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Nano Nickel-Cobalt Ferrite Catalyzed One Pot Synthesis of 14-Aryl-14H-dibenzo[a, j]xanthenes and 12-Aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one Derivatives

RAGHU BABU KORUPOLU[1], SRIVIDHYA MARIPI[1]*, SURI BABU MADASU[1], RAVI KUMAR MAJJI[1], RAVI KUMAR GANTA[1] and PANDU NAIDU CHILLA[1]

[1]Department of Engineering Chemistry, A. U. College of Engineering (A), Andhra University, Visakhapatnam - 530 003, Andhra Pradesh, India.
*Corresponding author E-mail: vidyasri.chem@gmail.com

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ABSTRACT

A simple, green and multi component, one pot synthesis of 14-Aryl-14H-dibenzo[a, j]xanthene derivatives by condensation of aryl aldehydes with 2-naphthol using magnetically separable and recyclable heterogeneous catalyst nano nickel cobalt ferrite ($Ni_{0.5}Co_{0.5}Fe_2O_4$), has been described. In addition, a one-pot three component condensation of aryl aldehydes, 2-naphthol and dimedone has been developed to furnish 12-Aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one derivatives in good to excellent yields under the same reaction conditions. The main advantage of this method is the nano catalyst can be reused up to five reaction cycles without losing the catalytic activity.

Keywords: Xanthenes, Naphthol, Nano nickel cobalt ferrite ($Ni_{0.5}Co_{0.5}Fe_2O_4$) catalyst and recyclable catalyst.

INTRODUCTION

One–pot, Multi Component Reactions (MCRs) are having momentous meaning due to formulation of mono product with elevated yields by the blending of two or more components in a one step process[1],[2]. The advantages of MCR's are atom economy, less time consuming, easy purification process and avoid protection – deprotection steps. Therefore, the design and development of efficient and green MCRs focussed on a target molecule is one of the most important challenges in organic synthesis in both medicinally and industrially.

Xanthenes and benzoxanthenes are an important class of oxygen heterocycles[3]. Xanthenes and benzoxanthenes are important intermediates in organic synthesis due to their wide range of biological and pharmaceutical activities such as antiviral[4], antibacterial[5] and anti-inflammatory activities[6]. These compounds are also being utilized as antagonists for the paralyzing action of zoxazolamine[7], in photodynamic therapy[8], as leuco-dyes in laser technology[9] and as P^H- sensitive fluorescent material for visualization of biomolecules[10].

Many synthetic strategies has been developed for synthesis of xanthenes and benzoxanthenes because of their pharmacological and biological activities such as cyclo-acylation of carbamates[11], trapping of benzynes by phenol [12], cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone[13], cyclodehydrations[14] and cyclization of polycyclic aryltriflate esters[15]. Recently the synthesis of benzoxanthenes has been achieved by the condensation of aromatic aldehydes with 2-naphthol by cyclodehydration in the presence of various catalysts such as amberlyst-15[16], sulfamic acid[17], molecular iodine[18], $Al(HSO_4)_3$[19], p-TSA[20], cyanuric chloride[21] and LiBr[22], dowex-50W[23], $NH_4H_2PO_4$[24], silica sulphuric acid[25], $HClO_4$-SiO_2[26] and H_2SO_4 in acetic acid as solvent[27]. The synthesis of 12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one derivatives involves the condensation of dimedone with aldehyde and 2-naphthol. The various catalysts have been reported for the synthesis of 12-aryl-tetrahydrobenzo[a]xanthene-11-one derivatives such as $InCl_3$ and P_2O_5[28], p-toluenesulfonic acid (PTSA)/ ionic liquid[29], proline triflate[30], ceric ammonium nitrate[31], iodine[32], sulfamic acid[33], cyanuric chloride[34], $Sr(OTf)_2$[35] and $HClO_4$-SiO_2[36].

The methods which are specified above are having its own advantages and merits, however many of these methods are unsatisfactory as they involve the use of halogenated solvents, unsatisfactory yields, catalyst loadings up to 30 mol%, prolonged reaction time and tedious experimental procedures. All of these disadvantages make further improvements for the synthesis of such molecules essential. Therefore, it is necessary to develop the alternate methods for the synthesis of 14-Aryl-14H-dibenzo [a, j] xanthenes and 12-Aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one derivatives. The synthesis mechanism should involve simple in process, efficient, eco friendly with high yields with novel catalysts.

Recently, nanomaterial-based catalysts as prominent heterogeneous catalysts are widely used in order to accelerate catalytic processes, particularly because they are accompanied with the principle of the green chemistry. The greener generation of nanoparticles and their eco-friendly applications in catalysis via magnetically recoverable and recyclable nano-catalysts for a variety of oxidation, reduction, and condensation reactions[37-40], has made an incredible impact on the development of sustainable pathways. Magnetically recyclable nano catalysts and their use in benign media is an ideal merge for the development of sustainable methodologies in organic synthesis.

Therefore, in order to accomplish the novel, high yielding and eco-friendly synthetic process, minimizing the by-products, with minimum number of separate reaction steps, improving the yields, our research work was extended by the application of nano catalysts in MCRs, we wish to report a clean and environmentally friendly approach to the synthesis of 14-Aryl-14H-dibenzo[a, j]xanthenes and tetrahydrobenzo[a]xanthen-11-ones via multi-component reaction of aldehydes, 2-naphthol and dimedone in the presence of nickel cobalt ferrite nanoparticles.

Due to the effective activity of magnetically separable nickel cobalt ferrite nano particles have the advantages of recyclability, easy work-up and clean reaction profiles apart from the lack of necessity ligands and in minimizing the organic waste generation when compared to the conventational catalytic systems. In this, we report 14-Aryl-14H-dibenzo[a, j]xanthenes and 12-Aryl-tetrahydrobenzo[a]xanthen-11-ones using magnetically separable and recyclable nano nickel cobalt ferrite as heterogeneous catalyst. The synthesised derivatives were characterised by IR, H^1-NMR and Mass spectral data.

MATERIALS AND METHODS

Experimental

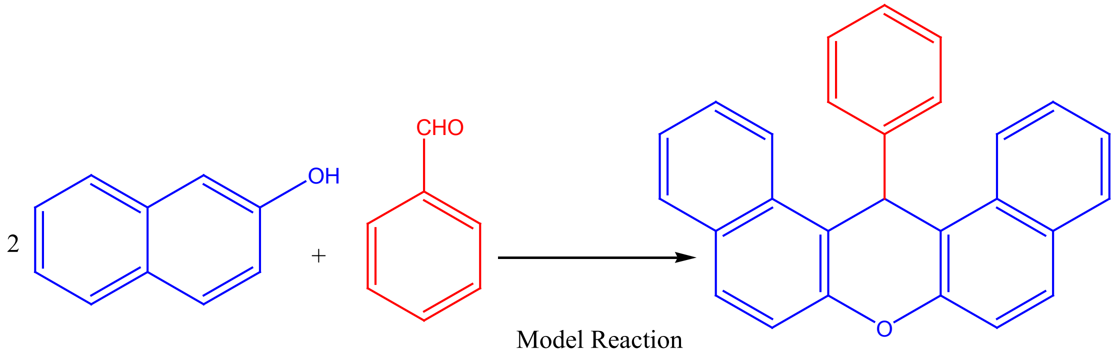
Sigma Aldrich has been selected as vendor for sourcing the chemicals. All chemicals were purchased, which is having the purity not less than 99.9%. Analytical Thin Layer Chromatography (TLC) was carried out by using silica gel 60 F254 pre-coated plates. Visualization was accomplished with UV lamp. All the products were characterized by their IR, H^1 NMR and Mass spectra. ^1H NMR was recorded on 300 MHz in $CDCl_3$/DMSO, and the chemical shifts were reported in parts per million (ppm, ä) downfield from the Tetramethyl silane (TMS).

Preparation of the Nickel –Cobalt Ferrite nano catalyst

Nickel-Cobalt Ferrites with formula $Ni_xCo_{1-x}Fe_2O_4$ (x= 1, 0.75, 0.5, 0.25 and 0). In this $Ni_{0.5}Co_{0.5}Fe_2O_4$ (x=0.5) has been chosen for the study and was synthesised by a chemical sol-gel co-precipitation method. In order to prepare $Ni_{0.5}Co_{0.5}Fe_2O_4$ nanoparticles, 0.05 moles of nickel nitrate, 0.05 moles of cobalt nitrate and 2 moles of iron nitrate are dissolved separately in a little amount of deionised water and then citric acid solution was prepared stoichiometric proportions. These two solutions were added in a 1:1 molar ratio and P^H adjusted to 7 by the addition of ammonia and ethylene glycol is added. The aqueous mixture was heated to 60^{0}C, it was converted to gel and then temperature increased to 200^{0}C finally to get powder. That powder was calcined to 600^{0}C and then characterised with XRD and SEM.

General experimental procedure for synthesis of 14-Aryl-14H-dibenzo[a, j]xanthenes

Aromatic aldehyde (2 mmol) and 2-naphthol (4 mmol) and nano nickel cobalt ferrite ($Ni_{0.5}Co_{0.5}Fe_2O_4$, 20 mol %) catalyst were taken in a round bottomed flask and the contents are dissolved in 5 mL of ethanol. Then the reaction mixture stirred for 20 min at reflux temperature (scheme-1). The progress of the reaction was monitored by TLC (n-hexane: ethyl acetate 4:1). After completion of the reaction the catalyst was separated by using an external strong Neodymium35 magnet. Then 10 mL of ethanol



Synthesis of 14-Aryl-14H-dibenzo[a, j]xanthenes

Table 1: Optimisation of reaction conditions

Entry	Catalyst	Solvent	Temperature(°C)	Time	Yield(%, w/w)
1	-	CH_2Cl_2	RT	5 hrs	<10
2	-	$CHCl_3$	RT	5 hrs	<10
3	-	CH_3CN	RT	5 hrs	<10
4	-	$ClCH_2CH_2Cl$	RT	5 hrs	<10
5	-	Ethanol	RT	5 hrs	<10
6	5 (mol %)	CH_2Cl_2	35-40	3 hrs	20
7	5 (mol %)	$CHCl_3$	60-65	3 hrs	24
8	5 (mol %)	CH_3CN	80-85	3 hrs	27
9	5 (mol %)	$ClCH_2CH_2Cl$	80-85	3 hrs	25
10	5 (mol %)	Ethanol	75-78	2 hrs	52
11	10 (mol %)	Ethanol	75-78	1 hr	65
12	15 (mol %)	Ethanol	75-78	40 min	85
13	20 (mol %)	Ethanol	75-78	20 min	95
14	25 (mol %)	Ethanol	75-78	20 min	95
15	30 (mol %)	Ethanol	75-78	20 min	95

was added to the reaction mixture and removal of solvent by rota vapor. After, the dried product was recrystallized from hot ethanol for several times to get the corresponding pure product 14-aryl-14H-dibenzo[a,j]xanthene derivatives in excellent yields. The products were confirmed by IR, H^1 NMR, and Mass spectras.

General experimental procedure for synthesis of 12-Aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one

A mixture of aromatic aldehyde (2 mmol) and 2-naphthol (2 mmol) dimedone (2 mmol) and nano nickel cobalt ferrite ($Ni_{0.5}Co_{0.5}Fe_2O_4$, 20 mol %) catalyst were taken in a round bottomed flask and the contents are dissolved in 5 mL of ethanol. Then the reaction mixture stirred for 30 min at reflux temperature (scheme-2). The progress of the reaction was monitored by TLC (n-hexane: ethyl acetate 4:1). After completion of the reaction the catalyst was separated by using an external strong Neodymium35 magnet. Then 10 mL of ethanol was added to the reaction mixture and removal of solvent by rota vapor. After, the dried product was recrystallized from hot ethanol for several times to get the corresponding pure product tetrahydrobenzo[a]xanthene-11-one derivatives in excellent yields. The products were confirmed by IR, H^1 NMR, and Mass spectras.

Table 2: $Ni_{0.5}Co_{0.5}Fe_2O_4$ Catalysed synthesis of 14-Aryl-14Hdibenzo[a,j]xanthene derivatives

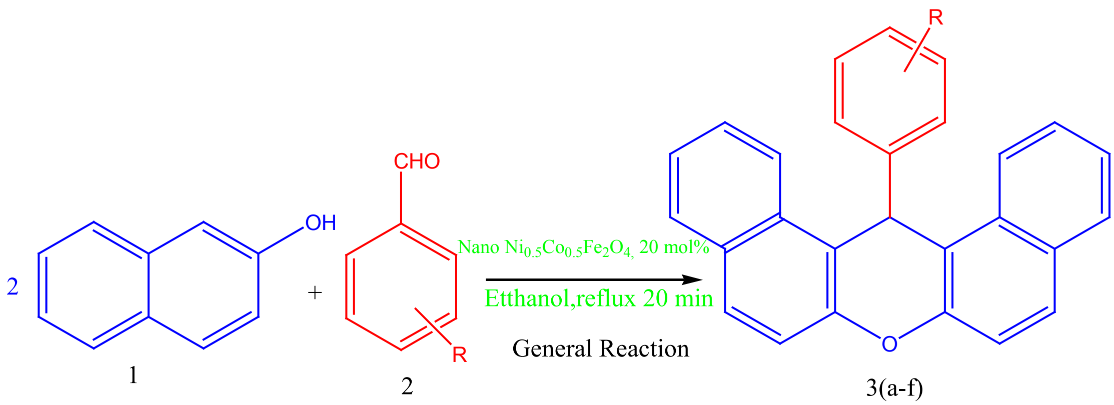
Entry	Product	R	Time (min)	Yield (%, w/w)
1	3a	H	20	92%
2	3b	2-OH	20	93%
3	3c	4-Cl	20	96%
4	3d	4-OH	20	95%
5	3e	4-NO_2	20	94%
6	3f	4-CH_3	20	95%

RESULTS AND DISCUSSIONS

Chemistry

Initially a model reaction is conducted at room temperature using different solvents and different mol% of catalyst for synthesis of 14-Aryl-14H-dibenzo[a, j]xanthenes and 12-Aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one to investigate the feasibility of the reaction.

Benzaldehyde and 2-naphthol were taken in different solvents (CH_2Cl_2, $CHCl_3$, CH_3CN, $ClCH_2CH_2Cl$ and ethanol), stirred for 5 hrs without catalyst at room temperature. It is observed that very low yield (<10%, Table-1, entry 1-5) of product is obtained even after 5 hrs of stirring. There was a slight increase in yield (10% to 52%, Table-1, entry 6-10), when the reaction mixture is added with 5 mol% nano nickel cobalt ferrite ($Ni_{0.5}Co_{0.5}Fe_2O_4$) catalyst even on stirring for just 3 hrs at refluxed temperatures. It was observed that yield 52% obtained was much better in ethanol solvent at the same reaction conditions. On increasing the catalyst to 10 and 15 mol%, there was increase in yield up to



Scheme 1: Nickel Cobalt Ferrite catalysed synthesis of 14-Aryl-14Hdibenzo[a,j]xanthene derivatives

65% and 85% respectively at the 75-78^0 C (Table-1, entry 11 and 12). Further increasing the catalyst to 20 mol% increased the yield to 95% (Table-1, entry 13) in 20 minutes. All the results are tabulated in Table 1. No change was observed on further enhancing the catalyst mol%.

With the optimised conditions in hand, the reaction was performed with different benzaldehydes (scheme 1) to explore the scope and generality of the present protocol and the results of these observations are summarized in Table 2. From the results, Benzaldehyde and other aromatic aldehydes containing electron-withdrawing and electron-donating groups were converted efficiently to the corresponding dibenzoxanthenes in excellent yields. The structures of synthesized dibenzo xanthenes were confirmed by IR, H[1] NMR and Mass spectral analysis.

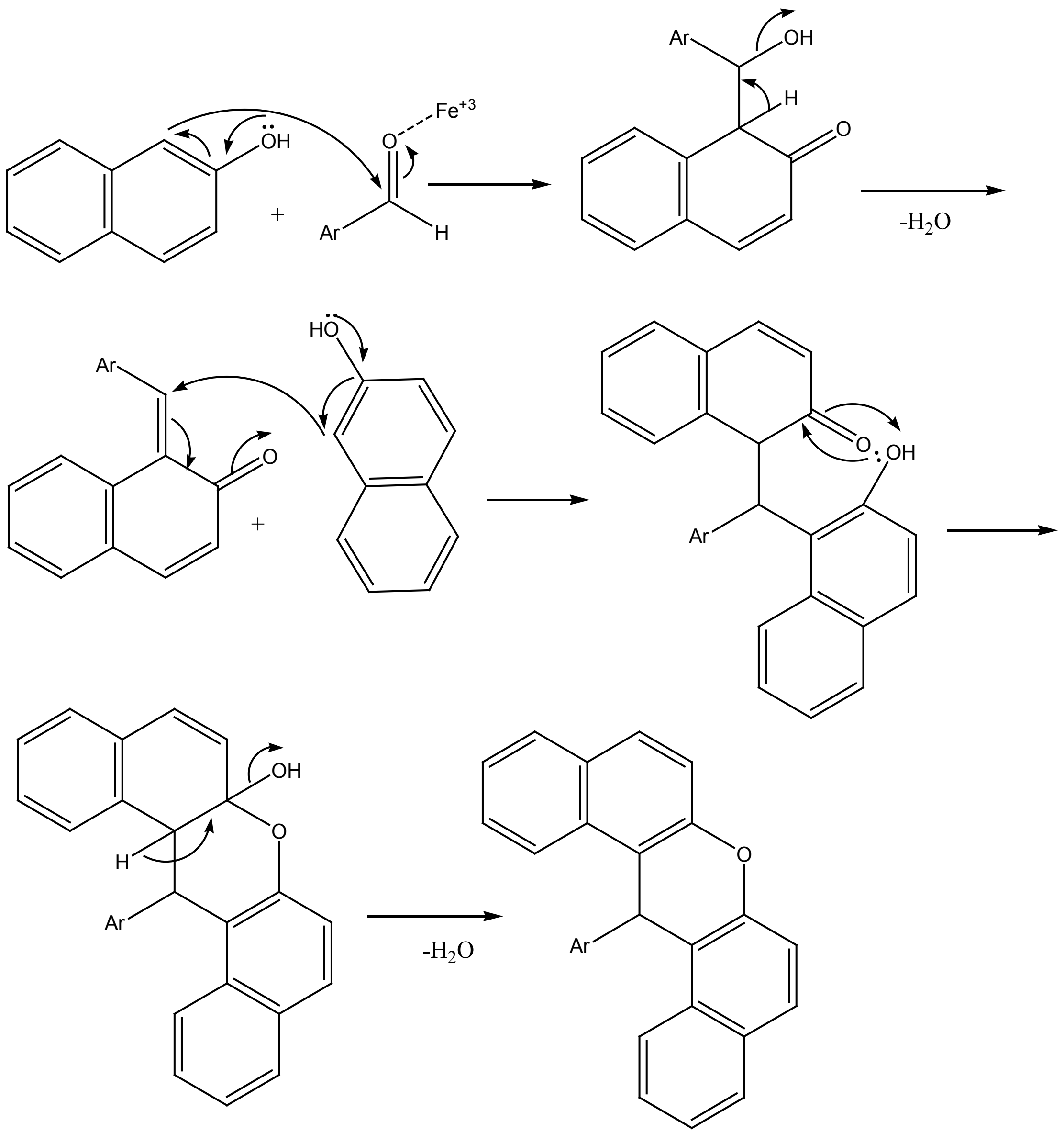


Fig. 1: Plausible mechanism for the formation of 14-Aryl-14H-dibenzo[a,j]xanthenes

The plausible mechanism for the formation of 14-Aryl-14H-dibenzo[a,j]xanthenes by using nickel cobalt ferrite NPs is shown in figure 1.

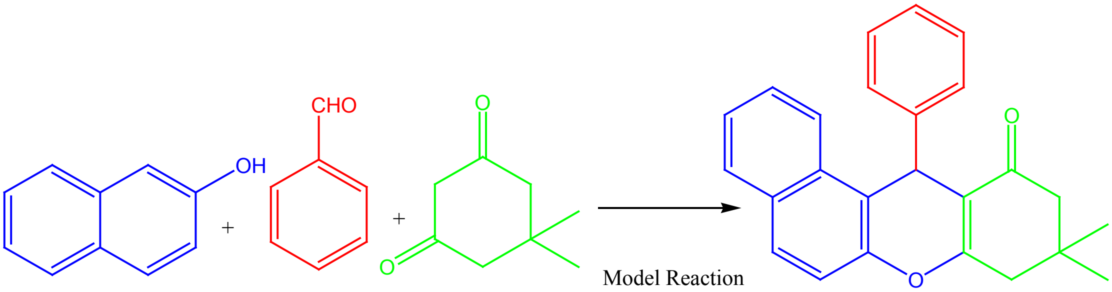
On the other hand a model reaction is conducted by using different solvents and different mol% of catalyst for synthesis of 12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one to investigate the feasibility of the reaction.

Dimedone, benzaldehyde and 2-naphthol were taken in different solvents chloroform ($CHCl_3$), acetonitrile (CH_3CN), tetrahydrofuran (THF), dichloroethane ($ClCH_2CH_2Cl$) and ethanol stirred for 8 hrs without catalyst at room temperature. It is observed that very low yield (<10%, Table-4, entry 1-5) of product is obtained even after 8 hrs of stirring. There was a slight increase in yield (10% to 55 %, Table-4, entry 6-10), when the reaction mixture is added with 5 mol% nano nickel cobalt ferrite ($Ni_{0.5}Co_{0.5}Fe_2O_4$) catalyst even on stirring for just 5 hrs at refluxed temperatures. It was observed that yield 55% obtained was much better in ethanol solvent at the same reaction conditions. On increasing the catalyst to 10 and 15 mol%, there was increase in yield up to 70% and 85% respectively at the 75-78^0 C. Further increasing the catalyst to 20 mol% increased the yield to 96% (Table-4, entry 13) in 30 minutes. All the results are tabulated in Table-4. No change was observed on further enhancing the catalyst mol%.

With the optimised conditions in hand, the reaction was performed with different benzaldehydes (scheme 2) to explore the scope and generality of the present protocol and the results of these observations are summarized in Table 5. From the results, aromatic aldehydes carrying either an electron donating groups or an electron withdrawing groups reacted successfully and gave the products in good to excellent yields. The structures of synthesized tetrahydrobenzo xanthenes were confirmed by IR, H^1NMR and Mass spectral analysis.

Table 3: Screening of various catalysts with nickel cobalt ferrite ($Ni_{0.5}Co_{0.5}Fe_2O_4$) in the synthesis of 14-Aryl-14H-dibenzo[a,j]xanthenes

Entry	Catalyst	Temperature(°C)	Time	Yield (%, w/w)	Reference
1	p-TSA	125	15-24 hrs	81-93	20
2	Sulfamic acid	125	6-12 hrs	90-95	17
3	Amberlyst-15	125	0.5-2 hrs	80-94	16
4	Iodine	90	0.5-1 hr	74-91	18
5	Dowex-50W	100	2 hrs	86-91	23
6	LiBr	130	1-2 hrs	80-84	22
7	Cyanuric chloride	110	32 min	91	21
8	Silica sulfuricacid	80	45 min	86	25
9	H_2SO_4/AcOH	80	73 hrs	60-90	27
10	$Ni_{0.5}Co_{0.5}Fe_2O_4$	75	20 min	95	Present work



Synthesis of 12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one

The plausible mechanism for the formation of 12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one by using nickel cobalt ferrite NPs is shown in figure 2.

Reusability of the catalyst

The reusability of nickel cobalt ferrite NPs is one of the most important advantages of this protocol that makes it useful for practical commercial applications. We have examined the recyclability of nickel cobalt ferrite NPs catalyst for the model reaction. Interestingly, the recovered catalyst could be reused for up to five cycles which is evident from Table 7. The catalyst was separated by using a magnet after completion of the reaction, washed with water followed by chloroform, dried in oven and reused for the next cycle.

Spectral data

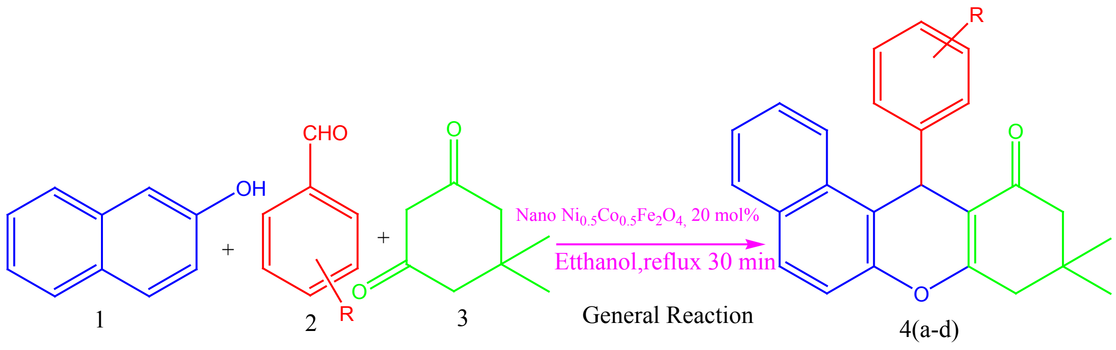
Spectral data of 14-Aryl-14H-dibenzo[a, j] xanthenes

14-Phenyl-14H-dibenzo[a,j]xanthene

White solid, Mp: 182-185^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.30 (2H, d, J = 8.4 Hz), 7.75 (2H, d, J = 7.8 Hz),), 7.80 (2H, d, J = 8.8 Hz), 7.60 (2H, t, J = 7.8 Hz), 7.53 (2H, d, J = 7.5 Hz), 7.55 (2H, d, J = 8.8 Hz), 7.42 (2H, t, J= 7.5 Hz), 7.15 (2H, t, J = 7.5 Hz), 7.10 (1H, t, J = 7.5 Hz), 6.50 (1H, s); FTIR

Table 4: Optimisation of reaction conditions

Entry	Catalyst	Solvent	Temperature(°C)	Time	Yield(%, w/w)
1	-	$CHCl_3$	RT	8 hrs	<10
2	-	CH_3CN	RT	8 hrs	<10
3	-	THF	RT	8 hrs	<10
4	-	$ClCH2CH_2Cl$	RT	8 hrs	<10
5	-	Ethanol	RT	8 hrs	<10
6	5 (mol %)	$CHCl_3$	60-65	5 hrs	40
7	5 (mol %)	CH_3CN	80-85	5 hrs	35
8	5 (mol %)	THF	64-68	5 hrs	42
9	5 (mol %)	$ClCH2CH_2Cl$	80-85	5 hrs	40
10	5 (mol %)	Ethanol	75-78	3 hrs	55
11	10 (mol %)	Ethanol	75-78	1.5 hr	70
12	15 (mol %)	Ethanol	75-78	40 min	85
13	20 (mol %)	Ethanol	75-78	30 min	96
14	25 (mol %)	Ethanol	75-78	30 min	96
15	30 (mol %)	Ethanol	75-78	30 min	96



Scheme 2: $Ni_{0.5}Co_{0.5}Fe_2O_4$ Catalysed synthesis of 12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one derivatives

(KBr, cm^{-1}): 3070, 3030, 2885, 1630 1591, 1520, 1490, 1460, 1252, 1070, 1020, 965, 830 744, 700; ESI-MS: m/z = 359 $(M+H)^+$

14-(2-Hydroxyphenyl)-14H-dibenzo[a,j] xanthene

Pink solid, Mp: 137-140⁰ C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.80 (br s, 1H) 6.15 (s, 1H), 7.05-7.35 (m, 4H J = 7.4-8.5), 7.83 (2H, d, J = 4.1 Hz), 7.75 (2H, d, J = 5.5 Hz), 7.55 (2H, d, J = 8.7 Hz), 7.25 (2H, t, J = 5.5 Hz), 7.60 (2H, d, J = 8.9 Hz), 7.55 (2H, t, J = 8 Hz); FTIR (KBr, cm^{-1}): 3400, 3020, 2890, 1650, 1592, 1520, 1450, 1410, 1251, 1240, 815; ESI-MS: m/z = 375.43 $(M+H)^+$

Table 5: $Ni_{0.5}Co_{0.5}Fe_2O_4$ Catalysed synthesis of 12-aryl-8, 9, 10, 12-tetrahydrobenzo[a] xanthene-11-one derivatives

Entry	Product	R	Time (min)	Yield (%, w/w)
1	4a	4-OCH_3	30	96%
2	4b	2-NO_2	30	94%
3	4c	2-OH	30	94%
4	4d	4-(2-pyridyl)	30	96%

14-(4-Chlorophenyl)-14H-dibenzo[a,j]xanthene

Brown solid, Mp: 285-288⁰C. ^{1}H NMR (300 MHz, $CDCl_3$) δ=6.45 (s, 1H), 8.12 (2H, d, J = 7.9 Hz), 7.55 (2H, d, J = 8.8 Hz), 7.60 (2H, d, J = 4.4 Hz), 7.82 (2H, d, J = 5.5 Hz), 7.55 (2H, d, J = 8.5 Hz), 7.65 (2H, t, J = 5.5 Hz), 7.45 (2H, d, J = 8.7 Hz), 7.45 (2H, t, J = 7.9 Hz); FTIR (KBr, cm^{-1}): 3130 1610, 1590, 1450, 1220 1110, 830, 776; ESI-MS: m/z = 393.8 $(M+H)^+$

14-(4-Hydroxyphenyl)-14H-dibenzo[a,j] xanthene

Pink solid, Mp: 138-140⁰C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.85 (br s, 1H), 6.42 (s, 1H), 8.15

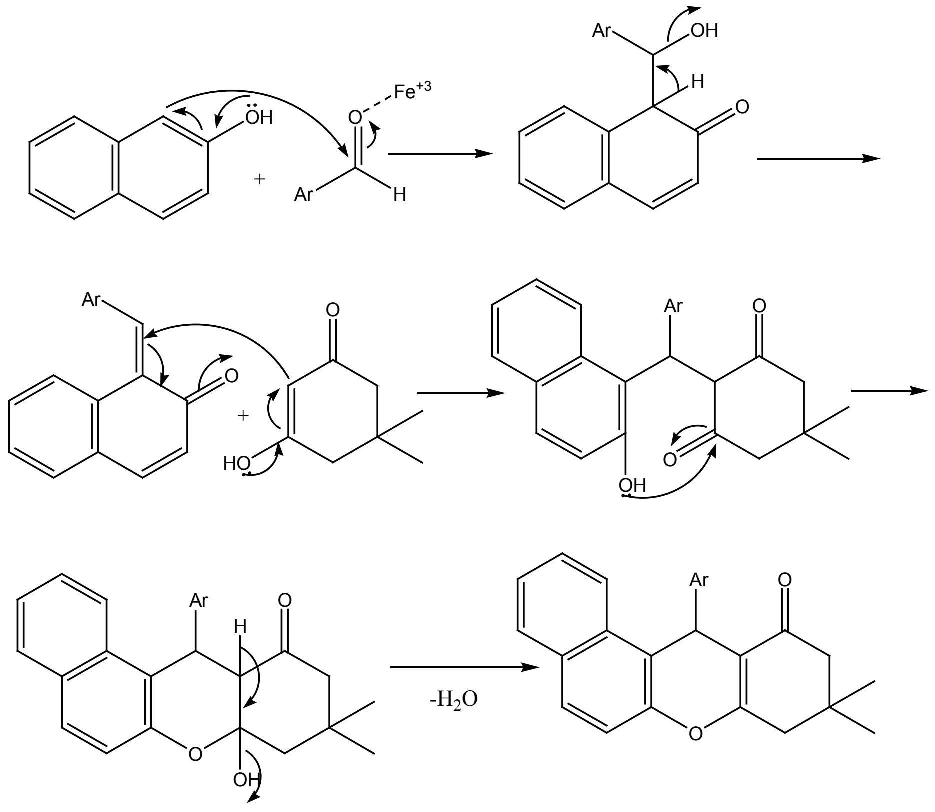


Fig. 2: Plausible mechanism for the formation of 12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one

(2H, d, J = 8.5 Hz), 7.75 (2H, d, J = 8.8 Hz), 7.75 (2H, d, J = 4.1 Hz), 7.85 (2H, d, J = 5.5 Hz), 7.75 (2H, d, J = 8.7 Hz), 7.65 (2H, t, J = 5.6 Hz), 7.58 (2H, d, J = 8.9 Hz), 7.55 (2H, t, J = 8 Hz); FTIR (KBr, cm^{-1}): 3410, 1580, 1511, 1410, 1240, 1240, 815; ESI-MS: m/z = 375.4 $(M+H)^+$

14-(4-Nitrophenyl)-14H-dibenzo[a,j]xanthene

Yellow solid, Mp: 182-185^0 C: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.21 (2H, d, J = 8.5 Hz), 7.85 (2H, d, J = 8.7 Hz), 7.85 (2H, d, J = 4.2 Hz), 7.85 (2H, d, J = 5.5 Hz), 7.65 (2H, d, J = 8.5 Hz), 7.60 (2H, t, J = 5.6 Hz), 7.55 (2H, d, J = 9 Hz), 7.45 (2H, t, J = 7.9 Hz), 6.42 (1H, s); FTIR (KBr, cm^{-1}):3070, 2920, 1620, 1592, 1612, 1592, 1615, 1450, 1410, 1345,, 1210, 1150, 1100 1020, 960, 850, 830, 740, 690; ESI-MS: m/z = 4 04.12 $(M+H)^+$

14-(4-Methylphenyl)-14H-dibenzo[a,j]xanthene

White solid, Mp: 227-229^0 C: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.12 (s, 3H), 6.42 (s, 1H), 7.80 (2H, d, J = 4.5 Hz), 7.75 (2H, d, J = 5.0 Hz), 7.75 (2H, d, J = 9 Hz), 7.73 (2H, t, J = 5.6 Hz), 7.55 (2H, d, J = 8.9 Hz), 7.55 (2H, t, J = 8 Hz), 7.15-7.38 (m, 4H); FTIR (KBr, cm^{-1}): 3400, 3050,1620, 1595, 1520,1450, 1412, 1355, 1230, 1140, 810, 750; ESI-MS: m/z = 373.42 $(M+H)^+$

Spectral data of 12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one

12-(4-Methoxyphenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydro-benzo[a] xanthen-11-one

White solid, Mp: 150-153^0 C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.8 (s, 3H), 0.85 (s, 3H), 1.10 (s, 3H), 2.05 (dd, J = 16.5 Hz, 2H) , 2.60 (s, 2H), 7.05-7.95 (m, 11H), 5.75 (s, 1H); FTIR (KBr, cm^{-1}): 3060,2950, 2885, 1652, 1375, 1230 1180 1060, 810; ESI-MS: m/z = 354.15 $(M+H)^+$

12-(2-Nitrophenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydro-benzo[a] xanthen-11-one

White solid, Mp: 220-222^0 C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.86 (s, 3H), 1.12 (s, 3H), 2.05 (dd, J = 16.5 Hz, 2H), 2.60 (s, 2H), 5.70 (s, 1H), 7.15-7.95 (m, 10H); FTIR (KBr, cm^{-1}):3030, 2950, 2871,1651, 1592, 1536, 1375, 1350, 1230 1170, 820; ESI-MS: m/z = 400.44 $(M+H)^+$

Table 6: Screening of various catalysts with $Ni_{0.5}Co_{0.5}Fe_2O_4$ in the synthesis of 12-aryl-8, 9, 10, 12-tetrahydrobenzo[a]xanthene-11-one derivatives

Entry	Catalyst	Temp.(°C)	Time	Yield (%, w/w)	Reference
1	$InCl_3$	120	30 min	84	28
2	Prolin triflate	100	300 min	79	30
3	CAN	120	30 min	94	31
4	I_2	60	75 min	90	32
5	$HClO_4/SiO_2$	80	72 min	89	36
6	PTSA	80	180 min	90	29
7	$Sr(oTf)_2$	80	300 min	85	35
8	Sulfamic acid	-	60 min	59	33
9	$Ni_{0.5}Co_{0.5}Fe_2O_4$ NPs	78	30 min	96	Present work

Table 7: Productivity with re-cycle catalyst

Entry	Catalystre-use	Yield(%, w/w)
1	1st cycle	94
2	2nd cycle	92
3	3rd cycle	90
4	4th cycle	89
5	5th cycle	87

12-(2-Hydroxyphenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydro-benzo[a] xanthen-11-one

White solid, Mp: 160-163^0 C; ^{1}H NMR (300 MHz, $CDCl_3$) δ =4.75 (br s, 1H), 0.95 (s, 3H), 1.15 (s, 3H), 2.02 (dd, J = 16.5 Hz, 2H), 2.60 (s, 2H), 5.75

(s, 1H), 7.15-7.95 (m, 10H); FTIR (KBr, cm^{-1}): 3400, 3020, 2955, 2872, 1651, 1595, 1530, 1385, 1352, 1235, 1170, 820; ; ESI-MS: m/z = 371.16 $(M+H)^+$

12-(4-(2-Pyridyl)-phenyl)-9, 9-dimethyl-8, 9, 10, 12-tetrahydro-benzo[a] xanthen-11-one

White solid, Mp: 230-233^0 C; ^{1}H NMR (300 MHz, $CDCl_3$) δ =0.92 (s, 3H), 1.12 (s, 3H), 2.02 (dd, J = 16.5 Hz, 2H), 2.60 (s, 2H), 5.75 (s, 1H), 7.15-7.95 (m, 14H); FTIR (KBr, cm^{-1}): 3030, 2962,2872, 1651, 1595, 1535, 1380, 1352, 1235, 1174, 810; ; ESI-MS: m/z = 432.19 $(M+H)^+$

CONCLUSION

Based on above conclusion it was concluded that, we have described a novel, efficient, multi-component one pot green synthetic method using nano nickel cobalt ferrite catalyst and ethanol as a solvent. The novelty and synthetic utility of this method is demonstrated in the efficient synthesis of 14-Aryl-14H-dibenzo xanthene and 12-aryl tetrahydrobenzo xanthene-11-one derivatives. The advantages of this method include its simplicity of operation, cleaner reaction, and good to excellent yields. Further, the purification of the product is simple filtration is involved. The catalyst is easily separated by using external magnet and is reusable up to five cycles.

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