Supporting Information

Table of Contents

I. General Information ................................................................. S2

II. Preparation of Substrates ......................................................... S3-S7
   a. Preparation of Organoboronates ........................................ S3
   b. Preparation of Epoxides .................................................. S6

III. General Experimental Procedures, Spectral Data and HPLC Analysis ........................................... S8-S19

IV. References ................................................................................ S19

V. NMR Spectra ............................................................................. S21-S55
I. General Information

a). Materials

All the reactions were carried out in oven-dried schlenk tubes under argon atmosphere (purity ≥99.999%). Copper(I) iodide was purchased from Sinopharm Chemical Reagent Co., Ltd as a off-white powder and refluxed in THF for further purification. The following chemicals were purchased and used as received: LiO\textsubscript{t}Bu(99.9%, Acros), KI(Sinopharm Chemical Reagent Co), K\textsubscript{t}Bu(Acros), NaOtBu(Acros), Arylboronic Acids(Alfa-Aesa or J&K), 1,2-Epoxyoctane(alfa,97%) 1,3-diphenylpropane-1,3-dione(95%, 9 Ding Chemistry), 2-(phenoxymethyl)oxirane(adamas,98%), 2-((benzylxy)methyl)oxirane(adamas,98%), (S)-2-((benzyloxy)methyl)oxirane(adamas,98%), tricyclohexylphosphine(98%, Sinocompound), triphenylphosphine(98%, Sinocompound), 4,4'-dimethoxy-2,2'-bipyridine(TCI), 4,7-diphenyl-1,10-phenanthroline(TCI), 2-isobutyrylcyclohexanone, xantphos(Acros), TMEDA(Sinopharm Chemical Reagent Co), Pybox(TCI).

Anhydrous DMF (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

\textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR and \textsuperscript{19}F-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in CDCl\textsubscript{3} unless otherwise noted; Data for \textsuperscript{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for \textsuperscript{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (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 Finnigan LCQ advantage Max Series MS System. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IC, AD, 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

a). Synthesis and characterization of organoboronates

Organoboronates were prepared according to literature procedure\textsuperscript{[1-5]}; Organoboronates were prepared from organoboronic acids and 2,2-dimethyl-1,3-propa-nediol in toluene.

\[
R - B(OH)_2 + HO\text{-}\text{DMPD} \xrightarrow{\text{Toluene, reflux, Dean-stark Trap}} R - B(OH)\text{O-DMPD}
\]

1 equiv 1.2 equiv

Characterization of organoboronates:

5, 5-dimethyl-2-phenyl-1,3,2-dioxaborinane (CAS: 5123-13-7)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.93–7.71 (m, 2H), 7.45–7.39 (m, 1H), 7.38–7.32 (m, 2H), 3.76 (s, 4H), 1.02 (s, 6H). \( ^13C \) NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 133.94, 130.80, 127.70, 72.41, 32.00, 22.02.

5,5-dimethyl-2-(p-tolyl)-1,3,2-dioxaborinane (CAS: 380481-66-3)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.69 (d, \( J = 7.9 \) Hz, 2H), 7.17 (d, \( J = 7.6 \) Hz, 2H), 3.76 (s, 4H), 2.36 (s, 3H), 1.01 (s, 6H). \( ^13C \) NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 140.71, 133.90, 128.43, 72.29, 31.91, 21.93, 21.69.

2-(4-bromophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (CAS: 183677-71-6)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.65 (d, \( J = 8.2 \) Hz, 2H), 7.51 – 7.43 (m, 2H), 3.75 (s, 4H), 1.01 (s, 6H). \( ^13C \) NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 135.50, 130.79, 125.59, 72.33, 31.90, 21.90.

5,5-dimethyl-2-(3-(trifluoromethoxy)phenyl)-1,3,2-dioxaborinane (CAS: 635305-40-7)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.71 (d, \( J = 7.3 \) Hz, 1H), 7.63 (s, 1H), 7.37 (t, \( J = 7.7 \) Hz, 1H), 7.30 – 7.23 (m, 1H), 3.77 (s, 4H), 1.02 (s, 6H).

3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-N,N-dimethylaniline (CAS: 1352304-48-3)
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 – 7.20 (m, 2H), 7.18 (d, $J$ = 7.1 Hz, 1H), 6.84 (dd, $J$ = 8.0, 2.0 Hz, 1H), 3.76 (s, 4H), 2.95 (s, 6H), 1.01 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.13, 128.40, 122.52, 118.04, 115.45, 72.32, 40.89, 31.90, 21.97.

2-(benzo[d][1,3]dioxol-5-yl)-5,5-dimethyl-1,3,2-dioxaborinane (CAS: 94838-83-2)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (dd, $J$ = 7.8, 0.9 Hz, 1H), 7.25 (d, $J$ = 5.7 Hz, 1H), 6.82 (d, $J$ = 7.8 Hz, 1H), 5.94 (s, 2H), 3.74 (s, 4H), 1.01 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.70, 147.16, 128.53, 113.23, 108.11, 100.63, 72.29, 31.89, 21.97.

5,5-dimethyl-2-(o-tolyl)-1,3,2-dioxaborinane (CAS: 91994-11-5)

Following general procedure. Purification by silica gel column chromatography gave the product as a colourless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J$ = 7.3 Hz, 1H), 7.35 – 7.25 (m, 1H), 7.15 (t, $J$ = 7.4 Hz, 2H), 3.77 (s, 4H), 2.51 (s, 3H), 1.03 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.97, 134.85, 130.6 (q, $J$ = 3.6 Hz), 129.98, 124.70, 122.43, 31.67, 22.43, 21.92.

5,5-dimethyl-2-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborinane (CAS: 635305-32-7)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (s, 1H), 7.97 (d, $J$ = 7.4 Hz, 1H), 7.66 (d, $J$ = 7.8 Hz, 1H), 7.45 (t, $J$ = 7.4 Hz, 1H), 3.78 (s, 4H), 3.78 (s, 4H), 1.02 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.1, 130.6 (q, $J$ = 3.6 Hz), 129.9 (q, $J$ = 33 Hz), 127.9, 127.2 (q, $J$ = 3.7 Hz), 125.9, 123.1, 72.4, 31.9, 21.9.

2-(furan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (CAS: 941320-88-3)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (s, 1H), 6.98 (d, $J$ = 3.3 Hz, 1H), 6.42 (dd, $J$ = 3.1, 1.4 Hz, 1H), 3.76 (s, 4H), 1.03 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.64, 121.47, 110.20, 72.29, 32.11, 21.88.

2-(3-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (CAS: 585524-80-7)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 1.5 Hz, 1H), 7.65 (d, $J$ = 7.3 Hz, 1H), 7.39 (m, 1H), 7.28 (t, $J$ = 5.9 Hz, 1H), 3.77 (s, 4H), 1.02 (s, 6H).
methyl 3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (CAS: 585524-77-2)
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.47\) (s, 1H), \(8.22 - 8.05\) (m, 1H), \(7.98\) (d, \(J = 7.4\) Hz, 1H), \(7.43\) (t, \(J = 7.6\) Hz, 1H), \(3.91\) (s, 3H), \(3.78\) (s, 4H), \(1.03\) (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 167.41, 138.33, 135.00, 131.78, 129.39, 127.68, 72.36, 52.01, 31.92, 21.89.

2-(4-(allyloxy)phenyl)-5,5-dimethyl-1,3,2-dioxaborinane (CAS: 1622082-57-8)
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.84 - 7.62\) (m, 2H), \(6.95 - 6.74\) (m, 2H), \(6.13 - 5.88\) (m, 1H), \(5.53 - 5.36\) (m, 1H), \(5.32 - 5.18\) (m, 1H), \(4.77 - 4.36\) (m, 2H), \(3.75\) (s, 4H), \(1.01\) (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 160.77, 135.50, 133.22, 117.68, 113.91, 72.27, 68.53, 31.91, 21.94.

3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzonitrile (CAS: 214360-45-9)
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.09\) (s, 1H), \(8.00\) (dd, \(J = 7.5, 1.1\) Hz, 1H), \(7.69\) (m, 1H), \(7.45\) (t, \(J = 7.6\) Hz, 1H), \(3.78\) (s, 4H), \(1.03\) (s, 6H).

2-(3-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (CAS: 1003858-50-1)
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.39\) (d, \(J = 7.2\) Hz, 1H), \(7.33\) (d, \(J = 2.6\) Hz, 1H), \(7.28 - 7.22\) (m, 1H), \(7.00 - 6.92\) (m, 1H), \(3.82\) (s, 3H), \(3.77\) (s, 4H), \(1.02\) (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 159.15, 128.89, 126.37, 118.00, 117.38, 72.44, 55.29, 32.01, 22.03.

5,5-dimethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborinane (CAS: 627906-96-1)
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.35\) (s, 1H), \(7.98 - 7.71\) (m, 4H), \(7.58 - 7.33\) (m, 2H), \(3.80\) (s, 4H), \(1.03\) (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 135.17, 134.99, 133.02, 130.05, 128.80, 127.79, 126.92, 125.75, 125.72, 72.55, 32.09, 22.08.

5,5-dimethyl-2-(3-(methylthio)phenyl)-1,3,2-dioxaborinane
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.70\) (s, 1H), \(7.57\) (d, \(J = 7.1\) Hz, 1H), \(7.43 - 7.26\) (m, 2H), \(3.77\) (s, 4H), \(2.50\) (s, 3H), \(1.03\) (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 137.65, 132.12, 130.71, 129.22, 128.21, 72.46, 32.03, 22.04, 16.09.
b. Synthesis and characterization of epoxides

**General procedure A**[6-8]. The respective phenol (1.0 eq) was dissolved in butanone (5 mL/mmol), K$_2$CO$_3$ (3.0 eq) and epibromohydrine (2.5 eq) were added and the mixture was heated to 80 °C for 24 h. K$_2$CO$_3$ was filtered off, the filter cake was washed extensively with acetone and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography.

**General procedure B**[9]. Alkene (10 mmol, 1 equiv) was dissolved in dichloromethane (15 mL) and placed in an ice bath. m-CPBA (12 mmol) was added in portions over 10 min and the reaction was stirred until TLC indicated complete conversion of the starting material. The reaction was quenched saturated sodium bicarbonate solution (15 mL) and then extracted with dichloromethane (3 x 15 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography.

**General procedure C**[10-11]. To a solution of potassium tertbutoxyde (12 mmol) in dimethylsulfoxide (12 mL) at room temperature was added trimethylsulfoxonium iodide (13.7 mmol) and stirred for 30 min. A solution of ketone (12 mmol) in dimethylsulfoxide (3 mL) was added and stirred overnight. The reaction mixture was diluted with EtOAc and water and the layers were separated. The aqueous layer was back-extracted with EtOAc. The combined organic extracts were washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure. The residue was purified by silica gel chromatography.

**Characterization of epoxide:**

2-methyl-2-((p-tolyloxy)methyl)oxirane (CAS: 857389-45-8)

Following general procedure B. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.06 (d, $J = 8.2$ Hz, 2H), 6.85 – 6.75 (m, 2H), 3.93 (dd, $J = 31.5$, 10.5 Hz, 2H), 2.84 (d, $J = 4.8$ Hz, 1H), 2.70 (d, $J = 4.8$ Hz, 1H), 2.27 (s, 3H), 1.46 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.61, 130.37, 129.95, 114.55, 71.63, 55.63, 52.04, 20.52, 18.55.
2-((2-fluoro-6-methylphenoxy)methyl)oxirane
Following general procedure A. ^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 6.93 (dd, \( J = 11.3, 8.2 \) Hz, 1H), 6.79 (dd, \( J = 8.1, 1.8 \) Hz, 1H), 6.73 – 6.63 (m, 1H), 4.25 (dd, \( J = 11.2, 3.1 \) Hz, 1H), 3.98 (dd, \( J = 11.2, 5.7 \) Hz, 1H), 3.35 (m, 1H), 2.91 – 2.85 (m, 1H), 2.74 (dd, \( J = 4.9, 2.6 \) Hz, 1H), 2.28 (s, 3H). ^1^C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 150.96 (d, \( J = 242.9 \) Hz), 146.04 (d, \( J = 10.8 \) Hz), 134.11 (d, \( J = 3.9 \) Hz), 122.10 (d, \( J = 6.6 \) Hz), 116.48 (d, \( J = 1.4 \) Hz), 115.84 (d, \( J = 18.2 \) Hz), 70.40, 50.10, 44.57, 21.00. ^19^F NMR (376 MHz, CDCl\textsubscript{3}) \( \delta \) -138.98.

2-(4-(benzyloxy)butyl)oxirane (CAS: 133617-19-3 )
Following general procedure B. ^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.44 – 7.07 (m, 5H), 4.50 (s, 2H), 3.48 (t, \( J = 6.4 \) Hz, 2H), 2.89 (dd, \( J = 7.0, 4.1 \) Hz, 1H), 2.79 – 2.63 (m, 1H), 2.54 – 2.40 (m, 1H), 1.73 – 1.61 (m, 2H), 1.60 – 1.48 (m, 4H).

2-((2-(thiophen-2-yl)ethoxy)methyl)oxirane (CAS: 1250057-30-7)
^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.12 (dd, \( J = 5.1, 1.2 \) Hz, 1H), 6.91 (m, 1H), 6.86 – 6.74 (m, 1H), 3.87 – 3.71 (m, 3H), 3.39 (dt, \( J = 12.2, 6.1 \) Hz, 1H), 3.17 – 3.12 (m, 1H), 3.10 (m, 2H), 2.77 (dd, \( J = 4.9, 4.3 \) Hz, 1H), 2.60 (dt, \( J = 7.4, 3.7 \) Hz, 1H). ^1^C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 141.07, 126.73, 125.22, 123.72, 72.00, 71.57, 50.83, 44.25, 30.46.

2-((3-(trifluoromethyl)phenoxy)methyl)oxirane (CAS: 585-45-5 )
Following general procedure A. ^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.39 (t, \( J = 8.0 \) Hz, 1H), 7.23 (d, \( J = 7.7 \) Hz, 1H), 7.15 (s, 1H), 7.10 (dd, \( J = 8.3, 2.4 \) Hz, 1H), 4.29 (dd, \( J = 11.0, 2.9 \) Hz, 1H), 3.96 (m, 1H), 3.37 (m, 1H), 3.04 – 2.85 (m, 1H), 2.77 (dd, \( J = 4.8, 2.6 \) Hz, 1H). ^19^F NMR (376 MHz, CDCl\textsubscript{3}) \( \delta \) -62.72. ^1^C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 158.58, 131.88 (q, \( J = 32.3 \) Hz), 130.07, 123.90 (q, \( J = 272.3 \) Hz), 118.15 (q, \( J = 1.0 \) Hz), 117.93 (q, \( J = 3.9 \) Hz), 111.44 (q, \( J = 3.8 \) Hz), 69.03, 49.94 (s), 44.53.

2-((2-bromo-4-chlorophenoxy)methyl)oxirane (CAS: 68224-01-1 )
Following general procedure A. ^1^H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.51 (d, \( J = 2.5 \) Hz, 1H), 7.19 (dt, \( J = 7.2, 3.6 \) Hz, 1H), 6.91 – 6.73 (m, 1H), 4.29 (dd, \( J = 11.2, 2.7 \) Hz, 1H), 3.97 (dd, \( J = 11.2, 5.4 \) Hz, 1H), 3.37 (m, 1H), 2.99 – 2.86 (m, 1H), 2.83 (dd, \( J = 5.0, 2.6 \) Hz, 1H). ^1^C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 153.80, 132.88, 128.34, 126.65, 114.39, 112.84, 69.88, 49.99, 44.50.
**Supporting Information**

**benzyl 1-oxa-6-azaspiro[2.5]octane-6-carboxylate**

Following general procedure C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 – 6.93 (m, 5H), 5.14 (s, 2H), 3.94 – 3.72 (m, 2H), 3.58 – 3.35 (m, 2H), 2.69 (d, $J$ = 1.5 Hz, 2H), 1.95 – 1.70 (m, 2H), 1.54 – 1.29 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.25, 136.70, 128.53, 128.07, 127.92, 67.24, 56.95, 53.75, 42.66, 32.86.

**5-(2-(2-methyloxiran-2-yl)ethyl)benzo[d][1,3]dioxole**

Following general procedure C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.82 – 6.42 (m, 3H), 5.90 (s, 2H), 2.92 – 2.45 (m, 4H), 1.99 – 1.67 (m, 2H), 1.36 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.61, 145.70, 135.42, 120.96, 108.73, 108.20, 100.81, 56.64, 53.91, 38.81, 31.18, 21.04.

**2-butyl-1-tosylaziridine (CAS: 116905-61-4)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J$ = 8.2 Hz, 2H), 7.34 (d, $J$ = 8.1 Hz, 2H), 2.76 – 2.68 (m, 1H), 2.65 – 2.60 (m, 1H), 2.45 (s, 3H), 2.06 (t, $J$ = 3.7 Hz, 1H), 1.63 – 1.49 (m, 1H), 1.39 – 1.31 (m, 1H), 1.28 – 1.18 (m, 4H), 0.81 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.43, 135.21, 129.63, 128.01, 40.44, 35.83, 31.01, 28.88, 22.13, 21.64, 13.85.

### III. General Experimental Procedures, Spectral Data and HPLC Analysis

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

In air, Cul (0.025 mmol), Base (0.5 mmol), KI (if necessary), Ligand (if necessary, 0.025 mmol) and 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (0.5 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Solvent (0.5 mL), 2-hexyloxirane (0.25 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at the mentioned temperature for the indicated amount of time. The reaction was quenched with H$_2$O (2 mL). The resulting solution was then extracted with CH$_2$Cl$_2$ (3 times, 10 mL each), dried over Na$_2$SO$_4$, and filtered. Dodecyl alcohol (0.25 mmol) was added as internal standard. The product was yielded by GC.
### Supporting Information

![Chemical Structures](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Ligand</th>
<th>Base</th>
<th>Solvent</th>
<th>T(°C)</th>
<th>Additive</th>
<th>Yield a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuI</td>
<td>-</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>-</td>
<td>6b</td>
</tr>
<tr>
<td>2</td>
<td>CuI</td>
<td>PPh₃</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Cu(PPh₃)Br</td>
<td>-</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>CuI</td>
<td>xantphos</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>CuI</td>
<td>dppm</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>CuI</td>
<td>PPh₃</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>110</td>
<td>-</td>
<td>10c</td>
</tr>
<tr>
<td>7</td>
<td>CuI</td>
<td>P(Cy)₃</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>110</td>
<td>-</td>
<td>18c</td>
</tr>
<tr>
<td>8</td>
<td>CuI</td>
<td>Dppb</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>110</td>
<td>-</td>
<td>20c</td>
</tr>
<tr>
<td>9</td>
<td>CuI</td>
<td>dppm</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>60</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>CuI</td>
<td>Johnphos</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>60</td>
<td>-</td>
<td>15c</td>
</tr>
<tr>
<td>11</td>
<td>CuI</td>
<td>TMEDA</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>60</td>
<td>-</td>
<td>8c</td>
</tr>
<tr>
<td>12</td>
<td>CuI</td>
<td>xantphos</td>
<td>KO'Me</td>
<td>DMF</td>
<td>80</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>13</td>
<td>CuCl</td>
<td>xantphos</td>
<td>Cs2CO₃</td>
<td>DMF</td>
<td>80</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>14</td>
<td>CuI</td>
<td>xantphos</td>
<td>NaO'Me</td>
<td>DMF</td>
<td>80</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>15</td>
<td>CuI</td>
<td>xantphos</td>
<td>LiO'Bu</td>
<td>Toluene</td>
<td>80</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>16</td>
<td>CuI</td>
<td>xantphos</td>
<td>LiO'Bu</td>
<td>DMSO</td>
<td>80</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>17</td>
<td>CuI</td>
<td>xantphos</td>
<td>LiO'Bu</td>
<td>THF</td>
<td>80</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>18</td>
<td>CuI</td>
<td>-</td>
<td>LiO'Bu</td>
<td>DMA</td>
<td>80</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td>19</td>
<td>CuI</td>
<td>xantphos</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>0.5 eq KI</td>
<td>48c</td>
</tr>
<tr>
<td>20</td>
<td>CuI</td>
<td>L₁</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>1 eq KI</td>
<td>75c</td>
</tr>
<tr>
<td>21</td>
<td>CuI</td>
<td>L₂</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>1 eq KI</td>
<td>35c</td>
</tr>
<tr>
<td>22</td>
<td>CuI</td>
<td>L₂</td>
<td>LiO'Bu</td>
<td>NMP</td>
<td>80</td>
<td>0.5 eq KI</td>
<td>tracec</td>
</tr>
<tr>
<td>23</td>
<td>CuI</td>
<td>dppf</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>1 eq KI</td>
<td>tracec</td>
</tr>
<tr>
<td>24</td>
<td>CuI</td>
<td>pybox</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>0.5 eq KI</td>
<td>50c</td>
</tr>
<tr>
<td>25</td>
<td>CuI</td>
<td>DPEphos</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>0.5 eq KI</td>
<td>30c</td>
</tr>
<tr>
<td>26</td>
<td>CuI</td>
<td>L3</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>0.5 eq KI</td>
<td>30c</td>
</tr>
<tr>
<td>27</td>
<td>CuI</td>
<td>L4</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>0.5 eq KI</td>
<td>30c</td>
</tr>
<tr>
<td>28</td>
<td>CuI</td>
<td>L5</td>
<td>LiO'Bu</td>
<td>DMF</td>
<td>80</td>
<td>0.5 eq KI</td>
<td>10c</td>
</tr>
</tbody>
</table>
Supporting Information

<table>
<thead>
<tr>
<th>29</th>
<th>CuI</th>
<th>L6</th>
<th>LiO\textsubscript{t}Bu</th>
<th>DMF</th>
<th>80</th>
<th>0.5 eq KI</th>
<th>trace\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>CuI</td>
<td>L1</td>
<td>LiO\textsubscript{t}Bu</td>
<td>DMF</td>
<td>80</td>
<td>1.5 eq KI</td>
<td>88(83)\textsuperscript{e}</td>
</tr>
<tr>
<td>31</td>
<td>-</td>
<td>L1</td>
<td>LiO\textsubscript{t}Bu</td>
<td>DMF</td>
<td>80</td>
<td>1.5 eq KI</td>
<td>() \textsuperscript{e}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: 1a (0.5 mmol), 2a (0.25 mmol), CuI (10 mol%), Base (2 equiv), ligand (10 mol%) in 0.5 mL solvent at 80 °C for 14 h under Ar atmosphere. \textsuperscript{b} Reaction conditions: 1a (0.5 mmol), 2a (0.25 mmol), CuI (10 mol%), Base (2 equiv), in 0.5 mL solvent at 80 °C for 14 h under Ar atmosphere. \textsuperscript{c} Reaction conditions: 1a (0.5 mmol), 2a (0.25 mmol), CuI (10 mol%), Base (2 equiv), KI, ligand (10 mol%) in 0.5 mL solvent at 80 °C for 14 h under Ar atmosphere. \textsuperscript{d} Reaction conditions: 1a (0.5 mmol), 2a (0.25 mmol), CuI (10 mol%), Base (2 equiv), ligand (10 mol%) in 0.5 mL solvent at the mentioned temperature for 14 h under Ar atmosphere. The yield was determined by GC using dodecyl alcohol as internal standard (average of two GC runs). \textsuperscript{e} Isolated yield. DMF = N,N-dimethylformamide. DMSO = dimethyl sulfoxide.

Experimental Procedures for Examples Described in Table 2.

In air, CuI (0.025 mmol), Li\textsubscript{o}Bu (0.5 mmol), KI (1.5 eq), 1,3-diphenylpropane-1,3-dione (0.025 mmol) and arylboronate (0.5 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMF (0.5 mL), epoxide (0.25 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 80 °C for 14 h. The reaction was quenched with H\textsubscript{2}O (2 mL). The resulting solution was then extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 times, 10 mL each), dried over Na\textsubscript{2}SO\textsubscript{4}, and filtered, concentrated, and purified by column chromatography.

Experimental Procedures for Examples Described in Table 3.

In air, CuBr (0.025 mmol), Li\textsubscript{o}Bu (0.5 mmol), Xantphos (0.025 mmol) and arylboronate (0.5 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMF (0.5 mL), 2-phenyloxirane (0.25 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 80 °C for 14 h. The reaction was quenched with H\textsubscript{2}O (2 mL). The resulting solution was then extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 times, 10 mL each), dried over Na\textsubscript{2}SO\textsubscript{4}, concentrated and purified by column chromatography.

Experimental Procedures for Examples Described in Scheme 2.

In air, CuBr (0.025 mmol), Li\textsubscript{o}Bu (0.5 mmol), xantphos (0.025 mmol) and arylboronate (0.5 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMF (0.5 mL), 2-butyl-1-tosylaziridine (0.25 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 80 °C for 14 h. The reaction was quenched with H\textsubscript{2}O (2 mL). The resulting solution was then extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 times, 10 mL each), dried over Na\textsubscript{2}SO\textsubscript{4}, concentrated and purified by column chromatography.
Experimental Procedures for Examples Described in Scheme 3

In air, CuI (0.025 mmol), LiOBU (0.5 mmol), KI (1.5 eq), 1,3-diphenylpropane-1,3-dione (0.025 mmol) and arylboronate (0.5 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMF (0.5 mL), epoxide (0.25 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 80 °C for 14 h. The reaction was quenched with H₂O (2 mL). The resulting solution was then extracted with CH₂Cl₂ (3 times, 10 mL each), dried over Na₂SO₄ and filtered, concentrated and purified by column chromatography.

Experimental Procedures for Examples Described in Scheme 4

In air, CuI (1 mmol), LiOBU (15 mmol), KI (1.5 eq), 1,3-diphenylpropane-1,3-dione (1 mmol) and 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (15 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMF (20 mL), 2-(phenoxy)methyloxirane (10 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 80 °C for 14 h. The reaction was quenched with H₂O (20 mL). The resulting solution was then extracted with CH₂Cl₂ (3 times, 15 mL each), dried over Na₂SO₄ and filtered, concentrated and purified by column chromatography.

Substrate scope

1-(p-tolyl)octan-2-ol (CAS: 936855-91-3)
Following general procedure, a colorless liquid.

1H NMR (400 MHz, CDCl₃) δ 7.22 – 7.02 (m, 4H), 3.90 – 3.65 (m, 1H), 2.93 – 2.70 ((dd, J = 13.5, 4.1 Hz, 1H), 2.67 – 2.53 (dd, J = 13.5, 8.5 Hz, 1H), 2.34 (s, 3H), 1.66 – 1.46 (m, 4H), 1.41 – 1.25 (m, 7H), 0.89 (t, J = 7.0 Hz, 3H).

13C NMR (101 MHz, CDCl₃) δ 136.05, 135.60, 129.42, 129.36, 72.85, 43.71, 36.93, 31.97, 29.47, 25.87, 22.75, 21.15, 14.22.

HRMS calcd for C₁₅H₂₄ONa (M+Na⁺):243.1719; found: 243.1720

1-(3-methoxyphenyl)octan-2-ol (CAS: 1285291-04-4)
Following general procedure, a colorless liquid.

1H NMR (400 MHz, CDCl₃) δ 7.36 – 7.13 (m, 1H), 6.89 – 6.78 (m, 3H), 3.92 – 3.71 (m, 4H), 2.81 (dd, J = 13.5, 4.1 Hz, 1H), 2.62 (dd, J = 13.5, 8.5 Hz, 1H), 1.66 – 1.45 (m, 4H), 1.39 – 1.22 (m, 7H), 0.89 (t, J = 6.8 Hz, 3H).

13C NMR (101 MHz, CDCl₃) δ 159.85, 140.40, 129.66, 121.85, 115.20, 111.89, 72.74, 55.27, 44.25, 36.98, 31.97, 29.45, 22.75, 14.22.

HRMS calcd for C₁₅H₂₄O₂Na (M+Na⁺):259.1669; found: 259.1669
1-(3-chlorophenyl)octan-2-ol (CAS: 1248186-42-6
Following general procedure, a colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.26 - 7.09\) (m, 3H), 7.07 – 6.99 (m, 1H), 3.86 – 3.62 (m, 1H), 2.73 (dd, \(J = 13.7, 4.2\) Hz, 1H), 2.57 (dd, \(J = 13.7, 8.3\) Hz, 1H), 1.56 – 1.39 (m, 4H), 1.33 – 1.16 (m, 7H), 0.82 (t, \(J = 6.8\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.98, 134.39, 129.84, 129.62, 127.76, 126.73, 72.64, 43.77, 37.06, 31.95, 29.40, 25.80, 22.74, 14.22. HRMS calcd for C\(_{14}\)H\(_{21}\)ClONa (M+Na\(^{+}\)): 263.1173; found: 263.1170

1-phenyloctan-2-ol (CAS: 19396-72-6
Following general procedure, a colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.45 - 6.73\) (m, 5H), 3.87 – 3.61 (m, 1H), 2.82 – 2.66 (m, 1H), 2.62 – 2.50 (m, 1H), 1.52 – 1.34 (m, 4H), 1.34 – 1.15 (m, 7H), 0.81 (t, \(J = 6.8\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 138.80, 129.56, 128.66, 126.54, 72.83, 44.18, 36.97, 31.97, 29.45, 25.86, 22.75, 14.22. HRMS calcd for C\(_{14}\)H\(_{22}\)ONa (M+Na\(^{+}\)): 229.1563; found: 229.1562

1-(4-bromophenyl)octan-2-ol (CAS: 1340103-80-1
Following general procedure, a colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.43\) (d, \(J = 9.4\) Hz, 2H), 7.08 (d, \(J = 9.4\) Hz, 2H), 3.91 – 3.65 (m, 1H), 2.77 (dd, \(J = 13.6, 4.2\) Hz, 1H), 2.61 (dd, \(J = 13.6, 8.3\) Hz, 1H), 1.63 – 1.41 (m, 4H), 1.38 – 1.22 (m, 7H), 0.88 (t, \(J = 6.7\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.82, 131.68, 131.30, 120.41, 72.67, 43.48, 37.01, 31.95, 29.41, 25.82, 22.75, 14.23. HRMS calcd for C\(_{14}\)H\(_{21}\)OBrNa (M+Na\(^{+}\)): 307.0668; found: 307.0663

1-(naphthalen-2-yl)octan-2-ol (CAS: 179396-36-2
Following general procedure, a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.81\) (t, \(J = 7.6\) Hz, 3H), 7.67 (s, 1H), 7.53 – 7.40 (m, 2H), 7.35 (dd, \(J = 8.4, 1.5\) Hz, 1H), 4.20 – 3.67 (m, 1H), 2.99 (dd, \(J = 13.5, 4.2\) Hz, 1H), 2.80 (dd, \(J = 13.6, 8.4\) Hz, 1H), 1.67 – 1.46 (m, 4H), 1.40 – 1.23 (m, 7H), 0.89 (d, \(J = 6.7\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 136.19, 133.56, 132.27, 128.20, 127.89, 127.82, 127.66, 127.53, 126.10, 125.48, 72.63, 44.23, 36.95, 31.87, 29.36, 25.78, 22.65, 14.12. HRMS calcd for C\(_{18}\)H\(_{24}\)ONa (M+Na\(^{+}\)): 279.1719; found: 279.1718

1-(4-(allyloxy)phenyl)octan-2-ol
Following general procedure, a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.12\) (d, \(J = 8.5\) Hz, 2H), 6.87 (d, \(J = 8.6\) Hz, 2H), 6.19 – 5.93 (m, 1H), 5.44 – 5.33 (m, 1H), 5.33 – 5.18 (m, 1H), 4.52 (d, \(J = 5.3\) Hz, 2H), 3.85 – 3.57 (m, 1H), 2.77 (dd, \(J = 13.7, 4.2\) Hz, 1H), 2.57 (dd, \(J = 13.7, 8.4\) Hz, 1H), 1.65 – 1.40 (m, 4H), 1.36 – 1.20 (m, 7H), 0.88 (t, \(J = 6.6\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 157.40, 133.49, 130.87, 130.48, 117.77, 114.94, 72.91, 68.97, 43.23, 36.87, 31.97, 29.47, 25.87, 22.75, 14.23. HRMS calcd for C\(_{17}\)H\(_{26}\)O\(_2\)Na (M+Na\(^{+}\)): 285.1825; found: 285.1824
1-(3-(methylthio)phenyl)octan-2-ol
Following general procedure, a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.23 (t, $J = 7.6$ Hz, 1H), 7.12 (d, $J = 8.6$ Hz, 2H), 6.99 (d, $J = 7.5$ Hz, 1H), 3.98 – 3.57 (m, 1H), 2.79 (dd, $J = 13.5$, 4.1 Hz, 1H), 2.61 (dd, $J = 13.5$, 8.5 Hz, 1H), 2.48 (s, 3H), 1.75 – 1.46 (m, 4H), 1.39 – 1.17 (m, 7H), 0.89 (t, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.46, 138.65, 128.98, 127.44, 126.18, 124.51, 72.61, 43.98, 36.90, 31.85, 29.33, 25.73, 22.64, 15.75, 14.12.

HRMS calcd for C$_{15}$H$_{24}$OSNa (M+Na$^+$): 275.1440; found: 275.1440

1-(3-(trifluoromethoxy)phenyl)octan-2-ol
Following general procedure, a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 – 6.88 (m, 4H), 3.81 – 3.64 (m, 1H), 2.75 (dd, $J = 13.7$, 4.0 Hz, 1H), 2.60 (dd, $J = 13.7$, 8.3 Hz, 1H), 1.65 – 1.35 (m, 4H), 1.29 – 1.13 (m, 7H), 0.81 (t, $J = 6.5$ Hz, 3H).$^{19}$F NMR (376 MHz, CDCl$_3$) δ -57.72.

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 148.33, 140.15, 128.67, 126.81, 120.88, 119.46 (q, $J = 256.9$ Hz), 117.79, 71.45, 42.63, 35.92, 30.78, 28.24, 24.63, 21.58, 13.04.

HRMS calcd for C$_{15}$H$_{21}$O$_2$F$_3$Na (M+Na$^+$): 313.1386; found: 313.1385

1-phenoxy-3-phenylpropan-2-ol (CAS: 42911-39-7)
Following general procedure, a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.19 (m, 7H), 6.97 (t, $J = 7.4$ Hz, 1H), 6.91 (d, $J = 8.6$, 0.8 Hz, 2H), 4.33 – 4.18 (m, 1H), δ 3.98 (dd, $J = 9.4$, 3.6 Hz, 1H), 3.90 (dd, $J = 9.3$, 6.6 Hz, 1H), 2.95 (d, $J = 6.7$ Hz, 2H), 2.31 (s, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.64, 137.66, 129.66, 129.52, 128.77, 126.81, 120.88, 119.46 (q, $J = 256.9$ Hz), 117.79, 71.45, 42.63, 35.92, 30.78, 28.24, 24.63, 21.58, 13.04.

HRMS calcd for C$_{15}$H$_{16}$O$_2$Na (M+Na$^+$): 251.1043; found: 251.1042

1-(3-(dimethylamino)phenyl)-3-phenoxypropan-2-ol
Following general procedure, a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.22 (m, 2H), 7.17 (t, $J = 7.9$ Hz, 1H), 6.95 (t, $J = 7.4$ Hz, 1H), 6.92 – 6.87 (m, 2H), 6.65 – 6.56 (m, 3H), 4.30 – 4.15 (m, 1H), 4.00 – 3.94 (m, 1H), 3.93 – 3.87 (m, 1H), 3.00 – 2.74 (m, 8H), 2.32 (s, 1H).$^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.72, 150.97, 138.33, 129.60, 129.46, 121.17, 117.67, 114.73, 113.63, 111.11, 71.24, 71.02, 40.69, 40.53.

HRMS calcd for C$_{17}$H$_{21}$O$_2$NNa (M+Na$^+$): 294.1465; found: 294.1460

1-(2-fluoro-6-methylphenoxy)-3-phenylpropan-2-ol
Following general procedure, a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.26 (m, 2H), 7.26 – 7.19 (m, 3H), 6.93 (dd, $J = 11.2$, 8.1 Hz, 1H), 6.76 – 6.59 (m, 2H), δ 4.23 (qd, $J = 6.7$, 3.6 Hz, 1H), 3.98 (dd, $J = 9.5$, 3.5 Hz, 1H), 3.90 (dd, $J = 9.5$, 6.7 Hz, 1H), 2.92 (d, $J = 6.8$ Hz, 2H), 2.45 (s, 1H),
2.26 (s, 3H)\(^{19}\text{F} \) NMR (376 MHz, CDCl\(_3\)) \(\delta\) -139.27.\(^{13}\text{C} \) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 150.99 (d, \(J = 242.7\) Hz), 146.16 (d, \(J = 10.8\) Hz), 137.58, 134.12 (d, \(J = 3.8\) Hz), 129.44, 128.64, 126.66, 121.94 (d, \(J = 6.6\) Hz), 116.28 (d, \(J = 1.2\) Hz), 115.85 (d, \(J = 18.2\) Hz), 72.63, 71.09, 39.72, 21.08.\(^1\) HRMS calcd for C\(_{16}\)H\(_{17}\)FO\(_2\)Na (M+Na\(^+\)): 283.1105; found: 283.1104

3-(2-hydroxy-3-phenoxypropyl)benzonitrile
Following general procedure, a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 (s, 1H), 7.55 – 7.48 (m, 2H), 7.40 (t, \(J = 7.7\) Hz, 1H), 7.35 – 7.21 (m, 2H), 7.02 – 6.93 (m, 1H), 6.92 – 6.77 (m, 2H), 4.29 – 4.17 (m, 1H), \(\delta\) 3.97 (dd, \(J = 9.3, 3.7\) Hz, 1H), 3.87 (dd, \(J = 9.3, 6.6\) Hz, 1H), 3.09 – 2.76 (m, 2H), 2.43 (s, 1H). \(^{13}\text{C} \) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.38, 139.50, 134.13, 133.05, 130.47, 129.72, 129.37, 121.53, 118.96, 114.66, 112.61, 71.03, 70.65, 39.30.
HRMS calcd for C\(_{16}\)H\(_{15}\)O\(_2\)NNa (M+Na\(^+\)): 276.0995; found: 276.0994

1-(furan-2-yl)-3-phenoxypropan-2-ol (CAS: 1552787-70-8)
Following general procedure, a colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 – 7.33 (m, 1H), 7.31 – 7.26 (m, 2H), 6.96 (t, \(J = 7.7\) Hz, 1H), 6.93 – 6.88 (m, 2H), 6.34 – 6.28 (m, 1H), 6.15 (d, \(J = 3.1\) Hz, 1H), \(\delta\) 4.30 (qd, \(J = 6.5, 3.9\) Hz, 1H), 4.00 (dd, \(J = 9.4, 3.8\) Hz, 1H), 3.91 (dd, \(J = 9.4, 6.6\) Hz, 1H), 2.98 (d, \(J = 6.4\) Hz, 2H), 2.21 (s, 1H). \(^{13}\text{C} \) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.62, 151.85, 141.88, 129.66, 121.33, 114.71, 110.56, 107.48, 71.10, 69.16, 32.45.
HRMS calcd for C\(_{13}\)H\(_{14}\)O\(_3\)Na (M+Na\(^+\)): 241.0835; found: 241.0833

6-(benzyloxy)-1-phenylhexan-2-ol
Following general procedure, a colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53 – 6.84 (m, 10H), 4.42 (s, 2H), 3.72 (dd, \(J = 8.3, 4.1\) Hz, 1H), 3.58 – 3.30 (m, 2H), 2.74 (dd, \(J = 13.5, 4.3\) Hz, 1H), 2.57 (dd, \(J = 13.5, 8.4\) Hz, 1H), 1.70 – 1.26 (m, 7H). \(^{13}\text{C} \) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.55, 128.53, 120.68, 114.05, 110.78, 67.78, 54.13, 44.81, 21.77.
HRMS calcd for C\(_{19}\)H\(_{24}\)O\(_2\)Na (M+Na\(^+\)): 307.1669; found: 307.1665

1-(3-methoxyphenyl)propan-2-ol (CAS: 34322-78-6)
Following general procedure, a colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.16 (dd, \(J = 13.4, 5.7\) Hz, 1H), 6.71 (dd, \(J = 14.8, 4.9\) Hz, 3H), 4.03 – 3.85 (m, 1H), 3.73 (s, 3H), 2.69 (dd, \(J = 13.4, 4.7\) Hz, 1H), 2.58 (dd, \(J = 13.4, 8.1\) Hz, 1H), 1.63 (s, 1H), 1.17 (d, \(J = 6.2\) Hz, 3H). \(^{13}\text{C} \) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.71, 139.09, 128.53, 120.68, 114.05, 110.78, 67.78, 54.13, 44.81, 21.77.
HRMS calcd for C\(_{10}\)H\(_{14}\)O\(_2\)Na (M+Na\(^+\)): 189.0886; found: 189.0880
1-(3-(dimethylamino)phenyl)-2-methyl-3-(p-tolyloxy)propan-2-ol
Following general procedure, a colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.18 (t, \(J = 7.8\) Hz, 1H), 7.12 (d, \(J = 8.5\) Hz, 2H), 6.86 (d, \(J = 8.5\) Hz, 2H), 6.70 – 6.55 (m, 3H), 3.75 (dd, \(J = 22.1, 8.8\) Hz, 2H), 2.97 (s, 2H), 2.85 (s, 6H), 2.33 (s, s, 4H), 1.35 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 156.62, 150.70, 137.81, 130.24, 129.99, 129.06, 118.84, 114.72, 114.54, 111.02, 73.37, 72.26, 45.60, 40.54, 24.33, 20.57.
HRMS calcd for C\(_{19}\)H\(_{25}\)O\(_2\)NNa (M+Na\(^+\)): 322.1778; found: 322.1775

\[
\begin{align*}
\text{Me} & \quad \text{O} \\
\text{O} & \quad \text{H} \\
\text{O} & \quad \text{H}
\end{align*}
\]

1-(3-methoxyphenyl)-2-methyl-3-(p-tolyloxy)propan-2-ol
Following general procedure, a colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.19 (t, \(J = 7.8\) Hz, 1H), 7.09 (d, \(J = 8.3\) Hz, 2H), 6.93 – 6.70 (m, 5H), 3.80 – 3.53 (m, 5H), 2.95 (s, 2H), 2.30 (s, 3H), 2.07 (s, 1H), 1.29 (s, 3H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.60, 156.56, 138.72, 130.49, 130.09, 129.37, 122.89, 115.90, 114.57, 112.39, 73.57, 72.34, 55.14, 45.30, 24.19, 20.62.
HRMS calcd for C\(_{18}\)H\(_{22}\)O\(_3\)Na (M+Na\(^+\)): 309.1462; found: 309.1460

methyl 3-(2-hydroxy-2-methyl-3-(p-tolyloxy)propyl)benzoate
Following general procedure, a colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 – 7.83 (m, 2H), 7.48 – 7.39 (m, 1H), 7.39 – 7.31 (m, 1H), 7.10 (d, \(J = 8.4\) Hz, 2H), 6.82 (d, \(J = 8.6\) Hz, 2H), 3.88 (s, 3H), 3.80 – 3.67 (m, 2H), 3.13 – 2.82 (m, 2H), 2.30 (s, 3H), 2.15 (s, 1H), 1.26 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 167.28, 156.48, 137.64, 135.18, 131.62, 130.64, 130.20, 130.10, 128.43, 127.98, 114.66, 74.01, 72.32, 52.23, 44.97, 24.00, 20.63.
HRMS calcd for C\(_{19}\)H\(_{22}\)O\(_4\)Na (M+Na\(^+\)): 337.1410; found: 337.1405

1-(3-methoxyphenyl)-3-(2-(thiophen-2-yl)ethoxy)propan-2-ol
Following general procedure, a colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.13 (dd, \(J = 8.9, 7.5\) Hz, 1H), 7.05 (dd, \(J = 5.1, 1.2\) Hz, 1H), 6.84 (dd, \(J = 5.1, 3.4\) Hz, 1H), 6.78 – 6.75 (m, 2H), 6.70 (dd, \(J = 9.9, 5.5\) Hz, 3H), 3.94 (dd, \(J = 6.6, 3.4\) Hz, 1H), 3.70 (s, 3H), 3.65 – 3.56 (m, 2H), 3.40 (dd, \(J = 9.5, 3.4\) Hz, 1H), 3.28 (dd, \(J = 9.5, 7.0\) Hz, 1H), 3.02 (t, \(J = 6.5\) Hz, 2H), 2.75 – 2.58 (m, 2H), 2.26 (s, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.62, 140.13, 138.53, 128.41, 125.66, 124.18, 122.76, 120.64, 113.98, 110.75, 73.07, 70.72, 70.19, 54.10, 38.84, 29.41.
HRMS calcd for C\(_{16}\)H\(_{20}\)O\(_3\)NaS (M+Na\(^+\)): 315.1025; found: 315.1024

1-phenyl-3-(3-(trifluoromethyl)phenoxy)propan-2-ol
Following general procedure, a colorless liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 – 7.28 (m, 3H), 7.28 – 7.19 (m, 4H), 7.12 (s, 1H), 7.08 – 7.01 (m, 1H), 4.37 – 4.15 (m, 1H), 3.98 (dd, \(J = 9.3, 3.6\) Hz, 1H), 3.91 (dd, \(J = 9.3, 6.4\) Hz, 1H), 3.10 – 2.78 (m, 2H), 2.25 (s, 1H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -
Supporting Information

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.69, 137.36, 131.93 (q, $J = 32.3$ Hz), 130.09, 129.40, 128.73, 126.80, 123.94 (q, $J = 272.4$ Hz), 118.03, 117.87 (q, $J = 3.8$ Hz), 111.51 (q, $J = 3.8$ Hz), 71.29, 71.00, 39.88.

HRMS calcd for C$_{16}$H$_{15}$O$_2$F$_3$Na (M+Na$^+$): 319.0916; found: 319.0915

1-(2-bromo-4-chlorophenoxy)-3-phenylpropan-2-ol
Following general procedure, a colorless liquid.  $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, $J = 2.5$ Hz, 1H), 7.27 – 7.04 (m, 6H), 6.64 (d, $J = 8.8$ Hz, 1H), 4.23 – 4.08 (m, 1H), 3.88 (dd, $J = 9.2$, 3.6 Hz, 1H), 3.78 (dd, $J = 9.1$, 6.3 Hz, 1H), 2.88 (d, $J = 7.2$ Hz, 2H), 2.39 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.77, 137.40, 132.85, 129.41, 128.70, 128.41, 126.76, 126.62, 114.22, 112.88, 72.45, 70.98, 39.76.

HRMS calcd for C$_{15}$H$_{14}$O$_2$ClBrNa (M+Na$^+$): 362.9758; found: 362.9755

benzyl 4-benzyl-4-hydroxypiperidine-1-carboxylate
Following general procedure, a colorless liquid.  $^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 – 6.87 (m, 10H), 5.04 (s, 2H), 3.95 – 3.67 (m, 2H), 3.26 – 2.88 (m, 2H), 2.66 (s, 2H), 1.69 – 1.26 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.22, 135.83, 134.87, 129.49, 127.45, 127.40, 126.93, 126.81, 125.83, 68.29, 66.00, 48.25, 38.88, 35.84.

HRMS calcd for C$_{20}$H$_{23}$O$_3$NNa (M+Na$^+$): 348.1570; found: 348.1570

benzyl 4-(benzo[d][1,3]dioxol-5-ylmethyl)-4-hydroxypiperidine-1-carboxylate
Following general procedure, a colorless liquid.  $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.12 (m, 5H), 6.82 – 6.48 (m, 3H), 5.92 (s, 2H), 5.11 (s, 2H), 4.16 – 3.76 (m, 2H), 3.16 (s, 2H), 2.65 (s, 2H), 1.78 – 1.34 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.28, 147.65, 146.54, 136.87, 129.54, 128.51, 127.99, 127.86, 123.41, 110.85, 108.22, 100.98, 69.30, 67.06, 48.95, 39.95, 36.53.

HRMS calcd for C$_{21}$H$_{23}$O$_5$NNa (M+Na$^+$): 392.1468; found: 392.1466

4-(benzo[d][1,3]dioxol-5-yl)-1-(3-methoxyphenyl)-2-methylbutan-2-ol
Following general procedure, a colorless liquid.  $^1$H NMR (400 MHz, CDCl$_3$) δ 7.23 (t, $J = 8.0$ Hz, 1H), 6.87 – 6.76 (m, 3H), 6.70 (dd, $J = 15.7$, 4.6 Hz, 2H), 6.64 (dd, $J = 7.9$, 1.5 Hz, 1H), 5.91 (s, 2H), 3.80 (s, 3H), 2.89 – 2.71 (m, 2H), 2.71 – 2.61 (m, 2H), 1.79 – 1.68 (m, 2H), 1.56 (s, 1H), 1.22 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.52, 147.58, 145.56, 138.83, 136.33, 129.27, 122.97, 120.98, 116.35, 111.86, 108.86, 108.21, 100.77, 72.32, 55.20, 48.29, 44.01, 30.16, 26.60.

HRMS calcd for C$_{19}$H$_{22}$O$_4$Na (M+Na$^+$): 337.1410; found: 337.1410
1-(o-tolyl)octan-2-ol (CAS: 1249825-56-6)
Following general procedure, a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 – 6.70 (m, 4H), 3.89 – 3.56 (m, 1H), 2.75 (dd, $J$ = 13.7, 4.1 Hz, 1H), 2.57 (dd, $J$ = 13.7, 8.8 Hz, 1H), 2.24 (s, 3H), 1.63 – 1.36 (m, 4H), 1.35 – 1.17 (m, 7H), 0.80 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.04, 136.68, 130.50, 130.18, 126.56, 126.03, 71.80, 41.34, 37.19, 31.90, 29.40, 25.83, 22.67, 19.71, 14.13.
HRMS calcd for C$_{15}$H$_{24}$ONa (M+Na$^+$): 243.1719; found: 243.1715

(S)-1-(benzyloxy)-3-(3-methoxyphenyl)propan-2-ol
Following general procedure, a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.27 (m, 5H), 7.25 – 7.15 (m, 1H), 6.86 – 6.71 (m, 3H), 4.61 – 4.42 (m, 2H), 4.14 – 3.94 (m, 1H), 3.77 (s, 3H), 3.50 (dd, $J$ = 9.5, 3.5 Hz, 1H), 3.40 (dd, $J$ = 9.4, 7.0 Hz, 1H), 2.78 (d, $J$ = 6.8 Hz, 2H), 2.24 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.71, 139.59, 137.99, 129.49, 129.49, 128.50, 127.83, 127.81, 121.72, 115.05, 111.86, 73.60, 73.43, 71.37, 55.17, 39.99.
HRMS calcd for C$_{17}$H$_{20}$O$_3$Na (M+Na$^+$): 295.1305; found: 295.1303

1-(benzyloxy)-3-(3-methoxyphenyl)propan-2-ol
Following general procedure, a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.27 (m, 5H), 7.26 – 7.17 (m, 1H), 6.86 – 6.74 (m, 3H), 4.54 (s, 2H), 4.14 – 3.98 (m, 1H), 3.78 (s, 3H), 3.56 – 3.47 (m, 1H), 3.47 – 3.34 (m, 1H), 2.78 (d, $J$ = 6.6 Hz, 2H), 2.31 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.70, 139.57, 137.97, 129.49, 128.50, 127.83, 127.81, 121.71, 115.05, 111.85, 73.59, 73.43, 71.37, 55.17, 39.98.
HRMS calcd for C$_{17}$H$_{20}$O$_3$Na (M+Na$^+$): 295.1305; found: 295.1300

2-(3-methoxyphenyl)-1-phenylethanol (CAS: 237763-20-1)
Following general procedure, a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 – 7.24 (m, 5H), 7.23 – 7.16 (m, 1H), 6.77 (dd, $J$ = 9.3, 4.1 Hz, 2H), 6.70 (s, 1H), 4.86 (dd, $J$ = 8.3, 5.0 Hz, 1H), 3.74 (s, 3H), 3.20 – 2.88 (m, 2H), 2.09 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.70, 139.57, 137.97, 129.49, 128.50, 127.83, 127.81, 121.71, 115.04, 111.85, 73.59, 73.43, 71.37, 55.17, 39.98.
HRMS calcd for C$_{15}$H$_{16}$O$_2$Na (M+Na$^+$): 251.1043; found: 251.1042

2-(3-(methylthio)phenyl)-1-phenylethanol
Following general procedure, a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.25 (m, 5H), 7.19 (t, $J$ = 7.6 Hz, 1H), 7.12 (dd, $J$ = 1.8, 1.2 Hz, 1H), 7.02 (t, $J$ = 1.6 Hz, 1H), 6.97 – 6.91 (m, 1H), 4.85 (dd, $J$ = 7.8, 5.5 Hz, 1H), 3.07 – 2.88 (m, 2H), 2.41 (s, 3H), 2.01 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.73, 138.80, 138.53, 128.89, 128.46, 127.69, 127.61, 126.34, 125.97, 124.80, 75.22, 45.94,
15.76.
HRMS calcd for C15H16OSNa (M+Na+): 267.0814; found: 267.0812

2-(4-bromophenyl)-1-phenylethanol (CAS: 214288-82-1)
Following general procedure, a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 – 7.15 (m, 7H), 7.02 (d, $J = 7.3$ Hz, 2H), 4.97 – 4.63 (m, 1H), 2.96 (d, $J = 6.5$ Hz, 2H), 2.02 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.54, 137.04, 131.47, 131.32, 128.52, 127.83, 125.92, 120.50, 75.22, 45.25.
HRMS calcd for C14H13OBrNa (M+Na+): 299.0042; found: 299.0040

2-(naphthalen-2-yl)-1-phenylethanol (CAS: 1484699-56-0)
Following general procedure, a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 – 7.75 (m, 3H), 7.66 (s, 1H), 7.52 – 7.43 (m, 2H), 7.42 – 7.21 (m, 6H), 4.99 (dd, $J = 8.4$, 4.9 Hz, 1H), 3.45 – 2.98 (m, 2H), 1.95 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.82, 135.58, 133.54, 132.36, 128.51, 128.17, 128.14, 127.83, 127.69, 127.62, 126.11, 125.96, 125.59, 75.27, 46.31.
HRMS calcd for C18H16ONa (M+Na+): 271.1093; found: 271.1093

4-methyl-N-(1-(p-tolyl)hexan-2-yl)benzenesulfonamide
Following general procedure, a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 8.2$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.00 (d, $J = 7.8$ Hz, 2H), 6.88 (d, $J = 7.9$ Hz, 2H), 4.39 (d, $J = 8.0$ Hz, 1H), 3.39 (dd, $J = 13.2$, 6.9 Hz, 1H), 2.77 – 2.54 (m, 2H), 2.41 (s, 3H), 2.30 (s, 3H), 1.67 (s, 1H), 1.49 – 1.35 (m, 1H), 1.34 – 1.23 (m, 2H), 1.15 (dd, $J = 12.5$, 5.9 Hz, 2H), 0.77 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.03, 137.89, 136.06, 134.04, 129.50, 129.36, 129.13, 127.01, 55.03, 40.75, 34.12, 27.52, 22.36, 21.53, 21.05, 13.93.
HRMS calcd for C20H28NO2S (M+H+): 346.1835; found: 346.1834

HPLC Analysis
### Supporting Information

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time (min)</th>
<th>Width (min)</th>
<th>Area (mAu*s)</th>
<th>Height (mAU)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.049</td>
<td>0.2960</td>
<td>486.63086</td>
<td>25.56818</td>
<td>49.7557</td>
</tr>
<tr>
<td>2</td>
<td>13.640</td>
<td>0.3486</td>
<td>491.40860</td>
<td>21.50571</td>
<td>50.2443</td>
</tr>
</tbody>
</table>

**IV. References**


V. NMR Spectra