Res Chem Intermed
DOI 10.1007/s11164-012-1008-9

Aqueous media preparation of 2-amino-4,6-diphenylnicotinonitriles using cellulose sulfuric acid as an efficient catalyst

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Received: 18 October 2012 / Accepted: 27 December 2012

Abstract A convenient approach to the synthesis of 2-amino-4,6-diphenylnicotinonitriles via four-component reaction of aromatic aldehydes, acetophenone derivatives, malononitrile and ammonium acetate is described. The reactions were done in water as solvent using cellulose sulfuric acid as catalyst. This simple protocol offer advantages such as shorter reaction times, simple work-up procedure, excellent yields and catalyst recovery.

Keywords Cellulose sulfuric acid · 2-Amino-4,6-diphenylnicotinonitrile · Catalyst recovery · Aqueous media preparation

Introduction

Multicomponent reactions (MCRs) have received substantial consideration from the organic community for their innumerable advantages over conventional multistep synthesis [1]. These reactions provide instantaneous access to large compound libraries with diverse functionality [2–6]. Moreover, MCRs are both atom and step economic as they avoid time consuming costly purification processes in addition to the protection and deprotection steps [7].

The prevalence of pyridines in nature and their central role as versatile building blocks in the synthesis of natural products as well as biologically active compounds has led to a continued interest in the practical synthesis of pyridine derivatives [8, 9]. The pyridine nucleus has also been found to be integral part of several potent inhibitors of phosphodiesterase 4 (PDE4) that are known to be beneficial for the potential treatment of asthma and chronic obstructive pulmonary disease (COPD)

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Published online: 13 January 2013

[10, 11]. 2-Amino-3-cyanopyridine derivatives are known to have multiple biological activities, such as anti-tumor activity [12], cardiotonic [13], anti-inflammatory [14] and anti-parkinsonism properties [15]. 2-Amino-3-cyano-pyridine derivatives were also reported as novel IKK-β inhibitors [14], A_{2A} adenosine receptor antagonists [15], potent inhibitor of HIV-1 integrase [16], and so on. 2-Amino-3-cyanopyridines are important and useful intermediates in preparing variety of heterocyclic compounds [17, 18]. Therefore, the synthesis of these compounds is of great significance.

A number of reports on this topic have appeared in the literature [19–27]. The common method used in the preparation of 2-amino-4,6-diphenylnicotinonitrile involves the chalcone or carbonyl compound condensation with malononitrile and ammonium acetate by conventional heating in the presence of ethyl alcohol as a solvent. Recently, the use of ultrasound [19], trifluoroethanol [20], ultrasonic irradiation and grindstone technology [21], silica-bound *N*-propyl triethylenetetramine sulfamic acid [22], microwave irradiation [23], ytterbium perfluorooctanoate [24], ionic liquid ethylammonium nitrate [25], [Bmim]BF_4 ionic liquid [26] and liquid liquid phase transfer catalysis conditions [27] have been developed for the synthesis of 2-amino-4,6-diphenylnicotinonitrile drivatives. However, some of these procedures have certain limitations such as harsh reaction conditions, long reaction time, toxic benzene as solvent, high temperature or microwave assistance, tedious work-up, and low yields. However, a straightforward and efficient one-pot reaction by catalysis in mild conditions is still limited. Hence, the development of novel methods for the synthesis of 2-amino-3-cyanopyridines is of great importance because of their potential biological and pharmaceutical activities.

During the course of our studies toward the development of new routes to the synthesis of heterocyclic compounds, such as 3,4-dihydropyrimidin-2(*1H*)-ones/-thiones/imines [28], β-amino ketone compounds [29], amidoalkyl naphthols [30] and 1,4-dihydropyridine derivatives [31] by multi-component reactions, we herein disclose a valid and an efficient procedure for the synthesis of 2-amino-4,6-diphenylnicotinonitrile derivatives via condensation of aromatic aldehydes, acetophenones, malononitrile and ammonium acetate in the presence of cellulose sulfuric acid (CSA), as an inexpensive and biodegradable solid acid catalyst in H_2O at a temperature of 60 °C. To the best of our knowledge, the use of cellulose sulfuric acid as a catalyst for the synthesis of 2-amino-4,6-diphenylnicotinonitriles previously has not been reported.

In the recent years, being focused on green chemistry using environmentally benign reagents and conditions is one of the most fascinating developments in synthesis of widely used organic compounds. The use of water as a promising solvent for organic reactions has received considerable attention in organic synthesis owing to its green credentials [32, 33] and organic synthesis in aqueous media offering key advantages such as rate enhancement and insolubility of the final products, which facilitates their isolation by simple filtration.

Heterogeneous catalysts for the synthesis of fine chemicals have attracted considerable interest from both environmental and economical points. The solid acids have high turnover numbers and easily separated from reaction mixtures [34]. Several interesting biopolymers have been utilized as a support for catalytic

applications, such as alginate [35], gelatin [36, 37], starch [38] and chitosan [39] derivatives. Cellulose and its derivatives, have some unique properties, which make them attractive alternatives for conventional synthetic organic or inorganic supports for catalytic applications [40]. The most frequently synthesized and used cellulose derivatives with functionalization patterns of high uniformity are important not only for comparison with statistically modified celluloses, but are particularly important as products with new properties and applications. Their importance also lies with respect to questions that remain open about the solution structure of cellulose derivatives and for the design of supra molecular architectures and has been widely studied during the past decades because of it is a biodegradable material and a renewable resource [41]. Thus, biopolymers are attractive candidates in the search for such solid support catalysts [42].

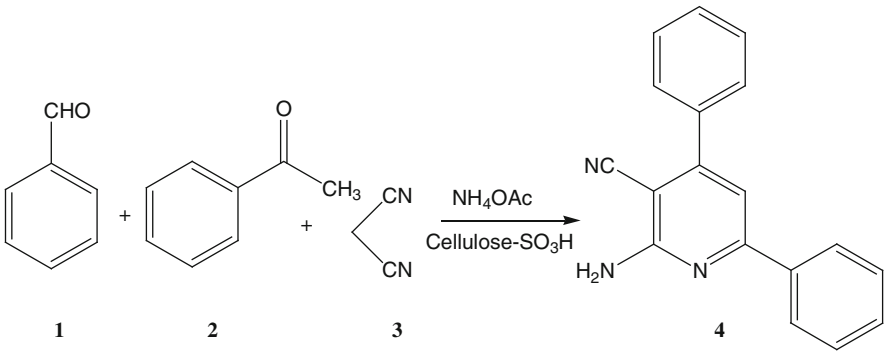
Cellulose sulfuric acid is easily prepared from the treatment of inexpensive cellulose with chlorosulfonic acid [43]. Recently, cellulose sulfuric acid has been utilized as a biopolymeric solid support acid catalyst for the synthesis of α-aminonitriles [43], quinolines [44], imidazoline, oxazolines, thiazolines [45], benzoxanthene derivatives [46], α-aminophosphonates [47], substituted pyrroles [48], 6-chloro-8-substituted-9*H*-purines [49], 1,4-dihydropyridines [50] and Ugi reaction [51].

Results and discussion

To find out the suitable conditions for the reaction, a series of experiments were performed with the standard reaction of benzaldehyde **1a**, acetophenone **2a**, malononitrile **3**, and ammonium acetate as a model reaction (Scheme 1).

Effect of catalyst

Our initial work started with screening of catalyst loading so as to identify optimal reaction conditions for the synthesis of 2-amino-4,6-diphenylnicotinonitrile derivatives. A mixture of benzaldehyde **1a** (1 mmol), acetophenone **2a** (1 mmol),



Scheme 1 Synthesis of 2-amino-4,6-diphenylnicotinonitrile (optimizing the reaction)

malononitrile **3** (1 mmol), and ammonium acetate (1 mmol) were stirred at 60 °C together with 5 ml water without catalyst. The yield was only 38 % (Table 1, Entry 1) after 7 h of the reaction. The same reaction was carried out in the presence of a catalytic amount of 0.015 mmol of cellulose–SO_3H under similar conditions. The yield of the product was increased to 66 % within 5 h. (Entry 2). Increasing the quantity of the catalyst to 0.03, 0.04 and 0.05 mmol gave the corresponding product in 72, 87 and 95 % yields in 3.5, 3 and 2.5 h, respectively. Use of just 0.05 mmol was sufficient to drive the reaction forward; larger amounts of the catalyst did not improve the results. Although the use of 0.06 mmol of cellulose–SO_3H permitted the reaction time to be decreased to 1.5 h and also the yield decreased to 88 % (Entry 6). A possible explanation for the low product yield is that the starting material or the product may have been destroyed during the reaction when an excess amount (0.06 mmol) of cellulose–SO_3H was used in the reaction. Hence 0.05 mmol of cellulose–SO_3H was sufficient to catalyze the reaction effectively.

Effects of the solvents

We try to optimize the model process mentioned above by detecting the efficiency of several classic solvents chosen as the medium for comparison. In each case, the substrates were mixed together with 5 ml solvent under high speed stirring conditions at 60 °C. Among the tested solvents such as methanol, ethanol, acetonitrile, THF, dichloromethane, water and solvent-free conditions, the formation of product **4a** was more facile and proceeded to give not only in high yield but also with high reaction rate in water (95 % yield in 2.5 h) (Table 2, entry 7).

Polar protic solvents such as ethanol and methanol afforded moderate yields of desired products but took comparatively longer reaction time (Table 1, entries 1 and 2). When the reaction was performed in acetonitrile, THF and dichloromethane (DCM), unfortunately, the desired product was only obtained in 42, 45 and 35 % yield respectively (Table 1, entries 3, 4, 5). In solvent-free conditions the desired product **4a** was obtained in low yield 76 % (Table 1, entry 6). The results show that water as solvent is effective for good yield (Table 2, entry 7).

Table 1 The reaction of benzaldehyde, acetophenone, malononitrile and ammonium acetate: effect of catalysis

Entry	Catalyst	Amount (mmol)	Time (h)	Yield (%)[a]
1	Cellulose–SO_3H	0.00	7.0	38
2	Cellulose–SO_3H	0.015	5.0	66
3	Cellulose–SO_3H	0.03	3.5	72
4	Cellulose–SO_3H	0.04	3.0	87
5	Cellulose–SO_3H	0.05	2.5	95
6	Cellulose–SO_3H	0.06	1.5	88

Reaction conditions: benzaldehyde (1 mmol), acetophenone (1 mmol), malononitrile (1 mmol) and ammonium acetate (1 mmol) and water (5 ml) at 60 °C

[a] Isolated yields

Table 2 The reaction of benzaldehyde, acetophenone, malononitrile and ammonium acetate: effect of solvent

Entry	Solvent	Amount of catalyst (mmol)	Time (h)	Yield (%)[a]
1	Ethanol	0.05	4.0	70
2	Methanol	0.05	4.0	65
3	Acetonitrile	0.05	8.0	42
4	THF	0.05	6.0	45
5	DCM	0.05	8.0	35
6	None	0.05	5.0	76
7	Water	0.05	2.5	95

Reaction conditions: benzaldehyde (1 mmol), acetophenone (1 mmol), malononitrile (1 mmol) and ammonium acetate (1 mmol) in water (5 ml) in the presence of Cellulose–SO_3H (0.05 mmol) at 60 °C

[a] Isolated yields

Table 3 Optimisation of temperature using cellulose–SO_3H (0.05 mmol) as catalyst in water

Entry	Temperature (°C)	Time (h)	Yield (%)[a]
1	40	3.5	70
2	50	3.0	88
3	60	2.5	95
4	70	2.5	86
5	80	2.5	80

Reaction conditions: benzaldehyde (1 mmol), acetophenone (1 mmol), malononitrile (1 mmol) and ammonium acetate (1 mmol) in water (5 ml) in the presence of cellulose–SO_3H (0.05 mmol)

[a] Isolated yields

Effects of reaction temperature

In order to further improve the yield of the reaction, we tried to perform the experiments in 40, 50, 60, 70 and 80 °C. It was observed that a lower reaction temperature led to a lower yield. As shown in Table 3, entry 3, we found that high temperature could improve the reaction yield and shorten the reaction time. As shown in Table 3, entry 5, the model reaction preceded in a considerably lower yield under 80 °C due to remove of ammonia from reaction vessel in high temperature. With having these results in hand, we selected the water as solvent for the one-pot reaction of aromatic aldehydes, malononitrile, acetophenones and ammonium acetate to give corresponding 2-amino-4,6-diphenylnicotinonitrile derivatives at 60 °C.

Reusability of the catalyst

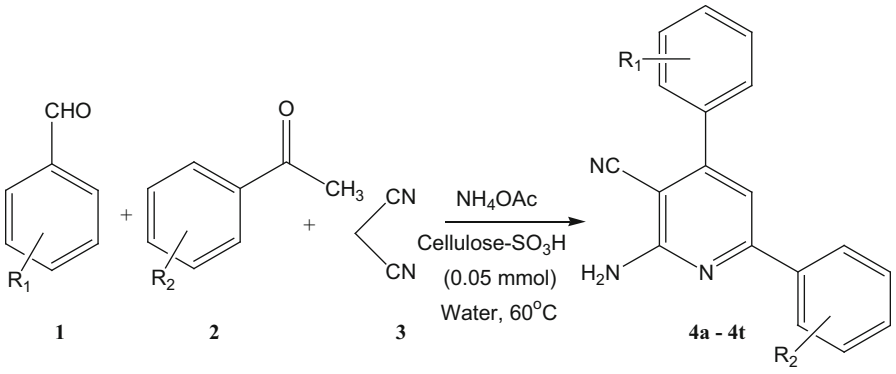
The reusability of the catalyst is one of the most important benefits and makes it useful for commercial applications. Thus the recovery and reusability of cellulose–

Table 4 The effect of recyclability of cellulose–SO_3H (0.05 mmol) catalyst on the product **4a** yield

Entry	Cycle	Time (h)	Yield (%)[a]
1	0	2.5	95
2	1	2.5	93
3	2	2.5	92
4	3	2.5	90

Reaction conditions: benzaldehyde (1 mmol), acetophenone (1 mmol), malononitrile (1 mmol) and ammonium acetate (1 mmol) in water (5 ml) in the presence of cellulose–SO_3H (0.05 mmol)

[a] Isolated yields



Scheme 2 Synthesis of various 2-amino-4,6-diphenylnicotinonitrile derivatives

SO_3H was investigated. After completion of the reaction, the reaction mixture was cooled to ambient temperature, CH_2Cl_2 was added, and the cellulose–SO_3H was filtered off. The recycled catalyst has been examined in the next run. The cellulose–SO_3H catalyst could be reused four times without any loss of its activity (Table 4).

Synthesis of various 2-amino-4,6-diphenylnicotinonitrile derivatives

With the optimized reaction conditions in hand, we proceeded to investigate the scope of the reaction by employing a wide range of aromatic aldehydes and acetophenones in the process (Scheme 2) (Table 5). The reaction performed well, providing the corresponding 2-amino-4,6-diphenylnicotinonitrile derivatives in good to high yields, demonstrating the generality of the method and its good tolerance of both electron-withdrawing and electron-donating substituents on the aromatic ring of the aldehyde. For example, aromatic aldehydes containing electron-donating substituents, including 4-OCH_3 and 4-CH_3 reacted with acetophenone derivatives, including 4-Br, 4-Cl and 4-F acetophenone under the optimized conditions, to provide the corresponding products in good to high yields (Table 5, entries 4, 8, 9, 14 and 15). Furthermore, aromatic aldehydes containing electron-withdrawing substituents, including 4-Cl, 4-F and 4-NO_2 reacted with 4-Br, 4-F,

Table 5 Synthesis of various 2-amino-4,6-diphenylnicotinonitriles derivatives in the presence of cellulose–SO_3H

Entry	R_1	R_2	Product	Time (h)	Yield (%)[a]	Mp (°C)	
						Found	Reported
1	H	H	**4a**	2.5	95	185–187	185–187 [20]
2	H	4-Br	**4b**	2.5	95	174–176	175 [21]
3	4-F	4-Br	**4c**	2.0	96	170–172	172 [21]
4	4-OCH_3	4-Br	**4d**	2.5	90	180–182	181 [21]
5	H	4-Cl	**4e**	2.5	93	241–243	240–242 [22]
6	4-F	4-Cl	**4f**	2.0	96	181–182	181 [21]
7	4-Cl	4-Cl	**4g**	2.0	95	230–232	230–231 [22]
8	4-CH_3	4-Cl	**4 h**	3.0	89	216–218	215–217 [22]
9	4-OCH_3	4-Cl	**4i**	3.0	90	204–206	204–205 [22]
10	4-Br	4-OH	**4j**	2.0	95	234–236	234–237 [19]
11	4-NO_2	4-OH	**4k**	2.0	94	206–208	205–208 [19]
12	4-F	4-OH	**4l**	2.0	96	202–204	201–203 [19]
13	4-Cl	4-F	**4m**	2.0	95	218–220	219–220 [23]
14	4-CH_3	4-F	**4n**	3.0	88	202–204	203–204 [22]
15	4-OCH_3	4-F	**4o**	3.0	89	195–197	194–196 [22]
16	4-Br	H	**4p**	2.5	94	226–228	225–228 [19]
17	4-Cl	4-CH_3	**4q**	2.5	93	172–174	172–173 [23]
18	4-Cl	4-OCH_3	**4r**	2.5	94	194–196	195–196 [23]
19	4-F	4-NO_2	**4s**	2.0	92	196–198	–
20	4-Br	4-NO_2	**4t**	2.0	94	208–210	–

Reaction conditions: substituted benzaldehyde (1 mmol), substituted acetophenone (1 mmol), malononitrile (1 mmol) and ammonium acetate (1 mmol) in water (5 ml) in the presence of cellulose–SO_3H (0.05 mmol). All reactions were carried out at 60 °C

[a] Isolated yields

4-Cl, 4-OH, 4-CH_3, 4-OCH_3 and 4-NO_2 acetophenone and malononitrile under the optimized conditions to afford the corresponding products in high yield (Table 5, entries 3, 6, 7, 10–13 and 16–20).

The structures of isolated products **4a**–**4t** were deducted by physical and spectroscopic data such as: IR, ^{1}H NMR and ^{13}C NMR spectroscopy, and elemental analysis. In IR spectra, symmetrical and unsymmetrical stretching frequency of NH_2 is formed in region between $\nu = 3{,}411$–$3{,}300$ cm^{-1}. The stretching vibration of C–N in nitrile group was appeared in the region between $\nu = 2{,}198$–$2{,}214$ cm^{-1}. In the ^{1}H NMR spectra in DMSO-d_6 was shown the two singlet signals around $\delta = 5.46$–6.98 and $\delta = 7.16$–7.28 ppm corresponding to NH_2 group and C–H of pyridine ring in 2-amino-4,6-diphenylnicotinonitriles. In the ^{13}C NMR spectra, one carbon link to C–C–N has chemical shift in $\delta = 84.8$–87.5 ppm because of anisotropic effect of triple bond of nitrile group and the signal around $\delta = 116.8$–118.0 is assigned by one carbon of C–N of nitrile group.

Experimental

General

All chemicals were purchased from Aldrich Chemical Co. and solvents were used without further purification. Analytical thin-layer chromatography was performed with E. Merck silica gel 60F glass plates. Visualisation of the developed chromatogram was performed by UV light (254 nm). Column chromatography was performed on silica gel 90, 200–300 mesh. Melting points were determined with Shimadzu DS-50 thermal analyser. ^{1}H nuclear magnetic resonance (NMR) (500 MHz) and ^{13}C NMR (125 MHz) spectra were obtained using Bruker DRX-500 Avance at ambient temperature, using tetramethylsilane (TMS) as internal standard. Fourier-transform infrared (FT-IR) spectra were obtained as KBr discs on Shimadzu spectrometer. Mass spectra were determined on a Varian—Saturn 2000 GC/MS instrument. Elemental analysis were measured by means of Perkin Elmer 2400 CHN elemental analyzer flowchart.

Preparation of cellulose sulfuric acid

To a magnetically stirred mixture of 5.0 g of cellulose in 20 ml of *n*-hexane, 1.0 g of chlorosulfonic acid (9 mmol) was added drop wise at 0 °C during 2 h. HCl gas was removed from the reaction vessel immediately. After the addition was complete, the mixture was stirred for 2 h. Then the mixture was filtered and washed with 30 ml of acetonitrile and dried at room temperature to afford 5.25 g of cellulose sulfuric acid as a white powder. Sulfur content of the samples by conventional elemental analysis, was 0.55 for cellulose sulfuric acid. The number of H^+ sites on the cellulose–SO_3H was determined by acid–base titration was 0.50 mequiv./g [43].

X-ray diffraction (XRD) for cellulose sulfuric acid

Powder X-ray diffraction measurements were performed using Advance diffract meter made by a Bruker AXS company in Germany. Scans were taken with a 2θ step size of 0.04 and a counting time of 30 s at room temperature. Specimens for XRD were prepared by compaction into a glass-backed aluminum sample holder. Data was collected over a 2θ range from 4° to 75°. The XRD pattern of cellulose sulfuric acid is presented in Fig. 1.

Typical procedure for the synthesis of 2-amino-4,6-diphenylnicotinonitrile (**4a**) in water

A mixture of benzaldehyde (1 mmol), acetophenone (1 mmol), malononitrile (1 mmol) and ammonium acetate (1 mmol) in the presence of cellulose sulfuric acid (0.05 mmol) was stirred in H_2O (5 ml) at 60 °C in a 50 ml flask for the appropriate time, as shown in Table 5. After completion of the reaction [thin-layer chromatography (TLC) monitoring], the reaction mixture was cooled to ambient

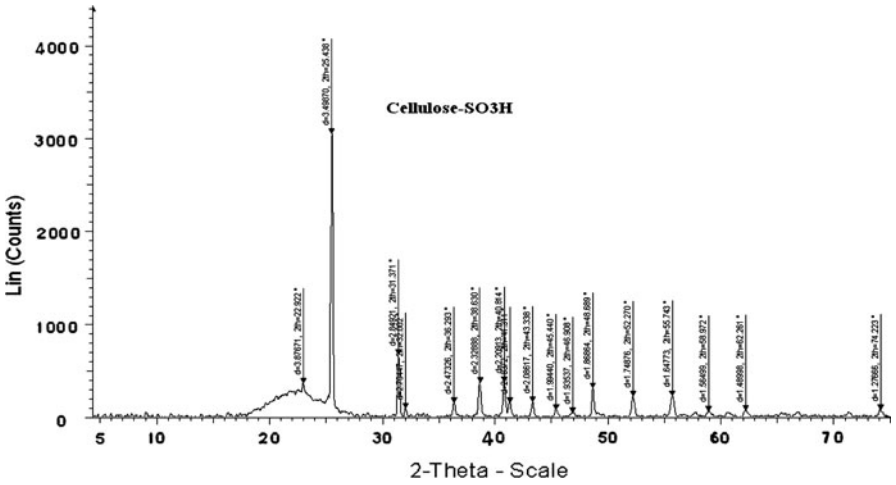


Fig. 1 XRD pattern of cellulose–SO_3H

temperature, CH_2Cl_2 was added, and the cellulose sulfuric acid was filtered off. The filtrate was concentrated to dryness, and the crude solid product was crystallized from EtOH to afford the pure 2-amino-4,6-diphenylnicotinonitrile (Table 5).

Spectral data for synthesized derivatives of 2-amino-4,6-diphenylnicotinonitrile (**4a**–**4t**)

*2-Amino-4,6-diphenylnicotinonitrile (**4a**)*

IR (KBr, cm^{-1}): 3,394 and 3,312 (NH_2), 3,177 (ArH), 2,211 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.04–8.16 (2H, m, ArH), 7.62–7.78 (3H, m, ArH), 7.40–7.47 (3H, m, ArH), 7.18 (1H, s, CH), 7.00 (2H, d, $J = 8.4$ Hz, ArH), 5.48 (2H, s, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 86.4, 109.0, 114.2, 117.8, 127.8, 129.4, 129.9, 130.3, 130.5, 138.1, 155.0, 158.9, 160.8, 161.4 ppm; MS(ESI): *m/z* 272 $(M + H)^+$; Anal. Calcd for $C_{18}H_{13}N_3$: C, 79.70; H, 4.80; N, 15.50 %. Found: C, 79.66; H, 4.76; N, 15.44 %.

*2-Amino-4-phenyl-6-(4-bromophenyl)nicotinonitrile (**4b**)*

IR (KBr, cm^{-1}): 3,388 and 3,308 (NH_2), 3,165 (ArH), 2,214 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.02–8.10 (2H, m, ArH), 7.65 (2H, d, $J = 8.4$ Hz, ArH), 7.50–7.55 (3H, m, ArH), 7.16 (1H, s, CH), 7.21 (2H, d, $J = 8.4$ Hz, ArH), 6.98 (2H, s, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 87.2, 108.9, 113.9, 117.85 127.3, 129.1, 129.5, 130.3, 130.8, 138.0, 153.9, 159.4, 161.0, 162.1 ppm; MS(ESI): *m/z* 350.9 $(M + H)^+$; Anal. Calcd for $C_{18}H_{12}BrN_3$: C, 61.73; H, 3.43; N, 12.00 %. Found: C, 61.66; H, 3.49; N, 12.12 %.

*2-Amino-4-(4-fluorophenyl)-6-(4-bromophenyl)nicotinonitrile (**4c**)*

IR (KBr, cm^{-1}): 3,400 and 3,307 (NH_2), 3,184 (ArH), 2,201 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.11–8.12 (2H, m, ArH), 7.66 (2H, d, $J = 8.4$ Hz, ArH), 7.44–7.48 (2H, m, ArH), 7.25 (1H, s, CH), 7.11 (2H, d, $J = 8.4$ Hz, ArH), 6.96 (2H, s, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 87.4, 108.5, 113.4, 118.0, 126.9, 128.9, 129.5, 130.1, 130.7, 138.1, 152.9, 157.9, 161.8, 162.6 ppm; MS(ESI): *m/z* 368.9 $(M + H)^+$; Anal. Calcd for $C_{18}H_{11}BrFN_3$: C, 58.71; H, 2.99; N, 11.44 %. Found: C, 58.70; H, 2.95; N, 11.40 %.

*2-Amino-4-(4-methoxyphenyl)-6-(4-bromophenyl)nicotinonitrile (**4d**)*

IR (KBr, cm^{-1}): 3,402 and 3,303 (NH_2), 3,180 (ArH), 2,201 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.16–8.19 (2H, m, ArH), 7.60 (2H, d, $J = 8.4$ Hz, ArH), 7.41–7.46 (2H, m, ArH), 7.20 (1H, s, CH), 7.12 (2H, d, $J = 8.4$ Hz, ArH), 5.63 (2H, s, NH_2), 3.81 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 87.0, 107.9, 114.2, 116.9, 128.0, 129.0, 129.8, 130.3, 130.6, 137.9, 155.5, 158.4, 161.8, 163.4 ppm; MS(ESI): *m/z* 380.9 $(M + H)^+$; Anal. Calcd for $C_{19}H_{14}BrN_3O$: C, 60.01; H, 3.68; N, 11.05 %. Found: C, 60.00; H, 3.62; N, 11.02 %.

*2-Amino-4-phenyl-6-(4-chlorophenyl)nicotinonitrile (**4e**)*

IR (KBr, cm^{-1}): 3,399 and 3,302 (NH_2), 3,177 (ArH), 2,212 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.04–8.09 (2H, m, ArH), 7.69 (2H, d, $J = 8.4$ Hz, ArH), 7.46–7.49 (3H, m, ArH), 7.21 (1H, s, CH), 7.17 (2H, d, $J = 8.4$ Hz, ArH), 5.60 (2H, s, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 86.9, 111.5, 115.6, 117.8, 127.3, 128.6, 129.5, 130.3, 131.6, 138.1, 154.9, 158.9, 160.8, 161.4 ppm; MS(ESI): *m/z* 306.45 $(M + H)^+$; Anal. Calcd for $C_{18}H_{12}ClN_3$: C, 70.71; H, 3.93; N, 13.75 %. Found: C, 70.66; H, 3.90; N, 13.72 %.

*2-Amino-4-(4-fluorophenyl)-6-(4-chlorophenyl)nicotinonitrile (**4f**)*

IR (KBr, cm^{-1}): 3,392 and 3,311 (NH_2), 3,177 (ArH), 2,211 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.11–8.15 (2H, m, ArH), 7.64 (2H, d, $J = 8.4$ Hz, ArH), 7.48–7.51 (2H, m, ArH), 7.19 (1H, s, CH), 7.11 (2H, d, $J = 8.4$ Hz, ArH), 5.69 (2H, s, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 84.8, 110.5, 114.0, 116.9, 128.7, 129.3, 129.6, 131.0, 131.7, 138.1, 154.9, 158.9, 162.8, 164.4 ppm; MS(ESI): *m/z* 324.45 $(M + H)^+$; Anal. Calcd for $C_{18}H_{11}FClN_3$: C, 66.78; H, 3.40; N, 12.98 %. Found: C, 66.74; H, 3.36; N, 12.96 %.

*2-Amino-4-(4-chlorophenyl)-6-(4-chlorophenyl)nicotinonitrile (**4g**)*

IR (KBr, cm^{-1}): 3,405 and 3,300 (NH_2), 3,184 (ArH), 2,200 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.00–8.06 (2H, m, ArH), 7.55 (2H, d, $J = 8.4$ Hz, ArH), 7.38–7.44 (2H, m, ArH), 7.19 (1H, s, CH), 7.14 (2H, d, $J = 8.4$ Hz, ArH), 5.62 (2H, s, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 87.9, 110.5, 116.8, 127.7, 129.1,

129.5, 130.3, 131.0, 140.1, 154.9, 158.9, 161.2, 163.4 ppm; MS(ESI): *m/z* 340.90 $(M + H)^+$; Anal. Calcd for $C_{18}H_{11}Cl_2N_3$: C, 63.55; H, 3.24; N, 12.36 %. Found: C, 63.52; H, 3.22; N, 12.30 %.

*2-Amino-4-(4-methylphenyl)-6-(4-chlorophenyl)nicotinonitrile (**4h**)*

IR (KBr, cm^{-1}): 3,411 and 3,309 (NH_2), 3,179 (ArH), 2,213 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.04–8.16 (2H, m, ArH), 7.58 (2H, d, $J = 8.4$ Hz, ArH), 7.42–7.49 (2H, m, ArH), 7.19 (1H, s, CH), 7.00 (2H, d, $J = 8.4$ Hz, ArH), 5.69 (2H, s, NH_2), 2.22 (3H, s, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 85.5, 111.5, 116.8, 127.5, 128.9, 129.4, 130.3, 132.0, 141.1, 156.2, 158.9, 162.0, 163.2 ppm; MS(ESI): *m/z* 320.45 $(M + H)^+$; Anal. Calcd for $C_{19}H_{14}ClN_3$: C, 71.37; H, 4.38; N, 13.15 %. Found: C, 71.32; H, 4.32; N, 13.14 %.

*2-Amino-4-(4-methoxyphenyl)-6-(4-chlorophenyl)nicotinonitrile (**4i**)*

IR (KBr, cm^{-1}): 3,401 and 3,311 (NH_2), 3,172 (ArH), 2,198 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.08–8.10 (2H, m, ArH), 7.61 (2H, d, $J = 8.4$ Hz, ArH), 7.44–7.46 (2H, m, ArH), 7.20 (1H, s, CH), 7.11 (2H, d, $J = 8.4$ Hz, ArH), 5.60 (2H, s, NH_2), 3.79 (3H, s, OCH_3). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 87.5, 108.9, 117.0, 128.0, 129.0, 129.6, 130.3, 131.0, 139.7, 153.9, 160.8, 162.5. MS(ESI): *m/z* 336.45 $(M + H)^+$; Anal. Calcd for $C_{19}H_{14}ClN_3O$: C, 67.97; H, 4.17; N, 12.52 %. Found: C, 67.90; H, 4.12; N, 12.58 %.

*2-Amino-4-(4-bromophenyl)-6-(4-hydroxyphenyl)nicotinonitrile (**4j**)*

IR (KBr, cm^{-1}): 3,388 and 3,355 (NH_2), 3,339 (OH), 3,222 (ArH), 2,200 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.14 (2H, d, $J = 8.4$ Hz, ArH), 7.54 (2H, d, $J = 8.4$ Hz, ArH), 7.16 (1H, s, CH), 7.07 (2H, d, $J = 8.4$ Hz, ArH), 7.03 (2H, d, $J = 8.4$ Hz, ArH), 6.87 (2H, s, NH_2), 9.82 (s, 1 H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 87.4, 108.9, 115.4, 116.8, 127.7, 129.1, 130.3, 132.0, 140.1, 154.9, 158.9, 160.8, 162.0 ppm; MS(ESI): *m/z* 366.90 $(M + H)^+$; Anal. Calcd for $C_{18}H_{12}N_3BrO$: C, 59.03; H, 3.28; N, 11.48 %. Found: C, 59.02; H, 3.24; N, 11.44 %.

*2-Amino-4-(4-nitrophenyl)-6-(4-hydroxyphenyl)nicotinonitrile (**4k**)*

IR (KBr, cm^{-1}): 3,404 and 3,300 (NH_2), 3,339 (OH), 3,170 (ArH), 2,210 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.09–8.18 (2H, m, ArH), 7.66 (2H, d, $J = 8.4$ Hz, ArH), 7.39–7.45 (2H, m, ArH), 7.22 (1H, s, CH), 7.00 (2H, d, $J = 8.4$ Hz, ArH), 6.93 (2H, s, NH_2) 9.90 (s, 1 H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 86.9, 110.5, 115.6, 116.8, 124.7, 127.1, 129.5, 130.3, 131.5, 137.9, 154.9, 158.9, 160.8, 162.0 ppm; MS(ESI): *m/z* 333 $(M + H)^+$; Anal. Calcd for $C_{18}H_{12}N_4O_3$: C, 65.06; H, 3.61; N, 16.87 %. Found: C, 65.02; H, 3.60; N, 16.84 %.

*2-Amino-4-(4-fluorophenyl)-6-(4-hydroxyphenyl)nicotinonitrile (**4l**)*

IR (KBr, cm^{-1}): 3,397 and 3,307 (NH_2), 3,339 (OH), 3,184 (ArH), 2,201 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.08–8.14 (2H, m, ArH), 7.58 (2H, d, $J = 8.4$ Hz, ArH), 7.35–7.43 (2H, m, ArH), 7.22 (1H, s, CH), 7.06 (2H, d, $J = 8.4$ Hz, ArH), 6.94 (2H, s, NH_2), 9.94 (s, 1 H, OH) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 86.5, 111.5, 115.0, 116.9, 126.9, 128.9, 129.4, 130.3, 131.5, 137.9, 154.9, 158.9, 160.5, 162.6 ppm; MS(ESI): *m/z* 306 $(M + H)^+$; Anal. Calcd for $C_{18}H_{12}FN_3O$: C, 70.82; H, 3.93; N, 13.77 %. Found: C, 70.80; H, 3.90; N, 13.74 %.

*2-Amino-4-(4-chlorophenyl)-6-(4-fluorophenyl)nicotinonitrile (**4m**)*

IR (KBr, cm^{-1}): 3,399 and 3,307 (NH_2), 3,184 (ArH), 2,201 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.06–8.13 (2H, m, ArH), 7.72 (2H, d, $J = 8.4$ Hz, ArH), 7.34–7.46 (2H, m, ArH), 7.18 (1H, s, CH), 7.14 (2H, d, $J = 8.4$ Hz, ArH), 6.97 (2H, s, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 87.5, 111.2, 115.3, 117.7, 127.6, 129.0, 129.5, 130.2, 130.7, 139.0, 153.9, 158.9, 160.8, 162.0 ppm; MS(ESI): *m/z* 324.45 $(M + H)^+$; Anal. Calcd for $C_{18}H_{11}ClFN_3$: C, 66.78; H, 3.40; N, 12.98 %. Found: C, 66.74; H, 3.38; N, 12.90 %.

*2-Amino-4-(4-methylphenyl)-6-(4-fluorophenyl)nicotinonitrile (**4n**)*

IR (KBr, cm^{-1}): 3,402 and 3,307 (NH_2), 3,184 (ArH), 2,201 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.14-8.19 (2H, m, ArH), 7.77 (2H, d, $J = 8.4$ Hz, ArH), 7.37–7.47 (2H, m, ArH), 7.25 (1H, s, CH), 7.09 (2H, d, $J = 8.4$ Hz, ArH), 6.00 (2H, s, NH_2), 2.22 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 86.0, 110.0, 114.4, 116.9, 128.0, 129.0, 129.6, 130.2, 130.6, 139.0, 155.2, 159.4, 160.4, 162.2 ppm; MS(ESI): *m/z* 304 $(M + H)^+$; Anal. Calcd for $C_{19}H_{14}FN_3$: C, 75.25; H, 4.62; N, 13.86 %. Found: C, 75.22; H, 4.60; N, 13.84 %.

*2-Amino-4-(4-methoxyphenyl)-6-(4-fluorophenyl)nicotinonitrile (**4o**)*

IR (KBr, cm^{-1}): 3,398 and 3,307 (NH_2), 3,184 (ArH), 2,201 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 7.98–8.08 (2H, m, ArH), 7.76 (2H, d, $J = 8.4$ Hz, ArH), 7.44–7.55 (2H, m, ArH), 7.28 (1H, s, CH), 7.20 (2H, d, $J = 8.4$ Hz, ArH), 5.58 (2H, s, NH_2), 3.36 (s, 3H, OCH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 85.7, 108.9, 115.6, 117.5, 126.0, 128.9, 129.6, 130.3, 131.0, 141.1, 154.4, 158.4, 160.8, 162.1 ppm; MS(ESI): *m/z* 320 $(M + H)^+$; Anal. Calcd for $C_{19}H_{14}FN_3O$: C, 71.47; H, 4.39; N, 13.17 %. Found: C, 71.44; H, 4.33; N, 13.18 %.

*2-Amino-4-(4-bromophenyl)-6-phenylnicotinonitrile (**4p**)*

IR (KBr, cm^{-1}): 3,411 and 3,307 (NH_2), 3,184 (ArH), 2,201 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 7.88–8.00 (2H, m, ArH), 7.78 (2H, d, $J = 8.4$ Hz, ArH), 7.33–7.44 (3H, m, ArH), 7.18 (1H, s, CH), 7.16 (2H, d, $J = 8.4$ Hz, ArH), 6.94 (2H, s, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 87.0, 110.5, 114.0, 116.9, 126.9,

128.5, 129.0, 130.3, 131.4, 139.5, 155.7, 158.5, 160.4, 161.9 ppm; MS(ESI): *m/z* 350.90 $(M + H)^+$; Anal. Calcd for $C_{18}H_{12}BrN_3$: C, 61.73; H, 3.43; N, 12.00 %. Found: C, 61.70; H, 3.40; N, 12.02 %.

*2-Amino-4-(4-chlorophenyl)-6-(4-methylphenyl)nicotinonitrile (**4q**)*

IR (KBr, cm^{-1}): 3,395 and 3,312 (NH_2), 3,180 (ArH), 2,208 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.16–8.19 (2H, m, ArH), 7.64 (2H, d, $J = 8.4$ Hz, ArH), 7.40–7.47 (2H, m, ArH), 7.24 (1H, s, CH), 7.16 (2H, d, $J = 8.4$ Hz, ArH), 6.95 (2H, s, NH_2), 2.18 (3H, s, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 86.4, 109.4, 114.4, 117.4, 127.4, 129.4, 129.9, 130.1, 130.6, 139.1, 155.2, 158.5, 160.5, 162.4 ppm; MS(ESI): *m/z* 320.45 $(M + H)^+$; Anal. Calcd for $C_{19}H_{14}ClN_3$: C, 71.37; H, 4.38; N, 13.15 %. Found: C, 71.34; H, 4.35; N, 13.12 %.

*2-Amino-4-(4-chlorophenyl)-6-(4-methoxyphenyl)nicotinonitrile (**4r**)*

IR (KBr, cm^{-1}): 3,392 and 3,307 (NH_2), 3,184 (ArH), 2,201 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 7.99-8.07 (2H, m, ArH), 7.78 (2H, d, $J = 8.4$ Hz, ArH), 7.35-7.42 (2H, m, ArH), 7.22 (1H, s, CH), 7.09 (2H, d, $J = 8.4$ Hz, ArH), 6.88 (2H, s, NH_2), 3.28 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 85.9, 107.9, 114.6, 117.8, 126.9, 128.9, 129.7, 130.5, 131.0, 141.1, 153.9, 158.9, 160.7, 161.9 ppm; MS(ESI): *m/z* 336.45 $(M + H)^+$; Anal. Calcd for $C_{19}H_{14}ClN_3O$: C, 67.97; H, 4.17; N, 12.52 %. Found: C, 67.94; H, 4.16; N, 12.44 %.

*2-Amino-4-(4-fluorophenyl)-6-(4-nitrophenyl)nicotinonitrile (**4s**)*

IR (KBr, cm^{-1}): 3,408 and 3,312 (NH_2), 3,188 (ArH), 2,207 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.01–8.09 (2H, m, ArH), 7.69 (2H, d, $J = 8.4$ Hz, ArH), 7.49–7.55 (2H, m, ArH), 7.29 (1H, s, CH), 7.19 (2H, d, $J = 8.4$ Hz, ArH), 5.46 (2H, s, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 87.7, 108.8, 113.6, 118.2, 127.0, 128.5, 129.4, 130.3, 130.9, 138.2, 152.7, 157.8, 161.6, 162.7 ppm; MS(ESI): *m/z* 335 $(M + H)^+$; Anal. Calcd for $C_{18}H_{11}FN_4O_2$: C, 64.67; H, 3.29; N, 16.76 %. Found: C, 64.58; H, 3.28; N, 16.77 %.

*2-Amino-4-(4-bromophenyl)-6-(4-nitrophenyl)nicotinonitrile (**4t**)*

IR (KBr, cm^{-1}): 3,399 and 3,317 (NH_2), 3,179 (ArH), 2,214 (CN). ^1H NMR (500 MHz, DMSO-d_6) δ: 8.08–8.15 (2H, m, ArH), 7.66 (2H, d, $J = 8.2$ Hz, ArH), 7.47–7.55 (2H, m, ArH), 7.18 (1H, s, CH), 7.16 (2H, d, $J = 8.4$ Hz, ArH), 5.51 (2H, s, NH_2) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 84.4, 110.4, 114.0, 116.7, 128.6, 129.4, 129.8, 131.2, 131.8, 138.3, 154.7, 158.8, 162.9, 164.6 ppm; MS(ESI): *m/z* 395.9 $(M + H)^+$; Anal. Calcd for $C_{18}H_{11}BrN_4O_2$: C, 54.69; H, 2.78; N, 14.18 %. Found: C, 54.64; H, 2.76; N, 14.15 %.

Conclusions

In summary, cellulose–SO_3H efficiently catalyzed the synthesis of 2-amino-4,6-diarylnicotinonitriles via a four component condensation reaction. The simplicity of this procedure, together with the eco-friendly, non-volatile, easy-to-handle, non-hazardous and recyclable nature of catalyst, represents the main advantages of this method. We expect this method will find extensive applications in the field of combinatorial chemistry, diversity-oriented synthesis and drug discovery.

Acknowledgments The authors are thankful to the Management of C. Abdul Hakeem College, Melvisharam—632509 (T.N), India for the support. The authors also thankful to Dr. W. Abdul Hameed, Principal, and Dr. M. S. Dastageer, Head of the Research Department of Chemistry for the facilities and support from the DST-FIST (Government of India) sponsored Department. The authors wish to thank to Dr. A. Abdul Rahuman, Unit of Nanotechnology and Bioactive Natural Products, for useful discussion and encouragement.

References

1. A. Domling, I. Ugi, Angew. Chem. Int. Ed. **39**, 3168 (2000)
2. X.-M. Wang, H.-L. Ye, Z.-J. Qaun, X.-C. Wang, Res. Chem. Intermed. doi:10.1007/s11164-012-0762-z
3. P. Karthikeyan, S.S.Kumar, A.S. Arunrao, M.P. Narayan, P.R. Bhagat, Res. Chem. Intermed. (2012). doi:10.1007/s11164-012-0689-4
4. Z. Song, X. Sun, L. Liu, Y. Cui, Res. Chem. Intermed. (2012). doi:10.1007/s11164-012-0744-1
5. C. Mukhopadhyay, P.K. Tapaswi, M.G.B. Drew, Tetrahedron Lett. **51**, 3944 (2010)
6. N.G. Kozlov, A.P. Kadutskii, Tetrahedron Lett. **49**, 4560 (2008)
7. D. Tejedor, F. Garcia-Tellado, Chem. Soc. Rev. **36**, 484 (2007)
8. G.D. Henry, Tetrahedron **60**, 6043 (2004)
9. M.C. Bagley, C. Glover, E.A. Merritt, Synlett 2459 (2007)
10. A. Kodimuthali, S.S.L. Jabaris, M. Pal, J. Med. Chem. **51**, 5471 (2008)
11. T.R. Reddy, G.R. Reddy, L.S. Reddy, S. Jammula, Y. Lingappa, R. Kapavarapu, C. Lakshmi, T. Meda, K.V.L. Parsa, M. Pal, Eur. J. Med. Chem. **48**, 265 (2012)
12. F. Zhang, Y. Zhao, L. Sun, L. Ding, Y. Gu, P. Gong, Eur. J. Med. Chem. **46**, 3149 (2011)
13. A.A. Bekhit, A.M. Baraka, Eur. J. Med. Chem. **40**, 1405 (2005)
14. T. Murata, M. Shimada, S. Sakakibara, T. Yoshino, H. Kadono, T. Masuda, M. Shimazaki, T. Shintani, K. Fuchikami, K. Sakai, H. Inbe, K. Takeshita, T. Niki, M. Umeda, K.B. Bacon, K.B. Ziegelbauer, T.B. Lowinger, Bioorg. Med. Chem. Lett. **13**, 913 (2003)
15. M. Mantri, O. De Graaf, J. Van Veldhoven, A. Göblyös, J.K. Von Frijtag Drabbe Kunzel, T. Mulder-Krieger, R. Link, H. De Vries, M.W. Beukers, J. Brussee, A.P. Ijzerman, J. Med. Chem. **51**, 4449 (2008)
16. J. Deng, T. Sanchez, L.Q. Al-Mawsawi, R. Dayam, R.A. Yunes, A. Garofalo, M.B. Bolger, N. Neamati, Bioorg. Med. Chem. **15**, 4985 (2007)
17. C.J. Shishoo, M.B. Devani, V.S. Bhadti, S. Ananthan, G.V. Ullas, Tetrahedron Lett. **24**, 4611 (1983)
18. M.A. Al-Haiza, M.S. Mostafa, M.Y. El-Kady, Molecules **8**, 275 (2003)
19. J. Safari, S.H. Banitaba, S.D. Khalili, Ultrason. Sonochem. **19**, 1061 (2012)
20. S. Khaksar, M. Yaghoobi, J. Fluor. Chem. **142**, 41 (2012)
21. R. Gupta, A. Jain, M. Jain, R. Joshi, Bull. Korean Chem. Soc. **31**, 3180 (2010)
22. K. Niknam, A. Jamali, M. Tajaddod, A. Deris, Chin. J. Catal. **33**, 1312 (2012)
23. F. Shi, S. Tu, F. Fang, T. Li, ARKIVOC **i**, 137 (2005)
24. J. Tang, L. Wang, Y. Yao, L. Zhang, W. Wang, Tetrahedron Lett. **52**, 509 (2011)
25. S.R. Sarda, J.D. Kale, S.K. Wasmatkar, V.S. Kadam, P.G. Ingole, W.N. Jadhav, R.P. Pawar, Mol. Divers. **13**, 545 (2009)
26. S.S. Mansoor, K. Aswin, K. Logaiya, S.P.N. Sudhan, J. Saudi Chem. Soc. doi:10.1016/j.jscs.2012.07.011

27. H.C. Shah, V.H. Shah, N.D. Desai, ARKIVOC **ii**, 76 (2009)
28. S.S. Mansoor, S.S. Shafi, S.Z. Ahmed, Arab. J. Chem. doi:10.1016/j.arabjc.2011.09.018
29. S.S. Mansoor, K. Aswin, K. Logaiya, S.P.N. Sudhan, J. Saudi Chem. Soc. doi:10.1016/j.jscs.2012.04.008
30. S.S. Mansoor, K. Aswin, K. Logaiya, S.P.N. Sudhan, J. Saudi Chem. Soc. doi:10.1016/j.jscs.2012.06.003
31. S.S. Mansoor, K. Aswin, K. Logaiya, S.P.N. Sudhan, S. Malik, Res. Chem. Intermed. (2012). doi:10.1007/s11164-012-0968-0
32. H. Chen, D.Q. Shi, J. Comb. Chem. **12**, 571 (2010)
33. Y. Zou, H. Wu, Y. Hu, H. Liu, X. Zhao, H. Ji, D. Shi, Ultrason. Sonochem. **18**, 708 (2011)
34. R.A. Sheldon, H. van Bekkum (eds.), *Fine Chemicals through Heterogeneous Catalysis* (Wiley-VCH, Weinheim, 2001)
35. W.L. Wei, H.Y. Zhu, C.L. Zhao, M.Y. Huang, Y.Y. Jiang, React. Funct. Polym. **59**, 33 (2004)
36. C. Crecchio, P. Ruggiero, M.D.R. Pizzigallo, Biotechnol. Bioeng. **48**, 585 (1995)
37. H. Gliemann, U. Nickel, S. Schneider, J. Raman, Spec. **29**, 89 (1998)
38. K. Huang, L. Xue, Y.C. Hu, M.Y. Huang, Y.Y. Jiang, React. Funct. Polym. **50**, 199 (2002)
39. E. Guibal, Prog. Polym. Sci. **30**, 71 (2005)
40. S.K. De, Synth. Commun. **35**, 653 (2005)
41. D. Klemm, B. Heublein, H.-P. Fink, A. Bohn, Angew. Chem. Int. Ed. **44**, 3358 (2005)
42. J.H. Clark, D.J. Macquarrie, *Green Chemistry and Technology* (Blackwell, Abingdon, 2002)
43. A. Shaabani, A. Maleki, Appl. Catal. A: Gen. **331**, 149 (2007)
44. A. Shaabani, A. Rahmati, Z. Badri, Catal. Commun. **9**, 13 (2008)
45. A. Shaabani, M. Seyyedhamzeh, A. Maleki, F. Rezazadeh, Appl. Catal. A: Gen. **358**, 146 (2009)
46. J.V. Madhav, Y.T. Reddy, P.N. Reddy, M.N. Reddy, J. Mol. Catal. A: Chem. **304**, 85 (2009)
47. K.S. Kumar, B.S. Krishna, C.B. Reddy, M.V.N. Reddy, C.S. Reddy, Arab. J. Chem. doi:10.1016/j.arabjc.2012.09.009
48. A. Rahmatpour, React. Funct. Polym. **71**, 80 (2011)
49. S. Maddila, M. Momin, P. Lavanya, C.V. Rao, J. Saudi Chem. Soc. doi:10.1016/j.jscs.2012.06.008
50. J. Safari, S.H. Banitaba, S.D. Khalili, J. Mol. Catal. A: Chem. **335**, 46 (2011)
51. H. Mofakham, Z. Hezarkhani, A. Shaabani, J. Mol. Catal. A: Chem. **360**, 26 (2012)