Supporting Information For

Synthesis and Cyclodehydration of Hydroxyphenols: A New Stereoselective Approach to 3-Aryl-2,3-Dihydrobenzofuranes

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General Methods. Diethylazadicarboxylate, triphenylphosphine, the solution of $BH_3 \cdot Me_2S$, and all phenols employed in this study were used as received. Anhydrous THF, CH_2Cl_2 (containing molecolar sieves) were purchased and used as such. Analytical TLC were performed on Alugram SIL G/UV254 silica gel sheets with detection by 0.5% Phosphomolybdic acid solution in 95% EtOH. Silica gel 60 was used for flash chromatography. Solvents for extraction and chromatography were HPLC grade.

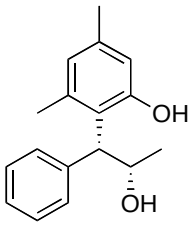
^{1}H NMR spectra were recorded at 200 or 250 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: **δ 7.26**, deuteromethanol: **δ 3.31**). ^{13}C NMR spectra were recorded at 50 MHz or at 62.5 MHz with complete proton decoupling. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: **δ 77.0**, deuteromethanol: **δ 49.0**).

1D NOESY spectrum was performed on a spectrometer operating at 600 MHz for 1H. The selective 1D NOE spectrum was acquired with 128 scans in 32K data points with a 15 s relaxation delay and a mixing time of 1.6 s by using selective pulse generated by means of an appropriate software.

Analytical high performance liquid chromatography (HPLC) were performed on a column with 0.5 mL solvent flow and detection at 254 nm.

GC/MS spectra were obtained operating at 70 eV.

Elemental analyses were performed at the Department of Pharmaceutical Sciences of the University of Pisa.



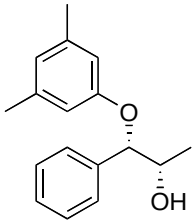
2-((*1R*, 2S)-2-Hydroxy-1-phenylpropyl)-3,5-dimethylphenol (3ab) (Table 1, entry 1).**

Using the general procedure, a solution of tris-(3,5-dimethylphenyl) borate **(1b)** (560.7 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at –78°C under argon to a solution of *trans*-β-methylstyrene oxide **(2a)** (134.1 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 18 hours at –40°C. The crude mixture, containing 35% of *O*-alkylated product, was purified by column chromatography eluting with hexanes/AcOEt 85:15 to give compound **3ab** (115.2 mg, 45%), as a white solid. M.p= 72- 75°C.

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.29 (d, 3H, *J*= 6.6 Hz); 2.21 (s, 3H); 2.29 (s, 3H); 4.40 (d, 1H, *J*= 4.1 Hz); 4.59- 4.75 (m, 1H); 6.60 (br, s, 1H); 6.70 (br, s, 1H); 7.14-7.21 (m, 5H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 20.5, 20.8, 21.1, 51.4, 70.9, 116.6, 123.3, 126.6, 128.2, 128.7, 137.9, 138.6, 139.1, 140.2, 155.2.

Anal. Calcd. For $C_{17}H_{20}O_2$: C, 79.65%; H, 7.86%. Found: C, 79.41%; H, 7.53%.

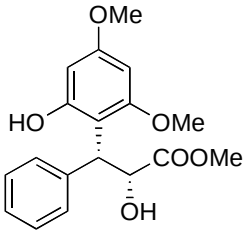


***(1S*, 2S**)-1-(3,5-Dimethylphenoxy)-1-phenylpropan-2-ol.**

The first eluting fractions of the above described column chromatography afforded pure *(1S*, 2S**)-1-phenyl-1-(3,5-dimethylphenoxy)-propan-2-ol, as a white solid (yield= 21%). M.p= 134-136°C.

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09 (d, 3H, *J*=6.4 Hz); 2.19 (s, 6H); 2.85 *OH* (br, s, 1H); 4.00-4.10 (m, 1H); 4.82 (d, 1H, *J*=7.3 Hz); 6.44-6.53 (m, 3H); 7.20-7.40 (m, 5H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 18.0, 21.3 (2C), 71.6, 85.4, 113.8, 123.1, 127.1, 128.1, 128.6, 138.3, 139.1, 157.8.



(2*R, 3*R**)-Methyl 2-hydroxy-3-(2-hydroxy-4,6-dimethoxyphenyl)-3-phenylpropanoate (3ca) (table 1, entry 3).**

Using the general procedure, a solution of tris-(3,5-dimethoxyphenyl) borate **(1a)** (705 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at –78°C to a solution of *trans*-methyl-2,3-epoxy-3-phenyl-propanoate **(2c)** (178 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 18 hours at –78°C. The crude mixture, containing 28% of *O*-alkylated product, was purified by column chromatography eluting with hexanes/AcOEt 7:3 to give compound **3ca** (containing 40% of *2R*,3S**-stereoisomer) **(**182.6 mg, 55%)**.**

^{1}H NMR (250 MHz, $CDCl_3$) δ 3.63 (s, 3H); 3.71 (s, 3H); 3.73 (s, 3H); 5.18 (d, 1H, *J*= 3.3 Hz); 5.35 (d, 1H, *J*= 3.3 Hz); 6.06 (d, 1H, *J*= 2.2 Hz); 6.14 (d, 1H, *J*= 2.2 Hz); 7.13-7.33 (m, 5H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 41.8, 52.6, 55.0, 55.8, 73.2, 91.1, 95.2, 106.0, 126.3, 127.4,128.2,139.6,157.5,158.9,160.6,173.8.

Representative signals of (*2R*,3S**) -stereoisomer **(*anti*-3ca)**:

^{1}H NMR (250 MHz, $CDCl_3$) δ 4.76 (d, 1H, *J*= 2.3 Hz, *CH*-Ar); 5.28 (d, 1H, *J*= 2.2 Hz, *CH*-OH).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 43.2 (*C*H-Ar), 52.9 (COO*C*H_3), 73.8 (*C*H-OH).

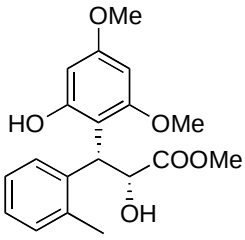
Clevage of epoxide 2c with borate 1b and directly cyclization of compound 3cb to the corrisponding 2,3-dihydrobenzofuranes 4cb and 5cb (table 1, entry 4).

Using the general procedure, a solution of tris-(3,5-dimethylphenyl) borate **(1b)** (560.7 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at rt under argon to a solution of *trans*-methyl-2,3-epoxy-3-phenyl-propanoate **(2c)** (178 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 18 hours at rt. The reaction was then quenched and the solvent was evaporated under a vacuum. To the crude mixture, containing 50% of *O*-alkylated product and a 89/11 mixture of *syn*-**3cb** and *anti*-**3cb** was not isolated but, dissolved in THF (2.0 mL) and additioned with triphenylphosphine (262.3 mg, 1.0 mmol) and diethylazodicarboxylate (130.7 mg, 0.118 mL, 0.75 mmol). The mixture was allowed to react for 2 hours at rt. The purification by flash column chromatography eluting with hexanes/Et_2O 9:1 afforded

(2*S**,3*R**)-2-carbomethoxy-3-phenyl-4,6-dimethyl-2,3-dihydrobenzofuran **(4cb)** (contaminated with 11% of (*2R*,3R**) steroisomer **5cb**), as a solid (107.2 mg, 38%).

^{1}H NMR (250 MHz, $CDCl_3$) δ 1.88 (s, 3H); 2.30 (s, 3H); 3.28 (s, 3H); 4.75 (d, 1H, *J*= 9.5 Hz); 5.43 (d, 1H, *J*= 9.5 Hz); 6.53 (s, 1H); 6.67 (s, 1H); 7.00 (d, 1H, *J*= 7.5 Hz); 7.10-7.33 (m, 2H); 7.73 (d, 1H, *J*= 7.5 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 18.3, 21.5, 50.7, 51.6, 84.9, 108.3, 124.0, 127.5,128.2, 128.5,129.0, 138.2, 139.4,168.8.

Representative signals of compound **5cb**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.66 (d, 1H, *J*=4.6 Hz), 4.97 (d, 1H, *J*=4.6 Hz).



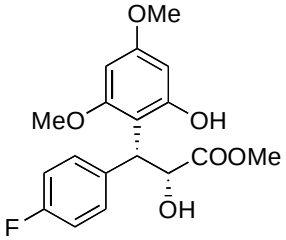
(2*R, 3*R**)-Methyl 2-hydroxy-3-(2-hydroxy-4,6-dimethoxyphenyl)-3-(2-methylphenyl)propanoate (3da) (table 1, entry 5).**

Using the general procedure, a solution of tris-(3,5-dimethoxyphenyl) borate **(1a)** (705 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at –78°C to a solution of *trans*-methyl-3-(2-methylphenyl)-2,3-epoxypropanoate (192 mg, 1.0 mmol) **(2d)** in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 18 hours at –78°C. The crude mixture, containing 30% of *O*-alkylated product, was purified by column chromatography eluting with hexanes/AcOEt 7:3 to give compound **3da** (179.9 mg, 52%) as a white solid. M.p= 153-155°C. R_F= 0.16 (hexanes/AcOEt 7:3).

^{1}H NMR (250 MHz, $CDCl_3$) δ 2.02 (s, 3H); 3.67 (s, 3H); 3.73 (s, 3H); 3.74 (s, 3H) 4.97-5.04 (m, 1H); 5.15 (d, 1H, *J*= 2.0 Hz); 5.99 (s, 2H); 7.05-7.24 (m, 3H); 7.69-7.72 (m, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 19.2, 41.0, 52.6, 55.0, 55.6, 73.2, 90.9, 95.2, 104.9, 125.9, 126.7, 127.2, 130.9, 136.6, 139.3, 157.6, 158.7, 160.4, 173.8.

Anal. Calcd. For $C_{19}H_{22}O_6$: C, 65.88%; H, 6.40%. Found: C, 65.51%; H, 6.32%.



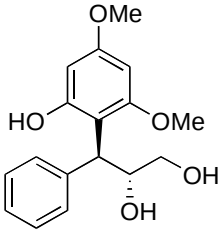
(2*R, 3*R**)-Methyl 3-(4-fluorophenyl)-2-hydroxy-3-(2-hydroxy-4,6-dimethoxyphenyl)propanoate (3ea) (table 1, entry 6).**

Using the general procedure, a solution of tris-(3,5-dimethoxyphenyl) borate **(1a)** (705 mg, 1.5 mmol) in

CH_2Cl_2 (1.0 mL) was added at –40°C to a solution of *trans*-methyl-2,3-epoxy-3-(4-fluorophenyl)propanoate **(2e)** (196 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 18 hours at -40°C. Column chromatography eluting with hexanes/AcOEt 7:3 afforded compound **3ea** (217 mg, 54% yield of **3ea**), as a solid, contaminated by an unseparable by-product (ca 15% of the mixture).

^{1}H NMR (200 MHz, $CDCl_3$) δ 3.68 (s, 3H); 3.72, (s, 3H); 3.75 (s, 3H); 4.21-4.34 *OH* (br, 1H); 5.08-5.18 (m, 1H); 5.25-5.35 (m, 1H); 6.05 (s, 2H); 7.94-7.40 (m, 4H); 8.30 *OH* (br, s, 1H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 41.2, 52.7, 55.1, 55.8, 73.3, 91.2, 95.2, 114.8, 115.3, 127.0, 129.1, 157.4, 159.8, 160.7, 163.8, 173.7.



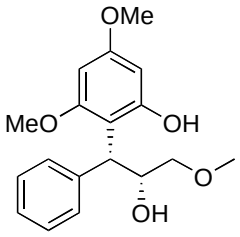
(*2R*,3S)-3-(2-Hydroxy-4,6-dimethoxy)-3-phenylpropane-1,2-diol (3fa) (table 1, entry 7).**

Using the general procedure, a solution of tris (3,5-dimethoxyphenyl) borate **(1a)** (705 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at –78°C to a solution of *trans*-2,3-epoxy-3-phenylpropanol **(2f)** (150 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 18 hours at –78°C. Column chromatography eluting with CH_2Cl_2/AcOEt 7:3 afforded pure **3fa** (258.4 mg, 85%), as a white solid. M.p= 107-109°C**.**

^{1}H NMR (250 MHz, MeOD) δ 3.37 (d, 1H, *J*= 7.7 Hz); 3.51-3.58 (m, 1H); 3.62 (s, 3H); 3.64 (s, 3H); 4.53 (d, 1H, *J*= 9.5 Hz); 4.81-4.97 (m, 1H); 5.97 (s,1H); 6.02 (s,1H); 7.01-7.08 (m, 1H); 7.16 (t, 2H, *J*= 7..5 Hz); 7.47 (d, 2H, *J*= 7.5 Hz).

^{13}C NMR (62.5 MHz, MeOD) δ 45.3, 55.5, 55.6, 66.6, 73.7, 91.5, 95.0, 111.4, 126.4, 128.5, 130.1, 144.4, 157.4, 160.3, 161.0.

Anal. Calcd. For $C_{17}H_{20}O_5$: C, 67.09%; H, 6.62%. Found: C, 67.32%; H, 6.50%.



2-((*1R*,2R)-2-Hydroxy-3-methoxy-1-phenylpropyl)-3,5-dimethoxyphenol (*Syn*-3ga) (table 1, entry 8).**

Using the general procedure, a solution of tris (3,5-dimethoxyphenyl) borate (**1a)** (705 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at –78°C to a solution of *trans*-2-(methoxymethyl)-3-phenyloxirane **(2g)** (164 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The

mixture was allowed to react for 18 hours at –78°C. The crude mixture, containing 23% of *O*-alkylated product, was purified by column chromatography eluting with hexanes/AcOEt 7:3 to give compound ***syn*-3ga** (contaminated with 5% of *O*-alkylated product, see below) (165.4 mg, 52%), as a white solid.

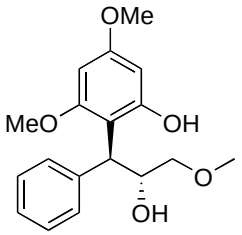
^{1}H NMR (250 MHz, $CDCl_3$) δ 3.15-3.27 (m, 4H); 3.46 (dd, 1H, J_1= 9.7 Hz, J_2= 2.5 Hz); 3.70 (s, 3H); 3.77 (s, 3H); 4.24 CH*OH* (br, s, 1H); 4.71-4.80 (m, 1H); 4.88 (d, 1H, *J*= 2.7 Hz); 6.07 (d, 1H, *J*= 2.2 Hz); 6.17 (d, 1H, *J*= 2.2 Hz); 7.11-7.40 (m, 5H); 9.40 Ar*OH* (br, s, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 40.8, 55.1, 55.8, 58.9, 72.9, 75.4, 90.9, 95.0, 106.4, 126.1, 127.8, 128.2, 140.4, 157.2, 159.1, 160.2.

Representative signals of the *O*-alkylated product:

^{1}H NMR (250 MHz, $CDCl_3$) δ 3.93-4.08 (m, 1H); 5.21 (d, 1H, *J*= 6.75 Hz)

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 59.1($CH_2O\mathit{CH_3}$), 74.4 (*CH*OH), 80.6 (*CH*OAr).

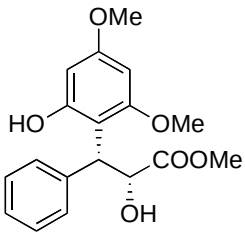


2-((*1S*,2R)-2-Hydroxy-3-methoxy-1-phenylpropyl)-3,5-dimethoxyphenol (*anti*-3ga) (table 1, entry 8).**

The first eluting fractions of the above described column chromatography afforded pure 2-((*1S**,*2R**)-2-hydroxy-3-methoxy-1-phenylpropyl)-3,5-dimethoxyphenol **(*anti*-3ga)** (contamined with 4% of *O*-alkylated product) (yield=14%), as an oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ 3.28-3.45 (m, 4H); 3.51 (dd, 1H, J_1= 9.75 Hz, J_2= 3.75 Hz); 4.50-4.60 (m, 1H); 4.64 (d, 1H, *J*= 4.0 Hz); 5.97 (d, 1H, *J*= 2.25 Hz); 6.11 (d, 1H, *J*= 2.25 Hz); 7.08-7.41 (m, 5H); 9.09 Ar*OH* (br, s, 1H).

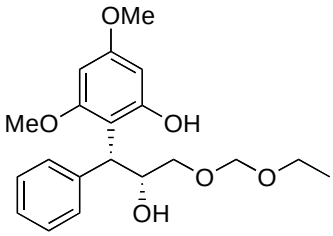
^{13}C NMR (62.5 MHz, $CDCl_3$) δ 42.5, 55.1, 56.6, 58.9, 71.7, 75.2, 91.2, 94.8, 110.2, 126.3, 127.7, 129.5, 156.4, 158.6, 159.8.



(2*R,3*R**)-Methyl 2-hydroxy-3-(2-hydroxy-4,6-dimethoxyphenyl)-3-phenylpropanoate (3ca) (table 1, entry 10).**

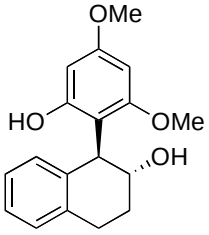
Using the general procedure, a solution of tris (3,5-dimethoxyphenyl) borate **(1a)** (705 mg, 1.5 mmol) in CH_2Cl_2

(1.0 mL) was added at –78°C to a solution of *cis*-methyl-2,3-epoxy-3-phenyl-propanoate[1] **(2i)** (178 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 18 hours at –78°C. The crude mixture, containing 12% of *O*-alkylated product, was purified by column chromatography eluting with hexanes/AcOEt 7:3 to give compound **3ca** (containing 13% of *trans*-stereoisomer) (172.6 mg, 52%).
For ^{1}H NMR and ^{13}C NMR data see above.



2-((*1R*,2R)-3-(Ethoxymethoxy)-2-hydroxy-1-phenyl propyl)-3,5-dimethoxyphenol (3ja) (table 1, entry 11).**

Using the general procedure, a solution of tris (3,5-dimethoxyphenyl) borate **(1a)** (705 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at –78°C to a solution of *cis*-2-((ethoxymethoxy)methyl)-3-phenyloxirane **2j** (208 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 18 hours at –78°C. Column chromatography eluting with hexanes/AcOEt 7:3 afforded pure **3ja** (253.4 mg, 70%), as an oil. R_F= 0.16 (hexanes/AcOEt 7:3).
^{1}H NMR (250 MHZ, $CDCl_3$) δ 1.20 (t, 3H, *J*= 7.1 Hz); 3.32 (dd, 1H, J_1= 11.5 Hz, J_2= 9.3 Hz) 3.50-3.73 (m, 3H); 3.71 (s, 3H); 3.76 (s, 3H); 3.83 (dd, 1H, J_1= 11.2 Hz, J_2= 2.4 Hz); 4.54-4.80 (m, 3H); 4.91 (d, 1H, *J*= 3.1 Hz); 6.07 (d, 1H, *J*= 2.4 Hz); 6.15 (d, 1H, *J*= 2.4 Hz); 7.11-7.39 (m, 5H); 9.42 Ar*OH* (br, s, 1H).
^{13}C NMR (62.5 MHz, $CDCl_3$) δ 15.0, 40.8, 55.1, 55.8, 63.8, 73.4, 73.5, 91.0, 95.2, 96.1, 106.5, 126.2, 127.8, 128.3, 140.6, 157.3, 159.2, 160.4.
Anal. Calcd. For $C_{20}H_{26}O_6$: C, 66.28%; H, 7.23%. Found: C, 66.30%; H, 7.23%.



(*1S*,2R)-1-(2-Hydroxy-4,6-dimethoxyphenyl)-1,2,3,4-tetra hydronaphtalen-2-ol (3ka) (table 1, entry 12).**

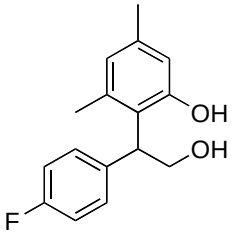
Using the general procedure, a solution of tris-(3,5-dimethoxyphenyl) borate **(1a)** (705 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at –80°C to a solution of dihydronaphtalene oxide **(2k)** (146 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 18 hours at –78°C. Column chromatography eluting with hexanes/AcOEt 6:4 afforded pure **3ka** (156 mg, 52%), as a solid. M.p= 150- 152 °C.

[1] Denis, J.N; Greene, A. E; Serra, A. A; Luche M. J. *J. Org. Chem.* **1986**, *51*, 46-50.

^{1}H NMR (250 MHz, $CDCl_3$) δ 1.75-1.92 (m,1H); 2.16-2.26 (m, 1H); 2.84-3.08 (m, 2H); 3.60 (br, s, 3H); 3.72 (s, 3H); 4.19 (ddd, 1H, J_1=11.0 Hz, J_2= 9.0 Hz, J_3= 3.5 Hz); 4.47 (d, 1H, *J*= 9.0 Hz); 6.03 (d, 1H, *J*= 2.3 Hz); 6.10 (d,1H, *J*= 2.3 Hz); 6.85 (d, 1H, *J*= 7.2 Hz); 6.93-7.10 (m, 3H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 28.6, 31.6, 44.0, 55.2, 55.7, 71.9, 92.0, 94.9, 126.3, 127.8,128.4,136.0,157.1, 159.8, 160.1.

Anal. Calcd. For $C_{18}H_{20}O_4$: C, 71.98%; H, 6.71%. Found: C, 72.03%; H, 6.44%.



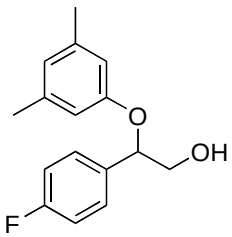
2-(1-(4-Fluorophenyl)-2-hydroxyethyl)-3,5-dimethylphenol (3mb) (substrate of table 2, entry 5)

Using the general procedure, a solution of tris (3,5-dimethylphenyl) borate **(1b)** (560.7 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at –78°C under argon to a solution of *p*-fluorophenyl oxirane **(2m)** (138.1 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 1.5 hours at –78°C. The crude mixture (containing 16% of *O*-alkylated product) was purified by column chromatography eluting with hexanes/AcOEt 7:3 to give compound **3mb** (150.8 mg, 58%)**,** as a white solid. M.p= 119- 121°C. R_f= 0.25 (hexanes/AcOEt 7:3).

^{1}H NMR (200 MHz, MeOD) δ 2.13-2.22 (m, 6H); 4.16-4.49 (m, 3H); 6.43-6.53 (m, 2H); 6.83-6.98 (m, 2H); 7.24-7.39 (m, 2H).

^{13}C NMR (50 MHz, MeOD) δ 20.3 (2 C), 47.1, 65.2, 114.4, 114.8, 115.2, 123.3, 124.5, 130.1, 130.3, 137.4, 138.3, 138.9, 156.0, 159.6, 164.2.

Anal. Calcd. For $C_{16}H_{17}FO_2$: C, 73.83%; H, 6.58%. Found: C, 73.53%; H, 6.48%.

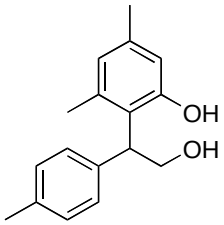


2-(3,5-Dimethylphenoxy)-2-(4-fluorophenyl)-ethanol.

The first eluting fractions of the above described column chromatography (R_f= 0.35 in hexanes/AcOEt 7:3) afforded pure 2-(3,5-dimethylphenoxy)-2-(4-fluorophenyl)-ethanol as a semisolid. (19.8 mg, 7.6%).

^{1}H NMR (200 MHz, $CDCl_3$) δ 2.22 (s, 6H); 3.68-3.95 (m, 2H); 5.24 (dd, 1H, J_1= 7.8 Hz, J_2= 4.0 Hz); 6.45-6.60 (m, 3H); 6.97-7.10 (m, 2H); 7.25-7.40 (m, 2H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 21.4 (2 C), 67.5, 80.2, 113.7, 115.5, 115.9, 123.2, 127.8, 128.0, 133.8, 139.2, 157.6, 164.9.



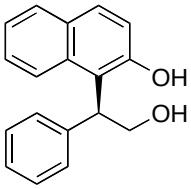
2-(2-Hydroxy-1-(4-methylphenyl)-ethyl)-3,5-dimethyl phenol[2] **(3nb) (substrate of table 2, entry 6).**

Using the general procedure, a solution of tris-(3,5-dimethylphenyl) borate **(1b)** (560.7 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at –78°C under argon to a solution of *p*-methylphenyl oxirane **(2n)** (134.1 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 1.5 hours at –78°C. The crude mixture (containing 13% of *O*-alkylated product) was purified by column chromatography eluting with hexanes/AcOEt 8:2 to give compound **3nb** (143.4 mg, 56%), as a liquid. R_f= 0.15 (hexanes/AcOEt 8:2).

^{1}H NMR (200 MHz, $CDCl_3$) δ 2.25 (s, 3H); 2.31 (s, 3H); 2.36 (s, 3H); 2.96-3.10 CH*OH* (br, 1H); 4.17-4.28 (m, 1H); 4.37-4.55 (m, 2H); 6.62-6.70 (m, 2H); 7.09-7.32 (m, 4H); 8.36-8.48 Ar*OH* (m, 1H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 20.8 (3 C), 45.9, 65.1, 116.4, 123.0, 123.5, 127.8, 129.5, 136.2, 136.4, 137.7, 138.1, 155.2.

Anal. Calcd. For $C_{17}H_{20}O_2$: C, 79.65%; H, 7.86%. Found: C, 79.74%; H, 7.63%.



1-((1*S*)-2-Hydroxy-1-phenylethyl)naphtalen-2-ol (3ld) (substrate of table 2, entry 7).

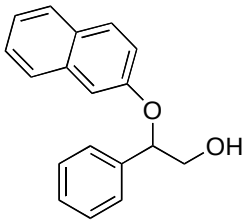
Using the general procedure, a solution of tris (β-naphtyl) borate **(1d)** (660 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at –78°C under argon to a solution of (*R*)-(+)-styrene oxide **(2l)** (120.1 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 1.5 hours –78°C. The crude mixture (containing 17% of *O*-alkylated product) was purified by column chromatography eluting with hexanes/AcOEt 8:2 to give compound **3ld** (179.5 mg, 68 %) (containing 24% of (*R*)-stereoisomer) as a white solid. M.p= 112-114°C. R_f= 0.26 (hexanes/AcOEt 7:3). $[\alpha]_D^{20}$= -49.6 (c=1.0, $CHCl_3$).

^{1}H NMR (250 MHz, $CDCl_3$) δ 2.75-3.20 *OH* (br, 1H); 4.32 (m, 1H); 4.47 (dd, 1H, J_1= 11.4 Hz, J_2= 4.9 Hz); 5.05-5.20 (m, 1H); 7.12-7.50 (m, 8H); 7.68-7.90 (m, 3H); 9.00-9.35 Ar*OH* (br, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 45.8, 65.4, 117.5, 120.3, 122.3, 122.8, 126.7, 126.9, 128.2, 128.8, 129.0, 129.3, 129.5, 133.7, 139.8, 153.4.

Anal. Calcd. For $C_{18}H_{16}O_2$: C, 81.79%; H, 6.10%. Found: C, 81.55%; H, 6.06%.

HPLC analysis performed on a Daicel Chiralcel ® OD-H column, flow rate: 0.5 mL/min, mobile phase: hexane/isopropanol 90/10, retention times (min): 27.3 (*R*, minor stereoisomer), 39.6 (*S*, major stereoisomer).

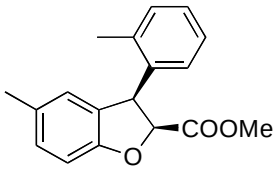


2-(Naphtalen-2-yloxy)-2-phenylethanol.

The first eluting fractions of the above described column chromatography (R_f= 0.35 in hexanes/AcOEt 7:3) afforded pure 2-naphtoxy-2-phenyl-ethanol as a semisolid. (15.8 mg, 6.6%).

^{1}H NMR (250 MHz, $CDCl_3$) δ 2.68- 2.88 *OH* (br, 1H); 3.80-4.06 (m, 2H); 5.41 (dd, 1H, J_1= 8.0 Hz, J_2= 3.7 Hz); 7.01-7.50 (m, 10H); 7.56 (d, 1H, *J*=7.9 Hz); 7.62-7.80 (m, 2H).

Synthesis of 2,3-dihydrobenzofuranes by Mitsunobu cyclodehydration (Table 2).



(2*S,3*R**)-Methyl 5-methyl-3-(2-methylphenyl)-2,3-dihydrobenzofuran-2-carboxylate(4dc) (table 2, entry 1).**

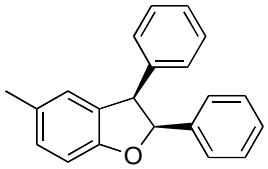
Using the general procedure described in the main text, to a solution of (2*R**,3*R**)-methyl-2-hydroxy-3-(2-hydroxy-5-methylphenyl)-3-(2-methylphenyl)propanoate[2] **(3dc)** (60.0 mg, 0.2 mmol) in anhydrous THF (0.8 mL) were added triphenylphosphine (104.9 mg, 0.4 mmol) and diethylazodicarboxylate (52.2 mg, 0.3 mmol). The mixture was allowed to react for 4 hours at rt. Column chromatography eluting with hexanes/Et_2O 9:1 afforded pure **4dc** (35.0 mg, 62%), as a solid. M.p= 105- 107 °C.

^{1}H NMR (200 MHz, $CDCl_3$) δ 2.26 (s, 3H); 2.48 (s, 3H); 3.19 (s, 3H); 5.25 (d, 1H, *J*=10.2 Hz); 5.50 (d, 1H, *J*=10.2 Hz); 6.81-6.96 (m, 3H); 6.99-7.22 (m, 4H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 19.3, 20.8, 47.3, 51.4, 83.7, 109.6, 125.8, 126.1, 127.4, 128.4, 129.3, 129.8, 131.0, 137.0, 174.1.

[2] Bertolini, F.; Crotti, P.; Macchia, F.; Pineschi, M. *Tetrahedron Lett*. **2006**, *47*, 61.

Anal. Calcd. For $C_{18}H_{18}O_3$: C, 76.57%; H, 6.43%. Found: C, 76.49%; H, 6.29%.



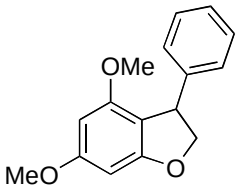
(2*S,3*R**)-5-Methyl-2,3-diphenyl-2,3-dihydrobenzofuran (4bc) (table 2, entry 2).**

Using the general procedure, to a solution of (2-((1*R**,2*R**)-1,2-diphenylethyl-2-hydroxy)-4-methylphenol[2] **(3bc)** (45.6 mg, 0.15 mmol) in anhydrous THF (0.6 mL) were added triphenylphosphine (78.8 mg, 0.3 mmol) and diethylazodicarboxylate (39.1 mg, 0.225 mmol). The mixture was allowed to react for 5 hours at rt. Column chromatography eluting with hexanes/Et_2O 8:2 afforded pure **4bc** (27.9 mg, 65%), as a solid. M.p= 70- 73°C.

^{1}H NMR (200 MHz, $CDCl_3$) δ 2.28 (s, 3H); 4.82 (d, 1H, *J*= 8.9 Hz); 6.00 (d, 1H, *J*= 8.9 Hz); 6.66- 6.73 (m, 2H); 6.91-7.09 (m, 10H); 7.26 (s, 1H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 20.8, 54.0, 88.7, 109.3, 126.5, 127.2, 127.6, 127.7, 129.2, 130.5, 130.7, 137.6, 139.2.

Anal. Calcd. For $C_{18}H_{18}O_3$: C, 88.08%; H, 6.34%. Found: C, 88.11%; H, 6.12%.



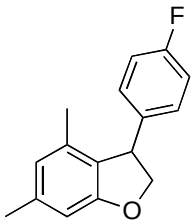
4,6-Dimethoxy-3-phenyl-2,3-dihydrobenzofuran (4la) (table 2, entry 3).

Using the general procedure, to a solution of 2-(2-hydroxy-1-phenylethyl)-3,5-dimethoxyphenol[2] **(3la)** (115.1 mg, 0.42 mmol) in anhydrous THF (1.7 mL) were added triphenylphosphine (220.3 mg, 0.84 mmol) and diethylazodicarboxylate (109.6 mg, 0.63 mmol). The mixture was allowed to react for 2 hours at rt. Column chromatography eluting with hexanes/Et_2O 9:1 afforded pure **4la** (102.1 mg, 95%), as a solid. M.p= 103- 105°C.

^{1}H NMR (200 MHz, $CDCl_3$) δ 3.65 (s, 3H); 3.82 (s, 3H); 4.49 (dd, 1H, J_1= 8.3 Hz, J_2= 4.2 Hz); 4.61 (dd, 1H, J_1= 8.9 Hz, J_2= 4.2 Hz); 4.89 (t, 1H, *J*= 8.7 Hz); 6.05 (d, 1H, *J*= 1.8 Hz); 6.19 (d, 1H, *J*= 1.8 Hz); 7.15-7.38 (m, 5H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 45.8, 55.2, 55.4, 80.3, 88.3, 91.5, 109.4, 126.5, 127.0, 128.4, 143.5, 157.0, 162.1.

Anal. Calcd. For $C_{18}H_{18}O_3$: C, 74.98%; H, 6.29%. Found: C, 75.11%; H, 6.22%.



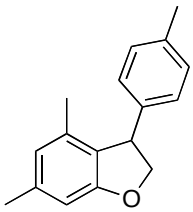
4,6-Dimethyl-3-(4-fluorophenyl)-2,3-dihydrobenzofuran (4mb) (table 2, entry 5).

Using the general procedure, to a solution of 2-(2-hydroxy-1-(4-fluorophenyl)-ethyl)-3,5-dimethylphenol **(3mb)** (109.2 mg, 0.42 mmol) in anhydrous THF (1.7 mL) were added triphenylphosphine (220.3 mg, 0.84 mmol) and diethylazodicarboxylate (109.6 mg, 0.63 mmol). The mixture was allowed to react for 2 hours at rt. Column chromatography eluting with hexanes/Et_2O 9:1 afforded pure **4mb** (89.4 mg, 88%), as a solid. M.p= 63- 65°C.

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.94 (s, 3H); 2.33 (s, 3H); 4.39 (dd, 1H, J_1= 8.4 Hz, J_2= 4.8 Hz); 4.49- 4.55 (m, 1H); 4.85 (t, 1H, J= 8.8 Hz); 6.52 (br, s, 1H); 6.60 (br, s, 1H); 6.94-7.15 (m, 4H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 18.5, 21.4, 46.8, 79.5, 107.9, 115.3, 115.7, 123.2, 128.8, 129.0, 134.9, 139.1, 159.2, 164,1.

Anal. Calcd. For $C_{16}H_{15}FO$: C, 79.32%; H, 6.24%. Found: C, 79.11%; H, 6.32%.



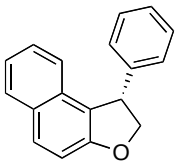
4,6-Dimethyl-3-(4-methylphenyl)-2,3-dihydrobenzofuran (4nb) (table 2, entry 6).

Using the general procedure, to a solution of 2-(2-hydroxy-1-(4-methylphenyl)-ethyl)-3,5-dimethylphenol **(3nb)** (61.4 mg, 0.24 mmol) in anhydrous THF (0.96 mL) were added triphenylphosphine (125.9 mg, 0.48 mmol) and diethylazodicarboxylate (62.6 mg, 0.36 mmol). The mixture was allowed to react for 2 hours at rt. Column chromatography eluting with hexanes/Et_2O 9:1 afforded pure **4nb** (48.6 mg, 85%), as an oil.

^{1}H NMR (200 MHZ, $CDCl_3$) δ 1.94 (s, 3H); 2.32 (s, 3H); 2.34 (s, 3H); 4.40 (dd, 1H, J_1= 8.2 Hz, J_2= 5.0 Hz); 4.51 (dd, 1H, J_1= 8.9 Hz, J_2= 5.0 Hz); 4.85 (t, 1H, J= 8.5 Hz); 6.51 (br, s, 1H); 6.59 (br, s, 1H); 7.00-7.15 (m, 4H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 18.5, 21.0, 21.4, 47.2, 79.7, 106.1, 107.7, 110.1, 123.0, 126.0, 127.4, 129.3, 135.1, 136.2, 138.8, 140.3, 160.3.

MS (relative intensity) 238 (M^+, 100), 223 (53), 208 (17), 195 (18), 165 (10), 119 (11). Anal. Calcd. For $C_{17}H_{18}O$: C, 85.67%; H, 7.61%. Found: C, 85.11%; H, 7.32%.



(*S*)-1-Phenyl-1,2-dihydronaphtho[2,1-*b*]furan (4ld) (table 2, entry 7).

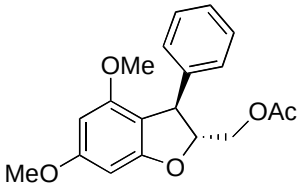
Using the general procedure, to a solution of 1-((1*S*)-2-hydroxy-1-phenylethyl)naphtalen-2-ol **(3ld)**[3] (127.7 mg, 0.48 mmol) in anhydrous THF (1.92 mL) were added triphenylphosphine (251.8 mg, 0.96 mmol) and diethylazodicarboxylate (125.3 mg, 0.72 mmol). The mixture was allowed to react for 3 hours at rt. The product (containing 22 % of (*R*)-stereoisomer) was isolated (112.2 mg, 95%) by column chromatography eluting with hexanes/AcOEt 8:2, as a light brown solid. M.p= 89-90°C. $[\alpha]_D^{20}$= + 45.2 (c = 3.7, $CHCl_3$).

^{1}H NMR (250 MHz, $CDCl_3$) δ 4.60 (dd, 1H, J_1=7.8 Hz, J_2= 4.4 Hz); 5.01- 5.26 (m, 2H); 7.18-7.45 (m, 9H); 7.72-7.90 (m, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 48.2, 80.3, 112.1, 121.0, 122.8, 126.6, 126.9, 127.6, 128.7, 128.8, 129.7, 130.0, 130.6, 143.3, 158.2.

Anal. Calcd. For $C_{19}H_{14}O$: C, 87.78%; H, 5.73%. Found: C, 87.90%; H, 5.65%.

HPLC analysis performed on a Daicel Chiralcel ® OD-H column, flow rate: 0.5 mL/min, mobile phase: hexane/isopropanol 98/2, retention times (min): 10.8 (*R*, minor stereoisomer), 15.7 (*S*, major stereoisomer).



(2 *R*, 3 R)-4,6-Dimethoxy-3-phenyl-2,3-dihydrobenzofuran-2-yl)methyl acetate (5fa) (table 2, entry 8).**

Using the general procedure, to a solution of (*2R*,3S**)-3-(2-hydroxy-4,6-dimethoxy)-3-phenylpropane-1,2-diol **(3fa)** (100.3 mg, 0.33 mmol) in anhydrous THF (1.32 mL) were added triphenylphosphine (173.1 mg, 0.66 mmol) and diethylazodicarboxylate (87.0 mg, 0.50 mmol). The mixture was allowed to react for 5 hours at rt and then the solvent was evaporated under a vacuum. To the crude mixture dissolved in pyridine (2.0 mL) was then added at 0°C acetic anhydride (673.2 mg, 0.62 mL, 6.6 mmol). The mixture was allowed to react for 24 hours at rt. The mixture was then quenched with aqueous $NaHCO_3$ saturated solution. The organic phase was then washed with HCl 10% and brine, dried over $MgSO_4$ and filtered. Column chromatography eluting with hexanes/AcOEt 9:1 afforded pure **5fa**, as an oil (64.9 mg, 60%).

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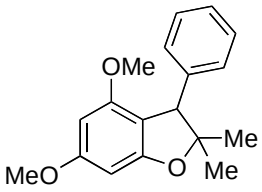
[3] Guss, C. O.; Jules, L. H. *J. Am. Chem. Soc.* **1950**, *72*, 3462.

^{1}H NMR (250 MHz, $CDCl_3$) δ 2.07 (s, 3H); 3.58 (s, 3H); 3.77 (s, 3H); 4.22-4.38 (m, 3H); 4.70-4.78 (m, 1H); 6.00 (d, 1H, *J*=2.0 Hz); 6.13 (d, 1H, *J*=2.0 Hz); 7.09-7.15 (m, 2H); 7.20-7.31 (m, 3H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 20.8, 48.6, 55.3, 55.5, 65.1, 88.4, 89.4, 91.9, 108.1, 126.8, 127.2, 128.6, 142.3, 157.2, 161.3, 162.3, 170.2.

Anal. Calcd. For $C_{19}H_{14}O$: C, 69.50%; H, 6.14%. Found: C, 69.87%; H, 5.89%.



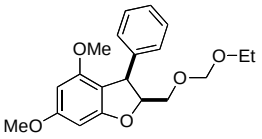
4,6-Dimethoxy-2,2-dimethyl-3-phenyl–2,3-dihydro benzofuran (4qa) (table 2, entry 9).

Using the general procedure, a solution of tris-(3,5-dimethyoxyphenyl) borate **(1a)** (705 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at rt under argon to a solution of 1,2-epoxy-2-methyl-1-phenyl-propane **(2q)** (148 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 18 hours at –40°C. The reaction was then quenched and the solvent was evaporated under a vacuum. To the crude mixture dissolved in toluene (18.5 mL) was then added with *p*-TsOH (28.5 mg, 0.15 mmol) and it was allowed to react for 3 hours at 100°C. The mixture was quenched with aqueous $NaHCO_3$ saturated solution, dried over $MgSO_4$ and filtered. Column chromatography eluting with hexanes/Et_2O 9:1 afforded pure **4qa**, as a solid (156.2 mg, 55%). M.p= 86-89°C.

^{1}H NMR (250 MHz, $CDCl_3$) δ 0.97 (s, 3H); 1.53 (s, 3H); 3.60 (s, 3H); 3.80 (s, 3H); 4.18 (s, 1H); 6.02 (s, 1H); 6.11 (s, 1H); 6.90-7.10 (m, 2H); 7.15-7.28 (m, 3H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ 24.5, 29.4, 55.3, 55.5, 55.6, 88.3, 90.4, 91.3, 109.4, 126.6, 127.0, 127.3, 140.4, 157.3, 160.7, 162.0

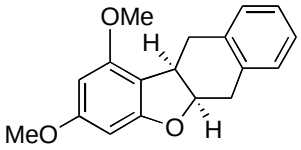
Anal. Calcd. For $C_{19}H_{14}O$: C, 76.03%; H, 7.09%. Found: C, 75.87%; H, 6.89%.



(2*S,3*R**)-2,3-Dihydro-4,6-dimethoxy-2-(ethoxymethoxy)methyl-3-phenyl-benzofuran (4ja) (Table 2, entry 10)**. Using the general procedure, triphenylphosphine (251.8 mg, 0.96 mmol) and diethylazodicarboxylate (125.3 mg, 114 μL, 0.72 mmol) were added to a solution of 2-((*1R**,*2R**)-3-(ethoxymethoxy)-2-hydroxy-1-phenylpropyl)-3,5-dimethoxy phenol (**3hi**) (173 mg, 0.48 mmol) in anhydrous THF (1.9 mL). The mixture was allowed to react for 2 hours at rt. Column chromatography eluting with hexanes/AcOEt 8:2, afforded pure **4ja** (128.8 mg, 78%), as an oil. ^{1}H

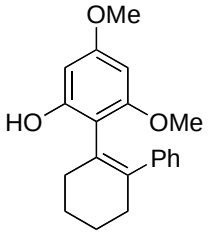
NMR (250 MHz, $CDCl_3$) δ 1.13 (t, 3H, *J*= 7.1 Hz); 3.25- 3.41 (m, 2H); 3.50 (q, 2H, *J*= 7.1 Hz); 3.56 (s, 3H); 3.76 (s, 3H); 4.49- 4.58 (m, 3H); 4.97- 5.25 (m, 1H); 6.00 (d, 1H, *J*= 2.0 Hz); 6.17 (d, 1H, *J*= 2.0 Hz); 6.90- 7.05 (m, 2H); 7.12- 7.25 (m, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 15.0, 47.6, 55.3, 55.5, 63.2, 67.9, 86.2, 88.5, 91.9, 95.2, 109.9, 126.9, 128.1, 128.3, 138.6, 156.8, 161.6, 162.2.

Anal. Calcd. For $C_{20}H_{24}O_5$: C, 69.75%; H, 7.02%. Found: C, 69.89%; H, 6.89%.



Compound 4ka (table 2, entry 11).

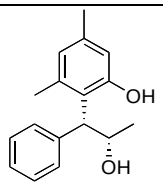
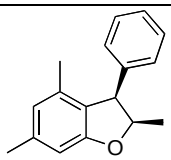
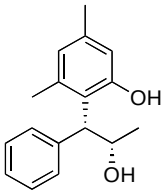
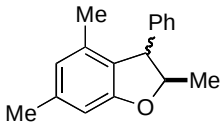
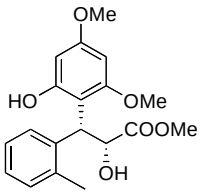
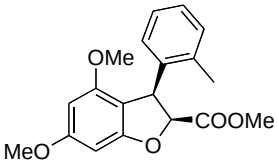
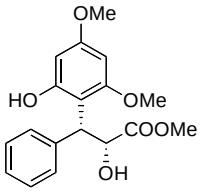
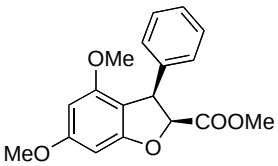
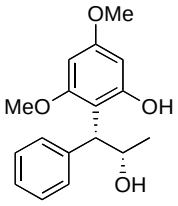
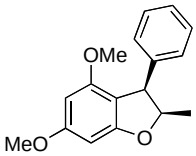
Using the general procedure, to a solution of (*1S*,2R**)-1-(2-hydroxy-4,6-dimethoxy phenyl)-1,2,3,4-tetahydronaphtalen-2-ol **(3ka)** (143.0 mg, 0.48 mmol) in anhydrous THF (1.92 mL) were added triphenylphosphine (251.8 mg, 0.96 mmol) and diethylazodicarboxylate (125.3 mg, 0.72 mmol). The mixture was allowed to react for 2 hours at rt. Column chromatography eluting with hexanes/AcOEt 8:2 afforded pure **4ka** (53.8 mg, 40%), as an oil. ^1H NMR (250 MHz, $CDCl_3$) δ 1.72-1.90 (m, 1H); 2.36-2.48 (m, 1H); 2.43-2.56 (m, 1H); 2.83-3.00 (m, 1H); 3.73 (s, 1H); 3.80 (s, 3H); 4.67 (d, 1H, *J*= 8.25 Hz); 5.21-5.30 (m, 1H); 5.95 (d, 1H, *J*=2.0 Hz); 6.03 (d, 1H, *J*= 2.0 Hz); 7.03-7.28 (m, 3H); 7.68 (d, 1H, *J*= 7.25 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 24.3, 27.9, 42.3, 55.2, 55.5, 83.1, 88.2, 91.4, 110.2, 125.9, 126.0, 128.2, 130.2, 136.2, 137.7, 157.3, 161.6, 161.7. Anal. Calcd. For $C_{19}H_{20}O_2$: C, 81.40%; H, 7.19%. Found: C, 81.33%; H, 7.21%.



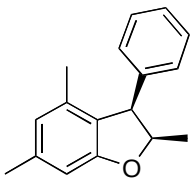
2-(2-Phenylcyclohex-1-enyl)-3,5-dimethoxyphenol (6). Using the general procedure, triphenylphosphine (141.6 mg, 0.40 mmol) and diethylazodicarboxylate (69.6 mg, 0.50 mmol) were added to a solution of compound **3ha** (88.6 mg, 0.27 mmol) in anhydrous THF (1.1 mL). The mixture was allowed to react for 5 hours at rt and then the solvent was removed *in vacuo*. Column chromatography eluting with hexanes/AcOEt 9:1 afforded pure **6** (50.2 mg, 60%), as an oil. ^1H NMR (250 MHz, $CDCl_3$) δ 1.62-1.85 (m, 4H); 2.12-2.25 (m, 2H); 2.42-2.71 (m, 2H); 3.62 (s, 3H); 3.77 (s, 3H); 5.36 Ar*OH* (br, s, 1H); 6.07 (d, 1H, *J*=2.3 Hz); 6.17 (d, 1H, *J*=2.3 Hz); 7.05-7.38 (m, 5H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 25.8, 27.4, 33.0 (2 C); 55.2, 55.7, 91.7, 92.3, 111.3, 123.0, 126.2, 127.8, 128.07, 141.3, 150.0, 153.6, 158.0, 160.5

Anal. Calcd. For $C_{20}H_{22}O_3$: C, 77.39%; H, 7.14%. Found: C, 77.64%; H, 7.04%.

TABLE 3. Additional Results of Cyclodehydration of Hydroxyphenols to 2,3-Dihydrobenzofuranes.

Entry	Hydroxyphenol	Conditions[a]	Product	Yield[b] (%)
1	 **3ab**	PPh_3/DEAD THF, rt	 **4ab**	75
2	 **3ab**	*p*-TsOH (20 mol%) Toluene, 100°C	 dr=68/32	91
3	 **3da**	PPh_3/DEAD THF, rt	 **4da**	70
4	 **3ca**	PPh_3/DEAD THF, rt	 **4ca**	77
5[c]	 **3aa**	PPh_3/DEAD THF, rt	 **4aa**	51

[a] All reactions were carried out in accordance with general procedures. [b]Isolated yield after chromatography on silica gel.[c] Compound **3aa** was not isolated but directly cyclized to **4aa** using the Mitsunobu-type cyclodehydration.



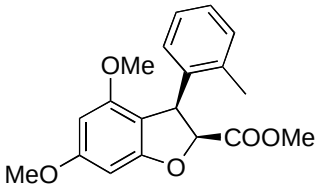
(2*R,3*R**)-2,4,6-Trimethyl-3-phenyl-2,3-Dihydrobenzofuran (4ab) (table 3, entry 1).**

Using the general procedure, to a solution of 2-((*1R*, 2S**)-2-hydroxy-1-phenylpropyl)-3,5-dimethylphenol **(3ab)** (59.5 mg, 0.25 mmol) in anhydrous THF (1.00 mL) were added triphenylphosphine (131.2 mg, 0.50 mmol) and diethylazodicarboxylate (66.1 mg, 0.38 mmol). The mixture was allowed to react for 1 hour at rt. The product (containing 3.6 % of *trans*-stereoisomer as determined by GC) was isolated (Yield=75 %) by column chromatography eluting with hexanes/Et_2O 9:1, as an oil.

^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.09 (d, 3H, *J*= 6.5 Hz); 1.93 (s, 3H); 2.32 (s, 3H); 4.35 (d, 1H, *J*= 8.2 Hz); 4.95-5.11 (m, 1H); 6.53 (s, 1H); 6.57 (s, 1H); 6.90–7.01 (m, 2H); 7.15-7.40 (m 3H).

^{13}C NMR ($CDCl_3$, 50 MHz) δ 17.0, 18.4, 21.6, 51.0, 83.2, 107.6, 123.0, 126.8, 127.6, 127.8, 128.3, 128.9, 135.1, 138.8, 139.0, 160.0.

MS (relative intensity) 238 (M^+, 100), 223 (85), 209 (20), 195 (40), 178 (16), 115 (21). Anal. Calcd. For $C_{17}H_{18}O$: C, 85.67%; H, 7.61%. Found: C, 85.90%; H, 7.55%.



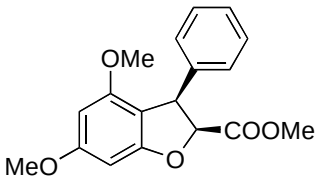
(2*S,3*R**)-Methyl 4,6-dimethoxy-3-(2-methylphenyl)-2,3-dihydrobenzofuran-2-carboxylate (4da) (table 3, entry 3).**

Using the general procedure, to a solution of (2*R**,3*R**)-methyl 2-hydroxy-3-(2-hydroxy-4,6-dimethoxyphenyl)-3-(2-methylphenyl)propanoate **(3da)** (126.7 mg, 0.37 mmol) in anhydrous THF (1.5 mL) were added triphenylphosphine (194.1 mg, 0.74 mmol) and diethylazodicarboxylate (52.2 mg, 0.3 mmol). The mixture was allowed to react for 1 hour at rt. The product was isolated (Yield=70%) by column chromatography eluting with hexanes/AcOEt 8:2, as a solid. M.p= 113- 114°C.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.47 (s, 3H); 3.23 (s, 3H); 3.60 (s, 3H); 3.80 (s, 3H); 5.13 (d, 1H, *J*= 9.5 Hz); 5.49 (d, 1H, *J*= 9.5 Hz); 6.03 (d, 1H, *J*=1.5 Hz); 6.80 (d, 1H, *J*= 7.2 Hz); 6.96-7.24 (m, 3H).

^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 19.8, 44.5, 51.5, 55.4, 55.6, 85.2, 88.5, 92.4, 108.7, 125.9, 126.9, 127.7, 129.6, 135.9, 136.9, 156.5, 161.2, 162.3, 168.9.

Anal. Calcd. For $C_{19}H_{14}O$: C, 69.50%; H, 6.14%. Found: C, 69.87%; H, 6.09%.



(2*S,3*R**)-Methyl 4,6-dimethoxy-3-phenyl-2,3-dihydro benzofuran-2-carboxylate (4ca) (table 3, entry 4).**

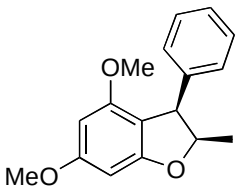
Following the procedure **A** described above, to a solution of (2*R**,3*R**)-methyl 2-hydroxy-3-(2-hydroxy-4,6-dimethoxyphenyl)-3-phenylpropanoate **(3ca)** (containing 13% of 2*S**,3*S**-stereoisomer) (66.8 mg, 0.20 mmol) in anhydrous THF (0.8 mL) were added triphenylphosphine (104.9 mg, 0.4 mmol) and diethylazodicarboxylate (52.2 mg, 0.3 mmol). The mixture was allowed to react for 1 hour at rt. The product (containing 13% of the *trans*-diastereoisomer **5ca**) was isolated (Yield=77%) by column chromatography eluting with hexanes/AcOEt 8:2, as a solid.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.27 (s, 3H); 3.58 (s, 3H); 3.80 (s, 3H); 4.79 (d, 1H, *J*= 9.25 Hz); 5.43 (d, 1H, *J*= 9.25 Hz); 6.03 (d, 1H, *J*= 2.0 Hz); 6.24 (d,1H, *J*= 2.0 Hz); 6.95-7.05 (m, 2H); 7.13- 7.23 (m, 3H).

^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 49.2, 51.6, 55.4, 55.5, 85.8, 88.6, 92.5, 108.2, 127.2, 127.9, 128.2, 138.4, 156.8, 161.1, 162.4, 168.7.

Anal. Calcd. For $C_{19}H_{14}O$: C, 68.78%; H, 5.77%. Found: C, 69.07%; H, 5.39%.

Representative signals of compound **5ca**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.71 (d, 1H, *J*=4.0 Hz), 4.98 (d, 1H, *J*=4.0 Hz). ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 50.3, 87.9.



(2 *R, 3 *R**)-4,6-Dimethoxy-2-methyl-3-phenyl-2,3-dihydro benzofuran (4aa) (table 3, entry 5).**

Using the general procedure for the stereoselective ring-opening of aryl epoxides, a solution of tris (3,5-dimethoxyphenyl) borate **(1a)** (705 mg, 1.5 mmol) in CH_2Cl_2 (1.0 mL) was added at rt under argon to a solution of *trans*-β-methyl-styrene **(2a)** (134 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The mixture was allowed to react for 18 hours at –78°C. The reaction was then quenched and the solvent was evaporated under a vacuum. To the crude mixture, containing 27% of *O*-alkylated product, dissolved in THF (2.9 mL) were then added triphenylphosphine (382.9 mg, 1.46 mmol) and diethylazodicarboxylate (189.7 mg, 1.09 mmol). The

mixture was allowed to react for 2 hours at rt. The purification by flash column chromatography eluting with hexanes/Et_2O 9:1 afforded (2*R**,3*R**)-4,6-dimethoxy-2-methyl-3-phenyl-2,3-dihydrobenzofuran **(4aa)** (contaminated with 19% of the *trans*-diastereoisomer **5aa**, see below), as an oil (137.7 mg, 51%).

^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.02 (d, 3H, *J*= 6.3 Hz); 3.60 (s, 3H); 3.78 (s, 3H); 4.38 (d, 1H, *J*=8.3 Hz); 4.93-5.10 (m, 1H); 6.01 (s, 1H); 6.13 (s, 1H); 6.92 (d, 2H, *J*=7.3 Hz); 7.10-7.27 (m, 3H).

^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 16.8, 49.3, 55.4, 55.5, 84.4, 88.3, 91.6, 126.6, 127.2, 128.4, 139.3, 156.8, 161.9 (2C).

Anal. Calcd. For $C_{17}H_{18}O_3$: C, 75.53%; H, 6.71%. Found: C, 75.47%; H, 6.49%.

Representative signals of (*2S*,3R**)-stereoisomer **(*trans*-5aa)**:

^{1}H NMR (250 MHz, $CDCl_3$) δ 4.11 (d, 1H, *J*= 5.0 Hz); 4.60-4.70 (m, 1H).