Scientia Iranica C (2013) 20(6), 1863–1870

Sharif University of Technology
**Scientia Iranica**
*Transactions C: Chemistry and Chemical Engineering*
www.scientiairanica.com

# Synthesis of 2-amino-4,6-diarylnicotininitriles using 3-propyldiethylenetriamine-silica as a recyclable solid base catalyst

**Kh. Niknam*, R. Rashidian and A. Jamali**

*Department of Chemistry, Faculty of Sciences, Persian Gulf University, Bushehr, P.O. Box 75169, Iran.*

Received 24 September 2012; accepted 12 March 2013

**KEYWORDS**
3-Propyldiethylenetriaminesilica;
2-amino-4,6-diarylnicotininitriles;
Solid base catalyst;
Pyridines;
Aldehydes;
Solvent-free.

**Abstract.** A simple and efficient procedure for the preparation of 3-propyldiethylenetriaminesilica (PDTAS) by reaction of 3-chloropropylsilica with diethylene-triamine is described. 3-propyldiethylenetriaminesilica is employed as a recyclable base catalyst for the synthesis of 2-amino-4,6-diarylnicotininitrile from the reaction of acetophenone derivatives, aromatic aldehydes, malononitrile, and ammonium acetate under solvent-free conditions at 100°C. The heterogeneous solid base catalyst was recycled for four runs upon the reaction of 4-chloroacetophenone, 4-chloroenzaldehyde, malononitrile, and ammonium acetate without losing its catalytic activity.



## 1. Introduction

Pyridine and its derivatives are important motifs present in a great number of pharmaceuticals and natural products [1-6]. The unique structural array and highly pronounced biological and physiological activies [1-6] displayed by the class of pyridine moieties have made them attractive synthetic targets. Especially, 2-amino-4,6-diarylnicotininitrile is considered to be an important class of bio-active agent [4-6]. For example, recently 2-aminopyridine derivatives have been identified as novel GPR54 antagonists with good brain exposure and in vivo efficacy for plasma LH levels in male rats [6], anti-microbial activity [7], IKK-$\beta$ inhibitors [8], potent inhibitor of HIV-1 integrase [9], anticonvulsant activity [10] and so on. Despite the existence of extensive literature for the synthesis of 2-amino-3-cyanopyridines, most common procedures need multiple steps [11], long reaction times, toxic benzene as solvents [12], high temperatures or microwave assistance [13], resulting in unsatisfactorily low yields. However, a straight-forward and efficient one-pot reaction by catalysis in mild conditions is still limited. Recent reports use two steps synthesis [14], Brönsted acidic ionic liquid at 150°C [15], $Yb(PFO)_3$ in refluxing ethanol [16], and silica-bound N-propyltriethylenetetramine sulfamic acid [17].

Based-catalysed condensation and addition reactions are industrially important in the production of drugs, fragrances and chemical intermediates [18]. One of the most important classes of these reactions is the C-C coupling reaction, such as Aldol and Knoevenagel condensations, as well as Michael reactions [19-21]. Conventionally, almost stoichiometric amounts of homogeneous bases are used for such purposes [18,22,23]. In such systems, there are many disadvantages, including isolation of products, the corrosive nature of the reaction mixture and the formation of large amounts of waste materials. Therefore, improved synthesis methods in terms of product purity, yield, and minimal waste formation are highly

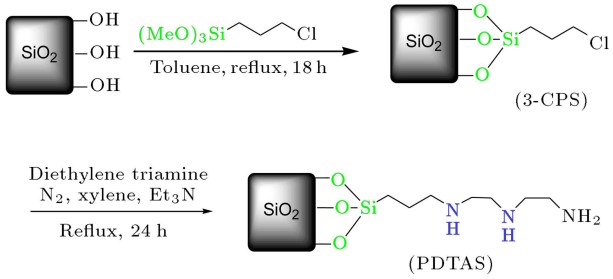
*. *Corresponding author. Tel.: +98 771 4541494; Fax: +98 771 4545188*
*E-mail addresses: khniknam@gmail.com, and niknam@pgu.ac.ir (Kh. Niknam)*

desirable. Moreover, replacement of liquid acids and bases with the corresponding cleaner, solid alternatives, possessing desirable characteristics such as being non-stoichiometric, non-corrosive and reusable, is necessary in view of environmentally benign industries. Solid base catalysts such as hydrotalcites and basic zeolites have been studied and applied in numerous reactions so far [24,25]. The potential use of microporous and mesoporous base catalysts in fine chemical production is enormous [19]. These heterogeneous catalysts are known to suppress side reactions, which include self-condensation and oligomerization, resulting in better selectivity and product yield. It also avoids the complex neutralization and separation steps needed to recover the homogeneous base catalysts from the reaction mixture. The recovered solid catalysts can be readily regenerated for further use.

## 2. Results and discussion

In continuation of our studies on the design and application of solid acid and solid base catalysts in organic transformations [26-34], herein, we describe the preparation of 3-propyldiethylenetriaminesilica (PDTAS) and its application as a catalyst for the synthesis of 2-amino-4,6-diarylnicotininitriles. PDTAS was prepared by the reaction of 3-chloropropylsilica (3-CPS) with diethylenetriamine in xylene, as illustrated in Scheme 1. The elemental analysis showed the $N$ content to be 4.07%; C, 11.07%; H, 2.40%.

The thermogravimetric analysis (TGA) curves of PDTAS show the mass loss of organic materials as they decompose upon heating (Figure 1). The initial weight




**Scheme 1.** Preparation of 3-propyldiethylenetriaminesilica (PDTAS).

loss from the PDTAS up to 100°C is due to removal of physically adsorbed solvent and surface hydroxyl groups.

The weight loss of about 22.59% between 120 and 600°C is contributed to the thermal decomposition of organic groups. This weight loss of organic components is equal to 1.55 mmol per 1 g of catalyst. The covalent chemical bonds connection made the catalyst have high thermal stability. This discovery made it possible for the catalyst to be used for high temperature applications.

Figure 2 shows Fourier transform infrared (FT-IR) spectra for PDTAS. The major peaks for silica ($SiO_2$) are broad anti symmetric Si-O-Si stretching from 1300 to 1000 $cm^{-1}$, and symmetric Si-O-Si stretching near 820-780 $cm^{-1}$. For the amine functional group, the FT-IR absorption range of the stretching mode lies in 3200-3300 $cm^{-1}$, which is covered by the silanol group. The FT-IR spectrum shows the overlapping asymmetric and symmetric stretching bands of O=C-O with Si-O-Si stretching bands in the silica

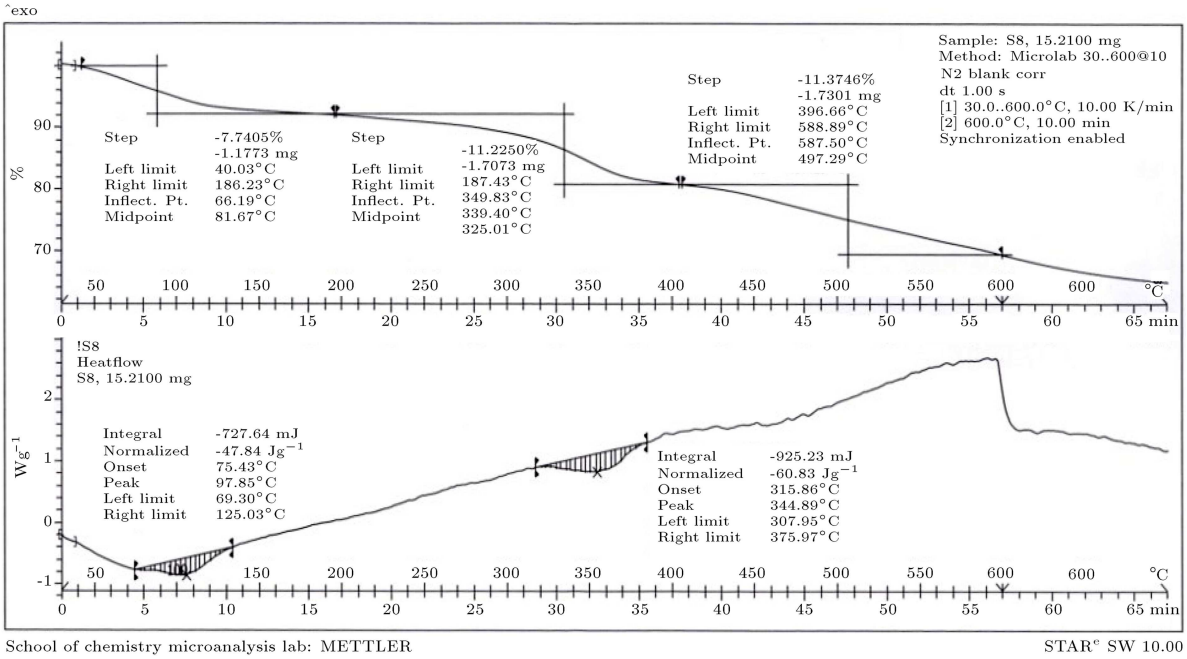



**Figure 1.** TGA of PDTAS.

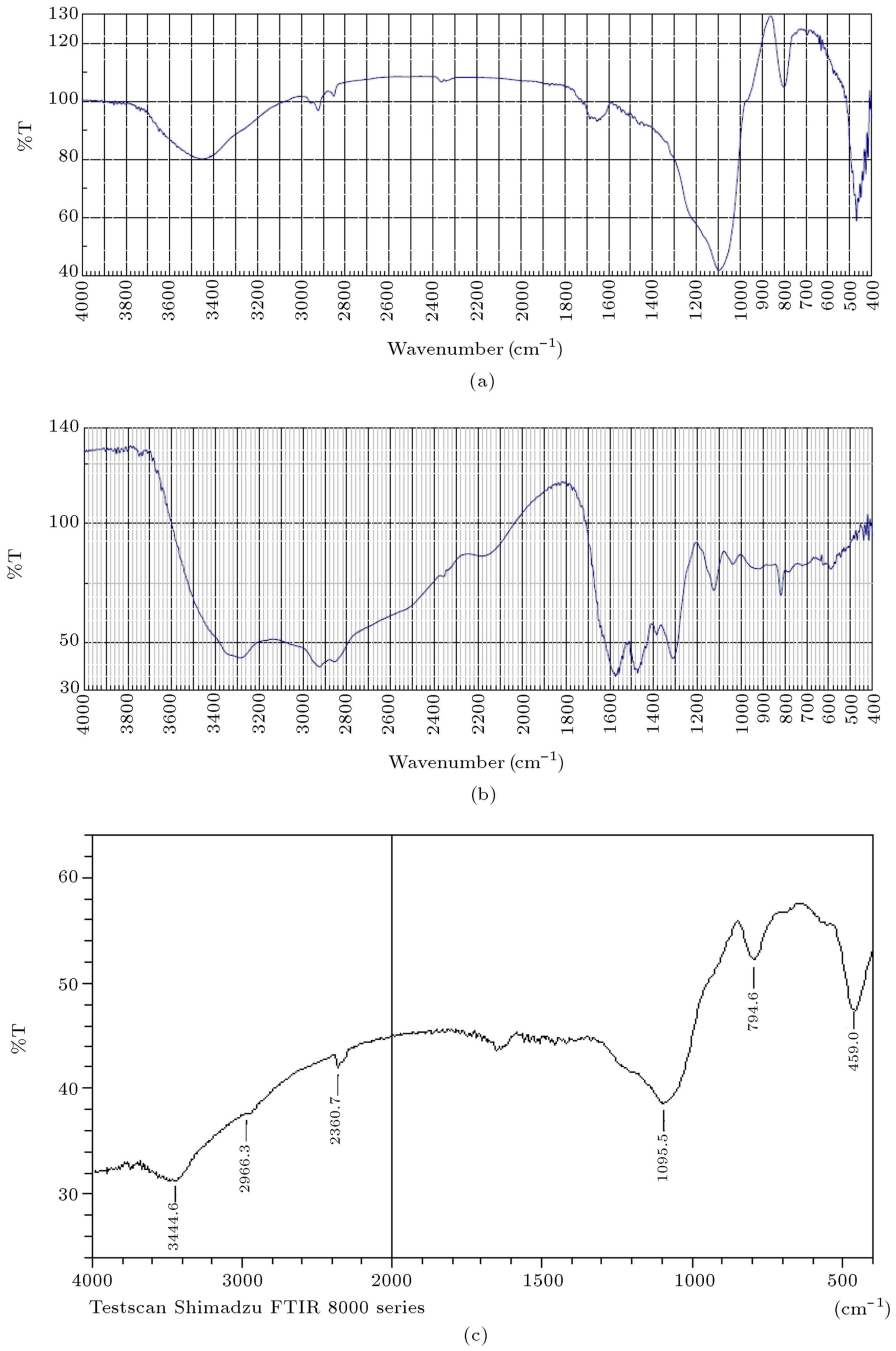



**Figure 2.** FT-IR of a) 3-chloropropylsilica, b) diethylenetriamine and c) PDTAS.

functionalized alkyl-amine. In the FT-IR of PDTAS, the bending mode of the amine group was shown in 1500-1600 cm$^{-1}$.

To study the effect of catalyst loading on the synthesis of 2-amino-4,6-diarylnicotinonitriles, the four-component condensation of 4-chlorobenzaldehyde, 4-chloroacetophenone, malononitrile, and ammonium acetate under different conditions, was selected as a model reaction.

The result shows that PDTAS is an effective catalyst for this condensation. In the absence of catalyst, the condensation reaction gave the corresponding product **1b** at 41% in the refluxing ethanol (Table 1, entry 1). The model reaction condensed in the presence of PDTAS in refluxing ethanol gave **1b** at 45% yield (Table 1, entry 3).

But, when the model reaction was treated with PDTAS under solvent-free conditions at 100°C, the yield was increased. In addition, the result of this condensation in the presence of bases, such as $Et_3N$, morpholine and diethylenetriamine, gave 68%, 66%, and 75% yields, respectively (Table 1, entries 9-

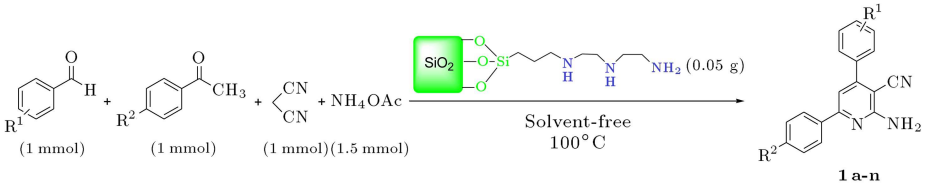
**Table 1.** Condensation reaction of 4-chloroacetophenone, 4-chlorobenzaldehyde, malononitrile, and ammonium acetate in the presence of different amounts of catalysts[a].

| Entry | Catalyst | Catalyst loading (g) | Conditions | Time (min) | Yield %[b] |
|---|---|---|---|---|---|
| 1 | - | - | EtOH, Reflux | 10 h | 41[c] |
| 2 | PDTAS | 0.05 | EtOH, Reflux | 10 h | 45[c] |
| 3 | PDTAS | 0.01 | Solvent-free, 100°C | 45 | 35 |
| 4 | PDTAS | 0.03 | Solvent-free, 100°C | 45 | 65 |
| 5 | PDTAS | 0.05 | Solvent-free, 100°C | 25 | 90 |
| 6 | PDTAS | 0.07 | Solvent-free, 100°C | 25 | 91 |
| 7 | PDTAS | 0.05 | Solvent-free, 90°C | 35 | 88 |
| 8 | $Et_3N$ | 11.8 (0.2 mmol) | Solvent-free, 100°C | 60 | 68 |
| 9 | Morpholine | 17.4 (0.2 mmol) | Solvent-free, 100°C | 60 | 66 |
| 10 | Diethylene triamine | 51.5 (0.5 mmol) | Solvent-free, 100°C | 50 | 75 |

[a]: Reaction conditions: 4-chlorobenzaldehyde (1 mmol), 4-chloroacetophenone (1 mmol), malononitrile (1 mmol), ammonium acetate (1.5 mmol).

[b]: Isolated yield.

[c]: Solvent (4 mL).




**Scheme 2.** Synthesis of 2-amino-4,6-diaryl-nicotininitriles catalyzed by PDTAS.

11). The optimized conditions were chosen as follows: acetophenone derivative (1 mmol), aldehyde (1 mmol), malononitrile (1 mmol), ammonium acetate (1.5 mmol), and PDTAS (0.05 g) and heated under solvent-free conditions at 100°C (Scheme 2). The lower temperature gave the corresponding product in lower yield and in longer reaction time (Table 1, entry 9).

A wide range of aromatic aldehydes was employed and all 2-amino-3-cyanopyridines were obtained in good to high yields. This demonstrated that this is a general method that tolerates both electron-withdrawing and electron-donating constituents. Aromatic aldehydes with electron-donating substituent, such as MeO, MeS, and Me, were reacted with acetophenone derivatives, such as 4-chloro, 4-fluoro, and 4-methoxy acetophenone, under optimized conditions in good to high yields (Table 2). Aromatic aldehydes with electron-deficiency, such as the 4-$NO_2$, 3-$NO_2$ group, reacted with 4-methyl-acetophenone and malononitrile under optimized conditions in high yield (Table 2, entries 9-10).

*Ortho*-substituted as well as *para*-substituted aromatic aldehydes were reacted in this four component condensation (Table 2, entry 7). This method not only affords the products in good to high yields but also avoids the problems associated with catalyst cost, handling, safety, and pollution.

The possibility of recycling the catalyst was examined using the reaction of 4-chlorobenzaldehyde, 4-chloroacetophenone, malononitrile, and ammonium acetate under optimized conditions. Upon completion, the reaction mixture was filtered, the solid washed with ethanol, and the recycled catalyst saved for the next reaction. The recycled catalyst could be reused four times without any further treatment. No observation of any appreciable loss in the catalytic activity of PDTAS was observed (Figure 3).

A plausible mechanism in the presence of a base was drawn in Scheme 3. The $\alpha$-cyanocinnamonitrile formed initially by Knoevenagel condensation in the presence of a solid base underwent subsequent reactions

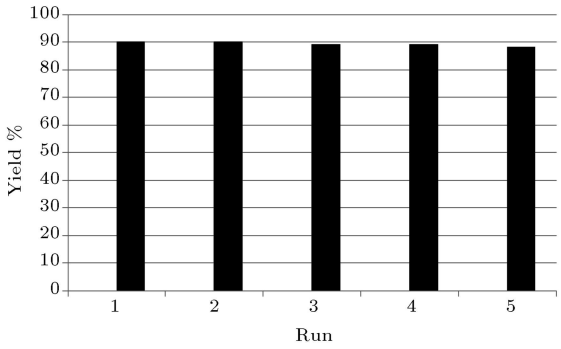


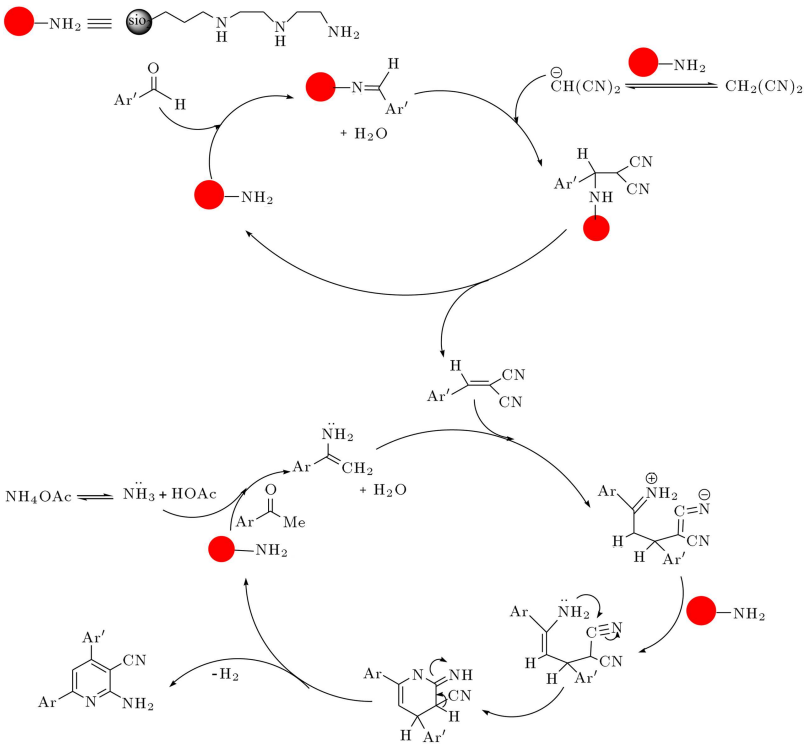

**Figure 3.** Recyclability of PDTAS in the reaction of 4-chloroacetophenone (1 mmol), 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol) and ammonium acetate (1.5 mmol) under solvent-free condition at 100°C. Reaction time = 25 min.

**Table 2.** Synthesis of various 2-amino-4,6-diarylnicotininitriles in the presence of PDTAS under solvent-free conditions at 100°C[a].

| Entry | $R^1$ | $R^2$ | Product | Time (min) | Yield (%)[b] | mp (°C) | Lit. mp (°C) |
|---|---|---|---|---|---|---|---|
| 1 | H | 4-Cl | **1a** | 25 | 89 | 240-242 | 240-241[13] |
| 2 | 4-Cl | 4-Cl | **1b** | 25 | 90 | 230-231 | 228-229[13] |
| 3 | 4-Cl | 4-F | **1c** | 25 | 90 | 204-206 | 219-220[13] |
| 4 | 4-MeS | 4-Cl | **1d** | 30 | 78 | 202-203 | 202-203[17] |
| 5 | 4-Me | 4-Cl | **1e** | 25 | 83 | 215-217 | 215-217[17] |
| 6 | 4-Me | 4-F | **1f** | 33 | 80 | 203-204 | 203-204[17] |
| 7 | 2-Cl | 4-F | **1g** | 30 | 74 | 202-203 | 202-203[17] |
| 8 | H | 4-Me | **1h** | 20 | 87 | 182-183 | 180-182[13] |
| 9 | 4-$O_2$N | 4-Me | **1i** | 18 | 85 | 201-203 | 201-203-[17] |
| 10 | 3-$O_2$N | 4-Me | **1j** | 17 | 90 | 188-190 | 188-190[17] |
| 11 | 4-Me | 3-Br | **1k** | 30 | 80 | 183-184 | - |
| 12 | 4-Me | 4-MeO | **1l** | 25 | 84 | 132-134 | - |
| 13 | 4-Cl | 4-MeO | **1m** | 22 | 82 | 199-200 | 195-196[13] |
| 14 | 4-MeO | 4-MeO | **1n** | 25 | 75 | 161-162 | 159-160[13] |

[a]: Reaction conditions: aldehyde (1 mmol), acetophenone derivative (1 mmol), malonitrile (1 mmol), ammonium acetate (1.5 mmol), PDTAS (0.05 g), solvent-free at 100°C, time was 10 minutes.

[b]:Isolated yield.



**Scheme 3.** A plausible mechanism for synthesis of pyridine derivatives.

with enamine, which was obtained by the reaction of aromatic methyl ketones and ammonium acetate in the presence of a solid base, followed by cyclization, to give the desired product.

## 3. Conclusion

In conclusion, we have shown that 3-propyldiethylenetriaminesilica (PDTAS), which can be prepared from commercially available and cheap starting materials, efficiently catalyzed this four component condensation reaction for the synthesis of 2-amino-4,6-diarylnicotinonitriles. The simplicity of the procedure, its eco-friendliness, non-volatility, easy handling, safety, and the reusability of the catalyst, are the advantages of this method.

## 4. Experimental section

### *4.1. Chemical and reagents*

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. All the products were characterized by comparison of their IR, $^1$H NMR and $^{13}$C NMR spectroscopic data, and their melting points, with the reported values [7-17]. Chloropropyl silica was prepared by a known procedure as previously reported [32].

### *4.2. Catalyst preparation*

#### *4.2.1. Synthesis of 3-propyldiethylenetriaminesilica (PDTAS)*

To a mixture of 3-chloropropyl silica (25 g) in anhydrous xylene (250 mL), an excess of diethylenetriamine (25 mL) was added and the mixture was refluxed with stirring for 24 h. After refluxing, the reaction was stopped and the modified silica was cooled to room temperature, transferred to a vacuum glass filter, and washed with xylene and a large excess of ethanol in turn. The silica that chemically bonded with propyldiethylenetriamine was dried under vacuum overnight at 80°C, and 26.23 g were obtained [32]. Elemental analysis showed the $N$ content to be 4.07%; C, 11.07%; H, 2.40%. The pH of PDTAS was determined by pH-ISE conductivity titration (Denver Instrument Model 270) and found to be pH = 8.7 at 25°C.

### *4.3. General procedure for the synthesis of 2-amino-4,6-diarylnicotinonitriles*

To a mixture of acetophenone derivative (1 mmol), aromatic aldehyde (1 mmol), malononitrile (1 mmol) and ammonium acetate (1.5 mmol), PDTAS (0.05 g, equal to $2.5 \times 10^{-7}$ mmol of $OH^-$) was added and heated at 100°C under solvent-free conditions. When the reaction was complete, as judged by TLC, ethanol (5 mL) was added, the reaction mixture was filtered and the remaining solid was washed with warm ethanol ($3 \times 5$ mL) in order to separate the catalyst. The products were recrystallized from ethanol. The recovered catalyst was dried and reused for subsequent runs.

**2-Amino-6-(3-bromophenyl)-4-p-tolylnicotinonitrile (1k):** IR (KBr): 3440, 3321, 2920, 2207, 1641, 1555, 1442, 1357, 1254, 1186, 782 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.47 (s, 3H), 5.38 (s, 2H), 7.19 (s, 1H), 7.35-7.42 (m, 3H), 7.56-7.62 (m, 3H), 7.94 (d, 1H, $J$ = 7.6 Hz), 8.20 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 21.4, 111.1, 123.0, 125.8, 128.0, 129.7, 130.2, 130.4, 133.0, 133.8, 140.0, 140.3, 155.4, 157.9, 160.1. Elemental analysis: for $C_{19}H_{14}BrN_3$: C, 62.65; H, 3.87; Br, 21.94; N, 11.54; Found: C, 62.43; H, 3.85; N, 11.31.

**2-Amino-6-(4-methoxyphenyl)-4-p-tolylnicotinonitrile (1l):** IR (KBr): 3455, 3363, 2924, 2205, 1621, 1565, 1508, 1440, 1369, 1304, 1241, 1173, 1114, 10294, 818 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.46 (s, 3H), 3.90 (s, 3H), 5.36 (s, 2H), 7.01 (d, 2H, $J$ = 8.8 Hz), 7.17 (s, 1H), 7.35 (d, 2H, $J$ = 7.6 Hz), 7.56 (d, 2H, $J$ = 7.6 Hz), 8.01 (d, 2H, $J$ = 8.8 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 21.4, 55.4, 110.3, 114.1, 117.5, 128.0, 128.8, 129.6, 130.4, 134.4, 140.0, 154.9, 159.2, 160.2, 161.4. Elemental analysis: for $C_{20}H_{17}N_3O$: C, 76.17; H, 5.43; N, 13.32; Found: C, 75.93; H, 5.39; N, 13.17.

## Acknowledgment

We are grateful for partial support of this work by the Persian Gulf University Research Council. We also appreciate the assistance of the School of Chemistry at Manchester University for running NMR, CHN, and TGA.

## References

1. Cocco, M.T., Congiu, C., Lilliu, V. and Onnis, V. "Synthesis and in vitro antitumoral activity of new 3,5-dicyanopyridine derivatives", *Bioorg. Med. Chem.*, **15**(4), pp. 1859-1867 (2007).
2. Fredholm, B.B., Ijzerman, A.P., Jacobson, K.A., Klotz, K.N. and Linden, J. "International union of pharmacology. XXV. Nomenclature and classification of adenosine receptors", *Pharmacol. Rev.*, **53**, pp. 527-552 (2001).
3. Mungra, D.C., Patel, M.P. and Patel, R.G. "An efficient one-pot synthesis and in vitro antimicrobial activity of new pyridine derivatives bearing the tetrazoloquinoline nucleus", *Arkivoc*, **xiv**, pp. 64-74 (2009).
4. May, B.C.H., Zorn, J.A., Witkop, J., Sherrill, J., Wallace, A.C., Legname, G., Prudiner, S.B. and Cohen, F.E. "Structure-activity relationship study of prion inhibition by 2-aminopyridine-3,5-dicarbonitrile-based compounds: Parallel synthesis, bioactivity, and in vitro pharmacokinetics", *J. Med. Chem.*, **50**(1), pp. 65-73 (2007).
5. Guo, K., Mutter, R., Heal, W., Reddy, T.R.K., Cope, H., Pratt, S., Thompson, M.J. and Chen, B. "Synthesis and evaluation of a focused library of pyridine dicarbonitriles against prion disease", *Eur. J. Med. Chem.*, **43**, pp. 93-106 (2008).
6. Kobayashi, T., Sasaki, S., Tomita, N., Fukui, S., Nakayama, M., Kiba, A., Kusaka, M., Matsumoto, S.I., Yamaguchi, M., Itoh, F. and Baba, A. "2-Acylamino-4,6-diphenylpyridine derivatives as novel GPR54 antagonists with good brain exposure and in vivo efficacy for plasma LH level in male rats", *Bioorg. Med. Chem.*, **18**, pp. 5157-5171 (2010).
7. Khidre, R.E., Abu-Hashem, A.A. and El-Shazly, M. "Synthesis and anti-microbial activity of some 1- substituted amino-4,6-dimethyl-2-oxo-pyridine-3-carbonitrile derivatives", *Eur. J. Med. Chem.*, **46**, pp. 5057-5064 (2011).

8. Murata, T., Shimada, M., Sakakibara, S., Yoshinno, T., Kadono, H., Masuda, T., Shimazaki, M., Shintani, T., Fuchikami, K., Saki, K., Inbe, H., Takeshita, K., Niki, T., Umeda, M., Bacon, K.B., Ziegelbauer, K.B. and Lowinger, T.B. "Discovery of novel and selective IKK-$\beta$ serine-threonine protein kinase inhibitors. Part 1", *Bioorg. Med. Chem. Lett.*, **13**(5), pp. 913-918 (2003).
9. Mantri, M., De Graaf, O., Van Valdhoven, J., Gobluos, A., Von Frijtag Drabbe Kunzel, J.K., Mulder-Krieger, T., Link, R., De Vries, H., Beukers, M.W., Brussee, J. and Ijzerman, A.P. "2-amino-6-furan-2-yl-4-substituted nicotinonitriles as $A_{2A}$ adenosine receptor antagonists", *J. Med. Chem.*, **51**(15), pp. 4449-4455 (2008).
10. Nadeem, S., Waquar, A., Shamsher, A.M., Ruhi, A. and Kamna, S. "Design, synthesis and evaluation of anticonvulsant activity of pyridinyl-pyrrolidones: A pharmacophore hybrid approach", *Arch. Pharm. Chem. Life Sci.*, **345**, pp. 185-194 (2012).
11. Girgis, A.S., Kalmouch, A. and Hosni, H.M. "Synthesis of novel 3-pyridinecarbonitriles with amino acid function and their fluorescence properties", *Amino Acids*, **26**(2), pp. 139-146 (2004).
12. Kambe, S., Saito, K., Sakurai, A. and Midorikawa, H. "A simple method for the preparation of 2-amino-4-aryl-3-cyanopyridines by the condensation of malononitrile with aromatic aldehydes and alkyl ketones in the presence of ammonium acetate", *Synthesis*, pp. 366-367 (1980).
13. Shi, F., Tu, S. J., Fang, F. and Li, T.J. "One-pot synthesis of 2-amino-3-cyanopyridine derivatives under microwave irradiation without solvent", *Arkivoc*, **i**, pp. 137-142 (2005).
14. Shah, H.C., Shah, V.H. and Desai, N.D. "An efficient one-pot synthesis and *in vitro* antimicrobial activity of new pyridine derivatives bearing the tetrazoloquinoline nucleus", *Arkivoc*, **ii**, pp. 76-74 (2009).
15. Davoodnia, A., Attar, P., Morsali, A., Eshghi, H., Tavakoli-Hoseini, N. and Khadem, S. "Experimental and theoretical studies on the tautomerism in 2-aminopyridines and 2(1*H*)-pyridinones: Synthesis of 2-Amino-4-aryl-3-cyano-6-(3,4-dimethoxyphenyl)-pyridines and 4-Aryl-3-cyano-6-(3,4-dimethoxyphenyl)-2(1*H*)-pyridinones", *Bull. Korean Chem. Soc.*, **32**(6), pp. 1873-1878 (2011).
16. Tang, J., Wang, L., Yao, Y., Zhang, L. and Wang, W. "One-pot synthesis of 2-amino-3-cyanopyridine derivatives catalyzed by ytterbium perfluorooctanoate [Yb(PFO)$_3$]", *Tetrahedron Lett.*, **52**, pp. 509-511 (2011).
17. Niknam, K., Jamali, A., Tajaddod, M. and Deris, A. "Synthesis of 2-amino-4,6-diarylnicotinonitriles using silica-bound *N*-propyl triethylenetetramine sulfamic acid as a recyclable solid acid cataly", *Chin. J. Catal.*, **33**, pp. 1312-1317 (2012).
18. Kelly, G.J., King, F. and Kett, M. "Waste elimination in condensation reactions of industrial importance", *Green Chem.*, **4**, pp. 392-399 (2002).
19. Weitkamp, J., Hunger, M. and Rymsa, U. "Base catalysis on microporous and mesoporous materials: recent progress and perspectives", *Micropor. Mesopor. Mater.*, **48**, pp. 255-270 (2001).
20. Sheldon, R.A. "Atom efficiency and catalysis in organic synthesis", *Pure Appl. Chem.*, **72**, pp. 1233-1246 (2000).
21. Zapf, A. and Beller, M. "Fine chemical synthesis with homogeneous palladium catalysts: examples, status and trends", *Top. Catal.*, **19**, pp. 101-109 (2002).
22. King, F. and Kelly, G.J. "Combined solid base/ hydrogenation catalysts for industrial condensation reactions", *Catal. Today*, **73**, pp. 75-81 (2002).
23. Poliakoff, M., Fitzpatrick, J.M., Farren, T.R. and Anastas, P.T. "Green chemistry: science and politics of change", *Science*, **297**, pp. 807-810 (2002).
24. (a) Debecker, D.P., Gaigneaux, E.M. and Busca, G. "Exploring, tuning, and exploiting the basicity of hydrotalcites for applications in heterogeneous catalysis", *Chem. Eur. J.*, **15**(16), pp. 3920-3935 (2009);

    (b) Sels, B.F., De Vos, D.E. and Jacobs, P.A. "Hydrotalcite-like anionic clays in catalytic organic reactions", *Catal. Rev.*, **43**, pp. 443-488 (2001).
25. Tanabe, K. and Holderich, W.F. "Industrial application of solid acid-base catalysts", *Appl. Catal. A*, **181**, pp. 399-434 (1999).
26. Niknam, K., Saberi, D. and Nouri Sefat, M. "Silica-bonded *S*-sulfonic acid as a recyclable catalyst for chemoselective synthesis of 1,1-diacetates", *Tetrahedron Lett.*, **50**, pp. 4058-4062 (2009).
27. Niknam, K. and Saberi, D. "Silica-bonded *N*-propyl sulfamic acid as an efficient catalyst for the formylation and acetylation of alcohols and amines under heterogeneous conditions", *Tetrahedron Lett.*, **50**, pp. 5210-5214 (2009).
28. Niknam, K. and Saberi, D. "Preparation of sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester: A new and recyclable catalyst for the formylation and acetylation of alcohols under heterogeneous conditions", *Appl. Catal. A: Gen.*, **366**, pp. 220-225 (2009).
29. Niknam, K., Mohammadizadeh, M.R., Mirzaee, S. and Saberi, D. "Silica-bonded *S*-sulfonic Acid: A recyclable catalyst for the synthesis of trisubstituted imidazoles under solvent-free conditions", *Chin. J. Chem.*, **28**, pp. 663-669 (2010).
30. Niknam, K., Mohammadizadeh, M.R. and Mirzaee, S. "Silica-bonded *S*-sulfonic acid as a recyclable catalyst for synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones", *Chin. J. Chem.*, **29**, pp. 1417-1422 (2011).
31. Niknam, K., Deris, A., Naeimi, F. and Majleci, F. "Synthesis of 1,2,4,5- tetrasubstituted imidazoles using silica-bonded propylpiperazine *N*-sulfamic acid as a recyclable solid acid catalyst", *Tetrahedron Lett.*, **52**, pp. 4642-4645 (2011).

32. Nouri Sefat, M., Deris, A. and Niknam, K. "Preparation of silica-bonded propyl-diethylene-triaminensulfamic acid as a recyclable catalyst for chemoselective synthesis of 1,1-diacetates", *Chin. J. Chem.*, **29**, pp. 2361-2367 (2011).

33. Ghaem Ahmadi-Ana, S.M., Baghernejad, M. and Niknam, K. "Synthesis of 2-aryl-1-arylmethyl-1*H*-1,3-benzimidazole derivatives using silica-bonded propyl-*S*-sulfonic acid as recyclable solid acid catalyst", *Chin. J. Chem.*, **30**, pp. 517-521 (2012).

34. Rahi, T., Baghernejad, M. and Niknam, K. "Silica-bonded *N*-propyl diethylenetriamine sulfamic acid as a recyclable solid acid catalyst for the synthesis of $\alpha$-aminonitriles", *Chin. J. Catal.*, **33**, pp. 1095-1100 (2012).

## Biographies

**Khodabakhsh Niknam** received a BS Degree in Pure Chemistry in 1993 from Shahid Beheshti University, and MS and PhD degrees in Organic Chemistry from Shiraz University in 1995 and 1999, respectively. He is currently Professor in the Department of Chemistry at the Persian Gulf University, Bushehr, Iran. His research interests include: design and synthesis of solid acid and base catalysts, preparation of nano-catalysts and investigation of catalytic activities in organic reactions, synthesis of heterocyclic compounds.

**Reza Rashidian** received BS and MS degrees in Pure and Organic Chemistry in 2010 and 2012, respectively, from the Persian Gulf University of Bushehr, Iran. His research interests include: synthesis of organic compounds and synthetic methods in organic chemistry. He is also co-author of some publications.

**Abbas Jamali** received a BS degree in Applied Chemistry in 2009 from the University of Birjand, Iran, and an MS degree in Organic Chemistry in 2012 from the Persian Gulf University of Bushehr, Iran. His research interests include: synthesis of organic compounds and synthetic methods in organic chemistry, phytochemical research of algae and marine chemistry. He is also co-author of some publications.