

## **Supporting Information**

# **Copper-Catalyzed/Mediated Borylation Reactions of Epoxides with Diboron Reagents: Access to $\beta$ -Hydroxyl Boronic Esters**

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## **Table of Contents**

|   |                |
|---|----------------|
| <b>I. General Information.....</b>  | <b>S2</b>      |
| <b>II. Preparation of Substrates.....</b>   | <b>S2</b>      |
| <b>III. General Experimental Procedures, Spectral Data and HPLC<br/>Analysis.....</b> | <b>S3-S14</b>  |
| <b>IV. References.....</b>  | <b>S15</b>     |
| <b>V. NMR Spectra.....</b>  | <b>S16-S56</b> |

## I. General Information

### a). Materials

All the reactions were carried out in oven-dried schlenk tubes under argon atmosphere (purity  $\geq 99.999\%$ ). Copper(I) iodide was purchased from Sinopharm Chemical Reagent Co., Ltd as a offwhite powder. Diboron reagents bis(pinacolato)diboron ( $B_2pin_2$ ) and neopentylglycolatediboron ( $B_2neop_2$ ) were purchased from Ally Chemical Co., Ltd and recrystallized in EtOAc and petroleum ether for further purification (as white solid). The following chemicals were purchased and used as received: LiO-*t*Bu (J & K, 99.9%), KO-*t*Bu (Acros), NaO-*t*Bu (Acros), 2-(phenoxymethyl)oxirane (adamas, 98%), (S)-2-((benzyloxy)methyl)oxirane (adamas, 98%), 2-((benzyloxy)methyl)oxirane (adamas, 98%).

Anhydrous solvents (DME, DMF, Diglyme, EtOAc, 1, 3-dioxane, THF) were purchased from Acros and used without further purification. Anhydrous THF (Acros) was stored over 4 Å molecular sieves under an argon atmosphere in a septum-capped bottle.

All the other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

### b). Analytical Methods

$^1H$ -NMR,  $^{13}C$ -NMR and  $^{19}F$ -NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in  $CDCl_3$  unless otherwise noted; Data for  $^1H$ -NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity, integration, and coupling constant (Hz). Data for  $^{13}C$ -NMR are reported in terms of chemical shift ( $\delta$  ppm), multiplicity, and coupling constant (Hz). Gas chromatography (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on FinniganLCQ advantage Max Series MS System. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IC, OD, AS, KM columns were purchased from Daicel Chemical Industries, LTD. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

## II. Preparation of Substrates

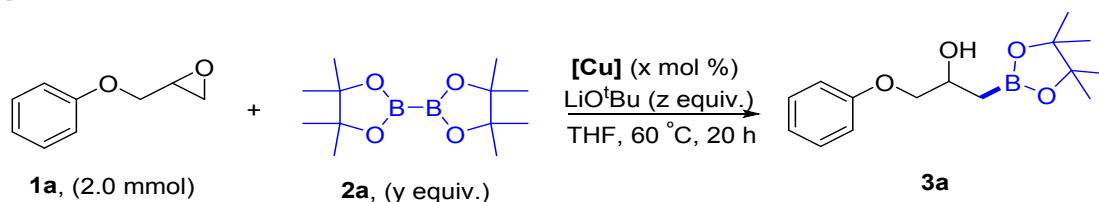
### Synthesis and characterization of epoxides

Epoxide substrates were prepared according to literature procedure, and NMR data have reported there.<sup>1-2</sup>

### III. General Experimental Procedures of Copper-Catalyzed Borylation Reactions of Epoxides with Diboron Reagents, Spectral Data and HPLC Analysis

#### Experimental Procedures for Examples Described in Table 1.

In air, schlenk tube was charged with Cu catalyst (0.03 mmol), base (0.6 mmol, 3 equiv.), and diboron reagent (0.6 mmol, 3 equiv.) which equipped with a stirring bar. The vessel was evacuated and refilled with argon three times. Under inert gas, 2-(phenoxy)methyl)oxirane substrate (0.2 mmol, 1 equiv.) and 1.0 mL of solvent were added. The resulting suspension was stirred for 20 h at 60 °C up to completion of reaction. Then 4 mL of H<sub>2</sub>O was added for reaction mixture, and extracted by EtOAc (3 x 5 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated and purified by thin layer chromatography plate over silic gel using petroleum ether/EtOAc (5/1, v/v) as eluent to obtain the  $\beta$ -hydroxyl boronic ester product.

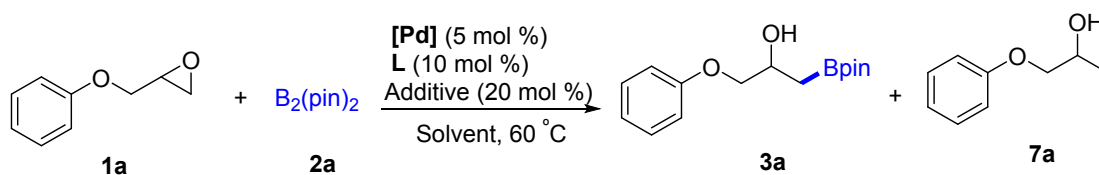


| Entry | [Cu] (x mol %) | B <sub>2</sub> pin <sub>2</sub> (y equiv.) | LiOtBu (z equiv.) | Yield (%) <sup>a</sup> |
|-------|----------------|--|-------------------|------------------------|
| 1     | (15)           | (1.5)                                      | (2.0)             | 43                     |
| 2     | (15)           | (2.0)                                      | (2.0)             | 54                     |
| 3     | (15)           | (3.0)                                      | (3.0)             | 85                     |
| 4     | (10)           | (3.0)                                      | (3.0)             | 60                     |
| 5     | (5)            | (3.0)                                      | (3.0)             | 26                     |
| 6     | -              | (3.0)                                      | (3.0)             | 0                      |

<sup>a</sup> Standard reaction conditions: epoxide (0.2 mmol), B<sub>2</sub>(pin)<sub>2</sub> reagent (y equiv.), CuI (x mol %), base (z equiv.), in 1 mL of THF at 60 °C for 20 h under Ar atmosphere. The yield was determined by GC (average of two GC runs) using diphenyl methanol as internal standard.

#### Experimental Procedures for Palladium-Catalyzed Borylation Reactions of Epoxides with Bis(pinacolato)diboron<sup>a</sup>

The reaction of epoxide **1a** with B<sub>2</sub>pin<sub>2</sub> **2a** was conducted according to procedure described in previous literature.<sup>3</sup>



| Entry             | [Pd]                               | Ligand                           | Solvent               | Additive | Yield (%) <sup>a</sup> | Yield (%) <sup>b</sup> |
|-------------------|------------------------------------|----------------------------------|-----------------------|----------|------------------------|------------------------|
|                   |                                    |                                  |                       |          | 3a                     | 7a                     |
| 1 <sup>c</sup>    | Pd(OAc) <sub>2</sub>               | P( <i>t</i> -Bu) <sub>2</sub> Me | MTBE/H <sub>2</sub> O | -        | 0                      | 0                      |
| 2                 | Pd <sub>2</sub> (dba) <sub>3</sub> | P( <i>t</i> -Bu) <sub>2</sub> Me | THF/H <sub>2</sub> O  | bpy      | 0                      | 0                      |
| 3                 | Pd <sub>2</sub> (dba) <sub>3</sub> | P( <i>t</i> -Bu) <sub>2</sub> Me | THF                   | bpy      | 0                      | 0                      |
| 4 <sup>d</sup>    | Pd <sub>2</sub> (dba) <sub>3</sub> | P( <i>t</i> -Bu) <sub>2</sub> Me | THF                   | -        | 0                      | 50                     |
| 5 <sup>d</sup>    | Pd <sub>2</sub> (dba) <sub>3</sub> | P( <i>t</i> -Bu) <sub>2</sub> Me | THF                   | bpy      | 0                      | 57                     |
| 6 <sup>d, e</sup> | Pd <sub>2</sub> (dba) <sub>3</sub> | P( <i>t</i> -Bu) <sub>2</sub> Me | THF                   | -        | 0                      | Trace                  |

<sup>a</sup> Standard reaction conditions: epoxide (0.1 mmol), B<sub>2</sub>(pin)<sub>2</sub> reagent (2.0 equiv.), Pd cat. (5 mol %), Ligand (10 mol %) in 0.6 mL of solvent (solvent/H<sub>2</sub>O = 12/1 v/v) at 60 °C from 3 up to 20 hrs under Ar atmosphere. <sup>b</sup> Yield represents isolated yield after purification by silica gel chromatography. <sup>c</sup> Pd<sub>2</sub>(dba)<sub>3</sub> was used instead of Pd(OAc)<sub>2</sub>, and same results were obtained. <sup>d</sup> (3 equiv.) of *t*-BuOLi was used. <sup>e</sup> (2 mol %/1 mol % of Pd<sub>2</sub>(dba)<sub>3</sub>/P(*t*-Bu)<sub>2</sub>Me was used. The yield was determined by GC using diphenyl methanol as internal standard. In entries (1, 2, 3) the recovery of substrate 1a was 80%. dba = dibenzylideneacetone, bpy = 2,2'-bipyridine.

### Experimental Procedures for Examples Described in Table 2.

In air, schlenk tube was charged with CuI (0.03 mmol), LiO<sup>t</sup>Bu (0.6 mmol, 3 equiv.), and diboron reagents (B<sub>2</sub>pin<sub>2</sub>, B<sub>2</sub>neop<sub>2</sub>) (0.6 mmol, 3 equiv.) which equipped with a stirring bar. The vessel was evacuated and refilled with argon three times. Oxirane substrate (0.2 mmol, 1 equiv.) and 1.0 mL of THF were added under inert gas. The reaction mixture was stirred for 20 hrs at 60 °C. After completing of reaction, 4 mL of H<sub>2</sub>O was added, and extracted by EtOAc (3 x 5 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated and purified by thin layer chromatography plate using petroleum ether/EtOAc (10/1 to 2/1, v/v) as eluent to afford the desired  $\beta$ -hydroxyl boronic ester products.

### Experimental Procedures for Examples Described in Scheme 2.

In air, the arylation reaction of  $\beta$ -hydroxyl boronic ester was performed according to previous literatures procedure with some modifications;<sup>4-7</sup> in schlenk tube which charged with Pd<sub>2</sub>(dba)<sub>3</sub> (0.005 mmol, 5 mol %), RuPhos (0.0075 mmol, 7.5 mol %), and KO<sup>t</sup>Bu (0.3 mmol, 3 equiv.). The vessel was evacuated and refilled with argon three times. Then THF (0.4 mL), toluene (0.5 mL) were added and the resulting mixture was stirred at room temperature for 10 min. Afterward,  $\beta$ -hydroxyl boronic ester (0.13 mmol) and haloaryls (0.1 mmol), and 0.1 mL of deionized H<sub>2</sub>O were added. The reaction mixture was stirred for 24 h at 70 °C up to end of reaction. 2 mL of H<sub>2</sub>O was added for reaction mixture which extracted by EtOAc (3 x 5 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated and purified by thin layer chromatography plate using petroleum ether/EtOAc (10/1 to 5/1, v/v) as eluent to afford the desired products.

### Experimental Procedures for Examples Described in Scheme 3.

In air, schlenk tube was charged with CuI (0.03 mmol), LiO<sup>t</sup>Bu (0.6 mmol, 3 equiv.), and bis(pinacolato)diboron (B<sub>2</sub>pin<sub>2</sub>) (0.6 mmol, 3 equiv.) which equipped with a stirring bar. The vessel was evacuated and refilled with argon three times. Under inert gas, benzyl epoxides (0.2 mmol, 1 equiv.) and 1.0 mL of THF were added. The reaction mixture was stirred for 20 hrs at 60 °C. After completing of reaction, the previously work-up was carried out and  $\beta$ -hydroxyl boronic ester was obtained as pure products using petroleum ether/EtOAc (5/1, v/v) as eluent.

- (I) The oxidation step of pinacolboronate alcohols (**3ba** & **3bb**) was performed for (0.2 mmol) scale according to previous literatures,<sup>2,8</sup> to afford 1,2-diol products which were purified by thin layer chromatography plate using petroleum ether/EtOAc (1/1, v/v).
- (II) The arylation reaction of pinacolboronate alcohols (**3ba** & **3bb**) was performed as followed; in 10 mL schlenk tube which charged with Pd<sub>2</sub>(dba)<sub>3</sub> (0.005 mmol, 5 mol %), RuPhos (0.0075 mmol, 7.5 mol %), and KO<sup>t</sup>Bu (0.3 mmol, 3 equiv.). The tube was evacuated and refilled with argon three times. THF (0.4 mL), toluene (0.5 mL) were added and the resulting mixture was stirred at room temperature for 10 min. Then borylated alcohol (0.13 mmol) and bromophenyl (0.1 mmol), and 0.1 mL of deionized H<sub>2</sub>O were added. The reaction mixture was stirred for 24 h at 70 °C up to end of reaction. Then the previous work-up was performed and the concentrated crude product was purified by thin layer chromatography plate using petroleum ether/EtOAc (5/1, v/v) as eluent to afford the desired products which subjected for HPLC analysis.
- (III) The enantiomeric purity of (S)-4-(benzyloxy)butane-1,3-diol and (S)-1-(benzyloxy)-3-phenylpropan-2-ol were determined by HPLC analysis (Chiralcel OD-H column, 90:10 hexanes/*i*-PrOH, 1.5 mL/min and 97:3 hexanes/*i*-PrOH, 1.0 mL/min respectively,  $\lambda$  = 210 nm).

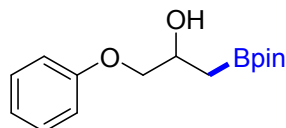
#### Experimental Procedures for Example Described in Scheme 4.

The Chan-Lam-Evans amination of  $\beta$ -hydroxyl boronic ester with *N*-methylaniline was conducted according to procedure described in previous literatures with some modifications.<sup>9-10</sup> 10 mL schlenk tube was charged by Cu(OAc)<sub>2</sub> (10 mol %, 0.02 mmol). The tube was evacuated and refilled with argon three times. Then  $\beta$ -hydroxyl boronic ester (1 equiv., 0.2 mmol), *N*-methylaniline (1.3 equiv. 0.26 mmol), and 0.5 mL of *m*-xylene were added. Under inert gas, di-*tert*-butyl peroxide (2 equiv., 0.4 mmol) was added to the mixture. The reaction mixture was stirred for 24 hrs at 100 °C up to end of reaction. Then the mixture was diluted with EtOAc and filtered through a pad of Celite and washed with EtOAc. Then concentrated under vacuo and purified by column chromatography using petroleum ether/EtOAc (5/1, v/v) to afford the desired product (25.4 mg, 49% yield) as brown oil.

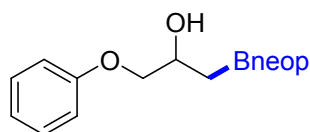
#### Experimental Procedures for Example Described in Scheme 5.

A gram-scale borylation reaction was performed in three-necked round-bottom flask which equipped with a stirring bar, CuI (0.15 mmol, 0.3 g), B<sub>2</sub>pin<sub>2</sub> (30 mmol, 7.6 g) LiO<sup>t</sup>Bu (30 mmol, 2.4 g), were put. The vessel was evacuated and refilled with argon three times. Under inert gas, epoxide substrate (10 mmol, 1 equiv.) and 50 mL of freshly distilled THF were added respectively. The resulting suspension was stirred for 20 h at 60 °C up to end of reaction. Thereafter, the work-up steps were conducted for the resulting reaction mixture, and the filtered crude product was concentrated under reduced pressure and then purified by flash column chromatography using petroleum ether/EtOAc (5/1, v/v) as eluent to afford the desired product (2.35 g, 85% yield).

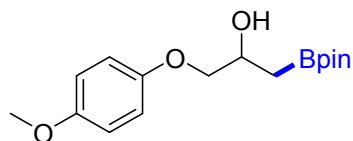
#### Scope of Epoxides


**1-phenoxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3a)**

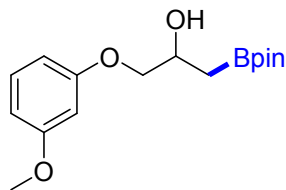
Following general procedure, (45.5 mg, 82% yield) as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 (t,  $J = 7.8$  Hz, 2H), 6.90 – 6.80 (m, 3H), 4.27 – 4.14 (m, 1H), 3.90 (dd,  $J = 9.4, 3.4$  Hz, 1H), 3.84 – 3.75 (m, 1H), 2.57 (br, 1H), 1.18 (s, 12H), 1.16 – 1.10 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.80, 129.54, 121.00, 114.75, 83.64, 73.31, 67.67, 24.91 (d,  $J = 3.7$  Hz), 16.55;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.28; HRMS calcd for  $\text{C}_{15}\text{H}_{23}\text{BO}_4[\text{H}]^+$ : 279.1762; found: 279.1750.


**1-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-3-phenoxypropan-2-ol (3b)**

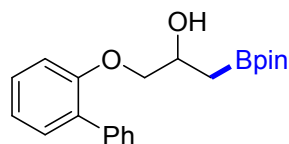
Following general procedure, (34.5 mg, 65% yield) as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.24 (m, 2H), 6.98 – 6.89 (m, 3H), 4.33 – 4.20 (m, 1H), 3.96 (dd,  $J = 9.4, 3.5$  Hz, 1H), 3.90 – 3.83 (m, 1H), 3.62 (s, 4H), 2.66 (br, 1H), 1.13 (d,  $J = 6.7$  Hz, 2H), 0.98 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.88, 129.53, 120.93, 114.73, 73.51, 72.16, 67.96, 31.82, 21.93, 19.78;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.74; HRMS calcd for  $\text{C}_{14}\text{H}_{21}\text{BO}_4[\text{H}]^+$ : 265.1606; found: 265.15912.


**1-(4-methoxyphenoxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3c)**

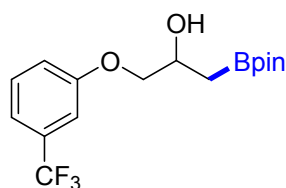
Following general procedure, (33.8 mg, 55% yield) as a colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 – 6.78 (m, 4H), 4.30 – 4.17 (m, 1H), 3.92 (dd,  $J = 9.4, 3.5$  Hz, 1H), 3.86 – 3.78 (m, 1H), 3.76 (s, 3H), 2.38 (br, 1H), 1.26 (s, 12H), 1.23 – 1.15 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  154.08, 153.04, 115.81, 114.74, 83.63, 74.26, 67.76, 55.84, 24.93 (d,  $J = 2.3$  Hz), 16.70;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.30; HRMS calcd for  $\text{C}_{16}\text{H}_{25}\text{BO}_5[\text{H}]^+$ : 309.1868; found: 309.18601.


**1-(3-methoxyphenoxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3d)**

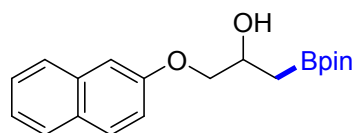
Following general procedure, (40 mg, 65% yield) as a colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 (t,  $J = 8.1$  Hz, 1H), 6.56 – 6.46 (m, 3H), 4.33 – 4.18 (m, 1H), 3.96 (dd,  $J = 9.4, 3.4$  Hz, 1H), 3.89 – 3.81 (m, 1H), 3.78 (s, 3H), 2.61 (br, 1H), 1.27 (s, 12H), 1.20 (d,  $J = 6.9$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  160.93, 160.10, 129.98, 106.91, 106.66, 101.28, 83.66, 73.42, 67.65, 55.38, 24.93 (d,  $J = 3.0$  Hz), 16.64;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.30; HRMS calcd for  $\text{C}_{16}\text{H}_{25}\text{BO}_5[\text{H}]^+$ : 309.1868; found: 309.18603.


**1-([1,1'-biphenyl]-2-yloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3e)**

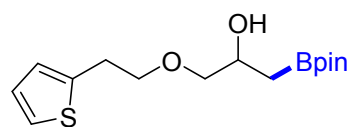
Following general procedure, (51.5 mg, 73% yield) as a colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.48 (m, 2H), 7.40 (t,  $J$  = 7.4 Hz, 2H), 7.35 – 7.24 (m, 3H), 7.09 – 6.94 (m, 2H), 4.22 – 4.08 (m, 1H), 4.07 – 3.91 (m, 1H), 3.88 – 3.74 (m, 1H), 2.41 (br, 1H), 1.25 (s, 12H), 1.16 – 1.05 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.61, 138.56, 131.46, 131.01, 129.55, 128.73, 128.17, 127.07, 121.51, 113.39, 83.56, 74.31, 67.56, 24.90 (d,  $J$  = 4.8 Hz), 16.47;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.34; HRMS calcd for  $\text{C}_{21}\text{H}_{27}\text{BO}_4[\text{H}]^+$ : 355.2075; found: 355.2068.


**1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(3-(trifluoromethyl)phenoxy)propan-2-ol (3f)**

Following general procedure, (47 mg, 68% yield) as light brown oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.34 (m, 1H), 7.24 – 7.18 (m, 1H), 7.18 – 7.06 (m, 2H), 4.35 – 4.21 (m, 1H), 4.02 (dd,  $J$  = 9.5, 3.4 Hz, 1H), 3.96 – 3.84 (m, 1H), 2.47 (br, 1H), 1.27 (s, 12H), 1.24 – 1.20 (m, 2H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.68 (s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.00, 131.95 (q,  $J$  = 32.2 Hz), 130.09, 124.07 (d,  $J$  = 272.3 Hz), 118.33 (d,  $J$  = 0.8 Hz), 117.72 (q,  $J$  = 3.8 Hz), 111.56 (t,  $J$  = 3.8 Hz), 83.77, 73.67, 67.53, 24.92 (d,  $J$  = 3.1 Hz), 16.63;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.24; HRMS calcd for  $\text{C}_{16}\text{H}_{22}\text{BF}_3\text{O}_4[\text{H}]^+$ : 347.1636; found: 347.1626.

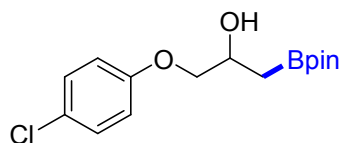

**1-(naphthalen-2-yloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3g)**

Following general procedure, (47.1 mg, 72% yield) as a colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 – 7.67 (m, 3H), 7.43 (t,  $J$  = 7.4 Hz, 1H), 7.38 – 7.28 (m, 1H), 7.26 – 7.11 (m, 2H), 4.47 – 4.26 (m, 1H), 4.09 (dd,  $J$  = 9.5, 3.4 Hz, 1H), 4.04 – 3.94 (m, 1H), 2.48 (br, 1H), 1.27 (s, 12H), 1.25 – 1.21 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  156.72, 134.56, 129.44, 129.10, 127.68, 126.81, 126.40, 123.71, 118.96, 106.99, 83.62, 73.41, 67.58, 24.87 (d,  $J$  = 3.6 Hz), 16.86;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.28; HRMS calcd for  $\text{C}_{19}\text{H}_{25}\text{BO}_4[\text{H}]^+$ : 329.1919; found: 329.1912.


**1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(2-(thiophen-2-yl)ethoxy)propan-2-ol (3h)**

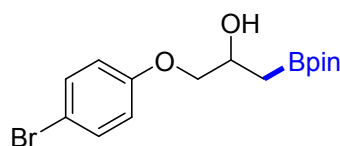
Following general procedure, (34.5 mg, 55% yield) as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13 (d,  $J$  = 4.7 Hz, 1H), 6.96 – 6.89 (m, 1H), 6.87 – 6.80 (m, 1H), 4.13 – 3.99 (m, 1H), 3.78 – 3.63 (m, 2H), 3.49 (dd,  $J$  = 9.5, 3.2 Hz, 1H), 3.37 – 3.29 (m, 1H), 3.10 (t,  $J$  = 6.7 Hz, 2H), 2.63 (br, 1H), 1.25 (s, 12H), 1.14 – 0.99 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.33, 126.79, 125.26, 123.82, 83.50,

76.62, 71.82, 67.89, 30.52, 24.91 (d,  $J = 5.5$  Hz), 16.60;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.21; HRMS calcd for  $\text{C}_{15}\text{H}_{25}\text{BO}_4\text{S}[\text{H}]^+$ : 313.1639; found: 313.1634.



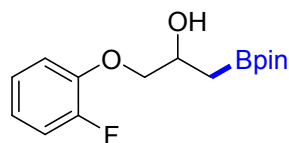
**1-(4-chlorophenoxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3i)**

Following general procedure, (49.8 mg, 80% yield) as pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 – 7.18 (m, 2H), 6.90 – 6.78 (m, 2H), 4.31 – 4.20 (m, 1H), 3.98 – 3.90 (m, 1H), 3.88 – 3.81 (m, 1H), 2.72 (br, 1H), 1.26 (s, 12H), 1.22 – 1.17 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.47, 129.41, 125.86, 116.05, 83.71, 73.73, 67.57, 24.92 (d,  $J = 4.1$  Hz), 16.64;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.25; HRMS calcd for  $\text{C}_{15}\text{H}_{22}\text{BClO}_4[\text{H}]^+$ : 313.1372; found: 313.1365.



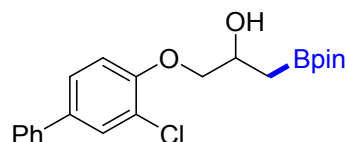
**1-(4-bromophenoxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3j)**

Following general procedure, (42.6 mg, 60% yield) as a colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.32 (m, 2H), 6.87 – 6.75 (m, 2H), 4.32 – 4.20 (m, 1H), 3.94 (dd,  $J = 9.4, 3.5$  Hz, 1H), 3.88 – 3.80 (m, 1H), 2.01 (br, 1H), 1.27 (s, 12H), 1.23 – 1.17 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  158.03, 132.39, 116.64, 113.23, 83.75, 73.72, 67.62, 24.96 (d,  $J = 2.9$  Hz);  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.53; HRMS calcd for  $\text{C}_{15}\text{H}_{22}\text{BBrO}_4[\text{H}]^+$ : 357.0867; found: 357.0848.



**1-(2-fluorophenoxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3k)**

Following general procedure, (37 mg, 63% yield) as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12 – 6.96 (m, 3H), 6.95 – 6.85 (m, 1H), 4.35 – 4.23 (m, 1H), 4.04 (dd,  $J = 9.2, 2.6$  Hz, 1H), 3.98 – 3.89 (m, 1H), 2.71 (br, 1H), 1.26 (s, 12H), 1.21 (d,  $J = 6.4$  Hz, 2H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -134.14 – -134.39 (m);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.96 (d,  $J = 245.7$  Hz), 146.96 (d,  $J = 10.6$  Hz), 124.38 (d,  $J = 3.9$  Hz), 121.56 (d,  $J = 6.8$  Hz), 116.38 (d,  $J = 18.2$  Hz), 115.60 (d,  $J = 1.5$  Hz), 83.68, 74.97, 67.62, 24.93 (d,  $J = 4.3$  Hz), 16.55;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.22; HRMS calcd for  $\text{C}_{15}\text{H}_{22}\text{BFO}_4[\text{H}]^+$ : 297.1668; found: 297.1660.

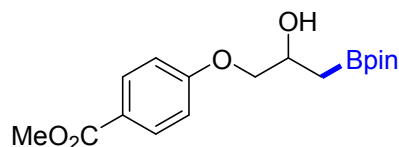


**1-((3-chloro-[1,1'-biphenyl]-4-yl)oxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3l)**

Following general procedure, (58.4 mg, 75% yield) as light yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.58 (m, 1H), 7.56 – 7.50 (m, 2H), 7.46 – 7.39 (m, 3H), 7.37 – 7.29 (m, 1H), 7.04 – 6.99 (m, 1H), 4.40 – 4.27 (m, 1H), 4.09 (dd,  $J = 9.3, 3.4$  Hz, 1H), 4.00 – 3.92 (m, 1H), 2.81 (br, 1H), 1.27 (s, 12H), 1.25 – 1.21 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  153.64, 139.54, 135.13, 128.85, 128.84,

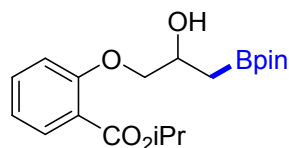


127.25, 126.74, 126.23, 123.53, 114.18, 83.58, 74.75, 67.47, 24.83 (d,  $J = 3.7$  Hz), 16.43;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.68; HRMS calcd for  $\text{C}_{21}\text{H}_{26}\text{BClO}_4[\text{H}]^+$ : 389.1685 found: 389.1657.



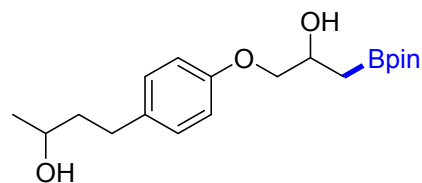
**Methyl 4-(2-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)benzoate (3m)**

Following general procedure, (39 mg, 58% yield) as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 – 7.95 (m, 2H), 6.99 – 6.90 (m, 2H), 4.34 – 4.24 (m, 1H), 4.03 (dd,  $J = 9.5, 3.4$  Hz, 1H), 3.97 – 3.91 (m, 1H), 3.88 (s, 3H), 2.70 (br, 1H), 1.27 (s, 12H), 1.24 – 1.20 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.98, 162.62, 131.70, 122.87, 114.35, 83.77, 73.48, 67.53, 52.01, 24.93 (d,  $J = 4.4$  Hz), 16.68;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.40; HRMS calcd for  $\text{C}_{17}\text{H}_{25}\text{BO}_6[\text{H}]^+$ : 337.1817; found: 337.1817.



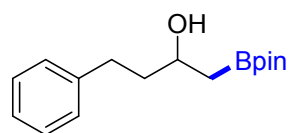
**Isopropyl 2-(2-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)benzoate (3n)**

Following general procedure, (29.3 mg, 40% yield) as pale green oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 – 7.75 (m, 1H), 7.48 – 7.40 (m, 1H), 7.04 – 6.94 (m, 2H), 5.32 – 5.19 (m, 1H), 4.32 – 4.17 (m, 2H), 3.89 – 3.78 (m, 1H), 2.88 (br, 1H), 1.36 (d,  $J = 6.3$  Hz, 6H), 1.26 (s, 12H), 1.18 – 1.06 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.04, 158.85, 133.53, 131.73, 121.32, 120.93, 114.93, 83.53, 75.57, 68.52, 67.28, 24.93 (d,  $J = 5.6$  Hz), 22.04 (d,  $J = 1.7$  Hz), 16.23;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.23; HRMS calcd for  $\text{C}_{19}\text{H}_{29}\text{BO}_6[\text{H}]^+$ : 365.2130; found: 365.2127.



**4-(4-(2-hydroxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)phenyl)butan-2-ol (3o)**

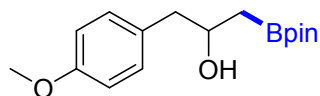
Following general procedure, (34.8 mg, 50% yield) as a colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17 – 7.04 (m, 2H), 6.92 – 6.79 (m, 2H), 4.33 – 4.12 (m, 1H), 4.00 – 3.89 (m, 1H), 3.88 – 3.72 (m, 2H), 2.77 – 2.53 (m, 2H), 1.88 (br 2H), 1.79 – 1.68 (m, 2H), 1.27 (s, 12H), 1.24 – 1.15 (m, 5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  157.06, 134.50, 129.38, 114.77, 83.66, 73.52, 67.73, 67.60, 41.16, 31.33, 24.94 (d,  $J = 2.4$  Hz), 23.73, 16.69;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.35; HRMS calcd for  $\text{C}_{19}\text{H}_{31}\text{BO}_5[\text{H}]^+$ : 351.2337; found: 351.2328.



**4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (3p)**

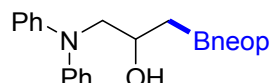
Following general procedure, (36 mg, 65% yield) as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.25 (m, 2H), 7.23 – 7.13 (m, 3H), 3.95 – 3.82 (m, 1H), 2.85 – 2.74 (m, 1H), 2.72 – 2.61 (m, 1H), 2.00 (br, 1H), 2.00 (br, 1H), 1.85 – 1.70 (m, 2H), 1.26 (s, 12H), 1.18 (dd,  $J = 16.1, 4.8$  Hz, 1H), 1.12 – 1.04 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.51, 128.57, 128.46, 125.80, 83.58, 68.64, 41.31,

32.39, 24.96 (d,  $J = 2.2$  Hz), 21.27;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.60; HRMS calcd for  $\text{C}_{16}\text{H}_{25}\text{BO}_3[\text{H}]^+$ : 277.1970; found: 277.1958.



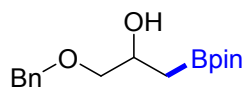
**1-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3q)**

Following general procedure, (40.9 mg, 70% yield) as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 – 7.10 (m, 2H), 6.87 – 6.80 (m, 2H), 4.04 (ddd,  $J = 13.1, 7.1, 5.6$  Hz, 1H), 3.79 (s, 3H), 2.80 – 2.64 (m, 2H), 2.23 (br, 1H), 1.26 (s, 12H), 1.16 – 1.04 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.27, 131.07, 130.55, 113.95, 83.53, 70.43, 55.39, 45.09, 24.96 (d,  $J = 4.5$  Hz);  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.55; HRMS calcd for  $\text{C}_{16}\text{H}_{25}\text{BO}_4[\text{H}]^+$ : 293.1919; found: 293.1919.



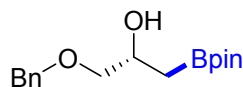
**1-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-3-(diphenylamino)propan-2-ol (3r)**

Following general procedure, (60.2 mg, 89% yield) as light brown oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.21 (m, 4H), 7.11 – 7.04 (m, 4H), 6.94 (t,  $J = 7.3$  Hz, 2H), 4.24 – 4.15 (m, 1H), 3.83 (dd,  $J = 14.8, 3.9$  Hz, 1H), 3.69 – 3.64 (m, 1H), 3.60 (s, 4H), 2.59 (br, 1H), 1.09 – 1.01 (m, 2H), 0.96 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.72, 129.35, 121.57, 121.44, 72.15, 66.96, 60.69, 31.83, 21.96;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.66; HRMS calcd for  $\text{C}_{20}\text{H}_{26}\text{BNO}_3[\text{H}]^+$ : 340.2079; found: 340.2074.



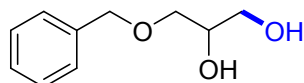
**1-(benzyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3ba)**

Following general procedure, (42.5 mg, 73% yield) as a colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.25 (m, 5H), 4.56 (s, 2H), 4.20 – 4.00 (m, 1H), 3.53 – 3.44 (m, 1H), 3.40 – 3.28 (m, 1H), 2.67 (br, 1H), 1.23 (s, 12H), 1.13 – 1.02 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  138.33, 128.49, 127.81, 127.74, 83.47, 75.80, 73.23, 68.07, 24.88 (d,  $J = 2.3$  Hz), 16.88;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.32; HRMS calcd for  $\text{C}_{16}\text{H}_{25}\text{BO}_4[\text{H}]^+$ : 293.1919; found: 293.1917.



**(S)-1-(benzyloxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-ol (3bb)**

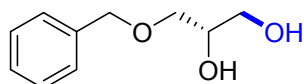
Following general procedure, (44.2 mg, 76% yield) as a colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.26 (m, 5H), 4.56 (s, 2H), 4.18 – 4.01 (m, 1H), 3.54 – 3.42 (m, 1H), 3.40 – 3.27 (m, 1H), 2.65 (br, 1H), 1.25 (s, 12H), 1.14 – 1.02 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  138.35, 128.52, 127.83, 127.76, 83.49, 75.83, 73.26, 68.10, 24.90 (d,  $J = 2.3$  Hz), 16.85;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  33.20; HRMS calcd for  $\text{C}_{16}\text{H}_{25}\text{BO}_4[\text{H}]^+$ : 293.1919; found: 293.1912.



**3-(benzyloxy)propane-1,2-diol (3bc)**

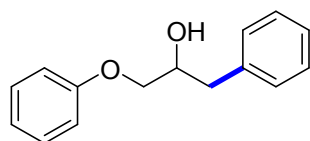
Following general procedure, (26.5 mg, 73% yield) as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.27 (m, 5H), 4.54 (s, 2H), 3.93 – 3.84 (m, 1H), 3.68 (dd,  $J = 11.5, 3.7$  Hz, 1H), 3.64 – 3.57 (m,

1H), 3.57 – 3.48 (m, 2H), 2.93 (br, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.77, 128.62, 128.03, 127.93, 73.67, 71.84, 70.80, 64.12; HRMS calcd for C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>[H]<sup>+</sup>: 183.1016; found: 183.1007.



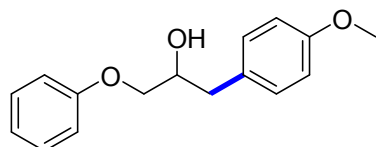
**(S)-3-(benzyloxy)propane-1,2-diol (3bd)**

Following general procedure, (29 mg, 80% yield) as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.27 (m, 5H), 4.55 (s, 2H), 3.95 – 3.86 (m, 1H), 3.70 (dd, *J* = 11.4, 3.8 Hz, 1H), 3.66 – 3.59 (m, 1H), 3.59 – 3.50 (m, 2H), 2.39 (br, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.76, 128.65, 128.07, 127.94, 73.72, 71.92, 70.74, 64.18; HRMS calcd for C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>[H]<sup>+</sup>: 183.1016; found: 183.1008.



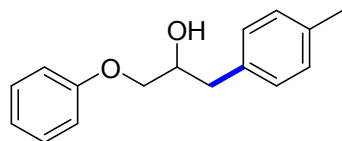
**1-phenoxy-3-phenylpropan-2-ol (4a)**

Following general procedure, (14.5 mg, 64% yield) as pale yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.18 (m, 7H), 7.01 – 6.84 (m, 3H), 4.29 – 4.15 (m, 1H), 3.95 (dd, *J* = 9.4, 3.7 Hz, 1H), 3.87 (dd, *J* = 9.3, 6.6 Hz, 1H), 2.98 – 2.87 (m, 2H), 2.21 (br, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 158.63, 137.68, 129.63, 129.50, 128.72, 126.74, 121.27, 114.71, 71.19, 71.04, 39.97; HRMS calcd for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>[H]<sup>+</sup>: 229.1223; found: 229.1227.



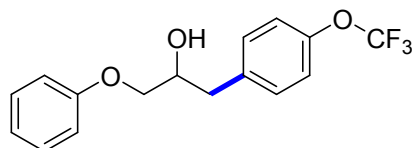
**1-(4-methoxyphenyl)-3-phenoxypropan-2-ol (4b)**

Following general procedure, (17.6 mg, 68% yield) as pale white solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.25 (m, 2H), 7.22 – 7.15 (m, 2H), 7.02 – 6.83 (m, 5H), 4.26 – 4.15 (m, 1H), 3.97 (dd, *J* = 9.4, 3.6 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.80 (s, 3H), 2.96 – 2.82 (m, 2H), 1.92 (br, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 158.69, 158.53, 130.48, 129.65, 129.59, 121.28, 114.75, 114.20, 71.33, 71.06, 55.40, 39.06; HRMS calcd for C<sub>16</sub>H<sub>18</sub>O<sub>3</sub>[H]<sup>+</sup>: 259.1329; found: 259.1323.

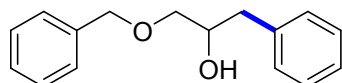


**1-phenoxy-3-(p-tolyl)propan-2-ol (4c)**

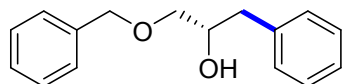
Following general procedure, (13.2 mg, 55% yield) as pale yellow solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.23 (m, 2H), 7.19 – 7.09 (m, 4H), 7.00 – 6.86 (m, 3H), 4.27 – 4.16 (m, 1H), 3.97 (dd, *J* = 9.4, 3.6 Hz, 1H), 3.93 – 3.85 (m, 1H), 2.96 – 2.86 (m, 2H), 2.33 (s, 3H), 1.88 (br, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 158.69, 136.34, 134.48, 129.64, 129.46, 129.39, 121.27, 114.75, 71.29, 71.09, 39.55, 21.17; HRMS calcd for C<sub>16</sub>H<sub>18</sub>O<sub>2</sub>[H]<sup>+</sup>: 243.1380; found: 243.1377.


**1-phenoxy-3-(4-(trifluoromethoxy)phenyl)propan-2-ol (4d)**

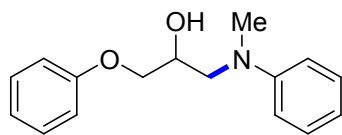
Following general procedure, (13.8 mg, 44% yield) as offwhite solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.24 (m, 4H), 7.20 – 7.13 (m, 2H), 6.98 (t,  $J = 7.3$  Hz, 1H), 6.93 – 6.87 (m, 2H), 4.29 – 4.16 (m, 1H), 3.98 (dd,  $J = 9.3, 3.5$  Hz, 1H), 3.93 – 3.85 (m, 1H), 3.01 – 2.88 (m, 2H), 1.63 (br, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.88 (s);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.52, 148.14, 148.13, 136.57, 130.83, 129.72, 121.46, 121.25, 114.71, 71.04, 70.99, 39.19; HRMS calcd for  $\text{C}_{16}\text{H}_{15}\text{F}_3\text{O}_3[\text{H}]^+$ : 313.1046; found: 313.1041.


**1-(benzyloxy)-3-phenylpropan-2-ol (5a)**

Following general procedure, (13.5 mg, 56% yield) as pale yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.26 (m, 7H), 7.25 – 7.17 (m, 3H), 4.60 – 4.50 (m, 2H), 4.12 – 4.00 (m, 1H), 3.52 (dd,  $J = 9.5, 3.5$  Hz, 1H), 3.45 – 3.34 (m, 1H), 2.86 – 2.76 (m, 2H), 1.88 (br, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  138.09, 138.08, 129.48, 128.62, 128.61, 127.95, 127.92, 126.59, 73.67, 73.55, 71.56, 40.03; HRMS calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_2[\text{H}]^+$ : 243.1380; found: 243.1380.

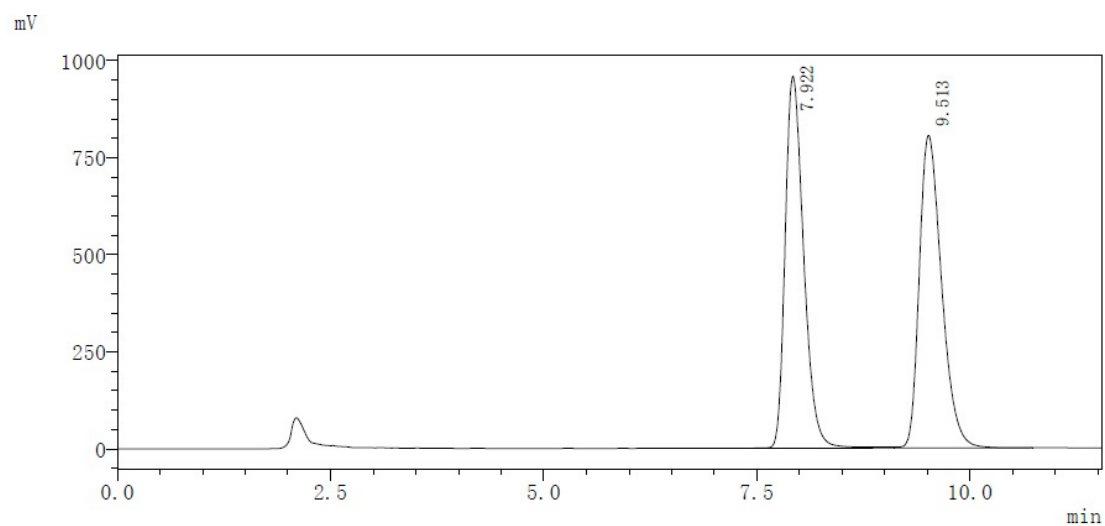
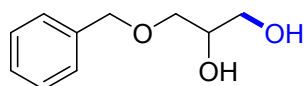

**(S)-1-(benzyloxy)-3-phenylpropan-2-ol (5b)**

Following general procedure, (13.8 mg, 57% yield) as pale yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.26 (m, 7H), 7.25 – 7.16 (m, 3H), 4.60 – 4.48 (m, 2H), 4.11 – 3.98 (m, 1H), 3.51 (dd,  $J = 9.5, 3.5$  Hz, 1H), 3.45 – 3.34 (m, 1H), 2.87 – 2.75 (m, 2H), 2.05 (br, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  138.09, 138.08, 129.47, 128.61, 128.60, 127.94, 127.92, 126.58, 73.66, 73.53, 71.56, 40.03; HRMS calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_2[\text{H}]^+$ : 243.1380; found: 243.1366.

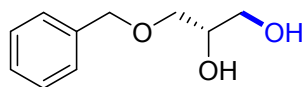

**1-(methyl(phenyl)amino)-3-phenoxypropan-2-ol (6a)**

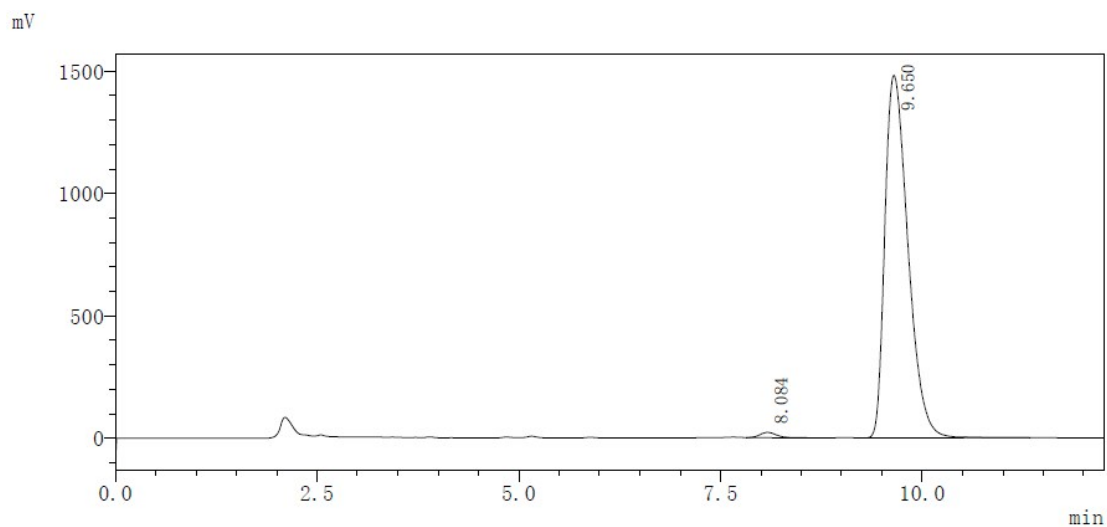
Following general procedure,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.19 (m, 4H), 7.02 – 6.94 (m, 1H), 6.94 – 6.89 (m, 2H), 6.84 – 6.78 (m, 2H), 6.78 – 6.71 (m, 1H), 4.35 – 4.24 (m, 1H), 4.05 (dd,  $J = 9.5, 4.0$  Hz, 1H), 3.99 (dd,  $J = 9.5, 5.4$  Hz, 1H), 3.57 – 3.49 (m, 2H), 2.99 (s, 3H), 2.52 (br, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  158.57, 149.83, 129.69, 129.41, 121.41, 117.43, 114.72, 112.98, 69.72, 68.32, 56.17, 39.64; HRMS calcd for  $\text{C}_{16}\text{H}_{19}\text{NO}_2[\text{H}]^+$ : 258.1489; found: 258.1481.

## HPLC Analysis

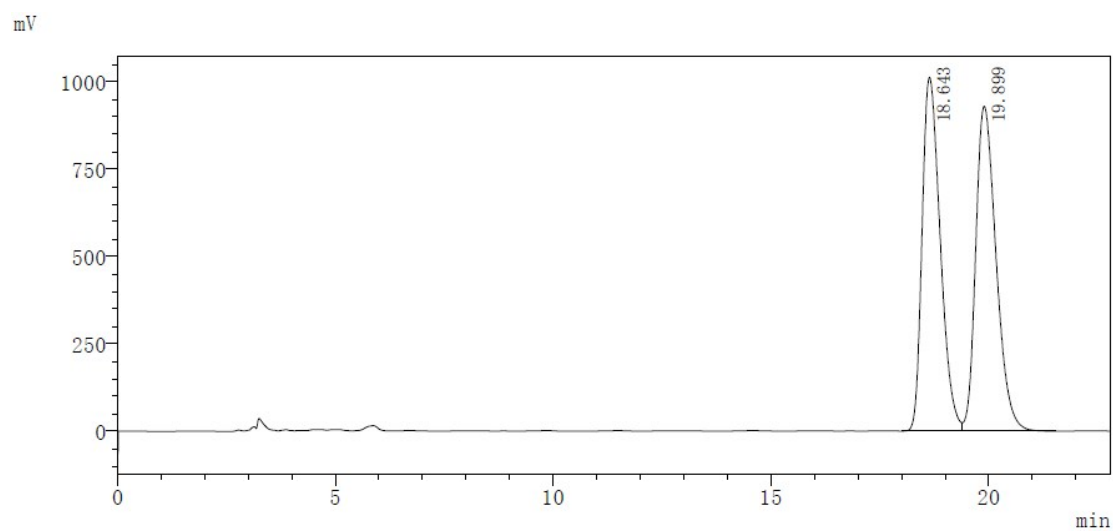
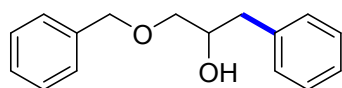


| Peak | Ret. Time (min) | Area ((mAu*s) | Height (mAU) | Area % |
|------|-----------------|---------------|--------------|--------|
| 1    | 7.922           | 14497776      | 958168       | 49.710 |
| 2    | 9.513           | 14666930      | 805137       | 50.290 |

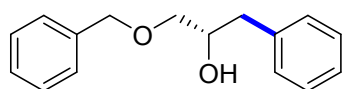


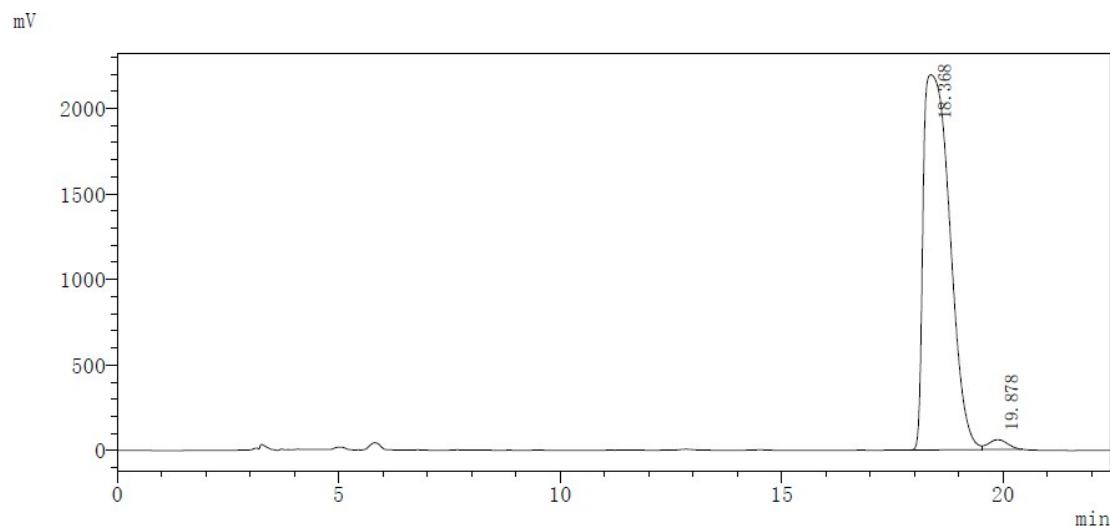


| Peak | Ret. Time (min) | Area ((mAu*s) | Height (mAU) | Area % |
|------|-----------------|---------------|--------------|--------|
| 1    | 8.084           | 311669        | 21517        | 1.046  |
| 2    | 9.650           | 29498319      | 1481655      | 98.954 |



| Peak | Ret. Time (min) | Area ((mAu*s) | Height (mAU) | Area % |
|------|-----------------|---------------|--------------|--------|
| 1    | 18.643          | 29323333      | 1012177      | 49.190 |
| 2    | 19.899          | 30288865      | 929767       | 50.810 |





| Peak | Ret. Time (min) | Area ((mAU*s) | Height (mAU) | Area % |
|------|-----------------|---------------|--------------|--------|
| 1    | 18.368          | 90180088      | 2185906      | 99.037 |
| 2    | 19.878          | 877158        | 38687        | 0.963  |

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## NMR Spectra

