Synthesis of CF_3-containing β-hetaryl-substituted enones

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A procedure was developed for the synthesis of previously unknown CF_3-containing β-azolyl-substituted enones by the reactions of 1,1,1-trifluoro-4-sulfonyl-3-butene-2,2-diols with various azoles. Quaternization of the azolyl group with methyl triflate afforded β-azolium-substituted enones in quantitative yields.

Key words: β-sulfonylvinyl(trifluoromethyl)methanediols, azoles, enones, methyl triflate, azolium cation, *ab initio* calculations, nucleophilic substitution.

β-Azolyl vinyl ketones attract attention of chemists as promising equivalents of the corresponding acylvinyl cations.[1,2] Several procedures have been developed for their synthesis.[3—10] The azolyl group in β-azolyl-substituted enones can be replaced under the action of nucleophiles,[11] the reaction being substantially accelerated by quaternization of the azolyl group with diiodomethane.[12,13] However, neither CF_3-containing β-azolyl-substituted enones nor β-azolium-substituted enones have been described.

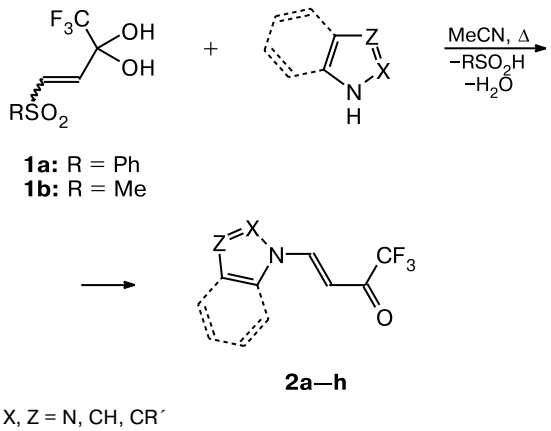
Earlier, we have studied the structures[14] and synthetic application of β-trifluoroacetylvinyl sulfones[15—19] and developed a procedure for the synthesis of CF_3-containing β-enaminoketones involving the nucleophilic substitution of the sulfonyl group at the vinyl carbon atom.[20]

In the present study, we investigated the reactions of readily accessible and stable sulfones **1a,b** [14] with various azoles. It was found that sulfones **1a,b** readily reacted with pyrazoles, imidazoles, triazoles, and their benzo analogs to give the corresponding β-azolyl-substituted enones **2a—h** in 47—92% yields (Scheme 1). The reactions proceeded stereoselectively to form only *E* isomers of enones (Table 1).

Sulfone **1b** is a less reactive electrophile than sulfone **1a**. Hence, it is necessary to use more reactive sulfone **1a** in the reactions with low-nucleophilic 2-(trifluoromethyl)-1*H*-benzimidazole for the preparation of product **2f** in good yield (72%),. It should also be noted that the reaction with imidazole proceeded at room temperature but the resulting β-imidazolyl-substituted enone **2g** was very unstable and underwent rapid polymerization. Tetrazoles were not involved in the reactions with sulfones **1a,b** even upon prolonged refluxing.

The reaction of benzotriazole with sulfone **1b** in acetonitrile at 0 °C followed by a slow increase in the temperature to 20 °C afforded compound **3**, which is an adduct of the azole at the C=C bond of vinyl sulfone. Ap-

Scheme 1



Scheme 2

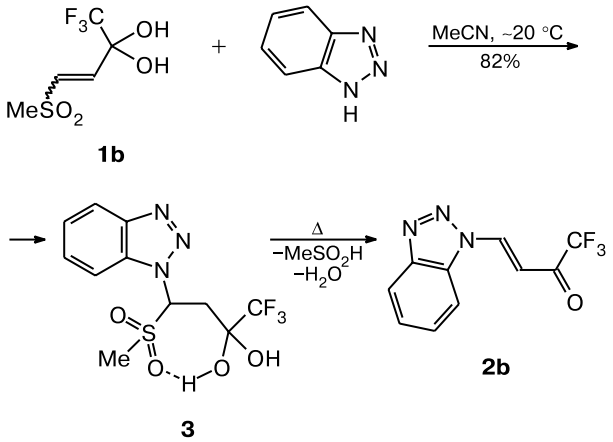


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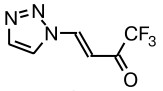
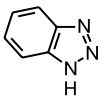
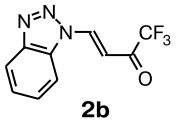
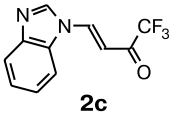
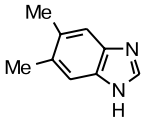
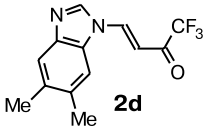
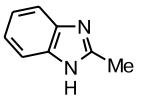
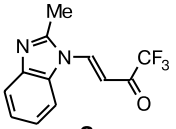
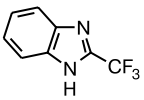
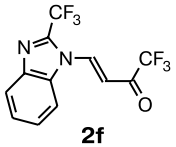
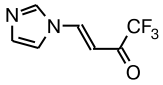
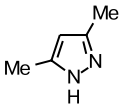
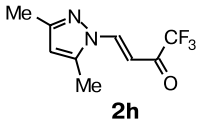
Table 1. Reactions of sulfones **1a,b** with azoles

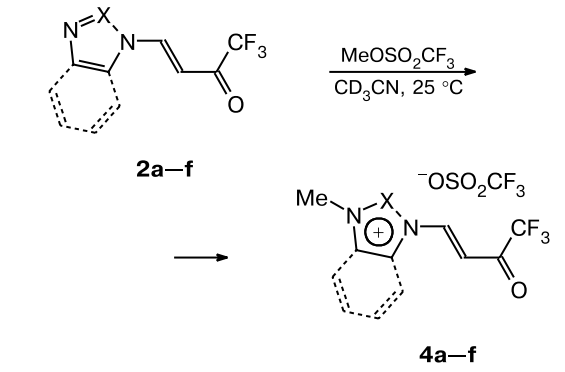
Azole	Product	Yield (%)*
	 **2a**	80 (85)
	 **2b**	92 (88)
	 **2c**	84 (81)
	 **2d**	84 (79)
	 **2e**	85 (80)
	 **2f**	72 (47)
	 **2g**	70 (60)
	 **2h**	90 (92)

* From sulfones **1a** (**1b**).

parently, this adduct is an intermediate in the synthesis of ketone **2b** and is converted into the latter with elimination of methanesulfinic acid and water upon heating of the reaction mixture (Scheme 2). Adduct **3** exists exclusively in the diol form due, apparently, to hydrogen bonding between the hydroxy and sulfonyl groups.

Since quaternization of the azolyl group increases the electrophilicity of β-azolyl-substituted enones,[11—13,21] we examined the possibility of preparing the quaternary salts from β-azolyl-substituted enones **2a—h**. It appeared that treatment of compounds **2a—f** with methyl triflate in acetonitrile at room temperature gave rise to salts **4a—f** in quantitative yields (Scheme 3).

Scheme 3

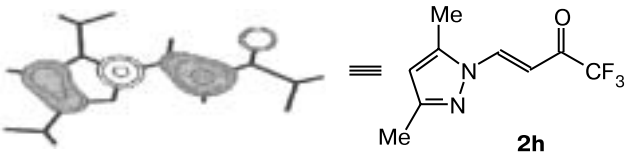


By contrast, β-pyrazolyl-substituted enone **2h** did not react with methyl triflate even upon prolonged refluxing. To explain the difference in the behavior of enones **2a—h**, we carried out quantum-chemical calculations of their nearly planar structures. The calculations were performed with the use of the PC-GAMESS program[22,23] at the RHF/6-31G* level, which provides (according to our earlier data) an adequate description of the reactivities of acceptor-dienophiles, *viz.*, (trifluoroacetyl)ethylene derivatives.[24] Stability of the results of optimization was confirmed by calculations of the eigenvalues of the Hessian of the total energy. All the structures under consideration correspond to minima on the potential energy surface.

The HOMO energy characterizes the nucleophilicity of a compound as a whole, whereas the orbital coefficients help in estimating the relative activities of atoms.[25] The fact that β-pyrazolyl-substituted enone **2h** is not involved in the reaction can be attributed to the very small orbital coefficient on the nitrogen atom in **2h**

Table 2. Energies (E) and the atomic contributions A(X) and A(Z) for HOMOs of β-azolyl-substituted enones **2a—h**

2	A(X)	A(Z)	E_{HOMO} /eV
	rel. units		
a	0.205	0.176	−10.05
b	0.044	0.205	−9.10
c	0.081	0.147	−8.86
d	0.169	0.255	−8.52
e	0.292	0.179	−8.74
f	0.034	0.188	−9.16
g	0.320	0.048	−9.52
h	0.025	0.322	−9.06



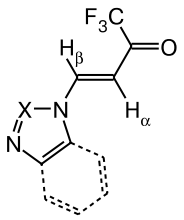
2h

Fig. 1. Schematic representation of the highest occupied molecular orbital in structure **2h**.

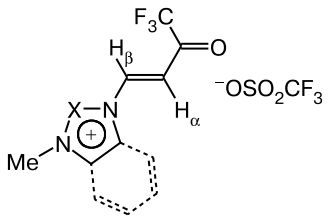
(A(X) = 0.025) compared to those in enones **2a—g** (Table 2, Fig. 1).

The structures of compounds **2** and **4** were confirmed by the data from ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectra, there is a substantial difference in the signals for the α-hydrogen atoms in the corresponding compounds **2** and **4** (Δδ = 0.27—0.45), whereas the shifts of the β-hydrogen atoms are virtually identical. There is also a substantial difference in the shifts of the protons H_X (Δδ = 1.50—1.52) for X = CH (compounds **2c,d/4c,d**) (Scheme 4).

Scheme 4



2a—f



4a—f

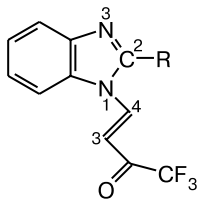
Compound	δH		ΔδH	
	H_α	H_β	H_α	H_β
2a—f	6.95—7.39	8.32—8.79	(−0.12)—0.07	0.27—0.45
4a—f	7.33—7.68	8.20—8.80		

Note. At X = CH, $\Delta\delta H_X$ = 1.50—1.52.

Table 3. Energies of LUMOs for planar structures **2a—g** and **4a—g**

Compound	E_{LUMO}/eV	
	2	**4**
a	1.17	−3.06
b	1.28	−3.17
c	1.48	−2.52
d	1.55	−2.19
e	1.60	−2.14
f	1.30	−2.81
g	1.44	−2.48

The LUMO energies of β-azolyl-substituted enones **2a—g** and the corresponding salts **4a—g** characterize their electrophilicity. The presence of a positive charge in salts **4a—g** leads to a substantial (by 3.74—4.45 eV) decrease in the LUMO energy compared to neutral molecules **2a—g**. Hence, salts **4a—g** hold promise as dieno- and electrophiles (Table 3).



2c,e,f, 4c,e,f

According to the results of calculations, the conjugation between the azole group and the (trifluoroacetyl)vinyl substituent in *N*-methylated azoles **4a—f** is substantially weakened, which is manifested in elongation of the C(4)—N(1) and C(2)—N(3) bonds by 0.04—0.06 Å and shortening of the C(3)—C(4) and N(1)—C(2) bonds by 0.01—0.02 and 0.05—0.06 Å, respectively. These facts reflect a more pronounced delocalization of the electron density in neutral compounds **2** compared to the corresponding charged salts **4**. The bond lengths in the calculated structures are given in Table 4.

Based on the calculated LUMO energies, one would expect that salt **4f** will be the most reactive dienophile among methylated benzimidazole derivatives **4c—f** due to the presence of the trifluoromethyl group in the benzimidazole moiety. However, the larger bond angles (see

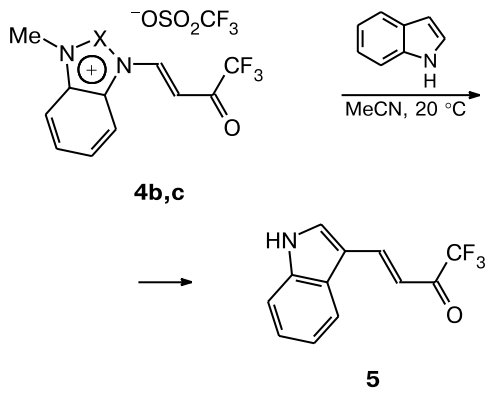
Table 4. Calculated bond lengths (d) and bond angles (ω) for optimized structures **2c,e,f** and **4c,e,f** (R = H (**c**), Me (**e**), CF_3 (**f**))

Compound	d (Δd)/Å				ω/deg		
	C(3)—C(4)	C(4)—N(1)	N(1)—C(2)	C(2)—N(3)	C(3)—C(4)—N(1)	C(4)—N(1)—C(2)	N(1)—C(2)—R
2c	1.3351	1.3691	1.3854	1.2696	127.3	128.2	121.0
4c	1.3197	1.4107	1.3262	1.3048	126.1	127.3	124.5
	(0.0154)	(−0.0416)	(0.0592)	(−0.0352)			
2e	1.3368	1.3698	1.4014	1.2737	130.4	131.3	124.3
4e	1.3201	1.4093	1.3403	1.3161	129.3	130.1	126.3
	(0.0167)	(−0.0341)	(0.0611)	(−0.0424)			
2f	1.3305	1.3823	1.3915	1.2681	131.0	133.4	125.0
4f	1.3176	1.4429	1.3359	1.3115	131.3	132.8	124.4
	(0.0129)	(−0.0606)	(0.0556)	(−0.0434)			

Table 4) in structure **4f** compared to those in structures **4c** and **4e** indicate that the steric repulsion between the (trifluoroacetyl)vinyl group and the substituents at position 2 of the benzimidazole moiety is increased in the order H < Me < CF_3. This fact, along with the above-mentioned weakening of conjugation, are responsible for a nonplanar structure of compound **4f**. The optimization of the *gauche* conformation of **4f** led to the structure with the C(2)—N(1)—C(4)—C(3) dihedral angle of 68°, the total energy being 4.1 kcal mol^{-1} lower than that of the planar form. The LUMO energy for the *gauche* conformation of **4f** is −2.26 eV, which is 0.55 eV higher than the corresponding value for the planar form. This is evidence that the *gauche* conformation is less electrophilic than the planar form.

To confirm experimentally the high electrophilicity of *N*-methylated cations **4a—f**, we studied the reactions of salts **4b,c** with indole. These reactions proceeded at room temperature in a few minutes to give the corresponding unsaturated ketone **5** in quantitative yield (Scheme 5).[15]

Scheme 5



To summarize, the reactions of *gem*-diols **1a,b** with various azoles proceed under mild conditions to give exclusively *E* isomers. This fact offers possibilities of preparing previously unknown trifluoroacetylvinyl-substituted azoles. Quaternization of the azolyl group with methyl triflate leads to a substantial decrease in the LUMO energy. The high electrophilicity of the resulting reagents was confirmed experimentally.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on Bruker AC 200P (200 and 50 MHz, respectively) and Varian VXR-400 (400 and 100 MHz, respectively) specrometers in $CDCl_3$ and CD_3CN with $SiMe_4$ as the internal standard. The IR spectra were measured on a UR-20 spectrometer in Nujol mulls. Thin-layer chromatography was carried out on Silufol UV-254 plates; visualization was perfromed with an acidified $KMnO_4$ solution and iodine vapor.

Synthesis of β-azolyl-substituted enones 2a—h (general procedure). Azole (1 mmol) was added to a solution of sulfone **1a,b** (1 mmol) in acetonitrile (15 mL) at ~20 °C. The reaction mixture was refluxed with stirring (the reaction with imidazole was performed at ~20 °C). The course of the reactions was monitored by TLC. The reaction time (on the average, 1 h) depends on the reactivity of azole. The β-azolyl-substituted enones were isolated by column chromatography on silica gel (dichlromethane as the eluent).

1,1,1-Trifluoro-(*E*)-4-(1*H*-1,2,3-triazol-1-yl)but-3-en-2-one (2a). The yield was 80% (85%), m.p. 82—84 °C. Found (%): C, 37.50; H, 2.32. $C_6H_4F_3N_3O$. Calculated (%): C, 37.71; H, 2.11. IR, ν/cm^{-1}: 1670. ^1H NMR (400 MHz, CD_3CN), δ: 8.66 (br.s, 1 H, Ar); 8.38 (d, 1 H, CH=, *J* = 13.8 Hz); 8.11 (br.s, 1 H, Ar); 7.12 (d, 1 H, CH=, *J* = 13.8 Hz). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.7 (C=O, *J* = 35.9 Hz); 155.2, 148.7, 141.2, 117.0 (CF_3, *J* = 288.1 Hz); 108.2.

(*E*)-4-(1*H*-1,2,3-Benzotriazol-1-yl)-1,1,1-trifluorobut-3-en-2-one (2b). The yield was 92% (88%), m.p. 114—116 °C. Found (%): C, 49.57; H, 2.62. $C_{10}H_6F_3N_3O$. Calculated (%): C, 49.80; H, 2.51. IR, ν/cm^{-1}: 1675. ^1H NMR (400 MHz, CD_3CN), δ: 8.79 (d, 1 H, CH=, *J* = 14.0 Hz); 8.38 (d, 1 H, Ar, *J* = 8.3 Hz); 7.98 (d, 1 H, Ar, *J* = 8.4 Hz); 7.73 and 7.56 (both t, 1 H each, Ar, *J* = 7.7 Hz); 7.39 (dd, 1 H, CH=, *J* = 14.0 Hz, *J* = 0.7 Hz). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.6 (C=O, *J* = 35.8 Hz); 147.6, 140.3, 132.9, 131.1, 127.2, 121.5, 117.0 (CF_3, *J* = 287.9 Hz); 112.3, 106.3.

(*E*)-4-(1*H*-Benzimidazol-1-yl)-1,1,1-trifluorobut-3-en-2-one (2c). The yield was 84% (81%), m.p. 108—110 °C. Found (%): C, 55.07; H, 3.11. $C_{11}H_7F_3N_2O$. Calculated (%): C, 55.01; H, 2.94. IR, ν/cm^{-1}: 1670. ^1H NMR (400 MHz, CD_3CN), δ: 8.36 (d, 1 H, CH=, *J* = 14.1 Hz); 8.25 (s, 1 H, Ar); 7.79 and 7.64 (both m, 1 H each, Ar); 7.37 (m, 2 H, Ar); 6.93 (d, 1 H, CH=, *J* = 14.1 Hz). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.6 (C=O, *J* = 35.8 Hz); 147.6, 140.3, 132.9, 131.1, 127.2, 121.5, 117.0 (CF_3, *J* = 288.0 Hz); 112.3, 106.3.

(*E*)-4-(5,6-Dimethyl-1*H*-benzimidazol-1-yl)-1,1,1-trifluorobut-3-en-2-one (2d). The yield was 84% (79%), m.p. 121—123 °C. Found (%): C, 58.05; H, 4.30. $C_{13}H_{11}F_3N_2O$. Calculated (%): C, 58.21; H, 4.13. IR, ν/cm^{-1}: 1670. ^1H NMR (400 MHz, CD_3CN), δ: 8.39 (d, 1 H, CH=, *J* = 14.4 Hz); 8.26, 7.54, and 7.48 (all s, 1 H each, Ar); 6.96 (d, 1 H, CH=, *J* = 14.4 Hz); 2.38 and 2.33 (both s, 3 H each, Me). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.4 (C=O, *J* = 35.8 Hz); 144.3, 143.7, 141.8, 135.8, 135.2, 131.2, 121.8, 117.5 (CF_3, *J* = 288.3 Hz); 113.5, 103.3, 20.4, 20.2.

1,1,1-Trifluoro-(*E*)-4-(2-methyl-1*H*-benzimidazol-1-yl)but-3-en-2-one (2e). The yield was 85% (80%), m.p. 119—121 °C. Found (%): C, 56.53; H, 3.72. $C_{12}H_9F_3N_2O$. Calculated (%): C, 56.70; H, 3.57. IR, ν/cm^{-1}: 1670. ^1H NMR (400 MHz, CD_3CN), δ: 8.34 (d, 1 H, CH=, *J* = 14.1 Hz); 7.78 and 7.63 (both m, 1 H each, Ar); 7.37 (m, 2 H, Ar); 6.95 (d, 1 H, CH=, *J* = 14.1 Hz); 2.69 (s, 3 H, Me). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.9 (C=O, *J* = 35.9 Hz); 155.1, 144.9, 142.1, 133.6, 125.8, 125.5, 120.7, 117.2 (CF_3, *J* = 288.1 Hz); 114.2, 103.7, 14.9.

1,1,1-Trifluoro-(*E*)-4-[2-(trifluoromethyl)-1*H*-benzimidazol-1-yl]but-3-en-2-one (2f). The yield was 72% (47%), m.p. 141—143 °C. Found (%): C, 46.55; H, 2.11. $C_{12}H_6F_6N_2O$. Calculated (%): C, 46.77; H, 1.96. IR, ν/cm^{-1}: 1680. ^1H NMR

(400 MHz, CD_3CN), δ: 8.32 (d, 1 H, CH=, J = 14.0 Hz); 7.95 (d, 1 H, Ar, J = 8.4 Hz); 7.91 (d, 1 H, Ar, J = 8.0 Hz); 7.62 (t, 1 H, Ar, J = 8.0 Hz); 7.62 (t, 1 H, Ar, J = 8.4 Hz); 7.13 (d, 1 H, CH=, J = 14.0 Hz). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.8 (C=O, J = 35.8 Hz); 142.7, 139.4, 134.2, 128.8, 127.1, 125.0, 123.1, 118.4 (CF_3, J = 290.2 Hz); 117.5 (CF_3, J = 288.3 Hz); 115.1, 109.3.

1,1,1-Trifluoro-(*E*)-4-(1*H*-imidazol-1-yl)but-3-en-2-one (2g). The yield was 70% (60%), red oil. Found (%): C, 44.01; H, 2.49. $C_7H_5F_3N_2O$. Calculated (%): C, 44.22; H, 2.65. IR, ν/cm^{-1}: 1675. ^1H NMR (400 MHz, CD_3CN), δ: 8.17 (d, 1 H, CH=, J = 13.8 Hz); 7.92, 7.36, and 7.24 (all br.s, 1 H each, Ar); 6.63 (d, 1 H, CH=, J = 13.8 Hz). ^{13}C NMR (100 MHz, CD_3CN), δ: 179.3 (C=O, J = 36.6 Hz); 140.4, 139.0, 132.7, 116.5 (CF_3, J = 288.1 Hz); 116.2, 105.1.

(*E*)-4-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-1,1,1-trifluorobut-3-en-2-one (2h). The yield was 90% (92%), m.p. 94—96 °C. Found (%): C, 49.39; H, 4.01. $C_9H_9F_3N_2O$. Calculated (%): C, 49.55; H, 4.16. IR, ν/cm^{-1}: 1670. ^1H NMR (400 MHz, CD_3CN), δ: 8.03 (d, 1 H, CH=, J = 13.7 Hz); 6.96 (d, 1 H, CH=, J = 13.7 Hz); 6.03 (br.s, 1 H, Ar); 2.36 (s, 3 H, Me); 2.26 (br.s, 3 H, Me). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.2 (C=O, J = 36.2 Hz); 155.4, 143.2, 139.6, 116.9 (CF_3, J = 287.9 Hz); 110.1, 102.8, 13.9, 10.7.

4-(1*H*-1,2,3-Benzotriazol-1-yl)-1,1,1-trifluoro-4-(methylsulfonyl)-2,2-butanediol (3). Benzotriazole (1 mmol) was added to a solution of sulfone **1b** (1 mmol) in acetonitrile (15 mL) at 0 °C. The reaction mixture was slowly warmed to ~20 °C and kept for 12 h. The crystals of diol **3** that precipitated were filtered off, washed with cold acetonitrile (5 mL), and dried in air. The yield was 82%, m.p. 180—181 °C. Found (%): C, 38.77; H, 3.32. $C_{11}H_{12}F_3N_3O_4S$. Calculated (%): C, 38.94; H, 3.56. IR, ν/cm^{-1}: 3150 (C—OH). ^1H NMR (400 MHz, $CDCl_3$), δ: 8.04, 7.90, 7.61, and 7.47 (all m, 1 H each, Ar); 6.35 (dd, 1 H, CH); 3.60 (s, 1 H, Me); 3.25 (m, 2 H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 155.2, 148.7, 141.2, 117.0 (CF_3, J = 288.1 Hz); 108.2, 80.7 (C—OH, J = 35.0 Hz); 54.5.

Quaternization of the azolyl group (general procedure). Methyl trifluoromethanesulfonate (0.1 mmol) was added to a solution of β-azolyl-substituted enone **2a—f** (0.1 mmol) in CD_3CN (0.5 mL) in an NMR tube. The reaction mixture was kept at ~20 °C for 1—10 min and then the ^1H and ^{13}C NMR spectra were recorded.

1-Methyl-3-[(*E*)-4,4,4-trifluoro-3-oxobuten-1-yl]-3*H*-1,2,3-triazolium trifluoromethanesulfonate (4a). ^1H NMR (400 MHz, CD_3CN), δ: 8.92 and 8.84 (both br.s, 1 H each, Ar); 8.41 and 7.39 (both d, 1 H each, CH=, J = 13.8 Hz); 4.00 (s, 3 H, Me). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.7 (C=O, J = 37.6 Hz); 148.2, 147.3, 139.7, 122.4 (CF_3, J = 319.1 Hz); 117.1 (CF_3, J = 288.8 Hz); 115.5, 36.7.

1-Methyl-3-[(*E*)-4,4,4-trifluoro-3-oxobuten-1-yl]-3*H*-1,2,3-benzotriazolium trifluoromethanesulfonate (4b). ^1H NMR (400 MHz, CD_3CN), δ: 8.80 (d, 1 H, CH=, J = 13.9 Hz); 8.40 (d, 1 H, Ar, J = 8.3 Hz); 8.26 (d, 1 H, Ar, J = 8.4 Hz); 8.03 (m, 2 H, Ar); 7.68 (dd, 1 H, CH=, J = 13.9 Hz); 4.68 (s, 3 H, Me). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.6 (C=O, J = 37.7 Hz); 138.3, 137.8, 136.4, 134.9, 133.5, 132.8, 122.6 (CF_3, J = 319.2 Hz); 117.2 (CF_3, J = 288.0 Hz); 116.2, 115.4, 40.8.

1-Methyl-3-[(*E*)-4,4,4-trifluoro-3-oxobuten-1-yl]-3*H*-benzimidazolium trifluoromethanesulfonate (4c). ^1H NMR (400 MHz, CD_3CN), δ: 9.76 (s, 1 H, Ar); 8.43 (d, 1 H, CH=, J = 14.1 Hz); 7.92 and 7.76 (both m, 1 H each, Ar); 7.64 (m, 2 H, Ar); 7.41 (d, 1 H, CH=, J = 14.1 Hz); 4.10 (s, 3 H, Me). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.6 (C=O, J = 37.0 Hz); 143.0, 140.3, 139.8, 139.3, 132.4, 130.5, 122.4 (CF_3, J = 319.0 Hz); 117.5 (CF_3, J = 288.4 Hz); 115.3, 115.0, 113.0, 35.6.

1,5,6-Trimethyl-3-[(*E*)-4,4,4-trifluoro-3-oxobuten-1-yl]-3*H*-benzimidazolium trifluoromethanesulfonate (4d). ^1H NMR (400 MHz, CD_3CN), δ: 9.78 (s, 1 H, Ar); 8.44 (d, 1 H, CH=, J = 14.3 Hz); 7.92 (s, 1 H, Ar); 7.74 (s, 1 H, Ar); 7.40 (d, 1 H, CH=, J = 14.3 Hz); 4.10, 2.44, and 2.42 (all s, 3 H each, Me). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.8 (C=O, J = 36.8 Hz); 142.8, 140.9, 140.3, 139.5, 132.4, 130.1, 122.5 (CF_3, J = 318.8 Hz); 117.6 (CF_3, J = 288.8 Hz); 115.3, 115.2, 113.2, 35.7, 21.1, 21.0.

1,2-Dimethyl-3-[(*E*)-4,4,4-trifluoro-3-oxobuten-1-yl]-3*H*-benzimidazolium trifluoromethanesulfonate (4e). ^1H NMR (400 MHz, CD_3CN), δ: 8.28 (d, 1 H, CH=, J = 14.1 Hz); 8.03 and 7.89 (both m, 1 H each, Ar); 7.72 (m, 2 H, Ar); 7.33 (d, 1 H, CH=, J = 14.1 Hz); 4.02 and 2.94 (both s, 3 H each, Me). ^{13}C NMR (100 MHz, CD_3CN), δ: 181.0 (C=O, J = 39.5 Hz); 156.1, 139.3, 133.8, 131.1, 129.6, 129.2, 122.4 (CF_3, J = 319.0 Hz); 118.1, 117.3 (CF_3, J = 288.2 Hz); 115.6, 115.2, 34.1, 13.2.

1-Methyl-2-(trifluoromethyl)-3-[(*E*)-4,4,4-trifluoro-3-oxobuten-1-yl]-3*H*-benzimidazolium trifluoromethanesulfonate (4f). ^1H NMR (400 MHz, CD_3CN), δ: 8.20 (d, 1 H, CH=, J = 14.0 Hz); 8.09 and 7.92 (both m, 2 H each, Ar); 7.43 (d, 1 H, CH=, J = 14.0 Hz); 4.30 (s, 3 H, Me). ^{13}C NMR (100 MHz, CD_3CN), δ: 180.3 (C=O, J = 37.7 Hz); 159.6, 137.9, 134.1, 132.3, 131.6, 126.5, 122.4, 122.4 (CF_3, J = 319.0 Hz); 118.8 (CF_3, J = 290.0 Hz); 117.1 (CF_3, J = 288.0 Hz); 116.2, 36.6.

1,1,1-Trifluoro-(*E*)-4-(3-indolyl)but-3-en-2-one (5). Methyl trifluoromethanesulfonate (1 mmol) was added dropwise to a solution of β-azolyl-substituted enone **2b,c** (1 mmol) in anhydrous MeCN (5 mL). The reaction mixture was kept at ~20 °C for 5 min. Then a solution of indole (1 mmol) in anhydrous MeCN (10 mL) was added dropwise. The course of the reaction was monitored by TLC. The reaction was brought to completion during 10 min. Compound **5** was isolated by column chromatography on silica gel. In both cases, the yields were close to quantitative. The IR and NMR spectra are identical with those published in the literature.[26]

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