First Propargyl Azides Bearing Strong Acceptor Substituents and Their Effective Conversion into Allenyl Azides: Influence of the Electronic Effects of Substituents on the Reactivity of Propargyl Azides[‡]

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Dedicated to Professor Harald Günther on the occasion of his 70th birthday

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We have succeeded in the synthesis of propargyl azides containing 1- or 3-phenylthio functionalities. The selective oxidation of their sulfur atoms to sulfoxides and sulfones allows access to the first propargyl azides bearing acceptor substituents. Interestingly, the prototropic rearrangement of the latter propargyl azides leads to the formation of allenyl azides with relatively high stabilities and with moderate to good yields. Propargyl azides containing phenylthio functionalities react in the presence of nucleophiles to afford the expected *N*-unsubstituted 1,2,3-triazoles via short-lived allenyl azides. These results are entirely different from those of the corresponding sulfoxides and sulfones, which react under the analogous conditions either to produce the corresponding bis(triazolo)pyrazine derivatives or to yield newly substituted vinyl azides. The latter compounds can successfully be used as starting material providing access to azirines.

Introduction

Due to their synthetic versatile character, organic azides are compounds of great interest.[1] Some organic azides can be synthesized by addition of XN_3 (X = H or halogen) to unsaturated compounds.[2] In the case with X = halogen, the latter azides can be converted to unsaturated derivatives by elimination of an HX molecule. This method is mainly used for the synthesis of vinyl azides.[2] Other methods to prepare organic azides include the nucleophilic substitution using the azide anion[3] as well as electrophilic azide transfer[4] and stepwise formation of the azido group from amines or diazo derivatives.[5]

Propargyl azides of type **1** are known to isomerize to allenyl azides **2** and **5** by [3,3] sigmatropic migration of the azido group (path A, Scheme 1) and by prototropic rearrangement (base-catalyzed path B, Scheme 1).[6–8] The species **2** and **5** proved to be short-lived intermediates that cyclized rapidly to the triazafulvenes **3** and **6**, which could be trapped by nucleophiles to afford the triazoles **4** and **7**, respectively.[8] If **1** is generated in situ starting with propargyl halides or sulfonates and sodium azide, the synthesis of the heterocycles **4** and **7** can be performed in one-pot procedures without isolation of dangerous azides.[9–11] Such a reaction cascade is based on simple and cheap starting materials to produce *N*-unsubstituted 1,2,3-triazoles bearing a functional group in the side chain. Thus, different groups have used this method successfully.[6–13]

In some special cases, allenyl azides can be directly characterized by ^1H and ^{13}C NMR spectroscopy.[8] However, isolation of these compounds is very difficult because the proportions of these quasi-stationary intermediates are rather low [**2a** ($\leq$ 3%), **2b** ($\leq$ 1%), **2c** ($\leq$ 3%), **2d** ($\leq$ 7%), **2e** ($\leq$ 8%), **2f** ($\leq$ 11%), **2g** ($\leq$ 0.32%), **2h** ($\leq$ 0.13%)].[6–8] Moreover, any other attempts to isolate or to observe azido allenes failed.[14–17] Investigations on the formation of azido allenes **2a**–**h** show that donor substituents accelerate the rate of the [3,3] sigmatropic rearrangement of **1** to **2**.[6–8] Unfortunately, the rate of the ring closure of **2** to **3** proved to be even more greatly increased by the donor substituents. By contrast, the CH_2Cl group (see **2d**) which can be regarded as a weak acceptor decreased the rate of the ring closure of **2d** to **3d**. These observations as well as the kinetic data of the transformations **2a**–**h** → **3a**–**h** led to the postulate[6–8] that allenyl azides are better stabilized by acceptor substituents than by sterically demanding alkyl substituents acting as donors.

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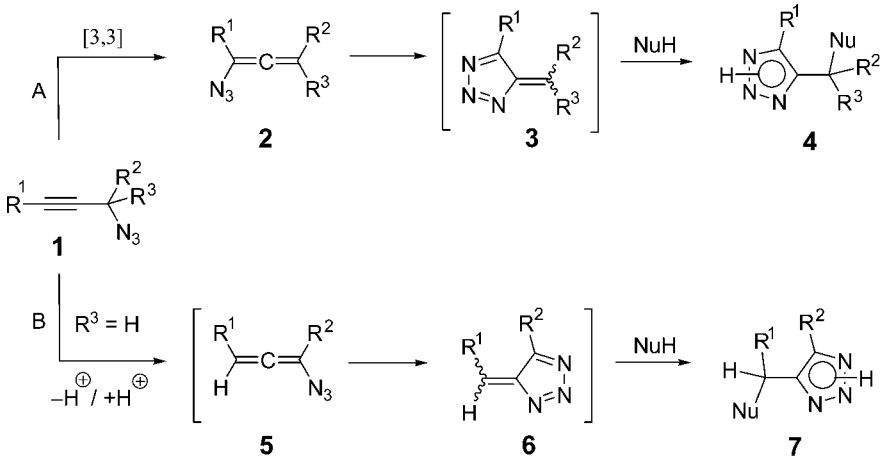


1, **2**, **3** and **4**	a	b	c	d	e	f	g	h
R^1	H	Me	CH_2OMe	CH_2Cl	CH_2OH	CH_2NH_2	H	H
R^2	H	H	H	H	H	H	Me	Me
R^3	H	H	H	H	H	H	H	Me

Scheme 1.

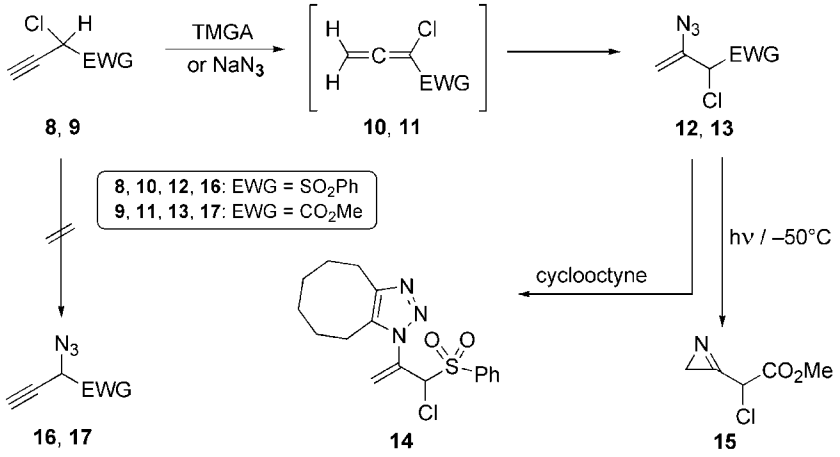
During this work, we faced a triple challenge. First of all, we were looking for an access to new propargyl azides bearing electron-withdrawing groups. Due to the postulated diminishing effect of the acceptor substituents on the rate of the ring closure of azido allenes to triazafulvenes, we expected to produce long-lived azido allenes in good yields from these propargyl azides. However, whereas numerous propargyl azides **1** bearing electron-donating groups (ERG) are known,[8,18] their analogs bearing strongly electron-withdrawing groups (R^1, R^2 and/or R^3 = EWG) are unknown to the best of our knowledge.[19,20] Moreover, we wanted to perform a rational comparison between the reactivity of the propargyl azides bearing acceptor substituents with the reactivity of those propargyl azides connected with electron-donating groups. Finally, we assume that a convenient access to allenyl azides will open the door to long-sought[14–16] methylene-2*H*-azirines which were unknown[21–23] until recently when they were generated by photolysis of allenyl azides[24,25] or other azides.[26]

Results and Discussion

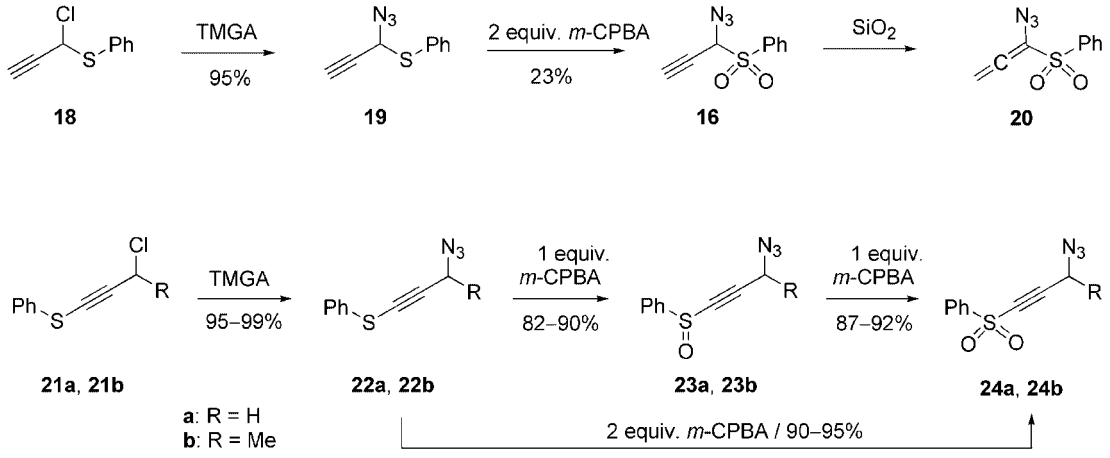
Synthesis of Propargyl Azides Bearing Acceptor Substituents

Our investigations showed that the synthesis of acceptor-substituted propargyl azides through direct substitution of the propargyl precursors bearing a leaving group is not appropriate. For example, the reaction of **8**[27] with tetramethylguanidinium azide (TMGA) led to the formation of the vinyl azide **12** instead of the propargyl azide **16** (Scheme 2). The reaction of the analogous compound **9** with sodium azide follows the same pathway producing the vinyl azide **13** instead of the propargyl azide **17**. Although a variety of different reaction conditions were tested, access to **16** and **17** was not possible by simple nucleophilic substitution. In fact, due to the presence of the acceptor substituent (EWG), which increases the acidity of the propargyl hydrogen, the prototropic isomerization of **8** to **10** and **9** to **11** was favored under the basic reaction conditions. Obviously, the allene intermediates **10** and **11** reacted under addition of hydrazoic acid (HN_3) to form the compounds **12** and **13**, respectively, in 65% and 95% yield. The proof of the presence of only one azido group in the structure of **12** was performed by its treatment with an excess of cyclooctyne to produce the triazole derivative **14** (82%). The structure of the vinyl azide **13** was proved not only by its spectroscopic data but also by its photochemical conversion into the 2*H*-azirine derivative **15** in 95% yield based on NMR spectroscopy. Moreover, Priebe has already shown that the reaction of methyl 4-chlorobut-2-ynoate (a structural isomer of **9**) with sodium azide led to the formation of the Michael addition product without substitution of the chloride at the propargylic position.[28]

To overcome the problem described above, we prepared the sulfur(II)-containing propargyl azides **19** (95%), **22a** (99%) and **22b** (99%) by the reaction of the corresponding propargyl chlorides **18**,[27] **21a**[29] and **21b**, respectively, with TMGA (Scheme 3). The compounds **19**, **22a** and **22b** offer an elegant possibility to produce the corresponding acceptor-substituted propargyl azides by oxidation of the thio-



Scheme 2.

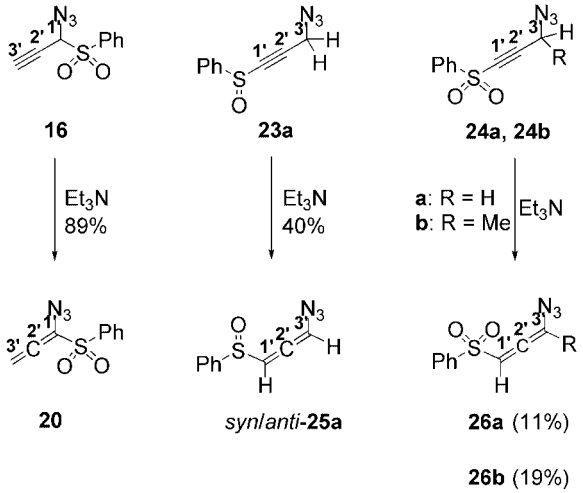


Scheme 3.

ethers to sulfoxides and sulfones. In this respect, treatment of **22a** and **22b** in each case with one equivalent of *m*-chloroperbenzoic acid (*m*-CPBA) at –20 °C for 12 h led to the formation of the desired sulfoxides **23a** and **23b** (mixture of diastereomers, 1.1:1) with good yields. All attempts to isolate the sulfoxide derived from **19** failed. In order to get also the sulfones derived from the propargyl azides **19**, **22a** and **22b**, treatment of each with two equivalents of *m*-CPBA was performed. Whereas **22a** and **22b** were easily oxidized to the sulfones **24a** (95%) and **24b** (90%), respectively, oxidation of **19** led to the formation of unstable compound **16** in only 23% yield after chromatography. In fact, **16** reacted especially during its purification on silica gel to afford surprisingly the azido allene **20**. The reaction of the sulfoxides **23a** and **23b** with one equivalent of *m*-CPBA also affords the sulfones **24a** and **24b** with 92% and 87% yield, respectively.

Reactivity of Propargyl Azides with Bases of Weak Nucleophilicity: Synthesis of Azido Allenes

Whereas the reaction of propargyl azides **19**, **22a** and **22b**, bearing only electron-donating groups, with bases like Et_3N or DABCO led to polymerization via short-lived allenyl azides and triazafulvenes without formation of any identifiable products, the oxidized derivatives **16**, **23a**, **24a** and **24b** isomerized under the same reaction conditions to afford the corresponding allenyl azides **20** (89%), **25a** (40%), **26a** (11%) and **26b** (19%), respectively (Scheme 4).

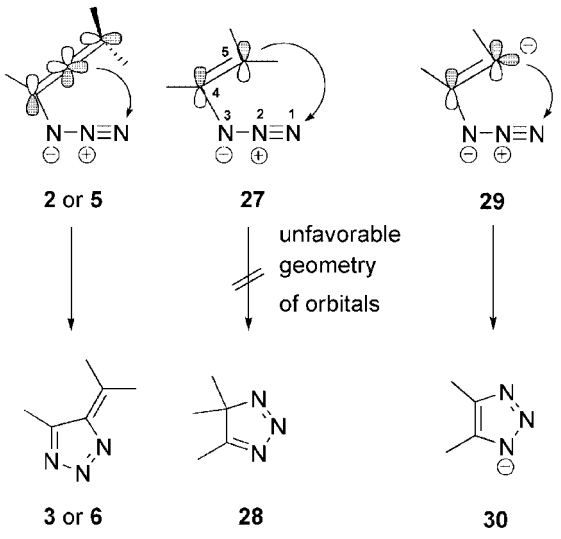


Scheme 4.

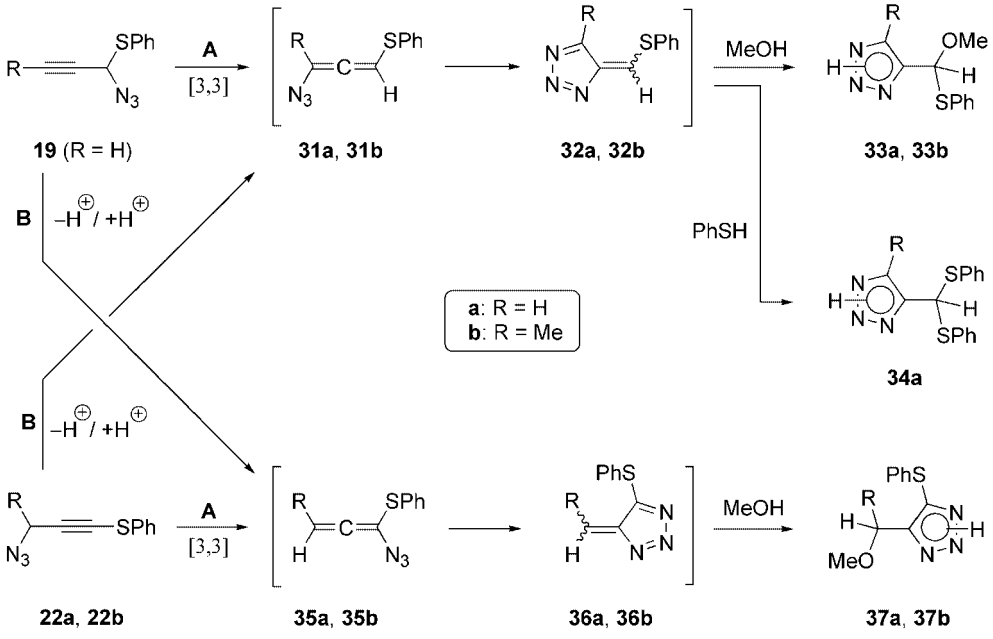
These yields were based on isolation by chromatography; yields determined by ^{1}H NMR were even higher. Due to the stereocenter on the sulfur(IV) atom and the chirality of the allene, **25a** was obtained as a 9:10 mixture of diastereoisomers. The high yield (89%) of the azido allene **20** compared to those of **25a** and **26a**,**b** was favored by the great acidity of the propargyl hydrogen of **16** which is bound directly at the α-position of the sulfone group. Consequently, the time for isomerization is reduced to only 10 min. These results show that azido allenes are stabilized by electron-withdrawing groups which prevent ring-closure to give triazafulvenes. However, the non-observation of azido allenes in the reaction of **19**, **22a** and **22b** is probably not only caused by the very rapid cyclization of their allenyl azide derivatives, which are connected to electron-donating groups, but also by lower rates of prototropic rearrangement of these propargyl azides.

In a diluted $CDCl_3$ solution, compound **26a** decomposes after one hour at room temperature to give a complex mixture of products. Under the same conditions, compound **25a** exhibits a longer life time (5 h). These observations show that the acceptor substituents do not only prevent cyclization to generate triazafulvenes, but also increase the sensitivity of the allenes to other reactions. Nevertheless, the latter effect of acceptor substituents is not surprising, because it is also known for other allenyl compounds.[30] When the hydrogen atom in the 3′-position of **26a** was replaced with a methyl group, the corresponding allenyl azide **26b** proved to be more stable. This can be rationalized by the compensation of the effect of the acceptor substituent by the electron-donating methyl group. The position of the azido groups with regard to those of the electron-withdrawing groups seems to play also an important role for the lifetime of the allenyl azides. It turned out through comparison of the lifetimes of the diluted solutions of **20** and **26a** that an azido allene is better stabilized when the azido group and the acceptor substituent are geminal to each other. No indication on the ring closure of the allenyl azides **20**, **25a**, **26a** and **26b** to the corresponding triazafulvenes of type **6** (Scheme 1) was obtained.

Due to the unfavorable distance between the orbitals of N-1 and C-5, simple vinyl azides **27** do not give triazoles of type **28** by intramolecular reaction,[31] whereas their anions **29** are known to cyclize to **30** rapidly (Scheme 5).[32] Considering the proposed mechanism[6–8] of the ring closure of azido allenes **2** or **5** to triazafulvenes **3** or **6**, we can say that the perpendicular geometry of the p orbitals of the central carbon atoms of the allenes **20**, **25a**, **26a** and **26b**, which may favor their ring closure to triazafulvenes, suffers from the decrease of the nucleophilicity of these central carbon atoms through the acceptor substituents.



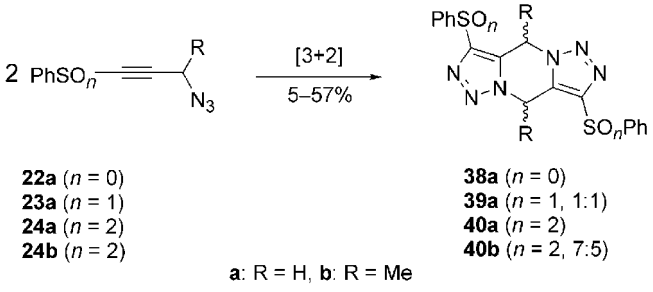
Scheme 5.



Scheme 6.

Succeeding Products from Propargyl Azides in Methanol

In methanol solutions, the propargyl azides **19**, **22a** and **22b** bearing donor substituents reacted at room temperature or above through [3,3] sigmatropic rearrangement to produce the 1,2,3-triazoles **33a** (47%), **37a** (68%) and **37b** (80%), respectively (Scheme 6, path A). When a very concentrated solution of **22a** in methanol was used, a small amount of the double [3+2] cycloaddition product **38a** (5.2%, Scheme 7) was found, together with **37a**. Under similar conditions, **22b** afforded a mixture, in which only the triazole **37b** was identifiable.



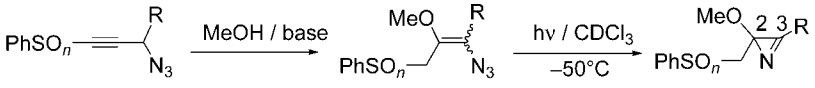
Scheme 7.

In contrast to the reactions of propargyl azides **19**, **22a** and **22b**, the reactions of the analogous compounds **23a** and **24a** bearing acceptor substituents afforded in methanol solutions after fourteen days at room temperature only the [3+2] cycloaddition products **39a** and **40a** in 23% and 57% yields, respectively (Scheme 7). Compound **39a** was obtained as a mixture of diastereomers (1:1). No evidence for the formation of the *N*-unsubstituted triazoles analogous to **33a**,**b** or **37a**,**b** was obtained. Under similar conditions, **24b** undergoes no significant reaction. However, when neat **24b** was left standing at room temperature for two days the corresponding [3+2] cycloaddition product **40b** was afforded in 8% yield as a mixture of diastereomers (7:5). The structures of the heterocycles **38a**, **39a**, **40a** and **40b** were determined by comparison of their NMR spectroscopic data with those of the parent compound.[33] As it is shown by these results, the yield of the [3+2] cycloaddition products is increased with the strengthening of the acceptor character of the sulfur substituents, whereas an additional methyl group decreased the yield due to steric hindrance.

Succeeding Products from Propargyl Azides in Methanol in the Presence of a Base

In order to continue our investigation on the influence of the electronic effect of substituents on the reactivity of propargyl azides, both propargyl azides bearing donor substituents and those with acceptor substituents were treated with methanol in the presence of base. When the methanol solutions of the propargyl azides **19** and **22a** were treated with sodium hydroxide at room temperature, the 1,2,3-triazoles **37a** (35%) and **33a** (20%), respectively, were obtained (Scheme 6, path B). In the case of **22a**, the formation of by-product **34a** (12%) was surprisingly observed. This product can be explained probably by in situ formation of thiophenol which then reacted with the intermediate **32a**. Under similar reaction conditions, **22b** led to the formation of **37b** (path A) rather than **33b** (path B). This can be rationalized by the weak acidity of the propargyl hydrogen of **22b**, which is situated geminal to the methyl group and the azido group, as well as the fact that an additional donor substituent like a methyl group accelerates the rate of the [3,3] sigmatropic rearrangement of propargyl azides.[6–8]

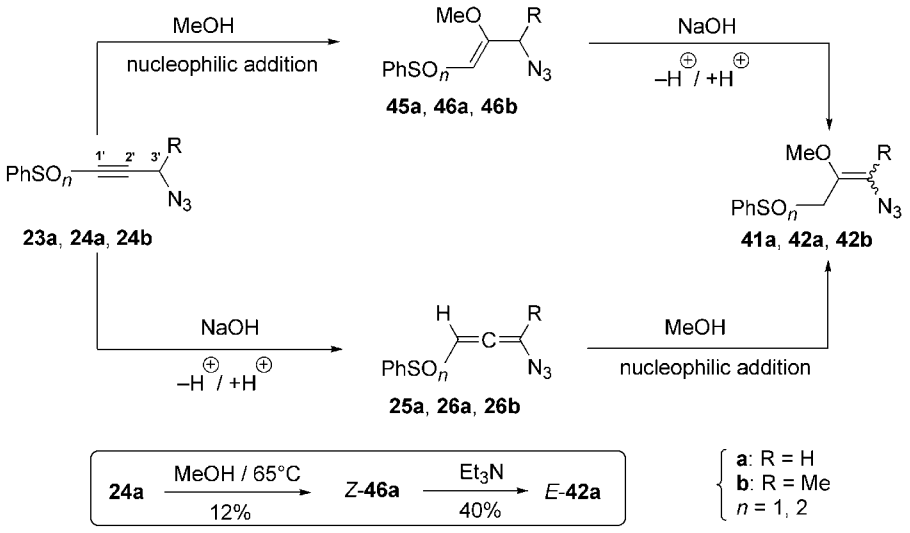
In contrast to the propargyl azides with donor substituents **19**, **22a** and **22b**, the analogous compounds **23a**, **24a** and **24b** react with methanol in the presence of base to afford the corresponding 1-azido-2-methoxyethenes. No evidence of the formation of the *N*-unsubstituted triazoles analogs of type **33a**,**b** or **37a**,**b** was obtained. In fact, treatment of **23a**, **24a** and **24b** with bases (NaOH, Et_3N) in methanol solution led to the formation of **41a** (73%), **42a** (77%) and **42b** (77%), respectively (Scheme 8). Only the *E*-isomers of **41a** and **42a** and in the case of **42b** a 3:2-mixture of *E*- and *Z*-isomers were found. This method provides an easy and efficient access to newly substituted vinyl azides. The position of the olefinic double bond in the structures of **41a**, **42a** and **42b** was determined by photochemical transformation to the 2*H*-azirines **43a** (*like*/*unlike* = 1:1), **44a** and **44b**, respectively.



23a, **24a**, **24b** **41a**, **42a**, **42b** **43a** (1:1), **44a**, **44b**

R	*n*	Starting material	Vinyl azide	Yield	Irradiation conditions	Azirine	Yield
H	1	**23a**	**41a**	73%[a]	$CDCl_3$ / –50°C	*like*/*unlike*-**43a**	~30%[b]
H	2	**24a**	**42a**	77%[a]	$CDCl_3$ / –55°C	**44a**	95%[b]
Me	2	**24b**	**42b**	77%[a]	$CDCl_3$ / –50°C	**44b**	80%[b]

Scheme 8. [a] Yield of isolated product. [b] Yield determined by NMR.



Scheme 9.

How are 1-Azido-2-methoxyethenes Formed from Acceptor-Substituted Propargyl Azides?

The formation of the compounds **41a**, **42a** and **42b** from the corresponding propargyl azide precursors allows two plausible mechanistic pathways (Scheme 9). In the first pathway, the nucleophile may first attack the most electrophilic carbon atom (C-2′) of the propargyl azides to form compounds of type **45a** or **46a**,**b**, followed by a prototropic rearrangement to afford the final products. To prove the plausibility of this pathway, a diluted solution of **24a** in methanol was heated for 20 h under reflux producing the bis(triazolo)pyrazine **40a** (Scheme 7) and the expected compound *Z*-**46a** (Scheme 9) in 12% yield after chromatography; *E*-**46a** was not found. In the presence of Et_3N, *Z*-**46a** isomerizes to *E*-**42a** (40%) showing the possibility of prototropic rearrangement. In the second pathway (Scheme 9), the prototropic isomerization of the propargyl azides takes place first to afford the corresponding azido allenes, which then react with methanol to form the final products. The first step of this pathway was already observed (Scheme 4). The formation of **42a** was also found when methanol and Et_3N was added to a $CDCl_3$ solution of **26a**. Thus, the observed products **41a**, **42a** and **42b** can be plausibly formed by concurrent reaction pathways.

Conclusion

In conclusion, we have developed an elegant and efficient method giving access to acceptor-substituted propargyl azides by selective oxidation of sulfur atoms of the corresponding thioethers. The base-catalyzed prototropic rearrangement of these propargyl azides afforded the desired allenyl azides in acceptable to very good yields. Propargyl azides bearing electron-withdrawing groups and those with electron-donating groups prove to undergo different reactions in methanol with and without the presence of a base. Under both reaction conditions, propargyl azides with donor substituents react as expected[6–13] by [3,3] sigmatropic rearrangement of the azido group or by prototropic isomerization (base catalysis) to short-lived azido allenes that cyclized rapidly to triazafulvenes. These intermediates undergo a nucleophilic addition to afford *N*-unsubstituted triazoles. In methanol solution, the acceptor-substituted propargyl azides yield the corresponding bis(triazolo)pyrazines by double [3+2] cycloaddition. Only two compounds containing the bis(triazolo)pyrazines unit were until now mentioned in the literature.[33,34] By treatment with bases in methanol solution, the title compounds produced 1-azido-2-methoxyethenes. The latter method provides a simple and efficient way to newly substituted vinyl azides.

Experimental Section

General Remarks: ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$, unless otherwise noted. Chemical shifts (δ) are reported in parts per million (ppm) downfield from TMS. Coupling constants (J) are reported in Hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet) t (triplet), q (quartet), m (multiplet). Infrared spectra were recorded as solutions in $CDCl_3$. TLC was performed on Macherey–Nagel precoated silica gel Polygram Sil G/UV_{254} plates and viewed by UV. Chromatography refers to flash chromatography,[35] carried out on Fluka silica gel 60. For the HPLC, the HPLC-pump 64 from Knauer was used. The detection ensued with a UV/Vis filter-photometer (λ = 254 nm) from Knauer. The photolyses were performed with a 150-W-Hg high pressure lamp (polychromatic) TQ 150 from Quarzlampen-Gesellschaft. For the elemental analyses, Vario El (Elementar Analysensystem GmbH) was employed. Mariner 5229 from Applied Biosystems was used for (HR)-MS-spectra. The method applied was the Electrospray Ionisation. For unstable compounds such as 2*H*-azirines, no elemental analyses could be measured.

***Warning*:** Elemental analyses of azides could not be performed because of explosive decomposition. Caution should be exercised during isolation of azide which may be explosive. In the case of solutions of tetrabutylammonium azide in CH_2Cl_2, an explosion proba-

bly caused by diazidomethane was reported.[36] Therefore, special caution is also necessary in the case of tetramethylguanidinium azide (TMGA) in CH_2Cl_2 although we never observed any incidence.

The known compounds **8**,[27] **18**[27] and **21a**[29] were synthesized according to the literature.

Methyl 2-Chlorobut-3-ynoate (9): This compound was synthesized in 95% yield based on NMR by analogy with the procedure described in the literature[37] starting with the corresponding alcohol methyl 2-hydroxybut-3-ynoate[38] and thionyl chloride. IR (CCl_4): $\tilde{\nu}$ = 3300 cm^{-1} (HC≡), 1740 (C=O). ^1H NMR ($CDCl_3$): δ = 2.76 (d, ^4J = 2.7 Hz, 1 H, HC≡), 3.88 (s, 3 H, CH_3), 5.01 (d, ^4J = 2.7 Hz, 1 H, H-2) ppm.

(2-Azido-1-chloroprop-2-enylsulfonyl)benzene (12): To a stirred solution of **8**[27] (0.73 g, 3.40 mmol) in CH_2Cl_2 (15 mL), was added a solution of tetramethylguanidinium azide (TMGA, 2.50 g, 15.8 mmol) in CH_2Cl_2 (15 mL) at 0 °C within 60 min. After additional stirring at this temperature for 30 min, the mixture was partially evaporated, and the residue was filtered on silica gel with Et_2O. The obtained solution was evaporated under vacuum, and the residue was crystallized from Et_2O/*n*-hexane to give **12** (0.50 g, 2.17 mmol, 65%) as a yellow solid; m.p. 108–110 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 2127 cm^{-1} (N_3), 1332 (SO_2), 1156 (SO_2). ^1H NMR ($CDCl_3$): δ = 5.03 (s, 1 H, H-1′), 5.17 (d, ^2J = 3.0 Hz, 1 H, H_2C=), 5.35 (d, ^2J = 3.0 Hz, 1 H, H_2C=), 7.60 (m, 2 H, Ph), 7.88 (m, 3 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 68.66 (d, C-1′), 103.10 (t, C-3′), 121.00 (s, C-2′), 124.57 (d, 2 C), 125.77 (d, 2 C), 130.44 (d, *p*-Ph), 133.53 (s, *i*-Ph) ppm.

Methyl (3-Azido-2-chlorobut-3-enoate (13): To a stirred solution of NaN_3 in a solvent mixture of water/CCl_4 (3 mL:3.3 mL), was added an etheric solution of **9** (2.5 mL, 0.75 mmol, 0.3 M). Stirring was continued for 2 h at room temperature affording the compound **13** with 95% yield based on NMR spectroscopy. IR ($CDCl_3$): $\tilde{\nu}$ = 2140 cm^{-1} (N_3), 1740 (C=O). ^1H NMR ($CDCl_3$): δ = 3.84 (s, 3 H, CH_3), 4.77 (s, 1 H, H-2), 5.01 (d, ^2J = 2.9 Hz, 1 H, H_2C=), 5.27 (d, ^2J = 2.9 Hz, 1 H, H_2C=) ppm.

[1-(α-Chlorophenylsulfonylmethyl)ethenyl]-4,5,6,7,8,9-hexahydro-1*H*-cyclooctatriazole (14): To a stirred solution of **12** (32.0 mg, 124 μmol) in CH_2Cl_2 (2 mL) was added cyclooctyne[39] (30.0 mg, 278 μmol). The mixture was stirred for 3 h at room temperature. The solvent was evaporated under vacuum, and the unreacted cyclooctyne was removed at 10^{-3} Torr. The residue was purified by flash chromatography on silica gel with Et_2O/*n*-hexane (1:1) to give the vinyl triazole **14** (37.0 mg, 101 μmol, 82%) as a yellowish oil. ^1H NMR ($CDCl_3$): δ = 1.51 (m, 4 H), 1.76 (m, 4 H), 2.86 (m, 4 H), 5.72 (d, *J* = 2.4 Hz, 1 H, H_2C=), 6.13 (d, *J* = 2.4 Hz, 1 H, H_2C=), 6.18 (s, 1 H, HCCl), 7.56 (m, 2 H, *m*-Ph), 7.70 (m, 1 H, *p*-Ph), 7.89 (m, 2 H, *o*-Ph). ^{13}C NMR ($CDCl_3$): δ = 22.36 (t), 24.28 (t), 24.97 (t), 25.58 (t), 27.18 (t), 27.89 (t), 71.73 (d, CCl), 118.62 (t, H_2C=), 129.16 (d, 2 C, Ph), 129.63 (d, 2 C, Ph), 134.30 (s), 134.38 (s), 134.84 (d, *p*-Ph), 135.30 (s), 145.38 (s) ppm. MS (ESI): *m*/*z* (%) = 366.00 (100) [M + H^+, ^{35}Cl]. $C_{17}H_{20}ClN_3O_2S$ (365.89): calcd. C 55.81, H 5.51, N 11.48, S 8.76; found C 55.79, H 5.54, N 11.50, S 8.95.

Methyl (2*H*-Azirin-3-yl)chloroacetate (15): The photolysis of **13** in $CDCl_3$ afforded after 8 h at –50 °C the desired azirine in 95% yield based on NMR spectroscopy. ^1H NMR ($CDCl_3$): δ = 1.89 (s, 2 H, N–CH_2), 3.90 (s, 3 H, CH_3), 5.55 (s, 1 H, Cl–CH) ppm.

(1-Azidoprop-2-ynylsulfanyl)benzene (19): The treatment of a solution of **18**[27] (1.76 g, 9.64 mmol) in CH_2Cl_2 (25 mL) with a solution of TMGA (3.70 g, 23.4 mmol) in CH_2Cl_2 (25 mL) afforded **19** (1.73 g, 9.15 mmol, 95%) as yellow oil (procedure: see synthesis of **12**). IR ($CDCl_3$): $\tilde{\nu}$ = 3305 cm^{-1} (HC≡), 2113 (N_3). ^1H NMR ($CDCl_3$): δ = 2.87 (d, ^4J = 2.1 Hz, 1 H, H-3′), 5.08 (d, ^4J = 2.1 Hz, 1 H, H-1′), 7.35 (m, 3 H, Ph), 7.55 (m, 2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 58.75 (d, C-1′), 75.83 (s, C-2′), 78.12 (d, C-3′), 129.17 (d, 2 C), 129.27 (d, *p*-Ph), 130.78 (s, *i*-Ph), 134.21 (d, 2 C) ppm.

(1-Azidoprop-2-ynylsulfonyl)benzene (16): Compound **19** (1.125 g, 5.95 mmol) was dissolved in CH_2Cl_2 (100 mL) and 70% *m*-chloroperbenzoic acid (*m*-CPBA, 4.37 g, 17.73 mmol) was added in small portions while stirring at 0 °C. After stirring at this temperature for additional 60 min, the mixture was washed three times with cooled $NaHSO_3$ solution, three times with cooled $NaHCO_3$ solution and three times with cooled water. The organic phase was dried with $MgSO_4$, filtered, and the solvent was evaporated under vacuum. The residue, which contained no **20** (yet), was separated by flash chromatography on silica gel with Et_2O/*n*-hexane (1:4). The first fractions gave **16** (0.30 g, 1.36 mmol, 23%) as a yellow oil whereas a mixture of **16** and the azido allene **20** (for the synthesis of **20**, see below) was obtained thereafter. IR ($CDCl_3$): $\tilde{\nu}$ = 3302 cm^{-1} (HC≡), 2109 (N_3), 1328 (SO_2), 1138 (SO_2). ^1H NMR ($CDCl_3$): δ = 2.98 (d, ^4J = 2.4 Hz, 1 H, H-3′), 4.82 (d, ^4J = 2.4 Hz, 1 H, H-1′), 7.58 (m, 2 H, *m*-Ph), 7.69 (m, 1 H, *p*-Ph), 7.94 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 70.11 (dd, $^2J_{C,H}$ = 50, $^2J_{C,H}$ = 9 Hz, C-2′), 70.70 (dd, $^1J_{C,H}$ = 162, $^3J_{C,H}$ = 4 Hz, C-1′), 81.32 (dd, $^1J_{C,H}$ = 258, $^3J_{C,H}$ = 4 Hz, C-3′), 129.13 (dm, 2 C), 129.70 (dm, 2 C), 134.28 (m, *i*-Ph), 134.93 (dm, *p*-Ph) ppm.

(1-Azidopropa-1,2-dienylsulfonyl)benzene (20): Compound **16** (45.0 mg, 204 μmol) was dissolved in dry $CDCl_3$ (0.50 mL) and treated with Et_3N (2.00 mg, 20.0 μmol). The reaction was monitored by ^1H NMR spectroscopy. After 10 min, the mixture was filtered over silica gel (1 g, filled in a Pasteur pipette) with Et_2O. The obtained filtrate was evaporated under vacuum to give **20** (40.0 mg, 181 μmol, 89%) as a yellow oil. IR ($CDCl_3$): $\tilde{\nu}$ = 2125 cm^{-1} (N_3), 1332 (SO_2), 1157 (SO_2). ^1H NMR ($CDCl_3$): δ = 5.98 (s, 2 H, H-3), 7.57 (m, 2 H, *m*-Ph), 7.67 (m, 1 H, *p*-Ph), 7.93 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 94.22 (t, C-3), 117.73 (s, C-1), 128.41 (d, 2 C), 129.25 (d, 2 C), 134.28 (d, *p*-Ph), 138.46 (s, *i*-Ph), 200.74 (s, C-2) ppm.

(3-Chlorobut-1-ynylsulfanyl)benzene (21b): Under argon, a solution of 3-chlorobut-1-yne[40] (2.00 g, 22.6 mmol) in dry Et_2O (30 mL) was cooled to –80 °C. *n*-Butyllithium (9.10 mL, 2.50 M in *n*-hexane) was added dropwise while stirring at –80 °C. After additional stirring at –80 °C for 45 min, PhSCl[41] (2.96 g, 20.5 mmol) was added dropwise at the same temperature. The mixture was stirred for 20 min and then warmed to room temperature within 45 min. Thereafter, the argon flow was stopped, and 35 mL of H_2O was added while stirring vigorously. The organic phase was separated in a funnel, and the aqueous phase was extracted several times with Et_2O. The combined organic phases were dried with $MgSO_4$ and filtered. The solvent was removed to give **21b** (3.99 g, 20.3 mmol, 99%) as a yellow oil. ^1H NMR ($CDCl_3$): δ = 1.85 (d, ^3J = 6.9 Hz, 3 H, Me), 4.90 (q, ^3J = 6.9 Hz, 1 H, H-3′), 7.26 (m, 1 H, *p*-Ph), 7.39 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 26.39 (q, Me), 44.88 (d, C-3′), 73.20 (s, Csp), 97.36 (s, Csp), 126.35 (d, 2 C), 126.79 (d, *p*-Ph), 129.28 (d, 2 C), 131.86 (s, *i*-Ph) ppm. HRMS (ESI): calcd. for $C_{10}H_9ClS$ [M + H^+, ^{35}Cl] 197.0139, found 197.0159.

(3-Azidoprop-1-ynylsulfanyl)benzene (22a): A solution of TMGA (5.00 g, 31.6 mmol) in CH_2Cl_2 (40 mL) was added dropwise to a solution of **21a**[29] (2.90 g, 15.9 mmol) in CH_2Cl_2 (40 mL) cooled to 0 °C. The mixture was stirred at this temperature for 8 h and kept overnight at 7 °C. After work-up (see synthesis of **12**), **22a** (3.00 g, 15.8 mmol, 99%) was obtained as a yellow oil. IR ($CDCl_3$): $\tilde{\nu}$ =2124 cm^{-1} (N_3). ^1H NMR ($CDCl_3$): δ = 4.17 (s, 2 H, H-3′), 7.28

(m, 1 H, *p*-Ph), 7.37 (m, 2 H), 7.44 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 41.10 (t, C-3′), 74.99 (s, Csp), 90.72 (s, Csp), 126.59 (d, 2 C), 126.86 (d, *p*-Ph), 129.25 (d, 2 C), 131.58 (s, *i*-Ph) ppm.

(3-Azidobut-1-ynylsulfanyl)benzene (22b): Compound **21b** (3.99 g, 20.3 mmol) was dissolved in CH_2Cl_2 (50 mL) and treated dropwise with a solution of TMGA (9.00 g, 57 mmol) in CH_2Cl_2 (15 mL) within 10 min while stirring at 0 °C. The mixture was kept for 4 days at 7–10 °C. After work-up (see synthesis of **12**), **22b** (4.07 g, 20.05 mmol, 99%) was obtained as a yellowish liquid. IR ($CDCl_3$): $\tilde{\nu}$ =2105 cm^{-1} (N_3), 1227 (N_3). ^{1}H NMR ($CDCl_3$): δ = 1.52 (d, ^3J = 6.9 Hz, 3 H, Me), 4.42 (q, ^3J = 6.9 Hz, 1 H, H-3′), 7.25 (m, 1 H, *p*-Ph), 7.39 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.34 (q, Me), 49.57 (d, C-3′), 73.56 (s, Csp), 95.00 (s, Csp), 126.47 (d, 2 C), 126.81 (d, *p*-Ph), 129.31 (d, 2 C), 131.81 (s, *i*-Ph) ppm.

(3-Azidoprop-1-ynylsulfinyl)benzene (23a): To a stirred solution of **22a** (1.31 g, 6.93 mmol) in $CHCl_3$ (25 mL), was added dropwise at –10 °C a solution of 70% *m*-CPBA (1.70 g, 7.19 mmol) in $CHCl_3$ (25 mL). The mixture was kept overnight at –23 °C. The unreacted *m*-CPBA was filtered from the cooled mixture, and the liquid phase was diluted with $CHCl_3$ and washed three times with a saturated Na_2CO_3 solution. The organic phase was dried with $MgSO_4$. After filtration, the solvent was removed under vacuum to give **23a** (1.27 g, 6.20 mmol, 90%) as a yellow oil. IR ($CDCl_3$): $\tilde{\nu}$ = 2129 cm^{-1} (N_3), 1053 (SO). ^{1}H NMR ($CDCl_3$): δ = 4.08 (s, 2 H, H-3′), 7.53 (m, 3 H), 7.79 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ = 39.79 (t, C-3′), 84.86 (s, Csp), 95.26 (s, Csp), 124.74 (d, 2 C), 129.54 (d, 2 C), 131.94 (d, *p*-Ph), 142.93 (s, *i*-Ph) ppm.

(3-Azidobut-1-ynylsulfinyl)benzene (23b): The oxidation of **22b** (0.90 g, 4.43 mmol) in CH_2Cl_2 (25 mL) with 70% *m*-CPBA (0.80 g, 4.64 mmol) in CH_2Cl_2 (20 mL) afforded the mixture of the diastereomers (1.1:1) of **23b** (0.80 g, 3.65 mmol, 82%) as a yellow oil (procedure: see synthesis of **23a**). IR ($CDCl_3$, mixture): $\tilde{\nu}$ = 2104 cm^{-1} (N_3), 1232 (N_3), 1054 (SO). ^{1}H NMR ($CDCl_3$, mixture): δ = 1.46 (d, ^3J = 7.2 Hz, 3 H, Me), 1.48 (d, ^3J = 7.2 Hz, 3 H, Me), 4.33 (q, ^3J = 7.2 Hz, 1 H, H-3′), 4.34 (q, ^3J = 7.2 Hz, 1 H, H-3′), 7.55 (m, 2×3 H), 7.81 (m, 2×2 H) ppm. ^{13}C NMR ($CDCl_3$, mixture): δ = 20.23 (q, 2 C, Me), 48.18 (d, 2 C, C-3′), 83.73 (s, 2 C, Csp), 99.21 (s, 2 C, Csp), 124.89 (d, 4 C), 129.62 (d, 4 C), 131.99 (d, 2 C, *p*-Ph), 143.17 (s, 2 C, *i*-Ph) ppm.

(3-Azidoprop-1-ynylsulfonyl)benzene (24a): Compound **22a** (0.73 g, 3.86 mmol) was dissolved in CH_2Cl_2 (15 mL) and treated dropwise with a cooled solution (0 °C) of 70% *m*-CPBA (2.50 g, 10.6 mmol) in CH_2Cl_2. The mixture was kept overnight at about 6 °C, then it was diluted with CH_2Cl_2 (50 mL) and washed three times with saturated Na_2CO_3 solution. The organic phase was dried with $MgSO_4$ and filtered. The solvent was removed to give **24a** (0.81 g, 3.67 mmol, 95%) as a yellow oil. Starting from **23a** (0.50 g, 2.44 mmol) and *m*-CPBA (0.71 g, 3.00 mmol), **24a** (0.49 g, 2.24 mmol, 92%) was also obtained. IR ($CDCl_3$): $\tilde{\nu}$ = 2112 cm^{-1} (N_3), 1333 (SO_2), 1166 (SO_2). ^{1}H NMR ($CDCl_3$): δ = 4.06 (s, 2 H, H-3′), 7.59 (m, 2 H, *m*-Ph), 7.70 (m, 1 H, *p*-Ph), 8.00 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 39.24 (t, C-3′), 83.18 (s, Csp), 86.86 (s, Csp), 127.43 (d, 2 C), 129.43 (d, 2 C), 134.60 (d, *p*-Ph), 140.71 (s, *i*-Ph) ppm.

(3-Azidobut-1-ynylsulfonyl)benzene (24b): For the oxidation of **22b** (0.81 g, 3.99 mmol) in CH_2Cl_2 (25 mL) with 70% *m*-CPBA (2.50 g, 10.6 mmol) in CH_2Cl_2 (15 mL) to yield **24b** (0.84 g, 3.57 mmol, 90%), see synthesis of **24a**. Starting from **23b** (0.71 g, 3.24 mmol) in CH_2Cl_2 (20 mL) and *m*-CPBA (1.00 g, 4.06 mmol) in CH_2Cl_2 (15 mL), **24b** (0.66 g, 2.81 mmol, 87%) was also obtained as a yellow oil. IR ($CDCl_3$): $\tilde{\nu}$ = 2105 cm^{-1} (N_3), 1232 (N_3), 1331 (SO_2), 1159 (SO_2). ^{1}H NMR ($CDCl_3$): δ = 1.47 (d, ^3J = 6.9 Hz, 3 H, Me), 4.29 (q, ^3J = 6.9 Hz, 1 H, H-3′), 7.59 (m, 2 H, *m*-Ph), 7.71 (m, 1 H, *p*-Ph), 8.02 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.82 (q, Me), 47.55 (d, C-3′), 82.30 (s, Csp), 90.48 (s, Csp), 127.52 (d, 2 C), 129.47 (d, 2 C), 134.57 (d, *p*-Ph), 141.00 (s, *i*-Ph) ppm.

(3-Azidopropa-1,2-dienylsulfinyl)benzene (25a): Compound **23a** (0.40 g, 1.95 mmol) was dissolved in dry CH_2Cl_2 (5 mL) and treated dropwise with Et_3N (0.20 g, 1.95 mmol) over a period of 15 min while stirring at 0 °C. The mixture was stirred for additional 45 min at 0 °C, and then the solvent was partially removed under cooling. The residue was chromatographed (column of Ø = 4 cm; filed with 150 cm^3 SiO_2) rapidly with 2 L of Et_2O/*n*-hexane (1:1). Fractions of 20 mL each were collected. Unreacted **23a** was collected first and then the desired allene. Removal of the solvent was performed under cooling affording a mixture of *syn*/*anti*-**25a** (0.16 g, 0.78 mmol, 40%) as a yellowish solid, which decomposed rapidly in contact with air. Diastereomeric ratio = 9:10. IR ($CDCl_3$, mixture): $\tilde{\nu}$ =2113 cm^{-1} (N_3), 1942 (C=C=C), 1272 (N_3), 1048 (SO). ^{1}H NMR ($CDCl_3$, mixture): δ = 6.41 (br. d, ^4J = 5.7 Hz, 1 H, H-3′), 6.43 (br. d, ^4J = 5.7 Hz, 1 H, H-3′), 6.61 (d, ^4J = 5.7 Hz, 1 H, H-1′), 6.62 (d, ^4J = 5.7 Hz, 1 H, H-1′), 7.55 (m, 2×3 H), 7.68 (m, 2×2 H) ppm. ^{13}C NMR ($CDCl_3$, mixture): δ = 108.50 (d), 110.10 (d), 113.71 (d), 114.02 (d), 124.25 (d, 4 C), 129.54 (d, 4 C), 131.65 (d, 2 C, *p*-Ph), 143.30 (s, *i*-Ph), 143.84 (s, *i*-Ph), 196.73 (s, C-2′), 197.45 (s, C-2′) ppm.

[(3-Azidopropa-1,2-dienyl)sulfonyl]benzene (26a): Compound **24a** (0.32 g, 1.44 mmol) was dissolved in dry benzene (5 mL) and treated dropwise with Et_3N (10 mg, 0.10 mmol) at 0 °C. The mixture was stirred for 30 min at 0 °C and filtered on silica gel with Et_2O. The solvent was removed under cooling and the residue diluted with dichloromethane (2 mL). The obtained solution was purified by HPLC [20 cm×2 cm Ø LiChrosphor Si 60 (5 μ)] with cooled CH_2Cl_2. Removal of the solvent under cooling afforded the allene **26a** (35 mg, 1.58 mmol, 11%) as a yellowish solid. The pure solid decomposed rapidly at room temperature to give a complex mixture of products. A small amount of the unreacted starting material **24a** was also isolated from other fractions. IR ($CDCl_3$): $\tilde{\nu}$ = 2117 cm^{-1} (N_3), 1324 (SO_2), 1153 (SO_2). ^{1}H NMR ($CDCl_3$): δ = 6.44 (br. d, ^4J = 5.7 Hz, 1 H, H-3′), 6.76 (d, ^4J = 5.7 Hz, 1 H, H-1′), 7.59 (m, 2 H, *m*-Ph), 7.68 (m, 1 H, *p*-Ph), 7.94 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 109.19 (d), 110.44 (d), 128.02 (d, 2 C), 129.32 (d, 2 C), 134.06 (d, *p*-Ph), 145.44 (s, *i*-Ph), 201.98 (s, C-2′) ppm.

[(3-Azidobuta-1,2-dienyl)sulfonyl]benzene (26b): Compound **24b** (0.30 g, 1.28 mmol) was dissolved in dry $CHCl_3$ (15 mL) and treated in small portions with 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.21 g, 1.91 mmol) while stirring at room temperature. After additional stirring for 1 h, the solvent was partially removed and the residue chromatographed on silica gel (150 g) with Et_2O. The fractions containing the major product were collected and evaporated to give 100 mg residue, which was dissolved in cooled Et_2O. This solution was used for HPLC [20 cm×2 cm Ø LiChrosphor Si 60 (5 μ)] using Et_2O/*n*-hexane (1:1) to give **26b** (ca. 56.0 mg, 238 μmol, 19%) as a yellowish oil. IR ($CDCl_3$): $\tilde{\nu}$ = 2125 cm^{-1} (N_3), 1332 (SO_2), 1157 (SO_2). ^{1}H NMR ($CDCl_3$): δ = 1.86 (d, ^5J = 2.7 Hz, 3 H, Me), 6.61 (q, ^5J = 2.7 Hz, 1 H, H-1′), 7.51 (m, 3 H), 7.91 (m, 2 H, *o*-Ph) PPM. ^{13}C NMR ($CDCl_3$): δ = 17.07 (q, Me), 108.40 (d, C-1′), 119.92 (s, C-3′), 127.95 (d, 2 C), 129.27 (d, 2 C), 133.85 (d, *p*-ph), 139.95 (s, *i*-Ph), 199.94 (s, C-2′) ppm.

4-[Methoxy(phenylsulfanyl)methyl]-1*H*-1,2,3-triazole (33a) from 19: Compound **19** (298 mg, 1.58 mmol) was dissolved in MeOH (25 mL) and stirred for 36 h at room temperature. Methanol was

removed under vacuum and the residue chromatographed on silica gel with Et_2O/*n*-hexane (1:1) to give **33a** (165 mg, 0.75 mmol, 47%) as a yellow oil. IR ($CDCl_3$): $\tilde{\nu}$ = 3439 cm^{-1} (NH). ^1H NMR ($CDCl_3$): δ = 3.62 (s, 3 H, MeO), 5.99 (s, 1 H, MeO*H*C), 7.26 (m, 3 H, Ph), 7.36 (m, 2 H, Ph), 7.43 (s, 1 H, H-5), 12.20 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.76 (q, MeO), 83.71 (d, MeO*H*C), 128.15 (d), 128.65 (d, 2 C, Ph), 129.36 (s, *i*-Ph), 131.34 (d), 133.95 (d, 2 C, Ph), 145.51 (s, C-4) ppm. MS (ESI): *m*/*z* (%) = 222.08 (42) [M + H^+], 190.05 (100). HRMS (ESI): calcd. for $C_{10}H_{11}N_3OS$ [M + H^+] 222.0701, found 222.0724.

4-[Methoxy(phenylsulfanyl)methyl]-1*H*-1,2,3-triazole (33a) and 4-[Bis(phenylsulfanyl)methyl]-1*H*-1,2,3-triazole (34a) from 22a: To a stirred solution of NaOH (0.26 g, 6.50 mmol) in MeOH (50 mL) was added **22a** (0.50 g, 2.65 mmol). Stirring was continued for 60 h at room temperature. Methanol was removed under vacuum, and the residue was dissolved in H_2O (40 mL). The obtained mixture was washed with Et_2O, and the aqueous layer was adjusted in ice bad with diluted (20%) H_2SO_4 to pH = 5–6. The mixture was extracted 5 to 6 times with Et_2O. After drying with $MgSO_4$, the solvent was removed under vacuum and the residue chromatographed on silica gel with Et_2O/*n*-hexane (1:1) to give **33a** (116 mg, 525 μmol, 20%) and **34a** (45.0 mg, 151 μmol, 12%) as a yellow oil. IR ($CDCl_3$): $\tilde{\nu}$ = 3438 cm^{-1} (NH). ^1H NMR ($CDCl_3$): δ = 5.79 (s, 1 H, HC–S), 7.27 (m, 2×3 H, Ph), 7.48 (m, 2×2 H, Ph), 7.58 (s, 1 H, H-5), 9.20 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 50.76 (d, HC–S), 128.38 (d, 2×1C), 129.00 (d, 2×2 C), 130.63 (d), 132.98 (s, 2×1 C), 133.09 (d, 2×2 C), 146.53 (s, C-4) ppm. MS (ESI): *m*/*z* (%) = 300.02 (45) [M + H^+], 190.01 (100). $C_{15}H_{13}N_3S_2$ (299.42): calcd. C 60.17, H 4.38, N 14.03, S 21.42; found C 59.73, H 4.39, N 13.61, S 21.03.

4-Methoxymethyl-5-phenylsulfanyl-1*H*-1,2,3-triazole (37a) from 22a: A solution of **22a** (500 mg, 2.65 mmol) in methanol (50 mL) was stirred for 60 h under reflux. The mixture, which contained traces of solid formed, was filtered. This solid proved to be **38a** [(2.0 mg, 5.25 μmol, 0.40%), for the synthesis of **38a** see below]. Removal of the solvent from the liquid phase afforded a residue, which was purified on silica gel with Et_2O/*n*-hexane (1:1) yielding **37a** (400 mg, 1.81 mmol, 68%) as a yellow oil and the unreacted starting material **22a** (45.0 mg, 238 μmol, 9%). IR ($CDCl_3$): $\tilde{\nu}$ = 3427 cm^{-1} (NH). ^1H NMR ($CDCl_3$): δ = 3.34 (s, 3 H, MeO), 4.55 (s, 2 H, MeOC*H*$_2$), 7.24 (m, 5 H, Ph), 13.25 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 58.59 (q, MeO), 63.95 (t, MeO*C*H_2), 126.87 (d, *p*-Ph), 129.03 (d, 2 C), 129.06 (d, 2 C), 134.16 (s, *i*-Ph), 137.02 (s), 144.53 (s) ppm. MS (ESI); *m*/*z* (%): 222.08 (57) [M + H^+], 190.03 (100). $C_{10}H_{11}N_3OS$ (221.28): calcd. C 54.23, H 5.01, N 18.99, S 14.49; found C 54.01, H 4.71, N 18.54, S 14.15.

4-Methoxymethyl-5-phenylsulfanyl-1*H*-1,2,3-triazole (37a) from 19: Starting from **19** (0.26 g. 1.38 mmol) and NaOH (0.13 g. 3.25 mmol) in methanol (50 mL), the mixture was stirred at 40 °C for 20 h. The work-up was done as in the synthesis of **33a**/**34a** to give **37a** (0.11 g, 0.50 mmol, 36%).

4-(1-Methoxyethyl)-5-phenylsulfanyl-1*H*-1,2,3-triazole (37b): A solution of **22b** (1.00 g, 4.93 mmol) in 75 mL of MeOH was heated at 60 °C for 3 days. After removal of the solvent under vacuum, the residue was purified on silica gel with Et_2O/*n*-hexane (11:9) to give the triazole **37b** (0.93 g, 3.96 mmol, 81%) as a yellow oil. IR ($CDCl_3$): $\tilde{\nu}$ =3425 cm^{-1} (NH). ^1H NMR ($CDCl_3$): δ = 1.46 (d, ^3J = 6.6 Hz, 3 H, *Me*(H)C), 3.17 (s, 3 H, MeO), 4.67 [q, ^3J = 6.6 Hz, 1 H, Me(*H*)C], 7.19 (m, 5 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.51 [q, *Me*(H)C], 56.63 (q, MeO), 70.48 [d, Me(H)*C*], 126.66 (d, *p*-Ph), 128.72 (d, 2 C), 129.97 (d, 2 C), 134.72 (s, *i*-Ph), 135.58 (br. s), 147.96 (br. s) ppm. $C_{11}H_{13}N_3OS$ (235.31): calcd. C 56.15, H 5.57, N 17.86, S 13.63; found C 56.43, H 5.45, N 17.89, S 13.88.

3,8-Bis(phenylsulfanyl)-4*H*,9*H*-bis[1,2,3]triazolo[1,5-*a*:1′,5′-*d*]pyrazine (38a): A solution of **22a** (250 mg, 1.32 mmol) in methanol (1 mL) was heated at 50 °C for 6 days with occasional addition of a few drops of methanol. The mixture was diluted with methanol (5 mL) and filtered. The precipitate was washed several times with small amounts of methanol to give **38a** (13.0 mg, 34.4 μmol, 5.2%) as a white powder; m.p. (MeOH) > 300 °C. ^1H NMR ([D_6]-DMSO): δ = 5.79 (s, 4 H, CH_2), 7.63 (m, 10 H, Ph) ppm. ^{13}C NMR ([D_6]DMSO): δ = 43.13 (t, 2 C, CH_2), 126.71 (d, 2 C, *p*-Ph), 127.89 (d, 4 C), 129.32 (d, 4 C), 130.68 (s, 2 C), 133.08 (s, 2 C), 134.46 (s, 2 C) ppm. $C_{18}H_{14}N_6S_2$ (378.48): calcd. C 57.12, H 3.73, N 22.20, S 16.94; found C 56.81, H 3.94, N 21.92, S 17.54.

3,8-Bis(phenylsulfinyl)-4*H*,9*H*-bis[1,2,3]triazolo[1,5-*a*:1′,5′-*d*]pyrazine (39a): Compound **23a** (220 mg, 1.07 mmol) was dissolved in MeOH (1 mL) and stirred at room temperature for 14 days with occasional addition of a few drops of MeOH. The yellowish powder formed was washed several times with small amounts of MeOH to give **39a** (50.1 mg, 122 μmol, 23%) as a diastereomeric mixture (*meso*/*rac* = 1:1); m.p. (MeOH, mixture) > 300 °C. ^1H NMR ([D_6]DMSO, mixture): δ = 5.57 (d, ^2J = 16.5 Hz, 2 H, CH_2), 5.62 (d, ^2J = 15.3 Hz, 2 H, CH_2), 5.88 (d, ^2J = 15.3, 2 H, CH_2), 5.90 (d, ^2J = 16.5 Hz, 2 H, CH_2) 7.59 (m, 2×6 H, Ph), 7.78 (m, 2×4 H, Ph) ppm. ^{13}C NMR ([D_6]DMSO, mixture): δ = 43.00 (t, 4 C, CH_2), 124.76 (d, 8 C, Ph), 129.64 (d, 8 C, Ph), 129.86 (s, 4 C), 131.75 (d, 4 C, *p*-Ph), 142.55 (s, 4 C), 143.83 (s, 4 C) ppm. $C_{18}H_{14}N_6O_2S_2$ (410.48): calcd. C 52.67, H 3.44, N 20.47, S 15.62; found C 52.50, H 3.40, N 20.17, S 16.05.

3,8-Bis(phenylsulfonyl)-4*H*,9*H*-bis[1,2,3]triazolo-[1,5-*a*:1′,5′-*d*]pyrazine (40a): A solution of **24a** (220 mg, 995 μmol) in MeOH (1 mL) was treated as in the case of **23a** → **39a** to give **40a** (125 mg, 283 μmol, 57%) as a white powder; m.p. (MeOH) > 300 °C. ^1H NMR ([D_6]DMSO): δ = 6.11 (s, 4 H, H_2C), 7.63 (m, 4 H, *m*-Ph), 7.74 (m, 2 H, *p*-Ph), 8.07 (m, 4 H, *o*-Ph) ppm. ^{13}C NMR ([D_6]DMSO): δ = 43.91 (t, 2 C, H_2C), 127.51 (d, 4 C), 129.74 (d, 4 C), 131.79 (s, 2 C), 134.75 (d, 2 C, *p*-Ph), 139.85 (s, 2 C), 141.14 (s, 2 C) ppm. $C_{18}H_{14}N_6O_4S_2$ (442.47): calcd. C 48.86, H 3.19, N 18.99, S 14.49; found C 48.44, H 3.47, N 18.50, S 14.66.

4,9-Dimethyl-3,8-bis(phenylsulfonyl)-4*H*,9*H*-bis[1,2,3]triazolo[1,5-*a*:1′,5′-*d*]pyrazine (40b): Compound **24b** (300 mg, 1.28 mmol) was kept at room temperature for two days without solvent. The product was washed three times with CH_2Cl_2 and two times with MeOH to give a diastereomeric mixture (7:5) of **40b** (25.5 mg, 53 μmol, 8.3%) as a whitish powder; m.p. (mixture) > 300 °C. ^1H NMR ([D_6]DMSO): δ = 2.00 (d, ^3J = 6.6 Hz, 2×6 H, Me), 6.46 [q, ^3J = 6.6 Hz, 2 H, Me(*H*)C, major isomer], 6.53 [q, ^3J = 6.6 Hz, 2 H, Me(*H*)C, minor isomer], 7.70 (m, 2×6 H), 8.06 (m, 2×4 H, *o*-Ph). ^{13}C NMR ([D_6]DMSO): δ = 22.12 (q, 2 C, Me), 23.63 (q, 2 C, Me), 51.62 (d, 2 C, Me(H)*C*), 52.14 (d, 2 C, Me(H)*C*), 127.53 (d, 4 C), 127.71 (d, 4 C), 129.71 (d, 4 C), 129.77 (d, 4 C), 134.56 (d, 4 C, *p*-Ph), 134.98 (s, 2 C), 139.62 (s, 2 C), 139.76 (s), 141.35 (s). Some signals could not be separated. $C_{20}H_{18}N_6O_4S_2$ (470.52): calcd. C 51.05, H 3.86, N 17.86, S 13.63; found C 50.96, H 4.01, N 17.79, S 14.04.

***(E)*-(3-Azido-2-methoxyprop-2-enylsulfinyl)benzene (*E*-41a):** To a solution of **23a** (50 mg, 244 μmol) in methanol (2 mL) was added Et_3N (50 μL). The mixture was stirred at room temperature for 1 h, then it was chromatographed on silica gel with Et_2O to give *E*-**41a** (42.0 mg, 177 μmol, 73%) as a yellow oil. *E*-**41a** was also obtained with lower yield using NaOH as base. IR ($CDCl_3$): $\tilde{\nu}$ = 2111 cm^{-1} (N_3), 1048 (SO). ^1H NMR ($CDCl_3$): δ = 3.50 (s, 3 H, MeO), 3.52

(d, ^2J = 12.6 Hz, 1 H, CH_2), 3.78 (d, ^2J = 12.6 Hz, 1 H, CH_2), 5.75 (s, 1 H, H-3′), 7.50 (m, 3 H, Ph), 7.64 (m, 2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): 55.61 (q, MeO), 57.90 (t, C-1′), 106.43 (d, C-3′), 124.16 (d, 2 C), 128.90 (d, 2 C), 131.29 (d, *p*-Ph), 142.55 (s), 143.52 (s) ppm. The stereochemistry of **41a** was determined by ^{1}H NMR NOE difference spectra.

(*E*)-(3-Azido-2-methoxyprop-2-enylsulfonyl)benzene (*E*-42a): The sulfone **24a** (0.32 g, 1.45 mmol) was dissolved in methanol (20 mL) and treated at room temperature with NaOH (1.00 mg, 25.0 μmol). The mixture was stirred for 30 min, evaporated and purified on silica gel with Et_2O/*n*-hexane (1:1) to give *E*-**42a** (0.28 g, 1.11 mmol, 77%) as yellow oil. IR ($CDCl_3$): $\tilde{\nu}$ = 2113 cm^{-1} (N_3), 1321 (SO_2), 1158 (SO_2). ^{1}H NMR ($CDCl_3$): δ = 3.48 (s, 3 H, MeO), 4.00 (s, 2 H, H-1′), 5.71 (s, 1 H, H-3′), 7.56 (m, 2 H, *m*-Ph), 7.66 (m, 1 H, *p*-Ph), 7.91 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.91 (q, MeO), 56.68 (t, C-1′), 107.38 (d, C-3′), 128.51 (d, 2 C), 128.77 (d, 2 C), 133.83 (d, *p*-Ph), 139.03 (s), 140.93 (s) ppm. The stereochemistry of **42a** was determined by NOE.

(*E*/*Z*)-(3-Azido-2-methoxybut-2-enylsulfonyl)benzene (*E*/*Z*-42b): To a stirred solution of **24b** (230 mg, 979 μmol) in methanol (15 mL) was added NaOH (1.00 mg, 25.0 μmol). After stirring for 2 h, the mixture was evaporated and chromatographed on silica gel with Et_2O/*n*-hexane (2:3) to give *E*-**42b** (105 mg, 393 μmol, 40%, yellow oil), *Z*-**42b** (66.0 mg, 247 μmol, 25%, yellow oil) and a mixture of *E*- and *Z*-**42b** (30.0 mg, 112 μmol, 11%); overall yield 77%. *E*-**42b**: IR ($CDCl_3$): $\tilde{\nu}$ = 2116 cm^{-1} (N_3), 1309 (SO_2), 1265 (N_3), 1154 (SO_2). ^{1}H NMR ($CDCl_3$): δ = 1.84 (s, 3 H, MeC), 3.51 (s, 3 H, MeO), 4.05 (2 H, H-1′), 7.55 (m, 2 H, *m*-Ph), 7.64 (m, 1 H, *p*-Ph), 7.90 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.06 (q, *Me*C), 53.45 (t, C-1′), 57.85 (q, MeO), 125.98 (s), 128.53 (d, 4 C), 133.76 (d, *p*-Ph), 133.88 (s), 138.68 (s) ppm. *Z*-**42b**: IR ($CDCl_3$): $\tilde{\nu}$ = 2113 cm^{-1} (N_3), 1309 (SO_2), 1148 (SO_2). ^{1}H NMR ($CDCl_3$): δ = 1.62 (s, 3 H, MeC), 3.49 (s, 3 H, MeO), 3.94 (s, 2 H, H-1′), 7.57 (m, 2 H, *m*-Ph), 7.67 (m, 1 H, *p*-Ph), 7.91 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.25 (q, *Me*C), 57.20 (t, C-1′), 58.71 (q, MeO), 124.63 (s), 128.36 (d, 2 C), 129.19 (d, 2 C), 133.36 (s), 133.97 (d, *p*-Ph), 138.68 (s) ppm. The stereochemistry of the isomers of **42b** was determined by NOE.

Photolysis of *E*-41a, *E*-42a and *E*/*Z*-42b (General Procedure): In order to determine the position of the olefinic double bonds, the compounds *E*-**41a** (20 mg, 84.4 μmol), *E*-**42a** (30.0 mg, 119 μmol) or *E*/*Z*-**42b** (30.0 mg, 112 μmol) were dissolved in $CDCl_3$ and irradiated at low temperature. The measurement of the NMR spectroscopic data was performed at 19 °C. Due to the decomposition, only a few signals of both diastereomers of **43a** (≈ 30%) could be assigned. The azirines **44a** (from *E*-**42a**) and **44b** (from *E*/*Z*-**42b**) were obtained with 95% and 80% yields (based on NMR), respectively.

2-Methoxy-2-phenylsulfinylmethyl-2*H*-azirine (*like*/*unlike*-43a): Irradiation of *E*-**41a** at –50 °C for 45 min. ^{1}H NMR ($CDCl_3$): δ = 2.92 (s, 3 H, MeO), 3.13 (s, 3 H, MeO), 2.60–3.80 (CH_2), 7.54 (m, 10 H, Ph), 10.34 (s, 1 H, H-3), 10.63 (s, 1 H, H-3) ppm. ^{13}C NMR ($CDCl_3$): 175.15 (d, C-3), 175.63 (d, C-3) ppm.

2-Methoxy-2-phenylsulfonylmethyl-2*H*-azirine (44a): Irradiation of *E*-**42a** at –55 °C for 45 min. IR ($CDCl_3$): $\tilde{\nu}$ = 1713 cm^{-1} (C=N), 1321 (SO_2), 1151 (SO_2). ^{1}H NMR ($CDCl_3$): δ = 2.88 (s, 3 H, MeO), 2.95 (d, ^2J = 14.6 Hz, 1 H, CH_2), 4.16 (d, ^2J = 14.6 Hz, 1 H, CH_2), 7.59 (m, 2 H, *m*-Ph), 7.67 (m, 1 H, *p*-Ph), 7.96 (m, 2 H, *o*-Ph), 10.48 (s, 1 H, H-3) ppm. ^{13}C NMR ($CDCl_3$): δ = 52.11 (q, MeO), 61.96 (s, C-2), 62.62 (t, CH_2), 128.05 (d, 2 C), 129.27 (d, 2 C), 134.01 (d, *p*-Ph), 139.40 (s, *i*-Ph), 172.99 (d, C-3) ppm.

2-Methoxy-3-methyl-2-phenylsulfonylmethyl-2*H*-azirine (44b): Irradiation of *E*/*Z*-**42b** at –50 °C for 50 min. IR ($CDCl_3$): $\tilde{\nu}$ = 1742 cm^{-1} (C=N), 1319 (SO_2), 1145 (SO_2). ^{1}H NMR ($CDCl_3$): δ = 2.54 (s, 3 H, MeC), 2.86 (s, 3 H, MeO), 2.88 (d, ^2J = 14.4 Hz, 1 H, CH_2), 4.18 (d, ^2J = 14.4 Hz, 1 H, CH_2), 7.56 (m, 2 H, *m*-Ph), 7.64 (m, 1 H, *p*-Ph), 7.92 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.61 (q, *Me*C), 51.74 (q, MeO), 62.90 (t, CH_2), 64.72 (s, C-2) 127.87 (d, 2 C), 129.03 (d, 2 C), 133.75 (d, *p*-Ph), 139.33 (s, *i*-Ph), 177.24 (s, C-3) ppm.

(*Z*)-(3-Azido-2-methoxyprop-1-enylsulfonyl)benzene (*Z*-46a): A solution of **24a** (500 mg, 2.26 mmol) in dry MeOH (500 mL) was heated for 20 h under reflux. The solid formed was filtered and proved to be **40a** (≈ 5 mg). The liquid phase was then concentrated and chromatographed on silica gel with Et_2O/*n*-hexane (4:1) to give *Z*-**46a** (70.0 mg, 277 μmol, 12%) as a yellow oil. IR ($CDCl_3$): $\tilde{\nu}$ = 2112 cm^{-1} (N_3), 1307 (SO_2), 1152 (SO_2). ^{1}H NMR ($CDCl_3$): δ = 3.77 (s, 3 H, MeO), 3.90 (br. s, 2 H, H-3′), 5.88 (s, 1 H, H-1′), 7.55 (m, 3 H), 7.96 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 49.72 (t, C-3′), 57.00 (q, MeO), 110.75 (d, C-1′), 127.57 (d, 2 C), 128.70 (d, 2 C), 133.02 (d, *p*-Ph), 142.33 (s, *i*-Ph), 160.60 (s, C-2′) ppm.

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