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Palladium-Catalyzed Regioselective Homocoupling of Arenes Using Anodic Oxidation: Formal Electrolysis of Aromatic Carbon−Hydrogen Bonds

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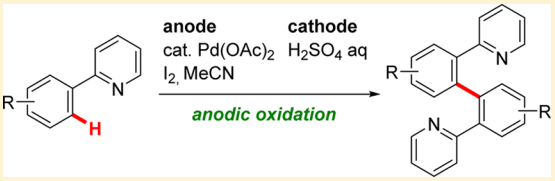
Supporting Information

ABSTRACT: Palladium-catalyzed regioselective homocoupling of arylpyridines under anodic oxidation conditions was achieved in the presence of I_2. The dimerization of meta-substituted arylpyridines proceeded selectively at less-sterically congested ortho-positions, and the selectivity is different from that reported for the palladium-catalyzed dimerization using Oxone as an oxidant. The dimerization also proceeds using catalytic amounts of both $Pd(OAc)_2$ and I_2 under the electrochemical reaction conditions.



In search of efficient, environmentally benign syntheses, transition-metal-catalyzed aromatic C−H functionalization has been extensively studied, because it may allow us to reduce synthetic steps and chemical wastes by avoiding the installation of reactive groups such as leaving groups and metals.[1] In order to form carbon−carbon bonds by these methods, however, most of the reported aromatic C−H functionalization processes still employ those groups as reaction sites in the coupling partners (Figure 1A). In this context, much effort has been devoted to development of direct coupling reactions of two carbon−hydrogen bonds, in which significant advances have been made in the past decade using stoichiometric amounts of oxidants (Figure 1B).[2,3]

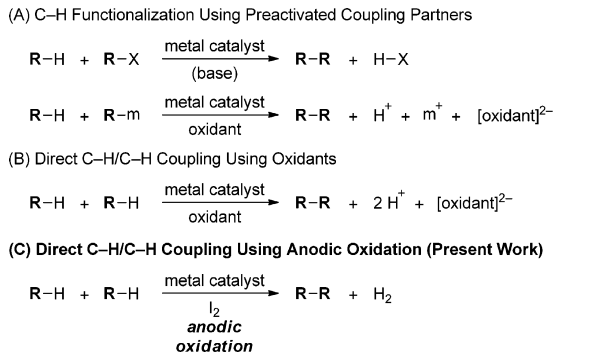


Figure 1. Strategies for carbon−carbon bond formation via cleavage of C−H bonds by transition metal catalysts.

In recent years, our group has been studying the use of anodic oxidation methods for transition-metal-catalyzed reactions, especially for aromatic C−H functionalization reactions.[4] Combining the palladium-catalyzed ortho-selective aromatic C−H bond cleavage and anodic oxidation of halogen sources, regioselective halogenation was achieved under simple reaction systems. In these reactions, protons are reduced to hydrogen gas at the cathode, while generating protons by cutting off from carbon−hydrogen bonds. Therefore, stoichiometric oxidants were not necessary for these processes. Construction of carbon−carbon bonds by combination of electrochemical oxidation with metal-catalyzed C−H bond cleavage has been reported by C−H alkenylation,[5] but this type of process has rarely been explored. It should be noted that in the absence of metal catalysts, anodic oxidation has been employed to form carbon−carbon bonds from two aromatic C−H bonds by using phenol derivatives[6,7a] or radical cation pools.[7b]

Here we report that palladium-catalyzed ortho-selective homocoupling of arylpyridines proceeds under anodic oxidation conditions in the presence of I_2 (Figure 1C). The reaction can be regarded as regioselective formal electrolysis of aromatic C−H bonds, considering that it forms a C−C bond and an H−H bond from two C−H bonds. The use of catalytic amounts of both a palladium salt and I_2 was also achieved.

For the palladium-catalyzed electrochemical C−H iodination we reported previously, substrates giving high yields were arylpyridines possessing a substituent at the ortho-position on the aryl group or the 3-position on the pyridyl group.[4b] On the other hand, 2-{3-(trifluoromethyl)phenyl}pyridine (**1a**) was found to have a high tendency to dimerize under the electrochemical reaction conditions. When the reaction of **1a** was performed at 90 °C for 5.4 h at 5 mA (4.0 F/mol),[8] the corresponding ortho-dimerization product **3a** was obtained in 53% yield along with 17% yield of iodination product **2a** (Table 1, entry 1). Although several examples of ortho-selective dimerization of arylpyridines were reported,[2] the selective formation of **3a** was intriguing, because Sanford and co-workers reported that $Pd(OAc)_2$-catalyzed dimerization of **1a** using Oxone as an oxidant gave a 1.7:1 mixture

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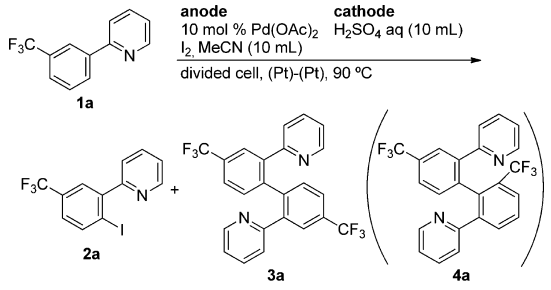
Table 1. Palladium-Catalyzed Electrochemical Regioselective Homocoupling of 1a[a]



						yields (%)	
entry	**1a** (mmol)	I_2 (equiv)	I (mA)	time (h)	F/mol	**2a**	**3a**
1	0.25	2	5	5.4	4.0	17	53
2	0.5	2	10	5.4	4.0	8	67
3	1.0	2	20	5.4	4.0	4	80
4	2.0	1	20	3.5	1.3	trace	82

[a]Reaction conditions: **1a**, $Pd(OAc)_2$ (10 mol %), I_2, MeCN (10 mL) [anode], and 2 M H_2SO_4 aq [cathode] in an H-type divided cell with two platinum electrodes and an anion-exchange membrane, 90 °C.

of dimers **3a** and **4a**.[2b] The major product **3a** was formed by carbon−carbon bond formation at the less-sterically congested ortho-positions, while the minor product **4a** was formed by connecting the less-sterically congested ortho-position with the more conjested one. They studied the reaction mechanism and proposed that the dimerization proceeds via regioselective C−H bond cleavage by a Pd(II) species (path a in Figure 2) and

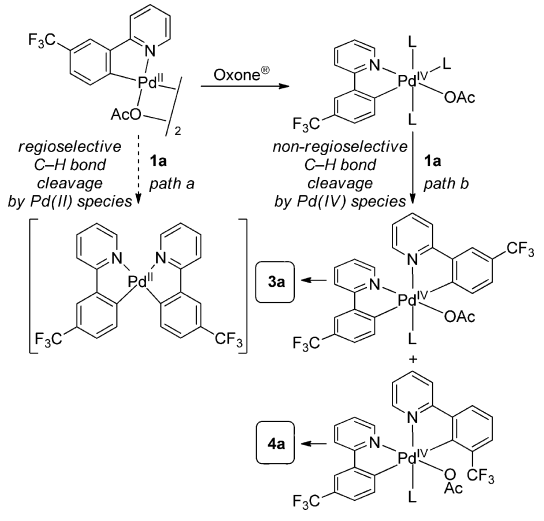


Figure 2. Reaction mechanism of the palladium-catalyzed homocoupling of **1a** with Oxone proposed by Sanford and co-workers.

oxidation of the Pd(II) species to Pd(IV) species with Oxone, followed by unselective cleavage of the ortho C−H bond of another molecule of **1a** by the Pd(IV) species and reductive elimination (path b in Figure 2). Sanford and co-workers also described that C−H bond cleavage by Pd(IV) species may be less selective compared to that by Pd(II) species.[9] The complete regioselectivity of the dimer formation in our reaction led us to speculate that the reaction may proceed by a different mechanism (Figure 3). The ortho C−H bond cleavage may first occur on a Pd(II) species twice to form a doubly chelated Pd(II) species which then oxidized by electrochemically generated I^+ species.[10,11] The other product **2a**

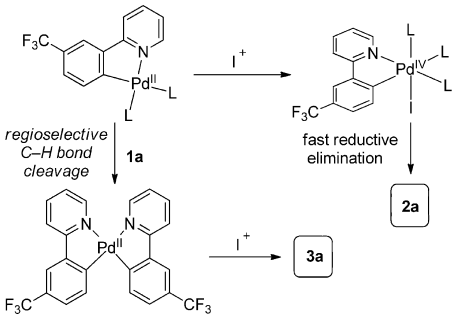


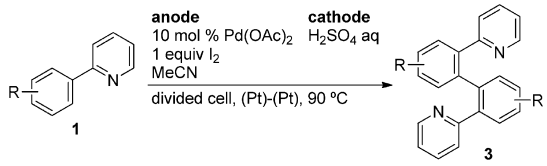
Figure 3. Our proposed reaction mechanism of the palladium-catalyzed electrochemical homocoupling of **1a** with I_2.

may be produced by the reaction of singly chelated Pd(II) species with I^+.

Based on the speculated mechanism, examination of the concentration of the substrate was conducted, because a higher concentration of the substrate may increase the concentration of the doubly chelated Pd(II) species. Indeed, when we increased the amount of substrate to 0.5 mmol with keeping the use of 10 mol % of $Pd(OAc)_2$ and 2 equiv of I_2, the yield of **3a** was improved to 67% while the yield of iodoarene **2a** was reduced to 8% (Table 1, entry 2). Further increase of the amount of **1a** to 1 mmol enhanced the yield of **3a** to 80% with reducing the yield of **2a** to 4% (entry 3). After optimization of the reaction conditions, the use of 2 mmol of **1a** with 1 equiv of I_2 allowed us to decrease the electrochemical equivalents to 1.3 F/mol (entry 4).

Under the optimized reaction conditions, the generality of the substrate was examined (Table 2). Arylpyridines having meta

Table 2. Palladium-Catalyzed Electrochemical Regioselective Homocoupling of Arylpyridines[a]



entry	**1**	R	I (mA)	time (h)	F/mol	yield (%)
1	**1b**	*m*-CO_2Me	20	3.5	1.3	80
2	**1c**	*m*-Ph	20	3.5	1.3	56
3	**1d**	*m*-Me	20	2.0	0.7	70
4	**1e**	*p*-CF_3	10	4.0	0.7	65
5	**1f**	*p*-CO_2Me	10	4.0	0.7	60
6	**1g**	*p*-Br	20	2.0	0.7	50
7	**1h**	*p*-Ph	10	4.0	0.7	65
8	**1i**	*p*-Me	20	1.0	0.4	66
9	**1j**	H	20	1.0	0.4	62

[a]Reaction conditions: **1**, $Pd(OAc)_2$ (10 mol %), I_2 (1 equiv) MeCN (10 mL) [anode], and 2 M H_2SO_4 aq [cathode] in an H-type divided cell with two platinum electrodes and an anion-exchange membrane, 90 °C.

substituents were first investigated. The reactions of arylpyridines with methoxycarbonyl and phenyl groups (**1b** and **1c**) gave 80% and 56% yields, respectively (entries 1 and 2). In the case of 2-(3-methylphenyl)pyridine (**1d**), the reaction for 2 h instead of 3.5 h gave a higher yield of dimer **3d**, probably due to the undesired iodination of **3d** (entry 3). The reactions of para-substituted arylpyridines were also performed. Arylpyridines with electron withdrawing groups such as trifluoromethyl, methoxycarbonyl, and

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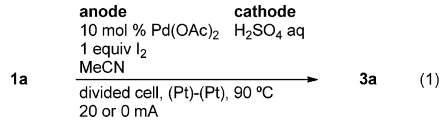
bromo groups were converted to the corresponding dimerization products **3e-g** in 50−65% yields using 0.7 F/mol of electricity (entries 4−6). The reaction of 2-(4-phenylphenyl)pyridine (**1h**) also gave dimer **3h** in 65% yield (entry 7). However, in the case of 2-(4-methylphenyl)pyridine and 2-phenylpyridine (**1i** and **1j**), the reaction using 0.4 F/mol of electricity gave 66% and 62% yields of dimerization products **3i** and **3j**, which indicates that the dimerization should proceed without applying electric current to some extent.

The progress of the dimerization of **1a** was then monitored with or without applying electric current (eq 1, Figure 4). As a



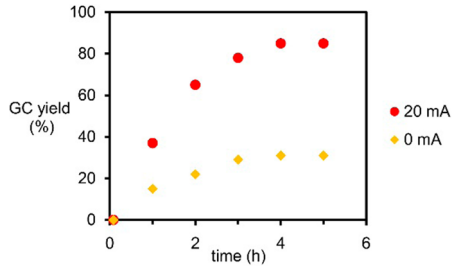
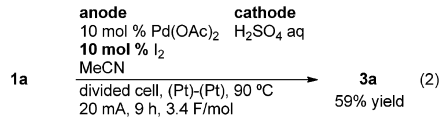


Figure 4. Plots of GC yield of **3a** versus time for the reactions with or without applying electric current.

result, the reaction with no electric current gave the product but with less efficiency. The formation of **3a** was slower from the beginning, and the GC yield of **3a** after 5 h was 31%, which is much lower than that obtained with 20 mA of electric current (85%).

The dimerization can be considered as formal electrolysis of carbon−hydrogen bonds at ortho-positions of arylpyridines, which means that I_2 only acts as a redox mediator for this reaction and theoretically the amount of I_2 can be used as a catalyst. Therefore, the use of 10 mol % of I_2 was examined and when the reaction was conducted for 9 h, dimerization product **3a** was obtained in 59% yield (eq 2).



In conlusion, palladium-catalyzed regioselective homocoupling of arylpyridines under anodic oxidation conditions was achieved in the presence of I_2. The reaction can be considered as formal electrolysis of aromatic C−H bonds. The dimerization of meta-substituted arylpyridines proceeded selectively at less-sterically congested ortho-positions. The dimerization can also proceed using catalytic amounts of both $Pd(OAc)_2$ and I_2. The results described here showed that the palladium-catalyzed formation of biaryl frameworks is possible, and further studies on metal-catalyzed electrochemical carbon−carbon bond formation are underway.

EXPERIMENTAL SECTION

General Procedure for Palladium-Catalyzed Electrochemical Homocoupling of Arylpyridines. The reaction was carried out in an H-type divided cell (anion-exchange membrane) equipped with two platinum electrodes (1.7 × 1.7 cm^2). The anodic chamber was charged with a solution of arypyridine, I_2 (1 equiv), and palladium acetate (10 mol %) in CH_3CN (10 mL). A 2 M aqueous solution (10 mL) of sulfuric acid was introduced into the cathodic chamber. An electric field was applied at 90 °C under a constant current condition and the mixture in the anodic chamber was stirred. After the reaction, the mixture was quenched with an aqueous solution of K_2CO_3 and was extracted twice with EtOAc. The obtained organic portions were washed with saturated $Na_2S_2O_3$, and then with brine. The resulting solution was dried over anhydride Na_2SO_4 and concentrated. The product was isolated by flash column chromatography.

2-(2-Iodo-5-trifluoromethylphenyl)pyridine (2a). The general procedure was followed with 56.2 mg (0.252 mmol) of 2-{3-(trifluoromethyl)phenyl}pyridine (**1a**), except that a 0.2 M aqueous solution (10 mL) of sulfuric acid was introduced into the cathodic chamber, and the reaction was carried out under a 5 mA constant current condition for 5.4 h. Column chromatography (Chromatorex NH, hexane) afforded 19.7 mg of **2a** (0.0564 mmol, 22% yield) as an yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.37 (m, 2H), 7.53 (d, J = 7.8 Hz, 1H), 7.70 (s, 1H), 7.81 (td, J = 7.8, 1.2 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 8.73 (d, J = 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 101.0, 119.6, 123.1, 123.8 (q, J = 272.5 Hz), 126.1 (q, J = 3.8 Hz), 126.9 (q, J = 3.8 Hz), 130.9 (q, J = 32.9 Hz), 136.3, 140.4, 145.8, 149.5, 159.5; HRMS (ESI-TOF) calcd for $[M + H]^+$ ($C_{12}H_8F_3IN$) m/z 349.9654. Found 349.9650.

2,2′-{4,4′-Bis(trifluoromethyl)-1,1′-biphenyl-2,2′-diyl}-bispyridine (3a). The general procedure was followed with 446 mg (2.00 mmol) of 2-{3-(trifluoromethyl)phenyl}pyridine (**1a**) and the reaction was carried out under a 20 mA constant current condition for 3.5 h. Column chromatography (Chromatorex NH, hexane, then 30:1 hexane/EtOAc) afforded 363 mg of **3a** (0.817 mmol, 82% yield) as a white solid. ^{1}H NMR spectroscopic data are in good agreement with those reported in literature.[2b]

2,2′-{4,4′-Bis(methoxycarbonyl)-1,1′-biphenyl-2,2′-diyl}-bispyridine (3b). The general procedure was followed with 427 mg (2.00 mmol) of 2-{3-(methoxycarbonyl)phenyl}pyridine (**1b**) and the reaction was carried out under a 20 mA constant current condition for 3.5 h. Column chromatography (silica gel 60N, 5:1 hexane/EtOAc, then 2:1 hexane/EtOAc) afforded 338 mg of **3b** (0.796 mmol, 80% yield) as a white solid: δ 3.92 (s, 6H), 6.86 (d, J = 7.8 Hz, 2H), 7.07 (ddd, J = 7.8, 4.9, 1.0 Hz, 2H), 7.38 (td, J = 7.8, 2.0 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 8.07 (dd, J = 7.8, 2.0 Hz, 2H), 8.21 (d, J = 2.0 Hz, 2H), 8.35 (ddd, J = 4.9, 2.0, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 52.1, 121.7, 124.2, 129.4, 129.8, 131.2, 131.3, 135.6, 140.0, 143.9, 149.2, 157.0, 166.6; HRMS (ESI-TOF) calcd for $[M + H]^+$ ($C_{26}H_{21}N_2O_4$) m/z 425.1501. Found 425.1493.

2,2′-(4,4′-Diphenyl-1,1′-biphenyl-2,2′-diyl)bispyridine (3c). The general procedure was followed with 463 mg (2.00 mmol) of 2-(3-phenylphenyl)pyridine (**1c**) and the reaction was carried out under a 20 mA constant current condition for 3.5 h. Column chromatography (silica gel 60N, 5:1 hexane/EtOAc, then 1:1 hexane/EtOAc) afforded 259 mg of **3c** (0.562 mmol, 56% yield) as a pale brown solid: δ 6.92 (d, J = 7.9 Hz, 2H), 7.06 (dd, J = 7.2, 4.9 Hz, 2H), 7.32−7.41 (m, 4H), 7.44 (t, J = 7.6 Hz, 4H), 7.49 (d, J = 7.9 Hz, 2H), 7.66−7.71 (m, 6H), 7.81 (d, J = 2.0 Hz, 2H), 8.38 (d, J = 4.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 121.3, 124.5, 127.0, 127.1, 127.4, 128.7, 128.8, 131.9, 135.4, 138.6, 140.3, 140.3, 140.4, 149.1, 158.1; HRMS (ESI-TOF) calcd for $[M + H]^+$ ($C_{34}H_{25}N_2$) m/z 461.2018. Found 461.2036.

2,2′-(4,4′-Dimethyl-1,1′-biphenyl-2,2′-diyl)bispyridine (3d). The general procedure was followed with 338 mg (2.00 mmol) of 2-(3-methylphenyl)pyridine (**1d**) and the reaction was carried out under a 20 mA constant current condition for 2 h. Column chromatography (silica gel 60N, 15:1 hexane/EtOAc, then 2:1 hexane/EtOAc) afforded 234 mg of **3d** (0.696 mmol, 70% yield) as a white solid. ^{1}H NMR spectroscopic data are in good agreement with those reported in literature.[2e]

2,2′-{5,5′-Bis(trifluoromethyl)-1,1′-biphenyl-2,2′-diyl}-bispyridine (3e). The general procedure was followed with 446 mg (2.00 mmol) of 2-{4-(trifluoromethyl)phenyl}pyridine (**1e**) and the reaction was carried out under a 10 mA constant current condition for 4 h. Column chromatography (silica gel 60N, 4:1 hexane/EtOAc, then 1:1 hexane/EtOAc) afforded 288 mg of **3e** (0.648 mmol, 65% yield) as a

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white solid. ^{1}H NMR spectroscopic data are in good agreement with those reported in literature.[2d]

2,2′-{5,5′-Bis(methoxycarbonyl)-1,1′-biphenyl-2,2′-diyl}-bispyridine (3f). The general procedure was followed with 427 mg (2.00 mmol) of 2-{4-(methoxycarbonyl)phenyl}pyridine (**1f**) and the reaction was carried out under a 10 mA constant current condition for 4 h. Column chromatography (silica gel 60N, 5:1 hexane/EtOAc, then 2:1 hexane/EtOAc) afforded 257 mg of **3f** (0.605 mmol, 60% yield) as a pale brown solid: δ 3.97 (s, 6H), 6.70 (d, J = 7.6 Hz, 2H), 7.05 (ddd, J = 7.6, 4.9, 0.9 Hz, 2H), 7.34 (td, J = 7.6, 1.8 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 8.10 (dd, J = 8.1, 1.8 Hz, 2H), 8.21 (d, J = 1.8 Hz, 2H), 8.35 (ddd, J = 4.9, 1.8, 0.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 52.3, 121.8, 124.3, 129.2, 130.3, 130.4, 132.4, 135.5, 139.2, 144.0, 149.2, 156.6, 166.7; HRMS (ESI-TOF) calcd for $[M + H]^+$ ($C_{26}H_{21}N_2O_4$) m/z 425.1501. Found 425.1520.

2,2′-(5,5′-Dibromo-1,1′-biphenyl-2,2′-diyl)bispyridine (3g). The general procedure was followed with 468 mg (2.00 mmol) of 2-(4-bromophenyl)pyridine (**1g**) and the reaction was carried out under a 20 mA constant current condition for 2 h. Column chromatography (silica gel 60N, 1:1 hexane/EtOAc) afforded 231 mg of **3g** (0.496 mmol, 50% yield) as a pale brown solid: δ 6.70 (d, J = 7.9 Hz, 2H), 7.05 (ddd, J = 7.4, 4.9, 0.9 Hz, 2H), 7.34−7.39 (m, 4H), 7.56 (dd, J = 8.3, 2.0 Hz, 2H), 7.62 (d, J = 2.0 Hz, 2H), 8.29 (d, J = 4.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 121.6, 122.7, 124.1, 131.2, 131.7, 133.6, 135.5, 138.7, 140.3, 149.1, 156.5; HRMS (ESI-TOF) calcd for $[M + H]^+$ ($C_{22}H_{15}Br_2N_2$) m/z 464.9602. Found 464.9604.

2,2′-(5,5′-Diphenyl-1,1′-biphenyl-2,2′-diyl)bispyridine (3h). The general procedure was followed with 463 mg (2.00 mmol) of 2-(4-phenylphenyl)pyridine (**1h**) and the reaction was carried out under a 10 mA constant current condition for 4 h. Column chromatography (silica gel 60N, 4:1 hexane/EtOAc, 1:1 hexane/EtOAc, then 1:2 hexane/EtOAc) afforded 299 mg of **3h** (0.649 mmol, 65% yield) as a white solid. ^{1}H NMR spectroscopic data are in good agreement with those reported in literature.[2e]

2,2′-(5,5′-Dimethyl-1,1′-biphenyl-2,2′-diyl)bispyridine (3i). The general procedure was followed with 339 mg (2.00 mmol) of 2-(4-methylphenyl)pyridine (**1i**) and the reaction was carried out under a 20 mA constant current condition for 1 h. Column chromatography (silica gel 60N, 1:10 hexane/ether) afforded 224 mg of **3i** (0.666 mmol, 66% yield) as a white solid. ^{1}H NMR spectroscopic data are in good agreement with those reported in literature.[2d,e]

2,2′-(1,1′-Biphenyl-2,2′-diyl)bispyridine (3j). The general procedure was followed with 311 mg (2.00 mmol) of 2-phenylpyridine (**1j**) and the reaction was carried out under a 20 mA constant current condition for 1 h. Column chromatography (silica gel 60N, 1:1 hexane/EtOAc, then EtOAc) afforded 193 mg of **3j** (0.626 mmol, 62% yield) as a white solid. ^{1}H NMR spectroscopic data are in good agreement with those reported in literature.[2a]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C{^{1}H} NMR spectra and IR data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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