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ORIGINAL ARTICLE

Pillar[5]arene-based *N*-heterocyclic carbene ligand for Pd-catalysed Suzuki reaction

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Abstract A pillar[5]arene-based *N*-heterocyclic carbene ligand was prepared by reaction of bromoethoxy pillar[5]arene with excess 1-methylimidazole at 130 °C in the absence of solvent and used as a catalyst for the Suzuki coupling reaction. Excellent yields were obtained when the Suzuki reactions were carried out under ambient atmosphere in ethanol, employing 0.2 mol% ligand, 1 mol% $PdCl_2(CH_3CN)_2$ and 1.5 mmol of K_2CO_3. The novel pillar[5]arene-based imidazolium salt is a promising material for the construction of highly active supramolecular catalytic systems.

Keywords Pillar[5]arene · *N*-Heterocyclic carbene · Supramolecular · Suzuki · Cross-coupling

Introduction

The Suzuki–Miyaura [1] reaction belongs to the valuable class of organic coupling reactions, using palladium(0) complexes to catalyse the coupling of boranes, boronic esters, and boronic acids with aryl halides [2–5]. This reaction has become one of the most important C–C bond forming methods in the synthesis of natural products, polymers, liquid crystals and organic materials [6].

Since their discovery by Arduengo in 1991 [7, 8], *N*-heterocyclic carbenes (NHCs) have demonstrated excellent performance in various catalytic reactions, including those catalysed by palladium [9–11]. Similarly, supramolecular *N*-heterocyclic carbene ligands (such as crown ethers [12–14], cyclodextrins [15, 16], calixarenes [17, 18] and porphyrins [19, 20]) play an important role in catalytic reactions, exhibiting excellent performance. The Mei-Ming [21] group reported Pd(II)–NHC crown ether complexes (Fig. 1a) in 2008, used to catalyse Suzuki–Miyaura reactions of various aryl bromides in water. These reactions did not require inert gas protection and exhibited high product yields and turnover numbers (TONs) of up to 99,000. We prepared a porphyrin-based NHC ligand (Fig. 1b) and investigated its catalytic activity in Suzuki coupling in 2009 [22, 23]. The Ulrich Darbost [24] group reported calix[4]arene-supported *N*-heterocyclic carbene palladium complexes (Fig. 1c) in 2014, and fully characterized their performance in Suzuki–Miyaura reactions with a variety of aryl bromides and heterocyclic substrates, revealing good catalytic performance.

Pillar[n]arenes, a new class of macrocyclic hosts, were first reported by Tomoki Ogoshi [25] and co-workers in 2008. Their structural repeating units are connected by methylene bridges in the two *para*-positions, forming a rigid pillar-like architecture [26]. Due to ease of synthesis and modification, pillar[n]arenes have attracted a lot of attention in the field of analytical chemistry. Tomoki Ogoshi and Yong Yao reported pillar[5]arene-based imidazolium salts in 2012. This kind of pillar[5]arenes were used in molecular recognition [27] and as a novel stabilizer to fabricate gold nanoparticles in water [28]. As part of our current research on supramolecular *N*-heterocyclic carbenes, we have found that pillar[5]arene-based imidazolium

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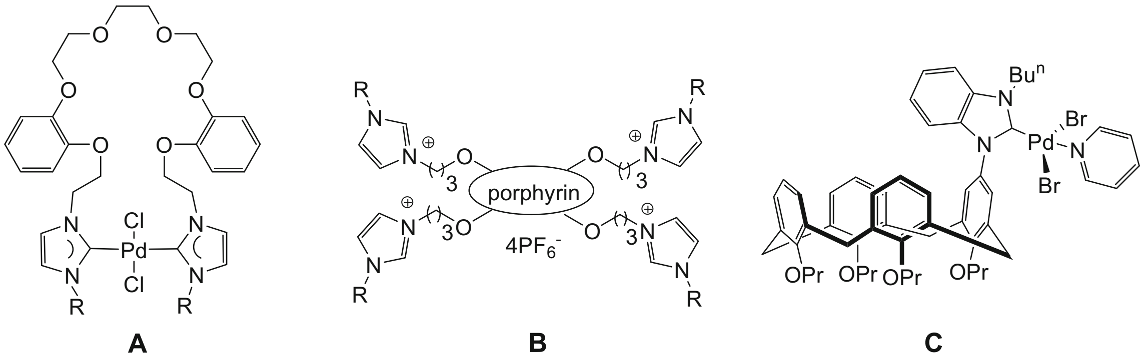
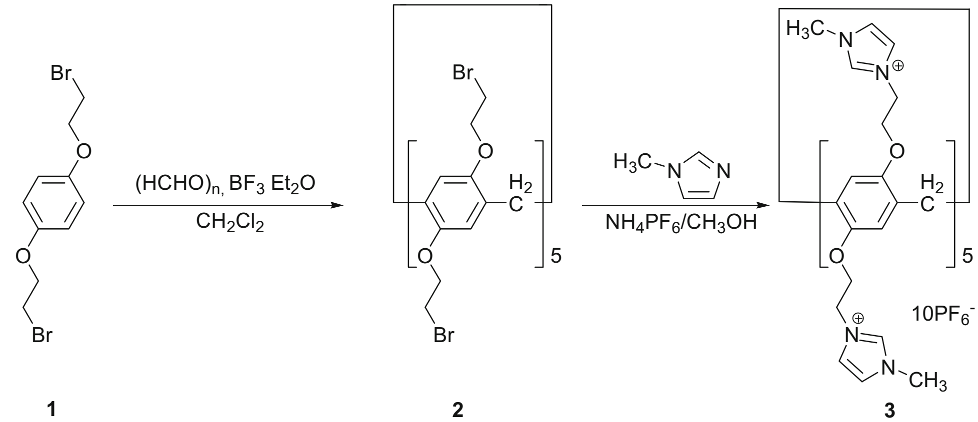


Fig. 1 Structures of the complexes **a**, **b** and **c**

Scheme 1 Synthesis of NHC ligand **3**



salts as *N*-heterocyclic carbene precursors, exhibit good organocatalytic properties.

Results and discussion

In this study, we synthesized pillar[5]arene-based imidazolium hexafluorophosphate according to previously reported procedures [27, 28]. The synthesis of NHC ligand is outlined in Scheme 1. Bromoethoxy pillar[5]arene **2** was prepared by stirring a mixture of 1,4-bis(2-bromoethoxy)benzene **1**, $BF_3·Et_2O$ and paraformaldehyde in dry CH_2Cl_2 for 150 min under N_2 atmosphere. Pillar[5]arene-based *N*-heterocyclic carbene ligand **3** was prepared by reacting bromoethoxy pillar[5]arene **2** with excess 1-methylimidazole at 130 °C in absence of solvent, followed by anion exchange with PF_6^- [27, 29, 30]. The product was characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis. The ^1H NMR resonance of the imidazolium proton of ligand **3** (NCHN) at δ 8.89 supports the formation of the expected carbene precursor.

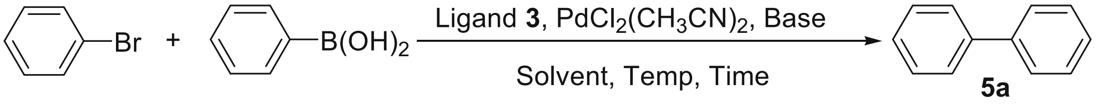
In the initial phase of the study, we tried to determine optimum conditions for the catalytic system, including base, solvent, temperature, etc. We used the reaction of bromobenzene with phenylboronic acid as a prototypical substrate combination to produce the biphenyl coupling product **5a** in presence of ligand **3**, with the results summarized in Table 1.

Initially, a good yield (99%, entry 10) was obtained using 1 mol% of ligand **3** and 5 mol% of $PdCl_2(CH_3CN)_2$. The amount of **3** was subsequently reduced to 0.2 mol%, still achieving a 99% yield (entry 11). During temperature screening, we conducted the reaction for 1.5 h at 65 °C, reaching a yield of 99% undoubtedly (entry 9). When the temperature was lowered to 50 °C, the yield was still satisfactory (entry 11). Surprisingly, when the reaction was performed at room temperature for 12 h, the yield reached 90% (entry 8), indicating the novel pillar[5]arene-based N-heterocyclic carbene ligand **3** exhibits excellent catalytic properties for the Suzuki cross-coupling reactions.

In order to explore the scope and limitations of ligand **3**, we coupled extensive aryl halide derivatives with phenylboronic acid derivatives under optimized reaction conditions, with the results summarized in Table 2.

Generally, the electronic properties of aryl halides significantly influence the outcome of coupling reactions, i.e. the presence of electron-withdrawing groups is proven

Table 1 Optimization of reaction conditions



Entry	Solvent	Base	T (°C)	T (h)	Yield (%)[a]
1	Ethanol	KOH	65	5	33
2	Ethanol	K_3PO_4	50	3	90
3	Ethanol	CH_3COONa	50	3	85
4	Ethanol	KO^tBu	50	3	61
5	Ethanol	NEt_3	50	3	82
6	Ethanol	NaO^tBu	50	3	45
7	Ethanol	Na_2CO_3	50	3	33
8	Ethanol	K_2CO_3	25	12	90
9	Ethanol	K_2CO_3	65	1.5	99
10	Ethanol	K_2CO_3	50	1.5	99[b]
11	**Ethanol**	**K_2CO_3**	**50**	**1.5**	**99**
12	DMF	K_2CO_3	50	3	15
13	THF	K_2CO_3	50	3	27
14	H_2O	K_2CO_3	50	3	Trace[c]
15	CH_3CN	K_2CO_3	50	3	40
16	1,4-dioxane	K_2CO_3	75	3	51

Reaction condition: 0.50 mmol of bromobenzene, 0.55 mmol of phenylboronic acid, 1.5 mmol of base, 0.2 mol% ligand **3**, 1 mol% $PdCl_2(CH_3CN)_2$, solvent 1.5 mL

Bold values indicate the best reaction condition

[a] Isolated yields

[b] The amount of ligand **3** is 1 mol%, $PdCl_2(CH_3CN)_2$ is 5 mol%

[c] Add TBAI 0.22 mmol

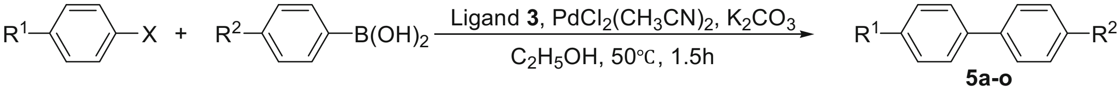
beneficial. In contrast, the presence of electron-donating groups or neutral groups results in moderate yields. In this experiment, we found that 4-bromotoluene and 4-bromoanisole, having electron-donating groups, are coupled with phenylboronic acid in yields of 95% or more (Table 2, entries 5 and 8). When 4-chlorophenylboronic acid was used as a substrate, the reaction yield was slightly decreased (Table 2, entry 6 and 9). Additionally, we tried to couple less reactive chlorobenzene derivatives, but the yields were relatively low (Table 2, entries 1 and 2).

After the NHC-pillar[5]arene was shown to be an effective catalyst for the Suzuki–Miyaura cross-coupling of aryl bromides and phenylboronic acid, the monomer-NHC ligand **4** lacking the pillar-shaped architecture was also prepared for comparison (Fig. 2). This new imidazolium salt was then compared with the NHC–pillar[5]arene **3** in standard Suzuki–Miyaura cross-coupling forming biaryls (Table 3).

Interestingly, both precursors gave comparable reaction yields in the simple coupling of aryl bromides and phenylboronic acid at 50 °C. It is surprising that the pillar[5]arene core seems to have a large impact on the coupling. Notably, with 0.2 mol% of NHC–pillar[5]arene **3** used, all of the aryl bromides and phenylboronic acid were converted to the corresponding biaryls in excellent yields (entries 1, 3, 5, 7, and 9). Ligand **4** was used in 1 mol% loading, providing the same number of imidazolium units as ligand **3**. However, the corresponding reaction yields were significantly reduced (entries 2, 4, 6, 8, and 10).

In order to further demonstrate the importance of supramolecular macrocyclic for this reaction, ^1H NMR spectroscopy (Fig. 3) was employed to study the inclusion interaction between ligand **3** and aryl bromide substrates. As shown in Fig. 3, when ligand **3** was added to bromobenzene solution, the signals of the homologous protons of the bromobenzene showed different shifts. (Other spectra in the Supplementary material) These facts suggest that the higher yields obtained with ligand **3** are attributable to its structural properties and capacity to strongly bind aryl bromides in its hydrophobic cavity (Fig. 4), which enhances the interaction with other reagents and palladium [31–35].

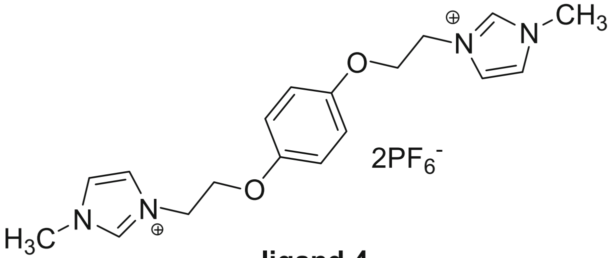
Table 2 Suzuki–Miyaura cross-coupling of aryl halide with different boronicacids



Entry	R^1	R^2	X	Product	Yield (%)[a]
1	H	H	Cl	5a	40
2	CH_3	H	Cl	5b	34
3	H	Cl	Br	5c	99
4	H	CH_3CH_2 O	Br	5d	99
5	CH_3	H	Br	5b	99
6	CH_3	Cl	Br	5e	82
7	CH_3	CH_3CH_2O	Br	5f	97
8	CH_3O	H	Br	5g	99
9	CH_3O	Cl	Br	5h	90
10	CH_3O	CH_3CH_2O	Br	5i	90
11	NO_2	H	Br	5j	99
12	NO_2	Cl	Br	5k	95
13	NO_2	CH_3CH_2O	Br	5l	91
14	CN	H	Br	5m	99
15	CN	Cl	Br	5n	96
16	CN	CH_3CH_2O	Br	5o	92

Reaction condition: 0.50 mmol of Ar–X, 0.55 mmol phenylboronic acid, 1.5 mmol of K_2CO_3, 0.2 mol% ligand 3, 1 mol% $PdCl_2(CH_3CN)_2$, ethanol 1.5 mL, 50 °C, 1.5 h

[a] Isolated yields after chromatographic purification



ligand 4

Fig. 2 Structure of the monomer-NHC ligand **4**

Conclusion

In summary, a convenient and efficient Suzuki–Miyaura cross-coupling for the synthesis of biaryls employing an NHC ligand was disclosed. The novel NHC-pillar[5]arene ligand was prepared and demonstrated to exhibit good catalytic activity in Suzuki–Miyaura cross-coupling of aryl bromides and phenylboronic acid under mild conditions, without the protection of an inert gas. The hydrophobic cavity present in the structure of pillar[5]arenes was found to play a very important role in this coupling reaction. Inspired by this, we are now pursuing a search for highly active supramolecular catalytic systems.

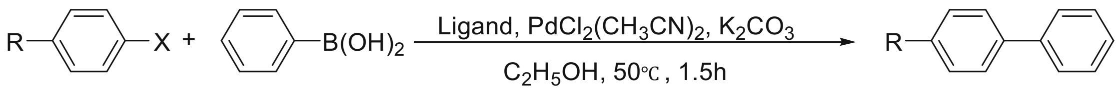
Experimental

All manipulations, reactions were performed under air atmosphere; solvents were purified using standard methods. Precursors 1, 2 and 3 were synthesized according to the previously reported [27, 28]. IR spectra were recorded on a Varian 660-IR spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE III HD 600 MHz spectrometer in $CDCl_3$ and d_6-DMSO with TMS as an internal reference. Coupling constants (*J*-values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal.

Preparation of the 1,4-bis(2-bromoethoxy)benzene (1) [27, 28]

A solution of 4-bis(2-hydroxyethoxy) benzene (6.0 g, 30 mmol) and triphenylphosphine (18.9 g, 72.1 mmol) in dry acetonitrile (200 mL) was cooled with an ice bath. Under vigorous stirring, carbon tetrabromide (24.0 g, 72.4 mmol) was slowly added. The mixture was stirred at room temperature for 12 h. Then cold water (200 mL) was added to the reaction mixture to give white precipitation.

Table 3 Suzuki–miyaura cross-coupling of bromobenzene derivatives with different catalysts



Entry	R	Ligand	t (h)	Yield (%)[a]
1	H	3	1.5	99
2	H	4	1.5	70
3	CH_3	3	1.5	99
4	CH_3	4	1.5	68
5	CH_3O	3	1.5	99
6	CH_3O	4	1.5	66
7	NO_2	3	1.5	99
8	NO_2	4	1.5	75
9	CN	3	1.5	99
10	CN	4	1.5	78

Reaction condition: 0.50 mmol of Ar–X, 0.55 mmol phenylboronic acid, 1.5 mmol of K_2CO_3, 0.2 mol% ligand **3**, 1 mol% ligand **4**, 1 mol% $PdCl_2(CH_3CN)_2$, ethanol 1.5 mL, 50 °C

[a] Isolated yields after chromatographic purification

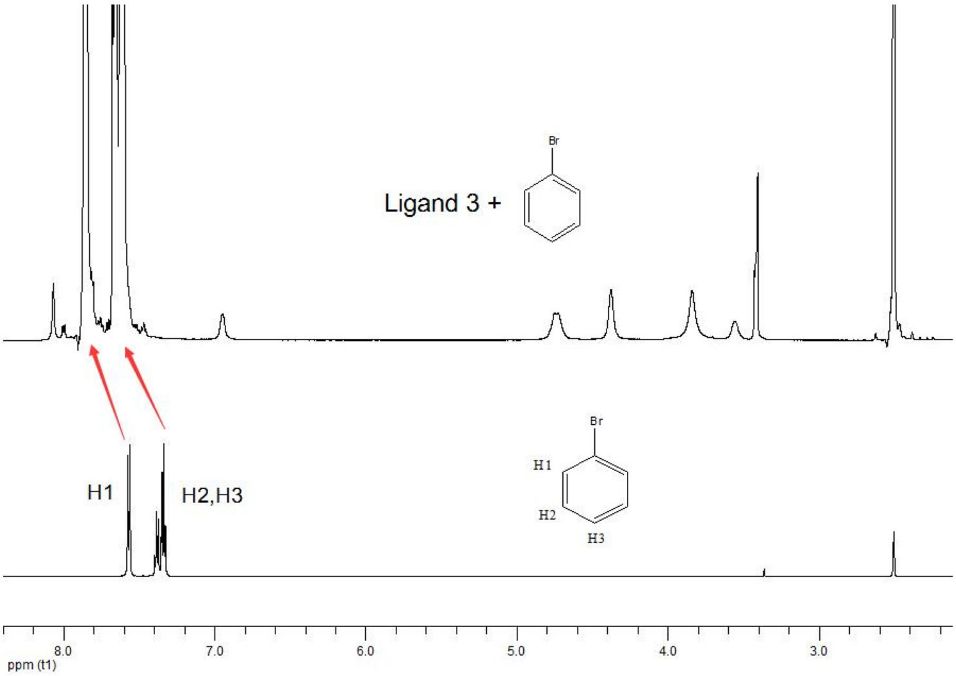


Fig. 3 Partial ^1H NMR spectra (600 MHz) of ligand **3** and bromobenzene in DMSO

The precipitate was collected, washed with methanol/water (3:2, 3 × 100 mL), recrystallized from methanol, and dried under vacuum to afford 1 as white crystals, 82.7% (14.5 g). ^1H NMR (600 MHz, $CDCl_3$): $\delta = 6.86$ (s, 4H), 4.24 (t, $J = 6.3$, 4H), 3.61 (t, $J = 6.3$, 4H) ppm.

Preparation of the pillar[5]arene (2) [27]

To a 500 mL Schlenk flask with magnetic stir bar was charged compound 1 (3.0 g 9.2 mmol), Paraformaldehyde (0.834 g, 27.8 mmol), CH_2Cl_2 (200 mL) was then charged, and the solution was cooled to 0 °C in an ice bath. Boron trifluoride etherate (3.0 mL, 23.7 mmol) was added to the solution cooling with ice bath under N_2 protection. The mixture was stirred for 2.5 h. The reaction mixture was filtration. Filtrate washed with 2.5 M NaOH (2 × 30 mL) and water (1 × 30 mL) and dried with anhydrous $MgSO_4$. The solvent was evaporated to provide a crude product. Recrystallized from ethyl acetate, and dried under vacuum to afford 2 as white or light yellow powder, 40% (1.2 g).

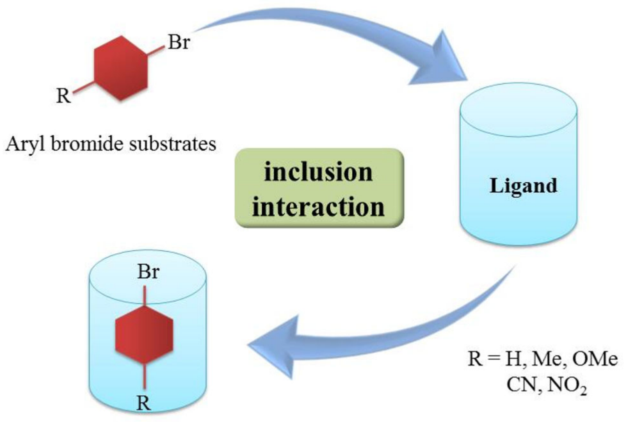


Fig. 4 The inclusion interaction mechanism for ligand **3** with aryl bromide substrates

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.91 (s, 10H), 4.22 (t, *J* = 5.6, 20H), 3.84 (s, 10H), 3.63 (t, *J* = 5.7, 20H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.7, 129.1, 116.0, 69.0, 30.7, 29.4 ppm.

Preparation of the NHC-pillar[5]arene ligand (3) [27, 28]

To solution of 1-methylimidazole (6 mL), compound 2 (0.50 g, 0.298 mmol) was added. The mixture was heated at 130 °C for 48 h. The resulting solution was poured into diethyl ether and the precipitate was collected by filtration. The reprecipitation process was repeated three times to afford white solid. White solid in methanol (20 mL), NH_4PF_6 (0.86 g, 5.28 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. The precipitate was collected by filtration to afford ligand 3 as white powder, 85% (0.71 g). Elemental Analysis: Calcd for C95H120F60N20O10P10 C, 36.19; H, 3.81; N, 8.89. Found: C, 36.04; H, 3.92; N, 8.93. ^{1}H NMR (600 MHz, d6-DMSO): δ = 8.89 (s, 10H), 7.81 (s, 10H), 7.47 (s, 10H), 6.70 (s, 10H), 4.62 (s, 20H), 4.29 (s, 20H), 3.74 (s, 30H), 3.50 (s, 10H) ppm. ^{13}C NMR (150 MHz, d_6-DMSO): δ = 149.1, 137.2, 128.4, 124.1, 123.1, 114.6, 66.8, 49.5, 36.2, 29.0 ppm.

Preparation of the ligand (4)

To a 100 mL round flask with magnetic stirbar was charged 1,4-bis(2-bromoethoxy)benzene 1 (0.50 g, 1.55 mmol) and 1-methylimidazole (0.51 g, 6.21 mmol) in THF (50 mL). This mixture was heated to reflux for 10 h. The resulting solution was poured into diethyl ether and the precipitate was collected by filtration. The reprecipitation process was repeated three times to afford white solid. White solid in methanol (20 mL), NH_4PF_6 (1.26 g, 7.75 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. The precipitate was collected by filtration to afford ligand 4 as white powder, 80% (0.77 g). Elemental Analysis: Calcd for C18H24F12N 4O2P2 C, 34.95; H, 3.88; N, 9.06. Found: C, 35.01; H, 3.79; N, 9.11. ^{1}H NMR (600 MHz, d_6-DMSO): δ = 9.16 (s, 2H), 7.79 (s, 2H), 7.71 (s, 2H), 6.90 (s, 4H), 4.55 (t, *J* = 4.8, 4H), 4.27 (t, *J* = 4.7, 4H), 3.87 (s, 6H) ppm. ^{13}C NMR (150 MHz, d_6-DMSO): δ = 152.7, 137.5, 124.0, 123.2, 116.1, 66.7, 49.0, 36.3 ppm.

Catalysis

General procedure for the Suzuki coupling reactions

In a typical run, a mixture of aryl bromide (0.50 mmol), phenylboronic acid (0.55 mmol), K_2CO_3 (1.5 mmol), 0.2 mol% ligand, 1 mol% $PdCl_2(CH_3CN)_2$ in 1.5 mL of ethanol were stirred at 50 °C for 1.5 h under air. Solvent ethanol was removed completely under vacuum degree 0.09 MPa at 45 °C to give a crude product. The pure product was isolated by column chromatography on silica.

*Diphenyl (**5a**)* White solid, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.4, 4H), 7.43 (t, *J* = 7.5, 4H), 7.34 (t, *J* = 7.4, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.2, 128.7, 127.2, 127.1 ppm.

*4-Methylbiphenyl (**5b**)* White solid, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51–7.50 (m, 2H), 7.42 (d, *J* = 8.1, 2H), 7.35 (dd, *J* = 5.7, 13.2, 2H), 7.25 (t, *J* = 7.4, 1H), 7.18–7.17 (m, 2H), 2.32 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 140.1, 137.3, 136.0, 128.4, 127.7, 126.0, 20.1 ppm.

*4-Chloro-1,1′-biphenyl (**5c**)* White solid; 99% yield (95 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48–7.47 (m, 2H), 7.45–7.44 (m, 2H), 7.38–7.37 (m, 2H), 7.34–7.33 (m, 2H), 7.29 (t, *J* = 7.4, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 127.9, 127.8, 127.3, 126.6, 126.0 ppm.

*4-Ethoxy-1,1′-biphenyl (**5d**)* White solid; 99% yield (100 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48 (td, *J* = 1.6, 8.1, 2H), 7.45–7.44 (m, 2H), 7.34 (dd, *J* = 5.0, 10.6, 2H), 7.24–7.21 (m, 1H), 6.90–6.89 (m, 2H), 4.01 (q, *J* = 7.0, 2H), 1.37 (dd, *J* = 4.5, 9.5, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.5, 139.9, 132.6, 127.7, 127.1, 125.7, 125.6, 113.7, 62.5, 13.9 ppm.

*4′-Chloro-4-Methylbiphenyl (**5e**)* White solid; 82% yield (83 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51–7.50 (m, 2H), 7.46–7.44 (m, 2H), 7.39–7.38 (m, 2H), 7.25 (d, *J* = 8.9, 2H), 2.39 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 139.6, 137.5, 137.1, 133.0, 129.6, 128.9, 128.2, 126.8, 21.1 ppm.

*4′-Methyl-4-ethoxy-1,1′-biphenyl (**5f**)* White solid; 97% yield (103 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50 (d,

$J = 8.5$, 2H), 7.45 (d, $J = 8.0$, 2H), 7.22 (d, $J = 7.8$, 2H), 6.95 (d, $J = 8.5$, 2H), 4.08–4.06 (m, 2H), 2.38 (s, 3H), 1.45–1.43 (m, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 158.3$, 138.0, 136.3, 133.6, 129.4, 127.9, 126.6, 114.7, 63.5, 21.1, 18.4 ppm.

4-Methoxybiphenyl ***(5g)*** White solid; 99% yield (90 mg). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.49$–7.45 (m, 4H), 7.34 (t, $J = 7.8$, 2H), 7.23–7.22 (m, 1H), 6.92–6.90 (m, 2H), 3.78 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 158.1$, 139.8, 132.8, 127.7, 127.1, 125.7, 125.6, 113.2, 54.3 ppm.

4′-Chloro-4-Methoxybiphenyl ***(5h)*** White solid; 90% yield (98 mg). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.50$–7.47 (m, 2H), 7.46–7.45 (m, 2H), 7.39–7.37 (m, 2H), 7.25 (d, $J = 8.9$, 2H), 2.39 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 139.6$, 137.5, 137.1, 133.0, 129.6, 128.9, 128.2, 126.8, 21.1 ppm.

4′-Methoxy-4-ethoxy-1,1′-biphenyl ***(5i)*** White solid; 63% yield (72 mg). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.40$ (t, $J = 8.0$, 4H), 6.89–6.87 (m, 4H), 4.00 (q, $J = 7.0$, 2H), 3.77 (s, 3H), 1.36 (t, $J = 7.0$, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 157.6$, 157.0, 132.5, 132.3, 131.2, 126.7, 113.7, 113.1, 62.5, 54.3, 13.9 ppm.

4-Nitrobiphenyl ***(5j)*** Yellow solid; 99% yield (100 mg). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.31$–8.30 (m, 2H), 7.75–7.74 (m, 2H), 7.64–7.62 (m, 2H), 7.52–7.50 (m, 2H), 7.46–7.44 (m, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 147.7$, 147.1, 138.8, 129.2, 128.9, 127.8, 127.4, 124.1 ppm.

4′-Chloro-4-Nitrobiphenyl ***(5k)*** Yellow solid; 95% yield (110 mg). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.31$–8.30 (m, 2H), 7.72–7.70 (m, 2H), 7.57–7.55 (m, 2H), 7.48–7.47 (m, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 146.3$, 145.3, 136.2, 134.3, 128.4, 127.6, 126.7, 123.2 ppm.

4′-Ethoxy-4-Nitrobiphenyl ***(5l)*** Yellow solid; 91% yield (111 mg). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.27$ (d, $J = 8.6$, 2H), 7.69 (d, $J = 8.7$, 2H), 7.57 (d, $J = 8.6$, 2H), 7.01 (d, $J = 8.6$, 2H), 4.10 (q, $J = 7.0$, 2H), 1.46 (t, $J = 7.0$, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.8$, 147.3, 146.5, 130.9, 128.6, 127.0, 124.1, 115.1, 63.7, 14.8 ppm.

4-Cyanobiphenyl ***(5m)*** White solid; 99% yield (90 mg). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.73$ (d, $J = 8.4$, 2H), 7.69 (d, $J = 8.3$, 2H), 7.59 (d, $J = 7.2$, 2H), 7.49 (t, $J = 7.6$, 2H), 7.43 (t, $J = 7.3$, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 145.7$, 139.2, 132.6, 129.1, 128.7, 127.8, 127.2, 119.0, 110.9 ppm.

4′-Chloro-4-cyanobiphenyl ***(5n)*** White solid; 96% yield (103 mg). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.73$ (d, $J = 8.4$, 2H), 7.65 (d, $J = 8.4$, 2H), 7.53–7.52 (m, 2H), 7.47–7.45 (m, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 144.4$, 137.6, 135.0, 132.7, 129.3, 128.5, 127.6, 118.8, 111.3 ppm.

4′-Ethoxy-4-cyanobiphenyl ***(5o)*** White solid; 92% yield (103 mg). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.69$ (d, $J = 8.2$, 2H), 7.64 (d, $J = 8.3$, 2H), 7.53 (d, $J = 8.6$, 2H), 6.99 (d, $J = 8.6$, 2H), 4.09 (q, $J = 7.0$, 2H), 1.45 (t, $J = 7.0$, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 159.6$, 145.3, 132.6, 131.3, 128.3, 127.1, 119.1, 115.1, 110.1, 63.6, 14.8 ppm.

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