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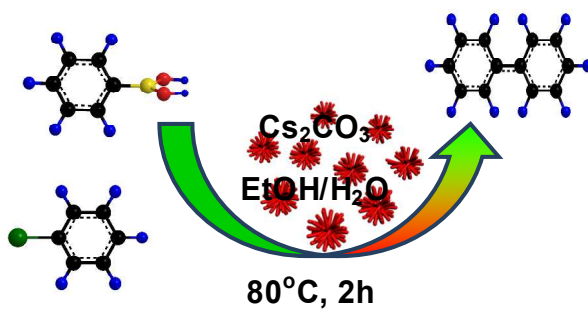
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Graphical Abstract



The Pd–Pt NDs were synthesized by a one-pot wet-chemical method, which showed enhanced catalytic activity toward Suzuki cross-coupling reaction.

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PAPER

Enhanced catalytic performance of Pd–Pt nanodendrites for ligand-free Suzuki cross-coupling reactions

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Pd–Pt nanodendrites were synthesized by a facile, environment-friendly, one-pot wet-chemical method, without using any seed, template, or toxic organic solvent. The as-obtained bimetallic nanocrystals exhibited efficient catalytic activity toward ligand-free Suzuki cross-coupling reaction in ethanol aqueous solution. And a series of biphenyl compounds were obtained with high yields under mild conditions. Furthermore, the catalyst can be easily recovered and reused at least 6 consecutive cycles, nearly without losing its catalytic activity.

Introduction

Palladium (Pd) is an excellent and all-purpose catalyst to a large number of reactions, such as carbon–carbon coupling,¹ alcohol oxidation,² olefin hydrogenation,³ and electrochemical formic acid oxidation,⁴ especially in carbon–carbon cross-coupling reactions.^{5, 6} However, catalytic reactions usually occur on the surface of a Pd catalyst.^{7–9} Thus, it becomes a huge challenge to take full advantages of Pd atoms and to reduce Pd usage without sacrificing the catalytic performance.

On the other hand, for promoting the reaction activity, these cross-coupling reactions are usually implemented with Pd catalyst along with phosphine ligands, which shows some shortcomings such as expensive, poisonous, and air sensitive.^{10–12} During the last decade, tremendous strategies have been proposed to enhance the performance of a catalyst without applying ligands for C–C cross coupling reactions.^{13–18} The usage of catalysts is much less at nano-scale level as compared to bulk materials, owing to their enlarged surface-to-volume ratio.^{19–21}

Recently, many efforts have been devoted to the synthesis of bimetallic nanomaterials because of their excellent catalytic activity and chemical/physical stability as respective to the monometallic counterparts.^{22–24} Particularly, Pt-based nanostructures have attracted significant research attention for their widespread potential applications deriving by their unique catalytic, electronic, and sensing properties.^{25–27}

Suzuki cross-coupling reaction, as a fascinating reaction for the formation of C–C bonds, plays a significant role in organic synthesis, due to its broad substrate scope, high level of functional group tolerance, and large turnover rates.^{11, 28–31} Therefore, it's highly indispensable to explore advanced Pd-based nanocatalysts.

Herein, we investigated the catalytic performance of Pd catalysts through alloying with Pt to form Pd–Pt alloyed nanodendrites (denoted as Pd–Pt NDs) by a facile modified wet-chemical method for Suzuki cross-coupling reaction, without

using any ligand. The catalytic activity of Pd–Pt NDs for the Suzuki cross-coupling reaction was investigated by changing the solvents, dosages of the catalyst, bases, reaction time and temperature.

Experimental

Materials

Phenylboronic acid (98 wt.%), chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), palladium chloride (PdCl_2), polyvinyl pyrrolidone (PVP, MW = 58 000), urea, hydrazine hydrate (80 wt.%), commercial Pd black and Pt black were purchased from Shanghai Aladdin Chemical Reagent Company (Shanghai, China). All the solvents (ethanol, toluene, acetone, acetonitrile, dimethyl formamide (DMF)), and other chemicals were of analytical grade and used without further purification.

Synthesis and characterization of Pd–Pt NDs

Pd–Pt NDs were prepared by a modified method as a previous work.³² Typically, 4 mL of 100 mM PdCl_2 , 20.6 mL of 38.6 mM $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, and 0.06 g urea were dissolved into 40 mL of 0.25 wt.% PVP solution under stirring. Then, the pH of the mixture was adjusted to 12 with freshly-prepared 0.1 M NaOH, and put into an ice-bath under stirring. After the addition of 400 μL hydrazine hydrate (16.5 M), the mixture promptly turned black and the reaction was continued for 1 h. Finally, the product was collected by centrifugation and washed several times with ethanol and water, and dried at 60 °C under vacuum for further use.

The morphology, composition, and elemental distribution of the samples were recorded by transmission electron microscopy (TEM), high resolution TEM (HRTEM), X-ray energy dispersive spectra (EDS), and EDS line scanning profiles on a JEM–2100F HR transmission electron microscope coupled with an energy-dispersive X-ray spectrometer (Oxford–INCA). X-ray diffraction (XRD) analysis was performed on a Bruker–D8–AXS diffractometer system equipped with Cu K α radiation (Bruker Co., Germany).

Catalytic measurements for Suzuki cross-coupling reactions

Suzuki–Miyaura cross-coupling reactions were conducted as follows: a mixture of aryl halides (0.5 mmol, 1 equiv), phenylboronic acid (0.6 mmol, 1.2 equiv), Cs₂CO₃ (0.6 mmol, 1.2 equiv), Pd–Pt NDs (4 mg), 2 mL of ethanol (EtOH) and water (v/v = 1/1) were put into in a Schlenk tube (10 mL), and then the mixture was stirred for desired time at 80 °C under air atmosphere. The reaction was monitored by thin layer chromatography (TLC). Afterward, the reaction mixture was cooled to room temperature. And the catalyst was recovered by filtration, and washed thoroughly with ethyl acetate and water. The combined organic layer was dried by Na₂SO₄, and the filtered residue was purified by flash column chromatography on silica gel. All the relevant experiments were performed in the sealed Schlenk tube under air atmosphere unless otherwise stated.

Results and discussion

Characterization of Pd–Pt NDs

As illustrated by the TEM images (Figure 1A, B), the as-prepared nanocrystals are dendrites in shape, containing several subunits and substantially uniform in size. The formation of Pd–Pt NDs is based on a speedy nucleation and particle attachment growth.³³ Firstly, the abundant Pt and Pd atoms grow into nuclei via the self-aggregation process to minimize the total surface free energy of the system. Then, with the co-directing effects by PVP and urea, the nuclei are self-organized by twinning and imperfectly oriented attachment to form dendritic nanostructures.^{32, 34}

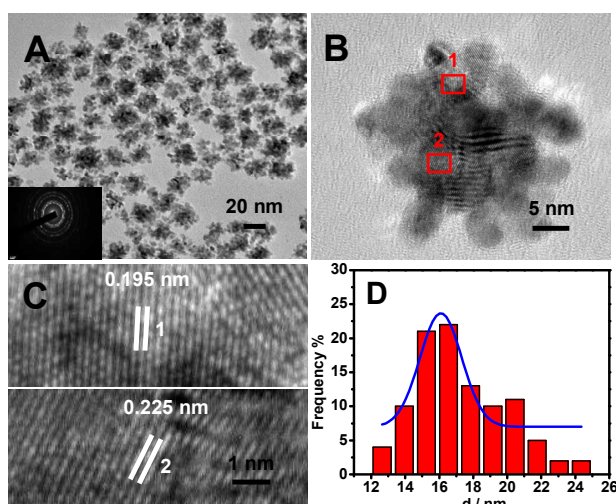


Figure 1. TEM image (A), and HRTEM images (B, C) of Pd–Pt NDs. The corresponding particle size distribution pattern (D).

The selected-area electron diffraction (SAED) pattern demonstrates polycrystalline nature of Pd–Pt NDs (inset in Figure 1A).³⁵ Besides, HRTEM images (Figure 1B, C) display well-defined lattice fringes with lattice spacing distances of ca. 0.195 and 0.225 nm from the marked square areas in an individual Pd–Pt nanodendrite, which are well assigned to the (200) and (111)

planes of the face-centered cubic (fcc) Pd–Pt alloy, respectively, as supported by the SAED data.^{36, 37} Besides, the nanoparticle size of Pd–Pt NDs is narrowly distributed from 12 to 24 nm, with a mean size of 17 nm (Figure 1D).

The XRD pattern was performed to investigate the compositions and crystal structures of Pd–Pt NDs (Figure 2A). It exhibits four representative diffraction peaks located at 39.9°, 46.4°, 68.0°, and 81.7°, which are well attributed to the (111), (200), (220), and (311) planes of the fcc Pd–Pt alloy, respectively. Meanwhile, these diffraction peaks are precisely situated between pure Pd (JCPDS–46–1043 Pd) and Pt (JCPDS–04–0802 Pt), convincingly showing the formation of the alloyed Pd–Pt nanocrystals.³⁸

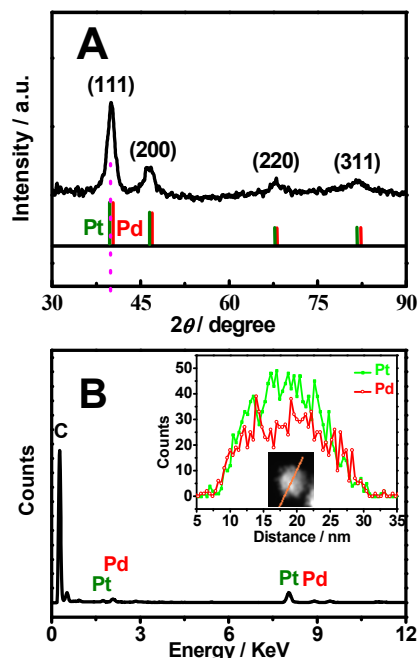


Figure 2. XRD pattern (A) and EDX spectrum (B) of Pd–Pt NDs. Insets show HAADF-STEM image and line scanning profiles of Pd–Pt NDs.

More importantly, the EDS line scanning profiles were provided to confirm the elemental distribution of Pd and Pt in Pd–Pt NDs (Inset in Figure 2A). It reveals homogeneous distribution of Pd and Pt throughout an intact Pd–Pt nanodendrite, further confirming the formation of Pd–Pt alloy. Moreover, the atomic ratio of Pd to Pt is estimated to be 1:1, which agrees well with the initial ratio of the precursors ([PdCl₂]:[H₂PtCl₆] = 1:1), as strongly supported by the EDS data (Figure 2B), reflecting the efficient reduction of Pd and Pt precursors in the present work.³⁹ The highly branched nanostructures and the well-dispersed nature of Pd–Pt NDs are expected to show high catalytic activity for practical catalysis reactions.

Catalytic activity of Pd–Pt NDs for Suzuki cross-coupling reaction

Suzuki cross-coupling reaction is one of the most powerful methods for the C–C bond formation.^{6, 40} Pd-catalyzed Suzuki cross-coupling reaction is extensively applied for the preparation of biaryl compounds in organic synthesis, which are pivotal intermediate products in pharmaceuticals, herbicides, and natural

products, as well as in engineering materials.⁴¹⁻⁴³ Figure 3 depicts the general process of the ligand-free Suzuki reaction, which mainly involves three steps:⁴⁴ (i) the oxidative addition of palladium(0) with halide to form organopalladium species, (ii) the coupling of organopalladium species with base to yield palladium complex by transmetalation, and (iii) the reductive elimination of the palladium complex to obtain desired product.⁴⁵

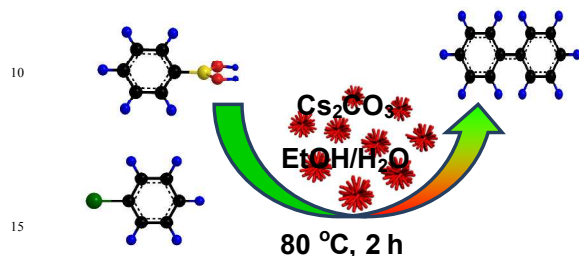


Figure 3. Schematic illustration for the Suzuki cross-coupling reaction catalyzed by Pd–Pt NDs.

The catalytic activity of Pd–Pt NDs was examined by the Suzuki cross-coupling reaction through the variation of solvents, dosages of the catalyst, bases, reaction time and temperature. The corresponding procedure for the Suzuki cross-coupling reactions, relevant physical properties, copies of ¹H and ¹³C NMR spectra and mass analysis data for the products were provided in Electronic Supplementary Information (ESI).

Table 1 Optimization of the conditions for the Suzuki cross-coupling reaction of bomobenzene with phenylboronic acid.

Entry	Solvents	Bases	Temp. (°C)	Time (h)	Yield (%) ^b
1	Ethanol/H ₂ O ^c	Cs ₂ CO ₃	80	2	98
2	Ethanol	Cs ₂ CO ₃	80	2	83
3	Toluene	Cs ₂ CO ₃	80	2	79
4	DMF	Cs ₂ CO ₃	80	2	85
5	Acetone	Cs ₂ CO ₃	80	2	90
6	Acetonitrile	Cs ₂ CO ₃	80	2	78 ³⁵
7	H ₂ O	Cs ₂ CO ₃	80	2	82
8	Ethanol/H ₂ O ^c	Na ₂ CO ₃	80	2	86
9	Ethanol/H ₂ O ^c	K ₂ CO ₃	80	2	95
10	Ethanol/H ₂ O ^c	NaOH	80	2	91
11	Ethanol/H ₂ O ^c	NaHCO ₃	80	2	82 ₄₀
12	Ethanol/H ₂ O ^c	Et ₃ N	80	2	84
13	Ethanol/H ₂ O ^c	NaOBu-t	80	2	92
14	Ethanol/H ₂ O ^c	NaOAc	80	2	87
15	Ethanol/H ₂ O ^c	Cs ₂ CO ₃	25	2	trace
16	Ethanol/H ₂ O ^c	Cs ₂ CO ₃	40	2	24 ⁴⁵
17	Ethanol/H ₂ O ^d	Cs ₂ CO ₃	60	2	32
18	Ethanol/H ₂ O ^e	Cs ₂ CO ₃	80	2	54
19	Ethanol/H ₂ O ^e	Cs ₂ CO ₃	80	2	98
20	Ethanol/H ₂ O ^e	Cs ₂ CO ₃	80	0.5	22 ⁵⁰
21	Ethanol/H ₂ O ^e	Cs ₂ CO ₃	80	1	52
22	Ethanol/H ₂ O ^e	Cs ₂ CO ₃	80	1.5	86

^a Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), catalyst (Pd–Pt NDs, 4 mg).

^b Isolated yields.

^c Ethanol/H₂O=1:1.

Firstly, different solvents were investigated (Table 1, entries 1–8). It can be observed that EtOH/H₂O (1:1) is the best candidates, possibly due to the good dispersion of reactants in EtOH and high solubility of bases in water to activate arylboronic acid and subsequently facilitate the reaction rate.⁴⁶ Meanwhile, Cs₂CO₃ is found to be the most effective base for the Suzuki cross-coupling reaction (Table 1, entries 9–14) via the screened measurements under the identical conditions among those of Et₃N, K₂CO₃ and other bases. Therefore, Cs₂CO₃ was ultimately chosen as the base for this system.⁴⁷

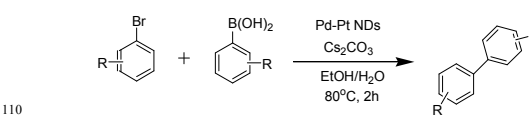
Next, the influence of Pd–Pt NDs with different dosages was explored in the control experiments. As shown in Table 1 (entry 1), the Suzuki cross-coupling reaction with 4 mg of the catalyst and Cs₂CO₃ as a base at 80 °C for 2 h in EtOH/H₂O (1:1) affords the maximum yield of 98%. When the reaction time, temperature, and dosage of the catalyst are decreased, the corresponding yields are remarkably reduced (Table 1, entries 15–22). These results indicate that 4 mg of the catalyst displays the best catalytic activity in the present work.

Under the optimized reaction conditions, we explored the general applicability of Pd–Pt NDs to the coupling of different aryl halides and arylboronic acids. It is known that aryl halides and arylboronic acids have different electronic and steric properties.⁴⁸ As displayed in Table 2, the presence of aryl chlorides gives moderate yields of the coupling products (Table 2, entries 3, 10), while bromobenzene and iodobenzene have the high yield of 98% among the non-substituted aryl halides (Table 2, entry 1, 2). These results are in good agreement with those in the literature, because the activation of C–Cl bond is much more difficult than those of C–Br and C–I bonds.^{49, 50}

It's important to note that aryl bromides and iodides with electron-donating groups such as CH₃ and OCH₃ show good yields above 90% (Table 2, entries 4–6, 8, 11, 13). However, substituting aryl halides with electron-withdrawing groups display slightly lower reactivity as compared to those containing electron-donating or neutral groups, owing to the nucleophilicity effects of the substituents on the arylboronic acid (Table 2, entries 7, 9, 12, 18, 19).⁵¹

Besides, *para*-bromoanisole gives the highest productivity, followed by *meta*-bromoanisole and *ortho*-bromoanisole with the decreased yield under the same conditions (Table 2, entries 4–6). This is due to different steric hindrance effects of the reactants.⁵² Specifically, the reactivity of mono-substituted aryl halides in this reaction is followed the sequence: *para* > *meta* > *ortho*.⁵³

Table 2 Suzuki cross-coupling reactions of aryl halides with arylboronic acids catalyzed by Pd–Pt NDs.



Entry	Aryl halide	Arylboronic acid	Products	Time (h)	Yield (%) ^a
1				2	98
5				2	98
3				2	76
10				2	90
5				2	94
15				2	98
7				2	89
20				2	86
9				2	82
25				4	78
11				2	95
30				2	83
13				2	98
35				2	98
14				2	98
15				2	96
40				2	94
16				2	94
17				2	91
45				2	91
18				2	84
50				2	87
19				2	87
55				2	74
20				2	74
21			24	N.R.

N.R.: No reaction.

a. Isolated yields.

Next, arylboronic acids with electron-donating and electron-withdrawing groups were also employed. Clearly, the arylboronic acids with electron-donating groups (such as CH₃ and OCH₃, Table 2, entries 14–17) exhibit higher reaction activity than the arylboronic acids with electron-withdrawing groups (such as Cl and F, Table 2, entries 18, 19). And the substitution pattern of arylboronic acid also agrees well with the above substituting aryl halides (Table 2, entries 14–16). A more sterically hindered double substitution in ortho positions of arylboronic acid was also tolerated in this reaction condition, albeit with a slightly lower yield of 74% (Table 2, entry 20). It is a pity that nearly no product is obtained for alkyl bromides with phenylboronic acid by prolonging the reaction even to 24 h (Table 2, entry 21). Thus, a variety of aryl halides, including sterically hindered, electron-donating, and electron-withdrawing aryl halides, have been successfully coupled in the present work.

The catalytic activity of Pd–Pt NDs was further compared with commercial Pd black and Pt black under the identical reaction conditions for the Suzuki cross-coupling reaction. Obviously, Pd–Pt NDs show better catalytic activity than Pd black and Pt black, which display the yield with 62 % and trace (Table 3, entries 2, 3), respectively. The results demonstrate that Pt is poor in catalyzing Suzuki cross coupling reaction, while its introduction into Pd–Pt NDs leads to the improved catalytic activity, possibly resulting from the variation of Pd electronic structures and the distinct nanodendrites feature of Pd–Pt NDs.⁵⁴ This result further reflects the improved catalytic activity of Pd–Pt NDs toward Suzuki cross-coupling reaction.

Table 3 The catalytic activity comparison of different catalysts in the Suzuki cross-coupling reaction.

Entry	Catalysts	Reaction conditions	Yield (%)	Ref.
1	Pd–Pt NDs	Cs ₂ CO ₃ , EtOH–H ₂ O, 4 mg catalyst, 80 °C, 2 h	98	This work
2	Pd black	Cs ₂ CO ₃ , EtOH–H ₂ O, 4 mg catalyst, 80 °C, 2 h	62	This work
3	Pt black	Cs ₂ CO ₃ , EtOH–H ₂ O, 8 mg catalyst, 80 °C, 2 h	trace	This work
4	Pd–Fe ₃ O ₄	Na ₂ CO ₃ , DMF–H ₂ O, 1 mol% catalysts, reflux, 24 h	70	55
5	Pd–Fe ₃ O ₄ @C	K ₂ CO ₃ , EtOH, 2 mg catalyst, 60 °C, 2 h	99	56
6	Pd/COF–LZUI	K ₂ CO ₃ , p-xylene, 0.5 mol% catalyst, 150 °C, 3 h	97	57
7	Pd–Ni ₂ O/ROGO	NaOH, EtOH–H ₂ O, 45 °C, 3 h	99	58
8	NAP–Mg–Pd(0)	K ₂ CO ₃ , Water, 0.5 mol% catalyst, r.t., 6 h	92	59
9	Pd–Co/Graphene	Na ₂ CO ₃ , EtOH–H ₂ O, 4 mol% catalyst, argon, 80 °C	76	60
10	Pd–CoFe ₂ O ₄ MNPs	Na ₂ CO ₃ , EtOH, 2 mg catalyst, reflux, 12 h	79	61
11	Pd@meso-SiO ₂	K ₂ CO ₃ , EtOH, 10 mg catalyst, 80 °C, 3 h	32.4	62

Additionally, we compared our results with those of magnetically reused Pd-based nano-catalysts for catalyzing the Suzuki cross-coupling reaction between bromobenzene and phenylboronic reported in the literature (Table 3, entries 4–11).^{55–62} Evidently, the Suzuki cross-coupling reaction catalyzed by Pd–Pt NDs owns the advantages such as facile preparation, mild reaction conditions, easy separation, and good stability, unlike some of the referenced work involved harsh reaction conditions (e.g., high reaction temperature,⁵⁷ long reaction time,^{55, 56} anaerobic,^{55, 60} and toxic solvents^{55, 57}). These results verify the enhanced catalytic activity of Pd–Pt NDs, making it a promising catalyst for promising applications in organic synthesis.

Catalyst reusability

The recovering and reusing of a catalyst are important to the coupling reactions. In order to test the recycling of Pd–Pt NDs, the Suzuki cross-coupling reaction between bromobenzene and phenylboronic acid was selected as a model system. After completion of the reaction, the catalyst was recovered by filtration and washed thoroughly with ethyl acetate and water, followed by drying in oven at 60 °C for the next cycles. The results demonstrate that Pd–Pt NDs can be recycled for at least 6 times, without any obvious loss of yield, affirming high stability of Pd–Pt NDs under the present conditions (Figure 4).

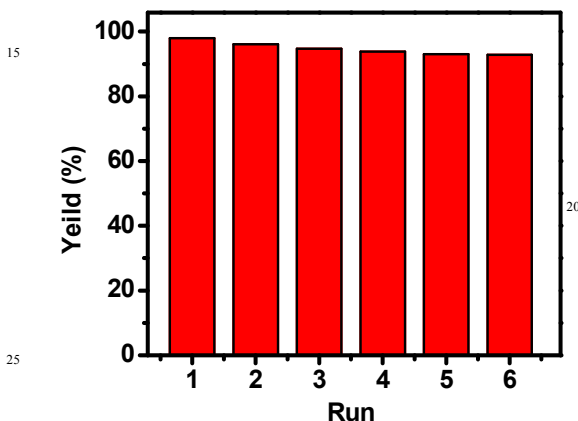


Figure 4. The recycling of Pd–Pt NDs for the Suzuki cross-coupling reaction.

The improved catalytic activity and better stability of Pd–Pt NDs is attributed to the unique dendritic nanostructures of Pd–Pt NDs to provide more active sites available for organic reactions.⁶³ Besides, the presence of Pt plays a significant role to enhance the shape stability, probably resulting from the higher energy barrier to reconstruct the surface structure induced by the incorporation of inert Pt on the surfaces of Pd–Pt NDs.^{64, 65}

Conclusions

In summary, a facile recyclable Pd–Pt NDs was firstly used for the Suzuki cross-coupling reaction under mild conditions. The hybrid nanocrystals showed high catalytic activity, long-term stability, which could be readily recovered and reused for at least 6 cycles, without any obvious loss of the catalytic activity. These results proved a promising alternative approach for synthesis of biphenyl compounds. Further work is in progress to broaden the scope of this catalytic system for other organic conversion.

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Notes and references

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