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The catalytic effects of in situ prepared N-heterocyclic carbenes from benzimidazole salts in Suzuki–Miyaura cross-coupling reaction and uses in catalytic preparation of 1,3,5-triphenyl-1,3,5-triazinane-2,4,6-trione from phenyl isocyanate

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Abstract: Many benzimidazole salts bearing a 3-phenylpropyl substituent (**1a**–**1h**) were synthesized and their structures were identified by ^{1}H NMR, ^{13}C NMR, and IR spectroscopic methods and elemental analysis. These N-heterocyclic carbene (NHC) precursors were used as a part of a catalytic system including $Pd(OAc)_2$ and the base in the Suzuki–Miyaura cross-coupling reaction under microwave irradiation. They were also used as catalysts in the cyclotrimerization of phenyl isocyanate to yield 1,3,5-triphenyl-1,3,5-triazinane-2,4,6-trione. It has been observed that benzimidazole salts made a positive contribution to both catalytic reactions as a NHC precursor.

Key words: Benzimidazole salt, NHC precursor, catalyst, Suzuki–Miyaura reaction, cyclotrimerization of phenyl isocyanate

1. Introduction

After the first report on N-heterocyclic carbenes (NHCs) in the early 1960s by Wanzlick and Schikora, a new window opened in organometallic chemistry.[1–11] Following the preparation of the first stable N-heterocyclic carbene by Arduengo et al. in 1991,[12] they became powerful and were widely used as ligands in many organometallic compound syntheses and in many catalytic reactions.[13–16] Due to their lower toxicity, stronger σ-donor/lower π-acceptor character, and higher stability toward heat, moisture, and air, NHCs have become an alternative to phosphine-based ligands in organometallic chemistry.[5,11,17–19] Most of the transition metals, such as iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold, yttrium, and samarium, can form stable complexes with NHC ligands.[3,5,20] Both NHCs and their organometallic derivatives have been used as catalysts in various organic reactions. These reactions include cross-coupling, olefin metathesis, transformation, reduction, rearrangement, telomerization, aryl amination, condensation, cyclotrimerization, polymerization, cyclization, addition, hydroformylation, dehydrogenation, borylation, and ring-opening metathesis polymerization.[3,10,18,21–24]

The Suzuki–Miyaura cross-coupling reaction is one of the most attractive methods for C-C bond-forming in organic syntheses.[25–29] It is used in diverse areas such as the preparation of pharmaceutically active compounds, biaryls, and *p*-terphenyls.[30,31] Although a great number of cross-coupling reactions are known, exploring environmentally benign, economical, and efficient catalysts or catalyst systems for the construction

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of C-C bonds is still an ongoing area of interest in catalyst chemistry. Most of the catalysts used for Suzuki–Miyaura reactions in previous studies have been focused on the use of palladium-phosphine or palladium-NHC complexes and palladium nanoparticles.[32–41] Moreover, microwave heating has been used successfully as an efficient heating technique in Suzuki–Miyaura type C-C coupling reactions.[33,42–52] Therefore, much attention has been paid to finding out the most effective and environmentally benign catalyst or catalyst system.

On the other hand, isocyanurates have been prepared by cyclotrimerization reaction from isocyanates and these types of heterocyclic and aromatic compounds have been used in a variety of materials.[53,54] Due to their excellent thermal and chemical properties, isocyanurates have been used to improve polymers, such as increasing the electrical properties and thermal stability of copolyimides,[55] syntheses of highly stable plastic[56] and amphiphilic polyethylene glycol gels,[57] and increasing the flame retardancy and thermal stability of epoxy resins[58,59] and polypropylene.[60,61] Isocyanurates are also an important class of compounds for improving coating and other properties of polyurethane.[62–65] Besides other applications, aryl isocyanurates are used as activators in the polymerization of ε-caprolactam to produce nylons.[66] Moreover, according to another report,[67] asymmetric 1,3,5-triazine-2,4,6-triones can be used as a novel class of gonadotropin-releasing hormone receptor antagonists.

Because of their important applications, the synthesis of isocyanurates is a remarkable topic in organic chemistry. Many various catalysts have been used for the synthesis of isocyanurates, such as amine bases;[53] alkoxyallenes;[68] sulfide anion and phase transfer catalysts;[54] hexamethyldisilazane;[69] proazaphosphatranes;[70,71] organometallic catalysts containing Ti, Co, Zr, Pd, Pr, Ln, Sn, W, Li, and Nb metals;[72–84] ketene cyclic N,O-acetals;[85] fluoride anions;[86] carbamate anions;[87] phosphines;[88] N-heterocyclic carbenes;[89,90] and tetrakis (dimethylamino)ethylene (TDAE).[91]

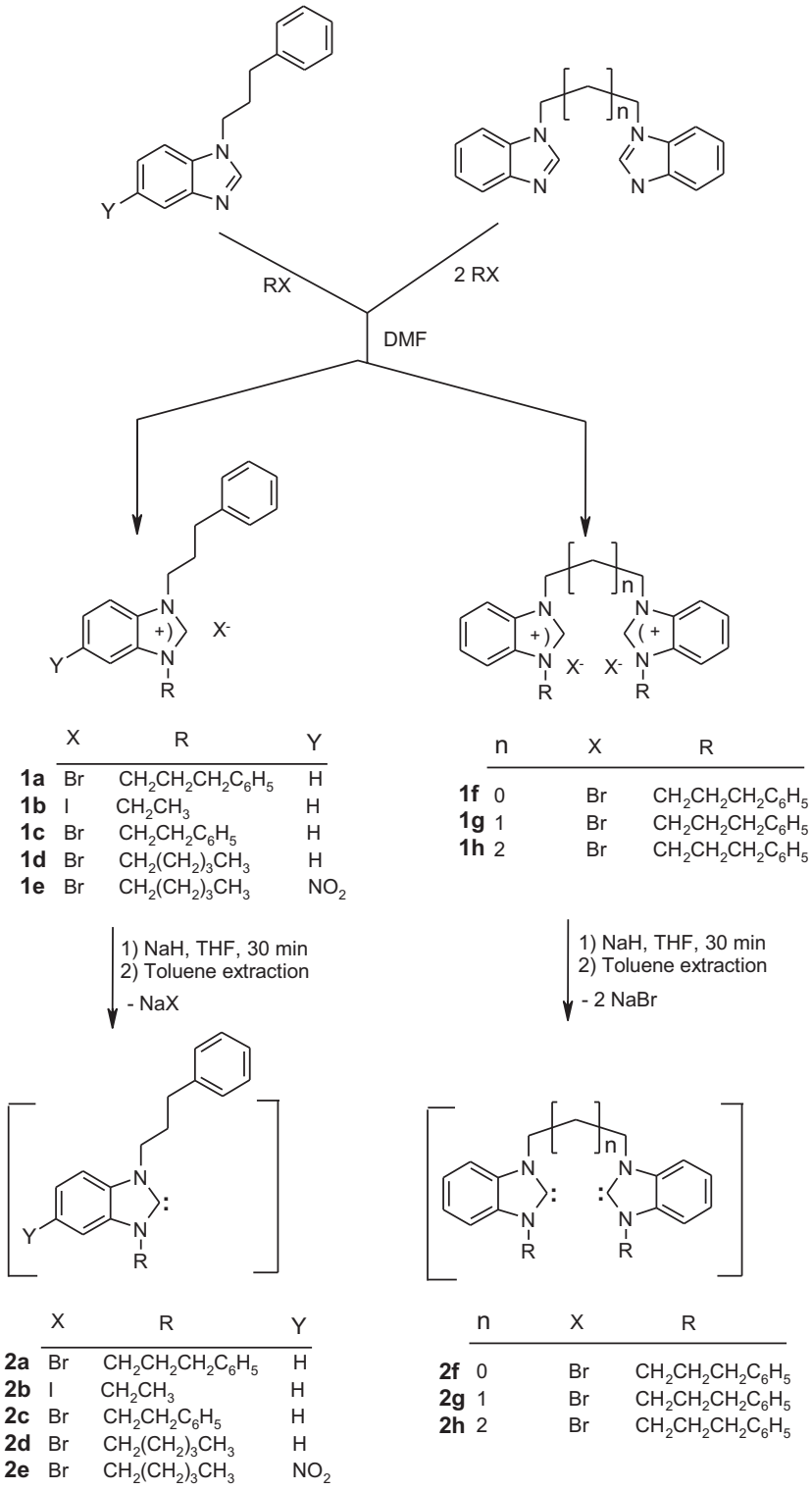
We were previously interested in the synthesis of electron-rich olefins and their derivatives.[92–94] When we tried to prepare the phenyl isocyanate derivative of electron-rich olefins, we obtained a small amount of unexpected trimerization product 1,3,5-triphenyl-1,3,5-triazinane-2,4,6-trione along with the expected 1,3-disubstituted-1',3'-diphenyl-1,3-dihydrospiro[benzo[d]imidazole-2,4'-imidazolidine]-2',5'-dione type spiro compounds.[95,96] In connection with this, we also tried to explore catalytic effectiveness of the catalytic system including Pd salt and novel benzimidazole ligands in the cyclotrimerization reaction of phenyl isocyanate.

In this work, we aimed to explore the catalytic activities of a catalytic system including benzimidazole salts as electron-rich NHC precursors (**1a**–**1h**), $Pd(OAc)_2$, and base in the Suzuki–Miyaura C-C coupling reaction and the catalytic activity of in situ prepared NHC ligands in the cyclotrimerization reaction of phenyl isocyanate.

2. Results and discussion

New benzimidazolium and bis-benzimidazolium salts (**1b**–**1h**) were synthesized from the treatment of 1-(3-phenylpropyl)benzimidazole with appropriate alkyl halides in refluxing DMF with good yields of 64%–83%. The synthesis of benzimidazolium salts **1b**–**1h** is summarized in Scheme 1. The structures of the benzimidazolium salts (**1b**–**1h**) were elucidated by ^{1}H and ^{13}C NMR, IR, and microanalyses. All spectral data were in accordance with the proposed structures. The characteristic NC*H*N resonance in the ^{1}H NMR spectra and N*C*HN resonance in the ^{13}C NMR spectra of benzimidazolium salts (**1b**–**1h**) were observed at around 9.84–10.32 ppm and 142.2–146.9 ppm, respectively. The benzimidazolium salts (**1b**–**1h**) showed IR absorption bands at

1566, 1567, 1560, 1560, 1562, 1561, and 1562 cm^{-1} for $\nu_{(C=N)}$. These values were in good agreement with the previously reported results.[97,98]



	X	R	Y
1a	Br	$CH_2CH_2CH_2C_6H_5$	H
1b	I	CH_2CH_3	H
1c	Br	$CH_2CH_2C_6H_5$	H
1d	Br	$CH_2(CH_2)_3CH_3$	H
1e	Br	$CH_2(CH_2)_3CH_3$	NO_2

	n	X	R
1f	0	Br	$CH_2CH_2CH_2C_6H_5$
1g	1	Br	$CH_2CH_2CH_2C_6H_5$
1h	2	Br	$CH_2CH_2CH_2C_6H_5$

	X	R	Y
2a	Br	$CH_2CH_2CH_2C_6H_5$	H
2b	I	CH_2CH_3	H
2c	Br	$CH_2CH_2C_6H_5$	H
2d	Br	$CH_2(CH_2)_3CH_3$	H
2e	Br	$CH_2(CH_2)_3CH_3$	NO_2

	n	X	R
2f	0	Br	$CH_2CH_2CH_2C_6H_5$
2g	1	Br	$CH_2CH_2CH_2C_6H_5$
2h	2	Br	$CH_2CH_2CH_2C_6H_5$

Scheme 1. Synthesis pathway of benzimidazolium salts and their NHCs.

2.1. Suzuki–Miyaura reaction

The Suzuki–Miyaura reaction is one of the most versatile and utilized reactions for the selective formation of carbon-carbon bonds.[25,42] Although there has been considerable research on this topic, it is still being studied to improve the catalytic system and reaction conditions. With this aim, we also continued to improve the catalytic system containing new benzimidazolium salts for the Suzuki–Miyaura reaction. To find the optimum reaction conditions for the Suzuki–Miyaura coupling reaction, a series of experiments were performed with 1-bromonaphthalene (1 mmol) and phenylboronic acid (1 mmol) in the presence of 1 mol% of $Pd(OAc)_2$. Test reactions were performed using different bases such as K_2CO_3, KOH, and Cs_2CO_3 and different solvents such as DMF/H_2O, PEG, and H_2O for 5 and 10 min at 60 °C, 80 °C, and 100 °C. To obtain good yields, inorganic bases like K_2CO_3, KOH, and Cs_2CO_3 were used and K_2CO_3 was the most effective (Table 1, entries 9 and 10). Among the solvents examined, DMF/H_2O (1:1) was found to be the best choice (Table 1, entries 9 and 10). Our next studies focused on the effect of temperature on the Suzuki–Miyaura reaction. There was no change in yields after increasing the reaction time from 5 min to 10 min at 100 °C (entry 10). After these test experiments, we found that use of the catalytic system consisting of 1% $Pd(OAc)_2$, 2% mol of **1a**–**1h**, and 2% mol K_2CO_3 in DMF/H_2O (1:1) at 100 °C/300 W microwave irradiation led to the best conversion within 5 min. Finally, the effect of $Pd(OAc)_2$ concentrations was investigated and the best result was obtained for 1 mol% $Pd(OAc)_2$, whereas 0.5 mol% yielded low coupling product under optimized conditions (Table 1, entries 9–11). As expected, the desired product was not obtained in the absence of $Pd(OAc)_2$ (Table 1, entry 12) and the yield of benzimidazolium salt **1g**, the catalytic, dramatically decreased to 31% (Table 1, entry 13).

According to these results, the optimized reaction conditions were determined as follows: 1 mol% of $Pd(OAc)_2$, 2 mol% benzimidazole salt (**1a**–**1h**), 2 mmol K_2CO_3, and DMF:H_2O (1:1) at 100 °C in the presence of microwave irradiation (300 W) for 5 min. No palladium nanoparticle formation was observed during the catalytic experiments in this work. When these optimized reaction conditions were compared with our previous work reported in 2013, it was concluded that reaction time and temperature play an important role in the formation of palladium nanoparticles.[32]

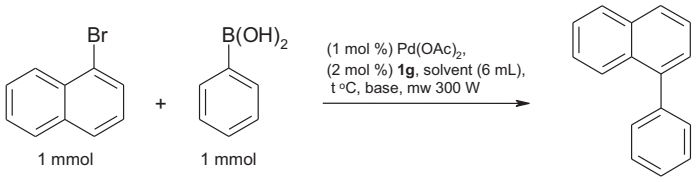
With the optimized reaction conditions in hand, we screened the catalytic activity of all benzimidazolium salts as ligands in the Suzuki–Miyaura cross-coupling reaction using different coupling partners such as phenyl bromide, 1-naphthyl bromide, phenylboronic acid, and 1,4-phenylenediboronic acid to explore the scope of the catalytic reaction. All the cross-coupling results are given in Table 2. Among the benzimidazole salts tested in optimized conditions, compound **1e** bearing a 5-nitro substituent at position 3 of the benzimidazole ring was found to be the least effective due to the strong electron-withdrawing effect of NO_2 group (Table 2, entry 5), whereas compound **1d** was the most effective benzimidazolium salt due to its good electron-donating ability of the n-pentyl substituent. When the isolated catalytic yields of the coupling reaction are compared, the catalytic activity decreases from A (biphenyl) to D (1,4-di(naphthalen-1-yl)benzene).

2.2. Catalytic preparation of 1,3,5-triphenyl-1,3,5-triazinane-2,4,6-trione from phenyl isocyanate (cyclotrimerization reaction)

2.2.1. Optimization of the cyclotrimerization reaction

Our initial screening efforts focused on compound **1d** for catalyzing the cyclotrimerization reaction of phenyl isocyanate (3 mol) at room temperature under argon atmosphere in toluene (5 mL and 1 mL) in 120 min and 20 min (Table 3, entries 1 and 2). As the reaction progressed, a white solid cyclotrimerization product began

Table 1. Test experiments for optimization of the Suzuki–Miyaura cross-coupling reaction.



Entry	Base	Solvent	Heat (°C)	Time (min)	Yield (%)[a]
1	K_2CO_3	DMF:H_2O (1:1)	60	5	57
2	K_2CO_3	DMF:H_2O (1:1)	80	5	81
3	K_2CO_3	EtOH:H_2O (1:1)	80	5	72
4	K_2CO_3	PEG^{300}	80	5	62
5	K_2CO_3	H_2O	80	5	29
6	KOH	DMF:H_2O (1:1)	80	5	73
7	Cs_2CO_3	DMF:H_2O (1:1)	80	5	77
8	K_2CO_3	DMF:H_2O (1:1)	100	3	86
9	K_2CO_3	DMF:H_2O (1:1)	100	5	97
10	K_2CO_3	DMF:H_2O (1:1)	100	10	97
11[b]	K_2CO_3	DMF:H_2O (1:1)	100	5	70
12[c]	K_2CO_3	DMF:H_2O (1:1)	100	5	-
13[d]	K_2CO_3	DMF:H_2O (1:1)	100	5	31

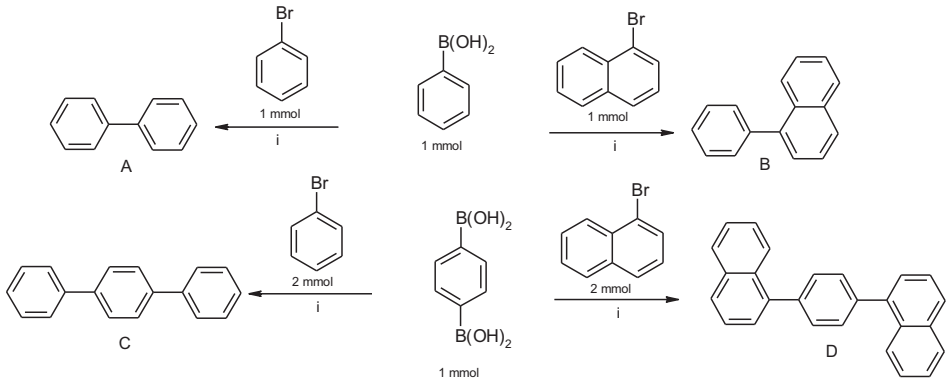
[a]Isolated yield. [b]$Pd(OAc)_2$, 0.5 mol% was used. [c]Without $Pd(OAc)_2$. [d]Without **1g**.

to form. According to these observations, the catalytic conversion was well performed in concentrated solution in a short time (Table 3, entry 2). The catalytic yield was found to be moderate in THF (1 mL) for 20 min. After obtaining these results, we decided to perform the reaction without solvent with 0.5 and 1 mol% in situ prepared NHC (**1d**) in 5 min. The reaction without solvent completed with a violent exothermic reaction in a short time (Table 3, entries 4 and 5). The reaction was not observed without benzimidazole salt (**1d**) (Table 3, entry 6). After performing a series of test experiments with phenyl isocyanate with **1d**, we obtained optimum reaction conditions for the cyclotrimerization reaction.

Having established the optimal catalytic reaction conditions for the trimerization reaction (Table 3) as 1 mol% NHC and 3 mol phenyl isocyanate in 5 min at room temperature under argon atmosphere without solvent, we then surveyed the scope and limitations of in situ prepared NHCs in this catalytic system. As seen in Table 4, all NHCs performed well for the cyclotrimerization reaction of phenyl isocyanate, except compound **1e**. Because of the electron-withdrawing properties of the nitro group at the 3 position of the benzimidazole ring, **1e** showed moderate activity under the optimized reaction conditions. Both monobenzimidazole (**1a**–**1e**) and bisbenzimidazole salts (**1f**–**1g**) as NHC sources showed similar catalytic activity in the cyclotrimerization reaction of phenyl isocyanate. When the catalytic activity of the in situ prepared benzimidazole-derived NHCs is compared with the literature values reported by Giuglio-Tonolo et al.,[91] it can be concluded that the present work has a shorter reaction time, lower catalyst amount, and relatively higher yields for the cyclotrimerization reaction.

A plausible catalytic cyclotrimerization reaction mechanism is suggested in Scheme 2.

Table 2. The Suzuki–Miyaura cross-coupling reactions of aryl bromides with phenylboronic and 1,4-phenylenediboronic acids.



Entry	Salt	A yield (%)	B yield (%)	C yield (%)	D yield (%)
1	**1a**	99	97	90	69
2	**1b**	98	94	91	64
3	**1c**	99	97	90	71
4	**1d**	99	97	93	75
5	**1e**	96	85	80	42
6	**1f**	99	90	88	55
7	**1g**	99	97	94	70
8	**1h**	99	94	92	62

Isolated yields; reaction time is 5 min. i: (1 mol%) $Pd(OAc)_2$, (2 mmol) K_2CO_3, (2 mol%) **1a**–**1e**, (1 mol%) **1f**–**1h**; 300 W; DMF:H_2O (3:3 mL). A = Biphenyl, B = 1-phenylnaphthalene, C = 1,1':4',1''-terphenyl, D = 1,4-Di(naphthalen-1-yl)benzene.

2.3. Conclusions

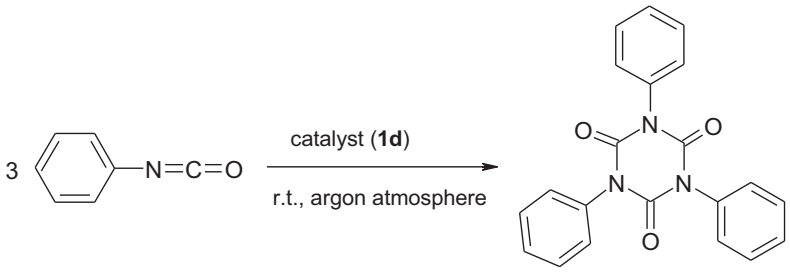
Benzimidazole salts containing 3-phenylpropyl substituents (**1a**–**1h**) were prepared from the reactions of appropriate alkyl halides and 1-(3-phenylpropyl)benzimidazole. These salts were used as ligands in the presence of $Pd(OAc)_2$ in a catalytic system for Suzuki–Miyaura reactions. They were also used as NHC precursors in the cyclotrimerization reaction of phenyl isocyanate. As far as we know, benzimidazole salts were used for the first time as catalysts in the cyclotrimerization reaction of phenyl isocyanate. It was observed that the benzimidazolium salts as NHC precursors (**1a**–**1h**) are highly effective catalysts for both the Suzuki–Miyaura cross-coupling reaction and the catalytic cyclotrimerization reaction of phenyl isocyanate to yield isocyanurate. Both monobenzimidazole (**1a**–1**e**) and bisbenzimidazole salts (**1f**–1**g**) as NHC sources showed similar catalytic activity in the Suzuki–Miyaura and cyclotrimerization reaction of phenyl isocyanate.

3. Experimental

3.1. General

The Suzuki–Miyaura reactions were carried out in a microwave oven system manufactured by Milestone (Milestone Start S Microwave Labstation for Synthesis) under aerobic conditions, whereas the cyclotrimerization reactions were performed under an atmosphere of purified argon using standard Schlenk techniques. Starting chemicals used in reactions were supplied commercially from Aldrich or Merck Chemical Co. Solvents were

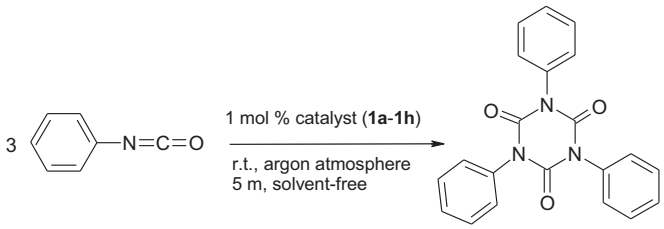
Table 3. Optimization of the conditions for cyclotrimerization reaction of phenyl isocyanate.



Entry	Salt	Yield (%)[a]		
1	Toluene (5 mL)	2 h	**1d** (0.5 mol%)	35
2	Toluene (1 mL)	20 m	**1d** (0.5 mol%)	70
3	THF (1 mL)	20 m	**1d** (0.5 mol%)	68
4	Solvent-free	20 m	**1d** (0.5 mol%)	81
5	Solvent-free	5 m	**1d** (1 mol%)	99
6	Solvent-free	2 h	Without **1d**	No reaction

Reaction conditions: phenyl isocyanate (2 mL, 18.30 mmol), room temperature.
[a]Isolated yields.

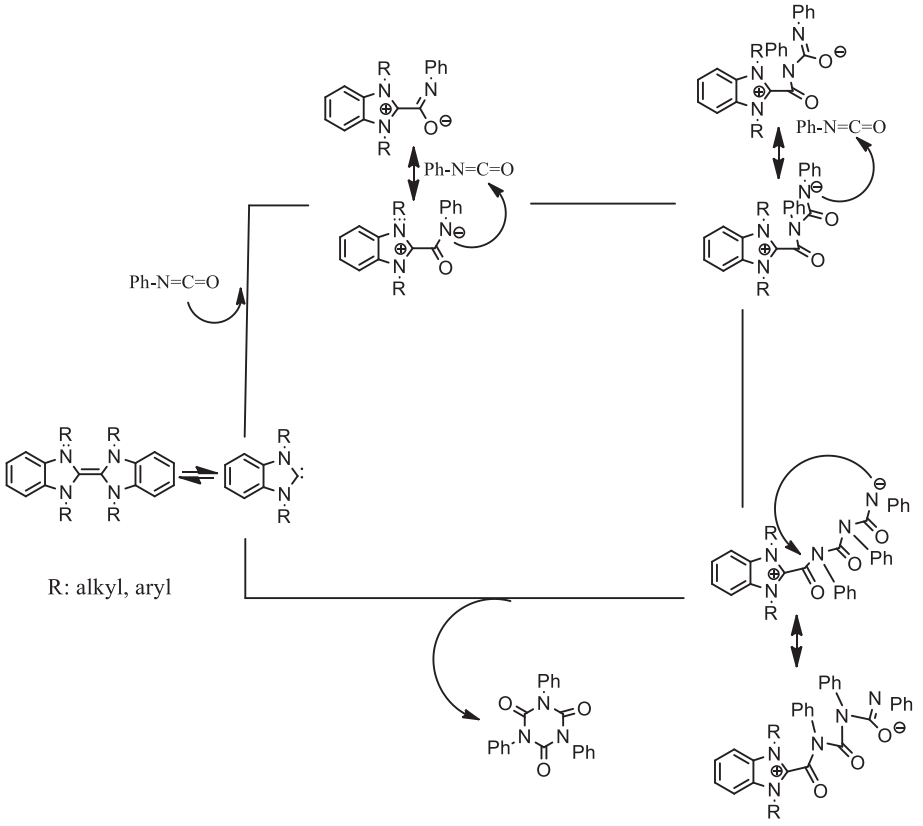
Table 4. Activities of all the NHC precursors in cyclotrimerization reaction of phenyl isocyanate.



Entry	Salt	Yield (%)[a]
1	**1a**	95
2	**1b**	90
3	**1c**	94
4	**1d**	99
5	**1e**	70
6	**1f**	86
7	**1g**	94
8	**1h**	99

Reaction conditions: catalyst (1 mol%), phenyl isocyanate (2 mL, 18.30 mmol), solvent-free, room temperature in 5 min.
[a]Isolated yields.

dried with standard methods and freshly distilled prior to use. ^{1}H NMR (300.13 MHz) and ^{13}C NMR (75.47 MHz) spectra were obtained using a Bruker Avance 300 UltraShield high-performance digital FT NMR spectrometer. IR spectra were recorded as KBr pellets in the range of 4000–400 cm^{-1} on a PerkinElmer FT-IR



Scheme 2. Proposed catalytic cyclotrimerization reaction mechanism.

spectrophotometer. Elemental analyses were performed by LECO CHNS-932 elemental analyzer. Melting points were recorded using an Electrothermal-9200 melting point apparatus and are uncorrected. The LC-MS chromatogram of phenyl isocyanurate was recorded with an Agilent 1100 Series LC/MSD SL. Please see the Supplementary data for the ^{1}H NMR, ^{13}C NMR, and IR spectra of these novel benzimidazolium salts and the catalytic products.

3.2. General procedure for synthesis

1,2-Bis(benzimidazole-1-yl)ethane, 1,3-bis(benzimidazole-1-yl)propane, 1,4-bis(benzimidazole-1-yl)butane, 1-(3-phenylpropyl)benzimidazole, compound **1a**, and 1-(3-phenylpropyl)-5-nitrobenzimidazole were synthesized according to the literature.[99−103]

3.2.1. Synthesis of 1-(3-phenylpropyl)-3-ethylbenzimidazolium iodide (1b)

A mixture of 1-(3-phenylpropyl)benzimidazole (1.5 g, 6.36 mmol) and ethyl iodide (1.04 g, 6.67 mmol) in dimethylformamide (5 mL) was refluxed for 4 h. Then all volatiles were removed in vacuo and the crude product was crystallized from ethanol/diethyl ether (1:5). Yield: 1.94 g, 78%; mp: 110–112 °C. IR (cm^{-1}): 1566 ($\upsilon_{C=N}$). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 1.55 (t, 3H, CH_2CH_3, J = 7.5 Hz); 2.27 (*quint*, 2H, J = 7.5 Hz, $CH_2CH_2CH_2C_6H_5$); 2.74 (t, 2H, J = 7.8 Hz, $CH_2CH_2CH_2C_6H_5$); 4.49 (q, 2H, J = 7.5 Hz, CH_2CH_3); 4.56 (t, 2H, J = 7.2 Hz, $CH_2CH_2CH_2C_6H_5$); 7.18–7.29 (m, 5H, C_6H_5); 7.67–7.72 (m, 2H, C_6H_4); 8.05–8.14

(m, 2H, C_6H_4); 9.84 (s, 1H, NCHN). ^{13}C NMR (DMSO-d_6): δ 14.6 (CH_2CH_3); 30.5 ($CH_2CH_2CH_2C_6H_5$); 32.4 ($CH_2CH_2CH_2C_6H_5$); 42.6 (CH_2CH_3); 47.0 ($CH_2CH_2CH_2C_6H_5$); 114.1, 114.2, 126.5, 126.9, 127.0, 128.7, 128.8, 131.4, 131.7, 141.0 (Ar-C); 142.3 (NCHN). Anal. Calc. for $C_{18}H_{21}N_2I$ (392.28): C, 55.11; H, 5.40; N, 7.14; found: C, 54.87; H, 5.28; N, 7.30.

Other benzimidazolium halides (**1c**–**1h**) were also synthesized with the corresponding alkyl halides via a procedure similar to the synthesis of **1a**.

3.2.2. 1-(3-Phenylpropyl)-3-(2-phenylethyl)benzimidazolium bromide (1c)

Yield: 1.88 g, 70%; mp: 104–105 °C. IR (cm^{-1}): 1567 ($\upsilon_{C=N}$). ^{1}H NMR (DMSO-d_6): δ 2.19 (*quint*, 2H, J = 7.5 Hz, $CH_2CH_2CH_2C_6H_5$); 2.62 (t, 2H, J = 7.8 Hz, $CH_2CH_2CH_2C_6H_5$); 3.28 (t, 2H, J = 7.2 Hz, $CH_2CH_2C_6H_5$); 4.54 (t, 2H, J = 7.2 Hz, $CH_2CH_2CH_2C_6H_5$); 4.80 (t, 2H, J = 7.2 Hz, $CH_2CH_2C_6H_5$); 7.15–7.30 (m, 10H, C_6H_5); 7.63–7.70 (m, 2H, C_6H_4); 8.06–8.12 (m, 2H, C_6H_4); 9.95 (s, 1H, NCHN). ^{13}C NMR (DMSO-d_6): δ 30.6 ($CH_2CH_2CH_2C_6H_5$); 32.2 ($CH_2CH_2CH_2C_6H_5$); 34.9 ($CH_2CH_2C_6H_5$); 46.9 ($CH_2CH_2CH_2C_6H_5$); 48.2 ($CH_2CH_2C_6H_5$); 114.2, 114.3, 126.5, 127.0, 127.3, 128.7, 128.8, 129.0, 129.3, 131.3, 131.4, 137.3, 137.4, 140.9 (Ar-C); 142.7 (NCHN). Anal. Calc. for $C_{24}H_{25}N_2Br$ (421.37): C, 68.41; H, 5.98; N, 6.65; found: C, 68.10; H, 5.96; N, 6.41.

3.2.3. 1-(3-Phenylpropyl)-3-pentylbenzimidazolium bromide (1d)

Yield: 1.77 g, 72%; mp: 83–84 °C. IR (cm^{-1}): 1560 ($\upsilon_{C=N}$). ^{1}H NMR (DMSO-d_6): δ 0.86 (t, 3H, J = 6.6 Hz, $CH_2CH_2CH_2CH_2CH_3$); 1.26–1.36 (m, 4H, $CH_2CH_2CH_2CH_2CH_3$); 1.92 (*quint*, 2H, J = 7.2 Hz, $CH_2CH_2CH_2CH_2CH_3$); 2.26 (*quint*, 2H, J = 7.5 Hz, $CH_2CH_2CH_2C_6H_5$); 2.71 (t, 2H, J = 7.8 Hz, $CH_2CH_2CH_2C_6H_5$); 4.49 (t, 2H, J = 7.2 Hz, $CH_2CH_2CH_2CH_2CH_3$); 4.58 (t, 2H, J = 7.2 Hz, $CH_2CH_2CH_2C_6H_5$); 7.13–7.28 (m, 5H, C_6H_5); 7.66–7.71 (m, 2H, C_6H_4); 8.08–8.15 (m, 2H, C_6H_4); 10.03 (s, 1H, NCHN). ^{13}C NMR (DMSO-d_6): δ 13.7 ($CH_2CH_2CH_2CH_2CH_3$); 21.6 ($CH_2CH_2CH_2CH_2CH_3$); 27.9 ($CH_2CH_2CH_2CH_2CH_3$); 28.2 ($CH_2CH_2CH_2CH_2CH_3$); 30.0 ($CH_2CH_2CH_2C_6H_5$); 31.9 ($CH_2CH_2CH_2C_6H_5$); 46.5 ($CH_2CH_2CH_2CH_2CH_3$); 46.6 ($CH_2CH_2CH_2C_6H_5$); 113.6, 113.7, 125.9, 126.4, 128.2, 128.3, 131.0, 131.1, 140.5 (Ar-C); 142.2 (NCHN). Anal. Calc. for $C_{21}H_{27}N_2Br$ (387.36): C, 65.11; H, 7.03; N, 7.23; found: C, 64.63; H, 7.20; N, 7.12.

3.2.4. 1-(3-Phenylpropyl)-3-pentyl-5(6)-nitrobenzimidazolium bromide (1e)

Yield: 1.48 g, 64%; mp: 113–114 °C. IR (cm^{-1}): 1560 ($\upsilon_{C=N}$), 1529 (υ_{Ar-NO2}). ^{1}H NMR (DMSO-d_6): δ 0.89 (m, 3H, $CH_2CH_2CH_2CH_2CH_3$); 1.37 (m, 4H, $CH_2CH_2CH_2CH_2CH_3$); 1.95 (m, 2H, $CH_2CH_2CH_2CH_2CH_3$); 2.29 (*quint*, 2H, J = 7.5 Hz, $CH_2CH_2CH_2C_6H_5$); 2.75 (t, 2H, J = 7.8 Hz, $CH_2CH_2CH_2C_6H_5$); 4.53–4.70 (m, 4H, $CH_2CH_2CH_2CH_2CH_3$ and $CH_2CH_2CH_2C_6H_5$); 7.17–7.28 (m, 5H, C_6H_5); 8.38–8.54 (m, 2H, C_6H_4); 9.15 (d, 1H, J = 2.1 Hz, C_6H_4); 10.32 (s, 1H, NCHN). ^{13}C NMR (DMSO-d_6): δ 14.3 ($CH_2CH_2CH_2CH_2CH_3$); 22.1 ($CH_2CH_2CH_2CH_2CH_3$); 28.3 ($CH_2CH_2CH_2CH_2CH_3$); 28.8 ($CH_2CH_2CH_2CH_2CH_3$); 30.5 ($CH_2CH_2CH_2C_6H_5$); 32.3 ($CH_2CH_2CH_2C_6H_5$); 47.7 ($CH_2CH_2CH_2CH_2CH_3$ and $CH_2CH_2CH_2C_6H_5$); 111.4, 115.6, 122.0, 126.5, 128.7, 128.8, 131.5, 135.4, 141.0, 146.2 (Ar-C); 146.9 (NCHN). Anal. Calc. for $C_{21}H_{26}N_3O_2Br$ (432.35): C, 58.34; H, 6.06; N, 9.72; found: C, 57.91; H, 5.90; N, 9.40.

3.2.5. 1,2-Bis[3-(3-phenylpropyl)-1-ylbenzimidazolium]ethane dibromide (1f)

Yield: 2.59 g, 69%; mp: 129–131 °C. IR (cm^{-1}): 1562 ($\upsilon_{C=N}$). ^{1}H NMR (DMSO-d_6): δ 2.16 (*quint*, 4H, J = 7.8 Hz, $CH_2CH_2CH_2C_6H_5$); 2.63 (t, 4H, J = 7.8 Hz, $CH_2CH_2CH_2C_6H_5$); 4.48 (t, 4H, J = 7.5 Hz, $CH_2CH_2CH_2C_6H_5$); 5.19 (m, 4H,CH_2CH_2); 7.18–7.32 (m, 10H, C_6H_5); 7.54–7.66 (m, 4H, C_6H_4); 7.89–8.10 (m, 4H, C_6H_4); 10.06 (s, 2H, NCHN). ^{13}C NMR (DMSO-d_6): δ 30.5 ($CH_2CH_2CH_2C_6H_5$); 32.2 ($CH_2CH_2CH_2C_6H_5$); 46.2 (CH_2CH_2); 47.0 ($CH_2CH_2CH_2C_6H_5$); 113.5, 114.3, 126.6, 127.1, 127.2, 128.7, 128.9, 131.4, 131.5, 141.0 (Ar-C); 143.5 (NCHN). Anal. Calc. for $C_{34}H_{36}N_4Br_2$ (660.50): C, 61.83; H, 5.49; N, 8.48; found: C, 61.07; H, 5.23; N, 8.16.

3.2.6. 1,3-Bis[3-(3-phenylpropyl)-1-ylbenzimidazolium]propane dibromide (1g)

Yield: 2.83 g, 77%; mp: 90–92 °C. IR (cm^{-1}): 1561 ($\upsilon_{C=N}$). ^{1}H NMR (DMSO-d_6): δ 2.26 (*quint*, 4H, J = 7.5 Hz, $CH_2CH_2CH_2C_6H_5$); 2.67 (*quint*, 2H, J = 6.9 Hz, $CH_2CH_2CH_2$); 2.74 (t, 4H, J = 7.2 Hz, $CH_2CH_2CH_2C_6H_5$); 4.57 (t, 4H, J = 7.2 Hz, $CH_2CH_2CH_2C_6H_5$); 4.78 (t, 4H, J = 7.2 Hz, $CH_2CH_2CH_2$); 7.14–7.27 (m, 10H, C_6H_5); 7.66–7.69 (m, 4H, C_6H_4); 8.11–8.23 (m, 4H, C_6H_4); 10.16 (s, 2H, NCHN). ^{13}C NMR (DMSO-d_6): δ 28.1 ($CH_2CH_2CH_2$); 30.0 ($CH_2CH_2CH_2C_6H_5$); 31.9 ($CH_2CH_2CH_2C_6H_5$); 43.9 ($CH_2CH_2CH_2$); 46.5 ($CH_2CH_2CH_2C_6H_5$); 113.7, 126.0, 126.4, 126.5, 128.2, 128.3, 131.0, 131.1, 140.5 (Ar-C); 142.4 (NCHN). Anal. Calc. for $C_{35}H_{38}N_4Br_2$ (674.51): C, 62.32; H, 5.68; N, 8.31; found: C, 62.02; H, 5.50; N, 8.39.

3.2.7. 1,4-Bis[3-(3-phenylpropyl)-1-ylbenzimidazolium]butane dibromide (1h)

Yield: 2.95 g, 83%; mp: 119–120 °C. IR (cm^{-1}): 1562 ($\upsilon_{C=N}$). ^{1}H NMR (DMSO-d_6): δ 2.04 (m, 4H, $CH_2CH_2CH_2CH_2$); 2.25 (*quint*, 4H, J = 7.5 Hz, $CH_2CH_2CH_2C_6H_5$); 2.71 (t, 4H, J = 7.8 Hz, $CH_2CH_2CH_2C_6H_5$); 4.55 (t, 4H, J = 7.2 Hz, $CH_2CH_2CH_2C_6H_5$); 4.59 (m, 4H, $CH_2CH_2CH_2CH_2$); 7.20–7.29 (m, 10H, C_6H_5); 7.63–7.72 (m, 4H, C_6H_4); 8.07–8.16 (m, 4H, C_6H_4); 10.02 (s, 2H, NCHN). ^{13}C NMR (DMSO-d_6): δ 25.9 ($CH_2CH_2CH_2CH_2$); 30.5 ($CH_2CH_2CH_2C_6H_5$); 32.4 ($CH_2CH_2CH_2C_6H_5$); 46.5 ($CH_2CH_2CH_2CH_2$); 47.0 ($CH_2CH_2CH_2C_6H_5$); 114.2, 126.5, 126.9, 127.0, 128.7, 128.8, 131.5, 131.6, 141.0 (Ar-C); 142.7 (NCHN). Anal. Calc. for $C_{36}H_{40}N_4Br_2$ (688.55): C, 62.80; H, 5.86; N, 8.14; found: C, 62.64; H, 5.67; N, 8.05.

3.3. General procedure for formation of Suzuki–Miyaura cross-coupling reactions

Bromobenzene (1 mmol) or 1-bromonaphthalene (1 mmol), phenylboronic acid (1 mmol), or benzene-1,4-diboronic acid (0,5 mmol), K_2CO_3 (2 mmol), $Pd(OAc)_2$ (1 mol%), **1a**–1**h** (2 mol%), and DMF (3 mL)-H_2O (3 mL) were added to an apparatus of microwave equipment. The mixture was stirred and heated at 100 °C by microwave irradiation (300 W) for 5 min. After the completion of the reaction, the product was extracted with ethyl acetate from the mixture. Then the purification was done by crystallization from ethyl acetate/n-hexane (1:1). The isolated yield was calculated. The product structures were determined by ^{1}H-NMR, ^{13}C-NMR, and LC-MS.

3.4. General procedure for formation of N-heterocyclic carbene and isocyanurate

A mixture of benzimidazolium salt (**1a**–**1h**) (0.18 mmol) and NaH (0.25 mmol) in tetrahydrofuran (5 mL) was stirred for 30 min at room temperature under an argon atmosphere. Then the solvent was removed in vacuo and the precipitate was extracted with hot toluene (5 mL) and filtered when hot. The solvent was removed again and phenyl isocyanate (2 mL, 18.30 mmol) was added under an argon atmosphere. An exothermic reaction was observed in seconds and white-colored needle-crystalline phenyl isocyanurate (1,3,5-triphenylperhydro-1,3,5-triazine-2,4,6-trione) occurred.[104] The product was washed with diethyl ether twice and dried.

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