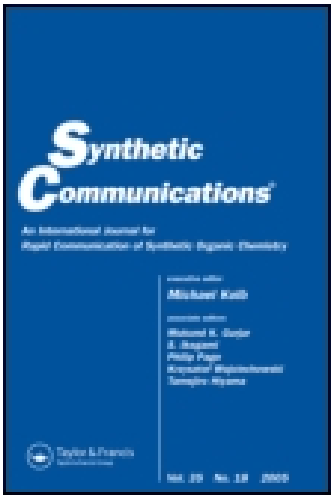

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Synthesis of 6-Amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles Catalyzed by Silica-Supported Tetramethylguanidine Under Solvent-Free Conditions

Amol B. Atar [a] , Jong Tae Kim [a] , Kwon Taek Lim [a] & Yeon Tae Jeong [a]
[a] Department of Image Science and Engineering , Pukyong National University , Busan , Korea
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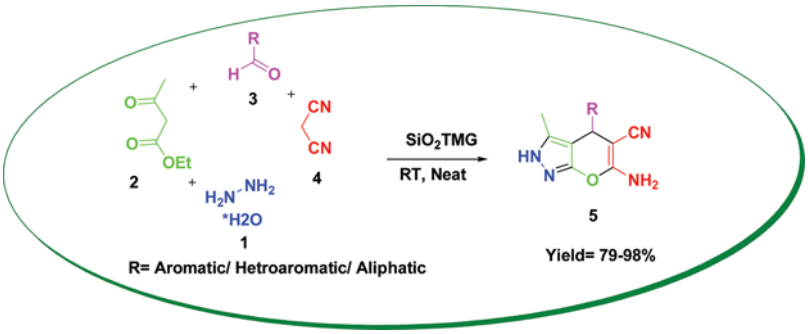
DOI: 10.1080/00397911.2014.913634

SYNTHESIS OF 6-AMINO-2,4-DIHYDROPYRANO-[2,3-*c*]PYRAZOL-5-CARBONITRILES CATALYZED BY SILICA-SUPPORTED TETRAMETHYLGUANIDINE UNDER SOLVENT-FREE CONDITIONS

Amol B. Atar, Jong Tae Kim, Kwon Taek Lim, and Yeon Tae Jeong

Department of Image Science and Engineering, Pukyong National University, Busan, Korea

GRAPHICAL ABSTRACT



Abstract *An efficient, high-yielding, and rapid protocol has been developed for the synthesis of diversity-oriented 6-amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles derivatives via a four-component, one-pot cyclocondensation reaction of ethyl acetoacetate, hydrazine hydrate, aldehydes, and malononitrile using silica-supported tetramethylguanidine as a heterogeneous catalyst for the first time. The protocol proves to be efficient and environmentally benign in terms of very easy workup, good yields, and ease of recovery of catalyst. In addition, the present method is superior in terms of green media, the amount of catalyst, and reaction time.*

Keywords Four-component reaction; heterogeneous catalyst; pyrano[2,3-c]pyrazole; silica-supported tetramethylguanidine

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Address correspondence to Yeon Tae Jeong, Department of Image Science and Engineering, Pukyong National University, Busan 608-737, Korea. E-mail: ytjeong@pknu.ac.kr

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INTRODUCTION

Pyrano[2,3-c]pyrazole derivatives are building blocks with a broad range of biological activities such as antimicrobial,[1] insecticidal,[2] and anti-inflammatory[3] activites. Furthermore, compounds containing pyrano[2,3-c]pyrazole moiety have been reported to exhibit enzyme inhibitiory,[4] anticancer,[5] and antifungal[6] activity apart from being significant intermediates for the construction of complex heterocycles.[7] The pharmaceutical importance of pyrano[2,3-c]pyrazole and their utilization in organic transformations has directed great research activity toward the construction of the skeletons of different kinds of heterocycles.[8] As a result of their biological and synthetic importance, a number of synthetic methods for the preparation of 6-amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles have been developed for the reaction of ethylacetoacetate, hydrazine hydrate, aldehyde, and malononitrile in the presence of different catalysts.[9–22] However, some of these procedures have certain limitations, such as prolonged reaction time, the use of toxic solvents, or poor yields. The recovery and reusability of the catalyst is also a problem. Therefore, it is still desirable to seek a green and ecofriendly protocol that uses a highly efficient and reusable catalyst for the preparation of 6-amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles.

Recently, heterogeneous catalysts have been highly acknowledged for the sustainable development of any catalytic process because of their easy recovery, recyclability, minimization of undesired toxic wastes, and E factor.[23] The usage of heterogeneous metal Lewis acid catalyst instead of traditional homogeneous metal Lewis and Brønsted acid catalysts could be a more environmentally friendly alternative. The problems usually connected with the homogeneous catalysts can be easily overcome by heterogenization of a homogeneous counterpart onto insoluble inorganic or organic solid support in which active components are strongly immobilized.[24] Solid catalysts provide numerous opportunities for recovering and recycling catalysts from reaction environments. Among the various heterogeneous catalysts, particularly, silica-supported tetramethylguanidine has the advantages of low cost, ease of preparation, environmental friendliness, high efficiency, and catalyst recyclability (Fig. 1).

It is evident from the previous literature that silica-supported tetramethylguanidine has generated enormous interest as a green and a potential solid catalyst to construct carbon–carbon and carbon–heteroatom bonds in various organic transformations.[25,26] Considering these subjects and based on our previous endeavors in exploring novel and practical multicomponent reactions to synthesize useful

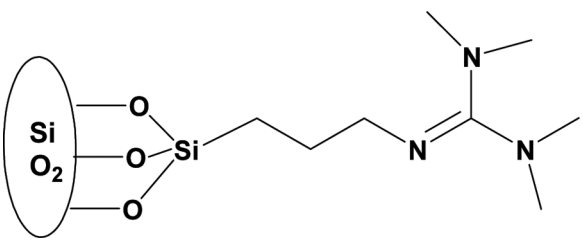
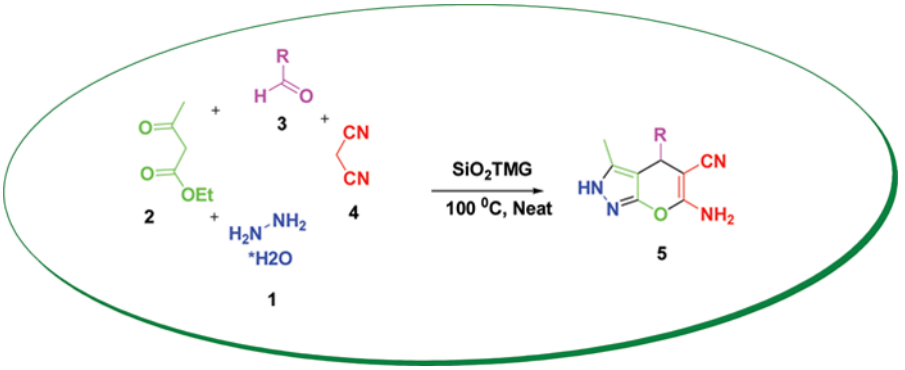


Figure 1. Silica-supported tetramethylguanidine.



Scheme 1. Synthesis of 6-amino-4-alkyl/aryl-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-carbonitriles catalyzed by SiO_2TMG under neat conditions.

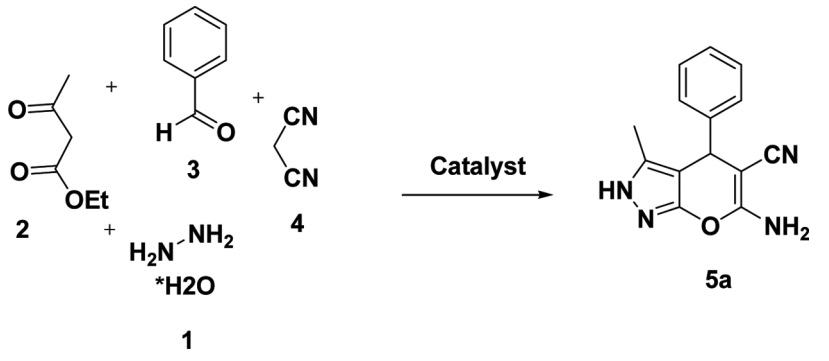
heterocyclic compounds,[27–30] we decided to investigate efficiency of silica-supported tetramethylguanidine catalyst for the synthesis of 6-amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles. Herein we report a tandem synthesis of 6-amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles derivatives from ethyl acetoacetate, hydrazine hydrate, aldehydes, and malononitrile using silica-supported tetramethylguanidine as expeditious reusable catalyst in an excellent yield (Scheme 1).

RESULTS AND DISCUSSION

The studies were initiated to optimize the reaction conditions for a model reaction of hydrazine hydrate **1**, ethyl acetoacetate **2**, benzaldehyde **3a**, and malononitrile **4** in the presence of different catalysts and solvents (Table 1). To establish the real effectiveness of the catalyst for the synthesis of 6-amino-3-methyl-4-(3-phenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile, a test reaction was performed without catalyst using hydrazine hydrate **1**, ethyl acetoacetate **2**, benzaldehyde **3a**, and malononitrile **4** in ethanol at reflux. It was found that only 10% yield of product was obtained in the absence of catalyst even after 6 h (Table 1, entry 1). To develop a viable approach, the model reaction was investigated by employing different heterogeneous catalysts such as SiO_2, $BF_3 \cdot SiO_2$, $Zn(OTf)_2 \cdot SiO_2$, $ZnCl_2 \cdot SiO_2$, $TiO_2 \cdot SiO_2$, SiO_2TMG, and $FeCl_3 \cdot SiO_2$. Among all screened catalysts SiO_2TMG gave the best result in view of yield and reaction time (Table 1, entry 9). In contrast, SiO_2, $BF_3 \cdot SiO_2$, $Zn(OTf)_2 \cdot SiO_2$, $ZnCl_2 \cdot SiO_2$, $TiO_2 \cdot SiO_2$, and $FeCl_3 \cdot SiO_2$ did not afford the desired product in good yields (Table 1, entries 2–6 and 8).

To see the effect of solvent, we screened different solvents such as EtOH, acetonitrile, methanol, and water at reflux. It was observed that under solvent conditions the reactions required longer times (2–4 h) to afford comparable yields (Table 1, entries 7 and 10–12). When the reaction was performed under solvent-free conditions, good yield of target product was obtained (Table 1, entry 9). Moreover, we found that the yields were obviously affected by the amount of SiO_2TMG loaded. When 5, 10, 15, and 20 mol% of SiO_2TMG were used, the yields were 81%, 96%, 95%, and 92%, respectively (Table 1, entries 9 and 13–15). Therefore, 10 mol% of SiO_2TMG was sufficient and optimal quantity for the completion of the reaction.

Table 1. Optimization[a] of promoters, solvents, and temperature in the synthesis of **5a**



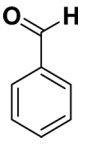
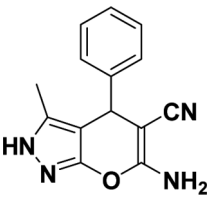
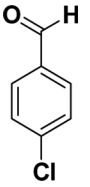
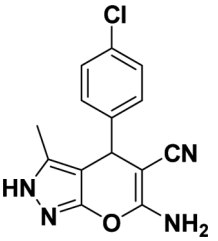
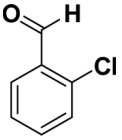
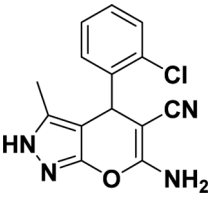
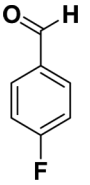
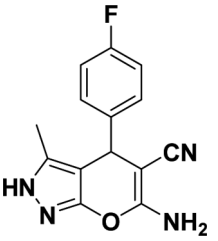
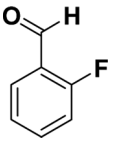
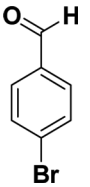
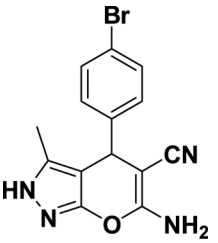
No.	Catalyst (10 mol%)	Solvent	Condition	Time	Yield[b] (%)
1	—	Ethanol	Reflux	6 h	10
2	SiO_2	Neat	100 °C	4 h	38
3	$BF_3 \cdot SiO_2$	Ethanol	Reflux	5 h	45
4	$Zn(OTf)_2 \cdot SiO_2$	Water	100 °C	6 h	51
5	$ZnCl_2.SiO_2$	Neat	100 °C	8 h	56
6	$TiO_2 \cdot SiO_2$	ACN	80 °C	10 h	48
7	SiO_2TMG	Ethanol	Reflux	2 h	85
8	$FeCl_3 \cdot SiO_2$	Neat	80 °C	4 h	60
9	SiO_2TMG	Neat	100 °C	30 min	96
10	SiO_2TMG	Water	100 °C	2 h	85
11	SiO_2TMG	ACN	Reflux	3 h	78
12	SiO_2TMG	Methanol	Reflux	4 h	82
13	SiO_2TMG (5 mol%)	Neat	100 °C	1 h	81
14	SiO_2TMG (15 mol%)	Neat	100 °C	30 min	95
15	SiO_2TMG (20 mol%)	Neat	100 °C	30 min	92

[a]Reaction conditions: hydrazine hydrate (1.5 mmol), ethyl acetoacetate (1 mmol), benzaldehyde (1 mmol), malononitrile (1 mmol), and catalyst (10 mol%, except entries 13, 14, and 15).
[b]Isolated yield.

Encouraged by the general interest of this convergent and experimentally simple transformation, we then evaluated its scope and efficiency in the generation of 6-amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles arrays by recourse to a diverse range of several substituted aryl/aliphatic aldehydes. It was gratifying to observe that most of the tested substrates exhibited satisfactory reactivity profiles, in all cases leading to a smooth heterocyclization sequence that readily afforded the target structures (Table 2). Compared with aromatic aldehydes, aliphatic aldehyde afforded relatively lower yields of the corresponding 6-Amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles. A possible mechanism of this one-pot reaction is expected on the basis of reported literature[15] (Scheme 2).

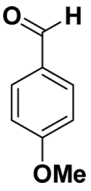
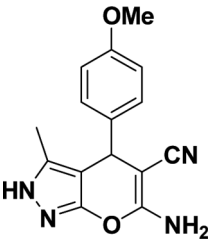
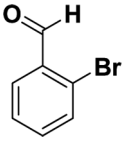
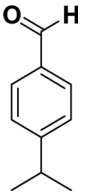
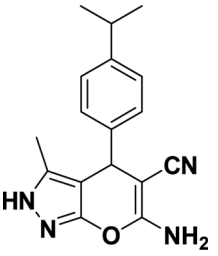
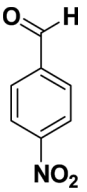
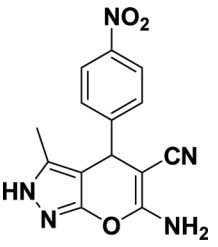
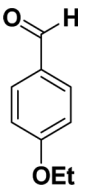
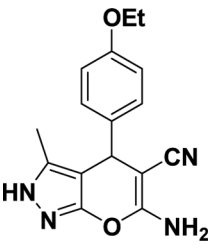
The probable mechanism for the formation of 6-amino-2,4-dihydropyrano-[2,3-c]pyrazol-5-carbonitriles using SiO_2TMG as a catalyst is outlined in Scheme 2. The condensation of C=O and NH_2 on the ethyl acetoacetate and hydrazine hydrate and the subsequent loss of ethanol occurred via intramolecular nucleophilic

Table 2. Synthesis[a] of 6-amino-4-alkyl/aryl-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-carbonitriles

No.	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C) [Ref.]
5a			30	96	245–246[13]
5b			20	98	233–234[13]
5c			30	95	147–148[13]
5d			20	96	244–245[19]
5e			30	95	260–262[19]
5f			20	95	179–180[13]

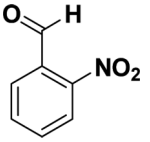
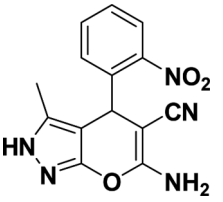
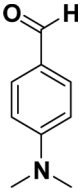
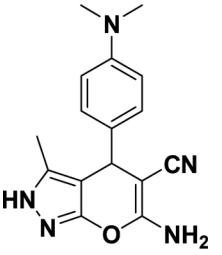
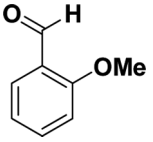
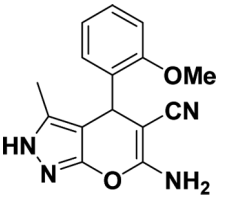
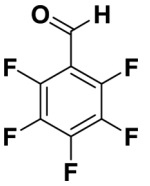
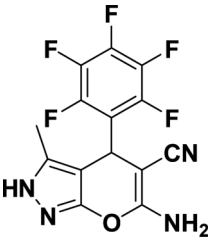
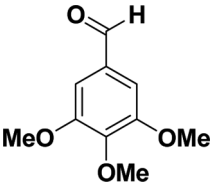
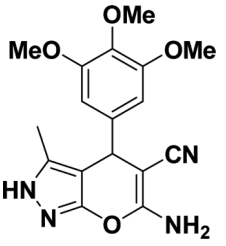
(*Continued*)

Table 2. Continued

No.	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C) [Ref.]
5g			40	92	211–212[13]
5h			35	91	247–248[21]
5i			45	89	182–183[15]
5j			20	98	250–251[13]
5k			55	90	189–190[–]

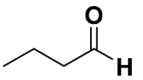
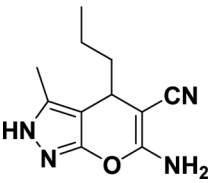
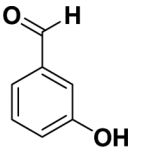
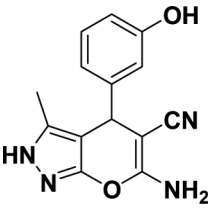
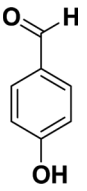
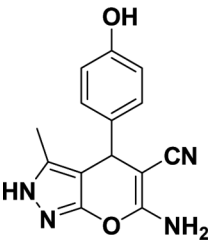
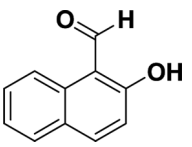
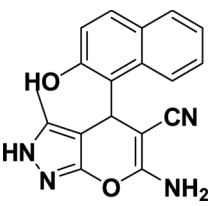
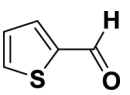
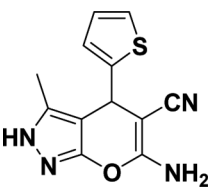
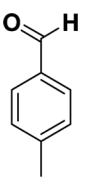
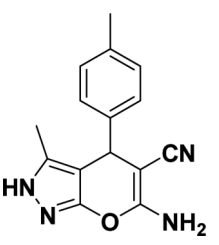
(*Continued*)

Table 2. Continued

No.	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C) [Ref.]
5l			25	93	221–222[13]
5m			40	90	168–169[21]
5n			35	88	250–252[19]
5o			15	98	248–249[22]
5p			45	90	210–211[13]

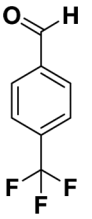
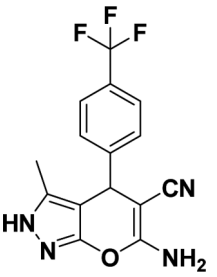
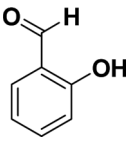
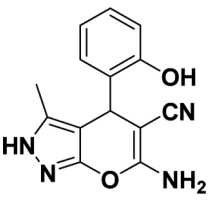
(*Continued*)

Table 2. Continued

No.	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C) [Ref.]
5q			60	79	143–144[12]
5r			35	92	259–260[21]
5s			30	93	225–226[13]
5t			55	85	248–250[–]
5u			40	85	190–191[21]
5v			35	87	175–176[13]

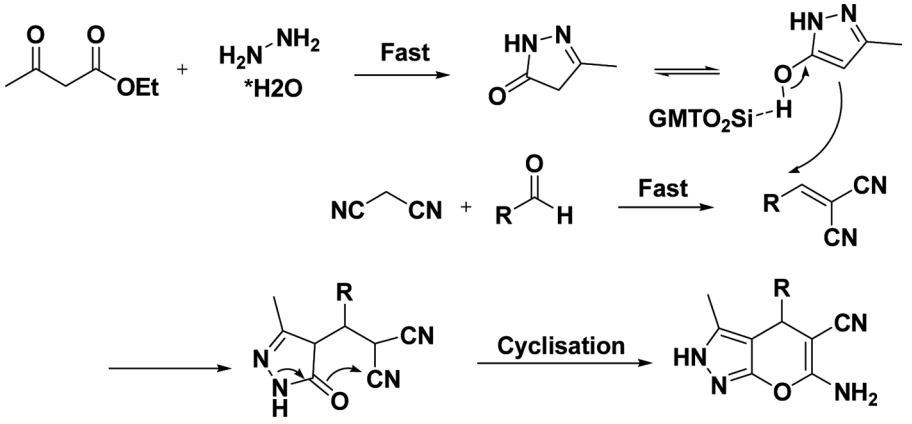
(*Continued*)

Table 2. Continued

No.	Aldehyde	Product	Time (min)	Yield[b] (%)	Mp (°C) [Ref.]
5w			25	95	244–245[19]
5x			40	90	209–211[15]

[a]Reaction conditions: hydrazine hydrate (1.5 mmol), ethyl acetoacetate (1 mmol), aldehydes (1 mmol), malononitrile (1 mmol), and SiO_2TMG catalyst (10 mol%).
[b]Isolated yield.

substitution to deliver intermediate pyrazole-5-one. Knoevenagel condensation between an malononitrile and aldehyde produced a species that underwent Michael addition with the pyrazole-5-one. Further rearrangement via the subsequent intramolecular nucleophilic attack of OH to CN may have generated the expected target product. The SiO_2TMG catalyst may have facilitated both the condensation reaction and the nucleophilic attack.



Scheme 2. Probable mechanism for the formation of 6-amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles using SiO_2TMG as a catalyst.

Table 3. Comparative study[a] of the efficacy of silica-supported tetramethylguanidine using phenyl hydrazine and hydrazine hydrate

No.	Aldehyde	Time (min)		Yield[b] (%)	
		H_2N-NH_2	Ph-NH-NH_2	H_2N-NH_2	Ph-NH-NH_2
1	p-Bromobenzaldehyde	20	45	95	92
2	p-Methoxybenzaldehyde	40	60	92	88
3	Benzaldehyde	30	55	96	93
4	m-Hydroxybenzaldehyde	35	65	92	90
5	p-Methylbenzaldehyde	35	60	87	88

[a]Reaction conditions: Phenyl hydrazine/hydrazine hydrate (1.5 mmol), ethyl acetoacetate (1 mmol), aldehydes (1 mmol), malononitrile (1 mmol), and SiO_2TMG catalyst (10 mol%).

Table 4. Recycling and reuse of SiO_2TMG

Entry	Reaction cycle	Yield[a] (%)
1	1 (fresh run)	96
2	2	96
3	3	95
4	4	95

[a]Isolated yield.

We also carried out the comparative study of the efficacy of silica-supported tetramethylguanidine between phenyl hydrazine and hydrazine hydrate as shown in Table 3. As compared to hydrazine hydate, phenyl hydrazine take more time for the completion of reaction with slightly lower yield.

The reusability of the SiO_2TMG catalyst is one of its most important benefits and makes it useful for commercial applications as well. Thus the recovery and reusability of the catalyst were investigated. The recyclability of the catalyst was checked with model reaction (Table 4, entries 1–4). The catalyst was recovered after completion of the first fresh run, the reaction mixture was cooled to room temperature, and then the residue was treated with boiling ethanol, filtered through a sintered funnel, and washed thoroughly with the same solvent. The catalyst was separated from the reaction mixture. The recovered SiO_2TMG was dried at 90–100 °C for 12 h and tested in up to three more reaction cycles. The same catalyst was reused for subsequent reactions (three runs) with fresh substrates under the same conditions. The catalyst showed excellent recyclability in all these reactions (Table 4), as the reaction times and yield remained almost the same without loss of catalytic activity.

EXPERIMENTAL

Chemicals were purchased from Aldrich, Merck, and Alfa Aesar chemical companies. The NMR spectra were recorded in dimethylsulfoxide (DMSO-d_6) on a Jeol JNM ECP 400 NMR instrument using Tetramethylsilane (TMS) as an

internal standard. High-resolution mass spectra (HRMS) were recorded on a Jeol JMS-700 mass spectrometer. Melting points were taken in open capillaries on an Electrothermal-9100 instrument (Japan).

Preparation of Silica-Supported Tetramethylguanidine (SiO_2TMG) Catalyst

Silica-supported tetramethylguanidine was prepared by adopting the literature precedent.[31] 1,1,3,3-Tetramethylguanidine (TMG, 0.2 mol) and mixed xylenes were mixed together and heated to 120 °C. Chloropropyl trimethoxysilane (0.081 mol) was added dropwise over 2 h, and the solution allowed to react for 2 h. It treated with activated silica in presence of triethyl amine, and the solution was allowed to react for 1 h. On cooling, a solid precipitate was filtered and dried at 85–90 °C to yield the desired product.

General Procedure for the Synthesis of 6-Amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles

To a prestirred mixture of ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), aldehydes (1 mmol), and malononitrile (1 mmol) were added, followed by SiO_2TMG (10 mol%). The reaction mixture was then heated at 100 °C. The reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled to room temperature. The residue was treated with boiling ethanol, filtered through a sintered funnel, and washed thoroughly with the same solvent. The combined filtrate was evaporated in vacuo to afford the crude product, which was recrystallized from ethanol to afford pure compound **5**. The spectral and analytical data of the model representative compound are given here.

6-Amino-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5a)

Yield 96%; white powder; mp 245–246 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.1 (s, 1H), 7.31 (t, $J = 12$ Hz, 2H), 7.22 (t, $J = 8$ Hz, 1H), 7.16 (d, $J = 8$ Hz, 2H), 6.88 (s, 2H), 4.59 (s, 1H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.9, 154.7, 144.4, 135.6, 128.4, 126.7, 120.8, 97.6, 57.2, 36.2, 9.7. HRMS (ESI, m/z): calcd. for $C_{14}H_{12}N_4O$ (m/z) 252.1011; found 252.1011.

CONCLUSION

In summary, we have described an efficient and environmentally benign protocol for the synthesis of fully substituted 6-amino-2,4-dihydropyrano[2,3-c]pyrazol-5-carbonitriles via reaction of ethyl acetoacetate, hydrazine hydrate, and malononitrile with diverse aldehydes using silica-supported tetramethylguanidine as expeditious reusable catalyst in excellent yields. The main advantages of this present methodology are the simple workup, easy recovery of catalyst, and lack of need for anhydrous conditions, base, or any additional activators.

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SUPPORTING INFORMATION

Supplemental data for this article can be accessed on the publisher's website.

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