# Cationic Palladium Complex Catalyzed Highly Enantioselective Intramolecular Addition of Arylboronic Acids to Ketones. 

 A Convenient Synthesis of Optically Active CycloalkanolsGuixia Liu and Xiyan Lu*<br>State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China<br>xylu@mail.sioc.ac.cn

## Supporting Information Part 1

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## I. General

All reactions were carried out under a nitrogen atmosphere unless otherwise noted. The progress of all reactions was monitored by thin-layer chromatography to ensure the reactions had reached completion. NMR spectra were recorded on a Varian Mercury V x 300 spectrometer. Infrared spectra were obtained on a Bio-Rad FTS-185 instrument. Mass spectra were provided on Agligent 5973 or Agilent 1100. The optical rotation was measured on a Perkin-Elmer 341 polarimeter and the enantiomeric excesses were determined after separation of the enantiomers by HPLC on a Perkin-Elmer (785A, 200 IC Pump) or Waters (515 Pump, 2487. Dual Absorbance Detector) instruments. Elemental analyses were carried out on Elementar Vario EL instruments. All solvents were dried and distilled before use according to the standard methods. All melting points were uncorrected. $\quad\left[\mathrm{Pd}(\mathrm{dppp})\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}(\mathrm{OTf})_{2} \quad(\mathbf{3 a}),{ }^{1} \quad\left[\mathrm{Pd}(R)-\operatorname{BINAP}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}(\mathrm{OTf})_{2} \quad(\mathbf{4 a}),{ }^{2}$ $\left[\{\mathrm{Pd}(R)-\mathrm{BINAP}(-\mathrm{OH})\}_{2}\right]^{2+}(\mathrm{OTf})_{2} \quad(\mathbf{4 b})^{2}$ were synthesized following the literature procedures. Amberlite IRA $400(\mathrm{Cl})$ were purchased from Lancaster. Before use, they were treated with NaOH solution ( 2 N ), then washed with water until neutrality and filtrated under vacuum.

## II. synthesis of substrates

(i) General procedure for preparation of the substrates $\mathbf{1 a}-\mathbf{-}^{3,4}$



Typical procedure for the preparation of $1 \mathrm{a}: \mathrm{K}_{2} \mathrm{CO}_{3}(3.036 \mathrm{~g}, 22 \mathrm{mmol})$ was added to a solution of phenacyl bromide $(4.403 \mathrm{~g}, 22 \mathrm{mmol})$ and 2-iodophenol $(4.845 \mathrm{~g}, 22 \mathrm{mmol})$ in acetone ( 13 mL ) and the resulting suspension heated under reflux for 4 h . The mixture was then allowed to cool to room temperature and poured into water $(100 \mathrm{~mL})$. The precipitate was collected by filtration and to afford crude product 2-(2-iodo-phenoxy)-1-phenyl-ethanone, which was used for the next step without purification. The crude product was added to a stirred solution of benzene ( 150 mL ), ethylene glycol ( $5.5 \mathrm{~g}, 89 \mathrm{mmol}$ ) and p-toluenesulfonic acid ( $120 \mathrm{mg}, 0.66 \mathrm{mmol}$ ), fitted with a Dean Stark trap and refluxed overnight. The reaction mixture was cooled and washed with saturated solution of $\mathrm{NaHCO}_{3}(20 \mathrm{~mL})$ and $\mathrm{NaCl}(20 \mathrm{~mL})$. The organic portion was dries $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, concentrated in vacuo and the residue was purified by flash column chromatography to obtain the product $\mathbf{3 a}(6.687 \mathrm{~g}, 80 \%$ for two steps $)$.

To 17.6 mmol of compound $\mathbf{3 a}$ dissolved in the mixture of $\mathrm{Et}_{2} \mathrm{O}(30 \mathrm{~mL})$ and THF $(60 \mathrm{~mL})$ in a flame dried 250 mL round-bottom flask was added at $-78{ }^{\circ} \mathrm{C} 13.1 \mathrm{~mL}(21$ mmol ) of a 1.6 M solution of $n \mathrm{BuLi}$ in hexanes. The mixture was stirred at $-78^{\circ} \mathrm{C}$ for 20 min followed by addition of $4 \mathrm{~mL}(35 \mathrm{mmol})$ of $\mathrm{B}(\mathrm{OMe})_{3}$ in one portion via syringes. The resulting mixture was allowed to stir at $-78^{\circ} \mathrm{C}$ for 0.5 h , warmed to ambient temperature, and stirred for further 2 h . Twenty milliliters of aq. 1 N HCl was added and the mixture was stirred for an additional 0.5 h . The organic layer was separated and the aqueous layer was extracted with EtOAc $(2 \times 30 \mathrm{~mL})$. The organic layers were combined, washed (water, then $10 \%$ aqueous $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$, then brine), dries $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, concentrated. The crude product was added to $\mathrm{MeOH}(20 \mathrm{~mL})$ plus 2 mL of $8 \mathrm{~N} \mathrm{H}_{2} \mathrm{SO}_{4}$ and the mixture was allowed to stand at room temperature overnight. After dilution with water and extracted with EtOAc
$(2 \times 20 \mathrm{~mL})$, The organic layers were combined, dries $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, concentrated. The pure compound $\mathbf{1 a}(2.591 \mathrm{~g}, 57 \%$ for two steps) was obtained by recrystillization in a mixture of EtOAc-petroleum ether.

Compound $\mathbf{3 b} \mathbf{- 3 f}, \mathbf{1 b} \mathbf{- 1 f}$ can be prepared by similar procedure using corresponding bromomethylkeones. ${ }^{5}$

## 2-(2'-iodo-phenoxy)-1-phenyl-ethanone ethylene acetal (3a)



White solid; mp 80-81 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.77-7.74(\mathrm{~m}, 1 \mathrm{H}), 7.67-7.63(\mathrm{~m}$, $2 \mathrm{H}), 7.42-7.36(\mathrm{~m}, 3 \mathrm{H}), 7.27-7.21(\mathrm{~m}, 1 \mathrm{H}), 6.75(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.72-6.67(\mathrm{~m}, 1 \mathrm{H})$, 4.41-4.37 (m, 2H), 4.18 (s, 2H), 4.02-3.97 (m, 2H). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 157.3$, 139.7, 139.5, 129.3, 128.6, 128.1, 126.2, 122.7, 112.1, 108.0, 86.2, 73.2, 66.0. IR (neat) $v$ 1578, 1473, 1436, $1289 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 305\left(\mathrm{M}^{+}+1-\mathrm{Ph}\right), 149$ (100). Anal. Calcd for $\mathrm{C}_{16} \mathrm{H}_{15} \mathrm{IO}_{3}$ : C, 50.28; H, 3.96; I, 33.20. Found: C, 50.24; H, 4.14; I, 32.96.


3b
3b: White solid; yield: $85 \%$; mp 54-56 ${ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.77-7.74$ ( m , $1 \mathrm{H}), 7.58-7.55(\mathrm{~m}, 2 \mathrm{H}), 7.27-7.21(\mathrm{~m}, 1 \mathrm{H}), 6.92(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.75(\mathrm{~d}, J=8.4 \mathrm{~Hz}$, $1 \mathrm{H}), 6.69(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.38-4.36(\mathrm{~m}, 2 \mathrm{H}), 4.16(\mathrm{~s}, 2 \mathrm{H}), 4.00-3.96(\mathrm{~m}, 2 \mathrm{H}), 3.82(\mathrm{~s}$, $3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 159.8,157.4,139.5,131.9,129.3,127.6,122.7,113.5$, 112.1, 108.0, 86.3, 73.3, 65.9, 55.3. IR (oil): v 1478, 1248, 837, $750 \mathrm{~cm}^{-1} ; \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI})$ : 387( $\mathrm{M}^{+}-\mathrm{I}+2$ ), 179 (100), 135, 91. Calcd for $\mathrm{C}_{17} \mathrm{H}_{17} \mathrm{IO}_{4}$ : C, 49.53; H, 4.16; I, 30.79. Found C, 49.48; H, 4.16; I, 30.88.


3c: oil; yield: $77 \% ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.75(\mathrm{dd}, J=7.5,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.61(\mathrm{dd}$, $J=6.9,2.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.36(\mathrm{dd}, J=6.3,1.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.25-7.22(\mathrm{~m}, 1 \mathrm{H}), 6.76-6.67(\mathrm{~m}, 2 \mathrm{H})$, 4.36-4.31 (m, 2H), $4.14(\mathrm{~s}, 2 \mathrm{H}), 3.99-3.91(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 157.1$, $139.5,138.2,134.5,129.3,128.3,127.9,122.8,112.0,107.6,86.1,73.0,65.9$. IR (oil): $v$ 3062, 2893, 1475, $1249 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 304\left(\mathrm{M}^{+}-\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{Cl}\right), 183$ (100), 141, 139. HRMS-EI calcd for $\mathrm{C}_{16} \mathrm{H}_{14} \mathrm{IO}_{3}\left(\mathrm{M}^{+}-\mathrm{Cl}\right) 380.9988$, found 380.9994 .


3d: oil; yield: $82 \%$; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.82-7.73(\mathrm{~m}, 3 \mathrm{H}), 7.65(\mathrm{~d}, J=8.1 \mathrm{~Hz}$, $2 H), 7.27-7.21(\mathrm{~m}, 1 \mathrm{H}), 6.75-6.67(\mathrm{~m}, 2 \mathrm{H}), 4.37-4.32(\mathrm{~m}, 2 \mathrm{H}), 4.17(\mathrm{~s}, 2 \mathrm{H}), 3.99-3.95(\mathrm{~m}$, $2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 157.1,143.6,139.6,129.4,127.0,125.1(\mathrm{q}, J=3.5$ $\mathrm{Hz}), 123.0,112.0,107.5,86.1,73.0,65.9 .{ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, d^{6}$-DMSO) $\delta-62.97$. IR (oil): v 3065, 1475, 1327, 846, $749 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 450\left(\mathrm{M}^{+}\right), 431,217(100), 173,145$. HRMS-EI calcd for $\mathrm{C}_{17} \mathrm{H}_{14} \mathrm{~F}_{3} \mathrm{IO}_{3}\left(\mathrm{M}^{+}\right) 449.9940$, found 449.9938 .


3d: oil; yield: $69 \% ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.77-7.74(\mathrm{~m}, 1 \mathrm{H}), 7.43-7.42(\mathrm{~m}, 1 \mathrm{H})$, $7.30-7.25(\mathrm{~m}, 1 \mathrm{H}), 6.86-6.83(\mathrm{~m}, 1 \mathrm{H}), 6.74-6.68(\mathrm{~m}, 1 \mathrm{H}), 6.54-6.53(\mathrm{~m}, 1 \mathrm{H}), 6.38-6.36(\mathrm{~m}$,

1H), 4.37-4.32 (m, 4H), 4.13-4.10 (m, 2H). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 157.3,151.6$, $142.9,139.4,129.3,122.9,112.3,110.1,108.2,104.3,86.3,71.0,66.2$. IR (oil): v 3062, 1475, 1291, 747. MS ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): $372\left(\mathrm{M}^{+}\right), 139$ (100), 95, 76, 65. HRMS-EI calcd for $\mathrm{C}_{14} \mathrm{H}_{13} \mathrm{IO}_{4}\left(\mathrm{M}^{+}\right) 371.9859$, found 371.9846 .


3f: oil; yield: $82 \%$; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.57-7.54(\mathrm{~m}, 2 \mathrm{H}), 6.90-6.83(\mathrm{~m}, 2 \mathrm{H})$, 4.23-4.19 (m, 2H), 4.10-4.05 (m, 2H), 3.99 (s, 2H), $1.56(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 155.0,133.3,128.4,122.0,112.9,112.0,107.7,72.4,65.6,22.3$. IR (oil): $v$ 3066, 1587, 1482, 1061. MS ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): $272\left(\mathrm{M}^{+}\right)$, 234, 149, 94, 87 (100). HRMS-EI calcd for $\mathrm{C}_{11} \mathrm{H}_{13} \mathrm{BrO}_{3}\left(\mathrm{M}^{+}\right)$272.0048, found 272.0049.

## 2-(2'-Oxo-2'-phenyl-ethoxy)-phenyl boronic acid (1a)



White solid; mp 133-135 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 8.02-7.99 (m, 2H), 7.94-7.91 (m, 1H), 7.67-7.44 (m, 4H), 7.12-7.07 (m, 1H), 6.93 (d, $J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{~s}, 2 \mathrm{H}), 5.42$ (s, 2H). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 193.3,162.8,137.3,134.3,133.8,132.6,129.0$, 127.7, 122.0, 111.3, 70.2. IR (neat) v 3360 (br), 3061, 1693, $1600 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 256$ $\left(\mathrm{M}^{+}\right), 212,105$ (100). Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{13} \mathrm{BO}_{4}: \mathrm{C}, 65.67$; H, 5.12. Found: C, 65.58; H, 5.11.


## 1b

White solid; yield: $56 \%$; mp $138-140{ }^{\circ} \mathrm{C},{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, d^{6}$-DMSO) $\delta 8.14(\mathrm{~s}, 2 \mathrm{H}$ ), $8.08(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.74(\mathrm{dd}, J=7.2,1.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.49-7.43(\mathrm{~m}, 1 \mathrm{H}), 7.18(\mathrm{~d}, J=8.1$ $\mathrm{Hz}, 1 \mathrm{H}), 7.12(\mathrm{~d}, J=9.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.02(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.60(\mathrm{~s}, 2 \mathrm{H}), 3.884(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 MHz, $d^{6}$-DMSO) $\delta 193.2,163.8,162.7,136.2,132.2,130.3,126.7,121.1,114.1$, 112.3, 70.4, 55.6. IR (neat) v 3420 (br), 3317 (br), 3010, 1686, 1601. MS ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): 225 $\left(\mathrm{M}^{+}-\mathrm{O}=\mathrm{B}(\mathrm{OH})-\mathrm{CH}_{3}\right), 44(100)$. Anal. Calcd for $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{BO}_{5}: \mathrm{C}, 62.97$; H, 5.28. Found: C, 62.75; H, 5.03.


White solid; yield: $47 \%$; mp 201-203 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.95-7.90(\mathrm{~m}, 3 \mathrm{H})$, 7.53-7.43(m, 3H), 7.12-7.07 (m, 1H), $6.91(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.31(\mathrm{~s}, 2 \mathrm{H}), 5.37(\mathrm{~s}, 2 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR (75 MHz, $d^{6}$-DMSO) $\delta 193.9,162.5,138.9,136.2,132.6,132.1,129.8,129.0$, 121.1, 112.2, 70.7. IR (neat) v 3359 (br), 1693, 1600, 1339. MS ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): $272\left(\mathrm{M}^{+}-\mathrm{H}_{2} \mathrm{O}\right)$, $229,165,139$ (100), 111. Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{12} \mathrm{BClO}_{4}$ : C, 57.88; H, 4.16. Found: C, 57.91; H, 4.30.


1d
White solid; yield: $53 \%$; mp $180-182{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.11(\mathrm{~d}, J=8.1 \mathrm{~Hz}$, $2 \mathrm{H}), 7.93-7.90(\mathrm{~m}, 1 \mathrm{H}), 7.81(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.47-7.44(\mathrm{~m}, 1 \mathrm{H}), 7.13-7.08(\mathrm{~m}, 1 \mathrm{H})$,
$6.92(\mathrm{~m}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.35(\mathrm{~s}, 2 \mathrm{H}), 5.42(\mathrm{~s}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.75 \mathrm{MHz}, d^{6}-\mathrm{DMSO}\right)$ $\delta 194.2,162.4,137.0,136.1,133.3,132.9,132.1,128.7,125.7(\mathrm{q}, J=3.5 \mathrm{~Hz}), 125.4$, 121.8, 121.1, 112.1, 70.9. ${ }^{19}$ F NMR (282 MHz, $d^{6}$-DMSO) $\delta$-62.09. IR (neat) v 3405 (br), $1702,1601 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 270\left(\mathrm{M}^{+}+1-\mathrm{F}\right), 173$ (100). Anal. Calcd for $\mathrm{C}_{15} \mathrm{H}_{12} \mathrm{BF}_{3} \mathrm{O}_{4}$ : C, 55.59; H, 3.73. Found: C, 55.75; H, 3.96.


White solid; yield: $45 \%$; mp $142-144{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.90(\mathrm{dd}, J=7.2$ and $1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.65(\mathrm{~d}, J=0.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.48-7.38(\mathrm{~m}, 2 \mathrm{H}), 7.11-7.06(\mathrm{~m}, 1 \mathrm{H}), 6.91(\mathrm{~d}, J$ $=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.65-6.63(\mathrm{~m}, 1 \mathrm{H}), 6.34-6.33(\mathrm{~m}, 2 \mathrm{H}), 5.27(\mathrm{~s}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $d^{6}$-DMSO) $\delta 183.3,162.4,149.4,148.5,136.1,132.1,121.2,119.6,112.7,112.1,69.6$. IR (neat) v 3318 (br), 1685, 1603, 1348. MS ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): 246 ( $\mathrm{M}^{+}$), 228, 95 (100). Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{11} \mathrm{BO}_{5}$ : C, $58.58 ; \mathrm{H}, 4.51$. Found: C, 58.70; $\mathrm{H}, 4.85$.


White solid; yield: $55 \%$; mp $146-148{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.88(\mathrm{dd}, J=7.5$ and $1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.43-40(\mathrm{~m}, 1 \mathrm{H}), 7.08(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.77(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H})$, 6.31-6.27 (m, 2H), $4.76(\mathrm{~s}, 2 \mathrm{H}), 2.26(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, d^{6}$-DMSO) $\delta 204.1$, $162.2,136.0,131.9,121.0,111.8,109.0,72.5,26.0$. IR (neat) v 3335 (br), 1732, 1604. MS $(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 194\left(\mathrm{M}^{+}\right), 151,121,107,43$ (100). Anal. Calcd for $\mathrm{C}_{9} \mathrm{H}_{11} \mathrm{BO}_{4}: \mathrm{C}, 55.72 ; \mathrm{H}, 5.72$. Found: C, 55.84; H, 5.90.

## (ii) General procedure for preparation of the substrates $\mathbf{1 g - i} \mathbf{i}^{\mathbf{4}}$



Typical procedure for the preparation of $1 \mathbf{g}: \mathrm{K}_{2} \mathrm{CO}_{3}(2.11 \mathrm{~g}, 15 \mathrm{mmol})$ was added to the solution of 2-Iodo-5-methoxy-phenol ${ }^{6}(3.75 \mathrm{~g}, 15 \mathrm{mmol})$ and phenacyl bromide in acetone $(10 \mathrm{~mL})$ and the resulting suspension heated under reflux for 4 h . The mixture was then allowed to cool to room temperature and poured into water $(100 \mathrm{~mL})$. The precipitate was collected by filtration and to afford crude product

2-(2'-iodo-5'-methoxy-phenoxy)-1-phenyl-ethanone, which was used for the next step without purification. The crude product was added to the solution of trimethyl orthoformate ( $4 \mathrm{~mL}, 37 \mathrm{mmol}$ ) and $p$-toluenesulfonic acid ( $82 \mathrm{mg}, 0.45 \mathrm{mmol}$ ) in methanol ( 70 mL ). The mixture was heated at $50{ }^{\circ} \mathrm{C}$ for 12 h , followed by the removal of methanol and methyl formate by distillation at $70{ }^{\circ} \mathrm{C}$. The resulting oil was treated with 15 mg of sodium methoxide in 1.5 mL of methanol, washed with ether, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, and concertrated under reduced pressure. The residue was purified by flash column chromatography to obtain the product $\mathbf{3 g}(4.81 \mathrm{~g}, 76 \%$ for two steps).
$\mathbf{1 g}$ was prepared by the similar procedure from $\mathbf{3 a}$ to $\mathbf{1 a}$. $\mathbf{1 h}$ and $\mathbf{1 i}$ was prepared by using the corresponding phenols ${ }^{7}$.

## 2-(2',2'-dimethoxy-2'-phenyl-ethoxy)-1-iodo-4-methoxybenzene (3g)


oil; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.69-68(\mathrm{~m}, 2 \mathrm{H}), 7.53(\mathrm{~d}, J=9.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.40-7.26$ $(\mathrm{m}, 3 \mathrm{H}), 6.28-6.20(\mathrm{~m}, 2 \mathrm{H}), 4.14(\mathrm{~s}, 2 \mathrm{H}), 3.71(\mathrm{~s}, 3 \mathrm{H}), 3.33(\mathrm{~s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 161.0,157.9,139.1,139.0,128.1,127.9,127.7,107.7,101.1,100.1,75.2,71.1$, 55.4, 49.2. IR (oil): v 3061, 1584, 748, 702. MS ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): 383 ( ${ }^{+}-\mathrm{OMe}$ ), 382 (100), 350, 151, 105. HRMS-EI calcd for $\mathrm{C}_{16} \mathrm{H}_{15} \mathrm{IO}_{3}\left(\mathrm{M}^{+}-\mathrm{CH}_{3} \mathrm{OH}\right) 382.0066$, found 382.0053.

## 4-Chloro-1-(2',2'-dimethoxy-2'-phenyl-ethoxy)-2-iodobenzene (3h)


oil; yield: $81 \%$; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.67-7.64(\mathrm{~m}, 3 \mathrm{H}), 7.38-7.34(\mathrm{~m}, 3 \mathrm{H})$, 7.17-7.13 (m, 1H), $6.51(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.14(\mathrm{~s}, 2 \mathrm{H}), 3.33(\mathrm{~s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 156.1,138.8,138.5,128.9,128.2,128.0,127.6,126.6,112.7,101.0,86.7,71.5$, 49.2. IR (oil): v 3089, 2943, 1578, 1564. MS ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): $388\left(\mathrm{M}^{+}-2 \mathrm{CH}_{3}\right), 152,151$ (100), 105, 91. HRMS-EI calcd for $\mathrm{C}_{16} \mathrm{H}_{16} \mathrm{ClIO}_{3}\left(\mathrm{M}^{+}\right)$417.9833, found 417.9829.

4-methyl-1-(2',2'-dimethoxy-2'-phenyl-ethoxy)-2-iodobenzene (3i)

oil; yield: $76 \%$; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.68-7.65(\mathrm{~m}, 2 \mathrm{H}), 7.52(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H})$, 7.40-7.31 (m, 3H), $6.97(\mathrm{dd}, J=7.8,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.49(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.13(\mathrm{~s}, 2 \mathrm{H})$, $3.33(\mathrm{~s}, 6 \mathrm{H}), 2.20(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 155.2,139.7,139.1,132.4,129.6$, 128.1, 127.9, 127.7, 112.2, 101.2, 86.4, 71.4, 49.2, 19.9. IR (oil): v 3060, 2943, 1600,
1490. MS ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): $398\left(\mathrm{M}^{+}\right), 366(100), 151,105,77$. HRMS-EI calcd for $\mathrm{C}_{17} \mathrm{H}_{19} \mathrm{IO}_{3}\left(\mathrm{M}^{+}\right)$ 398.0379, found 398.0363.

## 4-Methoxy-2-(2'-oxo-2'-phenylethoxy)-phenyl boronic acid (1g)



White solid; yield: $43 \%$; mp $156-157{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.00-7.97(\mathrm{~m}, 2 \mathrm{H})$, $7.83(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.66-7.51(\mathrm{~m}, 3 \mathrm{H}), 6.63-6.60(\mathrm{~m}, 1 \mathrm{H}), 6.46(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H})$, $6.14(\mathrm{~s}, 2 \mathrm{H}), 5.36(\mathrm{~s}, 2 \mathrm{H}), 3.86(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, d^{6}$-DMSO) $\delta$ 194.6, 164.0, $162.9,137.4,134.1,133.8,128.8,127.9,106.3,99.2,70.7,55.3$. IR (neat) v 3513 (br), 1705, $1606 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / z, \mathrm{EI}): 242\left(\mathrm{M}^{+}-\mathrm{O}=\mathrm{BOH}\right), 105(100), 91$. Anal. Calcd for $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{BO}_{5}: \mathrm{C}, 62.97 ; \mathrm{H}, 5.28$. Found: C, 63.02; H, 5.52.

## 5-Chloro-2-(2-oxo-2-phenyl-ethoxy)-phenyl boronic acid (1h) <br> 

White solid; yield: $55 \%$; $\mathrm{mp} 180-182{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.00-7.97(\mathrm{~m}, 2 \mathrm{H})$, 7.86-7.37 (m, 5H), $6.86(\mathrm{~d}, J=9.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.34(\mathrm{~s}, 2 \mathrm{H}), 5.38(\mathrm{~s}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $d^{6}$-DMSO) $\delta 194.5,161.1,135.1,134.1,133.7,131.1,128.8,127.9,125.1,114.3,71.1$. IR (neat) v 3490 (br), $3383,1695 \mathrm{~cm}^{-1}$. MS ( $\mathrm{m} / \mathrm{z}$, EI): $211\left(\mathrm{M}^{+}-\mathrm{Cl}-\mathrm{O}=\mathrm{BOH}\right), 77,43$ (100). Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{12} \mathrm{BClO}_{4}$ : C, 57.88; H, 4.16. Found: C, 58.20; H, 4.28.

## 5-Methyl-2-(2'-oxo-2'-phenylethoxy)-phenyl boronic acid (1i)



White solid; yield: $58 \%$; mp 159-161 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.00-7.97(\mathrm{~m}, 2 \mathrm{H})$,
$7.70-7.63(\mathrm{~m}, 2 \mathrm{H}), 7.53(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.26-7.23(\mathrm{~m}, 1 \mathrm{H}), 6.82(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H})$, 6.35-6.34 (m, 2H), $5.38(\mathrm{~s}, 2 \mathrm{H}), 2.32(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, d^{6}$-DMSO) $\delta$ 194.9, $160.6,136.6,134.1,133.9,132.4,129.5,128.9,127.9,112.1,70.7,20.1$. IR (neat) v 3370, $3216,1693 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 151\left(\mathrm{M}^{+}-\mathrm{CH}_{2} \mathrm{COPh}, 100\right), 134,105$. Anal. Calcd for $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{BO}_{4}: \mathrm{C}, 66.70 ; \mathrm{H}, 5.60$. Found: C, 66.73; H, 5.60.

## (iii) procedure for preparation of the substrates $\mathbf{1 j}{ }^{\mathbf{8}}$


$\mathbf{4} \mathbf{j}$ was prepared according to the literature method. ${ }^{\mathbf{9}} \mathbf{3} \mathbf{j}$ was prepared from $\mathbf{4} \mathbf{j}$ by using ethylene glycol and catalyzed amount of p-toluenesulfonic acid in benzene with a Dean Stark trap. 1j was prepared by similar procedure from 3a to $\mathbf{1 a}$.

2-(2'-Bromo-phenyl)-ethy-2-phenyl-1,3-dioxolane (3j)


3j: oil; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.53-7.46(\mathrm{~m}, 3 \mathrm{H}), 7.38-7.26(\mathrm{~m}, 3 \mathrm{H}), 7.18(\mathrm{~d}, J=$ $4.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.04-7.00(\mathrm{~m}, 1 \mathrm{H}), 4.11-4.06(\mathrm{~m}, 2 \mathrm{H}), 3.86-3.81(\mathrm{~m}, 2 \mathrm{H}), 2.85-2.79(\mathrm{~m}, 2 \mathrm{H})$, 2.22-2.16 (m, 2H). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 142.3,141.2,132.6,130.1,128.0,127.8$, 127.4, 127.3, 125.6, 124.3, 109.8, 64.5, 40.3, 30.4. IR (oil): v 3060, 2887, 1567, 1472, 1038. MS ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): $303\left(\mathrm{M}^{+}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 149$ (100), 105, 77. HRMS-EI calcd for
$\mathrm{C}_{11} \mathrm{H}_{12} \mathrm{BrO}_{2}\left(\mathrm{M}^{+}-\mathrm{Ph}\right)$ 255.0021, found 255.0018 .

## 2-(3-Oxo-3-phenyl-propyl)-phenyl boronic acid (1j)



White solid; yield: $49 \% ; \mathrm{mp} 115-117^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.98-7.95(\mathrm{~m}, 2 \mathrm{H})$, 7.66-7.55 (m, 2H), 7.47-7.19 (m, 5H), $6.90(\mathrm{~s}, 2 \mathrm{H}), 3.62-3.58(\mathrm{~m}, 2 \mathrm{H}), 3.20(\mathrm{~d}, J=6.3 \mathrm{~Hz}$, $2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, d^{6}$-DMSO) $\delta 199.4,144.7,136.5,133.1,128.7,128.5,127.9$, 124.9, 40.9, 30.2. IR (neat) v 3176 (br), 1678, $1597 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 254\left(\mathrm{M}^{+}\right), 131,135$, 105 (100). Anal. Calcd for $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{BO}_{3}$ : C, $70.90 ; \mathrm{H}, 5.95$. Found: C, $70.58 ; \mathrm{H}, 6.00$.
(iv) procedure for preparation of the substrates 1 k

$\mathbf{4 k}$ was prepared according to the literature method. ${ }^{10}$
2-iodophenol ( $2.652 \mathrm{~g}, 12.1 \mathrm{mmol}$ ) dissolved in DMF ( 15 mL ) was treated with $50 \%$ NaH suspended in mineral oil ( $482 \mathrm{mg}, 12.1 \mathrm{mmol}$ ) and the resultant was stirred 0.5 h . A solution of $\mathbf{4 k}(2.236 \mathrm{~g}, 10.1 \mathrm{mmol})$ in $\mathrm{DMF}(8 \mathrm{~mL})$ was then added and the mixture refluxed for 40 h . The reaction was quenched with $\mathrm{H}_{2} \mathrm{O}$ and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ layer was dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, and concertrated under reduced pressure. The residue was purified by flash column chromatography to obtain the product 3 k ( $2.178 \mathrm{~g}, 55 \%$ ).
$\mathbf{1 k}$ was prepared by similar procedure from $\mathbf{3 j}$ to $\mathbf{1} \mathbf{j}$.

## 2-[2-(2-Iodo-phenoxy)-ethyl]-2-phenyl-1,3-dioxolane (3k)



3k: oil; yield: $62 \%$; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.75-7.23(\mathrm{~m}, 7 \mathrm{H}), 6.77(\mathrm{dd}, J=7.8$, $0.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.70-6.65(\mathrm{~m}, 1 \mathrm{H}), 4.14(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.08-4.03(\mathrm{~m}, 2 \mathrm{H}), 3.83-3.78(\mathrm{~m}$, $2 \mathrm{H}), 2.52(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 157.3,141.9,139.3,129.3$, $128.2,128.1,125.4,122.3,112.0,108.8,86.5,64.8,64.5,39.3$. IR (oil): v 3060, 1467, 1049, 748, 703. MS ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): 395 ( $\mathrm{M}^{+}-1$ ), 149 (100), 105, 77. HRMS-EI calcd for $\mathrm{C}_{17} \mathrm{H}_{17} \mathrm{IO}_{3}\left(\mathrm{M}^{+}\right)$396.0222, found 396.0220 .

## 2-(3-Oxo-3-phenyl-propoxy)-phenyl boronic acid (1k) <br> 

White solid; yield: $52 \%$; mp 97-99 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.03-8.00(\mathrm{~m}, 2 \mathrm{H})$, 7.85 (dd, $J=7.2,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.62-7.59(\mathrm{~m}, 1 \mathrm{H}), 7.53-7.42(\mathrm{~m}, 3 \mathrm{H}), 7.07-6.99(\mathrm{~m}, 2 \mathrm{H})$, $5.96(\mathrm{~s}, 2 \mathrm{H}), 4.55(\mathrm{t}, J=6.3 \mathrm{~Hz}, 2 \mathrm{H}), 3.53(\mathrm{t}, J=6.3 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right)$ $\delta 197.4,163.4,136.9,136.7,133.7,132.8,128.8,128.2,121.5,111.0,63.5,37.8$. IR (neat) $v 3379$ (br), 1681, $1600 \mathrm{~cm}^{-1} . \mathrm{MS}\left(\mathrm{m} / \mathrm{z}\right.$, EI): $270\left(\mathrm{M}^{+}\right), 252$, 44 (100). Anal. Calcd for $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{BO}_{4}$ : C, 66.70; H, 5.60. Found: C, 66.55; H,5.81.

## II. Enantioselective Intramolecular Addition of Arylboronic Acids to Ketones

(i) Non-asymmetric cyclization of $\mathbf{1 a}$ catalyzed by $\left[\mathrm{Pd}(\mathrm{dppp})\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]^{2+}(\mathrm{OTf})_{2}(\mathbf{3 a})$

Under argon, $\mathrm{K}_{3} \mathrm{PO}_{4}(128.1 \mathrm{mg}, 0.6 \mathrm{mmol})$ was added to a solution of $\mathbf{1 a}(76.6 \mathrm{mg}, 0.3$ mmol ), 3a ( $12.6 \mathrm{mg}, 0.015 \mathrm{mmol}$ ) and water ( $10.8 \mu \mathrm{~L}, 0.6 \mathrm{mmol}$ ) in dioxane ( 3 mL ). The reaction mixture was stirred at $80{ }^{\circ} \mathrm{C}$ for 1 h . After the reaction was completed as monitored by TLC, the reaction mixture was quenched with $\mathrm{H}_{2} \mathrm{O}$ and the aqueous layer was extracted with $\mathrm{EtOAc}(3 \times 20 \mathrm{~mL})$. The organic layers were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, and concertrated under reduced pressure. The residue was purified by flash column chromatography to obtain the product $\mathbf{2 a}$ ( $58 \mathrm{mg}, 91 \%$ ).

## 3-phenyl-3-hydroxy-2,3-dihydrobenzofuran $2 \mathbf{a n}^{11}$


$2 a$
Oil; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.51-6.91(\mathrm{~m}, 9 \mathrm{H}), 4.67$ and $4.49(\mathrm{AB} \mathrm{q}, J=10.2 \mathrm{~Hz}$, $2 \mathrm{H}), 2.54(\mathrm{br} \mathrm{s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 160.5,142.5,132.1,130.6,128.2$, $127.5,126.0,124.4,121.4,110.7,86.0,82.5$. IR (oil) v 3437 (br), $3061,1600 \mathrm{~cm}^{-1} . \mathrm{MS}$ ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): $212\left(\mathrm{M}^{+}, 100\right), 194,77$.
(ii) General Procedure for Table 2

Under argon, Amberlite $\operatorname{IRA}(\mathrm{OH})(100 \mathrm{mg}, 1.5$ equiv) was added to a solution of $\mathbf{1}$ ( $51.2 \mathrm{mg}, 0.2 \mathrm{mmol}), \mathbf{4 b}(9.0 \mathrm{mg}, 0.005 \mathrm{mmol})$ in toulene $(2 \mathrm{~mL})$ or in the mixture of toluene ( 1 mL ) and dioxane ( 1 mL ). The reaction mixture was stirred at $40{ }^{\circ} \mathrm{C}$ for 12 h . After the reaction was completed as monitored by TLC, the reaction mixture was quenched with $1 \mathrm{~N} \mathrm{NaOH}(8 \mathrm{~mL})$ and the aqueous layer was extracted with $\mathrm{EtOAc}(3 \times 20$ $\mathrm{mL})$. The organic layers were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, and concertrated under reduced pressure. The residue was purified by flash column chromatography to obtain the product $\mathbf{2}$.

## 3-phenyl-3-hydroxy-2,3-dihydrobenzofuran (2a)



Entry 1. Oil; yield: 85\%; The ee was determined by chiral HPLC using a Chiralcel OD-H column with hexane $:$ isopropanol $=90: 10$, flow $=0.7 \mathrm{~mL} / \mathrm{min}$; ee: $92 \% ;[\alpha]_{\mathrm{D}}{ }^{20}=-114.5$ (c $1.00, \mathrm{CHCl}_{3}$ ).

## 3-(4-Methoxy-phenyl)-2,3-dihydro-benzofuran-3-ol (2b)



2b

Entry 2. Oil; yield: 92\%; The ee was determined by chiral HPLC using a Chiralcel OD-H column with hexane $:$ isopropanol $=90: 10$, flow $=0.7 \mathrm{~mL} / \mathrm{min}$; ee: $91 \% ;[\alpha]_{\mathrm{D}}{ }^{20}=-111.4$ (c $1.10, \mathrm{CHCl}_{3}$ ).
${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.43-7.38(\mathrm{~m}, 2 \mathrm{H}), 7.32-7.26(\mathrm{~m}, 1 \mathrm{H}), 7.12-7.09(\mathrm{~m}, 1 \mathrm{H})$, 6.96-6.87 (m, 4H), 4.65 and $4.45(\mathrm{AB} \mathrm{q}, J=10.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 2.61-2.59(\mathrm{~m}, 1 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 160.4,158.8,134.7,132.2,130.4,127.2,124.3,121.2$, $113.5,110.6,85.9,82.1,55.2$. IR (oil) v 3453 (br), $1508,832,752 \mathrm{~cm}^{-1} . \mathrm{MS}(m / z, \mathrm{EI}): 242$ $\left(\mathrm{M}^{+}\right), 224$ (100), 209, 152. HRMS-EI calcd for $\mathrm{C}_{15} \mathrm{H}_{14} \mathrm{O}_{3}\left(\mathrm{M}^{+}\right)$242.0943, found 242.0942.

## 3-(4-Chloro-phenyl)-2,3-dihydro-benzofuran-3-ol (2c)



Entry 3. Oil; yield: 90\%; The ee was determined by chiral HPLC using a Chiralcel OD-H column with hexane $:$ isopropanol $=90: 10$, flow $=0.7 \mathrm{~mL} / \mathrm{min} ;$ ee: $87 \% ;[\alpha]_{\mathrm{D}}{ }^{20}=-89.5(c$ $\left.1.15, \mathrm{CHCl}_{3}\right)$.
${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ 87.43-7.26(m, 5H), 7.06-6.91 (m, 3H), 4.62 and 4.42 (AB q, $J=10.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.78(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 160.4,141.07$, $133.41,131.68,130.74,128.31,127.50,124.25,121.51,110.78,85.84,82.07$. IR (oil) $v$ 3438 (br), 1598, 1478, $1093 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 246\left(\mathrm{M}^{+}\right), 229$, 121 (100). HRMS-EI calcd for $\mathrm{C}_{14} \mathrm{H}_{11} \mathrm{ClO}_{2}\left(\mathrm{M}^{+}\right) 246.0448$, found 246.0453

## 3-(4-Trifluoromethyl-phenyl)-2,3-dihydro-benzofuran-3-ol (2d)



## 2d

Entry 4. White solid; yield: $86 \%$; The ee was determined by chiral HPLC using a Chiralcel OD-H column with hexane $:$ isopropanol $=90: 10$, flow $=0.7 \mathrm{~mL} / \mathrm{min}$; ee: $93 \%$; $[\alpha]_{D}{ }^{20}=-81.7\left(c \quad 1.00, \mathrm{CHCl}_{3}\right)$. mp 78-80 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR (300 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta$ 7.65-7.59 (m, 4H), 7.35-7.26 (m, 1 H ), 7.06-6.93 (m, 3 H ), 4.68 and $4.49(\mathrm{AB} \mathrm{q}, J=10.5 \mathrm{~Hz}, 2 \mathrm{H}), 2.64(\mathrm{br} \mathrm{s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 160.5,146.6,131.6,131.0,130.0,129.6,126.5,125.2(\mathrm{q}, J=3.7 \mathrm{~Hz})$, 124.3, 121.7, 110.9, 86.0, 82.3. ${ }^{19} \mathrm{~F}$ NMR ( $282 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$-62.92. IR (neat) v 3483 (br), 1620, 1329, $1122 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 280\left(\mathrm{M}^{+}\right), 263,135$ (100). HRMS-EI calcd for $\mathrm{C}_{15} \mathrm{H}_{11} \mathrm{~F}_{3} \mathrm{O}_{2}\left(\mathrm{M}^{+}\right)$280.0711, found 280.714 .

## 3-Furan-3-yl-2,3-dihydro-benzofuran-3-ol (2e)



Entry 5. oil; yield: 84\%; The ee was determined by chiral HPLC using a Chiralcel OD-H column with hexane $:$ isopropanol $=90: 10$, flow $=0.7 \mathrm{~mL} / \mathrm{min}$; ee: $84 \% ;[\alpha]_{\mathrm{D}}{ }^{20}=-60.9(c$ $\left.0.83, \mathrm{CHCl}_{3}\right)$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.43(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.42-7.26(\mathrm{~m}, 2 \mathrm{H}), 6.99-6.91(\mathrm{~m}$, $2 \mathrm{H}), 6.39-6.38(\mathrm{~m}, 2 \mathrm{H}), 4.75$ and $4.67(\mathrm{AB} \mathrm{q}, J=10.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.66-2.65(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 160.2,154.1,142.9,131.0,129.4,124.2,121.2,110.9,110.4$, $107.1,82.3,78.8 . \operatorname{IR}$ (neat) $v 3338(\mathrm{br}), 1603,1475,1015 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 202\left(\mathrm{M}^{+}\right)$, 185, 173 (100), 128.HRMS-EI calcd for $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{O}_{3}\left(\mathrm{M}^{+}\right)$202.0630, found 202.0635.

## 3-Methyl-2,3-dihydro-benzofuran-3-ol (2f) ${ }^{\mathbf{1 2}}$



Entry 6. White solid; yield: 58\%; The ee was determined by chiral HPLC using a Chiralcel OD-H column with hexane $:$ isopropanol $=90: 10$, flow $=0.7 \mathrm{~mL} / \mathrm{min}$; ee: $96 \%$; $[\alpha]_{D}{ }^{20}=-42.5\left(c \quad 1.00, \mathrm{CHCl}_{3}\right)$. mp 48-49 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.34(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.26-7.23(\mathrm{~m}, 1 \mathrm{H})$, 6.98-6.86(m, 1H), $6.87(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.49$ and $4.30(\mathrm{AB} \mathrm{q}, J=10.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.03$ (br s, 1H), $1.69(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 159.7, 131.9, 130.3, 122.9, 121.0, $110.6,83.9,77.8,24.8$. IR (oil) $v 3400$ (br), 1601, $1479,749 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 150\left(\mathrm{M}^{+}\right)$, 135 (100), 107, 77.

6-Methoxy-3-phenyl-2,3-dihydro-benzofuran-3-ol (2g)


Entry 7. Oil; yield: 91\%; The ee was determined by chiral HPLC using a Chiralcel AD-H column with hexane $:$ isopropanol $=95: 5$, flow $=0.7 \mathrm{~mL} / \mathrm{min}$; ee: $89 \% ;[\alpha]_{\mathrm{D}}{ }^{20}=-86.5(c$ $\left.1.00, \mathrm{CHCl}_{3}\right)$.
${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.52-7.49(\mathrm{~m}, 2 \mathrm{H}), 7.39-7.26(\mathrm{~m}, 3 \mathrm{H}), 7.00-6.97(\mathrm{~m}, 1 \mathrm{H})$,
6.51-6.48 (m, 2H), 4.71 and $4.51(\mathrm{AB} \mathrm{q}, J=10.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 2.39-2.35(\mathrm{~m}, 1 \mathrm{H})$.
${ }^{13}{ }^{2} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right) \delta 162.2,142.7,128.2,127.5,126.1,124.7,124.4,107.9,96.3$, 87.1, 82.2, 55.5. IR (oil) v 3459, 1627, 1496, 1152. MS ( $\mathrm{m} / \mathrm{z}, \mathrm{EI}$ ): 242(M ${ }^{+}$), 224 (100), 209, 152. HRMS-EI calcd for $\mathrm{C}_{15} \mathrm{H}_{14} \mathrm{O}_{3}\left(\mathrm{M}^{+}\right)$242.0943, found 242.0943 .

## 5-Chloro-3-phenyl-2,3-dihydro-benzofuran-3-ol (2h)



Entry 8. Oil; yield: 83\%; The ee was determined by chiral HPLC using a Chiralcel OD-H column with hexane $:$ isopropanol $=90: 10$, flow $=0.7 \mathrm{~mL} / \mathrm{min}$; ee: $89 \% ;[\alpha]_{\mathrm{D}}{ }^{20}=-109.4$ (c $1.00, \mathrm{CHCl}_{3}$ ).
${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.49-7.23(\mathrm{~m}, 6 \mathrm{H}), 7.05(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.89(\mathrm{~d}, J=8.7$ $\mathrm{Hz}, 1 \mathrm{H}), 4.71$ and $4.54(\mathrm{AB} \mathrm{q}, J=10.5 \mathrm{~Hz}, 2 \mathrm{H}), 2.51(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right)$ $\delta 159.1,141.8,133.9,130.5,128.4,127.8,126.0,125.9,124.5,111.9,86.6,82.4$. IR (oil) $v$ 3421 (br), 1470, $700 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / \mathrm{z}, \mathrm{EI}): 246$ (100), 228, 155, 105. HRMS-EI calcd for $\mathrm{C}_{14} \mathrm{H}_{11} \mathrm{ClO}_{2}\left(\mathrm{M}^{+}\right)$246.0448, found 246.0459.

## 5-Methyl-3-phenyl-2,3-dihydro-benzofuran-3-ol (2i)


$2 i$
Entry 9. Oil; yield: 82\%; The ee was determined by chiral HPLC using a Chiralcel OD-H column with hexane $:$ isopropanol $=90: 10$, flow $=0.7 \mathrm{~mL} / \mathrm{min} ;$ ee: $93 \% ;[\alpha]_{\mathrm{D}}{ }^{20}=-97.0(c$ $\left.1.00, \mathrm{CHCl}_{3}\right)$.
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.52-7.50(\mathrm{~m}, 2 \mathrm{H}), 7.41-7.26(\mathrm{~m}, 3 \mathrm{H}), 7.12-7.08(\mathrm{~m}, 1 \mathrm{H})$, 6.88-6.84(m, 2H), 4.65 and $4.49(\mathrm{AB} \mathrm{q}, J=10.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.56(\mathrm{~s}, 1 \mathrm{H}), 2.27(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right) \delta 158.4,142.6,132.1,131.1,130.8,128.2,127.4,126.0,124.5$,
110.2, 86.2, 82.6, 20.7.IR (oil) v 3439 (br), 1613, $1492 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / z, \mathrm{EI}): 226\left(\mathrm{M}^{+}, 100\right)$, 208, 209, 135, 77. HRMS-EI calcd for $\mathrm{C}_{15} \mathrm{H}_{14} \mathrm{O}_{2}\left(\mathrm{M}^{+}\right)$226.0994, found 226.0996.

1-Phenyl-indan-1-ol (2j) ${ }^{\mathbf{1 3}}$


Entry 10. Oil; yield: 53\%; The ee was determined by chiral HPLC using a Chiralcel OD-H column with hexane : isopropanol $=90: 10$, flow $=0.7 \mathrm{~mL} / \mathrm{min}$; ee: $66 \% ;[\alpha]_{\mathrm{D}}{ }^{20}=-$ 27.0 ( $c 1.60, \mathrm{CHCl}_{3}$ ). The absolute configuration was determined to be $(R)$ according to literature. [ lit. ${ }^{13}[\alpha]_{\mathrm{D}}{ }^{20}=-48.5\left(\mathrm{c} 1.56, \mathrm{CHCl}_{3}\right)$ for pure ( $R$ )-1-Phenyl-indan-1-ol] ${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.42-7.20(\mathrm{~m}, 8 \mathrm{H}), 7.10(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.23-3.13(\mathrm{~m}$, $1 \mathrm{H}), 3.00-2.91(\mathrm{~m}, 1 \mathrm{H}), 2.53-2.47(\mathrm{~m}, 2 \mathrm{H}), 2.11(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 147.9,146.3,144.1,128.5,128.0,127.0,126.9,125.7,125.0,124.0,85.5,44.8,29.9$. IR (oil) v 3376 (br), 1602, $1447 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / z, \mathrm{EI}): 208\left(\mathrm{M}^{+}\right), 192$ (100), 133.

## 4-phenyl-chroman-4-ol (2k) ${ }^{14}$



Entry 11. Oil; yield: 82\%; The ee was determined by chiral HPLC using a Chiralcel OD-H column with hexane : isopropanol $=90: 10$, flow $=0.7 \mathrm{~mL} / \mathrm{min}$; ee: $53 \% ;[\alpha]_{\mathrm{D}}{ }^{20}=$ -18.2 (c 1.00, $\mathrm{CHCl}_{3}$ ).
${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.42-7.18(\mathrm{~m}, 6 \mathrm{H}), 6.96-6.81(\mathrm{~m}, 3 \mathrm{H}), 4.44-4.35(\mathrm{~m}, 1 \mathrm{H})$, 4.27-4.20 (m, 1H), 2.38-2.30 (m, 2H), 2.23-2.16 (m, 1H). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 155.0,147.0,129.5,129.0,128.1,128.0,127.0,126.3,120.8,117.1,71.5,63.1,39.6$. IR (oil) v 3453 (br), 1608, $1487 \mathrm{~cm}^{-1} . \mathrm{MS}(\mathrm{m} / z, \mathrm{EI}): 226\left(\mathrm{M}^{+}\right), 197(100), 149$.

## References:

1. Stang, P. J.; Cao, D. H.; Poulter, G. T.; Arif, A. M. Orgaometallics 1995, 14, 1110.
2. Hagiwara, E.; Fujii, A.; Sodeoka, M. J. Am. Chem. Soc. 1998, 120, 2474.
3. Moody, C. J.; Doyle, K. J.; Elliott, M. C.; Mowlem, T. J. J. Chem. Soc. Perkin Trans. 1 1997, 16, 2413.
4. Michellys, P.-Y.; Ardecky, R. J.; Chen, J.-H.; D'Arrigo, J.; Grese, T. A.; Karanewsky, D. S.; Leibowitz, M. D.; Liu, S.; Mais, D. A.; Mapes, C. M.; Montrose-Rafizadeh, C.; Ogilvie, K. M.; Reifel-Miller, A.; Rungta, D.; Thompson, A. W.; Tyhonas, J. S.; Boehm, M. F. J. Med. Chem. 2003, 46, 4087.
5. Rival, Y.; Grassy, G.; Michel, G. Chem. Pharm. Bull. 1992, 40, 1170.
6. Tsukayama, M.; Utsumi, H.; Kunugi, A.; Nozaki, H. Heterocycles 1997, 45, 1131.
7. Edgar, K. J.; Falling, S. N. J. Org. Chem. 1990, 55, 5287.
8. de Koning, C. B.; Michael, J. P.; Rousseau, A. L. J. Chem. Soc. Perkin Trans. 1 2000, 5, 787.
9. Wursthorn, K. R.; Kuivila, H. G.; Smith, G. F. J. Am. Chem. Soc. 1978, 100, 2779.
10. Speare, D. M.; Fleming, S. M.; Beckett, M. N.; Li, J.-J.; Bugg, T. D. H. Org. Biomol. Chem. 2004, 2, 2942.
11. Wagner, P. J.; Meador, M. A.; Park, B. S. J. Am. Chem. Soc. 1990, 112, 5199.
12.Casiraghi, G.; Sartori, G.; Casnati, G.; Bigi, F. J. Chem. Soc. Perkin Trans. 1 1983, 8, 1649.
12. Jaouen, G.; Meyer, A. J. Am. Chem. Soc. 1975, 97, 4667.
13. Kodama, Y.; Nakabayashi, T.; Segawa, K.; Hattori, E.; Sakuragi, M.; Nishi, N.;

Sakuragi, H. J. Phys. Chem. A 2000, 104, 11478.

