Supporting Information

For

Facile Regio- and Stereoselective Carbon-Carbon Coupling of Phenol Derivatives with Aryl Aziridines

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General Methods. THF, CH₂Cl₂ 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.

¹H 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). ¹³C 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) were performed on a Waters 600E equipped with Varian Prostar 325 detector using Daicel Chiralcel OD-H and AD-H column with detection at 254 nm.

Mass spectra ESIMS were measured on a Finnigan LC-Q Deca Termoquest spectrometer, equipped with a software Xcalibur.

Synthesis of aromatic borates

Following a previously described procedure for the preparation of triphenyl borate¹, a solution of substituted phenol (90 mmol) in degassed THF (20 mL) was added at 0°C to BH₃·Me₂S (30.0 mmol) under argon. The mixture was allowed to react up to complete evolution of H₂. Evaporation of organic solution afforded aromatic borates **1a-f**, which were not further purified and used immediately after their preparation.

Ring-opening of aziridines

General Procedure as follows: a solution of aryl borate (0.75 mmol) in CH₂Cl₂ (0.5 mL) was added under argon protection at -78°C to a solution of aziridine (0.5 mmol) in CH₂Cl₂ (1.5 mL) under a magnetic stirring. The reaction was followed by TLC and was quenched, after the times indicated in Table 1 and Scheme 2, with brine (2.0 mL). The solution was diluted with Et₂O or CH₂Cl₂ (20 mL) and washed with brine. Evaporation of the dried organic solution afforded a crude reaction mixture that was purified by semipreparative TLC or by silica gel column chromatography to give the pure compounds.

(2S)-2-Phenyl-2-(2-hydroxyphenyl)-N-(4-methylphenylsulfonyl)-ethanamine (3aa), (Scheme 2).

Using the general procedure described above, a solution of triphenyl borate (**1a**) (217.5 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at -78°C under argon to a solution of (*S*)-*N*-Ts aziridine of styrene (**2a**) (136.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 18 hours at -78 °C. The product was isolated (Yield=33.3%) by column chromatography eluting with hexanes/AcOEt 7:3, as a solid. M.p= 182-185°C. R_f= 0.22 (hexanes/AcOEt 8:2).

¹ Brown, C. A.; Krishnamurthy, S. *J. Org. Chem.* **1978**, *43*, 2731.

^1H NMR (MeOD) δ 2.40 (s, 3H); 3.42 (d, 1H, J = 8.0 Hz); 4.51 (t, 1H, J = 8.0 Hz); 6.63- 6.76 (m, 2H); 6.88- 7.05 (m, 2H); 7.09- 7.25 (m, 5H); 7.31 (d, 2H, J = 8.0 Hz); 7.66 (d, 1H, J = 8.0 Hz).

^{13}C NMR (MeOD) δ 21.46, 45.16, 47.49, 116.08, 120.41, 127.28, 128.07, 128.51, 129.20, 129.28, 129.51, 129.56, 130.64, 138.72, 143.17, 144.47, 156.13.

ESIMS (neg.): m/z 366 [M-H].

HPLC analysis performed on a Daicel Chiralpak[®] AD-H column, flow rate: 1.0 mL/min, mobile phase: hexane/isopropanol 90/10, retention times (min): 51.41 (*S*, major stereoisomer), 55.98 (*R*, minor stereoisomer).

The first eluting fractions of the above described column chromatography afforded pure **(2*R*)-2-phenyl-2-phenoxy-*N*-(4-methylphenylsulfonyl)-ethanamine (4aa)**, (Scheme 2), as a semisolid (yield= 34.2%).

^1H NMR (CDCl_3) δ 2.41 (s, 3H); 3.24 (ddd, 1H, J_1 = 13.3 Hz, J_2 = 9.0 Hz; J_3 = 3.8 Hz); 3.43 (ddd, 1H, J_1 = 13.3 Hz, J_2 = 9.2 Hz; J_3 = 3.6 Hz); 4.96-5.05 NH (m, 1H); 5.11 (dd, 1H, J_1 = 9.0 Hz, J_2 = 3.6 Hz); 6.70 (d, 2H, J = 8.3 Hz); 6.88 (t, 1H, J = 7.3 Hz); 7.09- 7.36 (m, 9H); 7.72 (d, 2H, J = 8.1 Hz).

^{13}C NMR (CDCl_3) δ 22.11, 50.12, 79.03, 116.36, 121.88, 126.63, 127.57, 128.93, 129.42, 129.88, 130.37, 137.62, 138.58, 144.09, 157.80.

(2*S*)-2-Phenyl-2-(2-hydroxyphenyl)-*N*-benzyloxycarbonyl-ethanamine (3ba), (Scheme 2).

Using the general procedure described above, a solution of triphenyl borate (**1a**) (217.5 mg, 0.75 mmol) in CH_2Cl_2 (0.5 mL) was added at -78°C under argon to a solution of (*S*)-*N*-Cbz aziridine of styrene (**2b**) (126.5 mg, 0.5 mmol) in CH_2Cl_2 (1.5 mL). The mixture was allowed to react for 2 hours at -78°C . The product was isolated (Yield=18%) by semipreparative TLC eluting with hexanes/AcOEt 85:15 (3 times), as a solid. M.p= 132-135°C.

^1H NMR (CDCl_3) δ 3.62- 3.96 (m, 2H); 4.54 (t, 1H, J = 7.7 Hz); 4.93- 5.17 (m, 3H); 6.61- 6.78 (m, 3H); 6.94 (d, 1H, J = 6.6 Hz); 7.06 (t, 1H, J = 7.1 Hz); 7.13- 7.40 (m, 10H).

^{13}C NMR (CDCl_3) δ 45.24, 45.35, 67.71, 116.85, 121.10, 127.59, 128.62, 128.85, 128.99, 129.21, 129.39, 129.56, 136.86, 141.31, 154.82 157.69.

ESIMS (neg.): m/z 346 $[\text{M}-\text{H}]$.

HPLC analysis performed on a Daicel Chiralpak[®] AD-H column, flow rate: 1.0 mL/min, mobile phase: hexane/isopropanol 90/10, retention times (min): 28.58 (*R*, minor stereoisomer), 30.43 (*S*, major stereoisomer).

The first eluting fractions of the above described column chromatography afforded pure **(2*R*)-2-phenyl-2-phenoxy-*N*-benzyloxycarbonyl-ethanamine (4ba)**, (Scheme 2), as a solid (yield= 25.3%). M.p= 87- 90°C.

^1H NMR (CDCl_3) δ 3.45 (ddd, 1H, J_1 = 13.6 Hz, J_2 = 8.9 Hz; J_3 = 4.3 Hz); 3.75 (ddd, 1H, J_1 = 13.6 Hz, J_2 = 11.1 Hz; J_3 = 4.5 Hz); 5.01- 5.19 (m, 2H); 5.20- 5.36 *CH*-OAr + *NH* (m, 2H); 6.75- 6.95 (m, 3H); 7.10- 7.43 (m, 12H).

^{13}C NMR (CDCl_3) δ 48.43, 67.58, 79.71, 116.51, 121.86, 126.80, 128.84, 129.24, 129.47, 130.09, 139.24, 157.02, 158.35.

Ring-opening of (*S*)-*N*-P(O)Ph₂ aziridine of styrene (**2c**) with triphenyl borate (**1a**), (Scheme 2).

Using the general procedure described above, a solution of triphenyl borate (**1a**) (217.5 mg, 0.75 mmol) in CH_2Cl_2 (0.5 mL) was added at -78°C under argon to a solution of (*S*)-*N*-P(O)Ph₂ aziridine of styrene (**2c**) (159.5 mg, 0.5 mmol) in CH_2Cl_2 (1.5 mL). The mixture was allowed to react for 18 hours at -78°C . The reaction afforded an inseparable mixture of *C*- and *O*-alkylated product, **3ca** and **4ca**, 41/59 ratio respectively. Representative signal for:

C-Alk product (**3c**) $\Rightarrow$ 4.86- 5.00 *CH*Ar (m, 1H).

O-Alk product (**4c**) $\Rightarrow$ 5.28- 5.39 *CH*Ar (m, 1H):

HPLC analysis of product **3ca** was performed on a Daicel Chiralpak[®] AD-H column, flow rate: 1.0 mL/min, mobile phase: hexane/isopropanol 90/10, retention times (min): 32.63 (*S*, major stereoisomer); 54.62 (*R*, minor stereoisomer).

(2*S*)-2-Phenyl-2-(4,6-dimethyl-2-hydroxyphenyl)-*N*-(4-methylphenylsulfonyl)-ethanamine (3ab), (Table 1, entry 1).

Using the general procedure described above, a solution of tris (3,5-dimethylphenyl) borate (**1b**) (280.5 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at –78°C under argon to a solution of (*S*)-*N*-Ts aziridine of styrene (**2a**) (136.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 2 hours at –78 °C. The product was isolated (Yield=73%) by column chromatography eluting with hexanes/AcOEt 8:2, as a solid. M.p= 175-178°C. R_f= 0.17 (hexanes/AcOEt 8:2).

¹H NMR (CDCl₃) δ 2.05 (s, 3H); 2.17 (s, 3H); 2.39 (s, 3H); 3.62- 3.87 (m, 2H); 4.35- 4.46 (m, 1H); 4.81- 4.97 CH₂NH (m, 1H); 5.69- 5.80 Ar-*OH* (br, 1H); 6.40 (s, 1H); 6.51 (s, 1H); 7.08- 7.27 (m, 7H); 7.65 (d, 1H, 8.3 Hz).

¹³C NMR (CDCl₃) δ 21.13, 21.41, 22.14, 45.00, 46.51, 115.97, 122.52, 125.09, 127.06, 127.63, 128.43, 129.07, 130.26, 137.53, 138.46, 139.67, 141.66, 143.89, 154.80.

ESIMS (neg.): *m/z* 394 [M-H].

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): 22.30 (*R*, minor stereoisomer), 26.03 (*S*, major stereoisomer).

Anal. Calcd. For C₂₃H₂₅NO₃S: C, 69.84%; H, 6.37%; N, 3.54%; S, 8.11%. Found: C, 70.45%; H, 6.18%; N, 3.34%; S, 8.11%.

(2*S*)-(+)-2-Phenyl-2-(4,6-dimethyl-2-hydroxyphenyl)-*N*-benzyloxy carbonyl-ethanamine (3bb), (Table 1, entry 2).

Using the general procedure described above, a solution of tris (3,5-dimethylphenyl) borate (**1b**) (280.5 mg, 0.75 mmol) in

CH₂Cl₂ (0.5 mL) was added at -78°C under argon to a solution of (*S*)-*N*-Cbz aziridine of styrene (**2b**) (126.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 16 hours at -78 °C. The product was isolated (Yield=51%) by column chromatography eluting with hexanes/AcOEt 8:2, as a solid. M.p= 0.28 (hexanes/AcOEt 8:2).

¹H NMR (CDCl₃) δ 2.15 (s, 6H); 3.82- 4.11 (m, 2H); 4.48- 4.56 (m, 1H); 4.96- 5.15 (m, 3H), 5.96- 6.10 Ar-*OH* (br, s, 1H); 6.41 (s, 1H); 6.52 (s, 1H); 7.09- 7.27 (m, 10H).

¹³C NMR (CDCl₃) δ 21.34, 21.48, 44.30, 44.60, 67.39, 116.03, 124.85, 126.90, 128.44, 128.68, 128.72, 129.04, 129.13, 137.04, 138.13, 139.47, 142.18, 155.14, 157.46.

ESIMS (neg.): *m/z* 374 [M-H].

[α]_D²⁰ = +9.61 (c 0.52, MeOH).

HPLC analysis performed on a Daicel Chiralcel[®] OD-H column, flow rate: 0.5 mL/min, mobile phase: hexane/isopropanol 92/8, retention times (min): 30.61 (*S*, major stereoisomer), 52.86 (*R*, minor stereoisomer).

(2*S*)-(+)-2-Phenyl-2-(4,6-dimethyl-2-hydroxyphenyl)-*N*-diphenylphosphinyl-ethanamine (3cb**), (Table 1, entry 3).**

Using the general procedure described above, a solution of tris (3,5-dimethylphenyl) borate (**1b**) (280.5 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at -78°C under

argon to a solution of (*S*)-*N*-P(O)Ph₂ aziridine of styrene (**2c**) (159.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 2 hours at -78 °C. The product was isolated (Yield=70%) by column chromatography eluting with CH₂Cl₂/AcOEt 7:3, as a solid. M.p= 100-103°C. R_f= 0.15 (CH₂Cl₂/AcOEt 7:3).

¹H NMR (CDCl₃) δ 2.16 (s, 3H); 2.19 (s, 3H); 3.15- 3.40 *NHdPPh* (m, 1H); 3.58- 3.80 (m, 1H); 3.82- 4.03 (m, 1H); 4.41- 4.59 (m, 1H); 6.49 (s, 1H); 6.81 (s, 1H); 7.04- 7.22 (m, 5H); 7.29- 7.54 (m, 6H); 7.73- 7.90 (m, 4H).

¹³C NMR (CDCl₃) δ 21.48, 21.53, 44.04, 46.94, 116.78, 123.91, 126.51, 128.64, 128.80, 129.12, 129.37, 132.62, 132.78, 132.94, 138.00, 138.72, 142.93, 156.85.

ESIMS (neg.): *m/z* 440 [M-H].

$[\alpha]_D^{20} = +20.63$ (c 0.48, MeOH).

HPLC analysis performed on a Daicel Chiralpak[®] AD-H column, flow rate: 0.7 mL/min, mobile phase: hexane/isopropanol 90/10, retention times (min): 22.64 (*S*, major stereoisomer), 52.86 (*R*, minor stereoisomer).

Anal. Calcd. For C₂₈H₂₈NO₂P: C, 76.17%; H, 6.39%; N, 3.17%; P, 7.02%. Found: C, 76.34%; H, 6.19%; N, 3.10%; P, 7.07%.

(2*S*)-2-Phenyl-2-(2-hydroxy-3,4,6-trimethylphenyl)-*N*-benzyloxycarbonyl-ethanamine (3bc), (Table 1, entry 4).

Using the general procedure described above, a solution of tris (2,3,5-trimethylphenyl) borate (**1c**) (312 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at –78 °C under argon to a solution of (*S*)-*N*-Cbz aziridine of styrene (**2b**) (126.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 2 hours at –78 °C. The product was isolated (Yield=40%) by column chromatography eluting with hexanes/AcOEt 8:2, as a semisolid. R_f = 0.28 (hexanes/AcOEt 8:2).

¹H NMR (CDCl₃) δ 2.04 (s, 3H); 2.20 (s, 6H); 3.79- 3.94 (m, 1H); 4.05- 4.25 (m, 1H); 4.56- 4.70 (m, 1H); 4.83- 4.98 NHCbz (m, 1H); 5.07 (s, 2H); 6.61 (s, 1H); 7.14- 7.39 (m, 10H).

¹³C NMR (CDCl₃) δ 12.21, 20.64, 21.22, 43.33, 44.00, 67.34, 124.54, 125.63, 127.22, 128.12, 128.73, 129.13, 129.38, 135.89, 136.84, 137.12, 141.72, 153.04, 157.23.

ESIMS (neg.): m/z 388 [M-H].

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): 26.43 (*R*, minor stereoisomer), 28.50 (*S*, major stereoisomer).

Anal. Calcd. For C₂₅H₂₇NO₃: C, 77.09%; H, 6.99%; N, 3.60%. Found: C, 76.14%; H, 7.01%; N, 3.35%.

(2S)-2-Phenyl-2-(4,6-dimethoxy-2-hydroxyphenyl)-N-benzyloxycarbonyl-ethanamine (3bd) (Table 1, entry 5).

Using the general procedure described above, a solution of tris (3,5-dimethoxyphenyl) borate (**1d**) (352.5 mg, 0.75 mmol) in CH_2Cl_2 (0.5 mL) was added at -78°C under argon to a solution of (*S*)-*N*-Cbz aziridine of styrene (**2b**) (126.5 mg, 0.5 mmol) in CH_2Cl_2 (1.5 mL). The mixture was allowed to react for 1 hour at -78°C . The product was isolated (Yield=88%) by column chromatography eluting with hexanes/AcOEt 7:3, as a semisolid. R_f = 0.11 (hexanes/AcOEt 7:3).

^1H NMR (CDCl_3) δ 3.67 (s, 3H); 3.69 (s, 3H); 3.89- 4.23 (m, 2H); 4.72- 4.88 (m, 1H); 4.96- 5.21 (m, 3H); 5.99- 6.12 (m, 2H); 7.10- 7.43 (m, 10H).

^{13}C NMR (CDCl_3) δ 40.77, 44.14, 55.75, 56.21, 67.45, 92.00, 95.07, 126.70, 128.61, 128.84, 129.16, 137.07, 143.08, 156.95, 157.70, 160.24, 160.38.

ESIMS (neg.): m/z 406 $[\text{M}-\text{H}]^-$.

HPLC analysis performed on a Daicel Chiralpak[®] AD-H column, flow rate: 0.7 mL/min, mobile phase: hexane/isopropanol 90/10, retention times (min): 49.63 (*S*, major stereoisomer), 61.21 (*R*, minor stereoisomer).

(2S)-2-Phenyl-2-(2-hydroxy-5-methoxyphenyl)-N-benzyloxycarbonyl-ethanamine (3be), (Table 1, entry 6).

Using the general procedure described above, a solution of tris (4-methoxyphenyl) borate (**1e**) (285 mg, 0.75 mmol) in CH_2Cl_2 (0.5 mL) was added at -78°C under argon to a solution of (*S*)-*N*-Cbz aziridine of styrene (**2b**) (126.5 mg, 0.5 mmol) in CH_2Cl_2 (1.5 mL). The mixture was allowed to react for 2 hours at -78°C . The product was isolated (Yield=59%) by column chromatography eluting with hexanes/AcOEt 7:3, as a semisolid.

^1H NMR (CDCl_3) δ 3.72 (s, 3H); 3.73- 4.01 (m, 2H); 4.53- 4.67 (m, 1H); 5.06- 5.23 (m, 3H); 6.42- 6.52 Ar-*OH* (br, s, 1H); 6.59- 6.66 (m, 1H); 6.71 (m, 1H); 6.77- 6.85 (m, 1H); 7.17- 7.50 (m, 10H).

^{13}C NMR (CDCl_3) δ 45.36 (2 carbon); 56.28, 67.63, 112.84, 115.24, 117.43, 127.57, 128.81, 129.15, 129.36, 129.79, 136.84, 141.20, 148.68, 154.02, 157.60.

ESIMS (neg.): m/z 376 $[\text{M}-\text{H}]$.

HPLC analysis performed on a Daicel Chiralpak[®] AD-H column, flow rate: 0.7 mL/min, mobile phase: hexane/isopropanol 85/15, retention times (min): 25.19 (*S*, major stereoisomer), 30.41 (*R*, minor stereoisomer).

2-(4-Fluorophenyl)-2-(4,6-dimethyl-2-hydroxyphenyl)-*N*-(4-methylphenylsulfonyl)-ethanamine (3db), (Table 1, entry 7).

Using the general procedure described above, a solution of tris (3,5-dimethylphenyl) borate (**1b**) (280.5.5 mg, 0.75 mmol) in CH_2Cl_2 (0.5 mL) was added at -78°C under argon to a solution of *N*-Ts aziridine of *p*-fluoro-styrene (**2d**) (136.5 mg, 0.5 mmol) in CH_2Cl_2 (1.5 mL). The mixture was allowed to react for 24 hours at -78°C . The product was isolated (Yield=87%) by column chromatography eluting with hexanes/AcOEt 7:3, as a solid. M.p= 45- 47°C. R_f = 0.24 (hexanes/AcOEt 7:3).

^1H NMR (CDCl_3) δ 2.07 (s, 3H); 2.18 (s, 3H); 2.42 (s, 3H); 3.66- 3.80 (m, 2H); 4.32- 4.42 (m, 1H); 4.99- 5.08 CH_2NH (m, 1H); 6.41 (s, 1H); 6.52 (s, 1H); 6.83- 6.92 (m, 2H); 7.10- 7.32 (m, 4H); 7.67 (d, 2H, J = 8.2 Hz).

^{13}C NMR (CDCl_3) δ 21.03, 21.34, 22.09, 44.54, 46.71, 115.53, 115.96, 125.17, 127.57, 129.67, 130.08, 130.30, 137.39, 138.57, 139.53, 144.00, 154.55, 159.57, 164.42.

2-(4-Methylphenyl)-2-(4,6-dimethyl-2-hydroxyphenyl)-*N*-(4-methylphenylsulfonyl)-ethanamine (3eb), (Table 1, entry 8).

Using the general procedure described above, a solution of tris (3,5-dimethylphenyl) borate (**1b**) (280.5 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at –78°C under argon to a solution of *N*-Ts aziridine of *p*-methyl-styrene (**2e**) (143.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 2 hours at –78 °C. The product was isolated (Yield=65%) by column chromatography eluting with hexanes/AcOEt 8:2, as a solid (M.p= 46- 49°C).

¹H NMR (CDCl₃) δ 2.11 (s, 3H); 2.20 (s, 3H); 2.27 (s, 3H); 2.41 (s, 3H); 3.72 (d, 2H, *J*= 8.0 Hz); 4.39 (t, 1H, *J*= 8.0 Hz); 6.37 (s, 1H); 6.55 (s, 1H); 6.97- 7.10 (m, 4H); 7.25 (d, 2H, *J*= 8.0 Hz); 7.66 (d, 2H, *J*= 8.3 Hz).

¹³C NMR (CDCl₃) δ 21.23, 21.32, 21.66, 22.21, 44.37, 46.24, 116.17, 125.33, 127.72, 128.17, 129.94, 130.29, 136.88, 137.60, 138.59, 139.72, 143.91, 154.61.

(1*S,2*S**)-1-Phenyl-1-(4,6-dimethoxy-2-hydroxyphenyl)-*N*-(4-methylphenylsulfonyl)-propan-2-amine (3fd),** (Table 1, entry 9).

Using the general procedure described above, a solution of tris (3,5-dimethoxyphenyl) borate (**1d**) (352.5 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at –78°C under argon to a solution of *N*-Ts aziridine of β-methyl-styrene (**2f**) (143.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 14 hour at –78 °C. The product was isolated (Yield=85%) by column chromatography eluting with hexanes/AcOEt 7:3, as a grey solid (M.p=75- 77 °C).

¹H NMR (MeOD) δ 0.98 (d, 3H, *J*= 6.2 Hz); 2.36 (s, 3H); 3.65 (s, 3H); 3.68 (s, 3H); 4.36 (d, 1H, *J*= 11.2 Hz); 4.63- 4.71 (m, 1H); 5.95- 5.98 (m, 2H); 6.93- 7.00 (m, 3H); 7.15 (d, 2H, *J*= 8.0 Hz); 7.25- 7.30 (m, 2H); 7.43 (d, 2H, *J*= 8.0 Hz).

^{13}C NMR (MeOD) δ 21.43, 21.65, 48.67, 52.30, 55.45, 55.83, 91.28, 94.80, 111.43, 126.31, 127.81, 128.39, 130.01, 130.37, 140.15, 143.74, 144.48, 157.44, 160.31, 160.97.

ESIMS (neg.): m/z 440 [M-H].

Synthesis of aryl triflates

Triflic anhydride (0.375 mmol) was added dropwise at 0°C under argon protection to a solution of aminophenol of type **3** (0.25 mmol) in pyridine (1.35 mL) under a magnetic stirring. The reaction was followed by TLC and was quenched with brine (2.0 mL). The solution was diluted with Et₂O or CH₂Cl₂ (20 mL) and washed with brine and dried with Na₂SO₄. Evaporation of the dried organic solution afforded corresponding aryl triflates.

2-Phenyl-2-(4,6-dimethyl-2-trifluoromethanesulfonylphenyl)-1-(4-methylphenylsulfonyl)-ethanamine (5ab**) (Table 2, entry 1)).**

Following the general procedure described above, triflic anhydride (0.548 mmol, 153.4 mg) was added dropwise at 0°C under argon protection to a solution of 2-phenyl-2-(2-hydroxy-4,6-dimethylphenyl)-*N*-(4-methylphenylsulfonyl)-ethanamine (**3ab**) (0.365 mmol, 144.1 mg) in pyridine (2.0 mL). The mixture was allowed to react for 2 hours at rt. The evaporation of dried organic solution afforded compound (**5ab**) (yield=94%), as a solid (M.p= 98-100°C).

¹H NMR (CDCl₃) δ 2.14 (s, 3H); 2.34 (s, 3H); 2.43 (s, 3H); 3.48- 3.64 (m, 1H); 3.82- 4.01 (m, 1H); 4.49- 4.62 CH₂NH (m, 1H); 4.65- 4.77 (m, 1H); 6.94- 6.99 (m, 2H); 7.04- 7.35 (m, 7H); 7.71 (d, 2H, *J*= 8.1 Hz).

¹³C NMR (CDCl₃) δ 21.56, 22.16, 30.30, 43.07, 45.03, 120.15, 127.48, 127.79, 128.91, 129.28, 129.71, 130.43, 133.02, 137.15, 139.86, 141.18, 144.21, 149.42.

2-Phenyl-2-(5-methyl-2-trifluoromethanesulfonylphenyl)-*N*-(4-methylphenylsulfonyl)-ethanamine (5af**) (Table 2, entry 2).**

Following the general procedure described above, triflic anhydride (0.345 mmol, 96.6 mg) was added dropwise at 0°C

under argon protection to a solution of (2*S*)-2-phenyl-2-(2-hydroxy-5-methylphenyl)-*N*-(4-methylphenylsulfonyl)-ethanamine (**3af**) (0.23 mmol, 87.7 mg) in pyridine (1.25 mL). The mixture was allowed to react for 2.5 hours at rt. The evaporation of dried organic solution afforded compound (**5af**) (yield=97%), as a yellow solid.

¹H NMR (CDCl₃) δ 2.29 (s, 3H); 2.38 (s, 3H); 3.42- 3.57 (m, 2H); 4.32 (t, 1H, *J*= 7.6 Hz); 4.44- 4.58 CH₂NH (m, 1H); 6.98- 7.42 (m, 10H); 7.63 (d, 2H, *J*= 7.0 Hz).

¹³C NMR (CDCl₃) δ 21.80, 22.20, 44.20, 47.06, 122.18, 125.96, 127.76, 128.20, 128.60, 128.90, 129.63, 129.71, 130.02, 130.14, 130.47, 139.52, 139.58, 144.30.

(2*S*)-2-Phenyl-2-(2-trifluoromethansulfonyloxyphenyl)-*N*-(4-methylphenylsulfonyl)-ethanamine (5aa**) (Table 2, entry 2).**

Following the general procedure described above, triflic anhydride (0.375 mmol, 105 mg) was added dropwise at 0°C under argon protection to a solution of (2*S*)-2-phenyl-2-(2-hydroxyphenyl)-*N*-(4-methylphenylsulfonyl)-ethanamine (**3aa**) (0.25 mmol, 90.6 mg) in pyridine (1.35 mL). The mixture was allowed to react for 2 hours at rt. The evaporation of dried organic solution afforded compound (**5aa**) (yield=91%), as a semisolid.

¹H NMR (CDCl₃) δ 2.43 (s, 3H); 3.50- 3.69 (m, 2H); 4.43 (t, 1H, *J*=7.7 Hz); 4.77- 4.90 NH (m, 1H); 7.11 (d, 2H, *J*= 7.3 Hz); 7.20- 7.40 (m, 9H); 7.68 (d, 2H, *J*= 7.6 Hz).

¹³C NMR (CDCl₃) δ 22.18, 44.31, 47.09, 122.36, 124.42, 127.72, 128.21, 128.62, 129.39, 129.62, 130.45, 134.41, 136.69, 139.44, 144.26, 148.30, 150.44.

2-(4-Fluorophenyl)-2-(4,6-dimethyl-2-trifluoromethansulfonyloxyphenyl)-*N*-(4-methylphenylsulfonyl)-ethanamine (5db**).**

Following the general procedure described above, triflic anhydride (0.548 mmol, 153.4 mg) was added dropwise at 0°C under argon protection to a solution of 2-(4-fluorophenyl)-2-(2-hydroxy-4,6-dimethylphenyl)-*N*-(4-methylphenylsulfonyl)-ethanamine (**3db**) (0.365 mmol, 150.7 mg) in pyridine (2.0 mL). The mixture was

allowed to react for 2 hours at rt. The evaporation of dried organic solution afforded compound (**5db**) (yield=81%), as a solid (M.p= 37- 40°C).

¹H NMR (CDCl₃) δ 2.09 (s, 3H); 2.25 (s, 3H); 2.27 (s, 3H); 3.45 (ddd, 1H, *J*₁=13.6 Hz, *J*₂=7.4 Hz, *J*₃=5.4 Hz); 3.84 (ddd, 1H, *J*₁=13.6 Hz, *J*₂=12.8 Hz, *J*₃=7.5 Hz); 4.56-4.71 (m, 1H); 5.10- 5.22 CH₂NH (m, 1H); 6.77- 7.37 (m, 8H); 7.64 (d, 2H, *J*=8.2 Hz).
¹³C NMR (CDCl₃) δ 21.44, 22.05, 30.31, 42.51, 45.19, 115.73, 116.15, 120.04, 127.61, 128.32, 129.30, 132.85, 135.42, 136.94, 139.83, 140.90, 144.13, 149.29, 159.65, 164.53.

(1*S,2*S**)-1-Phenyl-1-(4,6-dimethoxyphenyl-2-trifluoromethansulfonyl)-*N*-(4-methylphenylsulfonyl)-propan-2-amine (**5gd**), (Table 2, entry 5).**

Following the general procedure described above, triflic anhydride (0.548 mmol, 153.4 mg) was added dropwise at 0°C under argon protection to a solution of (1*S**,2*S**)-1-phenyl-1-(2-hydroxy-4,6-dimethoxyphenyl)-*N*-(4-methylphenylsulfonyl)-propan-2-amine (**3fd**) (0.365 mmol, 161.0 mg) in pyridine (2.0 mL). The mixture was allowed to react for 2 hours at rt. The evaporation of dried organic solution afforded compound (**5gd**) (yield= 91%), as a solid.

¹H NMR (CDCl₃) δ 1.15 (d, 3H, *J*= 6.3Hz); 2.39 (s, 3H); 3.70 (s, 3H); 3.73 (s, 3H); 4.05 (d, 1H, *J*= 10.4Hz); 4.28- 4.38 CHNH (m, 1H); 4.48- 4.61 (m, 1H); 6.32- 6.40 (m, 2H); 7.00- 7.27 (m, 7H); 7.64 (d, 2H, *J*= 8.1Hz).
¹³C NMR (CDCl₃) δ 21.72, 50.16, 51.76, 56.26, 56.47, 99.41, 99.92, 111.12, 121.94, 127.44, 127.92, 129.03, 129.13, 130.03, 140.22, 143.52, 149.18, 159.76, 160.58.

General Procedure for the Synthesis of 3-aryl indolines.

Following a slightly modification of a previously described procedure for the intramolecular amination of aryl halides², in a Schlenk apparatus the substrate (**compounds of type 5**) (0.22 mmol) was added to a small amount of dry benzene. The solution was evacuated and backfilled with argon. Then degassed DMSO (1.1 mL), CsOAc (213 mg, 1.1 mmol, 5 equiv.) and CuI (84 mg, 0.44 mmol, 2 equiv.) were added under argon protection. The reaction mixture was then warmed to 120°C, followed by TLC and quenched after the times indicated in Table 2. The resulting solution was then quenched with ammoniacal aq NaCl and extracted for three times with diethyl ether. The organic layer was dried with MgSO₄, filtered and evaporated in vacuo. Purification by column chromatography afforded pure cyclized compounds (**compounds of type 6**).

4,6-Dimethyl-3-phenyl-1-(4-methylphenylsulfonyl)-indoline (**6ab**), (Table 2, entry 1).

Following the general procedure described above, a solution of 2-phenyl-2-(4,6-dimethyl-2-trifluoromethanesulfonyl phenyl)-*N*-(4-methylphenylsulfonyl)-ethanamine (**5ab**) (0.22 mmol, 115.9 mg) in degassed DMSO (1.1 mL) was added to a dried mixture of CuI (0.44 mmol, 84 mg) and CsOAc (1.1 mmol, 213 mg) under argon protection. The solution was then warmed to 120°C. The mixture was allowed to react for 12 hours. The product was isolated (Yield=72%) by column chromatography eluting with hexanes/AcOEt 7:3, as a solid (M.p= 185-187°C).

¹H NMR (CDCl₃) δ 1.78 (s, 3H); 2.37 (s, 3H); 2.39 (s, 3H); 3.79- 3.93 (m, 1H); 4.18- 4.32 (m, 2H); 6.62 (br, s, 1H); 6.67- 6.76 (m, 2H); 7.04- 7.23 (m, 5H); 7.47 (br, s, 1H); 7.66 (d, 2H, *J*= 8.3 Hz).

² Yamada, K.; Kubo, T.; Tukuyama, H.; Fukuyama, T. *Synlett* **2002**, 231.

^{13}C NMR (CDCl_3) δ 19.16, 22.23, 30.37, 45.56, 59.59, 113.58, 127.05, 127.26, 127.89, 128.00, 129.25, 130.30, 134.59, 135.92, 139.41, 143.69, 144.57.

5-Methyl-3-phenyl-1-(4-methylphenylsulfonyl)-indoline (6af), (Table 2, entry 2).

Following the general procedure described above, a solution of 2-phenyl-2-(5-methyl-2-trifluoromethansulfonylphenyl)-1-(4-methylphenylsulfonyl)-ethanamine (**5af**) (0.22 mmol, 112.9 mg) in degassed DMSO (1.1 mL) was added to a dried mixture of CuI (0.44 mmol, 84 mg) and CsOAc (1.1 mmol, 213 mg) under argon protection. The solution was then warmed to 120°C. The mixture was allowed to react for 12 hours. The product was isolated (Yield=77%) by column chromatography eluting with hexanes/AcOEt 8:2, as a solid. R_f = 0.34 (hexanes/AcOEt 8:2).

^1H NMR (CDCl_3) δ 2.20 (s, 3H); 2.38 (s, 3H); 3.74 (dd, 1H, J_1 =7.9 Hz, J_2 = 4.4 Hz); 4.24- 4.48 (m, 2H); 6.64 (br, s, 1H); 6.80- 6.91 (m, 2H); 7.03- 7.34 (m, 6H); 7.67- 7.75 (m, 2H).

^{13}C NMR (CDCl_3) δ 30.37, 30.99, 47.05, 59.29, 115.49, 126.79, 127.70, 127.76, 128.11, 128.45, 129.36, 130.01, 130.16, 130.35, 133.94, 134.29, 139.58, 144.40.

4,6-Dimethyl-3-(4-fluorophenyl)-1-(4-methylphenylsulfonyl)-indoline (6db), (Table 2, entry 4).

Following the general procedure described above, a solution of 2-(4-fluorophenyl)-2-(4,6-dimethyl 2-trifluoromethansulfonylphenyl)-1-(4-methylphenylsulfonyl)-ethanamine (**5db**) (0.22 mmol, 119.8 mg) in degassed DMSO (1.1 mL) was added to a dried mixture of CuI (0.44 mmol, 84 mg) and CsOAc (1.1 mmol, 213 mg) under argon protection. The solution was then warmed to 120°C. The mixture was allowed to react for 12 hours. The product was isolated (Yield=90%) by column chromatography eluting with hexanes/AcOEt 8:2, as a solid (M.p= 155-157°C). R_f = 0.29 (hexanes/AcOEt 8:2).

^1H NMR (CDCl_3) δ 1.79 (s, 3H); 2.37 (s, 3H); 2.39 (s, 3H); 3.76- 3.88 (m, 1H); 4.11- 4.31 (m, 2H); 6.58- 6.88 (m, 5H); 7.19 (d, 2H, J = 8.2 Hz); 7.47 (br, s, 1H); 7.64 (d, 2H, J = 8.2 Hz).

^{13}C NMR (CDCl_3) δ 19.10, 22.17, 30.38, 44.71, 59.57, 113.73, 115.85, 116.26, 127.16, 127.97, 129.25, 129.41, 130.16, 130.30, 134.62, 135.81, 142, 73, 144.68.

(2*S,3*S**)-4,6-Dimethoxy-2-methyl-3-phenyl-1-(4-methylphenylsulfonyl)-indoline (6fd), (Table 2, entry 5).**

Following the general procedure described above, a solution of (1*S**, 2*S**)-1-phenyl-1-(4,6-dimethoxyphenyl)-2-trifluoromethanesulfonyl-2-(4-methylphenylsulfonyl)-propan-2-amine (**5fd**), (0.22 mmol, 126.1 mg) in degassed DMSO (1.1 mL) was added to a dried mixture of CuI (0.44 mmol, 84 mg) and CsOAc (1.1 mmol, 213 mg) under argon protection. The solution was then warmed to 120°C. The mixture was allowed to react for 12 hours. The product was isolated (Yield=22%) by column chromatography eluting with hexanes/AcOEt 8:2, as a solid (M.p= 109-110°C).

^1H NMR (CDCl_3) δ 1.05 (d, 3H, J = 6.1 Hz); 2.39 (s, 3H); 3.48 (s, 3H); 3.88 (s, 3H); 4.33- 4.42 (m, 2H); 6.14 (d, 1H, J = 2.0 Hz); 6.90- 6.97 (m, 2H); 7.07 (d, 1H, J = 2.0 Hz); 7.16- 7.23 (m, 5H); 7.65 (d, 2H, J = 8.3 Hz).

^{13}C NMR (CDCl_3) δ 30.45, 49.66, 56.00, 56.47, 64.45, 94.87, 96.25, 106.91, 110.89, 127.45, 128.17, 128.53, 129.60, 130.37, 139.33, 144.71, 145.20, 157.50, 162.35.

Demonstration of the absolute configuration of compound 6aa

(2S)-(+)-3-Phenyl-1-(4-methylphenylsulfonyl)-indoline (6aa)³, (Table 2, entry 3).

Following the general procedure described above, a solution of 2-phenyl-2-(2-trifluoromethansulfonyloxyphenyl)-1-(4-methylphenylsulfonyl)-ethanamine (**5aa**) (0.22 mmol, 109.8 mg) in degassed DMSO (1.1 mL) was added to a dried mixture of CuI (0.44 mmol, 84 mg) and CsOAc (1.1 mmol, 213 mg) under argon protection. The solution was then warmed to 120°C. The mixture was allowed to react for 12 hours. The product was isolated (Yield=45%) by column chromatography eluting with hexanes/AcOEt 85:15, as a solid.³

¹H NMR (CDCl₃) δ 2.39 (s, 1H); 3.67- 3.84 (m, 1H); 4.31- 4.38 (m, 2H); 6.84- 7.09 (m, 4H); 7.17- 7.28 (m, 6H); 7.68 (d, 2H, *J*= 8.2 Hz); 7.74 (d, 1H, *J*= 8.3 Hz).

[α]_D²⁰ = +55.4 (*c* 0.35, CHCl₃).

The absolute configuration (*S*) was assigned after comparison of the sign of the optical rotatory power with the value reported in the literature (Lit. [α]_D²⁰ = +88.9).³

HPLC analysis performed on a Daicel Chiralcel[®] OD-H column, flow rate: 0.5 mL/min, mobile phase: hexane/isopropanol 80/20, retention times (min): 16.02 (*S*, major stereoisomer); 20.67 (*R*, minor stereoisomer).

³ Kuwano, R.; Kaneda, K.; Ito, T.; Sato, K.; Kurokawa, T.; Ito, Y. *Org. Lett.* **2004**, 6, 2213.

TABLE 3. Additional results of the uncatalyzed carbon-carbon coupling of different aryl borates with styrenyl aziridines.^a

entry	aziridine	conditions	Ar ₃ B (Ar=) ^b	C-Alk /O-Alk	C-alkylated product (yield) ^c	Anti/Syn
1	Rac-2a	18h, -78°C	1f	75/25	3af (65)	N/A
2	(S)-2a	5h, -78°C	1d	>95/<5	3ad (84)	>99/<1
3	Rac-2g	8h, -78°C	1d	>95/<5	3gd (63)	N/A
4	Rac-2d	24h, -78°C to rt	1d	>95/<5	3dd (89)	N/A
5	Rac-2g	24h, -78°C	1b	>95/<5	3gb (68)	N/A

^a All reactions were carried out in accordance with general procedure. ^b All phenols were treated with BH₃·Et₂O to form corresponding aryl borates immediately before use. ^c Isolated yield after chromatography on silica gel.

2-Phenyl-2-(2-hydroxy-5-methylphenyl)-N-(4-methylphenylsulfonyl)-ethanamine (3af), (Table 3, entry 1).

Using the general procedure described above, a solution of tris (*p*-methylphenyl) borate (**1f**) (249 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at –78°C under argon to a solution of *N*-Ts aziridine of styrene (**2a**) (136.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 18 hours at –78 °C. The product was isolated (Yield=65%) by column chromatography eluting with hexanes/AcOEt 7:3, as a solid. M.p= 110-112°C.

¹H NMR (CDCl₃) δ 2.14 (s, 3H); 2.41 (s, 3H); 3.48- 3.62 (m, 2H); 4.44 (t, 1H, *J*= 7.9 Hz); 4.70- 4.86 *NH* (m, 1H); 6.59- 6.69 (m, 2H); 6.80- 6.89 (m, 1H); 7.08- 7.32 (m, 7H); 7.65 (d, 1H, *J*= 8.3 Hz).

¹³C NMR (CDCl₃) δ 22.31, 22.21, 44.50, 47.15, 116.56, 127.57, 127.80, 128.81, 129.18, 129.33, 129.50, 130.37, 141.25, 144.08, 152.08.

ESIMS (neg.): *m/z* 380 [M-H].

Anal. Calcd. For C₂₂H₂₃NO₃S: C, 69.26%; H, 6.08%; N, 3.67%; S, 8.41%. Found: C, 71.15%; H, 6.10%; N, 3.30%; S, 8.39%.

The first eluting fractions of the above described column chromatography afforded pure **2-phenyl-2-(4-methylphenoxy)-N-(4-methylphenylsulfonyl)-ethanamine (4af)**, (Table 3, entry 1), as a white solid (yield= 6%). M.p= 75-77°C.

¹H NMR (CDCl₃) δ 2.21 (s, 3H); 2.40 (s, 3H); 3.23 (ddd, 1H, *J*₁= 13.2 Hz, *J*₂= 9.0 Hz; *J*₃= 3.8 Hz); 3.41 (ddd, 1H, *J*₁= 13.2 Hz, *J*₂= 9.0 Hz; *J*₃= 3.6 Hz); 5.03- 5.17 *CH-OAr* + *NH* (m, 2H); 6.55- 6.66 (m, 2H); 6.70- 6.79 (m, 1H); 6.94 (d, 2H, *J*= 8.2 Hz); 7.03 (d, 1H, *J*= 8.2 Hz); 7.13- 7.39 (m, 5H); 7.67- 7.78 (m, 2H).

¹³C NMR (CDCl₃) δ 21.12, 22.19, 50.17, 79.22, 116.29, 126.72, 127.67, 128.97, 129.46, 130.44, 130.67, 131.34, 137.60, 138.70, 144.21, 155.6.

(2S)-2-Phenyl-2-(4,6-dimethoxy-2-hydroxy-phenyl)-N-(4-methylphenylsulfonyl)-ethanamine (3ad), (Table 3, entry 2).

Using the general procedure described above, a solution of tris (3,5-dimethoxyphenyl)borate (**1d**) (352.5 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at –78°C under argon to a solution of (*S*)-N-Ts aziridine of styrene (**2a**) (136.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 5 hours at –78 °C. The product was isolated (Yield=84%) by column chromatography eluting with hexanes/AcOEt 6:4, as a solid. M.p= 116- 118°C. R_f= 0.33 (hexanes/AcOEt 6:4).

¹H NMR (CDCl₃) δ 2.39 (s, 3H); 3.57 (s, 3H); 3.60- 3.80 (m, 5H); 4.68- 4.59 CH-OAr + NH (m, 2H); 5.92 – 5.98 (m, 2H); 7.05- 7.24 (m, 7H); 7.64 (d, 2H, *J*= 8.0 Hz).

¹³C NMR (CDCl₃) δ 22.19, 40.40, 45.85, 55.90, 56.13, 92.38, 95.09, 108.29, 126.97, 127.76, 128.37, 128.95, 130.23, 142.04, 143.82, 156.31, 160.15, 160.69.

HPLC analysis performed on a Daicel Chiralcel[®] OD-H column, flow rate:0.5 mL/min, mobile phase: hexane/isopropanol 92/8, retention times (min): 49.80 (*R*, minor stereoisomer); 58.17 (*S*, major stereoisomer).

2-(4-Fluorophenyl)-2-(4,6-dimethoxy-2-hydroxy-phenyl)-N-benzyloxycarbonyl-ethanamine (3gd), (Table 3, entry 3).

Using the general procedure described above, a solution of tris (3,5-dimethoxyphenyl) borate (**1d**) (352.5 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at –78°C under argon to a solution of *N*-Cbz aziridine of *p*-fluoro-styrene (**2g**) (135.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 8 hours at –78 °C. The product was isolated (Yield=63%) by column chromatography eluting with hexanes/AcOEt 7:3, as a solid (M.p= 55- 56°C).

^1H NMR (CDCl_3) δ 3.67 (s, 3H); 3.71 (s, 3H); 3.83- 4.00 (m, 1H); 4.02- 4.20 (m, 1H); 4.71 (t, 1H, J = 7.8 Hz); 4.95- 5.20 (m, 3H); 5.98- 6.08 (m, 2H); 6.88 (t, 2H, J = 8.7 Hz); 7.18- 7.42 (m, 7H).

^{13}C NMR (CDCl_3) δ 40.22, 44.16, 55.71, 56.15, 67.69, 91.89, 95.04, 115.21, 115.63, 128.64, 128.75, 129.14, 129.99, 130.13, 137.02, 138.68, 156.76, 159.43, 160.42, 164.25.

2-(4-Fluorophenyl)-2-(4,6-dimethoxy-2-hydroxyphenyl)-N-(4-methylphenylsulfonyl)-ethanamine (3dd), (Table 3, entry 4).

Using the general procedure described above, a solution of tris (3,5-dimethoxyphenyl) borate (**1d**) (352.5 mg, 0.75 mmol) in CH_2Cl_2 (0.5 mL) was added at -78°C under argon to a solution of *N*-Ts aziridine of *p*-fluoro-styrene (**2d**) (136.5 mg, 0.5 mmol) in CH_2Cl_2 (1.5 mL). The mixture was allowed to react for 20 hours at -78°C and for 4 hours at rt. The product was isolated (Yield=89%) by column chromatography eluting with hexanes/AcOEt 7:3, as a solid. M.p= 40- 41 $^\circ\text{C}$. R_f = 0.19 (hexanes/AcOEt 7:3).

^1H NMR (CDCl_3) δ 2.40 (s, 3H); 3.56 (s, 3H); 3.66 (s, 3H); 3.59- 3.84 (m, 2H); 4.54- 4.67 (m, 1H); 4.81- 4.95 CH_2NH (m, 1H); 5.91- 6.10 (m, 2H); 6.84 (t, 2H, J = 8.7 Hz); 7.11- 7.30 (m, 4H); 7.65 (d, 2H, J = 8.2 Hz).

^{13}C NMR (CDCl_3) δ 22.13, 40.05, 46.10, 55.80, 55.96, 92.18, 94.86, 108.12, 115.20, 115.61, 127.63, 129.87, 130.00, 130.25, 143.95, 156.30, 160.05, 160.57, 164.27.

2-(4-Fluorophenyl)-2-(4,6-dimethyl-2-hydroxyphenyl)-N-benzyloxycarbonyl-ethanamine (3gb), (Table 3, entry 5).

Using the general procedure described above, a solution of tris (3,5-dimethylphenyl) borate (**1b**) (280.5 mg, 0.75 mmol) in CH_2Cl_2 (0.5 mL) was added at -78°C under argon to a solution of *N*-Cbz aziridine of *p*-fluoro-styrene (**2g**) (135.5 mg, 0.5 mmol) in CH_2Cl_2 (1.5 mL). The mixture was allowed to react for 1 hour at -78°C . The

product was isolated (Yield=68%) by column chromatography eluting with hexanes/AcOEt 8:2, as a semisolid.

^1H NMR (CDCl_3) δ 2.20 (s, 6H); 3.83- 3.96 (m, 1H); 4.08- 4.18 (m, 1H); 4.46- 4.54 (m, 1H); 5.07 (s, 2H); 6.43 (s, 1H); 6.58 (s, 1H); 6.86- 6.95 (m, 2H); 7.19- 7.32 (m, 7H).

^{13}C NMR (CDCl_3) δ 21.36, 21.47, 44.29, 44.53, 67.48, 115.52, 115.93, 124.94, 128.70, 128.83, 129.19, 129.93, 130.07, 136.99, 137.90, 138.35, 139.41, 155.04, 164.39.

ESIMS (neg.): m/z 392 $[\text{M-H}]$.

Anal. Calcd. For $\text{C}_{24}\text{H}_{24}\text{FNO}_3$: C, 73.26%; H, 6.15%; F, 4.83% N, 3.56%. Found: C, 73.40%; H, 6.18%; F, 4.77; N, 3.45%.

TABLE 4. Additional results of the uncatalyzed carbon-carbon coupling of different aryl borates with disubstituted aziridines.

entry	aziridine	Conditions	Ar ₃ B (Ar=) ^b	C-Alk /O-Alk	C-alkylated product (yield) ^c	Anti/syn
1	2h	14h, -78°C	1d	90/10	3hd (90)	>99/<1
2	2i	2.5h, rt	1d	>95/<5	3id (82)	>99/<1
3	2l	1h, 0°C	1d	Nd	Complex mixture	N/A
4	2m	18h, rt	1d	Nd	7^d (30)	Nd
5	2n	18h, -78°C	1b	Nd	Complex mixture	N/A

^a All reactions were carried out in accordance with general procedure. ^b All phenols were treated with BH₃·Et₂O to form corresponding aryl borates immediately before use. ^c Isolated yield after chromatography on silica gel. ^d Obtained after deprotection with BF₃·Et₂O as described in literature (*vide infra*).⁴

(1*S,2*S**)-1-Phenyl-1-(2-hydroxy-4,6-dimethoxyphenyl)-*N*-benzyloxycarbonyl-propan-2-amine (3hd), (Table 4, entry 1).**

Using the general procedure described above, a solution of tris (3,5-dimethoxyphenyl) borate (**1d**) (352.5 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at –78 °C under argon to a solution of *N*-Cbz aziridine of β-methyl-styrene (**2h**) (133.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 1 hour at –78 °C. The product was isolated (Yield=90%) by column chromatography eluting with hexanes/AcOEt 7:3, as a solid (M.p=65- 68 °C). R_f= 0.13 (hexanes/AcOEt 7:3).

¹H NMR (CDCl₃) δ 1.23 (d, 3H, *J*= 6.4 Hz); 3.59 (s, 3H); 3.79 (s, 3H); 4.38 *CH*-Ar (d, 1H, *J*= 11.2 Hz); 4.75- 4.85 *CH-NH* (m, 1H); 5.06 (s, 2H); 5.32- 5.49 *CH*-NH (m, 1H); 6.00 (d, 1H, *J*= 2.3 Hz); 6.13 (d, 1H, *J*= 2.3 Hz); 7.08- 7.37 (m, 8H); 7.55- 7.67 (m, 2H).

¹³C NMR (CDCl₃) δ 21.54, 48.29, 49.00, 55.54, 56.36, 67.03, 91.21, 94.69, 110.40, 126.48, 128.12, 128.61, 129.14, 129.38, 137.10, 143.44, 157.17, 159.43, 160.04.

ESIMS (neg.): *m/z* 420 [M-H].

Anal. Calcd. For C₂₅H₂₇NO₅: C, 71.24%; H, 6.46%; N, 3.32%. Found: C, 71.34%; H, 6.39%; N, 3.10%.

(1*S, 2*S**)-1-Phenyl-1-(4,6-dimethoxy-2-hydroxy phenyl)-*N*-diphenylphosphinyl-propan-2-amine (3id), (Table 4, entry 2).**

Using the general procedure described above, a solution of tris (3,5-dimethoxyphenyl) borate (**1d**) (352.5 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at rt under argon to a solution of *N*-P(O)Ph₂ aziridine of β-methyl-styrene (**2i**) (173.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 2.5 hours at rt. The product

was isolated (Yield=82%) by column chromatography eluting with hexanes/AcOEt 7:3, as a solid.

¹H NMR (CDCl₃) δ 1.24 (d, 1H, *J*= 6.0 Hz); 3.62 (s, 3H); 3.69 (s, 3H); 4.40- 4.55 (m, 2H); 5.97 (d, 1H, *J*= 2.4

Hz); 6.23 (d, 1H, J = 2.4 Hz); 7.15- 7.46 (m, 13H), 7.72- 7.82 (m, 2H).

^{13}C NMR (DMSO) δ 23.85, 49.06, 49.19, 54.75 (2 carbon); 90.12, 94.01, 110.28, 125.42, 127.31, 127.73, 127.96, 128.17, 129.64, 130.79, 131.12, 131.46, 131.63, 131.94, 132.11, 156.34, 158.70, 158.86.

Ring-opening of *N*-Cbz aziridine of stilbene (2l**) with tris (3,5-dimethoxyphenyl) borate (**1d**), (Table 4, entry 3).**

Using the general procedure described above, a solution of tris (3,5-dimethoxyphenyl) borate (**1d**) (352.5 mg, 0.75 mmol) in CH_2Cl_2 (0.5 mL) was added at 0°C under argon to a solution of *N*-Cbz aziridine of stilbene (**2l**) (164.5 mg, 0.5 mmol) in CH_2Cl_2 (1.5 mL). The mixture was allowed to react for 1 hour at 0°C. The reaction afforded a complex mixture.

1,2-Diphenyl-1-(2-hydroxy-4,6-dimethoxyphenyl)-ethanamine (7**), (Table 4, entry 4).**

Using the general procedure described above, a solution of tris (3,5-dimethoxyphenyl) borate (**1d**) (352.5 mg, 0.75 mmol) in CH_2Cl_2 (0.5 mL) was added at rt under argon to a solution of *N*-P(O)Ph₂ aziridine of stilbene (**2m**) (211.5 mg, 0.5 mmol) in CH_2Cl_2 (1.5 mL). The mixture was allowed to react for 18 hours at rt. The *C*-alkylated product (**3md**) was isolated (Yield=71%) by column chromatography eluting with $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 7:3, as a solid. The deprotection of compound **3md** (122.5 mg, 0.22 mmol) with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (312.4 mg, 2.2 mmol) in MeOH (4.4 mL) and CH_2Cl_2 (4.4 mL) at rt⁴ afforded compound **7** (overall yield= 30%), as a solid (m.p= 152-155 °C). R_f = 0.07 (hexanes/AcOEt 6:4).

^1H NMR (CDCl_3) δ 3.61 (s, 3H); 3.80 (s, 3H); 4.62 (br, s, 1H); 4.99 (br, s, 1H); 5.97 (d, 1H, J =2.5 Hz); 6.22 (d, 1H, J =2.5 Hz); 6.85- 6.93 (m, 2H); 7.03- 7.39 (m, 8H). ^{13}C NMR (CDCl_3) δ 49.43, 55.88, 56.57, 57.39, 90.86, 95.57, 110.93, 126.83, 127.44, 127.91, 128.54, 129.04, 130.72, 132.45, 138.33, 145.44, 159.27, 159.85.

⁴ Cantrill, A. A.; Osborn, H. M. I.; Sweeney, J. *Tetrahedron*, **1998**, 54, 2181- 2208.

Ring-opening of *N*-Ts aziridine of indene (2n**) with tris (3,5-dimethylphenyl) borate (**1b**), (Table 4, entry 5).**

Using the general procedure described above, a solution of tris (3,5-dimethylphenyl) borate (**1b**) (280.5 mg, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added at -78°C under argon to a solution of *N*-Ts aziridine of indene (**2n**) (142.5 mg, 0.5 mmol) in CH₂Cl₂ (1.5 mL). The mixture was allowed to react for 18 hours at -78°C. The reaction afforded a complex mixture.