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Synthesis and characterization of amino glucose-functionalized silica-coated $NiFe_2O_4$ nanoparticles: a heterogeneous, new and magnetically separable catalyst for the solvent-free synthesis of pyrano[3,2-*c*]chromen-5(4*H*)-ones

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A novel, efficient and one-pot multi-component procedure for the synthesis of simple pyrano[3,2-*c*]chromen-5(4*H*)-ones or pyrazolyl pyrano[3,2-*c*]chromen-5(4*H*)-ones *via* reaction of aryl aldehydes, acetophenones and 4-hydroxycoumarin promoted by amino glucose-functionalized silica-coated $NiFe_2O_4$ nanoparticles under solvent-free conditions without using any other harmful organic reagents was reported. The structure of this nanoparticle was characterized by transmission electron microscopies, X-ray diffraction and Fourier transform infrared spectroscopies. The catalyst could easily be separated from the reaction mixture by using an external magnetic field and it was reusable. The high purity of the desired products, eco-friendliness, short reaction time and easy workup procedure can be mentioned as the other advantages of this method.

Introduction

Pyranochromenes are a class of important heterocycles with a wide range of pharmaceutical and biological properties such as anti-coagulant, spasmolytic, analgesic, myorelaxant, anti-cancer, cytotoxic, anti-HIV, anti-microbial, anti-tuberculosis, diuretic and anti-anaphylactic activity.[1–9] Moreover, they can be used as cognitive enhancers for the treatment of neurodegenerative diseases, including Huntington's disease, schizophrenia and myoclonus disease, amyotrophic lateral sclerosis, Alzheimer's disease, Parkinson's disease, AIDS associated dementia and Down's syndrome.[1] They can act also as additives in perfumes, food, cosmetics, optical brighteners, dispersed fluorescence and laser dyes.[10,11] So far, only a few methods have been reported for the synthesis of pyrano[3,2-*c*]chromen-5(4*H*)-ones.[12–15]

Multicomponent reactions (MCRs) are one of the most efficient tools in modern synthetic organic chemistry. They have advantages such as being fast, simple and easy to implement, with high atom efficiency. They offer a model for target- and diversity-oriented synthesis.[16–20]

Transition-metal nanoparticles are materials: containing a few tens to several thousand metal atoms, which are stabilized by ligands, polymers or dendrimers as protecting agents for their surfaces. They are heterogeneous catalysis that benefits from easy removal of catalyst materials and possible use at high temperatures, suffered for a long time from lack of selectivity and understanding of the mechanistic aspects that are indispensable in parameter improvements.[21] Amino glucose-functionalized silica-coated $NiFe_2O_4$ nanoparticles have attracted a lot of chemists because of its unique properties such as chemical inertness, easy synthesis and functionalization, low toxicity and low cost, high surface area, small crystallite size, superior controlled selectivity, more active sites and facile removing with aid of external magnet from the reaction mixture.

Results and discussion

The multicomponent reaction of benzaldehydes, acetophenones and 4-hydroxycoumarin, simple in nature, is essentially a condensation reaction. The reaction can be assisted by activating the carbonyl group of aldehydes with an acidic species or by improving the nucleophilic property of 4-hydroxycoumarin in basic media. In continuation of our research for the green synthesis of heterocyclic compounds,[22–29] herein we describe the synthesis of pyrano[3,2-*c*]chromen-5(4*H*)-ones using $NiFe_2O_4$@SiO_2@amino glucose magnetic nanoparticle as a new catalyst (Scheme 1).

As shown in Scheme 2, the $NiFe_2O_4$@SiO_2@amino glucose magnetic nanoparticle was synthesized in three steps from commercially available materials. MNPs were coated by silica using a sol–gel process. The $NiFe_2O_4$@SiO_2 core–shell structures

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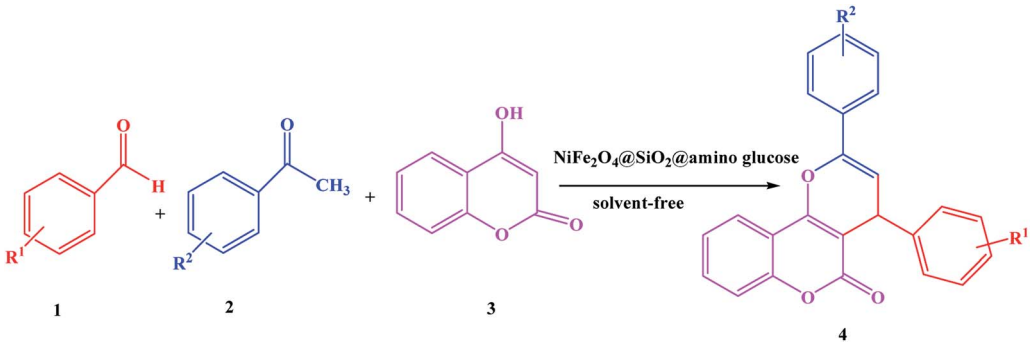
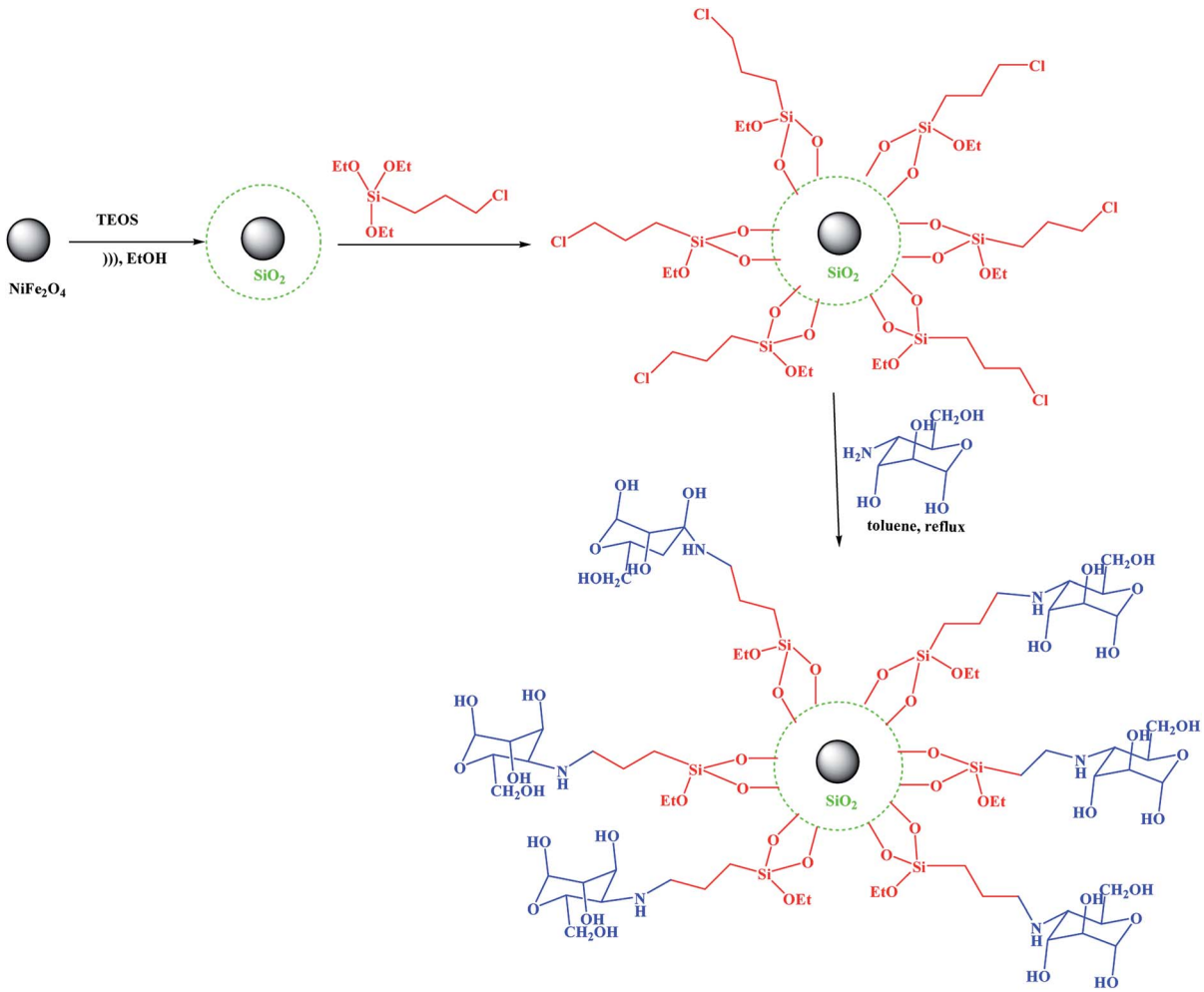


Scheme 1 Multicomponent synthesis of pyrano[3,2-*c*]chromen-5(4*H*)-ones using $NiFe_2O_4$@SiO_2@amino glucose.

were then sequentially treated with 3-chloropropyltrimethoxysilane. Next, it was treated with aminoglucose to obtain the amino glucose-functionalized silica-coated $NiFe_2O_4$ nanoparticles.

In the FT-IR spectrum of the $NiFe_2O_4$@SiO_2@amino glucose magnetic nanoparticle (Fig. 1), the absorption band of Fe–O was appeared in 590 cm^{-1}, the absorption band of Si–O–Si in SiO_2 shell were appeared in 1088, 912 and 512 cm^{-1}. The peaks in region 2930, 3120 and 3415 cm^{-1} refer to the stretching band of C–H aliphatic, OH stretching and NH stretching, in order.

The structure of $NiFe_2O_4$@SiO_2@glucose amine was also analyzed by XRD analysis. In Fig. 2 the XRD patterns of $NiFe_2O_4$@SiO_2@glucose amine and pure $NiFe_2O_4$ are illustrated. The comparison of the XRD patterns indicated that both patterns exhibits peaks at 30°, 36°, 45°, 50°, 54°, 58° and 62° which are



Scheme 2 Stepwise synthesis pathway of $NiFe_2O_4$@SiO_2@amino glucose.

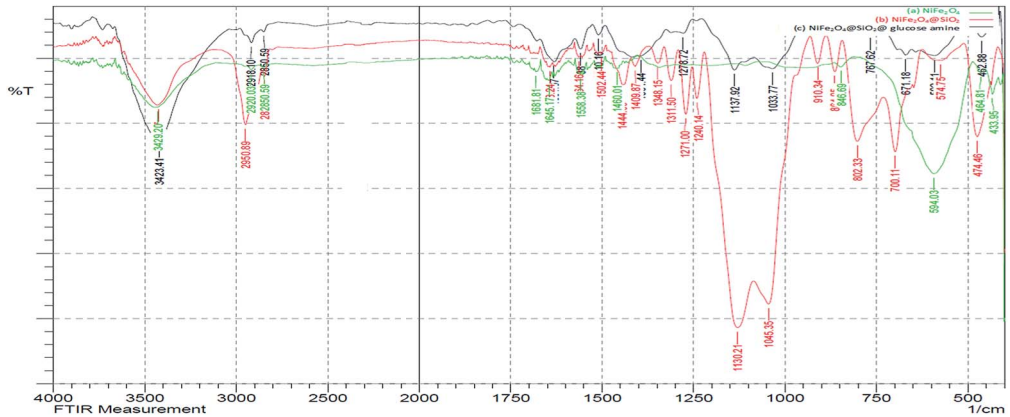


Fig. 1 FT-IR spectra of (a) $NiFe_2O_4$, (b) $NiFe_2O_4$@SiO_2, (c) $NiFe_2O_4$@SiO_2@glucose amine.

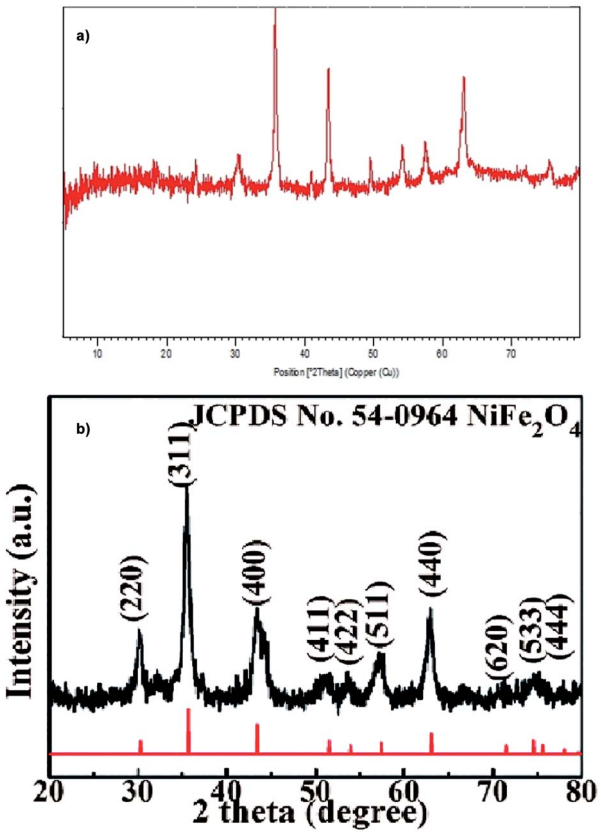


Fig. 2 The XRD of (a) $NiFe_2O_4$@SiO_2@glucose amine and (b) $NiFe_2O_4$.

representative of HNTs structure (JCPDS no. 54-0964) and broad peak in 10–30° is related to $NiFe_2O_4$ covered by SiO_2.

Next, the morphology and nanoparticle size of the synthesized magnetic catalyst was characterized by Transmission Electron Microscope (TEM) (Fig. 3). As shown in Fig. 2, the catalyst particles possess near spherical morphology with average diameter of about 20–40 nm. Furthermore, TEM images show some aggregation, which was illustrated the successful grafting of the polymer on to magnetic nanoparticles.

The most common method to determine concentration of acidic sites is temperature programmed desorption (TPD) of a basic probe molecule, mostly ammonia. For this test, the sample were pretreated at 573 K for 2 h. Afterwards, ammonia was adsorbed onto the surface of the samples at 393 K. The total amount of desorbed ammonia was determined by reaction with a diluted solution of sulphuric acid and titration with sodium hydroxide. The results are shown in Table 1. It can be seen that the numbers of acidic sites increase from $NiFe_2O_4$ and $NiFe_2O_4$@SiO_2 to $NiFe_2O_4$@SiO_2@glucose amine.

In order to evaluate the catalytic capability of the synthesized heterogeneous catalyst ($NiFe_2O_4$@SiO_2@glucose amine) in organic reactions, we chose to examine its activity in a one-pot reaction for the synthesis of pyrano[3,2-*c*]chromen-5(4*H*)-ones.

Initially, we observed that the reaction of 4-nitrobenzaldehyde with 4-hydroxycoumarin and acetophenone in $NiFe_2O_4$@SiO_2@glucose amine could be a suitable choice for the synthesis of pyrano – chromene **4b**. This protocol proceeds smoothly at room temperature to afford product **4b** in fairly high yield. We have also carried out the sample reaction in the $NiFe_2O_4$, $NiFe_2O_4$@SiO_2, SiO_2 or in the absence of catalyst. On the other hand, variables affecting on the reaction yields such as the type of solvent, the amount of catalyst, different temperatures, and solvent-free conditions were studied (Table 2). As

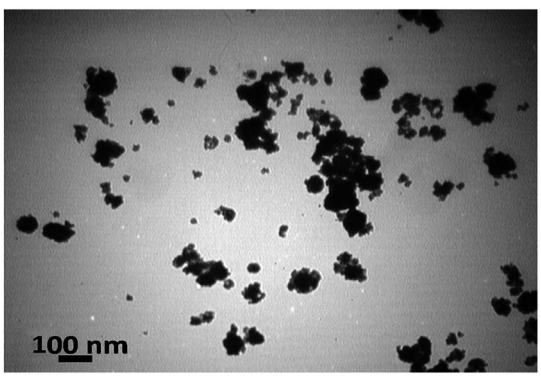


Fig. 3 The TEM image of synthesized $NiFe_2O_4$@SiO_2@glucose amine.

Table 1 Concentration of acidic sites determined by the method NH_3-TPD

Catalyst	$NiFe_2O_4$	$NiFe_2O_4$@SiO_2	$NiFe_2O_4$@SiO_2@glucose amine
Acid surface sites (μmol g^{-1})	180	315	1450

shown in Table 2, the reaction under solvent-free conditions is more efficient.

To check the generality of this method, different derivatives of benzaldehydes and acetophenones were subjected to the reaction with 4-hydroxycoumarin. The results are summarized in Table 3.

All of the synthesized compounds were characterized by IR, NMR, HR-Ms, elemental analysis and by comparison with authentic samples for known compounds.

In continuation of our study, we triggered to synthesize a new category of pyrazolylpyrano chromenes **4k–m** and bis pyranochromene **4n** as shown in Scheme 3.

A plausible mechanism for the formation of pyranochromene **4** is shown in Scheme 4. Initially, $NiFe_2O_4$@SiO_2@glucose amine can increase the electrophilic character of the carbonyl species by virtue of its inherent Brønsted acidity. Nucleophilic addition of the enolic form of the ketone and subsequent dehydration can lead to chalcone **6**. Then, Michael addition of **3** to **6** to produce intermediate **8**, followed by simple condensation of the hydroxyl group with the carbonyl and dehydration, forms product **4**.

We compared the efficiency of this method with recently reported methods (Table 4).

The recyclability and reusability of catalyst was studied in the model one-pot three-component reaction between 4-nitrobenzaldehyde, acetophenone and 4-hydroxycoumarin. At the end of the reaction, the separated catalyst can be reused after being washed with warm EtOH and drying at 80 °C. $NiFe_2O_4$@SiO_2@glucose amine was used again for subsequent experiments under similar reaction conditions. The catalyst could be reused for the next cycle without any notable loss of its activity. Yields of the product decreased only slightly after reusing the catalyst five times.

Experimental section

Materials and methods

Chemicals were purchased from Merck and Fluka. All solvents used were dried and distilled according to standard procedures. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were determined on a Shimadzu FT-IR

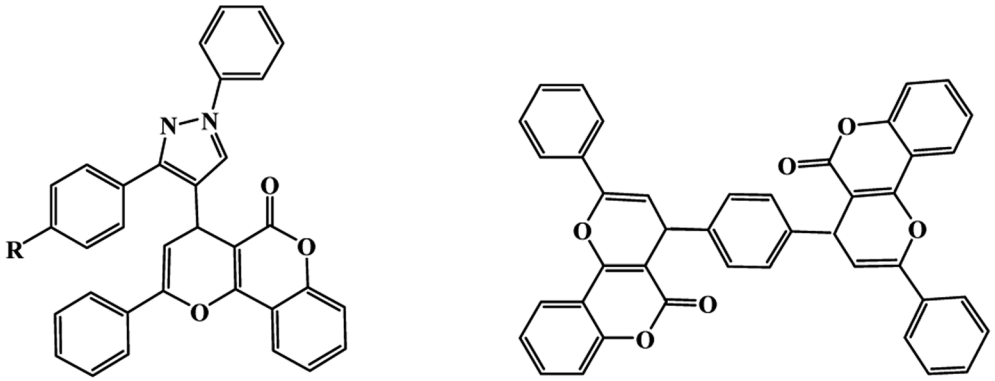
Table 2 Optimization of reaction condition

Entry	Catalyst	Catalyst amount	Reaction condition	Time (min)	Yield (%)
1	—	—	Reflux in EtOH	720	Trace
2	SiO_2	0.05 g	Stir, rt, EtOH	750	15
3	$NiFe_2O_4$	0.05 g	Stir, rt, EtOH	720	24
4	$NiFe_2O_4$@SiO_2	0.05 g	Stir, rt, EtOH	300	53
5	$NiFe_2O_4$@SiO_2@glucose amine	0.05 g	Stir, rt, EtOH	40	90
6	$NiFe_2O_4$@SiO_2@glucose amine	0.07 g	Stir, rt, EtOH	40	87
7	$NiFe_2O_4$@SiO_2@glucose amine	0.03 g	Stir, rt, EtOH	60	85
8	$NiFe_2O_4$@SiO_2@glucose amine	0.05 g	Stir, rt, CH_3CN	60	76
9	$NiFe_2O_4$@SiO_2@glucose amine	0.05 g	Stir, rt, H_2O	45	84
10	$NiFe_2O_4$@SiO_2@glucose amine	0.05 g	Solvent free, rt	25	96
11	$NiFe_2O_4$@SiO_2@glucose amine	0.05 g	Solvent free, 80 °C	25	94

Table 3 Synthesis of pyrano[3,2-*c*]chromen-5(4*H*)-ones using $NiFe_2O_4$@SiO_2@glucose amine

Entry	Benzaldehyde	Acetophenones	Product	Time (min)	Yield (%)	Mp (°C) (Lit mp)	Ref.
1	3-Nitro	Acetophenone	**4a**	10	95	123–125 (122–123)	14
2	4-Nitro	Acetophenone	**4b**	10	98	228–230 (230–231)	13 and 15
3	4-Hydroxy	Acetophenone	**4c**	15	93	167–169	This work
4	Benzaldehyde	Acetophenone	**4d**	12	95	166–168 (170–171)	12–15 and 30
5	4-Methoxy	Acetophenone	**4e**	15	90	143–144 (143–144)	12[a,b] and 30
6	4-Chloro	4-Chloro	**4f**	10	94	238–240 (239–241)	12 and 15
7	4-Chloro	3-Nitro	**4g**	10	95	189–190	This work
8	4-Methyl	3-Nitro	**4h**	15	93	152–154	This work
9	4-Chloro	Acetophenone	**4i**	10	97	176–178 (176–177)	13 and 14
10	Benzaldehyde	4-Chloro	**4j**	10	96	145–147 (149–151)	12 and 14

[a] All the isolated products were characterized on the basis of their elemental analyses, physical properties and IR, ^1H, ^{13}C NMR spectral analysis, HR-Ms or by direct comparison with authentic materials. [b] Isolated yields.



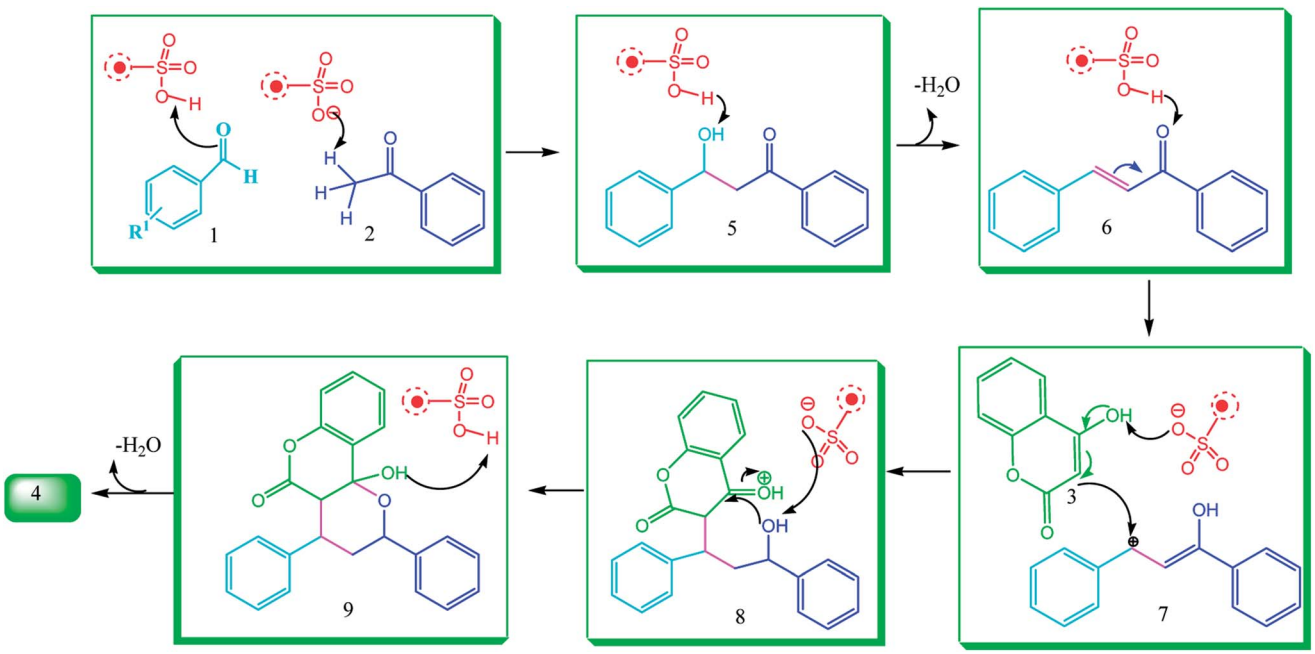
4k: R=H ;10min, 94%, mp >300 °C

4l: R=4-OCH_3; 12min, 92%, mp 287-289°C

4m: R= 4-Methyl; 15min, 93%, mp 265-267°C

4n 20min, 86%, mp > 300°C

Scheme 3 Synthesis of pyrazolyl and bis pyrano[3,2-c]chromenes.



Scheme 4 Proposed mechanism for the synthesis of pyranochromene 4.

8600 spectrophotometer. ^{1}H and ^{13}C NMR spectra were determined on a Bruker 400 DRX Avance instrument at 500 and 125 MHz. Elemental analyses were recorded on a Carlo-Erba EA1110CNNO-S analyser.

Thin layer chromatography (TLC) was carried out with ethyl acetate : *n*-hexane 1 : 4 on TLC Silica gel 60 F_{254}.

Synthesis of silica-coated $NiFe_2O_4$ ($NiFe_2O_4$@SiO_2 MNPs). Typically, 500 mg of the $NiFe_2O_4$ nanoparticle were dispersed by ultrasonic vibration in a mixture of ethanol (20 ml), deionized water (3 ml) and 1 ml of 25 wt% concentrated aqueous ammonia solution for 20 min. Subsequently, 0.7 ml of tetraethylorthosilicate (TEOS) was added dropwise. After stirring for 12 h at room temperature under N_2 atmosphere, the products was collected from the solution using a magnet, and then washed several times with water and ethanol and dried at 25 °C under vacuum.

Synthesis of $NiFe_2O_4$@SiO_2–Cl MNPs. 500 mg $NiFe_2O_4$@SiO_2 nanoparticles were dispersed into 50 ml toluene and sonicated for 20 min, followed by the addition of 0.5 ml (3-chloropropyl) trimethoxysilane (CPTES). Then, the mixture was refluxed at 110 °C with continuous stirring for 12 h under a nitrogen flow. The resulting $NiFe_2O_4$@SiO_2–Cl MNPs was collected by magnetic separation followed by washing with toluene and ethanol several times and drying at 60 °C for 6 h.

Table 4 Comparison of present method for the synthesis of **4d** with some previous methods

Entry	Condition	Time (min)	Yield (%)	Ref.
1	MWI, 60 °C	15	92	30
2	I_2, AcOH, 100 °C	50	98	14[a]
3	$AuCl_3$, AgOTf (3 mol%), reflux	360	78	15[a]
4	$Ca(OTf)_2$, $BuNPF_6$, 120 °C	240	92	13[a]

[a] This pyranochromene was synthesized in a two step protocol, synthesis of chalcone followed by reaction with 4-hydroxycoumarin.

Synthesis of $NiFe_2O_4$@SiO_2@amino glucose. 500 mg $NiFe_2O_4$@SiO_2–Cl MNPs were dispersed into 50 ml toluene and sonicated for 30 min, followed by the addition of 0.5 ml glucose amine. Then, the mixture was refluxed at 110 °C with continuous stirring for 12 h under a nitrogen flow. The resulting functionalized $NiFe_2O_4$@SiO_2@aminoglucose was collected by magnetic separation followed by washing with toluene and ethanol several times and drying at 80 °C for 8 h.

General procedure for preparation of pyrano[3,2-*c*]chromen-5(4*H*)-ones 4a–n. A mixture of aldehyde 1 (1.0 mmol), acetophenone derivative 2 (1.0 mmol), 4-hydroxycoumarin 3 (1.0 mmol) and 0.05 g $NiFe_2O_4$@SiO_2@aminoglucose were stirred at room temperature under solvent free condition for the required reaction time according to Tables 2 and 3 After completion of the reaction, as indicated by TLC (TLC Silica gel 60 F_{254}, ethyl acetate : *n*-hexane 1 : 4), the resulting mixture was diluted with hot ethanol (10 ml) and the catalyst separated by an external magnet and washed with hot distilled water (5 ml) and ethanol (3 ml) two times. The filtrate was cooled down to room temperature and the crude products which precipitated were collected and recrystallized from ethanol if necessary. All of the synthesized compounds were characterized by their physical constants, IR, ^{1}H NMR, ^{13}C NMR spectroscopy, HR-Ms and elemental analysis. Some derivatives of the pyranochromenes are known and were compared with authentic samples matching melting points and spectras.

Analytical data for the selected compounds

*4-(3-Nitrophenyl)-2-phenylpyrano[3,2-c]chromen-5(4H)-one (**4a**).* White solid, mp: 123–125 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.41 (s, 1H), 7.05–7.92 (m, 14H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 34.34, 103.34, 105.65, 109.28, 111.62, 111.74, 114.72, 115.82, 119.03, 119.38, 121.92, 127.72, 130.29, 135.87, 137.63, 139.72, 142.49, 145.83, 147.87, 151.54, 154.75, 162.09 ppm. FT-IR (KBr): 3077, 2938, 1707 (C=O), 1613, 1495, 1510 and 1388 (NO_2), 1237 (C–O) cm^{-1}. HRMs (*m*/*z* 397.1). Anal calc. for $C_{24}H_{15}NO_5$: C, 72.54; H, 3.80; N, 3.52. Found: C, 72.51; H, 3.83; N, 3.55.

*4-(4-Nitrophenyl)-2-phenylpyrano[3,2-c]chromen-5(4H)-one (**4b**).* White solid, mp: 228–230 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.42 (s, 1H), 7.23–7.97 (m, 14H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 37.82, 103.60, 105.92, 109.54, 111.98, 111.19, 115.04, 116.04, 119.82, 121.62, 130.59, 133.72, 137.82, 139.48, 142.80, 145.27, 147.48, 151.38, 154.73, 162.24 ppm. FT-IR (KBr): 2918, 1663 (C=O), 1523 and 1356 (NO_2), 1600, 1400, 1233 (C–O) cm^{-1}. HRMs (*m*/*z* 397.1). Anal calc. for $C_{24}H_{15}NO_5$: C, 72.54; H, 3.80; N, 3.52. Found: C, 72.53; H, 3.81; N, 3.54.

*4-(4-Hydroxyphenyl)-2-phenylpyrano[3,2-c]chromen-5(4H)-one (**4c**).* White solid, mp: 167–169 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.4 (s, 1H), 6.88–7.92 (m, 14H), 9.8 (s, 1H, phenolic O–H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 37.63, 103.56, 105.78, 109.72, 111.04, 111.37, 115.84, 116.50, 119.24, 121.97, 130.21, 133.83, 137.72, 139.05, 142.756, 143.64, 149.62, 151.58, 154.48, 160.48 ppm. FT-IR (KBr): 3239, 3069, 2930, 1707 (C=O), 1572, 1486, 1237 (C–O) cm^{-1}. HRMs (*m*/*z* 368.1). Anal alc. for $C_{24}H_{16}O_4$: C, 78.25; H, 4.38. Found: C, 78.21; H, 4.40.

*2,4-Diphenylpyrano[3,2-c]chromen-5(4H)-one (**4d**).* White solid, mp: 166–168 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.41 (s, 1H), 6.78–7.64 (m, 15H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 36.71, 103.12, 105.21, 109.11, 111.13, 111.38, 114.78, 115.03, 121.45, 126.76, 128.14, 135.87, 142.09, 143.91, 145.12, 145.67, 147.16, 151.09, 153.98, 165.41 ppm. FT-IR (KBr): 3099, 2987, 1665 (C=O), 1609, 1487, 1234 (C–O) cm^{-1}. HRMs (*m*/*z* 352.1). Anal calc. for $C_{24}H_{16}O_3$: C, 81.80; H, 4.58. Found: C, 81.81; H, 4.56.

*4-(4-Methoxyphenyl)-2-phenylpyrano[3,2-c]chromen-5(4H)-one (**4e**).* White solid, mp: 143–144 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 3.50 (s, 3H), 5.59 (s, 1H), 7.19–8.17 (m, 14H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 36.65, 54.58, 103.27, 105.82, 109.09, 111.27, 111.83, 114.62, 115.24, 123.74, 125.87, 129.87, 135.87, 142.38, 143.84, 145.63, 145.43, 151.87, 152.41, 153.49, 163.09 ppm. FT-IR (KBr): 2938, 1666 (C=O), 1495, 1388, 1261 (C–O), 1102 cm^{-1}. HRMs (*m*/*z* 382.12). Anal calc. for $C_{25}H_{18}O_4$: C, 78.52; H, 4.74. Found: C, 78.51; H, 4.71.

*2,4-Bis(4-chlorophenyl)pyrano[3,2-c]chromen-5(4H)-one (**4f**).* White solid, mp: 238–240 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.10 (s, 1H), 7.07–8.09 (m, 13H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 36.80, 103.72, 105.47, 109.71, 111.38, 111.06, 113.49, 115.05, 123.29, 123.93, 129.04, 135.62, 142.40, 143.21, 143.63, 145.63, 148.38, 151.09, 152.32, 161.32 ppm. FT-IR (KBr): 2934, 1675 (C=O), 1605, 1495, 1221 (C–O), 1098, 1016 cm^{-1}. HRMs (*m*/*z* 420.03). Anal calc. for $C_{24}H_{14}Cl_2O_3$: C, 68.43; H, 3.35. Found: C, 68.41; H, 3.37.

*4-(4-Chlorophenyl)-2-(3-nitrophenyl)pyrano[3,2-c]chromen-5(4H)-one (**4g**).* White solid, mp: 189–190 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.64 (s, 1H), 7.37–8.09 (m, 10H), 8.32 (s, 1H), 8.58 (s, 1H), 8.83 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 36.29, 103.72, 105.48, 109.76, 111.39, 111.38, 115.41, 116.03, 119.61, 121.92, 130.04, 131.32, 133.72, 137.43, 139.85, 142.28, 144.93, 145.38, 147.72, 151.48, 154.05, 162.51 ppm. FT-IR (KBr): 3065, 2934, 1667 (C=O), 1609, 1572, 1392, 1245 (C–O), 1171 (C–Cl) cm^{-1}. HRMs (*m*/*z* 431.06). Anal calc. for $C_{24}H_{14}ClNO_5$: C, 66.75; H, 3.27; N, 3.24. Found: C, 66.71; H, 3.29; N, 3.27.

*2-(3-Nitrophenyl)-4-p-tolylpyrano[3,2-c]chromen-5(4H)-one (**4h**).* White solid, mp: 152–154 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.31 (s, 3H), 5.61 (s, 1H), 7.11–8.11 (m, 8H), 8.25 (d, J = 8.2 Hz, 1H), 8.53–8.59 (m, 1H), 8.79 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 31.29, 37.58, 103.40, 105.78, 109.72, 111.49, 111.48, 113.87, 116.28, 119.98, 121.76, 130.28, 131.73, 133.28, 133.69, 137.68, 139.29, 142.72, 145.63, 147.59, 151.73, 154.21, 161.82 ppm. FT-IR (KBr): 3089, 2922, 1675 (C=O), 1604, 1527, 1495, 1347, 1216 (C–O) cm^{-1}. HRMs (*m*/*z* 411.11). Anal calc. for

$C_{25}H_{17}NO_5$: C, 72.99; H, 4.16; N, 3.40. Found: C, 72.98; H, 4.19; N, 3.41.

*4-(4-Chlorophenyl)-2-phenylpyrano[3,2-c]chromen-5(4H)-one (**4i**).* White solid, mp: 176–178 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.63 (s, 1H), 7.14–7.83 (m, 9H), 7.89–8.02 (m, 2H), 8.14 (d, J = 8.0 Hz, 2H), 8.72 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 36.46, 103.21, 105.51, 109.12, 110.93, 111.21, 113.63, 118.09, 119.27, 123.27, 130.05, 131.18, 133.72, 136.20, 138.51, 142.72, 145.63, 151.06, 154.18, 160.93 ppm. FT-IR (KBr): 3087, 2987, 1673 (C=O), 1613, 1565, 1475, 1323, 1256 (C–O) cm^{-1}. HRMs (*m*/*z* 386.07). Anal calc. for $C_{24}H_{15}ClO_3$: C, 74.52; H, 3.91. Found: C, 74.58; H, 3.99.

*2-(4-Chlorophenyl)-4-phenylpyrano[3,2-c]chromen-5(4H)-one (**4j**).* White solid, mp: 145–147 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.58 (s, 1H), 7.27–7.85 (m, 8H), 8.01 (d, J = 7.8 Hz, 2H), 8.09 (d, J = 7.8 Hz, 2H), 8.23–8.32 (m, 1H), 8.74 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 36.51, 103.18, 105.93, 109.62, 111.04, 111.32, 113.61, 118.17, 119.40, 123.36, 130.12, 131.14, 133.63, 136.72, 138.90, 142.24, 145.05, 151.20, 156.82, 161.14 ppm. FT-IR (KBr): 3011, 2965, 1679 (C=O), 1600, 1545, 1432, 1278 (C–O) cm^{-1}. HRMs (*m*/*z* 386.05). Anal calc. for $C_{24}H_{15}ClO_3$: C, 74.52; H, 3.91. Found: C, 74.54; H, 3.95.

***4k**).* Off white solid, mp: >300 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.63 (s, 1H), 7.07 (d, J = 7.6 Hz, 2H), 7.11–8.03 (m, 18H), 8.12 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 56.9, 101.9, 105.6, 111.0, 111.7, 112.9, 117.7, 119.4, 119.8, 121.1, 123.3, 129.5, 129.7, 131.0, 131.6, 133.4, 133.7, 135.0, 135.4, 138.0, 138.2, 139.5, 140.4, 145.8, 151.7, 153.7, 163.0 ppm. FT-IR (KBr): 2973, 1721 (C=O), 1672, 1632, 1481, 1209 (C–O), 1108 cm^{-1}. HRMs (*m*/*z* 494.16). Anal calc. for $C_{33}H_{22}N_2O_3$: C, 80.15; H, 4.48; N, 5.66; found: C, 80.10; H, 4.41, N, 5.67.

***4l**).* Off white solid, mp: 287–289 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.31 (s, 3H), 5.59 (s, 1H), 7.11 (d, J = 7.8 Hz, 2H), 7.13–8.05 (m, 17H), 8.09 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 43.5, 57.3, 101.3, 103.6, 111.4, 111.8, 113.6, 117.9, 119.8, 120.2, 121.0, 128.7, 129.8, 129.9, 130.5, 131.4, 133.3, 133.9, 135.3, 135.5, 139.0, 139.8, 139.9, 140.5, 143.6, 150.5, 153.4, 161.4 ppm. FT-IR (KBr): 2991, 1709 (C=O), 1657, 1641, 1492, 1235 (C–O), 1128 cm^{-1}. HR-Ms (508.18 *m*/*z*). Anal calc. for $C_{34}H_{24}N_2O_3$: C, 80.30; H, 4.76; N, 5.51; found: C, 80.24; H, 4.76, N, 5.57.

***4m**).* Off white solid, mp: 265–267 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 3.63 (s, 3H), 5.41 (s, 1H), 7.10 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 7.15–8.08 (m, 15H), 8.14 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 56.9, 59.6, 101.6, 105.9, 111.6, 112.7, 113.5, 118.0, 119.0, 119.7, 120.6, 125.7, 129.3, 129.7, 130.6, 131.5, 133.9, 135.5, 135.7, 137.4, 138.5, 139.7, 140.0, 143.7, 148.9, 151.2, 153.4, 161.3 ppm. FT-IR (KBr): 2962, 1709 (C=O), 1652, 1641, 1493, 1226 (C–O), 1170 cm^{-1}. HR-Ms (524.17 *m*/*z*). Anal calc. for $C_{34}H_{24}N_2O_4$: C, 77.85; H, 4.61; N, 5.34. Found: C, 77.84; H, 4.66, N, 5.32.

***4n**).* White solid, mp: >300 °C, ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 5.44 (s, 2H), 7.10–7.14 (m, 4H), 7.16–7.34 (m, 4H), 7.136–8.05 (m, 16H) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 56.9, 101.6, 104.8, 111.2, 111.7, 113.0, 119.6, 119.9, 125.4, 129.6, 129.9, 131.6, 133.2, 135.8, 142.0, 151.5, 152.6, 161.0. FT-IR (KBr): 3057, 2983, 1723 (C=O), 1655, 1647, 1462, 1219 (C–O), 1151 cm^{-1}. HR-Ms (*m*/*z* 657.23). Anal calc. for $C_{44}H_{33}O_6$: C, 80.35; H, 5.06. Found: C, 80.34; H, 5.11.

Conclusion

In conclusion, we have developed $NiFe_2O_4$@SiO_2@glucose amine as a new, mild and efficient avenue for the synthesis of pyrano[3,2-*c*]chromen-5(4*H*)-ones. This nano particles were synthesized for the first time and can act as a promoter to activate the substrate molecule for the synthesis of pyrano[3,2-*c*]chromen-5(4*H*)-ones. The operational simplicity, the excellent yields of products, ease of separation and recyclability of the magnetic catalyst, waste reduction and high selectivity are the main advantages of this method. Furthermore, this new avenue is cheap and environmentally benign. This novel concept is expected to use to development of more benign reactions.

Conflicts of interest

There are no conflicts to declare.

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