β-Oxo Amides: Inexpensive and Efficient Ligands for the Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling Reaction

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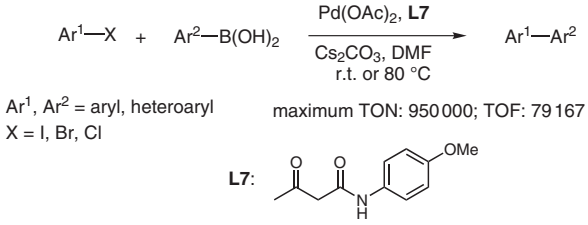
Abstract: β-Oxo amides were found to be inexpensive and efficient ligands for the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction. In the presence of palladium(II) acetate and *N*-(4-methoxyphenyl)-3-oxobutanamide (**L7**), a variety of aryl halides, including deactivated aryl chlorides and heteroaryl halides, were successfully coupled to arylboronic acids in moderate to excellent yields providing very high turnover numbers (maximum TON <950,000 and TOF <79,167). It is noteworthy that the reaction is conducted under mild and aerobic conditions.

Key words: palladium(II) acetate, β-oxo amide, Suzuki–Miyaura cross-coupling reaction, aryl halides, arylboronic acids

The palladium-catalyzed Suzuki–Miyaura coupling reaction is one of the most widely used C–C bond-forming reactions in organic synthesis.[1] Generally, the Suzuki–Miyaura coupling reaction is conducted using a palladium–ligand (often a phosphine or a carbene ligand) complex as the catalyst at high temperatures.[2,3] However, many of these phosphine and carbene ligands are expensive or they are sensitive to air and/or moisture. Therefore, a wide range of alternative ligands, such as oxazolines,[4] amines,[5] amino acids,[6] heterocycles,[7] diazabutadienes,[8] ureas,[9] guanidine,[10] hydrazones,[11] surfactants,[12] and others,[13,14] have been developed to overcome these drawbacks in recent years. Although most of these ligands are inexpensive and stable, many are not commercially available and provide low turnover numbers (the loading of palladium/ligand is often >1 mol%). In view of economic and industrial interests, the development of a high turnover number catalytic system that includes an inexpensive ligand as an alternative to these palladium/phosphine or palladium/carbene catalytic systems is still significant. Recently, 1,3-dicarbonyls including 1,3-diketones and β-oxo esters were employed as highly active ligands for the copper-catalyzed Ullmann-type coupling reaction,[15] which raised the possibility of creating a more robust catalytic system for palladium-catalyzed cross-coupling reactions. Indeed, β-oxo amides, in particular *N*-(4-methoxyphenyl)-3-oxobutanamide (**L7**), were found to be efficient ligands for the palladium-catalyzed Suzuki–Miyaura coupling reaction (Scheme 1). In the presence of palladium(II) acetate and *N*-(4-methoxyphenyl)-3-oxobutanamide (**L7**), a variety of aryl halides were smoothly coupled with arylboronic acids under mild conditions giving the products in moderate to excellent yields. Moreover, the catalytic system is highly efficient for the couplings of aryl iodides and bromides (the maximal TON <950,000 and TOF <79,167).



Scheme 1

The palladium(II) acetate catalyzed cross-coupling of 4-bromoanisole (**1a**) with phenylboronic acid (**2a**) was conducted as a model reaction to optimize the reaction reactions, and the results are summarized in Table 1. Initially, a number of 1,3-dicarbonyls, including β-oxo esters, diketones, β-oxo nitriles, and β-oxo amides, were tested as ligands. It was found that most 1,3-dicarbonyls were highly efficient in promoting the reaction, and β-oxo amides were more effective than the other 1,3-dicarbonyls (entries 1–17). Without any ligand, treatment of 4-bromoanisole (**1a**) with phenylboronic acid (**2a**), palladium(II) acetate, and cesium carbonate in *N*,*N*-dimethylformamide at room temperature after 12 hours afforded the corresponding product **3** in a rather low yield (entry 1). Thus, we attempted to perform the reaction using 1,3-dicarbonyls as ligands. The results indicated that the yield of the target product **3** was increased slightly when either β-oxo ester **L1** or **L2** or β-oxo nitrile **L5** was added (entries 2, 3, and 6), and the presence of diketones **L3** and **L4** even disfavored the reaction (entries 4 and 6). To our delight, the yield of **3** was enhanced dramatically when using β-oxo *N*-arylamides **L6**–**L10** as the ligand (entries 7–11), and β-oxo *N*-arylamides bearing a methyl or methoxy group on the benzene ring **L7**–**L9** gave the best results in terms of the reaction rate. While 3-oxo-*N*-phenylbutanamide (**L6**) enhanced the yield of the reaction of 4-bromoanisole (**1a**) with phenylboronic acid (**2a**) to 93% after 12 hours, the ligands **L7**–**L9** provided ca. 96% yield of **3** in three hours.

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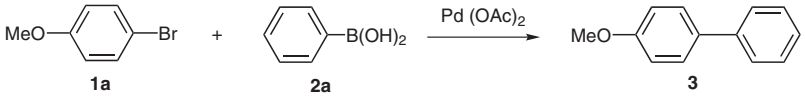
Table 1 Screening Conditions[a]



1a 2a 3

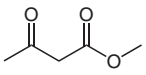
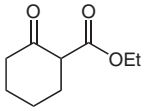
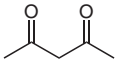
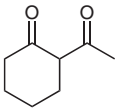
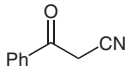
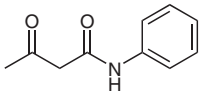
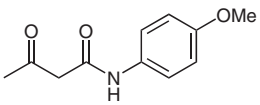
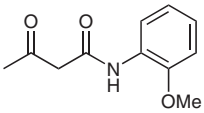
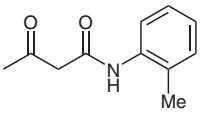
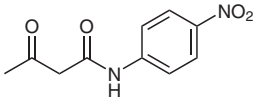
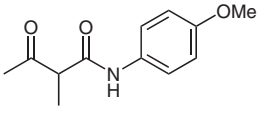
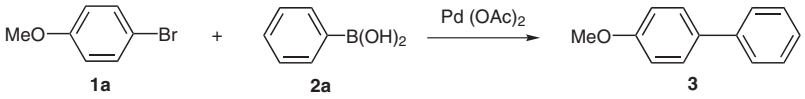
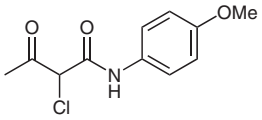
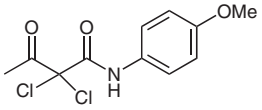
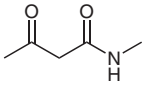
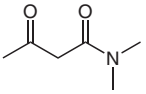
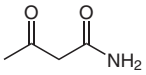
Entry	Ligand	Base	Time (h)	Yield[b] (%)
1	–	Cs_2CO_3	12	11
2	 **L1**	Cs_2CO_3	12	30
3	 **L2**	Cs_2CO_3	12	22
4	 **L3**	Cs_2CO_3	3	6
5	 **L4**	Cs_2CO_3	3	<5
6	 **L5**	Cs_2CO_3	3	12
7	 **L6**	Cs_2CO_3	12	93
8	 **L7**	Cs_2CO_3	3	96
9	 **L8**	Cs_2CO_3	3	96
10	 **L9**	Cs_2CO_3	3	95
11	 **L10**	Cs_2CO_3	3	90
12	 **L11**	Cs_2CO_3	3	27

Table 1 Screening Conditions[a] (continued)



1a **2a** **3**

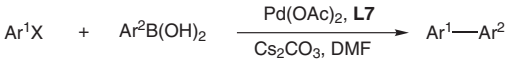
Entry	Ligand	Base	Time (h)	Yield[b] (%)
13	 **L12**	Cs_2CO_3	3	35
14	 **L13**	Cs_2CO_3	3	trace
15	 **L14**	Cs_2CO_3	12	82
16	 **L15**	Cs_2CO_3	12	23
17	 **L16**	Cs_2CO_3	12	45
18[c]	**L7**	Cs_2CO_3	3	97
19[d]	**L7**	Cs_2CO_3	3	35
20	**L7**	K_2CO_3	3	81
21	**L7**	Na_2CO_3	3	68
22	**L7**	K_3PO_4	3	50
23	**L7**	Et_3N	3	11
24[e]	**L7**	Cs_2CO_3	3	43
25[f]	**L7**	Cs_2CO_3	3	80
26[g]	**L7**	Cs_2CO_3	3	85
27[h]	**L7**	Cs_2CO_3	12	35
28[h,i]	**L7**	Cs_2CO_3	12	98
29[i,j]	**L7**	Cs_2CO_3	12	30

[a] Reaction conditions: 1a (0.5 mmol), 2a (0.6 mmol), $Pd(OAc)_2$ (1 mol%), ligand (2 mol%), base (1 mmol), DMF (1 mL), r.t.
[b] Isolated yield.
[c] L7 (3 mol%).
[d] L7 (1 mol%).
[e] EtOH (1 mL) instead of DMF.
[f] Dioxane (1 mL) instead of DMF.
[g] H_2O–DMF (1:10, 1 mL) instead of DMF.
[h] $Pd(OAc)_2$ (0.1 mol%) and ligand (0.2 mol%).
[i] At 80 °C.
[j] $Pd(OAc)_2$ (0.01 mol%) and ligand (0.02 mol%).

However, the catalytic activity was reduced sharply when there are substituents at the 2-position of the β-oxo *N*-arylamides **L11**–**L13** (entries 12–14). For example, β-oxo *N*-arylamide **L11** bearing a methyl group at the 2-position gave the target product **3** in only 27% yield (entry 12). Satisfactory results were still achieved using β-oxo *N*-alkylamide **L14** as the ligand (entry 15). However, the two other amide ligands **L15** and **L16**, whether N-disubstituted or unsubstituted, both display less active for the reaction based on the yield (entries 16 and 17). In addition, the screening results showed that the better palladium/**L7** ratio is 1:2 in view of yield and the reaction cost (entries 8, 18, and 19). Subsequently, a series of bases and solvents were evaluated. The results showed that cesium carbonate combined with *N*,*N*-dimethylformamide afforded the best results (entries 20–26), and the catalytic efficiency was decreased to some extent by adding water (entries 8 and 26). Finally, the catalytic activity of the palladium(II) acetate/**L7** system was further examined (entries 27–29). In the presence of 0.1 mol% of palladium(II) acetate and 0.2 mol% of **L7**, substrate **1a** (0.5 mmol) was reacted with boronic acid **2a** (0.6 mmol) in *N*,*N*-dimethylformamide at room temperature for 12 hours to give the corresponding product **3** in 35% yield (TON = 350; entry 27), whereas the yield of **3** was enhanced to 98% at 80 °C (TON = 980; entry 28). However, further decreasing the loading of palladium to 0.01 mol% produced a low yield of **3** even at 80 °C (TON = 3,000; entry 29).

As shown in Table 2, the palladium(II) acetate/**L7** system displayed highly catalytic activity for the Suzuki–Miyaura coupling reaction, and the scope of the aryl halides was extended to some deactivated aryl chlorides and heteroaryl halides. In the presence of palladium(II) acetate and **L7**, substrate **1a** with boronic acids **2b**–**d** could also be converted completely in three hours into the corresponding cross-coupled products **4**–**6** in satisfactory yields (entries 1–3). Subsequently, the reactions of three aryl iodides **1b**–**d** with **2a** were examined under the standard conditions (entries 5–9). Treatment of 4-iodoanisole (**1b**) (0.5 mmol) with phenylboronic acid (**2a**) (0.6 mmol), palladium(II) acetate (1 mol%), and **L7** (2 mol%) for one hour afforded the target product **3** in quantitative yield (entry 4). However, only 43% yield of **3** was observed after 12 hours at a loading of 0.1 mol% palladium (entry 5), fortunately **3** could also be obtained in quantitative yield under these conditions when the reaction was performed at 80 °C (entry 6). Noteworthy is that the successfully reaction of **1b** with **2a** for 12 hours to give **3** in good yield in the presence of 0.0001 mol% of palladium and 0.0002 mol% of **L7** (TON = 900,000, TOF = 75,000; entry 7). The other two iodides **1c** and **1d** could also smoothly undergo coupling with **2a** at a loading of 0.0001 mol% palladium in satisfactory yields (entries 8 and 9).

Table 2 Palladium(II) Acetate/**L7** Catalyzed Suzuki–Miyaura Cross-Couplings of Aryl Halides **1** with Arylboronic Acids **2**[a]



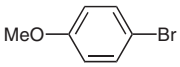
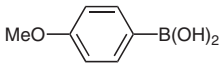
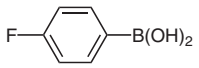
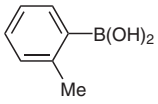
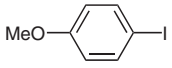
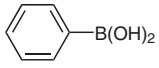
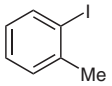
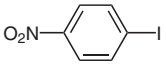
Entry	Ar^1X	$Ar^2B(OH)_2$	Time (h)	Product	Yield[b] (%)
1	 **1a**	 **2b**	3	**4**	95
2	**1a**	 **2c**	3	**5**	98
3	**1a**	 **2d**	3	**6**	70
4	 **1b**	 **2a**	1	**3**	100
5[c]	**1b**	**2a**	12	**3**	43
6[c,d]	**1b**	**2a**	12	**3**	98
7[d,e]	**1b**	**2a**	12	**3**	90
8[d,e]	 **1c**	**2a**	12	**7**	78
9[d,e]	 **1d**	**2a**	12	**8**	95

Table 2 Palladium(II) Acetate/**L7** Catalyzed Suzuki–Miyaura Cross-Couplings of Aryl Halides **1** with Arylboronic Acids **2**[a] (continued)

$Ar^1X + Ar^2B(OH)_2 \xrightarrow[Cs_2CO_3,\ DMF]{Pd(OAc)_2,\ \mathbf{L7}} Ar^1{-}Ar^2$

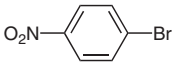
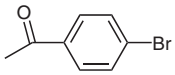
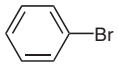
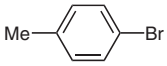
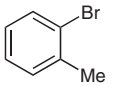
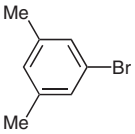
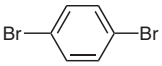
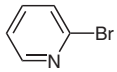
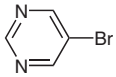
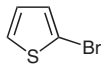
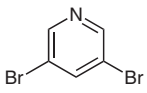
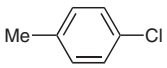
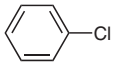
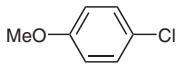
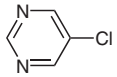
Entry	Ar^1X	$Ar^2B(OH)_2$	Time (h)	Product	Yield[b] (%)
10	 **1e**	**2a**	4	**8**	99
11[d,f]	**1e**	**2a**	12	**8**	99
12	 **1f**	**2a**	4	**9**	93
13	 **1g**	**2a**	1	**10**	100
14	 **1h**	**2a**	1	**11**	98
15[d]	 **1i**	**2a**	12	**7**	71
16	 **1j**	**2a**	1	**12**	83
17	 **1k**	**2a**	3	**13**	80
18	 **1l**	**2a**	16	**14**	33
19[d]	**1l**	**2a**	16	**14**	85
20[c,d]	**1l**	**2a**	20	**14**	80
21[d]	 **1m**	**2a**	6	**15**	100
22[d]	 **1n**	**2a**	3	**16**	89
23[d,g]	 **1o**	**2a**	3	**17**	72
24[d]	 **1p**	**2a**	16	**11**	21
25[d,h]	**1p**	**2a**	16	**11**	57
26[d,h]	 **1q**	**2a**	16	**10**	65

Table 2 Palladium(II) Acetate/**L7** Catalyzed Suzuki–Miyaura Cross-Couplings of Aryl Halides **1** with Arylboronic Acids **2**[a] (continued)

$Ar^1X + Ar^2B(OH)_2 \xrightarrow[Cs_2CO_3,\ DMF]{Pd(OAc)_2,\ \mathbf{L7}} Ar^1—Ar^2$

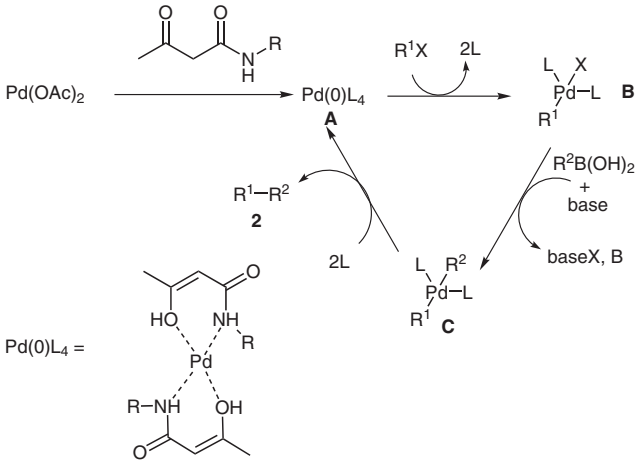
Entry	Ar^1X	$Ar^2B(OH)_2$	Time (h)	Product	Yield[b] (%)
27[d,h]	 **1r**	**2a**	16	**3**	46
28[d,h]	 **1s**	**2a**	16	**15**	85

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), $Pd(OAc)_2$ (1 mol%), **L7** (2 mol%), Cs_2CO_3 (1 mmol), DMF (1 mL), r.t.
[b] Isolated yield.
[c] $Pd(OAc)_2$ (0.1 mol%) and **L7** (0.2 mol%).
[d] At 80 °C.
[e] $Pd(OAc)_2$ (0.0001 mol%) and **L7** (0.0002 mol%).
[f] $Pd(OAc)_2$ (0.01 mol%) and **L7** (0.02 mol%).
[g] **2** (1.2 mmol).
[h] $Pd(OAc)_2$ (3 mol%), **L7** (6 mol%) and TBAB (20 mol%).

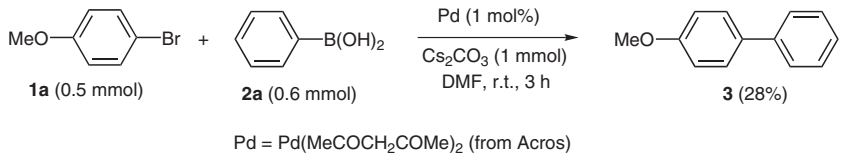
Encouraged by these results, a variety of aryl bromides and heteroaryl bromides were employed as the substrates for the palladium(II) acetate/**L7** catalyzed Suzuki–Miyaura coupling reaction (entries 10–23). It was observed that the palladium(II) acetate/**L7** system is still efficient for the reaction of aryl bromides, which underwent coupling with **2a** smoothly in good to excellent yield at 1 mol% to 0.01 mol% loadings of palladium (entries 10–17). However, the catalytic activity of the palladium(II) acetate /**L7** system decreased to some extent for the couplings of heteroaryl bromides, and higher reaction temperatures were required (entries 18–23). The reaction of 2-bromopyridine (**1l**) with **2a**, for example, afforded a low yield of the target product **14** at room temperature, whereas the yield of **14** increased sharply to 85% at 80 °C (entries 18 and 19). The results also showed that the reaction of substrate **1l** with **2a** could be conducted smoothly in good yield under 0.1 mol% of palladium (TON = 800; entry 20). It is worth noting that substrates **1k** and **1o** can performed the Suzuki–Miyaura coupling reaction with boronic acid **2a** to synthesize the corresponding polyaryls **13** and **17** in good yields (entries 17 and 23).

To our delight, aryl chlorides, including deactivated chlorides, were also suitable substrates under the palladium(II) acetate/**L7** catalyzed Suzuki–Miyaura coupling conditions in the presence of tetrabutylammonium bromide.[16] Although the reaction of 4-chlorotoluene (**1p**) with **2a**, 1 mol% of palladium(II) acetate and 2 mol% of **L7** provided a low yield of **11** even at 80 °C (entry 24), substrate **1p** could work well with **2a** to provide a moderate yield of **11** when 3 mol% of palladium and 20 mol% of tetrabutylammonium bromide were added (entry 25). Moderate to good yields were still achieved from the couplings of the other aryl chlorides **1q**,**r** and heteroaryl chloride **1s** with **2a** under the same conditions (entries 26–28).

A working mechanism was proposed as outlined in Scheme 2 on the basis of the previously proposed mechanism.[1] To elucidate the present results, a $Pd(0)L_4$ intermediate **A** was proposed.[1,17] The screening results of the ligands indicated that β-oxo amides were more efficient that β-oxo esters, 1,3-diketone, and β-oxo nitrile, which suggested that the coordination of nitrogen atom with palladium occurred. On the other hand, a control reaction disclosed that palladium(II) acetylacetonate provided a 28% yield of the desired product **3** after three hours (Scheme 3), whereas palladium(II) acetate combined with acetylacetonate (**L3**) gave only 6% yield of **3** (Table 1, entry 4). These results demonstrated that the coordination of the oxygen atom with palladium to form the enolate plays an important role in the reaction. The results in Table 1 further support this (Table 1, entries 7–15). Satisfactory results were obtained using β-oxo amides **L6**–**L10** and **L14** ligand, whereas the yield was reduced sharply using β-oxo amides **L11** and **L12** having a substituent at the 2-



Scheme 2 A possible mechanism



Scheme 3 A control reaction

position. Furthermore, no reaction was observed using ligand **L13**, which does not have an enol form (Table 1, entry 14). Thus, we deduced that the $Pd(0)L_4$ intermediate may be presented as intermediate **A**. The ^1H NMR data of palladium(II) acetate/**L7** (1:2) in situ also support the generation of intermediate **A** (Figure 1).

In summary, an inexpensive and efficient ligand for the palladium-catalyzed Suzuki–Miyaura coupling reaction of aryl halides with arylboronic acids has been developed. In the presence of palladium(II) acetate and **L7**, a variety of aryl halides including aryl chlorides and heteroaryl halides were smoothly coupled with arylboronic acids in moderate to excellent yields. Based on the results, several features were established: (1) The reaction was carried out under mild conditions. Many coupling reactions proceeded at room temperature. (2) The palladium(II) acetate/**L7** system is highly efficient (the maximal turnover numbers are <950,000 and turnover frequencies are <79,167). The coupling of aryl iodides could be conducted smoothly at a loading of 0.001 mol% palladium, and the reaction of aryl bromides were also worked well in the presence of 1 mol% to 0.01 mol% of palladium. (3) The reaction is general because its scope was extended to deactivated aryl chlorides and heteroaryl halides. Further efforts to extend the application of these ligands in other cross-coupling reactions and organic synthesis are underway in our laboratory.

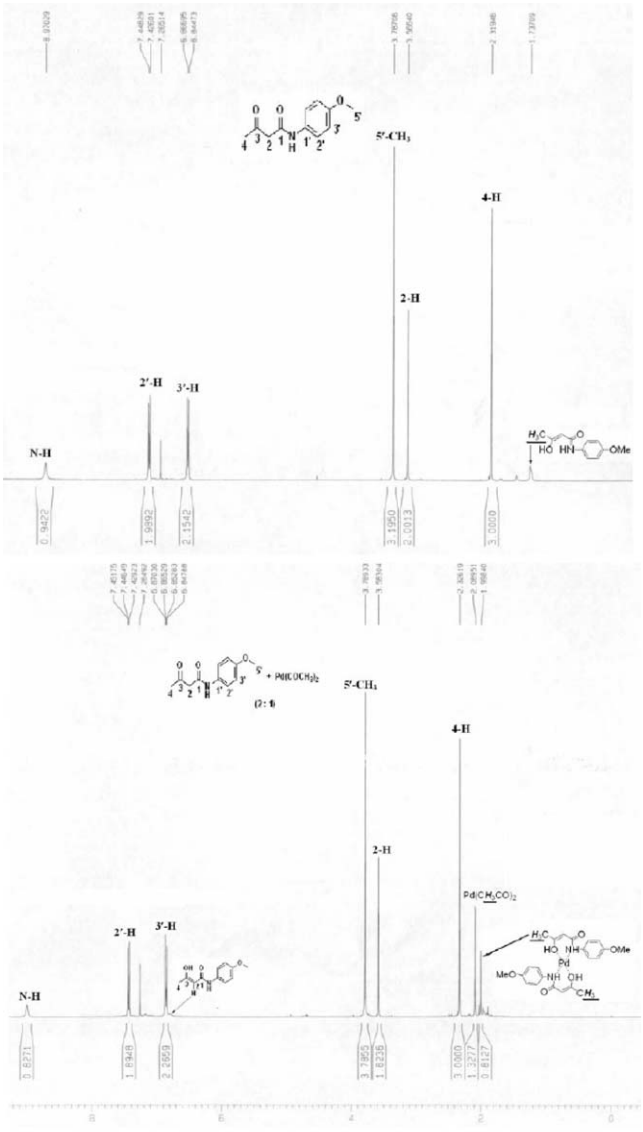


Figure 1 ^1H NMR of palladium(II) acetate/**L7** (1:2) in situ

NMR spectroscopy was performed on an Inova-400 (Varian), an Inova-500 (Varian) or a Bruck-300 (Bruck) spectrometer operating at 400 MHz (^1H NMR) and 100 MHz (^{13}C NMR), 500 MHz (^1H NMR) and 125 MHz (^{13}C NMR) or 300 MHz (^1H NMR) and 75 MHz (^{13}C NMR) with $CDCl_3$ as the solvent and TMS as internal standard. MS analysis was performed on GC-MS analysis (Shimadzu GCMS-QP2010).

Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling Reactions; General Procedure

A mixture of aryl halide **1** (0.5 mmol), arylboronic acid **2** (0.6 mmol), $Pd(OAc)_2$ (the indicated amount in Table 1 and Table 2), **L7** (the indicated amount in Table 1 and Table 2), Cs_2CO_3 (1 mol), and DMF (1 mL) was stirred at r.t. or 80 °C for the indicated time until complete consumption of starting material as monitored by TLC. After the mixture was filtered and evaporated, the residue was then purified by flash column chromatography (hexane or hexane–EtOAc) to afford the corresponding coupled product.

4-Methoxybiphenyl (3)[2a]

^1H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.53 (m, 4 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.33 (t, *J* = 7.25, 1 H), 6.98 (d, *J* = 8.8, 2 H), 3.86 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

LRMS (EI, 70 eV): *m*/*z* (%) = 184 (M^+, 100).

4,4′-Dimethoxybiphenyl (4)[17]

^1H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.4 Hz, 4 H), 6.95 (d, *J* = 8.87 Hz, 4 H), 3.84 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 133.5, 127.7, 114.1, 59.3.

LRMS (EI, 70 eV): *m*/*z* (%) = 214 (M^+, 100).

4-Fluoro-4′-methoxybiphenyl (5)[2d]

^1H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.45 (m, 4 H), 7.09 (t, *J* = 8.4 Hz, 2 H), 6.96 (d, *J* = 8.7 Hz, 2 H), 3.83 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7, 160.4, 159.0, 132.7, 128.2 (d, *J* = 9.3 Hz, 1 C), 128.0, 115.5 (d, *J* = 28.2 Hz, 1 C), 114.2, 55.3.

LRMS (EI, 70 eV): *m*/*z* (%) = 202 (M^+, 100).

4′-Methoxy-2-methylbiphenyl (6)[2d]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.22 (m, 6 H), 6.95 (d, *J* = 8.4 Hz, 2 H), 3.85 (s, 3 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 141.5, 135.5, 134.3, 130.3, 130.2, 129.9, 127.0, 125.8, 113.5, 55.3, 20.6.

LRMS (EI, 70 eV): *m*/*z* (%) = 198 (M^+, 100).

2-Methylbiphenyl (7)[2d]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (t, *J* = 7.2 Hz, 2 H), 7.32 (t, *J* = 6.8 Hz, 3 H), 7.25–7.23 (m, 4 H), 2.27 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 125.6, 20.4.

LRMS (EI, 70 eV): *m*/*z* (%) = 168 (M^+, 100).

4-Nitrobiphenyl (8)[2c]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 8.8 Hz, 2 H), 7.74 (d, *J* = 8.8 Hz, 2 H), 7.64 (d, *J* = 6.9 Hz, 2 H), 7.52–7.44 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6, 147.1, 138.8, 129.2, 128.91, 127.8, 127.4, 124.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 199 (M^+, 100).

1-Biphenyl-4-ylethanone (9)[2c]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.4 Hz, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.64 (d, *J* = 7.6 Hz, 2 H), 7.48 (t, *J* = 7.2 Hz, 2 H), 7.41 (t, *J* = 7.2 Hz, 1 H), 2.65 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.1, 146.1, 140.2, 136.2, 130.1, 129.2, 128.6, 127.6, 118.5, 27.0.

LRMS (EI, 70 eV): *m*/*z* (%) = 196 (M^+, 100).

Biphenyl (10)[2c]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.4 Hz, 4 H), 7.45 (t, *J* = 7.4 Hz, 4 H), 7.35 (t, *J* = 7.8 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.6, 129.1, 127.6, 127.5.

LRMS (EI, 70 eV): *m*/*z* (%) = 154 (M^+, 100).

4-Methylbiphenyl (11)[2a]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (t, *J* = 7.6 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1, 138.3, 137.0, 129.5, 128.7, 127.3, 127.2, 127.0, 21.1.

LRMS (EI, 70 eV): *m*/*z* (%) = 168 (M^+, 100).

3,5-Dimethylbiphenyl (12)[2a]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.4 Hz, 2 H), 7.44 (t, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 7.2 Hz, 1 H), 7.23 (s, 2 H), 7.02 (s, 1 H) 2.40 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 138.1, 128.9, 128.7, 127.9, 127.2, 127.1, 125.1, 21.4.

LRMS (EI, 70 eV): *m*/*z* (%) = 182 (M^+, 100).

1,4-Diphenylbenzene (13)[12c]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72–7.68 (m, 8 H), 7.50 (t, *J* = 7.2 Hz, 4 H), 7.40 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.8, 140.2, 128.8, 127.5, 127.3, 127.0.

LRMS (EI, 70 eV): *m*/*z* (%) = 230 (M^+, 100).

2-Phenylpyridine (14)[18]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, *J* = 4.8 Hz, 1 H), 7.99 (d, *J* = 6.8 Hz, 2 H), 7.78–7.71 (m, 2 H), 7.48 (t, *J* = 8.8 Hz, 2 H), 7.42 (t, *J* = 7.2 Hz, 1 H), 7.26–7.21 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 149.6, 139.3, 136.7, 128.9, 128.7, 126.9, 122.1, 120.5.

LRMS (EI, 70 eV): *m*/*z* (%) = 155 (M^+, 100).

5-Phenylpyrimidine (15)[19]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.21 (s, 1 H), 8.97 (s, 2 H), 7.59 (d, *J* = 8.8 Hz, 2 H), 7.53 (t, *J* = 8.8 Hz, 2 H), 7.47 (t, *J* = 7.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 154.8, 134.2, 134.1, 129.3, 128.9, 126.7.

LRMS (EI, 70 eV): *m*/*z* (%) = 156 (M^+, 100).

2-Phenylthiophene (16)[20]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.57 (m, 2 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.29–7.23 (m, 3 H), 7.05 (t, *J* = 4.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 134.3, 128.8, 127.9, 127.4, 125.9, 124.7, 123.0.

LRMS (EI, 70 eV): *m*/*z* (%) = 160 (M^+, 100).

3,5-Diphenylpyridine (17)[21]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (s, 2 H), 8.10 (s, 1 H), 7.66 (d, *J* = 8.4 Hz, 4 H), 7.52 (t, *J* = 8.0 Hz, 4 H), 7.45 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.0, 137.8, 136.7, 133.0, 129.2, 128.3, 127.3.

LRMS (EI, 70 eV): *m*/*z* (%) = 231 (M^+, 100.

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