FeCl₃.nano SiO₂: An Efficient Heterogeneous Nano Catalyst for the Synthesis of 14-Aryl-14*H*-dibenzo[a,j]xanthenes and 1,8-Dioxo-octahydro-xanthenes under Solvent-free Conditions

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ABSTRACT

A novel, efficient and eco-friendly procedure for the synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthenes and 1,8-dioxo-octahydro-xanthenes is described through one-pot condensation of 2-naphthol and dimedone with aryl aldehydes in the presence of nano silica-supported ferric chloride under solvent-free conditions. The present approach offers several advantages such as short reaction times, high yields, easy purification, recovery and reusability of the catalyst.

KEYWORDS

Xanthenes, nano silica, ferric chloride, multi-component reactions, solvent-free.

1. Introduction

Solid acids have attracted much attention in organic synthesis owing to their easy work-up procedures, easy filtration and minimization of cost and waste generation due to reuse and recycling of these catalysts.[1] Recent advances in nanoscience and nanotechnology have led to a new research interest in employing nanometre-sized particles as an alternative matrix for supporting catalytic reactions. In comparison with conventional supports like solid-phase, nanoparticular matrixes have a higher catalyst loading capacity due to their very large surface area.[2] Recently, silica-supported ferric chloride has been used as an efficient heterogeneous catalyst with some advantages such as low cost, ease of preparation, and catalyst recycling.[3,4] Among various solid supports, nano silica gel is one of the extensively used surface material supports for different chemical transformations in organic chemistry. Nano silica is usually preferred since it displays many significant properties such as high surface area, excellent stability (thermal and chemical) and good accessibility. Furthermore, organic groups can be robustly anchored to the surface, to provide catalytic canters.[5,6] According to the above results we modified nano silica gel surfaces using FeCl₃.6H₂O, which has been supported on silica nanoparticles for the synthesis of xanthene derivatives.

The synthesis of xanthene derivatives has received a great attention because of their wide range of therapeutic and biological properties including antibacterial,[7] antiviral,[8] and anti-inflammatory characteristics.[9] In addition, these compounds are used extensively in dyes,[10] laser technologies[11] and as pH-sensitive fluorescent materials for visualization of biomolecules.[12] There are several methods reported in the literature for the synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthene derivatives including the reaction of aryloxy magnesium halides and triethylorthoformate,[13] cyclodehydration,[14] trapping of benzynes by phenols,[15] intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones,[16] cyclization of polycyclic aryl triflate esters[17] and cyclocondensation between 2-hydroxy

aromatic aldehydes and 2-tetralon.[18] In addition, the preparation of 14-aryl-14*H*-dibenzo[a,j]xanthenes has been achieved *via* the reaction of various aldehydes and 2-naphthols by cyclodehydration in the presence of diverse catalysts, including: H₄[SiW₁₂O₄₀],[19] PEG-SO₃H,[20] WCl₆,[21] ruthenium chloride hydrate,[22] poly(4-vinylpyridinium)hydrogen sulfate,[23] DABCO,[24] silica sulfuric acid,[25] Cu(CH₃CN)₄PF₆,[26] trichloroacetic acid,[27] bismuth(III) chloride,[28] sulfonic acid functionalized silica (SiO₂-Pr-SO₃H),[29] Sc[N(SO₂C₈F₁₇)₂]₃,[30] silica-supported ferric hydrogensulfate,[31] P₂O₅ or InCl₃,[32] and polystyrene-supported aluminum chloride.[33]

The classical method for the synthesis of 1,8-dioxo-octahydro-xanthenes involves the condensation of two equivalents of dimedone (5,5-dimethyl-1,3-cyclohexane dione) with various aromatic aldehydes,[34] catalyzed by different catalysts such as alum,[35] [cmmim][BF₄],[36] [TMGT],[37] Fe-{3-montmorilonite,[38] NaHSO₄-SiO₂ or silica chloride,[39] SmCl₃,[40] and silica sulfuric acid.[41] However, many of these methods suffer from disadvantages such as unsatisfactory yields, expensive catalysts, long reaction times, toxic organic solvents, laborious work-up procedures, the requirement of special apparatus, and harsh reaction conditions. Thus, the development of simple, efficient, high-yielding, and eco-friendly methods using new catalysts for the synthesis of these compounds would be highly desirable. With the purpose to develop more efficient synthetic processes, reduce the number of separate reaction steps, and minimize by-products here we report a novel and efficient method for the preparation of xanthene derivatives *via* multi-component coupling of dimedone and 2-naphthol with various aryl-aldehydes in the presence of nano silica-supported ferric chloride. FeCl₃-SiO₂ (np) as an efficient, non-volatile, recyclable, non-explosive, easy to handle, and eco-friendly catalyst can be used as catalyst in many organic reactions.

2. Results and Discussion

To optimize the reaction conditions, the reaction was performed using different amounts of the catalyst, varying temperatures and solvents for carbon-carbon and carbon-oxygen bond forma-

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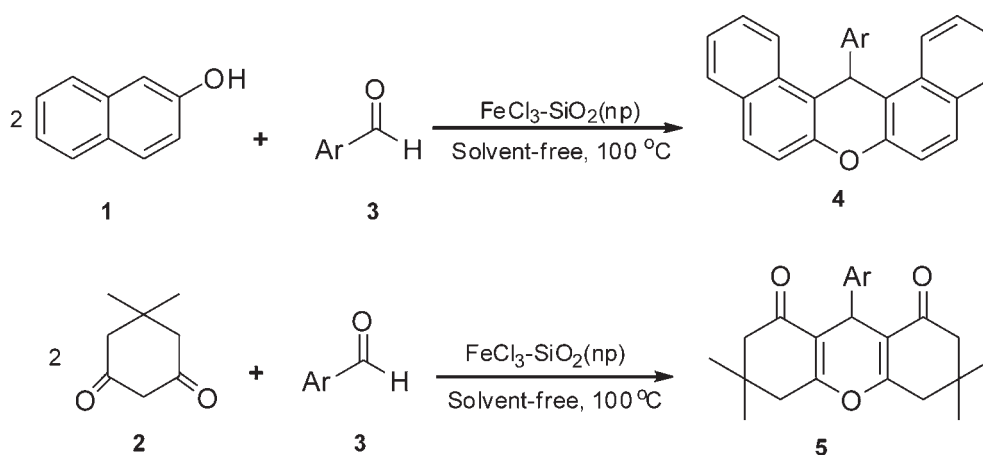
Scheme 1
FeCl$_3$-SiO$_2$ (np) catalyzed synthesis of xanthenes under solvent-free conditions.
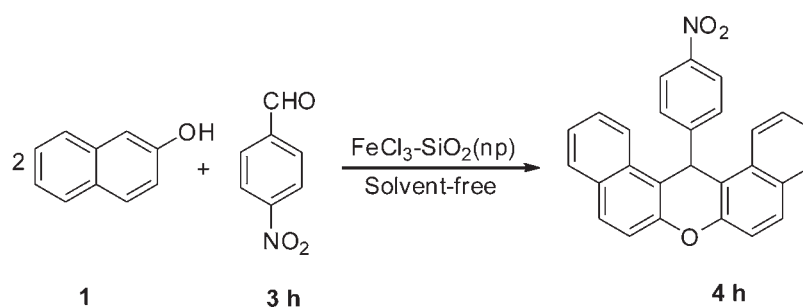
Scheme 2
The model reaction for the preparation of xanthenes using FeCl$_3$-SiO$_2$ (np).

tions. Therefore, we run the model reaction using 2-naphthol **1** and 4-nitrobenzaldhyde **3h** to afford the corresponding 14-aryl-14*H*-dibenzo[a,j]xanthene **4h** (Scheme 2).

No product was obtained in the absence of the catalyst (Table 1, entry 1) and in the presence of the catalyst at room temperature (Table 1, entry 2), indicating that the catalyst and high temperature are necessary for the reaction conditions. We found that the best results were obtained when the reaction was carried out at 100 °C.

To evaluate the catalytic efficiency we used various catalysts in this condensation reaction. As shown in Table 2 FeCl$_3$-SiO$_2$ (np) is the most efficient catalyst for the synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthenes, So we carried out the model reaction using various amounts of this catalyst. The results summarized in Table 1 show the optimum amount of the catalyst was 0.05 g (0.2 mmol, 20 mol%) FeCl$_3$-SiO$_2$ (np).

The increased catalytic activity of FeCl$_3$-SiO$_2$ (np) over the bulk silica-supported ferric chloride may be attributed to the higher surface area of nanomaterials. This is concluded to be due to morphological differences which have been shown in the SEM image (Fig. 2). As shown in Fig. 2 the particle size of the FeCl$_3$-SiO$_2$ (np) has been found to be 45–50 nm.

During optimization of the reaction conditions, the model reaction was carried out in different solvents and also under solvent-free conditions. According to Tables 1 and 2 the best yield and shortest time were obtained in the presence of FeCl$_3$-SiO$_2$ under solvent-free conditions.

The significant results of the above-mentioned experiments prompted us to investigate catalytic activity of FeCl$_3$-SiO$_2$ in the synthesis of 1,8-dioxo-octahydro-xanthene deriatives. Thus, we used the optimized reaction conditions in the presence of FeCl$_3$-SiO$_2$ (np) to produce 1,8-dioxo-octahydro-xanthenes.

Table 1 Influence of catalyst amount FeCl$_3$-SiO$_2$ (np), solvent and temperature on the model reaction.[a]

Entry	Catalyst/g	Solvent	T/°C	Time/min	Yields[b]/%
1	None	Solvent-free	100	300	None
2	0.05	Solvent-free	r.t.	300	None
3	0.01	Solvent-free	100	50	40
4	0.02	Solvent-free	100	45	65
5	0.03	Solvent-free	100	35	70
6	0.04	Solvent-free	100	25	85
7	0.05	Solvent-free	100	20	95
8	0.06	Solvent-free	100	20	95
9	0.05	EtOH	Reflux	210	50
10	0.05	CH$_2$Cl$_2$	Reflux	150	45
11	0.05	CH$_3$CN	Reflux	120	60

[a] Reaction conditions: 2-naphthol (2 mmol) and aldehydes (1 mmol).
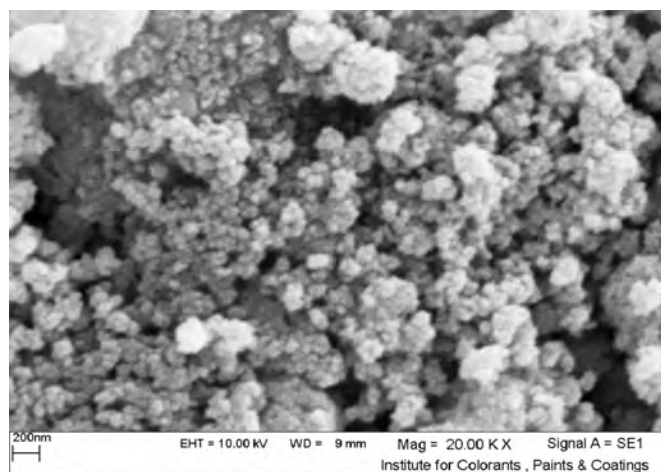[b] Isolated yields.
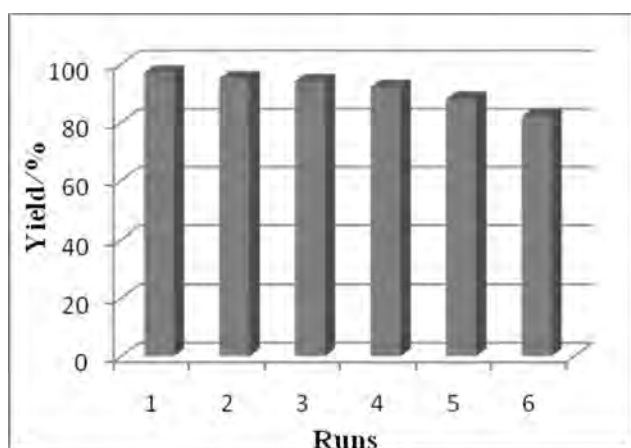
Figure 1 Recoverability of $FeCl_3$-SiO_2 (np).

Figure 2 SEM image of the $FeCl_3$-SiO_2 (np).

Table 2 Reaction of 4-nitrobenzaldehyde and 2-naphthol in various catalysts at 100 °C.[a]

Entry	Catalyst	Time	Yields [b]/%
1	None	4 h	0
2	$FeCl_3.6H_2O$	2 h	60
3	SiO_2	2.5 h	35
4	$FeCl_3$-SiO_2	1 h	70
5	Nano-SiO_2	1.5 h	65
6	$FeCl_3$-SiO_2 (np)	20 min	95

[a] The reaction was carried out under solvent-free conditions.
[b] Isolated yield.

Series of experiments were carried out and as a result of these we prepared a number of 1,8-dioxo-octahydro-xanthenes in high yields and short reaction times. $FeCl_3$-SiO_2 (np) was thus shown to be an effective catalytic system which gave the desired products in excellent yields (Table 3). To study the scope of this procedure, we next used a diversity of aldehydes to investigate three component reactions under the optimized conditions.

We observed various aryl aldehydes could be introduced in high efficiency and produced high yields of products in high purity (≥95 % by ^{1}H NMR). In addition, aromatic aldehydes

bearing electron-withdrawing groups such as NO_2, Cl, and Br in the *p*-position reacted very smoothly, while reactants with electron-releasing groups such as isopropyl and methoxy decreased both the rate of the reaction and the yield of the corresponding product. Sterically hindered aldehydes reacted more slowly in comparison with unhindered aldehydes (Table 3).

2.1. Recycling and Reuse of the Catalyst

In the recycling procedure of $FeCl_3$-SiO_2 (np), dichloromethane was added to dilute the reaction mixture after terminating the reaction. The catalyst was insoluble in the solvent and was separated by easy filtration. The recovered $FeCl_3$-SiO_2 (np) was washed with CH_2Cl_2 (5 × 5 mL). The separated catalyst was used for six cycles with a slightly decreased activity as shown in Fig. 1.

In conclusion, we were able to demonstrate that a range of 14-aryl-14*H*-dibenzo[a,j]xanthenes and 1,8-dioxo-octahydro-xanthenes could be obtained by the catalytic application of nano silica-supported ferric chloride under solvent-free conditions.

3. Experimental

Chemicals were purchased from Sigma-Aldrich and Merck in high purity. All of the materials were of commercial reagent grade and were used without further purification. Melting

Table 3 One-pot synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthenes (**4**) and 1,8-dioxo-octahydro-xanthenes (**5**) catalyzed by $FeCl_3$-SiO_2 (np).

Entry	Aldehyde	Products **4a-o** Time/min | Yield [a]/%	M.p./°C [ref.]	Products **5a-o** Time/min | Yield [a]/%	M.p./°C [ref.]
1	C_6H_5	30|85	181–183 [19]	20|92	201–203 [35]
2	4-$CH_3C_6H_4$	33|80	227–229 [19]	30|88	214–215 [35]
3	4-OHC_6H_4	25|80	137–139 [19]	25|90	248–250 [35]
4	4-$OMeC_6H_4$	35|78	203–204 [19]	32|85	241–243 [35]
5	4-$(CH_3)_2CHC_6H_4$	40|75	152–154 [32]	35|80	203–205 [b]
6	4-ClC_6H_4	20|92	288–289 [19]	15|95	227–229 [35]
7	4-BrC_6H_4	25|90	296–297 [19]	18|92	240–241 [35]
8	4-$NO_2C_6H_4$	20|95	310–312 [19]	15|95	225–226 [35]
9	3-$NO_2C_6H_4$	25|88	211–212 [19]	20|93	166–168 [35]
10	3-ClC_6H_4	25|85	211–212 [21]	25|90	183–184 [35]
11	4-FC_6H_4	20|90	239–240 [19]	18|92	225–226 [35]
12	2-$NO_2C_6H_4$	30|85	213–215 [21]	32|85	246–248 [34]
13	4-$CHOC_6H_4$	25|90	252–254 [b]	22|92	211–213 [b]
14	4-CNC_6H_4	30|90	218–219 [b]	18|93	216–217 [b]
15	4-$SMeC_6H_4$	35|88	264–266 [b]	30|85	256–257 [b]

[a] Isolated yield.
[b] New products.

points were measured on an Electrothermal 9200 apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHZ spectrometer with CDCl$_3$ as solvent and tetramethyl-silane (TMS) as an internal standard. The chemical shift values are in δ. FT-IR spectra were recorded on a Magna-IR, spectrometer 550 Nicolet in KBr pellets in the range of 400–4000 cm^{-1}. Mass spectra were recorded on a Finnigan MAT 44S by Electron Ionization (EI) mode with an ionization voltage of 70 eV. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. Microscopic morphology of products was visualized by SEM (LEO 1455VP).

3.1. Preparation of Nano Silica-supported Ferric Chloride

Nano silica gel (25 g) and FeCl$_3$.6H$_2$O (2 g) (8 % of the weight of nano-SiO$_2$) were vigorously stirred under solvent-free conditions at room temperature for 24 h to achieve a homogeneous adsorption. A yellowish powder was obtained. This powder was heated for 1 h at 100 °C to give a brownish powder ('active' FeCl$_3$-SiO$_2$ reagent).

3.2. General Procedure for the Synthesis of 14-Aryl-14*H*-dibenzo[a,j]xanthenes (4a-o)

A mixture of 2-naphthol (0.28 g, 2 mmol), aldehyde (1 mmol) and FeCl$_3$-SiO$_2$ (np) (0.05 g, 0.2 mmol, 20 mol%) was heated at 100 °C for 20–40 min. During the procedure, the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and dichloromethane was added. The catalyst was insoluble in CH$_2$Cl$_2$ and it could therefore be recycled by a simple filtration. The solvent was evaporated and the solid obtained recrystallized from EtOH to afford the pure xanthenes.

3.3. General Procedure for the Preparation of 1,8-Dioxo-octahydro-xanthenes (5a-o)

A mixture of 5,5-dimethyl-1,3-cyclohexanedione (0.28 g, 2 mmol), various aldehydes (1 mmol) and FeCl$_3$-SiO$_2$ (np) (0.05 g, 0.2 mmol, 20 mol%) was heated at 100 °C for 15–35 min. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature and the obtained residue was dissolved in dichloromethane, the catalyst was insoluble in CH$_2$Cl$_2$ and was separated by a simple filtration. The solvent was evaporated and the solid obtained recrystallized from ethanol to afford the pure 1,8-dioxo-octahydro-xanthenes.

3.4. Spectral Data of New Products

4-(14H-Dibenzo[a,j]xanthene-14-yl)benzaldehyde (**4m**). Pink crystal; m.p. = 252–254 °C; IR (KBr)/ υ (cm^{-1}): 3060, 2923, 2852 (CHO), 2765 (CHO), 1691, 1595 (C=C, Ar), 1513 (C=C, Ar), 1243 (C-O), 819; ^{1}H NMR (CDCl$_3$)/ δ ppm: δ 6.58 (s, 1H, CH), 7.17–7.19 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.42–7.45 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.50–7.68 (m, 4H), 7.70–7.78 (m, 4H), 7.82–7.86 (t, *J* = 7.6 Hz, 2H, Ar-H), 8.33–8.35 (d, *J* = 8.0 Hz, 2H, Ar-H), 9.79 (s, 1H, CHO); ^{13}C NMR (CDCl$_3$)/ δ ppm: 33.5, 117.6, 118.1, 122.8, 124.2, 126.4, 126.5, 126.7, 128.7, 128.8, 131.1, 131.5, 142.3, 146.6, 148.8, 192.3; MS (EI) (*m/z*): 386 (M$^+$); (Found: C, 87.26; H, 4.51 %. Calc. for C$_{28}$H$_{18}$O$_2$ (386.45); C, 87.03; H, 4.69 %).

14-(4-Cyanophenyl)-14H-dibenzo[a,j]xanthene (**4n**). White crystal; m.p. = 218–219 °C; FT-IR (KBr, cm^{-1}): 3041, 2218 (C≡N), 1622 (C=C, Ar), 1583, 1242 (C-O), 809. ^{1}H NMR (CDCl$_3$): δ 6.61 (s, 1H, CH) 7.43–7.45 (d, *J* = 8 Hz, 2H, Ar-H), 7.51–7.53 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.59–7.61 (t, 2H, Ar), 7.68–7.70 (d, *J* = 8 Hz, 2H, Ar-H), 7.84–7.87 (m, 4H, Ar), 8.00–8.02 (d, *J* = 7.8 Hz, 2H, Ar-H), 8.28–8.30 (d, 2H, Ar). ^{13}C NMR (CDCl$_3$): 36.9, 95.1, 115.9, 116.2, 117.1, 120.2,

122.5, 124.8, 126.1, 128.1, 129.7, 132.6, 134.1, 135.9, 148.3, 159.1. MS (EI) (*m/z*): 383 (M$^+$); (Found: C, 87.58; H, 4.59; N, 3.78 %. Calc. for C$_{28}$H$_{17}$NO (383.45); C, 87.71; H, 4.47; N 3.65 %).

14-(4-Thiomethyl)-14H-dibenzo[a,j]xanthene (**4o**). Yellow crystal; m.p. = 264–266 °C; FT-IR (KBr, cm^{-1}): 3046, 1621 (C=C, Ar), 1592, 1510 (C=C, Ar), 1228 (C-O), 1196 (C-S), 815. ^{1}H NMR (CDCl$_3$): δ 2.81 (s, 3H, CH$_3$), 6.42 (s, 1H, CH), 6.82–6.84 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.34–7.42 (m, 4H, Ar), 7.51–7.56 (m, 4H, Ar), 7.66–7.74 (m, 4H, Ar), 8.24–7.26 (d, *J* = 7.9 Hz, 2H, Ar-H). ^{13}C NMR (CDCl$_3$): 31.2, 55.2, 112.1, 116.9, 117.1, 121.9, 123.9, 126.5, 129.1, 128.8, 129.1, 130.9, 131.5, 138.1, 147.5, 156.1. MS (EI) (*m/z*): 404 (M$^+$); (Found: C, 83.27; H, 4.86 %. Calc. for C$_{28}$H$_{20}$OS (372.47); C, 83.14; H, 4.98 %).

9-(4-Isopropylphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (**5e**). Yellow solid. m.p. = 203–206 °C; FT-IR (KBr, cm^{-1}): 3071, 2961, 1665 (C=O), 1624 (C=C, Ar), 1359, 1198 (C-O). ^{1}H NMR (CDCl$_3$): δ 1.00 (s, 6H), 1.10 (s, 6H, 2 × CH$_3$), 1.18 (d, 6H, 2 × CH$_3$), 2.16–2.26 (m, 4H, 2 × CH$_2$), 2.46 (s, 4H, 2 × CH$_3$), 2.78–2.81 (m, 1H, CH), 4.73 (s, 1H, CH), 7.04–7.06 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.17–7.19 (d, *J* = 8.1 Hz, 2H, Ar-H). ^{13}C NMR (CDCl$_3$): 23.9, 27.4, 29.2, 31.3, 32.2, 33.6, 40.8, 50.8, 115.8, 126.1, 128.1, 141.3, 146.5, 162.1, 196.4. MS (EI) (*m/z*): 392 (M$^+$); (Found: C, 79.39, H 8.36 %. Calc. for C$_{26}$H$_{32}$O$_3$ (392.54); C 79.56, H 8.22 %).

4-(3,3,6,6-Tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthene-9-yl)benzaldehyde (**5m**). White solid. mp = 211–213; FT-IR (KBr, cm^{-1}): 2959, 2873 (CH, CHO), 1728 (C=O, CHO), 1663 (C=O), 1618 (C=C, Ar), 1517, 1358, 1200 (C-O). ^{1}H NMR (CDCl$_3$): δ 0.99 (s, 6H, 2 ×CH$_3$), 1.10 (s, 6H, 2 × CH$_3$), 2.14–2.25 (m, 4H, 2 × CH$_2$), 2.45 (s, 4H, 2 × CH$_3$), 4.70 (s, 1H, CH), 7.34–7.36 (d, *J* = 8Hz, 2H, Ar-H), 7.75–7.77 (d, *J* = 8 Hz, 2H, Ar-H), 9.65 (s, 1H). ^{13}C NMR (CDCl$_3$): 27.3, 29.2, 31.5, 32.2, 40.8, 50.76, 115.1, 120.2, 130.1, 131.1, 143.2, 162.4, 196.4, 205.1. MS (EI) (*m/z*): 378 (M$^+$); (Found: C 76.05, H 7.09 %. Calc. for C$_{24}$H$_{28}$O$_3$S (378.47); C 76.17, H 6.92 %).

4-(3,3,6,6-Tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthene-9-yl)benzonitrile (**5n**). Yellow solid. mp = 216–217 °C; FT-IR (KBr, cm^{-1}): 2960, 2225 (C≡N), 1663 (C=O), 1620 (C=C, Ar), 1362, 1199 (C-O), ^{1}H NMR (CDCl$_3$): δ 0.99 (s, 6H, 2 × CH$_3$), 1.12 (s, 6H, 2 × CH$_3$), 2.15–2.28 (m, 4H, 2 × CH$_2$), 2.49 (m, 4H, 2 × CH$_2$), 4.77 (s, 1H, CH), 7.41–7.43 (d, *J* = 8 Hz, 2H, Ar-H), 7.52–7.54 (d, *J* = 8Hz, 2H, Ar-H). ^{13}C NMR (CDCl$_3$): 27.3, 29.2, 32.2, 32.4, 40.8, 50.6, 110.2, 114.6, 119.0, 129.2, 132.0, 149.4, 162.9, 196.3. MS (EI) (*m/z*): 375 (M$^+$); (Found: C 76.77, H 6.71, N 3.73 %. Calc. for C$_{24}$H$_{25}$NO$_3$ (375.47); C 76.77, H 6.71, N 3.73 %).

3,4,6,7-Tetrahydro-3,3,6,6-tetramethyl-9-(4-methylthiophenyl)-2H-xanthene-1,8(5H,9H)-dione (**5o**). White solid. mp = 256–257 °C; FT-IR (KBr, cm^{-1}): 2963, 1661 (C=O), 1621 (C=C, Ar), 1368, 1221 (C-O), 1166 (C-S). ^{1}H NMR (CDCl$_3$): δ 1.02 (s, 6H, 2 × CH$_3$), 1.11 (s, 6H, 2 × CH$_3$), 2.14–2.25 (m, 4H, 2 × CH$_2$), 2.45 (m, 4H, 2 × CH$_2$), 2.78 (s, 3H, CH$_3$-Ar), 4.95 (s, 1H, CH), 7.14–7.16 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.25–7.27 (d, *J* = 8.1 Hz, 2H, Ar-H). ^{13}C NMR (CDCl$_3$): 27.3, 29.2, 30.9, 32.1, 40.8, 50.7, 52,1, 113.4, 115.7, 129.3, 136.5, 157.9, 162.1, 196.4. MS (EI) (*m/z*): 364 (M$^+$); (Found: C 72.82, H 6.99 %. Calc. for C$_{24}$H$_{28}$O$_3$S (364.49); C 72.69, H 7.12 %).

4. Conclusion

In summary, an efficient, facile and economical method for the preparation of xanthenes has been developed using nano silica-supported ferric chloride as a catalyst under solvent-free conditions. The products were obtained in excellent yields and the reaction times were significantly reduced compared to the use of bulk FeCl$_3$-SiO$_2$. The present protocol represents a simple method for the three-component reaction of 2-naphthol and

dimedone with aldehydes for the synthesis of some 14-aryl-14*H*-dibenzo[a,j]xanthene and 1,8-dioxo-octahydro-xanthene derivatives in the presence of novel nano-scale materials.

Acknowledgements

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