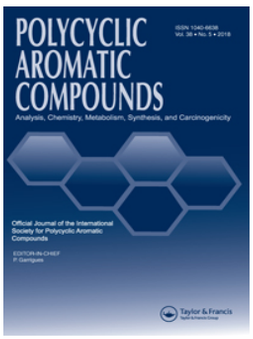

Polycyclic Aromatic Compounds

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An Efficient and Rapid Synthesis of 1,4-Dihydropyrano [2,3-c]Pyran and 1,4-Dihydropyrano[2,3-c]Quinoline Derivatives Using Copper Nanoparticles Grafted on Carbon Microspheres

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ABSTRACT

A rapid and efficient one-pot three-component synthesis of 2-amino-3-cyano-4-aryl-7-methyl-5-oxo-4,5-dihydro-pyrano-[3,2-*c*]pyran and 2-amino-3-cyano-4-aryl-6-methyl5,6-dihydro-5-oxo-4*H*-pyrano-[3,2-c]quinoline derivatives catalyzed by copper nanoparticles grafted on carbon microspheres is developed. The use of heterogeneous catalyst, mild reaction conditions, and excellent yield of the corresponding products are the key features of the present protocol.

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KEYWORDS
Cu-NP/C; pyranopyran; pyranoquinoline

Introduction

Multicomponent reactions (MCRs) are the convergent reactions in which three or more reactants combine resulting in molecular complexity.[1–2] MCRs are beneficial in terms of their atom economic, time saving, cost effective and environmentally benign nature.[3] During the past decades, MCRs have attracted the attention of organic and medicinal chemists and constitute the efficient tools of green chemistry.[4]

4*H*-Pyran skeleton containing compounds constitute an important class of organic compounds exhibiting a wide range of pharmacological and biological properties.[5] Pyran is one of the important structural motifs found widely in natural products, such as coumarins, benzopyrans, sugars, flavonoids, xanthones, etc.[6] Epicalyxins F and G, isolated from the seeds of *Alpinia blepharocalyx*, are the most potent members of this class that act as anticancer agents against human HT-1080 fibrosarcoma and murine 26-L5 carcinoma. Some biologically significant 4*H*-pyran derivatives are depicted in Figure 1. The synthesis of such compounds has attracted a strong interest owing to their biological potential.[7] Various methods have been reported for the synthesis of these compounds and their analogues such as the use of 1*H*-imidazol-3-ium tricyanomethanide,[8] iron oxide/phenyl sulfonic acid,[9] $PtCl_4$,[10] KF/Al_2O_3,[11] NH_4OAc,[12] ultrasonic irradiation,[13] β-cyclodextrin,[14] Fe_3O_4 nanoparticles,[15] and $ES/Cu(OH)_2$ nanocomposite.[16]

Pyranoquinolines constitute an important group of heterocyclic compounds present in many natural products possessing different therapeutic activities.[17] These compounds are biologically

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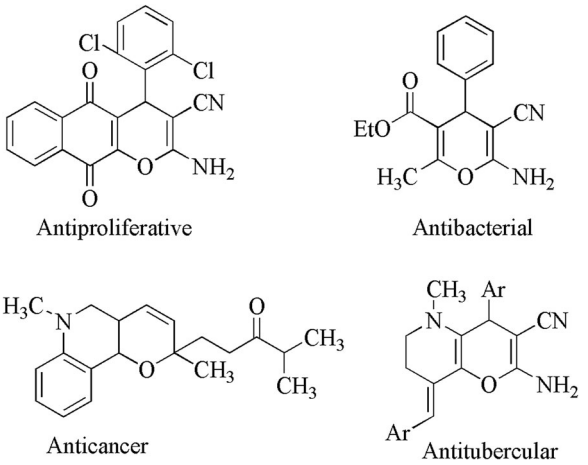


Figure 1. Some representative examples of biologically potent pyrano-pyrans.

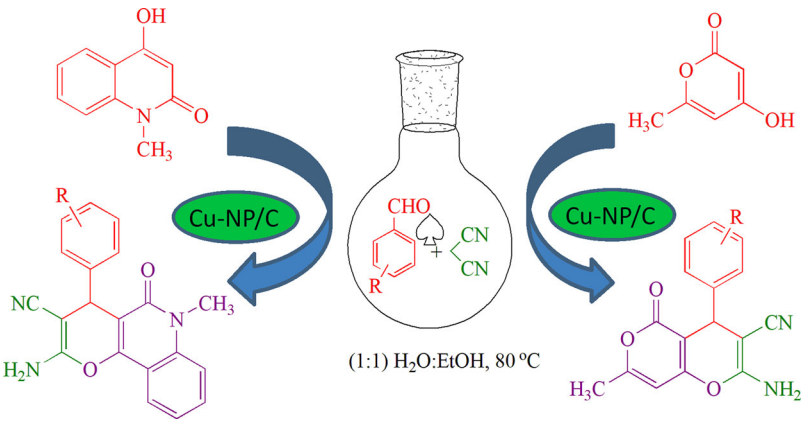
significant for exhibiting numerous activities such as antiallergic, antifungal, antibacterial, antipyretic, insecticidal, analgesic, antipyretic, cytotoxic, antiplatelet aggregation agents, and anticancer.[18] Pyranoquinoline containing alkaloids such as fusaricide, melicobisquinolinone-B, zanthosimuline, and huajiaosimuline exhibit cytotoxicity against cancer cells as potential anticancer agents. Many methods involving one-pot three-component reaction of aldehydes, malononitrile, and 4-hydroxy-2-quinolone have been documented under the catalytic influence of Et_3N,[19] L-Proline,[20] DABCO,[21] and $CoFe_2O_4$,[22] Fe_3O_4@GO-naphthalene-SO_3H,[23] *N*-butylsulfonate-functionalized MWCNTs-D-NH_2,[24] Fe_3O_4@DNH$(CH_2)_4SO_3H$,[25] SO_3H-functionalized nano-MGO-D-NH_2,[26] and [BMIM][HSO_4][27]. However, most of the methods are inconvenient due to certain drawbacks which include elaborate and tedious workup, use of toxic reagents, and large amounts of catalysts. Consequently, a new, eco-friendly, and low-cost protocol for the synthesis of pyranoquinoline derivatives is highly desirable.

Nano catalysts of copper are important nanoparticles.[28] Copper nanoparticle catalyzed reactions are advantageous over the conventional metal-catalyzed reactions in terms of low catalyst loading, high atom economy, better yields, inexpensive, shorter reaction times, and recyclability of the catalyst. Nanoparticles undergo self-aggregation and it is difficult to separate them from the reaction mixture. This limitation can be overcome by anchoring them on some supports. These developed catalytic metallic nanoparticles are inexpensive, non or minimally poisonous, highly active, stable, and easily separable from reaction mixture. Thus in continuation of our previous work on copper nanoparticles grafted on carbon microspheres;[29–30] in the present work we report a simple and convenient method for the synthesis of 2-amino-3-cyano-4-aryl-7-methyl-5-oxo-4,5-dihydro-pyrano-[3,2-*c*]-pyran and 2-amino-3-cyano-4-aryl-6-methyl-4-hydro-pyrano-[3,2-c]-quinoline derivatives via one-pot three-component condensation of an aromatic aldehyde, malononitrile and the enolisable ketone, 4-hydroxy-6-methylpyran-*2H*-one/1-methyl-4-hydroxyquinoline-*2H*-one, under catalysis of copper nanoparticles grafted on carbon microspheres (Cu-NP/C) (Scheme 1).

Experimental section

General details

All the chemicals were Sigma Aldrich, Alpha Aeser or Spectrochem made and used without further purification. Thin Layer Chromatography (TLC) was monitored on Merck made silica gel



Scheme 1. One-pot synthesis of pyrano-pyran and pyrano-quinoline derivatives

60-F-254 aluminum plates. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer using the specified solvents using tetramethylsilane as the internal standard. Mass spectrometric data were recorded by electron spray ionization (ES) technique on a Q-tof-micro quadruple mass spectrometer (Micro mass).

General procedure for the synthesis of 6-amino-4-aryl-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano [2,3-c]pyrazoles

A mixture of aromatic aldehyde (1 mmol), malononitrile (1.1 mmol), 4-hydroxy- 6-methyl-2-pyrone or 1-methyl 4-hydroxy-2-quinolone (1 mmol) was refluxed at 80 °C with constant stirring in 1:1 water: ethanol (5 mL) in the presence of Cu-NP/C (10 wt%) for an appropriate time as mentioned in Table 2. The progress of the reaction was monitored by TLC using 5% methanol: dichloromethane as the mobile phase. After completion of the reaction, the reaction mixture was diluted with hot ethanol (10 mL) and filtered off to separate catalyst as the residue. The residue was further washed with hot ethanol (2 × 5 mL); the combined filtrates were concentrated on rotary evaporator to get the desired products which were of enough purity that required no purification.

Spectral data of the representative compounds is mentioned below:

2-Amino-3-cyano-4-(2-carboxyphenyl)-7-methyl-5-oxo-4,5-dihydro-5-oxopyrano[3,2-*c*]pyran, entry 9, (4 h): MP: 238-240 °C; IR (cm^{-1}) 752, 956, 1033, 1134, 1253, 1373, 1490, 1575, 1604, 1670, 2202, 2976, 3103, 3367, 3468; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ ppm 2.20 (s, 3H, CH$_3$), 5.69 (s, 1H, CH, chiral), 6.25 (s, 1H, =CH), 7.09 (s, 2H, NH$_2$), 7.17-7.10 (d, 1H, Ar-H, J = 8.8 Hz), 7.27-7.31 (t, 1H, Ar-H, J = 8.6 Hz), 7.46-7.50 (t, 1H, ArH, J = 7.53 Hz), 7.77-7.79 (d, 1H, ArH, J = 7.53 Hz), 12.86 (s, 1H, COOH); HRMS (ES^{+}) m/z 325.07.

2-Amino-3-cyano-4-(4-cyanophenyl)-6-methyl-5,6-dihydro-5-oxo-4*H*-pyrano[3,2-c]quinoline, entry 14, (5 b): MP: 278-280 °C; IR (cm^{-1}) 754, 839, 1095, 1253, 1375, 1597, 1629, 1674, 2189, 2231, 3192, 3336, 3441; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ ppm 3.53 (s, 3H, CH$_3$), 4.64 (s, 1H, CH chiral), 7.39 (s, 2H, NH$_2$), 7.42-7.44 (d, 3H, Ar-H, J = 8.52), 7.57-7.59 (d, 1H, ArH, J = 8.00), 7.71-7.76 (m, 3H, Ar-H), 8.02-8.04 (d, 1H, ArH, J = 7.2); ^{13}C NMR (500 MHz, DMSO-d$_6$): δ ppm 29.1, 37.3, 38.8, 39.0, 56.6, 107.6, 109.4, 112.4, 114.6, 114.6, 119.2, 122.1, 128.5, 131.6, 132.2, 138.6,149.7, 150.3, 158.7, 159.5; HRMS (ES^{+}) m/z 353.11 (M-1).

2-Amino-3-cyano-4-(4-(2-amino-3-cyano-5,6-dihydro-6-methyl-5-oxo-4*H*-pyrano[3,2-c]quinolin-4-yl)phenyl)-5,6-dihydro-6-methyl-5-oxo-4H-pyrano[3,2-c]quinoline (entry 15, 5c): MP: 279-282 °C; IR (cm^{-1}) 752, 1095, 1290, 1377, 1462, 1627, 1672, 2194, 2229, 3190, 3327, 3371, 3431, 3587; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ ppm 3.53 (s, 6H, 2CH$_3$), 4.47 (s, 1H, CH, chiral), 4.63 (s, 1H, CH, chiral), 7.10 (s, 1H, ArH), 7.23 (s, 1H, ArH), 7.38 (s, 4H, 2 NH$_2$), 7.43-7.48 (d, 2H, ArH,

J = 8.3 Hz), 7.54-7.59 (m, 2H, Ar-H), 7.71-7.74 (m, 2H, ArH), 7.86-7.89 (m, 2H, ArH), 7.98-8.04 (m, 2H, ArH); ^{13}C NMR (500 MHz, DMSO-d_6): δ ppm 29.2, 29.2, 36.8, 37.5, 38.9, 40.0, 56.7, 57.8, 107.6, 108.9, 112.5, 113.2, 114.9, 119.3, 122.0, 114.1, 122.2, 127.3, 128.6, 129.8, 130.7, 131.7, 138.7, 150.1, 150.4, 151.1, 158.7, 159.7, 161.0; HRMS (ES^+) m/z 581.23.

Results and discussion

In the present work, we report an efficient and facile protocol for the synthesis of 2-amino-3-cyano-4-aryl-7-methyl-5-oxo-4,5-dihydro-pyrano[3,2-*c*]pyran and 2-amino-3-cyano-4-aryl-6-methyl-4-hydro-pyrano [3,2-c]quinoline derivatives by the one-pot three-component condensation from aromatic aldehydes, malononitrile, and 4-hydroxy 6-methyl-2-pyrone or 1-methyl-4-hydroxy-2-quinolone by using Cu NP/C as a reusable and safe catalyst in 1:1 water-ethanol mixture at 80^0C.

The present work was carried by using Cu NP/C catalyst for the synthesis of pyrano-pyran and pyrano-quinoline derivatives. Initially, 3-bromo benzaldehyde (1 mmol), malononitrile (1.1 mmol), 4-hydroxy 6-methyl 2-pyrone (1 mmol) were selected for the optimization of reaction conditions at 80 °C in a 5 mL water-ethanol (1:1). The effect of solvent and amount of catalyst was also studied (Table 1). A better yield was found using 10 wt% of the catalyst in 1:1 H_2O-EtOH (Table 1).

Thereafter, a series of reactions was carried out by using diversely substituted aldehydes under the optimized reaction conditions. All the aldehydes used underwent the three-component reaction with malononitrile and 4-hydroxy 6-methyl-2-pyrone to produce a library of 2-amino-3-cyano-4-aryl-7-methyl-5-oxo-4, 5-dihydro-pyrano [3,2-*c*]pyran derivatives in good to excellent yields. Similarly, 2-amino-3-cyano-4-aryl-6-methyl-4-hydro-pyrano [3,2-c]quinoline derivatives were synthesized by using 1-methyl 4-hydroxy 2-quinolone (Table 2).

Table 1. Optimization of the reaction conditions.

Entry	Solvent	Catalyst (wt%)	Temperature (°C)	Time (min.)	Yield (%)
1	CH_3CN	10	80	98	62
2	CH_2Cl_2	10	40	137	65
3	H_2O	05	80	114	67
4	EtOH	05	80	28	76
5	1:1 H_2O - EtOH	05	80	25	80
6	1:1 H_2O - EtOH	10	**80**	**14**	**92**

Table 2. Synthesis of 2-amino-3-cyano-4-aryl-7-methyl-5-oxo-4,5-dihydro-pyrano[3, 2-*c*] pyran and 2-amino-3-cyano-4-aryl-6-methyl-5,6-dihydro-5-oxo-4*H*-pyrano[3,2-c] quinoline derivatives catalyzed by copper nanoparticles grafted on carbon microspheres.

Entry	Aldehyde[a]	Enolisable Ketone	Time (min.)	Product	Yield[b] (%)	**Melting point (°C)**
1	Benzaldehyde	3a	20	4a	86	249–251[7]
2	3-Bromo benzaldehyde	3a	18	4b	88	258–260[7]
3	2-Fluorobenzaldehyde	3a	20	4c	90	238–240[7]
4	2-Chloro benzaldehyde	3a	17	4d	90	267–268[11]
5	4-Cyano benzaldehyde	3a	15	4e	88	230–232[7]
6	3-Nitro benzaldehyde	3a	15	4f	93	234–235[7]
7	4-Bromo benzaldehyde	3a	18	4g	88	214–215[7]
8	2-Carboxy benzaldehyde	3a	24	4h	85	230–232 [Present work]
9	Thiophene-2-carbaldehyde	3a	30	4i	84	242–243[11]
10	4-Hydroxy benzaldehyde	3b	16	5a	91	130–132[18]
11	4-Cyano benzaldehyde	3b	36	5b	86	254–256 [Present work]
12	Terphthaldehyde	3b	24	5c	88	279–282 [Present work]
13	Indole 3-carboxaldehyde	3b	28	5d	85	192–194[18]
14	Benzaldehyde	3b	20	5e	91	153–154[18]
15	3-Nitro benzaldehyde	3b	22	5f	90	190–192[18]

[a]Substituted aromatic aldehyde (1 mmol), malononitrile (1 mmol), enolizable ketone (1 mmol), and Cu NP/C (10 wt%), H_2O: EtOH (1:1) 5 mL, 80 °C; [b]Isolated yield.

Table 3. Reusability of catalyst for the model reaction.

Sr. No.	Run	Yield (%)[a]
1	Fresh	88
2	I	85
3	II	81
4	III	81

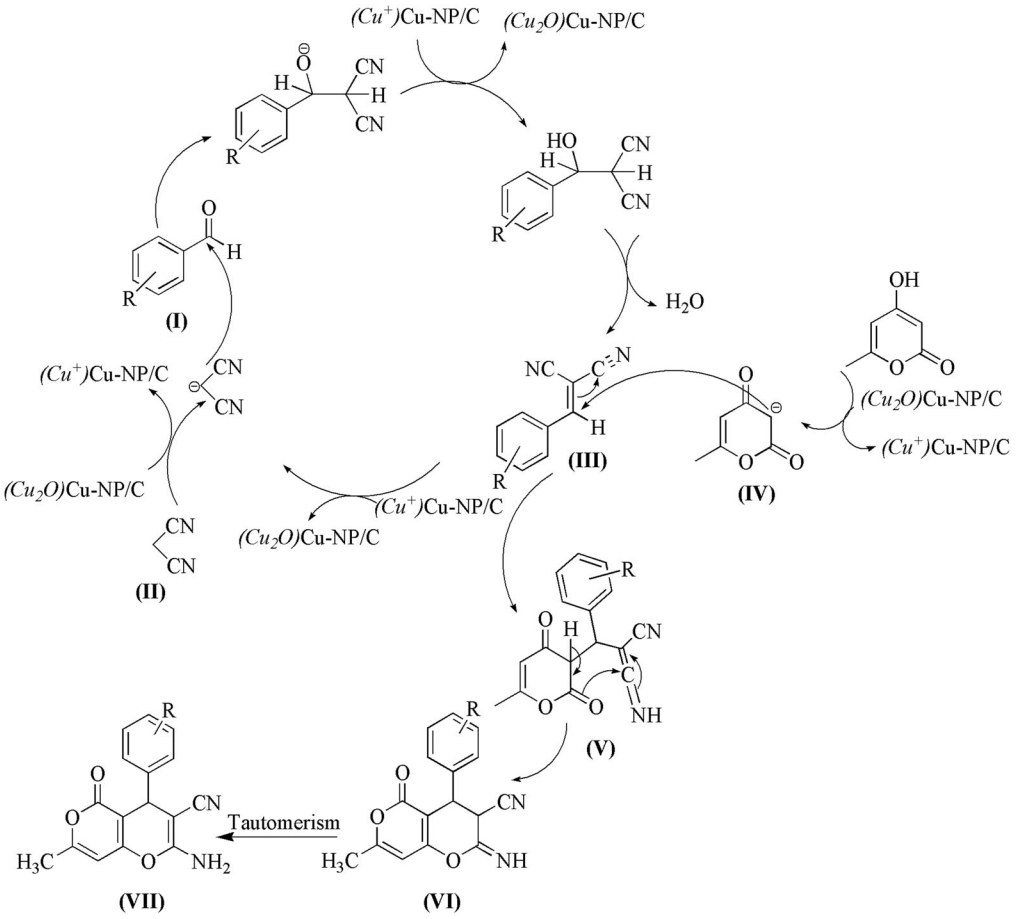
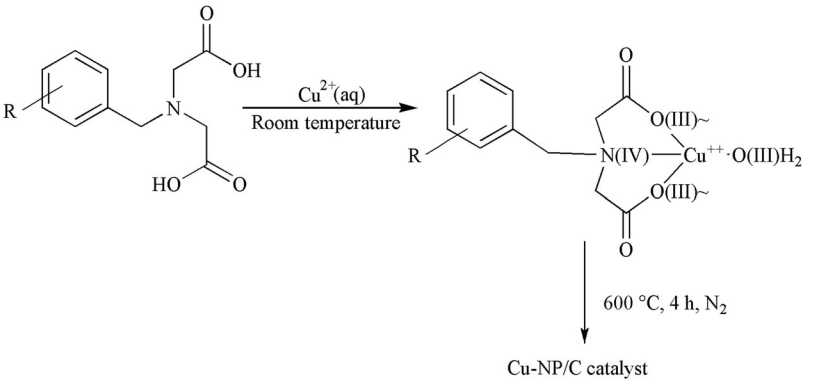


Figure 2. The plausible mechanism for the synthesis of pyrano-pyrans by using Cu-NP/C catalyst.

The reactions of aromatic aldehydes with electron-withdrawing substituents such as chloro and nitro groups proceeded at faster rates and gave better yields than those with electron-donating groups such as methoxy and methyl.

After completion of the reaction as monitored by TLC, the reaction mass was diluted with hot ethanol (3×5 mL) and the catalyst was separated by filtration. The combined filtrate was collected to get crude product which was purified by recrystallization in hot ethanol. Reusability is an important aspect of a heterogeneous catalyst. We studied the catalyst reusability in case of the model reaction of 3-bromobenzaldehyde, malononitrile, and 4-hydroxy-6-methyl-2-pyrone to form the corresponding pyrano-pyran (***Entry 2***, Table 3). The catalyst was found to work well in successive runs without an appreciable loss of its catalytic activity.



Scheme 2. The synthesis of catalyst.

Table 4. Comparison of literature methods for the synthesis of 1,4-dihydropyrano[2,3-c]pyran and 1,4-dihydropyrano[2,3-c]quinoline derivatives with the present protocol.

Sr. No.	Conditions	Catalyst amount	Reference
1	Magnetic iron oxide/phenylsulfonic acid, Distilled water, 50 °C, 10–45 min	0.2 mol%	8
2	KF/Al_2O_3 EtOH, R. T. 5–10 h	50 mg / mmol of aldehyde	10
3	Ammonium acetate, Grinding, 10–18 min	10 mol %	11
4	DABCO 80 °C, 20 min	25 mol%	21
5	Nano Cobalt Ferrite EtOH, MW irradiation	0.5 mg/10 mmol of aldehyde	22
6	Fe_3O_4@ NS-GO, water, R.T., 2- 10 min	0.01 g / mmol of aldehyde	23
7	MMWCNTs-D-$(CH_2)_4$-SO_3H nanocomposite EtOH: H_2O, Reflux, 10–30 min	0.04 g / mmol of aldehyde	24
8	$[CH_2O(CH_2)_2NH_3]_2(CF_3COO)_2$ ionic liquid, solvent free, 80 °C, 12–30 min	7 mol%	31
9	{[HIM]C$(CN)_3$}, neat, 50 °C, 10–25 min	2 mol%	32
10	Cu NP/C EtOH: H_2O (1:1), 80 °C, 15–30 min	10 wt%	Present work

Thus Cu-NP/C can be easily separated and reused several times successfully without a significant loss of activity. Another important aspect of the present work is the use of aqueous ethanol (1:1) as solvent for the reaction.

The plausible mechanism for the synthesis of pyrano-pyrans by using Cu-NP/C catalyst is depicted in Figure 2. Cu NPs are partially oxidized on surface by air. The Cu_2O generated on surface of the catalyst [(Cu_2O)Cu-NP/C)] acts as a base to remove protons from malononitrile and the reacting 2H-pyrone, whereby it turns into (Cu^+)Cu-NP/C and not into (Cu)Cu-NP/C. The Cu^+ left on surface of the catalyst can act as Lewis acid to activate I and III toward the relevant nucleophilic attacks. (Cu^+)Cu-NP/C is transformed into (Cu_2O)Cu-NP/C during protonation of intermediate anions. It involves formation of the intermediate **(III)** via condensation of an aldehyde with malononitrile. Simultaneously, 4-hydroxy-6-methyl-2-pyrone is transformed by the catalyst into the intermediate (**IV**), which undergoes a nucleophilic addition onto (**III**) in Michael manner to give the intermediate (**V**). The intermediate (**V**) undergoes cyclization followed by tautomerism to form the desired product (**VII**).

A similar mechanism can be proposed for the Cu-NP/C catalyzed synthesis of 2-amino-3-cyano-4-aryl-6-methyl-4-hydro-pyrano [3,2-c]quinolone by replacing the 4-hydroxy-6-methyl-2-pyrone with 1-methyl-4-hydroxy-2-quinolone.

The protocol for detailed synthesis and characterization of the catalyst is already reported in our previous work.[29–30] It was prepared from a styrene-based divinylbenzene and acrylonitrile-modified and iminodiacetate (-$CH_2N(CH_2COOH)_2$) functionalized resin. The resin was treated with copper (II) sulfate solution and then the dried Cu-loaded resin was carbonized at 600 °C for 4 h in a high purity dry nitrogen stream (Scheme 2). A comparison of the present method with

some of the literature methods for the synthesis of these heterocyclic compounds is depicted in Table 4.

Conclusion

In summary, in the present work, we report an efficient and rapid method for one-pot three-component synthesis of 2-amino-3-cyano-4-aryl-7-methyl-5-oxo-4,5-dihydro-pyrano [3,2-*c*]pyrans and 2-amino-3-cyano-4-aryl-6-methyl-5,6-dihydro-5-oxo-4*H*-pyrano [3,2-c]quinolones catalyzed by Cu-NP/C under heterogeneous conditions. The present method provides a valuable addition to the synthesis of these biologically significant heterocycles in terms of mild, environmentally benign reaction conditions and excellent yields of the products.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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