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A SIMPLE METHOD FOR THE SYNTHESIS OF γ-FUNCTIONALIZED VINYL AND ALLYL SULFONES

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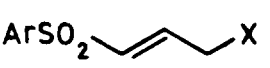
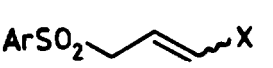
Abstract: The synthesis of γ-functionalized vinyl sulfones **3** have been carried out directly starting from dibromides **2** derived from allyl sulfones **1** by reaction with different nucleophiles. The process is stereoselective affording compounds **3** with *E* configuration except in the case of methallylic derivatives. The regioisomeric γ-functionalized allyl sulfones **4** were obtained from dibromides **2** or from vinyl sulfones **3**, with *Z* configuration, except when triphenylphosphine was used as nucleophile, in this case the corresponding (*E*)-vinylphosphonium bromide **4al** was obtained.

Vinyl and allyl sulfones are the most synthetically useful sulfones in Organic Chemistry.[1] The reactivity of vinyl sulfones[1,2] is based in three types of general reactions: (a) Michael type additions, (b) cycloadditions reactions, and (c) formation of vinylic anions. In the case of allyl sulfones[1] the most interesting reactions are: (a) formation of allylic anions, (b) nucleophilic or radical substitution of the arylsulfonyl group, and (c) allylic 1,3-rearrangement. In connection with our studies on carbanions derived from vinyl sulfones[3] we were interested in the synthesis of γ-functionalized vinyl **I** and also in their regioisomeric allyl sulfones **II**. The general methods described for the synthesis of this type of compounds are based on the nucleophilic substitution of: (1) 3-bromo- or 3-chloro-alkenyl aryl sulfones[4] and (2) allylidene disulfones.[5] The first method is more convenient for the synthesis of the corresponding sulfones **I** and **II** since the second one works only with α-alkylated acyclic derivatives.



I

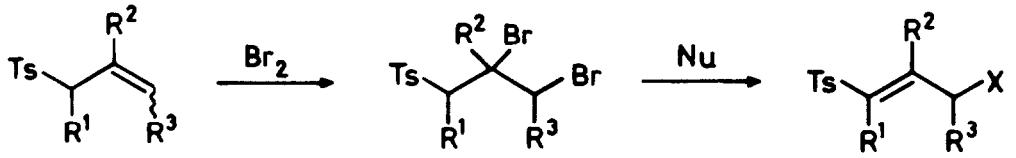


II

We now report a simpler and more convenient method for the synthesis of γ-functionalized vinyl and allyl sulfones of the type **I** and **II** respectively, starting from the dibromo derivatives of allyl sulfones based on the in situ generation of 3-bromo-1-alkenyl *p*-tolyl sulfones.[4]

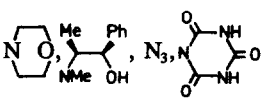
RESULTS AND DISCUSSION

The reaction of dibromo derivatives **2**, easily prepared by addition of bromine in carbon tetrachloride to allyl sulfones **1**, with different nucleophilic reagents afforded γ-functionalized vinyl sulfones **3** in good yields (Scheme 1 and Table 1). The process takes place, in general, with two equivalents of the nucleophile under different reaction conditions depending on the nature of both reactants and is steroselective affording the corresponding *E* isomers except in the case of methallylic derivatives of **2b**. In general, the in situ generated γ-tosylated allyl bromides **3** (X=Br) suffered the corresponding nucleophilic displacement S_N2^{4a} before their isomerization[7] to the corresponding unwanted vinyl bromides **4** (X=Br) took place.



1 **2** **3**

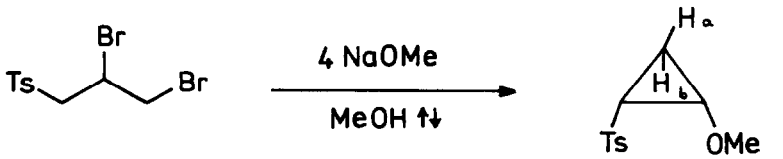
a: $R^1 = R^2 = R^3 = H$
b: $R^1 = R^3 = H$, $R^2 = Me$
c: $R^1 = R^2 = H$, $R^3 = Me$
d: $R^1 - R^3 = -(CH_2)_3-$, $R^2 = H$

[X = Br, OMe, OAc, OH, NHPh,  , N_3, , Ts, $CH(CO_2Me)_2$]

Scheme 1

When sodium methoxide was used as nucleophile at room temperature only the dehydrobromination reaction was observed affording the corresponding γ-tosylated allylic bromides **3aa-3da** (Table 1, entries 1-4). Compound **3aa** was obtained impurified by its regioisomer (*Z*)-**4aa** and not by its stereoisomer (*Z*)-**3aa**

as it has been described for the dehydrobromination of 1,2-dibromo-3-(phenylsulfonyl)propane with triethylamine[8] (see below). The corresponding methoxy derivatives **3ab-3db** have been achieved using one equivalent of sodium methoxide under methanol reflux (Table 1, entries 5-7). When compound **2a** was allowed to react with an excess of sodium methoxide the *cis*-cyclopropyl sulfone **5**[9] was obtained (Scheme 2 and Table 1, entry 8). Compound **5** results from the Michael addition of methoxide anion to the in situ generated (*E*)-3-bromo-1-tosyl-1-propene (**3aa**) following the cyclopropanation reaction[10]. This type of sulfones has been used as homoenolate precursors[11] being our method more direct than the described[12] for the synthesis of such type of compounds.



2a **5**

Scheme 2

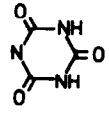
The acetates derivatives **3ac-3dc** were prepared by reaction of compounds **2** with two equivalents of sodium acetate in DMSO (Table 1, entries 9-12). In the case of sodium nitrite the reaction with dibromide **2a** failed and it was necessary to start from the monobromide **3aa**, which reacted with this nucleophile in anhydrous conditions to yield alcohol **3ad** (Table 1, entry 13). This product arises probably from the *O*-allylation of the nitrite anion and further hydrolysis of the allyl nitrite during the work-up.

As nitrogen-containing nucleophiles have been tested amines, sodium azide, and potassium cyanate. With three or four equivalents of amines such as aniline or morpholine in dichloromethane or THF, the secondary or tertiary γ-tosylated allylic amines **3ae**, **3ce** or **3af-3df** were respectively obtained (Table 1, entries 14-19). In order to prepare a quiral amine derivative, potentially useful in asymmetric induction, (*L*)-(-)-ephedrine was allowed to react with **2a** at room temperature giving the allylic amine **3ag** together with the morpholine derivatives **6**. Products **3ag** and **6** can be separated by column chromatography and products **6** can be exclusively obtained when the reaction was carried out under dichloromethane reflux (Scheme 3 and Table 1, entries 20 and 21). Compounds **6** were obtained as a mixture of diastereoisomers **6a** and **6b** in a 3/1 molar ratio (^{1}H-NMR) as result of the intramolecular Michael addition of the hydroxy group from ephedrine to the vinyl sulfone. The mayor isomer **6a** was obtained in pure form by recrystallization and its configuration was assigned according to the positive NOE effect observed between 2-H and 6-H.

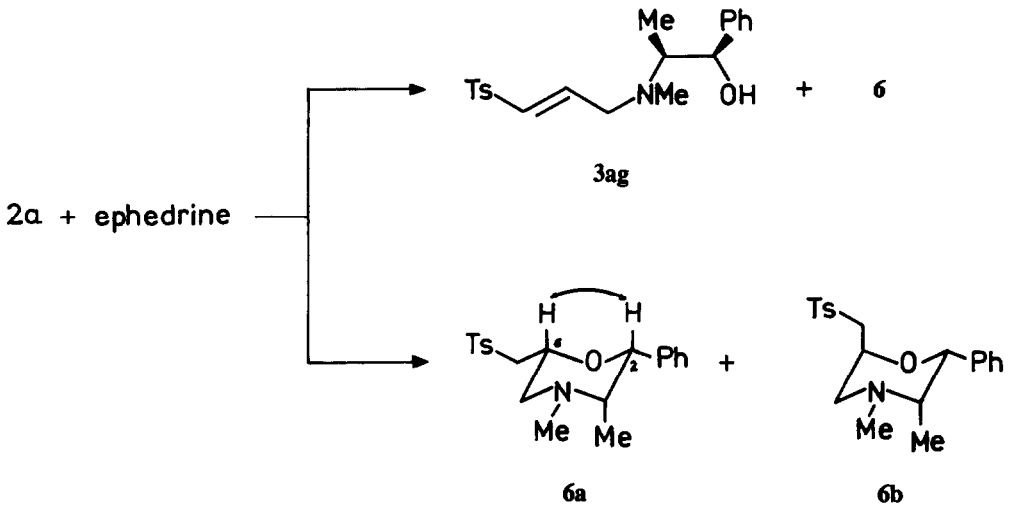
Table 1. Synthesis of γ-Functionalized Vinyl Sulfones **3**.

Entry	Starting compound	Reaction conditions				Product		
		Nu (equiv.)	Solvent	T (°C)	Time	no.	X	Yield (%)[a]
1	**2a**	NaOMe (1)	MeOH	rt	1d	**3aa**[b]	Br	78
2	**2b**	NaOMe (1)	MeOH	rt	1d	**3ba**[c]	Br	98[d]
3	**2c**	NaOMe (0.6)	MeOH	rt	1d	**3ca**	Br	50
4	**2d**	NaOMe (3)	MeOH	rt	30 min.	**3da**	Br	98
5	**2a**	NaOMe (1)	MeOH	reflux	6d	**3ab**	OMe	95
6	**2c**	NaOMe (1)	MeOH	reflux	7d	**3cb**	OMe	75
7	**2d**	NaOMe (1)	MeOH	reflux	7d	**3db**	OMe	69
8	**2a**	NaOMe (4)	MeOH	reflux	7d	**5**	-	61
9	**2a**	NaOAc (2)	-[e]	rt	1d	**3ac**[f]	OAc	99[d]
10	**2b**	NaOAc (2)	-[e]	rt	1d	**3bc**[c]	OAc	90[d]
11	**2c**	NaOAc (2)	DMSO	100	1d	**3cc**[f]	OAc	60
12	**2d**	NaOAc (2)	DMSO	100	3d	**3dc**	OAC	51
13	**3aa**	$NaNO_2$ (2)	DMSO	rt	3h	**3ad**[g]	OH	87
14	**2a**	$PhNH_2$ (4)	CH_2Cl_2	reflux	2d	**3ae**	NHPh	99[d]
15	**2c**	$PHNH_2$ (3)	THF	reflux	1d	**3ce**	NHPh	62
16	**2a**	Morpholine (3)	CH_2Cl_2	reflux	4h	**3af**		99

Table 1. Cont.

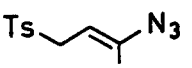
17	**2b**	Morpholine (3)	CH_2Cl_2	reflux	1d	**3bf**[a]		98[d]
18	**2c**	Morpholine (3)	CH_2Cl_2	reflux	1d	**3cf**		97
19	**2d**	Morpholine (3)	CH_2Cl_2	reflux	2d	**3df**		66
20	**2a**	Ephedrine (4)[i]	CH_2Cl_2	rt	1d	**3ag**		46[j]
21	**2a**	Ephedrine (4)[i]	CH_2Cl_2	reflux	1d	**6**	-	80[k]
22	**2a**	NaN_3 (2)	-[e]	rt	3h	**3ah**	N_3	59
23	**2b**	NaN_3 (2)	-[e]	rt	1d	**3bh**[c]	N_3	90[d]
24	**2c**	NaN_3 (1.75)	DMF	rt	1d	**3ch**	N_3	78
25	**2d**	NaN_3 (2)	-[e]	rt	1d	**3dh**	N_3	90
26	**2a**	KNCO (2)	-[e]	reflux	1d	**3ai**		37
27	**2a**	NaTs (2)	DMF	reflux	1d	**3aj**	Ts	61
28	**2a**	$NaCH(CO_2Me)_2$ (2)[l]	THF	rt	1d	**3ak**	$CH(CO_2Me)_2$	40[m]

[a]Based on starting dibromide **2**, after column chromatography. [b]A 15% of compound (*Z*)-**4aa** has been also obtained. [c]Mixture of *Z*/*E*-stereoisomers (1/1). [d]Isolated crude pure compound (^{1}H-NMR, tlc). [e]A 1:1 mixture of CH_2Cl_2/DMSO was used. [f]See reference 6. [g]See reference 3c. [h]Mixture of *Z*/*E*-stereoisomers (1/2). [i]Prepared from the corresponding chlorhydrate. [j]A 40% of compound **6** was also obtained. [k]Mixture of diastereoisomers all *cis*/*trans*:3/1. [l]Prepared from dimethyl malonate and sodium hydride in THF. [m]A 25% of compound **7** was also obtained.



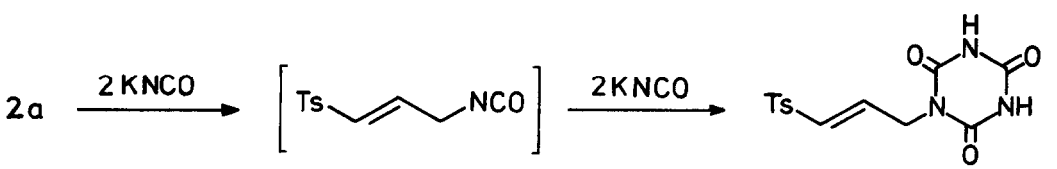
Scheme 3

The corresponding γ-tosylated allylic azides **3ah-3dh** (Table 1, entries 22-25) were prepared by treatment of dibromides **2** with two equivalents of sodium azide in CH_2Cl_2-DMSO or DMF as solvents. In the case of compound **3ch**, 1.75 equivalents of nucleophile have to be used in order to avoid its isomerization to the allyl sulfone **4ch** (see below).



4ch

The last nitrogen-containing nucleophile used was potassium cyanate, which by reaction with dibromide **2a** in a mixture of CH_2Cl_2-DMSO afforded the cyanuric acid derivative **3ai** (Table 1, entry 26), probably formed by reaction of the intermediate allylic isocyanate with potassium cyanate (Scheme 4).



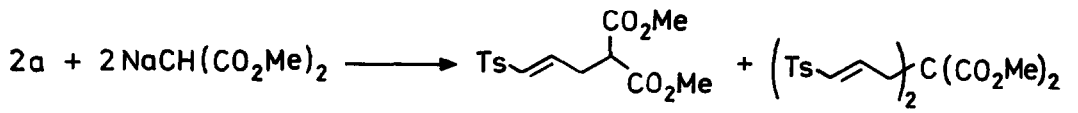
3ai

Scheme 4

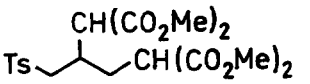
Disulfone **3aj**[13] was prepared by reaction of **2a** with two equivalents of sodium *p*-toluenesulfinate

under DMF reflux (Table 1, entry 27). This class of compounds has been used in the synthesis of electron-deficient dienes by Knoevenagel-type condensation.[14]

Finally, sodium dimethyl malonate reacted with dibromide **2a** to give a mixture of products **3ak** and **7** in 1.6:1 molar ratio resulting from mono- and diallylation of dimethyl malonate (Scheme 5 and Table 1, entry 28). These products can be easily separated by column chromatography. Attempts to avoid the formation of compound **7** changing the addition order (**2a** over sodium dimethyl malonate) exclusively gave compound **8** (40% yield, Scheme 5).



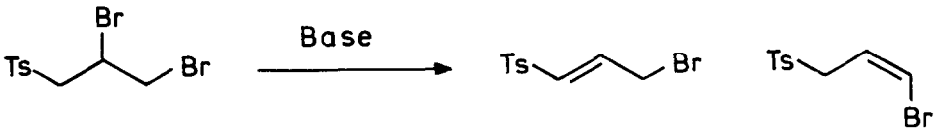
3ak **7**



8

Scheme 5

From these results we conclude that this method constitutes an easy way to prepare γ-functionalized vinyl sulfones **3** starting from dibromides derived from allyl sulfones, avoiding the isolation of γ-tosylated allyl bromides when the nucleophile is basic enough to carry out the in situ dehydrobromination reaction. Only in the case of sodium nitrite the reaction has to be carried out with the allylic bromide **3aa**. The need of the corresponding monobromides when poor basic nucleophiles have to be used prompted us to study the elimination reaction specially for compound **2a** (see above). Thus, we studied the reaction of dibromide **2a** with one equivalent of different bases (Scheme 6 and Table 2). The reaction with triethylamine or sodium methoxide gave the same mixture of regioisomers **3aa** and **4aa** in 3:1 molar ratio (from ^{13}C- and ^{1}H-NMR spectra of the crude reaction mixture). The *Z*-isomer of **3aa** was no detected as it has been previously



2a **3aa** **4aa**

Scheme 6

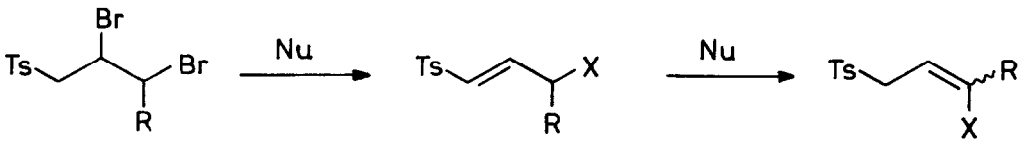
Table 2. Reaction of Dibromide **2a** with Bases.

Base	Reaction conditions			Product	
	Solvent	T (°C)	Time	no.	Yield %[a]
Et_3N	THF	0	3h	**3aa** + **4aa**[b]	87
NaOMe	MeOH	rt	1d	**3aa** + **4aa**[b]	98
Morpholine	CH_2Cl_2	reflux	1d	**3aa**	74
NaN_3	-[c]	rt	2d	**2a** + **3aa** + **3ah**[d]	100
NaOAc	DMSO	rt	1d	**3aa**	82

[a]Based on compound **2a**. Isolated crude product. [b]Molar ratio : 3/1. [c]A 1/1 mixture of CH_2Cl_2/DMSO was used. [d]Molar ratio : 2/1/3.

reported.[8] Morpholine and sodium acetate gave regioselectively compound **3aa** but sodium azide afforded a mixture of unreacted **2a**, **3aa**, and **3ah**. Consequently the best bases, tried by us, for the synthesis of **3aa** are morpholine and sodium acetate, under these conditions no isomerization to vinyl bromide **4aa** was observed.

The synthesis of thermodynamically more stable[15] γ-functionalized allyl sulfones of the type II (e.g. compounds **4**) was tried to carried out treating dibromides **2** with an excess of nucleophile or by isomerization of vinyl sulfones **3** (Scheme 7 and Table 3). The direct preparation of compounds **4** from **2** took place with sodium methoxide and sodium azide affording the bromide **4ca** and the vinyl azides **4ah**, and **4ch** respectively (Table 3, entries 1-3). Triethylamine also gave the vinyl bromide **4aa** when starting from compound **2a** (Table 3, entry 4). The isomerization of vinyl to allyl sulfones was only observed when acetate **3ac** was treated with triethylamine affording the vinyl acetate **4ac**. The stereochemistry of compounds **4** was



2 **3** **4**

Scheme 7

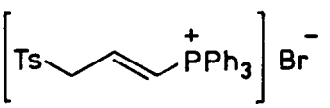
exclusively *Z* for R=H and mainly *Z* for R=Me.[16] We assigned the most shielded signal of the methyl groups in the ^{1}-H-NMR spectra of compounds **4** (R=Me) to the *Z* isomer and not to the *E* as it was previously made.[4a] Finally, triphenylphosphine reacted with monobromide **3aa** in toluene reflux to afford

Table 3. Synthesis of γ-Functionalized Allyl Sulfones 4.

Entry	Starting compound	Nu or Base (equiv.)	Reaction conditions			Product		
			Solvent	T (°C)	Time	no.	X	Yield %[a]
1	2c	NaOMe (2)	MeOH	rt	12h	4ca[b]	Br	79
2	2a	NaN_3 (2.5)	-[c]	rt	1d	4ah	N_3	79
3	2c	NaN_3 (4)	-[c]	reflux	1d	4ch[d]	N_3	32
4	2a	Et_3N (1.5)	THF	rt	1d	4aa	Br	78[e]
5	3ac	Et_3N (1)	CH_2Cl_2	rt	2d	4ac	OAc	86
6	3aa	PPh_3 (1)	$PhCH_3$	reflux	1d	4al	PPh_3	99

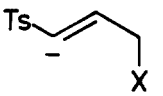
[a]Based on starting compound. Isolated compound after purification. [b]Mixture 7/1 of *Z/E* stereoisomers. [c]A 1/1 mixture of CH_2Cl_2/DMSO was used. [d]Mixture 10/1 of *Z/E* stereoisomers. [e]A 25% of **3aa** was also obtained.

regio and stereoselectively the vinylphosphonium salt **4al** with *E* configuration. This compound can be presumably used in the synthesis of substituted cyclopentadienes via a [3+2] anulation process.[17]

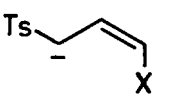


4al

Studies are also in course on the use of these γ-functionalized vinyl and allyl sulfones as precursors of functionalized vinylic and allylic anions of the type III and IV.



III



IV

EXPERIMENTAL

General. Melting points were obtained with a Reichert thermovar apparatus and are uncorrected. Spectra were recorded with the following instruments: IR, Pye Unicam SP3-200; NMR, Bruker AC-300 , recorded in $CDCl_3$ with TMS as internal standard, ^{13}C NMR assignments were done on the basis of DEPT experiments ; MS, Hewlett-Packard 5988A (EI, 70eV). $[\alpha]_D$, Optical Activity AA-100 polarimeter. Microanalyses were performed by the Microanalyses Service of the University of Zaragoza. T.l.c. analyses were carried out on Merck Kieselgel 60F-254 plates (visualization by UV) and column chromatography was performed on Merck Kieselgel 60 (70-230 mesh). Solvents were dried as usually.

Synthesis of Allyl Sulfones Dibromides 2. General Procedure.[8] To a solution of allyl sulfone 1[3e] (45 mmol)

in CCl_4 (25 ml) was droped a solution of bromine (2.5 ml, 50 mmol) in CCl_4 (25 ml). After 4h stirring the precipitate[18] was filtered off, washed with CCl_4 and purified by recrystallization yielding compounds **2**.

1,2-Dibromo-3-tosylpropane (**2a**): 90%; mp 86-87°C (CH_2Cl_2/hexane); ν_{max} ($CHCl_3$) 1300 and 1140 cm^{-1} (SO_2); δ_H 2.46 (s, 3H, CH_3), 3.60 (dd, J=6.5, 15.0 Hz, 1H, 1xCH_2S), 3.78 (dd, J=6.5, 11.0Hz, 1H, 1xCH_2Br), 3.96 (m, 2H, 1xCH_2S and 1xCH_2Br), 4.53 (m, 1H, CHBr), 7.39, and 7.82 (2d, J=8.0Hz, 4H, ArH); δ_C 21.59 (CH_3), 36.49 (CH_2Br), 40.91 (CHBr), 61.90 (CH_2S), 128.09, 130.06, 135.88, and 145.45 (ArC); *m/z* 358 (M^++4, 3%), 356 (M^++2, 6), 354 (M^+, 3), 277 (24), 275 (23), 201 (26), 156 (45), 155 (41), 139 (43), 121 (31), 119 (32), 92 (47), 91 (100), 89 (20), 65 (50), and 41 (20). Anal. Calcd. for $C_{10}H_{12}Br_2S$: C, 33.73; H, 3.40. Found: C, 33.94; H, 3.48.

1,2-Dibromo-2-methyl-3-tosylpropane (**2b**): 99%; R_f 0.68 (hexane/ether:1/2); ν_{max} (film) 1300 and 1140 cm^{-1} (SO_2); δ_H 2.16 (s, 3H, CH_3CBr), 2.45 (s, 3H, CH_3Ar), 3.79, 3.95 (2d, J=14.5Hz, 2H, CH_2S), 4.13 (s, 2H, CH_2Br), 7.37, and 7.83 (2d, J=8.3Hz, 4H, ArH); δ_C 21.60 (CH_3Ar), 30.50 (CH_3CBr), 43.11 (CH_2Br), 58.37 (CBr), 65.17 (CH_2S), 127.89, 130.00, 137.50, and 145.21 (ArC); *m/z* 372 (M^++4, 1%), 370 (M^++2, 1), 368 (M^+, 1), 291 (34), 289 (33), 215 (28), 157 (88), 155 (36), 139 (21), 135 (41), 133 (41), 92 (51), 91 (100), 65 (46), 55 (34), and 53 (24).

(erythro/threo)-*2,3-Dibromo-1-tosylbutane* (**2c**): 82%; mp 66-68°C (CH_2Cl_2/hexane); ν_{max} ($CHCl_3$) 1300 and 1140 cm^{-1} (SO_2); δ_H 1.75, 1.80 (2d, $J_{erythro}$=6.6Hz, J_{threo}=6.3Hz, 3H, CH_3CH), 2.46 (s, 3H, CH_3Ar), 3.65, 3.92 (2m, 2H, CH_2S), 4.49 (m, 2H, 2xCHBr), 7.39, and 7.82 (2d, J=8.0Hz, 4H, ArH); δ_C 21.63 (CH_3Ar), 23.09 (CH_3CH-*threo*), 23.53 (CH_3CH-*erythro*), 48.71, 51.33 (2xCHBr-*erythro*), 49.04, 50.20 (2xCHBr-*threo*), 61.61 (CH_2-*erythro*), 62.05 (CH_2-*threo*), 128.11, 128.20, 130.04, 130.05, 135.92, and 145.41 (ArC); *m/z* 372 (M^++4, 1%), 370 (M^++2, 1), 368 (M^+, 1), 291 (34), 289 (33), 215 (28), 157 (88), 156 (24), 155 (36), 139 (21), 135 (41), 133 (41), 92 (51), 91 (100), 65 (46), 55 (34), and 53 (24). Anal. Calcd. for $C_{11}H_{14}Br_2O_2S$: C, 35.70; H, 3.81. Found: C, 36.05; H, 3.90.

(1R*, 2R*, 3R*)-*1,2-Dibromo-3-tosylcyclohexane* (**2d**): 89%; mp 142-143°C (CH_2Cl_2/hexane); ν_{max} ($CHCl_3$) 1300 and 1140cm^{-1} (SO_2); δ_H 1.70-2.15 (m, 6H, 3xCH_2), 2.46 (s, 3H, CH_3), 3.83 (m, 1H, CHS), 4.69 (m, 2H, 2xCHBr), 7.38 and 7.81 (2d, J=8.0Hz, 4H, ArH); δ_C 19.61, 20.64, 27.17 (3xCH_2), 21.61 (CH_3), 47.28, 52.79 (2xCHBr), 61.09 (CHS), 129.04, 129.81, 134.57, and 145.12 (ArC); *m/z* 317 (M^+-79, <1%), 315 (M^+-81, <1), 157 (15), 92 (21), 91 (38), 81 (18), 80 (15), 79 (100), 77 (21), 65 (32), and 53 (11). Anal. Calcd. for $C_{13}H_{16}Br_2O_2S$: C, 39.42; H, 4.07. Found: C, 39.19; H, 4.01.

Synthesis of γ-Functionalized Vinyl Sulfones 3 and Derivatives. General Procedure. A mixture of dibromide **2** (0.5 mmol) and nucleophile[19] (see Tables 1 and 2) in the corresponding solvent (ca. 5 ml) was stirred at the temperature and for the time indicated on Tables 1 and 2. The reaction was followed by t.l.c. and after extractive work-up compounds **3**, **5**, **6**, **7**, and **8** were isolated and purified by column chromatography or and by recrystallization.

(E)-*3-Bromo-1-tosyl-1-propene* (**3aa**): R_f 0.41 (hexane/ether:1/2); ν_{max} (film) 3020, 1620, 960 (CH=C), 1300, and 1140 cm^{-1} (SO_2); δ_H 2.44 (s, 3H, CH_3), 4.00 (d, J=7.0Hz, 2H, CH_2), 6.57 (d, J=14.5Hz, 1H, CHS), 6.98 (dt, J=14.5, 7.0Hz, 1H, $CHCH_2$), 7.35, and 7.67 (2d, J=8.0Hz, 4H, ArH); δ_C 21.54 (CH_3), 27.32 (CH_2), 127.79, 130.01, 136.54, 144.79 (ArC), 134.18, and 138.87 (CH=CH); *m/z* 276 (M^++2, 9%), 274 (M^+, 8), 155 (10), 139 (100), 131 (21), 92 (11), 91 (50), and 65 (26).

(Z,E)-*3-Bromo-2-methyl-1-tosyl-1-propene* (**3ba**): R_f 0.57 (hexane/ether:1/2); ν_{max} (film) 3030, 1610 (CH=C), 1300, and 1140 cm^{-1} (SO_2); δ_H 2.02, 2.26 (2s, 3H, CH_3CCH_2), 2.44 (s, 3H, CH_3Ar), 3.88, 4.57 (2s, 2H, CH_2), 6.18, 6.47 (2s, 1H, CHS), 7.35, 7.37, 7.78, and 7.82 (4d, J=8.0Hz, 4H, ArH); δ_C 16.16, 23.37 (CH_3CCH_2), 21.48, 21.52 (CH_3Ar), 27.11, 36.47 (CH_2), 127.19, 127.38, 129.84, 129.81, 138.24, 144.44, 144.55 (ArC), 128.28, 129.61,

148.75, and 149.39 (*C*H=*C*CH$_2$).

(E)-*3-Bromo-1-tosyl-1-butene* (**3ca**): R_f 0.52 (hexane/ether:1/2); ν_{max} (film) 3030, 1610, 960 (CH=C), 1300, and 1135 cm^{-1} (SO_2); δ_H 1.80 (d, J=6.7Hz, 3H, C*H*$_3$CH), 2.44 (s, 3H, C*H*$_3$Ar), 4.69 (m, 1H, CHBr), 6.49 (d, J=14.8Hz, 1H, CHS), 7.02 (dd, J=14.8, 6.7Hz, 1H, C*H*CHS), 7.36, and 7.77 (2d, J=8.1Hz, 4H, ArH); δ_C 21.43 (*C*H$_3$Ar), 24.12 (*C*H$_3$CH), 42.78 (CHBr), 127.59, 129.85, 136.50, 144.61 (ArC), 130.73, and 144.24 (CH=CH).

3-*Bromo-3-tosyl-1-cyclohexene* (**3da**): mp 96-97°C (hexane/ether); ν_{max} ($CHCl_3$) 3010, 1630 (CH=C), 1300, and 1140 cm^{-1} (SO_2); δ_H 1.75-2.45 (m with s at 2.44, 9H, 3xCH_2 and CH_3), 4.86 (m, 1H, CHBr), 7.06 (m, 1H, CHCS), 7.34, and 7.44 (2d, J=8.0Hz, 4H, ArH); δ_C 18.14, 22.50, 30.99 (3xCH_2), 21.53 (CH_3), 43.84 (CHBr), 128.12, 129.85, 135.27, 144.61 (ArC), 135.42, and 142.15 (*C*=*C*HCH$_2$); *m/z* 316 (M^++2, <1%), 314 (M^+, <1), 139 (100), 91 (11), 79 (15), and 77 (11). Anal. Calcd. for $C_{13}H_{15}BrO_2S$: C, 49.53; H, 4.80. Found: C, 50.02; H, 4.85.

(E)-*3-Methoxy-1-tosyl-1-propene* (**3ab**): mp 81-82°C (hexane/CH_2Cl_2); ν_{max} ($CHCl_3$) 3050, 1620, 940 (CH=C), 1300, and 1140 cm^{-1} (SO_2); δ_H 2.43 (s, 3H, C*H*$_3$Ar), 3.36 (s, 3H, CH_3O), 4.11 (dd, J=3.5, 2.5Hz, 2H, CH_2O), 6.56 (dt, J=15.0, 2.5Hz, 1H, CHS), 6.91 (dt, J=15.0, 3.5Hz, 1H, C*H*CH$_2$), 7.30, and 7.74 (2d, J=8.0Hz, 4H, ArH); δ_C 21.55 (*C*H$_3$Ar), 58.84 (CH_3O), 70.01 (CH_2O), 127.68, 129.86, 137.29, 144.35 (ArC), 130.62, and 141.66 (CH=CHS); *m/z* 226 (M^+, 26%), 183 (21), 149 (26), 139 (39), 91 (48), 71 (100), 65 (32), and 41 (22). Anal. Calcd. for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24. Found: C, 56.53; H, 6.18.

(E)-*3-Methoxy-1-tosyl-1-butene* (**3cb**): R_f 0.45 (hexane/ether:1/2); ν_{max} (film) 3020, 1620, 960 (CH=C), 1300, and 1140 cm^{-1} (SO_2); δ_H 1.27 (d, J=6,5Hz, 3H, CH_3CO), 2.43 (s, 3H, C*H*$_3$Ar), 3.29 (s, 3H, CH_3O), 3.96 (m, 1H, CHO), 6.52 (dd, J=15.0, 1.3Hz, 1H, CHS), 6.85 (dd, J=15.0, 4.9Hz, 1H, C*H*CHO), 7.34, and 7.77 (2d, J=8.0Hz, 4H, ArH); δ_C 19.59 (*C*H$_3$CO), 21.50 (*C*H$_3$Ar), 56.72 (CH_3O), 75.09 (CHO), 127.61, 129.84, 137.24, 144.34 (ArC), 130.48, and 146.12 (CH=CH); *m/z* 240 (M^+,5%), 140 (18), 139 (80), 129 (10), 91 (100), 89 (27), 85 (76), 77 (18), 65 (80), and 59 (57).

3-Methoxy-1-tosyl-1-cyclohexene (**3db**): R_f 0.53 (hexane/ether:1/2); ν_{max} (film) 3020, 1630, 810 (CH=C), 1300, and 1140 cm^{-1} (SO_2); δ_H 1.55, 1.83, 2.14 (3m, 6H, 3xCH_2), 2.43 (s, 3H, C*H*$_3$Ar), 3.42 (s, 3H, CH_3O), 3.92 (m, 1H, CHO), 7.01 (m, 1H, C*H*CHO), 7.33, and 7.74 (2d, J=8.1Hz, 4H, ArH); δ_C 19.15, 22.93, 26.95 (3xCH_2), 21.51 (*C*H$_3$Ar), 56.43 (CH_3O), 74.10 (CHO), 128.16, 129.73, 135.67, 144.32 (ArC), 135.50, and 142.80 (*C*H=*C*CH$_2$); *m/z* 267 (M^++1, 1%), 266 (M^+, 7), 140 (14), 139 (18), 127 (21), 111 (100), 110 (28), 95 (10), 91 (57), 89 (12), 83 (11), 81 (15), 79 (34), 77 (30), 71 (20), 67 (14), 65 (60), 63 (15), 55 (22), 53 (19), 51 (16), 45 (11), and 41 (19).

(cis)-*1-Methoxy-2-tosylcyclopropane* (**5**): mp 71-72°C (hexane/ether); ν_{max} ($CHCl_3$) 1300 and 1140 cm^{-1} (SO_2); δ_H 1.41 (m, 1H, H_b), 1.59 (q, J=6.7Hz, 1H, H_a), 2.45-2.53 (m with s at 2.45, 4H, CH_3 and CHS), 3.25 (s, 3H, CH_3O), 3.81 (m, 1H, CHO), 7.36, and 7.78 (2d, J=8.1Hz, 4H, ArH); δ_C 14.25 (CH_2), 21.55 (CH_3), 39.09 (CHS), 58.71 (CH_3O), 59.48 (CHO), 127.44, 129.85, 137.43, and 144.43 (ArC); *m/z* 211 (M^+-15, 2%), 91 (63), 89 (28), 71 (100), 65 (75), 63 (29), and 41 (37). Anal. Calcd. for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24. Found: C, 58.07; H, 6.33.

(E)-*3-Tosyl-2-propenyl acetate* (**3ac**):[6] R_f 0.31 (hexane/ether:1/2); ν_{max} (film) 3040, 1630, 945 (CH=C), 1730 (C=O), 1300, and 1140 cm^{-1} (SO_2); δ_H[6] 2.10 (s, 3H, CH_3CO), 2.45 (s, 3H, C*H*$_3$Ar), 4.78 (dd, J=4.0, 2.0Hz, 2H, CH_2), 6.58 (dt, J=15.0, 2.0Hz, 1H, CHS), 6.96 (dt, J=15.0, 4.0Hz, 1H, C*H*CH$_2$), 7.36, and 7.78 (2d, J=8.0Hz, 4H, ArH); δ_C 20.39 (*C*H$_3$CO), 21.43 (*C*H$_3$Ar), 61.28 (CH_2), 127.65, 129.88, 136.76, 144.54 (ArC), 131.46, and 138.74 (CH=CHS); *m/z* 254 (M^+, 5%), 212 (34), 183 (17), 157 (13), 139 (52), 119 (13), 99 (78), 92 (48), 91 (97),

89 (16), 77 (17), 65 (55), 63 (17), and 43 (100).

(Z,E)-*2-Methyl-3-tosyl-2-propenyl acetate* (**3bc**): R_f 0.51 (hexane/ether:1/5); ν_{max} (film) 3020, 1625 (CH=C), 1725 (C=O), 1300, and 1140 cm^{-1} (SO_2); δ_H 1.90, 2.09, 2.10, 2.13 (4s, 6H, CH_3CO and CH_3CCO), 2.45 (s, 3H, CH_3Ar), 4.55, 5.25 (2s, 2H, CH_2), 6.24, 6.39 (2s, 1H, CHS), 7.36, 7.80, and 7.82 (3d, J=8.0Hz, 4H, ArH); δ_C 14.44, 20.37, 20.41, 21.27, 21.42 (3xCH_3), 61.20, 65.95 (CH_2), 125.98, 127.03, 127.15, 128.02, 129.69, 138.24, 138.69, 144.15, 144.28, 149.16, and 149.85 (ArC and CH=C).

(E)-*1-Methyl-3-tosyl-2-propenyl acetate* (**3cc**):[6] R_f 0.43 (hexane/ether:1/2); ν_{max} (film) 3040, 1630, 950 (CH=C), 1720 (C=O), 1300, and 1140 cm^{-1} (SO_2); δ_H[6] 1.36 (d, J=6.5Hz, 3H, CH_3CH), 2.05 (s, 3H, CH_3CO), 2.43 (s, 3H, CH_3Ar), 5.51 (m, 1H, $CHCH_3$), 6.41 (dd, J=15.0, 1.5Hz, 1H, CHS), 6.80 (dd, J=15.0, 4.5Hz, 1H, CHCO), 7.25, and 7.67 (2d, J=8.0Hz, 4H, ArH); δ_C 19.23, 20.75, 21.41 (3xCH_3), 67.78 (CHO), 127.61, 129.83, 136.85, 144.47 (ArC), 130.59, 143.55 (CH=CHS), and 169.42 (C=O); *m/z* 268 (M^+, 17%), 226 (25), 209 (14), 183 (56), 157 (17), 139 (81), 113 (100), 92 (26), 91 (68), 89 (13), 71 (53), 65 (34), and 43 (66).

3-*Tosyl-2-cyclohexenyl acetate* (**3dc**): R_f 0.36 (hexane/ether:1/2); ν_{max} (film) 3040, 1640 (CH=C), 1720 (C=O), 1300, and 1140 cm^{-1} (SO_2); δ_H 1.63, 1.84, 2.22 (3m, 6H, 3xCH_2), 2.07 (s, 3H, CH_3CO), 2.43 (s, 3H, CH_3Ar), 5.41 (m, 1H, CHO), 6.87 (dt, J=3.5, 2.0Hz, 1H, CHCO), 7.34, and 7.74 (2d, J=8.0Hz, 4H, ArH); δ_C 18.93, 22.65, 26.91 (3xCH_2), 20.93 (CH_3CO), 21.50 (CH_3Ar), 67.14 (CHO), 128.19, 129.80, 135.34, 144.55 (ArC), 133.84, 144.46 ($CH=CCH_2$), and 170.11 (C=O); *m/z* 294 (M^+, 16%), 251 (23), 140 (18), 139 (100), 97 (47), 95 (18), 92 (43), 91 (97), 89 (21), 79 (36), 78 (18), 77 (53), 67 (24), 65 (77), 63 (21), 53 (13), 51 (17), 43 (99), and 41 (14).

(E)-*3-Tosyl-2-propen-1-ol* (**3ad**).[3c]

(E)-*Phenyl(3-tosyl-2-propenyl)amine* (**3ae**): mp 108-109°C (CH_2Cl_2/hexane); ν_{max} ($CHCl_3$) 3370 (NH), 3040, 1590, 940 (CH=C), 1300, and 1140 cm^{-1} (SO_2); δ_H 2.41 (s, 3H, CH_3), 3.95 (m, 2H, CH_2), 4.02 (br s, 1H, NH), 6.51 (d, J=8.0Hz, 2H, *o*-Ph), 6.55 (d, J=15.0Hz, 1H, CHS), 6.71 (t, J=7.5Hz, 2H, *p*-Ph), 7.02 (dt, J=15.0, 3.5Hz, 1H, $CHCH_2$), 7.15 (t, J=8.0Hz, *m*-Ph), 7.30, 7.72 (2d, J=8.0Hz, 4H, *p*-TolH); δ_C 21.45 (CH_3), 44.22 (CH_2), 112.77, 118.07, 128.77, 146.78 (Ph), 127.45, 129.19, 137.25, 144.25 (*p*-TolC); *m/z* 287 (M^+, 20%), 132 (80), 131 (17), 130 (100), 117 (11), 106 (53), 91 (16), 77 (40), 65 (18), and 51 (11). Anal. Calcd. for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 67.24; H, 6 26; N, 4.63.

(E)-*(1-Methyl-3-tosyl-2-propenyl)phenylamine* (**3ce**): mp 113-114°C (CH_2Cl_2/hexane); ν_{max} ($CHCl_3$) 3370 (NH), 3070, 1620, 960 (CH=C), 1300, and 1135 cm^{-1} (SO_2); δ_H 1.37 (d, J=6.8Hz, 3H, CH_3CH), 2.41 (s, 3H, CH_3Ar), 3 73 (br s, 1H, NH), 4.14 (m, 1H, CHN), 6.49 (m, 3H, *o*-Ph and CHS), 6.71 (t, J=7.5Hz, 1H, *p*-Ph), 6.97 (dd, J=15.0, 4 6Hz, 1H, CHCHN), 7.10 (t, J=7.8Hz, 2H, *m*-Ph), 7.28, and 7.68 (2d, J=8.1Hz, 4H, *p*-TolH); δ_C 20.24 (CH_3CH), 21.34 (CH_3Ar), 49.72 (CHN), 113.36, 118.02, 129.01, 145.83 (Ph), 127.24, 129.63, 137.16, 144.05 (*p*-TolC), 130.29, and 147.80 (CH=CHS); *m/z* 301 (M^+, 7%), 146 (55), 144 (39), 130 (100), 120 (61), 118 (21), 91 (80), 77 (68), and 65 (69). Anal. Calcd. for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.18; H, 6.56; N, 4 69.

(E)-N-*(3-Tosyl-2-propenyl)morpholine* (**3af**): R_f 0.41 (ether); ν_{max} (film) 3040, 1620, 950 (CH=C), 1300, and 1140 cm^{-1} (SO_2); δ_H 2.44 (br s, 7H, CH_3 and 2xCH_2CH_2O), 3.16 (d, J=5.4Hz, 2H, $CHCH_2N$), 3.68 (deform. t, J=4.5Hz, 4H, 2xCH_2O), 6.57 (d, J=15.0Hz, 1H, CHS), 6.91 (dt, J=15.0, 5.4Hz, 1H, $CHCH_2N$), 7.35, and 7 77 (2d, J=8.0Hz, 4H, ArH); δ_C 21.33 (CH_3), 53.31 (2xCH_2CH_2O), 58.08 ($CHCH_2N$), 66.50 (2xCH_2O), 127.44, 129.71, 137.10, 144.21 (ArC), 132.49, and 141.90 (CH=CHS); *m/z* 281 (M^+, 6%), 126 (57), 100 (100), 96 (32), 95 (27),

91 (34), 68 (21), 65 (23), 56 (22), 42 (27), and 41 (20).

(Z,E)-N-*(2-Methyl-3-tosyl-2-propenyl)morpholine* (**3bf**): R_f 0.51 (ether); ν_{max} (film) 3020, 1615 (CH=C), 1280, and 1130 cm^{-1} (SO_2); δ_H 1.96, 2.12 (2s, 3H, CH_3CCH_2), 2.37 (m, 4H, 2xCH_2CH_2O), 2.44 (s, 3H, CH_3Ar), 2.92, 3.48 (2s, 2H, CH_2C), 3.65 (m, 4H, 2xCH_2O), 6.33, 6.52 (2s, 1H, CHS), 7.35, and 7.80 (2d, J=7.8Hz, 4H, ArH); δ_C 16.00, 22.69 (CH_3CCH_2), 21.31 (CH_3Ar), 53.22, 53.28 (2xCH_2CH_2O), 57.15, 65.70 (CH_2CCH_3), 66.56, 66.66 (2xCH_2O), 126.84, 127.04, 129.56, 139.50, 143.92, 152.50, and 153.80 (ArC and C=CHS).

(E)-N-*(1-Methyl-3-tosyl-2-propenyl)morpholine* (**3cf**): R_f 0.43 (AcOEt); ν_{max} (film) 3030, 1610, 950 (CH=C), 1300, and 1140 cm^{-1} (SO_2); δ_H 1.18 (d, J=6.7Hz, 3H, CH_3CH), 2.35-2.48 (m with s at 2.44, 7H, CH_3Ar and 2xCH_2N), 3.18 (q, J=6.7Hz, 1H, $CHCH_3$), 3.68 (t, J=4.4Hz, 2XCH_2O), 6.47 (d, J=15.2Hz, 1H, CHS), 6.91 (dd, J=15.2, 6.8Hz, 1H, CHCHN), 7.35, and 7.77 (2d, J=8.0Hz, 4H, ArH); δ_C 15.38 (CH_3CH), 21.32 (CH_3Ar), 49.76 (2xCH_2N), 60.03 (CHN), 66.76 (2xCH_2O), 127.37, 129.72, 137.21, 144.18 (ArC), 131.58, and 146.83 (CH=CHS); *m/z* 295 (M^+, 13%), 280 (46), 140 (36), 139 (34), 124 (100), 114 (72), 108 (11), 91 (23), 65 (14), and 56 (14).

N-*(3-Tosyl-2-cyclohexenyl)morpholine* (**3df**): mp 145-146°C (CH_2Cl_2); ν_{max} ($CHCl_3$) 3010, 1620 (C=CH), 1300, and 1140 cm^{-1} (SO_2); δ_H 1.50, 1.80, 1.90, 2.20 (4m, 6H, 3xCH_2C), 2.45 (s, 3H, CH_3), 2.59 (m, 4H, 2xCH_2N), 3.35 (m, 1H, CHN), 3.71 (t, J=4.5Hz, 2xCH_2O), 7.05 (m, 1H, CHCHN), 7.34, and 7.74 (2d, J=8.0Hz, 4H, ArH); δ_C 20.86, 21.94, 22.83 (3xCH_2C), 21.35 (CH_3), 49.15 (2xCH_2N), 60.55 (CHN), 67.05 (2xCH_2O), 127.85, 129.61, 135.93, 144.09 (ArC), 138.31, and 142.58 ($CH=CCH_2$); *m/z* 321 (M^+, 8%), 166 (98), 139 (31), 138 (100), 91 (26), 79 (15), 77 (14), and 65 (15). Anal. Calcd. for $C_{17}H_{23}NO_3S$: C, 63.52; H, 7.21; N, 4.36. Found: C, 62.93; H, 7.28; N, 4.03.

(1R:2S)-(E)-*2-[N-Methyl-N-(3-tosyl-2-propenyl)amino]-1-phenyl-1-propanol* (**3ag**): $[\alpha]_D$ -10.5 (c=1, $CHCl_3$); mp 122-123°C (CH_2Cl_2/hexane); ν_{max} ($CHCl_3$) 3440 (OH), 3050, 1620, 930 (CH=C), 1300, and 1140 cm^{-1} (SO_2); δ_H 0.94 (d, J=6.5Hz, 3H, CH_3CH), 2.22 (s, 3H, CH_3N), 2.43 (s, 3H, CH_3Ar), 2.78 (m, 1H, $CHCH_3$), 3.05 (br s, 1H, OH), 3.21 (d, J=5.0Hz, 2H, CH_2N), 4.68 (d, J=5.0Hz, 1H, CHO), 6.29 (d, J=15.0Hz, 1H, CHS), 6.82 (dt, J=15.0, 5.0Hz, 1H, $CHCH_2$), 7.21 (s, 5H, Ph), 7.32, and 7.72 (2d, J=8.0Hz, 4H, *p*-TolH); δ_C 9.58 (CH_3CH), 21.48 (CH_3Ar), 39.24 (CH_3N), 54.05 (CH_2N), 63.79 (CHN), 74.06 (CHO), 125.93, 127.06, 127.92, 142.38 (Ph), 127.52, 129.76, 137.36, 144.19 (*p*-TolC), 129.76, and 143.58 (CH=CHS); *m/z* 358 (M^+-1, <1%), 253 (14), 252 (100), 139 (20), 91 (13), and 77 (10). Anal. Calcd. for $C_{20}H_{25}NO_3S$: C, 66.82; H, 7.01; N, 3.90. Found: C, 66.47; H, 7.28; N, 3 79.

(2R:3S:6R)-3,4-*Dimethyl-2-phenyl-6-(tosylmethyl)morpholine* (**6a**):$[\alpha]_D$ -70.3 (c=0.9, $CHCl_3$); mp 199-200°C (CH_2Cl_2/hexane); ν_{max} ($CHCl_3$) 1300 and 1140 cm^{-1} (SO_2); δ_H 0.62 (d, J=6.6Hz, 3H, CH_3CH), 2.45, 2.47 (2s, 6H, CH_3N and CH_3Ar), 2.54, 2.68 (2d, J=11.3Hz, 2H, CH_2N), 3.05 (m, 1H, $CHCH_3$), 3.34 (dd, J=14.6, 4.1Hz, 1H, 1xCH_2S), 3.61 (dd, J=14.6, 7.3Hz, 1H, 1xCH_2S), 4.30 (m, 1H, CH_2CHO), 4.77 (d, J=2.1Hz, 1H, CHPh), 6.99 (m, 2H, Ph), 7.29-7.33 (m, 5H, 3H of Ph and 2H of *p*-TolH), and 7.87 (d, J=8.1Hz, 2H of *p*-TolH); δ_C 2.13 (CH_3CH), 21.54 (CH_3Ar), 42.50 (CH_3N), 50.87 (CH_2N), 57.57 (CHN), 59.93 (CH_2S), 71.48 ($CHCH_2$), 80.69 (CHPh), 125.20, 126.78, 128.23, 139.27 (Ph), 127.76, 129.68, 136.97, and 144.49 (*p*-TolC); *m/z* 359 (M^+, <1%), 204 (3), 99 (7), 98 (100), 91 (8), 65 (3), 56 (4), 42 (3) and 41 (6). Anal. Calcd. for $C_{20}H_{25}NO_3S$: C, 66.82; H, 7.01; N, 3.90. Found: C, 66.56; H, 7.19; N, 3.78.

(E)-*3-Azido-1-tosyl-1-propene* (**3ah**): mp 62-63°C (CH_2Cl_2/hexane); ν_{max} ($CHCl_3$) 3040, 1620, 960 (CH=C), 2090 (N_3), 1300, and 1140 cm^{-1} (SO_2); δ_H 2.44 (CH_3), 4.09 (d, J=2.5Hz, 2H, CH_2N), 6.61 (d, J=15.0Hz, 1H, CHS), 6 88 (d, J=15.0, 4.5Hz, 1H, $CHCH_2$), 7.35, and 7.77 (2d, J=8.0Hz, 4H, ArH); δ_C 21.46 (CH_3), 50.16 (CH_2N),

127.67, 129.91, 136.72, 144.66 (ArC), 132.78, and 138.28 (CH=CHS); *m/z* 237 (M^+, 2%), 139 (100), 131 (27), 107 (13), 92 (12), 91 (81), 89 (25), 77 (21), 65 (63), 63 (26), 55 (11), and 51 (12). Anal. Calcd. for $C_{10}H_{11}N_3O_2S$: C, 50.62; H, 4.67; N, 17.71. Found: C, 51.04; H, 4.94; N, 16.88.

(Z,E)-*3-Azido-2-methyl-1-tosyl-1-propene* (**3bh**): R_f 0.44 (hexane/ether:1/2); ν_{max} ($CDCl_3$) 3020, 1620 (CH=C), 2080 (N_3), 1300, and 1140 cm^{-1} (SO_2); δ_H (60 MHz, Varian EM-360L) 2.0, 2.1 (2s, 3H, CH_3CCH_2), 2.4 (CH_3Ar), 3.8, 4.5 (2s, 2H, CH_2), 6.2, 6.4 (2s, 1H, CHS), 7.3, and 7.7 (2d, J=8.0Hz, 4H, ArH); δ_C 15.60, 22.71 (2xCH_3CCH_2), 21.53 (CH_3Ar), 49.54, 56.78 (CH_2), 127.25, 127.34, 129.84, 129.98, 138.23, 138.71, 144.38, 144.64 (ArC), 127.79, 129.46, 148.32, and 148.71 (CH=C).

(E)-*3-Azido-3-methyl-1-tosyl-1-propene* (**3ch**): R_f 0.51 (hexane/ether:1/2); ν_{max} ($CHCl_3$) 3010, 1610, 960 (CH=C), 2100 (N_3), 1300, and 1140 cm^{-1} (SO_2); δ_H 1.39 (d, J=6.8Hz, 3H, CH_3CH), 2.43 (s, 3H, CH_3Ar), 4.23 (m, 1H, $CHCH_3$), 6.54 (d, J=14.9Hz, 1H, CHS), 6.81 (dd, J=14.9, 5.0Hz, 1H, CHCHS), 7.34, and 7.76 (2d, J= 8.0Hz, 4H, ArH); δ_C 18.81 (CH_3CH), 21.52 (CH_3Ar), 56.40 (CHN), 127.72, 129.95, 136.80, 144.68 (ArC), 131.91, and 142.80 (CH=CHS).

3-Azido-1-tosylcyclohexene (**3dh**): R_f 0.48 (hexane/ether:1/2); ν_{max} (film) 3030, 1630 (CH=C), 2070 (N_3), 1300, and 1140 cm^{-1} (SO_2); δ_H 1.64, 1.85, 2.19 (3m, 6H, 3xCH_2), 2.42 (s, 3H, CH_3), 4.07 (m, 1H, CHN), 6.88 (m, 1H, CHCHN), 7.32, and 7.72 (2d, J=8.0Hz, 4H, ArH); δ_C 19.10, 22.57, 27.13 (3xCH_2), 21.51 (CH_3), 55.55 (CHN), 128.19, 129.85, 135.25, 144.67 (ArC), 133.07, and 144.67 ($CH=CCH_2$); *m/z* 277 (M^+, <1%), 139 (100), 92 (48), 91 (81), 77 (23), 67 (25), and 65 (75).

1-[(E)-3--Tosyl-2-propenyl]-1,3,5-triazin-2,4,6-triona (**3ai**): mp 132-134°C (CH_2Cl_2/hexane); ν_{max} ($CHCl_3$) 3260 (NH), 1680 (C=O), 1300, and 1140 cm^{-1} (SO_2); δ_H 2.43 (s, 3H, CH_3), 4.56 (d, J=4.0Hz, CH_2), 6.59 (d, J=15.0Hz, 1H, CHS), 6.85 (dt, J=15.0, 5.5Hz, 1H, $CHCH_2$), 7.33, and 7.71 (2d, J=8.0Hz, 4H, ArH); δ_C 21.59 (CH_3), 42.54 (CH_2N), 127.75, 129.87, 130.04, 136.58, 144.77, 148.02 (ArC, 2xC=O), 133.81, and 137.72 (CH=CHS); *m/z* 323 (M^+, 3%), 168 (100), 139 (51), 92 (25), 91 (78), 82 (37), 65 (49), and 56 (21). Anal. Calcd. for $C_{13}H_{13}N_3O_5S$: C, 48.29; H, 4.05; N, 13.00. Found: C, 48.94; H, 4.19; N, 12.60.

(E)-*1,3-Ditosyl-1-propene* (**3aj**): mp 146-147°C (CH_2Cl_2/hexane); ν_{max} ($CHCl_3$) 3020, 1620, 960 (CH=C), 1310, and 1140 cm^{-1} (SO_2); δ_H 2.40, 2.46 (2s, 6H, 2xCH_3), 3.91 (d, J=7.5Hz, 2H, CH_2), 6.34 (d, J=15.0Hz, 1H, CHS), 6.74 (dt, J=15.0, 7.5Hz, 1H, $CHCH_2$), 7.23, 7.35, 7.62, and 7.68 (4d, J=8.0Hz, 8H, ArH); δ_C 21.57, 21.58 (2xCH_3), 57.72 (CH_2), 127.91, 128.22, 129.91, 129.97, 134.56, 136.23, 144.93, 145.37 (ArC), 130.89, and 138.60 (CH=CHS); *m/z* 350 (M^+, 20%), 195 (16), 155 (90), 139 (68), 131 (17), 92 (11), 91 (100), and 65 (23). Anal. Calcd. for $C_{17}H_{18}O_4S_2$: C, 58.26; H, 5.18. Found: C, 57.97; H, 5.06.

Methyl (E)-*2-(Methoxycarbonyl)-5-tosyl-4-pentenoate* (**3ak**): R_f 0.71 (ether); ν_{max} (film) 3030, 1620, 970 (CH=C), 1720 (C=O), 1300, and 1140 cm^{-1} (SO_2); δ_H 2.43 (s, 3H, CH_3Ar), 2.80 (td, J=7.2, 1.5Hz, 2H, CH_2), 3.54 (t, J=7.3Hz, 1H, CHCO), 3.69 (s, 6H, 2xCH_3O), 6.40 (dt, J=15.0, 1.5Hz, 1H, CHS), 6.88 (dt, J=15.0, 7.0Hz, 1H, $CHCH_2$), 7.33, and 7.73 (2d, J=8.5Hz, 4H, ArH); δ_C 21.43 (CH_3Ar), 30.15 (CH_2CH), 49.75 ($CHCH_2$), 52.66 (2xCH_3O), 127.55, 129.77, 137.05, 144.35 (ArC), 133.33, 140.88 (CH=CHS) and 168.18 (C=O); *m/z* 326 (M^+, <1%), 171 (100), 155 (18), 139 (67), 111 (34), 107 (24), 92 (14), 91 (61), 71 (11), 65 (35), 59 (34), and 53 (13).

Methyl 2,2-bis[(E)-*3-tosyl-2-propenyl]malonate* (**7**): R_f 0.47 (ether); ν_{max} (film) 3030, 1630, 970 (CH=C), 1720 (C=O), 1300, and 1140 cm^{-1} (SO_2); δ_H 2.43 (s, 3H, CH_3Ar), 2.71 (dd, J=7.5, 1.0Hz, 4H, 2xCH_2), 3.67 (s, 6H, 2xCH_3O), 6.22 (dt, J=15.0, 1.0Hz, 2H, 2xCHS), 6.73 (dt, J=15.0, 7.5Hz, 2H, 2x$CHCH_2$), 7.33, and 7.71 (2d,

J=8.0Hz, 8H, ArH); δ_C 21.57 (2x*C*H$_3$Ar), 35.33 (2xCH$_2$), 53.05 (2xCH$_3$O), 56.46 (*C*CH$_2$), 127.71, 129.96, 136.91, 144.64 (ArC), 135.07, 138.64 (2xCH=CHS), and 169.30 (2xC=O); *m/z* 520 (M^+, 1%), 155 (19), 139 (45), 92 (14), 91 (100), 79 (11), 77 (18), 65 (35), and 59 (13).

Methyl 2,5-bis(methoxycarbonyl)-3-(tosylmethyl)adipate (**8**): R_f 0.50 (ether); ν_{max} (film) 1720 (C=O), 1300, and 1140 cm^{-1} (SO$_2$); δ_H 2.16, 2.29 (2m, 2H, C*H*$_2$CHCO), 2.45 (s, 3H, C*H*$_3$Ar), 2.66 (m, 1H, C*H*CH$_2$S), 3.25 (dd, J=15.0, 6.0Hz, 1H, 1xCH$_2$S), 3.51 (m, 2H, 1xCH$_2$S and CH$_2$C*H*CO), 3.69, 3.72, 3.73, 3.74 (4s, 12H, 4xCH$_3$O), 3.93 (d, J=4.0Hz, 1H, CHC*H*CO), 7.37, and 7.78 (2d, J=8.0Hz, 4H, ArH); δ_C 21.51 (*C*H$_3$Ar), 31.00 (*C*H$_2$CO), 31.63 (*C*HCH$_2$S), 49.43, 52.99 (2xCHCO), 52.56, 52.60, 52.61, 52.63 (4xCH$_3$O), 57.17 (CH$_2$S), 127.97, 129.85, 136.17, 144.79 (ArC), 168.06, 168.14, 168.87, and 168.97 (4xC=O); *m/z* 428 (M^+-30, <1%), 396 (M^+-62, 1), 303 (25), 271 (28), 239 (39), 179 (63), 139 (55), 92 (22), 91 (100), 65 (44), 59 (71), and 55 (20).

Synthesis of γ-Functionalized Allyl Sulfones. General Procedure. A mixture of compound **2** or **3** (0.5 mmol) and nucleophile or base (see Table 3) in the corresponding solvent (*ca.* 5 ml) was stirred at the temperature and for the time shown in Table 3. After extractive work-up compounds **4** were isolated and purified as above.

(Z,E)-*1-Bromo-1-methyl-3-tosyl-1-propene* (**4ca**): R_f 0.52 (hexane/ether:1/2); ν_{max} (film) 3070, 1655 (CH=C), 1300, and 1140 cm^{-1} (SO$_2$); δ_H (of *Z*-isomer) 2.27 (s, 3H, CH$_3$CBr), 2.45 (s, 3H, C*H*$_3$Ar), 3.96 (d, J=7.3Hz, 2H, CH$_2$S), 5.77 (t, J=7.3Hz, 1H, C*H*CH$_2$), 7.34, and 7.76 (2d, J=8.0Hz, 4H, ArH); δ_C (of *Z*-isomer) 21.54 (*C*H$_3$Ar), 28.92 (*C*H$_3$CBr), 59.10 (CH$_2$S), 116.11 (*C*HCH$_2$), 128.28, 129.61, 135.46, 144.73 (ArC), 131.13 (CBr); *m/z* 209 (M^+-Br, 27%), 135 (68), 133 (69), 92 (52), 91 (68), 89 (23), 65 (68), 63 (21), and 53 (100).

(Z)-*1-Azido-3-tosyl-1-propene* (**4ah**): mp 81-82 °C (hexane/ether); ν_{max} (CHCl$_3$) 3010, 1630, 960 (CH=C), 2100 (N$_3$), 1300, and 1140 cm^{-1} (SO$_2$); δ_H 2.45 (s, 3H, C*H*$_3$Ar), 3.86 (dd, J=7.8, 1.0Hz, 2H, CH$_2$S), 4.91 (q, J=7.8Hz, 1H, C*H*CH$_2$), 6.39 (dt, J=7.8, 1.0Hz, 1H, CHN), 7.35, and 7.78 (2d, J=8.0Hz, 4H, ArH); δ_C 21.56 (*C*H$_3$Ar), 53.59 (CH$_2$S), 105.36, 135 57 (CH=CHN), 128.47, 129.52, 132.70, and 144.75 (ArC); *m/z* 237 (M^+, 1%), 155 (14), 92 (37), 91 (100), 89 (21), 65 (52), 63 (20), and 54 (13). Anal. Calcd. for $C_{10}H_{11}N_3O_2S$: C, 50.62; H, 4.67; N, 17.71. Found: C, 50.96; H, 4.82; N, 17.53.

(Z,E)-*1-Azido-1-methyl-3-tosyl-1-propene* (**4ch**): R_f 0.50 (hexane/ether:1/2); ν_{max} 3010, 1610 (CH=C), 2100 (N$_3$), 1300, and 1140 cm^{-1} (SO$_2$); δ_H (of *Z*-isomer) 1.96 (s, 3H, CH$_3$CN), 2.45, (s, 3H, C*H*$_3$Ar), 3.82 (d, J=7.8Hz, 2H, CH$_2$), 4.75 (m, 1H, C*H*CH$_2$), 7.34, and 7.76 (2d, J=8.0Hz, 4H, ArH); δ_C (of *Z*-isomer) 18.20 (*C*H$_3$CN), 21.60 (*C*H$_3$Ar), 54.50 (CH$_2$), 102.20 (CN), 128.50, 129.50, 136.00, 144.60 (ArC), and 139.30 (*C*HCH$_2$)); *m/z* 251 (M^+, 1%), 155 (28), 139 (42), 135 (29), 133 (27), 92 (22), 91 (100), 68 (61), 65 (43), and 42 (45).

(Z)-*1-Bromo-3-tosyl-1-propene* (**4aa**): R_f 0.40 (hexane/ether:1/5); ν_{max} (film) 3070, 3040, 1615, 775 (CH=C), 1300, and 1140 cm^{-1} (SO$_2$); δ_H 2.45 (s, 3H, CH$_3$), 4.03 (d, J=7.5Hz, 2H, CH$_2$), 6.23 (dd, J= 7.5, 7.3Hz, 1H, C*H*CH$_2$), 6.49 (d, J=7.3Hz, 1H, CHBr), 7.34, and 7.77 (2d, J=8.0Hz, 4H, ArH); δ_C 21.62 (CH$_3$), 57.27 (CH$_2$), 116.09, 122.07 (CH=CHBr), 128.41, 129.75, 135.30, and 144.98 (ArC); *m/z* 276 (M^++1, 5%), 274 (M^+-1, 5), 195 (27), 155 (35), 149 (17), 139 (100), 121 (29), 119 (40), 91 (94), and 55 (38).

(Z)-*3-Tosyl-1-propenyl acetate* (**4ac**): R_f 0.51 (hexane/ether:1/5); ν_{max} (film) 3040, 1660, 740 (CH=C), 1750 (C=O), 1300, and 1140 cm^{-1} (SO$_2$); δ_H 1 94 (s, 3H, CH$_3$CO), 2.43 (s, 3H, C*H*$_3$Ar), 3.94 (d, J=7.8Hz, 2H, CH$_2$), 4.95 (td, J=7.8, 6.3Hz, 1H, C*H*CH$_2$), 7.19 (d, J=6.3Hz, 1H, CHO), 7.34, and 7.77 (2d, J=8.0Hz, 4H, ArH); δ_C 19.92 (*C*H$_3$CO), 21.27 (*C*H$_3$Ar), 52.57 (CH$_2$), 99.54 (*C*HCH$_2$), 128.25, 129.32, 135.12, 144.53 (ArC), and 139.27 (CHO); *m/z* 254 (M^+, <1%), 212 (M^+-42, 8), 150 (20), 99 (26), 91 (43), 65 (30), and 43 (100).

(E)-*(3-Tosyl-1-propenyl)triphenylphosphonium bromide* (**4al**): mp 220-221°C (CH_2Cl_2/hexane); ν_{max} ($CHCl_3$) 3000, 1610, 990 (CH=C), 1300, and 1140 cm^{-1} (SO_2); δ_H 2.41 (s, 3H, CH_3), 4.87 (d, J=7.0Hz, 2H, CH_2), 6.49 (m, 1H, C*H*CH_2), 7.34 (d, J=8.0Hz, 2H, 2x*p*-TolH), 7.5-8.0 (m, 17H, 2x*p*-TolH and 3xPh), 8.68 (dd, J=21.5, 16.5Hz, 1H, CHP); δ_P 19.18; δ_C 21.58 (CH_3), 59.82 (d, J=19.5Hz, CH_2), 117.22 (d, J=90.0Hz, 3xC_i-Ph), 119.69 (d, J=81.0Hz, CHP), 146.88 (d, J=4.5Hz, *C*HCH_2), 130.42 (d, J=13.0Hz, 6xC_m-Ph), 133.89 (d, J=10.5Hz, 6xC_o-Ph), 135.32 (d, J=3.0Hz, 3xC_p-Ph), 128.14, 129.95, 135.32, and 145.03 (*p*-TolH); *m/z* 459 (M^++2, 2%), 278 (39), 277 (100), 262 (36), 246 (30), 199 (22), 183 (57), 123 (34), 91 (21), and 77 (29). Anal. calcd. for $C_{28}H_{26}BrO_2PS$: C, 62.57; H, 4.88. Found: C, 61.98; H, 4.90.

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