

**General Considerations:** Infrared (IR) spectra were recorded on a Bruker Tensor II FT-IR Spectrometer,  $\nu_{\max}$  in  $\text{cm}^{-1}$ . Bands are characterized as broad (br), strong (s), medium (m), and weak (w).  $^1\text{H}$  NMR spectra were recorded at room temperature on a Varian I400 (400 MHz), Varian VXR400 (400 MHz), Varian I500 (500 MHz), or a Varian I600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ( $\text{CHCl}_3$ : 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration.  $^{13}\text{C}$  NMR spectra were recorded on a Varian I400 (100 MHz), Varian VXR400 (100 MHz), or a Varian I500 (125 MHz) spectrometer with complete proton decoupling.  $^{19}\text{F}$  NMR spectra were recorded on a Varian VXR400 (375 MHz) spectrometer or a Varian I500 (470 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ( $\text{CDCl}_3$ : 77.16 ppm). Most of High-resolution mass spectrometry (HRMS) was performed on either a Waters/Micromass LCT Classic (ESI-TOF) or a Thermo Electron Corporation MAT 95XP-Trap (GC/MS). Samples 15 and 16 were analyzed by low energy electron ionization (EI, 15 V) on an Agilent G7250 QTOF mass spectrometer. This instrument was purchased with funds from NSF award CHE 1726633. Melting points were obtained on a Thomas Hoover capillary melting point apparatus without correction. The diastereomeric and regioisomeric ratios were determined using NMR, GC or GC-MS analysis of unpurified reaction mixtures. GC analyses were performed by means of Agilent 6850 Gas Chromatograph equipped with Agilent 19091Z-413E, 30 m x 320  $\mu\text{m}$  x 0.25  $\mu\text{m}$  column. Air was used as the GC carrier gas and maintained at a constant flow rate of 25.0 mL/min. The initial temperature was 60 °C and subsequently ramped at a rate of 20 °C /min to a final temperature of 300 °C, and held for 5 min. Total run time was 17 min. Unless otherwise noted, all reactions have been carried out with distilled and degassed solvents under an atmosphere of dry  $\text{N}_2$  in oven- (150 °C) and flame-dried glassware with standard vacuum-line techniques. Tetrahydrofuran and DMF were purified under a positive pressure of dry argon by passage through two columns of activated alumina. Toluene was purified under a positive pressure of dry argon by passage through columns of activated alumina and Q5 (Grubbs apparatus). All work-up and purification procedures were carried out with reagent grade solvents (purchased from Sigma-Aldrich) in air. Standard column chromatography techniques using ZEOprep 60/40-63  $\mu\text{m}$  silica gel were used for purification.

## ■ Reagents and Catalysts:

**(2-Methylpropenyl)benzene** was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**(3-Bromophenyl)methanol** was purchased from CombiBlocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**1-(2-(4-Bromophenoxy)ethyl)pyrrolidine** was purchased from CombiBlocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**1-(4-Bromophenyl)pyrrolidine** was purchased from Ark Pharm and was used as received.

**1-Bromo-2-chlorobenzene** was purchased from CombiBlocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**1-Bromo-3,5-dimethylbenzene** was purchased from Oakwood and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**1-Bromo-3-chlorobenzene** was purchased from Oakwood and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**1-Bromo-4-chlorobenzene** was purchased from Sigma-Aldrich and used as received.

**1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI)** was purchased from Oakwood and used as received.

**1*H*-Indene** was purchased from TCI and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**1-Phenyl-1-cyclohexene** was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**2-Bromonaphthalene** was purchased from Oakwood and used as received.

**2-Bromotoluene** was purchased from Oakwood and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**2-Ethyl-1*H*-indene** was purchased from Alfa Aesar and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**2-Methyl-1*H*-indene** was purchased from Accela and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**3-Bromoanisole** was purchased from Oakwood and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**3-Bromofuran** was purchased from CombiBlocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**4-Bromo-1,2-methylenedioxybenzene** was purchased from CombiBlocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**4-Bromoanisole** was purchased from TCI and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**4-Bromofluorobenzene** was purchased from Oakwood and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**4-Dimethylaminopyridine** was purchased from Oakwood and used as received.

**5-Bromo-1-methylindole** was purchased from CombiBlocks and used as received.

**5-Bromo-2-methoxypyridine** was purchased from CombiBlocks and used as received.

**Benzyltriphenylphosphonium bromide** was purchased from CombiBlocks and used as received.

**Bis(1,5-cyclooctadiene)nickel** was purchased from Strem and used as received.

**Bis(1,5-cyclooctadiene)nickel(0)** was purchased from Strem and used as received.

**Bis(pinacolato)diboron** was purchased from Oakwood and purified via recrystallization from pentane prior to use.

**Bromobenzene** was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**Diethyl benzylphosphonate** was purchased from Oakwood and used as received.

**di-tert-Butyl dicarbonate** was purchased from Oakwood and used as received.

**Dodecane** was purchased from Aldrich and used as received.

**Hydrogen Peroxide (30 wt% in water)** was purchased from Macron and used as received.

**Methyl 2-(3-bromophenyl)acetate** was purchased from CombiBlocks and used as received.

**N, N-Dimethylacetamide (DMA, anhydrous, septum-sealed bottle DriSolv®)** was purchased from Sigma-Aldrich and used as received.

**N-Boc-nortropinone** was purchased from CombiBlocks and used as received.

**Nickel(II) chloride ethylene glycol dimethyl ether complex (NiCl<sub>2</sub>DME)** was purchased from Strem and used as received.

**Nickel(II) dichloride (NiCl<sub>2</sub>)** was purchased from Strem and used as received.

**N-Methylmorpholine N-oxide** was purchased from Sigma-Aldrich and used as received.

**Phenyl cyanate** was purchased from Sigma-Aldrich and used as received.

**Potassium ethoxide** was purchased from Sigma-Aldrich and used as received.

**Potassium methoxide** was purchased from Alfa Aesar and used as received.

**Potassium tert-butoxide** was purchased from Strem and used as received.

**tert-butyl 3-oxoazetidine-1-carboxylate** was purchased from CombiBlocks and used as received.

**tert-Butyl 5-bromo-1H-indole-1-carboxylate** was purchased from CombiBlocks and used as received.

**tert-Butyldimethylsilyl chloride** was purchased from Oakwood and used as received.

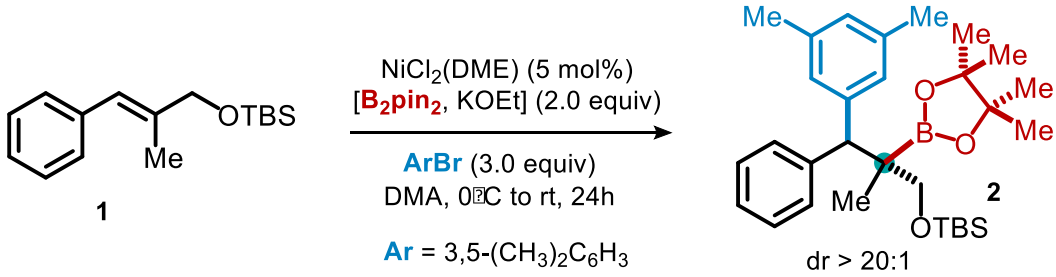
**Tetrapropylammonium perruthenate (TPAP)** was purchased from Oakwood and used as received.

**trans-Anethole** was purchased from TCI and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**trans-β-Methylstyrene** was purchased from TCI and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**α-Methylstyrene** was purchased from Accela and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipet prior to use.

**Table S-1: Variations from Standard Reaction Conditions<sup>[a]</sup>**



entry	Change from standard conditions	<b>2</b> (%) <sup>[b]</sup>
1	Ni(COD) <sub>2</sub> instead of NiCl <sub>2</sub> (DME)	<5
2	Ni(dppf)Cl <sub>2</sub> instead of NiCl <sub>2</sub> (DME)	trace
3	Ni(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> instead of NiCl <sub>2</sub> (DME)	trace
4	NiCl <sub>2</sub> instead of NiCl <sub>2</sub> (DME)	56
5	none	98
6	no premixing B <sub>2</sub> pin <sub>2</sub> and KOEt	79
7	1.5 equiv ArBr instead of 3.0 equiv ArBr	65
8	2 mol% NiCl <sub>2</sub> (DME) instead of 5 mol% NiCl <sub>2</sub> (DME)	75
9	toluene instead of DMA	trace
10	THF instead of DMA	21
11	DMF instead of DMA	25
12	ArI instead of ArBr	<10
13	KOtBu instead of KOEt	90
14	NaOEt instead of KOEt	72
15	glovebox free reaction setup	94

[a] reactions performed on 0.2 mmol scale. [b] Yield determined by <sup>1</sup>H NMR analysis of the unpurified reactions mixture with an internal standard.

#### ■ General Procedure A for Arylboration Reaction in Table S-1:

*Preparation of NiCl<sub>2</sub>(DME) stock solution in DMA (0.02 M):* In an oven-dried 5-mL vial with a magnetic stir bar, NiCl<sub>2</sub>(DME) (8.8 mg, 0.04 mmol) was added in the N<sub>2</sub>-filled glovebox. The vial was sealed with a rubber septum and removed from the glovebox. DMA (2.0 mL) was added to the vial, and the mixture was stirred for 5 minutes until the solution became completely homogeneous as a blue solution.

In an N<sub>2</sub>-filled glovebox, KOEt (33.7 mg, 0.400 mmol, 2.00 equiv) and bis(pinacolato)diboron (B<sub>2</sub>pin<sub>2</sub>) (0.102 g, 0.400 mmol, 2.00 equiv) were added to a separate oven-dried 16 x 100 mm screw-capped vial containing a magnetic stir bar. The vial was sealed with a rubber septum and removed from the glovebox. DMA (1.0 mL) was added to the vial, and the mixture was stirred vigorously at r.t. for 1 h to afford a suspension. Thereafter, the vial was cooled to 0 °C, the alkene (0.20 mmol, 1.0 equiv) and Aryl bromide (0.60 mmol, 3.0 equiv) were added to the reaction mixture via syringe under an N<sub>2</sub> atmosphere. The pre-prepared NiCl<sub>2</sub>(DME) stock solution in DMA (0.50 mL, 0.02 M) was added to the reaction mixture. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was warmed to r.t. and stirred for 24 h. The reaction was quenched upon the addition of water (2.0 mL), and the solution was diluted with EtOAc (15 mL), the organic layer was washed with KOH aqueous (3 x 4.0 mL, 1.0 M), dried over MgSO<sub>4</sub>, gravity

filtered, and concentrated. dibromomethane was added as an internal standard and a small aliquot was analyzed via  $^1\text{H}$  NMR.

### ■ General Procedure B for the Arylboration Reaction in Scheme 2 and 3

*Preparation of NiCl<sub>2</sub>(DME) stock solution in DMA (0.04 M):* In the N<sub>2</sub>-filled glovebox, an oven-dried 5-mL vial with a magnetic stir bar was charged NiCl<sub>2</sub>(DME) (17.6 mg, 0.08 mmol). The vial was sealed with a rubber septum and removed from the glovebox. DMA (2.0 mL) was added to the vial, and the mixture was stirred for 5 minutes until the solution became completely homogeneous as a blue solution.

In an N<sub>2</sub>-filled glovebox, KOEt (67.4 mg, 0.800 mmol, 2.00 equiv) and bis(pinacolato)diboron (B<sub>2</sub>pin<sub>2</sub>) (0.203 g, 0.800 mmol, 2.00 equiv) were added to a separate 16 x 100 mm screw-capped vial. The vial was sealed with a rubber septum and removed from the glovebox. DMA (2.5 mL) was added to the vial, and the mixture was stirred vigorously at r.t. for 1 h to afford a suspension. Thereafter, the vial was cooled to 0 °C, the alkene (0.40 mmol, 1.0 equiv) and aryl bromide (1.2 mmol, 3.0 equiv) were added to the reaction mixture via syringe under an N<sub>2</sub> atmosphere. (*Note:* if the alkene or aryl bromide is solid, it was dissolved in a minimal DMA (0.20 mL) and was added via syringe, followed by a DMA rinsing (0.20 mL)). The pre-prepared NiCl<sub>2</sub>(DME) stock solution in DMA (0.50 mL, 0.04 M) was added to the reaction mixture. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was warmed to r.t. and stirred for 24 h. The reaction was quenched upon the addition of water (2.0 mL), and the solution was diluted with EtOAc (20 mL), the organic layer was washed with KOH aqueous (3 x 5.0 mL, 1.0 M), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated. dibromomethane was added as an internal standard and a small aliquot was analyzed via  $^1\text{H}$  NMR.

### ■ General Procedure C for the Arylboration under Glovebox Free

*Preparation of NiCl<sub>2</sub>(DME) stock solution in DMA (0.02 M):* A 5-mL vial containing a magnetic stir bar was flame-dried under vacuum. After cooling to room temperature, the vial was back filled with nitrogen and removed from vacuum-line. NiCl<sub>2</sub>(DME) (8.8 mg, 0.040 mmol) was added to the vial in the air. The vial was sealed with a rubber septum and was evacuated and backfilled with nitrogen three times. DMA (2.0 mL) was added to the vial, and the mixture was stirred for 5 minutes until the solution becomes homogeneous as a blue solution.

KOEt (33.7 mg, 0.400 mmol, 2.00 equiv) and bis(pinacolato)diboron (0.102 g, 0.400 mmol, 2.00 equiv) were added to a separate flame-dried 16 x 100 mm screw-capped vial containing a magnetic stir bar. The vial was sealed with a rubber septum, and then evacuated under high vacuum and backfilled with nitrogen. The evacuate-refill cycle was repeated three times, DMA (1.0 mL) was added to the vial, and the mixture was stirred vigorously at r.t. for 1 h to afford a suspension. Thereafter, the vial was cooled to 0 °C, the alkene (0.20 mmol, 1.0 equiv) and Aryl bromide (0.60 mmol, 3.0 equiv) were added to the reaction mixture via syringe under an N<sub>2</sub> atmosphere. The pre-prepared NiCl<sub>2</sub>(DME) stock solution in DMA (0.50 mL, 0.02 M) was added to the reaction mixture. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was warmed to r.t. and stirred for 24 h. The reaction was quenched upon the addition of water (2.0 mL), and the solution was diluted with EtOAc (15 mL), the organic layer was washed with KOH aqueous (3 x 4.0 mL, 1.0 M), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated. dibromomethane was added as an internal standard and a small aliquot was analyzed via  $^1\text{H}$  NMR.

### ■ General Procedure D for the Arylboration of Alkenes and Subsequent Oxidation

*Preparation of NiCl<sub>2</sub>(DME) stock solution in DMA (0.04 M):* In a 5-mL vial containing a magnetic stir bar was oven-dried, NiCl<sub>2</sub>(DME) (17.6 mg, 0.080 mmol) was added in the N<sub>2</sub>-filled glovebox (the glovebox is not required). The vial was sealed with a rubber septum and removed from the glovebox. DMA (2.0 mL) was added to the vial, and the mixture was stirred for 5 minutes until the solution became completely homogeneous as a blue solution.

In an N<sub>2</sub>-filled glovebox, KOEt (67.4 mg, 0.800 mmol, 2.00 equiv) and B<sub>2</sub>pin<sub>2</sub> (0.203 mg, 0.800 mmol, 2.00 equiv) were added to a separate 16 x 100 mm screw-capped vial containing a magnetic stir bar was oven-dried. The vial was sealed with a rubber septum and removed from the glovebox. DMA (2.5 mL) was added to the vial, and the mixture was stirred vigorously at r.t. for 1 h to afford a suspension. Thereafter, the vial was cooled to 0 °C, the alkene (0.40 mmol, 1.0 equiv) and Aryl bromide (1.2 mmol, 3.0 equiv) were added to the reaction mixture via syringe under an N<sub>2</sub> atmosphere. (*Note:* if the alkene or aryl bromide is solid, it was dissolved in a minimal DMA (0.20 mL) and was added via syringe, followed by a DMA rinsing (0.20 mL)). The pre-prepared NiCl<sub>2</sub>(DME) stock solution in DMA (0.50 mL, 0.04 M) was added to the reaction mixture. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was warmed to r.t. and stirred for 24 h. The reaction was quenched upon the addition of water (2.0 mL), and the solution was diluted with EtOAc (20 mL), the organic layer was washed with KOH aqueous (3 x 5.0 mL, 1.0 M), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated. Dibromomethane was added as an internal standard and a small aliquot was analyzed via <sup>1</sup>H NMR.

The unpurified material was then dissolved in THF (5.0 mL) and NaOH (2.0 mL, 2.0 M aqueous solution, 4.0 mmol, 10 equiv.) was added. The reaction flask was placed in an ice bath and cooled to 0 °C. Then, H<sub>2</sub>O<sub>2</sub> (0.20 mL, 30% aqueous solution, 2.0 mmol, 5.0 equiv.) was added via syringe. The ice bath was removed and the reaction was stirred at room temperature for 5h then quenched upon the addition of water (5 mL). The aqueous layer was extracted with EtOAc (3 x 8 mL) and the combined organic layers were dried over anhydrous MgSO<sub>4</sub>, gravity filtered, and concentrated. The residue material was purified via silica gel column chromatography.

### ■ General Procedure E: Arylboration in Toluene for Cyclic Alkenes in Scheme 5

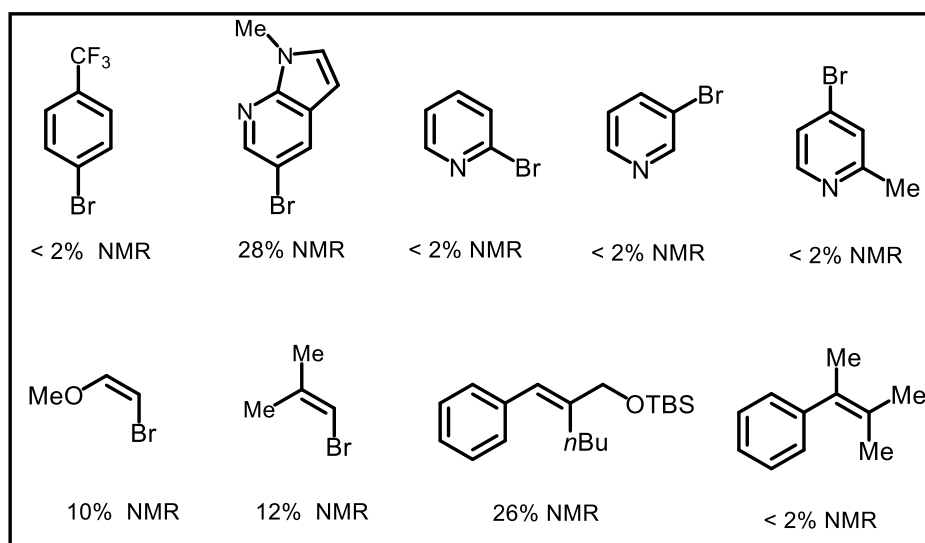
In an N<sub>2</sub>-filled glovebox, NiCl<sub>2</sub>(DME) (13.2 mg, 0.060 mmol, 15 mol%), KOEt (67.4 mg, 0.800 mmol, 2.00 equiv) and B<sub>2</sub>pin<sub>2</sub> (0.203 mg, 0.800 mmol, 2.00 equiv) were added to a 16 x 100 mm screw-capped vial containing a magnetic stir bar was oven-dried. The vial was sealed with a rubber septum and removed from the glovebox. The alkene (0.40 mmol, 1.0 equiv) and aryl bromide (0.48 mmol, 1.2 equiv) in toluene (2.0 mL) were added to the reaction mixture via syringe under an N<sub>2</sub> atmosphere. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 60 °C for 24 h in a preheated aluminum block. The reaction was quenched upon the addition of water (2.0 mL), and the solution was diluted with EtOAc (20 mL), the organic layer was washed with KOH aqueous (3 x 5.0 mL, 1.0 M), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated. Dibromomethane was added as an internal standard and a small aliquot was analyzed via <sup>1</sup>H NMR.

### ■ General Procedure F: Arylboration in Toluene for Acyclic Alkenes in Scheme 5

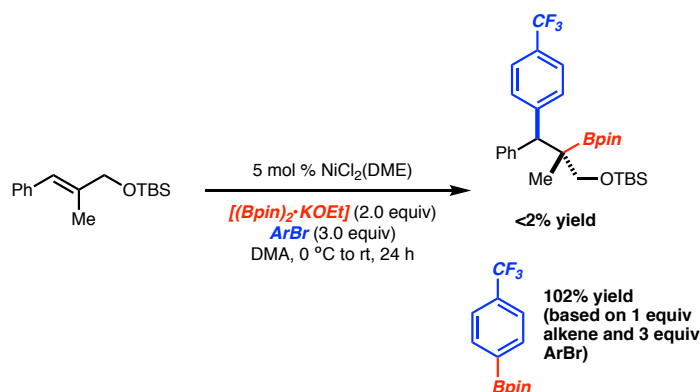
NiCl<sub>2</sub>(DME) (13.2 mg, 0.06 mmol, 15 mol%), KOEt (67.4 mg, 0.800 mmol, 2.00 equiv) and B<sub>2</sub>pin<sub>2</sub> (0.203 mg, 0.800 mmol, 2.00 equiv) were added to a 16 x 100 mm screw-capped vial containing a

magnetic stir bar was oven-dried in an N<sub>2</sub>-filled glovebox. The vial was sealed with a rubber septum and removed from the glovebox. The alkene (0.80 mmol, 2.0 equiv) and aryl bromide (0.40 mmol, 1.0 equiv) in toluene (2.0 ml) were added to the reaction mixture via syringe under an N<sub>2</sub> atmosphere. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 60 °C for 24 h in a preheated aluminum block. The reaction was quenched upon the addition of water (2.0 mL), and the solution was diluted with EtOAc (20 mL), the organic layer was washed with KOH aqueous (3 x 5.0 mL, 1.0 M), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated. Dibromomethane was added as an internal standard and a small aliquot was analyzed via <sup>1</sup>H NMR.

### ■ Substrate Limitations:

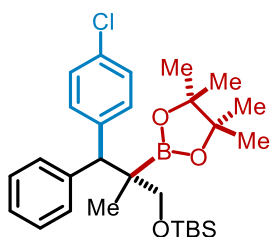


In the case of aryl bromides that have electron withdrawing group, formation of significant quantities of ArBpin was observed.



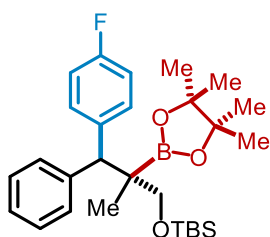
### ■ Characterization Data for Arylboration Products:

In <sup>13</sup>C NMR spectra, signals of carbons directly bonded to boron were not detected because of quadrupolar relaxation. Unless noted, the minor diastereomer is not detected via NMR.



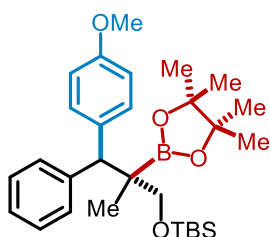
**tert-butyl(-3-(4-chlorophenyl)-2-methyl-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (3):**

The title compound was prepared according to general procedure B. The crude material (65% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **3** as a white solid (61 % avg. yield of two runs). **M.P.:** 70-73 °C. **IR (neat):** 2928 (m), 2856 (m), 1491 (w), 1470 (w), 1371 (w), 1314 (m), 1256 (m), 1141 (m), 1076 (s), 1075 (s), 833 (s), 774 (m), 738 (m), 702 (m), 585 (w). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.37 – 7.33 (m, 2H), 7.30 – 7.11 (m, 7H), 4.22 (s, 1H), 3.68 (d, *J* = 8.9 Hz, 1H), 3.27 (d, *J* = 8.9 Hz, 1H), 1.14 (s, 6H), 1.11 (s, 3H), 1.08 (s, 6H), 0.90 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 142.8, 142.2, 131.7, 131.2, 130.2, 128.0, 127.9, 126.2, 83.4, 70.6, 54.6, 26.1, 25.0, 24.9, 18.5, 17.5, -5.36, -5.38. **HRMS (ESI):** Calcd for C<sub>28</sub>H<sub>42</sub>BClO<sub>3</sub>SiNa [M+Na]<sup>+</sup>: 523.2582, Found: 523.2574.



**tert-butyl(-3-(4-fluorophenyl)-2-methyl-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (4):**

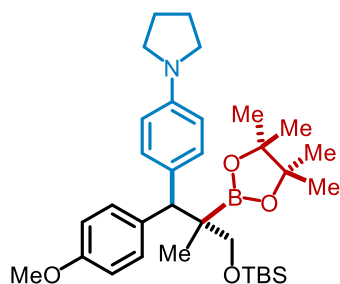
The title compound was prepared according to general procedure B. The crude material (82% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **4** as a white solid (76 % avg. yield of two runs). **M.P.:** 42-45 °C. **IR (neat):** 2928 (m), 2856 (m), 1604 (s), 1508 (w), 1371(m), 1314 (m), 1142 (m), 1075 (s), 834 (s), 774 (s), 701 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.42 – 7.38 (m, 2H), 7.27 – 7.21 (m, 4H), 7.19 – 7.15 (m, 1H), 6.96 – 6.90 (m, 2H), 4.25 (s, 1H), 3.72 (d, *J* = 8.9 Hz, 1H), 3.30 (d, *J* = 8.9 Hz, 1H), 1.15 (s, 9H), 1.08 (s, 6H), 0.92 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 161.4 (d, *J* = 242.7 Hz), 142.4, 140.0 (d, *J* = 3.2 Hz), 131.2 (d, *J* = 7.5 Hz), 130.2, 127.8, 126.1, 114.6 (d, *J* = 20.7 Hz), 83.4, 70.8, 54.5, 26.1, 25.0, 24.9, 18.5, 17.5, -5.36, -5.39. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -117.8. **HRMS (ESI):** Calcd for C<sub>28</sub>H<sub>42</sub>BFO<sub>3</sub>SiNa [M+Na]<sup>+</sup>: 507.2873, Found: 507.2872.





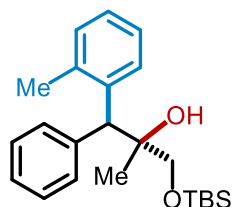
***tert*-butyl(3-(4-methoxyphenyl)-2-methyl-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (5):**

The title compound was prepared according to general procedure B. The crude material (92% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 4% Et<sub>2</sub>O/Hexanes) to provide **5** as a white solid (75 % avg. yield of two runs). **M.P.:** 45-48 °C. **IR (neat):** 2929 (m), 2856 (m), 1609 (w), 1511 (m), 1463 (w), 1313 (m), 1249 (s), 1142 (m), 1077 (m), 834 (s), 775 (s), 702 (m), 593 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.40 – 7.35 (m, 2H), 7.28 – 7.22 (m, 4H), 7.19 – 7.14 (m, 1H), 6.83 – 6.78 (m, 2H), 4.22 (s, 1H), 3.78 (s, 4H), 3.29 (d, *J* = 8.8 Hz, 1H), 1.18 (s, 3H), 1.16 (s, 6H), 1.10 (s, 6H), 0.94 (s, 9H), 0.02 (d, *J* = 6.3 Hz, 6H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 157.9, 142.9, 136.5, 130.7, 130.2, 127.7, 125.9, 113.3, 83.2, 71.1, 55.3, 54.5, 26.1, 25.0, 24.9, 18.5, 17.4, -5.35, -5.39. **HRMS (ESI):** Calcd for C<sub>29</sub>H<sub>45</sub>BO<sub>4</sub>SiNa [M+Na]<sup>+</sup>: 519.3072, Found: 519.3068



**1-(4-(3-((*tert*-butyldimethylsilyl)oxy)-1-(4-methoxyphenyl)-2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)pyrrolidine (6):**

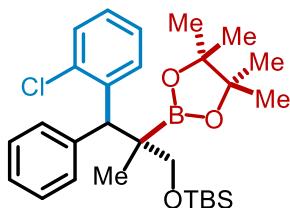
The title compound was prepared according to general procedure B. The crude material (72% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 50% Et<sub>2</sub>O/Hexanes) to provide **6** as a pale yellow oil (68 % avg. yield of two runs). **IR (neat):** 2929 (m), 2856 (m), 1610 (m), 1509 (s), 1312 (m), 1248 (s), 1178 (m), 1142 (s), 1071 (s), 832 (s), 773 (m), 735 (m), 562 (w). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.25 – 7.20 (m, 2H), 7.16 – 7.11 (m, 2H), 6.78 – 6.72 (m, 2H), 6.44 (d, *J* = 8.3 Hz, 2H), 4.06 (s, 1H), 3.76 (s, 3H), 3.26 – 3.19 (m, 4H), 1.99 – 1.93 (m, 4H), 1.14 (s, 6H), 1.13 (s, 3H), 1.08 (s, 6H), 0.89 (s, 9H), -0.02 (d, *J* = 4.0 Hz, 6H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 157.6, 146.4, 136.0, 131.6, 131.1, 130.3, 113.0, 111.3, 83.2, 71.5, 55.3, 53.6, 47.8, 26.1, 25.5, 25.1, 25.0, 18.5, 17.3, -5.30, -5.34. **HRMS (ESI):** Calcd for C<sub>33</sub>H<sub>53</sub>O<sub>4</sub>NBSi [M+H]<sup>+</sup>: 566.3931, Found: 566.3838



**3-((*tert*-butyldimethylsilyl)oxy)-2-methyl-1-phenyl-1-(*o*-tolyl)propan-2-ol (7):**

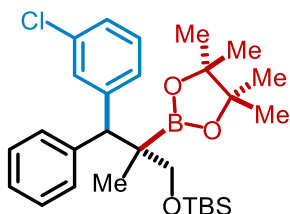
The title compound was prepared according to general procedure D. The crude material (84% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 60% Et<sub>2</sub>O/Hexanes) to provide **7** as a colorless oil (72 % avg. yield of two runs). **IR (neat):** 2928 (m), 2856 (m), 11462 (m), 1251 (m), 1079 (s), 1005 (w), 943 (w), 775 (s), 744 (m), 729 (m), 700 (m), 575 (m). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.17 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.38 – 7.30 (m, 2H), 7.30 – 7.21 (m, 2H), 7.20 – 7.12 (m, 2H), 4.35 (s, 1H), 3.66 – 3.49 (m, 2H), 2.38 (s, 3H), 1.30 (s, 3H), 0.94

(s, 9H), 0.02 (d,  $J = 13.0$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.0, 140.4, 136.7, 130.6, 130.5, 129.2, 128.2, 126.3, 126.2, 125.8, 75.5, 69.1, 51.8, 30.1, 26.0, 25.9, 20.7, 18.4, -5.5. HRMS (ESI): Calcd for  $\text{C}_{23}\text{H}_{34}\text{O}_2\text{SiNa}$   $[\text{M}+\text{Na}]^+$ : 393.2220, Found: 393.2222.



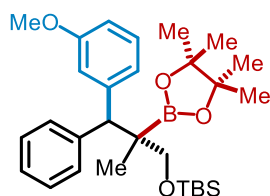
**tert-butyl(3-(2-chlorophenyl)-2-methyl-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (8):**

The title compound was prepared according to general procedure B. The crude material (43% yield as determined by internal standard) was purified by MPLC (12 g  $\text{SiO}_2$ , 0 to 2%  $\text{Et}_2\text{O}$ /Hexanes) to provide **8** as a white solid (37 % avg. yield of two runs). **M. P.:** 91-93°C. **IR (neat):** 2928 (m), 2856 (m), 1470 (m), 1370 (m), 1315 (s), 1256 (s), 1142 (s), 1079 (s), 966 (w), 834 (s), 774 (m), 747 (m), 701(m).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 (dd,  $J = 7.9, 1.6$  Hz, 1H), 7.31 – 7.26 (m, 1H), 7.26 – 7.21 (m, 3H), 7.21 – 7.14 (m, 3H), 7.12 (td,  $J = 7.6, 1.6$  Hz, 1H), 4.74 (s, 1H), 3.81 (d,  $J = 8.8$  Hz, 1H), 3.38 (d,  $J = 8.7$  Hz, 1H), 1.17 (s, 3H), 1.13 (s, 6H), 0.99 (s, 6H), 0.93 (s, 9H), 0.04 (s, 3H), -0.00 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.2, 140.3, 135.4, 130.7, 129.9, 129.8, 127.5, 127.3, 126.2, 126.0, 83.3, 71.0, 50.5, 26.1, 25.0, 24.7, 18.4, 18.0, -5.3, -5.4. HRMS (ESI): Calcd for  $\text{C}_{28}\text{H}_{42}\text{O}_3\text{BClNaSi}$   $[\text{M}+\text{Na}]^+$ : 523.2577, Found: 523.2574



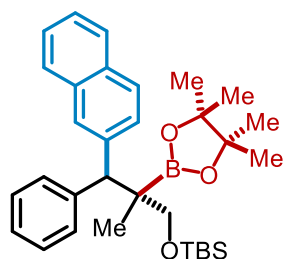
**tert-butyl(3-(3-chlorophenyl)-2-methyl-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (9):**

The title compound was prepared according to general procedure B. The crude material (51% yield as determined by internal standard) was purified by MPLC (12 g  $\text{SiO}_2$ , 0 to 2%  $\text{Et}_2\text{O}$ /Hexanes) to provide **9** as a colorless oil (44 % avg. yield of two runs). **IR (neat):** 2928 (m), 2856 (m), 1593 (w), 1471 (m), 1352 (m), 1255 (m), 1141 (s), 1077 (s), 834 (s), 774 (s), 703 (s), 578 (w).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49 – 7.46 (m, 1H), 7.29 (dt,  $J = 7.1, 1.9$  Hz, 1H), 7.27 – 7.24 (m, 4H), 7.21 – 7.17 (m, 1H), 7.16 – 7.13 (m, 2H), 4.26 (s, 1H), 3.68 (d,  $J = 9.0$  Hz, 1H), 3.32 (d,  $J = 9.0$  Hz, 1H), 1.18 (s, 6H), 1.14 (s, 3H), 1.11 (s, 6H), 0.93 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.4, 141.9, 133.7, 130.3, 129.8, 129.1, 128.2, 127.9, 126.2, 126.1, 83.4, 70.5, 54.9, 26.1, 25.0, 24.9, 18.5, 17.6, -5.37, -5.39. HRMS (ESI): Calcd for  $\text{C}_{28}\text{H}_{42}\text{O}_3\text{BClNaSi}$   $[\text{M}+\text{Na}]^+$ : 523.2577, Found: 523.2575.



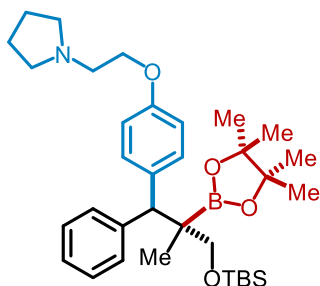
***tert*-butyl((-3-(3-methoxyphenyl)-2-methyl-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (10):**

The title compound was prepared according to general procedure B. The crude material (85% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 4% Et<sub>2</sub>O/Hexanes) to provide **10** as a colorless oil (79 % avg. yield of two runs). **M. P.:** 51-53°C. **IR (neat):** 2929 (m), 2855 (m), 1579 (w), 1464 (m), 1312(m), 1256 (s), 1142 (s), 1071 (s), 966 (w), 857 (s), 834 (s), 773 (s), 740 (m), 701 (s), 664 (w). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.29 – 7.20 (m, 4H), 7.21 – 7.12 (m, 2H), 7.07 – 7.02 (m, 2H), 6.72 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H), 4.22 (s, 1H), 3.79 – 3.76 (m, 4H), 3.31 (d, *J* = 8.8 Hz, 1H), 1.17 (s, 3H), 1.15 (s, 6H), 1.08 (s, 6H), 0.92 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 159.3, 145.8, 142.4, 130.2, 128.8, 127.7, 126.0, 122.3, 115.7, 111.4, 83.3, 71.1, 55.3, 55.2, 26.1, 25.0, 24.9, 18.5, 17.6, -5.35, -5.39. **HRMS (ESI):** Calcd for C<sub>29</sub>H<sub>45</sub>O<sub>4</sub>BNaSi [M+Na]<sup>+</sup>: 519.3072, Found: 519.3067.



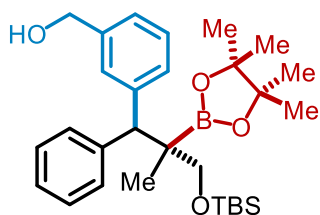
***tert*-butyldimethyl(2-methyl-3-(naphthalen-2-yl)-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)silane (11):**

The title compound was prepared according to general procedure B. The crude material (66% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 4% Et<sub>2</sub>O/Hexanes) to provide **11** as a white solid (61 % avg. yield of two runs). **M. P.:** 102-104°C. **IR (neat):** 2929 (m), 2855 (m), 1599 (w), 1470 (w), 1313 (m), 1257 (m), 1141 (s), 1076 (s), 965 (w), 852 (s), 774 (m), 736 (s), 702 (s), 477 (m). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.03 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.49 – 7.36 (m, 3H), 7.31 – 7.21 (m, 4H), 7.21 – 7.12 (m, 1H), 4.47 (s, 1H), 3.84 (d, *J* = 8.8 Hz, 1H), 3.36 (d, *J* = 8.8 Hz, 1H), 1.27 (s, 3H), 1.13 (s, 6H), 1.02 (s, 6H), 0.95 (s, 9H), 0.03 (d, *J* = 6.8 Hz, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 142.4, 142.0, 133.3, 132.0, 130.6, 129.4, 127.9, 127.7, 127.6, 127.4, 127.0, 126.1, 125.8, 125.3, 83.3, 71.3, 55.0, 26.2, 25.0, 24.9, 18.5, 17.5, -5.31, -5.34. **HRMS (ESI):** Calcd for C<sub>32</sub>H<sub>45</sub>O<sub>3</sub>BNaSi [M+Na]<sup>+</sup>: 539.3123; Found: 539.3122



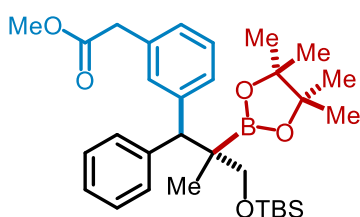
**1-(2-(4-(4-(*tert*-butyldimethylsilyloxy)-2-methyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenoxy)ethyl)pyrrolidine (12):**

The title compound was prepared according to general procedure B. The crude material (62% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 80% Et<sub>2</sub>O/Hexanes) to provide **12** as a white solid (54% avg. yield of two runs). **M. P.:** 78-80°C. **IR (neat):** 2928 (m), 2855 (m), 1610 (m), 1312 (m), 1247 (s), 1142 (m), 1069 (m), 833 (s), 774 (m), 700 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.34 – 7.27 (m, 2H), 7.19 – 7.22 (m, 4H), 7.17 – 7.08 (m, 1H), 6.81 – 6.74 (m, 2H), 4.16 (s, 1H), 4.09 – 4.02 (m, 2H), 3.73 (d, *J* = 8.8 Hz, 1H), 3.23 (d, *J* = 8.8 Hz, 1H), 2.86 (t, *J* = 6.1 Hz, 2H), 2.63 – 2.57 (m, 4H), 1.84 – 1.74 (m, 4H), 1.11 (d, *J* = 3.4 Hz, 9H), 1.05 (s, 6H), 0.88 (s, 9H), -0.02 (s, 3H), -0.04 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 157.1, 142.9, 136.6, 130.7, 130.2, 127.7, 125.8, 114.0, 83.3, 71.2, 67.2, 55.3, 54.9, 54.4, 26.1, 25.0, 24.94, 24.91, 23.6, 18.5, 17.3, -5.35, -5.39. **HRMS (ESI):** Calcd for C<sub>34</sub>H<sub>55</sub>BN<sub>2</sub>O<sub>4</sub>Si [M+H]<sup>+</sup>: 580.3988; Found: 580.3995



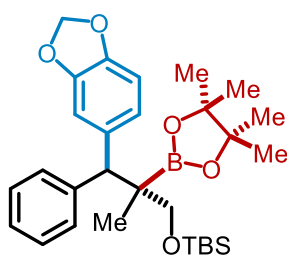
**(3-(4-(4-(*tert*-butyldimethylsilyloxy)-2-methyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenoxy)propyl)phenylmethanol (13):**

The title compound was prepared according to general procedure B. The crude material (63% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 60% Et<sub>2</sub>O/Hexanes) to provide **13** as a colorless oil (56% avg. yield of two runs). **IR (neat):** 3386 (w) 2927 (m), 2855 (m), 1600 (w), 1470 (m), 1371 (w), 1311 (m), 1255 (m), 141 (s), 1070 (s), 967 (w), 854 (s), 834 (s), 774 (s), 702 (s), 665 (w). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.39 – 7.36 (m, 2H), 7.28 – 7.18 (m, 5H), 7.18 – 7.10 (m, 2H), 4.62 (d, *J* = 5.8 Hz, 2H), 4.23 (s, 1H), 3.72 (d, *J* = 8.9 Hz, 1H), 3.27 (d, *J* = 8.8 Hz, 1H), 1.14 (s, 3H), 1.11 (s, 6H), 1.04 (s, 6H), 0.89 (s, 9H), -0.02 (s, 3H), -0.03 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 144.6, 142.4, 140.5, 130.3, 129.1, 128.5, 128.2, 127.8, 126.0, 124.7, 83.3, 71.0, 65.7, 55.3, 26.1, 25.0, 24.9, 18.5, 17.6, -5.35, -5.39. **HRMS (ESI):** Calcd for C<sub>29</sub>H<sub>45</sub>O<sub>4</sub>BNaSi [M+Na]<sup>+</sup>: 519.3072; Found: 519.3071



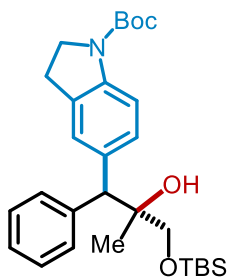
**methyl 2-(3-(3-((*tert*-butyldimethylsilyl)oxy)-2-methyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)acetate (14):**

The title compound was prepared according to general procedure B. The crude material (71% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 2 to 5% Et<sub>2</sub>O/Hexanes) to provide **14** as a colorless oil (61% avg. yield of two runs). **IR (neat):** 2928 (w), 2855 (m), 1740 (s), 1470 (w), 1255 (m), 1141 (s), 1070 (m), 965 (w), 854 (s), 834 (s), 773 (m), 702 (m). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.36 (d, *J* = 7.8 Hz, 1H), 7.31 (s, 1H), 7.24 – 7.18 (m, 5H), 7.18 – 7.11 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 4.20 (s, 1H), 3.74 (d, *J* = 8.8 Hz, 1H), 3.66 (s, 3H), 3.56 (s, 2H), 3.26 (d, *J* = 8.8 Hz, 1H), 1.14 (s, 3H), 1.10 (s, 6H), 1.03 (s, 6H), 0.89 (s, 9H), -0.02 (s, 3H), -0.03 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 172.1, 144.5, 142.3, 133.4, 130.9, 130.3, 128.5, 128.2, 127.7, 126.8, 126.0, 83.3, 71.1, 55.2, 52.0, 41.4, 26.1, 25.0, 24.9, 24.8, 18.5, 17.4, -5.37, -5.41. **HRMS (ESI):** Calcd for C<sub>31</sub>H<sub>47</sub>O<sub>5</sub>BNaSi [M+Na]<sup>+</sup>: 561.3178; Found: 561.3182.



**(3-(benzo[d][1,3]dioxol-5-yl)-2-methyl-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)(*tert*-butyl)dimethylsilane (15):**

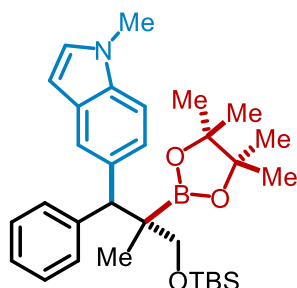
The title compound was prepared according to general procedure B. The crude material (92% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 3% Et<sub>2</sub>O/Hexanes) to provide **15** as a white solid (81% avg. yield of two runs). **M. P.:** 77-79°C. **IR (neat):** 2928 (m), 2855 (m), 1486 (m), 1371 (m), 1249 (s), 1142 (s), 1073 (s), 1040 (s), 967 (m), 854 (s), 834 (s), 774 (s), 701 (m). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.33 – 7.19 (m, 4H), 7.17 – 7.12 (m, 1H), 7.00 – 6.84 (m, 2H), 6.69 (d, *J* = 7.9 Hz, 1H), 5.86 (br s, 2H), 4.16 (s, 1H), 3.71 (d, *J* = 9.0 Hz, 1H), 3.28 (d, *J* = 8.9 Hz, 1H), 1.16 (s, 6H), 1.12 (s, 3H), 1.11 (s, 6H), 0.91 (s, 9H), -0.00 (s, 3H), -0.01 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 147.3, 145.6, 142.8, 138.2, 130.1, 127.8, 126.0, 122.6, 110.6, 107.7, 100.7, 83.3, 70.8, 55.0, 26.1, 25.01, 24.97, 24.9, 18.5, 17.7, -5.36, -5.38. **HRMS (ESI):** Calcd for C<sub>29</sub>H<sub>43</sub>BO<sub>5</sub>SiNa [M+Na]<sup>+</sup>: 533.2865; Found: 533.2866.



***tert*-butyl 5-(3-((*tert*-butyldimethylsilyl)oxy)-2-hydroxy-2-methyl-1-phenylpropyl)indoline-1-carboxylate (16):**

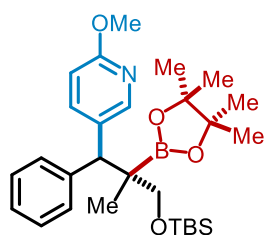
The title compound was prepared according to general procedure D. The crude material (80% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 60% Et<sub>2</sub>O/Hexanes) to provide **16** as a colorless oil (70% avg. yield of two runs). **IR (neat):** 2928 (m), 2855 (m), 11694

(m), 1491 (m), 1389 (s), 1334 (m), 1250 (m), 1172 (m), 1143 (s), 1085 (s), 1019 (m), 938 (w), 834 (s), 776 (m), 736 (m), 701 (m).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.56 – 7.47 (m, 2H), 7.31 – 7.21 (m, 4H), 7.21 – 7.12 (m, 1H), 3.99 – 3.85 (m, 3H), 3.40 – 3.26 (m, 2H), 3.07 – 2.95 (m, 2H), 1.60 (s, 9 H), 1.18 (s, 3H), 0.90 (s, 9H), -0.01 (s, 6H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.7, 142.4, 135.4, 130.0, 129.0, 128.3, 126.3, 114.4, 75.2, 69.4, 57.2, 47.8, 28.6, 26.0, 24.6, 18.3, -5.37, -5.39. **HRMS (ESI)**: Calcd for  $\text{C}_{29}\text{H}_{43}\text{NO}_4\text{SiNa}$   $[\text{M}+\text{Na}]^+$ : 520.2854; Found: 520.2853.



**5-(3-((tert-butyl)dimethylsilyloxy)-2-methyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1-methyl-1H-indole (17):**

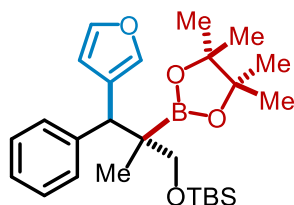
The title compound was prepared according to general procedure B. The crude material (79% yield as determined by internal standard) was purified by MPLC (12 g  $\text{SiO}_2$ , 10 to 60%  $\text{Et}_2\text{O}$ /Hexanes) to provide **17** as a white solid (73% avg. yield of two runs). **M. P.:** 112-115°C. **IR (neat)**: 2928 (m), 2855 (m), 1479 (m), 1310 (m), 1248 (m), 1141 (s), 1076 (s), 966 (w), 857 (s), 834 (s), 774 (m), 703 (s).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.77 (d,  $J$  = 1.3 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.21 (t,  $J$  = 7.6 Hz, 2H), 7.18 – 7.09 (m, 3H), 6.98 (d,  $J$  = 3.1 Hz, 1H), 6.41 (d,  $J$  = 3.0 Hz, 1H), 4.35 (s, 1H), 3.83 (d,  $J$  = 8.8 Hz, 1H), 3.73 (s, 3H), 3.30 (d,  $J$  = 8.8 Hz, 1H), 1.21 (s, 3H), 1.12 (s, 6H), 1.02 (s, 6H), 0.92 (s, 9H), 0.00 (d,  $J$  = 5.3 Hz, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.7, 135.3, 135.2, 130.4, 128.6, 128.2, 127.6, 125.6, 124.6, 121.0, 108.6, 101.0, 83.2, 71.6, 55.1, 32.9, 26.2, 25.0, 18.5, 17.6, -5.30, -5.34. **HRMS (ESI)**: Calcd for  $\text{C}_{31}\text{H}_{46}\text{BO}_3\text{NSiNa}$   $[\text{M}+\text{Na}]^+$ : 542.3232; Found: 542.3232.



**5-(3-((tert-butyl)dimethylsilyloxy)-2-methyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2-methoxypyridine (18):**

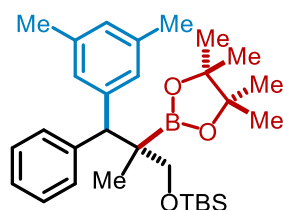
The title compound was prepared according to general procedure B. The crude material (57% yield as determined by internal standard) was purified by MPLC (12 g  $\text{SiO}_2$ , 10 to 60%  $\text{Et}_2\text{O}$ /Hexanes) to provide **18** as a white solid (52% avg. yield of two runs). **M. P.:** 50-53 °C. **IR (neat)**: 2929 (m), 2856 (m), 1602 (m), 1491 (m), 1388 (w), 1257 (m), 1142 (m), 1077 (m), 1030 (m), 966 (w), 833 (s), 774 (m), 702 (m).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.21 (d,  $J$  = 2.5 Hz, 1H), 7.66 (dd,  $J$  = 8.6, 2.6 Hz, 1H), 7.29 – 7.20 (m, 4H), 7.18 – 7.12 (m, 1H), 6.62 (d,  $J$  = 8.6 Hz, 1H), 4.16 (s, 1H), 3.89 (s, 3H), 3.65 (d,  $J$  = 9.0 Hz, 1H), 3.29 (d,  $J$  = 9.0 Hz, 1H), 1.13 (s, 6H), 1.11 (s, 3H), 1.09 (s, 6H), 0.90 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.6, 147.3, 142.1, 140.4,

132.4, 130.1, 127.9, 126.2, 109.8, 83.4, 70.3, 53.4, 52.3, 26.1, 25.0, 24.9, 18.5, 17.6, -5.39. **HRMS (ESI)**: Calcd for C<sub>28</sub>H<sub>45</sub>BO<sub>4</sub>NSi [M+H]<sup>+</sup>: 498.3205; Found: 498.3213.



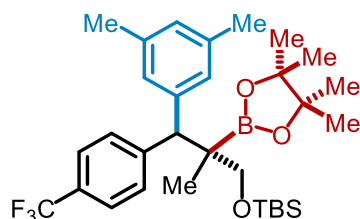
**tert-butyl(3-(furan-3-yl)-2-methyl-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (19):**

The title compound was prepared according to general procedure B. The crude material (49% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 3% Et<sub>2</sub>O/Hexanes) to provide **19** as a colorless (58% avg. yield of two runs). **IR (neat)**: 2929 (m), 2856 (m), 1470 (w), 1370 (m), 1255 (m), 1072 (s), 1028 (m), 966 (w), 855 (s), 833(s), 774 (s), 702 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**: δ 7.54 (d, *J* = 1.4 Hz, 1H), 7.35 – 7.23 (m, 3H), 7.21 (d, *J* = 7.4 Hz, 3H), 6.34 (s, 1H), 4.15 (s, 1H), 3.76 (d, *J* = 8.8 Hz, 1H), 3.16 (d, *J* = 8.8 Hz, 1H), 1.20 (s, 6H), 1.16 (s, 6H), 1.08 (s, 3H), 0.91 (s, 9H), 0.00 (s, 3H), -0.01 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**: δ 141.9, 141.3, 140.1, 130.0, 127.7, 127.3, 126.3, 112.6, 83.4, 71.14, 46.1, 26.1, 25.0, 24.9, 18.5, 16.1, -5.3, -5.4. **HRMS (ESI)**: Calcd for C<sub>26</sub>H<sub>41</sub>BO<sub>4</sub>NaSi [M+Na]<sup>+</sup>: 479.2759; Found: 479.2758.



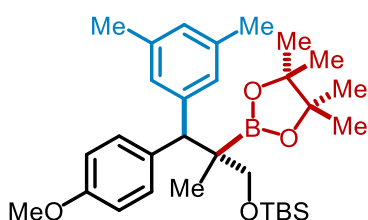
**tert-butyl(3-(3,5-dimethylphenyl)-2-methyl-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (2):**

The title compound was prepared according to general procedure B. The crude material (98% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **2** as a white solid (90% avg. yield of two runs). **M. P.**: 69-71 °C. **IR (neat)**: 2928 (m), 2856 (m), 1491 (w), 1314 (m), 1141 (m), 1076 (s), 966 (w), 822 (s), 773 (m), 701 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**: δ 7.25 – 7.17 (m, 4H), 7.19 – 7.10 (m, 1H), 7.02 (d, *J* = 1.6 Hz, 2H), 6.77 (s, 1H), 4.13 (s, 1H), 3.74 (d, *J* = 8.8 Hz, 1H), 3.24 (d, *J* = 8.8 Hz, 1H), 2.24 (s, 6H), 1.12 (s, 3H), 1.12 (s, 6H), 1.04 (s, 6H), 0.89 (s, 9H), -0.02 (s, 3H), -0.04 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**: δ 144.1, 142.7, 137.1, 130.3, 127.7, 127.6, 127.6, 125.9, 83.2, 76.90, 71.3, 55.1, 26.1, 25.0, 24.9, 21.5, 18.5, 17.5, -5.33, -5.38. **HRMS (ESI)**: Calcd for C<sub>30</sub>H<sub>47</sub>BO<sub>3</sub>NaSi [M+Na]<sup>+</sup>: 517.3279; Found: 517.3280. X-ray crystal structure is available (see attached spectrum).



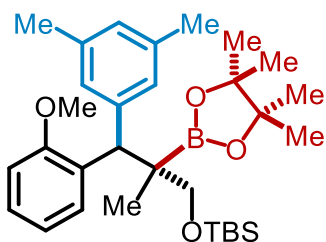
***tert*-butyl(3-(3,5-dimethylphenyl)-2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-(trifluoromethyl)phenyl)propoxy)dimethylsilane (20):**

The title compound was prepared according to general procedure B. The crude material (64% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **20** as a colorless oil (61% avg. yield of two runs). **IR (neat):** 2928 (m), 2856 (m), 1601 (w), 1361 (s), 1255 (m), 1123 (s), 1067 (s), 1018 (w), 834 (s), 774 (s), 671 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.02 (s, 2H), 6.82 (s, 1H), 4.25 (s, 1H), 3.69 (d, *J* = 9.0 Hz, 1H), 3.32 (d, *J* = 9.0 Hz, 1H), 2.27 (s, 6H), 1.16 (s, 6H), 1.13 (s, 3H), 1.09 (s, 6H), 0.93 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 147.3, 143.1, 137.4, 130.6, 128.0, 128.0, 127.6, 127.1 (q, *J* = 270.0 Hz), 124.6 (q, *J* = 3.9 Hz), 83.4, 70.3, 55.1, 26.14, 26.12, 24.96, 24.93, 24.9, 21.5, 18.5, 17.9, -5.37, -5.40. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -62.3. **HRMS (ESI):** Calcd for C<sub>31</sub>H<sub>46</sub>BO<sub>3</sub>F<sub>3</sub>NaSi [M+Na]<sup>+</sup>: 585.3151; Found: 585.3154.



***tert*-butyl(3-(3,5-dimethylphenyl)-3-(4-methoxyphenyl)-2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (21):**

The title compound was prepared according to general procedure B. The crude material (85% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 4% Et<sub>2</sub>O/Hexanes) to provide **21** as a colorless oil (76% avg. yield of two runs). **IR (neat):** 2928 (m), 2856 (m), 1606 (w), 1509 (m), 1310 (s), 1249 (s), 1142 (m), 1071 (m), 966 (w), 833 (s), 774 (m), 736 (m), 698 (m). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.21 – 7.12 (m, 2H), 7.04 (d, *J* = 1.5 Hz, 2H), 6.84 – 6.75 (m, 3H), 4.11 (s, 1H), 3.77 (s, 4H), 3.27 (d, *J* = 8.8 Hz, 1H), 2.27 (s, 6H), 1.16 (s, 3H), 1.14 (s, 6H), 1.06 (s, 6H), 0.92 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 157.7, 144.4, 137.0, 134.9, 131.1, 127.5, 127.5, 113.1, 83.1, 71.34, 55.2, 54.2, 26.1, 24.93, 24.88, 21.5, 18.5, 17.4, -5.3, -5.4. **HRMS (ESI):** Calcd for C<sub>31</sub>H<sub>49</sub>BO<sub>4</sub>NaSi [M+Na]<sup>+</sup>: 547.3385; Found: 547.3387.

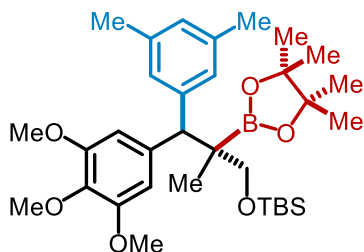


***tert*-butyl(3-(3,5-dimethylphenyl)-3-(2-methoxyphenyl)-2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (22):**

The title compound was prepared according to general procedure B. The crude material (98% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 4% Et<sub>2</sub>O/Hexanes) to provide **22** as a colorless oil (83% avg. yield of two runs). **M. P.:** 88-91 °C. **IR (neat):** 2928 (m), 2856 (m), 1599 (w), 1462 (m), 1360 (m), 1312 (m), 1239 (s), 1142 (s), 071 (s), 967 (m), 835 (s), 774 (s), 752 (m), 699 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.31 – 7.24 (m, 1H), 7.13 (td, *J* = 7.8,

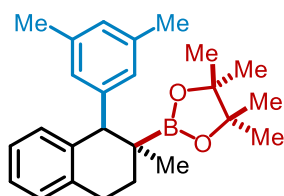


1.6 Hz, 1H), 7.07 (s, 2H), 7.87 – 7.84 (m, 2H), 6.78 (s, 1H), 4.80 (s, 1H), 4.01 (d,  $J = 8.9$  Hz, 1H), 3.83 (s, 3H), 3.17 (d,  $J = 8.9$  Hz, 1H), 2.27 (s, 6H), 1.19 (s, 3H), 1.16 (s, 6H), 1.04 (s, 6H), 0.92 (s, 9H), 0.01 (s, 3H), 0.01 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.2, 144.8, 136.9, 132.1, 131.4, 127.7, 127.3, 126.7, 119.9, 110.3, 83.0, 72.0, 55.2, 45.2, 26.1, 24.9, 24.8, 21.5, 18.5, 17.9, -5.3, -5.4. **HRMS (ESI):** Calcd for  $\text{C}_{31}\text{H}_{49}\text{BO}_4\text{NaSi}$   $[\text{M}+\text{Na}]^+$ : 547.3385; Found: 547.3390.



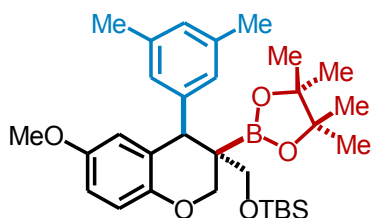
***tert*-butyl((2*R*,3*R*)-3-(3,5-dimethylphenyl)-2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(3,4,5-trimethoxyphenyl)propoxy)dimethylsilane (**23**):**

The title compound was prepared according to general procedure B. The crude material (99% yield as determined by internal standard) was purified by MPLC (12 g  $\text{SiO}_2$ , 0 to 4%  $\text{Et}_2\text{O}$ /Hexanes) to provide **23** as a white solid (96% avg. yield of two runs). **M. P.:** 58-61 °C. **IR (neat):** 2928 (m), 2856 (m), 1588 (w), 1507 (m), 1462 (m), 1371 (m), 1322 (m), 1251 (m), 1129 (s), 1073 (m), 1010 (m), 836 (m), 775 (m).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.00 (s, 2H), 6.77 (s, 1H), 6.58 (s, 2H), 4.07 (s, 1H), 3.81 (br s, 9H), 3.72 (d,  $J = 9.0$  Hz, 1H), 3.32 (d,  $J = 9.0$  Hz, 1H), 2.25 (s, 6H), 1.13 (br s, 9H), 1.06 (s, 6H), 0.91 (s, 9H), -0.00 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.4, 143.8, 138.6, 137.1, 136.3, 127.7, 127.4, 107.7, 83.2, 70.7, 60.9, 56.2, 55.5, 26.1, 25.0, 24.8, 21.5, 18.5, 17.9, -5.3, -5.4. **HRMS (ESI):** Calcd for  $\text{C}_{33}\text{H}_{53}\text{BO}_6\text{NaSi}$   $[\text{M}+\text{Na}]^+$ : 607.3597; Found: 607.3602.



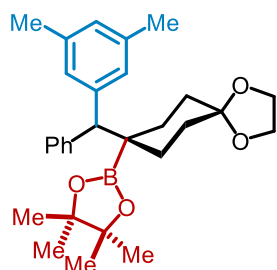
**2-(1-(3,5-dimethylphenyl)-2-methyl-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**24**):**

The title compound was prepared according to general procedure B. The crude material (97% yield as determined by internal standard) was purified by MPLC (12 g  $\text{SiO}_2$ , 0 to 2%  $\text{Et}_2\text{O}$ /Hexanes) to provide **24** as a colorless oil (88% avg. yield of two runs). **IR (neat):** 2928 (m), 2856 (m), 1598 (w), 1451 (m), 1369 (m), 1310 (m), 1145 (s), 1119 (m), 1093 (m), 847 (s), 743 (s), 690 (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.21 – 7.07 (m, 2H), 7.03 (t,  $J = 7.5$  Hz, 1H), 6.93 (d,  $J = 7.7$  Hz, 1H), 6.81 – 6.76 (m, 3H), 3.90 (s, 1H), 2.97 – 2.89 (m, 2H), 2.38 – 2.24 (m, 1H), 2.24 (s, 6H), 1.70–1.62 (m, 1H), 1.16 (s, 6H), 1.14 (s, 3H), 0.99 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.0, 138.7, 136.8, 136.0, 131.4, 128.8, 128.1, 127.6, 125.8, 125.5, 82.9, 52.8, 25.3, 25.1, 24.4, 22.1, 21.5. **HRMS (ESI):** Calcd for  $\text{C}_{25}\text{H}_{33}\text{BO}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 399.2466; Found: 399.2466.



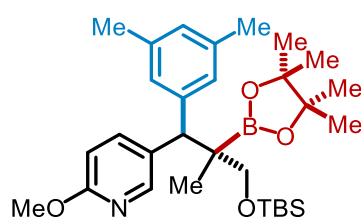
**tert-butyl((4-(3,5-dimethylphenyl)-6-methoxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)chroman-3-yl)methoxy)dimethylsilane (25):**

The title compound was prepared according to general procedure B. The crude material (56% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 4% Et<sub>2</sub>O/Hexanes) to provide **25** as a white solid (46% avg. yield of two runs). **M. P.:** 103-105 °C. **IR (neat):** 2928 (m), 2856 (m), 1599 (w), 1497 (s), 1386 (m), 1337 (m), 1259 (m), 1212 (m), 1144 (m), 1121 (m), 1079 (m), 1043 (m), 968 (w), 847 (s), 777 (m), 717 (m). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 6.85 – 6.76 (m, 4H), 6.69 (dd, *J* = 2.9, 1H), 6.34 (d, *J* = 2.9 Hz, 1H), 4.41 (d, *J* = 11.6, 1H), 4.29 (d, *J* = 11.6 Hz, 1H), 3.74 (d, *J* = 8.8 Hz, 1H), 3.66 – 3.56 (m, 5H), 2.23 (s, 6H), 1.07 (s, 6H), 0.89 (s, 9H), 0.87 (s, 6H), 0.04 (s, 3H), 0.02 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 153.2, 148.6, 144.7, 137.3, 128.1, 128.0, 124.4, 117.1, 115.4, 114.0, 83.2, 65.9, 62.9, 55.7, 44.4, 26.1, 25.2, 24.4, 21.5, 18.5, -5.4, -5.5. **HRMS (ESI):** Calcd for C<sub>31</sub>H<sub>47</sub>BO<sub>5</sub>NaSi [M+Na]<sup>+</sup>: 561.3178; Found: 561.3180



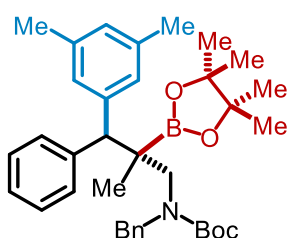
**2-(8-((3,5-dimethylphenyl)(phenyl)methyl)-1,4-dioxaspiro[4.5]decan-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26):**

The title compound was prepared according to general procedure B. The crude material (82% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 4% Et<sub>2</sub>O/Hexanes) to provide **26** as a colorless oil (74% avg. yield of two runs). **IR (neat):** 2928 (m), 2856 (m), 1598 (w), 1371 (m), 1305 (m), 1231 (m), 1141 (s), 1101 (s), 1035 (w), 967 (w), 850 (s), 734 (s). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.99 (s, 2H), 6.77 (s, 1H), 3.91 – 3.82 (m, 4H), 3.79 (s, 1H), 2.25 (s, 6H), 2.12 – 1.99 (m, 2H), 1.78 – 1.60 (m, 4H), 1.53 – 1.35 (m, 2H), 1.14 (d, *J* = 3.8 Hz, 12H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 143.1, 142.9, 137.0, 130.1, 127.85, 127.82, 127.8, 126.0, 109.0, 83.5, 64.3, 64.2, 62.1, 33.9, 33.8, 32.6, 32.1, 25.2, 21.6. **HRMS (ESI):** Calcd for C<sub>29</sub>H<sub>39</sub>BO<sub>4</sub>Na [M+Na]<sup>+</sup>: 485.2834; Found: 485.2832.



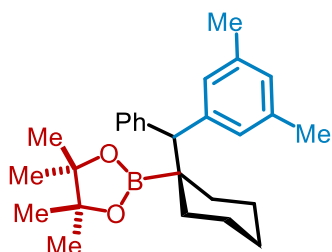
**5-(3-((*tert*-butyldimethylsilyloxy)-1-(3,5-dimethylphenyl)-2-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2-methoxy-pyridine (27):**

The title compound was prepared according to general procedure B. The crude material (76% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 5% Et<sub>2</sub>O/Hexanes) to provide **27** as a colorless oil (68% avg. yield of two runs). **IR (neat):** 2928 (m), 2856 (m), 1603 (m), 1490 (s), 1470 (m), 1389 (m), 1255 (m), 1142 (m), 1071 (m), 1030 (m), 966 (w), 832 (s), 773 (m), 732 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 8.05 (d, *J* = 2.4 Hz, 1H), 7.51 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.99 (s, 2H), 6.77 (s, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 4.08 (s, 1H), 3.89 (s, 3H), 3.71 (d, *J* = 8.9 Hz, 1H), 3.28 (d, *J* = 8.9 Hz, 1H), 2.24 (s, 6H), 1.12 (s, 9H), 1.04 (s, 6H), 0.89 (s, 9H), -0.01 (s, 3H), -0.03 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 162.6, 147.5, 143.5, 140.6, 137.3, 131.1, 127.8, 127.4, 109.8, 83.3, 70.6, 53.3, 51.7, 26.1, 24.91, 24.86, 21.5, 18.5, 17.7, -5.37, -5.42. **HRMS (ESI):** Calcd for C<sub>30</sub>H<sub>49</sub>BO<sub>4</sub>NSi [M+H]<sup>+</sup>: 526.3518; Found: 526.3526.



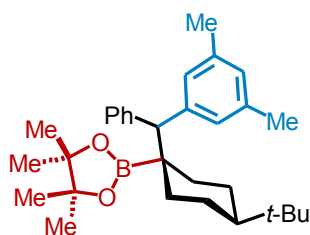
***tert*-butyl benzyl(3-(3,5-dimethylphenyl)-2-methyl-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate (28):**

The title compound was prepared according to general procedure B. The crude material was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 50% Et<sub>2</sub>O/Hexanes) to provide **28** as a colorless oil (48% avg. yield of two runs). **IR (neat):** 2975 (w), 2929 (w), 1689 (s), 1600 (w), 1365 (m), 1313 (m), 1166 (m), 1136 (s), 969 (m), 852 (w), 700 (m). **<sup>1</sup>H NMR (500 MHz, Toluene-*d*<sub>8</sub>, 80 °C):** δ 7.24 (d, *J* = 7.7 Hz, 2H), 7.19 – 7.13 (m, 4H), 7.13 – 7.04 (m, 2H), 7.04 – 6.99 (m, 2H), 6.98 – 6.88 (m, 2H), 6.64 (s, 1H), 4.58 – 4.32 (m, 2H), 4.03 (s, 1H), 3.77 (d, *J* = 14.1 Hz, 1H), 3.50 (d, *J* = 14.1 Hz, 1H), 2.13 (s, 6H), 1.41 (s, 3H), 1.31 (s, 9H), 1.04 (s, 6H), 0.96 (s, 6H). **<sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 60 °C):** δ 156.6, 144.4, 143.0, 139.9, 137.4, 131.1, 128.6, 128.5, 128.4, 128.2, 128.0, 127.2, 126.2, 83.6, 79.2, 58.9, 28.5, 25.7, 25.4, 21.5, 21.4, 18.9. **HRMS (ESI):** Calcd for C<sub>36</sub>H<sub>48</sub>BO<sub>4</sub>NBNa [M+H]<sup>+</sup>: 592.3569; Found: 592.3573.



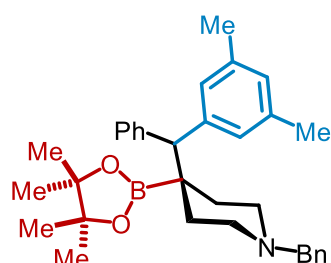
**2-(1-((3,5-dimethylphenyl)(phenyl)methyl)cyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29):** The title compound was prepared according to general procedure B. The crude material (98% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **29** as a white solid (91% avg. yield of two runs). **M. P.:** 98-99 °C. **IR (neat):** 2921 (m), 2852 (m), 1598 (w), 1450 (w), 1376 (m), 1304 (m), 1235 (m), 1138 (s), 971 (m), 859 (m), 705 (m). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):** δ 7.38 – 7.33 (m, 2H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.14 (t, *J* = 7.4 Hz,

1H), 6.99 (s, 2H), 6.78 (s, 1H), 3.79 (s, 1H), 2.27 (s, 6H), 2.15 – 2.05 (m, 2H), 1.68 – 1.61 (m, 2H), 1.59 – 1.53 (m, 1H), 1.47 – 1.37 (m, 2H), 1.18 – 1.08 (m, 2H), 1.00 – 0.94 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 143.3, 143.2, 136.9, 130.4, 128.1, 127.71, 127.66, 125.9, 83.1, 62.0, 35.0, 34.4, 26.3, 25.6, 25.5, 25.1, 21.6. HRMS (ESI): Calcd for C<sub>27</sub>H<sub>37</sub>BO<sub>2</sub>Na [M+Na]<sup>+</sup>: 427.2779; Found: 427.2777.



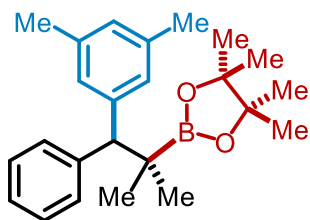
**2-(4-(tert-butyl)-1-((3,5-dimethylphenyl)(phenyl)methyl)cyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30):**

The title compound was prepared according to general procedure B. The crude material (98% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **30** as a white solid (90% avg. yield of two runs). **M. P.:** 107-109 °C. **IR (neat):** 2934 (m), 2865 (m), 1598 (w), 1447 (m), 1364 (m), 1301 (m), 1238 (w), 1143 (s), 1034 (w), 965 (w), 856 (m), 736 (m), 703 (s). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.62 – 7.54 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.17 (m, 1H), 7.16 (s, 2H), 6.85 (s, 1H), 4.34 (s, 1H), 2.34 (s, 6H), 2.03 – 1.92 (m, 2H), 1.61 – 1.45 (m, 6H), 1.32 (s, 6H), 1.30 (s, 6H), 1.17 – 1.08 (m, 1H), 0.97 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 143.9, 143.6, 137.0, 130.2, 127.9, 127.8, 127.6, 125.7, 82.9, 53.6, 47.7, 32.8, 31.43, 31.41, 27.6, 25.0, 24.9, 21.6, 21.30, 21.28. HRMS (ESI): Calcd for C<sub>31</sub>H<sub>45</sub>BO<sub>2</sub>Na [M+Na]<sup>+</sup>: 484.3405; Found: 483.3402.



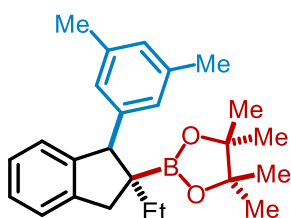
**1-benzyl-4-((3,5-dimethylphenyl)(phenyl)methyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine (31):**

The title compound was prepared according to general procedure B. The crude material (63% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 50% Et<sub>2</sub>O/Hexanes) to provide **31** as a colorless oil (54% avg. yield of two runs). **IR (neat):** 2976 (w), 2923 (m), 1599 (w), 1494 (m), 1372 (s), 1309 (s), 1237 (m), 1142 (s), 968 (w), 853 (m), 767 (m), 699 (s). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.38 – 7.33 (m, 2H), 7.32 – 7.20 (m, 7H), 7.17 – 7.12 (m, 1H), 6.98 (s, 2H), 6.79 (s, 1H), 3.82 (s, 1H), 3.51 (s, 2H), 2.91 – 2.75 (m, 2H), 2.27 (s, 6H), 2.21 – 2.00 (m, 4H), 1.62 – 1.47 (m, 2H), 1.04 (s, 6H), 1.03 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 142.9, 142.7, 137.6, 137.1, 130.3, 129.7, 128.1, 128.0, 127.84, 127.79, 127.0, 126.0, 83.3, 63.5, 61.4, 52.6, 52.45, 34.1, 33.7, 25.0, 21.6. HRMS (ESI): Calcd for C<sub>33</sub>H<sub>43</sub>BO<sub>2</sub>N [M+H]<sup>+</sup>: 496.3381; Found: 496.3386.



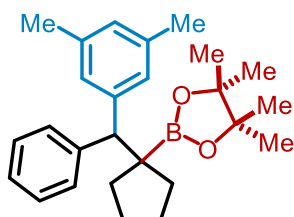
**2-(1-(3,5-dimethylphenyl)-2-methyl-1-phenylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32):**

The title compound was prepared according to general procedure B. The crude material (99% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **32** as a white solid (87% avg. yield of two runs). **M.P.:** 53-54 °C. **IR (neat):** 2976 (w), 2864 (w), 1599 (m), 1470 (m), 1370 (m), 1307 (m), 1133 (s), 965 (m), 847 (m), 724 (m). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.31 – 7.18 (m, 4H), 7.19 – 7.09 (m, 1H), 6.91 (s, 2H), 6.78 (s, 1H), 4.01 (s, 1H), 2.25 (s, 6H), 1.10 (s, 6H), 1.08 (s, 6H), 1.03 (s, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 143.6, 143.5, 136.9, 130.2, 127.9, 127.6, 127.5, 125.8, 83.1, 58.5, 24.7, 24.6, 24.5, 23.6, 21.6. **HRMS (ESI):** Calcd for C<sub>24</sub>H<sub>33</sub>BO<sub>2</sub> [M]<sup>+</sup>: 364.2572; Found: 364.2574.



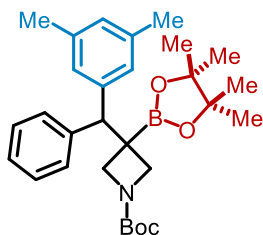
**2-(1-(3,5-dimethylphenyl)-2-ethyl-2,3-dihydro-1H-inden-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (34):**

The title compound was prepared according to general procedure B. The crude material (99% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **34** as a white solid (94% avg. yield of two runs). **M.P.:** 44-46 °C. **IR (neat):** 2976 (m), 2918 (w), 1599 (m), 1457 (w), 1371 (m), 1312 (m), 1263 (w), 1143 (s), 976 (w), 849 (m), 759 (m), 685 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.31 (d, *J* = 7.4 Hz, 1H), 7.19 (td, *J* = 7.4, 1.2 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.76 (s, 1H), 6.68 (s, 2H), 4.01 (s, 1H), 3.53 (d, *J* = 16.5 Hz, 1H), 2.86 (d, *J* = 16.5 Hz, 1H), 2.23 (s, 6H), 1.89 – 1.74 (m, 1H), 1.51 – 1.43 (m, 1H), 0.98 – 0.91 (m, 15H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 147.2, 144.7, 143.5, 137.4, 127.8, 126.6, 126.5, 126.4, 125.5, 125.0, 83.1, 62.3, 38.2, 32.1, 25.0, 24.7, 21.4, 11.4. **HRMS (ESI):** Calcd for C<sub>25</sub>H<sub>33</sub>BO<sub>2</sub>Na [M+Na]<sup>+</sup>: 399.2464; Found: 399.2464.



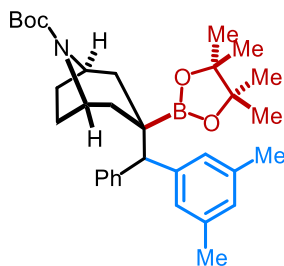
**2-(1-(3,5-dimethylphenyl)(phenyl)methyl)cyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35):**

The title compound was prepared according to general procedure B. The crude material (96% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **35** as a white solid (90% avg. yield of two runs). **M.P.:** 60-63°C. **IR (neat):** 2974 (m), 2866 (w), 1598 (w), 1368 (m), 1304 (m), 1141 (s), 961 (w), 851 (m), 701 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.32 – 7.26 (m, 2H), 7.24 – 7.20 (m, 2H), 7.17 – 7.10 (m, 1H), 6.92 (s, 2H), 6.78 (s, 1H), 4.19 (s, 1H), 2.25 (s, 6H), 2.09 – 1.97 (m, 2H), 1.62 – 1.53 (m, 2H), 1.52 – 1.40 (m, 2H), 1.39 – 1.25 (m, 2H), 1.02 (s, 6H), 1.00 (s, 6H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 144.03, 144.01, 137.1, 130.5, 128.2, 127.8, 127.6, 125.9, 83.2, 57.1, 33.8, 33.1, 25.3, 25.1, 24.68, 24.66, 21.7. **HRMS (ESI):** Calcd for C<sub>26</sub>H<sub>35</sub>BO<sub>2</sub>Na [M+Na]<sup>+</sup>: 413.2622; Found: 413.2618



***tert*-butyl 3-((3,5-dimethylphenyl)(phenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)azetidine-1-carboxylate (**36**):**

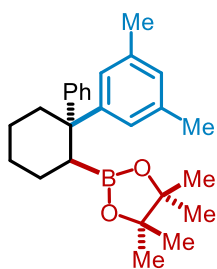
The title compound was prepared according to general procedure B. The crude material (75% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 50% Et<sub>2</sub>O/Hexanes) to provide **36** as a colorless oil (70% avg. yield of two runs). **IR (neat):** 2976 (m), 2878 (w), 1697 (m), 1600 (w), 1363 (s), 1136 (s), 964 (m), 847 (m), 721 (m), 702 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.29 – 7.25 (m, 2H), 7.23 – 7.12 (m, 3H), 6.83 (s, 1H), 6.76 (s, 2H), 4.24 (s, 1H), 4.14 – 4.05 (m, 2H), 3.96 (s, 1H), 3.94 (s, 1H), 2.27 (s, 6H), 1.34 (s, 9H), 1.09 (s, 12H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 156.3, 137.5, 129.5, 128.20, 128.19, 127.3, 126.5, 83.9, 79.0, 54.4, 28.4, 24.6, 24.5, 21.5. **HRMS (ESI):** Calcd for C<sub>29</sub>H<sub>40</sub>BO<sub>4</sub>NaN [M+Na]<sup>+</sup>: 500.2943; Found: 500.2942.



***tert*-butyl (*1R,3R*)-3-((3,5-dimethylphenyl)(phenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-azabicyclo[3.2.1]octane-8-carboxylate (**37**):**

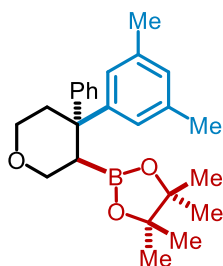
The title compound was prepared according to general procedure B. The crude material (68% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 80% Et<sub>2</sub>O/Hexanes) to provide **37** as a white solid (61% avg. yield of two runs). **M. P.:** 44-46 °C. **IR (neat):** 2974 (m), 2872 (w), 1693 (s), 1365 (s), 1305 (s), 1250 (m), 1158 (s), 1141 (s), 1099 (m), 855 (m), 744 (m), 701 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.39 – 7.33 (m, 2H), 7.24 – 7.20 (m, 2H), 7.17 – 7.10 (m, 1H), 6.99 (s, 2H), 6.78 (s, 1H), 4.31 (br s, 2H), 3.81 (s, 1H), 2.73 (q, *J* = 11.2 Hz, 2H), 2.26 (s, 6H), 1.63 (s, 2H), 1.41 (s, 9H), 1.30 – 1.21 (m, 4H), 1.06 (s, 12H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 156.9, 143.0, 142.7, 137.0, 130.3, 128.1, 127.8, 127.8, 126.0, 83.2, 79.2, 59.6, 53.3, 51.5, 38.9,

31.9, 31.2, 28.5, 27.4, 25.3, 21.5. **HRMS (ESI):** Calcd for  $C_{33}H_{46}BO_4NaN$   $[M+Na]^+$ : 554.3412; Found: 554.3412.



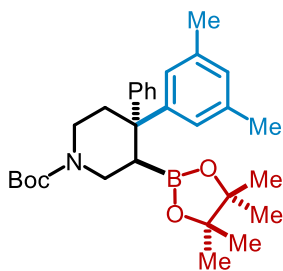
**2-(2-(3,5-dimethylphenyl)-2-phenylcyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38):**

The title compound was prepared according to general procedure B. The crude material (84% yield as determined by internal standard) was purified by MPLC (12 g  $SiO_2$ , 0 to 2%  $Et_2O$ /Hexanes) to provide **38** as a white solid (76% avg. yield of two runs). **M.P.:** 135-137 °C. **IR (neat):** 2924 (m), 2858 (w), 1599 (m), 1455 (w), 1371 (s), 1322 (m), 1144 (s), 1072 (w), 970 (w), 846 (m), 706 (m).  **$^1H$  NMR (600 MHz,  $CDCl_3$ ):**  $\delta$  7.47 – 7.35 (m, 2H), 7.27 (t,  $J = 7.8$  Hz, 2H), 7.10 (t,  $J = 7.3$  Hz, 1H), 6.91 (s, 2H), 6.68 (s, 1H), 2.70 – 2.55 (m, 3H), 2.22 (s, 6H), 1.99 – 1.86 (m, 1H), 1.76 – 1.60 (m, 2H), 1.57 – 1.49 (m, 2H), 1.22 – 1.12 (m, 1H), 0.99 (s, 6H), 0.96 (s, 6H).  **$^{13}C$  NMR (150 MHz,  $CDCl_3$ ):**  $\delta$  150.9, 147.7, 136.9, 128.3, 127.6, 126.7, 125.0, 124.7, 82.5, 46.1, 32.9, 24.7, 24.6, 24.5, 24.1, 22.8, 21.6. **HRMS (ESI):** Calcd for  $C_{26}H_{35}BO_2Na$   $[M+Na]^+$ : 413.2622; Found: 413.2620. X-ray crystal structure is available (see attached spectrum).



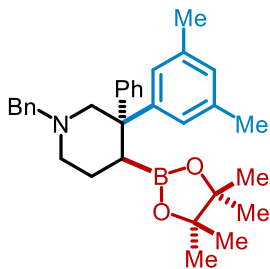
**2-(4-(3,5-dimethylphenyl)-4-phenyltetrahydro-2H-pyran-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39):**

The title compound was prepared according to general procedure B. The crude material (86% yield as determined by internal standard) was purified by MPLC (12 g  $SiO_2$ , 0 to 2%  $Et_2O$ /Hexanes) to provide **39** as a white solid (76% avg. yield of two runs). **M. P.:** 137-139 °C. **IR (neat):** 2977 (w), 2904 (w), 1689 (s), 1429 (m), 1383 (m), 1329 (m), 1244 (m), 1163(s), 1140 (s), 1099 (m), 960 (w), 863 (m), 736 (m), 705 (m).  **$^1H$  NMR (600 MHz,  $CDCl_3$ ):**  $\delta$  7.35 – 7.28 (m, 2H), 7.27 – 7.24 (m, 2H), 7.13 – 7.07 (m, 1H), 6.87 (s, 2H), 6.69 (s, 1H), 3.98 – 3.86 (m, 3H), 3.43 – 3.35 (m, 1H), 2.97 – 2.89 (m, 1H), 2.53 – 2.46 (m, 2H), 2.22 (s, 6H), 1.05 (s, 6H), 0.92 (s, 6H).  **$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):**  $\delta$  149.6, 146.4, 137.3, 128.6, 127.5, 127.2, 125.5, 124.3, 83.0, 66.6, 65.1, 44.6, 33.7, 25.2, 24.7, 24.3, 21.6. **RMS (ESI):** Calcd for  $C_{25}H_{33}O_3BNa$   $[M+Na]^+$ : 415.2415; Found: 415.2416.



**tert-butyl (4-(3,5-dimethylphenyl)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate (40):**

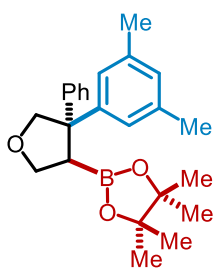
The title compound was prepared according to general procedure B. The crude material (84% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 60% Et<sub>2</sub>O/Hexanes) to provide **40** as a white solid (68% avg. yield of two runs). **M.P.:** 137-139 °C. **IR (neat):** 2974 (w), 2917 (w), 1602 (w), 1446 (w), 1338 (m), 1266 (w), 962 (w), 867 (m), 709(s). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.36 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.14 – 7.07 (m, 1H), 6.88 (s, 2H), 6.69 (s, 1H), 4.25 – 3.91 (m, 2H), 3.17 – 3.36 (m, 1H), 2.87 – 2.80 (m, 1H), 2.75 – 2.46 (m, 3H), 2.21 (s, 6H), 1.44 (s, 9H), 1.00 (s, 6H), 0.91 (s, 6H). **<sup>13</sup>C NMR (125 MHz, Toluene-*d*<sub>6</sub>, 60 °C):** δ 154.3, 150.2, 146.5, 137.6, 137.3, 129.2, 127.4, 125.7, 125.0, 83.0, 78.4, 45.8, 33.1, 28.9, 24.9, 24.5, 21.5. **HRMS (ESI):** Calcd for C<sub>30</sub>H<sub>42</sub>BO<sub>4</sub>NaN [M+Na]<sup>+</sup>: 514.3099; Found: 514.3101.



**1-benzyl-3-(3,5-dimethylphenyl)-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine (41):**

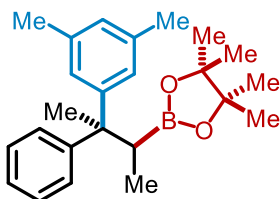
The title compound was prepared according to general procedure B. The crude material (93% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 60% Et<sub>2</sub>O/Hexanes) to provide **41** as a colorless oil (84% avg. yield of two runs). **IR (neat):** 2976 (w), 2917 (w), 1599 (m), 1494 (w), 1369 (m), 1316 (m), 1142 (s), 1024 (w), 968 (w), 848 (m), 733 (m), 697 (s). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.38 – 7.31 (m, 6H), 7.30 – 7.25 (m, 3H), 7.18 – 7.13 (m, 1H), 6.96 (s, 2H), 6.76 (s, 1H), 3.68 – 3.61 (m, 2H), 3.41 (s, 1H), 3.22 (d, *J* = 11.4 Hz, 1H), 2.69– 2.47 (m, 3H), 2.27 (s, 6H), 2.10– 2.01 (m, 1H), 1.77 – 1.69 (m, 1H), 1.14 (s, 6H), 1.07 (s, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 148.4, 148.1, 139.3, 136.9, 129.2, 128.1, 127.8, 127.8, 127.2, 126.9, 125.1, 82.8, 63.7, 52.8, 47.1, 31.7, 24.7, 24.6, 21.7. **HRMS (ESI):** Calcd for C<sub>32</sub>H<sub>41</sub>BO<sub>2</sub>N [M+H]<sup>+</sup>: 482.3225; Found: 482.3231.





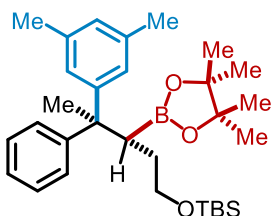
**2-(4-(3,5-dimethylphenyl)-4-phenyltetrahydrofuran-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (42):**

The title compound was prepared according to general procedure B. The crude material (45% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **42** as a colorless oil (42% avg. yield of two runs). **IR (neat):** 2976 (w), 2927 (w), 1749 (m), 1445 (m), 1371 (m), 1320 (m), 1141 (s), 1045 (w), 961 (w), 850 (m), 765 (w), 691 (s). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.42 – 7.36 (m, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 6.82 (s, 2H), 6.78 (s, 1H), 4.60 (d, *J* = 8.2 Hz, 1H), 4.19 (t, *J* = 8.5 Hz, 1H), 4.10 (t, *J* = 8.5 Hz, 1H), 3.99 (d, *J* = 8.2 Hz, 1H), 2.52 (t, *J* = 8.8 Hz, 1H), 2.22 (s, 6H), 1.06 (s, 6H), 0.98 (s, 6H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 146.5, 146.1, 137.0, 128.2, 127.9, 127.9, 126.2, 126.2, 83.3, 80.0, 70.5, 58.0, 24.9, 24.7, 21.6. **HRMS (ESI):** Calcd for C<sub>24</sub>H<sub>31</sub>BO<sub>3</sub>Na [M+Na]<sup>+</sup>: 401.2258; Found: 401.2259.



**2-(3-(3,5-dimethylphenyl)-3-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (43):**

The title compound was prepared according to general procedure B. The crude material (98% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **43** as a colorless oil (89% avg. yield of two runs). **IR (neat):** 2975 (w), 2918 (w), 1598 (m), 1456 (w), 1349 (m), 1316 (m), 1142 (s), 1027 (w), 964 (w), 846 (m), 776 (w), 699 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.34 – 7.23 (m, 4H), 7.19 – 7.12 (m, 1H), 6.96 (s, 2H), 6.79 (s, 1H), 2.28 (s, 6H), 2.21 (q, *J* = 7.4 Hz, 1H), 1.84 (s, 3H), 1.14 (s, 12H), 0.96 (d, *J* = 7.4 Hz, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 150.8, 149.6, 136.9, 127.8, 127.5, 127.1, 125.4, 125.2, 82.7, 47.3, 24.7, 24.6, 23.5, 21.7, 12.2. **HRMS (ESI):** Calcd for C<sub>24</sub>H<sub>33</sub>BO<sub>2</sub>Na [M+Na]<sup>+</sup>: 387.2466; Found: 387.2466.

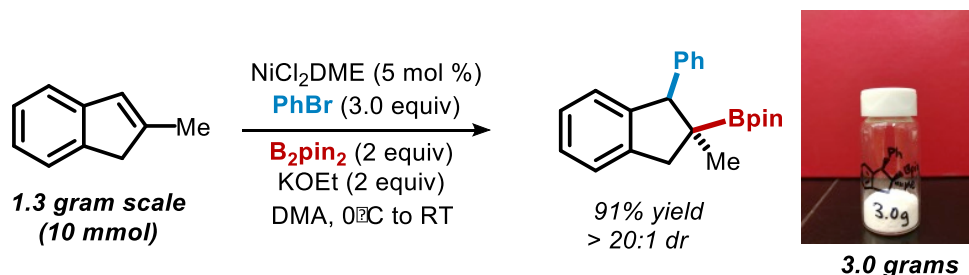


**tert-butyl((4-(3,5-dimethylphenyl)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)dimethylsilane (44):**

The title compound was prepared according to general procedure B. The crude material (83% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to

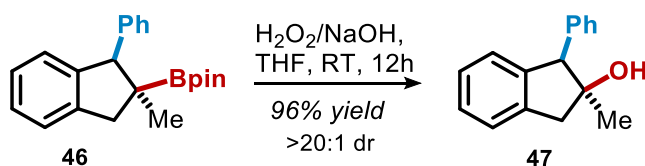
provide **44** as a colorless oil (66% avg. yield of two runs). **IR (neat):** 2928 (w), 2856 (w), 1741 (w), 1599 (w), 1362 (m), 1235(m), 11443 (s) ,1092 (s), 834 (s), 774 (s), 699 (m). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.31 – 7.27 (m, 2H), 7.22 – 7.16 (m, 2H), 7.09 – 7.04 (m, 1H), 6.86 (s, 2H), 6.68 (s, 1H), 3.63 (ddd, *J* = 9.9, 8.5, 5.2 Hz, 1H), 3.50 (dt, *J* = 9.9, 7.9 Hz, 1H), 2.18 (s, 6H), 2.13 (dd, *J* = 10.5, 3.6 Hz, 1H), 1.77 (s, 3H), 1.67 (ddt, *J* = 10.8, 7.8, 4.3 Hz, 2H), 1.01 (s, 6H), 0.97 (s, 6H), 0.87 (s, 9H), 0.00 (d, *J* = 2.7 Hz, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 150.2, 149.4, 136.9, 127.9, 127.5, 127.1, 125.3, 125.3, 82.8, 63.5, 46.9, 31.7, 26.23, 26.20, 24.91, 24.86, 24.0, 21.7, 18.6, -5.07, -5.11. **HRMS (ESI):** Calcd for C<sub>31</sub>H<sub>49</sub>BO<sub>3</sub>NaSi [M+Na]<sup>+</sup>: 531.3436; Found: 531.3434.

## ■ Gram Scale and Functional Group Transformations



### 4,4,5,5-tetramethyl-2-(2-methyl-1-phenyl-2,3-dihydro-1H-inden-2-yl)-1,3,2-dioxaborolane (**46**):

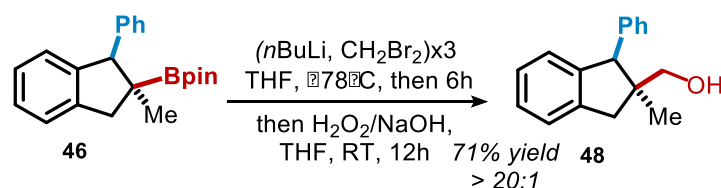
In an N<sub>2</sub>-filled glovebox, an oven-dried 100 mL round-bottom flask was charged with KOEt (1.68 g, 20.0 mmol, 2.00 equiv) and bis(pinacolato)diboron (5.08 g, 20.0 mmol, 2.00 equiv). The flask was sealed with a rubber septum and removed from the glovebox. DMA (70 mL) was added to the vial, and the mixture was stirred vigorously at r.t. for 1 h to afford a suspension. Thereafter, the flask was cooled to 0°C, the alkene **45** (1.34 mL, 10.0 mmol, 1.00 equiv) and bromobenzene (3.15 mL, 30.0 mmol, 3.00 equiv) were added to the reaction mixture via syringe under an N<sub>2</sub> atmosphere. The solution of NiCl<sub>2</sub>(DME) (110 mg, 0.500 mmol, 5 mol%) in DMA (4.0 mL) was added to the reaction mixture via syringe, followed by a DMA rinsing (2.0 mL). The reaction was warmed to r.t. and stirred for 24 h. The reaction was quenched upon the addition of water (10 mL), and the solution was diluted with EtOAc (150 mL), the organic layer was washed with KOH aqueous (3 x 30 mL, 1.0 M), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated. The crude material was purified by MPLC (80 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **46** as a white solid (3.0 g, 91% yield). **M.P.:** 88-90 °C. **IR (neat):** 2976 (w), 2862 (w), 1452 (w), 1378 (s), 1359 (w), 1311 (s), 1253 (w), 1144 (s), 1106 (s), 968 (w), 854 (m), 742 (s), 697 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.31 (d, *J* = 7.5 Hz, 1H), 7.22 – 7.15 (m, 3H), 7.15 – 7.08 (m, 2H), 7.08 – 7.02 (m, 3H), 4.03 (s, 1H), 3.61 (d, *J* = 16.2 Hz, 1H), 2.63 (d, *J* = 16.2 Hz, 1H), 1.23 (s, 3H), 0.95 (s, 6H), 0.90 (s, 6H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 146.6, 144.9, 143.4, 128.7, 128.2, 126.8, 126.6, 126.2, 125.8, 125.2, 83.2, 62.6, 42.5, 26.1, 24.8, 24.6. **HRMS (ESI):** Calcd for C<sub>22</sub>H<sub>27</sub>BO<sub>2</sub>Na [M+Na]<sup>+</sup>: 357.1996; Found: 357.1997



### 2-methyl-1-phenyl-2,3-dihydro-1H-inden-2-ol (**47**):

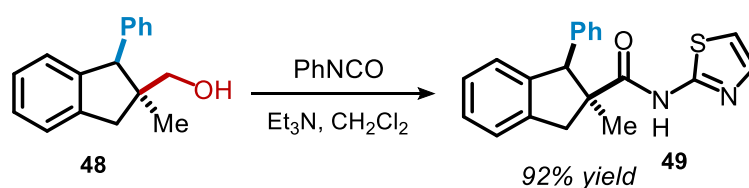
To a cooled (0 °C) solution of boronic ester **46** (530 mg, 1.58 mmol, 1.00 equiv) in THF (15.0 mL) was added a solution of 30% H<sub>2</sub>O<sub>2</sub>/2.0 M NaOH (1:2 v/v, 12 mL) under nitrogen. The ice bath was removed and the reaction was stirred at room temperature for 4 h and then diluted with water (10.0 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL) and the combined organic layers were dried over anhydrous MgSO<sub>4</sub>, gravity filtered, and concentrated. The crude material was purified by MPLC (40 g SiO<sub>2</sub>, 10 to 40% Et<sub>2</sub>O/Hexanes) to provide **47** as a white solid (0.34 g, 96% yield). **M. P.:** 52-54 °C. **IR (neat):** 3426 (w), 3024 (w), 2964 (w), 1602 (m), 1452 (w), 1375 (w), 1088 (m), 931 (w), 734 (s), 701 (m), 570 (w). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.48 – 7.42 (m, 2H), 7.42 – 7.34 (m, 2H), 7.32 – 7.27 (m, 3H), 7.27 – 7.21 (m, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 4.30 (s, 1H), 3.27 – 3.10 (m, 2H), 1.53 (s, 3H), 1.36 (s, 1H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 144.2, 142.2,

137.6, 130.3, 128.6, 127.5, 127.2, 126.7, 125.5, 124.9, 81.5, 62.2, 46.8, 26.6. **HRMS (ESI):** Calcd for C<sub>16</sub>H<sub>16</sub>ONa [M+Na]<sup>+</sup>: 247.1093; Found: 247.1093.



### (2-methyl-1-phenyl-2,3-dihydro-1H-inden-2-yl)methanol (**48**):

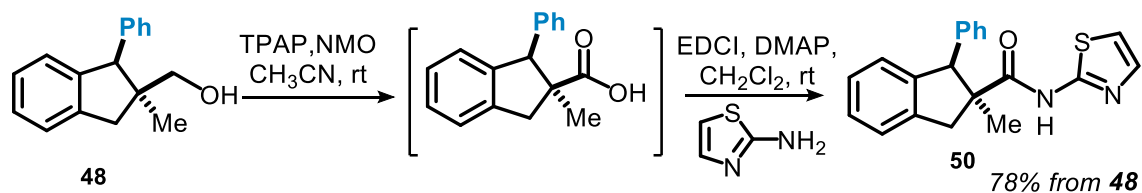
To a cooled (-78 °C, dry ice/acetone bath) solution of the boronic ester **46** (200 mg, 0.598 mmol, 1.00 equiv) in THF was added dibromomethane (0.105 mL, 1.50 mmol, 2.50 equiv) under nitrogen. *n*-BuLi (0.530 mL, 1.32 mmol, 2.50 M in hexanes, 2.20 equiv) was added dropwise over 5–10 min with vigorous stirring, and the mixture was left to stir for an additional 30 min. The addition of the dibromomethane (0.105 mL, 1.50 mmol, 2.50 equiv) and *n*-BuLi (0.530 mL, 1.32 mmol, 2.50 M in hexanes, 2.20 equiv) was repeated two more times. The cooling bath was removed and the mixture was allowed to warm to room temperature for 2 h, before being cooled to 0 °C. The solution of 30% H<sub>2</sub>O<sub>2</sub>/2.0 M NaOH (1:2 v/v, 6 mL) was added to the mixture. The cooling bath was removed and the mixture was stirred for 5 h. The mixture was diluted with water (5.0 mL) and extracted with diethyl ether (3 × 10 mL). The organic extract was washed with brine (10 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude material was purified by MPLC (24 g SiO<sub>2</sub>, 10 to 40% Et<sub>2</sub>O/Hexanes) to provide **48** as a white solid (101.3 mg, 71%). **M. P.:** 76-79 °C. **IR (neat):** 3426 (w), 3024 (w), 2964 (w), 1602 (m), 1452 (w), 1375 (w), 1088 (m), 931 (w), 734 (s), 701 (m), 570 (w). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.37 – 7.27 (m, 3H), 7.27 – 7.22 (m, 2H), 7.19 (t, *J* = 7.4, 1H), 7.12 (d, *J* = 7.3 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 4.17 (s, 1H), 3.29 (dd, *J* = 11.2, 6.8 Hz, 1H), 3.23 (dd, *J* = 11.2, 5.5 Hz, 1H), 3.12 (d, *J* = 15.9 Hz, 1H), 2.74 (d, *J* = 15.9 Hz, 1H), 1.34 (s, 3H), 0.97 (dd, *J* = 6.9, 5.5 Hz, 1H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 145.4, 142.7, 140.7, 129.1, 128.6, 127.1, 127.0, 126.7, 125.6, 124.9, 68.2, 61.0, 49.7, 42.2, 24.6. **HRMS (ESI):** Calcd for C<sub>17</sub>H<sub>18</sub>O [M]<sup>+</sup>: 238.1352; Found: 238.1355.



### 2-Methyl-1-phenyl-2,3-dihydro-1H-inden-2-yl)methyl phenylcarbamate (**49**):

To a solution of **48** (75.0 mg, 0.314 mmol, 1.00 equiv) in methylene chloride was added triethylamine (48.0 μL, 0.345 mmol, 1.10 equiv) and Phenyl cyanate (34.0 μL, 0.314 mmol, 1.00 equiv) at room temperature under nitrogen. After stirring for 1.5 h, the reaction was concentrated under vacuum. The crude material was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 50% Et<sub>2</sub>O/Hexanes) to provide **49** as a white solid (99.2 mg, 92%). **M. P.:** 82-85 °C. **IR (neat):** 3311 (m), 3025 (w), 2958 (w), 1703 (s), 1599 (m), 1526 (m), 1443 (m), 1313 (m), 1219 (s), 1058 (m), 1029 (w), 736 (s), 700 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.42 – 7.22 (m, 10H), 7.14 (m, 4H), 6.64 – 6.54 (br s, 1H), 4.26 (s, 1H), 3.89 (d, *J* = 10.7 Hz, 1H), 3.80 (d, *J* = 10.7 Hz, 1H), 3.20 (d, *J* = 15.8 Hz, 1H), 2.84 (d, *J* = 15.8 Hz, 1H), 1.42 (s, 3H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 153.5, 145.1, 142.2, 139.7, 137.9,

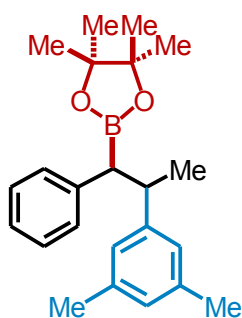
129.2, 129.0, 128.4, 128.3, 127.1, 126.9, 126.7, 125.4, 124.8, 123.3, 118.6, 70.0, 61.1, 48.0, 42.3, 24.5. **HRMS (ESI):** Calcd for C<sub>24</sub>H<sub>23</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>: 380.1621; Found: 380.1624.



### 2-Methyl-1-phenyl-N-(thiazol-2-yl)-2,3-dihydro-1H-indene-2-carboxamide (**50**):

To a solution of **48** (90.0 mg, 0.377 mmol, 1.00 equiv) in CH<sub>3</sub>CN was added 4-Methylmorpholine *N*-oxide (0.509 g, 3.77 mmol, 10.0 equiv) and Tetrapropylammonium perruthenate (13.3 mg, 0.0337 mmol, 10 mol%) at room temperature under nitrogen. After stirring for 3 h, the reaction was quenched with isopropyl alcohol (2 mL) and was left to stir for 30 min. The solvent was removed under reduced pressure. The crude material was dissolved in EtOAc (15 mL) and washed with HCl (3 × 5.0 mL, 2.0 M) to afford the pure carboxylic acid compound which was used in the next step without further purification.

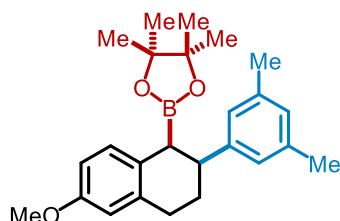
To a cooled (0 °C) solution of thiazol-2-amine (43.4 mg, 0.468 mmol, 1.30 equiv) in methylene chloride (3.0 mL) was added 4-Dimethylaminopyridine (66 mg, 0.54 mmol, 1.5 equiv) under nitrogen. The carboxylic acid (91 mg, 0.36 mmol, 1.0 equiv) in methylene chloride (1.0 mL+ 0.5 mL rinsing) was added followed by EDCI (0.104 mg, 0.540 mmol, 1.50 equiv). The cooling bath was removed and the reaction was allowed to warm to room temperature and stirred for 12h. The reaction was quenched with water (2.0 mL), extracted with methylene chloride (3 × 5.0 mL). The combined organic layers were washed with HCl (2 × 4.0 mL, 2.0 M), saturated Na<sub>2</sub>CO<sub>3</sub> aqueous, brine, dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude material was purified by MPLC (12 g SiO<sub>2</sub>, 10 to 100% Et<sub>2</sub>O/Hexanes) to provide **50** as a white solid (98.4 mg, 78%). **M.P.:** 134-136 °C. **IR (neat):** 3178 (w), 3025 (w), 2932 (w), 1677 (m), 1529 (s), 1481 (w), 1318 (m), 1266 (m), 1159 (m), 937 (w), 736 (m), 699 (s). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 9.51 (s, 1H), 7.39 (d, *J* = 3.6 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.23 – 7.14 (m, 1H), 7.14 – 7.07 (m, 3H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.85 (d, *J* = 3.6 Hz, 1H), 4.33 (s, 1H), 3.91 (d, *J* = 16.2 Hz, 1H), 2.94 (d, *J* = 16.2 Hz, 1H), 1.57 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 172.8, 158.9, 143.8, 141.3, 139.9, 137.0, 128.5, 128.2, 127.8, 127.4, 127.3, 125.6, 125.0, 113.7, 62.5, 56.5, 42.2, 25.5. **HRMS (ESI):** Calcd for C<sub>20</sub>H<sub>19</sub>ON<sub>2</sub>Na [M+H]<sup>+</sup>: 335.1215; Found: 335.1214.



### 2-(2-(3,5-dimethylphenyl)-1-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**52**):

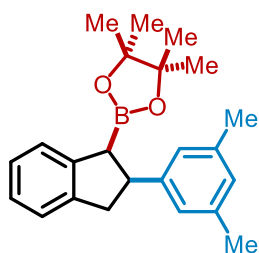
The title compound was prepared according to general procedure F. The crude material (60% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to

provide **52** as a colorless oil (54% avg. yield of two runs). **IR (neat):** 2975 (w), 2917 (w), 1601 (w), 1355 (s), 1319 (s), 1140 (s), 968 (w), 846 (m), 765 (m), 701 (s). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.38 – 7.31 (m, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.19 – 7.12 (m, 1H), 6.95 (s, 2H), 6.81 (s, 1H), 3.27 – 3.01 (m, 1H), 2.49 (d, *J* = 11.7 Hz, 1H), 2.29 (s, 6H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 6H), 0.89 (s, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 147.4, 141.8, 137.5, 129.3, 128.4, 127.7, 125.6, 125.5, 83.1, 42.95, 24.6, 24.2, 22.0, 21.5. **HRMS (ESI):** Calcd for C<sub>23</sub>H<sub>31</sub>BO<sub>2</sub>Na [M+Na]<sup>+</sup>: 373.2309; Found: 373.2310.

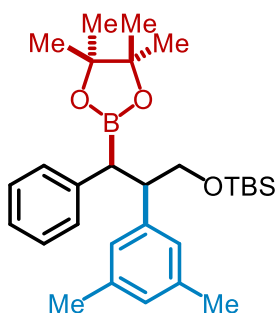


**2-(2-(3,5-dimethylphenyl)-6-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (53):**

The title compound was prepared according to general procedure E. The crude material (94% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 5% Et<sub>2</sub>O/Hexanes) to provide **53** as a white solid (83% avg. yield of two runs). **M. P.:** 64-67 °C. **IR (neat):** 2976 (w), 2929 (w), 1604 (m), 1497 (m), 1354 (m), 1323 (m), 1264 (m), 1234 (m), 1107 (s), 1040 (m), 967 (w), 844 (m), 735 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.05 (d, *J* = 7.8 Hz, 1H), 7.00 (s, 2H), 6.86 (s, 1H), 6.72 (s, 1H), 6.71 – 6.69 (m, 1H), 3.81 (s, 3H), 3.14 (ddd, *J* = 12.2, 6.0, 2.5 Hz, 1H), 3.04 – 2.91 (m, 3H), 2.61 – 2.51 (m, 1H), 2.33 (s, 6H), 2.13 – 2.07 (m, 1H), 1.05 (s, 6H), 0.98 (s, 6H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 157.1, 145.8, 137.31, 137.29, 130.1, 129.4, 127.6, 125.5, 113.9, 111.9, 82.8, 55.2, 41.5, 30.4, 25.6, 24.7, 24.3, 21.5. **HRMS (ESI):** Calcd for C<sub>25</sub>H<sub>33</sub>BO<sub>3</sub>Na [M+Na]<sup>+</sup>: 415.2415; Found: 415.2415.

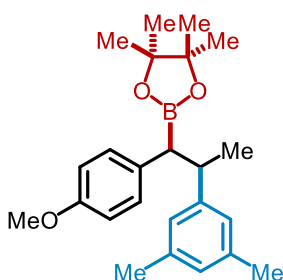


**2-(2-(3,5-dimethylphenyl)-2,3-dihydro-1H-inden-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (54):** The title compound was prepared according to general procedure E. The crude material (49% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **54** as a colorless oil (42% avg. yield of two runs). **IR (neat):** 2975 (w), 2917 (w), 1603 (w), 1747 (w), 1358 (s), 1324 (m), 1140 (s), 966 (w), 845 (s), 738 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.30 – 7.24 (m, 2H), 7.19 – 7.12 (m, 2H), 6.88 (s, 2H), 6.81 (s, 1H), 3.88 (q, *J* = 8.1 Hz, 1H), 3.32 (d, *J* = 7.8 Hz, 2H), 3.27 (d, *J* = 8.7 Hz, 1H), 2.26 (s, 6H), 0.96 (s, 6H), 0.94 (s, 6H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 145.1, 144.9, 143.7, 137.5, 127.7, 126.5, 125.7, 125.5, 124.42, 124.39, 83.0, 47.2, 39.5, 24.6, 24.5, 21.5. **HRMS (ESI):** Calcd for C<sub>23</sub>H<sub>29</sub>BO<sub>2</sub>Na [M+Na]<sup>+</sup>: 371.2153; Found: 371.2154.



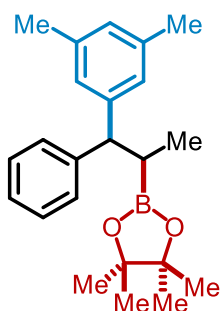
**tert-butyl(2-(3,5-dimethylphenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (55):**

The title compound was prepared according to general procedure F. The crude material (50% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **55** as a white solid (47% avg. yield of two runs). **M. P.:** 78-80 °C. **IR (neat):** 2927 (w), 2855 (w), 1601 (w), 1470 (w), 1358 (m), 1323 (m), 1251 (m), 1141 (m), 108 (m), 968 (w), 834 (s), 773 (m), 701 (m). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):** δ 7.41 – 7.36 (m, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.99 (s, 2H), 6.80 (s, 1H), 3.51 (dd, *J* = 9.8, 2.8 Hz, 1H), 3.46 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.08 (ddd, *J* = 12.3, 5.6, 2.8 Hz, 1H), 2.95 (d, *J* = 12.3 Hz, 1H), 2.28 (s, 6H), 0.90 (s, 6H), 0.87 (s, 6H), 0.79 (s, 9H), -0.26 (s, 3H), -0.27 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 143.9, 141.5, 136.9, 129.4, 128.3, 127.7, 127.1, 125.5, 83.1, 65.3, 50.4, 26.0, 24.5, 24.2, 21.4, 18.3, -5.6, -5.7. **HRMS (ESI):** Calcd for C<sub>29</sub>H<sub>45</sub>BO<sub>3</sub>NaSi [M+Na]<sup>+</sup>: 503.3123; Found: 503.3122. X-ray crystal structure is available (see attached spectrum).



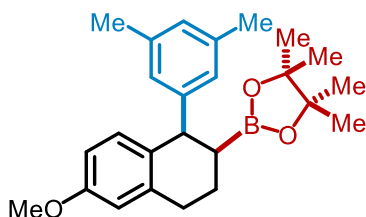
**2-(2-(3,5-dimethylphenyl)-1-(4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56):**

The title compound was prepared according to general procedure F. The crude material (78% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 5% Et<sub>2</sub>O/Hexanes) to provide **56** as a white solid (69% avg. yield of two runs). **M. P.:** 43-45 °C. **IR (neat):** 2974 (w), 2919 (w), 1605 (w), 1508 (s), 1354 (m), 1320 (m), 1245 (s), 1140 (s), 1036 (m), 968 (m), 847 (m), 771 (m). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.25 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 2H), 6.87 – 6.76 (m, 3H), 3.79 (s, 3H), 3.09 – 3.01 (m, 1H), 2.43 (d, *J* = 11.7 Hz, 1H), 2.29 (s, 6H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.92 (s, 6H), 0.90 (s, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 157.7, 147.5, 137.4, 133.7, 130.1, 127.6, 125.6, 113.8, 83.0, 55.3, 43.1, 24.6, 24.2, 21.9, 21.4. **HRMS (ESI):** Calcd for C<sub>24</sub>H<sub>33</sub>BO<sub>3</sub>Na [M+Na]<sup>+</sup>: 403.2419; Found: 403.2415.



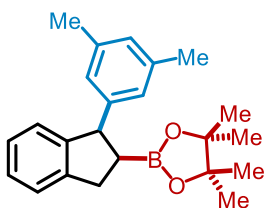
**2-(1-(3,5-dimethylphenyl)-1-phenylpropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51):**

The title compound was prepared according to general procedure B. The crude material (98% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **51** as a white solid (93% avg. yield of two runs). **M. P.:** 75-78 °C. **IR (neat):** 2923 (m), 2853 (w), 1598 (w), 1455 (m), 1378 (m), 1320 (m), 1142 (s), 1007 (m), 967 (w), 843 (m), 696 (m). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.27 – 7.19 (m, 4H), 7.10 (t, *J* = 7.0 Hz, 1H), 6.91 (s, 2H), 6.70 (s, 1H), 3.73 (d, *J* = 12.2 Hz, 1H), 2.20 (s, 6H), 1.96 – 1.87 (m, 1H), 0.99 (s, 6H), 0.96 (s, 6H), 0.87 (d, *J* = 7.2 Hz, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 145.7, 145.1, 137.5, 128.5, 128.1, 127.7, 126.0, 125.9, 83.0, 54.7, 24.50, 24.47, 21.5, 14.7. **HRMS (ESI):** Calcd for C<sub>23</sub>H<sub>31</sub>BO<sub>2</sub>Na [M+Na]<sup>+</sup>: 373.2309; Found: 373.2310.



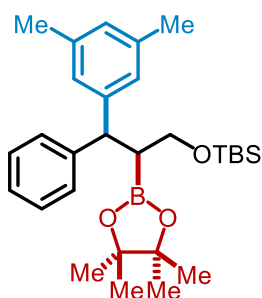
**2-(1-(3,5-dimethylphenyl)-6-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (57):**

The title compound was prepared according to general procedure B. The crude material (63% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 5% Et<sub>2</sub>O/Hexanes) to provide **57** as a colorless oil (62% avg. yield of two runs). **IR (neat):** 2976 (m), 2930 (w), 1606 (w), 1499 (m), 1376 (m), 1315 (m), 1231 (m), 1141 (s), 1039 (m), 969 (m), 846 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 6.84 (d, *J* = 8.5 Hz, 1H), 6.76 – 6.74 (s, 3H), 6.68 (d, *J* = 2.8 Hz, 1H), 6.61 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.29 (d, *J* = 5.5 Hz, 1H), 3.78 (s, 3H), 2.93 (ddd, *J* = 16.9, 5.7, 2.2 Hz, 1H), 2.87 – 2.70 (m, 1H), 2.22 (s, 6H), 2.03 – 1.93 (m, 1H), 1.88 – 1.82 (m, 1H), 1.68 (ddd, *J* = 13.3, 5.5, 2.6 Hz, 1H), 1.18 (s, 6H), 1.05 (s, 6H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 157.4, 146.3, 138.2, 136.7, 132.6, 131.3, 127.7, 127.5, 113.1, 112.2, 82.9, 55.1, 44.3, 30.0, 25.0, 24.7, 21.3, 19.2. **HRMS (ESI):** Calcd for C<sub>25</sub>H<sub>33</sub>BO<sub>3</sub>Na [M+Na]<sup>+</sup>: 415.2419; Found: 415.2416.



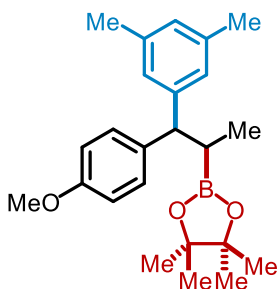


**2-(1-(3,5-dimethylphenyl)-2,3-dihydro-1H-inden-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (58):** The title compound was prepared according to general procedure B. The crude material (99% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **58** as a colorless oil (87% avg. yield of two runs). **IR (neat):** 2976 (m), 2916 (w), 1599 (m), 1457 (w), 1370 (s), 1319 (m), 1141 (s), 966 (m), 852 (m), 743 (s), 705 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.35 (d, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.3, 1H), 7.18 – 7.09 (m, 2H), 6.79 (s, 1H), 6.72 (s, 2H), 4.56 (d, *J* = 9.2 Hz, 1H), 3.44 (dd, *J* = 16.2, 11.0 Hz, 1H), 3.08 (dd, *J* = 16.2, 9.2 Hz, 1H), 2.43 (dt, *J* = 11.1, 9.4 Hz, 1H), 2.25 (s, 6H), 1.00 (d, *J* = 2.4 Hz, 12H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 148.0, 145.3, 144.7, 137.4, 127.8, 126.6, 126.5, 126.2, 125.1, 124.4, 83.0, 53.5, 34.4, 24.8, 24.7, 21.4. **HRMS (ESI):** Calcd for C<sub>23</sub>H<sub>29</sub>BO<sub>2</sub>Na [M+Na]<sup>+</sup>: 371.2153; Found: 371.2153.



**tert-butyl((2S,3S)-3-(3,5-dimethylphenyl)-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethylsilane (59):**

The title compound was prepared according to general procedure B. The crude material (67% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes) to provide **59** as a colorless oil (64% avg. yield of two runs). **IR (neat):** 2927 (m), 2955 (w), 1599 (w), 1471 (m), 1362 (m), 1323 (m), 1256 (m), 1144 (s), 1089 (m), 965 (w), 836 (s), 774 (m). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.36 – 7.30 (m, 2H), 7.30 – 7.25 (m, 2H), 7.20 – 7.12 (m, 1H), 7.01 (s, 2H), 6.78 (s, 1H), 3.95 (d, *J* = 12.5 Hz, 1H), 3.69 – 3.55 (m, 2H), 2.36 – 2.30 (m, 1H), 2.28 (s, 6H), 1.06 (s, 6H), 1.04 (s, 6H), 0.91 (s, 9H), 0.01 (s, 3H), -0.01 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 145.1, 144.9, 137.5, 128.5, 128.1, 127.7, 127.6, 126.1, 83.0, 64.6, 50.2, 26.1, 24.7, 21.4, 18.4, -5.3, -5.4. **HRMS (ESI):** Calcd for C<sub>29</sub>H<sub>45</sub>BO<sub>3</sub>NaSi [M+Na]<sup>+</sup>: 503.3123; Found: 503.3124.

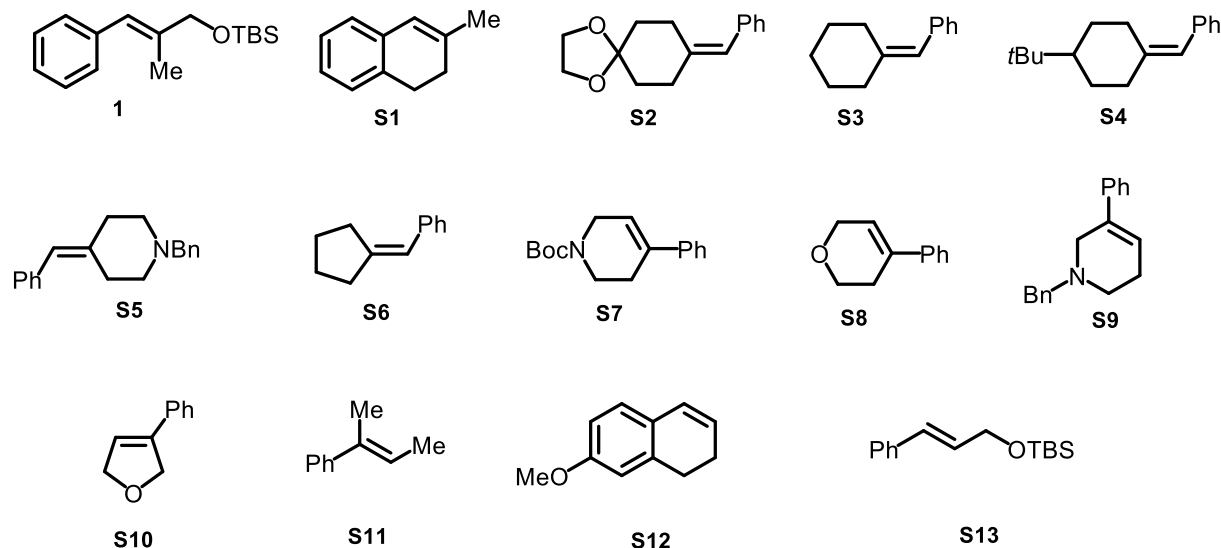


**2-(1-(3,5-dimethylphenyl)-1-(4-methoxyphenyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (60):**

The title compound was prepared according to general procedure B. The crude material (98% yield as determined by internal standard) was purified by MPLC (12 g SiO<sub>2</sub>, 0 to 5% Et<sub>2</sub>O/Hexanes) to provide **60** as a white solid (90% avg. yield of two runs). **M. P.:** 120-123 °C. **IR (neat):** 2974 (m), 2927 (w), 1606 (m), 1509 (s), 1378 (m), 1319 (m), 1247 (m), 1142 (s), 1036 (m), 966 (w), 844 (m), 739 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.25 – 7.17 (m, 2H), 6.95 (s, 2H), 6.86 – 6.80 (m, 2H),

6.75(s, 1H), 3.76 – 3.73 (m, 4H), 2.26 (s, 6H), 1.93 (dq,  $J = 12.1, 7.2$  Hz, 1H), 1.04 (s, 6H), 1.01 (s, 6H), 0.94 (d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.8, 146.1, 137.4, 137.2, 128.9, 127.5, 125.8, 113.8, 82.9, 55.2, 53.9, 24.5, 24.4, 21.4, 14.6. HRMS (ESI): Calcd for  $\text{C}_{24}\text{H}_{33}\text{BO}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ : 403.2419; Found: 403.2415.

### Alkene Substrate Synthesis

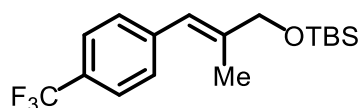


**1**<sup>[1]</sup>, **S1**<sup>[2]</sup>, **S2**<sup>[3]</sup>, **S3**<sup>[4]</sup>, **S4**<sup>[5]</sup>, **S5**<sup>[6]</sup>, **S6**<sup>[7]</sup>, **S7**<sup>[4]</sup>, **S8**<sup>[8]</sup>, **S9**<sup>[9]</sup>, **S10**<sup>[10]</sup>, **S11**<sup>[11]</sup>, **S12**<sup>[12]</sup>, **S13**<sup>[13]</sup> were prepared according to known literature procedures.

### General Procedure G for the Synthesis of Substrates



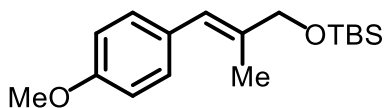
To a solution of the alcohol (1.0 equiv) in methylene chloride in a 100 mL round-bottom flask was added 4-Dimethylaminopyridine (0.1 equiv), triethylamine (1.2 equiv) and *tert*-butyldimethylsilyl chloride (1.2 equiv) at room temperature under nitrogen. The mixture was allowed to stir for overnight. The reaction was quenched with water and extracted two times with methylene chloride. The combined organic layers were washed with brine, dried over  $\text{MgSO}_4$ , filtered and concentrated under vacuum. The crude mixture was purified by MPLC ( $\text{SiO}_2$ ) to provide the silyl ether compound.



### **(E)-tert-butyldimethyl((2-methyl-3-(4-(trifluoromethyl)phenyl)allyl)oxy)silane (S15):**

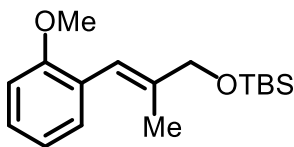
The title compound was prepared according to general procedure G starting from *(E)*-2-methyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol<sup>[14]</sup> (2.16 g, 10.0 mmol). The crude material was purified by MPLC (80 g  $\text{SiO}_2$ , 0-1%  $\text{Et}_2\text{O}$ /Hexanes) to provide **S15** as a colorless oil (87% yield). IR (neat):

2930 (m), 2857 (w), 1615 (m), 1322 (s), 1252 (w), 1163 (m), 1108 (m), 1066 (s), 834 (s), 774 (s). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.59 (s, 1H), 4.27 – 4.19 (m, 2H), 1.84 (s, 3H), 0.97 (s, 9H), 0.14 (s, 6H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 141.9, 140.0, 129.2, 128.2 (q, *J* = 32.1 Hz), 125.1 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 270.2 Hz, 2H), 122.4, 68.2, 26.1, 18.6, 15.2, -5.2. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):** δ -62.4. **HRMS (ESI):** Calcd for C<sub>17</sub>H<sub>25</sub>FOSi [M]<sup>+</sup>: 330.1621; Found: 330.1630.



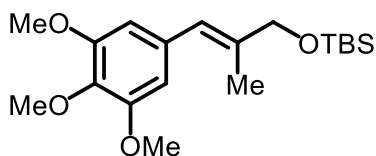
**(E)-tert-butyl((3-(4-methoxyphenyl)-2-methylallyl)oxy)dimethylsilane (S16):**

The title compound was prepared according to general procedure G starting from (*E*)-3-(4-methoxyphenyl)-2-methylprop-2-en-1-ol<sup>[14]</sup> (0.76 g, 4.27 mmol). The crude material was purified by MPLC (80 g SiO<sub>2</sub>, 0-2% Et<sub>2</sub>O/Hexanes) to provide **S16** as a colorless oil (81% yield). **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.15 – 7.07 (m, 2H), 6.80 – 6.71 (m, 2H), 6.36 (s, 1H), 4.10 – 4.03 (m, 2H), 3.68 (s, 3H), 1.72 (s, 3H), 0.88 – 0.80 (m, 9H), 0.04 – -0.02 (m, 6H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 158.1, 136.0, 130.7, 130.1, 123.5, 113.6, 68.9, 55.3, 26.1, 18.6, 15.1, -5.1. **HRMS (ESI):** Calcd for C<sub>17</sub>H<sub>28</sub>FO<sub>2</sub>Si [M]<sup>+</sup>: 292.1853; Found: 292.1858.



**(E)-tert-butyl((3-(2-methoxyphenyl)-2-methylallyl)oxy)dimethylsilane (S17):**

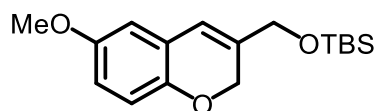
The title compound was prepared according to general procedure G starting from (*E*)-3-(2-methoxyphenyl)-2-methylprop-2-en-1-ol<sup>[14]</sup> (1.78 g, 10.0 mmol). The crude material was purified by MPLC (80 g SiO<sub>2</sub>, 0-2% Et<sub>2</sub>O/Hexanes) to provide **S17** as a colorless oil (83% yield). **IR (neat):** 2952 (m), 2855 (w), 1597 (m), 1487 (m), 1243 (s), 1111(m), 833 (s), 774 (m), 749 (s). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.27 – 7.19 (m, 2H), 6.98 – 6.90 (m, 1H), 6.87 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.63 (s, 1H), 4.24 (s, 2H), 3.82 (s, 3H), 1.81 (s, 3H), 0.97 (m, 9H), 0.14 (m, 6H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 157.3, 137.5, 130.3, 127.8, 127.0, 120.1, 119.8, 110.5, 68.9, 55.5, 26.1, 18.6, 15.2, -5.1. **HRMS (ESI):** Calcd for C<sub>17</sub>H<sub>28</sub>O<sub>2</sub>NaSi [M+Na]<sup>+</sup>: 315.1751; Found: 315.1753.



**(E)-tert-butyl((2-methyl-3-(3,4,5-trimethoxyphenyl)allyl)oxy)dimethylsilane (S18):**

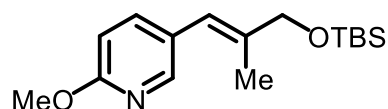
The title compound was prepared according to general procedure G starting from (*E*)-2-methyl-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-ol<sup>[15]</sup> (2.60 g, 10.0 mmol). The crude material was purified by MPLC (80 g SiO<sub>2</sub>, 0-2% Et<sub>2</sub>O/Hexanes) to provide **S18** as a colorless oil (96% yield). **IR (neat):** 2929 (m), 2855 (w), 1579 (m), 1505 (m), 1462 (m), 1413 (m), 1333(m), 1237 (m), 1125 (s), 1006 (m), 834 (s), 774 (m). **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 6.49 (s, 2H), 6.46 (s, 1H), 4.17 (s, 2H), 3.85 (s, 9H), 1.85 (s, 3H), 0.95 (s, 9H), 0.12 (s, 6H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 153.0, 137.4,

136.7, 133.8, 123.9, 106.3, 68.6, 61.0, 56.2, 26.1, 18.6, 15.3, -5.1. **HRMS (ESI):** Calcd for  $C_{19}H_{32}O_4SiNa$   $[M-CH_2+Na]^+$ : 375.1962.; Found: 375.1963.



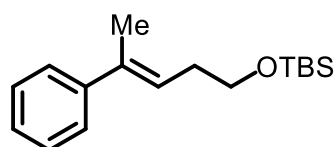
***tert*-butyl((6-methoxy-2H-chromen-3-yl)methoxy)dimethylsilane (S19):**

The title compound was prepared according to general procedure G starting from (6-methoxy-2H-chromen-3-yl)methanol<sup>[16]</sup> (1.00 g, 5.25 mmol). The crude material was purified by MPLC (80 g  $SiO_2$ , 0 to 2%  $Et_2O$ /Hexanes) to provide **S19** as a colorless oil (94% yield). **IR (neat):** 2928 (m), 2855 (w), 1583 (m), 1493 (w), 1253(m), 1210 (m), 1069 (w), 844 (s), 755 (m). **<sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ):**  $\delta$  6.76 – 6.70 (m, 1H), 6.65 (dd,  $J = 8.7, 3.0$  Hz, 1H), 6.57 (d,  $J = 3.0$  Hz, 1H), 6.32 (s, 1H), 4.69 (s, 2H), 4.22 (s, 2H), 3.76 (s, 3H), 0.93 (s, 9H), 0.11 (s, 6H). **<sup>13</sup>C NMR (125 MHz,  $CDCl_3$ ):**  $\delta$  154.3, 147.4, 135.3, 123.4, 118.8, 116.0, 113.8, 111.9, 66.4, 63.6, 55.9, 26.0, 18.5, -5.2. **HRMS (ESI):** Calcd for  $C_{17}H_{25}O_3Si$   $[M-H]^+$ : 305.1567; Found: 305.1570.



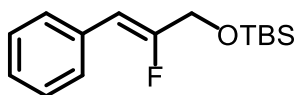
***(E)*-5-(3-((*tert*-butyldimethylsilyloxy)-2-methylprop-1-en-1-yl)-2-methoxypyridine (S20):**

The title compound was prepared according to general procedure G starting from (*E*)-3-(6-methoxypyridin-3-yl)-2-methylprop-2-en-1-ol<sup>[17]</sup> (1.80 g, 10.0 mmol). The crude material was purified by MPLC (80 g  $SiO_2$ , 10-20%  $Et_2O$ /Hexanes) to provide **S20** as a colorless oil (79% yield). **IR (neat):** 2928 (m), 2855 (w), 1601 (w), 1491 (s), 1371 (m), 1286 (m), 1251 (m), 1074 (m), 1027 (m), 833 (s), 774 (s). **<sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ):**  $\delta$  8.08 (d,  $J = 2.4$  Hz, 1H), 7.49 (dd,  $J = 8.6, 2.5$  Hz, 1H), 6.70 (d,  $J = 8.5$  Hz, 1H), 6.40 (s, 1H), 4.17 (s, 2H), 3.93 (s, 3H), 1.80 (s, 3H), 0.94 (s, 9H), 0.11 (s, 6H). **<sup>13</sup>C NMR (125 MHz,  $CDCl_3$ ):**  $\delta$  162.6, 146.9, 139.1, 138.0, 127.0, 120.0, 110.3, 68.5, 53.5, 26.1, 18.6, 15.1, -5.1. **HRMS (ESI):** Calcd for  $C_{16}H_{28}O_2SiN$   $[M+H]^+$ : 294.1884; Found: 294.1886



***(E)*-*tert*-butyldimethyl((4-phenylpent-3-en-1-yl)oxy)silane (S21):**

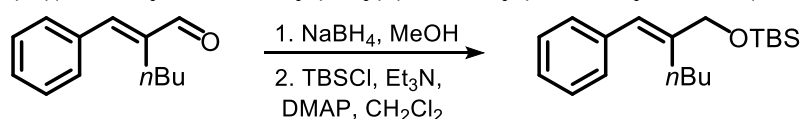
The title compound was prepared according to general procedure G starting from (*E*)-4-phenylpent-3-en-1-ol<sup>[18]</sup> (1.10 g, 6.78 mmol). The crude material was purified by MPLC (80 g  $SiO_2$ , 100% Hexanes) to provide **S21** as a colorless oil (82% yield). **IR (neat):** 2928 (m), 2855 (w), 1493 (w), 1252 (m), 1092 (m), 935 (w), 833 (s), 773 (m), 694 (m). **<sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ):**  $\delta$  7.32 – 7.27 (m, 2H), 7.24 – 7.19 (m, 2H), 7.15 – 7.10 (m, 1H), 5.72 – 5.67 (m, 1H), 3.65 – 3.60 (m, 2H), 2.36 (q,  $J = 7.1$  Hz, 2H), 1.97 (s, 3H), 0.83 (s, 9H), 0 -0.01 (s, 6H). **<sup>13</sup>C NMR (125 MHz,  $CDCl_3$ ):**  $\delta$  144.0, 136.6, 128.3, 126.7, 125.8, 124.5, 62.9, 32.8, 26.1, 18.5, 16.1, -5.1. **HRMS (ESI):** Calcd for  $C_{16}H_{25}OSi$   $[M-CH_3]^+$ : 261.1669; Found: 261.1674.



### (*Z*)-*tert*-butyl((2-fluoro-3-phenylallyl)oxy)dimethylsilane (**70**):

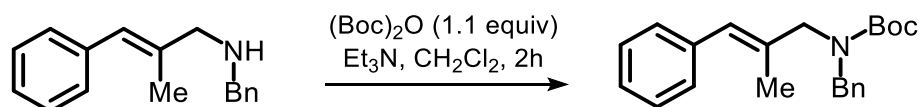
The title compound was prepared according to general procedure G starting from (*Z*)-2-fluoro-3-phenylprop-2-en-1-ol<sup>[19]</sup> (1.72 g, 11.3 mmol). The crude material was purified by MPLC (80 g SiO<sub>2</sub>, 100%Hexanes) to provide **70** as a colorless oil (72% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.54 – 7.36 (m, 2H), 7.30 – 7.18 (m, 2H), 7.18 – 7.07 (m, 1H), 5.69 (d, *J* = 39.1 Hz, 1H), 4.21 (d, *J* = 10.3, 2H), 0.88 (s, 9H), 0.07 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 158.8 (d, *J* = 266.8 Hz), 133.3 (d, *J* = 2.4 Hz), 128.7 (d, *J* = 7.1 Hz), 128.6, 127.3 (d, *J* = 2.3 Hz), 106.2 (d, *J* = 6.0 Hz), 61.9 (d, *J* = 36.0 Hz), 25.9, 18.5, -5.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -113.06 (dt, *J* = 39.1, 10.4 Hz). HRMS (ESI): Calcd for C<sub>15</sub>H<sub>23</sub>OFSi [M]<sup>+</sup>: 266.1497; Found: 266.1496.

### Synthesis of the (*E*)-((2-benzylidenehexyl)oxy)(*tert*-butyl)dimethylsilane (**S22**):



To a cooled (0 °C) solution of the (*E*)-2-benzylidenehexanal<sup>[20]</sup> (3.00 g, 15.9 mmol, 1.00 equiv) in MeOH (50.0 mL) was added NaBH<sub>4</sub> (905 mg, 23.9 mmol, 1.50 equiv) under nitrogen. After 30 min, the reaction was quenched with saturated aqueous NH<sub>4</sub>Cl solution (20.0 mL). The aqueous layer was separated and extracted with Et<sub>2</sub>O (3 × 25 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated. To a solution of the crude alcohol in methylene chloride (80 mL) in a 150 mL round-bottom flask was added 4-Dimethylaminopyridine (194 mg, 1.59 mmol, 0.10 equiv), triethylamine (2.66 mL, 19.1 mmol, 1.2 equiv) and *tert*-butyldimethylsilyl chloride (2.88 g, 19.1 mmol, 1.2 equiv) at room temperature under nitrogen. The mixture was allowed to stir for overnight. The reaction was quenched with water (50 mL) and extracted with methylene chloride (3 × 40 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The crude mixture was purified by MPLC (80 g SiO<sub>2</sub>, 100%Hexanes) to provide **S22** as a colorless oil (92% yield, 2 steps). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.23 – 7.16 (m, 2H), 7.16 – 7.11 (m, 2H), 7.11 – 7.05 (m, 1H), 6.41 (s, 1H), 4.11 (s, 2H), 2.16 – 2.08 (m, 2H), 1.40 – 1.30 (m, 2H), 1.27 – 1.15 (m, 2H), 0.84 (s, 9H), 0.77 (t, *J* = 7.3 Hz, 3H), 0.00 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 142.2, 138.2, 128.8, 128.2, 126.2, 123.9, 66.9, 30.8, 28.6, 26.1, 23.2, 18.6, 14.1, -5.1. HRMS (ESI): Calcd for C<sub>19</sub>H<sub>32</sub>OSi [M]<sup>+</sup>: 304.2217; Found: 304.2217.

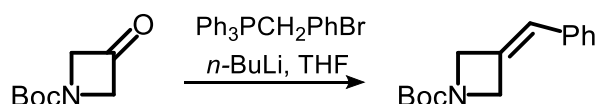
### Synthesis of the *tert*-Butyl (*E*)-benzyl(2-methyl-3-phenylallyl)carbamate (**S23**)



To a cooled (0 °C) solution of (*E*)-*N*-benzyl-2-methyl-3-phenylprop-2-en-1-amine<sup>[21]</sup> (1.24 g, 5.22 mmol, 1.00 equiv) in methylene chloride (40 mL), was added triethylamine (1.10 mL, 7.83 mmol, 1.50 equiv). The di-*tert*-butyl dicarbonate (1.25 g, 5.74 mmol, 1.1 equiv) was added in three portions under nitrogen. The reaction was allowed to warm to room temperature and monitored by TLC (about 2 hours). Water (25 mL) was added and the mixture was extracted with methylene

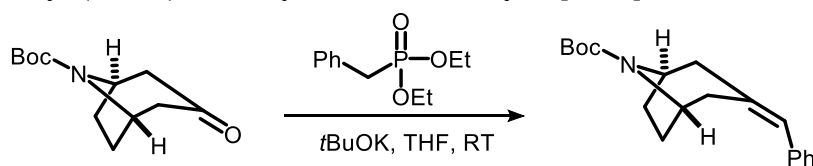
chloride (2 × 20 mL). The combined organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated under vacuum. The crude mixture was purified by MPLC (80 g SiO<sub>2</sub>, 5% EtOAc/Hexanes) to provide the title compound **S23** as a white solid. **M.P.:** 31-33 °C. **IR (neat):** 2975 (m), 2829 (w), 1690 (s), 1451 (m), 1414 (m), 1364 (m), 1241 (m), 1163 (s), 1115 (m), 884 (m), 697 (m). **<sup>1</sup>H NMR (500 MHz, Toluene-*d*<sub>8</sub>, 80 °C):** δ 7.22 – 7.18 (m, 2H), 7.14 – 7.08 (m, 5H), 7.06 – 6.98 (m, 2H), 6.97 – 6.90 (m, 1H), 6.21 (s, 1H), 4.40 (s, 2H), 3.88 (s, 2H), 1.68 (s, 3H), 1.43 (s, 9H). **<sup>13</sup>C NMR (125 MHz, Toluene-*d*<sub>8</sub>, 60 °C):** 155.9, 139.3, 138.3, 137.6, 135.1, 129.3, 128.7, 128.4, 127.4, 126.7, 79.5, 54.5, 49.8, 28.6, 15.7. **HRMS (ESI):** Calcd for C<sub>22</sub>H<sub>27</sub>O<sub>2</sub>NaN [M+Na]<sup>+</sup>: 360.1934; Found: 360.1936.

#### Synthesis of the *tert*-Butyl 3-benzylideneazetidone-1-carboxylate (**S24**):



To a cooled (0 °C) solution of Benzyltriphenylphosphonium bromide (3.45 g, 7.96 mmol, 1.10 equiv) in THF (50 mL) was added *n*-BuLi (5.40 mL, 8.68 mmol, 1.6 M in hexanes, 1.2 equiv) dropwise under nitrogen. After stirring for an additional 30 minutes at the same temperature, the solution of *t*-Butyl 3-oxoazetidone-1-carboxylate (1.23 g, 7.23 mmol, 1.00 equiv.) in dry THF (15 mL) was added dropwise. After the addition, the cold bath was removed and the reaction mixture was stirred at room temperature for 12 h. The saturated NH<sub>4</sub>Cl aqueous (50 mL) was added to quench the reaction, which was extracted with EtOAc (3 × 40 mL). The combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude material was purified by MPLC (80 g SiO<sub>2</sub>, 10 to 50% Et<sub>2</sub>O/Hexanes) to provide **S24** as a colorless oil (0.726 g, 41 %). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):** δ 7.33 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.25 (s, 1H), 4.83 (q, *J* = 3.0 Hz, 2H), 4.64 (q, *J* = 3.0 Hz, 2H), 1.49 (s, 9H). **<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):** δ 156.4, 136.2, 130.7, 128.8, 127.2, 127.1, 122.4, 76.9, 58.8, 28.5.

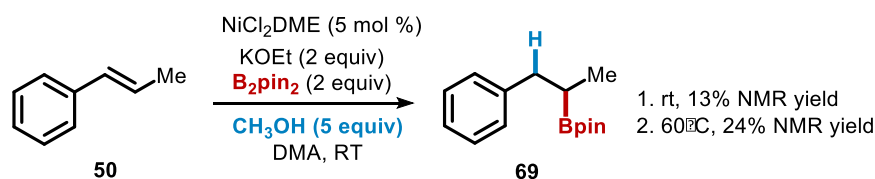
#### Synthesis of *tert*-Butyl (*1R,5S*)-3-benzylidene-8-azabicyclo[3.2.1]octane-8-carboxylate (**S25**):



To a solution of diethyl benzylphosphonate (3.2 mL, 15 mmol, 1.5 equiv) in THF (50 mL) was added *t*-BuOK (14 mL, 14 mmol, 1.0 M in THF, 1.4 equiv) dropwise under nitrogen. After stirring for additional 30 minutes at the same temperature, the solution of *N*-Boc-nortropinone (1.39 g, 10.0 mmol, 1.00 equiv.) in dry THF (15 mL) was added dropwise. After the addition, the reaction mixture was stirred at room temperature for 12 h. The saturated NH<sub>4</sub>Cl aqueous (40 mL) was added to quench the reaction, which was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated. The crude material was purified by MPLC (80 g SiO<sub>2</sub>, 10 to 50% Et<sub>2</sub>O/Hexanes) to provide **S25** as a white solid (2.21 g, 74 %). **M. P.:** 84-86 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.28 – 7.33 (m, 2H), 7.22 – 7.15 (m, 3H), 6.44 (s, 1H), 4.31 (s, 1H), 4.19 (s, 1H), 2.73 (d, *J* = 14.2 Hz, 1H), 2.68 – 2.56 (m, 1H), 2.46 (d, *J* = 14.2 Hz, 1H), 2.21 – 2.09 (m, 1H), 1.96 – 1.77 (m, 2H), 1.71 – 1.62 (m, 1H), 1.50 (s, 9H), 1.48 – 1.40 (m, 1H). **<sup>13</sup>C NMR**

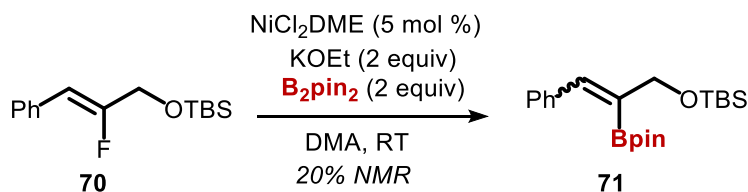
(125 MHz, CDCl<sub>3</sub>):  $\delta$  153.6, 137.5, 135.6, 128.9, 128.6, 128.1, 126.3, 76.9, 54.4, 53.9, 42.6, 36.0, 28.6, 28.5, 28.2. HRMS (ESI): Calcd for C<sub>19</sub>H<sub>25</sub>O<sub>2</sub>N [M]<sup>+</sup>: 299.1880; Found: 299.1880.

### ■ Procedure for the Protoboration



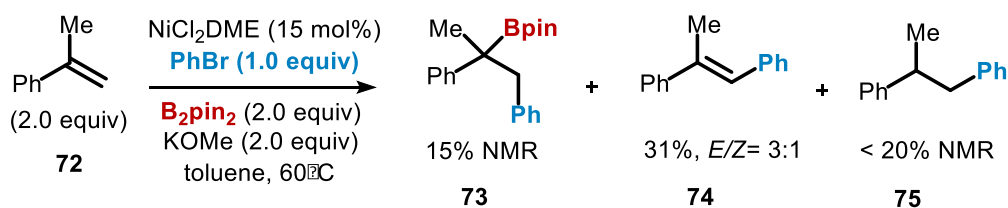
In an N<sub>2</sub>-filled glovebox, an oven-dried 16 x 100 mm vial with magnetic stir bar was charged with KOEt (67.4 mg, 0.800 mmol, 2.00 equiv) and B<sub>2</sub>pin<sub>2</sub> (0.203 g, 0.800 mmol, 2.00 equiv). The vial was sealed with a rubber septum and removed from the glovebox. DMA (2.5 mL) was added to the vial, and the mixture was stirred vigorously at room temperature for 1 h to afford a suspension. Thereafter, the vial was cooled to 0 °C, the *trans*- $\beta$ -methylstyrene **50** (52  $\mu$ L, 0.40 mmol, 1.0 equiv) and MeOH (81  $\mu$ L, 2.0 mmol, 5.0 equiv) were added to the reaction mixture via syringe under an N<sub>2</sub> atmosphere. The pre-prepared NiCl<sub>2</sub>(DME) stock solution in DMA (0.50 mL, 0.04 M) was added to the reaction mixture. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was warmed to r.t. or 60 °C and stirred for 24 h. The solution was passed through a 3 cm x 3 cm pad of celite and silica gel and washed with EtOAc (3 x 4 mL). The filtrate was washed with KOH aqueous (3 x 3.0 mL, 1.0 M), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated. Dibromomethane (28  $\mu$ L) was added as an internal standard and a small aliquot was analyzed via <sup>1</sup>H NMR in a 13% yield of **69**. When the reaction was setup at 60 °C, 24% yield was observed. This compound has been previously reported and the crude <sup>1</sup>H NMR matches it described.<sup>[22]</sup>

### ■ Borylation of (*Z*)-*tert*-Butyl((2-fluoro-3-phenylallyl)oxy)dimethylsilane



In an N<sub>2</sub>-filled glovebox, an oven-dried 16 x 100 mm vial with magnetic stir bar was charged with KOEt (67.4 mg, 0.800 mmol, 2.00 equiv) and B<sub>2</sub>pin<sub>2</sub> (0.203 g, 0.800 mmol, 2.00 equiv). The vial was sealed with a rubber septum and removed from the glovebox. DMA (2.5 mL) was added to the vial, and the mixture was stirred vigorously at r.t. for 1 h to afford a suspension. Thereafter, the vial was cooled to 0 °C, the (*Z*)-*tert*-butyl((2-fluoro-3-phenylallyl)oxy)dimethylsilane **70** (0.107 g, 0.400 mmol, 1.00 equiv) was added to the reaction mixture via syringe under an N<sub>2</sub> atmosphere. The pre-prepared NiCl<sub>2</sub>(DME) stock solution in DMA (0.50 mL, 0.04 M) was added to the reaction mixture. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was warmed to r.t. and stirred for 24 h. The reaction was quenched upon the addition of water (2.0 mL), and the solution was diluted with EtOAc (20.0 mL), the organic layer was washed with KOH aqueous (3 x 5.0 mL, 1.0 M), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated. Dibromomethane (28.0  $\mu$ L) was added as an internal standard and a small aliquot was analyzed via <sup>1</sup>H NMR indicated 20 % yield and 7:1 dr. The compound **71** was further confirmed by GC-MS.

## ■ Arylboration of $\alpha$ -Methylstyrene in Toluene



In an N<sub>2</sub>-filled glovebox, an oven-dried 16 x 100 mm screw-capped vial with a magnetic stir bar was charged with NiCl<sub>2</sub>(DME) (13.2 mg, 0.06 mmol, 15 mol%), KOEt (67.4 mg, 0.80 mmol, 2.00 equiv) and B<sub>2</sub>pin<sub>2</sub> (0.203 g, 0.800 mmol, 2.00 equiv). The vial was sealed with a rubber septum and removed from the glovebox. The  $\alpha$ -Methylstyrene (104  $\mu$ L, 0.800 mmol, 2.00 equiv) and bromobenzene (42  $\mu$ L, 0.40 mmol, 1.0 equiv) in toluene (2.0 ml) were added to the reaction mixture via syringe under an N<sub>2</sub> atmosphere. The septum was quickly replaced by a Teflon-lined screw cap and the reaction was stirred at 60 °C for 24 h in a preheated aluminum block. The reaction was quenched upon the addition of water (2.0 mL), and the solution was diluted with EtOAc (20 mL), the organic layer was washed with KOH aqueous (3 x 5.0 mL, 1.0 M), dried over MgSO<sub>4</sub>, gravity filtered, and concentrated. Dibromomethane(28  $\mu$ L) was added as an internal standard and a small aliquot was analyzed via <sup>1</sup>H NMR indicated 15 % yield of **73** and 20% yield of **75**. The Heck product **74** is commercially available, the yield and E/Z ratio were determined by GC analysis using dodecane as a calibrated internal standard. All the compounds were further confirmed by GC-MS. The compound **73** was isolated as a colorless oil (13% yield) by MPLC (12 g SiO<sub>2</sub>, 0 to 2% Et<sub>2</sub>O/Hexanes). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.35 – 7.20 (m, 4H), 7.20 – 7.07 (m, 4H), 7.02 – 6.89 (m, 2H), 3.20 (d, *J* = 13.1 Hz, 1H), 2.94 (d, *J* = 13.1 Hz, 1H), 1.27 (s, 3H), 1.20 (s, 6H), 1.17 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  146.6, 139.7, 130.6, 128.1, 127.6, 127.3, 125.9, 125.4, 83.7, 45.8, 24.9, 24.6, 20.6. HRMS (ESI): Calcd for C<sub>21</sub>H<sub>28</sub>O<sub>2</sub>B [M+H]<sup>+</sup>: 323.2177; Found: 323.2179.

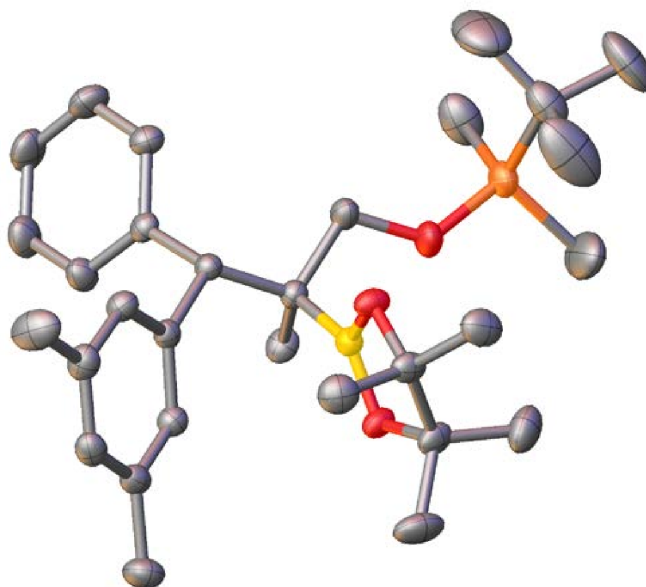
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## X-Ray Crystallography of 2:



Formula unit, hydrogen atoms omitted for clarity.

**Table S-2. Crystal Data and Structure Refinement for Compound 2**

Empirical formula	C <sub>30</sub> H <sub>47</sub> B O <sub>3</sub> Si
Formula weight	494.57
Crystal color, shape, size	colorless block, 0.27 × 0.25 × 0.19 mm <sup>3</sup>
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 10.6297(4) Å                      α = 74.1839(12)° b = 10.6434(4) Å                      β = 71.2012(12)° c = 14.9830(6) Å                      γ = 89.9118(12)°
Volume	1537.00(10) Å <sup>3</sup>
Z	2
Density (calculated)	1.069 Mg/m <sup>3</sup>
Absorption coefficient	0.103 mm <sup>-1</sup>
F(000)	540

### ***Data collection***

Diffractometer	Kappa Apex II Duo, Bruker
Theta range for data collection	1.499 to 27.536°.
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -18 ≤ l ≤ 19
Reflections collected	18682
Independent reflections	6992 [R <sub>int</sub> = 0.0309]
Observed Reflections	5880
Completeness to theta = 25.242°	98.8 %

### ***Solution and Refinement***

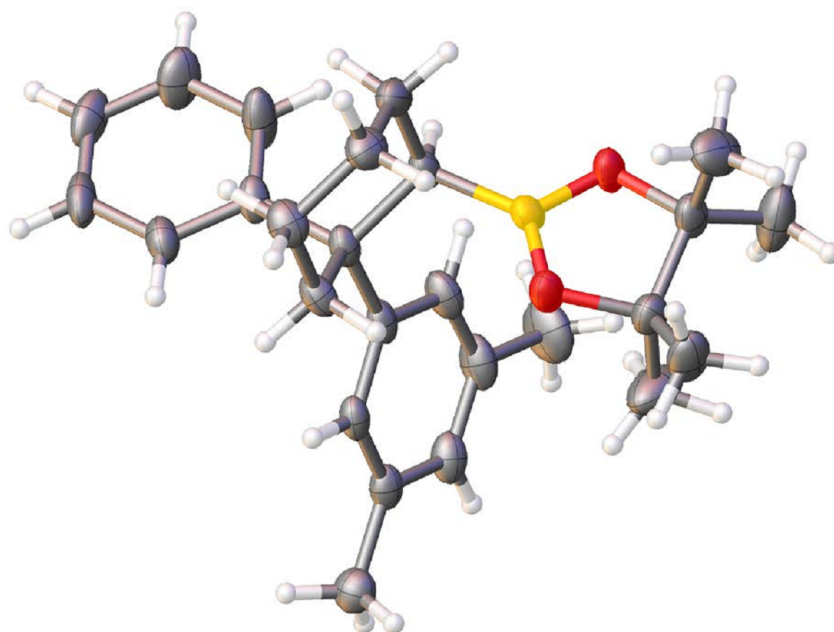
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6570
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Weighting scheme	$w = [\sigma^2 F_o^2 + AP^2 + BP]^{-1}$ , with $P = (F_o^2 + 2 F_c^2)/3$ , A = 0.0657, B = 0.4337
Data / restraints / parameters	6992 / 0 / 328
Goodness-of-fit on F <sup>2</sup>	1.041
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0439, wR2 = 0.1212
R indices (all data)	R1 = 0.0528, wR2 = 0.1281
Largest diff. peak and hole	0.434 and -0.419 e.Å <sup>-3</sup>

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Goodness-of-fit =  $[\sum [w(F_o^2 - F_c^2)^2] / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$ , all data.

$R1 = \sum (|F_o| - |F_c|) / \sum |F_o|$ .       $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

### **X-Ray Crystallography of 38:**



**Table S-3. Crystal Data and Structure Refinement for Compound 38**

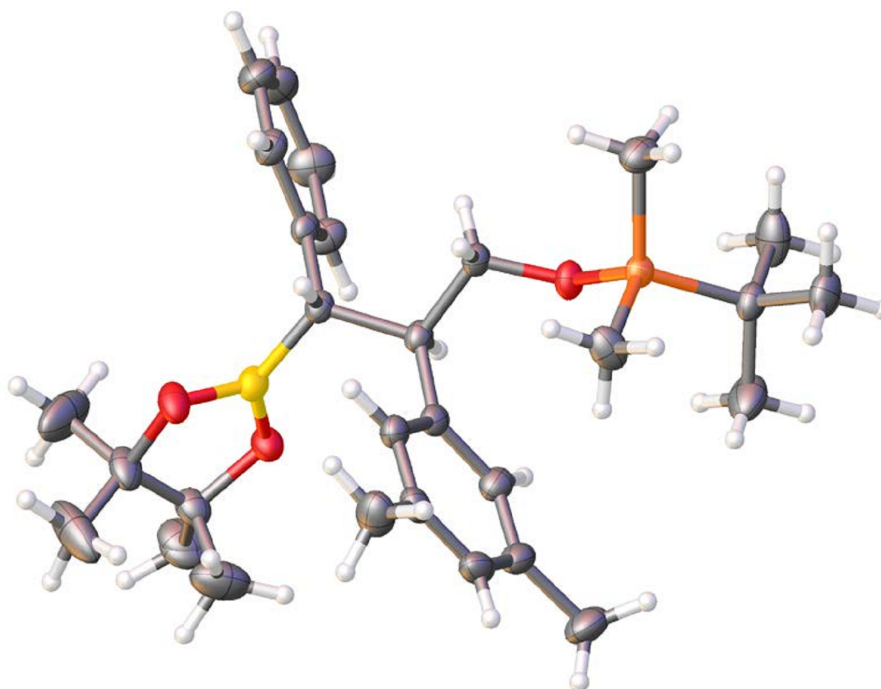
Empirical formula	C <sub>26</sub> H <sub>35</sub> B O <sub>2</sub>	
Formula weight	390.35	
Crystal color, shape, size	colorless needle, 0.40 × 0.15 × 0.15 mm <sup>3</sup>	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /c	
Unit cell dimensions	a = 13.6156(7) Å	α = 90°.
	b = 9.2138(4) Å	β = 110.491(3)°.
	c = 19.1403(9) Å	γ = 90°.
Volume	2249.25(19) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.153 Mg/m <sup>3</sup>	
Absorption coefficient	0.070 mm <sup>-1</sup>	
F(000)	848	
<b>Data collection</b>		
Diffractometer	Kappa Apex II Duo, Bruker	
Theta range for data collection	1.597 to 27.612°.	
Index ranges	-17 ≤ h ≤ 17, -10 ≤ k ≤ 11, -24 ≤ l ≤ 24	
Reflections collected	29472	
Independent reflections	5166 [R <sub>int</sub> = 0.0408]	
Observed Reflections	3836	
Completeness to theta = 25.242°	99.4 %	
<b>Solution and Refinement</b>		
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6762	
Solution	Intrinsic methods	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Weighting scheme	w = [σ <sup>2</sup> F <sub>o</sub> <sup>2</sup> + AP <sup>2</sup> + BP] <sup>-1</sup> , with P = (F <sub>o</sub> <sup>2</sup> + 2 F <sub>c</sub> <sup>2</sup> )/3, A = 0.062400, B = 1.015900	
Data / restraints / parameters	5166 / 0 / 268	
Goodness-of-fit on F <sup>2</sup>	1.025	
Final R indices [I > 2σ(I)]	R1 = 0.0506, wR2 = 0.1285	
R indices (all data)	R1 = 0.0710, wR2 = 0.1443	
Largest diff. peak and hole	0.438 and -0.302 e.Å <sup>-3</sup>	

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Goodness-of-fit =  $[\sum[w(F_o^2 - F_c^2)^2]/N_{\text{observns}} - N_{\text{params}}]^{1/2}$ , all data.

R1 =  $\sum(|F_o| - |F_c|) / \sum |F_o|$ .      wR2 =  $[\sum[w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

## X-Ray Crystallography of 55:



**Table S-4. Crystal Data and Structure Refinement for Compound 55**

Empirical formula	C <sub>29</sub> H <sub>45</sub> B O <sub>3</sub> Si	
Formula weight	480.55	
Crystal color, shape, size	colorless block, 0.350 × 0.280 × 0.220 mm <sup>3</sup>	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 10.2153(9) Å	α = 97.081(4)°.
	b = 11.1298(10) Å	β = 90.919(4)°.
	c = 12.9937(13) Å	γ = 97.217(4)°.
Volume	1453.7(2) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.098 Mg/m <sup>3</sup>	
Absorption coefficient	0.107 mm <sup>-1</sup>	
F(000)	524	

### ***Data collection***

Diffractometer	Kappa Apex II Duo, Bruker
Theta range for data collection	1.580 to 27.596°.
Index ranges	-11 ≤ h ≤ 13, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	22117
Independent reflections	6678 [R <sub>int</sub> = 0.0293]
Observed Reflections	5577
Completeness to theta = 25.242°	99.5 %

### ***Solution and Refinement***

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6621
Solution	Intrinsic methods
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Weighting scheme	$w = [\sigma^2 F_o^2 + AP^2 + BP]^{-1}$ , with $P = (F_o^2 + 2 F_c^2)/3$ , $A = 0.0667$ , $B = 0.5981$
Data / restraints / parameters	6678 / 405 / 347
Goodness-of-fit on F <sup>2</sup>	1.058
Final R indices [I > 2σ(I)]	R1 = 0.0450, wR2 = 0.1228
R indices (all data)	R1 = 0.0551, wR2 = 0.1348
Largest diff. peak and hole	0.581 and -0.279 e.Å <sup>-3</sup>

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Goodness-of-fit =  $[\Sigma[w(F_o^2 - F_c^2)^2]/N_{\text{observns}} - N_{\text{params}}]^{1/2}$ , all data.

$$R1 = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|. \quad wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}.$$

# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra

