DOI: 10.1002/ejic.200800154

N-Heterocyclic Benzhydrylamines as New *N*,*N*-Bidentate Ligands in Palladium Complexes: Synthesis, Characterization and Catalytic Activity

Vincent Terrasson,[a] Damien Prim,*[a] and Jérome Marrot[a]

Keywords: Nitriles / Benzhydrylamines / *N*,*N*-Ligands / Palladium

The synthesis of new *N*,*N*-bidentate ligands based on a π-deficient N-heterocyclic benzhydrylamine core is described. The corresponding air-stable palladium complexes are obtained in high yields and fully characterized by NMR spectroscopy and X-ray structure determination. These new phosphane-free catalytic systems proved efficient in the Suzuki–Miyaura reaction, enabling us to obtain biaryl products in good yields, also for reactions with *o*-substituted phenyl chlorides as starting materials. The effects of both electronic and steric modulations at the benzhydrylamine core on the catalytic activity are also described.

Introduction

Transition-metal-catalyzed bond formation has become a powerful chemical tool over the last decades. Among these catalyzed transformations, the Suzuki–Miyaura reaction has emerged as one of the most popular and general way to create carbon–carbon bonds and has thus found widespread applications in organic synthesis.[1] This Pd-assisted process offers many advantages over other transition-metal-catalyzed reactions, such as commercial availability of a large panel of boronic acid derivatives, easy handling, easy removal of boron residues, and high functional group tolerance, explaining the increasing interest not only in academic research but also in the industrial scientific community. Indeed, numerous drugs, materials, optical devices, or products of industrial significance, prepared by using at least one catalyzed C–C bond formation, have been recently patented and commercialized.[2] The catalytic system (ligand–Pd combination), of course, plays a crucial role in such processes.[3] The most often used ligands, which paved the way to the current success of Pd-catalyzed reactions, are tertiary phosphanes. Recent investigations[4] have shown that phosphane-free catalytic systems efficiently compete with P-based catalytic systems and overcome some of their known drawbacks such as cost, air-stability, degradation, or P-based waste management. The selection of a robust ligand involves an overall compromise between several significant criteria. If the whole efficiency of the catalytic system (catalyst loading, yields, conversion, etc.) is a key parameter, rapid access to the ligand, stability of both ligand and transition-metal complex, common starting materials, as well as ease of purification should also be taken into account. Even if significant progresses have been made, there is a steady demand for alternative, new, easy to prepare, stable ligands, and efficient catalytic systems. Herein, we report on a new series of *N*,*N*-bidentate ligands and their corresponding palladium complexes based on a N-heterocyclic benzhydrylamine framework (Figure 1).

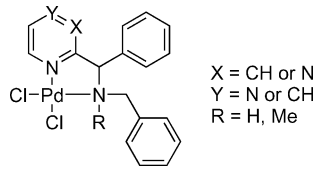


Figure 1. N-Heterocyclic benzhydrylamine-based Pd complexes.

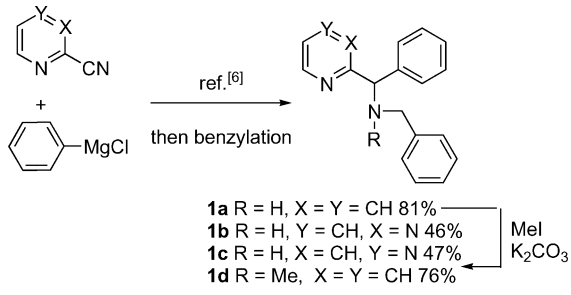
Such ligands are readily obtained in high yields from commercially available common reactants, and the access methodology allows facile structural modulation of the ligand. In addition, the corresponding Pd complexes are air-stable and reveal highly efficiency in the Suzuki–Miyaura reaction.

Results and Discussion

We first focused our attention on model compound **1a**, whose structure is based on a benzylamine core substituted by a pyridine ring. Although access to arylmethylamines can be envisioned through several metal-catalyzed processes,[5] methylamine **1a** was prepared in a one-pot sequence involving addition of phenylmagnesium chloride to 2-cyanopyridine and subsequent reduction according to our previously described methodology.[6] Benzylation of the primary amine proved judicious in increasing the solubility of

[a] Institut Lavoisier UMR CNRS 8180, Université de Versailles-Saint-Quentin-en-Yvelines,
45, avenue des Etats-Unis, 78035 Versailles, France
Fax: +33-1-39254452
E-mail: prim@chimie.uvsq.fr

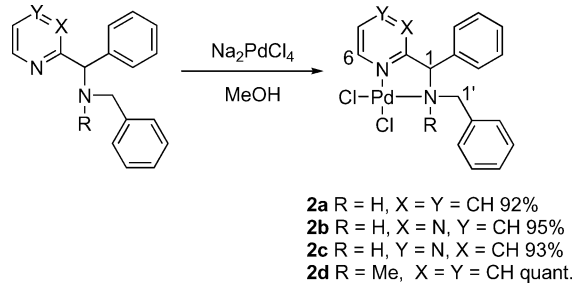
the complex in most common solvents (CH_2Cl_2, EtOAc, etc.), thus making isolation, purification, and characterization easier. With the aim to develop new ligand series, we chose to modulate both electronic and steric effects over model compound **1a**. Indeed, using the same straightforward methodology, we were able to prepare new pyrimidine and pyrazine analogues, **1b** and **1c**, respectively (Scheme 1). The question was whether the presence of a second nitrogen atom and its relative position in the π-deficient heterocycle could influence complexation properties, structures of the complexes, and their catalytic activities. Substitution at the methylamine nitrogen atom was also modified by further alkylation, leading to a tertiary amine.



Scheme 1. Preparation of hetero-biarylmethylamine ligands.

In order to prepare the corresponding Pd complexes **2a**–**2d**, complexation reactions were next examined. Compounds **1a**–**d** were treated with Na_2PdCl_4 under classical conditions[7] to give the expected Pd^{II} complexes **2** in high yields ranging from 92% to quantitative (Scheme 2). The reaction proceeded smoothly at room temperature in freshly distilled methanol. After several hours, precipitation of complexes **2a**–**c** was observed. In contrast, after 16 h, **2d** remained soluble. In all cases, the solvent was removed, and the solid residue was purified by simple filtration through a silica gel pad to afford the corresponding palladium complex. These complexes are perfectly air-stable, both in the solid state and in solution.

It is worth noting that increasing nitrogen atom substitution from **1a** to **1d** did not affect complexation yields. Similarly, moving from pyridine in **1a** to pyrimidine and pyrazine in **1b** and **1c**, respectively led to no significant variation in isolated yields for the corresponding complexes. NMR spectroscopic data of complexes **2a**–**2d** are in good agreement with their respective structures. In addition, the presence of only one set of signals in the ^1H NMR spectra



Scheme 2. Preparation of Pd complexes **2**.

for all complexes indicates that the complexation process selectively afforded only one of the possible (*rac*-)diastereomers. Selected ^1H NMR chemical shifts are gathered in Table 1.

Characteristic positive shieldings ranging from 0.46 to 0.82 ppm for benzyl protons H(1) and H(1′) are observed between ligands **1a**–**1d** and their complexes **2a**–**2d**, thus confirming coordination by the metal center. However, it is worth noting that close chemical shifts of benzyl protons H(1) and H(1′) in both ligands **1a**–**1c** and the corresponding complexes **2a**–**2c** are observed, regardless of the heterocyclic substituent. Interestingly, H(6) protons exhibit only poor shielding regardless of the heterocycle and the presence of additional substituents at the methylamine fragment.

Single crystals suitable for X-ray analysis were obtained by slow evaporation of dmso solutions of complexes **2a**, **2c**, and **2d** (Figure 2).[8]

It is worth noting that all structures present similar arrangements. Selected bond lengths and angles are presented in Table 2. For example, Pd–N(1) and Pd–N(8), as well as Pd–Cl(1) and Pd–Cl(2) bond lengths in all complexes are very close. Similarly, C(2)–N(1)–Pd and C(7)–N(8)–Pd angles range from 113.7 to 115.3° and from 105.4 to 108.9°, respectively. Only a small variation of the Pd-plane deviation between **2a**, **2c**, and **2d** has been observed.

It is also worth to note that large substituents at C(7) and N(8) arranged in an *anti* fashion during the complexation process. Minimization of steric factors between these substituents in the corresponding ligands probably account for these preferred relative configurations at the rigid diazametallacyclopentane in **2a**, **2c**, and **2d**. Thus, obtention of one (*rac*-)diastereomer is strongly supported by both ^1H NMR spectroscopic data in solution (Table 2) and crystallographic data in the solid state.

Table 1. Selected ^1H NMR chemical shifts.

Entry	Series	$\delta_{(H1')}$ [ppm]			$\delta_{(H1)}$ [ppm]			$\delta_{(H6)}$ [ppm]		
		1	**2**	$\delta_{H(complex)} - \delta_{H(ligand)}$	**1**	**2**	$\delta_{H(complex)} - \delta_{H(ligand)}$	**1**	**2**	$\delta_{H(complex)} - \delta_{H(ligand)}$
1	**a**	3.62	4.09	0.47	4.85	5.42	0.57	8.47	8.53	0.06
2	**b**	3.64	4.14	0.50	4.94	5.51	0.57	8.75	8.75	0
3	**c**	3.65	4.11	0.46	4.95	5.57	0.62	8.49	8.57	0.08
4	**d**	3.43	4.17	0.74	4.63	5.45	0.82	8.46	8.67	0.21

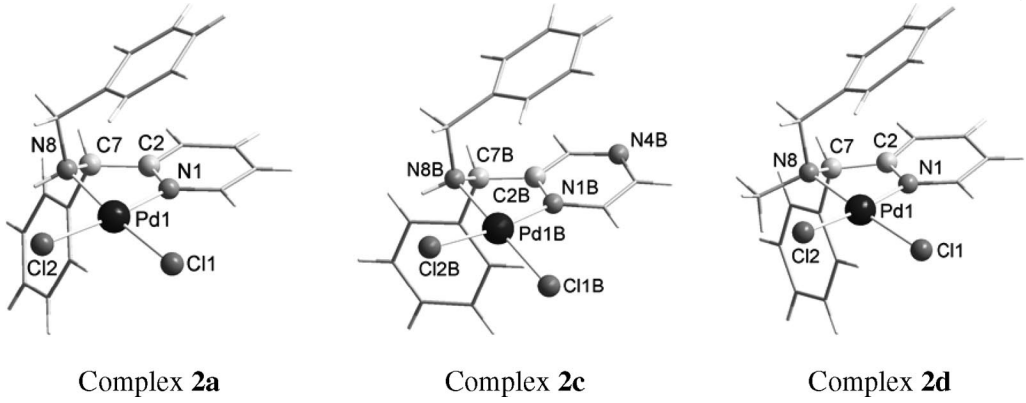


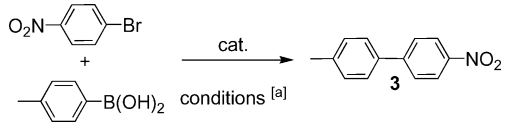
Figure 2. X-ray structures of complexes **2a**, **2c**, and **2d**.

Table 2. Selected crystallographic data for complexes **2a**, **2c**, and **2d**.

Complex	Bond lengths [Å]				Angles [°]		Pd-plane
	N(1)–Pd	N(8)–Pd	Cl(1)–Pd	Cl(2)–Pd	C(2)–N(1)–Pd	C(7)–N(8)–Pd	deviation
2a	2.021	2.031	2.303	2.282	114.9	108.9	0.062
2c	2.023	2.043	2.289	2.281	113.7	105.4	0.043
2d	2.020	2.083	2.293	2.300	115.3	107.1	0.039

At this stage, we started to evaluate the catalytic activity of methylamine-based complexes **2a**–**2d**. The preliminary study and comparison of our four catalytic systems for the preparation of 4-methyl-4′-nitro-1,1′-biphenyl (**3**) are shown in Table 3. The behavior of complex **2a** was first examined in the Suzuki reaction shown in Table 3. The model compound could be easily obtained in quantitative yield by using classical reaction conditions (Table 3, entry 1). When the catalyst loading was lowered to 0.01 mol-%, longer reaction courses (4 h) were required to reach quantitative conversions (compare entries 2 and 3). Attempts to further decrease the catalyst loading to 10^{-3} mol-% failed, leading to poor conversion even after prolonged heating times. The nature of the base was next examined. Under the same conditions, moving from K_2CO_3 to K_3PO_4 (entry 4) and Cs_2CO_3 (entry 5) gave various results. The use of K_3PO_4 afforded a lower conversion rate. In contrast, Cs_2CO_3 as the base was found to be superior, significantly enhancing the reaction rate and allowing quantitative access to the model compound within 2 h (entry 7). These preliminary results clearly demonstrate that this first catalytic system represents a good compromise between the overall catalytic activity and the easy obtention of the methylamine ligand. It was then debatable, whether electronic and steric modifications of catalyst **2a** would modulate the catalytic activity and improve the results we already described. The steric effect was next examined. Comparison of catalysts **2a** and **2d** under identical reaction conditions (entries 5 and 8) led to similar conversion after 30 min, indicating that an increase in substitution at the methylamine nitrogen atom only poorly affected the catalytic process. The same procedure was applied for complexes **2b** and **2c**, bearing pyrimidine and pyrazine heterocycles, respectively. Interestingly, the use of the latter catalytic systems afforded higher conversions in the same 30-minute time frame (entries 9 and 10). Moreover, the relative positions of the two nitrogen atoms in the heterocycle seemed to affect the overall coupling process. Indeed, pyrazine-based complex **2c** compared favorably to

Table 3. Evaluation of catalytic activity.



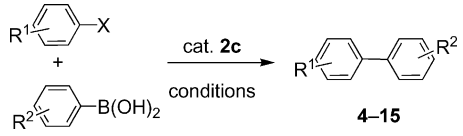
Entry	Cat. (mol-%)	Base	Time [h]	Conversion[b] [%]
1	**2a** (1)	K_2CO_3	0.5	quant.
2	**2a** (0.01)	K_2CO_3	1	43
3	**2a** (0.01)	K_2CO_3	4	quant.
4	**2a** (0.01)	K_3PO_4	1	31
5	**2a** (0.01)	Cs_2CO_3	0.5	34
6	**2a** (0.01)	Cs_2CO_3	1	62
7	**2a** (0.01)	Cs_2CO_3	2	96
8	**2d** (0.01)	Cs_2CO_3	0.5	28
9	**2b** (0.01)	Cs_2CO_3	0.5	50
10	**2c** (0.01)	Cs_2CO_3	0.5	70
11	**2c** (0.01)	Cs_2CO_3	1	quant. (92)[c]
12	**2c** (0.01)[d]	K_2CO_3	2	82
13	**2c** (0.1)[e]	Cs_2CO_3	18	quant.

[a] Conditions: Bromonitrobenzene (0.5 mmol), 4-methylbenzeneboronic acid (0.6 mmol, 1.2 equiv.), base (1.25 mmol, 2.5 equiv.), dmf/H_2O (95:5, 1 mL), 100 °C. [b] Based on ^{1}H NMR spectra. [c] Isolated yield [%]. [d] Reaction conducted in water. [e] Reaction conducted at 50 °C.

pyrimidine-based complex **2b** and quantitatively afforded the expected coupling product **3** within 1 h (entry 11). At this stage, the exact role of the two nitrogen atoms and the influence of their relative position on the outcome of the catalytic process are not fully stated. Also worth noting are the results obtained in pure aqueous media and at lower temperatures. Interestingly, biphenyl **3** could be obtained in high yield (82%) by using complex **2c** as the catalyst (entry 12) in environmentally more friendly pure aqueous media. In addition, all coupling reactions were run at 100 °C in aqueous dmf, which potentially hampers the use of thermally sensitive substrates. Thus, we envisioned decreasing the reaction temperature. Although no coupling reaction could be observed at 25 °C, even for prolonged reaction times, quantitative conversions have been obtained in 18 h at 50 °C (entry 13).

Table 4 gathers the results of an aromatic substitution survey for this reaction. Variously substituted bromobenzenes were successfully coupled with substituted phenylboronic acids by using **2c** as the catalyst. Disappearance of the starting aromatic halides was monitored by TLC (times indicated in Table 4) and confirmed by ^{1}H NMR spectroscopy of the crude material. Compounds **4** to **15** were obtained in high yields after easy isolation and filtration of the crude product over a silica gel pad.

Table 4. Suzuki reaction.



Entry	R^1	X	R^2	Cat. [mol-%] - Conditions[a]	Time [h]	Comp.	Conv. (%)[b]
1	4-NO_2	Br	2,4-$(MeO)_2$	0.01 - A	4	**4**	quant. (95)
2	4-NO_2	Br	4-CF_3	0.01 - A	5	**5**	quant. (95)
3	4-CHO	Br	H	0.01 - A	2	**6**	95 (90)
4	4-CHO	Br	2-Me	0.01 - A	3	**7**	quant. (95)
5	4-CHO	Br	3-NO_2	0.01 - A	5	**8**	quant. (97)
6	4-Ac	Br	H	0.01 - A	2	**9**	44
7	4-Ac	Br	H	0.01 - B	2	**9**	quant. (93)
8	4-OH	Br	H	0.01 - B	4	**10**	quant. (95)
9	4-OMe	Br	H	0.1 - A	72	**11**	85
10	4-OMe	Br	H	0.1 - B	18	**11**	quant. (89)
11	2-CN	Br	2-Me	0.05 - A	12	**12**	quant. (89)
12	4-CN	Cl	2-Me	0.2 - A	24	**13**	quant. (75)
13	2-CHO	Cl	4-MeO	0.2 - A	24	**14**	quant. (74)
14	2-NO_2	Cl	4-MeO	0.2 - A	24	**15**	quant. (78)

[a] Conditions: Aromatic halide (0.5 mmol), boronic acid (0.6 mmol, 1.2 equiv.), base (1.25 mmol, 2.5 equiv.), solvent (1 mL), 100 °C, A: Cs_2CO_3, dmf/H_2O (95:5), B: K_2CO_3, H_2O. [b] Conversion based on ^{1}H NMR spectra, isolated yields are within brackets.

A first set of aromatic bromides reacted with phenylboronic acids bearing either electronic donating or withdrawing groups under the aforementioned catalytic conditions (entries 1–10). For reaction times of 2 to 5 h, regardless of the substituent on the phenylboronic acid (entries 1–8), the presence of a strong donating group at the halide partner affected the reaction course. Indeed, complete conversions required increased reaction times and higher catalyst loadings (entries 9–10). Biphenyl **12**, bearing two *o*,*o*′-substituents, was successfully prepared and isolated in 89% yield by using 0.05 mol-% of catalyst **2c** (entry 11). It is worth noting that the use of pure water instead of aqueous dmf may afford increased conversions and yields. Indeed, biphenyls **9** and **11** were readily obtained in 93 and 89% respective yield in inorganic media (compare entries 6–7 and 9–10). Finally, catalytic system **2c** (0.2 mol-%) also proved to be efficient in the coupling reaction of aromatic chlorides and boronic acids substituted in an *ortho* or *para* fashion (entries 12–14).

Conclusion

We have developed efficient and robust phosphane-free catalytic systems based on a N-heterocyclic benzhydrylamine core for Suzuki couplings. Such new, stable Pd^{II} complexes represent a useful compromise between catalyst efficiency (catalyst loading, yields), facile and short preparation of ligands and complexes, compatibility with chloride substrates, *ortho*-substituted coupling partners, and pure aqueous and mild reaction conditions.

Experimental Section

General Remarks: Reactions were carried out in round-bottomed flasks equipped with a magnetic stirring bar and capped with a septum. Diethyl ether was distilled from Na/benzophenone and methanol over Mg/I_2. TLC analyses were performed on Merck silica gel 60 F_{254} TLC plates (0.5 mm thickness). FTIR spectra were recorder with a Perkin–Elmer Spectrum BX spectrometer, and ^{1}H and ^{13}C spectra were recorded with Bruker 200 and Advance-300 spectrometers and referenced to $CDCl_3$ or $[D_6]$dmso. Mass spectra were obtained at the mass spectrometry facilities operated by the ENSC Clermont-Ferrand.

Synthesis of the Phenyl(pyrazin-2-yl)methylamine: Biarylmethylamines were synthesized by following our previously described procedure:[6] to a stirred solution of pyrazine-2-carbonitrile (1 g, 9.50 mmol) in freshly distilled diethyl ether (25 mL) at 0 °C under argon was added dropwise a solution of phenylmagnesium chloride (7.50 mL, 1.9 M, 14.27 mmol) in thf. The reaction mixture was stirred at room temperature for 16 h, and the solvent was removed by evaporation. The residue was then dissolved in MeOH (25 mL), $NaBH_4$ (360 mg, 9.50 mmol) was added at 0 °C, and the mixture was stirred at room temperature for 4 h. After concentration of the solution under vacuum, saturated aqueous NH_4Cl solution (25 mL) was added, and the aqueous phase was extracted with EtOAc (3 × 25 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel to give the pure methylamine (1.11 g, 5.99 mmol, 63%) as an orange oil. R_f = 0.15 (5% MeOH in EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 2 H, NH_2), 5.20 (s, 1 H), 7.15–7.27 (m, 3 H), 7.29–7.33 (m, 2 H), 8.32 (d, J = 2.50 Hz, 1 H), 8.41 (dd, J = 1.50 and 2.50 Hz, 1 H), 8.49 (d, J = 1.50 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 59.0, 126.8 (2 C), 127.5, 128.7 (2 C), 142.9, 143.4, 143.6, 143.7, 158.6 ppm. IR (film): $\tilde{\nu}$ = 3360, 3288, 3058, 3027, 2919, 1685, 1491, 1470, 1450, 1399, 1143, 1050, 1020, 851, 753, 697, 600 cm^{-1}. MS (CI, CH_4): *m*/*z* (%) = 371 (20) $[2M + H]^+$, 352 (35), 186 (95) [M +

H]$^+$, 169 (100) [M – NH_2]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 186.1031; found 186.1026.

Benzylation of Primary Amines: To a stirred solution of biarylmethylamine (2 mmol) and $MgSO_4$ (481 mg, 4 mmol) in MeOH (20 mL) was added benzaldehyde (202 μL, 212 mg, 2 mmol). The mixture was stirred at room temperature for 12 h, then cooled to 0 °C, and $NaBH_4$ (76 mg, 2 mmol) was added. The reaction mixture was stirred at room temperature for 4 h. The solution was then concentrated under vacuum, and saturated aqueous NH_4Cl solution (25 mL) were added. The aqueous phase was extracted with EtOAc (3 × 25 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel.

***N*-Benzyl-*N*-[phenyl(pyridin-2-yl)methyl]amine (1a):** Yield 490 mg (90%); yellow oil; R_f = 0.20 (20% EtOAc in cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.88 (s, 1 H, NH), 3.60 (d, J = 13.3 Hz, 1 H), 3.67 (d, J = 13.3 Hz, 1 H), 4.86 (s, 1 H), 6.93 (ddd, J = 1.0, 4.9, and 7.4 Hz, 1 H), 7.07–7.13 (m, 2 H), 7.16–7.24 (m, 7 H), 7.34–7.37 (m, 2 H), 7.40 (td, J = 1.8 and 7.6 Hz, 1 H), 8.42 (d, J = 4.8 Hz, 1 H) ppm. ^{1}H NMR (300 MHz, [D_6]dmso): δ = 3.26 (s, 1 H, NH), 3.62 (t, J = 14.6 Hz, 2 H), 4.85 (s, 1 H), 7.19–7.24 (m, 3 H), 7.25–7.32 (m, 6 H), 7.39–7.43 (m, 2 H), 7.50 (d, J = 7.9 Hz, 1 H), 7.73 (td, J = 1.8 and 7.7 Hz, 1 H), 8.47 (d, J = 4.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 50.6, 66.6, 121.4, 122.0, 126.6, 126.9, 127.4 (2 C), 128.0 (2 C), 128.1 (2 C), 128.3 (2 C), 136.7, 140.5, 143.1, 148.7, 162.8 ppm. IR (film): $\tilde{\nu}$ = 3324, 3083, 3063, 3027, 2832, 1670, 1583, 1568, 1496, 1475, 1450, 1434, 1117, 1025, 989, 743, 697, 615, 543 cm^{-1}. MS (CI, NH_3): m/z (%) = 275 (100) [M + H]$^+$. HRMS (ESI):calcd. for [M + H]$^+$ 275.1548; found 275.1551.

***N*-Benzyl-*N*-[phenyl(pyrimidin-2-yl)methyl]amine (1b):** Yield 436 mg (79%); brown solid; R_f = 0.30 (50% EtOAc in cyclohexane); m.p. 73 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.48 (s, 1 H, NH), 3.64 (d, J = 13.1 Hz, 1 H), 3.73 (d, J = 13.1 Hz, 1 H), 5.03 (s, 1 H), 7.06 (t, J = 5.0 Hz, 1 H), 7.15–7.30 (m, 8 H), 7.38–7.41 (m, 2 H), 8.62 (d, J = 5.0 Hz, 2 H) ppm. ^{1}H NMR (300 MHz, [D_6]dmso): δ = 3.36 (s, 1 H, NH), 3.64 (s, 2 H), 4.94 (s, 1 H), 7.21–7.24 (m, 2 H), 7.27–7.32 (m, 6 H), 7.36 (t, J = 4.9 Hz, 1 H), 7.40–7.43 (m, 2 H), 8.77 (d, J = 4.9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.3, 67.5, 119.2, 127.0, 127.5, 127.8 (2 C), 128.4 (2 C), 128.5 (2 C), 128.6 (2 C), 139.9, 141.3, 157.2 (2 C), 170.9 ppm. IR (in KBr): $\tilde{\nu}$ = 3304, 3083, 3053, 3017, 2940, 2843, 1783, 1562, 1491, 1460, 1419, 1117, 1020, 820, 748, 697, 595, 549 cm^{-1}. MS (CI, CH_4): m/z (%) = 276 (100) [M + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 276.1501; found 276.1519.

***N*-Benzyl-*N*-[phenyl(pyrazin-2-yl)methyl]amine (1c):** Yield 414 mg (75%); yellow solid; R_f = 0.30 (30% EtOAc in cyclohexane); m.p. 79 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.59 (s, 1 H, NH), 3.62 (d, J = 13.2 Hz, 1 H), 3.69 (d, J = 13.2 Hz, 1 H), 4.90 (s, 1 H), 7.13–7.18 (m, 2 H), 7.20–7.26 (m, 6 H), 7.32–7.36 (m, 2 H), 8.28 (d, J = 2.7 Hz, 1 H), 8.37 (dd, J = 1.5 and 2.5 Hz, 1 H), 8.52 (d, J = 1.50 Hz, 1 H) ppm. ^{1}H NMR (300 MHz, [D_6]dmso): δ = 3.41 (s, 1 H, NH), 3.62 (d, J = 13.7 Hz, 1 H), 3.68 (d, J = 13.7 Hz, 1 H), 4.95 (s, 1 H), 7.20–7.26 (m, 2 H), 7.30–7.35 (m, 6 H), 7.43–7.46 (m, 2 H), 8.49 (d, J = 2.5 Hz, 1 H), 8.54 (dd, J = 1.5 and 2.5 Hz, 1 H), 8.83 (d, J = 1.50 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.4, 65.3, 127.0, 127.6 (2 C), 127.7, 128.1 (2 C), 128.3 (2 C), 128.7 (2 C), 139.6, 141.2, 142.9, 143.7, 144.0, 157.8 ppm. IR (in KBr): $\tilde{\nu}$ = 3298, 3048, 3022, 2919, 2832, 1470, 1450, 1404, 1112, 1061, 1015, 835, 753, 697, 620, 589, 538 cm^{-1}. MS (CI, CH_4): m/z (%) = 276 (100) [M + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 276.1501; found 276.1502.

Methylation of Amine 1a: To a stirred solution of methylamine **1a** (362 mg, 1.32 mmol) and K_2CO_3 (274 mg, 1.98 mmol) in MeCN (10 mL) was added dropwise methyl iodide (82 μL, 187 mg, 1.32 mmol). The mixture was stirred at room temperature for 16 h, and the reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (15 mL). The aqueous phase was extracted with EtOAc (3 × 25 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel to give tertiary amine **1d** (288 mg, 1 mmol, 76%) as a yellow oil.

***N*-Benzyl-*N*-methyl-*N*-[phenyl(pyridin-2-yl)methyl]amine (1d):** R_f = 0.45 (20% EtOAc in cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98 (s, 3 H), 3.34 (d, J = 13.5 Hz, 1 H), 3.49 (d, J = 13.5 Hz, 1 H), 4.55 (s, 1 H), 6.90 (ddd, J = 1.20, 4.90 and 7.40 Hz, 1 H), 7.05–7.22 (m, 6 H), 7.26–7.29 (m, 2 H), 7.44–7.48 (m, 3 H), 7.59 (d, J = 7.90 Hz, 1 H), 8.36 (d, J = 4.90 Hz, 1 H) ppm. ^{1}H NMR (300 MHz, [D_6]dmso): δ = 1.96 (s, 3 H), 3.38 (d, J = 13.5 Hz, 1 H), 3.48 (d, J = 13.5 Hz, 1 H), 4.63 (s, 1 H), 7.19–7.24 (m, 3 H), 7.26–7.40 (m, 6 H), 7.52–7.55 (m, 2 H), 7.71–7.80 (m, 2 H), 8.46 (d, J = 4.60 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.2, 59.6, 77.4, 121.8, 121.9, 126.7, 127.1, 128.1 (4 C), 128.4 (2 C), 128.5 (2 C), 136.5, 139.3, 141.6, 148.8, 162.6 ppm. IR (film): $\tilde{\nu}$ = 3083, 3058, 3027, 307, 2955, 2929, 2843, 2786, 1665, 1588, 1496, 1455, 1429, 1588, 1312, 1281, 1132, 1020, 917, 779, 743, 697, 615, 554 cm^{-1}. MS (CI, CH_4): m/z (%) = 289 (100) [M + H]$^+$. HRMS (ESI): calcd. for [M + H]$^+$ 289.1705; found 289.1698.

Preparation of Palladium Complexes: To a stirred solution of amine **1a**–**d** (0.25 mmol) in freshly distilled MeOH (5 mL) was added Na_2PdCl_4 (74 mg, 0.25 mmol). The mixture was stirred at room temperature for 16 h, and the solvent was removed by evaporation under vacuum. The residue was then filtered through a silica gel pad [firstly eluting with cyclohexane/EtOAc (7:3) to remove traces of free amine, then eluting with EtOAc] to give the corresponding palladium complexes.

Complex 2a: Yield 103 mg (92%); yellow powder; R_f = 0.60 (EtOAc). ^{1}H NMR (300 MHz, [D_6]dmso): δ = 3.95 (dd, J = 2.5 and 13.1 Hz, 1 H), 4.30 (dd, J = 4.2 and 13.1 Hz, 1 H), 5.46 (s, 1 H), 6.99 (s, 1 H, NH), 7.23–7.32 (m, 3 H), 7.34–7.39 (m, 2 H), 7.46–7.58 (m, 3 H), 7.88 (td, J = 1.4 and 7.7 Hz, 1 H), 7.95 (d, J = 7.1 Hz, 4 H), 8.57 (d, J = 5.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D_6]dmso): δ = 57.8, 73.0, 123.4, 124.2, 128.6 (2 C), 128.8 (3 C), 129.5 (2 C), 129.6, 131.7 (2 C), 134.7, 137.9, 140.5, 148.9, 166.2 ppm. IR (in KBr): $\tilde{\nu}$ = 3452, 3109, 3058, 3032, 2930, 2858, 1609, 1496, 1475, 1455, 1440, 1424, 1163, 1143, 912, 764, 692, 554 cm^{-1}. MS [ESI, MeCN/MeOH (4:1)]: m/z (%) = 462–453 (100) [M – Cl + MeCN]$^+$, 426–417 (50) [M – Cl – HCl + MeCN]$^+$, 416–407 (10), 386–377 (15) [M – Cl – HCl]$^+$. HRMS (ESI): calcd. for ([M – Cl – HCl]$^+$, ^{104}Pd) 377.0432; found 377.0444. $C_{19}H_{18}Cl_2N_2Pd$ (451.69): calcd. C 50.52, H 4.02, N 6.20; found C 50.59, H 4.10, N 6.28.

Complex 2b: Yield 107 mg (95%); yellow powder; R_f = 0.65 (EtOAc). ^{1}H NMR (300 MHz, [D_6]dmso): δ = 3.97 (d, J = 12.7 Hz, 1 H), 4.31 (dd, J = 3.7 and 12.7 Hz, 1 H), 5.51 (s, 1 H), 7.08 (s, 1 H, NH), 7.20–7.28 (m, 3 H), 7.39 (t, J = 5.3 Hz, 1 H), 7.45–7.54 (m, 3 H), 7.93 (d, J = 6.8 Hz, 2 H), 7.99 (d, J = 6.5 Hz, 2 H), 8.64 (dd, J = 2.1 and 6.0 Hz, 1 H), 8.75 (dd, J = 2.1 and 4.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D_6]dmso): δ = 57.5, 72.4, 120.5, 128.2 (2 C), 128.4 (2 C), 128.5, 129.0 (2 C), 129.3, 131.5 (2 C), 134.2, 136.2, 155.7, 159.7, 173.9 ppm. IR (in KBr): $\tilde{\nu}$ = 3447, 3150, 3073, 3027, 2925, 2848, 1778, 1588, 1552, 1501, 1450, 1419, 1363, 1255, 1096, 1035, 820, 769, 748, 707, 697, 661, 554 cm^{-1}. MS [ESI, MeCN/MeOH (4:1)]: m/z (%) = 463–454 (100) [M – Cl +MeCN]$^+$, 425–414 (60), 413–406 (65), 387–378 (15) [M – Cl –

HCl]$^+$. HRMS (ESI): calcd. for ([M – Cl – HCl]$^+$, ^{104}Pd) 378.0384; found 378.0381. $C_{18}H_{17}Cl_2N_3Pd$ (452.67): calcd. C 47.76, H 3.79, N 9.28; found C 48.01, H 3.82, N 9.29.

Complex 2c: Yield 105 mg (93%); orange powder; R_f = 0.60 (EtOAc). ^{1}H NMR (300 MHz, [D$_6$]dmso): δ = 3.93 (d, J = 13.3 Hz, 1 H), 4.30 (dd, J = 3.9 and 13.3 Hz, 1 H), 5.58 (s, 1 H), 7.19–7.28 (m, 3 H), 7.46–7.55 (m, 3 H), 7.88–7.95 (m, 4 H), 8.50 (d, J = 2.3 Hz, 1 H), 8.57 (d, J = 3.1 Hz, 1 H), 8.69 (s, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]dmso): δ = 57.3, 70.8, 128.3 (2 C), 128.4 (2 C), 128.5, 129.1 (2 C), 129.4, 131.2 (2 C), 134.0, 136.3, 141.4, 144.8, 145.6, 160.3 ppm. IR (in KBr): $\tilde{\nu}$ = 3437, 3088, 3063, 3022, 2914, 1783, 1588, 1491, 1445, 1404, 1255, 1148, 1055, 748, 692, 554, 482 cm^{-1}. MS [ESI, MeCN/MeOH (4:1)]: m/z (%) = 496–487 (50) [M – Cl + MeCN + MeOH]$^+$, 463–454 (70) [M – Cl + MeCN]$^+$, 425–414 (100), 413–406 (90), 387–378 (30) [M – Cl – HCl]$^+$. HRMS (ESI): calcd. for ([M – Cl – HCl]$^+$, ^{104}Pd) 378.0384; found 378.0378. $C_{18}H_{17}Cl_2N_3Pd$ (452.67): calcd. C 47.76, H 3.79, N 9.28; found C 47.48, H 3.61, N 9.12.

Complex 2d: Yield 115 mg (99%); yellow powder; R_f = 0.40 (EtOAc). ^{1}H NMR (300 MHz, [D$_6$]dmso): δ = 2.33 (s, 3 H), 4.01 (d, J = 12.7 Hz, 1 H), 4.31 (d, J = 12.7 Hz, 1 H), 5.45 (s, 1 H), 7.24–7.56 (m, 10 H), 7.86 (td, J = 1.5 and 7.7 Hz, 1 H), 8.03 (dd, J = 1.9 and 7.3 Hz, 2 H), 8.66 (d, J = 5.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]dmso): δ = 48.5, 68.5, 80.2, 123.3, 123.8, 128.1 (2 C), 128.8, 129.4 (4 C), 129.7, 132.6 (2 C), 132.7, 135.7, 140.3, 148.6, 163.9 ppm. IR (in KBr): $\tilde{\nu}$ = 3447, 3058, 3032, 2925, 1726, 1609, 1491, 1475, 1450, 1373, 1286, 1240, 1153, 1045, 912, 892, 784, 753, 702, 559 cm^{-1}. MS [ESI, MeCN/MeOH (4:1)]: m/z (%) = 474–465 (10) [M – Cl + MeCN]$^+$, 440–431 (50) [M – Cl – HCl + MeCN]$^+$, 428–419 (100), 400–391 (70) [M – Cl – HCl]$^+$. HRMS (ESI): calcd. for ([M – Cl – HCl]$^+$, ^{104}Pd) 391.0588; found 391.0585. $C_{20}H_{20}Cl_2N_2Pd$ (465.71): calcd. C 51.58, H 4.33, N 6.02; found C 51.31, H 4.28, N 5.91.

General Procedure for the Suzuki Reaction: To a stirred solution of aromatic halide (0.5 mmol), boronic acid (0.6 mmol), and Cs_2CO_3 (407 mg, 1.25 mmol) in dmf/H_2O (95:5, 1 mL) was added the palladium complex (33 μL, 1.5×10^{-3} M, 5×10^{-5} mmol, 0.01% or 67 μL, 7.5×10^{-3} M, 5×10^{-4} mmol, 0.1%). The mixture was stirred at 100 °C until the reaction was complete. EtOAc (10 mL) and water (10 mL) were then added, and the aqueous phase was extracted with EtOAc (3×5 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel to give the biaryl product.

For reactions conducted in water, water (1 mL) and K_2CO_3 (173 mg, 1.25 mmol) were used instead of dmf/H_2O (95:5) and Cs_2CO_3, respectively.

4-Methyl-4′-nitro-1,1′-biphenyl (3): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 7.32 (d, J = 8.0 Hz, 2 H), 7.54 (d, J = 8.0 Hz, 2 H), 7.72 (d, J = 9.0 Hz, 2 H), 8.28 (d, J = 9.0 Hz, 2 H) ppm. Data in accordance with previously reported results.[9]

2,4-Dimethoxy-4′-nitro-1,1′-biphenyl (4): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 3.88 (s, 3 H), 6.61 (m, 2 H), 7.28 (d, J = 8.8 Hz, 1 H), 7.67 (d, J = 8.3 Hz, 2 H), 8.23 (d, J = 8.3 Hz, 2 H) ppm. Data in accordance with previously reported results.[10]

4-Nitro-4′-trifluoromethyl-1,1′-biphenyl (5): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.73–7.80 (m, 6 H), 8.32 (d, J = 9.0 Hz, 2 H) ppm. Data in accordance with previously reported results.[11]

4-Phenylbenzaldehyde (6): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.42–7.55 (m, 3 H), 7.65 (m, 2 H), 7.76 (d, J = 8.3 Hz, 2 H), 7.97 (d, J = 8.3 Hz, 2 H), 10.07 (s, 1 H) ppm. Data in accordance with previously reported results.[12]

4-Formyl-2′-methyl-1,1′-biphenyl (7): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 7.25–7.33 (m, 4 H), 7.51 (d, J = 8.6 Hz, 2 H), 7.95 (d, J = 8.6 Hz, 2 H), 10.08 (s, 1 H) ppm. Data in accordance with previously reported results.[12]

4-Formyl-3′-nitro-1,1′-biphenyl (8): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.67 (t, J = 8.0 Hz, 1 H), 7.79 (d, J = 8.3 Hz, 2 H), 7.94–8.03 (m, 3 H), 8.22–8.28 (m, 1 H), 8.47 (t, J = 2.0 Hz, 1 H), 10.08 (s, 1 H) ppm. Data in accordance with previously reported results.[13]

4-Phenylacetophenone (9): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.64 (s, 3 H), 7.37–7.53 (m, 3 H), 7.60–7.72 (m, 4 H), 8.05 (d, J = 8.8 Hz, 2 H) ppm. Data in accordance with previously reported results.[14]

4-Phenylphenol (10): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.99 (s, 1 H), 6.92 (d, J = 8.8 Hz, 2 H), 7.28–7.59 (m, 7 H) ppm. Data in accordance with previously reported results.[15]

4-Methoxy-1,1′-biphenyl (11): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.91 (s, 3 H), 7.06 (d, J = 8.8 Hz, 2 H), 7.34–7.54 (m, 3 H), 7.58–7.69 (m, 4 H) ppm. Data in accordance with previously reported results.[14]

2-Cyano-2′-methyl-1,1′-biphenyl (12): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.22 (s, 3 H), 7.21–7.42 (m, 5 H), 7.47 (td, J = 1.4 and 7.6 Hz, 1 H), 7.65 (td, J = 1.4 and 7.6 Hz, 1 H), 7.77 (dd, J = 1.4 and 7.7 Hz, 1 H) ppm. Data in accordance with previously reported results.[16]

4-Cyano-2′-methyl-1,1′-biphenyl (13): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 7.19–7.35 (m, 4 H), 7.45 (d, J = 8.7 Hz, 2 H), 7.72 (d, J = 8.7 Hz, 2 H) ppm. Data in accordance with previously reported results.[12]

2′-Formyl-4-methoxy-1,1′-biphenyl (14): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 7.00 (d, J = 8.8 Hz, 2 H), 7.30 (d, J = 8.8 Hz, 2 H), 7.47 (m, 2 H), 7.61 (td, J = 1.6 and 7.3 Hz, 1 H), 8.01 (m, 1 H), 10.00 (s, 1 H) ppm. Data in accordance with previously reported results.[17]

4-Methoxy-2′-nitro-1,1′-biphenyl (15): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 6.96 (d, J = 8.8 Hz, 2 H), 7.27 (d, J = 8.8 Hz, 2 H), 7.40–7.48 (m, 2 H), 7.59 (m, 1 H), 7.80 (m, 1 H) ppm. Data in accordance with previously reported results.[18]

Acknowledgments

We are grateful to the Ministère de l'Education Nationale de la Recherche et de la Technologie (MENRT)-France for a grant (V. T.) and to Centre National de la Recherche Scientifique (CNRS) and the Université de Versailles-Saint-Quentin-en-Yvelines for financial support.

[1] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483 and the references cited therein; b) A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147; c) F. Alonso, I. P. Beletskaya, M. Yus, *Tetrahedron* **2008**, *64*, 3047–3101; d) B. Puget, J.-P. Roblin, D. Prim, Y. Troin, *Tetrahedron Lett.* **2008**, *49*, 1706–1709.

[2] For recent review see: J.-P. Corbet, G. Mignani, *Chem. Rev.* **2006**, *106*, 2651–2710 and the references cited therein.

[3] P. W. van Leuuwen, P. Kamer, J. Reek, P. Dierkes, *Chem. Rev.* **2000**, *100*, 2741–2770.

[4] For recent phosphane-free catalytic systems, see: a) Z.-X. Wang, Z.-Y. Chai, *Eur. J. Inorg. Chem.* **2007**, 4492–4499; b) M. Bröring, C. Kleeberg, E. C. Tejero, *Eur. J. Inorg. Chem.* **2007**, 3208–3216; c) S. Haneda, Z. Gan, K. Eda, M. Hayashi, *Orga-*

nometallics **2007**, *26*, 6551–6555; d) S. Haneda, C. Ueba, K. Eda, M. Hayashi, *Adv. Synth. Catal.* **2007**, *349*, 833–835; e) C. Bianchini, G. Lenoble, W. Oberhauser, S. Parisel, F. Zanobini, *Eur. J. Inorg. Chem.* **2005**, 4794–4800 and the references cited therein.

[5] a) V. Terrasson, S. Marque, M. Georgy, J.-M. Campagne, D. Prim, *Adv. Synth. Catal.* **2006**, *348*, 2063–2067; b) J. Michaux, V. Terrasson, S. Marque, J. Wehbe, D. Prim, J.-M. Campagne, *Eur. J. Org. Chem.* **2007**, 2601–2603.

[6] V. Terrasson, S. Marque, A. Scarpacci, D. Prim, *Synthesis* **2006**, 1858–1862.

[7] a) L. Keller, M. Vargas-Sanchez, D. Prim, F. Couty, G. Evano, J. Marrot, *J. Organomet. Chem.* **2005**, *690*, 2306–2311; b) V. V. Dunina, L. G. Kuz′mina, M. Y. Kazakova, O. N. Gorunova, Y. K. Grishin, E. I. Kazakova, *Eur. J. Inorg. Chem.* **1999**, 1029–1039.

[8] Crystal data and structure refinements for **2a**, **2c**, and **2d**: Analyses were carried out by using a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector with Mo-K_α monochromatized radiation (λ = 0.71073 Å). Crystal data **2a**: $C_{19}H_{18}Cl_2N_2Pd$, M_w = 451.65, monoclinic, space group C_c; dimensions: a = 8.5312(1) Å, b = 18.0606(3) Å, c = 12.2962(2) Å, β = 95.703(1)°, V = 1885.20(5) Å^3; Z = 4; μ = 1.270 mm^{-1}; 19418 reflections measured at room temperature; independent reflections: 5422 [5098 $F_o > 4\sigma(F_o)$]; data were collected up to a $2\Theta_{max}$ value of 60.12° (99.6% coverage). Number of variables: 217; R_1 = 0.0202, wR_2 = 0.0432, S = 1.034; highest residual electron density: 0.336 e Å^{-3} (all data R_1 = 0.0230, wR_2 = 0.0442). Crystal data **2c**: $C_{18}H_{17}Cl_2N_3Pd$, M_w = 452.65, monoclinic, space group $P2_1/c$; dimensions: a = 16.9212(15) Å, b = 15.2833(12) Å, c = 16.4784(14) Å, β = 118.744(3)°, V = 3736.4(5) Å^3; Z = 8; μ = 1.283 mm^{-1}; 54638 reflections measured at room temperature; independent reflections: 10941 [9053 $F_o > 4\sigma(F_o)$]; data were collected up to a $2\Theta_{max}$ value of 60.24° (99.3% coverage). Number of variables: 434; R_1 = 0.0860, wR_2 = 0.2192, S = 1.206; highest residual electron density 2.423 e Å^{-3} (all data R_1 = 0.0989, wR_2 = 0.2263). Crystal data **2d**: $C_{20}H_{20}Cl_2N_2Pd$, M_w = 465.68, monoclinic, space group $P2_1/n$; dimensions: a = 10.4772(11) Å, b = 12.8641(13) Å, c = 14.3890(13) Å, β = 103.478(4)°, V = 1885.9(3) Å^3; Z = 4; μ = 1.272 mm^{-1}; 102328 reflections measured at 100 K; independent reflections: 5569 [5205 $F_o > 4\sigma(F_o)$]; data were collected up to a $2\Theta_{max}$ value of 60.64° (98.3% coverage). Number of variables: 227; R_1 = 0.0297, wR_2 = 0.0810, S = 1.226; highest residual electron density 0.336 e Å^{-3} (all data R_1 = 0.0346, wR_2 = 0.0945). Data reduction was performed with the SAINT software. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set by using the SADABS program based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares with use of the SHELX-TL package. CCDC-677262 (for **2a**), -677263 (for **2c**), and -677264 (for **2d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[9] K. Shudo, T. Ohta, T. Okamoto, *J. Am. Chem. Soc.* **1981**, *103*, 645–653.

[10] S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *J. Am. Chem. Soc.* **2006**, *128*, 11748–11749.

[11] L. Liu, Y. Zhang, Y. Wang, *J. Org. Chem.* **2005**, *70*, 6122–6125.

[12] N. Kataoka, Q. Shelby, J. P. Stambuli, J. F. Hartwig, *J. Org. Chem.* **2002**, *67*, 5553–5566.

[13] B. Tao, D. W. Boykin, *J. Org. Chem.* **2004**, *69*, 4330–4335.

[14] T. Mino, Y. Shirae, T. Saito, M. Sakamoto, T. Fujita, *J. Org. Chem.* **2006**, *71*, 9499–9502.

[15] I. Ryu, H. Matsubara, S. Yasuda, H. Nakamura, D. P. Curran, *J. Am. Chem. Soc.* **2002**, *124*, 12946–12947.

[16] S. Y. Liu, M. J. Choi, G. C. Fu, *Chem. Commun.* **2001**, 2408–2409.

[17] H. J. Wu, C. F. Lin, J. L. Lee, W. D. Lu, C. Y. Lee, C. C. Chen, M. J. Wu, *Tetrahedron* **2004**, *60*, 3927–3934.

[18] A. N. Cammidge, V. H. M. Goddard, H. Gopee, N. L. Harrison, D. L. Hughes, C. J. Schubert, B. M. Sutton, G. L. Watts, A. J. Whitehead, *Org. Lett.* **2006**, *8*, 4071–4074.

Received: February 11, 2008
Published Online: May 6, 2008

