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[Bmim]PF_6-Promoted Ligandless Suzuki−Miyaura Coupling Reaction of Potassium Aryltrifluoroborates in Water

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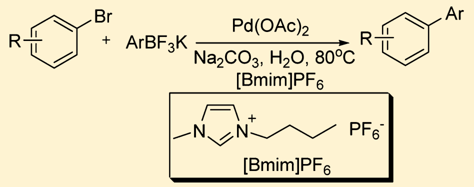
Supporting Information

ABSTRACT: The Suzuki−Miyaura coupling reactions of potassium aryltrifluoroborates with aryl bromides in water are promoted by the addition of [bmim]PF_6 using $Pd(OAc)_2$ as a catalyst and Na_2CO_3 as a base under air. The quantity of [bmim]PF_6 used is crucial to the efficiency of the catalytic system. A wide range of biaryls and polyaryls can be easily prepared in good to excellent yields.



The palladium-catalyzed Suzuki−Miyaura coupling reaction of aryl halides with organoboron nucleophiles has become an extremely versatile and powerful synthetic tool for the construction of unsymmetrical biaryls,[1] which are important structural components in natural products, agrochemicals, pharmaceuticals, and functional materials.[2] Organoboronic acids are the most widely used organoboron nucleophiles in the Suzuki−Miyaura coupling reactions. Tremendous effort has been exerted on the Suzuki−Miyaura coupling reactions of organoboronic acids.[1−3] However, organoboronic acids are not ideal substrates because they suffer from several problems.[4] First, organoboronic acids often exist as dimeric and cyclic trimeric anhydrides with loss of water, which results in difficulties in purification and determination of precise stoichiometry. Second, organoboronic acids are easier to give proto-deboronation and homocoupling products, and an excess of these compounds is often required. Finally, organoboronic acids are rarely used in the modification of organic substrates due to their sensitivities to reagents that commonly used in routine organic synthesis. These shortcomings can be overcome by the use of potassium organotrifluoroborates. Potassium organotrifluoroborates are generally crystalline and monomeric solids and show high stability toward air and water. They can be prepared easily and efficiently from organoboron compounds with two labile substituents by treatment with inexpensive KHF_2 in aqueous acetone or methanol.[5] Unlike organoboronic acids, potassium organotrifluoroborates withstand a number of routine organic reaction conditions and can be utilized to elaborate the organic substructures.[6] Therefore, potassium organotrifluoroborates have emerged as attractive and promising alternatives to organoboronic acids.[7] Significant progress has been achieved for the Suzuki−Miyaura coupling reactions of potassium organotrifluoroborates using phosphine-base and nitrogen-containing ligands,[8] microwave techniques,[9] and heterogeneous catalysts.[10]

Water is an ideal solvent in organic synthesis with regard to its safety, cost and environmental effects.[11] The first ligandless catalytic system for the Suzuki−Miyaura coupling reaction of potassium organotrifluoroborates in water was developed by Molander and co-workers.[12] They found that only substrates containing an −OH or −COOH group could be coupled in water using $Pd(OAc)_2$ as a catalyst and K_2CO_3 as a base. Later, Stefani and co-workers reported a catalytic system for the synthesis of α-aryl-β-ketoesters by the Suzuki−Miyaura coupling reactions of potassium aryltrifluoroborates with 5-iodo-1, 3-dioxin-4-ones in water using $Pd_2(dba)_3$ as a catalyst and n-Bu_4NOH as a base under N_2 atmosphere.[13] Unfortunately, this catalytic system showed poor activity toward bromine-substituted substrates. Very recently, our group developed a highly efficient, ligandless catalytic system for the Suzuki−Miyaura coupling reactions of potassium aryltrifluoroborates with aryl and heteroaryl halides in water using $Pd(OAc)_2$ as a catalyst and Na_2CO_3 as a base in which poly(ethylene glycol) (PEG) was used as additive.[14]

Ionic liquids (ILs) based on 1, 3-dialkylimidazolium cations have been widely used as green solvents in metal-mediated transformations due to their peculiar properties, such as extremely low vapor pressure, good thermal and chemical stability, high compatibility with transition-metal catalysts, and immiscibility with many organic solvents.[15] The use of ionic liquids as reaction medium offers the advantages of the elimination of highly toxic solvents, simplicity of workup procedures, and the possibility of recycling ionic liquids and the catalyst. The only report about the Suzuki−Miyaura coupling reactions of potassium organotrifluoroborates using ionic liquids as medium showed that the Suzuki−Miyaura coupling reactions of potassium organotrifluoroborates with aryldiazonium tetrafluoroborates could proceed smoothly using an azapalladacycle as a catalyst in [bmim]BF_4/MeOH mixture under N_2.[16] During our research on the development of ligandless catalytic systems for the Suzuki−Miyaura coupling reaction in water,[14,17] we found that [bmim]PF_6 could promote the Suzuki−Miyaura coupling reactions of potassium aryltri-

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fluoroborates with aryl bromides in water using $Pd(OAc)_2$ as a catalyst and Na_2CO_3 as a base. Herein, we report our findings.

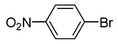
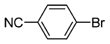
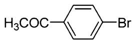
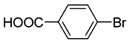
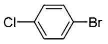
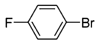
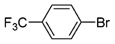
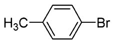
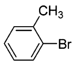
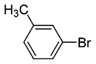
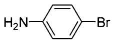
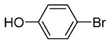
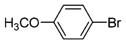
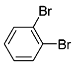
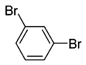
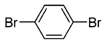
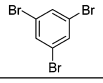
Initial studies focused on optimizing reaction conditions for the coupling of 4-bromonitrobenzene (0.5 mmol) with potassium phenyltrifluoroborate (0.6 mmol) using $Pd(OAc)_2$ (1 mol %) as a catalyst and Na_2CO_3 (1 mmol) as a base at 80 °C for 1.5 h in water (3 mL). Little reaction was observed when pure water was used as the solvent (Table 1, entry 1). A dramatic increase in yield was found when $[bmim]PF_6$ (3 g) was added to water (Table 1, entry 2). These results suggested that the efficiency of this catalytic system was promoted by the addition of $[bmim]PF_6$. It should be noted that only a trace amount of product was found when pure $[bmim]PF_6$ was used (Table 1, entry 3). Under the same reaction conditions, we studied the effect of anions of the ILs on the reaction and found much lower yield of the product was achieved when $[bmim]BF_4$ (3 g) or [bmim]Cl (3 g) was used in water (Table 1, entries 4 and 5). The effect of the amount of $[bmim]PF_6$ used in this system in water was next investigated. To our surprise, a decrease in the amount of $[bmim]PF_6$ in the reaction showed little influence on the efficiency of this system (Table 1, entries 6–8). To explore the importance of the cation in $[bmim]PF_6$, the effect of addition of the same mole quantity of KPF_6 as 0.1 g of $[bmim]PF_6$ in water was studied, and little product was found (Table 1, entry 9). Other bases were also studied in this system (Table 1, entries 10–17), and Na_2CO_3 was chosen as the optimal base in the following studies. It was noteworthy that only 2 equiv of base was needed in this catalytic system.

Table 1. Optimization of the Reaction Conditions[a]

entry	base	solvent	yield[c] (%)
1	Na_2CO_3	H_2O (3 mL)	trace
2	Na_2CO_3	$H_2O-[bmim]PF_6$ (3/3 g)	99
3	Na_2CO_3	$[bmim]PF_6$ (3 g)	trace
4	Na_2CO_3	$H_2O-[bmim]BF_4$ (3/3 g)	45
5	Na_2CO_3	$H_2O-[bmim]Cl$ (3/3 g)	trace
6	Na_2CO_3	$H_2O-[bmim]PF_6$(3/0.2 g)	99
7	Na_2CO_3	$H_2O-[bmim]PF_6$ (3/0.1 g)	99
8	Na_2CO_3	$H_2O-[bmim]PF_6$ (3/0.05 g)	95
9[b]	Na_2CO_3	H_2O-KPF_6	7
10	K_2CO_3	$H_2O-[bmim]PF_6$ (3/0.1 g)	99
11	K_3PO_4	$H_2O-[bmim]PF_6$ (3/0.1 g)	97
12	NaOH	$H_2O-[bmim]PF_6$ (3/0.1 g)	92
13	KOH	$H_2O-[bmim]PF_6$ (3/0.1 g)	93
14	NaOAc	$H_2O-[bmim]PF_6$ (3/0.1 g)	20
15	$NaHCO_3$	$H_2O-[bmim]PF_6$ (3/0.1 g)	54
16	NEt_3	$H_2O-[bmim]PF_6$ (3/0.1 g)	85
17	pyridine	$H_2O-[bmim]PF_6$ (3/0.1 g)	7

[a] Reaction conditions: 4-bromonitrobenzene (0.5 mmol), $PhBF_3K$ (0.6 mmol), $Pd(OAc)_2$ (1 mol %), base (1 mmol), 80 °C, 1.5 h. [b] KPF_6 (0.3 mmol). [c] Isolated yield.

Table 2. $[Bmim]PF_6$-Promoted Suzuki–Miyaura Coupling Reactions of Aryl Bromides with $PhBF_3K$ in Water[a]

Entry	ArBr	Conditions [b]	Yield [e] (%)
1		**A**, 1.5 h	99
2		**A**, 1.5 h	98
3		**A**, 2 h	99
4		**A**, 2 h	97
5		**A**, 2 h	69
		A, 6 h	75
		B, 2 h	84
		B, 4 h	87
6		**A**, 2 h	63
		B, 2 h	83
		B, 4 h	99
7		**A**, 2 h	60
		B, 2 h	87
		B, 4 h	92
8		**A**, 3 h	59
		B, 3 h	85
		B, 6 h	98
9		**B**, 6 h	84
10		**B**, 6 h	96
11		**B**, 6 h	94
12		**B**, 6 h	92
13		**B**, 6 h	90
14 [c]		**A**, 12 h	80
15 [c]		**A**, 12 h	87
16 [c]		**A**, 12 h	84
17 [d]		**A**, 12 h	62
		B, 12 h	96

[a] Reaction conditions: ArBr (0.5 mmol), $PhBF_3K$ (0.6 mmol), Na_2CO_3 (1 mmol), $Pd(OAc)_2$ (1 mol %), 80 °C. [b] A: $H_2O/[bmim]PF_6$ (3/0.1 g). B: $H_2O/[bmim]PF_6$ (3/3 g). [c] $PhBF_3K$ (1.2 mmol), Na_2CO_3 (2 mmol), $Pd(OAc)_2$ (2 mol %). [d] $PhBF_3K$ (1.8 mmol), Na_2CO_3 (3 mmol), $Pd(OAc)_2$ (3 mol %). [e] Isolated yield.

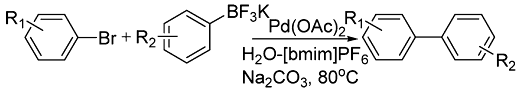
The generality of this $[bmim]PF_6$-promoted ligandless Suzuki–Miyaura coupling reaction of potassium organotrifluoroborates in water was next examined with a wide range of aryl bromides with various potassium aryltrifluoroborates using $Pd(OAc)_2$ as a catalyst and Na_2CO_3 as a base at 80 °C under air. As shown in Table 2, good to excellent yields were obtained for aryl bromides containing both electron-withdrawing groups and electron-donating groups, and a wide range of functional groups was tolerated. It should be noted that the quantity of the $[bmim]PF_6$ used had a great influence on the efficiency of this system toward different substrates. For the couplings of 4-bromonitrobenzene, 4-bromobenzonitrile, 4-bromoacetophenone and 4-bromobenzoic acid with potassium phenyltrifluoroborate, excellent yields were found when these reactions were conducted in $H_2O/[bmim]PF_6$ (3/0.1 g) within short reaction times (Table 2, entries 1–4). In contrast, much lower yields were obtained for aryl bromides containing −Cl, −F, $-CF_3$, and −Me when the coupling reactions were carried out in $H_2O/[bmim]PF_6$ (3/0.1 g) (Table 2, entries 5–8), and no significant increase in yield was found even with longer reaction time (Table 2, entry 5). Much higher yields were achieved when these reactions were conducted in $H_2O/$

$[bmim]PF_6$ (3/3 g) (Table 2, entries 5−8). Aryl bromides containing −Me, $-NH_2$, −OH, and −OMe groups delivered the corresponding products in high yields using H_2O/$[bmim]PF_6$ (3/3 g) as the reaction medium (Table 2, entries 8−13). Sterically demanding 1-bromo-2-methylbenzene could be coupled smoothly with potassium phenyltrifluoroborate, affording the desired product in good yield (Table 2, entry 9).

To explore the efficiency of this new system toward the synthesis of polyaryls, the Suzuki−Miyaura coupling reactions of several dibromobenzene substrates with $PhBF_3K$ were studied (Table 2, entries 14−17). To our delight, this new system was very applicable for the couplings of *o*-, *p*-, and *m*-dibromobenzene, and the desired polyaryls could be obtained in good yields (Table 2, entries 14−16). The yield of 1, 3, 5-tribromobenzene with $PhBF_3K$ in $H_2O/[bmim]PF_6$ (3/3 g) was much higher yield than that in $H_2O/[bmim]PF_6$ (3/0.1 g) (Table 2, entry 17).

The effect of the potassium aryltrifluoroborate partner on the Suzuki−Miyaura reaction was next investigated. Potassium aryltrifluoroborates containing both electron-donating groups and electron-withdrawing groups underwent the coupling smoothly to deliver the products in good to excellent yields (Table 3). Good yields were also obtained for the coupling of potassium 2-methylphenyltrifluoroborate with 4-bromonitrobenzene (Table 3, entry 3). For the coupling of 1-bromo-2-methylbenzene with potassium 2-methylphenyltrifluoroborate, the product was obtained in moderate yield (Table 3, entry 8).

Table 3. Suzuki−Miyaura Coupling Reactions of Aryl Bromides with Potassium Aryltrifluoroborate in $H_2O/[bmim]PF_6$[a]



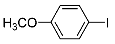
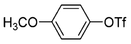
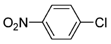
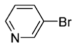
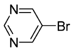
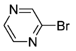
entry	R_1	R_2	conditions[b]	yield[c] (%)
1	$4-NO_2$	4-OMe	**A**, 1.5 h	99
2	$4-NO_2$	$4-CH_3$	**A**, 1.5 h	99
3	$4-NO_2$	$2-CH_3$	**A**, 1.5 h	85
4	$4-NO_2$	$3-CH_3$	**A**, 1.5 h	98
5	$4-NO_2$	$4-CF_3$	**A**, 1.5 h	83
6	$4-CH_3$	$4-CH_3$	**B**, 6 h	98
7	$4-CH_3$	$4-CF_3$	**B**, 6 h	75
8	$2-CH_3$	$2-CH_3$	**B**, 12 h	44

[a]Reaction conditions: ArBr (0.5 mmol), $ArBF_3K$ (0.6 mmol), Na_2CO_3 (1 mmol), $Pd(OAc)_2$ (1 mol %), 80 °C. [b]A: $H_2O/[bmim]PF_6$ (3/0.1 g). B: $H_2O/[bmim]PF_6$ (3/3 g). [c]Isolated yield.

The Suzuki−Miyaura coupling reaction of other aryl electrophiles with potassium phenyltrifluoroborate was also studied in this catalytic system. For the coupling of 4-iodoanisole, the desired product was obtained in moderate yield (Table 4, entry 1). However, this catalytic system was not applicable to the couplings of aryl chloride and triflate (Table 4, entries 2 and 3). Excellent yields were achieved in the coupling of 5-bromopyrimidine and 2-bromopyrazine (Table 4, entries 5 and 6), while only 26% isolated yield was found in the coupling of 3-bromopyridine (Table 4, entry 4).

The immobilization of the catalyst in ILs and the potential reusability of ILs prompted us to explore the recyclability of this catalytic system using the reaction of 4-bromonitrobenzene with $PhBF_3K$ in the presence of $Pd(OAc)_2$ and Na_2CO_3 in $H_2O/[bmim]PF_6$ (3/0.1 g) at 80 °C for 1.5 h. As expected, this catalytic system could be recycled, and the yields for the first five runs were 99%, 95%, 90%, 81%, and 64%, respectively.

Table 4. Suzuki−Miyaura Coupling Reactions of Other Aryl Electrophiles with $PhBF_3K$ in $H_2O/[bmim]PF_6$[a]

Entry	Aryl electrophile	Time (h)	Yield[b] (%)
1		6 h	48
2		6 h	Trace
3		12 h	No
4		6 h	26
5		6 h	99
6		6 h	95

[a]Reaction conditions: aryl electrophile (0.5 mmol), $PhBF_3K$ (0.6 mmol), Na_2CO_3 (1 mmol), $Pd(OAc)_2$ (1 mol %), 80 °C, $H_2O/[bmim]PF_6$ (3/3 g). [b]Isolated yield.

Mechanistic investigations on the Suzuki−-Miyaura coupling reactions involving organoboronic acids in ILs have been reported in the literature.[18−21] Several active palladium species were suggested to be responsible for the Suzuki−Miyaura reaction of arylboronic acids in ILs, such as palladium metal stabilized by the reaction medium,[18] Pd nanoparticles,[19] and Pd−carbene species generated in situ,[20] in addition to others.[21] It was reported in the literature that Pd nanoparticles could be formed in ILs and the catalytic properties of these nanoparticles were affected by both the cation and anion of the ionic liquids.[22] In the coupling reaction of 4-bromonitrobenzene with potassium phenyltrifluoroborate, we found that $H_2O/[bmim]PF_6$ was the optimal reaction medium, while $H_2O/[bmim]BF_4$, $H_2O/[bmim]Cl$, and H_2O/KPF_6 were inferior to afford much lower yields. Based on these results and the literature, we proposed that Pd nanoparticles might be formed in this catalytic system, and the size of the Pd nanoparticles was dependent on the reaction medium. When more $[bmim]PF_6$ was used, the dispersion of the Pd nanoparticles in ionic liquids would be increased to enhance the coupling efficiency. A further mechanistic investigation on this $[bmim]PF_6$-promoted ligandless Suzuki−Miyaura coupling reaction of potassium organotrifluoroborates in water is underway in our laboratory.

In conclusion, we have developed an efficient, ligandless, and recyclable catalytic system for the Suzuki−Miyaura coupling reaction of potassium organotrifluoroborates with aryl bromides in water using $Pd(OAc)_2$ as a catalyst and Na_2CO_3 as a base. A wide range of functional groups was tolerated. Additionally, this catalytic system, $Pd(OAc)_2-H_2O-[bmim]PF_6$, could be recycled up to five times with good yield.

■ EXPERIMENTAL SECTION

General Method. All reactions were carried out under air without any protection of inert gases. Potassium aryltrifluoroborates used were prepared by corresponding arylboronic acids following the method reported in literature.[5a] Other starting materials were purchased from common commercial sources and used without further purification. All products were isolated by chromatography on a silica gel (300−400 mesh) using petroleum ether (60−90 °C) and ethyl acetate.

^1H NMR spectra were recorded on a 300 or 400 MHz spectrometer using TMS as internal standard ($CDCl_3$: δ 7.26 ppm, *d*-DMSO: δ 2.50 ppm). Datas are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants

(Hz) and integration. Mass spectroscopy data were collected on a GC−MS instrument.

General Procedure for the Suzuki−Miyaura Coupling Reaction. A mixture of aryl bromide (0.5 mmol), ArBF$_3$K (0.6 mmol; for dihalides, 1.2 mmol; for trihalides, 1.8 mmol), Na$_2$CO$_3$ (1 mmol; for dihalides, 2 mmol; for trihalides, 3 mmol), Pd(OAc)$_2$ (1 mol %; for dihalides, 2 mol %; for trihalides, 3 mol %), distilled water (3 mL), and [bmim]PF$_6$ was stirred at 80 °C for the indicated time under air. The reaction solution was extracted by Et$_2$O (4 × 10 mL) after being cooled to room temperature. The combined organic layer was then concentrated, and the residue was subjected to flash chromatography on a silica gel (300−400 mesh) column using petroleum and ethyl acetate to afford the corresponding biaryl product.

General Procedure for the Reusability of Pd(OAc)$_2$−H$_2$O−[bmim]PF$_6$ in the Suzuki−Miyaura Coupling Reaction of 4-Bromonitrobenzene with PhBF$_3$K. A mixture of 4-bromonitrobenzene (0.5 mmol), PhBF$_3$K (0.60 mmol), Na$_2$CO$_3$ (1 mmol), Pd(OAc)$_2$ (1 mol %), and H$_2$O/[bmim]PF$_6$ (3/0.1 g) was stirred at 80 °C for 1.5 h under air. The mixture was cooled to room temperature and extracted by diethyl ether (4 × 10 mL). The residue (Pd(OAc)$_2$−H$_2$O−[bmim]PF$_6$) was subjected to the next run by charging with the same substrates (4-bromonitrobenzene (0.5 mmol), PhBF$_3$K (0.60 mmol), and Na$_2$CO$_3$ (1 mmol)) under the same reaction conditions. The combined organic layer was concentrated under reduced pressure, and the residue was isolated by chromatography on a silica gel (300−400 mesh) column using petroleum and ethyl acetate to afford the product.

4-Nitro-1,1′-biphenyl:[23] 98.8 mg, 99% [CAS: 92-93-3, T1]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.30 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 7.7 Hz, 2H), 7.48 (m, 3H); MS (EI) m/e 200 (10), 199 (71), 169 (28), 153 (29), 152 (100), 151 (29), 141 (19), 127 (10), 115 (12), 76 (14), 63 (7), 51 (7).

1,1′-Biphenyl-4-carbonitrile:[23] 88.2 mg, 98% [CAS: 2920-38-9, T2-2]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.49 (t, J = 7.4 Hz, 2H), 7.46−7.36 (m, 1H); MS (EI) m/e 180 (15), 179 (100), 178 (24), 152 (9), 151 (20), 89 (10), 76 (38).

1-[1,1′-Biphenyl]-4-yl-ethanone:[23] 97.5 mg, 99% [CAS: 92-91-1, T2-3]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 7.7 Hz, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.1 Hz, 1H), 2.65 (s, 3H); MS (EI) m/e 197 (6), 196 (54), 182 (20), 181 (100), 153 (54), 152 (78), 128 (5), 127 (5), 91 (5), 84 (5), 76 (24), 75 (5), 63 (5), 39 (6).

4-Biphenylcarboxylic acid:[21b] 96.4 mg, 97% [CAS: 92-2-2, T2-4]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.18 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.68−7.60 (m, 2H), 7.49 (t, J = 7.4 Hz, 2H), 7.42 (d, J = 7.3 Hz, 1H); MS (EI) m/e 198 (100), 179 (60), 152 (45), 76 (20).

4-Chloro-1,1′-biphenyl:[24] 82.1 mg, 87% [CAS: 2051-62-9, T2-5]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (m, 4H), 7.48−7.31 (m, 5H); MS (EI) m/e 188 (100), 152 (70), 76 (40), 63 (15), 51 (10).

4-Fluoro-1,1′-biphenyl:[25] 85.0 mg, 99%; [CAS: 324-74-3, T2-6]: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67−7.49 (m, 4H), 7.44 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.14 (t, J = 8.6 Hz, 2H); MS (EI) m/e 173 (12), 172 (100), 171 (37), 170 (24), 154 (5), 152 (5), 146 (5), 87 (7), 86 (12), 76 (5).

4-Trifluoromethyl-1,1′-biphenyl:[23] 102.0 mg, 92% [CAS: 398-36-7, T2-7]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.71 (s, 4H), 7.61 (d, J = 7.8 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H); MS (EI) m/e 223 (15), 222 (100), 153 (24), 152 (29), 151 (10), 86 (7).

4-Methyl-1,1′-biphenyl:[23] 82.6 mg, 98% [CAS: 644-08-6, T2−8]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, J = 7.8 Hz, 2H), 7.50 (s, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 7.7 Hz, 2H), 2.39 (s, 3H); MS (EI) m/e 169 (12), 168 (100), 167 (51), 165 (15), 154 (7), 153 (24), 152 (24), 115 (7), 84 (7), 83 (10).

2-Methyl-1,1′-biphenyl:[23] 71.0 mg, 84% [CAS: 643-58-3, T2-9]; ^{1}H NMR (400 MHz, DMSO) δ 7.45 (m, 2H), 7.40−7.22 (m, 6H), 7.19 (m, 1H), 2.23 (s, 3H); MS (EI) m/e 168 (100), 153 (48), 128 (5), 115 (9), 83 (17), 76 (6).

3-Methyl-1,1′-biphenyl:[24] 80.7 mg, 96%; [CAS: 643-93-6, T2-10]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, J = 7.6 Hz, 2H), 7.44 (m, 4H), 7.35 (t, J = 7.4 Hz, 2H), 7.19 (d, J = 7.4 Hz, 1H), 2.44 (s, 3H); MS (EI) m/e 168 (100), 152 (25), 115 (5), 83 (10), 63 (7), 51 (5).

1,1′-Biphenyl-4-amine:[23] 79.8 mg, 96% [CAS: 92-67-1, T2-11]; ^{1}H NMR (400 MHz, DMSO) δ 7.60−7.48 (m, 2H), 7.36 (t, J = 7.9 Hz, 4H), 7.20 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 8.5 Hz, 2H), 5.24 (s, 2H); MS (EI) m/e 169 (100), 139 (10), 115 (9), 83 (10). MS (EI) m/e 169 (100), 139 (10), 115 (9), 83 (10).

1,1′-Biphenyl-4-ol:[24] 78.5 mg, 92% [CAS: 92-69-3, T2-12]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, J = 7.9 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 8.3 Hz, 2H), 4.74 (s, 1H); MS (EI) m/e 170 (100), 169 (90), 141 (33), 115 (24), 83 (10).

4-Methoxy-1,1′-biphenyl:[23] 83.2 mg, 90% [CAS: 613-37-6, T2-13]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (t, J = 8.6 Hz, 4H), 7.42 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 6.98 (d, J = 8.5 Hz, 2H), 3.86 (s, 3H); MS (EI) m/e 184 (100), 169 (57), 141 (71), 139 (15), 115 (45).

1,1′:2′,1″-Terphenyl:[23] 92.6 mg, 80% [CAS: 84-15-1, T2-14]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 (m, 4H), 7.20 (m, 6H), 7.17−7.10 (m, 4H); MS (EI) m/e 230 (100), 215 (30), 114 (25), 101 (15).

1,1′:3′,1″-Terphenyl:[23] 100.2 mg, 87% [CAS: 92-06-8, T2-15]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (t, J = 1.6 Hz, 1H), 7.69−7.61 (m, 4H), 7.62−7.55 (m, 2H), 7.55−7.42 (m, 5H), 7.41−7.33 (m, 2H); MS (EI) m/e 230 (100), 115 (15), 101 (12).

1,1′:4′,1″-Terphenyl:[23] 98.1 mg, 85% [CAS: 92-94-4, T2-16]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 (s, 4H), 7.66 (m, 4H), 7.47 (m, 4H), 7.42−7.33 (m, 2H); MS (EI) m/e 230 (100), 115 (25), 101 (10).

5′-Phenyl-1,1′:3′,1″-terphenyl:[23] 147.5 mg, 96% [CAS: 612-71-5, T2-17]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80 (s, 3H), 7.72 (m, 6H), 7.49 (t, J = 7.5 Hz, 6H), 7.41 (m, 3H); MS (EI) m/e 306 (100).

4′-Methoxy-4-nitrobiphenyl:[24] 114.0 mg, 99%; [CAS: 2143-90-0, T3-1]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.27 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.2 Hz, 2H), 3.88 (s, 3H); MS (EI) m/e 229 (100), 199 (20), 183 (12), 171 (10), 168 (24), 156 (7), 153 (20), 139 (49), 128 (10).

4′-Methyl-4-nitrobiphenyl:[26] 113.5 mg, 99% [CAS: 2143-88-6, T3-2]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.29 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 7.9 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H); MS (EI) m/e 214 (15), 213 (100), 183 (27), 165 (46), 152 (83), 139 (10), 128 (7), 115 (15).

2′-Methyl-4-nitro-1,1′-biphenyl:[27] 97.5 mg, 85% [CAS: 33350-73-1, T3-3]; ^{1}H NMR (400 MHz, DMSO) δ 8.29 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 3.7 Hz, 2H), 7.31 (d, J = 4.5 Hz, 1H), 7.26 (d, J = 7.1 Hz, 1H), 2.25 (s, 3H); MS (EI) m/e 213 (100), 165 (88), 152 (78), 151 (12), 115 (27), 82 (15), 77 (5), 63 (11), 51 (7), 39 (7).

3′-Methyl-4-nitro-1,1′-biphenyl:[27] 111.7 mg, 80% [CAS: 952-21-6, T3-4]; ^{1}H NMR (400 MHz, DMSO) δ 8.30 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 8.8 Hz, 2H), 7.65−7.52 (m, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 2.40 (s, 3H); MS (EI) m/e 213 (88), 183 (29), 165 (53), 152 (100), 115 (20), 82 (12), 63 (10), 51 (7), 39 (7).

4-Nitro-4′-(trifluoromethyl)-1,1′-biphenyl:[24] 111.0 mg, 83% [CAS: 80245-34-7, T3-5]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.34 (d, J = 8.4 Hz, 2H), 7.80−7.71 (m, 6H); MS (EI) m/e 268 (15), 267 (100), 266 (7), 248 (7), 237 (33), 221 (7), 209 (27), 201 (34), 170 (7), 153 (7), 152 (59), 151 (17), 75 (7).

4,4′-Dimethyl-1,1′-biphenyl:[28] 89.5 mg, 98% [CAS: 613-33-2, T3-6]; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53−7.43 (m, 4H), 7.23 (d, J = 7.9 Hz, 4H), 2.39 (s, 6H); MS (EI) m/e 182 (100), 167 (50), 152 (10), 89 (20).

4-Methyl-4′-(trifluoromethyl)-1,1′-biphenyl:[23] 89.0 mg, 75% [CAS: 97067-18-0, T3-7]: ^{1}H NMR (400 MHz, DMSO) δ 7.87 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H); MS (EI) m/e 236 (100), 167 (42), 152 (9), 91 (8).

2,2′-Dimethyl-1,1′-biphenyl:[29] 40.3 mg, 44%; [CAS: 605-39-0, T3-8]: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31−7.16 (m, 6H), 7.10 (d, J =

7.0 Hz, 2H), 2.05 (s, 6H); MS (EI) *m/e* 182 (65), 167 (100), 152 (22), 115 (10), 89 (20), 76 (10), 51 (5), 39 (8).

3-Phenylpyridine:[30] 19.8 mg, 26% [CAS: 1008-88-4, T4-4]; ^{1}H NMR (400 MHz, DMSO) δ 8.89 (d, *J* = 2.1 Hz, 1H), 8.57 (m, 1H), 8.10−8.01 (m, 1H), 7.76−7.67 (m, 2H), 7.48 (m, 3H), 7.41 (m, 1H); MS (EI) *m/e* 155 (100), 127 (15), 102 (11), 76 (10).

5-Phenylpyrimidine:[30] 77.4 mg, 99% [CAS: 34771-45-4, T4-5]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.95 (s, 2H), 7.61−7.55 (m, 2H), 7.55−7.49 (m, 2H), 7.47 (m, 1H); MS (EI) *m/e* 156 (100), 102 (73), 76 (15), 51(22).

2-Phenylpyrazine:[31] 74.0 mg, 95%; [CAS: 29460-97-7, T4-6]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.73−8.58 (m, 1H), 8.52 (d, *J* = 2.4 Hz, 1H), 8.02 (m, 2H), 7.64−7.36 (m, 3H); MS (EI) *m/e* 156 (100), 129 (22), 103 (91), 76 (25), 51 (18), 39 (5).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR spectra of the products. 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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