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N,N-Dimethylbenzimidazolium Iodide as a Green Catalyst for Cross-Coupling of Aromatic Aldehydes with Unactivated Imines

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ABSTRACT

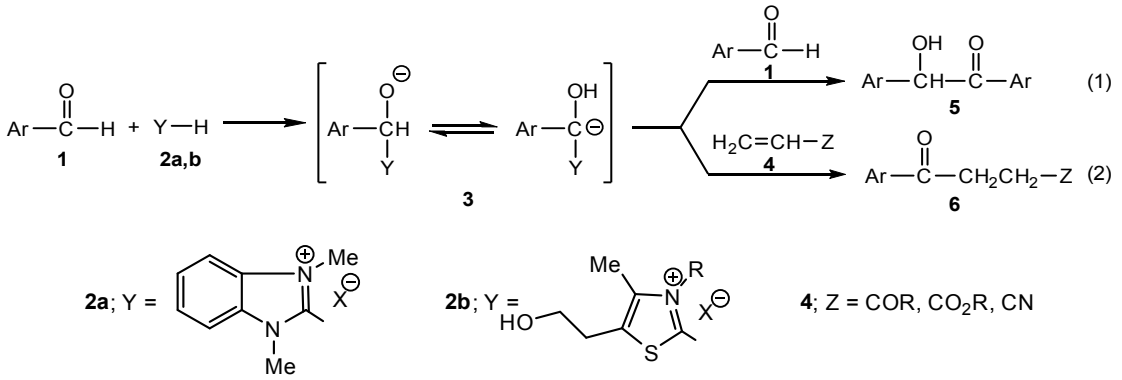
Cross-coupling of aromatic aldehydes with unactivated imines catalyzed by *N,N*-dimethylbenzimidazolium iodide in ethanolic sodium hydroxide solution gave á-amino ketones in satisfactory yields. Benzoin condensation and further oxidation of the resulted aroins also occurred as side reactions.

Key words: *N,N*-dimethylbenzimidazolium iodide, green catalyst, ross-coupling, unactivated imines, α-amino ketones.

INTRODUCTION

Acyl anion equivalents 3 resulted from treatment of aromatic aldehydes 1 with either benzimidazolium salt 2a or thiazolium salt 2b in the presence of base have been successfully utilized in benzoin condensation[1-4] (eq.1) and Stetter reaction[5-9] (eq.2), as illustrated in Scheme 1.

In addition to aromatic aldehyde 1 and electrophilic alkene 4, unactivated imines have also been employed as aroyl anion receptors.[10] As shown in Scheme 2, cross-coupling of aromatic aldehydes 1 with unactivated imines 7 catalyzed by thiazolium chloride 2b and trimethylamine in ethanol at 70 ^{o}C for 2 days provided exclusively á-amino ketones 8 in 58-85 %yields.



Scheme 1:

As part of our continuing interest in catalytic reactivity of *N,N*-dimethylbenzimidazolium iodide (2a) and its reusability, we report herein the cross-coupling of aromatic aldehydes with imines catalyzed by 2a in ethanolic sodium hydroxide solution.

EXPERIMENTAL

Chemicals were perchased from Fluka, Aldrich and Merck chemical company and used without further purification. Melting points were determined on a Sanyo Gallenkamp melting point apparatus and compared with those of known samples. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer. ^{1}H and ^{13}C NMR spectra were obtained using a VARIAN MERCURY plus (400 MHz FT NMR).

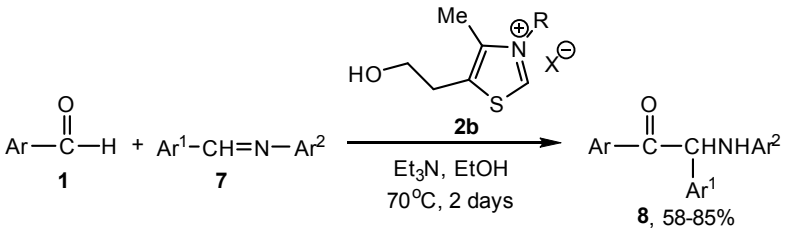
N,N-Dimethylbenzimidazolium iodide was prepared following our previously reported reference.[11]

General procedure for the preparation of unactivatedimines

Aniline (9) (9.30 g, 0.10 mol) was added to a vigorously stirred aromatic aldehyde (0.10 mol). Stirring was continued for 15 minutes. The reaction mixture was poured, with rapid stirring, into 95% ethanol (33 ml) and the resulting mixture was allowed to stand, first ten minutes at room temperature and then thirty minutes in an ice bath. The pale yellow precipitates of imine were filtered and washed with cold ethanol. The filtrate was concentrated under reduced pressure and purified by using column chromatography with 20% EtOAc:hexane as eluant to give an additional amount of the imine.

N-Benzylideneaniline (10a).Yellow crystals, mp 51 °C (lit.[12]50-52 °C), FTIR (KBr, í, cm^{-1}) n_{max} 3059, 3026, 1626, 1590, 1483, 1450, 1366, 1192, 1169, 760, 693 cm^{-1}; ^{1}H NMR($CDCl_3$, 400 MHz) d 8.45 (1H, s, C*H*), 7.90 (2H, brd, *J* = 9.6 Hz, 2- and 6-*H*), 7.46 (3H, m, 3¢-, 4- and 5¢-*H*), 7.39 (2H, t, *J* = 8.1 Hz, 3- and 5-*H*), 7.22 (3H, m, 2¢-, 4¢- and 6¢-*H*); ^{13}C NMR ($CDCl_3$) d 120.9, 125.9, 128.8, 129.1, 131.4, 152.1, 160.4.

N-(4-Methylbenzylidene)aniline (10b). Yellow crystals, mp 44-45 °C (lit.[12] 44-45 °C), FTIR (KBr, í, cm^{-1}) n_{max} 3061, 2884, 1624, 1586, 1483, 1448, 1367, 1191, 1169, 814, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) d 8.41 (1H, s, C*H*), 7.79 (2H, d, *J* = 8.1 Hz, 2- and 6-*H*), 7.38 (2H, t, *J* = 8.1 Hz, 3¢-,



Scheme 1:

and 5¢-*H*), 7.27 (2H, d, *J* = 8.0 Hz, 3- and 5-*H*), 7.21 (3H, m, 2¢-, 4¢- and 6¢-*H*), 2.41 (3H, s, ArCH_3); ^{13}C NMR($CDCl_3$) d 21.6, 120.9, 125.7, 128.8, 129.1, 129.5, 133.8, 141.8, 152.3, 160.3.

N-(4-Methoxybenzylidene)aniline (10c). Yellow crystals, mp 59-60 °C (lit.[13] 59-60 °C), FTIR (KBr, í, cm^{-1}) n_{max} 3004, 2839, 1604, 1576, 1511, 1485, 1422, 1370, 1308, 251, 1163, 1029, 833 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) d 8.38 (1H, s, C*H*), 7.85 (2H, d, *J* = 8.7 Hz, 2- and 6-*H*), 7.38 (2H, t, *J* = 8.2 Hz, 3¢-, and 5¢-*H*), 7.20 (3H, m, 2¢-, 4¢- and 6¢-*H*), 6.98 (2H, d, *J* = 8.8 Hz, 3- and 5-*H*), 3.86 (3H, s, ArOCH_3); ^{13}C NMR ($CDCl_3$) d 55.4, 114.2, 120.9, 125.5, 129.1, 129.3, 130.5, 152.4, 159.6, 162.3.

N-(4-Chlorobenzylidene)aniline (10d). Yellow crystals, mp 64-65 °C (lit.[14] 63-64 °C), FTIR (KBr, í, cm^{-1}) n_{max} 3060, 2983, 2873, 1621, 1584, 1563, 1485, 1401, 1353, 1084, 828, 761, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) d 8.40 (1H, s, C*H*), 7.83 (2H, d, *J* = 8.5 Hz, 2- and 6-*H*), 7.43 (2H, d, *J* = 8.5 Hz, 3-, and 5-*H*), 7.39 (2H, t, *J* = 7.7 Hz, 3¢- and 5¢-*H*), 7.23 (1H, t, *J* = 7.4 Hz, 4¢-*H*), 7.20 (2H, d, *J* = 7.3 Hz, 2¢- and 6¢-*H*); ^{13}C NMR ($CDCl_3$) d 120.8, 126.1, 129.1, 129.2, 129.9, 134.7, 137.3, 151.7, 158.7.

General procedure for cross-coupling of aromatic aldehydes with unactivated imines catalyzed by *N,N*-dimethylbenzimidazoliumiodide (2a) in ethanolic sodium hydroxide solution

An imine (20.00 mmol) and an aromatic aldehyde (24.00 mmol) were added to a solution of *N,N*-dimethylbenzimidazolium iodide (2a) (1.10 g, 4.00 mmol) and NaOH (0.16 g, 4.00 mmol) in ethanol (20 ml). The reaction mixture was heated at reflux for 5 hours.The pale yellow precipitates of á-amino ketone were filtered and washed with cold ethanol. The filtrate was concentrated under reduced pressure and dissolved in dichloromethane (40 ml). The dichloromethane solution was washed with water (2×20 ml), dried (anh.Na_2SO_4) and evaporated to dryness. The residue was purified by using preparative thin layer chromatography with 20% EtOAc:hexane as eluant to give an additional amount of the á-amino ketone, aroin, and aril.

N,N-dimethylbenzimidazolium iodide (2a) was recovered from the aqueous layer by evaporation to dryness and recrystallization of the brown residue with ethanol.

1,2-Diphenyl-2-(phenylamino)ethanone (11a). Yellow crystals; mp 99-100 °C (lit.[15] 98-99 °C); FTIR (KBr, í, cm^{-1}) n_{max} 3396, 3054, 3026, 1679, 1599, 1504, 1449, 1319, 1247, 1175, 748, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) d 7.80 (2H, d, *J* = 7.4 Hz, 2- and 6-*H*), 7.53 (1H, t, *J* = 7.5 Hz, 4-*H*), 7.44 (4H, m, 2¢¢-, 3-, 5- and 6¢-*H*), 7.27 (2H, t, *J* = 7.7 Hz, 3¢¢- and 5¢¢-*H*), 7.21 (1H, t, *J* = 7.3 Hz, 4¢¢-*H*), 7.13 (2H, t, *J* = 7.2 Hz, 3¢- and 5¢-*H*), 6.68 (3H, m, 2¢-,4¢- and 6¢-*H*), 6.02 (1H, d, *J* = 6.1 Hz, C*H*), 5.40 (1H, br d, *J* = 5.8 Hz, N*H*); ^{13}C NMR ($CDCl_3$) d 62.8, 113.5, 117.9, 128.1, 128.1, 128.7, 128.9, 129.0, 129.2, 133.5, 135.1, 137.8, 146.2, 197.1.

2-Phenyl-2-(phenylamino)-1-p-tolylethanone (11b). Yellow crystals; mp 134-135 °C (lit.[16] 137°C); FTIR (KBr, í, cm^{-1}) n_{max} 3396, 3051, 3028, 1676, 1603, 1504, 1430, 1319, 1249, 1175, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz)d 7.91 (2H, d, *J* = 8.1 Hz, 2- and 6-*H*), 7.44 (2H, d, *J* = 7.7 Hz, 2¢¢- and 6¢¢-*H*), 7.29-7.61 (5H, m, 3-, 3¢-, 4¢¢-, 5- and 5¢¢-*H*), 7.12 (2H, t, *J* = 7.7 Hz, 3¢- and 5¢-*H*), 6.67 (3H, m, 2¢-, 4¢- and 6¢-*H*), 6.00 (1H, d,*J* = 6.3 Hz, C*H*), 5.41 (1H, d,*J* = 5.9 Hz, N*H*), 2.36 (1H, s, ArCH_3); ^{13}C NMR ($CDCl_3$) d 21.7, 62.6, 113.5, 113.6, 117.8, 128.0, 128.1, 129.1, 129.3, 129.4, 132.6, 138.1, 144.5, 146.3, 196.6.

1-(4-Methoxyphenyl)-2-phenyl-2-(phenylamino)ethanone (11c). White crystals; mp 149-150 °C (lit.[15] 143-144 °C); FTIR (KBr, í, cm^{-1}) n_{max} 3394, 3052, 1671, 1600, 1505, 1419, 1318, 1258, 1169, 1027, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) d 8.01 (2H, d, *J* = 8.8 Hz, 2- and 6-*H*), 7.45 (2H, d, *J* = 7.6 Hz, 2¢¢- and 6¢¢-*H*), 7.27 (2H, t,*J* = 7.4 Hz, 3¢¢- and 5¢¢-*H*), 7.19 (1H, t, *J* = 7.3 Hz, 4¢¢-*H*), 7.12 (2H, t, *J* = 7.9 Hz, 3¢- and 5¢-*H*), 6.90 (2H, d, *J* = 8.8 Hz, 3- and 5-*H*), 6.67 (3H, m, 2¢-, 4¢- and 6¢-*H*), 5.98 (1H, s, C*H*), 5.42 (1H, br s, N*H*), 3.83 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) d 55.5, 62.3, 113.5, 113.6, 113.9, 117.3, 127.8, 128.0, 129.0, 129.2, 131.3, 138.3, 146.3, 163.9, 195.4.

1-(4-Chlorophenyl)-2-phenyl-2-(phenylamino)ethanone (11d). Yellow crystals; mp 153-155 °C (lit.[15] 153-154 °C); FTIR (KBr, í, cm^{-1}) n_{max} 3399, 3054, 1683, 1602, 1588, 1504, 1454,

1400, 1317, 1248, 1093, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) d 7.93 (2H, d, *J* = 8.6 Hz, 2- and 6-*H*), 7.41 (4H, m, 2¢-, 3-, 5- and 6¢¢-*H*), 7.29 (2H, t, *J* = 7.2 Hz, 3¢¢- and 5¢¢-*H*), 7.22 (1H, m, 4¢¢-*H*), 7.13 (2H, t, *J* = 7.5 Hz, 3¢- and 5¢-*H*), 6.68 (3H, m, 2¢-, 4¢- and 6¢-*H*), 5.96 (1H, d, *J* = 5.5 Hz, C*H*), 5.36 (1H, brd, *J* = 5.0 Hz, N*H*); ^{13}C NMR ($CDCl_3$) d 62.9, 113.5, 113.6, 118.0, 128.1, 128.3, 129.1, 129.2, 129.3, 130.2, 130.3, 133.4, 137.5, 140.0, 146.0, 195.9.

2-(Phenylamino)-1,2-dip-tolylethanone (11e). Yellow crystals; mp 117-118°C; FTIR (KBr, í, cm^{-1}) n_{max} 3396, 3021, 2916, 1674, 1604, 1504, 1430, 1410, 1375, 1316, 1246, 1170, 1000, 747 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) d 7.91 (2H, d, *J* = 8.1 Hz, 2- and 6-*H*), 7.33 (2H, d, *J* = 8.0 Hz, 2¢¢- and 6¢¢-*H*), 7.22 (2H, t, *J* = 8.0 Hz, 3- and 5-*H*), 7.10 (4H, m, 3¢-, 3¢¢-, 5¢- and 5¢¢-*H*), 6.66 (3H, m, 2¢-, 4¢- and 6¢-*H*), 5.97 (1H, d, *J* = 6.5 Hz, C*H*), 5.38 (1H, brd, *J* = 6.5 Hz, N*H*), 2.37-2.24 (6H, s, 2(Ar-CH_3)); ^{13}C NMR ($CDCl_3$) d 21.0, 21.7, 62.2, 113.4, 113.6, 117.8, 120.9, 128.0, 129.0, 129.2, 129.3, 129.4, 129.8, 132.4, 135.0, 137.8, 144.5, 146.3, 196.7.

1,2-Bis(4-methoxyphenyl)-2-(phenylamino) ethanone (11f). Yellow crystals; mp 108-109 °C (lit.[17] 114-115°C); FTIR (KBr, í, cm^{-1}) n_{max} 3395, 2933, 1672, 1600, 1508, 1462, 1420, 1316, 1255, 1170, 1029, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) d 8.00 (2H, d, *J* = 8.8 Hz, 2- and 6-*H*), 7.36 (2H, d, *J* = 8.7 Hz, 2¢¢- and 6¢¢-*H*), 7.12 (2H, t, *J* = 8.5 Hz, 3¢- and 5¢-*H*), 6.90 (2H, d, *J* = 8.9 Hz, 3- and 5-*H*), 6.81 (2H, d, *J* = 8.7 Hz, 3¢¢- and 5¢¢-*H*), 6.66 (3H, m, 2¢-, 4¢- and 6-*H*), 6.22 (1H, d, *J* = 6.2 Hz, C*H*), 5.35 (1H, brd, *J* = 6.1 Hz, N*H*), 3.84-3.72 (6H, s, 2(Ar-OCH_3)); ^{13}C NMR ($CDCl_3$) d 55.1, 55.3, 61.5, 113.4, 113.6, 113.8, 114.0, 114.4, 114.5, 117.5, 127.9, 129.2, 130.1, 131.1, 131.3, 146.3, 159.2, 163.8, 195.5.

1,2-Bis(4-chlorophenyl)-2-(phenylamino) ethanone (11g). Yellow crystals; mp 99-100 °C; FTIR (KBr, í, cm^{-1}) n_{max} 3398, 3052, 1682, 1603, 1589, 1504, 1488, 1400, 1312, 1245, 1174, 1092, 747 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) d 7.90 (2H, d, *J* = 8.6 Hz, 2- and 6-*H*), 7.41 (2H, d, *J* = 8.5, 3- and 5-*H*), 7.35 (2H, d, *J* = 8.5, 2¢¢- and 6¢¢-*H*), 7.25 (2H, d, *J* = 8.4 Hz, 3¢¢- and 5¢¢-*H*), 7.13 (2H, t, *J* = 8.1 Hz, 3¢- and 5¢-*H*), 6.70 (1H, t, *J* = 7.4, 4¢-*H*), 6.63 (2H, d, *J* = 7.9, 2¢- and 6¢-*H*), 5.93 (1H, d, *J* = 6.2 Hz, C*H*), 5.36 (1H, brd, *J* = 6.1 Hz, N*H*); ^{13}C NMR ($CDCl_3$) d 62.1, 113.5, 113.6, 118.3, 129.2, 129.3, 129.4, 130.2, 133.1, 134.2, 136.1, 140.3, 145.7, 195.5.

Benzoin (12a). White crystals; mp 136-137 °C (lit.[18] 135 °C); FTIR (KBr, í, cm^{-1}) n_{max} 3381, 3060, 2932, 1678, 1595, 1449, 1388, 1262, 1204, 1067, 977, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) ä 7.91 (2H, d, *J* = 7.4 Hz, 2- and 6-*H*), 7.49 (1H, t, *J* = 7.8 Hz, 4-*H*), 7.33 (2H, t, *J* = 7.8 Hz, 3-and 5-*H*), 7.30-7.25 (5H, m, Ar*H*), 5.95 (1H, d, *J* = 6.1 Hz, C*H*); 4.55 (1H, d, *J* = 6.1 Hz, O*H*); ^{13}C NMR ($CDCl_3$) d 76.2, 127.8, 128.6, 128.7, 129.2, 129.1, 133.5, 133.9, 139.0, 199.0.

4,4¢-Dimethylbenzoin (12b). White crystals; mp 73-74 °C (lit.[3] 75-76 °C); FTIR (KBr, í, cm^{-1}) n_{max} 3458, 3030, 2921, 1673, 1606, 1511, 1409, 1391, 1277, 1077, 787 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) d 7.82 (2H, d, *J* = 8.1 Hz, 2- and 6-*H*), 7.22 (2H, d, *J* = 7.9 Hz, 3- and 5-*H*), 7.18 (2H, d, *J* = 8.1 Hz, 2¢- and 6¢-*H*), 7.11 (2H, d, *J* = 8.0 Hz, 3¢-*H* and 5¢-*H*), 5.90 (1H, s, C*H*), 2.35 (3H, s, Ar-CH_3), 2.28 (3H, s, Ar-CH_3); ^{13}C NMR ($CDCl_3$) d 21.1, 21.7, 75.8, 127.6, 129.3, 129.4, 129.8, 131.0, 136.4, 138.4, 144.9, 198.6.

Anisoin (12c). White crystals; mp 110-112 °C (lit.[18] 111 °C); FTIR (KBr, í, cm^{-1}) n_{max} 3454, 3005, 2936, 2839, 1668, 1598, 1509, 1462, 1307, 1252, 1074, 1027, 828 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) d 7.89 (2H, d, *J* = 8.9 Hz, 2- and 6-*H*), 7.24 (2H, d, *J* = 8.7 Hz, 2¢- and 6¢-*H*), 6.86 (2H, d, *J* = 6.4 Hz, 3- and 5-*H*), 6.84 (2H, d, *J* = 6.1 Hz, 3¢- and 5¢-*H*), 5.84 (1H, d, *J* = 6.0 Hz, C*H*), 4.56 (1H, d, *J* = 6.0 Hz, O*H*), 3.82-3.75 (6H, s, 2(OCH_3)); ^{13}C NMR ($CDCl_3$) d 55.2, 55.5, 75.2, 113.9, 114.5, 126.3, 129.0, 131.6, 131.9, 159.6, 164.0, 197.3.

4,4¢-Dichlorobenzoin (12d). Yellow crystals; mp 89-90 °C (lit.[19] 88 °C); FTIR (KBr, í, cm^{-1}) n_{max} 3424, 3091, 3072, 687, 1674, 1590, 1488, 1401, 1252, 1093, 979, 812 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) d 7.81 (2H, d, *J* = 8.6 Hz, 2- and 6-*H*), 7.36 (2H, d, *J* = 8.6 Hz, 3- and 5-*H*), 7.28 (2H, d, *J* = 8.5 Hz, 3¢- and 5¢-*H*), 7.24 (2H, d, *J* = 8.5 Hz, 2¢- and 6¢-*H*), 5.88 (1H, d, *J* = 6.0 Hz, C*H*), 4.51 (1H, d, *J* = 6.0 Hz, O*H*); ^{13}C NMR ($CDCl_3$) d 75.5, 129.1, 129.2, 129.4, 130.4, 131.6, 134.8, 137.2, 140.7, 197.5.

Benzil (13a). Yellow crystals; mp 95-96 °C (lit.[18] 95 °C), FTIR (KBr, í, cm^{-1}) n_{max} 3065, 1662, 1594, 1580, 1450, 1211, 1174, 875, 719 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) d 7.98 (4H, d, *J* = 7.4 Hz, 2-, 2¢-, 6- and 6¢-*H*), 7.66 (2H, t, *J* = 7.5 Hz, 4- and 4¢-*H*), 7.52 (4H, t, *J* = 7.7 Hz, 3-, 3¢-, 5- and 5¢-*H*); ^{13}C NMR ($CDCl_3$) d 129.1, 130.0, 133.1, 134.9, 194.6.

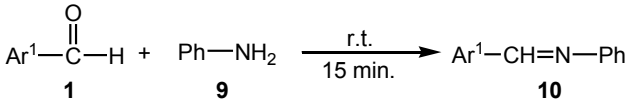
4,4¢-Dimethylbenzil (13b). Yellow crystals; mp 99-100 °C (lit.[18] 103°C), FTIR (KBr, í, cm^{-1}) n_{max} 2922, 1667, 1604, 1572, 1440, 1410, 1379, 1321, 1219, 1173, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) d 7.86 (4H, d, *J* = 8.2 Hz, 2-, 2¢-, 6- and 6¢-*H*), 7.04 (4H, d, *J* = 8.0 Hz, 3-, 3¢-, 5- and 5¢-*H*), 2.43 (6H, s, 2(Ar-CH_3)); ^{13}C NMR ($CDCl_3$) d 21.7, 126.5, 129.2, 130.2, 144.6, 171.4.

p-Anisil (13c). White crystals; mp 132-133 °C (lit.[18] 133°C); FTIR (KBr, í, cm^{-1}) n_{max} 2959, 1655, 1598, 1572, 1509, 1424, 1312, 1263, 1161, 1016, 832 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) d 7.87 (4H, d, *J* = 8.8 Hz, 2-, 2¢- and 6-, 6¢-*H*), 6.89 (4H, d, *J* = 8.9 Hz, 3-, 3¢- and 5-, 5¢-*H*), 3.80 (6H, s, 2(OCH_3)); ^{13}C NMR ($CDCl_3$) d 55.6, 114.3, 126.3, 132.4, 164.8, 193.6.

4,4¢-Dichlorobenzil (13d). Yellow crystals; mp 197-198 °C (lit.[20] 197-198 °C), FTIR (KBr, í, cm^{-1}) n_{max} 3094, 1661, 1587, 1425, 1316, 1210, 1173, 1094, 881, 835 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) d 7.85 (4H, d, *J* = 8.6 Hz, 2-, 2¢-, 6- and 6¢-*H*), 7.43 (4H, d, *J* = 8.6 Hz, 3-, 3¢-, 5- and 5¢-*H*); ^{13}C NMR ($CDCl_3$) d 129.5, 131.1, 131.3, 141.8, 192.4.

RESULTS AND DISCUSSION

Imines 10 used in our study were prepared in very good yields, as shown in Scheme 3, by condensation between the corresponding aromatic aldehydes 1 with aniline (9) in the absence of solvent at room temperature for 15 minutes.[21]

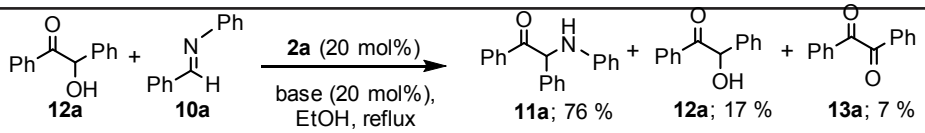


1 **9** **10**

1a Ar = C_6H_5 **10a**; 92%
1b Ar = 4-$CH_3C_6H_4$ **10b**; 92%
1c Ar = 4-$CH_3OC_6H_4$ **10c**; 96%
1d Ar = 4-ClC_6H_4 **10d**; 94%

Scheme 3

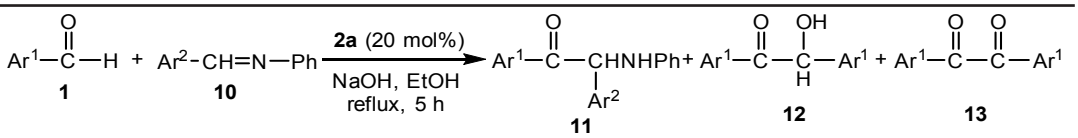
Table 1: Optimization of the reaction conditions for the cross-coupling of benzaldehyde (1a) with N-benzylideneaniline (10a)



Base	Reaction time (hour)	Temperature	% Mol of 2a	Yield (%) 11a	12a	13a
TEA	48	70 °C	20	4[a]	28[b]	26[b]
NaOH	48	70 °C	20	27[a]	12[b]	61[b]
	48	Reflux	20	76[a]	9[b]	10[b]
	5	Reflux	20	76[a]	14[b]	14[b]

[a] %yield base on mol of N-benzylideneaniline (10a)
[b] %yield base on mol of benzaldehyde (1a)

Table 2: The generality and scope of the cross-coupling of aromatic aldehydes with imines



1 **10** **11** **12** **13**

1b Ar^1 = 4-$CH_3C_6H_4$	**10a** Ar^2 = C_6H_5	**11b**; 79%	**12b**; 19%	**13b**; 7%
1c Ar^1 = 4-$CH_3OC_6H_4$	**10a** Ar^2 = C_6H_5	**11c**; 12%	**12c**; 19%	**13c**; 16%
1d Ar^1 = 4-ClC_6H_4	**10a** Ar^2 = C_6H_5	**11d**; 87%	**12d**; 18%	**13d**; 23%
1b Ar^1 = 4-$CH_3C_6H_4$	**10b** Ar^2 = 4-$CH_3C_6H_4$	**11e**; 80%	**12b**; 1%	**13b**; 14%
1c Ar^1 = 4-$CH_3OC_6H_4$	**10c** Ar^2 = 4-$CH_3OC_6H_4$	**11f**; 11%	**12c**; 23%	**13c**; 19%
1d Ar^1 = 4-ClC_6H_4	**10d** Ar^2 = 4-ClC_6H_4	**11g**; 87%	**12d**; 10%	**13d**; 22%

We had examined cross-coupling betweenbenzaldehyde (1a) and *N*-benzylideneaniline (10a) under similar conditions as reported in the literature by using 20 mol% of *N*,*N*-dimethylbenzimidazolium iodide (2a) and triethylamine in ethanol at 70°C for 2 days.[10] Unfortunately, this reaction gave only 4% yield of the desired 1,2-diphenyl-2-(phenylamino)ethanone (11a) together with benzoin (12a) and benzil (13a) in 28 and 26% yields, respectively. Benzoin (12a) was resulted from benzoin condensation which underwent further oxidation to give benzil (13a) *via* the mechanism proposed by Miyashita *et al.*[22] Replacement of triethylamine with sodium hydroxide, on the other hand, was found to give á-amino ketone 11a along with benzoin (12a) and benzil (13a) in 27, 12 and 61% yields, respectively, as shown in Table 1. Increasing the reaction temperature led to a higher yield of á-amino ketone 11a, *i.e.*, 76% yield. The two side products, 12a and 13a, were still obtained in 9 and 10% yields, respectively. Similar results were obtained despite of the shorten of the reaction time to only 5 hours, *i.e.*, 11a, 12a and 13a were obtained in 76, 14 and 14% yields, respectively.

Among various conditions studied, cross-coupling of benzaldehyde (1a) with *N*-benzylideneaniline (10a) using 20 mol% of benzimidazoliumsalt2a as a catalyst in ethanolic sodium hydroxide solution at reflux for 5 hours was chosen as the optimum conditions. Although the conditions at reflux for 48 hours also gave the same yield of 1,2-diphenyl-2-(phenylamino) ethanone (11a), it took longer time and also provided comparable yields of the two side products.

Cross-coupling between a variety of substituted aromatic aldehydes 1 with imines 10 were carried out and the results are shown in Table 2. Aromatic aldehydes having a weak electron-donating group, *i.e.*, 1b, as well as the one with a weak electron-withdrawing group, *i.e.*, 1d, reacted with *N*-benzylideneaniline (10a), affording good yields of á-amino ketones 11b and 11d, respectively. Reactions between aromatic aldehydes 1b and 1d with imines 10b and 10d, derived from the same aldehydes, also provided good yields of the corresponding á-amino ketones 11e and 11g, respectively. On the other hand, crossing-coupling of aromatic aldehydes 1c bearing strong electron-donating group with *N*-benzylideneaniline (10a) as well as *N*-(4-methoxybenzylidene)aniline (10c) gave poor yields of á-amino ketones 11c and 11f, respectively. Corresponding aroins 12b-d and arils 13b-d were obtained from all cases as side products.

Replacement of an aromatic aldehyde with a half equivalent of benzoin (12a) under the optimum conditions gave 1,2-diphenyl-2-(phenylamino) ethanone (11a) together with benzoin (12a) and benzil (13a) in 76, 17 and 7% yields, respectively.

After separation of organic products, *N,N*-dimethylbenzimidazolium iodide (2a) could be recovered by evaporation of the aqueous solution of the benzimidazolium salt to dryness. Recrystallization of the residue in ethanol gave recovered purified *N,N*-dimethylbenzimidazolium iodide (2a).

CONCLUSION

N,N-Dimethylbenzimidazolium iodide (2a) in the presence of NaOH satisfactorily catalysed cross-coupling between aromatic aldehydes and unactivated imines to afford expected á-amino ketones. Aromatic aldehydes also underwent benzoin condensation and some resulted aroins went through oxidation as evidenced by isolation of aroins and corresponding arils as minor products. Expected á-amino ketone could be obtained from treatment of benzoin with an imine. Benzimidazolium salt could be recovered and reused.

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