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MICROWAVE-ASSISTED *N,N'*-DIMETHYLBENZIMIDAZOLIUM IODIDE AS A POWERFUL AND EFFICIENT CATALYTIC SYSTEM FOR THE INTERMOLECULAR STETTER REACTION AND THE SYNTHESIS OF 1,2-DIARYLETHANE-1,2-DIONE DERIVATIVES IN THE ABSENCE OF ORGANIC SOLVENT

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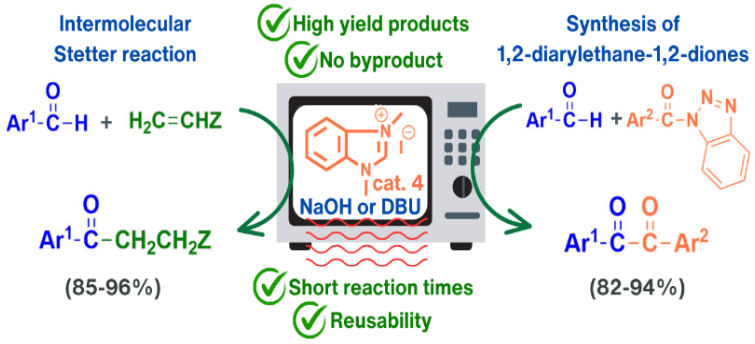
1,4-addition products were successfully synthesized through intermolecular Stetter reactions involving aromatic aldehydes and *α,β*-unsaturated compounds, as well as 1,2-dicarbonyl compound derivatives via cross-coupling reactions between aromatic aldehydes and *N*-acylbenzotriazoles. These reactions yielded appreciable quantities of products with significantly reduced reaction times when performed under microwave irradiation. These results were achieved using just 50 mol% of *N,N*-dimethylbenzimidazolium iodide along with suitable bases like NaOH and DBU, which further contributed to the high yields of products while minimizing the formation of unwanted side products. This method is not only efficient but also clean, practical, and straightforward. Moreover, the *N,N*-dimethylbenzimidazolium iodide catalyst, once recovered after extraction and in the absence of organic solvents, can be reused multiple times without experiencing a significant loss of catalytic efficiency. This aspect is particularly noteworthy for promoting eco-friendly chemistry practices.



INTRODUCTION

N-Heterocyclic carbenes (NHCs), stable carbenes discovered in the last decade of the 20th century, have recently gained significant attention as catalysts in organic synthesis.[1–5] Over the years, numerous reports have detailed carbene-catalyzed reactions, primarily due to their ability to generate acyl anion equivalents.[6,7] Among the diverse types of NHCs, including thiazolium and imidazolium salts, there has been a growing interest in their applications across various organic reactions. These encompass crucial processes such as the transesterification of alcohols,[8] cyanosilylation of aldehydes,[9] benzoin reactions,[10–17] nucleophilic acylation of haloarenes,[18–21] nucleophilic acylation of benzyl and activated alkyl halides,[22,23] and even the Stetter reaction.[24]

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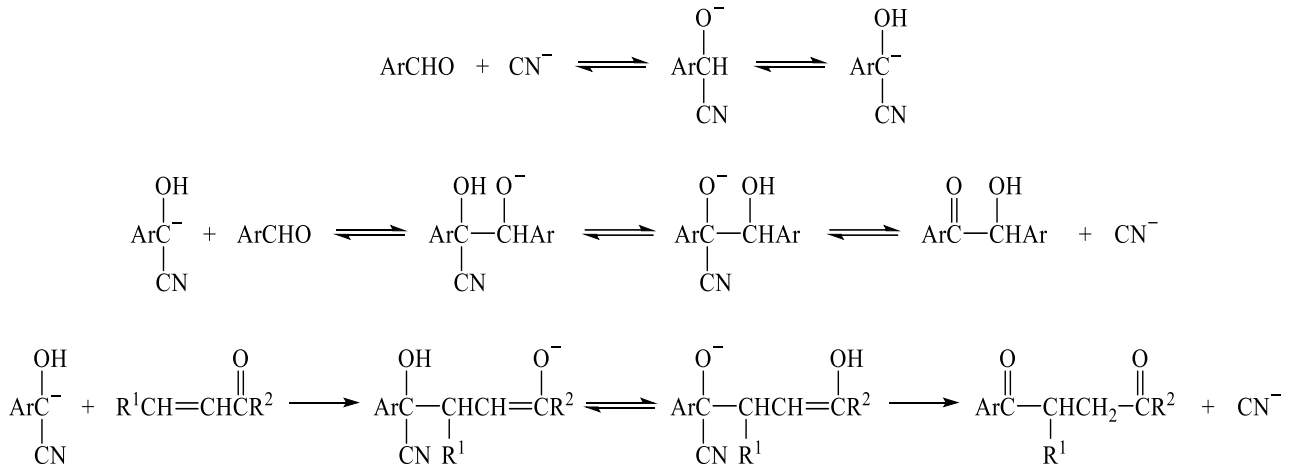
The Stetter reaction is a well-known chemical process involving the coupling of an aldehyde with an electron-deficient alkene, resulting in a 1,4-addition (conjugate addition) of the aldehyde to an *α,β*-unsaturated ketone, ester, or nitrile. This reaction can be catalyzed by various agents, including cyanide and thiazolium or imidazolium salts. Cyanide-catalyzed Stetter reactions are typically limited to aromatic aldehydes, as aliphatic aldehydes tend to undergo unwanted aldol condensation. In the case of aromatic aldehydes, the Stetter reaction competes with the benzoin condensation, as illustrated in Scheme 1. It's important to note that the benzoin condensation is a reversible process. However, since the Stetter reaction yields more stable products, the primary product formed in this scenario is typically derived from the Stetter reaction.[25,26]



Scheme 1 – The Stetter reaction competes with the benzoin condensation.

Over time, researchers have explored a range of *N*-heterocyclic carbenes (NHCs) to enhance the quality of Stetter reactions. Notably, Stetter and co-workers[27] discovered that the benzyl-substituted thiazolium salt **2** (depicted in Fig. 1) yielded optimal results when used for the addition of aliphatic aldehydes. In contrast, for the addition of aromatic aldehydes, they selected compounds **1** and **3**. Interestingly, any one of these three NHCs proved suitable for additions involving heterocyclic aldehydes.

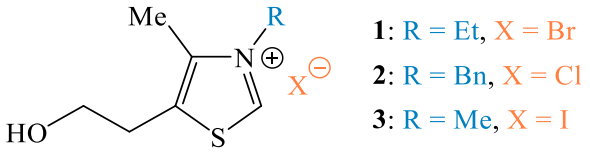
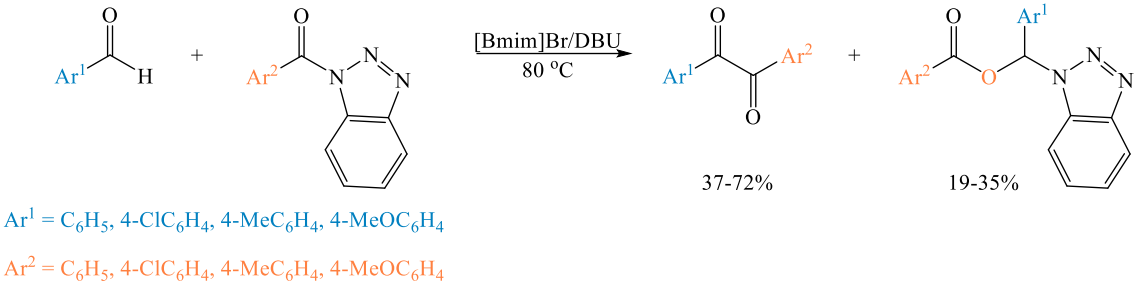


Fig. 1 – Selected thiazolium salts for the Stetter reaction.

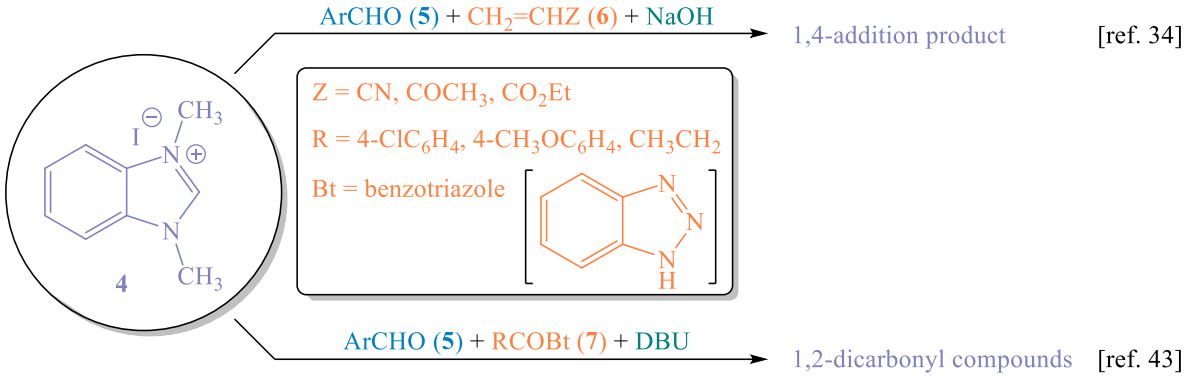
Furthermore, a plethora of other NHC catalysts have found application in Stetter reactions, as extensively documented in the literature. Examples include chiral thiazolium salts facilitating asymmetric Stetter reactions,[28–31] chiral triazolium salts enabling asymmetric intramolecular Stetter reactions,[32,33] benzimidazolium salts catalyzing intramolecular Stetter reactions,[34] and even the utilization of imidazolium salts within ionic liquids as both solvents and precatalysts for Stetter reactions.[35]

Significant advancements in the use of *N*-acylbenzotriazoles in organic synthesis as activated derivatives of carboxylic acids were made prior to the late 20th century.[36] Efficient *N*-acylbenzotriazole reagents can be directly synthesized from acid chlorides and 1*H*-benzotriazole (BtH).[37] These stable, crystalline *N*-acylbenzotriazoles have garnered interest due to their effectiveness as alternatives to often unstable and challenging-to-prepare acid chlorides.[38] Consequently, *N*-acylbenzotriazoles find utility in various processes, such as the *N*-acylation of amines,[39] *C*-acylation of ketones,[40] and reactions with Grignard and heteroaryllithium reagents.[41] Notably, in a recent study, 1-butyl-3-methylimidazolium bromide ([Bmim]Br), a type of *N*-heterocyclic carbene (NHC), was employed as a catalyst for the cross-coupling reaction between aromatic aldehydes and *N*-aroylbenzotriazoles, resulting in satisfactory yields of 1,2-diarylethane-1,2-dione derivatives (benzil), as depicted in Scheme 2.[42]



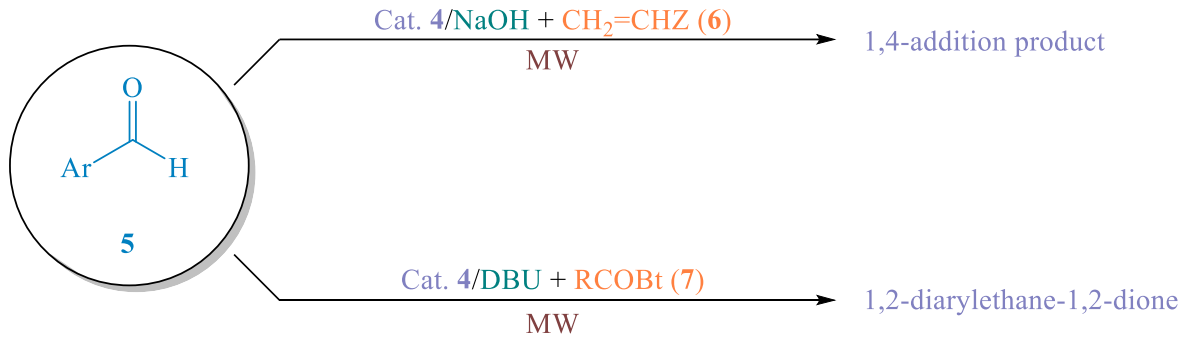
Scheme 2 – Cross-coupling reaction between aromatic aldehydes and *N*-acylbenzotriazoles performing in [Bmim]Br.

We have previously published studies on Stetter reactions involving *α,β*-unsaturated compounds (**6**) and aromatic aldehydes (**5**).[34] In our research, we observed that this reaction proceeds smoothly in an aqueous medium when employing *N,N*-dimethylbenzimidazolium iodide (**4**) as the catalyst and a base (NaOH). Furthermore, a similar reaction has been documented in the literature,[43] where cross-coupling between aromatic aldehydes (**5**) and *N*-acylbenzotriazoles (**7**) was catalyzed by a benzimidazolium salt (**4**) in the presence of the base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in tetrahydrofuran (THF), as illustrated in Scheme 3.



Scheme 3 – Benzimidazolium salt 4 catalyzed for Stetter reaction between *α,β*-unsaturated compounds 6 and aromatic aldehydes 5 and cross-coupling reaction of aromatic aldehydes **5** with *N*-acylbenzotriazoles **7**.

Continuing our exploration of the catalytic reactivity of *N,N*-dimethylbenzimidazolium iodide (**4**), we present in this study the benzimidazolium-catalyzed intermolecular Stetter reaction involving aromatic aldehydes (**5**) and *α,β*-unsaturated compounds (**6**). Additionally, we investigate the cross-coupling reaction of aromatic aldehydes (**5**) with *N*-acylbenzotriazoles (**7**) under solvent-free conditions using microwave irradiation, as illustrated in Scheme 5



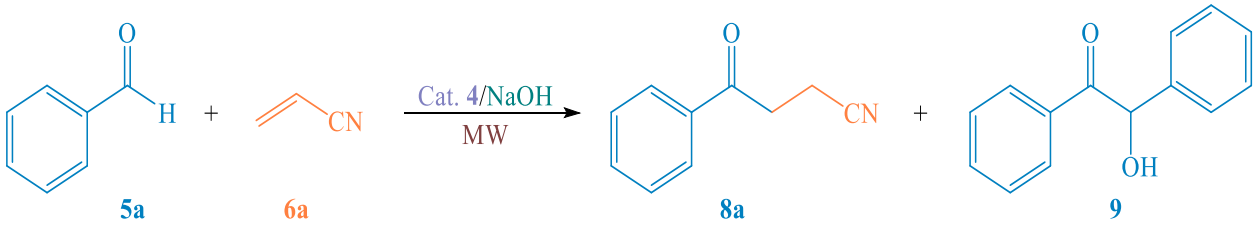
Scheme 4 – The intermolecular Stetter reaction involves the reaction of *α,β*-unsaturated compounds 6 with aromatic aldehydes 5. Additionally, a cross-coupling reaction occurs between aromatic aldehydes **5** and *N*-acylbenzotriazoles **7** catalyzed by *N,N*-dimethylbenzimidazolium iodide (**4**). These reactions take place in the absence of organic solvent and are facilitated by microwave irradiation.

RESULTS AND DISCUSSION

In our initial investigation of the intermolecular Stetter reaction, we began with a simple substrate, benzaldehyde (**5a**), and acrylonitrile (**6a**). We followed a methodology similar to that reported in the literature,[34] with slight modifications to the catalyst (**4**) and NaOH percentages to optimize conditions for a solvent-free environment under microwave irradiation, as detailed in Table 1.

Table 1

Optimization of the reaction between benzaldehyde (**5a**) and acrylonitrile (**6a**) in different mol% of catalyst **4** and base (NaOH) in a solvent-free environment under microwave irradiation at 700W



5a **6a** **8a** **9**

Entry	Cat. **4** (mol%)	NaOH (mol%)	Time (min)	Yield **8a** (%)	Yield **9** (%)
1	10	10	300	65	28
2	20	20	150	77	14
3	30	30	130	79	12
4	40	40	120	85	6
5	50	50	90	92	n.d.
6	100	100	90	93	n.d.

n.d.: not detected.

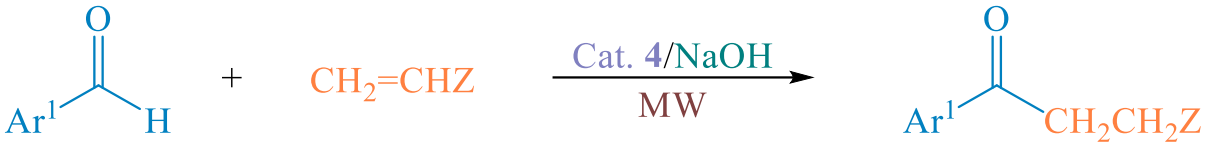
The initiation of the reaction was observed to depend on the quantities of both catalyst **4** (*N*,*N*-dimethylbenzimidazolium iodide) and the base (NaOH). Initially, the reaction proceeded very slowly, taking 300 minutes when 10 mol% of catalyst **4** and 10 mol% of NaOH were used. However, as we increased the amounts of catalyst (20, 30, and 40 mol%) and NaOH (20, 30, and 40 mol%) and conducted the reaction in a microwave irradiation setup at 700W, the reaction time improved to 150, 130, and 120 minutes. Notably, with these increased amounts of catalyst and base, the reaction produced not only the major product **8a** but also side product **9** (Entries 1–4, Table 1).

Further investigation revealed that by increasing the mol% of catalyst **4** and NaOH to 50 and 100, respectively, the reaction completed within 90 minutes, and the maximum yields reached 90 and 91%, respectively, without the formation of side products **9** (Entries 5 and 6, Table 1). Consequently, we selected to use 50 mol% of catalyst **4** and NaOH (Entry 5, Table 1) over 100 mol% (Entry 6, Table 1) since it provided similar yields of product **8a** without extending reaction times. With the optimized conditions for catalyst and base percentages (Table 1), we proceeded to investigate various intermolecular Stetter reactions between acrylonitrile (**6a**), methyl vinyl ketone (**6b**), ethyl acrylate (**6c**), or methyl acrylate (**6d**) and aldehydes **5a-c**. These reactions were conducted in the absence of an organic solvent using microwave irradiation (Table 2).

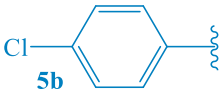
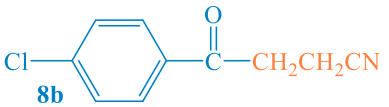
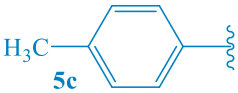
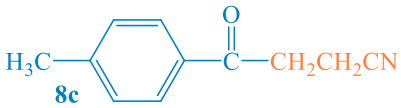
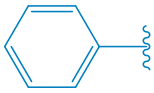
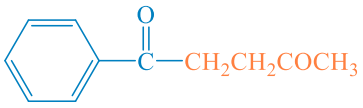
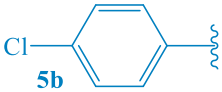
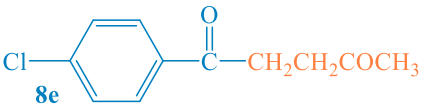
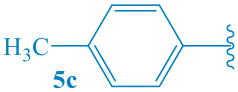
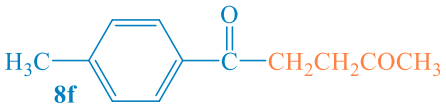
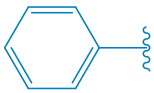
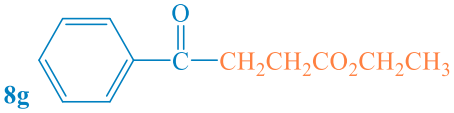
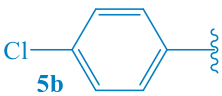
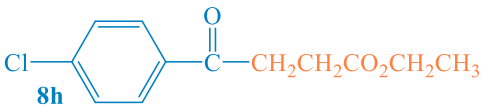
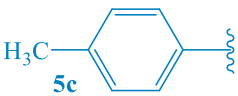
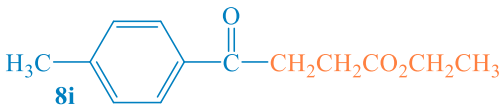
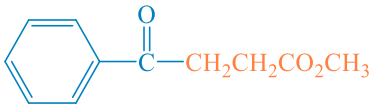
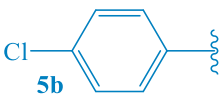
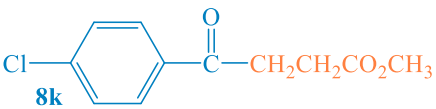
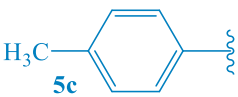
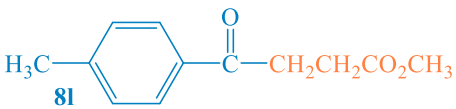
Our examination revealed that the yield of the 1,4-addition product **8** in the Stetter reaction consistently exceeded 90% in most cases (Entries 1–4, 7, and 10, Table 2). In a few instances, a slightly lower but still satisfactory yield was obtained, ranging from 85% to 88% (Entries 5–6, 8–9, and 11, Table 2). In conclusion, we found that the use of 50 mol% *N*,*N*-dimethylbenzimidazolium iodide (**3**) catalyst in combination with NaOH proved highly effective in facilitating the intermolecular Stetter reaction between aromatic aldehydes (**5a-d**) and *α*,*β*-unsaturated compounds (**6a-d**) in the absence of an organic solvent, employing microwave irradiation to achieve excellent product yields.

Table 2

Intermolecular Stetter reaction of aromatic aldehydes **5a-d** with acrylonitrile (**6a**), methyl vinyl ketone (**6b**) ethyl acrylate (**6c**) or methyl acrylate (**6d**) catalyzed by *N*,*N*-dimethylbenzimidazolium iodide (**4**) (50 mol%) and NaOH (50 mol%) in the absence of organic solvent under microwave irradiation



5 **6** **8**

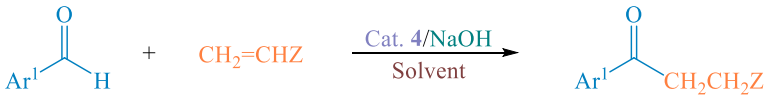
Entry	Ar	Z	Time (min)	Product	Yield (%)
1	 **5b**	CN (**6a**)	70	 **8b**	96
2	 **5c**	CN (**6a**)	110	 **8c**	90
3	 **5a**	$COCH_3$ (**6b**)	100	 **8d**	90
4	 **5b**	$COCH_3$ (**6b**)	80	 **8e**	93
5	 **5c**	$COCH_3$ (**6b**)	120	 **8f**	88
6	 **5a**	$CO_2CH_2CH_3$ (**6c**)	100	 **8g**	88
7	 **5b**	$CO_2CH_2CH_3$ (**6c**)	80	 **8h**	92
8	 **5c**	$CO_2CH_2CH_3$ (**6c**)	120	 **8i**	85
9	 **5a**	CO_2CH_3 (**6d**)	90	 **8j**	89
10	 **5b**	CO_2CH_3 (**6d**)	80	 **8k**	90
11	 **5c**	CO_2CH_3 (**6d**)	130	 **8l**	86

To further assess our findings, we compared the product yields (1,4-addition products **8**, as indicated in Table 2) with our previous study using *N*,*N*-dimethylbenzimidazolium iodide (**4**) as an efficient catalyst for an environmentally friendly intermolecular Stetter reaction in water.[34] In our earlier report, we employed *N*,*N*-dimethylbenzimidazolium iodide (**4**) as the

catalyst in water without microwave assistance (refer to Tables 3). By using microwave-assisted intermolecular Stetter reactions between aromatic aldehydes (**5a-c**) and unsaturated double bonds (**6a-c**) with *N*,*N*-dimethylbenzimidazolium iodide (**4**) as the catalyst in the absence of an organic solvent, we consistently achieved high yields: 92% for **8a**, 96% for **8b**, 90% for **8c**, 90% for **8d**, 93% for **8e**, 88% for **8f**, 88% for **8g**, 92% for **8h**, and 85% for **8i**. In contrast, when using catalyst **4** in a water-based reaction without microwave assistance, the yields for products **8a**, **8b**, **8c**, **8d**, **8e**, **8f**, **8g**, **8h**, and **8i** were 75%, 77%, 71%, 73%, 75%, 70%, 62%, 66%, and 58%, respectively. Importantly, the reaction times in the water-based reactions (without microwave assistance) were significantly longer compared to those conducted in the absence of an organic solvent (with microwave assistance). While the conditions varied slightly between the solvent and solvent-free setups in the Stetter reaction catalyzed by *N*,*N*-dimethylbenzimidazolium iodide (**4**), making a direct comparison somewhat challenging, there still appears to be a relative correlation between the two. This is due to the formation of water from the deprotonation of the C2-hydrogen of the imidazolium ring in *N*,*N*-dimethylbenzimidazolium iodide by NaOH, as reported in the literature.[44] The resulting water can hydrate the hydroxide anion, potentially hindering carbene formation and leading to lower product yields.[44] However, microwave irradiation disrupts the hydrogen bond in the hydration of the hydroxide ion by water.[45] This disruption results in the generation of free water molecules and hydroxyl ions. Moreover, it's widely recognized that some chemical reactions conducted under microwave agitation proceed up to 200 times faster compared to thermally activated processes.[46] Therefore, by involving of microwave irradiation can enhance the potential of the reaction conditions for water formation.

Table 3

Comparison of Stetter reaction between aromatic aldehydes and *a*,*β*-unsaturated compounds of current work with literature



5 **6** **8**

Z = CN, $COCH_3$, $CO_2CH_2CH_3$

Entry	Solvent conditions	Yield (%)								
		8a	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**	**8h**	**8i**
1	Solvent-free under MW, 70-120 min (current work)	92	96	90	90	93	88	88	92	85
2	Solvent (water) without MW, 3.5-6 h (ref. 34)	75	77	71	73	75	70	62	66	58

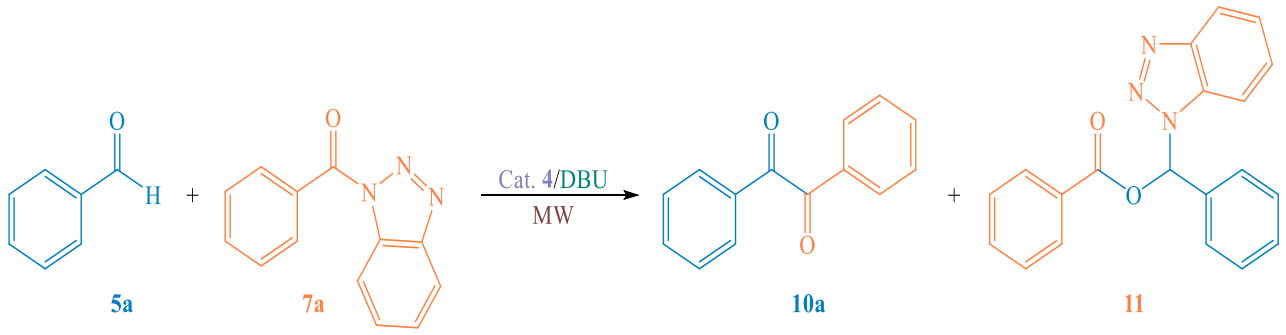
In the subsequent step, we synthesized acylated reagents, specifically *N*-acylbenzotriazoles (**7a-d**), following a previously reported procedure.[43] For the reaction involving aromatic aldehyde **5a** and *N*-benzoylbenzotriazole (**7a**), including the choice of base (in this case, DBU), in the cross-coupling reaction catalyzed by *N*,*N*-dimethylbenzimidazolium iodide (**4**) in the absence of an organic solvent using microwave irradiation, we initially followed a ratio similar to what had been reported in the literature.[43] Moreover, we explored the influence of the mol% of catalyst **4** and DBU in these reactions, as documented in Table 1. This involved increasing the mol% of both catalyst **4** and the base, as illustrated in Table 4.

We conducted cross-coupling reactions between benzaldehyde (**5a**) and *N*-benzoylbenzotriazole (**7a**) using varying mol% of catalyst **4** and DBU under microwave-assisted conditions. Notably, employing 10, 20, 30, and 40 mol% of both **4** and DBU resulted in extended reaction times of 360, 180, 150, and 120 minutes, respectively. These reactions also led to the formation of side product **11** as impurities, which emerged during the reaction (Entries 1–4, Table 4). Conversely, when 50 or 100 mol% of both catalyst **4** and DBU were used, the cross-coupling reactions yielded the

desired product 10 in satisfactory yields of 89% and 90%, respectively. Importantly, these reactions required less time and did not produce side product **11** (Entries 5–6, Table 4). Therefore, using 50 mol% of both **4** and DBU, as opposed to 100 mol%, resulted in no significant difference in yield or reaction times, establishing it as the optimum condition for the cross-coupling reaction between aromatic aldehyde **5a** and *N*-benzoylbenzotriazole **7a**.

Table 4

Optimization conditions of microwave-assisted reaction between benzaldehyde (**5a**) and *N*-benzoylbenzotriazole (**7a**) in the presence of different mol% of catalyst **4** and base (DBU) in a solvent-free environment under microwave irradiation at 700W



Entry	Cat. **4** (mol%)	DBU (mol%)	Time (min)	Yield **10a** (%)	Yield **11** (%)
1	10	10	360	44	37
2	20	20	180	53	28
3	30	30	150	61	19
4	40	40	120	78	9
5	50	50	100	89	n.d.
6	100	100	100	90	n.d.

n.d.: not detected.

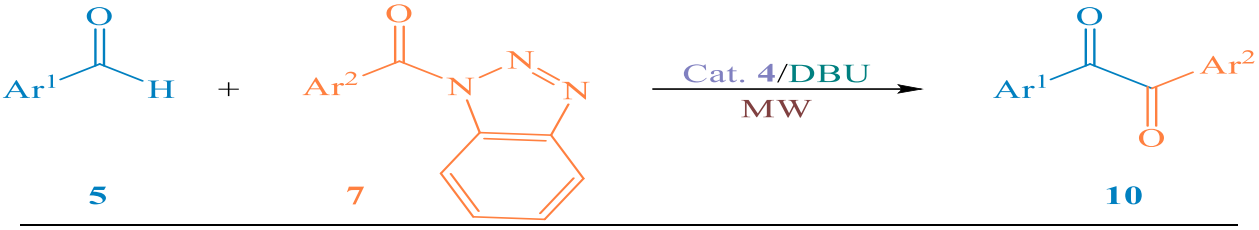
To assess the general applicability of these reactions, we extended the cross-coupling reactions to various aromatic aldehydes (**5a-f**) and *N*-acylbenzotriazoles (**7a-d**) in the absence of an organic solvent using microwave irradiation under the standardized conditions (Entries 5, Table 4). The results are summarized in Table 5.

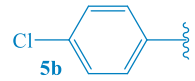
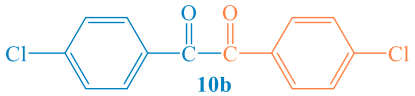
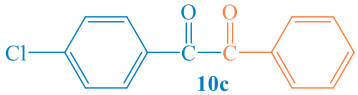
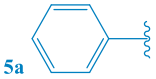
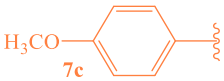
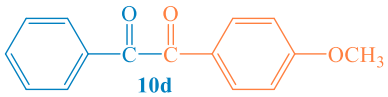
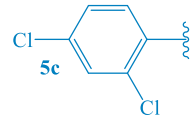
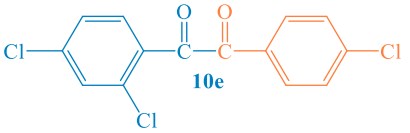
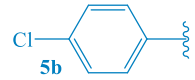
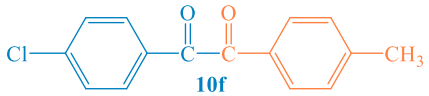
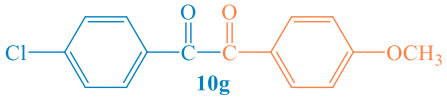
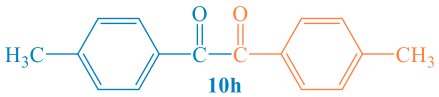
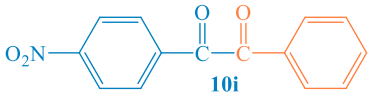
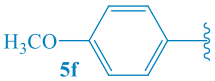
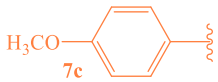
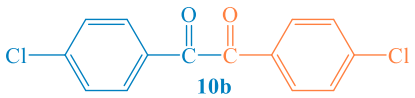
Examining the results in Table 5, we observe that the cross-coupling reactions between aromatic aldehydes (**5a-f**) and *N*-acylbenzotriazoles (**7a-d**) yielded the corresponding 1,2-dicarbonyl compound derivatives (**10b-j**) without any occurrence of side products. Interestingly, we found that substitutions at the ortho- or para-positions of the aromatic aldehyde ring did not hinder the reaction's progress. This held true for various substitution groups in both the aromatic rings **5** and **7**, including chloro (Cl-), methyl (CH_3-), methoxy (CH_3O-), and nitro (NO_2-) groups. Importantly, these substitutions did not significantly affect the product yields of **10b-j**. We further observed that chloride substitution at the para-positions of the aromatic aldehyde ring consistently resulted in high yields ranging from 90% to 94% for compounds **10g** (90%), **10f** (91%), **10c** (92%), **10e** (93%), and **10b** (94%). In contrast, other para-substituted groups, including cases where no substitution was present, exhibited slightly lower yields ranging from 82% to 87%. Nevertheless, these yields remained highly satisfactory, considering both the yields and reaction times under the given conditions.

We compared the results of this experiment with our previous work,[43] where we used *N*,*N*-dimethylbenzimidazolium iodide (**4**) as a catalyst for cross-coupling reactions between aromatic aldehydes and *N*-acylbenzotriazoles conducted in organic solvents (tetrahydrofuran; THF) without microwave irradiation.

Table 5

Cross-coupling reaction between aromatic aldehydes **5a-f** and *N*-acylbenzotriazoles **7a-d** in the presence of 50 mol% of catalyst **4** and DBU under microwave irradiation in the absence of organic solvent



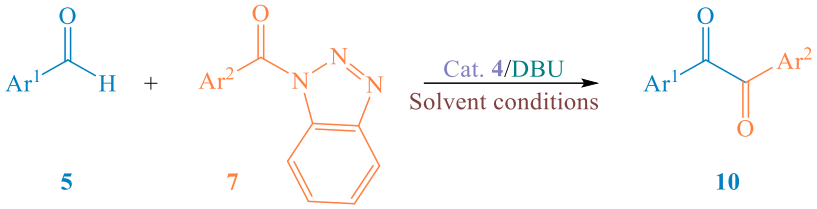
Entry	Ar^1	Ar^2	Time (min)	Product	Yield (%)
1			90		94
2			100		92
3			120		87
4			100		93
5			110		91
6			130		90
7			140		86
8			130		84
9			150		82

The comparison revealed that under the absence of an organic solvent and using microwave irradiation, we achieved excellent yields of 94% for **10b**, 92% for **10c**, 87% for **10d**, 91% for **10f**, 90% for **10g**, and 82% for **10j**, respectively. In contrast, when catalyst **4** was employed in THF without

microwave assistance, the yields for products **10b**, **10c**, **10d**, **10f**, **10g**, and **10j** were substantially lower, ranging from 35% to 61%. Additionally, it's worth noting that the reaction times in THF without microwave assistance were significantly longer, spanning 16–20 hours, in contrast to the shorter reaction times under microwave irradiation in solvent-free conditions (70–120 minutes) (Tables 6).

Table 6

Comparison of cross-coupling reaction between aromatic aldehydes and *N*-acylbenzotriazole of current work with literature



Ar^1 = 4-ClC_6H_4, C_6H_5, 4-$CH_3OC_6H_4$

Ar^2 = 4-ClC_6H_4, C_6H_5, 4-$CH_3OC_6H_4$, 4-$CH_3C_6H_4$

Entry	Solvent conditions	Yield (%)					
		10b	**10c**	**10d**	**10f**	**10g**	**10j**
1	Solvent-free under MW, 90–150 min (current work)	94	92	87	91	90	82
2	Solvent (THF) without MW, 16–20 h (ref. 43)	61	54	47	40	55	35

We conducted recycling experiments to examine the feasibility of intermolecular Stetter reactions between aromatic aldehydes and *α,β*-unsaturated compounds, as well as the cross-coupling reactions of aromatic aldehydes with *N*-acylbenzotriazoles in the absence of organic solvent under microwave irradiation. To represent the Stetter reaction, we chose the reaction between benzaldehyde (**5a**) and acrylonitrile (**6a**), and for the synthesis of 1,2-dicarbonyl compound derivatives, we used the reactions between benzaldehyde (**5a**) and *N*-benzoylbenzotriazole (**7a**).

Table 7

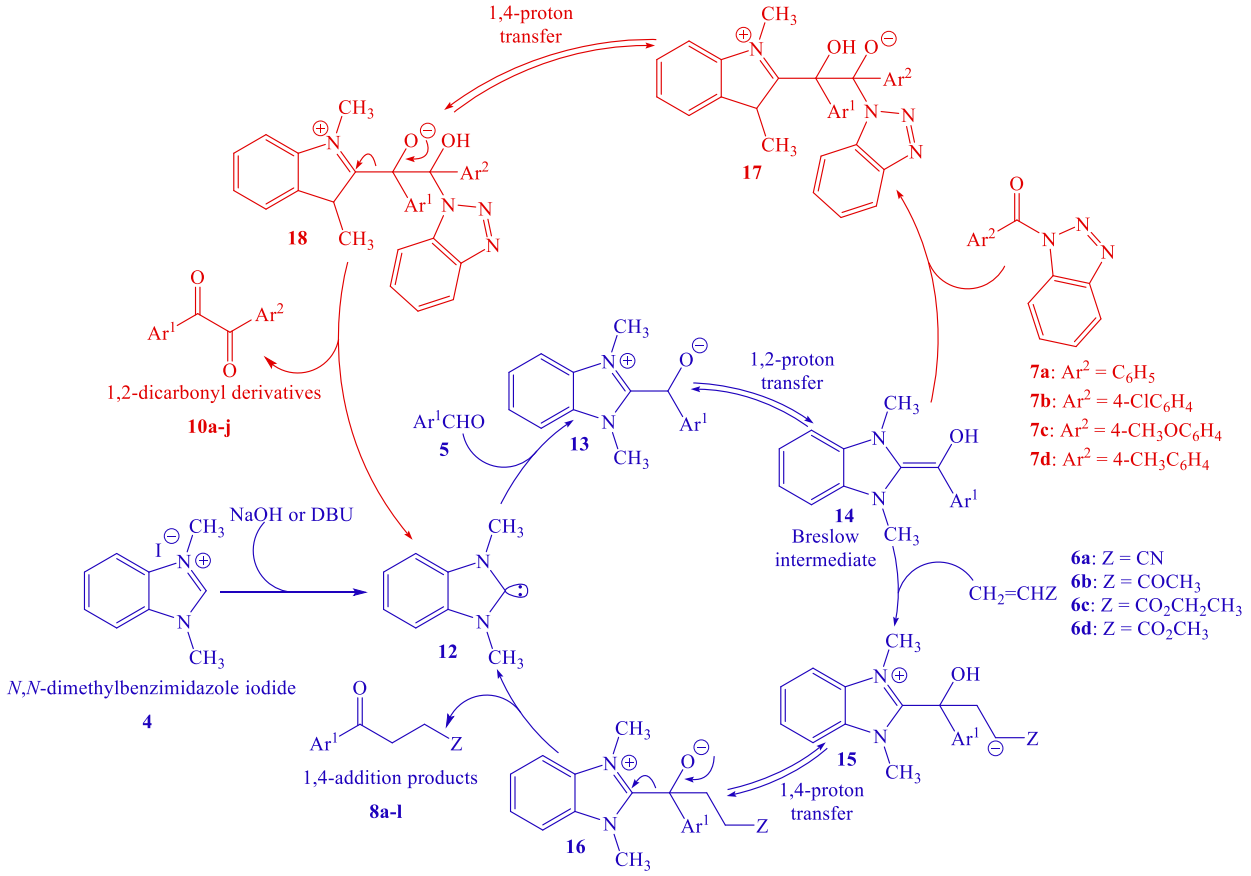
Catalyst reusability of *N*,*N*-dimethylbenzimidazolium iodide (**4**) in intermolecular Stetter reaction of **5a** with **6a** and cross-coupling reaction between **5a** and **7a** in solvent free conditions under microwave irradiation

Product	Run				
	1	2	3	4	5
Yield **8a** (%) from the reaction between **5a** and **6a**	92	90	87	84	80
Yield **10a** (%) from the reaction between **5a** and **7a**	89	84	81	76	73

In the Stetter reaction, after the initial run involving **5a** and **6a**, which yielded 4-phenyl-4-oxobutanenitrile (**8a**) with a 92% yield, we reused the *N*,*N*-dimethylbenzimidazolium iodide and NaOH under solvent-free conditions with microwave irradiation at 700W. After simple extraction and separation, no additional treatment was applied, and the catalyst was used for at least four cycles. In each subsequent cycle, the recovered catalyst from the previous run was employed in the same type of reaction. The product yield of **8a** for the second cycle was 90%, followed by 87%, 84%, and 80% for the third, fourth, and fifth cycles, respectively. This approach was also applicable to the synthesis of 1,2-diphenylethane-1,2-dione (**10a**) from the reaction between benzaldehyde (**5a**) and *N*-benzoylbenzotriazole (**7a**). The results indicate a slight decrease in product yields from the first to the fifth cycles, yet they remained consistently high at 73% (Table 7). This decrease might stem from the conversion of hydroxide ions from NaOH to water, as these ions play a key role in deprotonating the C2-hydrogen of the imidazolium ring in *N*,*N*-dimethylbenzimidazolium iodide, forming a reactive *N*-heterocyclic carbene. Water can also hydrate the hydroxide anion, potentially hindering carbene formation, as observed in

previous study.[44] Nevertheless, the results presented in Table 7 demonstrate the remarkable recyclability of the Stetter reaction and cross-coupling of aromatic aldehydes with *N*-acylbenzotriazole systems, with no significant loss of catalytic activity observed over at least four runs.

The mechanism of the intermolecular Stetter reaction leading to the formation of 1,4-addition products (**8a-l**) provides insights into the mechanisms of subsequent NHC-catalyzed acyl anion additions. The process initiates with the nucleophilic attack of the aldehyde (**5**) by the NHC (**12**), represented as *N*,*N*-dimethylbenzimidazol-2-ylidene, forming the benzimidazolium salt adduct (**13**). This adduct then undergoes proton transfer, yielding intermediate **14**. The NHC moiety plays a crucial role in stabilizing the resulting carbanion by accepting electron density, thus facilitating the proton transfer. This key intermediate, known as the 'Breslow intermediate,' (**14**) is pivotal in explaining the umpolung reactivity of aldehydes induced by NHC catalysts. In the next step, *α*,*β*-unsaturated compounds (**6**) undergo nucleophilic attack by intermediate **14**, leading to the formation of intermediate **16**. Subsequently, elimination reactions occur, yielding the Stetter products (**8a-l**), and regenerating the original carbene catalyst (**12**). This pathway is represented by the blue pathway in Scheme 5.



Scheme 5 – Catalytic cycles of intermolecular Stetter reaction of aldehydes with *α*,*β*-unsaturated compounds (blue pathway)/cross-coupling reaction between aromatic aldehydes and *N*-acylbenzotriazole (red pathway).

For a plausible catalytic cycle explaining the formation of 1,2-dicarbonyl derivative compounds (**10a-j**), we propose an alternative pathway (red pathway in Scheme 1). *N*,*N*-dimethylbenzimidazol-2-ylidene (**12**), generated in situ from the deprotonation of benzimidazolium salt **4** by DBU, reacts with the aromatic aldehyde (**5**) to produce the Breslow intermediate (**14**). This intermediate subsequently reacts with *N*-acylbenzotriazole (**7**), forming intermediate **17**. The collapse of intermediate **17**, followed by the liberation of benzimidazol-2-ylidene (**12**) from the resulting intermediate **18**, results in the formation of 1,2-dicarbonyl compounds (**10a-j**) and completes the catalytic cycle.

MATERIAL AND METHODS

This study was conducted using chemicals and reagents of analytical grade, which were used directly without any further purification. This includes the *N*-acylbenzotriazole derivatives **7a-d**, as previously reported in our earlier works.[48] Our experimental setup involved a domestic microwave oven (Electrolux, EMM2023MW, 700W, 2450 MHz). Melting points were determined using a Buchi B-545 apparatus and compared with the values of known reference samples. We analyzed ^{1}H-NMR and ^{13}C-NMR spectra in $CDCl_3$ on a Varian Mercury 400 spectrometer and obtained IR spectra using KBr disks on a Shimadzu spectrometer. For routine monitoring of reactions, we employed TLC, using Kieselgel 60 F_{254} precoated aluminum sheets, readily available from Merck.

General procedure for the microwave-enhanced intermolecular Stetter reaction between aromatic aldehydes and various substates, including acrylonitrile (6a), methyl vinyl ketone (6b) ethyl acrylate (6c) or methyl acrylate (6d) catalyzed by *N*,*N*-dimethylbenzimidazolium Iodide (4) in the absence of organic solvent

The reaction was initiated by grinding a mixture of *N*,*N*-dimethylbenzimidazolium iodide (**4**) (1 mmol) and NaOH (0.2 mmol) in a mortar at room temperature for 5 minutes. Subsequently, aromatic aldehydes (1.0 mmol) and either acrylonitrile (**6a**), methyl vinyl ketone (**6b**), ethyl acrylate (**6c**), or methyl acrylate (**6d**) (2.0 mmol) were added to the mixture. The reaction was then subjected to microwave irradiation at 700W for a duration ranging from 70 to 130 minutes. Upon completion of the reaction, confirmed by TLC (using a 50% hexane/dichloromethane solvent mixture), we extracted the product with ethyl acetate (3 × 25 mL). The organic phase was dried, and the solvent was removed under reduced pressure. The resulting residue was purified by preparative liquid chromatography (PLC) using a 50% hexane-dichloromethane solvent mixture, yielding compounds **8a-l**.

4-Phenyl-4-oxobutanenitrile **(8a)**

R_f = 0.35 (50% hexane/dichloromethane), white crystals, m.p.: 75-77 °C (lit. 74-76 °C);[47] IR (KBr): ν_{max} 3062 (aromatic C-H stretching), 2940 (aliphatic C-H stretching), 2250 (C≡N stretching), 1683 (C=O stretching), 1595 (aromatic C=C stretching) and 1210 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.96 (2H, d, *J* = 7.2 Hz, 2′-*H* and 6′-*H*), 7.62 (1H, t, *J* = 7.6 Hz, 4′-*H*), 7.50 (2H, t, *J* = 7.6 Hz, 3′-*H* and 5′-*H*), 3.39 (2H, t, *J* = 7.2 Hz, CH_2CH_2CN) and 2.78 (2H, t, *J* = 7.2 Hz, CH_2CH_2CN); ^{13}C NMR δ 11.8, 34.3, 119.2, 128.0, 128.9, 133.9, 135.6 and 195.3.

4-(4′-Chlorophenyl)-4-oxobutanenitrile **(8b)**

R_f = 0.21 (50% hexane/dichloromethane), yellow crystals, m.p.: 72-73 °C (lit. 72-73 °C);[48] IR (KBr): ν_{max} 3091, 3060 (aromatic C-H stretching), 2924 (aliphatic C-H stretching), 2250 (C≡N stretching), 1675 (C=O stretching), 1590 (aromatic C=C stretching) and 1212 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.89 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.47 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 3.35 (2H, t, *J* = 7.2 Hz, CH_2CH_2CN) and 2.77 (2H, t, *J* = 7.2 Hz, CH_2CH_2CN); ^{13}C NMR δ 11.7, 34.2, 119.0, 129.2, 129.4, 133.9, 140.5 and 194.1.

4-(4′- Methylphenyl)-4-oxobutanenitrile **(8c)**

R_f = 0.31 (50% hexane/dichloromethane), yellow crystals, m.p. 75-76 °C (lit. 75-77 °C);[35] IR (KBr): ν_{max} 3040 (aromatic C-H stretching), 2924, 2891 (aliphatic C-H stretching), 2251 (C≡N stretching), 1681 (C=O stretching), 1594 (aromatic C=C stretching), 1313 and 1229 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.78 (2H, d, *J* = 7.6 Hz, 2′-*H* and 6′-*H*), 7.22 (2H, d, *J* = 7.6 Hz, 3′-*H* and 5′-*H*), 3.29 (2H, t, *J* = 7.2 Hz, CH_2CH_2CN) and 2.70 (2H, t, *J* = 7.2 Hz, CH_2CH_2CN) and 2.36 (3H, s, Ar-CH_3); ^{13}C NMR δ 11.8, 29.7, 34.1, 119.2, 128.1, 129.5, 133.2, 144.9 and 201.4.

1-Phenyl-1,4-pentanedione **(8d)**

R_f = 0.56 (50% hexane/dichloromethane), yellow crystals, m.p. 70-72 °C (lit. 70-72 °C);[34] IR (KBr): ν_{max} 3073 (aromatic C-H stretching), 2900 (aliphatic C-H stretching), 1718, 1676 (C=O stretching), 1596 (aromatic C=C stretching), 1347 and 1211 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.84 (2H, d, *J* = 7.2 Hz, 2-*H* and 6-*H*), 7.71 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.44 (2H, t, *J* = 7.6 Hz, 3-*H* and 5-*H*), 3.23 (2H, t, *J* = 13.1 Hz, $CH_2CH_2COCH_3$), 2.84 (2H, t, *J* = 13.1 Hz, $CH_2CH_2COCH_3$) and 2.17 (3H, s, $CH_2CH_2COCH_3$); ^{13}C NMR δ 29.8, 32.3, 36.9, 127.8, 128.4, 132.9, 136.6, 198.3 and 206.9.

1-(4′-Chlorophenyl)-1,4-pentanedione **(8e)**

R_f = 0.50 (50% hexane/dichloromethane), yellow crystals, m.p. 71-72 °C (lit. 71-73 °C);[34] IR (KBr): ν_{max} 3100 (aromatic C-H stretching), 2902 (aliphatic C-H stretching), 1718, 1673 (C=O stretching), 1590 (aromatic C=C stretching), 1335, 1317 and 1214 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.90 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.41 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 3.21 (2H, t, *J* = 13.2

Hz, $CH_2CH_2COCH_3$), 2.75 (2H, t, *J* = 13.2 Hz, $CH_2CH_2COCH_3$) and 2.18 (3H, s, $CH_2CH_2COCH_3$); ^{13}C NMR δ 29.7, 32.1, 36.8, 128.1, 128.8, 134.9, 139.3, 197.1 and 206.8.

***1-(4′- Methylphenyl)-1,4-pentanedione* (8f)**

R_f = 0.48 (50% hexane/dichloromethane), yellow crystals, m.p. 84-85 °C (lit. 83-85 °C);[34] IR (KBr): ν_{max} 3091 (aromatic C-H stretching), 2914 (aliphatic C-H stretching), 1708, 1679 (C=O stretching), 1584 (aromatic C=C stretching), 1321 and 1217 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.88 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.31 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 3.22 (2H, t, *J* = 13.2 Hz, $CH_2CH_2COCH_3$), 2.78 (2H, t, *J* = 13.2 Hz, $CH_2CH_2COCH_3$), 2.41 (3H, s, Ar-CH_3) and 2.16 (3H, s, $CH_2CH_2COCH_3$); ^{13}C NMR δ 11.9, 29.6, 32.2, 36.7, 128.9, 130.1, 134.5, 138.7, 198.1 and 206.7.

***Ethyl 4-phenyl-4-oxobutanoate* (8g)**

R_f = 0.43 (50% hexane/dichloromethane), yellow liquid;[35] IR (neat): ν_{max} 3063 (aromatic C-H stretching), 2983, 2933 (aliphatic C-H stretching), 1733 , 1687 (C=O stretching), 1597 (aromatic C=C stretching), 1365, 1219 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.97 (2H, d, *J* = 7.2 Hz, 2′-*H* and 6′-*H*), 7.55 (1H, t, *J* = 7.2 Hz, 4′-*H*), 7.45 (2H, t, *J* = 7.2 Hz, 3′-*H* and 5′-*H*), 4.15 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 3.30 (2H, t, *J* = 6.8 Hz, $CH_2CH_2CO_2CH_2CH_3$), 2.75 (2H, t, *J* = 6.8 Hz, $CH_2CH_2CO_2CH_2CH_3$) and 1.25 (3H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$); ^{13}C NMR δ 14.2, 28.3, 33.4, 60.6, 128.0, 128.6, 133.2, 136.6, 172.9 and 198.1.

***Ethyl 4-(4′-chlorophenyl)-4-oxobutanoate* (8h)**

R_f = 0.41 (50% hexane/dichloromethane), yellow crystal, m.p. 56-57 °C (lit. 56-58 °C);[47] IR (KBr): ν_{max} 3091 (aromatic C-H stretching), 2981, 2945 (aliphatic C-H stretching), 1732, 1671 (C=O stretching), 1588 (aromatic C=C stretching), 1319, 1251 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.85 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.37 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-H), 4.09 (2H, q, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 3.20 (2H, t, *J* = 6.8 Hz, $CH_2CH_2CO_2CH_2CH_3$), 2.68 (2H, t, *J* = 6.8 Hz, $CH_2CH_2CO_2CH_2CH_3$) and 1.20 (3H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$); ^{13}C NMR δ 14.2, 28.2, 33.3, 60.7, 128.9, 129.4, 134.9, 139.7, 172.8 and 197.0.

***Ethyl 4-(4′- methylphenyl)-4-oxobutanoate* (8i)**

R_f = 0.41 (50% hexane/dichloromethane), white crystals, m.p. 64-66 °C (lit. 64-65 °C);[35] IR (KBr): ν_{max} 3091(aromatic C-H stretching), 2981, 2930 (aliphatic C-H stretching), 1732, 1671 (C=O stretching), 1589 (aromatic C=C stretching), 1379, 1298 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.85 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.37 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 4.09 (2H, q, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 3.21 (2H, t, *J* = 6.4 Hz, $CH_2CH_2CO_2CH_2CH_3$), 2.68 (2H, t, *J* = 6.4 Hz, $CH_2CH_2CO_2CH_2CH_3$), 2.10 (3H , s, Ar-CH_3), 1.20 (3H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$); ^{13}C NMR δ 14.2, 28.2, 30.9, 33.0, 60.7, 128.9, 129.4, 134.9, 139.6, 172.8 and 196.9.

***Methyl 4-phenyl-4-oxobutanoate* (8j)**

R_f = 0.43 (50% hexane/dichloromethane), yellow liquid;[49] IR (neat): ν_{max} 3063 (aromatic C-H stretching), 2983, 2933 (aliphatic C-H stretching), 1733 , 1687 (C=O stretching), 1597 (aromatic C=C stretching), 1365, 1219 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.93 (2H, d, *J* = 7.2 Hz, 2′- and 6′-*H*), 7.50 (1H, t, *J* = 7.2 Hz, 4′-*H*), 7.39 (2H, t, *J* = 7.2 Hz, 3′- and 5′-*H*), 3.65 (3H, s, $CH_2CH_2CO_2CH_3$), 3.33 (2H, t, *J* = 6.8 Hz, $CH_2CH_2CO_2CH_3$) and 2.71 (2H, t, *J* = 6.8 Hz, $CH_2CH_2CO_2CH_3$); ^{13}C NMR δ 27.8, 33.4, 51.6, 128.0, 128.6, 133.2, 136.6, 173.3 and 198.1.

***Methyl 4-(4′-chlorophenyl)-4-oxobutanoate* (8k)**

R_f = 0.41 (50% hexane/dichloromethane), white solid,[49] m.p. 47-49 °C; IR (KBr): ν_{max} 3091 (aromatic C-H stretching), 2981, 2945 (aliphatic C-H stretching), 1732, 1671 (C=O stretching), 1588 (aromatic C=C stretching), 1319, 1251 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.90 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.41 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-H), 3.68 (3H, s, $CH_2CH_2CO_2CH_3$), 3.26 (2H, t, *J* = 6.8 Hz, $CH_2CH_2CO_2CH_3$) and 2.77 (2H, t, *J* = 6.8 Hz, $CH_2CH_2CO_2CH_3$); ^{13}C NMR δ 27.9, 33.3, 52.0, 128.9, 129.4, 134.8, 139.7, 173.0 and 196.9.

***Methyl 4-(4′- methylphenyl)-4-oxobutanoate* (8l)**

R_f = 0.41 (50% hexane/dichloromethane), white solid,[49] m.p. 66–67 °C; IR (KBr): ν_{max} 3091(aromatic C-H stretching), 2981, 2930 (aliphatic C-H stretching), 1732, 1671 (C=O stretching), 1589 (aromatic C=C stretching), 1379, 1298 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.87 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.26 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 3.71 (3H, s, $CH_2CH_2CO_2CH_3$), 3.29 (2H, t, *J* = 6.4 Hz, $CH_2CH_2CO_2CH_3$), 2.75 (2H, t, *J* = 6.4 Hz, $CH_2CH_2CO_2CH_3$) and 2.42 (3H, s, Ar-CH_3); ^{13}C NMR δ 21.6, 28.1, 33.3, 52.0, 128.1, 129.3, 134.1, 144.0, 173.4 and 197.8.

***Benzoin* (9)**

R_f = 0.19 (50% hexane/dichloromethane), white crystals; m.p. 133-135 °C (lit. 134-136 °C);[13] IR

(KBr): ν_{max} 3418 (O-H stretching), 3067, 3024 (aromatic C-H stretching), 2931 (aliphatic C-H stretching), 1678 (C=O stretching), 1596 (aromatic C=C stretching), 1256 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.91 (2H, d, *J* = 7.6 Hz, 2-*H* and 6-*H*), 7.51 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.39 (2H, t, *J* = 7.6 Hz, 3-*H* and 5-*H*), 7.25–7.32 (5H, m, Ar*H*), 5.95 (1H, s, C*H*), 4.52 (1H, br s, OH); ^{13}C NMR δ 76.1, 127.8, 128.6, 128.7,129.1, 133.6, 133.9, 139.0 and 198.8.

General procedure for the microwave-enhanced cross-couping reaction between aromatic aldehydes and N-acylbenzotriazoles 7a-d catalyzed by *N*,*N*-dimethylbenzimidazolium iodide (4) in the absence of organic solvent

The reaction was begun by grinding a mixture of *N*,*N*-dimethylbenzimidazolium iodide (**4**) (1.0 mmol) and DBU (0.2 mmol) together in a mortar at room temperature for 5 minutes. Aromatic aldehydes (**5**) (1.0 mmol) and one of the following *N*-acylbenzotriazoles, *N*-benzoylbenzotriazole (**7a**), *N*-(4-chlorobenzoyl)-1*H*-benzotriazole (**7b**), *N*-(4-methylbenzoyl)-1*H*-benzotriazole (**7c**), or *N*-(4-methoxybenzoyl)-1*H*-benzotriazole (**7d**) (2.0 mmol), were then added slowly to the mixture. The resulting mixture was subjected to microwave irradiation at 700W for a duration ranging from 90 to 150 minutes. Upon completion of the reaction, as confirmed by TLC (using a 50% hexane/dichloromethane solvent mixture), we extracted the product with ethyl acetate (3 × 25 mL). The organic phase was dried, and the solvent was removed under reduced pressure. The resulting residue was purified by preparative liquid chromatography (PLC) using a 50% hexane/dichloromethane solvent mixture, yielding compounds **10a-j**.

1,2-Diphenylethane-1,2-dione **(10a)**

R_f = 0.66 (50% hexane/dichloromethane), yellow solid, m.p. 94–96 °C (lit. 95-96 °C);[44] IR (KBr): ν_{max} 3064 (aromatic C-H stretching), 1662 (C=O stretching), 1589 (aromatic C=C stretching), 1349 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.97 (4H, d, *J* = 7.6 Hz, 2-*H*, 6-*H*, 2′-*H* and 6′-*H*), 7.65 (2H, t, *J* =7.6 Hz, 4-*H* and 4′-*H*) and 7.52 (4H, t, *J* = 7.6 Hz, 3-*H*, 5-*H*, 3′-*H* and 5′-*H*); ^{13}C NMR δ 129.0, 129.9, 133.0, 134.8 and 194.4.

1,2-Di(4-chlorophenyl)ethane-1,2-dione **(10b)**

R_f = 0.63 (50% hexane/dichloromethane), yellow crystals, m.p. 197-198 °C (lit. 197-198 °C);[48] IR(KBr): νmax 3090 (aromatic C-H stretching), 1665 (C=O stretching), 1591 (aromatic C=C stretching), 1317, 1214 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.92 (4H, d, *J* = 8.8 Hz, 2-*H*, 6-*H*, 2′-*H* and 6′-*H*) and 7.51 (4H, d, *J* = 8.4 Hz, 3-*H*, 5-*H*, 3′-*H* and 5′-*H*); ^{13}C NMR δ 129.4, 131.2, 131.3, 141.9 and 192.3.

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione **(10c)**

R_f = 0.64 (50% hexane/dichloromethane), yellow crystals, m.p. 74-75 °C (lit. 75-76 °C);[50] IR (KBr): ν_{max} 3081 (aromatic C-H stretching), 1667 (C=O stretching), 1587 (aromatic C=C stretching), 1309, 1281 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.90 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.92 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.68 (1H, t, *J* = 7.2 Hz, 4′-*H*), 7.52 (2H, d, *J* = 7.6 Hz, 3-*H* and 5-*H*) and 7.51 (2H, d, *J* = 8.4 Hz, 3′-H and 5′-H); ^{13}C NMR δ 129.0, 129.3, 129.9, 131.3, 131.4, 132.8, 135.1, 141.6, 193.1 and 193.7.

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione **(10d)**

R_f = 0.54 (50% hexane/dichloromethane), yellow oil;[50] IR (KBr): ν_{max} 3065, 3009 (aromatic C-H stretching), 2951, 2859 (aliphatic C-H stretching), 1678 (C=O stretching), 1597 (aromatic C=C stretching), 1300, 1265 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.96 (4H, t, *J* = 8.4 Hz, 2-*H*, 6-*H*, 2′-*H* and 6′-*H*), 7.64 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.52 (2H, t, *J* = 8.0 Hz, 3-*H* and 5-*H*), 6.99 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*) and 3.89 (3H, s, Ar-OCH_3); ^{13}C NMR δ 55.5, 114.4, 126.1,128.8, 129.9, 132.5, 133.2, 134.7, 165.1, 193.1 and 194.9.

1-(4-Chlorophenyl)-2-(2,4-dichlorophenyl)-ethane-1,2-dione **(10e)**

R_f = 0.62 (50% hexane/dichloromethane), yellow solid, m.p. 79–81 °C (lit. 80–82 °C);[51] IR (KBr): ν_{max} 3074 (aromatic C-H stretching), 1661 (C=O stretching), 1581 (aromatic C=C stretching), 1369 (C-O stretching) cm^{-1}; ^{1}H NMR δ 7.97 (2H, d, *J* = 8.4 Hz, 5-*H* and 6-*H*), 7.85 (1H, d, *J* = 8.0 Hz, 3-*H*), 7.52 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*) and 7.43–7.46 (2H, m, 2′-*H* and 6′-*H*); ^{13}C NMR δ 128.0, 129.3, 130.4, 130.5, 131.6, 132.2, 132.9, 134.3, 140.6, 141.4, 190.2 and 192.2.

1-(4-Chlorophenyl)-2-(4-methylphenyl)ethane-1,2-dione **(10f)**

R_f = 0.61 (50% hexane/dichloromethane), yellow solid, m.p. 114–115 °C (lit. 116–117 °C);[51] IR (neat): ν_{max} 3073 (aromatic C-H stretching), 2937 (aliphatic C-H stretching), 1663 (C=O stretching), 1585 (aromatic C=C stretching), 1335,

1271 (C-O stretching) cm^{-1}; ^1H NMR δ 7.92 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.86 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.48 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.31 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*) and 2.44 (3H, s, Ar-CH_3); ^{13}C NMR δ 21.8, 129.4, 129.9, 130.1, 130.4,131.3, 131.5, 141.4, 146.5, 193.1 and 193.5.

***1-(2-Chlorophenyl)-2-(4-methoxyphenyl)-ethane-1,2-dione* (10g)**

R_f = 0.58 (50% hexane/dichloromethane), yellow liquid;[42] IR (neat): ν_{max} 3095, (aromatic C-H stretching), 2963 (aliphatic C-H stretching), 1669 (C=O stretching), 1579 (aromatic C=C stretching), 1313, 1265 (C-O stretching) cm^{-1}; ^1H NMR δ 7.93 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.91 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.49 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 6.98 (2H, d, *J* = 8.0 Hz, 3-*H* and 5-*H*) and 3.88 (3H, s, Ar-OCH_3); ^{13}C NMR δ 55.6, 114.5, 125.9, 129.4, 131.2, 131.6, 132.5, 141.2, 165.2, 192.5 and 193.5.

***1,2-Di(4-methylphenyl)ethane-1,2-dione* (10h)**

R_f = 0.59 (50% hexane/dichloromethane), yellow crystals, m.p. 99-101 °C (lit. 99-100 °C);[44] IR (KBr): ν_{max} 3068 (aromatic C-H stretching), 2956 (aliphatic C-H stretching), 1666 (C=O stretching), 1601, 1579 (aromatic C=C stretching), 1328, 1227 (C-O stretching) cm^{-1}; ^1H NMR δ 7.85 (4H, d, *J* = 8.4 Hz, 2-*H*, 6-*H*, 2′-H and 6′-*H*), 7.03 (4H, d, *J* = 8.4 Hz, 3-*H*, 5-*H*, 3′-*H* and 5′-*H*) and 2.43 (6H, s, 2(Ar-CH_3)); ^{13}C NMR δ 21.7, 126.6, 129.3, 130.2, 144.6 and 171.5.

***1-(4-Nitrophenyl)-2-phenylethane-1,2-dione* (10i)**

R_f = 0.57 (50% hexane/dichloromethane), yellow solid, m.p. 149-151 °C (lit. 151-152 °C);[52] IR (KBr): ν_{max} 3105 (aromatic C-H stretching), 1664 (C=O stretching), 1597 (aromatic C=C stretching), 1378 (C-O stretching) cm^{-1}; ^1H NMR δ 8.36 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 8.18 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.99 (2H, d, *J* = 7.2 Hz, 2′-H and 6′-*H*), 7.70–7.74 (1H, m, 4′-*H*) and 7.54–7.58 (2H, m, 2′-H and 6′-*H*); ^{13}C NMR δ 124.1, 129.3, 130.0, 130.9, 132.4, 135.5, 137.3, 151.2, 192.1 and 192.8.

***1,2-Di(4-methoxyphenyl)ethane-1,2-dione* (10j)**

R_f = 0.62) (50% hexane/dichloromethane), yellow solid, m.p. 132-133 °C (lit. 132-134 °C);[44] IR (KBr): ν_{max} 3061 (aromatic C-H stretching), 2962, 2848 (aliphatic C-H stretching), 1658 (C=O stretching), 1593 (aromatic C=C stretching), 1302, 1263 (C-O stretching) cm^{-1}; ^1H NMR δ 7.96 (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*) and 3.89 (6H, s, 2(Ar-OCH_3)); ^{13}C NMR δ 55.6, 114.4, 126.4, 132.5, 164.9 and 193.4.

***1H-1,2,3-Benzotriazol-1-yl(phenyl)methyl benzoate* (11)**

R_f = 0.14) (50% hexane/dichloromethane), colour-less liquid;[42] IR (neat): ν_{max} 3069 (aromatic C-H stretching), 1737 (C=O stretching of ester), 1607 (aromatic C=C stretching), 1258 (C-O stretching) cm^{-1}; ^1H NMR δ 8.76 (1H, s, ArC-*H*), 8.15 (2H, d, *J* = 8.4 Hz, C_2-*H* and C_6-*H* of Ar-*H*), 8.09 (1H, d, *J* = 7.6 Hz, C_7′-*H* of Ar-*H*), 7.62 (1H, t, *J* = 7.6 Hz, C_6′-*H* of Ar-*H*), 7.51-7.45 (9H, m, Ar-*H*) and 7.36 (1H, t, *J* = 7.6 Hz, C5′-*H* of Ar-*H*); ^{13}C NMR δ δ 80.9, 110.6, 120.4, 124.4, 126.4, 128.2, 128.6, 128.8, 128.9, 129.7, 130.2, 132.1, 134.1, 134.3, 146.5 and 164.4.

CONCLUSIONS

In summary, we have developed an efficient and environmentally friendly method for conducting intermolecular Stetter reactions between aromatic aldehydes and *α,β*-unsaturated compounds, as well as cross-coupling reactions between aromatic aldehydes and *N*-acylbenzotriazoles. This method harnesses the power of microwave irradiation and utilizes *N,N*-dimethylbenzimidazolium iodide as the catalyst. The reactions consistently yield high quantities of 1,4-addition products (**8a-l**), ranging from 85% to 96% for the Stetter reactions, and 1,2-dicarbonyl products (**10a-j**), with yields between 82% and 94% for the cross-coupling reactions. Notably, the recovered *N,N*-dimethylbenzimidazolium iodide can be reused up to four times without a significant loss of catalytic efficiency. This reusability aspect is particularly advantageous for sustainable and environmentally conscious green chemistry practices.

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