NJC

PAPER

View Article Online
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Cite this: DOI: 10.1039/c5nj03450g

A 2-((4-Arylpiperazin-1-yl)methyl)phenol ligated Pd(II) complex: an efficient, versatile catalyst for Suzuki–Miyaura cross-coupling reactions†

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Received (in Montpellier, France)
4th December 2015,
Accepted 4th July 2016

DOI: 10.1039/c5nj03450g

www.rsc.org/njc

N,N,O-Tridentate palladium(II) complexes [Pd(OAc){R-$C_4H_8N_2(CH_2Ar)$}] (R = Ph, Ar = 4-*t*Bu-C_6H_3–OH (**4a**)) and [2,4-di-*t*Bu-C_6H_2–OH, R = benzyl (**4b**)] **4a** and **4b** have been synthesized from the corresponding 2-((4-arylpiperazin-1-yl)methyl)phenol ligands **3a** and **3b** in quantitative yields. The synthesized ligands and their palladium(II) complexes were characterized by NMR, IR and HRMS analyses. Complex **4a** has been used as an efficient catalyst for the Suzuki cross-coupling reaction of 5-iodovanillin and 5-bromosalicylaldehyde with various arylboronic acids in low catalytic amounts (0.01–0.05 mol% of **4a**). Moreover, this catalytic system is even applicable for Suzuki coupling reactions of deactivated aryl bromides and aryl chlorides, affording the cross-coupling products in good to excellent yields with a broad substrate scope.

Introduction

Design and development of simple, economical, suitable organometallic catalysts that can maintain environmentally benign conditions have become an important goal for C–C cross-coupling reactions in organic synthesis.[1] The Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids is one of the most popular palladium catalyzed C–C bond-forming reactions.[2] This reaction has vast importance in the total synthesis of various natural products, pharmaceuticals, polymers and agrochemicals.[3] Its synthetic attractiveness is due to the coupling capability of sterically demanding substrates and the enormous extent of different functional groups under mild experimental conditions.[4] There is a great demand to incorporate non-toxic reagents to make this process industrially viable for scale-up production.[5] Thus there is a great demand in the market for the development of new palladium catalysts with high turnover number, reaction rate, yields and selectivity.[6] Development of air and moisture-stable Pd-catalysts for C–C cross-coupling reactions still remains as an important challenge to be solved.[7] In particular, C–C cross-coupling reactions catalyzed by phosphine-free Pd complexes have great value due to their low cost and ease of handling.[8] Many nitrogen ligands coordinated with palladium(II) complexes have been reported for different C–C cross-coupling reactions.[9]

The Suzuki–Miyaura cross-coupling reaction brings enormous ease for synthesis of acid, hydroxyl, amine and aldehyde functional group containing biphenyl derivatives.[10] The Suzuki coupling products of 5-iodovanillin derivatives have great importance in food materials, pesticides, plant cell walls and key structural elements in natural products.[11] Nantenine is an alkaloid which contains 5-arylvanillin as a basic scaffold and it acts as an antagonist at the 5-HT_{2A} serotonin receptor.[12] 6-Arylmethyl-5-hydroxy-7-phenyl-chromone derivatives that inhibit the replication of HCV (chronic hepatitis C virus) activities are also synthesized from 5-arylvanilline units (Fig. 1).[13] The direct preparation of 5-arylvanillin is particularly attractive in the context of biaryl synthesis, and a few 5-arylvanillin compounds have been synthesized and published previously by using magnesium and indium reagents with high catalyst loading (4 mol% of palladium) along with expensive phosphine ligands at elevated temperatures.[14]

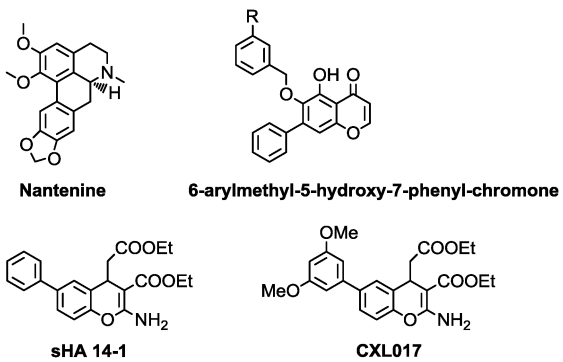

Fig. 1 Structures of bioactive compounds.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5nj03450g

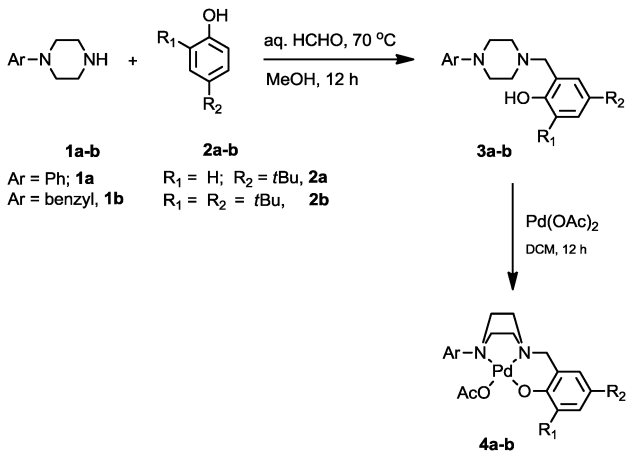
Recently, B. Schmidt and coworkers reported a Pd/C catalyzed Suzuki coupling of 5-iodovanillin.[15] Similarly 5-bromosalicylaldehyde coupled products were found to be useful intermediates in organic syntheses and the pharmaceutical industry with high biological activities.[16,17] Bioactive molecules like sHA 14-1 and CXL017 were prepared from 5-arylsalicylaldehyde, which were proved to be promising candidates for the treatment of cancer with multiple drug resistance (Fig. 1).[18] The Suzuki cross-coupling reaction of 5-bromosalicylaldehyde with arylboronic acid under different reaction conditions was unsuccessful.[19]

As part of our ongoing research, we report herein the synthesis and characterization of 2-((4-arylpiperazin-1-yl)methyl)phenol ligated palladium(II) complexes, as well as the investigation of their catalytic activity in the Suzuki cross-coupling reaction. To date very few reports have been published in the literature on piperazine moiety containing ligands to accelerate Pd-catalyzed Suzuki–Miyaura coupling reactions. M. S. Balakrishna and co-workers have documented piperazine based palladium catalysts for Heck and Suzuki cross-coupling reactions.[20] Z. G. Zhou's group has reported the Suzuki reaction of aryl halides and homo-coupling of arylboronic acids with piperazine ligands using Pd(II) salts.[21]

All the methods reported for biphenyl synthesis from 5-iodovanillin and 5-bromosalicylaldehyde employed high amounts of catalyst (4–5 mol%) and expensive phosphine ligands. Therefore, it is crucial to develop simple and efficient Pd catalytic systems for the Suzuki cross-coupling reaction. In this regard we describe our results on the optimization and scope of cross-coupling reactions of 5-iodovanillin, 5-bromosalicylaldehyde, deactivated aryl bromides and aryl chlorides with different arylboronic acids, catalyzed by Pd(II) complex **4a**.

Results and discussion

The piperazine ligands **3a–b** were prepared as shown in Scheme 1.[20] This involves the reaction between *N*-arylpiperazine, aqueous HCHO and phenol derivatives in methanol under reflux conditions to afford ligands **3a–b** in almost quantitative yields. The resulting *N,N,O* tridentate ligands **3a–b** were further treated with $Pd(OAc)_2$ in dichloromethane to give the desired palladium(II) complexes **4a–b** in high yields. These complexes are soluble in polar and nonpolar solvents. We observed the solubility of these complexes to be normal in hexane, but high in chloroform, dichloromethane, acetonitrile and *N,N*-dimethylformamide. The air and moisture stable Pd(II) complexes were characterized by NMR, mass and IR spectroscopy. All the ligands and their palladium(II) complexes were in good conformity with the results of NMR.

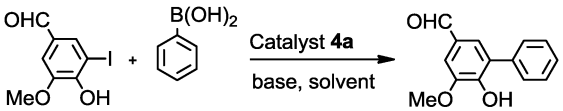


Scheme 1 Synthesis of ligands **3a–b** and their palladium(II) complexes **4a–b**.

The phenolic OH proton signals of the ligands **3a–b** disappeared in their corresponding Pd(II) complexes, which confirms the coordination of the metal ion with the oxygen atom by deprotonation. This results in the loss of one acyl group as acetic acid from $Pd(OAc)_2$. The NMR spectra of these complexes showed one set of methyl proton signals in the range δ 1.29–1.98. Further, the positive-mode spectra of High Resolution Mass Spectrometry (HRMS) also confirm the formation of Pd(II) complexes **4a** and **4b**.

To evaluate the catalytic activity of the palladium(II) complexes (**4a–b**), the Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids was studied. 5-Iodovanillin **5a** and phenylboronic acid **6a** were chosen to establish a model reaction for the optimization of the reaction conditions. The preliminary results are shown in Table 1. We screened different bases for the coupling reaction of **5a** with **6a** in a 1 : 1 ratio of water and methanol system. We observed that the reaction proceeded well with high yields of the desired coupling product **7a** with inorganic (K_2CO_3, $LiOH{\cdot}H_2O$ and K_3PO_4) as well as organic (DABCO and Et_3N) bases (entries 1–3 and 5, 6). This coupling reaction afforded high conversion with the majority of screened bases with only variation in the reaction time. In the case of $LiOH{\cdot}H_2O$, **7a** was observed in high yield within 5 h, whereas K_2CO_3 requires 8 h for product formation. Gratifyingly,

Table 1 Optimization reaction of 5-iodovanillin with phenylboronic acid[a]



Entry	Base	Solvent	Time (h)	Yield[b] (%)
1	K_2CO_3	H_2O + MeOH	8	97
2	$LiOH{\cdot}H_2O$	H_2O + MeOH	5	99
3	K_3PO_4	H_2O + MeOH	12	96
4	$NaOAc{\cdot}3H_2O$	H_2O + MeOH	24	20
5	DABCO	H_2O + MeOH	20	96
6	Et_3N	H_2O + MeOH	24	95
7	–	H_2O + MeOH	24	Nr[c]
8	$LiOH{\cdot}H_2O$	H_2O + MeOH	24	≤ 5[d]
9	$LiOH{\cdot}H_2O$	H_2O	20	60
10	$LiOH{\cdot}H_2O$	MeOH	24	85
11	$LiOH{\cdot}H_2O$	CH_3CN	24	Nr[c]
12	$LiOH{\cdot}H_2O$	Toluene	24	20
13	$LiOH{\cdot}H_2O$	DMF	24	10

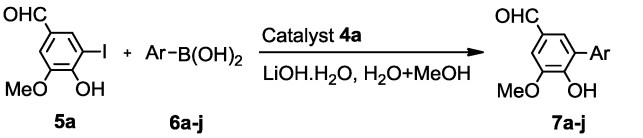
[a] Reaction conditions: 5-iodovanillin (1 mmol), phenylboronic acid (1.2 mmol), base (2 mmol), catalyst **4a** 0.01 mol%, solvent (H_2O + MeOH 1 : 1, 2 mL) at room temperature. [b] Isolated yield. [c] Nr = no reaction. [d] Without catalyst **4a**.

excellent product formation was observed with K_3PO_4 in a prolonged reaction time of 12 h. Low product formation was observed with NaOAc·3H_2O base even under long-standing conditions (entry 4). Moreover, strong base LiOH·H_2O is more suitable for the coupling of **5a** with arylboronic acids than other bases (K_2CO_3, K_3PO_4, DABCO, Et_3N and NaOAc·3H_2O). Without a base no reaction was observed (entry 7). As expected poor yields of **7a** ($\leq$5%) were observed under catalyst-free conditions (entry 8). Next, we studied the solvent effect on the above coupling reaction with LiOH·H_2O as base. In contrast to the aqueous methanol system, independent reactions of water and methanol solvents gave **7a** in low yields (entries 9 & 10). No or poor yield of **7a** was observed in the case of acetonitrile, toluene and DMF (entries 11–13). It clearly showed that the solvent plays a key role in the cross-coupling reaction. Thus from all the screenings, the best results were observed with the LiOH·H_2O–H_2O/MeOH system using 0.01 mol% of catalyst **4a** at room temperature (entry 2).

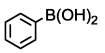
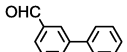
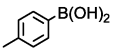
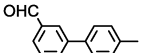
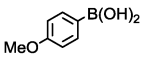
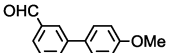
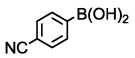
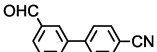
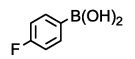
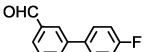
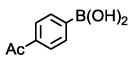
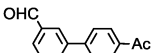
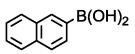
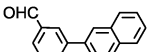
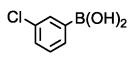
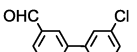
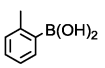
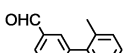
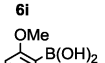
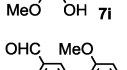
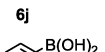
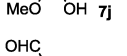
With the appropriate solvent and base in hand, next we studied the scope of Pd(II) complex **4a** for the Suzuki–Miyaura cross-coupling reaction of 5-iodovanillin **5a** with a variety of phenylboronic acids **6a–j**. The results are summarised in Table 2. A range of arylboronic acids were converted to the corresponding coupled products **7a–h** with **5a** in excellent yields at room temperature (entries 1–8). However, arylboronic acids bearing electron-withdrawing or electron-donating groups showed a trivial effect on the coupling reaction. Next, we observed the substituent effect of arylboronic acids showing the variation of reaction time for their cross-coupling reactions. Phenylboronic acid **6a**, 4-methylbenzeneboronic acid **6b**, 4-fluorobenzeneboronic acid **6e** and 2-naphthylboronic acids **6g** took 6 h for conversion into their corresponding products **7a**, **7b**, **7e** and **7g** (entries 1, 2, 5 and 7). Whereas 4-OMe, 4-CN and 4-OAc substituted arylboronic acids **6c**, **6d** and **6f** require 8 h of reaction time for successful couplings (entries 3, 4 and 6). However, when 3-chlorobenzeneboronic acid **6h** was used as the substrate for **5a** coupling, the reaction completed within 3 h with 97% yield (entry 8). We also used sterically hindered arylboronic acids to obtain *ortho*-Me and OMe groups substituted 5-arylvanillins **7i** and **7j** in good yields, 85% and 80%, respectively (entries 9 and 10). Next, we observed 84% and no yield of **7a** for 5-bromovanillin **5b** and 5-chlorovanillin **5c** as partners in Suzuki cross-coupling reactions (entry 11).

Further we extended the above-optimized reaction conditions to the Suzuki–Miyaura cross-coupling reaction of 5-bromosalicylaldehyde **5d** with different arylboronic acids (Table 3). We observed low yield for the **5d** coupling reaction with **6a** at room temperature by using 0.01 mol% of catalyst **4a**. Here we required high temperature and catalyst loading for efficient cross-coupling of substrates to complete the reaction. When the concentration of catalyst **4a** was increased from 0.01 mol% to 0.05 mol%, the yield of the corresponding coupling product **8a** increased from 40% to 86% at 60 °C (entry 1). In comparison with the reported 5-phenylsalicylaldehyde synthesis, the present catalyst amount (0.05 mol%) was very low.[19] A variety of arylboronic acids bearing electron-withdrawing groups such as

Table 2 Coupling reactions of 5-iodovanillin with a various arylboronic acids[a]



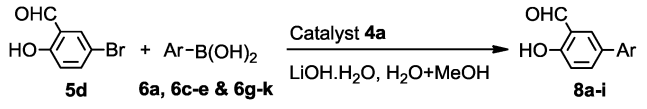
5a **6a-j** **7a-j**

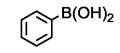
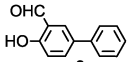
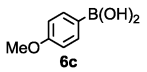
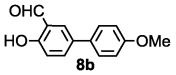
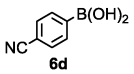
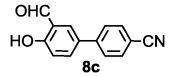
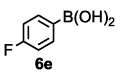
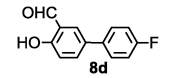
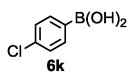
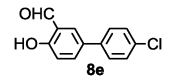
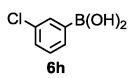
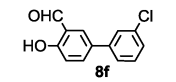
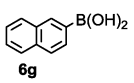
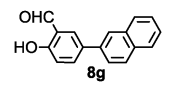
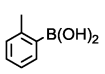
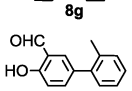
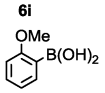
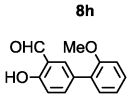
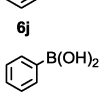
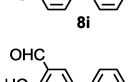
Entry	Ar	Product	Time (h)	Yield[b] (%)	Ref.
1	 **6a**	 **7a**	6	99, 94[c]	—
2	 **6b**	 **7b**	6	97	—
3	 **6c**	 **7c**	8	96	—
4	 **6d**	 **7d**	8	97	—
5	 **6e**	 **7e**	6	96	—
6	 **6f**	 **7f**	8	94	—
7	 **6g**	 **7g**	6	95	—
8	 **6h**	 **7h**	3	97	—
9	 **6i**	 **7i**	24	85	—
10	 **6j**	 **7j**	24	80	—
11	 **6a**	 **7a**	24	84[d], Nr[e]	—

[a] Reaction conditions: 5-iodovanillin (1.0 mmol), arylboronic acid (1.2 mmol), catalyst **4a** 0.01 mol%, LiOH·H_2O (1 mmol), H_2O + MeOH (2 mL, 1 : 1) at room temperature. [b] Isolated yield. [c] Carried out with 0.01 mol% of catalyst **4b**. [d] Reaction with 5-bromovanillin and catalyst 0.05 mol% of **4a** at 60 °C. [e] Reaction with 5-chlorovanillin and catalyst 0.05 mol% of **4a** at 100 °C. Nr = no reaction.

4-cyano **6d**, 4-fluoro **6e** and 4-chloro **6k** moieties and electron-donating group 4-methoxy substituted arylboronic acids **6c** reacted well with **5d**, resulting in 5-aryl substituted salicylaldehydes (**8c–e** and **8b**) in excellent yields (entries 2–5). However, the reaction of 3-chlorobenzeneboronic acid **6h** with **5d** preferred K_3PO_4 base over LiOH·H_2O for efficient coupling (entry 6). When sterically hindered 2-methylphenylboronic acid **6i** and 2-methoxyphenylboronic acid **6j** were used as substrates, coupling products **8h** and **8i** were formed with moderate yields in 30 h of reaction time (entries 8 and 9). No coupling product

Table 3 Coupling reactions of 5-bromosalicylaldehyde with various arylboronic acids[a]



Entry	Ar	Product	Time (h)	Yield[b] (%)	Ref.
1	 6a	 8a	15	86, 40[c]	16
2	 6c	 8b	15	94	18*a*
3	 6d	 8c	15	92	—
4	 6e	 8d	15	90	16
5	 6k	 8e	15	88	16
6	 6h	 8f	12	86[d]	—
7	 6g	 8g	15	88	18*b*
8	 6i	 8h	30	79	—
9	 6j	 8i	30	74	18*a*
10	 6a	 8a	24	84[d], Nr[e]	16

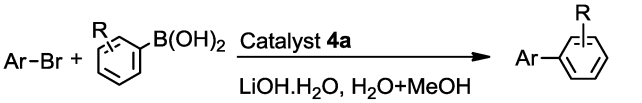
[a] Reaction conditions: 5-bromosalicylaldehyde (1.0 mmol), arylboronic acid (1.2 mmol), catalyst **4a** 0.05 mol%, $LiOH{\cdot}H_2O$ (2 mmol), H_2O (2 mL) at 60 °C. [b] Isolated yield. [c] Reaction with 0.01 mol% catalyst **4a** at room temperature. [d] K_3PO_4 (2 mmol) used as base. [e] Reaction with 5-chlorosalicylaldehyde and 1 mol% of **4a** at 100 °C. Nr = no reaction.

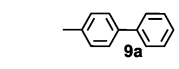
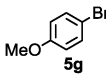
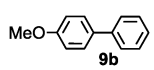
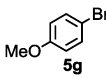
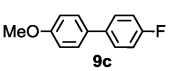
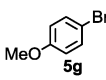
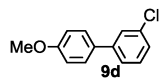
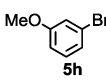
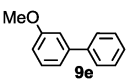
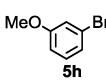
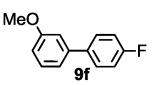
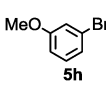
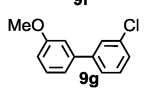
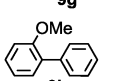
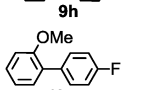
was noticed for 5-chlorosalicylaldehyde **5e** as a partner in the Suzuki cross-coupling reaction (entry 10).

On the other hand, we examined the efficiency of this catalyst **4a** for the Suzuki reaction of deactivated aryl bromides **5f–j** with different arylboronic acids (**6a**, **6e** and **6h**) under the above-optimized reaction conditions at 50 °C. The cross-coupling reactions of deactivated aryl bromides were carried out well, and obtained good yields for all the corresponding biaryl products **9a–m**. This reaction proceeded smoothly with the electron-rich aryl bromides bearing 4-Me and OMe groups at *para*-, *meta*- and *ortho*-positions (entries 1–10). However, we observed good yields for the most challenging substrate 4-SMe group containing aryl bromide **5j** when employed as a coupling partner with different arylboronic acids for a prolonged reaction time of 15–24 h (entries 11–13).

To understand the efficiency of our complex **4a**, we extended the Suzuki cross-coupling reaction of aryl chlorides with a variety of arylboronic acids using 3 mol% of **4a**, 2 mmol $LiOH{\cdot}H_2O$, and 2 mL of DMF at 100 °C for 24 h. We observed good yields of the desired products **9n–q** for electron-deficient aryl chlorides such as 1-chloro-4-nitrobenzene **5k**, 4-chloroacetophenone **5l** and 4-chlorobenzophenone **5m** (entries 1–4). In the case of chlorobenzene **5n** and 4-chlorotoluene **5o** as reaction partners, low to moderate yields of the coupled products **9r**, **9a** and **9b** were obtained only after 30 h (entries 5–8). However, we observed less than 10% of homo-coupling products of arylboronic acids for the Suzuki cross-coupling of aryl chlorides.

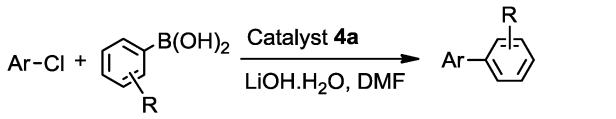
Table 4 Coupling reactions of arylboronic acids with a variety of aryl bromides[a]



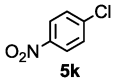
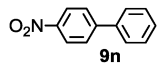
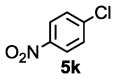
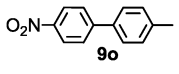
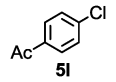
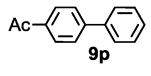
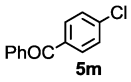
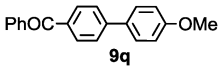
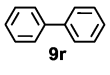
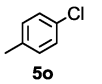
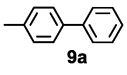
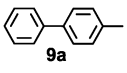
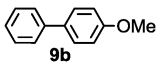
Entry	Aryl halide	R	Product	Yield[b] (%)	Ref.
1	 5f	H	 9a	96	2*b*
2	 5g	H	 9b	94	2*b*
3	 5g	F	 9c	92	22*a*
4	 5g	Cl	 9d	94	22*e*
5	 5h	H	 9e	86	2b
6	 5h	F	 9f	90	22*a*
7	 5h	Cl	 9g	82	22*e*
8	 5i	H	 9h	86	2*b*
9	 5i	F	 9i	90	22*a*
10	5i	Cl	9j	82	22*d*
11	5j	H	9k	92[c]	8*a*
12	5j	F	9l	90[c]	22*c*
13	5j	Cl	9m	88[c]	—

[a] Reaction conditions: aryl halide (1 mmol), arylboronic acid (1.2 mmol), catalyst **4a** 0.01 mol%, $LiOH{\cdot}H_2O$ (2 mmol), H_2O + MeOH (2 mL, 1 : 1) at 50 °C for 15 h. [b] Isolated yield. [c] Reaction time: 24 h.

Table 5 Coupling reactions of arylboronic acids with a variety of aryl chlorides[a]



5k-o 6a-c 9a-b & 9n-r

Entry	Aryl halide	R	Product	Yield[b] (%)	Ref.
1	 5k	H	 9n	80	2*b*
2	 5k	Me	 9o	81	1*c*
3	 5l	H	 9p	76	2*b*
4	 5m	OMe	 9q	80	22*b*
5	 5n	H	 9r	64[c]	2*b*
6	 5o	H	 9a	62[c]	2*b*
7	 5n	Me	 9a	56[c]	2*b*
8	 5n	OMe	 9b	60[c]	2*b*

[a] Reaction conditions: aryl chloride (1 mmol), arylboronic acid (1.2 mmol), catalyst **4a** 3 mol%, $LiOH{\cdot}H_2O$ (2 mmol), DMF (2 mL) at 100 °C for 24 h. [b] Isolated yield. [c] Reaction time: 30 h.

The catalytic efficiency of complex **4a** exhibits several advantages, observed from the above results (Tables 1–5). (1) The low catalyst loading is sufficient for efficient coupling of iodo- and bromoaryl compounds (0.01–0.05 mol%). (2) The operation of this reaction is very simple without the use of any susceptible reagents. (3) Hydroxy- and aldehyde-substituted aryl halide coupling reactions proceeded well under aqueous systems with the air stable catalyst **4a**. (4) The main feature of this process was the efficient synthesis of 5-arylvanillin from a particular solvent system and all the inorganic bases. (5) Lastly, the developed complex **4a** is even applicable for non-activated chloro coupling reactions.

Conclusion

In conclusion, we have developed a new *N*,*N*,*O*-tridentate derived palladium(II) complex for the Suzuki reaction of 5-iodovanillin, 5-bromosalicylaldehyde and deactivated aryl bromides in an aqueous system. We obtained a variety of 5-arylvanillin and 5-arylsalicylaldehyde derivatives in excellent yields. These biaryl units can serve as key structural elements in different pharmaceutical intermediates. Coupling reactions of various deactivated aryl bromides with different arylboronic acids proceeded well using low catalyst loadings (0.01 mol%). This catalytic system is even applicable for challenging ArCl couplings. An excellent functional group tolerance with high yields in aqueous systems makes this method more economically viable in terms of green perspectives.

Experimental section

General procedure for the synthesis of ligands 3a–b

In a 100 mL round bottom flask piperazine (10 mmol), 40% aqueous formaldehyde solution (2.1 mL, 30 mmol) and methanol (50 mL) were added and refluxed for 2 h. This reaction mixture was allowed to cool to room temperature. Phenol derivatives (**2a** or **2b**) (20 mmol) were directly added to the reaction mixture and again refluxed for 12 h. Then the reaction mixture was allowed to stand at room temperature for cooling and the resulting solid (90–95% yield) was filtered off and dried under vacuum.

General procedure for the preparation of Pd(II) complexes 4a–b

To a flask containing ligand (**3a** or **3b**) (0.5 mmol) and $Pd(OAc)_2$ (0.5 mmol), 30 mL of CH_2Cl_2 was added at room temperature and stirred for 12 h. The reaction mixture was washed with water to remove AcOH generated in the reaction mixture. The solvent was removed under reduced pressure and the resulting brown solid was dried under high vacuum to obtain the pure Pd(II) complexes (**4a** or **4b**) in 94–96% yield.

Pd(II) complex 4a. Brown solid, m.p.: 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.36 (t, J = 8.84 Hz, 2H), 7.15 (d, J = 8.58 Hz, 1H), 7.03–6.94 (m, 4H), 6.78 (d, J = 8.58 Hz, 1H), 3.94 (d, J = 10.10 Hz, 2H), 3.74 (s, 2H), 3.57 (d, J = 12.88 Hz, 2H), 3.42 (t, J = 11.11 Hz, 2H), 3.05 (d, J = 12.88 Hz, 2H), 1.29 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 150.4, 138.5, 129.2, 127.0, 126.5, 123.8, 119.9, 118.5, 115.5, 55.3, 52.8, 43.6, 33.7, 31.5, 29.6; FTIR (KBr): $\tilde{\nu}$ = 2955, 1722, 1573 cm^{-1}; HRMS: calcd for $C_{21}H_{27}N_2OPd$ $(M–OAc)^+$ = 429.1158, found: 429.1080.

Pd(II) complex 4b. Brown solid, m.p.: 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38 (m, 6H), 6.84 (s, 1H), 4.22 (s, 2H), 4.14 (s, 2H), 3.57–3.12 (m, 4H), 2.61–2.25 (m, 4H), 1.98 (s, 3H), 1.44 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 163.5, 140.5, 136.9, 131.4, 130.3, 128.9, 128.6, 126.2, 125.6, 125.0, 62.3, 61.8, 59.7, 54.9, 54.8, 35.2, 33.9, 31.6, 30.8, 29.5, 23.6; FTIR (KBr): $\tilde{\nu}$ = 2954, 1718, 1573 cm^{-1}; HRMS: calcd for $C_{26}H_{37}N_2OPd$ $(M–OAc)^+$ = 499.1941, found: 499.1935.

General procedure for the Suzuki–Miyaura cross-coupling reaction of 5-iodovanillin

A mixture of 5-iodovanillin (1.0 mmol), arylboronic acid (1.2 mmol), $LiOH{\cdot}H_2O$ (2.0 mmol) and Pd complex **4a** (0.01 mol% in 0.1 mL DMF) in a 1 : 1 ratio of water and methanol system (2 mL) was stirred at room temperature for 6 h. After confirmation of completion of the reaction by TLC, the reaction mixture was extracted with ethyl acetate and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was

purified by column chromatography on silica gel using ethyl acetate/hexane as the eluent to afford the desired products.

6-Hydroxy-5-methoxybiphenyl-3-carbaldehyde 7a (entry 1, Table 2). White solid, m.p.: 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 9.73 (s, 1H), 7.51 (s, 2H), 7.39–7.25 (m, 5H), 6.61 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.1, 159.1, 148.8, 147.5, 136.3, 129.1, 128.7, 128.4, 127.8, 127.6, 107.4, 56.4; HRMS: exact mass calculated for $C_{14}H_{13}O_3$ $[M + H]^+$ = 229.0865, found m/z = 229.0856.

6-Hydroxy-5-methoxy-4′-methyl-[1,1′-biphenyl]-3-carbaldehyde 7b (entry 2, Table 2). White solid, m.p.: 148 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 9.73 (s, 1H), 7.41–7.39 (m, 3H), 7.28 (s, 1H), 7.16 (d, J = 7.83 Hz, 2H), 6.51 (s, 1H), 3.84 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.1, 148.6, 147.3, 137.4, 133.2, 129.0, 128.8, 128.5, 127.5, 107.1, 56.2, 21.1; HRMS: exact mass calculated for $C_{15}H_{15}O_3$ $[M + H]^+$ = 243.1021, found m/z = 243.0989.

4′-Methoxy-6-hydroxy-5-methoxybiphenyl-3-carbaldehyde 7c (entry 3, Table 2). Light yellow solid, m.p.: 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 9.78 (s, 1H), 7.50 (d, J = 9.09 Hz, 2H), 7.41 (m, 1H), 7.31 (s, 1H), 6.92 (d, J = 9.09 Hz, 2H), 6.43 (s, 1H), 3.91 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.1, 159.2, 148.6, 147.4, 130.2, 129.2, 128.6, 128.4, 127.3, 113.9, 107.1, 56.4, 55.3; HRMS: exact mass calculated for $C_{15}H_{15}O_4$ $[M + H]^+$ = 259.0970, found m/z = 259.0949.

4′-Cyano-6-hydroxy-5-methoxybiphenyl-3-carbaldehyde 7d (entry 4, Table 2). Light yellow solid, m.p.: 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 9.79 (s, 1H), 7.66 (m, 4H), 7.42 (d, J = 19.95 Hz, 2H), 6.78 (s, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.7, 148.8, 147.6, 141.5, 132.1, 129.8, 129.4, 127.7, 118.8, 111.2, 108.6, 56.5; HRMS: exact mass calculated for $C_{15}H_{12}NO_3$ $[M + H]^+$ = 254.0817, found m/z = 254.0802.

4′-Fluoro-6-hydroxy-5-methoxybiphenyl-3-carbaldehyde 7e (entry 5, Table 2). White solid, m.p.: 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 9.76 (s, 1H), 7.50 (s, 2H), 7.38 (d, J = 26.77 Hz, 2H), 7.04 (s, 2H), 6.53 (s, 1H), 3.90 (s, 3H); ^{19}F NMR (376.46 MHz, $CDCl_3$) δ:$\tilde{\nu}$ −114.31 (s, 1 F); ^{13}C NMR (100 MHz, $CDCl_3$) 190.9, 163.5 (d, J = 248.09 Hz), 148.5, 147.3, 132.1, 130.7 (d, J = 8.05 Hz), 129.1, 128.2, 126.5, 115.4 (d, J = 21.95 Hz), 107.4, 56.3; HRMS: exact mass calculated for $C_{14}H_{12}FO_3$ $[M + H]^+$ = 247.0770, found m/z = 247.0776.

4′-Acetyl-6-hydroxy-5-methoxy-[1,1′-biphenyl]-3-carbaldehyde 7f (entry 6, Table 2). Orange solid, m.p.: 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 9.85 (s, 1H), 8.02 (m, 2H), 7.73 (m, 2H), 7.52–7.33 (m, 2H), 7.04 (s, 1H), 3.97 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 198.0, 190.9, 149.0, 147.6, 147.3, 136.1, 135.9, 129.3, 128.3, 128.1, 126.3, 108.7, 56.4, 26.6; HRMS: exact mass calculated for $C_{16}H_{15}O_4$ $[M + H]^+$ = 271.0970, found m/z = 271.0960.

4-Hydroxy-3-methoxy-5-(naphthalen-2-yl)benzaldehyde 7g (entry 7, Table 2). White solid, m.p.: 164 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 9.76 (s, 1H), 7.96 (s, 1H), 7.80–7.75 (m, 3H), 7.65 (m, 1H), 7.49 (s, 1H), 7.39–7.37 (m, 2H), 7.31 (s, 1H), 6.30 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.1, 148.9, 147.5, 133.8, 133.3, 132.7, 129.3, 128.8, 128.2, 128.1, 127.8, 127.6 (d), 127.0, 126.3, 126.2, 107.9, 56.4; HRMS: exact mass calculated for $C_{18}H_{15}O_3$ $[M + H]^+$ = 279.1021, found m/z = 279.1023.

3′-Chloro-6-hydroxy-5-methoxybiphenyl-3-carbaldehyde 7h (entry 8, Table 2). White solid, m.p.: 136 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 9.58 (s, 1H), 7.98 (s, 1H), 7.62 (s, 1H), 7.51–7.47 (m, 2H), 7.41 (s, 1H), 7.35–7.34 (m, 1H), 6.85 (s, 1H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.9, 162.7, 148.8, 147.5, 138.1, 134.1, 129.6, 129.1, 128.2, 127.7, 127.2, 126.2, 107.9, 56.4; HRMS: exact mass calculated for $C_{14}H_{12}ClO_3$ $[M + H]^+$ = 263.0475, found m/z = 263.0443.

6-Hydroxy-5-methoxy-2′-methyl-[1,1′-biphenyl]-3-carbaldehyde 7i (entry 9, Table 2). White solid, m.p.: 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 9.75 (s, 1H), 7.73 (s, 1H), 7.37 (s, 1H), 7.25–7.22 (m, 3H), 7.15–7.13 (m, 1H), 6.36 (s, 1H), 3.92 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.9, 148.6, 147.1, 136.7, 135.8, 130.0, 129.8, 129.1, 129.0, 128.1, 128.0, 125.7, 107.4, 56.2, 19.8; HRMS: exact mass calculated for $C_{15}H_{15}O_3$ $[M + H]^+$ = 243.1021, found m/z = 243.1021.

6-Hydroxy-2′,5-dimethoxy-[1,1′-biphenyl]-3-carbaldehyde 7j (entry 10, Table 2). Light yellow solid, m.p.: 138 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 9.73 (s, 1H), 7.34 (m, 2H), 7.30 (t, J = 8.33 Hz, 1H), 7.24 (d, J = 7.57 Hz, 1H), 6.99–6.92 (m, 2H), 6.49 (s, 1H), 3.87 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 190.9, 156.4, 149.1, 147.6, 131.4, 130.2, 129.7, 129.5, 128.9, 125.1 (d), 120.8, 111.2, 107.5, 56.1, 55.6; HRMS: exact mass calculated for $C_{15}H_{15}O_4$ $[M + H]^+$ = 259.0970, found m/z = 259.0974.

General procedure for the Suzuki–Miyaura cross-coupling reaction of 5-bromosalicylaldehyde

A mixture of 5-bromosalicylaldehyde 5d (1.0 mmol), arylboronic acid (1.2 mmol), $LiOH{\cdot}H_2O$ (2.0 mmol) and Pd complex **4a** (0.05 mol% in 0.1 mL DMF) in a 1 : 1 ratio of water and methanol system (2 mL) was stirred at 60 °C for 24 h. To the cooled solution water was added, extracted with ethyl acetate and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using ethyl acetate/hexane as the eluent to give the desired products.

3′-Formyl-4′-hydroxy-[1,1′-biphenyl]-4-carbonitrile 8c (entry 3, Table 3). White solid, m.p.: 149 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 11.11 (s, 1H), 10.01 (s, 1H), 7.81–7.67 (m, 6H), 7.14 (d, J = 8.58 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 161.8, 143.6, 135.4, 134.0, 132.7, 132.0, 131.0, 127.8, 127.0, 120.7, 118.5, 110.8; HRMS: exact mass calculated for $C_{14}H_{10}NO_2$ $[M + H]^+$ = 223.0633, found m/z = 223.0797.

5-(-3-Chlorophenyl)salicylaldehyde 8f (entry 6, Table 3). Light yellow solid, m.p.: 70 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.95 (s, 1H), 9.89 (s, 1H), 7.65 (m, 2H), 7.45 (m, 1H), 7.35–7.23 (m, 3H), 7.01 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 161.4, 141.1, 135.5, 134.9, 131.8, 130.2, 127.4, 126.7, 124.7, 120.7, 118.3, 113.7; HRMS: exact mass calculated for $C_{13}H_{10}ClO_2$ $[M + H]^+$ = 233.0369, found m/z = 233.0370.

4-Hydroxy-2′-methyl-[1,1′-biphenyl]-3-carbaldehyde 8h (entry 8, Table 3). Brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.93 (s, 1H), 9.83 (s, 1H), 7.42 (s, 2H), 7.19–7.12 (m, 4H), 6.98 (d, J = 8.84 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 160.5, 139.9, 137.9, 135.3, 133.8, 133.7, 130.4, 129.6, 127.6, 126.0, 120.2, 117.3, 20.3; HRMS: exact mass calculated for $C_{14}H_{13}O_2$ $[M + H]^+$ = 213.0916, found m/z = 213.0910.

General procedure for the Suzuki–Miyaura cross-coupling reaction of aryl bromides

A mixture of aryl bromide (1.0 mmol), phenylboronic acid **6a** (1.2 mmol), $LiOH{\cdot}H_2O$ (2.0 mmol), H_2O + MeOH (1 : 1, 2 mL), and Pd complex **4a** in freshly prepared DMF solution (0.01 mol% in 0.1 mL DMF) was stirred at 50 °C for the desired reaction time. Further, the reaction mixture was extracted with ethyl acetate and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using ethyl acetate/hexane as the eluent to give the corresponding coupling products.

(3′-Chloro-[1,1′-biphenyl]-4-yl)(methyl)sulfane 9m (entry 13, Table 4). Light yellow solid, m.p.: 48 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 7.54 (s, 1H), 7.49–7.42 (m, 3H), 7.36–7.28 (m, 4H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 142.3, 138.5, 136.4, 134.7, 130.0, 127.4, 127.1, 126.9, 126.8, 124.9, 15.7; HRMS: exact mass calculated for $C_{13}H_{11}ClS$ $[M]^+$ = 234.0270, found m/z = 234.0261.

General procedure for the Suzuki–Miyaura cross-coupling reaction of aryl chlorides

A mixture of aryl chloride (1.0 mmol), phenylboronic acid **6a** (1.2 mmol), $LiOH{\cdot}H_2O$ (2.0 mmol), DMF (2 mL), and Pd complex **4a** (3 mol%) was stirred at 100 °C for the desired reaction time. Further, a reaction procedure the same as above was performed.

Acknowledgements

KS thanks the University Grants Commission (UGC), New Delhi, for Dr D. S. Kothari postdoctoral research fellowship. SP thanks the CSIR, New Delhi, for a Senior Research Associateship. Special thanks to Professor Samudranil Pal for the support.

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