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Microwave Assisted Benzoin Condensation using *N*,*N*-Dimethylbenzimidazolium Iodide as an Efficient Greener Catalyst in Neutral Ionic Liquid [Bmim]BF_4

Baramee Phungpis[1,*], Pakin Noppawan[2] and Kanokkan Worawut[1]

[1]Faculty of Natural Resources, Rajamangala University of Technology Isan Sakonnakhon Campus, Sakon Nakhon 47160, Thailand
[2]Department of Chemistry, Faculty of Science, Mahasarakham University, Maha Sarakham 44150, Thailand

*Corresponding author: E-mail: barameephungpis@yahoo.com

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The utilization of *N*,*N*-dimethylbenzimidazolium iodide as a catalyst in [Bmim]BF_4 for benzoin condensation under microwave irradiation demonstrates its efficiency and eco-friendliness. This method enables the synthesis of α-hydroxy carbonyl compounds from various aromatic and heteroaromatic aldehydes with significant yields, ranging from good to high (89-96%). The reactions proceed swiftly, yielding no detectable byproducts. Moreover, the recycled reaction media, comprising benzimidazolium salt and NaOH after extraction, can be reused multiple times without a significant loss of efficiency.

Keywords: Benzoin, [Bmin]BF_4, *N*,*N*-Dimethylbenzimidazolium iodide, Hydroxy carbonyl, Microwave irradiation.

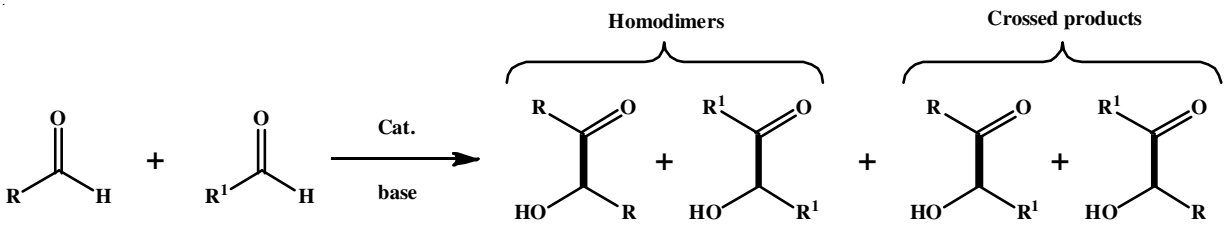
INTRODUCTION

Microwave-assisted synthesis is an innovative and eco-friendly method that offers a simple yet powerful technique for quickly and efficiently processing chemical products. This approach not only enhances yields but also ensures consistent results. By leveraging microwaves, it becomes possible to directly interact with molecules, facilitating the rapid generation of thermal conductivity. Consequently, this technology has proven successful in a wide range of laboratory applications, including solid-state chemistry, nanotechnology [1], nanomaterial synthesis [2-5], agglomerates, film coatings, gel beads, microspheres, tablets, nanosystems, tablets, solid dispersions [6] and organic synthesis [7]. Considering these remarkable advantages, microwave assisted synthesis presents an intriguing avenue for the advancement of processes in organic synthesis.

The benzoin condensation is a chemical reaction where aldehyde reacts to another aldehyde, resulting in the formation of homo-dimers. A fascinating variation of this reaction is the cross-benzoin condensation, which involves the coupling of different aldehydes or aldehydes with ketones, leading to the formation of cross products. In the case of the crossed intermolecular benzoin reaction, it is typical to observe that none of the four possible products, known as single α-hydroxy carbonyls or benzoin/acyloin dominates over the others [8] (**Scheme-I**).

Benzoin, an acyloin derivative, is widely employed in the diverse organic reactions, particularly in the synthesis of significant compounds for drug development. A notable characteristic of benzoin is its secondary alcohol group, which contributes to its antimicrobial properties. Through the conversion of benzoin into α-haloketones, a wide array of valuable compounds can be generated by reacting with various nucleophiles [9]. Moreover, benzoin intermediates can undergo substitution with crucial functional groups, enabling the synthesis of amino ketones and amino alcohols that possess necrotizing effects on mammalian tumors [10]. Additionally, substituted acyloin derivatives have emerged as vital intermediates in the production of non-prostanoid prostacyclin mimetics [11], as well as compounds exhibiting central nervous system (CNS) activity and acting as inhibitors of cholesterol biosynthesis [12]. These versatile applications highlight the significance of benzoin and its derivatives in pharmaceutical synthesis.

N,*N*-Dimethylbenzimidazolium iodide (**1**) stands out among various *N*-heterocyclic carbenes (NHCs) as an efficient catalyst for green organic synthesis, particularly in the benzoin reactions and Stetter reactions. It has demonstrated its effectiveness in promoting benzoin condensation under environmental friendly



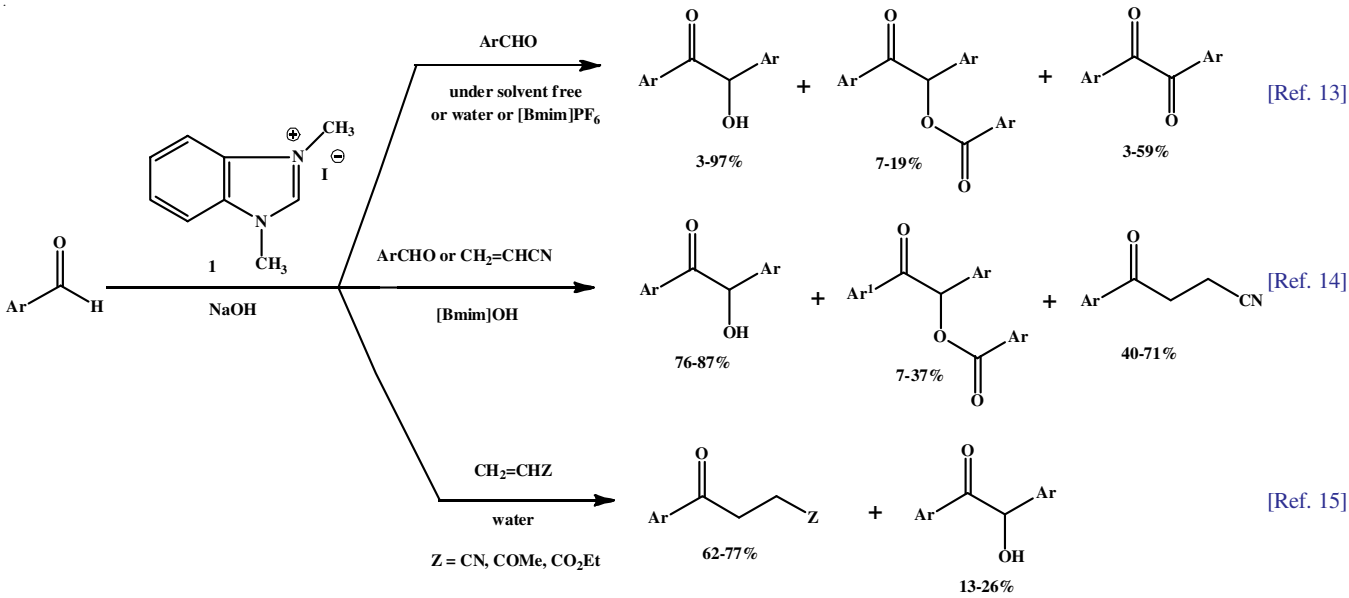
Scheme-I: Four possible products from intermolecular cross-benzoin condensation

conditions [13], facilitating benzoin condensation and Stetter reactions in [Bmim][OH] (an ionic liquid) [14] and enabling Stetter reactions in water [15] (**Scheme-II**). Moreover, in addition to its catalytic role in benzoin condensation and Stetter reactions, *N*,*N*-dimethylbenzimidazolium iodide (**1**) has successfully found as a green catalyst for the cross-coupling of aromatic aldehydes with unactivated imines [16] (**Scheme-III**). The versatility of *N*,*N*-dimethylbenzimidazolium iodide (**1**) as a catalyst in several green reaction processes is demonstrated, which enhances its potential uses in organic synthesis.

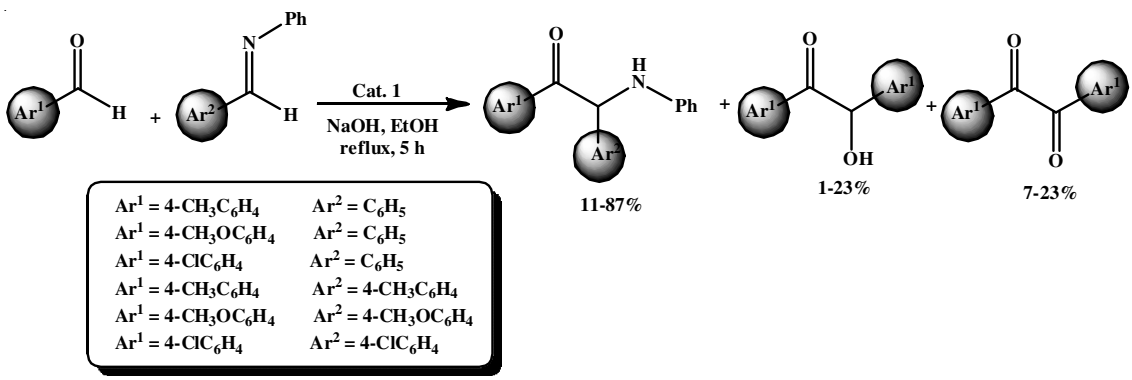
Based on the provided information, it is clear that *N*,*N*-dimethylbenzimidazolium iodide (**1**) is widely recognized as an efficient and commonly used green catalyst. Its primary application lies in the synthesis of organic compounds, including 1,2-adducts such as benzoin [13,14] and α-amino ketones [16], as well as 1,4-adducts like Stetter products [14,15]. As part of our ongoing investigation on the catalytic characteristics as well as the ability to be reusability of *N*,*N*-dimethylbenzimidazolium iodide (**1**), a study is conducted that focused on the benzoin condensation of aromatic aldehydes using microwave technique. This innovative approach offers an alternative method for producing acyloin derivatives, which play a crucial role in the drug development.

EXPERIMENTAL

The reactions were performed using a domestic microwave oven (Electrolux, EMM2023MW, 700 W, 2450 MHz). All chemicals, including the solvent, were of analytical grade



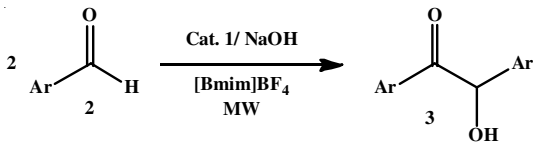
Scheme-II: *N*,*N*-Dimethylbenzimidazolium iodide (**1**) as a catalyst in benzoin condensation and Stetter reaction under green conditions



Scheme-III: *N*,*N*-Dimethylbenzimidazolium iodide (**1**) as a catalyst for cross-coupling between aromatic aldehydes and unactivated imines

and used without the need for additional purification. Melting points were determined using a BUCHI B-545 apparatus and compared with known samples. For NMR analysis, a Varian Mercury plus spectrophotometer operating at 400 MHz was utilized. Infrared (IR) spectra of the synthesized compounds were recorded using KBr pellets on a Shimadzu spectrometer in the 4000-400 cm^{-1} range.

Microwave enhanced benzoin condensation of aromatic/heteroaromatic aldehydes catalyzed by *N,N*-dimethylbenzimidazolium iodide (1) in [Bmim]BF_4: To conduct the reaction, a mixture of 1.0 mmol of aromatic/heteroaromatic aldehydes **2a-o**, *N,N*-dimethylbenzimidazolium iodide (**1**) and NaOH (0.2 mmol) in [Bmim]BF_4 (5 mL) was prepared. The mixture was then exposed to microwave irradiation at 700 W for 30-50 min. Subsequently, the reaction mixture was cooled to room temperature and extracted with diethyl ether (3 × 60 mL), followed by dilution with distilled water. The organic layer was then dried using Na_2SO_4 and concentrated under vacuum. To obtain pure α-hydroxy carbonyl compounds **3a-o**, the resulting mixture was purified using preparative TLC on silica gel, utilizing dichloromethane as eluent (**Scheme-IV**).



Scheme-IV: Microwave-assisted benzoin condensation catalyzed by *N,N*-dimethylbenzimidazolium (**1**) and NaOH in neutral ionic liquid [Bmim]BF_4

2-Hydroxy-1,2-diphenylethan-1-one (3a): R_f = 0.42 (50% ethyl acetate/hexane), white solid, yield: 91%, m.p.: 134-136 ºC (lit. 134-136 ºC) [17]; IR (KBr, ν_{max}, cm^{-1}): 3419 (O-H *str.*), 3055, 3027 (aromatic C-H *str.*), 2938 (aliphatic C-H *str.*), 1674 (C=O *str.*), 1595 (aromatic C=C *str.*) and 1263 (C-O *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 7.91 (2H, d, *J* = 8.0 Hz, 2-*H* and 6-*H*), 7.52 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.39 (2H, t, *J* = 7.8 Hz, 3-*H* and 5-*H*), 7.27-7.33 (5H, m, 2′-*H*, 3′-*H*, 4-*H*, 5′-*H* and 6′-*H*), 5.95 (1H, s, C*H*) and 4.54 (1H, s, O*H*); ^{13}C NMR ($CDCl_3$) δ ppm: 76.4, 128.1, 128.9, 129.0, 129.5, 129.5, 133.8, 134.6, 139.3 and 199.0.

1,2-*Bis*(4-fluorophenyl)-2-hydroxyethan-1-one (3b): R_f = 0.39 (50% ethyl acetate/hexane), white crystals, yield: 89%, m.p.: 81-82 ºC (lit. 81-82 ºC) [18]; IR (KBr, ν_{max}, cm^{-1}): 3451 (O-H *str.*), 3074 (aromatic C-H *str.*), 2927 (aliphatic C-H *str.*), 1676 (C=O *str.*), 1596, 1516 (aromatic C=C *str.*), 1231 (C-O *str.*) and 1019 (C-F *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 7.93 (2H, dd, *J* = 8.8 Hz and 5.2 Hz, 2-*H* and 6-*H*), 7.30 (2H, dd, *J* = 8.8 Hz and 5.2 Hz, 2′-*H* and 6′-*H*), 7.08 (2H, t, *J* = 8.8 Hz, 3-*H* and 5-*H*), 7.02 (2H, t, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 5.90 (1H, s, C*H*) and 4.54 (1H, s, O*H*); ^{13}C NMR ($CDCl_3$) δ ppm: 75.3, 116.0, 116.1, 116.2, 116.3, 129.4, 129.5, 129.6, 129.7, 131.8, 131.9, 134.7, 134.8, 161.5, 164.0, 164.8, 167.4 and 197.2.

1,2-*Bis*(4-chlorophenyl)-2-hydroxyethan-1-one (3c): R_f = 0.41 (50% ethyl acetate/hexane), white crystals, yield: 90%, m.p.: 87-88 ºC (lit. 88 ºC) [19]; IR (KBr, ν_{max}, cm^{-1}): 3425 (O-H *str.*), 3072 (aromatic C-H *str.*), 2929 (aliphatic C-H *str.*), 1674 (C=O *str.*), 1590 (aromatic C=C *str.*), 1262 (C-O *str.*) and 963 (C-Cl *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 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*) and 4.49 (1H, s, O*H*); ^{13}C NMR ($CDCl_3$) δ ppm: 77.3, 129.1, 129.2, 129.4, 130.4, 131.6, 134.8, 137.2, 140.7 and 197.5.

1,2-*Bis*(3-chlorophenyl)-2-hydroxyethan-1-one (3d): R_f = 0.42 (50% ethyl acetate/hexane), white solid, yield: 89%, m.p.: 78-79 ºC (lit. 78-79 ºC) [20]; IR (KBr, ν_{max}, cm^{-1}): 3439 (O-H *str.*), 3058 (aromatic C-H *str.*), 2932, 2860 (aliphatic C-H *str.*), 1675 (C=O *str.*), 1580 (aromatic C=C *str.*), 1219 (C-O *str.*) and 709 (C-Cl *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 7.74 (1H, d, *J* = 7.8 Hz, 6-*H*), 7.36 (1H, s, 2-*H*), 7.32 (1H, d, *J* = 8.4 Hz, 4-*H*), 7.27 (1H, t, *J* = 7.6 Hz 5-*H*), 7.28-7.26 (2H, m, 4′-*H* and 5′-*H*), 7.20 (1H, d, 6′-*H*), 5.88 (1H s, C*H*) and 4.45 (1H, s, O*H*); ^{13}C NMR ($CDCl_3$) δ ppm: 76.0, 126.2, 127.5, 128.2, 129.4, 129.4, 130.5, 130.9, 134.5, 135.1, 135.5, 135.6, 140.6 and 197.7.

1,2-*Bis*(4-bromophenyl)-2-hydroxyethan-1-one (3e): R_f = 0.42 (50% ethyl acetate/hexane), white solid, yield: 90%, m.p.: 93-94 ºC (lit. 93-94 ºC) [21]; IR (KBr, ν_{max}, cm^{-1}): 3418 (O-H *str.*), 3070 (aromatic C-H *str.*), 2922, 2849 (aliphatic C-H *str.*), 1678 (C=O *str.*), 1591 (aromatic C=C *str.*), 1209 (C-O *str.*) and 711 (C-Br *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 7.79-7.69 (2H, m, 2-*H* and 6-*H*), 7.59–7.51 (2H, m, 3′-*H* and 5′-*H*), 7.49-7.42 (2H, m, 3-*H* and 5-*H*), 7.21-7.14 (2H, m, 2′-*H* and 6′-*H*), 5.85 (1H, s, C*H*) and 4.47 (1H, s, O*H*); ^{13}C NMR ($CDCl_3$) δ ppm: 75.9, 123.3, 129.7, 129.9, 130.8, 132.3, 132.6, 132.8, 138.0 and 198.0.

2-Hydroxy-1,2-di-*p*-tolylethan-1-one (3f): R_f = 0.44 (50% ethyl acetate/hexane), white solid, yield: 95%, m.p.: 75-76 ºC (lit. 75-76 ºC) [22]; IR (KBr, ν_{max}, cm^{-1}): 3448 (O-H *str.*), 3030 (aromatic C-H *str.*), 2921 (aliphatic C-H *str.*), 1673 (C=O *str.*), 1607, 1542 (aromatic C=C *str.*) and 1198 (C-O *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 7.81 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.21 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*), 7.18 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.11 (2H, d, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 5.89 (1H, s, C*H*), 4.50 (1H, s, O*H*), 2.35 (3H, s, CH_3) and 2.28 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ ppm: 21.1, 21.7, 75.8, 127.6, 129.3, 129.4, 129.8, 131.0, 136.4, 138.3, 144.9 and 198.5.

2-Hydroxy-1,2-di-*m*-tolylethan-1-one (3g): R_f = 0.43 (50% ethyl acetate/hexane), white solid, yield: 93%, m.p.: 73-74 ºC (lit. 73-74 ºC) [20]; IR (KBr, ν_{max}, cm^{-1}): 3444 (O-H *str.*), 3051 (aromatic C-H *str.*), 2933 (aliphatic C-H *str.*), 1677 (C=O *str.*), 1601, 1536 (aromatic C=C *str.*) and 1188 (C-O *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 7.76 (1H, d, *J* = 8.0 Hz, 6-*H*), 7.69 (1H, s, 6-*H*), 7.32 (1H, t, *J* = 7.6 Hz, 5′-*H*), 7.28–7.24 (1H, m, 5-*H*), 7.20 (1H, d, *J* = 8.0 Hz, 4-*H*), 7.13 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 7.07 (1H, d, *J* = 7.5 Hz, 4′-*H*), 5.90 (1H, s, C*H*), 4.52 (1H, s, O*H*), 2.35 (3H, s, CH_3) and 2.30 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ ppm: 21.7, 21.7, 76.5, 125.3, 126.8, 128.6, 128.8, 129.3, 129.7, 129.9, 133.8, 135.0, 138.9, 139.2, 139.3 and 199.5.

1,2-*Bis*(4-ethylphenyl)-2-hydroxyethan-1-one (3h): R_f = 0.42 (50% ethyl acetate/hexane), white solid, yield: 94%, m.p.: 88-89 ºC (lit. 88-89 ºC) [23]; IR (KBr, ν_{max}, cm^{-1}): 3439 (O-H *str.*), 3078 (aromatic C-H *str.*), 2941 (aliphatic C-H *str.*), 1674 (C=O *str.*), 1599, 1517 (aromatic C=C *str.*) and 1238 (C-O

str.); ^{1}H NMR ($CDCl_3$) δ ppm: 7.85 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.24 (2H, d, *J* = 8.0 Hz, 3′-*H* and 5′-*H*), 7.22 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.15 (2H, d, *J* = 8.0 Hz, 2′-*H* and 6′-*H*), 5.90 (1H, s, C*H*), 4.53 (1H, s, O*H*), 2.65 (2H, q, *J* = 7.6 Hz, CH_2CH_3), 2.59 (2H, q, *J* = 7.6 Hz, CH_2CH_3) and 1.23-1.16 (6H, m, 2(CH_2CH_3)); ^{13}C NMR ($CDCl_3$) δ ppm: 15.3, 15.7, 28.9, 29.3, 76.2, 128.0, 128.5, 129.0, 129.8, 131.5, 136.9, 144.6, 151.3 and 198.9.

2-Hydroxy-1,2-*bis*(4-isopropylphenyl)ethen-1-one (3i): R_f = 0.41 (50% ethyl acetate/hexane), white solid, yield: 93%, m.p.: 91-92 ºC (lit. 91-92 ºC) [24]; IR (KBr, ν_{max}, cm^{-1}): 3450 (O-H *str.*), 3042 (aromatic C-H *str.*), 2923 (aliphatic C-H *str.*), 1680 (C=O *str.*), 1600, 1519 (aromatic C=C *str.*) and 1292 (C-O *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 7.91-7.81 (2H, m, 3-*H* and 5-*H*), 7.27 – 7.23 (4H, m, 2′-*H* and 3′-*H*, 5′-*H* and 6′-*H*), 7.18 (2H, d, *J* = 8.2 Hz, 2-*H* and 6-*H*), 5.90 (1H, s, C*H*), 4.52 (1H, s, O*H*), 2.87 (2H, m, 2(C*H*(CH_3)$_2$)) and 1.24-1.16 (12H, m, 2(CH(C*H*$_3$)$_2$)); ^{13}C NMR ($CDCl_3$) δ ppm: 23.8, 23.9, 24.2, 24.2, 34.1, 34.6, 76.1, 127.2, 127.6, 128.0, 129.8, 131.6, 137.0, 149.6, 155.9 and 198.8.

2-Hydroxy-1,2-*bis*(4-isobutylphenyl)ethan-1-one (3j): R_f = 0.40 (50% ethyl acetate/hexane), white solid, yield: 93%, m.p.: 94-95 ºC (lit. 94-95 ºC) [23]; IR (KBr, ν_{max}, cm^{-1}): 3455 (O-H *str.*), 3070 (aromatic C-H *str.*), 2951 (aliphatic C-H *str.*), 1679 (C=O *str.*), 1600, 1542 (aromatic C=C *str.*) and 1268 (C-O *str.*); ^{1}H NMR ($CDCl_3$): δ 7.87-7.78 (2H, m, 2′-*H* and 6′-*H*), 7.26-7.22 (2H, m, 3′-*H* and 5′-*H*), 7.18-7.13 (2H, m, 3-*H* and 5-*H*), 7.11–7.06 (2H, m, 2-*H* and 6-*H*), 5.89 (1H, s, C*H*), 4.54 (1H, s, O*H*), 2.47 (2H, d, *J* = 7.2 Hz, $CH_2CH(CH_3)_2$), 2.41 (2H, d, *J* = 7.2 Hz, $CH_2CH(CH_3)_2$), 1.76-1.89 (2H, m, 2($CH_2CH(CH_3)_2$)) and 0.86 (12H, d, *J* = 7.6 Hz, 2(CH_2CH-(CH_3)$_2$)); ^{13}C NMR ($CDCl_3$): δ 22.7, 22.7, 30.3, 30.5, 45.4, 45.8, 76.2, 127.9, 129.5, 129.7, 130.2, 131.6, 136.9, 142.5, 148.9 and 198.9.

1,2-*Bis*(4-(*tert*-butyl)phenyl)-2-hydroxyethan-1-one (3k): R_f = 0.41 (50% ethyl acetate/hexane), white solid, yield: 92%, m.p.: 111-112 ºC (lit. 111-112 ºC) [20]; IR (KBr, ν_{max}, cm^{-1}): 3458 (O-H *str.*), 3021 (aromatic C-H *str.*), 2971 (aliphatic C-H *str.*), 1675 (C=O *str.*), 1603, 1522 (aromatic C=C *str.*) and 1248 (C-O *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 7.89 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 7.42 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.34 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.27 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 5.91 (1H, s, C*H*), 4.51 (1H, s, O*H*), 1.29 (9H, s, C(CH_3)$_3$) and 1.27 (9H, s, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$) δ ppm: 31.3, 31.6, 34.9, 35.6, 76.0, 126.0, 126.4, 127.7, 129.6, 131.2, 136.6, 151.8, 158.1 and 198.7.

2-Hydroxy-1,2-*bis*(4-methoxyphenyl)ethan-1-one (3l): R_f = 0.41 (50% ethyl acetate/hexane), white solid, yield: 96%, m.p.: 105-108 ºC (lit. 105-108 ºC) [22]; IR (KBr, ν_{max}, cm^{-1}): 3454 (O-H *str.*), 3025 (aromatic C-H *str.*), 2936, 2839 (aliphatic C-H *str.*), 1668 (C=O *str.*), 1598, 1502 (aromatic C=C *str.*) and 1252 (C-O *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 7.89 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.24 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 6.85 (2H, d, *J* = 6.0 Hz, 3-*H* and 5-*H*), 6.83 (2H, d, *J* = 6.0 Hz, 3′-*H* and 5′-*H*), 5.85 (1H, s, C*H*), 3.81 (3H, s, OCH_3) and 3.74 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ ppm: 55.2, 55.5, 75.2, 113.9, 114.5, 126.3, 129.0, 131.6, 131.8, 159.6, 164.0 and 197.3.

2-Hydroxy-1,2-di(thiophen-2-yl)ethan-1-one (3m): R_f = 0.45 (50% ethyl acetate/hexane), white solid, yield: 89%, m.p.: 103-104 ºC (lit. 103-104 ºC) [25]; IR (KBr, ν_{max}, cm^{-1}): 3450 (O-H *str.*), 3022 (aromatic C-H *str.*), 2926, 2849 (aliphatic C-H *str.*), 1672 (C=O *str.*), 1598 (aromatic C=C *str.*) and 1251 (C-O *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 7.75 (1H, s, 5-*H*), 7.70 (1H, s, 5′-*H*), 7.30 (1H, d, *J* = 3.2 Hz, 3-*H*), 7.13-7.06 (2H, m, 4′-*H* and 4′-*H*), 6.97 (1H, d, *J* = 3.2 Hz, 3′-*H*), 6.03 (1H, s, C*H*) and 4.35 (1H, s, O*H*); ^{13}C NMR ($CDCl_3$) δ ppm: 72.0, 127.2, 127.3, 127.6, 128.7, 134.6, 135.7, 139.6, 142.4 and 190.3.

1,2-Di(furan-2-yl)-2-hydroxyethan-1-one (3n): R_f = 0.43 (50% ethyl acetate/hexane), yellow crystals, yield: 90%, m.p.: 138-139 ºC (lit. 138-139 ºC) [26]; IR (KBr, ν_{max}, cm^{-1}): 3418 (O-H *str.*), 3077 (aromatic C-H *str.*), 2964 (aliphatic C-H *str.*), 1680 (C=O *str.*), 1560 (aromatic C=C *str.*) and 1252 (C-O *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 7.61 (1H, s, 5-*H*), 7.37 (1H, s, 5′-*H*), 7.24 (1H, d, *J* = 3.2 Hz, 3-*H*), 6.53 (1H, d, *J* = 3.6 Hz, 4-*H*), 6.39 (1H, d, *J* = 3.2 Hz, 4′-*H*), 6.34 (1H, d, *J* = 3.2 Hz, 3′-*H*), 5.79 (1H, s, C*H*) and 4.15 (1H, s, O*H*); ^{13}C NMR ($CDCl_3$) δ ppm: 69.2, 109.1, 110.8, 112.6, 120.1, 143.2, 147.7, 149.4, 151.2 and 184.4.

2-Hydroxy-1,2-di(pyridin-2-yl)ethan-1-one (3o): R_f = 0.43 (50% ethyl acetate/hexane), yellow crystals, yield: 91%, m.p.: 154-156 ºC (lit. 154-156 ºC) [27]; IR (KBr, ν_{max}, cm^{-1}): 3464 (O-H *str.*), 3068 (aromatic C-H *str.*), 2981, 2850 (aliphatic C-H *str.*), 1668 (C=O *str.*), 1591, 1513 (aromatic C=C *str.*) and 1275 (C-O *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 8.77 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 8.55 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 7.94 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.20 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*) and 6.09 (1H, s, C*H*); ^{13}C NMR ($CDCl_3$) δ ppm: 75.6, 122.2, 122.6, 135.1, 137.5, 145.2, 150.5 and 197.8.

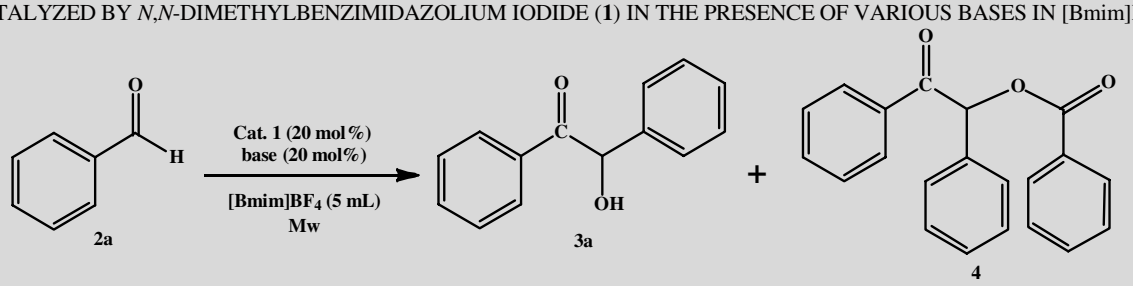
O-Benzoylbenzoin (4): R_f = 0.61 (50% ethyl acetate/hexane), yellow crystals, yield: 91%, m.p.: 123-124 ºC (lit. 123-125 ºC) [13]; IR (KBr, ν_{max}, cm^{-1}): 3061, 3041 (aromatic C-H *str.*), 2966 (aliphatic C-H *str.*), 1716, 1694 (C=O *str.*), 1597 (aromatic C=C *str.*), 1275, 1111 (C-O *str.*); ^{1}H NMR ($CDCl_3$) δ ppm: 8.12 (2H, d, *J* = 7.6 Hz, 2″-*H* and 6″-*H*), 8.02 (2H, d, *J* = 8.0 Hz, 2-*H* and 6-*H*), 7.38-7.61 (11H, m, Ar*H*), 7.11 (1H, s, C*H*); ^{13}C NMR ($CDCl_3$) δ ppm: 77.9, 128.5, 128.6, 128.9, 129.1, 129.3, 129.5, 130.0, 133.3, 133.4, 133.9, 134.8, 166.1 and 193.6.

RESULTS AND DISCUSSION

During the initial study, the application of microwave-assisted benzoin condensation for benzaldehyde was investigated. Following the methodology described in the literature [13], 20 mol% *N*,*N*-dimethylbenzimidazolium iodide (**1**) as catalyst as introduced and incorporated 20 mol% of different bases in the presence of green solvent, 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim]BF_4. The outcomes of this experiment are compiled in Table-1, offering a comprehensive overview of the obtained results.

When *N*,*N*-dimethylbenzimidazolium iodide (**1**) was used as catalyst in conjunction with K_2CO_3 and Na_2CO_3 as inorganic bases and TEA and DBU as organic bases, the reaction proceeded at a sluggish pace, resulting in low yields of the desired α-hydroxy carbonyl products. Specifically, the formation of

TABLE-1
OPTIMIZATION CONDITIONS OF MICROWAVE-ASSISTED BENZOIN CONDENSATION OF BENZALDEHYDE (**2a**) CATALYZED BY *N,N*-DIMETHYLBENZIMIDAZOLIUM IODIDE (**1**) IN THE PRESENCE OF VARIOUS BASES IN [Bmim]BF_4

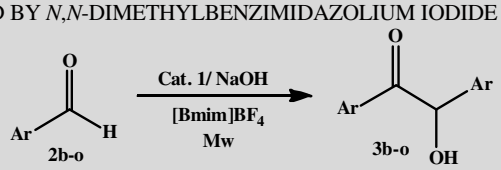


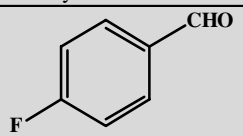
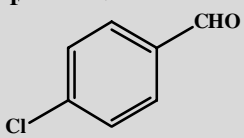
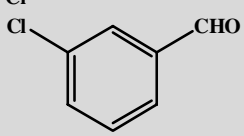
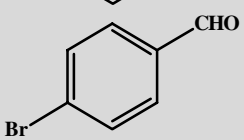
Entry	Base	Time (min)	Yield **3a** (%)	Yield **4** (%)
1	K_2CO_3	45	56	32
2	Na_2CO_3	50	59	29
3	TEA	60	58	26
4	DBU	40	79	7
5	KOH	40	87	–
6	NaOH	40	91	–

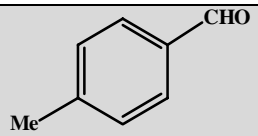
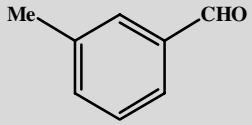
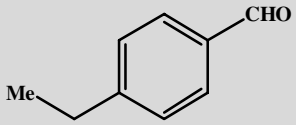
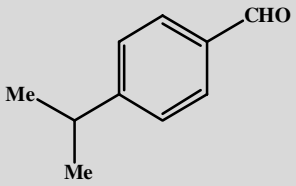
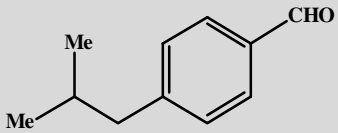
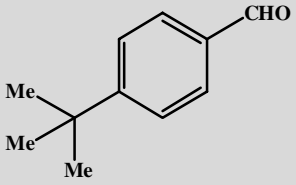
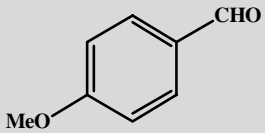
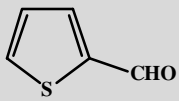
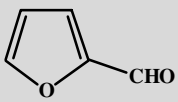
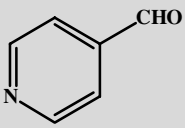
2-hydroxy-1,2-diphenylethan-1-one (**3a**) produced yields of 56%, 59%, 58% and 79%, alongside the detection of the by-product O-benzoylbenzoin (**4**) with yields of 32%, 29%, 26% and 7%, respectively (entry 1-4, Table-1). In contrast, when strong inorganic bases like KOH and NaOH were employed, no O-benzoylbenzoin formation was observed. It is revealed that the combination of catalytic **1** in [Bmim]BF_4 with KOH and NaOH under microwave irradiation at 700 W substantially increased the benzoins' yields to 87% and 91%, respectively, while concurrently reducing the reaction times (entry 5 and 6, Table-1). Based on these compelling results, NaOH was chosen as the preferred base for the benzoin reaction conducted under microwave conditions (700 W) in the presence of *N,N*-dimethylbenzimidazolium iodide (**1**) as catalyst. This optimized reaction condition was then successfully applied to benzoin condensations involving both electron-deficient and electron-rich aromatic aldehydes, as well as heteroaromatic aldehydes, as demonstrated in Table-1, entry 6.

A study on the conversion efficiency of microwave-enhanced benzoin condensation, starting with benzaldehyde (**2a**) was conducted. By optimizing the reaction conditions using *N,N*-dimethylbenzimidazolium iodide (**1**) as catalyst and NaOH at 20 mol% in [Bmim]BF_4 as the reaction medium, we expanded the scope of this benzoin condensation to include other aromatic aldehydes **2b-o**. The results, summarized in Table-2, demonstrated the successful formation of the desired acyloin products **3b-o** with consistently good to high yields and no byproduct **4** was observed in the benzoin reaction.

TABLE-2
BENZOIN CONDENSATION OF AROMATIC/HETEROAROMATIC ALDEHYDE **2b-o** UNDER MICROWAVE IRRADIATION CATALYZED BY *N,N*-DIMETHYLBENZIMIDAZOLIUM IODIDE (**1**) AND NaOH IN [Bmim]BF_4



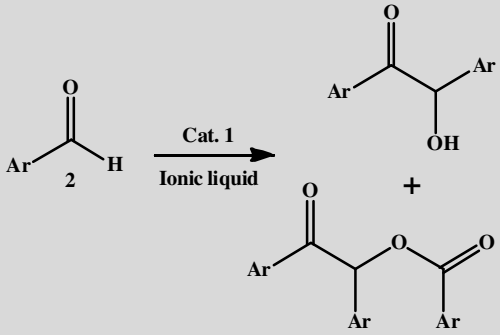
Entry		Aldehyde **2**	Time (min)	Yield **3** (%)	m.p. (°C)
1	**2b**		50	89 (**3b**)	81-82
2	**2c**		45	90 (**3c**)	87-88
3	**2d**		45	89 (**3d**)	78-79
4	**2e**		45	90 (**3e**)	93-94

5	**2f**		35	95 (**3f**)	75-76
6	**2g**		35	93 (**3g**)	73-74
7	**2h**		35	94 (**3h**)	88-89
8	**2i**		35	93 (**3i**)	91-92
9	**2j**		35	93 (**3j**)	94-95
10	**2k**		35	92 (**3k**)	111-112
11	**2l**		30	96 (**3l**)	105-108
12	**2m**		45	89 (**3m**)	103-104
13	**2n**		45	90 (**3n**)	138-139
14	**2o**		45	91 (**3o**)	154-156

The data presented in Table-2 underscore the effectiveness of *N*,*N*-dimethylbenzimidazolium iodide (**1**) and NaOH under microwave irradiation in [Bmim]BF_4 for conducting benzoin reactions with a range of substituted benzaldehydes. Significantly, the benzoin reactions involving F-, Cl-, Br-, CH_3-, CH_3CH_2-, $(CH_3)_2CH$-, $(CH_3)_2CHCH_2$-, $(CH_3)_3C$- and *p*-methoxy substituted benzaldehydes, as well as Cl- and CH_3- *m*-substituted benzaldehydes, exhibited excellent yields, ranging from 89% to 96% (Table-2, entry 1-11). Furthermore, when heteroaromatic aldehydes (**2m-o**) were subjected to microwave irradiation with catalytic **1** in the presence of NaOH in [Bmim]BF_4, the desired benzoin products were obtained with yields ranging from 89% to 91% (Table-2, entry 12-14). Remarkably, there were no significant differences in the overall yields of products **3a-o**. Importantly, all reactions were free from byproducts and the reaction times were short, ranging from 30 to 50 min.

We compared the yields of various benzoins, as shown in Table-2, with our previous report on benzoin condensation [13,14]. Previously, we used *N*,*N*-dimethylbenzimidazolium iodide (**1**) as catalyst in neutral ionic liquid [Bmim]PF_6 and basic ionic liquid [Bmim]OH without microwave assistance (Table-3). By employing microwave-assisted benzoin reactions with *N*,*N*-dimethylbenzimidazolium iodide (**1**) as catalyst in [Bmim]BF_4, we achieved good to high yields of 91% for **3a**, 89% for **3b**, 90% for **3c**, 95% for **3f** and 90% for **3n**. These results were compared with the yields obtained using catalyst **1** in [Bmim]PF_6 and [Bmim]OH without microwave assistance. In [Bmim]PF_6, the yields for products **3a**, **3c**, **3f** and **3n** were

TABLE-3
COMPARISON OF BENZOIN CONDENSATION OF AROMATIC/HETEROAROMATIC ALDEHYDES OF CURRENT WORK WITH LITERATURE



[Bmim]BF_4 (under MW); 3a , 3b, 3c, 3f and 3n; (see Table-3)
[Bmim]PF_6 (without MW); 3a, 3c, 3f and 3n; (see Table-3)
[Bmim]OH (without MW); 3a, 3b, 3c and 3f; (see Table-3)

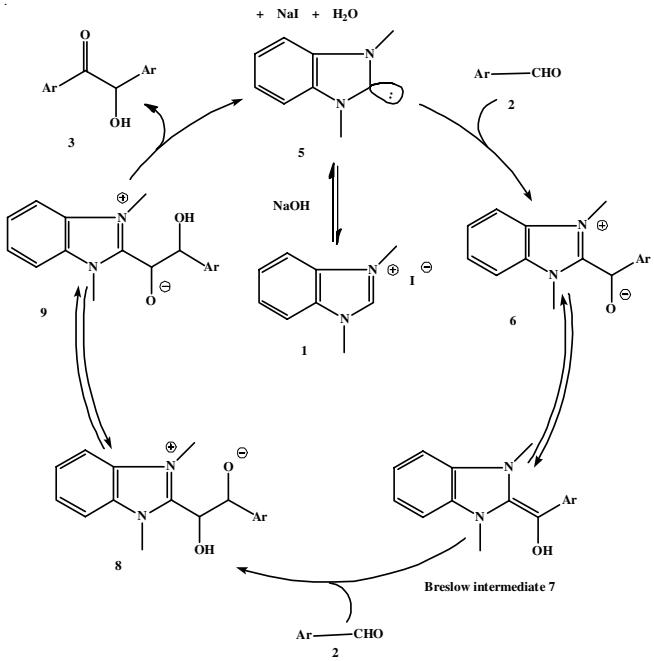
[Bmim]BF_4 (under MW); not detect
[Bmim]PF_6 (without MW); 4a (9%), 4c (19%), 4f (12%) and 4n (18%)
[Bmim]OH (without MW); 4a (7%), 4b (12%), 4c (21%) and 4f (37%)

Entry	Benzoin **3**	Yield **3** (%)		
		Solvent ([Bmim)BF_4) under MW, 30-50 min [Present work]	Solvent ([Bmim)PF_6) without MW, 4.5-8 h [Ref. 13]	Solvent ([Bmim)OH) without MW, 4-8 h [Ref. 14]
1	**3a**	91	83	87
2	**3b**	89	–	83
3	**3c**	90	60	76
4	**3f**	95	78	62
5	**3n**	90	62	–

83%, 60%, 78% and 62%, respectively, while in [Bmim]OH, the yields for products **3a**, **3b**, **3c** and **3f** were 87%, 83%, 76% and 62%, respectively. Thus, the reaction times for [Bmim]OH and [Bmim]PF_6 (without microwave assistance) were longer compared to [Bmim]BF_4 (with microwave assistance).

When [Bmim]OH and [Bmim]PF_6 were used as solvents (without microwave assistance), the formation of similar by-products **4** was observed, which required a longer reaction time. These byproducts were identified as aroylacyloins **4a-c**, **4f** and **4n**, in accordance with the mechanism reported by Miyashita *et al*. [28]. The catalytic formation of products **3** involved the ylide **5** derived from benzimidazolium salt **1**, following **Scheme-V** and proceeding through a carbanionic intermediate **7**, as described in previous literature [15]. The catalytic activity of *N*,*N*-dimethylbenzimidazolium iodide (**1**) stems from the deprotonation of the 2-H proton of the benzimidazolium cation, leading to the formation of *N*-heterocyclic carbine **5** (NHC). The reaction between aldehyde **2a-o** and 1 equiv. of the nucleophilic catalyst yields adduct **6** and subsequent proton transfer results in the formation of the Breslow intermediate **7**. Further nucleophilic addition of 1 equiv. generates adduct **9**, which can undergo reversible transformation into adduct **8**. The transformation of adduct **9** occurs through the elimination of the catalyst, giving rise to the formation of **3a-o** and the regeneration of NHC catalyst **5**.

A brief investigation was also indicated into the reusability of a mixture containing pre-catalyst **1** and NaOH in [Bmim]BF_4 for the benzoin condensation of benzaldehyde **2a** using microwave irradiation. In the first run, we achieved a yield of 91% for benzoin **3a** within a 40 min reaction time. The ionic liquid was then extracted using diethyl ether and concentrated. For the second cycle, we reused the recovered ionic liquid by adding 1 equiv. of benzaldehyde **2a**, resulting in a yield of 90% for **3a** within 40 min. Subsequently, in the third, fourth and fifth cycles, the yields of **3a** were 88% (40 min), 85% (45 min) and 82% (50 min), respectively (Table-4).



Scheme-V: Catalytic cycle of benzoin condensation

TABLE-4
REUSE OF A MIXTURE OF PRE-CATALYST **1** AND NaOH IN THE BENZOIN CONDENSATION OF **2a** IN [Bmim]BF_4 UNDER MICROWAVE IRRADIATION

Cycle	Time (min)	Yield **3a** (%)
1	40	91
2	40	90
3	40	88
4	45	85
5	50	82

Conclusion

In conclusion, a benzoin condensation method was successfully developed which is applicable to aromatic/heteroaromatic

aldehydes **2a-o**. This method offers a rapid, clean and practical approach to obtain α-hydroxy carbonyl products (benzoins) with high efficiency. By utilizing the microwave irradiation and *N*,*N*-dimethylbenzimidazolium iodide (**1**) as catalyst in [Bmim]BF_4, we achieved excellent yields ranging from 89% to 96% for the α-hydroxy carbonyls **3a-o**. Remarkably, no byproducts were detected during the process. The catalyst itself is stable and easy to handle and the mixture of benzimidazolium salt **1** and NaOH can be reused up to four times without significant loss of efficiency. Furthermore, this method aligns with the principles of green chemistry by promoting environmental friendly conditions. It provides the valuable insights into the catalytic utility of **1** through the use of microwave irradiation in an ionic liquid condition.

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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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