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ARTICLE

TiO_2-nanoparticles as efficient catalysts for the synthesis of pyridine dicarbonitriles

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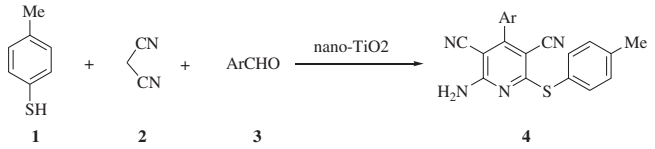
The catalytic effects of two forms of nano-TiO_2, which are prepared via an ordinary or a magnetized process, are investigated in the synthesis of pyridine dicarbonitriles by one-pot multicomponent reaction of 4-methyl thiophenol, malononitrile, and aryl aldehydes. The results have shown that both prepared nano-TiO_2 exhibited high catalytic activities toward the synthesis of pyridine dicarbonitrile derivatives but the nano-TiO_2, which is prepared *via* a magnetized process, has shown better catalytic activity. Furthermore, this new catalytic method for the synthesis of pyridine dicarbonitriles provides rapid access to the desired compounds in high yields and so a simple work-up procedure in the presence of water at room temperature. Therefore, this method represents a significant improvement incompatible of the other methods that are available for the synthesis of pyridine dicarbonitriles.

KEYWORDS
fast synthesis, multicomponent reaction, nano-TiO_2, pyridine dicarbonitriles

1 | INTRODUCTION

Among the nitrogen-containing heterocycles, densely substituted pyridine derivatives are one of the most important classes of compounds as they widely occur as key structural subunits in numerous natural products that exhibit many interesting biological activities.[1] In addition, these heterocyclic compounds have found a variety of applications in medicinal and pharmaceutical sciences.[2] Among these pyridine derivatives, 2-amino-6-(arylthio)pyridine-3,-5-dicarbonitrile is a privileged scaffold for developing pharmaceutical agents because various compounds with this structural motif display significant and diverse biological activities. For example, adenosine receptors are associated with Parkinson's disease, hypoxia, asthma, epilepsy, cancer, and cardiovascular diseases.[3] These pyridine compounds have been shown to be active inhibitors of the adenosine receptors and, therefore, can be used for treating these diseases.[3] They are also inhibitors of cholinesterases and may be used for treating neurodegenerative diseases. These compounds have also been studied as potential anti-HBV, antibacterial, antibiofilm, and anti-infective agents and as potassium channel openers with applications in treating urinary incontinence. Moreover, some of these derivatives also inhibit prion replication and may be used for treating Creutzfeldt–Jacob disease.[4] Many synthetic protocols were developed to accelerate the rate of pyridine dicarbonitrile reaction and to improve the yield. These compounds have been synthesized in the presence of various catalyst such as Et_3N,[5] IBX,[6] DABCO,[7] K_2CO_3,[8] KOH,[9] MS 4A,[10] Nano-CuI,[11] Nano-MgO,[12] and have been utilized in the construction of the pyridine dicarbonitriles. Major drawbacks of these procedures include expensive reagents, use of large amounts of organic solvents, and prolonged heating and side reactions. In recent years, economic and environmental concerns encourage the application of heterogeneous



SCHEME 1 Synthesis of pyridine dicarbonitriles catalyzed by nano-TiO_2

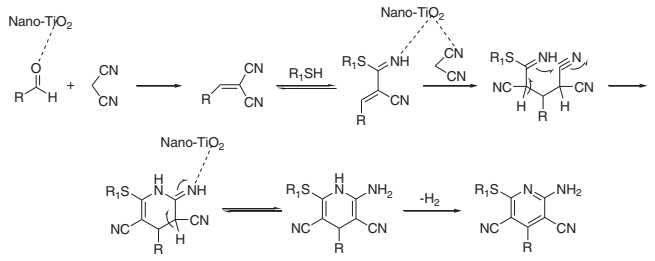
catalysts to carry out various organic transformations.[13] These catalysts have very high catalytic activities due to their large specific surface area and make the processes clean, safe, high-yielding, and inexpensive.[14] Nowadays, application of magnetic nanocomposites as heterogeneous catalysts is an interesting research area. The surface functionalization of these materials is an elegant way to bridge the gap between heterogeneous and homogeneous catalyses.[15]

As a part of our research in developing efficient methods of organic synthesis that involve reusable catalysts, we studied application of nano-TiO_2 prepared *via* an ordinary or a magnetized process as an efficient acid catalyst in the synthesis of pyridine dicarbonitrile derivatives by the reaction of thiophenol **1**, malononitrile **2**, and aryl aldehydes **3**. Nano-TiO_2 could be removed from the reaction mixture through filtration and reused several times. However, there were no reports on application of FGOSA as an acidic heterogeneous catalyst in the synthesis of pyridine dicarbonitriles (Scheme 1).

2 | RESULTS AND DISCUSSION

In this study, nano-TiO_2 structures were prepared via ordinary or magnetized processes. In both pathways, TiO_2nanostructures were synthesized using a hydrothermal process. In the magnetized process, NaOH was obtained from magnetized water. The model of water magnetization is discussed in the experimental section. The SEM image of the prepared nano-TiO_2 *via* an ordinary process is shown in Figure 1. The average size of TiO_2 nanoparticles is about 38 nm and they are exactly distinguishable from each other.

Figure 2 shows SEM images of the prepared TiO_2 via a magnetized process. In this pathway, water was magnetized



SCHEME 2 Mechanism for the synthesis of pyridine dicarbonitriles

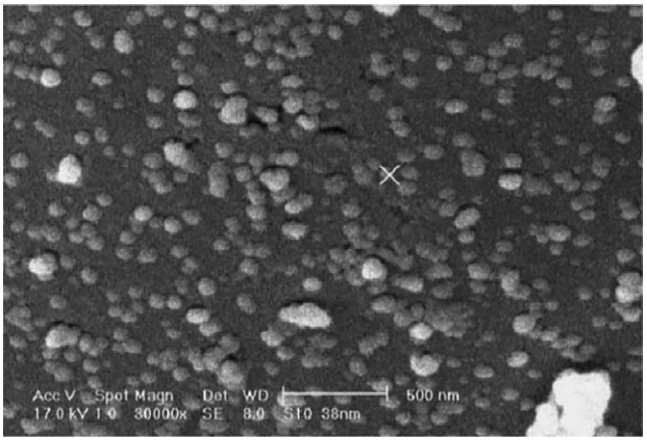


FIGURE 1 SEM image of prepared nano-TiO_2 *via* ordinary process

for **1h** and then utilized for the preparation of NaOH. Subsequently, the obtained sodium hydroxide was applied for the synthesis of nano-TiO_2 via a hydrothermal method. The hydrothermal process is discussed in the experimental. Interestingly, when water is magnetized, the morphology of final prepared samples is totally different. Therefore, it is clear that the property of water changed by applying the permanent magnetic field (0.6Tesla or 6,000 Guass) and the properties are reserved at least for 48 hr even at high temperature and pressure.

2.1 | Catalytic activity of TiO_2 nanostructures prepared via magnetized process in the synthesis of pyridine dicarbonitrile derivatives

The catalytic activity of this material was evaluated in the synthesis of pyridine dicarbonitrile derivatives. Synthesis of compound **4b** was selected as a model reaction for optimizing the reaction conditions. The reaction was carried out with 4-methyl thiophenol **1**, malononitrile **2**, and 4-chlorobenzaldehyde **3b** in the presence of different amounts of catalysts and in various solvents and also under solvent-free conditions (Table 1). Long reaction times and poor yields of the product **4b** were obtained in the absence of the catalyst in all cases (entries 1–5). Also, low yields of the desired product were obtained under solvent-free conditions in the presence or absence of the catalyst (entries 4–6). The presence of temperature was necessary for all situations. Therefore, the best results were reached under catalytic conditions upon refluxing solvents, preferably ethanol (entries 12–16). According to the final outcomes, the reaction was more facile and proceeded to give the highest yield (97%), and a short reaction time (14 min), using 0.06 g of the catalyst in ethanol (5 mL) at reflux temperature (entry 12). An increase of the catalyst amount up to 0.08 g did not improve the product yield or shorten the reaction time (entry 12).

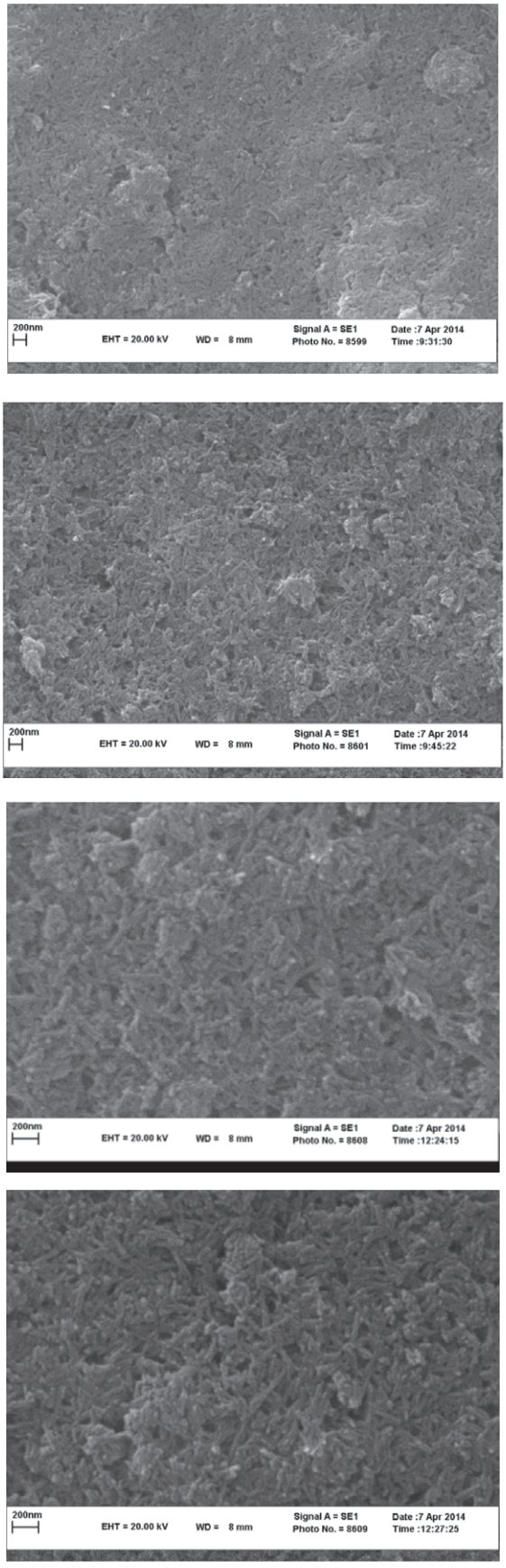


FIGURE 2 The SEM images of prepared nano-TiO_2 *via* magnetized process

TABLE 1 Optimization of reaction conditions for the synthesis of compound **4b** catalyzed by nano-TiO_2prepared via magnetized process[a]

Entry	Catalyst (g)	Solvent	T/°C	Time/min	Isolated yield/%
1	—	H_2O	Reflux	135	32
2	—	EtOH	Reflux	135	44
3	—	EtOH	r.t.	180	34
4	—	—	100	150	16
5	—	—	120	150	19
6	0.06	—	120	100	31
7	0.02	EtOH	Reflux	60	76
8	0.04	EtOH	Reflux	40	88
9	0.06	EtOH	80	45	89
10	0.06	EtOH	r.t.	30	78
11	0.08	EtOH	Reflux	20	96
12	**0.06**	**EtOH**	**Reflux**	**14**	**97**
13	0.06	H_2O	Reflux	25	83
14	0.06	MeOH	Reflux	40	63
15	0.06	CH_3CN	Reflux	50	51
16	0.06	CH_2Cl_2	Reflux	60	41

[a]Reaction conditions: 4-methyl thiophenol **1**, malononitrile **2**, and 4-chlorobenzaldehyde **3b** (1.5 mmol).

Catalytic effects of the both prepared TiO_2 were evaluated in the synthesis of pyridine dicarbonitrile derivatives under optimized conditions. According to the optimization experiments, both nanocatalysts involved demonstrated good catalytic effects in the model reaction but the nano-TiO_2 catalyst prepared via magnetized process promoted the reaction more efficiently than the other, leading to higher yields of products **4** in a shorter reaction time (Table 2).

TABLE 2 Synthesis of pyridine dicarbonitriles with different aldehydes[a]

Entry	Ar	Product	Time (min)		Yield (%)	
			TiO_2[b]	TiO_2[c]	TiO_2[b]	TiO_2[c]
1	C_6H_5	**4a**	28	20	87	93
2	4-Cl-C_6H_4	**4b**	21	14	91	97
3	3-Cl-C_6H_4	**4c**	32	21	89	95
4	4-Br-C_6H_4	**4d**	33	23	88	90
5	3-Br-C_6H_4	**4e**	27	19	85	89
6	3-NO_2-C_6H_4	**4f**	37	24	89	93
7	4-NO_2-C_6H_4	**4g**	31	26	90	94
8	4-CH_3O-C_6H_4	**4h**	36	27	87	94

[a]Reaction conditions: 4-methyl thiophenol, malononitrile, and aryl aldehydes, and TiO_2(0.06 g) in refluxing water.
[b]TiO_2 prepared via ordinary process.
[c]TiO_2 prepared via magnetized process.

Probably, the catalyst could act as a Lewis acid and, therefore, promote the reactions. The catalyst would play a significant role in increasing the electrophilic character of the electrophiles in the reaction (Scheme 2).

3 | CONCLUSIONS

In this article, we synthesized pyridine dicarbonitrile derivatives in the presence of nano-TiO_2 via an ordinary or a magnetized process as highly effective heterogeneous catalysts. This method provided these products in high yields over a short reaction time in both the forms of nano-TiO_2, but the nano-TiO_2 prepared *via* magnetized process showed better yields in the shorter reaction times. Also, the catalyst was inexpensive and easily obtainable, stable, and storable.

4 | EXPERIMENTAL

All products were characterized by m.p., IR, ^{1}H NMR, and GC/MS. Melting points were measured by using the capillary tube method with an electro thermal 9,200 apparatus. ^{1}H and ^{13}CNMR spectra were recorded on a Bruker DRX Avance spectrometer at 300 and 75 MHz, respectively, with CDCl3 as solvent. IR spectra were recorded from KBr disk on the FT-IR Bruker Tensor 27. GC/MS spectra were recorded on an Agilent Technologies 6,890 network GC system and an Agilent 5,973 network Mass selective detector. Thin layer chromatography (TLC) on commercial aluminum-backed plates of silica gel, 60 F254 was used to monitor the progress of reactions. All products were characterized by spectra and physical data.

4.1 | Solvent-magnetizing apparatus

The permanent magnet in a compact form, a unit called "AQUA CORRECT," was used. This equipment is a coaxial static magnetic system with field strength of 0.6 Tor 6,000 G (H.P.S Co., Germany). The equipment was connected from one end to the liquid pump and the other end to the pipelines of the solvent reservoir. Solutions flow through a coaxial static magnetic field and came back to the solvent reservoir.[16,17] Therefore, solution could pass through the field many times, in a closed cycle (Figure 3).

4.2 | Synthesis of nano-TiO_2 *via* magnetized process

Hydrothermal method is a very simple and common method. In this method, TiO_2 powder is first released in sodium hydroxide that was prepared by magnetized water and then it is mixed. The prepared solution is placed inside the autoclave and the reaction takes place at constant temperature in a given time. In this part of the process (transmission and heat), there are some parameters that affect Nanotube properties including the particle size and primary powder shape, molarity of potassium hydroxide solution (in the range 5–15 mol), the ratio of TiO_2 in gram to potassium solution in milliliter (in the range 0.25–20 g in 300 mL), reaction temperature (in the range 110–160°C), duration of reaction time (20–110 hr). The effect of these parameters has been studied in various resources.[18,19] After the completion of reaction, the solution should be allowed to cool slowly to room temperature. Then, the white precipitate is removed from the solution and washed with distilled water so that the solution reaches pH = 7. After this phase, it is washed with sulfuric acid (0.05 M) and distilled water, respectively. The resulting wet powder is dried under vacuum (50–80°C), though in some articles drying is performed under atmospheric pressure.[20] In this regard, the effect of atmospheric drying on nanotube properties has not been studied yet.

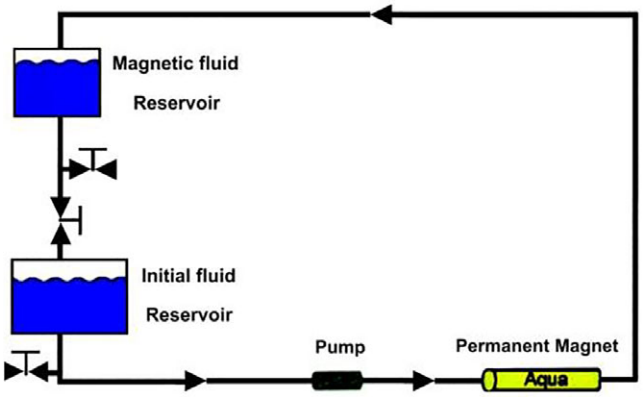


FIGURE 3 The model of solvent-magnetizing apparatus (SMA)

4.3 | Typical procedure for the preparation of pyridine dicarbonitriles

To a magnetically stirred solution of aldehyde (1 mmol), 4-methyl thiophenol (1 mmol), malononitrile (2 mmol), and nano-TiO2 (5 mol%) in ethanol (5 mL) were added and stirring was continued for appropriate time. The reaction was monitored by TLC. Upon completion of the transformation, the catalyst was filtered under hot conditions. The catalyst was washed with a small portion of hot ethanol. After cooling, the combined filtrate was allowed to stand at room temperature. The precipitated solid was collected by filtration, and recrystallized from ethanol to give a desired compound in high yields.

4.3.1 | 3-amino-5-(p-tolylthio)-[1,1′-biphenyl]-2,6-dicarbonitrile (4a)

IR (KBr) (ν_{max}/cm^{-1}): 3,432, 3,374, 3,073, 2,922, 2,231, 1,621, 1,585, 1,456, 1,073, and 723; ^{1}H NMR (DMSO, 300 MHz) (δ, ppm): 2.38 (s, 3H, CH_3), 7.32 (d, J = 7.1 Hz, 2H, aromatic H), 7.33–7.55 (m, 5H, aromatic H), 7.57 (d, J = 7.3 Hz, 2H, aromatic H), 7.60 (s, 1H, aromatic H), and 7.76 (br., s, 2H, NH_2); ^{13}C NMR (DMSO, 75 MHz) (δ, ppm): 167.51, 161.12, 159.31, 141.23, 135.54, 134.63, 135.21, 133.89, 130.11,129.54, 128.89, 124.37, 116.58, 115.87, 95.21, 86.25, and 22.48; GC/MS: 341 (M^+).

4.3.2 | 3-amino-4′-chloro-5-(p-tolylthio)-[1,1′-biphenyl]-2,6-dicarbonitrile (4b)

IR (KBr) (ν_{max}/cm^{-1}): 3,421, 3,374, 3,101, 2,965, 2,219, 1,647, 1,585, 1,421, 1,225, and 852; ^{1}H NMR ($CDCl_3$, 300 MHz) (δ, ppm): 2.39 (s, 3H, CH_3), 7.28 (d, J = 6.9 Hz, 2H, aromatic H), 7.30–7.40(m, 2H, aromatic H), 7.43-7.60 (m, 4H, aromatic H), and 7.79 (br., s, 2H, NH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) (δ, ppm): 170.21, 160.23, 159.21, 142.32, 137.23, 136.54, 132.65, 130.30, 130.01,129.11, 122.99, 116.32, 115.54, 97.01, 87.63, and 23.29; GC/MS: 375 (M^+).

4.3.3 | 3-amino-3′-chloro-5-(p-tolylthio)-[1,1′-biphenyl]-2,6-dicarbonitrile (4c)

IR (KBr) (ν_{max}/cm^{-1}): 3456, 3,372, 3,099, 2,903, 2,221, 1,671, 1,559, 1,486, 1,001, and 803; ^{1}H NMR ($CDCl_3$, 300 MHz) (δ, ppm): 2.47 (s, 3H, CH_3), 7.32 (t, J = 7.1 Hz, 2H, aromatic H), 7.38 (d, J = 7.3 Hz, 2H, aromatic H), 7.40–7.55 (m, 4H, aromatic H), 7.57 (s, 1H, aromatic H), and 7.80 (br., s, 2H, NH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) (δ, ppm): 169.89, 159.21, 157.92, 143.13, 142.03, 139.28, 136.67, 135.09, 132.54,130.98, 130.85, 128.62, 125.81, 116.52, 115.11, 96.11, 88.23, and 22.13; GC/MS: 375 (M^+).

4.3.4 | 3-amino-4′-bromo-5-(p-tolylthio)-[1,1′-biphenyl]-2,6-dicarbonitrile (4d)

IR (KBr) (ν_{max}/cm^{-1}): 3,441, 3,336, 3,122, 3,962, 2,231, 1,628, 1,571, 1,560, 1,006, and 811; ^{1}H NMR (DMSO, 300 MHz) (δ, ppm): 2.35 (s, 3H, CH_3), 7.30-7.70 (m, 6H, aromatic H), 7.75 (s, 1H, aromatic H), 7.79 (d, J = 7.1 Hz, 2H, aromatic H), and 7.83 (br., s, 2H, NH_2); ^{13}C NMR (DMSO, 75 MHz) (δ, ppm): 167.65, 161.58, 158.41, 141.52, 135.82, 134.14, 133.03, 132.69, 131.26,125.45, 124.65, 117.01, 115.21, 93.96, 88.11, and 22.07; GC/MS: 420 (M^+).

4.3.5 | 3-amino-3′-bromo-5-(p-tolylthio)-[1,1′-biphenyl]-2,6-dicarbonitrile (4e)

IR (KBr) (ν_{max}/cm^{-1}): 3,441, 3,326, 3,025, 2,998, 2,231, 1,678, 1,589, 1,521, 1,229, 998, and 796; ^{1}H NMR (DMSO, 300 MHz) (δ, ppm): 2.37 (s, 3H, CH_3), 7.31 (d, J = 6.9 Hz, 2H, aromatic H), 7.35–7.75 (m, 7H, aromatic H), and 7.81 (br, s, 2H, NH_2); ^{13}C NMR (DMSO, 75 MHz) (δ, ppm): 167.56, 162.25, 158.58, 142.20, 140.99, 138.55, 135.89, 134.11, 133.22,131.78, 130.41, 125.25, 124.31, 116.28, 115.66, 94.52, 87.66, and 20.73; GC/MS: 420 (M^+).

4.3.6 | 3-amino-3′-nitro-5-(p-tolylthio)-[1,1′-biphenyl]-2,6-dicarbonitrile (4f)

IR (KBr) (ν_{max}/cm^{-1}): 3,413, 3,258, 3,023, 2,969, 2,245, 1,639, 1,528, 1,468, 1,247, 985, and 729; ^{1}H NMR (DMSO, 300 MHz) (δ, ppm): 2.79 (s, 3H, CH_3), 7.33 (d, J = 7.3 Hz, 2H, aromatic H), 7.47 (d, J = 7.3 Hz, 2H, aromatic H), 7.61 (s, 1H, aromatic H), 7.66 (m, 1H, aromatic H), 7.68 (d, J = 7.1 Hz, 1H, aromatic H), 7.69–7.78 (m, 2H, aromatic H), and 8.13 (br., s, 2H, NH_2); ^{13}C NMR (DMSO, 75 MHz) (δ, ppm): 166.33, 159.52, 158.12, 141.23, 137.48, 136.20, 135.41, 133.77, 132.71, 131.01, 129.66, 128.21, 126.27, 116.89, 114.22, 95.21, 88.01, and 23.11; GC/MS: 386 (M^+).

4.3.7 | 3-amino-4′-nitro-5-(p-tolylthio)-[1,1′-biphenyl]-2,6-dicarbonitrile (4g)

IR (KBr) (ν_{max}/cm^{-1}): 3,503, 3,458, 3,058, 2,968, 2,214, 1,652, 1,565, 1,497, 1,341, 1,254, 1,037, and 789; ^{1}H NMR (DMSO,300 MHz) (δ, ppm): 2.26 (s, 3H, CH_3), 7.36 (d, J = 7.1 Hz, 2H, aromatic H), 7.39 (d, J = 7.1 Hz, 2H, aromatic H), 7.40–7.75 (m, 5H, aromatic H), and 8.31 (br, s, 2H); ^{13}C NMR (DMSO, 75 MHz) (δ, ppm):165.73, 160.71, 158.21, 137.72, 136.01, 134.92, 132.21, 130.42,129.33, 128.52, 126.21, 116.31, 114.71, 91.95, 88.27, and 24.10; GC/MS: 386 (M^+).

4.3.8 | 3-amino-4′-methoxy-5-(p-tolylthio)-[1,1′-biphenyl]-2,6-dicarbonitrile (4h)

IR (KBr) (ν_{max}/cm^{-1}): 3,468, 3,329, 3,029, 2,909, 2,215, 1,667, 1,559, 1,545, 1,459, 1,371, 1,073, and 868; ^{1}H NMR ($CDCl_3$, 300 MHz) (δ, ppm): 2.37 (s, 3H, CH_3), 3.91 (s, 3H, OCH_3), 7.10–7.20 (m, 4H, aromatic H), 7.34 (d, J = 7.2 Hz, 2H, aromatic H), 7.56 (s, 1H, aromatic H), 7.66 (d, J = 7.2 Hz, 2H, aromatic H), and 7.72 (br., s, 2H, NH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) (δ, ppm): 167.51, 161.42, 159.72,142.21, 136.61, 133.20, 132.06, 131.13, 127.33, 125.03, 122.62, 115.33, 113.42, 93.66, 88.63, and 22.33; GC/MS: 371 (M^+).

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REFERENCES

[1] A. Davoodnia, A. Nakhaei, *Synth. React. Inorg. M.* **2016**, *46*, 1073.
[2] S. Yadegarian, A. Davoodnia, A. Nakhaei, *Orient. J. Chem.* **2015**, *31*, 573.
[3] L. C. Chang, R. F. Spanjersberg, J. K. von Frijtag Drabbe Künzel, T. Mulder-Krieger, G. van den Hout, M. W. Beukers, J. Brussee, A. P. IJzerman, *J. Med. Chem.* **2004**, *47*, 6529.
[4] L. Garuti, M. Roberti, D. Pizzirani, *Mini Rev. Med. Chem.* **2007**, *7*, 481.
[5] N. M. Evdokimov, A. S. Kireev, A. A. Yakovenko, M. Y. Antipin, I. V. Magedov, A. Kornienko, *J. Org. Chem.* **2007**, *72*, 3443.
[6] S. Takale, J. Patil, V. Padalkar, R. Pisal, A. Chaskar, *J. Braz. Chem. Soc.* **2012**, *23*, 966.
[7] N. M. Evdokimov, I. V. Magedov, A. S. Kireev, A. Kornienko, *Org. Lett.* **2006**, *8*, 899.
[8] S. Mishra, R. Ghosh, *Synth. Commun.* **2012**, *42*, 2229.
[9] M. N. Khan, S. Pal, T. Parvin, L. H. Choudhury, *RSC Adv.* **2012**, *2*, 12305.
[10] P. V. Shinde, V. B. Labade, B. B. Shingate, M. S. Shingare, *J. Mol. Catal. A Chem.* **2011**, *336*, 100.
[11] J. Safaei-Ghomi, M. A. Ghasemzadeh, *J. Sulfur Chem.* **2013**, *34*, 233.
[12] M. Lakshmi Kantam, K. Mahendar, S. Bhargava, *J. Chem. Sci.* **2010**, *122*, 63.
[13] I. W. Davies, L. Matty, D. L. Hughes, P. J. Reider, *J. Am. Chem. Soc.* **2001**, *123*, 10139.
[14] M. Ledoux, C. Pham-Huu, *Catal. Today* **1992**, *15*, 263.
[15] C. S. Gill, B. A. Price, C. W. Jones, *J. Catal.* **2007**, *251*, 145.
[16] Z. Eshaghi, M. Gholizadeh, *Talanta* **2004**, *64*, 558.
[17] E. Esmaeilnezhad, H. J. Choi, M. Schaffie, M. Gholizadeh, M. Ranjbar, *J. Clean. Prod.* **2017**, *161*, 908.
[18] T. R. Reddy, R. Mutter, W. Heal, K. Guo, V. J. Gillet, S. Pratt, B. Chen, *J. Med. Chem.* **2006**, *49*, 607.
[19] M. D. Fletcher, T. E. Hurst, T. J. Miles, C. J. Moody, *Tetrahedron* **2006**, *62*, 5454.
[20] A. V. Rao, E. Nilsen, M.-A. Einarsrud, *J. Non-Cryst. Solids* **2001**, *296*, 165.

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