

New Way to Methylene-2*H*-azirines and Their Use as Powerful Intermediates for the Stereo- and Regioselective Synthesis of Compounds with Vinylamine Substructure^[‡]

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New and relatively stable methylene-2*H*-azirines **1** have been prepared by photolysis of allenyl azides or from 2-halo-2*H*-azirines by elimination of HX (X = halogen). The reaction of these methylene-2*H*-azirines with nucleophiles led to the highly stereo- and regio-selective formation of novel 1-aminovinyl derivatives with good to excellent yields. The trapping reactions of the less stable methylene-2*H*-azirines gave

rise to similar results. Moreover, we were able to prove that the previous report on 2-(phenylsulfonyl)acrylonitrile (**9**) was based on incorrect data. For this reason, the latter compound can be supposed to be firstly described in this paper.

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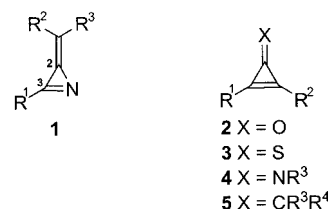
Introduction

2-Methylene-2*H*-azirines **1** form a long-sought^[1–3] compound class which was unknown^[4–6] until 1990 when the first examples were generated in our group by photolysis of allenyl azides.^[7,8] Thereby, the difficult access to considerable amounts of these first heterocyclic triafulvenes was attributed to their thermal and photochemical sensitivity as well as the difficult handling of the allenyl azides which served as precursors. Fortunately, we recently developed a new synthetic strategy that allows us to isolate some relatively stable allenyl azides.^[9] The photochemical transformation of the latter compounds is described in this paper.

Another method for the generation of methylene-2*H*-azirines based on matrix photolysis of 1,3-diazidophenyl derivatives, monitored by IR spectroscopy, has been reported by Tomioka and co-workers in 2003.^[10] However, the estimated yields of the methylene-2*H*-azirines formed by this method were very low (<10%).

In both methods mentioned above, the stability of the obtained methylene-2*H*-azirines **1** proved to depend strongly on the electronic nature of the substituent R¹ at the 3-position (Scheme 1). Thus, methylene-2*H*-azirines with R¹ = H are extremely unstable whereas those with R¹ = ERG (ERG = electron releasing group) show better stabilities. Nevertheless, the lifetime of the latter compounds

is rather short (less than one hour for solutions at room temperature). Therefore, our first challenge was to find out how the stability of methylene-2*H*-azirines can be improved. It is well known that compounds like cyclopropenones **2**,^[11–13] cyclopropenthiones **3**,^[11a,13] cyclopropenimines **4**,^[14] and methylenecyclopropenes **5**,^[12,15] which are structurally similar to methylene-2*H*-azirines, can be stabilized by donor substituents R¹ and R² at the cyclopropene ring. Noteworthy, the stability of methylenecyclopropenes **5** can be improved by the introduction of donor substituents R¹ and R² at the ring and acceptor substituents R³ and R⁴ at the methylene terminus.^[16] Therefore, we assumed that the introduction of both the acceptor substituents at the methylene group and a donor substituent at the azirine ring of the title compounds **1** might also increase their lifetime. In this context, we describe here the generation and characterization of some methylene-2*H*-azirines with improved stabilities using a new, simple, and inexpensive method. Moreover, the conversion of the latter compounds by nucleophiles and the analogous trapping reactions of the less stable azatriafulvenes **1** to form their 1-aminovinyl derivatives are reported. In fact, due to their presence in a range of naturally occurring compounds and synthetic biological



Scheme 1.

[‡] Reactions of Unsaturated Azides, 21. Part 20: K. Banert, S. Grimme, R. Herges, K. Heß, F. Köhler, C. Mück-Lichtenfeld, E.-U. Würthwein, *Chem. Eur. J.*, manuscript accepted.

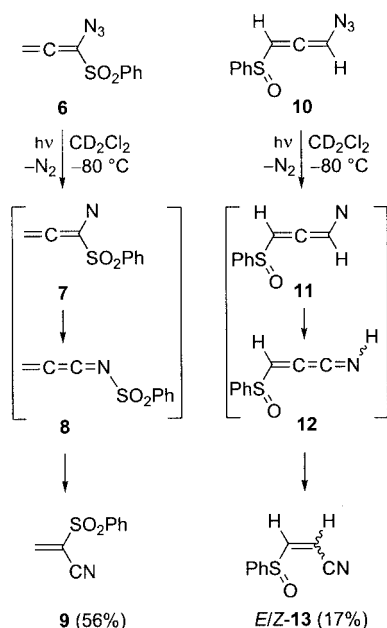
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active ones, compounds with the title substructure, such as α,β -dehydro amino acids and α,β -dehydro amino acid esters,^[17] peptides,^[17f,18] and α,β -dehydro amino ketones,^[19] have received increased attention in the last decades.

Results and Discussion

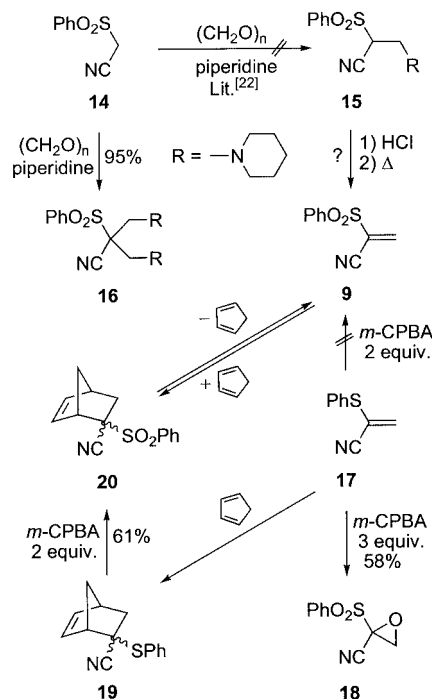
Methylene-2*H*-azirines from Allenyl Azides

Photolysis of solutions of the recently synthesized allenyl azides **6**^[9a] and **10**^[9a] in CD_2Cl_2 at -80°C affords the acrylonitrile derivatives **9** (56%) and **13**^[20] (*E/Z*, 17%), respectively, instead of the expected methylene-2*H*-azirines (Scheme 2). Compound **9** is also obtained by photolysis of **6** in CDCl_3 at -55°C or by the thermal decomposition of **6**. The formations of **9** and **13** probably proceed via the short-lived cumulenes **7**, **8** and **11**, **12**, respectively. Analogous intermediates were reported earlier.^[21] However, in the case of **7** and **11**, direct 1,2-migration of the sulfonyl group or the hydrogen atom, respectively, can also explain the formation of the products **9** and **13**.



Scheme 2.

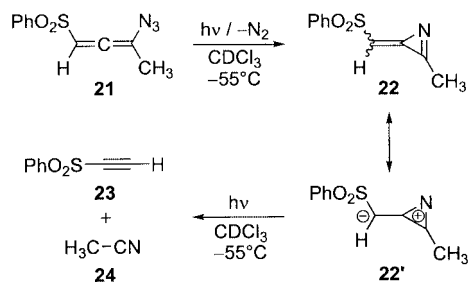
According to Bazavova and co-workers,^[22] compound **9** can also be obtained from the reaction of (phenylsulfonyl)-acetonitrile (**14**), piperidine, and paraformaldehyde via the Mannich base **15** (Scheme 3). However, the ^1H NMR spectroscopic data published for **9** ($\delta = 4.11$ and 4.99 for the signals of the olefinic hydrogen atoms) were not compatible with the structure of such acceptor substituted alkenes. Moreover, performing the reaction by analogy with the reported procedure gave rise to **16** (>95% based on **14**) instead of **15**.



Scheme 3.

In order to prove the structure of **9** generated from **6** (Scheme 2), 2-(phenylsulfonyl)acrylonitrile (**17**)^[23] was treated with two equivalents of *m*-chloroperbenzoic acid (*m*-CPBA, Scheme 3). This reaction afforded a mixture of compounds none of which gave rise to a ^1H NMR signal attributable to **9**. When using three equivalents of *m*-CPBA, only the oxirane **18** was identified. Fortunately, the Diels–Alder reaction of **17** and cyclopentadiene forming **19**^[24] followed by oxidation of the latter compound to produce **20** and its subsequent flash vacuum pyrolysis led to the desired product **9** by *retro*-Diels–Alder reaction. However, the yield of **9** was low (ca. 5%) since renewed [4+2] cycloaddition of **9** and cyclopentadiene could not be suppressed completely even at low temperature because of the high reactivity of both compounds. Our spectroscopic data of **9** and especially the ^1H NMR spectroscopic data are compatible with the structure of this acceptor-substituted alkene in contrast to the data published by Bazavova^[22] and co-workers.

Contrary to the photolysis of **6** and **10**, irradiation of **21**^[9a] yielded a product mixture including the desired heterocycles *E/Z*-**22** which were identified by their ^1H NMR spectroscopic data (14% yield based on ^1H NMR, Scheme 4). In fact, the observation of **22** is the consequence of its better stabilization, which can be rationalized as postulated in the introductory part and explained with the help of the mesomeric form **22'** in consideration of the methyl group (donor) at 3-position and the phenylsulfonyl group (acceptor) at the methylene terminus. In addition to **22**, signals ascribable to (phenylsulfonyl)acetylene (**23**)^[25] (6%) and acetonitrile (**24**) (6%) were also detected in the product mixture. The formation of **23** and **24** can be rationalized by the well-known photochemical fragmentation of methylene-2*H*-azirines.^[7]



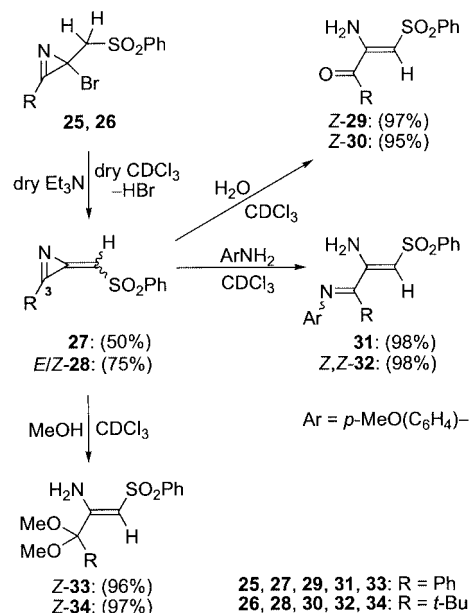
Scheme 4.

Although electron-withdrawing groups are necessary for a better stabilization of both azido allenes^[9] and methylene-2*H*-azirines, the low yield of **22** generated by the photolysis of the allenyl azide **21** and the non-formation of methylene-2*H*-azirines by the photolysis of **6** and **10** provide an evidence that compounds of type **1** bearing strong acceptor substituents at the methylene terminus can undergo rapid reactions if compared to other methylene-2*H*-azirines described in the literature.^[7,8]

Methylene-2*H*-azirines from 2-Halo-2*H*-azirines

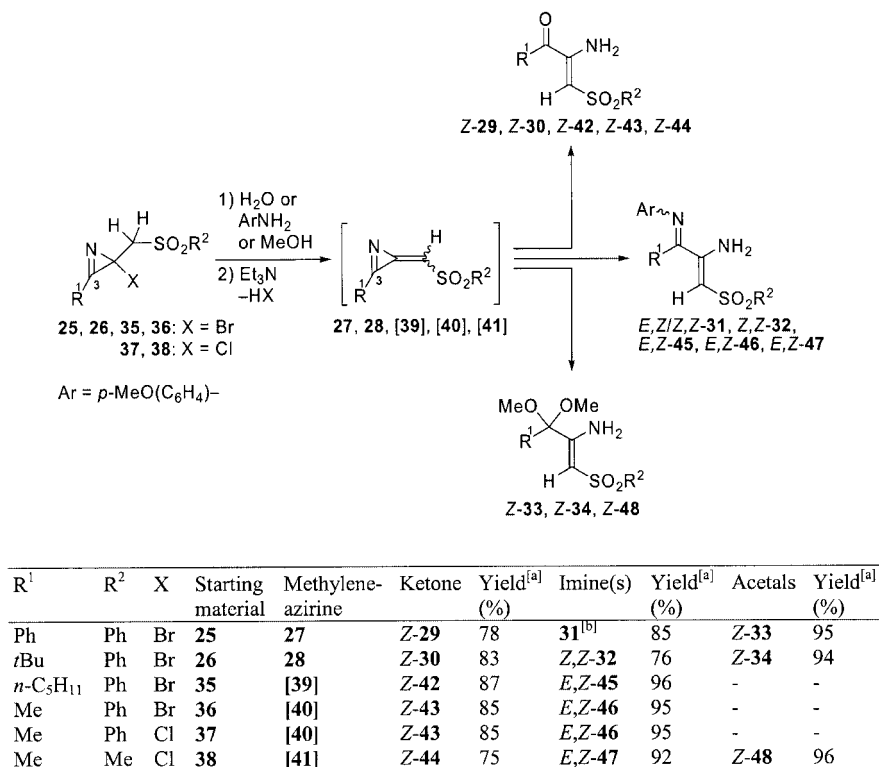
In order to find an appropriate method for the production of stable methylene-2*H*-azirines, dry CDCl_3 solutions of the recently synthesized 2-bromo-2*H*-azirines **25**^[26] and **26**^[26] were treated with dry Et_3N at room temperature under nitrogen atmosphere (Scheme 5). The reaction was monitored by ^1H NMR spectroscopy. The formation of the desired methylene-2*H*-azirines **27** (only one stereoisomer, 50% yield based on ^1H NMR) and *E/Z*-**28** (75% yield based on ^1H NMR, ratio of isomers = 1:15) from **25** and **26**, respectively, was observed. Compounds **27** and **28** could be detected in CDCl_3 solutions at room temperature for 2 and 36 hours, respectively. Hitherto, the maximal lifetime observed for a methylene-2*H*-azirine was one hour at room temperature. At -18°C , **28** could be conserved for several weeks without any remarkable decomposition. The stabilizing character of the bulky *tert*-butyl group in **28**, which has an +I effect accompanied with a strong kinetically stabilizing mode, is clearly more effective than that of the phenyl group in **27**. However, despite their relative long lifetime, **27** and **28** could not be isolated. This was attributed to their rapid succeeding reactions in contact with silica gel and the difficulties on attempts of crystallization from the product mixtures.

The methylene-2*H*-azirines **27** and *E/Z*-**28** proved to be powerful electrophiles. In fact, their treatment with water, *p*-anisidine, and methanol led to the corresponding addition reactions with subsequent ring-opening to form 1-amino-vinyl ketones *Z*-**29**^[27] and *Z*-**30**, 3-amino-1-azabuta-1,3-dienes **31** and *Z,Z*-**32** as well as 2-aminoacrolein acetals *Z*-**33** and *Z*-**34**, respectively, with very good yields (Scheme 5). These reactions took place with complete site selectivity at C-3. Except for **31**, which was obtained as mixture of isomers (ratio of isomers = 1:14, unknown assignment), only one stereoisomer was formed in each case. The *one-pot* syn-

Scheme 5. Generation of methylene-2*H*-azirines and subsequent reactions with nucleophiles.

thesis of the ketones *Z*-**29**, *Z*-**30**, the imines **31**, *Z,Z*-**32**, and the acetals *Z*-**33**, *Z*-**34** by direct trapping of the produced methylene-2*H*-azirines gave rise to similar results and overall yields in the range of 85–96% (Scheme 6).

When the 2-halo-2*H*-azirines **35**,^[26] **36**,^[26] **37**,^[26] and **38**^[26] were treated with dry Et_3N at room temperature under the conditions mentioned above, no signals of the corresponding methylene-2*H*-azirines **39**, **40**, and **41** could be observed (Scheme 6). This was ascribed to the low kinetically stabilizing character of the donor substituents at C-3 and the relatively high reaction temperatures. However, performing the reactions at lower temperatures led only to complex mixtures. Fortunately, the one-pot trapping reactions of compounds **39**, **40**, and **41** with water, *p*-anisidine or methanol as nucleophiles afforded the corresponding 1-aminovinyl ketones *Z*-**42**, *Z*-**43**, and *Z*-**44**, 3-amino-1-azabuta-1,3-dienes *E,Z*-**45**, *E,Z*-**46**, and *E,Z*-**47** as well as 2-aminoacrolein acetal *Z*-**48**, respectively, with very good yields. Compound *Z*-**44** had already been synthesized using another method,^[28] however, without any report on the NMR spectroscopic data and the stereocontrol. Using the one-pot procedure described above, the nucleophiles attacked in the same way as in the two-step procedure selectively at C-3 of the intermediate methylene-2*H*-azirine, and the products were formed with complete stereoselectivity. In all cases, the configuration of the vinylamine substructure was proved to be *Z* whereas that of the imine double bond was found to depend on the steric interactions with the substituent R^1 . For the bulky *tert*-butyl group, a *Z* configuration was found whereas the *E* configuration was adopted for $\text{R}^1 = \text{methyl}$ or *n*-pentyl. Except for *Z*-**29**, for which the stereochemistry was assigned by X-ray crystal structure analysis,^[27] the configurational assignments of all compounds were supported by ^1H NMR NOE experiments.



Scheme 6. One-pot synthesis of ketones, imines, and acetals including trapping of methylene-2*H*-azirines. [a] Yield of isolated compound. [b] Mixture of isomers.

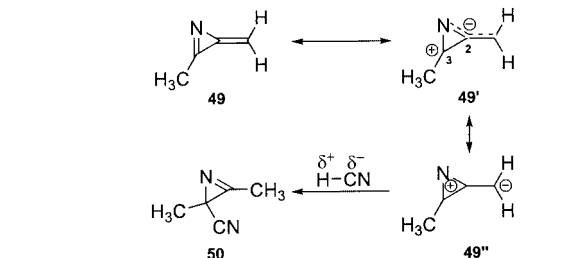
Both the generation of methylene-2*H*-azirines from 2-halo-2*H*-azirines and the subsequent nucleophilic transformation into 1-aminovinyl derivatives by two-step or one-pot procedures are new chemical transformations. Although the nature of the halogen do not influence the yield of the final product in the one-pot procedures, as shown for **43** and **46** (Scheme 6), it might be significantly relevant in the two-step pathway because the elimination of HCl in the first step to produce the short-lived methylene-2*H*-azirine is relatively difficult, taking longer time, if compared to that of HBr.

Mechanistic Aspects for the Formation of 1-Aminovinyl Derivatives

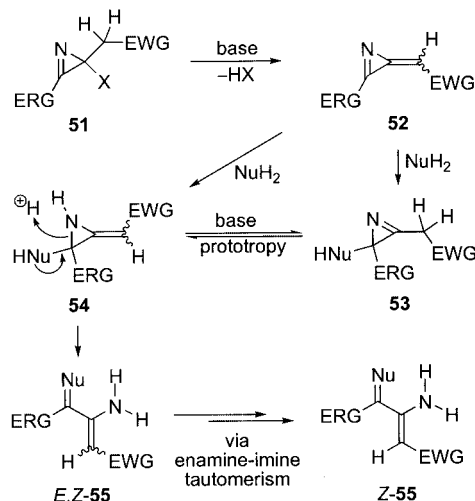
For the reactions of nucleophiles with methylene-2*H*-azirines, previous work in our group had predicted the regioselective attack of the nucleophile at C-3 (Scheme 7).^[8] However, the only known example of such reactions (**49** → **50**)^[7] afforded exclusively a normal 2*H*-azirine as product of simple 1,4-addition.

The formation of the ring-opening products described in this paper can be explained by the direct formation of intermediates of type **54** from **52** or by the formation of the azirines of type **53** and their rapid prototropic isomerization^[29] into **54** followed by ring opening to the thermodynamically more stable final products of type **55** (Scheme 8).

The isomerization of **53** into **54** could be facilitated by the acceptor substituent (EWG), which increased the acid-

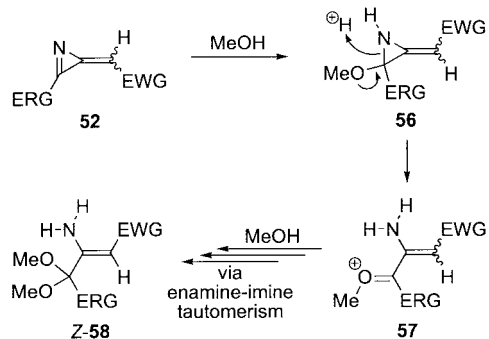


Scheme 7.



Scheme 8. Mechanism of the reaction of binucleophiles with methylene-2*H*-azirines.

ity of the α -EWG hydrogen. As far as the stereochemistry is concerned, the highly favorable *Z* configuration might be adopted via an enamine-imine tautomerism. In the case of the formation of the acetals, NuH_2 is replaced by two molecules of methanol, and the reaction with **52** might produce an intermediate of type **57**, which is attacked by a second molecule of methanol. The sequence is finished by the above-mentioned enamine-imine tautomerism to afford the final acetals *Z*-**58** (Scheme 9).



Scheme 9. Mechanism of the reaction of methanol with methylene-2*H*-azirines.

Conclusions

A new, simple, and efficient approach towards methylene-2*H*-azirines was developed. Some of these strained heterocycles proved to possess relatively high stabilities. The latter compounds could be regio- and stereoselectively converted to 1-aminovinyl derivatives with very good yields. Both the generation and the transfer of methylene-2*H*-azirines to 1-aminovinyl derivatives were combined in a one-pot procedure starting from 2-halo-2*H*-azirines to afford products with similar regio- and stereoselectivities and also with high yields. Using the one-pot synthesis strategy, less stable methylene-2*H*-azirines could be generated and trapped directly with nucleophiles to form the corresponding 1-aminovinyl derivatives likewise with high regio- and stereoselectivities and very good yields. The synthesis of 1-aminovinyl ketones and the analogous imines described in this paper represents new aspects of the azirine chemistry.

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). Assignments of configuration were supported by homonuclear NOE experiments except for **29**^[27] for which the configuration was ascertained by X-ray crystal structure analysis. Infrared spectra were recorded as solutions in CDCl_3 . TLC was performed on Macherey–Nagel precoated silica gel Polygram Sil G/UV₂₅₄ plates and viewed by UV. Chromatography refers to flash chromatography,^[30] carried out on Fluka silica gel 60. For the elemental analyses, Vario El

(Elementar Analysensystem GmbH) was employed. Mariner 5229 from Applied Biosystems was used for mass spectra. The method applied was the electrospray ionization.

The photolyses were performed with a 150-W Hg high-pressure lamp (polychromatic) TQ 150 from Heraeus GmbH. Quartz equipment was used for cooling the lamp with the help of an ethanol cryostat (Lauda GmbH). Solutions of the substrates in normal NMR sample tubes were cooled in the same way while being irradiated. 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. Monitoring the photolyses by ^1H NMR spectroscopy means that spectra were recorded at low temperature, e.g. -50°C , after a definite time of irradiation at the same temperature.

The known compounds **6**,^[9a] **10**,^[9a] **17**,^[23] **19**,^[24] **21**,^[9a] **25**,^[26] **26**,^[26] and (**35–38**)^[26] were synthesized according to the literature.

2-(Phenylsulfonyl)acrylonitrile (9): The allenyl azide **6**^[9a] (25.0 mg, 113 μmol) in CD_2Cl_2 (0.5 mL) was irradiated at -80°C . The reaction was monitored by ^1H NMR spectroscopy at -50°C . After 2 h, the formation of **9** was observed with 56% yield based on ^1H NMR spectroscopy. Photolysis of **6** in CDCl_3 at -55°C led to similar result. The formation of **9** was also observed during the thermal decomposition of compound **6** at room temperature. Neat **9** polymerizes rapidly at room temperature. The assignments of the NMR signals of **9** was performed with the help of ^{13}C , ^1H NMR correlation spectroscopy. IR (CDCl_3): $\tilde{\nu} = 1334\text{ cm}^{-1}$ (SO_2), 1154 (SO_2). ^1H NMR (CDCl_3): $\delta = 6.71$ (d, $^2J = 1.1\text{ Hz}$, 1 H, $\text{H}_2\text{C}=\text{C}$), 7.12 (d, $^2J = 1.1\text{ Hz}$, 1 H, $\text{H}_2\text{C}=\text{C}$), 7.62 (m, 3 H), 7.98 (m, 2 H, *o*-Ph). The chemical shifts of the signals assigned to the olefinic protons correspond well with δ values calculated using an empirical system of increments^[31] ($\delta = 6.93, 6.96$). ^{13}C NMR (CDCl_3): $\delta = 111.7$ (s, C-1), 128.1 (s, C-2), 129.9 (d, 2 C), 129.8 (d, 2 C), 135.2 (d, *p*-Ph), 136.4 (s, *i*-Ph), 139.6 (t, C-3).

3-(Phenylsulfonyl)acrylonitrile (*E/Z*-13): The allene **10**^[9a] (20.0 mg, 97.6 μmol) in CD_2Cl_2 (0.5 mL) was irradiated at -80°C . The reaction was monitored by ^1H NMR spectroscopy at -50°C . After 90 min, the formation of *E/Z*-**13**^[20] was observed with a combined yield of 17% based on ^1H NMR spectroscopy. For *E*-**13**, only one signal at $\delta = 6.41$ (d, $^3J = 15.0\text{ Hz}$, 1 H) was clearly identified in the ^1H NMR spectrum of the reaction mixture whereas two signals at $\delta = 5.89$ (d, $^3J = 10.3\text{ Hz}$, 1 H) and 7.12 (d, $^3J = 10.3\text{ Hz}$, 1 H) were identifiable for *Z*-**13**.

2-(Phenylsulfonyl)-1,3-dipiperidinopropane-2-carbonitrile (16): Treatment of the mixture of (phenylsulfonyl)acetonitrile **14** (6.13 g, 33.9 mmol), piperidine (32 mL) and 4.00 g of paraformaldehyde $[(\text{CH}_2\text{O})_n]$ by analogy with the literature^[22] led to **16** (12.07 g, 32.2 mmol, 95%), instead of **15** as reported by the authors. Compound **16** was obtained as white solid, m.p. $86\text{--}88^\circ\text{C}$ (*n*-hexane). ^1H NMR (CDCl_3): $\delta = 1.33$ (m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.39 (m, 8 H, NCH_2CH_2), 2.52 (br. t, $J = 4.5\text{ Hz}$, 8 H, NCH_2CH_2), 2.94 (d, $^2J = 14.1\text{ Hz}$, 2 H, CH_2CS), 3.04 (d, $^2J = 14.1\text{ Hz}$, 2 H, CH_2CS), 7.57 (m, 2 H, *m*-Ph), 7.70 (m, 1 H, *p*-Ph), 8.05 (m, 2 H, *o*-Ph). ^{13}C NMR (CDCl_3): $\delta = 23.7$ (t, 2 C, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 25.9 (t, 4 C, NCH_2CH_2), 55.8 (t, 4 C, NCH_2CH_2), 59.0 (t, 2 C, CH_2CS), 67.3 (s, C-2), 117.6 (CN), 128.7 (d, 2 C), 130.5 (d, 2 C), 134.4 (d, *p*-Ph), 136.9 (s, *i*-Ph). MS (ESI); m/z : 376.20 $[\text{M} + \text{H}^+]$. $\text{C}_{20}\text{H}_{29}\text{N}_3\text{O}_2\text{S}$ (375.53): calcd. C 63.97, H 7.78, N 11.19, S 8.52; found C 63.70, H 7.46, N 11.17, S 8.24.

1-(Phenylsulfonyl)oxirane-1-carbonitrile (18): Compound **17**^[23] (600 mg, 3.73 mmol) in CH_2Cl_2 (15 mL) was treated dropwise at 0°C with a solution of 70% *m*-CPBA (3.00 g, 12.15 mmol, remain-

der 3-chlorobenzoic acid) in CH_2Cl_2 (15 mL) and then allowed to stay overnight at 6 °C. The reaction mixture was diluted with CH_2Cl_2 , washed three times with a saturated aqueous solution of Na_2CO_3 and dried with MgSO_4 . The solvent was then removed, and the residue was chromatographed on silica gel with $\text{Et}_2\text{O}/n$ -hexane (1:1) to give **18** (450 mg, 2.15 mmol, 58%) as white solid, m.p. 59–60 °C ($\text{Et}_2\text{O}/n$ -hexane). ^1H NMR (CDCl_3): δ = 3.57 (d, 2J = 5.7 Hz, 1 H, CH_2), 3.86 (d, 2J = 5.7 Hz, 1 H, CH_2), 7.69 (m, 2 H, *m*-Ph), 7.82 (m, 1 H, *p*-Ph), 8.02 (m, 2 H, *o*-Ph). ^{13}C NMR (CDCl_3): δ = 52.1 (t, C-2), 60.0 (s, C-1), 112.0 (s, CN), 129.8 (d, 2 C), 129.9 (d, 2 C), 133.9 (s, *i*-Ph), 136.0 (d, *p*-Ph). $\text{C}_9\text{H}_7\text{NO}_3\text{S}$ (209.22): calcd. C 51.67, H 3.37, N 6.69, S 15.33; found C 51.56, H 3.38, N 6.51, S 15.40.

2-(Phenylsulfonyl)bicyclo[2.2.1]hept-5-ene-2-carbonitrile (20): The mixture *endo*-**19**^[24] (1.00 g, 4.41 mmol) was treated with two equivalents of *m*-CPBA under similar reaction conditions as described for **18**. The reaction mixture was then chromatographed over silica gel with $\text{Et}_2\text{O}/n$ -hexane (1:1) to give *exo*-**20** (690 mg, 2.66 mmol, 61%) as white solid, m.p. 110–113 °C ($\text{Et}_2\text{O}/n$ -hexane, 7:4 mixture). $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{S}$ (259.32): calcd. C 64.84, H 5.05, N 5.40, S 12.37; found C 64.20, H 5.09, N 5.22, S 12.60.

Minor Isomer: ^1H NMR (CDCl_3): δ = 1.50–3.50 (m, 6 H), 6.24 (m, 1 H), 6.49 (m, 1 H), 7.13 (m, 2 H, *m*-Ph), 7.73 (m, 1 H, *p*-Ph), 8.04 (m, 2 H, *o*-Ph). ^{13}C NMR (CDCl_3): δ = 36.9 (t), 42.4 (d), 46.1 (t), 50.0 (d), 67.0 (s, C-2), 118.7 (s, CN), 129.6 (d, 2 C), 130.4 (d), 134.9 (d), 135.6 (s, *i*-Ph), 139.1 (d), 142.4 (d).

Major Isomer: ^1H NMR (CDCl_3): δ = 1.50–3.50 (m, 6 H), 6.17 (m, 1 H), 6.42 (m, 1 H), 7.13 (m, 2 H, *m*-Ph), 7.73 (m, 1 H, *p*-Ph), 7.96 (m, 2 H, *o*-Ph). ^{13}C NMR (CDCl_3): δ = 36.9 (t), 43.0 (d), 49.7 (t), 52.6 (d), 66.8 (s, C-2), 119.8 (s, CN), 129.3 (d, 2 C), 130.2 (d), 134.8 (d), 136.4 (s), 139.1 (d), 142.4 (d).

After treating *exo*-**20** by flash vacuum pyrolysis at 550 °C and 10^{-5} Torr (for this technique, see ref.^[32]), **9** is collected at low temperature and identified by its NMR spectroscopic data, which were identical with those of **9** generated by photolysis of **6**.

3-Methyl-2-[(phenylsulfonyl)methylene]-2H-azirine (E/Z-22): The azido allene **21**^[9a] (8 mg, 34 μmol) in CDCl_3 (0.5 mL) was irradiated at –55 °C. The reaction was monitored by ^1H NMR spectroscopy at –55 °C. After 45 min of irradiation, the methylene-2H-azirines *E/Z*-**22** were obtained in ca. 14% yield based on ^1H NMR (ratio of products: 3:2). (Phenylsulfonyl)acetylene (**23**),^[25] acetonitrile (**24**), and the unreacted starting material were also observed in the products mixture in each case with ca. 6% yield based on ^1H NMR spectroscopy. The ^{13}C NMR spectroscopic data of the desired methylene-2H-azirines *E/Z*-**22** could not be obtained.

Minor Isomer: ^1H NMR (CDCl_3 , –55 °C): δ = 2.65 (s, 3 H, H_3C), 5.88 (s, 1 H, HC-SO_2), 7.90–8.60 (m, 5 H, Ph).

Major Isomer: ^1H NMR (CDCl_3 , –55 °C): δ = 2.96 (s, 3 H, H_3C), 5.90 (s, 1 H, HC-SO_2), 7.90–8.60 (m, 5 H, Ph).

3-Phenyl-2-[(phenylsulfonyl)methylene]-2H-azirine (27): Compound **25**^[26] (80 mg, 229 μmol) was dried for several hours at 10^{-3} Torr and dissolved under nitrogen atmosphere in dry CDCl_3 (0.6 mL). The solution was treated in a NMR tube with 40 μL dry Et_3N . The reaction was monitored by ^1H NMR, while the mixture was occasionally shaken up. The complete transformation of the starting material could be observed after 10 min. At that moment, the desired product **27** (only one stereoisomer) was detected with 50% yield based on ^1H NMR spectroscopy. This compound **27** was stable to be observed for ca. 2 h at room temperature, but it could not be isolated due to the rapid decomposition on silica gel. IR (CDCl_3 , mixture): $\tilde{\nu}$ = 1869 cm^{-1} (C=N), 1309 (SO_2), 1145 (SO_2). ^1H NMR (CDCl_3): δ = 5.94 (s, 1 H, HC-SO_2), 7.35–7.86 (m, 8 H), 8.52 (m, 2 H). ^{13}C NMR (CDCl_3): δ = 87.8 (d, HC-SO_2), 120.4 (s, *i*-Ph at C-3), 126.5 (d, 2 C), 128.9 (d, 2 C), 129.7 (d, 2 C), 132.4 (d), 132.4 (d, 2 C), 137.0 (d), 143.1 (s), 143.7 (s), 180.4 (s, C-3).

E/Z-3-tert-Butyl-2-[(phenylsulfonyl)methylene]-2H-azirine (E/Z-28): Under similar conditions as described for **27**, compound **26**^[26] (40 mg, 229 μmol) was treated with 1.5 equivalents of Et_3N to give *E/Z*-**28** with 75% yield based on ^1H NMR, ratio of isomers = 1:15. IR (CDCl_3 , mixture): $\tilde{\nu}$ = 1868 cm^{-1} (C=N), 1314 (SO_2), 1145 (SO_2).

Minor Isomer: ^1H NMR (CDCl_3): δ = 1.28 (s, 9 H, H_3C), 5.74 (s, 1 H, HC-SO_2), 7.41 (m, 3 H, Ph), 7.86 (m, 2 H, *o*-Ph). ^{13}C NMR (CDCl_3): δ = 25.1 (q, 3 C, H_3C); other signals could not be detected.

Major Isomer: ^1H NMR (CDCl_3): δ = 1.42 (s, 9 H, H_3C), 5.77 (s, 1 H, HC-SO_2), 7.41 (m, 3 H, Ph), 7.71 (m, 2 H, *o*-Ph). ^{13}C NMR (CDCl_3): δ = 24.9 (q, 3 C, H_3C), 34.6 (s, H_3CC), 88.0 (d, HC-SO_2), 126.1 (d, 2 C), 129.0 (d, 2 C), 132.3 (d, *p*-Ph), 142.8 (s), 145.8 (s), 193.4 (s, C-3).

Synthesis of 1-Aminovinyl Ketones Z-29, Z-30, Z-42, Z-43, and Z-44. Two-Step Procedure: This procedure is only applicable to the synthesis of **Z-29**, **Z-30**. Starting from **25** or **26**, the methylene-2H-azirines **27** and **28** were produced as shown above and treated with excess of water to give after 5 min the 1-aminovinyl ketones **Z-29** (97% with regard to **27**) and **Z-30** (95% with regard to **28**), respectively. The yields were based on ^1H NMR spectroscopy.

One-Pot Procedure: To a stirred emulsion of compounds **25**, **26**, **35**, **36**, **37**, or **38** in a mixture of water and dichloromethane, Et_3N was added (Table 1). After stirring at room temperature for the time given in Table 1, the reaction mixture was treated with dichloromethane, and the layers were separated. The aqueous phase was extracted several times with small amount of dichloromethane. The combined organic layers were dried with MgSO_4 and chromatographed on silica gel with $\text{Et}_2\text{O}/n$ -hexane to give the 1-aminovinyl ketones **Z-29**, **Z-30**, **Z-42**, **Z-43**, and **Z-44**,^[28] respectively.

(Z)-2-Amino-1-phenyl-3-(phenylsulfonyl)prop-2-en-1-one (Z-29): Yellow crystals (crystallization at –18 °C), m.p. 137–138 °C (ace-

Table 1. One-pot synthesis of 1-aminovinyl ketones.

Starting material	$\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$	Et_3N	Time	$\text{Et}_2\text{O}/n$ -hexane	Product	Yield ^[a]
(mmol)	(mL/mL)	(mmol)	(min)		(mmol)	(%)
25	0.428	5:1	1.287	60	1:1	Z-29 0.334 78
26	0.454	1:0.5	0.891	60	2:3	Z-30 0.378 83
35	0.581	1:0.5	1.089	40	1:4	Z-42 0.505 87
36	0.410	5:1	1.188	50	1:1	Z-43 0.346 85
37	0.410	5:1	1.188	60	1:1	Z-43 0.346 85
38	0.661	2:0.5	1.287	45	1:2	Z-44 0.496 75

[a] Yield of isolated product.

tone/Et₂O). IR (CDCl₃): $\tilde{\nu}$ = 3492 cm⁻¹ (NH), 3376 (NH), 1676 (C=O), 1610 (NH), 1304 (SO₂), 1140 (SO₂). ¹H NMR (CDCl₃): δ = 5.34 (s, 1 H, H-3), ca. 6.20 (br. s, 2 H, NH₂), 7.40–7.61 (m, 6 H), 7.72 (m, 2 H), 7.91 (m, 2 H). ¹³C NMR (CDCl₃): δ = 101.6 (d, C-3), 126.3 (d, 2 C), 128.6 (d, 2 C), 129.2 (d, 2 C), 129.7 (d, 2 C), 133.2 (d), 133.6 (d), 134.6 (s), 143.0 (s), 147.3 (s, C-2), 191.8 (s, C-1). C₁₅H₁₃NO₃S (287.33): calcd. C 62.70, H 4.56, N 4.87, S 11.16; found C 62.39, H 4.61, N 4.79, S 11.63. The stereochemistry was determined by X-ray structure analysis.^[27]

(*Z*)-2-Amino-4,4-dimethyl-1-(phenylsulfonyl)pent-1-en-3-one (*Z*-30): White Powder, m.p. 108–110 °C (Et₂O/*n*-hexane). IR (CDCl₃): $\tilde{\nu}$ = 3489 cm⁻¹ (NH), 3371 (NH), 1695 (C=O), 1610 (NH), 1301 (SO₂), 1138 (SO₂). ¹H NMR (CDCl₃): δ = 1.24 (s, 9 H, H₃C), 5.39 (s, 1 H, H-1), 6.03 (br. s, 2 H, NH₂), 7.55 (m, 3 H), 7.90 (m, 2 H, *o*-Ph). ¹³C NMR (CDCl₃): δ = 27.7 (q, 3 C, H₃C), 44.0 (s, C-4), 96.0 (d, C-1), 126.0 (d, 2 C), 129.1 (d, 2 C), 132.9 (d, *p*-Ph), 143.3 (s, *i*-Ph), 148.0 (s, C-2), 203.2 (s, C-3). C₁₃H₁₇NO₃S (264.34): calcd. C 58.40, H 6.41, N 5.24, S 11.99; found C 58.45, H 6.18, N 5.16, S 12.02.

(*Z*)-2-Amino-1-(phenylsulfonyl)oct-1-en-3-one (*Z*-42): White powder, m.p. 69–71 °C (Et₂O/*n*-hexane). IR (CDCl₃): $\tilde{\nu}$ = 3491 cm⁻¹ (NH), 3376 (NH), 1704 (C=O), 1613 (NH), 1304 (SO₂), 1139 (SO₂). ¹H NMR (CDCl₃): δ = 0.84 (t, ³*J* = 7.2 Hz, 3 H, H-8), 1.25 (m, 4 H), 1.57 (quint, *J* = 7.5 Hz, 2 H), 2.61 (t, *J* = 7.5 Hz, 2 H, H-4), 5.61 (s, 1 H, H-1), ca. 6.10 (br. s, 2 H, NH₂), 7.56 (m, 3 H, Ph), 7.91 (m, 2 H, *o*-Ph). ¹³C NMR (CDCl₃): δ = 13.8 (q, C-8), 22.3 (t), 23.5 (t), 31.0 (t), 36.8 (t, C-4), 97.7 (d, C-1), 126.3 (d, 2 C), 129.2 (d, 2 C), 133.1 (d, *p*-Ph), 142.9 (s, *i*-Ph), 146.1 (s, C-2), 196.2 (s, C-3). C₁₄H₁₉NO₃S (281.37): calcd. C 59.76, H 6.80, N 4.98, S 11.39; found C 59.25, H 6.96, N 4.97, S 11.23.

(*Z*)-3-Amino-4-(phenylsulfonyl)but-3-en-2-one (*Z*-43): Yellow solid, m.p. 73–75 °C (Et₂O/*n*-hexane). IR (CDCl₃): $\tilde{\nu}$ = 3492 cm⁻¹ (NH), 3376 (NH), 1706 (C=O), 1614 (NH), 1305 (SO₂), 1139 (SO₂). ¹H NMR (CDCl₃): δ = 2.33 (s, 3 H, H₃C), 5.61 (s, 1 H, H-4), ca. 6.20 (br. s, 2 H, NH₂), 7.53 (m, 2 H, *m*-Ph), 7.61 (m, 1 H, *p*-Ph), 7.92 (m, 2 H, *o*-Ph). ¹³C NMR (CDCl₃): δ = 24.8 (q, H₃C), 98.7 (d, C-4), 126.3 (d, 2 C), 129.2 (d, 2 C), 133.2 (d, *p*-Ph), 142.8 (s), 146.1 (s), 193.7 (s, C-2). C₁₀H₁₁NO₃S (225.26): calcd. C 53.32, H 4.92, N 6.22, S 14.23; found C 53.32, H 4.98, N 6.14, S 14.13.

(*Z*)-3-Amino-4-(methylsulfonyl)but-3-en-2-one (*Z*-44): This compound **44** had already been synthesized using a different procedure.^[28] However, neither the NMR spectroscopic data nor the details on its stereochemistry were mentioned. Beige powder. IR (CDCl₃): $\tilde{\nu}$ = 3491 cm⁻¹ (NH), 3377 (NH), 1708 (C=O), 1614 (NH), 1307 (SO₂), 1142 (SO₂). ¹H NMR (CDCl₃): δ = 2.42 (s, 3 H, H₃CC), 3.04 (s, 3 H, H₃CSO₂), 5.60 (s, 1 H, H-4), ca. 6.00 (br. s, 2 H, NH₂). ¹³C NMR (CDCl₃): δ = 24.8 (q, H₃CC), 44.3 (q, H₃CSO₂), 97.4 (d, C-4), 146.9 (s, C-3), 193.6 (s, C-2).

Synthesis of 3-Amino-1-azabuta-1,3-dienes **31, *Z,Z*-**32**, *E,Z*-**45**, *E,Z*-**46**, and *E,Z*-**47**.** Two-Step Procedure: This procedure is only

applicable for the synthesis of **31** and *Z,Z*-**32**. Starting from **25** and **26**, the methylene-2*H*-azirines **27** and **28** were produced as shown above and treated with an excess of dry *p*-anisidine to give after about 10 min the imines **31** (mixture) and *Z,Z*-**32** both with 98% yield based on ¹H NMR and calculated with regard to the respective methylene-2*H*-azirines **27** and **28**.

One-Pot Procedure: To a stirred solution of compounds **25**, **26**, **35**, **36**, **37**, or **38** in dry dichloromethane, dry *p*-anisidine and Et₃N were added successively (Table 2). After stirring at room temperature for the time given in Table 2, the reaction mixture was concentrated, and the residue was filtered through silica gel with Et₂O. Solvent was removed from the filtrate to give a solid, which was washed three times with small amounts of Et₂O. In some cases, purification on silica gel with Et₂O or Et₂O/*n*-hexane was necessary. The corresponding imine derivatives **31** (ratio of isomers = 1:14), *Z,Z*-**32**, *E,Z*-**45**, *E,Z*-**46**, and *E,Z*-**47** were obtained, respectively.

3-Amino-1-(4-methoxyphenyl)-2-phenyl-4-(phenylsulfonyl)-1-azabuta-1,3-diene (31**):** Yellow solid (Et₂O, mixture). IR (CDCl₃, mixture): $\tilde{\nu}$ = 3479 cm⁻¹ (NH), 3362 (NH), 1600 (NH), 1300 (SO₂), 1137 (SO₂). C₂₂H₂₀N₂O₃S (392.47): calcd. C 67.33, H 5.14, N 7.14, S 8.17; found C 66.84, H 5.12, N 7.12, S 8.71.

Minor Isomer: ¹H NMR (CDCl₃): δ = 3.77 (s, 3 H, H₃CO), 4.76 (s, 1 H, H-4), 6.58 (d, *J* = 9.0 Hz, 2 H), 6.65 (d, *J* = 9.0 Hz, 2 H), 7.01 (m, 2 H, *o*-Ph at C-2), 7.27 (m, 3 H), 7.52 (m, 3 H), 7.89 (m, 2 H, *o*-Ph-SO₂). The ¹³C NMR signals of this isomer could not be observed.

Major Isomer: ¹H NMR (CDCl₃): δ = 3.70 (s, 3 H, H₃CO), 4.96 (s, 1 H, H-4), 6.58 (d, *J* = 9.0 Hz, 2 H), 6.65 (d, *J* = 9.0 Hz, 2 H), 7.01 (m, 2 H, *o*-Ph at C-2), 7.27 (m, 3 H), 7.52 (m, 3 H), 7.89 (m, 2 H, *o*-Ph-SO₂). The ¹H NMR signal of NH₂ could not be detected. ¹³C NMR (CDCl₃): δ = 55.3 (q, H₃C), 99.5 (C-4), 113.7 (d, 2 C), 123.4 (d, 2 C), 126.1 (d, 2 C), 128.4 (d, 2 C), 129.0 (d, 2 C), 129.1 (d, 2 C), 129.3 (d), 132.6 (d), 132.9 (s), 141.0 (s), 143.7 (s), 151.0 (s), 157.2 (s), 160.7 (s).

(1*Z*,3*Z*)-3-Amino-2-(*tert*-butyl)-1-(4-methoxyphenyl)-4-(phenylsulfonyl)-1-azabuta-1,3-diene (*Z,Z*-32**):** Yellow solid, m.p. 140–142 °C (Et₂O). IR (CDCl₃): $\tilde{\nu}$ = 3506 cm⁻¹ (NH), 3363 (NH), 1609 (NH), 1295 (SO₂), 1136 (SO₂). ¹H NMR (CDCl₃): δ = 1.29 (s, 9 H, H₃CC), 3.73 (s, 3 H, H₃CO), 4.49 (s, 1 H, H-4), ca. 5.80 (br. s, 2 H, NH₂), 6.54 (s, 4 H), 7.36 (m, 2 H), 7.48 (m, 3 H). ¹³C NMR (CDCl₃): δ = 28.5 (q, 3 C, H₃CC), 39.8 (s, H₃CC), 55.1 (q, H₃CO), 93.1 (d, C-4), 113.7 (d, 2 C), 120.0 (d, 2 C), 125.7 (d, 2 C), 128.7 (d, 2 C), 132.2 (d), 142.5 (s), 143.5 (s), 151.6 (s), 156.1 (s), 173.6 (s). C₂₀H₂₄N₂O₃S (372.48): calcd. C 64.49, H 6.49, N 7.52, S 8.61; found C 64.15, H 6.39, N 7.47, S 8.84.

(1*E*,3*Z*)-3-Amino-1-(4-methoxyphenyl)-2-pentyl-4-(phenylsulfonyl)-1-azabuta-1,3-diene (*E,Z*-45**):** Yellow solid, m.p. 129–131 °C

Table 2. One-pot synthesis of 3-amino-1-azabuta-1,3-dienes.

Starting material (mmol)	<i>p</i> -Anisidine (mmol)	CH ₂ Cl ₂ (mL)	Et ₃ N (mmol)	Time (min)	Et ₂ O/ <i>n</i> -hexane ^[a]	Product (mmol)	Yield ^[b] (%)
25	0.571	1.143	2	1.089	30	1:0	31 ^[c] 0.487 85
26	0.606	1.212	2	1.139	30	1:1	<i>Z,Z</i> - 32 0.462 76
35	0.727	1.453	2	1.188	30	1:0	<i>E,Z</i> - 45 0.697 96
36	0.616	1.250	2	1.188	30	1:0	<i>E,Z</i> - 46 0.586 95
37	0.616	1.232	2	1.188	30	1:0	<i>E,Z</i> - 46 0.585 95
38	1.377	2.066	2	1.980	30	1:0	<i>E,Z</i> - 47 1.263 92

[a] Purification by filtration through silica gel using Et₂O or Et₂O/*n*-hexane. [b] Yield of isolated product. [c] Mixture of isomers with unknown stereochemistry.

Table 3. One-pot synthesis of 2-aminoacrolein acetals.

Starting material (mmol)	MeOH (mL)	Et ₃ N (mmol)	Time (min)	Et ₂ O/ <i>n</i> -hexane ^[a]	Product (mmol)	Yield ^[b] (%)
25	0.229	1	30	1:0	Z-33	0.217
26	0.364	1	30	1:1	Z-34	0.342
38	0.386	1	30	1:0	Z-48	0.369

[a] Purification by chromatography on silica gel with Et₂O or Et₂O/*n*-hexane. [b] Yield of isolated product.

(Et₂O). IR (CDCl₃): $\tilde{\nu}$ = 3476 cm⁻¹ (NH), 3358 (NH), 1597 (NH), 1301 (SO₂), 1137 (SO₂). ¹H NMR (CDCl₃): δ = 0.74 (t, ³J = 6.9 Hz, 3 H, H₃CC), 1.09 (m, 4 H), 1.37 (m, 2 H), 2.32 (m, 2 H, H₂CC-2), 3.79 (s, 3 H, H₃CO), 5.41 (s, 1 H, H-4), ca. 6.60 (br. s, 2 H, NH₂), 6.63 (d, *J* = 8.7 Hz, 2 H, H-2'), 6.88 (d, *J* = 8.7 Hz, 2 H, H-3'), 7.54 (m, 3 H), 7.96 (m, 2 H, *o*-Ph-SO₂). ¹³C NMR (CDCl₃): δ = 13.7 (q, H₃CC), 21.9 (t), 28.1 (t), 28.2 (t), 31.5 (t), 55.4 (q, H₃CO), 95.0 (d, C-4), 114.3 (d, 2 C), 120.1 (d, 2 C), 126.0 (d, 2 C), 129.0 (d, 2 C), 132.6 (d), 142.1 (s), 143.8 (s), 149.6 (s), 156.6 (s), 164.4 (s). C₁₇H₁₈N₂O₃S (386.51): calcd. C 65.26, H 6.78, N 7.25, S 8.30; found C 64.92, H 6.75, N 7.22, S 8.53.

(1E,3Z)-3-Amino-1-(4-methoxyphenyl)-2-methyl-4-(phenylsulfonyl)-1-azabuta-1,3-diene (E,Z-46): Yellow solid, m.p. 128–130 °C (acetone/Et₂O). IR (CDCl₃): $\tilde{\nu}$ = 3478 cm⁻¹ (NH), 3360 (NH), 1721 (C=N), 1599 (NH), 1302 (SO₂), 1137 (SO₂). ¹H NMR (CDCl₃): δ = 1.99 (s, 3 H, H₃CC), 3.80 (s, 3 H, H₃CO), 5.42 (s, 1 H, H-4), ca. 6.60 (br. s, 2 H, NH₂), 6.69 (d, *J* = 8.7 Hz, 2 H, H-2'), 6.89 (d, *J* = 8.7 Hz, 2 H, H-3'), 7.52 (m, 3 H), 7.97 (m, 2 H, *o*-PhSO₂). ¹³C NMR (CDCl₃): δ = 15.4 (q, H₃CC), 55.4 (q, H₃CO), 95.2 (d, C-4), 114.3 (d, 2 C), 121.0 (d, 2 C), 126.2 (d, 2 C), 129.0 (d, 2 C), 132.7 (d), 141.8 (s), 143.8 (s), 150.6 (s), 157.0 (s), 159.7 (s). C₁₇H₁₈N₂O₃S (314.40): calcd. C 61.80, H 5.49, N 8.48, S 9.71; found C 61.93 H 5.56, N 8.52, S 9.76.

(1E,3Z)-3-Amino-1-(4-methoxyphenyl)-2-methyl-4-(methylsulfonyl)-1-azabuta-1,3-diene (E,Z-47): Yellow solid, m.p. 151–153 °C (Et₂O). IR (CDCl₃): $\tilde{\nu}$ = 3476 cm⁻¹ (NH), 3360 (NH), 1602 (NH), 1297 (SO₂), 1119 (SO₂). ¹H NMR (CDCl₃): δ = 2.05 (s, 3 H, H₃CC), 3.05 (s, 3 H, H₃CSO₂), 3.81 (s, 3 H, H₃CO), 5.40 (s, 1 H, H-4), 6.44 (br. s, 2 H, NH₂), 6.72 (d, *J* = 8.7 Hz, 2 H, H-2'), 6.91 (d, *J* = 8.7 Hz, 2 H, H-3'). ¹³C NMR (CDCl₃): δ = 15.3 (q, H₃CC), 44.2 (q, H₃CSO₂), 55.5 (q, H₃CO), 94.4 (d, C-4), 114.3 (d, 2 C), 121.0 (d, 2 C), 141.7 (s), 151.3 (s), 157.0 (s), 159.6 (s). MS (ESI): *m/z*: 269.07 [M+H⁺]. C₁₂H₁₆N₂O₃S (268.33): calcd. C 53.71, H 6.01, N 10.44, S 11.95; found C 53.75, H 6.07, N 10.25, S 11.59.

Synthesis of 2-Aminoacrolein Acetals Z-33, Z-34, and Z-48. Two-Step Procedure: This procedure is only applicable for the synthesis of **33** and **34**. Starting from **25** and **26**, the methylene-azirines **27** and **28** were produced as shown above and treated with an excess of dry methanol to give after 5 to 10 min the acetals **Z-33** and **Z-34** with 96% and 97% yield, respectively, based on NMR spectroscopy. The yields were calculated with regard to the corresponding methyleneazirines.

One-Pot Procedure: To a stirred solution of compounds **25**, **26**, or **38** in dry methanol, Et₃N was added (Table 3). After stirring at room temperature for the time given in Table 3, the reaction mixture was concentrated, and the residue was purified on silica gel with Et₂O or Et₂O/*n*-hexane to give the acetals **Z-33**, **Z-34**, and **Z-48**, respectively.

(Z)-1-[Dimethoxy(phenyl)methyl]-2-(phenylsulfonyl)vinylamine (Z-33): Yellow oil. IR (CDCl₃): $\tilde{\nu}$ = 3497 cm⁻¹ (NH), 3374 (NH), 1618 (NH), 1297 (SO₂), 1134 (SO₂). ¹H NMR (CDCl₃): δ = 3.10 (s, 6 H, H₃CO), 5.28 (s, 1 H, H-2), ca. 6.10 (br. s, 2 H, NH₂), 7.30 (m,

3 H), 7.40–7.51 (m, 5 H), 7.80 (m, 2 H). ¹³C NMR (CDCl₃): δ = 49.7 (q, 2 C, H₃CO), 91.3 (d, C-2), 100.9 (s, COCH₃), 125.6 (d, 2 C), 126.1 (d, 2 C), 128.3 (d, 2 C), 128.7 (d, 2 C), 128.8 (d), 132.1 (d), 138.2 (s, *i*-Ph), 144.5 (s, *i*-Ph), 157.0 (s, C-1). HRMS (ESI): *m/z* calcd. for C₂₀H₂₀NO₄S [M+H⁺] 334.1110; found 334.1108.

(Z)-2,2-Dimethoxy-3,3-dimethyl-1-[(phenylsulfonyl)methylene]butylamine (Z-34): Yellow oil. IR (CDCl₃): $\tilde{\nu}$ = 3501 cm⁻¹ (NH), 3373 (NH), 1612 (NH), 1290 (SO₂), 1133 (SO₂). ¹H NMR (CDCl₃): δ = 0.89 (s, 9 H, H₃CC), 3.26 (s, 6 H, H₃CO), 4.87 [s, 1 H, C(H)SO₂], 7.48 (m, 3 H, Ph), 7.87 (m, 2 H, *o*-Ph). The ¹H NMR signal of NH₂ could not be detected. ¹³C NMR (CDCl₃): δ = 26.7 (q, 3 C, H₃CC), 40.8 (s, C-3), 52.3 (q, H₃CO), 92.2 [d, C(H)SO₂], 105.6 (s, C-2), 125.5 (d, 2 C), 128.8 (d, 2 C), 132.1 (d, *p*-Ph), 144.7 (s, *i*-Ph), 155.7 (s, C-1). HRMS (ESI): *m/z* calcd. for C₁₅H₂₄NO₄S [M+H⁺] 314.1421; found 314.1421.

(Z)-2,2-Dimethoxy-1-[(methylsulfonyl)methylene]propylamine (Z-48): Yellow oil. IR (CDCl₃): $\tilde{\nu}$ = 3499 cm⁻¹ (NH), 3376 (NH), 1620 (NH), 1289 (SO₂), 1117 (SO₂). ¹H NMR (CDCl₃): δ = 1.45 (s, 3 H, H₃CC), 2.93 (s, 3 H, H₃CSO₂), 3.19 (s, 6 H, H₃CO), 5.03 [s, 1 H, C(H)SO₂], ca. 5.80 (br. s, 2 H, NH₂). ¹³C NMR (CDCl₃): δ = 23.8 (q, H₃CC), 44.6 (q, H₃CSO₂), 49.4 (q, 2 C, H₃CO), 88.9 [d, C(H)SO₂], 100.0 (s, C-2), 158.5 (s, C-1). HRMS (ESI): *m/z* calcd. for C₇H₁₆NO₄S [M+H⁺] 210.0798; found 210.0795.

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