Potential N-Heterocyclic Carbene Precursors in the Palladium-Catalyzed Heck Reaction

Serpil Demir, Rukiye Zengin, and İsmail Özdemir

Department of Chemistry, Faculty of Science and Art, Inönü University, 44280 Malatya, Turkey

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ABSTRACT: A novel 1-(cyclobutylmethyl)-substituted imidazolidinium/benzimidazolium salts as Nheterocyclic carbene (NHC) precursors were successfully synthesized and characterized by ¹H NMR, ¹³C NMR, IR, and elemental analysis techniques. These compounds were easily prepared from the reaction of N-alkyl imidazoline/N-alkyl benzimidazole with bromomethylcyclobutane in high yields. The in situ formed catalytic system derived from the NHC precursor and $Pd(OAc)_2$ was used in the Heck reaction between aryl halides and styrene with potassium hydroxide in water. The corresponding Heck products were obtained in good yields. © 2012 Wiley Periodicals, Inc. Heteroatom Chem. 24:77-83, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21065

INTRODUCTION

The palladium-catalyzed Mizoroki—Heck reaction, or more often the Heck reaction, arylation of olefins with aryl halides was independently discovered by Heck [1] and Mizoroki [2] ca. 40 years ago. It has since become one of the most celebrated tools for constructing sp² C—C bonds in synthetic chemistry [3, 4]. Its significance has been highlighted by the 2010 Nobel Prize in chemistry to Professor Richard Heck along with Professors Ei-ichi Negishi and Akira

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Suzuki. Of all the work undertaken, the area that has perhaps received most research effort is the development of new catalysts and ligands for Heck coupling reactions and the use of these catalyst systems in, for example, natural product synthesis. As the choice of ligand plays a major role in the efficiency of the catalyst, phosphine ligands are the first choice to catalyze the Heck reaction more actively and efficiently [5–9]. However, they are often toxic, air-sensitive, or quite expensive. In the past 15 years, the employment of N-heterocyclic carbene (NHC) ligands has gained an enormous popularity in catalysis due to their potential advantages over tertiary phosphines specifically, easy accessibility, better σ donor ability, and improved thermal stability of the complexes [10–13]. An exceptionally large number of NHC complexes have emerged and have been used successfully in many catalytic transformations, notably the C-C and C-N cross-coupling reactions [14–21] as well as the extremely useful metathesis reaction [22–26]. While a variety of media, such as ionic liquids [27], fluorous solvents [28], and supercritical carbon dioxide [29-31] have been promoted as replacements to organic solvents in metalcatalyzed reactions, the use of water as the solvent is considered as a key characteristic from environmental, nontoxicity, industrial, and economical points of view [32-34]. The use of water in Pd-catalyzed crosscoupling reactions goes back to the early development of the Suzuki coupling with the first example being reported by Calabrese and co-workers in 1990 [35, 36]. Recently, we have shown the influence of imidazodinium/benzimidazolium salts as NHC precursors with Pd(OAc)₂ for the C-C coupling reactions [37-39,41,42]. Now, we report synthesis, structure, and the use of 1,3-dialkyl imidazolidinium or

Correspondence to: İsmail Özdemir; e-mail: ismail.ozdemir@ inonu.edu.tr.

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SCHEME 1 Synthesis of imidazolidinium salts (path A) and benzimidazolium salts (path B). 1-alkylimidazoline or 1-alkylbenzimidazole (5 mmol), bromomethylcyclobutane (5 mmol) in DMF (10 mL) at 60°C for 10 h.

benzimidazolium salts that consist of the cyclobutylmetyl moiety as ligands for Pd(II)-catalyzed Heck coupling reactions of aryl halides in water.

RESULTS AND DISCUSSION

The new NHC precursors (**1a–1c** and **2a–2c**) were readily prepared upon treatment of the 1-alkyl imidazoline or benzimidazole with bromomethylcyclobutane in DMF (Scheme 1).

We chose the cyclobutyl ring as a substituent. Because we thought that this group can exhibit different catalytic activities due to the cyclic structure. All compounds are air and moisture-stable in the solid state as well as in solution, and they were isolated as solids in very good yields and fully characterized by ¹H NMR, ¹³C NMR, and IR spectroscopy, elemental analyses, and their melting points were determined. They can dissolve in water, dichloromethane, chloroform, methanol, and acetonitrile. Although they have not water-soluble side groups such as sugar, sulfonate, and amino, they are perfectly solvable in water.

A fine study of the chemical shifts of the acidic C(2) protons shows that they are located in the range 9.15–11.68 ppm, which indicates a significant difference in the acidity of these protons (Table 1). Comparison of the chemical shifts in the two series where the aromatic substituents are identical as in (1a, 2a), (1b, 2b), and (1c, 2c) reveals the order $\delta(1) < \delta(2)$, which is an indication of the influence of the core structure of the properties of these salts. The ¹³C NMR spectra of 1a–1c exhibit the NCHN resonances between δ 157.7 and 156.9 ppm, which are also typical values previously reported for imidazolidinium

TABLE 1 ¹H NMR and ¹³C NMR Spectroscopic Data for the C(2)H Proton and Carbon (δ , ppm); ν (CN) (cm⁻¹) of the NHC Salts

NHC Salt	¹ H NMR	¹³ C NMR	ν (CN)	NHC Salt	¹ H NMR	¹³ C NMR	ν (CN)
1a	9.92	157.7	1658	2a	11.68	142.5	1552
1b	9.53	157.4	1649	2b	11.31	142.8	1550
1c	9.15	156.9	1643	2c	10.70	142.2	1552

salts [37]. The NCHN δ [¹³C[¹H]] signal of the benzimidazolium salts is usually around 142 ± 4 ppm. For the benzimidazolium salts **2a–c**, it was found to be 142.5, 142.8, and 142.2 ppm, respectively. These values are in good agreement with the previously reported results [39–42].

The compounds (**1a–c** and **2a–c**) show IR absorption bands at wavelengths and that vary from 1550 to 1658 cm⁻¹, which are assigned to ν (CN). These IR absorption values are in good agreement with previously reported values for NHC salts [37–42].

Pd(*OAc*)₂/*NHC Precursor Catalyzed the Heck Reaction Performed in Water*

The Heck reaction of aryl halides with alkenes is promoted by palladium catalysts and meanwhile one of the most important methods for C–C coupling in organic synthesis [43], in the synthesis of intermediates for pharmaceuticals [44], and also for the preparation of conducting polymers [45]. NHCs are potential ligands for formation of complexes with transition metals that can be used as catalysts in organic synthesis. The ligand-free systems consist of $Pd(OAc)_2$ or $Pd(O_2CCF_3)_2$; base and solvents have also been used as a catalyst system in Heck coupling reactions [46-48]. However, using the Pd(OAc)₂-catalytic systems containing ligands has been shown more effective catalytic activity than ligand-free palladium-containing systems [49,51]. Pd(OAc)₂-benzimidazole or imidazoline ligands could be very effective catalytic systems, particularly in cross-coupling reactions [37-42]. Heck reactions are most frequently performed in dipolar aprotic organic solvents such as DMF [52], DMA [53], and dioxane [37]. Compared to organic solvents, water is safe, nontoxic, nonflammable, and inexpensive. Therefore, development of organic reactions in water is still attractive enough [54–61].

The in situ formed catalytic systems derived from the NHC salts and Pd(OAc)₂ have been used successfully for the Heck reaction in water. Initially, the reaction conditions were optimized starting from 4-bromoacetophenone and styrene catalyzed by the NHC salts/Pd(OAc)₂ system in water at 80° C with various bases as shown in Table 2. No good yield was observed when either potassium carbonate or cesium carbonate was used as the base (Table 2, entries 1 and 5), whereas a good yield was observed with potassium tert-butoxide, potassium hydroxide, and sodium hydroxide (Table 2, entries 2, 3, and 4). We observed almost same results with potassium tertbutoxide and potassium hydroxide and preferred to potassium hydroxide as a base because it was cheaper than others. It was noted that in the absence of the NHC precursor, there was no detectable amount of the desired coupled product formed as judged by the GC analysis (Table 2, entry 8).

The effect of temperature and reaction time on the reaction of 4-bromoacetophenone and styrene in water using the $1a/(Pd(OAc)_2 \text{ and KOH} \text{ as a base}$ (Table 2, entries 6 and 7) was also studied. Having optimized conditions, we applied these conditions to the coupling reactions of varieties of aryl halides with styrene (Table 3).

The coupling of aryl iodides and bromides was superior and afforded the desired products in excellent yields. Reactions involving deactivated aryl bromides bearing a methyl or methoxy group with styrene gave high yields of the coupled product. The reaction between 1-bromo-4-nitrobenzene and styrene also work well to give product for 2 h. 4-iodoanisole and 4-iodoacetophenone were completely converted into the coupled products after

		Br-COCH ₃	Water	COCH3	
Entry	NHC Salt	Base	Temperature (° C)	Time (h)	Yield (%)
1	1a	Cs ₂ CO ₃	80	3	40
2	1a	KÖBu ^t	80	3	93
3	1a	KOH	80	3	95
4	1a	NaOH	80	3	87
5	1a	K ₂ CO ₃	80	3	35
6	1a	KOH	60	3	55
7	1a	KOH	80	1	75
8	-	KOH	80	15	10

TABLE 2 Effect of Different Bases on Product Yield in the Heck Coupling of 4-Bromoacetophenone and Styrene in Water

Reaction conditions: All reactions were carried out using styrene (1.5 mmol), 4-bromoacetophenone (1.0 mmol), KOH (2.0 mmol), **1a** (2.0 mmol%), Pd(OAc)₂ (1.0 mmol%), water (5 mL). All reactions were monitored by TLC and GC.

		x—Q—R	LHX/Pd(OA 80°C / Water		R	
R/X	1a	1b	1c	2a	2b	2c
COCH ₃ /Br CHO/Br OCH ₃ /Br	95 (3 h) 92 (5 h) 85 (10 h) 95 (10 h) ^a	93 (3 h) 81 (5 h) 92 (10 h) ^a	92 (3 h) 89 (5 h) 72 (10 h) ^a	55 (3 h) 51 (5 h) 53 (10 h) ^a	47 (3 h) 37 (5 h) 55 (10 h) ^a	68 (3 h) 35 (5 h) 42 (10 h) ^a
CH ₃ /Br	63 (10 h) 91 (10 h) ^a	84 (10 h) ^a	89 (10 h) ^a	83 (10 h) ^a	81 (10 h) ^a	51 (10 h) ^a
NO ₂ /Br H/Br	87 (2 h) 47 (5 h) 69 (5 h) ^a	83 (2 h)	81 (2 h)	78 (2 h)	76 (2 h)	72 (2 h)
OCH ₃ /I COCH ₃ /I COCH ₃ /CI	97 (Ì/2 ĥ) ^a 93 (1/2 h) No (24 h) No (24 h) ^b					

TABLE 3 Heck Reaction between Aryl Halides and Styrene in the Presence of LHX/Pd(OAc)₂ and KOH in Water

Reaction conditions: All reactions were carried out using styrene (1.5 mmol), aryl halide (1.0 mmol), KOH (2.0 mmol), LHX (2.0 mmol%), Pd(OAc)₂ (1.0 mmol%), water (5 mL), 80°C. All reactions were monitored by TLC and GC. ^a100°C.

^b120°C.

30 min. The ideal substrates for coupling reactions are aryl chlorides, since they tend to be cheaper and more widely available than their bromide or iodide counterparts. Unfortunately, the high C-Cl bond strength compared with C-Br and C-I bonds disfavor oxidative addition, the first step in catalytic coupling reactions. We also investigated the scope of this method on aryl chlorides, but found that the coupling of aryl chloride with styrene did not work; even on heating the reaction mixture vigorously stirred at 120°C in oil bath and extending the reaction time. We found that all these Pd(OAc)₂/LHX catalytic systems are very active for aryl bromide and iodide in the Heck reaction. Like other type of palladiumcatalyst coupling reactions, the Mizoroki-Heck reaction's activity is also highly dependent on the nature of the ligand, for example, its electronic and steric effect [62]. The activity of the catalysts (1a-1c and 2a-2c) was also tested in the Heck reaction. The NHC ligands with a imidazolidinium group (1a-1c) are much more active than those NHC ligands with benzimidazolium groups (2a-2c). Thus, we reported that the electronic properties of the NHC ligands with the cyclobutylmethyl substituent have a significant effect on the reactivity. When compared to literature results [37,63], new NHC precursors are a very active catalyst for the Heck coupling reaction. Gülcemal and co-workers reported the benzimidazolium bromides bearing oligoether side chains - $(CH_2CH_2O)n - (n = 1, 2, \text{ or } 3)$ as a catalyst for the Heck reaction of bromoacetophenone with styrene and Cs₂CO₃ at 100°C and 4 h in the presence of water. A great advantage of our catalysts is to generate the styrene derivatives in aqueous media with economic KOH at short time and lower temperature as indicated in the literature. We believe that the cyclobutylmethyl group has a significant effect on this reaction. The carbene ligand with the 4-methyl– substituted imidazolidinium group is much more active than those carbene ligands with other substituted groups.

CONCLUSIONS

In conclusion, we prepared cyclobutylmethyl functionalized imidazolidinium/benzimidazolium salts (1–2) whose structures were confirmed by ¹H NMR, ¹³C NMR, IR, and elemental analysis. The in situ catalytic activities of all salts, in combination with Pd(OAc)₂, were tested for the Heck reaction in water. The advantages offered by this method are simple procedure, mild conditions, and good yields of product. Research in our laboratory is currently on going to extend the coordination chemistry of functionalized NHCs to transition metals and explore their potential applications in catalysis.

EXPERIMENTAL

All procedures were carried out under an inert atmosphere using standard Schlenk line techniques. Chemicals and solvents were purchased from Sigma Aldrich (Dorset, UK). 1-Alkylbenzimidazole and alkylimidazoline were synthesized in our

laboratory. Solvents were dried with standard methods and freshly distilled prior to use. Elemental analyses were performed by a LECO CHNS-932 elemental analyzer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. FT-IR spectra were recorded as KBr pellets in the range of 400–4000 cm^{-1} on a Perkin Elmer spectrum 100. ¹H NMR and ¹³C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (¹H), 100 MHz (¹³C) in CDCl₃ with tetramethylsilane as an internal reference. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (J values) are given in Hertz. NMR multiplicities are abbreviated as fallows: s = singlet, d = doublet, t = triplet, m = multiplet, hept = heptet signal. All catalytic reactions were monitored on an Agilent 6890N GC system by GC-FID with a HP-5 column of 30 m length, 0.32 mm diameter, and 0.25-µm film thickness. Column chromatography was performed using silica gel 60 (70-230 mesh). Solvent ratios are given as v/v.

General Procedure for the Preparation of the NHC Precursors

To a solution of 1-alkylimidazoline or 1alkylbenzimidazole (5 mmol) in DMF (10 mL), bromomethylcyclobutane (5 mmol) at 25° C was added slowly and the resulting mixture was stirred at 60°C for 10 h. Diethyl ether (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with diethyl ether (3 × 15 mL), dried under vacuum. The crude product was recrystallized from EtOH/Et₂O.

[1-(Cyclobutylmethyl)-3-(4-methylbenzyl)] imidazolidinium Bromide, **1a**

Yield: 2.65 g (82%), mp: 109–110°C, IR $\nu_{(CN)} = 1658$ cm⁻¹. ¹H NMR (399.9 MHz, CDCl₃) δ (ppm) = 1.80–1.74 (m, 2H, CH₂, CH₂-cyclobutane), 1.98–1.81 (m, 2H, CH₂, CH₂-cyclobutane), 2.16–2.05 (m, 2H, CH₂, CH₂-cyclobutane), 2.31 (s, 3H, CH₂C₆H₄(CH₃)-4), 2.67 (hept., 1H, J = 7.8 Hz, CH, CH₂-cyclobutane), 3.89–3.79 (m, 4H, NCH₂CH₂N), 4.82 (s, 2H, CH₂C₆H₄(CH₃)-4), 7.28 (d, 2H, J = 8.1 Hz, CH₂C₆H₄(CH₃)-4), 7.28 (d, 2H, J = 8.1 Hz, CH₂C₆H₄(CH₃)-4), 7.14 (d, 2H, J = 7.8 Hz, CH₂C₆H₄(CH₃)-4), 9.92 (s, 1H, NCHN). ¹³C NMR (100.5 MHz, CDCl₃) δ (ppm) =

18.2 (CH₂, CH₂-cyclobutane), 21.2 (CH₂C₆H₄(CH₃)-4), 25.9 (CH₂, CH₂-cyclobutane), 32.9 (CH, CH₂cyclobutane), 47.7 and 48.9 (NCH₂CH₂N), 51.7 (CH₂C₆H₄(CH₃)-4), 53.5 (CH₂-cyclobutane), 128.9, 129.6, 129.8, and 138.9 (CH₂C₆H₄(CH₃)-4), 157.7 (NCHN), Anal. Calcd for C₁₆H₂₃N₂Br: C: 59.45; H: 7.17; N: 8.67. Found C: 59.48; H: 7.15; N: 8.69.

[1-(Cyclobutylmethyl)-3-(2,4,6-trimethylbenzyl)] imidazolidinium Bromide, **1b**

Yield: 3.27 g (93%), mp: 163–164°C, IR $\nu_{(CN)}$ = 1649 cm⁻¹. ¹H NMR (399.9 MHz, CDCl₃) δ $(ppm) = 1.81-1.72 (m, 2H, CH_2, CH_2-cyclobutane),$ 1.99-1.88 (m, 2H, CH₂, CH₂-cyclobutane), 2.17-2.05 (m, 2H, CH₂, CH₂-cyclobutane), 2.34 and 2.25 (s, 9H, $CH_2C_6H_2(CH_3)_3$ -2,4,6), 2.68 (hept., 1H, J = 7.5 Hz, CH, CH₂-cyclobutane), 3.61 (d, 2H, J = 7.8 Hz, CH_2 -cyclobutane), 3.98–3.74 (m, 4H, NC H_2 C H_2 N), 4.90 (s, 2H, C H_2 C₆H₂(CH₃)₃-2,4,6), 6.86 (s, 2H, $CH_2C_6H_2(CH_3)_3$ -2,4,6), 9.53 (s, 1H, NCHN). ¹³C NMR (100.5 MHz, CDCl₃) δ (ppm) = 18.1 (CH₂, CH₂-cyclobutane), 20.2 and 20.9 (CH₂C₆H₂(CH₃)₃-2,4,6), 25.8 (CH₂, CH₂cyclobutane), 32.9 (CH, CH₂-cyclobutane), 47.7 and 46.2 (NCH₂CH₂N), 48.8 (CH₂C₆H₂(CH₃)₃-2,4,6), 53.2 (CH₂-cyclobutane), 125.4, 129.8, 137.6, and 139.0 (CH₂C₆H₂(CH₃)₃-2,4,6), 157.4 (NCHN), Anal. Calcd for C₁₈H₂₇N₂Br: C: 61.54; H: 7.75; N: 7.97. Found C: 61.55; H: 7.78; N: 7.94.

[1-(Cyclobutylmethyl)-3-(2,3,4,5,6-pentamethylbenzyl)]imidazolidinium Bromide, **1c**

Yield: 3.30 g (87%), mp: 242–243°C, IR $\nu_{(CN)}$ = 1643 cm⁻¹. ¹H NMR (399.9 MHz, CDCl₃) δ (ppm) = 1.81–1.72 (m, 2H, CH₂, CH₂-cyclobutane), 2.01– 1.89 (m, 2H, CH₂, CH₂-cyclobutane), 2.16-2.05 (m, 2H, CH₂, CH₂-cyclobutane), 2.30, 2.24, and 2.22 (s, 15H, $CH_2C_6(CH_3)_5$ -2,3,4,5,6), 2.67 (hept., 1H, J = 7.8Hz, CH, CH₂-cyclobutane), 3.61 (d, 2H, J = 7.5 Hz, CH_2 -cyclobutane), 4.01–3.82 (m, 4H, N CH_2CH_2N), 4.94 (s, 2H, CH₂C₆(CH₃)₅-2,3,4,5,6), 9.15 (s, 1H, NCHN). ¹³C NMR (100.5 MHz, CDCl₃) δ (ppm) = 16.9, 17.1, and 17.2 $(CH_2C_6(CH_3)_5-2,3,4,5,6)$, 18.2 (CH₂, CH₂-cyclobutane), 25.8 (CH₂, CH₂cyclobutane), 32.9 (CH, CH₂-cyclobutane), 47.3 and 48.1 (NCH₂CH₂N), 48.9 (CH₂C₆(CH₃)₅-2,3,4,5,6), 53.6 (CH₂-cyclobutane), 125.6, 133.4, 133.6, and 136.5 (CH₂C₆(CH₃)₅-2,3,4,5,6), 156.9 (NCHN), Anal. Calcd for C₂₀H₃₁N₂Br: C: 63.32; H: 8.24; N: 7.38. Found C: 63.29; H: 8.25; N: 7.41.

[1-(Cyclobutylmethyl)-3-(4-methylbenzyl)] benzimidazolium Bromide, **2a**

Yield: 2.93 g (79%), mp: 210–211°C, IR $\nu_{(CN)}$ = 1552 cm⁻¹. ⁱH NMR (399.9 MHz, CDCl₃) δ (ppm) = 2.09-1.87 (m, 4H, CH₂, CH₂-cyclobutane), 2.20-2.12 (m, 2H, CH₂, CH₂-cyclobutane), 2.31 (s, 3H, $CH_2C_6H_4(CH_3)-4)$, 3.07 (hept., 1H, J = 7.8 Hz, CH, CH₂-cyclobutane), 4.62 (d, 2H, J = 7.8 Hz, CH₂-cyclobutane), 5.88 (s, 2H, CH₂C₆H₄(CH₃)-4), 7.41 (d, 2H, J = 8.1 Hz, $CH_2C_6H_4(CH_3)$ -4), 7.15 (d, 2H, J = 7.5 Hz, $CH_2C_6H_4(CH_3)-4$), 7.72–7.52 (m, 4H, NC₆ H_4 N), 11.68 (s, 1H, NCHN). ¹³C NMR $(100.5 \text{ MHz}, \text{ CDCl}_3) \delta \text{ (ppm)} = 17.9 \text{ (CH}_2, \text{ CH}_2)$ *cyclobutane*), 21.2 (CH₂C₆H₄(CH₃)-4), 25.8 (CH₂, CH₂-cyclobutane), 34.5 (CH, CH₂-cyclobutane), 51.2 (CH₂C₆H₄(CH₃)-4), 52.3 (CH₂-cyclobutane), 113.0, 113.9, 127.1, 127.2, 131.1, and 131.5 (NC₆H₄N), 128.3, 129.8, 129.9, and 139.2 (CH₂C₆H₄(CH₃)-4), 142.5 (NCHN), Anal. Calcd for C₂₀H₂₃N₂Br: C: 64.69; H: 6.24; N: 7.54. Found C: 64.71; H: 6.21; N: 7.55.

[1-(Cyclobutylmethyl)-3-(2,4,6-trimethylbenzyl)] benzimidazolium Bromide, **2b**

Yield: 3.39 g (85%), mp: 219–220°C, IR $v_{(CN)} =$ 1550 cm⁻¹. ¹H NMR (399.9 MHz, CDCl₃) δ (ppm) = 2.02-1.94 (m, 4H, CH₂, CH₂-cyclobutane), 2.15-2.05 (m, 2H, CH₂, CH₂-cyclobutane), 2.31 and 2.29 (s, 9H, $CH_2C_6H_2(CH_3)_3$ -2,4,6), 3.04 (hept., 1H, J =7.5 Hz, CH, CH₂-cyclobutane), 4.64 (d, 2H, J = 7.8Hz, CH₂-cyclobutane), 5.92 (s, 2H, CH₂C₆H₂(CH₃)₃-2,4,6), 6.93 (s, 2H, $CH_2C_6H_2(CH_3)_3$ -2,4,6), 7.18 (d, 1H, J = 8.7 Hz, NC₆H₄N), 7.45 (t, 1H, J = 6.6 Hz, NC_6H_4N), 7.58 (t, 1H, J = 6.6 Hz, NC_6H_4N), 7.71 (d, 1H, J = 8.4 Hz, NC₆ H_4 N), 11.31 (s, 1H, NCHN). ¹³C NMR (100.5 MHz, CDCl₃) δ (ppm) = 17.9 (CH₂, CH₂-cyclobutane), 21.1 and 20.3 (CH₂C₆H₂(CH₃)₃-2,4,6), 25.7 (CH₂, CH₂-cyclobutane), 34.5 (CH, CH₂-cyclobutane), 47.5 (CH₂C₆H₂(CH₃)₃-2,4,6), 52.2 (CH₂-cyclobutane), 113.0, 113.9, 127.0, 127.2, 131.3, and 131.6 (NC₆H₄N), 125.1, 130.2, 137.9, and 139.7 (CH₂C₆H₂(CH₃)₃-2,4,6), 142.8 (NCHN), Anal. Calcd for C₂₂H₂₇N₂Br: C: 66.16; H: 6.81; N: 7.01. Found C: 66.15; H: 6.78; N: 7.04.

[1-(Cyclobutylmethyl)-3-(2,3,4,5,6-pentamethylbenzyl)]benzimidazolium Bromide, **2c**

Yield: 3.10 g (67%), mp: 254–255°C, IR $\nu_{(CN)} =$ 1552 cm⁻¹. ¹H NMR (399.9 MHz, CDCl₃) δ (ppm) = 2.00–1.88 (m, 4H, CH₂, CH₂-cyclobutane), 2.09–2.04 (m, 2H, CH₂, CH₂-cyclobutane), 2.28, 2.27, and 2.24 (s, 15H, CH₂C₆(CH₃)₅-2,3,4,5,6), 2.96 (hept., 1H, J = 7.5 Hz, CH, CH₂-cyclobutane), 4.70 (d,

2H, J = 7.5 Hz, CH_2 -cyclobutane), 5.86 (s, 2H, $CH_2C_6(CH_3)_5$ -2,3,4,5,6), 7.47 (d, 1H, J = 7.8 Hz, NC_6H_4N), 7.60 (t, 1H, J = 7.5 Hz, NC_6H_4N), 7.71 (t, 1H, J = 7.8 Hz, NC_6H_4N), 7.94 (d, 1H, J = 7.2 Hz, NC_6H_4N), 10.7 (s, 1H, NCHN). ¹³C NMR (100.5 MHz, CDCl₃) δ (ppm) = 16.6, 17.1, and 17.2 ($CH_2C_6(CH_3)_5$ -2,3,4,5,6), 17.9 (CH_2 , CH_2 -cyclobutane), 25.7 (CH_2 , CH_2 -cyclobutane), 34.6 (CH, CH_2 -cyclobutane), 48.3 ($CH_2C_6(CH_3)_5$ -2,3,4,5,6), 52.2 (CH_2 -cyclobutane), 113.1, 113.8, 127.0, 127.2, 131.4, and 131.7 (NC_6H_4N), 124.9, 133.4, 133.9, and 137.3 ($CH_2C_6(CH_3)_5$ -2,3,4,5,6), 142.2 (NCHN), Anal. Calcd for $C_{27}H_{31}N_2Br$: C: 69.97; H: 6.74; N: 6.04. Found C: 69.95; H: 6.71; N: 6.05.

General Procedure for the Heck Reaction

Aryl halide (1.0 mmol), styrene (1.5 mmol), KOH (2.0 mmol), NHC precursor (2.0 mmol%), and Pd(OAc)₂ (1.0 mmol%) were taken in a 25-mL Schlenk tube in which 5 mL of water was added. The reaction mixture was stirred for 1/2-24 h at 80–120°C. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered and the filtrate extracted with ethyl acetate (10 mL × 2). The combined organic layer was dried over anhydrous MgSO₄ and evaporated under reduced pressure. The crude material was purified by column chromatography with EtOAc/hexane (1/5) over silica gel to afford the corresponding product in high purity.

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