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The *N*-heterocyclic carbene-catalyzed cross-coupling of aromatic aldehydes with *N*-aroylbenzotriazoles: A novel approach to synthesis of diaryl 1,2-diketones

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ABSTRACT

The new NHC-catalyzed cross-coupling between N-acylbenzotrizoles and aromatic aldehydes is described. This reaction offers a novel approach to synthesis of symmetrical and unsymmetrical diaryl 1,2-diketones.

Key words: *N*-Aroylbenzotrizoles, NHCs, diaryl 1,2-diketones

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INTRODUCTION

N-Acylbenzotrizoles are well recognized as acylating reagents. They have been used as such reagents for *N*-acylation of amines [1], *O*-acylation of aldehydes [2], and *C*-acylation of ketones [3], and Grignard and heteroaryllithium reagents [4]. Intriguingly, the analogous reaction with the Breslow intermediates, generated *in situ* from aromatic aldehydes and *N*-heterocyclic carbenes (NHCs), has never been reported. As part of our continue effort to explore the reactivity of carbene resulted from deprotonation of *N*,*N*-dimethylbenzimidazolium iodide [5-8], we report herein, for the first time, the NHC-catalyzed cross-coupling of aromatic aldehydes with *N*-aroylbenzotriazoles. This cross-coupling offers a novel approach to synthesis of symmetrical and unsymmetrical diaryl 1,2-diketones, a class of compounds that exhibit antitumor activity [9] and inhibition of mammalian carboxylesterases [10].

MATERIALS AND METHODS

Solvents were purified according to standard methods prior to use, while all other chemicals were used as received from commercial sources. Melting points were determined on a Sanyo Gallenkamp melting point apparatus and compared with those of known samples. IR spectra were measured with a Perkin Elmer Spectrum One FT-IR Spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a VARIAN MERCURY plus (400 MHz FT NMR).
N,*N*-Dimethylbenzimidazolium iodide was prepared following our previously reported procedure [11].

General procedure for the preparation of *N*-acylbenzotriazoles 2
Benzotriazole (**1**) (2.38 g, 20.0 mmol) and potassium carbonate (5.53 g, 40.0 mmol) and an appropriate acyl halide (24.0 mmol) were ground altogether with a pestle and mortar at room temperature for 1-2 hours. After completion of the reaction, as indicated by TLC (50% dichloromethane/hexane), the reaction mixture was extracted with dichloromethane (3 × 30 ml). The extracts were dried (anh.Na_2SO_4) and concentrated at reduced pressure. The residue was purified by PLC (50% dichloromethane/hexane) to give the *N*-acylbenzotriazole.

***N*-(4-Methoxybenzoyl)-1H-benzotriazole (2a) [1]**
White crystals; mp 95-97 °C; IR (KBr) (ν): 3076, 2994, 2842, 1697, 1607, 1513, 1371, 1270, 1180, 1046, 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.37 (1H, d, *J* = 8.0 Hz, 7-*H*), 8.29 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 8.16 (1H, d, *J* = 8.0 Hz, 4-*H*), 7.69 (1H, t, *J* = 8.0 Hz, 6-*H*), 7.54 (1H, t, *J* = 8.0 Hz, 5-*H*), 7.06 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 3.93 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.6, 113.9, 114.8, 120.1, 123.5, 126.1, 130.1, 132.6, 134.4, 145.7, 164.2, 165.7.

***N*-(4-Chlorobenzoyl)-1H-benzotriazole (2b) [1]**
White crystals; mp 136-138 °C; IR (KBr) (ν): 3065, 2930, 1717, 1594, 1488, 1371, 1266, 1026 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.39 (1H, d, *J* = 8.4 Hz, 7-*H*), 8.22 (1H, d, *J* = 8.8 Hz, 2′-*H*), 8.18 (1H, d, *J* = 8.4 Hz, 4-*H*), 8.08 (1H, d, *J* = 8.8 Hz, 6′-*H*), 7.73 (1H, t, *J* = 8.4 Hz, 6-*H*), 7.58 (1H, t, *J* = 8.4 Hz, 5-*H*), 7.57 (1H, d, *J* = 8.8 Hz, 3′-*H*), 7.51 (1H, d, *J* = 8.8 Hz, 5′-*H*); ^{13}C NMR ($CDCl_3$) δ: 114.8, 120.3, 126.5, 128.8, 129.4, 130.6, 131.9, 133.2, 140.4, 145.8, 161.3.

***N*-Propionyl-1H-benzotriazole (2c) [12]**
White crystals; mp 79-81 °C; IR (KBr) (ν): 2983, 2938, 1739, 1599, 1455, 1382, 1209, 1173, 1069, 776 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.29 (1H, d, *J* = 8.0 Hz, 7-*H*), 8.11 (1H, d, *J* = 8.0 Hz, 4-*H*), 7.65 (1H, t, *J* = 8.0 Hz, 6-*H*), 7.50 (1H, t, *J* = 8.0 Hz, 5-*H*), 3.46 (2H, q, *J* = 7.6 Hz, CH_2), 1.42 (3H, t, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 8.3, 29.1, 114.4, 120.1, 126.0, 130.3, 131.1, 146.1, 173.3.

General procedure for the cross-coupling between aromatic aldehydes and *N*-acylbenzotriazoles in the presence of *N*,*N*-dimethylbenzimidazolium iodide and DBU in THF
A stirred solution of *N*,*N*-dimethylbenzimidazolium iodide (**4**) (0.137 g, 0.5 mmol), aromatic aldehyde (1.0 mmol) and *N*-acylbenzotriazole (2.0 mmol) in THF (5 ml) was heated at reflux for 0.5 hour. DBU (0.152 g, 1.0 mmol) was then added and reflux was continued for a further 16-20 hours, as indicated by TLC (50% dichloromethane/hexane). The reaction mixture was extracted with dichloromethane (3 × 30 ml) and the combined organic extracts was dried (anh.Na_2SO_4). Evaporation of the solvent gave the crude products, which were purified by PLC (50% dichloromethane/hexane).

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (5a) [13]
Yellow solid; mp 65-66 °C; IR (KBr) (ν): 3065, 3009, 2957, 2928, 2850, 1677, 1597, 1451, 1265, 1166, 1097, 1026, 1167 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.97 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.95 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.65 (1H, t, *J* = 8.0 Hz, 4′-*H*), 7.51 (2H, t, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 6.98 (2H, d, *J* = 8.8 Hz, 3-H and 5-*H*), 3.89 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.6, 114.4, 126.1, 128.9, 129.9, 132.4, 133.2, 134.7, 165.0, 193.1, 194.8.

1-(4-Chlorophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (5b)
Yellow liquid; IR (neat) (ν): 3095, 2968, 2924, 1666, 1572, 1510, 1487, 1313, 1265, 1167, 1094, 879, 743 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.94 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.92 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.48 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*), 6.98 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 3.89 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.6, 114.4, 125.9, 129.3, 131.2, 131.6, 132.4, 141.3, 165.1, 192.4, 193.3.

1-(4-Fluorophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (5c)
Yellow liquid; IR (neat) (ν): 3074, 3007, 2958, 2925, 1668, 1656, 1601, 1573, 1270, 1176 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.01 (2H, dd, *J* = 8.4 and 6.0 Hz, 2-*H* and 6-*H*), 7.94 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.18 (2H, t, *J* = 8.4 Hz, 3-*H* and 5-*H*), 6.98 (2H, d, *J* = 8.8 Hz, 3′- and 5′-*H*), 3.89 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.6, 114.4, 116.2, 116.4, 126.0, 129.7, 132.4, 132.6, 132.7, 132.8, 165.1, 165.4, 167.9, 192.6, 193.0.

1-(4-Methoxyphenyl)-2-p-tolylethane-1,2-dione (5d)
Yellow liquid; IR (neat) (ν): 2929, 2850, 1666, 1596, 1510, 1456, 1309, 1260, 1024 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.94 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.86 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.30 (2H, d, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 6.97 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 3.88 (3H, s, Ar-OCH_3), 2.43 (3H, s, Ar-CH_3); ^{13}C NMR ($CDCl_3$) δ: 21.9, 55.6, 114.3, 126.2, 129.6, 130.0, 130.8, 132.3, 145.9, 164.9, 193.3, 194.6.

4,4′-Dimethoxybenzil (5e) [14]
Yellow solid; mp 132-134 °C; IR (KBr) (ν): 2959, 2849, 1655, 1598, 1572, 1509, 1424, 1312, 1263, 1161, 1016 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.95 (4H, d, *J* = 8.8 Hz, 2-*H*, 6-*H*, 2′-*H* and 6′-*H*), 6.97 (4H, d, *J* = 8.8 Hz, 3-*H*, 5-*H*, 3′-*H* and 5′-*H*), 3.89 (6H, s, 2(Ar-OCH_3)); ^{13}C NMR ($CDCl_3$) δ: 55.6, 114.3, 126.4, 132.4, 164.9, 193.5.

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (5f) [15]
Yellow crystals; mp 69-71 °C; IR (KBr) (ν): 3092, 3065, 2924, 2854, 1668, 1587, 1449, 1320, 1209, 834, 712 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.93 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.91 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.68 (1H, t, *J* = 8.0 Hz, 4′-*H*), 7.53 (2H, d, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 7.50 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*); ^{13}C NMR ($CDCl_3$) δ: 129.0, 129.4, 129.9, 131.2, 131.4, 132.8, 135.0, 141.6, 193.0, 193.8.

4,4′-Dichlorobenzil (5g) [16]
Yellow crystals; mp 197-198 °C; IR (KBr) (ν): 3094, 2925, 1661, 1587, 1486, 1317, 1210, 1094 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.91 (4H, d, *J* = 8.4 Hz, 2-*H*, 6-*H*, 2′-*H* and 6′-*H*), 7.50 (4H, d, *J* = 8.4 Hz, 3-*H*, 5-*H*, 3′-*H* and 5′-*H*); ^{13}C NMR ($CDCl_3$) δ: 129.5, 131.2, 131.3, 141.8, 192.3.

1-(4-Chlorophenyl)-2-(4-fluorophenyl)ethane-1,2-dione (5h)
Yellow liquid; IR (neat) (ν): 3075, 2960, 2925, 2855, 1664, 1595, 1455, 1232, 1157, 841, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.02 (2H, dd, *J* = 8.8 and 5.2 Hz, 2′-*H* and 6′-*H*), 7.92 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.50 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*), 7.20 (2H, t, *J* = 8.8 Hz, 3′-*H* and 5′-*H*); ^{13}C NMR ($CDCl_3$) δ: 116.3, 116.5, 128.8, 129.3, 129.5, 131.2, 131.5, 132.7, 132.8, 141.7, 165.6, 168.2, 192.0, 192.5.

1-(4-Chlorophenyl)-2-p-tolylethane-1,2-dione (5i)
Yellow liquid; IR (neat) (ν): 3093, 3065, 2924, 2856, 1663, 1585, 1484, 1315, 1211, 1171, 1091, 831, 736 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.92 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.86 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.48 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*), 7.31 (2H, d, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 2.44 (3H, s, Ar-CH_3); ^{13}C NMR ($CDCl_3$) δ: 21.9, 129.4, 129.8, 130.0, 130.4, 131.2, 131.5, 141.4, 146.4, 193.2, 193.5.

1-(4-Chlorophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (5j)
Yellow liquid; IR (neat) (ν): 3095, 2968, 2924, 1666, 1572, 1510, 1487, 1313, 1265, 1167, 1094, 879, 743 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.94 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.92 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.48 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*), 6.98 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 3.89 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.6, 114.4, 125.9, 129.3, 131.2, 131.6, 132.4, 141.3, 165.1, 192.4, 193.3.

1*H*-1,2,3-Benzotriazol-1-yl(phenyl)methyl 4-methoxybenzoate (6a)
Yellow liquid; IR (neat) (ν): 3066, 2963, 2924, 2841, 1731, 1605, 1512, 1454, 1255, 1168 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.73 (1H, s, ArC*H*), 8.08 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 8.07 (1H, d, *J* = 7.6 Hz, 7′-*H*), 7.50-7.54 (2H, m, 4′-*H*, 2″-*H* and 6″-*H*), 7.40-7.44 (4H, m, 6′-*H*, 3″-*H*, 4″-*H* and 5″-*H*), 7.34 (1H, t, *J* = 7.6 Hz, 5′-*H*), 6.91 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 3.82 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.5, 80.6, 110.7, 114.0, 120.2, 120.7, 124.4, 126.3, 128.1, 128.9, 129.6, 132.1, 132.2, 134.5, 146.3, 164.1, 164.2.

1*H*-1,2,3-Benzotriazol-1-yl(4-chlorophenyl)methyl 4-methoxybenzoate (6b)
Yellow liquid; IR (neat) (ν): 3071, 2961, 2937, 2845, 1725, 1605, 1579, 1453, 1257, 1171 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.67 (1H, s, ArC*H*), 8.07 (1H, d, *J* = 7.6 Hz, 7′-*H*), 8.05 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.56 (1H, d, *J* = 7.6 Hz, 4′-*H*), 7.46 (2H, d, *J* = 8.0 Hz, 3″-*H* and 5″-*H*), 7.44 (1H, t, *J* = 7.6 Hz, 6′-*H*), 7.34-7.39 (3H, m, 5′-*H*, 2″-*H* and 6″-*H*), 6.91 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*), 3.83 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.5, 79.9, 110.5, 114.0, 120.3, 120.4, 124.5, 127.8, 128.3, 129.2, 132.0, 132.2, 133.1, 135.7, 146.3, 164.0, 164.3.

1*H*-1,2,3-Benzotriazol-1-yl(4-fluorophenyl)methyl 4-methoxybenzoate (6c)
Yellow liquid; IR (neat) (ν): 3078, 3040, 2959, 1725, 1606, 1579, 1451, 1263, 1171, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.67 (1H, s, ArC*H*), 8.08 (1H, d, *J* = 8.0 Hz, 7′-*H*), 8.06 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.56 (1H, d, *J* = 8.0 Hz, 4′-*H*), 7.52 (2H, dd, *J* = 8.8 and 5.2 Hz, 2″-*H* and 6″-*H*) 7.45 (1H, t, *J* = 8.0 Hz, 6′-*H*), 7.37 (2H, t, *J* = 8.0 Hz, 5′-*H*), 7.12 (2H, t, *J* = 8.8 Hz, 3″-*H* and 5″-*H*), 6.92 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 3.84 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.5, 80.0, 110.5, 114.0, 115.9, 116.1, 120.3, 120.5, 124.5, 128.2, 128.4, 128.5, 130.4, 130.5, 132.0, 130.2, 146.3, 162.0, 164.0, 164.3, 164.5.

1*H*-1,2,3-Benzotriazol-1-yl(4-methylphenyl)methyl 4-methoxybenzoate (6d)
Colorless liquid; IR (neat) (ν): 3064, 2961, 2841, 1731, 1606, 1581, 1493, 1259, 1167 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.70 (1H, s, ArC*H*), 8.06 (1H, d, *J* = 7.6 Hz, 7′-*H*), 8.07 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.55 (1H, d, *J* = 7.6 Hz, 4′-*H*), 7.39-7.43 (3H, m, 6′-*H*, 2″-*H* and 6″-*H*), 7.33 (1H, t, *J* = 7.6 Hz, 5′-*H*), 7.20 (2H, d, *J* = 8.4 Hz, 3″-*H* and 5″-*H*), 6.90 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 3.80 (3H, s, Ar-OCH_3), 2.33 (3H, s, Ar-CH_3); ^{13}C NMR ($CDCl_3$) δ: 21.2, 55.5, 80.7, 110.8, 114.0, 120.1, 120.7, 124.4, 126.2, 128.0, 129.6, 131.5, 132.1, 132.2, 139.6, 146.3, 164.1, 164.2.

1*H*-1,2,3-Benzotriazol-1-yl(4-methoxyphenyl)methyl 4-methoxybenzoate (6e)
Colorless liquid; IR (neat) (ν): 3072, 3006, 2935, 2840, 1731, 1606, 1515, 1493, 1166 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.67 (1H, s, ArC*H*), 8.06 (3H, d, *J* = 8.8 Hz, 2-*H*, 6-*H* and 7′-*H*), 7.54 (1H, d, *J* = 8.8 Hz, 4′-*H*), 7.40-7.47 (3H, m, 2′′-*H* and 6′′-*H* and 6′-*H*), 7.34 (1H, t, *J* = 8.8 Hz, 5′-*H*), 6.93 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 6.91 (2H, d, *J* = 8.8 Hz, 3′′-*H* and 5′′-*H*), 3.82 (3H, s, Ar-OCH_3), 3.78 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.3, 55.5, 80.6, 110.8, 113.6, 114.0, 114.3, 120.1, 120.8, 124.3, 126.5, 127.7, 128.0, 132.0, 132.2, 146.3, 160.5, 164.1.

1*H*-1,2,3-Benzotriazol-1-yl(phenyl)methyl 4-chlorobenzoate (6f)
Yellow liquid; IR (neat) (ν): 3103, 2965, 2924, 2853, 1734, 1590, 1492, 1453, 1402, 1256, 1176, 1072, 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.72 (1H, s, ArC*H*), 8.09 (1H, d, *J* = 7.6 Hz, 7′-*H*), 8.06 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.52-7.49 (2H, m, Ar*H*), 7.47-7.43 (7H, m, Ar*H*), 7.38 (1H, t, *J* = 7.6 Hz, 5′-*H*); ^{13}C NMR ($CDCl_3$) δ: 80.9, 110.5, 120.3, 124.4, 126.2, 127.0, 128.2, 129.0, 129.1, 129.8, 131.4, 132.0, 134.0, 140.6, 146.4, 163.7.

1*H*-1,2,3-Benzotriazol-1-yl(4-chlorophenyl)methyl 4-chlorobenzoate (6g)
Colorless liquid; IR (neat) (ν): 3093, 3063, 2963, 2925, 1736, 1591, 1490, 1451, 1257, 1174, 1067, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.10 (1H, s, ArC*H*), 8.09 (1H, d, *J* = 7.6 Hz, 7′-*H*), 8.04 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.53-7.38 (9H, m, Ar*H*); ^{13}C NMR ($CDCl_3$) δ: 80.2, 110.3, 120.5, 124.6, 126.7, 127.8, 128.4, 129.1, 129.3, 131.4, 131.9, 132.6, 136.0, 140.8, 146.4, 163.6.

1*H*-1,2,3-Benzotriazol-1-yl(4-fluorophenyl)methyl 4-chlorobenzoate (6h)
Colorless liquid; IR (neat) (ν): 3101, 3071, 2963, 2926, 1735, 1591, 1452, 1322, 1258, 1157, 1073, 804, 751 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.66 (1H, s, ArC*H*), 8.09 (1H, d, *J* = 7.6 Hz, 7′-*H*), 8.04 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.55-7.51 (3H, m, 3-*H*, 5-*H* and 6′-*H*), 7.48 (1H, d, *J* = 7.6 Hz, 4′-*H*), 7.44 (2H, d, *J* = 8.8 Hz, 2′′-*H* and 6′′-*H*), 7.39 (1H, t, *J* = 7.6 Hz, 5′-*H*), 7.14 (2H, t, *J* = 8.8 Hz, 3′′-*H* and 5′′-*H*); ^{13}C NMR ($CDCl_3$) δ: 80.3, 110.3, 116.0, 116.2, 120.4, 124.6, 126.8, 128.3, 128.4, 128.5, 129.1, 130.0, 131.4, 132.0, 132.8, 140.8, 146.3, 162.1, 163.6, 164.6.

1*H*-1,2,3-Benzotriazol-1-yl(4-methylphenyl)methyl 4-chlorobenzoate (6i)
Colorless liquid; IR (neat) (ν): 3094, 3068, 2963, 2920, 1731, 1592, 1452, 1322, 1258, 1174, 1072, 829, 793 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.70 (1H, s, ArC*H*), 8.08 (1H, d, *J* = 7.6 Hz, 7′-*H*), 8.05 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.51 (1H, d, *J* = 7.6 Hz, 4′-*H*), 7.40-7.45 (5H, m, 6′-*H*, 3-*H*, 5-*H*, 2′′-*H* and 6′′-*H*), 7.36 (1H, t, *J* = 7.6 Hz, 5′-*H*), 7.23 (2H, d, *J* = 8.0 Hz, 3′′-*H* and 5′′-*H*), 2.36 (3H, s, Ar-CH_3); ^{13}C NMR ($CDCl_3$) δ: 21.2, 81.1, 110.6, 120.3, 124.4, 126.2, 127.0, 128.1, 129.0, 129.7, 131.1, 131.4, 132.0, 130.8, 140.6, 146.4, 163.7.

1*H*-1,2,3-Benzotriazol-1-yl(4-methoxyphenyl)methyl 4-chlorobenzoate (6j)
Colorless liquid; IR (neat) (ν): 3093, 3066, 2997, 2958, 1729, 1592, 1452, 1351, 1255, 1175, 1069, 836, 799 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.65 (1H, s, ArC*H*), 8.09 (1H, d, *J* = 7.6 Hz, 7′-*H*), 8.04 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.42-7.51 (6H, m, 6′-*H*, 4′-*H*, 3-*H*, 5-*H*, 2′′-*H* and 6′′-*H*), 7.37 (1H, t, *J* = 7.6 Hz, 5′-*H*), 6.95 (2H, d, *J* = 8.8 Hz, 3′′-*H* and 5′′-*H*), 3.82 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.4, 81.0, 110.5, 114.3, 120.3, 124.4, 126.0, 127.0, 127.8, 128.1, 129.0, 131.4, 132.0, 140.6, 146.3, 160.6, 163.7.

1*H*-1,2,3-Benzotriazol-1-yl(phenyl)methyl propanoate (6k)
Yellow liquid; IR (neat) (ν): 3066, 2982, 2943, 1755, 1614, 1591, 1452, 1336, 1283, 1144 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.50 (1H, s, ArC*H*), 8.06 (2H, d, *J* = 8.4 Hz, 7-*H*), 7.32-7.43 (9H, m, Ar*H*), 2.43-2.57 (2H, m, CH_2), 1.17 (3H, t, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 8.8, 27.3, 80.2, 110.7, 120.2, 124.4, 126.2, 128.0, 128.9, 129.6, 132.0, 134.2, 146.3, 172.3.

1*H*-1,2,3-Benzotriazol-1-yl(4-chlorophenyl)methyl propanoate (6l)
Yellow liquid; IR (neat) (ν): 3093, 2981, 2943, 1737, 1696, 1590, 1490, 1285, 1169 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.44 (1H, s, ArC*H*), 8.07 (1H, d, *J* = 8.4 Hz, 7-*H*), 7.44 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.35-7.40 (5H, m, Ar*H*), 2.42-2.57 (2H, m, CH_2), 1.16 (3H, t, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 8.7, 27.3, 79.5, 110.4, 120.3, 124.5, 127.7, 128.2, 129.1, 131.9, 132.8, 135.7, 146.3, 172.2.

1*H*-1,2,3-Benzotriazol-1-yl(4-fluorophenyl)methyl propanoate (6m)
Yellow liquid; IR (neat) (ν): 3073, 2957, 2925, 2854, 1758, 1733, 1608, 1512, 1453, 1278, 1144 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.44 (1H, s, ArC*H*), 8.06 (1H, d, *J* = 8.4 Hz, 7-*H*), 7.36-7.47 (5H, m, Ar*H*), 7.12 (2H, t, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 2.42-2.57 (2H, m, CH_2), 1.17 (3H, t, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 8.7, 27.3, 79.6, 110.4, 115.9, 116.1, 120.3, 124.5, 128.1, 128.3, 128.4, 128.5, 130.1, 131.9, 146.3, 162.0, 164.5, 172.2.

1*H*-1,2,3-Benzotriazol-1-yl(4-methylphenyl)methyl propanoate (6n)
Yellow liquid; IR (neat) (ν): 3093, 3069, 2935, 2840, 1756, 1614, 1516, 1492, 1452, 1287, 1148 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.46 (1H, s, ArC*H*), 8.07 (1H, d, *J* = 8.4 Hz, 7-*H*), 7.35-7.42 (3H, m, Ar*H*), 7.33 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.21 (2H, d, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 2.43-2.57 (2H, m, CH_2), 2.35 (3H, s, Ar-CH_3), 1.17 (3H, t, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 8.8, 21.2, 27.3, 80.3, 110.7, 120.1, 124.3, 126.1, 127.9, 129.5, 130.2, 131.9, 139.7, 146.3, 172.3.

1*H*-1,2,3-Benzotriazol-1-yl(4-methoxyphenyl)methyl propanoate (6o)
Yellow liquid; IR (neat) (ν): 3068, 2954, 2923, 2851, 1731, 1676, 1600, 1513, 1425, 1296, 1163 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.43 (1H, s, ArC*H*), 8.04 (1H, d, *J* = 8.4 Hz, 7-*H*), 7.31-7.43 (5H, m, Ar*H*), 6.90 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 3.78 (3H, s, Ar-OCH_3), 2.40-2.52 (2H, m, CH_2), 1.15 (3H, t, *J* = 7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 8.7, 27.4, 55.3, 80.2, 110.7, 114.2, 120.2, 124.3, 126.3, 127.7, 127.9, 131.9, 146.3, 160.5, 172.3.

Benzoin (14a) [17]
White crystals; mp 134-136 °C; IR (KBr) (ν): 3413, 3058, 3027, 2931, 1678, 1595, 1449, 1262, 1206, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.91(2H, d, *J* = 7.6 Hz, 2-*H* and 6-*H*), 7.52 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.39 (2H, t, *J* = 7.6 Hz, 3-*H* and 5-*H*), 7.26-7.33 (5H, m, Ar*H*), 5.95 (1H, s, C*H*), 4.54 (1H, br s, O*H*); ^{13}C NMR ($CDCl_3$) δ: 76.2, 127.8, 128.6, 128.7, 129.1, 133.5, 133.9, 139.0, 198.9.

4,4′-Dichlorobenzoin (14b) [17]
White crystals; mp 87-88 °C; IR (KBr) (ν): 3425, 3072, 2929, 1674, 1590, 1488, 1401, 1252, 1207, 1093 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.75 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.32 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*), 7.24 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.18 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 5.81 (1H, s, C*H*); ^{13}C NMR ($CDCl_3$) δ: 77.3, 129.1, 129.2, 129.4, 130.4, 131.6, 134.8, 137.2, 140.7, 197.5.

4,4′-Dimethoxybenzoin (14e) [17]
White crystals; mp 106-108 °C; IR (KBr) (ν): 3454, 3005, 2936, 2839, 1668, 1598, 1462, 1307, 1252, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.89 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.24 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 6.85 (2H, d, *J* = 6.0 Hz, 2′-*H* and 6′-*H*), 6.83 (2H, d, *J* = 6.0 Hz, 3′-*H* and 5′-*H*), 5.85 (1H, s, C*H*), 3.81 (3H, s, Ar-OCH_3), 3.74 (3H, s, Ar-OCH_3); ^{13}C NMR ($CDCl_3$) δ: 55.2, 55.5, 75.2, 113.9, 114.5, 126.3, 129.0, 131.6, 131.8, 159.6, 164.0, 197.3.

***O*-Propionylbenzoin (15a)**
Yellow liquid; IR (neat) (ν): 3065, 3035, 2980, 2882, 1737, 1695, 1597, 1497, 1366, 1225, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.94 (2H, d, *J* = 7.6 Hz, 2-*H* and 6-*H*), 7.51 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.48 (2H, t, *J* = 7.6 Hz, 3-*H* and 5-*H*), 7.34-7.42 (5H, m, Ar′-*H*), 6.87 (1H, s, C*H*), 2.44-2.58 (2H, m, CH_2), 1.19 (3H, t, *J* = 7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 8.9, 27.3, 77.4, 128.6, 128.8, 129.1, 129.2, 133.4, 133.7, 134.7, 173.9, 194.0.

***O*-(Propionyl)-4,4′-dichlorobenzoin (15b)**
Yellow liquid; IR (neat) (ν): 3094, 3045, 2981, 2943, 1733, 1695, 1589, 1490, 1286, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.85 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.39 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 7.36 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 7.34 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 6.76 (1H, s, C*H*), 2.43-2.56 (2H, m, CH_2), 1.18 (3H, t, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 8.9, 27.3, 77.3, 129.1, 129.4, 129.8, 130.1, 131.9, 132.8, 135.6, 140.2, 173.8, 192.6.

***O*-(Propionyl)-4,4′-difluorobenzoin (15c)**
Yellow liquid; IR (neat) (ν): 3078, 3015, 2983, 2945, 2885, 1736, 1696, 1597, 1509, 1462, 1298, 1155cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.95 (2H, dd, *J* = 8.8 Hz and 5.2 Hz, 2-*H* and 6-*H*), 7.44 (2H, dd, *J* = 8.8 Hz and 5.6 Hz, 2′-*H* and 6′-*H*), 7.09 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 7.04 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 6.80 (1H, s, C*H*), 2.43-2.56 (2H, m, CH_2), 1.18 (3H, t, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 8.9, 27.3, 77.3, 115.8, 116.0, 116.1, 116.3, 129.4, 129.5, 130.4, 130.5, 130.9, 131.0, 131.4, 131.5, 162.0, 164.4, 164.6, 167.1, 173.9, 192.3.

***O*-(Propionyl)-4,4′-dimethylbenzoin (15d)**
Yellow liquid; IR (neat) (ν): 3032, 3006, 2921, 2857, 1717, 1692, 1608, 1450, 1277, 1177. 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.84 (2H, d, *J* = 8.0 Hz, 2-*H* and 6-*H*), 7.34 (2H, d, *J* = 8.0 Hz, 3-*H* and 5-*H*), 7.18 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.16 (2H, d, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 6.83 (1H, s, C*H*), 2.42-2.57 (2H, m, CH_2), 2.35 (3H, s, Ar-CH_3), 2.31 (3H, s, Ar-CH_3), 1.18 (3H, t, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 9.0, 21.2, 21.6, 27.4, 77.3, 128.6, 128.9, 129.3, 129.8, 131.0, 132.1, 139.2, 144.3, 174.0, 193.5.

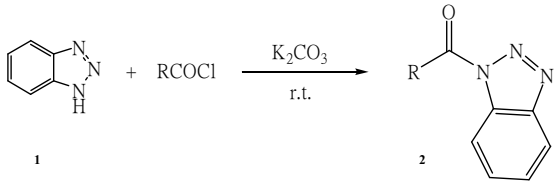
***O*-(Propionyl)-4,4′-dimethoxybenzoin (15e)**

Yellow liquid; IR (neat) (ν): 2984, 2939, 1746, 1697, 1588, 1493, 1361, 1151, 1011 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.85 (2H, d, *J* = 8.0 Hz, 2-*H* and 6-*H*), 7.45 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.01 (2H, d, *J* = 8.0 Hz, 3-*H* and 5-*H*), 6.82 (2H, d, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 6.37 (1H, s, C*H*), 3.89 (3H, s, Ar-OCH_3), 3.83 (3H, s, Ar-OCH_3), 2.37-2.45 (2H, m, CH_2), 1.16 (3H, t, *J* = 8.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 8.7, 27.2, 55.3, 55.4, 73.2, 114.5, 114.6, 116.4, 124.0, 129.5, 129.6, 132.3, 161.1, 172.5, 194.9.

RESULTS AND DISCUSSION

It has been suggested that reactivity of *N*-aroylbenzotriazole is influenced by the substituent on the aromatic ring. With weak electron-withdrawing groups as bromine in the *para* position, the *N*-acylation of amines are promoted [18]. In our opinion, the increase of reactivity probably causes by the electron-donating effect from non-bonding electrons of bromine. Therefore, we decided to perform cross-coupling reactions of aromatic aldehydes with *N*-4-methoxybenzoylbenzotriazole (**2a**) and *N*-4-chlorobenzoylbenzotriazole (**2b**). Cross-coupling reactions between aromatic aldehydes and *N*-propionylbenzotriazole (**2c**) were also attempted.

N-Acylbenzotriazoles **2a-c** were readily obtained in 83-96% yields from treatment of benzotriazole (**1**) with the appropriate acid chloride and potassium carbonate in the absence of solvent at room temperature [12], as shown in Scheme 1.

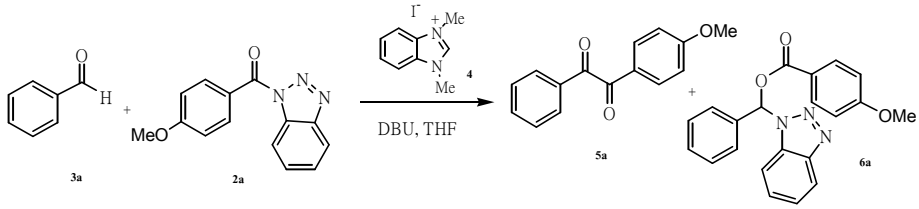


a; R = $MeOC_6H_5$, 83%
b; R = ClC_6H_5, 96%
c; R = CH_3CH_2, 83%

Scheme 1. Preparation of *N*-acylbenzotriazoles 2a-c

Our study commenced with the treatment of benzaldehyde (**3a**) with two equivalents of *N*-4-methoxybenzoylbenzotriazole (**2a**), in the presence of 20 mol% of *N*,*N*-dimethylbenzimidazolium iodide (**4**) and either NEt_3 or DBU, in CH_3CN at refluxing temperature. No reaction, however, occurred due to these attempts (Table 1, entries 1, 2). Although carrying out this treatment using NEt_3 as a base in THF at refluxing temperature also failed to give any reaction, the expected 1-(4-methoxyphenyl)-2-phenylethane-1,2-dione (**5a**) was delightedly obtained in 36% yield, along with 1*H*-1,2,3-benzotriazol-1-yl(phenyl)methyl 4-methoxybenzoate (**6a**) in 29% yield when NEt_3 was replaced by DBU (Table 1, entries 3, 4). The yield of ethane-1,2-dione **5a** increased to 47 and 50% when the amount of benzimidazolium salt **4** was increased from 20 mol% to 50 and 100 mol%, respectively (Table 1, entries 5, 6). The yield of benzotriazol-1-yl(phenyl)methyl ester **6a** also increased to 35 and 38% yields, respectively.

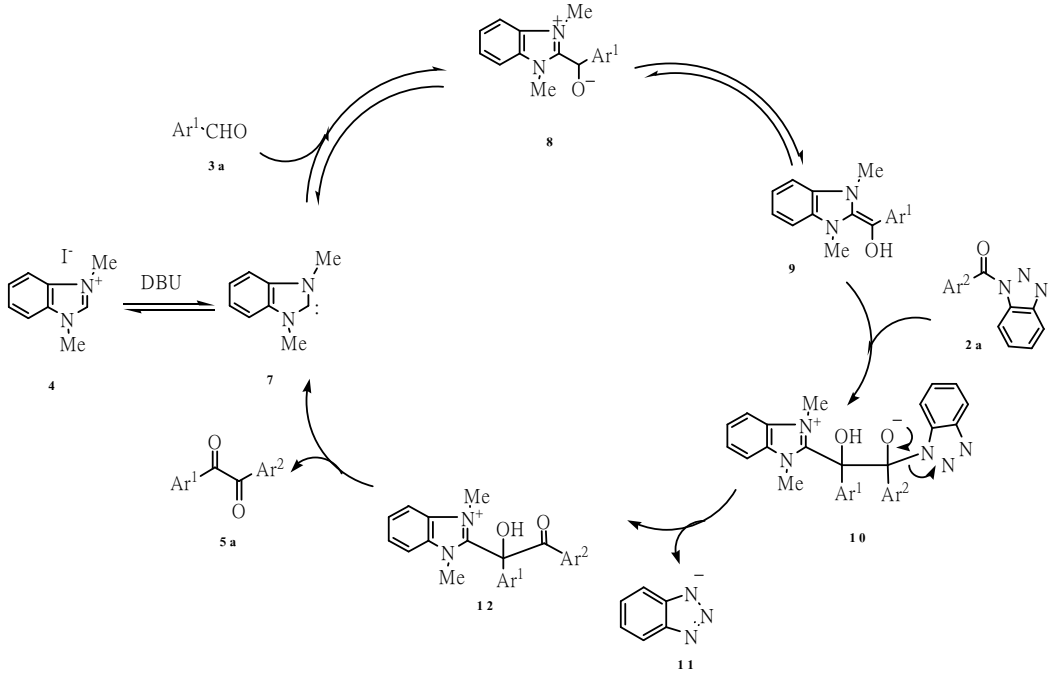
Table 1. Optimization for cross-coupling of benzaldehyde (3a) with *N*-4- methoxybenzoylbenzotriazole (2a)



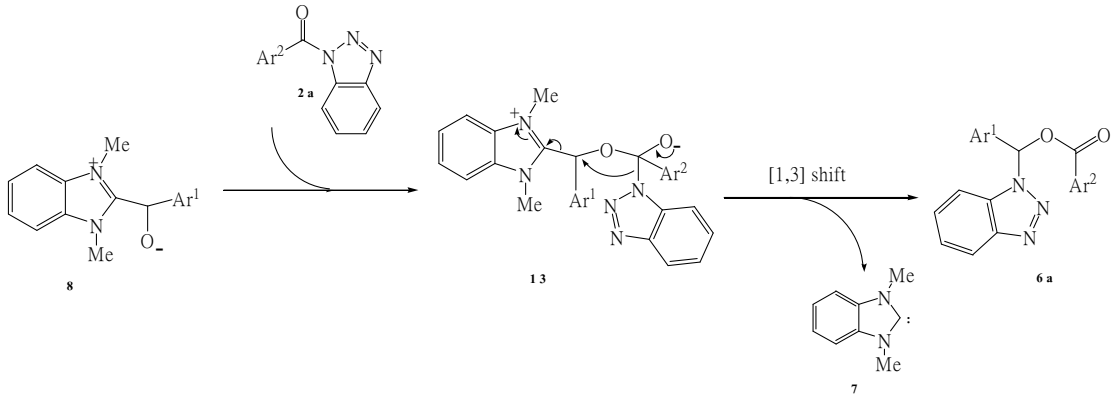
Entry	Base/ Solvent	%Mol of 4	%Yield (5a)	%Yield (6a)
1	TEA/ CH_3CN	20	-	-
2	DBU/ CH_3CN	20	-	-
3	TEA/ THF	20	-	-
4	DBU/ THF	20	36	29
5	DBU/ THF	50	47	35
6	DBU/ THF	100	50	38

A plausible catalytic cycle for the formation of unsymmetrical aril **5a** ($Ar^1 \neq Ar^2$) was proposed, as illustrated in Scheme 2. *N*,*N*-Dimethylbenzimidazol-2-ylidene (**7**), generated *in situ* from deprotonation of benzimidazolium salt **4** by DBU reacted with aromatic aldehyde **3a** to give the Breslow intermediate **9** which reacted with *N*-4-methoxybenzoylbenzotriazole (**2a**) to give the intermediate **10**. Collapse of the intermediate **10** followed by

liberation of benzimidazol-2-ylidene **7** from the resulting intermediate **12** gave aril **5a** and complete the catalytic cycle.



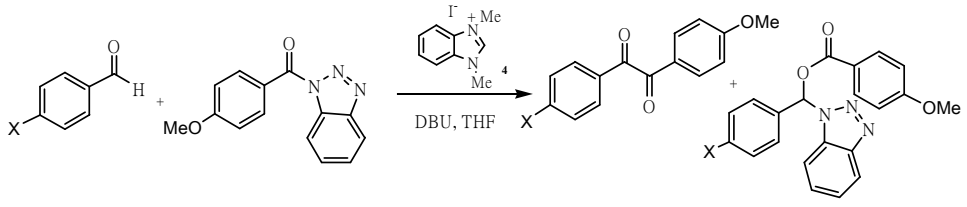
Scheme 2. Proposed catalytic cycle for cross-coupling between aromatic aldehyde 3a and *N*-4-methoxybenzoylbenzotriazole (2a)



Scheme 3. Pathway for the formation of aromatic acid 1*H*-1,2,3-benzotriazol-1-yl(phenyl)methyl ester 6a

The formation of aromatic acid 1*H*-1,2,3-benzotriazol-1-yl(aryl)methyl ester **6a** was rationalized by a pathway illustrated in Scheme 3. Accordingly, the aroylbenzotriazole **2a** underwent nucleophilic attack by the adduct **8** to give the alkoxy intermediate **13.** Subsequent [1,3] shift of benzotriazolyl group led to expulsion of benzimidazol-2-ylidene **7** to provide aromatic acid ester **6a**.

We had chosen cross-coupling of aromatic aldehyde **3a** with *N*-benzoylbenzotriazole **2a** in the presence of 50 mol% of benzimidazolium salt **4** and DBU in THF at reflux as the optimum conditions and performed this cross-coupling using aromatic aldehydes **3b-e** in place of **3a**. As shown in Scheme 4, the expected cross-coupling ethane-1,2-diones **5b-e** along with the corresponding 1*H*-1,2,3-benzotriazol-1-yl(aryl)methyl esters **6b-e** were obtained in satisfied yields.



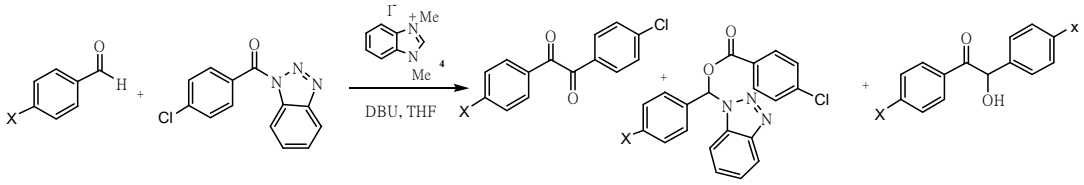
3b; X = Cl
3c; X = F
3d; X = Me
3e; X = OMe

2a

5b; 55% **6b**; 28%
5c; 65% **6c**; 27%
5d; 39% **6d**; 36%
5e; 35% **6e**; 33%

Scheme 4. Cross-coupling of aromatic aldehydes 3b-e with *N*-4-methoxybenzoylbenzotriazole (2a)

Treatment of *N*-4-chlorobenzoylbenzotriazole **2b** with aromatic aldehydes **3a-e** under the same conditions gave the expected cross-coupling ethane-1,2-diones **5f-j** together with the corresponding 1*H*-1,2,3-benzotriazol-1-yl(aryl)methyl 4-chlorobenzoates **6f-j** in satisfied yields, as illustrated in Scheme 5. Additionally, aroins **14a**,**b**,**e**, resulted from benzoin condensation, also occurred as minor side products.



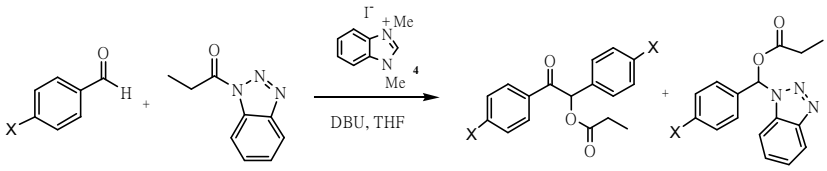
3a; X = H
3b; X = Cl
3c; X = F
3d; X = Me
3e; X = OMe

2b

5f; 54% **6f**; 21% **14a**; 5%
5g; 61% **6g**; 25% **14b**; 4%
5h; 70 % **6h**; 25% **14c**; 0%
5i; 40% **6i**; 27% **14d**; 0%
5j; 32% **6j**; 13% **14e**; 8%

Scheme 5. Cross-coupling of aromatic aldehydes 3a-e with *N*-4-chlorobenzoylbenzotriazole (2b)

No expected ethane-1,2-diketones was detected upon treatment of *N*-propionylbenzotriazole (**2c**) with aromatic aldehydes **3a-e**. Isolated products were corresponding *O*-propionylaroins **15a-e** and 1*H*-1,2,3-benzotriazol-1-yl(aryl)methyl propanoates **6k-o** as shown in Scheme 6.



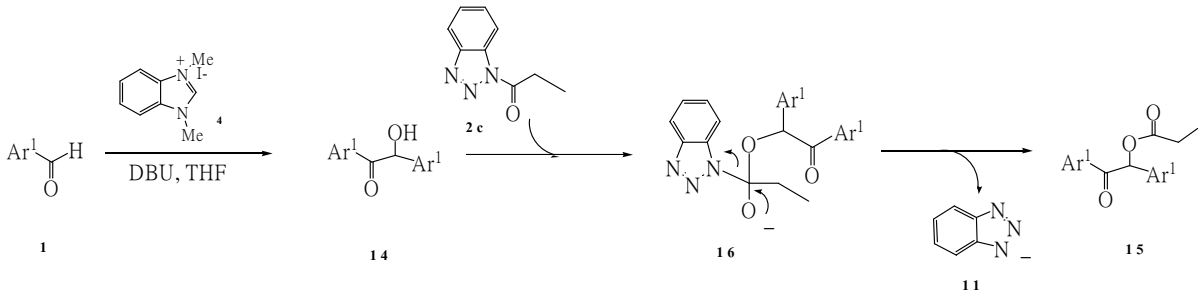
3a; X = H
3b; X = Cl
3c; X = F
3d; X = Me
3e; X = OMe

2c

15a; 45% **6k**; 43%
15b; 42% **6l**; 40%
15c; 46% **6m**; 41%
15d; 40% **6n**; 37%
15e; 41% **6o**; 39%

Scheme 6. Cross-coupling of aromatic aldehydes 3a-e with *N*-propionylbenzotriazole (2c)

The carbonyl group of *N*-acylbenzotriazole **2c** is less electrophilic than that of aldehydes **3a-e**, consequently, benzoin condensation occurred and resulting aroins **14a-e** transformed further to the corresponding *O*-propionylaroins **15a-e** by a proposed mechanism shown in Scheme 7.



Scheme 7. Proposed mechanism for *O*-propionylaroins 15a-e

CONCLUSION

N-Aroylbenzotriazoles bearing electron-donating group on aromatic ring underwent cross-coupling with aromatic aldehydes in the presence of *N,N*-dimethylbenzimidazolium iodide and DBU in THF to produce 1,2-diarylethane-1,2-diones in satisfied yields. Aromatic acid 1*H*-1,2,3-benzotriazolyl(aryl)methyl esters and some aroins were also obtained as minor side products. Treatment of *N*-propionylbenzotriazole with aromatic aldehydes, on the other hand, provided none of corresponding ethane-1,2-diones. Isolated products were *O*-propionylaroins and also 1*H*-1,2,3-benzotriazolyl(aryl)methyl propionates.

Acknowledgement
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