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The catalytic activity of a novel recyclable alkoxypalladium complex in Suzuki reaction

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ABSTRACT

A novel palladium complex based on *N*,*O*-ligand was synthesized, which shows a high catalytic activity in the Suzuki cross-coupling reaction without using any phosphine ligand. More importantly, no significant loss of the catalytic activity was observed after six recycles. We suggest that this catalyst has commercial and industrial potential in the future.

1. Introduction

The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction[1] has been one of the most studied catalytic reactions in the last two decades. Up to now, it was widely used in the synthesis of poly-olefins and substituted biaryls, which are important skeletons in the structures of natural products, agrochemicals, pharmaceuticals, and advanced materials.[2] Generally, phosphine ligands are often used in palladium-catalyzed processes, but most of them are water- and air-sensitive.[3] Thus, a number of phosphine-free ligands for the Suzuki–Miyaura reaction have been reported, which were successfully applied to this reaction, such as palladacycles,[4] *N*-heterocyclic carbenes,[5] imines,[6] diazabutadienes,[7] amines,[8] pyrazoles,[9] and bipyridine-based systems.[3a,10] Some of these palladium catalysts have not only high catalytic activity but also recyclability. More recently, Gülcemal et al.[11] tested the palladium catalysts based on *N*,*N*- or *N*,*O*-ligands for the Suzuki cross-coupling reaction of aryl bromides with boronic acid in water. In this case, the obtained turnover number (TON) was up to 100,000. It is well known that compounds containing pyridine moiety represent one of the most widespread ligands in chemistry of coordinated and organometallic derivatives. It may be explained by the formation of the additional interactions between nitrogen and metal atoms. Whereas, palladium complexes based on pyridine-containing alcohols have not employed in modified Suzuki reaction. According to these factors, in this paper we will report the synthesis of a novel palladium catalyst based on 2,6-$PyCH_3(CH_2CPh_2O)^-$ fragment, and study its catalytic activity in the modified Suzuki cross-coupling reaction.

2. Results and discussion

The reaction between $Pd(OAc)_2$ and alcohol **2** is a standard approach to synthesize di(alkoxy)palladium(II).[12] We used this method for the synthesis of complex **3**, which was isolated as a white solid in an excellent yield (91%) (Scheme 1). The structure of complex **3** was confirmed by elemental analysis and high resolution mass spectrometry. Unfortunately, NMR spectra were not recorded due to insolubility of **3** in all of accessible organic solvents. According to the data of elemental analysis, we found that each molecule **3** contains two molecules of AcOH. But the data of high resolution mass spectrometry shows that in the solution state these two molecules of AcOH are dissolved in solvent. Therefore, it is proved that these two molecules of AcOH are coordinated to palladium complex *via* a coordinated bond.

In our initial investigation, we studied to explore the optimized reaction conditions of complex **3** in modified Suzuki reaction, as shown in Table 1. The results show that this reaction proceeded smoothly with Cs_2CO_3 and KOH in C_2H_5OH at 50 °C to give the product **6a** in excellent yield (99%) (Table 1, entries 3 and 5). Either

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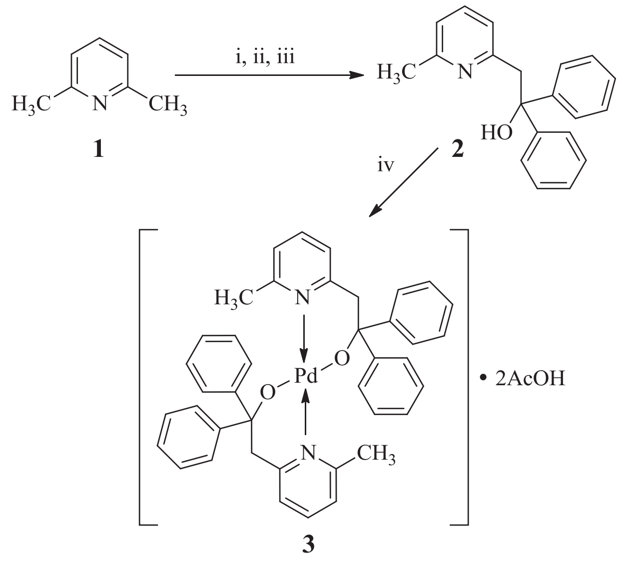


Scheme 1. Reagents and conditions: (i) *n*-BuLi (1.01 equiv), THF, −60 °C; (ii) $Ph_2C{=}O$ (1.01 equiv); (iii) 2 N HCl; (iv) $Pd(OAc)_2$ (0.5 equiv), toluene, rt, 3 days.

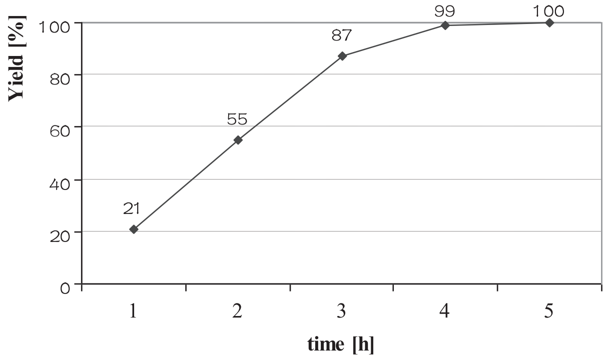
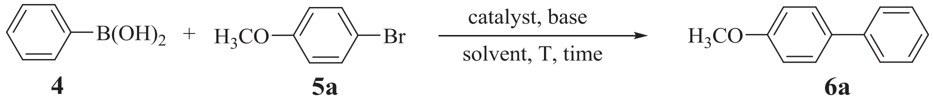


Fig. 1. Effect of time on the yield (GC determined) of **6a** in the coupling reaction with 0.1 mol % catalyst (KOH as a base, C_2H_5OH as a solvent).

the polarity of solvents or the bases were changed, the yield of compound **6a** was sharply reduced (Table 1, entries 1–11). In addition, the yield of the desired product **6a** was decreased at lower temperatures, which could be explained due to the decrease of the solubility of catalyst in solvent (Table 1, entries 12 and 13). Meanwhile, the effective catalyst loading was also studied (Table 1, entries 15–20). High yield (98%) and a TON of 32,667 were obtained even at catalyst loading as low as 0.003 mol % (Table 1, entry 20). According to experimental data demonstrated in Fig. 1, it was found that the optimized time for this reaction is 4 h with 0.1 mol % catalyst **3**. Therefore, the optimized conditions for the palladacycle-catalyzed Suzuki cross-coupling reaction of aryl bromides include the following parameters: boronic acid (1.5 mmol), aryl bromide (1.0 mmol), palladacycle complex **3** (0.1 mol %), KOH (2.0 mmol), C_2H_5OH (3.0 mL), under air atmosphere, at 50 °C in 4 h.

To explore the generality and scope of catalyst **3**, the modified Suzuki reaction of different aryl bromides was carried out under the optimized reaction conditions (Table 2). The results demonstrate that complex **3** really exhibits high catalytic activity in the modified Suzuki cross-coupling reaction for a broad variety of aryl bromides containing either electron-donating or electron-withdrawing groups to give excellent yields (Table 2, entries 1–10). It should be noted that methyl 4-bromobenzoate **5h** reacts with phenyl boronic acid in C_2H_5OH to give compound **6h** instead of **6i**. We proposed that the ester exchange proceeded in this process (Table 2, entry 8). In order to confirm our proposition, we repeated this reaction in CH_3OH. Not surprisingly, the compound **6i** was obtained in excellent yield, 99% (Table 2, entry 9). In addition, aryl bromides with electron-withdrawing groups could react more quickly than aryl bromides containing electron-donating groups. Especially, *p*-bromonitrobenzene **5j** had completely transformed to compound **6j** in 1 h at room temperature (Table 2, entry 10). To further extend the

Table 1
Screening of bases, solvents and temperatures for the coupling reaction of aryl bromide with phenyl boronic acid[a]



Entry	Base	*T* [°C]	Solvent	Time [h]	Cat. [mol %]	Yield[b] [%]
1	K_3PO_4	50	C_2H_5OH	1	1	97
2	K_2CO_3	50	C_2H_5OH	1	1	98
3	Cs_2CO_3	50	C_2H_5OH	1	1	99
4	KOAc	50	C_2H_5OH	1	1	80
5	KOH	50	C_2H_5OH	1	1	99
6	KF	50	C_2H_5OH	1	1	60
7	KOH	50	CH_3OH	1	1	86
8	KOH	50	THF	1	1	6
9	KOH	50	$(C_2H_5)_2O$	1	1	NR[c]
10	KOH	50	DMF	1	1	4
11	KOH	50	H_2O	1	1	34
12	KOH	40	C_2H_5OH	1	1	75
13	KOH	25	C_2H_5OH	1	1	4
14	KOH	50	C_2H_5OH	0.5	0.5	20
15	KOH	50	C_2H_5OH	1	0.5	97
16	KOH	50	C_2H_5OH	3.5	0.2	98
17	**KOH**	**50**	**C_2H_5OH**	**4**	**0.1**	**99**
18	KOH	50	C_2H_5OH	10	0.02	99
19	KOH	50	C_2H_5OH	10	0.01	99
20	KOH	50	C_2H_5OH	20	0.003	98

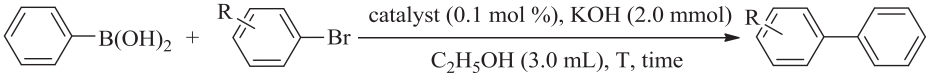
The values in bold represent the optimized conditions for the studied reaction.

[a] Reaction conditions: boronic acid (1.5 mmol), 4-bromoanisole (1.0 mmol), base (2.0 mmol), solvent (3.0 mL), under air atmosphere.

[b] Isolated yield.

[c] No reaction.

Table 2
Modified Suzuki cross-coupling reaction of aryl bromides with boronic acid[a]



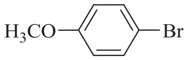
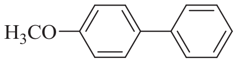
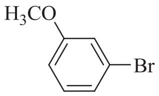
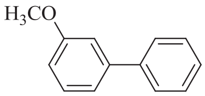
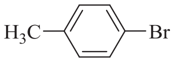
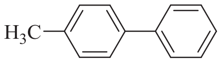
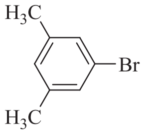
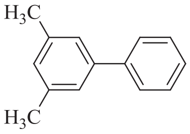
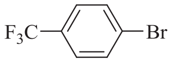
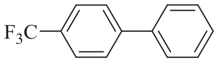
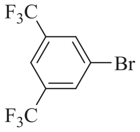
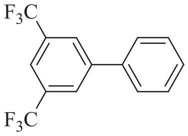
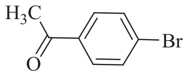
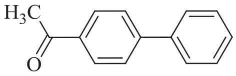
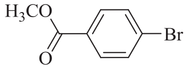
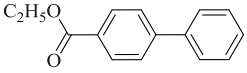
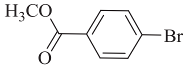
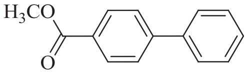
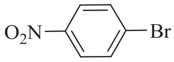
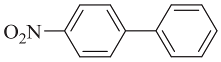
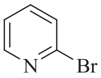
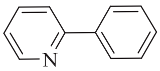
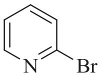
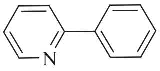
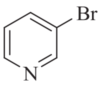
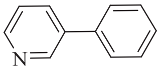
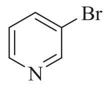
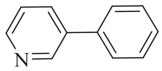
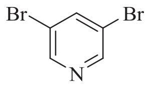
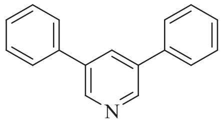
Entry	Aryl bromide	Product	T [°C]	Time [h]	Yield[b] [%]
1	 **5a**	 **6a**	50	4	99
2	 **5b**	 **6b**	50	2	97
3	 **5c**	 **6c**	50	1	99
4	 **5d**	 **6d**	50	1.5	98
5	 **5e**	 **6e**	50	1	99
6	 **5f**	 **6f**	50	1	99
7	 **5g**	 **6g**	50	1	99
8	 **5h**	 **6h**	50	1	99
9[c]	 **5i**	 **6i**	50	1	99
10	 **5j**	 **6j**	rt	1	99
11	 **5k**	 **6k**	50	24	40
12	 **5k**	 **6k**	78	12	68
13	 **5l**	 **6l**	50	24	41

Table 2 (*continued*)

Entry	Aryl bromide	Product	*T* [°C]	Time [h]	Yield[b] [%]
14	 **5l**	 **6l**	78	12	92
15[d]	 **5m**	 **6m**	50	7	78

[a] Reaction conditions: boronic acid (1.5 mmol), aryl bromide (1.0 mmol), KOH (2.0 mmol), catalyst (0.1 mol %), C_2H_5OH (3.0 mL), under air atmosphere.
[b] Isolated yield.
[c] Reaction conditions: CH_3OH (3.0 mL), under air atmosphere.
[d] Reaction conditions: boronic acid (1.5 mmol), aryl bromide (0.5 mmol).

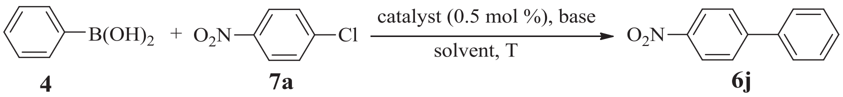
scope of this catalytic system, we tried to carry out the coupling reaction of heteroaryl bromides **5k**–**m** with phenyl boronic acid. It was found that the standard conditions used for aryl bromides were not suitable for 2-bromopyridine and 3-bromopyridine, and low yields (only 40%) were obtained in 24 h at 50 °C (Table 2, entries 11 and 13). Increasing the temperature to 78 °C, the corresponding products could be obtained in moderate to excellent yields (Table 2, entries 12 and 14). On the other hand, the Suzuki reaction of 3,5-dibromopyridine **5m** with phenyl boronic acid could proceed at 50 °C to give moderate yield (Table 2, entry 15).

In light of the high reactivity of this new catalyst in reaction with aryl bromides, we investigated the modified Suzuki coupling reaction of aryl chlorides. However, the reaction conditions optimized for aryl bromides were ineffective for aryl chlorides. Thus, the new reaction conditions for aryl chlorides were selected (Table 3). It was found that the reaction of aryl chloride **7a** could proceed in the presence of K_2CO_3 in DMF at 100 °C to give the product **6j** in excellent yield (Table 3, entry 3).

Under optimized conditions, the Suzuki cross-coupling reaction of aryl chlorides with phenyl boronic acid was studied (Table 4). The results suggest that there is a great difference in the reaction rate of various aryl chlorides. The cross-coupling reaction of 4-chlorobenzonitrile **7b** with phenyl boronic acid could proceed easily to give an excellent yield (92%). However, 2-chlorotoluene **7h** did not react with phenyl boronic acid under the same conditions (Table 4, entries 2 and 8). Aryl chlorides with electron-withdrawing substituents (Table 4, entries 1–5) react more easily than aryl chlorides with electron-donating groups (Table 4, entries 6–8).

Recently, the catalyst recycling has attracted chemists' attention in organic synthesis. A large number of polymer-supported organometallic catalysts were synthesized and used in different catalytic reactions. For example, Ley et al.[13] used 0.4 mol % MC-[Pd] at 100 °C for 4-bromoanisole only a 60% conversion was observed, and this catalyst could only be recycled four times. At the same year, the catalytic activity of 2 mol % polymer-supported palladium was confirmed in the reaction of aryl iodides with aryl boronic acid with excellent yield. However, authors did not investigate recyclable character of the catalyst.[14] Using the recycling of a salen-type palladium(II) catalyst, N.T.S. Phan et al.[15] studied the Suzuki reaction of 4-bromoanisole at 90 °C for 24 h. After three cycles, the yield of the reaction reduced from 99% to 82%. Although the iron oxide–Pd exhibits a high activity toward the Suzuki cross-coupling reaction, authors only used this supported catalyst for aryl iodides and bromides.[16] Therefore, due to the insolubility and high activity of complex **3**, we investigated the possibility of the reuse of catalyst for the modified Suzuki reaction of phenyl boronic acid with **5a**, and the results were shown in Fig. 2. Upon completion of each reaction, the solid catalyst was isolated by centrifugation, washed with ethyl acetate and reused without further purification. The product **6a** was obtained in 99% yield from the first to fifth cycles, 95% for the eighth cycle, and 88% for the 10th cycle. From the data of recycling experiments we found that no significant loss of the catalytic activity was observed for complex **3** after six consecutive reactions, and proposed that this catalyst could be used within eight-recycle runs. Comparing our catalyst **3** to above-mentioned supported catalysts, it was found that the catalyst **3** has some advantages over all others in Suzuki reaction.

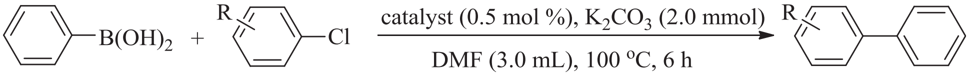
Table 3
Screening of bases, solvents and temperatures for the coupling reaction of aryl chloride with boronic acid[a]

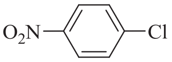
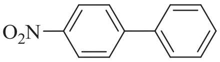
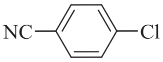
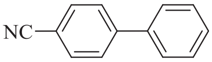
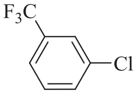
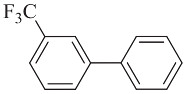
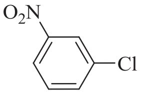
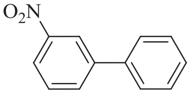
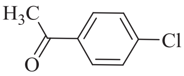
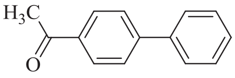
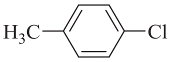
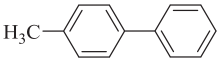
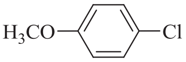
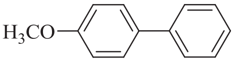
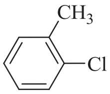
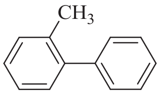


Entry	Base	*T* [°C]	Solvent	Time [h]	Yield[b] [%]
1	KOH	110	DMF	16	86
2	KOH	110	DMSO	16	80
3	**K_2CO_3**	**100**	**DMF**	**6**	**90**
4	K_2CO_3	80	DMF	12	62

The values in bold represent the optimized conditions for the studied reaction.
[a] Reaction conditions: boronic acid (1.5 mmol), 4-chloronitrobenzene (1.0 mmol), catalyst (0.5 mol %), base (2.0 mmol), solvent (3.0 mL), under air atmosphere.
[b] GC yield.

Table 4
Modified Suzuki cross-coupling reaction of aryl chlorides with boronic acid[a]



Entry	Aryl chloride	Product	Yield[b] [%]
1	 **7a**	 **6j**	82
2	 **7b**	 **6n**	92
3	 **7c**	 **6o**	60
4	 **7d**	 **6p**	35
5	 **7e**	 **6g**	35
6	 **7f**	 **6c**	30
7	 **7g**	 **6a**	31
8	 **7h**	 **6q**	Trace[c]

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[a] Reaction conditions: boronic acid (1.5 mmol), aryl chloride (1.0 mmol), K$_2$CO$_3$ (2.0 mmol), catalyst (0.5 mol %), DMF (3.0 mL), 100 °C, 6 h, under air atmosphere.
[b] Isolated yield.
[c] Determined by GC.

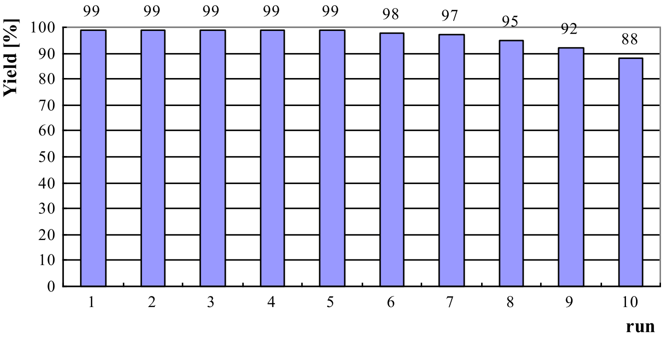

Fig. 2. Recycling experiments of catalyst **3** in the palladium-catalyzed Suzuki cross-coupling reaction.

3. Conclusion

In summary, we synthesized a novel palladium(II) catalyst based on *N*,*O*-ligand. This catalyst is insoluble in various organic solvents, but exhibits high catalytic activity in the modified Suzuki cross-coupling reaction. More importantly, there is no significant loss of catalytic activity after six recycles. In addition, a series of biaryl derivatives were obtained in moderate to excellent yields in mild conditions from the reaction of phenyl boronic acid with aryl bromides or chlorides. Therefore we consider that this catalyst has commercial and industrial potential in the future.

4. Experimental

4.1. General

All reactions were carried out under air atmosphere. Compound 2,6-PyCH$_3$(CH$_2$CPh$_2$OH) was prepared according to the literature procedure.[12] Other chemical reagents were purchased from commercial suppliers and used without further purification. All organic solvents were purified prior to use. The products **6a–p** were known, and the purified products were identifiable by comparison of melting points, ^{1}H NMR, ^{13}C NMR spectra with the literature. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 instrument using $CDCl_3$ as the solvent and TMS as the internal standard. High resolution mass spectrometry data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS instrument. Elemental analyses (EA) data were recorded on Elementar Vario ELIII spectrometer. Melting points were measured using a WC-1 microscopic apparatus and are uncorrected.

4.2. Synthesis of $[PyCH_3(CH_2CPh_2O)]_2Pd\cdot 2AcOH$ (3)

A solution of $PyCH_3(CH_2CPh_2OH)$ (318.3 mg, 1.10 mmol) in toluene (10 mL) was added to a stirred solution of $Pd(OAc)_2$ (123.5 mg, 0.55 mmol) in toluene (10 mL). The mixture was stirred at room temperature. After 3 days, the solid was filtered off to give **3** as a white solid. Yield: 91%. HRMS (ESI): calcd for $C_{40}H_{36}N_2O_2Pd$ $[M+H]^+$ 683.1812; found 683.1902. Anal. Calcd for $C_{44}H_{44}N_2O_6Pd\cdot 2AcOH$ (802.2234): C, 65.79; H, 5.52; N, 3.49. Found: C, 65.55; H, 5.51; N, 3.81%.

4.3. General procedures for synthesis compounds 6a–q

4.3.1. General procedures of aryl bromides To a flask were added complex **3** (0.7 mg, 0.001 mmol, 0.1 mol %), phenyl boronic acid (182.9 mg, 1.5 mmol), KOH (112.2 mg, 2.0 mmol), aryl bromide (1.0 mmol), and C_2H_5OH (3.0 mL). Unless the otherwise note, the reaction mixture was stirred at 50 °C. After the completion of the reaction it was cooled to room temperature. The reaction mixture was dissolved in H_2O, and extracted with ethyl acetate (3×5.0 mL). The organic layer was collected and dried by Na_2SO_4, then concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the desired product.

4.3.2. General procedures of aryl chlorides To a flask were added with complex **3** (3.4 mg, 0.005 mmol, 0.5 mol %), phenyl boronic acid (182.9 mg, 1.5 mmol), K_2CO_3 (276.4 mg, 2.0 mmol), aryl chloride (1.0 mmol), and DMF (3.0 mL). Unless the otherwise note, the reaction mixture was stirred at 100 °C for 6 h. After the completion of the reaction it was cooled to room temperature. The reaction mixture was dissolved in H_2O, and extracted with ethyl acetate (3×5.0 mL). The organic layer was collected and dried by Na_2SO_4, then concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the desired product.

4.4. Analytical data for compounds 6a–p

*4.4.1. 4-Methoxybiphenyl (**6a**).*[17] White solid, mp 84–86 °C (lit. mp 83–84 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.53, 7.47–7.40, 7.36–7.29, 7.03–6.97 (9H, 4m, aromatic hydrogens), 3.87 (3H, s, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.14, 140.81, 133.77, 128.69, 128.13, 126.71, 126.63, 114.19 (aromatic carbons), 55.31 (OCH_3).

*4.4.2. 3-Methoxybiphenyl (**6b**).*[3b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.58, 7.49–7.43, 7.42–7.34, 7.23–7.19, 7.16–7.13, 6.95–6.89 (9H, 6m, aromatic hydrogens), 3.89 (3H, s, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.84, 142.71, 141.03, 129.72, 128.70, 127.38, 127.17, 119.64, 112.82, 112.60 (aromatic carbons), 55.26 (OCH_3).

*4.4.3. 4-Methylbiphenyl (**6c**).*[17] White solid, mp 42–43 °C (lit. mp 44–46 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.55, 7.52–7.47, 7.45–7.40, 7.36–7.29, 7.26–7.23 (9H, 5m, aromatic hydrogens), 2.39 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.10, 138.29, 137.00, 129.45, 128.69, 126.97, 126.94 (aromatic carbons), 21.10 (CH_3).

*4.4.4. 3,5-Dimethylbiphenyl (**6d**).*[17] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.58, 7.50–7.41, 7.40–7.32 (5H, 3 m), 7.24 (2H, s), 7.03 (1H, s) (aromatic hydrogens), 2.41 (6H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.41, 141.21, 138.22, 128.86, 128.60, 127.16, 127.05, 125.07 (aromatic carbons), 21.41 (CH_3).

*4.4.5. 4-(Trifluoromethyl)-biphenyl (**6e**).*[18] Colorless solid, mp 68–69 °C (lit. mp 70–71 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–7.68, 7.64–7.60, 7.52–7.45, 7.44–7.39 (9H, 4m, aromatic hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.73, 139.76, 128.97, 128.74, 128.17, 127.40, 127.26, 127.15 (aromatic carbons), 125.69 (q, CF_3).

*4.4.6. 3,5-Bis(trifluoromethyl)-biphenyl (**6f**).*[19] Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (2H, s), 7.89 (1H, s), 7.64–7.60, 7.56–7.44 (5H, 2 m) (aromatic hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.35, 138.25, 129.27, 128.87, 127.23, 124.76, 122.05, 120.90 (aromatic carbons), 132.14 (q, CF_3).

*4.4.7. 1-Biphenyl-4-yl-ethanone (**6g**).*[18] Colorless solid, mp 112–114 °C (lit. mp 121–122 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.01, 7.72–7.60, 7.50–7.38 (9H, 3m, aromatic hydrogens), 2.64 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.68 (C=O), 145.74, 139.85, 135.84, 128.92, 128.88, 128.19, 127.23, 127.19 (aromatic carbons), 26.62 (CH_3).

*4.4.8. 4-Ethylphenylbenzoate (**6h**).*[20] White solid, mp 46–47 °C (lit. mp 47–48 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–8.09, 7.70–7.59, 7.51–7.36 (9H, 3m, aromatic hydrogens), 4.41 (2H, q, J=7.2 Hz, CH_2), 1.42 (3H, t, J=7.2 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.48 (C=O), 145.47, 140.00, 130.02, 129.18, 128.88, 128.07, 127.24, 126.96 (aromatic carbons), 60.95 (CH_2), 14.34 (CH_3).

*4.4.9. Methyl 4-phenylbenzoate (**6i**).*[17] White solid, mp 111–112 °C (lit. mp 113 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–8.08, 7.70–7.60, 7.51–7.37 (9H, 3m, aromatic hydrogens), 3.95 (3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.99 (C=O), 145.61, 139.97, 130.07, 128.90, 128.12, 127.26, 127.19, 127.03 (aromatic carbons), 52.13 (CH_3).

*4.4.10. 4-Nitrobiphenyl (**6j**).*[3b] Yellow solid, mp 110–112 °C (lit. mp 113–115 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32–8.26, 7.77–7.70, 7.66–7.60, 7.54–7.42 (9H, 4m, aromatic hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.55, 147.03, 138.70, 129.10, 128.86, 127.72, 127.32, 124.03 (aromatic carbons).

*4.4.11. 2-Phenylpyridine (**6k**).*[3b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72–8.69, 8.02–7.97, 7.79–7.70, 7.54–7.39, 7.25–7.20 (9H, 5m, aromatic and Py hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.40, 149.62, 139.33, 136.73, 128.91, 128.71, 126.86, 122.07, 120.55 (aromatic and Py carbons).

*4.4.12. 3-Phenylpyridine (**6l**).*[3b] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87–8.84, 8.60–8.56, 7.89–7.83, 7.60–7.55, 7.52–7.44, 7.42–7.32 (9H, 6m, aromatic and Py hydrogens). ^{13}C NMR

(100 MHz, $CDCl_3$): δ 148.38, 148.25, 137.76, 136.56, 134.25, 128.99, 128.01, 127.07, 123.45 (aromatic and Py carbons).

*4.4.13. 3,5-Diphenylpyridine (**6m**).*[21] White solid, mp 136–138 °C (lit. mp 137–138 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 8.85–8.80, 8.08–8.04, 7.68–7.63, 7.54–7.48, 7.47–7.40 (13H, 5m, aromatic and Py hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.98, 137.73, 136.57, 132.86, 129.09, 128.19, 127.23 (aromatic and Py carbons).

*4.4.14. 4-Phenylbenzonitrile (**6n**).*[22] White solid, mp 80–82 °C (lit. mp 84–88 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 7.76–7.66, 7.62–7.57, 7.53–7.40 (9H, 3m, aromatic hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.61, 139.10, 132.55, 129.07, 128.62, 127.68, 127.18, 118.94, 110.82 (aromatic carbons).

*4.4.15. 3-(Trifluoromethyl)-biphenyl (**6o**).*[23] Yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (1H, s), 7.81–7.76, 7.64–7.53, 7.52–7.45, 7.44–7.38 (8H, 4m, aromatic hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.95, 139.72, 130.93, 130.41, 129.21, 128.98, 128.01, 127.17, 125.52, 122.81 (aromatic carbons), 123.91 (q, CF_3).

*4.4.16. 3-Nitrobiphenyl (**6p**).*[3b] Yellow solid, mp 57–58 °C (lit. mp 59–60 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 8.50–8.44, 8.24–8.19, 7.94–7.89, 7.66–7.58, 7.54–7.41 (9H, 5m, aromatic hydrogens). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.65, 142.81, 138.61, 133.04, 129.69, 129.13, 128.51, 127.13, 122.01, 121.92 (aromatic carbons).

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