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Solvent-free synthesis of 14-aryl(alkyl)-14*H*-dibenzo[*a,j*]xanthene, 9-aryl(alkyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-dione and 2-Amino-5,6,7,8-tetrahydro-5-oxo-4-aryl-7,7-dimethyl-4*H*-benzo-[*b*]-pyran derivatives using $InCl_3$ as catalyst

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Abstract: An efficient synthesis route to dibenzoxanthene, xanthene and benzopyran derivatives from reaction of divergent aldehydes with β-naphthol, dimedone and ethyl cyanoacetate respectively under solvent-free conditions by indium chloride as a relative inexpensive, eco-friendly, easy available, non-volatile, non-explosion, thermally robust, recyclable and easy to handle catalyst at 90°C with good to excellent yields is described. Unenhanced reaction times, simple reaction protocol and work-up, improved synthesis of these materials in the presence of this heterogeneous catalyst.

Keywords: Dibenzoxanthene; Xanthene, Benzopyran; Solvent-free; Indium chloride

Introduction

Xanthenes and benzoxanthenes have received much attention because of their wide range of therapeutic and biological properties, such as antibacterial [1], antiviral [2], and anti-inflammatory activities [3]. These compounds have emerged as sensitizers in photodynamic therapy [4,5], and are used as leuco-dyes [6] and in laser technology [7]. Furthermore, benzoxanthenes are used as dyes [6,8], in laser technologies [9] and in fluorescent materials [10]. they are also utilized as antagonists for paralyzing action of zoxazolamine [11,12]. Thus, the synthesis of benzoxanthene derivatives currently is of great interest. 4*H*-Benzo[*b*]pyrans are an important class of compounds which have received considerable attention in recent years due to their wide range of biological activities [13]. Compounds with these ring systems have diverse pharmacological activities such as anti-coagulant, anticancer, spasmolytic, diuretic, anti-ancaphylactia [14] and served as important regulators for potassium cation channel [15]. 4*H*-Pyrans also constitute the structural unit of a series of natural products [16]. A number of 2-amino-4*H*-pyrans are useful as photoactive materials [17]. Dibenzoxanthenes has been prepared by different methods. However, many of these methods suffer from certain drawbacks including longer reaction times, unsatisfactory yields, harsh reaction conditions and necessity of excess of reagents and catalysts.

One of the best methods is the reaction of β-naphthol with aldehydes or acetals under acidic conditions and other catalysts [18]. There are several methods for synthesis of 4*H*-Benzo[*b*]pyrans [19] and xanthenes [20]. In spite of potential utility of aforementioned routes for the synthesis of 14*H*-dibenzo[*a,j*]xanthene, 1,8-dioxo-octahydro-xanthenes and 4*H*-benzo[*b*]pyrans derivatives, many of these methods involve expensive reagents, strong acidic conditions, long reaction times, low yields, use of excess of reagents/catalysts and use of toxic organic solvents.

Therefore, to avoid these limitations, the discovery of a new and efficient catalyst with high catalytic activity, short reaction time and simple work-up for the preparation of these three compounds under neutral, mild and practical conditions is of prime interest. The aim of this study is to utilize the $InCl_3$ as catalyst for the synthesis of these compounds.

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Results and discussion

Role of metal salts as Lewis acid catalysts in carbon–carbon bond formation and other organic transformations is well established [21]. Following recent studies directed towards the development of practical, safe and environmentally friendly procedures for some important transformations with Indium compounds [22], we wish to report an efficient, convenient and facile method for preparation of these three compounds. In the course of optimization of the reaction conditions, increase in reaction time did not prove fruitful. $InCl_3$ (0.10 mmol) was the optimum amount of catalyst and larger amounts of the catalyst did not improve the yields while decreasing the amount of catalyst decreased the yields. The reaction worked well with aromatic as well as aliphatic aldehydes (Tables 1, 2 and 3), giving products in 82–96% yields. As it is shown in Tables 1, 2 and 3 the method is general and tolerates a variety of functional groups. The yields are high to excellent. Next, we investigated the reusability and recycling of $InCl_3$. At first, we put β-naphthol, *p*-methoxybenzaldehyde and 0.10 mmol of $InCl_3$ together and then the mixture was stirred at 90°C under solvent-free media. When the reaction was completed, the catalyst was separated by simple filtration by dichloromethane and recovered 0.10 mmol of $InCl_3$ was reused in subsequent reactions without significant decrease in activity even after six runs (Table 4). The suggested mechanism of the $InCl_3$ catalyzed synthesis of these compounds is shown in Schemes 4, 5 and 6.

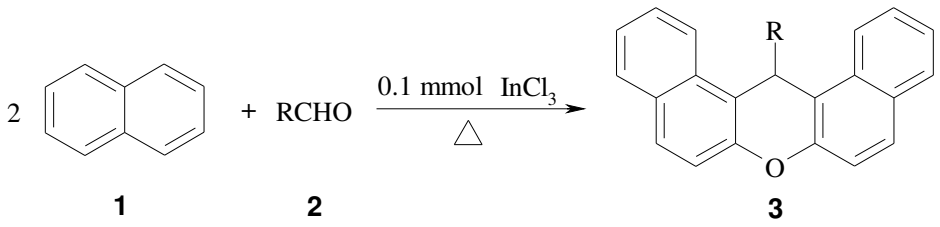
Experimental

Melting points were measured on a Stuart Scientific SMP_2 apparatus and are uncorrected. IR spectra were recorded on a Philips PU-9716 spectrophotometer. All aldehydes, β-naphthol, dimedone and ethyl cyanoacetate were purchased from Merck and $InCl_3$ purchased from Aldrich and used without further purification.

Synthesis of 14-alkyl or aryl dibenzo[*a,j*]xanthenes

General procedure (Scheme 1)

Aldehyde **2** (1 mmol), 2-naphthol **1** (2 mmol, 0.29 g) and $InCl_3$ (0.10 mmol, 0.022 g) were mixed for 1 min at room temperature and stirred at 90°C for the appropriate time (given in Table 1). After completion of the reaction (monitored by TLC), catalyst was separated by simple filtration by EtOH-H_2O (1:3). Then the resulting solid products **3** were collected and were recrystallized from ethanol.



Scheme 1.

Table 1. Synthesis of 14*H*-dibenzo[*a,j*]xanthene derivatives in presence of $InCl_3$ (0.10 mmol) as catalyst from β-naphthol and aldehydes under thermal (bath oil 90°C) and solvent-free conditions

Product	R	Time(min)	Yield[a](%)	Mp(°C) Found	Mp(°C) Reported
3a	C_6H_5	5	89	182-184	183 [18d]
3b	2-$NO_2C_6H_4$	5	91	290-291	293 [18h]
3c	3-$NO_2C_6H_4$	4	93	212-214	213 [18e]
3d	4-$NO_2C_6H_4$	4	95	310-312	312 [18d]
3e	4-MeC_6H_4	4	93	225-228	228 [18d]
3f	4-BrC_6H_4	4	95	295-297	296 [18d]
3g	4-ClC_6H_4	4	93	285-287	287 [18e]
3h	4-FC_6H_4	4	94	235-237	238 [18e]
3i	2,4-$(Cl)_2C_6H_3$	4	93	249-251	228 [18b]
3j	4-$(CH_3)_2CHC_6H_4$	6	86	235-237	—[b]
3k	2-BrC_6H_4	4	95	210-212	214 [18d]
3l	2-ClC_6H_4	4	95	211-213	215 [18e]
3m	2,6-$(Cl)_2C_6H_4$	11	82	267-269	—[b]
3n	2-$MeOC_6H_4$	10	84	254-257	258 [18e]
3o	3-$MeOC_6H_4$	5	90	178-180	180-181 [18m]

Table 2. Continued

3p	4-$MeOC_6H_4$	10	83	201-203	205 [18e]
3q	4-NCC_6H_4	4	94	325-327	—[b]
3r	*n*-C_3H_7	11	82	150-152	152-154 [18q]
3s	$C_6H_5CH_2CH_2$	10	86	167-169	—[b]

[a]Yields refer to pure isolated products. All known products have been reported previously in the literature and were characterized by comparison of ^{1}H NMR and IR spectra with authentic samples.
[b]New compound

Synthesis of 2,2-Arylmethylene Bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives 5a–r

General procedure (Scheme 2)

Aldehyde **2** (1 mmol), dimedone **4** (2.2 mmol) and $InCl_3$ (0.10 mmol, 0.022 g) were mixed for 1 min at room temperature and stirred at 90°C for the appropriate time (given in Table 2). The progress of the reaction was monitored by thin-layer chromatography, TLC (eluent, petroleum ether–ethyl acetate 1:3). After completion of the reaction, the products **5** was filtered and washed with water. Further purification was carried out by crystallization from EtOH.

Table 2. Synthesis of 1,8-dioxo-octahydro-xanthene derivatives in presence of $InCl_3$ (0.10 mmol) as catalyst from dimedone and aldehydes under thermal (bath oil 90°C) and solvent-free conditions

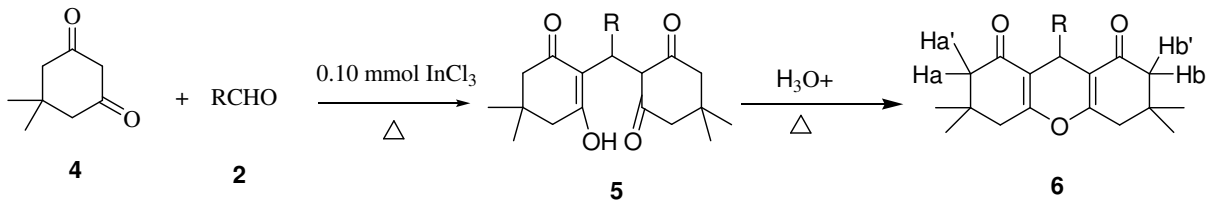
Product	R	Time(min)	Yield[a](%)	Mp(°C)Found	Mp(°C)Reported
6a	3-$MeOC_6H_4$	4	92	160-162	160-162 [20a]
6b	4-$MeOC_6H_4$	5	94	239-242	241-243 [20f]
6c	3,4-$(MeO)_2C_6H_3$	7	90	183-185	—[b]
6d	3-$NO_2C_6H_4$	4	94	165-167	167-168 [20f]
6e	4-$NO_2C_6H_4$	3	95	219-221	221-223 [20f]
6f	C_6H_5	3	90	201-203	201-203 [20a]
6g	4-HOC_6H_4	6	82	244-246	246-248 [20f]
6h	*trans*-C_6H_5CH=CH	7	87	176-178	177-179 [20f]
6i	4-ClC_6H_4	4	94	228-230	230-232 [20a]
6j	2,4-$(Cl)_2C_6H_3$	4	95	253-255	254-255 [20a]
6k	$C_6H_5CH_2CH_2$	5	90	164-166	—[b]
6l	4-NCC_6H_4	2	96	214-216	215-217 [20h]
6m	4-$(CH_3)_2CHC_6H_4$	4	93	169-171	—[d]
6n	2-BrC_6H_4	4	95	222-224	226-228 [20g]
6o	4-FC_6H_4	3	95	221-223	224-226 [20g]
6p	3,5-$(MeO)_2$-4-HOC_6H_2	6	93	204-206	—[b]
6q	4-MeC_6H_4	4	93	214-216	216-217 [20f]
6r	CH_3	7	82	173-175	176-177[20l]
6s	4-Br C_6H_4	5	94	156-158	158-159[19g]

[a]Yields refer to pure isolated products. All known products have been reported previously in the literature and were characterized by comparison of ^{1}H NMR and IR spectra with authentic samples.
[b]New compound

Synthesis of 1,8-dioxo-octahydro-xanthene derivatives 6a–r

General procedure (Scheme 2)

To a mixture of 1 mmol of **3a–j** in 20 ml of MeOH, concentrated sulfuric acid (0.1ml) was added. The reaction mixture was stirred at room temperature for 15 min. The solid was filtered, and the remaining solution was neutralized with NaOH 1N solution. The solid products were collected.



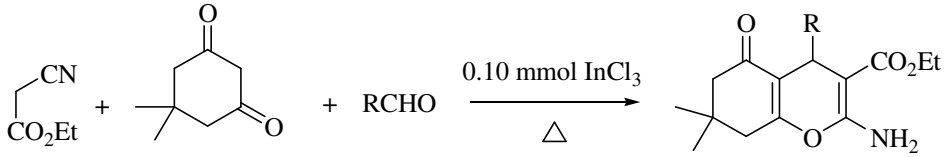
4 **2** **5** **6**

Scheme 2.

Synthesis of 4*H*-Benzo[*b*]pyran derivatives

General procedure (Scheme 3)

A mixture of aldehyde **2** (1.1 mmol), dimedone **4** (1.1 mmol, 0.28 g), ethyl cyanoacetate **7** (1.2 mmol, 0.22 g) and $InCl_3$ (0.10 mmol, 0.022 g) were mixed for 1 min at room temperature and stirred at 90°C for the appropriate time (given in Table 3). After completion of the reaction (monitored by TLC), catalyst was separated by simple filtration and the aqueous solution was evaporated. Then the resulting solid products **8** were collected and were recrystallized from ethanol.



7 **4** **2** **8**

Scheme 3.

Table 3. Synthesis of 4*H*-Benzo[*b*]pyran derivatives in presence of $InCl_3$ (0.10 mmol) as catalyst from dimedone, ethyl cyanoacetate and aldehydes under thermal (bath oil 90°C) and solvent-free conditions

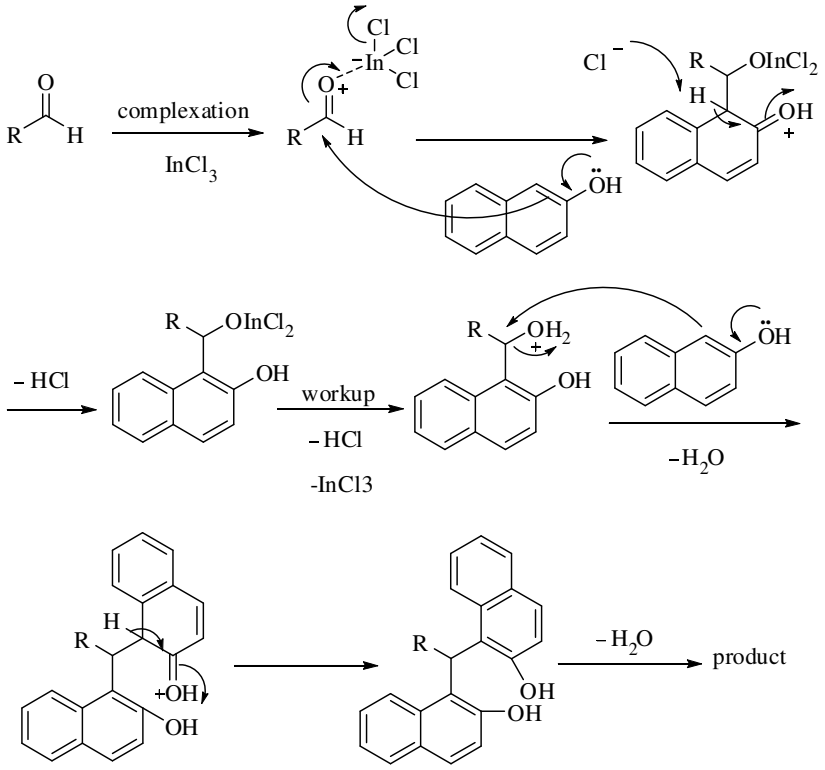
Product	R	Time(min)	Yield[a](%)	Mp(°C) Found	Mp(°C) Reported
8a	C_6H_5	15	84	159-161	161-163 [19c]
8b	4-$NO_2C_6H_4$	8	83	181-183	183-185 [19i]
8c	4-MeC_6H_4	15	88	154-156	155-157 [19c]
8d	2-ClC_6H_4	12	89	164-166	166-168 [19b]
8e	4-ClC_6H_4	10	87	147-149	149-150 [19b]
8f	2,4-$(Cl)_2C_6H_3$	8	90	174-176	176-178 [19c]
8g	4-$MeOC_6H_4$	18	87	137-139	137-139 [19c]
8h	4-BrC_6H_4	10	88	137-139	137-139 [19c]
8i	3-NO_2-C_6H_4	10	86	178-180	181-183 [19n]

[a]Yields refer to pure isolated products. All known products have been reported previously in the literature and were characterized by comparison of IR spectra with authentic samples.

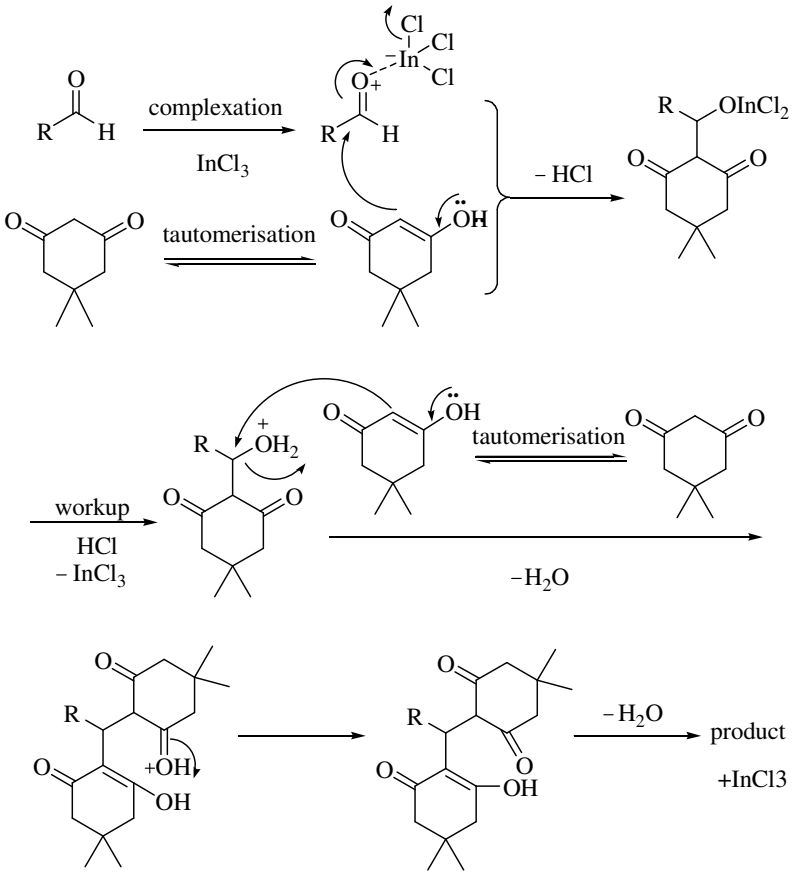
Table 4. Recycling of 0.10 mmol of $InCl_3$

Entry	Time(min)	Yield[a](%)
1	10	83
2	12	82
3	14	81
4	16	79
5	18	77
6	20	75

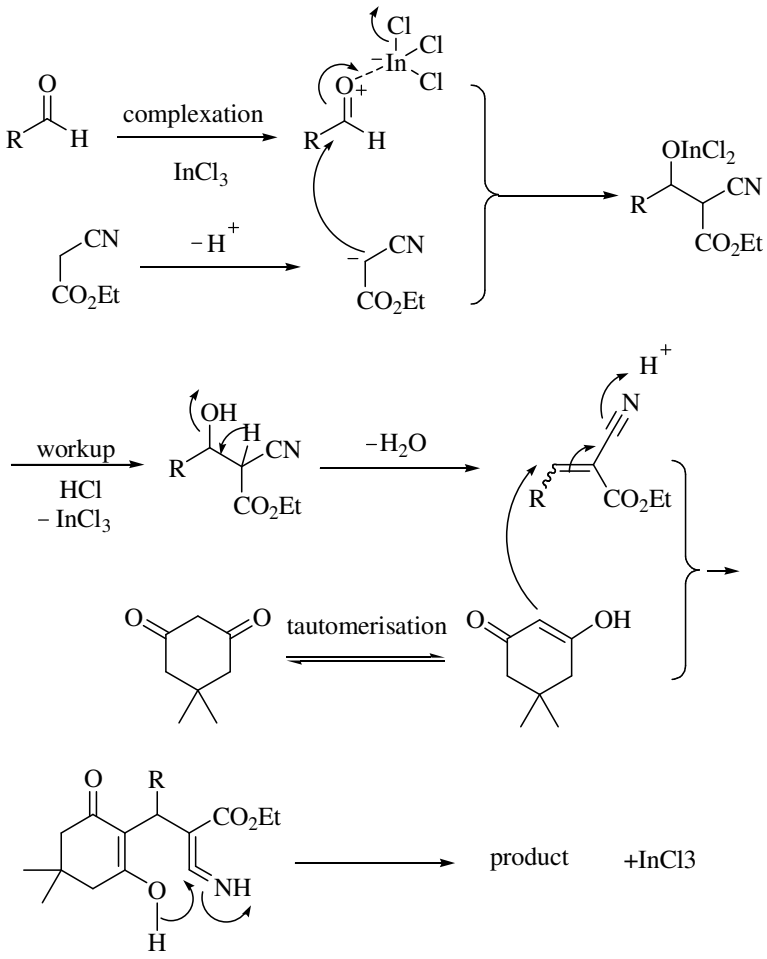
[a]Isolated yields



Scheme 4



Scheme 5



Scheme 6

Typical spectroscopic data

3a: 14-Phenyl-14*H*-dibenzo[*a,j*]xanthene (Table 1, [18d]): white solid: ^{1}H NMR (300 MHz, $CDCl_3$), δ6.48 (s, 1H), 6.93–7.13 (m, 3H), 7.36–7.61 (m, 8H), 7.76–7.83 (m, 4H), 8.38 (d, 2H, *J*=8.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ38.1, 117.4, 118.1, 122.7, 124.3, 126.4, 126.8, 128.3, 128.5, 128.8, 128.9, 131.1, 131.5, 145.1, 148.8; IR ($CHCl_3$, υ/cm^{-1}): 2923, 1591, 1461, 1377, 1249; Found (%): C, 90.30; H, 4.98. Calc. for $C_{27}H_{18}O$ (%): C, 90.47; H, 5.06.

3q: 4-(14*H*-Dibenzo[*a,j*]xanthen-14-yl)-benzonitrile (Table 1): white solid: ^{1}H NMR (300 MHz, $CDCl_3$), δ6.54 (s, 1H), 7.27–7.49 (m, 4H), 7.50–7.51 (m, 2H), 7.59–7.62 (m, 4H), 7.82-7.87 (m, 4H),8.27-8.28 (d, 2H, *J*=5.1 Hz); IR (KBr ,υ/cm^{-1}): 2237, 1605, 1245, 804, 727.

3j: 14-(4-Isopropyl-phenyl)-14*H*-dibenzo[*a,j*]xanthene (Table 1): white solid: ^{1}H NMR (300 MHz, $CDCl_3$), δ1.09-1.10 (d, 6H, *J*=4.9 Hz), 2.70-2.73 (m, H), 6.49 (s, H), 7.00-7.02 (d, 2H, *J*=6.6 Hz), 7.40-7.46 (m, 4H) ,7.48.-7.52 (d, 2H), 7.59-7.62 (t, 2H), 7.79-7.81 (d, 2H, *J*=9.9 Hz), 7.84-7.85 (d, 2H), 7.8.43-8.44 (d, 2H); IR (KBr, υ/cm^{-1}): 2987, 1602, 1247, 805, 732.

3m: 14-(2,6-Dichloro-phenyl)-14*H*-dibenzo[*a,j*]xanthene (Table 1): white solid: ^{1}H NMR (300 MHz, $CDCl_3$), δ6.92-6.97 (m, 2H), 7.03 (s, H,CH), 7.35-7.39 (m, 4H,4CH), 7.44 (s, H,CH), 7.51-7.54 (t, 2H, *J*=7.5 Hz)7.79-7.81 (d, 4H, 4CH), 8.57-8.59 (d, 2H, *J*=7.5 Hz); IR ($CHCl_3$, υ/cm^{-1}): 1608, 1447 , 1252, 803, 754,713.

3s: 14-Phenethyl-14*H*-dibenzo[*a,j*]xanthene (Table 1): Yellow solid:^{1}H NMR (300 MHz, $CDCl_3$), δ2.34-2.39 (m,2H), 2.40-2.46(m, 2H, 2CH), 5.69-5.71 (t, 1H, *J*=4.9 Hz, CH), 6.83–6.84 (d, 2H), 7.03–7.11 (m, 3H), 7.44–7.46(d, 2H, 2CH), 7.49-7.52 (t, 2H), 7.64–7.67 (t, 2H), 7.82–7.84 (d, 2H), 7.92–7.93 (d, 2H, 2CH), 8.29-8.31 (d, 2H, 2CH) ; IR (KBr ,υ/cm^{-1}): 2943, 1587, 1247, 804, 763.

5c: 2-[(3,4-Dimethoxy-phenyl)-(2-hydroxy-4,4-dimethyl-6-oxo-cyclohex-1-enyl)-methyl]-5,5-dimethyl-cyclohexane-1,3-dione (Table 2, [20a]); white solid: Mp. 178-180°C; (300 MHz, $CDCl_3$), δ.99 (s, 6H, 2Me)), 1.09 (s, 6H, 2Me), 2.15-2.24(q, 4H, *J*=9.8Hz, $2CH_2$), 2.45 (s, 4H ,$2CH_2$), 3.78 (s, 3H, Me), 3.84 (s, 3H, Me), 4.69 (s, H ,CH), 6.69-6.71 (m, H, CH), 6.74-6.76 (m, H,CH), 6.89-6.90 (s, H, CH) , 12.0 (brs, 1H, OH); IR (KBr, υ/cm^{-1}):3453, 3015, 2953, 1585.

5m: 2-[(2-Hydroxy-4,4-dimethyl-6-oxo-cyclohex-1-enyl)-(4-isopropyl-phenyl)-methyl]-5,5-dimethyl-cyclohexane-1,3-dione; (Entry 6b, Table 2, [20a]); white solid: Mp. 165-167°C; (300 MHz, $CDCl_3$), δ1.11 (s, 6H, 2Me), 1.21-1.27 (s, 12H, 4Me),),2.31-2.44(m, 8H, $4CH_2$), 2.86-2.89 (m, H, CH), 5.52 (s, H, CH), 7.02-7.27 (m, 4H, 4CH) , 11.91 (brs, 1H, OH) ; IR (KBr, υ/cm^{-1}):3463, 2959, 2928, 1738, 1731, 1599.

5p: 2-[(4-Hydroxy-3,5-dimethoxy-phenyl)-(2-hydroxy-4,4-dimethyl-6-oxo-cyclohex-1-enyl)-methyl]-5,5-dimethyl-cyclohexane-1,3-dione(Entry 6b, Table 2, [20a]):white solid: Mp. 198-200°C; ^{1}H NMR (300 MHz, $CDCl_3$), δ1.01 (s, 6H, 2Me); 1.10 (s, 6H, 2Me); 2.21-2.22 (q, *J*=5.8Hz, 4H, $2CH_2$); 2.45-2.47 (q, *J*=5.8Hz, 4H, $2CH_2$); 3.82 (s, 6H, 2Me); 4.68 (s, H, CH), 5.37 (s, H, CH), 6.52 (s, 2H, 2CH), 12.0 (brs, 1H, OH); IR (KBr, υ/cm^{-1}):3459, 3016, 2952, 1718, 1620.

5k: 2-[1-(2-Hydroxy-4,4-dimethyl-6-oxo-cyclohex-1-enyl)-3-phenyl-propyl]-5,5-dimethyl-cyclohexane-1,3-dione (Entry 6b, Table 2, [20a]): white solid: Mp. 173-175°C; ^{1}H NMR (300 MHz, $CDCl_3$), δ1.06-1.08 (d, 12H, 4Me), 2.25-2.37 (m, 10H, $5CH_2$), 2.48-2.51 (s, 2H, CH_2), 4.00-4.03 (s, H, CH), 7.14-7.28 (m, 5H, 5CH) , 11.66 (brs, 1H, OH); IR (KBr, υ/cm^{-1}):3455, 3014, 2952, 1714, 1621.

6f: 3,3,6,6-Tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-dione (Entry **6b**, Table 2, [20a]): Mp. 201-203°C; ^{1}H NMR (300 MHz, $CDCl_3$), δ0.99 (s, 6H, CMe_2); 1.11 (s, 6H, CMe_2); 2.14-2.23 (q, *J*=15.86Hz, 4H, $2xCH_2$); 2.43 (s, 4H, $2xCH_2$); 4.68 (s, 1H, CH); 7.04-7.25 (m, 5H, Ar).

6c: 9-(3,4-Dimethoxy-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-dione(Table 2): Mp. 183-185°C; IR (KBr, υ/cm^{-1}): 3011, 2955, 1741, 1671.

6p: 9-(4-Hydroxy-3,5dimethyl-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-dione (Table 2): Mp. 204-206°C ; IR (KBr, υ/cm^{-1}):3375, 2959, 1745, 1669, 1651.

6k: 3,3,6,6-Tetramethyl-9-phenethyl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-dione (Table 2): Mp. 164-166°C; IR (KBr, υ/cm^{-1}) :3040,2951, 1688, 1658.

6m: 9-(4-Isopropyl-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-dione(Table 2): Mp. 169-171°C; IR (KBr, υ/cm^{-1}):3040, 2960, 1695, 1659, 1623.

8f: 2-Amino-5,6,7,8-tetrahydro-5-oxo-4-(2,4-dichlorophenyl)-7,7-dimethyl-4*H*-benzo-[*b*]-pyran (Table 3, [19c]): ^{1}H NMR (300 MHz, $CDCl_3$), δ1.04 (3H, s, Me), 1.14 (3H, s, Me), 1.18 (3H, t, *J*=7.1 Hz, Me), 2.18 (1H, d, *J*=16.0 Hz, H-6), 2.26 (1H, d, *J*=16.0 Hz, H-6), 2.46 (2H, m, CH_2), 4.06 (2H, m, OCH_2), 5.0 (1H, s, H-4), 6.30 (2H, br, NH_2) 7.15 (1H, dd, *J*=4.6, 1.3 Hz, H–Ar), 7.28 (1H, d, *J*=4.6 Hz, H–Ar), 7.29 (1H, br, H–Ar); IR (KBr, υ/cm^{-1}) 3429, 3306, 2957, 1699.

8i: 2-Dimethylamino-7,7-dimethyl-4-(3-nitro-phenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylic acid ethyl ester(Table 3, [19n]): ^{1}H NMR (300 MHz, $CDCl_3$), δ1.03 (3H, s, Me), 1.16 (3H, s, Me), 1.19 (3H, t, *J*=7.1 Hz, Me), 2.21 (1H, d, *J*=16.0 Hz, H-6), 2.28 (1H, d, *J*=16.0 Hz, H-6), 2.51 (2H, m, CH_2), 4.07 (2H, m, OCH_2), 4.85 (1H, s, H-4), 6.28 (2H, br, NH_2) 7.40 (1H, t, *J*=7.9Hz, H–Ar), 7.68 (1H, d, *J*=7.90Hz, H–Ar), 8.0 (1H, d, *J*=7.90Hz, H–Ar); IR (KBr, υ/cm^{-1}) 3438, 3328, 2961, 1686,1525.

Conclusion

We have developed a simple, efficient and green protocol for the synthesis of 14*H*-dibenzo[*a,j*]xanthene, 1,8-dioxo-octahydro-xanthene and 4*H*-benzo[*b*]pyran derivatives using $InCl_3$ under solvent-free conditions. The short reaction times, simple work-up in isolation of the products in good yields with high purity, mild reaction conditions and recyclability of catalyst are features of this new procedure.

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