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# Iron-catalyzed sulfonylimine synthesis under neutral conditions

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ABSTRACT

A convenient $FeCl_3$-catalyzed synthesis of *N*-sulfonylimines via the condensation of aldehydes with *N*-sulfonylamides in mild and neutral conditions (in ethanol at room temperature) is reported. This procedure constitutes the first iron-catalyzed synthesis of *N*-sulfonylimines and is adapted to the condensation of both aromatic and aliphatic aldehydes.



## 1. Introduction

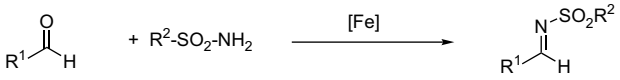
*N*-Sulfonylimines have been increasing in importance during the two last decades because they are one of the few types of imines bearing electron-withdrawing *N*-substituents that are stable enough to be isolated but also enough reactive to be useful intermediates[1] in organic synthesis and industrial applications. They were used in numerous reactions such as nucleophilic addition,[2] hetero Diels–Alder,[3] or ene reactions.[4] In addition, they were excellent precursors for the preparation of aziridines[5] and oxaziridines.[6]

A lot of synthetic routes[7] toward *N*-sulfonylaldimines have already been developed based on Lewis acid catalyzed reactions[8] of sulfonamides with aldehyde precursors, rearrangement of oxime *O*-sulfinates,[9] tellurium mediated reaction of aldehydes with chloramine-T,[10] via the reaction of *N*-trimethylsilylaldimine with various sulfonyl chlorides…[11]

The straightforward route is still the direct condensation of carbonyl compounds with sulfonamides.[12] Due to the weak nucleophilicity of sulfonamide derivatives, harsh acidic conditions and high temperatures were usually required and dehydrating agents or apparatus were oftenly used. In a synthetic point of view, those drastic conditions were not compatible with the resulting imine derivatives. Furthermore, some other procedures needed cumbersome experimental and multi-step procedure.

In another hand, iron, one of the most abundant metals on the earth, and consequently one of the most inexpensive and environmentally friendly ones, has seen a rise of its use as catalyst. Very efficient processes, which are now able to compete with other metal-catalyzed ones have emerged in the C–C bond formation,[13] hydrosilylation,[14] oxidation,[15] epoxidation,[16] even hydrogenation areas.[17]

In continuing our work on the use of iron as catalyst[18], we described herein the first iron-catalyzed synthesis of *N*-sulfonylaldimines using an efficient and simple procedure for the direct condensation of aldehydes with *N*-sulfonamides (Scheme 1).




**Scheme 1.** Iron-catalyzed *N*-sulfonylimine synthesis from aldehydes and sulfonylamides.

## 2. Results and discussion

In an initial attempt to synthesize *N*-sulfonylimine using iron-catalyzed procedure, we have investigated the condensation reaction of benzaldehyde **1a** (1 mmol) with *N*-tosylamide **2** (1 mmol) in ethanol as solvent. Our catalytic system consisted on commercially available iron salt such as dry $FeCl_3$. A systematic study was first undertaken to define the best reaction conditions, and Table 1 lists the representative data obtained for the synthesis of *N*-tosylbenzylimine **3a** with various commercially available iron salts.

In general, 10 mol % of iron salt was applied as catalyst precursor in ethanol and the reaction mixture was stirred at room temperature for 1 h.

First of all, when iron(II) salts were employed as catalyst, low to moderate GC-yields ranging from 4 to 50% were observed. Among the different iron(II) salt precursors tested, the best result was achieved when the reaction was performed in presence of $FeCl_2$, furnishing the *N*-tosylbenzylimine **3a** in 50% GC-yield (Table 1, entry 2). Interestingly, the use of iron(III) salts, and more especially $FeCl_3$ is crucial for the success of this reaction as a promising GC-yield of 75% was obtained (Table 1, entry 11). Interestingly, the

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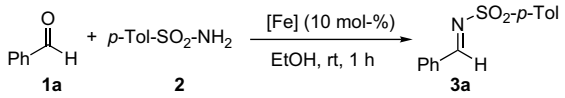
**Table 1**
Iron salt screening for the addition of *p*-tosylamide to benzaldehyde




1a 2 3a

| Entry | Iron salt 10 mol %[a] | GC-yield (%)[b] |
|---|---|---|
| 1 | — | 0 |
| 2 | $FeCl_2$ | 50 |
| 3 | $FeBr_2$ | 46 |
| 4 | $Fe(acac)_2$ | 5 |
| 5 | $Fe(OAc)_2$ | 4 |
| 6 | $FeSO_4{\cdot}7H_2O$ | 28 |
| 7 | $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ | 7 |
| 8 | $Fe(ClO_4)_3{\cdot}xH_2O$ | 44 |
| 9 | $Fe_2O_3$ | 1 |
| 10 | $FeCl_3{\cdot}6H_2O$ | 60 |
| 11 | $FeCl_3$ | 75 |
| 12 | $Fe(acac)_3$ | 5 |

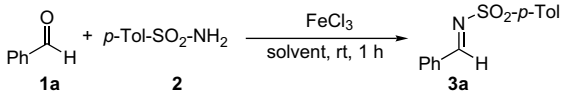
[a] Experimental conditions: benzaldehyde (1 mmol), *p*-tosylamide (1 mmol), iron salt (10 mol %) in 3 mL of ethanol for 1 h.
[b] Determined by GC.

conversion was moderate (61%) when $FeCl_3{\cdot}6H_2O$ was used, which shows the far better Lewis acid ability of $FeCl_3$.[18b,19] Control experiments in absence of iron salt (Table 1, entry 1) confirmed the crucial role, which the iron catalyst plays in the described condensation reaction as it did not occur.

To get more information on the optimal catalytic conditions, we carried out also intensive investigations to define the best solvent for this transformation. Eight different solvents were tested at room temperature for 1 h using 10 mol % of dry $FeCl_3$ as catalyst. Table 2 lists representative data collected for the synthesis of *N*-tosylbenzylimine **3a** as model reaction.

Ethanol has been found to be a far better solvent than other classical organic ones tested: *N*-tosylbenzylimine **3a** was obtained with rather good GC-yield (75%) (Table 2, entry 8). In other classical solvents, the GC-yields were moderate and surprisingly, no reaction occurred in DMF and *N*-methylpyrrolidone (NMP) (Table 2, entries 3 and 4).

**Table 2**
Investigation of solvents on the model reaction




1a 2 3a

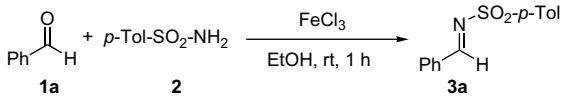
| Entry | $FeCl_3$ (mol %)[a] | Solvent | GC-yield (%)[b] |
|---|---|---|---|
| 1 | 10 | DCE | 58 |
| 2 | 10 | THF | 65 |
| 3 | 10 | NMP | 0 |
| 4 | 10 | DMF | 0 |
| 5 | 10 | Toluene | 50 |
| 6 | 10 | Acetone | 54 |
| 7 | 10 | AcOEt | 41 |
| 8 | 10 | EtOH | 75 |

[a] Experimental conditions: benzaldehyde (1 mmol), *p*-tosylamide (1 mmol), iron salt (10 mol %) in 3 mL of solvent for 1 h.
[b] Determined by GC.

Variation of the ratio of aldehyde to *N*-tosylamide had significant impact on the conversion. With a 1:1 ratio, the GC-yield was 75% (Table 3, entry 1). When we increased the amount of aldehyde to a ratio 1.5:1, the GC-yield didn't increase significantly (76%) (Table 3, entry 2). But when the ratio reached 2:1, a good and promising GC-yield of 85% was observed (Table 3, entry 3).

At this stage, we studied the variation of the amount of catalyst on the conversion of the reaction. By changing the amount of iron from 10 mol % to 4 mol %, the yield increased to 92% (Table 3, entry 4). But when the lower amount of $FeCl_3$ was used (1 mol %), the GC-yield decreased to 80%.

**Table 3**
Investigation of benzaldehyde and catalyst amount on the model reaction




1a 2 3a

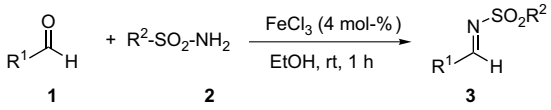
| Entry | $FeCl_3$ (mol %)[a] | Benzaldehyde (equiv) | GC-yield(%)[b] |
|---|---|---|---|
| 1 | 10 | 1 | 75 |
| 2 | 10 | 1.5 | 76 |
| 3 | 10 | 2 | 85 |
| 4 | 4 | 2 | 100 (92[c]) |
| 5 | 1 | 2 | 80 |

[a] Experimental conditions: benzaldehyde, *p*-tosylamide (1 mmol), iron salt in 3 mL of ethanol for 1 h.
[b] GC-yield of tosylamide, determined by GC.
[c] Isolated yield.

Hence, the optimized conditions found for the synthesis of *N*-tosylaldimines starting from aldehyde and *N*-tosylamide are the use of 2 equiv of aldehyde, 1 equiv of *N*-tosylamide in the presence of 4 mol % of dry $FeCl_3$ in ethanol at room temperature for 1 h.

The substrate scope was then investigated. A variety of aldehydes and *N*-sulfonylamides were tested under the optimized conditions using $FeCl_3$ as catalyst (Table 4).

**Table 4**
Scope of the reaction[a]




1 2 3

| Entry | $R^1$ | $R^2$ | Time (h) | | GC-yield | Isolated yield |
|---|---|---|---|---|---|---|
| 1 | Ph | *p*-Tol | 1 | **3a** | 100 | 92 |
| 2 | 4-$CF_3$–$C_6H_4$ | *p*-Tol | 1 | **3b** | 96 | 83 |
| 3 | 4-OMe–$C_6H_4$ | *p*-Tol | 1 | **3c** | 90 | 72 |
| 4 | 4-Br–$C_6H_4$ | *p*-Tol | 1 | **3d** | 100 | 80 |
| 5 | 4-Cl–$C_6H_4$ | *p*-Tol | 1 | **3e** | 95 | 70 |
| 6 | Furan-2-yl | *p*-Tol | 1 | **3f** | 86 | 67 |
| 7 | Thiophen-2-yl | *p*-Tol | 1 | **3g** | 87 | 74 |
| 8 | Thiophen-3-yl | *p*-Tol | 1 | **3h** | 56 | 30 |
| 9 | | | 2 | | 80 | 45 |
| 10 | | | 4[b] | | 100 | 71 |
| 11 | 5-Methylthio-phen-2-yl | *p*-Tol | 4 | **3i** | 57 | 30 |
| 12 | | | 4[b] | | 80 | 62 |
| 13 | 5-Ethylthio-phen-2-yl | *p*-Tol | 48 | **3j** | 100 | 71 |
| 14 | 4-Br–$C_6H_4$ | *p*-$ClC_6H_4$ | 16 | **3k** | 100 | 70 |
| 15 | 4-Cl–$C_6H_4$ | *p*-$ClC_6H_4$ | 16 | **3l** | 100 | 48 |
| 16 | 4-Br–$C_6H_4$ | Ph | 16 | **3m** | 90 | 66 |
| 17 | 4-Cl–$C_6H_4$ | Ph | 16 | **3n** | 86 | 57 |
| 18 | 4-Br–$C_6H_4$ | Me | 16 | **3o** | 95 | 54 |
| 19 | Cyclohexyl | *p*-Tol | 16[b] | **3p** | 100 | — |
| 20 | Propyl | *p*-Tol | 16[b] | **3q** | >90 | — |

[a] Experimental conditions: aldehyde (2 mmol), *p*-tosylamide (1 mmol), $FeCl_3$ (0.04 mmol, 4 mol %) in 3 mL of ethanol for 1 h.
[b] The reaction was performed at 60 °C.

In general, all reactions were clean, and the *N*-sulfonylimines **3** were obtained in moderate to good yields under the previously optimized conditions. The purification of the desired compound was made by simple recrystallization. It turned out that our iron-catalyzed condensation could adapt to various aldehydes. For aromatic aldehydes such as benzaldehyde or *p*-substituted benzaldehydes, the reaction proceeded smoothly and gave rise to the aromatic *N*-tosylimines **3a–e** in moderate to good GC-yields reaching 100% and isolated yields ranging from 70 to 92% (Table 4, entries 1–5). When 2-furaldehyde and 2-thiophenecarboxaldehyde were used, good GC-yields were observed (86 and 87%,

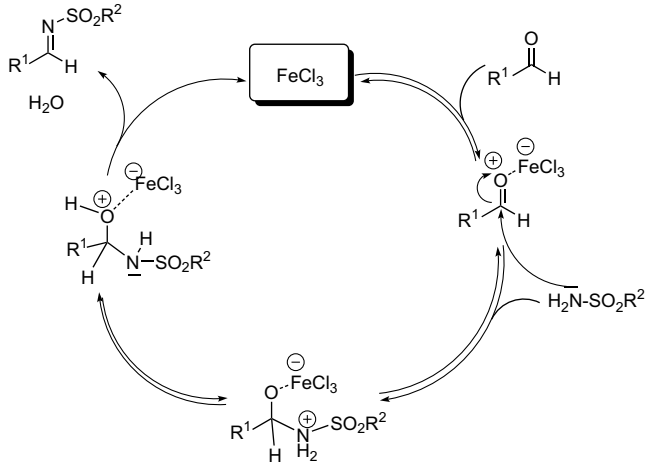
respectively) and good isolated yields were obtained (**3f**, 67% and **3g**, 74%) (Table 4, entries 6 and 7). Using the same reaction conditions (room temperature, 1 h), 3-thiophenecarboxaldehyde gave only a moderate GC-yield of 56% and an isolated yield of 30% (Table 4, entry 8). Increasing the reaction time to 2 h had a beneficial effect (GC-yield=80%, isolated yield=45%, entry 9). However, enhancing the temperature to 60 °C for 4 h improved both GC-yield (100%) and isolated yield (71%) (Table 4, entry 10). In like manner, the 5-methylthiophen-2-yltosylimine **3i** was obtained in 62% yield when the reaction mixture was warmed at 60 °C for 4 h instead of 30% after 4 h at room temperature (Table 4, entries 11and 12). The 5-ethylthiophen-2-yltosylimine **3j** was obtained with 71% isolated yield after 48 h at room temperature (Table 4, entry 13).

We were successful in extending the procedure to include other sulfonamides such as *p*-chlorophenylsulfonamide (entries 14 and 15), phenylsulfonamide (entries 16 and 17) and methylsulfonamide (entry 18). In those cases, the reactions proceeded at room temperature for 16 h and led to the corresponding sulfonaldimines with moderate to good isolated yields (48–70%).

We must underline that the conversion rate of *p*-toluenesulfonamide with aldehydes was higher than the other sulfonamides used, certainly due to a difference of nucleophilicity of the amino part.

Due to mild and neutral condensation reaction conditions, enolizable aliphatic aldehydes were also good candidates for the reaction (Table 4, entries 19 and 20) and gave the desired *N*-tosylimines **3p**,**q** with good GC-yields ranging from 90 to 100%. Those two aliphatic *N*-Ts imines were not purified because of their instability.

At this stage of the project, although the mechanism of the present reaction has not been studied in details and if any mechanistic discussion is speculative, we believe that the catalyzed transformation proceeds via an iron Lewis acid activation of the carbonyl group of the aldehyde. Therefore, iron-coordinated carbonyl increases its electrophilicity to trigger the nucleophilic attack by the sulfonylamide (Scheme 2).




**Scheme 2.** Plausible mechanism for iron-catalyzed sulfonylimine synthesis.

## 3. Conclusion

In conclusion, we have developed the first iron-catalyzed addition of *N*-sulfonylamides on aldehydes, which involves a commercially available catalyst, $FeCl_3$. This efficient and simple method provides in most cases the desired *N*-sulfonylimines in moderate to good yields. Overall the novel iron-catalyzed *N*-sulfonylimines synthesis reported here constitutes a promising process because of its operational simplicity: it must be pointed out that this *N*-sulfonylimine synthesis is conducted in mild and neutral conditions (room temperature in ethanol as solvent). Its increased efficiency and enlargement of the substrate scope are currently under investigation by our research group.

## 4. Experimental section

### 4.1. General information

All reagents and solvents were used as received. Reactions were performed under ambient atmosphere. Technical grade solvents were used. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker DPX 200 and AM300WB spectrometers at ambient temperature in $CDCl_3$. Chemical shifts are given in parts per million (ppm) relative to $CDCl_3$ ($^1H$: 7.26 ppm, $^{13}C$: 77.00 ppm). Coupling constants are given in hertz (Hz). High resolution mass spectra (HRMS) were recorded by the HRMS unit of the CMRPO (Rennes) using EI (Electron ionization, 70 eV) or electrospray ionization (ESI). Gas chromatography (GC) was performed on a GC-2014 (Shimadzu) Gas Chromatograph equipped with a 30-m capillary column (Supelco, Equity™-5, fused silica capillary column, 30 M×0.25 mm×0.25 μm film thickness), using $N_2$/air as vector gas. GC–MS were measured by GCMS-QP2010S (Shimadzu) with GC-2010 equipped with a 30-m capillary column (Supelco, SLB™-5ms, fused silica capillary column, 30 M×0.25 mm×0,25 μm film thickness), using helium as vector gas. The following GC conditions were used: initial temperature 100 °C, for 2 min, then rate 10 °C/min until 250 °C and kept at 250 °C for 15 min.

### 4.2. General procedure

In a 10 mL vial equipped with a magnetic stirring bar, 4 mol % of commercially available dry $FeCl_3$ was added to the solution of sulfonylamide (1 mmol) in ethanol (3 mL). Aldehyde (2 mmol) was then added.

The solution was stirred at room temperature for 1 h. Volatile components were then removed under reduced pressure and the residue was recrystallized in a mixture of 2 mL of hot AcOEt and 6 mL of hexane. After 5 h in fridge, the solid was filtered, washed, and dried.

Compounds **3a**,[2c,12b,g,h] **3b**,[20] **3c**,[2c,12g,20] **3d**,[21] **3e**,[8a,12b,g] **3f**,[12c] **3g**,[8a,12b] **3h**,[8a] **3l**[22], **3m**,[23] and **3n**[23] were characterized by comparing their NMR spectra with the literature data.

#### *4.2.1. N-Benzylidene-4-methylbenzenesulfonamide **3a***

The compound was prepared as described in the general procedure (92% isolated yield). GC: $t_R$=19.4 min. MS (EI): *m*/*z* 259 ($M^+$, 80), 195 (40), 155 (100), 104 (90), 91 (90), 77 (90), 65 (90), 51 (90). $^1H$ NMR (200.13 MHz, $CDCl_3$): $\delta$ ppm 2.46 (s, 3H), 7.37 (d, 2H, *J*=8), 7.45–7.55 (m, 2H), 7.60–7.75 (m, 1H), 7.85–8.00 (m, 4H), 9.06 (s, 1H). $^{13}C$ NMR (50.75 MHz, $CDCl_3$): $\delta$ ppm 170.6, 145.1, 135.4, 132.8, 131.8, 130.3, 129.6, 128.5, 126.9, 22.1.

#### *4.2.2. N-(4-Trifluoromethylbenzylidene)-4-methylbenzenesulfonamide **3b***

The compound was prepared as described in the general procedure (83% isolated yield). GC: $t_R$=18.4 min. MS (EI): *m*/*z* 327 ($M^+$, 60), 155 (100), 145 (30), 91 (100), 65 (100), 51 (30). $^1H$ NMR (200.13 MHz, $CDCl_3$): $\delta$ ppm 2.48 (s, 3H), 7.39 (d, 2H, *J*=8.4), 7.77 (d, 2H, *J*=8.0), 7.92 (d, 2H, *J*=7.8), 8.07 (d, 2H, *J*=8.0), 9.10 (s, 1H). $^{13}C$ NMR (50.75 MHz, $CDCl_3$): $\delta$ ppm 169.3, 144.9, 125.5–143.7 (m), 129.3 (q, $^1J_{C-F}$=260), 22.3.

#### *4.2.3. N-(4-Methoxybenzylidene)-4-methylbenzenesulfonamide **3c***

The compound was prepared as described in the general procedure (72% isolated yield). GC: $t_R$=26.9 min. MS (EI): *m*/*z* 289 ($M^+$, 15), 155 (15), 134 (70), 91 (80), 77 (15), 65 (30). $^1H$ NMR

(200.13 MHz, $CDCl_3$): δ ppm 2.45 (s, 3H), 3.91 (s, 3H), 6.98 (d, 2H, *J*=8.8), 7.35 (d, 2H, *J*=8.0), 7.91 (d, 2H, *J*=8.8), 7.90 (d, 2H, *J*=8.2), 8.96 (s, 1H). $^{13}C$ NMR (50.75 MHz, $CDCl_3$): δ ppm 169.7, 165.7, 144.7, 136.1, 134.2, 130.2, 128.3, 125.6, 115.1, 56.1, 22.1.

*4.2.4. N-(4-Bromobenzylidene)-4-methylbenzenesulfonamide* ***3d***

The compound was prepared as described in the general procedure (80% isolated yield). GC: $t_R$=21.4 min. MS (EI): *m*/*z* 339 ($M^+$, 10), 337 ($M^+$, 10), 184 (10), 182 (10), 155 (60), 91 (100), 65 (25). $^1H$ NMR (200.13 MHz, $CDCl_3$): δ ppm 2.46 (s, 3H), 7.37 (d, 2H, *J*=8.0), 7.64 (d, 2H, *J*=7.7), 7.80 (d, 2H, *J*=8.0), 7.90 (d, 2H, *J*=7.7), 8.99 (s, 1H). $^{13}C$ NMR (50.75 MHz, $CDCl_3$): δ ppm 169.3, 145.3, 135.3, 133.0, 132.8, 131.6, 130.7, 130.3, 128.6, 22.1.

*4.2.5. N-(4-Chlorobenzylidene)-4-methylbenzenesulfonamide* ***3e***

The compound was prepared as described in the general procedure (70% isolated yield). GC: $t_R$=20.4 min. MS (EI): *m*/*z* 295 ($M^+$, 5), 293 ($M^+$, 10), 155 (50), 91 (100), 65 (25). $^1H$ NMR (200.13 MHz, $CDCl_3$): δ ppm 2.47 (s, 3H), 7.37 (d, 2H, *J*=6.9), 7.49 (d, 2H, *J*=7.2), 7.88 (m, 4H), 9.02 (s, 1H). $^{13}C$ NMR (50.75 MHz, $CDCl_3$): δ ppm 169.2, 145.3, 141.9, 135.3, 132.8, 131.2, 130.3, 130.2, 128.6, 22.1.

*4.2.6. N-(2-Furylmethylene)-4-methylbenzenesulfonamide* ***3f***

The compound was prepared as described in the general procedure (67% isolated yield). GC: $t_R$=17.8 min. MS (EI): *m*/*z* 249 ($M^+$, 80), 155 (100), 139 (40), 91 (100), 65 (100), 51 (30). $^1H$ NMR (200.13 MHz, $CDCl_3$): δ ppm 2.45 (s, 3H, $CH_3$), 7.10–7.50 (m, 3H), 7.70–8.00 (m, 4H), 9.13 (s, 1H). $^{13}C$ NMR (50.75 MHz, $CDCl_3$): δ ppm 162.7, 144.9, 139.6, 138.6, 137.2, 135.8, 130.2, 129.3, 128.4, 22.1.

*4.2.7. 4-Methyl-N-(2-thienylmethylene)-benzenesulfonamide* ***3g***

The compound was prepared as described in the general procedure (74% isolated yield). GC: $t_R$=20.8 min. MS (EI): *m*/*z* 265 ($M^+$, 80), 174 (60), 155 (100), 110 (100), 91 (100), 83 (30), 65 (100), 51 (30). $^1H$ NMR (200.13 MHz, $CDCl_3$): δ ppm 2.45 (s, 3H), 7.18–7.30 (m, 1H), 7.36 (d, 2H, *J*=8.2), 7.80 (d, 2H, *J*=4.2), 7.88 (d, 2H, *J*=8.4), 9.13 (s, 1H). $^{13}C$ NMR (50.75 MHz, $CDCl_3$): δ ppm 162.7, 144.0, 139.5, 138.6, 135.8, 130.2, 129.3, 128.4, 126.9, 22.1.

*4.2.8. 4-Methyl-N-(thiophen-3-ylmethylene)-benzenesulfonamide* ***3h***

The compound was prepared as described in the general procedure (71% isolated yield). GC: $t_R$=20 min. MS (EI): *m*/*z* 265 ($M^+$, 10), 210 (100), 174 (90), 155 (100), 110 (45), 91 (100), 83 (35), 65 (100). $^1H$ NMR (200.13 MHz, $CDCl_3$): δ ppm 2.46 (s, 3H), 7.25–7.35 (m, 2H), 7.62 (d, 1H, *J*=5.0), 7.89 (d, 2H, *J*=8.2), 8.16 (m, 2H), 9.02 (s, 1H). $^{13}C$ NMR (50.75 MHz, $CDCl_3$): δ ppm 163.5, 145.0, 138.6, 137.5, 135.7, 130.2, 128.5, 128.2, 126.9, 22.1.

*4.2.9. 4-Methyl-N-((5-methylthiophen-2-yl)methylene)-benzenesulfonamide* ***3i***

The compound was prepared as described in the general procedure (62% isolated yield). GC: $t_R$=20.7 min. MS (EI): *m*/*z* 281 ($M^+$, 8), 279 (20), 207 (25), 155 (20), 124 (55), 91 (100), 65 (30), 53 (20). $^1H$ NMR (300.13 MHz, $CDCl_3$): δ ppm 2.44 (s, 3H), 2.58 (s, 3H), 6.89–7.88 (m, 6H), 9.00 (s, 1H). $^{13}C$ NMR (75.47 MHz, $CDCl_3$): δ ppm 161.9, 153.7, 144.2, 140.1, 136.0, 135.8, 129.7, 127.8, 21.6, 16.5. HRMS (EI, 70 eV): calcd for $C_{13}H_{13}NO_2S_2$ [$M^+$] 279.0388, found 279.0388.

*4.2.10. N-((5-Ethylthiophen-2-yl)methylene)-4-methylbenzenesulfonamide* ***3j***

The compound was prepared as described in the general procedure (71% isolated yield). GC: $t_R$=21.2 min. MS (EI): *m*/*z* 293 ($M^+$, 20), 155 (15), 138 (75), 122 (15), 91 (100), 65 (30). $^1H$ NMR (300.13 MHz, $CDCl_3$): δ ppm 1.30 (t, 3H, *J*=7.5), 2.41 (s, 3H), 2.88 (q, 2H, *J*=7.5), 6.90–7.85 (m, 6H), 9.00 (s, 1H). $^{13}C$ NMR (50.75 MHz, $CDCl_3$): δ ppm 162.0, 161.3, 144.1, 140.1, 135.7, 135.3, 129.6, 127.6, 126.0, 24.2, 21.5, 15.2. HRMS (EI, 70 eV): calcd for $C_{14}H_{15}NO_2S_2$ [$M^+$] 293.0544, found 293.0534.

*4.2.11. N-(4-Bromobenzylidene)-4-chlorobenzenesulfonamide* ***3k***

The compound was prepared as described in the general procedure (70% isolated yield). GC: $t_R$=21.7 min. MS (EI): *m*/*z* 359 ($M^+$, 10), 357 ($M^+$, 8), 184 (20), 182 (20), 177 (25), 175 (65), 113 (35), 111 (100), 76 (25), 75 (55), 51 (20), 50 (10). $^1H$ NMR (300.13 MHz, $CDCl_3$): δ ppm 7.52 (d, 2H, *J*=8.7), 7.66 (d, 2H, *J*=8.5), 7.79 (d, 2H, *J*=8.6), 7.96 (d, 2H, *J*=8.8), 9.02 (s, 1H). $^{13}C$ NMR (75.46 MHz, $CDCl_3$): δ ppm 169.6, 140.4, 136.5, 132.7, 132.5, 131.0, 130.7, 129.5, 129.5. HRMS (ESI): calcd for $C_{13}H_9NO_2SClBrNa$ [M+Na]$^+$ 379.9124, found 379.9122.

*4.2.12. N-(4-Chlorobenzylidene)-4-chlorobenzenesulfonamide* ***3l***

The compound was prepared as described in the general procedure (48% isolated yield). GC: $t_R$=20.6 min. MS (EI): *m*/*z* 315 ($M^+$, 8), 313 ($M^+$, 10), 177 (15), 175 (45), 140 (10), 138 (25), 113 (35), 111 (100), 76 (10), 75 (45), 51 (10), 50 (15). $^1H$ NMR (300.13 MHz, $CDCl_3$): δ ppm 7.50 (d, 2H, *J*=8.4), 7.55 (d, 2H, *J*=8.5), 7.89 (d, 2H, *J*=8.3), 7.96 (d, 2H, *J*=8.4), 9.04 (s, 1H). $^{13}C$ NMR (75.46 MHz, $CDCl_3$): δ ppm 169.4, 141.9, 140.4, 136.5, 132.5, 130.6, 129.7, 129.6, 129.5.

*4.2.13. N-(4-Bromobenzylidene)-benzenesulfonamide* ***3m***

The compound was prepared as described in the general procedure (66% isolated yield). GC: $t_R$=20.3 min. MS (EI): *m*/*z* 325 ($M^+$, 5), 323 ($M^+$, 5), 184 (15), 182 (15), 141 (45), 77 (100), 51 (25), 50 (10). $^1H$ NMR (300.13 MHz, $CDCl_3$): δ ppm 7.61 (m, 5H), 7.79 (m, 2H), 8.00 (m, 2H), 9.03 (s, 1H). $^{13}C$ NMR (75.46 MHz, $CDCl_3$): δ ppm 169.6, 140.4, 136.4, 132.7, 132.5, 130.9, 130.7, 129.52, 129.50.

*4.2.14. N-(4-Chlorobenzylidene)-benzenesulfonamide* ***3n***

The compound was prepared as described in the general procedure (57% isolated yield). GC: $t_R$=19.3 min. MS (EI): *m*/*z* 281 ($M^+$, 4), 279 ($M^+$, 10), 141 (45), 138 (25), 113 (12), 111 (4), 77 (100), 51 (25), 50 (10). $^1H$ NMR (300.13 MHz, $CDCl_3$): δ ppm 7.49 (d, 2H, *J*=7.7), 7.57 (m, 3H), 7.89 (d, 2H, *J*=7.8), 8.02 (d, 2H, *J*=7.0), 9.04 (s, 1H). $^{13}C$ NMR (75.46 MHz, $CDCl_3$): δ ppm 169.1, 141.6, 137.9, 133.7, 132.4, 130.7, 129.6, 129.2, 128.0.

*4.2.15. N-(4-bromobenzylidene)-methanesulfonamide* ***3o***

The compound was prepared as described in the general procedure (54% isolated yield). GC: $t_R$=14.9 min. MS (EI): *m*/*z* 263 ($M^+$, 25), 261 ($M^+$, 25), 184 (100), 182 (100), 157 (45), 155 (45), 102 (30), 101 (20), 80 (50), 79 (55), 76 (75), 75 (75), 65 (20), 51 (15), 50 (50). $^1H$ NMR (200.13 MHz, $CDCl_3$): δ ppm 3.15 (s, 3H), 7.67 (d, 2H, *J*=7.7), 7.84 (d, 2H, *J*=8.0), 9.00 (s, 1H). $^{13}C$ NMR (75.46 MHz, $CDCl_3$): δ ppm170.4, 132.7, 132.4, 130.9, 130.5, 40.2. HRMS (EI, 70 eV): calcd for $C_8H_8NO_2{}^{79}BrS$ [$M^+$] 260.9459, found 260.9473.

*4.2.16. N-(Cyclohexylmethylene)-4-methylbenzenesulfonamide* ***3p***

The compound was prepared as described in the general procedure. It was not purified because of its instability. GC: $t_R$=18.4 min. MS (EI): *m*/*z* 265 ($M^+$, 35), 210 (40), 197 (70), 155 (85), 133 (80), 110 (100), 91 (100), 83 (40), 65 (100), 55 (100).

*4.2.17. N-Butylidene-4-methylbenzenesulfonamide* ***3q***

The compound was prepared as described in the general procedure. It was not purified because of its instability. GC: $t_R$=14 min. MS (EI): *m*/*z* 225 ($M^+$, 10), 197 (100), 155 (100), 133 (100), 106 (60), 91 (100), 70 (100), 65 (100), 51 (30).

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## Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.07.029.

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