3200341	0.6757125	-1.6108698
C	-2.1889543	0.2352973	-1.3205923
H	-1.3890345	0.8543329	-1.7154743

H	-2.3559157	-0.5530103	-2.0456206
H	-2.3731875	-1.2093753	0.2396248
H	1.1884471	-2.3204726	-0.3746705
H	-0.3348751	-3.9557863	-1.3670276
H	-0.9450370	-3.4321828	0.1946357
H	-1.6594392	-2.8141486	-1.2785081

5m-Anion

E (TPSS-D3/def2-TZVP) = -765.0433373667 (conv)

Lowest Freq. = 46.88 cm⁻¹

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5m-Anion (037/c1/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	-0.4632337	2.8595416	-1.4501206
C	0.3434057	2.2069817	-0.3344786
C	0.1775917	2.9955618	0.9585290
H	0.7582202	2.5515926	1.7590093
H	-0.8561584	3.0214827	1.2884754
H	0.4993577	4.0320667	0.8467954
B	0.1059910	0.5683444	-0.2187394
O	0.6482982	0.0058846	1.0475151
C	1.9515144	-0.4588264	0.8575839
C	2.9528434	0.6440544	1.2011146
H	2.8504366	1.4966840	0.5466490
H	2.7617786	0.9754238	2.2158515
H	3.9765427	0.2893864	1.1487947
C	2.2034325	-1.6134607	1.8128104
H	1.4482093	-2.3803067	1.7089624
H	2.1725353	-1.2463333	2.8335389
H	3.1782244	-2.0614692	1.6487663
C	1.9853457	-0.8643823	-0.6568617
C	1.6691489	-2.3415308	-0.8740733
H	0.7634580	-2.6312301	-0.3636267
H	1.5248228	-2.5085925	-1.9362269
H	2.4781676	-2.9813322	-0.5377209
O	0.9838368	-0.0845184	-1.2467567
C	3.3129186	-0.5753264	-1.3404099
H	3.5399110	0.4820880	-1.3253454
H	3.2581847	-0.8926922	-2.3768545
H	4.1307927	-1.1122099	-0.8699667
C	-1.4601188	0.1203558	-0.4042201
C	-1.6418197	-1.3900045	-0.4973229
H	-1.0513471	-1.7726802	-1.3212755
C	-3.0910923	-1.8237900	-0.6587896
C	-3.9623389	-1.2700369	0.4550489
C	-3.8304401	0.2403153	0.5378706
C	-2.3775305	0.6703726	0.6855015
H	-2.3324863	1.7527102	0.7028734
H	-2.0066957	0.3351053	1.6542174
H	-4.4276345	0.6245545	1.3621366
H	-4.2380918	0.6788765	-0.3725196
H	-5.0009104	-1.5557131	0.3086371

H	-3.6482153	-1.7071776	1.4022720
H	-3.1648904	-2.9090718	-0.6874389
H	-3.4691745	-1.4611466	-1.6143956
H	-1.2372830	-1.8463914	0.4052048
H	-1.8126099	0.5342228	-1.3536448
H	1.3905621	2.3099161	-0.6214705
H	-1.5268931	2.8489311	-1.2277857
H	-0.1799042	3.9004723	-1.6094072
H	-0.3283727	2.3361981	-2.3929235

5j-TS_iPr

E(TPSS-D3/def2-TZVP) = -1063.315486138 (conv)

Lowest Freq. = -903.16 cm⁻¹

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5j-TS_iPr (038TS1/c1a/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	-0.4884846	-3.2530355	-0.6032375
C	-0.8318207	-2.3988750	0.5931306
C	-0.0067270	-2.7617822	1.8072793
H	-0.0749746	-3.8188375	2.0542093
H	-0.3164411	-2.1888577	2.6748804
H	1.0431117	-2.5410590	1.6301964
H	-1.9582936	-2.7400045	0.8977551
B	-0.9266945	-0.7838365	0.3029377
O	-1.7616184	-0.4458657	-0.8717037
C	-2.9273983	0.2275956	-0.4873939
C	-4.0846001	-0.7621543	-0.4489327
H	-3.9321344	-1.5021938	0.3196609
H	-4.1347944	-1.2721050	-1.4042783
H	-5.0364073	-0.2729995	-0.2713269
C	-3.2482679	1.2966466	-1.5166125
H	-4.0996115	1.8970008	-1.2115791
H	-2.4030967	1.9515935	-1.6781297
H	-3.4943273	0.8246929	-2.4623781
C	-2.5797122	0.7879232	0.9282630
C	-1.9395427	2.1722557	0.8727090
H	-1.1003583	2.1918194	0.1936153
H	-1.5733442	2.4224292	1.8621068
H	-2.6482585	2.9352320	0.5697764
C	-3.7633572	0.8552412	1.8768552
H	-4.1729291	-0.1283616	2.0607275
H	-3.4405738	1.2689254	2.8267142
H	-4.5494272	1.4929003	1.4850193
O	-1.6524805	-0.1357867	1.4208931
C	0.6320674	-0.2390301	0.0806108
H	-1.1451270	-3.0321633	-1.4371765
H	0.5317630	-3.0581778	-0.9282444
H	-0.5544913	-4.3179554	-0.3860652
C	-3.0980246	-3.6785213	1.3770679
F	-2.5446092	-4.7619973	1.9131987
F	-3.8889805	-3.1365536	2.2984999
F	-3.8665461	-4.0834031	0.3703721
C	1.2469813	0.5419859	1.2661678
H	1.9296713	-0.0873425	1.8296271
H	0.4782814	0.8648295	1.9556697

C	0.8690320	0.6666521	-1.1314024
H	0.0552953	1.3735012	-1.2543283
H	0.9260161	0.1016940	-2.0565644
C	2.1557328	1.4128888	-0.8091968
H	2.3228801	2.2903811	-1.4275840
H	3.0083474	0.7505270	-0.9446061
C	1.9895526	1.7494940	0.6680467
H	2.9318296	1.9585100	1.1642669
H	1.3770927	2.6423029	0.7616554
H	1.2750164	-1.1024931	-0.0833126

5j-TS_cPent

E(TPSS-D3/def2-TZVP) = -1063.316481635 (conv)

Lowest Freq. = -806.60 cm⁻¹

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5j-TS_cPent (038TS2/c4a/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	-0.6928212	-3.1815739	-0.2637927
C	-1.1107778	-2.2257121	0.8441411
C	-0.3845426	-2.5707516	2.1370460
H	-0.5891831	-3.5923413	2.4575218
H	-0.6773278	-1.9073983	2.9454547
H	0.6912336	-2.4852184	2.0233012
H	-2.1695023	-2.4065959	1.0309804
B	-1.0277579	-0.6420680	0.4137881
O	-1.5727833	-0.4051897	-0.9445308
C	-2.8808929	0.0854616	-0.8685553
C	-3.8677082	-1.0778440	-0.9401490
H	-3.7542518	-1.7447330	-0.0977168
H	-3.6672339	-1.6412258	-1.8448066
H	-4.8962592	-0.7355799	-0.9742725
C	-3.1396361	0.9911390	-2.0592821
H	-4.1178871	1.4570740	-1.9969907
H	-2.3912675	1.7683966	-2.1319577
H	-3.1062579	0.4049200	-2.9718043
C	-2.9142644	0.8197911	0.5103839
C	-2.5070969	2.2859574	0.4068038
H	-1.5712834	2.3971310	-0.1196745
H	-2.3753139	2.6756368	1.4100528
H	-3.2598869	2.8846172	-0.0947366
C	-4.2610633	0.7566212	1.2107222
H	-4.5427257	-0.2650462	1.4258743
H	-4.2037040	1.2957416	2.1507708
H	-5.0423171	1.2133311	0.6111912
O	-1.9662935	0.1333797	1.2773307
H	-1.2694247	-3.0019117	-1.1639960
H	0.3538915	-3.0617712	-0.5244664
H	-0.8289297	-4.2249480	0.0217228
C	2.5875345	-1.6133839	-0.2291815
F	2.8639592	-2.6473664	0.5538318
F	2.5153392	-2.0501055	-1.4799300
F	3.6022265	-0.7631440	-0.1533517
C	0.4999177	0.0028309	0.5116401
H	1.2566203	-0.8653391	0.1796165
C	0.9750069	0.4262523	1.9041256
H	1.4322579	-0.3839490	2.4598480

C	0.8500456	1.1816106	-0.4090096
H	1.6560259	0.9103830	-1.0873836
H	0.0105742	1.4557758	-1.0328948
H	0.1078978	0.7503116	2.4725486
C	1.9228344	1.6020461	1.6949925
H	2.9159226	1.2412825	1.4420679
H	2.0177348	2.2360758	2.5709160
C	1.3169026	2.3195953	0.4987581
H	0.4625898	2.9044555	0.8268202
H	2.0077233	2.9979822	0.0088797

5m-TS_iPr

E(TPSS-D3/def2-TZVP) = -1102.629239442 (conv)

Lowest Freq. = -896.07 cm⁻¹

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5m-TS_iPr (037TS1/c2/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	-1.9371069	-2.9752367	1.3285185
C	-0.6678092	-2.2876381	0.8856719
C	0.0265389	-3.0459043	-0.2236166
H	0.1950758	-4.0891704	0.0334116
H	0.9844073	-2.5979914	-0.4661620
H	-0.5773797	-3.0326807	-1.1274287
H	0.0900638	-2.4099291	1.8286710
B	-0.8058066	-0.6635310	0.6400325
O	-1.4801761	0.0305691	1.7582500
C	-0.5917112	0.8577450	2.4532051
C	-0.1173926	0.1388702	3.7097145
H	0.4653723	-0.7319100	3.4591455
H	-0.9865760	-0.1862021	4.2702353
H	0.4810345	0.7807628	4.3474066
C	-1.3196452	2.1216127	2.8762743
H	-0.6443149	2.8311620	3.3440484
H	-1.7955357	2.5999209	2.0313240
H	-2.0899796	1.8687848	3.5977459
C	0.5658686	1.0990021	1.4317598
C	0.3296870	2.3280628	0.5591328
H	-0.6470705	2.3019028	0.0990925
H	1.0725341	2.3383981	-0.2306283
H	0.4217717	3.2494086	1.1237968
C	1.9378078	1.2336716	2.0690567
H	2.2156366	0.3293630	2.5925661
H	2.6772566	1.4162890	1.2960293
H	1.9716619	2.0649676	2.7661272
O	0.5446899	-0.0517624	0.6365446
H	-2.3691941	-2.4726564	2.1861753
H	-2.6766298	-2.9560725	0.5302061
H	-1.7748385	-4.0206205	1.5864161
C	0.9821269	-3.1446432	2.8706329
F	1.1868017	-4.3866375	2.4421976
F	2.1749902	-2.5841844	3.0515546
F	0.3906193	-3.2293276	4.0588993
C	-1.6566508	-0.4618605	-0.7786614
H	-2.1200948	-1.4188288	-1.0317401
C	-0.7689617	-0.1040156	-1.9669798
H	0.0318021	-0.8307448	-2.0664722

C	-2.8153906	0.5262318	-0.6888544
H	-3.4749288	0.2398897	0.1234159
H	-2.4418246	1.5135848	-0.4275624
H	-0.2827797	0.8485392	-1.7742349
C	-1.5435312	-0.0072811	-3.2735350
H	-1.9417447	-0.9893035	-3.5270359
H	-0.8854117	0.2821444	-4.0901335
C	-3.6005393	0.6282719	-1.9889031
H	-4.3963896	1.3649181	-1.9002387
H	-4.0823482	-0.3281599	-2.1895846
C	-2.6956872	0.9776110	-3.1592818
H	-2.2917095	1.9779756	-3.0081407
H	-3.2647220	1.0081535	-4.0849470

5m-TS_cHex

E (TPSS-D3/def2-TZVP) = -1102.625792651 (conv)

Lowest Freq. = -905.29 cm⁻¹

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5m-TS_cHex (037TS2/c2a/bhlyp-d3.def2-TZVP_COSMO_37.5)

C	-3.2185287	0.7666502	0.2230236
C	-2.0020013	0.4510709	1.0831045
C	-2.4445560	0.0748365	2.4914642
H	-3.0416087	0.8620595	2.9532684
H	-1.5970777	-0.1188070	3.1402632
H	-3.0449100	-0.8280371	2.4829432
H	-1.4638405	1.3947166	1.1747077
B	-0.9503070	-0.6645431	0.4086673
O	-1.0038314	-2.0056455	1.0309092
C	-1.7126886	-2.9019378	0.2232728
C	-3.1594204	-2.9879509	0.7019479
H	-3.6659727	-2.0389884	0.6146448
H	-3.1585353	-3.2713475	1.7485356
H	-3.7237506	-3.7315529	0.1500663
C	-1.1005353	-4.2849037	0.3697918
H	-1.5755821	-5.0006894	-0.2934612
H	-0.0405237	-4.2678130	0.1633672
H	-1.2405771	-4.6312164	1.3887307
C	-1.5807925	-2.2947881	-1.2170981
C	-0.4261823	-2.8929126	-2.0102290
H	0.4921777	-2.8572230	-1.4494510
H	-0.2913520	-2.3069136	-2.9124718
H	-0.6156829	-3.9218233	-2.2972244
C	-2.8395318	-2.4281280	-2.0598686
H	-3.6735736	-1.9100780	-1.6079074
H	-2.6621440	-1.9899475	-3.0366405
H	-3.1128485	-3.4684528	-2.2053599
O	-1.3197243	-0.9386753	-0.9962795
H	-2.9227597	1.1098855	-0.7614133
H	-3.8474083	-0.1041796	0.0714376
H	-3.8410031	1.5382494	0.6780336
C	2.5075949	-1.9012232	-0.1087591
F	2.2647466	-3.1732067	0.1906735
F	2.7530777	-1.8317777	-1.4142866
F	3.6301272	-1.5603389	0.5191933
C	0.5706698	-0.0358791	0.5474760
H	1.3199997	-0.9560299	0.2450629
C	0.9854748	0.3439315	1.9585527
H	0.9335387	-0.5313043	2.6004279

C	0.8658639	1.0626655	-0.4531350
H	0.7166209	0.6768804	-1.4559721
H	0.1207440	1.8488773	-0.3193672
H	0.2469100	1.0427380	2.3462986
C	2.3527385	1.0051202	2.0819591
H	3.1352497	0.2784740	1.8919615
H	2.4971343	1.3586194	3.0997430
C	2.2462991	1.6890151	-0.3201208
H	2.3478281	2.5196392	-1.0137881
H	3.0062583	0.9609696	-0.5961149
C	2.5029978	2.1562212	1.1021454
H	1.7886119	2.9392174	1.3535690
H	3.4926246	2.5966573	1.1854222

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9. NMR Spectra of New Compounds

