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Preparation and Synthetic Applications of Lithiated Vinyl Sulfones Derived from 3-Buten-1-ol and 4-Penten-1-ol

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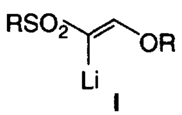
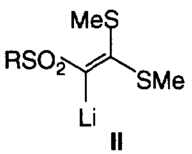
Abstract: Vinyl sulfones (*E*)-4-tosyl-3-buten-1-ol (**2**) and its MOM-derivative **6**, prepared by iodosulfonylation-dehydroiodination of 3-buten-1-ol (**1**), are regio and stereoselectively lithiated at the 4-position to afford intermediates **3** and **7**, respectively. The protected derivative **7** can be alkylated and acylated at the vinylic position and both intermediates can also react with carbonyl compounds to give 1,5-diols which cyclize to the corresponding dihydropyrans **9**. The MOM-derivative of (*E*)-5-tosyl-4-penten-1-ol (**16**), obtained by protection of the homologous 4-penten-1-ol (**14**) followed by iodosulfonylation-dehydroiodination, is regio and stereoselectively lithiated at the 5-position to provide monoanion **17** which reacts with electrophiles at this position affording products **18**. Cyclization and desulfonylation reactions of representative obtained products **18** are studied.

INTRODUCTION

Vinyllithium intermediates stabilized by the sulfone group[1] can be prepared by direct lithiation of vinyl sulfones,[2] this reaction being facilitated by the presence of chelating functional groups through the so called CIPE-effect.[3] Thus, intermediates of the type **I**[4] and **II**[5] with alkoxy and thioalkoxy groups at the β-position of the vinyl sulfone have been used as acetaldehyde and ketene anion enolate synthons, respectively. β-Acylvinyl anions **III**[6] and **IV**[7] derived from acrylic systems are useful intermediates in the synthesis of 1,4-dicarbonyl compounds,[6,7] cyclopentenones,[6b] and butenolides.[7] Organolithium compounds derived from γ-functionalized vinyl sulfones with amine,[8] oxido[9] or methoxymethoxy (MOMO)[10] groups of the type **V** have been applied to the synthesis of *Z*-allylamines,[8] dihydrofurans,[9b] furans,[9b] lactones,[10a] butenolides,[9b,10a] and polypropionate chains.[10b] As a part of our current interest concerning remote anions derived from δ-functionalized vinyl sulfones,[11] we describe here the preparation and synthetic applications of lithium derivatives of δ or ε-functionalized vinyl sulfones of the type **VI** with an oxido or methoxymethoxy (MOMO) groups. These intermediates should allow the synthesis of cyclic ethers which are present in polyether antibiotics and other natural products.[12]



I



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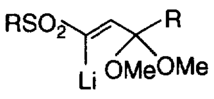
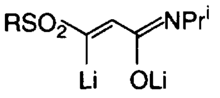
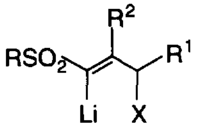


III

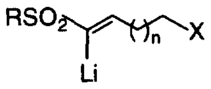


IV



[X = $N(CH_2)_4O$, OLi, OMOM]

V



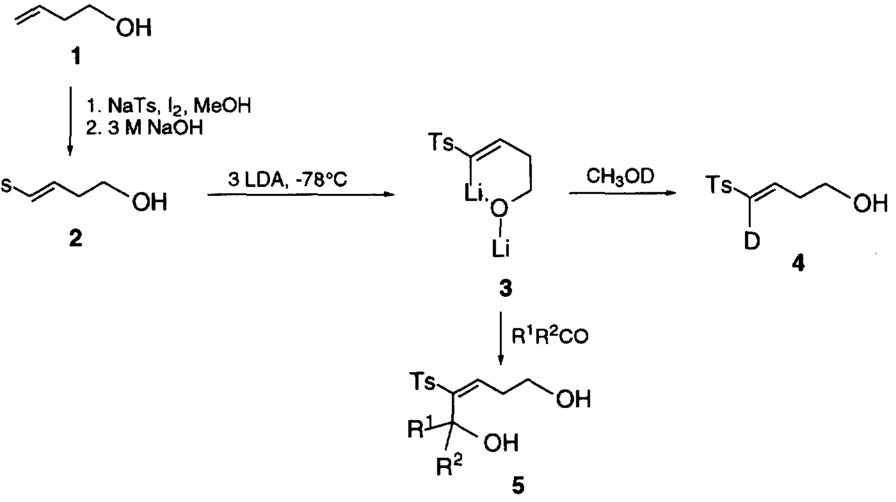
[X = OLi, OMOM] n = 1,2

VI

RESULTS AND DISCUSSION

1. Vinyl sulfones derived from 3-buten-1-ol.

The one-pot iodosulfonylation-dehydroiodination[13,11] of 3-buten-1-ol (**1**)[15] with sodium *p*-toluenesulfinate and iodine in MeOH followed by treatment with 3 M NaOH afforded stereoselectively (*E*)-4-tosyl-3-buten-1-ol (**2**) in 83% yield. The lithiation of this alcohol with 3 equiv of LDA at -78°C for 30 min gave dianion **3** which was characterized as its deuterated equivalent **4** by reaction with CH_3OD (90% yield and 81% of deuterium incorporation[16]). Dilithiated intermediate **3** reacted with carbonyl compounds under the reaction conditions described on Table 1 to give steroselectively unsaturated 1,5-diols **5** (Scheme 1).



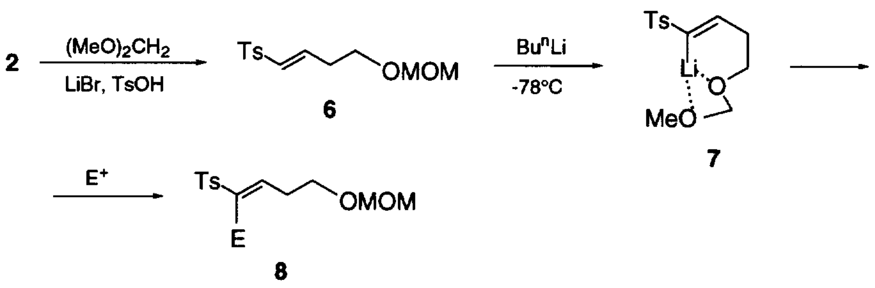
Scheme 1.

The reaction of dianion **3** with other electrophiles such as alkyl halides and acyl chlorides failed. However, the methoxymethyl derivative **6** of vinyl sulfone **2**, obtained by protection with dimethoxymethane[17] in 90% yield, was regio and stereoselectively lithiated at the vinylic position with n-butyllithium at -78 °C to give monoanion **7** which reacted with different electrophiles such as CH_3OD, alkyl halides, carbonyl compounds, benzoyl chloride, and cyclohexyl isocyanate to provide derivatives **8** (Scheme 2 and Table 2).

Table 1. Reaction of Dilithiated Vinyl Sulfone **3** with Carbonyl Compounds.

Carbonyl compound	reaction conditions	product no.	R^1	R^2	yield (%)[a]	*R*f[b]
EtCHO	2.5 h, -78 to -30°C	**5a**	Et	H	67	0.28
Pr^{i}CHO	3 h, -78 to -30°C	**5b**	Pr^i	H	72[c]	0.34
Bu^{t}CHO	3 h, -78 to 0°C	**5c**	Bu^t	H	53	0.49
PhCHO	3 h, -78 to -25°C	**5d**	Ph	H	72	0.51
$(CH_2)_5CO$	3 h, -78 to -25°C	**5e**	$(CH_2)_5$		54	0.48

[a] Based on alcohol **2**, after column chromatography on silica gel. [b] Hexane/EtOAc: 1/3. [c] Isolated crude yield, prior to transformation into dihydropyran **9a**.



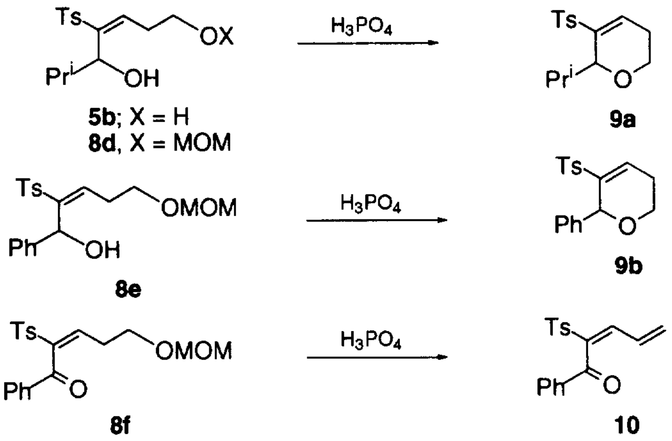
Scheme 2.

Table 2. Reaction of Monoanion **7** with Electrophiles.

Electrophile	reaction conditions	product no.	E	yield (%)[a]	mp (°C)[b] or *R*f[c]
CH_3OD	15 min, -78°C	**8a**	D	90[d]	0.54
MeI	1 h, -78 to -50°C	**8b**	Me	72	0.58
$PhCH_2Br$	1 h, -78 to -50°C	**8c**	$PhCH_2$	53	0.62
Pr^{i}CHO	3 h, -78 to -25°C	**8d**	Pr^{i}CHOH	85[e]	0.54
PhCHO	3 h, -78 to -25°C	**8e**	PhCHOH	73	0.46
PhCOCl	1 h, -78 to -50°C	**8f**	PhCO	58	0.60
CyNCO	1 h, -78 to -50°C	**8g**	CyNHCO	56	133-134

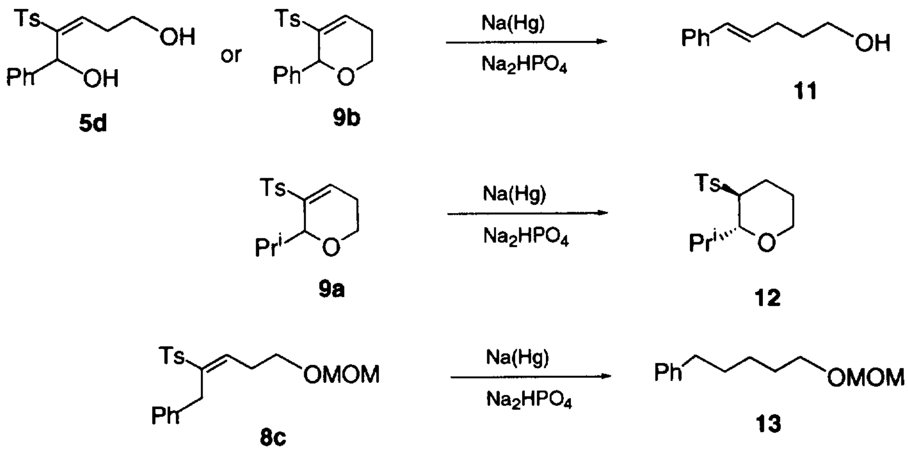
[a] Based on sulfone **6**, after column chromatography on silica gel. [b] Hexane/EtOAc. [c] Hexane/EtOAc: 1/1. [d] 81% of deuterium incorporation (300 MHz ^1H NMR). [e] Isolated crude yield, prior to transformation into dihydropyran **9a**.

Representative crude 1,5-diol derivatives **5b**, **8d** and **8e** were transformed into dihydropyrans **9a** and **9b** by treatment with H_3PO_4 under toluene reflux in 40, 41 and 58% yield, respectively, based on starting vinyl sulfones **2** and **6**, respectively. Under the same reaction conditions the ketone **8f** suffered β-elimination instead of cyclization to give the dienone **10** in 75% yield (Scheme 3).



Scheme 3.

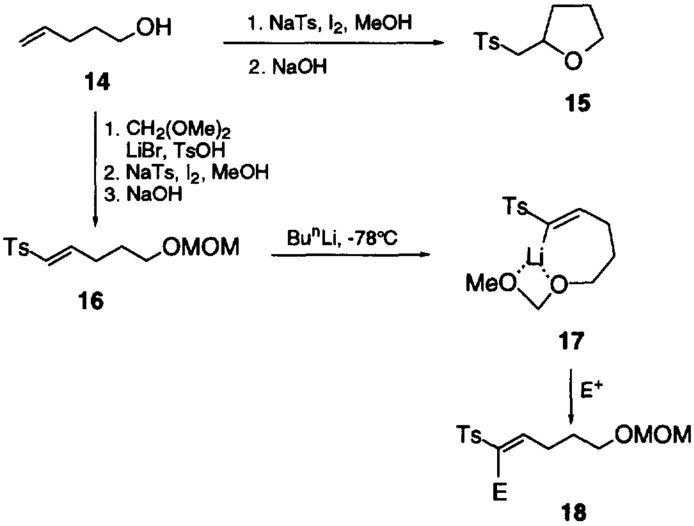
The reductive elimination of the tosyl group with representative derivatives such as diol **5d** and dihydropyran **9b** was carried out with sodium amalgam[18] giving rise stereoselectively to the same alcohol **11** in 69 and 45% yield, respectively. These results can be explained by reduction of the carbon-carbon double bond followed by Julia olefination. Reduction of the double bond was also observed when the dihydropyran **9a**, derived from isobutanal, was treated with sodium amalgam[18] affording the tetrahydropyran **12** in 45% yield. The benzylated derivative **8c** suffered also reduction of the carbon-carbon double bond and reductive desulfonylation to lead to the formation of the saturated protected alcohol **13** in 87% yield (Scheme 4).



Scheme 4.

2. Vinyl sulfones derived from 4-penten-1-ol.

The iodosulfonylation-dehydroiodination of 4-penten-1-ol (**14**)[7] provided the 2-(tosylmethyl) tetrahydrofuran (**15**) in 65% yield due to intramolecular conjugate addition of the alcohol to the vinyl sulfone. Therefore, the alcohol **14** was protected and the resulting MOM-derivative was iodosulfonylated-dehydroiodinated to afford the vinyl sulfone **16** in 77% yield. Lithiation of this sulfone with n-butyllithium, as it was described above for **2**, led to the formation of monoanion **17** which reacted with different electrophiles: CH_3OD, alkyl halides, carbonyl compounds, benzoyl chloride and cyclohexyl isocyanate, under the conditions described on Table 3, affording compounds **18** (Scheme 5).



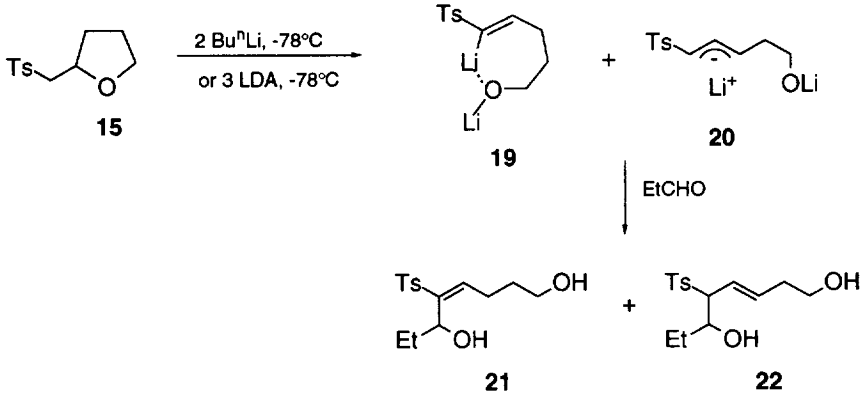
Scheme 5.

Table 3. Reaction of Monoanion **17** with Electrophiles.

Electrophile	reaction conditions	product no.	E	yield (%)[a]	mp (°C)[b] or R_f[c]
CH_3OD	15 min, -78°C	**18a**	D	88[d]	0.48
MeI	1 h, -78 to -50°C	**18b**	Me	76	0.56
$PhCH_2Br$	1 h, -78 to -50°C	**18c**	$PhCH_2$	62	0.63
EtCHO	1 h, -78 to -60°C	**18d**	EtCHOH	73	0.38
Bu^tCHO	1 h, -78 to -60°C	**18e**	Bu^tCHOH	83	0.49
PhCHO	1 h, -78 to -60°C	**18f**	PhCHOH	89	0.41
PhCOCl	30 min, -78°C	**18g**	PhCO	53	0.55
CyNCO	40 min, -78°C	**18h**	CyNHCO	62	83-84

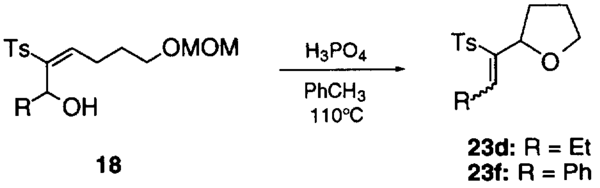
[a] Based on sulfone **16**, after column chromatography on silica gel. [b] Hexane/EtOAc. [c] Hexane/EtOAc: 1/1. [d] 92% of deuterium incorporation (300 MHz ^1H NMR).

When the tetrahydrofuran derivative **15** was treated with 2 equiv of n-butyllithium or 3 equiv of LDA at -78°C and then with propanal as electrophile a *ca.* 1/1 mixture of alcohols **21** and **22** in 42% yield was obtained. That means that the sulfone **15** could be used as starting material for the preparation of intermediate **19** by a β-elimination process, but unfortunately this dianion partially isomerizes to intermediate **20**, probably through an intramolecular deprotonation promoted by the lithium alcoholate (Scheme 6).



Scheme 6.

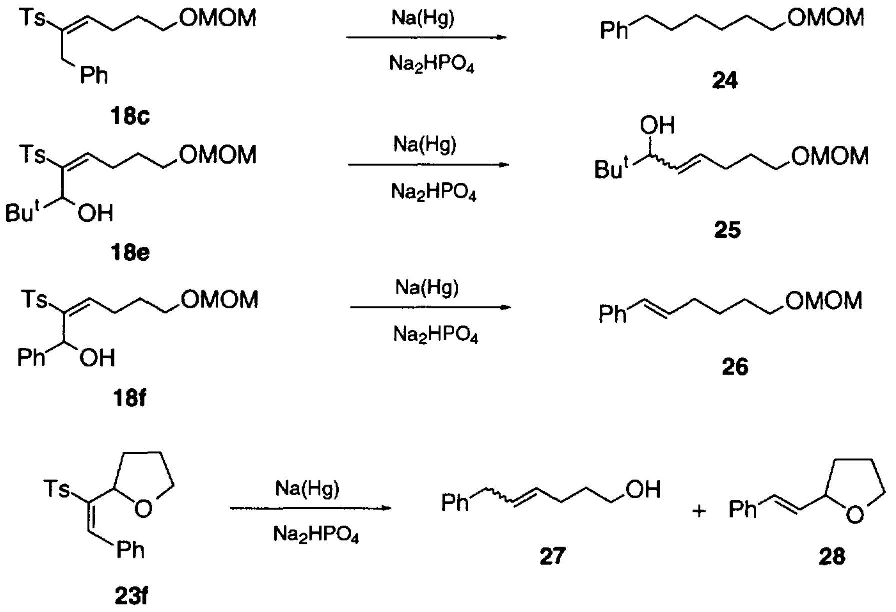
The treatment of 1,6-diol derivatives **18d** and **18f** with H_3PO_4 under toluene reflux led to the formation of tetrahydrofurans **23** in 55 and 61% yield, respectively, instead to the corresponding tetrahydroepanes (Scheme 7). Compound **23d** was isolated as a 1/1 mixture of *Z/E* diastereomers and **23f** was stereoselectively obtained with *E*-configuration according to the observed 2% of NOE effect at the *ortho*-position of the tosyl when the olefinic hydrogen was irradiated.



Scheme 7.

When representative systems **18c**, **18e**, **18f**, and **23f** were submitted to reduction with sodium amalgam[18] compounds **24-28** were obtained (Scheme 8). The benzylated sulfone **18c** suffers the same process than compound **8c**: reduction of the carbon-carbon double bond and subsequent desulfonylation to afford the MOM-protected 6-phenyl-1-hexanol **24** in 89% yield. The diol **18e** derived from pivalaldehyde experiments desulfonylation to give the monoprotected diol **25** as a 1/3 mixture of *Z/E* diastereomers in 73% yield. However, diol **18f** derived from benzaldehyde underwent reduction of the double bond and Julia olefination to provide compound **26** in 67% yield as in the case of compound **5d** derived from 3-buten-1-ol (see text above and Scheme 4). Finally, the tetrahydrofuran **23f** gave mainly product **27** as a 1/3 mixture of *Z/E* diastereomers in 60% yield together with 35% of detosylated tetrahydrofuran **28**.

We concluded that remote vinylic anions derived from vinyl sulfones, easily prepared from 3-buten-1-ol and 4-penten-1-ol, are appropriate nucleophiles that can be functionalized at the δ- and ε-positions, respectively, affording 1,5- and 1,6-bifunctionalized products which can be transformed into dihydropyrans and tetrahydrofurans derivatives.



Scheme 8.

EXPERIMENTAL SECTION

General. Melting points were obtained with a Reichert Thermovar apparatus and are uncorrected. FT-IR spectra were obtained on a Nicolet Impact 400D spectrophotometer as neat liquids. NMR spectra were recorded on a Bruker AC-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) using $CDCl_3$ as solvent and TMS as internal standard; chemical shifts are given in δ (ppm) and coupling constants (*J*) are measured in Hz. ^{13}C NMR assignments were made on the basis of DEPT experiments. Mass spectra (EI, 70 eV) were obtained on a Hewlett-Packard 5988A and a Shimadzu QP-5000 spectrometers, using in the latter a HP-1 capillary column (12 m X 0.2 mm i.d.; stationary phase 5% methyl silicone). High resolution mass spectra were measured in the Mass Spectrometry Service at the University of Zaragoza. Elemental analyses were performed by the Microanalyses Service at the University of Alicante. Thin layer chromatography (TLC) was carried out on Schleicher & Schuell F1400/LS 254 plates coated with a 0.2 mm layer of silica gel and UV visualization. Column chromatography was performed using silica gel 60 of 70-230 mesh. All starting materials were commercially available (Aldrich, Fluka, Across) of the best grade and were used without further purification. THF was dried over benzophenone ketyl under an argon atmosphere and distilled before use.

Synthesis of (*E*)-4-Tosyl-3-buten-1-ol (2): A suspension of 3-buten-1-ol (**1**) (0.72 g, 10 mmol) and sodium *p*-toluenesulfinate (5.16 g, 20 mmol) and iodine (3.05 g, 12 mmol) in methanol (50 mL) was stirred for 2 d at room temperature. Then, solvent was removed in vacuo (15 Torr) and the resulting residue was dissolved in EtOAc (50 mL) and washed with aqueous 0.2 M $Na_2S_2O_3$. The organic layer was decanted and aqueous 3 M NaOH was added and stirred for 1 d. The organic layer was separated, washed with brine (3x30 mL), dried (Na_2SO_4) and evaporated (15 Torr) and the resulting residue was purified by column chromatography affording 1.876 g (83% yield) of pure compound **2**: R_f 0.34 (hexane/EtOAc: 1/3); ν 3508 (OH), 1634, 966 (C=CH), 1303, and 1143 cm^{-1} (SO_2); δ_H 2.42-2.49 (m with s at 2.42, 5H, C*H*$_3$Ar, CHC*H*$_2$), 2.82 (s, 1H, OH), 3.72 (t, *J*=6.1, 2H, C*H*$_2$OH), 6.44 (d, *J*=14.7, 1H, CHS), 6.97 (dt, *J*=14.7, 7.1, 1H, SCH=C*H*), 7.33, and 7.75 (2d, *J*=8.1, 4H, ArH); δ_C 21.41 (*C*H$_3$Ar), 34.30 (CH*C*H$_2$), 60.00 (CH$_2$OH), 132.02, 143.23 (CH=CH), 127.42, 129.77, 137.12, and 144.26 (ArC); *m/z* 226 (*M*$^+$, 2%), 196 (100), 179 (21), 161 (46), 157 (33), 139 (75), 131 (12), 130 (26), 129 (47), 115 (12), 108 (11), 107 (16), 92 (43), 91 (91), 89 (18), 77 (19), 70 (26), 65 (54), 63 (19), 51 (12), 43 (13), and 41 (15) (Found: *M*$^+$ 226.0666. Calcd. for $C_{11}H_{14}O_3S$: 226.0664).

Lithiation of (*E*)-4-Tosyl-3-buten-1-ol (2) and Reaction with Electrophiles. General Procedure. To a solution of (*E*)-4-tosyl-3-buten-1-ol (**2**) (68 mg, 0.3 mmol) in dry THF (2 mL) cooled at -78° C was added a solution of LDA (0.9 mmol) freshly prepared in THF (1 mL). After 30 min stirring, the corresponding electrophile was added (0.36 mmol) (see Table 1 for reaction conditions) and the reaction mixture was hydrolyzed with saturated aqueous NH_4Cl and extracted with EtOAc (3x20 mL). The organic layer was dried (Na_2SO_4) and evaporated (15 Torr) and the residue was purified by flash chromatography (hexane/EtOAc) to afford compounds **4** and **5**. Yields and physical data are included in Table 1, spectral and analytical data follow:

***(E)-4-Deuterio-4-tosyl-3-buten-1-ol* (4):** ν 3508 (OH), 1634, 966 (C=CH), 1303, and 1143 cm^{-1} (SO_2); δ_H 2.43-2.50 (m with s at 2.43, 6H, C*H*$_3$Ar, CHC*H*$_2$, OH), 3.74 (t, *J*=6.1, 2H, C*H*$_2$OH), 6.97 (t, *J*=6.1, 1H, CD=CH), 7.33, and 7.75 (2d, *J*=8.1, 4H, ArH); δ_C 21.46 (*C*H$_3$Ar), 34.31 (CH*C*H$_2$), 60.09 (CH$_2$OH), 127.49, 129.81, 137.21, 144.28 (ArC), 131.85 (t, *J*=26.9, CDS), and 143.06 (CD=*C*H); *m/z* 227 (*M*$^+$, 3%), 198 (12), 197 (85), 196 (26), 180 (29), 162 (45), 157 (49), 139 (90), 132 (10), 131 (25), 130 (49), 129 (17), 116 (10), 108 (12), 107 (18), 93 (10), 92 (64), 91 (100), 90 (11), 89 (19), 77 (19), 71 (27), 65 (51), 63 (19), 51 (12), 43 (14), 42 (10), and 41 (12).[19]

***(E)-4-Tosyl-3-heptene-1,5-diol* (5a):** ν 3472 (OH), 1640, 983 (C=CH), 1284, and 1145 cm^{-1} (SO_2); δ_H 0.82 (t, *J*=7.3, 3H, C*H*$_3$CH$_2$), 1.54, 1.72 (2m, 2H, CH$_3$C*H*$_2$), 2.02 (s, 1H, OH), 2.43-2.58 (m with s at 2.43, 4H, C*H*$_3$Ar, *H*CHCH$_2$OH), 2.83 (m, 1H, HC*H*CH$_2$OH), 3.18 (s, 1H, OH), 3.78 (m, 2H, C*H*$_2$OH), 4.42 (dd, *J*=8.7, 5.0, 1H, C*H*OH), 7.02 (t, *J*=7.9, 1H, C=CH), 7.32, and 7.75 (2d, *J*=8.1, 4H, ArH); δ_C 10.44 (*C*H$_3$CH$_2$), 21.57 (*C*H$_3$Ar), 29.83 (CH$_3$*C*H$_2$), 31.44 (CH*C*H$_2$CH$_2$), 60.49 (CH$_2$OH), 70.14 (CHOH), 127.91, 129.80, 137.22, 141.27, 144.28, and 145.66, (ArC, C=CH); *m/z* 248 (*M*$^+$-36, 0.2%), 237 (21), 226 (11), 225 (100), 157 (12), 139 (21), 133 (11), 128 (16), 92 (12), 91 (37), 65 (15), and 41 (14).[19]

***(E)-6,6-Dimethyl-4-tosyl-3-heptene-1,5-diol* (5c):** ν 3489 (OH), 1632, 975 (C=CH), 1293, and 1146 cm^{-1} (SO_2); δ_H 1.00 [s, 9H, (CH$_3$)$_3$C], 2.41-2.47 (m with s at 2.41, 5H, C*H*$_3$Ar, CHC*H*$_2$), 2.90, 3.32 (2s, 2H, 2xOH), 3.69 (m, 2H, C*H*$_2$OH), 4.36 (s, 1H C*H*OH), 6.97 (t, *J*=7.6, 1H, C=CH), 7.30, and 7.76 (2d, *J*=8.2, 4H, ArH); δ_C 21.52 (*C*H$_3$Ar), 27.02 [(*C*H$_3$)$_3$C], 32.90 [(CH$_3$)$_3$*C*], 37.61 (CH*C*H$_2$), 60.59 (CH$_2$OH), 76.81 (CHOH), 127.72, 129.71, 138.41, 143.96, 144.94, and 145.56, (ArC, C=CH); *m/z* 264 (*M*$^+$-48, 0.5%), 256 (14), 238 (15), 225 (44), 157 (58), 140 (26), 139 (46), 101 (16), 100 (100), 99 (14), 93 (15), 92 (26), 91 (53), 83 (34), 77 (10), 69 (11), 65 (19), 58 (10), 57 (46), 55 (14), 53 (12), 43 (20), and 41 (42).[19]

***(E)-1-Phenyl-2-tosyl-2-pentene-1,5-diol* (5d):** ν 3473 (OH), 1640 (C=CH), 1299, and 1145 cm^{-1} (SO_2); δ_H 2.23, 2.49 (2m, 2H, CHC*H*$_2$), 2.37 (s, 3H, C*H*$_3$Ar), 2.98, 4.38 (2s, 2H, 2xOH), 3.66 (m, 2H, C*H*$_2$OH), 5.70 (s, 1H, C*H*OH), 7.14-7.26 (m, 8H, C=CH, ArH), and 7.61 (d, *J*=8.2, 2H, ArH); δ_C 21.50 (*C*H$_3$Ar), 31.31 (CH*C*H$_2$), 59.92 (CH$_2$OH), 68.31 (CHOH), 125.48, 127.13, 127.99, 128.11, 129.70, 136.44, 140.58, 142.69, 144.19, and 146.29 (ArC, C=CH); *m/z* 314 (M^+-18, 0.3%), 177 (12), 176 (100), 157 (24), 139 (16), 130 (14), 129 (27), 128 (19), 120 (47), 115 (22), 105 (48), 92 (12), 91 (46), 79 (13), 77 (35), and 65 (18).[19]

***(E)-4-(1-Hydroxycyclohexyl)-4-tosyl-3-buten-1-ol* (5e):** ν 3505 (OH), 1283, and 1142 cm^{-1} (SO$_2$); δ_H 1.15 (m, 1H, Cy), 1.44-1.89 (m, 9H, Cy), 2.41 (s, 3H, CH_3Ar), 2.63, 2.97 (2s, 2H, 2xOH), 2.78 (dt, *J*=7.7, 6.3, 2H, C=CHCH_2), 3.84 (t, *J*=6.3, 2H, CH_2OH), 7.09 (t, *J*=7.7, 1H, C=CH), 7.28, and 7.68 (2d, *J*=8.0, 4H, ArH); δ_C 21.15, 24.84, 37.19, [(CH$_2$)$_5$], 21.51 (CH$_3$Ar), 33.04 (C=CHCH$_2$), 61.09 (CH$_2$OH), 73.70 (COH), 139.81, 149.15 (C=CH), 127.03, 129.46, 139.23, and 143.38 (ArC); *m/z* 324 (M^+, 0.9%), 169 (20), 168 (100), 157(19), 151 (12), 139 (57), 129 (13), 125 (17), 112 (11), 107 (12), 105 (10), 97 (21), 95 (10), 92 (13), 91 (44), 81 (22), 79 (17), 77 (12), 69 (11), 67 (17), 65 (19), 55 (25), 43 (13), and 41 (16) (Found: M^+ 324.1393. Calcd. for $C_{17}H_{24}O_4S$: 324.1395).

Synthesis of (*E*)-4-(Methoxymethoxy)-1-butenyl *p*-Tolyl Sulfone (6) from Alcohol 2. A suspension of alcohol **2** (1.13 g, 5 mmol), LiBr (87 mg, 1 mmol) and *p*-TsOH·H$_2$O (95 mg, 0.5 mmol) in dimethoxymethane (10 mL) was stirred for 1 d and then brine was added. The resulting solution was extracted with ether (3x20 mL) and the organic layers were dried with Na$_2$SO$_4$ and concentrated in vacuo to give a crude product which was purified by flash chromatography (hexane/EtOAc) affording pure compound **6** (82% yield): R_f 0.54 (hexane/EtOAc: 1/1); ν 1638, 961 (C=CH), 1303, and 1145 cm^{-1} (SO$_2$); δ_H 2.43 (s, 3H, CH_3Ar), 2.52 (m, 2H, CHCH_2), 3.31 (s, 3H, OCH$_3$), 3.64 (t, *J*=6.3, 2H, CH$_2$CH_2O), 4.58 (s, 2H, OCH$_2$O), 6.41 (dt, *J*=15.0, 1.5, 1H, CHS), 6.98 (dt, *J*=15.0, 6.8, 1H, SCH=CH), 7.33, and 7.76 (2d, *J*=8.1, 4H, ArH); δ_C 21.51 (CH$_3$Ar), 31.72 (CHCH$_2$), 55.26 (OCH$_3$), 65.10 (CH$_2$$CH_2$O), 96.35 (OCH$_2$O), 132.27, 142.91 (CH=CH), 127.60, 129.80, 137.49, and 144.22 (ArC); *m/z* 239 (M^+-31, 0.2%), 139 (16), 91 (19), 85 (28), 65 (12), and 45 (100).[19]

Lithiation of (*E*)-4-(Methoxymethoxy)-1-butenyl *p*-Tolyl Sulfone (6) and Reaction with Electrophiles. General Procedure. To a solution of (*E*)-4-(methoxymethoxy)-1-butenyl *p*-tolyl sulfone (6) (71 mg, 0.25 mmol) in dry THF (3 mL) cooled at -78° C was added a 1.6M solution of n-butyllithium (188 μL, 0.3 mmol) in hexanes. After 30 min stirring, the corresponding electrophile was added (0.3 mmol) (see Table 2 for reaction conditions) and the reaction mixture was hydrolyzed with saturated aqueous NH$_4$Cl and extracted with EtOAc (3x20 mL). The organic layers were dried (Na$_2$SO$_4$), evaporated (15 Torr) and the residue was purified by flash chromatography (hexane/EtOAc) to give compounds **8**. Yields and physical data are included in Table 2, spectral and analytical data follow:

***(E)-4-Deuterio-4-(methoxymethoxy)-1-butenyl* p*-Tolyl Sulfone* (8a):** ν 1638, 961 (C=CH), 1303, and 1145 cm^{-1} (SO$_2$); δ_H 2.43 (s, 3H, CH_3Ar), 2.52 (m, 2H, CHCH_2), 3.31 (s, 3H, OCH$_3$), 3.64 (t, *J*=6.3, 2H, CH$_2$CH_2O), 4.58 (s, 2H, OCH$_2$O), 6.97 (m, 1H, SCD=CH), 7.33, and 7.76 (2d, *J*=8.2, 4H, ArH); δ_C 21.49 (CH$_3$Ar), 31.65 (CHCH$_2$), 55.24 (OCH$_3$), 65.08 (CH$_2$$CH_2$O), 96.32 (OCH$_2$O), 132.25 (t, *J*=24.4, CDS), 142.80 (SCD=CH), 127.58, 129.78, 137.48, and 144.19 (ArC); *m/z* 180 (M^+-91, 0.7%), 86 (14), and 45 (100).[19]

***(E)-1-Methyl-4-(methoxymethoxy)-1-butenyl* p*-Tolyl Sulfone* (8b):** ν 1641 (C=CH), 1301, and 1148 cm^{-1} (SO$_2$); δ_H 1.85 (d, *J*=0.9, 3H, CH$_3$C), 2.43-2.50 (m with s at 2.43, 5H, CHCH_2, CH_3Ar), 3.35 (s, 3H, OCH$_3$), 3.64 (t, *J*=6.4, 2H, CH$_2$CH_2O), 4.61 (s, 2H, OCH$_2$O), 6.91 (m, 1H, C=CH), 7.32, and 7.73 (2d, *J*=8.4, 4H, ArH); δ_C 11.64 (CH$_3$C), 21.53 (CH$_3$Ar), 29.03 (CHCH$_2$), 55.26 (OCH$_3$), 65.62 (CH$_2$$CH_2$O), 96.41 (OCH$_2$O), 128.10, 129.68, 136.17, 144.04 (ArC), 137.10, and 138.72 (C=CH); *m/z* 223 (M^+-61, 0.6%), 139 (20), 99(22), 91 (15), 65 (12), and 45 (100).[19]

(E)-1-Benzyl-4-(methoxymethoxy)-1-butenyl* p-*Tolyl Sulfone **(8c)**: ν 3061, 3028, 1645, 1597 (C=CH), 1301, and 1145 cm^{-1} (SO_2); δ_H 2.36 (s, 3H, CH_3Ar), 2.43 (m, 2H, $CHCH_2$), 3.33 (s, 3H, OCH_3), 3.58 (t, J=6.4, 2H, CH_2CH_2O), 3.70 (s, 2H, CH_2C), 4.57 (s, 2H, OCH_2O), 6.97-7.18 (m, 8H, C=CH, ArH), and 7.61 (d, J=8.2, 2H, ArH); δ_C 21.45 (CH_3Ar), 29.44 ($CHCH_2$), 32.12 (CH_2C), 55.26 (OCH_3), 65.43 (CH_2CH_2O), 96.35 (OCH_2O), 126.24, 128.10, 128.18, 128.29, 129.49, 136.69, 140.22, 141.77, and 143.85 (C=CH, ArC); *m/z* 360 (M^+, 0.2%), 172 (35), 160 (18), 159 (27), 143 (13), 142 (14), 141 (14), 139 (38), 131 (18), 129 (24), 128 (30), 115 (18), 91 (38), 65 (14), and 45 (100) (Found: M^+ 360.1392. Calcd. for $C_{20}H_{24}O_4S$: 360.1395).

(E)-1-Phenyl-5-(methoxymethoxy)-2-tosyl-2-penten-1-ol **(8e)**: ν 1638, 961 (C=CH), 1303, and 1145 cm^{-1} (SO_2); δ_H 2.27-2.62 (m with s at 2.39, 5H, $CHCH_2$, CH_3Ar), 3.30 (s, 3H, OCH_3), 3.57 (m, 2H, CH_2CH_2O), 3.75 (d, J=7.6, 1H, OH), 4.56 (s, 2H, OCH_2O), 5.73 (d, J=7.6, 1H, CHOH), 7.14-7.26 (m, 8H, C=CH, ArH), and 7.59 (d, J=8.2, 2H, ArH); δ_C 21.50 (CH_3Ar), 28.93 ($CHCH_2$), 55.36 (OCH_3), 64.97 (CH_2CH_2O), 68.61 (CHOH), 96.24 (OCH_2O), 125.49, 127.16, 127.94, 128.14, 129.59, 136.88, 140.60, 142.28, 144.08, and 146.03 (C=CH, ArC); *m/z* 331 (M^+-45, 5%), 176 (10), 175 (29), 158 (14), 139 (15), 130 (17), 129 (16), 128 (17), 115 (11), 105 (42), 91 (27), 77 (20), 65 (13), 53 (11), 51 (10), 45 (100), 44 (29), and 43 (11).[19]

(E)-5-(Methoxymethoxy)-2-tosyl-1-phenyl-2-penten-1-one **(8f)**: ν 3063, 1596 (C=CH), 1667 (C=O), 1319, and 1149 cm^{-1} (SO_2); δ_H 2.29 (dt, J=13.7, 6.1, 2H, $CHCH_2$), 2.43 (s, 3H, CH_3Ar), 3.29 (s, 3H, OCH_3), 3.55 (t, J=6.3, 2H, CH_2CH_2O), 4.53 (s, 2H, OCH_2O), 7.31 (m, 3H, C=CH, ArH), 7.44-7.93 (m, 7H, ArH); δ_C 21.62 (CH_3Ar), 30.20 ($CHCH_2$), 55.27 (OCH_3), 64.89 (CH_2CH_2O), 96.22 (OCH_2O), 128.47, 128.78, 129.67, 129.92, 134.46, 136.16, 136.64, 142.71, 143.54, 144.69 (C=CH, ArC), and 190.99 (C=O); *m/z* 329 (M^+-CH_2OCH_3, 1%), 105 (53), 91 (20), 77 (39), 65 (11), 45 (100).[19]

(E)-*N*-Cyclohexyl-5-(methoxymethoxy)-2-tosyl-2-pentenamide **(8g)**: ν 3231, 3069 (NH), 1651 (C=CH, C=O), 1302, and 1151 cm^{-1} (SO_2); δ_H 1.13-1.88 (m, 11H, Cy), 2.42 (s, 3H, CH_3Ar), 2.77 (dt, J=7.6, 6.0, 2H, C=$CHCH_2$), 3.37 (s, 3H, OCH_3), 3.70-3.82 (m with t at 3.72, J=6.0, 3H, CHN, CH_2CH_2O), 4.63 (s, 2H, OCH_2O), 7.08 (d, J=7.9, 1H, NH), 7.31 (m, 3H, C=CH, ArH), and 7.74 (d, J=8.2, 2H, ArH); δ_C 21.61 (CH_3Ar), 24.63, 25.41, 32.68 (Cy), 30.26 (C=$CHCH_2$), 48.48 (CHN), 55.46 (OCH_3), 65.35 (CH_2CH_2O), 96.35 (OCH_2O), 139.99, 146.04 (C=CH), 128.15, 129,75, 136.27, 144.73 (ArC), and 159.55 (C=O); *m/z* 364 (M^+-31, 2%), 350 (11), 333 (11), 332 (10), 253 (22), 252 (22), 139 (20), 98 (13), 91 (38), 55 (16), 53 (10), 45 (100), and 41 (17) (Found: C, 60.17; H, 7.07; N, 2.87; S, 7.33. Calcd. for $C_{20}H_{29}NO_5S$: C, 60.74; H, 7.39; N, 3.54; S, 8.11).

Cyclization of 1,5-Diols Derivatives 5b and 8e. General Procedure. A mixture of crude diol (0.25 mmol) and H_3PO_4 (98 μL, 1.68 mmol) in toluene (2 mL) was stirred under reflux during 1 h and then saturated aqueous $NaHCO_3$ was added at room temperature and this mixture was extracted with EtOAc. The organic layer was washed with $NaHCO_3$, dried (Na_2SO_4) and evaporated (15 Torr) and the residue was purified by flash chromatography (hexane/EtOAc) to afford compounds **9**. Yields are mentioned in the text and physical, spectral and analytical data follow:

(E)-6-Isopropyl-3,6-dihydro-2H-5-pyranyl* p-*Tolyl Sulfone **(9a)**: R_f 0.66 (hexane/EtOAc: 1/1); ν 1629 (C=CH), 1301, and 1148 cm^{-1} (SO_2); δ_H 0.49, 0.99 [2d, J=6.9, 6H, $(CH_3)_2CH$], 2.15-2.52 [m with s at 2.44, 6H, CH_3Ar, $(CH_3)_2CH$, $CHCH_2$], 3.41 (td, J=10.8, 3.1, 1H, HCHO), 3.96 (dd, J=10.8, 5.6, 1H, HCHO), 4.27 (m, 1H, CHO), 7.22 (m, 1H, C=CH), 7.33, and 7.74 (2d, J=8.1, 4H, ArH); δ_C 14.65, 19.57 [$(CH_3)_2CH$], 21.57 (CH_3Ar), 26.22 ($CHCH_2$), 30.00 [$(CH_3)_2CH$], 62.04 (CH_2O), 77.50 (CHO), 128.02, 129.71, 137.38, 144.22

(ArC), 139.73, and 142.86 (C=CH); *m/z* 280 (M^+, 3%), 239 (18), 238 (100), 237 (96), 139 (10), 91 (39), 83 (16), 81 (11), 65 (16), 53 (14), 43 (15), and 41 (12) (Found: M^+ 280.1121. Calcd. for $C_{15}H_{20}O_3S$: 280.1133).

(E)-6-Phenyl-3,6-dihydro-2H-5-pyranyl* p-*Tolyl Sulfone **(9b)**: mp 101-102° C (hexane/EtOAc); ν 3062, 3031, 1636 (C=CH), 1302, and 1149 cm^{-1} (SO_2); δ_H 2.32 (s, 3H, CH_3Ar), 2.51 (m, 2H, $CHCH_2$), 3.65 (dt, J=11.5, 5.6, 1H, *H*CHO), 3.82 (dd, J=11.5, 5.7, 1H, HC*H*O), 5.45 (d, J=0.9, 1H, CHO), 6.98-7.26 (m, 9H, C=CH, ArH), and 7.42 (m, 1H, ArH); δ_C 21.39 (CH_3Ar), 25.97 ($CHCH_2$), 59.43 (CH_2O), 74.91 (CHO), 127.65, 127.92, 128.30, 129.17, 129.21, 136.63, 136.88, 138.73, 142.06, and 143.50 (C=CH, ArC); *m/z* 314 (M^+, 41%), 159 (19), 158 (69), 157 (18), 131 (13), 130 (100), 129 (28), 128 (36), 127 (13), 115 (19), 105 (16), 102 (16), 91 (36), 77 (24), 65 (20), 53 (10), and 51 (14) (Found: C, 68.52; H, 5.35; S, 10.25. Calcd. for $C_{18}H_{18}O_3S$: C, 68.77; H, 5.77; S, 10.20).

Synthesis of (2*E*)-2-Tosyl-1-phenyl-2,4-pentadien-1-one (10): A mixture of crude ketone **8f** (0.25 mmol) and H_3PO_4 (98 μL, 1.68 mmol) in toluene (2 mL) was refluxed during 1 h and then saturated aqueous $NaHCO_3$ was added at room temperature and this mixture was extracted with EtOAc. The organic layer was washed with $NaHCO_3$, dried (Na_2SO_4) and evaporated (15 Torr) and the residue was purified by flash chromatography (hexane/EtOAc) to afford compound **10** in 75% yield: mp 72-73°C (hexane/EtOAc); ν 3064, 1665, 1596 (C=O,C=CH), 1304, and 1149 cm^{-1} (SO_2); δ_H 2.43 (s, 3H, CH_3Ar), 5.57 (d, J=10.3, 1H, *H*CH), 5.80 (d, J=16.8, 1H, HC*H*), 6.08 (ddd, J=16.8, 11.1, 10.3, 1H, C*H*=CH_2), and 7.30-7.89 (m, 10H, C=CH, ArH); δ_C 21.67 (CH_3Ar), 128.53, 128.88, 129.75, 130.03, 130.30, 130.40, 134.52, 136.45, 136.89, 141.10, 141.19, 144.79 (C=CHCH=CH_2, ArC), and 190.72 (CO); *m/z* 312 (M^+, 20%), 141 (21), 139 (14), 129 (12), 128 (20), 105 (100), 91 (33), 77 (64), 65 (17), 57 (11), 51 (19), and 43 (27) (Found: C, 68.97; H, 5.45; S, 9.71. Calcd. for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16; S, 10.26).

Reduction of Compounds 5d, 8c, 9a and 9b with Sodium Amalgam. General Procedure. To a suspension of anhydrous Na_2HPO_4 (113 mg, 0.80 mmol) and ca. 5% sodium amalgan (1.84 g, 4 mmol) in dry methanol (3.5 mL) was dropped at 0° C a solution of the corresponding sulfone (0.2 mmol) in methanol (1.5 mL). The reaction mixture was stirred at room temperature during 90 min. Then, the reaction was hydrolyzed with water and extracted with dichloromethane (3x15 mL). The organic layer was dried (Na_2SO_4), concentrated in vacuo (15 Torr) and the residue was purified by flash chromatography (hexane/EtOAc) to yield compounds **11**, **12** and **13**. Yields are included in the text, physical, spectroscopic and analytical data follow:

(E)-5-Phenyl-4-penten-1-ol **(11)**[20]: R_f 0.42 (hexane/EtOAc: 1/1); ν 3354 (OH), 3080, 3058, 1600, and 965 cm^{-1} (C=CH); δ_H 1.76 (m, 2H, $CH_2CH_2CH_2$), 2.32 (m, 2H, $CHCH_2$), 3.72 (t, J=6.4, 2H, CH_2OH), 6.24 (dt, J=15.9, 6.9, 1H, ArCH=C*H*), 6.43 (d, J=15.9, 1H, ArC*H*), and 7.18-7.36 (m, 5H, ArH); δ_C 29.32 ($CH_2CH_2CH_2$), 32.25 ($CHCH_2$), 62.43 (CH_2OH), 125.95, 126.95, 128.49, 130.03, 130.39, and 137.62 (ArC, CH=CH); *m/z* 162 (M^+, 37%), 144 (21), 143 (22), 130 (14), 129 (100), 128 (29), 118 (21), 117 (60), 116 (21), 115 (67), 105 (14), 104 (26), 92 (22), 91 (88), 78 (17), 77 (23), 66 (10), 65 (23), 63 (16), 51 (30), 50 (10), and 43 (52) (Found: M^+ 162.1043. Calcd. for $C_{11}H_{14}O$: 162.1045).

trans-*2-Isopropyl-3-tosyl-2*H*-pyran* **(12)**: mp 129-130° C (hexane/EtOAc); ν 1102, 1085 (C-O), 1308, and 1141 cm^{-1} (SO_2); δ_H 0.94, 1.01 [2d, J=6.9, 6H, $(CH_3)_2CH$], 1.53-1.77 [m, 4H, $SCH(CH_2)_2$], 2.46-2.58 [m with s at 2.46, 4H, CH_3Ar, $(CH_3)_2CH$], 3.11 (ddd, J=11.0, 9.0, 4.3, 1H, *H*CHO), 3.29 (td, J=11.3, 2.7, 1H, CHS), 3.48 (dd, J=9.0, 2.4, 1H, HC*H*O), 3.89 (m, 1H, CHO), 7.36, and 7.74 (2d, J=8.2, 4H, ArH); δ_C 14.82, 20.07 [$(CH_3)_2CH$], 21.61 (CH_3Ar), 25.13, 25.56, 29.79 [$SCH(CH_2)_2$, $(CH_3)_2CH$], 61.50 (CH_2O), 67.21, (CHS), 80.87 (CHO), 128.70, 129.74, 135.34, and 144.60 (ArC); *m/z* 239 (M^+-43, 32%), 155 (47), 139 (35), 127 (22), 126 (81), 111 (15), 109 (20), 92 (19), 91 (70), 83 (37), 71 (96), 67 (17), 65 (32), 57 (18), 56 (13), 55 (80), 53 (12), 44 (14), 43 (100), and 42 (10).[19]

***1-(5-Methoxymethoxypentyl)benzene* (13)**[21, 22]**:** R_f 0.72 (hexane/EtOAc: 2/1); ν 3084, 3062 (C=CH), 1147, 1112, and 1045 cm^{-1} (C-O); δ_H 1.36-1.70 [m, 6H, $(CH_2)_3CH_2O$], 2.62 (t, J=7.9, 2H, CH_2Ar), 3.35 (s, 3H, OCH_3), 3.52 (t, J=6.4, 2H, CH_2CH_2O), 4.61 (s, 2H, OCH_2O), 7.16-7.30 (m, 5H, ArH); δ_C 25.90, 29.61, 31.29, 35.91 [$Ar(CH_2)_4$], 55.08 (OCH_3), 67.72 (CH_2CH_2O), 96.39 (OCH_2O), 125.62, 128.24, 128.37, and 142.61 (ArC); *m/z* 177 (M^+-31, 1%), 145 (44), 117 (28), 105 (10), 104 (14), 92 (12), 91 (94), 65 (18), and 45 (100).[19]

Synthesis of 2-(Tosylmethyl)tetrahydrofuran (15): This compound was prepared by iodosulfonylation-dehydroiodination of 4-penten-1-ol (**14**) in the same manner that for alcohol **2** and isolated in 65% yield: mp 58-59° C (hexane/EtOAc); ν 1086, 1056 (C-O), 1303, and 1142 cm^{-1} (SO_2); δ_H 1.65, 1.87, 2.10 [3m, 4H, $CH(CH_2)_2$], 2.44 (s, 3H, CH_3Ar), 3.20, 3.41 (2dd, J=14.1, 6.4, 6.0, 2H, SCH_2), 3.65-3.82 (m, 2H, CH_2O), 4.23 (m, 1H, CHO), 7.35, and 7.80 (2d, J=8.1, 4H, ArH); δ_C 21.44 (CH_3Ar), 25.11, 31.42 [$CH(CH_2)_2$], 61.04 (CH_2O), 67.82 (CH_2S), 72.76 (CHO), 127.90, 129.63, 136.74, and 144.50 (ArC); *m/z* 197 (M^+-43, 0.3%), 92 (15), 91 (29), 85 (27), 84 (100), 71 (44), 65 (21), 56 (17), 55 (16), 44 (13), 43 (66), 42 (18), 41 (30), and 40 (23) (Found: C, 59.81; H, 6.87; S, 13.18. Calcd. for $C_{12}H_{16}O_3S$: C, 59.98; H, 6.71; S, 13.34).

Synthesis of (*E*)-5-(Methoxymethoxy)-1-pentenyl *p*-Tolyl Sulfone (16): 4-Penten-1-ol (**14**) was protected as MOM ether in the way indicated above for alcohol **2** in quantitative yield. Then, compound **16** was prepared by iodosulfonylation-dehydroiodination of protected alcohol **14** under the same reaction conditions mentioned before for alcohol **1** in 85% yield: R_f 0.48 (hexane/EtOAc: 1/1); ν 1634 (C=CH), 1303, and 1146 cm^{-1} (SO_2); δ_H 1.75 (m, 2H, CH_2CH_2O), 2.35 (m, 2H, $CHCH_2$), 2.43 (s, 3H, CH_3Ar), 3.31 (s, 3H, OCH_3), 3.51 (t, J=6.1, 2H, CH_2CH_2O), 4.57 (s, 2H, OCH_2O), 6.33 (d, J=15.0, 1H, CHS), 6.97 (dt, J=15.0, 6.9, 1H, SCH=C*H*), 7.33, and 7.75 (2d, J=8.1, 4H, ArH); δ_C 21.50 (CH_3Ar), 27.74, 28.24 [$CH(CH_2)_2$], 55.11 (OCH_3), 66.38 (CH_2CH_2O), 96.35 (OCH_2O), 131.04, 145.67 (CH=CH), 127.54, 129.80, 137.66, and 144.15 (ArC); *m/z* 284 (M^+, 0.1%), 139 (29), 129 (11), 97 (42), 91 (27), 71 (12), 65 (16), and 45 (100) (Found: M^+ 284.1084. Calcd. for $C_{14}H_{20}O_4S$: 284.1082).

Lithiation of (*E*)-5-(Methoxymethoxy)-1-pentenyl *p*-Tolyl Sulfone (16) and Reaction with Electrophiles. General Procedure. Metallation of (*E*)-5-(methoxymethoxy)-1-pentenyl *p*-tolyl sulfone (**16**) was carried out in the same way as for compound **6**. Then, the corresponding electrophiles were added (0.3 mmol) (see Table 3 for reaction conditions). After the treatment above-mentioned, compounds **18** were obtained with yields and physical data indicated in Table 3. Spectral and analytical data follow:

***(E)-1-Deuterio-5-(methoxymethoxy)-1-pentenyl* p*-Tolyl Sulfone* (18a):** ν 1634 (C=CH), 1303, and 1146 cm^{-1} (SO_2); δ_H 1.75 (m, 2H, CH_2CH_2O), 2.34 (m, 2H, $CHCH_2$), 2.43 (s, 3H, CH_3Ar), 3.31 (s, 3H, OCH_3), 3.51 (t, J=6.3, 2H, CH_2CH_2O), 4.57 (s, 2H, OCH_2O), 6.96 (t, J=6.9, 1H, SCD=CH), 7.33, and 7.75 (2d, J=8.2, 4H, ArH); δ_C 21.50 (CH_3Ar), 27.73, 28.20 [$CH(CH_2)_2$], 55.12 (OCH_3), 66.38 (CH_2CH_2O), 96.35 (OCH_2O), 130.71 (t, J=27.5, CDS), 145.58 (SCD=*C*H), 127.54, 129.80, 137.65, and 144.16 (ArC); *m/z* 285 (M^+, 0.1%), 139 (28), 130 (11), 98 (33), 91 (25), 65 (13), and 45 (100).[19]

***(E)-6-(Methoxymethoxy)-2-tosyl-2-hexene* (18b):** ν 1649 (C=CH), 1300, and 1150 cm^{-1} (SO_2); δ_H 1.76 (m, 2H, $CHCH_2CH_2$), 1.82 (d, J=1.5, 3H, CH_3C), 2.28 (m, 2H, $CHCH_2$), 2.43 (s, 3H, CH_3Ar), 3.33 (s, 3H, OCH_3), 3.51 (t, J=6.3, 2H, CH_2CH_2O), 4.59 (s, 2H, OCH_2O), 6.87 (m, 1H, C=CH), 7.32, and 7.73 (2d, J=8.2, 4H, ArH); δ_C 11.42 (CH_3C), 21.53 (CH_3Ar), 25.10, 28.30 [$(CH_2)_2CH_2O$], 55.16 (OCH_3), 66.74 (CH_2CH_2O), 96.42 ($\mathrm{OCH_2O}$), 137.49, 139.71 (C=CH), 128.04, 129.70, 136.20, and 144.02 (ArC); *m/z* 267 (M^+-31, 1%), 139 (13), 45 (100), 44 (27), and 43 (15).[19]

(E)-6-(Methoxymethoxy)-1-phenyl-2-tosyl-2-hexene **(18c):** ν 3061, 3028, 1641 (C=CH), 1301, and 1147 cm^{-1} ($\mathrm{SO_2}$); δ_{H} 1.70 (m, 2H, $\mathrm{CHCH_2C}H_2$), 2.27 (m, 2H, $\mathrm{CHC}H_2$), 2.36 (s, 3H, $\mathrm{C}H_3\mathrm{Ar}$), 3.30 (s, 3H, $\mathrm{OCH_3}$), 3.46 (t, J=6.3, 2H, $\mathrm{CH_2C}H_2\mathrm{O}$), 3.68 (s, 2H, $\mathrm{CH_2C}$), 4.54 (s, 2H, $\mathrm{OCH_2O}$), 6.96-7.18 (m, 8H, C=CH, ArH), 7.60 (d, J=8.2, 2H, ArH); δ_{C} 21.43 ($C\mathrm{H_3Ar}$), 25.68, 28.29 [$(C\mathrm{H_2})_2\mathrm{CH_2O}$], 31.97 ($\mathrm{CH_2C}$), 55.15 ($\mathrm{OCH_3}$), 66.58 ($\mathrm{CH_2}C\mathrm{H_2O}$), 96.34 ($\mathrm{OCH_2O}$), 126.20, 128.09, 128.11, 128.25, 129.48, 136.84, 136.87, 140.62, 142.86, and 143.79 (C=CH, ArC); *m/z* 373 (M^+-1, 0.2%), 342 (13), 187 (31), 186 (50), 185 (18), 174 (19), 173 (46), 169 (14), 157 (17), 156 (18), 155 (20), 145 (25), 143 (18), 142 (17), 141 (30), 139 (64), 131 (21), 130 (51), 129 (66), 128 (47), 127 (13), 117 (19), 115 (40), 105 (13), 92 (12), 91 (86), 77 (12), 71 (10), 65 (21), and 45 (100).[19]

(E)-8-(Methoxymethoxy)-4-tosyl-4-octen-3-ol **(18d):** ν 3504 (OH), 1637 (C=CH), 1299, and 1145 cm^{-1} ($\mathrm{SO_2}$); δ_{H} 0.82 (t, J=7.3, 3H, $\mathrm{C}H_3\mathrm{CH_2}$), 1.49-1.88 (m, 4H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$, $\mathrm{CH_3C}H_2$), 2.43-2.63 (m with s at 2.43, 5H, $\mathrm{C}H_3\mathrm{Ar}$, $\mathrm{C{=}CHC}H_2$), 2.80 (br. s, 1H, OH), 3.31 (s, 3H, $\mathrm{OCH_3}$), 3.54 (t, J=6.1, 2H, $\mathrm{CH_2C}H_2\mathrm{O}$), 4.46 (dd, J=8.9, 5.5, 1H, $\mathrm{C}H\mathrm{OH}$), 4.57 (s, 2H, $\mathrm{OCH_2O}$), 6.93 (t, J=7.6, 1H, C=CH), 7.31, and 7.74 (2d, J=8.4, 4H, ArH); δ_{C} 10.42 ($C\mathrm{H_3CH_2}$), 21.50 ($C\mathrm{H_3Ar}$), 25.31, 28.54, 29.83 [$(C\mathrm{H_2})_2\mathrm{CH_2O}$, $\mathrm{CH_3}C\mathrm{H_2}$], 55.16 ($\mathrm{OCH_3}$), 66.59 ($\mathrm{CH_2}C\mathrm{H_2O}$), 70.31 (CHOH), 96.36 ($\mathrm{OCH_2O}$), 127.78, 129.67, 137.96, 143.79, and 144.04 (C=CH, ArC); *m/z* 313 (M^+-29, 0.4%), 281 (24), 252 (10), 251 (71), 157 (15), 141 (19), 139 (27), 125 (12), 124 (21), 95 (15), 92 (10), 91 (35), 79 (11), 67 (13), 65 (14), 57 (12), 55 (13), 45 (100), and 41 (13).[19]

(E)-8-(Methoxymethoxy)-2,2-dimethyl-4-tosyl-4-octen-3-ol **(18e):** ν 3507 (OH), 1631 (C=CH), 1300, and 1145 cm^{-1} ($\mathrm{SO_2}$); δ_{H} 1.02 [s, 9H, $(\mathrm{CH_3})_3\mathrm{C}$], 1.68 (m, 2H, $\mathrm{CHCH_2C}H_2$), 2.30-2.63 (m with s at 2.42, 6H, $\mathrm{C}H_3\mathrm{Ar}$, $\mathrm{CHC}H_2$, OH), 3.27 (s, 3H, $\mathrm{OCH_3}$), 3.40 (t, J=6.1, 2H, $\mathrm{CH_2C}H_2\mathrm{O}$), 4.41 (d, J=6.7, 1H, $\mathrm{C}H\mathrm{OH}$), 4.47 (s, 2H, $\mathrm{OCH_2O}$), 6.76 (t, J=7.3, 1H, C=CH), 7.30, and 7.78 (2d, J=8.4, 4H, ArH); δ_{C} 21.46 ($C\mathrm{H_3Ar}$), 26.83, 28.43 [$(C\mathrm{H_2})_2\mathrm{CH_2O}$], 26.90 [$(C\mathrm{H_3})_3\mathrm{C}$], 37.61 [$(\mathrm{CH_3})_3C$], 55.09 ($\mathrm{OCH_3}$), 66.41 ($\mathrm{CH_2}C\mathrm{H_2O}$), 77.16 (CHOH), 96.23 ($\mathrm{OCH_2O}$), 127.55, 129.59, 139.31, 143.82, 144.06, and 147.29 (C=CH, ArC); *m/z* 339 (M^+-31, 0.3%), 282 (15), 281 (25), 252 (17), 251 (100), 157 (14), 139 (29), 127 (15), 109 (10), 95 (13), 92 (11), 91 (29), 81 (11), 67 (13), 65 (11), 57 (30), 45 (76), and 41 (28).[19]

(E)-6-(Methoxymethoxy)-1-phenyl-2-tosyl-2-hexen-1-ol **(18f):** ν 3477 (OH), 3061, 3029, 1638 (C=CH), 1300, and 1146 cm^{-1} ($\mathrm{SO_2}$); δ_{H} 1.69 (m, 2H, $\mathrm{CHCH_2C}H_2$), 2.22-2.42 (m with s at 2.37, 5H, $\mathrm{C}H_3\mathrm{Ar}$, $\mathrm{CHC}H_2$), 3.29 (s, 3H, $\mathrm{OCH_3}$), 3.44 (t, J=6.1, 2H, $\mathrm{CH_2C}H_2\mathrm{O}$), 3.67 (s, 1H, OH), 4.53 (s, 2H, $\mathrm{OCH_2O}$), 5.77 (s, 1H, $\mathrm{C}H\mathrm{OH}$), 7.09-7.18 (m, 8H, C=CH, ArH), and 7.52 (d, J=8.2, 2H, ArH); δ_{C} 21.45 ($C\mathrm{H_3Ar}$), 25.39, 28.10 [$(C\mathrm{H_2})_2\mathrm{CH_2O}$], 55.16 ($\mathrm{OCH_3}$), 66.41 ($\mathrm{CH_2}C\mathrm{H_2O}$), 68.74 (CHOH), 96.23 ($\mathrm{OCH_2O}$), 125.42, 127.09, 127.75, 128.06, 129.52, 137.24, 140.28, 143.87, 143.88, and 145.47 (C=CH, ArC); *m/z* 345 (M^+-45, 12%), 190 (11), 189 (36), 172 (11), 146 (24), 145 (15), 143 (15), 139 (27), 128 (13), 115 (17), 105 (74), 91 (43), 79 (13), 77 (30), 65 (16), and 45 (100).[19]

(E)-6-(Methoxymethoxy)-2-tosyl-1-phenyl-2-hexen-1-one **(18g):** ν 3063, 1633 (C=CH), 1668 (C=O), 1305, and 1148 cm^{-1} ($\mathrm{SO_2}$); δ_{H} 1.70 (m, 2H, $\mathrm{CHCH_2C}H_2$), 2.12 (m, 2H, $\mathrm{CHC}H_2$), 2.43 (s, 3H, $\mathrm{C}H_3\mathrm{Ar}$), 3.24 (s, 3H, $\mathrm{OCH_3}$), 3.39 (t, J=6.1, 2H, $\mathrm{CH_2C}H_2\mathrm{O}$), 4.47 (s, 2H, $\mathrm{OCH_2O}$), 7.23 (t, J=7.9, 1H, C=CH), 7.30-7.91 (m, 9H, ArH); δ_{C} 21.62 ($C\mathrm{H_3Ar}$), 26.83, 28.15 [$(C\mathrm{H_2})_2\mathrm{CH_2O}$], 55.13 ($\mathrm{OCH_3}$), 66.31 ($\mathrm{CH_2}C\mathrm{H_2O}$), 96.27 ($\mathrm{OCH_2O}$), 128.43, 128.80, 129.67, 129.79, 134.41, 136.35, 136.78, 142.32, 144.64, 145.33 (C=CH, ArC), and 191.05 (C=O); *m/z* 357 (M^+-31, 2%), 279 (17), 139 (13), 105 (100), 91 (29), 77 (48), 65 (12), and 45 (84).[19]

(E)-N-Cyclohexyl-6-(methoxymethoxy)-2-tosyl-2-hexenamide **(18h)**: ν 3365 (NH), 1669 (C=O), 1636 (C=CH), 1304, and 1146 cm^{-1} (SO_2); δ_H 1.13-1.36, 1.59-1.88 (2m, 12H, Cy, $CHCH_2CH_2$), 2.42 (s, 3H, CH_3Ar), 2.62 (m, 2H, $CHCH_2$), 3.35 (s, 3H, OCH_3), 3.56 (t, *J*=6.0, 2H, CH_2CH_2O), 3.75 (m, 1H, CHN), 4.60 (s, 2H, OCH_2O), 6.97 (d, *J*=8.6, 1H, NH), 7.26 (t, *J*=7.8, 1H, C=CH), 7.31, and 7.71 (2d, *J*=8.1, 4H, ArH); δ_C 21.57 (CH_3Ar), 24.63, 25.35, 32.62 (Cy), 26.80, 28.36 [$C=CH(CH_2)_2$], 48.48 (CHN), 55.20 (OCH_3), 66.75 (CH_2CH_2O), 96.34 (OCH_2O), 138.06, 149.66 (C=CH), 127.91, 129.79, 136.01, 144.74 (ArC), and 159.45 (C=O); *m/z* 409 (*M*$^+$, 0.6%), 267 (22), 266 (15), 257 (19), 139 (24), 119 (10), 98 (19), 91 (47), 67 (13), 65 (15), 56 (15), 55 (21), 45 (10), and 41 (19) (Found: C, 61.48; H, 7.83; N, 3.54; S, 7.62. Calcd. for $C_{21}H_{31}NO_5S$: C, 61.59; H, 7.63; N, 3.42; S, 7.83).

Lithiation of 2-(Tosylmethyl)tetrahydrofuran (15) and Reaction with Propanal. Metallation of 2-(tosylmethyl)tetrahydrofuran (**15**) was carried out in the same way as for compound **6** with 2 equiv of n-butyllithium or 3 equiv of LDA. Then propanal was added (0.3 mmol, 22 μL) and after the treatment indicated before, a ca. 1/1 mixture of alcohols **21** and **22** was obtained. Yield is included in the text, physical, spectral and analytical data follow:

(E)-5-Tosyl-4-octen-1,6-diol **(21)** ***and (E)-5-Tosyl-3-octen-1,6-diol*** **(22)**[23]**:** R_f 0.38 (hexane/EtOAc: 1/3);[24] ν 3470 (OH), 1640 (C=CH), 1284, and 1145 cm^{-1} (SO_2);[24] δ_H 0.82, 0.92 (2t, *J*=7.3, 3H, CH_2CH_3), 1.31-1.83 (m, 3H, CH_3CH_2, $CH_2CH_2CH_2$), 2.24-2.73 (m with 2s at 2.44, 2.46, 6H, CH_3Ar, $CHCH_2CH_2$, OH), 3.19 (s, 1H, OH), 3.44-3.64 (m, 2.5H, CH_2OH, CHS), 4.33 (m, 0.5H, CHCHOH), 4.45 (dd, *J*=8.9, 5.5, 0.5H, CCHOH), 5.47 (dt, *J*=15.6, 7.2, 1H, $CH=CHCH_2$), 5.75 (dd, *J*=15.6, 9.9, 1H, $CH=CHCH_2$), 6.95 (td, *J*=7.9, 2.1, 0.5H, C=CH), 7.33, 7.36, 7.73, and 7.74 (4d, *J*=8.4, 4H, ArH); δ_C 9.91, 10.46 (CH_3CH_2), 21.55, 21.61 (CH_3Ar), 24.80, 27.74, 29.87, 30.86, 36.03 [$(CH_2)_2CH_2OH$, CH_3CH_2, $CHCH_2CH_2OH$], 119.79, 127.82, 128.86, 129.62, 129.78, 134.46, 137.41, 138.50, 143.88, 144.22, and 145.01 (ArC, C=CH, CH=CH); *m/z* 262 (*M*$^+$-36, 0.2%), 251 (20), 240 (15), 239 (100), 157 (12), 143 (15), 139 (21), 92 (12), 91 (35), 65 (15), and 41 (11).[19, 24]

Cyclization of 1,6-Diols Derivatives 18d and 18f. General Procedure. These cyclizations were carried out in the same way as for 1,5-diols to afford compounds **23d** and **23f** whose yields are mentioned in the text and physical, spectral and analytical data follow:

(E/Z)-1-Tosyl-1-(tetrahydro-2-furanyl)-1-butene **(23d):** R_f 0.56, 0.49 (hexane/EtOAc:2/1);[24] ν 1639 (C=CH), 1301, and 1139 cm^{-1} (SO_2);[24] δ_H 0.96, 1.11 (2t, *J*=7.6, 3H, CH_2CH_3), 1.83-2.68 (m with s at 2.43, 9H, CH_3Ar, $OCH(CH_2)_2$, CH_2CH_3], 3.65-4.00 (m, 2H, CH_2O), 4.64 (m, 1H, CHO), 6.34 (t, *J*=7.5, 0.5H, C=CH, *Z*), 7.00 (t, *J*=7.5, 0.5H, C=CH, *E*), 7.29, 7.31, 7.73, and 7.78 (4d, *J*=8.2, 4H, ArH); δ_C 13.20, 13.29 (CH_3CH_2), 21.56 (CH_3Ar), 21.66, 21.75, 25.56, 26.28, 32.90, 33.66 [$OCH(CH_2)_2$, CH_3CH_2], 68.39, 68.63 (CH_2O), 75.41, 77.53 (CHO), 127.17, 127.71, 129.46, 129.65, 138.42, 139.18, 143.62, 144.05, (ArC), 141.24, 141.88, 143.19, and 145.63 (C=CH); *m/z* 280 (*M*$^+$, 2%), 251 (23), 237 (10), 157 (21), 141 (57), 139 (21), 125 (28), 124 (100), 123 (21), 109 (14), 107 (15), 97 (15), 96 (52), 95 (31), 92 (17), 91 (53), 83 (45), 82 (77), 81 (30), 79 (21), 77 (17), 71 (29), 69 (10), 67 (19), 65 (32), 55 (41), 53 (24), 43 (26), and 41 (37)[24] (Found: *M*$^+$ 280.1130. Calcd. for $C_{15}H_{20}O_3S$: 280.1133).[24]

(E)-2-Phenyl-1-tosyl-1-(tetrahydro-2-furanyl)-1-ethene **(23f):** mp 91-92°C (hexane/EtOAc); ν 3060, 3027, 1620 (C=CH), 1300, and 1147 cm^{-1} (SO_2); δ_H 1.79-2.50 [m with s at 2.42, 7H, $CH(CH_2)_2$, CH_3Ar], 3.64, 3.90 (2m, 2H, CH_2O), 4.88 (t, *J*=7.9, 1H, CHO), 7.26-7.41 (m, 7H, ArH), 7.81 (d, *J*=8.2, 2H, ArH), and 8.00 (s, 1H, C=CH); δ_C 21.58 (CH_3Ar), 26.37, 32.43 [$(CH_2)_2CH_2O$], 68.70 (CH_2O), 75.19 (CHO), 127.59, 128.51, 129.34, 133.36, 139.72, 141.17, 142.72, and 143.55 (C=CH, ArC); *m/z* 189 (53), 188 (15), 173 (M^+-Ts, 70%), 172 (100), 171 (49), 157 (13), 144 (10), 131 (58), 130 (25), 129 (21), 128 (18), 116 (17), 115 (29), 103 (30), 102 (24), 91 (46), 89 (11), 77 (27), 71 (20), 65 (34), 63 (12), 53 (11), 51 (17), 44 (97), 43 (43), and 42 (41) (Found: C, 69.58; H, 6.27; S, 9.57. Calcd. for $C_{19}H_{20}O_3S$: C, 69.49; H, 6.14; S, 9.76).

Reduction of Compounds 18c, 18e, 18f and 23f with Sodium Amalgam. General Procedure. The desulfonylation of these compounds was carried out under the same reaction conditions indicated above yielding compounds **24-28**. Yields are included in the text, physical, spectroscopic and analytical data follow:

1-(6-Methoxymethoxyhexyl)benzene (**24**)[22]: R_f 0.87 (hexane/EtOAc: 1/1); ν 3059, 3026 (C=CH), 1147, 1112, and 1045 cm^{-1} (C-O); δ_H 1.36-1.73 [m, 8H, $(CH_2)_4CH_2O$], 2.61 (t, *J*=7.6, 2H, CH_2Ar), 3.35 (s, 3H, OCH_3), 3.51 (t, *J*=6.6, 2H, CH_2CH_2O), 4.62 (s, 2H, OCH_2O), 7.15-7.30 (m, 5H, ArH); δ_C 26.07, 29.05, 29.65, 31.39, 35.87 [$Ar(CH_2)_5$], 55.07 (OCH_3), 67.78 (CH_2CH_2O), 96.37 (OCH_2O), 125.57, 128.21, 128.36, and 142.74 (ArC); *m/z* 191 (M^+-31, 2%), 190 (15), 159 (22), 131 (15), 118 (19), 117 (66), 105 (15), 104 (27), 92 (24), 91 (100), 81 (12), 65 (21), 55 (11), and 45 (100).

(E/Z)-2,2-Dimethyl-8-(methoxymethoxy)-4-octen-3-ol (**25**): R_f 0.67 (hexane/EtOAc: 1/1);[24] ν 3487 (OH), 1149, 1112, and 1041 cm^{-1} (C-O);[24] δ_H 0.90, 0.91 [2s, 9H, $(CH_3)_3C$], 1.43 (s, 1H, OH), 1.69 (m, 2H, $CH_2CH_2CH_2$), 2.15 (m, 2H, $CHCH_2$), 3.37 (s, 3H, OCH_3), 3.53 (m, 2H, CH_2CH_2O), 3.70, 4.09 (2d, *J*=6.7, 8.2, 1H, CHOH), 4.62 (s, 2H, OCH_2O), and 5.59 (m, 2H, CH=CH); δ_C 25.47, 25.68 [$(CH_3)_3C$], 28.95, 29.32, 29.40 [$CH(CH_2)_2$], 34.73, 34.93 [$(CH_3)_3C$], 55.12, 55.22 (OCH_3), 66.99, 67.08 (CH_2CH_2O), 74.65, 80.97 (CHOH), 96.41 (OCH_2O), 130.09, 130.38, 132.33, and 132.66 (CH=CH); *m/z* 159 (M^+-Bu^t, 4%), 127 (22), 98 (10), 97 (100), 95 (12), 93 (10), 83 (11), 81 (15), 79 (16), 71 (26), 70 (11), 69 (27), 67 (18), 57 (45), 55 (60), 45 (82), 43 (47), and 42 (14).[19, 24]

1-(6-Methoxymethoxy-1-hexenyl)benzene (**26**)[25]: R_f 0.81 (hexane/EtOAc: 1/1); ν 3060, 3026, 1601 (C=CH) and 1050 cm^{-1} (C-O); δ_H 1.65 [m, 4H, $(CH_2)_2CH_2O$], 2.25 (m, 2H, $CHCH_2$), 3.36 (s, 3H, OCH_3), 3.55 (t, *J*=6.3, 2H, CH_2CH_2O), 4.63 (s, 2H, OCH_2O), 6.21 (dt, *J*=15.6, 6.8, 1H, $CHCH_2$), 6.39 (d, *J*=15.6, 1H, CH=$CHCH_2$), 7.16-7.35 (m, 5H, ArH); δ_C 25.98, 29.27, 32.75 [$CH(CH_2)_3$], 55.12 (OCH_3), 67.59 (CH_2CH_2O), 96.41 (OCH_2O), 125.91, 126.83, 128.46, 130.10, 130.60, and 137.80 (ArC, CH=CH); *m/z* 189 (M^+-31, 0.6%), 157 (19), 130 (11), 129 (37), 117 (16), 115 (32), 104 (17), 91 (54), and 45 (100).

(E/Z)-6-Phenyl-4-hexen-1-ol (**27**)[20c]: R_f 0.38 (hexane/EtOAc: 1/1);[24] ν 3352 (OH), 3084, 3062, 3026, 1603, 968 (C=CH), and 1055 cm^{-1} (C-O);[24] δ_H 1.58 (s, 1H, OH), 1.66 (m, 2H, $CHCH_2CH_2$), 2.13, 2.26 (2m, 2H, $CHCH_2CH_2$), 3.34, 3.42 (2d, *J*=6.1, 6.7, 2H, $ArCH_2$), 3.66 (m, 2H, CH_2O), 5.57 (m, 2H, CH=CH), and 7.16-7.32 (m, 5H, ArH); δ_C 28.80, 29.04 (CH_2CH_2O), 32.32, 32.70 ($CHCH_2CH_2$), 39.00 ($ArCH_2$), 62.54, 63.02 (CH_2O), 125.61, 125.92, 128.23, 128.29, 128.37, 128.44, 129.59, 131.05, 140.83, and 142.72 (ArC, CH=CH); *m/z* 176 (M^+, 3%), 130 (15), 129 (18), 117 (31), 115 (17), 104 (54), 92 (29), 91 (100), 77 (11), 65 (24), and 51 (13).[24]

(E)-2-Phenyl-1-(tetrahydro-2-furanyl)-1-ethene (**28**)[26]: R_f 0.74 (hexane/EtOAc: 2/1); ν 3081, 3058, 3025, 1599, 966 (C=CH), and 1053 cm^{-1} (C-O); δ_H 1.66-2.19 [m, 4H, $OCH(CH_2)_2$], 3.85, 3.98 (2m, 2H, CH_2O), 4.48 (c, *J*=6.8, 1H, CHO), 6.21 (dd, *J*=15.9, 6.8, 1H, CHCHO), 6.59 (d, *J*=15.9, 1H, CH=CHCHO), 7.20-7.40 (m, 5H, ArH); δ_C 25.90, 32.39 [$OCH(CH_2)_2$], 68.16 (CH_2O), 79.65 (CHO), 126.45, 127.47, 128.49, 130.43, 130.53, and 136.87 (CH=CH, ArH); *m/z* 174 (M^+, 51%), 173 (19), 131 (34), 129 (13), 128 (16), 115 (19), 104 (33), 103 (20), 91 (19), 78 (17), 77 (24), 70 (22), 63 (11), 55 (22), 51 (26), 44 (14), 43 (16), and 42 (100).

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REFERENCES AND NOTES

1. (a) Simpkins, N. S. *Tetrahedron* **1990**, *46*, 6951-6984. (b) Simpkins, N. S. In *Sulphones in Organic Synthesis* , Pergamon Press, Oxford: 1993.
2. (a) Eisch, J. J., Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3279-3280. (b) Eisch, J. J., Behrooz, M. *Tetrahedron Lett.* **1984**, *25*, 4851-4854. (c) Holmes, A. B.; Pooley, G. R. *Tetrahedron* **1992**, *48*, 7775-7792. (d) Müller, J.; Neuburger, M.; Zehnder, M. *Helv. Chim. Acta* **1995**, *78*, 615-618.
3. Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356-363
4. (a) Simpkins, N. S. *Tetrahedron Lett.* **1987**, *28*, 989-992. (b) McCombie, S. W.; Shankar, B. B.; Ganguly, A. K.*Tetrahedron Lett.* **1987**, *28*, 4123-4126. (c) McCombie, S. W.; Shankar, B. B.; Ganguly, A. K.; Padwa, A.; Bullock, W. H.; Dyszlewski, A. D. *Tetrahedron Lett.* **1987**, *28*, 4127-4130.
5. Yamamoto, M.; Takemori, T.; Iwasa, S.; Kohmoto, S.; Yamada, K. *J. Org. Chem.* **1989**, *54*, 1757-1760.
6. (a) Nájera, C.; Yus, M. *Tetrahedron Lett.* **1987**, *28*, 6709-6712. (b) Nájera, C.; Yus, M. *J. Org. Chem.* **1988**, *53*, 4708-4715. (c) Parrain, J.-L.; Beaudet, I.; Duchêne, A.; Watrelot, S.; Quintard, J.-P. *Tetrahedron Lett.* **1993**, *34*, 5445-5448.
7. Nájera, C.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1387-1391.
8. Ibañez, P. L.; Nájera, C. *Tetrahedron Lett.* **1993**, *34*, 2003-2006.
9. (a) Eisch, J. J., Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3277-3279. (b) Nájera, C.; Yus, M. *J. Org. Chem.* **1989**, *54*, 1491-1499.
10. (a) Rojo, J.; García, M.; Carretero, J. C. *Tetrahedron* **1993**, *49*, 9787-9800. (b) Carretero, J. C.; Dominguez, E. *J. Org. Chem.* **1993**, *58*, 1596-1600. (c) Alcaraz, C.; Carretero, J. C.; Dominguez, E. *Tetrahedron Lett.* **1991**, *32*, 1385-1388.
11. Caturla, F.; Nájera, C. *Tetrahedron Lett.* **1996**, *37*, 2833-2836.
12. Kotsuki, H. *Synlett* **1992**, 97-106.
13. This methodology is a simple and easy way for preparing vinyl sulfones[14] and avoids the use of chlorinated solvents and the preparation of the very unstable tosyl iodide.
14. Nájera, C.; Sansano, J. M.; Yus, M. *J. Chem. Educ.* **1995**, *72*, 664-665.
15. Purchased from Aldrich.
16. Deduced by 300 MHz ^{1}H NMR.
17. Gras, J.-L.; Kong Win Chang, Y. Y.; Guerin, A. *Synthesis* **1985**, 74-75.
18. Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477-3478.
19. In this case was not possible to obtain the corresponding HRMS due to the absence of the M^+ signal.
20. (a) Riobé, O. *C. R. Acad. Sci.* **1947**, *225*, 334-345. (b) Riobé, O. *Ann. Chim.* **1949**, *4*, 593-638. (c) Collins, R. F.; Davis, M. *J. Chem. Soc.* **1961**, 1863-1879.
21. For the corresponding alcohol see: Drukker, E. A., Beets, M. G. J. *Rec. Trav. Chim. Pays-Bas* **1953**, *72*, 989-992.
22. For the corresponding alcohol see ref. 20c.
23. For the major diastereomer.
24. Mixture of compounds.
25. For the corresponding alcohol see: Cousseau, J.; Lamant, M. *Bull. Soc. Chim. Fr.* **1967**, 4702-4707.
26. Montaudon, E.; Thepeniez, J.; Lalande, R. *J. Heterocycl. Chem.* **1979**, *16*, 113-121.

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