

# Polyaniline supported palladium catalyzed Suzuki–Miyaura cross-coupling of bromo- and chloroarenes in water<sup>☆</sup>

M. Lakshmi Kantam,<sup>a,\*</sup> Moumita Roy,<sup>a</sup> Sarabindu Roy,<sup>a</sup> B. Sreedhar,<sup>a</sup>  
S. Sakunthala Madhavendra,<sup>a</sup> B. M. Choudary<sup>b</sup> and Rajib Lal De<sup>c</sup>

<sup>a</sup>*Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India*

<sup>b</sup>*Ogene Systems (I) Pvt. Ltd, #11-6-56, GSR Estates, Hyderabad 500037, India*

<sup>c</sup>*Department of Chemistry, Jadavpur University, Kolkata 700032, India*

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**Abstract**—Polyaniline supported palladium catalysts were prepared from different palladium precursors and all the catalysts are well characterized using ICP-AES, FTIR, TGA–DTA, SEM-EDX and XPS analysis. All the catalysts were tested for Suzuki–Miyaura coupling of bromo- and chloroarenes in water and the catalyst prepared from PdCl<sub>2</sub> precursor was found to be the most effective catalyst. The catalyst can easily be recovered by simple filtration and reused for several cycles with almost consistent activity.

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## 1. Introduction

Organic reactions in aqueous medium have been the subject of considerable attention in terms of achieving more environmentally friendly synthetic transformations.<sup>1</sup> Palladium catalyzed Suzuki–Miyaura<sup>2</sup> cross-coupling reaction is one of the most important tools in modern organic synthesis for the formation of symmetrical and unsymmetrical biaryl compounds, which are the key components of many natural products as well as in the field of engineering materials, such as conducting polymers, molecular wires and liquid crystals.<sup>3</sup> Most of the catalytic systems for Suzuki–Miyaura coupling, which are combination of palladium salts with various ligands such as phosphines, *N*-heterocyclic carbenes, etc. operate with high efficiency only in organic or in a mixture of water and organic solvents.<sup>4</sup> So there is still scope for the development by which inexpensive and readily available chloroarenes can be activated without using any ancillary ligand and more importantly, which allows water as reaction media. Bedford et al. first showed that Pd(OAc)<sub>2</sub> without any ligand can be used to catalyze Suzuki–Miyaura coupling of chloroarenes in tetrabutylammonium bromide (TBAB) using water as an additive.<sup>5</sup>

As the system is homogeneous in nature, it precludes the recovery of precious palladium. So it is highly desirable to

develop a reusable catalytic system for Suzuki–Miyaura coupling of haloarenes in aqueous medium. Baleizao et al. reported the effective immobilization of an oxime–carbapalladacycle complex onto a silica matrix and used it as a reusable heterogeneous catalyst for Suzuki–Miyaura coupling of chloroarenes in water.<sup>6</sup> Recently Lysen and Kohler reported palladium on activated carbon as a recyclable catalyst for Suzuki–Miyaura coupling of aryl chlorides in water.<sup>7</sup> Earlier, we reported layered double hydroxides supported nanopalladium catalysts for Suzuki–Miyaura coupling of chloroarenes in dioxane–water<sup>8a</sup> and later nanocrystalline magnesium oxide supported palladium catalyzed Suzuki–Miyaura coupling of iodo- and bromoarenes in water.<sup>8b</sup>

Polyaniline (PANI) is one of the most widely studied conducting polymers for electronic and optical applications<sup>9</sup> due to its environmental stability and interesting redox properties but only a few reports are available using not well characterized PANI supported metal catalysts.<sup>10</sup> We conceived the use of interactive PANI prompted by its highly conducting and redox properties as a support that holds metal complexes securely during catalytic reactions. Further its easy preparative protocol from non-expensive starting material (aniline), controllable doping levels through an acid doping/base dedoping process, inert nature and non-solubility in most of the organic solvents and water are essential qualities for using it as support in heterogeneous catalysis. We have already reported our preliminary investigation on polyaniline supported palladium catalyzed Suzuki–Miyaura reaction of iodo- and bromoarenes in organic solvents.<sup>11</sup> Herein we wish to report a detailed study involving the

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\* Corresponding author. Tel.: +91 40 27193510; fax: +91 40 27160921; e-mail: mlakshmi@iict.res.in

polyaniline supported palladium (PANI–Pd) catalysts prepared from different palladium precursors for the activation of chloroarenes in water.

## 2. Results and discussion

### 2.1. Characterization of PANI–Pd catalysts

We have prepared four types of polyaniline supported palladium catalysts namely PA–Pd1, PA–Pd2, PA–Pd3 and PA–Pd4 using acetonitrile solution of different palladium precursors i.e., Pd(OAc)<sub>2</sub>, PdCl<sub>2</sub>(PhCN)<sub>2</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and PdCl<sub>2</sub>, respectively. All the catalysts prepared were well characterized by ICP–AES, FTIR, TGA–DTA, SEM–EDX and XPS analysis. ICP–AES technique was used to determine the palladium loading in the respective catalysts and the results are summarized in Table 1. It is observed that when the palladium source is coordinated to acetonitrile then better loading occurred. It can be proposed that the reactions between PANI and Pd<sup>2+</sup> complexes present in the solutions involve the ligand exchange as it is known that acetonitrile molecules coordinating to the metal ions can be easily replaced by other ligands.<sup>12</sup> Here most probably PANI replaced the ligands i.e., CH<sub>3</sub>CN, PhCN and PPh<sub>3</sub>. As PPh<sub>3</sub> is strongly bonded to Pd a very small loading was observed.

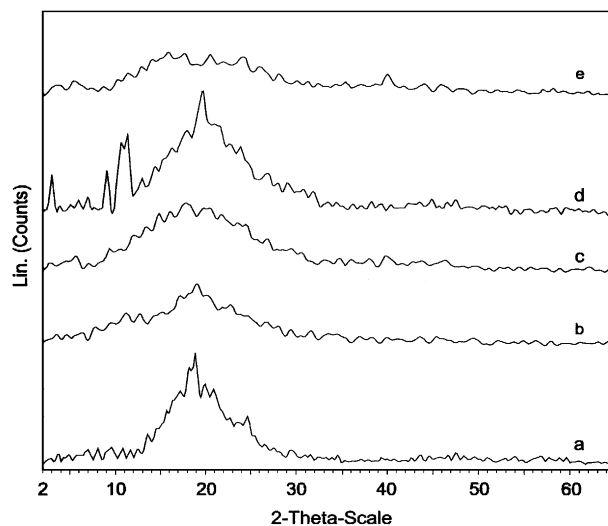
The most important bands in the FTIR spectrum of PANI are located at 1584, 1494, 1376, 1308, 1163 and 830 cm<sup>-1</sup> (see Supplementary data). They are due to the stretching vibrations of quinoid ( $\nu_{C=N} + \nu_{C=C}$ ) and benzenoid ( $\nu_{C=C}$ ) units of the polymer, deformations of the C–N bond, stretching vibrations of the C–N bond, in plane deformations of CH bonds present in the aromatic rings of the undoped polymer and the out of plane deformations of CH bonds in 1,4-substituted aromatic ring, respectively.<sup>13</sup> Upon incorporation of Pd<sup>2+</sup> ions into PANI in all the catalysts no shifts in the quinoid or benzenoid ring band positions have been observed, which is in accord with earlier studies.<sup>12a</sup>

All the PA–Pd catalysts were subjected to TGA–DTA analysis (see Supplementary data). As in PA–Pd1 the presence of acetate moiety was not detected by FTIR analysis due to interference by PANI backbone but the TGA–DTA analysis appears to be fruitful. Almost near identical endotherms were observed in the TGA–DTA of PA–Pd1 and Pd(OAc)<sub>2</sub> at 260–270 °C, which confirm the presence of acetate moiety in PA–Pd1. PA–Pd2 did not show any endotherms or weight loss in the TGA–DTA for PhCN but PA–Pd3 showed a minor weight loss for PPh<sub>3</sub>, which indicates that PPh<sub>3</sub> being a strong ligand was not completely exchanged by PANI or some adsorbed precursor (i.e., PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>) was there, which was not completely removed by washing. Scanning electron microscopic

**Table 1.** Loading of palladium in different polyaniline–palladium catalysts

Entry	Catalyst	Palladium precursor	Loading (mmol/g)	Efficiency of Pd loading <sup>a</sup> (%)
1	PA–Pd1	Pd(OAc) <sub>2</sub>	0.43	21.5
2	PA–Pd2	PdCl <sub>2</sub> (PhCN) <sub>2</sub>	0.34	17
3	PA–Pd3	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	0.076	3.8
4	PA–Pd4	PdCl <sub>2</sub>	0.51	25.5

<sup>a</sup> (Pd bounded with PANI/total Pd charged) × 100.

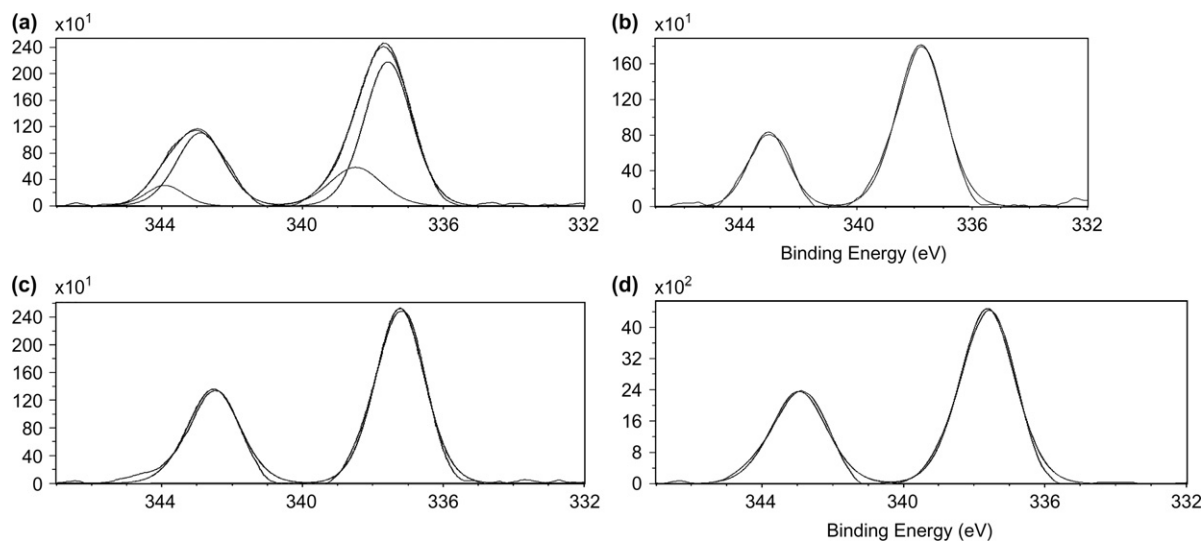


**Figure 1.** XRD patterns of: (a) PANI, (b) PA–Pd1, (c) PA–Pd2, (d) PA–Pd3 and (e) PA–Pd4.

images of PANI and PANI supported palladium catalysts did not show any appreciable differences (SI-Fig. S3). Powdered X-ray diffraction of PANI and PANI supported palladium catalysts show almost similar amorphous nature (Fig. 1). XPS data of PANI supported palladium catalysts (Fig. 2) are summarized in Table 2. In all the catalysts, palladium is present in +2 oxidation state, Pd(II).<sup>14</sup> The observed binding energy peaks of Cl 2p<sub>3/2</sub> at 197.8 eV and Cl 2p<sub>1/2</sub> at 199 eV clearly indicate the presence of Cl in PA–Pd2 and PA–Pd4 catalysts (please see Supplementary data). XPS analysis of PA–Pd3 showed the signal for ‘P’ but the intensity was very low, which is in agreement with the TGA–DTA analysis.

### 2.2. Suzuki–Miyaura coupling of bromo- and chloroarenes

Initially we tried the Suzuki–Miyaura coupling of 4-bromoanisole with phenylboronic acid in 1,4-dioxane at 100 °C using Cs<sub>2</sub>CO<sub>3</sub> base in the presence of PA–Pd1 (2 mol %). We got an excellent yield of corresponding biaryl (95%) with a very little amount (<2%) of biphenyl (homo-coupled product from phenylboronic acid) within 6 h. Then we changed the solvent system to pure water and under identical conditions we attained the cross-coupled product in 89% yield after 2 h. When we replaced Cs<sub>2</sub>CO<sub>3</sub> with K<sub>2</sub>CO<sub>3</sub>, reaction was complete within 70 min giving 98% of the product. K<sub>3</sub>PO<sub>4</sub> and KF were also found to be fairly active under these conditions (95% and 94% product within 3 h, respectively). But organic bases like Et<sub>3</sub>N and Bu<sub>3</sub>N were found to be less active. Then we compared the catalytic activity of PANI supported different palladium catalysts in the Suzuki–Miyaura coupling of 4-bromoanisole and phenylboronic acid in water under the optimized conditions and the results are summarized in Table 3. It was found that the activity order of the catalysts is PA–Pd4 > PA–Pd2 > PA–Pd1 > PA–Pd3. Next, several bromoarenes were examined in Suzuki–Miyaura coupling using PA–Pd4 catalyst to explore the scope and limitation of the present catalytic protocol (Scheme 1) and the results are summarized in Table 4. It was found that the catalyst was compatible to several



**Figure 2.** XPS narrow scan survey for Pd 3d in: (a) PA–Pd1, (b) PA–Pd2, (c) PA–Pd3 and (d) PA–Pd4.

**Table 2.** XPS analysis results of all the polyaniline supported palladium catalysts

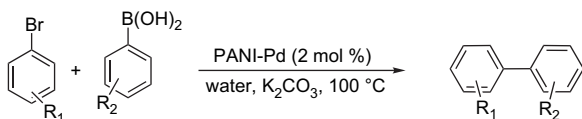
Entry	Catalyst	Binding energy (eV)		
		Pd 3d <sub>3/2</sub>	Pd 3d <sub>5/2</sub>	N 1s
1	PANI	—	—	398; 399.4; 400.2
2	PA–Pd1	338.03	343	398.5; 399.4; 400.3
3	PA–Pd2	337.78	343.06	398.48; 399.72
4	PA–Pd3	337.24	342.54	398.44; 399.63
5.	PA–Pd4	337.64	342.96	398.40; 399.30

**Table 3.** Comparison of catalytic activity of polyaniline supported different palladium catalysts in Suzuki–Miyaura reaction of 4-bromoanisole and phenylboronic acid in water<sup>a</sup>

Entry	Catalyst	Yield <sup>b</sup> (%)
1	PA–Pd1	67
2	PA–Pd2	87
3	PA–Pd3	80
4	PA–Pd4	92

<sup>a</sup> Reaction conditions: 4-bromoanisole (1 mmol), phenylboronic acid (1.2 mmol), catalyst (2 mol %), K<sub>2</sub>CO<sub>3</sub> (3 mmol), water (3 mL), 100 °C, reaction time 60 min.

<sup>b</sup> GC yield using tridecane as an internal standard.



**Scheme 1.**

functionalities like CHO, CN, NO<sub>2</sub>, etc. Bromoarenes with electron-withdrawing functionalities reacted at a faster rate than the bromoarenes-bearing electron-donating functionalities, which is in agreement with earlier studies. On the other hand arylboronic acids with electron-withdrawing group required longer duration than the arylboronic acids with electron-donating group. Sterically hindered arylboronides as well as arylboronic acids reacted sluggishly. When we reduced the catalyst loading to 0.5 mol % and to 0.1 mol % then also we got excellent yield albeit with longer duration

(Table 4, entries 5–7). Table 5 shows the effect of palladium loading in the coupling of 4-bromoanisole and phenylboronic acid. From Table 5, it can be seen that near identical activities are observed irrespective of the loading levels of palladium in the PA–Pd4 catalyst, in the range of 0.035–0.51 mmol/g, while maintaining the concentration of palladium in the reaction at 2 mol %.

The rate accelerating effect observed in water needs some clarifications. When we monitored the reaction between phenylboronic acid and 4-bromoanisole in water and in 1,4-dioxane at 100 °C in the presence of K<sub>2</sub>CO<sub>3</sub> using PA–Pd4, we found the induction period to be 3 min and 25 min in water and 1,4-dioxane, respectively (Fig. 3). We envisioned that the long induction period observed in organic solvent compared to water is correlated to the reduction time of Pd(II) to Pd(0). To confirm this hypothesis we examined the used catalyst by XPS from each of the reaction. It was observed that in aqueous medium Pd(II) in the catalyst was completely reduced to Pd(0) (as Pd 3d<sub>5/2</sub> signal shifted from 337.64 eV to 335 eV) only after 5 min of reaction whereas for the reduction in dioxane it required 30 min (see Supplementary data). This clearly indicates that Pd(0) is the actual catalyst. It was also observed that boronic acid and base were needed for the reduction of palladium(II). In addition to this, may be some other factors such as less solubility of inorganic base in dioxane than water are also responsible for the better activity of the catalyst in water. As Pd(0) was formed before the initiation of the reaction, we prepared a catalyst PA–Pd5 from Pd<sub>2</sub>(dba)<sub>3</sub> (Pd: 0.18 mmol/g) and it was tested in the Suzuki–Miyaura coupling of 4-bromoanisole and phenylboronic acid (Table 4, entries 17 and 18).

It was observed that the activity of PA–Pd5 was much lower than PA–Pd4. When PA–Pd5 was analyzed by XPS for Pd, it was observed that all Pd was present as Pd(II) instead of Pd(0) (see Supplementary data). Most probably during catalyst preparation Pd(0) was oxidized by exposure to air.

Next we turned our attention towards the activation of chloroarenes in aqueous medium. First we tested 4-chloroacetophenone with phenylboronic acid under identical conditions and

**Table 4.** Suzuki–Miyaura coupling of bromoarenes in water<sup>a</sup>

Entry	Bromoarene	Boronic acids	Time (min)	Yield (%)
1	C <sub>6</sub> H <sub>5</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	60	95 (92) [1]
2	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	25	97 (95) [2]
3	4-CH <sub>3</sub> CO-C <sub>6</sub> H <sub>4</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	30	96 (93) [3]
4	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	70	95 (92) [4]
5	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	70	98 (95) [5]
6 <sup>b</sup>	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	120	95 [5]
7 <sup>c</sup>	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	480	92 [5]
8	2-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	90	98 (94) [6]
9	4-CHO-C <sub>6</sub> H <sub>4</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	45	99 (95) [7]
10	4-CN-C <sub>6</sub> H <sub>4</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	30	99 (93) [8]
11	C <sub>6</sub> H <sub>5</sub> -Br	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>	45	95 [5]
12	C <sub>6</sub> H <sub>5</sub> -Br	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>	45	97 [4]
13	C <sub>6</sub> H <sub>5</sub> -Br	2-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>	80	92 [6]
14	C <sub>6</sub> H <sub>5</sub> -Br	4-CH <sub>3</sub> CO-C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>	80	95 [3]
15	C <sub>6</sub> H <sub>5</sub> -Br	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>	90	95 (90) [9]
16 <sup>c</sup>	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -Br	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>	50	(92) [10]
17 <sup>d</sup>	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	60	48 [5]
18 <sup>d</sup>	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -Br	C <sub>6</sub> H <sub>5</sub> -B(OH) <sub>2</sub>	140	96 [5]

<sup>a</sup> Reaction conditions: bromoarene (1 mmol), arylboronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (3 mmol), PA–Pd4 (2 mol %), water (3 mL), 100 °C, under N<sub>2</sub>. GC yield using tridecane as an internal standard and in parenthesis isolated is yield given.

<sup>b</sup> Catalyst of 0.5 mol % was used.

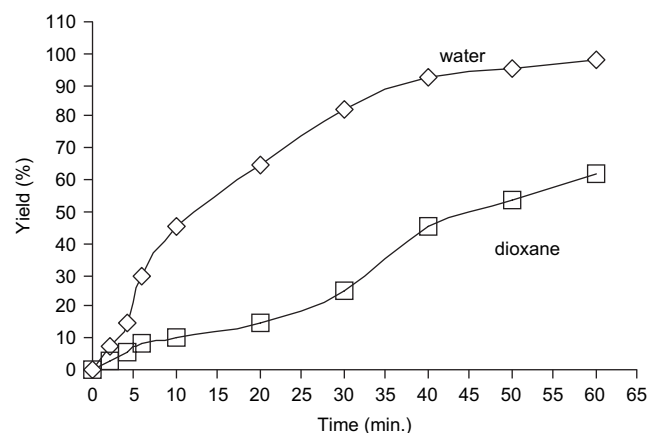
<sup>c</sup> Catalyst of 0.1 mol % was used.

<sup>d</sup> PA–Pd5 of 2 mol % was used.

**Table 5.** Effect of Pd concentration in PA–Pd4 on the Suzuki–Miyaura coupling of 4-bromoanisole and phenylboronic acid<sup>a</sup>

Entry	Loading of Pd (mmol g <sup>-1</sup> )	Yield (%)
1	0.51	95
2	0.23	96
3	0.12	95
4	0.035	95

<sup>a</sup> Reaction conditions: 4-bromoanisole (1 mmol), phenylboronic acid (1.2 mmol), catalyst (2 mol %), K<sub>2</sub>CO<sub>3</sub> (2 mmol), water (3 mL), 100 °C, 70 min, N<sub>2</sub>.

**Figure 3.** Comparison of catalytic activity of PA–Pd4 in Suzuki coupling of 4-bromoanisole and phenylboronic acid in water and dioxane solvent.

we could observe about 25% product formation after 24 h. Then by considering the rate enhancing effect of TBAB in palladium catalyzed Suzuki–Miyaura reaction,<sup>4h,i,1,5</sup> we added 10% TBAB and got 55% yield in 24 h. Then by optimizing the amount of TBAB, we found that 50% TBAB is sufficient to drive the reaction towards completion within 12 h. Several other chloroarenes were reacted under identical conditions and the results are summarized in Table 6. Several other boronic acids were also tested to widen the scope of our catalyst (Table 7). It was observed that the boronic acid containing electron-

**Table 6.** Suzuki–Miyaura reaction of chloroarenes with phenylboronic acid in water using PA–Pd4 catalyst<sup>a</sup>

Entry	Chloroarene	Time (h)	Yield (%)
1	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -Cl	12	94 (90) [2]
2	4-CH <sub>3</sub> CO-C <sub>6</sub> H <sub>4</sub> -Cl	12	93, 25 <sup>b</sup> , 92 <sup>c</sup> [3]
3	4-CN-C <sub>6</sub> H <sub>4</sub> -Cl	12	88 [8]
4	4-CHO-C <sub>6</sub> H <sub>4</sub> -Cl	18	86 [7]
5	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -Cl	24	62 (58) [5]
6	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -Cl	24	64 (57) [4]
7	2-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -Cl	24	17 [6]
8	2,6-CH <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> -Cl	24	No reaction

<sup>a</sup> Reaction conditions: Chloroarene (1 mmol), phenylboronic acid (1.2 mmol), TBAB (0.5 mmol), K<sub>2</sub>CO<sub>3</sub> (3 mmol), PA–Pd4 (2 mol %), water (3 mL), 100 °C, under N<sub>2</sub>. GC yields using tridecane as an internal standard and in parenthesis isolated yield is given.

<sup>b</sup> Without TBAB.

<sup>c</sup> Yield after fifth cycle.

**Table 7.** Suzuki–Miyaura coupling of 4-CH<sub>3</sub>CO-C<sub>6</sub>H<sub>4</sub>-Cl with different arylboronic acids in water using PA–Pd4 catalyst<sup>a</sup>

Entry	Arylboronic acid	Time (h)	Yield (%)
1	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>	20	92 [11]
2	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>	12	93 [12]
3	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>	10	94 [13]
4	4-F-C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>	18	90 [14]
5	2-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>	24	88 [15]
6	<i>trans</i> -2-Phenylvinylboronic acid	15	90 [16]

<sup>a</sup> Reaction conditions: chloroarene (1 mmol), arylboronic acid (1.2 mmol), catalyst (2 mol %), TBAB (0.5 mmol), water (3 mL), 100 °C, under N<sub>2</sub>, isolated yield.

withdrawing group reacted for a longer duration (Table 7, entries 1 and 4). Sterically hindered boronic acid also reacted sluggishly (Table 7, entry 5).

### 2.3. Reusability and leaching test

For every supported catalyst it is important to know the reusability of the catalyst. The polyaniline supported palladium catalysts can easily be recovered from the reaction mixture by simple filtration and reused in the second run

after washing with water followed by acetone and air drying. To study the reusability of the polyaniline–palladium catalysts we have chosen PA–Pd4 as the model catalyst as it was found to be the most effective among all the catalysts prepared. PA–Pd4 was employed in the coupling of 4-chloroacetophenone with phenylboronic acid. The catalyst was used for five consecutive cycles (Table 6, entry 2). The difference in palladium content between the fresh and used catalyst was ca. 2% (fresh: 0.5100 mmol/g; used after fifth cycle: 0.4998 mmol/g). Next to know whether the reaction takes place on the solid surface or with palladium dissolved from the catalyst,<sup>15</sup> we conducted a reaction between 4-bromoanisole and phenylboronic acid using 2 mol % PA–Pd4 in water at 100 °C and the reaction was terminated at 42% conversion. The catalyst was separated by hot filtration and the filtrate was stirred under reaction condition for an additional 10 h. The conversion remained same. When the filtrate was tested for palladium by ICP-AES technique, no palladium was detected. According to Lipshutz et al.<sup>16</sup> a significant amount of supported palladium metal can be dissolved during the reaction and could be redeposit quickly on the solid during the filtration as a result of unavoidable minor temperature difference during the filtration. It may be assumed in this case that also during filtration the solid matrix can trap palladium species dissolved from the catalyst during the reaction. The ‘three-phase’ test developed by Rebek et al.<sup>17</sup> is used to detect the presence of catalytically active homogeneous metal species, in which one of the substrate is anchored on a solid different from the catalyst and can only react if a soluble, catalytic palladium source is present. If the substrate, which is immobilized, causes leaching of the pre-catalyst, it is necessary to add a soluble component as well.<sup>18</sup> To check the metal leaching, we have prepared modified silica functionalized with *p*-bromobenzamide and conducted a Suzuki–Miyaura coupling reaction of 4-bromoanisole and phenylboronic acid using PA–Pd4 in the presence of silica-bound BrPhCONH (Scheme 2). After the complete consumption of 4-bromoanisole, the solid was filtered, washed and air-dried. The filtrate was analyzed after usual workup and 92% of 4-methoxybiphenyl was obtained from the coupling of two soluble reagents. Then the solid (silica-bound reagent and catalyst) was treated with an aqueous solution of NaOH at 100 °C for 24 h. Afterwards the solution was filtered and the filtrate was acidified and extracted with ether. Then the ether layer was analyzed by using GC and GC–MS, and 4-bromobenzoic acid and 4-phenylbenzoic acid were obtained in a 3:1 ratio. These studies clearly prove that during reaction some amount of catalytically active

palladium was leached out of the polyaniline support. However, the strong ligand or support effect of polyaniline on the activity of the palladium catalyst cannot be denied because when we conducted the same reaction using PdCl<sub>2</sub> under identical conditions only small amount of the product was formed along with the inactive palladium black formation.

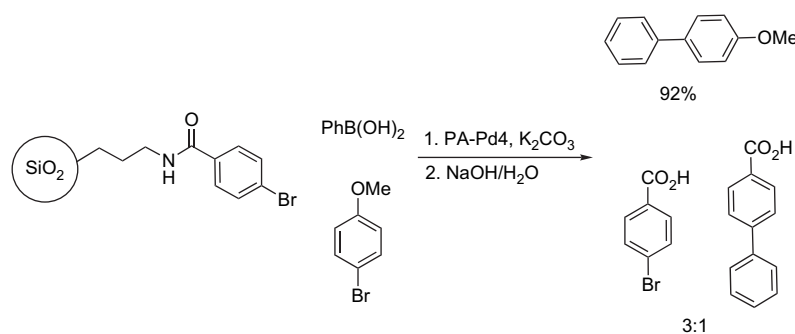
### 3. Conclusions

In conclusion, we have prepared polyaniline supported palladium catalysts using different palladium precursors and all the catalysts were well characterized using ICP, XPS, XRD, TGA–DTA, FTIR and SEM analysis. All the catalysts were evaluated for Suzuki–Miyaura coupling of bromo- and chloroarenes with arylboronic acids in water and it was found that the catalyst prepared from PdCl<sub>2</sub> was the best in terms of activity. Moreover the catalyst was reused for five consecutive cycles with consistent activity.

### 4. Experimental

#### 4.1. General methods

IR spectra were recorded on BIORAD 175C FTIR spectrometer for samples as KBr pellets. <sup>1</sup>H NMR spectra were recorded on a Varian Gemini 200 MHz and Avance 300 MHz spectrometers. Chemical shifts ( $\delta$ ) are reported in parts per million, using TMS as an internal standard for <sup>1</sup>H NMR. SEM-EDX (Scanning electron microscopy-energy dispersive X-ray analysis) was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. X-ray photoemission spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg K $\alpha$  anode. The pressure in the spectrometer was about 10<sup>–9</sup> Torr. For energy calibration, we have used the C1s photoelectron line. The C1s binding energy was taken to be 285.0 eV. Spectra were deconvoluted using Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species was first determined using the spectrum of a pure sample. The location and FWHM of products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible within  $\pm 0.1$  eV. ACME silica gel (100–200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck pre-coated silica gel 60-F<sub>254</sub> plates. GC analyses were performed



Scheme 2. Three-phase test using PA–Pd4 catalyst.

by using SHIMADZU GC 2010 with ZB5 capillary column. All the palladium complexes, aryl halides and arylboronic acids, 3-aminopropyl-modified silica gel and 4-bromobenzoyl chloride were purchased from Aldrich and used as received. Aniline and other solvents were distilled, and dried before use. All other chemicals were procured from commercial sources and used as such without further purification.

## 4.2. Preparation of PANI

Freshly distilled aniline (4.9 g, 53 mmol) was added to water (350 mL) containing H<sub>2</sub>SO<sub>4</sub> (15 mL) and the solution was kept under continuous stirring at 0 °C. To this solution ammonium persulfate (12 g, 53 mmol) in water (125 mL) was added drop wise over 4 h. The precipitated polyaniline-sulfate salt was recovered by filtration, and the precipitate was washed with copious amount of water followed by acetone. Thus obtained polyaniline-sulfate salt was stirred for 12 h at ambient temperature with sodium hydroxide solution (1 N, 500 mL). Then the deprotonated polyaniline base (PANI) was filtered off and washed with water, followed by acetone.

## 4.3. Preparation of polyaniline supported different palladium catalysts

PANI (300 mg) was charged into a round-bottomed flask containing an acetonitrile solution (25 mL) of palladium acetate (300 mg, 0.6 mmol) and stirred under nitrogen atmosphere for 48 h. The resultant catalyst was filtered off and washed with acetonitrile followed by acetone. The residue was dried in air for 24 h to afford the black catalyst PA–Pd1 (440 mg). The amount of palladium was measured by ICP-AES technique (Pd 0.43 mmol/g).

Similarly PA–Pd2, PA–Pd3 and PA–Pd4 were prepared from PdCl<sub>2</sub>(PhCN)<sub>2</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and PdCl<sub>2</sub>, respectively, using 0.6 mmol of palladium salts for 300 mg of PANI.

## 4.4. Suzuki–Miyaura coupling of bromoarenes in water

In an oven dried 10-mL round-bottomed flask, bromoarene (1 mmol), arylboronic acid (1.2 mmol), tridecane (122 μL) (internal standard), K<sub>2</sub>CO<sub>3</sub> (3 mmol), PA–Pd4 (2 mol %) and water (3 mL) were charged and stirred at 100 °C under N<sub>2</sub> atmosphere and the reaction was monitored by GC. For GC analysis, approximately 0.1 mL of reaction mixture was taken out by syringe, filtered and washed with ethyl acetate. Then the organic layer was separated and volume was made up to 1 mL and directly analyzed by GC. After completion of the reaction as monitored by GC, the catalyst was filtered. The filtrate was diluted with ethyl acetate and washed with 10% aqueous NaOH solution and finally with saturated aqueous NaCl solution. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated to get the crude product. The crude product was column chromatographed using hexane and ethyl acetate mixture as an eluent. All the products were characterized by <sup>1</sup>H NMR and mass spectrometry.

## 4.5. Suzuki–Miyaura coupling of chloroarenes in water

In an oven dried 10-mL round-bottomed flask, chloroarene (1 mmol), arylboronic acid (1.2 mmol), tridecane (122 μL),

K<sub>2</sub>CO<sub>3</sub> (3 mmol), TBAB (0.5 mmol), PA–Pd4 (2 mol %) and water (3 mL) were charged and stirred at 100 °C under N<sub>2</sub> atmosphere. After completion of the reaction as monitored by GC, the catalyst was filtered. The filtrate was diluted with ethyl acetate and washed with 10% aqueous NaOH solution and finally with saturated aqueous NaCl solution. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated to get the crude product. The crude product was column chromatographed using hexane and ethyl acetate mixture as an eluent. All the products were characterized by using <sup>1</sup>H NMR and mass spectrometry.

## 4.6. Spectroscopic characterization of products

**4.6.1. Biphenyl (1).**<sup>4</sup> White solid; mp: 68–70 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.28 (t, 2H, *J*=7.55 Hz), 7.37 (t, *J*=8.3 Hz, 4H), 7.53 (d, *J*=8.3 Hz, 4H); EIMS (*m/z*): 154 (M<sup>+</sup>).

**4.6.2. 4-Nitrobiphenyl (2).**<sup>4</sup> Yellow solid; mp: 112–114 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.38–7.54 (m, 3H), 7.55–7.65 (m, 2H), 7.73 (d, *J*=8.9 Hz, 2H), 8.31 (d, *J*=8.9 Hz, 2H); EIMS (*m/z*): 199 (M<sup>+</sup>), 152, 141, 76, 50.

**4.6.3. 4-Acetylbiphenyl (3).**<sup>4</sup> White solid; mp: 116–118 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.63 (s, 3H), 7.31–7.52 (m, 3H), 7.54–7.76 (m, 4H), 8.00 (d, *J*=8.2 Hz, 2H); EIMS (*m/z*): 196 (M<sup>+</sup>), 180, 152, 76, 43.

**4.6.4. 4-Methylbiphenyl (4).**<sup>4</sup> White solid; mp: 44–46 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.38 (s, 3H), 7.19 (d, *J*=7.55 Hz, 2H), 7.24–7.46 (m, 5H), 7.51 (d, *J*=7.55 Hz, 2H); EIMS (*m/z*): 168 (M<sup>+</sup>), 166, 163, 150, 113, 90, 75, 50.

**4.6.5. 4-Methoxybiphenyl (5).**<sup>4</sup> White solid; mp: 88–90 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.84 (s, 3H), 6.92 (d, *J*=8.9 Hz, 2H), 7.23–7.30 (m, 1H), 7.32–7.42 (m, 2H), 7.44–7.57 (m, 4H); EIMS (*m/z*): 184 (M<sup>+</sup>), 169, 141, 115, 89, 63.

**4.6.6. 2-Methylbiphenyl (6).**<sup>4</sup> Colourless liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.26 (s, 3H), 7.10–7.21 (m, 4H), 7.24–7.31 (m, 3H), 7.32–7.41 (m, 2H); EIMS (*m/z*): 168 (M<sup>+</sup>), 167, 149, 109, 81, 69, 57, 43.

**4.6.7. 4-Formylbiphenyl (7).**<sup>4</sup> Colourless liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.32–7.51 (m, 3H), 7.59 (dt, *J*=6.8 Hz, 1.70 Hz, 2H), 7.72 (d, *J*=8.5 Hz, 2H), 7.92 (d, *J*=8.5 Hz, 2H), 10.04 (s, 1H); EIMS (*m/z*): 182 (M<sup>+</sup>), 152, 76, 63, 51.

**4.6.8. 4-Cyanobiphenyl (8).**<sup>4</sup> White solid; mp: 84–86 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.35–7.49 (m, 3H), 7.52–7.57 (m, 2H), 7.66 (d, *J*=8.3 Hz, 2H), 7.72 (d, *J*=8.3 Hz, 2H); EIMS (*m/z*): 180 (M+1), 179 (M<sup>+</sup>), 142, 43.

**4.6.9. 3-Nitrobiphenyl (9).**<sup>4</sup> Yellow solid; mp: 58–59 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.38–7.53 (m, 3H), 7.54–7.66 (m, 3H), 7.89 (dd, *J*=8.17 Hz, 1.48 Hz, 1H), 8.19 (dd, *J*=8.17 Hz, 1.48 Hz, 1H), 8.43 (s, 1H); EIMS (*m/z*): 199 (M<sup>+</sup>), 141, 77, 51, 43.

**4.6.10. 4-Nitro-4'-methoxybiphenyl (10).**<sup>4</sup> Yellow solid; mp: 109–110 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.85 (s,

3H), 6.96 (d,  $J=8.4$  Hz, 2H), 7.52 (d,  $J=8.4$  Hz, 2H), 7.65 (d,  $J=8.9$  Hz, 2H), 8.25 (d,  $J=8.9$  Hz, 2H); EIMS ( $m/z$ ): 229 ( $M^+$ ), 199, 168, 139.

**4.6.11. 4-Acetyl-3'-nitrobiphenyl (11).** White solid; mp: 108–110 °C; IR (KBr)  $\nu$  593, 718, 1264, 1357, 1531, 1603, 1672, 1751, 3098  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.63 (s, 3H), 7.65 (t,  $J=8.3$  Hz, 1H), 7.71 (d,  $J=8.3$  Hz, 2H), 7.92 (d,  $J=7.55$  Hz, 1H), 8.06 (d,  $J=8.3$  Hz, 2H), 8.26 (d,  $J=7.55$  Hz, 1H), 8.49 (s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  25.63, 121.49, 122.30, 126.67, 128.35, 129.17, 132.28, 136.44, 141, 142.67, 148.49, 197.10; EIMS ( $m/z$ ): 241 ( $M^+$ , 32%), 226 (100%), 180, 152, 141, 129, 90, 76, 55, 43. Anal. Calcd for  $\text{C}_{14}\text{H}_{11}\text{NO}_3$  (241.07): C, 69.70; H, 4.60; N, 5.81. Found: C, 69.59; H, 4.62; N, 5.68.

**4.6.12. 4-Acetyl-4'-methylbiphenyl (12).**<sup>19</sup> White solid; mp: 122–124 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.45 (s, 3H), 2.64 (s, 3H), 7.26 (d,  $J=8.3$  Hz, 2H), 7.50 (d,  $J=8.3$  Hz, 2H), 7.66 (d,  $J=8.3$  Hz, 2H), 8.01 (d,  $J=8.3$  Hz, 2H); EIMS ( $m/z$ ): 210 ( $M^+$ ), 209, 194, 151, 76, 43.

**4.6.13. 4-Acetyl-4'-methoxybiphenyl (13).**<sup>20</sup> White solid; mp: 148–150 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.62 (s, 3H), 3.85 (s, 3H), 6.97 (d,  $J=8.2$  Hz, 2H), 7.52 (d,  $J=8.2$  Hz, 2H), 7.66 (d,  $J=8.5$  Hz, 2H), 8.02 (d,  $J=8.5$  Hz, 2H); EIMS ( $m/z$ ): 226 ( $M^+$ ), 195, 183, 115, 76.

**4.6.14. 4-Acetyl-4'-fluorobiphenyl (14).**<sup>4</sup> White solid; mp: 102–104 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.62 (s, 3H), 7.14 (t,  $J=8.3$  Hz), 7.53–7.63 (m, 4H), 7.98 (d,  $J=8.3$  Hz, 2H); EIMS ( $m/z$ ): 214 ( $M^+$ ), 194, 170, 76, 43.

**4.6.15. 4-Acetyl-2'-methylbiphenyl (15).**<sup>21</sup> Yellowish liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.27 (s, 3H), 2.62 (s, 3H), 7.13–7.27 (m, 4H), 7.39 (d,  $J=8.6$  Hz, 2H), 7.99 (d,  $J=8.6$  Hz, 2H); EIMS ( $m/z$ ): 210 ( $M^+$ ), 195, 76, 50, 43.

**4.6.16. 4-Acetyl-trans-stilbene (16).**<sup>22</sup> White solid; mp: 134–136 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.6 (s, 3H), 7.12 (d,  $J=16.6$  Hz, 1H), 7.22 (d,  $J=16.6$  Hz, 1H), 7.28–7.41 (m, 3H), 7.53 (d,  $J=6.8$  Hz, 2H), 7.59 (d,  $J=8.3$  Hz, 2H), 7.95 (d,  $J=8.3$  Hz, 2H); EIMS ( $m/z$ ): 222 ( $M^+$ ), 207, 178, 152, 89, 76, 43.

#### 4.7. Reusability study

After the completion of the reaction, catalyst was filtered off. Then it was washed with water followed by acetone and air-dried. After drying the recovered catalyst was charged in the next run.

#### 4.8. Three-phase test

*Procedure for synthesis of BrPhCONH–SiO<sub>2</sub>.* To anchor the *p*-bromobenzamide, a solution of the *p*-bromobenzoyl chloride (550 g, 2.5 mmol) in dry THF (10 mL) was placed in a round-bottomed flask in the presence of aminopropyl-modified solid (1 g) and pyridine (3 mmol) under nitrogen atmosphere. The suspension was stirred magnetically at 40 °C under nitrogen atmosphere for 12 h. The solid was separated by centrifugation and washed with 20 mL of HCl/H<sub>2</sub>O (5% v/v, three times), 20 mL of aqueous solution

of K<sub>2</sub>CO<sub>3</sub> (0.02 M, two times), neat water (two times) and ethanol (two times). Then the solid was Soxhlet extracted with CH<sub>2</sub>Cl<sub>2</sub> for 24 h. After drying the solids (at 50 °C under reduced pressure, the anchored amount was determined by combustion chemical analysis and confirmed by thermogravimetric analysis. BrPhCONH–SiO<sub>2</sub>: 0.35 mmol/g.

A solution of 4-bromoanisole (1 mmol), phenylboronic acid (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (3 mmol), BrPhCONH–SiO<sub>2</sub> (350 mg) and PA–Pd<sub>4</sub> (2 mol %) in water (4 mL) was stirred at 100 °C under nitrogen until the complete consumption of 4-bromoanisole (~2 h). The solid was separated by filtration, washed with ethanol and Soxhlet extracted with ethanol for 24 h. After that the solid was hydrolyzed in a 2 M solution of NaOH (20 mL) at 90 °C for 24 h. The solution was filtered, and the filtrate was acidified with 10% HCl and extracted with ether, concentrated and analyzed by GC–MS.

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#### Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.05.064.

#### References and notes

- (a) Narayan, S.; Muldoon, J.; Finn, M. G.; Fokin, V. V.; Kolb, H. C.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2005**, *44*, 3275; (b) Li, C.-J. *Chem. Rev.* **2005**, *105*, 3095; (c) Li, C.-J.; Chan, T.-H. *Organic Reactions in Aqueous Media*; Wiley: Chichester, UK, 1997.
- (a) Suzuki, A. *J. Organomet. Chem.* **1999**, *54*, 147; (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
- (a) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359; (b) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633; (c) Like, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176; (d) Bolm, C.; Hildebrand, J. P.; Muniz, K.; Hermanns, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 3284.
- (a) Mino, T.; Shirae, Y.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2005**, *70*, 2191; (b) Lemo, J.; Henze, K.; Astruc, D. *Org. Lett.* **2005**, *7*, 2253; (c) Kwong, F. Y.; Lam, W. H.; Yeung, C. H.; Chan, K. S.; Chan, A. S. C. *Chem. Commun.* **2004**, 1922; (d) Li, J.-H.; Liu, W.-J.; Xie, Y. X. *J. Org. Chem.* **2005**, *70*, 5409; (e) Kim, J. H.; Kim, J. W.; Shokouhimehr, M.; Lee, Y. S. *J. Org. Chem.* **2005**, *70*, 6714; (f) Xiong, Z.; Wang, N.; Dai, M.; Li, A.; Chen, J.; Yang, Z. *Org. Lett.* **2004**, *6*, 3337; (g) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1871; (h) Li, J.-H.; Liu, W.-J. *Org. Lett.* **2004**, *6*, 2809; (i) Jensen, J. F.; Johannsen, M. *Org. Lett.* **2003**, *5*, 3025; (j) Leadbeater, N.; Marco, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1407; (k) Stambuli, J. P.; Kuwano, R.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 4746; (l) Botella, L.; Najera, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 179; (m) Alonoso, D. A.; Najera, C.; Pacheco, M. C. *J. Org. Chem.* **2002**, *67*, 5588; (n) Bedford,

- R. B.; Cazin, C. S. *J. Chem. Commun.* **2001**, 1540; (o) Zapf, A.; Ehrentraut, A.; Beller, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4253; (p) Reetz, M. T.; Westermann, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 165.
5. Bedford, R. B.; Blake, M. E.; Butts, C. P.; Holder, D. *Chem. Commun.* **2003**, 466.
6. (a) Baleizao, C.; Corma, A.; Garcia, H.; Leyva, A. *Chem. Commun.* **2003**, 606; (b) Baleizao, C.; Corma, A.; Garcia, H.; Leyva, A. *J. Org. Chem.* **2004**, *69*, 439.
7. (a) Lysen, M.; Kohler, K. *Synthesis* **2006**, 692; (b) Lysen, M.; Kohler, K. *Synlett* **2005**, 1671.
8. (a) Choudary, B. M.; Madhi, S.; Chowdari, N. S.; Kantam, M. L.; Sreedhar, B. *J. Am. Chem. Soc.* **2002**, *124*, 14127; (b) Kantam, M. L.; Roy, S.; Roy, M.; Sreedhar, B.; Choudary, B. M. *Adv. Synth. Catal.* **2005**, *347*, 2002.
9. (a) Skoheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*, 2nd ed.; Marcel Dekker: New York, NY, 1998; (b) *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: Chichester, UK, 1997; Vols. 1–4.
10. (a) Velusamy, S.; Ahamed, M.; Punniyamurthy, T. *Org. Lett.* **2004**, *6*, 4821; (b) Kowalski, G.; Pielichowski, J. *Synlett* **2002**, 2107; (c) Prabhakaran, E. N.; Iqbal, J. *J. Org. Chem.* **1999**, *64*, 3339; (d) Das, B. C.; Iqbal, J. *Tetrahedron Lett.* **1997**, *38*, 1235; (e) Pielichowski, K.; Pielichowski, J.; Iqbal, J.; Gurtat, P. *Appl. Catal., A: Gen.* **1997**, *161*, L25.
11. Choudary, B. M.; Roy, M.; Roy, S.; Kantam, M. L.; Sreedhar, B.; Kumar, K. V. *Adv. Synth. Catal.* **2006**, *348*, 1734.
12. (a) Hasik, M.; Paluszkiwicz, C.; Bielanska, E. *J. Mol. Struct.* **2005**, *744–747*, 677; (b) Gutmann, V. *Coordination Chemistry in Non-aqueous Solutions*; Springer: New York, NY, 1968.
13. (a) Ping, Z.; Nauer, G. E.; Neugebauer, H.; Theiner, J.; Neckel, A. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 121; (b) Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth. Met.* **1988**, *24*, 211.
14. Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer: Minnesota, MN, 1992.
15. (a) Zhao, F.; Bhanage, B. M.; Shirai, M.; Arai, M. *Chem.—Eur. J.* **2000**, *6*, 843; (b) Zhao, F.; Shirai, M.; Ikushima, Y.; Arai, M. *J. Mol. Catal. A: Chem.* **2002**, *180*, 211; (c) Prockl, S. S.; Kleist, W.; Gruber, M. A.; Kohler, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1881; (d) Andrews, S. P.; Stepan, A. F.; Tanaka, H.; Ley, S. V.; Smith, M. D. *Adv. Synth. Catal.* **2005**, *347*, 647.
16. Lipshutz, B. H.; Tasler, S.; Chrisman, W.; Spliethoff, B.; Tecsche, B. *J. Org. Chem.* **2003**, *68*, 1177.
17. (a) Rebek, J.; Gavina, F. *J. Am. Chem. Soc.* **1974**, *96*, 7112; (b) Rebek, J.; Brown, D.; Zimmerman, S. *J. Am. Chem. Soc.* **1975**, *97*, 454.
18. Davies, I. W.; Matty, L.; Hughes, D. L.; Reider, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 10139.
19. Ueda, M.; Daito, A.; Oh-Tani, S.; Miyaura, N. *Tetrahedron* **1998**, *54*, 13079.
20. Calo, V.; Nacci, A.; Monopoli, A.; Montigelli, F. *J. Org. Chem.* **2005**, *70*, 6040.
21. Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 2719.
22. Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989.