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1-Butyl-3-methylimidazol-2-ylidene as an Efficient Catalyst for Cross-Coupling between Aromatic Aldehydes and *N*-Aroylbenzotriazoles

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Cross-coupling of aromatic aldehydes with *N*-aroylbenzotriazoles in [Bmim]Br in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) provided an efficient procedure for the synthesis of 1,2-diarylethane-1,2-diones.

Keywords: [Bmim]Br, 1-Butyl-3-methylimidazol-2-ylidene, 1,2-Diarylethane-1,2-diones.

INTRODUCTION

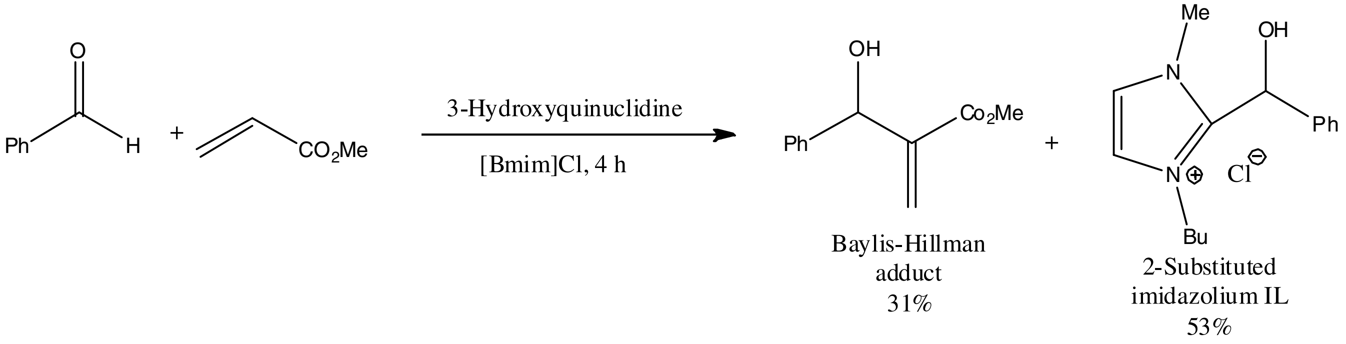
Ionic liquids (ILs) made up of 1,3-dialkylimidazolium cation are the most studied class of ionic liquids because of their low melting points and viscosity, stability to oxidative, and reductive conditions and their ease of preparation and handling [1,2]. This class of ionic liquids has been successfully employed as efficient reaction media for various reactions. For example, synthesis of coumarins *via* the $POCl_3$ catalyzed Pechman condensation of phenols and ethyl acetoacetate in either 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6) or 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4)] proceeds smoothly at ambient temperature to give coumarins in excellent yields (91-95%) [3].

[Bmim]BF_4 is the solvent of choice for shorter reaction time and much better yield of 2-amino-4,5-diphenylpyridine-3-carbonitrile derivatives from one pot condensation of aromatic aldehydes, methyl ketones, malonitrile and ammonium acetate [4]. Performing condensation of 1,2-diamines with 1,2-diketones using 1-butyl-3-methylimidazolium bromide ([Bmim]Br) as reaction media under microwave irradiation conditions also offers an efficient method for the synthesis of quinoxaline derivatives in excellent yields and short reaction times [5]. The proton at the C2 position of imidazolium cation easily undergoes deprotonation under strong or mild basic conditions to generate a highly stabilized *N*-heterocyclic carbene (NHC), *i.e.*, imidazol-2-ylidene [6]. Palladium(II) acetate employed as catalyst for the Heck olefination reactions of aryl halides with acrylates performing in [Bmim]Br has been reported to react readily with the imidazolium cation *via* deprotonation to give NHC complexes of palladium. The generated carbene complexes are catalytically active for the C-C bond forming reaction [7].

On the contrary, the Baylis-Hillman reaction between benzaldehyde and methyl acrylate catalyzed by mild base DABCO or 3-hydroxyquinuclidine carrying out in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) gives low yield of the Baylis-Hillman adduct (**Scheme-I**).

Addition reaction between benzaldehyde and the NHC, generated from imidazolium cation under mild basic reaction conditions, giving the 2-substituted imidazolium ionic liquid is responsible for low yield of the desired Baylis-Hillman product. Formation of 2-substituted imidazolium ionic liquid is the initial step for the benzoin condensation. However, no benzoin has been detected in the Baylis-Hillman reaction performing in [Bmim]Cl [8,9].

The NHC generated from [Bmim]Br in the presence of NaOH, on the other hand, can be used as efficient catalyst for benzoin condensation and Stetter reaction [10,11]. In the presence of NaOH, abstraction of 2-H proton of imidazolium ion trans-



Scheme-I: Mild basic catalyzed Baylis-Hillman reaction

forms [Bmim]Br (**1**) to imidazol-2-ylidene (**2**). Addition of the carbene catalyst **2** to aromatic aldehyde **3** leads to Breslow intermediate **5** which further reaction with second equivalent of aromatic aldehyde **3** generates adduct **6**. Proton transfer and regeneration of catalyst **2** produces benzoin (**8**) (**Scheme-II**). Alternatively, addition of Breslow intermediate **5** to the Michael acceptor **9** provides conjugate adduct **10**. Proton transfer and also liberation of catalyst **2** affords 1,4-addition product **12** (**Scheme-II**).

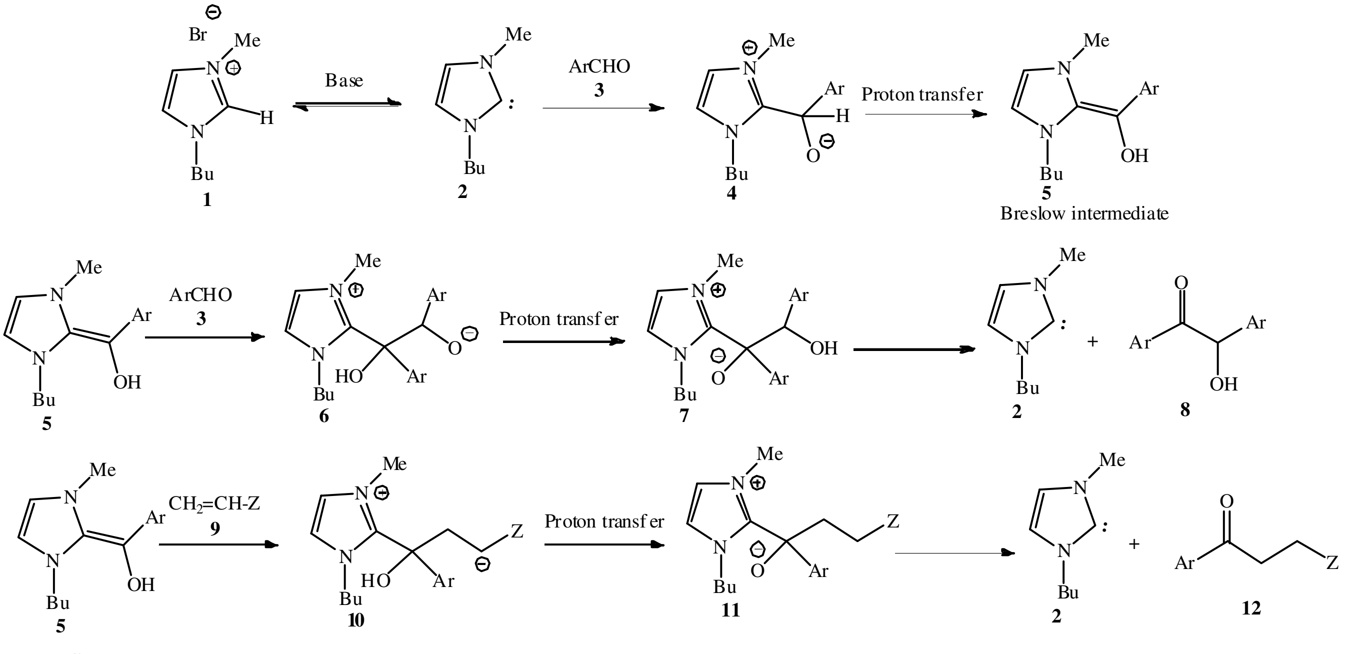
Besides aromatic aldehydes and Michael acceptors, NHC catalyzed cross-coupling between aromatic aldehydes and *N*-aroylbenzotriazoles also proceeds well to give 1,2-diarylethane-1,2-diones. This cross-coupling has been performed in THF, a conventional organic solvent, using NHC catalyst derived from *N*,*N*-dimethylbenzimidazolium iodide [12]. 1,2-Diarylethane-1,2-diones is a class of compounds which has received a great deal of attention because of their photoluminescence properties [13], antioxidant activity [14] and antimicrobial activity [15]. Synthesis of imidazoles and quinoxalines, heterocyclic compounds which possess various biological activities such as antibacterial, anticancer and antifungal activities, commonly used ethane-1,2-diones as precursor [16-19].

As part of our continuing interest in the effectiveness of NHC as organocatalyst [12,20-23], we reported herein the cross-coupling of aromatic aldehydes with *N*-aroylbenzotriazoles using [Bmim]Br as precatalyst and reaction media. This cross-coupling would provide a more convenient and eco-friendly method for the synthesis of 1,2-diarylethane-1,2-diones.

EXPERIMENTAL

Chemicals were used as received from the commercial sources. Melting points were determined with a Buchi B-545 apparatus and compared with those of known samples. IR spectra were recorded on a FTIR Perkin-Elmer instrument. Spectra of solids were carried out using KBr pellets. The ^{1}H and ^{13}C NMR spectra were obtained using a VARIAN MERCURY plus (400 MHz FT NMR). *N*-Aroylbenzotriazoles used in this study were synthesized according to our reported method [12].

General procedure for the cross-coupling between aromatic aldehydes (3a-d) and *N*-acylbenzotriazoles (13a-d) in [Bmim]Br (1): To a stirred solution of corresponding aromatic aldehyde **3** (1.0 mmol) and corresponding *N*-aroylbenzotriazole **13** (2.0 mmol) in [Bmim]Br (**3**) (0.219 g, 1.0 mmol)



Scheme-II: Reaction pathway for benzoin condensation and Setter reaction catalyzed by 1-butyl-3-methylimidazol-2-ylidene was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.076 g, 0.5 mmol). The reaction mixture was stirred at 80 ºC for 9-19 h. On completion of the reaction, as indicated by TLC, the reaction mixture was diluted with water (10 mL). The mixture was extracted with dichloromethane (3 × 30 mL). The organic layers were combined and washed with water and dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified using preparative thin layer chromatography on silica gel (dichloromethane/hexane, 1:1 as eluant). The purified compounds (**14a-j** and **15a-p**) with their physical data are listed below.

1,2-Diphenylethane-1,2-dione (14a): Yellow crystals. m.p.: 95-96 ºC (lit. 95 ºC) [24]; IR (KBr, ν_{max}, cm^{-1}): 3065, 1664, 1596, 1451, 1325, 1214 and 720; ^1H NMR ($CDCl_3$): δ 7.99 (d, 4H, C_2-H, C_6-H, C_2'-H and C_6'-H of Ar-H, J = 8.4 Hz), 7.65 (t, 2H, C_4-H and C_4'-H of Ar-H, J = 8.4 Hz) and 7.53 (t, 4H, C_3-H, C_5-H, C_3'-H and C_5'-H of Ar-H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$): δ 129.1, 129.9, 133.1, 134.9 and 194.8.

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (14b): Yellow solid. m.p.: 68-70 ºC (lit. 66-67 ºC) [25]; IR (KBr, ν_{max}, cm^{-1}): 3090, 3062, 2921, 2858, 1670, 1591, 1450, 1321, 1207 and 719; ^1H NMR ($CDCl_3$): δ 7.94 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.8 Hz), 7.92 (d, 2H, C_2'-H and C_6'-H of Ar-H, J = 8.4 Hz), 7.69 (t, 1H, C_4'-H of Ar-H, J = 8.4 Hz), 7.54 (d, 2H, C_3'-H and C_5'-H of Ar-H, J = 8.4 Hz), 7.51 (d, 2H, C_3-H and C_5-H of Ar-H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$): δ 129.1, 129.5, 129.8, 131.3, 131.5, 132.9, 135.2, 141.8, 193.1 and 193.9.

1-(4-Methylphenyl)-2-phenylethane-1,2-dione (14c): Yellow crystals. m.p.: 98-100 ºC (lit. 99-101 ºC) [22]; IR (KBr, ν_{max}, cm^{-1}): 3023, 2989, 2848, 1659, 1598, 1423, 1263, 1158 and 834; ^1H NMR ($CDCl_3$): δ 8.02 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.4 Hz), 7.97 (d, 2H, C_2'-H and C_6'-H of Ar-H, J = 8.0 Hz), 7.67 (t, 1H, C_4'-H of Ar-H, J = 8.0 Hz), 7.46 (t, 2H, C_3'-H and C_5'-H of Ar-H, J = 8.0 Hz), 7.20 (d, 2H, C_3-H and C_5-H of Ar-H, J = 8.4 Hz) and 2.35 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$): δ 21.3, 128.5, 128.9, 129.4, 129.6, 129.8, 132.9, 136.3, 139.8 and 193.0.

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (14d): Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 3059, 3012, 2960, 2929, 2855, 1680, 1594, 1449, 1259, 1160 and 1161; ^1H NMR ($CDCl_3$): δ 7.98 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.4 Hz), 7.96 (d, 2H, C_2'-H and C_6'-H of Ar-H, J = 8.8 Hz), 7.66 (t, 1H, C_4'-H of Ar-H, J = 8.8 Hz), 7.52 (t, 2H, C_3'-H and C_5'-H of Ar-H, J = 8.8 Hz), 6.99 (d, 2H, C_3-H and C_5-H, J = 8.4 Hz), 3.88 (s, 3H, Ar-OCH_3); ^{13}C NMR ($CDCl_3$): δ 55.7, 114.4, 126.2, 128.9, 129.9, 132.6, 133.3, 134.7, 165.1, 193.2 and 194.9.

1,2-Di(4-chlorophenyl)ethane-1,2-dione (14e): Yellow solid. m.p.: 196-197 ºC (lit. 197-198 ºC) [26]; IR (KBr, ν_{max}, cm^{-1}): 3090, 2931, 1664, 1589, 1489, 1221 and 1090; ^1H NMR ($CDCl_3$): δ 7.93 (d, 4H, C_2-H, C_6-H, C_2'-H and C_6'-H of Ar-H, J = 8.8 Hz) and 7.52 (d, 4H, C_3-H, C_5-H, C_3'-H and C_5'-H of Ar-H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$): δ 129.6, 131.3, 131.5, 141.7 and 192.4.

1-(4-Chlorophenyl)-2-*p*-tolylethane-1,2-dione (14f): Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 3089, 3062, 2931, 2860, 1665, 1584, 1481, 1317, 1209, 1169 and 731; ^1H NMR ($CDCl_3$): δ 7.93 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.8 Hz), 7.87 (d, 2H, C_2'-H and C_6'-H of Ar-H, J = 8.4 Hz), 7.49 (d, 2H, C_3-H and C_5-H of Ar-H, J = 8.8 Hz), 7.32 (d, 2H, C_3'-H and C_5'-H of Ar-H, J = 8.4 Hz), 2.45 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$): δ 21.8, 129.4, 129.9, 130.0, 130.5, 131.2, 131.5, 141.4, 146.4, 193.4 and 193.6.

1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-ethane-1,2-dione (14g): Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 3090, 2970, 2927, 1669, 1570, 1515, 1489, 1310, 1267, 1171, 1089 and 741; ^1H NMR ($CDCl_3$): δ 7.95 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.8 Hz), 7.93 (d, 2H, C_2'-H and C_6'-H of Ar-H, J = 8.4 Hz), 7.49 (d, 2H, C_3-H and C_5-H of Ar-H, J = 8.8 Hz), 6.99 (d, 2H, C_3'-H and C_5'-H of Ar-H, J = 8.4 Hz), 3.88 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$): δ 55.7, 114.5, 125.8, 129.3, 131.2, 131.7, 132.4, 141.3, 165.2, 192.5 and 193.4.

1,2-Di(4-methylphenyl)ethane-1,2-dione (14h): Yellow solid. m.p.: 99-100 ºC (lit. 99-100 ºC) [27]; IR (KBr, ν_{max}, cm^{-1}): 2922, 1667, 1604, 1573, 1440, 1410, 1321, 1220 and 1173; ^1H NMR ($CDCl_3$): δ 7.87 (d, 4H, C_2-H, C_6-H, C_2'-H and C_6'-H of Ar-H, J = 8.8 Hz), 7.05 (d, 4H, C_3-H, C_5-H, C_3'-H and C_5'-H of Ar-H, J = 8.8 Hz) and 2.44 (s, 6H, 2(Ar-CH_3)); ^{13}C NMR ($CDCl_3$): δ 21.8, 126.5, 129.3, 130.2, 144.7 and 171.5.

1-(4-Methoxyphenyl)-2-*p*-tolylethane-1,2-dione (14i): Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 2932, 2857, 1668, 1595, 1519, 1466, 1311, 1263 and 1023; ^1H NMR ($CDCl_3$): δ 7.95 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.4 Hz), 7.87 (d, 2H, C_2'-H and C_6'-H of Ar-H, J = 8.4 Hz), 7.31 (d, 2H, C_3'-H and C_5'-H of Ar-H, J = 8.4 Hz), 6.98 (d, 2H, C_3-H and C_5-H of Ar-H, J = 8.4 Hz), 3.89 (s, 3H, Ar-OCH_3) and 2.44 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$): δ 21.9, 55.7, 114.3, 126.3, 129.6, 130.1, 130.8, 132.4, 145.9, 164.9, 193.4 and 194.7.

1,2-Di(4-methoxyphenyl)ethane-1,2-dione (14j): Yellow crystals. m.p.: 131-133 ºC (lit. 131-134 ºC) [28]; IR (KBr, ν_{max}, cm^{-1}): 2960, 2841, 1657, 1592, 1569, 1427, 1312, 1266 and 1154; ^1H NMR ($CDCl_3$): δ 7.96 (d, 4H, C_2-H, C_6-H, C_2'-H and C_6'-H of Ar-H, J = 8.4 Hz), 6.98 (d, 4H, C_3-H, C_5-H, C_3'-H and C_5'-H of Ar-H, J = 8.4 Hz) and 3.89 (s, 6H, 2(Ar-OCH_3)); ^{13}C NMR ($CDCl_3$): δ 55.7, 114.3, 126.5, 132.3, 164.8 and 193.7.

1*H*-1,2,3-Benzotriazol-1-yl(phenyl)methyl benzoate (15a): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3069, 2963, 1737, 1607, 1511, 1451, 1258, 1157 and 751; ^1H NMR ($CDCl_3$): δ 8.76 (s, 1H, ArC-H), 8.14 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.4 Hz), 8.09 (d, 1H, C_7'-H of Ar-H, J = 7.6 Hz), 7.61 (t, 1H, C_6'-H of Ar-H, J = 7.6 Hz), 7.52-7.44 (m, 9H, Ar-H) and 7.37 (t, 1H, C_5'-H of Ar-H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$): δ 80.9, 110.7, 120.4, 124.5, 126.4, 128.2, 128.6, 128.7, 128.9, 129.7, 130.2, 132.1, 134.0, 134.3, 146.5 and 164.5.

1*H*-1,2,3-Benzotriazol-1-yl(phenyl)methyl 4-chlorobenzoate (15b): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3101, 2967, 2921, 2852, 1735, 1593, 1489, 1441, 1401, 1256, 1180, 1071 and 760; ^1H NMR ($CDCl_3$): δ 8.71 (s, 1H, ArC-H), 8.08 (d, 1H, C_7'-H of Ar-H, J = 7.8 Hz), 8.05 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.8 Hz), 7.51-7.48 (m, 2H, Ar-H), 7.46-7.42 (m, 7H, Ar-H), 7.37 (t, 1H, C_5'-H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$): δ 80.8, 110.4, 120.2, 124.3, 126.1, 127.1, 128.3, 129.2, 129.3, 129.9, 131.5, 132.1, 134.1, 140.5, 146.5 and 163.8.

1*H*-1,2,3-Benzotriazol-1-yl(phenyl)methyl 4-methylbenzoate (15c): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3035, 2953, 2924, 2856, 1716, 1612, 1578, 1493, 1450, 1270, 1177, 1094 and 804; ^{1}H NMR ($CDCl_3$): δ 8.71 (s, 1H, ArC-H), 7.99-8.02 (m, 3H, C_7'-H, C_2-H and C_6-H of Ar-H), 7.93 (d, 1H, C_4'-H of Ar-H, J = 7.6 Hz), 7.87 (t, 1H, C_6'-H, J = 7.6 Hz), 7.57 (d, 2H, $C2''$-H and $C6''$-H of Ar-H, J = 8.4 Hz), 7.48-7.56 (m, 3H, Ar-H), 7.31 (t, 1H, $C5'$-H of Ar-H, J = 7.6 Hz), 7.14 (d, 2H, $C3''$-H and $C5''$-H of Ar-H, J = 8.4 Hz) and 2.25 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$): δ 21.3, 82.2, 111.9, 119.7, 124.3, 127.7, 127.8, 128.1, 128.6, 128.8, 128.9, 129.8, 131.1, 136.8, 139.8, 146.6 and 165.9.

1*H*-1,2,3-Benzotriazol-1-yl(phenyl)methyl 4-methoxybenzoate (15d): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3059, 2961, 2928, 2847, 1732, 1609, 1510, 1451, 1249 and 1168; ^{1}H NMR ($CDCl_3$): δ 8.74 (s, 1H, ArC-H), 8.09 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.4 Hz), 8.08 (d, 1H, C_7'-H of Ar-H, J = 7.8 Hz), 7.51-7.55 (m, 2H, C_4'-H, C_2''-H and C_6''-H of Ar-H), 7.39-7.43 (m, 4H, C_6'-H, C_3''-H, C_4''-H and C_5''-H), 7.33 (t, 1H, C_5'-H of Ar-H, J = 7.8 Hz), 6.92 (d, 2H, C_3-H and C_5-H of Ar-H, J = 8.4 Hz), 3.89 (s, 3H, Ar-OCH_3); ^{13}C NMR ($CDCl_3$): δ 55.6, 80.7, 110.8, 114.2, 120.3, 120.8, 124.5, 126.5, 128.3, 128.8, 129.8, 132.2, 132.4, 134.6, 146.5, 164.3 and 164.4.

1*H*-1,2,3-Benzotriazol-1-yl(4-chlorophenyl)methyl benzoate (15e): Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 3063, 2963, 2925, 2854, 1736, 1591, 1490, 1451, 1257, 1067 and 738; ^{1}H NMR ($CDCl_3$): δ 8.74 (s, 1H, ArC-H), 8.10 (d, 1H, C_7'-H of Ar-H, J = 7.8 Hz), 8.07 (d, 2H, C_2-H and C_6'-H of Ar-H, J = 8.8 Hz), 7.42-7.54 (m, 9H, Ar-H) and 7.39 (t, 1H, C_5'-H of Ar-H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$): δ 80.8, 110.4, 120.4, 124.5, 126.3, 127.2, 128.3, 129.1, 129.2, 129.9, 131.6, 132.1, 134.1, 140.7, 146.6 and 163.9.

1*H*-1,2,3-Benzotriazol-1-yl(4-chlorophenyl)methyl 4-chlorobenzoate (15f): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3090, 3049, 2957, 1735, 1590, 1493, 1451, 1260, 1164 and 742; ^{1}H NMR ($CDCl_3$): δ 8.71 (s, 1H, ArC-H), 8.11 (d, 1H, C_7'-H of Ar-H, J = 7.8 Hz), 8.06 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.8 Hz), 7.55-7.39 (m, 9H, Ar-H); ^{13}C NMR ($CDCl_3$): δ 80.3, 110.2, 120.4, 124.7, 126.8, 127.9, 128.5, 129.2, 129.4, 131.3, 131.8, 132.5, 136.2, 140.9, 146.7 and 163.8.

1*H*-1,2,3-Benzotriazol-1-yl(4-chlorophenyl)methyl 4-methylbenzoate (15g): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3094, 3068, 2963, 1731, 1592, 1452, 1322, 1258, 1174 and 793; ^{1}H NMR ($CDCl_3$): δ 8.71 (s, 1H, ArC-H), 8.09 (d, 1H, C_7'-H, J = 7.8 Hz), 8.06 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.4 Hz), 7.52 (d, 1H, C_4'-H of Ar-H, J = 7.8 Hz), 7.39-7.46 (m, 5H, Ar-H), 7.35 (t, 1H, C_5'-H of Ar-H, J = 7.8 Hz), 7.24 (d, 2H, C_3''-H and C_5''-H, J = 8.8 Hz) and 2.38 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$): δ 21.3, 81.1, 110.7, 120.3, 124.3, 126.2, 127.0, 128.2, 129.0, 129.7, 131.1, 131.4, 132.0, 130.8, 140.7, 146.8 and 163.9.

1*H*-1,2,3-Benzotriazol-1-yl(4-chlorophenyl)methyl 4-methoxybenzoate (15h): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3069, 2958, 2939, 2840, 1728, 1605, 1579, 1451, 1258 and 1170; ^{1}H NMR ($CDCl_3$): δ 8.66 (s, 1H, ArC-H), 8.06 (d, 1H, C_7'-H, J = 7.8 Hz), 8.04 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.8 Hz), 7.57 (d, 1H, C_4'-H of Ar-H, J = 7.8 Hz), 7.47 (d, 2H, C_3''-H and C_5''-H of Ar-H, J = 8.4 Hz), 7.43 (t, 1H, C_6'-H of Ar-H, J = 7.8 Hz), 7.33-7.40 (m, 3H, C_5'-H, C_2''-H and C_6''-H of Ar-H), 6.90 (d, 2H, C_3-H and C_5-H, J = 8.8 Hz), 3.87 (s, 3H, Ar-OCH_3); ^{13}C NMR ($CDCl_3$): δ 55.6, 79.8, 110.6, 114.1, 120.2, 120.3, 124.7, 127.9, 128.4, 129.3, 132.1, 132.3, 133.0, 135.6, 146.4, 164.0 and 164.4.

1*H*-1,2,3-Benzotriazol-1-yl(4-methylphenyl)methyl benzoate (15i): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3066, 3036, 2959, 2855, 1731, 1612, 1493, 1452, 1259 and 1178; ^{1}H NMR ($CDCl_3$): δ 8.76 (s, 1H, ArC-H), 8.09 (d, 1H, C_7'-H of Ar-H, J = 7.8 Hz), 8.03 (d, 2H, C_2-H and C_6-H, J = 8.4 Hz), 7.54-7.57 (m, 3H, C_6'-H, C_2''-H and C_6''-H of Ar-H), 7.40-7.46 (m, 4H, C_3''-H, C_4''-H, C_5''-H and C_4'-H of Ar-H), 7.36 (t, 1H, C_5'-H of Ar-H, J = 7.8 Hz), 7.26 (d, 2H, C_3-H and C_5-H of Ar-H, J = 8.4 Hz) and 2.39 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$): δ 21.9, 80.5, 110.8, 120.2, 124.4, 126.3, 128.1, 129.0, 129.4, 129.6, 130.1, 145.1, 146.5 and 164.5.

1*H*-1,2,3-Benzotriazol-1-yl(4-methylphenyl)methyl 4-chlorobenzoate (15j): Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 3089, 3059, 2965, 2921, 1733, 1591, 1450, 1322, 1258, 1184, 1072 and 793; ^{1}H NMR ($CDCl_3$): δ 8.71 (s,1H, ArC-H), 8.09 (d, 1H, C_7'-H of, J = 7.8 Hz), 8.06 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.8 Hz), 7.52 (d, 1H, C_4'-H of Ar-H, J = 7.8 Hz), 7.41-7.46 (m, 5H, C_6'-H, C_3-H, C_5-H, C_2''-H and C_6''-H of Ar-H), 7.35 (t, 1H, C_5'-H of Ar-H, J = 7.8 Hz), 7.24 (d, 2H, C_3''-H and C_5''-H of Ar-H, J = 8.4 Hz), 2.39 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$): δ 21.3, 81.2, 110.7, 120.4, 124.3, 126.1, 127.1, 128.2, 129.1, 129.6, 131.0, 131.3, 132.1, 132.8, 140.8, 146.5 and 163.8.

1*H*-1,2,3-Benzotriazol-1-yl(4-methylphenyl)methyl 4-methylbenzoate (15k): Yellow solid. m.p.: 175-176 ºC; IR (KBr, ν_{max}, cm^{-1}): 3091, 3064, 2924, 2855, 1731, 1608, 1514, 1453, 1261 and 1076; ^{1}H NMR ($CDCl_3$): δ 8.68 (s, 1H, ArC-H), 8.09 (d, 1H, C_7'-H of Ar-H, J = 7.6 Hz), 8.02 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.4 Hz), 7.54 (d, 1H, C_4'-H of Ar-H, J = 7.6 Hz), 7.39-7.44 (m, 3H, C_6'-H, C_2''-H and C_6''-H of Ar-H), 7.35 (t, 1H, C_5'-H of Ar-H, J = 7.6 Hz), 7.26 (d, 2H, C_3-H and C_5-H of Ar-H, J = 8.4 Hz), 7.22 (d, 2H, C_3''-H and C_5''-H of Ar-H, J = 8.4 Hz), 2.45 (s, 3H, Ar-CH_3) and 2.39 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$): δ 21.2, 21.7, 80.8, 110.7, 120.2, 124.3, 125.8, 126.2, 128.0, 129.4, 129.6, 130.1, 131.4, 132.1, 139.6, 144.9, 146.4 and 164.6.

1*H*-1,2,3-Benzotriazol-1-yl(4-methylphenyl)methyl 4-methoxybenzoate (15l): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3061, 2956, 2851, 1733, 1601, 1588, 1493, 1259 and 1171; ^{1}H NMR ($CDCl_3$): δ 8.71 (s, 1H, ArC-H), 8.08 (d, 1H, C_7'-H of Ar-H, J = 7.6 Hz), 8.07 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.4 Hz), 7.54 (d, 1H, C_4'-H of Ar-H, J = 7.6 Hz), 7.38-7.44 (m, 3H, C_6'-H, C_2''-H and C_6''-H of Ar-H), 7.34 (t, 1H, C_5'-H of Ar-H, J = 7.6 Hz), 7.21 (d, 2H, C_3''-H and C_5''-H, J = 8.8 Hz), 6.89 (d, 2H, C_3-H and C_5-H of Ar-H, J = 8.4 Hz), 3.82 (s, 3H, Ar-OCH_3), 2.31 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$): δ 21.4, 55.5, 80.9, 110.9, 114.0, 120.1, 120.6, 124.4, 126.2, 128.0, 129.6, 131.4, 132.1, 132.2, 139.7, 146.3, 164.1 and 164.3.

1*H*-1,2,3-Benzotriazol-1-yl(4-methoxyphenyl)methyl benzoate (15m): Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 3066, 2963, 2841, 1731, 1605, 1512, 1454, 1255 and 1168; ^{1}H NMR ($CDCl_3$): δ 8.72 (s, 1H, ArC-H), 8.07 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.4 Hz), 8.08 (d, 1H, C_7'-H of Ar-H, J = 7.8 Hz), 7.51-7.55 (m, 3H, C_4'-H, C_2''-H and C_6''-H of Ar-H), 7.39-7.43 (m, 4H, C_6'-H, C_3''-H, C_4''-H and C_5''-H of Ar-H), 7.33 (t, 1H, C_5'-H of Ar-H, J = 7.8 Hz), 6.92 (d, 2H, C_3-H and C_5-H, J = 8.4 Hz) and 3.89 (s, 3H, Ar-OCH_3); ^{13}C NMR ($CDCl_3$): δ 55.6, 80.6, 110.8, 114.0, 120.3, 120.8, 124.5, 126.2, 128.1, 128.9, 129.6, 132.1, 132.2, 134.5, 146.4, 164.2 and 164.3.

1*H*-1,2,3-Benzotriazol- 1-yl(4-methoxyphenyl)methyl 4-chlorobenzoate (15n): Yellow liquid; IR (neat, ν_{max}, cm^{-1}): 3089, 3056, 2991, 2953, 1731, 1593, 1450, 1351, 1255, 1177, 1069 and 799; ^{1}H NMR ($CDCl_3$): δ 8.66 (s, 1H, ArC-H), 8.10 (d, 1H, C_7'-H of Ar-H, J = 7.8 Hz), 8.05 (d, 2H, C_2-H and C_6-H, J = 8.8 Hz), 7.44-7.52 (m, 6H, C_6'-H, C_4'-H, C_3-H, C_5-H, C_2''-H and C_6''-H of Ar-H), 7.36 (t, 1H, C_5'-H of Ar-H, J = 7.8 Hz), 6.96 (d, 2H, C_3''-H and C_5''-H of Ar-H, J = 8.4 Hz), 3.84 (s, 3H, Ar-OCH_3); ^{13}C NMR ($CDCl_3$): δ 55.5, 81.1, 110.4, 114.4, 120.4, 124.3, 126.1, 127.1, 127.9, 128.0, 129.1, 131.3, 132.1, 140.5, 146.4, 160.7 and 163.8.

1*H*-1,2,3-Benzotriazol-1-yl(4-methoxyphenyl)methyl 4-methylbenzoate (15o): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3064, 2961, 2841, 1731, 1606, 1581, 1493, 1259 and 1167; ^{1}H NMR ($CDCl_3$): δ 8.71 (s, 1H, ArC-H), 8.08 (d, 2H, C_2-H and C_6-H of Ar-H, J = 8.4 Hz), 8.07 (d, 1H, C_7'-H of Ar-H, J = 7.8 Hz), 7.54 (d, 1H, C_4'-H of Ar-H, J = 7.8 Hz), 7.38-7.44 (m, 3H, C_6'-H, C_2''-H and C_6''-H of Ar-H), 7.34 (t, 1H, C_5'-H of Ar-H, J = 7.8 Hz), 7.21 (d, 2H, C_3''-H and C_5''-H of Ar-H, J = 8.8 Hz), 6.89 (d, 2H, C_3-H and C_5-H of Ar-H, J = 8.4 Hz), 3.81 (s, 3H, Ar-OCH_3) and 2.34 (s, 3H, Ar-CH_3); ^{13}C NMR ($CDCl_3$): δ 21.3, 55.5, 80.9, 110.8, 114.0, 120.1, 120.8, 124.3, 126.2, 128.0, 129.5, 131.5, 132.1, 132.2, 139.7, 146.3, 164.1 and 164.2.

1*H*-1,2,3-Benzotriazol-1-yl(4-methoxyphenyl)methyl 4-methoxybenzoate (15p): Colourless liquid; IR (neat, ν_{max}, cm^{-1}): 3081, 3009, 2936, 2840, 1730, 1609, 1515, 1490 and 1165; ^{1}H NMR ($CDCl_3$): δ 8.66 (s, 1H, ArC-H), 8.05 (d, 3H, C_2-H, C_6-H and C_7'-H of Ar-H, J = 8.4 Hz), 7.55 (d, 1H, C_4'-H of Ar-H, J = 7.8 Hz), 7.41-7.46 (m, 3H, C_2''-H and C_6''-H and C_6'-H), 7.33 (t, 1H, C_5'-H of Ar-H, J = 7.8 Hz), 6.94 (d, 2H, C_3-H and C_5-H, J = 8.4 Hz), 6.92 (d, 2H, C_3''-H and C_5''-H of Ar-H, J = 8.4 Hz), 3.83 (s, 3H, Ar-OCH_3), 3.79 (3H, s, $OC\mathit{H}_3$); ^{13}C NMR ($CDCl_3$): δ 55.4, 55.5, 80.9, 110.9, 113.7, 114.0, 114.3, 120.1, 120.9, 124.2, 126.5, 127.7, 128.0, 132.0, 132.3, 146.3, 160.5 and 164.1.

RESULTS AND DISCUSSION

Reaction conditions for the cross-coupling of aromatic aldehydes with *N*-aroylbenzotriazoles reported herein were similar to described procedure [12] except 1-butyl-3-methylimidazolium bromide [Bmim]Br was used as precatalyst and reaction medium at 80 ºC.

An appropriate amount of [Bmim]Br (**1**) required for cross-coupling between benzaldehyde (**3a**) and two equivalents of *N*-benzoylbenzotriazole (**13a**) in the presence of 50 mol% of DBU as catalyst was initially examined. As shown in Table-1, use of 100 mol% of [Bmim]Br (**1**) gave highest yields of expected 1,2-diphenylethane-1,2-dione (**14a**) and 1*H*-1,2,3-benzotriazol-1-yl(phenyl)methyl benzoate (**15a**) as side product.

The scope of the cross-coupling reaction performing in [Bmim]Br in the presence of DBU was then demonstrated using both electron deficient and electron rich aromatic aldehydes as well as *N*-aroylbenzotriazoles under the optimized reaction conditions (Table-1, entry 3). To our delight, treatment of aromatic aldehydes **3a-d** with *N*-aroylbenzotriazoles **13a-d** as illustrated in Table-2 afforded satisfied yields of the expected 1,2-diarylethane-1,2-diones **14b-j** together with the corresponding 1*H*-1,2,3-benzotriazol-1-yl(aryl)methyl esters **15b-p**.

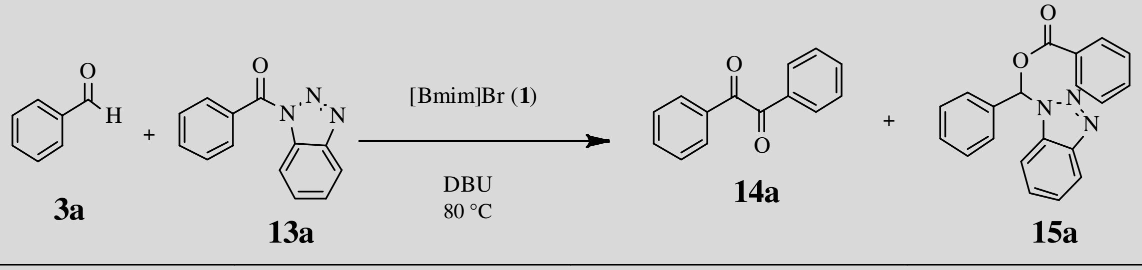
The mechanism of this cross-coupling between aromatic aldehydes **3** and *N*-aroylbenzotriazoles **13** was analogous as depicted in **Scheme-II** for benzoin condensation and Stetter reaction. Following the usual formation of Breslow intermediate **5**, the nucleophilic attrack on carbonyl carbon of *N*-aroylbenzotriazoles **13** followed by elimination of benzotriazolate anion **17** gives intermediate **18**. Departure of imidazol-2-ylidene **2** to complete the catalytic cycle finally gives 1,2-diarylethane-1,2-diones product **14** (**Scheme-III**).

On the other hand, nucleophilic addition of the adduct **4** to *N*-aroylbenzotriazole **13** gives intermediate **19**, which undergoes benzotriazolyl [1,3] shift to furnish 1*H*-1,2,3-benzotriazol-1-yl(aryl)methyl esters side product **15** (**Scheme-IV**).

Conclusion

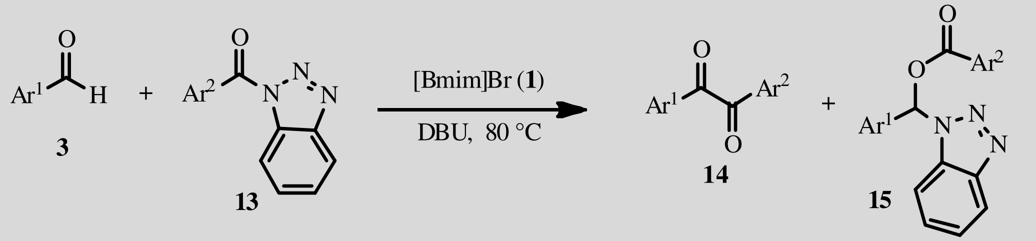
1-Butyl-3-methylimidazol-2-ylidine, generated *in situ* from treatment of [Bmim]Br with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), successfully catalyzed cross-coupling between various aromatic aldehydes and *N*-aroylbenzotriazoles to afford

TABLE-1
OPTIMIZATION FOR CROSS-COUPLING OF BENZALDEHYDE (**3a**) WITH
N-BENZOYLBENZOTRIAZOLE (**13a**) PERFORMING IN [Bmim]Br (**1**)

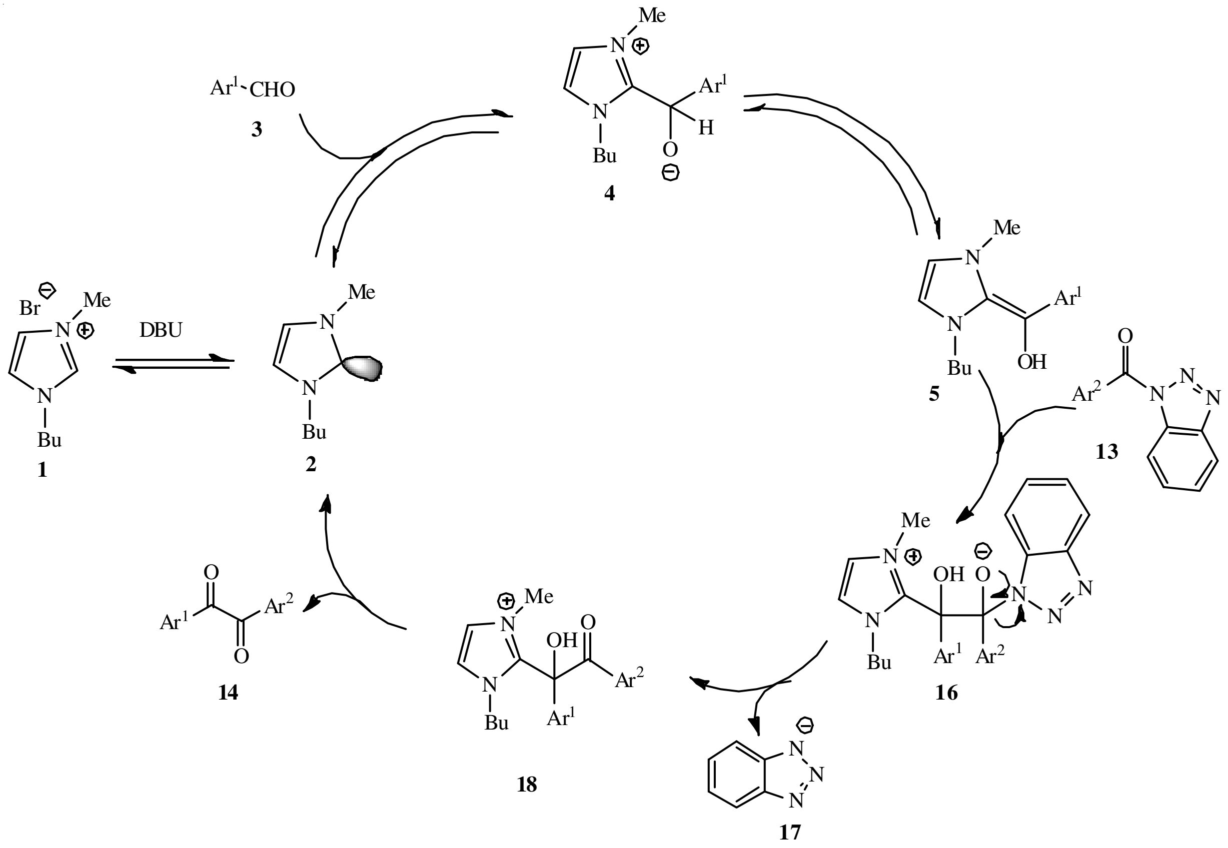


Entry	Mol % **1**	Yield **14a** (%)	Yield **15a** (%)
1	20	39	13
2	50	70	19
3	100	72	19

TABLE-2
CROSS-COUPLING REACTIONS WITH VARIOUS SUBSTRATES



Entry	Ar^1	Ar^2	Yield (%)	Yield (%)
1	4-ClC_6H_5 (**3b**)	C_6H_5 (**13a**)	54 (**14b**)	29 (**15b**)
2	4-MeC_6H_5 (**3c**)	C_6H_5 (**13a**)	40 (**14c**)	34 (**15c**)
3	4-$MeOC_6H_5$ (**3d**)	C_6H_5 (**13a**)	37 (**14d**)	29 (**15d**)
4	C_6H_5 (**3a**)	4-ClC_6H_5 (**13b**)	61 (**14b**)	28 (**15e**)
5	4-ClC_6H_5 (**3b**)	4-ClC_6H_5 (**13b**)	65 (**14e**)	32 (**15f**)
6	4-MeC_6H_5 (**3c**)	4-ClC_6H_5 (**13b**)	48 (**14f**)	31 (**15g**)
7	4-$MeOC_6H_5$ (**3d**)	4-ClC_6H_5 (**13b**)	51 (**14g**)	31 (**15h**)
8	C_6H_5 (**3a**)	4-MeC_6H_5 (**13c**)	60 (**14c**)	30 (**15i**)
9	4-ClC_6H_5 (**3b**)	4-MeC_6H_5 (**13c**)	65 (**14f**)	30 (**15j**)
10	4-MeC_6H_5 (**3c**)	4-MeC_6H_5 (**13c**)	43 (**14h**)	35 (**15k**)
11	4-$MeOC_6H_5$ (**3d**)	4-MeC_6H_5 (**13c**)	49 (**14i**)	33 (**15l**)
12	C_6H_5 (**3a**)	4-$MeOC_6H_5$ (**13d**)	44 (**14d**)	34 (**15m**)
13	4-ClC_6H_5 (**3b**)	4-$MeOC_6H_5$ (**13d**)	59 (**14g**)	30 (**15n**)
14	4-MeC_6H_5 (**3c**)	4-$MeOC_6H_5$ (**13d**)	43 (**14i**)	32 (**15o**)
15	4-$MeOC_6H_5$ (**3d**)	4-$MeOC_6H_5$ (**13d**)	39(**14j**)	30 (**15p**)



Scheme-III: Catalytic cycle for cross-coupling between aromatic aldehyde **3** and *N*-aroylbenzotriazole **13** catalyzed by 1-butyl-3-methylimidazol-2-ylidene (**2**)

satisfied yields of expected 1,2-diarylethane-1,2-diones. Corresponding 1*H*-1,2,3-benzotriazol-1-yl(aryl)methyl esters were also obtained as side products.

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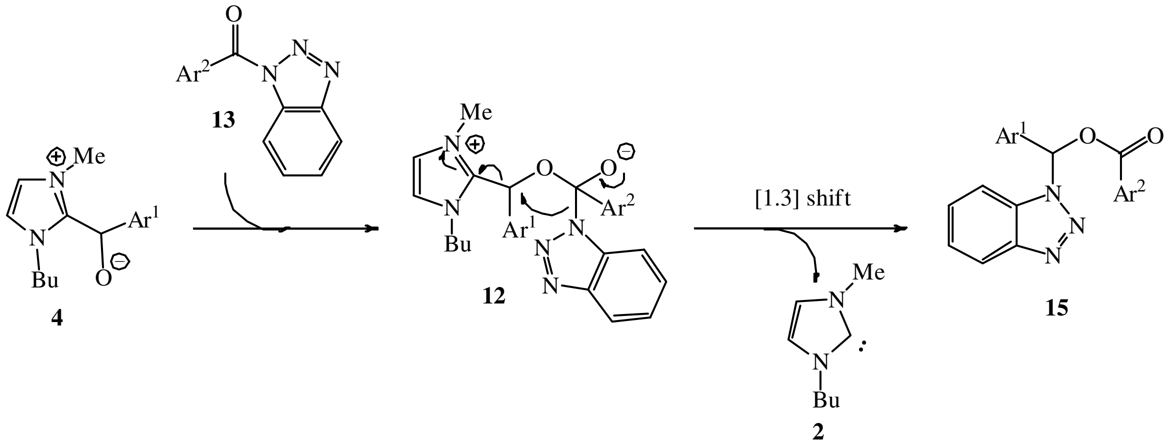

Scheme-IV: Plausible mechanism for the formation of 1*H*-1,2,3-benzotriazol-1-yl(aryl)methyl esters **15**

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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