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Pd/TEMPO-catalyzed electrooxidative synthesis of biaryls from arylboronic acids or arylboronic esters

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ABSTRACT

A facile electrooxidative method for synthesizing biaryls from arylboronic acids or arylboronic esters is described. In the presence of a catalytic amount of $Pd(OAc)_2$ and TEMPO, the electrooxidation of arylboronic acids or arylboronates gave the corresponding biaryls in moderate to excellent yields.

1. Introduction

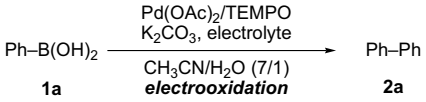
Biaryls are key skeletons of functional materials and pharmaceutical compounds. Various methods for preparing biaryl compounds have been reported. One of the most straightforward methods for preparing unsymmetrical biaryls is a Pd-catalyzed cross-coupling reaction such as Suzuki–Miyaura coupling.[1] In contrast, preparing symmetric biaryls, one of the simplest methods for preparing symmetric biaryls is the palladium-catalyzed homo-coupling of aryl halides,[2] arylboronic acids,[3] or arylboronic esters.[3b,d,h,j,4] We have been interested in electrochemical organic syntheses,[5] and recently reported both the electrooxidative synthesis of cationic Pd complexes ($[Pd(CH_3CN)_4][Y]_2$, $Y=BF_4^-$, PF_6^-, and ClO_4^-) and the integration of this system into electrooxidative Wacker-type reactions.[5b] We also reported the electrooxidative homo-coupling reaction of arylboronic acids catalyzed by electrogenerated cationic Pd^{II} catalysts. This electrooxidation could be applied to each arylboronic acids bearing electron-withdrawing or -donating substituents.[6] Under appropriate conditions, a wide variety of arylboronic acids could be converted to the corresponding biaryls at room temperature. We later discovered that the homo-coupling of arylboronic esters could be achieved under similar conditions. We described here the details of the electrooxidation of a series of arylboronic acids as well as arylboronic esters, to give the corresponding biaryls in moderate to high yields.

2. Results and discussion

2.1. Optimization of the reaction conditions for the electrooxidative homo-coupling of phenylboronic acid

The electrooxidative coupling of phenylboronic acid (**1a**) was carried out under various conditions. Previously, we reported that the electrooxidation of $Pd(OAc)_2$ gave a cationic palladium complex bearing a counter anion which came from the electrolyte.[5b] Therefore, the effect of the supporting electrolyte was examined first (Table 1). The electrooxidation of **1a** in the presence of $Pd(OAc)_2$ (10 mol %), TEMPO (30 mol %), and Et_4NBF_4 (0.05 M) afforded **2a** in 64% yield (entry 1). With the use of Et_4NPF_6, **2a** was obtained in 76% yield (entry 2). With Et_4NClO_4, the yield of **2a**

Table 1
Effect of electrolytes[a]



Entry	Electrolyte	Yield (%)[b]
1	Et_4NBF_4	64
2	Et_4NPF_6	76
3	Et_4NClO_4	88 (61)[c]
4	Et_4NOTs	60
5	Et_4NOAc	66
6	Bu_4NClO_4	56
7	$LiClO_4$	86
8	$NaClO_4$	73

[a] Reaction conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), TEMPO (30 mol %), K_2CO_3 (2 equiv), electrolyte (0.05 M), CH_3CN/H_2O (7/1, 10 mL), 5 mA, 3 F/mol.
[b] Isolated yield.
[c] $Pd(OAc)_2$ (5 mol %).

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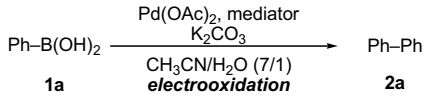
drastically increased to 88% (entry 3). In contrast, with the electrooxidation of **1a** in the presence of Et_4NOTs or Et_4NOAc, the product **2a** was obtained in yields of only 60% and 66%, respectively (entries 4 and 5). These results suggest that ammonium and/or alkaline metal salts of strong acids may be favorable supporting electrolytes for the reaction.

The proper choice of mediator plays a significant role in the electrooxidative coupling of **1a** (Table 2). Without any mediator, the reaction did not proceed. Even with a stoichiometric amount of $Pd(OAc)_2$, **2a** was obtained in only 51% yield (entry 1). While **2a** was obtained in 73% yield with TEMPO (entry 2), the yield of **2a** decreased to 36% with 4-benzoyl-TEMPO (entry 3). With hydroquinone, a frequently used mediator, **2a** was obtained in only 49% yield (entry 4). Triphenylamine (Ph_3N) was also ineffective for the reaction (entry 5). These results suggest that Pd^0 species generated in situ could not be oxidized to Pd^{II} directly on the anode, and an efficient catalyst would be generated in situ only with the use of TEMPO. When TEMPO was used as a mediator, it would act not only as a mediator, but also as a ligand of the Pd catalyst.

Table 2
Effect of mediators[a]

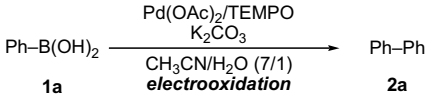


Entry	Mediator	Yield (%)[b]
1	None	n.d. (51)[c]
2	TEMPO	73
3	4-Benzoyl-TEMPO	36
4	Hydroquinone	49
5	Ph_3N	36

[a] Reaction conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), mediator (30 mol %), K_2CO_3 (2 equiv), $NaClO_4$ (0.05 M), CH_3CN/H_2O (7/1, 10 mL), 5 mA, 3 F/mol.
[b] Isolated yield.
[c] Performed with $Pd(OAc)_2$ (1 equiv).

The amount of TEMPO strongly dominated the reactivity of the reaction (Table 3). TEMPO at 30 mol % was the best amount for the reaction (86%, entry 2). With either more or less TEMPO, the yield of **2a** decreased (entries 1 and 3).

Table 3
Effect of the amount of TEMPO[a]

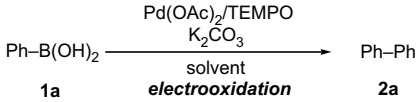


Entry	Amount of TEMPO (mol %)	Yield (%)[b]
1	20	55
2	30	86
3	40	57

[a] Reaction conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), K_2CO_3 (2 equiv), $LiClO_4$ (0.05 M), CH_3CN/H_2O (7/1, 10 mL), 5 mA, 3 F/mol.
[b] Isolated yield.

We next examined the effect of the solvent in the electrooxidative homo-coupling of **1a** (Table 4). Mixtures of several organic solvents and water (7/1) were used for the reaction. When the reaction was carried out in acetone/H_2O, THF/H_2O, DMA/H_2O, or DMF/H_2O, the yield of the product **2a** varied within a range of 13–39% (entries 2–5). Among the solvents that have been examined thus far, CH_3CN/H_2O was the most suitable combination for the electrooxidative coupling of **1a** (entry 1), which suggests that CH_3CN would coordinate to the Pd center to stabilize the catalyst. The ratio of CH_3CN and H_2O was also important. While **2a** was obtained in 86% yield with a CH_3CN/H_2O ratio of 7/1, with a 5/1 or 9/1 solution of CH_3CN/H_2O, the reaction efficiency was quite low, and **2a** was obtained in respective yields of 25% and 39% (entry 1). In these cases, the reaction media was apparently separated into organic and aqueous phases, and this could help to explain why the reaction did not proceed efficiently. Interestingly, water was also an efficient solvent, in which the reaction proceeded smoothly to afford **2a** in 78% yield (entry 6).

Table 4
Effect of solvent[a]



Entry	Solvent	Yield (%)[b]
1	CH_3CN/H_2O (7/1)	86 (25)[c] (39)[d]
2	Acetone/H_2O (7/1)	39
3	THF/H_2O (7/1)	36
4	DMA/H_2O (7/1)	14
5	DMF/H_2O (7/1)	13
6	H_2O	78

[a] Reaction conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), TEMPO (30 mol %), K_2CO_3 (2 equiv), $LiClO_4$ (0.05 M), 5 mA, 3 F/mol.
[b] Isolated yield.
[c] CH_3CN/H_2O (5/1).
[d] CH_3CN/H_2O (9/1).

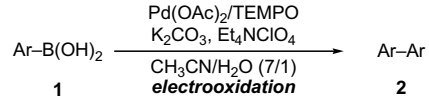
2.2. Scope and limitations of the Pd/TEMPO-catalyzed homo-coupling of arylboronic acids

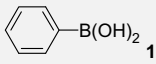
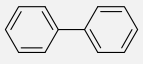
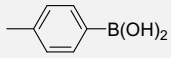
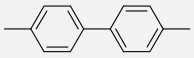
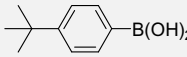
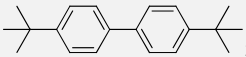
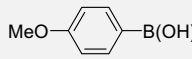
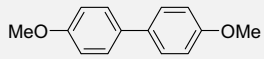
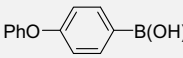
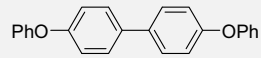
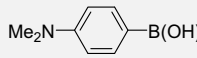
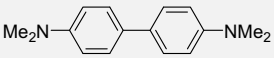
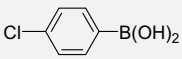
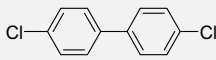
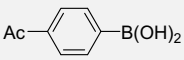
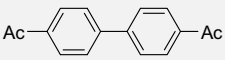
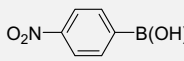
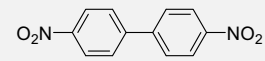
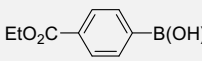
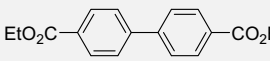
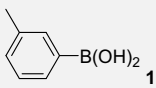
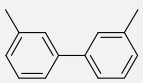
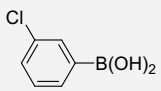
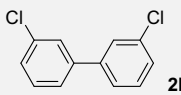
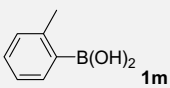
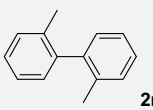
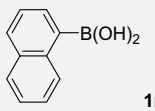
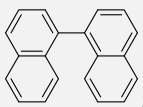
As mentioned above, the homo-coupling of **1a** gave the best results with K_2CO_3 as a base, Et_4NClO_4 as an electrolyte, and TEMPO as a mediator. The homo-coupling of several arylboronic acids was carried out under the optimized conditions (Table 5). First, arylboronic acids bearing electron-donating groups at the *p*-position were examined (entries 2–6). The reaction of *p*-tolylboronic acid (**1b**) and *p*-*tert*-butylphenylboronic acid (**1c**) proceeded smoothly to give 4,4′-dimethylbiphenyl (**2b**) and 4,4′-di-*tert*-butylbiphenyl (**2c**) in respective yields of 91% and 89% (entries 2 and 3). In contrast, the reaction of *p*-methoxyphenylboronic acid (**1d**) gave the desired product in only 34% yield under the condition. Further optimization revealed that aq $NaClO_4$ was a suitable solvent for substrate **1d**, and the yield of **2d** increased to 95% (entry 4). The homo-coupling of *p*-phenoxyphenylboronic acid (**1e**) proceeded smoothly under the typical conditions to give **2e** in 95% yield (entry 5). Next, the Pd/TEMPO-catalyzed reaction of several arylboronic acids bearing electron-withdrawing groups was examined (entries 7–10). The reactions of *p*-chlorophenylboronic acid (**1g**), *p*-acetylphenylboronic acid (**1h**), and *p*-nitrophenylboronic acid (**1i**) proceeded smoothly to give biaryls **2g**–**i** in respective yields of 93%, 95%, and 98%. Unfortunately, *p*-(ethoxycarbonyl)phenylboronic acid (**1j**) suffered from hydrolysis under these conditions and **2j** was obtained in only 23% yield (entry 10). *m*- and *o*-Substituted phenylboronic acids could also be used in the reaction (entries 11–14). The reaction of *m*-tolylboronic acid (**1k**) and *m*-chlorophenylboronic acid (**1l**) gave the corresponding biaryls (**2k** and **2l**) in respective yields of 85% and 87% (entries 11 and 12). Similarly, the homo-coupling of *o*-tolylboronic acid (**1m**) proceeded to afford **2m** in 74% yield (entry 13). 1-Naphthylboronic acids could also be used for the reaction, and 1,1′-binaphthyl was obtained in 97% yield (entry 14).

2.3. Pd/TEMPO-catalyzed homo-coupling of arylboronic esters

To elucidate the scope and limitations of the reaction conditions, we next extended this procedure to the homo-coupling of

Table 5
Electrooxidative homo-coupling of several arylboronic acids[a]



Entry	Ar–B(OH)$_2$	Ar–Ar	Yield (%)[b]
1	 **1a**	 **2a**	88
2	 **1b**	 **2b**	91
3	 **1c**	 **2c**	89
4[c]	 **1d**	 **2d**	95
5	 **1e**	 **2e**	95
6[d]	 **1f**	 **2f**	69
7	 **1g**	 **2g**	93
8	 **1h**	 **2h**	95
9	 **1i**	 **2i**	98
10	 **1j**	 **2j**	23
11	 **1k**	 **2k**	85
12	 **1l**	 **2l**	87
13	 **1m**	 **2m**	74
14	 **1n**	 **2n**	97

[a] Reaction conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), TEMPO (30 mol %), K_2CO_3 (2 equiv), Et_4NClO_4 (0.05 M), 5 mA, 3 F/mol.
[b] Isolated yield.
[c] Performed in aq $NaClO_4$.
[d] 4-$PhCO_2$-TEMPO was used instead of TEMPO.

arylboronic esters (Table 6). First, the homo-coupling of phenylboronic esters was carried out. Under the optimized conditions for arylboronic acids, the electrooxidative homo-coupling of phenylboronic esters **3a** and **4a** gave biphenyl (**2a**) in respective yields of 67% and 64% (entries 1 and 2). Further optimization revealed that the yield of **2a** was highly influenced by the solvent, and the reaction of **3a** gave the product in up to 88% yield in H_2O (entry 1). We next examined arylboronic esters bearing electron-donating groups at the *p*-position (entries 3–5). The electrooxidative homo-coupling of *p*-tolylboronic ester **3b** afforded 4,4′-bitolyl (**2b**) in 72% yield, while the electrolysis of **4b** gave **2b** in 99% yield (entry 4). The yield of 4-dimethylaminophenylboronic ester was similar to that of 4-dimethylaminophenylboronic acid (69%, entry 5). Next, the electrooxidation of arylboronic esters bearing electron-withdrawing groups at the *p*-position (entries 6–8) was examined. The electrooxidation of *p*-chloroboronic esters **3g** and **5g** gave 4,4′-dichlorobiphenyl (**2g**) in respective yields of 92% and 96% (entries 6 and 7). *p*-Nitrophenylboronic ester (**3i**) gave **2i** in 92% yield (entry 8). *o*-Substituted arylboronic esters could also be used in the reaction (entries 9 and 10). The electrooxidation of **3k** and **3l** gave corresponding biaryl **2k** and **2l** in the respective yields of 69% and 81% (entries 9 and 10). As with the reaction of arylboronic acids, arylboronic esters bearing electron-donating or withdrawing groups could be used in the reaction to give the corresponding biaryls in moderate to high yields.

2.4. A plausible mechanism

The Pd/TEMPO-catalyzed electrooxidative homo-coupling of arylboronic acids and esters exhibited high reactivity under mild conditions in contrast to previously reported O_2-oxidative reactions. This high reactivity was probably due to the generation of oxygen-free active Pd^{II} species. Amatore and Jutand reported that the air-oxidation of Pd^0 generates $(\eta^2\text{-}O_2)PdL_2$.[3h] They also found that a Pd/benzoquinone-catalyzed electrooxidation of arylboronic acids and esters proceeded smoothly under anaerobic conditions to afford biaryls.[3b] They noted that oxygen-free Pd species might play a key role in the reaction. Since our electrooxidative reaction was carried out under an argon atmosphere, oxygen-free Pd^{II} species would be generated. Although the intermediate has not been identified, it should be a Pd^{II} species bearing ClO_4^- or TEMPO as a counteranion.[7] A plausible mechanism is illustrated in Figure 1. First, the electrooxidation of $Pd(OAc)_2$ would proceed to generate a Pd^{II} species ($Pd^{II}[Y]_2$, Y=ClO_4^-) through Kolbe oxidation.[5b] Transmetallation would then occur with an arylborate, which was generated by the reaction of an arylboronic acid/ester with base, to give Ar–Pd^{II}[Y]. A second transmetallation would give Ar–Pd^{II}–Ar, and subsequent reductive elimination would give biaryl and Pd^0 species (Pd^0). The Pd^0 species would be oxidized to Pd^{II} by the *N*-oxoammonium cation generated by the electrooxidation of TEMPO on the anode, and the active Pd^{II} catalyst would be regenerated.

3. Conclusion

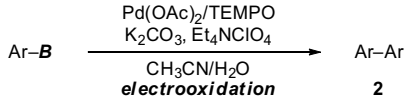
The Pd/TEMPO-catalyzed electrooxidative homo-coupling of arylboronic acids has been developed. Arylboronic acids **1a**–**n**, bearing electron-donating or -withdrawing groups, were successfully used for the reaction, and the corresponding biaryls **2a**–**n** were obtained in good to excellent yields under mild conditions. The electrooxidative homo-coupling of arylboronic esters took place under similar conditions. In the presence of a catalytic amount of Pd/TEMPO, several arylboronic esters were oxidized to give the corresponding biaryls.

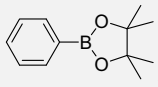
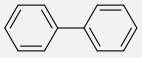
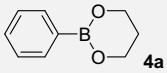
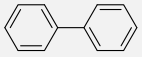
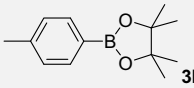
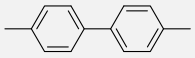
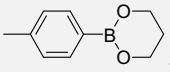
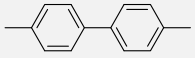
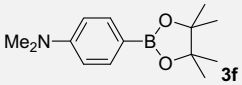
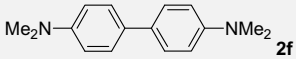
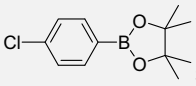
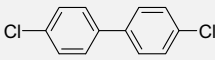
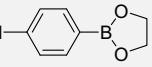
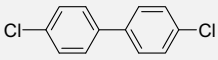
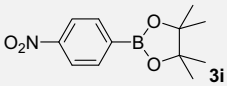
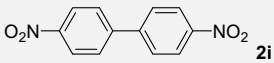
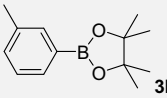
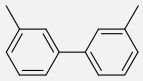
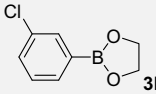
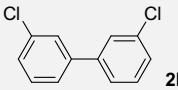
4. Experimental

4.1. General procedure of electrooxidative Pd-catalyzed homo-coupling of arylboronic acids

The electrooxidation was carried out in an H-type divided cell (separated by a glass filter) equipped with two platinum electrodes (1.0×1.5 cm^2). In the anodic chamber was placed a solution of phenylboronic acid (**1a**, 25 mg, 0.21 mmol), $Pd(OAc)_2$ (4.3 mg, 0.02 mmol), TEMPO (9.4 mg, 0.06 mmol), and K_2CO_3 (55 mg, 0.40 mmol) in a 0.05 M Et_4NClO_4 solution of CH_3CN/H_2O (7/1, 5 mL). In the cathodic chamber was placed a 0.05 M Et_4NClO_4 solution of

Table 6
Electrooxidative homo-coupling of several arylboronic esters[a]



Entry	Ar–B	Ratio of CH_3CN/H_2O	Ar–Ar	Yield (%)[b]
1	 **3a**	0/1	 **2a**	88 (67)[c]
2	 **4a**	7/1	 **2a**	64
3	 **3b**	1/1	 **2b**	72
4	 **4b**	7/1	 **2b**	99
5	 **3f**	1/1	 **2f**	69
6	 **3g**	1/3	 **2g**	92
7	 **5g**	7/1	 **2g**	96
8	 **3i**	3/1	 **2i**	92
9	 **3k**	1/1	 **2k**	69
10	 **3l**	7/1	 **2l**	81

[a] Reaction conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), TEMPO (30 mol %), K_2CO_3 (2 equiv), Et_4NClO_4 (0.05 M), 5 mA, 3 F/mol.
[b] Isolated yield.
[c] Performed in CH_3CN/H_2O (7/1).

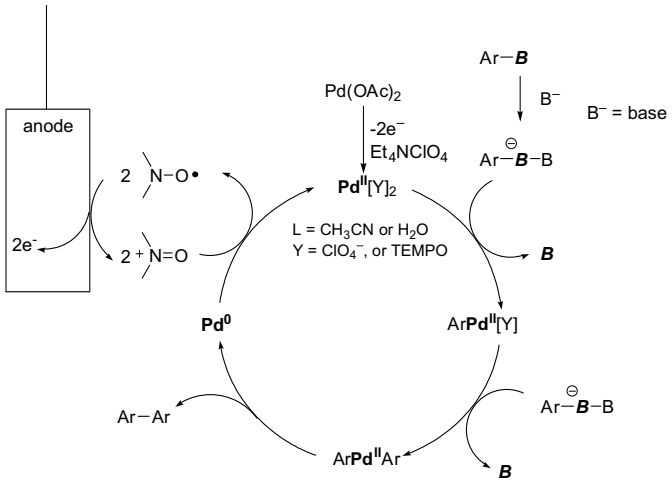


Figure 1. A plausible mechanism for the electrooxidative homo-coupling of arylboronic acids and esters.

CH_3CN/H_2O (7/1, 5 mL). Under argon, a constant current (5 mA, 3 F/mol) was supplied at room temperature with vigorous stirring. To the resulting mixture was added aq satd NaCl (10 mL) and extracted with Et_2O (3×10 mL). The combined organic phase was washed with aq satd NaCl (15 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to afford biphenyl (**2a**, 88%).

*4.1.1. Biphenyl (**2a**).* Colorless solid; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35–7.38 (m, 2H), 7.45–7.48 (m, 4H), 7.61–7.62 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 127.1, 127.2, 128.7, 141.2; IR (KBr) 3062, 3034, 1568, 1480, 1428, 729, 697 cm^{-1}.

*4.1.2. 4,4′-Dimethylbiphenyl (**2b**).* Colorless solid; ^1H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 6H), 7.22–7.24 (m, 4H), 7.46–7.48 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.1, 126.8, 129.4, 136.7, 138.3; IR (KBr) 2919, 1903, 1561, 1502, 1447, 1311, 1179, 1113, 1038 cm^{-1}.

*4.1.3. 4,4′-Di-tert-butylbiphenyl (**2c**).* Colorless solid; ^1H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 18H), 7.44 (dd, J=6.8, 2.0 Hz, 4H), 7.52 (dd,

J=6.8, 2.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.4, 34.5, 125.6, 126.6, 138.2, 149.9; IR (KBr) 3087, 3053, 3029, 2959, 2901, 2867, 1495 cm^{-1}.

*4.1.4. 4,4′-Dimethoxybiphenyl (**2d**).* Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (s, 6H), 6.94–6.97 (m, 4H), 7.47–7.49 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.2, 114.0, 127.6, 133.3, 158.5; IR (KBr) 2957, 1500, 1438, 1275, 1248, 1041 cm^{-1}.

*4.1.5. 4,4′-Diphenoxybiphenyl (**2e**).* Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05–7.08 (m, 8H), 7.11–7.14 (m, 2H), 7.34–7.38 (m, 4H), 7.51–7.54 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 119.0, 119.1, 123.3, 128.2, 129.8, 135.6, 156.6, 157.1; IR (KBr) 3056, 3039, 2923, 2853, 1590, 1492, 1255 cm^{-1}.

*4.1.6. 4,4′-Bis(dimethylamino)biphenyl (**2f**).* Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.97 (s, 12H), 6.80 (d, J=8.4 Hz, 4H), 7.45 (d, J=8.4 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.8, 113.1, 126.9, 129.8, 149.2; IR (KBr) 2799, 1611, 1352, 1227 cm^{-1}.

*4.1.7. 4,4′-Dichlorobiphenyl (**2g**).* Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.42 (m, 4H), 7.47–7.49 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 128.2, 129.0, 133.7, 138.4; IR (KBr) 2962, 2356, 1474, 1388, 1261, 1088, 1002 cm^{-1}.

*4.1.8. 4,4′-Diacetylbiphenyl (**2h**).* Colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.66 (s, 6H), 7.72–7.73 (m, 4H), 8.06–8.07 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 26.7, 127.4, 128.9, 136.4, 144.2, 197.6; IR (KBr) 3343, 3044, 2920, 1681 cm^{-1}.

*4.1.9. 4,4′-Dinitrobiphenyl (**2i**).* Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J=9.0 Hz, 4H), 8.37 (d, J=9.0 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 124.4, 128.3, 145.0, 148.0; IR (KBr) 2935, 1598, 1511, 1477, 1375, 1343, 1108 cm^{-1}.

*4.1.10. 4,4′-Bis(ethoxycarbonyl)biphenyl (**2j**).* Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (t, J=7.0 Hz, 6H), 4.41 (q, J=7.0 Hz, 4H), 7.68 (dt, J=8.5, 2.0 Hz, 4H), 8.13 (dt, J=8.5, 2.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 61.1, 127.2, 130.0, 130.1, 144.3, 166.3; IR (KBr) 2981, 2906, 1707, 1607,1279 cm^{-1}.

*4.1.11. 3,3′-Dimethylbiphenyl (**2k**).* Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 6H), 7.15 (d, J=7.3 Hz, 2H), 7.24 (s, 2H), 7.31 (t, J=7.3 Hz, 2H), 7.37–7.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 124.3, 127.9, 128.0, 128.6, 138.2, 141.3; IR (neat) 3028, 2949, 2919, 2859, 2732 cm^{-1}.

*4.1.12. 3,3′-Dichlorobiphenyl (**2l**).* Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.45 (m, 6H), 7.53–7.55 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.2, 127.2, 127.7, 130.1, 134.8, 141.6; IR (neat) 3064, 2924, 2853, 1591, 1561, 1462, 1395, 1101 cm^{-1}.

*4.1.13. 2,2′-Dimethylbiphenyl (**2m**).* Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.05 (s, 6H), 7.10–7.27 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8, 125.5, 127.1, 129.3, 129.8, 135.8, 141.6; IR (neat) 3059, 3017, 2922, 1599, 1477, 1453, 754, 728 cm^{-1}.

*4.1.14. 1,1′-Binaphthyl (**2n**).* Colorless solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.30 (m, 2H), 7.38–7.60 (m, 8H), 7.92–7.95 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 125.4, 125.8, 125.9, 127.0, 127.8, 127.9, 128.1, 132.8, 133.5, 138.4; IR (KBr) 3040, 1822, 1586, 1504, 1384 cm^{-1}.

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Supplementary data

Spectroscopic and analytical data and selected experimental procedure associated with this article can be found, in the online version. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.08.004.

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