Introduction

Biaryls have been widely applied in the syntheses of natural products, polyaromatic molecules, and pharmaceuticals. Transition-metal (TM) catalyzed cross-coupling reactions are very powerful tools for constructing such structural units. However, various issues remain, including high costs and the poor stability of many TM catalysts and ligands, and the necessity of disposal of heavy-metal residues. Transition-metal-free (TM-free) cross-coupling methods have attracted significant attention in recent years.

Phenol derivatives have some advantages: (1) phenol derivatives are easily available and are less expensive than the corresponding halides; (2) the use of halides, which pollute the environment is avoided; and (3) phenol derivatives can exhibit orthogonal reactivity to organohalides. There are many known methods for cross-coupling phenols derivatives. However, no examples utilize simple phenol derivatives (e.g. pivalate esters, sulfonates, carbamates, and sulfamates) for cross-coupling by SET processes. Organozinc reagents have emerged as attractive candidates due to their easy preparation and high functional group tolerance in cross-coupling reactions for the construction of biaryl and aryl–vinyl structural scaffolds.

Herein, we report the first cross-coupling reactions of phenol derivatives with arylzinc reagents to construct C–C bonds under SET-catalyzed cross-coupling reaction conditions.

Results and discussion

We started our investigation by utilizing phenyl pivalate ester 1a as a model substrate. The desired biaryl 3a was not obtained using 1 equiv. of the 4-methoxyphenylzinc reagent prepared from the corresponding arylmagnesium bromide and zinc bromide (Table 1, entry 1).
utilized to prepare the arylzinc reagent is crucial for smooth conversion.

No matter if 1 or 2 equiv. of the arylmagnesium bromide is mixed with 1 equiv. of zinc bromide (Table 1, entries 2 and 3), the reaction was very poor. The reaction yield was improved slightly by adding 1 equiv. of lithium chloride (Table 1, entries 4 and 5); however, the reaction proceeded sparingly or not at all when lithium bromide or magnesium bromide were added (Table 1, entries 6 and 7). The yield reached 46% using 2 equiv. of lithium chloride (Table 1, entry 8), but the yield did not increase significantly when 3 equiv. of lithium chloride were added (Table 1, entry 9).

Under the same conditions as those in entry 9, microwave (MW) heating led to a yield of 68% (Table 1, entry 10). Actually, the arylzinc iodide/lithium chloride complex reported by Knochel27 gave lower yields of the product, even in the presence of an external magnesium salt (Table 1, entries 11 and 12). The use of N,N-dimethylacetamide (DMA), PrO, and 1,4-dioxane as solvents were demonstrated to be of no effect (Table 1, entries 13, 15, and 16). When N,N-dimethylformamide (DMF) was used, a yield of 5% was obtained (Table 1, entry 17). The use of 1-methylpyrrolidin-2-one (NMP), 2-Me-Tetrahydrofuran (THF), diglyme, and toluene led to the desired product, and 2-Me-THF gave the highest yield (Table 1, entries 14 and 18–20). Mixtures (1:1) of 2-Me-THF/toluene, 2-Me-THF/NMP, or 2-Me-THF/diglyme behaved better than a single solvent, with 2-Me-THF/NMP (1:1) leading to the highest yield (Table 1, entries 21–23). The reaction yield did not increase on extending the reaction time, with only 0.5 h being required to obtain the highest yield (Table 1, entries 24–26). When the reaction was run at 80 °C, a 93% yield was achieved. A reaction temperature higher than 80 °C did not further improve the yield, while a temperature lower than 80 °C led to a decrease in the yield (Table 1, entries 25, 27, and 28). However, conventional heating led, under the same conditions, to a yield of only 25% (Table 1, entry 29).

With promising results in hand, we next tested the analogous cross-coupling of several other electrophilic partners (Table 2). In addition to the aryl pivalate ester (Table 2, entry 1), the corresponding carbamate and sulfamate were deemed competent substrates (Table 2, entries 2 and 3). Furthermore, sulfonate derivatives of phenol also gave high yields of the coupled product (Table 2, entries 4–6), and aryl sulfonates (in particular, tosylates) were relatively unreactive compared to triflates; however, tosylates were more easily handled, stable and considerably less expensive than aryl triflates. Moreover, the use of a phenyl methyl ether did not lead to the desired product under our optimized conditions (Table 2, entry 7).

Having identified optimized reaction conditions (Table 1, entry 25), we next investigated the scope of the substrates (Table 3). Aryl pivalates/tosylates containing electron-donating groups were efficiently coupled to provide the corresponding biaryl products in good to excellent yields (Table 3, entries 3b, 3c, 3d, and 3e), with the ortho methyl-substituted aryl pivalates/tosylates giving lower yields compared to their meta- and para-substituted analogues. More sterically hindered 2,6-xylyl pivalate underwent the reaction with 2a to afford 3g in 49% yield (Table 3, entry 3g); however, 2,6-xylyl triflate gave a more satisfactory yield under the same conditions. Aryl pivalates/tosylates containing electron-withdrawing groups (Table 3, entries 3i, 3j, and 3k) and naphthyl pivalates/tosylates (Table 3, entry 3l) were efficiently coupled to provide the corresponding biaryl products in excellent isolated yields. It is worth mentioning that an aryl triflate containing chloride reacted with 2a occurred efficiently, with the potentially reactive C–Cl bond untouched (Table 3, entry 3k), p-Bromophenyl pivalate reacted with 2a to give product 3l in 35% yield (Table 3, entry 3l) along with 1,4-bis(4-methoxyphenyl)benzene (16%) as a by-product. Various sensitive functional groups, including unprotected phenol (Table 3, entry 3h), ester (Table 3, entries 3n and 3o), and amide (Table 3, entry 3m) groups were well tolerated. N-Methylindolyl and pyridyl pivalates/tosylates also gave good yields of the expected products (Table 3, entries 3p and 3q).

We further inspected the reactivity of different zinc reagents (Table 4). Both electron-rich and electron-deficient (het)aryl zinc reagents (Table 4, entries 3r, 3s, 3t, 3u, 3v, 3w, 3ae) were smoothly participated in the cross-coupling. Compared with 3w, the reaction of 3v was not sensitive to the steric hindrance of (het)aryl zinc reagents. Heteroaryl zinc reagents were efficiently coupled with aryl pivalates/tosylates in excellent yields (Table 4, entries 3i, 3x, 3y, 3z, 3af, 3ah, 3aj, and 3ak). A variety of functional groups was also compatible under these reaction conditions, including nitrile, ketone, amide, and ester (Table 4, entries 3aa, 3ab, 3ae, 3ad, and 3ai). It is worth noting that an easily enolizable ketone (Table 4, entry 3ah) was well tolerated, and no notable byproducts resulting from the addition of Grignard reagents to these groups were found.

The SET-catalyzed cross-coupling reactions are more sensitive to steric hindrance. However, the promising results obtained for para- and meta-substituted aryl pivalates/tosylates render this system a new and useful tool in SET-catalyzed cross-coupling reactions. For instance, under these conditions, the selective one-pot synthesis of disubstituted phenol sulfonates gave unsymmetrically substituted terphenyl compounds in satisfactory yields (Scheme 1).

In Hayashi’s report,28 the occurrence of SET initiation in the coupling of aryl Grignard reagents with aryl halides was confirmed by the observation that the addition of lithium 4,4-di-tert-butylphenylide (LDBB) drastically accelerated the coupling. This result may be rationally understood by inferring that LDBB works as an easily enolizable ketone (Table 4, entry 3ah) was well tolerated, and no notable byproducts resulting from the addition of Grignard reagents to these groups were found.

The SET-catalyzed cross-coupling reactions are more sensitive to steric hindrance. However, the promising results obtained for para- and meta-substituted aryl pivalates/tosylates render this system a new and useful tool in SET-catalyzed cross-coupling reactions. For instance, under these conditions, the selective one-pot synthesis of disubstituted phenol sulfonates gave unsymmetrically substituted terphenyl compounds in satisfactory yields (Scheme 1).

In Hayashi’s report,28 the occurrence of SET initiation in the coupling of aryl Grignard reagents with aryl halides was confirmed by the observation that the addition of lithium 4,4-di-tert-butylphenylide (LDBB) drastically accelerated the coupling. This result may be rationally understood by inferring that LDBB works as a much more efficient single-electron donor than Grignard reagents in the slow initiation step, and thus, the overall reaction rate is increased. We conducted similar experiments on the arylzinc coupling using LDBB as a single-electron donor. The reactivity of PhOPiv (1a) toward (4-MeOC,H,)_2Zn 2a was quite low at 50 °C over 30 min, when giving only a 45% yield of the coupling product 3a (Scheme 2). By contrast, treatment of 1a with LDBB (0.2 equiv.) gave 3a in 54% yield. The observed acceleration is compatible with SET initiation, and it is likely that [PhOPiv]−, generated by SET, has a lifetime long enough to react with 1a before undergoing decomposition to Ph−.29,30,31
Considering the above result in conjunction with similarities in the intrinsic character between arylzinc and arylmagnesium reagents, the present coupling reaction likely follows a Grignard cross-coupling mechanism\textsuperscript{2,4,32–34} as shown in Scheme 3, and exemplified by the reaction of PhOPiv\textsuperscript{1a} with (4-MeOC\textsubscript{6}H\textsubscript{4})\textsubscript{2}Zn\textsuperscript{2a}. The reaction is initiated by SET from (4-MeOC\textsubscript{6}H\textsubscript{4})\textsubscript{2}Zn to PhOPiv to give the anion radical [PhOPiv]•\textsuperscript{−}, which reacts with (4-MeOC\textsubscript{6}H\textsubscript{4})\textsubscript{2}Zn. SET from the resulting anion radical, [4-MeOC\textsubscript{6}H\textsubscript{4}-Ph]•\textsuperscript{−}, to PhOPiv gives the coupling product 4-MeOC\textsubscript{6}H\textsubscript{4}-Ph and regenerates [PhOPiv]•\textsuperscript{−}, thereby beginning another propagation cycle.

**Conclusion**

The reactions of (het)aryl pivalates/tosylates with di(het)arylzincs gave biaryl compounds in short reaction times under microwave irradiation. The reaction is suitable for a broad scope of substrates and exhibits good functional group compatibility. This reaction is applicable to simple hydroxybenzenes that are widely distributed in nature. No catalyst or ligand is required, and a simple work-up procedure is employed. The reaction is believed to occur via a SET mechanism for activation of the aryl pivalates.

**Experimental**

**General information**

The reactions were carried out at 50–80 W in a CEM Discover (0–600 W, 2450M) focused microwave reactor equipped with a pressure controller under isothermal conditions. Standard 5 mL glass reaction vessels were used as supplied with the CEM reactor. The reaction mixtures were

| Entry | Organic zinc reagent | Solvent | Time (h) | Temperature (°C) | Mode of heating\textsuperscript{a} | Yield\textsuperscript{c} |
|-------|----------------------|---------|----------|------------------|----------------------------------|-----------------|
| 1     | 1ArMgBr + 1ZnCl\textsubscript{2} | THF     | 8        | 80              | ∆                                | –               |
| 2     | 1ArMgBr + 1ZnBr\textsubscript{2} | THF     | 8        | 80              | ∆                                | <5%             |
| 3     | 1ArMgBr + 1ZnBr\textsubscript{2} + 1LiBr | THF     | 8        | 80              | ∆                                | 10%             |
| 4     | 1ArMgBr + 1ZnBr\textsubscript{2} + 1LiCl | THF     | 8        | 80              | ∆                                | 18%             |
| 5     | 2ArMgBr + 1ZnBr\textsubscript{2} + 1LiCl | THF     | 8        | 80              | ∆                                | 39%             |
| 6     | 2ArMgBr + 1ZnBr\textsubscript{2} + 1LiCl | THF     | 8        | 80              | ∆                                | <5%             |
| 7     | 2ArMgBr + 1ZnBr\textsubscript{2} + 1MgBr\textsubscript{2} | THF     | 8        | 80              | ∆                                | –               |
| 8     | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | THF     | 8        | 80              | ∆                                | 46%             |
| 9     | 2ArMgBr + 1ZnBr\textsubscript{2} + 3LiCl | THF     | 8        | 80              | ∆                                | 47%             |
| 10    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | THF     | 8        | 80              | MW                               | 68%             |
| 11\textsuperscript{d} | 2ArZnLiCl | THF     | 8        | 80              | MW                               | 23%             |
| 12\textsuperscript{d} | 2ArZnLiCl + 2MgBr\textsubscript{2} | THF     | 8        | 80              | MW                               | 24%             |
| 13    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | DMA     | 8        | 80              | MW                               | –               |
| 14    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | NMP     | 8        | 80              | MW                               | 35%             |
| 15    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | iPr\textsubscript{2}O | 8        | 80              | MW                               | –               |
| 16    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | 1,4-dioxane | 8        | 80              | MW                               | –               |
| 17    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | DMF     | 8        | 80              | MW                               | 5%              |
| 18    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | 2-Me-THF | 8        | 80              | MW                               | 75%             |
| 19    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | Diglyme  | 8        | 80              | MW                               | 32%             |
| 20    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | Toluene  | 8        | 80              | MW                               | 37%             |
| 21    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | 2-Me-THF/toluene (1:1) | 8 | 80       | MW                               | 56%             |
| 22    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | 2-Me-THF/NMP (1:1) | 8 | 80       | MW                               | 87%             |
| 23    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | 2-Me-THF/diglyme (1:1) | 8 | 80       | MW                               | 61%             |
| 24    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | 2-Me-THF/NMP (1:1) | 1 | 80       | MW                               | 92%             |
| 25    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | 2-Me-THF/NMP (1:1) | 0.5 | 80       | MW                               | 93% (91%)       |
| 26    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | 2-Me-THF/NMP (1:1) | 10 min | 80 | MW | 88% |
| 27    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | 2-Me-THF/NMP (1:1) | 0.5 | 50 | MW | 45% |
| 28    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | 2-Me-THF/NMP (1:1) | 0.5 | 100 | MW | 92% |
| 29    | 2ArMgBr + 1ZnBr\textsubscript{2} + 2LiCl | 2-Me-THF/NMP (1:1) | 0.5 | 80 | MW | 25% |

MW: microwave.

\textsuperscript{a}Conditions: 1a (0.2 mmol) was treated with 2a (0.3 mmol, 1.5 equiv.) in solvent (3 mL) by heating under argon.

\textsuperscript{b}∆ conventional heating.

\textsuperscript{c}GC yield using tridecane as an internal standard; isolated yield is given in parentheses.

\textsuperscript{d}See Chen et al.\textsuperscript{13}
### Table 2. Survey of cross-coupling partners.a

| Entry | X         | Yield (%)<sup>b</sup> |
|-------|-----------|----------------------|
| 1     | OPiv      | 93                   |
| 2     | OSO₂-NMe₂ | 75                   |
| 3     | OCONEt₂  | 56                   |
| 4     | OTs       | 88                   |
| 5     | OMs       | 85                   |
| 6     | OTf       | 96                   |
| 7     | OMe       | –                    |

<sup>a</sup>Conditions: 1a (0.2 mmol), 2a (0.3 mmol, 1.5 equiv.), in 2-Me-THF/NMP (1:1) (3 mL), MW irradiation, 80 °C, 0.5 h.  
<sup>b</sup>GC yield using tridecane as an internal standard.

### Table 3. Cross-couplings of aryl pivalate esters and sulfonates with the 4-methoxyphenylzinc reagent.a,b

| Ar<sup>1</sup> | X         | Yield (%)<sup>b</sup> |
|----------------|-----------|----------------------|
| 3b             | OPiv      | 87% (X = OPiv)       |
|                |           | 89% (X = OTs)        |
| 3c             | OPiv      | 69% (X = OPiv)       |
|                |           | 72% (X = OTs)        |
| 3d             | OPiv      | 81% (X = OPiv)       |
|                |           | 83% (X = OTs)        |
| 3e             | OPiv      | 69% (X = OPiv)       |
|                |           | 77% (X = OTs)        |
| 3f             | OPiv      | 93% (X = OPiv)       |
|                |           | 91% (X = OTs)        |
| 3g             | OPiv      | 93% (X = OPiv)       |
|                |           | 85% (X = OTf)        |
| 3h             | OPiv      | 65% (X = OPiv)       |
|                |           | 80% (X = OTs)        |
| 3i             | OPiv      | 89% (X = OPiv)       |
|                |           | 87% (X = OTs)        |
|                |           | 86% (X = OMs)        |
| 3j             | OPiv      | 91% (X = OPiv)       |
|                |           | 93% (X = OTs)        |
| 3k             | OTf       | 81% (X = OTf)        |
| 3l             | OTf       | 35% (X = OTf)        |
| 3m             | OTs       | 81% (X = OTs)        |
| 3n             | OTs       | 84% (X = OTs)        |
|                |           | 83% (X = OMs)        |
| 3o             | OTs       | 65% (X = OTs)        |
|                |           | 82% (X = OTf)        |
| 3p             | OPiv      | 84% (X = OPiv)       |
|                |           | 82% (X = OTs)        |
| 3q             | OPiv      | 77% (X = OPiv)       |
|                |           | 83% (X = OTs)        |

<sup>a</sup>Conditions: 1 (0.2 mmol), 2 (0.3 mmol, 1.5 equiv.), 2-Me-THF/NMP (1:1) (3 mL), MW irradiation, 80 °C, 0.5 h.  
<sup>b</sup>Isolated yields.
Table 4. Cross-coupling of aryl pivalate esters and sulfonates with different zinc reagents.\textsuperscript{a,b}

\[
\begin{array}{cccc}
\text{Ar}^1 & X & + & (\text{Ar}^2)_2Zn \\
\text{1} & \text{2} & \text{3} \\
\otimes 1 \text{MgBr} & \text{2LiCl} & \text{2-Me-THF/NMP (1:1)} & 0.5 \text{h, 80 °C, MW} \\
\text{X = OPiv, OTs, OTf, OMs} \\
\end{array}
\]

\begin{tabular}{llllll}
& 3r & 65% (X = OPiv) & 78% (X = OTs) & 76% (X = OMs) \\
& & & & & \\
& 3s & 86% (X = OPiv) & 87% (X = OTs) & 83% (X = OMs) \\
& & & & & \\
& & & & & \\
& 3t & 81% (X = OPiv) & 83% (X = OTs) & 83% (X = OMs) \\
& & & & & \\
& & & & & \\
& 3u & 85% (X = OPiv) & 86% (X = OTs) & 86% (X = OMs) \\
& & & & & \\
& & & & & \\
& 3v & 78% (X = OPiv) & 81% (X = OTs) & 76% (X = OMs) \\
& & & & & \\
& & & & & \\
& 3w & 45% (X = OPiv) & 81% (X = OTf) & 78% (X = OTs) \\
& & & & & \\
& & & & & \\
& 3x & 77% (X = OPiv) & 78% (X = OTs) & 76% (X = OMs) \\
& & & & & \\
& & & & & \\
& 3y & 78% (X = OPiv) & 79% (X = OTs) & 75% (X = OMs) \\
& & & & & \\
& & & & & \\
& 3z & 75% (X = OPiv) & 78% (X = OTs) & 76% (X = OMs) \\
& & & & & \\
& & & & & \\
& 3aa & 78% (X = OPiv) & 79% (X = OTs) & 76% (X = OMs) \\
& & & & & \\
& & & & & \\
& 3ab & 65% (X = OPiv) & 68% (X = OTs) & 68% (X = OTs) \\
& & & & & \\
& & & & & \\
& 3ac & 76% (X = OPiv) & 79% (X = OTs) & 76% (X = OMs) \\
& & & & & \\
& & & & & \\
& 3ad & 75% (X = OPiv) & 77% (X = OTs) & 76% (X = OMs) \\
& & & & & \\
& & & & & \\
& 3ae & 81% (X = OPiv) & 80% (X = OTs) & 81% (X = OTs) \\
& & & & & \\
& & & & & \\
& 3af & 83% (X = OPiv) & 85% (X = OTs) & 83% (X = OTs) \\
& & & & & \\
& & & & & \\
& 3ag & 83% (X = OPiv) & 85% (X = OTs) & 85% (X = OTs) \\
& & & & & \\
& & & & & \\
& 3ah & 78% (X = OPiv) & 82% (X = OTs) & 83% (X = OTs) \\
& & & & & \\
& & & & & \\
& 3ai & 81% (X = OPiv) & 83% (X = OTs) & 83% (X = OTs) \\
& & & & & \\
& & & & & \\
& 3aj & 82% (X = OPiv) & 83% (X = OTs) & 83% (X = OTs) \\
& & & & & \\
& & & & & \\
& 3ak & 83% (X = OPiv) & 85% (X = OTs) & 85% (X = OTs) \\
& & & & & \\
& & & & & \\
& 3ak & 83% (X = OPiv) & 85% (X = OTs) & 85% (X = OTs) \\
& & & & & \\
& & & & & \\
\end{tabular}

\textsuperscript{a}Conditions: 1 (0.2 mmol), 2 (0.3 mmol, 1.5 equiv.), 2-Me-THF/NMP (1:1) (3 mL), MW irradiation, 80 °C, 0.5 h.

\textsuperscript{b}Isolated yields.

stirred magnetically. LiCl, ZnBr\textsubscript{2}, ZnCl\textsubscript{2}, and LiBr were purchased from Aldrich. MgBr\textsubscript{2} was purchased from Alfa Aesar. Other reagents are available commercially and were used without further purification, unless otherwise indicated. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. THF was dried over alumina under N\textsubscript{2} using a Grubbs-type solvent purification system. All arylzinc reagents were prepared from the corresponding arylmagnesium bromides, LiCl and ZnBr\textsubscript{2}. All aromatic phenols were purchased from Alfa Aesar. Spectroscopic data for known compounds match with the data reported in the corresponding references. Reactions were monitored with Agilent GC Series 6890N and instruments GCMS 7890A. All compounds were characterized by \textsuperscript{1}H NMR spectroscopy using a Bruker 400 M spectrometer (Bruker Avance III 400 MHz NMR). New compounds are characterized by HRMS (TripleTOF\textsuperscript{TM} 5600+). \textsuperscript{1}H NMR was recorded in CDCl\textsubscript{3} using tetramethylsilane (TMS) and deuterium oxide as the internal standard. Chemical shifts were reported in parts per million. The signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; and m, multiplet. Coupling constants, \textit{J}, are reported in Hertz (Hz). The products were purified by column chromatography on Aladdin silica gel 300–400 mesh under an argon atmosphere.
Scheme 1. One-pot synthesis of an unsymmetric terphenyl compound.

| Additive (equiv) | Conv. of 1a | Yield of 3a |
|-----------------|------------|------------|
| none            | 47%        | 45%        |
| LDBB (0.2)      | 54%        | 54%        |

Scheme 2. Effect of the addition of single-electron donors.

Scheme 3. A plausible mechanism.

**Experimental procedures**

General procedure for the reaction between (het)aryl pivalates 1 and diarylzinc reagents 2. In a glovebox, (het)aryl pivalate 1 (0.2 mmol) and NMP (1.5 mL) were added to the diarylzinc 2 (0.3 mmol, prepared by mixing zinc bromide, lithium chloride, and the corresponding aryl magnesium bromide in 1.5 mL of THF) in a reaction tube. The reaction mixture was then heated at 80 °C for 0.5 h under MW irradiation. After completion of the reaction, the mixture was concentrated under vacuum, and saturated NH₄Cl added. The mixture was extracted with CH₂Cl₂ several times. The combined organic layers were dried over anhydrous MgSO₄, concentrated in vacuo, and the residue was purified by column chromatography on silica gel to give the coupling product 3.

*(2,6-Dimethylphenyl)-5-methoxypyridine (3w)*. Product 3w was obtained following the general procedure. Purification via silica gel column chromatography (petroleum ether/EtOAc=10:1, v/v) afforded the desired product. ¹H NMR (400 MHz, CDCl₃): δ 7.99 (dd, J=2.4, 0.8 Hz, 1H), 7.39 (dd, J=8.4, 2.4 Hz, 1H), 7.21-7.12 (m, 3H), 6.84 (dd, J=8.4, 0.7 Hz, 1H), 4.01 (s, 3H), 2.07 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 163.1, 146.6, 139.7, 137.9, 136.9,
129.4, 127.5, 110.7, 53.4, 21.0. HRMS (ESI): m/z [M + H]⁺ calced for C₁₄H₁₅NO: 214.1154; found: 214.1229.

4'-Benzoyl-[1,1'-biphenyl]-2-carbonitrile (3ai). Product 3ai was obtained following the general procedure. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1, v/v) afforded the desired product. 1H NMR (400 MHz, CDCl₃): δ 7.93 (dt, J = 8.2, 1.7 Hz, 2H), 7.87~7.85 (m, 2H), 7.82~7.81 (m, 1H), 7.70~7.67 (m, 3H), 7.62~7.56 (m, 2H), 7.54~7.49 (m, 3H). 13C NMR (100 MHz, CDCl₃): δ 196.2, 144.4, 142.1, 137.7, 137.4, 134.0, 133.1, 132.8, 130.6, 130.2, 128.9, 128.5, 118.5, 111.4. HRMS (ESI): m/z [M + H]⁺ calcd for C₂₀H₁₃NO: 284.0997; found: 284.1075.

Acknowledgements
The author is thankful to Hebei University of Science & Technology for 1H NMR, 13C NMR, and HRMS (ESI) facilities.

Declaration of conflicting interests
The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding
The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: The author gratefully acknowledges the financial support from Hebei Chemical & Pharmaceutical College.

ORCID iD
Chun-Jing Li https://orcid.org/0000-0002-3874-9936

Supplemental material
Supplemental material for this article is available online.

References
1. Diederich F and Stang PJ (eds). Metal-catalyzed cross-coupling reactions. New York: Wiley, 1998.
2. Miyaura N (ed.) Cross-coupling reactions: a practical guide. Berlin: Springer, 2002.
3. Kertesz M, Choi CH and Yang S. Chem Rev 2005; 105: 3448.
4. Sun CL and Shi ZJ. Chem Rev 2014; 114: 9219.
5. Zhang N, Samanta SR, Rosen BM, et al. Chem Rev 2014; 114: 5848.
6. De Carolis M, Protti S, Fagnoni M, et al. Angew Chem Int Ed 2005; 44: 1232.
7. Protti S, Fagnoni M and Albini A. Angew Chem Int Ed 2005; 44: 5675.
8. Dichiariante V, Fagnoni M and Albini A. Angew Chem Int Ed 2007; 46: 6495.
9. Studer A and Curran DP. Angew Chem 2016; 55: 58.
10. Holmberg-Douglas N and Nicewicz DA. Org Lett 2019; 21: 7114.
11. Liu W, Li J and Li CJ. J Am Chem Soc 2019; 141: 6755.
12. Liu W, Li J, Huang CY, et al. Angew Chem Int Ed 2020; 59: 1786.
13. Chen Q, Lejn T and Knochel P. Angew Chem Int Ed 2014; 53: 8746.
14. Murarka S and Studer A. Angew Chem Int Ed 2012; 51: 12362.
15. Dunsford JJ, Clark ER and Ingleson MJ. Angew Chem Int Ed 2015; 54: 5688.
16. Shirakawa E, Tamakuni F, Kusano E, et al. Angew Chem Int Ed 2014; 53: 521.
17. Minami H, Saito T, Wang C, et al. Angew Chem Int Ed 2015; 54: 4665.
18. He Q, Wang L, Liang Y, et al. J Org Chem 2016; 81: 9422.
19. Shirakawa E. J Synth Org Chem Jpn 2013; 71: 526.
20. Wang DY, Morimoto KK, Yang ZK, et al. Chem Asian J 2017; 12: 2554.
21. Shirakawa E, Hayashi Y, Itoh KI, et al. Angew Chem Int Ed 2012; 51: 218.
22. Haines BE and Wiest O. J Org Chem 2014; 79: 2771.
23. Li BJ, Xu L, Wu ZH, et al. J Am Chem Soc 2009; 131: 14656.
24. Molander GA and Beaumard F. Org Lett 2010; 12: 4022.
25. Knochel P and Jones P. Organozinc reagents: a practical approach. New York: Oxford, 1999.
26. Erdik E. Organozinc Reagents in Organic Synthesis. Boston, MA: CRC Press, 1996.
27. Krasovskiy A, Malakhov V, Gavryushin A, et al. Angew Chem Int Ed 2006; 45: 6040.
28. Shirakawa E, Hayashi Y, Itoh K, et al. Angew Chem Int Ed 2012; 51: 218.
29. Russell GA, Norris RK and Panek EJ. J Am Chem Soc 1971; 93: 5839.
30. Costentin C, Robert M and Savéant JM. J Am Chem Soc 2004; 126: 16051.
31. Takeda N, Poliakov PV, Cook ARM, et al. J Am Chem Soc 2004; 126: 4301.
32. Uchiyama N, Shirakawa E and Hayashi T. Chem Commun 2013; 49: 364.
33. Shirakawa E, Watabe R, Murakami T, et al. Chem Commun 2013; 49: 5219.
34. Chan TL, Wu Y, Choy PY, et al. Chem Eur J 2013; 19: 15802.