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FULL PAPER

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Efficient and green catalytic system incorporating new benzimidazolium salts for the Sonogashira cross-coupling reaction

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A number of novel benzimidazole salts were synthesized and their structures were determined using ^{1}H NMR, ^{13}C NMR and infrared spectroscopic techniques and elemental analysis. A catalyst system consisting of $Pd(OAc)_2$ and copper nanoparticles in the presence of Cs_2CO_3 and incorporating the novel benzimidazole salts in poly(ethylene glycol) solvent significantly improved the yields of Sonogashira reactions between aryl halides and phenylacetylene under microwave irradiation in 10 min.

KEYWORDS
benzimidazole salts, copper nanoparticles, cross-coupling, homocoupling, microwave, Sonogashira reaction

1 | INTRODUCTION

The first cross-coupling reaction with terminal alkynes and aryl or vinyl halides in the presence of a palladium and copper iodide catalyst was reported in 1975 by Sonogashira and co-workers.[1] Since then, this protocol has been popularized as the Sonogashira cross-coupling reaction. Today, the Sonogashira coupling reaction is known as a powerful method for the synthesis of novel alkynes derived from terminal acetylenes and aryl or vinyl halides.[2–11] Although palladium–phosphine complexes and copper-based catalysts have been mostly used in the Sonogashira reaction, the addition of copper(I) salts as co-catalysts has some drawbacks such as Glaser-type homocoupling and phosphine-based ligands causing environmental pollution.[2] In order to prevent these unwanted effects, many researchers have also tried copper-free and metal-free Sonogashira reaction protocols.[4,12–19] Many of these methods involve long reaction times and low reaction yields. After the isolation of stable N-heterocyclic carbenes by Arduengo and co-workers in 1991, a new window was opened for scientists who worked on metal-mediated catalytic syntheses due to the ease of synthesis of N-heterocyclic carbene ligands which have better σ-donor ability, lower toxicity and better thermal stability than phosphine-based ligands.[20,21] Microwave irradiation accelerates chemical reactions and increases reaction yields and decreases reaction times and electricity costs, and the use of metal catalysis in conjunction with microwave heating provides significant advantages.[22,23] In our previous studies, we used several *in situ* prepared palladium–N-heterocyclic carbenes derived from benzimidazole for the Suzuki, Heck and Buchwald–Hartwig reactions under microwave irradiation conditions and obtained promising catalytic results.[24–30]

The use of a metal catalyst as nanoparticles generally accelerates the catalytic conversion and the use of nanoparticles in cross-coupling reactions has attracted a great deal of interest because of their effectiveness. Therefore, several studies have been reported relating to the use of palladium nanoparticles in cross-coupling reactions.[31–34] However, as far as we know, there has been only one report of the use of copper nanoparticles as a co-catalyst in the Sonogashira cross-coupling reaction which was also reported by us.[26] Palladium-catalysed reactions are important in synthetic organic chemistry.[35–38] In this context, both homogenous and heterogeneous catalyst systems incorporating palladium have been used. Comparing these systems, homogeneous systems seem to be more active due to their acting at the molecular scale whereas heterogeneous systems are active only on the catalytic surface. Immobilization is a method to improve catalytic activity and recyclability of homogeneous catalysts using an appropriate supporting system such as polymers, resins etc.[39–42] However, it has been reported that

palladium immobilization is generally complicated and involves multiple steps with undesirable palladium black formation and relatively long reaction times.[40,41]

In our previous work, we investigated the catalytic activity of *N*-phthalimidoethyl and 4-substituted benzyl-bearing benzimidazolium salts in the Sonogashira cross-coupling reaction. With the hope of obtaining the most efficient catalyst for Sonogashira cross-coupling reactions, the work presented here focused on a catalyst system containing a series of novel benzimidazole compounds (having 2-oxo-2-phenylethyl, alkyl, substituted alkyl and benzyl), $Pd(OAc)_2$, copper nanoparticles (CuNPc) and $CsCO_3$ for reaction in poly(ethylene glycol) (PEG) under microwave irradiation.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and characterization of new Benzimidazole salts

Benzimidazole salts are good source for *in situ* formation of palladium–N-heterocyclic carbene complexes from $Pd(OAc)_2$ in the presence of an appropriate base. Substituents in benzimidazole salts incorporated in the catalytic system also play a role in catalytic activity, and electron-donating substituents slightly enhance catalytic activity whereas electron-withdrawing substituents slightly decrease it. In this context, new benzimidazole salts were prepared in good yields by treating appropriate alkyl halide with 1-benzyl-1*H*-benzo[*d*]imidazole (**I**) or 2-(1*H*–benzo[*d*]imidazol-1-yl)-1-phenylethanone (**II**) or 1-phenethyl-1*H*-benzo[*d*]imidazole (**III**). All benzimidazole salts were smoothly crystallized from an EtOH–Et_2O mixture. The structures of benzimidazole complexes **1**–**10** were elucidated using ^{1}H NMR, ^{13}C NMR and infrared (IR) spectrometric analyses. All spectral data were in agreement with the proposed structures. IR spectra of compounds show strong $\nu_{(C=O)}$ and $\nu_{(C=N)}$ bands at 1682–1703 and 1560–1595 cm^{-1}, respectively. The IR spectrum of **4** shows a $\nu_{(C\&-N)}$ band at 2200 cm^{-1}. The characteristic CH resonances for the proton at the 2-position of benzimidazole salts **1**–**10** were observed between 9.71 and 10.29 ppm. As expected, salt formation shifts the ^{1}H NMR signals of the benzimidazolium salts downfield from those of the naked benzimidazole ($\Delta\delta \approx 0.63$ to 2.21 ppm) for the proton at the 2-position of benzimidazole ring. The carbon resonances for the carbon at the 2-position of benzimidazole salts **1**–**10** were observed between 142.3 and 144.9 ppm. Salt formation shifts the ^{13}C NMR signals of the benzimidazolium salts downfield from those of the naked benzimidazole ($\Delta\delta \approx 0.8$ to 3.4 ppm) for the carbon at the 2-position of the benzimidazole salt. All other aliphatic and aromatic protons and carbons were observed at expected regions.

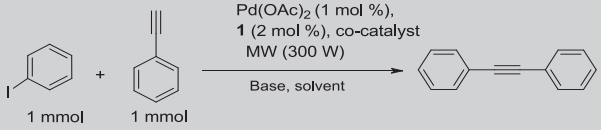
2.2 | Optimization of Sonogashira reactions

In order to determine the optimum reaction conditions for the Sonogashira coupling reaction we chose to study the coupling of iodobenzene with phenylacetylene as model compounds. The test reactions were performed in the presence of 0.05 or 1 mol% of $Pd(OAc)_2$ and 1 or 0.05 mol% of CuI or 2 or 4 mol% of CuNPc as co-catalyst using different bases such as KOH, K_2CO_3 and Cs_2CO_3 in various solvents such as DMF, EtOH, DME, $C_2H_4(OH)_2$, glycerol and PEG^{300} for 5, 10 and 20 min at 60, 80, 100 and 120 °C under microwave irradiation. Solvents can play an important role in organic synthesis. In this context, PEG has been used as a solvent, phase-transfer catalyst and to enhance the recyclability of catalysts.[43–45] Optimization data are shown in Table 1. It was found that the Sonogashira coupling reaction catalysed by **1**, 1 mol% of $Pd(OAc)_2$, 4 mol% of CuNPc as co-catalyst and base catalyst system gave the highest yield when using PEG as a solvent and Cs_2CO_3 as a base at 100 °C with microwave heating in 10 min (Table 1, entry 19). Having established the optimal reaction conditions, the recycling of the catalyst was investigated. The catalyst can be recycled at least three times without significant loss of activity (Table 1, entry 19). Neither prolonging the reaction time from 10 to 20 min nor enhancing the reaction temperature from 100 to 120 °C affected significantly the coupling product yields. Experiments showed that the yields of Sonogashira coupling reaction were decreased in the absence of **1** in 10 min under optimized conditions (Table 1, entry 21). We also explored whether the reaction can be effected using conventional heating system in a preheated oil bath for 10 min under optimized reaction conditions. However, we did not detect desired coupling product under the optimal reaction conditions using conventional heating (Table 1, entry 23).

2.3 | Sonogashira coupling reaction of Aryl halides with Phenylacatylene

After having established the optimized coupling reaction conditions (Table 1).we investigated the reaction using a variety of aryl halides having electron-neutral, electron-rich and electron-poor properties, such as iodobenzene, bromobenzene, chlorobenzene, 4-iodotoluene, 4-bromonitrobenene, 4-iodoanisole, 4-bromobenzaldehyde and 4-bromoacetophenone, with phenylacetylene as substrate under the optimized conditions. The results are given in Table 2. Regardless of aryl halide reactivity, both aryl iodides and aryl bromides coupled smoothly with phenylacetylene to form the desired corresponding products in good to excellent yields (Table 2, entries 1–20 and 32–81). Among the aryl halides, phenyl iodide and aryl bromides bearing electron-withdrawing substituent such as nitro, formyl and acetyl gave excellent Sonogashira-type coupling yields (Table 2, entries

TABLE 1 Optimization of Sonogashira coupling reactions under microwave irradiation[a]



			Co-catalyst					
Entry	**Salt**	**Base**	**CuI (mol%)**	**CuNPc (mol%)**	**Solvent**	**Time (min)**	**Temperature (°C)**	**Yield (%)**
1	1	KOH	0.01	—	DMF	10	60	38
2	1	KOH	0.01	—	DMF	20	60	43
3	1	KOH	0.01	—	DMF	10	100	51
4	1	KOH	0.01	—	DMF	10	120	57
5	1	K_2CO_3	0.01	—	DMF	10	100	60
6	1	K_2CO_3	0.01	—	DMF	20	100	63
7	1	Cs_2CO_3	0.01	—	DMF	10	60	45
8	1	Cs_2CO_3	0.01	—	DMF	10	80	50
9	1	Cs_2CO_3	0.01	—	DMF	10	100	59
10	1	Cs_2CO_3	0.01	—	DMF	10	120	60
11	1	Cs_2CO_3	0.05	—	DMF	10	120	53
12	1	Cs_2CO_3	—	0.02	DMF	10	100	71
13	1	Cs_2CO_3	—	0.02	DMF	10	120	73
14	1	Cs_2CO_3	—	0.02	EtOH	10	100	43
15	1	Cs_2CO_3	—	0.02	DME	10	100	35
16	1	Cs_2CO_3	—	0.02	Ethylene glycol	10	100	61
17	1	Cs_2CO_3	—	0.02	Glycerol	10	100	52
18	1	Cs_2CO_3	—	0.02	PEG^{300}	10	100	90
19	1	Cs_2CO_3	—	0.04	PEG^{300}	10	100	100, 97[b], 92[c]
20	1	Cs_2CO_3	—	0.04	PEG^{300}	10	100	74[d]
21	None	Cs_2CO_3	—	0.04	PEG^{300}	10	100	59[e]
22	1	Cs_2CO_3	—	0.04	PEG^{300}	5	100	92
23	1	Cs_2CO_3	—	0.04	PEG^{300}	10	100	n.d.[f]

[a]Yields are based on aryl iodide. Reactions were monitored by GC–MS.

[b]Second run.

[c]Third run.

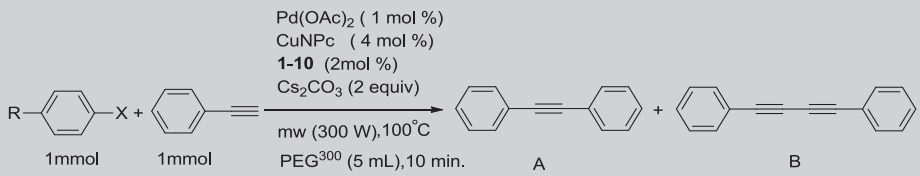
[d]0.5% $Pd(OAc)_2$ was used.

[e]Salt was not used.

[f]On preheated oil bath, for 10 min with thermal heating at 100 °C; n.d., not detected.

1–10, 42–51, 62–71 and 72–81). On the other hand, a strong electron-donating methoxy group and weak electron-donating methyl group on the aryl iodide gave a moderate or good yield using the optimized conditions (Table, 2, entries 52–61 and 32–41). It is noteworthy that only aryl chloride gave low Sonogashira cross-coupling yields and Glaser-type homocoupling products under optimized reaction conditions (Table 2, entries 21–31). We investigated the reactivity of chlorobenzene with phenylacetylene in the Sonogashira coupling reaction with extending the reaction time from 10 to 20 min. The extended reaction time slightly decreased the Sonogashira coupling yield but increased the homocoupling yield (Table 2, entry 22). We did not detect any Glaser-type homocoupling product from the other aryl bromides or iodides having electron-neutral, electron-poor or electron-rich substituents. Whereas significant differences were not observed among the substituents at position 3 of the benzimidazole ring incorporated in the catalytic system, the more electron-donating substituents led to desired Sonogashira-type coupling and slightly improved the catalytic yields. Comparing the catalytic activities of benzimidazolium salts incorporated in the catalytic system in our previous work[24] and the present work, benzimidazolium salts having 2-oxo-2-phenylethyl substituent showed slightly better catalytic activity than benzimidazolium salts bearing *N*-phthalimidoethyl substituent. Aryl chlorides were also

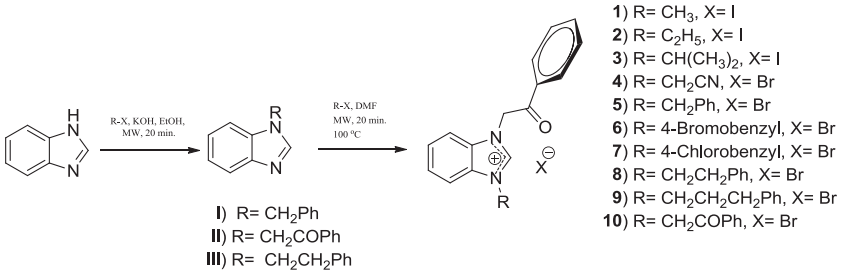
TABLE 2 Sonogashira coupling reactions of aryl halides with phenylacetylene



Entry	X	R	Salt	Yield A (%)	Yield B (%)	Entry	X	R	BimHX	Yield A (%)	Yield B (%)
1	I	H	1	90	n.d.	42	Br	NO_2	1	95 (90)[a]	n.d.
2	I	H	2	95	n.d.	43	Br	NO_2	2	92	n.d.
3	I	H	3	97	n.d.	44	Br	NO_2	3	96 (91)[a]	n.d.
4	I	H	4	98	n.d.	45	Br	NO_2	4	92	n.d.
5	I	H	5	95	n.d.	46	Br	NO_2	5	91	n.d.
6	I	H	6	94	n.d.	47	Br	NO_2	6	91	n.d.
7	I	H	7	96	n.d.	48	Br	NO_2	7	90	n.d.
8	I	H	8	98	n.d.	49	Br	NO_2	8	93	n.d.
9	I	H	9	100 (94)[a]	n.d.	50	Br	NO_2	9	90	n.d.
10	I	H	10	98 (92)[a]	n.d.	51	Br	NO_2	10	90	n.d.
11	Br	H	1	80	n.d.	52	I	OCH_3	1	88	n.d.
12	Br	H	2	80	n.d.	53	I	OCH_3	2	81	n.d.
13	Br	H	3	80	n.d.	54	I	OCH_3	3	82	n.d.
14	Br	H	4	86	n.d.	55	I	OCH_3	4	76	n.d.
15	Br	H	5	83	n.d.	56	I	OCH_3	5	83	n.d.
16	Br	H	6	82	n.d.	57	I	OCH_3	6	90	n.d.
17	Br	H	7	83	n.d.	58	I	OCH_3	7	86	n.d.
18	Br	H	8	84	n.d.	59	I	OCH_3	8	84	n.d.
19	Br	H	9	85	n.d.	60	I	OCH_3	9	89	n.d.
20	Br	H	10	82	n.d.	61	I	OCH_3	10	82	n.d.
21	Cl	H	1	50	42	62	Br	CHO	1	85	n.d.
22[b]	Cl	H	1	47	44	63	Br	CHO	2	92	n.d.
23	Cl	H	2	52	40	64	Br	CHO	3	92	n.d.
24	Cl	H	3	47	43	65	Br	CHO	4	91	n.d.
25	Cl	H	4	35	45	66	Br	CHO	5	93	n.d.
26	Cl	H	5	37	49	67	Br	CHO	6	92	n.d.
27	Cl	H	6	47	50	68	Br	CHO	7	90	n.d.
28	Cl	H	7	39	45	69	Br	CHO	8	92	n.d.
29	Cl	H	8	56	44	70	Br	CHO	9	96 (92)[a]	n.d.
30	Cl	H	9	56	26	71	Br	CHO	10	90	n.d.
31	Cl	H	10	64	35	72	Br	CH_3CO	1	91	n.d.
32	I	CH_3	1	92	n.d.	73	Br	CH_3CO	2	90	n.d.
33	I	CH_3	2	89	n.d.	74	Br	CH_3CO	3	91	n.d.
34	I	CH_3	3	86	n.d.	75	Br	CH_3CO	4	93	n.d.
35	I	CH_3	4	85	n.d.	76	Br	CH_3CO	5	93	n.d.
36	I	CH_3	5	82	n.d.	77	Br	CH_3CO	6	91	n.d.
37	I	CH_3	6	90	n.d.	78	Br	CH_3CO	7	88	n.d.
38	I	CH_3	7	87	n.d.	79	Br	CH_3CO	8	94 (90)[a]	n.d.
39	I	CH_3	8	87	n.d.	80	Br	CH_3CO	9	92	n.d.
40	I	CH_3	9	94	n.d.	81	Br	CH_3CO	10	92	n.d.
41	I	CH_3	10	80	n.d.						

[a]Isolated yield.

[b]Temperature ramped to 100 °C (3 min) and held for 20 min.



SCHEME 1 Synthesis of the benzimidazole derivatives

investigated in the present work and it is noteworthy that, besides the Sonogashira cross-coupling products, Glaser-type homocoupling products were also obtained.

3 | CONCLUSIONS

We have developed an efficient, simple and environmentally benign catalytic system incorporating novel benzimidazole salts for the Sonogashira cross-coupling reaction. The Sonogashira coupling yields were found to be excellent for aryl iodide bearing electron-neutral and electron-withdrawing substituents at position 4 of the phenyl ring. Aryl bromide bearing only electron-withdrawing substituents at position 4 of the phenyl ring gave excellent yields. Aryl chloride gave both Sonogashira cross-coupling and Glaser-type homocoupling products, each in yields of approximately 50%. Furthermore, the catalyst system consisting of $Pd(OAc)_2$, CuNPc, benzimidazole salts and Cs_2CO_3 in PEG^{300} can be recycled at least three times without loss of activity in short reaction time (10 min) without any palladium black formation.

4 | EXPERIMENTAL

4.1 | Materials and methods

Starting materials and reagents used in reactions were supplied commercially by Aldrich or Merck. All catalytic activity experiments were carried out in a microwave oven system manufactured by Milestone (Milestone Starts S Microwave Labstation for Synthesis) under aerobic conditions. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded using a Bruker DPX-300 high-performance digital FT NMR spectrometer. Elemental analyses were performed with a LECO CHNS-932 elemental analyser. IR spectra were recorded with ATR equipment in the range 650–4000 cm^{-1} using a PerkinElmer Spectrum One FTIR spectrophotometer. Melting points were recorded using an Electrothermal-9200 melting point apparatus and are uncorrected.

4.2 | GC–MS analysis

GC–MS spectra were recorded using an Agilient 6890 N GC and 5973 mass selective detector using with an HP-INNOWAX column of 60 m in length, 0.25 mm in diameter and 0.25 μm film thicknesses. GC–MS parameters for Sonogashira coupling reactions were as follows: initial temperature, 60 °C; initial time, 5 min; temperature ramp 1, 30 °C min^{-1}; final temperature, 200 °C; ramp 2, 20 °C min^{-1}; final temperature, 250 °C; run time, 30.17 min; injector port temperature, 250 °C; detector temperature, 250 °C; injection volume, 1.0 μl; carrier gas, helium; mass range, *m*/*z* between 50 and 550.

4.3 | Synthesis of Benzimidazolium salts

1-Benzyl-1*H*-benzo[*d*]imidazole (**I**),[46] 2-(1*H*–benzo[*d*]imidazol-1-yl)-1-phenylethanone (**II**)[47,48] and 1-phenethyl-1*H*-benzo[*d*]imidazole (**III**)[49] used in this work as starting compounds were prepared by treating benzimidazole with (chloromethyl)benzene, 2-bromo-1-phenylethanone and (2-bromoethyl)benzene, respectively, according to a modified literature procedure (Scheme 1). Compounds **1**[46,48] and **10**[50] have been reported in the literature but their synthesis methods need multi-step reactions and long reaction times. Thus, these compounds were prepared using a new one-step, easy synthetic method according to our previous studies (Scheme 1).[51]

4.4 | General method for synthesis of compounds 1–10

A mixture of 1 eq. of 1-substituted benzimidazole derivatives (**I**, **II** or **III**) and 1.1 eq. of appropriate alkyl halide was subjected to microwave irradiation (300 W, 100 °C) in DMF (10 ml) for 20 min. After completion of the reaction, all volatiles were removed under reduced pressure and the obtained crude product was crystallized from ethanol–diethyl ether (1:2).

4.4.1 | 3-Methyl-1-(2-oxo-2-phenylethyl)-1*H*–benzo[*d*]imidazol-3-ium iodide (1)

Yield 0.53 g (cream crystals), 66%; m.p. 164–166 °C. IR (ν_{max}, cm^{-1}): 1566 (C═N), 1682 (C═O). Anal. Found (%): C 51.39, H 3.84, N 7.66. Calcd for $C_{16}H_{15}IN_2O$ (378.2) (%): C 50.81, H 4.00, N 7.41. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.71 (*s*, 1H, NC*H*N), 7.66–8.17 (*m*, 9H, Ar-*H*), 6.48

(*s*, 2H, CH_2COPh), 4.22 (*s*, 3H, CH_3). ^{13}C NMR (DMSO-d_6, δ, ppm): 191.8 (CH_2*C*OPh), 144.1 (N*C*HN), 135.1, 134.2, 132.3, 132.0, 129.6, 129.0, 127.2, 127.0, 114.3, 114.2 (Ar-*C*), 53.8 (*C*H_2COPh), 34.2 (CH_3).

4.4.2 | 3-Ethyl-1-(2-oxo-2-phenylethyl)-1*H*–benzo[*d*]imidazol-3-ium iodide (2)

Yield 0.51 g (cream crystals), 52%; m.p. 94–95 °C. IR (ν_{max}, cm^{-1}): 1570 (C=N), 1699 (C=O). Anal. Found (%): C 51.80, H 4.17, N 6.90. Calcd for $C_{17}H_{17}IN_2O$ (392.2) (%): C 52.06, H 4.37, N 7.14. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.77 (*s*, 1H, NC*H*N), 8.09–8.18 (Ar-H, 4H), 7.80 (Ar-H, 1H), 7.68–7.75 (Ar-H, 4H), 6.43 (*s*, 2H, CH_2COPh), 4.66 (*q*, 4H, CH_2CH_3, J = 3.6 Hz), 1.59 (*t*, 3H, CH_3, J = 3.6 Hz). ^{13}C NMR (DMSO-d_6, δ, ppm): 191.7 (CH_2*C*OPh), 143.4 (N*C*HN), 135.1, 134.2, 132.5, 131.0, 129.6, 128.9, 127.3, 127.0, 114.5, 114.2 (Ar-*C*), 53.7 (*C*H_2COPh), 42.8 (CH_2), 14.7 (CH_3).

4.4.3 | 1-Isopropyl-3-(2-oxo-2-phenylethyl) benzimidazolium iodide (3)

Yield 0.70 g (cream crystals), 76.9%; m.p. 182–183 °C. IR (ν_{max}, cm^{-1}): 1595 (C=N), 1685 (C=O). Anal. Found (%): C 53.49, H 4.82, N 6.99. Calcd for $C_{18}H_{19}IN_2O$ (406.1) (%): C 53.22, H 4.71, N 6.90. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.77 (*s*, 1H, NC*H*N), 8.05–8.21 (*m*, 4H, Ar-H), 7.66–7.81 (*m*, 6H, Ar-H), 6.35 (*s*, 2H, CH_2COPh), 5.16 (*m*, 1H, $CH(CH_3)_2$), 1.67 (*d*, 6H, $CH(CH_3)_2$, J = 6.6 Hz). ^{13}C NMR (DMSO-d_6, δ, ppm): 191.7 (CH_2*C*OPh), 142.3 (N*C*HN), 135.28, 134.2, 132.7, 130.6, 129.6, 128.9, 127.3, 127.0, 114.5, 114.4 (Ar-*C*), 53.5 (CH_2COPh), 51.3 *C*$H(CH_3)_2$), 22.0 ($CH(CH_3)_2$).

4.4.4 | 3-(Cyanomethyl)-1-(2-oxo-2-phenylethyl)-1*H*–benzo[*d*]imidazol-3-ium bromide (4)

Yield 0.75 g (cream crystals), 71%; m.p. 199–200 °C. IR (ν_{max}, cm^{-1}): 1566 (C=N), 1689 (C=O), 2200 (C&-N). Anal. Found (%): C 56.98, H 3.95, N 11.76. Calcd for $C_{17}H_{14}BrN_3O$ (355.0) (%): C 57.32, H 3.96, N 11.80. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.93 (*s*, 1H, NC*H*N), 8.15–8.22 (*m*, 4H, Ar-H), 7.67–7.84 (*m*, 5H, Ar-H), 6.55 (*s*, 2H,CH_2COPh), 6.11 (*s*, 2H, CH_2CN). ^{13}C NMR (DMSO-d_6, δ, ppm): 191.5 (CH_2*C*OPh), 144.9 (N*C*HN), 144.8, 135.1, 134.2, 132.3, 130.5, 129.5, 129.0, 127.8, 115.0, 114.8 (Ar-*C*), 113.9 (CH_2*C*N), 54.2 (*C*H_2COPh), 35.9 (CH_2CN).

4.4.5 | 1-Benzyl-3-(2-oxo-2-phenylethyl) benzimidazolium bromide (5)[35,37]

Yield 1.78 g (white crystals), 90%; m.p. 170–171 °C. IR (ν_{max}, cm^{-1}): 1562 (C=N), 1695 (C=O). Anal. Found (%): C 80.72, H 5.86, N 8.62. Calcd for $C_{22}H_{19}BrN_2O$ (327.1))%): C 80.71, H 5.85, N 8.56. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.86 (*s*, 1H, NC*H*N), 7.40–8.15 (*m*, 14H, Ar-H), 6.45 (*s*, 2H, CH_2COPh), 5.92 (*s*, 2H, CH_2Ph). ^{13}C NMR (DMSO-d_6, δ, ppm): 191.7 (CH_2*CO*Ph), 144.0 (N*C*HN), 135.1, 134.4, 134.3, 134.2, 132.6, 131.0, 129.6, 129.5, 129.3, 128.9, 128.8, 127.4, 127.3, 114.6, 114.4 (Ar-*C*), 53.8 (CH_2COPh), 50.45 (CH_2Ph).

4.4.6 | 3-(4-Bromobenzyl)-1-(2-oxo-2-phenylethyl)-1*H*–benzo[*d*]imidazol-3-ium bromide (6)

Yield 1.5 g (cream crystals), 88.2%; m.p. 245–246 °C. IR (ν_{max}, cm^{-1}): 1567 (C=N), 1696 (C=O). Anal. Found (%): C 54.65, H 3.76, N 5.87. Calcd for $C_{22}H_{18}Br_2N_2O$ (484.0) (%): C 54.35, H 3.73, N 5.76. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.84 (*s*, 1H, NC*H*N), 8.04–8.15 (*m*, 4H, Ar-H), 7.51–7.83 (*m*, 9H, Ar-H), 6.44 (s, 2H, $CH_2COC_6H_5$), 5.91 (s, 2H, $CH_2C_6H_4Br$). ^{13}C NMR (DMSO-d_6, δ, ppm): 191.2 (CH_2*C*OC_6H_5), 143.6 (N*C*HN), 134.5, 133.7, 133.2, 132.1, 132.0, 130.6, 130.4, 129.0, 128.4, 126.9, 126.8, 122.2, 114.1, 113.8, (Ar-C), 53.3 (*C*$H_2COC_6H_5$), 49.3 (*C*$H_2C_6H_4Br$).

4.4.7 | 3-(4-Chlorobenzyl)-1-(2-oxo-2-phenylethyl)-1*H*–benzo[*d*]imidazol-3-ium bromide (7)

Yield 1.3 g (white crystals), 87.2%; m.p. 216–217 °C. IR (ν_{max}, cm^{-1}): 1567 (C=N), 1696 (C=O). Anal. Found (%): C 59.30, H 4.17, N 6.63. Calcd for $C_{22}H_{18}BrClN_2O$ (440.0) (%): C 59.82, H 4.11, N 6.34. ^{1}H NMR (DMSO-d_6, δ, ppm): 10.29 (*s*, 1H, NC*H*N), 8.17–8.23 (*m*, 4H, Ar-H), 7.46–7.76 (*m*, 9H, Ar-H), 6.72 (s, 2H, $CH_2COC_6H_5$), 6.11 (s, 2H, $CH_2C_6H_4Cl$). ^{13}C NMR (DMSO-d_6, δ, ppm): 191.8 (CH_2*C*OC_6H_5), 144.1 (N*C*HN), 144.0, 135.0, 134.2, 134.0, 133.4, 132.6, 131.0, 130.9, 129.5, 129.0, 127.3, 127.2, 114.8, 114.5 (Ar-C), 54.3 (*C*$H_2COC_6H_5$), 49.7 (*C*$H_2C_6H_4Cl$).

4.4.8 | 1-(2-Oxo-2-phenylethyl)-3-phenethyl-1*H*-benzo[*d*]imidazol-3-ium bromide (8)

Yield 0.8 g (cream crystals), 84.2%; m.p. 157–158 °C. IR (ν_{max}, cm^{-1}): 1563 (C=N), 1695 (C=O). Anal. Found (%): C 65.75, H 5.03, N 6.86. Calcd for $C_{23}H_{21}BrN_2O$ (420.1) (%): C 65.57, H 5.02, N 6.63. ^{1}H NMR (DMSO-d_6, δ,

ppm): 9.72 (*s*, 1H, NC*H*N), 8.05–8.15 (4H, Ar-H), 7.65–7.83 (6H, Ar-H), 7.23–7.30 (*m*, 4H, Ar-H), 6.43 (*s*, 2H, CH_2COPh), 4.90 (*t*, 2H, CH_2CH_2Ph, J = 7.2 Hz), 3.29 (*t*, 2H, CH_2CH_2Ph, J = 7.2 Hz). ^{13}C NMR (DMSO-d_6, δ, ppm): 191.6 (CH_2*C*OPh), 143.7 (N*C*HN), 137.3, 135.1, 134.2, 132.3, 131.2, 129.5, 129.4, 129.0, 128.9, 127.4, 127.2, 127.0, 114.4, 114.3 (Ar-*C*), 53.7 (CH_2COPh), 48.4 (*C*H_2CH_2Ph), 35.2 (CH_2*C*H_2Ph).

4.4.9 | 1-(2-Oxo-2-phenylethyl)-3-(3-phenylpropyl)-1*H*–benzo[*d*]imidazol-3-ium bromide (9)

Yield 0.56 g (cream crystals), 54.5%; m.p. 156–157 °C. IR (ν_{max}, cm^{-1}): 1564 (C═N), 1703 (C═O). Anal. Found (%): C 65.56, H 5.27, N 6.87. Calcd for $C_{24}H_{23}BrN_2O$ (434.1) (%): C 66.21, H 5.32, N 6.43. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.81 (*s*,1H, NC*H*N), 8.09–8.17 (*m*, 4H, Ar-H), 7.67–7.81(*m*, 5H, Ar-H), 7.20–7.30 (*m*, 5H, Ar-H), 6.43 (*s*, 2H, CH_2COPh), 4.68 (*t*, 2H, NC$H_2CH_2CH_2$Ph, J = 3.4 Hz), 2.72 (*t*, 2H, $CH_2CH_2CH_2$Ph, J = 3.9 Hz), 2.28 (*q*, 2H, $CH_2CH_2CH_2$Ph, J = 3.8 Hz). ^{13}C NMR (DMSO-d_6, δ, ppm): 191.8 (CH_2*C*OPh), 143.9 (N*C*HN), 140.9, 135.1, 134.2, 132.5, 131.2, 129.6, 128.9, 128.8, 128.7, 127.3, 127.1, 126.6, 114.5, 114.2 (Ar-C), 53.6 (*C*H_2COPh), 47.1 (*C*$H_2CH_2CH_2$Ph), 32.2 (CH_2CH_2*C*H_2Ph), 30.6 (CH_2*C*H_2CH_2Ph).

4.4.10 | 1,3-Bis(2-oxo-2-phenylethyl)-1*H*–benzo[*d*]imidazol-3-ium bromide (10)[39]

Yield 2.9 g (cream crystals), 61.5%; m.p. 219–220 °C. IR (ν_{max}, cm^{-1}): 1563 (C═N), 1690 (C═O). Anal. Found (%): C 63.34, H 4.46, N 6.69. Calcd for $C_{23}H_{19}BrN_2O_2$ (434.1) (%): C 63.46, H 4.40, N 6.44. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.76 (*s*, 1H, NC*H*N), 8.15–8.18 (*m*, 6H, Ar-H), 7.80–7.82 (*m*, 2H, Ar-H), 7.68–7.72 (*m*, 6H, Ar-H), 6.60 (*s*, 4H, CH_2COPh). ^{13}C NMR (DMSO-d_6, δ, ppm): 191.7 (CH_2*C*OPh), 144.9 (N*C*HN), 135.0, 134.3, 132.1, 129.5, 128.9, 127.3, 114.5 (Ar-*C*), 54.1 (*C*H_2COPh).

4.5 | General procedure for Sonogashira reactions

$Pd(OAc)_2$ (1 mmol%), CuNPc (4 mol%), benzimidazolium halides **1–10** (2 mmol%), aryl halide (1 mmol), phenylacetylene (1 mmol), Cs_2CO_3 (2 mmol) and PEG^{300} (6 ml) were added to the microwave apparatus and the mixture was heated at 100 °C (300 W) for 10 min after a ramp time of 3 min to reach to 100 °C. At the end of the reaction, the mixture was cooled and the product extracted with ethyl acetate–*n*-hexane (1:5) and filtered through a pad of silica gel with copious washing. The purity and yield of coupling products was determined by GC–MS using the normalizing peak areas method. Some coupling yields were also determined through isolated coupling products.

4.6 | General procedure for recycling of catalyst for Sonogashira reaction

After completing the first catalytic cycle, a mixture of ethyl acetate–*n*-hexane (1:5) (10 ml) was added to the reaction mixture and coupling product was extracted into the organic phase. Insoluble palladium–N-heterocyclic carbene complex formed *in situ* from $Pd(OAc)_2$, benzimidazolium salt and CuNPc was recovered by decantation of the reaction mixture and transferred to a microwave tube with PEG. After reloading the coupling partners and Cs_2CO_3 (1 mmol%) the reaction was repeated following the general Sonogashira reaction procedure described above.

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