ORIGINAL RESEARCH PAPER

High Catalytic Ability of Fe_3O_4/EDTA Magnetic Nanocatalyst in Comparison with Various Deep Eutectic Solvents for One-Pot Synthesis of 4H-Pyrans

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ABSTRACT

In this work, various 3-cyano-4-aryl-4H-pyran derivatives were prepared efficiently through a one-pot, multicomponent synthesis between aromatic aldehyde, malononitrile and acetophenone derivatives or ethyl acetoacetate using Fe_3O_4/EDTA magnetic nanocatalyst and ethanol as solvent. The reactions were completed at room temperature in 10 min using 5 mg of catalyst and 2 mL of solvent to prepare 1 mmol of the product. The employed catalyst has consisted of magnetite nanoparticles core, which coated with EDTA to modify its surface and prevent the aggregation. In addition, the catalytic abilities of different deep eutectic solvents (DESs) such as choline chloride/tin (II) chloride, choline chloride/zinc chloride and choline chloride/urea were compared with the nanomagnetic catalyst via this synthesis. The nanomagnetic catalyst showed higher ability in comparison with various DESs for the title reaction. The employed nanomagnetic catalyst has been recycled 4 times without important loss of its activity which shows its high efficiency and small leaching.

Keywords: *4H-Pyran; magnetite nanoparticle; Multicomponent reaction; Deep Eutectic Solvent.*

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INTRODUCTION

Multicomponent reactions (MCRs) have been an important class of synthetic method during last decades [1] because of their advantages such as an allowance to the construction of several bonds at one phase, high bond forming efficiency, molecular diversity, reduction of work-up, extraction, and purification processes [2]. Many natural products and bioactive compounds [3-6] including 4H-pyrans, which showed interesting biological activities [7-10], have been obtained via MCRs. Among different 4H-Pyran derivatives, their annulated heterocycles have attracted more interests because of their wide range of biological and

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pharmacological properties [11]. The 4H-Pyrans are responsible for its biological, pharmacological and other activities [12]. Furthermore, substitution of a pyran's hydrogen atom with amino or cyano makes these compounds as synthons of natural compounds [13,14]. Thus, researchers have made considerable effort towards synthesis of these compounds. Traditionally, 4H-pyran derivatives were conventionally prepared by refluxing active methylene compounds (malononitrile and cyanoacetic acid esters), with an aldehyde and 1,3-diketone (coumarin, methylacetoacetate and cyclic-1,3-dione) in the presence of a base such as piperidine and triethylamine in organic solvents [15]. Recently, the most of reported methods are consisted of using organic bases/catalysts [16,17] which require special work-up and separation technique for the purification of product and recycling the catalyst from the reaction environment. In addition, other catalysts such as ionic liquids [18], SiO_2 nanoparticle [19], tetra butyl ammonium bromide [20], tetra butyl ammonium fluoride [21], $(NH_4)_2HPO_4$ [22], heteropoly acids [23], KF–Al_2O_3 [24] and $CeCl_3$ [25] were also used to prepare these structures. Both employed organic and inorganic catalytic methods are authoritative but they suffer from some drawbacks such as expensive catalyst, low yields, tedious or difficult work-up and poor recyclability. Thus, the search of inoffensive, inexpensive, readily available, and convenient catalyst for preparation of these compounds is still eligible. The existing methods are not well suited for the catalyst one-pot multi-component condensations. Therefore, after our successes in previous studies related to the Multicomponent synthesis and preparation of heterocycles [26-30]. we have decided to make an effort for the synthesis of 4H-Pyran derivatives using new methodologies. In this work, simple and efficient method has been employed for the synthesis of 4H-Pyran derivatives from aromatic aldehyde derivatives, malononitrile and acetophenone derivatives or ethyl acetoacetate in presence of Fe_3O_4/EDTA magnetic nanocatalyst.

EXPERIMENTAL

All initial compounds and used solvents were purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich (Taufkirchrn, Germany) companies with high purities (>99%) and used without further purification. Melting points were measured in capillary tubes using Gallen Kamp melting point instrument. IR spectra were recorded with KBr pellets on JASCO FT-IR spectrometers. ^1H and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 400 MHz spectrometer in $CDCl_3$ solution (University of Isfahan, Isfahan, Iran). CHN analyses were recorded with LECO CHNS-932 elementary chemical analyzer (Model NO: 601-800-500). To prepare the sample DES, a mixture of choline chloride/tin (II) chloride with 1:2 ratio was heated with stirring until a clear and colorless liquid was obtained. Other DESs were prepared with the same method (only tin chloride was replaced with zinc chloride or urea).

Preparation of Fe_3O_4/EDTA

Nanostructured Fe_3O_4 was prepared by chemical co-precipitation method as described in previous reports [31]. To coat the nanocatalyst with organic layer, the reported methodology [32] was employed. Therefore, 0.2 g Fe_3O_4 was dispersed in 20 mL deionized water under ultrasound irradiation. The resulting suspension was stirred at 70°C and then, 8 mL of disodium EDTA solution (in water, 0.025 mol/L) was added dropwise and the mixture was allowed to stir for 2h. Finally, the synthesized precipitates were separated, washed 4 times (with deionized water) and dried. All characterization analyses of this catalyst could be found in the reported work [32].

General procedure for the synthesis of 4H-Pyran derivatives using magnetic nanocatalyst

In a 10 mL round-bottom flask over the stirrer, aromatic aldehyde (1.0 mmol), malononitrile (1.1 mmol), acetophenone or ethyl acetoacetate (1.0 mmol) and Fe_3O_4/EDTA (0.005 g) were mixed in 2 mL ethanol. The reaction mixture has been stirred for 10 min at 25°C. The progress of the reaction was monitored by TLC (eluent phase: n-hexane: EtOAc with 3:1 volume ratio). After completion of the reaction, the nanomagnetic catalyst was separated with magnet and was washed several times with ethanol (to be used in the next run). The ethanol was evaporated to obtain the pure Fe_3O_4/EDTA. Then, the reaction mixture was overflowed and held constant to precipitate. The crude product was recrystallized in ethanol to give the pure product. All products were known compounds and their physical and spectroscopic data (mp, IR, ^1H NMR, ^{13}C NMR and elemental analysis) were compared with those of authentic samples in the references [33,34]. All yields were obtained by

weighting the pure and dry product and deviding the experimental weight to the expected theoretical weight. The physical and spectroscopic data for selected compounds are listed below.

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

Pale yellow solid, Yield 95%, mp= 169–170°C, FT-IR (KBr): ν_{max}(cm^{-1})= 837, 1059, 1173, 1267, 1409, 1608, 1648, 1696, 2193, 2981, 3332, 3409. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm)= 1.14 (t, 3H, *J*= 7 Hz), 2.40 (s, 3H), 4.06 (m, 2H), 4.46 (s, 1H), 4.49 (s, 2H), 7.16 (d, 2H, *J*= 8 Hz,), 7.30 (d, 2H, *J*= 8 Hz,). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)= 13.9, 18.5, 38.3, 60.8, 107.6, 118.6, 128.8, 128.9, 133.0, 142.3, 152.8, 157.1, 157.4, 165.6. Elemental analysis for $C_{16}H_{15}N_2O_3Cl$: C 60.29, H 4.71, N 8.79; Found: C 60.30, H 4.75, N 8.81.

Ethyl 6-amino-4-(4-bromophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (4b)

Pale yellow solid, Yield 93%, mp= 174–175°C, FT-IR (KBr): ν_{max}(cm^{-1})= 835, 1068, 1264, 1370, 1485, 1608, 1691, 2194, 2980, 3329, 3409. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 1.14 (t, 3H, *J*= 7 Hz,), 2.40 (s, 3H), 4.06 (m, 2H), 4.44 (s, 1H), 4.52 (s, 2H), 7.11 (d, 2H, *J*= 8 Hz,), 7.45 (d, 2H, *J*= 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)= 13.9, 18.4, 38.4, 60.8, 105.6, 115.9, 118.5, 129.3, 131.7, 144.5, 157.5, 159.9, 160.2, 165.8. Elemental analysis for $C_{16}H_{15}N_2O_3Br$: C 52.89, H 4.13, N 7.71; Found: C 52.82, H 4.19, N 7.66.

Ethyl 6-amino-4-(4-nitrophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (4d)

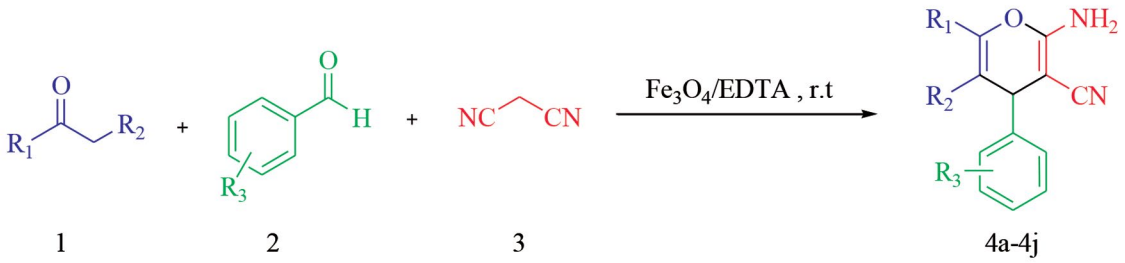
Pale yellow solid, Yield 95%; mp= 172–173°C, FT-IR (KBr): ν_{max}(cm^{-1})= 850, 1059, 1173, 1270, 1345, 1519, 1608, 1691, 2199, 2982, 3332, 3403. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 1.13 (t, 3H, *J*= 7 Hz), 2.45 (s, 3H), 4.07 (q, 2H, *J*= 7 Hz), 4.57 (s, 2H), 4.59 (s, 1H), 7.40 (d, 2H, *J*= 8 Hz,), 8.21 (d, 2H, *J*= 8 Hz,). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)= 14.0, 18.7, 38.8, 61.0, 106.8, 118.2, 124.1, 128.4, 151.0, 152.1, 153.1, 157.6, 158.1, 165.3. Elemental analysis for $C_{16}H_{15}N_3O_5$: C 58.36, H 4.56, N 12.76; Found: C 57.54, H 3.00, N 12.80.

General procedure for the synthesis of the 4H-Pyran derivatives using DESs

In a 10 mL round-bottom flask over the stirrer, aromatic aldehyde (1.0 mmol), malononitrile (1.1 mmol), acetophenone or ethyl acetoacetate (1.0 mmol) and 5 mol% DES were mixed without solvent. The reaction mixture has been stirred for 1.5 hours at 80°C. The progress of the reaction was monitored by TLC (eluent phase: n-hexane:EtOAc with 3:1 volume ratio). After completion of the reaction, the mixture was diluted with water (5 mL) and the organic part was extracted with Et_2O (2×5 mL). The DES obtained by evaporation of water from aqueous layer and reused. The organic layer was dried over $MgSO_4$ and its solvent was evaporated. The crude product was recrystallized in ethanol to give the pure product.

RESULTS AND DISCUSSION

Initially, we chose the model reaction between ethyl acetoacetate (130.1 mg, 1.0 mmol), 4-Chlorobenzaldehyde (140.6 mg, 1.0 mmol) and malononitrile (72.7 mg, 1.1 mmol) in the presence of catalyst (Fe_3O_4/EDTA) to optimize the reaction parameters and obtain the best conditions for the general reaction according to Scheme 1.



Scheme. 1. The general reaction for the synthesis of 4H-pyran derivatives in presence of Fe_3O_4/EDTA.

Different reaction conditions such as the amount of nano-sized Fe_3O_4/EDTA (0.005, 0.05, 0.01 and 0.1 g), the reaction temperature (r.t, 60, 90°C), the solvent (water and ethanol) and the reaction time (5, 10, 20, 30 and 60 minutes) were changed and the preparation of product was monitored. The results were listed in Table 1. The change of solvent from ethanol to water reduced the yield. Moreover, although we used 0.1 g of catalyst at the first experiment, reducing this value to 0.05, 0.01 and 0.001 g does not reduce the reaction yield, which shows the high potency of this catalyst. The addition of reaction temperature from 25 °C to 60 °C and 90 °C has not any effect on the reaction. Therefore, these experiments showed the best (optimized) conditions for this reaction are 25°C in the presence of 0.005 g of catalyst at 10 min (Table 1, entry 10). By the increase of each of these parameters, the reaction yield has not changed meaningfully and by decreasing the reaction time to 5 min, the yield was decreased. In addition, using the catalyst less than 0.005 g has some handling difficulties. Therefore, we employed these conditions to prepare other derivatives of 2-amino-4,6-diphenyl-4H-pyran-3-carbonitriles and ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylates according to the general reaction (Scheme 1).

Moreover, to determine the catalytic effect of the desired DESs (ChCl.2$SnCl_2$, ChCl.2$ZnCl_2$ and ChCl.2Urea), the model reaction was monitored in the presence of different values of these DESs (without our nanomagnetic catalyst) at various conditions. The results; consisted of using 5, 10 and 20 mol percent of DES and different times (0.5, 1.0, 1.5 and 50 h), were listed in Table 2. The reported values in Table 2 show that although the reaction could be performed in presence of DES, ~~but~~ it needs to the higher temperature and more times to successfully prepare the desired product using DES. Therefore, Fe_3O_4/EDTA nanomagnetic catalyst was used as our catalyst for preparation of the other derivatives.

Table 1. Optimization of the reaction conditions for the model reaction[a] in presence of nanomagnetic catalyst

Entry	Catalyst	Solvent	Cat (g)	T (°C)	Time (h)	Yiald (%)[b]
1	-	EtOH	-	25	60	-
2	Fe_3O_4/EDTA	EtOH	0.1	25	60	95
3	Fe_3O_4/EDTA	EtOH	0.1	60	60	94
4	Fe_3O_4/EDTA	EtOH	0.1	90	60	92
5	Fe_3O_4/EDTA	EtOH	0.05	25	60	95
6	Fe_3O_4/EDTA	EtOH	0.01	25	60	95
7	Fe_3O_4/EDTA	EtOH	0.005	25	60	95
8	Fe_3O_4/EDTA	EtOH	0.005	25	30	95
9	Fe_3O_4/EDTA	EtOH	0.005	25	20	95
10	Fe_3O_4/EDTA	EtOH	0.005	25	10	95
11	Fe_3O_4/EDTA	EtOH	0.005	25	5	45
12	Fe_3O_4/EDTA	Water	0.005	25	10	56
13	Fe_3O_4	EtOH	0.005	25	10	41

[a]The model reaction: ethyl acetoacetate (1.0 mmol), 4-Chlorobenzaldehyde (1.0 mmol) and malononitrile (1.0 mmol). [b]Isolated yield.

After the optimization of the reaction conditions, to show the versatility and generality of the presented method for preparation of 4H-pyrans, different derivatives have been prepared using the optimized conditions (only the reaction times are different for different derivatives to obtain the best yield, based on the monitoring of reaction). The details of all prepared 4H-pyrans (4a-4j) and obtained products were shown in Table 3. According to this table, a variety of aromatic aldehydes containing electron-withdrawing and electron-donating groups and different enolizable ketones (ethyl acetoacetate, acetophenone and phenyl acetophenone) were used to prepare 4H-pyrans consisted of the amino group at C2 position, cyano group at C3 position, and one, two or three aryl group at C4-C6 positions.

As the above table, using the optimized conditions, the desired 4H-pyrans were obtained by yield between 46% to 95%. These results clearly show that using Fe_3O_4/EDTA nanomagnetic catalyst, various 4H-pyran derivatives could be successfully synthesized at mild condition. By comparing the results, aromatic aldehydes with electron withdrawing and halogen substituent at C4 were produced in higher yields. However, any meaningful relation?? between the structures of enolizable ketones and obtained yields has not been observed.

Since we obtained valuable results, we have compared the results of this work with some of the most important studies for the synthesis of 4H-pyrans using the same reaction. The brief results of this comparison were listed in Table 4. According to this table, the present work produces the comparable (or more appropriate) results than the previous reports.

Table 2. Optimization of the reaction conditions for the model reaction[a] in presence of various DESs

Entry	Catalyst type	Cat (mol%)	T (°C)	Time (h)	Yield (%)[b]
1	-	-	80	5	-
2	ChCl.2$SnCl_2$	10	25	5	65
3	ChCl.2$SnCl_2$	10	60	5	72
4	ChCl.2$SnCl_2$	10	80	5	94
5	ChCl.2$SnCl_2$	10	80	1.5	92
6	ChCl.2$SnCl_2$	20	80	1.5	92
7	ChCl.2$SnCl_2$	5	80	1.5	94
8	ChCl.2$SnCl_2$	5	80	1	82
9	ChCl.2$SnCl_2$	5	80	0.5	71
10	ChCl.2urea	5	80	1.5	65
11	ChCl. 2$ZnCl_2$	5	80	1.5	80

[a]The model reaction: ethyl acetoacetate (1.0 mmol), 4-Chlorobenzaldehyde (1.0 mmol) and malononitrile (1.0 mmol).
[b]Isolated yield.

Table 3. One-pot, multi-component synthesis of 4H-pyran derivatives catalyzed by Fe_3O_4/EDTA[a]

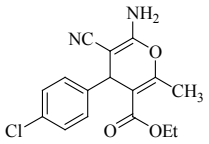
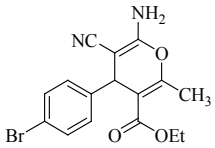
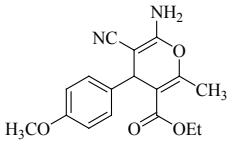
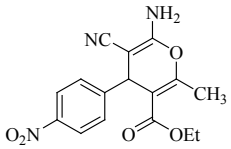
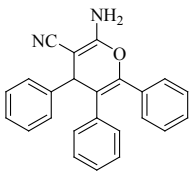
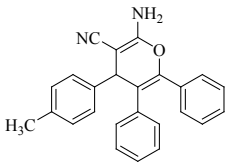
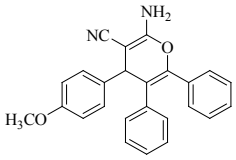
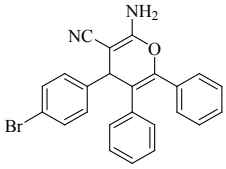
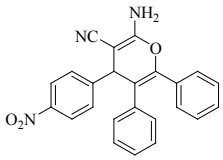
No	R_1	R_2	R_3	Product	Time (min)	Yield (%)[b]	mp (°C)	Ref
4a	CH_3	CO_2Et	4-Cl		13	95	169-170	[33]
4b	CH_3	CO_2Et	4-Br		13	93	174-175	[33]
4c	CH_3	CO_2Et	4-OCH_3		15	65	134-136	[33]
4d	CH_3	CO_2Et	4-NO_2		13	95	172-173	[33]
4e	C_6H_5	C_6H_5	H		15	65	225-228	[34]
4f	C_6H_5	C_6H_5	4-CH_3		13	86	204-207	[34]

Table 3. Continued

No	R_1	R_2	R_3	Product	Time (min)	Yield (%)[b]	mp (°C)	Ref
4g	C_6H_5	C_6H_5	4-OCH_3		25	46	186-188	[34]
4i	C_6H_5	C_6H_5	4-Br		10	94	195-198	[34]
4j	C_6H_5	C_6H_5	4-NO_2		10	95	126-137	[34]

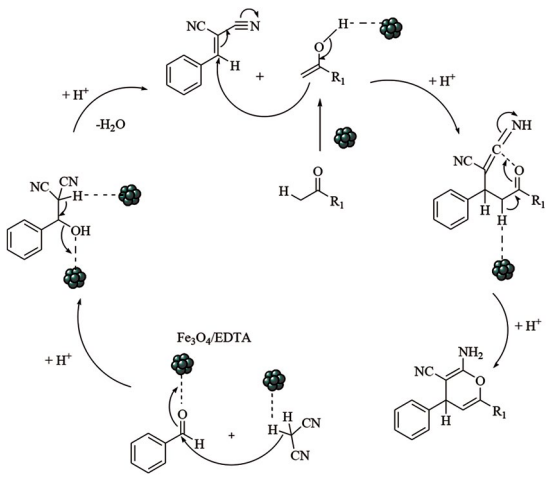
[a]Reaction conditions: a mixture of aromatic aldehyde derivatives (1.0 mmol), malononitrile (1.0 mmol), acetophenone derivatives or ethyl acetoacetate (1.0 mmol) and Fe_3O_4/EDTA (0.005 g) were stirred at room temperature.

[b]Isolated yield: obtained by weighting the pure and dry product and deviding the experimental weight to the expected theoretical weight.

Table 4. The comparison between the results of this work with previous reports

Cat. structure	Cat. Value (for 1 mmol product)	T (°C)	Time (min)	Yield range (%)[b]	Ref. No.
Fe_3O_4/DES	0.1 g	25	55-150	45-94	35
PDA/MeSO3	0.026 g	60	3-15	82-95	36
Fe_3O_4/SiO2/IL/Ferrocene	0.05	25-110	10-40	80-90	37
Potassium phthalimide + Ball-milling	5 mol%	Ambient	7-25	97-99	38
Fe_3O_4/EDTA	0.005 g	25	10-25	46-95	This work

To define the role of employed Fe_3O_4/EDTA in the reaction and based on the previous report about this mechanism [39], a reliable mechanism was proposed according to Scheme 2. Fe_3O_4 plays an important role because it catalyzes the most steps of the reaction by its Lewis acid nature (according to the proposed mechanism). Moreover, EDTA covers the Fe_3O_4 core with an organic layer to prevent the aggregations of nanomagnetite and reducing its catalytic effect.



Scheme. 2. Proposed mechanism for the synthesis of 4H-pyran derivatives, catalyzed by Fe3O4/EDTA.

At the final step of this study, the reusability of Fe_3O_4/EDTA has been explored in the model reaction. To examine the reusability of the catalyst, after completion of each run of the reaction, the nanomagnetic catalyst was separated with magnet and was washed several times with ethanol. The ethanol was evaporated to obtain the pure Fe_3O_4/EDTA and reused (for next three times) without further purification. The results were listed in Table 5 and they showed that the employed Fe_3O_4/EDTA could be used at least four times with only 6% loss in the yield of the product.

Table 5. The result of the reusability of the Fe_3O_4/EDTA in the model reaction

Entry	Cycle	Time (min)	Yield (%)
1	1st run	10	95
2	2nd run	10	92
3	3nd run	10	90
4	4nd run	10	89

CONCLUSION

In this report, various 4H-pyran derivatives were synthesized using the three-component reaction between aromatic aldehydes, acetophenone derivatives (or ethyl acetoacetate) and malononitrile in the ethanol as solvent. Several catalysts such as choline chloride- based DESs have been employed and based on the results, Fe3O4/EDTA nanomagnetic particles showed the highest efficiencies for this reaction. The reaction only needs to 5 mg of catalyst and maximum 25 min time to be completed at acceptable yields. The aldehydes with electron-withdrawing groups showed the higher yields than the other derivatives of benzaldehyde. However, the yield obtained from acetophenone derivatives is comparable with that of ethyl acetoacetate. Finally, the recyclability of the employed catalyst was examined that after 4 times, the yield was decreased by only 6%.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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