An aerobic ligandless palladium acetate catalysed Suzuki–Miyaura cross-coupling reaction in an aqueous solvent

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The Suzuki–Miyaura reaction of aryl iodides and aryl bromides was catalysed by $Pd(OAc)_2$ (1 mol%) using $K_3PO_4{\cdot}3H_2O$ (2 equiv) as base in dimethyl acetamide DMA-H_2O (1 : 1) at room temperature. Changes in the loading of $Pd(OAc)_2$ (from 1 mol% to 2 mol%), temperature (from room temperature to 80 °C) and the ratio of DMA to water (from 1 : 1 to 5 : 1) resulted in the successful coupling of activated aryl chlorides with phenylboronic acid.

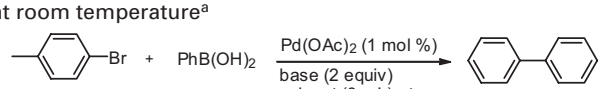
Keywords: Suzuki–Miyaura reaction, ligandless, palladium acetate, aqueous solvent

The palladium–catalysed Suzuki–Miyaura cross-coupling of aryl halides with arylboronic acids has become one of the most important methods for the synthesis of unsymmetrical biaryls.[1,2] Generally, phosphine ligands[3,4] have been used to guarantee the excellent yields of the cross-coupling reaction. However, many phosphine ligands are sensitive to air; and there are other problems associated with the ligands usage, such as phosphonium salt formation[5] and aryl–aryl exchange reaction.[6] Consequently the development of ligandless palladium-catalysed Suzuki–Miyaura reactions has received attention in the past decade.[7-15]

Our research interests in Suzuki–Miyaura cross-coupling lie in the development of highly efficient water-soluble ligands for cross-coupling reactions. In the course of studies, we found that 1 mol% of $Pd(OAc)_2$ was able to catalyse the Suzuki–Miyaura cross-coupling of 4-bromotoluene with phenylboronic acid in aqueous acetonitrile at 80 °C without added ligands. This afforded 4-methylbiphenyl in a yield of 98% with sodium carbonate as the base (Table 1, entry 1). However, the yield decreased dramatically to only 30% when reaction was carried out at room temperature (entry 2). In aqueous ethereal solvents such as THF (entry 3) and DME (entry 4), the reaction gave 4-methylbiphenyl in the yield of 52% and 76% respectively. Encouragingly, when polar aprotic solvents such as DMF and DMA (*N,N*-dimethylacetamide) were used, excellent yields (≥ 92%) of 4-methylbiphenyl were attained at room temperature (entries 5–7). When $K_3PO_4{\cdot}3H_2O$ was used instead of Na_2CO_3 in aqueous DMF and DMA (entries 8 and 9), almost quantitative yields of 4-methylbiphenyl were obtained. Compared with DMF, DMA was the choice of organic solvent since it resulted in an even higher yield of 4-methylbiphenyl with a smaller amount used in the reaction (entries 8 and 9). It was worth noting that the yield of cross-coupling product was not affected when the reaction was carried out in air (entries 5, 6, 8 and 9). Further decreasing the total volume of aqueous DMA from 6 ml (entry 9) to 4 ml produced an unchanged yield of 4-methylbiphenyl. Thus, a convenient ligandless procedure for the Suzuki–Miyaura cross-coupling reaction was developed which was run in air at room temperature (Scheme 1).

Under these optimised reaction conditions, aryl iodides and aryl bromides were coupled with arylboronic acids providing the corresponding cross-coupling products in excellent yields. Two aryl iodides, 4-iodoanisole (Table 2, entry 1) and 2-nitroiodobenzene (entry 2) were tested, and excellent yields of cross-coupling products were obtained after 6 hours. Except for two bromobenzoic acids, the coupling reactions of all other aryl bromides, *para*-substituted or even *ortho*-substituted aryl bromides (either electron withdrawing or electron donating groups) were completed within 1 hour, affording the desired cross-coupling products in excellent yields (entries 3–11 and entries 14–17). As for the two bromobenzoic acids, 4-bromobenzoic acid (entry 12) and 3-bromobenzoic acid (entry 13), the coupling reaction needed 9h and 3h respectively for the full conversion of substrates. It was worth noting that aryl bromides or arylboronic acids containing *ortho*-substituents

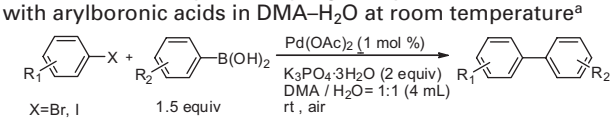
Table 1 Effects of solvents and bases on $Pd(OAc)_2$-catalysed coupling reaction of 4-bromotoluene with phenylboronic acid at room temperature[a]



Entry	Base	Solvent	Yield/%[b]
1[c]	Na_2CO_3	CH_3CN/H_2O (1 : 1)	98
2	Na_2CO_3	CH_3CN/H_2O (1 : 1)	30
3	Na_2CO_3	THF/H_2O (2 : 1)	52
4	Na_2CO_3	DME/H_2O (2 : 1)	76
5	Na_2CO_3	DMF/H_2O (2 : 1)	92
6[d]	Na_2CO_3	DMF/H_2O (2 : 1)	92
7	Na_2CO_3	DMA/H_2O (2 : 1)	96
8	$K_3PO_4{\cdot}3H_2O$	DMF/H_2O (2 : 1)	97
9[d]	$K_3PO_4{\cdot}3H_2O$	DMA/H_2O (1 : 1)	98

[a]Unless otherwise indicated, all reactions were performed with 1.0 mmol of 4-bromotoluene at room temperature for 16–17 h under N_2. [b]Isolated yield. [c]Reaction was run at 80 °C. [d]Coupling reaction was carried out in air.

Table 2 Suzuki–Miyaura coupling of aryl iodides and bromides with arylboronic acids in DMA–H_2O at room temperature[a]



Entry	X	R^1	R^2	Time/h	Yield/%[b]
1[c]	I	4-OMe	H	6	94
2	I	2-NO_2	H	6	98
3	Br	4-Me	H	0.5	98
4	Br	4-CN	H	0.2	98
5	Br	4-OMe	H	0.4	99
6	Br	4-CHO	H	0.5	98
7	Br	4-OH	H	0.8	98
8	Br	4-NHAc	H	0.8	99
9	Br	4-NO_2	H	0.5	98
10	Br	4-COOEt	H	0.8	95
11	Br	4-Me	4-OMe	0.5	99
12[d]	Br	4-COOH	H	9	96
13[d]	Br	3-COOH	H	3	90
14	Br	4-Me	2-OMe	0.5	99
15	Br	2-Me-4-OMe	H	0.5	99
16	Br	2-Me	2-OMe	0.5	89
17	Br	2-Me	H	0.5	90

[a]Unless otherwise indicated, all reactions were performed with 1.0 mmol of aryl iodides or aryl bromides. [b]Isolated yield. [c]Conversion was 96%. [d]Three equivalents of $K_3PO_4{\cdot}3H_2O$ were used.

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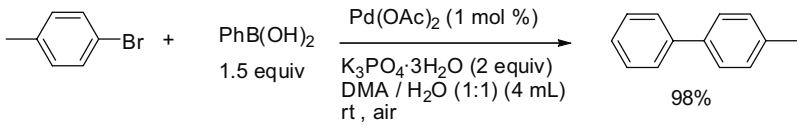


Scheme 1 Optimal reaction conditions for $Pd(OAc)_2$-catalysed Suzuki–Miyaura coupling reaction of 4-bromotoluene.

on the aromatic rings also worked well in the cross-coupling reaction (entries 14–17). Typically, the successful coupling of 2-bromotoluene with 2-methoxyphenylboronic acid gave 2'-methoxy-2-methylbiphenyl in a yield of 89% after 30 min (entry 16).

Although excellent results were achieved for aryl iodides and aryl bromides, aryl chlorides did not work very well under the standard conditions. It was observed that the cross-coupling reaction of 4-chloroacetophenone with phenylboronic acid was largely affected by the ratio of DMA to H_2O. Both higher (DMA–H_2O, 1 : 1) and lower (DMA–H_2O, 20 : 1) water amount had a deleterious effect on coupling reaction, resulting in low yields of 4-acetylbiphenyl (Table 3, entries 1 and 7). Through fine tuning of the volumetric ratio of DMA to H_2O, the ratio of 5 : 1 was found to be the best value (entries 2–6) since the highest yield of 4-acetylbiphenyl (77%) was achieved in this solvent system (entry 3).

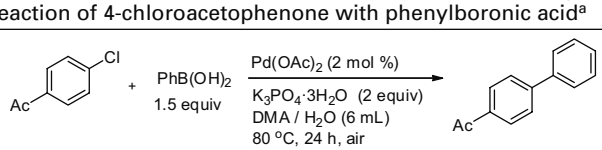
Various aryl chlorides with electron-withdrawn groups could be coupled with phenylboronic acid in the same solvent system providing 78–97% yields of desired cross-coupling products (Table 4, entries 1–4). However, 4-chlorotoluene, an electron-neutral aryl chloride, gave only moderate yield of 4-methylbiphenyl (entry 5). Thus, compared with the optimal reaction system for aryl bromides (Scheme 1), changes in catalyst loading, temperature and volumetric ratio of DMA–H_2O made this catalytic system applicable to activated aryl chlorides.

In summary, a convenient protocol has been developed for the ligandless $Pd(OAc)_2$-catalysed Suzuki–Miyaura reaction of aryl halides with arylboronic acids in aqueous DMA in air without the aid of phase-transfer reagent. This protocol allows the efficient coupling of various aryl bromides with arylboronic acids at room temperature in a quite short reaction times. A strong solvent effect was observed and DMA–H_2O (5 : 1) was found to be the best solvent system, in which activated aryl chlorides were efficiently coupled to provide the cross-coupling products in good to excellent yields.

Experimental

All reagents were purchased from commercial suppliers and used without further purification. All solvents were distilled before use. The ^{1}H NMR spectra were recorded at 300 MHz or 400 MHz and ^{13}C NMR spectra were measured at 75 MHz or 100 MHz, using $CDCl_3$, acetone-d_6, DMSO-d_6 as the solvents.

Table 3 Effect of DMA–H_2O volumetric ratio on cross-coupling reaction of 4-chloroacetophenone with phenylboronic acid[a]



Entry	DMA/H_2O	Yield/%[b]	Conversion/%
1	1 : 1	23	30
2	4 : 1	40	52
3	5 : 1	77	80
4	6 : 1	47	53
5	10 : 1	39	48
6	15 : 1	29	31
7	20 : 1	20	23

[a]Unless otherwise indicated, all reactions were performed with 1.0 mmol of 4-chloroacetophenone. [b]Isolated yield.

General procedure for Suzuki–Miyaura reaction

A mixture of 1 mmol of aryl iodides or aryl bromides, arylboronic acid (1.5 mmol), $K_3PO_4·3H_2O$ (533 mg, 2 mmol) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) in 4 ml of DMA-H_2O (1 : 1) was stirred at room temperature. Upon complete consumption of substrates as determined by TLC, NaOH (1 M) solution 10 ml was added and the mixture was then extracted with EtOAc (4 × 20 ml). The combined organic layer was washed with water (3 × 20 ml) and brine once. It was dried over anhydrous $MgSO_4$, filtered, and concentrated. Preparative TLC or column chromatography on silica and elution with petroleum ether/EtOAc afforded the cross-coupling products. Products were confirmed by comparison of their ^{1}H NMR and ^{13}C NMR data with those reported in the literature.

4-Methoxybiphenyl (Table 2, entry 1):[16] M.p. 90–91 °C (Lit.[16] 87–88 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (t, J = 8.8 Hz, 4H), 7.42 (t, J = 8 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.12, 140.81, 133.76, 128.69, 128.14, 126.70, 126.64, 114.18, 55.32.

2-Nitrobiphenyl (Table 2, entry 2):[17] M.p. 37–38 °C (Lit.[17] 34–35 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.0 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.51–7.40 (m, 5H), 7.34–7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.12, 137.26, 136.10, 132.15, 131.78, 128.53, 128.05, 127.92, 127.74, 123.88.

4-Methylbiphenyl (Table 2, entry 3)[16]: M.p. 47–48 °C (Lit.[16] 47 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.25 (d, J = 6.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.13, 138.32, 136.95, 129.44, 128.68, 127.13, 126.94, 21.05.

4-Cyanobiphenyl (Table 2, entry 4):[16] M.p. 86–87 °C (Lit.[16] 88–89 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 8.4, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 8.0 Hz, 2H), 7.47–7.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.53, 139.03, 132.49, 129.02, 128.57, 127.62, 127.13, 118.87, 110.78.

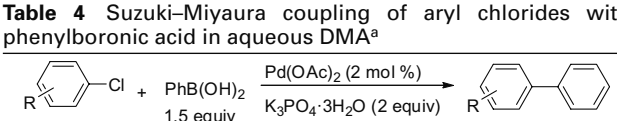
Biphenyl-4-carbaldehyde (Table 2, entry 6)[16]: M.p. 57–58 °C (Lit.[16] 59 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.51-7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.87, 147.14, 139.66, 135.15, 130.23, 128.69, 128.42, 127.63, 127.32.

Biphenyl-4-ol (Table 2, entry 7):[18] M.p. 159–161 °C (Lit.[18] 164–165 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.32 (d, J = 7.2 Hz, 2H), 6.91 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.00, 140.73, 134.07, 129.40, 128.71, 128.39, 126.71, 115.62.

N-biphenyl-4-yl-acetamide (Table 2, entry 8):[19] M.p. 167–169 °C (Lit.[19] 168–170 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.54 (m, 6H), 7.43 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.20 (s, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.73, 140.70, 137.41, 135.86, 128.99, 127.80, 127.32, 127.04, 120.50, 24.82.

4-Nitrobiphenyl (Table 2, entry 9):[16] M.p. 112–113 °C (Lit.[16] 113 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H), 7.51–7.47 (m,

Table 4 Suzuki–Miyaura coupling of aryl chlorides with phenylboronic acid in aqueous DMA[a]



Entry	R	Yield/)[b]	Conversion/%
1	4-NO_2	97	99
2[c]	4-Ac	77	80
3	4-CN	87	93
4	4-CF_3	78	100
5	4-Me	50	65

[a]Unless otherwise indicated, all reactions were performed with 1.0 mmol of aryl chlorides. [b]Isolated yield. [c]Biphenyl was obtained in the yield of 36%.

3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.56, 147.02, 138.69, 129.11, 128.87, 127.74, 127.32, 124.03.

Biphenyl-4-carboxylic acid ethyl ester (Table 2, entry 10):[20] M.p. 45–46 °C (Lit.[20] 47–48 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 8.4 Hz, 2H), 7.67–7.64 (m, 4H), 7.47 (t, J = 7.4 Hz, 2H), 7.40 (d, J = 7.2 Hz, 2H), 4.40 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.47, 145.47, 140.00, 130.02, 129.20, 128.87, 128.06, 127.23, 126.96, 60.93, 14.34.

4'-Methoxy-4-methylbiphenyl (Table 2, entry 11):[21] M.p. 110–112 °C (Lit.[21] 109–110 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.967 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.88, 137.90, 136.29, 133.67, 129.40, 127.90, 126.53, 114.11, 55.23, 21.01.

Biphenyl-4-carboxylic acid (Table 2, entry 12):[18] M.p. 225–227 °C (Lit.[18] 227–229 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.99 (bs, 1H), 8.02 (d, J = 8.0, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.2 Hz, 2H), 7.43 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.50, 144.57, 139.22, 130.25, 129.82, 129.29, 128.48, 127.14, 127.00

Biphenyl-3-carboxylic acid (Table 2, entry 13):[18] M.p. 165–167 °C (Lit.[18] 163–166 °C). ^{1}H NMR (300 MHz, Acetone-d_6): δ 11.39 (bs, 1H), 8.30 (s, 1H), 8.05 (d, J = 7.2 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.2 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H); ^{13}C NMR (75.5 MHz, Acetone-d_6): δ 206.12, 167.52, 142.25, 140.90, 132.22, 130.03, 129.90, 129.32, 128.79, 128.69, 127.84.

2-Methoxy-4'-methylbiphenyl (Table 2, entry 14):[3] M.p. 70–72 °C (Lit.[3] 71–72 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.0 Hz, 2H), 7.32–7.29 (m, 2H), 7.22 (t, J = 7.4 Hz, 2H), 7.03–6.96 (m, 2H), 3.80 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.42, 136.50, 135.53, 130.72, 130.61, 129.34, 128.67, 128.30, 120.72, 111.09, 55.42, 21.14.

4-Methoxy-2-methylbiphenyl (Table 2, entry 15):[22] Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 6.8 Hz, 2H), 7.26–7.19 (m, 3H), 7.09 (d, J = 8.4 Hz, 1H), 6.74 (s, 2H), 3.77 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.67, 141.58, 136.59, 134.53, 130.74, 129.32, 127.94, 126.38, 115.65, 111.00, 55.07, 20.67.

2-Methoxy-2'-methylbiphenyl (Table 2, entry 16):[23] M.p. 41–43 °C (Lit.[23] 42–44 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (t, J = 7.2 Hz, 1H), 7.26–7.14 (m, 5H), 7.03–6.96 (m, 2H), 3.77 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.54, 138.60, 136.75, 130.94, 130.79, 129.96, 129.52, 128.51, 127.24, 125.40, 120.39, 110.59, 55.30, 19.88.

2-Methylbiphenyl (Table 2, entry 17):[11] Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.36 (m, 3H), 7.34–7.25 (m, 2H), 7.20–7.17 (m, 4H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.90, 141.88, 135.23, 130.27, 129.76, 129.14, 128.02, 127.21, 126.71, 125.74, 20.42.

4-Acetylbiphenyl (Table 4, entry 2):[16] M.p. 120–121 °C (Lit.[16] 117–118 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 6.4 Hz, 2H), 7.70 (d, J = 6.8 Hz, 2H), 7.64 (d, J = 5.2 Hz, 2H), 7.48 (m, 2H), 7.42 (d, J = 6.0 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.61, 145.62, 139.72, 135.72, 128.86, 128.81, 128.14, 127.16, 127.10, 26.56.

4-Trifluoromethylbiphenyl (Table 4, entry 4)[20]: M.p. 69–70 °C (Lit.[20] 64–65 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 4H), 7.60 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 1H); ^{13} C NMR (100 MHz, $CDCl_3$) δ 144.71, 139.73, 129.17, 128.96, 128.17, 127.38, 127.24, 125.70, 125.66.

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