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In situ generation of palladium nanoparticles: ligand-free palladium catalyzed ultrafast Suzuki–Miyaura cross-coupling reaction in aqueous phase at room temperature

Zhengyin Du [a,b,*], Wanwei Zhou [a,b], Fen Wang [a,b], Jin-Xian Wang [a,b]

[a] Key Laboratory of Eco-Environment Related Polymer Materials of Ministry of Education, Northwest Normal University, Lanzhou 730070, PR China
[b] Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, PR China

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ABSTRACT

An ultrafast and highly efficient ligand-free Suzuki–Miyaura cross-coupling reaction between aryl bromides/iodides and arylboronic acids using palladium chloride as catalyst in PEG400/H_2O in air at room temperature has been developed. TEM showed that palladium nanoparticles were generated in situ from $PdCl_2$/PEG400/H_2O without use of other reductants. The catalyst system can be recycled to reuse three times with good yields.

1. Introduction

The palladium catalyzed Suzuki–Miyaura cross-coupling reaction[1,2] between arylboronic acids and aryl halides or triflates has proved to be one of the most powerful and well-known chemical tools for forming the carbon–carbon single bonds of biaryls.[3] The general Suzuki–Miyaura coupling procedure involves the use of palladium–ligand complexes as catalysts, and the reactions are performed at high temperature under oxygen-free conditions to avoid side reactions. Nevertheless, all of these catalysts are toxic, expensive, usually unrecoverable, and the resulting products are often contaminated by Pd metal and ligands. In recent years, ligand-free palladium catalysts[4] have attracted much attention in the cross-coupling reactions due to the increasing international momentum for the development of an economically and environmentally friendly reaction in terms of green chemistry.

On the other hand, the use of environmentally benign reaction medium for replacing of volatile and poisonous organic solvents is one of hot topics in green chemistry. Water has clear advantages as a solvent for use in chemistry because it is cheap, readily available, and nontoxic. Recently, the Suzuki coupling reaction was investigated in aqueous phase under conventional thermal conditions and microwave irradiation.[5–13] Polyethylene glycol (PEG), being regarded as a high prospective solvent to replace volatile organic solvents in separation, catalysis and synthesis due to its some interesting characteristics, including high polarity, high boiling points, low toxicity, and good environmental compatibility,[14] has also been used in Suzuki coupling reactions.[15–18] Zhang and co-workers[19] reported that $Pd(OAc)_2$ in a mixture of water and PEG2000 was an active catalyst for the Suzuki reaction of aryl iodides and bromides.

As a convenient and inexpensive source of palladium, palladium chloride has been directly used in the Suzuki reactions and good results were obtained.[20–24] However, they suffered from low TON (TON was only 20 when used up to 5 mol % of catalyst),[21,22,24] long reaction times[20,22–24] and higher temperature.[21,22] To the best of our knowledge, there are few in situ formed palladium nanoparticles from $PdCl_2$ catalyzed Suzuki–Miyaura coupling reactions in the literature.[21]

We herein report the ligand-free Suzuki–Miyaura cross-coupling reaction catalyzed by in situ generated palladium nanoparticles from $PdCl_2$ in PEG400/H_2O under ambient conditions in air.

2. Results and discussion

To optimize the reaction conditions, a series of experiments under varied conditions in terms of solvents, the amount of base, catalyst, and reaction time for a model coupling reaction of

* Corresponding author. Tel./fax: +86 (931) 7971989; e-mail address: clinton_du@126.com (Z. Du).

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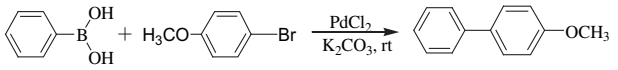
Table 1
Optimized conditions via the coupling of phenylboronic acid with 4-bromoanisole[a]



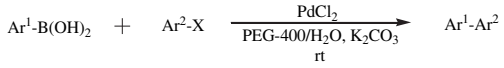
Entry	Solvents	K_2CO_3 (mmol)	$PdCl_2$ (mol %)	Time (min)	Yield[b] (%)
1	PEG400	1.75	0.5	20	44
2	PEG400/H_2O (3 mL/0.05 g)	1.75	0.5	20	56
3	PEG400/H_2O (2/1 mL)	1.75	0.5	8	96
4	PEG400/H_2O (1.5/1.5 mL)	1.75	0.5	8	99
5	PEG400/H_2O (1/2 mL)	1.75	0.5	10	67
6	PEG400/H_2O (0.05 g/3 mL)	1.75	0.5	20	Trace
7	H_2O (3 mL)	1.75	0.5	8	NR
8	PEG400/H_2O (1.5/1.5 mL)	1.75	0.5	6	93
9	PEG400/H_2O (1.5/1.5 mL)	1.5	0.5	8	83
10	PEG400/H_2O (1.5/1.5 mL)	1.75	0.25	15	87
11	PEG400/H_2O (1.5/1.5 mL)	1.75	0.1	20	37
12	PEG400/H_2O (1.5/1.5 mL)	1.75	None	10	Trace

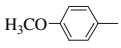
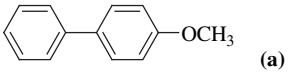
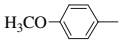
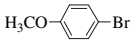
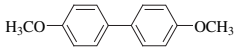
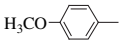
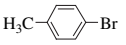
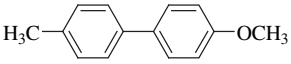
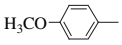
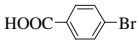
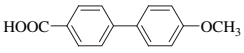
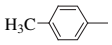
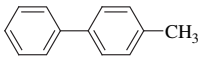
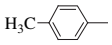
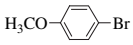
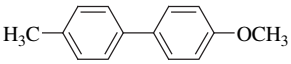
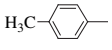
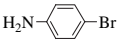
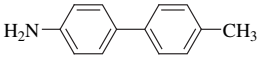
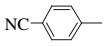
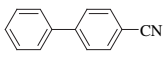
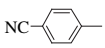
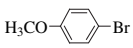
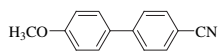
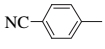
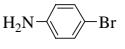
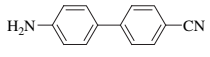
[a] Reaction conditions: phenylboronic acid (0.5 mmol), 4-bromoanisole (0.6 mmol).
[b] Isolated yield.

4-bromoanisole and phenylboronic acid were carried out in air as illustrated in Table 1. The effect of solvent on the Suzuki reaction was initially examined by using 0.5 mol % $PdCl_2$ (relative to phenylboronic acid). From the results in Table 1, it could be seen that the yield of the product was not promising, and only a 44% yield was obtained in PEG400 in the absence of H_2O (Table 1, entry 1). With the increase of the amount of water in PEG400, the yield increased first, then decreased until the reaction could not occur in pure water, and the high yield of 99% was achieved when the volume ratio of PEG to water was 1/1and the reaction lasted only 8 min (Table 1, entries 2–7), which might be due to the good solubility of the two substrates in this mixture. Under this condition, the TON of this reaction was 100, and the TOF was up to 742.5 h^{-1}, which was rare in the previously reported literatures of free-ligand palladium catalyzed Suzuki reactions. When the reaction time was prolonged from 6 to 8 min, the yield rose correspondingly from 93% to 99% (Table 1, entries 8 and 4). As known, base plays an important role in this reaction. If the amount of K_2CO_3 decreased from 3.5 equiv to 3.0 equiv of phenylboronic acid, the yield declined evidently from 99% to 83% (Table 1, entries 4 and 9). The amount of catalyst was also examined. When the amount of $PdCl_2$ was 0.25 mol %, the reaction was progressed well in 15 min with the yield of 87%. Further decrease the amount of $PdCl_2$ to 0.1 mol %, the yield declined significantly (Table 1, entry 11). It was noteworthy that trace of the biaryl was obtained when no catalyst was used (Table 1, entry 12).

Under the above optimized conditions, the scopes and limitations of this reaction were investigated, as seen in Table 2. It was obvious that a wide range of aryl bromides and iodides with varied substituents underwent cross-coupling with several diversely substituted phenylboronic acids by this procedure to produce the corresponding biaryls. Both the electron-rich and electron-deficient substituents on phenylboronic acid could not almost affect the yields

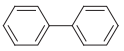
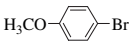
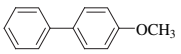
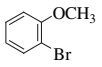
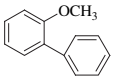
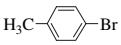
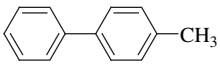
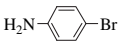
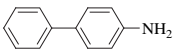
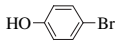
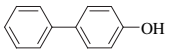
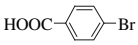
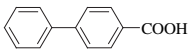
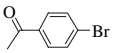
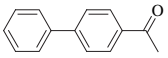
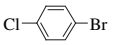
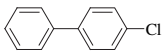
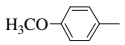
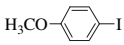
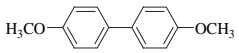
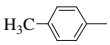
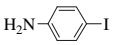
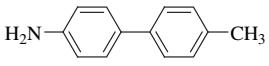
Table 2
Suzuki coupling reactions of aryl halides with arylboronic acids[a]



Entry	Ar^1	Ar^2-X	Time (min)	Product	Yield[b] (%)
1			8	 **(a)**	99
2			8	 **(b)**	99
3			8	 **(c)**	92
4			8	 **(d)**	99
5			8	 **(e)**	97
6			8	 **(c)**	97
7			15	 **(f)**	85
8			8	 **(g)**	99
9			8	 **(h)**	99
10			15	 **(i)**	87

(*continued on next page*)

Table 2 (*continued*)

Entry	Ar^1	Ar^2-X	Time (min)	Product	Yield[b] (%)
11			8	 **(j)**	99
12			8	 **(a)**	99
13			8	 **(k)**	93
14			8	 **(e)**	83
15			15	 **(l)**	84
16			8	 **(m)**	84
17			8	 **(n)**	99
18			8	 **(o)**	94
19			8	 **(p)**	97
20			8	 **(b)**	99
21			8	 **(f)**	90

[a] Reaction conditions: arylboronic acid (0.5 mmol), aryl halide (0.6 mmol), $PdCl_2$ (0.0025 mmol), K_2CO_3 (1.75 mmol), and PEG400/H_2O (1.5 mL/1.5 mL).
[b] Isolated yield.

of the products (e.g., Table 2, entries 1, 5, 8 and 11). For aryl bromides, the electronic effect of substituents showed different slightly. Initially, bromobenzene without any substituents coupled with varied phenylboronic acids to produce very high yields. The substituted HO–, CH_3–, and NH_2– groups resulted in a slight decline of the yields in comparison with the same electron-donating group CH_3O–, which gave almost quantitative yields, whereas the examined electron-withdrawing groups produced excellent yields in 8–15 min (e.g., Table 2, entries 12–18). Furthermore, sterically demanding aryl bromide also gave high yield (Table 2, entries 13). Subsequently, two aryl iodides were chosen to examine this reaction and the excellent yields were obtained (Table 2, entries 20 and 21).

To check the reusability of the reaction medium as well as the catalyst, the coupling of phenylboronic acid with 1-bromo-4-methoxybenzene in Table 2, entry 12 was chosen as a model reaction. The reaction mixture was extracted with ether after completion. The residual ether in reaction medium was removed under reduced pressure. Then, the reaction medium and Pd catalyst were subjected to the next run of the Suzuki reaction by charging with the same substrates. The results for the reuse of this catalyst system are summarized in Table 3. It can be seen that the activity of the catalyst decreases so significantly in recycle 2 that only 83% of yield is obtained even if the reaction time is prolonged from 8 min to 3 h.

Table 3
Recycle of the catalyst system[a]

Entry	Recycle number	Time	Yield [%][b]
1	Fresh	8 min	99
2	Recycle 1	8 min	82
3	Recycle 2	3 h	83
4	Recycle 3	3 h	81

[a] Reaction conditions: phenylboronic acid (0.5 mmol), 1-bromo-4-methoxybenzene (0.6 mmol), $PdCl_2$ (0.0025 mmol), K_2CO_3 (1.75 mmol), PEG400/H_2O (1.5 mL/1.5 mL), rt.
[b] Isolated yield.

In our previous work, we have confirmed that Pd nanoparticles are formed from $PdCl_2$ in PEG400 wherein PEG400 acts as both reductant and stabilizer.[25] In order to further clarify the active species in this Suzuki reaction, transmission electron microscope (TEM) was used for the analysis of the size and distribution of palladium nanoparticles. It showed that nano-Pd particles were fabricated and the average dimension was around 6–10 nm before the substrates were added into $PdCl_2$/PEG400 system (Fig. 1). It is obvious that the active species of the catalyst is in situ formed nano-Pd particles. TEM results of recovered Pd catalyst show that the Pd nanoparticles aggregate to form micrometer particles. This might be the major cause of slow deactivation. The details are under investigation.

3. Conclusion

In conclusion, we have successfully developed a highly efficient ligand-free method for the Suzuki coupling of aryl bromides and iodides with various phenylboronic acids by using $PdCl_2$ as catalyst

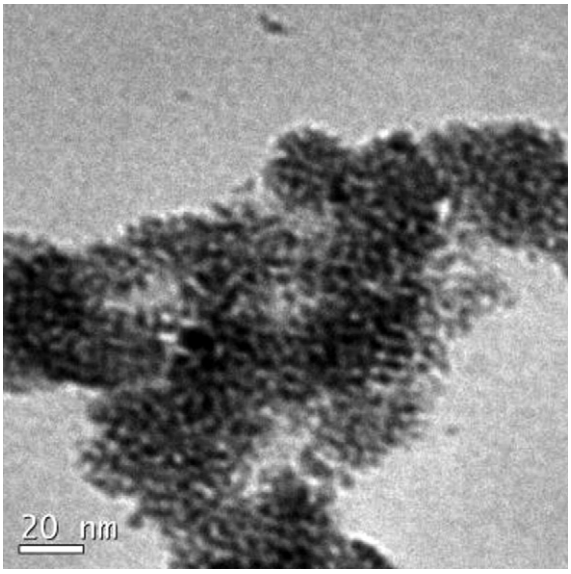


Fig. 1. TEM picture of nano-Pd in $PdCl_2$/PEG400/H_2O.

and PEG400/H_2O as medium in air at room temperature. The advantages of this protocol include low amount of the catalyst, mild conditions, very short reaction time, high to excellent yield, wide scope of substrates, and simple operation.

4. Experimental section

4.1. General remarks

All reagents were used as obtained from commercial sources without further purification. Melting points were determined on an XT-4 electrothermal micro-melting point apparatus. The ^1H and ^{13}C NMR spectra were recorded on a Bruker MERCURY-PLUS 400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm, δ). IR was measured on an Alpha Centauri FT-IR spectrometer and MS was analyzed by a QP-1000A GC–MS with EI sources. Elemental analyses were performed on a Carlo-Erba 1106 Elemental Analysis instrument. TEM pictures were obtained by JEM-2010 High-Resolution Transmission Electron Microscope.

4.2. General procedure for Suzuki–Miyaura reaction

A mixture of arylboronic acid (0.5 mmol), aryl bromides/iodides (0.6 mmol), $PdCl_2$ (0.0025 mmol), K_2CO_3 (1.75 mmol), PEG400 1.5 mL, and H_2O 1.5 mL were added to a 50 mL round-flask, and stirred at room temperature for the desired time until complete consumption of starting material as judged by TLC. Then, the reaction mixture was extracted with ether (10 mL×4) and the combined organic layers were dried over anhydrous $MgSO_4$ (acidification was needed for carboxyl substituted substrates before extraction). The solvent was removed by evaporation under reduced pressure to afford the crude products, which were further purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

4.3. Analytical data for the Suzuki–Miyaura coupling products

*4.3.1. 4-Methoxybiphenyl (**a**).* White solid, mp: 88–89 °C (lit.[26] 87–88 °C). ^1H NMR (400 MHz, $CDCl_3$): δ=7.56–7.51 (m, 4H), 7.43–7.39 (m, 2H), 7.32–7.28 (m, 1H), 6.99–6.96 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.09, 140.79, 133.73, 128.70, 128.13, 126.71, 126.63, 114.16, 55.32; EI-MS (m/z): 185 [M^++1], 184 [M^+], 169, 76; IR (ν/cm^{-1}): 1605, 1485, 1249, 1117, 833, 759, 687; Anal. Calcd for $C_{13}H_{12}O$ (184.09): C 84.75, H 6.57. Found: C 84.33, H 6.51.

*4.3.2. 4-Methoxy-4′-methoxybiphenyl (**b**).* White solid, mp: 181–182 °C (lit.[27] 178–180 °C). ^1H NMR (400 MHz, $CDCl_3$): δ=7.48 (d, J=7.6 Hz, 4H), 6.96 (d, J=7.2 Hz, 4H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.68, 133.46, 127.70, 114.14, 55.30; EI-MS (m/z): 215 [M^++1], 214 [M^+], 199, 183, 107, 76; IR (ν/cm^{-1}): 1605, 1498, 1246, 1180, 824; Anal. Calcd for $C_{14}H_{14}O_2$ (214.10): C 78.48, H 6.59. Found: C 78.12, H 6.54.

*4.3.3. 4-Methyl-4′-methoxybiphenyl (**c**).* White solid, mp 111–112 °C (lit.[27] 110–112 °C). ^1H NMR (400 MHz, $CDCl_3$): δ=7.51–7.49 (m, 2H), 7.45 (d, J=8 Hz, 2H), 7.22 (d, J=6.8 Hz, 2H), 6.97–6.94 (m, 2H), 3.83 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.90, 137.94, 136.32, 133.72, 129.41, 127.93, 126.55, 55.30, 21.03; EI-MS (m/z): 199 [M^++1], 198 [M^+], 183, 152, 76; IR (ν/cm^{-1}): 1606, 1499, 1249, 1180, 806; Anal. Calcd for $C_{14}H_{14}O$ (198.10): C 84.81, H 7.12. Found: C 84.43, H 7.05.

*4.3.4. 4-(4-Methoxyphenyl) benzoic acid (**d**).* White solid, mp: 265–266 °C (lit.[28] 250.0–251.7 °C). ^1H NMR (400 MHz, DMSO-d_6): δ=12.89 (s, 1H), 7.99 (d, J=8 Hz, 2H), 7.76 (d, J=8.4 Hz, 2H), 7.70 (d, J=8.8 Hz, 2H), 7.06 (d, J=8.8 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=167.16, 159.54, 143.93, 131.20, 129.92, 128.81, 128.12, 126.11, 114.49, 55.23; EI-MS (m/z): 229 [M^++1], 228 [M^+], 213, 185, 168, 44; IR (ν/cm^{-1}): 1681, 1601, 1525, 1495, 1429, 1289, 1247, 1193, 937, 835, 773, 706; Anal. Calcd for $C_{14}H_{12}O_3$ (228.08): C 73.67, H 5.30. Found: C 73.99, H 5.25.

*4.3.5. 4-Methylbiphenyl (**e**).* White solid, mp: 43–44 °C (lit.[29] 46–47 °C). ^1H NMR (400 MHz, $CDCl_3$): δ=7.58 (d, J=8 Hz, 2H), 7.49 (d, J=7.6 Hz, 2H), 7.43–7.39 (m, 2H), 7.32–7.28 (m, 1H), 7.24–7.20 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.14, 138.34, 136.98, 129.45, 128.68, 126.94, 21.07; EI-MS (m/z): 168 [M^+], 167 [M^+–1], 153, 91, 76; IR (ν/cm^{-1}): 1600, 1565, 822, 752, 688; Anal. Calcd for $C_{13}H_{12}$ (168.09): C 92.81, H 7.19. Found: C 93.26, H 7.13.

*4.3.6. 4-Methyl-4′-aminobiphenyl (**f**).* Yellowish-brown solid, mp: 91–93 °C (lit.[30] 98–99 °C). ^1H NMR (400 MHz, $CDCl_3$): δ=7.43–7.37 (m, 4H), 7.22–7.18 (m, 2H), 6.74 (d, J=8.8 Hz, 2H), 3.64 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.53, 138.25, 135.84, 131.52, 129.33, 127.76, 126.20, 115.34, 20.99; EI-MS (m/z): 184 [M^++1], 183 [M^+], 168, 167, 152, 77; IR (ν/cm^{-1}): 3422, 3381, 1617, 1498, 806; Anal. Calcd for $C_{13}H_{13}N$ (183.10): C 85.21, H 7.15. Found: C 85.55, H 7.09.

*4.3.7. 4-Cyanobiphenly (**g**).* White solid, mp: 85–86 °C (lit.[26] 85–86 °C). ^1H NMR (400 MHz, $CDCl_3$): δ=7.73–7.66 (m, 4H), 7.60–7.57 (m, 2H), 7.50–7.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.61, 139.11, 132.54, 129.07, 128.61, 127.68, 127.18, 118.90, 110.84; EI-MS (m/z): 180 [M^++1], 179 [M^+], 152, 76; IR (ν/cm^{-1}): 2223, 1602, 1480, 844, 768, 696; Anal. Calcd for $C_{13}H_9N$ (179.07): C 87.12, H 5.06. Found: C 86.76, H 5.10.

*4.3.8. 4-Methoxy-4′-cyanobipheny (**h**).* White solid, mp: 104–105 °C (lit.[31] 103–104 °C). ^1H NMR (400 MHz, $CDCl_3$): δ=7.70–7.62 (m, 4H), 7.55 (d, J=8 Hz, 2H), 7.01 (d, J=8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=160.19, 145.19, 132.54, 131.48, 128.34, 127.08, 119.07, 114.53, 110.09, 55.39; EI-MS (m/z): 210 [M^++1], 209 [M^+], 194, 177, 151, 76; IR (ν/cm^{-1}): 2220, 1603, 1490, 1239, 1173, 823; Anal. Calcd for $C_{14}H_{11}NO$ (209.08): C 80.36, H 5.30. Found: C 80.03, H 5.27.

*4.3.9. 4-Amino-4′-cyanobiphenyl (**i**).* Yellowish-brown solid, mp: 187–188 °C (lit.[32] 181–183 °C). ^1H NMR (400 MHz, CDCl3):

δ=7.66–7.59 (m, 4H), 7.43–7.40 (m, 2H), 6.78–6.74 (m, 2H), 3.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.17, 145.48, 132.47, 128.89, 128.15, 126.53, 119.25, 115.31, 109.35; EI-MS (m/z): 195 [M^++1], 194 [M^+], 178, 169, 152, 76; IR (ν/cm^{-1}): 3443, 3361, 2224, 1633, 1593, 1491, 820; Anal. Calcd for $C_{13}H_{10}N_2$ (194.08): C 80.39, H 5.19. Found: C 80.07, H 5.23.

*4.3.10. Biphenyl (**j**).* White solid, mp: 70–71 °C (lit.[17] 69–70 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.60–7.57 (m, 4H), 7.45–7.41 (m, 4H), 7.36–7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.19, 128.72, 127.22, 127.13; EI-MS (m/z): 154 [M^+], 76; IR (ν/cm^{-1}): 1567, 1473, 728, 692; Anal. Calcd for $C_{12}H_{10}$ (154.08): C 93.46, H 6.54. Found: C 93.11, H 6.61.

*4.3.11. 2-Methoxylbiphenyl (**k**).* Colorless viscous liquid (lit.[17] Oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.53–7.50 (m, 2H), 7.41–7.37 (m, 2H), 7.32–7.28 (m, 3H), 7.03–6.95 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=156.40, 138.49, 130.84, 130.65, 129.50, 128.57, 127.93, 126.86, 120.77, 111.16, 55.47; EI-MS (m/z): 185 [M^++1], 184 [M^+], 169, 152, 76; IR (ν/cm^{-1}): 1603, 1485, 1249, 1119, 763, 759, 687; Anal. Calcd for $C_{13}H_{12}O$ (184.09): C 84.75, H 6.57. Found: C 85.16, H 6.52.

*4.3.12. 4-Aminobiphenyl (**l**).* Yellowish-brown solid, mp: 52–54 °C (lit.[29] 53–54 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.54–7.52 (m, 2H), 7.41–7.36 (m, 4H), 7.28–7.21 (m, 1H), 6.74 (d, J=8.4 Hz, 2H), 3.69 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.78, 141.07, 131.45, 128.60, 127.94, 126.33, 126.20, 115.31; EI-MS (m/z): 170 [M^++1], 169 [M^+], 152, 77; IR (ν/cm^{-1}): 3423, 3391, 1620, 1483, 1260, 835, 761, 693; Anal. Calcd for $C_{12}H_{11}N$ (169.09): C 85.17, H 6.55. Found: C 85.54, H 6.51.

*4.3.13. 4-Phenylphenol (**m**).* White solid, mp: 169–170 °C (lit.[26] 165 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.55–7.52 (m, 2H), 7.49–7.46 (m, 2H), 7.43–7.39 (m, 2H), 7.32–7.28 (m, 1H), 6.92–6.88 (m, 2H), 4.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=155.02, 140.73, 134.04, 128.70, 128.38, 126.70, 115.62; EI-MS (m/z): 171 [M^++1], 170 [M^+], 153, 76; IR (ν/cm^{-1}): 3412, 1602, 1485, 1258, 832, 757, 686; Anal. Calcd for $C_{12}H_{10}O$ (170.07): C 84.68, H 5.92. Found: C 84.45, H 5.99.

*4.3.14. 4-Phenylbenzoic acid (**n**).* White solid, mp: 228–230 °C (lit.[29] 225–226 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ=12.98 (s, 1H), 8.02 (d, J=8.4 Hz, 2H), 7.79 (d, J=8 Hz, 2H), 7.72 (d, J=7.6 Hz, 2H), 7.50–7.46 (m, 2H), 7.42–7.38 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=167.15, 144.32, 139.02, 129.97, 129.60, 129.09, 128.30, 126.98, 126.83; EI-MS (m/z): 199 [M^++1], 198 [M^+], 181, 153, 76; IR (ν/cm^{-1}): 1682, 1606, 1485, 1421, 1294, 939, 862, 750, 696; Anal. Calcd for $C_{13}H_{10}O_2$ (198.07): C 78.77, H 5.09. Found: C 79.11, H 4.91.

*4.3.15. 1-Biphenyl-4-yl-ethanone (**o**).* White solid, mp: 122–123 °C (lit.[17,26] 120–121 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.04–8.02 (m, 2H), 7.70–7.67 (m, 2H), 7.64–7.62 (m, 2H), 7.49–7.45 (m, 2H), 7.42–7.38 (m, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.76, 145.77, 139.85, 135.82, 128.93, 128.89, 128.22, 127.26, 127.21, 26.66; EI-MS (m/z): 197 [M^++1], 196 [M^+], 181, 153, 76; IR (ν/cm^{-1}): 1678, 1261, 837, 764, 686; Anal. Calcd for $C_{14}H_{12}O$ (196.09): C 85.68, H 6.16. Found: C 85.99, H 6.10.

*4.3.16. 4-Chlorobiphenyl (**p**).* White solid, mp: 72–74 °C (lit.[31] 75–76 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.56–7.49 (m, 4H), 7.45–7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.97, 139.65, 133.35, 128.89, 128.86, 128.37, 127.57, 126.97; EI-MS (m/z): 190 [M^++2], 188 [M^+], 152, 76; IR (ν/cm^{-1}): 1651, 1560, 1514, 1473, 831, 756, 686; Anal. Calcd for $C_{12}H_9Cl$ (188.04): C 76.40, H 4.81. Found: C 76.12, H 4.87.

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Supplementary data

The general procedures and spectra of products. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.04.093.

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