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A facile approach for the synthesis of 14-aryl- or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes under solvent-free condition

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ABSTRACT

A facile, efficient and environment-friendly protocol for the synthesis of 14-aryl- or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes has been developed by one-pot condensation of 2-naphthol with aliphatic and aromatic aldehydes in the presence of P_2O_5 or $InCl_3$ as catalysts under solvent-free conditions. The present approach offers the advantages of clean reaction, simple methodology, short reaction time, high yield, easy purification, and economic availability of the catalyst.

Organic syntheses involving greener process and under solvent-free conditions have been investigated world wide due to stringent environment and economic regulations.[1] In addition, the implementation of several transformations in a single manipulation is highly compatible with the goals of sustainable and green chemistry. The synthesis of xanthenes, especially benzoxanthenes (Fig. 1), has attracted great interest in recent years due to their wide range of biological and pharmaceutical properties such as antiviral,[2] antibacterial,[3] and anti-inflammatory[4] activities as well as sensitizers in photodynamic therapy[5] (PDT; a method of treating tumours by combined use of a photosensitizer and light) and antagonists for the paralyzing action of zoxazolamine.[6] Furthermore, these compounds can be used as leuco-dyes,[7] pH-sensitive fluorescent materials for visualization of biomolecules[8] and utilized in laser technologies.[9]

In view of great importance of benzoxanthenes, various methods have been reported for the construction of benzoxanthene scaffolds, including the reaction of β-naphthol with formamide,[10] 2-naphthol-1-methanol,[11] carbon monoxide,[12] the cyclocondensation reaction of 2-hydroxyaromatic aldehydes with 2-tetralone,[13] the reaction of benzaldehydes with acetophenones,[14] palladium-catalyzed cyclization of polycyclic aryltriflate esters[15] and trapping of benzynes by phenols.[16] Recently, the synthesis of benzoxanthenes has been achieved by the condensation of aldehydes with β-naphthol by cyclodehydration in the presence of various catalysts (Scheme 1), such as AcOH–H_2SO_4,[17] *p*-TSA,[18] $MeSO_3H$,[19] sulfamic acid,[20a] ionic liquid,[20b] iodine,[21] heteropolyacid,[22] silica sulfuric acid,[23] Amberlyst-15,[24] cyanuric chloride,[25] LiBr,[26] $CoPy_2Cl_2$,[27] $Yb(OTf)_3$,[28a] $Sc[N(SO_2C_8F_{17})_2]_3$,[28b] $NaHSO_4$[29a] and $Al(HSO_4)_3$.[29b]

However, these methods show varying degrees of success as well as limitations such as prolonged reaction times, low yields, use of toxic solvents, requirement of excess of reagents/catalysts, laborious work-up procedures, the requirement of special apparatus, or harsh reaction conditions. Thus, the development of an alternate milder and clean procedure is highly demanding for the synthesis of benzoxanthenes, which surpasses those limitations. The use of phosphorous pentoxide has given many advantages in organic synthesis. P_2O_5 is mild and selective catalyst, easy to handle and readily biodegradable, which has earlier been used widely in various organic transformations such as Beckmann rearrangement,[30] olefin dimerisation,[31] tetrahydropyranylation of alcohols[32] and formation of 1,1-diacetate.[33]

As part of our research program directed towards the development of highly expedient methods and the syntheses of diverse

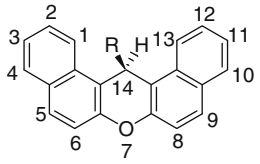

Figure 1. Benzoxanthenes.

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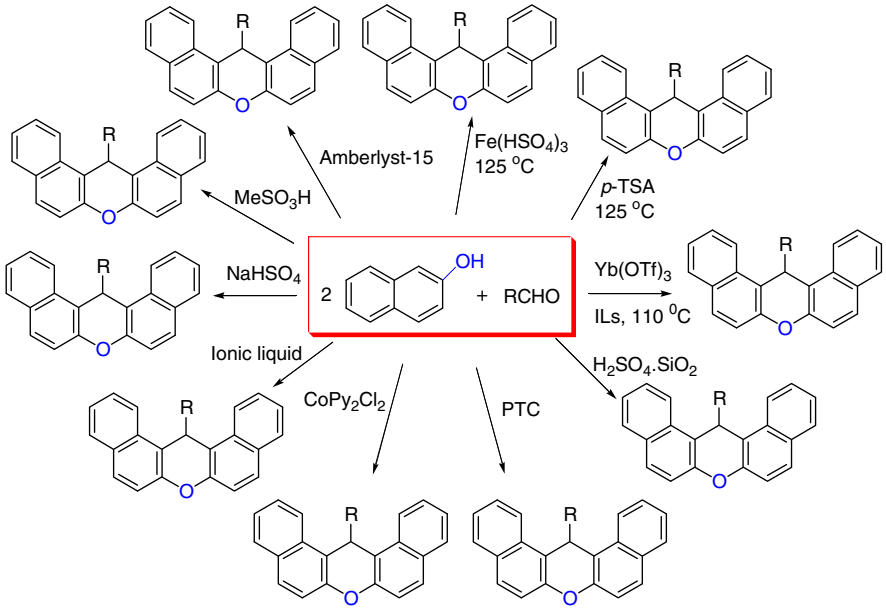
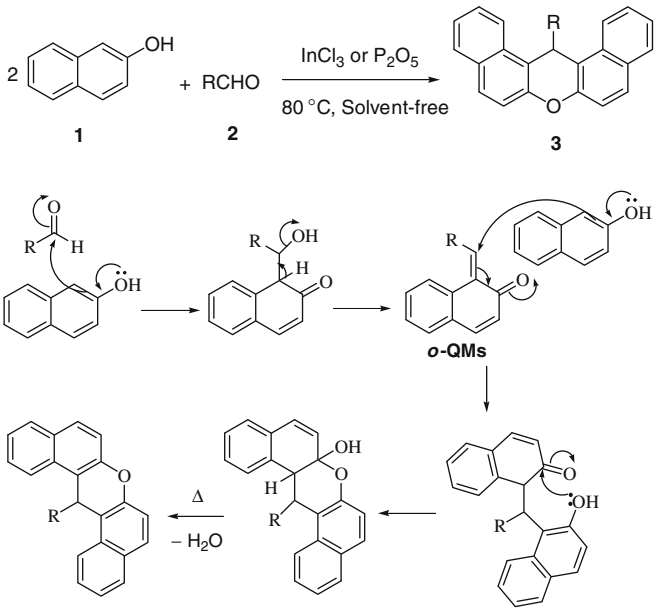


Scheme 1. Preparation of 14-substituted-14*H*-dibenzo[*a*,*j*] xanthenes by condensation of 2-naphthol and aldehydes.



Scheme 2. Proposed mechanism for the synthesis of 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes.

heterocyclic compounds[34] of biological significance, we herein disclose a new, convenient, and one-pot synthesis of 14-aryl- or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes from aldehydes and β-naphthol catalyzed by P_2O_5 or $InCl_3$ under solvent-free conditions in excellent yields (Scheme 2). To the best of our knowledge in the open literature, one-pot syntheses of benzoxanthenes catalyzed by P_2O_5 or $InCl_3$ have not been reported.

In our initial experiments, the condensation of 4-bromobenzaldehyde and β-naphthol (mole rate 1:2) was performed in the presence of catalysts $InCl_3$ and P_2O_5 separately, in refluxing dichloromethane (DCM). Both catalysts facilitated the formation of dibenzo[*a*,*j*]xanthene in good yields (92% and 97%, respectively), but require long reaction time (7 h and 6 h, respectively). Then, it was decided to carry out the reactions under solvent-free conditions with the above catalysts separately, and it was found that the reactions proceeded smoothly in shorter reaction time giving good yields. The results show that under solvent-free conditions, the catalytic activities of P_2O_5 and $InCl_3$ were increased and in all the cases P_2O_5 was found to be a better catalyst than $InCl_3$ (Table 2).

A test reaction using 4-bromobenzaldehyde and β-naphthol (mole rate 1:2) at 80 °C without catalyst was performed in order to establish the real effectiveness of the catalyst. It was found that no conversion to product occurred even after 10 h of heating. We then focused on optimising the reaction conditions. In order to evaluate the most appropriate catalyst loading a model reaction using 4-bromobenzaldehyde and β-naphthol (mole rate 1:2) was carried out using 10 mol %, 15 mol % and 20 mol % of P_2O_5 at 80 °C without solvent. It was found that 20 mol% of the catalyst showed maximum yield in minimum time (Table 1, entry 20). A

Table 1
Comparison of the efficiency of P_2O_5 with other catalysts for the synthesis dibenzoxanthenes

Entry	Catalyst	Temp (°C)	Time	Yields[a] (%)
1	*p*-TSA	125	15–24 h	81–93
2	$H_2SO_4{\cdot}SiO_2$	125	4–8 h	78–95
3	Selecfluor®	125	6–11 h	74–93
4	Sulfamic acid	125	6–12 h	90–95
5	$Fe(HSO_4)_3$	125	23 min	72–90
6	$K_5CoW_{12}O_{40}{\cdot}3H_2O$	125	3 h	64–78
7	Amberlyst-15	125	0.5–2 h	80–94
8	Montmorillonite K10	120	2–4 h	75–87
9	PTC	110	2–3 h	87–93
10	LiBr	130	1–2 h	80–84
11	Dowex-50 W	100	1–2 h	78–91
12	Heteropoly acid	100	0.5–1.5 h	80–91
13	$Yb(OTf)_3$/ILs	110	3–7 h	78–95
14	Iodine	90	2.5–5 h	82–95
15	$NaHSO_4$	90	0.5–1 h	74–91
16	$CoPy_2Cl_2$	85	2–8 h	65–94
17	H_2SO_4	80	73 h	60–90
18	P_2O_5 (10 mol %)	80	5–8 h	72–84
19	P_2O_5 (15 mol %)	80	3–5 h	78–92
20	P_2O_5 (20 mol %)	80	0.5–1 h	87–97
21	P_2O_5 (25 mol %)	80	2–4 h	76–88

[a] Yields of isolated pure products.

Table 2
P_2O_5 and $InCl_3$ catalyzed synthesis of 14-substituted-14*H*-dibenzo[*a*,*j*]-xanthenes

Entry	R	Product	Method A (P_2O_5) Time (min)/yield (%)	Method B ($InCl_3$) Time (min)/yield (%)	Mp (°C)/(lit.)
1	4-NO_2·C_6H_4	**3a**	50/97	60/94	310–311 (311–312)[21]
2	3-NO_2·C_6H_4	**3b**	52/90	60/82	210–211 (211–212)[19]
3	2-NO_2·C_6H_4	**3c**	30/84	45/75	214–215 (214)[21]
4	4-Cl·C_6H_4	**3d**	47/92	55/84	287–288 (288–289)[19]
5	2-Cl·C_6H_4	**3e**	52/85	60/75	214–215 (215–216)[19]
6	4-OMe·C_6H_4	**3f**	50/89	60/80	202–203 (203–204)[19]
7	4-Me·C_6H_4	**3g**	55/84	65/76	227–228 (228–229)[19]
8	C_6H_5	**3h**	45/88	55/78	182–183 (181–183)[21]
9	3-OH·C_6H_4	**3i**	52/86	60/80	242–243
10	4-Br·C_6H_4	**3j**	52/94	60/85	295–296 (296)[26]
11	4-F·C_6H_4	**3k**	50/91	65/82	239–240 (239)[19]
12	3-OEt, 2-OH·C_6H_3	**3l**	60/84	75/75	206–208
13	2-OH, 3-OMe·C_6H_3	**3m**	58/83	75/72	266–267
14	2,4-Cl_2·C_6H_3	**3n**	45/90	55/82	227–228 (227)[23]
15	2-OMe·C_6H_4	**3o**	56/83	65/77	258–260 (260–261)[20b]
16	4-OH·C_6H_4	**3p**	58/88	65/79	139–140 (140)[28b]
17	2-OH·C_6H_4	**3q**	60/82	70/75	127–128
18	Me_2CH	**3r**	62/75	75/71	152–153 (153–154)[19]
19	$C_6H_5CH{=}CH$	**3s**	70/54	75/50	178–180
20	Me_2CHCH_2	**3t**	62/70	75/62	112–113 (113–114)[19]
21	CH_3CH_2	**3u**	60/75	75/67	149–150 (151–152)[19]

further increasing of catalyst loading does not affect the yield, but slightly slowed down the reaction (Table 1, entry 21). Thus, 20 mol % of catalyst was found to be the optimal quantity and sufficient to push the reaction forward.

With the optimized conditions in hand, to explore the generality of the reaction, we extended our study with different aromatic and aliphatic aldehydes to prepare a series of dibenzo[*a*,*j*]xanthenes (**3a**–**u**, Table 2). In all the cases the corresponding benzoxanthenes were obtained in good to excellent yields. However, with aromatic aldehydes with electron-withdrawing groups as substrates, the reaction time is shorter than those with electron-donating groups. Though *meta*- and *para*-substituted aromatic aldehydes gave good results, *ortho*-substituted aromatic aldehydes (such as 2-nitrobenzadehyde) gave lower yields because of the steric effects. Interestingly, 4-hydroxybenzaldehyde also gave the desired product in excellent yield. On the other hand, reactions with aliphatic and α,β-unsaturated aldehydes provided somewhat lower yields than those with aromatic aldehydes (Table 2, entries 18–21) probably due to less stability of *o*-quinonemethide intermediate (*o*-QMs)[35] and the bulkiness of aldehydes.

In order to show the accessibility of the present work in comparison with the reported results, we summarized some of the results for the preparation of dibenzoxanthenes[36] in Table 2, which shows that P_2O_5 is the most efficient catalyst with respect to the reaction time and temperature and exhibits broad applicability in terms of yield.

A mechanistic rationale portraying the probable sequence of events is given in Scheme 2. The reaction proceeds through the in situ formation of *ortho*-quinone methide intermediate by the nucleophilic addition of β-naphthol to aldehyde (a highly reactive and ephemeral intermediate[35] that have been extensively harnessed by nature), which is further attacked by second molecule of β-naphthol followed by cyclodehydration to give the benzoxanthenes. Phosphorous pentoxide acts as a water scavenger, which assists in the reaction.

In conclusion we have developed a facile protocol for the synthesis of 14-substituted-14*H*-dibenzo[*a*,*j*]-xanthenes[36]. The remarkable catalytic activity of P_2O_5 and $InCl_3$ is superior to the reported other catalytic methods with respect to reduced reaction times. The pure products were obtained by column chromatography. The higher yields, mild reaction condition, easy purification, and economic availability of the catalyst make the ecofriendly procedure an attractive alternative to the existing methods for the synthesis of 14-substituted-14*H*-dibenzo[*a*,*j*]-xanthene. Further application of P_2O_5 and *o*-QM intermediate on the extension of this protocol are ongoing in our group.

Acknowledgements

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36. *General procedure for synthesis of 14-substituted-14H-dibenzo[a,j]xanthenes*: To a nicely ground mixture of 2-naphthol (2 mmol) and aldehyde (1 mmol), P_2O_5 (20 mol %) or $InCl_3$ (30 mol %) was added and the reaction mixture was heated at 80 °C for the appropriate time (Table 2). After completion (monitored by TLC), the reaction mixture was cooled to room temperature, water (50 mL) was added and extracted with ethyl acetate (3 × 25 mL). The combined extract was washed with brine, dried over anhydrous $MgSO_4$ and evaporated to dryness under vacuum to give the crude product, which was purified by column chromatography over silica gel (hexane/AcOEt = 19:1). The desired pure products were characterized by spectral (IR, ^1H and ^{13}C NMR) and analytical data, and by comparison of their physical and spectral data with those of known benzoxanthenes.[17–31]Data for some selected compounds: *14-(3-Hydroxyphenyl)-14H-dibenzo[a,j]-xanthene* (**3i**): mp 242–243 °C. IR (KBr, cm^{-1}): 3412, 1588, 1507, 1413, 1258, 1237, 813; ^1H NMR (300 MHz, $CDCl_3$): δ 8.37 (d, J = 8.7 Hz, 2H), 7.83–7.76 (m, 4H), 7.59–7.54 (m, 2H), 7.47–7.37 (m, 4H), 7.18 (d, J = 7.8 Hz, 1H), 7.03 (t, J = 8.1 Hz, 1H), 6.86 (s, 1H), 6.64–6.43 (m, 2H), 4.54 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.8, 147.9, 145.9, 130.6, 130.2, 128.6, 128.1, 128.0, 126.0, 123.5, 121.9, 120.1, 117.2, 116.3, 114.6, 112.8, 37.0. Anal. Calcd for $C_{27}H_{18}O_2$: C, 86.61; H, 4.85. Found: C, 86.50; H, 4.73.

14-(4-Bromophenyl)-14H-dibenzo[a,j]-xanthene (**3j**): mp 295–296 °C. IR (KBr, cm^{-1}): 3056, 2922, 1622, 1590, 1514, 1456, 1392, 1243, 1231, 1207, 1143, 1062, 957, 816, 772, 741; ^1H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, J = 8.4 Hz, 2H), 7.85–7.78 (m, 4H), 7.60–7.55 (m, 2H), 7.48–7.37 (m, 5H), 7.25–7.23 (m, 3H), 6.46 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.9, 144.8, 131.2, 130.7, 130.6, 130.0, 129.2, 128.6, 127.0, 124.6, 123.2, 119.4, 117.6, 116.8, 36.8. Anal. Calcd for $C_{27}H_{17}BrO$: C, 74.15; H, 3.92. Found: C, 74.23; H, 3.80.

14-(3-Ethoxy-2-hydroxyphenyl)-14H-dibenzo[a,j]-xanthene (**3l**): mp 206–208 °C. IR (KBr, cm^{-1}): 3412, 2961, 1583, 1509, 1408, 1258, 1247, 1032, 957; ^1H NMR (300 MHz, $CDCl_3$): δ 8.70 (d, J = 8.4 Hz, 2H), 7.80–7.73 (m, 4H), 7.58–7.36 (m, 6H), 6.85 (s, 1H), 6.76 (d, J = 7.2 Hz, 1H), 6.54–6.44 (m, 3H), 4.03–3.97 (m, 2H), 1.46 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.7, 145.2, 140.2, 132.0, 131.6, 130.7, 128.4, 128.3, 126.7, 124.1, 123.4, 122.3, 120.3, 118.1, 117.8, 108.9, 64.5, 36.4, 14.8. Anal. Calcd for $C_{29}H_{22}O_3$: C, 83.23; H, 5.30. Found: C, 83.15; H, 5.16.

14-Isopropyl-14H-dibenzo[a,j]xanthene (**3r**): mp 152–153 °C. IR (KBr, cm^{-1}): 3057, 2953, 1593, 1509, 1438, 1388, 1245, 819, 746; ^1H NMR (300 MHz, $CDCl_3$): δ 8.70 (d, J = 8.4 Hz, 2H), 7.80–7.73 (m, 4H), 7.58–7.36 (m, 6H), 6.76 (d, J = 7.2 Hz, 1H), 2.11 (m, 1H), 1.06 (d, J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.2, 145.7, 139.7, 132.4, 131.1, 129.3, 128.8, 127.8, 126.9, 124.7, 123.9, 122.7, 119.8, 118.6, 117.5, 109.9, 36.7, 30.4, 14.8. Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.67; H, 6.13.