



## An efficient method for the synthesis of novel *N*-sulfonylimines using TBAB under solvent-free conditions

Wahida Boufas, Billel Belhani, Hadjer Cheloufi, Hacène K'tir, Nour-Eddine Aouf and Malika Berredjem\*

Laboratory of Applied Organic Chemistry, Synthesis of biomolecules and molecular modelling Group, Chemistry Department, Sciences Faculty, Badji Mokhtar - Annaba University, Annaba, Algeria

### ABSTRACT

The condensation of various sulfonamides with aromatic aldehydes was effectively promoted in the presence of TBAB to produce the corresponding sulfonylimine products in good yields under solvent-free conditions. The sulfonamides were prepared starting from chlorosulfonylisocyanate (CSI), primary amine in three steps (carbamoylation, sulfamoylation and deprotection).

**Keywords:** TBAB, Microwave, sulfonylimine, solvent-free, catalyst.

### INTRODUCTION

*N*-sulfonylimines have received considerable attention for organic chemists, they also serve as useful synthetic intermediates as versatile synthetic intermediates [1-2]. In addition, they are excellent substrates in nucleophilic additions [3] reductions [4], hetero Diels–Alder [5], for stable alkenes in stereochemically controlled reactions [6], and excellent precursors for the preparation of aziridines [7] and oxaziridines synthesis [8]. Several methods for the synthesis of *N*-sulfonylimines have been developed via the condensation of aldehyde with sulfonamide catalyzed by silica sulfate solid acid [9], Silica-supported  $P_2O_5(P_2O_5/SiO_2)$  [10], reaction of arylaldehydes and *p*-toluene sulfonamide in methylene chloride using trifluoroacetic anhydride as a dehydrating agent [11], rearrangement of oxime *O*-sulfinates [12], Lewis acid  $FeCl_3$  catalyzed reactions of sulfonamides with aldehyde precursors [13], the addition of *N*-sulfonylsulfonamide to aldehyde in the presence of boron-trifluoride etherate [14], tellurium mediated reaction of aldehydes with chloramine-T [15], using tetraethyl ortho silicate [16] and the reaction of trimethylsilylaldimine with various sulfonyl chlorides [17]. Each of these methods has its own merits, but some of these methods are plagued by the limitation of long reaction times, expensive and hazardous reagent and requiring use of a microwave oven. Consequently, there is scope for further renovation toward mild conditions, increased of variation of the substituents in the components, and better yields.

Tetra-*n*-butyl ammonium bromide (TBAB) was reported to be the most effective out of six catalysts they tried under solid–liquid mode of operation, it has emerged as an extremely useful homogeneous catalyst in various organic transformations [18] including conjugate addition of thiols to electron deficient alkenes [19], transthioacetalisation of acetals [20], trimethylsilylation of alcohols [21] and in the synthesis of aryl-14H-dibenzo [a,j] xanthenes [22]. TBAB is an inexpensive readily available ionic liquid with inherent properties like environmental compatibility, greater selectivity, operational simplicity, non-corrosive nature and ease of reusability. Herein, we describe a new efficient and practical route for the synthesis of *N*-sulfonylimines by the condensation of sulfonamide **1** with aryl aldehyde **2** catalyzed by TBAB under solvent-free.

## EXPERIMENTAL SECTION

Melting points were determined in open capillary tubes on an Electro thermal apparatus and uncorrected. IR spectra were recorded on a Perkin-Elmer FT-600 spectrometer. Proton nuclear magnetic resonance was determined with a 360 WB or AC 250-MHz Bruker spectrometer using CDCl<sub>3</sub> and DMSO-d<sub>6</sub> as a solvent and TMS as an internal standard. Chemical shifts are reported in  $\delta$  units (ppm). All coupling constants (*J*) are reported in Hertz. Multiplicity is indicated as s (singlet), d (doublet), t (triplet), m (multiplet) and combination of these signals. Electron ionization mass spectra (30 ev) were recorded in positive mode on a Water Micro Mass ZQ. All reactions were monitored by TLC on silica Merck h60 F254 (Art. 5554) precoated aluminum plates and were developed by spraying with ninhydrin solution.

**1. General Procedure for the preparation of carboxylsulfamide**

To a stirred solution of chlorosulfonyl isocyanate (CSI) (1.62 g, 11.48 mmol) in (10 ml) of anhydrous methylene chloride at 0°C was added (0.85 g, 11.48 mmole) of *tert*-butanol in the same solvent. After a period of 30 min, the resulting solution and (1.75 ml, 1.1 equiv.) of triethylamine was slowly added to a solution containing (1 equiv.) of primary amine in (10 ml) of anhydrous methylene chloride at 0 °C. The resulting reaction solution was allowed to warm up to room temperature for over 2 hour. The reaction mixture diluted with (30 ml) of methylene chloride and washed with HCl 0.1 N and then with water. The organic layer was dried over anhydrous sodium sulphate and concentrated in vacuum, to give carboxylsulfamides in excellent yields.

Spectroscopic data for:

***Tert*-butyl (1-phenyl)aminosulfonylcarbamate 1a**

Yield: 95%. M = 272 g/mol [C<sub>11</sub>H<sub>16</sub>O<sub>4</sub>N<sub>2</sub>S]. mp: 129-131 °C. R<sub>f</sub> = 0.7 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.50-7.25 (m, 5H, **H-Ar**); 1.45 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 149.89; 135.77; 129.48; 126.61; 122.86; 84.16; 27.28;. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1718(C=O), 3447 and 3268.5(2NH), 1655 (C=C), 1358.2 and 1151.1 (SO<sub>2</sub>). MS-ESI<sup>+</sup> 30ev m/z: 273 [M+H]<sup>+</sup>.

***Tert*-butyl (3-fluorophenyl)aminosulfonylcarbamate 1b**

Yield: 88%. M = 290 g/mol [C<sub>11</sub>H<sub>15</sub>O<sub>4</sub>N<sub>2</sub>SF]. mp:137-138 °C. R<sub>f</sub>=0.9 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 10.52 (s, 1H, NH); 7.55-6.75 (m, 4H, **H-Ar**); 1.35 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 164; 156; 141;131; 112; 110; 100; 75; 30.2;. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1716.5 (C=O), 3442.7 and 3261.4 (2NH), 1651.0 (C=C), 1361.7 and 1143.7 (SO<sub>2</sub>).MS-ESI<sup>+</sup> 30ev m/z: 291 [M+H]<sup>+</sup>.

***Tert*-butyl (1-phenylethyl)aminosulfonylcarbamate 1c**

Yield: 94%. M = 300 g/mol [C<sub>13</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub>S]. mp: 130-131 °C. R<sub>f</sub> = 0.75 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.35 (m, 5H, **H-Ar**); 5.90 (d, 1H, *J* = 7.52 Hz, NH-CH\*); 4.75 (m, 1H, CH\*); 1.52 (d, 3H, *J* = 6.93 Hz, CH<sub>3</sub>); 1.45 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 153; 145; 130; 126, 125; 79; 45; 29; 19. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1723 (C=O), 3421.5 and 3251.5 (2NH), 1643.6 (C=C), 1363 and 1135 (SO<sub>2</sub>). MS-ESI<sup>+</sup>30 ev m/z: 301 [M+H]<sup>+</sup>.

***Tert*-butyl (4-methoxyphenyl)aminosulfonylcarbamate 1d**

Yield: 92%. M = 302 g/mol [C<sub>12</sub>H<sub>18</sub>O<sub>5</sub>N<sub>2</sub>S]. mp: 139-141°C. R<sub>f</sub> = 0.8 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.50-7.20 (m, 4H, **H-Ar**); 3.82 (s, 3H, CH<sub>3</sub>-O); 1.35 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 125.71; 114.60; 126.61; 55.50; 27.93. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1718 (C=O), 3447 and 3268.5(2NH), 1655 (C=C), 1358.2 and 1151.1 (SO<sub>2</sub>). MS-ESI+ 30ev m/z: 273 [M+H]<sup>+</sup>.

***Tert*-butyl (1-cyclohexyl)aminosulfonylcarbamate 1e**

Yield: 90%. M = 278 g/mol [C<sub>11</sub>H<sub>22</sub>O<sub>4</sub>N<sub>2</sub>S]. mp: 109-110 °C. R<sub>f</sub> = 0.9 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.25 (s, 1H, NH-Boc); 5.15 (d, 1H, *J* = 7.35, NH-cyl); 3.30 (m, 1H, CH\*-NH); 1.90 (m, 2H, CH<sub>2</sub> cyc); 1.80 (m, 2H, CH<sub>2</sub>-cyc); 1.60 (m, 2H, CH<sub>2</sub>-cyc); 1.50 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>); 1.25 (m, 4H, 2CH<sub>2</sub>-cyc). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 159; 78; 44; 35; 26; 25; 22. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1720.1 (C=O), 3420.5 and 3221.4 (2NH), 1367 and 1132 (SO<sub>2</sub>). MS-ESI+ 30ev m/z: 279 [M+H]<sup>+</sup>.

***Tert*-butyl (benzyl)aminosulfonylcarbamate 1f**

Yield: 75%. M = 286 g/mol [C<sub>12</sub>H<sub>18</sub>O<sub>4</sub>N<sub>2</sub>S]. mp: 123-125°C. R<sub>f</sub> = 0.7 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.55-7.20 (m, 5H, **H-Ar**); 3.65 (m, 2H, CH<sub>2</sub>-Ar); 1.45 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 149.89; 135.77; 129.48; 126.61; 122.86; 84.16; 43.6; 27.28;. IR (KBr,  $\nu$  cm<sup>-1</sup>): 1718(C=O), 3447 and 3268.5 (2NH), 1655 (C=C), 1358.2 and 1151.1 (SO<sub>2</sub>). MS-ESI+ 30ev m/z: 287 [M+H]<sup>+</sup>.

## 2. General Procedure for the preparation of sulfonamide

The deprotection reaction of carboxylsulfamide (**1a-f**) was carried out in distilled water, the reaction mixture was refluxed for 15-30 min, and then it was extracted 3× (30 ml) with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure, to give sulfonamides (**2a-f**) in good yields

Spectroscopic data for:

### *N*-(1-phenyl)sulfamide **2a**

Yield: 90%. M = 172 g/mol [C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S]. mp: 96-98°C. R<sub>f</sub> = 0.55 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (DMSO, δ ppm): 7.65-7.20 (m, 5H, **H**-Ar); 4.90 (s, 2H, **NH**<sub>2</sub>). <sup>13</sup>C NMR (DMSO, δ ppm): 136; 129.58; 125.29; 120.82. IR (KBr, ν cm<sup>-1</sup>): 3368-3257(**NH**, **NH**<sub>2</sub>); 1658(**C=C**); 1364.8 and 1159 (**SO**<sub>2</sub>). MS-ESI+ 30ev m/z: 173 [M+H]<sup>+</sup>.

### *N*-(3-fluorophenyl)sulfamide **2b**

Yield: 78%. M = 190 g/mol [C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>SF]. mp: 91-93°C. R<sub>f</sub>=0.68 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (DMSO, δ ppm): 7.75-7.55 (m, 4H, **H**-Ar); 4.70 (s, 2H, **NH**<sub>2</sub>). <sup>13</sup>C NMR (DMSO, δ ppm): 164; 139; 129; 119; 111; 105. IR (KBr, ν cm<sup>-1</sup>): 3370-3262 (**NH**,**NH**<sub>2</sub>); 1652(**C=C**); 1361 and 1155 (**SO**<sub>2</sub>). MS-ESI+ 30ev m/z: 191 [M+H]<sup>+</sup>.

### *N*-(1-phenylethyl)sulfamide **2c**

Yield: 91%. M = 200 g/mol [C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S]. mp: 100-102-176 °C. R<sub>f</sub>=0.58 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (DMSO, δ ppm): 7.35 (m, 5H, **H**-Ar); 5.25 (d, 1H, J= 6.93Hz, **NH**-CH); 4.55 (m, 1H, **CH**\*); 4.45 (s, 2H, **NH**<sub>2</sub>); 1.57 (d, 3H, J= 6.93 Hz, **CH**<sub>3</sub>). <sup>13</sup>C NMR (DMSO, δ ppm): 145; 130; 125.1; 125; 43; 19. IR (KBr, ν cm<sup>-1</sup>): 3373-3260 (**NH**,**NH**<sub>2</sub>); 1642 (**C=C**); 1360 and 1153 (**SO**<sub>2</sub>). MS-ESI+ 30ev m/z: 201 [M+H]<sup>+</sup>.

### *N*-(4-methoxy-phenyl)sulfamide **2d**

Yield: 90%. M = 203 g/mol [C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>S]. mp: 98-100°C. R<sub>f</sub>= 0.62 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (DMSO, δ ppm): 7.60-7.20 (m, 4H, **H**-Ar); 4.90 (s, 2H, **NH**<sub>2</sub>), 3.95 (s, 3H, **CH**<sub>3</sub>-O). <sup>13</sup>C NMR (DMSO, δ ppm): 136; 129.58; 125.29; 120.82. IR (KBr, ν cm<sup>-1</sup>): 3368-3257 (**NH**, **NH**<sub>2</sub>); 1658 (**C=C**); 1364.8 and 1159 (**SO**<sub>2</sub>). MS-ESI+ 30ev m/z: 204 [M+H]<sup>+</sup>.

### *N*-(1-cyclohexyl)sulfamide **2e**

Yield: 87%. M = 178 g/mol [C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S]. mp: 85-87 °C. R<sub>f</sub>=0.6 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (DMSO, δ ppm): 4.90 (d, 1H, J = 6.2, **NH** cyc); 3.60 (s, 2H, **NH**<sub>2</sub>); 3.25 (m, 1H, **CH**\*NH), 1.85 (m, 2H, **CH**<sub>2</sub> cyc), 1.55 (m, 2H, **CH**<sub>2</sub>-cyc), 1.35 (m, 2H, **CH**<sub>2</sub>-cyc); 1.25 (m, 4H, 2**CH**<sub>2</sub>-cyc). <sup>13</sup>C NMR (DMSO, δ ppm): 42.9; 33.5; 26.1; 25.9; 20. IR (KBr, ν cm<sup>-1</sup>): 3374-3269 (**NH**, **NH**<sub>2</sub>); 1368 and 1150 (**SO**<sub>2</sub>). MS-ESI+ 30ev m/z: 179 [M+H]<sup>+</sup>.

### *N*-(benzyl)sulfamide **2f**

Yield: 80%. M = 186 g/mol [C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S]. mp: 97-99°C. R<sub>f</sub> = 0.48 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (DMSO, δ ppm): 7.70-7.90 (m, 5H, **H**-Ar); 4.90 (s, 2H, **NH**<sub>2</sub>); 3.65 (m, 2H, **CH**<sub>2</sub>-Ar); <sup>13</sup>C NMR (DMSO, δ ppm): 136; 129.58; 125.29; 120.82; 43.6. IR (KBr, ν cm<sup>-1</sup>): 3368-3257(**NH**, **NH**<sub>2</sub>); 1658(**C=C**); 1364.8 and 1159 (**SO**<sub>2</sub>). MS-ESI+ 30ev m/z: 186 [M+H]<sup>+</sup>.

## 3. General Procedure for the preparation of *N*-sulfonylimines

A mixture of sulfonamide (2 mmol), aromatic aldehyde (2 mmol) and TBAB (0.2 mmol, 10%) was heated at 100°C under nitrogen atmosphere and solvent-free conditions for 3h. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature then diluted with methylene chloride. The residue was purified by silica gel chromatography diluted with CH<sub>2</sub>Cl<sub>2</sub> to give *N*-sulfonylimines (**3a-e**) in high yields. All products were known and characterized by <sup>1</sup>H NMR and IR spectral data.

Spectroscopic data for:

### *N*-(4-Methoxybenzylidene)-1-phenylsulfamide **3a**

Yield: 90%. M = 290 g/mol [C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S]. mp: 171-173°C. R<sub>f</sub> = 0.75 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 7.82-7.10 (2d, 4H, J<sub>1</sub>=J<sub>2</sub>= 8.73Hz, Ar-OCH<sub>3</sub>); 7.20 (m, 5H, Ar-NH); 7.05 (s, 1H, **CH**=N); 4.80 (m, H, **NH**); 3.95 (s, H, **CH**<sub>3</sub>-O). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 181.4; 162.9; 137.7; 130.2; 129.5; 124.5; 119.5; 114.4; 55.8. IR (KBr, ν cm<sup>-1</sup>): 3320 (**NH**); 1620 (**N=C**); 1323 and 1159 (**SO**<sub>2</sub>).

### *N*-(4-Methoxybenzylidene)-3-fluorophenylsulfamide **3b**

Yield: 78%. M = 303 g/mol [C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>SF]. mp: 186-188 °C. R<sub>f</sub>=0.70 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 7.90 (s, 1H, **CH**=N); 7.75-7.50 (m, 8H, **H**-2Ar); 4.65 (m, 1H, **NH**); 3.85 (s, H, **CH**<sub>3</sub>-O). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 177.2; 163.7; 160.9; 139.7; 131.2; 127.1; 124.5; 115.5; 114.5; 110.4; 49.7. IR (KBr, ν cm<sup>-1</sup>): 3340 (**NH**); 1623 (**N=C**); 1343 and 1185 (**SO**<sub>2</sub>).

***N*-(4-Methoxybenzylidene)-1-phenylethylsulfamide 3c**

Yield: 91%. M = 318 g/mol [C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S]. mp :173-175 °C. R<sub>f</sub> =0.67 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 8.60 (s, 1H, CH=N); 7.80-7.10 (2d, 4H, J<sub>1</sub>=J<sub>2</sub>=8.73Hz, Ar-OCH<sub>3</sub>); 7.45 (m, 5H, Ar-CH\*); 5.15 (d, 1H, J=7.27Hz, NH-CH); 4.75 (m, 1H, CH\*); 3.90 (s, 3H, CH<sub>3</sub>-O); 1.65 (d, 3H, J= 7.02Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 181.4; 162.9; 143.5; 130.2; 128.5; 126.9; 124.5; 115.5; 114.5; 55.8; 47.3; 20.3. IR (KBr, ν cm<sup>-1</sup>): 3340 (NH); 1611 (N=C); 1343 and 1159 (SO<sub>2</sub>).

***N*-(4-Methoxybenzylidene)-4-methoxy-phenylsulfamide 3d**

Yield: 90%. M = 320 g/mol [C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S]. mp: 182-184°C. R<sub>f</sub> = 0.78 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 7.50 (s, 1H, CH=N), 6.75-6.90 (m, 8H, H-2Ar), 3.90 (s, 9H, 2CH<sub>3</sub>-O). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 181.4; 162.9; 153.3; 130.0; 130.2; 124.5; 115.5; 114.5; 55.8. IR (KBr, ν cm<sup>-1</sup>): 3244 (NH); 1596.95 (N=C); 1323 and 1149 (SO<sub>2</sub>).

***N*-(4-Methoxybenzylidene)-1-cyclohexylsulfamide 3e**

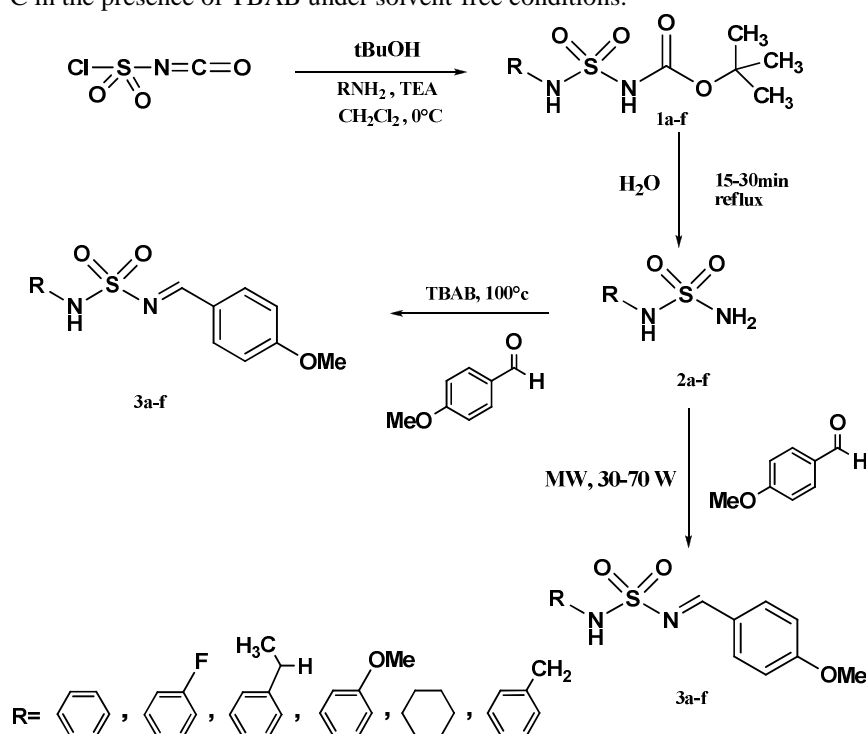
Yield: 85%. M = 296 g/mol [C<sub>14</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>S]. mp: 125-126°C. R<sub>f</sub> =0.83 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 8.50 (s, 1H, CH=N); 7.10-7.90 (2d, 4H, J<sub>1</sub>=J<sub>2</sub>=2.7Hz, H-Ar); 4.44 (d, 1H, J=7.62, NH cyc); 3.95 (s, 3H, CH<sub>3</sub>-O); 3.40 (m, 1H, CH-NH); 2.15 (m, 2H, CH<sub>2</sub> cyc), 1.75 (m, 2H, CH<sub>2</sub>-cyc), 1.65 (m, 2H, CH<sub>2</sub>-cyc); 1.35 (m, 4H, 2CH<sub>2</sub>-cyc). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 181.4; 162.9; 130.2; 124.5; 115.5; 114.5; 55.8; 44.4; 32.6; 25.7; 24.6. IR (KBr, ν cm<sup>-1</sup>): 3248 (NH); 1630 (N=C); 1323 and 1149 (SO<sub>2</sub>).

***N*-(4-Methoxybenzylidene)-benzylsulfamide 3f**

Yield: 75%. M = 304 g/mol [C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>S]. mp: 170-172°C. R<sub>f</sub> = 0.66 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH:9/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 7.90 (s, 1H, CH=N); 7.65-7.25 (m, 9H, H-2Ar); 4.85 (m, H, NH); 3.90 (s, 3H, CH<sub>3</sub>-O); 3.50 (m, 2H, CH<sub>2</sub>-Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 185.2; 156.8; 143.6; 129.1; 128.5; 126.7; 126.5; 124.5; 113.7; 111.5; 52.3; 47.3. IR (KBr, ν cm<sup>-1</sup>): 3320 (NH); 1600 (N=C); 1356 and 1159 (SO<sub>2</sub>).

**RESULTS AND DISCUSSION**

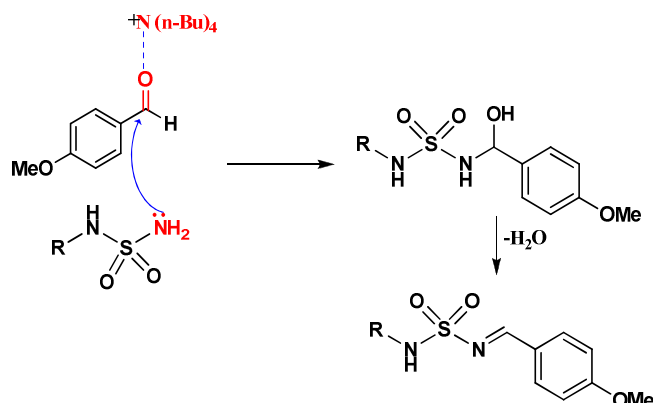
In order to find the suitable conditions, the condensation of sulfonamide (**1a-f**) with aromatic aldehyde was performed at 100°C in the presence of TBAB under solvent-free conditions.



Scheme 1. Synthesis of *N*-sulfonylimines

The sulphonamides (**1a-f**) were prepared by a simple and efficient method [23] by the reaction of the *tert*-butanol and chlorosulfonyl isocyanate in anhydrous methylene chloride at 0°C. After 30 min the *N*-chlorosulfonyl carbamate and triethylamine were added to a solution of primary amine in the same solvent. The deprotection reaction of sulfonamide was carried out in distilled water at 100°C for 30-60 min to give sulphonamides (**2a-f**) with quantitative

yields. Preparation of *N*-sulfonylimines includes the condensation of sulfonamides with aldehyde in the presence of TBAB at 100°C under solvent free conditions for 3 h.



**Scheme 2.** Plausible reaction mechanism for the formation of *N*-sulfonylimine in the presence of TBAB catalyst

To find the effect of TBAB (Table 1), the same reaction was carried out under the same conditions in the absence of TBAB. No reaction occurs after 10 h working time, this shows the essential role of TBAB.

**Table 1.** Synthesis of *N*-sulfonylimines

Entry	R	Product	Cat	t (°C)	t(h)	Yield (%)
1	C <sub>6</sub> H <sub>5</sub>	3a	TBAB	100	3	80
2	3-F-C <sub>6</sub> H <sub>4</sub>	3b	TBAB	100	3	82
3	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )	3c	TBAB	100	2	90
4	4-MeO-C <sub>6</sub> H <sub>4</sub>	3d	TBAB	100	3	75
5	C <sub>6</sub> H <sub>11</sub>	3e	TBAB	100	4	85
6	C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub>	3f	TBAB	100	2	75
7	C <sub>6</sub> H <sub>5</sub>	3a	FeCl <sub>3</sub> -6H <sub>2</sub> O	100	10	10
8	C <sub>6</sub> H <sub>5</sub>	3a	FeCl <sub>3</sub>	100	10	10
9	C <sub>6</sub> H <sub>5</sub>	3a	SnCl <sub>4</sub>	100	10	NR
10	C <sub>6</sub> H <sub>5</sub>	3a	AlCl <sub>3</sub>	100	10	NR
11	C <sub>6</sub> H <sub>5</sub>	3a	TiCl <sub>4</sub>	100	10	NR

In order to explore the specificity of this method, we also attempted the synthesis of *N*-sulfonylimines under microwave conditions (Table 2), in the case of the TBAB catalyst reaction we obtained *N*-sulfonylimines under solvent free with good yield, when the same reaction was subjected to microwave assisted reactions; only poor yield of the product (40%) was obtained with incomplete consumption of the starting material (entry 6, Table 2). Additionally, we find that the TBAB catalyst reactions under free solvent are more efficient, convenient and high yielding.

**Table 2.** A comparison of the results obtained using microwave and TBAB catalyst

Entry	R	Procedure				
		TBAB catalyst		Microwave heating		
		Temp °C	Yields (%)	Temp °C	Power (w)	Yields (%)
1	3a	100	80	165	70	38
2	3b	100	82	175	65	38
3	3c	100	90	180	55	35
4	3d	100	75	185	50	35
5	3e	100	85	187	45	36
6	3f	100	75	192	30	40

## CONCLUSION

A new series of *N*-sulfonylimines derivatives were synthesized in four steps (carbamoylation, sulfamoylation, deprotection and condensation with aldehyde) starting from chlorosulfonyl isocyanate (CSI) and primary amine in the presence of TBAB as catalyst. This efficient and simple method provides in most cases the desired *N*-sulfonylimines in good yields. This new procedure offers advantages like minimum pollution of the environment, non-toxic catalyst, which makes it a useful and attractive process for the preparation of these compounds.

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