Supporting Information

Base-Free Ni-Catalyzed Suzuki-Type Cross-Coupling
Reactions of Epoxides with Boronic Acids

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1. General Information

1.1 Materials

The following chemicals were purchased and used as received: NiBr₂-diglyme (Aldrich, CAS: 312696-09-6), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbpy, CAS: 72914-19-3, Aldrich), Nickel(II) iodide (CAS: 13462-90-3, Alfa), NiCl₂(PPh₃)₂ (CAS: 14264-16-5, Adamas-beta), Cyclohexene oxide (CAS: 286-20-4, Adamas-beta), Isobutylene Oxide (CAS: 558-30-5, TCI), Cyclopentene oxide (CAS: 285-67-6, J&K), 2-hexyloxirane (CAS: 2984-50-1, Alfa), NaI (dry, anhydrous, Sinopharm Chemical Reagent Co., Ltd.), EtOH (Hengyue Chemical Technology Co., Ltd., 4 Å molecular sieves).

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

1.2 Analytical Methods

¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker 400 MHz spectrometer at 295 K in CDCl₃ unless otherwise noted. ¹⁹F NMR were reported as ¹⁹F exp. comp. pulse decoupling (F19CPD) unless otherwise noted. Data for ¹H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ¹³C-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 ESI-mass data were acquired on Thermo LTQ Orbitrap XL instrument. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).
2. Preparation of Substrates

2.1 Synthesis of substrates

To a solution of potassium tertbutoxyde (20 mmol) in DMSO (20 mL) at room temperature was added trimethylsulfoxonium iodide (1.1 equiv.) and stirred for 30 min. A solution of acetophenone (20 mmol) in DMSO (15 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 to provide the product. ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.35 (m, 4H), 7.33-7.28 (m, 1H), 3.01 (d, J = 5.3 Hz, 1H), 2.84 (d, J = 5.5 Hz, 1H), 1.76 (s, 3H).

To a solution of dimethylsulfoxonium methyldide, which was prepared under Ar from NaH of 60% dispersion in mineral oil (11.0 mmol) and trimethylsulfanium iodide (11.0 mmol) in 5 mL of anhydrous DMSO, was added benzyl 4-oxopiperidine-1-carboxylate (10.0 mmol) in 5 mL of DMSO dropwise. The resulting mixture was stirred at 55 ºC for 6 h. The cooled reaction mixture was poured into water and extracted with EtOAc. The combined organic layers were washed with H₂O, brine and then dried over Na₂SO₄. The mixture was purified by column chromatography to afford the desired products.
3. General Experimental Procedures

3.1 General procedure for Table 1

In air, Catalyst (10 mol%), Ligand (12 mol%), Phenylboronic acid (0.5 mmol) acid and NaI (50 mol%) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). Solvent (0.8 mL), Base (1.5 equiv.) and cyclohexene oxide (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. Benzophenone was added as internal standard. The product was yielded by GC.

Table S1. Optimization of the reaction conditions

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<th>Entry</th>
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<th>Solvent</th>
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<td>dtbpy</td>
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<td>H₂O</td>
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</table>
3.2 General procedure for Table 2

In air, NiBr₂·diglyme (10 mol%), dtbpy (12 mol%), Boronic acid (0.5 mmol) and NaI (50 mol%) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). To these solids, EtOH (0.8 mL) and epoxy (0.25 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 70 °C for 20 h. The mixture was purified by column chromatography to afford the desired products. The d.r. ratio was determined by ¹H & GC.

3.3 General procedure for Table 3

In air, NiBr₂·diglyme (10 mol%), dtbpy (12 mol%), (E)-styrylboronic acid (0.5 mmol) and NaI (50 mol%) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). EtOH (0.8 mL) and epoxy (0.25 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 70 °C for 20 h. The mixture was purified by column chromatography to afford the desired products.

3.3 General procedure for Table 4

In air, NiBr₂·diglyme (10 mol%), dtbpy (12 mol%), Boronic acid (1.5 equiv.) and NaI (50 mol%) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). EtOH (0.8 mL) and epoxy (0.3 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 70 °C for 20 h. The mixture was purified by column chromatography to afford the desired products.

3.3 General procedure for scheme 2

In air, NiBr₂·diglyme (10 mol%), dtbpy (12 mol%), (E)-styrylboronic acid (0.5 mmol) and NaI (50 mol%) were added to a schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). EtOH (0.8 mL) and 3,4-Epoxy-1-butene (0.25 mmol) were added in turn by syringe. The resulting reaction mixture was stirred vigorously at 70 °C for 20 h. The mixture was purified by column chromatography to afford the desired products.
4. Substrate Scope and Spectral Data

2-(3-(trifluoromethyl)phenyl)cyclohexan-1-ol
Prepared according to the general procedure, as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 – 7.47 (m, 2H), 7.46 – 7.40 (m, 2H), 3.68 (td, $J = 10.1$, 4.4 Hz, 1H), 2.57 – 2.45 (m, 1H), 2.17 – 2.06 (m, 1H), 1.92 – 1.83 (m, 2H), 1.81 – 1.73 (m, 1H), 1.57 – 1.28 (m, 5H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.95. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.64, 131.38 (q, $J = 1.1$ Hz), 130.95 (q, $J = 32.0$ Hz), 129.05, 124.54 (q, $J = 3.8$ Hz), 124.21 (q, $J = 272.3$ Hz), 123.59 (q, $J = 3.8$ Hz), 74.18, 52.97, 34.87, 33.37, 25.88, 24.97. HRMS (APCI) calcd for C13H15F3NaO (M+Na+): 267.0967; found: 267.0961.

2-phenylcyclohexan-1-ol
Prepared according to the general procedure, as a sticky solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.28 (m, 2H), 7.27 – 7.19 (m, 3H), 3.64 (td, $J = 10.1$, 4.3 Hz, 1H), 2.51 – 2.25 (m, 1H), 2.15 – 1.99 (m, 1H), 1.89 – 1.79 (m, 2H), 1.77 – 1.68 (m, 1H), 1.64 (br s, 1H), 1.57 – 1.25 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.35, 128.75, 127.94, 126.81, 74.40, 53.23, 34.47, 33.35, 26.08, 25.09. HRMS (APCI) calcd for C12H16NaO (M+Na+): 199.1093; found: 199.1098.

1-(4-(2-hydroxy-2-methylpropyl)phenyl)ethan-1-one
Prepared according to the general procedure, as a liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.3$ Hz, 2H), 2.83 (s, 2H), 2.58 (s, 3H), 1.24 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.01, 143.85, 135.42, 130.69, 128.15, 70.83, 49.68, 29.32, 26.56. HRMS (APCI) calcd for C12H16NaO2 (M+Na+): 215.1043; found: 215.1045.
**2-((1,1’-biphenyl]-4-yl)cyclohexan-1-ol**

Prepared according to the general procedure, as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.62 – 7.52 (m, 4H), 7.48 – 7.39 (m, 2H), 7.38 – 7.31 (m, 3H), 3.71 (td, \(J = 10.1, 4.3\) Hz, 1H), 2.49 (ddd, \(J = 13.2, 10.0, 3.5\) Hz, 1H), 2.15 (dd, \(J = 6.0, 2.7\) Hz, 1H), 1.96 – 1.83 (m, 2H), 1.79 (dd, \(J = 10.9, 4.6\) Hz, 1H), 1.62 – 1.56 (m, 1H), 1.56 – 1.46 (m, 1H), 1.46 – 1.30 (m, 3H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 142.39, 140.91, 139.80, 128.76, 128.31, 127.52, 127.17, 127.04, 74.46, 52.89, 34.56, 33.36, 26.07, 25.09. HRMS (APCI) calcd for C\(_{18}\)H\(_{20}\)NaO (M+Na\(^+\)): 275.1406; found: 275.1409.

**2-(naphthalen-2-yl)cyclohexan-1-ol**

Prepared according to the general procedure, as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 – 7.75 (m, 3H), 7.70 (s, 1H), 7.51 – 7.35 (m, 3H), 3.75 (td, \(J = 10.1, 4.3\) Hz, 1H), 2.59 (ddd, \(J = 13.2, 10.0, 3.6\) Hz, 1H), 2.24 – 2.01 (m, 1H), 1.96 – 1.84 (m, 2H), 1.78 (dd, \(J = 10.9, 4.1\) Hz, 1H), 1.69 – 1.55 (m, 2H), 1.53 – 1.30 (m, 3H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.75, 133.64, 132.64, 128.51, 127.67, 127.64, 126.73, 126.15, 125.97, 125.57, 74.29, 53.38, 34.51, 33.35, 26.11, 25.12. HRMS (APCI) calcd for C\(_{16}\)H\(_{18}\)NaO (M+Na\(^+\)): 249.1250; found: 249.1253.

**2-((1,1’-biphenyl]-4-yl)cyclopentan-1-ol**

Prepared according to the general procedure, as a pale-yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.62 – 7.48 (m, 4H), 7.45 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 4.16 (q, \(J = 7.2\) Hz, 1H), 2.90 (dd, \(J = 17.1, 8.0\) Hz, 1H), 2.26 – 2.05 (m, 2H), 1.93 – 1.62 (m, 5H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 142.51, 141.02, 139.42, 128.79, 127.88, 127.32, 127.15, 127.04, 80.45, 54.12, 34.07, 31.92, 21.82. HRMS (APCI) calcd for C\(_{17}\)H\(_{18}\)NaO (M+Na\(^+\)): 261.1250;
2-(4-(trifluoromethyl)phenyl)cyclohexan-1-ol

Prepared according to the general procedure, as a pale-yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J$ = 8.1 Hz, 2H), 7.34 (d, $J$ = 8.0 Hz, 2H), 3.67 – 3.54 (m, 1H), 2.55 – 2.41 (m, 1H), 2.13 – 1.98 (m, 1H), 1.78 (ddd, $J$ = 39.7, 16.6, 4.1 Hz, 4H), 1.57 – 1.23 (m, 4H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.35. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.98 (q, $J$ = 1.1 Hz), 128.90 (q, $J$ = 32.3 Hz), 128.23, 125.50 (q, $J$ = 3.7 Hz), 124.29 (q, $J$ = 271.8 Hz), 74.07, 52.94, 34.91, 33.32, 25.83, 24.95. HRMS (APCI) calcd for C$_{13}$H$_{15}$F$_3$NaO (M+Na$^+$): 267.0967; found: 267.0972.

4-(2-hydroxy-2-methylpropyl)benzonitrile

Prepared according to the general procedure, as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J$ = 8.2 Hz, 2H), 7.35 (d, $J$ = 8.2 Hz, 2H), 2.82 (s, 2H), 1.61 (br s, 1H), 1.24 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.76, 131.79, 131.25, 119.01, 110.27, 70.85, 49.67, 29.41. HRMS (APCI) calcd for C$_{11}$H$_{13}$NNaO (M+Na$^+$): 198.0889; found: 198.0887.

2-methyl-1-(3-(trifluoromethoxy)phenyl)propan-2-ol

Prepared according to the general procedure, as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (t, $J$ = 7.8 Hz, 1H), 7.21 – 7.04 (m, 3H), 2.78 (s, 2H), 1.46 (br s, 1H), 1.23 (s, 6H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.77. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.08, 140.17, 129.35, 128.87, 122.99, 120.50 (q, $J$ = 256.9 Hz), 118.95, 70.75, 49.35, 29.22. HRMS (APCI) calcd for C$_{11}$H$_{13}$F$_3$NaO$_2$ (M+Na$^+$): 257.0760; found: 257.0765.

1-phenyloctan-2-ol
Prepared according to the general procedure, as a pale-yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32 (t, \(J = 7.2\) Hz, 2H), 7.25 – 7.20 (m, 3H), 3.81 (ddd, \(J = 13.0, 7.9, 4.5\) Hz, 1H), 2.83 (dd, \(J = 13.5, 4.2\) Hz, 1H), 2.64 (dd, \(J = 13.5, 8.4\) Hz, 1H), 1.53 – 1.44 (m, 3H), 1.36 – 1.24 (m, 7H), 0.88 (t, \(J = 6.8\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 138.66, 129.43, 128.55, 126.43, 72.71, 44.06, 36.85, 31.84, 29.33, 25.74, 22.63, 14.10. (APCI) calcd for C\(_{14}\)H\(_{22}\)NaO (M+Na\(^+\)): 229.1563; found: 229.1567.

\[
\text{HO} \quad \text{C} \quad \text{HO}
\]

### 2-(4-fluorophenyl)cyclohexan-1-ol

Prepared according to the general procedure, as a pale-yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.25 – 7.18 (m, 2H), 7.11 – 6.96 (m, 2H), 3.61 (td, \(J = 10.1, 4.3\) Hz, 1H), 2.52 – 2.30 (m, 1H), 2.10 (ddd, \(J = 7.5, 4.6, 1.9\) Hz, 1H), 1.88 – 1.80 (m, 2H), 1.79 – 1.73 (m, 1H), 1.53 – 1.25 (m, 4H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -116.34. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 161.73 (d, \(J = 244.6\) Hz), 139.02 (d, \(J = 3.1\) Hz), 129.23 (d, \(J = 7.8\) Hz), 115.50 (d, \(J = 21.0\) Hz), 74.50, 52.42, 34.61, 33.50, 26.01, 25.03. HRMS (APCI) calcd for C\(_{12}\)H\(_{15}\)FNaO (M+Na\(^+\)): 217.0999; found: 217.0991.

\[
\text{O} \quad \text{C} \quad \text{OH}
\]

### 1-(3-(2-hydroxy-2-methylpropyl)phenyl)ethan-1-one

Prepared according to the general procedure, as a pale-yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.83 – 7.57 (m, 2H), 7.35 (m, 2H), 2.76 (s, 2H), 2.53 (s, 3H), 1.68 (br s, 1H), 1.16 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 198.44, 138.53, 137.02, 135.27, 130.17, 128.33, 126.59, 70.77, 49.46, 29.26, 26.69. HRMS (APCI) calcd for C\(_{12}\)H\(_{16}\)NaO\(_2\) (M+Na\(^+\)): 215.1043; found: 215.1046.

\[
\text{O} \quad \text{C} \quad \text{OH}
\]

### 2,2-diphenylethan-1-ol
Prepared according to the general procedure, as a pale-yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 – 6.93 (m, 10H), 4.29 – 3.88 (m, 3H), 1.71 (br s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.43, 128.77, 128.37, 126.87, 66.17, 53.68. HRMS (APCI) calcd for C14H14NaO (M+Na+): 221.0937; found: 221.0933.

![OH](Ph) \[2-(\{1,1'-biphenyl\}-4-yl)-2-phenylethan-1-ol]

Prepared according to the general procedure, as a pale-yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 – 7.48 (m, 4H), 7.47 – 7.37 (m, 2H), 7.36 – 7.27 (m, 7H), 7.27 – 7.23 (m, 1H), 4.85 – 3.43 (m, 3H), 1.59 (br s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.38, 140.80, 140.53, 139.79, 128.84, 128.83, 128.78, 128.39, 127.50, 127.31, 127.09, 126.96, 66.18, 53.38. HRMS (APCI) calcd for C20H18NaO (M+Na+): 297.1250; found: 297.1257.

![OH](Ph) | ![N](Boc)

**tert-butyl 4-([(1,1'-biphenyl]-4-ylmethyl)-4-hydroxypiperidine-1-carboxylate**

Prepared according to the general procedure, as a pale-yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 – 7.47 (m, 4H), 7.46 – 7.39 (m, 2H), 7.36 – 7.30 (m, 1H), 7.27 – 7.22 (m, 2H), 3.86 (d, $J$ = 13.1 Hz, 2H), 3.33 – 2.88 (m, 2H), 2.78 (s, 2H), 1.69 – 1.50 (m, 4H), 1.46 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.89, 140.75, 139.70, 135.23, 131.04, 128.84, 127.31, 127.08, 127.02, 79.46, 69.58, 48.93, 39.47, 36.67, 28.52. HRMS (APCI) calcd for C23H29NNaO3 (M+Na+): 390.2040; found: 390.2049.

![O](HO)

**1-((3-(2-hydroxycyclohexyl)phenyl)ethan-1-one**

Prepared according to the general procedure, as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (s, 1H), 7.83 (dt, $J$ = 7.3, 1.5 Hz, 1H), 7.49 – 7.37 (m, 2H), 3.73 (td, $J$ = 10.1, 4.3 Hz, 1H), 2.62 (d, $J$ = 4.1 Hz, 3H), 2.57 – 2.48 (m, 1H), 2.19 – 2.05 (m, 1H), 1.95 – 1.84 (m, 2H), 1.78 (dd, $J$ = 11.1, 4.6 Hz, 1H), 1.57 – 1.22 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$
(E)-2-methyl-5-phenylpent-4-en-2-ol
Prepared according to the general procedure, as a pale-yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.35 (m, 2H), 7.34 – 7.27 (m, 2H), 7.23 – 7.19 (m, 1H), 6.46 (d, \(J = 15.8\) Hz, 1H), 6.35 – 6.24 (m, 1H), 2.39 (d, \(J = 7.5\) Hz, 2H), 1.27 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.35, 133.70, 128.56, 127.28, 126.16, 125.79, 70.92, 47.36, 29.27. HRMS (APCI) calcd for C\(_{12}\)H\(_{16}\)NaO (M+Na\(^+\)): 199.1093; found: 199.1096.

trans-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)cyclohexan-1-ol
Prepared according to the general procedure, as a pale-yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.34 (m, 2H), 7.31 (t, \(J = 7.5\) Hz, 2H), 7.25 – 7.17 (m, 1H), 6.53 (d, \(J = 15.9\) Hz, 1H), 6.07 (dd, \(J = 15.9, 8.9\) Hz, 1H), 3.34 (td, \(J = 9.9, 4.4\) Hz, 1H), 2.13 – 2.00 (m, 2H), 1.87 – 1.77 (m, 3H), 1.73 – 1.65 (m, 1H), 1.35 – 1.24 (m, 4H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.07, 132.16, 131.98, 128.56, 127.38, 126.18, 73.25, 50.59, 33.89, 31.44, 25.22, 24.82. HRMS (APCI) calcd for C\(_{14}\)H\(_{18}\)NaO (M+Na\(^+\)): 225.1250; found: 225.1257.

(E)-3-methyl-5-phenylpent-4-en-2-ol
Prepared according to the general procedure, as a pale-yellow liquid. The d.r. ratio was determined to be 1.6:1 by \(^1\)H NMR. \(^1\)H NMR of a mixture of two diastereomers (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.18 (m, 1H), 6.47 (dd, \(J = 16.0, 12.1\) Hz, 1H), 6.15 (ddd, \(J = 17.5, 16.0, 8.3\) Hz, 1H), 3.82 – 3.51 (m, 1H), 2.53 – 2.19 (m, 1H), 1.62 (s, 1H), 1.26 – 1.16 (m, 3H), 1.14 – 1.05 (m, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 137.53, 137.29, 132.23, 131.80, 130.91, 128.70, 128.68, 127.48, 127.35, 126.30, 126.26, 71.49, 71.40, 45.62, 44.55, 20.48, 20.37, 16.73, 15.65. HRMS (APCI) calcd for C\(_{12}\)H\(_{16}\)NaO
(M+Na+): 199.1093; found: 199.1087.

(E)-5-phenylpent-4-en-2-ol
Prepared according to the general procedure, as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J = 7.3$ Hz, 2H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.21 (dd, $J = 13.2$, 6.0 Hz, 1H), 6.48 (d, $J = 15.9$ Hz, 1H), 6.29 – 6.16 (m, 1H), 3.93 (dd, $J = 12.2$, 6.2 Hz, 1H), 2.46 – 2.22 (m, 2H), 1.25 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.27, 133.18, 128.56, 127.30, 126.29, 126.13, 67.42, 42.93, 22.91. HRMS (APCI) calcd for C$_{11}$H$_{14}$NaO (M+Na+): 185.0937; found 185.0941.

(E)-1-phenylundeca-1,11-dien-4-ol
Prepared according to the general procedure, as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J = 7.5$ Hz, 2H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.22 (t, $J = 7.2$ Hz, 1H), 6.48 (d, $J = 15.8$ Hz, 1H), 6.28 – 6.10 (m, 1H), 5.87 – 5.70 (m, 1H), 5.04 – 4.87 (m, 2H), 2.49 – 2.39 (m, 1H), 2.34 – 2.25 (m, 1H), 2.04 (dd, $J = 13.6$, 6.4 Hz, 3H), 1.55 – 1.46 (m, 3H), 1.43 – 1.28 (m, 8H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.16, 137.25, 133.13, 128.55, 127.27, 126.37, 126.10, 114.19, 71.16, 41.16, 36.89, 33.78, 29.49, 29.08, 28.85, 25.66. HRMS (APCI) calcd for C$_{18}$H$_{26}$NaO (M+Na+): 281.1876; found 281.1872.

(E)-4-phenyl-2-vinylbut-3-en-1-ol
Prepared according to the general procedure, as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.34 (m, 2H), 7.35 – 7.27 (m, 2H), 7.27 – 7.18 (m, 1H), 6.50 (d, $J = 16.0$ Hz, 1H), 6.13 (dd, $J = 16.0$, 7.7 Hz, 1H), 5.88 – 5.63 (m, 1H), 5.34 – 5.13 (m, 2H), 3.65 (d, $J = 6.8$ Hz, 2H), 3.22 – 2.95 (m, 1H), 1.69 (br s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.38, 137.06, 132.25, 128.61, 128.58, 127.50, 126.24, 117.28, 65.24, 50.04. HRMS (APCI) calcd for C$_{12}$H$_{14}$NaO (M+Na+): 197.0937; found: 197.0933. The isolated product matched spectra previously reported in the literature. (Ref. J. Am. Chem. Soc., 2016, 138, 3655-3658).
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(2E,5E)-6-phenylhexa-2,5-dien-1-ol
Prepared according to the general procedure, as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 – 7.32 (m, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.20 (t, $J = 7.2$ Hz, 1H), 6.41 (d, $J = 15.8$ Hz, 1H), 6.28 – 6.15 (m, 1H), 5.84 – 5.64 (m, 2H), 4.14 (d, $J = 5.1$ Hz, 2H), 3.00 – 2.93 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.50, 130.96, 130.56, 130.28, 128.51, 128.03, 127.10, 126.04, 63.63, 35.49. HRMS (APCI) calcd for C$_{12}$H$_{14}$NaO (M+Na$^+$): 197.0937; found: 197.0939. The isolated product matched spectra previously reported in the literature. (Ref. Org. Lett., 2019, 21, 3606-3609).

F

2-(4-fluorophenyl)-2-phenylethan-1-ol
Prepared according to the general procedure, as a pale-yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.28 (m, 3H), 7.28 – 7.16 (m, 4H), 7.06 – 6.91 (m, 2H), 4.25 – 3.99 (m, 3H), 1.70 (br s, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -116.14. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.71 (d, $J = 245.2$ Hz), 141.27, 137.24 (d, $J = 3.2$ Hz), 129.81 (d, $J = 7.9$ Hz), 128.83, 128.27, 126.98, 115.52 (d, $J = 21.2$ Hz), 66.12, 52.82. HRMS (APCI) calcd for C$_{14}$H$_{13}$FNaO (M+Na$^+$): 239.0843; found: 239.0840.

O

1-(3-(2-hydroxy-1-phenylethyl)phenyl)ethan-1-one
Prepared according to the general procedure, as a pale-yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 (t, $J = 1.7$ Hz, 1H), 7.80 (dt, $J = 7.6$, 1.5 Hz, 1H), 7.44 (ddd, $J = 30.3$, 10.7, 4.5 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.21 (m, 3H), 4.30 – 4.22 (m, 1H), 4.21 – 4.15 (m, 2H), 2.56 (s, 3H), 1.91 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.40, 142.37, 140.95, 137.42, 133.28, 128.95, 128.87, 128.32, 127.96, 127.07, 127.03, 65.88, 53.50, 26.74. HRMS (APCI)
calcd for C16H16NaO2 (M+Na+): 263.1043; found: 263.1046.

4-(2-hydroxy-1-phenylethyl)benzonitrile
Prepared according to the general procedure, as a pale-yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 – 7.54 (m, 2H), 7.42 – 7.30 (m, 4H), 7.29 – 7.17 (m, 3H), 4.33 – 4.05 (m, 3H), 1.75 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.38, 140.13, 132.42, 129.24, 129.02, 128.34, 127.38, 118.87, 110.54, 65.54, 53.52. HRMS (APCI) calcd for C15H13NNaO (M+Na+): 246.0889; found: 246.0885.

2-((1E,3E)-penta-1,3-dien-1-yl)cyclopentan-1-ol
Prepared according to the general procedure, as a pale-yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (br s, 1H), 7.45 – 7.35 (m, 2H), 7.33 – 7.18 (m, 6H), 6.99 (d, $J$ = 7.6 Hz, 1H), 4.43 – 3.71 (m, 3H), 2.08 (s, 3H, -CH$_3$), 2.04 (br s, 3H, -OH). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.90, 142.55, 141.30, 138.27, 129.27, 128.71, 128.29, 126.85, 124.34, 119.89, 118.52, 65.89, 53.51, 24.46. HRMS (APCI) calcd for C16H17NNaO2 (M+Na+): 278.1151; found: 278.1156.

(E)-2,4-diphenylbut-3-en-1-ol
Prepared according to the general procedure, as a pale-yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.32 (m, 4H), 7.32 – 7.25 (m, 4H), 7.24 – 7.19 (m, 2H), 6.52 (d, $J$ = 16.0 Hz, 1H), 6.37 (dd, $J$ = 15.9, 7.8 Hz, 1H), 3.97 – 3.80 (m, 2H), 3.69 (q, $J$ = 7.3 Hz, 1H), 1.65 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.87, 136.99, 132.19, 129.75, 128.89, 128.61, 128.06, 127.57, 127.07, 126.32, 66.43, 51.87. HRMS (APCI) calcd for C16H16NaO (M+Na+):
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247.1093; found: 247.1096.

\[ \text{Cl} \quad \text{OH} \]

**2-(3-chlorophenyl)-2-phenylethan-1-ol**

Prepared according to the general procedure, as a pale-yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.27 (m, 4H), 7.26 – 7.17 (m, 4H), 7.13 (d, \(J = 7.1\) Hz, 1H), 4.24 – 3.92 (m, 3H), 1.96 (s, 1H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.69, 140.73, 134.53, 129.95, 128.90, 128.51, 128.33, 127.13, 127.03, 126.59, 65.86, 53.30. HRMS (APCI) calcd for C\(_{14}\)H\(_{13}\)ClNaO (M+Na\(^+\)): 255.0547; found: 255.0542.

\[ \text{HO} \quad \text{Ph} \quad \text{O} \quad \text{O} \]

**6-((1,1'-biphenyl)-4-yl)-2,2-dimethyl-1,3-dioxepan-5-ol**

Prepared according to the general procedure, as a pale-yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.63 – 7.51 (m, 4H), 7.43 (ddd, \(J = 8.5, 4.4, 1.9\) Hz, 2H), 7.39 – 7.30 (m, 3H), 4.52 (dt, \(J = 7.9, 6.0\) Hz, 1H), 4.08 – 3.91 (m, 3H), 3.71 (t, \(J = 8.0\) Hz, 1H), 3.16 – 2.95 (m, 1H), 1.71 (d, \(J = 24.7\) Hz, 1H), 1.35 (d, \(J = 2.6\) Hz, 6H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.76, 140.16, 137.33, 129.40, 128.80, 127.56, 127.29, 127.06, 109.03, 67.15, 64.42, 49.84, 26.51, 25.53. HRMS (APCI) calcd for C\(_{19}\)H\(_{22}\)NaO\(_3\) (M+Na\(^+\)): 321.1461; found: 321.1463.

\[ \text{HO} \quad \text{MeO} \quad \text{2} \quad \text{C} \]

**methyl 3-(2-hydroxycyclohexyl)benzoate**

Prepared according to the general procedure, as a pale-yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 – 7.83 (m, 2H), 7.54 – 7.29 (m, 2H), 3.90 (s, 3H), 3.75 – 3.64 (m, 1H), 2.60 – 2.40 (m, 1H), 2.21 – 2.00 (m, 1H), 1.85 (ddd, \(J = 8.5, 7.1, 2.6\) Hz, 2H), 1.81 – 1.74 (m, 1H), 1.60 – 1.18 (m, 5H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 167.16, 144.03, 132.83, 130.49, 128.80, 128.72, 128.02, 74.19, 52.96, 52.15, 34.79, 33.43, 25.96, 25.03. HRMS (APCI) calcd for C\(_{14}\)H\(_{18}\)NaO\(_3\) (M+Na\(^+\)): 257.1148; found: 257.1143.
3-((1,1'-biphenyl)-4-yl)butan-2-ol
Prepared according to the general procedure, as a pale-yellow liquid. The d.r. ratio was determined to be 1.8:1 by $^1$H NMR. $^1$H NMR of a mixture of two diastereomers (400 MHz, CDCl$_3$) $\delta$ 7.53 – 7.43 (m, 4H), 7.35 (M, 2H), 7.27 – 7.17 (m, 3H), 4.02 – 3.63 (m, 1H), 2.79 – 2.47 (m, 1H), 1.30 – 1.20 (m, 3H), 1.19 – 0.99 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.39, 142.74, 140.96, 140.91, 139.69, 139.39, 128.82, 128.53, 128.34, 127.37, 127.30, 127.24, 127.17, 127.07, 127.05, 125.92, 72.44, 72.38, 47.64, 46.84, 21.13, 20.76, 17.95, 16.06. HRMS (APCI) calcd for C$_{16}$H$_{18}$NaO (M+Na$^+$): 249.1250; found: 249.1255.

3-((1,1'-biphenyl)-4-yl)methyl)cyclopentan-1-ol
Prepared according to the general procedure, as a pale-yellow solid. The d.r. ratio was determined to be 1.2:1 by $^1$H NMR. $^1$H NMR of a mixture of two diastereomers (400 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J$ = 7.6 Hz, 2H), 7.50 (d, $J$ = 7.9 Hz, 2H), 7.42 (t, $J$ = 7.5 Hz, 2H), 7.31 (t, $J$ = 7.3 Hz, 1H), 7.26 – 7.19 (m, 2H), 4.56 – 4.15 (m, 1H), 2.81 – 2.54 (m, 2H), 2.21 – 2.07 (m, 1H), 2.05 – 1.87 (m, 1H), 1.85 – 1.64 (m, 2H), 1.55 – 1.38 (m, 2H), 1.36 – 1.16 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.13, 140.98, 140.88, 138.70, 129.24, 128.81, 128.76, 127.24, 127.04, 127.02, 127.00, 126.94, 73.71, 73.62, 42.53, 42.31, 42.20, 41.68, 40.34, 39.24, 35.44, 35.16, 30.39, 30.24. HRMS (APCI) calcd for C$_{18}$H$_{20}$NaO (M+Na$^+$): 275.1406; found: 275.1403.

benzyl 4-benzyl-4-hydroxypiperidine-1-carboxylate
Prepared according to the general procedure, as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.22 (m, 8H), 7.17 (d, $J$ = 7.1 Hz, 2H), 5.12 (s, 2H), 3.95 (br s, 2H), 3.16 (br s, 2H), 2.75 (s, 2H), 1.71 – 1.34 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.29, 136.89, 135.89, 130.55, 128.52, 128.50, 128.00, 127.89, 126.92, 69.36, 67.07, 49.31, 39.94, 36.63. HRMS
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(APCI) calcd for C20H23NNaO3 (M+Na+): 348.1570; found: 348.1573.

[Chemical structure image]

4-phenylisochromane

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.26 (m, 2H), 7.26 – 7.15 (m, 4H), 7.11 (t, $J = 7.4$ Hz, 1H), 7.04 (d, $J = 7.5$ Hz, 1H), 6.94 (d, $J = 7.7$ Hz, 1H), 4.89 (q, $J = 15.0$ Hz, 2H), 4.16 (q, $J = 5.0$ Hz, 2H), 3.89 (dd, $J = 12.7$, 8.4 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.11, 136.43, 134.89, 129.64, 129.06, 128.55, 126.79, 126.77, 126.46, 124.19, 72.22, 68.56, 44.51. HRMS (APCI) calcd for C15H15O (M+H+): 211.1117; found: 211.1119. The isolated product matched spectra previously reported in the literature. (Ref. Angew. Chem., Int. Ed., 2018, 57, 319 – 323).

[Chemical structure image]

2-(p-tolyl)cyclohexan-1-ol

Prepared according to the general procedure, as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.20 – 7.01 (m, 4H), 3.92 – 3.39 (m, 1H), 2.44 – 2.35 (m, 1H), 2.33 (s, 3H), 2.14 – 2.07 (m, 1H), 1.89 – 1.80 (m, 2H), 1.78 – 1.72 (m, 1H), 1.56 – 1.25 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.14, 136.39, 129.49, 127.77, 74.49, 52.80, 34.41, 33.39, 26.11, 25.09, 21.03. HRMS (APCI) calcd for C13H18NaO (M+Na+): 213.1250; found: 213.1253.

[Chemical structure image]

2-(3,4-dimethylphenyl)-2-phenylethan-1-ol

Prepared according to the general procedure, as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.15 (m, 5H), 7.08 (d, $J = 7.7$ Hz, 1H), 7.05 – 6.95 (m, 2H), 4.22 – 4.03 (m, 3H), 2.23 (s, 3H), 2.22 (s, 3H), 1.51 (br s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.71, 138.72, 136.97, 135.17, 130.01, 129.69, 128.72, 128.25, 126.73, 125.55, 66.22, 53.33, 19.93, 19.39. HRMS (APCI) calcd for C16H18NaO (M+Na+): 249.1250; found: 249.1256.
2-(3,4,5-trifluorophenyl)cyclohexan-1-ol

Prepared according to the general procedure, as a pale-yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.01 – 6.72 (m, 2H), 3.57 (td, $J$ = 10.0, 4.3 Hz, 1H), 2.54 – 2.30 (m, 1H), 2.19 – 2.02 (m, 1H), 2.00 – 1.65 (m, 3H), 1.55 – 1.19 (m, 5H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -134.46, -134.51, -163.32, -163.37, -163.43. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.23 (ddd, $J$ = 249.7, 9.8, 4.1 Hz), 140.14 (td, $J$ = 6.6, 4.6 Hz), 138.40 (dt, $J$ = 249.8, 15.3 Hz), 111.67 (dd, $J$ = 15.4, 5.5 Hz), 74.12, 52.42, 34.98, 33.24, 25.70, 24.86. HRMS (APCI) calcd for C$_{12}$H$_{13}$F$_3$NaO (M+Na$^+$): 253.0811; found: 253.0815.

1-(4-(2-hydroxycyclohexyl)phenyl)ethan-1-one

Prepared according to the general procedure, as a pale-yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 – 7.77 (m, 2H), 7.66 – 7.30 (m, 2H), 3.83 – 3.66 (m, 1H), 2.63 – 2.44 (m, 4H), 2.26 – 2.09 (m, 1H), 1.96 – 1.74 (m, 3H), 1.57 – 1.29 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.79, 149.50, 135.74, 128.78, 128.09, 74.11, 53.17, 34.87, 33.22, 26.56, 25.86, 24.99. HRMS (APCI) calcd for C$_{14}$H$_{18}$NaO$_2$ (M+Na$^+$): 241.1199; found: 241.1197.

2-(4-(hydroxymethyl)phenyl)-2-phenylethan-1-ol

Prepared according to the general procedure, as a pale-yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.16 (m, 9H), 4.64 (s, 2H), 4.27 – 4.11 (m, 3H), 1.77 (br s, 1H), 1.63 (br s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.30, 140.93, 139.41, 128.76, 128.53, 128.27, 127.46, 126.88, 66.09, 65.05, 53.35. HRMS (APCI) calcd for C$_{15}$H$_{16}$NaO$_2$ (M+Na$^+$): 251.1043; found: 251.1046.
**4-(2-hydroxycyclohexyl)benzaldehyde**

Prepared according to the general procedure, as a pale-yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.98 (s, 1H), 7.85 (d, \(J = 8.3\) Hz, 2H), 7.43 (d, \(J = 8.3\) Hz, 2H), 3.83 – 3.60 (m, 1H), 2.64 – 2.42 (m, 1H), 2.29 – 2.04 (m, 1H), 1.94 – 1.75 (m, 3H), 1.63 – 1.27 (m, 5H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 191.93, 151.12, 135.20, 130.19, 128.57, 74.14, 53.37, 34.93, 33.22, 25.82, 24.97. HRMS (APCI) calcd for C\(_{13}\)H\(_{16}\)NaO\(_2\) (M+Na\(^+\)): 227.1043; found: 227.1041.

![](image)

**2-(benzofuran-2-yl)cyclohexan-1-ol**

Prepared according to the general procedure, as a pale-yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54 – 7.48 (m, 1H), 7.43 (ddd, \(J = 3.2, 1.9, 0.9\) Hz, 1H), 7.26 – 7.13 (m, 2H), 6.51 (d, \(J = 0.6\) Hz, 1H), 3.87 – 3.48 (m, 1H), 2.77 – 2.58 (m, 1H), 2.13 (ddd, \(J = 7.6, 4.7, 1.5\) Hz, 1H), 2.03 (ddd, \(J = 13.2, 6.0, 2.8\) Hz, 1H), 1.89 – 1.77 (m, 2H), 1.74 – 1.59 (m, 1H), 1.47 – 1.27 (m, 4H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.27, 154.68, 128.51, 123.57, 122.68, 120.54, 111.00, 102.71, 72.68, 46.36, 34.29, 30.10, 25.36, 24.60. HRMS (APCI) calcd for C\(_{14}\)H\(_{16}\)NaO\(_2\) (M+Na\(^+\)): 239.1043; found: 239.1046.

![](image)

**(S)-1-([1,1'-biphenyl]-4-yl)butan-2-ol**

Prepared according to the general procedure, as a pale-yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.56 (dd, \(J = 15.1, 7.8\) Hz, 4H), 7.43 (t, \(J = 7.5\) Hz, 2H), 7.31 (dd, \(J = 19.9, 7.5\) Hz, 3H), 4.01 – 3.55 (m, 1H), 2.87 (dd, \(J = 13.6, 3.9\) Hz, 1H), 2.69 (dd, \(J = 13.5, 8.4\) Hz, 1H), 1.66 – 1.34 (m, 3H), 1.01 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.95, 139.41, 137.80, 129.89, 128.80, 127.30, 127.19, 127.05, 74.08, 43.22, 29.71, 10.13. HRMS (APCI) calcd for C\(_{16}\)H\(_{18}\)NaO (M+Na\(^+\)): 249.1250; found: 249.1252.
Scheme S1. Experiment of chiral epoxide

\[
\begin{align*}
\text{Ph} & \quad \text{B(OH)}_2 \\
0.5 \text{ mmol} & \quad \text{NiBr}_2 \text{diglyme, 8 mol\%} \\
\text{(S)-1,2-Epoxybutane} & \quad \text{dtbpy, 10 mol\%} \\
0.25 \text{ mmol} & \quad \text{Nal, 50 mol\%} \\
\text{EtOH, 20 mL} & \quad 70^\circ \text{C, 20 h} \\
79\% \text{ yield, >99\% ee} & \quad \text{L:B > 15:1}
\end{align*}
\]

**Chiralpak AD-H column, λ = 214 nm, n-hexane/i-PrOH (90:10)**

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**Scheme S2. Mechanism experiment of chiral epoxide**

\[
\begin{align*}
\text{Ar-B(OH)}_2 & \quad \text{NiBr}_2 \text{diglyme, 10 mol\%} \\
0.5 \text{ mmol} & \quad \text{dtbpy, 12 mol\%} \\
0.25 \text{ mmol} & \quad \text{Nal, 50 mol\%} \\
>98\% \text{ ee} & \quad \text{EtOH, 0.8 mL} \\
70^\circ \text{C, 20 h} & \quad 75\% \text{ yield racemic}
\end{align*}
\]

**Chiralpak OJ-H column, λ = 214 nm**

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S20
Scheme S3. Hammett analysis of the reaction

\[
\begin{align*}
\text{Ph-B(OH)}_2 + \text{Ar-B(OH)}_2 & \quad \text{NiBr}_2 \cdot \text{diglyme, 10 mol\%} \\
& \quad \text{dbpy, 12 mol\%} \\
& \quad \text{NaI, 50 mol\%} \\
& \quad \text{EtOH, 0.8 mL} \\
& \quad 70 \, ^\circ\text{C, 20 h}
\end{align*}
\]
Supporting Information

Scheme S4. X-ray diffraction analysis

CCDC Deposition Number: 1967481
## Supporting Information

### 5. NMR Spectra

#### Spectrum 1

![NMR Spectrum 1](image1)

#### Spectrum 2

![NMR Spectrum 2](image2)

#### Spectrum 3

![NMR Spectrum 3](image3)
Supporting Information


f1 (ppm)

-57.77

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{OH} & \quad \text{OH} \\
\text{F} & \quad \text{F} & \quad \text{F}
\end{align*}
\]

-57.77

29.22

49.35

70.75

118.95

119.23

121.78

122.99

128.87

129.35

140.17

149.08

-70.75

-49.35

-29.22

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{OH} & \quad \text{OH} \\
\text{F} & \quad \text{F} & \quad \text{F}
\end{align*}
\]
Supporting Information
Supporting Information

Chemical shifts for the compounds:

- C: 140.14, 139.49, 136.39, 135.14
- H: 74.49, 52.80, 34.41, 26.11
- CH₃: 21.03

Structures of the compounds:

1. Structure with chemical shifts: 7.32, 7.31, 7.29, 7.28, 7.26, 7.24, 7.23, 7.22, 7.21
2. Structure with chemical shifts: 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22
3. Structure with chemical shifts: 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22
Supporting Information

![Chemical Structure](image)

![NMR Spectrum](image)