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Regio- and stereoselective ring opening of epoxides. Enantioselective synthesis of 2,3,4-trisubstituted five-membered heterocycles†

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Abstract—By using the appropriate protecting groups, the opening of (2*S*,3*S*,4*E*)-5-benzenesulfonyl-2,3-epoxy-pent-4-en-1-ol (−)-**2** could be controlled and used for the synthesis of the enantiomeric pyrrolidines (+)- and (−)-**18** and the tetrahydrofuran analogs (+)- and (−)-**19**. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The discovery of the asymmetric epoxidation of allylic epoxides by Sharpless[1] was a milestone in asymmetric synthesis and following on from this, the regio- and stereoselective opening of chiral epoxides have been the subject of many studies in recent years.[2]

Five-membered oxa and aza ring systems are widely distributed in nature and have attracted the interest of the scientific community, particularly in conjunction with the total synthesis of polyether natural products,[3] or pyrrolidines with glycosidase inhibiting activity.[4] Our laboratory has been involved in a program seeking to exploit the reactivity of 1-hydroxymethyl-4-sulfonylbutadienes for the synthesis of functionalized oxygen and nitrogen five-membered heterocycles.

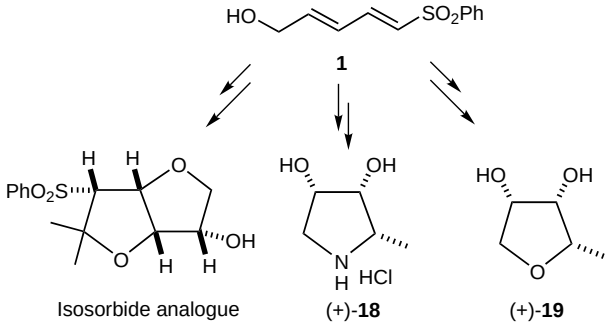
The vinyl sulfone **1** has been transformed into an isosorbide analogue exploiting its chemo- and enantioselective epoxidation and the reactivity of the α position of the vinyl sulfone towards electrophiles.[5] Similarly, **1** has been transformed into a biologically active 2,3,4-trisubstituted pyrrolidine (+)-**18**, and tetrahydrofuran (+)-**19** using the regio- and stereoselective opening of the corresponding epoxide (Scheme 1).

2. Results and discussion

In this work we wished to investigate the regio- and stereoselective opening of chiral epoxides and disclose the possibility of obtaining enantiomeric compounds by the use of appropriate protecting groups (Scheme 2).

The starting material chosen for these studies was compound (−)-**2**, obtained by Sharpless epoxidation of **1** with L-(+)-DET,[1c] with e.e. of 95% (measured by Mosher's ester derivatization).[6] Compound (−)-**2** was protected with various groups under the usual conditions (Scheme 3).

In a recent paper we reported the influence of several protecting groups on the cyclization of δ-hydroxyepoxides.[7] In this paper, control of the opening of epoxides



Scheme 1.

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† In memoriam of Dr. B. del Rey.

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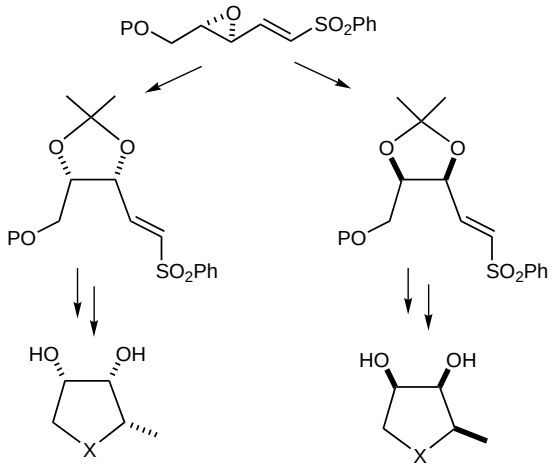
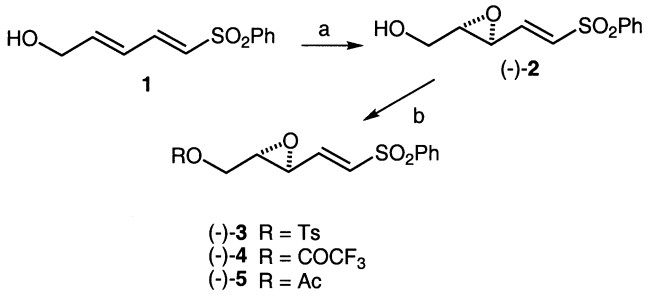


Scheme 2.



Scheme 3. *Reagents and conditions*: (a) L-(+)-DET, $Ti(^iPrO)_4$, TBHP, CH_2Cl_2, −20°C, 12 h, 85%; (b) TsCl, Py, 80% or CF_3COCl, Py, 71%, or Ac_2O, Py, 95%.

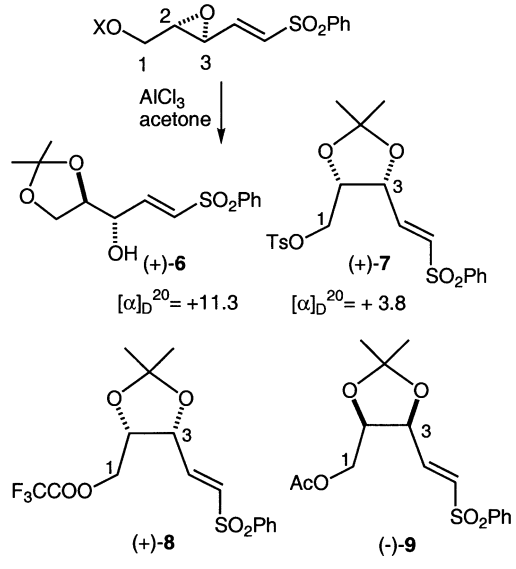
obtained from 1-hydroxymethyl-4-sulfonylbutadiene by the use of different protecting groups is reported. Treatment of compounds (−)-**2**, (−)-**3**, (−)-**4** and (−)-**5**, with $AlCl_3$ in acetone[8] gave only one compound for each starting material as shown in Scheme 4.

As can be seen, the opening of the epoxide could be controlled by choosing a suitable protecting group. If there is no 'internal nucleophile' on C-1, as for (−)-**3** and (−)-**4**, inversion at C-3 occurs, giving rise to compounds (+)-**7** and (+)-**8**, respectively. The existence of an 'internal nucleophile' on C-1, as is the case for (−)-**2** and (−)-**5**, produced opening on C-2 with inversion of configuration in both cases, giving compounds (+)-**6** and (−)-**9**, respectively (Scheme 4).

The regio- and stereoselective opening of these epoxides could easily be rationalized. Compound (+)-**6** would be produced by Payne rearrangement[1b] and transformation of the corresponding epoxide into the acetal,[9] while compounds (+)-**7** and (+)-**8** would arise from nucleophilic opening at C-3 by acetone, as described by Sharf[8] and Colvin.[10] The result for (−)-**9** could be understood by the intervention of an acetoxonium cation and acetone acting as nucleophile, as described by Rastetter and Oppolzer.[11]

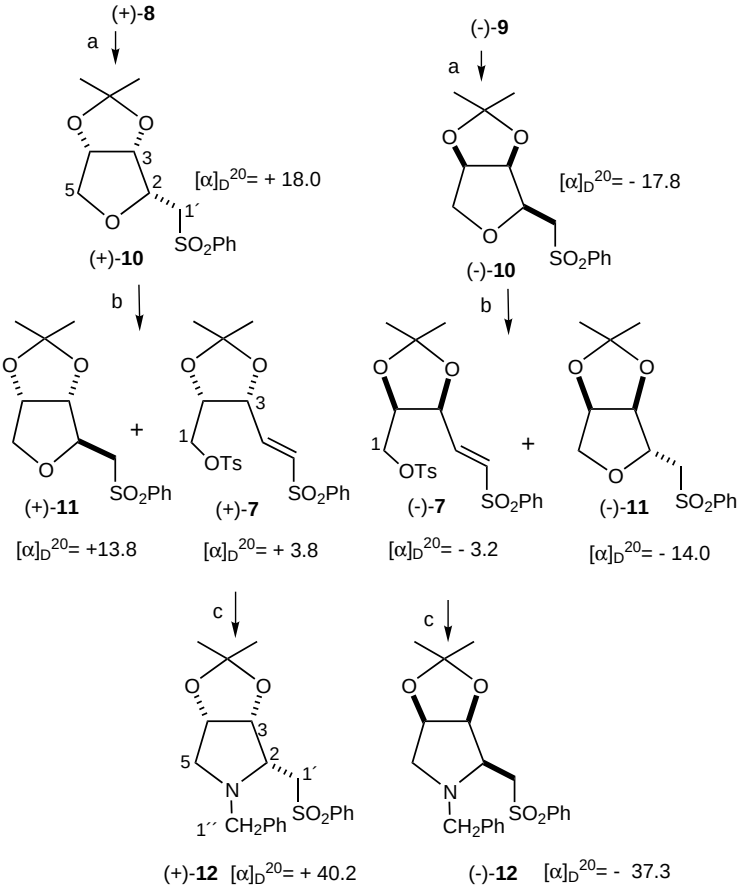
The stereochemistry of these compounds was established in the following way. The stereochemistry of (+)-**7** has been reported.[5] Treatment of compounds (+)-**8** and (−)-**9** under basic conditions gave the enantiomeric tetrahydrofurans (+)-**10** and (−)-**10**, respectively, in a diastereoselective way. In order to establish unequivocally the configuration of each molecule, both were transformed into known compounds. Treatment of (+)-**10** and (−)-**10** separately with *n*-BuLi in THF and quenching with TsCl led to compounds (+)-**7** and (−)-**7**, respectively, in 60% yield with 20% starting material recovered and 5% of the diastereoisomers of (+)-**10** and (−)-**10** at the C-2 center, compounds (+)-**11** and (−)-**11**, respectively. These derivatives, (+)-**7** and (−)-**7**, already demonstrate the stereochemistry of the parent compounds, but due to the low value of the specific rotation, were transformed to give the enantiomeric pyrrolidines (+)-**12** and (−)-**12**, respectively, by treatment with benzylamine in methanol. No other diastereomer was detected, confirming the stereochemical outcome of the epoxide ring-opening reaction (Scheme 5).

The stereochemistry of (+)-**6** remained to be established. This was carried out as shown in Scheme 6. Deprotection of (+)-**6** with HCl/MeOH followed by treatment under basic conditions, gave a 1:1 mixture of diastereoisomers at C-2, (−)-**13** and (−)-**14**. These compounds were protected under the usual conditions, without isolation, to give (−)-**10** and (−)-**11** in 80% yield for the two steps. The specific rotation value and the rest of the physical properties for (−)-**10** and (−)-**11** were concordant with compounds obtained before, confirming the inversion at C-2 during the opening of the epoxide in the reaction of (−)-**2** with $AlCl_3$ in acetone. The stereochemical assignment was confirmed by deprotection of (−)-**10** and (−)-**11** to give (−)-**13** and (−)-**14** respectively, in excellent yield (Scheme 6).

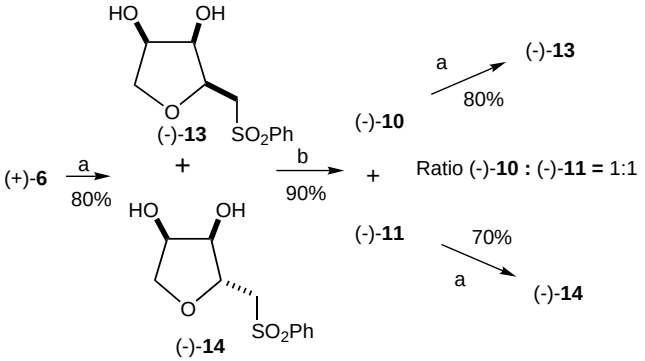


X	H, (-)-2	Ts, (-)-3	$COCF_3$, (-)-4	Ac, (-)-5
	(+)-6 (82%)	(+)-7 (65%)	(+)-8 (63%)	(-)-9 (80%)

Scheme 4.



Scheme 5. *Reagents and conditions*: (a) K_2CO_3, MeOH, quantitative; (b) 1. *n*-BuLi, THF, −78°C, 2. TsCl, THF, 60%; (c) $BnNH_2$, MeOH, Et_3N, 78%.



Scheme 6. *Reagents and conditions*: (a) 1. 2 M HCl, MeOH; 2. Na_2CO_3, MeOH; (b) *p*-TsOH, acetone.

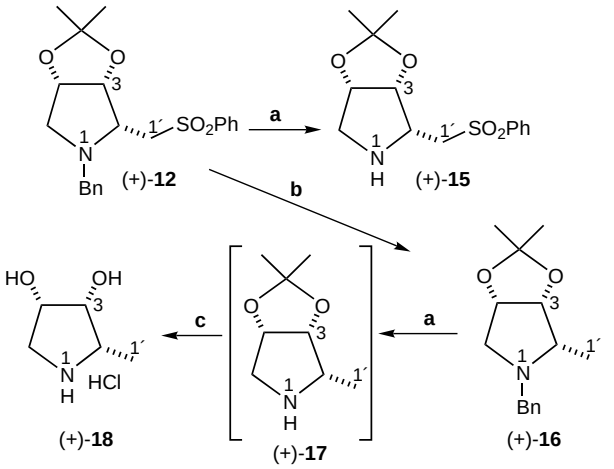
Having determined the stereochemical outcome of the epoxide ring-opening reactions, we then synthesized the corresponding heterocycles. Compound (+)-**12** was transformed into pyrrolidine (+)-**18** as shown in Scheme 7.

Deprotection of (+)-**12** with H_2, Pd/C led to (+)-**15** in a 95% yield. The stereochemistry of this compound was assigned by ^{1}H NMR and NOE experiments.[5] Desulfonation of (+)-**15** proceed in low yield, so (+)-**12** was first treated with sodium amalgam under the usual conditions to produce (+)-**16** in 77% yield. Compound (+)-**16** was then debenzylated under the same conditions as before to produce (+)-**17**. Without isolation, (+)-**17** was subjected to treatment with 6 M HCl to give pyrrolidine (+)-**18** in an excellent yield (80%) as its hydrochloride salt, over two steps. This compound shows the same physical properties as described in the literature.[4d]

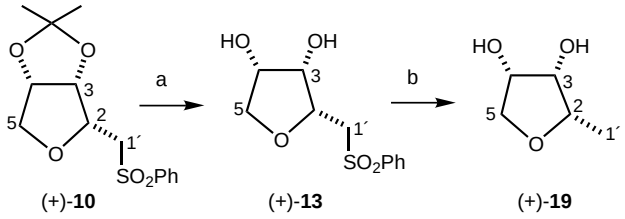
The versatility of this procedure for obtaining enantiomeric compounds could be seen as compound (−)-**7** having been transformed above into (−)-**12**. This compound could easily be transformed into the enantiomer of pyrrolidine (+)-**18**, following an identical procedure.

The synthesis of the tetrahydrofuran analogues was straightforward. Tetrahydrofuran (+)-**10** was transformed into diol (+)-**19**, as shown in Scheme 8. Deprotection of the acetal under acidic conditions gave diol (+)-**13**, confirming the assignment of (−)-**13** made above. Desulfonylation of (+)-**13** as before gave the oxygen analogue of pyrrolidine (+)-**18**, the tetrahydrofuran (+)-**19**. The enantiomeric tetrahydrofuran (−)-**19** could be obtained starting from (−)-**10** following the same procedure.

Thus, using different protecting groups, the regio- and stereoselectivity of the epoxide ring-opening reaction of (2*S*,3*S*,4*E*)-5-benzenesulfonyl-2,3-epoxy-pent-4-en-1-ol



Scheme 7. *Reagents and conditions*: (a) H_2, Pd/C, MeOH, 90%; (b) Na(Hg), MeOH, 77%; (c) 6 M HCl, MeOH, 80%.



Scheme 8. *Reagents and conditions*: (a) 6 M HCl, MeOH, 80%; (b) Raney-Ni, MeOH, 77%.

could be controlled to give enantiomeric pyrrolidine and tetrahydrofuran analogues. Compounds with tosylate or trifluoroacetate groups at C(1) undergo ring-opening under the above conditions with inversion at C-3, while compounds with no protecting group or an acetate group at C-1 undergo inversion at the C-2 center. Thus, employing only natural L-(+)-DET in the Sharpless epoxidation can be used in combination with this methodology to obtain both enantiomeric series.

The fact that both enantiomeric series can be obtained by the use of either isomer of DET in the Sharpless epoxidation reaction opens interesting possibilities. Either the route from epoxide to heterocycle with the best yield can be selected, or, where additional stereocenters are present in the starting material, it should be possible to use the enantiomer of DET that gives the best selectivity and yield in the Sharpless oxidation step, adjusting the subsequent chemistry to give the desired stereochemistry at the three centers in the heterocycles produced using the method described here.

In this paper, we have also reported the transformation of compound (−)-**2** into a 2,3,4-trisubstituted pyrrolidine, which has glycosidase inhibiting activity,[5] its tetrahydrofuran analogue and a route to synthesize the enantiomers of both compounds. Tetrahydrofurans with an extra side chain are used in the synthesis of amphiphilic structures[11] so this methodology opens new ways to obtain derivatives of these compounds easily in both enantiomeric forms.

3. Experimental

3.1. General

Unless otherwise stated, all chemicals were purchased as the highest purity commercially available and were used without further purification. Melting points were determined with a Kofler hot stage melting point apparatus and are uncorrected. IR spectra were recorded on a BOMEM 100 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were performed in deuterochloroform and referenced to the residual peak of $CHCl_3$ at δ 7.26 and δ 77.0 ppm for ^{1}H and ^{13}C, respectively, in a Bruker WP-200 SY and a BRUKER DRX 400 MHz. Chemical shifts are reported in δ, ppm and coupling constants (J) are given in Hz. MS were performed in a VG-TS 250 spectrometer at 70 eV ionizing voltage. Mass spectra are presented as m/z (% rel. int.). HRMS were recorded on a VG Platform spectrometer using Electronic Impact (EI) or Fast Atom Bombardment (FAB) technique. Optical rotations were determined in a Perkin–Elmer 241 polarimeter in 1 dm cells. Diethyl ether, THF and benzene were distilled from sodium, and pyridine and dichloromethane were distilled under argon from CaH_2.

3.2. (2*S*,3*S*,4*E*)-5-Benzenesulfonyl-2,3-epoxy-pent-4-en-1-ol (−)-2

To a solution of L-(+)-DET (460 mg, 2.23 mmol) in CH_2Cl_2 (10 mL) cooled at −23°C was added titanium isopropoxide (0.61 mL, 2.23 mmol). The mixture was stirred for 15 min before the addition of a solution of compound **1** (500 mg, 2.23 mmol) in CH_2Cl_2 (12 mL) and finally a solution of *t*-butyl hydroperoxide (5.5 M in decane, 0.80 mL, 4.46 mmol) was added. The resulting mixture was then stored (~48 h) in the freezer at ~20°C. Then the flask was placed in a bath at −23°C and 10% aqueous tartaric acid solution (7 mL) was added. After 30 min the cooling bath was removed and stirring was continued at room temperature for 1 h until the aqueous layer became clear. The organic layer was washed once with water. The resulting solution was cooled in an ice bath and then 1N sodium hydroxide solution (8 mL) was added and the mixture was stirred for 30 min. The organic layer was washed with water and brine, dried with sodium sulfate and concentrated to give a yellow oil. It was purified by flash chromatography (*n*-hexane/EtOAc, 7:3) to give (−)-**2** (454 mg, 85%) as a white oil: $[\alpha]_D^{20} = -11.7$ ($c = 1.90$, $CHCl_3$), IR (film) ν (cm^{-1}): 3600, 1447, 1308, 1148, 1086; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.90–7.51 (5H, m, Ar), 6.77 (1H, dd, $J = 15.0$, and 5.9, H-4), 6.67 (1H, d, $J = 15.0$, H-5), 3.93 (1H, d, $J = 13.0$, H_a-1), 3.71 (1H, d, $J = 13.0$, H_b-1), 3.57 (1H, dd, $J = 5.9$ and 1.8, H-3), 3.09 (1H, d, $J = 1.8$, H-2); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 142.0 (CH-4), 139.8 (C-*ipso*), 133.7 (CH-*para*), 132.9 (CH-5), 129.4 (2CH-*meta*), 127.7 (2CH-*ortho*), 61.4 (CH-3), 60.5 (CH_2-1), 52.2 (CH-2); EIMS m/z (%) 241 (M^++1, 3) 197 (30), 125 (45), 77 (100) 64 (15), HRMS (EI) m/z calcd for $C_{11}H_{12}O_4S$ 240.0456; found 241.0453 (M^++1).

3.3. (2*S*,3*S*,4*E*)-5-Benzenesulfonyl-2,3-epoxy-pent-4-en-1-yl tosylate (−)-3

To a solution of (−)-**2** (400 mg, 1.67 mmol) in pyridine (4 mL) was added TsCl (476 mg, 2.50 mmol) at 0°C. The mixture was stirred for 8 h and ice was added. The mixture was stirred for 30 min and then extracted with EtOAc. The combined organic extracts were washed with aqueous HCl (2N), $NaHCO_3$ (5%) and brine. After drying and concentration the residue was purified by flash chromatography (*n*-hexane/EtOAc, 8:2) to gave (−)-**3** (526 mg, 80%): $[\alpha]_D^{20}=-12.2$ ($c=0.78$, $CHCl_3$), IR (film) ν (cm^{-1}): 1362, 1177, 1150, 1086, 966; ^1H NMR ($CDCl_3$, 200 MHz) δ 8.01–7.30 (9H, m, Ar), 6.68 (1H, dd, $J=15.0$, and 5.2, H-4), 6.64 (1H, d, $J=15.0$, H-5), 4.20 (1H, dd, $J=12.2$ and 3.8, H_a-1), 4.10 (1H, dd, $J=12.2$ and 4.6, H_b-1), 3.40 (1H, dd, $J=5.2$, and 1.8, H-3), 3.13 (1H, m, H-2), 2.44 (3H, s, CH_3-Ts); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 145.4 (C-*ipso*, -Ts), 140.1 (CH-4), 139.6 (C-*ipso*, SO_2Ph), 134.1 (CH-5), 133.8 (CH-*para*, SO_2Ph), 132.6 (C-*para*, -Ts), 130.0 (2CH-*meta*, -Ts), 129.4 (2CH-*meta*, -SO_2Ph), 127.9 (2CH-*ortho*, -Ts), 127.8 (2CH-*ortho*, -SO_2Ph), 68.1 (CH_2-1), 57.6 (CH-3), 52.9 (CH-2), 21.9 (CH_3-Ts); EIMS m/z (%) 394 (M^+, 5) 351 (5), 155 (42), 125 (55), 91 (100), HRMS (EI) m/z calcd for $C_{18}H_{18}O_6S_2$ 394.0545; found 394.0546.

3.4. (2*S*,3*S*,4*E*)-5-Benzenesulfonyl-2,3-epoxy-pent-4-en-1-yl trifluoroacetate (−)-4

To a solution of (−)-**2** (300 mg, 1.25 mmol) in pyridine (4 mL) was added trifluoracetic anhydride (0.30 mL, 1.87 mmol) at 0°C. The mixture was stirred for 6 h and quenched with water. The organic layer was separated, washed with water and brine and dried over Na_2SO_4. The residue obtained by filtration was purified by flash chromatography (*n*-hexane/EtOAc, 8:2) to give (−)-**4** (300 mg, 71%): $[\alpha]_D^{20}=-20.5$ ($c=0.92$, $CHCl_3$), IR (film) ν (cm^{-1}): 1790, 1449, 1319, 1150, 1086; ^1H NMR ($CDCl_3$, 200 MHz) δ: 7.91–7.53 (5H, m, Ar), 6.77 (1H, dd, $J=15.0$, and 5.2, H-4), 6.71 (1H, d, $J=15.0$, H-5), 4.70 (1H, dd, $J=12.0$ and 2.8, H_a-1), 4.34 (1H, dd, $J=12.0$ and 5.0, H_b-1), 3.50 (1H, dd, $J=5.2$, and 1.8, H-3), 3.26 (1H, m, H-2); ^{13}C NMR ($CDCl_3$, 50.3 MHz): 171.0 (CO-CF_3), 139.4 (CH-4), 139.8 (C-*ipso*), 134.5 (CH-5), 134.1 (CH-*para*), 129.7 (2CH-*meta*), 128.1 (2CH-*ortho*), 65.9 (CH_2-1), 57.2 (CH-3), 52.9 (CH-2); EIMS m/z (%): 336 (M^+, 12), 197 (35), 163 (100), 125 (100), 77 (92); HRMS (EI) m/z calcd for $C_{13}H_{11}O_5F_3S$ 336.0279; found 336.0285.

3.5. (2*S*,3*S*,4*E*)-5-Benzenesulfonyl-2,3-epoxy-pent-4-en-1-yl acetate (−)-5

To a solution of (−)-**2** (300 mg, 1.25 mmol) in pyridine (5 mL) was added acetic anhydride (1 mL). The solution was stirred for 30 min and quenched with ice. After 15 min ethyl acetate (15 mL) was added. The organic layer was separated, washed with aqueous 2N HCl, $NaHCO_3$ (5%), water and brine and dried over Na_2SO_4. Concentration followed by chromatography on silica gel (*n*-hexane/EtOAc, 8:2) gave (−)-**5** (318 mg, 95%): $[\alpha]_D^{20}=-40.6$ ($c=1.17$, $CHCl_3$), IR (film) ν (cm^{-1}): 3055, 1744, 1148; ^1H NMR ($CDCl_3$, 200 MHz) δ: 7.91–7.53 (5H, m, Ar), 6.78 (1H, dd, $J=15.0$, and 5.6, H-4), 6.69 (1H, d, $J=15.0$, H-5), 4.40 (1H, dd, $J=12.6$ and 3.4, H_a-1), 4.06 (1H, dd, $J=12.6$ and 5.0, H_b-1), 3.46 (1H, dd, $J=5.6$, and 1.8, H-3), 3.18 (1H, m, H-2), 2.09 (3H, s, CH_3-Ac); ^{13}C NMR ($CDCl_3$, 50.3 MHz): 170.7 (CO-Ac), 140.9 (CH-4), 139.8 (C-*ipso*), 134.0 (CH-5), 133.8 (CH-*para*), 129.7 (2CH-*meta*), 128.1 (2CH-*ortho*), 63.2 (CH_2-1), 58.4 (CH-3), 53.3 (CH-2), 20.9 (CH_3-Ac).

3.6. (2*R*,3*S*,4*E*)-5-Benzenesulfonyl-1,2-isopropylidene-dioxy-pent-4-en-3-ol (+)-6

To a solution of (−)-**2** (350 mg, 1.04 mmol) in acetone (10 mL) was added a catalytic amount of $AlCl_3$. The mixture was stirred for 24 h then neutralized with a solution of $NaHCO_3$ (5%) and extracted with EtOAc. The combined organic layers washed with water and brine. The residue was purified by flash chromatography (*n*-hexane/EtOAc, 8.5:1.5) to give (+)-**6** (254 mg, 82%): $[\alpha]_D^{20}=+11.3$ ($c=0.60$, $CHCl_3$), IR (film) ν (cm^{-1}): 2928, 1308, 1148, 1071, 843; ^1H NMR ($CDCl_3$, 200 MHz) δ: 7.90–7.50 (5H, m, Ar), 6.95 (1H, dd, $J=15.0$, and 3.4, H-4), 6.69 (1H, dd, $J=15.0$ and 2.2, H-5), 4.52 (1H, brs, H-3), 4.13 (1H, m, H-2), 3.92 (1H, dd, $J=8.4$, and 6.6, H_a-1), 3.84 (1H, dd, $J=8.4$, and 6.0, H_b-1), 1.42 (3H, s, CH_3), 1.35 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 143.1 (CH-4), 140.3 (C-*ipso*), 133.7 (CH-*para*), 131.9 (CH-5), 129.6 (2CH-*meta*), 127.9 (2CH-*ortho*), 110.3 (C-acetonide), 77.1 (CH-2), 70.3 (CH-3), 64.8 (CH_2-1), 26.6 (CH_3 -acetonide), 25.1 (CH_3-acetonide); MS (FAB) m/z (%) 299 (M^++1, 10), 241 (10), 136 (100), 91 (42), 69 (57); HRMS (FAB) m/z calcd for $C_{14}H_{19}O_5S$ 299.0953; found 299.0958.

3.7. (2*S*,3*R*,4*E*)-5-Benzenesulfonyl-2,3-isopropylidene-dioxy-pent-4-en-1-yl tosylate (+)-7

Starting from (−)-**3** (90 mg, 0.23 mmol) and following an identical procedure to that described for the preparation of (+)-**6** compound, (+)-**7** (67 mg, 65%) was obtained: $[\alpha]_D^{20}=+3.8$ ($c=1.05$, $CHCl_3$), IR (film) ν (cm^{-1}): 2990, 1368, 1177, 1150, 980; ^1H NMR ($CDCl_3$, 200 MHz) δ: 7.91–7.39 (9H, m, Ar), 6.91 (1H, dd, $J=15.0$, and 3.8, H-4), 6.63 (1H, dd, $J=15.0$ and 1.4, H-5), 4.85 (1H, m, H-3), 4.44 (1H, q, $J=6.6$, H-2), 3.93 (1H, dd, $J=10.3$ and 6.6, H_a-1), 3.79 (1H, dd, $J=10.3$ and 6.6, H_b-1), 2.46 (3H, s, CH_3-Ts) 1.37 (3H, s, CH_3-acetonide), 1.31 (3H, s, CH_3-acetonide); ^{13}C NMR ($CDCl_3$, 50.3 MHz), δ: 145.2 (C-*ipso*-Ts), 139.8 (C-*ipso*-SO_2Ph), 138.6 (CH-4), 133.6 (CH-*para*-SO_2Ph), 133.1 (CH-5), 132.4 (C-*para*-Ts) 130.0 (2CH-*meta*-Ts), 129.4 (2CH-*meta*, -SO_2Ph), 128.0 (2CH-*ortho*-SO_2Ph), 127.9 (2CH-*ortho*, -Ts) 110.3 (C-acetonide), 75.0 (2CH-2,3), 67.0 (CH_2-1); 27.3 (CH_3-acetonide), 25.3 (CH_3-acetonide), 21.6 (CH_3-Ts); EIMS m/z (%) 452 (M^+, 28), 426 (55), 414 (100); HRMS (EI) m/z calcd for $C_{21}H_{24}O_7S_2$ 452.0963; found 452.0965.

3.8. (2*S*,3*R*,4*E*)-5-Benzenesulfonyl-2,3-isopropylidenedioxy-pent-4-en-1-yl trifluoroacetate (+)-8

Starting from (−)-**4** (65 mg, 0.9 mmol) and following an identical procedure to that described for the preparation of (+)-**6**, compound (+)-**8** (47 mg, 63%) was obtained: $[\alpha]_D^{20}=+4.3$ ($c=0.15$, $CHCl_3$), IR (film) ν (cm^{-1}): 2938, 1790, 1221, 1148, 1086; ^1H NMR ($CDCl_3$, 200 MHz) δ: 7.90–7.50 (5H, m, Ar), 6.98 (1H, dd, $J=15.0$, and 3.8, H-4), 6.70 (1H, d, $J=15.0$, H-5), 4.90 (1H, m, H-3), 4.54 (1H, q, $J=4.4$, H-2), 4.20 (2H, d, $J=4.4$, H-1), 1.47 (3H, s, CH_3-acetonide), 1.37 (3H, s, CH_3-acetonide); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 170.3 (CO-CF_3), 138.0 (CH-4), 137.0 (C-*ipso*), 134.0 (CH-5), 133.7 (CH-*para*), 129.8 (2CH-*meta*), 128.0 (2CH-*ortho*), 110.3 (C-acetonide), 74.9 (CH-3), 74.6 (CH-2), 65.7 (CH_2-1), 27.4 (CH_3-acetonide), 25.3 (CH_3-acetonide).

3.9. (2*R*,3*S*,4*E*)-5-Benzenesulfonyl-2,3-isopropylidenedioxy-pent-4-en-1-yl acetate (−)-9

Starting from (−)-**5** (88 mg, 0.31 mmol) and following an identical procedure to that described for the preparation of (+)-**6**, compound (−)-**9** (84 mg, 80%) was obtained: $[\alpha]_D^{20}=-5.0$ ($c=0.42$, $CHCl_3$), IR (film) ν (cm^{-1}): 2926, 1740, 1229, 1148; ^1H NMR ($CDCl_3$, 200 MHz) δ: 7.90–7.50 (5H, m, Ar), 6.98 (1H, dd, $J=15.0$ and 4.0, H-4), 6.72 (1H, dd, $J=15.0$ and 1.4, H-5), 4.87 (1H, m, H-3), 4.47 (1H, q, $J=6.2$, H-2), 3.94 (2H, dd, $J=6.2$, and 2.6, H-1), 2.06 (3H, s, CH_3-Ac), 1.47 (3H, s, CH_3-acetonide), 1.36 (3H, s, CH_3-acetonide); ^{13}C NMR ($CDCl_3$, 50.3 MHz) 170.5 (CO-Ac), 139.8 (C-*ipso*), 139.7 (CH-4), 133.8 (CH-*para*), 132.5 (CH-5), 129.6 (2CH-*meta*), 127.9 (2CH-*ortho*), 110.3 (C-acetonide), 75.5 (CH-3), 75.3 (CH-2), 62.6 (CH_2-1); 27.7 (CH_3-acetonide), 25.3 (CH_3-acetonide), 20.9 (CH_3-Ac).

3.10. (2*R*,3*R*,4*S*)-2-Benzenesulfonylmethyl-3,4-isopropylidenedioxy-tetrahydrofuran (+)-10

To a solution of (+)-**8** (60 mg, 0.15 mmol) in MeOH (3 mL) was added a solution of Na_2CO_3 (10%) (0.5 mL). The mixture was stirred for 2 h, neutralized with 2N HCl and extracted with EtOAc. The combined organic layers washed with water and brine. The residue was purified by flash chromatography (*n*-hexane/EtOAc, 7.5:2.5) to give (+)-**10** (40 mg, 88%): $[\alpha]_D^{20}=+18.0$ (c 0.25, $CHCl_3$); IR (film) ν (cm^{-1}): 2932, 1308, 1148, 1086; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.96–7.19 (5H, m, -Ar), 4.73 (1H, dd, $J=5.8$ and 3.2 Hz, H-4), 4.60 (1H, dd, $J=5.8$ and 3.6 Hz, H-3), 3.97 (1H, m, H-2), 3.95 (1H, d, $J=11.0$ Hz, H_α-5), 3.60 (1H, dd, $J=14.8$ and 4.8 Hz H_a-1′), 3.46 (1H, d, $J=14.8$ Hz, H_b-1′), 3.44 (1H, dd, $J=11.0$ and 3.2 Hz, H_β-5), 1.41 (3H, s, Me-acetonide), 1.28 (3H, s, Me-acetonide); ^{13}C NMR ($CDCl_3$, 50.3 MHz). 140.0 (C-*ipso*), 133.9 (CH-*para*), 129.4 (2CH-*meta*), 128.3 (2CH-*ortho*), 111.7 (C-acetonide), 81.3 (CH-3), 80.9 (CH-4), 72.2 (CH-2), 73.2 (CH_2-5), 56.1 (CH_2-1′), 26.1 (Me-acetonide), 24.9 (Me-acetonide); MS (FAB) m/z (%) 299 (M^++1, 5), 154 (100), 107 (22), 69 (28); HRMS (FAB) m/z calcd for $C_{14}H_{19}O_5S$ 299, 0953; found 299.0958.

3.11. (2*S*,3*S*,4*R*)-2-Benzenesulfonylmethyl-3,4-isopropylidenedioxy-tetrahydrofuran (−)-10

Compound (−)-**9** (70 mg, 0.20 mmol) was dissolved in a solution of K_2CO_3 in MeOH (3%) (2 mL). The mixture was stirred for 2 h, neutralized with 2 M HCl and extracted with EtOAc. The combined organic layers washed with water and brine. The residue was purified by flash chromatography (*n*-hexane/EtOAc, 7.5:2.5) to give (−)-**10** (54 mg, 90%): $[\alpha]_D^{20}=-17.8$ (c 0.67, $CHCl_3$)

3.12. (2*S*,3*R*,4*E*)-5-Benzenesulfonyl-2,3-isopropylidenedioxy-pent-4-en-1-yl tosylate (+)-7 and (2*S*,3*R*,4*S*)-2-benzenesulfonylmethyl-3,4-isopropylidenedioxy-tetrahydrofuran (+)-11

To a solution of (+)-**10** (100 mg, 0.33 mmol) in THF (3.5 mL) was added *n*-BuLi (0.2 mL, 0.33 mmol) at −78°C. The mixture was stirred for 5 min and then a solution of TsCl (314 mg, 1.65 mmol) in THF (4 mL) was added via cannula. The mixture was allowed to warm to room temperature and then quenched with saturated aqueous ammonium chloride. The organic layer was separated, washed with water and brine, dried over Na_2SO_4. Concentration followed by flash chromatography on silica gel (*n*-hexane/EtOAc, 8.5:1.5) gave (+)-**7** (88 mg, 60%), starting material (+)-**10** (20 mg, 20%) and (+)-**11** (5 mg, 5%): $[\alpha]_D^{20}=+13.8$ (c 0.30, $CHCl_3$); IR (film) ν (cm^{-1}): 2932, 1308, 1144, 1080; ^1H NMR ($CDCl_3$, 200 MHz) δ: 7.96–7.19 (5H, m, -Ar), 4.77 (1H, m, H-4), 4.68 (1H, dd, $J=6.2$ and 1.6 Hz, H-3), 4.39 (1H, dt, $J=6.6$ and 1.6 Hz, H-2), 3.86 (1H, d, $J=10.9$ Hz, H_α-5), 3.65 (1H, dd, $J=10.9$ and 4.3 Hz, H_β-5), 3.28 (1H, dd, $J=14.4$ and 6.8 Hz, H_a-1′), 3.20 (1H, dd, $J=14.4$ and 6.6 Hz, H_b-1′), 1.41 (3H, s, Me-acetonide), 1.28 (3H, s, Me-acetonide); ^{13}C NMR ($CDCl_3$, 50.3 MHz), δ: 139.4 (C-*ipso*), 133.9 (CH-*para*), 129.2 (2CH-*meta*), 128.2 (2CH-*ortho*), 113.3 (C-acetonide), 84.3 (CH-2), 80.4 (CH-3), 79.0 (CH-4), 72.2 (CH_2-5), 56.5 (CH_2-1′), 26.1 (Me-acetonide), 24.9 (Me-acetonide); MS (FAB) m/z (%) 299 (M^++1, 5), 154 (100), 107 (22), 69 (28); HRMS (FAB) m/z calcd for $C_{14}H_{19}O_5S$ 299.0953; found 299.0958.

3.13. (2*R*,3*S*,4*E*)-5-Benzenesulfonyl-2,3-isopropylidenedioxy-penta-4-en-1-yl tosylate (−)-7 and (2*R*,3*S*,4*R*)-2-benzenesulfonylmethyl-3,4-isopropylidenedioxy-tetrahydrofuran (−)-11

Starting from (−)-**10** (60 mg, 0.20 mmol) and following an identical procedure to that described for the preparation of (+)-**7** and (+)-**11**, compounds (−)-**7** (53 mg, 60%): $[\alpha]_D^{20}=-3.2$ (c 0.21, $CHCl_3$) and (−)-**11** (3 mg, 5%): $[\alpha]_D^{20}=-14.0$ (c 0.26, $CHCl_3$) were obtained.

3.14. (2*R*,3*R*,4*S*)-*N*-Benzyl-2-benzenesulfonylmethyl-3,4-isopropylidenedioxypyrrolidine (+)-12

To a solution of (+)-**7** (70 mg, 0.15 mmol) in MeOH (2 mL) was added $BnNH_2$ (66 μL, 0.60 mmol) and Et_3N (30 μL, 0.22 mmol). The mixture was heated under reflux for 12 h and was then allowed to cool at room temperature. The mixture was diluted with EtOAc (15

mL), the organic layer was separated, washed with water and dried over Na_2SO_4. Filtration and concentration gave a yellow oil which was flash chromatographed (*n*-hexane/EtOAc, 85:15) to give (+)-**12** (45 mg, 78%): $[\alpha]_D^{20}=+40.2$ (*c* 0.94, $CHCl_3$); IR (film) *v* (cm^{-1}): 2938, 2805, 1447, 1306, 1150, 1086; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.96–7.19 (10H, m, -Ar), 4.57 (1H, dd, *J*= 10.8 and 4.4 Hz, H-4), 4.53 (1H, dd, *J*=10.8 and 5.1 Hz, H-3), 3.88 (1H, d, *J*=13.9, Ha-1″), 3.87 (1H, dd, *J*=14.5 and 8.6 Hz, H_β-1′), 3.20 (1H, d, *J*=14.5, H_α-1′), 3.13 (1H, d, *J*=13.9 Hz, Hb-1″), 3.01 (1H, d, *J*=11.2, H_α-5), 2.77 (1H, m, H-2), 2.03 (1H, dd, *J*= 11.2 and 4.4, H_β-5); 1.45 (3H, s, Me-acetonide), 1.26 (3H, s, Me-acetonide). ^{13}C NMR ($CDCl_3$, 100 MHz), δ: 139.8 (C-*ipso*, SO_2Ph), 137.7 (C-*ipso*, Bn), 133.6 (CH-*para*, SO_2Ph), 129.1 (2CH-*meta*, SO_2Ph), 128.3 (4CH-2*ortho*, SO_2Ph, 2*meta*, Bn), 128.0 (2CH-*ortho*, Bn), 127.0 (CH-*para*, Bn), 111.4 (C-acetonide), 79.8 (CH-3), 77.8 (CH-4), 62.1 (CH-2), 58.7 (CH_2-5), 56.5 (CH_2-1″), 53.7 (CH_2-1′); 26.1 (Me-acetonide), 25.3 (Me-acetonide); MS (FAB) *m*/*z* (%) 388 (M^++1, 21), 376 (100), 370 (30), 364 (25); HRMS (FAB) *m*/*z* calcd for $C_{21}H_{26}O_4SN$ 388.1582; found 388.1588.

3.15. (2*S*,3*S*,4*R*)-*N*-Benzyl-2-benzenesulfonylmethyl-3,4-isopropylidenedioxypyrrolidine (−)-12

Starting from (−)-**7** (50 mg, 0.11 mmol) and following an identical procedure to that described for the preparation of (+)-**12**, compound (−)-**12** was obtained (25 mg, 78%): $[\alpha]_D^{20}=-37.3$ (*c* 0.32, $CHCl_3$).

3.16. Deprotection of (+)-6

Compound (+)-**6** (40 mg, 0.13 mmol) was dissolved in MeOH (1.5 mL) and three drops of aqueous 6 M HCl were added and stirred overnight. Then, aqueous Na_2CO_3 (10%) was added until the pH became basic. The mixture was stirred for 2 h, neutralized with aqueous 2 M HCl and extracted with EtOAc. The combined organic layers were washed with water and brine and dried over Na_2SO_4. After evaporation of the solvent a mixture of compounds (−)-**13** and (−)-**14** in a 1:1 ratio was obtained (29 mg, 90%). This mixture was dissolved in acetone (2 mL) and a catalytic amount of *p*-TsOH was added and stirred for 6 h. The reaction was quenched with $NaHCO_3$ (5%) and extracted with EtOAc. The combined organic layers washed with water and brine and dried with Na_2SO_4. The crude mixture was chromatographed on silica gel flash to give (−)-**10** (13 mg, 33%) and (−)-**11** (10 mg, 25%).

3.17. (2*S*,3*R*,4*R*)-2-Benzenesulfonylmethyl-tetrahydrofuran-3,4-diol (−)-13

To a solution of (−)-**10** (100 mg, 0.33 mmol) in 5 mL of MeOH was added five drops of 6N HCl. The reaction was stirred at room temperature for 12 h, neutralized with $NaHCO_3$ (5%) and extracted with EtOAc. The combined organic layers washed with water then dried over Na_2SO_4 before concentration to give (−)-**13** (74 mg, 80%): $[\alpha]_D^{20}=-2.1$ (*c* 0.68, $CHCl_3$); IR (film) *v* (cm^{-1}): 3445, 1304, 1146, 1088, 1034, 822; ^1H NMR ($CDCl_3$, 200 MHz) δ: 8.0–7.4 (5H, m, Ar), 4.32 (2H, m, H-3, H-4), 3.83 (1H, dd, *J*=9.4 and 5.8, H_α-5), 3.76 (1H, dd, *J*=14.0 and 7.2, H_a-1′), 3.73 (1H, dd, *J*=9.4 and 5.2, H_β-5), 3.66 (1H, m, H-2), 3.47 (1H, dd, *J*= 14.0 and 5.2, H_b-1′); ^{13}C NMR ($CDCl_3$, 50.3 MHz), δ: 139.4 (C-*ipso*), 134.2 (CH-*para*), 129.6 (2CH-*meta*), 128.1 (2CH-*ortho*), 75.4 (CH-2) 72.2 (CH_2-5), 71.7 (2CH, CH-3, 4), 56.4 (CH_2-1′).

3.18. (2*R*,3*R*,4*R*)-2-Benzenesulfonylmethyl-tetrahydrofuran-3,4-diol (−)-14

To a solution of (−)-**11** (10 mg, 0.03 mmol) in 1 mL of MeOH was added two drops of 6 M HCl. The reaction was stirred at room temperature for 12 h, neutralized with $NaHCO_3$ (5%) and extracted with EtOAc. The combined organic layers washed with water then dried over Na_2SO_4 before concentration to give (−)-**14** (5.1 mg, 70%): $[\alpha]_D^{20}=-5.6$ (*c*=0.16, $CHCl_3$); IR (film) *v* (cm^{-1}): 3445, 1304, 1146, 1088, 1034; ^1H NMR ($CDCl_3$, 200 MHz) δ: 8.00–7.50 (5H, m, Ar), 4.29 (1H, m, H-4), 4.07 (3H, m, H-2, H-3, H_a-5), 3.79 (1H, dd, *J*=10.2 and 2.2, H_b-5), 3.52 (1H, dd, *J*=14.0 and 4.8, H_a-1′), 3.41 (1H, dd, *J*=14.0 and 7.0, H_b-1′); ^{13}C NMR ($CDCl_3$, 50.3 MHz), δ: 140.0 (C-*ipso*), 134.4 (CH-*para*), 129.7 (2CH-*meta*), 128.3 (2CH-*ortho*), 76.3 (CH-3), 75.7 (CH-2), 73.5 (CH_2-5), 71.3 (CH-4), 59.9 (CH_2-1′).

3.19. (2*R*,3*R*,4*S*)-2-Benzenesulfonylmethyl-3,4-isopropylidenedioxypyrrolidine (+)-15

Compound (+)-**12** (40 mg, 0.10 mmol) was dissolved in MeOH (2 mL) and a catalytic amount of Pd/C was added. After being flushed and stirred under hydrogen for 24 h, the mixture was filtered over Celite and after concentration was obtained (+)-**15** (29 mg, 97%). For physical properties, see Ref. 5.

3.20. (2*S*,3*R*,4*S*)-*N*-Benzyl-3,4-isopropylidenedioxy-2-methylpyrrolidine (+)-16

Compound (+)-**12** (40 mg, 0.10 mmol) was dissolved in MeOH (1.5 mL) and the solution was cannulated into a flask containing Na(Hg) 2% (100 mg). The mixture was stirred for 3 h and concentrated. The residue was dissolved in EtOAc (15 mL) and the organic layer was separated and washed with water and brine. After drying (Na_2SO_4) and concentration, the residue was flash chromatographed on silica gel (*n*-hexane/EtOAc, 7.5:3.5) to give (+)-**16** (19 mg, 77%): $[\alpha]_D^{20}=+33.4$ (*c*= 0.70, $CHCl_3$); IR (film) *v* (cm^{-1}): 2934, 1377, 1208, 1119, 1005; ^1H NMR ($CDCl_3$, 200 MHz) δ: 7.32 –7.25 (5H, m, -Ar), 4.58 (1H, dd, *J*=6.6 and 4.4 Hz, H-4), 4.50 (1H, dd, *J*=6.2 and 4.4 Hz, H-3), 4.00 (1H, d, *J*=13.4, H_a-1″), 3.06 (1H, d, *J*=13.4, H_b-1″), 2.99 (1H, d, *J*=11.4 Hz, H_α-5), 2.20 (1H, m, H-2), 1.96 (1H, dd, *J*=11.4 and 4.4 Hz, H_β-5), 1.56 (3H, s, Me-acetonide), 1.33 (3H, s, Me-acetonide), 1.22 (3H, d, *J*=6.6, CH_3-1′). ^{13}C NMR ($CDCl_3$, 50.3 MHz), δ: 139.8 (C-*ipso*), 128.8 (2CH-*meta*), 128.4 (2CH-*ortho*), 126.9 (CH-*para*), 111.3 (C-acetonide), 82.7 (CH-3), 78.3 (CH-4), 63.0 (CH-2), 59.7 (CH_2-5), 56.8 (CH_2-1″), 26.6 (Me-ace-

tonide), 26.0 (Me-acetonide), 12.8 (Me-1′); EIMS m/z (%) 247 (M^+, 60), 219 (72) 232 (100); HRMS (EI) m/z calcd for $C_{15}H_{21}NO_2$ 247.1572 found 247.1560.

3.21. (2*S*,3*R*,4*S*)-2-Methylpyrrolidine-3,4-diol hydrochloride (+)-18

Compound (+)-**16** (30 mg, 0.12 mmol) was dissolved in MeOH and a catalytic amount of Pd/C was added. After being flushed and stirred under hydrogen for 24 h the mixture was filtered over Celite. After concentration the crude was dissolved in MeOH (2 mL) and treated with four drops of 6 M HCl. The reaction was stirred at room temperature for 12 h and after concentration afforded a white solid of (+)-**18** (11 mg, 80%). For physical properties, see Refs. 4d and 5.

3.22. (2*R*,3*S*,4*S*)-2-Benzenesulfonylmethyl-tetrahydrofuran-3,4-diol (+)-13

Starting from (+)-**10** (52 mg, 0.18 mmol) and following an identical procedure to that described for the preparation of (−)-**13**, compound (+)-**13** (37 mg, 80%) was obtained: $[\alpha]_D^{20}=+1.5$ ($c=0.68$, $CHCl_3$)

3.23. (2*S*,3*S*,4*S*)-2-Methyl-tetrahydrofuran-3,4-diol (+)-19

To a solution of (+)-**13** (70 mg, 0.29 mmol) in MeOH (3 mL) was added Raney-Ni. The mixture was heated under reflux with vigorous agitation for 16 h and then filtered over Celite to give after concentration (+)-**19** (27 mg, 93%): $[\alpha]_D^{20}=+8.0$ ($c=0.50$, $CHCl_3$); IR (film) ν (cm^{-1}): 3500, 1117, 1080, 1024; ^1H NMR ($CDCl_3$, 200 MHz) δ: 4.40 (1H, m, H-4), 4.01 (1H, m, H-3), 3.80 (3H, m, H-2, 2H-5), 1.30 (3H, d, $J=6.6$, Me); ^{13}C NMR ($CDCl_3$, 50.3 MHz), δ: 77.7 (CH-2), 72.8 (CH-3), 72.7 (CH-4), 72.6 (CH_2-5), 14.5 (CH_3-1′); HRMS (EI) m/z calcd for $C_5H_{10}O_3$ 118.0630; found 118.0633.

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