Supporting Data

General Methods. NMR spectra were recorded on a Varian Unity 300 spectrometer in the specified solvent and at a probe temperature of 23 ˚C. Radial Chromatography was carried out using a Chromatotron (Harrison Research Inc.) using glass plates coated with Merck type 60 P.F.$_{254}$ silica gel. All other details as previously reported.[1]

(1*S*,4*R*)-1-(10-Camphorsulfonyl)pyrrole-2-carboxaldehyde 9a and [*formyl-d*]-(1*S*,4*R*)-1-(10-camphorsulfonyl)pyrrole-2-carboxaldehyde 9b. To a stirred suspension of sodium hydride (1.2 equiv) in THF (5 mL) was added **8a** (20 mg, 0.21 mmol) in THF (2 mL). After stirring at rt for 15 min, (1*S*,4*R*)-(+)-10-camphorsulfonyl chloride (63 mg, 0.25 mmol) in THF (2 mL) was slowly added and stirring was continued for 1 h at rt. Water (10 mL) was added, the THF was removed under reduced pressure and the aqueous residue was extracted with dichloromethane (3x15 mL). The combined organic phases were washed with saturated aqueous sodium hydrogen carbonate (10 mL), water (10 mL), brine (10 mL), dried and concentrated under reduced pressure. The residue was purified by flash chromatography on silica (ethyl acetate/petroleum ether, 1:3) to give **9a** (62 mg, 95%) as a colorless oil which solidified at 0 ºC, mp 97 °C (petroleum ether); IR ($CHCl_3$) 1747, 1678, 1377, 1171 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.95 (s, 3H), 1.20 (s, 3H), 1.48 (m, 1H), 1.78 (m, 1H), 1.92 – 2.17 (m, 3H), 2.36 – 2.55 (m, 2H), 3.94 and 4.08 (ABq, J = 14.7 Hz, 2H), 6.41 (m, 1H), 7.22 (m, 1H), 7.61 (m, 1H), 9.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.6, 19.7, 25.2, 27.0, 42.5, 42.7, 48.3, 52.6, 58.9, 111.3,

128.9, 130.7, 133.1, 178.2, 213.9; HRMS calcd for $C_{15}H_{19}NO_4S$ 309.1035, found 309.1037.

The reaction was repeated using **8b** (20 mg, 0.21 mmol) to give **9b** (64 mg, 99%): ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.4, 19.5, 25.0, 26.7, 42.2, 42.4, 48.1, 52.4, 58.7, 111.2, 128.7, 130.5, 132.8, 177.8 (t, *J* = 28.2 Hz), 213.7; HRMS calcd for $C_{15}H_{18}DNO_4S$ 310.1098, found 310.1094.

(1*S*,4*R*)-2-Hydroxymethyl-1-(10-camphorsulfonyl)pyrrole 10a. The *N*-camphorsulfonylpyrrole **9a** (27 mg, 0.09 mmol) was reduced with zinc borohydride (1 equiv) in ether. Purification of the residue by flash chromatography on silica (ethyl acetate/petroleum ether, 1:2) gave **10a** (24 mg, 88%) as a colorless oil: IR ($CHCl_3$) 3514, 1746, 1369, 1175 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.87 (s, 3H), 1.10 (s, 3H), 1.50 (m, 1H), 1.85 (m, 1H), 1.95 – 2.17 (m, 3H), 2.37 – 2.50 (m, 2H), 3.29 and 3.83 (ABq, *J* = 14.7 Hz, 2H), 3.63 (bs, 1H, O*H*), 4.73 and 4.88 (ABq, *J* = 13.2 Hz, 2H, CH_2OH), 6.23 (m, 1H), 6.29 (m, 1H), 7.15 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.5, 19.6, 25.3, 26.8, 42.5, 42.8, 48.3, 52.8, 56.4, 58.7, 111.0, 115.1, 123.1, 134.2, 214.7; HRMS calcd for $C_{15}H_{21}NO_4S$ 311.1191, found 311.1193.

(1*S*,4*R*)-2-Chloromethyl-1-(10-camphorsulfonyl)pyrrole 12a. A solution of **10a** (7 mg, 0.02 mmol) in $CDCl_3$ (150 μL) containing N,N-diisopropylethylamine (11 μL, 0.06 mmol) in a 3 mm NMR tube was cooled in an ice bath under a stream of N_2. Methanesulfonyl chloride (5 μL, 0.06 mmol) was added with mixing and the progress of the reaction was monitored by ^1H NMR. When no starting material was observed by ^1H

NMR, the reaction was poured into dichloromethane (10 mL), washed with ice-cold water (10 mL), cold 10% aqueous hydrochloric acid (10 mL), and saturated aqueous sodium hydrogen carbonate (10 mL). The organic phase was then dried and evaporated under reduced pressure. The residual oil was dried under high vacuum (oil pump) for 3 h to give the crude **12a** (7 mg) as a yellow oil. Selected ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (s, 3H), 1.20 (s, 3H), 1.48 (m, 1H), 1.79 (m, 1H), 1.94 – 2.15 (m, 3H), 2.37 – 2.62 (m, 2H), 3.56 and 3.82 (ABq, *J* = 14.7 Hz, 2H), 4.86 and 5.07 (ABq, *J* = 12.7 Hz, 2H, C*H*$_2$Cl), 6.27 (m, 1H), 6.43 (m, 1H), 7.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.7, 19.9, 25.2, 27.0, 38.0, 42.5, 42.7, 48.1, 52.9, 59.0, 111.3, 117.1, 124.5, 129.8, 213.8; HRMS calcd for $C_{15}H_{20}ClNO_3S$ 329.0852, found 329.0851.

[*methylene-d*$_1$]-(1*S*,4*R*)-2-Chloromethyl-1-(10-camphorsulfonyl)pyrroles 12b and 12c. *S*-Alpine borane sequence: General procedure C (reference 1) was carried out using **9b** (12 mg, 0.04 mmol) and *S*-Alpine borane (86 μL of 0.5 M solution in THF, 0.04 mmol). Purification of the residue by flash chromatography on silica (ethyl acetate/petroleum ether, 1:2) gave a mixture of **10b** and **10c** (9 mg, 70%, 19:1) as a colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.87 (s, 3H), 1.11 (s, 3H), 1.51 (m, 1H), 1.86 (m, 1H), 1.95 – 2.17 (m, 3H), 2.37 – 2.50 (m, 2H), 3.28 and 3.84 (ABq, *J* = 14.7 Hz, 2H), 3.58 (bs, 1H, O*H*), 4.72 (s, 0.95H, C*H*DOH **10b**), 4.87 (s, 0.05H, C*H*DOH **10c**), 6.23 (m, 1H), 6.30 (m, 1H), 7.15 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.6, 19.7, 25.4, 26.9, 42.5, 42.9, 48.3, 52.9, 56.3 (t, *J* = 21.9 Hz), 58.7, 111.1, 115.1, 123.2, 134.4, 214.7; HRMS calcd for $C_{15}H_{20}DNO_4S$ 312.1254, found 312.1260.

The preceding sample of **10b** and **10c** (5 mg, 0.02 mmol) in $CDCl_3$ (150 μL) in a 3 mm NMR tube was treated with methanesulfonyl chloride (4 μL, 0.05 mmol) under the conditions used for the preparation of **12a**. ^{1}H NMR spectral analysis of the crude reaction mixture showed a mixture of **12b** and **12c** (~2:3). Selected ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.86 (s, 0.6H, C*H*DCl **12c**), 5.05 (s, 0.4H, C*H*DCl **12b**). Subsequent work up of the reaction mixture by the method described for **12a** gave a crude mixture of **12b** and **12c** (8 mg, ~1:1 by ^{1}H NMR) as a pale yellow oil. Selected ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.86 (s, 0.5H, C*H*DCl **12c**), 5.05 (s, 0.5H, C*H*DCl **12b**). HRMS calcd for $C_{15}H_{19}DClNO_3S$ 330.0915, found 330.0918.

***R*-Alpine borane sequence:** General procedure C (reference 1) was carried out using the deuterated *N*-camphorsulfonylpyrrole **9b** (12 mg, 0.04 mmol) and *R*-Alpine borane (83 μL of 0.5 M solution in THF, 0.04 mmol). Purification by flash chromatography on silica (ethyl acetate/petroleum ether, 1:2) gave a mixture of **10b** and **10c** (9 mg, 76%, 1:19) as a colourless oil: Selected ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.72 (s, 0.05H, C*H*DOH **10b**), 4.87 (s, 0.95H, C*H*DOH **10c**).

The preceding sample of **10b** and **10c** (5 mg, 0.02 mmol) in $CDCl_3$ (150 μL) in a 3 mm NMR tube was treated with methanesulfonyl chloride (4 μL, 0.05 mmol, 3 equiv) under the conditions used for the preparation of **12a**. ^{1}H NMR spectral analysis of the crude reaction mixture showed a mixture of **12b** and **12c** (~3:2). Selected ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.86 (s, 0.4H, C*H*DCl **12c**), 5.05 (s, 0.6H, C*H*DCl **12b**). Subsequent work up of the reaction mixture by the method described for **12a** gave a

crude mixture of **12b** and **12c** (6 mg, ~1:1) as a pale yellow oil. Selected ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.86 (s, 0.5H, C*H*DCl **12c**), 5.05 (s, 0.5H, C*H*DCl **12b**).

Reaction of [*methylene-d*$_1$]-(1*S*,4*R*)-2-hydroxymethyl-1-(10-camphorsulfonyl)pyrrole 10b and 10c with methanesulfonic anhydride. A sample of **10b** and **10c** (4 mg, 0.01 mmol, 19:1), obtained from the *S*-Alpine borane sequence described above, in $CDCl_3$ (0.5 mL) containing N,N-diisopropylethylamine (3 μL, 0.02 mmol, 1.5 equiv) was cooled to –78 °C in a 5 mm NMR tube under a stream of N_2. Methanesulfonic anhydride (3 mg, 0.02 mmol, 1.5 equiv) dissolved in $CDCl_3$ (0.2 mL) was added with mixing. The NMR tube was then inserted into the cooled NMR spectrometer (–20 °C probe temperature) and a ^{1}H NMR spectrum of the reaction mixture was recorded (t = 0 min). Spectral analysis of the crude reaction mixture showed a mixture of **11b** and **11c** (~4:1). Selected ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.39 (s, 0.2H, C*H*DOMs **11c**), 5.45 (s, 0.8H, C*H*DOMs **11b**). The reaction mixture was then kept at –20 °C and ^{1}H NMR spectra were recorded at regular intervals in order to monitor the progress of the reaction. A ^{1}H NMR spectrum of the reaction mixture after 30 min showed an equal mixture of the *O*-mesylated pyrroles **11b** and **11c** (~1:1). Selected ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.39 (s, 0.5H, C*H*DOMs **11c**), 5.45 (s, 0.5H, C*H*DOMs **11b**).

A sample of **10b** and **10c** (3 mg, 0.01 mmol, 1:19), obtained from the *R*-Alpine borane sequence above, was treated with methanesulfonic anhydride (3 mg, 0.02 mmol, 1.5 equiv) as described in above. ^{1}H NMR spectral analysis of the crude reaction mixture showed a mixture of **11b** and **11c** (~1:4). Selected ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.39 (s, 0.8H, C*H*DOMs **11c**), 5.45 (s, 0.2H, C*H*DOMs **11b**). The reaction mixture was then kept

at –20 °C and ^{1}H NMR spectra were recorded at regular intervals in order to monitor the progress of the reaction. A ^{1}H NMR spectrum of the reaction mixture after 90 min showed an equal mixture of the *O*-mesylated pyrroles **11b** and **11c** (~1:1). Selected ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.39 (s, 0.5H, C*H*DOMs **11c**), 5.45 (s, 0.5H, C*H*DOMs **11b**).