Supplementary Material

**Enantioselective synthesis of 3-aryl-phthalides through a nickel-catalyzed stereoconvergent cross-coupling reaction**

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1. General Information

All reagents were obtained commercially unless otherwise noted. Anhydrous solvents were obtained using standard drying techniques. Commercial grade reagents were used without further purification. Flash chromatography was performed on 300-400 mesh silica gel with the indicated solvent systems. High-resolution mass spectra were determined on an Agilent 6545 Accurate-Mass Q-TOF spectrometer. Nuclear Magnetic Resonance (NMR) spectra were acquired on a Bruker Avance-600 HD instrument operating at 600, 150 and 565 MHz for $^1$H, $^{13}$C and $^{19}$F. Chemical shifts are reported in $\delta$ ppm referenced to an internal SiMe4 standard for 1H NMR, chloroform-d ($\delta$ 77.00) for $^{13}$C NMR. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad resonance.

2. Preparation of 3-Bromoisobenzofuran-1(3H)-ones 1

All 3-bromoisobenzofuran-1(3H)-ones 3 were prepared as the following general procedures according to the known literature.\(^1\),\(^2\)

Under N$_2$ atmosphere, a mixture of alkylbenzoic acid (20.0 mmol), Na$_2$S$_2$O$_8$ (60.0 mmol) and TBAB (40.0 mmol) in MeCN (250 mL) was stirred at 80 °C for 18 h in a 500 mL three-necked, round-bottomed flask. The reaction mixture was diluted with water and extracted with EtOAc. The organic layer was washed with brine and dried over MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography to afford isobenzofuran-1(3H)-one.

Isobenzofuran-1(3H)-one (15.0 mmol), N-bromosuccinimide (18 mmol) and azo-bisisobutyronitrile (1.5 mmol) were combined in 100 mL of CCl$_4$ and refluxed under N$_2$ atmosphere for 4 h. The reaction mixture was cooled to room temperature, filtered and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (petroleum ether/EtOAc = 10/1) to yield 3-bromoisobenzofuran-1(3H)-one.

3. Asymmetrice Nickel-Catalyzed Cross-Coupling of 3-Bromophthalides and Arylboronic Acids

General Procedures: A 20 mL Schlenk tube was charged with 3-bromophthalide 1 (0.30 mmol), arylboronic acids 2 (0.6 mmol), K$_2$CO$_3$ (0.6 mmol), NiCl$_2$•glyme (0.03 mmol, 10 mol%), chiral ligand (0.036 mmol, 12 mol%) under N$_2$ atmosphere. THF (3 mL) was added and the mixture was stirred at rt for 10 min. The reaction mixture was then heated at 70 °C for additional 12 h. The mixture was concentrated under reduced pressure, and the residue was purified by silica-gel column chromatography (petroleum ether/EtOAc = 10/1 to 3/1) to afford pure 3-aryl-phthalides 3.
(R)-3-phenylisobenzofuran-1(3H)-one (3a)³

\[ \text{\textit{H} NMR (600 MHz, Chloroform-}d\text{\textit{)}} \delta 7.96 (d, J = 7.7 \text{ Hz}, 1H), 7.65 (t, J = 7.5 \text{ Hz}, 1H), 7.55 (t, J = 7.5 \text{ Hz}, 1H), 7.43 – 7.35 (m, 3H), 7.34 (d, J = 7.7 \text{ Hz}, 1H), 7.28 (dd, J = 6.7, 2.9 Hz, 2H), 6.41 (s, 1H). \text{\textit{C} NMR (150 MHz, Chloroform-}d\text{\textit{)}} \delta 170.48, 149.66, 136.39, 134.29, 129.33, 129.27, 128.94, 126.94, 125.62, 125.58, 122.83, 82.69. [\alpha]^{25}_D = -37.30 \text{ (c=1.0 in CHCl}_3\text{, 84\% ee sample). HRMS (ESI): calcld for C}_{14}H_{11}O_2 ([M+ H]^+) 211.0754, found 211.0756. HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 7.07 min (major) and 8.90 min (minor), 84\% ee.}

(R)-3-(p-tolyl)isobenzofuran-1(3H)-one (3b)³

\[ \text{\textit{H} NMR (600 MHz, Chloroform-}d\text{\textit{)}} \delta 7.96 (d, J = 7.7 \text{ Hz}, 1H), 7.64 (t, J = 7.5 \text{ Hz}, 1H), 7.54 (t, J = 7.5 \text{ Hz}, 1H), 7.43 – 7.35 (m, 3H), 7.34 (d, J = 7.7 \text{ Hz}, 1H), 7.28 (dd, J = 6.7, 2.9 Hz, 2H), 6.41 (s, 1H). \text{\textit{C} NMR (150 MHz, Chloroform-}d\text{\textit{)}} \delta 170.48, 149.66, 136.39, 134.29, 129.33, 129.27, 128.94, 126.94, 125.62, 125.58, 122.83, 82.69. [\alpha]^{25}_D = -37.30 \text{ (c=1.0 in CHCl}_3\text{, 84\% ee sample). HRMS (ESI): calcld for C}_{14}H_{11}O_2 ([M+ H]^+) 211.0754, found 211.0756. HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. t_R = 7.07 min (major) and 8.90 min (minor), 84\% ee.}
7.55 (t, $J = 7.5$ Hz, 1H), 7.32 (d, $J = 7.7$ Hz, 1H), 7.21 – 7.13 (m, 4H), 6.38 (s, 1H), 2.35 (s, 3H). $^{13}$C NMR (150 MHz, Chloroform-d) δ 170.55, 149.81, 139.32, 134.23, 133.40, 129.62, 129.26, 127.04, 125.74, 125.59, 122.85, 82.75, 21.21 [α]$^{D}_{[a]}$ = -16.22 (c=1.0 in CHCl$_3$, 79% ee sample). HRMS (ESI): calcd for C$_{15}$H$_{13}$O$_2$ ([M+ H]$^+$) 225.0910, found 225.0912. HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R = 7.12$ min (major) and 9.33 min (minor), 79% ee.
(R)-3-(4-methoxyphenyl)isobenzofuran-1(3H)-one (3c)

$^1$H NMR (600 MHz, Chloroform-d) $\delta$ 7.96 (d, $J$ = 7.7 Hz, 1H), 7.65 (t, $J$ = 7.4 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.32 (d, $J$ = 7.7 Hz, 1H), 7.18 (d, $J$ = 8.7 Hz, 2H), 6.89 (d, $J$ = 8.9 Hz, 2H), 6.37 (s, 1H), 3.81 (s, 3H). $^1$C NMR (150 MHz, Chloroform-d) $\delta$ 170.49, 160.42, 149.75, 134.22, 129.28, 128.78, 128.29, 125.95, 125.57, 122.92, 114.32, 82.71, 55.33.

[α]$^D_{25} = +7.08$ (c=1.0 in CHCl$_3$, 85% ee sample). HRMS (ESI): calcd for C$_{15}$H$_{13}$O$_3$ ([M+ H]$^+$) 241.0859, found 241.0863. HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R$ = 9.34 min (major) and 11.39 min (minor), 85% ee.
(R)-3-(4-fluorophenyl)isobenzofuran-1(3H)-one (3d)

$^1$H NMR (600 MHz, Chloroform-d) δ 7.97 (d, $J$ = 7.7 Hz, 1H), 7.67 (td, $J$ = 7.5, 1.1 Hz, 1H), 7.58 (t, $J$ = 7.5 Hz, 1H), 7.32 (dq, $J$ = 7.7, 0.9 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.10 – 7.03 (m, 2H), 6.40 (s, 1H).

$^{13}$C NMR (150 MHz, Chloroform-d) δ 170.22, 163.19 (d, $J$ = 248.6 Hz), 149.35, 134.39, 132.25 (d, $J$ = 3.2 Hz), 129.50, 129.06 (d, $J$ = 8.4 Hz), 125.70, 125.63, 122.80, 116.00 (d, $J$ = 21.8 Hz), 81.97.

$^{19}$F NMR (565 MHz, Chloroform-d) δ -111.77.

$[\alpha]_{25}^{25D}$ = -25.1 (c=1.0 in CHCl$_3$, 82% ee sample).

HRMS (ESI): calcd for C$_{14}$H$_{10}$FO$_2$ ([M+ H]$^+$) 229.0659, found 229.0660. HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R$ = 8.06 min (major) and 10.15 min (minor), 82% ee.
(R)-3-(4-chlorophenyl)isobenzofuran-1(3H)-one (3c)

$^1$H NMR (600 MHz, Chloroform-d) $\delta$ 7.96 (d, $J = 7.5$ Hz, 1H), 7.70 – 7.64 (m, 1H), 7.58 (d, $J = 7.5$ Hz, 1H), 7.39 – 7.34 (m, 2H), 7.34 – 7.30 (m, 1H), 7.25 – 7.19 (m, 2H), 6.38 (s, 1H).

$^{13}$C NMR (150 MHz, Chloroform-d) $\delta$ 170.19, 149.19, 135.26, 134.95, 134.44, 129.56, 129.20, 128.34, 125.76, 125.47, 122.74, 81.80. [α]$^2_{D}$ = -34.52 ($c$=1.0 in CHCl$_3$, 79% ee sample).

HRMS (ESI): calcd for C$_{14}$H$_{10}$ClO$_2$ ([M+ H]$^+$) 245.0364, found 245.0368. HPLC analysis: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R$ = 13.60 min (minor) and 15.85 min (major), 79% ee.
Peak RetTime Type Width Area Height Area %
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2 15.850 MM R 0.3338 2835.13403 141.54086 89.2987
(R)-3-(4-bromophenyl)isobenzofuran-1(3H)-one (3f)

$^1$H NMR (600 MHz, Chloroform-$d$) δ 7.96 (d, $J = 7.7$ Hz, 1H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.57 (t, $J = 7.3$ Hz, 1H), 7.54 – 7.48 (m, 2H), 7.32 (d, $J = 7.7$ Hz, 1H), 7.16 (d, $J = 6.8$ Hz, 2H), 6.36 (s, 1H).

$^{13}$C NMR (150 MHz, Chloroform-$d$) δ 170.17, 149.11, 135.46, 134.44, 132.15, 129.56, 128.57, 125.75, 125.43, 123.42, 122.72, 81.82. $[\alpha]_{D}^{25}$ = -25.10 ($c$=1.0 in CHCl$_3$, 88% ee sample).

HRMS (ESI): calcd for C$_{14}$H$_{10}$BrO$_2$ ([M+ H]$^+$) 288.9859, found 288.9861.

HPLC analysis: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R$ = 13.87 min (minor) and 15.99 min (major), 88% ee.
(R)-3-(4-(trifluoromethyl)phenyl)isobenzofuran-1(3H)-one (3g)

\(^1\)H NMR (600 MHz, Chloroform-d) \(\delta\) 7.99 (d, \(J = 7.7\) Hz, 1H), 7.71 – 7.64 (m, 3H), 7.59 (t, \(J = 7.5\) Hz, 1H), 7.44 (d, \(J = 7.8\) Hz, 2H), 7.34 (dd, \(J = 7.7, 0.9\) Hz, 1H), 6.46 (s, 1H). \(^1\)C NMR (150 MHz, Chloroform-d) \(\delta\) 170.08, 148.94, 140.27, 134.60, 131.46 (q, \(J = 32.6\) Hz), 129.74, 127.09, 126.03 (q, \(J = 3.8\) Hz), 125.96, 125.30, 123.74 (q, \(J = 272.4\) Hz), 122.67, 81.54. \(^19\)F NMR (565 MHz, Chloroform-d) \(\delta\) -62.77. \([\alpha]_{D}^{25} = -57.30\) (c=1.0 in CHCl\(_3\), 78% ee sample).

HRMS (ESI): calcd for C\(_{15}\)H\(_{10}\)F\(_3\)O\(_2\) ([M+ H]+) 279.0627, found 279.0629. HPLC analysis: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min.

\(t_R = 12.19\) min (minor) and 15.61 min (major), 78% ee.

(R)-4-(3-oxo-1,3-dihydroisobenzofuran-1-yl)benzaldehyde (3h)

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\[1 12.187 VB R 0.2537 8834.08594 525.94617 10.9389\]
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$^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 10.03 (s, 1H), 7.99 (dd, $J = 7.6$, 2.7 Hz, 1H), 7.92 (d, $J = 7.8$ Hz, 2H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 7.7$ Hz, 1H), 6.47 (s, 1H). $^{13}$C NMR (150 MHz, Chloroform-$d$) $\delta$ 191.43, 170.07, 148.87, 142.89, 136.87, 134.58, 130.30, 129.73, 127.22, 125.96, 125.20, 122.63, 81.60. $[\alpha]_{D}^{25} = -108.56$ (c=1.0 in CHCl$_3$, 77% ee sample). HRMS (ESI): calcd for C$_{15}$H$_{11}$O$_3$ ([M+ H]$^+$) 239.0703, found 239.0705. HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R$ = 16.18 min (major) and 24.28 min (minor), 77% ee.
methyl (R)-4-(3-oxo-1,3-dihydroisobenzofuran-1-yl)benzoate (3i)

$^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 8.06 (dt, $J$ = 8.5, 1.6 Hz, 2H), 7.98 (d, $J$ = 7.7 Hz, 1H), 7.67 (td, $J$ = 7.5, 1.2 Hz, 1H), 7.58 (t, $J$ = 7.5 Hz, 1H), 7.39 (d, $J$ = 8.4 Hz, 2H), 7.34 (d, $J$ = 7.7 Hz, 1H), 6.45 (s, 1H), 3.92 (s, 3H). $^{13}$C NMR (150 MHz, Chloroform-$d$) $\delta$ 170.20, 166.38, 149.12, 141.30, 134.50, 131.01, 130.28, 129.63, 126.65, 125.90, 125.32, 122.68, 81.81, 52.27. $[\alpha]_D^{25}$ = -79.48 ($c$=1.0 in CHCl$_3$, 81% ee sample). HRMS (ESI): calcd for C$_{16}$H$_{13}$O$_4$ ([M+ H]$^+$) 269.0808, found 269.0811. HPLC analysis: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R$ = 19.91 min (minor) and 23.76 min (major), 81% ee.
\([R]-3-(m\text{-}tolyl)\text{isobenzofuran-1}(3\text{H})\text{-one (3)}^8\)

\(^1\text{H NMR}\) (600 MHz, Chloroform-\(d\)) \(\delta\) 7.97 (d, \(J = 7.7\) Hz, 1H), 7.65 (td, \(J = 7.5, 1.1\) Hz, 1H), 7.55 (t, \(J = 7.5\) Hz, 1H), 7.36 – 7.31 (m, 1H), 7.27 (t, \(J = 7.6\) Hz, 1H), 7.18 (d, \(J = 7.6\) Hz, 1H), 7.11 – 7.05 (m, 2H), 6.37 (s, 1H), 2.33 (s, 3H).

\(^{13}\text{C NMR}\) (150 MHz, Chloroform-\(d\)) \(\delta\) 170.57, 149.79, 138.82, 136.31, 134.26, 130.04, 129.28, 128.81, 127.45, 125.61, 125.58, 124.04, 122.83, 82.79, 21.34. \([\alpha]_{25}^D = -42.26\) (c=1.0 in CHCl\(_3\), 82% ee sample). 

\textit{HRMS} (ESI): calcd for C\(_{15}\)H\(_{13}\)O\(_2\) ([M+ H]+) 225.0910, found 225.0912. 

\textit{HPLC analysis:}\n
Daicel CHIRALPAK AD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. \(t_R = 11.17\) min (minor) and 14.09 min (major), 82% ee.
(R)-3-(o-tolyl)isobenzofuran-1(3H)-one (3k)

$^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.98 (d, $J = 7.7$ Hz, 1H), 7.67 (td, $J = 7.5$, 1.1 Hz, 1H), 7.58 (tt, $J = 7.5$, 0.8 Hz, 1H), 7.35 (dd, $J = 7.6$, 0.9 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.16 – 7.10 (m, 1H), 6.92 (d, $J = 7.6$ Hz, 1H), 6.69 (s, 1H), 2.50 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-$d$) $\delta$ 170.58, 149.27, 137.15, 134.16, 134.08, 131.11, 129.35, 129.30, 127.25, 126.43, 126.40, 125.74, 123.00, 80.51, 19.32. $\left[\alpha\right]D_{25}^{25} = +48.28$ (c=1.0 in CHCl$_3$, 75% ee sample). HRMS (ESI): calcd for C$_{15}$H$_{13}$O$_2$ ([M+ H]$^+$) 225.0910, found 225.0912.

HPLC analysis: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 90:10; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R = 9.74$ min (minor) and 13.28 min (major), 75% ee.
(R)-3-(naphthalen-2-yl)isobenzofuran-1(3H)-one (3l)

$^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 8.00 (d, $J = 7.7$ Hz, 1H), 7.84 (m, 4H), 7.64 (td, $J = 7.5$, 1.2 Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.55 – 7.49 (m, 2H), 7.34 (s, 1H), 7.23 (dd, $J = 7.5$, 0.9 Hz, 1H). $^1$C NMR (150 MHz, Chloroform-$d$) $\delta$ 170.55, 149.70, 134.35, 133.67, 133.57, 133.06, 129.41, 129.06, 128.06, 127.78, 126.81, 126.68, 126.67, 125.70, 125.61, 123.76, 122.90, 82.89. $[\alpha]_{D}^{25}$ = -52.72 ($c$=1.0 in CHCl$_3$, 77% ee sample).

HRMS (ESI): calcd for C$_{16}$H$_{13}$O$_2$ ([M+ H]$^+$) 261.0910, found 261.0913.

HPLC analysis: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R$ = 15.37 min (minor) and 18.84 min (major), 77% ee.
(S)-3-(thiophen-3-yl)isobenzofuran-1(3H)-one (3m)

$^1$H NMR (600 MHz, Chloroform-d) δ 7.96 (d, $J = 7.6$ Hz, 1H), 7.69 (t, $J = 7.5$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.42 (d, $J = 7.7$ Hz, 1H), 7.36 – 7.32 (m, 2H), 6.94 (d, $J = 4.9$ Hz, 1H), 6.51 (s, 1H). $^{13}$C NMR (150 MHz, Chloroform-d) δ 170.17, 148.99, 137.19, 134.25, 129.45, 127.19, 125.89, 125.80, 125.73, 124.45, 122.81, 78.41. $[\alpha]_D^{25}$ = +59.36 ($c$=1.0 in CHCl$_3$, 85% ee sample). HRMS (ESI): calcd for C$_{12}$H$_9$O$_2$S ([M+ H]$^+$) 217.0318, found 217.0320.

HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:10; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R$ = 9.21 min (major) and 11.61 min (minor), 85% ee.
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(S)-3-(6-methoxypyridin-3-yl)isobenzofuran-1(3H)-one (3n)

$^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 8.21 (d, $J = 2.5$ Hz, 1H), 7.98 (d, $J = 7.7$ Hz, 1H), 7.69 (td, $J = 7.5$, 1.1 Hz, 1H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.32 (dd, $J = 7.7$, 0.9 Hz, 1H), 7.28 (dd, $J = 8.7$, 2.6 Hz, 1H), 6.73 (d, $J = 8.6$ Hz, 1H), 6.39 (s, 1H), 3.95 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-$d$) $\delta$ 170.11, 164.98, 148.92, 146.48, 137.39, 134.46, 129.64, 125.97, 125.78, 124.91, 122.86, 111.72, 80.40, 53.69.

$[\alpha]_{D}^{25}$ = +17.12 (c=1.0 in CHCl$_3$, 85% ee sample).

HRMS (ESI): calcd for C$_{14}$H$_{12}$NO$_3$ ([M+H]$^+$) 242.0812, found 242.0814.

HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R$ = 9.00 min (major) and 10.84 min (minor), 85% ee.
(3S)-3-(3a,7a-dihydrobenzofuran-2-yl)isobenzofuran-1(3H)-one (3o)

\[^1\text{H NMR}\] (600 MHz, Chloroform-\text{d}) \quad \delta \quad 8.01 \ (d, J = 7.7 \ Hz, 1H), 7.73 \ (td, J = 7.5, 1.1 \ Hz, 1H), 7.63 \ (t, J = 7.5 \ Hz, 1H), 7.59 \to 7.53 \ (m, 2H), 7.44 \ (dd, J = 8.3, 0.9 \ Hz, 1H), 7.32 \ (ddd, J = 8.4, 7.2, 1.3 \ Hz, 1H), 7.24 \ (td, J = 7.6, 1.0 \ Hz, 1H), 6.79 \ (s, 1H), 6.58 \ (s, 1H).

\[^{13}\text{C NMR}\] (150 MHz, Chloroform-\text{d}) \quad \delta \quad 169.72, 155.49, 151.21, 146.28, 134.39, 129.97, 127.34, 126.06, 125.95, 125.35, 123.22, 123.04, 121.54, 111.58, 106.74, 75.83.

\[^{[\alpha]}_{25D}^B\] = +77.46 \ (c=1.0 \ in \ CHCl_3, 82\% \ ee \ sample). HRMS (ESI): calcd for C_{16}H_{11}O_3 ([M+ H]^+) 251.0703, found 251.0705.

**HPLC analysis**: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. \( t_R = 15.11 \ \text{min (minor)} \) and 21.81 min (major), 82\% ee.
(R)-5-fluoro-3-phenylisobenzofuran-1(3H)-one (3p)
$^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.95 (dd, $J = 8.3, 4.8$ Hz, 1H), 7.38 – 7.41 (m, 3H), 7.28 – 7.23 (m, 3H), 7.00 (dd, $J = 7.7, 2.2$ Hz, 1H), 6.36 (s, 1H). $^{13}$C NMR (150 MHz, Chloroform-$d$) $\delta$ 169.22, 166.65 (d, $J = 256.7$ Hz), 152.46 (d, $J = 9.96$ Hz), 135.76, 129.50, 129.07, 128.00 (d, $J = 10.4$ Hz), 126.82, 121.60, 117.65 (d, $J = 24.1$ Hz), 110.14 (d, $J = 24.5$ Hz), 81.97 (d, $J = 2.7$ Hz). $^{19}$F NMR (565 MHz, Chloroform-$d$) $\delta$ -102.15. $[\alpha]^{25}_D$ = -41.00 ($c = 1.0$ in CHCl$_3$, 76% ee sample). HRMS (ESI): calcd for C$_{14}$H$_{10}$FO$_2$ ([M+ H$^+$]) 229.0659, found 229.0667. HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R$ = 6.72 min (major) and 13.93 min (minor), 76% ee.
\textbf{H NMR} (600 MHz, Chloroform-\textit{d}) $\delta$ 7.89 (d, $J = 8.2$ Hz, 1H), 7.52 (ddd, $J = 8.2$, 1.7, 0.7 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.33 – 7.30 (m, 1H), 7.32 – 7.26 (m, 2H), 6.37 (s, 1H). \textbf{C NMR} (150 MHz, Chloroform-\textit{d}) $\delta$ 169.28, 151.27, 141.05, 135.67, 130.17, 129.54, 129.10, 126.85, 126.81, 124.03, 123.24, 82.07. $[\alpha]^{25}_D = +30.52$ (c=1.0 in CHCl$_3$, 77% ee sample). \textbf{HRMS} (ESI): calcd for C$_{14}$H$_{10}$ClO$_2$ ([M+ H]$^+$) 245.0364, found 245.0371. \textbf{HPLC analysis}: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R = 7.04$ min (major) and 12.56 min (minor), 77% ee.
(R)-5-bromo-3-phenylisobenzofuran-1(3H)-one (3r)

$^1$H NMR (600 MHz, Chloroform-\textit{d}) $\delta$ 7.81 (d, $J$ = 8.1 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.49 (dt, $J$ = 1.5, 0.7 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.29 – 7.23 (m, 2H), 6.37 (s, 1H). $^1$C NMR (150 MHz, Chloroform-\textit{d}) $\delta$ 169.41, 151.36, 135.63, 133.00, 129.56, 129.54, 129.10, 126.90, 126.85, 126.25, 124.48, 82.03. $[\alpha]_{D}^{25}$ = +50.16 ($c$=1.0 in CHCl$_3$, 74% ee sample). **HRMS** (ESI): calcd for C$_{14}$H$_{10}$BrO$_2$ ([M+ H$^+$]) 288.9859, found 288.9868. **HPLC analysis**: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R$ = 7.39 min (major) and 11.58 min (minor), 74% ee.
methyl (R)-1-oxo-3-phenyl-1,3-dihydroisobenzofuran-5-carboxylate (3s)

$^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 8.23 (dd, $J = 8.2, 3.8$ Hz, 1H), 8.05 – 8.01 (m, 1H), 8.00 (s, 1H), 7.42 – 7.38 (m, 3H), 7.29 – 7.27 (m, 2H), 6.46 (s, 1H), 3.93 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-$d$) $\delta$ 169.39, 165.59, 149.65, 135.69, 135.63, 130.62, 129.50, 129.14, 129.07, 126.90, 125.67, 124.20, 82.73, 52.68. [$\alpha$]$^D_{25}$ = +43.38 ($c = 1.0$ in CHCl$_3$, 74% ee sample).

HRMS (ESI): calcld for C$_{16}$H$_{13}$O$_4$ ([M+H]$^+$) 269.0808, found 269.0818.

HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R = 8.63$ min (major) and 10.87 min (minor), 74% ee.
(R)-5-methyl-3-phenylisobenzofuran-1(3H)-one (3t)

$^1$H NMR (600 MHz, Chloroform-d) $\delta$ 7.83 (d, $J = 7.9$ Hz, 1H), 7.41 – 7.34 (m, 3H), 7.37 – 7.32 (m, 1H), 7.31 – 7.25 (m, 2H), 7.11 (d, $J = 0.7$ Hz, 1H), 6.34 (s, 1H), 2.43 (s, 3H). $^1$C NMR (150 MHz, Chloroform-d) $\delta$ 170.54, 150.26, 145.60, 136.65, 130.51, 129.18, 128.92, 126.90, 125.36, 123.06, 122.98, 82.41, 22.02. $[\alpha]_{D}^{25}$ = +3.16 (c=1.0 in CHCl$_3$, 83% ee sample). HRMS (ESI): calcd for C$_{15}$H$_{13}$O$_2$ ([M+ H]$^+$) 225.0910, found 225.0914. HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R = 7.53$ min (major) and 9.61 min (minor), 83% ee.
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(R)-5-methoxy-3-phenylisobenzofuran-1(3H)-one (3u)

$^1$H NMR (600 MHz, Chloroform-d) $\delta$ 7.86 (d, $J = 8.5$ Hz, 1H), 7.38 (dd, $J = 5.2$, 1.9 Hz, 3H), 7.32 – 7.25 (m, 2H), 7.05 (dd, $J = 8.5$, 2.2 Hz, 1H), 6.72 (d, $J = 2.0$ Hz, 1H), 6.31 (s, 1H), 3.83 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-d) $\delta$ 170.20, 164.90, 152.50, 136.58, 129.25, 128.96, 127.12, 127.01, 117.89, 116.84, 106.64, 82.08, 55.82. $[\alpha]^25_D = +34.44$ (c=1.0 in CHCl$_3$, 76% ee sample).

HRMS (ESI): calcd for C$_{15}$H$_{13}$O$_3$ ([M+ H]$^+$) 241.0859, found 241.0860.

HPLC analysis: Daicel CHIRALPAK AD-3; hexane: i-PrOH = 80:20; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R = 10.41$ min (major) and 12.77 min (minor), 76% ee.
(R)-6-methyl-3-phenylisobenzofuran-1(3H)-one (3v)\textsuperscript{\textbf{6}}

\textbf{\textsuperscript{1}H NMR} (600 MHz, Chloroform-\textit{d}) \(\delta\) 7.75 (dt, \(J = 1.7, 0.8\) Hz, 1H), 7.45 (dd, \(J = 7.8, 0.8\) Hz, 1H), 7.41 – 7.33 (m, 3H), 7.29 – 7.24 (m, 2H), 7.21 (d, \(J = 7.9\) Hz, 1H), 6.37 (s, 1H), 2.47 (s, 3H).

\textbf{\textsuperscript{13}C NMR} (150 MHz, Chloroform-\textit{d}) \(\delta\) 170.64, 147.11, 139.66, 136.67, 135.46, 129.19, 128.91, 126.94, 125.80, 125.57, 122.53, 82.61, 21.24. \([\alpha]_{D}^{25} = -31.14\) (c=1.0 in CHCl\textsubscript{3}, 81\% ee sample). \textbf{HRMS} (ESI): calcld for C\textsubscript{15}H\textsubscript{13}O\textsubscript{2} ([M+ H\textsuperscript{+}]\textsuperscript{+}) 225.0910, found 225.0914. \textbf{HPLC analysis}: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. \(t_{R}\) = 11.60 min (minor) and 15.00 min (major), 81\% ee.
(R)-4-methyl-3-phenylisobenzofuran-1(3H)-one (3w)

$^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.82 (d, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.43 (d, $J = 7.4$ Hz, 1H), 7.42 - 7.31 (m, 3H), 7.22 - 7.17 (m, 2H), 6.33 (s, 1H), 2.03 (s, 3H).

$^{13}$C NMR (150 MHz, Chloroform-$d$) $\delta$ 170.72, 147.55, 135.57, 135.27, 133.43, 129.77, 129.50, 128.92, 128.14, 126.12, 123.05, 82.98, 17.87. $[\alpha]_D^{25} = +1.66$ (c=1.0 in CHCl$_3$, 7% ee sample). HRMS (ESI): calcd for C$_{15}$H$_{13}$O$_2$ ([M+ H]$^+$) 225.0910, found 225.0912. HPLC analysis: Daicel CHIRALPAK OD-3; hexane: i-PrOH = 90:10; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R = 9.25$ min (minor) and 12.58 min (major), 7% ee.
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(R)-7-methyl-3-phenylisobenzofuran-1(3H)-one (3x)

$^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.49 (t, $J = 7.6$ Hz, 1H), 7.41 – 7.33 (m, 3H), 7.32 – 7.25 (m, 3H), 7.12 (d, $J = 7.6$ Hz, 1H), 6.33 (s, 1H), 2.75 (s, 3H). $^{13}$C NMR (150 MHz, Chloroform-$d$) $\delta$ 170.68, 150.21, 139.68, 136.84, 133.97, 130.89, 129.14, 128.90, 126.95, 123.03, 120.17, 81.79, 17.38. $[\alpha]_{D}^{25} = -90.18$ ($c = 1.0$ in CHCl$_3$, 81% ee sample). HRMS (ESI): calcd for C$_{15}$H$_{13}$O$_2$ ([M+ H$^+$]) 225.0910, found 225.0912. HPLC analysis: Daicel CHIRALPAK OD-3; hexane:i-PrOH = 95:5; detection wavelength = 220 nm; flow rate = 5.0 mL/min. $t_R = 9.86$ min (minor) and 12.66 min (major), 81% ee.
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4. Copies of $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectras
3i
5. References


