Preparation of *N*-(α,β-unsaturated acyl)-sulfonamides

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Dedicated to Prof. Alexander Pozharskii on the occasion of his 70 th anniversary

Abstract

N-(α,β-Unsaturated acyl)sulfonamides are prepared (i) by the *N*-acylation of sulfonamides with *N*-(α,β-unsaturated acyl)benzotriazoles in the presence of potassium *tert*-butoxide or sodium hydride and (ii) by reactions of appropriate α,β-unsaturated carboxamides with sulfonylbenzotriazoles in the presence of sodium hydride.

Keywords: Acylating agent, *N*-(α,β-unsaturated acyl)sulfonamides, α,β-unsaturated carboxamides, β-heteroarylacroylbenzotriazoles

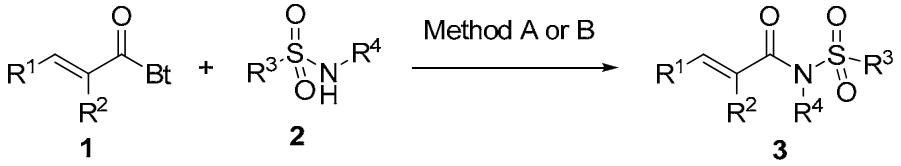
Introduction

N-(α,β-Unsaturated acyl)sulfonamides are plant disease control agents,[1] selective EP_3 antagonists,[2,3] anti-inflammatory agents[3] and useful intermediates in asymmetric 1,4-addition,[4a-4c] for the synthesis of substituted *β*-lactams,[4d] γ-butyrolactams,[4e] and 2-quinolinones.[5a,5b]

Published preparations of *N*-(α,β-unsaturated acyl)sulfonamides include (i) the acylation of sulfonamides (RSO_2NH_2) by (a) unsaturated acyl chlorides (R'CH=CHCOCl) in the presence of a base (such as triethylamine,[3,5a] *n*-butyllithium,[4d] or NaH [6,7]) or a copper powder catalyst;[8] (b) unsaturated carboxylic acids via mixed anhydride in the presence of Lewis acid catalyst;[9] (ii) reactions of aryl isocyanates (RSO_2NCO) with 1-alkenyltrialkylstannanes, di-1-alkenyldibutylstannanes in the presence of aluminium trichloride[10a] or with substituted alkenes;[10b] (iii) reactions of sulfonamide with the Wittig adduct obtained from (triphenylphosphoranylidene)ketene and an aldehyde; [11] (iv) coupling of unsaturated acids with sulfonamides in the presence of 1-ethyl-3-(3'-dimethylaminopropyl)carbodiimide (EDCI);[2,3,12] (v) dehydrogenation of the corresponding saturated analogs by using LDA followed by *N*-*tert*-butylbenzenesulfinimidoyl chloride.[5a,13]

Herein, we report the acylation of sulfonamides with stable, crystalline *N*-(α,β-unsaturated acyl)benzotriazoles to give *N*-(α,β-unsaturated acyl)sulfonamides.

Table 1. Preparation of *N*-(α,β-unsaturated acyl)sulfonamides (**3**)



Bt = Benzotriazol-1-yl

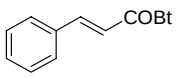
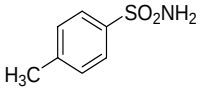
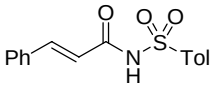
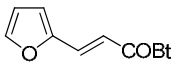
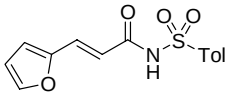
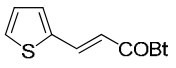
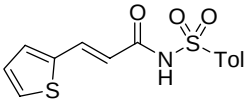
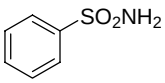
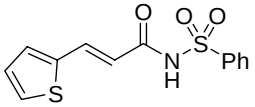
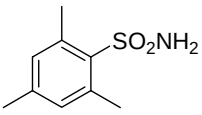
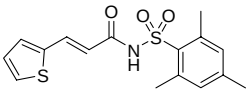
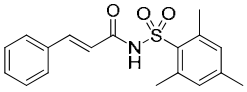
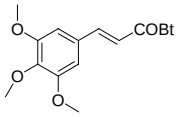
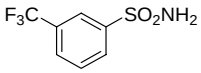
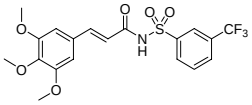
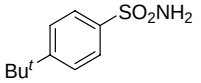
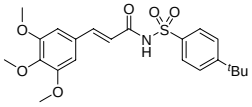
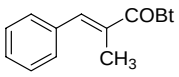
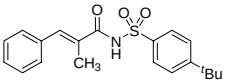
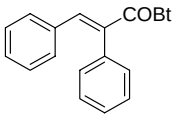
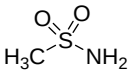
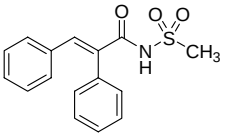
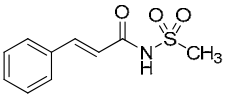
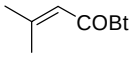
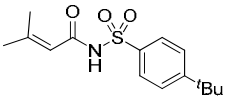
Entry	Compounds			Method[a]	Yield (%)[b]	Mp (°C)	Lit. mp (°C)
1	 **1a**	 **2a**	 **3a**	A	80	136–137	137–138
2	 **1b**	**2a**	 **3b**	A	89	149–150	Novel
3	 **1c**	**2a**	 **3c**	A	91	167–169	Novel
4	**1c**	 **2b**	 **3d**	A	48	143–146	Novel
5	**1c**	 **2c**	 **3e**	B[2]	87	88–91	Novel
6	**1a**	**2c**	 **3f**	B[1]	65	185–186	Novel
7	 **1d**	 **2d**	 **3g**	B[1]	84	103–104	Novel
8	**1d**	 **2e**	 **3h**	B[1]	56	98–101	Novel

Table 1. Continued

Entry	Compounds			Method[a]	Yield (%)[b]	Mp (°C)	Lit. mp (°C)
9	 **1e**	**2e**	 **3i**	B^1	84	189–190	Novel
10	 **1f**	 **2f**	 **3j**	B^1	60	198–200	Novel
11	**1a**	**2f**	 **3k**	B^1	63	167–169	Novel
12	 **1g**	**2e**	 **3l**	B^1	70	155–157	Novel

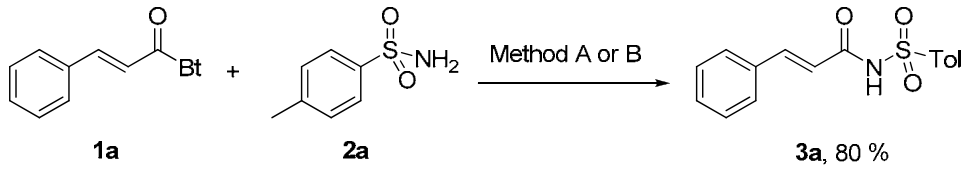
[a]Method A: KO^{t}Bu/THF, 0 °C–r.t., 3 h; Method B^1: NaH/THF, r.t., 2 h., Method B^2: NaH/THF,reflux,1h. [b]Isolated yield.

Results and Discussion

The acylating agents (**1a–g**) were prepared in 74–95 % yield from the corresponding carboxylic acids and benzotriazole with thionyl chloride.[14] Sulfonamides (**2c–e**) were prepared by the reaction of the corresponding sulfonyl chloride with ammonia (28 % solution).[15]

N-Acylation of *p*-toluene sulfonamide (**2a**) with cinnamoyl benzotriazole (**1a**) in the presence of sodium hydride failed at 0 °C but occurred at higher temperature.[16] When, *n*-butyl lithium was used in acylation of **2a** with **1a**, at -78 °C to r.t. for 12 h, a mixture of products was obtained one of which was the conjugate addition product as detected by ^{1}H NMR. This reaction was repeated in the presence potassium *tert*-butoxide at 0 °C to room temperature (Method A), which gave the desired α,β-unsaturated acyl sulfonamide **3a** in 80 % yield. A similar result was obtained when sodium hydride was used as base at room temperature (Method B) or by refluxing (Method B^2) (Scheme 1). Under the optimized conditions (Method A, B^1 or B^2), *N*-(α,β-unsaturated acyl)sulfonamides (**3**) were obtained in good yields from the reaction of a range of acylating agents (**1**) and sulfonamides (**2**) (Table 1). β-Heteroarylacroyl benzotriazoles also react readily with sulfonamides (Table 1, entries 2–5). Methyl substituents at both the ortho positions of

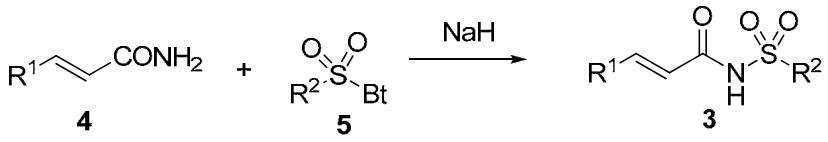
sulfonamide group did not hinder the reaction (Table 1, entry 5). Electronic variation in the sulfonamide derivatives also affected relatively little efficiency of the reaction (Table 1, entry 7 and 8). Methyl or phenyl groups at the α-position to the carbonyl group of the acylating agent did not prevent the formation of the corresponding substituted sulfonamide (Table 1, entry 9 and 10). Alkenyl acylating agent (**1g**) also reacted with sulfonamide (**2e**) (Table 1, entry 12).

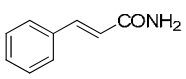
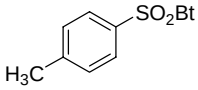
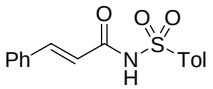
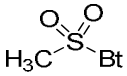
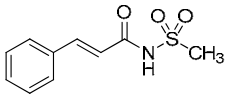
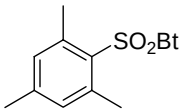
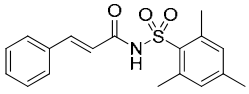
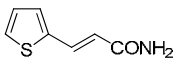
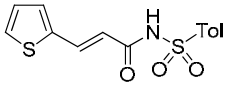
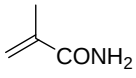
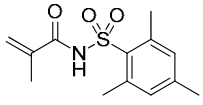


Method A: KO^{t}Bu/THF, 0 °C-r.t., 3h; Method B^1: NaH/THF, r.t. 2h,Method B^2: NaH/THF, reflux 1h

Scheme 1

Table 2. Preparation of *N*-(α,β-unsaturated acyl)sulfonamides (**3**)



Entry	Compounds			Method[a]	Yield (%)[a]	Mp (°C)	Lit. mp (°C)
1	 **4a**	 **5a**	 **3a**	B^1	71	137–138	137–138
2	**4a**	 **5b**	 **3k**	B^1	25	167–169	Novel
3	**4a**	 **5c**	 **3f**	B^1	30	185–186	Novel
4	 **4b**	**5a**	 **3m**	B^1	30	167–169	Novel
5	 **4c**	**5c**	 **3n**	B^1	30	196–198	Novel

[a]Isolated yield.

An alternative route to **3** involves reaction of α,β-unsaturated carboxamide (**4**) with sulfonyl benzotriazoles (**5**) in the presence of a base. The reaction of cinnamamide (**4a**), with *p*-toluenesulfonylbenzotriazole (**5a**) in the presence of potassium *tert*-butoxide at room temperature, failed to give product in 24 h. However, reaction of **4a** with **5a** in the presence of sodium hydride at room temperature for 1 h, gave the expected *N*-(α,β-unsaturated acyl)sulfonamide (**3a**) in 71 % yield. Similarly, carboxamides (**4a-c**) reacted with sulfonylbenzotriazoles (**5a-c**) as shown in the Table 2, to provide the products **3k**, **3f**, **3m** and **3n** in 25-30 % yields.

Conclusions

A general method for the preparation of *N*-(α,β-unsaturated acyl)sulfonamides from the corresponding sulfonamides by *N*-acylation with *N*-(α,β-unsaturated acyl)benzotriazoles has been developed. An alternative route involves reaction of an unsaturated carboxamide with the sulfonylbenzotriazoles. This method involves readily available starting materials, stable and crystalline benzotriazole derivatives and short reaction times.

Experimental Section

General Procedures. All reactions were carried out under nitrogen atmosphere and solvents were dried according to standard procedures. Carboxylic acids, sulfonamides, sulfonyl chlorides, benzotriazoles and potassium *tert*-butoxide were purchased and used without further purification. The strength of *n*-BuLi used was 1.6 M. Purification by column chromatography was carried out using silica gel. Melting points are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ (with TMS for ^{1}H and chloroform-*d* for ^{13}C as the internal standard). Elemental analyses were carried out by the Analytical Laboratory in the Center for Heterocyclic Compounds, Department of Chemistry, University of Florida.

General procedure for preparation of unsaturated *N*-acylbenzotriazoles 1a–g

To a solution of 1*H*-1,2,3-benzotriazole (11.9 g, 100 mmol) in CH_2Cl_2 (125 mL), $SOCl_2$ (1.9 mL, 25 mmol) was added drop wise with stirring at room temperature. After 30 min unsaturated acid (25 mmol) was added. After 3 h, the solid was filtered and washed with CH_2Cl_2 (50 mL). The combined filtrate was washed with 2N NaOH (2 × 100 mL), water (100 mL) and brine (30 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the solvent evaporated under vacuum to obtain a solid, which was recrystallized to afford *N*-acylbenzotriazoles (**1a–g**).

(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-3-phenyl-2-propen-1-one (1a). Yield 94 %; colorless needles (from hexane/AcOEt); mp 152–153 °C (lit.[14] mp 151–152 °C).

(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-3-(2-furyl)-2-propen-1-one (1b). Yield 90 %; light pink needles (from hexane/ CH_2Cl_2); mp 142–143 °C (lit.[14] mp 142–144 °C).

(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-3-(2-thienyl)-2-propen-1-one (1c). Yield 95 %; yellow plates (from hexane/AcOEt); mp 169–170 °C (lit.[14] mp 169–170 °C).
(*E*)-1-(1*H*-1,2,3-Benzotriazole-1-yl)-3-(3,4,5-trimethoxyphenyl)-2-propen-1-one (1d). Yield 74%; yellow crystals (from hexane / CH_2Cl_2); mp 136–137 °C (lit.[17] mp 136–137 °C).
(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-2methyl-3-phenyl-2-propen-1-one (1e). Yield 78 %; cream plates (from hexane / CH_2Cl_2); mp 50.5–51.5 °C). ^{1}H NMR δ 2.46 (s, 3H), 7.36-7.48 (m, 3H), 7.52-7.57 (m, 3H), 7.66-7.72 (m, 2H), 8.15-8.18 (m, 1H) 8.29-8.31 (m, 1H); ^{13}C NMR δ 16.0, 114.6, 120.1, 126.1, 128.5, 129.0, 129.8, 129.9, 130.1, 132.3, 135.1, 143.6, 145.8, 169.0. Anal. Calcd for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96. Found: C, 73.05; H, 4.93; N, 15.93.
(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-2,3-diphenyl-2-propen-1-one (1f). Yield 85 %; white crystals (from hexane / CH_2Cl_2); mp 133.4–135.0 °C). ^{1}H NMR δ 7.19–7.29 (m, 5H), 7.38–7.45 (m, 5H), 7.50–7.56 (m, 1H), 7.65–7.71 (m, 2H), 8.12–8.16 (m, 1H), 8.30–8.33 (m, 1H); ^{13}C NMR δ 114.6, 120.1, 126.1, 128.3, 128.5, 128.9, 129.5, 129.8, 130.2, 130.6, 132.2, 134.0, 134.3, 135.2, 142.6, 145.8, 167.8. Anal. Calcd for $C_{21}H_{15}N_3O$: C, 77.52; H, 4.65; N, 12.91. Found: C, 77.48; H, 4.52; N, 12.89.
1-(1*H*-1,2,3-Benzotriazol-1-yl)-3-methyl-2-buten-1-one (1g). Yield 95 %; colorless needle (from hexane); mp 96.0–97.0 °C (lit.[14] mp 95–97 °C).

General procedure for preparation of sulfonamides 2c–e
To a solution of a sulfonyl chloride (40 mmol) in $CHCl_3$ was added NH_3 (200 mmol, 28 % solution. After stirring vigorously at room temperature for 2 h, the reaction mixture was extracted with $CHCl_3$. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give the corresponding sulfonamide (**2c–e**).
2,4,6-Trimethylbenzenesulfonamide (2c). Yield 90 %; colorless microcrystals (from hex/EtOAc); mp 143–144 °C; (lit.[18] mp 141.5–142.5 °C).
3-(Trifluoromethyl)benzenesulfonamide (2d). Yield 82 %; colorless plates (from chloroform); mp 119–120 °C; (lit.[19] mp 111–112 °C).
4-(tert-Butyl)benzenesulfonamide (2e). Yield 80 %; white microcrystals (from hex/EtOAc); mp 133–134 °C (lit.[20] mp 133–134 °C).

General procedure for preparation *N*-(α,β-unsaturated acyl)sulfonamides 3a–l
To a suspension of potassium *t*-butoxide (0.08 g, 0.72 mmol) in THF (3 mL) at 0 °C was added a solution of sulfonamide (0.6 mmol) in THF (5 mL). The resulting mixture was stirred at room temperature for 1 h. It was again cooled to 0 °C and a solution of unsaturated *N*-acylbenzotriazole (0.6 mmol) in THF (7 mL) was added and stirred at room temperature for 3 h. The reaction was quenched with addition of saturated solution of ammonium chloride (5 mL), ethyl acetate (15 mL) was added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (15 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration the solvent was evaporated to get the crude product which was purified

by column chromatography (silica gel) eluting ethyl acetate/hexanes (1:3) to get the corresponding *N*-(α,β-unsaturated acyl)sulfonamides **3a–l** (Table 1).

4-Methyl-*N*-[(*E*)-3-phenyl-2-propenoyl]benzenesulfonamide (3a). Yield 80 %; white microcrystals (from hexane/EtOAc); mp 136–137 °C (lit.[4d] mp 137–138 °C).

***N*-[(*E*)-3-(2-Furyl)-2-propenoyl]-4-methylbenzenesulfonamide (3b).** Yield 89 %; white needles (from hexane/EtOAc); mp 149–150 °C; ^{1}H NMR δ 2.43 (s, 3H), 6.28 (d, *J* = 15.3 Hz, 1H), 6.46–6.48 (m, 1H), 6.64 (d, *J* = 3.3 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 15.3 Hz, 1H), 7.47–7.50 (m, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 8.35–8.60 (br s, 1H); ^{13}C NMR δ 21.7, 112.6, 114.7, 116.5, 128.4, 129.6, 132.0, 135.6, 145.1, 145.3, 150.4, 163.4. Anal. Calcd for $C_{14}H_{13}NO_4S$: C, 57.72; H, 4.50; N, 4.81. Found: C, 57.74; H, 4.45; N, 4.76.

4-Methyl-*N*-[(*E*)-3-(2-thienyl)-2-propenoyl]benzenesulfonamide (3c). Yield 91 %; colorless plates (from hexane/EtOAc); mp 167–169 °C; ^{1}H NMR δ 2.43 (s, 3H), 6.21 (d, *J* = 15.3 Hz, 1H), 7.04 (dd, *J* = 4.8, 3.7 Hz, 1H), 7.25 (d, *J* = 3.7 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 4.9 Hz, 1H), 7.80 (d, *J* = 15.6 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 8.54–8.76 (br s, 1H); ^{13}C NMR δ 21.6, 115.9, 128.3, 128.4, 129.5, 129.6, 132.1, 135.6, 138.3, 138.9, 145.1, 163.4. Anal. Calcd for $C_{14}H_{13}NO_3S_2$: C, 54.70; H, 4.26; N, 4.56. Found: C, 55.07; H, 4.14; N, 4.52.

***N*-[(*E*)-3-(2-Thienyl)-2-propenoyl]benzenesulfonamide (3d).** Yield 48 %; white needles (from hexane/EtOAc); mp 143–146 °C; ^{1}H NMR δ 6.24 (d, *J* = 15.2 Hz, 1H), 7.02-7.05 (m, 1H), 7.14-7.17 (m, 1H), 7.4 (d, *J* = 5.1 Hz, 1H), 7.53-7.58 (m, 2H), 7.63-7.68 (m, 1H), 7.8 (d, *J* = 15.4 Hz, 1H), 8.11-8.14 (m, 2H), 8.72 (br s, 1H); ^{13}C NMR δ 115.6, 127.6, 128.3, 128.4, 129.0, 129.5, 132.4, 134.0, 138.6, 138.6, 138.8, 163.0. Anal. Calcd for $C_{13}H_{11}NO_3S_2$: C, 53.22; H, 3.78; N, 4.77. Found: C, 53.37; H, 3.67; N, 4.71.

2,4,6-Trimethyl-*N*-[(*E*)-3-(2-thienyl)-2-propenoyl]benzenesulfonamide (3e). Yield 87 %; white powder (from hexane/EtOAc); mp 88–91 °C; ^{1}H NMR δ 2.30 (s, 3H), 2.75 (s, 6H), 6.20 (d, *J* = 15.2 Hz, 1H), 6.99 (s, 2H), 7.03-7.05 (m, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.40 (d, *J* = 4.9 Hz, 1H), 7.78 (d, *J* = 15.2 Hz, 1H), 8.65 (brs, 1H); ^{13}C NMR δ 21.1, 22.8, 115.6, 128.3, 129.4, 132.1, 132.2, 132.5, 138.4, 138.9, 140.4, 143.8, 163.4. Anal. Calcd for $C_{16}H_{17}NO_3S_2$.EtOAc: C, 56.72; H, 5.95; N, 3.31. Found: C, 56.71; H, 6.01; N, 3.25.

2,4,6-Trimethyl-*N*-[(*E*)-3-phenyl-2-propenoyl]benzenesulfonamide (3f). Yield 65 %; white powder (from hexane/EtOAc); mp 185–186 °C; ^{1}H NMR δ 2.31 (s, 3H), 2.76 (s, 6H), 6.40 (d, *J* = 15.5 Hz, 1H), 7.00 (s, 2H), 7.37-7.39 (m, 3H), 7.46-7.49 (m, 2H), 7.68 (d, *J* = 15.5 Hz, 1H), 8.62 (br s, 1H); ^{13}C NMR δ 21.1, 22.8, 117.2, 128.4, 128.9, 130.9, 132.2, 132.3, 133.7, 140.5, 143.9, 146.0, 163.7. Anal. Calcd for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25. Found: C, 65.51; H, 6.04; N, 4.10.

3-(Trifluoromethyl)-*N*-[(*E*)-3-(3,4,5-trimethoxyphenyl)-2-propenoyl]benzenesulfonamide (3g). Yield 84 %; white microcrystals (from hexane/EtOAc); mp 103–104 °C; ^{1}H NMR δ 3.85 (br s, 6H), 3.88 (br s, 3H), 6.27 (d, *J* = 15.5 Hz, 1H), 6.69 (s, 2H), 7.60 (d, *J* = 15.5 Hz, 1H), 7.73 (t, *J* = 8.41 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 8.35-8.38 (m, 2H), 8.54 (br s, 1H)); ^{13}C NMR δ 56.2, 61.0, 105.8, 116.4, 123.1 (q, *J* = 273.1 Hz), 125.4 (q, *J* = 3.4 Hz), 129.1, 129.8, 130.6 (q, *J*

= 3.4 Hz), 131.7 (q, *J* = 33.6 Hz), 132.0, 140.0, 140.8, 146.5, 153.4, 163.3. Anal. Calcd for $C_{19}H_{18}F_3NO_6S.H_2O$: C, 49.24; H, 4.35; N, 3.02. Found: C, 49.27; H, 4.08; N, 3.02.

4-(*tert*-Butyl)-*N*-[(*E*)-3-(3,4,5-trimethoxyphenyl)-2-propenoyl]benzenesulfonamide (3h). Yield 56 %; white microcrystals (from hexane/EtOAc); mp 98–101 °C; ^{1}H NMR δ 1.29 (s, 9H), 3.68 (s, 3H), 3.79 (s, 6H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.91(s, 2H), 7.50 (d, *J* = 15.8 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR δ 30.7, 35.0, 55.9, 60.1, 105.6, 118.4, 126.0, 127.5, 129.4, 136.6, 139.6, 143.9, 153.1, 156.8, 163.8. Anal. Calcd for $C_{22}H_{27}NO_6S$: C, 60.95; H, 6.28; N, 3.23. Found: C, 60.60; H, 6.63; N, 3.28.

4-(*tert*-Butyl)-*N*-[(*E*)-2-methyl-3-phenyl-2-propenoyl]benzenesulfonamide (3i). Yield 84 %; white microcrystals (from hexane/EtOAc); mp 188–190 °C; ^{1}H NMR δ 1.35 (s, 9H), 2.07 (s, 3H), 7.31-7.41 (m, 6H), 7.57 (d, *J* = 8.7 Hz, 2H), 8.07 (d, *J* = 8.7 Hz, 2H), 8.65-8.85 (br s, 1H); ^{13}C NMR δ 13.9, 31.0, 35.3, 126.0, 128.4, 128.4, 128.8, 129.6, 129.6, 134.9, 135.4, 138.1, 157.9, 166.5. Anal. Calcd for $C_{20}H_{23}NO_3S$: C, 67.20; H, 6.49; N, 3.92. . Found: C, 67.37; H, 6.67; N, 3.89.

***N*-[(*E*)-2,3-Diphenyl-2-propenoyl]methanesulfonamide (3j).** Yield 60 %; white microcrystals (from hexane/EtOAc); mp 198–200 °C; ^{1}H NMR δ 3.37 (s, 3H), 7.00 (d, *J* = 7.3 Hz, 2H), 7.15-7.23 (m, 3H), 7.28-7.30 (m, 2H), 7.50-7.52 (m, 3H), 7.60 (br s, 1H), 7.97 (s, 1H).); ^{13}C NMR δ 41.6, 128.4, 129.6, 129.7, 130.0, 130.4, 130.9, 131.4, 133.7, 133.9, 142.0, 165.2. Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65. Found: C, 64.07; H, 5.45; N, 4.49.

***N*-[(*E*)-3-Phenyl-2-propenoyl]methanesulfonamide (3k).** Yield 63 %; white microcrystals (from hexane/EtOAc); mp 167–169 °C; ^{1}H NMR δ 3.37 3.41(s, 3H),6.45 (d, *J* = 15.8 Hz, 1H), 7.41-7.43 (m, 3H), 7.53-7.56 (m, 2H), 7.80 (d, *J* = 15.8 Hz, 1H), 8.54 (br s, 1H)); ^{13}C NMR δ 41.8, 117.1, 128.5, 129.1, 131.2, 133.5, 146.6, 164.2. Anal. Calcd for $C_{10}H_{11}NO_3S$: C, 53.32; H, 4.92; N, 6.22. Found: C, 52.95; H, 4.80; N, 6.20.

4-(*tert*-Butyl)-*N*-(3-methyl-2-butenoyl)benzenesulfonamide (3l). Yield 70 %; white microcrystals (from hexane/EtOAc); mp 155–157 °C; ^{1}H NMR δ 1.34 (s, 9H), 1.87 (s, 3H), 2.13 (s, 3H), 5.57 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 8.6 Hz, 2H), 8.08 (br s, 1H); ^{13}C NMR δ 20.6, 27.7, 31.0, 35.3, 115.4, 126.0, 128.1, 135.8, 157.7, 160.4, 163.0. Anal. Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74. Found: C, 61.25; H, 7.33; N, 4.62.

General procedure for preparation of sulfonylbenzotriazoles (5a-c)

To a solution of benzotriazole was added $SOCl_2$ at rt with stirring. After half an hour, α,β-unsaturated acid was added in one portion and stirring was continued for 3 h. The precipitate was filtered off and washed with CH_2Cl_2. The filtrate was washed with $NaHCO_3$ solution, brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to obtain the corresponding sulfonylbenzotriazoles (**5a-c**).

***p*-Tolylsulfonylbenzotriazole (5a).** Yield 54 %; cream prisms (from ethyl ether); mp 128.0–129.0 °C (lit.[21] mp 133–134 °C).

1-(Methylsulfonyl)-1*H*-1,2,3-benzotriazole (5b). Yield 81 %; white flats (from benzene); mp 110.0–112.0 °C (lit.[22] mp 110.0–112.0 °C).

1-(Mesitylsulfonyl)-1*H*-1,2,3-benzotriazole (5c). Yield 85 %; white crystals (from Hex/CH_2Cl_2); mp 120.0–121.0 °C). Compound described [23] but no mp and spectra provided. ^{1}H NMR δ 2.32 (s, 3H), 2.66 (s, 6H), 7.01 (s, 2H), 7.48 (t, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 8.09-8.12 (m, 2H); ^{13}C NMR δ 21.1, 23.0, 112.3, 120.4, 125.5, 129.9, 131.4, 132.0, 132.5, 141.6, 144.8, 145.6. Anal. Calcd for $C_{15}H_{15}N_3O_2S$: C, 59.78; H, 5.02; N, 13.94 Found: C, 60.10; H, 5.03; N, 14.05.

General procedure for preparation *N*-(α,β-unsaturated acyl)sulfonamides 3a,3k,3f,3m and 3n

To a suspension of NaH (0.14 g, 3.4 mmol, 60 %) in THF (3 mL) at room temperature was added a solution of carbonyl amide (0.09 g, 1 mmol) in THF (3 mL) dropwise. The resulting mixture was stirred at room temperature for 1 h. A solution of sulfonyl-benzotriazole (0.301g, 1 mmol) in THF (5 mL) was added and stirred for 1 h. The reaction was quenched by addition of saturated solution of ammonium chloride (15 mL), ethyl acetate (15 mL) was added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (15 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration the solvent was evaporated to give the crude product which was purified by column chromatography (silica gel) eluting ethyl acetate/hexanes (1:3) to afford the corresponding *N*-(α,β-unsaturated acyl)sulfonamides (**3a**,**3k**,**3f**,**3m** and **3n**) (Table 2).

4-Methyl-*N*-[(*E*)-3-phenyl-2-propenoyl]benzenesulfonamide (3a). Yield 71 %; white microcrystals (from hexane/EtOAc); mp 137–138 °C (lit.[4d] mp 137–138 °C).

***N*-[(*E*)-3-Phenyl-2-propenoyl]methanesulfonamide (3k).** Yield 25%; white microcrystals (from hexane/EtOAc); mp 167–169 °C.

2,4,6-Trimethyl-*N*-[(*E*)-3-phenyl-2-propenoyl]benzenesulfonamide (3f). Yield 30 %; white powder (from hexane/EtOAc); mp 185–186 °C.

4-Methyl-*N*-[(*E*)-3-(2-thienyl)-2-propenoyl]benzenesulfonamide (3m). Yield 30 %; white microcrystals (from hexane/EtOAc); mp 167–169 °C; ^{1}H NMR δ 2.43 (s, 3H), 6.21 (d, *J* = 15.2 Hz, 1H), 7.02-7.05 (m, 1H), 7.24-7.26 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 5.1 Hz, 1H), 7.79 (d, *J* = 15.4 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 2H), 8.6 (br s, 1H).; ^{13}C NMR δ 21.7, 115.7, 128.3, 128.4, 129.5, 129.7, 132.2, 135.6, 138.4, 138.9, 145.2, 163.0. Anal. Calcd for $C_{14}H_{13}NO_3S_2$: C, 54.70; H, 4.26; N, 4.56. Found: C, 54.70; H, 4.27; N, 4.34.

4-Methyl-*N*-[(*E*)-3-phenyl-2-propenoyl]benzenesulfonamide (3n). Yield 30 %; white microcrystals (from hexane/EtOAc); mp 196–198 °C; ^{1}H NMR δ 1.95 (s, 3H), 2.36 (s, 3H), 2.78 (s, 6H), 5.64 (s, 1H), 5.91(s, 1H), 7.04 (s, 2H), 9.08 (br s, 1H).; ^{13}C NMR δ 18.1, 21.1, 22.8, 123.6, 132.1, 138.0, 140.6, 143.8, 165.5. Anal. Calcd for $C_{13}H_{17}NO_3S_2$: C, 58.40; H, 6.41; N, 5.24. Found: C, 58.53; H, 6.38; N, 5.20.

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