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## Dilithiated 3-Tosylpropanal Dimethyl Acetal as $\beta,\beta$ -Acylvinyl Dianion or Homoenate Dianion Equivalent<sup>1</sup>

Pedro Bonete and Carmen Nájera\*

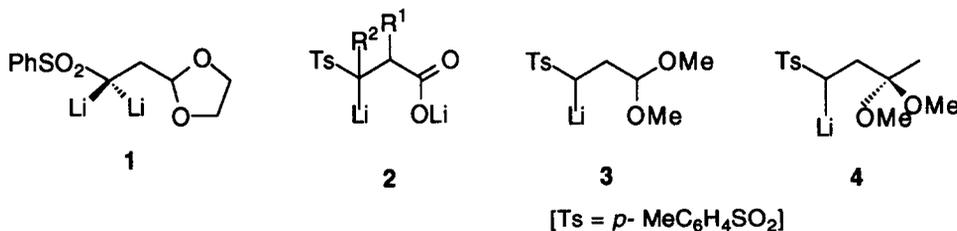
Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain

**Abstract:** 3,3-Dilithio-1,1-dimethoxy-3-tosylpropane (**6**) reacts with mono and dielectrophiles to give dialkylated products **7** and carbocyclic derivatives **8**, respectively. Hydrolysis of the acetal function followed by DBU dehydrosulfonylation of these products affords  $\beta,\beta$ -disubstituted propanal derivatives **11** and **12**. Reductive desulfonylation of compounds **8g-j** provides  $\beta,\beta$ -disubstituted propanal acetals **14**.

### INTRODUCTION

The ability of the sulfone group to generate *gem*-dianions is unique, especially in the case of alkyl and allyl sulfones<sup>2</sup>.  $\alpha,\alpha$ -Dilithiated sulfones have been mainly used as super-nucleophilic sulfonyl carbanions in the reaction with poor nucleophiles and as dinucleophiles they can react with two equiv. of an electrophile<sup>3</sup> or with one dielectrophile in cyclization reactions<sup>3b,3e,4</sup>. Monolithium derivatives of protected  $\gamma$ -oxosulfones have been used as sulfonyl-stabilized homoenolates in many carbon-carbon bond forming reactions<sup>5</sup>. However, the only described  $\alpha,\alpha$ -di-lithio derivative **1** of these  $\gamma$ -oxosulfones has only been chemically characterized by deuterolysis<sup>6</sup>.

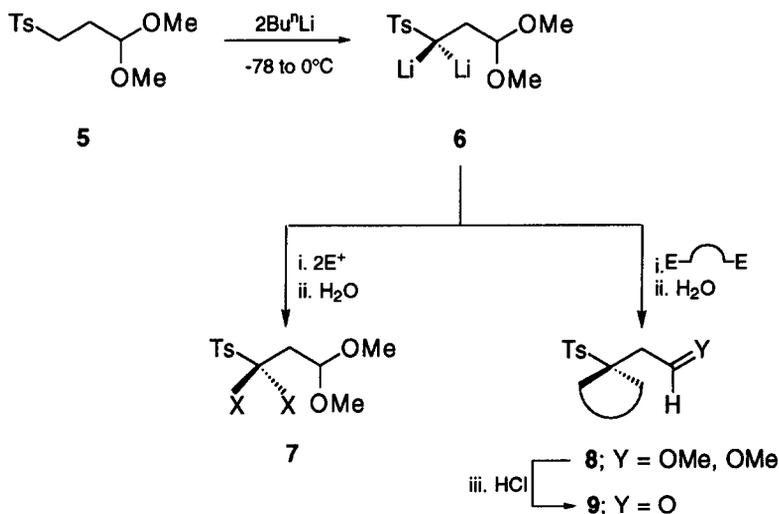
In connection with our studies about the preparation and synthetic applications of lithiated 3-tosylalkanoates (**2**)<sup>7</sup>, 3-tosylpropanal (**3**)<sup>5</sup> and 4-tosyl-2-butanone (**4**)<sup>5</sup> dimethyl ketals as versatile  $\beta$ -acylvinyl anion equivalents, we describe here the reactivity of 3,3-dilithio-3-tosylpropanal dimethyl acetal and its synthetic applications as a  $\beta,\beta$ -acylvinyl dianion as well as a homoenate dianion equivalent.



### RESULTS AND DISCUSSION

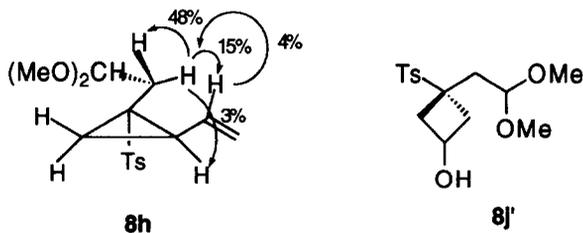
When 1,1-dimethoxy-3-tosylpropane (**5**), prepared by addition of sodium *p*-toluenesulfinate to acrolein followed by acetalization with trimethyl orthoformate<sup>5</sup>, was allowed to react with two equiv. of *n*-butyllithium in THF at temperatures between -78 and 0°C<sup>8</sup> the corresponding dilithiated intermediate **6** was obtained, which

was characterized by deuterolysis with  $d_4$ -methanol to provide dideuterated product **7a** (Scheme 1 and Table 1). This *gem*-dilithio derivative was dialkylated with *n*-butyl iodide or benzyl bromide to afford compounds **7b** or **7c**, respectively (Table 1, entries 2 and 3). The synthetic utility of sulfonyl dianion **6** in annellation reactions was studied with dielectrophiles. The carbocyclization reaction took place with different dihalides or electrophilic bifunctional compounds to yield products **8** (Scheme 1 and Table 1).



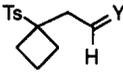
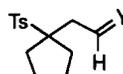
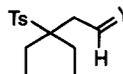
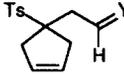
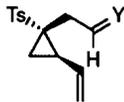
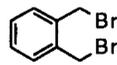
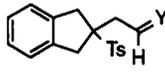
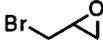
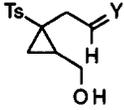
Scheme 1.

Intermediate **6** reacted with alkyl  $\alpha,\omega$ -dihalides to give the corresponding 4-, 5- and 6-membered carbocycles **8d-f** in good yields (Table 1, entries 4, 6 and 8), together with less than 9% of monoalkylated compounds, which could be easily separated by simple column chromatography (silica gel). The reaction with (*Z*)-1,4-dichloro-2-butene gave the corresponding cyclopentene **8g**, while the *E*-isomer underwent 1,2-substitution to lead stereoselectively to the more stable *trans*-substituted cyclopropane **8h**. The stereochemistry of this vinylcyclopropane **8h** was determined by using NOE  $^1\text{H}$  NMR spectroscopy. Irradiation of one of the protons of the methylene group at the  $\beta$ -position respect to the acetal group showed an enhancement of the methine at the vinyl group and *viceversa*.



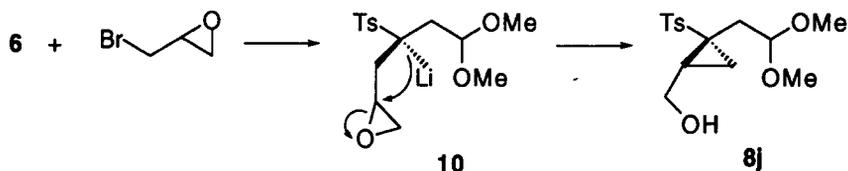
In the case of  $\alpha,\alpha'$ -dibromo-*o*-xylene the expected indan derivative **8i** was obtained (Table 1, entry 14). The reaction of dianion **6** with epibromohydrin gave the cyclopropane derivative **8j** and the cyclobutanol **8j'** in

**Table 1.** Preparation of Compounds **7**, **8**, and **9**.

entry	electrophile	product			
		no.	X or structure	Y	yield (%) <sup>a,b</sup> mp (°C) <sup>c</sup> or <i>R</i> <sub>F</sub> <sup>d</sup>
1	d <sup>4</sup> -MeOH	<b>7a</b>	D		95 <sup>e</sup> 0.37
2	n-BuI	<b>7b</b>	Bu <sup>n</sup>		97 0.59
3	PhCH <sub>2</sub> Br	<b>7c</b>	PhCH <sub>2</sub>		81 74-76
4	I(CH <sub>2</sub> ) <sub>3</sub> I	<b>8d</b>		(OMe) <sub>2</sub>	84 (3) 0.45
5		<b>9d</b>		O	99 <sup>f</sup> 0.30
6	I(CH <sub>2</sub> ) <sub>4</sub> I	<b>8e</b>		(OMe) <sub>2</sub>	87 (9) 0.43
7		<b>9e</b>		O	96 <sup>f</sup> 0.38
8	I(CH <sub>2</sub> ) <sub>5</sub> I	<b>8f</b>		(OMe) <sub>2</sub>	82 (8) 0.55
9		<b>9f</b>		O	93 <sup>f</sup> 0.39
10		<b>8g</b>		(OMe) <sub>2</sub>	95 0.50
11		<b>9g</b>		O	93 <sup>f</sup> 0.41
12		<b>8h</b>		(OMe) <sub>2</sub>	69 <sup>g</sup> 0.59
13		<b>9h</b>		O	78 0.41
14		<b>8i</b>		(OMe) <sub>2</sub>	71 (2) 0.45
15		<b>9i</b>		O	72 <sup>f</sup> 0.32
16		<b>8jh</b>		(OMe) <sub>2</sub>	70 <sup>i</sup> 0.20

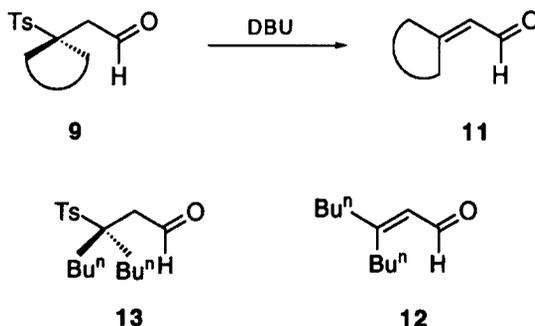
<sup>a</sup> Based on starting sulfone after column chromatography (silica gel, hexane/ether). <sup>b</sup> In parenthesis yield of monoalkylated product. <sup>c</sup> From hexane/CH<sub>2</sub>Cl<sub>2</sub>. <sup>d</sup> Hexane/EtOAc: 2/1. <sup>e</sup> 96% of double deuterium incorporation (deduced by <sup>1</sup>H NMR). <sup>f</sup> Isolated crude yield. <sup>g</sup> Only the *trans*-diastereomer was detected. <sup>h</sup> A *ca.* 1/1 diastereomer mixture was obtained (deduced by <sup>1</sup>H NMR). <sup>i</sup> A mixture of compounds **8j** and **8j'** was obtained in 92/8 molar ratio and were separated by column chromatography.

92/8 molar ratio (deduced by <sup>13</sup>C NMR). Compound **8j** was isolated as *ca.* 1/1 mixture of diastereomers. These results are the opposite to those observed in the reaction of this electrophile with [(phenylsulfonyl)methylene]-dilithium<sup>3b</sup>, which afforded the cyclobutanol derivative. The different behaviour of both dilithiated sulfones can be explained by the difference between the initial attack of dianion **6** respect to methyl phenyl sulfone dianion to the epibromohydrin. The most substituted dilithio derivative **6** attacked at the carbon-bromine bond to give intermediate **10**, which cyclized to provide cyclopropane **8j** (Scheme 2). However, dilithiated methyl phenyl sulfone opened first the epoxide followed by attack at the carbon-bromine bond<sup>3b</sup>.



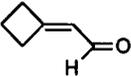
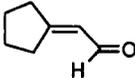
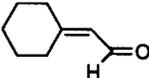
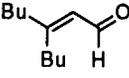
Scheme 2.

Acetals **8** were transformed into aldehydes **9** by refluxing in acetone/water (3/1) containing a catalytic amount of concd. hydrochloric acid<sup>6</sup> (Scheme 1 and Table 1). Treatment of aldehydes **9** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave  $\beta,\beta$ -disubstituted  $\alpha,\beta$ -unsaturated aldehydes **11** (Scheme 3 and Table 2). Dialkylated compound **7b** suffered partial dehydrosulfinylation during the hydrolysis step to give a mixture of compounds **12** and **13**. This mixture was treated with DBU, being compound **12** exclusively obtained (Scheme 3 and Table 2).



Scheme 3.

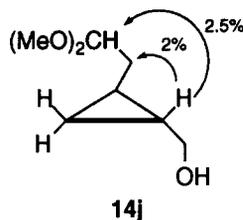
**Table 2.** Synthesis of Unsaturated Aldehydes **11** and **12**.

entry	starting compound		product			
	no.	no.	structure	yield (%) <sup>a</sup>	bp (°C) <sup>b</sup> or <i>R<sub>f</sub></i> <sup>c</sup>	
1	<b>9d</b>	<b>11d</b>		86	65-70 <sup>d,e</sup>	
2	<b>9e</b>	<b>11e</b>		88	80-85 <sup>f,g</sup>	
3	<b>9f</b>	<b>11f</b>		91	100-105 <sup>f,h</sup>	
4	<b>7b</b>	<b>12</b>		94	0.78	

<sup>a</sup> Based on starting compound after distillation or column chromatography. <sup>b</sup> Kugelrohr. <sup>c</sup> Hexane/EtOAc: 2/1. <sup>d</sup> Normal pressure. <sup>e</sup> Lit.<sup>10</sup>, <sup>f</sup> 55 Torr. <sup>g</sup> Lit.<sup>11</sup> bp 80-85/16 Torr. <sup>h</sup> Lit.<sup>12</sup> bp 30-35/0.5 Torr.

This methodology, can be considered a Wittig-like formation of  $\beta,\beta$ -disubstituted  $\alpha,\beta$ -unsaturated aldehydes, through a different strategy based on dialkylation of dilithiated 3-tosylpropanal dimethyl acetal and subsequent hydrolysis and dehydrosulfinylation. Thus, the present method allows the transformation of acrolein into  $\beta,\beta$ -disubstituted propenals.

In the case of aldehydes **9g** and **9i** (Table 1, entries 11 and 15) a complex mixture of products was obtained under DBU elimination reaction conditions, whereas compound **9h** (Table 1, entry 13) did not eliminate under the same reaction conditions. For compounds **8g-j** reductive desulfonylation using sodium amalgam<sup>9</sup> worked nicely to give desulfonylated acetals **14** (Table 3). Compound *trans*-**8h** isomerized to provide **14h** (Table 3, entry 2) as a *ca.* 1/1: *cis/trans* mixture of diastereomers under the reduction conditions, whereas *cis/trans*-**8j** gave only the *trans*-isomer of compound **14j** (Table 3, entry 4), which stereochemistry was also determined by <sup>1</sup>H NMR NOE-difference techniques. Thus, selective irradiation of the cyclopropane proton at the  $\beta$ -position of the alcohol resulted in significant enhancements of the methylene group at the  $\beta$ -position of the acetal and of the acetal proton conforming the *trans*-configuration of this cyclopropane derivative.

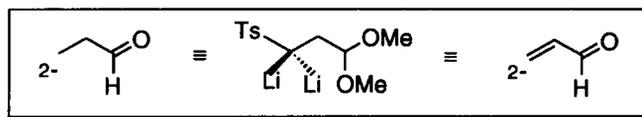
**Table 3.** Reductive Desulfonylation of Compounds **8g-j**

entry	starting compound		product			
	no.	no.	structure	yield (%) <sup>a</sup>	<i>R<sub>f</sub></i> <sup>b</sup>	
1	<b>8g</b>	<b>14g</b>		71	0.79 <sup>c</sup>	
2	<b>8h</b>	<b>14h</b>		74 <sup>d</sup>	0.79	
3	<b>8i</b>	<b>14i</b>		83	0.73	
4	<b>8j</b>	<b>14j</b>		46 <sup>e</sup>	0.15	

<sup>a</sup> Based on compound **8**, after column chromatography (silica gel). <sup>b</sup> Hexane/EtOAc: 2/1. <sup>c</sup> Lit.<sup>13</sup>.

<sup>d</sup> Ca. 1/1 mixture of diastereomers (deduced by <sup>1</sup>H NMR). <sup>e</sup> Only the *trans*-diastereomer was obtained.

In summary, readily accessible 3-tosylpropanal is also a useful precursor for the sulfonyl dianion 3,3-dilithio-3-tosylpropanal dimethyl acetal which is a good synthon for the  $\beta,\beta$ -acylvinyl dianion derived from acrolein and also for the homoenolate dianion derived from propanal. This simple methodology allows the formal dialkylation at the  $\beta$ -position of acrolein and also of propanal starting from acrolein and by means of its  $\gamma$ -oxosulfone.



## EXPERIMENTAL

**General.** Melting points were obtained with a Reichert Thermovar or on a Büchi and are uncorrected. IR spectra were obtained as films on a Pye Unicam SP3-200 or on a Nicolet 510 P-FT spectrophotometers.  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded on a Bruker AC-300 spectrometer with  $\text{SiMe}_4$  as internal standard and using  $\text{CDCl}_3$  as solvent.  $^{13}\text{C}$  NMR assignments were made on the basis of DEPT experiments. MS spectra were measured on a HP5988A (EI, 70eV). High resolution mass spectra were performed by the corresponding service of the University of Valencia. Elemental analyses were performed by the Microanalyses Service of the University of Alicante. GC were determined using a Hewlett-Packard HP-5890 instrument equipped with a 25 m WCOT capillary column (0.22 mm diam., 0.2 $\mu\text{m}$  film thickness OV-101 stationary phase) using nitrogen (2 ml/min) as the carrier gas,  $T_{\text{injector}}=270^\circ\text{C}$ ,  $T_{\text{column}}=60^\circ\text{C}$ , and 60-270 (15 $^\circ\text{C}/\text{min}$ ). Thin layer chromatography (TLC) was carried out on Schleicher & Schuell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel with UV or iodine visualization. Column chromatography was performed using silica gel 60 of 70-230 mesh. All starting materials were commercially available (Aldrich, Fluka), of the best grade and were used without further purification. THF was dried with  $\text{LiAlH}_4$  under an argon atmosphere,  $\text{CH}_2\text{Cl}_2$  was dried over  $\text{P}_2\text{O}_5$  and MeOH over magnesium.

### Preparation of Dianion 6 and Reaction with Electrophiles. Synthesis of Compounds 7 and 8.

**General Procedure.** To a solution of acetal **5**<sup>5</sup> (1 mmol) in dry THF (15 ml) was slowly added a 1.6 M solution of *n*-BuLi (1.38 ml, 2.2 mmol) in hexane at  $-78^\circ\text{C}$  under Ar. The resulting solution was stirred for 10 min at the same temperature, 1 h at  $0^\circ\text{C}$  and recooled to  $-78^\circ\text{C}$ , then the electrophile was added (2.2 mmol for monoelectrophiles or 1.1 mmol in the case of dielectrophiles). The reaction mixture was allowed to rise rt overnight, quenched with water (10 ml) and extracted with ether (3x10 ml). The organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated (15 Torr) to give crude compounds **7** or **8**, which were purified by column chromatography on silica gel. Yields and physical data are included in Table 1, analytical and spectral data follow.

**1,1-Dideuterio-3,3-dimethoxy-1-tosylpropane (7a):**  $\nu$  ( $\text{CHCl}_3$ ) 2820 (H-C-O), 1312, 1302, 1295 and 1139  $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $\delta_{\text{H}}$  1.98 (d,  $J=5.2\text{Hz}$ , 2H,  $\text{CH}_2$ ), 2.45 (s, 3H,  $\text{CH}_3\text{Ar}$ ), 3.29 (s, 6H,  $2\times\text{CH}_3\text{O}$ ), 4.41 (t,  $J=5.2\text{Hz}$ , 1H,  $\text{CHOCH}_3$ ), 7.36 and 7.78 (2d,  $J=8.2\text{Hz}$ , 4H, ArH);  $\delta_{\text{C}}$  21.4 ( $\text{CH}_3\text{Ar}$ ), 26.1 ( $\text{CH}_2$ ), 51.4 (quintet,  $J=21.4\text{Hz}$ ,  $\text{CD}_2$ ), 53.4 ( $2\times\text{CH}_3\text{O}$ ), 102.3 ( $\text{CHOCH}_3$ ), 127.7, 129.7, 135.8, 144.5 (ArC);  $m/z$  260 ( $M^+$ , <1%), 91 (20), 75 (100), 71 (42), 65 (17) and 41 (10).

**3-Butyl-1,1-dimethoxy-3-tosylheptane (7b):**  $\nu$  ( $\text{CDCl}_3$ ) 2660 (H-C-O), 1310 and 1140  $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $\delta_{\text{H}}$  0.90 (t,  $J=7.3\text{Hz}$ , 6H,  $2\times\text{CH}_2\text{CH}_3$ ), 1.27 (sextet,  $J=7.3\text{Hz}$ , 4H,  $2\times\text{CH}_2\text{CH}_3$ ), 1.43 (quintet,  $J=7.3\text{Hz}$ , 4H,  $2\times\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.68 (t,  $J=7.3\text{Hz}$ , 4H,  $2\times\text{CH}_2\text{C}$ ), 1.97 (d,  $J=4.5\text{Hz}$ , 2H,  $\text{CH}_2\text{CH}$ ), 2.44 (s, 3H,  $\text{CH}_3\text{Ar}$ ), 3.34 (s, 6H,  $2\times\text{CH}_3\text{O}$ ), 4.86 (t,  $J=4.5\text{Hz}$ , 1H,  $\text{CHOCH}_3$ ), 7.35 and 7.75 (2d,  $J=8.2\text{Hz}$ , 4H, ArH);  $\delta_{\text{C}}$  13.7 ( $2\times\text{CH}_3$ ), 21.4 ( $\text{CH}_3\text{Ar}$ ), 23.2, 25.5, 32.2, 36.5 ( $4\times\text{CH}_2$ ), 53.1 ( $2\times\text{CH}_3\text{O}$ ), 68.0 (C), 101.7 ( $\text{CHOCH}_3$ ), 129.3, 130.0, 133.6 and 144.3 (ArC);  $m/z$  355 ( $M^+-\text{CH}_3$ , <1%), 157 (10), 91 (5), 75 (100) and 71 (8).

**2-Benzyl-4,4-dimethoxy-1-phenyl-2-tosylbutane (7c):**  $\nu$  ( $\text{CHCl}_3$ ) 3014, 1530 (CH=C), 2856 (H-C-O), 1300, 1285 and 1139 $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $\delta_{\text{H}}$  1.99 (d,  $J=4.9\text{Hz}$ , 2H,  $\text{CH}_2\text{CH}$ ), 2.42 (s, 3H,  $\text{CH}_3\text{Ar}$ ), 3.13, 3.34 (2d,  $J=14.2\text{Hz}$ , 4H,  $2\times\text{CH}_2\text{Ph}$ ), 3.28 (s, 6H,  $2\times\text{CH}_3\text{O}$ ), 4.95 (t,  $J=4.9\text{Hz}$ , 1H,  $\text{CHCH}_2$ ), 7.17 (m, 10H, ArH), 7.27, 7.69 (2d,  $J=8.3\text{Hz}$ , 4H, ArH);  $\delta_{\text{C}}$  21.5 ( $\text{CH}_3\text{Ar}$ ), 36.7 ( $\text{CH}_2\text{CH}$ ), 39.8 ( $2\times\text{CH}_2\text{Ph}$ ), 53.4 ( $2\times\text{CH}_3\text{O}$ ), 69.5

(CCH<sub>2</sub>), 102.0 (CHCH<sub>2</sub>), 126.8, 128.0, 129.3, 130.7, 131.5, 134.2, 135.48 and 144.4 (ArC); *m/z* 407 (*M*<sup>+</sup>-CH<sub>3</sub>O, <1%), 157 (16), 91 (100), 77 (18), 75 (32) and 71 (13). Anal. Calcd. for C<sub>26</sub>H<sub>30</sub>O<sub>4</sub>S: C, 71.20; H, 6.89. Found: C, 71.31; H, 6.88.

**1-(2,2-Dimethoxyethyl)-1-tosylcyclobutane (8d):**  $\nu$  (film) 2830 (H-C-O), 1300 and 1130 cm<sup>-1</sup> (SO<sub>2</sub>);  $\delta_{\text{H}}$  1.94 (m with d at 1.98, *J*=5.0Hz, 4H, CH<sub>2</sub>CH and CH<sub>2</sub>CH<sub>2</sub>C), 2.18, 2.82 (2m, 4H, CH<sub>2</sub>CCH<sub>2</sub>), 2.45 (s, 3H, CH<sub>3</sub>Ar), 3.33 (s, 6H, 2xCH<sub>3</sub>O), 4.73 (t, *J*=5.0Hz, 1H, CHCH<sub>2</sub>), 7.35 and 7.76 (2d, *J*=8.1Hz, 4H, ArH);  $\delta_{\text{C}}$  14.7, 26.5, 36.8 (3xCH<sub>2</sub>), 21.6 (CH<sub>3</sub>Ar), 53.3 (2xCH<sub>3</sub>O), 63.5 (C), 102.4 (CHOCH<sub>3</sub>), 129.7, 132.9, 144.6 (ArC); *m/z* 283 (*M*<sup>+</sup>-CH<sub>3</sub>, <1%), 111 (13), 91 (17), 85 (39), 75 (100), 65 (14) and 47 (15); [Found: *M*<sup>+</sup>-(CH<sub>3</sub>O)<sub>2</sub>CH, 223.0796. Calcd. for C<sub>12</sub>H<sub>15</sub>O<sub>2</sub>S, 223.0793].

**1-(2,2-Dimethoxyethyl)-1-tosylcyclopentane (8e):**  $\nu$  (film) 2770 (H-C-O), 1305 and 1160 cm<sup>-1</sup> (SO<sub>2</sub>);  $\delta_{\text{H}}$  1.74 [m, 6H, 6x(CH<sub>2</sub>)<sub>4</sub>], 1.99 (d, *J*=4.9Hz, 2H, CH<sub>2</sub>CH), 2.34 [m, 2H, 2x(CH<sub>2</sub>)<sub>4</sub>], 2.44 (s, 3H, CH<sub>3</sub>Ar), 3.30 (s, 6H, 2xCH<sub>3</sub>O), 4.67 (t, *J*=4.9Hz, 1H, CHCH<sub>2</sub>), 7.34 and 7.78 (2d, *J*=8.1Hz, 4H, ArH);  $\delta_{\text{C}}$  21.5 (CH<sub>3</sub>Ar), 25.9, 32.5, 38.5 (3xCH<sub>2</sub>), 52.9 (2xCH<sub>3</sub>O), 71.2 (C), 102.0 (CHCH<sub>2</sub>), 129.4, 130.2, 133.4 and 144.4 (ArC); *m/z* 297 (*M*<sup>+</sup>-CH<sub>3</sub>, <1%), 125 (13), 91 (12), 75 (100), 67 (11), 47 (13), 45 (10), 43 (10) and 41 (15) (Found: *M*<sup>+</sup>-CH<sub>3</sub>, 297.1156. Calcd. for C<sub>15</sub>H<sub>21</sub>O<sub>4</sub>S, 297.1161).

**1-(2,2-Dimethoxyethyl)-1-tosylcyclohexane (8f):**  $\nu$  (film) 2830 (H-C-O), 1295 and 1130 cm<sup>-1</sup> (SO<sub>2</sub>);  $\delta_{\text{H}}$  1.65 (m, 10H, 5xCH<sub>2</sub>), 2.04 (d, *J*=4.8Hz, 2H, CH<sub>2</sub>CH), 2.45 (s, 3H, CH<sub>3</sub>Ar), 3.39 (s, 6H, 2xCH<sub>3</sub>O), 5.07 (t, *J*=4.8Hz, 1H, CH), 7.35 and 7.74 (2d, *J*=8.1Hz, ArH);  $\delta_{\text{C}}$  21.1, 24.6, 29.1, 34.1 (4xCH<sub>2</sub>), 21.5 (CH<sub>3</sub>Ar), 53.8 (2xCH<sub>3</sub>O), 65.1 (C), 102.5 (CH), 129.3, 130.6, 132.2 and 144.4 (ArC); *m/z* 311 (*M*<sup>+</sup>-CH<sub>3</sub>, 1%), 139 (58), 113 (67) and 75 (100)

**4-(2,2-Dimethoxyethyl)-4-tosylcyclopentene (8g):**  $\nu$  (film) 3062, 1600 (CH=C), 2830 (H-C-O), 1310, 1299, 1288 and 1145 cm<sup>-1</sup> (SO<sub>2</sub>);  $\delta_{\text{H}}$  2.04 (d, *J*=4.9Hz, 2H, CH<sub>2</sub>CHOCH<sub>3</sub>), 2.44 (s, 3H, CH<sub>3</sub>Ar), 2.51, 3.21 (2d, *J*=13.2Hz, 4H, CH<sub>2</sub>CCH<sub>2</sub>), 3.25 (s, 6H, 2xCH<sub>3</sub>O), 3.21 (d, *J*=13.2Hz, 2xCH<sub>2</sub>CCH<sub>2</sub>), 4.42 (t, *J*=4.9Hz, 1H, CHOCH<sub>3</sub>), 5.57, (s, 2H, CH=CH), 7.34 and 7.77 (2d, *J*=8.2Hz, 4H, ArH);  $\delta_{\text{C}}$  21.4 (CH<sub>3</sub>Ar), 38.9 (CH<sub>2</sub>CCH<sub>2</sub>), 53.0 (2xCH<sub>3</sub>O), 69.2 (CCH<sub>2</sub>), 101.6 (CHOCH<sub>3</sub>), 127.8, 129.4, 129.9, 133.1 and 144.5 (CH=CH and ArH); *m/z* 295 (*M*<sup>+</sup>-CH<sub>3</sub>, <1%), 139 (12), 123 (92), 97 (13), 91 (88), 79 (27), 77 (16), 75 (100), 66 (11), 65 (20), 47 (45) and 45 (21) (Found: *M*<sup>+</sup>-CH<sub>3</sub>O, 279.1055. Calcd. for C<sub>15</sub>H<sub>19</sub>O<sub>3</sub>S, 279.1055).

**trans-1-(2,2-Dimethoxyethyl)-1-tosyl-2-vinylcyclopropane (8h):**  $\nu$  (film) 3085, 1636, 967, 922 (CH=C), 3065 (ring), 2833 (H-C-O), 1313, 1301, 1289 and 1140 cm<sup>-1</sup> (SO<sub>2</sub>);  $\delta_{\text{H}}$  1.40 (dd, *J*=7.0, 5.8Hz, 1H, 1xCH<sub>2</sub>CHCH), 1.61 (dd, *J*=16.0, 7.9Hz, 1H, 1xCH<sub>2</sub>CHOCH<sub>3</sub>), 1.98 (ddd, *J*=9.8, 5.8, 0.9Hz, 1H, 1xCH<sub>2</sub>CHCH), 1.98 (ddd, *J*=16.0, 2.4, 1.1Hz, 1H, 1xCH<sub>2</sub>CHOCH<sub>3</sub>), 2.45 (s, 3H, CH<sub>3</sub>Ar), 2.51 (m, 1H, CHCH=CH<sub>2</sub>), 3.25, 3.32 (2s, 6H, 2xCH<sub>3</sub>O), 4.58 (dd, *J*=7.9, 2.4Hz, 1H, CHOCH<sub>3</sub>), 5.18 (ddd, *J*=10.1, 1.5, 0.8Hz, 1H, 1xCH<sub>2</sub>=CH), 5.20 (ddd, *J*=17.1, 1.5, 0.9Hz, 1H, 1xCH<sub>2</sub>=CH), 5.52 (ddd, *J*=17.1, 10.1, 7.3Hz, 1H, CH<sub>2</sub>=CH), 7.36 and 7.76 (2d, *J*=8.2Hz, 4H, ArH);  $\delta_{\text{C}}$  14.7 (CH<sub>2</sub>CHCH), 21.5 (CH<sub>3</sub>Ar), 26.3 (CHCH=CH<sub>2</sub>), 30.3 (CH<sub>2</sub>CHOCH<sub>3</sub>), 43.6 (C), 53.3, 54.8 (2xCH<sub>3</sub>O), 103.7 (CHOCH<sub>3</sub>), 119.2, 132.7 (CH=CH<sub>2</sub>), 128.2, 129.8, 135.6 and 144.4 (ArC); *m/z* 279 (*M*<sup>+</sup>-CH<sub>3</sub>O, 2%), 91 (15), 79 (11), 75 (100) y 47 (12).

**2-(2,2-Dimethoxyethyl)-2-tosylindan (8i):**  $\nu$  (CDCl<sub>3</sub>) 3080, 3040 (CH=C), 2830 (H-C-O), 1300 and 1130 cm<sup>-1</sup> (SO<sub>2</sub>);  $\delta_{\text{H}}$  2.14 (d, *J*=5.1Hz, 2H, CH<sub>2</sub>CH), 2.41 (s, 3H, CH<sub>3</sub>Ar), 2.99 (s, 6H, 2xCH<sub>3</sub>O), 3.06, 3.83 (2d, *J*=16.4Hz, 4H, 4xCH<sub>2</sub>C), 4.19 (t, *J*=5.1Hz, 1H, CHOCH<sub>3</sub>), 7.10 (s, 4H, ArH), 7.31 and 7.78 (2d, *J*=8.1Hz, 4H, ArH);  $\delta_{\text{C}}$  21.5 (CH<sub>3</sub>Ar), 39.1 (2xCH<sub>2</sub>), 53.0 (2xCH<sub>3</sub>O), 70.5 (C), 101.6 (CHOCH<sub>3</sub>), 123.9,

126.8, 129.5, 130.0, 133.1, 139.7 and 144.7 (ArC);  $m/z$  204 ( $M^+$ -TsH, 1%), 173 (30), 172 (20), 141 (11), 129 (30), 128 (12), 115 (20), 91 (27), 75 (100), 71 (52), 69 (12), 65 (13), 57 (18), 55 (17), 47 (17), 45 (44), 43 (35) and 41 (24).

**cis, trans-1-(2,2-Dimethoxyethyl)-2-(hydroxymethyl)-1-tosylcyclopropane (8j):** 1:1 diastereomers mixture.  $\nu$  (film) 3503 (OH), 2835 (H-C-O), 1312, 1300, 1288 and 1139  $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $\delta_{\text{H}}$  0.76 (dd,  $J=7.0$ , 5.7Hz, 1H,  $1\times\text{CH}_2\text{CH}$ ), 1.23 (dd,  $J=9.2$ , 5.5Hz, 1H,  $1\times\text{CH}_2\text{CH}$ ), 1.50 (dd,  $J=15.4$ , 7.0Hz, 1H,  $1\times\text{CH}_2\text{CHOCH}_3$ ), 1.64 (dd,  $J=10.4$ , 5.7Hz, 1H,  $1\times\text{CH}_2\text{CH}$ ), 1.70 (dd,  $J=7.9$ , 5.5Hz, 1H,  $1\times\text{CH}_2\text{CH}$ ), 1.82 (dd,  $J=16.1$ , 6.7Hz, 1H,  $1\times\text{CH}_2\text{CHOCH}_3$ ), 1.88 (dd,  $J=15.4$ , 4.0Hz, 1H,  $1\times\text{CH}_2\text{CHOCH}_3$ ), 2.04 (dd,  $J=16.1$ , 4.6Hz, 1H,  $1\times\text{CH}_2\text{CHOCH}_3$ ), 2.35 (m, 1H,  $\text{CHCH}_2\text{OH}$ ), 2.45, 2.46 (2s, 6H,  $2\times\text{CH}_3\text{Ar}$ ), 2.68 (m, 1H,  $\text{CHCH}_2\text{OH}$ ), 3.20-3.35 (m with s at 3.23, 3.28, 3.30, 3.34, 16H,  $4\times\text{OCH}_3$ ,  $2\times\text{CH}_2\text{OH}$ ), 4.00, 4.21 (2br s, 2H,  $\text{CH}_2\text{OH}$ ), 4.57 (dd,  $J=7.0$ , 4.0Hz, 1H,  $\text{CHOCH}_3$ ), 4.77 (dd,  $J=6.7$ , 4.6Hz, 1H,  $\text{CHOCH}_3$ ), 7.37, 7.78 (2d,  $J=8.2\text{Hz}$ , 8H, ArH);  $\delta_{\text{C}}$  14.3, 17.6 ( $\text{CH}_2\text{CHCH}_2\text{OH}$ ), 21.5 ( $\text{CH}_3\text{Ar}$ ), 25.5, 30.3 ( $\text{CHCH}_2\text{OH}$ ), 31.3 ( $2\times\text{CH}_2\text{CHOCH}_3$ ), 42.2, 43.5 (C), 53.3, 53.6, 54.6, 54.6 ( $2\times\text{CH}_3\text{O}$ ), 60.2, 60.4 ( $\text{CH}_2\text{OH}$ ), 102.8, 103.1 ( $\text{CHOCH}_3$ ), 128.4, 128.4, 129.8, 129.8, 135.7, 135.8, 144.5 and 144.9 (ArC);  $m/z$  283 ( $M^+$ - $\text{CH}_3\text{O}$ , 1%), 157 (25), 156 (10), 139 (28), 91 (19), 83 (12), 75 (100), 67 (15), 65 (17) and 41 (11) [Found:  $M^+$ - $\text{C}_2\text{H}_6\text{O}_2$ , 252.0769. Calcd. for  $\text{C}_{13}\text{H}_{16}\text{O}_3\text{S}$ , 252.0820).

**Preparation of Compounds 9. General Procedure.** To a solution of purified compounds 7 or 8 (prepared in 1 mmol scale) in acetone (6 ml) and water (2 ml) HCl conc. (ca. 0.1 ml) was added. The reaction mixture was stirred under reflux until complete reaction (TLC), acetone was removed (15 Torr) and water (20 ml) was added. The resulting solution was extracted with ether (3x20 ml), the organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated (15 Torr) to give pure compounds 9. Yields and physical data are included in Table 1, analytical and spectral data follow.

**2,2-Trimethylene-2-tosylpropanal (9d):**  $\nu$  ( $\text{CHCl}_3$ ) 2740, 1720 ( $\text{CH}=\text{O}$ ), 1295 and 1145  $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $\delta_{\text{H}}$  2.10, 2.93 [2m, 6H, ( $\text{CH}_2$ )<sub>3</sub>], 2.45 (s, 3H,  $\text{CH}_3\text{Ar}$ ), 2.70 (d,  $J=2.6\text{Hz}$ , 2H,  $\text{CH}_2\text{CHO}$ ), 7.38, 7.72 (2d,  $J=8.1\text{Hz}$ , 4H, ArH) and 9.75 (t,  $J=2.6\text{Hz}$ , 1H, CHO);  $\delta_{\text{C}}$  14.7, 27.2, 46.6 ( $3\times\text{CH}_2$ ), 21.5 ( $\text{CH}_3\text{Ar}$ ), 62.8 (C), 129.6, 129.9, 131.8, 145.2 (ArC) and 198.4 (CHO);  $m/z$  197 ( $M^+$ -Ts, <1%), 157 (16), 139 (20), 113 (100), 97 (18), 95 (15), 92 (31), 91 (51), 71 (84), 69 (19), 67 (39), 65 (37), 63 (11), 55 (10), 45 (12), 43 (23) and 41 (38).

**2,2-Tetramethylene-2-tosylpropanal (9e):**  $\nu$  ( $\text{CHCl}_3$ ) 1715 ( $\text{C}=\text{O}$ ), 1300 and 1140  $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $\delta_{\text{H}}$  1.75 (m, 6H,  $3\times\text{CH}_2$ ), 2.44-2.65 (m with s at 2.46, 5H,  $\text{CH}_3\text{Ar}$  and  $2\times\text{CH}_2$ ), 2.61 (d,  $J=2.5\text{Hz}$ , 2H,  $\text{CH}_2\text{CH}$ ), 7.38, 7.76 (2d,  $J=8.2\text{Hz}$ , 4H, ArH) and 9.82 (t,  $J=2.5\text{Hz}$ , 1H, CHO);  $\delta_{\text{C}}$  21.6 ( $\text{CH}_3\text{Ar}$ ), 25.7, 33.7, 48.9 ( $3\times\text{CH}_2$ ), 71.1 (C), 129.8, 130.2, 132.7, 135.2 (ArC) and 199.2 (CHO);  $m/z$  265 ( $M^+$ -1, <1%), 157 (61), 139 (12), 111 (12), 109 (18), 92 (17), 91 (33), 81 (18), 67 (100), 65 (23) and 41 (23) (Found:  $M^+$ -H, 265.0898. Calcd. for  $\text{C}_{14}\text{H}_{17}\text{O}_3\text{S}$ , 265.0898).

**2,2-Pentamethylene-2-tosylpropanal (9f):**  $\nu$  (film) 2755, 1730 ( $\text{CH}=\text{O}$ ), 1300 and 1140  $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $\delta_{\text{H}}$  1.75 [m, 10H, ( $\text{CH}_2$ )<sub>5</sub>], 2.46 (s, 3H,  $\text{CH}_3\text{Ar}$ ), 2.66 (d,  $J=3.0\text{Hz}$ , 2H,  $\text{CH}_2\text{CHO}$ ), 7.38, 7.72 (2d,  $J=8.1\text{Hz}$ , 4H, ArH) and 9.95 (t,  $J=3.0\text{Hz}$ , 1H, CHO);  $\delta_{\text{C}}$  21.0, 24.5, 28.9, 42.2 ( $4\times\text{CH}_2$ ), 21.6 ( $\text{CH}_3\text{Ar}$ ), 66.0 (C), 129.6, 130.6, 131.2, 145.0 (ArC) and 199.6 ( $\text{C}=\text{O}$ );  $m/z$  281 ( $M^+$ +1, 1%), 157 (18), 139 (16), 123 (12), 95 (25), 92 (25), 91 (100), 89 (20), 81 (64), 80 (12), 79 (24), 77 (19), 67 (28), 73 (65), 63 (16), 57 (17), 55 (38), 53 (20), 51 (11), 43 (26) and 41 (48).

**2-(1-Tosyl-2-vinylcyclopropyl)acetaldehyde (9h):**  $\nu$  (film) 3087, 3064, 3029 (CH=C), 2740, 1727 (CH=O), 1313, 1302, 1290 and 1140  $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $\delta_{\text{H}}$  1.14 (dd,  $J=6.9, 6.1\text{Hz}$ , 1H,  $1\times\text{CH}_2\text{CH}$ ), 1.98 (dd,  $J=9.8, 6.1\text{Hz}$ , 1H,  $1\times\text{CH}_2\text{CH}$ ), 2.46 (m with s at 2.46, 5H,  $\text{CH}_3\text{Ar}$ ,  $\text{CH}_2\text{CHO}$ ), 2.80 (m, 1H,  $\text{CHCH}=\text{CH}_2$ ), 5.25-5.33 (m, 2H,  $\text{CH}_2=\text{CH}$ ), 5.78 (ddd,  $J=17.0, 10.1, 7.0\text{Hz}$ , 1H,  $\text{CH}=\text{CH}_2$ ), 7.38, 7.71 (2d,  $J=8.3\text{Hz}$ , 4H, ArH) and 9.57 (t,  $J=2.4\text{Hz}$ , 1H, CHO);  $\delta_{\text{C}}$  17.0 ( $\text{CH}_2\text{CH}$ ), 21.6 ( $\text{CH}_3\text{Ar}$ ), 25.3 ( $\text{CHCH}_2$ ), 40.9 ( $\text{CH}_2\text{CHO}$ ), 43.0 (C), 120.5, 128.1, 130.1, 131.4, 145.2 (CH=CH, ArC) and 199.2 (CHO);  $m/z$  235 ( $M^+-\text{CHO}$ , 5%), 157 (22), 139 (28), 109 (18), 92 (25), 91 (80), 89 (21), 81 (44), 80 (15), 79 (100), 78 (12), 77 (70), 65 (80), 63 (29), 55 (15), 53 (51), 52 (30), 50 (16), 45 (17), 43 (21) and 41(52).

**2-(2-Tosyl-2-indanyl)acetaldehyde (9i):**  $\nu$  ( $\text{CHCl}_3$ ) 3020, 1600 (CH=C), 1720 (C=O), 1300 and 1140  $\text{cm}^{-1}$  ( $\text{SO}_2$ );  $\delta_{\text{H}}$  2.40 (s, 3H,  $\text{CH}_3\text{Ar}$ ), 2.76 (d,  $J=2.5\text{Hz}$ , 2H,  $\text{CH}_2\text{CHO}$ ), 3.08, 3.84 (2d,  $J=16.5\text{Hz}$ , 4H,  $2\times\text{CH}_2\text{C}$ ), 7.11 (m, 4H, ArH), 7.31, 7.73 (2d,  $J=8.1\text{Hz}$ , 4H, ArH) and 9.66 (t,  $J=2.5\text{Hz}$ , 1H, CHO);  $\delta_{\text{C}}$  21.4 ( $\text{CH}_3\text{Ar}$ ), 39.5 ( $2\times\text{CH}_2\text{C}$ ), 47.7 ( $\text{CH}_2\text{CHO}$ ), 70.8 (C), 124.4, 127.4, 129.7, 129.9, 138.4, 145.3 (ArC) and 198.1 (CHO);  $m/z$  314 ( $M^+$ , <1%), 141 (11), 115 (20), 75 (100), 71 (18), 69 (15), 67 (18), 55 (13), 45 (40), 43 (31) and 41 (40).

**Preparation of  $\beta$ ,  $\beta$ -Disubstituted  $\alpha$ ,  $\beta$ -Unsaturated Aldehydes 11 and 12. General Procedure.** To a solution of compound 9 (0.5 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (5 mL), DBU (0.082 ml, 0.55 mmol) was added at  $0^\circ\text{C}$  and stirred at room temperature until elimination was complete (TLC). The reaction mixture was poured into an aqueous saturated solution of  $\text{NaHCO}_3$  (25 ml) and extracted with ether (3x10 ml). The ethereal layers were washed with aqueous 2N HCl and brine, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated (15 Torr) to yield crude compounds 11 and 12, which were purified by column chromatography on silica gel or by distillation. Yields and physical data are include in Table 2, spectral data follow

**Cyclobutylidenacetaldehyde (11d)<sup>10</sup>:**  $\nu$  ( $\text{CDCl}_3$ ) 3080, 3020, 1630, 815 (CH=C), 2730 and 1670  $\text{cm}^{-1}$  (CH=O);  $\delta_{\text{H}}$  2.19 (quintet,  $J=8.0\text{Hz}$ , 2H,  $\text{CH}_2$ ), 2.97, 3.18 (2br t,  $J=8.0\text{Hz}$ , 4H,  $2\times\text{CH}_2$ ), 5.84 (dq,  $J=8.2, 2.1\text{Hz}$ , 1H,  $\text{CHCHO}$ ), 9.65 (d,  $J=8.2\text{Hz}$ , 1H, CHO);  $\delta_{\text{C}}$  17.6, 31.2, 33.5 ( $3\times\text{CH}_2$ ), 123.4, 173.7 (CH=C) and 190.3 (CHO);  $m/z$  97 ( $M^++1$ , 2%), 96 ( $M^+$ , 24), 95 (100), 81 (96), 68 (43), 67 (99), 66 (11), 65 (22), 53 (43), 51 (15), 50 (14), 43 (11), 42 (11) and 41 (47)

**Cyclopentylidenacetaldehyde (11e)<sup>11</sup>:**  $\nu$  (film) 3020, 2965, 1620, 830 (CH=C), 2890 and 1670  $\text{cm}^{-1}$  (CH=O);  $\delta_{\text{H}}$  1.73, 1.84 [2m, 4H,  $(\text{CH}_2)_2\text{CH}_2\text{C}$ ], 2.54, 2.81 (2m,  $\text{CH}_2\text{CCH}_2$ ), 6.01 (dq,  $J=8.0, 2.0\text{Hz}$ , 1H,  $\text{CHCHO}$ ), 9.85 (d,  $J=8.0\text{Hz}$ , 1H, CHO);  $\delta_{\text{C}}$  24.9, 36.4, 30.3, 35.8 ( $4\times\text{CH}_2$ ), 123.2, 168.5 (C=CH) and 191.8 (CHO);  $m/z$  111 ( $M^++1$ , 5%), 110 ( $M^+$ , 73), 109 (29), 95 (41), 91 (36), 82 (15), 81 (82), 79 (82), 77 (32), 68 (21), 67 (91), 66 (100), 65 (17), 55 (23), 54 (26), 53 (71), 52 (19), 51 (41), 50 (29), 43 (10) and 41 (62).

**Cyclohexylidenacetaldehyde (11f)<sup>12</sup>:**  $\nu$  ( $\text{CHCl}_3$ ) 3020, 1620 (CH=C), 2960, 2890 and 1685  $\text{cm}^{-1}$  (CH=O);  $\delta_{\text{H}}$  1.69 [m, 6H,  $(\text{CH}_2)_3\text{CH}_2\text{C}$ ], 2.30, 2.71 (2m, 4H,  $\text{CH}_2\text{CCH}_2$ ), 5.83 (d,  $J=8.2\text{Hz}$ , 1H,  $\text{CHC}$ ) and 10.02 (d,  $J=8.2\text{Hz}$ , 1H, CHO);  $\delta_{\text{C}}$  26.2, 28.2, 28.4, 29.6, 38.1 ( $5\times\text{CH}_2$ ), 125.3, 168.2 (C=CH) and 190.7 (CHO);  $m/z$  125 ( $M^++1$ , 5%), 124 ( $M^+$ , 64), 109 (32), 95 (100), 93 (11), 91 (24), 83 (10), 82 (11), 81 (83), 80 (73), 79 (39), 78 (13), 77 (21), 68 (18), 67 (76), 66 (15), 65 (19), 55 (46), 54 (12), 53 (39), 52 (11), 50 (12), 43 (10) and 41 (49).

**3-Butyl-2-heptenal (12):**  $\nu$  ( $\text{CHCl}_3$ ) 3010, 1630 (CH=C) and 1670  $\text{cm}^{-1}$  (C=O);  $\delta_{\text{H}}$  0.93, 0.94 (2t,  $J=7.2\text{Hz}$ , 6H,  $2\times\text{CH}_3$ ), 1.43 (m, 8H,  $2\times\text{CH}_2\text{CH}_2$ ), 2.27, 2.56 (2t,  $J=7.7\text{Hz}$ , 4H,  $2\times\text{CH}_2\text{C}$ ), 5.86 (d,

$J=8.3\text{Hz}$ , 1H, CH) and 9.99 (d,  $J=8.3\text{Hz}$ , 1H, CHO);  $\delta_{\text{C}}$  13.8 (2xCH<sub>3</sub>), 22.4, 22.7, 29.6, 31.1, 31.8, 37.7 (6xCH<sub>2</sub>), 127.1, 169.0 (CH=C) and 191.1 (CHO);  $m/z$  169 ( $M^+ + 1$ , 1%), 168 ( $M^+$ , 2), 111 (63), 97 (17), 95 (16), 93 (20), 84 (100), 83 (54), 81 (24), 79 (29), 77 (11), 69 (26), 67 (26), 57 (31), 56 (16), 55 (84), 53 (34), 51 (11), 43 (73) and 41 (99) (Found:  $M^+$ , 168.1525. Calcd. for C<sub>11</sub>H<sub>20</sub>O, 168.1514).

#### Reductive Desulfonylation of Compounds 8. Preparation of Compounds 14. General Procedure.

To a suspension of 10% Na-Hg (1.61g, 7mmol) and Na<sub>2</sub>HPO<sub>4</sub> (0.5g, 3.5mmol) in dry methanol (8 ml) at 0°C under Ar was added a solution of compound 8 (0.7mmol) in dry methanol (3 ml). After stirring at room temperature until complete desulfonylation, the reaction mixture was poured into water (30 ml) and extracted with ether (3x15 ml). The ethereal layer was washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated (15 Torr) to yield crude compounds 14, which were purified by column chromatography on silica gel. Yields and physical data are include in Table 3, spectral data follow.

**4-(2,2-Dimethoxyethyl)cyclopentene (14g)**<sup>13</sup>:  $\nu$  (film) 3040, 756 (CH=C), 2855 cm<sup>-1</sup> (H-C-O);  $\delta_{\text{H}}$  1.73 (dd,  $J=7.3, 5.8\text{Hz}$ , 2H, CH<sub>2</sub>CHOCH<sub>3</sub>), 2.10 (m, 2H, 2xCH<sub>2</sub>CHCH<sub>2</sub>), 2.33 (sept,  $J=7.3\text{Hz}$ , CHCH<sub>2</sub>CHOCH<sub>3</sub>), 2.50 (m, 2H, 2xCH<sub>2</sub>CHCH<sub>2</sub>), 3.33 (s, 6H, 2xCH<sub>3</sub>O), 4.41 (t,  $J=5.8\text{Hz}$ , 1H, CHOCH<sub>3</sub>) and 5.67 (s, 2H, CH=CH);  $\delta_{\text{C}}$  33.7 (CHCH<sub>2</sub>CHOCH<sub>3</sub>), 38.9 (CH<sub>2</sub>CH=CH, CH<sub>2</sub>CHOCH<sub>3</sub>), 52.6 (2xCH<sub>3</sub>O), 104.0 (CHOCH<sub>3</sub>) and 129.8 (CH=C);  $m/z$  155 ( $M^+ - 1$ , <1%), 125 (24), 124 (57), 95 (26), 94 (27), 93 (64), 92 (17), 91 (33), 79 (24), 77 (33), 76 (15), 75 (100), 71 (19), 68 (24), 67 (63), 66 (91), 65 (28), 59 (14), 58 (36), 55 (14), 53 (21), 51 (13), 47 (71), 45 (60), 43 (31), 41 (66) and 40 (21).

**cis, trans-1-(2,2-Dimethoxyethyl)-2-vinylcyclopropane (14h)**: 1:1 diastereomers mixture.  $\nu$  (CHCl<sub>3</sub>) 3020, 972 (CH=C), 2870 and 2854 cm<sup>-1</sup> (H-C-O);  $\delta_{\text{H}}$  0.29 (q,  $J=5.3\text{Hz}$ , 1H, 1xCH<sub>2</sub>CHCH=CH<sub>2</sub>), 0.59 (m, 2H, CH<sub>2</sub>CHCH=CH<sub>2</sub>), 0.78-1.77 (several m, 9H), 3.33, 3.35, 3.36, 3.37 [4s, 12H, 4xCH<sub>3</sub>O], 4.42, 4.43 (2t,  $J=5.7\text{Hz}$ , 2H, 2xCHOCH<sub>3</sub>), 4.84 (dd,  $J=10.2, 1.8\text{Hz}$ , 1H, 1xCH<sub>2</sub>=CH), 5.01 (ddd,  $J=10.2, 1.5, 0.6\text{Hz}$ , 1H, 1xCH<sub>2</sub>=CH), 5.03 (dd,  $J=17.1, 1.5\text{Hz}$ , 1H, 1xCH<sub>2</sub>=CH), 5.12 (ddd,  $J=10.2, 1.8, 0.6\text{Hz}$ , 1H, 1xCH<sub>2</sub>=CH), 5.40 (ddd,  $J=17.1, 10.2, 8.6\text{Hz}$ , 1H, 1xCH<sub>2</sub>=CH), 5.57 (ddd,  $J=17.1, 10.1, 8.6\text{Hz}$ , 1H, 1xCH<sub>2</sub>=CH);  $\delta_{\text{C}}$  12.0, 13.5 (CH<sub>2</sub>CHCH=CH<sub>2</sub>), 14.0, 16.4 (CHCH<sub>2</sub>CHO), 19.2, 22.1 (CHCH=CH<sub>2</sub>), 32.1, 36.9 (CH<sub>2</sub>CHO), 52.8, 52.9, 53.1 (CH<sub>3</sub>), 104.6, (H-C-O), 111.6, 114.6 (CH<sub>2</sub>=CH), 137.8 and 141.5 (CH<sub>2</sub>=CH);  $m/z$  125 ( $M^+ - \text{CH}_3\text{O}$ , 7%), 98 (45), 97 (28), 93 (17), 91 (16), 79 (14), 77 (20), 75 (100), 71 (20), 67 (40), 66 (15), 53 (15), 47 (70), 45 (44) and 41 (59);  $m/z$  125 ( $M^+ - \text{CH}_3\text{O}$ , 2%), 97 (77), 97 (53), 93 (50), 91 (28), 79 (22), 77 (32), 75 (100), 71 (24), 67 (57), 66 (24), 55 (21), 53 (25), 47 (84), 45 (73) and 41 (76).

**2-(2,2-Dimethoxyethyl)indan (14i)**:  $\nu$  (CHCl<sub>3</sub>) 3080, 3051, 3020 (CH=C) and 2831 cm<sup>-1</sup> (H-C-O);  $\delta_{\text{H}}$  1.84 (dd,  $J=6.9, 5.8\text{Hz}$ , 2H, CH<sub>2</sub>CHOCH<sub>3</sub>), 2.60 (m, 3H, 2xCH<sub>2</sub>CHCH<sub>2</sub> and CH<sub>2</sub>CHCH<sub>2</sub>), 3.07 (dd,  $J=14.2, 6.9\text{Hz}$ , 2H, 2xCH<sub>2</sub>CHCH<sub>2</sub>), 3.34 (s, 6H, 2xCH<sub>3</sub>O), 4.49 (t,  $J=5.8\text{Hz}$ , 1H, CHOCH<sub>3</sub>) and 7.15 (m, 4H, ArH);  $\delta_{\text{C}}$  36.3 (CHCH<sub>2</sub>CHOCH<sub>3</sub>), 38.1 (CH<sub>2</sub>CHOCH<sub>3</sub>), 39.3 (CH<sub>2</sub>Ar), 52.7 (2xCH<sub>3</sub>O), 103.8 (CHOCH<sub>3</sub>), 124.3, 126.1 and 143.2 (ArC);  $m/z$  175 ( $M^+ - \text{CH}_3\text{O}$ , 12%), 174 (33), 143 (44), 142 (14), 129 (14), 128 (23), 117 (40), 116 (100), 115 (23), 91 (19), 75 (49), 65 (10), 51 (11), 47 (35) and 45 (28) (Found:  $M^+$ , 206.1307. Calcd. for C<sub>13</sub>H<sub>18</sub>O<sub>2</sub>, 206.1307).

**trans-1-(2,2-Dimethoxyethyl)-2-(hydroxymethyl)cyclopropane (14j)**:  $\nu$  (film) 3422 (OH), 3065, 2995 (CH-ring), 2832 cm<sup>-1</sup> (H-C-O);  $\delta_{\text{H}}$  0.39 (dt,  $J=8.2, 4.9\text{Hz}$ , 1H, 1xCH<sub>2</sub>CHCH<sub>2</sub>OH), 0.45 (dt,  $J=8.5, 4.9\text{Hz}$ , 1H, 1xCH<sub>2</sub>CHCH<sub>2</sub>OH), 0.64 (m, 1H, CHCH<sub>2</sub>CHOCH<sub>3</sub>), 0.91 (m, 1H, CHCH<sub>2</sub>OH), 1.43 (ddd,  $J=14.1, 7.9, 5.9\text{Hz}$ , 1H, 1xCH<sub>2</sub>CHOCH<sub>3</sub>), 1.69 (dt,  $J=14.1, 5.9\text{Hz}$ , 1H, 1xCH<sub>2</sub>CHOCH<sub>3</sub>), 1.86 (br s, 1H, OH), 3.28 (dd,

$J=11.0, 7.9\text{Hz}$ , 1H, 1x $\text{CH}_2\text{OH}$ ), 3.34, 3.35 (2s, 6H,  $\text{CH}_3\text{O}$ ), 3.60 (dd,  $J=11.0, 6.4\text{Hz}$ , 1H, 1x $\text{CH}_2\text{OH}$ ), 4.46 (t,  $J=6.9\text{Hz}$ , 1H,  $\text{CHOCH}_3$ );  $\delta_{\text{C}}$  9.4 ( $\text{CH}_2\text{CHCH}_2\text{OH}$ ), 12.6 ( $\text{CHCHCH}_2\text{OH}$ ), 18.4 ( $\text{CHCH}_2\text{OH}$ ), 36.1 ( $\text{CH}_2\text{CHOCH}_3$ ), 52.6, 53.0 (2x $\text{CH}_3\text{O}$ ), 67.0 ( $\text{CH}_2\text{OH}$ ) and 104.6 ( $\text{CHOCH}_3$ );  $m/z$  129 ( $M^+-\text{CH}_3\text{O}$ , 15%), 97 (19), 79 (35), 77 (12), 76 (28), 75 (100), 71 (23), 69 (18), 67 (36), 59 (26), 58 (28), 55 (38), 53 (22), 47 (75), 45 (57), 43 (52), 42 (16) and 41 (70) (Found:  $M^+-\text{CH}_3\text{O}$ , 129.0916. Calcd. for  $\text{C}_7\text{H}_{13}\text{O}_2$ , 129.0916).

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