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# Three-Component Reaction of Sulfonamides with Acetylene and Amines

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**Abstract**—*N*-(2-Phenyl-1-piperidin-1-ylethylidene)tosylamide was synthesized by oxidative coupling of arenesulfonamides, acetylenes, and secondary amines. The reaction of phenylacetylene or propargyl alcohol with triflamide and piperidine under the same conditions unexpectedly gave *N*-[(1*E*)-piperidin-1-ylmethylidene]triflamide TfN=CHNC$_5$H$_{10}$ as a result of cleavage of the triple bond in the alkyne. A similar reaction with benzoylacetylene gave (2*E*)-1-phenyl-3-piperidin-1-ylprop-2-en-1-one, while triflamide did not react. Adducts of a series of acetylenes with triflamide were obtained using triflamide sodium salt. Attempted synthesis of an *N*-triflyl-substituted analog of amidine **1** by the reaction of benzoylacetylene with triflamide and piperidine or morpholine in the presence of Cu(OTf)$_2$ and hydrogen peroxide as an oxidant unexpectedly gave 1-piperidin-1-yl- or 1-morpholin-1-ylmethanimine, respectively.

**Keywords:** amidines, sulfonamides, acetylenes, amines, oxidative coupling, XRD analysis

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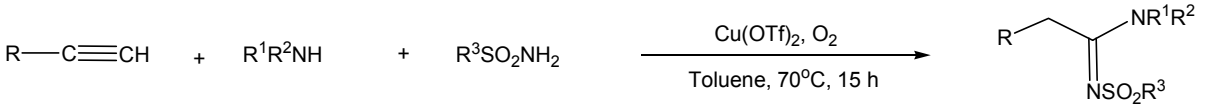
Amidines containing an electron-acceptor group on the imino nitrogen atom present interest in view of the strong conjugation in the >N–CH=N–X triad. A number of synthetic approaches to perfluoroalkylsulfonylamidines R$_f$SO$_2$N=CHNR$_2$ are known, including the reaction of R$_f$SO$_2$F with DMF [1], Vilsmeier−Haack reaction of salts R$_F$SO$_2$NHNa with POCl$_3$ and R$_2$NCHO [2], three-component reaction of azides R$_f$SO$_2$N$_3$ with ketones and secondary amines [3, 4], and some other [5]. We previously synthesized the simplest amidine of this type, TfN=CH–NMe$_2$ (Tf = CF$_3$SO$_2$), by the reaction of 2-phenyl-2H-1,2,3-triazole-4-carboxylic acid chloride with TfNHNa in DMF [6], and recently developed a method of synthesis of *N*-triflylamidines from *N*-formylamines and *N*-sulfinyltriflamide [7]. Proceeding with this research we made an attempt to bring triflamide into a Cu(OTf)$_2$-catalyzed three-component oxidative coupling reaction with terminal acetylenes and secondary amines under the conditions described by Kim and Stahl [8] for the reaction of arylacetylenes with dialkylamines and arenesulfonamides (Scheme 1).

The reaction by Scheme 1 resulted in the successful synthesis of *N*-[2-phenyl-1-(piperidin-1-yl)ethylidene)-4-methylbenzenesulfonamide **1**. The structure of compound **1** was established by X-ray diffraction (XRD) analysis (Fig. 1). Selected structural parameters of the synthesized compound are listed in the table.

The independent part of the unit cell of amidine **1** contains one molecule. Molecules **1** are held together by short S–O···H–C contacts of 2.5–2.7 Å. The N$^2$–C$^6$ and C$^6$=N$^1$ bonds in molecule **1** have almost equal lengths, which suggests strong conjugation, even though it is not as strong as in its C-unsubstituted triflyl analog TfN=CH–N(CH$_2$)$_5$ [7]. Note that the N–C and C=N bond lengths in the structurally related molecule TsN=CH–NEt$_2$ are equal to each other (1.307 Å) [9].

**Scheme 1.**



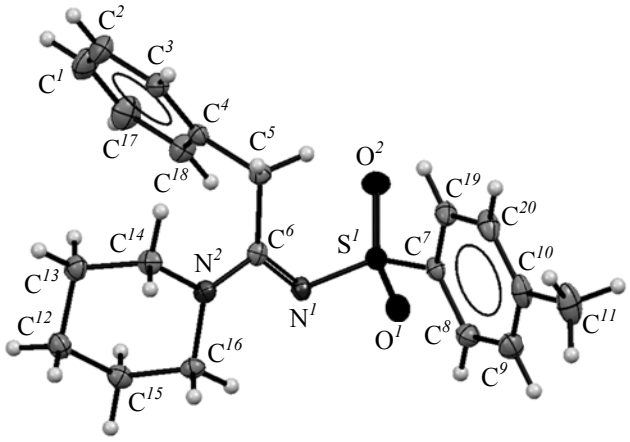



**Fig. 1.** Molecular structure of compound **1**.

Under the conditions of the reaction in Scheme 1, phenylacetylene did not react with triflamide and piperidine or diisopropylamine as an amine component. However, by changing the reaction conditions, specifically, by replacing the $Cu(OTf)_2$ catalyst by CuI, the $O_2$ oxidant by $NaIO_4$, and the solvent by acetonitrile, we unexpectedly obtained *N*-[(piperidin-1-yl)methylidene]triflamide **2**, which we synthesized earlier [7]. The reaction result is independent on the substituent at the triple bond, as judged from the fact that amine **2** is also formed, when phenylacetylene is replaced by propargyl alcohol (Scheme 2).

The unusual nature of this reaction is that it formally involves the cleavage of the triple bond, so that the final product contains only one carbon atom from the parent acetylene. Obviously, this can only occur as the result of addition to the triple bond, i.e. its saturation to an ordinary bond, and subsequent cleavage of the latter. An example of such a cleavage in the reaction of ketones with arylacetylenes and guanidine was recently reported by Schmidt et al. [10].

The driving force of the elimination of fragments of the starting arylacetylene in [10] is aromatization of the intermediate cycloadduct to 2-aminopyrimidine. In our case, such a driving force, apparently, is the oxidation of the intermediate adduct with sodium periodate (Scheme 3).

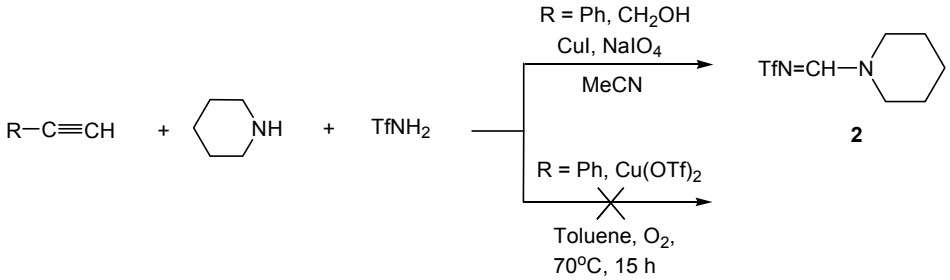
With benzoylacetylene, the single product of the three-component reaction with piperidine and triflamide is compound **3** (Scheme 4) formed as the *trans*-isomer through the addition of the amine, which is more basic than triflamide, to the activated triple bond. The NMR spectra of the product coincide with the spectra of (2*E*)-1-phenyl-3-piperidin-1-ylprop-2-en-1-one prepared in different ways [11–15].

Attempted addition of triflamide to benzoylacetylene under the same conditions but in the absence of amina failed because of the extremely low basicity of triflamide. The adduct of triflamide to

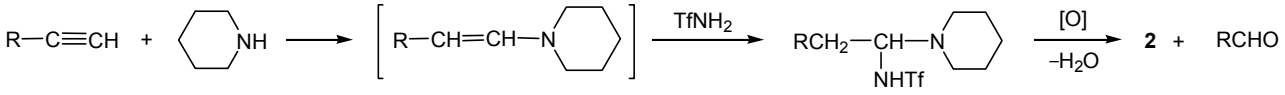
Some bond lengths, valence and torsion angles in a molecule **1**.

| Bond | *l*, Å | Angle | φ, deg | Angle | θ, deg |
|---|---|---|---|---|---|
| $S^1$–$O^1$ | 1.4434(11) | $O^1$–$S^1$–$O^2$ | 115.92(7) | $O^1$–$S^1$–$N^1$–$C^6$ | –169.50(12) |
| $S^1$–$O^2$ | 1.4475(12) | $O^1$–$S^1$–$N^1$ | 105.48(7) | $O^2$–$S^1$–$N^1$–$C^6$ | –40.41(14) |
| $S^1$–$N^1$ | 1.6069(13) | $O^2$–$S^1$–$N^1$ | 115.08(7) | $C^7$–$S^1$–$N^1$–$C^6$ | 77.28(13) |
| $S^1$–$C^7$ | 1.7670(15) | $O^1$–$S^1$–$C^7$ | 107.84(7) | $S^1$–$N^1$–$C^6$–$N^2$ | –167.22(11) |
| $N^1$–$C^6$ | 1.3282(18) | $O^2$–$S^1$–$C^7$ | 108.00(7) | $S^1$–$N^1$–$C^6$–$C^5$ | 15.6(2) |
| $N^2$–$C^6$ | 1.3341(19) | $N^1$–$S^1$–$C^7$ | 103.65(7) | $C^{12}$–$N^2$–$C^6$–$N^1$ | –178.12(13) |
| $N^2$–$C^{12}$ | 1.4730(19) | $C^6$–$N^1$–$S^1$ | 125.37(11) | $C^{16}$–$N^2$–$C^6$–$N^1$ | –3.18(19) |
| $N^2$–$C^{16}$ | 1.4758(19) | $C^6$–$N^2$–$C^{12}$ | 125.02(13) | $C^{12}$–$N^2$–$C^6$–$C^5$ | –0.7(2) |
| $C^5$–$C^6$ | 1.520(2) | $C^6$–$N^2$–$C^{16}$ | 122.55(12) | $C^{16}$–$N^2$–$C^6$–$C^5$ | 174.25(12) |
| | | $C^{12}$–$N^2$–$C^{16}$ | 112.27(12) | $C^4$–$C^5$–$C^6$–$N^1$ | 106.49(16) |
| | | $N^1$–$C^6$–$N^2$ | 116.87(13) | $C^4$–$C^5$–$C^6$–$N^2$ | –70.70(16) |
| | | $N^1$–$C^6$–$C^5$ | 125.43(13) | $N^1$–$S^1$–$C^7$–$C^8$ | 83.45(13) |
| | | $N^2$–$C^6$–$C^5$ | 117.64(12) | $N^1$–$S^1$–$C^7$–$C^{19}$ | –92.15(13) |

**Scheme 2.**




**Scheme 3.**



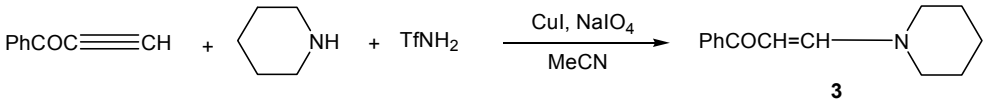

benzoylacetylene could only be obtained, when the basicity of triflamide was increased by using its sodium salt TfNHNa, and the reaction was performed in the presence of $Cu(OTf)_2$ as a catalyst and in the absence of oxidant. Similar reactions of TfNHNa with other activated acetylenes, specifically dibenzoylacetylene, methyl acetylenecarboxylate, and dimethyl acetylenedicarboxylate gave adducts **5–7** (Scheme 5).

According to the $^1$H and $^{13}$C NMR data, adducts **4–7** are formed as mixtures of two isomers in comparable proportions, but, depending on the substituents, either *Z* or *E* isomer is prevailing: *Z*-**4** : *E*-**4** = 3 : 10, *Z*-**5** : *E*-**5** = 2.2 : 1, *Z*-**6** : *E*-**6** = 1 : 3, and *Z*-**7** : *E*-**7**= 1 : 1.8. Isomer *E*-**4** was isolated pure by column chromatography on silica gel, and this allowed us to assign the signals in its $^{13}$C NMR spectrum.

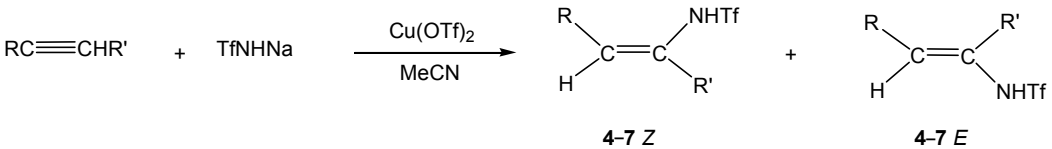
As follows from Scheme 5, products **4–7** are formed as the enamine tautomers. However, according to the $^1$H and $^{13}$C NMR data, the reaction with benzoylacetylene in methanol gave, along with *Z*-**4** and *E*-**4**, the imine tautomer $PhC(O)CH_2CH{=}NTf$ (**8**), and the *Z*,*E*-**4** : **8** ratio was 0.7 : 1. The formation of compound **8** is confirmed by the fact that the $^1$H NMR spectrum contains, along with signals of *Z*,*E*-**4**, a doublet at 3.3 ppm and a triplet at 4.9 ppm (ratio 2 : 1), split by mutual coupling with a constant of 5.6 Hz characteristic of the $–CH_2CH{=}N–$ fragment and belonging to the methylene and azomethine protons of this fragment. The $^{13}$C NMR spectrum displays the methylene and carbonyl carbon signals at 53.3 and 196.9 ppm, respectively. The carbonyl carbon signal of compound **8** is downfield to the respective signal of isomer **4**, as would be expected for an unconjugated C=O group. Presumably, the formation of imine **8** is promoted by the involvement of methanol into a solvation complex and keto-enol isomerization of the latter (Scheme 6).

Attempted synthesis of an *N*-triflyl-substituted analog of amidine **1** by the reaction of benzoylacetylene with triflamide and piperidine in the presence of 5 mol % of $Cu(OTf)_2$ in dioxane and hydrogen peroxide as an oxidant unexpectedly gave 1-(piperidin-1-ylmethanimine **9**. Similarly, the reaction with morpholine in acetonitrile or ethyl methyl ketone resulted in the synthesis of 1-(morpholin-1-yl)methanimine **10**. Seemingly, there results are reasonably

**Scheme 4.**

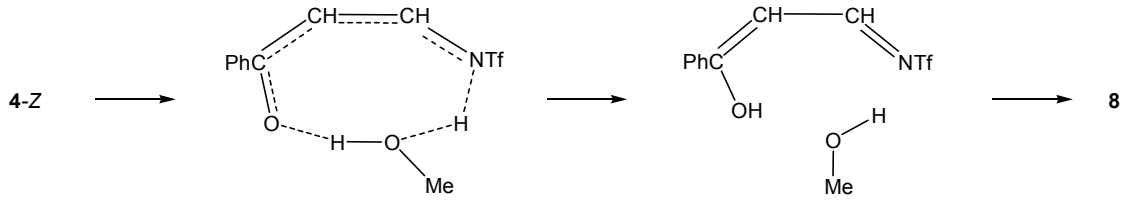



**Scheme 5.**

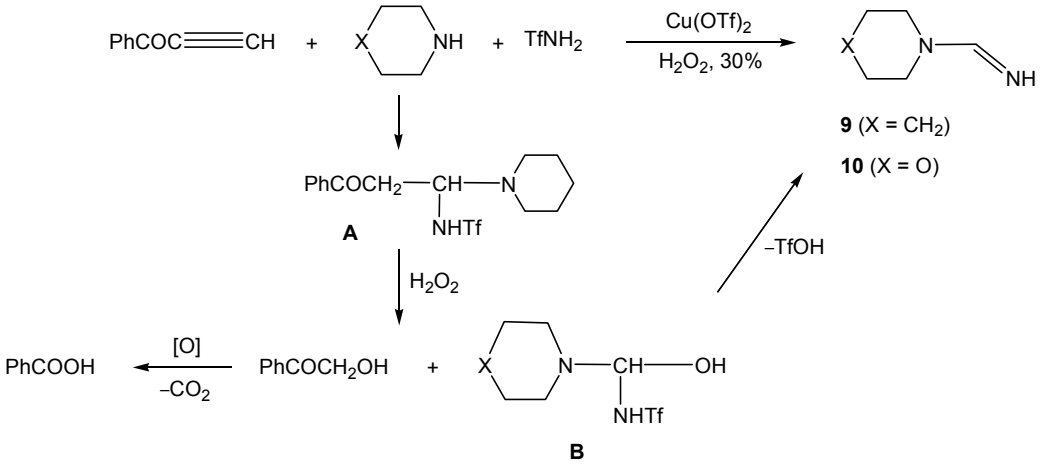



R = PhC(O), R' = H (**4**); R = R' = PhC(O) (**5**); R = MeOC(O), R' = H (**6**); R = R' = MeOC(O) (**7**).

**Scheme 6.**




**Scheme 7.**




explained in terms of the oxidation of intermediate **A**, like that in Scheme 3, with C–C bond cleavage and formation of benzoic acid and *N*-[amino(hydroxy)-methyl]triflamide **B**, followed by TfOH elimination from the latter (Scheme 7).

Evidence for Scheme 7 is provided by the isolation of benzoic acid by preparative chromatography and its and identification of $^{1}$H NMR spectroscopy. The structure of products **9** and **10** was confirmed by IR and NMR spectroscopy.

## EXPERIMENTAL

The IR spectra were measured on a Varian 3100 FTIR spectrometer. The $^{1}$H, $^{13}$C, and $^{19}$F NMR spectra were run on a Bruker DPX 400 spectrometer at 400 ($^{1}$H), 100 ($^{13}$C), and 376 ($^{19}$F) MHz in DMSO-$d_6$. The $^{1}$H and $^{13}$C chemical shifts were measured against residual proton signals of the deuterated solvent and given in ppm relative to TMS, and those of $^{19}$F, relative to $CFCl_3$. The single crystal of compound **1** was obtained by crystallization of the eluate (ethyl acetate–hexane) after column chromatography. Reaction progress was monitored by TLC on Sorbfil plates. XRD analysis was performed on a Bruker D8 Venture diffractometer (Mo$K_\alpha$ radiation, λ 0.71073 Å, φ and ω scans). The structure was solved by the direct method using SHELX [16]. Absorption was included using SADABS. Non-hydrogen atoms were refined with anisotropic displacement parameters using SHELX [16]. The crystal data are deposited at the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk/data_request/cif), CCDC 1826686.

***N*-[2-Phenyl-1-(piperidin-1-yl)ethylidene]-4-methylbenzenesulfonamide (1).** A solution of 1.03 g (6 mmol) of tosylamide in 20 mL of dry toluene containing 0.05 g (0.15 mmol) of $Cu(OTf)_2$ was evacuated 3 times and purged with oxygen, after which 0.31 g (3 mmol) of phenylacetylene, 0.51 g (6 mmol) of piperidine, and 10 mL of toluene were added. A stream of oxygen was passed through the mixture for 15 h under vigorous stirring and heating at 70°C. After cooling, a precipitate formed and was dissolved in 10 mL of ethyl acetate, the solution was filtered through a bed of silica gel, the solvent was removed in a vacuum, and the residue was chromatographed on an alumina column with hexane–ethyl acetate, 1 : 1. $^{1}$H NMR spectrum, δ, ppm: 1.08 m (2H, $NCH_2CH_2C\underline{H}_2$), 1.45 m (4H, $NCH_2C\underline{H}_2$), 3.33 and 3.65 m (4H, $NCH_2$), 4.39 s (2H, $PhCH_2$), 7.18–7.34 m (7H, Ph and $H^{3,5}$ in Tol) 7.68 d (2H, $H^{2,6}$ in Tol, $J$ 8.1 Hz). $^{13}$C NMR spectrum, δ, ppm: 20.8 ($CH_3$), 23.2 ($NCH_2CH_2\underline{C}H_2$), 24.9 and 25.4 ($NCH_2\underline{C}H_2$), 35.8 ($Ph\underline{C}H_2$), 45.3 and 47.3 ($NCH_2$), 125.7 ($C^{2,6}$ in Tol), 126.5 ($C^{p}$ in Ph), 128.0 ($C^{m}$ in Ph),

128.5 ($C^{3,5}$ in Tol), 129.2 ($C^{o}$ in Ph), 134.9 ($C^{1}$ in Ph), 141.47 ($C^{4}$ in Tol), 141.54 ($C^{1}$ in Tol), 164.0 (C=N). Found, %: C, 67.85; H, 6.45; N, 7.85; S, 8.98 $C_{20}H_{24}N_2O_2S$. Calculated, %: C, 67.38; H, 6.79; N, 7.86; S, 8.99.

XRD analysis of compound **1**: $C_{20}H_{24}N_2O_2S$, *m* 356.48, colorless plate-like crystals, 0.08 × 0.20 × 0.30 mm, monoclinic, space group $P2_1/c$; $\theta_{min}/\theta_{max}$ 2.67/30.25; *T* 100 K, *a* 19.522(1), *b* 8.325(1), *c* 11.354(1) Å; β 97.906(2)°, *V* 1827.8(2) Å$^3$, *Z* 4, $d_{calc}$ 1.295 g/cm$^3$, *F*(000) 760; absorption coefficient μ 0.193 mm$^{-1}$; 77175 reflections, including 5412 unique; 227 refined parameters; *R* 4.40, $R_w$ (on all reflections) 0.068; goodness of fit on $F^2$ 1.054; $\Delta\rho_{max}/\Delta\rho_{min}$ 0.350/–0.396 e/Å$^3$; weight scheme $w = [\sigma^2 (F_0^2) + (0.0392P)^2 + 1.3952P]^{-1}$, where $P = (F_0^2 + 2Fc^2)/3$.

***N*-(Piperidin-1-ylmethylidene)trifluoromethanesulfonamide (2).** To a solution of 1.0 g (6.7 mmol) of triflamide in 15 mL of dry acetonitrile, cooled to 10°C we added 0.13 g (0.67 mmol) of CuI and 0.34 g (3.4 mmol) of phenylacetylene and then slowly, dropwise, a solution 0.57 g (6.7 mmol) of 5 mL of dry; therewith, the mixture slightly warmed up and acquired a blue-green color. After cooling to room temperature, 2.15 g (10 mmol) of $NaIO_4$ was added in small portions. The mixture was allowed to stand for 30 min and heated to 40°C, after which it spontaneously warmed up to ~50°C and became brown. The mixture was stirred for 1 h at 50°C and then 3 h at room temperature, monitoring the reaction progress by TLC. The reaction mixture was filtered, the solvent was removed at reduced pressure, and the residue was purified by column chromatography on silica gel, eluent hexane–ether–acetonitrile, 1 : 2 : 1, to obtain colorless plate-like crystals, mp 88–89°C, identical to those obtained in [7].

**1-Phenyl-3-piperidin-1-ylprop-2-en-1-one (3).** To a solution of 1.49 g (10 mmol) of triflamide in 20 mL of dry acetonitrile we added 0.13 g (0.67 mmol) of CuI and 0.87 g (6.7 mmol) of benzoylacetylene (the mixture acquired a bright orange color) and then slowly, dropwise, a solution of 0.85 g (10 mmol) of piperidine in 5 mL of dry acetonitrile (the mixture slightly warmed up and acquired a brown green color). After cooling to room temperature, 2.9 g (13.4 mmol) of $NaIO_4$ was added in small portions. The mixture was allowed to stand for 30 min, heated to ~50°C, and stirred for 3 h, monitoring the reaction progress by TLC. The reaction mixture was filtered, the solvent was removed at reduced pressure, and the residue was purified by column chromatography on silica gel, eluent hexane–ether–acetonitrile, 1 : 2 : 1, to obtain yellow crystals, mp 89–91°C (91–92°C [11], 90–91.5°C [12]). $^1$H NMR spectrum, δ, ppm: 1.57 m (6H, $3CH_2$), 3.41 m [4H, $(CH_2)_2N$], 5.98 d (1H, *J* 12.4 Hz), 7.65 d (1H, *J* 12.4 Hz), 7.40–7.49 m (3H, $H^{m+p}$) 7.88 m (2H, $H^{o}$). $^{13}$C NMR spectrum, δ, ppm: 24.6, 25.4 br, 45.8 br, 54.0 br, 90.1, 127.1, 128.0, 130.6, 140.3, 152.7, 186.0.

Compound **3** was also prepared by the reaction of 0.87 g (6.7 mmol) of benzoylacetylene and 0.13 g (0.67 mmol) of CuI in 20 mL of dry acetonitrile with a solution of 0.85 g (10 mmol) of piperidine in 5 mL of dry acetonitrile with a raw yield of 1.59 g (92 %).

***N*-(3-Oxo-3-phenylprop-1-en-1-yl)trifluoromethanesulfonamide (4).** To a solution of 1 g (7.7 mmol) of benzoylacetylene in 20 mL of dry acetonitrile we added 0.14 g (0.39 mmol) of $Cu(OTf)_2$ and 1.97 g (11.5 mmol) of triflamide sodium salt. The mixture was stirred at 40–45°C for 4–5 h, cooled, the precipitate was filtered off, and the solvent was removed at reduced pressure. According to the NMR data, the yellow green residue contained a mixture of the *Z* and *E* isomers of compound **4**. IR spectrum, KBr, ν, cm$^{-1}$: 3444 (NH), 3063 (CH), 1641 (C=O), 1584 (C=C), 1557 (arom), 1197, 1177 (CF). Isomer (*Z*)-**4**: $^1$H NMR spectrum, δ, ppm: 5.77 d (1H, COCH=, *J* 8.1 Hz), 7.15 d (1H, =CHNTf, *J* 8.1 Hz). The aromatic proton signals of the two isomers overlap. $^{13}$C NMR spectrum, δ, ppm: 100.8 (CO<u>C</u>H=), 127.4 ($C^{o}$), 128.1 ($C^{m}$), 130.9 ($C^{p}$), 140.6 ($C^{ipso}$), 152.6 (=CHN), 187.1 (C=O). $^{19}$F NMR spectrum, δ, ppm: –78.72. The (*E*)-**4** isomer was isolated by column chromatography on silica gel (eluent hexane–ether–acetonitrile, 1 : 2 : 1) as a broght yellow solid amorphous material, yield 65%. $^1$H NMR spectrum, δ, ppm: 6.27 d (1H, COCH=, *J* 12.5 Hz), 7.44 t (2H, $H^{m}$, *J* 7.6 Hz), 7.50 t (1H, $H^{p}$, *J* 7.3 Hz), 7.83 d (2H, $H^{o}$, *J* 7.7 Hz), 8.02 d (1H, =CHNTf, *J* 12.5 Hz). $^{13}$C NMR spectrum, δ, ppm: 100.8 (CO*C*H=), 120.6 q ($CF_3$, *J* 323.9 Hz), 127.3 ($C^{o}$), 128.2 ($C^{m}$), 131.1 ($C^{p}$), 139.8 ($C^{ipso}$), 157.7 (=CHN), 189.0 (C=O). $^{19}$F NMR spectrum, δ, ppm: –79.06. HRMS, *m/z*: 280.0298 $[M + H]^+$. Calculated for $C_{10}H_9F_3NO_3S$: 280.0255.

The reactions of TfNHNa with dibenzoylacetylene, methyl acetylenecarboxylate, and dimethyl acetylenedicarboxylate were performed in a similar way. The residue after removal of the solvent was analyzed by $^1$H, $^{13}$C, and $^{19}$F NMR spectroscopy, not isolating analytically pure samples.

***N*-[3-Oxo-3-phenyl-1-(phenylcarbonyl)prop-1-en-1-yl]trifluoromethanesulfonamide *Z*,*E*-5.** IR spectrum, KBr, ν, $cm^{-1}$: 3390, 3278 (NH), 3065, 2927 (CH), 1700, 1659 (C=O), 1621, (C=C), 1597, 1576, 1508 (arom), 1223, 1191, 1176, 1120 (CF). *Z*-**5** (major isomer). $^1$H NMR spectrum, δ, ppm: 6.95 s (1H, CH=), 7.38–7.64 m (6H, $Ph^{m+p}$), 7.74 d (2H, 4-$Ph^o$, *J* 7.4 Hz), 7.85 d (2H, 1-$Ph^o$, *J* 7.4 Hz). $^{13}$C NMR spectrum, δ, ppm: 101.1 (CH=), 121.0 q ($CF_3$, *J* 327.4 Hz), 127.2 ($C^o$ in 4-Ph), 128.2 ($C^o$ in 1-Ph), 128.4 ($C^m$ in 4-Ph), 128.6 ($C^m$ in 1-Ph), 131.8 ($C^p$ in 4-Ph), 132.4 ($C^p$ in 1-Ph), 135.3 ($C^{ipso}$ in 4-Ph), 138.8 ($C^{ipso}$ in 1-Ph), 164.2 (=CHN), 186.7 ($C^4$=O), 193.9 ($C^1$=O). $^{19}$F NMR spectrum, δ, ppm: –76.39. *E*-**5** (minor isomer). $^1$H NMR spectrum, δ, ppm: 5.75 s (1H, CH=), 7.38–7.64 m (6H, $Ph^{m+p}$), 7.80 d (2H, 4-$Ph^o$, *J* 7.5 Hz), 7.92 d (2H, 1-$Ph^o$, *J* 7.5 Hz). $^{13}$C NMR spectrum, δ, ppm: 104.0 (CH=), 120.5 q ($CF_3$, *J* 325.5 Hz), 127.6 ($C^o$ in 4-Ph), 129.3 ($C^o$ in 1-Ph), 128.3 ($C^m$ in 4-Ph), 128.4 ($C^m$ in 1-Ph), 131.5 ($C^p$ in 4-Ph), 132.9 ($C^p$ in 1-Ph), 136.0 ($C^{ipso}$ in 4-Ph), 140.0 ($C^{ipso}$ in 1-Ph), 157.9 (=CHN), 188.1 ($C^4$=O), 196.2 ($C^1$=O). $^{19}$F NMR spectrum, δ, ppm: –77.51.

**Methyl 3-(trifluoromethanesulfonamido)prop-2-enoate *Z*,*E*-6.** IR spectrum (ATR), ν, $cm^{-1}$: 3329 (NH), 2959 (CH), 1678 (C=O), 1605 (C=C), 1172, 1146 1120 (CF). *Z*-**6** (minor isomer). $^1$H NMR spectrum, δ, ppm: 3.50 s (3H, $OCH_3$), 4.58 d [1H, =CHC(O), *J* 8.3 Hz], 6.94 d (1H, =CHN, *J* 8.3 Hz). $^{13}$C NMR spectrum, δ, ppm: 49.7 ($OCH_3$), 94.1 [=CHC(O)], 120.9 q ($CF_3$, *J* 327.0 Hz), 151.8 (=CHN), 166.5 (C=O). $^{19}$F NMR spectrum, δ, ppm: –77.20. *E*-**6** (major isomer). $^1$H NMR spectrum, δ, ppm: 3.51 s (3H, $OCH_3$), 4.96 d [1H, =CHC(O), *J* 13.0 Hz], 7.75 d (1H, =CHN, *J* 13.0 Hz). $^{13}$C NMR spectrum, δ, ppm: 50.0 ($OCH_3$), 96.7 [=CHC(O)], 120.9 q ($CF_3$, *J* 327.0 Hz), 155.4 (=CHN), 167.14 ($C^2$=O), 169.1 (C=O). $^{19}$F NMR spectrum, δ, ppm: –77.51.

**Dimethyl 2-(trifluoromethanesulfonamido)but-2-enedioate *Z*,*E*-7.** IR spectrum (film), ν, $cm^{-1}$: 3313 (NH), 2959, 2922, 2855 (CH), 1712 (C=O), 1599 (C=C), 1188, 1120 (CF). *Z*-**7** (minor isomer). $^1$H NMR spectrum, δ, ppm: 3.49 s (3H, $OCH_3$), 5.33 s (1H, CH=). $^{13}$C NMR spectrum, δ, ppm: 50.24 (3-$COOCH_3$), 51.5 (2-$COOCH_3$), 94.7 (CH=), 121.0 q ($CF_3$, *J* 327.8 Hz), 155.9 (=CHN), 167.14 ($C^2$=O), 167.18 ($C^3$=O). $^{19}$F NMR spectrum, δ, ppm: –76.55. *E*-**7** (major isomer). $^1$H NMR spectrum, δ, ppm: 3.53 s (3H, $OCH_3$), 5.31 s (1H, CH=). $^{13}$C NMR spectrum, δ, ppm: 50.17 (3-$COOCH_3$), 51.9 (2-$COOCH_3$), 103.2 (CH=), 120.9 q ($CF_3$, *J* 326.6 Hz), 149.2 (=CHN), 165.7 ($C^2$=O), 167.8 ($C^3$=O). $^{19}$F NMR spectrum, δ, ppm: –77.74.

**1-(Piperidin-1-yl)methanimine (9).** To a solution of 0.65 g (5 mmol) of benzoylacetylene, 0.97 g (6.5 mmol) of triflamide, and 0.09 g (0.25 mmol) of $Cu(OTf)_2$ in 15 mL of dioxane we slowly added dropwise a solution of 0.64 g (7.5 mmol) of piperidine in 5 mL of dioxane. The mixture was allowed to stand for 30 min at room temperature and then for 2 h at 60°C; therewith, the mixture changed color from green to dark yellow. After cooling to 10°C, 3 mL of 30% $H_2O_2$ was slowly added dropwise, and the mixture was stirred for 2 h at room temperature and filtered. The solvent was removed in a vacuum to leave a light yellow material. Part of the residue was distilled (bp 90–96°C/3 mmHg). However, the mixture could not be separated in this way, and therefore, compound **9** was isolated by preparative chromatography on an Agilent 1200 Preparative HPLC System. IR spectrum ($CH_2Cl_2$), ν, $cm^{-1}$: 3414 (NH), 1657 (C=N). $^1$H NMR spectrum ($CD_3CN$), δ, ppm: 1.48 m (2H, 4-$CH_2$), 1.55 and 1.66 m (4H, 3,5-$CH_2$), 3.31 and 3.40 m (4H, $NCH_2$), 6.84 br.s (1H, NH), 7.93 s (1H, CH=N). $^{13}$C NMR spectrum ($CD_3CN$), δ, ppm: 25.4 ($CH_2$), 26.0 ($CH_2$), 27.3 ($CH_2$), 41.1 ($CH_2$), 47.4 ($CH_2$), 161.9 (C=N).

**1-(Morpholin-1-yl)methanimine (10)** was prepared in a similar way in acetonitrile or ethyl methyl ketone and isolated by column chromatography on silica gel. $^1$H NMR spectrum ($CD_3CN$), δ, ppm: 3.36 m (2H, $NCH_2$), 3.45 m (2H, $NCH_2$), 3.57 m (2H, $OCH_2$), 3.62 m (2H, $OCH_2$), 7.98 s (1H, CH=N). The NH proton signal was not observed in the $^1$H NMR spectrum in acetonitrile, probably, because of fast exchange with the solvent. $^{13}$C NMR spectrum ($CD_3CN$), δ, ppm: 41.1 ($NCH_2$), 46.5 ($NCH_2$), 67.0 ($OCH_2$), 67.9 ($OCH_2$), 162.1 (C=N).

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## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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