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A study for the synthesis of dibenzo [*a,j*] xanthenes and 1-amidoalkyl 2-naphthols catalyzed by [Hmim][HSO_4] as a green, efficient and reusable catalyst under solvent-free conditions

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ABSTRACT

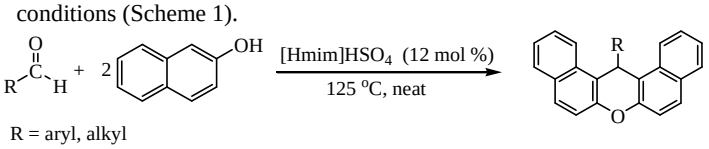
A convenient and efficient procedure for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthenes by condensation of 2-naphthol and aldehydes in the presence of Methylimidazolium hydrogensulfate, as a Brönsted acidic ionic liquid ([Hmim]HSO_4), is described. Both aromatic and aliphatic aldehydes reacted easily to afford the corresponding 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthenes in good yields under solvent-free conditions. Moreover, the synthesis of 1-amidoalkyl 2-naphthols is studied by condensation of aromatic aldehydes with amides or urea and 2-naphthol in the presence of [Hmim]HSO_4. Using solvent-free conditions, non-toxic and inexpensive materials, simple and clean work-up, short reaction times and high yields of the products are the advantages of this method.

Keywords: Methylimidazolium hydrogen sulfate, Dibenzoxanthene, Amidoalkyl naphthols, 2-Naphthol, Aldehyde.

1. Introduction

Recently, using ionic liquids (ILs) is increasing with a very fast rate because of their beneficial properties such as undetectable vapor pressure, non-inflammability, wide liquid range, reusability and high thermal stability [1-2]. A subdivision of ILs is protic ionic liquids (PILs), which are produced through the combination of a Brönsted acid and Brönsted base [3]. These acidic ionic liquids have widely been applied in electrochemistry, synthesis of nanostructure materials, reaction media and catalyst. Furthermore, Brönsted acidic ionic liquids can be designed to replace traditional mineral liquid acids such as sulfuric acid and hydrochloric acid in organic synthesis. Although, there are various Brönsted acidic ionic liquids applied in organic synthesis [3], the majority of these ionic liquids are synthesized with a time-consuming and expensive procedure. Methyl imidazolium hydrogen sulfate ([Hmim][HSO_4]) has easily been synthesized and used as an efficient, inexpensive and reusable catalyst in organic synthesis [4-6]. Moreover, the present ionic liquid is halogen free and because of less carbon numbers, this ionic liquid has less toxicity [7]. Therefore, [Hmim][HSO_4] can be introduced as a green ionic liquid. Xanthenes, especially benzoxanthens, are important intermediates in organic synthesis due to their wide range of biological and therapeutic properties such as antibacterial [8], antiviral [9] and anti-inflammatory activities [10]. Moreover, these heterocyclic compounds are used as sensitizers in photodynamic therapy for destroying the tumor cells [11], leuco-dyes in laser technology [12], antagonists of the paralyzing action of zoxazolamine [13], pH-sensitive fluorescent materials for visualization of biomolecules [14] and in the laser technology [15].The reported methods for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthenes involve the mixing of 2-naphthol with aldehydes in the presence of an acidic catalyst. A number of Brönsted and Lewis acidic catalysts such as *p*-TSA [16], LiBr [17], Amberlyst-15 [18], silica sulfuric acid [19], I_2 [20], sulfamic acid [21], $HClO_4$–SiO_2 [22], ionic liquid [23], $Yb(OTf)_3$ [24], alum [25], $BF_3.SiO_2$ [26], heteropoly acid [27], Montmorillonite K10 [28] and P_2O_5/Al_2O_3 [29] are used for the synthesis of these compounds.

Herein we report, an efficient and convenient procedure for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthenes by condensation of 2-naphthol with aldehydes in the presence of catalytic amount of methylimidazolium hydrogen sulfate as a green and reusable Brönsted acidic ionic liquid under solvent-free conditions (Scheme 1).



R = aryl, alkyl

Scheme 1. An efficient and convenient procedure for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[a,j]xanthenes.

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2. Experimental

All reagents were purchased from Merck and Aldrich and used without further purification. [Hmim]HSO_4 was synthesized according to the previous works [4-6]. All yields refer to the isolated products after purification. The products were characterized by comparison with authentic samples and by spectroscopic data (IR, ^{1}HNMR, ^{13}C NMR spectra and melting point). All melting points were taken on a Gallenkamp melting apparatus and were uncorrected. IR spectra were recorded on a JASCO FT/IR-680 PLUS spectrometer. ^{1}H NMR spectra were recorded on a Bruker 400 MHz.

2.1. General procedure for the synthesis of aryl or alkyl-14H-dibenzo [a,j] xanthenes.

A mixture of 2-naphthol (10 mmol), aldehyde (5 mmol), and [Hmim]HSO_4 (0.11 g, 12 mol %) was added to a round-bottomed flask. The reaction mixture was placed in an oil bath at 125 ºC and stirred for the specified time. The reaction was followed by TLC (EtOAc/cyclohexane, 20:80). After completion, the reaction mixture was cooled to room temperature and then water was added to the reaction mixture and stirred for 5–10 min. The crystalline product was collected by filtration, washed with ice-cold water (15 ml) and then recrystallized from ethanol to afford the pure product.

The spectral data of some dibenzo [a,j] xanthenes:

Table 2, entry 2: ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ = 6.50 (s, 1 H), 7.30 (d, *J* = 8.5 Hz, 2 H), 7.42-7.48 (m, 4 H), 7.52 (d, *J* = 8.9 Hz, 2 H), 7.63 (t, *J* = 7.2 Hz, 2 H), 7.85 (d, *J* = 8.9 Hz, 2 H), 7.88 (d, *J* = 8.0 Hz, 2 H), 8.36 (d, *J* = 8.5 Hz, 2 H). IR (KBr) cm^{-1}: 3068, 2905, 1620, 1590, 1481, 1456, 1430, 1400, 1238, 1072, 1008, 961, 826, 808, 739.

Table 2, entry 3: ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ = 6.51 (s, 1 H), 7.15 (d, *J* = 8.5 Hz, 2 H), 7.45-7.49 (m, 4 H), 7.52 (d, *J* = 8.9 Hz, 2 H), 7.61 (t, *J* = 7.3 Hz, 2 H), 7.85 (d, *J* = 8.9 Hz, 2 H), 7.88 (d, *J* = 8.0 Hz, 2 H), 8.36 (d, *J* = 8.5 Hz, 2 H). IR (KBr) cm^{-1}: 3025, 1620, 1590, 1483, 1457, 1400, 1239, 1082, 1012, 958, 831, 806, 740.

Table 2, entry 4: ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ = 6.85 (s, 1 H), 6.93-6.99 (m, 2 H), 7.30 (d, *J* = 7.1 Hz, 1 H), 7.44 (d, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 7.54 (d, *J* = 8.8 Hz, 2 H), 7.67 (t, *J* = 7.5 Hz, 2 H), 7.84 (d, *J* = 8.9 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 8.79 (d, *J* = 8.5 Hz, 2 H). IR (KBr) cm^{-1}: 3056, 1620, 1592, 1514, 1459, 1429, 1402, 1254, 1032, 964, 828, 810, 749, 739.

Table 2, entry 5: ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ = 6.51 (s, 1 H), 7.02 (d, *J* = 8.4 Hz, 1 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 7.46-7.50 (m, 4 H), 7.53 (d, *J* = 8.9 Hz, 2 H), 7.65 (t, *J* = 7.1 Hz, 2 H), 7.85 (d, *J* = 8.9 Hz, 2 H), 7.89 (d, *J* = 8.0 Hz, 2 H), 8.37 (d, *J* = 8.5 Hz, 2 H). IR (KBr) cm^{-1}: 3067, 1621, 1590, 1572, 1514, 1455, 1430, 1397, 1245, 1065, 959, 811, 755, 746.

Table 2, entry 6: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.03 (s, 1 H), 7.11-7.21 (m, 2 H), 7.39-7.47 (m, 4 H), 7.55 (t, *J* = 8.0 Hz, 2 H), 7.65-7.69 (m, 1 H), 7.95 (m, 4 H), 8.48 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 36.79, 112.77, 118.16, 124.26, 126.33, 126.95, 128.81, 129.19, 130.23, 131.34, 132.79, 138.40, 150.31. IR (KBr) cm^{-1}: 3057, 1622, 1598, 1515, 1463, 1429, 1404, 1353, 1252, 1186, 1075, 973, 833, 804, 769, 735.

Table 2, entry 8: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.82 (s, 3 H), 6.55 (s, 1 H), 7.45-7.48 (m, 2 H), 7.54 (d, *J* = 8.9 Hz, 2 H), 7.61-7.64 (m, 2 H), 7.66 (d, *J* = 8.5 Hz, 2 H), 7.84 (d, *J* = 8.9 Hz, 2 H), 7.86-7.89 (m, 4 H), 8.37 (d, *J* = 8.5 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 38.53, 52.36, 116.87, 118.45, 122.86, 124.82, 128.74, 129.32, 129.64, 130.31, 131.48, 131.73, 149.12, 150.42, 167.04. IR (KBr) cm^{-1}: 3060, 2996, 2948, 1707, 1591, 1512, 1457, 1431, 1402, 1288, 1250, 1241, 1189, 1115, 958, 818, 804, 746.

Table 2, entry 9: ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ = 6.53 (s, 1 H), 7.38 (t, *J* = 7.9 Hz, 2 H), 7.45 (d, *J* = 8.9 Hz, 2 H), 7.54 (t, *J* = 7.9 Hz, 2 H), 7.61 (d, *J* = 8.3 Hz, 2 H), 7.65 (d, *J* = 8.3 Hz, 2 H), 7.76-7.79 (m, 4 H), 8.29 (d, *J* = 8.5 Hz, 2 H), 9.73 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ = 38.51, 116.54, 118.37, 122.65, 124.84, 127.42, 129.23, 129.28, 129.71, 130.37, 131.36, 131.54, 149.05, 152.02, 191.85. IR (KBr) cm^{-1}: 3055, 2829, 2741, 1691, 1600, 1591, 1572, 1514, 1457, 1431, 1402, 1251, 1240, 1215, 1170, 963, 821, 806, 743, 671.

Table 2, entry 10: ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ = 6.57 (s, 1 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 7.49 (d, *J* = 7.8 Hz, 2 H), 7.54 (d, *J* = 8.9 Hz, 2 H), 7.62-7.66 (m, 4 H), 7.87 (d, *J* = 8.9 Hz, 2 H), 7.89 (d, *J* = 8.2 Hz, 2 H), 8.31 (d, *J* = 8.50 Hz, 2 H). ^{13} C NMR (100 MHz, $CDCl_3$/DMSO-d_6) δ = 38.45, 110.74, 116.36, 118.46, 119.01, 122.51, 124.97, 127.56, 129.29, 129.46, 129.91, 131.48, 131.55, 132.81, 149.23, 150.43. IR (KBr) cm^{-1}: 3056, 2225, 1621, 1604, 1590, 1514, 1500, 1431, 1413, 1397, 1237, 1064, 954, 836, 808, 780, 738.

Table 2, entry 11: ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ = 6.60 (s, 1 H), 7.29 (t, *J* = 7.7 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 7.55 (d, *J* = 8.9 Hz, 2 H), 7.66 (t, *J* = 7.7 Hz, 2 H), 7.84-7.88 (m, 6 H), 8.33 (d, *J* = 8.5 Hz, 2 H), 8.47 (s, 1 H). IR (KBr) cm^{-1}: 3080, 1621, 1592, 1529, 1458, 1430, 1401, 1347, 1251, 1140, 1081, 964, 825, 808, 744.

Table 2, entry 12: ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ = 6.65 (s, 1 H), 7.48 (t, *J* = 7.8 Hz, 2 H), 7.55 (d, *J* = 8.9 Hz, 2 H), 7.65 (t, *J* = 7.0 Hz, 2 H), 7.72 (d, *J* = 8.8 Hz, 2 H), 7.89 (t, *J* = 7.8 Hz, 4 H), 8.04 (d, *J* = 8.8 Hz, 2 H), 8.33 (d, *J* = 8.5 Hz, 2 H). IR (KBr) cm^{-1}: 3069, 1621, 1590, 1513, 1457, 1430, 1400, 1340, 1250, 1238, 1105, 964, 851, 827, 808, 742.

Table 2, entry 13: ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ = 2.18 (s, 3 H), 6.50 (s, 1 H), 7.00 (d, *J* = 8.0 Hz, 2 H), 7.44-7.48 (m, 4 H), 7.53 (d, *J* = 8.9 Hz, 2 H), 7.63 (t, *J* = 7.0 Hz, 2 H), 7.83 (d, *J* = 8.9 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 8.44 (d, *J* = 8.5 Hz, 2 H). IR (KBr) cm^{-1}: 3019, 2901, 1620, 1590, 1508, 1457, 1429, 1401, 1247, 961, 808, 739, 609.

Table 2, entry 15: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.59 (s, 3 H), 6.42 (s, 1 H), 6.48 (d, *J* = 8.2 Hz, 1 H), 7.04 (t, *J* = 8.4 Hz, 2 H), 7.13 (d, *J* = 7.5 Hz, 1 H), 7.37 (t, *J* = 7.2 Hz, 2 H), 7.44 (d, *J* = 9.0 Hz, 2 H), 7.55 (t, *J* = 7.6 Hz, 2 H), 7.71-7.82 (m, 4 H), 8.36 (d, *J* = 8.7 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 38.17, 55.23, 111.19, 115.16, 117.40, 118.23, 121.00, 122.94, 124.45, 127.00, 128.99, 129.07, 129.50, 131.27, 131.68, 145.01, 148.96, 159.97. IR (KBr) cm^{-1}: 3070, 3015, 2961, 2934, 2899, 1603, 1593, 1581, 1514, 1486, 1457, 1431, 1401, 1271, 1252, 1241, 1051, 964, 809, 775, 745.

Table 2, entry 16: ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ = 3.66 (s, 3 H), 6.49 (s, 1 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 7.43-7.47 (m, 4 H), 7.52 (d, *J* = 8.9 Hz, 2 H), 7.63 (t, *J* = 8.1 Hz, 2 H), 7.82 (d, *J* = 8.9 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 8.43 (d, *J* = 8.5 Hz, 2 H). IR (KBr) cm^{-1}: 3072, 2833, 1591, 1457, 1430, 1399, 1248, 1177, 1027, 961, 830, 808, 741.

Table 2, entry 17: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.46 (s, 1 H), 6.68 (d, *J* = 8.4 Hz, 2 H), 7.20 (m, 4 H), 7.42 (m, 4 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 7.58 (m, 2 H), 8.39 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (100

MHz, $CDCl_3$) δ = 37.09, 113.84, 117.53, 117.99, 122.68, 124.20, 126.74, 128.71, 128.79, 129.14, 131.07, 131.41, 137.36, 148.68, 157.85. IR (KBr) cm^{-1}: 3060, 1591, 1509, 1457, 1430, 1399, 1249, 1177, 1029, 961, 830, 808, 742.

Table 2, entry 18: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.76 (s, 1 H), 6.91 (m, 1 H), 7.14 (d, *J* = 8.0 Hz, 1 H), 7.34 (m, 1 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 7.58 (t, *J* = 7.6 Hz, 2 H), 7.83 (d, *J* = 8.8 Hz, 4 H), 8.54 (d, *J* = 4.8 Hz, 1 H), 8.68 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 41.93, 116.00, 117.90, 121.23, 123.84, 123.99, 124.38, 126.92, 128.39, 129.18, 130.90, 131.92, 137.10, 147.74, 148.20, 164.70. IR (KBr) cm^{-1}: 3044, 1620, 1588, 1513, 1458, 1429, 1407, 1255, 1244, 1147, 967, 831, 805, 773, 754.

Table 2, entry 19: ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ = 0.88 (d, *J* = 6.9 Hz, 6 H), 2.33 (m, 1 H), 5.50 (d, *J* = 3.8 Hz, 1 H), 7.47 (d, *J* = 8.7 Hz, 2 H), 7.50 (d, *J* = 7.1 Hz, 2 H), 7.64 (t, *J* = 6.9 Hz, 2 H), 7.83 (d, *J* = 8.8 Hz, 2 H), 7.91 (d, *J* = 8.1 Hz, 2 H), 8.35 (d, *J* = 8.5 Hz, 2 H). IR (KBr) cm^{-1}: 3068, 2959, 1590, 1515, 1456, 1432, 1398, 1250, 1237, 955, 815,739.

2.2. General procedure for the preparation of amidoalkyl naphthols.

A mixture of aldehyde (5 mmol), 2-naphthol (5 mmol), urea or amide (6 mmol) and [Hmim][HSO_4] (0.1 g, 10 mol %) was stirred at 115°C in oil bath. The completion of the reaction was followed by TLC (ethyl acetate/cyclohexane, 25:75), after 15 minutes, the reaction mixture was cooled to room temperature, then water was added to the reaction mixture to remove the catalyst and unreacted amide. The residue was filtered and if necessary, the obtained product was recrystallized from ethanol to give the pure product.

The spectral data of some amidoalkyl naphthols:

Table 4, entry 1: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.97 (s, 3 H), 7.11-7.16 (m, 4 H), 7.20-7.25 (m, 4 H), 7.33-7.37 (m, 1 H), 7.75-7.81 (m, 3 H), 8.44 (d, *J* = 8.0 Hz, 1 H), 9.99 (s, 1 H). IR (KBr) cm^{-1}: 3400, 3246, 1639,1516, 1437, 1338, 1278, 808, 742.

Table 4, entry 2: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.90 (s, 3 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 7.23-7.33 (m, 4 H), 7.38 (t, *J* = 8.0 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.96 (d, *J* = 8.0 Hz, 1 H), 8.56 (d, *J* = 8.0 Hz, 1 H), 9.80 (s, 1 H). IR (KBr) cm^{-1}: 3419, 3065, 1656, 1514, 1439, 1334, 1271, 815, 752.

Table 4, entry 4: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.88 (s, 3 H), 7.0 (d, *J* = 8.8 Hz, 1 H), 7.12 (d, *J* = 8.0 Hz, 1 H), 7.20 (t, *J* = 9.0 Hz, 1 H), 7.27-7.34 (m, 3 H), 7.47 (t, *J* = 8.0 Hz, 1 H), 7.72 (t, *J* = 8.8 Hz, 1 H), 7.81 (t, *J* = 8.4 Hz, 2 H), 8.60 (d, *J* = 8.8 Hz, 1 H), 9.40 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ =22.60,49.58,115.7,119.4, 122.38, 122.84, 127.30, 128.39, 128.62, 129.15, 129.49, 130.14, 133.14, 133.65,135.46, 137.97, 154.44, 168.75. IR (KBr) cm^{-1}:3424, 3274, 1649, 1517, 1435, 1370, 1274, 822, 764, 741.

Table 4, entry 7: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 2.01 (s, 3 H), 7.16 (d, *J* = 7.6 Hz, 1 H), 7.21 (d, *J* = 8.8 Hz, 1 H), 7.27 (t, *J* = 7.2 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 3 H), 7.81 (t, *J* = 8.8 Hz, 3 H), 8.13 (d, *J* = 8.8 Hz, 2 H), 8.59 (d, *J* = 8.0 Hz, 1 H), 10.13 (s, 1 H). IR (KBr) cm^{-1}:3391, 3075, 1640, 1524, 1351, 1439, 1351, 1281, 853, 825, 752.

Table 4, entry 12: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.88 (s, 3 H), 3.48 (s, 3 H), 3.65 (s, 3 H), 6.73 (dd, J_1 = 8.6, J_2 = 2.8, Hz, 1 H), 6.79 (d, *J* = 8.8 Hz, 1 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 1 H), 7.24 (t, *J* = 7.6 Hz, 1 H), 7.41 (t, *J* = 7.6 Hz, 1 H), 7.67 (d, *J* = 9.2 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 8.16 (d, *J* = 8.8 Hz, 1 H), 8.33 (d, *J* = 8.4 Hz, 1 H), 9.81 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ =23.11, 44.90, 55.72, 56.38, 111.47, 112.23, 116.3, 119.09, 119.37, 122.64, 123.84, 126.28, 128.62, 128.71, 129.20, 132.13, 133.03, 151, 21, 153.23, 153.72, 168.81. IR (KBr) cm^{-1}: 3365, 3173, 3003, 2834, 1644, 1496, 1437, 1278, 1219, 1053, 1027, 820, 752.

Table 4, entry 13: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 2.0 (s, 3 H), 7.13 (d, *J* = 8.4 Hz, 1 H), 7.21 (d, *J* = 8.8 Hz, 1 H), 7.25-7.40 (m,4 H), 7.72 (d, *J* = 8.4 Hz, 2 H), 7.80 (t, *J* = 8.8 Hz, 3 H), 8.53 (d, *J* = 8.0 Hz, 1 H), 10.09 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ =23.0, 48.34, 109.26, 118.39, 118.86, 119.45, 123.03, 123.42, 127.12, 127.42, 128.89, 129.13, 130.26, 132.44, 132.67, 149.40, 153.79, 170.15. IR (KBr) cm^{-1}:3380, 3075, 2958, 2231, 1629, 1510, 1439, 1333, 1280, 1247, 819, 753.

Table 4, entry 14: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.99 (s, 3 H), 3.80 (s, 3 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 7.19-7.38 (m, 5 H), 7.75-7.87 (m, 5 H), 8.51 (d, *J* = 8.0 Hz, 1 H), 10.05 (s, 1H), ^{13}C NMR (100 MHz, DMSO-d_6) δ =23.04, 48.27, 52.44, 118.80, 118.88, 122.95, 123.60, 126.73, 126.95, 127.95, 128.93, 129.07, 129.46, 130.06, 132.72, 149.14, 153.73, 166.60, 170.07. IR (KBr) cm^{-1}:3388, 3249, 3064, 2955, 1710, 1647, 1516, 1438, 1281, 1114, 822, 746.

Table 4, entry 15: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.84 (s, 2 H), 6.93 (s, 2 H), 7.06-7.30 (m, 8 H), 7.39 (s, 1 H), 7.73-7.83 (m, 2 H), 9.96 (s, 1 H). IR (KBr) cm^{-1}: 3447, 3404, 3212, 1650, 1600, 1531, 1439, 1355, 1271, 815, 746.

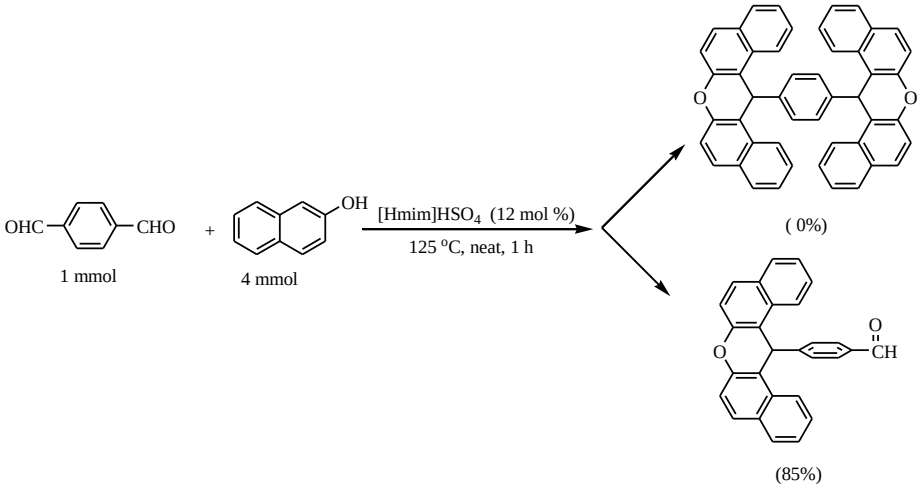
Table 2, entry 16: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.94 (s, 2 H), 6.97-7.06 (m, 2 H), 7.20 (d, *J* = 8.8 Hz, 1 H), 7.31 (t, *J* = 8.8 Hz, 1 H), 7.43-7.55 (m, 3 H), 7.78-7.86 (m, 3 H), 8.02-8.09 (m, 2 H), 10.15 (s, 1 H). IR (KBr) cm^{-1}: 3479, 3375, 3186, 1657, 1517, 1349, 1270, 810, 734.

Table 4, entry 20: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.18-7.33 (m, 4 H), 7.43-7.56 (m, 7 H), 7.77-7.87 (m, 4 H), 8.04 (d, *J* = 8.0 Hz, 1 H), 9.02 (d, *J* = 8.0 Hz, 1 H), 10.35 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 49.24, 118.29, 119.08, 120.04, 123.19, 127.32, 127.71, 128.84, 128.94, 129.19, 130.07, 131.50, 131.96, 132.69, 134.62, 141.99, 153.72, 166.38. IR (KBr) cm^{-1}: 3418, 3185, 1629, 1512, 1486, 1440, 1341, 1266, 811, 725.

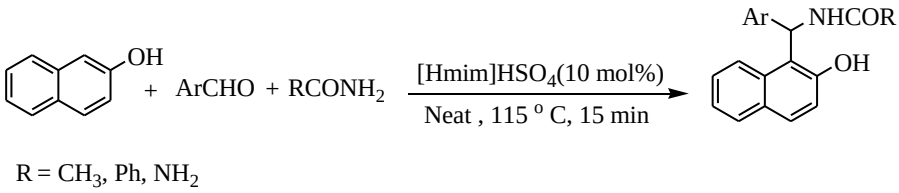
Table 4, entry 24: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.60 (s, 3 H), 3.66 (s, 3 H), 6.76 (dd, J_1 = 8.0 Hz, J_2 = 2.8 Hz, 1 H), 6.89 (d, *J* = 9.2 Hz, 1 H), 7.06 (s, 1 H), 7.17 (d, *J* = 8.8 Hz, 1 H), 7.27 (t, *J* = 8.8 Hz, 1 H), 7.41-7.51 (m, 5 H), 7.71-7.84 (m, 4 H), 8.23 (d, *J* = 8.4 Hz, 1 H), 8.83 (d, *J* = 8.8 Hz, 1 H), 10.16 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ =45.80, 55.66, 56.62, 111.19, 112.53, 116.52, 119.05, 119.24, 122.92, 123.71, 126.59, 127.63, 128.73, 128.81, 128.85, 129.41, 131.39, 131.65, 132.95, 135.07, 151.36, 153.34, 153.74, 165.47. IR (KBr) cm^{-1}: 3420, 3167, 2993, 2831, 1639, 1577, 1493, 1340, 1276, 1218, 1054, 814, 746.

3. Results and Discussion

Initially, to optimize the reaction conditions, we studied the reaction of 2-naphthol (2 mmol) and 4-chlorobenzaldehyde (1 mmol) as a simple model substrate in the presence of catalytic amount of [Hmim]HSO_4 (0.022 g, 12 mol %) under different conditions. We found that the best result was obtained when the reaction carried out at 125 °C under solvent-free conditions (Table 1, entry 7). In the



Scheme 2. The reaction between terephthaldialdehyde and excess amount of 2-naphtol.



Scheme 3. An efficient, fast, and convenient procedure for the one-pot three-component synthesis of amidoalkyl naphthol derivatives.

Table 1
Solvent effect on the reaction of 2-naphthol and 4-chlorobenzaldehyde using catalytic amount of $[Hmim]HSO_4$. [a,b]

Entry	Solvent	conditions	Time (h)	Yield (%)
1	Ethanol	Reflux	6	Trace
2	Acetonitrile	Reflux	6	0
3	Toluene	Reflux	8	0
4	1,2-Dichloroethane	Reflux	6	Trace
5	Solvent-free	rt	15	0
6	Solvent-free	100 °C	3	65
7	Solvent-free	125 °C	1	90
8 [c]	Solvent-free	125 °C	6	15

[a] The yields refer to the isolated pure products.
[b] The molar ratio of aldehyde/ 2-naphthol/ IL was 1:2:0.12.
[c] The reaction was carried out in the absence of $[Hmim]HSO_4$

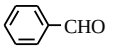
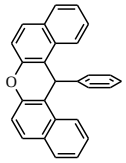
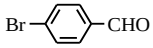
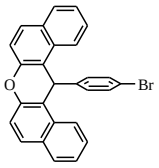
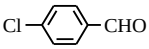
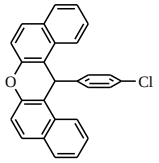
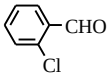
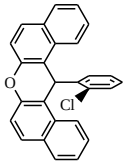
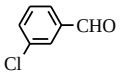
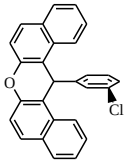
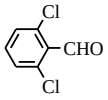
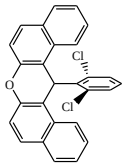
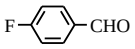
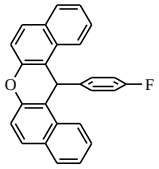
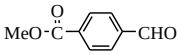
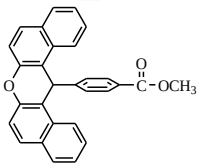
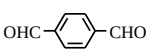
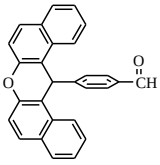
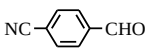
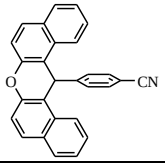
absence of catalyst, the reaction was carried out in low yield under the same conditions (Table 1, entry 8).

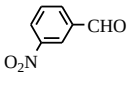
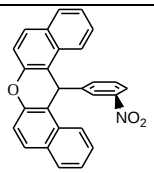
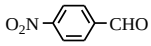
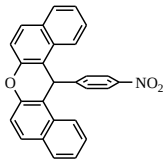
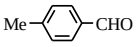
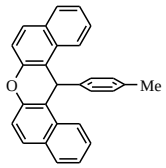
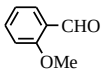
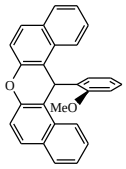
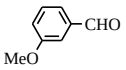
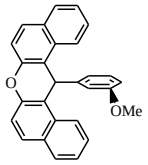
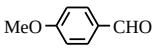
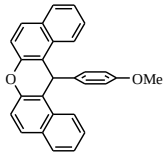
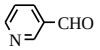
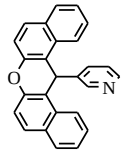
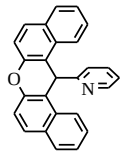
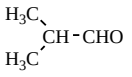
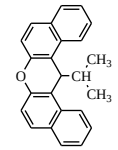
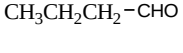
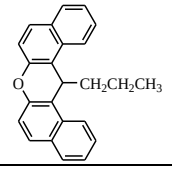
After optimization of the reaction conditions, we studied the generality of this method. Using this procedure, different kinds of aromatic and aliphatic aldehydes were treated with 2-naphtol to produce the corresponding 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes under solvent-free conditions (Table 2). Aromatic aldehydes with different functional groups were subjected to the condensation reaction and the corresponding products were synthesized in good to high yields and short reaction times. We also studied the reaction between terephthaldialdehyde (1 mmol) and 2-naphtol (4 mmol), we expected that both of the formyl groups on the aromatic ring of terephthaldialdehyde would react with 2-naphtol. However, we observed that one of the formyl groups was condensed with 2-naphtol and another group was intact due to the steric effects between *o*-hydrogens of benzene ring and the xanthene ring (Scheme 2).

As shown in Table 2, electronic effects were observed on these reactions. The substituted functional groups on the aryl aldehydes affected the yield and reaction time. In comparison with electron with-drawing groups, we found that electron-donating groups on the aryl aldehdes decreased both the reaction rate and the yield of the product (Table 2, entry 13-16). Moreover, when aliphatic aldehydes were used as the starting materials, the corresponding 14-alkyl-14*H*-dibenzo[*a*,*j*]xanthenes were obtained in good yields (Table 2, entries 19, 20). Using 12 mol% of Methylimidazolium hydrogen sulfate was sufficient to progress the reaction and an increase of the catalyst amount did not improve the yield. It is found that compounds containing 1,3-amino-oxygenated functional groups are frequently used as biologically active natural products and potent drugs such as nucleoside antibiotics and HIV protease inhibitors [30]. It is noteworthy that 1-amidoalkyl 2-naphthols can be converted to useful and important biological building blocks. For example, 1-amidoalkyl 2-naphthols can be hydrolyzed to 1-aminoalkyl 2-naphthol derivatives that these compounds show hypotensive and bradycardiac effects [31]. 1-Amidoalkyl

Table 2

Synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthenes in the presence of catalytic amount of [Hmim]HSO_4.[a]

Entry	Aldehyde	Product	Time (h)	Yield (%)	M.p. (°C)	
					Found	Reported
1			1.5	85	183-185	183-184 [26]
2			1.5	90	298-300	297-298 [26]
3			1.5	92	289-291	289-290 [26]
4			1.5	87	211-213	214-216 [26]
5			1.5	89	207-209	209-211 [26]
6			2	77	257-259	258-260 [23 b]
7			1.5	90	236-238	238-240 [29]
8			1.2	85	254-256	249-250 [28]
9 [b]			1	85	310-312	308-312 [27]
10			0.6	86	293-295	291-292 [24]

11			0.8	91	211-213	210-211 [26]
12			0.5	90	312-314	311-312 [26]
13			4	82	225-227	226-228 [29]
14			4	76	258-259	258-259 [29]
15			4	81	175-177	174-176 [23 b]
16			4	80	204-207	202-204 [29]
17			2	66	200-202	200-202 [29]
18			2	62	235-236	236-237 [29]
19			1.5	76	154-155	154-156 [29]
20			1.5	78	150-152	152-154 [29]

[a] The yields refer to the isolated pure products which were characterized from their spectral data by comparison with authentic samples. The reaction was carried out at 125°C under solvent–free conditions and the molar ratio of aldehyde/ 2-naphthol/ IL was 1:2:0.12.

[b] The molar ratio of terephthaldialdehyde/2-naphtol is 1:4.

2-naphthols can be prepared by multicomponent condensation of aldehydes, 2-naphthols and acetonitrile or various amides in the presence of Lewis or Brønsted acids such as *p*-TSA [32], montmorillonite K10 [33], $Ce(SO_4)_2$ [34], Iodine [35], $Fe(HSO_4)_3$

Table 3

Optimization of temperature and the amount of [Hmim][HSO_4] for the reaction of 2-naphtol, acetamide and 3-nitrobenzaldehyde [a]

Entry	[Hmim][HSO_4] (mol %)	Temperature (°C)	Time (min)	Yield (%) [b]
1	0	115	30	15
2	1	115	30	58
3	3	115	30	72
4	5	115	15	85
5	10	115	15	91
6	15	115	15	88
7	10	60	60	32
8	10	80	60	56
9	10	100	15	80

[a] The reactions were carried out under solvent-free conditions.
[b] The yields refer to the isolated pure products.

[36], $Sr(OTf)_2$ [37], $K_5CoW_{12}O_{40}.3H_2O$ [38], sulfamic acid [39],molybdophosphoric acid [40], cation-exchange resins [41], silicasulfuric acid [42], $HClO_4$-SiO_2 [43], ionic liquid [44], P_2O_5 [45] and Thiamine hydrochloride [46]. However, some of the reported methods suffer from certain drawback of green chemistry such as prolonged reaction time, low yield of the products, using organic solvents, the use of toxic, corrosive and expensive catalysts. Furthermore, the reusability of the catalyst is a problem. Therefore, the introduction of a clean procedure by using green and efficient catalyst with economic aspects which can be easily recycled is needed for the production of 1-amidoalkyl 2-naphthols. Herein we report an efficient, fast, and convenient procedure for the one-pot three-component synthesis of amidoalkyl naphthol derivatives from a variety of aryl aldehydes, 2-naphthol and different kinds of amides (acetamide, benzamide and urea) in the presence of [Hmim][HSO_4] as an efficient and reusable catalyst under solvent-free conditions (Scheme 3).

Initially, to optimize the reaction conditions, we studied the reaction of 2-naphthol (1 mmol), 3-nitrobenzaldehyde (1 mmol) and acetamide (1.2 mmol) as a simple model by using different quantities of [Hmim][HSO_4] at different temperatures under solvent-free conditions (Table 3). It was found that the best result was obtained when the reaction was carried out at 115°C in the presence of 10 mol% of ionic liquid (Table 3, entry 5). In the absence of catalyst, the reaction was carried out in low yield under the same conditions. Using 10 mol% of the catalyst was sufficient to progress the reaction and an increase of the catalyst amount did not improve the yield.

After optimization of the reaction conditions, we studied the generality of this method. Using this procedure, different kinds of aromatic aldehydes reacted with amides or urea and 2-naphtol to produce the corresponding 1-aminoalkyl 2-naphthol derivations under solvent-free conditions (Table 4). Aromatic aldehydes with different functional groups were subjected to the condensation reaction and the corresponding products were synthesized in good to high yields and short reaction time. The substituted functional groups on the aromatic ring of the aldehyde did not remarkably affect the yield and reaction time. In addition, we did not observe the steric effect of *ortho*-substituents on the reaction time and yield. It was noteworthy that no product of the corresponding dibenzo[*a,j*]xanthene was observed during the process of the reaction. The notable advantage of this method was the simplicity of work-up, so that ionic liquid and the excess amount of amide were washed off with water and if necessary, the residue was recrystallized from ethanol to obtain the pure product.

Table 4

Preparation of amidoalkyl naphthols using catalytic amount of [Hmim][HSO_4] under solvent-free conditions [a]

Entry	Ar	Urea/ Amide R	Yield (%)[b]	M. P.	
				Found	Reported
1	C_6H_5-	CH_3	89	239-241	245-246 [43]
2	2-ClC_6H_4-	CH_3	91	198-200	194-196 [39]
3	4-ClC_6H_4-	CH_3	92	218-220	223-225 [43]
4	2,6-$Cl_2C_6H_3$-	CH_3	90	222-224	223-224 [44]
5	4-BrC_6H_4-	CH_3	88	229-231	229-231 [44]
6	3-$O_2NC_6H_4$-	CH_3	93	246-248	241-242 [43]
7	4-$O_2NC_6H_4$-	CH_3	90	234-236	237-238 [45]
8	4-MeC_6H_4-	CH_3	87	214-216	214-216 [44]
9	2-$MeOC_6H_4$-	CH_3	85	250-252	241-242 [45]
10	3-$MeOC_6H_4$-	CH_3	88	224-226	218-220 [44]
11	4-$MeOC_6H_4$-	CH_3	86	176-178	183-185 [43]
12	2,5-$(MeO)_2C_6H_3$-	CH_3	85	233-235	228-230 [44]
13	4-NCC_6H_4-	CH_3	90	242-244	232-234 [44]
14	4-$CH_3OCOC_6H_4$-	CH_3	92	223-225	225-227 [44]
15	C_6H_5-	NH_2	78	176-178	176-178 [44]
16	3-$O_2NC_6H_4$-	NH_2	81	194-196	192-193 [44]
17	4-ClC_6H_4-	NH_2	80	170-171	168-169 [39]
18	C_6H_5-	C_6H_5	87	234-236	234-236 [44]
19	3-$MeOC_6H_4$-	C_6H_5	90	217-219	214-216 [44]
20	4-BrC_6H_4-	C_6H_5	85	186-188	182-184 [44]
21	4-ClC_6H_4-	C_6H_5	86	180-182	180-182 [44]
22	3-$O_2NC_6H_4$-	C_6H_5	87	230-232	233-235 [44]
23	4-MeC_6H_4-	C_6H_5	86	211-213	209-211 [44]
24	2,5-$(MeO)_2C_6H_3$-	C_6H_5	88	242-244	238-240 [44]

[a] The reaction was carried out at 115°C and the molar ratio of aldehyde/urea or amide/2-naphthol/IL was 1:1.2:1:0.1.
[b] The yields refer to the isolated pure products which were characterized from their spectral data by comparison with authentic samples.

To show the advantage of the present work in comparison with reported results in the literature, we compared results of methyl imidazolium hydrogen sulfate with some catalyst in the synthesis of *N*-[(3-nitro phenyl)-(2-hydroxy-naphthalen-1-yl)-methyl]-acetamide from 3-nitro benzaldehyde, acetamide and 2-naphthol. As shown in Table 5 (entries 1-8), [Hmim][HSO_4] can act as an effective catalyst with respect to reaction times, yields and simplified conditions of the obtained products.

Finally, the reusability of the present catalyst was also studied so that after each run, water was added to the reaction mixture and the product was filtered. To recycle the catalyst, all the water added for filtering and washing the product, was collected and washed with CH_2Cl_2 (3 × 10 ml) to remove organic impurities. Then water was evaporated and the catalyst was dried at 65 °C under reduced pressure for 2 h. It was found that the catalyst could be employed three times, although its activity gradually decreased Table 5 (entries 9-11).

Table 5
Synthesis of *N*-[(3-nitro phenyl)-(2-hydroxy-naphthalen-1-yl)-methyl]-cetamide via reaction of 3-nitro benzaldehyde, 2-naphthol and acetamide using different acidic catalysts.

Entry	Catalyst (mol%)	Solvent	Conditions	Time	Yield (%)	Ref.
1	*p*-TSA (10)	DCE	rt	10 h	96	32
2	*p*-TSA (10)	-	125 °C	4 h	93	32
3	Montmorillonite K10 (0.1 g)	-	125 °C	30 min	96	33
4	$K_5CoW_{12}O_{40}.3H_2O$ (1)	-	125 °C	3h	78	38
5	$K_5CoW_{12}O_{40}.3H_2O$ (1)	DCE	rt	12h	89	38
6	Sulfamic acid(0.05g)	DCE	28-30 °C	90 min	93	39
7	$HClO_4$-SiO_2 (0.6)	-	110 °C	30 min	95	43
8	Thiamine hydrochloride (10)	EtOH	80 °C	4h	88	46
9	[Hmim][HSO_4] (10) (first run)	-	115 °C	15 min	93	-
10	[Hmim][HSO_4] (10) (2nd run)	-	115 °C	15 min	88	-
11	[Hmim][HSO_4] (10) (3rd run)	-	115 °C	15 min	82	-

4. Conclusion

In summary, we introduced methyl imidazolium hydrogen sulfate ([Hmim][HSO_4]) as an inexpensive, easily available, non-corrosive and environmentally benign catalyst. A convenient and efficient procedure for the preparation of 14-aryl or alkyl-14H-dibenzo[*a*,*j*] xanthenes in good yields and short reaction times was reported in this work. Furthermor, In this work, we reported a facile and convenient method for the one-pot synthesis of amidoalkyl naphthols by using [Hmim][HSO_4] as an efficient and reusable catalyst. The notable advantages of this methodology were operational simplicity, availability of the reactants, short reaction times, high yields and easy work-up.

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