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Reactions of Thioacetamide Derivatives with Sulfonyl Azides: An Approach to Active-Methylene *N*-Sulfonylacetamidines

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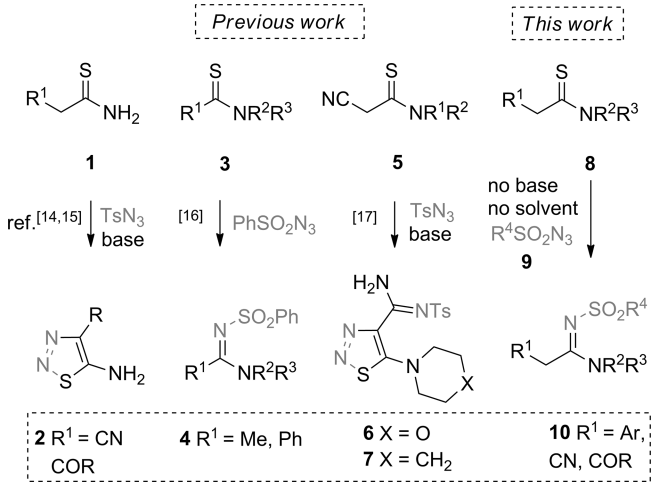
Reactions of functionalized [CN, CO_2Et, C(O)NHR, C(S)NR^1R^2] derivatives of thiomalonic acid and 2-arylthioacetamides with sulfonyl azides were shown to give active-methylene *N*-sulfonylamidines in 62–98 % yields. Various procedures for the reactions, including the use of pyridine, boiling ethanol, and water, or running the reactions in the absence of a base and solvent at 80 °C, were carried out and compared. The solvent-free variant was the best in terms of yield, and also because it does not require the use of an excess of the toxic and hazardous azides. The reaction was shown to tolerate electron-withdrawing substituents such as carbonyl, cyano, and aryl groups at the C-2 position. The presence of alkyl and phenyl groups on the nitrogen atom of the thioacetamide fragment, and the presence of substituents on the sulfonyl group were also tolerated. Thus, an efficient solvent-free, catalyst-free, and base-free synthetic approach for the synthesis of *N*-sulfonylmalonacetamidines and 2-arylacetamidines was found.

Introduction

Sulfonyl azides, mostly tosyl and mesyl azides, show a wide range of reactivities, and are widely used in organic synthesis.[1–3] They serve as diazo-transfer agents, and allow the synthesis of various types of diazo compounds from C–H-acidic compounds,[4,5] of azides from amines,[6] and of *N*-unsubstituted 1,2,3-triazoles from enamines.[7] They can undergo cycloaddition reactions with acetylenes to give 1-sulfonyl-1,2,3-triazoles, in which they are the source of the sulfonyl triaza fragment.[8] They can react with enamines to form *N*-sulfonyl derivatives of diamino alkenes, and here they serve as the source of the sulfonyl imino fragments.[7,9] In the last decade, two powerful synthetic methods were developed based on metal-catalyzed processes for the generation of *N*-sulfonylazavinyl carbenoids[10–12] and *N*-sulfonyl-substituted ketenimines[3] from acetylenes and sulfonyl azides, followed by reaction with various nucleophilic reagents to form a huge variety of different types of valuable heterocyclic and organic compounds, such as amidines, sulfonamides, azadienes, α-amino ketones, cyclopentadienes, etc. Also in these reactions, sulfonyl azides provide the sulfonyl imine fragments for the reaction products. Rh- and Ir-catalyzed insertion of a sulfonyl imino group into C–H bonds in reaction with sulfonyl azides has also been reported.[13]

We turned our attention to reactions of thioamides bearing active methylene groups with sulfonyl azides. It is well known that the reaction of thioamides of malonic and cyanoacetic acids **1** with sulfonyl azides represents a good method for the synthesis of 5-amino-1,2,3-thiadiazoles **2** (Scheme 1).[14,15] The reaction of mesyl and benzenesulfonyl azides with thioacetamides **3**, in which the methylene group is not activated, takes a different direction, leading to the formation of acetamidines **4**.[16] Recently, we discovered that tosyl azide can react with *N*,*N*-disubstituted cyano-



Scheme 1. Reactions of sulfonyl azides with thioacetamide derivatives.

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thiocetamide **5** in the presence of triethylamine to give 4-tosylamidino-1,2,3-thiadiazoles **6** and **7**; in this reaction it acts as the source of both diazo and sulfonyl imino groups.[17] Thus, sulfonyl azides could be donors of diazo and sulfonyl imino fragments in reactions of thioamides with sulfonyl azides.

In contrast to similar reactions in the presence of bases, the reactions of thioamides bearing an active methylene group with sulfonyl azides have, to the best of our knowledge, never been studied under base-free conditions. To develop a new and efficient approach to functionalized derivatives of *N*-sulfonylacetamidines **10**, a detailed study of the reactions of thiomalonamides and 2-arylthioacetamides **8** with arylsulfonyl and mesyl azides **9** under various conditions was carried out.

Results and Discussion

Two papers, apart from ours,[17] have been published on the reactions of thioamides with sulfonyl azides. The first report, from O. V. Zelenskaya et al., deals with the preparation of sulfonyl amidines by the reaction of thioamides with tosyl azide under relatively harsh conditions: heating at 90–100 °C in pyridine for 5 h.[18] Conversely, M. Aswad et al. found that thioamides of acetic and benzoic acids **3** and cyclic thioamides react with benzenesulfonyl and mesyl azides under very mild conditions in ethanol or other organic solvents, or even in water, under catalyst-free conditions, to form the corresponding amidines (i.e., **4**) in very good yields.[16] Based on literature data on the reaction of thioamides with azides,[14–18] apart from amidines, various heterocyclic compounds could be formed as a result of the reactions of malonic acid thioamides and 2-arylthioacetamides **8** with sulfonyl azides **9** (Figure 1). This complicates the development of a selective and efficient method for a base-catalyzed preparation of *N*-sulfonylacetamidines of type **10**. We started our experiments by studying the reaction of tosyl azide (**9b**) with cyanothioacetamide **8a** (Scheme 2). Thioamide **8a** was found to be unreactive when we used ethanol at room temperature, under the conditions of Aswad.[17] We also found that the reaction of thioamide **8a** with tosyl azide in pyridine, according to Zelenskaya et al.,[18] led to an oily brown residue containing traces of cyanoacetamidine **10a**. All our attempts to improve this protocol failed. Luckily, we found that cyanothioacetamide **8a** reacted smoothly with an equimolar amount of tosyl azide (**9b**) in the absence of solvent at 80 °C to form cyanoacetamidine **10a** in 97% yield (Scheme 2). Encouraged by this result, we expanded the reaction to a variety of sulfonyl azides **9**, and to primary, secondary, and tertiary thioamides of cyanoacetic acid, functionalized derivatives of thiocarbamoyl acetic acid, mono- and dithioamides of malonic acid, and thioamides of arylacetic acid **8a**–**8m** (Figure 1). We found that the reaction tolerates electron-withdrawing substituents such as carbonyl, cyano, and aryl groups at the C-2 position, and also tolerates the introduction of alkyl groups and phenyl substituents onto the nitrogen atom of the thioacetamides. Indeed, a small series of *N*-sulfonyl cyanoacetamidines **10A** were prepared in 80–97% isolated yields. We also demonstrated that sulfonyl azides such as tosyl, mesyl, 4-fluorophenyl, 2,4-dimethylphenyl, and benzothiadiazolylsulfonyl azides **9a**–**9e** readily react with 2-arylthioacetamides **8f**–**8h** and functionalized derivatives of thiocarbamoyl acetic acid **8i**–**8m** to form amidines **10B**–**10D** in 62–98% yields. Interestingly, both substituted and unsubstituted thioamide groups of malondithioamides **7k**–**7m** react with tosyl azide to form bis-acetamidines **10q**–**10s**. All our attempts to induce 4-nitrophenyl and 1-methyl-4-nitroimidazol-5-yl azides into reaction with thioamides **8** failed. Working with tosyl azide and other sulfonyl azides at 80 °C can be considered safe, certainly on the scale we worked on, but at temperatures above 120 °C, rapid decomposition may occur, so we advise against working at such high temperatures or on a scale where the reaction energy could not be effectively dissipated. The elimination of dinitrogen results in the formation of amidines **10**, as evidenced by the presence of cyano (2254 cm^{-1}) and carbonyl (1740 cm^{-1}) stretching in the IR spectra. Mass spectral data and further NMR sectroscopic data were all in good agreement with the structures of compounds **10**: proton signals typical for the methylene group at δ = 3.80–4.32 ppm, and for the cyclic amines at δ = 1.14–4.01 ppm in the ^1H NMR spectra; carbon signals at δ = 18.8–51.1 ppm (CH_2) and at δ = 154.9–168.5 ppm (C=NTs) in the ^{13}C NMR spectra; two ^{15}N signals due to the nitrogen atoms of the amidine fragment at δ = 121.5 and 123.5 ppm derived from ^1H,^{15}N HMBC spec-

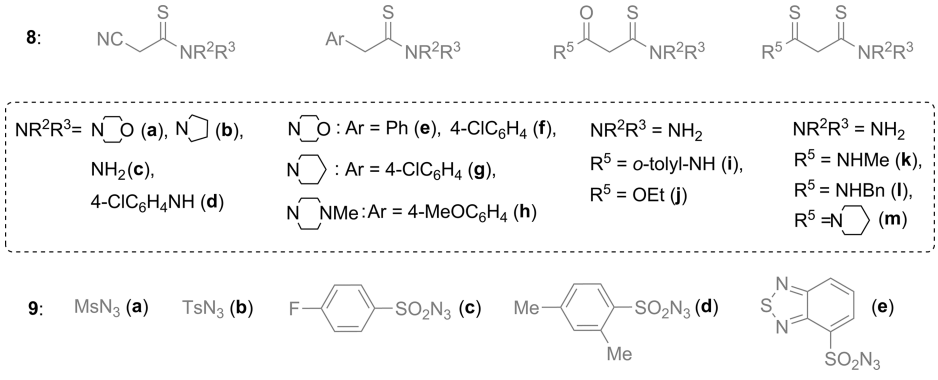
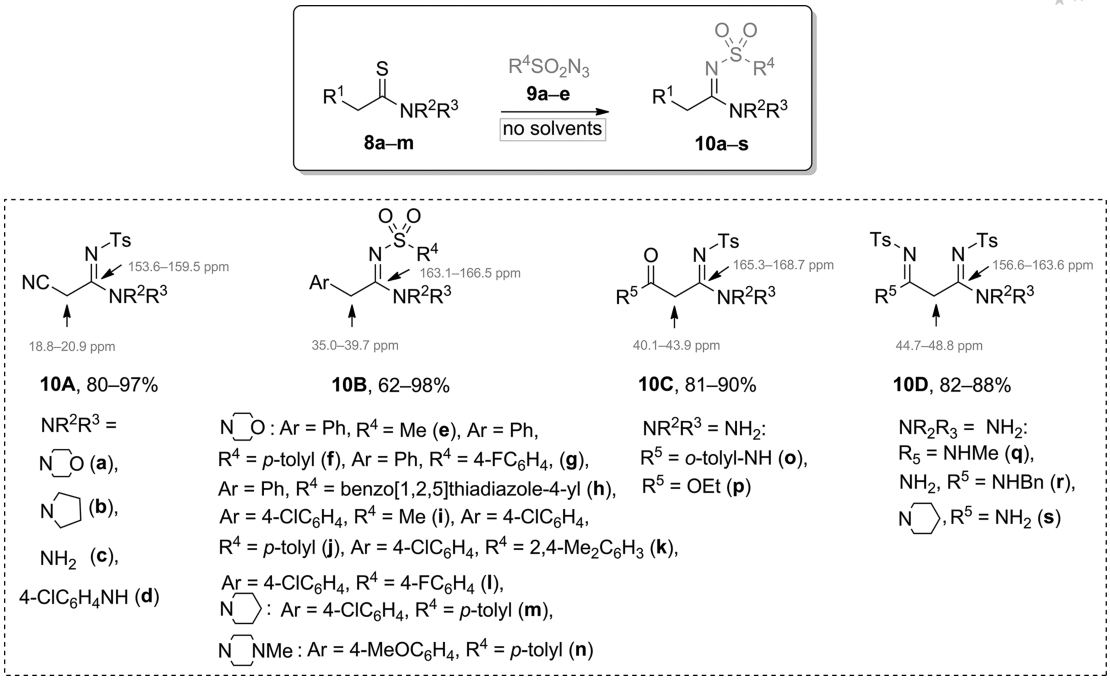


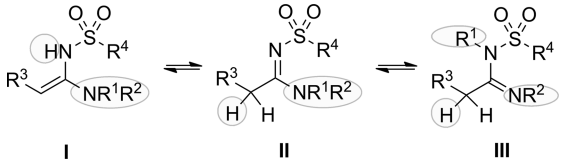
Figure 1. Structures of starting thioamides **8** and azides **9**.



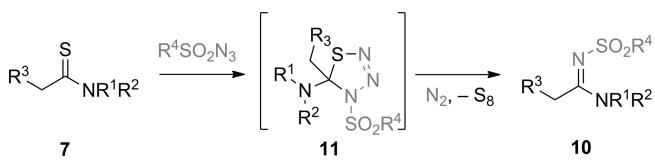
Scheme 2. Reactions of thioamides **8a**–**8m** with sulfonyl azides **9a**–**9e**.

tra. Final proof of the structures of amidines **10**, and the connectivity of the methylene, cyano, and sulfonyl groups and nitrogen atoms, came from 2D HSQC data and HMBC ^{1}H,^{13}C and ^{1}H,^{15}N spectra. The HSQC spectrum of amidine **10a** showed cross-peaks for all of the carbon and hydrogen atoms of each of the C–H bonds. The HMBC spectrum of amidine **10a** showed cross-peaks between the proton signals of the methylene group at δ = 4.31 ppm and the carbon of the cyano group at δ = 113.1 ppm and the carbon of the amidine group at δ = 154.9 ppm, and also between the signals of the morpholine OCH_2 fragment at δ = 3.63 and 3.69 ppm and the amidine carbon atom signal at δ = 154.9 ppm. Remarkably, cross-peaks between the methylene signals at δ = 4.31 ppm and both nitrogen atoms of the amidine fragment at δ = 121.5 and 123.5 ppm were observed in the ^{1}H,^{15}N HMBC spectrum of compound **10a**.

Acetamidines **10** bearing electron-withdrawing groups can exist as a mixture of possible tautomeric forms **I**–**III** (Scheme 3). Form **I** was rejected based on the ^{1}H NMR spectra. The ^{1}H NMR spectra of all compounds **10** contain singlet signals due to the protons of the methylene group; *N*,*N*-disubstituted amidines **10a**, **10b**, and **10e**–**10n** do not contain NH proton signals, confirming their existence in form **II**. Because the ^{1}H NMR spectra of *N*-methyl- (**10q**) and *N*-benzyl-acetamidines (**10r**) show signals for NH protons bound to Me and CH_2, we can conclude that *N*-monosubsituted amidines **10q** and **10r** also exist in tautomeric form **II**. Interestingly, in the ^{1}H NMR spectra of amidines **10c** and **10o**–**10r**, which contain an NH_2 group, the NH protons appear as two singlets. This fact could be interpreted in favor of tautomer **III**. Alternatively, this can be explained by the nonequivalence of the protons of the amino group, as we can see in the NMR spectra of thioamide **8k**. The 2D HSQC and HMBC ^{1}H,^{15}N spectra of compound **10p** give evidence that the two hydrogen atoms are directly connected to the same nitrogen atom, as expected for tautomer **II** (see Supporting Information). Thus, all unsubstituted, monosubstituted, and disubstituted *N*-sulfonyl amidines **10** exist in tautomeric form **II**. A plausible mechanism for the formation of amidines **10** is presented in Scheme 4. We propose the formation of intermediate thiatriazolines **11** as the result of a 1,3-dipolar cycloaddition reaction between the azido group of the sulfonyl azides and the C=S bond of thioamides **7**. Thiatriazolines are known to be produced by the reaction of azides with *N*-tosyl isothiocyanates.[19,20] They are proposed intermediates in reaction of mono- and dithioacids with sulfonyl azides to form *N*-sulfonylamides and thioamides.[20] Aswad et al.[16] proposed a stepwise mechanism for the formation of thiatriazolines based on the evidence of the increased rate of the reaction of thioamides



Scheme 3. Tautomerism in *N*-sulfonylacetamidines.



Scheme 4. Plausible mechanism of the formation of amidines **10**.

with mesyl and benzenesulfonyl azides in polar solvents. In any case, elimination of dinitrogen and sulfur from thiatriazoline **11** finalizes the formation of amidines **10**; this degradation process is typical for 1,2,3,4-thiatriazoles.[19]

We also found that sulfonylacetamidines **10** can be prepared by the reaction of thioamides **8f**, **8j**, and **8m** with azide **9b** in either boiling ethanol or water. But for the reaction to go to completion, 5 equiv. of azide **9b** was required, probably because of hydrolysis of the latter compound under these conditions. The synthesis of amidines **10f**, **10j**, and **10m** in the absence of a solvent has some advantages over the reactions in ethanol and water in terms of yield and reaction time, and also as a lower amount of hazardous azides **9b** was required (see Table 1).

Table 1. Comparative studies of the reaction of thioamides **8f**, **8j**, and **8m** with azide **9b**.

Product	Yield [%][a]	Yield [%][b]	Yield [%][c]
10f	83	61	79
10j	92	65	82
10m	86	58	84

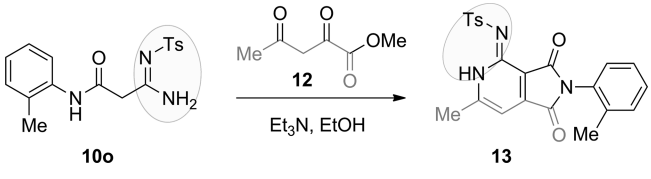
[a] In the absence of solvent at 80 °C for 0.5 h. [b] Reflux in anhydrous EtOH with **9b** (5 mol) for 20–30 h. [c] Reflux in boiling water with **9b** (5 mol) for 20 h.

Thus, we have developed an efficient and environmentally friendly approach to highly *C*- and N^2-substituted N^1-sulfonylacetamidines. Amidines are found in many biologically active natural products,[21] and have been identified as important pharmacophores.[22] Recently, amidines containing sulfonyl groups were identified as osteoclast differentiation inhibitors.[23] Unlike amidines in general, *N*-sulfonylacetamidines bearing electron-withdrawing groups on the carbon atom are represented in the literature only by a very few examples, and their chemical properties have been poorly studied.[24–26] As they have both nucleophilic and electrophilic functionalities, they are promising chemical reagents for organic synthesis.

Our preliminary experiments with reaction of amidine **10o** with methyl 2,4-dioxovalerate (**12**) in ethanol solution at room temperature in the presence of triethylamine have shown that both the amine and methylene groups can be involved in a cyclization process to form pyrrolo[3,4-*c*]pyridine **13** in 69% yield (Scheme 5). This reaction is similar to the earlier reported reaction of unsubstituted carbamoylacetamidines.[27]

Conclusions

Reactions of diversely substituted thioacetamides with aryl- and heteroarylsulfonyl azides and mesyl azide have been shown to take place in either ethanol or water at reflux, or under solvent-free conditions at 80 °C, to form *N*-sulfonylacetamidines and *N*-sulfonylmalonamidines in good yields. The solvent-free procedure is the best in terms of yield; it is also more environmentally friendly and safer because it requires only an equimolar amount of the toxic azides, rather than the five-fold excess required in solvents. The reaction has a wide scope. Obviously, the reaction has a rather general character with respect to the thioamides, and is limited to sulfonyl azides. Thus, an efficient, solvent-free and catalyst-free method to prepare functionalized derivatives of *N*-sulfonylmalonacetamidines and 2-arylacetamidines has been developed.



Scheme 5. Reaction of amidine **10o** with methyl 2,4-dioxovalerate (**12**).

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with a Bruker DRX 400 instrument in [D_6]DMSO or $CDCl_3$. $SiMe_4$ was used as an internal reference, and δ values are given in ppm. The mass spectra of **8m** and **10a**–**10s** were obtained (EI, 70 eV) with a Shimadzu GC–MS-QP2010 Ultra spectrometer with direct introduction of the sample into the ion source. The mass spectrum of compound **10a** was recorded with a Bruker Daltonics instrument using electrospray ionization. IR spectra were recorded with a Bruker Alpha FTIR spectrometer (ZnSe ATR accessory). Microanalysis was carried out with a CHNS/O Perkin–Elmer 2400 II elemental analyzer. Reactions were monitored by TLC (Silyfol® on aluminium foil plates), eluting with $CHCl_3$/hexane (9:1), $CHCl_3$/benzene (7:1), EtOAc/hexane (1:3), or EtOAc/hexane (1:6). TLC plates were visualized under UV light. Melting points were determined with a Stuart SMP-10 apparatus.

Thiomalonamides **8a**, **8b**, and **8d**,[28] thioamides **8c**, **8i**, and **8j**,[15,28] thioamides **8e**–**8h**,[29] and dithioamides **8k**–**8m**[30] were prepared according to known procedures. Azides **9a**–**9e** were bought from commercial suppliers.

3-(Piperidin-1-yl)-3-thioxopropanethioamide (8m): The compound was obtained by analogy[30] from 2-(piperidin-1-yl)-2-thioxoacetonitrile.[29] Yellow needles (35%), m.p. 119–121 °C. ^{1}H NMR ([D_6]-DMSO): δ = 1.66–1.69 (m, 6 H, CH_2), 3.85–3.78 (m, 2 H, CH_2), 4.14 (s, 2 H, CH_2), 4.20–4.17 (m, 2 H, CH_2), 8.90 (s, 1 H, NH), 9.53 (s, 1 H, NH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 23.3, 25.0, 26.1, 50.7, 51.7, 57.6, 192.0, 200.0 ppm. IR: $\tilde{\nu}$ = 3266 (NH), 3140 (NH) cm^{-1}. MS (EI): *m*/*z* (%) = 202 [M]$^+$ (18), 142 (17), 91 (100), 60 (30). $C_8H_{14}N_2S_2$ (202.34): calcd. C 47.49, H 6.97, N 13.84; found C 47.88, H 7.34, N 13.57.

General Procedures for the Preparation *N*-Sulfonylamidines 10a–10s

General Procedure A: A mixture of the corresponding thiomalonamide **8** (1.0 equiv.) and azide **9** (1.0 equiv.) was heated at 80 °C for 0.5–1 h. The reaction mixture was cooled, and ethanol was added. The precipitate was collected by filtration, and purified by flash chromatography on silica gel (60–120) using EtOAc/hexane mixtures. To achieve better separation, the composition of the eluent was gradually changed from 1:6 to 1:2, EtOAc/hexane.

***N*-(2-Cyano-1-morpholinoethylidene)-4-methylbenzenesulfonamide (10a):** Colorless powder (97%), m.p. 125–127 °C. ^{1}H NMR ([D_6]-DMSO): δ = 2.37 (s, 3 H, CH_3), 3.60–3.68 (m, 8 H, CH_2), 4.47 (s, 2 H, CH_2), 7.36 (d, *J* = 8.0 Hz, 2 H, ArH), 7.73 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 19.3, 21.4, 45.7, 47.7, 65.8, 114.6, 126.3, 130.0, 140.7, 142.9, 156.1 ppm. IR: $\tilde{\nu}$ = 2255

(CN) cm^{-1}. MS (EI): *m/z* (%) = 307 $[M]^+$ (2), 152 (100), 91 (46), 86 (46). MS (ESI): *m/z* = 308 $[M + H]^+$. $C_{14}H_{17}N_3O_3S$ (307.37): calcd. C 54.72, H 5.53, N 13.68; found C 54.56, H 5.69, N 13.47.

***N*-[2-Cyano-1-(pyrrolidin-1-yl)ethylidene]-4-methylbenzenesulfonamide (10b):** Colorless powder (80%), m.p. 118–120 °C. ^1H NMR ([D$_6$]DMSO): δ = 1.89–1.94 (m, 2 H, CH_2), 1.97–2.04 (m, 2 H, CH_2), 2.40 (s, 3 H, CH_3), 3.45 (t, *J* = 8.0 Hz, 2 H, CH_2), 3.68 (t, *J* = 8.0 Hz, 2 H, CH_2), 4.30 (s, 2 H, CH_2), 7.30 (d, *J* = 8.0 Hz, 2 H, ArH), 7.70 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 20.2, 21.5, 24.1, 25.8, 48.3, 49.7, 112.9, 126.4, 129.4, 140.2, 142.7, 153.3 ppm. IR: $\tilde{\nu}$ = 2254 (CN) cm^{-1}. MS (EI): *m/z* (%) = 291 $[M]^+$ (5), 136 (48), 91 (48), 70 (100). $C_{14}H_{17}N_3O_2S$ (291.37): calcd. C 57.71, H 5.88, N 14.42; found C 57.51, H 5.61, N, 14.23.

2-Cyano-*N*′-tosylacetimidamide (10c): Colorless powder (92%), m.p. 128–130 °C. ^1H NMR ([D$_6$]DMSO): δ = 2.38 (s, 3 H, CH_3), 3.80 (s, 2 H, CH_2), 7.37 (d, *J* = 8.0 Hz, 2 H, ArH), 7.75 (d, *J* = 8.0 Hz, 2 H, ArH), 8.13 (s, 1 H, NH), 8.86 (s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 20.9, 26.1, 115.8, 126.3, 130.1, 139.7, 143.2, 154.9 ppm. IR: $\tilde{\nu}$ = 2254 (CN) cm^{-1}. MS (EI): *m/z* (%) = 237 $[M]^+$ (19), 155 (36), 91 (100), 65 (28). $C_{10}H_{11}N_3O_2S$ (237.28): calcd. C 50.62, H 4.67, N 17.71; found C 50.43, H 4.61, N 17.97.

***N*-(4-Chlorophenyl)-2-cyano-*N*′-tosylacetimidamide (10d):** Pale yellow powder (85%), m.p. 132–134 °C. ^1H NMR ([D$_6$]DMSO): δ = 2.39 (s, 3 H, CH_3), 4.20 (s, 2 H, CH_2), 7.38–7.46 (m, 4 H, ArH), 7.57 (d, *J* = 8.0 Hz, 2 H, ArH), 7.78 (d, *J* = 8.0 Hz, 2 H, ArH), 10.92 (s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 20.7, 22.7, 114.8, 123.3, 125.9, 128.9, 129.5, 136.2, 139.6, 142.8, 153.7 ppm. IR: $\tilde{\nu}$ = 2254 (CN) cm^{-1}. MS (EI): *m/z* (%) = 347 $[M]^+$ (7), 155 (33), 91 (100), 65 (28). $C_{16}H_{14}ClN_3O_2S$ (347.82): calcd. C 55.25, H 4.06, N 12.08; found C 55.12, H 3.86, N 12.17.

***N*-(1-Morpholino-2-phenylethylidene)methanesulfonamide (10e):** Colorless powder (60%), m.p. 85–88 °C. ^1H NMR ([D$_6$]DMSO): δ = 2.96 (s, 3 H, CH_3), 3.23–3.41 (m, 4 H, CH_2), 3.55–3.65 (m, 2 H, CH_2), 3.67–3.75 (m, 2 H, CH_2), 4.39 (s, 2 H, CH_2), 7.21–7.31 (m, 3 H, ArH), 7.34 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 36.3, 44.0, 44.9, 47.0, 66.0, 126.9, 128.5, 129.0, 135.3, 165.0 ppm. MS (EI): *m/z* (%) = 282 $[M]^+$ (24), 116 (100), 86 (91), 79 (50). $C_{13}H_{18}N_2O_3S$ (282.36): calcd. C 55.30, H 6.43, N 9.92; found C 55.59, H 6.69, N 9.73.

4-Methyl-*N*-(1-morpholino-2-phenylethylidene)benzenesulfonamide (10f):[27] Colorless powder (83%), m.p. 153–155 °C (ref. 148–150 °C). ^1H NMR ([D$_6$]DMSO): δ = 2.35 (s, 3 H, CH_3), 3.28–3.35 (m, 4 H, CH_2), 3.54–3.56 (m, 2 H, CH_2), 3.67–3.70 (m, 2 H, CH_2), 4.44 (s, 2 H, CH_2), 7.20–7.26 (m, 3 H, ArH), 7.29–7.34 (m, 4 H, ArH), 7.70 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 21.4, 36.0, 45.2, 47.3, 66.0, 126.3, 127.0, 128.4, 129.1, 129.7, 135.1, 141.7, 142.2, 165.4 ppm. MS (EI): *m/z* (%) = 358 $[M]^+$ (4), 155 (61), 91 (100), 86 (87). $C_{19}H_{22}N_2O_3S$ (358.45): calcd. C 63.66, H 6.19, N 7.82; found C 63.45, H 6.09, N 7.60.

4-Fluoro-*N*-(1-morpholino-2-phenylethylidene)benzenesulfonamide (10g): Colorless powder (62%), m.p. 130–133 °C. ^1H NMR ([D$_6$]-DMSO): δ = 3.32–3.34 (m, 4 H, CH_2), 3.50–3.62 (m, 2 H, CH_2), 3.66–3.72 (m, 2 H, CH_2), 4.44 (s, 2 H, CH_2), 7.13–7.41 (m, 7 H, ArH), 7.80–7.90 (m, 2 H, ArH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 35.5, 44.8, 46.8, 66.5, 115.7, 115.9, 126.7, 127.8, 128.6, 128.7, 134.3, 140.3, 162.3, 164.8, 164.9 ppm. MS (EI): *m/z* (%) = 362 $[M]^+$ (3), 159 (47), 116 (86), 86 (100). $C_{18}H_{19}FN_2O_3S$ (362.42): calcd. C 59.65, H 5.28, N 7.73; found C 59.42, H 5.59, N 7.91.

***N*-(1-Morpholino-2-phenylethylidene)benzo[*c*][1,2,5]thiadiazole-4-sulfonamide (10h):** Colorless powder (55%), m.p. 123–126 °C. ^1H NMR ([D$_6$]DMSO): δ = 3.30–3.35 (m, 2 H, CH_2), 3.41–3.43 (m, 2 H, CH_2), 3.47–3.49 (m, 2 H, CH_2), 3.64–3.66 (m, 2 H, CH_2), 4.58 (s, 2 H, CH_2), 7.20–7.29 (m, 5 H, ArH), 7.74–7.77 (m, 1 H, ArH), 8.18–8.21 (m, 2 H, ArH) ppm. ^{13}C NMR ($CDCl_3$): δ = 37.2, 45.3, 47.1, 66.1, 125.5, 127.2, 127.8, 128.1, 129.0, 129.1, 133.6, 135.0, 150.0, 155.6, 165.5 ppm. MS (EI): *m/z* (%) = 402 $[M]^+$ (10), 338 (13), 135 (53), 86 (100). $C_{18}H_{18}N_4O_3S_2$ (402.49): calcd. C 53.71, H 4.51, N 13.92; found C 53.42, H 4.45, N 13.71.

***N*-[2-(4-Chlorophenyl)-1-morpholinoethylidene]methanesulfonamide (10i):** Colorless powder (85%), m.p. 127–129 °C. ^1H NMR ([D$_6$]-DMSO): δ = 2.97 (s, 3 H, CH_3), 3.30–3.40 (m, 4 H, CH_2), 3.57–3.60 (m, 2 H, CH_2), 3.67–3.75 (m, 2 H, CH_2), 4.39 (s, 2 H, CH_2), 7.31 (d, *J* = 8.0 Hz, 2 H, ArH), 7.40 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 35.0, 43.4, 44.4, 46.5, 66.0, 129.0, 131.0, 131.3, 134.0, 164.2 ppm. MS (EI): *m/z* (%) = 316 $[M]^+$ (25), 150 (100), 125 (44), 79 (21). $C_{13}H_{17}ClN_2O_3S$ (316.80): calcd. C 49.29, H 5.41, N 8.84; found C 49.49, H 5.64, N 9.03.

***N*-[2-(4-Chlorophenyl)-1-morpholinoethylidene]-4-methylbenzenesulfonamide (10j):** Colorless powder (92%), m.p. 130–132 °C. ^1H NMR ([D$_6$]DMSO): δ = 2.36 (s, 3 H, CH_3), 3.30–3.37 (m, 4 H, CH_2), 3.56–3.58 (m, 2 H, CH_2), 3.67–3.70 (m, 2 H, CH_2), 4.43 (s, 2 H, CH_2), 7.22 (d, *J* = 8.0 Hz, 2 H, ArH), 7.30 (d, *J* = 8.0 Hz, 2 H, ArH), 7.38 (d, *J* = 8.0 Hz, 2 H, ArH), 7.69 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 21.6, 35.2, 45.2, 47.3, 66.0, 126.3, 129.1, 129.7, 130.3, 131.8, 134.0, 141.6, 142.3, 164.8 ppm. MS: *m/z* (%) = 393 $[M]^+$ (2), 155 (79), 91 (100), 86 (66). $C_{19}H_{21}ClN_2O_3S$ (392.90): calcd. C 58.08, H 5.39, N 7.13; found C 57.87, H 5.20, N 7.09.

***N*-[2-(4-Chlorophenyl)-1-morpholinoethylidene]-2,4-dimethylbenzenesulfonamide (10k):** Colorless powder (68%), m.p. 120–122 °C. ^1H NMR ($CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 2.70 (s, 3 H, CH_3), 3.30–3.42 (m, 4 H, CH_2), 3.60–3.70 (m, 2 H, CH_2), 3.70–3.85 (m, 2 H, CH_2), 4.41 (s, 2 H, CH_2), 7.02 (d, *J* = 8.0 Hz, 2 H, ArH), 7.10 (d, *J* = 8.0 Hz, 2 H, ArH), 7.28 (d, *J* = 8.0 Hz, 2 H, ArH), 7.88 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.6, 21.3, 36.3, 45.0, 47.0, 66.3, 126.3, 127.8, 129.3, 129.4, 132.7, 132.9, 133.1, 137.0, 138.8, 142.5, 164.5 ppm. MS (EI): *m/z* (%) = 407 $[M]^+$ (8), 169 (89), 105 (100), 86 (83). $C_{20}H_{23}ClN_2O_3S$ (406.93): calcd. C 59.03, H 5.70, N 6.88; found C 59.28, H 5.42, N 7.07.

***N*-[2-(4-Chlorophenyl)-1-morpholinoethylidene]-4-fluorobenzenesulfonamide (10l):** Colorless powder (98%), m.p. 164–166 °C. ^1H NMR ([D$_6$]DMSO): δ = 3.37 (br. s, 4 H, CH_3), 3.59 (br. s, 2 H, CH_2), 3.71 (br. s, 2 H, CH_2), 4.44 (s, 2 H, CH_2), 7.21 (d, *J* = 8.0 Hz, 2 H, ArH); 7.30–7.40 (m, 4 H, ArH), 7.87 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 35.6, 45.0, 47.6, 66.1, 116.2, 116.4, 129.1, 129.2, 130.3, 130.2, 132.0, 140.8, 162.9, 164.9, 165.4 ppm. MS (EI): *m/z* (%) = 396 $[M]^+$ (11), 159 (47), 150 (100), 95 (91). $C_{18}H_{18}ClFN_2O_3S$ (396.86): calcd. C 54.48, H 4.57, N, 7.06; found C 54.58, H 4.49, N 6.82.

***N*-[2-(4-Chlorophenyl)-1-(piperidin-1-yl)ethylidene]-4-methylbenzenesulfonamide (10m):** Yellow powder (86%), m.p. 125–127 °C. ^1H NMR ($CDCl_3$): δ = 1.53–1.60 (m, 6 H, CH_2), 2.39 (s, 3 H, CH_3), 3.26–3.29 (m, 2 H, CH_2), 3.72–3.77 (m, 2 H, CH_2), 4.38 (s, 2 H, CH_2), 7.11 (d, *J* = 8.0 Hz, 2 H, ArH), 7.20–7.26 (m, 4 H, ArH), 7.80 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 20.8, 23.1, 24.8, 35.0, 45.3, 47.3, 125.6, 128.4, 129.1, 131.0, 141.3, 141.5, 166.5 ppm. MS (EI): *m/z* (%) = 390 $[M]^+$ (2), 155 (25), 91 (52), 84 (100). $C_{20}H_{23}ClN_2O_2S$ (390.93): calcd. C 61.45, H 5.93, N 7.17; found C 61.58, H 5.69, N 6.92.

***N*-[2-(4-Methoxyphenyl)-1-(4-methylpiperazin-1-yl)ethylidene]-4-methylbenzenesulfonamide (10n):** Yellow powder (79%), m.p. 103–

105 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 2.02 (t, J = 4.0 Hz, 2 H, CH$_2$), 2.11 (s, 3 H, N-CH$_3$), 2.27 (t, J = 4.0 Hz, 2 H, CH$_2$), 2.38 (s, 3 H, CH$_3$), 3.34 (t, J = 4.0 Hz, 2 H, CH$_2$), 3.66 (t, J = 4.0 Hz, 2 H, CH$_2$), 3.74 (s, 3 H, OCH$_3$), 4.29 (s, 2 H, CH$_2$), 6.82 (d, J = 8.0 Hz, 2 H, ArH), 7.11 (d, J = 8.0 Hz, 2 H, ArH), 7.27 (d, J = 8.0 Hz, 2 H, ArH), 7.66 (d, J = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 26.2, 39.7, 49.7, 51.1, 51.8, 59.0, 60.1, 119.6, 131.3, 131.9, 134.4, 146.7, 147.7, 163.1, 170.1 ppm. MS (EI): m/z (%) = 401 [M]$^+$ (4), 246 (60), 91 (61), 70 (100). $C_{21}H_{27}N_3O_3S$ (401.52): calcd. C 62.82, H 6.78, N, 10.47; found C 62.68, H 6.56, N 10.77.

3-Amino-*N*-*o*-tolyl-3-(tosylimino)propanamide (10o): Colorless powder (81%), m.p. 153–155 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 2.15 (s, 3 H, CH$_3$), 2.36 (s, 3 H, CH$_3$), 3.46 (s, 2 H, CH$_2$), 7.0–7.15 (m, 3 H, ArH), 7.18–7.21 (m, 3 H, ArH), 7.73 (d, J = 8.0 Hz, 2 H, ArH), 8.16 (s, 1 H, NH), 8.73 (s, 1 H, NH), 9.47 (s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 16.2, 21.4, 43.9, 125.2, 125.8, 126.4, 129.6, 130.8, 132.1, 136.4, 140.4, 142.6, 164.4, 165.3 ppm. IR: $\tilde{\nu}$ = 3429 (NH), 3325 (NH), 3239 (NH), 1670 (C=O) cm^{-1}. MS (EI): m/z (%) = 345 [M]$^+$ (3), 147 (63), 106 (89), 91 (100). $C_{17}H_{19}N_3O_3S$ (345.42): calcd. C 59.11, H 5.54, N 12.17; found C 59.22, H 5.64, N 12.37.

Ethyl 3-Amino-3-(tosylimino)propanoate (10p): Colorless powder (90%), m.p. 122–124 °C. ^{1}H NMR (CDCl$_3$): δ = 1.27 (t, J = 8.0 Hz, 3 H, CH$_3$), 2.42 (s, 3 H, CH$_3$), 3.37 (s, 2 H, CH$_2$), 4.20 (q, J = 8.0 Hz, 2 H, CH$_2$), 7.29 (d, J = 8.0 Hz, 2 H, ArH), 7.74 (br. s, 1 H, NH), 7.82 (d, J = 8.0 Hz, 2 H, ArH), 8.17 (br. s, 1 H, NH) ppm. ^{13}C NMR (CDCl$_3$): δ = 13.8, 21.9, 40.1, 62.0, 126.5, 129.3, 138.8, 143.1, 161.6, 168.7 ppm. IR: $\tilde{\nu}$ = 3386 (NH), 3305 (NH), 1740 (C=O) cm^{-1}. MS (EI): m/z (%) = 284 [M]$^+$ (14), 155 (18), 91 (100), 65 (25). $C_{12}H_{16}N_2O_4S$ (284.33): calcd. C 50.69, H 5.67, N 9.85; found C 50.43, H 5.61, N 9.96.

***N*^{1}-Methyl-*N*$'^1$,*N*$'^3$-ditosylmalonimidamide (10q):** Colorless powder (87%), m.p. 214–216 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 2.35 (s, 3 H, CH$_3$), 2.37 (s, 3 H, CH$_3$), 2.68 (d, J = 4.0 Hz, 3 H, CH$_3$), 3.73 (s, 2 H, CH$_2$), 7.25 (d, J = 8.0 Hz, 2 H, ArH), 7.29 (d, J = 8.0 Hz, 2 H, ArH), 7.62 (d, J = 8.0 Hz, 2 H, ArH), 7.69 (d, J = 8.0 Hz, 2 H, ArH), 7.97 (s, 1 H, NH$_2$), 8.63 (s, 1 H, NH$_2$), 8.69 (q, J = 4.0 Hz, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 21.1, 28.4, 125.8, 129.0, 139.8, 141.2, 142.0, 161.2, 163.6 ppm. MS (EI): m/z (%) = 357 [M – Ts]$^+$ (30), 155 (30), 91 (100), 65 (28). $C_{18}H_{22}N_4O_4S_2$ (422.52): calcd. C 51.17, H 5.25, N 13.26; found C 50.92, H 5.27, N 13.03.

***N*^{1}-Benzyl-*N*$'^1$,*N*$'^3$-ditosylmalonimidamide (10r):** Colorless powder (82%), m.p. 170–172 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 2.34 (s, 3 H, CH$_3$), 2.36 (s, 3 H, CH$_3$), 3.80 (s, 2 H, CH$_2$), 4.38 (d, J = 4.0 Hz, 2 H, CH$_2$), 7.15–7.35 (m, 9 H, ArH), 7.55 (d, J = 8.0 Hz, 2 H, ArH), 7.70 (d, J = 8.0 Hz, 2 H, ArH), 7.99 (s, 1 H, NH), 8.71 (s, 1 H, NH), 9.15 (t, J = 4.0 Hz, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 20.8, 20.9, 44.7, 125.7, 126.0, 126.9, 127.5, 128.1, 128.9, 129.0, 137.0, 139.8, 141.1, 141.4, 142.0, 160.8, 163.6 ppm. MS (EI): m/z (%) = 343 [M – Ts]$^+$ (48), 155 (30), 106 (35), 91 (100). $C_{24}H_{26}N_4O_4S_2$ (498.62): calcd. C 57.81, H 5.26, N 11.24; found C 57.68, H 5.11, N 11.15.

3-(Piperidin-1-yl)-*N*$'$-tosyl-3-(tosylimino)propanimidamide (10s): Colorless powder (88%), m.p. 195–197 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 1.44–1.60 (m, 6 H, CH$_2$), 2.40 (s, 3 H, CH$_3$), 2.42 (s, 3 H, CH$_3$), 3.25–3.40 (m, 2 H, CH$_2$), 3.50–3.62 (m, 2 H, CH$_2$), 4.10 (s, 2 H, CH$_2$), 7.22 (d, J = 8.0 Hz, 2 H, ArH), 7.28 (d, J = 8.0 Hz, 2 H, ArH), 7.63 (d, J = 8.0 Hz, 2 H, ArH), 7.68 (d, J = 8.0 Hz, 2 H, ArH), 7.95 (s, 1 H, NH), 8.67 (br. s, 1 H, NH) ppm. ^{13}C NMR (CDCl$_3$): δ = 21.5, 21.5, 23.9, 25.4, 39.8, 47.1, 48.8, 126.2, 126.6, 129.3, 129.5, 138.8, 140.1, 142.7, 143.4, 156.6, 161.7 ppm. MS (EI): m/z (%) = 231 [M – Ts]$^+$ (25), 155 (20), 91 (69), 84 (100). $C_{22}H_{28}N_4O_4S_2$ (476.61): calcd. C 55.44, H 5.92, N 11.76; found C 55.49, H 6.26, N 11.62.

General Procedure B: A solution of the corresponding thiomalonamide **8e**–**8g** (1.0 equiv.) and tosyl azide (**9b**; 5.0 equiv.) in anhydrous EtOH was heated at reflux for 20–30 h. The reaction mixture was concentrated in vacuo to dryness, and the residue was purified by flash chromatography on silica gel (60–120) using EtOAc/hexane mixtures. To achieve better separation, the composition of the eluent was gradually changed from 1:6 to 1:2, EtOAc/hexane.

General Procedure C: A suspension of the corresponding thiomalonamide **8e**–**8g** (1.0 equiv.) and tosyl azide (**9b**; 5.0 equiv.) was heated at reflux in H$_2$O for 10–20 h. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (60–120) using EtOAc/hexane mixtures. To achieve better separation, the composition of the eluent was gradually changed from 1:6 to 1:2, EtOAc/hexane.

4-Methyl-*N*-[6-methyl-1,3-dioxo-2-*o*-tolyl-2,3-dihydro-1*H*-pyrrolo-[3,4-*c*]pyridin-4(5*H*)-ylidene]benzenesulfonamide (13): Methyl 2,4-dioxovalerate (**12**; 0.53 g, 3.6 mmol) and triethylamine (0.5 mL, 3.6 mmol) were added to a suspension of malonamidine **10o** (1.24 g, 3.6 mmol) in ethanol (5 mL). The reaction mixture was stirred at room temperature for 3 h. The yellow precipitate of compound **12** was collected by filtration, and washed with ethanol and hexane. Colorless powder (71%), m.p. 173–175 °C. ^{1}H NMR (CDCl$_3$): δ = 2.15 (s, 3 H, CH$_3$), 2.43 (s, 3 H, CH$_3$), 2.63 (s, 3 H, CH$_3$), 7.15 (d, J = 4.0 Hz, 1 H, ArH), 7.24 (s, 1 H, =CH), 7.31–7.37 (m, 5 H, ArH), 7.15 (d, J = 4.0 Hz, 2 H, ArH), 8.69 (s, 1 H, NH) ppm. ^{13}C NMR (CDCl$_3$): δ = 17.8, 21.6, 25.4, 106.7, 111.5, 126.9, 128.5, 129.1, 129.7, 131.4, 136.4, 136.6, 142.6, 144.6, 147.0, 165.6, 166.8, 167.3 ppm. MS (EI): m/z (%) = 421 [M]$^+$ (3), 356 (100), 266 (35), 91 (58). $C_{22}H_{19}N_3O_4S$ (421.47): calcd. C 62.69, H 4.54, N 9.97; found C 62.28, H 4.25, N 10.19.

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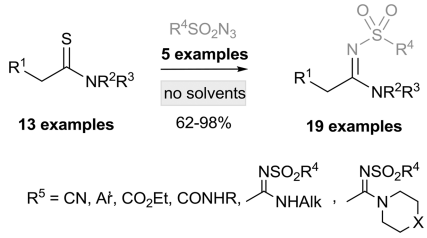
Sulfonyl Azides

An efficient, solvent-free and base-free approach to active-methylene *N*-sulfonylacetamidines has been developed.



Keywords: Synthetic methods / Azides / Sulfonamides / Thioamides

