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Highly Efficient Method for Suzuki Reactions in Aqueous Media

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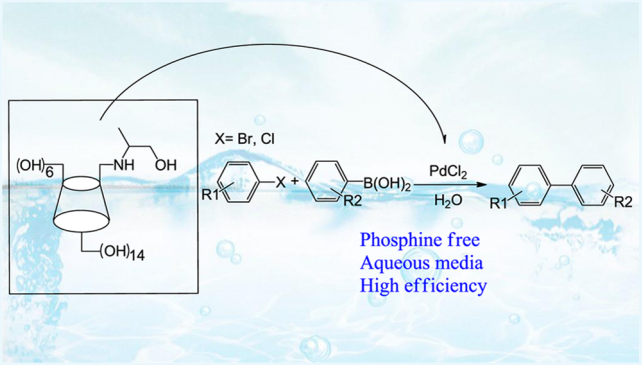
Supporting Information

ABSTRACT: Herein, we report the crystal structure and characterization of mono-6-(L-aminopropanol)-deoxy-β-cyclodextrin (L_n@β-CD). A highly efficient, in situ generated catalyst, $PdCl_2$(L_n@β-CD), was synthesized for palladium-catalyzed cross-coupling reactions under mild reaction conditions, and the use of this catalyst in Suzuki cross-couplings was investigated. Low palladium loadings of 0.01 mol % $PdCl_2$(L_n@β-CD) (Pd accounted for approximately 8.4% of the catalyst by mass) were found to be highly efficient for Suzuki cross-couplings in water and afforded the corresponding biaryl compounds in excellent yields. The catalyst can be recycled and reused.



INTRODUCTION

Over the past few decades, water-soluble catalysts have gained great interest for the development of novel catalysts for greener chemical processes and synthetic methods.[1−3] Water-soluble catalysts and ligands are widely utilized in organic reactions because of environmental and economical considerations.[4]

Cross-coupling has been established as a preferred method for generating C−C bonds in synthetic chemistry.[5] Palladium-catalyzed cross-coupling reactions are recognized as highly versatile tools for C−C bond formation.[6] Although Suzuki coupling reactions are among the most useful methods for the synthesis of carbon skeletons, there are still improvements that could be made to render this technique even more effective. It has also been demonstrated that the use of palladium phosphine species[3,7,8] is an excellent strategy for Suzuki couplings under very low palladium loadings. However, phosphine ligands are expensive, toxic, and usually hydrophobic and air-sensitive;[7] therefore, cross-coupling reactions under phosphine-free conditions are still an important challenge for researchers.[9−11] Recently, different phosphine-free ligands as diverse as N-heterocyclic carbenes,[12] diimines,[13] diamines,[14] and amides[15] have attracted considerable attention as competent ligands for Suzuki reactions.

Cyclodextrins (CDs) are good candidates for involvements in aqueous and reusable reactions.[16] They are also inexpensive and nontoxic. CDs are macrocyclic oligosaccharides possessing hydrophobic cavities and hydrophilic group,[17] and this allows them to be used in various applications. β-CD and its derivatives have been extensively used as catalysts in aqueous reactions as diverse as reduction,[18] hydrolysis,[19] oxidation,[20] and coupling reaction[21] because of their ability to solubilize hydrophobic compounds and their ability to recognize different molecules.[22] However, β-CD is poorly soluble in cold water; thus, chemical modifications[23] of β-CD are necessary to improve their selectivity and solubility. In addition, modified β-CDs, which are often highly soluble in water, can be easily separated from organic products.[24] Recently, Qi et al.[25] reported a palladium(II)−dipyrazole complex for Suzuki−Miyaura coupling reactions. Kaboudin et al.[26] have also reported a Pd(II)−β-cyclodextrin complex for Suzuki−Miyaura couplings in water. However, catalyst recycling was not possible and high catalyst loading was used in the reaction described in their reports.

In this article, we describe the synthesis and crystal structure of the L_n@β-CD ligand. Furthermore, we have developed an in situ-generated catalyst system (ligand + $PdCl_2$ in water) that is an excellent catalyst for aqueous Suzuki cross-coupling reactions. It has shown that $PdCl_2$(L_n@β-CD) (Scheme 1) is an excellent catalyst for Suzuki reactions. $PdCl_2$(L_n@β-CD) shows good performance parameters, such as a high efficiency, low toxicity, low required palladium loading (only 0.00084 wt %), and good recyclability, which should make it broadly applicable for future industrial processes.

RESULTS AND DISCUSSION

The in situ-generated catalyst system was prepared in three consecutive steps that are depicted in Scheme 1 by adopting L_n@β-CD as the ligand and $PdCl_2$ as the palladium source, which coordinated with each other in water. The structure of

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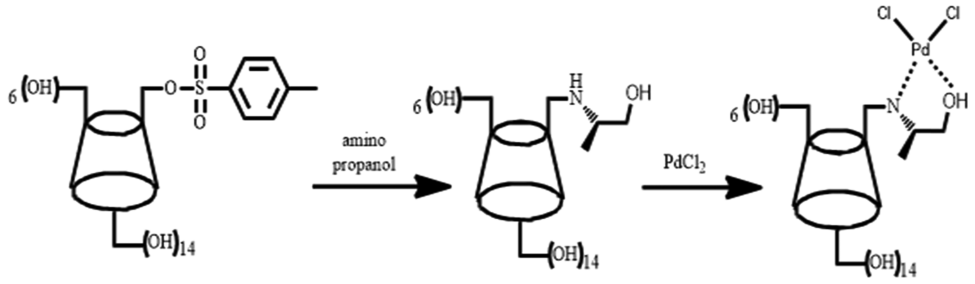
Scheme 1. Synthesis of L_n@β-CD·H_2O and $PdCl_2$(L_n@β-CD)



L_n@β-CD·H_2O was characterized by single-crystal X-ray crystallography (Figure 1).

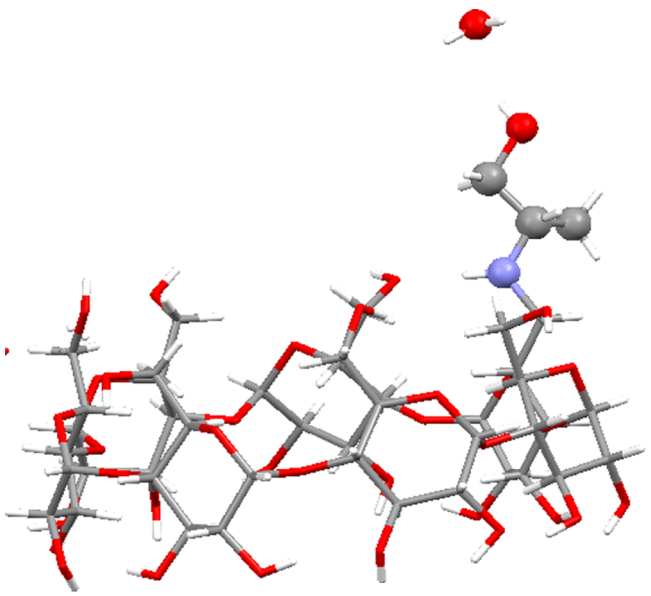


Figure 1. Single-crystal analysis of L_n@β-CD·H_2O.

The initial experiments with L_n@β-CD·H_2O revealed that it was poorly soluble in cold water; thus, we heated the solution containing the $PdCl_2$(L_n@β-CD) complex to 90 °C to obtain a clear solution. Electrospray ionization mass spectrometry (ESI-MS) is an important method for investigating complex formation in aqueous solutions. Figure S3 in the Supporting Information shows the experimental isotopic distribution for the peaks at m/z: 1391.36, which was assigned to $[M + Na]^+$, and m/z: 1356.38, which was assigned to $[M + Na - Cl]^+$. These results clearly confirm the binding between $PdCl_2$ and L_n@β-CD.

The catalytic behavior of the $PdCl_2$(L_n@β-CD) complex was studied in the Suzuki coupling reaction of aryl boronic acids with aryl halides in water. When the reaction was carried out using aryl bromides and the $PdCl_2$(L_n@β-CD) complex (0.01 mol %) for 4 h in water, the biaryl derivatives were obtained in isolated yields of 80−100% in the presence of K_3PO_4·$7H_2O$ as the base (Table 1, entries 1−15). The control experiments showed that without the $PdCl_2$(L_n@β-CD) complex, only a trace amount of the product was obtained (Table 1, entry 20). To further study the difference of the influences between the three ligands and β-CD, a comparative experiment (Table 1, entry 21) was conducted. The result showed that with only a trace amount of β-CD and palladium chloride, *p*-bromotoluene and phenylboronic acid as the substrates, only 6% of the coupling product was obtained. This may be because of the poor solubility and no coordination site of raw β-CD. The result clearly indicated the importance of our ligand.

As shown in Table 1, the heterocoupling of boronic acid derivatives with various aryl bromides gave the corresponding biaryl compounds in good to excellent yields, and only *o*-methyl bromobenzene gave a low yield (entries 4, 9, and 14). We think this is due to steric hinderance.

For the coupling reaction of 1-chloro aryl derivatives with phenylboronic acid (Table 1, entries 16−19), the catalytic activity of the $PdCl_2$(L_n@β-CD) complex at 0.01 mol % loading was not satisfactory and only 71% of the coupling product was obtained using *p*-nitrochlorobenzene (Table 1, entry 18) as the substrate. The yields with other substrates were very low under the same conditions. The optimal reaction conditions will be examined to determine the applicability of the present catalytic system in the Suzuki cross-couplings of various aryl chlorides with different aryl boronic acids in the next stage.

By screening different bases, including K_3PO_4·$7H_2O$, K_2CO_3, Li_2CO_3, Cs_2CO_3, $NaHCO_3$, and $KOC(CH_3)_3$ (Table 2), we found that K_3PO_4 and Li_2CO_3 were best when using the $PdCl_2$(L_n@β-CD) complex (0.01 mol %) for 4 h in water. For $KOC(CH_3)_3$, the yield was not satisfactory. This may be because of the poor solubility of $KOC(CH_3)_3$ in water.

Our next stage focused on the reaction temperature and catalyst loading. As seen from Table 3, the yield of coupling product decreased when the catalyst loadings were below 0.01 mmol %. Thus, the optimized reaction temperature was 90 °C. Under the above optimized catalyst loading levels, effects of temperature on the coupling yield and turnover number (TON) were noticeable. Below 10 °C, the TON for this reaction was limited to 5900. At 80 °C, a TON of 9.02×10^5 was observed. The yield of the coupling reaction decreases to 5% when the reaction temperature was decreased to 10 °C even if the amount of catalyst was 0.1 mol % (Table 3, entry 11). This may be because the L_n@β-CD ligand is poorly soluble in cold water and thus proper heating of the reaction system is necessary.

Remarkably, the PdL_n@β-CD catalyst showed highly efficient catalytic activity for Suzuki reactions, which afforded good to excellent yield with a high turnover number (TON) up to 3.1×10^6 (Table 3, entry 5).

From a green chemistry perspective, the focus is on the recycling of the metal catalysts. We verified that after the work up of the Suzuki coupling reaction of *p*-bromotoluene and phenylboronic acid as a model reaction, the aqueous phase can still catalyze the reaction with a fresh batch of substrates. The results obtained in our experiments confirmed that it was possible to recycle and reuse the catalyst complex at least six times after extraction of the products with ethyl ether without significant loss of catalytic activity (Table 4). Notably, catalyst

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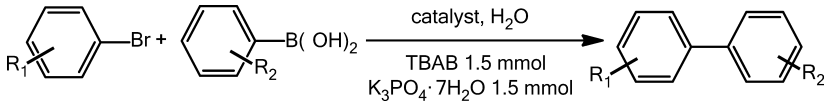
Table 1. $PdCl_2(L_n@\beta\text{-CD})$-Catalyzed Suzuki Couplings of Different Substrates[a]



entry	R_1	X	R_2	time (h)	yield (%)[b]
1	4-H	−Br	4-H	4	98
2	4-CH_3	−Br	4-H	4	100
3	4-OCH_3	−Br	4-H	4	94
4	2-CH_3	−Br	4-H	4	83
5	3-OCH_3	−Br	4-H	4	94
6	4-H	−Br	4-CH_3	4	100
7	4-CH_3	−Br	4-CH_3	4	92
8	4-OCH_3	−Br	4-CH_3	4	90
9	2-CH_3	−Br	4-CH_3	4	80
10	3-OCH_3	−Br	4-CH_3	4	96
11	4-H	−Br	4-OCH_3	4	100
12	4-CH_3	−Br	4-OCH_3	4	95
13	4-OCH_3	−Br	4-OCH_3	4	100
14	2-CH_3	−Br	4-OCH_3	4	88
15	3-OCH_3	−Br	4-OCH_3	4	97
16	4-CH_3	−Cl	4-H	12	4
17	2-CH_3	−Cl	4-H	12	3
18	4-NO_2	−Cl	4-H	12	71
19	4-OCH_3	−Cl	4-H	12	1
20[c]	4-CH_3	−Br	4-H	4	0.2
21[d]	4-CH_3	−Br	4-H	4	6

[a]Reaction conditions: arylhalides, 1 mmol; arylboronic acid, 1.5 mmol; in situ generated catalyst system, 100 μL; $K_3PO_4{\cdot}7H_2O$, 1.5 mmol; tetra-*n*-butylammonium bromide (TBAB), 1.5 mmol; H_2O, 2 mL; 90 °C. [b]Detected and analyzed by gas chromatography (GC) with biphenyl as an internal standard. [c]The reaction was conducted under ligandless conditions and with a trace amount of palladium chloride. [d]The reaction was conducted with a trace amount of β-CD and palladium chloride.

Table 2. Screening of Different Bases[a]

entry	cata. loading (mol %)	base	*T* (°C)	yield (%)[b]
1	0.01	$K_3PO_4{\cdot}7H_2O$	90	100
2	0.01	K_2CO_3	90	95.0
3	0.01	Li_2CO_3	reflux	99.0
4	0.01	Cs_2CO_3	reflux	80.5
5	0.01	$NaHCO_3$	90	91.5
6	0.01	$KOC(CH_3)_3$	90	70

[a]Reaction conditions: *p*-bromotoluene, 1 mmol; arylboronic acid, 1.5 mmol; $PdCl_2(L_n@\beta\text{-CD})$ complex, 0.01 mol %; TBAB, 1.5 mmol; H_2O, 2 mL; 4 h. [b]Detected and analyzed by GC with biphenyl as an internal standard.

Table 3. Effects of Reaction Temperature and Catalyst Loading[a]

entry	cata. (mol %)	*T* (°C)	yield (%)[b]	TON
1	0.02	90	100	500 000
2	0.01	90	100	1 000 000
3	0.008	90	99	1 237 500
4	0.005	90	95	1 900 000
5	0.003	100	93	3 100 000
6	0.01	90	100	1 000 000
7	0.01	80.0	90	902 000
8	0.01	60.0	65	655 000
9	0.01	40.0	15	158 000
10	0.01	rt	10	107 000
11	0.1	10.0	5	5900

[a]Reaction conditions: *p*-bromotoluene, 1 mmol; arylboronic acid, 1.5 mmol; in situ generated catalyst complex; $K_3PO_4{\cdot}7H_2O$, 1.5 mmol; TBAB, 1.5 mmol; H_2O, 2 mL; 4 h. [b]Detected and analyzed by GC with biphenyl as an internal standard.

decomposition to palladium black is not observed in the reaction, and $L_n@\beta$-CD was found to effectively stabilize the catalyst against decomposition and facilitate recycling.

CONCLUSIONS

In conclusion, we have demonstrated that $PdCl_2(L_n@\beta\text{-CD})$, a cheap, readily available, and highly stable catalyst complex, can be used to tolerate a wide variety of substrates in high yields from aqueous Suzuki coupling reactions in air. All reactions can be directly conducted in aqueous media. More importantly, the catalyst system can be recycled and reused several times without significant loss of catalytic activity. We herein presented an improved and generally applicable aqueous protocol for a range of substrates with broad functional group tolerance. Suzuki reactions can be performed under phosphine- and organic solvent-free conditions based on $PdCl_2$ and $L_n@\beta$-CD in water. Additionally, we demonstrated an exceedingly simple, economically convenient, and sustainable protocol for efficient Suzuki couplings. Explorations of reactions with 1-chloro aryl derivatives and phenylboronic acids as the coupling partners using the same method are currently underway.

EXPERIMENTAL SECTION

General Information. The NMR spectra were recorded on a Bruker-400 NMR spectrometer. DMSO-d_6 was used as a solvent. Chemical Shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal

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Table 4. Recyclability of the Catalytic System[a]

entry	time (h)	run	T (°C)	yield (%)
1	4	1st	100	96
2	4	2nd	100	90
3	4	3rd	100	88
4	4	4th	100	86
5	4	5th	100	81
6	4	6th	100	72

[a]Reaction conditions: *p*-bromotoluene, 1 mmol; arylboronic acid, 1.5 mmol; aqueous phase after the extraction of the coupled products; $K_3PO_4 \cdot 7H_2O$, 1.5 mmol; TBAB, 1.5 mmol; H_2O, 2 mL. [b]Detected and analyzed by GC with biphenyl as an internal standard.

standard. Crystal data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation (l = 0.71073 Å). Intensities were corrected for Lorentz and polarization effects and empirical absorption, and the data reduction was carried out using the SADABS program. The structure was solved by direct methods using SHELXS-97. ESI-MS was performed on Exactive Orbitrap produced by Thermofisher. Gas chromatography was performed on CP-3800 produced by Varian.

Materials. All reagents were used as received from commercial sources. L-Aminopropanol and mono-6-(*p*-tolylsulfonyl)-deoxy-β-CD were purchased from an online merchant without further purification. All reagents were weighed and handled in air.

Typical Procedure for the Synthesis of L_n@β-CD. All chemicals were purchased directly from commercial suppliers and were used without further purification. The L_n@β-CD ligand was obtained from a mixture of L-aminopropanol and mono-6-(*p*-tolylsulfonyl)-deoxy-β-CD. Mono-6-OTS-β-CD (0.7 g, 0.53 mmol) and L-aminopropanol (3.27 g, 43.4 mmol) were stirred at 80 °C for 8 h in air. Then, 1.5 mL of water was added into the mixture and it was washed three times with acetone to give a white solid. Single crystals suitable for X-ray measurements were obtained by recrystallization from water. The desired product was obtained in 82% yield based on mono-6-OTS-β-CD.

Typical Procedure for the Preparation of $PdCl_2$(L_n@β-CD). $PdCl_2$(L_n@β-CD) was formed in situ and was directly obtained in water by mixing mono-6-(L-aminopropanol)-deoxy-β-CD and palladium dichloride in 2:1 molar ratio. L_n@β-CD (0.040 g, 0.0334 mmol) was dissolved in H_2O (16.7 mL), and palladium dichloride (0.003 g, 0.0167 mmol) was added. The mixture was stirred for 20 min at 90 °C in air by refluxing.

Typical Procedure for the Suzuki Coupling Reaction. A Schlenk flask equipped with a magnetic stir bar was charged with aryl halide (1 mmol), phenylboronic acid (1.5 mmol), $PdCl_2$(L_n@β-CD) catalyst (100 μL of a solution prepared from 16.7 mL of the above in situ-synthesized catalyst system), base (1.5 mmol), TBAB (1.5 mmol), and water (2 mL). After completion of the reaction, the mixture was cooled to room temperature and then extracted with ethyl ether. The ethyl ether fraction was washed with 2 mol/L hydrochloric acid and water three times each, and then it was dried over anhydrous sodium sulfate. The resulting crude product was purified and isolated by column chromatography using 200−300 mesh silica gel to give the final product.

Mono 6-(L-Aminopropanol)-deoxy-β-CD (L_n@β-CD). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 5.81−5.68 (m, 14H, O(2) and O(3) of β-CD), 4.83 (s, 7H, C(1) of β-CD), 4.55−4.43 (s, 6H, O(6) of β-CD), 3.65−3.30 (m, 46H, overlaps with C(2)H, C(3)H, C(4)H, C(5)H, and C(6) of β-CD and H_2O), 3.17 (s, 2H, C(6′) of β-CD), 2.93−2.91 (d, 1H, −OH of aminopropanol), 2.75−2.72 (d, 1H, −CH of aminopropanol), 2.58−2.57 (d, 2H, $-CH_2$ of aminopropanol), 1.62 (s, 1H, −NH of aminopropanol), 0.89−0.88 (d, 3H, −CH3 of aminopropanol). ^{13}C NMR (400 MHz, DMSO-d_6): δ (ppm) = 102.35 (C1 of β-CD), 82.12 (C4 of β-CD), 73.5 (C3 of β-CD), 72.88 (C2 of β-CD), 72.50 (C5 of β-CD), 66.08 (C6′ of β-CD), 60.37 (C6 of β-CD), 54.86, 46.72, 17.52 (C of aminopropanol). Crystal data: $C_{45}NO_{35}H_{77}$, orthorhombic, P_{212121}, a = 13.1062(5) Å, b = 19.3742(9) Å, c = 27.0246(11) Å, α = 90°, β = 90°, γ = 90°, V = 6862.1(5) Å^3, Z = 4, ρ_{calcd} = 1.079, 64 180 reflections were collected, T = 289.03 K.

1-Methyl-2-(4-methylphenyl)benzene. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.358 (m, 8H, H of phenyl), 2.535 (s, 3H, H of $-CH_3$), 2.418 (s, 3H, H of $-CH_3$).

1-Methoxy-4-(2-methylphenyl)benzene. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.368−7.286 (m, 6H, H of phenyl), 7.065 (d, 2H, H of phenyl), 3.939 (s, 3H, H of $-OCH_3$), 2.388 (s, 3H, H of $-CH_3$).

2-Methylbiphenyl. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.458 (m, 2H, H of phenyl), 7.365 (m, 3H, H of phenyl), 7.286 (m, 4H, H of phenyl), 2.402 (s, 3H, H of $-CH_3$).

3-Methoxy-4′-methyl-1,1′-biphenyl. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.79−7.62 (m, 2H, H of phenyl), 7.60−7.58 (m, 1H, H of phenyl), 7.50−7.45 (m, 4H, H of phenyl), 7.16−7.13 (m, 1H, H of phenyl), 4.05 (s, 3H, H of $-OCH_3$), 2.65 (s, 3H, H of $-CH_3$).

3,4′-Dimethoxy-1,1′-biphenyl. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.67−7.65 (m, 2H, H of phenyl), 7.47−7.43 (m, 1H, H of phenyl), 7.30−7.29 (m, 2H, H of phenyl), 7.28−7.10 (m, 2H, H of phenyl), 7.08−6.97 (m, 1H, H of phenyl), 3.94−3.92 (d, 6H, H of $-OCH_3$).

4,4′-Dimethyl-1,1′-biphenyl. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.481−7.465 (d, 4H, H of phenyl), 7.237−7.221 (d, 4H, H of phenyl), 2.382 (s, 1H, H of $-CH_3$).

4-Methoxy-4′-methyl-1,1′-biphenyl. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.553−7.535 (d, 2H, H of phenyl), 7.491−7.475 (d, 2H, H of phenyl), 7.287−7.552 (m, 2H, H of phenyl), 7.008−6.991 (d, 2H, H of phenyl), 3.879 (s, 3H, H of $-OCH_3$), 2.417 (s, 3H, H of $-CH_3$).

4-Methyl-1,1′-biphenyl. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.668 (d, 2H, H of phenyl), 7.583 (d, 2H, H of phenyl), 7.516 (m, 2H, H of phenyl), 7.414 (m, 1H, H of phenyl), 7.349−7.333 (d, 2H, H of phenyl), 2.488 (s, 3H, H of $-CH_3$).

4-Methoxy-1,1′-biphenyl. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.552−7.523 (m, 4H, H of phenyl), 7.438−7.407 (m, 2H, H of phenyl), 7.326−7.293 (m, 1H, H of phenyl), 7.002−6.972 (m, 2H, H of phenyl), 3.858 (s, 3H, H of $-OCH_3$).

4-Nitro-1,1′-biphenyl. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 8.34−8.31 (d, 2H, H of phenyl), 7.78−7.76 (m, 2H, H of phenyl), 7.75−7.67 (d, 2H, H of phenyl), 7.66−7.48 (m, 3H, H of phenyl).

3-Methoxy-1,1′-biphenyl. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.82−7.80 (d, 2H, H of phenyl), 7.64−7.52 (m, 4H, H of phenyl), 7.41−7.37 (m, 2H, H of phenyl), 7.11−7.09 (m, 1H, H of phenyl), 4.00 (s, 3H, H of $-OCH_3$).

1,1′-Biphenyl. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) = 7.627−7.612 (d, 4H, H of phenyl), 7.481−7.450 (m, 4H, H of phenyl), 7.386−7.356 (m, 2H, H of phenyl).

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00469.

^{1}H NMR for all compounds and ESI-MS and ^{13}C NMR for some of the compounds (PDF)

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Author Contributions

F.J. conceived the project and wrote the paper; X.Z. performed the experiments and contributed references; X.G. and G.W. designed the experiments and analyzed the data; and all authors read and approved the final manuscript.

Notes

The authors declare no competing financial interest.

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