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Naphthidine di(radical cation)s-stabilized palladium nanoparticles for efficient catalytic Suzuki–Miyaura cross-coupling reactions

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Abstract

Stable Pd(0) nanoparticles were prepared at room temperature in 1,4-dioxane from $PdCl_2$ using *N*,*N*′-bis(4-methoxyphenyl)-(1,1′-binaphthyl)-4,4′-diamine (naphthidine) as reducing and stabilizing agent. This procedure resulted in Pd(0) particles possessing an average diameter of ca. 25 nm stabilized against aggregation due to a barrier of the naphthidine di(radical cation) $Napht^{2,2+}$. These particles were evaluated for their capability to act as catalysts in Suzuki–Miyaura coupling reactions. The Pd(0)/$Napht^{2,2+}$ provides a general and convenient method to prepare biaryls from aryl bromides or iodides and boronic acids with a broad range of functional groups in 1,4-dioxane at 80 °C and under aerobic conditions.

Keywords: Naphthidines; Pd nanoparticles; Catalysis; C–C coupling; Recycle

1. Introduction

The Suzuki–Miyaura reaction is one of the most versatile and utilized method for the selective construction of carbon–carbon bonds in particular for the formation of biaryls, structural units found in natural products, pharmaceuticals, and advanced materials.[1] There has recently been considerable interest in the preparation of new and highly active catalysts that can be used in the Suzuki–Miyaura coupling.[2] However, industrial applications of these reactions are still rare mainly due to the following two problems: (i) palladium and many phosphines are expensive and (ii) phosphine ligands are poisonous, air sensitive, and subject to P–C bond degradation at elevated temperatures. Accordingly, one of the current focuses in the field is the development of efficient catalysts that utilize inexpensive, preferentially nonphosphine, ligands.

The application of metal particles in catalysis has become an important frontier of research in recent years.[3] Due to their high surface area and the density of the unsaturated surface coordination sites, nanocatalysts offer increased catalytic efficiency with respect to bulk materials.[4] Since metal nanoparticles are unstable with respect to aggregation and precipitation to the bulk metal, stabilizers such as surfactants,[5] organic ligands,[6] polymers,[7] dendrimers,[3a,8] ionic liquids,[9] and aerogels[10] are generally used during their preparation to prevent agglomeration and to control the particle size. The surface properties of these metal nanoparticles and their catalytic activity are crucially controlled by the nature of these stabilizers. Once the metal salt (generally Pd(II)) added to a solution of the stabilizer, a reducing agent, $NaBH_4$, molecular H_2, hydrazine, or an alcohol, is used to generate the metal(0) nanoparticles. A prominent area of application of palladium nanoparticles prepared by this method in organic chemistry concerns coupling reactions.

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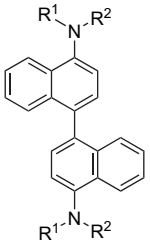
Recently, a great number of nanomaterials containing Pd(0) nanoparticles have been developed for carbon–carbon bond-forming reactions, and especially for Suzuki–Miyaura[8a,7g,11] and Hiyama[12] couplings.

Naphthidines **1** (Fig. 1) are new reducing agents that can easily be prepared in two steps from 1-chloronaphthalene by Ni(0)-catalyzed aryl amination[13] reactions followed by $TiCl_4$-mediated oxidative homocoupling of the intermediate 1-naphthylamines.[14] We have recently shown that naphthidines react with oxidants such as phenyliodine(III)bis(trifluoroacetate) (PIFA) or thianthrenium perchlorate ($ThClO_4$) to generate under mild conditions stable di(radical cation)s $\mathbf{1}^{2.2+}$.[14]

We report here the preparation of Pd(0) nanoparticles using naphthidines as reducing agent of $PdCl_2$ and the catalytic activity in Suzuki–Miyaura cross-coupling reactions of the Pd(0)/Napht$^{2.2+}$ nanomaterial thus produced. Although amines like DABCO,[15] dicyclohexylamine,[16] hydrazones,[17] ureas,[18] or supported poly(allylamine)s[19] have already been used in Suzuki–Miyaura reactions, this report describes the first use of a Pd(0) nanocatalyst in situ generated by an aromatic diamine and stabilized by its radical cations.



1 (R^1, R^2 = H, alkyl or aryl)

Figure 1. Structure of naphthidines.

2. Results and discussion

Our exploratory experiments started with the reduction of $PdCl_2$ with *N*,*N*′-bis(4-methoxyphenyl)-(1,1′-binaphthyl)-4,4′-diamine **1a** (R^1=C_6H_4-*p*-OMe, R^2=H). All materials were handled and the reaction conducted in air. Addition of $PdCl_2$ (1 equiv) to a solution of **1a** (1 equiv) in CH_2Cl_2, THF, dioxane, CH_3CN, or DMF at room temperature resulted immediately in a color change from pale yellow to dark red in THF or dioxane and to deep blue in CH_2Cl_2 or CH_3CN. Analysis of the CH_2Cl_2 solution obtained after 1 h reduction by EPR reveals a single broad line with a spectral width of ca. 30 G (Fig. 2). The spectra obtained suggests that $PdCl_2$ oxidizes **1a** into the di(radical cation) $\mathbf{1a}^{2.2+}$.[14]

Electrochemistry was used to further point out the presence of this di(radical cation) $\mathbf{1a}^{2.2+}$ in the medium, via the in situ monitoring of its formation upon Pd^{2+} reduction by means of hydrodynamic voltammetry measurements performed in acetonitrile medium (Fig. 3). The electrochemical behavior of the **1a**/$\mathbf{1a}^{2.2+}$ system is well-known, displaying a reversible behavior at the characteristic mid-wave potential of +0.71 V.

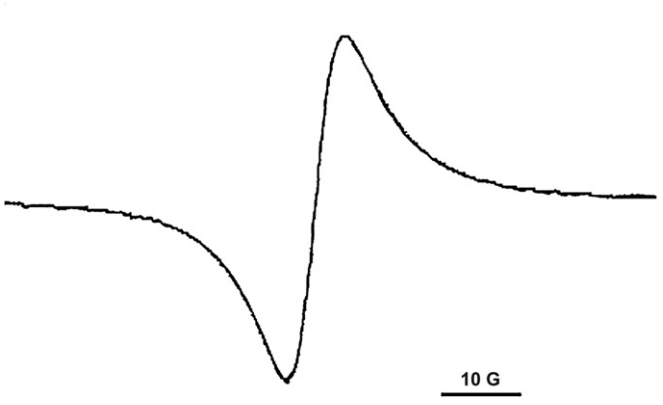


Figure 2. EPR spectra of the CH_2Cl_2 solution containing the Pd(0)/Napht$^{2.2+}$ material recorded at 293 K.

Applying a more cathodic potential (i.e., +0.2 V) to a rotating disk electrode thus provides an easy way to monitor the appearance of free $\mathbf{1a}^{2.2+}$ species as a function of reaction time with $PdCl_2$ (Pd^{2+} was not electroactive at the working potential of +0.2 V). As shown in Figure 3, the amount of free $\mathbf{1a}^{2.2+}$ species started to grow slowly, then more rapidly and then tended to level off after 2 h, the same trend being also observed when performing the experiment in CH_2Cl_2. The concomitant observation of the dark blue color and the fact that $\mathbf{1a}^{2.2+}$ species were only detected by electrochemistry after several minutes suggest that some di(radical cation)s are immobilized onto the surface of Pd(0) nanoparticles (see also observations by electron microscopy below). In addition, both measurements of zero-current potential values after reaction completion (i.e., +0.45 V in CH_3CN) and control experiments by cyclic voltammetry confirm that **1a** has been effectively oxidized by $PdCl_2$ into the di(radical cation) $\mathbf{1a}^{2.2+}$ and that the amount of free $\mathbf{1a}^{2.2+}$ species (non-bonded onto Pd(0)

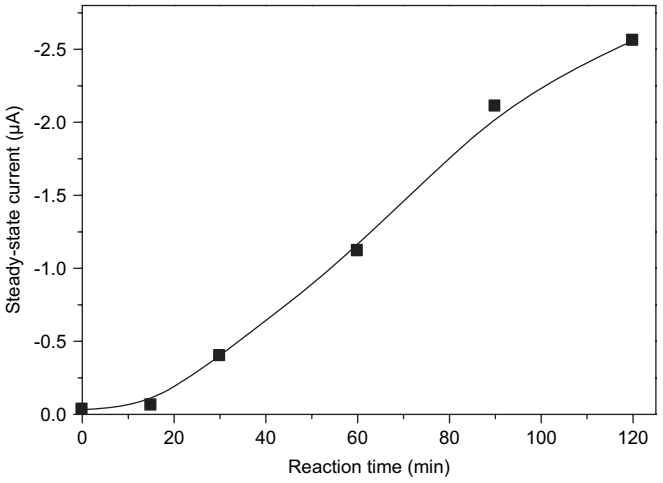


Figure 3. Variation of the steady-state currents measured at a rotating disk carbon electrode as a function of time in acetonitrile solution containing 2 mM $PdCl_2$ to which 2×10^{-2} M **1a** was added at time t=0. Applied potential: +0.2 V; electrode rotation speed: 1500 rd min^{-1}; supporting electrolyte: Bu_4NPF_6 (0.1 M).

particles) is rather low, supporting again the fact that a great part of these species would be used to stabilize the nanoparticles.

SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy) analyses of the dioxane solution reveal that Pd(0) nanoparticles were formed during the process (Figs. 4 and 5). The SEM micrograph (Fig. 4) shows roughly spherical separated aggregates that are ca. 4 μm in size. At higher magnifications on the dark field TEM micrograph (Fig. 5), small subunits forming the aggregates can be observed. Pd(0) nanoparticles appear as white spots at the surface of organic wires. It is not unreasonable to assume that these wires are formed from **1a**$^{2.2+}$ (as also supported by electrochemistry data, see above) and that positive charges of the di(radical cation)s stabilize particles toward coagulation. Dispersion of Pd(0) particles on the surface of these wires is, however, not homogeneous and aggregation of metal particles at different places was observed. The average diameter of Pd(0) particles was estimated to be 25.0 nm. No changes were observed in the materials by TEM after several weeks' storage at room temperature under air.

The nanomaterial obtained after 2 h reaction between $PdCl_2$ and naphthidine **1a** was also subjected to X-ray photoelectron spectroscopy (XPS). The results are shown in Figure 6. The N 1s spectra (Fig. 6a) can be separated into two major components at 399.1 and 400.4 eV, attributed, respectively, to the N═ and NH and to the N^+ units of the naphthidine and of its di(radical cation).[20,21] The Pd 3d spectra is shown in Figure 6b. The spectra were deconvoluted to determine the differences in the shares of individual peak components in the Pd

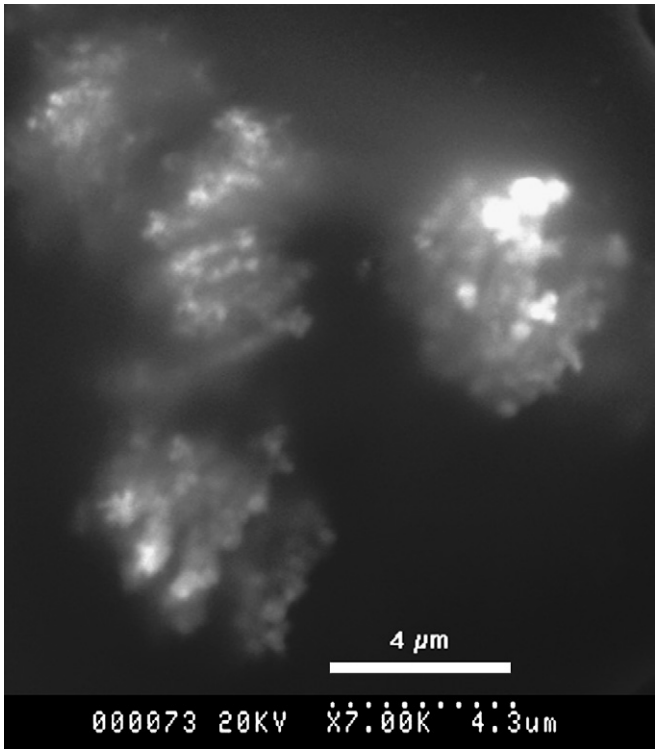


Figure 4. SEM micrograph of the Pd(0)/**1a**$^{2.2+}$ nanomaterial.

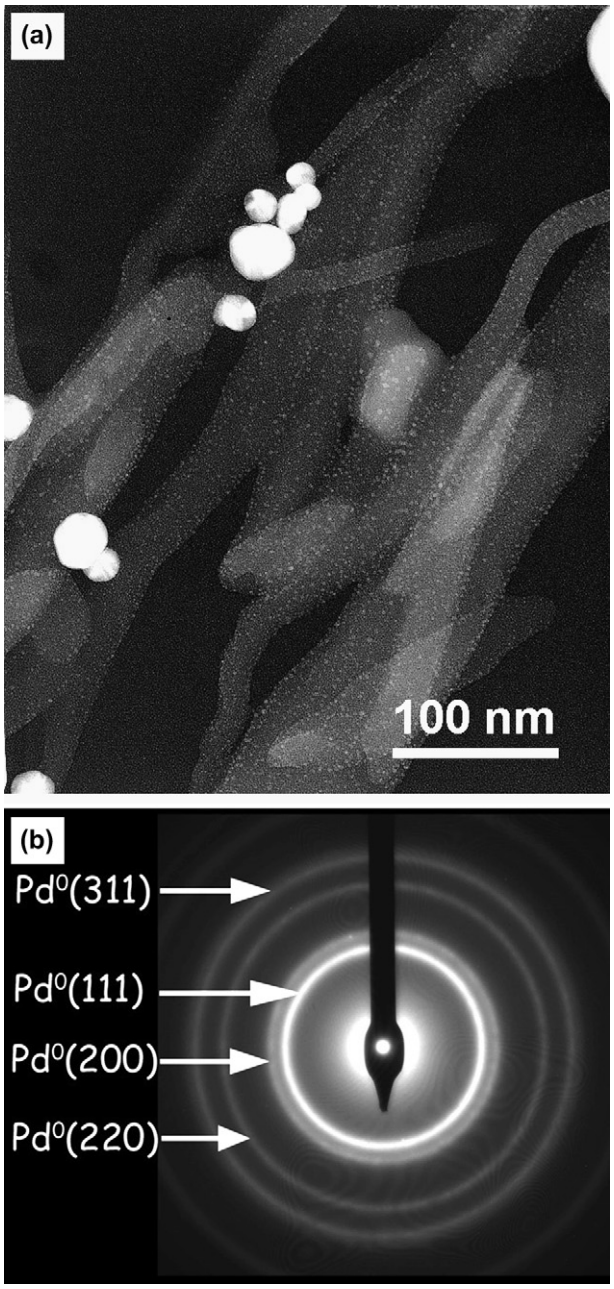


Figure 5. (a) TEM micrograph of the Pd(0)/**1a**$^{2.2+}$ nanomaterial and (b) electron diffraction pattern of palladium nanoparticles.

containing nanomaterial. The presence of Pd(0) was confirmed by the Pd $3d_{5/2}$ peak at 334.3 eV. The component peak with binding energy at 335.6 eV can be assigned to Pd(+2) species.[22] According to the literature,[21] the third peak at 337.2 eV can be assigned to Pd–N bonds. Chemical analysis of the particle surface shows finally that the atomic ratio of Pd(0)/Pd(+2) is 2.1.

With the well-defined and air-stable nanocatalyst available, we performed optimization studies to determine how naphthidines, solvents, bases, and temperature affect the catalytic activity.

Three naphthidines were first screened as potential reducers and ligands, using a model coupling reaction of 4-bromoanisole

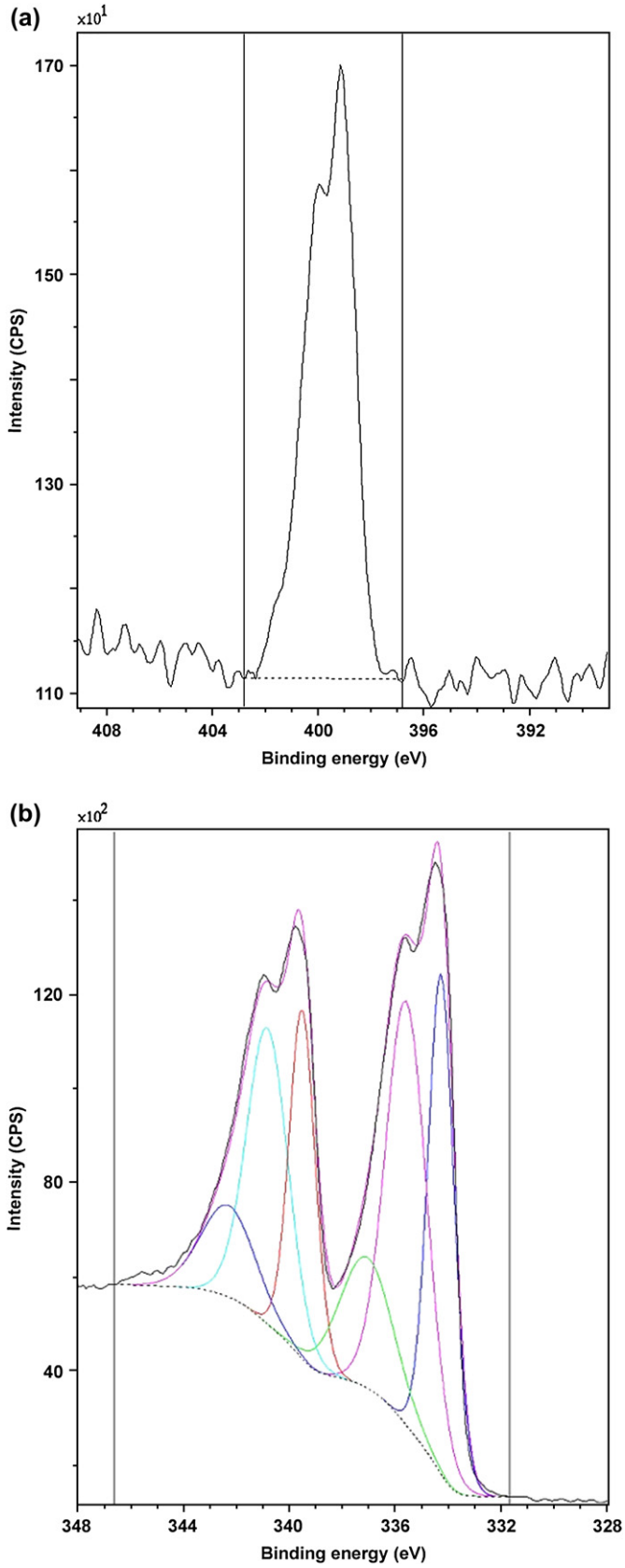


Figure 6. XPS analysis of the Pd/Napht$^{2,2+}$ nanomaterial: the binding energy spectrum of (a) N 1s and (b) Pd 3d.

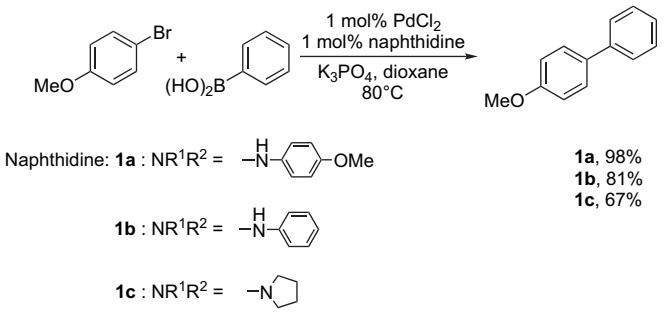


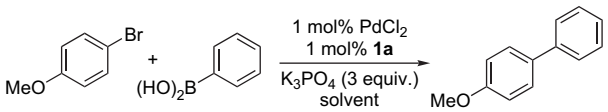
Figure 7. Effect of the naphthidine's structure on Suzuki–Miyaura cross-coupling of 4-bromoanisole.

and phenylboronic acid in the presence of 1 mol % $PdCl_2$, 1 mol % naphthidine, and 2 equiv of K_3PO_4 in 1,4-dioxane at 80 °C (Fig. 7).

Among the naphthidines investigated, compound **1c** displayed moderate efficiency giving the coupling product in 67% yield. More bulky amines in which the di(radical cation)s generated upon oxidation are stabilized by extended delocalization across a benzenic ring were found to be better ligands. Naphthidine **1a** was found to be the best ligand, giving the coupling product in a nearly quantitative yield in 5 h. These results suggest that steric bulk and electronic delocalization are important to the activity of the catalyst. *N*,*N*′-Diphenylnaphthidines **1a** and **1b** appear to be better ligands than comparable alkylated because the former have a greater ability to stabilize the catalytic active Pd species responsible for the catalytic cycle. It is also noteworthy that couplings were conducted with a **1**/Pd ratio of 1/1. Increasing this ratio to 2/1 has no influence on the activity of the nanocatalyst.

The same coupling reaction for the ligand-screening experiments was used as a model for solvent optimization studies (Table 1). The non-polar solvent toluene gave a low yield of 4-methoxybiphenyl (entry 1) and Pd black formation was observed during the coupling. Polar aprotic or protic solvents do not benefit the reaction and only moderate yields of the coupling product were obtained in DMF or EtOH (entries 2 and 3). Contrary to results obtained with amines and hydrazone ligands in Suzuki–Miyaura couplings,[15–17] ethereal

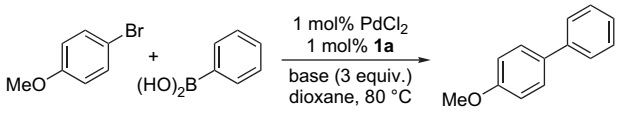
Table 1
Solvent effect[a]



Entry	Solvent/*T*(°C)	Yield[b] (%)
1	Toluene/80	7[c]
2	DMF/80	39
3	EtOH/80	53
4	THF/65	78
5	Dioxane/80	98

[a] Reactions conditions: 4-bromoanisole (3 mmol), phenylboronic acid (4.5 mmol), base (9 mmol), $PdCl_2$ (1 mol %), **1a** (1 mol %), solvent (5 mL).
[b] Isolated yields.
[c] Determined by GC/MS.

Table 2
Effect of the base on the Pd/**1a**$^{2.2+}$-catalyzed Suzuki–Miyaura coupling reaction[a]



Entry	Base	Conversion[b] (%)	Time[b] (h)	Yield[c] (%)
1	Cs_2CO_3	100		98
2	CsF	100		95
3	KF	100		95
4	Na_2CO_3	94	15	91
5	$NaHCO_3$	73	15	52
6	K_3PO_4	100		98
7	LiOH	56	15	48
8	NaOH	46	15	40
9	KOH	52	15	45
10	AcONa	33	15	—
11	*t*-BuONa	10	15	—
12	Et_3N	37	15	—
13	*i*-Pr_2NEt	25	15	—

[a] Reaction conditions: 4-bromoanisole (3 mmol), phenylboronic acid (4.5 mmol), base (9 mmol), $PdCl_2$ (1 mol %), **1a** (1 mol %), dioxane (5 mL), 80 °C.
[b] Determined by GC/MS.
[c] Isolated yields.

solvents like THF and dioxane gave the best results (entries 4 and 5). Dioxane, which gave the fastest reaction, was chosen for further experiments. Attempts to conduct the reaction at lower temperatures in dioxane resulted only in a decrease in the conversion of 4-bromoanisole (50 °C, 12 h, 47%).

Investigations into the optimal base showed that the rate of reaction and the activity of the catalyst were significantly influenced by the base used (Table 2). Inorganic bases such as Cs_2CO_3, CsF, KF, and K_3PO_4 provided 4-methoxybiphenyl in excellent yields (entries 1–3 and 6). Sodium carbonate (Na_2CO_3) can also be used (entry 4) but hydrogenocarbonate ($NaHCO_3$) gave only a modest yield in product (entry 5). Finally, when hydroxides, AcONa, *t*-BuONa, and organic bases (Et_3N, *i*-Pr_2NEt) were used (entries 7–13), poor conversions of 4-bromoanisole were observed and precipitation of palladium black occurred within a few hours. Noteworthy is also that no beneficial effect of strong bases was observed with our catalyst contrary to phosphine-based systems.[23]

Among the palladium compounds screened for use as catalyst precursor ($Pd(OAc)_2$, $PdCl_2$, $PdBr_2$), the best result was obtained with $PdCl_2$. The effect of catalyst loading was also examined. A range of 0.1–2.0 mol % of the Pd(0)/**1a**$^{2.2+}$ catalyst was evaluated and it was found that 0.6 mol % gave the most consistent results. The couplings involving activated aryl halides can be carried out efficiently under lower Pd loadings (0.2 mol %). Further decreasing the Pd loading to 0.1 or 0.05 mol % led to moderate conversion (<50%). It is finally noteworthy that no product was formed when the coupling of phenylboronic acid and 4-bromoanisole was conducted in the absence of $PdCl_2$.

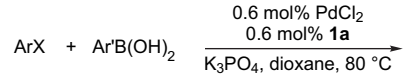
Compared to recently developed ligand-free methodologies using Pd for Suzuki–Miyaura reactions like $PdCl_2$ in pyridine,[24] polyaniline supported Pd,[25] or microwave-promoted couplings in water,[26] the stability of the Pd(0)/**1a**$^{2.2+}$ catalyst allowed reactions to be performed under mild conditions and at low Pd loading.

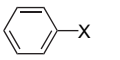
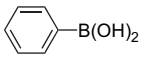
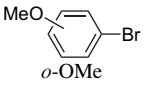
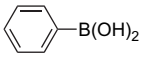
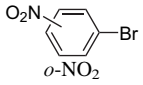
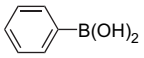
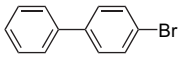
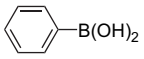
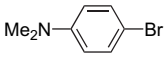
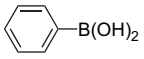
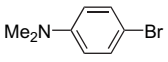
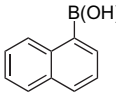
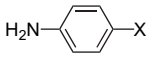
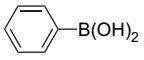
On the basis of the optimized reaction conditions, the coupling reactions between a range of aryl halides and several arylboronic acids were carried out to explore the general effectiveness of the Pd(0)/**1a**$^{2.2+}$ catalyst (Table 3). With iodo- and bromobenzene, the couplings proceeded very rapidly and afforded quantitatively biphenyl (entries 1 and 2). No reaction was observed with chlorobenzene (entry 3). Using 4- or 3-substituted aryl bromides led to good yields of the corresponding unsymmetrical biaryls. Reaction times of sterically demanding *ortho*-substituted aryl bromides were slightly increased (entries 4, 7, and 18–19). An *ortho*-substitution is well-tolerated, both in the aryl bromide and in the arylboronic acid and biaryls possessing a 2,2′-disubstituted pattern could be prepared (entries 23 and 24). Even very hindered substrates like 2,4,6-trimethylphenylboronic acid could be coupled to 4-bromonitrobenzene to give the desired product in 93% yield with low catalyst loading (0.6 mol %) after 13 h reaction (entry 25). 2- or 3-Bromopyridines are also excellent substrates giving coupling products in excellent yields (entries 26 and 27). The reaction of 5-bromo-2-chloropyridine with phenylboronic acid gave exclusively 2-chloro-5-phenylpyridine (entry 28), showing the good chemoselectivity. The coupling between 5-bromopyrimidine and 1-naphthylboronic acid was found to be more difficult (entry 29). 3-Thienylboronic acid can also be used (entries 30 and 31). However, with substrates bearing strong coordinating groups of palladium (NH_2, OH, S; entries 13–16, 30, and 31), conversions observed after 15 h reaction were only poor using aryl bromides and it was found advantageous to use aryl iodides. It can also be noted that the Pd(0)/**1a**$^{2.2+}$ catalytic system can tolerate a broad range of functional groups such as NO_2, NH_2, NMe_2, SMe, CHO, $COCH_3$, CO_2Me, CN, and CH_2OH.

Finally, the catalyst was found recyclable without loss of activity. After the reaction of 4-bromoanisole with phenylboronic acid in dioxane at 80 °C had reached completion, the Pd(0)/**1a**$^{2.2+}$ catalyst was recovered from the reaction mixture by centrifugation and reused under identical reaction conditions to those of the first run. As shown in Table 4, only a slight decrease of activity was observed after three cycles.

In conclusion, we have developed a novel and efficient catalyst system for the Suzuki–Miyaura reaction by using naphthidine di(radical cation)s-stabilized palladium nanoparticles as catalyst and K_3PO_4 as base in dioxane. Pd(0) nanoparticles possessing an average diameter of ca. 25 nm were in situ generated by reduction of $PdCl_2$ with the naphthidine. The organic/inorganic material thus produced was found air- and moisture stable allowing the reactions to be conducted under aerobic conditions. The cross-coupling of arylboronic acids with aryl bromides and aryl iodides gave the corresponding biaryl products in excellent yields under the present conditions. We are currently pursuing the further application of this procedure.

Table 3
Pd(0)/**1a**$^{2.2+}$-catalyzed Suzuki–Miyaura cross-couplings of aryl halides with arylboronic acids[a]



Entry	Aryl halide	X	Arylboronic acid	Time[b] (h)	Yield[c] (%)
1		I		1	Quant
2		Br		3	Quant
3		Cl		15	0
4	 *o*-OMe			8	98
5	*m*-OMe			5	99
6	*p*-OMe			5	99
7	 *o*-NO_2			12	50
8	*m*-NO_2			6	97
9	*p*-NO_2			4	98
10				5	Quant
11				8	Quant
12				10	92
13		Br		15	31[d]
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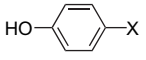
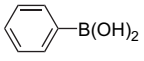
15		Br		15	48[d]
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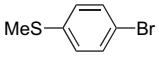
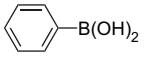
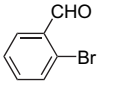
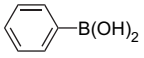
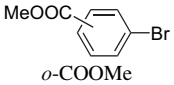
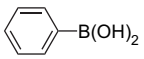
17		Br		12	83
18				6	95
19	 *o*-COOMe			8	86
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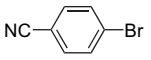
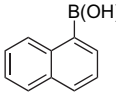
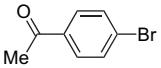
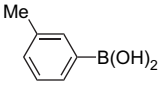
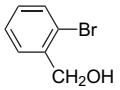
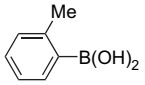
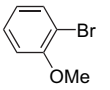
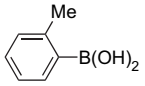
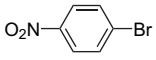
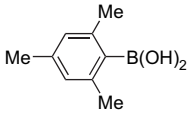
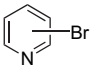
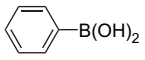
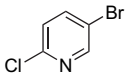
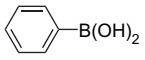
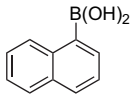
21				12	92
22				6	99

Table 3 (*continued*)

Entry	Aryl halide	X	Arylboronic acid	Time[b] (h)	Yield[c] (%)
23				10	89
24				8	98
25				13	93
26		2-Br		6	95
27		3-Br		5	98
28				5	99
29				15	45
30		Br		15	42[d]
31		I		7	99

[a] Reaction conditions: aryl halide (3 mmol), arylboronic acid (4.5 mmol), K_3PO_4 (9 mmol), $PdCl_2$ (0.6 mol %), **1a** (0.6 mol %), dioxane (5 mL), 80 °C.
[b] Determined by GC/MS.
[c] Isolated yields.
[d] Yields determined by GC/MS.

Table 4
Recycling of the Pd(0)/**1a**$^{2.2+}$ catalyst[a]

Run	Catalyst recovery (%)	Product yield[b] (%)
1	98	96
2	91	87
3	89	84

[a] Pd(0)/**1a**$^{2.2+}$ (0.6 mol %), 4-bromoanisole (3 mmol), phenylboronic acid (4.5 mmol), K_3PO_4 (9 mmol), and dioxane (5 mL) were stirred for 5 h at 80 °C under open air conditions.
[b] Isolated yields.

3. Experimental section

3.1. General experimental procedures

TLC plates (Merck Silica Gel 60 F254) were used for analytical TLC and Merck Kieselgel 60 was used for preparative column chromatography. ^{1}H NMR spectra were acquired on a Brucker AM 400 operating at 400 MHz, in $CDCl_3$ (δ values are referred to $CHCl_3$ at 7.26 ppm). ^{13}C NMR spectra were

acquired on a Brucker AM 400 operating at 100 MHz, in $CDCl_3$ (δ values are referred to $CDCl_3$ at 77.0 ppm). IR spectra were recorded using NaCl cells or mixture compounds/KBr. Mass spectra were obtained on a GC/MS Shimadzu QP-5050 (EI, 70 eV). Melting points were determined on a Tottoli capillary melting point apparatus and are uncorrected. EPR spectra were recorded at 25 °C using a computer-controlled Brucker ER 200 D spectrometer operating at the X band with 100 kHz modulation frequency. The following conditions were used: 10 mW; modulation amplitude, 4 G; receiver gain, from 1.25×10^3 to 25×10^3. Colloidal Pd(0)/Napht$^{2.2+}$ solutions were analyzed by Scanning Electron Microscopy (SEM) using a HITACHI S2500 instrument. Transmission Electron Microscopy (TEM) images were taken by placing a drop of Pd(0)/Napht$^{2.2+}$ in dioxane onto a carbon film supported copper grid. Samples were studied using a Philips CM20 instrument with LaB6 cathode operating at 200 kV.

Each compound prepared herein was characterized by GC/MS, IR, and ^1H and ^{13}C NMR spectroscopies. All reported yields are based on the weight of the isolated product.

Gas chromatographic analyses were performed on a Shimadzu GC-17 capillary gas chromatograph fitted with an 'Optima 5' column (22 m×0.25 mm, ID×0.25 μm). All quantifications of reaction constituents were achieved by gas chromatography using a known quantity of decane or dodecane as reference standard.

All reagents were obtained commercially and used without further purification.

3.2. Preparation of the Pd(0)/Napht$^{2.2+}$ nanocatalyst

Typical procedure for reactions performed with 0.6 mol % catalyst: in a 10 mL Schlenk tube were introduced successively 2 mL anhydrous dioxane, $PdCl_2$ (0.018 mmol), and the naphthidine **1a** (0.018 mmol). The solution was stirred at room temperature for 2 h before use as catalyst.

3.3. Typical procedure for the Suzuki–Miyaura reaction

A Schlenk tube was charged with the arylboronic acid (4.5 mmol), the aryl halide (3.0 mmol), K_3PO_4 (9.0 mmol), and 4 mL dioxane. After stirring at room temperature for 5 min, the colloidal solution of Pd(0)/Napht$^{2.2+}$ previously prepared was added and the mixture was heated at 80 °C. The reaction was followed by GC or GC/MS analysis. When completion was reached, the reaction mixture was cooled to room temperature and dioxane was evaporated under reduced pressure. The crude material obtained was purified by silica gel column chromatography.

3.4. Reusability study

After the completion of the reaction, the Pd(0)/**1a**$^{2.2+}$ catalyst was recovered from the reaction mixture by centrifugation (4000 rpm for 10 min) and reused under identical reaction conditions to those for the first run.

3.5. Spectroscopic characterization of products

3.5.1. Biphenyl (Table 1, entries 1–3)[25b]

White solid; mp: 68–70 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J=8.3 Hz, 4H), 7.37 (d, J=8.3 Hz, 4H); 7.28 (t, J=7.5 Hz, 2H). EIMS (m/z): 154 (M^+).

3.5.2. 2-Methoxybiphenyl (Table 3, entry 4)[27]

Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (td, J=7.0, J'=1.5 Hz, 2H), 7.39 (td, J=7.1 and 1.1 Hz, 2H), 7.30 (td, J=7.4 and 1.6 Hz, 3H), 7.04–6.94 (m, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 138.5, 130.9, 130.6, 130.0, 128.6, 128.0, 126.9, 120.8, 111.1, 55.5. EIMS (m/z): 184 (M^+).

3.5.3. 3-Methoxybiphenyl (Table 3, entry 5)[28]

Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.51–7.59 (m, 2H), 7.34–7.44 (m, 2H), 7.24–7.34 (m, 2H), 7.06–7.18 (m, 2H), 6.85 (ddd, J=0.9, 2.5 and 8.2 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 142.6, 141.0, 129.7, 128.7, 127.3, 127.1, 119.6, 112.8, 112.5, 55.1. EIMS (m/z): 184 (M^+).

3.5.4. 4-Methoxybiphenyl (Table 3, entry 6)[25b]

White solid; mp: 90–91 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54–7.44 (m, 4H), 7.42–7.35 (m, 2H), 7.28–7.23 (m, 1H), 6.98 (d, J=8.3 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 140.8, 133.8, 128.7, 128.1, 126.8, 126.7, 114.2, 55.4. EIMS (m/z): 184 (M^+).

3.5.5. 2-Nitrobiphenyl (Table 3, entry 7)[29]

Yellow solid; mp: 37–38 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (q, J=2.5 Hz, 1H), 7.65–7.58 (m, 1H), 7.47–7.43 (m, 5H), 7.33–7.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 137.7, 136.6, 132.6, 132.3, 129.0, 128.5, 128.5, 128.3, 128.2, 124.4. IR (ν, cm^{-1}) (KBr): 2920, 2850, 1598, 1353, 1110, 1025, 847, 709. EIMS (m/z): 199 (M^+).

3.5.6. 3-Nitrobiphenyl (Table 3, entry 8)[25b]

Yellow solid; mp: 59–60 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.19 (dd, J=8.2 and 1.5 Hz, 1H), 7.88 (dd, J=8.2 and 1.5 Hz, 1H), 7.52–7.68 (m, 3H), 7.35–7.49 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 142.9, 138.7, 133.2, 129.9, 129.3, 128.7, 127.3, 122.1, 122.0. IR (ν, cm^{-1}) (KBr): 2920, 1598, 1572, 1514, 1349, 1097, 1005, 843, 701. EIMS (m/z): 199 (M^+).

3.5.7. 4-Nitrobiphenyl (Table 3, entry 9)[29]

Yellow solid; mp: 113–115 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J=8.7 Hz, 2H), 7.70 (d, J=8.7 Hz, 2H), 7.60 (t, J=7.5 Hz, 2H), 7.51–7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 147.0, 138.7, 129.1, 128.9, 127.7, 127.4, 124.1. IR (ν, cm^{-1}) (KBr): 2920, 2850, 1598, 1097, 1005, 843, 701. EIMS (m/z): 199 (M^+).

3.5.8. 1,4-Diphenylbenzene (Table 3, entry 10)[30]

White solid; mp: 212 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74–7.70 (m, 8H), 7.50 (t, J=7.2 Hz, 2H), 7.40

(t, J=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 140.1, 128.7, 127.5, 127.2, 127.0. EIMS (m/z): 230 (M^+).

3.5.9. 4-(N,N-Dimethylamino)biphenyl (Table 3, entry 11)[31]

White solid; mp: 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.25 (m, 5H), 7.50–6.82 (m, 4H), 3.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 136.4, 129.3, 128.8, 127.9, 127.7, 126.0, 114.8, 40.6. EIMS (m/z): 197 (M^+).

3.5.10. N,N-Dimethyl-4-(naphthyl)benzenamine (Table 3, entry 12)

White solid; mp: 109–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.37 (m, 7H), 7.29–7.23 (m, 2H), 6.55–6.47 (m, 2H), 2.84 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 140.6, 134.0, 131.8, 130.9, 128.3, 126.9, 126.4, 125.6, 40.5. EIMS (m/z): 247 (M^+).

3.5.11. 4-Phenylaniline (Table 3, entries 13 and 14)[32]

Brown solid; mp: 45–47 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J=8.4 Hz, 2H), 7.38 (d, J=8.4 Hz, 2H), 7.38–7.12 (m, 3H), 6.68 (d, J=8.4 Hz, 2H), 3.58 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 141.2, 132.0, 131.5, 128.7, 128.0, 126.4, 126.3, 116.7, 115.4. IR (ν, cm^{-1}) (KBr): 3424, 3382, 3206, 1617, 1493, 1461, 1443, 1298, 1146, 1122, 1070, 764. EIMS (m/z): 171 (M^+).

3.5.12. 4-Hydroxybiphenyl (Table 3, entry 15 and 16)[33]

White solid; mp: 165–167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J=8.2 Hz, 2H), 7.42 (d, J=8.2 Hz, 2H), 7.35–7.20 (m, 5H), 1.15 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 139.5, 129.2, 128.3, 127.4, 121.8, 121.1, 116.9. IR (ν, cm^{-1}) (KBr): 3491, 3419, 3032, 3014, 1697, 1573, 1487, 1427, 1328, 1205, 1167, 1087, 1027, 884, 791. EIMS (m/z): 170 (M^+).

3.5.13. 4-Phenylthioanisole (Table 3, entry 17)[34]

Yellow solid; mp: 107–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.39 (m, 5H), 7.31 (m, 2H), 7.22 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 138.0, 137.6, 128.8, 127.4, 127.1, 126.9, 126.8. EIMS (m/z): 200 (M^+).

3.5.14. [1,1′-Biphenyl]-2-carbaldehyde (Table 3, entry 18)[8a]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 8.02 (dd, J=7.5 and 1.8 Hz, 1H), 7.63 (dd, J=7.5 and 1.4 Hz, 1H), 7.51–7.34 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 146.0, 137.7, 133.7, 133.5, 130.7, 130.1, 128.4, 128.1, 127.8, 127.5. IR (ν, cm^{-1}) (NaCl): 3061, 2849, 2753, 1692, 1597, 1196, 747, 702, 645. EIMS (m/z): 182 (M^+).

3.5.15. 2-Carbomethoxybiphenyl (Table 3, entry 19)[35]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.35 (m, 8H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 142.7, 141.6, 131.5, 131.0, 130.0, 129.0, 128.6, 127.5, 127.4, 66.1, 52.2. IR (ν, cm^{-1}) (NaCl): 2949, 1731, 1478, 1451, 1439, 1431, 1283, 1249, 1126, 1090, 1050. EIMS (m/z): 212 (M^+).

3.5.16. 4-Carbomethoxybiphenyl (Table 3, entry 20)[8a]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J=8.4 Hz, 2H), 7.69–7.63 (m, 4H), 7.50–7.38 (m, 3H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 145.4, 140.0, 130.2, 129.0, 128.2, 127.3, 127.0, 52.2. IR (ν, cm^{-1}) (NaCl): 2955, 1726, 1474, 1442, 1289, 1251, 1128, 1090. EIMS (m/z): 212 (M^+).

3.5.17. 4-[1]Naphthylbenzonitrile (Table 3, entry 21)[36]

Red solid; mp: 76–77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.83 (m, 2H), 7.75–7.63 (m, 3H), 7.51–7.43 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 138.2, 133.9, 132.2, 131.0, 128.9, 128.7, 126.8, 126.3, 125.5, 125.2, 119.0, 111.2. IR (ν, cm^{-1}) (KBr): 2255, 1509, 1473, 1457, 1441, 1289, 1269, 1129, 1095, 1070, 790. EIMS (m/z): 229 (M^+).

3.5.18. 4-Acetyl-3′-methylbiphenyl (Table 3, entry 22)[37]

White solid; mp: 84–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J=8.5 Hz, 2H), 7.68 (d, J=8.5 Hz, 2H), 7.33–7.44 (m, 3H), 7.20–7.26 (m, 1H), 2.64 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 145.8, 139.7, 138.5, 135.7, 128.9, 128.8, 127.9, 127.1, 124.3, 26.5, 21.4. IR (ν, cm^{-1}) (KBr): 3019, 1683, 1483, 1469, 1298, 1270, 787. EIMS (m/z): 210 (M^+).

3.5.19. 2-(2′-Methylphenyl)benzyl alcohol (Table 3, entry 23)[38]

White solid; mp: 81–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.44 (m, 2H), 7.40–7.26 (m, 2H), 7.17–7.11 (m, 4H), 4.71 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 140.5, 134.3, 132.1, 132.0, 131.3, 128.6, 127.5, 127.1, 126.2, 126.0, 125.8, 41.8, 40.9. IR (ν, cm^{-1}) (KBr): 3350, 3061, 2958, 2926, 1596, 1512, 1476, 1465, 1443, 1376, 1246, 1109, 1023, 945, 846, 753. EIMS (m/z): 198 (M^+).

3.5.20. 2-Methoxy-2′-methylbiphenyl (Table 3, entry 24)[39]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, J=8.2 and 1.7 Hz, 1H), 7.36–7.24 (m, 5H), 7.10 (dd, J=7.4 and 0.9 Hz, 1H), 7.05 (d, J=8.2 Hz, 1H), 3.84 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 138.6, 136.7, 130.9, 130.8, 129.9, 129.5, 128.5, 127.2, 125.4, 120.4, 110.5, 55.3, 19.9. EIMS (m/z): 199 (M^+).

3.5.21. 4′-Nitro-2,4,6-trimethylbiphenyl (Table 3, entry 25)[40]

Yellow solid; mp: 90–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J=8.0 Hz, 2H), 7.29 (d, J=8.0 Hz, 2H), 6.96 (s, 2H), 2.32 (s, 3H), 2.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 146.7, 137.5, 136.7, 135.0, 130.4, 128.4, 123.6, 20.9, 29.5. IR (ν, cm^{-1}) (KBr): 2920, 2850, 1598, 1572, 1514, 1343, 1105, 1097, 1005, 843, 701. EIMS (m/z): 243 (M^+).

3.5.22. 2-Phenylpyridine (Table 3, entry 26)[41]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70–8.67 (m, 1H), 8.00–7.96 (m, 2H), 7.73–7.68 (m, 2H), 7.50–7.44 (m, 2H), 7.42–7.36 (m, 1H), 7.23–7.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 149.5, 139.3, 136.5, 128.8, 128.7, 126.7, 122.1, 120.4. EIMS (*m*/*z*): 155 (M^+).

3.5.23. 3-Phenylpyridine (Table 3, entry 27)[41]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (d, J=1.8 Hz, 1H), 8.59 (d, J=1.8 Hz, 1H), 7.87–7.85 (m, 1H), 7.58–7.55 (m, 2H), 7.50–7.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 148.2, 137.8, 136.7, 134.5, 129.1, 128.1, 127.2, 123.6. EIMS (*m*/*z*): 155 (M^+).

3.5.24. 2-Chloro-5-phenylpyridine (Table 3, entry 28)[42]

White solid; mp: 55 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J=1.8 Hz, 1H), 7.87–7.81 (dd, J=8.0 and 2.5 Hz, 1H), 7.58–7.37 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 139.6, 133.3, 128.9, 128.8, 128.4, 127.5, 127.0. EIMS (*m*/*z*): 188 (M^+).

3.5.25. 5-(1-Naphthyl)pyrimidine (Table 3, entry 29)

White solid; mp: 140–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.92 (m, 3H), 7.59–7.54 (m, 1H), 7.48–7.42 (m, 3H), 7.40–7.35 (m, 1H), 7.28–7.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 134.0, 133.9, 133.2, 128.6, 128.5, 128.3, 128.2, 126.9, 126.4, 126.2, 125.8. EIMS (*m*/*z*): 206 (M^+).

3.5.26. 3-Phenylthiophene (Table 3, entries 30 and 31)[43]

Pale yellow solid; mp: 89–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J=7.2 Hz, 2H), 7.42 (m, 1H), 7.38–7.35 (m, 4H), 7.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 136.4, 129.3, 128.3, 128.2, 127.5, 121.6. EIMS (*m*/*z*): 160 (M^+).

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