Reactions of Unsaturated Azides; Part 17:[1] An Efficient Strategy for the Synthesis of Small-Ring Heterocycles via Isomerization of 2-Halo-2*H*-azirines

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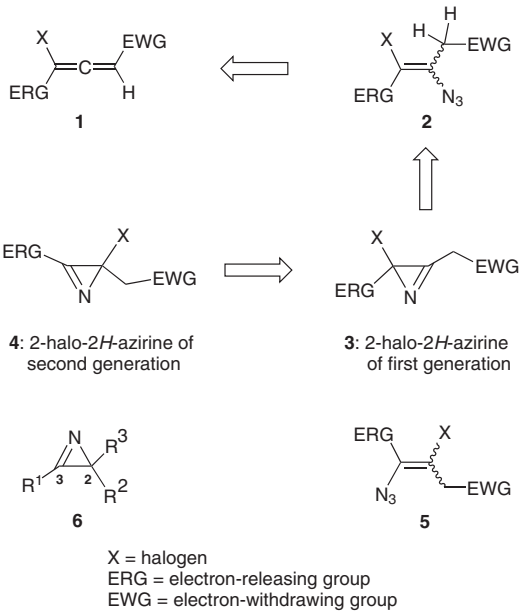
Abstract: New acceptor-substituted allenyl halides were synthesized. The addition of hydrazoic acid (HN_3) to these allenyl halides led to the formation of new 1-azido-2-haloethene derivatives. The photolysis of the latter compounds afforded the corresponding 2-halo-2*H*-azirines. At room temperature or below, they isomerized irreversibly by [1,2]-rearrangement of halogen to form other azirine isomers in very good yields. It is the first time that such a complete rearrangement of 2-halo-2*H*-azirines is observed. This synthetic strategy offers the possibility to observe both azirine isomers in their pure forms from single 1-azido-2-haloethene precursor.

Key words: allenes, azides, 2-halo-2*H*-azirines, addition reactions, rearrangements, photochemistry, thermolysis

2*H*-Azirines are highly strained nitrogen-containing heterocycles. Most of them are synthetic.[2] However, examples of naturally occurring ones are also known.[3] Methods for their synthesis include thermolysis and photolysis of vinyl azides[2a,b,e] and isoxazoles,[2a,b] Neber and modified Neber reactions[2a,b] as well as thermolysis of oxazaphospholines.[2a,b] 2*H*-Azirines are synthetic versatile compounds, and their reactions have been intensively explored. They can undergo thermal or photochemical ring opening to afford 1,3-dipolar species, which can be trapped through inter- and intramolecular reactions.[2a–d] 2*H*-Azirines are also known as good electrophiles.[4] Some amino derivatives such as amino acids,[2a,4a,5] aziridines,[4c,5] pyrazines,[2h,4b] and indoles[6] can be prepared from 2*H*-azirines. In addition to all these possibilities, 2-halo-2*H*-azirines offer another reaction site by their halogen atoms. Up to 1997, there were just a few 2-halo-2*H*-azirine derivatives mentioned in the literature.[7] This was mainly due to the difficult access to appropriate precursors, the synthesis of which needed the use of explosive XN_3 reagents (X = Cl, Br, I).[7b,c] But since 1997, with the development of a new method[8] for producing some 1-azido-2-haloethenes, which are known as good precursors for the 2-halo-2*H*-azirines, several of the latter compounds have been prepared[9] and utilized as intermediates[9b,d] in the synthesis of many useful compounds. However, access to 1-azido-2-haloethenes by this method was limited to specific structures. On the other hand, some 2-halo-2*H*-azirines proved to have a great tendency to equilibrate with their azirine isomers through a [1,2]-shift of the halogen atom.[7b,c] This rapid establishment of equilibrium made the observation, isolation and conservation of pure isomers only possible at low temperature.[7b] Consequently, studies on this [1,2]-halogen shift in 2-halo-2*H*-azirines were limited to some kinetic investigations[7b,c] without use in preparative synthesis.



Scheme 1

Here we report on how to turn this method into an efficient one, which can be used in the preparation of pure azirines of type **4** (Scheme 1). Compounds of type **4** may be ideal precursors for the long-sought[10–12] methylene-2*H*-azirines, which were unknown[13–15] until recently when they were generated by photolysis of allenyl azides[16,17] or other azides.[18] 1-Azido-2-haloethenes of type **5** are possible precursors for the azirines of type **4**. However, access to such 1-azido-2-haloethenes **5** proved to be very difficult. In our synthetic strategy, the newly synthesized 1-azido-2-haloethenes **2** are supposed to produce 2-halo-2*H*-azirines of first generation **3**, which have sufficiently high internal energies to cause an irreversible conversion into more stable isomers **4**. Note that 2*H*-azirines **6** are better stabilized by donor substituents (R^1) at the 3-position of the ring, contrary to electron-withdrawing groups, which induced instability when fixed at this position. Therefore, the substitution pattern of 2-halo-2*H*-azirines of type **3** described in this paper has been especially built up with the

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aim of facilitating their rearrangement into isomers of type **4**. On the way to the azirines of type **4**, some key steps were: a) access to new allenyl halides **1** bearing acceptor substituents, b) synthesis of new 1-azido-2-haloethenes **2**, c) generation of 2-halo-2*H*-azirines of type **3** and d) implementation of the irreversible rearrangement of the 2-halo-2*H*-azirines **3** into the final azirines **4**.

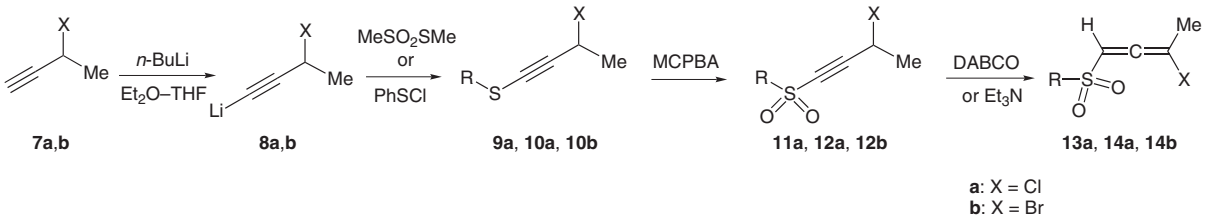
Synthesis of Allenes of Type 1

In order to produce the allenyl halides of type **1**, two different synthetic pathways were used. In the first one, propargyl halides **7a**[19] and **7b**[19] were treated with *n*-butyllithium by analogy with the procedure described in the literature[19] followed by addition of $MeSO_2SMe$[20] or PhSCl[21] leading to thioethers **9a**, **10a** and **10b** (Table 1). The reaction of **9a**, **10a** and **10b** with two equivalents of *m*-chloroperoxybenzoic acid afforded the sulfone derivatives **11a**, **12a** and **12b**, respectively. By prototropic rearrangement of **11a**, **12a** and **12b** using triethyl amine or 1,4-diazabicyclo[2.2.2]octane (DABCO) as base, the desired sulfonyl substituted allenyl halides **13a**, **14a** and **14b** were obtained in good to very good yields.

In the second pathway, the propargyl compounds **15a**,[22] **16a**,[23] **17c**,[24] and **18c** were treated with potassium thiophenolate (PhSK) by analogy with the procedure described in the literature[25] affording the propargyl thioethers **19**,[26] **20**, **21**[27] and **22**, respectively, in very good yields (Table 2). By treatment of **19**–**22** with two equivalents of *m*-chloroperoxybenzoic acid, the corresponding sulfones **23**, **24**, **25**,[27] and **26**, were obtained in very good yields.

Addition of bromine to the alkynyl sulfones **23**–**26** in dichloromethane led to the corresponding vicinal vinyl dibromides (*E*)-**27b**, (*E*)-**28b**, (*E*)-**29b** and (*E*/*Z*)-**30b** in good to very good yields (Table 3). Finally, treatment of **27b**–**30b** with triethyl amine afforded the required allenyl halides **31b**–**34b**. Except for **30b**, which was obtained as a mixture of *E*- and *Z*-isomers (*E*/*Z* = 26:1), the exclusive formation of *E*-isomers was observed. Examples for the stereoselective formation of *E*-isomers by addition of bromine to alkynes are known.[28,29] In many cases, acetic acid was used as solvent instead of dichloromethane as we used here.

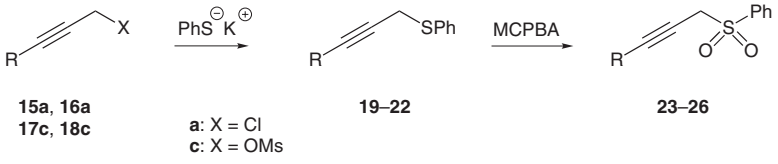
Table 1 Synthesis of Sulfonyl-Substituted Allenyl Halides **13a**, **14a** and **14b**



Starting alkyne	Thioether	Yield (%)[a]	Alkynyl sulfone	Yield (%)[a]	Base	Allenyl sulfone	Yield (%)[a]
7a (X = Cl)	**9a** (R = Me)	94	**11a**	95	DABCO	**13a**	82
7a (X = Cl)	**10a** (R = Ph)	99	**12a**	96	DABCO	**14a**	94
7b (X = Br)	**10b** (R = Ph)	60	**12b**	93	Et_3N	**14b**	92

[a] All yields refer to isolated compounds.

Table 2 Synthesis of Sulfones **23**–**26**



R	Starting alkyne	Thioether	Yield (%)[a]	Sulfone	Yield (%)$_a$
$MeOCH_2$	**15a** (X = Cl)	**19**	92	**23**	96
n-C_5H_{11}	**16a** (X = Cl)	**20**	95	**24**	97
Ph	**17c** (X = OMs)	**21**	90	**25**	92
t-Bu	**18c** (X = OMs)	**22**	88	**26**	95

[a] All yields refer to isolated compounds.

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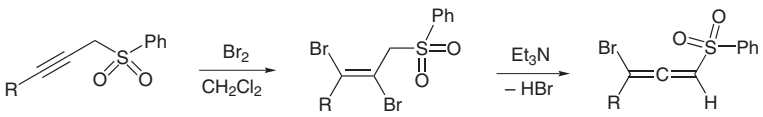
Table 3 Synthesis of Allenyl Halides **31b–34b**



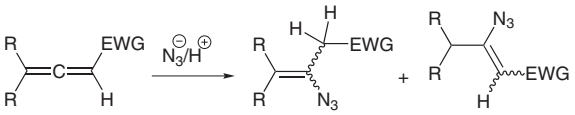
23–26 (*E*)-**27b**-(*E*)-**29b** (*E*/*Z*)-**30b** **31b–34b**

R	Propargyl sulfone	*vic*-Vinyl dibromide	Yield (%)[a]	*E*/*Z* ratio	Allenyl bromide	Yield (%)[a]
$MeOCH_2$	**23**	(*E*)-**27b**	93	1:0	**31b**	70
n-C_5H_{11}	**24**	(*E*)-**28b**	94	1:0	**32b**	44
Ph	**25**	(*E*)-**29b**	89	1:0	**33b**	67
t-Bu	**26**	(*E*/*Z*)-**30b**	86	26:1	**34b**	82

[a] All yields refer to isolated compounds.

Synthesis of 1-Azido-2-haloethenes of Type 2

Previous results[30] on the addition of hydrazoic acid to acceptor-substituted allenes of type **35** led to the formation of vinyl azides of type **37** (Scheme 2). In some cases the formation of mixtures of isomers of type **36** and **37** had been observed.[2h,30] The latter reaction course was also observed when tetramethylguanidinium azide (TMGA) was used as source of HN_3.[30]



35 **36** **37**

Scheme 2

However, treatment of the novel sulfonyl substituted allenyl halides with TMGA at about 0 °C for shorter reaction times led only to 1-azido-2-haloethenes of type **36** (Scheme 2). In fact, the reaction of **13a**, **14a**,**b** and **31b–34b** with TMGA gave the corresponding 1-azido-2-haloethenes (*E*/*Z*)-**38a**, (*E*/*Z*)-**39a**, (*E*/*Z*)-**39b**, (*E*/*Z*)-**40b**, (*E*/*Z*)-**41b**, (*E*/*Z*)-**42b** and (*Z*)-**43b**, in excellent yields (Table 4). The exclusive formation of (*Z*)-**43b** was rationalized by the stereodirecting effect of the bulky *tert*-butyl group.

Photolysis of 1-Azido-2-haloethenes and Rearrangement of the Resulting 2-Halo-2*H*-azirines of Type 3

As we already mentioned in the introduction, some 2-halogen-2*H*-azirines undergo a thermal rearrangement through [1,2] halogen shift.[7b,c] However, this rearrangement always led to an equilibrium between the isomers formed. The ratio of the isomers at equilibrium proved to depend on the solvent polarity, whereas the thermodynamically more stable isomer was always the major one. Consequently, we thought that it would be possible to isolate exclusively the thermodynamically more stable isomer, if the energy difference between the isomers is high enough.

In this connection, we first irradiated a solution of 1-azido-2-haloethenes (*E*)-**40b** and (*Z*)-**40b** in $CDCl_3$ at –30 °C with UV light affording the 2-bromo-2*H*-azirine **44b** together with traces of the isomer **46b** (Scheme 3). Since the observed rearrangement is a thermal process,[7b,c] traces of **46b** were formed during the measurement of ^1H NMR data, which took place at 19 °C. At room temperature the equilibrium between both isomers was established 10–15 minutes later (ratio of isomers at equilibrium **44b**/**46b** = 1:1). This equilibrium showed that the difference between the electronic effects of the substituents at 2- and 3-position of the azirines **44b** and **46b** is small. In fact, the $PhSO_2CH_2$ group and the $MeOCH_2$ group[31] can be considered as weak acceptor substituents, which consequently led to approximately the same thermodynamic stability of the isomers **44b** and **46b**. The rearrangement itself is known[7b] to take place through an intermediate cation, which should have the structure of **45b** in our case. The establishment of this equilibrium is a result comparable to those reported in the literature.[7b,c]

When $CDCl_3$ solutions of (*E*/*Z*)-**39b**, (*E*/*Z*)-**41b**, (*Z*)-**43b** were irradiated under the same conditions followed by measurement of NMR data at 19 °C, the corresponding azirines **48b**, **49b**, **51b** were obtained, together with their rearranged isomers **53b**, **54b** and **56b**, respectively (Table 5). However, in contrary to the equilibrium obtained before, the complete rearrangement of the azirines **48b**, **49b**, **51b** into more stabilized isomers **53b**, **54b** and **56b**, respectively, was observed by keeping the samples at room temperature. The stability of the azirines **53b**, **54b** and **56b** has been induced by the +I-effect of methyl, *n*-pentyl and *tert*-butyl groups, respectively, which are fixed at the 3-position of the corresponding azirines. Thus the

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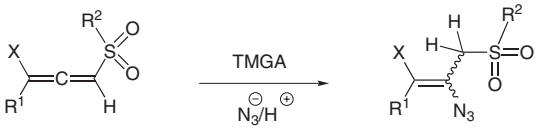
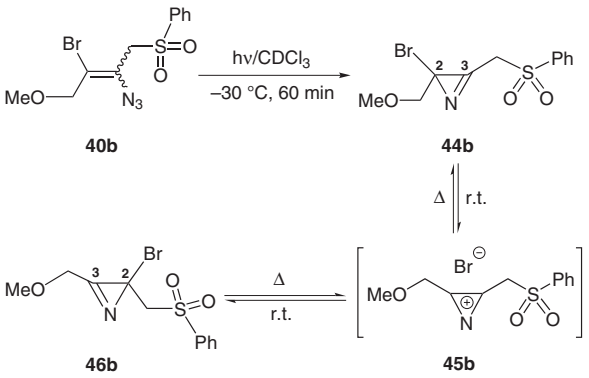
Table 4 Synthesis of 1-Azido-2-haloethenes



13a, **14a**,**b** **31b–34b** **38a**, **39a**,**b** **40b–43b**

X	R^1	R^2	Allene	Ethene	*E*/*Z* ratio	Yield (%)[a]
Cl	Me	Me	**13a**	(*E*/*Z*)-**38a**	5:1.5	98
Cl	Me	Ph	**14a**	(*E*/*Z*)-**39a**	3:2	97
Br	Me	Ph	**14b**	(*E*/*Z*)-**39b**	5:1	92
Br	$MeOCH_2$	Ph	**31b**	(*E*/*Z*)-**40b**	2:1	95
Br	*n*-C_5H_{11}	Ph	**32b**	(*E*/*Z*)-**41b**	3:1	99
Br	Ph	Ph	**33b**	(*E*/*Z*)-**42b**	1:2	92
Br	*t*-Bu	Ph	**34b**	(*Z*)-**43b**	0:1	94

[a] All yields refer to the isolated compounds.



40b **44b** **46b** **45b**

Scheme 3

yields of the rearrangement products were excellent. In the case of the transformation of (*E*/*Z*)-**42b** (R^1 = Ph) into **55b** (97%), the rearrangement was so fast that the corresponding azirine intermediate **50b** could only be observed at lower temperature. The half-lifetime of the conversion of **50b** was found to be ca. 709 seconds in $CDCl_3$ at –30 °C with k = ca 9.77×10^{-4} s^{-1}.

In order to study the influence of the halogen on the rearrangement process, (*E*/*Z*)-**39a** (X = Cl) was irradiated to give **48a** (X = Cl, 99%), and the rate of its rearrangement to yield **53a** was then compared with the analogous transformation of **48b** (X = Br) into **53b**. We found that at room temperature the complete rearrangement of **48a** into **53a** took about four hours, which corresponded to approximately 24 times the duration of **48b** → **53b** (ca. 10 min). Therefore, we can say that the time of the halogen displacement considerably depends on the strength of the C–X bond (Cl > Br). The stronger the C–X bond is, the longer is the rearrangement time. By variation of the substituent R^2, for example **38a** (R^2 = Me) and **39a** (R^2 = Ph), the time necessary for the rearrangement of the resulting azirines (**47a** → **52a** and **48a** → **53a**) proved to be only weakly influenced if compared to the effects of the substituents R^1 and X (X = halogen). In each rearrangement described in this paper, the formation of the rearranged azirines took place in excellent yield, without any evidence of polymerization.

In summary, we succeeded in the synthesis of new acceptor-substituted allenyl halides and their conversion into novel vicinal vinyl azidohalides. Their photolysis led to new 2-halo-2*H*-azirines. The first irreversible rearrangement of such small-ring heterocycles into more stable isomeric azirines is highlighted in this paper as a newly adapted and effective way to 2-halo-2*H*-azirines. This isomerization took place under mild conditions and in excellent yields. From the first step, substituents were selectively introduced into intermediates with aim of facilitating the irreversible conversion of the first azirines into their rearranged azirine isomers. Since the C–X bonds have to be broken and recombined during the process, the nature of halogen also greatly influences the rate of the rearrangement because of the difference in strengths of the C−X bonds. Although there was a possibility of reaction between the nitrogen lone pair and the intermediate cation, no evidence of polymerization was found. The strategy developed in this paper is very efficient although several steps are involved. It opens a way to new and clean 2-halo-2*H*-azirines. In a further publication we will show that these compounds are very convenient precursors to generate 2-methylene-2*H*-azirines.

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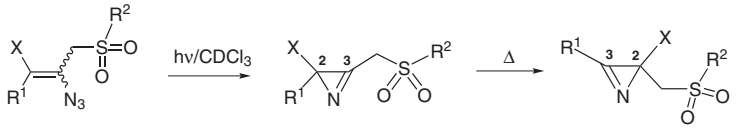
Table 5 Synthesis of Azirines



38a, **39a**,**b** **41b–43b** | **47b**, **48a**,**b**, **49b** **50b**, **51b** | **52a**, **53a**,**b** **54b–56b**

X	R^1	R^2	Ethene	First azirine	Yield (%) or remark	Time (min)	Rearranged azirine	Yield (%)
Cl	Me	Me	(*E*/*Z*)-**38a**	**47a**	99[a]	180[b]	**52a**	99[a]
Cl	Me	Ph	(*E*/*Z*)-**39a**	**48a**	99[a]	240[b]	**53a**	99[a]
Br	Me	Ph	(*E*/*Z*)-**39b**	**48b**	**48b**/**53b** = 1:1[c]	~10[b]	**53b**	96[a,d]
Br	*n*-C_5H_{11}	Ph	(*E*/*Z*)-**41b**	**49b**	**49b**/**54b** = 1:4[c]	~5[b]	**54b**	97[d,e]
Br	Ph	Ph	(*E*/*Z*)-**42b**	**50b**	**50b**/**55b** = 5:2[f]	~709 s[g]	**55b**	97[a,d]
Br	*t*-Bu	Ph	(*Z*)-**43b**	**51b**	**51b**/**56b** = 1:3[c]	~10[b]	**56b**	99[a,d]

[a] Yield determined by NMR.
[b] Relative rearrangement time at 19 °C.
[c] Ratio determined from the first ^{1}H NMR spectrum taken at 19 °C after photolysis at –30 °C.
[d] Yield based on the ethene compound.
[e] Yield of isolated product.
[f] Ratio determined from the first ^{1}H NMR spectrum taken at –50 °C after photolysis at –50 °C.
[g] Half-lifetime at –30 °C.

^{1}H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, on a Varian Gemini in $CDCl_3$, unless otherwise noted. Chemical shifts (δ) are reported in ppm downfield from TMS. Coupling constants (*J*) are reported in Hz, and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). IR spectra were recorded as solutions in $CDCl_3$. TLC analyses were performed on Macherey–Nagel precoated silica gel Polygram Sil G/UV_{254} plates and visualized by UV. Chromatography refers to flash chromatography[32] carried out on Fluka silica gel 60. The photolyses were performed with a 150-W-Hg high-pressure lamp (polychromatic) TQ 150 from Quarzlampen-Gesellschaft. In order to get good yields of the 2*H*-azirines by preventing succeeding photochemical reactions, solutions in $CDCl_3$, which function as UV filter, were used. For the elemental analyses, Vario El instrument (Elementar Analysensystem GmbH) was employed. Mariner 5229 from Applied Biosystems was used for HRMS spectra. The method applied was the electrospray ionization. But, in the case of vinyl azides, the intensity of the M+ signal was so small that high resolution could not be realized.

Elemental analyses of azides could not be performed because of explosive decomposition. For a few compounds, derivatives were prepared to perform the elemental analysis or HRMS, respectively, or this characterization was realized for the next product within a sequence of synthetic steps. Caution should be exercised during isolation of azide, which may be explosive. In the case of solutions of tetrabutylammonium azide in dichloromethane, an explosion probably caused by diazidomethane was reported.[33] Therefore special caution is also necessary in the case of TMGA in dichloromethane although we never observed any incidence.

The known compounds were synthesized according to the corresponding literature for **7a**,[19] **7b**,[19] **15a**,[22] **16a**,[23] and **17c**[24] or according to the literature[25] for **19**[26] and **21**.[27] The synthesis of **25**[27] was performed according to the procedure used for **11a**. The stereochemistry and the assignment of the ^{1}H NMR signals were clarified with aid of NOE experiments or by comparison of the NMR data.

(3-Chlorobut-1-ynylsulfanyl)benzene (10a)

Under Ar atmosphere, a solution of 3-chlorobut-1-yne (**7a**;[19] 2.00 g, 22.6 mmol) in anhyd Et_2O (30 mL) was cooled to –80 °C. A solution of *n*-BuLi (9.10 mL, 2.5 M) in *n*-hexane was added dropwise while stirring at –80 °C. After additional stirring at –80 °C for 45 min, PhSCl[21] (2.96 g, 20.5 mmol) was added dropwise at the same temperature. The mixture was stirred for 20 min and then warmed to r.t. within 45 min. Then H_2O (35 mL) was added while stirring vigorously. The organic phase was separated, and the aqueous phase was extracted several times with Et_2O. The combined organic layers were dried over $MgSO_4$ and the solvent was removed to give **10a** (3.99 g, 20.3 mmol, 99%) as a yellow oil.

^{1}H NMR ($CDCl_3$): δ = 1.85 (d, ^3J = 6.9 Hz, 3 H, CH_3), 4.90 (q, ^3J = 6.9 Hz, 1 H, H-3′), 7.24–7.28 (m, 1 H, *p*-Ph), 7.35–7.45 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 26.4 (q, CH_3), 44.9 (d, C-3′), 73.2 (s, C≡), 97.4 (s, C≡), 126.4 (d, 2 × C), 126.8 (d, *p*-Ph), 129.3 (d, 2 × C), 131.9 (s, *i*-Ph).

HRMS (ESI): *m*/*z* [M + H^+, ^{35}Cl] calcd for $C_{10}H_9ClS$: 197.0139; found: 197.0159.

(3-Bromobut-1-ynylsulfanyl)benzene (10b)

According to the procedure used for **10a**, compound **10b** (2.03 g, 8.4 mmol) was obtained in 60% yield as a yellow oil from the propargyl bromide **7b**,[19] *n*-BuLi (2.5 M solution in hexane) and PhSCl.[21]

^{1}H NMR ($CDCl_3$): δ = 2.02 (d, ^3J = 6.9 Hz, 3 H, CH_3), 4.89 (q, ^3J = 6.9 Hz, 1 H, H-3′), 7.28–7.48 (m, 5 H, Ph).

^{13}C NMR ($CDCl_3$): δ = 27.2 (q, CH_3), 32.1 (d, C-3′), 73.9 (s, C≡), 98.0 (s, C≡), 126.3 (d, 2 × C), 126.8 (d, *p*-Ph), 129.3 (d, 2 × C), 132.0 (s, *i*-Ph).

3-Chloro-1-methylsulfonylbut-1-yne (11a)

According to the literature,[19] we obtained **9a** (94%) as a colorless oil from the propargyl chloride (**7a**),[19] *n*-BuLi (2.5 M solution in hex-

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ane) and *S*-methyl methanethiosulfonate ($MeSO_2SMe$).[20] In contact with air, **9a** was oxidized from colorless to dark-brown.

9a

^{1}H NMR ($CDCl_3$): δ = 1.73 [d, ^3J = 6.9 Hz, 3 H, C(CH_3)], 2.37 (s, 3 H, SCH_3), 4.75 (q, ^3J = 6.9 Hz, 1 H, H-3).

^{13}C NMR ($CDCl_3$): δ = 18.9 (q, SCH_3), 26.4 [q, C(CH_3)], 45.2 (d, C-3), 78.3 (s, C≡), 91.4 (s, C≡).

While stirring at 0 °C, a solution of the compound **9a** (1.50 g, 11.2 mmol) in CH_2Cl_2 (40 mL) was treated dropwise with a solution of 70% MCPBA (6.00 g, 24.3 mmol) in CH_2Cl_2 (20 mL). This mixture was kept overnight at 6 °C. Thereafter, it was diluted with CH_2Cl_2 and washed with a sat. solution of Na_2CO_3 (3 ×). The organic layer was dried over $MgSO_4$ and concentrated to afford the sulfone **11a** (1.75 g, 10.5 mmol, 95%) as a colorless liquid.

IR ($CDCl_3$): 2202 (C≡C), 1325 (SO_2), 1150 (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.78 [d, ^3J = 6.9 Hz, 3 H, C(CH_3)], 3.21 (s, 3 H, SO_2CH_3), 4.70 (q, ^3J = 6.9 Hz, 1 H, H-3).

^{13}C NMR ($CDCl_3$): δ = 24.6 [q, C(CH_3)], 40.9 (q, SO_2CH_3), 46.4 (d, C-3), 80.1 (s, C≡), 90.0 (s, C≡).

MS (ESI): *m*/*z* = 166.98 [M + H$^+$, ^{35}Cl].

Anal. Calcd for $C_5H_7ClO_2S$: C, 36.04; H, 4.23; S, 19.24. Found: C, 36.12; H, 4.26; S, 18.89.

(3-Chlorobut-1-ynylsulfonyl)benzene (12a)

According to the procedure used for **11a**, compound **10a** was treated with 70% MCPBA to afford **12a** (96%) as a yellow oil.

IR ($CDCl_3$): 2200 (C≡C), 1331 (SO_2), 1159 (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.74 (d, ^3J = 6.9 Hz, 3 H, CH_3), 4.66 (q, ^3J = 6.9 Hz, 1 H, H-3′), 7.57–7.63 (m, 2 H, *m*-Ph), 7.68–7.74 (m, 1 H, *p*-Ph), 7.98–8.02 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 24.7 (q, CH_3), 41.1 (d, C-3′), 81.7 (s, C≡), 91.8 (s, C≡), 127.5 (d, 2 × C), 129.4 (d, 2 × C), 134.5 (d, *p*-Ph), 140.8 (s, *i*-Ph).

Anal. Calcd for $C_{10}H_9ClO_2S$: C, 52.52; H, 3.96; S, 13.98. Found: C, 53.02; H, 4.01; S, 13.62.

(3-Bromobut-1-ynylsulfonyl)benzene (12b)

According to the procedure used for **11a**, compound **10b** was treated with 70% MCPBA to afford **12b** (93%) as a yellow oil.

IR ($CDCl_3$): 2195 (C≡C), 1333 (SO_2), 1162 (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.85 (d, ^3J = 6.9 Hz, 3 H, CH_3), 4.56 (q, ^3J = 6.9 Hz, 1 H, H-3′), 7.55–7.61 (m, 2 H, *m*-Ph), 7.65–7.69 (m, 1 H, *p*-Ph), 7.95–7.99 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 25.2 (q, CH_3), 26.3 (d, C-3′), 81.1 (s, C≡), 92.6 (s, C≡), 127.3 (d, 2 × C), 129.4 (d, 2 × C), 134.4 (d, *p*-Ph), 140.7 (s, *i*-Ph).

MS (ESI): *m*/*z* (%) = 272.94 (90) [M + H$^+$, ^{79}Br], 274.93 (100) [M + H$^+$, ^{81}Br].

3-Chloro-1-methylsulfonylbuta-1,2-diene (13a)

While stirring at 15 °C, compound **11a** (1.10 g, 6.61 mmol) in $CHCl_3$ (4 mL) was treated with DABCO (0.67 g, 5.98 mmol). The mixture was stirred for 50 min at 15–20 °C and then filtered on silica gel with Et_2O. After removal of the solvent and crystallization from Et_2O–*n*-pentane, the allene **13a** (0.90 g, 5.41 mmol, 82%) was obtained as white crystals; mp 60–61 °C.

IR ($CDCl_3$): 1968 (C=C=C), 1318 (SO_2), 1138 (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.28 [d, ^5J = 3 Hz, 3 H, C(CH_3)], 3.04 (s, 3 H, SO_2CH_3), 6.35 (q, ^5J = 3 Hz, 1 H, H-1).

^{13}C NMR ($CDCl_3$): δ = 22.5 [q, C(CH_3)], 42.8 (q, SO_2CH_3), 103.2 (d, C-1), 110.8 (s, C-3), 202.6 (s, C-2).

Anal. Calcd for $C_5H_7ClO_2S$: C, 36.04; H, 4.23. Found: C, 36.14; H, 4.36.

(3-Chlorobuta-1,2-dienylsulfonyl)benzene (14a)

To a stirred solution of **12a** (65 mg, 284 μmol) in $CDCl_3$ (0.5 mL), DABCO (32 mg, 286 μmol) was added. After 2 h, the mixture was filtered on silica gel with Et_2O, and the solvent was removed to afford **14a** (0.06 g, 263 μmol, 94%) as a yellow oil. For larger amounts, the reaction was repeated in CH_2Cl_2 at 15–20 °C for 2.5 h.

IR ($CDCl_3$): 1966 (C=C=C), 1321 (SO_2), 1147 (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.16 (d, ^5J = 3.0 Hz, 3 H, CH_3), 6.34 (q, ^5J = 3.0 Hz, 1 H, H-1′), 7.54–7.60 (m, 2 H, *m*-Ph), 7.64–7.68 (m, 1 H, *p*-Ph), 7.90–7.94 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 22.4 (q, CH_3), 104.5 (d, C-1′), 110.7 (s, C-3′), 127.9 (d, 2 × C), 129.3 (d, 2 × C), 133.9 (d, *p*-Ph), 139.8 (s, *i*-Ph), 202.6 (s, C-2′).

Anal. Calcd for $C_{10}H_9ClO_2S$: C, 52.52; H, 3.96; S, 13.98. Found: C, 52.78; H, 4.02; S, 13.71.

(3-Bromobuta-1,2-dienylsulfonyl)benzene (14b)

While stirring at 0 °C, compound **12b** (1.20 g, 4.40 mmol) in CH_2Cl_2 (5 mL) was treated with Et_3N (1.33 g, 13.2 mmol). The mixture was stirred for 100 min at 5 °C and then filtered on silica gel with Et_2O to afford the allene **14b** (1.10 g, 4.03 mmol, 92%) as a colorless oil.

IR ($CDCl_3$): 1320 (SO_2), 1145 (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.29 (d, ^5J = 3.0 Hz, 3 H, CH_3), 6.11 (q, ^5J = 3.0 Hz, 1 H, H-1′), 7.53–7.59 (m, 2 H, *m*-Ph), 7.62–7.68 (m, 1 H, *p*-Ph), 7.89–7.92 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 23.8 (q, CH_3), 95.8 (s, C-3′), 103.0 (d, C-1′), 127.9 (d, 2 × C), 129.3 (d, 2 × C), 133.9 (d, *p*-Ph), 139.9 (s, *i*-Ph), 201.1 (s, C-2′).

MS (ESI): *m*/*z* (%) = 272.94 (95) [M + H$^+$, ^{79}Br], 274.94 (100) [M + H$^+$, ^{81}Br].

HRMS (ESI): *m*/*z* [M + H$^+$, ^{79}Br] calcd for $C_{10}H_9BrO_2S$: 272.9532; found: 272.9516.

(4,4-Dimethylpent-2-ynylsulfanyl)benzene (22)

By analogy with the procedure described in the literature,[24] compound **18c** was obtained as a colorless liquid in quantitative yield from the corresponding alcohol.[34]

Compound 18c

^{1}H NMR ($CDCl_3$): δ = 1.20 [s, 9 H, C(CH_3)], 3.09 (s, 3 H, SO_2CH_3) 4.81 (s, 2 H, H-1).

^{13}C NMR ($CDCl_3$): δ = 27.5 [s, C(CH_3)], 30.4 [q, 3 × C, C(CH_3)], 38.9 (q, SO_2CH_3) 58.7 (t, C-1), 70.8 (s, C≡), 98.8 (s, C≡).

Compound **22** (88%) was obtained as a colorless oil from **18c** according to the procedure described in the literature.[25] On contact with air, its colorless aspect changes slowly to yellow. This was due to its oxidation to the corresponding sulfoxide.

MS (ESI): *m*/*z* = 221.10 [M + H$^+$].

Compound 22

^{1}H NMR ($CDCl_3$): δ = 1.16 (s, 9 H, CH_3), 3.61 (s, 2 H, H-1′), 7.25–7.33 (m, 3 H, Ph), 7.45–7.48 (m, 2 H, Ph).

^{13}C NMR ($CDCl_3$): δ = 23.3 (t, C-1′), 27.4 (s, C-4′), 30.9 (q, 3 × C, CH_3), 74.0 (s, C≡), 92.7 (s, C≡), 126.7 (d, *p*-Ph), 128.7 (d, 2 × C), 130.5 (d, 2 × C), 135.4 (s, *i*-Ph).

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MS (ESI): m/z = 205.09 [M + H^+].

GC–MS: m/z = 204 [M^+].

(4-Methoxybut-2-ynylsulfonyl)benzene (23)
Compound **23** (96%, yellow oil) was obtained from **19**[26] according to the procedure used for **11a**.

IR ($CDCl_3$): 1327 (SO_2), 1141 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.22 (s, 3 H, OCH_3), 4.01 (t, ^5J = 2.2 Hz, 2 H), 4.05 (t, ^5J = 2.2 Hz, 2 H), 7.52–7.57 (m, 2 H, *m*-Ph), 7.62–7.66 (m, 1 H, *p*-Ph), 7.92–7.95 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 48.5 (t, C-1′), 57.4 (q, OCH_3), 59.5 (t, C-4′), 74.0 (s, C≡), 83.7 (s, C≡), 128.6 (d, 2 × C), 129.0 (d, 2 × C) 134.1 (d, *p*-Ph), 137.5 (s, *i*-Ph).

HRMS (ESI): m/z [M + H^+] calcd for $C_{11}H_{12}O_3S$: 225.0580; found: 2251.0582.

(Oct-2-ynylsulfonyl)benzene (24)
Compound **20** (95%) was obtained as a colorless oil from **16a**[23] according to the procedure described in the literature.[25]

Compound 20
^1H NMR ($CDCl_3$): δ = 0.90 (t, ^3J = 7.2 Hz, 3 H, H-8′), 1.31 (m, 4 H), 1.47 (m, 2 H), 2.17 (tt, ^3J = 7.2 Hz, ^5J = 2.4 Hz, 2 H, H-4′), 3.64 (t, ^5J = 2.4 Hz, 2 H, H-1′), 7.20–7.25 (m, 1 H, *p*-Ph), 7.29–7.34 (m, 2 H, Ph), 7.42–7.47 (m, 2 H, Ph).

^{13}C NMR ($CDCl_3$): δ = 13.9 (q, C-8′), 18.7 (t), 22.1 (t), 22.9 (t), 28.2 (t), 30.9 (t), 75.4 (s, C≡), 84.1 (s, C≡), 126.4 (d, *p*-Ph), 128.7 (d, 2 × C), 129.6 (d, 2 × C), 135.6 (s, *i*-Ph).

Compound **24** (97%) was then obtained as a colorless oil from **20** according to the procedure used for **11a**.

IR ($CDCl_3$): 1324 (SO_2), 1137 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.85 (t, ^3J = 7.2 Hz, 3 H, H-8′), 1.23 (m, 4 H), 1.40 (m, 2 H), 2.11 (tt, ^3J = 7.2 Hz, ^5J = 2.4 Hz, 2 H, H-4′), 3.93 (t, ^5J = 2.4 Hz, 2 H, H-1′), 7.53–7.58 (m, 2 H, *m*-Ph), 7.64–7.70 (m, 1 H, *p*-Ph), 7.93–7.97 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 13.9 (q, C-8′), 18.6 (t), 22.0 (t), 27.7 (t), 30.8 (t), 48.9 (t, C-1′), 67.3 (s, C≡), 88.9 (s, C≡), 128.7 (d, 2 × C), 128.9 (d, 2 × C), 134.0 (d, *p*-Ph) 137.7 (s, *i*-Ph).

MS (ESI): m/z = 251.09 [M + H^+].

HRMS (ESI): m/z [M + H^+] calcd for $C_{14}H_{18}O_2S$: 251.1100; found: 251.1117.

(4,4-Dimethylpent-2-ynylsulfonyl)benzene (26)
The sulfone **26** (4.20 g, 17.7 mmol, 95%) was obtained as white crystals (mp 55–57 °C) from **22** according to the procedure used for **11a**.

IR ($CDCl_3$): 1324 (SO_2), 1137 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.10 (s, 9 H, CH_3), 3.91 (s, 2 H, H-1′), 7.52–7.58 (m, 2 H, *m*-Ph), 7.64–7.70 (m, 1 H, *p*-Ph), 7.94–7.97 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 27.4 (s, C-4′), 30.4 (q, 3 × C, CH_3), 48.9 (t, C-1′), 66.3 (s, C-2′), 96.6 (s, C-3′), 128.8 (d, 2 × C), 129.0 (d, 2 × C), 134.0 (d, *p*-Ph), 137.5 (s, *i*-Ph).

Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.06; H, 6.82; S, 13.57. Found: C, 65.61; H, 6.61; S, 13.77.

(*E*)-(2,3-Dibromo-4-methoxybut-2-enylsulfonyl)benzene [(*E*)-27b]
The sulfone **23** (2.90 g, 13.1 mmol) in anhyd CH_2Cl_2 (50 mL) was treated dropwise at 0 °C with a solution of bromine (2.30 g, 14.4 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred for 100 min at 7 °C. The solvent was then removed at 0 °C under vacuum using a flask-receptor cooled at –10 °C and previously filled with a CH_2Cl_2 solution of cyclohexene as trap for the rest of bromine. The residue was purified by chromatography on silica gel eluting with Et_2O–*n*-hexane (11:9) to give (*E*)-**27b** (4.60 g, 12.0 mmol, 93%) as a white solid; mp 55–57 °C (Et_2O).

IR ($CDCl_3$): 1327 (SO_2), 1153 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.23 (s, 3 H, OCH_3), 4.27 (s, 2 H, H-4′), 4.54 (s, 2 H, H-1′), 7.50–7.56 (m, 2 H, *m*-Ph), 7.62–7.68 (m, 1 H, *p*-Ph), 7.90–7.94 (m, 2 H, *o*-Ph); the assignment of the signals was supported by NOE experiments.

^{13}C NMR ($CDCl_3$): δ = 57.7 (q, OCH_3), 66.3 (t, C-1′), 75.0 (t, C-4′), 109.3 (s, CBr), 128.1 (s, CBr), 128.7 (d, 2 × C), 129.2 (d, 2 × C), 134.3 (d, *p*-Ph), 138.3 (s, *i*-Ph).

Anal. Calcd for $C_{11}H_{12}Br_2O_3S$: C, 34.40; H, 3.15; S, 8.35. Found: C, 34.45; H, 3.07; S, 8.13.

(*E*)-(2,3-Dibromooct-2-enylsulfonyl)benzene [(*E*)-28b]
Compound **24** (4.00 g, 16.0 mmol) in anhyd CH_2Cl_2 (30 mL) was treated dropwise at 0 °C with bromine (5.00 g, 31.25 mmol) in CH_2Cl_2 (20 mL). After stirring for 2 h at 10 °C, the mixture was washed with a sat. solution of Na_2SO_3 (3 ×). The organic layer was dried over $MgSO_4$ and evaporated to give (*E*)-**28b** (6.14 g, 15.0 mmol, 94%) as a colorless oil.

IR ($CDCl_3$): 1325 (SO_2), 1151 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.89 (t, ^3J = 7.2 Hz, 3 H, H-8′), 1.26 (m, 4 H), 1.42 (m, 2 H), 2.61 (t, J = 7.5 Hz, 2 H, H-4′), 4.50 (s, 2 H, H-1′), 7.51–7.57 (m, 2 H, *m*-Ph), 7.64–7.70 (m, 1 H, *p*-Ph) 7.93–7.95 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 13.9 (q, C-8′), 22.3 (t), 26.9 (t), 30.6 (t), 41.2 (t, C-4′), 66.4 (t, C-1′), 105.7 (s, CBr), 129.0 (d, 2 × C), 129.1 (d, 2 × C), 132.0 (s, CBr), 134.2 (d, *p*-Ph), 138.9 (s, *i*-Ph).

MS (ESI): m/z = 410.92 [M + H^+, ^{81}Br].

(*E*)-(1,2-Dibromo-3-phenylsulfonylprop-1-enyl)benzene [(*E*)-29b]
Compound (*E*)-**29b** (89%) was obtained as a white solid from **25**[27] according to the procedure used for (*E*)-**28b**; mp 108–110 °C (Et_2O–*n*-pentane).

IR ($CDCl_3$): 1326 (SO_2), 1148 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 4.69 (s, 2 H, H-3′), 7.15–7.20 (m, 2 H, PhC-1′), 7.33–7.36 (m, 3 H, PhC-1′), 7.59–7.65 (m, 2 H, *m*-$PhSO_2$), 7.70–7.76 (m, 1 H, *p*-$PhSO_2$), 8.03–8.07 (m, 2 H, *o*-$PhSO_2$).

^{13}C NMR ($CDCl_3$): δ = 66.8 (t, C-3′), 107.9 (s), 126.1 (s), 128.3 (d, 2 × C), 128.4 (d, 2 × C), 129.1 (d, 2 × C), 129.2 (d, 2 × C), 129.3 (d), 134.4 (d), 138.3 (s), 139.7 (s).

Anal. Calcd for $C_{15}H_{12}Br_2O_2S$: C, 43.30; H, 2.91; S, 7.71. Found: C, 43.40; H, 2.90; S, 7.26.

(2,3-Dibromo-4,4-dimethylpent-2-enylsulfonyl)benzene [(*E*/*Z*)-30b]
Compound **26** (3.50 g, 13.06 mmol) in anhyd CH_2Cl_2 (50 mL) was treated dropwise at 0 °C with bromine (4.00 g, 25.0 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at 20 °C for 4 h. The workup was performed according to the procedure used for (*E*)-**28b** to afford a yellow liquid (4.45 g, 11.24 mmol, 86%) containing (*E*)-**30b** and (*Z*)-**30b** in a ratio of 26:1.

IR ($CDCl_3$, mixture): 1323 (SO_2), 1145 (SO_2) cm^{-1}.

MS (ESI, mixture): m/z = 396.90 [M + H^+, ^{81}Br].

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(*E*)-30b
^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 9 H, CH_3), 4.69 (s, 2 H, H-1′), 7.51–7.57 (m, 2 H, *m*-Ph), 7.64–7.70 (1 H, *p*-Ph), 7.93–7.97 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 30.6 (q, 3 × C, CH_3), 41.4 (s, C-4′), 70.8 (t, C-1′), 103.6 (s, CBr), 128.9 (d, 2 × C), 129.1 (d, 2 × C), 134.1 (d, *p*-Ph), 138.5 (s), 141.5 (s).

(*Z*)-30b
^{1}H NMR ($CDCl_3$): δ = 1.43 (s, 9 H, CH_3), 4.75 (s, 2 H, H-1′), 7.46–7.51 (m, 2 H, Ph), 7.64–7.70 (1 H, *p*-Ph), 8.00–8.06 (m, 2 H, Ph).

^{13}C NMR ($CDCl_3$): δ = 32.1 (q, 3 × C, CH_3).

Due to the low concentration, only one ^{13}C NMR signal of (*Z*)-**30b** was detected.

Synthesis of the Allenyl Bromides 30b–34b (Table 6); General Procedure
The synthesis of **31b**, **32b**, **33b** and **34b** was performed by treatment of the anhyd CH_2Cl_2 solutions of the vinyl bromides (*E*)-**27b**, (*E*)-**28b**, (*E*)-**29b** and (*E*/*Z*)-**30b**, respectively, with Et_3N at 0 °C. After stirring at the temperature and for the time given in Table 6, purification was performed with the help of chromatography on silica gel using Et_2O–*n*-hexane as eluent.

(3-Bromo-4-methoxybuta-1,2-dienylsulfonyl)benzene (31b)
White solid; mp 41–42 °C (Et_2O–*n*-hexane).

IR ($CDCl_3$): 1322 (SO_2), 1160 (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.32 (s, 3 H, OCH_3), 4.12 (d, ^5J = 2.4 Hz, 2 H, H-4′), 6.27 (t, ^5J = 2.4 Hz, 1 H, H-1′), 7.50–7.56 (m, 2 H, *m*-Ph), 7.60–7.66 (m, 1 H, *p*-Ph), 7.86–7.90 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 58.1 (q, O*C*H_3), 72.8 (t, C-4′), 97.1 (s, C-3′), 105.3 (d, C-1′), 127.8 (d, 2 × C), 129.3 (d, 2 × C), 134.0 (d, *p*-Ph), 139.8 (s, *i*-Ph), 200.8 (s, C-2′).

Anal. Calcd for $C_{11}H_{11}BrO_3S$: C, 43.58; H, 3.66; S, 10.57. Found: C, 43.48; H, 3.72; S, 10.38.

(3-Bromoocta-1,2-dienylsulfonyl)benzene (32b)
Yellowish oil.

IR ($CDCl_3$): 1322 (SO_2), 1146 (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.87 (t, ^3J = 7.2 Hz, 3 H, H-8′), 1.26 (m, 4 H), 1.44 (m, 2 H), 2.41 (td, ^3J = 7.5 Hz, ^5J = 2.7 Hz, 2 H, H-4′), 6.16 (t, ^5J = 2.7 Hz, 1 H, H-1′), 7.55–7.59 (m, 2 H, *m*-Ph), 7.63–7.66 (m, 1 H, *p*-Ph) 7.89–7.93 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 13.8 (q, C-8′), 22.1 (t), 27.0 (t), 30.4 (t), 36.7 (t, C-4′), 101.3 (s, C-3′), 103.6 (d, C-1′), 127.8 (d, 2 × C), 129.2 (d, 2 × C), 133.8 (d, *p*-Ph), 139.9 (s, *i*-Ph), 201.0 (s, C-2′).

MS (ESI): *m*/*z* (%) = 143.00 (100), 329.00 (65) [M + H$^+$, ^{79}Br].

HRMS (ESI): *m*/*z* [M + H$^+$, ^{79}Br] calcd for $C_{14}H_{17}BrO_2S$: 329.0159; found: 329.0149.

(1-Bromo-3-phenylsulfonylpropa-1,2-dienyl)benzene (33b)
White solid; mp 121–122 °C (Et_2O–*n*-hexane).

IR ($CDCl_3$): 1323 (SO_2), 1153 (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 6.51 (s, 1 H, H-3′), 7.34–7.39 (m, 3 H, Ph), 7.44–7.49 (m, 2 H, Ph), 7.51–7.58 (m, 2 H, Ph), 7.62–7.68 (m, 1 H, Ph), 7.94–7.98 (m, 2 H, Ph).

^{13}C NMR ($CDCl_3$): δ = 100.8 (s, C-1′), 105.5 (d, C-3′), 127.6 (d, 2 × C), 128.0 (d, 2 × C), 128.7 (d, 2 × C), 129.3 (d, 2 × C), 130.1 (d), 130.5 (s, *i*-Ph at C-1), 134.1 (d), 139.9 (s, *i*-PhSO_2), 203.1 (s, C-2′).

Anal. Calcd for $C_{15}H_{11}BrO_2S$: C, 53.75; H, 3.31; S, 9.56. Found: C, 53.48; H, 3.35; S, 9.39.

(3-Bromo-4,4-dimethylpenta-1,2-dienylsulfonyl)benzene (34b)
White solid; mp 75–76 °C (*n*-hexane).

IR ($CDCl_3$): 1961 (C=C=C), 1334 (SO_2), 1156 (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.08 (s, 9 H, CH_3), 6.17 (s, 1 H, H-1′), 7.52–7.58 (m, 2 H, *m*-Ph), 7.62–7.67 (1 H, *p*-Ph), 7.89–7.92 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 28.3 (q, 3 × C, CH_3), 37.2 (s, C-4′), 103.8 (d, C-1′), 113.2 (s, C-3′), 128.0 (d, 2 × C), 129.2 (d, 2 × C), 133.1 (d, *p*-Ph), 139.7 (s, *i*-Ph), 199.0 (s, C-2′).

Anal. Calcd for $C_{13}H_{15}BrO_2S$: C, 49.53; H, 4.79; S, 10.17. Found: C, 49.47; H, 4.75; S, 10.24.

Synthesis of the 1-Azido-2-haloethenes 38a, 39a,b and 40b–43b (Table 7); General Procedure
The 1-azido-2-haloethenes (*E*/*Z*)-**38a**, (*E*/*Z*)-**39a**, (*E*/*Z*)-**39b**, (*E*/*Z*)-**40b**, (*E*/*Z*)-**41b**, (*E*/*Z*)-**42b** and (*Z*)-**43b** were obtained by treatment of the stirred CH_2Cl_2 solutions of the allenes **13a**, **14a**, **14b**, **31b**, **32b**, **33b** and **34b**, respectively, with TMGA at 0 °C. After stirring at the temperature and for the time given in Table 7, the solvent was partially removed. Purification was performed by filtration of the residue through silica gel using Et_2O.

(*E*/*Z*)-2-Azido-3-chloro-1-methylsulfonylbut-2-ene [(*E*/*Z*)-38a]
Yellowish solid; mp 74–77 °C (Et_2O–*n*-hexane, mixture).

IR ($CDCl_3$, mixture): 2160 (N_3), 2113 (N_3), 1319 (SO_2), 1127 (SO_2) cm^{-1}.

MS (ESI, mixture): *m*/*z* (%) = 182.03 (100), 210.11 (ca. 3) [M + H$^+$, ^{35}Cl].

(*E*)-38a
^{1}H NMR ($CDCl_3$): δ = 2.19 [s, 3 H, C(CH_3)], 3.01 (s, 3 H, SO_2CH_3), 4.22 (s, 2 H, H-1).

Table 6 Synthesis of Compounds **31b**–**34b**

Dibromide	n (mmol)	CH_2Cl_2 (mL)	Et_3N (mmol)	Temp (°C)	Time (min)	Et_2O–*n*-hexane	Allene	n (mmol)	Yield[a] (%)
(*E*)-**27b**	6.12	15	15.8	16	60	1:1	**31b**	4.29	70
(*E*)-**28b**	2.44	10	7.32	5	240	1:4	**32b**	1.06	44
(*E*)-**29b**	0.84	8	2.52	6	60	1:1	**33b**	0.56	67
(*E*)-**30b**	10.1	30	40.4	20	720	1:3	**34b**	8.23	82

[a] Yield of isolated compound.

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Table 7 Synthesis of 1-Azido-3-haloethenes

Starting allene	n (mmol)	CH_2Cl_2 (mL)	TMGA (mmol)	Temp (°C)	Time (min)	1-Azido-2-haloethene	*E*/*Z* ratio	n (mmol)	Yield[a] (%)
13a	3.840	2	4.110	5	15	(*E*/*Z*)-**38a**	5:1.5	3.770	98
14a	0.263	1	0.534	5	15	(*E*/*Z*)-**39a**	3:2	0.254	97
14b	0.249	1	0.498	20	20	(*E*/*Z*)-**39b**	5:1	0.228	92
31b	0.264	1	0.506	15	20	(*E*/*Z*)-**40b**	2:1	0.249	95
32b	0.182	1	0.275	5	25	(*E*/*Z*)-**41b**	3:1	0.180	99
33b	0.191	1	0.478	15	20	(*E*/*Z*)-**42b**	1:2	0.209	92
34b	0.209	1	0.838	5	240	(*Z*)-**43b**	0:1	0.223	94

[a] Yield of isolated compound.

^{13}C NMR ($CDCl_3$): δ = 21.3 [q, C(*C*H_3)], 40.9 (q, SO_2CH_3), 54.6 (t, C-1), 122.8 (s), 125.8 (s).

(*Z*)-38a

^{1}H NMR ($CDCl_3$): δ = 2.25 [s, 3 H, C(CH_3)], 3.01 (s, 3 H, SCH_3), 3.94 (s, 2 H, H-1).

^{13}C NMR ($CDCl_3$): δ = 22.9 [q, C(*C*H_3)], 40.9 (q, SCH_3), 55.2 (t, C-1), 120.9 (s), 126.4 (s).

(*E*/*Z*)-(2-Azido-3-chlorobut-2-enylsulfonyl)benzene [(*E*/*Z*)-39a]

Yellow solid; mp 64–67 °C (Et_2O–*n*-hexane, mixture).

IR ($CDCl_3$, mixture): 2155 (N_3), 2110 (N_3), 1325 (SO_2), 1143 (SO_2) cm^{-1}.

MS (ESI, mixture): *m*/*z* (%) = 244.05 (100), 272.13 (ca. 3) [M + H^+, ^{35}Cl].

(*E*)-39a

^{1}H NMR ($CDCl_3$): δ = 2.02 (s, 3 H, CH_3), 4.28 (s, 2 H, H-1′), 7.53–7.73 (m, 3 H, Ph), 7.91–7.95 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 21.1 (q, *C*H_3), 56.0 (t, C-1′), 122.0 (s), 126.8 (s), 128.7 (d, 2 × C), 129.2 (d, 2 × C), 134.4 (d, *p*-Ph), 137.9 (s, *i*-Ph).

(*Z*)-39a

^{1}H NMR ($CDCl_3$): δ = 1.83 (s, 3 H, CH_3), 4.03 (s, 2 H, H-1′), 7.53–7.73 (m, 3 H, Ph), 7.91–7.95 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 22.1 (q, CH_3), 56.5 (t, C-1′), 121.1 (s), 125.3 (s), 128.5 (d, 2 × C), 129.6 (d, 2 × C), 134.5 (d, *p*-Ph), 137.7 (s, *i*-Ph).

(*E*/*Z*)-(2-Azido-3-bromobut-2-enylsulfonyl)benzene [(*E*/*Z*)-39b]

Mixture of isomers obtained as a yellow oil.

IR ($CDCl_3$, mixture): 2145 (N_3), 2104 (N_3), 1325 (SO_2), 1310 (SO_2), 1143 (SO_2), 1132 (SO_2) cm^{-1}.

(*E*)-39b

^{1}H NMR ($CDCl_3$): δ = 2.21 (s, 3 H, CH_3), 4.32 (s, 2 H, H-1′), 7.53–7.59 (m, 2 H, *m*-Ph), 7.66–7.72 (m, 1 H, *p*-Ph), 7.91–7.95 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 23.5 (q, CH_3), 58.0 (t, C-1′), 118.2 (s), 123.5 (s), 128.6 (d, 2 × C), 129.1 (d, 2 × C), 134.3 (d, *p*-Ph), 137.7 (s, *i*-Ph).

(*Z*)-39b

^{1}H NMR ($CDCl_3$): δ = 1.94 (s, 3 H, CH_3), 4.07 (s, 2 H, H-1′), 7.53–7.59 (m, 2 H, *m*-Ph), 7.66–7.72 (m, 1 H, *p*-Ph), 7.91–7.95 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 24.0 (q, CH_3), 55.6 (t, C-1′), 115.1 (s), 122.8 (s), 128.4 (d, 2 × C), 129.4 (d, 2 × C), 134.4 (d, *p*-Ph), 137.3 (s, *i*-Ph).

(*E*/*Z*)-(2-Azido-3-bromo-4-methoxybut-2-enylsulfonyl)benzene [(*E*/*Z*)-40b]

Mixture of isomers obtained as a yellow oil.

IR ($CDCl_3$, mixture): 2152 (N_3), 2110 (N_3), 1327 (SO_2), 1159 (SO_2) cm^{-1}.

(*E*)-40b

^{1}H NMR ($CDCl_3$): δ = 3.18 (s, 3 H, OCH_3), 4.12 (s, 2 H, CH_2), 4.37 (s, 2 H, CH_2), 7.50–7.59 (m, 2 H, *m*-Ph), 7.63–7.68 (m, 1 H, *p*-Ph), 7.85–7.92 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 57.4 (q, OCH_3), 58.0 (t, C-1′), 70.5 (t, C-4′), 119.2 (s), 127.5 (s), 128.6 (d, 2 × C), 129.2 (d, 2 × C), 134.4 (d, *p*-Ph), 137.6 (s, *i*-Ph).

(*Z*)-40b

^{1}H NMR ($CDCl_3$): δ = 3.17 (s, 3 H, OCH_3), 3.80 (s, 2 H, CH_2), 4.23 (s, 2 H, CH_2), 7.50–7.59 (m, 2 H, *m*-Ph), 7.63–7.68 (m, 1 H, *p*-Ph), 7.85–7.92 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 55.6 (t, C-1′), 57.7 (q, OCH_3), 72.8 (t, C-4′), 115.1 (s), 126.9 (s), 128.3 (d, 2 × C), 129.4 (d, 2 × C), 134.5 (d, *p*-Ph), 137.4 (s, *i*-Ph).

(*E*/*Z*)-(2-Azido-3-bromooct-2-enylsulfonyl)benzene [(*E*/*Z*)-41b]

(E)-41b

Yellow oil.

IR ($CDCl_3$): 2104 (N_3), 1325 (SO_2), 1158 (SO_2) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, ^3J = 7.2 Hz, 3 H, H-8′), 1.27 (m, 6 H), 2.45 (t, *J* = 7.5 Hz, 2 H, H-4′), 4.35 (s, 2 H, H-1′), 7.52–7.57 (m, 2 H, *m*-Ph), 7.65–7.71 (m, 1 H, *p*-Ph), 7.91–7.96 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 13.9 (q, C-8′), 22.3 (t), 27.4 (t), 30.6 (t), 35.8 (t), 58.2 (t, C-1′), 123.2 (s), 124.9 (s), 128.9 (d, 2 × C), 129.2 (d, 2 × C), 134.3 (d, *p*-Ph), 137.8 (s, *i*-Ph).

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(*Z*)-41b
Yellow oil.

IR ($CDCl_3$): 2107 (N_3), 1325 (SO_2), 1141 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.86 (t, ^3J = 7.2 Hz, 3 H, H-8′), 1.15 (m, 2 H), 1.24 (m, 2 H), 1.41 (m, 2 H), 2.12 (t, J = 7.5 Hz, 2 H, H-4′), 4.07 (s, 2 H, H-1′), 7.58–7.64 (m, 2 H, *m*-Ph), 7.69–7.75 (m, 1 H, *p*-Ph), 7.91–7.96 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 13.9 (q, C-8′), 22.3 (t), 28.0 (t), 30.8 (t), 36.3 (t), 56.0 (t, C-1′), 122.6 (s), 122.6 (s), 128.6 (d, 2 × C), 129.6 (d, 2 × C), 134.6 (d, *p*-Ph), 137.7 (s, *i*-Ph).

(*E*/*Z*)-(2-Azido-1-bromo-3-phenylsulfonylprop-1-enyl)benzene [(*E*/*Z*)-42b]
Mixture of isomers obtained as a yellow oil.

IR ($CDCl_3$, mixture): 2160 (N_3), 2113 (N_3), 1325 (SO_2), 1154 (SO_2) cm^{-1}.

MS (ESI, mixture): *m*/z (%) = 157.05 (100), 163.09 (63), 348.11 (50), 350.08 (15), 378.13 (ca. 5) [$M + H^+$, ^{79}Br].

^1H NMR ($CDCl_3$, mixture): δ = 4.11 (s, 2 H, H-3′, *Z*-isomer), 4.48 (s, 2 H, H-3′, *E*-isomer), 6.85–8.05 (m, 20 H, Ph).

^{13}C NMR ($CDCl_3$, mixture): δ = 56.5 (t, C-3′), 59.7 (t, C-3′), 125.1 (s), 125.6 (s), 128.2 (d), 128.5 (d), 129.0 (d), 129.1 (d), 134.3 (d), 134.5 (d), 136.6 (s), 136.8 (s), 137.9 (s).

Some signals were not detected. The assignment of the NMR signals and the stereochemistry was performed by comparison with the data of (*E*/*Z*)-**39a**,**b** and (*E*/*Z*)-**40b**.

(*Z*)-(2-Azido-3-bromo-4,4-dimethylpent-2-enylsulfonyl)benzene [(*Z*)-43b]
White crystals (Et_2O–*n*-hexane); decompose at 40 °C.

IR ($CDCl_3$): 2148 (N_3), 2106 (N_3), 1325 (SO_2), 1149 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.32 (s, 9 H, CH_3), 4.37 (s, 2 H, H-1′), 7.57–7.63 (m, 2 H, *m*-Ph), 7.68–7.74 (1 H, *p*-Ph), 7.92–7.96 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 31.6 (q, 3 × C, CH_3), 40.6 (s, C-4′), 56.5 (t, C-1′), 121.8 (s), 128.4 (d, 2 × C), 129.5 (d, 2 × C), 134.5 (d, *p*-Ph), 136.2 (s), 138.6 (s).

Azirine 44b and its Rearrangement into Azirine 46b
Compound (*E*/*Z*)-**40b** (86 mg, 249 μmol) in $CDCl_3$ (0.6 mL) was irradiated at –30 °C for 60 min. The first ^1H NMR spectrum, measured at 19 °C, proved the formation of **44b** and traces of **46b**. By keeping the mixture at r.t. for 10 min, a second ^1H NMR spectrum showed both isomers in a 1:1 ratio of **44b**:**46b**. This ratio remained unchanged for the rest of time, although decomposition was observed after long storage. The initial combined NMR yield was 98%.

IR ($CDCl_3$, 1:1 mixture): 1746 (C=N), 1325 (SO_2), 1158 (SO_2), 1141 (SO_2) cm^{-1}.

2-Bromo-2-methoxymethyl-3-phenylsulfonylmethyl-2*H*-azirine (44b)
^1H NMR ($CDCl_3$): δ = 3.18 (s, 3 H, OCH_3), 3.81 (d, ^2J = 12.0 Hz, 1 H, OCH_2), 3.86 (d, ^2J = 12.0 Hz, 1 H, OCH_2), 4.74 (s, 2 H, O_2SCH_2), 7.55–7.62 (m, 2 H, *m*-Ph), 7.66–7.73 (m, 1 H, *p*-Ph), 7.80–8.03 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 51.0 (s, C-2), 53.6 (t, O_2SCH_2), 58.9 (q, OCH_3), 75.9 (t, OCH_2), 128.6 (d, 2 × C), 129.5 (d, 2 × C), 134.8 (d, *p*-Ph), 138.1 (s, *i*-Ph), 173.0 (s, C-3).

2-Bromo-3-methoxymethyl-2-phenylsulfonylmethyl-2*H*-azirine (46b)
^1H NMR ($CDCl_3$): δ = 3.55 (s, 3 H, OCH_3), 3.65 (d, ^2J = 15.0 Hz, 1 H, O_2SCH_2), 4.34 (d, ^2J = 15.0 Hz, 1 H, O_2SCH_2), 4.87 (d, ^2J = 18.6 Hz, 1 H, OCH_2), 5.00 (d, ^2J = 18.6 Hz, 1 H, OCH_2), 7.55–7.62 (m, 2 H, *m*-Ph), 7.66–7.73 (m, 1 H, *p*-Ph), 7.87–7.92 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 41.4 (s, C-2), 59.8 (q, OCH_3), 66.7 (t, CH_2), 67.8 (t, CH_2), 128.3 (d, 2 × C), 129.4 (d, 2 × C), 134.4 (d, *p*-Ph), 138.7 (s, *i*-Ph), 176.9 (s, C-3).

Azirine 47a and its Rearrangement into Azirine 52a
Compound (*E*/*Z*)-**38a** (50.0 mg, 239 μmol) in $CDCl_3$ (0.6 mL) was irradiated at –30 °C for 45 min to afford the azirine **47a** in over 99% NMR yield. By keeping the obtained solution at r.t. for 3 h, **47a** rearranged to give **52a** in over 99% NMR yield.

2-Chloro-2-methyl-3-methylsulfonylmethyl-2*H*-azirine (47a)
^1H NMR ($CDCl_3$): δ = 1.96 [s, 3 H, $C(CH_3)$], 3.13 (s, 3 H, SO_2CH_3), 4.62 (s, 2 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = 27.8 (q, [$C(CH_3)$], 41.9 (q, SO_2CH_3), 51.9 (t, CH_2), 57.0 (s, C-2), 175.7 (s, C-3).

2-Chloro-3-methyl-2-methylsulfonylmethyl-2*H*-azirine (52a)
White crystals; mp 74–75 °C (Et_2O).

IR ($CDCl_3$): 1766 (C=N), 1320 (SO_2), 1134 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.67 [s, 3 H, $C(CH_3)$], 3.02 (s, 3 H, SO_2CH_3), 3.38 (d, ^2J = 15.9 Hz, 1 H, CH_2), 4.16 (d, ^2J = 15.9 Hz, 1 H, CH_2).

^{13}C NMR ($CDCl_3$): δ = 12.2 [q, $C(CH_3)$], 42.2 (q, SO_2CH_3), 52.5 (s, C-2), 64.9 (t, CH_2), 175.6 (s, C-3).

Anal. Calcd for $C_5H_8ClNO_2S$: C, 33.06; H, 4.44; N, 7.71; S, 17.65. Found: C, 33.09; H, 4.68; N, 7.71; S, 16.68.

Azirine 48a and its Rearrangement into Azirine 53a
Compound (*E*/*Z*)-**39a** (0.03 g, 110 μmol) in of $CDCl_3$ (0.5 mL) was irradiated at –30 °C for 90 min to afford the azirine **48a** in over 99% NMR yield. By keeping the obtained solution at r.t. for 4 h or by warming at 35 °C for 3 h, **48a** rearranged to give **53a** in over 99% NMR yield.

2-Chloro-2-methyl-3-phenylsulfonylmethyl-2*H*-azirine (48a)
^1H NMR ($CDCl_3$): δ = 1.87 (s, 3 H, CH_3), 4.68 (d, ^2J = 15.9 Hz, 1 H, CH_2), 4.74 (d, ^2J = 15.9 Hz, 1 H, CH_2), 7.59–7.65 (m, 2 H, *m*-Ph), 7.70–7.76 (m, 1 H, *p*-Ph), 7.96–8.00 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 27.8 (q, CH_3), 53.7 (t, CH_2), 57.0 (s, C-2), 128.3 (d, 2 × C), 129.6 (d, 2 × C), 134.9 (d, *p*-Ph), 138.0 (s, *i*-Ph), 175.5 (s, C-3).

2-Chloro-3-methyl-2-phenylsulfonylmethyl-2*H*-azirine (53a)
IR ($CDCl_3$): 1766 (C=N), 1323 (SO_2), 1143 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.66 (s, 3 H, CH_3), 3.40 (d, ^2J = 15.3 Hz, 1 H, CH_2), 4.28 (d, ^2J = 15.3 Hz, 1 H, CH_2), 7.57–7.63 (m, 2 H, *m*-Ph), 7.67–7.73 (m, 1 H, *p*-Ph), 7.91–7.96 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 12.2 (q, CH_3), 51.7 (s, C-2), 67.1 (t, CH_2), 128.3 (d, 2 × C), 129.4 (d, 2 × C), 134.3 (d, *p*-Ph), 138.9 (s, *i*-Ph), 174.8 (s, C-3).

Anal. Calcd for $C_{10}H_{10}ClNO_2S$: C, 49.28; H, 4.14; N, 5.74; S, 13.15. Found: C, 49.66; H, 4.66; N, 5.25; S, 12.84.

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Azirine 48b and its Rearrangement into Azirine 53b
Compound (*E*/*Z*)-**39b** (0.03 g, 110 μmol) in $CDCl_3$ (0.5 mL) was irradiated at –30 °C for 60 min. The first ^1H NMR spectrum, measured at 19 °C, proved the presence of a mixture (1:1) of **48b** and **53b**. By keeping this mixture at r.t. for about 10 min, a second ^1H NMR spectrum proved only the presence of **53b** in over 96% NMR yield.

2-Bromo-2-methyl-3-phenylsulfonylmethyl-2*H*-azirine (48b)
^1H NMR ($CDCl_3$): δ = 2.05 (s, 3 H, CH_3), 4.69 (d, ^2J = 15.9 Hz, 1 H, CH_2), 4.75 (d, ^2J = 15.9 Hz, 1 H, CH_2), 7.59–7.64 (m, 2 H, *m*-Ph), 7.67–7.73 (m, 1 H, *p*-Ph), 7.96–8.00 (m, 2 H, *o*-Ph).

Due to the rapid rearrangement, the ^{13}C NMR data of **48b** are not available.

2-Bromo-3-methyl-2-phenylsulfonylmethyl-2*H*-azirine (53b)
Yellow oil.

IR ($CDCl_3$): 1764 (C=N), 1322 (SO_2), 1142 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.67 (s, 3 H, CH_3), 3.61 (d, ^2J = 15.0 Hz, 1 H, C*H*$_2$), 4.28 (d, ^2J = 15.0 Hz, 1 H, CH_2), 7.59–7.64 (m, 2 H, *m*-Ph), 7.67–7.73 (m, 1 H, *p*-Ph), 7.89–7.93 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 12.4 (q, CH_3), 41.7 (s, C-2), 68.3 (t, CH_2), 128.4 (d, 2 × C), 129.4 (d, 2 × C), 134.3 (d, *p*-Ph), 138.9 (s, *i*-Ph), 176.3 (s, C-3).

MS (ESI): *m*/*z* = 288.23 [M + H^+, ^{81}Br].

Azirine 49b and its Rearrangement into Azirine 54b
Compound (*E*/*Z*)-**41b** (0.03 g, 80.6 μmol) in $CDCl_3$ (0.5 mL) was irradiated at –30 °C for 60 min. The first ^1H NMR spectrum, measured at 19 °C, proved the presence of a mixture (1:2) of **49b** and **54b**. By keeping this mixture at r.t. for about 5 min, a second ^1H NMR spectrum proved only the presence of **54b** (28 mg, 78.2 μmol, 96%).

2-Bromo-2-pentyl-3-phenylsulfonylmethyl-2*H*-azirine (49b)
^1H NMR ($CDCl_3$): δ = 0.85 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.24 (m, 2 H), 1.39 (m, 4 H), 1.82 (m, 2 H, CH_2 at C-2), 4.70 (s, 2 H, SO_2CH_2), 7.51–7.63 (m, 2 H, *m*-Ph), 7.66–7.72 (m, 1 H, *p*-Ph), 7.98–8.02 (m, 2 H, *o*-Ph).

Due to the rapid rearrangement, the ^{13}C NMR data of **49b** are not available.

2-Bromo-3-pentyl-2-phenylsulfonylmethyl-2*H*-azirine (54b)
Yellow oil.

IR ($CDCl_3$): 1753 (C=N), 1323 (SO_2), 1141 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.92 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.41 (m, 4 H), 1.83 (m, 2 H), 2.94 (dt, ^2J = 17.4 Hz, ^3J = 7.5 Hz, 1 H, CH_2 at C-3), 3.05 (dt, ^2J = 17.4 Hz, ^3J = 7.5 Hz, 1 H, CH_2 at C-3), 3.62 (d, ^2J = 15.3 Hz, 1 H, SO_2CH_2), 4.35 (d, ^2J = 15.3 Hz, 1 H, SO_2CH_2), 7.51–7.63 (m, 2 H, *m*-Ph), 7.66–7.72 (m, 1 H, *p*-Ph), 7.89–7.93 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 13.8 (q, CH_3), 22.1 (t), 23.4 (t), 26.8 (t), 31.1 (t), 42.3 (s, C-2), 68.4 (t, SO_2CH_2), 128.3 (d, 2 × C), 129.4 (d, 2 × C), 134.3 (d, *p*-Ph), 138.9 (s, *i*-Ph), 178.8 (s, C-3).

HRMS (ESI): *m*/*z* [M + H^+, ^{79}Br] calcd for $C_{14}H_{18}BrNO_2S$: 344.0267; found: 344.0275.

Azirine 50b and its Rearrangement into Azirine 55b
Compound (*E*/*Z*)-**42b** (50.0 mg, 132 μmol) in $CDCl_3$ (0.5 mL) was irradiated at –30 °C for 60 min. The ^1H NMR spectrum, measured at 19 °C, proved only the presence of the rearranged azirine **55b** in 97% NMR yield. When the irradiation and the measurement of the NMR data were performed in $CDCl_3$ at –50 °C, **50b** could be observed. However, even at that temperature (–50 °C), the rearrangement of **50b** to **55b** took place slowly.

2-Bromo-2-phenyl-3-phenylsulfonylmethyl-2*H*-azirine (50b)
Yellow in $CDCl_3$ solution at –50 °C.

^1H NMR ($CDCl_3$, –50 °C): δ = 4.76 (d, ^2J = 13.0 Hz, 1 H, CH_2), 4.82 (d, ^2J = 13.0 Hz, 1 H, CH_2), 7.15–7.17 (m, 2 H), 7.29–7.32 (m, 3 H), 7.44–7.50 (m, 2 H), 7.57–7.73 (m, 3 H).

^{13}C NMR ($CDCl_3$, –50 °C): δ = 50.1 (s, C-2), 52.7 (t, CH_2), 126.5 (d), 128.2 (d), 128.8 (d), 130.8 (d, overlaps of two signals), 135.0 (d), 136.5 (s), 138.1 (s), 171.2 (s, C-3).

2-Bromo-3-phenyl-2-phenylsulfonylmethyl-2*H*-azirine (55b)
Whitish solid; mp 82–83 °C (Et_2O–CH_2Cl_2).

IR ($CDCl_3$): 1736 (C=N), 1324 (SO_2), 1159 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$, 19 °C): δ = 3.85 (d, ^2J = 15.3 Hz, 1 H, CH_2), 4.53 (d, ^2J = 15.3 Hz, 1 H, CH_2), 7.52–7.74 (m, 6 H), 7.90–7.93 (m, 2 H), 8.11–8.15 (m, 2 H).

^{13}C NMR ($CDCl_3$, 19 °C): δ = 42.7 (s, C-2), 68.0 (t, CH_2), 121.3 (s), 128.3 (d, 2 × C), 129.3 (d, 2 × C), 129.4 (d, 2 × C), 130.8 (d, 2 × C), 134.2 (d), 134.9 (d), 139.2 (s), 173.3 (s, C-3).

Anal. Calcd for $C_{15}H_{12}BrNO_2S$: C, 51.44; H, 3.45; N, 4.00; S, 9.15. Found: C, 51.34; H, 3.51; N, 3.98; S, 8.87.

Azirine 51b and its Rearrangement into Azirine 56b
The vinyl azide (*Z*)-**43b** (60.0 mg, 167 μmol) in $CDCl_3$ (0.6 mL) was irradiated at –30 °C for 60 min. The first ^1H NMR spectrum, measured at 19 °C, proved the presence of a mixture (1:3) of **51b** and **56b**. By keeping this mixture at r.t. for approximately 10 min, a second ^1H NMR spectrum proved only the presence of **56b** in 99% NMR yield.

2-Bromo-2-*tert*-butyl-3-phenylsulfonylmethyl-2*H*-azirine (51b)
^1H NMR ($CDCl_3$): δ = 0.97 (s, 9 H, CH_3), 4.68 (s, 2 H, SO_2CH_2), 7.54–7.62 (m, 2 H, *m*-Ph), 7.64–7.70 (m, 1 H, *p*-Ph), 8.02–8.06 (m, 2 H, *o*-Ph).

Due to the rapid rearrangement, the ^{13}C NMR data of this compound are not available.

2-Bromo-3-*tert*-butyl-2-phenylsulfonylmethyl-2*H*-azirine (56b)
White solid; mp 68–70 °C.

IR ($CDCl_3$): 1741 (C=N), 1323 (SO_2), 1146 (SO_2) cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.42 (s, 9 H, CH_3), 3.70 (d, ^2J = 15.0 Hz, 1 H, CH_2), 4.29 (d, ^2J = 15.0 Hz, 1 H, CH_2), 7.54–7.62 (m, 2 H, *m*-Ph), 7.64–7.70 (m, 1 H, *p*-Ph), 7.92–7.96 (m, 2 H, *o*-Ph).

^{13}C NMR ($CDCl_3$): δ = 25.9 (q, CH_3), 34.5 [s, *C*(CH_3)], 44.0 (s, C-2), 68.3 (t, CH_2), 128.5 (d, 2 × C), 129.3 (d, 2 × C), 134.2 (d, *p*-Ph), 139.4 (s, *i*-Ph), 184.2 (s, C-3).

Anal. Calcd for $C_{13}H_{16}BrNO_2S$: C, 47.28; H, 4.88; N, 4.24; S, 9.71. Found: C, 47.18; H, 4.84; N, 4.24; S, 10.00.

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References

(1) Fotsing, J. R.; Banert, K. *Eur. J. Org. Chem.* **2005**, 3704.

(2) (a) Backes, J. In *Houben-Weyl*, Vol. E16c, 4th ed.; Klamann, D., Ed.; Thieme: Stuttgart, **1992**, 17. (b) Nair, V. In *The Chemistry of Heterocyclic Compounds, Small-Ring Heterocycles*, Vol. 42; Hassner, A., Ed.; Wiley: New York, **1983**, 215. (c) Pearson, W. H.; Lian, B. W.; Bergmeier, S. C. In *Comprehensive Heterocyclic Chemistry II*, Vol. 1A; Katritzky, A. R.; Rees, C. W.; Scriven, E. F.; Padwa, A., Eds.; Pergamon: Exeter, **1996**, 1. (d) Heimgartner, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 238; *Angew. Chem.* **1991**, *103*, 271. (e) L'abbé, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 775; *Angew. Chem.* 1975, *87*, 831. (f) Smolinsky, G. *J. Am. Chem. Soc.* **1961**, *83*, 4483. (g) Smolinsky, G. *J. Org. Chem.* **1962**, *27*, 3557. (h) Harvey, G. R.; Ratts, K. W. *J. Org. Chem.* **1966**, *31*, 3907. (i) Nair, V. *J. Org. Chem.* **1972**, *37*, 802. (j) Banert, K.; Köhler, F. *Angew. Chem. Int. Ed.* **2001**, *40*, 174; *Angew. Chem*. 2001, *113*, 173.

(3) (a) Miller, T. W.; Tristram, E. W.; Wolf, F. J. *J. Antibiot.* **1971**, *24*, 48. (b) Molinski, T. F.; Ireland, C. M. *J. Org. Chem.* **1988**, *53*, 2103. (c) Salomon, C. E.; Williams, D. H.; Faulkner, D. J. *J. Nat. Prod.* **1995**, *58*, 1463. (d) Stapley, E. O.; Hendlin, D.; Jackson, M.; Miller, A. K.; Hernandez, S.; Mata, J. M. *J. Antibiot.* **1971**, *24*, 42. (e) Davis, F. A.; Reddy, G. V.; Liu, H. *J. Am. Chem. Soc.* **1995**, *117*, 3651. (f) Davis, F. A.; Liu, H.; Liang, C.-H.; Reddy, G. V.; Zhang, Y.; Fang, T.; Titus, D. D. *J. Org. Chem.* **1999**, *64*, 8929.

(4) (a) Bucher, C. B.; Heimgartner, H. *Helv. Chim. Acta* **1996**, *79*, 1903. (b) Drögemüller, M.; Jautelat, R.; Winterfeldt, E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1572; *Angew. Chem.* **1996**, *107,* 1669. (c) Davis, F. A.; Liang, C.-H.; Liu, H. *J. Org. Chem.* **1997**, *62*, 3796.

(5) Haddach, M.; Pastor, R.; Riess, J. G. *Tetrahedron Lett.* **1990**, *31*, 1989.

(6) Russell, G. A.; Yao, C.-F. *J. Org. Chem.* **1992**, *57*, 6508.

(7) (a) Gallagher, T. C.; Storr, R. C. *Tetrahedron Lett.* **1981**, *22*, 2905. (b) Ciabattoni, J.; Cabell, M. *J. Am. Chem. Soc.* **1971**, *93*, 1482. (c) Padwa, A.; Blacklock, T. J.; Carlsen, P. H. J.; Pulwer, M. *J. Org. Chem.* **1979**, *44*, 3281. (d) Banks, R. E.; Moore, G. J. *J. Chem. Soc. C* **1966**, 2304. (e) Morawietz, J.; Sander, W. *J. Org. Chem.* **1996**, *61*, 4351.

(8) Rocha Gonsalves, A. M. d'A.; Cabral, A. M. T. D. P. V.; Pinho e Melo, T. M. V. D.; Gilchrist, T. L. *Synthesis* **1997**, 673.

(9) (a) Pinho e Melo, T. M. V. D.; Rocha Gonsalves, A. M. d'A.; Lopes, C. S. J.; Gilchrist, T. L. *Tetrahedron Lett.* **1999**, *40*, 789. (b) Pinho e Melo, T. M. V. D.; Lopes, C. S. J.; Rocha Gonsalves, A. M. d'A.; Beja, A. M.; Paixão, J. A.; Silva, M. R.; Da Veiga, L. A. *J. Org. Chem.* **2002**, *67*, 66. (c) Pinho e Melo, T. M. V. D.; Lopes, C. S. J.; Rocha Gonsalves, A. M. d'A.; Storr, R. C. *Synthesis* **2002**, 605. (d) Pinho e Melo, T. M. V. D.; Cardoso, A. L.; Gomes, C. S. B.; Rocha Gonsalves, A. M. d'A. *Tetrahedron Lett.* **2003**, *44*, 6313.

(10) L'abbé, G.; Bollyon, M.; Germain, G.; Scheefer, G. *Bull. Soc. Chim. Belg.* **1983**, *92*, 881.

(11) L'abbé, G. *Bull. Soc. Chim. Belg.* **1984**, *93*, 579.

(12) Hassner, A.; Keogh, J. *J. Org. Chem.* **1986**, *51*, 2767.

(13) An alleged 2-methylene-2*H*-azirine[14] proved to be a structurally isomeric product.[15]

(14) Kallury, R. K. M. R.; Devi, P. S. U. *Tetrahedron Lett.* **1977**, 3655.

(15) (a) Anderson, D. J. *J. Org. Chem.* **1986**, *51*, 945. (b) Ashok, K.; Sridevi, G.; Umadevi, Y. *Synthesis* **1993**, 623.

(16) Banert, K.; Hagedorn, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 103; *Angew. Chem.* **1990**, *102*, 90.

(17) Banert, K.; Hagedorn, M.; Knözinger, E.; Becker, A.; Würthwein, E.-U. *J. Am. Chem. Soc.* **1994**, *116*, 60.

(18) Chapyshev, S. V.; Tomioka, H. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2075.

(19) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, **1992**.

(20) Scholz, D. *Synthesis* **1983**, 944.

(21) Barrett, A. G. M.; Dhanak, D.; Graboski, G. G.; Taylor, S. J. *Org. Synth.* **1990**, *68*, 8.

(22) Banert, K. *Chem. Ber.* **1989**, *122*, 911.

(23) Condon–Gueugnot, S.; Linstrumentelle, G. *Tetrahedron* **2000**, *56*, 1851.

(24) Robin, S.; Rousseau, G. *Eur. J. Org. Chem.* **2000**, 3007.

(25) Effenberger, F.; Gaupp, S. *Tetrahedron: Asymmetry* **1999**, *10*, 1765.

(26) Diefenbach, S. P. U.S. Patent, 4704377, **1987**; *Chem. Abstr.* **1988**, *108*, 96627g.

(27) Fortes, C. C.; Garrote, C. F. D.; Clevia, F. D. *Synth. Commun.* **1997**, *27*, 2993.

(28) Rathore, R.; Deselnicu, M. I.; Burns, C. L. *J. Am. Chem. Soc.* **2002**, *124*, 14832.

(29) Sasson, Y. In *The Chemistry of Halides, Pseudo-halides and Azides*; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, **1995**, 535.

(30) Banert, K.; Lehman, J. In *Modern Allene Chemistry*; Krause, N.; Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, **2004**, 359 (see especially the chapter on pp 379–386 and references cited therein).

(31) Taft, R. W. Jr. *J. Am. Chem. Soc.* **1953**, *75*, 4231.

(32) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(33) (a) Dharanipragada, R.; VanHulle, K.; Bannister, A.; Bear, S.; Kennedy, L.; Hruby, V. J. *Tetrahedron* **1992**, *48*, 4733. (b) Hruby, V. J.; Boteju, L.; Li, G. *Chem. Eng. News* **1993**, *71 (Oct. 11)*, 2.

(34) Maclnnes, I.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1077.

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