

Supporting Information

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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 off-white powder and refluxed in THF for further purification. The following chemicals were purchased and used as received: LiOtBu(99.9%,Acros), KI(Sinopharm Chemical Reagent Co), KOtBu(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-((benzyloxy)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.

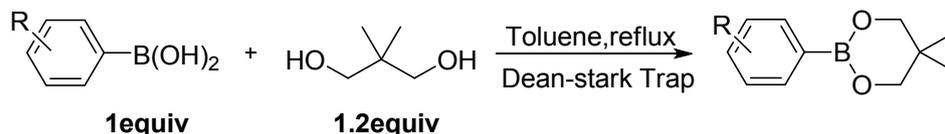
b). Analytical Methods

$^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and $^{19}\text{F-NMR}$ spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in CDCl_3 unless otherwise noted; Data for $^1\text{H-NMR}$ are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for $^{13}\text{C-NMR}$ 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).

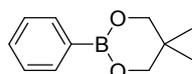
II. Preparation of Substrates

a). Synthesis and characterization of organoboronates

Organoboronates were prepared according to literature procedure^[1-5]: Organoboronates were prepared from organoboronic acids and 2,2-dimethyl-1,3-propanediol in toluene.

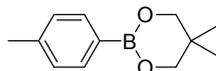


Characterization of organoboronates:



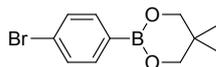
5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane(CAS: 5123-13-7)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 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, CDCl₃) δ 133.94, 130.80, 127.70, 72.41, 32.00, 22.02.



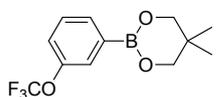
5,5-dimethyl-2-(p-tolyl)-1,3,2-dioxaborinane (CAS: 380481-66-3)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 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, CDCl₃) δ 140.71, 133.90, 128.43, 72.29, 31.91, 21.93, 21.69.



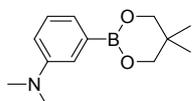
2-(4-bromophenyl)-5,5-dimethyl-1,3,2-dioxaborinane(CAS: 183677-71-6)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 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, CDCl₃) δ 135.50, 130.79, 125.59, 72.33, 31.90, 21.90.



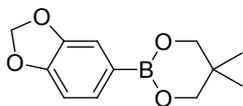
5,5-dimethyl-2-(3-(trifluoromethoxy)phenyl)-1,3,2-dioxaborinane(CAS: 635305-40-7)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 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).



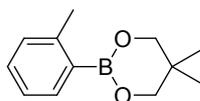
3-(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)-N,N-dimethylaniline(CAS: 1352304-48-3)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 150.13, 128.40, 122.52, 118.04, 115.45, 72.32, 40.89, 31.90, 21.97.



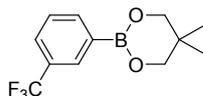
2-(benzo[d][1,3]dioxol-5-yl)-5,5-dimethyl-1,3,2-dioxaborinane(CAS: 94838-83-2)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 149.70, 147.16, 128.53, 113.23, 108.11, 100.63, 72.29, 31.89, 21.9



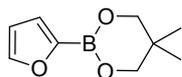
5,5-dimethyl-2-(o-tolyl)-1,3,2-dioxaborinane(CAS: 91994-11-5)

Following general procedure. Purification by silica gel column chromatography gave the product as a colourless liquid. ^1H NMR (400 MHz, CDCl_3) δ 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 (101 MHz, CDCl_3) δ 143.97, 134.85, 130.07, 129.98, 124.70, 72.29, 31.67, 22.43, 21.92.



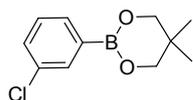
5,5-dimethyl-2-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborinane(CAS: 635305-32-7)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 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), 1.02 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 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.



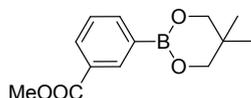
2-(furan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane(CAS: 941320-88-3)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 146.64, 121.47, 110.20, 72.29, 32.11, 21.88.



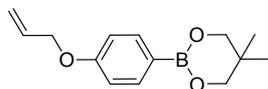
2-(3-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane(CAS: 585524-80-7)

Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 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).

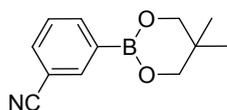


methyl 3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (CAS: 585524-77-2)

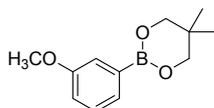
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.47 (s, 1H), 8.22 – 8.05 (m, 1H), 7.98 (d, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 3.91 (s, 3H), 3.78 (s, 4H), 1.03 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 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)**

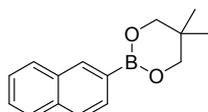
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.84 – 7.62 (m, 2H), 6.95 – 6.74 (m, 2H), 6.13 – 5.88 (m, 1H), 5.53 – 5.36 (m, 1H), 5.32 – 5.18 (m, 1H), 4.77 – 4.36 (m, 2H), 3.75 (s, 4H), 1.01 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 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)**

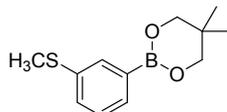
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (s, 1H), 8.00 (dd, $J = 7.5, 1.1$ Hz, 1H), 7.69 (m, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 3.78 (s, 4H), 1.03 (s, 6H).

**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. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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)**

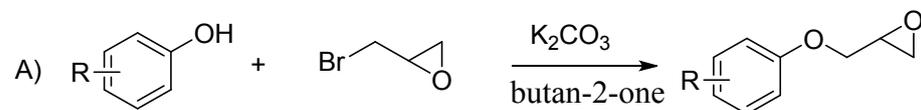
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 8.35 (s, 1H), 7.98–7.71 (m, 4H), 7.58–7.33 (m, 2H), 3.80 (s, 4H), 1.03 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.17, 134.99, 133.02, 130.05, 128.80, 127.79, 126.92, 126.75, 125.72, 72.55, 32.09, 22.08.

**5,5-dimethyl-2-(3-(methylthio)phenyl)-1,3,2-dioxaborinane**

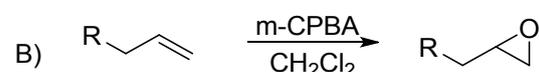
Following general procedure. Purification by silica gel column chromatography gave the product as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (s, 1H), 7.57 (d, $J = 7.1$ Hz, 1H), 7.43–7.26 (m, 2H), 3.77 (s, 4H), 2.50 (s, 3H), 1.03 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.65, 132.12, 130.71, 129.22, 128.21, 72.46, 32.03, 22.04, 16.09.

HRMS (EI) calcd for C₁₂H₁₇BO₂S (M⁺): 236.1042; found: 236.1041.

b). Synthesis and characterization of epoxides



General procedure A^[6-8]. The respective phenol (1.0 eq) was dissolved in butanone (5 mL/mmol), K₂CO₃ (3.0 eq) and epibromohydrine (2.5 eq) were added and the mixture was heated to 80 °C for 24 h. K₂CO₃ 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.

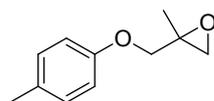


General procedure B^[9]. Alkene (10 mmol, 1 equiv) was dissolved in dichloromethane (15 mL) and placed in an ice bath. m-CPBA (12 mmol) was added in portions over 10 min and the reaction was stirred until TLC indicated complete conversion of the starting material. The reaction was quenched saturated 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.



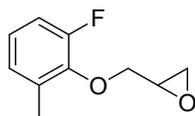
General procedure C^[10-11]. To a solution of potassium tertbutoxyde (12 mmol) in dimethylsulfoxide (12 mL) at room temperature was added trimethylsulfoxonium iodide (13.7 mmol) and stirred for 30 min. A solution of ketone (12 mmol) in dimethylsulfoxide (3 mL) was added and stirred overnight. The reaction 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 Na₂SO₄. The solvent was removed under reduced pressure. The residue was purified by silica gel chromatography.

Characterization of epoxide:

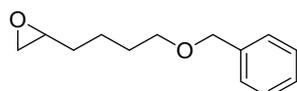


2-methyl-2-((p-tolyloxy)methyl)oxirane (CAS: 857389-45-8)

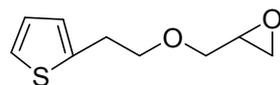
Following general procedure B. ¹H NMR (400 MHz, CDCl₃) δ 7.06 (d, *J* = 8.2 Hz, 2H), 6.85 – 6.75 (m, 2H), 3.93 (dd, *J* = 31.5, 10.5 Hz, 2H), 2.84 (d, *J* = 4.8 Hz, 1H), 2.70 (d, *J* = 4.8 Hz, 1H), 2.27 (s, 3H), 1.46 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 156.61, 130.37, 129.95, 114.55, 71.63, 55.63, 52.04, 20.52, 18.55.


2-((2-fluoro-6-methylphenoxy)methyl)oxirane

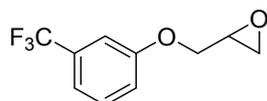
Following general procedure A. ^1H NMR (400 MHz, CDCl_3) δ 6.93 (dd, $J = 11.3, 8.2$ Hz, 1H), 6.79 (dd, $J = 8.1, 1.8$ Hz, 1H), 6.73 – 6.63 (m, 1H), 4.25 (dd, $J = 11.2, 3.1$ Hz, 1H), 3.98 (dd, $J = 11.2, 5.7$ Hz, 1H), 3.35 (m, 1H), 2.91 – 2.85 (m, 1H), 2.74 (dd, $J = 4.9, 2.6$ Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 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_3) δ -138.98.


2-(4-(benzyloxy)butyl)oxirane (CAS: 133617-19-3)

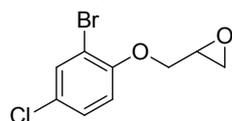
Following general procedure B. ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.07 (m, 5H), 4.50 (s, 2H), 3.48 (t, $J = 6.4$ Hz, 2H), 2.89 (dd, $J = 7.0, 4.1$ Hz, 1H), 2.79 – 2.63 (m, 1H), 2.54 – 2.40 (m, 1H), 1.73 – 1.61 (m, 2H), 1.60 – 1.48 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.58, 128.39, 127.65, 127.56, 72.94, 70.12, 52.27, 47.10, 32.30, 29.56, 22.75.


2-((2-(thiophen-2-yl)ethoxy)methyl)oxirane (CAS: 1250057-30-7)

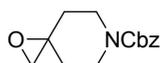
^1H NMR (400 MHz, CDCl_3) δ 7.12 (dd, $J = 5.1, 1.2$ Hz, 1H), 6.91 (m, 1H), 6.86 – 6.74 (m, 1H), 3.87 – 3.71 (m, 3H), 3.39 (dt, $J = 12.2, 6.1$ Hz, 1H), 3.17 – 3.12 (m, 1H), 3.10 (m, 2H), 2.77 (dd, $J = 4.9, 4.3$ Hz, 1H), 2.60 (dt, $J = 7.4, 3.7$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.07, 126.73, 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. ^1H NMR (400 MHz, CDCl_3) δ 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_3) δ -62.72. ^{13}C NMR (101 MHz, CDCl_3) δ 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.

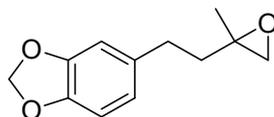

2-((2-bromo-4-chlorophenoxy)methyl)oxirane (CAS: 68224-01-1)

Following general procedure A. ^1H NMR (400 MHz, CDCl_3) δ 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). ^{13}C NMR (101 MHz, CDCl_3) δ 153.80, 132.88, 128.34, 126.65, 114.39, 112.84, 69.88, 49.99, 44.50.



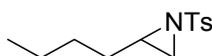
benzyl 1-oxa-6-azaspiro[2.5]octane-6-carboxylate

Following general procedure C. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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)

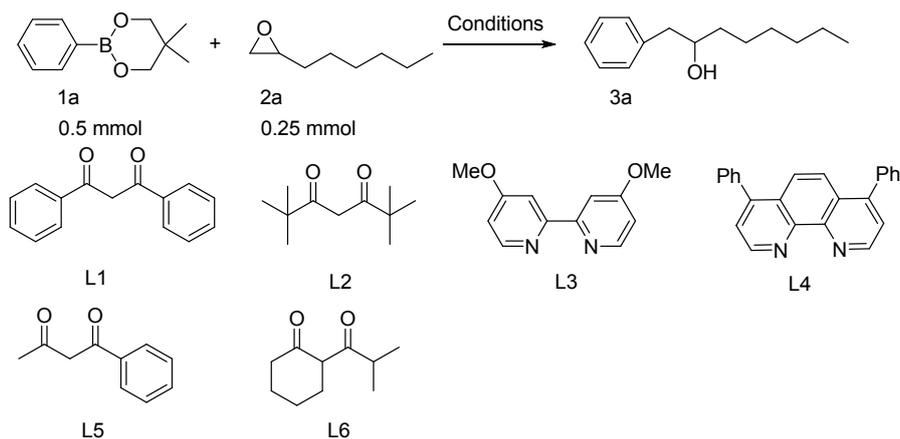
^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 2.76 – 2.68 (m, 1H), 2.65 – 2.60 (m, 1H), 2.45 (s, 3H), 2.06 (t, J = 3.7 Hz, 1H), 1.63 – 1.49 (m, 1H), 1.39 – 1.31 (m, 1H), 1.28 – 1.18 (m, 4H), 0.81 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.43, 135.21, 129.63, 128.01, 40.44, 33.83, 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, CuI (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_2O (2 mL). The resulting solution was then extracted with CH_2Cl_2 (3 times, 10 mL each), dried over Na_2SO_4 , and filtered. Dodecyl alcohol (0.25mmol) was added as internal standard. The product was yielded by GC.



Entry	Catalyst	Ligand	Base	Solvent	T(°C)	Additive	Yield ^a
1	CuI	-	LiO ^t Bu	DMF	80	-	6 ^b
2	CuI	PPh ₃	LiO ^t Bu	DMF	80	-	5
3	Cu(PPh ₃)Br	-	LiO ^t Bu	DMF	80	-	trace
4	CuI	xantphos	LiO ^t Bu	DMF	80	-	40
5	CuI	dppm	LiO ^t Bu	DMF	80	-	3
6	CuI	PPh ₃	LiO ^t Bu	DMF	110	-	10 ^d
7	CuI	P(Cy) ₃	LiO ^t Bu	DMF	110	-	18 ^d
8	CuI	Dppb	LiO ^t Bu	DMF	110	-	20 ^d
9	CuI	dppm	LiO ^t Bu	DMF	60	-	trace ^e
10	CuI	Johnphos	LiO ^t Bu	DMF	60	-	15 ^e
11	CuI	TMEDA	LiO ^t Bu	DMF	60	-	8 ^e
12	CuI	xantphos	KOMe	DMF	80	-	trace
13	CuCl	xantphos	Cs ₂ CO ₃	DMF	80	-	2
14	CuI	xantphos	NaOMe	DMF	80	-	trace
15	CuI	xantphos	LiO ^t Bu	Toluene	80	-	trace
16	CuI	xantphos	LiO ^t Bu	DMSO	80	-	5
17	CuI	xantphos	LiO ^t Bu	THF	80	-	trace
18	CuI	-	LiO ^t Bu	DMA	80	-	16
19	CuI	xantphos	LiO ^t Bu	DMF	80	0.5 eq KI	48 ^c
20	CuI	L1	LiO ^t Bu	DMF	80	1 eq KI	75 ^c
21	CuI	L2	LiO ^t Bu	DMF	80	1 eq KI	35 ^c
22	CuI	L2	LiO ^t Bu	NMP	80	0.5 eq KI	trace ^c
23	CuI	dppf	LiO ^t Bu	DMF	80	1 eq KI	trace ^c
24	CuI	pybox	LiO ^t Bu	DMF	80	0.5 eq KI	50 ^c
25	CuI	DPEphos	LiO ^t Bu	DMF	80	0.5 eq KI	30 ^c
26	CuI	L3	LiO ^t Bu	DMF	80	0.5 eq KI	30 ^c
27	CuI	L4	LiO ^t Bu	DMF	80	0.5 eq KI	30 ^c
28	CuI	L5	LiO ^t Bu	DMF	80	0.5 eq KI	10 ^c

29	CuI	L6	LiO ^t Bu	DMF	80	0.5 eq KI	trace ^c
30	CuI	L1	LiO^tBu	DMF	80	1.5 eq KI	88(83%)^e
31	-	L1	LiO ^t Bu	DMF	80	1.5 eq KI	0 ^e

^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. ^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. ^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. ^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). ^e Isolated yield. DMF = N,N-dimethylformamide. DMSO = dimethyl sulfoxid.

Experimental Procedures for Examples Described in Table 2.

In air, CuI (0.025 mmol), Li^tOBu (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 Table 3.

In air, CuBr (0.025 mmol), Li^tOBu (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 H₂O (2 mL). The resulting solution was then extracted with CH₂Cl₂ (3 times, 10 mL each), dried over Na₂SO₄, concentrated, and purified by column chromatography.

Experimental Procedures for Examples Described in Scheme 2.

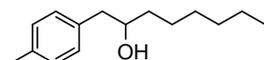
In air, CuBr (0.025 mmol), Li^tOBu (0.5 mmol), xantphos (0.025 mmol) and arylboronate (0.5 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMF (0.5 mL), 2-butyl-1-tosylaziridine (0.25 mmol) were added in turn by syringe. The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

Experimental Procedures for Examples Described in Scheme 3

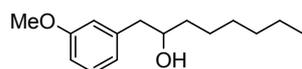
In air, CuI (0.025 mmol), Li^tOBu (0.5 mmol), KI (1.5 eq), 1,3-diphenylpropane-1,3-dione (0.025 mmol) and arylboronate (0.5 mmol) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). DMF (0.5 mL), epoxide (0.25 mmol) were added in turn 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), Li^tOBu (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)methyl)oxirane (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.

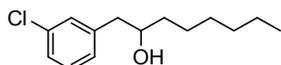
Substrate scope**1-(p-tolyl)octan-2-ol (CAS: 936855-91-3)**

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 C₁₅H₂₄O₂Na (M+Na⁺):243.1719; found: 243.1720

**1-(3-methoxyphenyl)octan-2-ol (CAS: 1285291-04-4)**

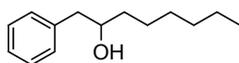
Following general procedure, a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.13 (m, 1H), 6.89 – 6.78 (m, 3H), 3.92 – 3.71 (m, 4H), 2.81 (dd, *J* = 13.5, 4.1 Hz, 1H), 2.62 (dd, *J* = 13.5, 8.5 Hz, 1H), 1.66 – 1.45 (m, 4H), 1.39 – 1.22 (m, 7H), 0.89 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) 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, 25.86, 22.75, 14.22.

HRMS calcd for C₁₅H₂₄O₂Na (M+Na⁺):259.1669; found: 259.1669



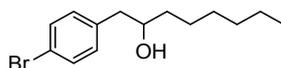
1-(3-chlorophenyl)octan-2-ol (CAS: 1248186-42-6)

Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.09 (m, 3H), 7.07 – 6.99 (m, 1H), 3.86 – 3.62 (m, 1H), δ 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) δ 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 $\text{C}_{14}\text{H}_{21}\text{ClO}_2\text{Na}$ ($\text{M}+\text{Na}^+$): 263.1173; found: 263.1170



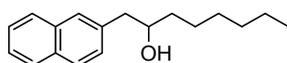
1-phenyloctan-2-ol (CAS: 19396-72-6)

Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{14}\text{H}_{22}\text{O}_2\text{Na}$ ($\text{M}+\text{Na}^+$): 229.1563; found: 229.1562



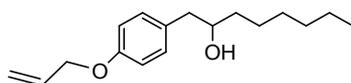
1-(4-bromophenyl)octan-2-ol (CAS: 1340103-80-1)

Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J = 9.4$ Hz, 2H), 7.08 (d, $J = 9.4$ Hz, 2H), 3.91 – 3.65 (m, 1H), δ 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) δ 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 $\text{C}_{14}\text{H}_{21}\text{OBrNa}$ ($\text{M}+\text{Na}^+$): 307.0668; found: 307.0663



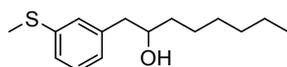
1-(naphthalen-2-yl)octan-2-ol (CAS: 179396-36-2)

Following general procedure, a white solid. ^1H NMR (400 MHz, CDCl_3) δ 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, $J = 6.7, 3\text{H}$). ^{13}C NMR (101 MHz, CDCl_3) δ 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 $\text{C}_{18}\text{H}_{24}\text{O}_2\text{Na}$ ($\text{M}+\text{Na}^+$): 279.1719; found: 279.1718



1-(4-(allyloxy)phenyloctan-2-ol

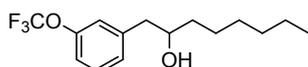
Following general procedure, a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (d, $J = 8.5$ Hz, 2H), 6.87 (d, $J = 8.6$ Hz, 2H), 6.19 – 5.93 (m, 1H), 5.44 – 5.33 (m, 1H), 5.33 – 5.18 (m, 1H), 4.52 (d, $J = 5.3$ Hz, 2H), 3.85 – 3.57 (m, 1H), δ 2.77 (dd, $J = 13.7, 4.2$ Hz, 1H), 2.57 (dd, $J = 13.7, 8.4$ 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) δ 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 $\text{C}_{17}\text{H}_{26}\text{O}_2\text{Na}$ ($\text{M}+\text{Na}^+$): 285.1825; found: 285.1824



1-(3-(methylthio)phenyl)octan-2-ol

Following general procedure, a colorless liquid. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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.

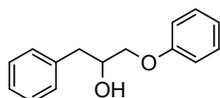
HRMS calcd for $\text{C}_{15}\text{H}_{24}\text{OSNa}$ ($\text{M}+\text{Na}^+$): 275.1440; found: 275.1440



1-(3-(trifluoromethoxy)phenyl)octan-2-ol

Following general procedure, a colorless liquid. $^1\text{H NMR}$ (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). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.72. $^{13}\text{C NMR}$ (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.

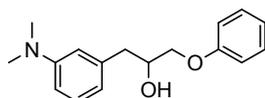
HRMS calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2\text{F}_3\text{Na}$ ($\text{M}+\text{Na}^+$): 313.1386; found: 313.1385



1-phenoxy-3-phenylpropan-2-ol (CAS: 42911-39-7)

Following general procedure, a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 – 7.19 (m, 7H), 6.97 (t, $J = 7.4$ Hz, 1H), 6.91 (dd, $J = 8.6, 0.8$ 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). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 158.64, 137.66, 129.66, 129.52, 128.77, 126.80, 121.30, 114.72, 71.24, 71.04, 39.99.

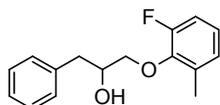
HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{Na}$ ($\text{M}+\text{Na}^+$): 251.1043; found: 151.1042



1-(3-(dimethylamino)phenyl)-3-phenoxypropan-2-ol

Following general procedure, a white solid. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $\text{C}_{17}\text{H}_{21}\text{O}_2\text{NNa}$ ($\text{M}+\text{Na}^+$): 294.1465; found: 294.1460

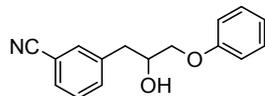


1-(2-fluoro-6-methylphenoxy)-3-phenylpropan-2-ol

Following general procedure, a colorless liquid. $^1\text{H NMR}$ (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)¹⁹F NMR (376 MHz, CDCl₃) δ -139.27.¹³C NMR (101 MHz, CDCl₃) δ 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

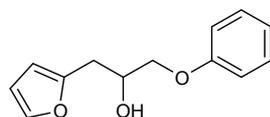
HRMS calcd for C₁₆H₁₇FO₂Na (M+Na⁺): 283.1105; found: 283.1104



3-(2-hydroxy-3-phenoxypropyl)benzonitrile

Following general procedure, a white solid. ¹H NMR (400 MHz, CDCl₃) δ 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), δ 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).¹³C NMR (101 MHz, CDCl₃) δ 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.

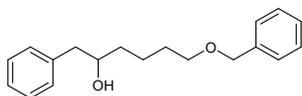
HRMS calcd for C₁₆H₁₅O₂NNa (M+Na⁺): 276.0995; found: 276.0994



1-(furan-2-yl)-3-phenoxypropan-2-ol (CAS: 1552787-70-8)

Following general procedure, a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.33 (m, 1H), 7.31 – 7.26 (m, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.93 – 6.88 (m, 2H), 6.34 – 6.28 (m, 1H), 6.15 (d, *J* = 3.1 Hz, 1H), δ 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).¹³C NMR (101 MHz, CDCl₃) δ 158.62, 151.85, 141.88, 129.66, 121.33, 114.71, 110.56, 107.48, 71.10, 69.16, 32.45.

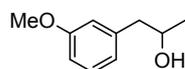
HRMS calcd for C₁₃H₁₄O₃Na (M+Na⁺): 241.0835; found: 241.0833



6-(benzyloxy)-1-phenylhexan-2-ol

Following general procedure, a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 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).¹³C NMR (101 MHz, CDCl₃) δ 137.55, 128.39, 127.52, 127.33, 126.62, 126.49, 125.41, 71.87, 71.52, 69.23, 43.02, 35.49, 28.63, 21.41.

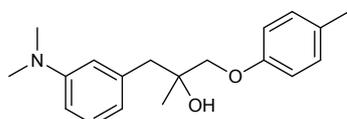
HRMS calcd for C₁₉H₂₄O₂Na (M+Na⁺): 307.1669; found: 307.1665



1-(3-methoxyphenyl)propan-2-ol (CAS: 34322-78-6)

Following general procedure, a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 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).¹³C NMR (101 MHz, CDCl₃) δ 158.71, 139.09, 128.53, 120.68, 114.05, 110.78, 67.78, 54.13, 44.81, 21.77.

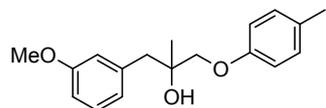
HRMS calcd for C₁₀H₁₄O₂Na (M+Na⁺): 189.0886; found: 189.0880



1-(3-(dimethylamino)phenyl)-2-methyl-3-(p-tolyloxy)propan-2-ol

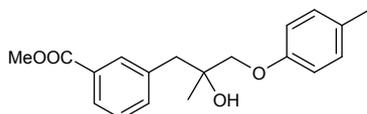
Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.18 (t, $J = 7.8$ Hz, 1H), 7.12 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 6.70 – 6.55 (m, 3H), 3.75 (dd, $J = 22.1, 8.8$ Hz, 2H), 2.97 (s, 2H), 2.85 (s, 6H), 2.33 (s, s, 4H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 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 $\text{C}_{19}\text{H}_{25}\text{O}_2\text{NNa}$ ($\text{M}+\text{Na}^+$): 322.1778; found: 322.1775

**1-(3-methoxyphenyl)-2-methyl-3-(p-tolyloxy)propan-2-ol**

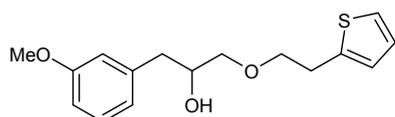
Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.19 (t, $J = 7.8$ Hz, 1H), 7.09 (d, $J = 8.3$ Hz, 2H), 6.93 – 6.70 (m, 5H), 3.80 – 3.53 (m, 5H), 2.95 (s, 2H), 2.30 (s, 3H), 2.07 (s, 1H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.60, 156.56, 138.72, 130.49, 130.09, 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 $\text{C}_{18}\text{H}_{22}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}^+$): 309.1462; found: 309.1460

**methyl 3-(2-hydroxy-2-methyl-3-(p-tolyloxy)propyl)benzoate**

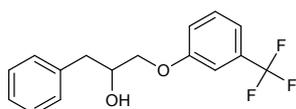
Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.98 – 7.83 (m, 2H), 7.48 – 7.39 (m, 1H), 7.39 – 7.31 (m, 1H), 7.10 (d, $J = 8.4$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 3.88 (s, 3H), 3.80 – 3.67 (m, 2H), 3.13 – 2.82 (m, 2H), 2.30 (s, 3H), 2.15 (s, 1H), 1.26 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 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 $\text{C}_{19}\text{H}_{22}\text{O}_4\text{Na}$ ($\text{M}+\text{Na}^+$): 337.1410; found: 337.1405

**1-(3-methoxyphenyl)-3-(2-(thiophen-2-yl)ethoxy)propan-2-ol**

Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 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, 1H), 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) δ 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.

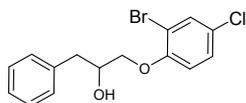
HRMS calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{NaS}$ ($\text{M}+\text{Na}^+$): 315.1025; found: 315.1024

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

Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 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) δ -

62.61. ^{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.

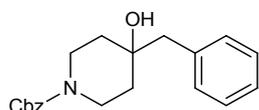
HRMS calcd for $\text{C}_{16}\text{H}_{15}\text{O}_2\text{F}_3\text{Na}$ ($\text{M}+\text{Na}^+$): 319.0916; found: 319.0915



1-(2-bromo-4-chlorophenoxy)-3-phenylpropan-2-ol

Following general procedure, a colorless liquid. ^1H 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.

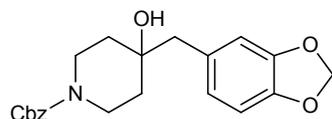
HRMS calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{ClBrNa}$ ($\text{M}+\text{Na}^+$): 362.9758; found: 362.9755



benzyl 4-benzyl-4-hydroxypiperidine-1-carboxylate

Following general procedure, a colorless liquid. ^1H 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.

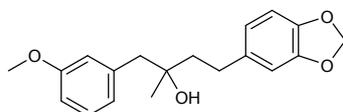
HRMS calcd for $\text{C}_{20}\text{H}_{23}\text{O}_3\text{NNa}$ ($\text{M}+\text{Na}^+$): 348.1570; found: 348.1570



benzyl 4-(benzo[d][1,3]dioxol-5-ylmethyl)-4-hydroxypiperidine-1-carboxylate

Following general procedure, a colorless liquid. ^1H 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.

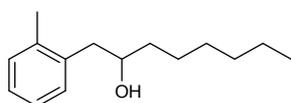
HRMS calcd for $\text{C}_{21}\text{H}_{23}\text{O}_5\text{NNa}$ ($\text{M}+\text{Na}^+$): 392.1468; found: 392.1466



4-(benzo[d][1,3]dioxol-5-yl)-1-(3-methoxyphenyl)-2-methylbutan-2-ol

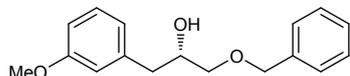
Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.23 (t, $J = 8.0$ Hz, 1H), 6.87 – 6.76 (m, 3H), 6.70 (dd, $J = 15.7, 4.6$ Hz, 2H), 6.64 (dd, $J = 7.9, 1.5$ Hz, 1H), 5.91 (s, 2H), 3.80 (s, 3H), 2.89 – 2.71 (m, 2H), 2.71 – 2.61 (m, 2H), 1.79 – 1.68 (m, 2H), 1.56 (s, 1H), 1.22 (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 $\text{C}_{19}\text{H}_{22}\text{O}_4\text{Na}$ ($\text{M}+\text{Na}^+$): 337.1410; found: 337.1410



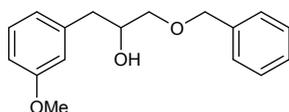
1-(*o*-tolyl)octan-2-ol (CAS: 1249825-56-6)

Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{15}\text{H}_{24}\text{ONa}$ ($\text{M}+\text{Na}^+$): 243.1719; found: 243.1715

**(S)-1-(benzyloxy)-3-(3-methoxyphenyl)propan-2-ol**

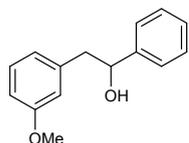
Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.27 (m, 5H), 7.25 – 7.15 (m, 1H), 6.86 – 6.71 (m, 3H), 4.61 – 4.42 (m, 2H), 4.14 – 3.94 (m, 1H), 3.77 (s, 3H), 3.50 (dd, $J = 9.5, 3.5$ Hz, 1H), 3.40 (dd, $J = 9.4, 7.0$ Hz, 1H), 2.78 (d, $J = 6.8$ Hz, 2H), 2.24 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.71, 139.59, 137.99, 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 $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}^+$): 295.1305; found: 295.1303

**1-(benzyloxy)-3-(3-methoxyphenyl)propan-2-ol**

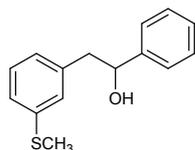
Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.27 (m, 5H), 7.26 – 7.17 (m, 1H), 6.86 – 6.74 (m, 3H), 4.54 (s, 2H), 4.14 – 3.98 (m, 1H), 3.78 (s, 3H), 3.56 – 3.47 (m, 1H), 3.47 – 3.34 (m, 1H), 2.78 (d, $J = 6.6$ Hz, 2H), 2.31 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 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 $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Na}$ ($\text{M}+\text{Na}^+$): 295.1305; found: 295.1300

**2-(3-methoxyphenyl)-1-phenylethanol (CAS: 237763-20-1)**

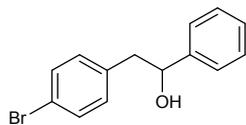
Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.24 (m, 5H), 7.23 – 7.16 (m, 1H), 6.77 (dd, $J = 9.3, 4.1$ Hz, 2H), 6.70 (s, 1H), 4.86 (dd, $J = 8.3, 5.0$ Hz, 1H), 3.74 (s, 3H), 3.20 – 2.78 (m, 2H), 2.09 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.70, 143.86, 139.68, 129.52, 128.45, 127.64, 125.98, 121.90, 115.14, 112.18, 75.25, 55.18, 46.17.

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

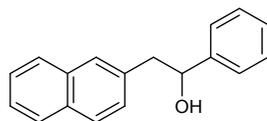
**2-(3-(methylthio)phenyl)-1-phenylethanol**

Following general procedure, a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 143.73, 138.80, 138.53, 128.89, 128.46, 127.69, 127.61, 126.34, 125.97, 124.80, 75.22, 45.94,

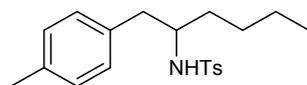
15.76.

HRMS calcd for C₁₅H₁₆OSNa (M+Na⁺): 267.0814; found: 267.0812**2-(4-bromophenyl)-1-phenylethanol (CAS: 214288-82-1)**

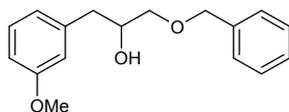
Following general procedure, a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.15 (m, 7H), 7.02 (d, *J* = 7.3 Hz, 2H), 4.97 – 4.63 (m, 1H), 2.96 (d, *J* = 6.5 Hz, 2H), 2.02 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.54, 137.04, 131.47, 131.32, 128.52, 127.83, 125.92, 120.50, 75.22, 45.25.

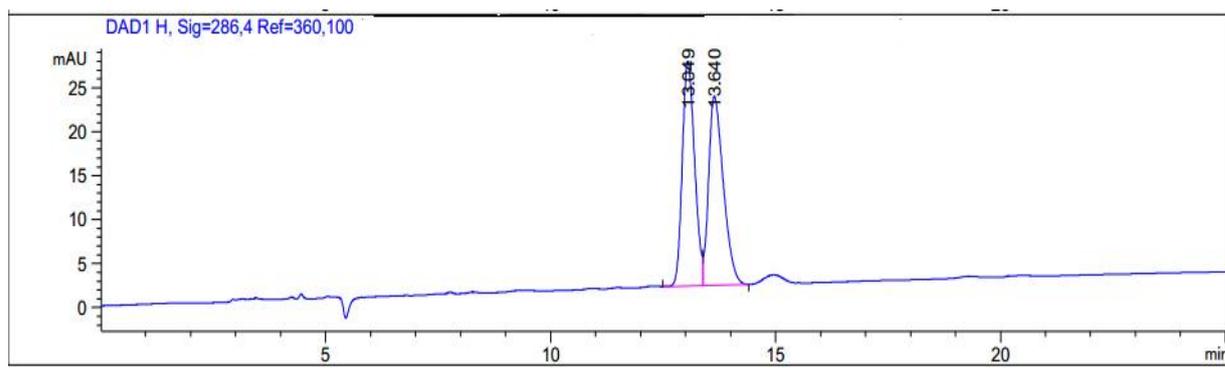
HRMS calcd for C₁₄H₁₃OBrNa (M+Na⁺): 299.0042; found: 299.0040**2-(naphthalen-2-yl)-1-phenylethanol (CAS: 1484699-56-0)**

Following general procedure, a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 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). ¹³C NMR (101 MHz, CDCl₃) δ 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.

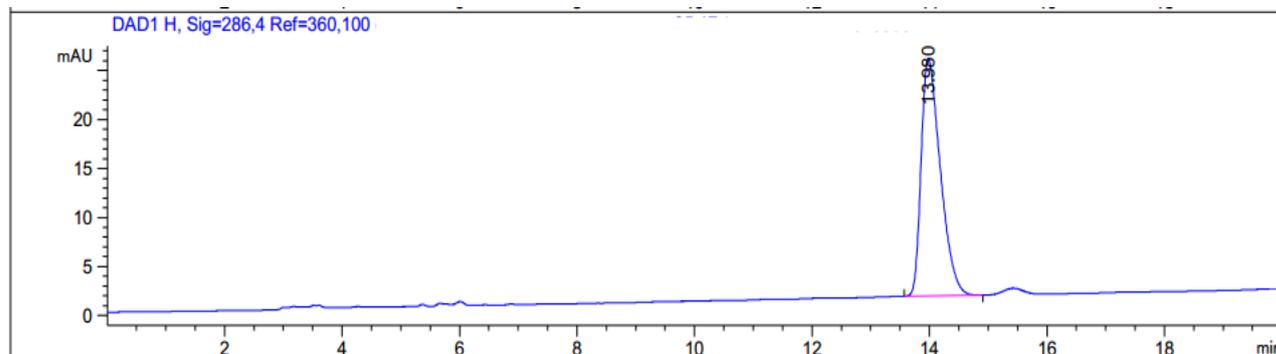
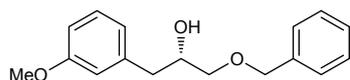
HRMS calcd for C₁₈H₁₆ONa (M+Na⁺): 271.1093; found: 271.1093**4-methyl-N-(1-(p-tolyl)hexan-2-yl)benzenesulfonamide**

Following general procedure, a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 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). ¹³C NMR (101 MHz, CDCl₃) δ 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**



Peak	Ret Time (min)	Width (min)	Area (mAu*s)	Height (mAU)	Area %
1	13.049	0.2960	486.63086	25.56818	49.7557
2	13.640	0.3486	491.40860	21.50571	50.2443



Peak	Ret Time (min)	Width (min)	Area (mAu*s)	Height (mAU)	Area %
1	13.980	0.3470	550.47296	24.23875	100.0000

IV. References

- (1) Ueno, S.; Chatani, N.; Kakiuchi, F. *J. Am. Chem. Soc.* **2007**, *129*, 6098.
- (2) Ukai, K.; Aoki, M.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.*, **2006**, *128*, 8706.
- (3) Carlson, B.; Phelan, G. D.; Kaminsky, W.; Dalton, L.; Jiang, X.; Liu, S.; Jen, A. K. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14162.
- (4) Tobisu, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.*, **2006**, *128*, 8152.

- (5) Gribkov, D. V.; Pastine, S. J.; Schnürch, M.; Sames, D. *J. Am. Chem. Soc.*, **2007**, 129, 11750.
- (6) Tasler, S.; Baumgartner, R.; Ammendola, A.; Schachtner, J.; Wieber, T.; Blisse, M.; Rath, S.; Zaja, M.; Klahn, P.; Quotschalla, U.; Ney, P. *Bioorg. Med. Chem. Lett.*, **2010**, 20, 6108.
- (7) Epple, R.; Urbina, H. D.; Russo, R.; Liu, H.; Mason, D.; Bursulaya, B.; Tumanut, C.; Li, J.; Harris, J. L. *Bioorg. Med. Chem. Lett.*, **2007**, 17, 1254.
- (8) Tasler, S.; Baumgartner, R.; Aschenbrenner, A.; Ammendola, A.; Wolf, K.; Wieber, T.; Schachtner, J.; Blisse, M.; Quotschalla, U.; Ney, P. *Bioorg. Med. Chem. Lett.*, **2010**, 20, 3399.
- (9) Taber, D. F.; Paquette, C. M.; Gu, P.; Tian, W. *J. Org. Chem.*, **2013**, 78, 9772.
- (10) Ciaccio, J. A.; Drahus, A. L.; Meis, R. M.; Tingle, C. T.; Smrtka, M.; Geneste, R. *Synth. Commu.*, **2003**, 33, 2135.
- (11) Hara, K.; Park, S. Y.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Chemistry, an Asian journal*, **2008**, 3, 1500.

