



# Solid catalysts for the production of fine chemicals: the use of natural phosphate alone and doped base catalysts for the synthesis of unsaturated arylsulfones

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**Abstract**—The inexpensive natural phosphate, both alone and doped with potassium fluoride, is a new basic catalyst for the synthesis of  $\alpha,\beta$ -unsaturated arylsulfones. Activation by water and benzyltriethylammonium chloride has also been investigated. When using an ammonium salt, natural phosphate doped with potassium fluoride is an excellent solid support for the synthesis of  $\alpha,\beta$ -unsaturated arylsulfones, leading to excellent yields in a few minutes.

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## 1. Introduction

Heterogeneous catalysis is an important application of porous solids possessing acid and Lewis basic sites. Studies on solid acid catalysts are enormous. Though little attention is devoted to basic catalysts in comparison with solid acid catalysts, high activities and selectivities are often obtained for many kinds of reaction.<sup>1</sup> Numerous reactions including isomerizations, additions, alkylations and cyclizations are carried out industrially using liquid bases as catalysts. Furthermore, many organic reactions require a stoichiometric amount of liquid bases. The advantages of heterogeneous catalysis over conventional homogeneous reactions is that it provides greater selectivity, enhanced reaction rates, cleaner product and manipulative simplicity. For these reasons, heterogeneous catalysis can be considered as a new attempt to develop the notion of ‘clean chemistry’.

Sulfones are important intermediates in organic synthesis.<sup>2</sup> Their importance is due to the fact that arylsulfonyl groups can stabilise adjacent carbanions<sup>3</sup> and may easily be removed by hydrolysis, reduction or elimination<sup>4</sup> and, when appropriate, may be eliminated to introduce carbon–carbon double bonds into organic molecule.<sup>5</sup> Thus they are

useful temporary activating groups for alkylation,<sup>6</sup> acylation<sup>7</sup> and addition reactions.<sup>8</sup>

The Knoevenagel condensation of arylsulfones and aldehydes is one of the most popular methods for synthesizing unsaturated arylsulfones. The deprotonation of phenylsulfonylalkanes generally involves strong bases such as sodium hydride,<sup>9</sup> butyl lithium<sup>10</sup> or lithium di-*isopropyl*-amide (LDA).<sup>11</sup> However, the deprotonation energy strongly depends on the presence of adjacent electron-withdrawing groups such as an ester,<sup>3</sup> nitrile or ketone.<sup>12</sup>

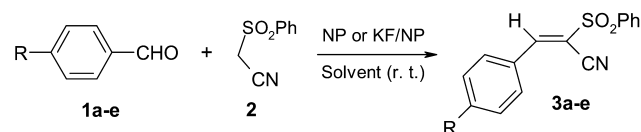
In recent years, the Knoevenagel condensation in heterogeneous media has been carried out in presence of zeolites,<sup>13</sup> organic resins,<sup>14</sup> mixed magnesium–aluminium oxides derived from hydrotalcites,<sup>15</sup> sepiolites,<sup>16</sup> aluminophosphonates oxynitrides (ALPON),<sup>17</sup> and more recently, synthetic phosphate  $\text{Na}_2\text{CaP}_2\text{O}_7$ .<sup>18</sup>

We have previously investigated the use of natural phosphate to promote organic transformations<sup>19</sup> and have shown that its mildly basic properties can be exploited in many synthetic applications.<sup>20</sup> We have also shown that doping with mineral salts increases the activity of natural phosphate.<sup>20</sup>

In continuation of our ongoing program to develop clean and economical processes for the production of fine chemicals, we describe in this paper, the use of natural phosphate (NP) alone and doped with KF as an inorganic

**Keywords:** Natural phosphate; Ammonium salt; Knoevenagel; Heterogeneous catalysis; Arylsulfones; Recyclable catalyst.

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Scheme 1.

support of the Knoevenagel condensation between phenylsulfonacetonitrile **2** and benzaldehyde or 4-substituted benzaldehydes **1**, at room temperature with a solvent (Scheme 1).

## 2. Preparation of the catalyst and structural characteristics

Natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco).<sup>21</sup> Prior to use this material requires initial treatments such as crushing and washing. For use in organic synthesis, the NP is treated by techniques involving attrition, sifting, calcinations (900 °C), washing, and recalcination. These treatments lead to a fraction between 100 and 400  $\mu\text{m}$  that is rich in phosphate and has following chemical composition  $\text{P}_2\text{O}_5$  (34.24%), CaO (54.12%),  $\text{F}^-$  (3.37%),  $\text{SiO}_2$  (2.42%),  $\text{SO}_3$  (2.21%),  $\text{CO}_2$  (1.13%),  $\text{Na}_2\text{O}$  (0.92%), MgO (0.68%),  $\text{Al}_2\text{O}_3$  (0.46%),  $\text{Fe}_2\text{O}_3$  (0.36%),  $\text{K}_2\text{O}$  (0.04%) and several metals (Zn, Cu, Cd, V, U, Cr) in the range of ppm. The structure of the material is similar to that of fluoroapatite ( $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ). In sedimentary rocks, phosphates are formed from compounds derived from apatite by partial isomorphic substitution:  $\text{Ca}^{2+}$  ions by  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ , or  $\text{Al}^{3+}$ ,  $\text{PO}_4^{3-}$  ions by  $\text{VO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  or  $\text{MnO}_4^{2-}$ , and  $\text{F}^-$  by  $\text{OH}^-$  or  $\text{Cl}^-$ . These different substitutions cause distortions of the structure which depends on the nature and the radii of the ions involved. This solid presented a very low surface area (BET) at ca.  $1 \text{ m}^2 \text{ g}^{-1}$ .

KF/NP has been prepared by adding 8 g of NP to a 1 g KF aqueous solution. The mixture was stirred, evaporated to dryness and dried at 150 °C for 2 h. The catalyst KF/NP (weight report KF/NP: 1:8)<sup>20c,d</sup> is a grey powder, the colour of NP itself. The IR data shows the presence of some additional H-bonded water at  $3250 \text{ cm}^{-1}$  and  $1636\text{--}1675 \text{ cm}^{-1}$  for the supported solid. On the other hand, the X-ray diffraction of KF/NP gives a diffraction pattern almost identical to that of NP itself. Peak positions and intensities are essentially unaltered. We showed previously<sup>20</sup> that supporting KF on NP causes the formation of a more open structure which incorporates KF in such a way that crystalline KF is not formed in significant quantities. However, it appears that the basic structure of NP is not destroyed, indicating a less profound interaction of KF with NP than is the case with alumina.<sup>22</sup> The morphology of the solid surface was observed in scanning electron micrograph (SEM) images of KF/NP in comparison with NP. It clearly appears that some modifications have taken place at the surface of the catalyst.

## 3. Results and discussion

The results for a variety of  $\alpha,\beta$ -unsaturated arylsulfones

**Table 1.** Synthesis of products **3** by Knoevenagel condensation using NP and KF/NP

Products	R	Solvent	Yield, % (time, h) <sup>a</sup>	
			NP (5 h)	KF/NP (1 h)
<b>3a</b>	H	MeOH	56	64
<b>3a</b>	H	EtOH	58	60
<b>3a</b>	H	MeOH <sup>b</sup>	60	68
<b>3a</b>	H	EtOH <sup>b</sup>	68	77
<b>3b</b>	$\text{NO}_2$	EtOH	72	82
<b>3b</b>	$\text{NO}_2$	EtOH <sup>b</sup>	87	95
<b>3c</b>	Cl	EtOH	66	75
<b>3c</b>	Cl	EtOH <sup>b</sup>	80	88
<b>3d</b>	Me	EtOH	50	60
<b>3d</b>	Me	EtOH <sup>b</sup>	64	76
<b>3e</b>	OMe	EtOH	46	58
<b>3e</b>	OMe	EtOH <sup>b</sup>	60	70

<sup>a</sup> Yields of pure products isolated by distillation under vacuum and identified by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, mass spectroscopy and IR spectroscopy.

<sup>b</sup> The solvent/water ratio is 90:10.

prepared by Knoevenagel condensation catalyzed by NP alone and doped with KF are summarized in Table 1.

In general, the use of NP as heterogeneous catalyst in the Knoevenagel condensation has allowed the isolation of  $\alpha,\beta$ -unsaturated arylsulfones in moderate yields (Table 1). The reactions are relatively slow. Only the isomer of configuration *E* has been isolated.<sup>18</sup>

Solid catalysts become particularly interesting when they can be regenerated. Indeed, in our case, NP was recovered quantitatively by simple filtration and regenerated by calcination for 15 min at 700 °C. The recovered catalyst was reused several times without loss of activity, even after the sixth, cycle product **3a** was obtained in the same yield.

Under similar conditions, the use of NP doped with KF, decreases remarkably the Knoevenagel reaction time (Table 1).

The addition of water slightly increases the reaction yields of the  $\alpha,\beta$ -unsaturated arylsulfones **3** with either catalyst (NP and KF doped NP). For example, the yield of alkene **3a** increases from 64 to 68% in methanol and from 64 to 77% in ethanol when using KF/NP as a catalyst. Various quantities of water have been used. Figure 1 shows that the best results are obtained when 10% of water is added. This activation is probably due to the interaction between water and the solid surface. If a large amount of water is used a thin film of water will be formed between the organic reagents and catalyst which explain the decreasing of the yields (Fig. 1).

The best conditions for synthesizing the alkene **3a** are generalized to **3b**, **3c**, **3d** and **3e** (Table 1).

We clearly show that water increases the catalytic activity of both NP alone and with KF/NP, in all cases. For example, for the alkene **3b**, the yield increases from 72 to 87% and from 82 to 95% for the two catalysts NP alone and KF/NP, respectively. However, under similar conditions, the best catalytic activity was observed with the NP doped by KF (Table 1).

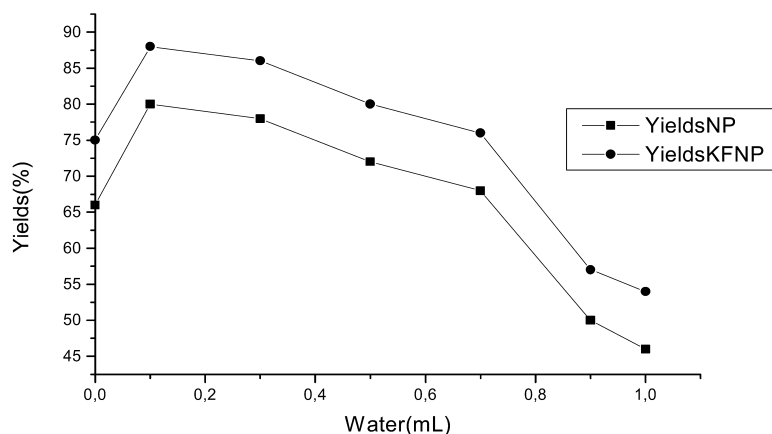


Figure 1. Influence of water in the synthesis of **3a**.

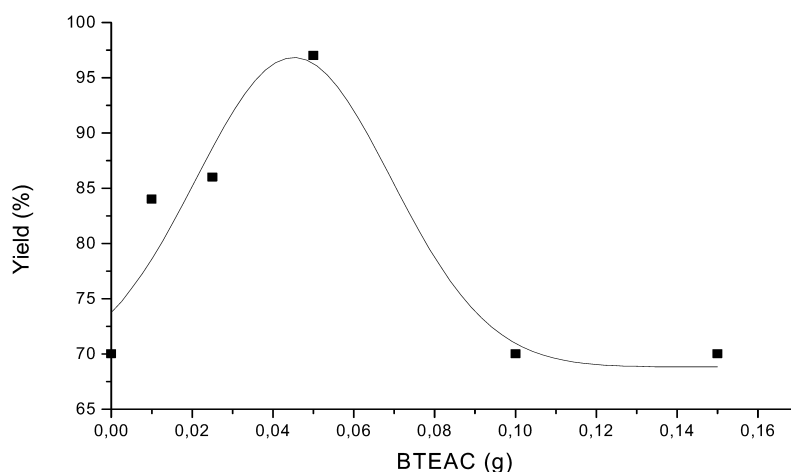


Figure 2. Influence of BTEAC in the synthesis of **3b** (KF/NP catalyst).

It has been shown previously that the addition of an ammonium salt to natural phosphate,<sup>23</sup> fluorapatite,<sup>24</sup> or hydroxyapatite<sup>25</sup> increases the activity of these catalysts. Therefore, we carried out the synthesis of the  $\alpha,\beta$ -unsaturated arylsulfone **3b** with KF/NP in ethanol using different amounts of benzyltriethylammonium chloride (BTEAC). The results obtained after 40 min show that the best yields are obtained with 0.050 g of BTEAC (Fig. 2). Moreover, the kinetic curves for the synthesis of the alkene **3b** in the absence and in the presence of BTEAC clearly show the enhancement of the catalytic activity of KF/NP by addition of the ammonium salt. The yields obtained after 10, 20, 30 and 40 min are 47, 75, 86, and 97% in the presence of BTEAC and 20, 39, 52, and 68% without BTEAC.

Finally, this method was extended to the preparation of several  $\alpha,\beta$ -unsaturated arylsulfones (Table 2). In all cases, the reaction afforded product **3** in high yields. The addition of BTEAC caused a significant increase in the reaction rate (Table 2). Similar effects were observed in the presence of NP alone catalyst (Table 2). It is important to note that BTEAC itself has no catalytic activity and seems to act only as a phase transfer catalyst.

The effect of electron acceptor or donor substituents on the aromatic ring of benzaldehyde in the Knövenagel condensation was carried out in the reaction of phenylsulfonyl-

acetonitrile **2** and substituted benzaldehyde derivatives (**1a–e**) using NP and KF/NP as catalysts. Results from Tables 1 and 2 show that the presence of electron acceptor groups on the aromatic ring increases the reaction rate proportionally to the value of the Hammett constant. Meanwhile, the presence of electron donor groups decreases the reaction rate, demonstrating the participation of the aldehyde in the controlling step of the reaction.

Table 2. Synthesis of products **3** by Knövenagel condensation using NP and KF/NP, in the presence and in the absence of BTEAC

Entry	Products	R	Solvent	Yield, % (time, h) <sup>a</sup>	
				NP	KF/NP
1	<b>3a</b>	H	EtOH	58 (5)	60 (1)
2	<b>3a</b>	H	EtOH <sup>b</sup>	75 (5)	73 (0.8)/91 (1)
3	<b>3b</b>	NO <sub>2</sub>	EtOH	72 (5)	68 (0.6)/82 (1)
4	<b>3b</b>	NO <sub>2</sub>	EtOH <sup>b</sup>	85 (3)/94 (4)	86 (0.5)/97 (0.6)
5	<b>3c</b>	Cl	EtOH	66 (5)	75 (1)
6	<b>3c</b>	Cl	EtOH <sup>b</sup>	86 (4)/93 (5)	77 (0.6)/97 (1)
7	<b>3d</b>	Me	EtOH	50 (5)	60 (1)
8	<b>3d</b>	Me	EtOH <sup>b</sup>	73 (5)	86 (1)
9	<b>3e</b>	OMe	EtOH	46 (5)	58 (1)
10	<b>3e</b>	OMe	EtOH <sup>b</sup>	70 (5)	92 (1)

<sup>a</sup> Yields of pure products isolated by distillation under vacuum and identified by <sup>1</sup>H, <sup>13</sup>C NMR, mass spectroscopy and IR spectroscopy.

<sup>b</sup> BTEAC 0.05 g.

Thus, we estimate that the surface of the catalyst (NP or KF/NP) presents multicatalytic active sites. The basic sites polarize the C–H bond of the active methylene compound. The acidic surface of NP<sup>26</sup> probably coordinates with the oxygen of the carbonyl carbon on which a partial positive charge appears. Consequently, the C–C bond formation is facilitated and the final alkene is obtained by the transfer of a proton followed by dehydration.

The activity of KF/NP/BTEAC seems to be higher than other known catalysts (entry 2–11; Table 3) and slightly lower than ALPON<sup>27</sup> (atomic ratio Al:P:N=1:0.95:0.42; entry 12; Table 3).

**Table 3.** Comparison of KF/NP/BTEAC with several heterogeneous catalysts in the synthesis of product **3a** by Knoevenagel condensation

Entry	Solid catalyst	Yields (time) [(%) (time/h)] <b>3a</b>
1	KF/NP/ BTEAC	91 (1)
2	KF/NP/Water	77 (1)
3	KF/NP	60 (1)
4	NP/ BTEAC	75 (5)
5	NP/water	68 (5)
6	NP	58 (5)
7	Na <sub>2</sub> CaP <sub>2</sub> O <sub>7</sub> <sup>18</sup>	58 (1)
8	Na <sub>2</sub> CaP <sub>2</sub> O <sub>7</sub> /water <sup>18</sup>	74 (1)
9	Zeolite–CsX <sup>25</sup>	35 (2)
10	MgO <sup>27</sup>	86 (2)
11	Mg–Al-hydrotalcite <sup>27</sup>	71 (2)
12	ALPON <sup>27</sup>	95 (2) <sup>a</sup>

<sup>a</sup> Atomic ratio Al:P:N=1:0.95:0.42.

#### 4. Conclusion

Natural phosphate doped with potassium fluoride is an efficient basic catalyst for the Knoevenagel reaction. Several  $\alpha,\beta$ -unsaturated arylsulfones can be synthesized with high yields using catalytic amounts of KF/NP. This catalyst brings advantages such as high catalytic activity under very mild liquid phase conditions, easy separation of the catalyst by simple filtration, possible recycling of the catalyst, use of non-toxic and inexpensive catalyst and especially, elimination of salts and by-product pollutants. This solid base catalyst then becomes a practical alternative to soluble bases. The addition of an ammonium salt increases the reaction rate for all  $\alpha,\beta$ -unsaturated arylsulfones synthesized and the products were obtained in high yields.

#### 5. Experimental

##### 5.1. General comments

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker DRX-400 spectrometer in CDCl<sub>3</sub>, using CDCl<sub>3</sub> as internal standard. The chemical shifts ( $\delta$ ) are expressed in ppm relative to CDCl<sub>3</sub> and coupling constant ( $J$ ) in Hertz. Mass spectra were obtained on a VG ZAB-HS mass spectrometer. IR spectra were obtained on a FTIR (ATI Mattson-Genesis Series) and reported in wave numbers (cm<sup>-1</sup>). Surface area and pore size analysis were carried out at 77 K on a Micromeritics ASAP2010 instrument using nitrogen as adsorbent. X-ray diffraction patterns of the catalysts were obtained on a

Philips 1710 diffractometer using Cu K $\alpha$  radiation and SEM images were taken on a Hitachi S-2400 microscope. Melting points were determined with a 'Thomas Hoover' melting (capillary method) apparatus and are uncorrected. Flash column chromatography was performed using Merck silica gel 60 (230–400 mesh ASTM).

All reactions were carried out under atmosphere air. Solvents and starting materials (Aldrich) were used without further purification. The natural phosphate alone and doped by potassium fluoride were prepared according to the method we described previously.<sup>20</sup>

##### 5.2. General procedure for the syntheses of $\alpha,\beta$ -unsaturated arylsulfones (**3a–e**)

To a flask containing an equimolar mixture (1 mmol) of aldehyde **1** and phenylsulfonylacetonitrile **2** in solvent (methanol or ethanol: 1 ml), phosphate catalyst (NP or KF/NP) 0.1 g was added and the mixture was stirred at room temperature for a specified time (Tables 1 and 2). The reaction mixture was filtered and the catalyst washed with dichloromethane. After concentration of the filtrate under reduced pressure the residue was subjected to chromatography or distillation under vacuum leading to the  $\alpha,\beta$ -unsaturated sulfone as a solid. The product structure was analysed by <sup>1</sup>H, <sup>13</sup>C NMR, mass spectroscopy and IR spectrometry.

The same procedure was used for the reactions carried out with NP or KF/NP (0.1 g) activated with water (0.1 ml) or BTEAC (0.050 g). Water or BTEAC were always added in the last place. In the case of BTEAC, the products were washed with water to eliminate the ammonium salt before purification.

##### 5.3. Identifications of products

**5.3.1.  $\alpha$ -Phenylsulfonyl cinnamionitrile, **3a**.** White solid; mp 130–132 °C;  $R_f$  (20% AcOEt/hexane) 0.46;  $\nu_{\max}$  (KBr) 3031, 2218, 1578 cm<sup>-1</sup>;  $\delta_H$  (400 MHz CDCl<sub>3</sub>) 8.24 (1H, s, =CH); 8.03 (2H, d,  $J=8.4$  Hz, HAr); 7.92 (2H, d,  $J=8.8$  Hz, HAr); 7.74–7.70 (1H, m, HAr); 7.64–7.57 (3H, m, HAr); 7.50 (2H, t,  $J=8.0$  Hz, HAr);  $\delta_C$  (100 MHz CDCl<sub>3</sub>) 151.5, 137.8, 134.6, 134.1, 131.0, 130.1, 129.7, 129.5, 128.7, 114.8, 113.1;  $m/z$  (EI): 271 (M<sup>2+</sup>, 5), 269 (63, M<sup>+</sup>), 128 (100), 101 (10), 77 (100), 51 (36%); HRMS (EI): M<sup>+</sup>, found 269.0513. C<sub>15</sub>H<sub>11</sub>NO<sub>2</sub>S requires 269.0511.

**5.3.2.  $\alpha$ -Phenylsulfonyl 4-nitrocinnamionitrile, **3b**.** White solid; mp 140–142 °C;  $R_f$  (20% AcOEt/hexane) 0.37;  $\nu_{\max}$  (KBr) 3113, 2218, 1596 cm<sup>-1</sup>;  $\delta_H$  (400 MHz CDCl<sub>3</sub>) 8.34 (2H, d,  $J=8.8$  Hz, HAr); 8.30 (1H, s, =CHAr); 8.08 (2H, d,  $J=8.8$  Hz, HAr); 8.04 (2H, d,  $J=7.6$  Hz, HAr); 7.77 (1H, t,  $J=7.6$  Hz, HAr).  $\delta_C$  (100 MHz CDCl<sub>3</sub>) 151.0, 148.0, 137.4, 136.0, 135.2, 131.5, 129.9, 129.0, 124.5, 115.5, 112.3;  $m/z$  (EI): 314 (13, M<sup>+</sup>), 181 (5), 141 (53), 77 (100), 51 (22), 40 (36%); HRMS (EI): M<sup>+</sup>, found 314.0367. C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>S requires 314.0361.

**5.3.3.  $\alpha$ -Phenylsulfonyl 4-chlorocinnamionitrile, **3c**.** White solid; mp 152–154 °C;  $R_f$  (20% AcOEt/hexane) 0.51;  $\nu_{\max}$  (KBr) 3031, 2227, 1596 cm<sup>-1</sup>;  $\delta_H$  (400 MHz

CDCl<sub>3</sub>) 8.18 (1H, s, =CHAr); 8.02 (2H, d, *J*=8.8 Hz, HAr); 7.87 (2H, d, *J*=8.8 Hz, HAr); 7.75–7.71 (1H, m, HAr); 7.65–7.60 (2H, m, HAr); 7.51–7.46 (2H, m, HAr); δ<sub>C</sub> (100 MHz CDCl<sub>3</sub>) 149.9, 140.5, 137.6, 134.8, 132.1, 129.9, 129.5, 128.7, 128.5, 115.2, 112.9; *m/z* (EI): 305 (30, M<sup>2+</sup>), 303 (57, M<sup>+</sup>), 162 (100), 126 (28), 77 (56), 51 (54), 40 (53); HRMS (EI): M<sup>+</sup>, found 303.0128. C<sub>15</sub>H<sub>10</sub>ClNO<sub>2</sub>S requires 303.0121.

#### 5.3.4. α-Phenylsulfonyl 4-methylcinnamitrile, 3d.

White solid; mp 144–146 °C; *R*<sub>f</sub> (20% AcOEt/hexane) 0.47; ν<sub>max</sub> (KBr) 3031, 2227, 1596 cm<sup>-1</sup>; δ<sub>H</sub> (400 MHz CDCl<sub>3</sub>) 8.20–7.20 (m, 9H, ArH and 1H, HC=C); 2.4 (s, 3H, CH<sub>3</sub>); δ<sub>C</sub> (100 MHz CDCl<sub>3</sub>) 159.0, 139.9, 138.2, 135.2, 132.4, 131.3, 131.2, 129.3, 129.2, 114.9, 99.1, 21.5; *m/z* (EI): 285 (20, M<sup>2+</sup>), 283 (100, M<sup>+</sup>), 142 (29), 115 (27), 77 (100); HRMS (EI): M<sup>+</sup>, found 283.0669. C<sub>16</sub>H<sub>13</sub>NO<sub>2</sub>S requires 283.0667.

#### 5.3.5. α-Phenylsulfonyl 4-methoxycinnamitrile, 3e.

White solid; mp 113–115 °C; *R*<sub>f</sub> (20% AcOEt/hexane) 0.23; ν<sub>max</sub> (KBr) 3022, 2218, 1589 cm<sup>-1</sup>; δ<sub>H</sub> (400 MHz CDCl<sub>3</sub>) 8.14 (1H, s, =CHAr); 8.01 (2H, d, *J*=7.6 Hz, HAr); 7.92 (2H, d, *J*=8.8 Hz, HAr); 7.69 (1H, t, *J*=7.6 Hz, HAr); 7.60 (2H, t, *J*=7.6 Hz, HAr); 6.98 (2H, d, *J*=8.8 Hz, HAr); 3.89 (3H, s, OCH<sub>3</sub>); δ<sub>C</sub> (100 MHz CDCl<sub>3</sub>) 164.5, 151.0, 138.5, 134.3, 133.7, 129.6, 128.4, 122.9, 115.0, 113.7, 110.9, 55.7; *m/z* (EI): 301 (10, M<sup>2+</sup>), 299 (44, M<sup>+</sup>), 157 (100), 77 (33), 51 (10), 40 (16); HRMS (EI): M<sup>+</sup>, found 299.0621. C<sub>16</sub>H<sub>13</sub>NO<sub>3</sub>S requires 299.0616.

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