

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

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

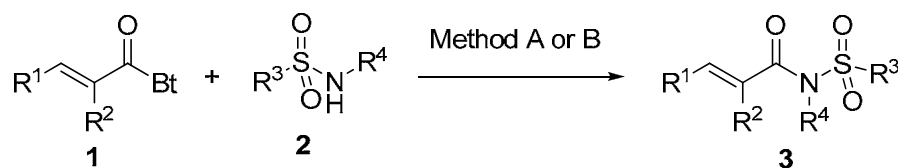
Keywords: Acylating agent, *N*-(α,β -unsaturated acyl)sulfonamides, α,β -unsaturated carboxamides, β -heteroarylacroylbenzotriazoles

Introduction

N-(α,β -Unsaturated acyl)sulfonamides are plant disease control agents,¹ selective EP₃ antagonists,^{2,3} anti-inflammatory agents³ 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 (RSO₂NH₂) 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 (RSO₂NCO) 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}

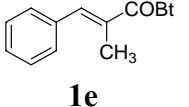
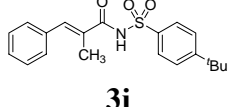
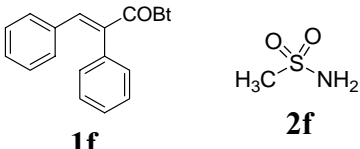
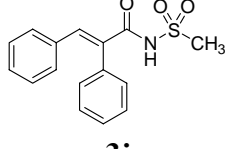
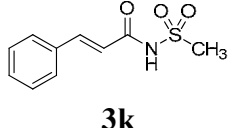
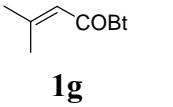
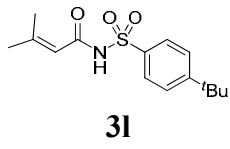
Herein, we report the acylation of sulfonamides with stable, crystalline *N*-(α,β -unsaturated acyl)benzotriazoles to give *N*-(α,β -unsaturated acyl)sulfonamides.

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				A	80	136–137	137–138
2				A	89	149–150	Novel
3				A	91	167–169	Novel
4				A	48	143–146	Novel
5				B ²	87	88–91	Novel
6				B ¹	65	185–186	Novel
7				B ¹	84	103–104	Novel
8				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

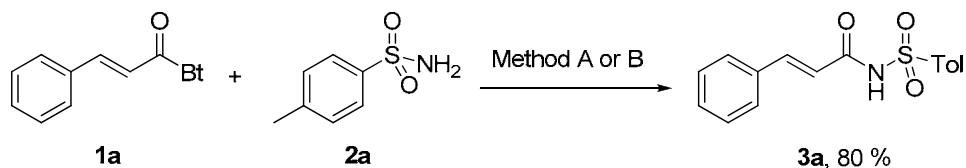
^aMethod A: KO^tBu/THF, 0 °C–r.t., 3 h; Method B¹: NaH/THF, r.t., 2 h., Method B²: NaH/THF, reflux, 1h. ^bIsolated yield.

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 ¹H 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 B²) (Scheme 1). Under the optimized conditions (Method A, B¹ or B²), *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

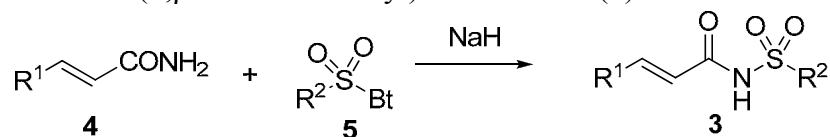
sulfonamide group did not hinder the reaction (Table 1, entry 5). Electronic variation in the sulfonamide derivatives also affected relatively little efficiency of the reaction (Table 1, entry 7 and 8). Methyl or phenyl groups at the α -position to the carbonyl group of the acylating agent did not prevent 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).

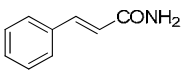
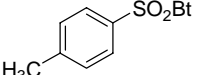
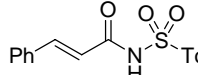

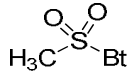
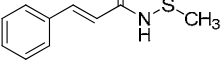

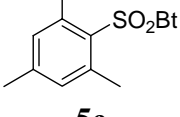
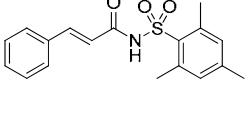
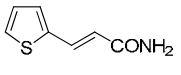

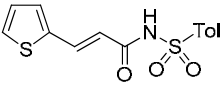
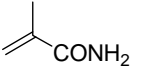

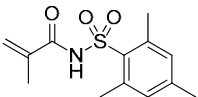


Method A: $\text{KO}^t\text{Bu}/\text{THF}$, 0 °C-r.t., 3h; Method B¹: NaH/THF , r.t. 2h, Method B²: NaH/THF , reflux 1h

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

^aIsolated 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. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded in CDCl₃ (with TMS for ¹H and chloroform-*d* for ¹³C 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 CH₂Cl₂ (125 mL), SOCl₂ (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 CH₂Cl₂ (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 MgSO₄, 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/ CH₂Cl₂); mp 142–143 °C (lit.¹⁴ mp 142–144 °C).

(E)-1-(1H-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-(1H-1,2,3-Benzotriazole-1-yl)-3-(3,4,5-trimethoxyphenyl)-2-propen-1-one (1d). Yield 74%; yellow crystals (from hexane / CH₂Cl₂); mp 136–137 °C (lit.¹⁷ mp 136–137 °C).

(E)-1-(1H-1,2,3-Benzotriazol-1-yl)-2methyl-3-phenyl-2-propen-1-one (1e). Yield 78 %; cream plates (from hexane / CH₂Cl₂); mp 50.5–51.5 °C). ¹H 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); ¹³C 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 C₁₆H₁₃N₃O: C, 72.99; H, 4.98; N, 15.96. Found: C, 73.05; H, 4.93; N, 15.93.

(E)-1-(1H-1,2,3-Benzotriazol-1-yl)-2,3-diphenyl-2-propen-1-one (1f). Yield 85 %; white crystals (from hexane / CH₂Cl₂); mp 133.4–135.0 °C). ¹H 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); ¹³C 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 C₂₁H₁₅N₃O: C, 77.52; H, 4.65; N, 12.91. Found: C, 77.48; H, 4.52; N, 12.89.

1-(1H-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 CHCl₃ was added NH₃ (200 mmol, 28 % solution). After stirring vigorously at room temperature for 2 h, the reaction mixture was extracted with CHCl₃. The organic layer was dried over anhydrous MgSO₄ 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 Na₂SO₄. 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; ¹H 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); ¹³C 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 C₁₄H₁₃NO₄S: 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; ¹H 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); ¹³C 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 C₁₄H₁₃NO₃S₂: 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; ¹H 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); ¹³C 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 C₁₃H₁₁NO₃S₂: 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; ¹H 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); ¹³C 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 C₁₆H₁₇NO₃S₂.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; ¹H 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); ¹³C 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 C₁₈H₁₉NO₃S: 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; ¹H 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); ¹³C 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 $C_{19}H_{18}F_3NO_6S \cdot H_2O$: 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; 1H 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; 1H 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; 1H 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; 1H NMR δ 3.37 (s, 3H), 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; 1H 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/CH₂Cl₂); mp 120.0–121.0 °C). Compound described²³ but no mp and spectra provided. ¹H 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); ¹³C 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 C₁₅H₁₅N₃O₂S: 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 Na₂SO₄. 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; ¹H 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).; ¹³C 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 C₁₄H₁₃NO₃S₂: 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; ¹H 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).; ¹³C NMR δ 18.1, 21.1, 22.8, 123.6, 132.1, 138.0, 140.6, 143.8, 165.5. Anal. Calcd for C₁₃H₁₇NO₃S₂: C, 58.40; H, 6.41; N, 5.24. Found: C, 58.53; H, 6.38; N, 5.20.

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