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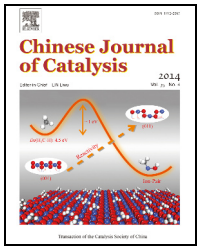

Article

Condensation of 2-naphtol with arylaldehydes using acetic acid functionalized ionic liquids as highly efficient and reusable catalysts

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ABSTRACT

An efficient solvent-free protocol for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes from the condensation of 2-naphthol with arylaldehydes, using acetic acid functionalized imidazolium salts (1-carboxymethyl-3-methylimidazolium bromide ([cmmim]Br) and 1-carboxymethy1-3-methylimidazolium tetrafluoroborate ([cmmim]BF_4) as reusable catalysts, has been developed. The turn over frequency on the catalysts is several times higher than the other previously reported catalysts. Also, thermal gravimetric analysis and powder X-ray diffraction pattern of the catalysts have been studied.

1. Introduction

Ionic liquids (based imidazolium or other organic cations) have received considerable interest as eco-friendly solvents, catalysts, and reagents in organic synthesis because of their unique properties, such as low volatility, non-flammability, high thermal stability, negligible vapor pressure, and the ability to dissolve a wide range of materials [1–9]. Among them, Brønsted acidic ionic liquids, which add the useful characteristics of solid acids and mineral liquid acids, have been designed to replace traditional mineral acids like H_2SO_4 and HCl in chemical procedures [10–25].

The 14-aryl-14H-dibenzo[a,j]xanthene group is a key structural element of many biologically active compounds, such as antibacterials [26], antivirals [27], anti-inflammatory agents [28], and in photodynamic therapy [29]. Xanthene-based compounds have also been investigated for agricultural bactericide activity and some other benzoxanthenes have found applications in industry as dyes for use in lasers [30] and as fluorescent materials for visualization of biomolecules [31]. Xanthene dyes can be extracted from soil and plants, such as Indigofera Longeracemosa [32,33]. Some methods for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes have been reported by condensing 2-naphthol with aldehydes in the presence of a protic or Lewis acid catalyst [34–45]. However, these catalytic systems suffer from some limitations, such as long reaction time, high catalyst loadings, the use of toxic solvents, or special apparatus. The search for milder and more environmentally benign conditions would therefore be of great benefit in the synthesis of these compounds.

Here, the acetic acid functionalized imidazolium salts 1-carboxymethyl-3-methylimidazolium bromide ([cmmim]Br)

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and 1-carboxymethy1-3-methylimidazolium tetrafluoroborate ([cmmim][BF_4]) as highly efficient and reusable catalysts for the preparation of 14-aryl-14H-dibenzo[a,j]xanthene derivatives was reported. Their effectiveness has been tested in the reaction of 2-naphthol with aromatic aldehydes under solvent-free conditions (Scheme 1).

2. Experimental

2.1. General

All chemicals were purchased from Merck or Fluka Chemical Companies. The products were identified by comparison of their melting points (MP) and spectral data in the literature. Acetic acid functionalized ionic liquids were prepared according to literature procedures [44,45]. The progress of each catalyzed reaction was monitored by TLC using silica gel SIL G/UV 254 plates. The ^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) were run on a Bruker Avance DPX-250 FT-NMR spectrometer (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

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

A mixture of arylaldehyde (1 mmol), 2-naphtol (2 mmol) and catalyst ([cmmim]Br or [cmmim]BF_4) (0.1 mmol, 10 mol%) was stirred at 115 °C. When the reaction was complete, as judged by TLC, H_2O (1 mL) was added to the reaction mixture, stirred and refluxed for 3 min. Then, the reaction mixture was filtered and all water in the filtrate was removed under reduced pressure to separate the catalyst from the crude product. The solid residue (crude product) was collected by filtration and recrystallized from hot ethanol (95%) to give the pure product. The recovered catalyst was washed with $CHCl_3$, dried under reduced pressure and reused for the next run.

14-phenyl-14H-dibenzo[a,j]xanthene (**1b**). IR (KBr, cm^{-1}): 3075, 1621, 1592, 1513, 1243, 1152, 803, 765; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 6.74 (s, 1H), 6.97 (t, J = 7.6 Hz, 1H), 7.14 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.62–7.66 (m, 4H), 7.91–7.93 (m, 4H), 8.70 (d, J = 8.8 Hz, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 37.0, 117.9, 118.1, 123.8, 124.9, 126.7, 127.4, 128.4, 128.8, 129.0, 129.4, 131.1, 131.3, 146.0, 148.4.

14-(2-chlorophenyl)-14H-dibenzo[a,j]xanthene (**2b**). IR (KBr, cm^{-1}): 3057, 1622, 1592, 1515, 1247, 1141, 809, 745; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 6.64 (s, 1H), 6.91–7.03 (m, 2H), 7.27 (d, J = 7.7 Hz, 2H), 7.38–7.50 (m, 5H), 7.57–7.70 (m, 2H), 7.76–7.90 (m, 4H), 8.54 (d, J = 8.4 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 34.8, 116.9, 118.2, 123.3, 124.9, 127.4, 128.5, 128.8, 129.2, 129.8, 130.2, 130.3, 130.9, 131.4, 132.0, 143.2, 148.7.

14-(3-chlorophenyl)-14H-dibenzo[a,j]xanthene (**3b**). IR (KBr, cm^{-1}): 3069, 1623, 1591, 1246, 1141, 813, 746; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 6.74 (s, 1H), 7.01 (d, J = 8.1 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.52–7.66 (m, 6H), 7.91 (d, J = 8.7 Hz, 4H), 8.67 (d, J = 8.7 Hz, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 36.5, 117.2, 118.1, 123.7, 125.1, 126.8, 127.0, 127.5, 127.9, 129.1, 129.7, 130.7, 131.1, 131.2, 133.5, 148.2, 148.5.

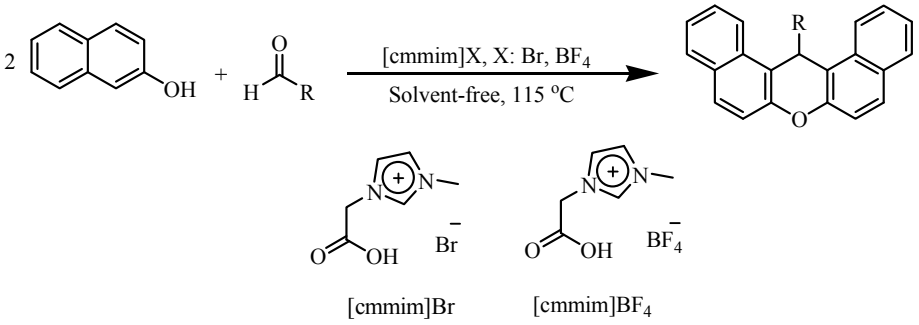
14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthene (**4b**). IR (KBr, cm^{-1}): 3076, 1622, 1593, 1515, 1254, 1153, 804, 745; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 6.76 (s, 1H), 7.18 (d, J = 6.8 Hz, 2H), 7.46–7.64 (m, 10H), 8.92 (d, J = 7.8 Hz, 2H), 8.66 (d, J = 7.6 Hz, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 36.3, 117.4, 118.1, 123.4, 123.7, 125.0, 127.4, 128.8, 129.1, 129.6, 130.1, 131.1, 131.2, 144.8, 148.4.

14-(2,3-dichlorophenyl)-14H-dibenzo[a,j]xanthene (**5b**). IR (KBr, cm^{-1}): 3058, 1633, 1594, 1255, 1141, 965, 817, 748, 676; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.86 (s, 1H), 7.11 (t, J = 1.1 Hz, 1H), 7.28 (s, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.44–7.52 (m, 4H), 7.65 (t, J = 7.9 Hz, 2H), 7.84 (t, J = 8.6 Hz, 4H), 8.69 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ 35.6, 117.7, 118.1, 123.3, 124.5, 127.1, 128.1, 128.7, 129.2, 129.9, 130.8, 131.6, 146.4, 148.9, 155,7.

14-(3-bromophenyl)-14H-dibenzo[a,j]xanthene (**6b**). IR (KBr, cm^{-1}): 3065, 1622, 1591, 1398, 1239, 1140, 810, 746; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 6.63 (s, 1H), 6.90–7.02 (m, 2H), 7.26 (d, J = 7.7 Hz, 2H), 7.37–7.49 (m, 5H), 7.58 (t, J = 7.9 Hz, 2H), 7.85–7.89 (m, 4H), 8.53 (d, J = 8.5 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 34.8, 116.9, 118.2, 123.3, 124.9, 127.4, 128.5, 128.8, 129.1, 129.8, 130.2, 130.3, 130.9, 131.4, 132.0, 143.2, 148.6.

14-(4-bromophenyl)-14H-dibenzo[a,j]xanthene (**7b**). IR (KBr, cm^{-1}): 3070, 1634, 1591, 1238, 1158, 940, 832, 740, 677; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.46 (s, 1H), 7.28–7.83 (m, 10H), 8.31 (s, 2H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ 37.4, 116.6, 118.0, 122.4, 124.4, 126.9, 128.9, 129.1, 129.9, 131.2, 131.6, 144.0, 148.6.

14-(4-fluorophenyl)-14H-dibenzo[a,j]xanthene (**8b**). IR (KBr, cm^{-1}): 3034, 1632, 1592, 1502, 1239, 1095, 813, 743; ^{1}H



Scheme 1. Synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes catalyzed by acetic acid functionalized imidazolium salts.