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Nano α-Al_2O_3 supported ammonium dihydrogen phosphate ($NH_4H_2PO_4/Al_2O_3$): preparation, characterization and its application as a novel and heterogeneous catalyst for the one-pot synthesis of tetrahydrobenzo[*b*]pyran and pyrano[2,3-*c*] pyrazole derivatives

Behrooz Maleki* and Samaneh Sedigh Ashrafi

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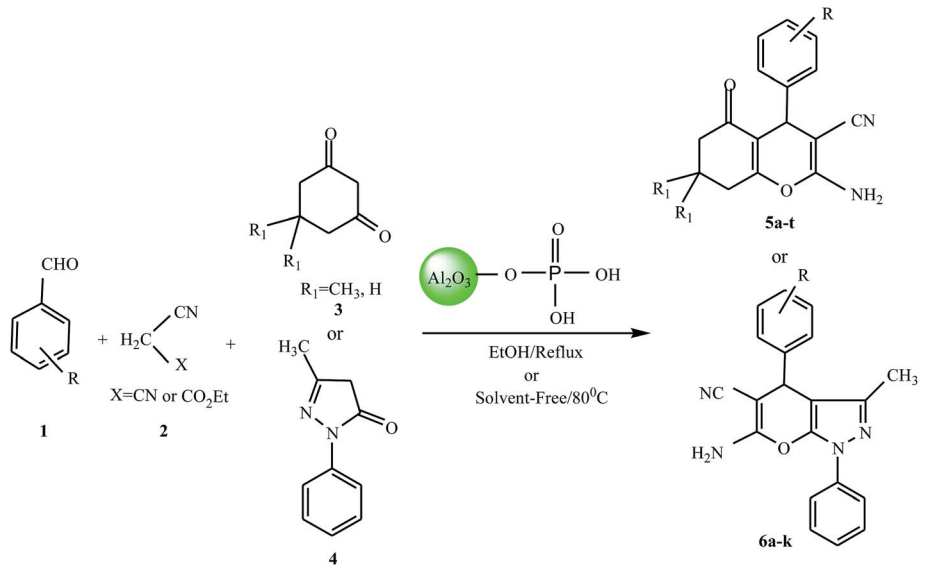
A simple, efficient, and environmentally benign route was developed for the preparation of 2-amino-3-cyano-4-aryl-7,7-dimethyl-5,6,7,8-tetrahydrobenzo[*b*]pyrans and 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles from the condensation of various aldehydes, malononitrile, and 1,3-dicarbonyl compounds (1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione) or 3-methyl-1-phenyl-2-pyrazoline-5-one, using $NH_4H_2PO_4/Al_2O_3$ with good yields. The use of easily available catalyst, shorter reaction times, better yields, the simplicity of the reaction, the heterogeneous system, and the easy work up are the advantages of the present method. Characterization of the catalyst was performed by FT-IR spectroscopy, X-ray diffraction (XRD) techniques, thermal analysis (TG/DTG) and Transmission electron microscopy (TEM).

Introduction

In recent years, synthetic chemists have shown tremendous interest in developing highly efficient transformations for the synthesis of 4*H*-pyrans and pyranopyrazoles and their derivatives due to their potential applications in the pharmaceutical and agrochemical industries and synthetic chemistry. These compounds have a wide range of biological and pharmalogical properties, such as anti-allergic, anti-flammatory, anti-tumor, spasmolytic, diuretic, anti-cancer, anti-coagulant and anti-anaphylactic activities.[1] Polyfunctionalized 4*H*-pyrans are a common structural unit in a number of natural products.[2] 4*H*-Pyrans ring can be transformed to pyridine systems, which relate to pharmacologically important calcium antagonist of the dihydropyridine type.[3] Also, 4*H*-benzo[*b*]pyrans can be used as cognitive enhancers, for the treatment of neurodegenerative disease, including Alzheimer's disease, amyotrophic lateral sclerosis, AIDS-associated dementia, and Down syndrome, as well as for the treatment of Schizophrenia and Huntington's diseases.[4]

Because of their extensive range of pharmacological activity and also their industrial and synthetic applications, several methods have been reported for the synthesis of 2-amino-3-cyano-4-aryl-7,7-dimethyl-5,6,7,8-tetrahydrobenzo[*b*]pyrans and 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles, which include bicomponent condensation of 1,3-dicarbonyl compounds (1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione) with α-cyanocinnamonitrile,[5] or through one-pot reaction three-component of aldehydes, malononitrile, and 1,3-dicarbonyl compounds (1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione) or 3-methyl-1-phenyl-2-pyrazoline-5-one, in the presence of various catalysts.[6] Also, a highly efficient synthesis of 4*H*-pyrano[2,3-*c*]pyrazole has been reported using four component cyclocondensation of hydrazine hydrate or phenylhydrazine, ethylacetoacetate, aldehydes and malononitrile in the presence of L-proline and [Bimim]BF_4 at 50 °C.[7] Generally, these compounds have been prepared through one-pot reaction three-component in the presence several catalyst such as, piperidine,[8] hexadecyltrimethyl ammonium bromide (HTMAB),[9] sodium bromide,[10] ionic liquids,[11] tetramethyl ammonium hydroxide,[12] diammunium hydrogen phosphate,[13] organocatalysts,[14] sodium selenate,[15] tetrabutylammonium bromide (TBAB),[16] polyaniline/silicagel,[17] alum [$KAl(SO_4)_2 \cdot 12H_2O$],[18] rare earth perfluorooctanoate [$Re(PFO)_3$],[19] caro's acid,[20] amine or amino acid,[21] potassium phosphate,[22] PPA/SiO_2,[23] the use of microwave irradiation,[24] $BF_3 \cdot OEt_2$,[25] $Pd(OAc)_2$, PPh_3, Na_2CO_3,[26] NEt_3, toluene/EtOH,[27] DABCO, EtOH,[28] TPPA,[29] *t*-BuOK/*t*-BuOH[30] and L-proline under ultrasound irradiation.[31] Many of these methods suffer from one or more limitations such as low yields, use of expensive reagents,

Department of Chemistry, Hakim Sabzevari University, Sabzevar 96179-76487, Iran. E-mail: b.maleki@hsu.ac.ir; malekibehrooz@gmail.com; Fax: +98-571-4410300; Tel: +98-571-4002643



Scheme 1 Synthesis of tetrahydrobenzo[*b*]pyrans and pyrano[2,3-*c*]pyrazoles using $NH_4H_2PO_4/Al_2O_3$ as catalyst.

long reaction times, tedious work-up procedures, and co-occurrence of several side reactions. In recent decade, many heterogeneous organic reactions have been performed using various reagents supported on solid materials.[32] $NH_4H_2PO_4/Al_2O_3$ is an inexpensive, easily available, non-toxic, low toxicity, heterogeneous, low cost and environmentally benign compound that is used in various organic transformations.

MCRs involve three or more starting materials reacting in a single flask to form a new product.[33] One example of an MCRs is a three-component, one-pot synthesis of tetrahydrobenzo[*b*]-pyrans and pyrano[2,3-*c*]pyrazoles.

As part of our work on one-pot multi-component reactions (MCRs) for the synthesis of various heterocyclic compounds of biological importance[34] and in continuation of our previous work on the development of new synthetic methodologies,[35] we now wish to report here a highly efficient procedure for the preparation of tetrahydrobenzo[*b*]pyrans and pyrano[2,3-*c*]pyr-azoles *via* a one-pot three-component reactions using $NH_4H_2PO_4/Al_2O_3$ as catalyst (Scheme 1).

Result and discussion

Our preliminary investigations were focused on systematic evaluation of different catalysts for the model reaction of benzaldehyde **1a** (1 mmol), dimedone (1 mmol), and malono-nitrile (1.2 mmol) in EtOH after reacting for 15 min at 80 °C (Table 1, entry 1). It was found that the conventional Lewis acids such as NH_4Cl, NH_4F, KH_2PO_4, K_2HPO_4, and H_3PO_4 as well as the condition of no catalyst showed poor effect to the yield of the product (entry 2–7). Even when large amount of catalyst was used, the result was still unsatisfactory (entry 8). With the use of $NH_4H_2PO_4/Al_2O_3$, the results seemed to be better (entry 9–14). On the optimized of amount catalyst (entry 15 and 16), we found that 0.03 g of $NH_4H_2PO_4/Al_2O_3$ could effectively catalyze the reaction for the synthesis of the desired product (entry 9). Then it continued to optimize the model reaction by detecting the efficiency of polar (CH_3CN, MeOH, H_2O) and nonpolar (CH_2Cl_2, CCl_4) solvents (entry 17–21). Ethanol was found to be the best in terms of yield and time (entry 9). The effect of temperature was also studied by carrying out the model reaction in the presence of $NH_4H_2PO_4/Al_2O_3$ (0.03 g) at room temperature (25 °C), 50 °C, 60 °C, and 70 °C (entry 22–25). It was observed that the yield increased was as the reaction temperature rose. Additionally, this reaction took place in the absence of solvent using 0.03 g of catalyst at 80 °C, interestingly; the same yield was achieved (entry 26). Also, the effect of the reaction parameters such as amount of catalyst and temperature were studied in detail. The best result was obtained with 0.03 g of catalyst at 80 °C (entry 27–30).

After optimization of the reaction conditions, we studied the generality of these conditions to other substrates. By using this method, different kinds of aldehydes reacted with 1,3-dicar-bonyl compounds (1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione) and malononitrile to produce the corre-sponding 2-amino-3-cyano-4-aryl-7,7-dimethyl-5,6,7,8-tetra-hydrobenzo[*b*]pyrans under both heterogeneous (in refluxing EtOH) and also solvent free conditions (Table 2). The property of substituent on the aromatic ring showed strongly obvious effects in terms of yields and time under this reaction condi-tion. Aldehydes containing electron-withdrawing groups (such as nitro, halide) reacted better to give the corresponding prod-ucts in higher yields than aromatic aldehydes containing electron-donating groups (such as alkyl, alkoxy, hydroxyl).

Encouraged by these results, we replaced the cyclic 1,3-dicarbonyl compounds (1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione) with 3-methyl-1-phenyl-2-pyrazoline-5-one in same conditions (Scheme 1). Initially, we optimized amount of $NH_4H_2PO_4/Al_2O_3$ for condensation of the reaction between 5,5-dimethyl-1,3-cyclohexanedione, benzldehyde (1 mmol), and malononitrile (1.2 mmol). The best result was

Table 1 Optimization of reaction conditions for the synthesis of 2-amino-3-cyano-4-(phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (**5a**)

Entry	Catalyst	Conditions	Time (min)	Yield[a] (%)
1	$NH_4H_2PO_4$ (30 mol%)	EtOH/reflux	20	71
2	NH_4Cl (30 mol%)	EtOH/reflux	40	52
3	NH_4F (30 mol%)	EtOH/reflux	40	50
4	KH_2PO_4 (30 mol%)	EtOH/reflux	40	64
5	K_2HPO_4 (30 mol%)	EtOH/reflux	50	60
6	H_3PO_4 (5 drop)	EtOH/reflux	20	48
7	—	EtOH/reflux	20	28
8	$NH_4H_2PO_4$ (40 mol%)	EtOH/reflux	20	72
9	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	EtOH/reflux	15	86
10	NH_4Cl/Al_2O_3 (0.03 gr)	EtOH/reflux	30	61
11	NH_4F/Al_2O_3 (0.03 gr)	EtOH/reflux	30	59
12	KH_2PO_4/Al_2O_3 (0.03 gr)	EtOH/reflux	30	72
13	K_2HPO_4/Al_2O_3 (0.03 gr)	EtOH/reflux	40	66
14	H_3PO_4/Al_2O_3 (0.03 gr)	EtOH/reflux	30	75
15	$NH_4H_2PO_4/Al_2O_3$ (0.02 gr)	EtOH/reflux	20	77
16	$NH_4H_2PO_4/Al_2O_3$ (0.04 gr)	EtOH/reflux	15	85
17	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	CH_3CN/reflux	15	60
18	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	CH_3OH/reflux	15	79
19	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	H_2O/reflux	15	46
20	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	CH_2Cl_2/reflux	60	38
21	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	CCl_4/reflux	60	34
22	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	EtOH/25 °C	60	Impure
23	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	EtOH/50 °C	40	60
24	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	EtOH/60 °C	40	64
25	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	EtOH/70 °C	30	80
26	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	Solvent-free/80 °C	20	84
27	$NH_4H_2PO_4/Al_2O_3$ (0.02 gr)	Solvent-free/80 °C	30	76
28	$NH_4H_2PO_4/Al_2O_3$ (0.04 gr)	Solvent-free/80 °C	20	83
29	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	Solvent-free/90 °C	20	85
30	$NH_4H_2PO_4/Al_2O_3$ (0.03 gr)	Solvent-free/70 °C	30	80

[a] Isolated yields.

obtained with 0.03 gr of $NH_4H_2PO_4/Al_2O_3$. To investigate the versatility of the catalyst, the reaction of cyclic 1,3-dicarbonyl compounds was carried out with various aldehydes and malononitrile for synthesis of 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles derivatives under solvent-free conditions at 80 °C and in refluxing EtOH (Table 3). All reactions proceeded efficiently within 15–40 minutes at 80 °C to provide the corresponding pyrano[2,3-*c*]pyrazoles derivatives in good yields ranging from 74–94%.

In order to broaden the scope of the present method, the replacement of malononitrile with ethyl cyanoacetate was examined. To our delight, the reaction underwent successful condensation under similar reaction conditions, to afford the corresponding tetrahydrobenzo[*b*]pyran and pyrano[2,3-*c*]pyrazole derivatives in high yields (Table 2, product **5p–q**). It was observed that with ethyl cyanoacetate a slightly longer reaction time was needed for reasonably high yields.

Finally, we have developed this synthetic method for one-pot efficient synthesis of 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles by polycondensation aldehydes with phenylhydrazine, malononitrile and ethylacetoacetate. To achieve the optimal reaction condition, the reaction of benzaldehyde **1a** (1 mmol) with phenylhydrazine (1.2 mmol), malononitrile (1.2 mmol) and ethylacetoacetate (1.2 mmol) in the presence of $NH_4H_2PO_4/Al_2O_3$ were selected as a model reaction and the effects of the reaction parameters such as amount of the catalyst and temperature were studied in detail. The best result was obtained with 0.03 gr of $NH_4H_2PO_4/Al_2O_3$ under thermal conditions in EtOH at 80 °C. Several structurally diverse aldehydes (Scheme 2, Table 2) were subjected to condensation with phenylhydrazine, malononitrile and ethylacetoacetate under the catalytic influence of $NH_4H_2PO_4/Al_2O_3$ (0.03 g).

After successfully synthesizing of a series of 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles in good yields, we replaced phenyl hydrazine with hydrazine hydrate in same conditions (Scheme 3). We began this study by subjecting 4-methoxybenzaldehyde (1 mmol), hydrazine hydrate (1.2 mmol), and ethylacetoacetate (1.2 mmol) to reactions with malononitrile (1.2 mmol) in the presence of $NH_4H_2PO_4/Al_2O_3$ under thermal conditions in EtOH at 80 °C. Unfortunately, complex mixtures were observed. To minimize the formation of byproducts, the hydrazine hydrate (1.2 mmol) and ethylacetoacetate (1.2 mmol) were first stirred in EtOH at 80 °C for 10 min. Next 4-methoxybenzaldehyde (1 mmol), and malononitrile (1.2 mmol) were added and the mixture was heated for 75 min in EtOH at 80 °C. The desired product was obtained in 72%

Table 2 Preparation of 2-amino-3-cyano-4-aryl-7,7-dimethyl-5,6,7,8-tetrahydrobenzo[*b*]pyrans derivatives using $NH_4H_2PO_4/Al_2O_3$ as catalyst[a]

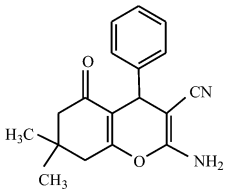
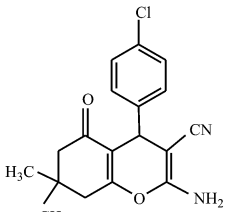
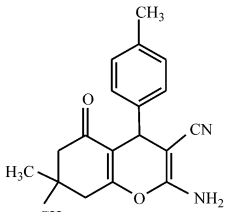
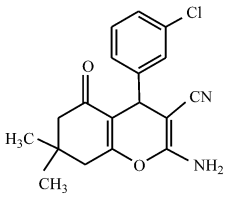
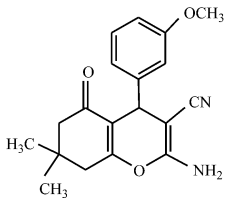
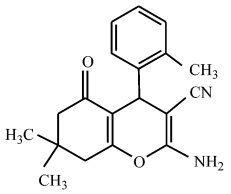
Product (5)	Ar	X	R^1	Time (min)	Yield[b] (%)	Mp (°C) Found	Mp (°C) Reported
 (5a)	C_6H_5	CN	CH_3	15 (20)	86 (84)	228–230	227–239 (ref. 9)
 (5b)	4-ClC_6H_4	CN	CH_3	15 (30)	92 (89)	209–211	206–207 (ref. 9)
 (5c)	4-$CH_3C_6H_4$	CN	CH_3	15 (15)	94 (88)	212–214	214–216 (ref. 9)
 (5d)	3-ClC_6H_4	CN	CH_3	35 (35)	91 (87)	229–230	233–234 (ref. 9)
 (5e)	3-$MeOC_6H_4$	CN	CH_3	20 (25)	90 (90)	196–198	—
 (5f)	2-MeC_6H_4	CN	CH_3	30 (25)	80 (80)	210–212	212–214 (ref. 14)

Table 2 (*Contd.*)

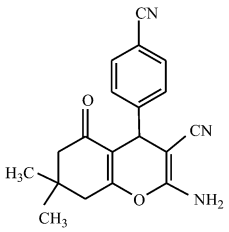
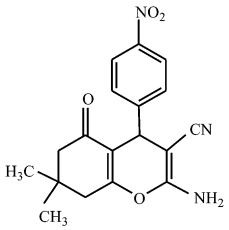
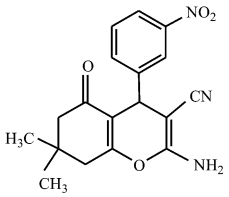
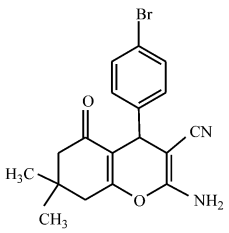
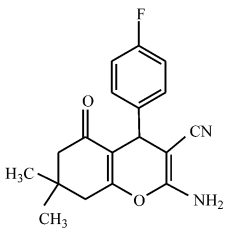
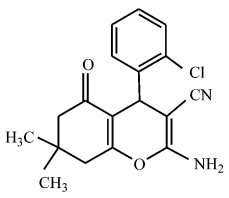
Product (5)	Ar	X	R^1	Time (min)	Yield[b] (%)	Mp (°C) Found	Mp (°C) Reported
 **(5g)**	4-CNC_6H_4	CN	CH_3	15 (25)	97 (89)	225–228	225–228 (ref. 14)
 **(5h)**	4-$NO_2C_6H_4$	CN	CH_3	15 (30)	98 (92)	180–182	177–179 (ref. 14)
 **(5i)**	3-$NO_2C_6H_4$	CN	CH_3	15 (30)	90 (82)	213–215	210–212 (ref. 14)
 **(5j)**	4-BrC_6H_4	CN	CH_3	15 (30)	94 (89)	197–199	196–198 (ref. 18)
 **(5k)**	4-FC_6H_4	CN	CH_3	20 (40)	90 (84)	190–191	191–193 (ref. 18)
 **(5l)**	2-ClC_6H_4	CN	CH_3	20 (30)	90 (84)	214–216	215–216 (ref. 18)

Table 2 (*Contd.*)

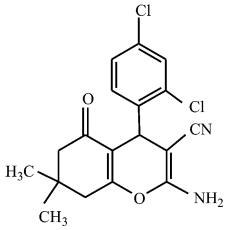
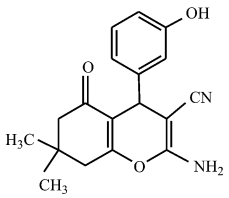
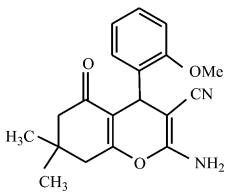
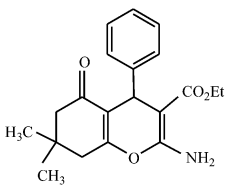
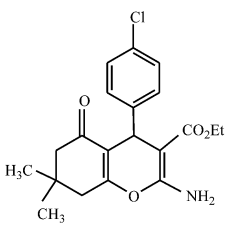
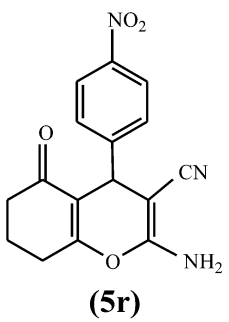
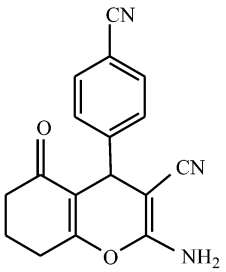
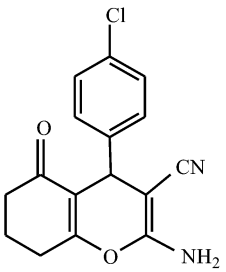
Product (5)	Ar	X	R^1	Time (min)	Yield[b] (%)	Mp (°C) Found	Mp (°C) Reported
 **(5m)**	2,4-ClC_6H_4	CN	CH_3	20 (20)	94 (90)	190–192	189–191 (ref. 18)
 **(5n)**	3-HOC_6H_5	CN	CH_3	60 (60)[c]	82 (74)	236–238	236–238 (ref. 18)
 **(5o)**	2-$MeOC_6H_4$	CN	CH_3	30 (25)	84 (82)	210–212	212–214 (ref. 21)
 **(5p)**	C_6H_5	CO_2Et	CH_3	10 (10)[c]	62 (45)	155–157	158–160 (ref. 13)
 **(5q)**	4-ClC_6H_4	CO_2Et	CH_3	6 (5)[c]	70 (68)	149–150	153–155 (ref. 13)
 **(5r)**	4-$NO_2C_6H_4$	CN	H	15 (15)	92 (90)	230–232	234–235 (ref. 24)

Table 2 (*Contd.*)

Product (5)	Ar	X	R^1	Time (min)	Yield[b] (%)	Mp (°C) Found	Mp (°C) Reported
 (5s)	4-CNC_6H_4	CN	H	15 (15)	90 (90)	229–232	234–236 (ref. 24)
 (5t)	4-ClC_6H_4	CN	H	25 (35)	84 (80)	224–226	226–228 (ref. 24)

[a] The reaction times and yields obtained under solvent-free conditions are given in parentheses. [b] Isolated yields. [c] The reaction time is hour.

yield. This two-step procedure allows the one-pot four component reaction to be controlled, avoiding the separation of intermediates, as well as time-consuming and costly purification processed. Subsequently, this study was used to develop a four-component synthesis of diverse pyranopyrazoles (Table 4).

Reusability of the catalyst was also investigated. For this purpose, the same model reaction was again studied under optimized conditions. After completion of the reaction, the reaction mixture was filtered in hot condition to separate the catalyst, dried at 120 °C for 4 h, and reused for similar reaction. The catalyst could be reused at least three times without significant loss of activity (Fig. 1).

The catalyst $NH_4H_2PO_4/Al_2O_3$ prepared by impregnation of nano-alumina support by $NH_4H_2PO_4$ was characterized by FT-IR spectroscopy, X-ray diffraction (XRD), thermal analysis (TGA/DTG) and Transmission electron microscopy (TEM).

The infrared spectra's of Al_2O_3 and catalyst, before and after using it, were shown in Fig. 2. Frequency comparison of IR spectra shows the appearance of absorption in region 1442 cm^{-1}. This absorption is due to the P═O stretching vibrations of OPO_3H_2 groups presence that were shown in Scheme 4.

The XRD pattern of the $NH_4H_2PO_4$/nano α-Al_2O_3 is also presented in Fig. 3. Marked peaks are attributed to nano-alumina support. Additional weak peaks are probably related to the formation of $NH_4H_2PO_4$/nano-Al_2O_3.[36–41]

Thermal analysis of initial powder of ADP/nano α-Al_2O_3 was performed at the temperature range 0 to 1000 °C. Thermal gravimetric (TGA) and differential thermal gravimetry (DTG) analysis of the ADP/nano α-Al_2O_3 was investigated by raising its temperature at the rate of 5°C min^{-1} in air up to 1000 °C to analyze its thermal decomposition behavior. According to the TGA curve and its derivative (DTG), two peak weight loss have been specified at temperatures 501 and 875 °C. Weight loss at 875 °C is possibly due to decomposition of ADP. Weight loss at 501 °C is due to decomposition of nano α-Al_2O_3. At temperatures above 600 °C, the phase diagram became Constant for the formation of the phase of ADP/nano α-Al_2O_3. Also, at temperatures above 900 °C the phase diagram became Constant for the formation of the phase II of ADP/nano α-Al_2O_3 (Fig. 4).

The supported catalyst was consisted with TEM results (Fig. 5). As shown in Fig. 5, the $NH_4H_2PO_4$/nano α-Al_2O_3 powder indicated strong agglomeration of particles with varied spherical sizes showed that the particles were of irregular shape with a wide size distribution. This is quite reasonable because of the varying particle size of the powder, as shown in XRD patterns.

A plausible mechanism for one-pot synthesis of 2-amino-3-cyano-4-aryl-7,7-dimethyl-5,6,7,8-tetrahydrobenzo[*b*]pyrans and 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles were given in Scheme 5.

Table 3 Preparation of 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles derivatives using $NH_4H_2PO_4/Al_2O_3$ as catalyst[a]

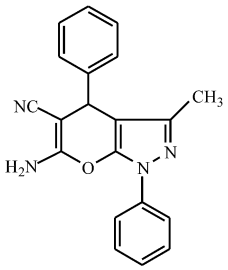
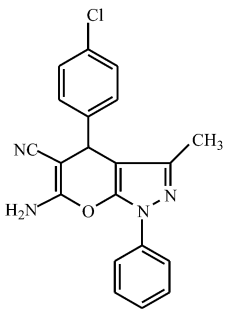
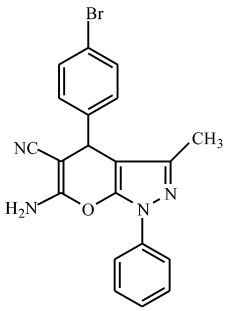
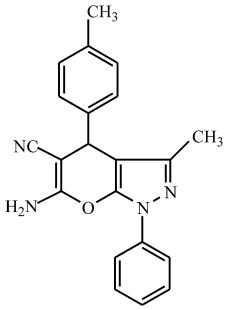
Product (6)	Ar	X	Time (min)	Yield[b] (%)	Mp (°C) Found	Mp (°C) Reported
 (6a)	C_6H_5	CN	15 (15)	84 (80)	165–166	168–170 (ref. 7)
 (6b)	4-ClC_6H_4	CN	20 (20)	94 (85)	182–184	186–187 (ref. 7)
 (6c)	4-BrC_6H_4	CN	40 (20)	94 (85)	185–186	183–184 (ref. 7)
 (6d)	4-$CH_3C_6H_4$	CN	30 (20)	89 (85)	176–178	174–175 (ref. 7)

Table 3 (*Contd.*)

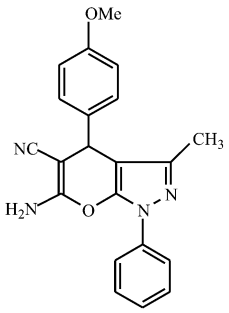
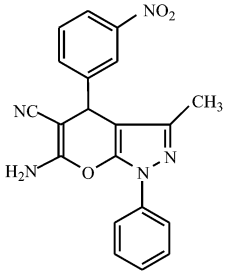
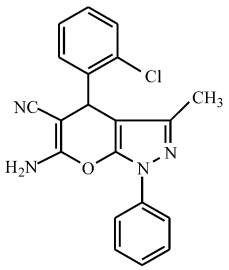
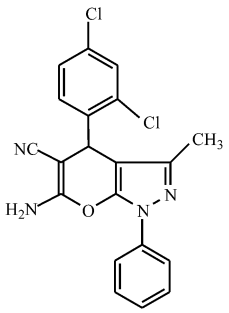
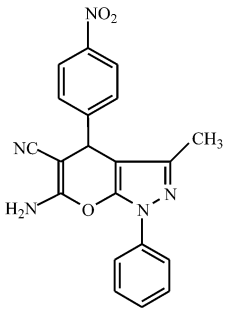
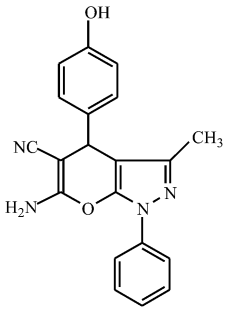
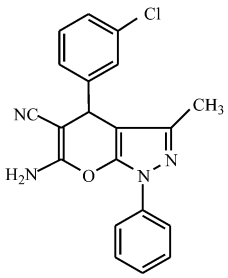
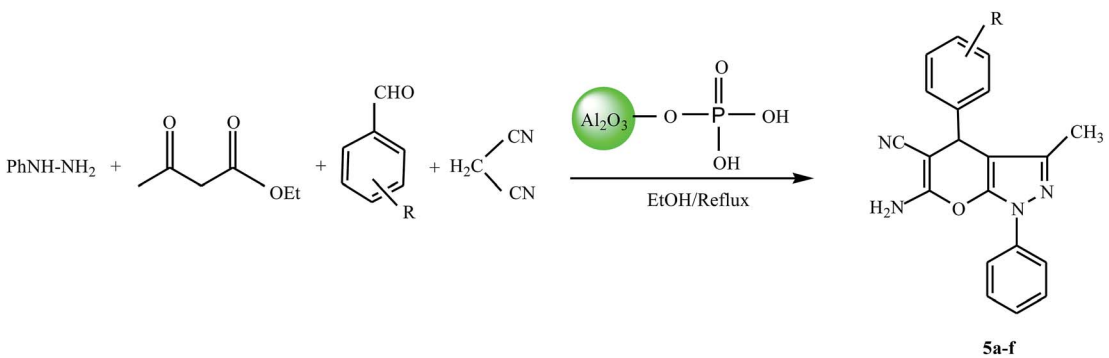
Product (6)	Ar	X	Time (min)	Yield[b] (%)	Mp (°C) Found	Mp (°C) Reported
 **(6e)**	4-$MeOC_6H_4$	CN	20 (20)	82 (80)	170–172	171–172 (ref. 7)
 **(6f)**	3-$NO_2C_6H_4$	CN	20 (15)	74 (86)	190–192	188–190 (ref. 7)
 **(6g)**	2-ClC_6H_4	CN	20 (15)	82 (80)	147–149	144–146 (ref. 7)
 **(6h)**	2,4-$Cl_2C_6H_4$	CN	20 (15)	90 (86)	180–182	182–184 (ref. 7)

Table 3 (*Contd.*)

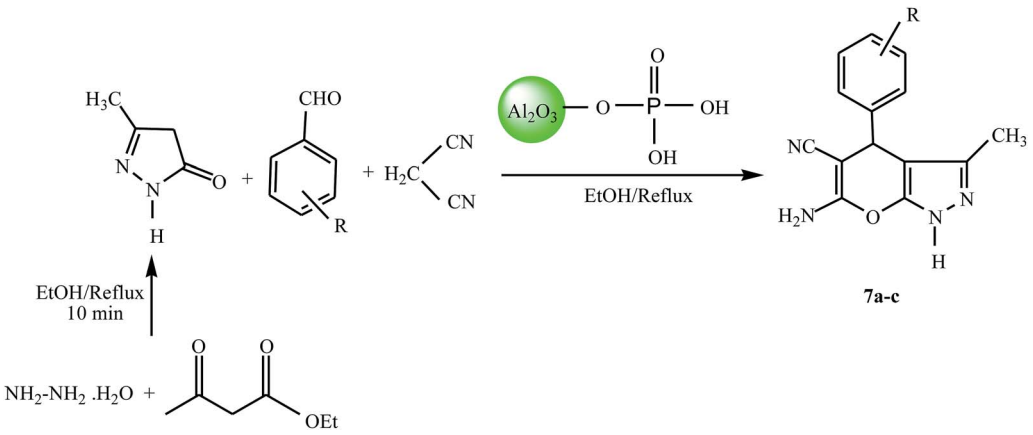
Product (6)	Ar	X	Time (min)	Yield[b] (%)	Mp (°C) Found	Mp (°C) Reported
 **(6i)**	4-$NO_2C_6H_4$	CN	20 (20)	82 (80)	199–197	194–196 (ref. 7)
 **(6j)**	4-HOC_6H_4	CN	15 (15)	90 (80)	208–210	206–207 (ref. 7)
 **(6K)**	3-ClC_6H_4	CN	20 (15)	91 (82)	152–154	148–150 (ref. 7)

[a] The reaction times and yields obtained under solvent-free conditions are given in parentheses. [b] Isolated yields.



5a-f

Scheme 2 Four-component synthesis of 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-c]pyrazoles.



Scheme 3 Preparation of 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles by condensation of four-component.

Experimental

IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer (KBr pellets). ^{1}H NMR spectra were obtained using a Bruker 300 MHz spectrometer in DMSO-d_6 or $CDCl_3$ using TMS as an internal reference. Melting points were determined in open capillary tubes in a Stuart BI Branstead Electrothermal Cat no.:IA9200 apparatus and uncorrected. TEM micrograph were characterized by Philips CM_{10}, TGA and DTG curves were characterized by Shimadzu 50.

General procedure for the synthesis of 2-amino-3-cyano-4-aryl-7,7-dimethyl-5,6,7,8-tetrahydrobenzo[*b*]pyrans and 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles

A mixture of aldehyde (**1**, 1 mmol), malononitrile (**2**, 2 mmol), 1,3-dicarbonyl compounds [1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione] (**3**, 1 mmol) or 3-methyl-1-phenyl-2-pyrazoline-5-one (**4**, 1 mmol) and $NH_4H_2PO_4/Al_2O_3$ (0.03 g) in EtOH (96%, 3 ml) was stirred on an oil bath under reflux condition for a suitable time (Table 1). The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered in hot condition to separate the catalyst, poured into crushed ice and the solid product, which was separated, filtered and recrystallized from ethanol to get pure crystalline 2-amino-3-cyano-4-aryl-7,7-dimethyl-5,6,7,8-tetrahydrobenzo[*b*]pyrans and 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles. In separated positions, this reaction carried out under solvent-free at 80 °C.

Preparation of the catalyst $NH_4H_2PO_4$/nano α-Al_2O_3

The catalyst was prepared by mixing nano α-Al_2O_3 (2.5 g) with a solution of $NH_4H_2PO_4$ (0.6 g, 5 mmol) in distilled water (10 ml). The resulting mixture was stirred for 30 min to absorb $NH_4H_2PO_4$ on surface of nano alumina. After removal of water in a rotary evaporator, the solid powder was dried at 120 °C for 2–3 h under reduced pressure. The drying temperature was maintained below the decomposition temperatures of the salts. The amount of H^+ in the $NH_4H_2PO_4$/nano α-Al_2O_3 determined by acid base titration was 0.5 mmol g^{-1}.

2-Amino-3-cyano-4-(phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5a). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.04 (s, 3H), 1.13 (s, 3H), 2.11–2.21 (m, 2H), 2.42 (s, 2H), 4.67 (s, 1H), 6.52 (brs, 2H, D_2O exchangeable), 7.14–7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 26.32, 27.65, 31.24, 35.09, 39.08, 49.98, 59.74, 113.09, 118.42, 125.86, 126.63, 127.54, 142.68, 158.54, 162.32, 194.24; IR (KBr disc, cm^{-1}): 3314, 3202, 2214, 1688, 1624, 1507, 1482, 1370.

2-Amino-3-cyano-4-(4-chloro phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5b). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.98 (s, 3H), 1.03 (s, 3H), 2.13–2.24 (m, 2H), 2.47 (s, 2H), 4.16 (s, 1H), 6.62 (brs, 2H, D_2O exchangeable), 7.16 (d, 2H), 7.42 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 25.63, 27.44, 31.68, 34.69, 39.98, 50.28, 60.54, 114.87, 119.62, 124.74, 127.89, 128.32, 141.76, 159.54, 161.56, 196.76; IR (KBr disc, cm^{-1}): 3370, 3178, 2198, 1678, 1620, 1507, 1490, 1384.

2-Amino-3-cyano-4-(4-methyl phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5c). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.97 (s, 3H), 1.05 (s, 3H), 2.14 (d, 1H), 2.21 (d, 1H), 2.47–2.76 (m, 2H), 4.45 (s, 1H), 6.92 (brs, 2H, D_2O exchangeable), 7.04 (d, 2H), 7.09 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 26.98, 28.34, 30.65, 33.98, 36.67, 39.08, 51.61, 61.54, 112.93, 118.82, 125.44, 126.61, 126.96, 142.64, 153.67, 162.32, 194.72; IR (KBr disc, cm^{-1}): 3392, 3205, 2190, 1670, 1630, 1598, 1486, 1410.

2-Amino-3-cyano-4-(3-chloro phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5d). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.98 (s, 3H), 1.06 (s, 3H), 2.09 (d, 2H), 2.26 (d, 2H), 4.78 (s, 1H), 6.64 (brs, 2H, NH_2, D_2O exchangeable), 7.09–7.16 (m, 3H), 7.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 26.30, 27.62, 31.33, 35.98, 39.43, 51.98, 59.96, 113.44, 118.19, 127.21, 129.89, 130.76, 142.76, 157.08, 162.61, 196.009; IR (KBr disc, cm^{-1}): 3398, 3201, 2196, 1676, 1622, 1506, 1482, 1370.

2-Amino-3-cyano-4-(3-methoxyphenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5e). ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ 0.92 (s, 3H), 1.01 (s, 3H), 2.05 (d, 2H), 2.66 (d, 2H), 3.45 (s, 3H), 4.17 (s, 1H), 7.06 (brs, 2H, D_2O exchangeable), 7.13–7.26 (m, 3H), 7.34 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 27.30, 28.78, 32.33, 35.52, 35.58, 38.43, 50.44, 58.41,

Table 4 Preparation of 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles derivatives by four component reaction using $NH_4H_2PO_4$/Al_2O_3 as catalyst

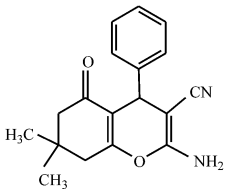
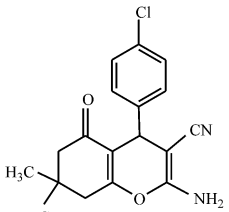
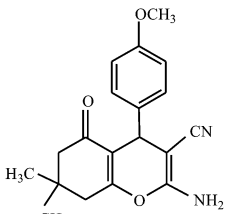
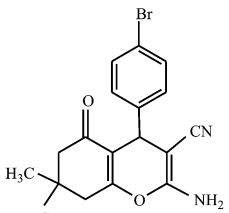
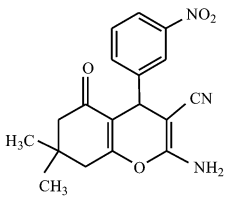
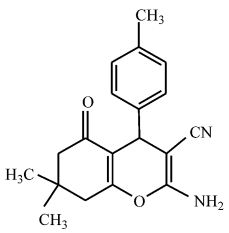
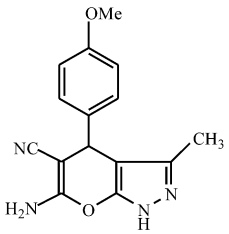
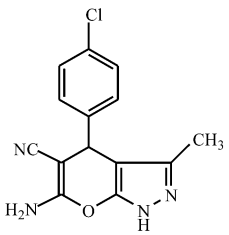
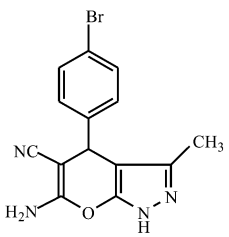
Products (5 or 7)	Ar	X	Time (min)	Yield[a] (%)	Mp (°C) Found	Mp (°C) Reported
 (5a)	C_6H_5	CN	160	78	165–166	168–170 (ref. 9)
 (5b)	4-ClC_6H_4	CN	80	80	174–175	174–175 (ref. 9)
 (5c)	4-$CH_3OC_6H_4$	CN	120	80	174–175	170–172 (ref. 9)
 (5d)	4-BrC_6H_4	CN	80	82	184–186	183–184 (ref. 9)
 (5e)	3-$NO_2C_6H_4$	CN	80	86	188–190	188–190 (ref. 9)
 (5f)	4-$CH_3C_6H_4$	CN	180	73	217–219	214–216 (ref. 9)

Table 4 (*Contd.*)

Products (5 or 7)	Ar	X	Time (min)	Yield[a] (%)	Mp (°C) Found	Mp (°C) Reported
 (7a)	4-$MeOC_6H_4$	CN	75	72	213–215	212–213 (ref. 7)
 (7b)	4-ClC_6H_4	CN	80	74	236–238	234–235 (ref. 7)
 (7c)	4-BrC_6H_4	CN	80	78	244–246	249–250 (ref. 7)

[a] Isolated yields.

112.74, 120.19, 128.91, 129.63, 131.80, 144.16, 158.98, 163.61, 197.00; IR (KBr disc, cm^{-1}): 3370, 3180, 2185, 1660, 1624, 1509, 1492, 1380.

2-Amino-3-cyano-4-(2-methyl phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5f). ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ 0.95 (s, 3H), 1.08 (s, 3H), 2.12 (d, 1H), 2.21 (d, 1H), 2.37–2.56 (m, 2H), 2.78 (s, 3H), 4.41 (s, 1H), 6.06 (brs, 2H, D_2O exchangeable), 7.35–7.58 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 25.30, 26.32, 32.33, 34.12, 36.08, 39.93, 51.64, 59.96, 113.65, 121.89, 124.76, 129.03, 132.09, 142.56, 156.06, 161.61, 193.64; IR (KBr disc, cm^{-1}): 3390, 3280, 2197, 1690, 1623, 1595, 1472, 1389.

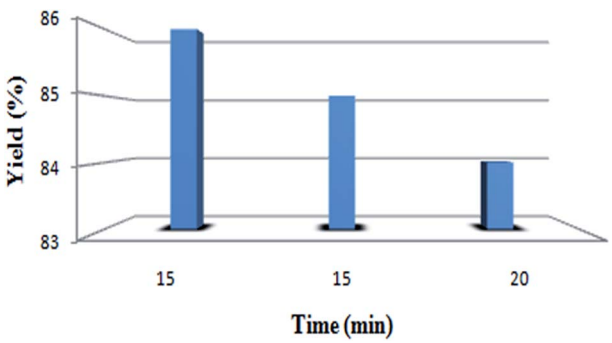


Fig. 1 Reuse of the $NH_4H_2PO_4/Al_2O_3$ for synthesis of **5a**.

2-Amino-3-cyano-4-(4-cyano phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5g). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.02 (s, 3H), 1.08 (s, 3H), 2.28–2.32 (m, 2H), 2.46 (s, 2H), 5.16 (s, 1H), 5.67 (brs, 2H, D_2O exchangeable), 7.43 (d, 2H), 7.77 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 25.63, 26.44, 30.68, 35.69, 39.08, 51.68, 61.54, 114.87, 119.62, 121.78, 126.74, 127.09, 128.02, 143.56, 160.91, 162.76, 197.06; IR (KBr disc, cm^{-1}): 3470, 3278, 2198, 1670, 1620, 1509, 1498, 1381.

2-Amino-3-cyano-4-(4-nitrophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5h). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.04 (s, 3H), 1.18 (s, 3H), 2.26–2.51 (m, 2H), 2.59 (s, 2H), 5.26 (s, 1H), 6.12 (brs, 2H, D_2O exchangeable), 7.56

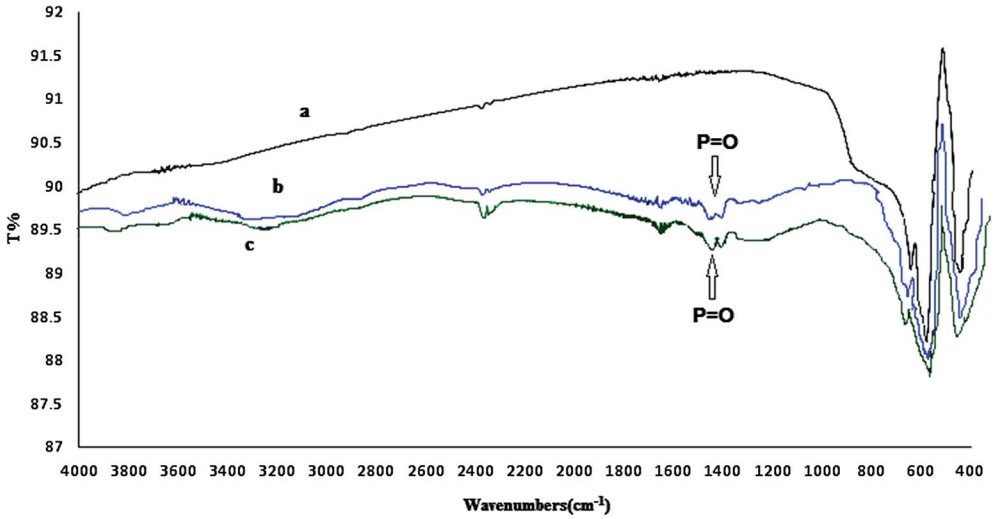
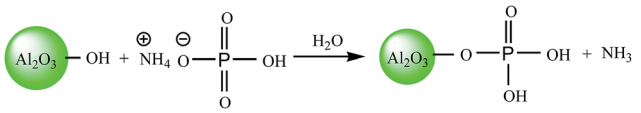


Fig. 2 FT-IR Spectra of (a) Al_2O_3, (b) fresh $NH_4H_2PO_4/Al_2O_3$, (c) recovered $NH_4H_2PO_4/Al_2O_3$.



Scheme 4 Preparation of $NH_4H_2PO_4/Al_2O_3$.

(d, 2H), 8.09 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 26.98, 27.44, 31.08, 35.87, 40.18, 51.88, 62.54, 113.67, 119.02, 127.74, 127.97, 129.02, 144.32, 161.61, 165.78, 197.24; IR (KBr disc, cm^{-1}): 3401, 3307, 2200, 1690, 1598, 1498, 1468, 1375.

2-Amino-3-cyano-4-(3-nitro phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5i). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.02 (s, 3H), 1.06 (s, 3H), 2.16–2.24 (m, 2H), 2.39 (s, 2H), 4.84 (s, 1H), 6.09 (brs, 2H, NH_2, D_2O exchangeable), 7.19–7.32 (m, 3H), 7.44 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 26.32, 27.98, 31.53, 35.05, 39.73, 51.24, 59.74, 113.04, 118.19, 126.21, 126.89, 130.65, 141.76, 156.08, 161.91, 193.65; IR (KBr disc, cm^{-1}): 3346, 3297, 2189, 1680, 1588, 1498, 1478, 1389.

2-Amino-3-cyano-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5j). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.96 (s, 3H), 1.01 (s, 3H), 2.12–2.21 (m, 2H), 2.37 (s, 2H), 4.15 (s, 1H), 6.02 (brs, 2H, D_2O exchangeable), 7.46 (d, 2H), 7.78 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 25.13, 27.44, 31.08, 35.76, 39.12, 50.74, 60.04, 113.45, 118.02, 123.12, 126.09, 128.13, 140.76, 157.34, 160.14, 193.97; IR (KBr disc, cm^{-1}): 3325, 3187, 2194, 1675, 1604, 1545, 1468, 1386.

2-Amino-3-cyano-4-(4-flouro phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5k). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.00 (s, 3H), 1.08 (s, 3H), 2.20–2.22 (m, 2H), 2.40 (s, 2H), 4.24 (s, 1H), 5.78 (brs, 2H, D_2O exchangeable), 7.17 (d, 2H), 7.28 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 26.14, 27.78, 30.89, 35.78, 38.12, 49.82, 61.54, 113.89, 118.98, 122.12, 127.56, 129.53, 141.86, 158.54, 160.05, 195.04; IR (KBr disc, cm^{-1}): 3376, 3200, 2201, 1678, 1624, 1589, 1466, 1380.

2-Amino-3-cyano-4-(2-chloro phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5l). ^{1}H NMR (300 MHz, $CDCl_3$,

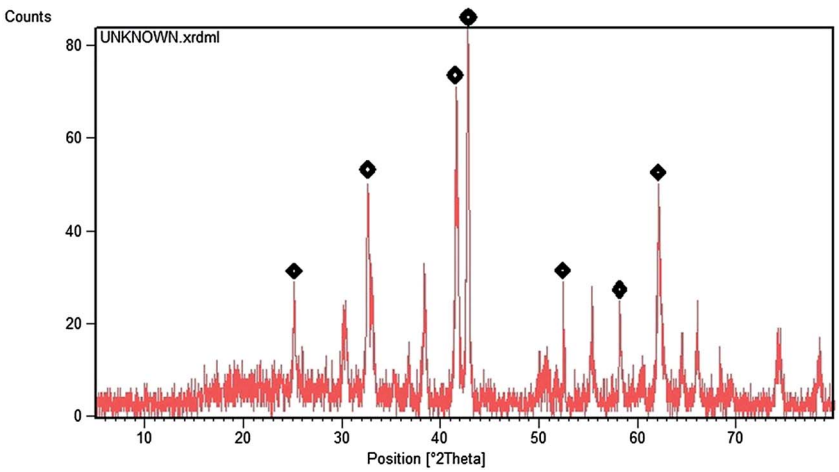


Fig. 3 XRD patterns of $NH_4H_2PO_4$/nano-Al_2O_3.

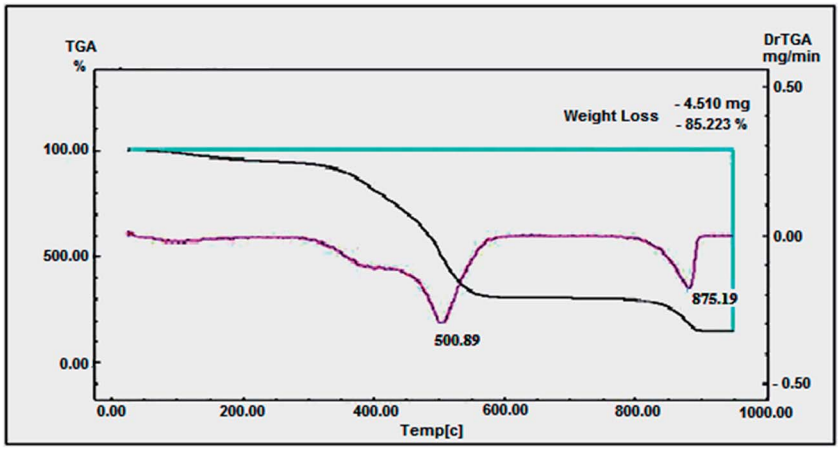


Fig. 4 TGA and DTG curves of $NH_4H_2PO_4$/nano α-Al_2O_3.

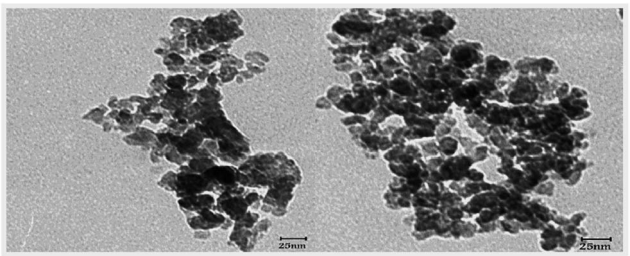


Fig. 5 TEM micrograph of $NH_4H_2PO_4$/nano α-Al_2O_3.

ppm) δ 0.97 (s, 3H), 1.02 (s, 3H), 2.08–2.22 (m, 2H), 2.42 (s, 2H), 4.56 (s, 1H), 5.96 (brs, 2H, D_2O exchangeable), 7.45–7.78 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 25.56, 26.02, 32.67, 36.08, 40.65, 50.65, 60.78, 113.56, 119.87, 123.46, 129.03, 131.09, 143.12, 156.06, 160.13, 195.67; IR (KBr disc, cm^{-1}): 3382, 3312, 2191, 1664, 1617, 1585, 1470, 1389.

2-Amino-3-cyano-4-(2,4-dichloro phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5m). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.01 (s, 3H), 1.12 (s, 3H), 2.13–2.22 (m, 2H), 2.47 (s, 2H), 4.45 (s, 1H), 5.85 (brs, 2H, D_2O exchangeable), 7.15–7.38 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 26.06, 26.42, 33.67, 35.12, 40.79, 51.45, 60.23, 113.12, 118.47, 122.12, 129.13, 130.18, 142.12, 155.45, 160.78, 193.14; IR (KBr disc, cm^{-1}): 3388, 3289, 2187, 1698, 1624, 1595, 1489, 1379.

2-Amino-3-cyano-4-(3-hydroxy phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5n). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.05 (s, 3H), 1.14 (s, 3H), 2.12–2.23 (m, 2H), 2.44 (s, 2H), 4.34 (s, 1H), 5.58 (brs, 2H, D_2O exchangeable), 7.01–7.33 (m, 3H), 8.14 (brs, 1H, D_2O exchangeable); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 26.35, 26.98, 31.03, 35.67, 39.54, 51.63, 59.24, 113.78, 118.98, 126.45, 127.76, 130.78, 140.79, 155.09, 164.13, 194.89; IR (KBr disc, cm^{-1}): 3650, 3325, 3120, 2195, 1679, 1645, 1586, 1478, 1382.

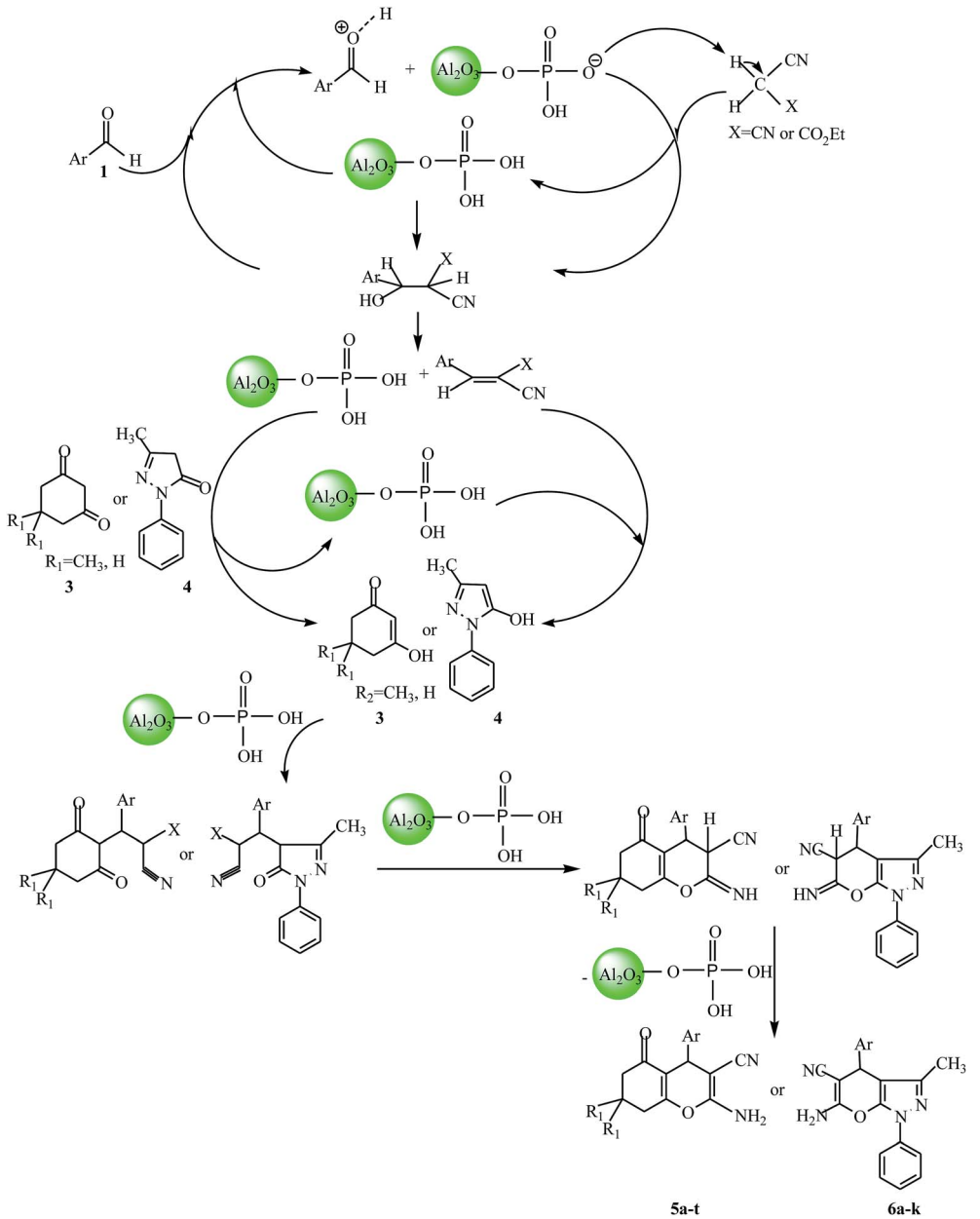
2-Amino-3-cyano-4-(2-methoxy phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5o). ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ 0.98 (s, 3H), 1.12 (s, 3H), 2.12–2.23 (m, 2H), 2.34 (s, 2H), 3.87 (s, 3H), 4.68 (s, 1H), 6.64 (brs, 2H, D_2O exchangeable), 7.24–7.61 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 25.42, 26.41, 29.87, 31.65, 36.08, 40.03, 51.04, 60.43, 113.12, 120.06, 123.76, 129.03, 133.09, 140.06, 154.06, 160.32, 194.04; IR (KBr disc, cm^{-1}): 3384, 3288, 2199, 1680, 1620, 1590, 1470, 1372.

2-Amino-3-ethylacetato-4-(phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5p). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.01 (s, 3H), 1.08 (s, 3H), 1.24 (t, 3H), 2.16–2.25 (m, 2H), 2.34 (s, 2H), 4.24 (q, 2H), 4.37 (s, 1H), 5.52 (brs, 2H, D_2O exchangeable), 7.12–7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 19.12, 26.52, 27.65, 31.44, 35.56, 39.68, 50.15, 60.63, 71.47, 113.09, 126.42, 126.86, 127.03, 142.54, 156.68, 161.87, 172.42, 196.01; IR (KBr disc, cm^{-1}): 3423, 3265, 3020, 2980, 1667, 1614, 1520, 1462, 1378.

2-Amino-3-ethylacetato-4-(phenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5q). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.04 (s, 3H), 1.09 (s, 3H), 1.12 (t, 3H), 2.26–2.35 (m, 2H), 2.62 (s, 2H), 4.05 (q, 2H), 4.26 (s, 1H), 5.98 (brs, 2H, D_2O exchangeable), 7.32 (d, 2H), 7.56 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 19.43, 26.56, 26.94, 31.78, 36.01, 40.04, 51.25, 61.42, 70.97, 113.24, 127.42, 127.96, 128.57, 143.54, 159.68, 161.05, 171.32, 195.62; IR (KBr disc, cm^{-1}): 3412, 3258, 3020, 2986, 1664, 1612, 1568, 1489, 1389.

2-Amino-3-cyano-4-(4-nitro phenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5r). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 2.10–2.20 (m, 2H), 2.41–2.55 (m, 2H), 2.80–2.88 (m, 1H), 2.93–3.00 (m, 1H), 5.68 (s, 1H), 6.09 (brs, 2H, D_2O exchangeable), 7.32 (d, 2H), 7.84 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 20.87, 27.98, 35.43, 37.61, 50.43, 61.21, 114.32, 118.76, 126.03, 126.68, 130.02, 142.02, 160.45, 163.18, 198.23; IR (KBr disc, cm^{-1}): 3388, 3345, 2219, 1687, 1598, 1490, 1468, 1389.

2-Amino-3-cyano-4-(4-cyano phenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5s). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 2.08–2.10 (m, 2H), 2.45–2.48 (m, 2H), 2.81–2.89 (m, 1H), 2.92–2.99 (m, 1H), 5.48 (s, 1H), 6.31 (brs, 2H, D_2O exchangeable), 7.32 (d, 2H), 7.74 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 20.46, 27.67, 35.00, 37.19, 51.44, 60.56, 113.78, 118.09, 126.34, 126.96, 131.34, 141.45, 161.05, 164.78, 196.01; IR (KBr disc, cm^{-1}): 3324, 3189, 2198, 1667, 1616, 1583, 1478, 1391.



Scheme 5 Proposed mechanisms.

2-Amino-3-cyano-4-(4-chloro phenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[*b*]pyran (5t). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 2.09–2.21 (m, 2H), 2.41–2.54 (m, 2H), 2.80–2.88 (m, 1H), 2.93–3.00 (m, 1H), 5.58 (s, 1H), 6.09 (brs, 2H, D_2O exchangeable), 7.15 (d, 2H), 7.44 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 20.50, 27.55, 33.15, 37.09, 50.45, 59.13, 113.24, 118.67, 126.45, 126.06, 130.14, 140.05, 159.05, 162.34, 192.46; IR (KBr disc, cm^{-1}): 3320, 3192, 2193, 1680, 1619, 1576, 1462, 1376.

6-Amino-3-methyl-5-cyano-4-(phenyl)1,4-dihydropyrano[2,3-*c*]pyrazole (6a). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.77 (s, 3H), 5.16 (s, 1H), 7.28–7.48 (m, 10H), 7.78 (brs, 2H, D_2O exchangeable); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 25.02, 40.43, 50.45, 59.13, 113.24, 118.67, 126.45, 126.06, 127.67, 128.03, 128.98, 129.14, 130.14, 140.05, 154.05, 162.34; IR (KBr disc, cm^{-1}): 3425, 3332, 2200, 1620, 1590, 1484, 1386.

6-Amino-3-methyl-5-cyano-4-(4-chlorophenyl)1,4-dihydropyrano[2,3-*c*]pyrazole (6b). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.98 (s, 3H), 5.32 (s, 1H), 7.08–7.57 (m, 9H), 6.50 (brs, 2H, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 26.32, 40.02, 51.35, 60.72, 113.05, 118.24, 125.09, 126.67, 126.98, 128.78, 129.09, 130.65, 131.43, 141.31, 152.54, 160.01; IR (KBr disc, cm^{-1}): 3432, 3298, 2194, 1612, 1594, 1459, 1367.

6-Amino-3-methyl-5-cyano-4-(4-bromophenyl)1,4-dihydropyrano[2,3-*c*]pyrazole (6c). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 2.01 (s, 3H), 4.89 (s, 1H), 6.05 (brs, 2H, D_2O exchangeable), 6.96–7.47 (m, 9H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 25.01, 40.76, 51.05, 61.63, 113.96, 119.04, 125.46, 126.09, 126.42,

128.01, 129.76, 130.05, 131.57, 142.42, 151.52, 161.43; IR (KBr disc, cm^{-1}): 3392, 3278, 2221, 1610, 1568, 1445, 1346.

6-Amino-3-methyl-5-cyano-4-(4-methylphenyl)1,4-dihydropyrano[2,3-*c*]pyrazole (6d). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.01 (s, 3H), 2.46 (s, 3H), 5.12 (s, 1H), 5.98 (brs, 2H, D_2O exchangeable), 7.11–7.79 (m, 9H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 25.18, 26.56, 41.04, 50.25, 60.63, 113.24, 118.04, 125.13, 126.45, 127.52, 128.18, 129.89, 130.68, 131.43, 141.67, 153.69, 160.11; IR (KBr disc, cm^{-1}): 3413, 3321, 2196, 1620, 1589, 1448, 1381.

6-Amino-3-methyl-5-cyano-4-(4-methoxyphenyl)1,4-dihydropyrano[2,3-*c*]pyrazole (6e). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.68 (s, 3H), 3.89 (s, 3H), 5.76 (s, 1H), 6.45 (brs, 2H, D_2O exchangeable), 7.09–7.98 (m, 9H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 25.32, 36.12, 40.04, 51.05, 59.61, 113.78, 119.14, 125.79, 126.54, 127.02, 128.38, 129.11, 130.18, 131.67, 140.67, 151.67, 158.52; IR (KBr disc, cm^{-1}): 3389, 3292, 2197, 1618, 1576, 1454, 1372.

6-Amino-3-methyl-5-cyano-4-(3-nitrophenyl)1,4-dihydropyrano[2,3-*c*]pyrazole (6f). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.79 (s, 3H), 5.16 (s, 1H), 6.05 (brs, 2H, D_2O exchangeable), 7.19–7.68 (m, 8H), 8.01 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 25.67, 41.12, 51.61, 61.05, 113.78, 119.14, 125.79, 126.54, 126.98, 127.32, 128.12, 128.67, 129.34, 130.78, 131.05, 140.67, 154.67, 159.89; IR (KBr disc, cm^{-1}): 3420, 3310, 2198, 1618, 1598, 1568, 1490, 1386.

6-Amino-3-methyl-5-cyano-4-(2-chlorophenyl)1,4-dihydropyrano[2,3-*c*]pyrazole (6g). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.09 (s, 3H), 5.01 (s, 1H), 6.65 (brs, 2H, D_2O exchangeable), 7.01–7.78 (m, 9H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 25.12, 39.46, 49.01, 60.14, 113.08, 118.14, 125.09, 126.78, 127.08, 127.32, 128.45, 128.98, 129.89, 131.12, 131.95, 139.07, 156.04, 160.34; IR (KBr disc, cm^{-1}): 3422, 3318, 2195, 1617, 1568, 1494, 1375.

6-Amino-3-methyl-5-cyano-4-(2,4-dichlorophenyl)1,4-dihydropyrano[2,3-*c*]pyrazole (6h). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.78 (s, 3H), 5.16 (s, 1H), 7.32–7.42 (m, 5H), 7.50 (brs, 2H, D_2O exchangeable), 7.63 (s, 1H), 7.78–7.80 (d, 2H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 25.07, 40.34, 50.43, 60.01, 113.45, 118.64, 125.12, 126.14, 126.78, 127.42, 128.11, 128.67, 129.89, 130.43, 131.45, 141.67, 153.43, 160.32; IR (KBr disc, cm^{-1}): 3450, 3320, 2200, 1614, 1590, 1482, 1390.

6-Amino-3-methyl-5-cyano-4-(4-nitrophenyl)1,4-dihydropyrano[2,3-*c*]pyrazole (6i). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 2.03 (s, 3H), 5.87 (s, 1H), 6.45 (brs, 2H, D_2O exchangeable), 7.43–7.98 (m, 9H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 25.01, 41.56, 51.65, 61.78, 113.76, 119.67, 125.76, 126.49, 126.89, 128.69, 129.06, 130.71, 131.07, 141.42, 153.64, 160.02; IR (KBr disc, cm^{-1}): 3410, 3317, 2193, 1620, 1586, 1570, 1493, 1393.

6-Amino-3-methyl-5-cyano-4-(4-hydroxyphenyl)1,4-dihydropyrano[2,3-*c*]pyrazole (6j). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.89 (s, 3H), 5.17 (s, 1H), 6.15 (brs, 2H, D_2O exchangeable), 7.13–7.87 (m, 9H), 8.24 (brs, 1H, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 25.78, 41.96, 51.02, 60.08, 113.54, 118.43, 125.92, 126.09, 126.59, 128.44, 129.32, 130.32, 131.49, 140.42, 152.21, 160.22; IR (KBr disc, cm^{-1}): 3654, 3379, 3289, 2198, 1610, 1576, 1471, 1382.

6-Amino-3-methyl-5-cyano-4-(3-chlorophenyl)1,4-dihydropyrano[2,3-*c*]pyrazole (6k). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.65 (s, 3H), 4.89 (s, 1H), 6.76 (brs, 2H, D_2O exchangeable), 7.43–7.84 (m, 8H), 8.65 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 26.07, 39.14, 50.24, 60.23, 113.08, 118.14, 125.79, 126.54, 126.08, 127.12, 128.02, 128.67, 129.89, 130.78, 131.75, 140.67, 152.67, 160.21; IR (KBr disc, cm^{-1}): 3421, 3318, 2211, 1605, 1576, 1492, 1393.

6-Amino-3-methyl-4-(4-methoxyphenyl)-1,4-dihydro-pyrano[2,3-*c*]pyrazole-5-carbonitrile (7a). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.79 (s, 3H), 3.45 (s, 3H), 4.56 (s, 1H), 6.88 (brs, 2H, D_2O exchangeable), 7.10 (d, 2H), 7.19 (d, 2H), 12.01 (s, 1H, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ) δ 10.22, 35.17, 36.01, 57.64, 97.82, 121.31, 126.04, 128.64, 136.19, 136.07, 141.64, 155.22, 161.35; IR (KBr disc, cm^{-1}): 3483, 3254, 2191, 1641, 1608, 1492, 1390.

6-Amino-3-methyl-4-(4-chloroxyphenyl)-1,4-dihydro-pyrano[2,3-*c*]pyrazole-5-carbonitrile (7b). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.78 (s, 3H), 4.86 (s, 1H), 6.78 (brs, 2H, D_2O exchangeable), 7.18 (d, 2H), 7.45 (d, 2H), 12.22 (s, 1H, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 10.02, 33.62, 55.17, 96.38, 120.71, 128.05, 129.36, 132.68, 133.30, 135.19, 140.64, 155.64, 161.08; IR (KBr disc, cm^{-1}): 3481, 3252, 2187, 1643, 1593, 1492, 1410.

6-Amino-3-methyl-4-(4-bromophenyl)-1,4-dihydro-pyrano[2,3-*c*]pyrazole-5-carbonitrile (7c). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.75 (s, 3H), 4.81 (s, 1H), 6.48 (brs, 2H, D_2O exchangeable), 7.09 (d, 2H), 7.32 (d, 2H), 12.12 (s, 1H, D_2O exchangeable); ^{13}C NMR (75 MHz, DMSO-d_6, ppm) δ 10.12, 33.62, 55.69, 96.23, 120.01, 128.45, 129.79, 132.54, 133.30, 135.21, 140.54, 155.89, 161.98; IR (KBr disc, cm^{-1}): 3444, 3238, 2195, 1637, 1600, 1491, 1394.

Conclusion

In conclusion, we have reported a simple new catalytic method for the synthesis of 2-amino-3-cyano-4-aryl-7,7-dimethyl-5,6,7,8-tetrahydrobenzo[*b*]pyrans and 6-amino-5-cyano-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles by one-pot condensation reaction of aldehydes, malononitrile, and 1,3-dicarbonyl compounds (1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione) or 3-methyl-1-phenyl-2-pyrazoline-5-one, respectively, using $NH_4H_2PO_4/Al_2O_3$ as an reusable, safe and green heterogeneous catalyst. The notable advantages of this methodology are operational simplicity, generality, inexpensive, availability of reactants, short reaction times and easy work-up.

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