Synthesis W. Liu et al. Feature

Pd-Catalyzed Homo Cross-Dehydrogenative Coupling of 2-Arylpyridines by Using I_2 as the Sole Oxidant

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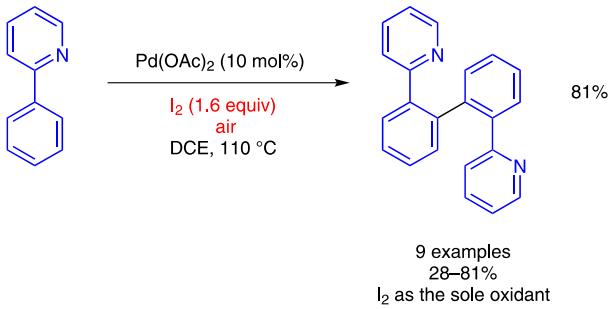
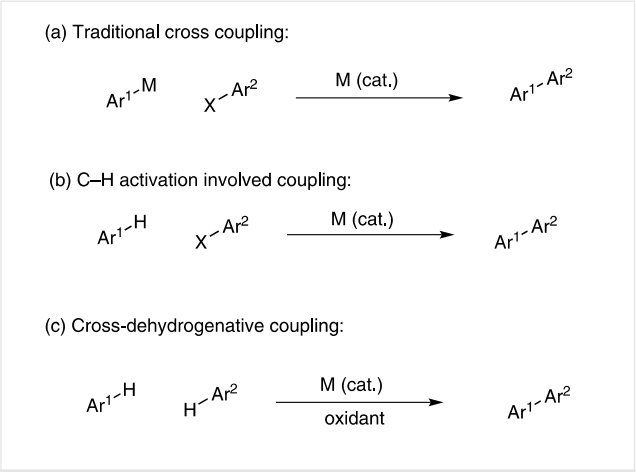


Received: 11.01.2016
Accepted after revision: 12.02.2016
Published online: 10.03.2016
DOI: 10.1055/s-0035-1561399; Art ID: ss-2016-z0022-fa

Abstract A palladium-catalyzed homo cross-dehydrogenative coupling (CDC) of 2-arylpyridines via C–H activation is described. This reaction employs I_2 as the sole oxidant without any other additives, which complements the hypervalent iodine chemistry, such as of phenyliodonium diacetate (PIDA) or IOAc, in C–H activation research field. A tentative mechanism involving a Pd(II)–Pd(IV) catalytic cycle is proposed to rationalize this homo CDC reaction.

Key words palladium, biaryl, iodine, C–H activation, cross-dehydrogenative coupling

Biaryl structural motifs are ubiquitous in natural products, pharmaceuticals, photo-electronics, and agrochemicals.[1] Over the past few decades, many elegant methods have been developed to synthesize biaryls, in which palladium-catalyzed cross-coupling reactions, such as the Suzuki and Negishi reactions, are the most efficient and reliable.[2] However, these traditional coupling reactions carry some fundamental limitations, such as entailing pre-synthesis of both coupling partners, i.e. the electrophiles (R-X) and the nucleophiles (R-M), which would generate additional waste and decrease the overall efficiency [Scheme 1 (a)]. A more economical strategy employ one C–H bond as the precursor, which could be coupled with another reactant.[3] This strategy has an advantage in that it only requires one pre-functionalized starting material [Scheme 1 (b)]. Clearly, if both substrates contribute C–H bonds as the coupling precursors ('cross-dehydrogenative coupling' CDC),[4] no pre-synthesized precursors would be mandatory [Scheme 1 (c)]. This type of reaction is superior to the first two types because: 1. they show higher atom economy since only two H atoms are removed from the starting materials; and 2. they avoid the pre-synthesis of both coupling partners, which would eliminate the waste from the beginning.



Scheme 1 Evolution of three strategies to synthesize biaryls

I_2 is a cheap and versatile oxidant widely utilized in organic synthesis.[5] However, I_2 has been rarely used as the sole oxidant in C–H activation protocols because it usually requires activation by other additives such as metal salts to form more reactive iodine species in situ.[6] In contrast to I_2, hypervalent iodine compounds, such as PIDA,[7] NIS,[8] and IOAc,[9] are extensively employed in C–H activation reactions. However, hypervalent iodine compounds are usually expensive and difficult to synthesize and store. Therefore, a C–H activation process, which can be mediated by I_2 without other additives to replace hypervalent iodine oxidants, is desirable and complementary to current hypervalent chemistry.

To circumvent the regioselectivity issue, directing groups, among which pyridine is popular, are necessary to coordinate with the metal catalyst.[10,11] For the dimerization of 2-arylpyridines (Scheme 2), Sanford and co-workers[12] reported a protocol that involved a Pd(II) and Pd(IV) cycle using oxone as the terminal oxidant. Although oxone[13] is relatively cheap and environmentally benign, its solubility issues in regular organic solvents limit its applicability. Moreover, Yu and co-workers[14] have developed another protocol to achieve the dimerization of 2-arylpyridines using a stoichiometric amount of a copper salt. Although copper is abundant, the use of a stoichiometric amount of copper salt would, unfortunately, categorize this method as 'not green'. Our group[15] also reported a reaction for the homo-coupling of 2-arylpyridines using a Ru catalyst and $FeCl_3$ as the stoichiometric oxidant. Herein, we wish to describe another method to homo-dimerize 2-arylpyridines by using a Pd catalyst and I_2 as the sole oxidant.

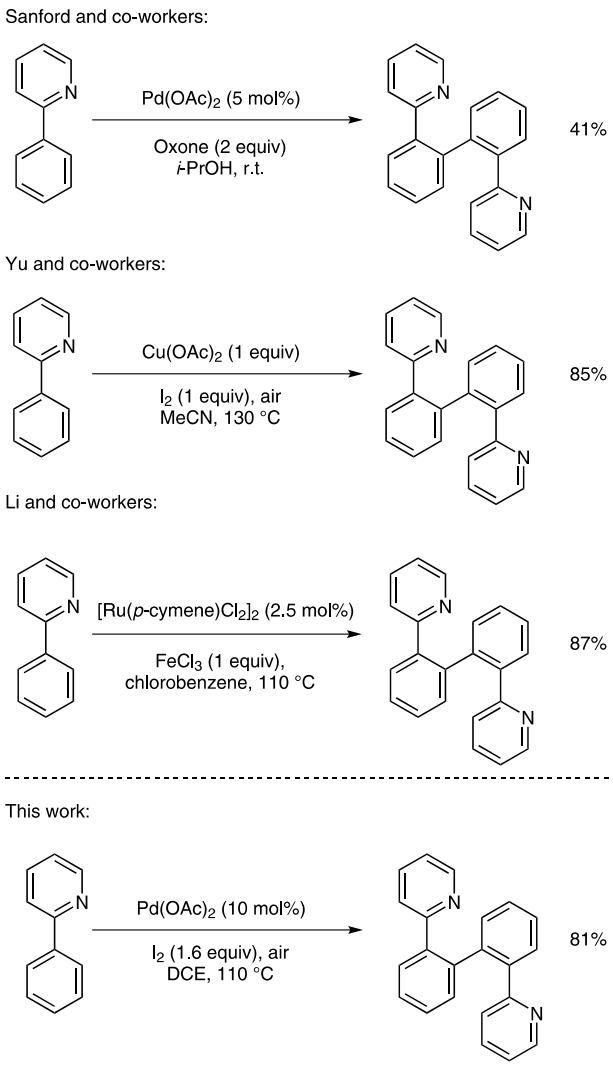
Recently, we initiated a program towards the application of UV photochemistry in organic synthesis. As an extension of previous work,[16] we envisioned to combine C–H activation with photochemistry to achieve the coupling of 2-phenylpyridine with non-activated alkyl halides. Unfortunately, when 2-phenylpyridine was reacted with cyclohexyl iodide under classical $Pd(OAc)_2$ catalyzed C–H activation conditions in the presence of both UV and heating, we could not detect any of the desired coupling product. However, by carefully examining the GC/MS trace, we could identify the homo-dimerization product at an approximate 5% yield [Scheme 3 (a)]. Inspired by this unexpected result, we designed a serial of control experiments and rapidly concluded that the iodine radical from cyclohexyl iodide

Biographical sketches

Wenbo Liu obtained his B.Sc from University of Science and Technology of China (Hefei, China) in 2010. He studied chemical biology under the supervision of Professor David M. Perrin at University of British Columbia (Vancouver, Canada), where he finished the total synthesis of two soluble carbocyclic Janus-AT phosphoramidites and obtained the M.Sc degree in 2013. Following that, he moved to McGill University (Montreal, Canada) to study green chemistry under the tutelage of Professor Chao-Jun Li. His current research interest focuses upon solving challenging synthetic problems by using organic photochemistry.

You-Quan Zhu received his Ph.D. in 2005 with Prof. H.-Z. Yang and has worked at Nankai University in Tianjin (China) as an associate professor since then. Currently, he is a visiting scholar in the group of Prof. Dr. C.-J. Li at McGill University in Montreal (Canada). His research interests focus on the development of new sustainable catalytic methodologies for selective constructions of carbon–carbon bonds and the discovery of novel ecofriendly pesticides.

Chao-Jun Li received his Ph.D. at McGill University (1992) and was a NSERC Postdoctoral Fellow at Stanford University (1992–1994). He was on the faculty at Tulane University (US) (1994–2003). Since 2003, he has been a Canada Research Chair in Green Chemistry and E. B. Eddy Chair Professor of Chemistry at McGill University. He is a Fellow of the Royal Society of Canada (Academy of Sciences), a Fellow of the American Association for the Advancement of Sciences (AAAS), a Fellow of the American Chemical Society, a Fellow of the Royal Society of Chemistry (UK), and a Fellow of the Chemical Institute of Canada.

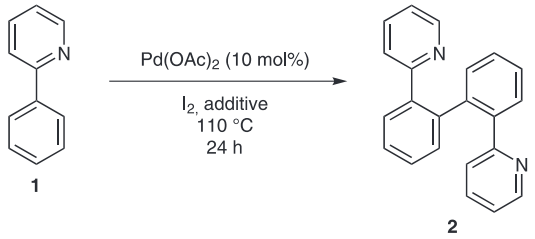


Scheme 2 Previous work on the homocoupling of 2-arylpyridine and this work

under UV irradiation was essential for dimerization. Therefore, we speculated whether I_2 was able to promote this reaction if heated. To our delight, when I_2 was added to the reaction, the dimerization product could be obtained in 35% yield [Scheme 3 (b)]. Encouraged by this result, we extensively investigated the temperature, concentration, reaction time,[17] solvent, and additive effects of this reaction (Table 1). Control experiments confirmed that both $Pd(OAc)_2$ and I_2 are indispensable for this reaction (entries 1 and 2). Various solvents were screened (entries 3–10) and 1,2-dichloroethane (DCE, entry 10) gave the highest yield (83%). We also investigated diverse additives, including common acids and bases (entries 11–16), but these are not beneficial to increasing the yields. Finally, the optimized conditions for this reaction were: 10 mol% $Pd(OAc)_2$, 1.6 equiv I_2, DCE as the solvent, at 110 °C for 24 hours.

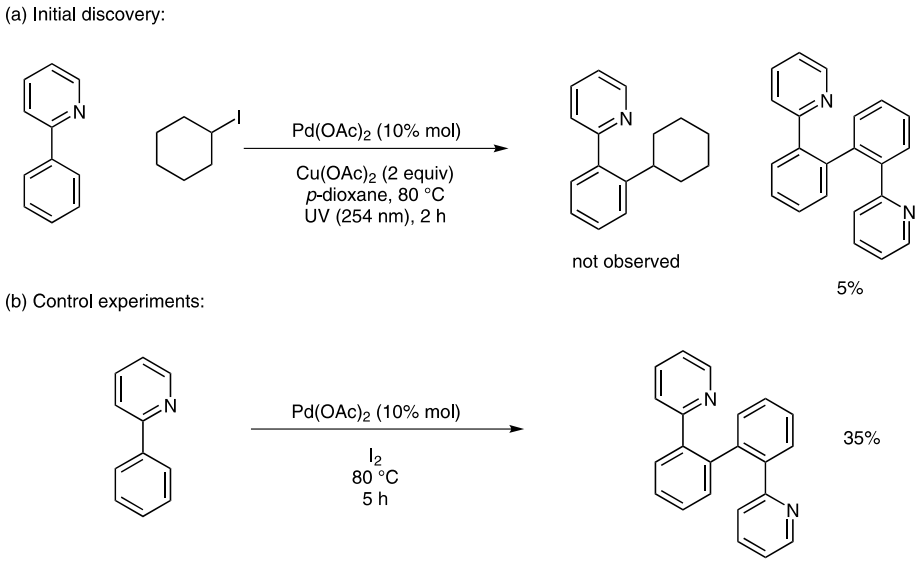
Having obtained the optimized reaction conditions, we briefly investigated the scope of this reaction (Figure 1). 2-(4-Methylphenyl)pyridine dimerized to give **2b** in a similar yield (76%) to 2-phenylpyridine, which gave **2a** in 81% yield. Substrates with the electron-withdrawing group (F) and electron-donating group (OMe) in the *para* position of phenyl ring gave the respective dimerization products **2c** and **2j** smoothly. When the Cl was at the *para* position of the phenyl ring, the reaction yield dropped dramatically to 28% (**2d**). 2-(Biphenyl-4-yl)pyridine and 2-(4-*tert*-butylphenyl)pyridine also produced the desired products **2e** and **2f**, respectively, albeit with slightly lower yields (51% and 40%). Besides the 2-phenylpyridine derivatives, 2-(2-naphthyl)pyridine was also applicable to our reaction conditions and gave **2g** in 68% yield. The methyl substitution of the pyridine ring in the phenylpyridine did not bring a significant change and the reaction proceeded to give **2h** in 63%

Table 1 Solvent and Additive Effects of this Reaction



Entry	Pd catalyst	Solvent	Additive (equiv)	Yield[a] (%)
1	–	DCE	–	0
2[b]	$Pd(OAc)_2$	DCE	–	0
3	$Pd(OAc)_2$	*p*-dioxane	–	65
4	$Pd(OAc)_2$	H_2O	–	0
5	$Pd(OAc)_2$	PhCl	–	15
6	$Pd(OAc)_2$	DCE/H_2O (1:4)	–	24
7	$Pd(OAc)_2$	DMSO/H_2O (1:4)	–	4
8	$Pd(OAc)_2$	$CHCl_3$	–	45
9	$Pd(OAc)_2$	DMF	–	0
10	$Pd(OAc)_2$	DCE	–	83 (81)[c]
11	$Pd(OAc)_2$	DCE	Cs_2CO_3 (0.5)	25
12	$Pd(OAc)_2$	DCE	Na_2CO_3 (0.5)	43
13	$Pd(OAc)_2$	DCE	NaOAc (0.5)	67
14	$Pd(OAc)_2$	DCE	AcOH (0.5)	65
15	$Pd(OAc)_2$	DCE	TfOH (0.5)	55
16	$Pd(OAc)_2$	DCE	Et_3N (0.5)	0

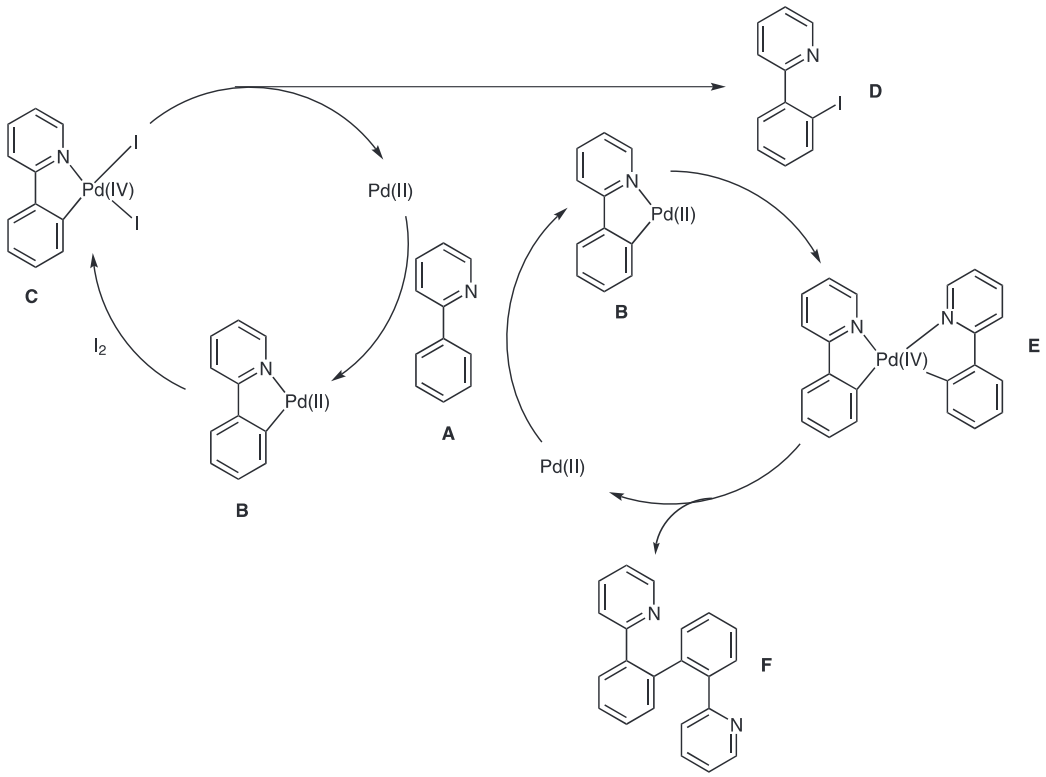
[a] The yield was determined by using ^1H NMR through using mesitylene as the internal standard.
[b] Without I_2.
[c] Isolated yield.



Scheme 3 A serendipitous discovery and control experiment

yield. The reaction did not take place using a *para*-acetyl substituted substrate probably because the carbonyl group competed with the N atom to coordinate with the catalyst.

A tentative mechanism was proposed to rationalize this transformation (Scheme 4). First, palladium(II) acetate could activate the *ortho* C–H bond of **A** through the N-direction to generate the intermediate **B**,[10] which possibly un-



Scheme 4 Proposed mechanism to rationalize this transformation

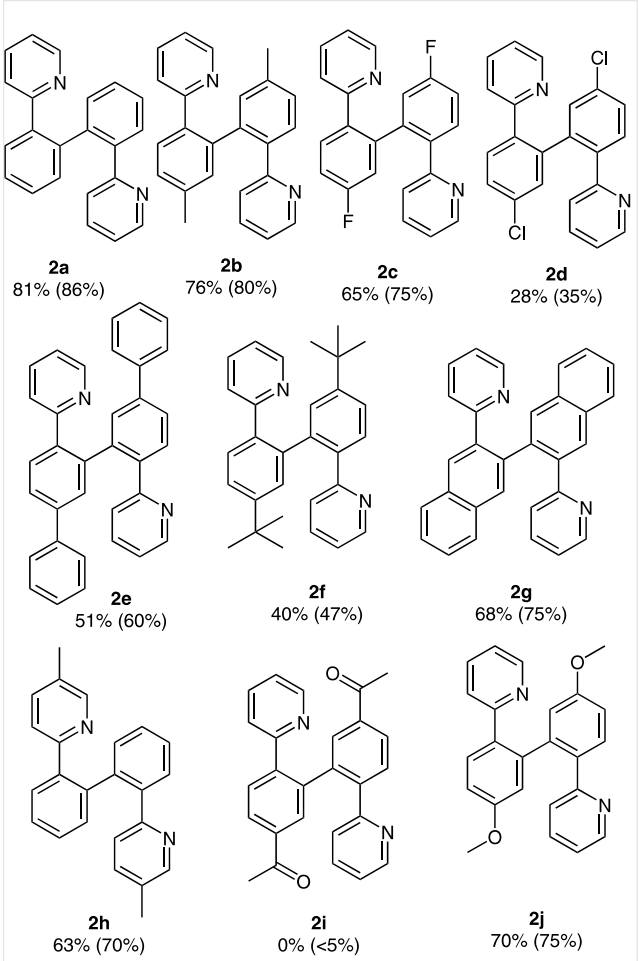


Figure 1 Scope of this reaction. *Reagents and conditions*: 2-arylpyridine (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol), I_2 (0.16 mmol), DCE (0.5 mL), 110 °C, 24 h. All yields refer to isolated yields and the average of two parallel runs, the conversion is indicated in parenthesis based on the ^{1}H NMR analysis of the crude mixture.

dergoes oxidative addition with I_2, producing the intermediate **C**. Subsequently, reductive elimination from **C** could result in the intermediate **D**, which could react with another **B** to generate the intermediate **E**. Finally, reductive elimination based on **E** would afford the desired coupling product **F** and regenerate the catalyst.

In summary, we have developed a Pd-catalyzed dimerization reaction of 2-arylpyridines through C–H activation. This reaction uses I_2 as the sole oxidant to achieve the catalytic cycle and has a relatively broad substrate scope. Complementary to the application of hypervalent iodine compounds in C–H activation, our protocol is expected to enrich iodine chemistry for C–H functionalization.

Solvents and reagents were purchased from Sigma-Aldrich and were used without further purification unless otherwise specified. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 MHz, or 500 MHz spectrometers and ^{19}F NMR spectra were recorded on a Bruker 400 MHz spectrometer; internal reference of δ = 7.26 or 77.0 $CHCl_3$ as standard. All NMR spectra were recorded at r.t. (23 °C) unless otherwise indicated. HRMS was conducted using electro-spraying ionization (ESI), and was performed by McGill University on a Thermo-Scientific Exactive Orbitrap. Protonated molecular ions $[M + H]^+$ or sodium adducts $[M + Na]^+$, were used for empirical formula confirmation. All preparative chromatography was performed through using gradient elution (hexanes/EtOAc) on a Biotage Isolera™ One automated chromatography system with SNAP ultra silica gel cartridges and sample cartridges.

Arylpyridines **1** are known compounds, with characterization data available in the literature: **1a**,**h**,**j**,[15] **1b–e**,[12] **1f**,[18] **1g**,[14] **1i**.[19]

2-Arylpyridines 1; General Procedure

2-Bromopyridine (191 µL, 2 mmol), $Pd(OAc)_2$ (10 mg, 0.02 mmol), and arylboronic acid (4 mmol) were added to a 25-mL round-bottom flask in air without any precautions. Subsequently, *i*-Pr_2NH (1 mL) and H_2O (4 mL) were added into the flask. Then a condenser was set on the round-bottom flask and the reaction was heated to reflux for 16 h. The mixture was then transferred to a 100-mL separation funnel and EtOAc (20 mL) and H_2O (20 mL) were added. The organic layer were collected and the solvent was removed used a rota-vapor. The crude product was purified by column chromatography.

2,2′-Di(pyridin-2-yl)biphenyl (2a);[15] Typical Procedure for Homo Cross-Dehydrogenative Coupling

To a 5-mL V-shape tube were added $Pd(OAc)_2$ (2.5 mg, 0.01 mmol), I_2 (40 mg, 0.16 mmol), 2-phenylpyridine (30 µL, 0.2 mmol), and DCE (0.5 mL). Then the tube was heated in a pre-heated 110 °C oil bath for 24 h. Subsequently, the volatiles were removed by rota-vapor and the residue was purified by column chromatography (30% EtOAc in hexane) to give the product as a white solid: yield: 24 mg (81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 4.8 Hz, 2 H), 7.53–7.56 (m, 2 H), 7.32–7.44 (m, 8 H), 7.01–7.05 (m, 2 H), 6.78 (d, J = 7.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 148.8, 139.7, 139.5, 135.1, 131.2, 129.9, 128.5, 127.6, 124.3, 121.1.

2,2′-(5,5′-Dimethylbiphenyl-2,2′-diyl)dipyridine(2b)[12]

White solid: yield: 25 mg (76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (dd, J_1 = 5.0 Hz, J_2 = 0.9, 2 H), 7.41 (d, J = 7.8 Hz, 2 H), 7.28 (m, 4 H), 7.21 (dd, J_1 = 7.8 Hz, J_2 = 0.9 Hz, 2 H), 6.96 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 2 H), 6.66 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 2 H), 2.43 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 148.7, 139.6, 138.3, 137.0, 135.0, 131.8, 129.8, 128.4, 124.2, 120.8, 21.2.

2,2′-(5,5′-Difluorobiphenyl-2,2′-diyl)dipyridine (2c)[12]

White solid: yield: 22 mg (65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (dd, J_1 = 5.0 Hz, J_2 = 0.9 Hz, 2 H), 7.48–7.53 (m, 2 H), 7.36 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 2 H), 7.01–7.14 (m, 6 H), 6.76 (d, J = 7.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6 (d, J_{C-F} = 989.1 Hz), 156.7, 149.0, 140.8 (d, J_{C-F} = 25.2 Hz), 136.0, 135.4, 132.0 (d, J_{C-F} = 29.7 Hz), 124.1, 121.4, 117.7 (d, J_{C-F} = 86.7 Hz), 115.0 (d, J_{C-F} = 81.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –113.37.

2,2′-(5,5′-Dichlorobiphenyl-2,2′-diyl)dipyridine (2d)[12]

White solid: yield: 11 mg (28%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (dd, J_1 = 5.1 Hz, J_2 = 0.9 Hz, 2 H), 7.32–7.46 (m, 8 H), 7.03 (dd, J_1 = 5.1 Hz, J_2 = 0.9 Hz, 2 H), 6.70 (dd, J_1 = 7.8 Hz, J_2 = 0.9 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 149.0, 140.1, 138.2, 135.5, 134.5, 131.5, 130.7, 128.3, 124.1, 121.5.

4′,6″-Di(pyridin-2-yl)-1,1′:3′,1″:3″,1‴-quaterphenyl (2e)[12]

White solid: yield: 23 mg (51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (dd, J_1 = 4.8 Hz, J_2 = 0.9 Hz, 2 H), 7.76 (d, J = 0.9 Hz, 2 H), 7.66–7.74 (m, 8 H), 7.47 (t, J = 7.8 Hz, 4 H), 7.38 (m, 4 H), 7.05 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 2 H), 6.90 (d, J = 7.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 149.0, 141.2, 140.0, 138.8, 135.2, 130.6, 129.8, 128.8, 127.5, 127.0, 126.4, 124.4, 121.2.

2,2′-(5,5′-Di-*tert*-butylbiphenyl-2,2′-diyl)dipyridine (2f)

White solid: yield: 17 mg (40%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, J = 4.9 Hz, 2 H), 7.61 (d, J = 8.2 Hz, 2 H), 7.43–7.35 (m, 4 H), 7.14 (d, J = 1.9 Hz, 2 H), 7.08–7.03 (m, 2 H), 7.00 (d, J = 8.0 Hz, 2 H), 1.20 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 151.0, 149.1, 139.6, 137.2, 135.1, 129.8, 129.2, 124.7, 124.2, 120.9, 34.4, 31.1.

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{30}H_{33}N_2$: 421.2638; found: 421.2635.

3,3′-Di(pyridin-2-yl)-2,2′-binaphthalene (2g)[14]

White solid: yield: 28 mg (68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, J_1 = 4.8 Hz, 2 H), 8.14 (s, 2 H), 8.03 (s, 2 H), 7.96 (d, J = 7.8 Hz, 2 H), 7.91 (d, J = 7.8 Hz, 2 H), 7.50–7.55 (m, 4 H), 7.27–7.19 (m, 2 H), 7.08–6.93 (m, 2 H), 6.71 (d, J = 7.9 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 149.2, 138.5, 135.5, 133.6, 133.1, 130.8, 129.7, 128.6, 127.9, 126.9, 126.6, 124.6, 121.5.

2,2′-Bis(5-methylpyridin-2-yl)biphenyl (2h)[15]

White solid: yield: 21 mg (63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 2 H), 7.54–7.56 (m, 2 H), 7.31–7.41 (m, 6 H), 7.13 (d, J = 8.0 Hz, 2 H), 6.70 (d, J = 8.0 Hz, 2 H), 2.25 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 149.4, 139.9, 139.7, 135.8, 131.4, 130.5, 130.0, 128.2, 127.6, 123.8, 18.2.

2,2′-(5,5′-Dimethoxybiphenyl-2,2′-diyl)dipyridine (2j)[15]

White solid: yield: 26 mg (70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (dd, J_1 = 5.1 Hz, J_2 = 0.9 Hz, 2 H), 7.49 (dd, J_1 = 6.6 Hz, J_2 = 2.7 Hz, 2 H), 7.29 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 2 H), 6.93–6.98 (m, 6 H), 6.72 (d, J = 7.8 Hz, 2 H), 3.81 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 157.5, 148.7, 141.0, 135.1, 132.6, 131.4, 124.1, 120.7, 116.0, 113.5, 55.2.

Acknowledgment

We are grateful to the Canada Research Chair (Tier I) Foundation (to C. J. Li), CFI, and NSERC for support of research. W. Liu is grateful for DDTP program for a scholarship.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561399.

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(17) Based on our research, higher temperature, longer reaction time and higher concentration produced a higher reaction yield. However, to make a comprimse on these three parameters, we decided to use 110 °C, 0.4 M, and 24 h to optimize the solvent and additive effects.
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