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# Synthesis of novel benzimidazole salts and microwave-assisted catalytic activity of in situ generated Pd nanoparticles from a catalyst system consisting of benzimidazol salt, $Pd(OAc)_2$, and base in a Suzuki-Miyaura reaction

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**Abstract:** Novel benzimidazolium salts having N-benzyl or N-(4-substitutedbenzyl) groups were synthesized and their microwave-promoted catalytic activity for the Suzuki–Miyaura cross-coupling reaction were determined using in situ formed palladium(0) nanoparticles (PdNPs) from a catalytic system consisting of $Pd(OAc)_2/K2CO_3$ in $DMF/H_2O$. PdNPs were characterized by X-ray diffraction (XRD) pattern and particle size of in situ generated PdNPs from the Pd(111) plane was determined to be of diameter 19.6 nm by the Debye–Scherrer equation. Moreover, the yield of the Suzuki–Miyaura reactions with aryl iodides and aryl bromides was found to be nearly quantitative. The synthesized benzimidazole salts (**1**–**5**) were identified by $^1H$ and $^{13}C$ NMR and IR spectroscopic methods, and micro analysis. The molecular structure of **5** was also determined by X-ray crystallography.

**Key words:** Benzimidazole salt, N-heterocyclic carbenes, palladium nanoparticles, cross-coupling reaction, Suzuki–Miyaura coupling, microwave

## 1. Introduction

The Suzuki–Miyaura reaction is one of the most versatile and utilized reactions for the selective construction of carbon–carbon bonds, in particular for the formation of biaryls.[1−8] Because of the excellent physical and chemical properties of biaryls, they can be used in several organic compound syntheses, such as of monomers for constructing polymers, supramolecular compounds, and natural, pharmaceutical, and agrochemical products.[9,10] Nowadays, the Suzuki–Miyaura reaction plays an important role in organic synthetic chemistry to obtain new generation organic materials with many important properties such as electronic, optical, or mechanical.[9] Therefore, in recent years, much effort has been devoted to develop and improve the reaction conditions. For these purposes, various catalysts or catalytic systems including tertiary phosphines and N-heterocyclic carbenes, solvent, base, and reaction conditions such as temperature and time, and conventional or microwave heating systems have been investigated.[11−20]

Among the catalysts, those having N-heterocyclic carbene ligands have gained enormous popularity due to their potential advantages over tertiary phosphines such as better $\sigma$-donor ability, low toxicity, and

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In memory of Prof Dr Ayhan S Demir

thermal stability.[8,21–24] In particular, Pd(II)-NHC complexes are more attractive as pre-catalysts because of their stability to air, moisture, and heating and they also have excellent long-term storage profiles.[8] $Pd(OAc)_2$/benzimidazole or imidazole ligands could be very effective catalytic systems in these reactions.[17,25]

In recent years, microwave-assisted organic synthesis has been considered a green technology owing to its high reaction rates, purity of products, increased yield, decreased electricity cost, and simplified course of reactions.[26–34] The use of metal catalysis in conjunction with microwave heating may also have significant advantages over traditional heating methods, since the inverted temperature gradients under microwave conditions may provide an increased lifetime of the catalyst through elimination of wall effects.[35]

There are extensive studies about the Suzuki-type C–C cross-coupling reaction incorporating microwave irradiation with high yield in a short time using various ligands other than benzimidazole moiety.[27,29–32,34–36] Recently, we have also investigated the catalytic activity of some in situ prepared N-heterocyclic carbene-Pd complexes for Suzuki–Miyaura cross coupling reactions under microwave heating.[37,38] Since the nature, size, and electronic properties of the substituent on the nitrogen atom(s) of the benzimidazole may play a crucial role in tuning the catalytic activity, to find more efficient palladium catalysts we have synthesized a series of new benzimidazolium halides, **1**–**5** (Scheme), containing benzyl, substituted benzyl, and 3-phenylpropyl moieties, and we aimed to investigate the activity of in situ Pd-carbene based catalytic systems for Suzuki cross-coupling reactions.

Reetz and co-workers were the first to report the use of Pd and Pd/Ni nanoparticles for the Suzuki coupling of aryl bromides and chlorides with phenylboronic acid.[39,40] PdNPs are effective catalysts for chemical transformations due to their large surface area and many research groups have used them as an active catalyst for Suzuki–Miyaura cross-coupling reactions.[16,41–49]

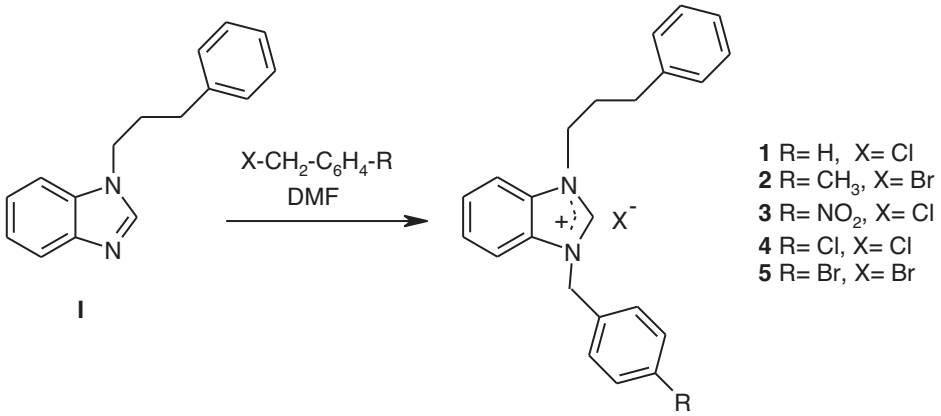
Herein, we report on the microwave-assisted catalytic activity of $Pd(OAc)_2$/benzyl and 3-phenylpropyl substituted benzimidazolium salts and base catalytic system through in situ formed PdNPs in Suzuki cross-coupling reactions. The X-ray structural analysis of compound **5** was also determined to clarify whether there is crystal water in the benzimidazolium compounds, as in our previous work.[50]

## 2. Experimental

All preparations were carried out in an atmosphere of purified argon using standard Schlenk techniques. The starting materials and reagents used in the reactions were supplied commercially by Aldrich or Merck. The solvents were dried by 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 aerobic conditions. $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) spectra were recorded using a Bruker DPX-300 high performance digital FT NMR spectrometer. Infrared spectra were recorded as KBr pellets in the range 4000–400 $cm^{-1}$ on a PerkinElmer FT-IR spectrophotometer. The structural characterization of the samples fabricated was investigated by X-ray diffraction (XRD). An automated Rigaku RadB Dmax X-ray diffractometer having CuK$\alpha$ radiation was used. Scan speed was selected as $2^\circ$ $min^{-1}$ in the range of $2\theta$ = 3–80°.

Elemental analyses were performed by LECO CHNS-932 elemental analyzer. Melting points were recorded using an Electrothermal-9200 melting point apparatus, and are uncorrected.

1-(3-Phenylpropyl)benzimidazole (**I**), used in this work as a starting compound, was prepared by treating benzimidazole and 3-bromopropylbenzene similar to the literature procedure.[51]




**Scheme.** Synthesis pathways of the benzimidazole derivatives.

### 2.1. GC-MS analysis

GC-MS spectra were recorded on an Agilient 6890 N GC and 5973 Mass Selective Detector using an HP-INNOWAX column of 60-m length, 0.25-mm diameter, and 0.25-$\mu$m film thicknesses. GC-MS parameters for both Suzuki and Heck 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 $\mu$L; carrier gas, helium; mass range between m/z 50 and 550.

### 2.2. Synthesis of benzimidazole salts

*Synthesis of 1-benzyl-3-(3-phenylpropyl)benzimidazolium chloride,* **1**

A mixture of 1-(3-phenylpropyl)benzimidazole (**I**) (1.00 g, 4.23 mmol) and benzyl chloride (0.50 mL, 4.34 mmol) in dimethylformamide (5 mL) was refluxed for 4 h. The mixture was then cooled and the volatiles were removed under vacuum. The solid was crystallized from ethanol/diethyl ether (1:1). White crystals of the title compound **1** (1.16 g, 75%) were obtained, mp 96–98 °C; $\upsilon_{max}$/cm$^{-1}$ = 1564 (CN). Anal. found: C 75.37, H 6.30, N 7.20. Calculated for $C_{23}H_{23}N_2Cl$ (362.90): C 76.12, H 6.39, N 7.72. $^1$H NMR ($\delta$, DMSO-$d_6$): 10.26 (s, 1H, NC$\underline{H}$N), 8.13–7.20 (m, 14H, $C_6\underline{H}_4$, $C_6\underline{H}_5$, $CH_2C_6\underline{H}_5$), 5.81 (s, 2H, $C\underline{H}_2C_6H_5$), 4.59 (t, 2H, $C\underline{H}_2CH_2CH_2C_6H_5$, $J$ = 7.2 Hz), 2.73 (t, 2H, $CH_2CH_2C\underline{H}_2C_6H_5$, $J$ = 7.8 Hz), 2.29 (quint, 2H, $CH_2C\underline{H}_2CH_2C_6H_5$, $J$ = 7.5 Hz). $^{13}$C NMR ($\delta$, DMSO-$d_6$): 143.1 (N$\underline{C}$HN), 141.0, 134.6, 131.8, 131.3, 129.4, 129.2, 129.1, 128.8, 128.7, 127.1, 127.0, 126.5, 114.4, and 114.3 ($\underline{C}_6H_4$, $\underline{C}_6H_5$, $CH_2\underline{C}_6H_5$), 50.3 ($\underline{C}H_2C_6H_5$), 47.1 ($\underline{C}H_2CH_2CH_2C_6H_5$), 32.4 ($CH_2CH_2\underline{C}H_2C_6H_5$), 30.4 ($CH_2\underline{C}H_2CH_2C_6H_5$).

### 2.3. General method for the synthesis of compounds 2–5

Equivalent amount of the 1-(3-phenylpropyl)benzimidazole and the appropriate alkyl halide were refluxed in dimethylformamide (5 mL) for 4 h. Then the mixture was cooled to room temperature and the volatiles were removed under reduced pressure. The residue was crystallized from ethanol/diethyl ether (1:1).

*1-(4-Methylbenzyl)-3-(3-phenylpropyl)benzimidazolium bromide,* **2.**

Yield, 1.64 g (white crystals), 92%; mp 207–208 °C; $\upsilon_{max}$/cm$^{-1}$ = 1565 (CN). Anal. found: C 68.27, H 6.09, N 6.49. Calculated for $C_{24}H_{25}N_2Br$ (421.37): C 68.41, H 5.98, N 6.65. $^1$H NMR ($\delta$, DMSO-$d_6$):

10.06 (s, 1H, NC$\underline{H}$N), 8.14–7.16 (m, 13H, $C_6\underline{H}_4$, $C_6\underline{H}_5$, $CH_2C_6\underline{H}_4CH_3$), 5.73 (s, 2H, $C\underline{H}_2C_6H_4CH_3$), 4.58 (t, 2H, $C\underline{H}_2CH_2CH_2C_6H_5$, $J$ = 7.2 Hz), 2.73 (t, 2H, $CH_2CH_2C\underline{H}_2C_6H_5$, $J$ = 7.8 Hz), 2.31 (quint, 2H, $CH_2C\underline{H}_2CH_2C_6H_5$, $J$ = 7.5 Hz), 2.29 (s, 3H, $CH_2C_6H_4C\underline{H}_3$). $^{13}$C NMR ($\delta$, DMSO-$d_6$): 142.8 (N$\underline{C}$HN), 141.0, 138.6, 131.8, 131.5, 131.3, 129.9, 128.8, 128.7, 127.1, 127.0, 126.5, and 114.4 ($\underline{C}_6H_4$, $\underline{C}_6H_5$, $CH_2\underline{C}_6H_4CH_3$), 50.2 ($\underline{C}H_2C_6H_4CH_3$), 47.1 ($\underline{C}H_2CH_2CH_2C_6H_5$), 32.4 ($CH_2CH_2\underline{C}H_2C_6H_5$), 30.5 ($CH_2\underline{C}H_2CH_2C_6H_5$), 21.2 ($CH_2C_6H_4\underline{C}H_3$).

*1-(4-Nitrobenzyl)-3-(3-phenylpropyl)benzimidazolium chloride,* **3.**

Yield, 1.53 g (yellow crystals), 88%; mp 154–156 °C; $\upsilon_{max}$/cm$^{-1}$ = 1557 (CN). Anal. found: C 67.12, H 5.57, N 10.01. Calculated for $C_{23}H_{22}N_3O_2Cl$ (407.89): C 67.73, H 5.44, N 10.30. $^1$H NMR ($\delta$, $CDCl_3$): 12.20 (s, 1H, NC$\underline{H}$N), 8.25–7.19 (m, 13H, $C_6\underline{H}_4$, $C_6\underline{H}_5$, $CH_2C_6\underline{H}_4NO_2$), 6.16 (s, 2H, $C\underline{H}_2C_6H_4NO_2$), 4.59 (t, 2H, $C\underline{H}_2CH_2CH_2C_6H_5$, $J$ = 7.5 Hz), 2.86 (t, 2H, $CH_2CH_2C\underline{H}_2C_6H_5$, $J$ = 7.2 Hz), 2.51 (quint, 2H, $CH_2C\underline{H}_2CH_2C_6H_5$, $J$ = 7.5 Hz). $^{13}$C NMR ($\delta$, $CDCl_3$): 148.3 (N$\underline{C}$HN), 144.2, 139.8, 139.3, 131.3 131.0, 129.5, 128.7, 128.4, 127.5, 127.4, 126.6, 124.5, 113.3, and 113.2 ($\underline{C}_6H_4$, $\underline{C}_6H_5$, $CH_2\underline{C}_6H_4NO_2$), 50.2 ($\underline{C}H_2C_6H_4NO_2$), 47.2 ($\underline{C}H_2CH_2CH_2C_6H_5$), 32.6 ($CH_2CH_2\underline{C}H_2C_6H_5$), 30.2 ($CH_2\underline{C}H_2CH_2C_6H_5$).

*1-(4-Chlorobenzyl-3-(3-phenylpropyl)benzimidazolium chloride,* **4.**

Yield, 1.41 g (white crystals), 84%; mp 142–143 °C; $\upsilon_{max}$/cm$^{-1}$ = 1559 (CN). Anal. found: C 68.93, H 5.73, N 6.80. Calculated for $C_{23}H_{22}N_2Cl_2$ (397.34): C 69.52, H 5.58, N 7.05. $^1$H NMR ($\delta$, $CDCl_3$): 12.00 (s, 1H, NC$\underline{H}$N), 7.54–7.16 (m, 13H, $C_6\underline{H}_4$, $C_6\underline{H}_5$, $CH_2C_6\underline{H}_4Cl$), 5.91 (s, 2H, $C\underline{H}_2C_6H_4Cl$), 4.59 (t, 2H, $C\underline{H}_2CH_2CH_2C_6H_5$, $J$ = 7.5 Hz), 2.82 (t, 2H, $CH_2CH_2C\underline{H}_2C_6H_5$, $J$ = 7.2 Hz), 2.46 (quint, 2H, $CH_2C\underline{H}_2CH_2C_6H_5$, $J$ = 7.5 Hz). $^{13}$C NMR ($\delta$, $CDCl_3$): 143.8 (N$\underline{C}$HN), 139.5, 135.2, 131.5, 131.3, 131.0, 129.9, 129.5, 128.6, 128.4, 127.2, 127.1, 126.5, 113.7, and 113.0 ($\underline{C}_6H_4$, $\underline{C}_6H_5$, $CH_2\underline{C}_6H_4Cl$), 50.6 ($\underline{C}H_2C_6H_4Cl$), 47.0 ($\underline{C}H_2CH_2CH_2C_6H_5$), 32.5 ($CH_2CH_2\underline{C}H_2C_6H_5$), 30.3 ($CH_2\underline{C}H_2CH_2C_6H_5$).

*1-(4-Bromobenzyl)-3-(3-phenylpropyl)benzimidazolium bromide,* **5.**

Yield, 1.42 g (white crystals), 69%; mp 196–197 °C; $\upsilon_{max}$/cm$^{-1}$ = 1563 (CN). Anal. found: C 56.27, H 4.40, N 5.67. Calculated for $C_{23}H_{22}N_2Br_2$ (486.24): C 56.81, H 4.56, N 5.76. $^1$H NMR ($\delta$, DMSO-$d_6$): 10.08 (s, 1H, NC$\underline{H}$N), 8.14–7.16 (m, 13H, $C_6\underline{H}_4$, $C_6\underline{H}_5$, $CH_2C_6\underline{H}_4Br$), 5.78 (s, 2H, $C\underline{H}_2C_6H_4Br$), 4.58 (t, 2H, $C\underline{H}_2CH_2CH_2C_6H_5$, $J$ = 7.2 Hz), 2.74 (t, 2H, $CH_2CH_2C\underline{H}_2C_6H_5$, $J$ = 7.8 Hz), 2.29 (quint, 2H, $CH_2C\underline{H}_2CH_2C_6H_5$, $J$ = 7.5 Hz). $^{13}$C NMR ($\delta$, DMSO-$d_6$): 143.1 (N$\underline{C}$HN), 141.0, 133.9, 132.3, 131.8, 131.2, 131.1, 128.8, 128.7, 127.2, 127.1, 126.5, 122.5, 114.4, and 114.3 ($\underline{C}_6H_4$, $\underline{C}_6H_5$, $CH_2\underline{C}_6H_4Br$), 49.6 ($\underline{C}H_2C_6H_4Br$), 47.1 ($\underline{C}H_2CH_2CH_2C_6H_5$), 32.4 ($CH_2CH_2\underline{C}H_2C_6H_5$), 30.4 ($CH_2\underline{C}H_2CH_2C_6H_5$).

### 2.4. Single-crystal X-ray diffraction analysis of 1-(4-bromobenzyl)-3-(3-phenylpropyl)benzimidazolium bromide (5)

The X-ray data were collected at 296(2) K on a STOE IPDS II diffractometer with Mo$K_\alpha$ radiation. Data collection, cell refinement, and data reduction were performed with X-AREA and XRED32.[52] Crystal structures were solved by direct methods using the SIR97 structure solution program and refined on $F^2$ by full matrix least-square methods on $F^2$ using the SHELXL97 program.[53,54]

All H atoms were positioned geometrically with C—H = 0.93-0.97 Å, and refined using a riding model with $U_{iso}$(H) = 1.2$U_{eq}$(C). A summary of the crystal data, experimental details, and refinement results for **5**

is given in Table 1. The molecular structure of **5** in Figure 1 was drawn with ORTEP-3.[55] The relevant bond lengths and bond angles are listed in Table 2.

**Table 1.** The crystal data, data collection, and refinement values of compound **5**.

| | |
|---|---|
| *Crystal data* | |
| $C_{23}H_{22}BrN_2.Br$ | $Z = 2$ |
| $M_r = 486.23$ | $D_x = 1.542$ Mg m$^{-3}$ |
| Triclinic, $P$-1 | $\alpha = 103.098$ (5)° |
| $a = 8.6978$ (5) Å | $\beta = 99.602$ (5)° |
| $b = 9.0916$ (5) Å | $\gamma = 105.739$ (5)° |
| $c = 14.5678$ (9) Å | $V = 1047.43$ (12) Å$^3$ |
| Mo $K\alpha$ radiation | $\mu = 3.88$ mm$^{-1}$ |
| $T = 296$ (2) K | Crystal shape and color: block, colorless |
| *Data collection* | |
| STOE IPDS 2 diffractometer | $R_{int} = 0.118$ |
| $\omega$ scans | $\theta_{max} = 26.5°$ |
| Absorption correction:integration | $h = -10 \rightarrow 10$ |
| $T_{min} = 0.106$, $T_{max} = 0.196$ | $k = -11 \rightarrow 11$ |
| 14,941 measured reflections | $l = -18 \rightarrow 18$ |
| 4337 independent reflections<br>3690 reflection with $I > 2\sigma(I)$ | |
| *Refinement* | |
| Refinement on $F^2$ | Calculated weights |
| $R[F^2 > 2\sigma(F^2)] = 0.048$ | $w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 0.5155P]$ |
| $wR(F^2) = 0.094$ | $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.09$ | $(\Delta/\sigma)_{max} < 0.0001$ |
| 4337 reflections | $\Delta\rho_{max} = 0.80$ e Å$^{-1}$ |
| 244 parameters | $\Delta\rho_{min} = -0.41$ e Å$^{-1}$ |
| H atoms constrained to parent site | Extinction correction: none |

**Table 2.** Selected bond lengths (Å), bond angles (°).

| | | | |
|---|---|---|---|
| Br1—C12 | 1.903 (3) | N2—C6 | 1.396 (4) |
| N1—C1 | 1.389 (4) | N2—C7 | 1.321 (4) |
| N1—C7 | 1.336 (4) | N2—C15 | 1.464 (4) |
| N1—C8 | 1.469 (4) | | |
| | | | |
| C1—N1—C7 | 108.4 (2) | N2—C6—C1 | 107.1 (2) |
| C1—N1—C8 | 126.4 (2) | N2—C6—C5 | 130.9 (2) |
| C7—N1—C8 | 125.0 (3) | N1—C7—N2 | 110.4 (2) |
| C6—N2—C7 | 108.0 (2) | N1—C8—C9 | 113.1 (2) |
| C6—N2—C15 | 124.3 (3) | Br1—C12—C11 | 119.0 (2) |
| C7—N2—C15 | 127.8 (3) | Br1—C12—C13 | 119.5 (3) |
| N1—C1—C2 | 132.2 (3) | N2—C15—C16 | 114.4 (3) |
| N1—C1—C6 | 106.2 (2) | | |

### 2.5. General procedure for the Suzuki–Miyaura reactions

$Pd(OAc)_2$ (1 mmol%), benzimidazolium halides (**1**–**5**) (2 mmol %), aryl halide (1 mmol), phenylboronic acid (1.2 mmol), $K_2CO_3$ (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. Temperature was ramped up to reach 120 °C in 3 min. At the end of the reaction, the mixture was cooled, and the product was extracted with ethyl acetate/*n*-hexane (1:5) and chromatographed on a silica gel column. The purity of coupling products was checked by NMR and GC-MS, and yields are based on aryl halide. The coupling products were confirmed by increasing the peaks on gas chromatograms and mass values from MS spectra. All coupling products were also isolated and characterized by $^1$H NMR or MS before the serial catalytic work up each time.

The Suzuki–Miyaura coupling yields between phenylboronic acid and 4-iodotoluene or 4–methylanisole were also determined as an isolated yield for comparison purposes with the GC-based yields. The isolated yields were determined as follows. At the end of the Suzuki–Miyaura coupling reaction, the mixture was cooled to room temperature and 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 4-methylbiphenyl or 4-methoxybiphenyl product as a pale white solid, which was characterized by comparison of NMR data with those in the literature. The palladium nanoparticles were obtained as follows. After separating the Suzuki–Miyaura coupling product at the end of the catalytic reaction, the residue including black palladium nanoparticles was washed 3 times with water and then ethanol to obtain pure palladium nanoparticles. The PdNPs were tested for the Suzuki–Miyaura coupling reaction at the optimized conditions after drying.

## 3. Results and discussion

1-(3-Phenylpropyl)benzimidazole (**I**) was synthesized from benzimidazole, 3-bromopropylbenzene, and KOH in refluxing EtOH in good yield of 86%. The molecular structure of compound **5** was confirmed by single crystal X-ray diffraction to clarify whether there is crystal water in the benzimidazolium compounds. Its molecular structure is depicted in Figure 1.

Benzimidazolium salts containing aryl alkyl moieties, **1**–**5**, were prepared by treatments of 1-(3-phenylpropyl)benzimidazole with appropriate benzyl halides in refluxing DMF with good yields of 69%–92%. The synthesis of the benzimidazolium salts **1**–**5** is summarized in the Scheme. The benzimidazolium salts are air- and moisture-stable both in the solid state and in solution. The new benzimidazole derivatives (**1**–**5**) were characterized by $^1$H NMR, $^{13}$C NMR, IR, and elemental analysis techniques, which support the proposed structures.

The value of $\delta[^{13}\mathrm{C}\{^1\mathrm{H}\}]$, N*C*HN in benzimidazolium salts is usually around 142 ± 4.[37] For benzimidazolium salts **1**–**5** it was found to be 143.1, 142.8, 148.3, 143.8, and 143.1 ppm, respectively. These values are in good agreement with the previously reported results.[17,38] The NC*H*N proton signals for the benzimidazolium salts were observed as singlets at 10.26, 10.06, 12.20, 12.00, and 10.08 ppm, respectively. As expected, the highest shifts to downfield of the NC*H*N proton signals were observed where bearing strong electron withdrawing nitro substituent on the phenyl ring. These chemical shift values are also typical for NC*H*N protons of benzimidazolium salts for increasing the acidity of the NC*H*N proton.[37,38]

The carbon–nitrogen band frequencies, $\nu_{(C=N)}$ for benzimidazole salts **1**–**5** were observed at 1564, 1565, 1557, 1559, and 1563 cm$^{-1}$, respectively. Similar to the $^{13}$C NMR and $^1$H NMR results, the highest red shift was observed for compound **3** due to its having a strong electron withdrawing nitro substituent on the phenyl ring.

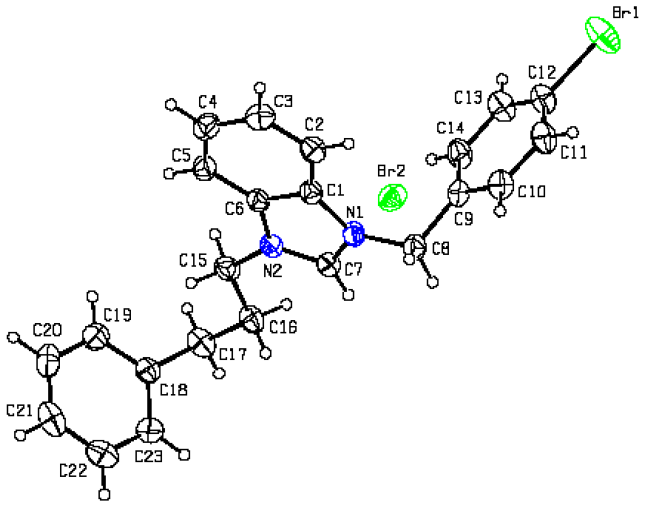


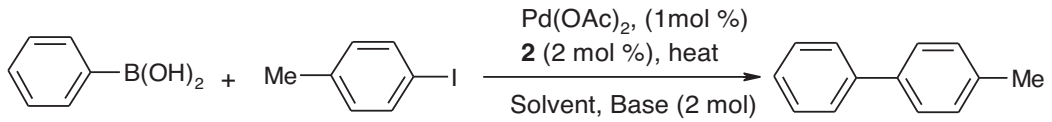

**Figure 1.** View of the title molecule **(5)**, showing the atom labeling scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

In order to find the optimum reaction conditions for the Suzuki coupling reaction, a series of experiments was performed with catalysis by *p*-iodotoluene and phenylboronic acid as model compounds. The test reactions were performed using different bases such as $Cs_2CO_3$, $K_2CO_3$, and DBU (1,8-diazabicyclo[5.4.0]undec-7-en) and different solvents such as DMF/$H_2O$, EtOH/$H_2O$, $H_2O$, $C_2H_4(OH)_2$/$H_2O$, and glycerine/$H_2O$ for 5, 10, 60, and 90 min at 60 °C, 80 °C, 100 °C, and 120 °C. It was found that the Suzuki coupling reaction catalyzed by **2**, $Pb(OAc)_2$, and the base catalyst system gave the highest yield when using DMF/$H_2O$ mixture as a solvent and $Cs_2CO_3$ or $K_2CO_3$ as a base at 120 °C microwave heating for 10 min. A considerable increase in the catalytic reactions' yield was not observed when prolonging the time from 5 to 30 min. After these results, we chose $K_2CO_3$ as a base as it is cheaper than $Cs_2CO_3$, and water/DMF as a solvent. We also tested the catalytic yields using a conventional heating system in a preheated oil bath over 5, 10, 30, 60, and 90 min at different temperatures. The test experiment results for optimization of the Suzuki–Miyaura coupling reaction are given in Table 3.

After having established the optimized coupling reaction conditions (Table 3) the scope of the reaction and efficiencies of the benzimidazolium salts were evaluated by investigating the coupling of the phenylboronic acid with various *p*-substituted aryl halides. Under the optimized conditions, reaction of *p*-bromoacetophenone, methyl *p*-bromobenzoate, *p*-iodoanisole, and *p*-iodotoluene with phenylboronic acid gave almost as high a yield as using a catalytic system consisting of 2 mol % benzimidazole salts (**1**–**5**), 1 mol % $Pd(OAc)_2$, and 2 equivs $K_2CO_3$ in DMF-$H_2O$ (1:1) at 120 °C by microwave irradiation (300 W) over 10 min. On the other hand, bearing strong electron donating group on the aryl chlorides such as methoxy, weak electron donating methyl, and medium electron withdrawing formyl group gave a moderate or good 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.[6] We also tested the catalytic yields using a conventional heating system in a preheated oil bath for 5, 10, and 30 min at 120 °C, but we obtained only 8%, 11%, and 61% yields, respectively, using benzimidazole salt, **2**, and *p*-iodotoluene in optimized conditions (Table 3, entries 6–8). Çetinkaya et al. also reported that a similar catalytic system containing some benzimidazolium salts

needed a longer reaction time (3–6 h) for the Suzuki coupling reaction under thermal conditions.[17,50] Control experiments showed that the yield of the Suzuki coupling reaction was decreased in the absence of **2** over 10 min under microwave heating (Table 4, entry 1). The results obtained from optimum conditions for the Suzuki reactions are given in Table 4. Of the 5 different aryl halides used in the Suzuki coupling with phenylboronic acid, those with electron-withdrawing substituents were found to give the highest yield (Table 4, entries 11–20).

**Table 3.** Test experiments for optimization of the Suzuki–Miyaura coupling reactions.



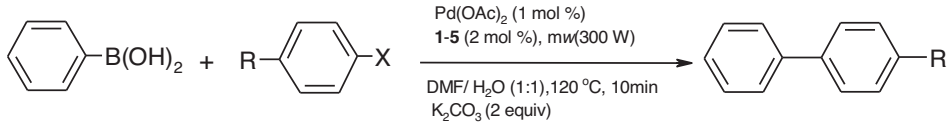

| Entry | Base | Solvent | Time (min) | Thermal heating | | | Microwave heating | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | °C | Yield,%; TOF($h^{-1}$) | | °C (300W) | Conv.[a],%; TOF($h^{-1}$) | | |
| 1 | $K_2CO_3$ | DMF/$H_2O$ | 5 | 60 | 00 | 00 | 60 | 67 | 402 | |
| 2 | $K_2CO_3$ | DMF/$H_2O$ | 5 | 80 | 03 | 18 | 80 | 73 | 438 | |
| 3 | $K_2CO_3$ | DMF/$H_2O$ | 10 | 80 | 15 | 90 | 80 | 82 | 492 | |
| 4 | $K_2CO_3$ | DMF/$H_2O$ | 60 | 100 | 68 | 408 | n.t. | | - | |
| 5 | $K_2CO_3$ | DMF/$H_2O$ | 90 | 100 | 87 | 522 | n.t. | | - | |
| 6 | $K_2CO_3$ | DMF/$H_2O$ | 5 | 120 | 08 | 48 | 120 | 90 88* | 540 | 528* |
| 7 | $K_2CO_3$ | DMF/$H_2O$ | 10 | 120 | 11 | 66 | 120 | 99 96* | 594 | 576* |
| 8 | $K_2CO_3$ | DMF/$H_2O$ | 30 | 120 | 61 | 366 | 120 | 99 96* | 594 | 576* |
| 9 | $Cs_2CO_3$ | DMF/$H_2O$ | 10 | | | | 120 | 99 | 594 | |
| 10 | $Cs_2CO_3$ | EtOH/$H_2O$ | 10 | | | | 120 | 76 | 556 | |
| 11 | $K_2CO_3$ | $H_2O$ | 10 | | | | 120 | 42 | 252 | |
| 12 | $K_2CO_3$ | $C_2H_4(OH)_2/H_2O$ | 10 | | | | 120 | 78 | 468 | |
| 13 | DBU | DMF/$H_2O$ | 10 | | | | 120 | 91 | 546 | |
| 14 | DBU | EtOH/$H_2O$ | 10 | | | | 120 | 89 | 534 | |
| 15 | $K_2CO_3$ | Glycerine/$H_2O$ | 10 | | | | 120 | 65 | 390 | |

[a]Conversions were determined by GC-MS based on the aryl halide. n.t.: not tested. *Isolated yield.

Benzimidazole salt bearing a strong electron-withdrawing nitro substituent at the benzyl group, **3**, is found the least effective of the salts examined in Suzuki coupling reactions (Table 4, entries 3, 8, 13, 18, 23, 28, and 32). On the other hand, benzimidazole salt **2**, which bears an electron-donating methyl group at the para-position of the N-benzyl group, is the most effective for the catalytic activity in the Suzuki coupling reactions among them. Similar catalytic results to ours for the Suzuki cross-coupling reactions have also been reported in the literature using the catalytic system consisting of palladium compound, base, and various benzimidazolium or imidazolium salts.[12,13,17,56,57]

Similar to our previous results, the endpoint of all these reactions was clearly observed black particles in the reaction mixture, which probably derived from palladium nanoparticles. These nanoparticles may act as a catalyst themselves or as a reservoir of Pd(0) molecular species, which would be the active catalysts. These nanoparticles generated from in situ formed Pd-NHC are probably more active than Pd(0) complexes.[58] With the aim of proving the catalytic role of the Pd nanoparticles, we also tested in situ formed palladium(0) nanoparticles at the optimized conditions for Suzuki cross-coupling reactions. As can be seen in Table 2 [entries 2 (TOF = 582 $h^{-1}$) and 22 (TOF = 462 $h^{-1}$)], PdNPs were an efficient catalyst at optimized conditions under microwave heating. The comparison of our results with the previous related studies[16,42–44,48,49] showed that the present study has some advantages, in particular short reaction times, better TOF values, and moderate reaction conditions.

**Table 4.** The Suzuki–Miyaura cross-coupling reactions of aryl halides with phenylboronic acid.




| Entry | R | X | Salt | Yield (%) | TOF ($h^{-1}$) |
|---|---|---|---|---|---|
| | | | | | |
| 1 | $CH_3$ | I | No | 48 | 288 |
| 2[b] | $CH_3$ | I | PdNPs | 97 | 582 |
| 3 | $CH_3$ | I | 1 | 99 95* | 594 570* |
| 4 | $CH_3$ | I | 3 | 96 89* | 576 534* |
| 5 | $CH_3$ | I | 4 | 98 83* | 588 498* |
| 6 | $CH_3$ | I | 5 | 99 89* | 594 534* |
| 7 | $OCH_3$ | I | 1 | 99 87* | 594 522* |
| 8 | $OCH_3$ | I | 2 | 99 96* | 594 576* |
| 9 | $OCH_3$ | I | 3 | 96 92* | 576 552* |
| 10 | $OCH_3$ | I | 4 | 97 90* | 582 540* |
| 11 | $OCH_3$ | I | 5 | 99 96* | 594 576* |
| 12 | $COCH_3$ | Br | 1 | 99 | 594 |
| 13 | $COCH_3$ | Br | 2 | 99 | 594 |
| 14 | $COCH_3$ | Br | 3 | 98 | 588 |
| 15 | $COCH_3$ | Br | 4 | 98 | 588 |
| 16 | $COCH_3$ | Br | 5 | 99 | 594 |
| 17 | $COOCH_3$ | Br | 1 | 99 | 594 |
| 18 | $COOCH_3$ | Br | 2 | 99 | 594 |
| 19 | $COOCH_3$ | Br | 3 | 97 | 582 |
| 20 | $COOCH_3$ | Br | 4 | 98 | 588 |
| 21 | $COOCH_3$ | Br | 5 | 99 | 594 |
| 22[c] | $CH_3$ | Cl | PNPs | 77 | 462 |
| 23 | $CH_3$ | Cl | 1 | 76 | 456 |
| 24 | $CH_3$ | Cl | 2 | 84 | 504 |
| 25 | $CH_3$ | Cl | 3 | 71 | 426 |
| 26 | $CH_3$ | Cl | 4 | 72 | 432 |
| 27 | $CH_3$ | Cl | 5 | 82 | 492 |
| 28 | $OCH_3$ | Cl | 1 | 77 | 462 |
| 29 | $OCH_3$ | Cl | 2 | 79 | 474 |
| 30 | $OCH_3$ | Cl | 3 | 68 | 408 |
| 31 | $OCH_3$ | Cl | 4 | 70 | 420 |
| 32 | $OCH_3$ | Cl | 5 | 74 | 444 |
| 33 | CHO | Cl | 1 | 81 | 486 |
| 34 | CHO | Cl | 2 | 85 | 510 |
| 35 | CHO | Cl | 3 | 76 | 456 |
| 36 | CHO | Cl | 4 | 73 | 438 |
| 37 | CHO | Cl | 5 | 79 | 474 |

Yields are based on the aryl halide. Reactions were monitored by GC-MS. Conditions: temperature ramped to 120 °C (3 min) and held for 10 min). * Isolated yields.
[b,c] Palladium(0) nanoparticles were used as catalyst. TOF = TON/time (h); TON = (Yield %) × (mol-substrate)/(mol-catalyst).

Figure 2 shows powder XRD diffraction patterns obtained for the in situ formed palladium(0) nanoparticles. According to XRD diffraction, the Pd nanoparticles have Fm-3m face centered cubic structure, and the crystal parameters using the Jade program according to the Rietveld-refinement method were calculated as a = b = c = 3.889 Å. The strong diffraction peaks at the Bragg angles of 40.2°, 46.7°, and 68.2° correspond to the 111, 200, and 220 facets of elemental palladium.[16,59] The particle size of the corresponding facets 111, 200, and 220 of elemental palladium were determined as 19.6, 15.5, and 19.6 nm (18.2 ± 2.4 nm) by using the Debye–Scherrer equation [d = (0.94. $\lambda_{CuK\alpha}$)/(FWHM.Cos$\theta$)], respectively. These values were also found experimentally as 19.3, 15.1, and 19.1 nm (17.8 ± 2.4 nm) from the XRD report, respectively.

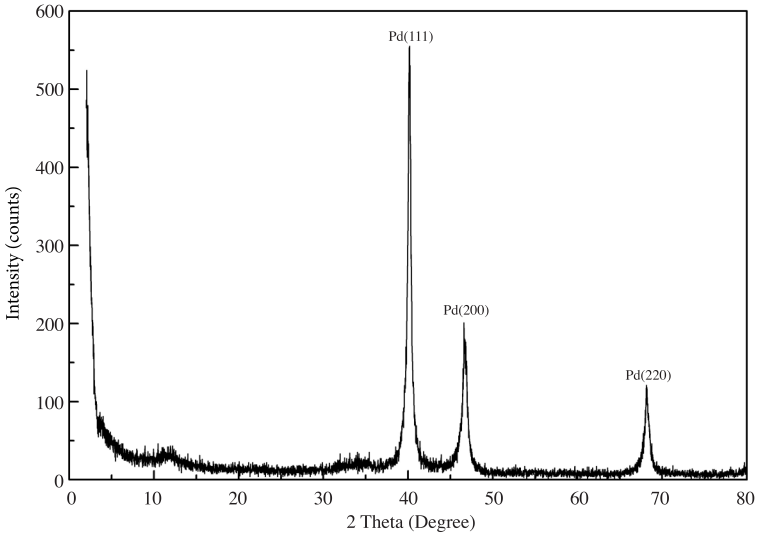



**Figure 2.** Powder XRD pattern of in situ formed palladium (0) nanoparticules showing the facets of the palladium.

### 3.1. Molecular structure of 5

The title compound, $C_{23}H_{22}BrN_2$.Br, crystallizes in the triclinic P-1 space group. All geometric parameters are comparable with results obtained from previous studies on related benzimidazole derivatives.[60,61] The

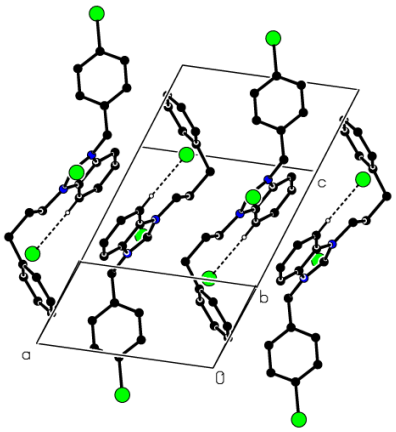



**Figure 3.** Packing view of **5** in the unit cell. Hydrogen bonds are indicated as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

benzimidazole ring (N1/N2/C1-C7) is planar with maximum deviation from planarity of 0.026(3) and 0.028(3) Å for atoms N1 and C4, respectively. The dihedral angles between the rings A(N1/N2/C1-C7), B(C9-C14), and C(C18-C23) are A/B = 86.08(13)°, A/C = 80.63(15)°, and B/C = 71.49(17)°. The crystal structure of **5** is stabilized by intermolecular C — H ··· Br interactions (Table 4; Figure 3). Furthermore, a C—H... $\pi$ interaction was found in the crystal structure (Table 5).

**Table 5.** Hydrogen-bond parameters (Å, °).

| | *D*—H | H...*A* | D...A | *D*—H...*A* |
|---|---|---|---|---|
| C5—H5...Br2$^{i}$ | 0.93 | 2.79 | 3.711 (3) | 171 |
| C7—H7...Br2$^{ii}$ | 0.93 | 2.68 | 3.488 (3) | 145 |
| C17—17B...Cg3$^{ii}$ | 0.97 | 2.75 | 3.691 (4) | 164 |

Symmetry codes: (i) 1 – x, 1 – y, 1 – z. (ii) 1 – x, 1 – y, 1 – z. Cg3 is the centroid of the C9-C14 benzene ring.

## 4. Conclusions

We prepared some new benzimidazole salts containing benzyl, *p*-substituted benzyl, and 3-phenylpropyl moieties (**1**–**5**). The use of the palladium catalyst system including the benzimidazolium salts in the Suzuki coupling reaction gave better yield under microwave-assisted conditions in short reaction times than thermal heating conditions and the yields of the reactions were increased even using aryl chlorides. In situ formed PdNPs (18.2 ± 2.4 nm) also showed good catalytic activity in the Suzuki–Miyaura cross coupling reactions under the optimized conditions.

## 5. Supporting information

CCDC holds the supplementary crystallographic data CCDC 838509. 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 e-mail deposit@ccdc.cam.ac.uk.

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## References

1. Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749–1758.
2. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.
3. Yan, J.; Zhou, Z.; Zhu, M. *Tetrahedron Lett.* **2005**, *46*, 8173–8175.
4. Alonso, F.; Beletskaya, I. P.; Yus, M. *Tetrahedron* **2008**, *64*, 3047–3101.
5. Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133–173.
6. Tudose, A.; Delaude, L.; Andre, B.; Demonceau, A. *Tetrahedron Lett.* **2006**, *47*, 8529–8533.
7. Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem. Int. Ed.* **2009**, *48*, 9792–9826.
8. Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem. Int. Ed.* **2007**, *46*, 2768–2813.

9. Suzuki, A. *ChemComm.* **2005**, 4759–4763.
10. Hajipour, A. R.; Karami, K.; Tavakoli, G. *Appl. Organomet. Chem.* **2011**, *25*, 567–576.
11. Dawood, K. M. *Tetrahedron* **2007**, *63*, 9642–9651.
12. Linninger, C. S.; Herdtweck, E.; Hoffmann, S. D.; Herrmann, W. A. *J. Mol. Struct.* **2008**, *890*, 192–197.
13. Singh, R.; Viciu, M. S.; Kramareva, N.; Navarro, O.; Nolan, S. P. *Org. Lett.* **2005**, *7*, 1829–1832.
14. Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440–1449.
15. Hahn, F. E.; Jahnke, M. C.; Pape, T. *Organometallics* **2006**, *25*, 5927–5936.
16. Durap, F.; Metin, Ö.; Aydemir, M.; Özkar, S. *Appl. Organomet. Chem.* **2009**, *24*, 498–503.
17. Gök, Y.; Gürbüz, N.; Özdemir, İ.; Çetinkaya, B.; Çetinkaya, E. *Appl. Organomet. Chem.* **2005**; *19*, 870–874.
18. Şireci, N.; Yılmaz, Ü.; Küçükbay, H. *Asian J. Chem.* **2010**, *22*, 7153–7158.
19. Chanthavong, F.; Leadbeater, N. E. *Tetrahedron Lett.* **2006**, *47*, 1909–1912.
20. Kappe, C. O.; *Angew. Chem. Int. Ed.* **2004**, *43*, 6250–6284.
21. Hahn, F. E.; Jahnke, M. C. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172.
22. Küçükbay, H.; Çetinkaya, B.; Guesmi, S.; Dixneuf, P. H. *Organometallics* **1996,** *5*, 2434–2439.
23. Mercan, D.; Çetinkaya, E.; Çetinkaya, B. *J. Organomet. Chem.* **2011**, *696*, 1359–1366.
24. Nolan, S. P. *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH: Weinheim, 2006.
25. Özdemir, İ.; Demir, S.; Yaşar, S.; Çetinkaya, B. *Appl. Organomet. Chem.* **2005**, *19*, 55–58.
26. Loupy, A. *Microwaves in Organic Synthesis*, 2nd ed., Wiley-VCH: Weinheim, 2006.
27. Prokopvova, H.; Ramirez, J.; Fernandez, E.; Kappe, C. O. *Tetrahedron Lett.* **2008**, 49, 4831–4835.
28. Glasnov, T. N.; Findenig, S.; Kappe, C.O. *Chem. Eur. J.* **2009**, *15*, 1001–1010.
29. Leadbeater, N. E.; Marco, M. *Org. Lett.* **2002**, *4*, 2973–2976.
30. Avery, K. B.; Devine, W. G.; Kormos, C. M.; Leadbeater, N. E. *Tetrahedron Lett.* **2009**, *50*, 2851–2853.
31. Arvela, R. K.; Leadbeater, N. E. *Org. Lett.* **2005**, *7*, 2101–2104.
32. Trejos, A.; Fardost, A.; Yahiaoui, S.; Larhed, M. *Chem. Commun.* **2009**, 7587–7589.
33. Lindh, J.; Enquist, P-A.; Pilotti, Å.; Nilsson, P.; Larhed, M. *J. Org. Chem.* **2007**, *72*, 7957–7962.
34. Zhou, Z-G.; Shi, J-C.; Hu, Q-S.; Xie, Y-R.; Du, Z-Y.; Zhang, S-Y. *Appl. Organomet. Chem.* **2011**, *25*, 616–619.
35. Singh, B. K.; Kaval, N.; Tomar, S.; Van der Eycken, E.; Parmar, V. S. *Org. Process Res. Dev.* **2008**, *12*, 468–474.
36. Appukkuttan, P.; Van der Eycken, E. *Eur. J. Org. Chem.* **2008**, 1133–1155.
37. Yılmaz, Ü.; Şireci, N.; Deniz, S.; Küçükbay, H. *Appl. Organomet. Chem.* **2010**, *24*, 414–420.
38. Yılmaz, Ü.; Küçükbay, H.; Şireci, N.; Akkurt, M.; Günal, S.; Durmaz, R.; Tahir, M. N. *Appl. Organomet. Chem.* **2011**, *25*, 366–373.
39. Balanta, A.; Godard, C.; Claver, C. *Chem. Soc. Rev.* **2011**, *40*, 4973–4985.
40. Reetz, M. T.; Breinbauer, R.; Wanninger, K. *Tetrahedron Lett.* **1996**, *37*, 4499–4502.
41. Astruc, D. *Inorg. Chem.* **2007**, *46*, 1884–1894.
42. Sawoo, S.; Srimani, D.; Dutta, P.; Lahiri, R.; Sarkar, A. *Tetrahedron,* **2009**, *65*, 4367–4374.
43. Mao, P.; Yang, L.; Xiao, Y.; Yuan, J.; Liu, X.; Song, M. *J. Organomet. Chem.* **2012**, *705*, 39–43.
44. Zawartka, W.; Gniewek, A.; Trzeciak, A. M.; Ziolkowsski, J. J.; Pernak, J. *J. Mol. Catal. A: Chem.* **2009**, *304*, 8–15.
45. Borkowski, T.; Trzeciak, A. M.; Bukowski, W.; Bukowska, A.; Tylus, W.; Kepinski, L. *Appl. Catal. A: Gen.* **2010**, *378*, 83–89.

46. Metin, Ö.; Durap, F.; Aydemir, M.; Özkar, S. *J. Mol. Catal. A: Chem.* **2011**, *337*, 39–44.
47. Li, Y.; Hong, X. M.; Collard, D. M.; El-Sayed, M. A. *Org. Lett.* **2000**, *2*, 2385–2388.
48. Ellis, P. J.; Fairlamb, I. J. A.; Hackett, S. F. J.; Wilson, K.; Lee, A. F. *Angew. Chem. Int. Ed.* **2010**, *49*, 1820–1824.
49. Martins, D. L.; Alvarez, H. M.; Aguiar, L. C. S. *Tetrahedron Lett.* **2010**, *51*, 6814–6817.
50. Yu, Y.; Hu, T.; Chen, X.; Xu, K.; Zhang, J.; Huang, J. *Chem. Commun.* **2011**, *47*, 3592–3594.
51. Magdesieva, T. V.; Nikitin, O. M.; Levitsky, O. A.; Zinovyeva, V. A.; Bezverkhyy, I.; Zolotukhina, E. V.; Vorotyntsev, M. A. *J. Mol. Catal. A.* **2012**, 353–354, 50–57.
52. Akkurt, M.; Yıldırım, Ö. S.; Şireci, N.; Küçükbay, H.; Büyükgüngör, O. *Acta Cryst.* **2008,** *E64*, o2136–o2137.
53. Pozharskii, A. F.; Simanov, A. M. *J. Gen. Chem. USSR,* **1963**, *33*, 172.
54. Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.
55. Altomare, A.; Burla, M.C.; Camalli, M.; Cascarano, G.L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.G.G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 339–340.
56. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122.
57. Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565–566.
58. Özdemir, İ.; Şahin, N.; Gök, Y.; Demir, S.; Çetinkaya, B. *J. Mol. Catal. A.* **2005**, *234*, 181–185.
59. Huang, W.; Guo, E. P.; Xiao, Y. J.; Zhu, M. F.; Zou, G.; Tang, J. *Tetrahedron* **2005**, *61*, 9783–790.
60. Illa, O.; Rodriguez-Garcia, C.; Acosta-Silva, C.; Favier, I.; Picurelli, D.; Oliva, A.; Gomez, M.; Branchadell, V.; Ortuno, R. M. *Organometallics* **2007**, *26*, 3306–3314.
61. Sun, Z.; Cheng, F.; Dai, X. *J. Autom Method. Manag.* **2009**, Art. ID 496281, doi: 10.1155/2009/496281, 1–5.
62. Türktekin, S.; Akkurt, M.; Orhan, E.; Küçükbay, F. Z.; Küçükbay, H.; Büyükgüngör, O. *Acta Cryst.* **2004**, *E60*, m1220–m1222.
63. Akkurt, M.; Öztürk, S.; Şireci, N.; Küçükbay, H.; Büyükgüngör, O. *Acta Cryst.* **2004**, *E60*, o1185–o1187.