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ARTICLE

An efficient synthesis of novel 3-hydroxy-12-arylbenzo[*a*]xanthen-11-ones and 5,12-diarylxantheno[2,1-*a*]xanthene-4,12-diones using *p*TSA in [bmim]BF_4

Sneha Yadav, Bhaskara Nand, and Jitender M. Khurana

Abstract: We introduce a simple, efficient, and environmentally benign synthesis of a series of novel xanthenes via one-pot condensation of 2,6-dihydroxynaphthalene, aldehydes, and dimedone in [bmim]BF_4 with *p*TSA as catalyst in high yields.

Key words: mono- and bis(tetrahydrobenzo[*a*]xanthen-11-ones), ionic liquid, one-pot condensation, *p*TSA.

Résumé : On présente une synthèse simple, efficace et respectueuse de l'environnement d'une série de nouveaux xanthènes au moyen d'une condensation monotope du 2,6-dihydroxynaphthalène, d'aldéhydes et de dimédone en solution dans [bmim]BF_4 en présence d'APTS comme catalyseur qui donne de hauts rendements. [Traduit par la Rédaction]

Mots-clés : mono- et bis(tétrahydrobenzo[3 *a*]xanthén-11-ones), liquide ionique, condensation monotope, APTS.

Introduction

Ionic liquids are rapidly substituting the classical organic solvents on account of the interesting advantages that they offer such as extremely low vapor pressure, excellent thermal stability, reusability, and ability to dissolve many organic and inorganic substrates.[1] The use of ionic liquids as reaction medium may offer a convenient solution to both the solvent emission problem and the catalytic recycling problem.[2] Room temperature ionic liquids,[3] especially those based on the 1-*N*-alkyl–3-methyl imidazolium cation, have attracted much attention in recent years as alternative green reaction media and have found growing applications in organic reactions. Several examples of these reactions include hydrogenations,[4] Friedel–Crafts reactions,[5] Heck reactions,[6] Bishler–Napieralski reactions,[7] olefin hydrodimerizations,[8] and olefin dimerizations.[9]

Xanthenes and related compounds have been of significant interest because of their broad spectrum of pharmaceutical importance, such as analgesic,[10] anti-bacterial,[11] anti-inflammatory,[12] and anti-viral activities.[13] These compounds are being used as antagonists for the paralyzing action of zoxazolamine[14] and in photodynamic therapy.[15]

Some xanthene derivatives have been investigated for agricultural bactericide activity.[16] Some other derivatives have commercial application as dyes in laser technology[17] and fluorescent materials for visualization of biomolecules.[18] Many procedures have been reported for the synthesis of xanthene derivatives, including cyclodehydrations,[19] γ-alkylations to the heteroatoms,[20] trapping of benzynes by phenols,[21] cyclocondensation between 2-hydroxyaromatic aldehydes and 2-tetralone,[22] the reaction of β-naphthol with aldehydes or acetals under acidic conditions, and intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones.[23] A variety of 12-aryl-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-ones have been synthesized from the condensation of β-naphthol, aldehydes, and cyclic 1,3-dicarbonyl compounds.[16,24]

Thus, a broad utility range has made xanthenes prime synthetic candidates thereby accentuating the need to develop newer synthetic routes for scaffold manipulation of xanthene derivatives. The synthesis of tetrahydrobenzo[*a*]xanthen-11-ones has been reported in the presence of strontium triflate,[25] NH_2SO_3H,[26] $NaHSO_4.SiO_2$ under reflux in halogenated solvents for long hours,[24] TBAF,[27] and manganese perchlorate.[28] As part of our ongoing research[29,30] on the synthesis of xanthenes, we report a facile route for the preparation of novel xanthenes from a one-pot reaction of aldehydes, 2,6-dihydoxynaphthalene, and 5,5-dimethylcyclohexane-1,3-dione (dimedone) in ionic liquid [bmim]BF_4 in the presence of a catalytic amount of *p*TSA.

Experimental

All of the chemicals used in the synthesis were purchased from Sigma-Aldrich and used as received. TLC was used to monitor reaction progress. Melting points were determined on a melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM ECX-400P (400 MHz) with $CDCl_3$ or DMSO-d_6 as solvent and TMS as the internal standard. IR spectra were recorded on a Perkin-Elmer FT-IR SPECTRUM-2000. The chemical shift values are recorded on the δ scale and the coupling constants (*J*) are in hertz. Mass spectra were recorded on a JEOL-AccuTOF JMS-T100 mass spectrometer having a DART source.

General procedure for the synthesis of 3-hydroxy-12-aryl-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (IIa–IIk)

A mixture of aldehyde (1 mmol), 2,6-dihydroxynaphthalene (1 mmol), dimedone (1.1 mmol), and *p*TSA (2 mol %) was placed into a 50 mL round-bottomed flask containing 0.5 mL of [bmim]BF_4. The mixture was stirred at 60 °C for an appropriate time as mentioned in Table 2. After completion of the reaction as monitored by TLC, the mixture was allowed to cool to room temperature and quenched with water (~10 mL). The precipitate formed was collected by filtration pump, washed with ethanol, and dried to obtain pure xanthen-11-one derivatives. The products were characterized by IR, ^1H NMR, ^{13}C NMR, and mass spectroscopy.

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S. Yadav, B. Nand, and J.M. Khurana. Department of Chemistry, University of Delhi, Delhi 110007, India.

Corresponding author: Jitender M. Khurana (e-mail: jmkhurana1@yahoo.co.in).

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Spectral data

12-(4-Chlorophenyl)-3-hydroxy-9,9-dimethyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one (IIa)

Colorless solid; yield 93%; mp 250–252 °C. IR (KBr, cm^{-1}) υ_{max}: 3101, 2963, 1617, 1588, 1489, 1388, 1223, 1212, 1162. δ_H (400 MHz, DMSO-d_6): 9.65 (s, 1H, OH), 7.76 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.60 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.26–7.24 (m, 1H, Ar-H), 7.21–7.14 (m, 4H, Ar-H), 7.06–7.05 (m, 1H, Ar-H), 6.99–6.96 (m, 1H, Ar-H), 5.43 (s, 2H, CH), 2.58 (d, *J* = 17.4 Hz, 1H, $CH_a.H_bCMe_2$), 2.43 (d, *J* = 11.9 Hz, 1H, $CH_a.H_bCMe_2$), 2.24 (d, *J* = 16.3 Hz, 1H, $CH_a.H_bCO$), 2.03 (d, *J* = 20.0 Hz, 1H, $CH_a.H_bCO$), 0.96 (s, 3H, CH_3), 0.78 (s, 3H, CH_3). δ_C (100 MHz, DMSO-d_6): 206.68, 196.03, 164.21, 154.72, 145.13, 144.04, 132.83, 130.73, 129.97, 128.14, 127.50, 124.82, 124.55, 119.43, 117.34, 116.83, 112.63, 110.04, 50.12, 33.72, 31.93, 30.73, 28.85, 26.24. MS (ESI) *m*/*z* calcd.: 404.12; found: 405.21 [M$^+$+H]. Anal. calcd. for $C_{25}H_{21}ClO_3$: C, 74.16; H, 5.23; Cl, 8.76%; found: C, 74.10; H, 5.18; Cl, 8.72%.

12-(4-Bromophenyl)-3-hydroxy-9,9-dimethyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one (IIb)

Colorless solid; yield 90%; mp 208–210 °C. IR (KBr, cm^{-1}) υ_{max}: 3093, 2962, 2771, 1589, 1484, 1391, 1234, 1221, 1163, 1010. δ_H (400 MHz, DMSO-d_6): 9.73 (s, 1H, OH), 7.82 (d, *J* = 9.5 Hz, 1H, Ar-H), 7.67 (d, *J* = 9.5 Hz, 1H, Ar-H), 7.37–7.33 (m, 3H, Ar-H), 7.20 (d, *J* = 8.04 Hz, 2H, Ar-H), 7.13–7.10 (m, 1H, Ar-H), 7.05–7.02 (m, 1H, Ar-H), 5.48 (s, 1H, CH), 2.64 (d, *J* = 18.3 Hz, 1H, $CH_a.H_bCMe_2$), 2.55–2.51 (m, 1H, $CH_a.H_bCMe_2$), 2.31 (d, *J* = 16.0 Hz, 1H, $CH_a.H_bCO$), 2.12–2.07 (m, 1H, $CH_a.H_bCO$), 1.03 (s, 3H, CH_3), 0.85 (s, 3H, CH_3). δ_C (100 MHz, DMSO-d_6): 195.96, 164.14, 154.70, 145.07, 144.43, 132.79, 131.02, 130.77, 130.34, 127.48, 124.78, 124.51, 119.40, 119.23, 117.30, 116.73, 112.53, 110.01, 50.08, 33.78, 31.91, 28.83, 28.64, 26.48, 26.23. MS (ESI) *m*/*z* calcd.: 448.07; found: 449.33 [M$^+$+H], 451.14 [(M$^+$+H)+2]. Anal. calcd. for $C_{25}H_{21}BrO_3$: C, 66.82; H, 4.71; Br, 17.78%; found: C, 66.74; H, 4.66; Br, 17.70%.

3-Hydroxy-9,9-dimethyl-12-(4-trifluoromethyl-phenyl)-8,9,10, 12-tetrahydro-benzo[a]xanthen-11-one (IIc)

Colorless solid; yield 90%; mp 245–247 °C. IR (KBr, cm^{-1}) υ_{max}: 3129, 3073, 2960, 1622, 1591, 1419, 1388, 1320, 1216, 1136. δ_H (400 MHz, DMSO-d_6): 9.74 (s, 1H, OH), 7.75 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.61 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.45–7.39 (m, 4H, Ar-H), 7.27 (d, *J* = 9.5 Hz, 1H, Ar-H), 7.05–7.04 (m, 1H, Ar-H), 6.98–6.96 (m, 1H, Ar-H), 5.51 (s, 1H, CH), 2.57 (d, *J* = 16.0 Hz, 1H, $CH_a.H_bCMe_2$), 2.44–2.41 (m, 1H, $CH_a.H_bCMe_2$), 2.25–2.18 (m, 1H, $CH_a.H_bCO$), 2.03–1.98 (m, 1H, $CH_a.H_bCO$), 0.94 (s, 3H, CH_3), 0.75 (s, 3H, CH_3). δ_C (100 MHz, DMSO-d_6): 196.27, 164.66, 154.86, 149.65, 145.24, 132.96, 129.10, 128.30, 127.80, 126.83, 125.66, 125.21, 124.85, 124.63, 119.64, 117.53, 116.58, 112.43, 110.22, 50.17, 40.12, 34.42, 32.05, 28.91, 26.36. MS (ESI) *m*/*z* calcd.: 438.14; found: 439.21 [M$^+$+H]. Anal. calcd. for $C_{26}H_{21}F_3O_3$: C, 71.23; H, 4.83; F, 13.00%; found: C, 71.19; H, 4.78; F, 12.97%.

12-(3-Bromophenyl)-3-hydroxy-9,9-dimethyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one (IId)

Colorless solid; yield 89%; mp 203–205 °C. IR (KBr, cm^{-1}) υ_{max}: 3344, 2926, 1654, 1623, 1517, 1376, 1289, 1226. δ_H (400 MHz, DMSO-d_6): 9.76 (s, 1H, OH), 7.84 (d, *J* = 9.5 Hz, 1H, Ar-H), 7.66 (d, *J* = 9.5 Hz, 1H, Ar-H), 7.43–7.41 (m, 1H, Ar-H), 7.31 (d, *J* = 10.2 Hz, 1H, Ar-H), 7.23–7.17 (m, 2H, Ar-H), 7.12–7.08 (m, 2H, Ar-H), 7.04–7.01 (m, 1H, Ar-H), 5.47 (s, 1H, CH), 2.66–2.51 (m, 2H, CH_2CMe_2), 2.29 (d, *J* = 16.1 Hz, 1H, $CH_a.H_bCO$), 2.08 (d, *J* = 15.3 Hz, 1H, $CH_a.H_bCO$), 1.01 (s, 3H, CH_3), 0.82 (s, 3H, CH_3). δ_C (100 MHz, DMSO-d_6): 195.99, 164.37, 154.76, 147.65, 145.14, 132.81, 130.72, 130.41, 129.18, 127.59, 127.19, 124.83, 124.50, 121.41, 119.49, 117.32, 116.57, 112.49, 110.04, 50.07, 33.94, 31.96, 30.72, 28.80, 26.16. MS (ESI) *m*/*z* calcd.: 448.07; found: 449.14 [M$^+$+H], 451.13 [(M$^+$+H)+2]. Anal. calcd. for $C_{25}H_{21}BrO_3$: C, 66.82; H, 4.71; Br, 17.78%; found: C, 66.76; H, 4.65; Br, 17.72%.

12-(2,4-Dichlorophenyl)-3-hydroxy-9,9-dimethyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one (IIe)

Yellow solid; yield 90%; mp 175 °C. IR (KBr, cm^{-1}) υ_{max}: 3399, 2929, 1645, 1595, 1468, 1378, 1233, 1214, 1159. δ_H (400 MHz, DMSO-d_6): 9.77 (s, 1H, OH), 7.85 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.65 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.41 (s, 1H, Ar-H), 7.28–7.22 (m, 3H, Ar-H), 7.10–7.09 (m, 1H, Ar-H), 7.03–6.99 (m, 1H, Ar-H), 5.68 (s, 1H, CH), 2.66 and 2.51 (AB system, *J* = 17.5 Hz, 2H, $CH_a.H_bCMe_2$), 2.46–2.45 (m, 1H, $CH_a.H_bCO$), 2.28 (d, *J* = 16.0 Hz, 1H, $CH_a.H_bCO$), 1.02 (s, 3H, CH_3), 0.85 (s, 3H, CH_3). δ_C (100 MHz, DMSO-d_6): 206.82, 195.95, 164.59, 154.76, 145.38, 141.21, 132.89, 132.79, 131.70, 128.96, 127.91, 127.59, 124.88, 124.51, 119.39, 117.45, 110.29, 79.24, 50.20, 40.43, 31.87, 30.78, 28.95, 26.25. MS (ESI) *m*/*z* calcd.: 438.08; found: 439.15 [M$^+$+H], 441.15 [(M$^+$+H)+2]. Anal. calcd. for $C_{25}H_{20}Cl_2O_3$: C, 68.35; H, 4.59; Cl, 16.14%; found: C, 68.32; H, 4.53; Cl, 16.08%.

3-Hydroxy-9,9-dimethyl-12-(4-methoxyphenyl)-8,9,10, 12-tetrahydro-benzo[a]xanthen-11-one (IIf)

Colorless solid; yield 88%; mp 238–240 °C. IR (KBr, cm^{-1}) υ_{max}: 3062, 2962, 1621, 1589, 1508, 1391, 1249, 1222, 1034. δ_H (400 MHz, DMSO-d_6): 9.61 (s, 1H, OH), 7.79 (d, *J* = 9.5 Hz, 1H, Ar-H), 7.58 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.24 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.07–7.03 (m, 3H, Ar-H), 6.98–6.95 (m, 1H, Ar-H), 6.89 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.36 (s, 1H, CH), 3.26 (s, 3H, OCH_3), 2.58 (d, *J* = 16.4 Hz, 1H, $CH_a.H_bCMe_2$), 2.44–2.42 (m, 2H, CH_2), 2.23 (d, *J* = 16.0 Hz, 1H, CH_2CO), 0.97 (s, 3H, CH_3), 0.79 (s, 3H, CH_3). δ_C (100 MHz, DMSO-d_6): 195.87, 163.80, 154.58, 145.02, 142.18, 135.12, 132.71, 128.66, 127.96, 127.08, 124.86, 124.65, 119.21, 117.55, 117.26, 113.08, 109.89, 50.12, 40.28, 33.76, 31.89, 28.88, 26.23, 20.49. MS (ESI) *m*/*z* calcd.: 400.17; found: 401.21 [M$^+$+H]. Anal. calcd for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04; found: C, 77.92; H, 5.99%.

12-(3,4-Dimethoxyphenyl)-3-hydroxy–9,9-dimethyl-8,9,10, 12-tetrahydro-benzo[a]xanthen-11-one (IIg)

Yellow solid; yield 91%; mp 260–265 °C. IR (KBr, cm^{-1}) υ_{max}: 3296, 2956, 1628, 1589, 1520, 1381, 1265, 1225, 1140, 1028. δ_H (400 MHz, DMSO-d_6): 9.67 (s, 1H, OH), 7.91 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.62 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.28 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.09–7.08 (m, 1H, Ar-H), 7.04–7.01 (m, 1H, Ar-H), 6.90–6.89 (m, 1H, Ar-H), 6.69–6.67 (m, 1H, Ar-H), 6.63–6.61 (m, 1H, Ar-H), 5.40 (s, 1H, CH), 3.61 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 2.62 (d, *J* = 17.6 Hz, 1H, $CH_a.H_bCMe_2$), 2.51 (d, *J* = 16.8 Hz, 1H, $CH_a.H_bCMe_2$), 2.28 (d, *J* = 16.1 Hz, 1H, $CH_a.H_bCO$), 2.08 (d, *J* = 16.0 Hz, 1H, $CH_a.H_bCO$), 1.01 (s, 3H, CH_3), 0.85 (s, 3H, CH_3). δ_C (100 MHz, DMSO-d_6): 196.05, 163.85, 154.60, 148.13, 147.05, 145.04, 137.71, 132.73, 127.05, 125.06, 124.76, 120.09, 119.22, 117.67, 117.27, 113.18, 112.22, 111.46, 109.89, 55.46, 55.30, 50.15, 33.58, 31.91, 28.92, 26.18. MS (ESI) *m*/*z* calcd.: 430.18; found: 431.25 [M$^+$+H]. Anal. calcd. for $C_{27}H_{26}O_5$: C, 75.33; H, 6.09%; found: C, 75.30; H, 6.02%.

3-Hydroxy-9,9-dimethyl-12-(2-methylphenyl)-8,9,10, 12-tetrahydrobenzo[a]xanthen-11-one (IIh)

Colorless solid; yield 90%; mp 245–248 °C. IR (KBr, cm^{-1}) υ_{max}: 3183, 2955, 1648, 1617, 1592, 1458, 1382, 1229, 1213, 1148. δ_H (400 MHz, DMSO-d_6): 9.63 (s, 1H, OH), 7.58–7.56 (m, 2H, Ar-H), 7.23 (d, *J* = 8.0 Hz, 1H, Ar), 7.03–6.96 (m, 3H, Ar-H), 6.86–6.82 (m, 3H, Ar-H), 5.44 (s, 1H, CH), 2.73 (s, 3H, CH_3), 2.57 (d, *J* = 16.8 Hz, 1H, $CH_a.H_bCMe_2$), 2.44–2.41 (m, 1H, $CH_a.H_bCMe_2$), 2.21 (d, *J* = 16.1 Hz, 1H, $CH_a.H_bCO$), 2.00 (d, *J* = 15.4 Hz, 1H, $CH_a.H_bCO$), 0.95 (s, 3H, CH_3), 0.76 (s, 3H, CH_3). δ_C (100 MHz, DMSO-d_6): 196.21, 163.91, 154.60, 145.20, 143.73, 134.59, 132.66, 130.45, 129.24, 127.17, 126.11, 126.00, 124.82, 124.35, 119.20, 118.38, 117.34, 113.63, 110.06, 50.24, 40.43, 31.74, 31.15, 28.83, 26.12, 19.43. MS (ESI) *m*/*z* calcd.: 384.17; found: 385.23 [M$^+$+H]. Anal. calcd. for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29%; found: C, 81.15; H, 6.27%.

3-Hydroxy-12-(4-isopropylphenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one (IIi)

Colorless solid; yield 92%; mp 240–242 °C. IR (KBr, cm^{-1}) υ_{max}: 3163, 2957, 1624, 1591, 1382, 1225, 1152, 1031. δ_H (400 MHz, DMSO-d$_6$): 9.59 (s, 1H, OH), 7.79 (d, *J* = 9.5 Hz, 1H, Ar-H), 7.53 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.20 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.06–7.01 (m, 3H, Ar-H), 6.95–6.89 (m, 3H, Ar-H), 5.34 (s, 1H, CH), 2.60–2.55 (m, 1H, CHMe$_2$), 2.46–2.37 (m, 2H, CH_2CMe_2), 2.17 (d, *J* = 16.0 Hz, 1H, $CH_a.H_bCO$), 1.99 (d, *J* = 16.1 Hz, 1H, $CH_a.H_bCO$), 0.94 (d, *J* = 6.6 Hz, 6H, CHMe$_2$), 0.91 (s, 3H, CH$_3$), 0.76 (s, 3H, CH$_3$). δ_C (100 MHz, DMSO-d$_6$): 196.53, 164.56, 155.23, 146.59, 145.66, 143.12, 133.34, 128.55, 127.64, 126.62, 125.45, 125.28, 119.90, 118.29, 117.92, 113.77, 110.55, 50.76, 40.92, 34.32, 33.47, 32.53, 29.37, 27.06, 24.44, 24.25. MS (ESI) *m/z* calcd.: 412.20, found: 413.26 [M$^+$+H]. Anal. calcd. for $C_{28}H_{28}O_3$: C, 81.52; H, 6.84%; found: C, 81.44; H, 6.80%.

3-Hydroxy-9,9-dimethyl-12-(1-naphthyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (IIj)

Yellow solid; yield 87%; mp 285 °C. IR (KBr, cm^{-1}) υ_{max}: 3448, 2935, 1623, 1516, 1374, 1287, 1238, 1225, 1155, 1024. δ_H (400 MHz, DMSO-d$_6$): 9.70 (s, 1H, OH), 7.81 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.67–7.59 (m, 5H, Ar-H), 7.51–7.47 (m, 1H, Ar-H), 7.34 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.26–7.23 (m, 1H, Ar-H), 7.15–7.13 (m, 1H, Ar-H), 7.05–7.04 (m, 1H, Ar-H), 6.74–6.71 (m, 1H, Ar-H), 6.20 (s, 1H, CH), 2.66 and 2.54 (AB system, *J* = 17.6 Hz, 2H, $CH_a.H_bCMe_2$), 2.24 (d, *J* = 16.1 Hz, 1H, $CH_a.H_bCO$), 1.97 (d, *J* = 16.1 Hz, 1H, $CH_a.H_bCO$), 1.00 (s, 3H, CH$_3$), 0.76 (s, 3H, CH$_3$). δ_C (100 MHz, DMSO-d$_6$): 196.19, 163.77, 154.50, 145.13, 132.71, 128.40, 127.11, 126.90, 126.11, 125.57, 125.04, 124.66, 118.99, 117.50, 110.01, 50.15, 48.62, 40.11, 31.76, 28.84, 26.15. MS (ESI) *m/z* calcd.: 420.17; found: 421.23 [M$^+$+H]. Anal. calcd. for $C_{29}H_{24}O_3$: C, 82.83; H, 5.75%; found: C, 82.78; H, 5.70%.

General procedure for the synthesis of 5,13-diaryl-2,2,10,10-tetramethyl-2,3,9,10,11,13-hexahydroxantheno[2,1-*a*]xanthene-4,12(1*H*,5*H*)-dione (IIIa–IIIk)

A mixture of aldehyde (2.0 mmol), 2,6-dihydroxynaphthalene (1.0 mmol), dimedone (2.2 mmol), and *p*TSA (5 mol%) was placed into a 50 mL round-bottomed flask containing 1 mL of [bmim]BF$_4$. The mixture was stirred at 90 °C for an appropriate time. After completion of the reaction as monitored by TLC, the mixture was allowed to cool to room temperature and quenched with water (~10 mL). The precipitate formed was collected by filtration at pump, recrystallized with chloroform, and dried to obtain pure xanthene-4,12-dione derivatives.

5,13-Bis(4-chlorophenyl)-2,2,10,10-tetramethyl-2,3,9,10,11,13-hexahydroxantheno [2,1-a]xanthene-4,12(1H,5H)-dione (IIIa)

Colorless solid; yield 92%; mp >300 °C. IR (KBr, cm^{-1}) υ_{max}: 2726, 1647, 1595, 1377, 1218, 1165, 1010. δ_H (400 MHz, CDCl$_3$): 7.84 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.27 (s, 1H, Ar-H), 7.20–7.18 (m, 5H, Ar-H), 7.10 (d, *J* = 8.0 Hz, 4H, Ar-H), 5.63 (s, 2H, CH), 2.54–2.43 (m, 4H, CH_2CMe_2), 2.27–2.16 (m, 4H, CH$_2$CO), 1.05 (s, 6H, CH$_3$), 0.92 (s, 6H, CH$_3$). δ_C (100 MHz, DMSO-d$_6$): 196.84, 164.02, 146.98, 142.63, 139.42, 132.02, 129.67, 129.31, 128.44, 124.34, 118.13, 113.49, 50.79, 41.30, 34.21, 32.26, 29.09, 27.24. MS (ESI) *m/z* calcd.: 648.18; found: 649.12 [M$^+$+H], 651.14 [(M$^+$+H)+2], 653.17 [(M$^+$+H)+4]. Anal. calcd. for $C_{40}H_{34}Cl_2O_4$: C, 73.96; H, 5.28; Cl, 10.92%; found: C, 73.91; H, 5.24; Cl, 10.85%.

5,13-Bis(4-bromophenyl)-2,2,10,10-tetramethyl-2,3,9,10,11,13-hexahydroxantheno [2,1-a]xanthene-4,12(1H,5H)-dione (IIIb)

Colorless solid; yield 91%; mp >300 °C. IR (KBr, cm^{-1}) υ_{max}: 2726, 1647, 1595, 1377, 1218, 1165, 1010. δ_H (400 MHz, CDCl$_3$): 7.84 (d, *J* = 10.5 Hz, 2H, Ar-H), 7.27–7.25 (m, 6 H, Ar-H), 7.13 (d, *J* = 8.6 Hz, 4H, Ar-H), 5.61 (s, 2H, CH), 2.51 and 2.45 (AB system, *J* = 17.7 Hz, 4H, $CH_a.H_bCMe_2$), 2.25 and 2.19 (AB system, *J* = 16.4 Hz, 4H, $CH_a.H_bCO$), 1.05 (s, 6H, CH$_3$), 0.92 (s, 6H, CH$_3$). δ_C (100 MHz, CDCl$_3$): 196.85, 164.04, 147.17, 143.58, 131.38, 130.05, 129.28, 124.33, 120.19, 118.14, 117.83, 113.38, 50.77, 41.27, 34.29, 32.26, 29.03, 27.25. MS (ESI) *m/z* calcd.: 738.08; found: 739.23 [M$^+$+H], 741.22 [(M$^+$+H)+2], 743.27 [(M$^+$+H)+4]. Anal. calcd. for $C_{40}H_{34}Br_2O_4$: C, 65.05; H, 4.64; Br, 21.64%; found: C, 64.98; H, 4.61; Br, 21.58%.

2,2,10,10-Tetramethyl-5,13-bis(4-nitrophenyl)-2,3,9,10,11,13-hexahydroxantheno [2,1-a]xanthene-4,12(1H,5H)-dione (IIIc)

Colorless solid; yield 89%; mp >300 °C. IR (KBr, cm^{-1}) υ_{max}: 3435, 2960, 1711, 1654, 1596, 1518, 1378, 1346, 1241, 1221. δ_H (400 MHz, CDCl$_3$): 8.0 (d, *J* = 8.7 Hz, 4H, Ar-H), 7.81 (d, *J* = 9.1 Hz, 2H, Ar-H), 7.46–7.42 (m, 4H, Ar-H), 7.30 (d, *J* = 9.1 Hz, 2H, Ar-H), 5.76 (s, 2H, CH), 2.54–2.45 (m, 4H, CH_2CMe_2), 2.28–2.17 (m, 4H, CH$_2$CO), 1.06 (s, 6H, CH$_3$), 0.89 (s, 6H, CH$_3$). δ_C (100 MHz, CDCl$_3$): 207.07, 196.70, 164.54, 151.52, 147.29, 146.32, 129.24, 124.47, 123.67, 118.46, 117.09, 112.60, 50.65, 41.24, 34.85, 32.25, 30.91, 29.01, 27.13. MS (ESI) *m/z* calcd.: 670.23; found: 671.33 [M$^+$+H]. Anal. calcd. for $C_{40}H_{34}N_2O_8$: C, 71.63; H, 5.11; N, 4.18%; found: C, 71.57; H, 5.06; N, 4.13%.

2,2,10,10-Tetramethyl-5,13-bis(4-(trifluoromethyl)phenyl)-2,3,9,10,11,13-hexahydroxantheno[2,1-a]xanthene-4,12(1H,5H)-dione (IIId)

Colorless solid; yield 93%; mp >300 °C. IR (KBr, cm^{-1}) υ_{max}: 2927, 1647, 1378, 1325, 1219, 1121, 1067. δ_H (400 MHz, CDCl$_3$): 7.87 (d, *J* = 9.1 Hz, 2H, Ar-H), 7.38–7.43 (m, 8H, Ar-H), 7.26 (d, *J* = 9.1 Hz, 2H, Ar-H), 5.74 (s, 2H, CH), 2.55 and 2.48 (AB system, *J* = 16.9 Hz, 4H, $CH_a.H_bCMe_2$), 2.28 and 2.22 (AB system, *J* = 16.4 Hz, 4H, $CH_a.H_bCO$), 1.08 (s, 6H, CH$_3$), 0.94 (s, 6H, CH$_3$). δ_C (100 MHz, CDCl$_3$): 196.81, 164.27, 148.34, 147.26, 129.28, 128.65, 128.21, 125.30, 124.41, 122.58, 118.28, 117.63, 113.19, 50.75, 41.29, 34.74, 32.28, 28.99, 27.29. MS (ESI) *m/z* calcd.: 716.24; found: 717.38 [M$^+$+H]. Anal. calcd. for $C_{42}H_{34}F_6O_4$: C, 70.38; H, 4.78; F, 15.90%; found: C, 70.33; H, 4.72; F, 15.86%.

2,2,10,10-Tetramethyl-5,13-bis(3-nitrophenyl)-2,3,9,10,11,13-hexahydroxantheno[2,1-a]xanthene-4,12(1H,5H)-dione (IIIe)

Colorless solid; yield 90%; mp >300 °C. IR (KBr, cm^{-1}) υ_{max}: 3425, 3097, 2960, 1642, 1594, 1528, 1409, 1349, 1220, 1165, 1011. δ_H (400 MHz, CDCl$_3$): 7.90–7.86 (m, 2H, Ar-H), 7.71–7.64 (m, 4H, Ar-H), 7.47–7.41 (m, 2H, Ar-H), 7.17–7.12 (m, 4H, Ar-H), 5.56 (s, 2H, CH), 2.35–2.27 (m, 4H, CH_2CMe_2), 2.10–1.93 (m, 4H, CH$_2$CO), 0.85 (s, 6H, CH$_3$), 0.69 (s, 6H, CH$_3$). δ_C (100 MHz, CDCl$_3$): 196.70, 164.37, 148.30, 147.38, 146.79, 134.68, 129.18, 124.52, 123.10, 121.67, 118.57, 112.83, 50.69, 41.26, 34.76, 32.31, 28.82, 27.12. MS (ESI) *m/z* calcd.: 670.23; found: 671.35 [M$^+$+H]. Anal. calcd. for $C_{40}H_{34}N_2O_8$: C, 71.63; H, 5.11; N, 4.18%; found: C, 71.55; H, 5.08; N, 4.11%.

5,13-Bis(2-chlorophenyl)-2,2,10,10-tetramethyl-2,3,9,10,11,13-hexahydroxantheno[2,1-a]xanthene-4,12(1H,5H)-dione (IIIf)

Colorless solid; yield 91%; mp >300 °C. IR (KBr, cm^{-1}) υ_{max}: 3168, 2954, 1651, 1629, 1599, 1471, 1371, 1236, 1166, 1010. δ_H (400 MHz, CDCl$_3$): 8.12 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.58 (d, *J* = 9.0 Hz, 1H, Ar-H), 7.31–7.28 (m, 1H, Ar-H), 7.23–7.18 (m, 2H, Ar-H), 7.10–7.09 (m, 2H, Ar-H), 7.08–6.97 (m, 5H, Ar-H), 5.94 (s, 2H, CH), 2.59–2.53 (m, 4H, CH_2CMe_2), 2.33–2.20 (m, 4H, CH$_2$CO), 1.13 (s, 6H, CH$_3$), 0.99 (s, 6H, CH$_3$). δ_C (100 MHz, CDCl$_3$): 212.57, 196.50, 153.01, 132.60, 130.89, 129.76, 127.49, 126.55, 125.60, 118.23, 117.10, 110.29, 50.55, 41.48, 31.83, 29.00, 26.54. MS (ESI) *m/z* calcd.: 648.18; found: 649.31 [M$^+$+H], 651.31 [(M$^+$+H)+2], 653.32 [(M$^+$+H)+4]. Anal. calcd. for $C_{40}H_{34}Cl_2O_4$: C, 73.96; H, 5.28; Cl, 10.92%; found: C, 73.89; H, 5.25; Cl, 10.87%.

5,13-Bis(4-methoxyphenyl)-2,2,10,10-tetramethyl-2,3,9,10,11,13-hexahydroxantheno[2,1-a]xanthene-4,12(1H,5H)-dione (IIIg)

Colorless solid; yield 85%. mp >300 °C. IR (KBr, cm^{-1}) υ_{max}: 2954, 1651, 1609, 1510, 1405, 1374, 1226, 1177. δ_H (400 MHz, CDCl$_3$): 7.91 (d, *J* = 9.1 Hz, 2H, Ar-H), 7.27–7.25 (m, 3H, Ar-H), 7.19–7.17 (m, 3H, Ar-H), 6.67–6.70 (m, 4H, Ar-H), 5.62 (s, 2H, CH), 3.68 (s, 6H, OCH$_3$), 2.52 and 2.45 (AB system, *J* = 17.4 Hz, 4H, $CH_a.H_bCMe_2$), 2.26 and 2.21 (AB system, *J* = 16.0 Hz, 4H, $CH_a.H_bCO$), 1.06 (s, 6H, CH$_3$), 0.94 (s, 6H, CH$_3$). δ_C (100 MHz, CDCl$_3$): 27.31, 29.01, 32.27, 33.85, 41.31, 50.87, 55.07, 113.61, 114.10, 117.92, 118.59, 124.23, 129.24, 129.42, 137.10, 147.07, 157.77, 163.68, 197.02. MS (ESI) *m/z* calcd.: 640.28; found: 641.40 [M$^+$+H]. Anal. calcd. for $C_{42}H_{40}O_6$: C, 78.73; H, 6.29%; found: C, 78.67; H, 6.26%.

Table 1. Effect of different ionic liquids and catalyst amount on the condensation of 4-chlorobenzaldehyde, 2,6-dihydroxynaphthalene, and dimedone (molar ratio 1:1:1.1).

Entry	Solvent	Temperature (°C)	Catalyst	mol%	Time (h)	Yield (**IIa**) (%)
1	[bmim]Br	60	*p*TSA	2	10	35[a]
2	[bmim]Br	120	*p*TSA	2	10	42[a]
3	[bmim]Cl	60	*p*TSA	2	10	45[a]
4	[bmim]Cl	120	*p*TSA	2	10	37[a]
5		120	*p*TSA	2	5	54[a]
6	[bmim]BF_4	60	*p*TSA	2	2	93
7	[bmim]BF_4	60			5	55[a]
8	[bmim]BF_4	60	*p*TSA	0.5	6	72
9	[bmim]BF_4	60	*p*TSA	1	5	80
10	[bmim]BF_4	60	*p*TSA	5	2	92

[a] Incomplete reaction.

Table 2. Synthesis of 3-hydroxy-12-aryl-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-ones **IIa–IIj**.

Entry	Ar (ArCHO)	Product	Time (h)	Yield (%)[a]
1	4-ClC_6H_4 (**Ia**)	**IIa**	2	93
2	4-BrC_6H_4 (**Ib**)	**IIb**	2	90
3	4-$F_3CC_6H_4$ (**Ic**)	**IIc**	1.5	90
4	3-BrC_6H_4 (**Id**)	**IId**	2	89
5	2,4-$Cl_2C_6H_3$ (**Ie**)	**IIe**	3	90
6	4-$CH_3OC_6H_4$ (**If**)	**IIf**	2	88
7	3,4-$(CH_3O)_2C_6H_3$ (**Ig**)	**IIg**	3	91
8	2-$H_3CC_6H_4$ (**Ih**)	**IIh**	2	90
9	4-$Me_2CHC_6H_4$ (**Ii**)	**IIi**	1.5	92
10	1-Naphthyl (**Ij**)	**IIj**	2.5	87

Note: Reaction conditions: aldehyde (1.0 mmol), 2,6-dihydroxynaphthalene (1.0 mmol), dimedone (1.1 mmol), *p*TSA (2 mol%), 60 °C.

[a] Isolated yields.

5,13-Bis(3,4-dimethoxyphenyl)-2,2,10,10-tetramethyl-2,3,9,10,11,13-hexahydroxantheno[2,1-a]xanthene-4,12(1H,5H)-dione (IIIh)

Yellow solid; yield 89%; mp >300 °C. IR (KBr, cm^{-1}) υ_{max}: 2957, 1647, 1593, 1513, 1464, 1377, 1266, 1219, 1141, 1027. δ_H (400 MHz, $CDCl_3$): 7.96–7.93 (m, 2H, Ar-H), 7.27 (d, *J* = 9.1 Hz, 2H, Ar-H), 6.92–6.89 (m, 2H, Ar-H), 6.72–6.61 (m, 4H, Ar-H), 5.64 (s, 2H, CH), 3.79 (s, 6H, OCH_3), 3.73 (s, 6H, OCH_3), 2.53–2.49 (m, 4H, CH_2CMe_2), 2.29–2.23 (m, 4H, CH_2CO), 1.08 (s, 6H, CH_3), 0.95 (s, 6H, CH_3). δ_C (100 MHz, $CDCl_3$): 197.12, 163.84, 148.54, 147.21, 137.45, 129.47, 124.29, 124.19, 120.47, 120.28, 118.44, 117.89, 114.06, 111.69, 110.75, 55.80, 55.64, 50.84, 41.32, 34.27, 34.13, 32.25, 29.36, 29.08, 27.17, 26.95. MS (ESI) *m*/*z* calcd.: 700.30; found: 701.45 [M^++H]. Anal. calcd. for $C_{44}H_{44}O_8$: C, 75.41; H, 6.33%; found: C, 75.35; H, 6.26%.

2,2,10,10-Tetramethyl-5,13-di(m-tolyl)-2,3,9,10,11,13-hexahydroxantheno[2,1-a]xanthene-4,12(1H,5H)-dione (IIIi)

Colorless solid; yield 91%; mp >300 °C. IR (KBr, cm^{-1}) υ_{max}: 2925, 1645, 1599, 1406, 1377, 1242, 1223, 1171, 1011. δ_H (400 MHz, $CDCl_3$): 7.95 (d, *J* = 9.2 Hz, 1H, Ar-H), 7.29–7.26 (m, 3H, Ar-H), 7.07–7.01 (m, 6H, Ar-H), 6.85–6.84 (m, 2H, Ar-H), 5.63 (s, 2H, CH), 2.54 and 2.45 (AB system, *J* = 17.4 Hz, 4H, $CH_a.H_bCMe_2$), 2.24–2.17 (m, 4H, CH_2CO), 1.06 (s, 6H, CH_3), 0.95 (s, 6H, CH_3). δ_C (100 MHz, $CDCl_3$): 196.82, 163.84, 147.13, 144.59, 137.71, 129.47, 128.95, 128.08, 127.09, 125.43, 124.25, 118.55, 117.97, 114.06, 50.88, 41.35, 34.66, 32.32, 28.95, 27.39, 21.48. MS (ESI) *m*/*z* calcd.: 608.29; found: 609.38 [M^++H]. Anal. calcd. for $C_{42}H_{40}O_4$: C, 82.86; H, 6.62%; found: C, 82.83; H, 6.58%.

Table 3. Synthesis of 5,13-diaryl-2,2,10,10-tetramethyl-2,3,9,10,11,13-hexahydroxantheno[2,1-*a*]xanthene-4,12(1*H*,5*H*)-diones **IIIa–IIIk**.

Entry	Ar (ArCHO)	Product	Time (h)	Yield (%)
1	4-ClC_6H_4 (**Ia**)	**IIIa**	2	92[a]
2	4-BrC_6H_4 (**Ib**)	**IIIb**	2.5	91[a]
3	4-$O_2NC_6H_4$ (**Ik**)	**IIIc**	3	89[a]
4	4-$F_3CC_6H_4$ (**Ic**)	**IIId**	1.5	93[a]
5	3-$O_2NC_6H_4$ (**Il**)	**IIIe**	2.5	90[a]
6	2-ClC_6H_4 (**Im**)	**IIIf**	2	91[a]
7	4-$CH_3OC_6H_4$ (**If**)	**IIIg**	3.5	85[b]
8	3,4-$(CH_3O)_2C_6H_3$ (**Ig**)	**IIIh**	3	89[b]
9	3-$H_3CC_6H_4$ (**In**)	**IIIi**	2	91[b]
10	4-$Me_2CHC_6H_4$ (**Ii**)	**IIIj**	1.5	88[b]
11	2-Naphthyl (**Ij**)	**IIIk**	1.5	90[a]

[a] Reaction of aldehyde, 2,6-dihydroxynaphthalene, and dimedone (2:1:2.2 molar ratio) at 90 °C.

[b] Reaction of aldehyde, 2,6-dihydroxynaphthalene, and dimedone (3:1:3.3 molar ratio) at 90 °C.

5,13-Bis(4-isopropylphenyl)-2,2,10,10-tetramethyl-2,3,9,10,11,13-hexahydroxantheno[2,1-a]xanthene-4,12(1H,5H)-dione (IIIj)

Colorless solid; yield 88%; mp >300 °C. IR (KBr, cm^{-1}) υ_{max}: 3423, 2960, 1669, 1652, 1598, 1405, 1377, 1243, 1221, 1165. δ_H (400 MHz, $CDCl_3$): 7.93 (d, *J* = 9.5 Hz, 2H, Ar-H), 7.26 (s, 1H, Ar-H), 7.15 (d, *J* = 8.0 Hz, 4H, Ar-H), 6.99–6.94 (m, 5H, Ar-H), 5.61 (s, 2H, CH), 2.75–2.68 (m, 2H, $CHMe_2$), 2.52 and 2.42 (AB system, *J* = 17.6 Hz, 4H, $CH_a.H_bCMe_2$), 2.26–2.17 (m, 4H, CH_2CO), 1.09 (d, *J* = 7.3 Hz, 12H, $CHMe_2$), 1.04 (s, 6H, CH_3), 0.93 (s, 6H, CH_3). δ_C (100 MHz, $CDCl_3$): 196.98, 163.79, 147.08, 146.09, 141.99, 129.42, 128.04, 126.29, 124.27, 118.65, 117.93, 114.15, 50.87, 41.33, 34.28, 33.51, 32.32, 28.88, 27.54, 23.85, 23.77. MS (ESI) *m*/*z* calcd.: 664.36; found: 665.46 [M^++H]. Anal. calcd. for $C_{46}H_{48}O_4$: C, 83.10; H, 7.28%; found: C, 83.05; H, 7.25%.

2,2,10,10-Tetramethyl-5,13-di(naphthalen-2-yl)-2,3,9,10,11,13-hexahydroxantheno[2,1-a]xanthene-4,12(1H,5H)-dione (IIIk)

Colorless solid; yield 90%; mp >300 °C. IR (KBr, cm^{-1}) υ_{max}: 3057, 2959, 1651, 1597, 1400, 1378, 1241, 1225, 1166, 1010. δ_H (400 MHz, $CDCl_3$): 8.01 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.75–7.72 (m, 4H, Ar-H), 7.69–7.62 (m, 4H, Ar-H), 7.41–7.38 (m, 3H, Ar-H), 7.36–7.34 (m, 3H, Ar-H), 7.29–7.26 (m, 2H, Ar-H), 5.84 (s, 2H, CH), 2.53 and 2.45 (AB system, *J* = 17.4 Hz, 4H, $CH_a.H_bCMe_2$), 2.24 and 2.17 (AB system, *J* = 16 Hz, 4H, $CH_a.H_bCO$), 1.04 (s, 6H, CH_3), 0.89 (s, 6H, CH_3). δ_C (100 MHz, $CDCl_3$): 196.88, 163.94, 147.23, 141.99, 133.23, 132.08, 129.52, 127.99, 127.40, 127.01, 126.54, 125.75, 125.45, 124.47, 118.25, 118.03, 113.60, 50.83, 41.32, 34.91, 32.23, 29.01, 27.29. MS (ESI) *m*/*z* calcd.: 680.29; found: 681.42 [M^++H]. Anal. calcd. for $C_{48}H_{40}O_4$: C, 84.68; H, 5.92%; found: C, 84.63; H, 5.87%.

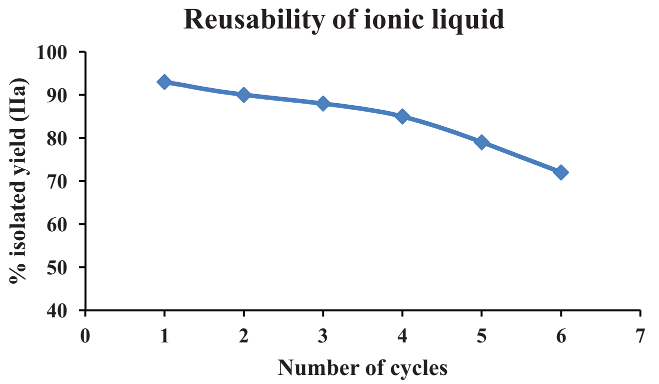
Recyclability of [bmim]BF_4

A reaction of 4-chlorobenzaldehyde (1 mmol), 2,6-dihydroxynaphthalene (1 mmol), and dimedone (1.1 mmol) was carried out in 2 mol% *p*TSA at 60 °C. The precipitate formed was collected by filtration pump, washed with water, and dried. The filtrate was concentrated under reduced pressure and dried at 100 °C to recover the ionic liquid for subsequent use.

Results and discussion

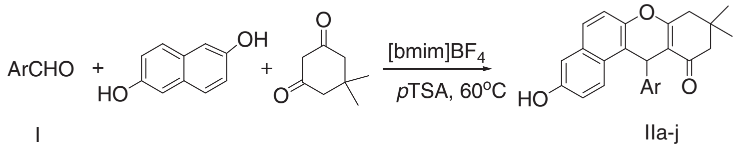
We herein report the synthesis of novel 3-hydroxy-12-aryl-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one (**IIa–IIj**) and 5,13-diaryl-2,2,10,10-tetramethyl-2,3,9,10,11,13-hexahydroxantheno[2,1-*a*]xanthene-4,12(1*H*,5*H*)-diones (**IIIa–IIIk**) by cyclocondensation of aldehydes, 2,6-dihydroxynaphthalene, and 5,5-dimethylcyclohexane-1,3-dione (dimedone) in [bmim]BF_4 in the presence of *p*TSA as catalyst. The initial reactions of 4-chlorobenzaldehyde (1.0 mmol) (**Ia**), 2,6-dihydroxynaphthalene (1.0 mmol), and dimedone (1.1 mmol) were attempted in different ionic liquids in the presence of *p*TSA to identify the most suitable ionic liquid. Reactions carried out in [bmim]Br and [bmim]Cl using 2 mol% *p*TSA at varied temperatures were incomplete even after 10 h but yielded a new product, 12-(4-chlorophenyl)-2-hydroxy-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (**IIa**). The reaction was then attempted under solvent-free conditions by heating the components at 120 °C. The reaction was incomplete after 5 h and yielded only 54% of **IIa** after workup. The reaction performed in [bmim]BF_4 as reaction medium in the presence of 2 mol% *p*TSA at 60 °C resulted in completion of the reaction in 2 h with the formation of **IIa** in 93% yield. The optimum amount of *p*TSA was observed to be 2 mol%. A lower amount of catalyst affected the yield of the product, while a higher concentration had no effect on the isolated yield. All of these results are summarized in Table 1.

Fig. 1. Reusability of [bmim]BF_4 and the effect on isolated yields of **IIa**.

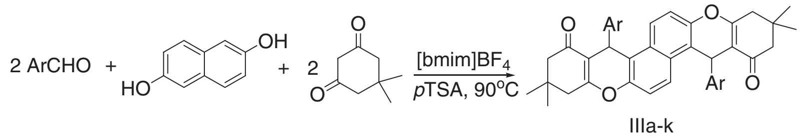


Having optimized the reaction conditions, a whole range of electronically divergent aromatic aldehydes were then exploited to successfully synthesize a series of xanthene derivatives in quantitative yields (eq. 1; Table 2):

(1)



(2)



Continuing our endeavours to form bis-condensation products harnessing the other phenolic –OH,[30] we focused our efforts on the formation of novel bis-condensation products by executing the reaction of 2,6-dihydroxynaphthalene with double molar ratios of aldehydes and dimedone under varied reaction conditions. The reaction between 4-chlorobenzaldehyde (2.0 mmol), 2,6-dihydroxynaphthalene (1.0 mmol), and dimedone (2.2 mmol) resulted in the formation of bis-condensed product 5,13-bis(4-chlorophenyl)-2,2,10,10-tetramethyl-2,3,9,10,11,13-hexahydroxantheno[2,1-*a*]xanthene-4,12(1*H*,5*H*)-dione **IIIa** in [bmim]BF_4 in the presence of 5 mol% *p*TSA at 90 °C. A variety of novel bis-condensed products were synthesized subsequently in high yields under the above conditions by changing the aromatic aldehydes (eq. 2; Table 3):

The reactions were complete in 1.5–3.5 h. It was noticed that the reactions with electron-deficient aldehydes gave the corresponding bis-products when the molar concentrations of aldehyde and dimedone were doubled but electron-rich aldehydes demanded higher concentrations (1:3:3) to afford the desired products.

The recyclability of the ionic liquid was also investigated for the synthesis of product **IIa**. The recovered ionic liquid gave comparable yields of 90%, 88%, and 85% in the second, third, and fourth cycles, respectively. However, the yields went down to 79% and 72% in the fifth and sixth cycles, respectively, as depicted in Fig. 1.

Conclusions

In conclusion, we have reported an efficient and convenient method for the synthesis of a new series of 3-hydroxy-12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one derivatives and 5,13-diaryl-2,2,10,10-tetramethyl-2,3,9,10,11,13-hexahydroxantheno [2,1-*a*]xanthene-4,12(1*H*,5*H*)-diones synthesized via condensation of 2,6-dihydroxynaphthalene, aromatic aldehydes, and dimedone in high yields using *p*TSA as a catalyst and [bmim]BF_4 as the reaction medium. Our method avoids the use of expensive reagents and harsh reaction conditions and is eco-friendly.

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