Accepted Manuscript

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PII: S0040-4020(13)01504-4

DOI: 10.1016/j.tet.2013.09.082

Reference: TET 24857

To appear in: *Tetrahedron*

Received Date: 10 August 2013

Revised Date: 17 September 2013

Accepted Date: 27 September 2013

Please cite this article as: Guo R-Y, An Z-M, Mo L-P, Yang S-T, Liu H-X, Wang S-X, Zhang Z-H, Meglumine promoted one-pot, four-component synthesis of pyranopyrazole derivatives, *Tetrahedron* (2013), doi: 10.1016/j.tet.2013.09.082.

Graphical Abstract

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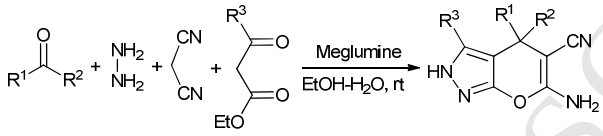

Biodegradable catalyst
Ethanol-water as solvent at RT
Atom economic one-pot four-component reaction
Excellent yields with broad substrate scope

Meglumine promoted one-pot, four-component synthesis of pyranopyrazole derivatives

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ABSTRACT—Meglumine, a bio-based chemical, was demonstrated to be a highly efficient and reusable catalyst for the synthesis of a series of pyranopyrazole derivatives via a one-pot, four-component reaction of carbonyl compound or isatin, hydrazine hydrate, malononitrile, and β-keto ester in EtOH-H_2O. The catalyst was found to work extremely for aldehydes, ketones or isatins at room temperature to give the corresponding dihydroprano[2,3-*c*]pyrazole or spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole] derivatives in high yields. The salient features of this new methodology are broad substrate scope, room temperature reaction conditions, short reaction times, high yields, easy work-up process, reusability of catalyst and the absence of hazardous organic solvents. All rights reserved.

Keywords:
Pyranopyrazoles
Multicomponent reaction
One-pot synthesis
Meglumine
biodegradable material

1. Introduction

Following the increasing demand of "green chemistry", the search for more environmentally benign forms of catalysis has received overwhelming attention, and one of the leading contestant for environmentally acceptable alternatives is biodegradable materials. Although some biodegradable materials such as chitosan,[1] gluconic acid,[2] cellulose sulfuric acid,[3] xanthan sulfuric acid,[4] starch sulfuric acid,[5] sulfuric acid-modified PEG (PEG-OSO_3H),[6] and eggshell[7] have been proposed as catalysts in some organic transformations. However, the number of available bio-based catalysts is far from abundant at this stage. Recently, Gu et al. introduced meglumine and gluconic acid aqueous solution as a promoting medium and catalyst for the multicomponent reaction of β-ketosulfones and formaldehyde.[8] Meglumine is an amino sugar derived from sorbitol with molecular formula $C_7H_{17}NO_5$. In particular, the low toxicity of meglumine allows its use in the formulation of pharmaceuticals as an excipient and in conjunction with iodinated compounds in contrast media such as diatrizoate meglumine and iodipamide meglumine. Meglumine possesses environmentally benign properties such as bio-degradablity and physiological inertness. Additionally, meglumine is inexpensive, non-corrosive, stabile to air and moisture and readily available in the market. It contains an amino group, primary and secondary hydroxyl groups and that can activate the nucleophilic as well as electrophilic components of the reactions by hydrogen bonding and donation of lone pair of electrons, respectively. Thus, such organic molecule may constitute alternative catalyst for the development of sustainable chemistry. Meanwhile, multicomponent reactions (MCRs) are known as a powerful tool for the construction of novel and structurally complex molecules in a single pot ensuring high atom-economy, good overall yields and high selectivity, lower costs, shorter reaction times, minimizing waste, labor, energy, and avoidance of expensive purification processes. It has been established that MCRs are generally much more environmentally friendly, and offer rapid access to large compound libraries with diverse functionalities.[9]

Potential biological activities and widespread synthetic utilities of pyranopyrazoles have led to their identification as a class of heterocyclic compounds which has created considerable interest in the pharmaceutical industry and in the diversified field of organic synthesis.[10] As a result, several strategies have been developed for the synthesis of pyranopyrazoles through a two-component[11] or three-component reaction.[12] Recently, Prasanna et al. have developed a four-component domino reaction from hydrazines, β-dicarbonyl compounds, nitriles in the presence of L-proline for the synthesis of densely functionalized 4*H*-pyrano[2,3-*c*]pyrazoles.[13] Zonouz and co-workers reported an efficient four-component reaction of dimethyl acetylenedicarboxylate, hydrazinehydrate, malononitrile, and aromatic aldehydes for the synthesis

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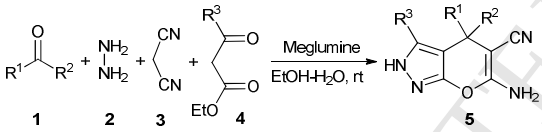
of 2,4-dihydropyrano[2,3-*c*]pyrazole-3-carboxylates in water.[14] One-pot, four-component syntheses of diverse pyranopyrazoles has also been accomplished and consists of condensation of aldehydes, ethyl acetoacetate, malononitrile and hydrazines. In this context, some catalysts have been used to promote these condensations such as Amberlyst A21,[15] triethylamine,[16] hexadecyl dimethyl benzyl ammonium chloride (HDBAC),[17] L-proline,[18] per-6-amino-β-cyclodextrin,[19] γ-alumina,[20] basic ionic liquids,[21] or piperidine.[22] Although these methods are quite satisfactory, some of them suffer from the absence of green chemistry, and have been associated with several shortcomings such as the use of volatile and hazardous organic solvents, low yields, extended reaction time, high temperature, and tedious procedure for the preparation of catalysts. Thus, the development of general, economically and environmentally benign synthetic methodologies for these heterocycles is highly desirable.

The combination of multicomponent reactions, an environmentally benign form of catalyst and a green solvent has become a promising frontier field of research in organic, medicinal and combinatorial chemistry.[23] Considering the above subjects and continuing our efforts on the development of new catalyst and environmental benign synthetic methodologies,[24] we report here on the first example of meglumine-catalyzed one-pot, four-component reaction of carbonyl compound, hydrazine hydrate, malononitrile, and β-keto ester for the synthesis of pyranopyrazole derivatives in ethanol-water mixture at room temperature (Scheme 1).

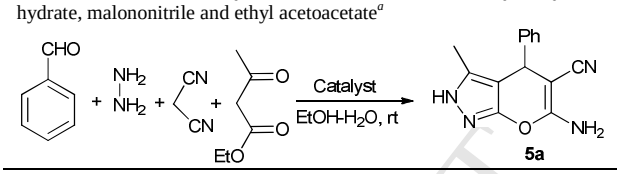


Scheme 1. Synthesis of pyranopyrazole derivatives.

2. Results and discussion

Initially, we selected benzaldehyde (1 mmol), hydrazine hydrate (1 mmol), malononitrile (1 mmol), ethyl acetoacetate (1 mmol) as model substrates to establish optimum reaction conditions. When the reaction was attempted without a catalyst, it was found that only a low yield of product was obtained even after 1 h (Table 1, entry 1). This result suggests that a catalyst plays a critical role in this reaction. A number of catalysts such as K_2CO_3, CH_3COONa, CH_3COONH_4, Al_2O_3, CeO_2, ZnO, CuO, MgO, Et_3N, and *L*-proline were examined to promote this transformation at room temperature. In comparison with these catalyst, meglumine proved to be the most efficient one which gave higher yield (95%) with 15 min (Table 1, entry 12).

Table 1
Influence of different catalysts on the reaction of benzaldehyde, hydrazine hydrate, malononitrile and ethyl acetoacetate[a]



Entry	Catalyst	Time (min)	Yield (%)
1	No	60	5
2	K_2CO_3	60	41
3	CH_3COONa	60	29
4	CH_3COONH_4	60	35
5	Al_2O_3	60	26
6	CeO_2	60	31
7	ZnO	60	28
8	CuO	60	26
9	MgO	60	21
10	Et_3N	60	22
11	*L*-Proline	60	66
12	Meglumine	15	95

[a] Experimental conditions: benzaldehyde (1 mmol), hydrazine hydrate (1 mmol), malononitrile (1 mmol), ethyl acetoacetate (1 mmol), catalyst (10 mol%), EtOH-H_2O (9:1, 2 ml).

With regard to the choice of solvents, we carried out the above reaction in various solvents. As shown in Table 2, when the reaction was performed under solvent-free conditions, low yield of target product was obtained. To find the best solvent for this transfortion, the present four-component reaction was screened in H_2O, PEG 400, THF, ^{i}PrOH, MeOH, EtOH and ethanol-water mixture. Among all these solvents, ethanol-water mixture (9:1) was found to be the best one and afforded the highest yield (Table 2, entry 9). Therefore, aqueous ethanol was selected as the solvent system for the subsequent reaction. Then the amount of the catalyst was evaluated in the model reaction at room temperature in EtOH-H_2O (9:1). The results showed that 10 mol% of catalyst was the best choice for the completing the reaction and the use of excessive catalyst had no impact either on the rate of the reaction or on the product yield.

Table 2
Optimization of reaction conditions[a]

Entry	Catalyst loading (mol%)	Solvent	Time (min)	Yield (%)
1	10	no	60	10
2	10	H_2O	60	30
3	10	PEG 400	60	62
4	10	THF	60	76
5	10	^{i}PrOH	60	81
6	10	MeOH	60	88
7	10	EtOH	15	92
8	5	EtOH: H_2O (9:1)	15	90
9	10	EtOH: H_2O (9:1)	15	95
10	15	EtOH: H_2O (9:1)	15	93
11[b]	10	EtOH: H_2O (9:1)	15	94
12[c]	10	EtOH: H_2O (9:1)	15	93, 92, 90

[a] Experimental conditions: benzaldehyde (1 mmol), hydrazine hydrate (1 mmol), malononitrile (1 mmol), ethyl acetoacetate (1 mmol), solvent (2 ml). [b] 50 mmol scale. [c] Catalyst was reused three times.

In addition, in order to demonstrate practical

usefulness of the present method, the model reaction was carried out in a scale of 50 mmol. As expected, the desired product could be obtained through recrystalization with 94% yield in 15 min. In this protocol, the product was separated from the reaction mixture by simple filtration, as it is not soluble in water and ethanol, while meglumine and the starting materials are soluble. The possibility of recycling the catalyst was examined in the model reaction. As shown in Table 2, meglumine can be reused three times without significant decrease in catalytic activity, the yields ranged from 93% to 90%.

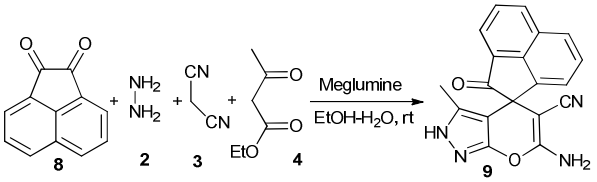
Encouraged by the efficiency of the reaction protocol described above, the scope and specificity of this protocol were further investigated. Firstly, a broad range of structurally diverse aldehydes were treated with hydrazine hydrate, malononitrile, and ethyl acetoacetate and the results are depicted in Table 3. As evident from Table 3, all reactions proceeded efficiently and the desired products were obtained in high to excellent yields in relatively short times without formation of any by-products. The nature of the functional group on the aromatic ring of the aldehyde exerted a slightly influence on the reaction time. A decrease of the reaction rate was observed with arylaldehyde carrying an electron-donating group in comparison to the unsubstituted benzaldehyde. The reaction was also sensitive to the steric environment of the aromatic aldehyde, and longer reaction times were required for benzaldehyde containing substituens at 2-position (Table 3, entries 2, 7, 12, 15 and 19). Heteroatomatic aldehydes, such as furan-2-carbaldehyde, thiophene-2-carbaldehyde, pyridine-4-carbaldehyde readily participated in this transformation, affording the potentially bio-important pyranopyrazoles in high yields (Table 3, entries 24-26). Furthermore, 1-naphthaldehyde was found to be a good substrate, and the target compound was obtained in 89% yield.

It is pertinent to note that aliphatic aldehydes are not appropriate starting materials in many reported procedures due to form unwanted byproducts via various side reactions such as aldo condensation and the Cannizzaro reaction. Fortunately, this meglumine-catalyzed transformation is not limited to aliphatic aldehydes and gave the pyranopyrazole product in high yields (Table 3, entries 28 and 29). Additionally, when the ethyl acetoacetate was switched to ethyl propionylacetate under above conditions, it exhibited analogous behavior to ethyl acetoacetate (Table 3, entries 30-32).

Having been inspired by these results, we have scrutinized the reactions of various of ketones. An extensive literature survey reveals that there are relatively fewer methods to synthesize pyranopyrazole derivatives from ketones due to the low reactivity of ketones as compared to aldehydes. Without any optimization, we were pleased to find that cyclic ketones such as cyclopenyanone, cyclohexanone and as well as alkyl-alkyl ketones, and aryl-alkyl ketones also underwent this one-pot conversion to afford the respective ketone-derived dihydroprano[2,3-*c*]pyrazoles in high yields under these conditions, albeit with a prolonged reaction time.

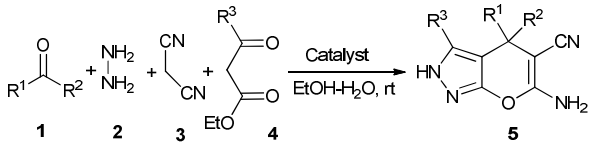
Istain is a privilieged lead molecule for designing potential pharmacological agents, and its derivatives have been shown to possess a broad spectrum of bioactivity. These interesting properties promoted us to widen the applicability of this procedure with isatins. Recently, Shestopalov and co-workers reported one-pot, two-step reaction of istain, hydrazine hydrate, malononitrile, and β-keto ester for synthesis of spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole] derivatives in the presence of Et_3N in refluxing EtOH.[16] Pleasantly, we found that one-step preparation of spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole] derivatives (**7**) could be accomplished using various isatins having electron-neutral, electron-deficient, and electron-rich substituents on the aryl ring under above optimized conditions (Table 4).

To explore the scope of this reaction to form new spiroheterocyclic compounds, we investigated the use of acenaphtylene-1,2-dione (**8**) as a substrate to react with hydrazine hydrate, malononitrile, ethyl acetoacetate under the optimized conditions. As expected the reaction proceeded well to afford spiro[acenaphthylene-1,4'-pyrano[2,3-*c*]pyrazole] derivative (**9**) in 35 min with 90% yield (Scheme 2). These successful results clearly indicate that the present catalytic approach is extendable to a wide variety of substrates.

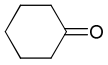
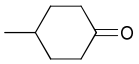


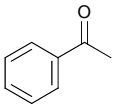
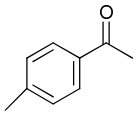
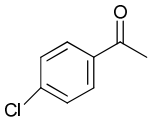
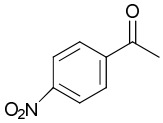
Scheme 2. Synthesis of spiro[acenaphthylene-1,4'-pyrano[2,3-c]pyrazole]

Table 3
Synthesis of dihydroprano[2,3-*c*]pyrazole **5** from carbonyl compounds



1 **2** **3** **4** **5**

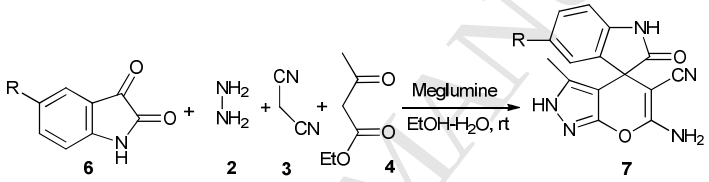
Entry	Carbonyl compounds	R^3	Product	Time (min)	Yield (%)[a]	m.p. (°C)
1	PhCHO	Me	**5a**	15	95	243-244 (244-245)[21a]
2	2-$OCH_3C_6H_4CHO$	Me	**5b**	30	90	249-250 (251-252)[21a]
3	4-$OCH_3C_6H_4CHO$	Me	**5c**	20	91	210-212 (211-213)[21a]
4	4-$CH_3(CH_2)_2OC_6H_4CHO$	Me	**5d**	18	92	175-176
5	4-$CH_3(CH_2)_4OC_6H_4CHO$	Me	**5e**	17	93	240-242
6	2-OMe-5-$CHMe_2C_6H_3CHO$	Me	**5f**	20	91	163-164
7	2,3,4-$(OMe)_3C_6H_2CHO$	Me	**5g**	25	89	223-225
8	3-$CH_3C_6H_4CHO$	Me	**5h**	17	90	170-171 (170-172)[19]
9	4-$C(CH_3)_3C_6H_4CHO$	Me	**5i**	22	91	223-225
10	4-$SCH_3C_6H_4CHO$	Me	**5j**	20	90	219-220
11	4-OHC_6H_4CHO	Me	**5k**	20	91	223-224 (224-226)[21a]
12	2-FC_6H_4CHO	Me	**5l**	16	92	261-262 (260-261)[25]
13	3-FC_6H_4CHO	Me	**5m**	10	91	242-243 (245-246)[25]
14	4-FC_6H_4CHO	Me	**5n**	11	92	244-245 (245-246)[21a]
15	2-ClC_6H_4CHO	Me	**5o**	22	90	245-246 (246-247)[21a]
16	3-ClC_6H_4CHO	Me	**5p**	12	92	230-231 (231-232)[16]
17	4-ClC_6H_4CHO	Me	**5q**	15	95	234-235 (233-234)[21a]
18	2,4-$Cl_2C_6H_3CHO$	Me	**5r**	17	92	229-230
19	2-$NO_2C_6H_4CHO$	Me	**5s**	13	92	243-244 (241-244)[21a]
20	4-$NO_2C_6H_4CHO$	Me	**5t**	10	93	248-249 (251-252)[21a]
21	3-$CF_3C_6H_4CHO$	Me	**5u**	7	94	201-202
22	4-$CF_3C_6H_4CHO$	Me	**5v**	8	94	243-244 (244-245)[26]
23	4-((4-Nitrobenzyl)oxy)benzaldehyde	Me	**5w**	20	93	206-207
24	Furan-2-carbaldehyde	Me	**5x**	17	90	230-231 (232-234)[21a]
25	Thiophene-2-carbaldehyde	Me	**5y**	12	92	224-226 (221-223)[27]
26	Pyridine-4-carbaldehyde	Me	**5z**	23	90	216-217 (214-215)[15]
27	1-Naphthaldehyde	Me	**5aa**	30	89	223-224 (226-228)[21a]
28	Decanal	Me	**5ab**	60	85	145-146
29	Cyclohexanecarbaldehyde	Me	**5ac**	20	86	170-171 (172-173)[19]
30	PhCHO	Et	**5ad**	15	90	216-217
31	4-$OCH_3C_6H_4CHO$	Et	**5ae**	23	90	193-195
32	4-ClC_6H_4CHO	Et	**5af**	20	92	218-220
33		Me	**5ag**	60	92	176-177 (175)[28]
34		Me	**5ah**	540	90	161-162
35		Me	**5ai**	540	91	165-166 (164-165)[15]
36		Me	**5aj**	540	92	148-149 (147-148)[15]
37		Me	**5ak**	540	90	196-197

38		Me	**5al**	480	86	178-179 (177-178)[15]
39		Me	**5am**	480	85	184-185 (183-184)[15]
40		Me	**5an**	360	87	183-184 (181-182)[15]
41		Me	**5ao**	300	88	220-221

[a] Isolated yield.

Table 4.

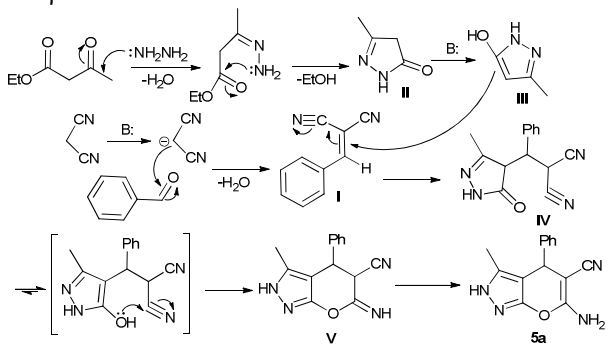
Synthesis of spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole] **7** from isatins



Entry	R	Product	Time (min)	Yield (%)[a]	m.p. (°C)
1	H	**7a**	35	92	286-287 (285-286)[29]
2	Me	**7b**	40	85	282-283 (279-281)[29]
3	F	**7c**	27	90	275-276 (274-275)[29]
4	Cl	**7d**	30	92	298-299 (297-298)[29]
5	Br	**7e**	27	93	283-284(282-283)[29]
6	NO_2	**7f**	25	93	273-274(270-271)[30]

[a] Isolated yield.

On the basis of the above results and previous studies,[19] a plausible mechanism can reasonably proposed for the synthesis of pyranopyrazole **5a** from benzaldehyde, hydrazine hydrate, malononitrile and ethyl acetoacetate (Scheme 3). We think that the presence of the amino group in the structure of meglumine plays a major role in its promoting activity for the formation of ylidenemalononitrile (**I**) from Knoevenagel condensation of benzaldehyde and malononitrile. The 3-methyl-1*H*-pyrazol-5(4*H*)-one (**I**) was formed from the condensation of ethyl acetoacetate and hydrazine, which would be converted to its corresponding enolate form **II** in the presence of meglumine. Subsequent Michael-type addition of **II** to the intermediate **I** to produce intermediated **IV**, which underwent intramolecular cyclization by the nucleophilic addition of enolate oxygen to nitrile group to generate intermediate **V**. Finally, the tautomerization of intermediate **V** gave dihydropyrano[2,3-*c*]pyrazole **5a**. Subsequent experiment showed that the formation of ylidenemalononitrile via Knoevenagel condensation of acetophenone and malononitrile was slower than istain in the presence of meglumine, which might be the part reason for longer time requirement for four-component reaction of ketones, hydrazine hydrate, malononitrile, and β-keto ester.



Scheme 3. Plausible mechanism for synthesis of pyrrole derivatives.

Finally, in order to show the efficiency of the proposed method, meglumine was compared with other catalysts reported earlier for the synthesis of **5a**. As demonstrated in Table 5, the use of meglumine leads to an improved protocol in terms of compatibility with environment, reaction time, and yield when compared with other catalyst.

Table 5 Comparison of our results with previously reported methods

Entry	Catalyst	Reaction conditions	Time (min)	Yield (%)
1	Amberlyst A21 (50 mg)	EtOH, rt	25	90[15]
2	Et_3N (20 mol%)	EtOH, reflux	15	65[16]
3	HDBAC (30 mol%)	EtOH, reflux	45	73[17]
4	L-Proline (10 mol%)	[Bmim]BF_4, 50 °C	10	90[18a]
5	L-Proline (10 mol%)	H_2O, reflux	10	90[18a]
6	γ-Alumina (30 mol%)	H_2O, reflux	50	80[20]
7	[bmim]OH (20 mol%)	50-60 °C	10	88[21a]
8	Piperidine (5 mol%)	H_2O, rt	10	83[22]
9	Meglumine (10 mol%)	EtOH: H_2O (9:1), rt	15	95

3. Conclusion

In summary, we have developed a highly efficient and greener approach for the one-pot, four-component synthesis of pyranopyrazole derivatives using meglumine as an inexpensive, biodegradable and reused catalyst. This method was found not only to applied to aromatic, heteroaromatic, and aliphatic aldehydes, but also to be useful for synthesis of ketone-derived dihydroprano[2,3-*c*]pyrazole and spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole] derivatives. The merits for the presented methodology are its efficient, generality, wide scope of substrates, high yield, short reaction time, simplicity, no elevated temperature, ease of product isolation, cleaner reaction profile, evasion of hazardous catalysts or solvents, and agreement with the green chemistry protocols, which make it a useful and attractive process for the synthesis of pyranopyrazoles.

4. Experimental

4.1 General information

All solvents and chemicals were obtained commercially and were used as received. All known compounds were identified by comparison of their melting points and ^{1}H NMR data with those in the authentic samples. Melting points were determined using an X-4 apparatus and are uncorrected. IR spectra were taken as KBrdiscs with a Bruker-TENSOR 27 spectrometer. NMR spectra were recorded on a Bruker DRX-500 spectrometer at 500 MHz (^{1}H) and 125 MHz (^{13}C) using DMSO-d_6 as the solvent with TMS as internal standard. Elemental analyses were obtained on a Vario EL III CHNOS elemental analyzer.

4.2 Typical procedure for synthesis of dihydropyrano[2,3-*c*]pyrazoles

Meglumine (10 mol%) was added to a mixture of carbonyl compound (**1**, 1 mmol), hydrazine hydrate (**2**, 1 mmol), malononitrile (**3**, 1 mmol), and β-keto ester (**4**, 1 mmol) in EtOH-H_2O (9:1, 2 ml). The resulting mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), the precipitated product was filtered and washed with aqueous ethanol (5 ml). The crude product was purified by recrystallization from ethanol to afford the desired product. In order to recover the catalyst, the filtrate was dried under reduced pressure and recovered catalyst was washed with diethyl ether (2 ml) twice and reused after drying.

4.3 Characterization data

*4.3.1 6-Amino-3-methyl-4-(4-propoxy-phenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5d**).* White solid; IR (KBr): 3473, 3236, 2189, 1641, 1597, 1491, 1402, 1255, 1055, 981, 746 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.97 (t, *J* = 7.5 Hz, 3H, CH_3), 1.67-1.74 (m, 2H, CH_2), 1.78 (s, 3H, CH_3), 3.88 (t, *J* = 6.5 Hz, 2H, CH_2), 4.52 (s, 1H, CH), 6.82 (s, 2H, NH_2), 6.85 (d, *J* = 8.5 Hz, 2H, HAr), 7.05 (d, *J* = 8.0 Hz, 2H, HAr), 12.1 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 10.2, 10.9, 22.3, 35.9, 58.0, 69.3, 98.4, 114.7, 121.3, 128.9, 136.0, 136.8, 155.2, 157.9, 161.1 ppm; Anal. Calcd for $C_{17}H_{18}N_4O_2$: C, 65.79; H, 5.85; N, 18.05. Found: C, 65.61; H, 5.62; N, 17.90.

*4.3.2 6-Amino-3-methyl-4-(4-pentyloxy-phenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5e**).* White solid; IR (KBr): 3444, 3238, 2195, 1637, 1600, 1491, 1394, 1236, 1055, 869, 756 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.89 (t, *J* = 6.5 Hz, 3H, CH_3), 1.32-1.41 (m, 4H, $2CH_2$), 1.68-1.71 (m, 2H, CH_2), 1.78 (s, 3H, CH_3), 3.92 (t, *J* = 6.0 Hz, 2H, CH_2), 4.52 (s, 1H, CH), 6.82 (s, 2H, NH_2), 6.84 (d, *J* = 8.0 Hz, 2H, HAr), 7.05 (d, *J* = 8.0 Hz, 2H, HAr), 12.1 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 10.2, 14.4, 22.4, 28.2, 28.9, 35.9, 58.0, 67.8, 98.4, 114.7, 121.3, 128.9, 136.0, 136.8, 155.2, 157.9, 161.1 ppm; Anal. Calcd for $C_{19}H_{22}N_4O_2$: C, 67.44; H, 6.55; N, 16.56. Found: C, 67.62; H, 6.73; N, 16.38.

*4.3.3 6-Amino-3-methyl-4-(5-isopropyl-2-methoxy-phenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5f**).* White solid; IR (KBr): 3375, 3173, 2195, 1647, 1602, 1487, 1396, 1249, 1105, 870 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.11 (d, *J* = 7.0 Hz, 6H, $2CH_3$), 1.78 (s, 3H, CH_3), 2.73-2.79 (m, 1H, CH), 3.73 (s, 3H, OCH_3), 4.91 (s, 1H, CH), 6.78 (s, 2H, NH_2), 6.83 (d, *J* = 1.5 Hz, 1H, HAr), 6.91 (d, *J* = 8.5 Hz, 1H, HAr), 7.07 (dd, *J* = 8.5 Hz, *J* = 2.0 Hz, 1H, HAr), 12.0 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 10.0, 24.5, 24.6, 33.0, 56.1, 56.7, 98.3, 111.8, 121.4, 125.6, 127.0, 132.0, 135.5, 140.9, 155.1, 155.6, 161.9 ppm; Anal. Calcd for $C_{18}H_{20}N_4O_2$: C, 66.65; H, 6.21; N, 17.27. Found: C, 66.83; H, 6.05; N, 12.46.

4.3.4 6-Amino-3-methyl-4-(2,3,4-trimethoxy-phenyl)-1,4-

*dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5g**).* White solid; IR (KBr): 3392, 3306, 3173, 2187, 1641, 1600, 1491, 1392, 1101, 898 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.78 (s, 3H, CH_3), 3.66 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 4.72 (s, 1H, CH), 6.71-6.76 (m, 2H, HAr), 6.79 (s, 2H, NH_2), 12.0 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 9.91, 31.0, 56.1, 57.3, 60.7, 61.3, 98.5, 108.4, 121.5, 123.8, 130.1, 135.6, 141.9, 151.6, 152.6, 155.4, 161.5 ppm; Anal. Calcd for $C_{17}H_{18}N_4O_4$: C, 59.64; H, 5.30; N, 16.37. Found: C, 59.80; H, 5.56; N, 16.53.

*4.3.5 6-Amino-3-methyl-4-(4-tert-butyl-phenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5i**).* White solid; IR (KBr): 3493, 3244, 2195, 1633, 1597, 1491, 1398, 1055, 761 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.26 (s, 9H, $3CH_3$), 1.79 (s, 3H, CH_3), 4.55 (s, 1H, CH), 6.86 (s, 2H, NH_2), 7.07 (d, *J* = 8.0 Hz, 2H, HAr), 7.33 (d, *J* = 7.5 Hz, 2H, HAr), 12.1 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 10.3, 31.6, 34.6, 36.2, 57.7, 98.3, 121.4, 125.6, 127.5, 135.9, 141.9, 149.3, 155.2, 161.4 ppm; Anal. Calcd for $C_{18}H_{20}N_4O$: C, 70.11; H, 6.54; N, 18.17. Found: C, 69.89; H, 6.38; N, 17.90.

*4.3.6 6-Amino-3-methyl-4-(4-methylsulfanyl-phenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5j**).* White solid; IR (KBr): 3483, 3254, 2191, 1641, 1608, 1492, 1390, 1053, 796 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.79 (s, 3H, CH_3), 2.45 (s, 3H, SCH_3), 4.56 (s, 1H, CH), 6.88 (s, 2H, NH_2), 7.10 (d, *J* = 8.0 Hz, 2H, HAr), 7.19 (d, *J* = 8.0 Hz, 2H, HAr), 12.1 (s, 1H, NH) ppm; ^{13}C NMR (DMSO, 125 MHz) δ 10.2, 15.1, 36.1, 57.6, 97.8, 121.3, 126.4, 128.6, 136.1, 136.7, 141.6, 155.2, 161.3 ppm; Anal. Calcd for $C_{15}H_{14}N_4OS$: C, 60.38; H, 4.73; N, 18.78. Found: C, 60.10; H, 4.56; N, 18.90.

*4.3.7 6-Amino-4-(2-fluorophenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5l**).* White solid; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.78 (s, 3H, CH_3), 4.63 (s, 1H, CH), 6.91 (s, 2H, NH_2), 7.14 (t, *J* = 9.0 Hz, 2H, HAr), 7.19-7.22 (m, 2H, HAr), 12.1 (s, 1H, NH) ppm.

4.3.8 *6-Amino-4-(2-chlorophenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5o**).* White solid; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.76 (s, 3H, CH_3), 5.06 (s, 1H, CH), 6.96 (s, 2H, NH_2), 7.17 (d, *J* = 7.0 Hz, 1H, HAr), 7.24-7.27 (m, 1H, HAr), 7.31 (t, *J* = 7.5 Hz, 1H, HAr), 7.41 (d, *J* = 8.0 Hz, 1H, HAr), 12.1 (s, 1H, NH) ppm.

4.3.9 6-Amino-3-methyl-4-(2,4-dichloro-phenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(5r).** White solid; IR (KBr): 3481, 3252, 2187, 1643, 1593, 1492, 1410, 1058, 871 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.77 (s, 3H, CH_3), 5.06 (s, 1H, CH), 7.02 (s, 2H, NH_2), 7.21 (d, *J* = 7.0 Hz, 1H, HAr), 7.40 (d, *J* = 8.0 Hz, 1H, HAr), 7.59 (s, 1H, HAr), 12.2 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 10.0, 33.6, 55.7, 96.8, 120.7, 128.5, 129.3, 132.6, 133.3, 135.9, 140.6, 155.4, 161.8 ppm; Anal. Calcd for $C_{14}H_{10}Cl_2N_4O$: C, 52.36; H, 3.14; N, 17.45. Found: C, 52.53; H, 2.88; N, 17.62.

4.3.10 *6-Amino-3-methyl-4-(2-nitrophenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5s**).* White solid; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.80 (s, 3H, CH_3), 5.12 (s, 1H, CH), 7.08 (s, 2H, NH_2), 7.35 (d, *J* = 8.0 Hz, 1H, HAr), 7.53 (t, *J* = 7.0 Hz, 1H, HAr), 7.70 (t, *J* = 7.5 Hz, 1H, HAr), 7.88 (d, *J* = 8.0 Hz, 1H, HAr), 12.2 (s, 1H, NH) ppm.

4.3.11 6-Amino-3-methyl-4-(3-trifluoromethyl-phenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(5u).** White solid; IR (KBr): 3481, 3238, 2191, 1637, 1597, 1491, 1404, 1122, 1057, 794 cm^{-1}; ^1H NMR (DMSO, 500 MHz) δ 1.78 (s, 3H, CH_3), 4.80 (s, 1H, CH), 7.00 (s, 2H, NH_2), 7.47 (d, *J* = 7.0 Hz, 1H, HAr), 7.53 (s, 1H, HAr), 7.56-7.63 (m, 2H, HAr), 12.2 (s, 1H, NH) ppm; ^{13}C NMR (DMSO, 125 MHz) δ 10.1, 36.3, 56.8, 97.4, 121.0, 124.1 (q, $^3J_{FC}$ = 3.8 Hz), 124.2 (q, $^3J_{FC}$ = 3.6 Hz), 124.8 (q, $^1J_{FC}$ = 270.3 Hz), 129.5 (q, $^2J_{FC}$ = 31.4 Hz), 130.3, 132.2, 136.3, 146.3, 151.2, 161.5 ppm; Anal. Calcd for $C_{15}H_{11}F_3N_4O$: C, 56.25; H, 3.46; N, 17.49. Found: C, 56.41; H, 3.28; N, 17.65.

4.3.12 6-Amino-3-methyl-4-[3-(4-nitro-benzyloxy)-phenyl]-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(5w).** White solid; IR (KBr): 3462, 3331, 2185, 1633, 1606, 1508, 1398, 1267, 1107 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.78 (s, 3H, CH_3), 4.55 (s, 1H, CH), 5.25 (s, 2H, CH_2), 6.84 (s, 2H, NH_2), 6.97 (d, *J* = 8.5 Hz, 2H, HAr), 7.09 (d, *J* = 8.5 Hz, 2H, HAr), 7.72 (d, *J* = 8.5 Hz, 2H, HAr), 8.25 (d, *J* = 8.5 Hz, 2H, HAr), 12.1 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 10.2, 35.9, 57.9, 68.5, 98.3, 115.1, 121.3, 124.1, 128.7, 129.1, 136.0, 137.6, 145.6, 147.5, 155.2, 157.2, 161.2 ppm; Anal. Calcd for $C_{21}H_{17}N_5O_4$: C, 62.53; H, 4.25; N, 17.36. Found: C, 62.38; H, 4.42; N, 17.18.

4.3.13 *6-Amino-4-(furan-2-yl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5x**).* White solid; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.97 (s, 3H, CH_3), 4.77 (s, 1H, CH), 6.17 (d, *J* = 3.0 Hz, 1H, HAr), 6.37 (t, *J* = 2.0 Hz, 1H, HAr), 6.96 (s, 2H, NH_2), 7.53 (d, *J* = 1.0 Hz, 1H, HAr), 12.2 (s, 1H, NH) ppm.

4.3.14 *6-Amino-3-methyl-4-(thiophen-2-yl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5y**).* White solid; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.95 (s, 3H, CH_3), 5.03 (s, 1H, CH), 6.96-6.99 (m, 3H, HAr, NH_2), 7.04 (d, *J* = 3.0 Hz, 1H, HAr), 7.41 (d, *J* = 5.0 Hz, 1H, HAr), 12.2 (s, 1H, NH) ppm.

4.3.15 *6-Amino-3-methyl-4-(pyridin-4-yl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5z**).* White solid; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.82 (s, 3H, CH_3), 4.66 (s, 1H, CH), 7.04 (s, 2H, NH_2), 7.19 (d, *J* = 6.0 Hz, 2H, HAr), 8.52 (d, *J* = 5.0 Hz, 2H, HAr), 12.2 (s, 1H, NH) ppm.

4.3.16 6-Amino-3-methyl-4-octyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(5ab).** White solid; IR (KBr): 3471, 3257, 2187, 1643, 1404, 1051, 723 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 0.83 (t, *J* = 7.0 Hz, 3H, CH_3), 0.96-0.98 (m, 1H, CH), 1.16-1.25 (m, 11H, CH_2), 1.54-1.60 (m, 2H, CH_2), 2.14 (s, 3H, CH_3), 3.55 (t, *J* = 4.0 Hz, 1H, CH), 6.77 (s, 2H, NH_2), 12.0 (s, 1H, NH) ppm; ^{13}C NMR

(DMSO-d_6, 125 MHz) δ 10.6, 14.4, 22.5, 24.2, 29.1, 29.4, 29.5, 30.1, 31.7, 35.3, 55.6, 97.3, 121.5, 135.3, 156.1, 162.3 ppm; Anal. Calcd for $C_{16}H_{24}N_4O$: C, 66.64; H, 8.39; N, 19.43. Found: C, 66.81; H, 8.20; N, 19.62.

4.3.17 6-Amino-3-ethyl-4-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(5ad).** White solid; IR (KBr): 3423, 3171, 2185, 1651, 1608, 1489, 1402, 1043, 871 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 0.76 (t, *J* = 7.5 Hz, 3H, CH_3), 2.12-2.19 (m, 2H, CH_2), 4.60 (s, 1H, CH), 6.87 (s, 2H, NH_2), 7.16 (d, *J* = 7.5 Hz, 2H, HAr), 7.22 (t, *J* = 7.0 Hz, 1H, HAr), 7.31 (t, *J* = 7.0 Hz, 1H, HAr), 12.1 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 12.9, 18.3, 36.8, 57.9, 97.4, 121.3, 127.2, 127.9, 128.9, 141.6, 145.3, 155.2, 161.2 ppm; Anal. Calcd for $C_{15}H_{14}N_4O$: C, 67.65; H, 5.30; N, 21.04. Found: C, 67.83; H, 5.15; N, 20.86.

4.3.18 6-Amino-3-ethyl-4-(4-methyl-phenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(5ae).** White solid; IR (KBr): 3234, 3119, 2189, 1639, 1489, 1406, 1033, 752 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 0.80 (t, *J* = 7.5 Hz, 3H, CH_3), 2.11-2.18 (m, 2H, CH_2), 3.72 (s, 3H, CH_3), 4.55 (s, 1H, CH), 6.81 (s, 2H, NH_2), 6.86 (d, *J* = 8.5 Hz, 2H, HAr), 7.07 (d, *J* = 8.0 Hz, 2H, HAr), 12.1 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 13.0, 18.3, 36.0, 55.5, 58.3, 97.6, 114.2, 121.3, 129.0, 137.3, 141.6, 155.2, 158.5, 161.0 ppm; Anal. Calcd for $C_{16}H_{16}N_4O_2$: C, 64.85; H, 5.44; N, 18.91. Found: C, 65.02; H, 5.26; N, 19.09.

4.3.19 6-Amino-3-ethyl-4-(4-chloro-phenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(5af).** White solid; IR (KBr): 3485, 3232, 2187, 1641, 1593, 1491, 1408, 1062, 750 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 0.80 (t, *J* = 7.0 Hz, 3H, CH_3), 2.13-2.18 (m, 2H, CH_2), 4.65 (s, 1H, CH), 6.92 (s, 2H, NH_2), 7.19 (d, *J* = 8.0 Hz, 2H, HAr), 7.37 (d, *J* = 8.0 Hz, 2H, HAr), 12.2 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 12.9, 18.3, 36.1, 57.4, 97.0, 121.1, 128.9 129.9, 131.7, 141.7, 144.4, 155.1, 161.2 ppm; Anal. Calcd for $C_{15}H_{13}ClN_4O$: C, 59.91; H, 4.36; N, 18.63. Found: C, 60.10; H, 4.52; N, 18.80.

4.3.20 6'-Amino-3'-methyl-1'H-spiro[cyclobutane-1,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile **(5ah).** White solid; IR (KBr): 3342, 3107, 2189, 1649, 1390, 995 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.93-2.00 (m, 2H, CH_2), 2.37-2.45 (m, 7H, CH_2, CH_3), 6.71 (s, 2H, NH_2), 12.1 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 11.0, 13.9, 35.3, 37.3, 63.5, 102.6, 121.0, 135.4, 154.2, 159.8 ppm; Anal. Calcd for $C_{11}H_{12}N_4O$: C, 61.10; H, 5.59; N, 25.91. Found: C, 60.91; H, 5.78; N, 26.06.

4.3.21 6'-Amino-3',4-dimethyl-1'H-spiro[cyclohexane-1,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile **(5ak).** White solid; IR (KBr): 3471, 3244, 2179, 1629, 1491, 1406, 1053, 717 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 0.93 (d, *J* = 6.0 Hz, 3H, CH_3), 1.46-1.52 (m, 2H, CH_2), 1.73 (d, *J* = 10.0 Hz, 2H, CH_2), 1.83-1.90 (m, 4H, $2CH_2$), 2.23 (s, 3H, CH_3), 6.58 (s, 2H, NH_2), 12.0 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 12.0, 22.9, 30.7, 31.7, 32.8, 60.8, 103.8, 124.6, 134.6, 154.8, 162.1 ppm; Anal. Calcd for $C_{14}H_{18}N_4O$: C, 65.09; H, 7.02; N, 21.69. Found: C, 64.90; H, 6.95; N, 21.86.

4.3.22 6-Amino-3,4-dimethyl-4-(4-nitro-phenyl)-1,4-dihydro-pyrano[2,3-c]pyrazole-5-carbonitrile **(5ao).** White solid; IR (KBr): 3439, 2980, 2185, 1645, 1516, 1349, 1026, 763 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.79 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 6.97 (s, 2H, NH_2), 7.52 (d, *J* = 9.0 Hz, 2H, HAr), 8.18 (d, *J* = 9.0 Hz, 2H, HAr), 12.2 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 10.6, 27.4, 38.4, 63.9, 102.0, 120.1, 123.9, 128.4, 135.9, 146.2, 154.3, 155.3, 160.7 ppm; Anal. Calcd for $C_{15}H_{14}N_4O$: C, 67.65; H, 5.30; N, 21.04. Found: C, 67.48; H, 5.52; N, 20.86.

*4.3.23 6'-Amino-3'-methyl-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile (**7a**)*. White solid; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.52 (s, 3H, CH_3), 6.90 (d, *J* = 7.5 Hz, 1H, HAr), 6.98-7.04 (m, 2H, HAr), 7.22-7.25 (m, 3H, HAr, NH_2), 10.6 (s, 1H, NH), 12.3 (s, 1H, NH) ppm.

*4.3.24 6'-Amino-3',5-dimethyl-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile (**7b**)*. White solid; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.54 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 6.78-6.84 (m, 2H, HAr), 7.04 (d, *J* = 7.0 Hz, 1H, HAr), 7.20 (s, 2H, NH_2), 10.5 (s, 1H, NH), 12.3 (s, 1H, NH) ppm.

4.3.25 6'-amino-5-fluoro-3'-methyl-2-oxo-1,2-dihydro-1'H-spiro[indole-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile **(7c).** White solid; IR (KBr): 3410, 3346, 3221, 2187, 1707, 1581, 1500, 1485, 1408, 1301, 1057, 792 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.57 (s, 3H, CH_3), 6.89-6.91 (m, 1H, HAr), 6.98 (d, *J* = 8.0 Hz, 1H, HAr), 7.08 (t, *J* = 8.5 Hz, 1H, HAr), 7.28 (s, 2H, NH_2), 10.6 (s, 1H, NH), 12.3 (s, 1H, NH) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 9.5, 48.3, 55.1, 95.3, 111.1 (d, $^3J_{CF}$ = 7.6 Hz), 112.7 (d, $^2J_{CF}$ = 24.5 Hz), 115.8 (d, $^2J_{CF}$ = 23.6 Hz), 119.1, 134.9 (d, $^3J_{CF}$ = 9.0 Hz), 135.2, 138.2, 155.7, 159.0 (d, $^1J_{CF}$ = 236.8 Hz), 162.9 ppm; Anal. Calcd for $C_{15}H_{10}FN_5O_2$: C, 57.88; H, 3.24; N, 22.50. Found: C, 57.70; H, 3.52; N, 22.35.

*4.3.26 6'-Amino-5-chloro-3'-methyl-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile (**7d**)*. White solid; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.61 (s, 3H, CH_3), 6.96 (d, *J* = 8.0 Hz, 1H, HAr), 7.08 (d, *J* = 2.0 Hz, 1H, HAr), 7.33-7.35 (m, 3H, HAr, NH_2), 10.8 (s, 1H, NH), 12.4 (s, 1H, NH) ppm.

*4.3.27 6'-amino-3'-methyl-2-oxo-2H,2'H-spiro[acenaphthylene-1,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile (**9**)*. Light yellow solid, mp: 245-246 °C (lit.[31] mp: 246 °C); IR (KBr): 3416, 3300, 2189, 1701, 1608, 1406 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.06 (s, 3H, CH_3), 7.31 (s, 2H, NH_2), 7.45 (d, *J* = 7.0 Hz, 1H, HAr), 7.77 (t, *J* = 7.5 Hz, 1H, HAr), 7.91 (t, *J* = 8.0 Hz, 1H, HAr), 8.05 (d, *J* = 7.0 Hz, 2H, HAr), 8.40 (d, *J* = 8.0 Hz, 1H, HAr), 12.20 (s, 1H, NH) ppm; Anal. Calcd for $C_{19}H_{12}N_4O_2$: C, 69.51; H, 3.68; N, 17.06. Found: C, 69.70; H, 3.85; N, 16.88.

Acknowledgement

The project was financially supported by the National Natural Science Foundation of China (Nos. 21272053, 21072042 and 20872025), Nature Science Foundation of Hebei Province (B2011205031) and the Training Programs of Innovation and Entrepreneurship for Undergraduates of Hebei Province (201310094021).

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