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FULL PAPER

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Polypyrrole/Fe_3O_4/CNT as a recyclable and highly efficient catalyst for one-pot three-component synthesis of pyran derivatives

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Polypyrrole (PPY)/Fe_3O_4/CNT has been synthesized and characterized by FT-IR, TEM and SEM techniques and its catalytic activity has been evaluated in the synthesis of several series of pyran derivatives. Tetrahydrobenzo[*b*]pyranes, 4H-pyran-3-carboxylates, 4H,5H-pyrano[3,2-*c*]chromenes and dihydropyrano[2,3-*c*]pyrazoles have been successfully prepared from one-pot three-component condensation of aldehyde, malononitrile and active methylene-containing compounds (dimedone /ethyl acetoacetate/4-hydroxycoumarin/3-methyl-2-pyrazoline-5-one) using PPY/Fe_3O_4/CNT as a new and reusable heterogeneous catalyst. The present method offer several advantages such as; high yields of products, short reaction times, easy work-up procedure and easy separation of the catalyst from the reaction mixture due to its magnetic character. Furthermore, chemoselective synthesis of bis-benzo[*b*]pyran from terephthalaldehyde can be achieved by this method.

KEYWORDS

one-pot synthesis, polypyrrole/Fe_3O_4/CNT nanocomposite, pyran derivatives, three-component reaction

1 | INTRODUCTION

Recently multi-component reaction (MCRs) have been gained considerable attention in combinatorial chemistry because of their ability for combination of more than two starting materials in a single flask to prepare a new product.[1,2] Pyrans are an important class of heterocyclic compounds that plays an important role in pharmaceutical chemistry.[3] Some pyran derivatives have been used as spasmolytic, diuretic, anti-tumor,[4] anti-cancer,[5] anti-anaphylactin[6] and anti-coagulant agents.[7] Furthermore, they can be used in several neurodegenerative diseases, such as parkinson, alzheimer, down syndrome, huntington, schizophrenia and myoclonus diseases as cognitive enhancer.[8] Numerous method have been reported for the synthesis of these compounds *via* three-component reaction of aldehyde, malononitrile and various β-diketones[9–13] using various conditions like microwave[14] and ultrasonic irradiation.[15] A variety of reagents such as $Yb(PFO)_3$,[16] LiBr,[17] SB-DABCO,[18] tetrabutylammonium bromide (TBAB),[19,20] Na_2SeO_4,[21] solid acids,[22,23] diammonium hydrogen phosphate,[24,25] silica bonded n-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride[18] and DBU[26] were employed for the preparation of pyrans. However, most of the reported methods suffer from some disadvantages including long reaction times, low yields of products and the use of toxic organic solvents such as DMF or acetic acid that make some complications in work-up procedure.[27] Therefore, there is still a need for design and development of new catalytic systems for mild and efficient synthesis of pyran derivatives with respect to economical and environmental aspects.

In recent years, design, synthesis and application of new nanomagnetic catalysts have been made a new field of challenge in chemistry especially in the synthesis of biologically active compounds and in drug discovery. Simple separation of magnetic nanocomposites from the reaction mixture, in combination with nano character of these compounds makes them an excellent choice for catalytic applications. Furthermore, the reusable systems are of great economical and environmental importance especially in industrial usages due to their reduction of costs and pollution.

2 | EXPERIMENTAL

Chemicals were purchased from Merck chemical companies. IR spectra were recorded on a shimadzu FT-IR 8440 s spectrophotometer. ^1H NMR spectra were reco-

rded on a Bruker AVANCE 300 MHZ spectrometer. Melting points were determined with Electrothermal 9100 apparatus and were uncorrected. The morphology of PPY/Fe_3O_4/CNT and size of nano particles were determined by scanning electron microscopy (SEM) model Leo 912 AB and Transmission electron microscopy (TEM) model Leo 1450 VP.

2.1 | Synthesis of PPY/Fe_3O_4/CNT

2.1.1 | CNTs functionalization

Recently, carbon nano particles have been extensively used in the preparation of various magnetic nanocomposites.[28–30] Herein, we wish to report the application of carbon nano tube (CNTs) as a suitable support in the preparation of PPY/Fe_3O_4/CNT and study its catalytic activity. To this aim, initially CNT was functionalized. 0.2 g of carbon nano tube (CNTs) and 50 ml of 60 % HNO_3 aqueous solution were added into 100 ml flask, and then were subjected to an ultrasonic bath for 30 min. Thereafter, the mixture was refluxed for 24 h. The resultant CNTs–COOH was filtered through a 0.22 μm membrane and washed with distilled water until neutralized and was dried under vacuum for 12 h at 60 °C.

2.2 | Synthesis of Fe_3O_4 magnetic nanoparticles

Magnetic nano-particles were synthesized by chemical co-precipitation method. First, 11.68 g $FeCl_3.6H_2O$ and 4.3 g $FeCl_2.4H_2O$ was dissolved in 400 ml of deionized water under nitrogen atmosphere with vigorous stirring at 60 °C. Then ammonia solution (NH_3 30%, 20 ml) was added slowly to the solution under nitrogen. The reaction was maintained at 60 °C for 60 min. The black precipitates obtained (Fe_3O_4 nano-particles) were collected using a magnet and washed repeatedly with deionized water until the pH of the washings became neutral and finally dried under vacuum at 60 °C for 24 h.

2.3 | Preparation of the catalyst

Nanomagnetic polypyrrole (PPY)/Fe_3O_4/CNT was prepared according to the reported procedure in articles with some modification.[31,32] The PPY/Fe_3O_4/CNT nanocomposites were synthesized via oxidative polymerization of pyrrole monomers in the presence of Fe_3O_4 NPs and CNTs (as the charge-balancing dopant in the polymer) using potassium persulfate as oxidant. 250 mg of the dried Fe_3O_4 NPs and 50 mg of CNT-COOH were added to 200 ml deionized water under stirring for 5 min and then, 0.5 ml of pyrrole monomers were added and stirred for 10 min. The reaction mixture was bubbled by nitrogen gas for 10 min under stirring to get rid of oxygen. Subsequently, 2.7 g of potassium persulfate was added to the mixture. After the addition of oxidant, the mixture was stirred for 16 h at room temperature. The resultant PPY/Fe_3O_4/CNT nano-composites were collected by a magnet and washed with deionized water, tetrahydrofuran and methanol several times to remove the unreacted materials, and dried at 60 °C under vacuum for 24 h and characterized by FT-IR, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) techniques.

The FT-IR spectra of Fe_3O_4 nanoparticle (a), Fe_3O_4/PPY (b) and PPY/Fe_3O_4/CNT have been shown in Figure 1.

In the IR spectrum of Fe_3O_4, absorptions peaks of Fe–O were observed at 587 and 3390 cm^{-1} which demonstrate the successful synthesis of Fe_3O_4 nanoparticles (Figure 1a). The IR spectrum of Fe_3O_4/PPy is presented in Figure 1b. The IR spectrum shows the typical characteristic pyrrole ring stretching vibration C-N, out-of-plane vibrations of C–H and ring deformation at about 1564 cm^{-1} and 1438 cm^{-1}; 1308 cm^{-1}, 1043 cm^{-1} and 923 cm^{-1}.[33] As it can be observed in Figure 1c, the PPY/Fe_3O_4/CNT nano-composite spectrum is the addition of spectra Fe_3O_4, CNT and PPy, and has the representative bands of these compounds. These absorption bands indicate successful synthesis of PPY/Fe_3O_4/CNT nanocomposite.

The morphology of PPY/Fe_3O_4/CNT and the size distribution of nano-particles were determined by scanning electron microscopy (SEM) (Figure 2) and Transmission electron microscopy (TEM) (Figure 3). These images clearly show that polypyrrole forms a compact and

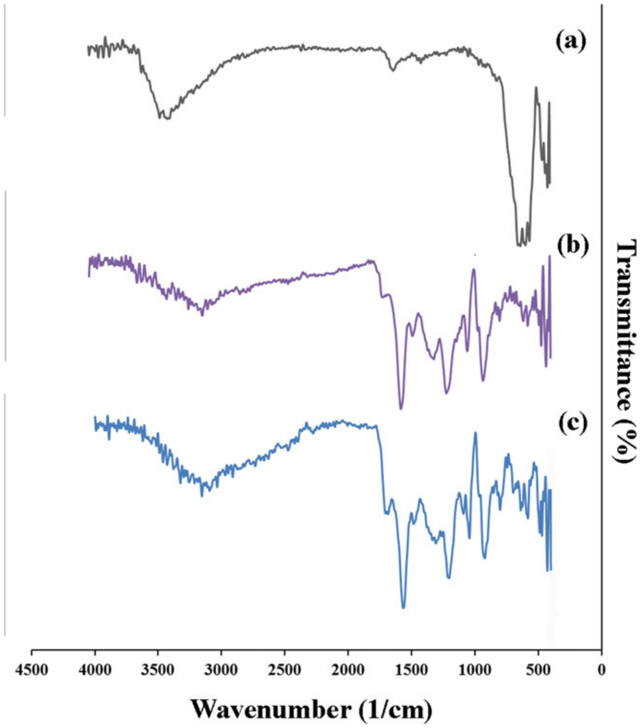


FIGURE 1 FT-IR spectra of a) Fe_3O_4 nanoparticles b) Fe_3O_4/PPy c) PPY/Fe_3O_4/CNT nanocomposite

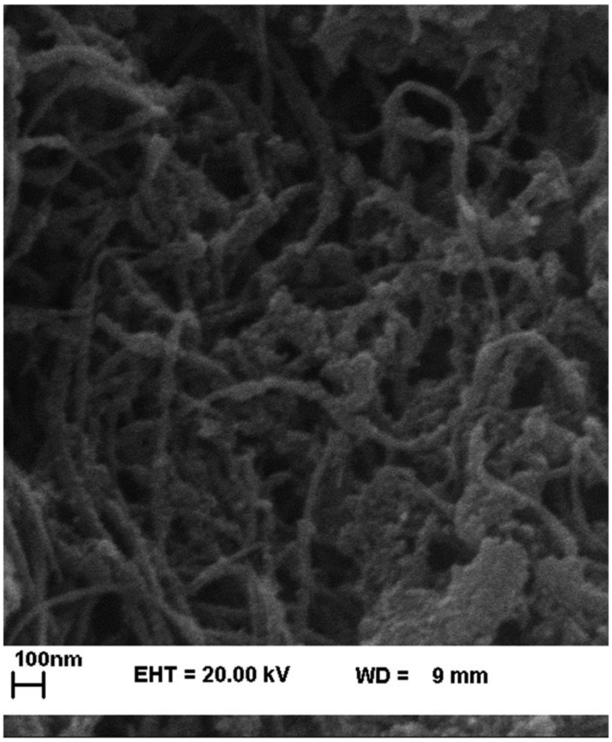


FIGURE 2 SEM micrograph of nano-magnetic PPY/Fe_3O_4/CNT

smooth film on Fe_3O_4/CNT. The average crystalline size of Fe_3O_4 nano-particles in PPY/Fe_3O_4/CNT was estimated about 30 nm.

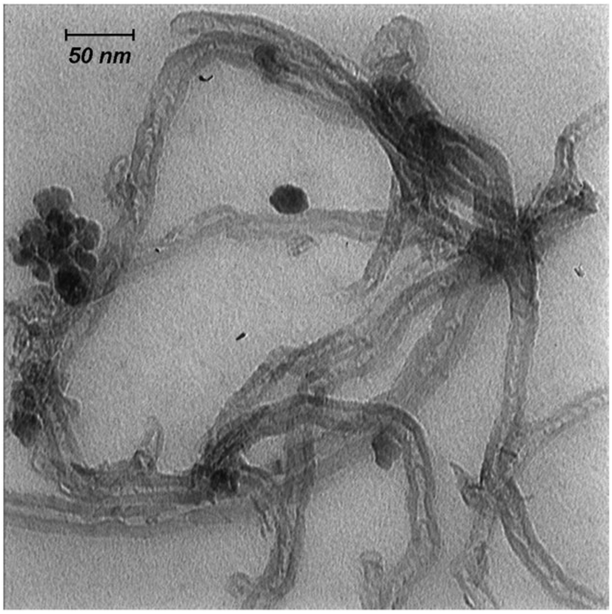


FIGURE 3 TEM micrograph of nano-magnetic PPY/Fe_3O_4/CNT

The megnetic property of PPY/Fe_3O_4/CNT was studied by measurement of saturation magnetization (M_s) and coercivity (H_c) values of this nanocomposite by Yang and co-workers.[32] The obtained results confirmed the good magnetic character of PPY/Fe_3O_4/CNT. Furthermore, the thermogeravimetric analysis of PPY/Fe_3O_4/CNT was shown a satisfactory thermal stability for this magnetic nanocomposite.[32] It was also shown that the conductivity of this nanocomposite is more than pure polypyrrole matrix.[34]

2.4 | General procedure for the synthesis of pyran derivatives using PPY/Fe_3O_4/CNT nanomagnetic catalyst

A mixture of aromatic aldehyde (1 mmol), malononitrile (1 mmol) and an active methylene-containing compound (dimedone/ cyclohexane-1,3-dione/ ethyl acetoacetate/ 4-hydroxycoumarin/ 3-methyl-2-pyrazoline-5-one) (1 mmol) was prepared and 0.032 gr of nanomagnetic catalyst was added to the mixture and heated at 90 °C under solvent-free condition. After completion of the reaction as monitored by TLC (eluent: EtOAc/ *n*-hexane, 1:1), ethanol (10 ml) was added and the catalyst was separated from the reaction mixture by an external magnet, washed with ethanol and dried at 60 °C under vacuum for 2 h. Crushed ice was added to the reaction mixture and the resulting precipitate was filtered and washed with ethanol to afford pure product in good to excellent yields (Table 2).

2.5 | Physical and Spectral Data of Some Products

2.5.1 | 2-Amino-3-cyano-4-phenyl-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[*b*]py-ran (4a)

IR (KBr disc, cm^{-1}): 3396, 3325, 3211, 2963, 2199, 1664, 1602, 1371, 1214, 1036; ^1H NMR (300 MHz, DMSO-d_6, ppm): δ_H 0.91 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 2.06 (d, *J*=16.1 Hz, 1H), 2.22 (d, *J* = 16.1 Hz, 1H), 3.58 (s, 2H, CH_2), 4.13 (s, 1H, CH), 7.09-7.18 (m, 3H, ArH), 7.23-7.28 (m, 2H, ArH).

2.5.2 | Ethyl-6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate (6a)

IR (KBr disc, cm^{-1}): 3412, 3334, 2199, 1693; ^1H NMR (300 MHz, DMSO-d_6, ppm): δ_H 1.09 (t, *J* = 7.12 Hz, 3H), 2.38 (s, 3H), 4.06-4.00 (m, 2H), 4.43 (s, 1H), 4.44 (s, 2H, NH_2), 7.31-7.19 (m, 5H, ArH).

2.5.3 | 2-Amino-4-phenyl-3-cyano-4H,5H-pyrano[3,2-*c*]chromene-5-one (8a)

IR (KBr disc, cm^{-1}): 3375, 3180, 2197, 1709; H NMR (300 MHz, DMSO-d_6, ppm): δ_H 4.46(s, 1H), 7.22-7.27(m, 3H, ArH) 7.30-7.34 (m, 2H, ArH),7.42 (s, 2H, NH_2), 7.46 (d, *J* = 8.3 Hz, 1H, ArH), 7.50 (td, *J* = 7.6, 0.9 Hz, 1H, ArH), 7.72 (td, *J* = 7.8, 1.6 Hz, 1H, ArH), 7.91 (dd, *J* = 7.9, 1.4 Hz, 1H, ArH).

2.5.4 | 6-Amino-3-methyl-4-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (10a)

IR (KBr disc, cm^{-1}): 3370, 3171, 2192, 1652, 1599, 1402, 1043; ^1H NMR (300 MHz, DMSO-d_6, ppm): δ_H 1.76 (s, 3H, CH_3), 4.58 (s, 1H), 6.86 (s, 2H, NH_2), 7.15 (d, 2H, *J* = 7.32 Hz), 7.19-7.22 (m, 1H), 7.28-7.32 (m, 2H), 12.08 (s, 1H, NH).

4,4′-(1,4-Phenylene)bis(2-amino-3-cyano-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahy-drob-enzo[*b*]pyran)

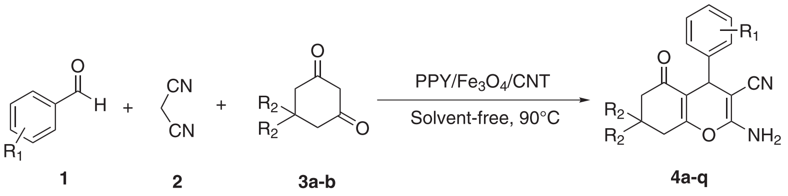
mp. 266–268 °C, m.p. 267–269 °C, lit.[35]; IR (KBr disc, cm^{-1}): 3448, 3327, 3189, 2960, 2194, 1655, 1602, 1363, 1210, 1148, 1029 cm^{-1}, ^1H NMR (300 MHz, DMSO-d_6, ppm): δ_H 0.985 (s, 6H, $2CH_3$), 1.035 (s, 6H, $2CH_3$), 2.16 (d, *J* = 16.4 Hz, 2H), 2.23 (d, *J* = 16.4 Hz, 2H), 2.50 (s, 4H), 4.14 (s, 2H), 6.98 (s, 4H, $2NH_2$), 7.04 (s, 4H, ArH).

3 | RESULT AND DISCUSSION

Here in, we wish to report a simple and convenient method for the preparation of several classes of pyran derivatives by condensation of aromatic aldehyde, malononitrile and β-diketone using PPY/Fe_3O_4/CNT as a new reusable nanomagnetic catalyst.

Initial studies were performed by the reaction of 4-chlorobenzaldehyde, malonitrile and dimedone as model reaction for the synthesis tetrahydrobenzo[*b*] pyran derivative under different reaction conditions (Scheme 1).

The effect of solvent, amount of catalyst and temperature were examined in model reaction (Table 1). The best result was obtained when the reaction was carried out in the presence of 32 mg of catalyst in the absence of solvent at 90 °C, which corresponding benzo[*b*]pyran was generated in 95 % yield after 10 minutes (Table 1, entry 3). The model reaction was also performed in the presence of CNT, Fe_3O_4 and PPY as catalyst and without the catalyst under optimized reaction conditions. The results show that CNT has low catalytic activity which led to the 35 % yields after 10 minutes (Table 1, entry 12). Fe_3O_4 successfully catalyze the reaction which 85%



1	R1
a	H
b	4-Cl
c	2-Cl
d	4-Br
e	4-NO_2
f	3-NO_2
g	CN

1	R1
h	4-OH
i	3-OH
j	4-OMe
k	3,4-$(OMe)_2$
l	4-$CHMe_2$
m	3-Cl
n	3-Br

3	R2
a	Me
b	H

SCHEME 1 Synthesis of tetrahydrobenzo[*b*]pyran derivatives using PPY/Fe_3O_4/CNT nanomagnetic catalyst

TABLE 1 Optimization of reaction conditions for **4b**[a]

Entry[a]	Catalyst (mg)	Conditions	Solvent	Time (min)	Yield[b] (%)
1	PPY/Fe_3O_4/CNT (15)	90 °C	_	10	80
2	PPY/Fe_3O_4/CNT (25)	90 °C	_	10	84
3	PPY/Fe_3O_4/CNT (32)	90 °C	_	10	97
4	PPY/Fe_3O_4/CNT (50)	90 °C	_	10	90
5	PPY/Fe_3O_4/CNT (32)	Rt	_	10	25
6	PPY/Fe_3O_4/CNT (32)	60 °C	_	10	37
7	PPY/Fe_3O_4/CNT (32)	90 °C	H_2O	10	20
8	PPY/Fe_3O_4/CNT (32)	85 °C	Ethanol	10	35
9	PPY/Fe_3O_4/CNT (32)	Reflux	Methanol	90	60
10	PPY/Fe_3O_4/CNT (32)	Reflux	Chloroform	150	45
11	PPY/Fe_3O_4/CNT (32)	90 °C	H_2O/ Ethanol(1:1)	30	75
12	CNT (32)	90 °C	_	10	35
13	Fe_3O_4 (32)	90 °C	_	10	85
14	PPY (32)	90 °C	_	10	Trace
15	_	90 °C	_	120	Trace

[a] Benzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol),

[b] Isolated yields.

product was obtained after 10 minutes, but it is not a good choice due to its non-reusability and the loss of its magnetic character (Table 1, entry 13). Furthermore, no catalytic activity was observed for the polymer (Table 1, entry 14) and no product was detected in the absence of catalyst after 120 minutes (Table 1, entry 15).

The generality of the current method was investigated in the reaction of aromatic aldehydes, malononitrile and dimedone or 1,3-cyclohexandion under optimized reaction condition (Scheme 1). The corresponding tetrahydrobenzo[*b*]pyran derivatives were obtained in good to excellent yields in appropriate times according to Table 2. It was observed that electron-withdrawing substituted aldehydes were reacted faster than electron-donating ones which represented in their high yields and short reaction times (Table 2, entries 1-17). T2

More ever, the efficiency of this method was studied for the synthesis of a series of pyran ring-structured compounds by replacing dimedone with some other active methylene-containing compounds (Scheme 2). To this aim, similar reactions were performed between aromatic aldehydes, malononitrile and ethyl acetoacete/4-hydroxy coumarin/3-methyl-2-pyrazoline-5-one in the presence of PPY/Fe_3O_4/CNT under optimized reaction conditions and corresponding 4H-pyrans (Table 2, entries 18-22), dihydropyrano[3,2,*c*]chromenes (Table 2, entries 23-24) and pyrano[2,3-*c*]pyrazoles (Table 2, entries 25-27) were successfully generated by the current procedure. Therefore, PPY/Fe_3O_4/CNT is a highly efficient catalyst for the synthesis of different substituted pyran moieties in different structures.

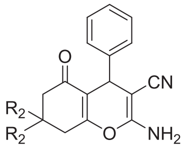
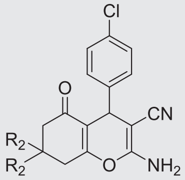
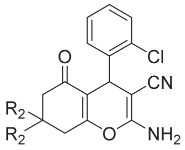
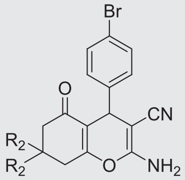
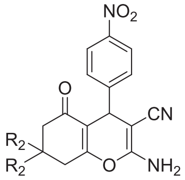
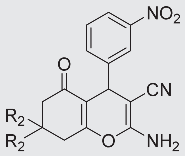
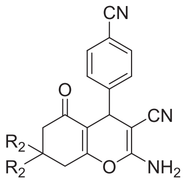
The chemoselectivity of the current method was also investigated in the reaction of terephthalaldehyde with 2 equivalents of dimedone and malononitrile under optimized conditions which corresponding bis-tetrahydrobenzo[*b*]pyran was exclusively produced in 90% yield after 40 minutes (Scheme 3). No mono-derivative was detected in the reaction mixture.

Although, the detailed mechanism of this reaction is unclear, a plausible mechanism may involve the following key steps (Scheme 4)

We compared the obtained results with some other methods for the preparation of 2-Amino-3-cyano-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[*b*]pyran in Table 3. These results clearly demonstrate that nanomagnetic PPY/Fe_3O_4/CNT is more efficient for this reaction.

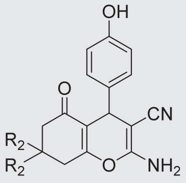
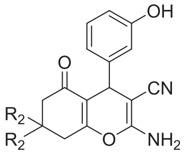
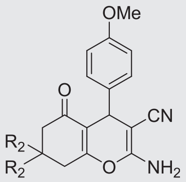
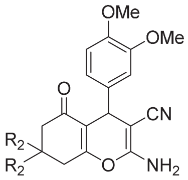
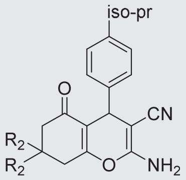
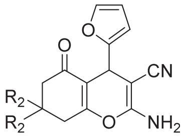
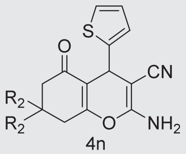
The reusability of the catalyst was also examined in the reaction of 4-chlorobenzaldehyde, malononitrile and dimedone under optimized reaction condition. After completion of the reaction, EtOH (10 ml) was added and the nanomagnetic catalyst was separated by an external magnet (Figure 4), washed with ethanol and dried at 60 °C under vacuum for 2 hours. The recovered PPY/Fe_3O_4/CNT was reused in the similar reaction for 10 times (Figure 5). The results show that catalyst can be reused at least 10 times in the preparation of pyran derivatives without significant loss in its catalytic activity.

TABLE 2 Syntheses of pyran derivatives in solvent-free condition catalyzed by nanomagnetic PPY/Fe_3O_4/CNT

Entry	Ar	β- diketone	product	Time (min)	Yield (%)[a]	mp (°C) found	mp (°C) reported
1	C_6H_5	3a	 4a	15	95	225-228	226-228[36]
2	$4\text{-(Cl)}C_4H_4$	3a	 4b	10	95	208-210	207-209[36]
3	$3\text{-(Cl)}C_4H_4$	3a	 4c	20	91	213-215	215-216[37]
4	$4\text{-(Br)}C_4H_4$	3a	 4d	15	94	199-201	201-203[38]
5	$4\text{-(NO}_2\text{)}C_4H_4$	3a	 4e	10	95	176-179	176-178[37]
6	$3\text{-(NO}_2\text{)}C_4H_4$	3a	 4f	15	92	212-213	213-214[37]
7	$4\text{-(CN)}C_4H_4$	3a	 4g	5	95	207-209	208-210[38]

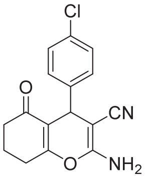
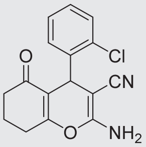
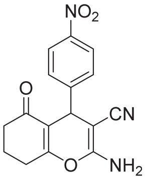
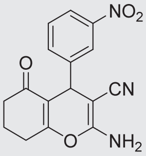
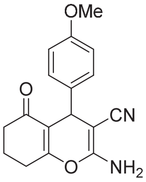
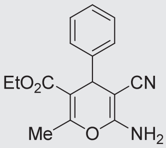
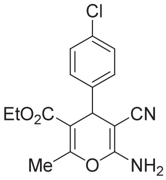
(Continues)

TABLE 2 (Continued)

Entry	Ar	*β*- diketone	product	Time (min)	Yield (%)[a]	mp (°C) found	mp (°C) reported
8	4-(OH)C_4H_4	3a	 4h	25	84	203-205	205-207[39]
9	3-(OH)C_4H_4	3a	 4i	20	86	228-231	229-231[39]
10	4-(OMe)C_4H_4	3a	 4j	30	90	199-202	199-201[40]
11	3,4-(OMe)$_2C_4H_4$	3a	 4k	40	84	167-169	168-170[40]
12	4-(iso-pr)C_4H_4	3a	 4l	35	83	197-198	198-200[38]
13	2-Furyl	3a	 4m	25	90	219-221	220-222[41]
14	2-Thionyl	3a	 4n	35	88	227-229	226-228[41]

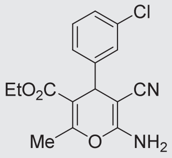
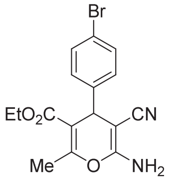
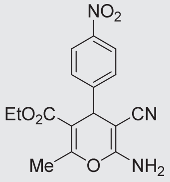
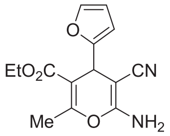
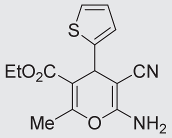
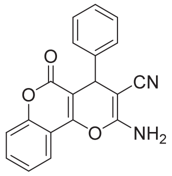
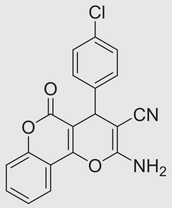
(Continues)

TABLE 2 (Continued)

Entry	Ar	*β*- diketone	product	Time (min)	Yield (%)[a]	mp (°C) found	mp (°C) reported
15	4-(Cl)C_4H_4	3b	 4o	12	95	226-229	226-229[37]
16	2-(Cl)C_4H_4	3b	 4p	15	90	212-214	213-215[37]
17	4-(NO_2)C_4H_4	3b	 4q	10	95	233-234	234-235[37]
18	3-(NO_2)C_4H_4	3b	 4r	15	93	197-200	198-200[37]
19	4-(OMe)C_4H_4	3b	 4s	40	82	191-193	193-195[37]
20	C_6H_5	5	 6a	75	75	186-189	189-191[42]
21	4-(Cl)C_4H_4	5	 6b	60	78	168-170	171-173[42]

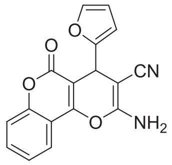
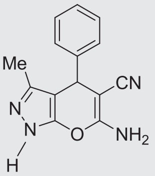
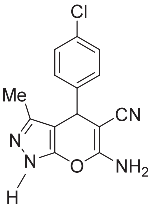
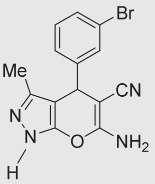
(Continues)

TABLE 2 (Continued)

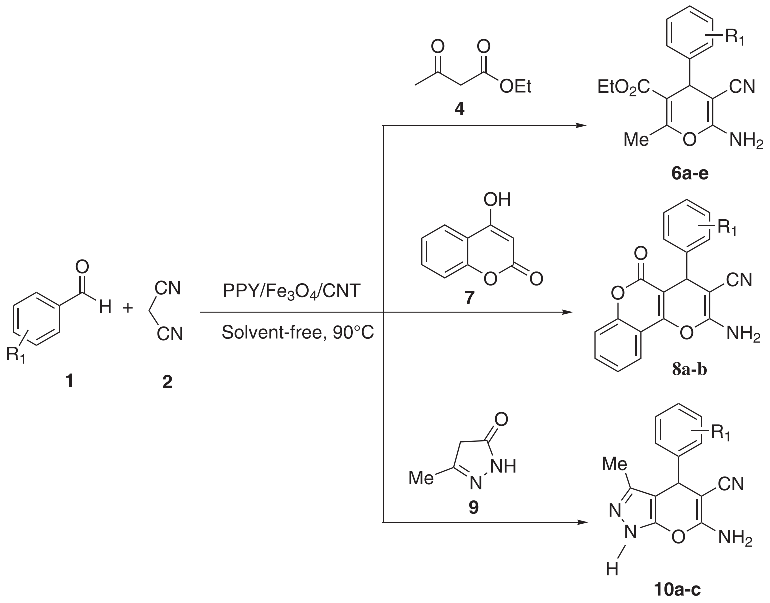
Entry	Ar	β- diketone	product	Time (min)	Yield (%)^a	mp (°C) found	mp (°C) reported
22	3-(Cl)C_4H_4	5	 6c	68	74	152-154	155-156[38]
23	4-(Br)C_4H_4	5	 6d	70	75	172-174	174-175[42]
24	4-(NO_2)C_4H_4	5	 6e	60	80	178-180	180-182[42]
25	2-Furyl	5	 6f	70	75	202-204	203-204[43]
26	2-Thionyl	5	 6g	75	70	204-206	203-205[44]
27	C_6H_5	7	 8a	30	89	254-255	255-257[40]
28	4-(Cl)C_4H_4	7	 8b	27	93	259-261	259-261[40]

(Continues)

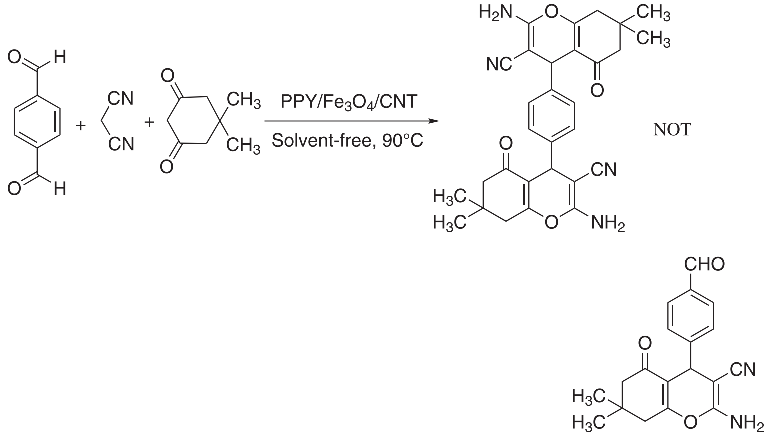
TABLE 2 (Continued)

Entry	Ar	β- diketone	product	Time (min)	Yield (%)[a]	mp (°C) found	mp (°C) reported
29	2-Furyl	7	 8c	25	90	251-253	252-253[45]
30	C_6H_5	9	 10a	35	92	243-245	244-245[46]
31	4-(Cl)C_4H_4	9	 10b	40	90	248-249	250-252[46]
32	3-(Br)C_4H_4	9	 10c	48	85	221-223	224-225[46]

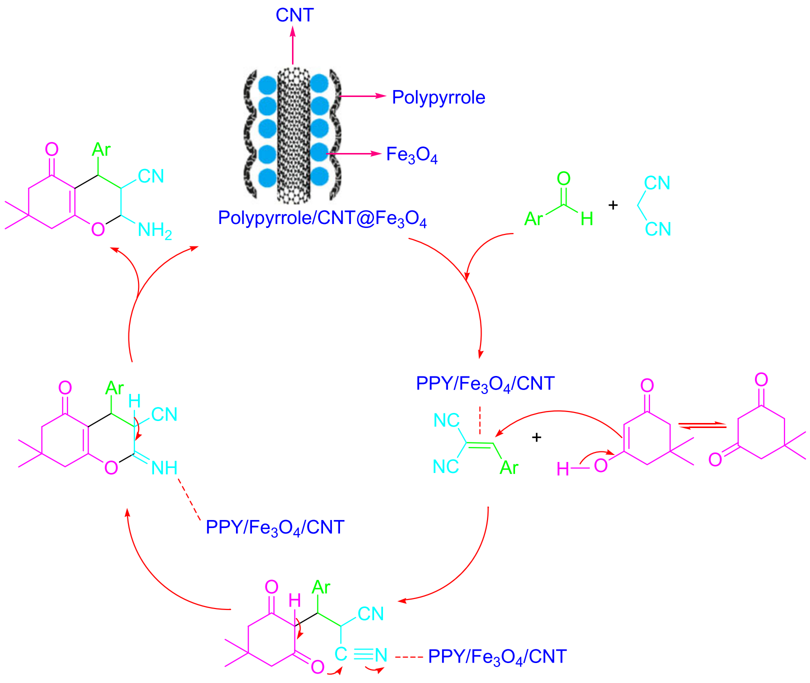
[a]Isolated Yields.



SCHEME 2 Synthesis of pyran derivatives using PPY/Fe_3O_4/CNT nanocomposite



SCHEME 3 Selective synthesis of bis-tetrahydrobenzo[*b*]pyran



SCHEME 4 Proposed mechanism for the synthesis of pyran derivatives

TABLE 3 The comparison of methods for the synthesis of 2-amino-3-cyano-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-4H-5,6,7,8-tetrahydrobenzo[*b*]pyran (4b)

Entry	Conditions	Time (min)	Yield (%)
1	PPY/Fe_3O_4/CNT/ Solvent-free/ 90 °C (Present work)	10	95
2	TBAB/ H_2O/ Reflux[39]	35	94
3	NaBr/ Solvent-free/ MW[47]	10	90
4	ZnO-beta zeolite/ EtOH/ Reflux[48]	35	95
5	$CeCl_3.7H_2O$/ aq EtOH/Reflux[49]	90	86
6	HDMBAB/ H_2O[50]	360	94
7	[bmim][BF_4]/ 80 °C[51]	180	95
8	MgO/ H_2O/EtOH(4:1)/ Reflux[52]	20	95
9	K_3PO_4/ H_2O/EtOH(80:20)/ rt[3]	60	93
10	PFPA/ H_2O/EtOH(1:1)/ rt[53]	60	92
11	[TEBSA].HSO_4 / H_2O/ 90 °C[54]	60	91

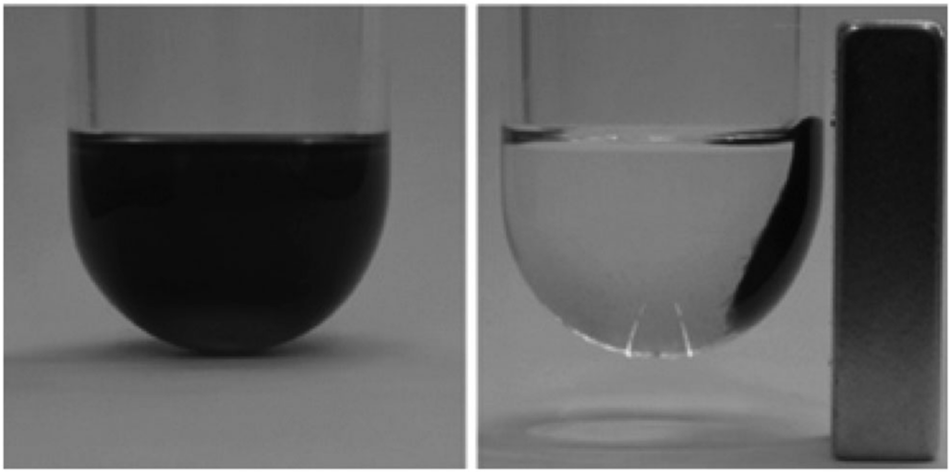


FIGURE 4 The use of an external magnetic field for separation of catalyst

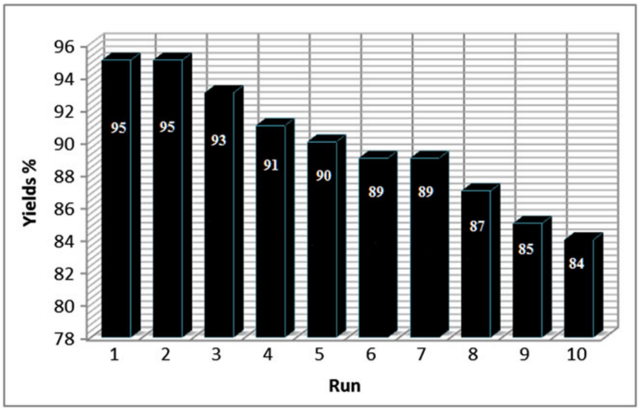


FIGURE 5 Reuse of the nanomagnetic polypyrrle/CNT@Fe_3O_4 for synthesis of 4b

4 | CONCLUSION

In conclusion, PPY/Fe_3O_4/CNT has been synthesized and characterized by FT-IR, TEM and SEM techniques and its catalytic activity has been evaluated in the synthesis of several series of pyran derivatives. Tetrahydrobenzo[*b*] pyranes, 4H-pyran-3-carboxylates, 4H,5H-pyrano[3,2-*c*] chromenes and dihydropyrano[2,3-*c*] pyrazoles have been successfully prepared from one-pot three-component condensation of aldehyde, malononitrile and dimedone (or ethyl acetoacetate/4-hydroxycoumarin/3-methyl-2-pyrazoline-5-one) using PPY/Fe_3O_4/CNT as a new, noncorrosive and reusable heterogeneous catalyst. The present method offer some advantages, such as high yields of products, short reaction times, easy work-up procedure and easy separation of the catalyst from the reaction mixture due to its magnetic character. Furthermore, chemoselective synthesis of bis-benzo[*b*]pyran from terephthalaldehyde can be achieved by this method. It must be noted that, it is the first report for the application of PPY/Fe_3O_4/CNT as a catalyst in organic transformations.

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