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Green synthesis of benzopyrans using Fe_3O_4 MNPs and multicomponent reaction

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Abstract: Application of Fe_3O_4 MNPs as a catalyst for the synthesis of pyran prepared by the reaction of dimedone, aldehydes, and malononitrile in water at room temperature. The catalyst was prepared according to a previously published literature procedure using inexpensive and readily available starting materials. Furthermore, the catalyst could be recovered conveniently and reused efficiently such that a considerable catalytic activity still could be achieved after fourth run. Other beneficial features of this new synthetic approach include short reaction time, high yields, clean reaction profiles, and a simple work-up procedure.

Keywords: Fe_3O_4MNPs, Pyrans, Green synthesis, Dimedone.

Introduction

Heterocyclic compounds hold a prominent position in medicinal chemistry owing to their wide spectrum of biological activities such as antimalarial,[1] antimicrobial[2], antitumor [3], anticancer [4], antidepressant [5], antiviral [6], antidiabetic [7], anti-inflammatory [8] and anti-HIV [9]. Moreover, they also contribute in the feld of material science [10], dyes and pigment science [11] as well as agrochemistry [12]. Therefore, there is considerable thrust for the development of efficient synthetic strategies for producing these compounds. MCRs open diverse avenues to create novel concatenations in one pot fashion leading to diverse biologically potent heterocyclic scaffolds [13, 14]. Having a cascade of reactions occurring in one pot is highly beneficial in the context of modern trends for organic synthesis, where sustainability is as relevant as efficiency and selectivity.

Multicomponent reactions being atom economic, efficient and extremely convergent in nature offer a number of advantages over stepwise sequential approaches [15–17] and could be performed in the presence of nanocatalyst and produce heterocyclic compounds [18-20]. Metal oxides are highly crystalline for their catalytic efficacy [21, 22] and the combination of two or more metals and their curing processes allow the tuning of the surface properties of the materials, making them opt for specific purpose [23, 24]. Pyrans are an important class of oxygen-containing heterocycles with diverse and interesting biological and pharmacological activities such as anti-coagulant, spasmolytic, diuretic, anti-cancer, and anti-anaphylactin characteristics [25–26]. They are also used for the treatment neurodegenerative disease, AIDS associated dementia and down's syndrome as well as for the treatment of schizophrenia and myoclonuse [27]. Some pyrans can be useful as photoactive materials [27]. Whereas polysubstituted pyran constitutes a structural unit of a series of natural products [28, 29]. According to these excellent properties of the pyrans, several methods have been reported for the synthesis of these compounds *via* three components one-pot reactions [30–37]. However,

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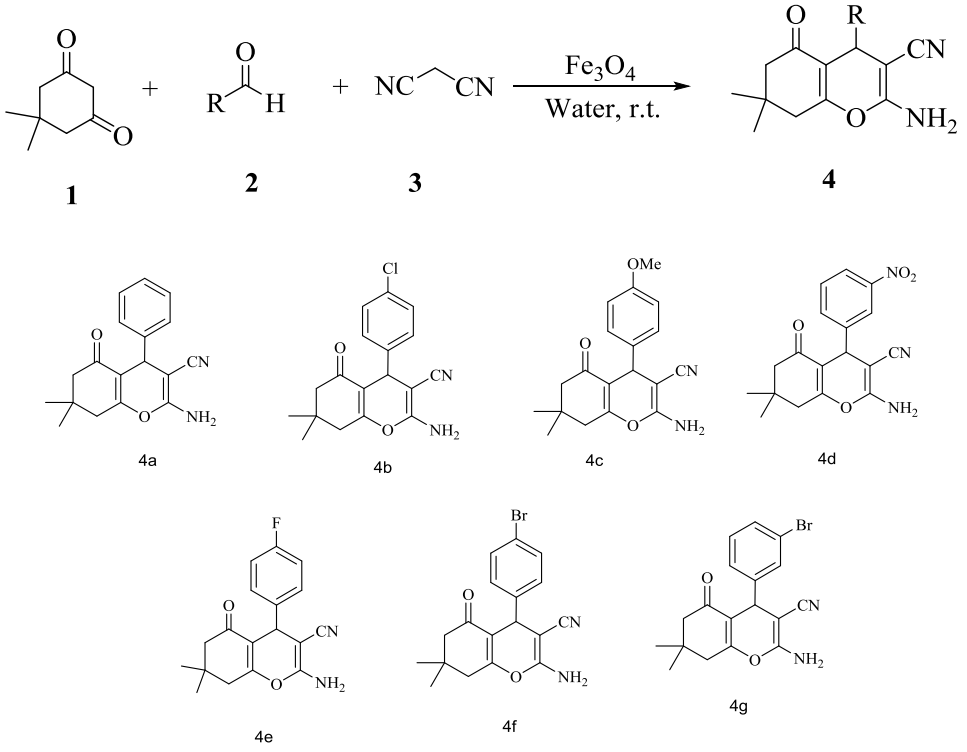
many of these methods were associated with use of hazardous organic solvents which is significantly harmful to environment, long duration of reaction, low yield of products, effluent pollution, hard to separate the catalyst and lack of general applicability. Therefore, the development of a new greener and more convenient method using a new catalyst with high catalytic activity for the synthesis of pyrans is highly desirable.

In this research was reported facile and efficient green synthesis of pyrans with short reaction time by the three-component reaction of dimedone, aldehydes and malononitrile using Fe_3O_4 MNPs as heterogeneous catalysts with high catalytic activity in water at room temperature in high yield (Scheme **1**).



Scheme 1: Fe_3O_4 MNPs catalyzed synthesis of pyrans

Results and discussion

The Fe_3O_4 MNPs catalyst was prepared according to a literature procedure [16].The analysis structure and size distribution of the nanoparticles was performed by scanning electron microscopy (SEM, Figure 1) and X-ray diffraction (XRD, Figure 2) methods. The average crystalline size (D) for Fe_3O_4 MNPs was calculated based on peak with the strongest intensity using the Debye–Scherrer equation ($D = K\lambda/\beta\cos\theta$); where is full-width at half-maximum or half-width in radians and K is the so-called shape factor (0.89), θ is Bragg's diffraction angle, and is the X-ray wavelength used (1.5406 Å for CuK_α line). Particles size of Fe_3O_4 MNPs has been found to be 21–23 nm. At first, the three-component reaction of dimedone, bnzaldehyde and malononitriles was investigated as a simple model for optimization of reaction conditions. Thereafter, the applicability of the method was evaluated for the synthesis of other pyrans using a wide range of aldehydes. The substituents in the aromatic ring of aldehydes or use of heteroaromatic aldehydes have no significant effect on the time of the reaction and yield of the products. Fe_3O_4 MNPs efficiently catalyzed the reactions, giving the desired products **4a-g** in high yields over relatively short reaction times.

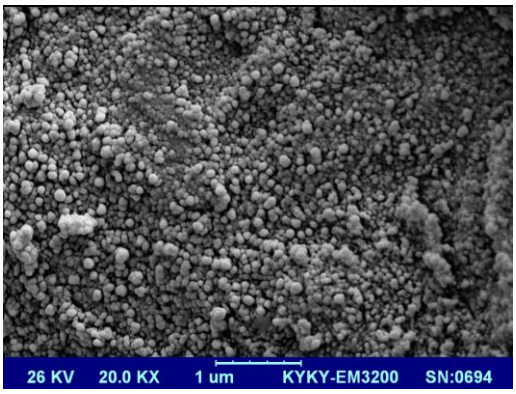


Figure 1. SEM image of Fe_3O_4 nanoparticles

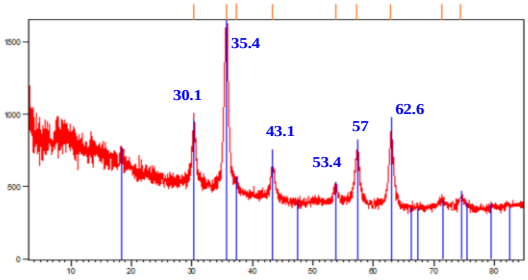


Figure 2. XRD spectra of Fe_3O_4 nanoparticles

Among the catalysts, Fe_3O_4 -MNPs was better to others and produced the best yield of the target 4*H*-chromene (**4a**). In the absence of catalyst only a trace amount of the product was formed (Table 1, entry 1). The Fe_3O_4MNPs are prepared according to literature procedure. The structure of Fe_3O_4 MNPs was confirmed by SEM and XRD spectra for nanostructure. The size of Fe_3O_4 MNPs from this method has been found to be 21–23 nm. Furthermore, we found that the yields were clearly affected by the amount of Fe_3O_4 loaded. It was found that 10 mol % of Fe_3O_4 was enough to produce **4a** with 92% isolated yield (Table 1, entry 14). The yield of reaction was decreased when the catalyst loading was increased to 20 mol % (Table 1, entry 16). Also, the change of reaction time hasn't any effect on yield of reaction. Also, the change of reaction time hasn't any effect on yield of reaction.

After this, we investigate the effect of solvents in the model reaction (Table 2). The best conversion was shown when the reaction was performed in water.

Table 1: Effect of different catalysts and catalyst loading for the synthesis of **4a**

Entry	Catalyst	Catalyst loading (mol%)	yield (%) [b]
1	-----	-----	15
2	KF/CP (NPs)	10	75
3	KF/CP (NPs)	15	80
4	KF/CP (NPs)	20	78
5	ZnO (NPs)	10	58
6	ZnO (NPs)	15	65
7	ZnO (NPs)	20	62
8	ZnO-NR	10	68
9	ZnO-NR	15	74
10	ZnO-NR	20	70
11	TiO_2-NPs	10	48
12	TiO_2-NPs	15	50

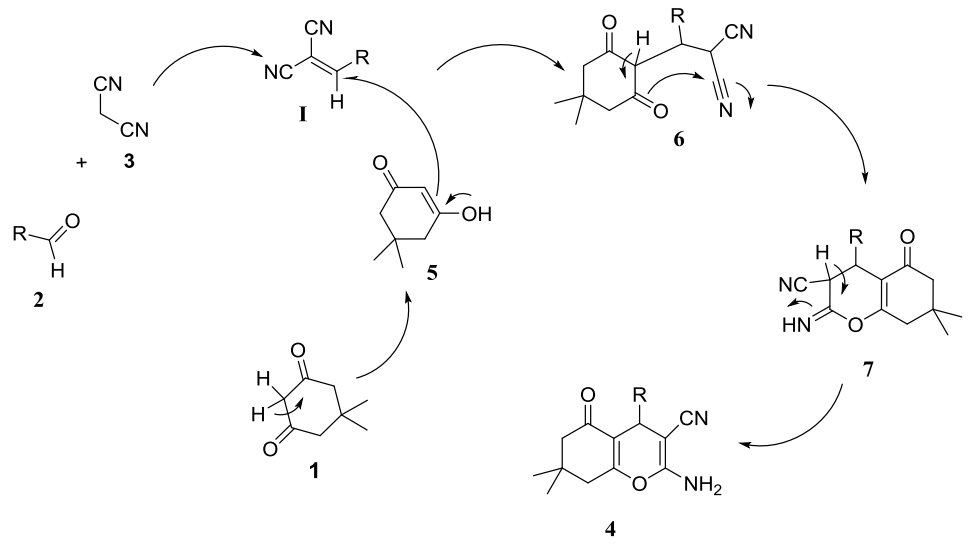
13	TiO_2-NPs	20	45
14	**Fe_3O_4-MNPs**	**10**	**92**
15	Fe_3O_4-MNPs	15	94
16	Fe_3O_4-MNPs	20	87

Table 2. Investigation of solvent and temperature effects on the synthesis of **4a**

Entry	Solvent	Temperature ^oC	Yield (%)[b]
1	CH_2Cl_2	-----	15
2	**H_2O**	------	**92**
3	H_2O	80	92
4	H_2O	100	93
5	CH_3CN	------	85
6	CH_3CN	70	87
7	CH_3CN	90	87
8	Et_2O	----	-----
9	toluene	----	68
10	toluene	80	70
11	toluene	120	72
12	DMF	----	75
13	DMF	80	78

The reusability is one of the significant properties of this catalyst. After the reaction was complete, the catalyst was separated by external magnetic field on stirring bar. The catalyst was then washed with ethyl acetate, air-dried, and employed directly under the same conditions without further purification. It was shown that the catalyst could be employed for five runs without considerable decreasing in the yield of product and its catalytic activity. Easy separation of obtained products from the catalyst makes this method useful for the synthesis of pyrans. Purity checks with melting points, TLC and the ^{1}H NMR spectroscopic data reveal that only one product is formed in all cases and no undesirable side-products are observed. The structures of all known products **4a-4g** were deduced from their ^{1}H NMR and FT-IR spectral data and a comparision of their melting points with those of authentic samples.

We compared the results we obtained using Fe_3O_4 MNPs as catalyst with previously reported results for the synthesis of pyrans in the presence of various catalysts. Our reaction conditions showed shorter reaction times than all the other conditions and gave high yields of the desired products.



Scheme 2: Plausible mechanism for the Fe_3O_4 MNPs catalyzed formation of tetrahydrobenzo[*b*]pyrans.

Experimental Section

All chemicals were available commercially and used without additional purification. The catalyst was synthesized according to the literature. The FT-IR spectra of the products were obtained with KBr disks, using a Tensor 27 Bruker spectrophotometer. The ^{1}H NMR (400 and 500 MHz) spectra were recorded using Bruker 400 and 500 spectrometers.

General experimental procedure:

A mixture of dimedone **1** (1 mmol), aldehyde **2** (1 mmol), malononitrile **3** (1 mmol) and Fe_3O_4 MNPs (0.09 g) as catalyst was heated in water for the appropriate time. The reaction was monitored by TLC. Upon completion of the transformation, hot ethanol was added and the catalyst filtered through sintered glass Büchner funnel under hot conditions. The catalyst was washed with a small portion of hot ethanol. After cooling, the combined filtrate was allowed to stand at room temperature. The precipitated solid was collected by filtration, and recrystallized from ethanol to give compounds **4** in high yields.

2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4a):

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.97 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.10 (d, 1H, *J* = 16.0 Hz, CH_2, diastereotopic proton), 2.27 (d, 1H, *J* = 16.0 Hz, CH_2, diastereotopic proton), 2.45–2.55 (m, 2H, CH2, diastereotopic protons overlapped with solvent), 4.18 (s, 1H, CH), 7.03 (s br., 2H, NH_2), 7.10–7.24 (m, 3H, arom-H), 8.16 (t, 2H, *J* = 7.2 Hz, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4b):

^{1}H NMR (500 MHz, DMSO-d_6): δ 0.95 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 2.10 (d, 1H, *J* = 16.0 Hz, CH_2, diastereotopic proton), 2.24 (d, 1H, *J* = 16.0 Hz, CH_2, diastereotopic proton), 2.45–2.55 (m, 2H, CH2, diastereotopic protons overlapped with solvent), 4.19 (s, 1H, CH), 7.05 (s br., 2H, NH_2), 7.17 (d, 2H, *J* = 8.4 Hz, arom-H), 7.34 (d, 2H, *J* = 8.4 Hz, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4c):

^{1}H NMR (500 MHz, DMSO-d_6): δ 0.94 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.08 (d, 1H, *J* = 16.0 Hz, CH_2, diastereotopic proton), 2.24 (d, 1H, *J* = 16.0 Hz, CH_2, diastereotopic proton), 2.42–2.56 (m, 2H, CH2, diastereotopic protons overlapped with solvent), 3.71 (s, 3H, OCH_3), 4.12 (s, 1H, CH), 6.83 (d, 2H, *J* = 8.7 Hz, arom-H), 6.93 (s br., 2H, NH_2), 7.04 (d, 2H, *J* = 8.7 Hz, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3 carbonitrile (4d):

^{1}H NMR (500 MHz, DMSO-d_6): δ 0.96 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.11 (d, 1H, *J* = 16.1 Hz, CH_2,

diastereotopic proton), 2.27 (d, 1H, *J* = 16.1 Hz, CH_2, diastereotopic proton), 2.55 (s, 2H, diastereotopic proton), 4.42 (s, 1H, CH), 7.17 (s br., 2H, NH_2), 7.55–7.50 (m, 2H, arom-H), 7.97 (t, 1H, *J* = 1.7 Hz, arom-H), 8.05–8.10 (m, 1H, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

2-amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4e):

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.96 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.11 (d, 1H, *J* = 16.2 Hz, CH_2, diastereotopic proton), 2.26 (d, 1H, *J* = 16.2 Hz, CH_2, diastereotopic proton), 2.41–2.55 (m, 2H, CH2, diastereotopic protons overlapped with solvent), 4.21 (s, 1H, CH), 7.07 (s br., 2H, NH_2), 7.08–7.23 (m, 4H, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

2-amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4f):

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.96 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.11 (d, 1H, *J* = 16.0 Hz, CH_2, diastereotopic proton), 2.26 (d, 1H, *J* = 16.0 Hz, CH_2, diastereotopic proton), 2.45–2.55 (m, 2H, CH2, diastereotopic protons overlapped with solvent), 4.19 (s, 1H, CH), 7.10 (s br., 2H, NH_2), 7.12 (d, 2H, *J* = 8.4 Hz, arom-H), 7.50 (d, 2H, *J* = 8.4 Hz, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

2-amino-4-(3-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4g):

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.97 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.14 (d, 1H, *J* = 16.0 Hz, CH_2, diastereotopic proton), 2.27 (d, 1H, *J* = 16.0 Hz, CH_2, diastereotopic proton), 2.45–2.55 (m, 2H, CH2, diastereotopic protons overlapped with solvent), 4.22 (s, 1H, CH), 7.13 (s br., 2H, NH_2), 7.15–7.20 (m, 1H, arom-H), 7.20-7.35 (m, 2H, arom-H), 7.37–7.45 (m, 1H, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

2-amino-7,7-dimethyl-5-oxo-4-(thiophen-2-yl)-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4h):

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.99 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 2.15 (d, 1H, *J* = 16.2 Hz, CH_2, diastereotopic proton), 2.31 (d, 1H, *J* = 16.2 Hz, CH_2, diastereotopic proton), 2.44 (d, 1H, *J* = 17.4 Hz, CH_2, diastereotopic proton), 2.56 (d, 1H, *J* = 17.4 Hz, CH_2, diastereotopic proton), 4.55 (s, 1H, CH), 6.87 (d, 1H, *J* = 2.8 Hz, arom-H), 6.92 (dd, 1H, J = 5.0, 3.4 arom-H), 7.15 (s br., 2H, NH_2), 7.40 (dd, 1H, *J* = 4.8, 0.8 Hz, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

Conclusion

In summary, we showed that Fe_3O_4 MNPs catalyzed the synthesis of pyrans by one-pot, three-component reaction of dimedone, aldehydes, and malononitrile, at in water at room temperature. The method was relatively fast and high yielding, and the work-up was easy. The catalyst can be recycled after simple handling, and used at least four times without any substantial reduction in its catalytic activity. The procedure is also advantageous in the sense that it is a fast reaction in water and therefore operates under environmentally friendly conditions.

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