High Pressure-Promoted [2+2] Cycloaddition Reactions of 4-Methylphenyl 1,2-Propadienyl Sulfone with Enol Ethers

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Under high pressure conditions, 4-methylphenyl 1,2-propadienyl sulfone (**1**) and enol ethers (**6**) undergo regioselective [2+2] cycloaddition reactions to give (3-alkoxycyclobutylidene)methyl 4-methylphenyl sulfones (**7**). The cycloaddition reaction has a broad scope with respect to the substituents allowed at the enol ether. The synthetic potential of the obtained cycloadducts is illustrated by a stereoselective addition of dimethylamine to the double bond of **7a** and **7b** to yield **11a** and **11b** and by a tertiary amine-induced double bond isomerisation of **7a** and **7b**, followed by ring-opening of the cyclobutene intermediate to yield 1-alkoxybuta-1,3-dienes **12a** and **12b**.

Introduction

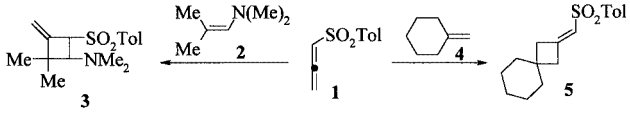
Allenes activated by electron-withdrawing or electron-donating substituents have been well investigated in cycloaddition reactions over the past decade, due to the potential for synthetic manipulation of their cycloadducts.[1−3]

We became interested in [2+2] cycloaddition reactions between 1,2-propadienyl sulfones and enol ethers, as these might provide alkoxy-methylenecyclobutanes, which seem attractive scaffolds for use in combinatorial chemistry. This is due to the presence of a sulfonyl group, a methylene function and an alkoxy group, while the cyclobutane ring can either be left as a basic structural unit or can be involved in further conversions.

Arenesulfonylallenes can be prepared readily, either from propargyl sulfones through an isomerisation reaction,[4] or from propargyl arenesulfinates through a [2,3]-sigmatropic rearrangement.[5]

Intramolecular [2+2] cycloaddition reactions of phenylsulfonyl-substituted allenes have been intensively studied by Pawda's group.[6] They found selective addition to the less activated β,γ-double bond of the allene, whereas these allenes react regioselectively with various 4π systems across the more activated α,β-double bond.[7]

Intermolecular [2+2] cycloadditions of 4-methylphenyl 1,2-propadienyl sulfone (**1**) have been reported with 1-dimethylamino-2-methylpropene (**2**)[8] and methylenecyclohexane (**4**)[9] as shown in Scheme 1.



Scheme 1

The cycloaddition with the enamine **2** occurs on the more activated α,β-double bond, whereas the reaction with **4** proceeds exclusively at the β,γ-double bond. In the latter case, the cycloadduct **5** is only obtained in 25% yield after 14 days at reflux in benzene in the presence of a Lewis acid catalyst.

This paper studies the scope of cycloaddition reactions of enol ethers **6** with **1** and illustrates the synthetic potential of the obtained cycloadducts.

Results and Discussion

A priori, cycloaddition of **1** with enol ethers could give two regioisomers. As the enol ethers are expected to be only slightly more reactive than **4**, we expected that forced conditions would be necessary to obtain satisfactory conversions.

Indeed, no conversion of **1** and enol ether **6b** was observed after 24 h at reflux in dichloromethane. We therefore decided to study this cycloaddition reaction under high pressure conditions, because it has been demonstrated that high pressure has a strong accelerating effect on polar [2+2] cycloaddition reactions.[10,11] On application of a pressure of 15 kbar overnight at room temperature, complete conversion was observed.

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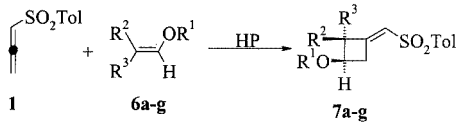
Table 1. Synthesis of (3-alkoxycyclobutylidene)methyl 4-methylphenyl sulfones **7a−g** from 4-methylphenyl 1,2-propadienyl sulfone (**1**) and enol ethers **6a−g**



1 **6a-g** **7a-g**

Vinyl ether	R^1	R^2	R^3	Equiv.	Temp. [°C]	Product	M.p. [°C]	Yield[a] [%]
6a	Et	H	H	4	50	**7a**	54−55	74
6b	*t*Bu	H	H	4	room temp.	**7b**	77−78	71
6c	Ph-CHMe	H	H	2	50	**7c**	oil	44
						7c′	oil	23
6d	*i*Pr	H	Me	4	50	**7d**	oil	75
6e	*i*Pr	Me	H	4	50	**7e**	oil	62
6f	Me	Me	Me	4	50	**7f**	39−41	65
6g	$-CH_2-CH_2-$		H	4	room temp.	**7g**	104−105	55

[a] After MPLC and recrystallization.

Of the four possible regioisomers, only **7** was formed, as is apparent from the ^1H NMR spectrum, in which the methylene proton appears as a narrow multiplet at about $\delta = 6.15$ ppm.

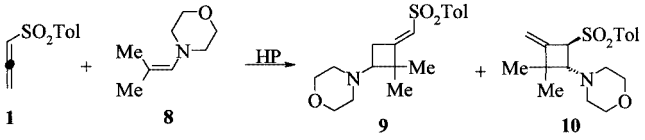
The results obtained with the enol ethers **6a−g** are presented in Table 1.

The results show that the reaction has a broad scope, as substitution in every position of the enol ether is possible. Regioselectivity is high in all cases, as the other regioisomers were only found in small amounts for enol ethers **6d** and **6e**. Enol ethers with β-substituents, such as **6d**, **6e**, **6g**, and **6f** could give *E*/*Z* mixtures with respect to the position of the tolylsulfonyl group. Only one isomer was isolated, however, most probably the one with the sulfonyl group at the side of the cyclobutane $-CH_2$ group. In addition, NMR of the crude high pressure reaction mixture showed only one sulfonyl methylene proton absorption, at about $\delta =$ 6 ppm.

The effect of a chiral auxiliary in the enol ether was studied with enol ether **6c**. Two diastereomers **7c** and **7c′** were found in a ratio of 2:1. This is similar to the induction recently found when this enol ether was used in a [4+2] cycloaddition reaction with an enone system.[11]

Interestingly, the substituents on the enol ether moiety do not affect the regioselectivity. It seems that the regioselectivity in this type of [2+2] cycloaddition reactions is determined by the electron−richness of the reacting alkene, as the strongly electron-rich enamine **2** exclusively gave addition at the α,β-double bond of **1**, while the weakly electron-rich alkene **4** exclusively underwent a [2+2] cycloaddition reaction at the β,γ-double bond (Scheme 1). We therefore also studied the cycloaddition of enamine **8**, which would be expected to have an electron-richness in between those of **2** and **6**. Indeed, a mixture of two regioisomers was now formed, as shown in Scheme 2.

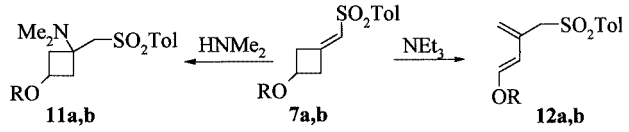
Compound **10** was isolated as a single isomer, most probably with the tosyl and morpholine groups in a *trans* arrangement, in agreement with a coupling constant of 6.9 Hz for the two vicinal cyclobutane protons.



1 **8** **9** **10**

Scheme 2

The synthetic potential of the methylene cyclobutanes is evident in some reactions with amines (Scheme 3.). Dimethylamine adds stereoselectively to the double bond of **7a** and **7b** to give addition products **11a** and **11b** as single isomers. In the presence of triethylamine, however, dienes **12a** and **12b** were isolated as the sole products. The triethylamine base probably causes isomerisation of the double bond in **7a** and **7b**, whereupon the formed cyclobutenes undergo fast ring-opening reactions to give the dienes **12a** and **12b**. We are now studying the scope and stereochemistry of these reactions.



11a,b **7a,b** **12a,b**

Scheme 3

Discussion and Conclusions

The mechanistic aspects of thermal [2+2] cycloaddition reactions of allenes have been a matter of much debate.[1a,12] The discussed mechanisms vary from concerted to stepwise, including diradical or dipolar intermediates. For intramolecular [2+2] cycloaddition reactions of phenylsulfonylallenes, a stepwise mechanism including initial carbon−carbon bond formation with the central allene carbon to give a diradical intermediate has been proposed.[6] Two regioisomers can be formed from this intermediate, depending on which part of the allylic radical is involved in

ring-closure. Regioselectivity is determined by the substitution pattern of the alkene part involved. High pressure favours cycloaddition reactions proceeding through concerted or dipolar reaction paths, as the diradical path has a lower negative activation volume.[13] The observed different results obtained for moderately and strongly electron-rich alkenes point to a more concerted reaction path in the cycloaddition with enol ethers, whereas for strongly electron-rich enamines such as **2**, dipolar intermediates are most probably formed and ring-closure occurs through the most stabilized dipoles. The cycloadducts **7** are interesting scaffolds for combinatorial chemistry, as is evident from the conversions to compounds **11a** and **11b** and **12a** and **12b** described in Scheme 3. We are now exploring these possibilities with aryl 1,2-propadienyl sulfones linked to a solid phase.

Experimental Section

General: The FTIR spectra were recorded on a Genesis Series Mattson instrument. The ^{1}H NMR were recorded on Bruker AM 400 (400 MHz) or Bruker AM 300 (300 MHz) spectrometers in $CDCl_3$ solutions. The ^{13}C NMR spectra were measured in $CDCl_3$ (75 MHz). Chemical shift values are reported as δ values in parts per million (ppm) relative to tetramethylsilane as a internal standard. Mass spectra were determined with a double focusing VG 7070E spectrometer. Melting points were measured on a Reichert Thermopan microscope and are uncorrected. The high pressure apparatus used in this study has been described before.[14] Chromatographic purification was carried out with a MPLC (Jobin Yvon) apparatus on Baker silica gel 60H. Enol ethers **6c**,[15] **6d**, **6e**,[16] and **6f**[17] were prepared by the literature methods indicated.

(3-Alkoxycyclobutylidene)methyl 4-Methylphenyl Sulfone

General Procedure for the Preparation of (7a−g) from 4-Methylphenyl 1,2-Propadienyl Sulfone (1) and Enol Ethers 6a−g: Compound **1** (0.3 g, 1.55 mmol) was added to enol ether **6a−g** (2 or 4 equiv.; see Table 1) in a 7.5 mL Teflon vessel, and the two compounds were mixed well. The resulting solution was diluted with dichloromethane until the vessel was full and then closed tightly with a cap. The vessel was pressurized at 15 kbar at room temperature or 50 °C for 16 h. After release of the pressure, the mixture was concentrated in vacuo at room temperature.

Compound 7a: Purification was achieved by MPLC (*n*-hexane/ethyl acetate, 85:15), followed by recrystallization from *n*-hexane. Yield: 305 mg (74%). ^{1}H NMR: δ = 1.20 (t, *J* = 4.5 Hz, 3 H), 2.43 (s, 3 H), 2.80−287 (m, 1 H), 2.99−3.09 (m, 2 H), 3.38−3.49 (m, 2 H), 3.56−3.65 (m, 1 H), 4.10 (quin, *J* = 6.3 Hz, 1 H), 6.17−6.19 (m, 1 H), 7.32 (d, *J* = 8.1 Hz), 7.75 (d, *J* = 8.1 Hz, with fine splitting) ppm. ^{13}C NMR: δ = 15.1, 21.6, 40.8, 41.1, 63.9, 69.1, 123.3, 127.1, 129.8, 138.9, 144.1, 155.1 ppm. $C_{14}H_{18}O_3S$ (266.36): calcd. C 63.13, H 6.81; found C 62.93, H 6.38.

Compound 7b: Purification was achieved by MPLC (*n*-hexane/ethyl acetate, 85:15), followed by recrystallization from *n*-hexane. Yield: 320 mg (71%). ^{1}H NMR: δ = 1.19 (s, 9 H), 2.43 (s, 3 H), 2.43−2.87 (m, 1 H), 2.96−3.04 (m, 2 H), 3.60−3.65 (m, 1 H), 4.21−4.24 (quin, 1 H, *J* = 6.6 Hz), 6.13−6.16 (m, *J* = 3 Hz, 1 H), 7.31 (d, *J* = 8 Hz, 2 H), 7.73 (d, *J* = 8 Hz, 2 H) ppm. ^{13}C NMR: δ = 21.6, 28.2, 43.4, 43.6, 62.7, 77.3, 122.6, 127.1, 129.7, 139.1, 155.8 ppm. $C_{16}H_{22}O_3S$ (294.42): calcd. C 65.27, H 7.53; found C 65.05, H 7.53.

Compound 7c and 7c′: ^{1}H NMR of the crude high pressure mixture showed that **7c** and **7c′** were present in 2:1 ratio. Purification was achieved by MPLC (*n*-hexane/ethyl acetate, 4:1).

Compound 7c: Oil. Yield: 230 mg (44%). ^{1}H NMR: δ = 1.43 (d, *J* = 6.5 Hz), 2.42 (s, 3 H), 2.73−2.78 (m, 2 H), 3.04−3.10 (m, 1 H), 3.54−3.61 (m, 1 H), 4.00 (quin, *J* = 6.4 Hz, 1 H), 4.42 (q, *J* = 6.5 Hz, 1 H), 6.09−6.10 (m, 1 H), 7.25−7.35 (m, 7 H), 7.69 (d, *J* = 8.4 Hz) ppm. ^{13}C NMR: δ = 21.5, 23.8, 40.9, 41.5, 67.3, 76.5, 121.9, 126.3, 127.0, 127.7, 128.4, 129.7, 138.9, 143.0, 144.0, 155.1 ppm. HRMS calcd. for $C_{20}H_{22}O_3S$: 342.1289; found 342.1277.

Compound 7c′: Oil. Yield: 120 mg (23%). ^{1}H NMR: δ = 1.44 (d, *J* = 6 Hz, 3 H), 2.42 (s, 3 H), 2.83−3.02 (m, 3 H), 3.34−3.40 (m, 1 H), 3.98−4.05 (m, 1 H), 4.38−4.42 (m, 1 H), 6.12−6.14 (m, 1 H), 7.25−7.36 (m, 7 H), 7.69 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR: δ = 21.6, 23.8, 41.1, 41.4, 67.3, 76.4, 123.1, 126.2, 127.1, 127.8, 128.5, 129.7, 138.9, 143.0, 144.0, 155.0 ppm. HRMS calcd. for $C_{20}H_{22}O_3S$: 342.1289; found 342.1289.

Compound 7d: Purification was achieved by MPLC (*n*-hexane/ethyl acetate, 4:1). Oil. Yield: 320 mg (75%). ^{1}H NMR: δ = 1.14 (9H [d, 6H and d, 3H]), 2.43 (s, 3 H), 2.80−2.87 (m, 1 H), 3.00−3.03 (m, 1 H), 3.59−3.71 (m, 3 × 1 H), 6.13−6.15 (m, 1 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.75 (d, *J* = 8.2 Hz, 2 H, with fine splitting) ppm. ^{13}C NMR: δ = 14.2, 21.5, 22.5, 39.5, 49.4, 70.5, 73.8, 121.5, 124.0, 129.7, 139.0, 143.9, 160.1 ppm. HRMS calcd. for $C_{16}H_{22}O_3S$: 294.1289; found 294.1285.

Compound 7e: Purification was achieved by MPLC (*n*-hexane/ethyl acetate, 85:15). Oil. Yield: 285 mg (62%). ^{1}H NMR: δ = 1.13 (9 H [d, 6 H and d, 3 H]), 2.43 (s, 3 H), 3.05−3.13 (m, 1 H), 3.19−3.24 (m, 1 H), 3.48−3.58 (m, 2 H), 4.16 (q, *J* = 7.0 Hz, 1 H), 6.14−6.16 (m, 1 H), 7.31 (d, *J* = 8.0 Hz), 7.75 (d, *J* = 8.1 Hz, 2 H) ppm. ^{13}C NMR: δ = 12.8, 21.5, 22.3, 39.5, 45.9, 69.0, 70.7, 122.2, 127.1, 129.7, 139.1, 143.9, 162.8 ppm. HRMS calcd. for $C_{16}H_{22}O_3S$: 294.1289; found 294.1283.

Compound 7f: Purification was achieved by MPLC (*n*-hexane/ethyl acetate, 4:1), followed by recrystallization from *n*-hexane. Yield: 280 mg (65%). ^{1}H NMR: δ = 1.17 (s, 3 H), 1.18 (s, 3 H), 2.43 (s, 3 H), 2.96 (ddd, *J* = 3.0, *J* = 6.2, *J* = 9.1 Hz, 1 H), 3.30 (s, 3 H), 3.52−3.64 (m, 2 H), 6.11−6.13 (m, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.54 (d, *J* = 8.1 Hz, 2 H) ppm. −^{13}C NMR: δ = 20.5, 21.5, 25.1, 36.4, 50.9, 57.0, 79.3, 121.0, 127.0, 129.7, 138.4, 143.9, 165.4 ppm. $C_{15}H_{20}O_3S$ (280.39): calcd. C 64.26, H 7.19; found C 64.10, H 7.04.

Compound 7g: Purification was achieved by MPLC (*n*-hexane/ethyl acetate, 4:1), followed by recrystallization from isopropyl ether. Yield: 225 mg (55%). ^{1}H NMR: δ = 1.82−1.95 (m, 2 H), 2.44 (s, 3 H), 3.01−3.08 (m, 1 H), 3.34−3.41 (m, 1 H), 3.63−3.66 (m, 1 H), 3.82−3.88 (m, 1 H), 4.10−4.15 (m, 1 H), 4.77−4.81 (m, 1 H), 6.19−6.21 (m, 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR: δ = 21.6, 31.7, 38.1, 50.3, 66.9, 75.8, 123.9, 127.2, 129.3, 138.8, 144.3, 161.4 ppm. $C_{14}H_{16}O_3S$ (264.35): calcd. C 63.61, H 6.10; found C 63.21, H 6.00.

Compound 9 and 10: The high-pressure mixture obtained after reaction between **1** (0.3 g, 1.55 mmol) and **8** (0.24 g, 1.7 mmol) in dichloromethane at room temp. and 15 kbar for 16 h. was concentrated at room temp./10 mm. Purification of the residue was achieved by MPLC (*n*-hexane/ethyl acetate, 7:3). Yield of compound **9**: 33 mg (6%). Yield of compound **10**: 165 mg (31%).

(2,2-Dimethyl-3-morpholinocyclobutylidene)methyl 4-Methylphenyl Sulfone (9): M.p. 140−142. ^{1}H NMR: δ = 1.15 (s, 3 H), 1.21 (s, 3

H), 2.26−2.29 (m, 2 H), 2.32−2.34 (m, 2 H), 2.44 (s, 3 H), 2.49 (dd, J = 7.6 Hz, 8.7 Hz, 1 H), 2.87 (ddd, J = 2.9, J = 8.8, J = 11.7 Hz, 1 H), 3.38 (ddd, J = 2, J = 7.5, J = 9.4 Hz, 1 H), 3.65−3.73 (m, 4 H), 6.08 (dd, J = 2.0, J = 2.8 Hz, 1 H), 7.33 (d, J = 8.5 Hz, 2 H with fine splitting), 7.74 (d, J = 8.3 Hz, 2 H with fine splitting) ppm. ^{13}C NMR: δ = 21.4, 21.6, 26.0, 33.4, 48.9, 51.9, 65.8, 66.6, 120.0, 127.1, 129.8, 139.2, 144.0, 166.7 ppm. $C_{18}H_{25}NO_3S$ (335.46): calcd. C 64.45, H 7.51, N 4.18; found C 64.48, H 7.45, N 4.18.

3,3-Dimethyl-2-methylene-4-morpholinocyclobutyl 4-Methylphenyl Sulfone (10): Oil. ^{1}H NMR: δ = 0.96 (s, 3 H), 1.15 (s, 3 H), 2.28−2.30 (m, 2 H), 2.39−2.45 (m, 2 H), 2.45 (s, 3 H), 2.75 (d, J = 6.9 Hz), 3.64−3.67 (m, 4 H), 4.35 (dt, J = 2.7, J = 6.9 Hz, 1 H), 5.05 (dd, J = 1.0, J = 3.0 Hz, 1 H), 5.17 (dd, J = 1.0, J = 2.5 Hz, 1 H), 7.35 (d, J = 8.2, 2 H with fine coupling), 7.78 (d, J = 8.3 Hz, 2 H, with fine coupling) ppm. ^{13}C NMR: δ = 21.8, 22.5, 26.9, 45.1, 52.3, 65.2, 66.5, 68.8, 109.1, 129.4, 129.7, 134.5, 144.9, 147.5 ppm. HRMS calcd. for $C_{18}H_{25}NO_3S$: 335.1555; found 335.1554.

***N*-{3-Ethoxy-1-[(4-methylphenylsulfonyl)methyl]cyclobutyl}-*N*,*N*-dimethylamine (11a):** Compound **7a** (100 mg, 0.38 mmol) was dissolved in acetonitrile (4 mL). The reaction mixture was saturated with dimethylamine. After 5 h the reaction mixture was concentrated in vacuo. The residue was recrystallized from *n*-pentane. Yield **11a**: 105 mg (90%). M.p. 75 °C. ^{1}H NMR: δ = 1.18 (t, J = 6.9 Hz, 3 H), 2.07 (s, 6 H), 2.07−2.17 (m, 2 H), 2.44 (s, 3 H), 2.73−2.80 (m, 2 H), 3.18 (s, 2 H), 3.41 (q, J = 6.9 Hz, 2 H), 4.02 (quin, J = 6.9 Hz, 1 H), 7.34 (d, J = 7.8 Hz, 2 H), 7.80 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR: δ = 15.3, 21.5, 37.1, 36.6, 55.8, 57.7, 63.3, 65.0, 127.7, 129.5, 139.0, 144.2 ppm. HRMS calcd. for $C_{16}H_{25}NO_3S$ [M + H]: 312.1633; found 312.1634.

***N*-{3-(*tert*-Butoxy)-1-[(4-methylphenylsulfonyl)methyl]cyclobutyl}-*N*,*N*-dimethylamine (11b):** Compound **7b** (100 mg, 0.34 mmol) was dissolved in acetonitrile (4 mL). The reaction mixture was saturated with dimethylamine. After 5 h the reaction mixture was concentrated in vacuo. The residue was recrystallized from *n*-hexane. Yield **11b**: 108 mg (94%). M.p. 100 °C. ^{1}H NMR: δ = 1.17 (s, 9 H), 2.05 (s, 6 H), 2.05−2.15 (m, 2 H), 2.45 (s, 3 H), 2.69−2.76 (m, 2 H), 3.19 (s, 2 H), 4.16 (quin, J = 7.5 Hz, 1 H), 7.34 (d, J = 7.8 Hz, 2 H), 7.81 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR: δ = 21.5, 28.3, 37.1, 41.5, 56.0, 57.6, 58.3, 73.6, 127.7, 129.5, 139.0, 144.1 ppm. HRMS calcd. for $C_{18}H_{29}NO_3S$ [M + H]: 340.1946; found 340.1944.

4-Ethoxy-2-methylene-3-butenyl 4-Methylphenyl Sulfone (12a): Compound **7a** (100 mg, 0.34 mmol) was dissolved in tetrahydrofuran (4 mL) and triethylamine (0.5 mL). The reaction mixture was heated at 65 °C for 16 h and then concentrated in vacuo, further purification of the residue not being necessary. Yield **12a**: 100 mg (100%). Oil. ^{1}H NMR: δ = 1.25 (t, J = 7.2 Hz, 3 H), 2.43 (s, 3 H), 3.74 (q, J = 7.2 Hz, 2 H), 3.87 (s, 2 H), 4.57 (s, 1 H), 4.99 (s, 1 H), 5.45 (d, J = 12.9 Hz, 1 H), 6.57 (d, J = 12.9 Hz, 1 H), 7.30 (d J = 8.1 Hz, 2 H, with fine splitting), 7.74 (d, J = 8.4 Hz, 2 H, with fine splitting) ppm. ^{13}C NMR: δ = 14.7, 21.5, 61.1, 65.9, 106.2, 117.9, 128.7, 129.4, 132.1, 135.3, 144.6, 149.6 ppm. HRMS calcd. for $C_{14}H_{18}O_3S$: 266.0976; found 266.09763.

4-(*tert*-Butoxy)-2-methylene-3-butenyl 4-Methylphenyl Sulfone (12b): Compound **7b** (100 mg, 0.38 mmol) was dissolved in tetrahydrofuran (4 mL) and triethylamine (0.5 mL). The reaction mixture was heated at 65 °C for 16 h and then concentrated in vacuo, further purification of the residue not being necessary. Yield **12a**: 100 mg (100%). Oil. ^{1}H NMR: δ = 2.43 (s, 9 H), 3.93 (s, 3 H), 4.50 (s, 1 H), 4.92 (s, 1 H), 5.60 (d, J = 12.3 Hz, 1 H), 36.78 (d, J = 12.3 Hz, 1 H), 7.31 (br. d, J = 7.8 Hz, 2 H), 7.74 (br. d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR: δ = 21.5, 28.0, 61.2, 77.4, 109.1, 117.9, 128.4, 129.7, 132.5, 135.1, 144.5, 144.8 ppm. HRMS calcd. for $C_{16}H_{22}O_3S$: 294.1289; found 294.1283.

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