

# Synthesis, characterization, and microwave-promoted catalytic activity of novel benzimidazole salts bearing silicon-containing substituents in Heck-Mizoroki and Suzuki-Miyaura cross-coupling reactions under aerobic conditions\*

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A number of benzimidazole derivatives (**1-8**) were synthesized and the catalytic activity of these compounds in a catalytic system including Pd(OAc)<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> in DMF-H<sub>2</sub>O was evaluated in Heck-Mizoroki and Suzuki-Miyaura cross-coupling reactions of aryl iodides, bromides, and chlorides with styrene and arylboronic acids under microwave irradiation and aerobic conditions. The yields of both the Heck-Mizoroki and the Suzuki-Miyaura cross coupling reactions with aryl iodides and aryl bromides were nearly quantitative.

The synthesized 1-substituted benzimidazole (**1**) and benzimidazole salts (**2-8**) were identified by <sup>1</sup>H- and <sup>13</sup>C-NMR and IR spectroscopic methods, and micro analysis. The molecular structure of **7** was also determined by X-ray crystallography.

**Key Words:** Benzimidazole salt, N-heterocyclic carbene, palladium catalysis, Heck-Mizoroki coupling reaction, Suzuki-Miyaura coupling reaction, microwave, crystal structure analysis

\*Dedicated to Prof. Dr. Christian Bruneu for his 60<sup>th</sup> birthday.

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## Introduction

During the past 50 years, the most important carbon-carbon bond forming methodologies have involved using transition metals to mediate the reactions in a controlled and selective manner.<sup>1</sup> In particular, the discovery of palladium catalyzed C-C coupling reactions, such as Heck-Mizoroki coupling<sup>2,3</sup> in the early 1970s and Suzuki-Miyaura coupling<sup>4</sup> in the early 1980s, has been applied to a diverse array of fields, ranging from natural products' synthesis to material science, including biologically important molecules using as drugs and agrochemicals.<sup>5</sup> Stilbene and biaryl moieties, which are products of Heck-Mizoroki and Suzuki-Miyaura cross coupling reactions, respectively, are high-value synthetic targets and can be found as substructures in many pharmaceutically and biologically active compounds.

Despite the fact that they are air-sensitive, degradable at high temperature, and toxic, tertiary phosphines are employed as ligand for palladium complexes in both Heck-Mizoroki and Suzuki-Miyaura cross-coupling reactions.<sup>6</sup> The major limitation with phosphine ligands in catalytic reactions is the termination of the catalytic cycle due to oxidation of phosphines to phosphine oxides, formation of stable phosphido-bridged catalytically inactive dimers, and the cleavage of the P-C bond, causing degradation of the ligand. These problems led chemists to discover new phosphorous free ligands.<sup>7</sup>

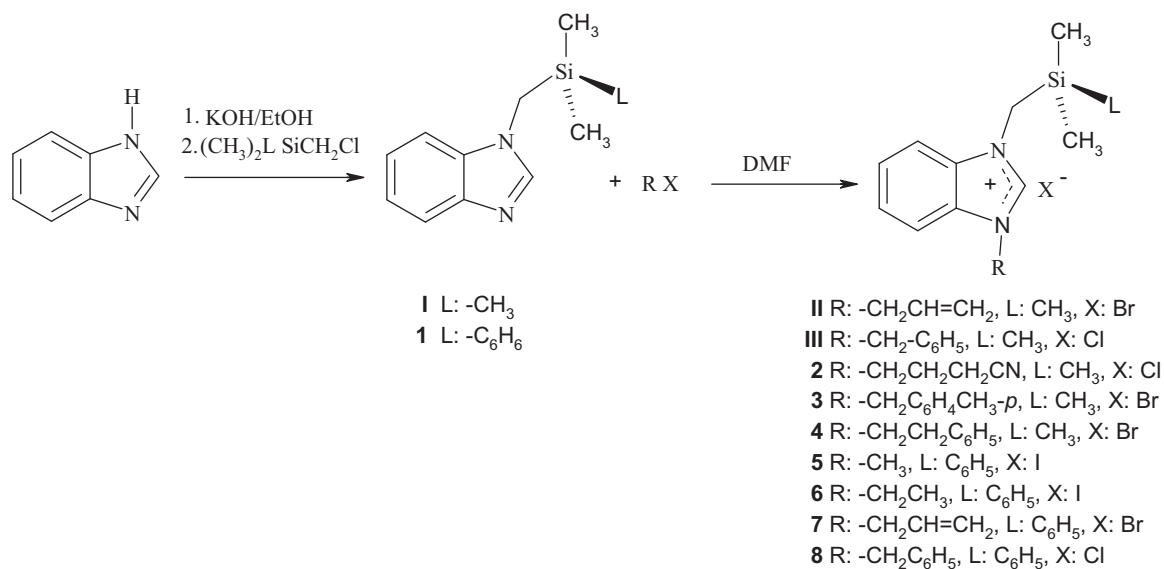
Since the first synthesis of N-heterocyclic carbene complexes, by Öfele and Wanzlick<sup>8,9</sup> in the 1960s and the isolation of free carbenes by Arduengo et al.<sup>10</sup> in 1991, N-heterocyclic carbenes (NHC) have gained remarkable attention.<sup>11-13</sup> They have become a very important class of ligands due to their stability to air and moisture, their low toxicity, and their strong  $\sigma$ -donor but  $\pi$ -acceptor abilities. They are considered alternatives to phosphine ligands in metal complexes. For this reason, the design and synthesis of novel and effective NHCs have attracted a great deal of attention from both academia and industry.<sup>14</sup>

However, both NHCs and electron-rich alkenes that can be used as a source of NHCs are highly air and moisture sensitive and require handling under strict inert conditions.<sup>15-17</sup> In contrast to the cumbersome preparation and isolation of NHCs and electron-rich alkenes, in situ generation of NHCs has the advantages of using a strong base, diazolium salts, and a common palladium source such as PdCl<sub>2</sub> or Pd(OAc)<sub>2</sub> under mild conditions in a number of catalytic syntheses, particularly C-C cross-coupling reactions. In particular, Pd(OAc)<sub>2</sub>/benzimidazole or imidazole ligands could be very effective catalytic system in these reactions.<sup>18-23</sup>

Furthermore, microwave-promoted synthesis is an area of increasing interest in both academic and industrial laboratories. In recent years, heating and driving chemical reactions by microwave energy has been an increasingly popular theme in the scientific community. The use of metal catalysts in conjunction with microwaves may have significant advantages over traditional heating methods since the inverted temperature gradient under microwave conditions may lead to an increased lifetime of catalyst through the elimination of wall effects.<sup>24</sup> There are extensive studies about Heck-Mizoroki and Suzuki-Miyaura type C-C cross-coupling reactions incorporating microwave irradiation using various ligands other than benzimidazole moiety.<sup>25-33</sup>

However, to the best of our knowledge, there is only one example about the catalytic properties of alkylsilyl substituted benzimidazole derivatives in Suzuki-Miyaura C-C cross-coupling reactions under microwave irradiation published in the literature.<sup>22</sup> The nature, size, and electronic properties of the substituents on the nitrogen atom(s) of the benzimidazole may play a crucial role in tuning the catalytic activity. In order to find a more efficient palladium catalyst, we synthesized a series of new benzimidazole salts, **II**, **III**, **2-8** (Scheme 1),

containing trimethylsilylmethyl or dimethylphenylsilylmethyl moieties, and we aimed to investigate the activity of in-situ prepared Pd-NHC based catalytic systems for the Heck-Mizoroki and Suzuki-Miyaura cross-coupling reactions under microwave heating.



**Scheme 1.** Synthesis pathways of the new silyl substituted benzimidazole derivatives.

Herein, we describe the synthesis of new benzimidazole (**1**) and benzimidazole salts (**1-8**) containing trimethylsilylmethyl or dimethylphenyl moieties. The compounds were fully characterized by elemental analysis, IR, <sup>13</sup>C-NMR, and <sup>1</sup>H-NMR spectroscopy and the molecular structure of **7** was determined by X-ray crystallography. We also report the microwave-assisted catalytic activity of Pd(OAc)<sub>2</sub>/trimethylsilylmethyl or dimethylphenyl substituted benzimidazole catalytic system in Heck-Mizoroki and Suzuki-Miyaura cross-coupling reactions.

## Experimental section

### General chemical procedure

All preparations were carried out in an atmosphere of purified argon using standard Schlenk techniques. Starting materials and reagents used in the reactions were supplied commercially by Aldrich or Merck Chemical Co. Solvents were dried with standard methods and freshly distilled prior to use. All catalytic activity experiments were carried out in a microwave oven system manufactured by Milestone (Milestone Start S Microwave Labstation for Synthesis) under the aerobic conditions. <sup>1</sup>H-NMR (300 MHz) and <sup>13</sup>C-NMR (75 MHz) spectra were recorded using a Bruker DPX-300 high performance digital FT NMR spectrometer. Infrared spectra were recorded as KBr pellets in the range 4000-400 cm<sup>-1</sup> on a Perkin-Elmer FT-IR 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.

Benzimidazole derivatives, **I**,<sup>34</sup> **II**,<sup>35</sup> and **III**,<sup>36</sup> used in this work were prepared according to the literature procedures.

## GC-MS analysis

GC-MS spectra were recorded on an Agilent 6890 N GC and 5973 Mass Selective Detector with an HP-INNOWAX column of 60 m length, 0.25 mm diameter, and 0.25  $\mu\text{m}$  film thicknesses. GC-MS parameters for both Suzuki and Heck-Mizoroki coupling reactions were as follows: initial temperature 60 °C; initial time, 5 min; temperature ramp 1, 30 °C/min; final temperature, 200 °C; ramp 2, 20 °C/min; final temperature 250 °C; run time 30.17 min; injector port temperature 250 °C; detector temperature 250 °C, injection volume, 1.0  $\mu\text{L}$ ; carrier gas, helium; mass range between  $m/z$  50 and 550.

## Synthesis of benzimidazole derivatives

*1-(Dimethylphenylsilylmethyl)benzimidazole*, **1**. To a mixture of benzimidazole (1.18 g; 10 mmol) and KOH (0.56 g, 10.0 mmol) in EtOH (10 mL) was added (chloromethyl)dimethylphenylsilane (1.85 mL, 10.2 mmol) and the mixture was heated under reflux for 4 h. The mixture was then cooled, after which potassium chloride was filtered off and washed with a little EtOH. The solvent was then removed from the filtrate in vacuo. After distillation of the crude product under reduced pressure, yellow oily compound **1** (1.74 g, 65%) was obtained, bp 89 °C/1 mmHg;  $\nu_{(C=N)}$  = 1590  $\text{cm}^{-1}$ . Anal. found: C 72.09, H 6.75, N 10.43%. Calculated for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{Si}$ : C 72.13, H 6.81, N 10.52%. <sup>1</sup>H-NMR ( $\delta$ , DMSO- $d_6$ ): 7.93 ppm (s, 1H, NCHN), 7.70-7.55 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 7.47-7.03 (m, 5H, C<sub>6</sub>H<sub>5</sub>Si), 4.11 (s, 2H, CH<sub>2</sub>Si) and 0.31 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C-NMR ( $\delta$ , DMSO- $d_6$ ): 139.6 (NCHN), 136.3, 134.2, 133.2, 130.1, 129.5 and 128.2 (C<sub>6</sub>H<sub>4</sub>), 124.5, 122.2, 119.7 and 111.1 (C<sub>6</sub>H<sub>5</sub>Si), 35.0 (CH<sub>2</sub>Si) and 1.1 (Si(CH<sub>3</sub>)<sub>2</sub>).

*3-(3-Cyanopropyl)-1-(trimethylsilylmethyl)benzimidazolium chloride*, **2**. A mixture of 1-(trimethylsilylmethyl)benzimidazole (1.02 g, 5.0 mmol) and 4-chlorobutyronitrile (0.5 mL, 5.6 mmol) in dimethylformamide (5 mL) was refluxed for 3 h. The mixture was then cooled and the volatiles were removed under vacuum. The residue was crystallized from dimethylformamide/ethanol (1:1). White crystals of the title compound **2** (1.13 g, 73%) were obtained, mp 133-134 °C:  $\nu_{(C=N)}$  = 1557  $\text{cm}^{-1}$ ,  $\nu_{(C\equiv N)}$  = 2247  $\text{cm}^{-1}$ , Anal. found: C 58.37, H 7.16, N 13.56%. Calculated for  $\text{C}_{15}\text{H}_{22}\text{N}_3\text{ClSi}$ : C 58.51, H 7.20, N 13.65%. <sup>1</sup>H-NMR ( $\delta$ , DMSO- $d_6$ ): 9.98 (s, 1H, NCHN), 8.18-8.07 (m, 2H, C<sub>6</sub>H<sub>4</sub>-C<sub>4</sub> and C<sub>7</sub>), 7.27-7.53 (m, 2H, C<sub>6</sub>H<sub>4</sub>-C<sub>5</sub> and C<sub>6</sub>), 4.64 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN,  $J=6.9$  Hz), 4.24 (s, 2H, CH<sub>2</sub>Si), 2.70 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN,  $J=6.9$  Hz), 2.25 (q, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN,  $J=6.9$  Hz) and 0.11 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si). <sup>13</sup>C-NMR ( $\delta$ , DMSO- $d_6$ ): 141.9 (NCHN), 132.4, 131.5, 126.9, 126.7, 114.5 and 113.9 (C<sub>6</sub>H<sub>4</sub>), 120.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN), 45.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN), 25.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN), and 14.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN), 38.4 (CH<sub>2</sub>Si) and -2.2 ((CH<sub>3</sub>)<sub>3</sub>Si).

## General method for the synthesis of compounds 3-8.

Equivalent amounts of the appropriate 1-substituted benzimidazole (**I**, **1**) and the alkyl halide were refluxed in dimethylformamide (5 mL) for 3 h. Then the mixture was cooled to room temperature and the volatiles were removed under reduced pressure. The residue was crystallized from dimethylformamide/ethanol (1:1) under an argon atmosphere to avoid bonding crystal water, as in some of our previous research.<sup>37</sup>

1-(Trimethylsilylmethyl)-3-*p*-xylylbenzimidazolium bromide, **3**. Yield 1.66 g (white crystals), 85%, mp 125-127 °C:  $\nu_{(C=N)}$  = 1558 cm<sup>-1</sup>. Anal. found: C 58.58, H 6.46, N 7.15%. Calculated for C<sub>19</sub>H<sub>25</sub>N<sub>2</sub>BrSi: C 58.60, H 6.47, N 7.19%. <sup>1</sup>H-NMR ( $\delta$ , DMSO-d<sub>6</sub>): 9.95 (s, 1H, NCHN), 8.12-8.10 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 8.02-7.98 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.70-7.62 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.42 (d, 2H, C<sub>6</sub>H<sub>4</sub> - *p*-xylyl,  $J$  = 8.0 Hz), 7.22 (d, 2H, C<sub>6</sub>H<sub>4</sub> - *p*-xylyl,  $J$  = 8.0 Hz), 5.78 (s, 2H, CH<sub>2</sub>*p*-xylyl), 4.29 (s, 2H, CH<sub>2</sub>Si), 2.28 (s, 3H, CH<sub>3</sub>*p*-xylyl) and 0.10 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si). <sup>13</sup>C-NMR ( $\delta$ , DMSO-d<sub>6</sub>): 141.6 (NCHN), 138.6, 132.4, 131.8, 131.1, 129.9 and 128.7 (C<sub>6</sub>H<sub>4</sub>), 127.1, 126.8, 114.6 and 114.3 (C<sub>6</sub>H<sub>5</sub>), 50.0 (CH<sub>2</sub>*p*-xylyl), 38.5 (CH<sub>2</sub>Si), 21.2 (CH<sub>3</sub> *p*-xylyl) and -2.2 ((CH<sub>3</sub>)<sub>3</sub>Si).

1-(Trimethylsilylmethyl)-3-phenethylbenzimidazolium bromide, **4**. Yield 1.70 g (white crystals), 87%, mp 231-232 °C:  $\nu_{(C=N)}$  = 1559 cm<sup>-1</sup>. Anal. found: C 58.53, H 6.47, N 7.13%. Calculated for C<sub>19</sub>H<sub>25</sub>N<sub>2</sub>BrSi: C 58.60, H 6.47, N 7.19%. <sup>1</sup>H-NMR ( $\delta$ , DMSO-d<sub>6</sub>): 9.59 (s, 1H, NCHN), 8.12-8.05 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.70-7.64 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.27-7.16 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 4.83 (t, 2H, CH<sub>2</sub> phenethyl,  $J$  = 6.9 Hz), 4.17 (s, 2H, CH<sub>2</sub>Si), 3.27 (t, 2H, CH<sub>2</sub> phenethyl,  $J$  = 6.9 Hz) and 0.01 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si). <sup>13</sup>C-NMR ( $\delta$ , DMSO-d<sub>6</sub>): 141.3 (NCHN), 137.3, 132.1, 131.2, 129.2, 129.0 and 127.4 (C<sub>6</sub>H<sub>4</sub>), 126.9, 126.8, 114.4 and 114.2 (C<sub>6</sub>H<sub>5</sub>), 48.1 (CH<sub>2</sub> phenethyl), 38.2 (CH<sub>2</sub>Si), 34.9 (CH<sub>2</sub> phenethyl) and -2.4 ((CH<sub>3</sub>)<sub>3</sub>Si).

1-(Dimethylphenylsilylmethyl)-3-methylbenzimidazolium iodide, **5**. A mixture of 1-(dimethylphenylsilylmethyl)benzimidazole (1.34 g, 5.0 mmol) and iodomethane (0.4 mL, 6.4 mmol) in dimethylformamide (5 mL) was refluxed for 3 h. The mixture was then cooled and the volatiles were removed under vacuum. The residue was crystallized from dimethylformamide/ethanol (1:1). White crystals of the title compound **5** (1.56 g, 76%) were obtained, mp 122-123 °C:  $\nu_{(C=N)}$  = 1559 cm<sup>-1</sup>. Anal. found: C 49.73, H 5.11, N 6.72%. Calculated for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>ISi: C 50.00, H 5.18, N 6.86%. <sup>1</sup>H-NMR ( $\delta$ , DMSO-d<sub>6</sub>): 9.48 (s, 1H, NCHN), 8.05-7.70 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 7.65-7.33 (m, 5H, C<sub>6</sub>H<sub>5</sub>Si), 4.44 (s, 2H, CH<sub>2</sub>Si), 4.08 (s, 3H, CH<sub>3</sub>) and 0.41 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C-NMR ( $\delta$ , DMSO-d<sub>6</sub>): 141.8 (NCHN), 134.9, 134.3, 132.1, 132.0, 131.9 and 130.5 (C<sub>6</sub>H<sub>4</sub>), 128.5, 126.8, 114.2 and 113.9 (C<sub>6</sub>H<sub>5</sub>Si), 37.9 (CH<sub>2</sub>Si), 33.8 (CH<sub>3</sub>) and -3.8 (Si(CH<sub>3</sub>)<sub>2</sub>).

1-(Dimethylphenylsilylmethyl)-3-ethylbenzimidazolium iodide, **6**. Yield 1.67 g (white crystals), 79%, mp 112-114 °C:  $\nu_{(C=N)}$  = 1559 cm<sup>-1</sup>. Anal. found: C 51.02, H 5.46, N 6.54%. Calculated for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>ISi: C 51.18, H 5.49, N 6.63%. <sup>1</sup>H-NMR ( $\delta$ , DMSO-d<sub>6</sub>): 9.62 (s, 1H, NCHN), 8.08-8.05 (m, 1H, C<sub>6</sub>H<sub>5</sub>), 7.94-7.91 (m, 1H, C<sub>6</sub>H<sub>4</sub>), 7.67-7.61 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.52-7.31 (m, 5H, C<sub>6</sub>H<sub>5</sub>Si), 4.47 (s, 2H, CH<sub>2</sub>Si), 4.45 (q, 2H, CH<sub>2</sub> ethyl,  $J$  = 7.2 Hz), 0.83 (t, 3H, CH<sub>3</sub> ethyl,  $J$  = 7.2 Hz) and 0.42 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C-NMR ( $\delta$ , DMSO-d<sub>6</sub>): 141.4 (NCHN), 134.8, 134.3, 132.0, 131.8, 131.3 and 130.5 (C<sub>6</sub>H<sub>4</sub>), 128.5, 126.9, 126.4 and 114.2 (C<sub>6</sub>H<sub>5</sub>Si), 48.4 (CH<sub>2</sub> ethyl), 37.8 (CH<sub>2</sub>Si), 22.6 (CH<sub>3</sub> ethyl) and -3.7 (Si(CH<sub>3</sub>)<sub>2</sub>).

1-(Dimethylphenylsilylmethyl)-3-allylbenzimidazolium bromide monohydrate, **7**. Yield 1.52 g (white crystals), 78%, mp 107-108 °C:  $\nu_{(C=N)}$  = 1558 cm<sup>-1</sup>. Anal. found: C 56.99, H 6.94, N 6.63%. Calculated for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>BrSi: C 57.00, H 6.94, N 6.65%. <sup>1</sup>H-NMR ( $\delta$ , DMSO-d<sub>6</sub>): 9.48 (s, 1H, NCHN), 7.96-7.90 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.67-7.56 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.51-7.32 (m, 5H, C<sub>6</sub>H<sub>5</sub>Si), 6.04 (m, 1H, CH allyl), 5.28 (m, 2H, CH<sub>2</sub> allyl), 5.14 (d, 2H, CH<sub>2</sub> allyl,  $J$  = 5.7 Hz), 4.45 (s, 2H, CH<sub>2</sub>Si) and 0.40 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C-NMR ( $\delta$ , DMSO-d<sub>6</sub>): 141.5 (NCHN), 134.7, 134.3, 132.2, 131.7, 131.2 and 130.5 (C<sub>6</sub>H<sub>4</sub>), 128.5, 127.0, 126.6 and 120.4 (C<sub>6</sub>H<sub>5</sub>Si), 114.5 (CH allyl), 114.1 (CH<sub>2</sub> allyl), 49.0 (CH<sub>2</sub> allyl), 38.0 (CH<sub>2</sub>Si) and -3.8 (Si(CH<sub>3</sub>)<sub>2</sub>).

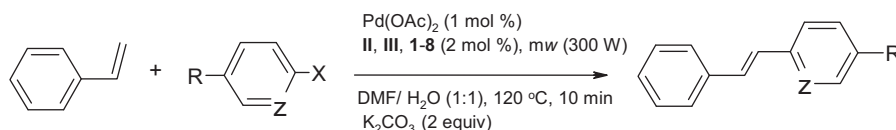
1-(Dimethylphenylsilylmethyl)-3-benzylbenzimidazolium chloride, **8**. Yield 1.62 g (white crystals), 82%,

mp 170-171 °C:  $\nu_{(C=N)} = 1557 \text{ cm}^{-1}$ . Anal. found: C 70.23, H 6.39, N 7.12%. Calculated for  $\text{C}_{23}\text{H}_{25}\text{N}_2\text{ClSi}$ : C 70.29, H 6.41, N 7.13%.  $^1\text{H-NMR}$  ( $\delta$ , DMSO- $d_6$ ): 9.80 (s, 1H, NCHN), 7.94-7.91 (m, 2H,  $\text{C}_6\text{H}_4$ ), 7.60-7.56 (m, 2H,  $\text{C}_6\text{H}_4$ ), 7.51-7.29 (m, 10H,  $\text{C}_6\text{H}_5$  benzyl and 5H  $\text{C}_6\text{H}_5\text{Si}$ ), 5.76 (s, 2H,  $\text{CH}_2$  benzyl), 4.49 (s, 2H,  $\text{CH}_2\text{Si}$ ) and 0.42 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C-NMR}$  ( $\delta$ , DMSO- $d_6$ ): 141.6 (NCHN), 134.6, 134.5, 134.3, 132.3, 131.0, 130.5, 129.5, 129.1, 128.8, 128.5, 127.1, 126.7, 114.6 and 114.1 ( $\text{C}_6\text{H}_4$ -ArH;  $\text{C}_6\text{H}_5$ -benzyl and  $\text{C}_6\text{H}_5\text{Si}$ ), 50.1 ( $\text{CH}_2$  benzyl), 38.0 ( $\text{CH}_2\text{Si}$ ) and -3.7 ( $\text{Si}(\text{CH}_3)_2$ ).

## General procedure for the Heck-Mizoroki reactions

$\text{Pd}(\text{OAc})_2$  (1 mmol%), benzimidazolium chlorides (**II**, **III**, **1-8**) (2 mmol%), the aryl halide (1 mmol), styrene (1.2 mmol),  $\text{K}_2\text{CO}_3$  (2 mmol), water (3 mL), and DMF (3 mL) were added to the microwave apparatus and the mixture was heated at 120 °C (300 W) for 10 min. It was carried out over a ramp time of 3 min to reach 120 °C. At the end of the reaction, the mixture was cooled and the product was extracted with ethyl acetate/*n*-hexane (1:5) and filtered through a pad of silica gel with copious washing. The percent conversion was determined by GC-MS based on aryl halide using the normalizing peak areas method.

**Table 1.** The Heck-Mizoroki coupling reactions of aryl halides with styrene.



Entry	R	Z	X	Salt	Conversion <sup>a</sup> (%)		TOF (h <sup>-1</sup> )	
1	H	CH	I	II	72 <sup>b</sup>		864	
2	H	CH	I	II	88 <sup>c</sup>		528	
3	H	CH	I	II	92 <sup>d</sup>		1104	
4	H	CH	I	II	97 <sup>e</sup>		291	
5	H	CH	I	no	nd <sup>f</sup>		—	
6	H	CH	I	no	09 <sup>g</sup>		27	
7	H	CH	I	II	10 <sup>h</sup>		60	
8	H	CH	I	II	97	89 <sup>i</sup>	582	534 <sup>i</sup>
9	H	CH	I	III	98	94 <sup>i</sup>	588	564 <sup>i</sup>
10	H	CH	I	2	99	92 <sup>i</sup>	594	552 <sup>i</sup>
11	H	CH	I	3	98		588	
12	H	CH	I	4	99	96 <sup>i</sup>	594	576 <sup>i</sup>
13	H	CH	I	5	98	91 <sup>i</sup>	588	546 <sup>i</sup>
14	H	CH	I	6	99	94 <sup>i</sup>	594	564 <sup>i</sup>
15	H	CH	I	7	98		588	
16	H	CH	I	8	98		588	
17	OCH <sub>3</sub>	CH	I	II	93	87 <sup>i</sup>	558	522 <sup>i</sup>
18	OCH <sub>3</sub>	CH	I	III	96	90 <sup>i</sup>	576	540 <sup>i</sup>

Table 1. Continued.

19	OCH <sub>3</sub>	CH	I	2	99		594
20	OCH <sub>3</sub>	CH	I	3	97		582
21	OCH <sub>3</sub>	CH	I	4	99	95 <sup>i</sup>	594 570 <sup>i</sup>
22	OCH <sub>3</sub>	CH	I	5	97	91 <sup>i</sup>	582 546 <sup>i</sup>
23	OCH <sub>3</sub>	CH	I	6	99	95 <sup>i</sup>	594 570 <sup>i</sup>
24	OCH <sub>3</sub>	CH	I	7	98		588
25	OCH <sub>3</sub>	CH	I	8	99		594
26	COCH <sub>3</sub>	CH	Br	II	94		564
27	COCH <sub>3</sub>	CH	Br	III	96		576
28	COCH <sub>3</sub>	CH	Br	2	98		588
29	COCH <sub>3</sub>	CH	Br	3	97		582
30	COCH <sub>3</sub>	CH	Br	4	98		588
31	COCH <sub>3</sub>	CH	Br	5	88		528
32	COCH <sub>3</sub>	CH	Br	6	98		588
33	COCH <sub>3</sub>	CH	Br	7	90		540
34	COCH <sub>3</sub>	CH	Br	8	91		546
35	H	N	Br	II	63		378
36	H	N	Br	III	64		384
37	H	N	Br	2	67		402
38	H	N	Br	3	64		384
39	H	N	Br	4	63		378
40	H	N	Br	5	68		408
41	H	N	Br	6	75		450
42	H	N	Br	7	70		420
43	H	N	Br	8	72		432
44	OCH <sub>3</sub>	CH	Cl	II	36		216
45	OCH <sub>3</sub>	CH	Cl	III	41		246
46	OCH <sub>3</sub>	CH	Cl	2	48		288
47	OCH <sub>3</sub>	CH	Cl	3	40		240
48	OCH <sub>3</sub>	CH	Cl	4	46		276
49	OCH <sub>3</sub>	CH	Cl	5	39		234
50	OCH <sub>3</sub>	CH	Cl	6	56		336
51	OCH <sub>3</sub>	CH	Cl	7	48		288
52	OCH <sub>3</sub>	CH	Cl	8	55		330

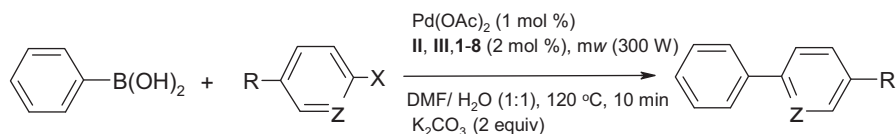
<sup>a</sup>Conversions were determined by GC-MS based on the aryl halide. Reaction conditions: temperature ramped to 80 °C (3 min) and held for 5<sup>b</sup> min and 10<sup>c</sup> min. Temperature ramped to 120 °C (3 min) and held for 5<sup>d</sup> min and 20<sup>e</sup> min. Temperature ramped to 120 °C (3 min) and held for 10<sup>f</sup> min and 20<sup>g</sup> min without salt (**II**). On preheated oil bath, 10<sup>h</sup> min with thermal heating at 120 °C. Isolated yields.<sup>i</sup> n.d., not detected. TOF = TON/time (h); TON = (% Conversion) × (mol-substrate)/(mol-Catalyst).

The Heck-coupling yields between styrene with phenyl iodide or *p*-iodoanisole were also determined as an isolated yield for comparison purposes with the GC based conversion (Table 1, entries 8, 9, 12-14, 17, 18, and 21-23). The isolated yields were determined as follows: at the end of the coupling reaction, the mixture was cooled to room temperature; the contents of the reaction vessel were poured into a separatory funnel. Water (3 mL) and ethyl acetate (5 mL) were added, and the coupling product was extracted and removed. After further extraction of the aqueous phase with ethyl acetate (5 mL) and combining the extracts, the ethyl acetate was removed in vacuo leaving the *trans*-stilbene or *trans-p*-methoxystilbene products as a pale white solid, which was characterized by comparison of NMR data with those in the literature.

## General procedure for the Suzuki reactions

In a typical run, a microwave reaction vessel was charged with a mixture of aryl halide (1 mmol), styrene (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol), Pd(OAc)<sub>2</sub> (1 mmol %), and benzimidazolium salt (2 mmol). To the mixture was then added DMF (3 mL) and water (3 mL). The mixture was reacted over a ramp time of 3 min to 120 °C and heated at 120 °C for 10 min. After completion of the reaction, work-up procedures similar to those described above for the Heck-Mizoroki reaction were performed.

**Table 2.** The Suzuki-Miyaura coupling reactions of aryl halides with phenylboronic acid.



Entry	R	Z	X	Salt	Conversion <sup>a</sup> (%)	TOF (h <sup>-1</sup> )		
1	H	CH	I	II	76 <sup>b</sup>	912		
2	H	CH	I	II	87 <sup>c</sup>	522		
3	H	CH	I	II	94 <sup>d</sup>	1128		
4	H	CH	I	II	98 <sup>e</sup>	294		
5	H	CH	I	no	nd <sup>f</sup>	—		
6	H	CH	I	no	11 <sup>g</sup>	33		
7	H	CH	I	II	09 <sup>h</sup>	54		
8	H	CH	I	II	97	91 <sup>i</sup>	582	546 <sup>i</sup>
9	H	CH	I	III	99	96 <sup>i</sup>	594	576 <sup>i</sup>
10	H	CH	I	2	99		594	
11	H	CH	I	3	99		594	
12	H	CH	I	4	99	97 <sup>i</sup>	594	582 <sup>i</sup>
13	H	CH	I	5	99	93 <sup>i</sup>	594	556 <sup>i</sup>
14	H	CH	I	6	99	94 <sup>i</sup>	594	564 <sup>i</sup>
15	H	CH	I	7	99		594	
16	H	CH	I	8	99		594	
17	OCH <sub>3</sub>	CH	I	II	99	90 <sup>i</sup>	594	540 <sup>i</sup>
18	OCH <sub>3</sub>	CH	I	III	99	93 <sup>i</sup>	594	558 <sup>i</sup>



Table 2. Continued.

19	OCH <sub>3</sub>	CH	I	2	99		594
20	OCH <sub>3</sub>	CH	I	3	99		594
21	OCH <sub>3</sub>	CH	I	4	99	95 <sup>i</sup>	594 570 <sup>i</sup>
22	OCH <sub>3</sub>	CH	I	5	99	92 <sup>i</sup>	594 552 <sup>i</sup>
23	OCH <sub>3</sub>	CH	I	6	99	97 <sup>i</sup>	594 582 <sup>i</sup>
24	OCH <sub>3</sub>	CH	I	7	99		594
25	OCH <sub>3</sub>	CH	I	8	99		594
26	COCH <sub>3</sub>	CH	Br	II	97		582
27	COCH <sub>3</sub>	CH	Br	III	96		576
28	COCH <sub>3</sub>	CH	Br	2	98		588
29	COCH <sub>3</sub>	CH	Br	3	98		588
30	COCH <sub>3</sub>	CH	Br	4	99		594
31	COCH <sub>3</sub>	CH	Br	5	98		588
32	COCH <sub>3</sub>	CH	Br	6	99		594
33	COCH <sub>3</sub>	CH	Br	7	98		588
34	COCH <sub>3</sub>	CH	Br	8	99		594
35	H	N	Br	II	69		414
36	H	N	Br	III	67		402
37	H	N	Br	2	69		414
38	H	N	Br	3	71		426
39	H	N	Br	4	76		456
40	H	N	Br	5	74		444
41	H	N	Br	6	80		480
42	H	N	Br	7	78		468
43	H	N	Br	8	77		462
44	OCH <sub>3</sub>	CH	Cl	II	50		300
45	OCH <sub>3</sub>	CH	Cl	III	57		342
46	OCH <sub>3</sub>	CH	Cl	2	62		372
47	OCH <sub>3</sub>	CH	Cl	3	58		348
48	OCH <sub>3</sub>	CH	Cl	4	60		360
49	OCH <sub>3</sub>	CH	Cl	5	68		408
50	OCH <sub>3</sub>	CH	Cl	6	65		390
51	OCH <sub>3</sub>	CH	Cl	7	70		420
52	OCH <sub>3</sub>	CH	Cl	8	76		456

<sup>a</sup>Conversions were determined by GC-MS based on the aryl halide. Reaction conditions: temperature ramped to 80 °C (3 min) and held for 5<sup>b</sup> min and 10<sup>c</sup> min. Temperature ramped to 120 °C (3 min) and held for 5<sup>d</sup> min and 20<sup>e</sup> min. Temperature ramped to 120 °C (3 min) and held for 10<sup>f</sup> min and 20<sup>g</sup> min without salt (**II**). On preheated oil bath, 10<sup>h</sup> min with thermal heating at 120 °C. <sup>i</sup>Isolated yields. n.d., not detected. TOF = TON/time (h); TON = (% Conversion) × (mol-substrate)/(mol-Catalyst).

The Suzuki-Miyaura coupling yields between phenylboronic acid with phenyl iodide or *p*-iodoanisole were also determined as an isolated yield for comparison purposes with the GC based conversion (Table 2, entries 8, 9, 12-14, 17, 18, and 21-23). The isolated yields for this purpose were determined using procedures similar to those described above for the Heck-Mizoroki reaction.

## Crystal structure determination of **7**

A good-quality single crystal of **7** was mounted with epoxy glue at the tip of glass capillaries for the X-ray diffraction experiments. X-ray measurements for **7** were carried out on a STOE IPDS 2 diffractometer with MoK $\alpha$  ( $\lambda = 0.71073$  Å) radiation at T = 296 K. Lattice parameters were obtained by least-squares fit to the optimized setting angles of the collected reflections by means of X-Area.<sup>38</sup> Data were reduced by using X-RED32<sup>38</sup> software applying integration absorption corrections. The molecular structure of **7** was solved by direct methods using the SIR-97 package<sup>39</sup> and refinements by full-matrix least-squares on F<sup>2</sup> using the SHELXL-97 program.<sup>40</sup> The water H atoms were located from a difference Fourier map and refined with distance restraints of O—H = 0.83(2) Å and H...H = 1.31 (2) Å, and with  $U_{iso}(\text{H}) = 1.5 U_{eq}(\text{O})$ . The other H atoms were positioned geometrically, with C—H = 0.93–0.97 Å, and refined as riding with  $U_{iso}(\text{H}) = 1.2$  or  $1.5 U_{eq}(\text{C})$ . Figures 1 and 2 were drawn by PLATON program.<sup>41</sup> The crystal data, data collection, and refinement details of compound **7** are given in Table 3.

## Results and discussion

In this work, non-symmetric benzimidazolium salts, which are conventional NHC precursors, bearing silicon-containing substituents, **II**, **III**, and **2-8**, were used. These salts were prepared from the treatment of 1-alkylbenzimidazoles (**I** and **1**) with appropriate alkyl halides in refluxing DMF with good yields of 73%–87%. The synthesis of the benzimidazoles (**I**, **II**, **III**, and **1-8**) is summarized in Scheme 1. All benzimidazolium salts synthesized in this work are air- and moisture-stable in the solid state as well as in solution. The new compounds **1-8** were identified by spectroscopic methods and elemental analysis. The NCHN  $\delta[^{13}\text{C}\{^1\text{H}\}]$  signal of the benzimidazolium salts is usually around  $142 \pm 4$  ppm.<sup>22,42</sup> For the benzimidazolium salts **2-8** it was found to be 141.9, 141.6, 141.3, 143.6, 141.8, 141.4, 141.5, and 141.6 ppm, respectively. These values are in good agreement with the previously reported results.<sup>20–22,43</sup> The NCHN protons of the benzimidazolium salts were observed as singlets in the <sup>1</sup>H-NMR spectrum at 9.98, 9.95, 9.59, 9.48, 9.62, 9.48, and 9.80 ppm, respectively. These chemical shift values are typical for NCHN protons of benzimidazolium salts because of their increased acidity.<sup>19–22</sup> In comparison, the corresponding values of the starting materials **I** and **1** are 8.10 and 7.93 ppm, which are significantly smaller than in benzimidazolium salts.

The benzimidazolium salts (**2-8**) show IR absorption bands at 1557, 1558, 1559, 1559, 1559, 1558, and 1557 cm<sup>-1</sup>, respectively, which are assigned to  $\nu(\text{C}=\text{N})$ . These IR absorption values are in good agreement with previously reported values for benzimidazolium salts.<sup>19–21</sup> These values are slightly smaller than expected for a standard  $\nu(\text{C}=\text{N})$  because of the  $\pi$ -electron delocalization on the imidazolium ring.

**Table 3.** The crystal data, data collection, and refinement details of compound **7**.

Empirical Formula	C <sub>19</sub> H <sub>23</sub> N <sub>2</sub> Si.H <sub>2</sub> O.Br
Formula weight	405.40
Temperature (K)	296
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
The number of reflections used to determine the unit cell	30505
Cell parameters (Å, °)	
a	8.8485 (4)
b	24.5969 (14)
c	11.0667 (5)
$\beta$	120.689 (3)
Volume (Å <sup>3</sup> )	2071.29 (19)
Z	4
Absorption coefficient, $\mu(\text{Mo K}\alpha)$ (mm <sup>-1</sup> )	2.05
Crystal size mm <sup>3</sup>	0.17 × 0.21 × 0.33
D <sub>x</sub> (Mg.m <sup>-3</sup> )	1.300
F(000)	840
$\theta_{\text{max}}$ (°)	26.5
Number of reflection measured	22205
Number of unique reflection	4288
Number of observed reflection $I > 2\sigma(I)$	3300
<i>h</i>	-11 → 11
<i>k</i>	-30 → 30
<i>l</i>	-13 → 13
<i>R</i> <sub>int</sub>	0.033
Number of refined parameters	224
Goodness of fit on <i>F</i> <sup>2</sup>	1.08
$R[F^2 > 2\sigma(F^2)]$ , <i>wR</i> <sub>2</sub>	0.052, 0.117
( $\Delta\sigma$ ) <sub>max</sub>	0.001
$\Delta\rho_{\text{max}}$ (e.Å <sup>-3</sup> )	0.62
$\Delta\rho_{\text{min}}$ (e.Å <sup>-3</sup> )	-0.51

## The Heck-Mizoroki coupling reaction

Palladium-catalyzed reactions for the formation of new carbon-carbon bonds are now recognized as essential in the tool box every synthetic chemist.<sup>44</sup> Of the many coupling reactions involving palladium catalysis, the

Heck-Mizoroki reaction, the coupling of aryl halides with terminal olefins, emerged as one of the most widely used transformations from both academic and industrial laboratories.<sup>45</sup>

The in situ generated catalytic system derived from the benzimidazolium salts and Pd(OAc)<sub>2</sub> has been used successfully in a series of carbon-carbon bond formation reactions. We recently reported the optimal reaction conditions for the Heck-Mizoroki coupling reactions including some benzimidazolium or bis-benzimidazolium salts/Pd(OAc)<sub>2</sub> and base as a catalyst system under microwave and conventional heating conditions.<sup>20–22</sup> In the present report, a series of aryl iodide, aryl bromide, aryl chloride, and 2-pyridyl bromide compounds were used for the coupling reaction with styrene. The recently reported optimal parameters for the base and solvent<sup>20</sup> were used to obtain stilbene derivatives, after test reactions to determine optimum reaction time and temperature using phenyl iodide and styrene (Table 1, entries 1-8). Finally, we found that use of the catalytic system consisting of 1% Pd(OAc)<sub>2</sub>, 2% mol of **II-III**, **2-8**, and 2% mol K<sub>2</sub>CO<sub>3</sub> in DMF-H<sub>2</sub>O (1:1) at 120 °C/300 W microwave heating led to the best conversion within 10 min.

It has been observed that no increase in catalytic reaction yield is found by prolonging the reaction time from 10 to 20 min (Table 1, entry 4). Furthermore, no coupling reaction occurred in the absence of **II** within 5 min (Table 1, entry 5) and very low yield was detected within 10 min (Table 1, entry 6). We also tested the catalytic yield using a conventional heating system (i.e. preheated oil bath) after 10 min at 120 °C and a low yield was detected, 10% (Table 1, entry 7). These experiments indicate that benzimidazole salts and microwave heating may play the crucial role in the catalytic system.

A complete list of the results obtained with optimal conditions is given in Table 1. Altogether 5 different aryl halides bearing electron-donating, electron-withdrawing groups and 2-bromopyridine, which is an electron-poor heterocyclic compound, reacted with styrene and gave the coupled products in almost high yield. As expected, the yields of the Heck-Mizoroki coupling reactions with styrene and aryl chlorides were low.

The benzimidazolium salt bearing dimethylphenyl substituents (**4-8**) are generally more effective than the other salts examined. Probably, acting as a Lewis base, the phenyl substituent on the silicon atom of the benzimidazolium salts affects positively the catalytic activity. It is noteworthy that 2-bromopyridine was also tolerated in this system, and the cross-coupling products were obtained in satisfactory yields (Table 1, entries 35-43). The reactivity of the aryl halide component on Heck-Mizoroki coupling reactions decreases in the order I > Br > Cl, which is in good agreement with previous reports.<sup>20,21,46</sup> In many studies, it was reported that the Heck-Mizoroki coupling reaction with aryl chlorides with electron withdrawing substituents did not give detectable amounts of Heck-Mizoroki coupling products in conventional heating systems.<sup>46–48</sup> In contrast, low or moderate yields were obtained for aryl chloride even bearing electron donating methoxy substituent with styrene using the microwave heating system (Table 1, entries 44-52). It is important to note that the end of all these reactions was clearly indicated by black particles in the reaction mixture, which are probably palladium nanoparticles.

## The Suzuki-Miyaura coupling reactions

Nowadays, the Suzuki-Miyaura reaction is one of the key techniques in the construction of molecular skeletons in organic synthesis. The catalytic yield of the coupling is dependent on a variety of parameters such as temperature, solvent, base, and nature of catalyst loading. We recently reported the optimum reaction conditions for the Suzuki-Miyaura/Heck-Mizoroki coupling reaction, including some benzimidazolium or bis-benzimidazolium

salts/Pd(OAc)<sub>2</sub> and base as a catalyst system under microwave and conventional heating conditions.<sup>20–22</sup> The recently reported optimal parameters (except time and temperature)<sup>20</sup> were used to obtain biaryl derivatives, after test reactions for optimization of the reacting time and temperature using phenyl iodide and phenylboronic acid (Table 2, entries 1-8). Finally, we found that use of the catalytic system consisting of 1% Pd(OAc)<sub>2</sub>, 2% mol of **II-III**, **2-8**, and 2% mol K<sub>2</sub>CO<sub>3</sub> in DMF-H<sub>2</sub>O (1:1) at 120 °C/300 W microwave heating led to the best conversion within 10 min.

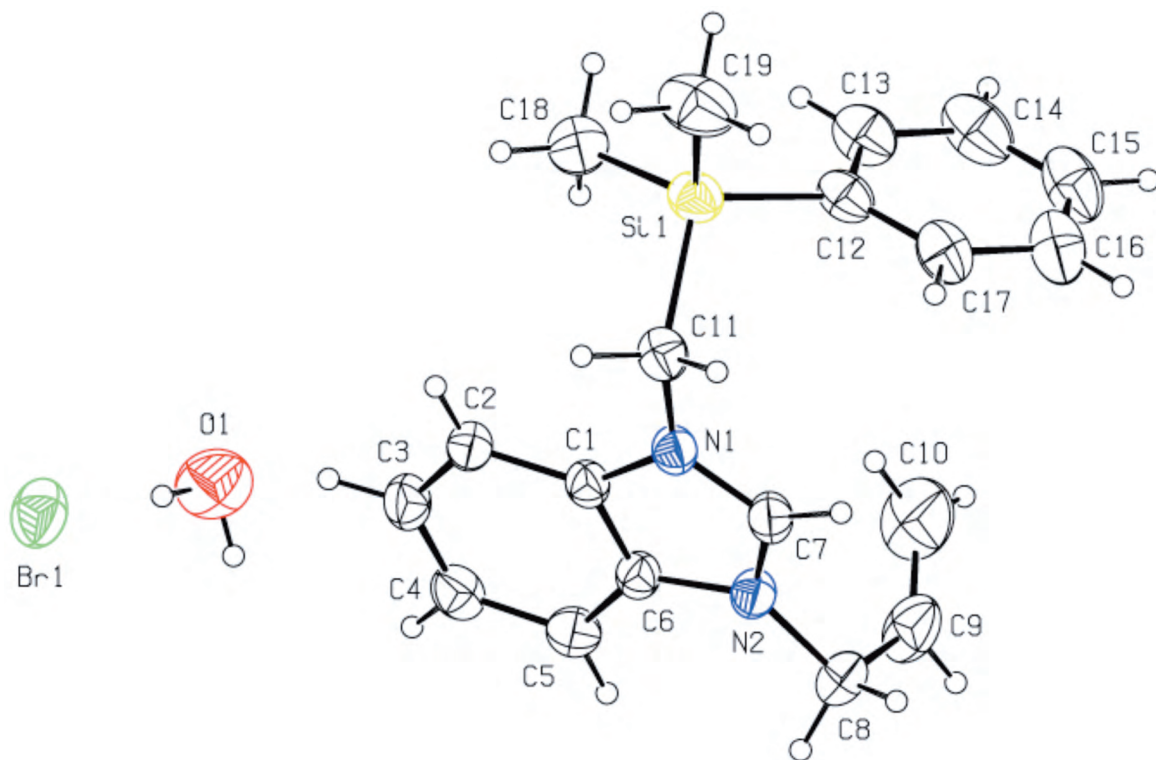
In the present report, a series of aryl iodide, aryl bromide, aryl chloride, and 2-pyridyl bromide were used for coupling partner with phenylboronic acid. The Suzuki-Miyaura cross coupling catalyzed by Pd(OAc)<sub>2</sub>-benzimidazole salt-K<sub>2</sub>CO<sub>3</sub> system is presented in detail (Table 2).

After having established the optimized coupling reaction conditions, the scope of the reaction and efficiencies of the benzimidazolium salts were evaluated by investigating the coupling of the phenylboronic acid with some *p*-substituted aryl halides. Under the optimized conditions, reaction of phenyl iodide, *p*-iodoanisole, and *p*-bromoacetophenone with phenylboronic acid gave almost as high a yield using a catalytic system consisting of 2 mol % benzimidazole salts (**II**, **III**, or **1-8**), 1 mol % Pd(OAc)<sub>2</sub> and 2 equivs K<sub>2</sub>CO<sub>3</sub> in DMF-H<sub>2</sub>O (1:1) at 120 °C by microwave irradiation (300 W) within 10 min. On the other hand, *p*-chloroanisole, which bears a strong electron donating methoxy group, gave a low or moderate yield using the optimized conditions. It is noteworthy that aryl chlorides are arguably the most useful substrates because of their lower cost and the wide range of commercially available compounds.<sup>6</sup> It is also worth noting that the satisfactory coupling products of 2-pyridyl bromide with phenylboronic acid were also obtained under optimized conditions. We also tested the catalytic yields using the conventional heating system in a preheated oil bath for 10 min at 120 °C, but we obtained only 9% yield using benzimidazole salt, **II**, and phenyl iodide optimized conditions (Table 2, entry 7). Control experiments showed that the Suzuki coupling reaction did not occur in the absence of **II** in 10 min (Table 2, entry 5) and very low yield was detected within 20 min (Table 2, entry 6) under microwave heating. A complete list of the results obtained with optimal conditions is given in Table 2. Of the 5 different aryl halides used in the Suzuki-Miyaura coupling with phenylboronic acid, those with electron-withdrawing substituents and aryl iodides were found to give the highest yield (Table 2, entries 1-34). Contrary to expectations, using 2-pyridyl bromide, which has an electron-deficient ring, as a coupling partner reduced the catalytic yield of the Suzuki-Miyaura reaction (Table 2, entries 35-43) As accepted, Suzuki-Miyaura cross-coupling yields of aryl chloride with electron-donating methoxy substituent were lower than those of aryl iodides and aryl bromides (Table 2, entries 44-52). These yields for the aryl chlorides may be acceptable due to their low cost and the challenge to activate the Csp<sup>2</sup>-Cl bond; it has attracted much attention from both the industry and scientific research laboratories to couple aromatic chlorides with arylboronic acids.<sup>42</sup>

The benzimidazolium salt bearing dimethylphenyl substituent on the silicon atoms (**4-8**) are also found to be more effective than other salts examined in Suzuki-Miyaura reactions (Table 2) and the tables indicate that the results for the Suzuki-Miyaura reaction are parallel to the Heck-Mizoroki data in general (Table 1). According to the previously reported results, electron-donating substituent on the nitrogen atoms of the benzimidazole salts may play a crucial role for the better catalytic activity in the catalytic system. It is important to note that, at the end of the all these reactions, palladium black was observed on the wall of the reaction vessel, probably derived from palladium nanoparticles. As can be seen in Table 2, a high C-C coupling product was obtained from the reaction of aryl iodides and aryl bromides with phenylboronic acid as expected.

## X-ray crystallography of **7**

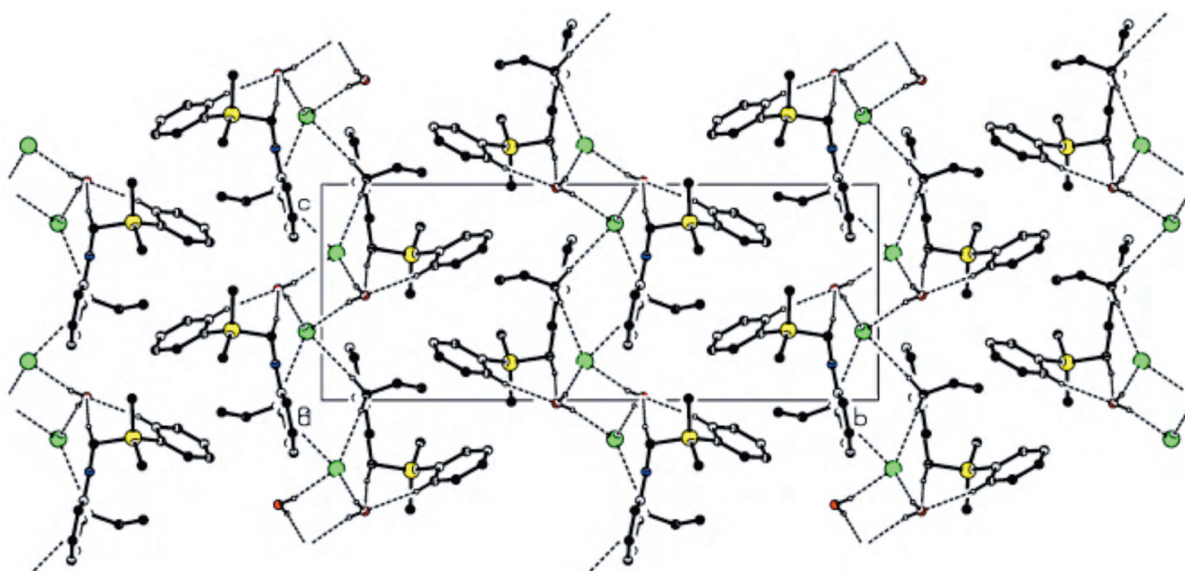
The structure of compound **7** was determined by X-ray diffraction analysis. Compound **7** crystallizes in the monoclinic space group  $P2_1/c$ . The general view and atom numbering scheme for **7** is shown in Figure 1.



**Figure 1.** View of the molecule, showing the atom labeling scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

The benzimidazole ring system (N1/N2/C1–C7) of the title compound (**I**) is almost planar [maximum deviation =  $-0.022(3)$  Å] and makes an angle of  $72.66(16)^\circ$  with the phenyl ring (C12–C17). The bond lengths and bond angles in (**I**) have reasonable values, and they are compatible with those found for similar compounds.<sup>35,36</sup> The angles around the Si atoms with a distorted tetrahedral geometry vary from  $103.84(17)^\circ$  to  $111.7(3)^\circ$ .

O—H...Br, C—H...Br, and C—H...O hydrogen bonds link the molecules (Table 4 and Figure 2). Furthermore,  $\pi - \pi$  stacking interactions are observed between the centroids of the benzene (C1–C6) and imidazole (N1/N2/C1/C6/C7) rings of the benzimidazole ring system [ $Cg1...Cg2(1-x, 1-y, 1-z) = 3.4970(17)$  Å and  $Cg2...Cg2(1-x, 1-y, 1-z) = 3.6740(18)$  Å,  $Cg1$  and  $Cg2$  are the centroids of the imidazole and benzene rings of the benzimidazole ring system, respectively].



**Figure 2.** The packing and hydrogen bonding interactions of (**I**), viewing down the a-axis. All hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

**Table 4.** Hydrogen-bond parameters ( $\text{\AA}$ ,  $^\circ$ ) for **7**.

	$D-H$	$H...A$	$D...A$	$D-H...A$
$O1-HO2...Br1$	0.85 (4)	2.55 (5)	3.385 (4)	169 (5)
$O1-HO1...Br1^i$	0.85 (4)	2.53 (4)	3.366 (5)	171 (4)
$C8-H8A...Br1^{ii}$	0.97	2.92	3.890 (4)	176
$C8-H8B...Br1^{iii}$	0.97	2.92	3.832 (4)	157
$C11-H11A...O1^{iv}$	0.97	2.57	3.471 (6)	155
$C17-H17...O1^{iv}$	0.93	2.54	3.453 (5)	168

Symmetry codes: (i)  $1 - x, 1 - y, 2 - z$ ; (ii)  $1 + x, y, z$ ; (iii)  $1 - x, 1 - y, 1 - z$ ; (iv)  $x, y, -1 + z$ .

## Conclusions

We prepared 1 new 1-substituted benzimidazole (**1**) and 7 non-symmetric 1,3-disubstituted benzimidazolium salts (**2-8**) bearing silicon containing alkyl groups on the 1 nitrogen atom of the azolium ring. The catalytic studies were done using in situ generated systems from  $Pd(OAc)_2$ /benzimidazolium salt and  $K_2CO_3$  for the Heck- Mizoroki and Suzuki-Miyaura cross coupling reactions. The catalyst systems in the Heck-Mizoroki and Suzuki-Miyaura reactions gave better yields under microwave-assisted moderate conditions and very short reaction times compared to those given in the literature.<sup>19,46,47</sup> The Heck-Mizoroki and Suzuki-Miyaura reactions were carried out using 300 W power microwave irradiation at 120  $^\circ C$  in only 10 min. It can be concluded that Heck-Mizoroki and Suzuki-Miyaura coupling reactions may be accelerated by microwave irradiation even using aryl chlorides bearing electron-donating methoxy substituent. In addition, coupling of 2-pyridyl bromide with

both styrene and phenylboronic acid affords corresponding stilbene and biaryl products in satisfactory yields over 10 min, respectively.

## Supporting Information

Supporting information can be found in the online version of this article. CCDC holds the supplementary crystallographic data 827530. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax (+44) 1223-336-033; or email [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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