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Highly efficient promoted zirconia solid acid catalysts for synthesis of α-aminonitriles using trimethylsilyl cyanide

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ABSTRACT

A straightforward and general method has been developed for the synthesis of α-aminonitriles from the reaction of aldehydes or ketones with amines and trimethylsilyl cyanides in the presence of a catalytic amount of promoted zirconia solid acid catalyst at room temperature. This simple experimental and product isolation procedure combined with easy recovery and reusability of the catalyst are expected to contribute to the development of clean and environmental friendly strategy for the synthesis of α-aminonitriles. A plausible reaction mechanism has been proposed for this multicomponent reaction.

1. Introduction

One of the fundamental aspects in Green Chemistry is linked to the number of steps in organic synthesis as well as atom economy. Multicomponent reactions (MCR) are thus becoming a more and more important class of reactions since they allow combining several starting materials in a single compound and in one-flask operation [1–3]. They exhibit economy of steps and often atom economy, most of the incoming atoms being linked together in a single product. Combining these aspects to heterogeneity and catalysis would reinforce the "greening" of such reactions. In order to offer solutions to such problems, we are currently exploiting promoted zirconia solid acid catalysts for organic synthesis [4,9], and in the present work we describe a solid acid-catalysed synthesis of α-aminonitriles through a three-component reaction (Scheme 1). A variety of homogeneous [10–20], heterogeneous catalysts [21–24], and other methodologies have been employed for α-aminonitriles synthesis under different reaction conditions [25,26]. However, efforts are still going onto develop clean and environmentally friendly strategy for the synthesis of α-aminonitriles.

α-Aminonitriles, often synthesized by Strecker reaction [27], are highly useful synthons for the synthesis of α-amino acids [28–34], nitrogen-containing heterocycles such as imidazoles and thiadiazoles [35,36], and other biologically useful molecules such as saframycin A, a natural product with anti-tumour activity or phthalascidi, a synthetic analogue, which exhibits even greater potency [37]. The Strecker reaction, discovered in 1850 [27], has been recognized as the first multicomponent reaction [2,38] published ever and has a central importance to the life sciences [39,40]. The classical procedure involves treatment of an aldehyde or a ketone with alkaline cyanides and salts of amines, and was discovered a century and a half ago [27]. The efficiency of the reaction has been increased by the use of catalysts, and reactive cyanide ion sources such as hydrogen cyanide [29], sodium or potassium cyanide, Bu_3SnCN, bis(dialkylamino) cyanoboranes, diethylphosphorocyanidate, and trimethylsilyl cyanide (TMSCN) [14,15,20,41]. TMSCN is a safer, more effective, and more easily handled anion source compared to others [11,13,22,23,25,42,43]. Although these methods [10–26] mentioned above are valuable, many of these procedures involve one or more disadvantages including the tedious isolation of pure α-aminonitriles from the reaction mixtures, extended reaction times, leading to the generation of a large amount of toxic waste, use of stoichiometric or relatively expensive reagents. Furthermore, many of these protocols are limited to aldehydes only, and many of the used catalysts are deactivated or sometimes decomposed by amines. In order to circumvent some of the problems associated with these procedures and in continuation of our ongoing work on solid acid catalysts, supported or not, to the organic synthesis [4–7,44–46], herein, we introduce promoted zirconia as an efficient solid acid catalyst for synthesis of α-aminonitriles. A few supported versions or versions based on heterogeneous catalysts have recently been described [21–24], but no zirconia-based catalysed version has so far been reported.

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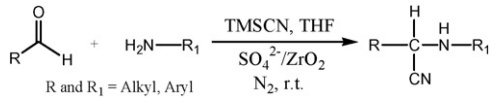


Scheme 1. SO_4^{2-}/ZrO_2 catalysed Strecker reaction at room temperature.

2. Experimental

2.1. Catalyst preparation

Zirconium hydroxide was prepared first from zirconium oxychloride by hydrolysis with dilute aqueous ammonia solution. For this purpose, the requisite quantity of $ZrOCl_2{\cdot}8H_2O$ (Loba Chime, GR grade) was dissolved in doubly distilled water and to this clear solution; aqueous NH_3 was added drop-wise with vigorous stirring until the pH of the solution reached 8. The obtained precipitate was washed with hot distilled water several times until free from chloride ions and dried at 393 K for 24 h. On the resulting hydrous zirconium hydroxide, sulfate, molybdate and tungstate promoters were deposited by a wet impregnation method. To incorporate these promoters, sulfuric acid, ammonium heptamolybdate and ammonium metatungstate (Aldrich, AR Grade) were used as the precursors respectively. Detailed procedure for the preparation of these catalysts could be found elsewhere [47,48].

2.2. Catalyst characterization

The powder X-ray diffraction patterns of the synthesized catalysts were recorded on a Siemens D-5000 diffractometer by using Cu Kα radiation source and scintillation counter detector. The XRD phases present in the samples were identified with the help of JCPDS data files. A conventional all glass volumetric high vacuum (1×10^{-6} Torr) system was used for BET surface area measurements. The BET surface areas were measured by nitrogen physisorption at liquid nitrogen temperature by taking 0.162 nm^2 as the area of cross-section of N_2 molecule. Raman spectra were recorded at ambient temperature on a DILOR XY spectrometer equipped with a CCD detector. The spectra were recorded in the range of 4000–100 cm^{-1} and at a spectral resolution of 2 cm^{-1} using the 514.5 nm excitation line from an argon ion laser (Spectra Physics, USA). The temperature programmed desorption measurements were carried on an Auto Chem 2910 instrument (Micromeritics, USA). A thermal conductivity detector was used for continuous monitoring of the desorbed ammonia and the areas under the peaks were integrated using GRAMS/32 software. Prior to TPD studies, samples were pretreated at 473 K for 1 h in a flow of ultra pure helium gas (40 ml min^{-1}). After pretreatment, the sample was saturated with 10% ultra pure anhydrous ammonia gas (balance He, 75 ml min^{-1}) at 353 K for 2 h and subsequently flushed with He (60 ml min^{-1}) at 373 K for 2 h to remove the physisorbed ammonia. The heating rate for the TPD measurements, from ambient to 1023 K, was 10 K min^{-1}. The SEM analyses were carried out with a Hitachi model-520 instrument. The finely powdered samples were mounted on a silver sample holder with the help of an adhesive to make the sample surface conductive and were coated with gold metal at 10 mmHg pressure.

2.3. Activity studies

All chemicals employed in this study were commercially available and used without further purification. A mixture of aldehyde (1 mmol), amine (1 mmol), TMSCN (1.2 mmol) and SO_4^{2-}/ZrO_2 solid acid catalyst (100 mg) in dry THF (1.5 ml) was stirred at room temperature for an appropriate time under N_2 atmosphere. After completion of the reaction, as indicated by TLC, the reaction mixture was filtered and washed with ethyl acetate (3×5 ml). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuum and purified by column chromatography on silica gel using ethyl acetate and hexane as an eluent to afford pure α-aminonitrile. All products were identified by comparing their spectral data with literature [4–23].

3. Results and discussion

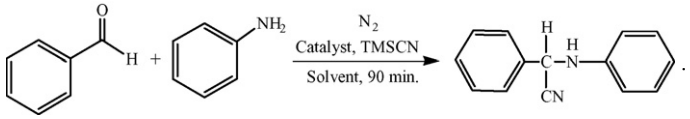
Incorporation of various promoters into $Zr(OH)_4$ shows a strong influence on the bulk and the surface properties of zirconia. XRD results revealed that addition of promoters enhanced the tetragonal zirconia phase and the surface acidity [47]. The ammonia-TPD results indicated that the impregnated sulfate ions show a strong influence and enhance the acidity of ZrO_2, which is followed by molybdate [47]. The Raman spectrum of unpromoted ZrO_2 calcined at 873 K exhibited the Raman bands pertaining to a mixture of monoclinic (180, 188, 221, 331, 380, 476, and 637 cm^{-1}) and tetragonal (148, 290, 311, 454, and 647 cm^{-1}) phases and the bands due to tetragonal phase were less intense than the lines due to monoclinic phase [8,9,47,48]. Whereas in the spectra of sulfate, molybdate and tungstate promoted catalysts bands representing the tetragonal phase were intense. To study the surface topography and to assess the surface dispersion of promoters namely sulfate, molybdate and tungstate over the ZrO_2, the SEM investigation was performed [8,9,48]. In the micrograph of zirconia, though crystallinity is observed, there were certain cracks on the surface that were attributed to the loss of water molecules during the calcination. As noted from the micrograph of tungstated zirconia sample, the WO_x were strongly interacted and highly dispersed on the surface of the zirconia support generating some porosity. From the micrograph of molybdated zirconia catalyst, it was noted that active component is equally spread on the surface of the support. The micrograph of sulfated zirconia indicated that the sulfate ions strongly interacted with the zirconia.

We initially carried out our investigation with the screening of various catalysts. We selected first a commonly used amine, aniline, reactive aldehyde, benzaldehyde, and trimethylsilyl cyanide as reactive cyanide ion source. The results are collected in Table 1. Preliminary experiments in various solvents revealed that the reaction performed well in THF (Entry 6) compared to non-polar or polar solvents CH_3CN or CH_2Cl_2 (Table 1, Entries 1 and 2). Indeed, sulfated zirconia (SO_4^{2-}/ZrO_2) is found to be most efficient than molybadated zirconia (MoO_x/ZrO_2) and tungstated zirconia (WO_x/ZrO_2) catalysts (Entries 6–8). Though these results are not directly correlated to BET surface area or NH_3 desorbed, the sulfated zirconia catalyst exhibited more BET SA (100 m^2/g) and more amount of ammonia desorption from NH_3-TPD (16 ml/g) measurements than that of molybadated or tungstated catalysts. Also an increase in the amount of catalyst showed a significant increase in the yield of product (Table 1, Entries 3–6). Of course, the reaction did not proceed without the catalyst under the identical conditions (Entry 9).

Heterogeneous catalysts offer ease of handling and purification, through simple filtration. They also allow catalyst recovery and recycling, another interesting eco-friendly aspect. In order to examine this possibility, after the reaction, the solid catalyst was conveniently removed by simple filtration from the reaction mixture. The wet catalyst was reused for the reaction and there was no big change in the catalytic activity in the next 3–5 cycles. With these "green" conditions in hand, we then explored the scope of this new promoted zirconia-based solid acid catalysed MCR. In the mean time, we also investigated the role of aldehyde and amine in this three-component condensation (Table 2 and Scheme 1).

Table 1

Search for optimal catalysts and conditions.[a]



Sr. no.	Catalyst	Amount of catalyst (mg)	Solvent[a]	Yield (%)[b]	BET SA ($m^2\ g^{-1}$)	NH_3 desorbed (ml/g)	Tetragonal ZrO_2 (%)
1.	SO_4^{2-}/ZrO_2	100	CH_3CN	95	100	16	80
2.	SO_4^{2-}/ZrO_2	100	CH_2Cl_2	98	100	16	80
3.	SO_4^{2-}/ZrO_2	75	THF	95	100	16	80
4.	SO_4^{2-}/ZrO_2	50	THF	93	100	16	80
5.	SO_4^{2-}/ZrO_2	25	THF	85	100	16	80
6.	SO_4^{2-}/ZrO_2	100	THF	~100	100	16	80
7.	WO_3/ZrO_2	100	THF	91	35	09	68
8.	MoO_3/ZrO_2	100	THF	88	94	11	84
9.	–	–	THF	NR	–	–	–

NR: no reaction.

[a] 1.5 ml solvent was used.

[b] Yields evaluated by ^{1}H NMR of the crude mixture.

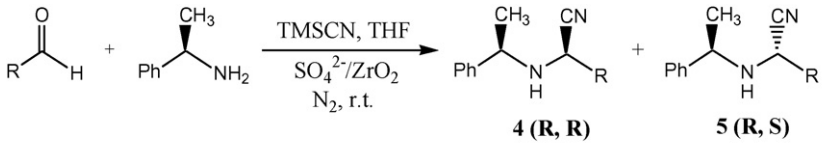
The influence of the amine as well as aldehyde was examined by submitting aromatic amines and aliphatic amines to different aldehydes or ketones with TMSCN. Aromatic amines provided the corresponding α-aminonitriles in excellent isolated yields. Aliphatic amines are found to be less reactive (Table 2, Entries 6–9), and with *iso*-butyl amine reaction did not work well (Table 2, Entry 3). The MCR is working smoothly with aromatic, heteroaromatic and aliphatic aldehydes, offering good to excellent yields. But ketones are found to be less reactive (Table 2, Entries 14–18). Similar observations were also made earlier with other reagents in the literature. Moreover, the reaction conditions are mild enough to perform the reactions in the presence of acid sensitive substrates, such as cinnamaldehyde and furfuraldehyde without any decomposition or polymerization (Table 2, Entries 4 and 10).

To evaluate the possibility of 1,3-asymmetric induction, we extended this MCR to the preparation of optically active α-aminonitriles derived from (R)-(+)-methylbenzylamine, aldehydes and the TMSCN. The reaction with both aryl and alkyl aldehydes in every case produced mixtures of diastereoisomers, with one diastereoisomer predominating. The relative stereochemistry of the products was determined by ^{1}H NMR spectroscopy using the literature methods [20,49,50]. For instance, the ^{1}H NMR of the crude α-(1-methylbenzyl)amino valeronitrile (R = *iso*-propyl, Scheme 2) showed two doublets, one at 2.85 ppm (J = 6.314 Hz) and the other at 3.33 ppm (J = 6.314 Hz) in a ratio of 64:36. Each doublet is derived from the proton attached to the carbon bearing the nitrile. On the basis of Ojima's finding the up field (major) doublet is from the S chiral center of the amino nitrile proton of the molecule and the downfield (minor) doublet is from the R chiral center [49]. According to the literature hypothesis [51–55], nucleophilic attack on the imine should take place antiperpendicular to the α-phenyl group.

The amines used are better nucleophiles than trimethylsilyl cyanide; hence, they react first with the carbonyl compound to produce the corresponding imine. Therefore, the reaction proceeds through the initial formation of an iminium from the starting amine and aldehyde. This iminium is then trapped by a cyanide ion *in situ* generated from TMSCN in the presence of solid acid catalyst. However, the iminium formation is equilibrated and this equilibrium could be influenced by solid acid. To check this possibility, we monitored by NMR the evolution of a mixture of aniline and benzaldehyde in the presence and absence of SO_4^{2-}/ZrO_2 at room temperature and THF as the solvent for a period of 30 min. The signal at ≈9 ppm typical of the iminium proton gradually grew and its relative integration reached a plateau. These results and the fact that iminium proportion was significantly higher in the presence of SO_4^{2-}/ZrO_2 than without it (Scheme 3) (94 vs. 76% respectively) tend to support an active role of solid acid for the formation of this intermediate. The probable mechanism for MCR is described in Scheme 4. The spectral data for some of the selected representative compounds is given below.

3.1. 2-(N-anilino)-2-phenylacetonitrile (Table 2, Entry 1)

Pale yellow crystalline solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ3.96 (d, J = 8.081 Hz, 1H), 5.36 (d, J = 8.081 Hz, 1H), 6.72 (d, J = 7.346 Hz, 2H), 6.86 (t, J = 7.346 Hz, 1H), 7.23 (t, J = 8.081 Hz, 2H), 7.41–7.49 (m, 3H), 7.55–7.61 (m, 2H); IR (neat) ν 3336, 3028, 2930, 2236, 1598, 1514, 1445, 1282, 1155, 996, 752 cm^{-1}. EIMS: m/z 208 (M^+), 180, 116, 91, 77.



R	4:5	Yield (%)
i-propyl	36:64	90
n-butyl	37:63	85
Phenyl	24:76	80
4-MeO-Ph	08:92	78

Scheme 2. 1,3-Asymmetric induction in Strecker reaction by SO_4^{2-}/ZrO_2 catalyst.

Table 2
Strecker reaction of a variety of aldehydes and amines with TMSCN in the presence of SO_4^{2-}/ZrO_2.

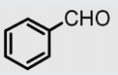
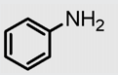
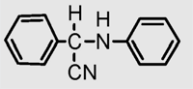
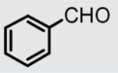
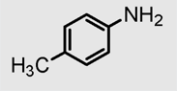
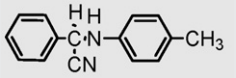
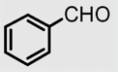
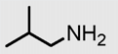
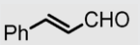
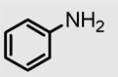
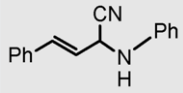
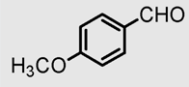
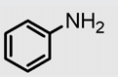
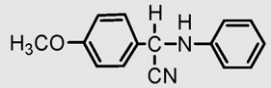
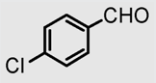
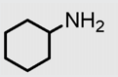
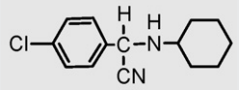
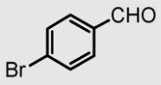
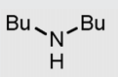
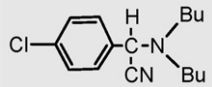
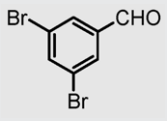
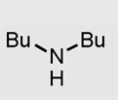
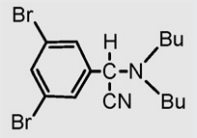
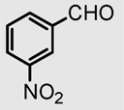
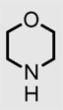
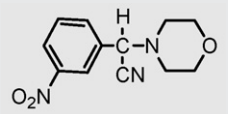
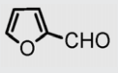
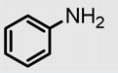
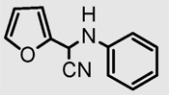
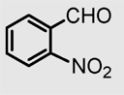
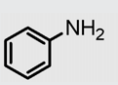
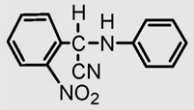
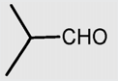
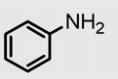
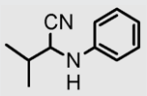
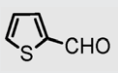
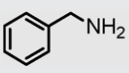
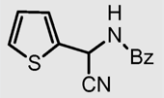
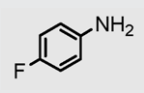
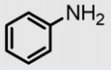
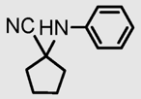
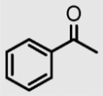
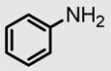
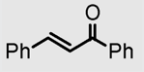
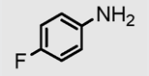
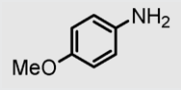
Entry	Aldehyde/ketone	Amine	Product	Time (min.)	Yield (%)[a]
1.				90	93
2.				120	76
3.			–	–[b]	NR
4.				30	73
5.				45	87
6.				120	46
7.				120	52
8.				120	80
9.				180	68
10.				20	82
11.				45	53
12.				180	89
13.				90	86
14.				360	88

Table 2 (*Continued*)

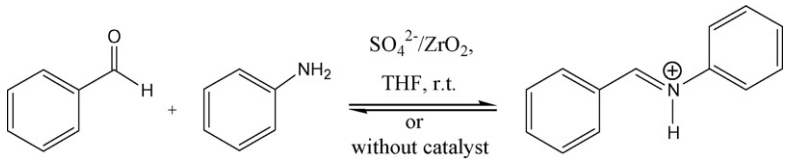
Entry	Aldehyde/ketone	Amine	Product	Time (min.)	Yield (%)[a]
15.				360	67
16.			–	–[b]	NR
17.			–	–[b]	Traces[c]
18.			–	–[b]	NR

NR: no reaction.

[a] Yields of isolated products after column chromatography otherwise mentioned.

[b] Reaction time is 12–15 h.

[c] From NMR.



Scheme 3. Equilibrated mixture obtained from aniline and benzaldehyde in the presence or not of SO_4^{2-}/ZrO_2.

3.2. 2-(N-p-tolylamino)-2-phenylacetonitrile (Table 2, Entry 2)

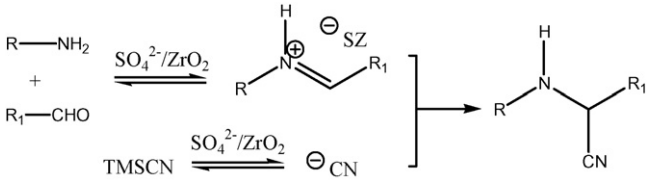
Dark brown crystalline solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ2.21 (s, 3H), 5.47 (d, J = 8.81 Hz, 1H), 5.77 (d, J= 8.81 Hz, 1H), 6.63 (d, J = 8.08 Hz, 2H), 6.94 (d, J = 8.08 Hz, 2H), 7.32–7.48 (m, 3H), 7.52–7.61 (m, 2H); IR (KBr): ν 3328, 2922, 2241, 1615, 1517, 1448, 1280, 1126, 924, 876, 804, 697 cm^{-1}; EIMS: m/z 222 (M^+), 116, 106, 89, 77, 51.

3.3. 2-(N-anilino)-2-cinnamylacetonitrile (Table 2, Entry 4)

Brick red solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ4.09 (d, J = 8.662 Hz, 1H), 5.43 (d, J = 8.662 Hz, 1H), 6.40 (m, 1H), 6.58 (m, 1H), 6.73 (d, J = 7.94 Hz, 2H), 6.87 (t, J = 7.218 Hz, 1H), 7.24 (t, J = 7.218 Hz, 2H), 7.46 (m, 1H); IR (neat) ν 3358, 2925, 2241, 1705, 1603, 1501, 1438, 1293, 1249, 1147, 1013, 877, 743 cm^{-1}; EIMS: m/z 198 (M^+), 169, 141, 115, 106, 92, 77, 51.

3.4. 2-(N-anilino)-2-(4-methoxy-phenyl)-acetonitrile (Table 2, Entry 5)

Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ3.83 (s, 3H), 3.90 (d, J = 8.08 Hz, 1H), 5.41 (d, J = 8.08 Hz, 1H), 6.76 (d, J = 8.08 Hz, 3H), 6.94 (d, J = 8.81 Hz, 2H), 7.20 (t, J = 8.08 Hz, 2H), 7.51 (d, J = 8.08 Hz,



Scheme 4. Proposed mechanism for MCR catalysed by SO_4^{2-}/ZrO_2.

2H); IR (neat): ν 3426, 2924, 2254, 1605, 1509, 1250, 1026, 1001, 825, 761 cm^{-1}; EIMS: m/z 238 (M^+), 210, 95, 81, 55, 41.

3.5. 2-(N-morpholino)-2-(3-nitrophenyl)acetonitrile (Table 2, Entry 9)

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ2.45–2.69 (m, 4H), 3.60–3.77 (m, 4H), 5.23 (s, 1H), 7.67 (t, J = 7.81 Hz, 1H), 7.92 (d, J = 7.81 Hz, 1H), 8.21–8.26 (m, 1H), 8.34–8.41 (m, 1H); IR (neat): ν 3398, 3084, 2916, 2229, 1615, 1532, 1451, 1291, 1113, 902, 866, 709 cm^{-1}; EIMS: m/z 247 (M^+), 216, 151, 106, 87, 57.

3.6. 3-Methyl-2-N-phenylamino-butyronitrile (Table 2, Entry 12)

Dark brown liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ1.12–1.20 (q, J = 6.25 Hz, 6H), 2.03–2.27 (m, 1H), 3.98 (q, J = 6.25 Hz, 1H), 5.45 (d, J = 6.25 Hz, 1H), 6.64–6.74 (m, 3H), 7.09–7.23 (m, 2H); IR (neat): ν 3373, 2966, 2924, 2249, 1726, 1604, 1505, 1465, 1313, 1271, 1154, 875, 751, 691 cm^{-1}; EIMS: m/z 174 (M^+), 131, 104, 77, 43.

3.7. 2-(N-benzylamino)-2-thiophenylacetonitrile (Table 2, Entry 13)

Colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ2.99 (bs, 1H), 3.96 (q, J = 12.842 Hz, 2H), 4.89 (s, 1H), 6.95–6.98 (m, 1H), 7.02–7.05 (m, 1H), 7.18–7.4 (m, 6H); IR (neat): ν 3315, 2922, 2231, 1633, 1495, 1356, 1217, 1163, 860, 758 cm^{-1}; EIMS: m/z 228 (M^+), 137, 122, 106, 91, 78, 66.

3.8. 1-(N-4-fluorophenylamino)-1-cyanocyclohexane (Table 2, Entry 14)

White crystalline solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ1.51–1.68 (m, 6H), 1.70–1.86 (m, 4H), 4.76 (bs, 1H), 6.82–6.94 (m, 4H); IR (KBr):

ν 3343, 2925, 2224, 1606, 1512, 1452, 1250, 1160 cm^{-1}; EIMS: m/z 218 (M^+), 175, 111, 95, 83, 41.

4. Conclusions

In summary, among the promoted zirconia solid acid catalysts, sulfated zirconia is found to be most efficient for the title reaction. Mild reaction conditions, experimental simplicity, inexpensive catalyst, high yield of the products and shorter reaction times are some of the advantages associated with this methodology.

Acknowledgments

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