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A General Method for the Synthesis of 2-Alkyl Substituted 1,3-Dienes Starting from 2-(Chloromethyl)-3-tosylpropene

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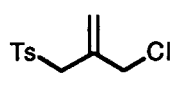
Abstract: **The alkylation of the monolithium derivative 5 of 2-(chloromethyl)-3-tosylpropene (1) with bromo- or iodo-methyltrimethylsilane affords the β-silyl sulfone 7, which after nucleophilic substitution of the chlorine atom followed by β-elimination of tosyltrimethylsilane, promoted by tetrabutylammonium fluoride (TBAF), gives 2-substituted conjugated dienes 6 and the outer-ring diene 14. Racemic ipsenol (10b), an aggregation pheromone of the bark beetle *Ips paraconfusus* Lanier, is prepared.**

INTRODUCTION

2-(Chloromethyl)-3-tosylpropene (**1**)[1] is a useful multicoupling reagent, with isobutene structure, which is easily prepared from commercially available 3-chloro-2-(chloromethyl)propene and has been used as: (a) a 1,3-dipole **2** in palladium catalyzed cyclopentannelation reactions with electrophilic olefins of its phenylsulfonyl homologous[2], (b) an allylic chlorinated dianion **3** in the synthesis of tosylated methylenecyclopropanes, furan derivatives, and cyclopentenes[3], and (c) a cationic or anionic synthon **4** in the preparation of different types of allyl sulfones[1].



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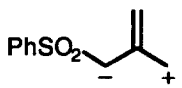

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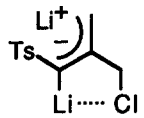

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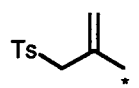

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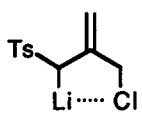
[* = + or -]



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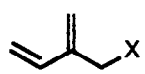
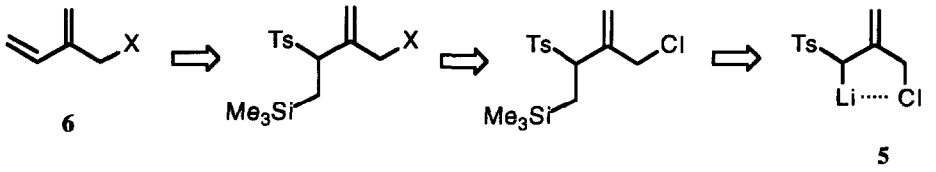


6

(Ts=*p*-$CH_3C_6H_4SO_2$)

Another possible application of this reagent **1** might be the straightforward three-step synthesis of functionalized 2-alkyl substituted 1,3-butadienes **6** applying its reactivity first as monolithium derivative **5**[4] with halomethyltrimethylsilanes, second as synthon **4**[1], and third carrying out the generation of the second double bond by fluoride induced β-elimination of tosyltrimethylsilane[5] (Kocienski's methodology) in the intermediate β-

silyl sulfone[6] (Scheme 1). The structure of this type of 2-substituted dienes **6** is present in terpenoids (e. g. myrcene derivatives, ipsdienol, and ipsenol) and are also useful in Diels-Alder reactions[7], specially in the synthesis of rings A and B of the taxane skeleton[8]. However, there are not general procedures for the synthesis of these type of dienes which start generally from isoprene[7e,f,9] or chloroprene[7c,d], and from other starting compounds[7b,10]. In this paper we describe a general synthesis of 2-substituted dienes of the type **6** starting from 2-(chloromethyl)-3-tosylpropene (**1**) according to the strategy indicated in Scheme 1[11].

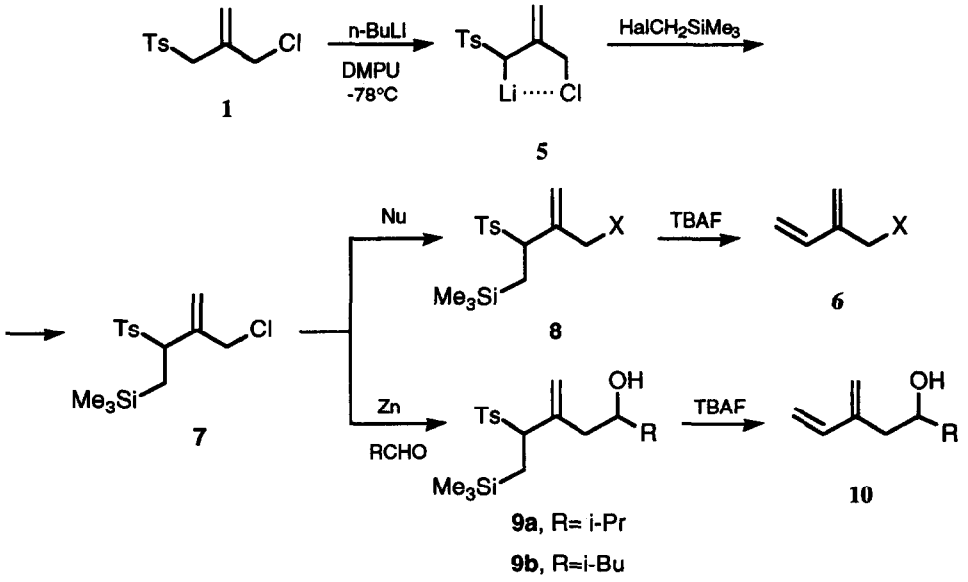


6 **5**

Scheme 1

RESULTS AND DISCUSSION

The lithiation of 2-(chloromethyl)-3-tosylpropene (**1**)[1] with n-butyllithium in the presence of *N,N'*-dimethylpropyleneurea (DMPU) in THF at -78°C for 10 min gave the monolithium intermediate **5**[4], which reacted with bromo- or iodo-methyltrimethylsilane[12] to give the β-silyl sulfone **7** in 62 or 70% yield, respectively (Scheme 2). The reaction of crude or pure compound **7** with different heteronucleophiles such as *(S)*-α-methylbenzylamine, morpholine, sodium azide, silver nitrite, sodium nitrite, benzoic acid, *(R)-O*-(4-chloro-2-methyl-



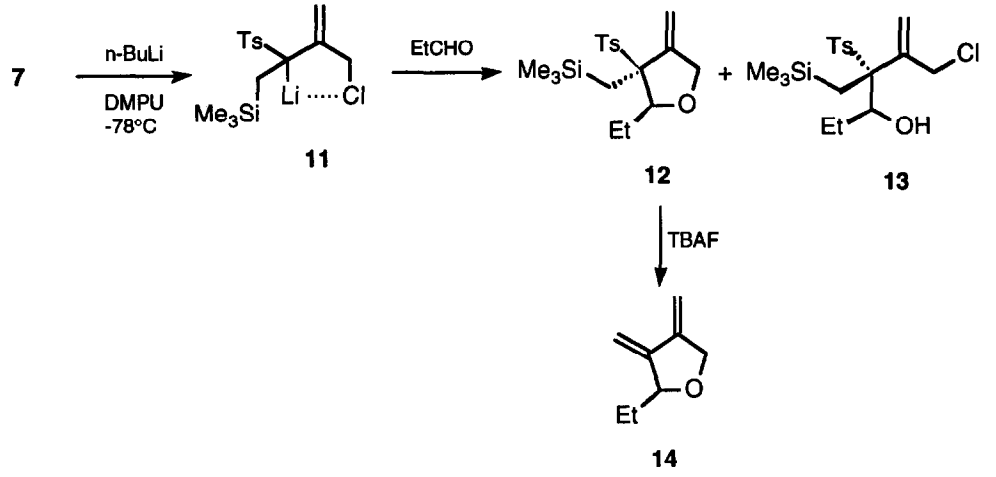
Scheme 2

phenyl)lactic acid[13], naproxene, and sodium thiophenolate, bromide, and iodide under appropriate reaction conditions afforded the corresponding functionalized β-silyl sulfones **8a-k** (Scheme 2 and Table 1). When Grignard reagents (*sec*- and *t ert*-butylmagnesium chloride and phenylmagnesium bromide) were allowed to react with pure compound **7** in THF at room temperature β-silyl sulfones **8l-n** were obtained (Scheme 2 and Table 1).

The obtained β-silyl sulfones **8** were transformed into dienes **6** by treatment with a solution of tetra-n-butylammonium fluoride (TBAF) in THF at 0°C (Scheme 2 and Table 2). Substituted butadienes **6** were isolated, in general, as pure compounds (>95%, GLC) after acidic extractive work-up; they were purified by kugelrohr distillation except the azide **8c** due to its thermal potential instability. Only in the case of aminodienes **6a** and **6b** they were isolated impurified with tri-n-butylamine and were separated by distillation. In some cases, **8d,e,l,m** decomposition of the diene took place, despite the mild elimination conditions used. Dienes **6** are, in general, very unstable compounds and decomposed on standing in hours or days.

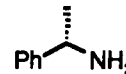
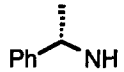
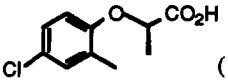
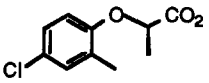
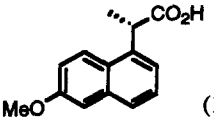
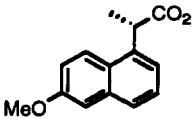
This methology has been applied to the synthesis of alcohol **10a** and racemic ipsenol (**10b**)[18], sex pheromone of the bark beetle *Ips paraconfusus* Lanier. By reaction of compound **7** with isobutanal and isopentanal in the presence of activated zinc[1] under Barbier reaction conditions, for 3 d under THF reflux alcohols **9a** and **9b** were obtained in 90 and 97% yield, respectively (Scheme 2). Further treatment of compounds **9** with TBAF in THF at 0°C during 30 min led to the corresponding dienic alcohols **10a** and **10b** (Scheme 2 and Table 2).

Starting from the chlorinated β-silyl sulfone **7** it is presumably possible to prepare more substituted dienes and as an example we tried the synthesis of the outer-ring diene **14**. The lithiation of compound **7**, under similar reaction conditions described for anion **5** (n-butyllithium/DMPU in THF at -78°C) gave intermediate **11**, which reacted with n-propanal to lead to the formation of two diastereoisomeric alcohols: only one of them cyclised, even at -78°C, to give the tetrahydrofuran **12** (Scheme 3). The configuration *cis* for compound **12** was assigned



Scheme 3

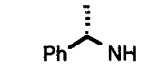
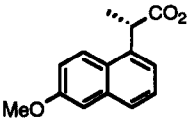
Table 1. Preparation of β-Silyl Sulfones **8**

Reaction conditions				Product			
Nu (equiv.)	Solvent	T (°C)	Time	No.	X	Yield(%)[a]	R_f[b]
 (4)	CH_3CN	reflux	2 d	**8a**		89[c]	0.36
Morpholine (4)	CH_3CN	reflux	2 d	**8b**		66	0.66[d]
NaN_3 (10)	EtOH/H_2O[e]	90[f]	2 d	**8c**	N_3	70	0.58
$AgNO_2$ (2)	Et_2O[g]	rt	4 d	**8d**	NO_2	68[c]	0.49[d]
$NaNO_2$ (2)	DMSO[g]	70[f]	2 d	**8e**	HO	73[c]	0.50
$PhCO_2H$ (1.5)[h]	DMF[g]	80	1.5 d	**8f**	$PhCO_2$	62	0.30
 (1.5)[h]	DMF[g]	80	1.5 d	**8g**		60	0.34
 (1.5)[h]	DMF[g]	80	2 d	**8h**		83[c]	0.40
NaSPh (2)	THF[g]	reflux	1 d	**8i**	PhS	73	0.55
NaBr (5)	CH_2Br_2/DMF[i]	90	20 h	**8j**	Br	98[c,j]	0.58[k]
NaI (5)	Me_2CO	reflux	1.5 d	**8k**	I	98[c,j]	0.47[d]
sec-BuMgCl (4)[l]	THF[g]	rt	2 d	**8l**	*sec*-Bu	85[c]	0.70
tert-BuMgCl (2)	THF[g]	rt	1 d	**8m**	*tert*-Bu	95[c,j]	0.69
PhMgBr (2)	THF[g]	rt	2 d	**8n**	Ph	83[c]	0.75

[a] Based on compound **1**, after column chromatography (silica gel, hexane/ether). [b] Hexane/ether:1/1. [c] Based on pure compound **7**. [d] Ether. [e] In 4/1 volume ratio. [f] Bath temperature. [g] Dry. [h] In the presence of sodium iodide (3 equiv.) and cesium fluoride (1.5 equiv.)[14]. [i] In 1/1 volume ratio. [j] Isolated crude pure product. [k] Mp 75-76°C (hexane/ether). [l] Copper bromide (2 equiv.) was added.

according to the positive n.O.e. effect (14%) between the methine and the methylene group bonded to the silicon. Compound **12** was isolated after flash chromatography in 60% yield together with the starting sulfone **7** (22%) and the *threo*-alcohol **13** (6%), which has sterical hindrance to cyclise. Final reaction of product **12** with TBAF at 0°C for 20 min in THF afforded pure dienic furan **14** in quantitative crude yield, which was purified by distillation (69%, bp 75°C/18 Torr) (Scheme 3).

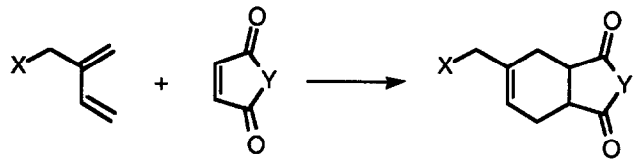
Table 2. Synthesis of 2-Substituted 1,3-Dienes **6** and **10**

β-Silyl sulfone	Reaction time	Diene			
		No.	X or R	Yield(%)[a]	Bp (°C/Torr)[b]
8a	15 min	**6a**		79	100/7
8b	1 h	**6b**		80	125/18
8c	1 h	**6c**	N_3	94[c]	-[d]
8f	30 min	**6f**	$PhCO_2$	75[e]	180/7
8h	15 min	**6h**		74[f]	-[g]
8i	90 min	**6i**	PhS	94[c,h]	175/7[i]
8j	30 min	**6j**	Br	76[e]	55/19[j]
8k	30 min	**6k**	I	80[e,h]	90/19
8n	30 min	**6n**	Ph	84	115/19[k]
9a	30 min	**10a**	i-Pr	88[e]	135/24
9b	30 min	**10b**	i-Bu	86	155/17[l]

[a] Based on starting sulfone after distillation. [b] Kugelrohr. [c] Isolated crude product (>95% pure, GLC). [d] R_f 0.50 (hexane/ether: 5/1). [e] 98% crude yield (>98% pure, GLC). [f] After purification by column chromatography on silica gel. [g] R_f 0.60 (hexane/ether: 3/1). [h] Decomposed by distillation. [i] Lit.[8f]. [j] Lit.[10c] 35-37°C/27 Torr. [k] Lit.[16] 71-75°C/ 5 Torr. [l] Lit.[17] bp 120-125°C/13 Torr.

The cycloaddition of this type of dienes with homochiral olefins has been carried out with 2-(benzyloxymethyl)-1,3-butadiene and takes place with high enantioselectivity[7e]. We have prepared homochiral dienes **6a** and **6h** in order to study their application in asymmetric Diels-Alder reaction. The cycloaddition reaction of dienes **6a** and **6h** with maleic anhydride (**15a**) and *N*-phenylmaleimide (**15b**) as dienophiles provided adducts **16** as mixture of diastereomers in *ca.* 1/1 molar ratio (^{13}C NMR) (Scheme 4 and Table 3). In the case of the reaction of ester **6h** and maleic anhydride (**15a**) aluminium trichloride was used as catalyst and with *N*-phenylmaleimide (**15b**) the reaction took place in 4 d at room temperature or in 1d in the presence of activated silica gel[19]. Homochiral dienic amine **6a** needed also the presence of activated silica gel and 3 d to react with *N*-phenylmaleimide to give compound **16d**.

In conclusion, this methodology allows the general synthesis of functionalized 2-substituted conjugated dienes and also of racemic ipsenol under mild reaction conditions.



6a,h **15a**, Y=O **16**
15b, Y=NPh

Scheme 4

Table 3. Diels-Alder Reaction of Homochiral Dienes **6a** and **6h**

		Reaction conditions			Product		
Diene	Dienophile	Reaction time	Catalyst	Solvent	No.	Yield(%)[a]	R_f[b]
6a	**15b**	3 d	SiO_2[c]	THF	**16a**	80	0.90[d]
6b	**15a**	4 d	$AlCl_3$	Et_2O	**16b**	60	0.50
6b	**15b**	4 d	-	THF	**16c**	77	0.48
6b	**15b**	1 d	SiO_2[c]	THF	**16c**	81	0.48

[a] Isolated crude yield based on diene **6**, deduced by ^1H NMR. [b] Ether. [c] Dried at 200°C during 16h. [d] AcOEt.

EXPERIMENTAL

General. Melting points were obtained with a Reichert Thermovar apparatus and are uncorrected. Optical rotation were measured in a Optical Activity AA-10 polarimeter. IR spectra were obtained as films in a Pye Unicam SP3-200 spectrophotometer as neat liquids. ^1H and ^{13}C spectra were recorded on a Bruker AC-300 spectrometer with $SiMe_4$ as internal standard and using $CDCl_3$ as solvent. ^{13}C-NMR assignments were made on the basis of DEPT experiments. MS spectra were measured in a Hewlett-Packard 5988A (EI, 70eV). High resolution mass spectra were measured in the corresponding Service at the University of Zaragoza. Elemental analyses were performed by the Microanalyses Service of the University of Alicante. Chromatographic analysis (GC) were determined with a Hewlett-Packard HP-5890 instrument equipped with a 25 m WCOT capillary column (0.22 mm diam., 0.2μm film thickness OV-101 stationary phase) using nitrogen (2 ml/min) as the carrier gas, $T_{injector}$=270°C, T_{column}=60°C, and 60-270 (15°C/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 and UV visualization. Column chromatography was performed using silica gel 60 of 70-270 mesh and hexane/ether as eluant. All starting materials were commercially available (Aldrich, Fluka, Janssen) of the best grade and were used without further purification. THF and ether were dried with $LiAlH_4$ under argon atmosphere.

Synthesis of 3-(Chloromethyl)-2-tosyl-1-(trimethylsilyl)-3-butene (7). To a solution of 2-(chloromethyl)-3-tosylpropene (**1**)[1] (98 mg, 0.4 mmol) and DMPU (0.053 mL, 0.44 mmol) in dry THF (3 mL) was added at -78 °C a 1.6 M solution of n-butyllithium (0.275 mL, 0.44 mmol) in hexane under an argon atmosphere. After 15 min stirring, the halomethyltrimethylsilane (0.44 mmol) was added and the reaction was warmed up at room temperature and an aqueous 3 M HCl solution (5 mL) was added (for iodomethyltrimethylsilane the reaction was quenched at -40 °C). The reaction mixture was extracted with ether (2x20 mL), the organic layer dried (Na_2SO_4) and evaporated *in vacuo* (15 Torr) to afford compound **7**, which was purified by column chromatography (silica gel, hexane/ether) and/or recystallized to give white crystals (62% and 70% yield for bromo- and iodo-methyltrimethylsilane, respectively): mp 57-58 °C (hexane/ether); ν (liq.) 3080, 1640, 825 (CH=C), 1260, 850, 750 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.06 [s, 9H, $(CH_3)_3Si$], 1.06 (dd, J=14.0, 14.0 Hz, 1H, CH_2Si), 1.33 (dd, J=14.0, 2.2 Hz, 1H, CH_2Si), 2.44 (s, 3H, CH_3Ar), 3.88 (dd, J=14.0, 2.2 Hz, 1H, CHS), 4.08, 4.28 (2d, J=12.5 Hz, 2H, CH_2Cl), 5.03, 5.51 (2s, 2H, CH_2=C), 7.31 and 7.67 (2d, J=8.0 Hz, 4H, ArH); δ_C -1.07 [$(CH_3)_3Si$], 15.24 (CH_2Si), 21.55 (CH_3Ar), 47.93 (CH_2Cl), 60.05 (CHS), 121.98, 132.74 (CH_2=C), 129.33, 129.62, 137.97 and 144.70 (ArC); *m/z* 295 (M^+-Cl, 2%), 180 (36), 149 (33), 93 (15), 91 (36), 73 (92), 67 (100), 65 (55), 63 (10) and 45 (49). Anal. calcd. for $C_{15}H_{23}ClO_2SSi$: C, 54.44; H, 7.00 and S, 9.69. Found: C, 54.17; H, 6.95 and S, 9.72.

Preparation of β-Silyl Sulfones 8a-k. General Procedure. A mixture of compound **7** (83 mg, 0.25 mmol) and the nucleophile (see Table 1) in the corresponding solvent (ca. 3 mL) was stirred under the conditions indicated in Table 1. The reaction was followed by TLC and after extractive work-up compounds **8a-k** were isolated and purified by column chromatography or and by recrystallization. Yields and physical data are included in Table 1, spectral and analytical data follow:

2-[(S)-(1-Phenylethyl)aminomethyl]-3-tosyl-4-(trimethylsilyl)-1-butene (mixture of diastereoisomers) (**8a**): ν (liq.) 3300 (NH), 3060, 1640, 810 (C=CH), 1240, 840, 730 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.10 [s, 9H, $(CH_3)_3Si$], 0.95-1.43 (m, 5H, CH_2Si and CH_3CN), 2.39 (s, 4H, CH_3Ar and NH), 2.85-3.30 (m, 2H, CH_2N), 3.50-3.96 (m, 2H, CHS and CHN), 5.13, 5.42 (2s, 2H, CH_2=C) and 7.27-7.80 (m, 9H, Ph and *p*-TolH); δ_C -0.95 [$(CH_3)_3Si$], 15.00 (CH_2Si), 21.54 (CH_3Ar), 24.40 (CH_3CN), 52.25 (CH_2N), 57.90 (CHN), 66.08 (CHS), 118.80, 126.50, 126.85, 128.34, 129.17, 129.54, 134.05, 141.43, 144.10 and 145.47 (ArC and C=C); *m/z* 415 (M^+, <0.01%), 260 (21), 149 (11), 105 (100), 82 (11), 73 (69) and 45 (11).

N-*[2-Methylene-4-(trimethylsilyl)-3-tosylbutyl]morpholine* (**8b**): ν (liq.) 3080, 1640, 810 (C=CH), 1250, 850, 760 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.10 [s, 9H, $(CH_3)_3Si$], 1.10 (dd, J=13.0 and 14.3 Hz, 1H, CH_2Si), 1.40 (dd, J=2.7 and 14.3 Hz, 1H, CH_2Si), 2.44 (s, 3H, CH_3Ar), 2.45 (m, 4H, CH_2CH_2N), 2.86, 3.17 (2d, J=15.0 Hz, 2H, CH_2C=C), 3.70 (m, 4H, 2xCH_2O), 3.85 (dd, J=2.7 and 13.3 Hz, 1H, CHS), 4.97, 5.36 (2s, 2H, CH_2=C), 7.33, and 7.71 (2d, J=8.1 Hz, 4H, ArH); δ_C -0.97 [$(CH_3)_3Si$], 15.21 (CH_2Si), 21.50 (CH_3Ar), 53.84 (2xCH_2CH_2N), 63.83 (CH_2C=C), 65.89 (CHS), 66.89 (2xCH_2O), 119.26, 129.10, 129.65, 133.30, 138.64 and 144.27 (ArC and C=C); *m/z* 264 (M^+-Ts, 16%), 149 (18), 138 (23), 100 (47), 91 (29), 73 (100), 67 (11), 65 (22), 56 (11), 45 (30) and 43 (11).

2-(Azidomethyl)-3-tosyl-4-(trimethylsilyl)-1-butene (**8c**): ν (liq.) 3080, 1640, 800 (C=CH), 2090 (N_3), 1245, 850, 755 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.10 [s, 9H, $(CH_3)_3Si$], 1.09 (dd, J=13.3 and 14.4 Hz, 1H, CH_2Si), 1.38 (dd, J=2.2 and 14.4 Hz, 1H, CH_2Si), 2.44 (s, 3H, CH_3Ar), 3.66 (dd, J=2.2 and 13.3 Hz, 1H, CHS), 3.85, 3.96 (2d, J=15.0 Hz, 2H, CH_2N), 4.98, 5.38 (2s, 2H, CH_2=C), 7.32 and 7.68 (2d, J=8.0 Hz, 4H, ArH); δ_C -1.13 [$(CH_3)_3Si$], 14.39 (CH_2Si), 21.59 (CH_3Ar), 54.87 (CH_2N), 66.33 (CHS), 120.35 (CH_2=C), 129.41, 129.54, 132.92, 137.15 and 144.75 (ArC); *m/z* 264 (M^+-$SiMe_3$, 1%), 180 (16), 149 (23), 91 (91), 73 (100), 65 (10) and 45 (13).

2-(Nitromethyl)-3-tosyl-4-(trimethylsilyl)-1-butene (**8d**): ν (liq.) 3085, 1630, 800 (C=CH), 1545 (NO_2), 1240, 830, 740 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.15 [s, 9H, $(CH_3)_3Si$], 1.07 (dd, J=13.0 and 14.5 Hz, 1H, CH_2Si), 1.35 (dd, J=2.5 and 14.5 Hz, 1H, CH_2Si), 2.39 (s, 3H, CH_3Ar), 3.99 (dd, J=2.5 and 13.0 Hz, 1H, CHS), 5.08, 5.37 (2d, J=13.3 Hz, 2H, CH_2N), 5.29, 5.65 (2s, 2H, CH_2=C), 7.39 and 7.72 (2d, J=8.1 Hz, 4H, ArH); δ_C -1.38 [$(CH_3)_3Si$], 14.84 (CH_2Si), 21.56 (CH_3Ar), 65.76 (CHS), 80.15 (CH_2N), 126.72, 129.48, 129.59, 132.17, 132.29 and 144.06 (ArC and C=C); *m/z* 295 (M^+-NO_2, 1%), 228 (26), 213 (11), 180 (57), 155 (29), 149 (76), 141 (28), 139 (12), 91 (35), 75 (26), 73 (100), 67 (45), 65 (29), 59 (11), 45 (32) and 41 (26).

2-Methylene-3-tosyl-4-(trimethylsilyl)-1-butanol (**8e**): ν (liq.) 3480 (OH), 3065, 1630, 810 (C=CH), 1240, 840, 740 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.10 [s, 9H, $(CH_3)_3Si$], 1.19 (dd, J=13.2 and 14.0 Hz, 1H, CH_2Si), 1.31 (dd, J=3.0 and 14.0 Hz, 1H, CH_2Si), 2.38 (s, 3H, CH_3Ar), 3.82 (dd, J=3.0 and 13.2 Hz, 1H, CHS), 4.10, 4.22 (2d, J=14.0 Hz, 2H, CH_2O), 5.02, 5.44 (2s, 2H, CH_2=C), 7.32 and 7.70 (2d, J=8.1 Hz, 4H, ArH); δ_C -1.08 [$(CH_3)_3Si$], 15.20 (CH_2Si), 21.62 (CH_3Ar), 65.29 (CHS), 65.62 (CH_2O), 119.34 (CH_2=C), 129.40, 129.60, 133.18, 141.23 and 144.69 (ArC and C=CH_2); *m/z* 312 (M^+, <0.01%), 230 (10), 228 (10), 180 (21), 157 (13), 139 (29), 91 (19), 75 (49), 73 (73), 67 (100), 65 (23), 45 (22) and 41 (17).

[2-Methylene-3-tosyl-4-(trimethylsilyl)]butyl Benzoate (**8f**): ν (liq.) 3085, 1650, 800 (C=CH), 1720 (CO), 1260, 840, 730 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.05 [s, 9H, $(CH_3)_3Si$], 1.15 (dd, J=13.5 and 14.5 Hz, 1H, CH_2Si), 1.38 (dd, J=2.5 and 14.5 Hz, 1H, CH_2Si), 2.38 (s, 3H, CH_3Ar), 3.74 (dd, J=2.5 and 13.5 Hz, 1H, CHS), 4.76, 4.90 (2d, J=14.0 Hz, 2H, CH_2O), 5.06, 5.45 (2s, 2H, CH_2=C), 7.27, 7.69 (2d, J=8.2 Hz, 4H, *p*-TolH), 7.38-7.68 (m, 3H, *m*- and *p*-Ph) and 8.00 (d, J=8.2 Hz, 2H, *o*-Ph); δ_C -1.16 [$(CH_3)_3Si$], 14.53 (CH_2Si), 21.53 (CH_3Ar), 65.91 (CHS and CH_2O), 120.41, 128.31, 129.31, 129.54, 129.57, 129.71, 133.07, 133.10, 137.12, 144.59 (ArC and C=C) and 165.75 (CO); *m/z* 416 (M^+, <0.01%), 261 (M^+-Ts, 11), 180 (24), 149 (27), 105 (56), 91 (12), 77 (22), 73 (100), 67 (20) and 65 (13).

[(2-Methylene-3-tosyl-4-(trimethylsilyl)]butyl (R)-*2-[(4-Chloro-2-methyl)phenoxy]propanoate* (mixture of diastereoisomers) (**8g**): ν (liq.) 1740 (CO), 1240, 840, 740 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.10 [s, 9H, $(CH_3)_3Si$], 0.80-1.65 (m, 5H, CH_3CH and CH_2Si), 2.25 (s, 3H, CH_3CCO), 2.39 (s, 3H, CH_3-*p*-Tol), 3.60-3.85 (m, 1H, CHS), 4.55-5.02 (m, 3H, CH_2O and CHO), 5.26, 6.05 (2s, 2H, CH_2=C) and 6.60-7.86 (m, 7H, ArH); δ_C -1.20 [$(CH_3)_3Si$], 14.00-14.44 (CH_2Si), 14.40-19.00 (CH_3CO), 20.75-21.05 (CH_3CO), 21.41-21.50 (CH_3-*p*-Tol), 65.86-66.14 (CH_2O and CHS), 72.96 (CHO), 112.82-154.28 (ArC and C=C) and 171.14 (CO); *m/z* 508 (M^+, 7%), 180 (21), 169 (22), 149 (24), 125 (10), 91 (14), 75 (11), 73 (100), 67 (16),

65 (12) and 45 (12).

[2-Methylene-3-tosyl-4-(trimethylsilyl)]butyl (S)-2-(6-Methoxy-2-naphthyl)propionate (mixture of diastereoisomers) (**8h**): ν (liq.) 1730 (CO), 1260, 840, 730 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.20 [s, 9H, $(CH_3)_3Si$], 1.05-1.22 (m, 2H, CH_2Si), 1.66 (m, 3H, CH_3CH), 2.39 (s, 3H, CH_3Ar), 3.62-4.30 (m, 5H, CH_3O, CHCO and CHS), 4.54-4.77 (m, 2H, CH_2O), 4.99-5.50 (m, 2H, CH_2=C) and 7.18-7.81 (m, 12H, ArH); δ_C -1.22 [$(CH_3)_3Si$], 14.36-15.04 (CH_2Si), 18.21-18.51 (CH_3CH), 21.41-21.46 (CH_3Ar), 45.12-45.26 (CHCO), 55.14 (CH_3O), 65.01-65.90 (CH_2O, CHS), 105.47, 118.86, 120.30, 125.87, 126.50, 127.09, 128.76, 129.15, 129.41, 132.96, 133.59, 135.30, 136.79, 141.19, 144.50, 157.51 (ArC and C=C) and 173.80 (CO); *m/z* 525 (M^++1, 1%), 524 (M^+, 2), 296 (35), 252 (20), 251 (87), 224 (13), 213 (10), 186 (11), 185 (100), 180 (12), 170 (15), 149 (22), 141 (17), 91 (11), 75 (11), 73 (99) and 45 (15).

2-(Phenylthiomethyl)-3-tosyl-4-(trimethylsilyl)-1-butene (**8i**): ν (liq.) 3075, 1640 (C=CH), 1250, 850, 750 ($SiMe_3$), 1300 and 1150 cm^{-1} (SO_2); δ_H 0.11 [s, 9H, $(CH_3)_3Si$], 1.10 (dd, J=13.0 and 14.0 Hz, 1H, CH_2Si), 1.39 (dd, J=2.2 and 14.0 Hz, 1H, CH_2Si), 2.45 (s, 3H, CH_3Ar), 3.82 (s, 2H, CH_2S), 3.92 (dd, J=2.2 and 13.0 Hz, 1H, CHS), 4.93, 5.47 (2s, 2H, CH_2=C), 7.19-7.36 (m, 7H, Ph and 2x*p*Tol), 7.66 (d, J=7.8 Hz, 2H, *p*-TolH); δ_C -0.98 [$(CH_3)_3Si$], 14.96 (CH_2Si), 21.58 (CH_3Ar), 39.14 (CH_2S), 67.03 (CHS), 121.07 (CH_2=C), 126.02, 128.77, 128.86, 129.24, 129.66, 133.00, 136.15, 137.52 and 144.48 (ArC and C=CH_2); *m/z* 404 (M^+, 0.1%), 295 (10), 249 (10), 176 (10), 149 (11), 109 (18), 91 (10), 73 (100), 65 (10) and 45 (12). Anal. calcd. for $C_{21}H_{28}O_2S_2Si$: C, 62.33, H, 6.97 and S, 15.85. Found: C, 62.25, H, 7.08 and S, 15.87.

2-(Bromomethyl)-3-tosyl-4-(trimethylsilyl)-1-butene (**8j**): ν (liq.) 3080, 1640, 800 (C=CH), 1255, 840, 750 ($SiMe_3$), 1300 and 1150 cm^{-1} (SO_2); δ_H 0.03 [s, 9H, $(CH_3)_3Si$], 1.03 (dd, J=13.3 and 14.5 Hz, 1H, CH_2Si), 1.32 (dd, J=2.4 and 14.5 Hz, 1H, CH_2Si), 2.44 (s, 3H, CH_3Ar), 3.94 (dd, J=2.4 and 13.3 Hz, 1H, CHS), 4.04, 4.27 (2d, J=11.0 Hz, 2H, CH_2Br), 5.03 , 5.55 (2s, 2H, CH_2=C), 7.31 and 7.68 (2d, J=8.0 Hz, 4H, ArH); δ_C -1.01 [$(CH_3)_3Si$], 15.46 (CH_2Si), 21.54 (CH_3Ar), 36.69 (CH_2Br), 65.20 (CHS), 122.51 (CH_2=C), 129.29, 129.67, 132.58, 137.97 and 144.70 (ArC and C=CH_2); *m/z* 228 (M^+-C_5H_7Br, 8%), 180 (25), 149 (24), 91 (28), 73 (100), 67 (77), 65 (31), 45 (29) and 41 (16). Anal. calcd. for $C_{15}H_{23}BrO_2SSi$: C, 47.99, H, 6.18 and S, 8.54. Found: C, 47.98, H, 6.16 and S, 8.48.

2-(Iodomethyl)-3-tosyl-4-(trimethylsilyl)-1-butene (**8k**): ν (liq.) 3080, 1620, 800 (C=CH), 1250, 840, 750 ($SiMe_3$), 1300 and 1150 cm^{-1} (SO_2); δ_H 0.08 [s, 9H, $(CH_3)_3Si$], 1.04 (dd, J=13.0 and 14.5 Hz, 1H, CH_2Si), 1.35 (dd, J=2.5 and 14.5 Hz, 1H, CH_2Si), 2.37 (s, 3H, CH_3Ar), 3.95 (dd, J=2.5 and 13.0 Hz, 1H, CHS), 4.06, 4.31 (2d, J=10.3 Hz, 2H, CH_2I), 5.00, 5.61 (2s, 2H, CH_2=C), 7.34 and 7.70 (2d, J=8.0 Hz, 4H, ArH); δ_C -0.82 [$(CH_3)_3Si$], 10.46 (CH_2I), 15.58 (CH_2Si), 21.61 (CH_3Ar), 66.02 (CHS), 121.73, 132.60 (CH_2=C), 129.32, 129.77, 138.79 and 144.75 (ArC); *m/z* 296 (M^++1-I, 1%), 267 (2), 180 (16), 149 (24), 91 (14), 75 (15), 73 (100), 67 (30), 65 (13) and 45 (16).

Preparation of β-Silyl Sulfones 8l-n. General Procedure. To a solution of compound **7** (83 mg, 0.25 mmol), in anhydrous THF (3 mL), cooled at 0°C, was added a solution of Grignard reagent (0.5 mmol) in ether or THF (see Table 1). The reaction was followed by TLC and after extractive work-up (NH_4Cl/H_2O/ether), compounds **8l-n** were obtained and purified by column chromatography. Yields and

physical data are included in Table 1, spectral and analytical data follow:

2-[1-Tosyl-2-(trimethylsilyl)ethyl]-4-methyl-1-hexene (mixture of diastereoisomers) (**8l**): ν (liq.) 3070, 1640, 800 (C=CH), 1250, 840, 740 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.10 [s, 9H, $(CH_3)_3Si$], 1.70-1.95 (m, 6H, 2xCH_3), 1.05-1.60 (m, 5H, CH_2Si and $CHCH_2CH_3$), 1.80-2.15 (m, 2H, CH_2C=C)C), 2.35 (s, 3H, CH_3Ar), 3.55 (d, J=12.0 Hz, 1H, CHS), 4.91, 5.00 (2d, J=0.5 Hz, 2H, CH_2=C), 7.28 and 7.69 (2d, J=8.0 Hz, 4H, ArH); δ_C -1.02, -0.99 [$(CH_3)_3Si$], 11.43, 11.50 (CH_3CH_2), 14.66, 14.80 (CH_2Si), 19.21, 19.27 (CH_3CH), 21.56 (CH_3Ar), 29.46, 29.56 (CH_2CH_3), 31.60, 32.35 ($CHCH_3$), 43.53, 43.54 (CH_2C=C), 69.27, 69.72 (CHS), 117.54, 117.55, 133.92, 134.08 (CH_2=C), 129.15, 129.55, 129.64 and 144.20 (ArC); *m/z* 352 (M^+, 0.01%), 180 (11), 149 (10) and 73 (100).

2-[1-Tosyl-2-(trimethylsilyl)ethyl]-4,4-dimethyl-1-pentene (**8m**): ν (liq.) 3075, 1630, 800 (C=CH), 1250, 850, 750 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.10 [s, 9H, $(CH_3)_3Si$], 1.08 [s, 9H, $(CH_3)_3C$], 1.20 (dd, J=11.0 and 14.5 Hz, 1H, CH_2Si), 1.36 (dd, J=4.0 and 14.5 Hz, 1H, CH_2Si), 1.92, 2.10 (2d, J=15.5 Hz, 2H, CH_2C=C), 2.45 (s, 3H, CH_3Ar), 3.77 (dd, J=4.0 and 11.0 Hz, 1H, CHS), 4.96, 5.09 (2s, 2H, CH_2=C), 7.36 and 7.75 (2d, J=8.2 Hz, 4H, ArH); δ_C -0.74 [$(CH_3)_3Si$], 16.09 (CH_2Si), 21.54 (CH_3Ar), 29.69 [$(CH_3)_3C$], 31.26 [$C(CH_3)_3$], 49.76 (CH_2C=C), 69.59 (CHS), 119.71 (CH_2=C), 129.03, 129.87, 133.52, 140.57 and 144.17 (ArC and C=CH_2); *m/z* 352 (M^+, 0.01%), 295 (10), 228 (10), 197 (45), 180 (10), 149 (16), 91 (10), 73 (100), 65 (10) and 57 (12). Anal. calcd. for $C_{19}H_{32}O_2SSi$: C, 64.72, H, 9.15 and S, 9.09. Found: C, 64.72, H, 9.09 and S, 8.50.

2-Benzyl-3-tosyl-4-(trimethylsilyl)-1-butene (**8n**): ν (liq.) 3060, 1630, 800 (C=CH), 1230, 840, 730 ($SiMe_3$), 1290 and 1140 cm^{-1} (SO_2); δ_H 0.90 [s, 9H, $(CH_3)_3Si$], 1.15 (dd, J=14.5 and 14.5 Hz, 1H, CH_2Si), 1.40 (dd, J=2.5 and 14.5 Hz, 1H, CH_2Si), 2.35 (s, 3H, CH_3Ar), 3.30, 3.50 (2d, J=16.2, 2H, CH_2Ph), 3.69 (dd, J=2.5 and 14.5 Hz, 1H, CHS), 4.78, 4.82 (2s, 2H, CH_2=C), 7.15-7.42 (m, 7H, Ph and 2x*p*-Tol) and 7.74 (d, J=8.2 Hz, 2H, ArH); δ_C -1.24 [$(CH_3)_3Si$],14.40 (CH_2Si), 21.47 (CH_3Ar), 42.02 (CH_2Ph), 67.98 (CHS), 119.30, 126.37,128.33, 129.1532, 129.55, 129.76, 133.40, 137.64, 142.11 and 144.31 (ArC and CH_2=C); *m/z* 372 (M^+, <0.01%), 293 (2), 157 (11), 149 (22), 142 (13), 139 (16), 91 (15), 73 (100), 67 (19), 65 (14) and 45 (19).

Reaction of Compound 7 with Aldehydes. Synthesis of Compounds 9. General Procedure. To a suspension of zinc powder (99.999%, 65 mg, 1mmol) in dry THF (2 mL) was added successively 1,2-dibromoethane (15 μL, 0.038 mmol) and chlorotrimethylsilane (8 μL, 0.03 mmol) under argon. The reaction mixture was stirred 1h and then, a solution of compound **7** (83 mg, 0.25 mmol) and the corresponding carbonyl compound (0.30 mmol) in THF (2 mL), was added. The resulting mixture was refluxed during three days. The suspension was filtered off and to the filtrate was added an aqueous saturated solution of ammonium chloride (10 mL). After extractive work-up the crude product was purified by column chromatography to give compounds **9**.

2-Methyl-5-methylene-6-tosyl-7-(trimethylsilyl)-3-heptanol (mixture of diastereoisomers) (**9a**): Yield 90%; R_f 0.40 (hexane/ether:1/1); ν (liq.) 3510 (OH), 3080, 1640, 800 (C=CH), 1255, 840, 740 ($SiMe_3$), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.05 [s, 9H, $(CH_3)_3Si$], 0.95 [d, J=6.8 Hz, 6H, $(CH_3)_2CH$], 1.16-1.28 (m, 2H, CH_2Si), 1.72 (m, 1H, $CHCH_3$), 2.05- 2.33 (m, 2H, CH_2CO), 2.45 (s, 3H, CH_3Ar), 2.50 (br. s, 1H, OH),

3.65 (m, 1H, CHO), 3.85 (dd, J=2.5 and 13.0 Hz, 1H, CHS), 5.04, 5.31 (2s, 2H, CH_2=C), 7.33 and 7.72 (2d, J=8.0 Hz, 4H, ArH); δ_C -1.16 [$(CH_3)_3Si$], 15.36 (CH_2Si), 17.24, 18.50 [$(CH_3)_2CH$], 21.43 (CH_3Ar), 31.54 [$CH(CH_3)_2$], 40.92 (CH_2CO), 68.54 (CHS), 74.31 (CHO), 119.77 (CH_2=C), 129.18, 129.45, 133.26, 139.75 and 144.40 (ArC and C=CH_2); *m/z* 368 (M^+, 0.1%), 229 (11), 213 (10), 180 (16), 139 (10), 123 (11), 91 (13), 81 (44), 75 (15), 73 (100), 67 (15), 55 (11), 45 (15) and 43 (15).

2-Methyl-6-methylene-7-tosyl-8-(trimethylsilyl)-4-octanol (mixture of diastereoisomers) (**9b**): Yield 97%; R_f 0.33 (hexane/ether:1/1); ν (liq.) 3500 (OH), 3080, 1630, 800 (C=CH), 1250, 850, 730 ($SiMe_3$), 1300 and 1145 cm^{-1} (SO_2); δ_H 0.05 [s, 9H, $(CH_3)_3Si$], 0.95, 0.96 [2d, J=6.5 Hz, 6H, $(CH_3)_2CH$], 1.13-1.30 (m, 4H, CH_2Si and CH_2CH), 1.46 (m, 1H, $CHCH_3$), 1.87 (m, 1H, CH_2C=C), 2.17 (m, 1H, CH_2C=C), 2.43 (s, 3H, CH_3Ar), 2.76 (br. s, 1H, OH), 2.50 (br. s, 1H, OH), 3.75 (2d, J=3.0 and 12.5 Hz, 1H, CHS), 3.94 (m, 1H, CHO), 5.08, 5.29 (2s, 2H, CH_2=C), 7.34 and 7.74 (2d, J=8.2 Hz, 4H, ArH); δ_C -1.17 [$(CH_3)_3Si$], 14.00 (CH_2Si), 21.49 (CH_3Ar), 21.96, 23.25 [$(CH_3)_2CH$], 24.55 ($CHCH_3$), 31.44 (CH_2CH), 46.78 (CH_2C=C), 66.73 (CHS), 68.05 (CHO), 120.21 (CH_2=C), 129.28, 129.38, 133.45, 139.69 and 144.44 (ArC and C=CH_2); *m/z* 296 (M^+-$C_5H_{11}O$, 3%), 229 (16), 180 (31), 139 (17), 95 (24), 92 (11), 91 (36), 81 (30), 75 (18), 73 (100), 69 (27), 65 (23), 45 (33), 43 (29) and 41 (25).

Synthesis of (*cis*)-2-Ethyl-4-methylene-3-[(trimethylsilyl)methyl]-3-tosyltetrahydrofuran (12). To a solution of **7** (83 mg, 0.25 mmol) and *N,N*-dimethylpropyleneurea (DMPU) (56 μL, 0.38 mmol) in THF (2.5 mL) cooled at -78°C, was added a 1.6M solution of n-butyllithium (238 μL, 0.38 mmol) in hexane. After 15 min stirring at the same temperature, was droped propanal (30 μL, 0.38 mmol) and the reaction was warmed up to room temperature. The reaction was hydroyzed with 3M hydrochloric acid (5 mL) and extracted with ether (2x10 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated *in vacuo* (15 torr). The crude product was purified by column chromatography yielding 53 mg of pure product **12** (60 %). R_f 0.48 (hexane/ether:1/1); ν (liq.) 3020, 1640, 900 (C=CH), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.01 [s, 9H, $(CH_3)_3Si$], 1.04 (t, J=7.3 Hz, 3H, CH_3CH_2), 1.49, 1.59 (2d, J=14.8 Hz, 2H, CH_2Si), 1.99, 2.17 (2m, 2H, CH_2CH_3), 2.38 (s, 3H, CH_3Ar), 3.74 (dd, J=10.8 and 2.0 Hz, 1H, CHO), 4.11 (dt, J=5.0 and 2.5 Hz, 2H, CH_2O), 4.97, 5.20 (2t, J=2.5 Hz, 2H, CH_2=C), 7.22 and 7.64 (2d, J=8.2 Hz, 4H, ArH). δ_C 0.64 [$(CH_3)_3Si$], 12.28 (CH_3CH_2), 16.61 (CH_2Si), 21.56 (CH_3Ar), 22.96 (CH_2CH_3), 70.10 (CH_2O), 77.38 (CS), 88.61 (CHO), 112.27 (CH_2=C), 128.74, 130.97, 134.71, 144.10 (ArC) and 146.11 (C=CH_2); *m/z* 198 (M^++1-Ts, 2%), 107 (18), 95 (10), 91 (41), 83 (11), 79 (13), 75 (19), 73 (100), 67 (10), 65 (18), 59 (10), 57 (14), 45 (16) and 43 (19).

Synthesis of Dienes 6, 10 and 14. General Procedure. To a solution of corresponding silyl sulfone **8**, **9** or **12** (0.75 mmol) in THF (10 mL) cooled at 0°C was added slowly a 1.0M solution of tetra-n-butylammonium fluoride (TBAF) (2.25 mL, 2.25 mmol) in THF. The reaction was warmed up to room temperature and then stirred for an additional time (see Table 2). After that, water (20 mL) was added and the resulting aqueous layer was extracted with ether (2x10 mL). The organic layer was dried (Na_2SO_4) and evaporated *in vacuo* (15 torr). The crude pure product was purified by distillation or by column chromatography to afford compounds **6**, **10** and **14**. Yields, physical, spectral and analytical data follow (for compounds **6** and **10** yields and physical data are included in Table 2).

(S)-N-*(Phenylethyl)*-N-*(2-methylene-3-butenyl)amine* (**6a**): R_f 0.60 (hexane/ether:5/1); $[\alpha]^{20}_D$=-31.6° (c=1.2, $CHCl_3$); ν (liq.) 3400 (NH), 3080, 3060, 1640, 1630 and 800 cm^{-1} (C=CH); δ_H 1.36 (d, J=6.5 Hz, 3H, CH_3CH), 2.10 (br. s, 1H, NH), 2.25 (d, J=4.0 Hz, 2H, CH_2N), 3.79 (q, J=6.5 Hz, 1H, CHN), 5.04 (d, J=11.0 Hz, 1H, CH_2=CH), 5.11, 5.16 (2s, 2H, CH_2=C), 5.18 (d, J=17.5 Hz, 1H, CH_2=CH), 6.35 (dd, J=11.0 and 17.5 Hz, 1H, CH=CH_2) and 7.28-7.35 (m, 5H, Ph); δ_C 24.24 (CH_3CH), 48.15 (CH_2N), 57.70 (CHN), 113.59, 116.32, 126.62, 126.84, 128.32, 137.52, 144.17 and 145.35 (Ph, C=CH_2 and CH=CH_2); *m/z* 187 (M^+, 18%), 172 (50), 105 (100), 104 (18), 103 (17), 91 (15), 83 (13), 82 (11), 79 (16), 77 (30) and 41 (22).

N-*(2-Methylene-3-butenyl)morpholine* (**6b**): R_f 0.50 (hexane/ether:5/1); ν (liq.) 3080, 3010, 1600, 1000, 900 and 880 cm^{-1} (C=CH); δ_H 2.37 (t, J=4.5 Hz, 4H, 2xCH_2CH_2N), 3.05 (s, 2H, CH_2C=C), 3.65 (t, J=4.5 Hz, 4H, 2xCH_2O), 5.05 (d, J=11.0 Hz, 1H, CH_2=CH), 5.11 (s, 2H, CH_2=C), 5.43 (d, J=17.5 Hz, 1H, CH_2=CH) and 6.32 (dd, J=11.0 and 17.5 Hz, 1H, CH=CH_2); δ_C 53.69 (CH_2CH_2N), 60.72 (CH_2C=C), 67.04 (CH_2O), 114.49, 117.89 (2xCH_2=C), 137.54 (CH=CH_2) and 141.99 (C=CH_2); *m/z* 154 (M^++1, 1%), 153 (M^+, 12), 100 (100), 94 (13), 68 (15), 67 (28), 65 (11), 56 (33), 55 (13), 43 (11), 42 (45) and 41 (49).

2-(Azidomethyl)-1,3-butadiene (**6c**): t_r 4.23 (35°C/3min, 15°C/min); ν (liq.) 3100, 3050, 1600, 1000, 910, 880 (C=CH) and 2100 cm^{-1} (N_3); δ_H 2.43 (s, 2H, CH_2N), 5.21 (d, J=11.0 Hz, 1H, CH_2=CH), 5.30 (2s, 2H, CH_2=C), 5.33 (d, J=17.5 Hz, 1H, CH_2CH) and 6.45 (dd, J=11.0 and 17.5 Hz, 1H, CH=CH_2); δ_C 51.87 (CH_2N), 115.03, 119.09 (2xCH_2=C), 136.27 (CH=CH_2) and 141.85 (C=CH_2); *m/z* 109 (M^+, 2%), 86 (18), 84 (33), 67 (28), 72 (43), 71 (43), 42 (100) and 41 (66).

(2-Methylene-3-butenyl) Benzoate (**6f**): R_f 0.70 (hexane/ether:5/1); ν (liq.) 3080, 3060, 1640, 1590, 880 (C=CH) and 1715 cm^{-1} (CO); δ_H 4.98 (s, 2H, CH_2O), 5.14 (d, J=11.0 Hz, 1H, CH_2=CH), 5.24 (s, 1H, CH_2=C), 5.30 (d, J=17.5 Hz, 1H, CH_2CH), 5.34 (s, 1H, CH_2=C), 6.40 (dd, J=11.0 and 17.5 Hz, 1H, CH=CH_2) 7.37-7.54 (m, 3H, *m*- and *p*-Ph) and 8.03 (d, J=8.5 Hz, 2H, *o*-Ph); δ_C 63.88 (CH_2O), 114.64, 117.94, 128.28, 129.52, 129.97, 132.92, 136.02, 140.54 (Ph, CH_2=C and CH=CH_2) and 166.08 (CO); *m/z* 189 (M^++1, 0.2%), 188 (M^+, 3%), 105 (100), 77 (26) and 51 (10).

(2-Methylene-3-butenyl) (S)-*2-(6-Methoxy-2-naphthyl)propionate* (**6h**): $[\alpha]^{20}_D$=+30.9° (c=1.65, $CHCl_3$); ν (liq.) 1730 cm^{-1} (CO); δ_H 1.59 (d, J=7.2 Hz, 3H, CH_3CH), 3.86 (s, 3H, CH_3O), 3.89 (q, J=7.2 Hz, 1H, $CHCH_3$), 4.76 (s, 2H, CH_2O), 5.02 (d, J=11.0 Hz, 1H, CH_2=CH), 5.10 (s, 2H, CH_2=C), 5.12 (d, J=18.0 Hz, 1H, CH_2=CH), 6.28 (dd, J=11.0 and 18.0 Hz, 1H, CH=CH_2) 7.09-7.15, 7.40 and 7.42-7.69 (3m, 6H, ArH); δ_C 18.29 (CH_3CH), 45.37 (CH_2CO), 55.12 (CH_3O), 63.65 (CH_2O), 105.48, 114.47, 117.65, 118.87, 125.94, 126.18, 127.02, 128.82, 129.17, 133.63, 135.35, 135.85, 140.41, 157.54 (ArC, C=CH_2 and CH=CH_2) and 174.11 (CO); *m/z* 298 (M^++2, 1%), 297 (M^++1, 8), 296 (M^+, 30), 185 (100), 170 (13), 153 (10), 141 (21), 115 (13) and 41 (15). High resolution mass spectrum required for $C_{19}H_{20}O_3$: *m/z* 296.1412. Found: 296.1410.

2-(Phenylthiomethyl)-1,3-butadiene (**6i**)[8f]: R_f 0.57 (hexane); ν (liq.) 3090, 3060, 990, 900 and 880 cm^{-1} (C=CH); δ_H 3.72 (s, 2H, CH_2S), 5.12, 5.15 (2s, 2H, CH_2=C), 5.19 (d, J=11.0 Hz, 1H, CH_2=CH), 5.38 (d, J=17.5 Hz, 1H, CH_2CH), 6.40 (dd, J=11.0 and 17.5 Hz, 1H, CH=CH_2) and 7.16-7.35 (m, 5H, Ph);

δ_C 35.77 (CH_2S), 114.76, 118.71 (2xCH_2=C), 126.24, 128.78, 129.81, 136.94 (Ph), 136.62 (*C*H=CH_2) and 141.20 (*C*=CH_2); *m/z* 178 (M^++2, 6%), 177 (M^++1, 17), (176 (M^+, 100), 175 (15), 162 (31), 128 (40), 123 (40), 109 (53), 91 (33), 85 (39), 67 (31), 65 (89), 51 (31), 45 (37) and 41 (68). High resolution mass spectrum required for $C_{11}H_{12}S$: *m/z* 176.2825. Found: 176.2830.

2-(Bromomethyl)-1,3-butadiene (**6j**)[10c]: R_f 0.51 (hexane); ν (liq.) 3080, 1590 cm^{-1} (C=CH); δ_H 3.65 (s, 2H, CH_2Br), 5.08 (s, 2H, CH_2C), 5.16 (d, *J*=11.0 Hz, 1H, C*H*$_2$=CH), 5.35 (d, *J*=15.5 Hz, 1H, CH_2=CH) and 6.37 (dd, *J*=17.5 and 11.0 Hz, 1H, C*H*=CH_2); δ_C 36.54 (CH_2Br), 114.73, 118.57 (2xCH_2=C), 136.50 (*C*H=CH_2) and 141.42 (*C*=CH_2); *m/z* 148 (M^++2, 6%), 146 (M^+, 7), 67 (11) and 53 (100).

2-(Iodomethyl)-1,3-butadiene (**6k**): R_f 0.61 (hexane); ν (liq.) 3060, 1590 and 890 cm^{-1} (C=CH); δ_H 3.95 (s, 2H, CH_2I), 5.06 (s, 2H, CH_2C), 5.10 (d, *J*=11.0 Hz, 1H, C*H*$_2$=CH), 5.26 (d, *J*=15.5 Hz, 1H, CH_2=CH) and 6.25 (dd, *J*=17.5 and 11.0 Hz, 1H, C*H*=CH_2); δ_C 36.54 (CH_2Br), 115.90, 123.94 (2xCH_2=C), 136.50, 134.44 =CH_2) and 143.34 (*C*=CH_2); *m/z* 194 (M^+, 2%), 141 (11), 67 (78) and 53 (100).

2-Benzyl-1,3-butadiene (**6n**)[16]: R_f 0.66 (hexane/ether:5/1); ν (liq.) 3080, 3060, 1600, 870 and 800 cm^{-1} (C=CH); δ_H 3.46 (s, 2H, CH_2Ph), 4.82 (s, 1H, CH_2=C), 4.96 (d, *J*=10.8 Hz, 1H, C*H*$_2$=CH), 5.08 (s, 1H, CH_2=C), 5.16 (d, *J*=17.6 Hz, 1H, C*H*$_2$CH), 6.34 (dd, *J*=10.8 and 17.6 Hz, 1H, C*H*=CH_2) and 7.05-7.22 (m, 5H, Ph); δ_C 38.02 (CH_2Ph), 114.26, 118.13 (2x*C*H$_2$=C), 125.96, 128.22, 128.79, 129.51, 138.42 and 139.41 (Ph, *C*H=CH_2 and *C*=CH_2); *m/z* 145 (M^++1, 5%), 144 (M^+, 44), 143 (16), 130 (10), 129 (100), 128 (39), 127 (10), 115 (20), 91 (38) and 65 (16).

2-Methyl-5-methylene-6-hepten-3-ol (**10a**): R_f 0.40 (hexane/ether:5/1); ν (liq.) 3400 (OH), 3090, 1630, 1600, 900, 870 and 800 cm^{-1} (C=CH); δ_H 0.92, 0.93 [2d, *J*=6.8 Hz, 6H, $(CH_3)_2C$)], 1.70 (m, 1H, C*H*CH_3), 2.10 (dd, *J*=10.0 and 14.0 Hz, 1H, CH_2CO), 2.51 (ddd, *J*=0.8, 2.8 and 14.0 Hz, 1H, CH_2CO), 2.93 (br. s, 1H, OH), 3.47 (m, 1H, CHO), 5.05 (d, *J*=11.0 Hz, 1H, C*H*$_2$=CH), 5.06 (s, 1H, CH_2=C), 5.10 (dd, *J*=0.5 and 0.8 Hz, 1H, CH_2=C), 5.19 (d, *J*=17.5 Hz, 1H, C*H*$_2$=CH) and 5.34 (dd, =11.0 and 17.5 Hz, 1H, C*H*=CH_2); δ_C 17.45, 18.49 [(*C*H_3)$_2$CH], 33.30 (*C*HCH_3), 36.55 (*C*H_2CO), 73.79 (CHO), 114.03, 118.16 (2x*C*H_2=C), 138.31 (*C*H=CH_2) and 143.42 (*C*=CH_2); *m/z* 140 (M^+, 3%), 122 (23), 73 (30), 72 (13), 68 (41), 67 (39), 55 (39), 53 (25), 52 (11), 51 (18), 43 (49) and 41 (100).

2-Methyl-6-methylene-7-octen-4-ol [(±)-Ipsenol] (**10b**)[17]: R_f 0.40 (hexane/ether:5/1); ν (liq.) 3400 (OH), 3080, 1600, 870 and 800 cm^{-1} (C=CH); δ_H 0.86 [2d, *J*=6.5 Hz, 6H, $(CH_3)_2C$)], 1.19, 1.39 (2m, 2H, C*H*$_2$CCH_3), 1.75 (m, 1H, C*H*CH_3), 1.95 (br. s, 1H, OH), 2.14 (dd, *J*=9.0 and 14.0 Hz, 1H, CH_2C=C), 2.42 (dd, *J*=3.5 and 14.0 Hz, 1H, CH_2C=C), 3.75 (m, 1H, CHO), 5.02 (s, 1H, CH_2=C), 5.03 (d, *J*=10.5 Hz, 1H, C*H*$_2$=CH), 5.09 (t, *J*=1 Hz, 1H, CH_2=C), 5.18 (d, *J*=17.5 Hz, 1H, C*H*$_2$=CH) and 6.32 (dd, =10.5 and 17.5 Hz, 1H, C*H*=CH_2); δ_C 22.10, 23.43 [(*C*H_3)$_2$CH], 24.71 (*C*HCH$_3$), 40.55 (*C*H_2C=C), 46.40 (*C*H_2CH), 67.62 (CHO), 114.20, 118.42 (2x*C*H_2=C), 138.50 (*C*H=CH_2) and 143.15 (*C*=CH_2); *m/z* 154 (M^+, <1%), 93 (16), 85 (22), 69 (67), 68 (100), 67 (43), 57 (13), 53 (11), 45 (13), 43 (24) and 41 (31).

2-Ethyl-3,4-bis(methylene)tetrahydrofuran (**14**): Yield 69 %; bp 75°C/18 torr; R_f 0.33 (hexane); ν (liq.) 3070, 1590 and 900 cm^{-1} (C=CH); δ_H 0.89 (t, *J*=7.0 Hz, 3H, CH_3), 1.60, 1.80 (2m, 2H, C*H*$_2$$CH_3$), 4.34,

4.44 (2dt, J=13.0 and 2.5 Hz, 2H, CH_2O), 4.82 (d, J=2.5 Hz, 1H, CH_2=CCH), 4.88 (t, J=2.5 Hz, 1H, CH_2=CCH_2), 5.32 (m, 1H, CHO), 5.36 (t, J=2.5 Hz, 1H, CH_2=CCH_2) and 5.40 d, J=2.5 Hz, 1H, CH_2=CCH); δ_C 9.28 (CH_3), 27.51 (CH_2CH_3), 70.84 (CH_2O), 83.16 (CHO), 102.23, 102.73 (2xCH_2=C), 145.14 and 147.57 (2xC=CH_2); m/z 124 (M^+, 19%), 95 (100), 67 (47), 65 (37), 57 (24), 53 (13), 51 (26), 43 (18), 42 (17) and 41 (29).

Diels-Alder Reaction of Compounds 6 with Dienophiles. General Procedure. A solution cooled at 0°C of corresponding diene **6** (0.01 mmol) and dienophile **15** (0.01 mmol) in THF or ether (1 mL) was stirred at room temperature for the time and in the presence of the catalyst (0.02 mmol for $AlCl_3$ and 0.1 mmol for SiO_2[19]) as indicated in Table 3. Water was added and the aqueous layer was extracted with ether (2x5 mL). The organic layer was dried over Na_2SO_4 and evaporated *in vacuo* (15 torr) to give crude pure products **16**. Yields and physical data are included on Table 3, spectral and analytical data follow:

4-[(S)-N-(1-Phenylethyl)aminomethyl]-4-cyclohexene-1,2-dicarboximide (1/1 mixture of diastereoisomers) (**16a**): ν (liq.) 1740, 1715 and 1700 cm^{-1} (3xC=O); δ_H 1.20 (2d, J=6.5 Hz, 3H, CH_3), 2.23, 2.59 (2m, 5H, 2xCH_2C=C and NH), 2.97, 2.99 (2s, 2H, CH_2N), 3.16 (m, 2H, 2xCHCO), 3.60 (m, 1H, CHN), 5.70 (m, 1H, CH=C) and 7.05-7.43 (m, 10H, ArH); δ_C 22.64, 22.66 (CH_3), 24.27, 24,28, 26.43, 26.61 (2xCH_2C=C), 39.31, 39.40 (CHCO), 52.15, 52.40 (CH_2N), 57.29, 57.65 (CHN), 126.11, 127.93, 128.49, 129.02, 129.17, 129.33, 130.10, 130.66, 131.19, 134.16 (ArC and C=C), 179.00 and 179.09 (CO); m/z 361 (M^++1, 1%), 360 (M^+, 4), 255 (23), 176 (13), 121 (10), 120 (100), 106 (73), 105 (71), 93 (38), 92 (12), 91 (50), 79 (30), 77 (52) 55 (14) and 43 (11).

(S)-*4-[2-(6-Methoxy-2-naphthyl)propanecarbonyloxymethyl]-1,2,3,6-tetrahydrophthalicAnhydride*(1/1 mixture of diastereoisomers) (**16b**): ν (liq.) 1740, 1720 and 1700 cm^{-1} (3xC=O); δ_H 1.57, 1.58 (2d, J=7 Hz, 3H, CH_3CH), 2.15-2.59 (m, 4H, 2xCH_2C=C), 3.28 (m, 2H, 2xCHCO$_2$), 3.86 (q, J=7.0 Hz, 1H, CHCH$_3$), 3.90 (s, 3H, CH_3O), 4.40-4.54 (m, 2H, CH_2O), 5.78-5.85 (m, 1H, CH=C) and 7.11-7.71 (m, 6H, ArH). δ_C 18.12, 18.17 (CH_3CCO), 23.64, 23.65, 24.56, 24.66 (2xCH_2C=C), 39.25, 39.64, 39.61 (2xCHCO$_2$), 45.33, 45.31 (CHCH$_3$), 55.26 (CH_3O), 66.42, 66.55 (CH_2O), 105.56, 118.98, 124.55, 124.73, 126.05, 126.20, 126.21, 127.12, 128.87, 129.24, 133.69, 134.94, 134.99, 135.31, 135.36, 157.63 (ArC and C=C), 173.49, 173.53 (COOCO), 174.18 and 174.27 (CO_2CH_2), m/z 396 (M^++2, 1%), 395 (M^++1, 6), 395 (M^+, 15), 229 (40), 212 (39), 186 (18), 185 (100), 151 (10) and 44 (50).

[4-(N-Phenyl-4-cyclohexene-1,2-dicarboximide)]methyl (S)-*2-(6-Methoxynaphthyl)propanoate* (1/1 mixture of diastereoisomers) (**16c**): ν (liq.) 1750, 1720 and 1700 cm^{-1} (3xC=O); δ_H 1.55, 1.58 (2d, J=7.2 Hz, 3H, CH_3CH), 2.33, 2.70 (2m, 4H, 2xCH_2C=C), 3.24 (m, 2H, 2xCHCO$_2$), 3.86 (q, J=7.2 Hz, 1H, CHCH$_3$), 3.94, 3.95 (2s, 3H, CH_3O), 4.4-4.54 (m, 2H, CH_2O), 5.87 (m, 1H, CH=C), 7.05-7.75 (m, 11H, ArH); δ_C 18.18, 18.50 (CH_3CCO), 21.64, 21.16, 24.98, 25.16 (2xCH_2C=C), 39.10, 39.11, 39.31, 39.33 (2xCHCON), 45.29, 45.37 (CHCO$_2$), 55.28 (CH_3O), 66.67, 66.80 (CH_2O), 105.58, 118.93, 124.61, 124.73, 125.94, 126.00, 126.26, 126.47, 126.52, 127.10, 128.59, 128.89, 129.08, 129.27, 129.40, 129.71, 131.99, 133.66, 135.17, 135.22, 135.54, 157.61 (ArC and CH=C), 174.23, 174.37 (COO), 178.46 and 178.82 (2xCON); m/z 471 (M^++2, 1%), 470 (M^++1, 5), 469 (M^+, 16), 229 (31), 212 (31), 186 (16), 185 (100), 170 (13), 141 (10), 93 (13), 91 (16) and 77 (13).

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REFERENCES AND NOTES

1. Nájera, C.; Sansano, J. M. *Tetrahedron* **1992**, *48*, 5179-5190.
2. (a) Breuilles, P.; Uguen, D. *Tetrahedron Lett.* **1988**, *29*, 201-204. (b) Breuilles, P.; Uguen, D. *Tetrahedron Lett.* **1987**, *28*, 6053-6056.
3. (a) Nájera, C.; Sansano, J. M. *Tetrahedron Lett.* **1992**, *33*, 6543-6546. (b) Nájera, C.; Sansano, J. M. *Tetrahedron* **1994**, in the press.
4. The corresponding monolithium intermediate derived from the homologous phenylsulfonyl compound has been described[2a].
5. (a) Kocienski, P. J. *Tetrahedron Lett.* **1979**, 2649-2650. (b) Kocienski, P. J. *J. Org. Chem.* **1980**, *45*, 2037-2039.
6. β-Stannyl sulfones gave the same elimination reaction to afford carbon-carbon double bonds: (a) Ochiai, M.; Tada, S.; Sumi, K.; Fujita, E. *Tetrahedron Lett.* **1982**, *23*, 2205-2208. (b) Pearlmann, B. A.; Putt, S. R.; Fleming, J. A. *J. Org. Chem.* **1985**, *50*, 3622-3624.
7. (a) Fringuelli, F.; Taticchi, A. In *Dienes in the Diels-Alder Reaction*; John Wiley & Sons: New York, 1990. (b) Bailey, W. J.; Carpenter, W. G.; Hermes, M. E. *J. Org. Chem.* **1962**, *27*, 1975-1978. (c) Sakurai, H.; Hosomi, A.; Saito, M.; Sasaki, K.; Iguchi, H.; Sasaki, J.; Araki, Y. *Tetrahedron* **1983**, *39*, 883-894. (d) Bloch, R.; Chaptal-Gradoz, N. *Tetrahedron Lett.* **1992**, *33*, 6147-6150. (e) Kozikowski, A. P.; Ognyanov, V. I.; Chen, C.; Kurian, P.; Crews, F. T. *Tetrahedron Lett.* **1993**, *34*, 219-222. (f) Chen, J-K.; Chen, C.-M.; Lin, W.-Y. *Tetrahedron Lett.* **1993**, *34*, 2961-2962. (g) Masuyama, Y.; Fuse, M.; Kurusu, Y. *Chem Lett.* **1993**, 1199-1202.
8. (a) Brown, P. A.; Jenkins, P. R. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1303-1309. (b) Bonnert, R. V.; Jenkins, P. R. *J. Chem. Soc., Perkin Trans. 1* **1989**, 413-418. (c) Shea, K. J.; Haffner, C. D. *Tetrahedron Lett.* **1988**, *29*, 1367-1370. (d) Jackson, R. W.; Highby, R. G.; Gilman, J. W.; Shea, K. J. *Tetrahedron* **1992**, *48*, 7013-7032. (e) Sakan, K.; Smith, D. A.; Babirad, S. A.; Fronczek, F. R.; Houk, K. N. *J. Org. Chem.* **1991**, *56*, 2311-2317.
9. (a) Riley, R. G.; Silverstein, R. M.; Katzenellenbogen, J. A.; Lenox, R. S. *J. Org. Chem.* **1974**, *39*, 1957-1958. (b) Borg-Visse, F.; Dawans, F. *Synthesis* **1979**, 817-818. (c) García Martínez, A.; Marco Contelles, J. L. *Synthesis* **1982**, 742-743. (d) Brown, H. C.; Randad, R. S. *Tetrahedron Lett.* **1990**, *31*, 455-458.
10. Arenz, T.; Frauenrath, H. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 932-933.
11. For preliminary communication, see: Nájera, C.; Sansano, J. M. *Tetrahedron Lett.* **1993**, *34*, 3781-3784.
12. The alkylation of α-lithiated sulfones with iodomethyltrimethyl-silane[5] or -stannane[6a,b] is the most simple way for β-silyl or β-stannyl sulfones, respectively.
13. Tottie, L.; Baeckström, P.; Moberg, C.; Tegenfeldt, J.; Heumann, A. *J. Org. Chem.* **1992**, *57*, 6579-6587.

14. Sato, T.; Otera, J.; Nozaki, H. *J. Org. Chem.* **1992**, *57*, 2166-2169. Sodium iodide was also added to generate *in situ* the iodine derivative **8k** (X=I).
15. For recent applications of this elimination reaction in synthesis of methylenecyclopropanes derivatives see: (a) Hsiao, C.; Hannick, S. M. *Tetrahedron Lett.* **1990**, *31*, 6609-6612. (b) Baldwin, J. E.; Adlington, R. M.; Bebbington., D.; Russell, A. T. *J. Chem. Soc., Chem. Commun.* **1992**, 1249-1251. (c) Ramaswamy, S.; Prasad, K.; Repic, O. *J. Org. Chem.* **1992**, *57*, 6344-6347. (d) Achmatowicz, B.; Kabat, M. M.; Krajewski, J.; Wicha, J. *Tetrahedron* **1992**, *48*, 10201-10210.
16. Nunomoto, S.; Kawakami, Y.; Yamashita, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2831-2832.
17. Imai, T.; Nishida, S. *J. Org. Chem.* **1990**, *55*, 4949-4852.
18. For syntheses of ipsenol see: Trost, B. M.; Rodríguez, M. S. *Tetrahedron Lett.* **1992**, *33*, 4675-4678 and references cited therein.
19. Veselovsky, V. V.; Gybin, A. S.; Lozanova, A. V.; Moiseenkov, A. M.; Smit, W. A.; Caple, R. *Tetrahedron Lett.* **1988**, *29*, 175-178.

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