Supplementary Information

Cu(I)-Catalyzed Asymmetric Intramolecular Addition of Aryl Pinacolboronic Esters to Unactivated Ketones: Enantioselective Synthesis of 2,3-Dihydrobenzofuran-3-ol Derivatives

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1. General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification.

**NMR spectrum:** $^1$H and $^{13}$C spectra are recorded on the Bruker AVANCE spectrometer, operating at 400 MHz (500 MHz) for $^1$H NMR and 100 MHz (125 MHz) for $^{13}$C NMR. Chemical shifts are reported in parts per million (ppm). Chemical shifts are reported downfield from CDCl$_3$ (δ: 7.26 ppm) and DMSO-d$_6$ (δ: 2.5 ppm) for $^1$H NMR. Chemical shifts of $^{13}$C NMR are reported in the scale relative to the solvent of CDCl$_3$ (δ: 77.0 ppm) and DMSO-d$_6$ (δ: 40.0 ppm) used as an internal reference. Multiplicities are recorded as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), q (quartet), m (multiplet). Coupling constants are reported in Hertz (Hz).

**Mass spectroscopy:** Mass spectra were in general recorded on Waters Micromass Q-TOF Premier Mass Spectrometer.

**Infrared Spectrometer:** Infrared spectra were obtained on Bruker TENSOR II instrument.

**High Performance Liquid Chromatography:** HPLC analysis was performed on Shimadzu 2030 equipment with Daicel Chiralpak OD-H or AD-H column.

**Spectropolarimeter:** Optical rotations were measured on Anton Paar MCP100 automatic polarimeter

**Chromatography:** Column chromatography was performed with silica gel (200-300 mesh ASTM).
2. Optimization of the Reaction Conditions

Table S1: Screening of Solvent

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<th>ee%</th>
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<td>THF</td>
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<tr>
<td>10$^d$</td>
<td>THF</td>
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$^a$Reaction conditions: The mixture of 1a (33.8 mg, 0.1 mmol), CuCl (0.5 mg, 0.005 mmol), (S,S)-QuinoxP* (1.8 mg, 0.0055 mmol), NaO-t-Bu (1 mg, 0.01 mmol) and i-PrOH (12.0 mg, 0.2 mmol) in solvent (0.5 mL) was stirred at RT for 16 h. $^b$Isolated yield. $^c$Determined by HPLC analysis. $^d$Used 20 mol% NaO-t-Bu.

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$^{293}$S3

Table S1: Screening of Solvent

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<td>10$^d$</td>
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$^a$Reaction conditions: The mixture of 1a (33.8 mg, 0.1 mmol), CuCl (0.5 mg, 0.005 mmol), (S,S)-QuinoxP* (1.8 mg, 0.0055 mmol), NaO-t-Bu (1 mg, 0.01 mmol) and i-PrOH (12.0 mg, 0.2 mmol) in solvent (0.5 mL) was stirred at RT for 16 h. $^b$Isolated yield. $^c$Determined by HPLC analysis. $^d$Used 20 mol% NaO-t-Bu.
Table S2: Screening of Base$^a$

![Chemical structure](image)

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<tr>
<td>7$^f$</td>
<td>NaCl-Bu</td>
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$^a$Reaction conditions: The mixture of 1a (33.8 mg, 0.1 mmol), CuCl (0.5 mg, 0.005 mmol), (S,S)-QuinoxP* (1.8 mg, 0.0055 mmol), Base (0.01 mmol) and i-PrOH (12.0 mg, 0.2 mmol) in THF (0.5 mL) was stirred at RT for 16 h. $^b$Isolated yield. $^c$Determined by HPLC analysis. $^d$Used 1.0 equiv. i-PrOH. $^e$Used 1.5 equiv. i-PrOH. $^f$Used 2.5 equiv. i-PrOH.
3. General Procedure for the Preparation of Substrates

The mixture of compound A and equal equiv. pinacol was refluxed with Dean-Stark in toluene (2 mL/mmol A) for 2 hours. After complete consumption of compound A (monitored by GC), toluene was removed and the residue was used for next reaction without further purification. (Note: Compound A were prepared according to the reported literature.)

To a 100 mL flask was added 2-aminophenylboronic acid pinacol ester (10 mmol), K$_2$CO$_3$ (2.08 g, 15 mmol), and DMF (30 mL) with stirring. After 15 minutes, BnBr (2.05 g, 12 mmol) was slowly added to the mixture over half an hour. After completion of the reaction (monitored by TLC), ethyl acetate (100 mL) and water (50 ml) were added to reaction mixture. The organic phase was separated and washed with water (3×50 mL). Then, the organic layer was concentrated under reduce pressure, which was directly used for the next step without further purification.

To a 100 mL flask was added C, 2-bromoacetophenone (2.39 g, 12 mmol), NaHCO$_3$ (1.68 g, 20 mmol), and DMF (30 mL). The reaction mixture was then heated to 50 °C. After completion of the reaction (monitored by TLC), ethyl acetate (100 mL) and water (50 ml) were added to reaction mixture. The organic phase was separated and washed with water (3×50 mL). Then, the organic layer was concentrated under reduce pressure and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give the substrate 3.
4. General Procedure for the Cu-Catalyzed Reactions

To a 4 mL sealed tube was added substrate 1 (0.1 mmol), CuCl (0.5 mg, 0.005 mmol), (S,S)-QuinoxP* (1.8 mg, 0.0055 mmol), NaOt-Bu (1 mg, 0.01 mmol) and i-PrOH (12.0 mg, 0.2 mmol) in THF (0.5 mL) in glovebox. Then the mixture was stirred at RT for 16 h. After that time, the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give the product 2.
5. Data for the Products

(R)-3-phenyl-2,3-dihydrobenzofuran-3-ol(2a)

![Chemical structure](image)

16.8 mg, 79% yield, oil.

$^1$H NMR (500 MHz, DMSO) $\delta$ 7.40 (d, $J = 7.5$ Hz, 2H), 7.38-7.31 (m, 2H), 7.30-7.22 (m, 2H), 7.01 (d, $J = 7.4$ Hz, 1H), 6.95-6.87 (m, 2H), 6.21 (s, 1H), 4.56 (d, $J = 9.9$ Hz, 1H), 4.46 (d, $J = 9.9$ Hz, 1H).

$^{13}$C NMR (125 MHz, DMSO) $\delta$ 160.3, 145.4, 134.0, 130.1, 128.5, 127.4, 126.1, 125.2, 121.3, 110.5, 85.9, 81.3.

HRMS (ESI) Calcd for C$_{14}$H$_{11}$O [M-H$_2$O+H]$^+$ 195.0810, found 195.0813.

$[\alpha]^{25}_D = -107.1$ (c = 0.7 in CH$_2$Cl$_2$); 96% ee [Chiralcel OD-H column, $n$-hexane / isopropanol = 90:10, 0.8 mL/min, $\lambda_{max}$ 254 nm, $t_R = 8.8$ min and 9.7 min].

(R)-3-(4-fluorophenyl)-2,3-dihydrobenzofuran-3-ol(2b)

![Chemical structure](image)

18.4 mg, 80% yield, oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53-7.46 (m, 2H), 7.36-7.30 (m, 1H), 7.13-7.04 (m, 3H), 6.97 (dd, $J = 11.4$, 4.3 Hz, 2H), 4.70 (d, $J = 10.3$ Hz, 1H), 4.48 (d, $J = 10.3$ Hz, 1H), 2.43 (s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.4, 160.8 (d, $J = 42.0$ Hz), 138.3 (d, $J = 3.0$ Hz), 131.92, 130.77, 127.9 (d, $J = 8.0$ Hz), 124.3, 121.5, 115.1 (d, $J = 22.0$ Hz), 110.9, 86.0, 82.2.

IR (oil) $\nu$ 3449 (br), 1593, 1472, 1057 cm$^{-1}$.

HRMS (ESI) Calcd for C$_{14}$H$_{10}$FO [M-H$_2$O+H]$^+$ 213.0716, found 213.0725.

$[\alpha]^{25}_D = -78.0$ (c = 0.9 in CH$_2$Cl$_2$); 96% ee [Chiralcel OD-H column, $n$-hexane / isopropanol = 90:10, 0.8 mL/min, $\lambda_{max}$ 254 nm, $t_R = 8.0$ min and 9.5 min].
(R)-3-(4-chlorophenyl)-2,3-dihydrobenzofuran-3-ol (2c)

$\text{H NMR (500 MHz, CDCl}_3 \text{)} \delta 7.46-7.42 (m, 2H), 7.32 (dd, J = 15.8, 8.4 \text{ Hz}, 3H), 7.07 (d, J = 7.4 \text{ Hz}, 1H), 6.98-6.93 (m, 2H), 4.68 (d, J = 10.3 \text{ Hz}, 1H), 4.46 (d, J = 10.3 \text{ Hz}, 1H), 2.42 (s, 1H).

$\text{C NMR (125 MHz, CDCl}_3 \text{)} \delta 160.5, 141.2, 133.5, 131.8, 130.8, 128.4, 127.5, 124.2, 121.6, 110.9, 86.0, 82.2.

The spectral data are consistent with those reported in the literature.\(^1\)

HRMS (ESI) Calcd for C\textsubscript{14}H\textsubscript{10}ClO [M-H\textsubscript{2}O+H]\(^+\) 229.0420, found 229.0421.

$[\alpha]_{D}^{25} = -75.9 \text{ (c = 0.9 in CH}_2\text{Cl}_2); 96\% \text{ ee [Chiralcel OD-H column, } n\text{-hexane / isopropanol = 90:10, 0.8 mL/min, } \lambda_{\text{max}} 254 \text{ nm, } t_R = 8.2 \text{ min and 9.9 min}].$

(R)-3-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzofuran-3-ol (2d)

$\text{H NMR (500 MHz, CDCl}_3 \text{)} \delta 7.65-7.60 (m, 4H), 7.33 (t, J = 7.8 \text{ Hz}, 1H), 7.06 (d, J = 7.5 \text{ Hz}, 1H), 6.97 (dd, J = 17.4, 8.0 \text{ Hz}, 2H), 4.71 (d, J = 10.4 \text{ Hz}, 1H), 4.51 (d, J = 10.4 \text{ Hz}, 1H), 2.43 (s, 1H).

$\text{C NMR (125 MHz, CDCl}_3 \text{)} \delta 160.6, 146.7, 131.7, 131.0, 130.0, 129.7, 126.5, 125.2 (q, J = 3.8 \text{ Hz}), 124.2, 121.7, 110.9, 86.0, 82.3.

The spectral data are consistent with those reported in the literature.\(^1\)

HRMS (ESI) Calcd for C\textsubscript{15}H\textsubscript{10}F\textsubscript{3}O [M-H\textsubscript{2}O+H]\(^+\) 263.0684, found 263.0684.

$[\alpha]_{D}^{25} = -108.8 \text{ (c = 0.9 in CH}_2\text{Cl}_2); 95\% \text{ ee [Chiralcel OD-H column, } n\text{-hexane / isopropanol = 90:10, 0.8 mL/min, } \lambda_{\text{max}} 254 \text{ nm, } t_R = 7.5 \text{ min and 9.0 min}].$
(R)-3-(p-tolyl)-2,3-dihydrobenzofuran-3-ol(2e)

\[
\begin{array}{c}
\text{H} \\
\text{Me} \\
\text{O} \\
\text{O} \\
\text{C} \\
\end{array}
\]

12.7 mg, 56% yield, oil.

\[ ^1\text{H} \text{NMR (500 MHz, CDCl}_3 \delta 7.39 (d, J = 8.1 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.12-7.08 (m, 1H), 6.95 (dd, J = 14.0, 7.7 Hz, 2H), 4.68 (d, J = 10.2 Hz, 1H), 4.49 (d, J = 10.2 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 1H).} \]

\[ ^{13}\text{C} \text{NMR (125 MHz, CDCl}_3 \delta 160.6, 139.6, 137.3, 132.3, 130.5, 128.9, 126.0, 124.3, 121.4, 110.7, 86.1, 82.5, 21.0.} \]

The spectral data are consistent with those reported in the literature.\(^2\)

HRMS (ESI) Calcd for C\(_{15}\)H\(_{13}\)O [M-H\(_2\)O+H\(^+\) 209.0966, found 209.0969.

[\(\alpha\)]\(_{D}^\text{25}\) = -127.3 (c = 0.4 in CH\(_2\)Cl\(_2\)); 96% ee [Chiralcel OD-H column, \(n\)-hexane / isopropanol = 90:10, 0.8 mL/min, \(\lambda_{\text{max}}\) 254 nm, \(t_R = 8.0 \text{ min and 9.2 min}\).

(R)-3-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-ol(2f)

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{Me} \\
\text{C} \\
\end{array}
\]

15.0 mg, 62% yield, oil.

\[ ^1\text{H} \text{NMR (400 MHz, CDCl}_3 \delta 7.39-7.33 (m, 2H), 7.27-7.21 (m, 1H), 7.05 (dd, J = 7.4, 0.8 Hz, 1H), 6.92-6.81 (m, 4H), 4.62 (d, J = 10.2 Hz, 1H), 4.40 (d, J = 10.2 Hz, 1H), 3.76 (s, 3H), 2.24 (s, 1H).} \]

\[ ^{13}\text{C} \text{NMR (100 MHz, CDCl}_3 \delta 160.6, 159.0, 134.6, 132.3, 130.5, 127.3, 124.4, 121.4, 113.6, 110.8, 86.0, 82.3, 55.3.} \]

The spectral data are consistent with those reported in the literature.\(^1\)

HRMS (ESI) Calcd for C\(_{15}\)H\(_{13}\)O\(_2\) [M-H\(_2\)O+H\(^+\) 225.0916, found 225.0915.

[\(\alpha\)]\(_{D}^\text{25}\) = -41.5 (c = 0.4 in CH\(_2\)Cl\(_2\)); 97% ee [Chiralcel OD-H column, \(n\)-hexane / isopropanol = 90:10, 0.8 mL/min, \(\lambda_{\text{max}}\) 254 nm, \(t_R = 11.1 \text{ min and 13.6 min}\).
(R)-3-([1,1'-biphenyl]-4-yl)-2,3-dihydrobenzofuran-3-ol (2g)

![Chemical Structure]

20.0 mg, 69% yield, white foam.

$^1$H NMR (400 MHz, DMSO) δ 7.67-7.63 (m, 4H), 7.47 (dd, $J = 15.1$, 8.0 Hz, 4H), 7.36 (t, $J = 7.3$ Hz, 1H), 7.29-7.24 (m, 1H), 7.08-7.03 (m, 1H), 6.97-6.89 (m, 2H), 6.27 (s, 1H), 4.59 (d, $J = 9.9$ Hz, 1H), 4.51 (d, $J = 9.9$ Hz, 1H).

$^{13}$C NMR (100 MHz, DMSO) δ 160.3, 144.6, 140.3, 139.3, 133.9, 130.1, 129.4, 127.9, 127.1, 126.8, 126.8, 125.3, 121.3, 110.5, 85.9, 81.2.

IR (neat) ν 3425 (br), 1601, 1460, 1126 cm$^{-1}$.

HRMS (ESI) Calcd for C$_{20}$H$_{15}$O [M-H$_2$O+H]$^+$ 271.1123, found 271.1126.

$\left[\alpha\right]^{25}_D = -74.9$ (c = 0.8 in CH$_2$Cl$_2$); 97% ee [Chiralcel OD-H column, n-hexane / isopropanol = 90:10, 0.8 mL/min, $\lambda_{max}$ 254 nm, $t_R$ = 11.1 min and 14.4 min].

(R)-3-(naphthalen-1-yl)-2,3-dihydrobenzofuran-3-ol (2h)

![Chemical Structure]

18.9 mg, 72% yield, oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.10 (s, 1H), 7.87-7.81 (m, 3H), 7.53-7.46 (m, 3H), 7.33 (t, $J = 7.8$ Hz, 1H), 7.12 (d, $J = 7.4$ Hz, 1H), 7.01 (d, $J = 8.2$ Hz, 1H), 6.96 (t, $J = 7.4$ Hz, 1H), 4.77 (d, $J = 10.3$ Hz, 1H), 4.62 (d, $J = 10.3$ Hz, 1H), 2.52 (s, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 160.7, 139.8, 132.9, 132.6, 132.1, 130.7, 128.2, 128.1, 127.6, 126.4, 126.2, 124.8, 124.4, 124.2, 121.5, 110.8, 85.9, 82.7.

The spectral data are consistent with those reported in the literature.$^2$

HRMS (ESI) Calcd for C$_{18}$H$_{13}$O [M-H$_2$O+H]$^+$ 245.0966, found 245.0965.

$\left[\alpha\right]^{25}_D = -40.6$ (c = 0.3 in CH$_2$Cl$_2$); 97% ee [Chiralcel OD-H column, n-hexane / isopropanol = 90:10, 0.8 mL/min, $\lambda_{max}$ 254 nm, $t_R$ = 12.8 min and 16.4 min].
(R)-3-(2-methoxyphenyl)-2,3-dihydrobenzofuran-3-ol(2i)

13.6 mg, 56% yield, oil.

\[ \text{H NMR (400 MHz, DMSO) } \delta 7.70 (d, J = 7.6 \text{ Hz}, 1\text{H}), 7.32-7.27 (m, 1\text{H}), 7.21-7.14 (m, 1\text{H}), 7.04-6.92 (m, 2\text{H}), 6.86 (dd, J = 12.0, 7.7 \text{ Hz}, 2\text{H}), 6.79 (t, J = 7.3 \text{ Hz}, 1\text{H}), 5.98 (s, 1\text{H}), 4.64 (d, J = 9.4 \text{ Hz}, 1\text{H}), 4.40 (d, J = 9.4 \text{ Hz}, 1\text{H}), 3.43 (s, 3\text{H}). \]

\[ \text{C NMR (100 MHz, DMSO) } \delta 160.5, 156.7, 134.0, 132.3, 129.4, 129.4, 127.3, 124.1, 120.4, 120.3, 112.8, 109.8, 83.9, 79.6, 56.0. \]

IR (oil) \( \nu \) 3457 (br), 1586, 1254, 849, 752 cm\(^{-1}\).

HRMS (ESI) Calcd for C\(_{15}\)H\(_{13}\)O\(_2\) [M-H\(_2\)O+H]\(^+\) 225.0916, found 225.0912.

\[ [\alpha]^{25}_D = -164.1 \text{ (c = 0.2 in CH}_2\text{Cl}_2); 85\% \text{ ee [Chiralcel OD-H column, } n\text{-hexane / isopropanol = 90:10, 0.8 mL/min, } \lambda_{\text{max}} 254 \text{ nm, } t_R = 30.3 \text{ min and 33.1 min].} \]

(R)-3-(thiophen-2-yl)-2,3-dihydrobenzofuran-3-ol(2j)

19.0 mg, 87% yield, oil. (Reactions was performed at 60 °C.)

\[ \text{H NMR (500 MHz, DMSO) } \delta 7.47 (dd, J = 5.1, 1.2 \text{ Hz}, 1\text{H}), 7.29-7.18 (m, 1\text{H}), 7.21-7.18 (m, 1\text{H}), 6.99 (dd, J = 5.1, 3.6 \text{ Hz}, 1\text{H}), 6.93 (t, J = 7.3 \text{ Hz}, 2\text{H}), 6.87 (dd, J = 3.5, 1.1 \text{ Hz}, 1\text{H}), 6.57 (s, 1\text{H}), 4.60 (d, J = 9.9 \text{ Hz}, 1\text{H}), 4.54 (d, J = 9.9 \text{ Hz}, 1\text{H}). \]

\[ \text{C NMR (125 MHz, DMSO) } \delta 159.9, 150.0, 135.0, 130.5, 127.5, 125.8, 125.1, 124.3, 121.3, 110.7, 85.4, 79.7. \]

IR (oil) \( \nu \) 3342 (br), 1621, 1468, 985 cm\(^{-1}\).

HRMS (ESI) Calcd for C\(_{12}\)H\(_9\)O\(_2\)S [M-H\(_2\)O+H]\(^+\) 201.0374, found 201.0374.

\[ [\alpha]^{25}_D = -94.6 \text{ (c = 0.9 in CH}_2\text{Cl}_2); 97\% \text{ ee [Chiralcel OD-H column, } n\text{-hexane / isopropanol = 90:10, 0.8 mL/min, } \lambda_{\text{max}} 254 \text{ nm, } t_R = 15.8 \text{ min and 17.1 min].} \]
(R)-3-methyl-2,3-dihydrobenzofuran-3-ol (2k)

![Chemical Structure](image)

7.8 mg, 52% yield, solid, mp 83-87 °C. (Reactions was performed at 60 °C.)

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.34 (d, $J = 7.4$ Hz, 1H), 7.26-7.22 (m, 1H), 6.96 (t, $J = 7.4$ Hz, 1H), 6.87 (d, $J = 8.1$ Hz, 1H), 4.50 (d, $J = 10.0$ Hz, 1H), 4.31 (d, $J = 10.0$ Hz, 1H), 2.01 (s, 1H), 1.69 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 159.8, 131.9, 130.3, 122.9, 121.0, 110.7, 84.0, 77.9, 24.9.

The spectral data are consistent with those reported in the literature.$^1$

HRMS (ESI) Calcd for C$_9$H$_9$O [M-H$_2$O+H]$^+$ 133.0653, found 133.0654.

$[^{[a]}]_{25}D = -62.4$ (c = 0.3 in CH$_2$Cl$_2$); 97% ee [Chiralcel OD-H column, n-hexane / isopropanol = 90:10, 0.8 mL/min, $\lambda_{max}$ 254 nm, $t_R$ = 7.4 min and 8.1 min].

(R)-3-(tert-butyl)-2,3-dihydrobenzofuran-3-ol (2l)

![Chemical Structure](image)

12.3 mg, 64% yield, solid, mp 80-84 °C.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.39 (dd, $J = 7.5$, 0.5 Hz, 1H), 7.26-7.22 (m, 1H), 6.91 (t, $J = 7.5$ Hz, 1H), 6.83 (d, $J = 8.1$ Hz, 1H), 4.69 (d, $J = 10.1$ Hz, 1H), 4.23 (d, $J = 10.1$ Hz, 1H), 2.04 (s, 1H), 1.05 (s, 9H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 160.6, 130.0, 129.8, 125.0, 120.4, 110.5, 85.7, 80.5, 37.6, 24.8.

The spectral data are consistent with those reported in the literature.$^3$

HRMS (ESI) Calcd for C$_{12}$H$_{15}$O [M-H$_2$O+H]$^+$ 175.1123, found 175.1126.

$[^{[a]}]_{25}D = -16.2$ (c = 0.7 in CH$_2$Cl$_2$); 94% ee [Chiralcel OD-H column, n-hexane / isopropanol = 90:10, 0.8 mL/min, $\lambda_{max}$ 254 nm, $t_R$ = 6.0 min and 6.8 min].

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(R)-2,2-dimethyl-3-phenyl-2,3-dihydrobenzofuran-3-ol (2m)

18.8 mg, 78% yield, white foam.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \text{)} \delta 7.52-7.48 \text{ (m, 2H), 7.42-7.25 \text{ (m, 5H), 6.98 \text{ (t, } J = 10.0 \text{ Hz, 1H), 6.91 \text{ (d, } J = 11.2 \text{ Hz, 1H), 2.09 \text{ (s, 1H), 1.62 \text{ (s, 3H), 0.88 \text{ (s, 3H)}}) \text{.}} \]

\[ ^13C \text{ NMR (100 MHz, CDCl}_3 \text{)} \delta 160.8, 130.1, 130.0, 125.0, 120.4, 110.5, 85.9, 80.6, 37.5, 24.8. \]

The spectral data are consistent with those reported in the literature.\(^4\)

HRMS (ESI) Calcd for C\(_{16}\)H\(_{17}\)O\(_2\) \([\text{M}+\text{H}]^+\) 241.1229, found 241.1236.

[\(\alpha\)]\(_{25}\)\(_D\) = -104.2 (c = 0.6 in CH\(_2\)Cl\(_2\)); 94% ee [Chiralcel AD-H column, \(n\)-hexane / isopropanol = 90:10, 0.8 mL/min, \(\lambda_{\text{max}}\) 254 nm, \(t_R = 8.4\) min and 9.4 min].

(R)-3-phenyl-2,3-dihydronaphtho[2,3-b]furan-3-ol (2n)

17.3 mg, 66% yield, oil.

\[ ^1H \text{ NMR (500 MHz, DMSO)} \delta 7.92-7.84 \text{ (m, 2H), 7.45 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.41 \text{ (d, } J = 7.3 \text{ Hz, 1H), 7.33 \text{ (t, } J = 7.7 \text{ Hz, 2H), 7.29 \text{ (d, } J = 8.8 \text{ Hz, 1H), 7.27-7.21 \text{ (m, 3H), 6.47 \text{ (d, } J = 1.1 \text{ Hz, 1H), 4.72 \text{ (d, } J = 10.0 \text{ Hz, 1H), 4.57 \text{ (d, } J = 9.9 \text{ Hz, 1H)}}) \text{.}} \]

\[ ^13C \text{ NMR (125 MHz, DMSO)} \delta 158.4, 146.1, 131.8, 130.1, 130.0, 129.2, 128.6, 127.3, 127.0, 125.8, 123.6, 123.4, 123.0, 113.1, 87.7, 82.6. \]

IR (oil) \(\nu\) 3438 (br), 1627, 1489, 1150 cm\(^{-1}\).

HRMS (ESI) Calcd for C\(_{18}\)H\(_{13}\)O \([\text{M-H}_2\text{O}+\text{H}]^+\) 245.0966, found 245.0965.

[\(\alpha\)]\(_{25}\)\(_D\) = -40.6 (c = 0.3 in CH\(_2\)Cl\(_2\)); 99% ee [Chiralcel OD-H column, \(n\)-hexane / isopropanol = 90:10, 0.8 mL/min, \(\lambda_{\text{max}}\) 254 nm, \(t_R = 13.1\) min and 33.0min].

(R)-5-chloro-3-phenyl-2,3-dihydrobenzofuran-3-ol (2o)

17.5 mg, 71% yield, oil.
\(^{1}\)H NMR (500 MHz, DMSO) δ 7.41 (d, \(J = 7.4\) Hz, 2H), 7.37 (dd, \(J = 10.4, 4.9\) Hz, 2H), 7.32-7.26 (m, 2H), 6.97 (dd, \(J = 9.0, 5.0\) Hz, 2H), 6.38 (s, 1H), 4.61 (d, \(J = 10.0\) Hz, 1H), 4.53 (d, \(J = 10.0\) Hz, 1H).

\(^{13}\)C NMR (125 MHz, DMSO) δ 159.1, 144.6, 136.1, 130.0, 128.6, 127.7, 126.1, 124.9, 124.7, 112.2, 86.5, 81.2.


\([\alpha]\)\(^{25}\)D = -43.6 (c = 0.4 in CH\(_2\)Cl\(_2\)); 86% ee [Chiralcel OD-H column, \(n\)-hexane / isopropanol = 90:10, 0.8 mL/min, \(\lambda_{\max}\) 254 nm, \(t_R = 7.9\) min and 9.0 min].

\((R)\)-6-methoxy-3-phenyl-2,3-dihydrobenzofuran-3-ol (2p)

\[\text{MeO} \]

15.3 mg, 63% yield, oil.

\(^{1}\)H NMR (400 MHz, DMSO) δ 7.43-7.38 (m, 2H), 7.34 (t, \(J = 7.6\) Hz, 2H), 7.25 (dd, \(J = 8.2, 6.2\) Hz, 1H), 6.88 (d, \(J = 8.3\) Hz, 1H), 6.53 (d, \(J = 2.2\) Hz, 1H), 6.47 (dd, \(J = 8.3, 2.2\) Hz, 1H), 6.08 (s, 1H), 4.57 (d, \(J = 9.8\) Hz, 1H), 4.45 (d, \(J = 9.8\) Hz, 1H), 3.74 (s, 3H).

\(^{13}\)C NMR (100 MHz, DMSO) δ 161.9, 161.6, 145.6, 128.4, 127.3, 126.2, 126.1, 125.6, 107.6, 96.4, 86.9, 81.0, 55.9.


\([\alpha]\)\(^{25}\)D = -93.3 (c = 0.9 in CH\(_2\)Cl\(_2\)); 99% ee [Chiralcel AD-H column, \(n\)-hexane / isopropanol = 90:10, 0.8 mL/min, \(\lambda_{\max}\) 254 nm, \(t_R = 14.3\) min and 21.7 min].

1-benzyl-3-phenylindolin-3-ol (4)

\[\text{Ph} \]

19.0 mg, 64% yield, oil.

\(^{1}\)H NMR (400 MHz, DMSO) δ 7.55 (d, \(J = 6.7\) Hz, 2H), 7.42-7.36 (m, 3H), 7.28 (d, \(J = 4.3\) Hz, 4H), 7.23-7.18 (m, 1H), 7.15 (s, 1H), 6.84 (d, \(J = 7.7\) Hz, 1H), 6.74 (t, \(J = 7.7\) Hz, 1H), 6.58 (d, \(J = 7.7\) Hz, 1H), 6.25 (d, \(J = 7.7\) Hz, 1H), 4.45 (d, \(J = 9.8\) Hz, 1H), 3.74 (s, 3H).
7.2 Hz, 1H), 6.65-6.57 (m, 2H), 4.58 (d, \( J = 16.3 \) Hz, 1H), 4.44 (d, \( J = 16.4 \) Hz, 1H), 3.36 (s, 2H).

\(^{13}\text{C} \) NMR (100 MHz, DMSO) \( \delta \) 142.9, 142.9, 139.0, 134.6, 128.8, 128.7, 128.5, 127.5, 127.2, 126.4, 121.7, 117.5, 116.9, 112.3, 94.9, 57.4, 54.3.

IR (oil) \( \nu \) 3396 (br), 2628, 1479, 1251, 1026 cm\(^{-1}\).

HRMS (ESI) Calcd for C\(_{21}\)H\(_{18}\)N [M-H\(_2\)O+H]\(^+\) 284.1439, found 284.1440.

\((R)-1\)-phenyl-2,3-dihydro-1H-inden-1-ol(6)

\[
\begin{align*}
\text{H} & \text{C} \\
& \text{Ph}
\end{align*}
\]

9.3 mg, 44% yield, oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.42-7.20 (m, 8H), 7.11-7.08 (m, 1H), 3.24-3.13 (m, 1H), 3.01-2.90 (m, 1H), 2.52-2.47 (m, 2H), 2.10 (s, 1H).

\(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 148.1, 146.1, 144.1, 128.6, 128.1, 127.0, 126.9, 125.6, 125.0, 124.2, 85.6, 44.8, 30.0.

The spectral data are consistent with those reported in the literature.\(^1\)

HRMS (ESI) Calcd for C\(_{15}\)H\(_{15}\)O [M+H]\(^+\) 211.1123, found 211.1119.

7% ee [Chiralcel AD-H column, \( n \)-hexane / isopropanol = 97:3, 0.8 mL/min, \( \lambda_{\text{max}} \) 254 nm, \( t_R \) = 12.5 min and 17.0 min].
6. References


7. NMR and HPLC Spectra

(R)-3-phenyl-2,3-dihydrobenzofuran-3-ol(2a)
(R)-3-(4-fluorophenyl)-2,3-dihydrobenzofuran-3-ol(2b)
(R)-3-((1,1'-biphenyl)-4-yl)-2,3-dihydrobenzofuran-3-ol (2g)
(R)-3-(thiophen-2-yl)-2,3-dihydrobenzofuran-3-ol(2j)
(R)-3-phenyl-2,3-dihydropaphtho[2,3-b]furan-3-ol (2n)
(R)-5-chloro-3-phenyl-2,3-dihydrobenzofuran-3-ol(2o)
(R)-6-methoxy-3-phenyl-2,3-dihydrobenzofuran-3-ol (2p)
1-benzyl-3-phenylindolin-3-ol(4)
(R)-3-phenyl-2,3-dihydrobenzofuran-3-ol(2a)

(Reaction was performed at RT.)

(Reaction was performed at 120 °C.)
(R)-3-(4-fluorophenyl)-2,3-dihydrobenzofuran-3-ol (2b)
(R)-3-(4-chlorophenyl)-2,3-dihydrobenzofuran-3-ol (2c)
(R)-3-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzofuran-3-ol (2d)
(R)-3-(p-tolyl)-2,3-dihydrobenzofuran-3-ol(2e)
(R)-3-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-ol(2f)
(R)-3-((1,1'-biphenyl)-4-yl)-2,3-dihydrobenzofuran-3-ol (2g)
(R)-3-(naphthalen-1-yl)-2,3-dihydrobenzofuran-3-ol(2h)
(R)-3-(thiophen-2-yl)-2,3-dihydrobenzofuran-3-ol(2j)

Reaction was performed at 60 °C.
**(R)-3-methyl-2,3-dihydrobenzofuran-3-ol (2k)**

Reaction was performed at 60 °C.
(R)-3-(tert-butyl)-2,3-dihydrobenzofuran-3-ol (21)
(R)-2,2-dimethyl-3-phenyl-2,3-dihydrobenzofuran-3-ol (2m)
(R)-3-phenyl-2,3-dihydnaphtho[2,3-b]furan-3-ol(2n)
(R)-5-chloro-3-phenyl-2,3-dihydrobenzofuran-3-ol(2o)
(R)-6-methoxy-3-phenyl-2,3-dihydrobenzofuran-3-ol(2p)
(R)-1-phenyl-2,3-dihydro-1H-inden-1-ol(6)