Enantiomerically Pure *cis*- and *trans*-2-Substituted Cyclopropanols from Allylic Sulfones

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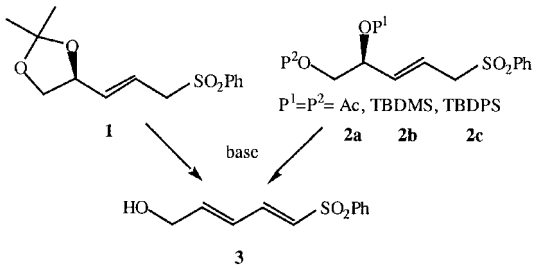
Abstract: Enantiomerically pure *cis*- and *trans*-2-substituted cyclopropanols have been obtained from allylic sulfones derived from (*R*)-glyceraldehyde, in good yields.

Key words: cyclopropanols, sulfones, cyclization, synthesis

1,2-disubstituted cyclopropanes can be found in natural and biologically active molecules.[1] Therefore, and because of their unique reactivity[2] the development of an asymmetric approach to these rings is of considerable interest. Among cyclopropanes, disubstituted cyclopropanols are quite rare, and their chemistry offers great potential[3] especially in the case of vinylic substituents.[4]

As part of our program on the elimination reaction of allylic sulfones such as **1**, we have found that, if the same protecting group is used for both hydroxyl groups,[5] these compounds give rise to 1-hydroxymethyl-4-sulfonylbutadienes (Scheme 1).



Scheme 1

In a recent paper, we differentiated the two hydroxyl groups.[6] The primary hydroxyl group was converted into a good leaving group (iodide) and the secondary one protected with a very stable group (tetrahydropyranyl). The stereogenic center was preserved in order to obtain cyclopropanols in enantiomerically pure form instead of dienes, in the above reaction. To extend the methodology, several protecting groups were tested, and the best conditions for obtaining enantiomerically enriched cyclopropanes are reported here.

Compound **1**, previously synthesized by us,[5] was deprotected with 2 N HCl in methanol, to yield diol **4**. This compound reacts selectively with *p*-toluenesulfonyl chloride in pyridine to give **5**, which was transformed under the usual conditions of protection and substitution into iodide **6**.[6] In order to obtain the different iodides, compound **6** was protected as its THP, TBDMS, and $C(CH_3)_2(OCH_3)$,[7] derivatives (**13**, **16** and **17** respectively). The MOM derivative was better prepared by protection of the tosylate **5** to give **11**, followed by conversion to iodide **14** (Scheme 2).

The benzyl derivative **15** was made from diol **4** by protection under the usual conditions to yield the acetal **7**. Reduction was attempted under a variety of conditions, with $NaCNBH_3$–TMSCl giving the best results, yielding compounds **8** and **9** in a 1:1 ratio. Compound **8** was transformed into the required **15** as usual by tosylation and reaction of the corresponding tosylate **12** with sodium iodide.

Once the starting materials **13**–**17** had been obtained, they were treated separately with LDA as base. In a recent paper, we showed that if the secondary alcohol was protected as its tetrahydropyranyl derivative, then treatment under basic conditions led to the protected cyclopropanes in good yield as a 70:30 mixture of **18** and **19**.[6] The same ratio was observed using 1.0 or 1.5 equivalents of LDA, but a better yield was achieved in the latter case (Scheme 3).

Here we show that this reaction can be extended to other protecting groups that add more versatility to our methodology. Treatment of compounds **13**–**17** with LDA as base led to the desired cyclopropanes in different, even reversed diastereomeric ratios, depending on the protecting group.

The configuration of the double bond in all vinylcyclopropanes was assigned according to the coupling constant of its vicinal hydrogens (^3J = 15.0 Hz).[6] The ratio of the diastereomeric cyclopropanes formed can be rationalized on the basis of the competition between the bulkiness of the protecting group, the chelating effect between the neighboring oxygenated group and the 1-sulfonylallyllithium intermediate with delocalization of the partial negative charge (Scheme 3).[8]

Deprotection under acidic conditions of **18** led to aldehyde **28** (Scheme 4). For this reason it was decided to hydrogenate first and then deprotect to obtain the required cyclopropanols.

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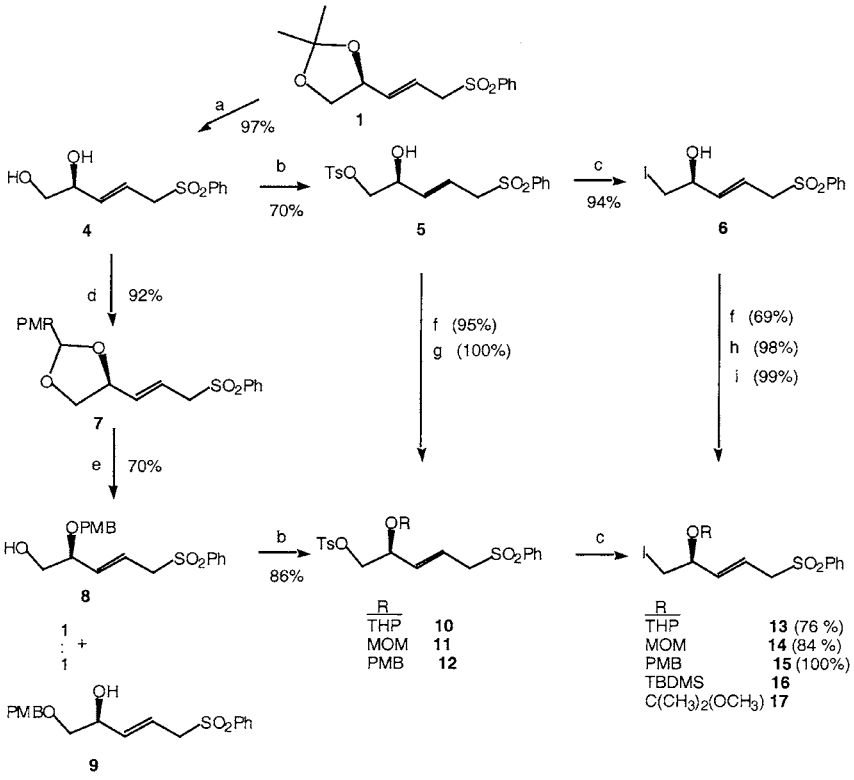
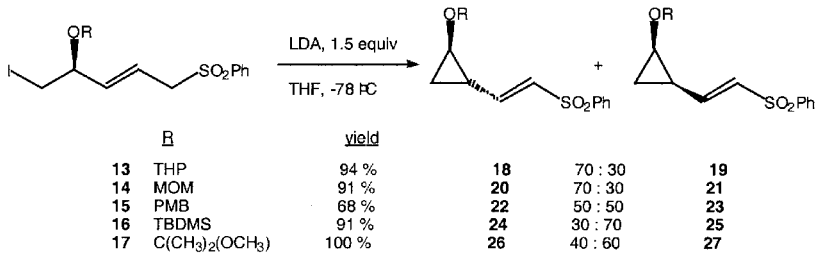
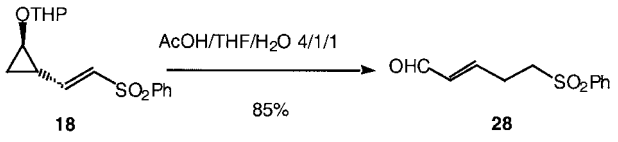


Scheme 2 *Reagents and conditions*: (a) HCl 2N, MeOH, r.t.; (b) TsCl, pyridine, r.t., (c) NaI, acetone, 80 ºC; (d) *p*-$MeOC_6H_4CH(OMe)_2$, TsOH, PhH, 130 ºC; (e) $NaCNBH_3$, TMSCl, MeCN, r.t.; (f) DHP, TsOH, CH_2Cl_2, r.t.; (g) $CH_2(OCH_3)_2$, P_2O_5, $CHCl_3$, r.t.; (h) TBDMSOTf, 2,6-lutidine, THF, r.t.; (i) 2-methoxypropene, PPTS, r.t.



Scheme 3



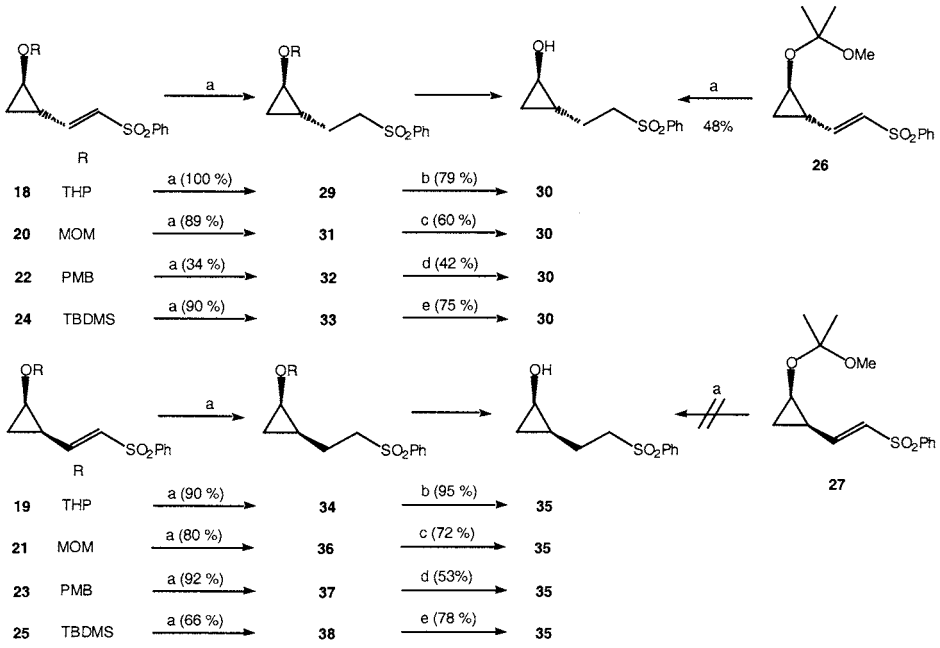
Scheme 4

While compounds **18**–**25** were hydrogenated giving saturated protected cyclopropanols **29**, **31**–**33**, **34**, **36**–**38** which were subsequently deprotected separately to yield **30** and **35**, compound **26** gave compound **30** directly on hydrogenation. Compound **27** decomposed, possibly due to steric encumbrance of the double bond (Scheme 5).

The configuration of these compounds was determined from the ^{1}H NMR spectra on the basis of the coupling constants J_{1-2} = 2.8 Hz for **30**, J_{1-2} = 6.4 Hz for **35**, and extensive NOE studies.

In conclusion, we have developed a convenient method for the synthesis of enantiomerically pure *cis*- and *trans*-2-substituted cyclopropanols with great synthetic potential. It is necessary to differentiate the two hydroxy groups of the 5-benzenesulfonyl-pent-3-ene-1,2-diol (**4**), to obtain the desired cyclopropanols on treatment with base, since undifferentiated protection of both hydroxyl groups led to elimination of the protecting group and diene formation.

^{1}H NMR spectra were recorded in $CDCl_3$ (ref. δ = 7.26) at 200 and 400 MHz on Varian 200 VX and BRUKER DRX 400 instruments, respectively. ^{13}C NMR spectra were recorded in $CDCl_3$ (ref. δ = 77.0) at 50 and 100 MHz on Varian 200 VX and BRUKER DRX 400 instruments, respectively, and multiplicities were determined by DEPT experiments. IR spectra were registered on a



Scheme 5 *Reagents and conditions*: (a) H_2, PtO_2, EtOAc; (b) TsOH, MeOH; (c) THF–H_2O–HCl 6M 1:5:2; (d) H_2, Pd/C, EtOAc; (e) TBAF, THF.

BOMEM 100 FT IR spectrophotometer. Optical rotations were determined using a Perkin-Elmer 241 polarimeter and 1 dm cells. The electron impact (EI) mass spectra were run on a VG-TS 250 spectrometer at 70 eV ionizing voltage. HRMS were recorded in a VG Platform (Fisons) spectrometer using Chemical Ionization (ammonia as gas) or Fast Atom Bombardment (FAB) technique. Column chromatography was performed with Merck silica gel 60 (70–230 mesh). Solvents and reagents were generally distilled immediately prior to use: THF from sodium benzophenone ketyl; CH_2Cl_2 and diisopropylamine from CaH_2; pyridine from KOH.

(–)-(2*S*)-5-Benzenesulfonyl-pent-3-ene-1,2-diol (4)

To a soln of **1** (1.02 g, 3.62 mmol) in MeOH (10 mL) were added an aq soln of 2 N HCl (2 mL), the mixture was left to stir for 2 h before completion. To stop the reaction, an aq soln of Na_2CO_3 (10%) was added until neutralization occured. The mixture was poured into an Erlenmeyer with Et_2O, dried over anhyd Na_2SO_4, filtered and the solvent removed in vacuo to give 0.85 g of diol **4** (97% yield).

$[\alpha]_D^{20}$ –6.1 (*c* 0.92, $CHCl_3$).

IR: 3100–3700, 3067, 2924, 2876, 1586, 1447, 1402, 1306, 1240, 1142, 1087, 1026, 974, 889, 772, 739, 689 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.31 (1 H, dd, *J* = 7.0, 11.4 Hz, H_A-1), 3.49 (1 H, dd, *J* = 3.2, 11.4 Hz, H_B-1), 3.76 (2 H, d, *J* = 7.0 Hz, H-5), 4.16 (1 H, m, H-2), 5.59 (1 H, dd, *J* = 4.8, 15.4 Hz, H-3), 5.69 (1 H, m, H-4), 7.53 (3 H, m, -SO_2Ph), 7.80 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 59.8 (C-5), 66.1 (C-1), 72.3 (C-2), 118.0 (C-3), 128.6 (C_{ortho}, -SO_2Ph), 129.5 (C_{meta}, -SO_2Ph), 134.3 (C_{para}, -SO_2Ph), 138.3 (C_{ipso}, -SO_2Ph), 140.0 (C-4).

MS: *m*/*z* (%) = 243 (9) [M^+], 176 (12), 154 (100), 107 (21), 77 (29).

HRMS: *m*/*z* calcd for $C_{11}H_{14}O_4S$, 242.0613; found, 243.0623.

Anal. calcd for $C_{11}H_{14}O_4S$ (242.3): C, 54.53; H, 5.82; S, 13.23. Found: C, 54.53; H, 5.88; S, 13.33.

(–)-(2*S*)- 5-Benzenesulfonyl-1-tosyloxy-pent-3-ene-2-ol (5)

To a soln of **4** (0.83 g, 3.44 mmol) in pyridine (5 mL) was added TsCl (0.66 g, 3.44 mmol). The soln was allowed to stir for 16 h, by which time TLC analysis showed that no starting material remained. Some drops of H_2O were added, the soln was poured into a separating funnel, extracted with Et_2O, the organic phase was washed with a soln of 2 N HCl, H_2O, sat. brine, dried with anhyd Na_2SO_4, filtered and the solvent removed in vacuo. The resultant oil was purified by flash silica column chromatography (hexane–EtOAc, 8:2) to yield 0.95 g (70%) of **5** as a white solid.

$[\alpha]_D^{20}$ –2.0 (*c* 0.94, $CHCl_3$).

IR: 3200–3600, 2924, 1447, 1358, 1308, 1177, 1144, 1086, 974 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.45 (3 H, s, CH_3-), 2.65 (1 H, br s, -OH), 3.79 (3 H, m, H_A-1, H-5), 3.90 (1 H, dd, *J* = 3.6, 10.2 Hz, H_B-1), 4.33 (1 H, m, H-2), 5.49 (1 H, dd, *J* = 5.2, 15.7 Hz, H-3), 5.74 (1 H, m, H-4), 7.36 (2 H, d, *J* = 8.4 Hz, H_{meta} Ts-), 7.58 (3 H, m, -SO_2Ph), 7.81 (4 H, m, H_{ortho} Ts-, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.0 (CH_3-), 59.6 (C-5), 69.5 (C-2) 72.5 (C-1), 120.1 (C-3), 128.2 (C_{ortho}, Ts-), 128.7 (C_{ortho}, -SO_2Ph), 129.5 (C_{meta}, -SO_2Ph), 130.3 (C_{meta}, Ts-), 132.5 (C_{ipso}, Ts-), 134.3 (C_{para}, -SO_2Ph), 137.2 (C-4), 138.3 (C_{ipso}, -SO_2Ph), 145.6 (C_{para}, Ts-).

MS: *m*/*z* (%) = 397 (10) [M^+], 307 (11), 154 (100), 107 (40), 77 (42).

HRMS: *m*/*z* calcd for $C_{18}H_{20}O_6S_2$, 396.0701; found, 397.0707.

Anal. calcd for $C_{18}H_{20}O_6S_2$ (396.5): C, 54.53; H, 5.08; S, 16.18. Found: C, 54.55; H, 5.18; S, 16.02.

(–)-(2*S*)-5-Benzenesulfonyl-1-iodo-pent-3-en-2-ol (6)

To a soln of **5** (0.31 g, 0.78 mmol) in acetone (4 mL) was added sodium iodide (0.40 g, 2.66 mmol). The soln was refluxed (80 °C) for 5 h under an argon atm, and allowed to cool. The solvent was removed in vacuo. The mixture was dissolved in H_2O, Et_2O and poured into a separating funnel. The organic phase was washed with a sat. soln of $Na_2S_2O_3$, a soln. of $NaHCO_3$ (5%), H_2O, brine, then dried with anhyd Na_2SO_4, filtered and the solvent removed in vac-

uo. The resultant oil was purified by flash silica column chromatography (hexane–EtOAc, 8:2) to yield 0.26 g (94%) of **6**.

$[\alpha]_D^{20}$ –6.3 (*c* 1.30, $CHCl_3$).

IR: 3200–3600, 3063, 2972, 2920, 1447, 1306, 1146, 1086, 972, 739, 689 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.52 (1 H, d, *J* = 5.2 Hz, -OH), 3.08 (1 H, dd, *J* = 6.4, 10.2 Hz, H_A-1), 3.20 (1 H, dd, *J* = 4.8, 10.2 Hz, H_B-1), 3.81 (2 H, d, *J* = 7.4 Hz, H-5), 4.12 (1 H, m, H-2), 5.57 (1 H, dd, *J* = 5.0 , 15.4 Hz, H-3), 5.78 (1 H, m, H-4), 7.60 (3 H, m, -SO_2Ph), 7.87 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.3 (C-1), 59.6 (C-5), 70.9 (C-2), 119.2 (C-3), 128.7 (C_{ortho}, -SO_2Ph), 129.5 (C_{meta}, -SO_2Ph), 134.2 (C_{para}, -SO_2Ph), 138.4 (C_{ipso}, -SO_2Ph), 140.4 (C-4).

MS: *m/z* (%) = 352 (2) [M^+], 225 (18), 211 (65), 169 (100), 125 (35), 77 (60).

HRMS: *m/z* calcd for $C_{11}H_{13}IO_3S$, 351.9630; found, 351.9631.

(+)-(2*S*)- 5-Benzenesulfonyl-1-iodo-2-(tetrahydropyran-2-yloxy)-pent-3-ene (13)

To a soln of **6** (0.12 g, 0.34 mmol) in CH_2Cl_2 (1 mL) was added dihydropyrane (80 μL, 0.88 mmol) and a catalytic amount of *p*-toluenesulfonic acid monohydrate. The reaction was left to stir for 19 h before addition of Et_2O. The soln was then poured into a separating funnel, washed with a soln of $NaHCO_3$ (5%), H_2O, and sat. brine. The organic phase was dried with anhyd Na_2SO_4, filtered and the solvent removed in vacuo. The resultant oil was then purified by flash silica column chromatography (hexane−EtOAc, 9:1) to yield 0.09 g (69%) of **13** as a colorless oil. Some starting material was also recovered from the column.

$[\alpha]_D^{20}$ +31.3 (*c* 1.04, $CHCl_3$).

IR: 2944, 2868, 1447, 1319, 1150, 1086, 1020, 972, 743, 689 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.42–1.85 (6 H, m, H-2′, H-3′, H-4′), 3.10 (2 H, m, H-1), 3.51 (1 H, m, H_A-5′), 3.84 (2 H, d, *J* = 7.4 Hz, H-5), 3.96 (1 H, m, H_B-5′), 4.14 (1 H, m, H-2), 4.48 and 4.72 (1 H, m, H-1′), 5.34–5.82 (2 H, m, H-3, H-4), 7.58 (3 H, m, -SO_2Ph), 7.86 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.5 (C-1), 19.1 and 19.5 (C-3′), 25.5 and 25.7 (C-4′), 30.6 (C-2′), 59.7 and 59.8 (C-5), 62.4 and 62.7 (C-5′), 74.3 and 74.6 (C-2), 95.7 and 97.8 (C-1′), 119.2 and 121.5 (C-3), 128.7 (C_{ortho}, -SO_2Ph), 129.4 (C_{meta}, -SO_2Ph), 134.0 (C_{para}, -SO_2Ph), 138.3 (C_{ipso}, -SO_2Ph), 138.7and 139.5 (C-4).

MS: *m/z* (%) = 436 (2) [M^+], 335 (10), 295 (20), 208 (10), 141 (15), 85 (100), 67 (60).

(–)-(2*S*)-5-Benzenesulfonyl-1-iodo-2-*tert*-butyldimethylsilyloxy-pent-3-ene (16)

To a soln of **6** (0.14 g, 0.39 mmol) in THF (2 mL) was added 2,6 lutidine (0.14 mL, 1.17 mmol). The mixture was cooled to 0 °C. Then *tert*-butyldimethylsilyl triflate (0.27 mL, 1.17 mmol) was added. The mixture was left to stir at r.t. for 30 min before addition of sat. $NaHCO_3$ soln, until neutralization. This soln was extracted with Et_2O and the organic extracts combined and washed with H_2O, $NaHCO_3$ soln (5%) and sat. brine. The organic phase was dried with anhyd Na_2SO_4, filtered and the solvent removed in vacuo. The resultant oil was purified by column chromatography (hexane–EtOAc, 95:5) to yield 0.18 g (98%) of **16**.

$[\alpha]_D^{20}$ –5.5 (*c* 1.38, $CHCl_3$).

IR: 2928, 2855, 1464, 1321, 1258, 1152, 1088, 970, 837, 779 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.00 (3 H, s, Me_A–Si), 0.07 (3 H, s, Me_B–Si), 0.87 [9 H, s, $(CH_3)_3$CSi], 3.01 (2 H, d, *J* = 5.8 Hz, H-1), 3.82 (2 H, d, *J* = 5.8 Hz, H-5), 4.15 (1 H, m, H-2), 5.63 (2 H, m, H-3, H-4), 7.58 (3 H, m, -SO_2Ph), 7.87 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –4.5 (Me_A–Si), –4.3 (Me_B–Si), 12.2 (C-1), 18.3 [$(CH_3)_3C$–Si], 26.0 [$(CH_3)_3$C–Si], 59.6 (C-5), 71.8 (C-2), 118.4 (C-3), 128.6 (C_{ortho}, -SO_2Ph), 129.4 (C_{meta}, -SO_2Ph), 134.0 (C_{para}, -SO_2Ph), 138.6 (C_{ipso}, -SO_2Ph), 141.3 (C-4).

(+)-(2*S*)-5-Benzenesulfonyl-1-iodo-2-(1-methoxy-1-methyl-ethoxy)-pent-3-ene (17)

To a soln of **6** (0.16 g, 0.47 mmol) in 2-methoxypropene (2 mL) was added a catalytic amount of pyridinium *p*-toluensulfonate. It was left to stir for 1 h before addition of some drops of Et_3N. The solvent was then removed in vacuo and the resultant oil purified by column chromatography (hexane–EtOAc, 9:1) to yield 0.20 g (100%) of **17**.

$[\alpha]_D^{20}$ +4.6 (*c* 1.13, $CHCl_3$).

IR: 2988, 2942, 1447, 1375, 1319, 1150, 1086, 1024, 972, 737, 689 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.26, (3 H, s, Me_2C), 1.33 (3 H, s, Me_2C), 2.98 (1 H, dd, *J* = 7.2, 9.8 Hz, H_A-1), 3.11 (1 H, dd, *J* = 4.4, 9.8 Hz, H_B-1), 3.16 (3 H, s, CH_3O-), 3.83 (2 H, d, *J* = 6.6 Hz, H-5), 4.17 (1 H, m, H-2), 5.63 (2 H, m, H-3, H-4), 7.58 (3 H, m, -SO_2Ph), 7.87 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.7 (C-1), 25.4 (Me_AC), 25.5 (Me_BC), 49.8 (CH_3O-), 59.7 (C-5), 69.9 (C-2), 101.6 [-O*C*$(CH_3)_2(OCH_3)$], 119.0 (C-3), 128.6 (C_{ortho}, -SO_2Ph), 129.4 (C_{meta}, -SO_2Ph), 134.0 (C_{para}, -SO_2Ph), 138.7 (C_{ipso}, -SO_2Ph), 140.8 (C-4).

MS: *m/z* (%) = 425 (5) [M + 1^+], 335 (7), 307 (15), 154 (100), 137 (58), 107 (25), 77 (30), 73 (25).

HRMS: *m/z* calcd for $C_{15}H_{22}IO_4S$, 425.0284; found, 425.0284.

(+)-(2*S*)-5-Benzenesulfonyl-2(tetrahydropyran-2-yloxy)-1-tosyloxy-pent-3-ene (10)

This experiment was carried out based on the procedure given for obtaining compound **13** from **6**. Compound **5** (0.19 g, 0.48 mmol), CH_2Cl_2 (0.5 mL), dihydropyrane (0.13 mL, 1.42 mmol), and *p*-toluenesulfonic acid monohydrate (cat.) were reacted for 16 h to yield 0.22 g (95%) of compound **10**.

$[\alpha]_D^{20}$ +44.7 (*c* 0.94, $CHCl_3$).

IR: 2945, 2870, 1447, 1360, 1308, 1177, 1146, 976, 816 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.37–1.71 (6 H, m, H-2′, H-3′, H-4′), 2.45 (3 H, s, CH_3-), 3.42 (1 H, m, H_A-5′), 3.65–4.00 (5 H, m, H_B-5′, H-5, H-1), 4.27 (1 H, m, H-2), 4.43 and 4.63 [1 H, m, H-1′ (3:1)], 5.30–5.76 (2 H, m, H-3, H-4), 7.34 (2 H, m, H_{meta} Ts-), 7.59 (3 H, m, -SO_2Ph), 7.80 (4 H, m, H_{ortho} Ts-, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.8 and 19.4 (C-3′), 21.9 (CH_3-), 25.5 (C-4′), 30.3 and 30.5 (C-2′), 59.7 and 59.8 (C-5), 61.8 and 62.8 (C-5′), 70.8 and 71.1 (C-1), 72.3 and 73.1 (C-2), 95.4 and 98.5 (C-1′), 120.1 and 122.2 (C-3), 128.2 (C_{ortho}, Ts-), 128.7 (C_{ortho}, -SO_2Ph), 129.3 (C_{meta}, -SO_2Ph), 130.1 (C_{meta}, Ts-), 133.1 (C_{ipso}, Ts-), 134.1 (C_{para}, -SO_2Ph), 135.7 and 136.6 (C-4), 138.3 (C_{ipso},-SO_2Ph), 145.2 (C_{para}, Ts-).

(+)-(2*S*)-5-Benzenesulfonyl-2-methoxymethoxy-1-tosyloxy-pent-3-ene (11)

To a soln of **5** (0.10 g, 0.24 mmol) in $CHCl_3$ (3 mL) was added dimethoxymethane (0.65 mL, 7.24 mmol). The mixture was cooled to 0 °C and P_2O_5 (0.47 g, 3.28 mmol) was added. The mixture was left to stir at r.t. for 1 h before addition of ice. This soln was extracted with Et_2O and the organic extracts combined and washed with $NaHCO_3$ soln (5%), H_2O (until pH 7) and sat. brine. The organic phase was dried over anhyd Na_2SO_4, filtered and the solvent removed in vacuo to yield 0.12 g of **11** (100%).

$[\alpha]_D^{20}$ +48.7 (*c* 1.05, $CHCl_3$).

IR: 3067, 2963, 2924, 1597, 1447, 1358, 1096, 1020, 802, 665 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.41 (3 H, s, CH_3C$_6$H$_4$SO$_2$-), 3.23 (3 H, s, -OCH$_2$OCH_3), 3.75 (2 H, d, *J* = 7.4 Hz, H-1), 3.84 (2 H, d, *J* = 5.2 Hz, H-5), 4.18 (1 H, m, H-2), 4.42 (2 H, s, -OCH_2OCH$_3$), 5.35 (1 H, dd, *J* = 6.6, 15.6 Hz, H-3), 5.69 (1 H, m, H-4), 7.31 (2 H, d, *J* = 8.4 Hz, H$_{meta}$ Ts-), 7.54 (3 H, m, -SO$_2$Ph), 7.76 (4 H, m, H$_{ortho}$ Ts, -SO$_2$Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.8 (*C*H$_3$C$_6$H$_4$SO$_2$-), 55.8 (-OCH$_2$O*C*H$_3$), 59.6 (C-5), 70.9 (C-1), 73.1 (C-2), 94.5 (-O*C*H$_2$OCH$_3$), 122.0 (C-3), 128.1 (C$_{ortho}$, Ts-), 128.6 (C$_{ortho}$, -SO$_2$Ph), 129.4 (C$_{meta}$, -SO$_2$Ph), 130.1 (C$_{meta}$, Ts-), 132.9 (C$_{ipso}$, Ts-), 134.2 (C$_{para}$, -SO$_2$Ph), 135.4 (C-4), 138.3 (C$_{ipso}$, -SO$_2$Ph), 145.3 (C$_{para}$, Ts-).

(+)-(2*S*)-5-Benzenesulfonyl-[1,2]-(4-methoxybenzyliden)-pent-3-ene-1,2-diol (7)

To a soln of **4** (0.11 g, 0.47 mmol) in benzene (20 mL) was added *p*-methoxybenzylidendimethylacetal (0.28 mL, 1.65 mmol) and a catalytic amount of *p*-toluensulfonic acid monohydrate. The soln was refluxed for 3 h using a Dean–Stark apparatus, and allowed to cool. The soln was then poured into a separating funnel, washed with a soln of $NaHCO_3$ (5%), H_2O and sat. brine. The organic phase was dried with anhyd Na_2SO_4, filtered and the solvent removed in vacuo. The resultant oil was purified by column chromatography (hexane–EtOAc, 8:2) to yield 0.16 g (92%) of **7**.

$[\alpha]_D^{20}$ +29.8 (*c* 1.61, $CHCl_3$).

IR: 3065, 2924, 1615, 1518, 1447, 1308, 1250, 1148, 1084, 1030, 974, 831, 741 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.47 and 3.58 [1 H, dd, *J* = 7.4, 8.4 Hz, *J* = 5.8, 8.0 Hz, H$_A$-1 (1:1)], 3.82 (5 H, m, *p*-C*H*$_3$OC$_6$H$_4$-, H-5), 4.05 and 4.21 (1 H, dd, *J* = 7.4, 8.0 Hz, *J* = 6.6, 8.4 Hz, H$_B$-1), 4.59 (1 H, m, H-2), 5.58 (1 H, m, H-3), 5.81 (2 H, m, H-4, *p*-CH$_3$OC$_6$H$_4$C*H*), 6.89 (2 H, m, H$_{meta}$ *p*-CH$_3$OC$_6$H$_4$-), 7.35 (2 H, m, H$_{ortho}$ *p*-CH$_3$OC$_6$H$_4$-), 7.57 (3 H, m, -SO$_2$Ph), 7.90 (2 H, m, -SO$_2$Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.6 (*p*-*C*H$_3$OC$_6$H$_4$-), 59.7 (C-5), 70.0 and 70.3 (C-1), 75.9 and 76.5 (C-2), 104.1 and 104.7 (*p*-CH$_3$OC$_6$H$_4$*C*H), 114.0 (C$_{meta}$, *p*-CH$_3$OC$_6$H$_4$-), 119.7 and 120.0 (C-3), 128.0 and 128.2 (C$_{ortho}$, *p*-CH$_3$OC$_6$H$_4$-), 128.8 (C$_{ortho}$, -SO$_2$Ph), 129.4 (C$_{meta}$, -SO$_2$Ph), 129.9 (C$_{ipso}$, *p*-CH$_3$OC$_6$H$_4$), 134.1 (C$_{para}$, -SO$_2$Ph), 138.0 and 138.3 (C-4), 138.3 (C$_{ipso}$, -SO$_2$Ph), 160.7 (C$_{para}$, *p*-CH$_3$OC$_6$H$_4$-).

MS: *m/z* (%) = 361 (1) [M + 1$^+$], 307 (12), 154 (100), 67 (80).

HRMS: *m/z* calcd for C$_{19}$H$_{21}$O$_5$S, 361.1110; found, 361.1110.

(+)-(2*S*)-5-Benzenesulfonyl-2-(4-methoxybenzyloxy)-pent-3-en-1-ol (8)

(–)-(2*S*)-5-Benzenesulfonyl-1-(4-methoxybenzyloxy)-pent-3-en-2-ol (9)

A soln of trimethylsilyl chloride (0.44 mL, 3.44 mmol) in CH_3CN (0.5 mL) was added dropwise to a stirred mixture containing compound **7** (0.16 g, 0.43 mmol), sodium cyanoborohydride (0.33 g, 5.20 mmol) in CH_3CN (8.5 mL). The reaction mixture was stirred for 1 h at r.t. The mixture was filtered through celite and poured into ice-cold sat. aq $NaHCO_3$. The aq phase was repeatedly extracted with CH_2Cl_2. The combined extracts were washed with sat. aq $NaHCO_3$, dried (Na_2SO_4), filtered and concentrated. The residue was purified by flash silica column chromatography (hexane–EtOAc, 7:3) to yield 0.10 g (70%) of compounds **8** and **9** (1:1).

8

$[\alpha]_D^{20}$ +54.7 (*c* 1.26, $CHCl_3$).

IR: 3200–3600, 2924, 2870, 1613, 1514, 1447, 1306, 1248, 1144, 1086, 1032, 976, 741, 689 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.06 (1 H, m, -OH), 3.42 (2 H, m, H-1), 3.80 (3 H, s, *p*-C*H*$_3$OC$_6$H$_4$CH$_2$-), 3.88 (3 H, m, H-2, H-5), 4.21 (1 H, d, *J* = 11.0 Hz, *p*-CH$_3$OC$_6$H$_4$C*H*$_A$H$_B$-), 4.41 (1 H, d, *J* = 11.0 Hz, *p*-CH$_3$OC$_6$H$_4$CH$_A$*H*$_B$-), 5.49 (1 H, dd, *J* = 7.0, 15.8 Hz, H-3), 5.76 (1 H, m, H-4), 6.87 (2 H, m, H$_{meta}$ *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 7.18 (2 H, m, H$_{ortho}$ *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 7.59 (3 H, m, -SO$_2$Ph), 7.88 (2 H, m, -SO$_2$Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.5 (*p*-*C*H$_3$OC$_6$H$_4$CH$_2$-), 59.9 (C-5), 65.2 (C-1), 70.7 (*p*-CH$_3$OC$_6$H$_4$*C*H$_2$-), 79.3 (C-2), 114.2 (C$_{meta}$, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 121.0 (C-3), 128.6 (C$_{ortho}$, -SO$_2$Ph), 129.4 (C$_{meta}$, -SO$_2$Ph), 129.8 (C$_{ortho}$, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 129.9 (C$_{ipso}$, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 134.2 (C$_{para}$, -SO$_2$Ph), 137.9 (C-4), 138.4 (C$_{ipso}$, -SO$_2$Ph), 159.6 (C$_{para}$, *p*-CH$_3$OC$_6$H$_4$CH$_2$-).

MS: *m/z* (%) = 362 (1) [M$^+$], 300 (5), 210 (5), 154 (20), 67 (80).

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$[\alpha]_D^{20}$ –2.1 (*c* 1.33, $CHCl_3$).

IR: 3200–3600, 3063, 2924, 2859, 1613, 1586, 1514, 1447, 1306, 1248, 1144, 1086, 1032, 974, 820, 739, 689 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.43 (1 H, m, -OH), 3.18 (1 H, dd, *J* = 7.8, 9.6 Hz, H$_A$-1), 3.37 (1 H, dd, *J* = 3.6, 9.6 Hz, H$_B$-1), 3.78 (2 H, d, *J* = 7.2 Hz, H-5), 3.81 (3 H, s, *p*-C*H*$_3$OC$_6$H$_4$CH$_2$-), 4.26 (1 H, m, H-2), 4.45 (2 H, s, *p*-CH$_3$OC$_6$H$_4$C*H*$_2$-), 5.52 (1 H, dd, *J* = 5.2, 15.4 Hz, H-3), 5.75 (1 H, m, H-4), 6.89 (2 H, m, H$_{meta}$ *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 7.23 (2 H, m, H$_{ortho}$ *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 7.56 (3 H, m, -SO$_2$Ph), 7.84 (2 H, m, -SO$_2$Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.5 (*p*-*C*H$_3$OC$_6$H$_4$CH$_2$-), 59.9 (C-5), 70.5 (C-2), 73.3 (C-1, *p*-CH$_3$OC$_6$H$_4$*C*H$_2$-), 114.1 (C$_{meta}$, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 118.5 (C-3), 128.8 (C$_{ortho}$, -SO$_2$Ph), 129.3 (C$_{meta}$, -SO$_2$Ph), 129.7 (C$_{ortho}$, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 129.9 (C$_{ipso}$, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 134.0 (C$_{para}$, -SO$_2$Ph), 138.3 (C$_{ipso}$, -SO$_2$Ph), 139.1 (C-4), 159.8 (C$_{para}$, *p*-CH$_3$OC$_6$H$_4$CH$_2$-).

(+)-(2*S*)-5-Benzenesulfonyl-2-(4-methoxybenzyloxy)-1-tosyloxy-pent-3-ene (12)

This experiment was carried out based on the procedure given for obtaining compound **5** from **4**. Compound **8** (29 mg, 0.08 mmol), pyridine (1 mL), and TsCl (45 mg, 0.24 mmol) were reacted for 2 d and 16 h to yield 35 mg (86%) of compound **12**.

$[\alpha]_D^{20}$ +22.4 (*c* 1.62, $CHCl_3$).

IR: 3065, 2959, 2872, 1613, 1514, 1447, 1362, 1308, 1250, 1177, 1146, 1080, 1032, 978, 818, 665 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.43 (3 H, s, C*H*$_3$C$_6$H$_4$SO$_2$-), 3.80 (3 H, s, *p*-C*H*$_3$OC$_6$H$_4$CH$_2$-), 3.80 (2 H, d, *J* = 7.4 Hz, H-5), 3.86 (2 H, m, H-1), 3.95 (1 H, m, H-2), 4.20 (1 H, d, *J* = 11.4 Hz, *p*-CH$_3$OC$_6$H$_4$C*H*$_A$H$_B$-), 4.35 (1 H, d, *J* = 11.4 Hz, *p*-CH$_3$OC$_6$H$_4$CH$_A$*H*$_B$-), 5.41 (1 H, dd, *J* = 6.2, 15.4 Hz, H-3), 5.73 (1 H, m, H-4), 6.84 (2 H, m, H$_{meta}$ *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 7.12 (2 H, m, H$_{ortho}$ *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 7.29 (2 H, d, *J* = 8.2 Hz, H$_{meta}$ Ts-), 7.58 (3 H, m, -SO$_2$Ph), 7.73 (2 H, d, *J* = 8.0 Hz, H$_{ortho}$ Ts-), 7.84 (2 H, m, -SO$_2$Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.9 (*C*H$_3$C$_6$H$_4$SO$_2$-), 55.5 (*p*-*C*H$_3$OC$_6$H$_4$CH$_2$-), 59.7 (C-5) 70.9 (C-1), 71.0 (*p*-CH$_3$OC$_6$H$_4$*C*H$_2$-), 75.8 (C-2), 114.0 (C$_{meta}$, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 122.0 (C-3), 128.2 (C$_{ortho}$, Ts-), 128.6 (C$_{ortho}$, -SO$_2$Ph), 129.5 (C$_{meta}$, -SO$_2$Ph), 129.6 (C$_{ortho}$, C$_{ipso}$, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 130.1 (C$_{meta}$, Ts-), 133.0 (C$_{ipso}$, Ts-), 134.2 (C$_{para}$, -SO$_2$Ph), 136.2 (C-4), 138.4 (C$_{ipso}$, -SO$_2$Ph), 145.2 (C$_{para}$, *p*-CH$_3$OC$_6$H$_4$CH$_2$-).

MS: *m/z* (%) = 517 (3) [M +1$^+$], 307 (10), 239 (5), 136 (80), 154 (40), 121 (100).

HRMS: *m/z* calcd for C$_{26}$H$_{29}$O$_7$S$_2$, 517.1355; found, 517.1355.

(+)-(2*S*)-5-Benzenesulfonyl-1-iodo-2-(tetrahydropyran-2-yloxy)-pent-3-ene (13)

This experiment was carried out based on the procedure given for obtaining compound **6** from **5**. Compound **10** (0.22 g, 0.46 mmol), acetone (5 mL), and sodium iodide (0.28 g, 1.84 mmol) were reacted for 14 h to yield 0.15 g (76%) of compound **13**.

(+)-(2*S*)-5-Benzenesulfonyl-1-iodo-2-methoxymethoxy-pent-3-ene (14)

This experiment was carried out based on the procedure given for obtaining compound **6** from **5**. Compound **11** (0.10 g, 0.24 mmol), acetone (3 mL), and sodium iodide (0.18 g, 1.20 mmol) were reacted for 20 h to yield 0.08 g (84%) of compound **14**.

$[\alpha]_D^{20}$ +44.7 (*c* 0.90, $CHCl_3$).

IR: 2955, 2892, 1447, 1308, 1146, 1086, 1024, 974, 741, 689 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.09 (2 H, d, *J* = 6.0 Hz, H-1), 3.38 (3 H, s, -OCH_2OCH_3), 3.83 (2 H, d, *J* = 7.2 Hz, H-5), 4.05 (1 H, m, H-2), 4.53 (2 H, s, -OCH_2OCH_3), 5.45 (1 H, dd, *J* = 7.0, 15.4, H-3), 5.73 (1 H, m, H-4), 7.60 (3 H, m, -SO_2Ph), 7.87 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.2 (C-1), 56,3 (-OCH_2OCH_3), 59.7 (C-5), 75.0 (C-2), 94.5 (-OCH_2OCH_3), 121.3 (C-3), 128.6 (C_{ortho}, -SO_2Ph), 129.5 (C_{meta}, -SO_2Ph), 134.1 (C_{para}, -SO_2Ph), 138.4 (C_{ipso}, -SO_2Ph), 138.7 (C-4).

(+)-(2*S*)-5-Benzenesulfonyl-1-iodo-2-(4-methoxybenzyloxy)-pent-3-ene (15)

This experiment was carried out based on the procedure given for obtaining compound **6** from **5**. Compound **12** (47 mg, 0.24 mmol), acetone (5 mL), and sodium iodide (54 mg, 0.36 mmol) were reacted for 3 d and 13 h to yield 44 mg (100%) of compound **15**.

$[\alpha]_D^{20}$ +28.3 (*c* 1.01, $CHCl_3$).

IR: 2959, 2924, 2853, 1613, 1586, 1514, 1447, 1308, 1248, 1175, 1148, 1086, 1032, 972, 822, 741, 689 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.06 (2 H, d, *J* = 5.8 Hz, H-1), 3.81 (3 H, s, *p*-$CH_3OC_6H_4CH_2$-), 3.81 (1 H, m, H-2), 3.86 (2 H, d, *J* = 7.4 Hz, H-5), 4.27 (1 H, d, *J* = 11.4 Hz, *p*-$CH_3OC_6H_4CH_AH_B$-), 4.40 (1 H, d, *J* = 11.4 Hz, *p*-$CH_3OC_6H_4CH_AH_B$-), 5.49 (1 H, dd, *J* = 6.8, 15.4 Hz, H-3), 5.74 (1 H, m, H-4), 6.87 (2 H, m, H_{meta} *p*-$CH_3OC_6H_4CH_2$-), 7.23 (2 H, m, H_{ortho} *p*-$CH_3OC_6H_4CH_2$-), 7.59 (3 H, m, -SO_2Ph) 7.88 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.2 (C-1), 55.5 (*p*-$CH_3OC_6H_4$-CH_2-), 59.7 (C-5), 70.8 (*p*-$CH_3OC_6H_4CH_2$-), 77.6 (C-2), 114.1 (C_{meta}, *p*-$CH_3OC_6H_4CH_2$-), 121.1 (C-3), 128.6 (C_{ortho}, -SO_2Ph), 129.5 (C_{meta}, -SO_2Ph), 129.7 (C_{ipso}, *p*-$CH_3OC_6H_4CH_2$-), 129.8 (C_{ortho}, *p*-$CH_3OC_6H_4CH_2$-), 134.2 (C_{para}, -SO_2Ph), 138.5 (C_{ipso}, -SO_2Ph), 139.2 (C-4), 159.6 (C_{para}, *p*-$CH_3OC_6H_4CH_2$-).

MS: *m/z* (%) = 472 (1) [M^+], 300 (5), 295 (5), 208 (5), 154 (40), 85 (70), 67 (100).

LDA Reaction; General Procedure

Reaction of compound **13** with LDA

LDA was generated by the addition of BuLi 1.6 M (0.17 mL, 0.27 mmol) to a soln of diisopropylamine (38 μL, 0.27 mmol) in THF (0.5 mL) at –78 °C. After 5 min, the mixture was allowed to warm to r.t., and then recooled to –78 °C.

Compound **13** (80 mg, 0.18 mmol) was then added to the reaction flask via cannula as a soln in THF (1 mL). The reaction mixture was left to stir for 1 h at –78 °C under Argon before the addition of sat. ammonium chloride soln (1 mL). The product was extracted into EtOAc (3 ×). The organic extracts were combined, washed with H_2O and sat. brine, then dried over anhyd Na_2SO_4, filtered and removed the solvent in vacuo. Cyclopropanes **18** and **19**, 53 mg (94%) were obtained in a 70:30 ratio separated by flash silica column chromatography (hexane–EtOAc, 9:1).

(+)-(1*R*,2*S*)-2-[2-(2-Benzenesulfonylvinyl)-1-(tetrahydropyran-2-yloxy)]-cyclopropane (18)

$[\alpha]_D^{20}$ +17.2 (*c* 0.79, $CHCl_3$).

IR: 3063, 2942, 2853, 1620, 1447, 1308, 1146, 1086, 1036, 974, 802 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.93 and 1.04 [1 H, q, *J* = 6.2 Hz, H_α-3 (3:7)], 1.24 and 1.43 (1 H, ddd, *J* = 4.0, 6.2, 9.8 Hz, H_β-3), 1.42–1.80 (6.3 H, m, H-2′, H-3′, H-4′, 0.3 H-2), 1.87 (0.7 H, dddd, *J* = 2.2, 6.2, 9.6, 9.6 Hz, 0.7 H-2), 3.56 (1.3 H, H_A-5′, 0.3 H-1), 3.71 (0.7 H, ddd, *J* = 2.2, 4.0, 6.6 Hz, 0.7 H-1), 3.88 (1 H, m, H_B-5′), 4.68 (1 H, m, H-1′), 6.28 and 6.25 (1 H, d, *J* = 15.0 Hz, -CH=C*H*SO_2Ph), 6.54 (1 H, dd, *J* = 9.6, 15.0 Hz, -C*H*=CH–SO_2Ph), 7.56 (3 H, m, -SO_2Ph), 7.86 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0 and 17.1 (C-3), 19.3 and 19.4 (C-3′), 21.5 and 22.2 (C-2), 25.5 (C-4′), 30.6 (C-2′), 59.0 (C-1), 62.6 and 62.8 (C-5′), 99.1 (C-1′), 127.5 and 128.2 (-CH=*C*H-SO_2Ph), 127.7 (C_{ortho}, -SO_2Ph), 129.5 (C_{meta}, -SO_2Ph), 133.4 (C_{para}, -SO_2Ph), 141.1 (C_{ipso}, -SO_2Ph), 147.9 and 148.0 (-*C*H=CHSO_2Ph).

MS: *m/z* (%) = 309 (2) [M^+], 279 (5), 167 (8), 149 (15), 125 (10), 85 (100).

HRMS: *m/z* calcd for $C_{16}H_{20}O_4S$, 308.1082; found, 308.1083.

(–)-(1*R*,2*R*)-2-[2-(2-Benzenesulfonylvinyl)-1-(tetrahydropyran-2-yloxy)]-cyclopropane (19)

$[\alpha]_D^{20}$ –41.7 (*c* 0.87, $CHCl_3$).

IR: 3063, 2945, 2870, 1618, 1447, 1317, 1144, 1086, 1038, 999, 754, 689 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.91 (1 H, m, H_β-3), 1.12–1.81 (8 H, m, H-2′, H-3′, H-4′, H-2, H_α-3), 3.52 (1 H, m, H_A-5′), 3.75–4.01 (2 H, m, H_B-5′, H-1), 4.42 and 4.72 (1 H, m, H-1′), 6.37 (1 H, m, -CH=C*H*SO_2Ph), 6.80 (1 H, m, -C*H*=CHSO_2Ph), 7.53 (3 H, m, -SO_2Ph), 7.87 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.8 and 16.9 (C-3), 19.3 and 19.5 (C-3′), 20.5 and 21.1 (C-2), 25.6 (C-4′), 30.3 and 30.6 (C-2′), 57.0 (C-1), 62.6 and 62.8 (C-5′), 99.3 (C-1′), 127.6 and 127.7 (C_{ortho}, -SO_2Ph), 128.5 and 128.6 (-CH=*C*HSO_2Ph), 129.3 and 129.4 (C_{meta}, -SO_2Ph), 133.2 (C_{para}, -SO_2Ph), 141.4 (C_{ipso}, -SO_2Ph), 146.8 and 147.4 (-*C*H=CH–SO_2Ph).

MS: *m/z* (%) = 308 (2) [M^+], 224 (5), 195 (8), 125 (15), 85 (100).

HRMS: *m/z* calcd for $C_{16}H_{20}O_4S$, 308.1082; found, 308.1087.

Reaction of compound **14** with LDA

This experiment was carried out based on the procedure given for the above reaction. BuLi, 1.6 M (0.19 mL, 0.30 mmol), diisopropylamine (42 μL, 0.30 mmol), THF (0.5 mL), compound **14** (79 mg, 0.20 mmol) in THF (1 mL) were reacted for 90 min to yield 49 mg (91%) of cyclopropanes **20** and **21** in a 70:30 ratio, and separated by column chromatography (hexane–EtOAc, 8:2).

(–)-(1*R*,2*S*)-2-(2-Benzenesulfonylvinyl)-1-methoxymethoxy-cyclopropane (20)

$[\alpha]_D^{20}$ –16.0 (*c* 0.83, $CHCl_3$).

IR: 3057, 2922, 2851, 1622, 1447, 1306, 1144, 1086, 1051, 999, 799 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.00 (1 H, q, *J* = 6.2 Hz, H_α-3), 1.33 (1 H, ddd, *J* = 4.0, 6.2, 9.8 Hz, H_β-3), 1.76 (1 H, dddd, *J* = 2.2, 6.2, 9.6, 9.6 Hz, H-2), 3.38, (3 H, s, -OCH_2OCH_3), 3.61 (1 H, ddd, *J* = 2.2, 4.0, 6.2 Hz, H-1), 4.62 (2 H, s, -OCH_2OCH_3), 6.28 (1 H, d, *J* = 14.6 Hz, -CH=C*H*–SO_2Ph), 6.53 (1 H, dd, *J* = 9.4, 14.6 Hz, -C*H*=CHSO_2Ph), 7.57 (3 H, m, -SO_2Ph), 7.86 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$):δ = 16.5 (C-3), 21.8 (C-2), 56.2 (-OCH_2OCH_3), 59.1 (C-1), 96.8 (-OCH_2OCH_3), 127.7 (C_{ortho}, -SO_2Ph), 128.1 (-CH=*C*HSO_2Ph), 129.5 (C_{meta}, -SO_2Ph), 133.4 (C_{para}, -SO_2Ph), 141.0 (C_{ipso}, -SO_2Ph), 147.5 (-*C*H=CHSO_2Ph).

MS: *m/z* (%) = 269 (1) [M + 1$^+$] 149 (10), 135 (10), 91 (100).

(+)-(1*R*,2*R*)-2-(2-Benzenesulfonylvinyl)-1-methoxymethoxy-cyclopropane (21)

$[\alpha]_D^{20}$ +6.8 (*c* 1.04, $CHCl_3$).

IR: 3054, 2926, 2853, 1622, 1447, 1306, 1283, 1142, 1086, 1032, 993, 797 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.07 (1 H, dt, *J* = 4.4, 6.2, 6.2 Hz, H_β-3), 1.25 (1 H, m, H_α-3), 1.64 (1 H, m, H-2), 3.40 (3 H, s, -OCH_2OCH_3), 3.83 (1 H, dt, *J* = 4.4, 6.2, 6.2 Hz, H-1), 4.55 (1 H, d, *J* = 6.6 Hz, -$OCH_AH_BOCH_3$), 4.63 (1 H, d, *J* = 6.6 Hz, -$OCH_AH_BOCH_3$), 6.41 (1 H, d, *J* = 15.0, -CH=C*H*SO_2Ph), 6.80 (1 H, dd, *J* = 10.2, 15.0 Hz, -C*H*=CHSO_2Ph), 7.54 (3 H, m, -SO_2Ph), 7.88 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.2 (C-3), 20.6 (C-2), 56.4 (-OCH_2OCH_3), 57.3 (C-1), 97.0 (-OCH_2OCH_3), 127.7 (C_{ortho}, -SO_2Ph), 128.9 (-CH=*C*HSO_2Ph), 129.4 (C_{meta}, -SO_2Ph), 133.3 (C_{para}, -SO_2Ph), 141.3 (C_{ipso}, -SO_2Ph), 146.6 (-*C*H=CHSO_2Ph).

MS: *m/z* (%) = 269 (1) [M + 1$^+$] 136 (20), 114 (10), 77 (100).

Reaction of compound **15** with LDA

This experiment was carried out based on the procedure given for the above reaction. BuLi 1.6 M (80 ml, 0.13 mmol), diisopropylamine (18 μL, 0.13 mmol), THF (0.5 mL), compound **15** (41 mg, 0.08 mmol) in THF (1 mL) were reacted for 1 h to yield 20 mg (68%) of cyclopropanes **22** and **23** in a 50:50 ratio and separated by flash silica column chromatography (hexane–EtOAc, 9:1).

(–)-(1*R*,2*S*)-2-(2-Benzenesulfonylvinyl)-1-(4-methoxybenzyloxy)-cyclopropane (22)

$[\alpha]_D^{20}$ –26.2 (*c* 0.98, $CHCl_3$).

IR: 3054, 2922, 2851, 1615, 1514, 1447, 1306, 1248, 1146, 1086, 1034, 802, 752, 689 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.97 (1 H, q, *J* = 6.2 Hz, H_α-3), 1.35 (1 H, ddd, *J* = 4.0, 6.2, 10.0 Hz, H_β-3), 1.66 (1 H, dddd, *J* = 2.2, 6.2, 10.0, 10.0 Hz, H-2), 3.39 (1 H, ddd, *J* = 2.2, 4.2, 6.2 Hz, H-1), 3.79 (3 H, s, *p*-C*H*$_3$OC$_6$H$_4$CH$_2$-), 4.47 (1 H, br s, *p*-$CH_3OC_6H_4CH_AH_B$-), 4.48 (1 H, s, *p*-$CH_3OC_6H_4CH_AH_B$-), 6.18 (1 H, d, *J* = 15.0 Hz, -CH=C*H*–SO_2Ph), 6.48 (1 H, dd, *J* = 10.0, 15.2 Hz, -C*H*=CHSO_2Ph), 6.84 (2 H, m, H_{meta} *p*-$CH_3OC_6H_4CH_2$-), 7.20 (2 H, m, H_{ortho} *p*-$CH_3OC_6H_4CH_2$-), 7.56 (3 H, m, -SO_2Ph), 7.86 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.9 (C-3), 22.4 (C-2), 55.5 (*p*-*C*H$_3$OC$_6$H$_4$CH$_2$-), 61.6 (C-1), 73.2 (*p*-$CH_3OC_6H_4CH_2$-), 114.1 (C_{meta}, *p*-$CH_3OC_6H_4CH_2$-), 127.7 (-CH=*C*H–SO_2Ph, C_{ortho}, -SO_2Ph), 129.3 (C_{ipso}, *p*-$CH_3OC_6H_4CH_2$-), 129.5 (C_{meta}, -SO_2Ph), 130.1 (C_{ortho}, *p*-$CH_3OC_6H_4CH_2$-), 133.4 (C_{para}, -SO_2Ph), 141.2 (C_{ipso}, -SO_2Ph), 147.9 (-*C*H=CH–SO_2Ph), 159.8 (C_{para}, *p*-$CH_3OC_6H_4CH_2$-).

MS: *m/z* (%) = 345 (5) [M + 1$^+$], 307 (14), 154 (85), 125 (25), 107 (50).

HRMS: *m/z* calcd for $C_{19}H_{21}O_4S$, 345.1161; found, 345.1161.

(+)-(1*R*,2*R*)-2-(2-Benzenesulfonylvinyl)-1-(4-methoxybenzyloxy)-cyclopropane (23)

$[\alpha]_D^{20}$ +8.7 (*c* 0.91, $CHCl_3$).

IR: 3057, 2926, 2855, 1615, 1514, 1447, 1306, 1250, 1144, 1086, 1032, 799, 754, 689 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.12 (1 H, dt, *J* = 4.0, 6.2, 6.2 Hz, H_β-3), 1.22 (1 H, m, H_α-3), 1.62 (1 H, m, H-2), 3.65 (1 H, dt, *J* = 4.0, 6.2, 6.2 Hz, H-1), 3.81 (3 H, s, *p*-C*H*$_3$OC$_6$H$_4$CH$_2$-), 4.38 (2 H, s, *p*-$CH_3OC_6H_4CH_2$-), 6.43 (1 H, d, *J* = 15.2Hz, -CH=C*H*SO_2Ph), 6.89 (3 H, m, -CH=C*H*SO_2Ph), H_{meta} *p*-$CH_3OC_6H_4CH_2$-), 7.24 (2 H, m, H_{ortho} *p*-$CH_3OC_6H_4CH_2$-), 7.54 (3 H, m, -SO_2Ph), 7.87 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.8 (C-3), 21.0 (C-2), 55.5 (*p*-*C*H$_3$OC$_6$H$_4$CH$_2$-), 59.7 (C-1), 73.4 (*p*-$CH_3OC_6H_4CH_2$-), 114.2 (C_{meta}, *p*-$CH_3OC_6H_4CH_2$-), 127.7 (C_{ortho}, -SO_2Ph), 128.6 (-CH=*C*HSO_2Ph), 129.2 (C_{ipso}, *p*-$CH_3OC_6H_4CH_2$-), 129.4 (C_{meta}, -SO_2Ph), 130.0 (C_{ortho}, *p*-$CH_3OC_6H_4CH_2$-), 133.2 (C_{para}, -SO_2Ph), 141.4 (C_{ipso}, -SO_2Ph), 146.9 (-*C*H=CH–SO_2Ph), 159.8 (C_{para}, *p*-$CH_3OC_6H_4CH_2$-).

MS: *m/z* (%) = 345 (2) [M + 1$^+$], 307 (5), 154 (26), 136 (25).

HRMS: *m/z* calcd for $C_{19}H_{21}O_4S$, 345.1161; found, 345.1166.

Reaction of compound **16** with LDA

This experiment was carried out based on the procedure given for the above reaction. BuLi 1.6 M (0.36 mL, 0.58 mmol), diisopropylamine (81 μL, 0.58 mmol), THF (1 mL), compound **16** (0.18 g, 0.38 mmol) in THF (1 mLwere reacted for 45 min to yield 0.12 g (91%) of cyclopropanes **24** and **25** in a 30:70 ratio and separated by flash silica column chromatography (hexane–EtOAc, 9:1).

(–)-(1*R*,2*S*)-2-(2-Benzenesulfonylvinyl)-1-*tert*-butyldimethylsililoxy-cyclopropane (24)

$[\alpha]_D^{20}$ –64.4 (*c* 0.50, $CHCl_3$).

IR: 3065, 2957, 2930, 2857, 1622, 1447, 1317, 1209, 1148, 1086, 916, 837, 801 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.08 (6 H, s, Me_ASi, Me_BSi), 0.86 [9 H, s, $(CH_3)_3CSi$], 0.96 (1 H, q, *J* = 6.2 Hz, H_α-3), 1.25 (1 H, ddd, *J* = 4.0, 6.2, 9.6 Hz, H_β-3), 1.64 (1 H, dddd, *J* = 2.2, 6.4, 9.4, 9.4 Hz, H-2), 3.49 (1 H, ddd, *J* = 2.2, 4.0, 6.2 Hz, H-1), 6.23 (1 H, d, *J* = 15.0 Hz, -CH=C*H*SO_2Ph), 6.53 (1 H, dd, *J* = 9.4, 15.0 Hz, -C*H*=CHSO_2Ph), 7.54 (3 H, m, -SO_2Ph), 7.85 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –4.8 (Me_ASi), –4.7 (Me_BSi), 18.2 [$(CH_3)_3C$–Si], 18.7 (C-3), 23.7 (C-2), 25.9 [$(CH_3)_3$CSi], 56.9 (C-1), 127.3 (-CH=*C*H–SO_2Ph), 127.6 (C_{ortho}, -SO_2Ph), 129.4 (C_{meta}, -SO_2Ph), 133.3 (C_{para}, -SO_2Ph), 141.3 (C_{ipso}, -SO_2Ph), 148.5 (-*C*H=CHSO_2Ph).

MS: *m/z* (%) = 339 (5) [M$^+$], 281 (20), 197 (15), 135 (10), 73 (100).

HRMS: *m/z* calcd for $C_{17}H_{27}O_3SSi$, 339.1450; found, 339.1450.

(–)-(1*R*,2*R*)-2-(2-Benzenesulfonylvinyl)-1-*tert*-butyldimethylsililoxy-cyclopropane (25)

$[\alpha]_D^{20}$ –59.5 (*c* 0.56, $CHCl_3$).

IR: 2957, 2930, 2857, 1624, 1447, 1317, 1260, 1146, 1086, 1020, 837, 793, 667 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.05 (3 H, s, Me_ASi), 0.08 (3 H, s, Me_BSi), 0.88 [9 H, s, $(CH_3)_3CSi$], 0.94 (1 H, dt, *J* = 4.0, 5.8, 5.8 Hz, H_β-3), 1.18 (1 H, dt, *J* = 9.6, 5.8, 5.8 Hz, H_α-3), 1.54 (1 H, m, H-2), 3.75 (1 H, dt, *J* = 4.2, 5.8, 5.8 Hz, H-1), 6.37 (1 H, d, *J* = 15.0 Hz, -CH=C*H*SO_2Ph), 6.83 (1 H, dd, *J* = 9.8, 15.0 Hz, -C*H*=CHSO_2Ph), 7.52 (3 H, m, -SO_2Ph), 7.88 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –5.0 (Me_ASi), –4.9 (Me_BSi), 18.3 [$(CH_3)_3$CSi, C-3], 21.0 (C-2), 25.9 [$(CH_3)_3C$–Si], 54.4 (C-1), 127.7 (C_{ortho}, -SO_2Ph), 128.5 (-CH=*C*HSO_2Ph), 129.3 (C_{meta}, -SO_2Ph), 133.2 (C_{para}, -SO_2Ph), 141.5 (C_{ipso}, -SO_2Ph), 147.8 (-*C*H=CHSO_2Ph).

MS: *m/z* (%) = 339 (5) [M$^+$], 281 (23), 197 (20), 136 (20), 73 (100).

HRMS: *m/z* calcd for $C_{17}H_{27}O_3SSi$, 339.1450; found, 339.1450.

Reaction of compound **17** with LDA

This experiment was carried out based on the procedure given for the above reaction. BuLi 1.6 M (0.12 mL, 0.19 mmol), diisopropylamine (26 μL, 0.19 mmol), THF (0.5 mL) compound **17** (53 mg, 0.13 mmol) in THF (1 mL) were reacted for 90 min to yield 43 mg (100%) of cyclopropanes **26** and **27** in a 40:60 ratio and separated by flash silica column chromatography (hexane–EtOAc, 9:1).

(–)-(1*R*,2*S*)-2-(2-Benzenesulfonylvinyl)-1-(1-Methoxy-1-methylethoxy)-cyclopropane (26)

$[\alpha]_D^{20}$ –7.5 (*c* 1.41, $CHCl_3$).

IR: 3059, 2992, 2944, 1624, 1447, 1373, 1308, 1283, 1211, 1146, 1086, 1067, 802 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.98 (1 H, q, *J* = 6.2 Hz, H_α-3), 1.30 (1 H, m, H_β-3), 1.32 (3 H, s, Me_AC), 1.33 (3 H, s, Me_BC), 1.65 (1 H, dddd, *J* = 2.2, 6.2, 9.6, 9.6 Hz, H-2), 3.21 (1 H, s, CH_3O-), 3.44 (1 H, ddd, 2.2, 4.4, 6.2 Hz, H-1), 6.25 (1 H, d, *J* = 15.0 Hz, -CH=C*H*–SO_2Ph), 6.53 (1 H, dd, *J* = 9.4, 15.0 Hz, -C*H*=$CHSO_2Ph$), 7.53 (3 H, m, -SO_2Ph), 7.85 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0 (C-3), 22.4 (C-2), 24.6 (Me_AC), 25.3 (Me_BC), 49.0 (CH_3O-), 54.4 (C-1), 102.0 [-O*C*$(CH_3)_2(OCH_3)$], 127.6 (C_{ortho}, -SO_2Ph), 127.7 (-CH=*C*HSO_2Ph), 129.4 (C_{meta}, -SO_2Ph), 133.4 (C_{para}, -SO_2Ph), 141.2 (C_{ipso}, -SO_2Ph), 148.1 (-*C*H=$CHSO_2Ph$).

(+)-(1*R*,2*R*)-2-(2-Benzenesulfonylvinyl)-1-(1-Methoxy-1-methylethoxy)-cyclopropane (27)

$[\alpha]_D^{20}$ +59.1 (*c* 1.16, $CHCl_3$).

IR: 3057, 2994, 2944, 1622, 1447, 1373, 1306, 1209, 1144, 1086, 1067, 1005, 820, 799, 752, 689 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.99 (1 H, dt, *J* = 4.4, 6.2, 6.2 Hz, H_β-3), 1.25 (3 H, s, Me_AC), 1.28 (1 H, m, H_α-3), 1.31 (3 H, s, Me_BC), 1.58 (1 H, m, H-2), 3.22 (3 H, s, CH_3O-), 3.72 (1 H, dt, *J* = 4.4, 6.2, 6.2 Hz, H-1), 6.36 (1 H, d, *J* = 15.0 Hz, -CH=C*H*SO_2Ph), 6.80 (1 H, dd, *J* = 10.4, 15.0 Hz, -C*H*=$CHSO_2Ph$), 7.53 (3 H, m, -SO_2Ph), 7.87 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.8 (C-3), 20.5 (C-2), 24.4 (Me_AC), 25.1 (Me_BC), 49.0 (CH_3O-), 52.5 (C-1), 101.8 [(-O*C*$(CH_3)_2(OCH_3)$], 127.6 (C_{ortho}, -SO_2Ph), 128.3 (-CH=*C*HSO_2Ph), 129.4 (C_{meta}, -SO_2Ph), 133.2 (C_{para}, -SO_2Ph), 141.5 (C_{ipso}, -SO_2Ph), 147.8 (-*C*H=$CHSO_2Ph$).

5-Benzenesulfonyl-pent-2-enal (28)

Cyclopropane **18** (13 mg, 0.04 mmol) was dissolved in AcOH–THF–H_2O, 4:1:1 (2 mL). It was left for 12 h before pouring into an Erlenmeyer with a buffer soln (pH = 7.2). The aq layer was extracted with EtOAc, and the organic layer dried over anhyd Na_2SO_4, filtered and the solvent removed in vacuo. The resultant oil was purified by flash silica column chromatography (hexane–EtOAc, 85:15) to yield 8 mg (80%) of **28**.

IR: 2930, 2868, 1690, 1449, 1308, 1146, 1086 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.79 (2 H, m, H-4), 3.27 (2 H, t, *J* = 7.4 Hz, H-5), 6.09 (1 H, dd, *J* = 15.8, 7.6 Hz, H-2), 6.76 (1 H, dt, *J* = 15.8, 6.6 Hz, H-3), 7.64 (3 H, m, -SO_2Ph), 7.93 (2 H, m, -SO_2Ph), 9.47 (1 H, d, *J* = 7.6 Hz, -CHO).

Hydrogenation Reaction; General Procedure

(+)-(1*R*,2*S*)-2-(2-Benzenesulfonylethyl)-1-(tetrahydropyran-2-yloxy)-cyclopropane (29)

To a soln of **18** (13 mg, 0.04 mmol) in EtOAc (1 mL) was added a catalytic amount of PtO_2. The mixture was left to stir under hydrogen for 15 h. The mixture was then filtered through celite and the solvent evaporated in vacuo. If necessary, the product was purified by column chromatography (hexane–EtOAc, 8:2) to yield 14 mg (100%) of **29**.

$[\alpha]_D^{20}$ +39.4 (*c* 0.69, $CHCl_3$).

IR: 3063, 2942, 2870, 1447, 1306, 1148, 1086, 1038, 993, 735, 691 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.32 and 0.46 (1 H, q and m, *J* = 5.8 Hz, H_α-3), 0.71 and 0.92 (1 H, ddd, *J* = 3.4, 5.8, 9.2 Hz, H_β-3), 0.92 (1 H, m, H-2), 1.41–1.82 (8 H, m, H-2′, H-3′, H-4′, -C*H*$_2$$CH_2SO_2Ph$), 3.21 (3 H, m, H-1, -$CH_2$C*H*$_2SO_2Ph$), 3.55 (1 H, m, H_A-5′), 3.87 (1 H, m, H_B-5′), 4.62 (1 H, m, H-1′), 7.62 (3 H, m, -SO_2Ph), 7.92 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.8 and 13.5 (C-3), 16.8 and 18.0 (C-2), 19.3 and 19.6 (C-3′), 25.3 (-*C*$H_2CH_2SO_2Ph$), 25.5 (C-4′), 30.5 (C-2′), 55.7 (-CH_2*C*H_2-SO_2Ph), 55.8 and 56.2 (C-1), 62.4 and 62.8 (C-5′), 98.8 and 99.1 (C-1′), 128.2 (C_{ortho}, -SO_2Ph), 129.4 (C_{meta}, -SO_2Ph), 133.8 (C_{para}, -SO_2Ph), 139.3 (C_{ipso}, -SO_2Ph).

(–)-(1*R*,2*R*)-2-(2-Benzenesulfonylethyl)-1-(tetrahydropyran-2-yloxy)-cyclopropane (34)

This experiment was carried out based on the procedure given for the hydrogenation reaction. Compound **19** (6 mg, 0.02 mmol) was reacted for 15 h to yield 5 mg (90%) of hydrogenated product **34**.

$[\alpha]_D^{20}$ –31.7 (*c* 0.52, $CHCl_3$).

IR: 3071, 2940, 2868, 1447, 1306, 1148, 1088, 1036, 741, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.13 and 0.33 (1 H, dt, *J* = 3.2, 6.0, 6.0 Hz, H_β-3), 0.62 and 0.73 (1 H, dt and m, *J* = 9.2, 6.0, 6.0 Hz, H_α-3), 0.87 (1 H, m, H-2), 130 and 2.07 (8 H, m, H-2′, H-3′, H-4′, -C*H*$_2$$CH_2SO_2Ph$), 3.21 (2 H, m, -$CH_2$C*H*$_2SO_2Ph$), 3.34 and 3.52 (1 H, ddd and m, *J* = 5.2, 10.8, 14.0 Hz, H-1), 3.52 (1 H, m, H_A-5′), 3.84 (1 H, m, H_B-5′), 4.55 and 4.60 (1 H, m, H-1′), 7.56 (2 H, m, -SO_2Ph), 7.64 (1 H, m, -SO_2Ph), 7.92 (2 H, m, -SO_2Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.9 and 11.2 (C-3), 14.7 and 15.5 (C-2), 19.1 and 19.5 (C-3′), 20.9 and 21.7 (-*C*$H_2CH_2SO_2Ph$), 25.1 and 25.3 (C-4′), 30.3 and 30.4 (C-2′), 52.9 and 53.7 (C-1), 55.9 and 56.4 (-CH_2*C*H_2SO_2Ph), 62.2 and 62.5 (C-5′), 98.9 and 99.3 (C-1′), 128.0 (C_{ortho}, -SO_2Ph) 129.1 (C_{meta}, -SO_2Ph), 133.4 (C_{para}, -SO_2Ph), 139.3 (C_{ipso}, -SO_2Ph).

(–)-(1*R*,2*S*)-2-(2-Benzenesulfonylethyl)-1-methoxymethoxy-cyclopropane (31)

This experiment was carried out based on the procedure given for the hydrogenation reaction. Compound **20** (16 mg, 0.06 mmol) was reacted for 15 h to yield 14 mg (89%) of the hydrogenated product **31**.

$[\alpha]_D^{20}$ –14.4 (*c* 1.23, $CHCl_3$).

IR: 3065, 2928, 2855, 1449, 1306, 1146, 1088, 1059, 1003, 920, 741, 691 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.38 (1 H, q, *J* = 6.2 Hz, H_α-3), 0.79 (1 H, ddd, *J* = 3.0, 6.2, 9.8 Hz, H_β-3), 1.14 (1 H, m, H-2), 1.58 (2 H, m, -C*H*$_2$$CH_2SO_2Ph$), 3.17 (3 H, m, H-1, –C*H*$_2$$CH_2SO_2Ph$), 3.37 (3 H, s, -$OCH_2OCH_3$), 4.58 (2 H, s, -O*C*$H_2OCH_3$), 7.58 (3 H, m, -$SO_2Ph$), 7.87 (2 H, m, -$SO_2Ph$).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.7 (C-3), 17.6 (C-2), 25.3 (-*C*$H_2CH_2SO_2Ph$), 55.7 (-CH_2*C*H_2SO_2Ph), 55.9 (-OCH_2O*C*H_3), 56.3 (C-1), 96.9 (-O*C*H_2OCH_3), 128.2 (C_{ortho}, -SO_2Ph), 129.5 (C_{meta}, -SO_2Ph), 133.9 (C_{para}, -SO_2Ph), 139.3 (C_{ipso}, -SO_2Ph).

MS: *m/z* (%) = 271 (1) [M + 1^+], 136 (20), 114 (10), 77 (100).

(–)-(1*R*,2*R*)-2-(2-Benzenesulfonylethyl)-1-methoxymethoxy-cyclopropane (36)

This experiment was carried out based on the procedure given for the hydrogenation reaction. Compound **21** (11 mg, 0.04 mmol) was

reacted for 15 h to yield 9 mg (80%) of the hydrogenated product **36**.

$[\alpha]_D^{20}$ –28.1 (*c* 0.88, $CHCl_3$).

IR: 3067, 2924, 2851, 1447, 1306, 1146, 1088, 1045, 741, 691 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.22 (1 H, dt, *J* = 3.2, 6.2, 6.2 Hz, H_β-3), 0.68 (1 H, dt, *J* = 9.2, 6.2, 6.2 Hz, H_α-3), 0.88 (1 H, m, H-2), 1.86 (2 H, m, -C*H*$_2$CH$_2$SO$_2$Ph), 3.23 (2 H, m, -CH$_2$C*H*$_2$SO$_2$Ph), 3.45 (3 H, m, -OCH$_2$OC*H*$_3$), 3.46 (1 H, dt, *J* = 3.4, 6.6, 6.6 Hz, H-1), 4.55 (1 H, d, *J* = 6.6 Hz, -OC*H*$_A$H$_B$OCH$_3$), 4.60 (1 H, d, *J* = 6.6 Hz, -OCH$_A$*H*$_B$OCH$_3$), 7.58 (3 H, m, -SO$_2$Ph), 7.90 (2 H, m, -SO$_2$Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.3 (C-3), 15.6 (C-2), 21.5 (-*C*H$_2$CH$_2$SO$_2$Ph), 54.1 (C-1), 56.0 (-OCH$_2$O*C*H$_3$), 56.3 (-CH$_2$*C*H$_2$SO$_2$Ph), 97.1 (-O*C*H$_2$OCH$_3$), 128.3 (C_{ortho}, -SO$_2$Ph), 129.4 (C_{meta}, -SO$_2$Ph), 133.8 (C_{para}, -SO$_2$Ph), 139.2 (C_{ipso}, -SO$_2$Ph).

MS: *m/z* (%) = 271 (1) [M + 1^+], 149 (20), 91 (40), 77 (100).

(–)-(1*R*,2*S*)-2-(2-Benzenesulfonylethyl)-1-(4-methoxybenzyloxy)-cyclopropane (32)

This experiment was carried out based on the procedure given for the hydrogenation reaction. Compound **22** (11 mg, 0.03 mmol) was reacted for 30 min to yield 3 mg (34%) of the hydrogenated product **32**.

$[\alpha]_D^{20}$ –18.9 (*c* 0.37, $CHCl_3$).

IR: 2922, 2853, 1613, 1514, 1447, 1304, 1260, 1146, 1086, 1032 cm^{-1}.

MS: *m/z* (%) = 347 (5) [M + 1^+], 121 (37), 99 (5), 49 (70).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.33 (1 H, q, *J* = 6.2 Hz, H_α-3), 0.80 (1 H, ddd, *J* = 3.0, 6.2, 9.8 Hz, H_β-3), 1.14 (1 H, m, H-2), 1.57 (2 H, m, -C*H*$_2$CH$_2$SO$_2$Ph), 3.00 (1 H, dt, *J* = 6.2, 3.0, 3.0 Hz, H-1), 3.11 (2 H, dd, *J* = 7.4, 8.8 Hz, -CH$_2$C*H*$_2$SO$_2$Ph), 3.80 (3 H, s, *p*-C*H*$_3$OC$_6$H$_4$CH$_2$-), 4.41 (1 H, s, *p*-CH$_3$OC$_6$H$_4$C*H*$_A$H$_B$-), 4.42 (1 H, s, *p*-CH$_3$OC$_6$H$_4$CH$_A$*H*$_B$-), 6.85 (2 H, m, H$_{meta}$ *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 7.22 (2 H, m, H$_{ortho}$ *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 7.60 (3 H, m, -SO$_2$Ph) 7.89 (2 H, m, -SO$_2$Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.0 (C-3), 18.0 (C-2), 25.2 (-*C*H$_2$CH$_2$SO$_2$Ph), 55.5 (*p*-*C*H$_3$OC$_6$H$_4$CH$_2$-), 55.8 (-CH$_2$*C*H$_2$SO$_2$Ph), 58.6 (C-1), 72.7 (*p*-CH$_3$OC$_6$H$_4$*C*H$_2$-), 114.1 (C_{meta}, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 128.2 (C_{ortho}, -SO$_2$Ph), 129.5 (C_{meta}, -SO$_2$Ph), 129.8 (C_{ortho}, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 129.9 (C_{ipso}, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 133.9 (C_{para}, -SO$_2$Ph), 139.3 (C_{ipso}, -SO$_2$Ph), 159.6 (C_{para}, *p*-CH$_3$OC$_6$H$_4$CH$_2$-).

HRMS: *m/z* calcd for $C_{19}H_{23}O_4S$, 347.1317; found, 347.1317.

(–)-(1*R*,2*R*)-2-(2-Benzenesulfonylethyl)-1-(4-methoxybenzyloxy)-cyclopropane (37)

This experiment was carried out based on the procedure given for the hydrogenation reaction. Compound **23** (10 mg, 0.03 mmol) was reacted for 18 h to yield 9 mg (92%) of the hydrogenated product **37**.

$[\alpha]_D^{20}$ –9.8 (*c* 0.53, $CHCl_3$).

IR: 2922, 2853, 1615, 1516, 1447, 1304, 1248, 1146, 1088, 1034 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.20 (1 H, dt, *J* = 3.4, 6.2, 6.2 Hz, H_β-3), 0.62 (1 H, dt, *J* = 9.2, 6.2, 6.2 Hz, H_α-3), 0.85 (1 H, m, H-2), 1.87 (2 H, q, *J* = 8.0 Hz, -C*H*$_2$CH$_2$SO$_2$Ph), 3.25 (3 H, m, H-1, -CH$_2$C*H*$_2$SO$_2$Ph), 3.81 (3 H, s, *p*-C*H*$_3$OC$_6$H$_4$CH$_2$-), 4.38 (1 H, s, *p*-CH$_3$OC$_6$H$_4$C*H*$_A$H$_B$-), 4.40 (1 H, s, *p*-CH$_3$OC$_6$H$_4$CH$_A$*H*$_B$-), 6.86 (2 H, m, H$_{meta}$ *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 7.17 (2 H, m, H$_{ortho}$ *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 7.57 (3 H, m, -SO$_2$Ph), 7.90 (2 H, m, -SO$_2$Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.4 (C-3), 16.2 (C-2), 21.4 (-*C*H$_2$CH$_2$SO$_2$Ph), 55.5 (*p*-*C*H$_3$OC$_6$H$_4$CH$_2$-), 56.2 (C-1), 56.4 (-CH$_2$*C*H$_2$SO$_2$Ph), 72.9 (*p*-CH$_3$OC$_6$H$_4$*C*H$_2$-), 114.0 (C_{meta}, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 128.3 (C_{ortho}, -SO$_2$Ph), 129.4 (C_{meta}, -SO$_2$Ph), 129.6 (C_{ortho}, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 130.2 (C_{ipso}, *p*-CH$_3$OC$_6$H$_4$CH$_2$-), 133.7 (C_{para}, -SO$_2$Ph), 139.3 (C_{ipso}, -SO$_2$Ph), 159.2 (C_{para}, *p*-CH$_3$OC$_6$H$_4$CH$_2$-).

MS: *m/z* (%) = 347 (5) [M + 1^+], 154 (40), 121 (100), 95 (40), 77 (70).

HRMS: *m/z* calcd for $C_{19}H_{23}O_4S$, 347.1317; found, 347.1317.

(–)-(1*R*,2*S*)-2-(2-Benzenesulfonylethyl)-1-*tert*-butyldimethylsililoxy-cyclopropane (33)

This experiment was carried out based on the procedure given for the hydrogenation reaction. Compound **24** (12 mg, 0.03 mmol) was reacted for 1 h to yield 11 mg (90%) of the hydrogenated product **33**.

$[\alpha]_D^{20}$ –36.4 (*c* 0.78, $CHCl_3$).

IR: 2957, 2950, 2857, 1447, 1308, 1148, 1086, 873, 779 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.06 (6 H, s, Me$_A$Si, Me$_B$Si), 0.27 (1 H, q, *J* = 5.8Hz, H_α-3), 0.65 (1 H, ddd, *J* = 2.8, 5.8, 9.4 Hz, H_β-3), 0.85 (1 H, m, H-2), 0.86 [9 H, s, (CH$_3$)$_3$CSi], 1.34 (1 H, m, -C*H*$_A$H$_B$CH$_2$SO$_2$Ph), 1.81 (1 H, m, -CH$_A$*H*$_B$CH$_2$SO$_2$Ph), 3.12 (3 H, m, H-1, -CH$_2$C*H*$_2$SO$_2$Ph), 7.59 (3 H, m, -SO$_2$Ph), 7.90 (2 H, m, -SO$_2$Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –4.6 (Me$_A$–Si, Me$_B$–Si), 14.3 (C-3), 18.2 [(CH$_3$)$_3$*C*–Si], 18.8 (C-2), 25.3 (-*C*H$_2$CH$_2$SO$_2$Ph), 26.0 [(*C*H$_3$)$_3$CSi], 53.4 (C-1), 55.7 (-CH$_2$*C*H$_2$SO$_2$Ph), 128.2 (C_{ortho}, -SO$_2$Ph), 129.5 (C_{meta}, -SO$_2$Ph), 133.9 (C_{para}, -SO$_2$Ph), 139.5(C_{ipso}, -SO$_2$Ph).

MS: *m/z* (%) = 341 (25) [M^+], 283 (35), 211 (8), 135 (25), 73 (100).

HRMS: *m/z* calcd for $C_{17}H_{29}O_3SSi$, 341.1607; found, 341.1607.

(–)-(1*R*,2*R*)-2-(2-Benzenesulfonylethyl)-1-*tert*-butyldimethylsililoxy-cyclopropane (38)

This experiment was carried out based on the procedure given for the hydrogenation reaction. Data are reported. Compound **25** (27 mg, 0.08 mmol) was reacted for 22 h to yield 18 mg (66%) of the hydrogenated product **38**.

$[\alpha]_D^{20}$ –36.8 (*c* 1.37, $CHCl_3$).

IR: 2957, 2930, 2857, 1447, 1306, 1148, 1088, 839, 779 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.01 (3 H, s, Me$_A$Si), 0.04 (3 H, s, Me$_B$Si), 0.62 (2 H, m, H-3), 0.75 (1 H, m, H-2), 0.81 [9 H, s, (CH$_3$)$_3$CSi], 1.71 (1 H, m, -C*H*$_A$H$_B$-CH$_2$SO$_2$Ph), 1.87 (1 H, m, -CH$_A$*H*$_B$-CH$_2$SO$_2$Ph), 3.07–3.38 (3 H, m, H-1, -CH$_2$C*H*$_2$SO$_2$Ph), 7.58 (3 H, m, -SO$_2$Ph), 7.90 (2 H, m, -SO$_2$Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –5.0 (Me$_A$Si), –4.8 (Me$_B$Si), 13.3 (C-3), 15.0 (C-2), 18.1 [(CH$_3$)$_3$*C*Si], 21.6 (-*C*H$_2$CH$_2$SO$_2$Ph), 25.9 [(*C*H$_3$)$_3$CSi], 50.2 (C-1), 56.4 (-CH$_2$*C*H$_2$SO$_2$Ph), 128.3 (C_{ortho}, -SO$_2$Ph), 129.4 (C_{meta}, -SO$_2$Ph), 133.7 (C_{para}, -SO$_2$Ph), 139.5 (C_{ipso}, -SO$_2$Ph).

MS: *m/z* (%) = 341 (35) [M^+], 283 (40), 199 (5), 135 (25), 73 (100).

HRMS: *m/z* calcd for $C_{17}H_{29}O_3SSi$, 341.1607; found, 341.1609.

(–)-(1*R*,2*S*)-2-(2-Benzenesulfonylethyl)-cyclopropanol (30)

To a soln of **26** (27 mg, 0.09 mmol) in EtOAc (1 mL) was added a catalytic amount of PtO_2. The mixture was left to stir under hydrogen for 15 h. It was filtered then through celite and the solvent evaporated in vacuo. The product was purified by column chromatography (hexane–EtOAc, 7:3) to yield 10 mg (48%) of **30**.

To a soln of **29** (8 mg, 0.02 mmol) in MeOH (1 mL) was added a catalytic amount of *p*-toluensulfonic acid monohydrate. The mixture was left to stir for 2 h. The soln was then diluted with Et_2O, and washed with a soln of $NaHCO_3$ (5%), H_2O and sat. brine. The organic phase was dried with anhyd Na_2SO_4, filtered and removed the

solvent in vacuo. The product was purified by column chromatography (hexane–EtOAc, 7:3) to yield 5 mg (79%) of **30**.

Compound **31** (10 mg, 0.04 mmol) was dissolved in 1 mL of the mixture: THF–H_2–HCl 6 N (1:5:2). The mixture was left to stir for 15 h before the addition of sat. NaCl soln (1 mL). The product was extracted into EtOAc (3 ×). The organic extracts were dried over anhyd Na_2SO_4, filtered and the solvent removed in vacuo. The product was purified by flash silica column chromatography (hexane–EtOAc, 7:3) to yield 7 mg (60%) of **30**.

To a soln of **32** (4 mg, 0.01 mmol) in EtOAc (1 mL) was added a catalytic amount of Pd–C. The mixture was left to stir under hydrogen for 1 h. It was then filtered through celite and the solvent evaporated in vacuo. The product was purified by column chromatography (hexane–EtOAc, 7:3) to yield 1 mg (42%) of **30**.

To a soln of **33** (8 mg, 0.02 mmol) in THF (0.5 mL) was added tretrabutylammonium fluoride 1.0 M soln (34 mL, 0.03 mmol). The mixture was left to stir for 20 h. Then, it was diluted with EtOAc, washed with H_2O and sat. brine. The organic layer was dried over anhyd Na_2SO_4, filtered and concentrated. The product was purified by column chromatography (hexane–EtOAc, 7:3) to yield 4 mg (78%) of **30**.

$[\alpha]_D^{20}$ –17.2 (*c* 0.43, $CHCl_3$).

IR: 3200–3600, 2926, 2855, 1447, 1304, 1142, 1086, 739, 689 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.37 (1 H, q, *J* = 6.0 Hz, H_α-3), 0.76 (1 H, ddd, *J* = 2.8, 5.6, 9.2 Hz, H_β-3), 0.95 (1 H, m, H-2), 1.56–1.73 (2 H, m, -C*H*$_2$CH$_2$SO$_2$Ph), 3.18 (2 H, ddd, *J* = 4.0, 6.4, 8.8 Hz, -CH$_2$C*H*$_2$SO$_2$Ph), 3.25 (1 H, dt, *J* = 6.4, 2.8, 2.8 Hz, H-1), 7.58 (2 H, m, -SO_2Ph), 7.65 (1 H, m, -SO_2Ph), 7.91 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.9 (C-3), 19.6 (C-2), 25.2 (-*C*H$_2$CH$_2$SO$_2$Ph), 52.8 (C-1), 56.0 (-CH$_2$*C*H$_2$SO$_2$Ph), 128.2 (C_{ortho}, -SO_2Ph), 129.5 (C_{meta}, -SO_2Ph), 133.9 (C_{para}, -SO_2Ph), 139.4 (C_{ipso}, -SO_2Ph).

MS: *m/z* (%) = 226 (5) [M^+], 184 (10), 143 (60), 125 (25), 84 (85), 77 (90).

HRMS: *m/z* calcd for $C_{11}H_{14}O_3S$, 226.0664; found, 226.0673.

(–)-(1*R*,2*R*)-2-(2-Benzenesulfonylethyl)-cyclopropanol (35)

To a soln of **34** (3 mg, 0.01 mmol) in MeOH (1 mL) was added a catalytic amount of *p*-toluensulfonic acid monohydrate. The mixture was left to stir for 15 h. The soln was then diluted with Et_2O, and washed with a soln of $NaHCO_3$ (5%), H_2O and sat. brine. The organic phase was dried with anhyd Na_2SO_4, filtered and the solvent removed in vacuo. The product was purified by column chromatography (hexane–EtOAc, 7:3) to yield 2 mg (95%) of **35**.

Compound **36** (10 mg, 0.04 mmol) was dissolved in the mixture: THF–H_2O–HCl 6 N (1:5:2, 1 mL). The mixture was left to stir for 15 h before the addition of sat. NaCl soln (1 mL). The product was extracted into EtOAc (3 ×). The organic extracts were dried over anhyd Na_2SO_4, filtered and the solvent removed in vacuo. The product was purified by flash silica column chromatography (hexane–EtOAc, 7:3) to yield 6 mg (72%) of **35**.

To a soln of **37** (5 mg, 0.01 mmol) in EtOAc (1 mL) was added a catalytic amount of Pd–C. The mixture was left to stir under hydrogen for 15 h. It was then filtered through celite and the solvent evaporated in vacuo. The product was purified by column chromatography (hexane–EtOAc, 7:3) to yield 2 mg (53%) of **35**.

To a soln of **38** (17 mg, 0.05 mmol) in THF (0.5 mL) was added tetrabutyl ammonium fluoride 1.0 M soln (77 mL, 0.08 mmol). The mixture was left to stir for 3 h. Then, it was diluted with EtOAc and washed with H_2O and sat. brine. The organic layer was dried over anhyd Na_2SO_4, filtered and concentrated. The product was purified by column chromatography (hexane–EtOAc, 7:3) to yield 9 mg (78%) of **35**.

$[\alpha]_D^{20}$ –8.5 (*c* 0.46, $CHCl_3$).

IR: 3200–3600, 3063, 2926, 2855, 1447. 1304, 1144, 1086, 689, 665 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.21 (1 H, m, H_β-3), 0.72 (2 H, m, H_α-3, H-2), 1.93 (2 H, m, -C*H*$_2$CH$_2$SO$_2$Ph), 2.26 (1 H, br s, -OH), 3.26 (2 H, m, -CH$_2$C*H*$_2$SO$_2$Ph), 3.52 (1 H, dt, *J* = 3.2, 6.4, 6.4 Hz, H-1), 7.61 (3 H, m, -SO_2Ph), 7.92 (2 H, m, -SO_2Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.3 (C-3), 16.7 (C-2), 20.7 (-*C*H$_2$CH$_2$SO$_2$Ph), 49.9 (C-1), 56.6 (-CH$_2$*C*H$_2$SO$_2$Ph), 128.2 (C_{ortho}, -SO_2Ph), 129.5 (C_{meta}, -SO_2Ph), 133.9 (C_{para}, -SO_2Ph), 139.5 (C_{ipso}, -SO_2Ph).

MS: *m/z* (%) = 226 (5) [M^+] 184 (15), 143 (65), 125 (30), 104 (20), 77 (100), 67 (25).

HRMS: *m/z* calcd for $C_{11}H_{14}O_3S$, 226.0664; found, 226.0639.

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