

## Electronic Supplementary Information

for

### **Mild metal-free *syn*-stereoselective ring opening of activated epoxides and aziridines with aryl borates.**

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- Text giving experimental procedures and characterization data for all new compounds 13-21 (pages 14-18)

**General Methods.** THF, CH<sub>2</sub>Cl<sub>2</sub> and DMF on molecular sieves were purchased from Fluka and used as such. Analytical TLC were performed on Alugram SIL G/UV254 silica gel sheets (Macherey-Nagel) with detection by 0.5% phosphomolybdic acid solution in 95% EtOH. Silica gel 60 (Macherey-Nagel 230-400 mesh) was used for flash chromatography. Solvents for extraction and chromatography were HPLC grade.

<sup>1</sup>H NMR spectra were recorded on a Bruker AC-200 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: δ 7.26). <sup>13</sup>C NMR spectra were recorded on a Bruker AC-200 (50 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: δ 77.7). Analytical high performance liquid chromatography (HPLC) was performed on a Waters 600E equipped with a Varian Prostar 325 detector using Daicel Chiralcel OD-H column with a 0.5 mL solvent flow and detection at 254 nm.

GC/MS spectra were obtained on a HP-5988-A operating at 70 eV. Mass spectra ESIMS were measured on a Finnigan LC-Q Deca Termoquest spectrometer, equipped with a software Xcalibur. High resolution mass spectra (HRMS) were recorded on a AEI MS-902 at the Department of Organic and Molecular Inorganic Chemistry, Stratingh Institute, University of Groningen, The Netherlands.

Elemental analyses were performed in our analytical laboratory with a Carlo Erba DP200 instrumentation and agreed with the theoretical values to within +/- 0.4%.

## Synthesis of aromatic borates.

**Triphenylborate (1a).**<sup>1</sup> Following a previously described procedure,<sup>1</sup> a solution of phenol (8.460 g, 90 mmol) in degassed THF (20 mL) was added at 0°C to BH<sub>3</sub>-Me<sub>2</sub>S (3.0 mL, 30 mmol) under argon. After stirring for 1h at rt, the solution was evaporated and to dryness to give **1a**, as a white solid (95% yield).

**Catechol butyl borate [butoxy-benzo[1,3,2]dioxaborole] (1b).**<sup>2</sup> A mixture of catechol (5.61 g; 50.9 mmol) and tributyl borate (15 ml; 12.9 g, 56 mmol) in toluene (50 mL) was refluxed for 17 hours. After removal of the solvent by means of distillation at ambient pressure, the product is purified by distillation (78°C, ca. 5 mmHg) to give 6.0 g of pure **1b** (62% yield), as a colorless liquid.

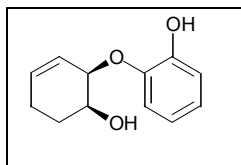
## Ring-opening of epoxides and aziridines

**Typical Procedure** as follows: aryl borate **1a** (1.2 mmol) or **1b** (2.0 mmol) was added at rt to a solution of 1.0 mmol of epoxide or aziridine in the appropriate solvent (1.0 mL) (see Table 1) under a magnetic stirring. The reaction was followed by TLC and was quenched, after the times indicated in Table 1, with 5% aqueous HCl (2.0 mL) for the reactions carried out with **1b**, or 5% aqueous NaOH (2.0 mL) for the reactions carried out with **1a**. The solution was diluted with Et<sub>2</sub>O or CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and washed twice with brine (3.0 ml each) for reactions carried out with borate **1b** and with 5% NaOH (2X3 mL) for reactions performed with **1a**. Evaporation of the dried organic solution afforded a crude reaction mixture which was subjected to flash chromatography to give the pure compounds.

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<sup>1</sup> C. A. Brown, S. Krishnamurthy, *J. Org. Chem.* 1978, **43**, 2731.

<sup>2</sup> W. Gerrard, M. F. Lappert, B. A. Mountfield *J. Chem. Soc.* 1959, 1529.



***syn*-2-(2-Hydroxyphenoxy)-3-cyclohexen-1-ol (2)**

Using the typical procedure described above, the product was isolated (63% yield) by column chromatography eluting with hexanes/AcOEt 7:3, as an oil.  $R_f=0.33$  (38% AcOEt in hexanes).

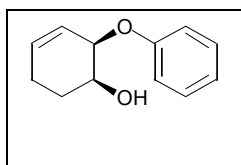
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.68-2.41 (m, 4H), 4.03-4.17 (m, 1H, -CH-OH), 4.51-4.58 (m, 1H, -CH-O-Ar), 5.72-6.02 (m, 2H), 6.71-6.98 (m, 4H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  23.7, 26.7, 68.5, 77.7, 116.8, 118.5, 120.8, 124.2, 124.6, 132.9, 146.1, 148.6.

MS 206 ( $\text{M}^+$ , 1), 110 (81), 96 (40), 78 (100), 67 (26), 54 (30), 39 (83).

Reference *anti*-2-(2-hydroxyphenoxy)-3-cyclohexen-1-ol was obtained in the following way: to a stirred solution of 1,2-epoxy-3-cyclohexene (96 mg, 1.0 mmol) in acetone (2.0 mL), catechol (132 mg, 1.2 mmol) and  $\text{K}_2\text{CO}_3$  (276.4 mg, 2.0 mmol) were added. The reaction was maintained under vigorous stirring for 24h at 55°C. After filtration, the resulting mixture was evaporated in vacuo to give a crude mixture containing mainly the reference *anti*-compound.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.79-4.08 (m, 1H, -CH-OH), 4.42-4.52 (m, 1H, -CH-OAr), 5.64-5.83 (m, 2H, olefinic protons).

*Syn/anti* stereoselectivity was more accurately measured by HPLC analysis on a Daicel Chiralcel<sup>®</sup> OD-H column, mobile phase: hexane/isopropanol 96/4, retention times (min): 32.4, 45.2 min (racemate of the *anti*-isomer), 28.7, 36.7 (racemate of the *syn*-isomer).



***syn*-2-Phenoxy-3-cyclohexen-1-ol (3).**

Using the typical procedure described above, the product was isolated in 65% yield after column chromatography eluting with hexanes/AcOEt 7:3 as a liquid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.72-2.12 (m, 4H), 4.02-4.18 (m, 1H, -CH-OH), 4.74-4.81 (m, 1H, -CH-O-Ph), 5.70-6.05 (m, 2H), 6.70-6.96 (m, 3H), 7.15-7.24 (m, 2H).

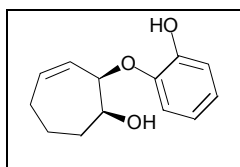
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  23.75, 27.0, 68.1, 73.8, 116.8, 121.0, 122.1, 124.1, 130.3, 133.3, 158.2.

ESIMS (pos.):  $m/z$  191 [M+H].

Anal. Calcd. for  $\text{C}_{12}\text{H}_{14}\text{O}_2$ : C, 75.76; H, 7.42. Found: C, 75.88, H, 7.34.

Reference ***anti*-2-phenoxy-3-cyclohexen-1-ol** was obtained using the Rh(I)-catalyzed *anti*-stereoselective ring-opening procedure developed by Lautens et al.<sup>3</sup>

*Syn/anti* stereoselectivity was determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The signals considered for the determination of the amount of the *anti*-isomer vs the *syn*-isomer **3** were:  $^1\text{H}$  NMR  $\delta$  3.95-4.03 (m, 1H, -CH-OH);  $^{13}\text{C}$  NMR  $\delta$  79.4 (C-O-Ph) and 71.2 (C-OH).



***syn*-2-(2-Hydroxyphenoxy)-3-cyclohepten-1-ol (4)**

Using the typical procedure described above, the product was isolated in 52% yield in mixture with the *anti*-stereoisomer after column chromatography eluting with hexane/AcOEt 7:3.

Further chromatographic purification on preparative TLC gave the pure *syn*-isomer **4** (38% yield), as a liquid.  $R_f=0.32$  (39% AcOEt in hexanes).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.50-2.40 (m, 6H), 4.19 (br d,  $J = 1.9$  Hz, 1H), 4.92 (br s, 1H), 5.50-5.60 (m, 1H), 5.95-6.15 (m, 1H), 6.70-7.00 (m, 4H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.2, 28.4, 34.4, 70.2, 80.9, 114.7, 115.8, 119.7, 122.4, 129.3, 134.1, 144.5, 147.3.

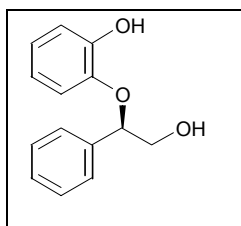
MS 202(13), 187(3), 174(5), 141(2), 121(5), 110(100), 82(32), 67(28), 53(29), 39(69).

Reference ***anti*-2-(2-hydroxyphenoxy)-3-cyclohepten-1-ol** was obtained in the following way: to a stirred solution of 1,2-epoxy-3-cycloheptene (110 mg, 1.0 mmol) in EtOH (2.0 mL), catechol (220 mg, 2.0 mmol) and NaH (40 mg, 1.66 mmol) were added. After a reflux of 18h the pH of the solution was adjusted to ca. 3 by addition of diluted HCl and then extracted several times with  $\text{Et}_2\text{O}$ . The

<sup>3</sup> K. Fagnou, M. Lautens *Org. Lett.* 2000, **2**, 2319.

evaporation of the washed (brine) and dried (MgSO<sub>4</sub>) organic solution afforded a crude reaction mixture (150 mg) which was not further purified.

*Syn/anti* stereoselectivity was determined by <sup>1</sup>H and <sup>13</sup>C NMR. Signals of the *anti*-isomer considered for integration were: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.52-4.68 (m, 1H, -CH-OAr), 3.81 (dt, 1H, *J*=3.9, 9.6 Hz, -CH-OH). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.5, 28.5, 36.9, 72.2, 84.2.



**(2*R*)-2-(2-Hydroxyphenoxy)-2-phenylethanol (5).**

Using the typical procedure described above using *R*-styrene oxide, the product was isolated in 75% yield after column chromatography eluting with hexanes/AcOEt 6:4, as a liquid.

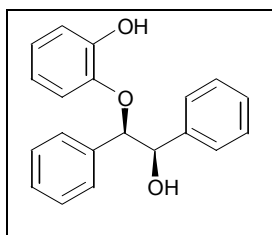
<sup>1</sup>H NMR δ 3.78-4.06 (m, 2H), 5.09 (dd, *J*=7.6, 3.7 Hz, 1H), 6.56-6.64 (m, 2H), 6.75-6.96 (m, 2H), 7.23-7.38 (m, 5H).

<sup>13</sup>C NMR δ 67.0, 82.8, 115.8 (2C), 119.9, 122.6, 126.3 (2C), 128.3, 128.7 (2C), 137.2, 145.3, 146.7.

MS(EI<sup>+</sup>) *m/z* = 230(M<sup>+</sup>, 6), 212(3), 179(1), 149(11), 121(33), 120(35), 110.0(100), 103(27), 91(20), 82.9(15), 77.0(10), 65.0(5).

HRMS(EI<sup>+</sup>) calculated for C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>: 230.09428, found: 230.09494.

The reference reaction proceeding with a complete *anti*-stereoselectivity (net inversion of configuration at the benzylic stereocenter) was prepared as the following: *R*-styrene oxide (60 mg, 0.5 mmol) was added to a stirred solution containing catechol (110 mg, 1.0 mmol) and NaH (13 mg, ca. 0.5 mmol). After 24h at 95°C the cold reaction mixture was diluted with Et<sub>2</sub>O (40 mL) and washed with brine several times. After evaporation of the dried organic solution the crude reaction mixture was subjected to HPLC analysis and compared with the reaction obtained with the use of catechol butyl borate (**1b**), which gives mainly retention of configuration. HPLC analysis performed on a Daicel Chiralcel<sup>®</sup> OD-H column, mobile phase: hexane/isopropanol 90/10, retention times (min): 15.5 (R, major stereoisomer), isomer 21.1 (S, minor stereoisomer).



**(1R\*, 2R\*)-2-(2-Hydroxyphenoxy)-1,2-diphenyl-1-ethanol (6).**

Stilbene oxide (196 mg, 1.0 mmol) was treated dropwise at rt with catechol butyl borate **1b** (384 mg, 2.0 mmol) under a vigorous stirring. The initial suspension became a light yellow solution and was treated after 4 h (ca. 85% conversion) with 2.0 mL of 5% HCl. Extraction with Et<sub>2</sub>O followed by evaporation of the washed organic solution (brine) afforded a crude product (350 mg) which was subjected to flash chromatography eluting with hexanes/AcOEt 8:2 to give 190 mg (62% yield) of compound **6**, as a solid. M.p.=111-114 °C.

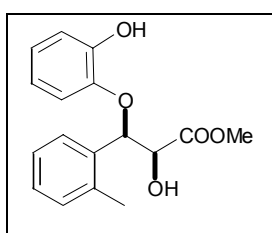
<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.96 (d, 1H, *J*=7.8 Hz), 5.04 (d, 1H, *J*=7.8 Hz), 6.62-7.30 (m, 14H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 79.14, 88.24, 116.7, 117.9, 120.4, 123.7, 127.8, 127.9, 128.6, 128.7, 138.0, 139.6, 146.2, 148.0.

ESIMS (neg.): *m/z* 305 [M-H].

*Syn/anti* stereoselectivity was determined by <sup>1</sup>H NMR. The signal of the *anti*-isomer considered for integration was: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.16 (d, 1H, -CH-OAr).

Reference **(1R\*, 2S\*)-2-(2-hydroxyphenoxy)-1,2-diphenyl-1-ethanol** (i.e. the *anti* isomer) was obtained using a described procedure.<sup>4</sup>



**(2S\*, 3R\*)-Methyl 3-(2-methylphenyl)-3-(2-hydroxyphenoxy)-2-hydroxy-propanoate (7).**

Using the typical procedure described above, the product was isolated in 82% yield after column chromatography eluting with hexanes/AcOEt 7:3, as a white solid. M.p.=148-151 °C.

<sup>1</sup>H NMR (MeOD) δ 7.32-7.38 (m, 1H), 7.07-7.19 (m, 3H), 6.66-6.82 (m, 2H), 6.59-6.42 (m, 2H), 5.87 (d, *J*=2.4 Hz, 1H), 4.47 (d, *J*=2.4 Hz, 1H), 3.70 (s, 3H), 2.45 (s, 3H).

<sup>4</sup> S. Kim, J. W. Wu, H. Y. Chen, F. DiNinno, *Org. Lett.* 2003, **5**, 685.

$^{13}\text{C}$  NMR (MeOD)  $\delta$  173.5, 147.8, 145.9, 135.9, 135.7, 131.5, 129.0, 128.5, 127.0, 122.9, 120.5, 116.7, 114.6, 78.9, 74.2, 52.8, 19.1.

Anal. Calcd. for  $\text{C}_{17}\text{H}_{18}\text{O}_3$ : C, 67.54; H, 6.00; Found: C, 68.18, H, 6.05.

*Syn/anti* stereoselectivity was determined by  $^1\text{H}$  NMR. Signals of the *anti*-isomer considered for integration were at 5.65 ppm (d, 1H,  $J=4.3$  Hz,  $-\text{CHO-Ar}$ ) and at 3.88 (s, 3H,  $-\text{OCH}_3$ ).

Demonstration of the relative stereochemistry of compound **7** was effected in two ways :

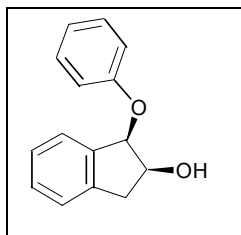
- 1) Conversion into **(2R\*, 3R\*)-methyl 3-(2-methylphenyl)-3-(2-hydroxyphenoxy)-2-chloro-propanoate** by a reaction proceeding with complete inversion of configuration. Following a previously described procedure<sup>5</sup>, a solution of compound **7** (70 mg, 0.025 mmol) in  $\text{CH}_3\text{CN}$  (0.2 mL) and  $\text{CCl}_4$  (0.5 mL) was treated with  $\text{PPh}_3$  (131 mg, 0.50 mmol) and refluxed for 24h. After evaporation of the solvent the crude mixture contained the title compound. Significant signals were in agreement with a previously described compound with the same stereochemistry:<sup>6</sup>  $^1\text{H}$  NMR  $\delta$  5.75 (d, 1H,  $J=9.0$  Hz,  $-\text{CH-OAr}$ ), 4.72 (d, 1H,  $J=9.0$  Hz,  $-\text{CH-Cl}$ ).
- 2) Conversion into the corresponding acetate **(2S\*, 3R\*)-methyl 3-(2-methylphenyl)-3-(2-acetoxyphenoxy)-2-acetoxy-propanoate (7-Ac)** and observation of  $J$  values, which were in agreement with closely related compounds.<sup>7</sup>  $^1\text{H}$  NMR  $\delta$  7.06-7.42 (m, 4H), 6.80-7.00 (m, 3H), 6.40 (d, 1H,  $J=8.0$  Hz), 5.79 (d, 1H,  $J=3.0$  Hz), 5.43 (d, 1H,  $J=3.0$  Hz), 3.69 (s, 3H), 2.43 (s, 3H), 2.30 (s, 3H), 2.00 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.65, 21.07, 21.30, 53.37, 73.48, 78.33, 114.89, 122.11, 124.11, 124.39, 126.96, 127.22, 128.15, 129.12, 131.31, 133.83, 136.66, 150.47, 168.05, 170.65.

<sup>5</sup> C. N. Barry, S. A. Evans Jr. *J. Org. Chem.* 1981, **46**, 3361.

<sup>6</sup> M. C. Cabaleiro, R. O. Garay, *J. Chem. Soc. Perkin Trans. II* 1987, 1473.

<sup>7</sup> S. B. Desai, N. P. Argade, K. N. Ganesh, *J. Org. Chem.* 1996, **61**, 6730.





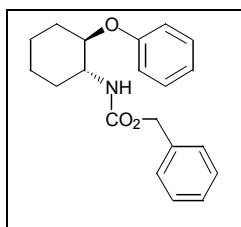
**(1R\*, 2S\*)-1-Phenoxy-indan-2-ol (8).**

Using the typical procedure described above (reaction carried out in DMF), the product was isolated in 70% yield after column chromatography eluting with hexane/AcOEt 7:3, as a white solid. M.p. 97-98°C

$^1\text{H NMR}$   $\delta$  7.04-7.41 (m, 9H), 5.62 (d, 1H,  $J=4.8$  Hz), 4.82-4.85 (m, 1H), **3.07-3.28 (m, 2H).**

$^{13}\text{C NMR}$   $\delta$  141.30, 139.91, 130.35, 129.80, 127.58, 126.13, 122.70, 117.12, 82.79, 73.64, 39.57.

*Syn/anti* stereoselectivity was determined by  $^1\text{H NMR}$  upon observation and integration of the signals corresponding to the methylene protons for each compound (indicated in **bold** in both spectra). The reference new **(1R\*, 2R\*)-1-phenoxy-indan-2-ol** (i.e. the *anti*-isomer) was prepared by the following procedure. A solution of indene oxide (66 mg, 0.5 mmol) in THF (3.0 mL) and  $\text{H}_2\text{O}$  (1.0 mL), was treated with phenol (282 mg, 3.0 mmol) and NaOH (120 mg, 3.0 mmol) and allowed to stir under reflux for 2h. After extraction with  $\text{Et}_2\text{O}$ , the dried ( $\text{MgSO}_4$ ) organic phase was evaporated to give a crude mixture containing the *anti*-isomer which was not further purified.  $^1\text{H NMR}$   $\delta$  7.04-7.40 (m, 9H), 5.59 (d, 1H,  $J=4.32$  Hz,  $-\text{CH}-\text{OPh}$ ), 4.59-4.68 (m, 1H,  $-\text{CH}-\text{OH}$ ), **3.36 (dd, 1H,  $J=6.6, 16.1$  Hz), 2.88 (d, 1H,  $J=6.6, 16.1$  Hz).**  $^{13}\text{C NMR}$   $\delta$  39.35, 78.70, 87.72, 116.42, 121.44, 126.04, 127.83, 129.73, 130.29, 140.23, 140.86, 159.32.



**(1R\*, 2R\*)-Cyclohexan-2-phenoxy-1-**

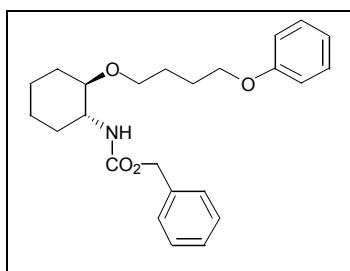
**carbobenzyloxyamina (9).**

Using the typical procedure described above (with the use of 2.0 equiv. of borate **1a**), the product was isolated in 82% yield after column chromatography eluting with hexanes/AcOEt 7:3, as a solid. M.p.=83-85°C (re-crystallized from hexanes).

$^1\text{H NMR}$   $\delta$  7.12-7.40 (m, 7H), 6.78-7.05 (m, 3H), 5.1 (s, 2H), 3.95-4.15 (m, 1H), 3.71-3.90 (m, 1H), 1.18-1.25 (m, 8H).

$^{13}\text{C}$  NMR  $\delta$  158.4, 156.8, 136.8, 130.1, 129.0, 128.6, 121.6, 120.6, 116.7, 116.0, 78.9, 67.4, 54.4, 31.49, 30.4, 24.5, 23.7.

Anal. Calcd. for  $\text{C}_{20}\text{H}_{23}\text{NO}_3$ : C, 73.82; H, 7.12; N, 4.30. Found: C, 73.98, H, 7.05, N, 4.32.



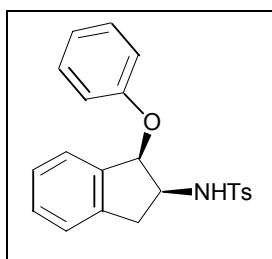
**(1*R*\*,2*R*\*)-2-Cyclohexan-[4-(phenoxy)-butoxy]-1-carbobenzyloxyamine (10).**

Aryl borate **1a** (290 mg, 1.0 mmol) was added at rt to a solution of *N*-Cbz aziridine derived from cyclohexene (115 mg, 0.5 mmol) in THF (0.7 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with 5% aqueous NaCl (2.0 mL) after 4h. The solution was diluted with  $\text{Et}_2\text{O}$  (30 mL) and washed with brine (3.0 mL) to give a crude product (295 mg) which was subjected to flash chromatography eluting with 20% AcOEt in hexanes to give 83 mg (42%) of a crude solid. M.p.=68-71 °C.

$^1\text{H}$  NMR  $\delta$  7.20-7.46 (m, 7H), 6.82-6.92 (m, 3H), 5.05 (s, 2H), 4.78-4.81 (m, 1H, NH), 3.86-3.92 (m, 2H), 3.28-3.66 (m, 3H), 3.00-3.12 (m, 1H), 1.90-2.15 (m, 2H), 1.50-1.85 (m, 5H), 1.05-1.40 (m, 5H).

$^{13}\text{C}$  NMR  $\delta$  158.3, 156.7, 130.1, 129.1, 128.7, 121.1, 115.1, 81.0, 68.7, 68.2, 67.2, 55.0, 32.0, 30.6, 27.4, 26.5, 24.6, 24.4.

Anal. Calcd. for  $\text{C}_{24}\text{H}_{31}\text{NO}_4$ : C, 72.52; H, 7.86; N, 3.52. Found: C, 72.77, H, 7.55, N, 3.32.



**(1*R*\*,2*S*\*)-1-Phenoxy-2-(4-methylphenylsulfonamido)-indane (11).**

Aryl borate **1a** (162.4 mg, 0.56 mmol) was added at rt to a solution of *N*-Ts aziridine derived from indene<sup>8</sup> (160 mg, 0.56 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with 5% aqueous NaCl (2.0 mL) after 2h. The solution was extracted with  $\text{CH}_2\text{Cl}_2$  (25 mL) and washed with

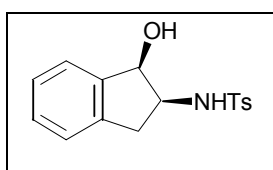
<sup>8</sup> T. P. Seden, R. W. Turner, *J. Chem. Soc. (C)*, 1968, 876.

brine (2.0 ml) to give a crude product which was subjected to flash chromatography eluting with 30% AcOEt in hexanes to give 123 mg (58%) of a solid. M.p=134-136 °C.  $R_f$ =0.33 (30% AcOEt in hexanes).

$^1\text{H}$  NMR  $\delta$  7.65- 7.70 (m, 2H), 7.04- 7.25 (m, 8H), 6.63- 6.94 (m, 3H), **5.09 (d,  $J$ =5.5 Hz, 1H)**, 4.03- 4.21 (m, 1H), **3.07 (d, 2H,  $J$ = 7.3 Hz)**, 2.32 (s, 3H).

$^{13}\text{C}$  NMR  $\delta$  160.91, 143.78, 139.22, 130.10, 129.98, 129.84, 127.42, 127.32, 125.89, 125.56, 122.38, 117.06, 79.59, 56.65, 31.11, 21.95.

ESIMS (pos.): m/z 380 [M+H].



The second eluting fractions of the above described flash chromatography ( $R_f$ =0.15 with 30% AcOEt in hexanes) afforded pure (**1R\***, **2S\***)-2-(4-Methylphenylsulfonamido)-indan-1-ol (**13**), as a solid. M.p 140- 143°C.

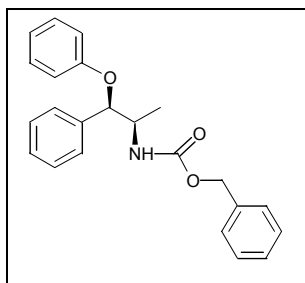
$^1\text{H}$  NMR  $\delta$  7.68- 7.72 (m, 2H), 7.12- 7.34 (m, 7H), 5.46- 5.50 (m, 1H, NH), 4.66 (d, 1H,  $J$ = 5.4 Hz, -CH-OH), 3.86- 4.01 (m, 1H), 2.77- 3.05 (m, 2H), 2.43 (s, 3H).

$^{13}\text{C}$  NMR  $\delta$  144.30, 143.78, 141.18, 138.09, 130.47, 130.07, 128.05, 127.84, 125.97, 125.71, 74.60, 57.33, 37.49, 22.26.

ESIMS (pos.): m/z 304 [M+H].

*Syn/anti* stereoselectivity (compound **11**) was determined by  $^1\text{H}$  NMR after integration of the signals indicated in **bold** in both spectra. The reference *anti*-isomer, namely (**1R\***,**2R\***)-1-phenoxy-2-(4-methylphenylsulfonamido)indane was prepared by the following procedure. A solution of *N*-Ts aziridine derived from indene<sup>8</sup> (40 mg, 0.14 mmol) in THF (1.5 mL) and H<sub>2</sub>O (0.5 mL), was treated with phenol (60 mg, 0.64 mmol) and NaOH (25 mg, 0.6 mmol) and allowed to stir under reflux for 6h. After extraction with Et<sub>2</sub>O, the dried (MgSO<sub>4</sub>) organic phase was evaporated to give a crude mixture containing the *anti*-isomer, which was not further purified.  $^1\text{H}$  NMR  $\delta$  **7.63- 7.67 (m, 2H)**, **7.11- 7.25 (m, 8H)**, **6.72- 6.93 (m, 3H)**, **5.42 (d, 1H,  $J$ =4.4 Hz)**, 5.00- 5.04 (m, 1H, NH), 4.00- 4.10 (m, 1H), **3.27 (dd, 1H,  $J_1$ = 7.1, 16.1 Hz)**, **2.65 (dd, 1H,  $J_1$ = 7.1, 16.1 Hz)**, 2.33 (s, 3H).

$^{13}\text{C}$  NMR  $\delta$  158.71, 144.30, 140.92, 139.76, 130.44, 130.29, 130.21, 130.10, 128.09, 127.85, 126.03, 125.91, 122.15, 116.43, 85.92, 60.28, 38.22, 22.25.



**(1*R*\*,2*R*\*)-1-Phenyl-1-phenoxy-2-**

**(carbobenzyloxy)propanamina (12).**

Aryl borate **1a** (174 mg, 0.60 mmol) was added at rt to a solution of *N*-Cbz aziridine derived from *trans*- $\beta$ -methyl styrene (80.1, 0.30 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.7 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with 5% aqueous NaCl (2.0 mL) after 3h. The solution was extracted with  $\text{CH}_2\text{Cl}_2$  (25 mL) and washed with brine (2.0 ml) to give a crude product which was subjected to semipreparative TLC eluting with 10% AcOEt in hexanes to give 43 mg (40%) of a semisolid.

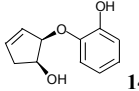
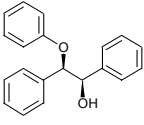
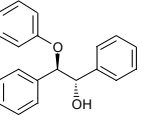
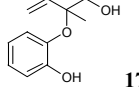
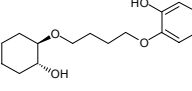
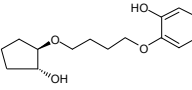
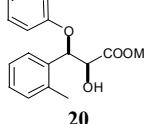
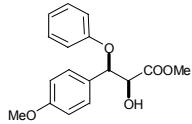
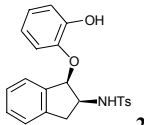
$^1\text{H}$  NMR  $\delta$  7.10-7.29 (m, 12H), 6.75-6.88 (m, 3H), 5.12 (d,  $J=2.9$  Hz, 1H), 5.00 (s, 2H), 4.08-4.28 (m, 1H), 1.24 (d,  $J=6.8$  Hz, 3H).

$^{13}\text{C}$  NMR  $\delta$  158.3, 156.2, 138.5, 137.0, 129.8, 128.9, 128.5, 127.1, 121.6, 116.2, 81.8, 67.1, 52.2, 18.1.

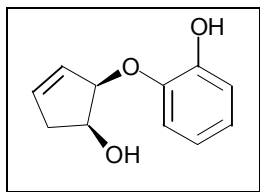
*Syn/anti* stereoselectivity was determined by  $^1\text{H}$  NMR. The reference *anti*-isomer was prepared by the following procedure. A solution of Cbz-aziridine of  $\beta$ -methyl styrene (53.4 mg, 0.20 mmol) in THF (0.6 mL) and  $\text{H}_2\text{O}$  (0.2 mL), was treated with phenol (56 mg, 0.60 mmol) and NaOH (24 mg, 0.6 mmol) and allowed to stir under reflux for 19h. After extraction with  $\text{Et}_2\text{O}$ , the washed organic solution (brine) and dried ( $\text{MgSO}_4$ ) afforded a crude reaction mixture which was not further purified. Signals of the *anti*-isomer considered for integration were:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.29 (d, 1H,  $J=2.4$  Hz) and 1.09 (d, 1H,  $J=6.8$  Hz).

# Supplementary Material (ESI) for Chemical Communications  
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**Table 2.** Additional results of the ring opening of epoxides and aziridines with aryl borates **1a,b**.<sup>a</sup>

Entry	Solvent Time	Product	<i>Syn/anti</i> . <sup>b</sup>	Yield (%) <sup>c</sup>
1	THF 1h	 <b>14</b>	N.d.	44
2	CH <sub>2</sub> Cl <sub>2</sub> 3h	 <b>15</b>	>95/<5	52
3	CH <sub>2</sub> Cl <sub>2</sub> 3h	 <b>16</b>	>95/<5	50
4	CH <sub>2</sub> Cl <sub>2</sub> 3h	 <b>17</b>	N.d.	44
5	THF 1h	 <b>18</b>	<5/>95	55 <sup>d</sup>
6	THF 1h	 <b>19</b>	<5/>95	60 <sup>d</sup>
7	THF 3h	 <b>20</b>	>95/<5	64
8	CH <sub>2</sub> Cl <sub>2</sub> 4h	 <b>21</b>	>95/<5	20 <sup>e</sup>
9	CH <sub>2</sub> Cl <sub>2</sub> 2h	 <b>22</b>	>95/<5	30

<sup>a-c</sup> See corresponding notes of Table 1. <sup>d</sup> A three component coupling involving THF occurred. <sup>e</sup> Obtained by preparative TLC.



**syn-2-(2-Hydroxyphenoxy)-3-cyclopenten-1-ol (14)** (Entry 1, Table 2)

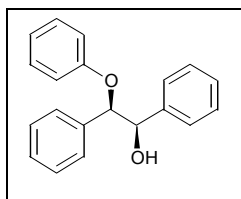
Aryl borate **1b** (384 mg, 2.0 mmol) was added at rt to a solution of 1,3-cyclopentadiene monoepoxide (82 mg, 1.0 mmol) in THF (1.0 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with 5% aqueous HCl (2.0 mL) after 1h. The solution was diluted with Et<sub>2</sub>O (30 mL) and washed with brine (3.0 ml) to give a crude product which was subjected to flash chromatography eluting with hexanes/AcOEt 7:3, to give 84 mg of pure **14** (44%), as an oil.

R<sub>f</sub>=0.19 with 30% AcOEt in hexanes.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.50-2.70 (m, 2H), 4.48-4.60 (m, 1H, -CH-OH), 4.80-4.99 (m, 1H, -CH-O-Ar), 5.89-6.11 (m, 2H), 6.65-6.94 (m, 4H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 39.6, 71.8, 84.1, 116.5, 116.7, 120.6, 123.3, 129.2, 135.5, 146.3, 147.6.

MS 192 (M<sup>+</sup>, 1), 174 (4), 110 (45), 82 (26), 54 (63), 39 (100).



**(1R\*, 2R\*)-2-Phenoxy-1,2-diphenyl-1-ethanol (15)**. (Entry 2, Table 2)

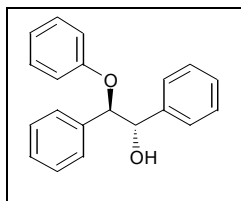
Aryl borate **1a** (348 mg, 1.2 mmol) was added at rt to a solution of *trans*-stilbene oxide (196.3 mg, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with 5% aqueous HCl (2.0 mL) after 3h (>95% conversion). The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and washed with brine (2.0 ml) to give a crude product which was subjected to column chromatography eluting with hexanes/AcOEt 8:2, to give 151 mg of pure **15** (52%), as a solid. M.p. 84-87°C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.86 (d, 1H, *J*=7.8 Hz, -CHOH), 5.06 (d, 1H, *J*=7.8 Hz, -CHOPh), 6.75-7.22 (m, 15H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 79.3, 86.1, 116.8, 122.0, 127.86, 128.1, 128.6, 128.23, 130.1, 137.8, 139.2.

ESIMS (pos.): *m/z* 290 [M+H].

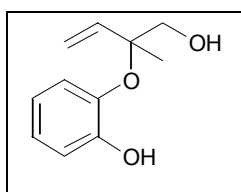
*Syn/anti* stereoselectivity was determined by <sup>1</sup>H NMR. In this case the minor *anti*-isomer is compound **16** (see below). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.16 (d, 1H, *J*=5.3 Hz).



**(1R\*, 2S\*)-2-Phenoxy-1,2-diphenyl-1-ethanol (16)**.<sup>9</sup> (Entry 3, Table 2).

Aryl borate **1a** (348 mg, 1.2 mmol) was added at rt to a solution of *cis*-stilbene oxide (196.3 mg, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with 5% aqueous HCl (2.0 mL) after 3h (>95% conversion). The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and washed with brine (2.0 mL) to give a crude product which was subjected to column chromatography eluting with hexanes/AcOEt 8:2, to give 145 mg of pure **16**<sup>9</sup> (50%).

*Syn/anti* stereoselectivity was determined by <sup>1</sup>H NMR. In this case the minor isomer is compound **15** (see above).



**2-(2-Hydroxyphenoxy)-2-methyl-3-buten-1-ol (17)** (Entry 4, Table 2)

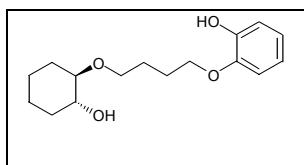
Aryl borate **1b** (384 mg, 2.0 mmol) was added at rt to a solution of isoprene monooxide (100 μL, ca. 1.0 mmol) in THF (1.0 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with 5% aqueous NaCl (2.0 mL) after 3h. The solution was diluted with Et<sub>2</sub>O (30 mL) and washed with brine (3.0 mL) to give a crude product which was subjected to flash chromatography eluting with hexanes/AcOEt 6:4, to give 83 mg of pure **17** (44%), as an oil.

R<sub>f</sub>=0.45 with 40% AcOEt in hexanes.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.33 (s, 3H), 3.64 (AB q, *J* = 11.23, 2H), 5.29 (dd, *J* = 11.0, *J* = 0.9, 1H), 5.39 (dd, *J* = 17.5, 0.9, 1H), 6.00 (dd, *J* = 17.5, *J* = 11.0, 1H), 6.65 (m, 4H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 19.6, 68.5, 83.1, 115.9, 117.0, 119.7, 120.9, 124.6, 139.3, 141.8, 143.8.

<sup>9</sup> H. Brunner, U. Obermann, P. Winner, *Organometallics*, 1989, **8**, 821.



**(1R\*, 2R\*)-2-[4-(2-Hydroxyphenoxy)-butoxy]-cyclohexan-1-ol (18)** (Entry 5, Table 2)

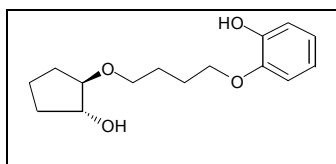
Aryl borate **1b** (384 mg, 2.0 mmol) was added at rt to a solution of cyclohexene oxide (100 mg, ca. 1.0 mmol) in THF (1.0 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with 5% aqueous NaCl (2.0 mL) after 1h. The solution was diluted with Et<sub>2</sub>O (30 mL) and washed with brine (3.0 ml) to give a crude product which was subjected to flash chromatography eluting with hexanes/AcOEt 7:3, to give 154 mg of pure **18** (55%), as an oil.

R<sub>f</sub>=0.25 with 30% AcOEt in hexanes.

<sup>1</sup>H NMR δ 1.09-1.44 (m, 4H), 1.56-2.15 (m, 8H), 2.89-3.15 (m, 1H), 3.42-3.56 (m, 2H), 3.62-3.78 (m, 1H), 3.98-4.14 (m, 2H), 6.78-6.98 (m, 4H).

<sup>13</sup>C NMR δ 24.6, 24.8, 26.7, 27.5, 29.9, 32.6, 68.7, 69.5, 74.6, 84.3, 112.6, 115.7, 120.6, 122.2, 146.7 (2C).

MS 280(M<sup>+</sup>, 7), 209(2), 171(56), 153(1), 123(7), 110(55), 99(14), 95(14), 81(52), 73(100), 55(81), 43(20), 41(34), 39(44).



**(1R\*, 2R\*)-2-[4-(2-Hydroxyphenoxy)-butoxy]-cyclopentan-1-ol (19)** (Entry 6, Table 2)

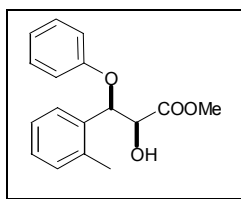
Aryl borate **1b** (384 mg, 2.0 mmol) was added at rt to a solution of cyclopentene oxide (90 mg, ca. 1.0 mmol) in THF (1.0 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with 5% aqueous NaCl (2.0 mL) after 1h. The solution was diluted with Et<sub>2</sub>O (30 mL) and washed with brine (3.0 ml) to give a crude product which was subjected to flash chromatography eluting with hexanes/AcOEt 7:3, to give 160 mg of pure **19** (60%), as an oil.

<sup>1</sup>H NMR δ 1.35-1.98 (m, 10H), 3.52 (t, 2H, *J*=6.3 Hz), 3.59-3.71 (m, 1H), 3.98 (t, 2H, *J*=6.2 Hz), 4.05-4.15 (m, 1H), 6.70-6.90 (m, 3H), 7.15-7.30 (m, 2H).

<sup>13</sup>C NMR δ 21.1, 26.8, 27.2, 30.0, 32.6, 68.2, 69.7, 77.9, 115.1, 121.1, 130.0, 159.6.

ESIMS (pos.): *m/z* 289 [M+Na<sup>+</sup>].





**(2*S*\*, 3*R*\*)-Methyl 3-(2-methylphenyl)-3-phenoxy-2-hydroxy-propanoate (20).** (Entry 7, Table 2)

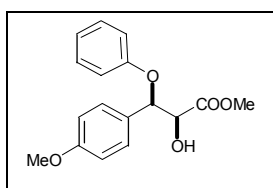
Aryl borate **1a** (348 mg, 1.2 mmol) was added at rt to a solution of methyl 3-(2-methylphenyl)-2,3-epoxy-propanoate (168 mg, 1.0 mmol) in THF (1.0 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with NaCl (2.0 mL) after 3h (>95% conversion). The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and washed with brine (2.0 ml) to give a crude product (407 mg) which was subjected to column chromatography eluting with hexanes/AcOEt 7:3, to give 145 mg of pure **20** (60%), as a white solid. M.p.= 115-117 °C.

R<sub>f</sub>=0.30 with 30% AcOEt in hexanes.

<sup>1</sup>H NMR δ 2.38 (s, 3H), 3.13 (d, *J*=8.0 Hz, 1H, -OH), 3.67 (s, 3H), 4.35 (dd, *J*=8.0, 2.2 Hz, 1H, -CHOH), 5.63 (d, *J*=2.2 Hz, 1H, -CHOPh), 6.63-6.82 (m, 3H), 7.03-7.11 (m, 6H), 7.32-7.37 (m, 1H).

<sup>13</sup>C NMR δ 19.7, 53.4, 73.6, 78.1, 116.3, 122.0, 126.89, 128.1, 128.7, 130.2, 131.2, 134.5, 135.1, 158.0, 173.0.

*Syn/anti* stereoselectivity was determined by <sup>1</sup>H NMR as reported before for compound **7** (vide supra).



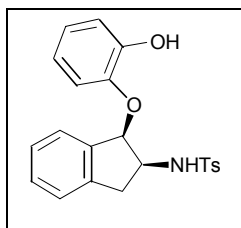
**(2*S*\*, 3*R*\*)-Methyl 3-(4-methoxyphenyl)-3-phenoxy-2-hydroxy-propanoate (21).** (Entry 8, Table 2)

Aryl borate **1a** (87 mg, 0.3 mmol) was added at rt to a solution of methyl 3-(4-methoxyphenyl)-2,3-epoxy-propanoate (55 mg, 0.3 mmol) in DMF/THF (1:1) (0.5 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with 5% aqueous NaCl (1.0 mL) after 2h (>95% conversion). The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and washed with brine (2.0 ml) to give a crude product which was subjected to semipreparative TLC, eluting with hexanes/AcOEt 7:3, to give pure **21**.

<sup>1</sup>H NMR δ 3.02-3.18 (m, 1H, -OH), 3.74 (s, 3H), 3.77 (s, 3H), 4.40-4.48 (m, 1H, -CHOH), 5.45 (d, *J*=2.7 Hz, 1H, -CHOPh), 6.75-6.95 (m, 5H), 7.18-7.38 (m, 4H).

<sup>13</sup>C NMR δ 53.4, 55.9, 75.7, 81.0, 114.8, 116.8, 122.1, 128.7, 128.9, 130.0, 158.2, 160.2, 172.9.

*Syn/anti* stereoselectivity was determined by  $^1\text{H}$  NMR as reported before for compound **7** (*vide supra*).



**(1R\*, 2S\*)-1-(2-Hydroxyphenoxy)-2-(4-methylphenylsulfonamido)indano (22).**

Aryl borate **1b** (115.2 mg, 0.6 mmol) was added at rt to a solution of *N*-Ts aziridine derived from indene (85.5 mg, 0.30 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.6 mL) under a magnetic stirring. The reaction was followed by TLC and quenched with 5% aqueous NaCl (2.0 mL) after 1.5h. The usual work-up afforded a crude product which was subjected to flash chromatography to give 40 mg of compound **22** (ca. 30% yield), contaminated by some amounts of the corresponding aminoalcohol.

$^1\text{H}$  NMR  $\delta$  7.73-7.77 (m, 2H), 7.05-7.31 (m, 4H), 6.61-6.93 (m, 2H), 5.14 (d,  $J=5.3$  Hz, 1H), 4.20-4.35 (m, 1H), 3.10 (d,  $J=7.7$  Hz, 2H), 2.37 (s, 3H).

$^{13}\text{C}$  NMR  $\delta$  147.7, 144.3, 141.4, 139.1, 137.7, 130.5, 130.4, 127.6, 126.3, 125.8, 124.0, 121.6, 120.6, 117.4, 116.5, 116.0, 82.0, 56.8, 37.8, 22.2.