

Synthesis of Biaryls via Decarbonylative Nickel-Catalyzed Suzuki–Miyaura Cross-Coupling of Aryl Anhydrides

Jing-Ya Zhou, Rui-Qing Liu, Cheng-Yi Wang, and Yong-Ming Zhu*



Cite This: <https://dx.doi.org/10.1021/acs.joc.0c02266>



Read Online

ACCESS |



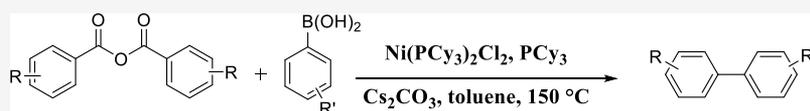
Metrics & More



Article Recommendations



Supporting Information



37 examples
up to 88% yield

- New C–C bond formation
- Broad substrate scope

ABSTRACT: Transition metal-catalyzed cross-couplings have been widely employed in the synthesis of many important molecules in synthetic chemistry for the construction of diverse C–C bonds. Conventional cross-coupling reactions require active electrophilic coupling partners, such as organohalides or sulfonates, which are not environmentally friendly enough. Herein, we disclose the first nickel-catalyzed Suzuki–Miyaura cross-coupling of aryl anhydrides and arylboronic acids for the synthesis of biaryls in a decarbonylation manner. The reaction tolerates a wide range of electron-withdrawing, electron-neutral, and electron-donating substituents in this process.

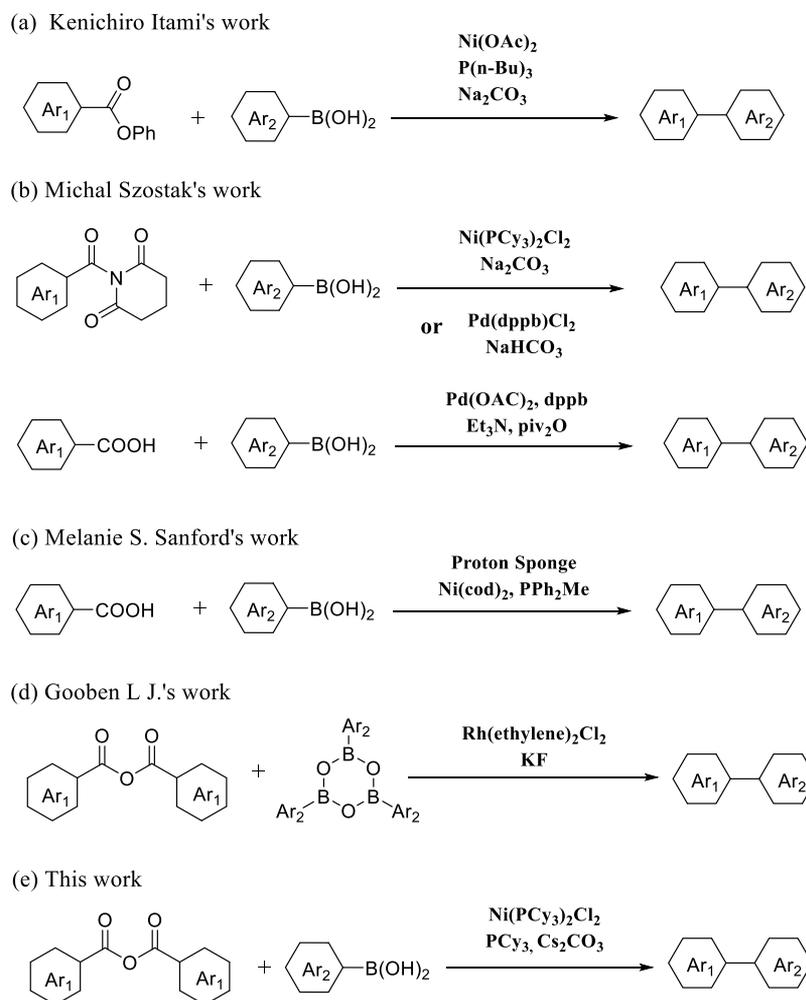
INTRODUCTION

Substituted biphenyls are key structural motifs in bioactive medicinal agents, natural products, and polymers.¹ Cross-coupling reactions catalyzed by transition metals have become indispensable tools for the construction of C–C bonds.² The Suzuki–Miyaura cross-coupling is one of the most important and prevalent methods for the construction of C–C bonds in organic and medicinal chemistry.³ Arylboronic acids appeared to be the preferred carbon nucleophile because they are readily available,⁴ nontoxic, and air- and moisture stable compounds that are resistant to the presence of a variety of sensitive functions. Although the traditional cross-coupling reaction between the organoboron nucleophile and haloaryl electrophile⁵ has been widely used in synthetic transformation, the generation of corrosive halogens is detrimental from synthetic and environmental perspectives. In recent years, with the rapid development of organometallic chemistry, there is a growing interest in the use of aroyl compounds in metal-catalyzed decarboxylative or decarbonylative coupling reactions.⁶ However, in catalytic cross-coupling reactions, the decarbonylation step was found to be less favorable and aryl ketones were easily formed.⁷ Therefore, in recent years, organic scientists have devoted to the development of cross-coupling methods that are beneficial to the decarbonylation process. At present, there have been reports of palladium, rhodium, and nickel transition metal-catalyzed decarbonylation cross-coupling reactions (Scheme 1). For example, Itami et al.⁸ reported using a user-friendly and inexpensive nickel catalyst; a range of phenyl esters of aromatic, heteroaromatic, and aliphatic carboxylic

acids react with arylboronic acids in a decarbonylative manner (Scheme 1a). Michal Szostak's group⁹ have successfully reported that nickel and palladium catalyze the amide decarbonylation Suzuki–Miyaura cross-coupling reaction for the synthesis of biaryl groups through the selective activation of the N–C(O) bond of the amide. At the same time, their research team also reported that palladium catalyzed the cross-coupling reaction between carboxylic acid and phenylboronic acid¹⁰ (Scheme 1b). Sanford's group developed a nickel-catalyzed coupling of arylboronic acids with acid fluorides, which are formed in situ from readily available carboxylic acids¹¹ (Scheme 1c). Gooßen first obtained an asymmetric biaryl group under the rhodium-catalyzed decarbonylation cross-coupling reaction of aryl anhydrides with triaryl boroxines¹² (Scheme 1d). In 2019, Rueping's research group reported an unconventional Suzuki-type method for synthesizing biaryls. This method through nickel-catalyzed aldehydes and organoboron reagents cross-couple under base-free conditions.¹³ For economic and environmental considerations, we chose to use nickel as a catalyst. Furthermore, the use of the earth-abundant first-row metal nickel as a catalyst in the target coupling makes this reaction commercially more appealing.

Received: September 21, 2020

Scheme 1. Different Catalytic Conditions for the Synthesis of Biphenyls



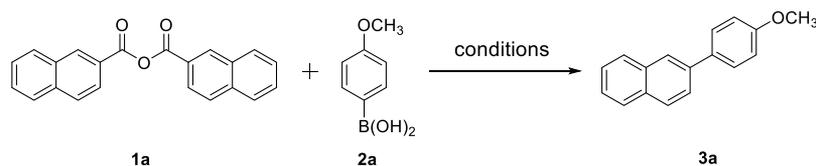
Our laboratory has previously reported that anhydrides and thiophenols build C–S bonds through decarbonylation or decarbonylation accompanied by decarboxylation under the catalysis of nickel.¹⁴ Because most carboxylic acids can be easily (and possibly in situ) converted to anhydrides,¹⁵ our primary goal is to develop a catalytic system capable of coupling anhydrides with arylboronic acids.

RESULTS AND DISCUSSION

We initiated this study by finding suitable catalytic conditions for the decarbonylative cross-coupling of aryl anhydrides and arylboronic acids, using 2-naphthoic anhydride (**1a**) and (4-methoxyphenyl) boronic acid (**2a**) as model substrates. We focused on the use of nickel(II) as a catalyst because of its low cost and stability under air and moisture conditions.^{16,17} Key optimization results are shown in Table 1. We found that in the presence of 5 mol % Ni(PCy₃)₂Cl₂, 10 mol % PCy₃, and 3.0 equiv of K₃PO₄, a small amount of decarbonylated cross-coupling target products was formed. Among various bases (Table 1, entry 1–6), a dramatic effect of Cs₂CO₃ was observed with 88% yield of **3a** (Table 1, entry 3). Under these reaction conditions, a decrease in the yield was observed by employing 1,4-dioxane as the solvent (Table 1, entry 7). It is worth noting that when the loading of Cs₂CO₃ was increased to 4.5 equiv, the yield of the target product decreased (Table 1, entry 8). The temperature effect was also examined and 150

°C was found to be optimal (Table 1, entry 9). With other air-stable nickel sources such as NiCl₂ and Ni(OAc)₂·4H₂O, the yield was reduced compared to the Ni(PCy₃)₂Cl₂ (Table 1, entry 10–11). Compared with other ligands, PCy₃ was the most optimal for this reaction (Table 1, entry 12–13). When no additional ligand is added, the yield of the target product decreased (Table 1, entry 14). No product was observed in the absence of a nickel catalyst (Table 1, entry 15).

After establishing optimal catalytic conditions [Ni(PCy₃)₂Cl₂, PCy₃, Cs₂CO₃ and toluene, 150 °C, and 24 h], the scope of this novel Suzuki–Miyaura biaryl cross-coupling of anhydrides was next investigated (Table 2). As shown in Table 2, we found that in this catalytic system, the reaction range is very wide and can tolerate the coupling of electron-rich (Table 2, **3a–h**, **3j–r**), electron-neutral (Table 2, **3i**), and electron-withdrawing (Table 2, **3t–x**) substrates. Phenylboronic acids of electron-rich groups such as methoxy, ethoxy, hydrocarbyl, and silane reacted smoothly to provide the corresponding substituted biphenyls. In addition to the low yield of some target products, such as **3j**, **3l**, **3m**, and **3q**, most electron-rich groups were transferred into the cross-coupling products in moderate to excellent yields. The hindered substrate showed good reactivity, and the target product was obtained in a moderate yield (Table 2, **3n–o**). Furthermore, in addition to the product **3t**, moderate yields were obtained with phenylboronic acids bearing electron-withdrawing substitu-

Table 1. Optimization of Ni-Catalyzed Suzuki Biaryl Synthesis Through Coupling of Anhydrides with Arylboronic Acids^a

entry	Ni cat.	ligand	base	solvent	yield (%)
1	Ni(PCy ₃) ₂ Cl ₂	PCy ₃	K ₃ PO ₄	toluene	trace
2	Ni(PCy ₃) ₂ Cl ₂	PCy ₃	K ₂ CO ₃	toluene	38
3	Ni(PCy ₃) ₂ Cl ₂	PCy ₃	Cs ₂ CO ₃	toluene	88
4	Ni(PCy ₃) ₂ Cl ₂	PCy ₃	CsF	toluene	30
5	Ni(PCy ₃) ₂ Cl ₂	PCy ₃	Bu ^t ONa	toluene	26
6	Ni(PCy ₃) ₂ Cl ₂	PCy ₃	Bu ^t OK	toluene	none
7	Ni(PCy ₃) ₂ Cl ₂	PCy ₃	Cs ₂ CO ₃	1,4-dioxane	72
8	Ni(PCy ₃) ₂ Cl ₂	PCy ₃	Cs ₂ CO ₃	toluene	40 ^b
9	Ni(PCy ₃) ₂ Cl ₂	PCy ₃	Cs ₂ CO ₃	toluene	37 ^c
10	NiCl ₂	PCy ₃	Cs ₂ CO ₃	toluene	none ^d
11	Ni(OAc) ₂ ·4H ₂ O	PCy ₃	Cs ₂ CO ₃	toluene	none
12	Ni(PPh ₃) ₂ Cl ₂	PPh ₃	Cs ₂ CO ₃	toluene	trace
13	Ni(dppp)Cl ₂	dppp	Cs ₂ CO ₃	toluene	21
14	Ni(PCy ₃) ₂ Cl ₂		Cs ₂ CO ₃	toluene	45
15		PCy ₃	Cs ₂ CO ₃	toluene	none

^aGeneral conditions: the reactions were run on 0.2 mmol 2-naphthoic anhydride in solvent (1.5 mL), (4-methoxyphenyl)boronic acid (1.5 equiv), catalyst (5 mol %), ligand (10 mol %), and base (3.0 equiv) under nitrogen in a sealed tube at 150 °C for 24 h. Isolated yield after purification of column chromatography. ^bCs₂CO₃ (4.5 equiv). ^c130 °C. ^dNiCl₂ (5 mol %), PCy₃ (20 mol %).

ents; it may be due to the strong electron-withdrawing effect, leading to a decrease in the yield of the product **3t**. Fluorinated biaryl compounds (Table 2, **3u–v**) are obtained in good yields. It has been reported in the literature that fluorinated biaryls have an important value in pharmaceutical and materials chemistry.¹⁸

The range of anhydride composition was investigated using 4-methoxyphenylboronic acid as a standard substrate (Table 3, **4a–4j**). In addition to the lower yield of sterically hindered anhydrides (Table 3, **4a**), coupling products of anhydrides with electron-neutral (Table 3, **4b**), electron-withdrawing (Table 3, **4f–g**), or electron-rich (Table 3, **4c–4e**, **4j**) groups all have moderate yields. To our surprise, proper addition of boric acid, cinnamic anhydride, and biphenyl anhydride can also be applicable to this reaction (Table 3, **4h–i**). At the same time, we also used different anhydrides to cross-react with different phenylboronic acids (Table 3, **4k–4m**) and also obtained moderate yields.

We conducted research using asymmetric anhydride as the raw material to clarify the mechanism (Scheme 2). It was found that two decarbonylation products can be separated. Therefore, we believe that anhydrides may react in two ways. It can be seen from Scheme 2 that the naphthyl moiety has higher reactivity than phenyl. The reactivity of electron-donating groups or electron-withdrawing groups attached to the benzene ring is almost the same. The steric hindrance has a little influence on the reactivity.

In order to prove the practicability of this method as a synthetic tool, we carried out a scale-up experiment on the product **3b** and the yield was 71% (Scheme 3).

Based on the abovementioned experimental results and previous literature reports,^{9a} a plausible mechanism of the Ni(II)-catalyzed decarbonylation cross-coupling reaction of anhydrides and phenylboronic acids is shown in Scheme 4. First, the substrate anhydride B undergoes oxidative addition

with Ni⁰ to form an intermediate C. The resulting acylnickel(II) intermediate C undergoes a transmetalation step with phenylboronic acid D, generating the acylnickel(II) species E. Decarbonylation of the intermediate E gives the compound F. Finally, the compound F undergoes reductive elimination to obtain cross-coupling products and the active Ni⁰ catalytic species.

CONCLUSIONS

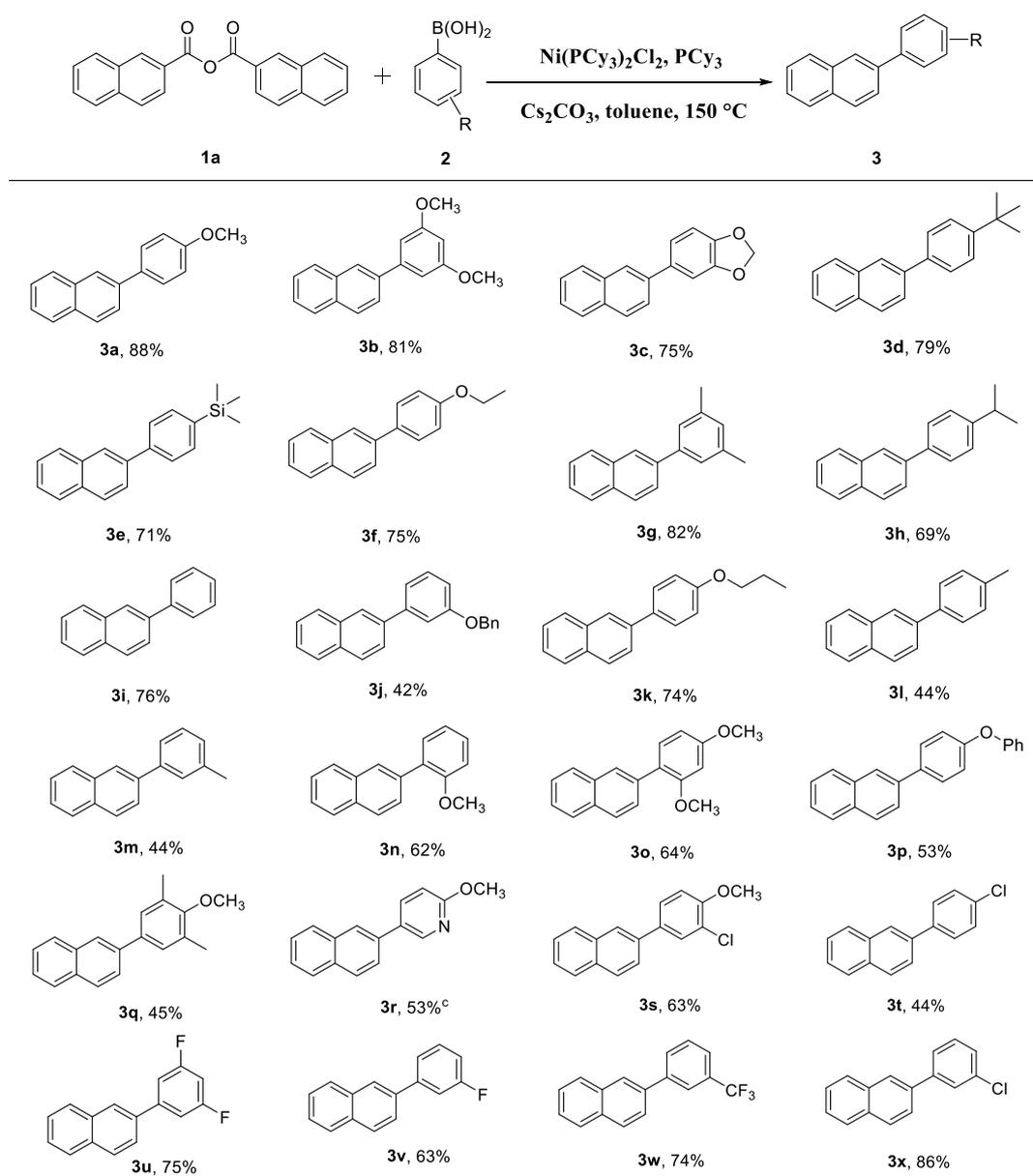
In summary, we have developed a nickel-catalyzed decarbonylative Suzuki–Miyaura coupling of anhydrides with arylboronic acids. The reaction has a wide substrate range and operational simplicity and employs a cost-effective, air-stable Ni(II) precatalyst. This process is a supplement to the traditional cross-coupling methods, which also indicates that decarbonyl cross-coupling may have a significant impact on the modern era of organic synthesis.

EXPERIMENTAL SECTION

General Information. In addition to benzoic anhydride, other monoanhydrides were prepared according to previously reported methods.^{15a} Reactants and reagents were purchased from commercial suppliers and used without further purification. All anhydrous solvents used in the reactions were dried and freshly distilled. Thin-layer chromatography (TLC) was performed on silica HSGF254 plates. Melting points were determined with a digital melting-point apparatus. ¹H (400 MHz) and ¹³C (101 MHz) NMR spectra were obtained from solutions in CDCl₃ or with tetramethylsilane as an internal standard using 400 MHz spectrometers. High-resolution mass spectrum (HRMS) analyses were carried out on an electrospray ionization or atmospheric pressure chemical ionization (ESI or APCI) apparatus using time-of-flight (TOF) mass spectrometry.

General Procedure for Decarbonylative Suzuki–Miyaura Coupling of Anhydrides. Anhydride (0.2 mmol), the arylboronic acid substrate (0.3 mmol), Ni(PCy₃)₂Cl₂ (6 mg, 0.01 mmol), PCy₃ (7 mg, 0.02 mmol), and Cs₂CO₃ (195 mg, 0.6 mmol) were successively added into a 15 mL sealed tube, using anhydrous toluene (1.5 mL) as

Table 2. Nickel-Catalyzed Suzuki Biaryl Synthesis Through Cross-Coupling of 2-Naphthoic Anhydride with Arylboronic Acids^{a,b}



^aGeneral conditions: the reactions were run on 0.2 mmol acid anhydride under nitrogen in a sealed tube, using R–B(OH)₂ (1.5 equiv), Ni(PCy₃)₂Cl₂ (5 mol %), PCy₃ (10 mol %), and Cs₂CO₃ (3.0 equiv) in toluene (1.5 mL) at 150 °C for 24 h. ^bIsolated yields. ^cR–B(OH)₂ (3.0 equiv).

the solvent. The mixture was stirred in a 150 °C oil bath under nitrogen for 24 h. Upon completion of the reaction as indicated by TLC, the mixture was diluted with EtOAc and then filtered through a pad of Celite. The solvent was removed under vacuum. The residue was purified on a silica gel column (petroleum ether) to give the pure target product.

2-Naphthoic Anhydride (1a).^{15a} White solid (568 mg, 85%). ¹H NMR (400 MHz, CDCl₃): δ 8.79 (s, 2H), 8.20 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 3H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 2H).

1-Naphthoic Anhydride (1b).^{15a} White solid (567 mg, 87%). ¹H NMR (400 MHz, CDCl₃): δ 9.15 (d, *J* = 8.6 Hz, 2H), 8.44 (d, *J* = 7.2 Hz, 2H), 8.15 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 2H), 7.66–7.50 (m, 4H).

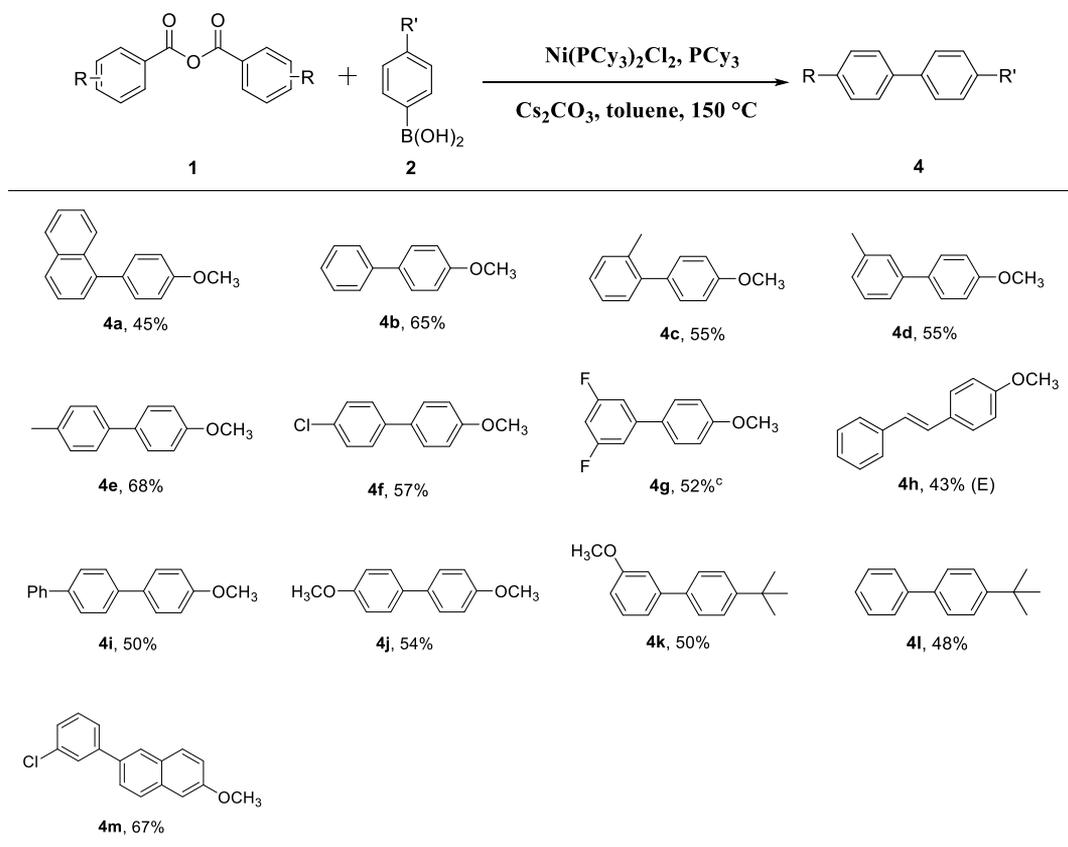
3-Chlorobenzoic Anhydride (1c).^{15a} White solid (529 mg, 90%). ¹H NMR (400 MHz, CDCl₃): δ 8.11 (s, 2H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 2H).

4-Chlorobenzoic Anhydride (1d).^{15a} White solid (513 mg, 87%). ¹H NMR (400 MHz, CDCl₃): δ 8.08 (d, *J* = 8.3 Hz, 4H), 7.52 (d, *J* = 8.3 Hz, 4H).

2-Methylbenzoic Anhydride (1e).^{15a} White solid (482 mg, 95%). ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.35–7.30 (m, 4H).

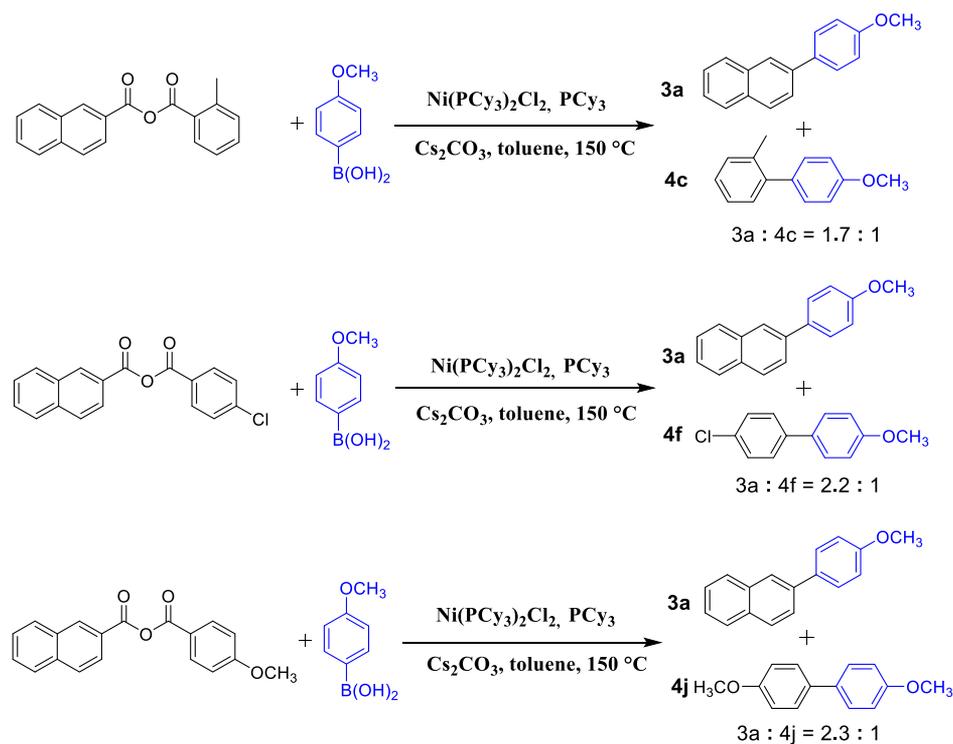
3-Methylbenzoic Anhydride (1f).^{15a} Yellow solid (442 mg, 85%). ¹H NMR (400 MHz, CDCl₃): δ 7.96 (s, 2H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 2.45 (s, 6H).

4-Methylbenzoic Anhydride (1g).^{15a} White solid (458 mg, 88%). ¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, *J* = 7.6 Hz, 4H), 7.32 (d, *J* = 7.6 Hz, 4H), 2.46 (s, 6H).

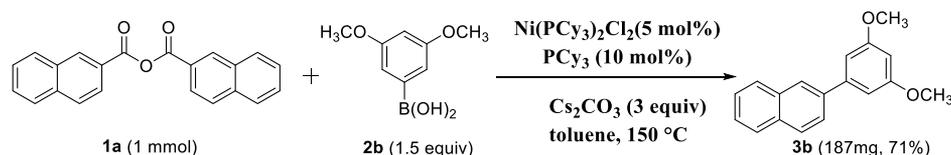
Table 3. Nickel-Catalyzed Suzuki Biaryl Synthesis Through Cross-Coupling of Anhydrides with Arylboronic Acid^{a,b}

^aGeneral conditions: the reactions were run on 0.2 mmol acid anhydride under nitrogen in a sealed tube, using R–B(OH)₂ (1.5 equiv), Ni(PCy₃)₂Cl₂ (5 mol %), PCy₃ (10 mol %), Cs₂CO₃ (3.0 equiv), and H₃BO₃ (1.5 equiv) in toluene (1.5 mL) at 150 °C for 24 h. ^bIsolated yields. ^cH₃BO₃ (2 equiv).

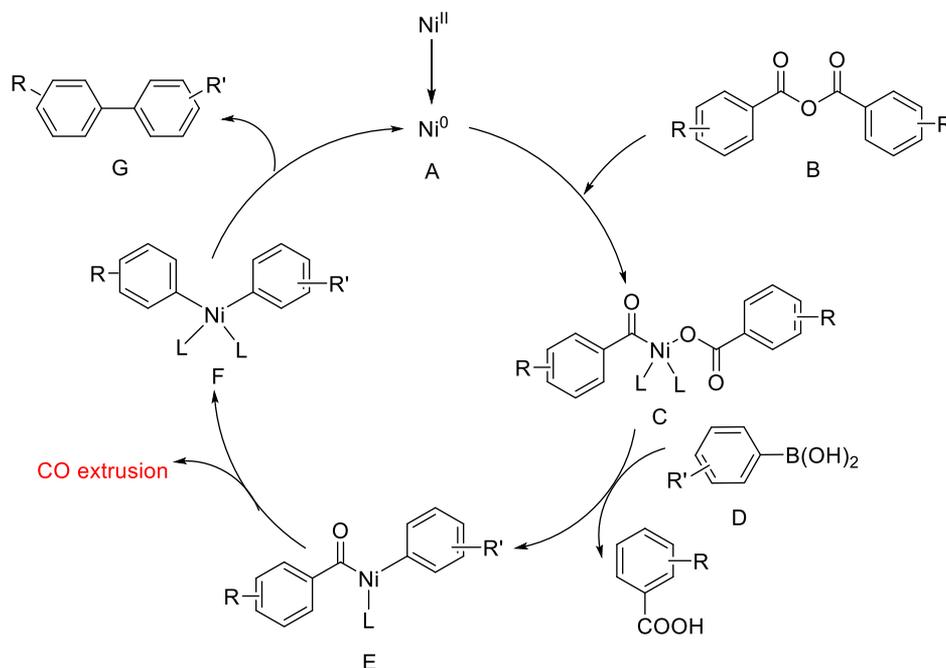
Scheme 2. Asymmetric Anhydride Selectivity Experiment



Scheme 3. Scale-Up Experiment



Scheme 4. Plausible Reaction Mechanism



3-Methoxybenzoic Anhydride (1h).^{15a} White solid (526 mg, 92%). ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.63 (s, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 3.86 (s, 6H).

4-Methoxybenzoic Anhydride (1i).^{15a} White solid (549 mg, 96%). ¹H NMR (400 MHz, CDCl₃): δ 8.10 (d, *J* = 8.5 Hz, 4H), 6.98 (d, *J* = 8.5 Hz, 4H), 3.90 (s, 6H).

3,5-Difluorobenzoic Anhydride (1j).^{15a} White solid (483 mg, 82%). ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 4.5 Hz, 4H), 7.17 (t, *J* = 7.8 Hz, 2H).

Cinnamic Anhydride (1k).^{15a} White solid (500 mg, 90%). ¹H NMR (400 MHz, CDCl₃): δ 7.87 (d, *J* = 15.9 Hz, 2H), 7.63–7.56 (m, 4H), 7.44 (d, *J* = 6.1 Hz, 6H), 6.54 (d, *J* = 15.9 Hz, 2H).

[1,1'-Biphenyl]-4-carboxylic Anhydride (1l).^{15a} White solid (642 mg, 85%). ¹H NMR (400 MHz, CDCl₃): δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.47 (dt, *J* = 26.5, 7.1 Hz, 2H), 7.26 (s, 1H).

2-(4-Methoxyphenyl)naphthalene (3a).¹⁹ White solid (41 mg, 88%); mp 116.8–117.3 °C. EtOAc/petroleum ether = 1:80. ¹H NMR (400 MHz, CDCl₃): δ 8.02 (s, 1H), 7.97–7.83 (m, 3H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.57–7.44 (m, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H). ¹³C{¹H} (101 MHz, CDCl₃): δ 159.2 (s), 138.1 (s), 133.7 (s), 133.6 (s), 132.3 (s), 128.4 (s), 128.3 (s), 128.0 (s), 127.6 (s), 126.2 (s), 125.6 (s), 125.4 (s), 125.0 (s), 114.3 (s), 55.3 (s).

2-(3,5-Dimethoxyphenyl)naphthalene (3b).¹⁹ Yellow oil (43 mg, 81%). EtOAc/petroleum ether = 1:40. ¹H NMR (400 MHz, CDCl₃): δ 8.03 (s, 1H), 7.93–7.82 (m, 3H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.57–7.44 (m, 2H), 6.86 (d, *J* = 1.6 Hz, 2H), 6.50 (s, 1H), 3.88 (s, 6H). ¹³C{¹H} (101 MHz, CDCl₃): δ 161.1 (s), 143.4 (s), 138.5 (s), 133.6 (s), 132.8 (s), 128.3 (s), 128.2 (s), 127.6 (s), 126.3 (s), 126.0 (s), 125.9 (s), 125.6 (s), 105.7 (s), 99.4 (s), 55.5 (s).

5-(Naphthalen-2-yl)benzo[d][1,3]dioxole (3c).²⁰ White solid (37 mg, 75%); mp 88.7–89.7 °C. EtOAc/petroleum ether = 1:80. ¹H NMR (400 MHz, CDCl₃): δ 7.94 (s, 1H), 7.85 (m, *J* = 8.6, 3.4 Hz, 3H), 7.66 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.52–7.41 (m, 2H), 7.21–7.15 (m, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.00 (s, 2H). ¹³C{¹H} (101 MHz, CDCl₃): δ 148.2 (s), 147.2 (s), 138.2 (s), 135.5 (s), 133.7 (s), 132.4 (s), 128.4 (s), 128.1 (s), 127.6 (s), 126.3 (s), 125.8 (s), 125.5 (s), 125.3 (s), 121.0 (s), 108.7 (s), 107.9 (s), 101.2 (s).

2-(4-(tert-Butyl)phenyl)naphthalene (3d).¹⁹ White solid (41 mg, 79%); mp 115.3–116.7 °C. Petroleum ether. ¹H NMR (400 MHz, CDCl₃): δ 8.03 (s, 1H), 7.93–7.82 (m, 3H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.55–7.43 (m, 4H), 1.38 (s, 9H). ¹³C{¹H} (101 MHz, CDCl₃): δ 150.4 (s), 138.4 (s), 138.2 (s), 133.7 (s), 132.5 (s), 128.2 (d, *J* = 17.2 Hz), 127.6 (s), 127.0 (s), 126.2 (s), 125.81 (s), 125.75 (s), 125.6 (s), 125.5 (s), 34.6 (s), 31.4 (s).

Trimethyl(4-(naphthalen-2-yl)phenyl)silane (3e).²¹ White solid (39 mg, 71%); mp 108.6–109.7 °C. EtOAc/petroleum ether = 1:60. ¹H NMR (400 MHz, CDCl₃): δ 8.07 (s, 1H), 7.96–7.85 (m, 3H), 7.80–7.71 (m, 3H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.56–7.46 (m, 2H), 0.34 (s, 9H). ¹³C{¹H} (101 MHz, CDCl₃): δ 141.5 (s), 139.4 (s), 138.5 (s), 133.9 (s), 133.7 (s), 132.7 (s), 128.4 (s), 128.2 (s), 127.6 (s), 126.7 (s), 126.3 (s), 125.9 (s), 125.8 (s), 125.5 (s), –1.1 (s).

2-(4-Ethoxyphenyl)naphthalene (3f).²² White solid (37 mg, 75%); mp 116.5–117.4 °C. EtOAc/petroleum ether = 1:80. ¹H NMR (400 MHz, CDCl₃): δ 7.99 (s, 1H), 7.92–7.82 (m, 3H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.53–7.41 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 4.10 (q, *J* = 6.9 Hz, 2H), 1.46 (t, *J* = 6.9 Hz, 3H). ¹³C{¹H} (101 MHz, CDCl₃): δ 158.6 (s), 138.2 (s), 133.7 (s), 133.4 (s), 132.3 (s), 128.4 (s), 128.3 (s), 128.0 (s), 127.6 (s), 126.2 (s), 125.6 (s), 125.4 (s), 125.0 (s), 114.9 (s), 63.5 (s), 14.9 (s).

2-(3,5-Dimethylphenyl)naphthalene (3g).¹⁹ White solid (38 mg, 82%); mp 62.5–63.3 °C. Petroleum ether. ¹H NMR (400 MHz, CDCl₃): δ 8.02 (s, 1H), 7.93–7.82 (m, 3H), 7.74 (d, *J* = 8.3

Hz, 1H), 7.54–7.43 (m, 2H), 7.34 (s, 2H), 7.03 (s, 1H), 2.42 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 141.1 (s), 138.8 (s), 138.4 (s), 132.6 (s), 129.0 (s), 128.2 (s), 128.1 (s), 127.6 (s), 126.2 (s), 125.8 (s), 125.7 (s), 125.7 (s), 125.3 (s), 21.4 (s).

2-(4-Isopropylphenyl)naphthalene (3h).²¹ White solid (33 mg, 69%); mp 72.6–73.4 °C. Petroleum ether. ^1H NMR (400 MHz, CDCl_3): δ 8.03 (s, 1H), 7.94–7.82 (m, 3H), 7.75 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.54–7.43 (m, 2H), 7.35 (d, J = 7.9 Hz, 2H), 3.03–2.93 (m, 1H), 1.32 (s, 3H), 1.30 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 148.1 (s), 138.6 (s), 138.5 (s), 133.7 (s), 132.5 (s), 128.3 (s), 128.1 (s), 127.6 (s), 127.3 (s), 127.0 (s), 126.2 (s), 125.7 (s), 125.6 (s), 125.5 (s), 33.8 (s), 24.0 (s).

2-Phenyl naphthalene (3i).¹⁹ White solid (31 mg, 76%); mp 105.6–106.7 °C. Petroleum ether. ^1H NMR (400 MHz, CDCl_3): δ 8.04 (s, 1H), 7.94–7.82 (m, 3H), 7.73 (t, J = 8.8 Hz, 3H), 7.55–7.43 (m, 4H), 7.37 (t, J = 7.2 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 141.1 (s), 138.5 (s), 133.7 (s), 132.6 (s), 128.8 (s), 128.4 (s), 128.2 (s), 127.6 (s), 127.4 (s), 127.3 (s), 126.3 (s), 125.9 (d, J = 12.6 Hz), 125.6 (s).

2-(3-(Benzyloxy)phenyl)naphthalene (3j).²³ White solid (26 mg, 42%); mp 157.3–159.5 °C. EtOAc/petroleum ether = 1:70. ^1H NMR (400 MHz, CDCl_3): δ 8.02 (s, 1H), 7.93–7.83 (m, 3H), 7.75–7.69 (m, 1H), 7.53–7.45 (m, 4H), 7.44–7.37 (m, 3H), 7.37–7.30 (m, 3H), 7.03–6.96 (m, 1H), 5.15 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 159.2 (s), 142.7 (s), 138.3 (s), 137.0 (s), 133.6 (s), 132.7 (s), 129.9 (s), 128.6 (s), 128.4 (s), 128.2 (s), 128.0 (s), 127.6 (s), 127.6 (s), 126.3 (s), 126.0 (s), 125.9 (s), 125.5 (s), 120.2 (s), 114.2 (s), 113.6 (s), 70.1 (s).

2-(4-Propoxyphenyl)naphthalene (3k). White solid (39 mg, 74%); mp 132.7–133.5 °C. EtOAc/petroleum ether = 1:80. ^1H NMR (400 MHz, CDCl_3): δ 7.97 (s, 1H), 7.91–7.79 (m, 3H), 7.70 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.52–7.39 (m, 2H), 7.00 (d, J = 8.4 Hz, 2H), 3.97 (t, J = 6.5 Hz, 2H), 1.89–1.78 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 158.8 (s), 138.2 (s), 133.7 (s), 133.4 (s), 132.3 (s), 128.4 (s), 128.3 (s), 128.0 (s), 127.6 (s), 126.2 (s), 125.6 (s), 125.4 (s), 125.4 (s), 125.0 (s), 114.9 (s), 69.6 (s), 22.6 (s), 10.5 (s). HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{O}$, 263.1436; found, 263.1437.

2-(*p*-Tolyl)naphthalene (3l).¹⁹ White solid (19 mg, 44%); mp 88.3–89.1 °C. Petroleum ether. ^1H NMR (400 MHz, CDCl_3): δ 8.02 (s, 1H), 7.94–7.82 (m, 3H), 7.74 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 7.8 Hz, 2H), 7.53–7.42 (m, 2H), 7.30 (d, J = 7.7 Hz, 2H), 2.42 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 138.5 (s), 138.2 (s), 137.2 (s), 133.7 (s), 132.5 (s), 129.6 (s), 128.3 (s), 128.1 (s), 127.6 (s), 127.2 (s), 126.2 (s), 125.8 (s), 125.5 (s), 125.4 (s), 21.1 (s).

2-(*m*-Tolyl)naphthalene (3m).¹⁹ Colorless oil (19 mg, 44%). Petroleum ether. ^1H NMR (400 MHz, CDCl_3): δ 8.03 (s, 1H), 7.94–7.82 (m, 3H), 7.74 (d, J = 8.4 Hz, 1H), 7.57–7.43 (m, 4H), 7.37 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 7.3 Hz, 1H), 2.46 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 141.1 (s), 138.7 (s), 138.4 (s), 133.7 (s), 132.6 (s), 128.8 (s), 128.3 (s), 128.2 (s), 128.2 (s), 128.1 (s), 127.6 (s), 126.2 (s), 125.8 (s), 125.7 (s), 125.7 (s), 124.5 (s), 21.6 (s).

2-(2-Methoxyphenyl)naphthalene (3n).²⁰ Yellow oil (29 mg, 62%). EtOAc/petroleum ether = 1:80. ^1H NMR (400 MHz, CDCl_3): δ 7.96 (s, 1H), 7.86 (d, J = 7.6 Hz, 3H), 7.69 (d, J = 8.4 Hz, 1H), 7.51–7.40 (m, 3H), 7.36 (t, J = 7.7 Hz, 1H), 7.13–6.98 (m, 2H), 3.82 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 156.7 (s), 136.2 (s), 133.4 (s), 132.4 (s), 131.1 (s), 130.7 (s), 128.8 (s), 128.1 (s), 128.1 (s), 127.6 (s), 127.2 (s), 125.9 (s), 125.8 (s), 120.9 (s), 111.3 (s), 55.6 (s).

2-(2,4-Dimethoxyphenyl)naphthalene (3o).²⁴ Yellow oil (34 mg, 64%). EtOAc/petroleum ether = 1:40. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (s, 1H), 7.84 (d, J = 8.4 Hz, 3H), 7.66 (d, J = 8.4 Hz, 1H), 7.50–7.41 (m, 2H), 7.35 (d, J = 8.4 Hz, 1H), 6.61 (d, J = 7.2 Hz, 2H), 3.88 (s, 3H), 3.82 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 160.4 (s), 157.7 (s), 136.0 (s), 133.5 (s), 132.2 (s), 131.5 (s), 128.2 (s), 128.0 (s), 127.8 (s), 127.5 (s), 127.1 (s), 125.8 (s), 125.6 (s), 123.6 (s), 104.7 (s), 99.1 (s), 55.5 (s).

2-(4-Phenoxyphenyl)naphthalene (3p). White solid (31 mg, 53%); mp 128.1–128.9 °C. EtOAc/petroleum ether = 1:80. ^1H

NMR (400 MHz, CDCl_3): δ 8.00 (s, 1H), 7.93–7.82 (m, 3H), 7.77–7.63 (m, 3H), 7.54–7.43 (m, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.19–7.01 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 157.1 (s), 156.9 (s), 137.8 (s), 136.1 (s), 133.7 (s), 132.4 (s), 129.8 (s), 128.7 (s), 128.4 (s), 128.1 (s), 127.6 (s), 126.3 (s), 125.8 (s), 125.4 (s), 123.4 (s), 119.1 (s), 119.0 (s). HRMS (APCI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{22}\text{H}_{16}\text{O}$, 296.1201; found, 296.1197.

2-(4-Methoxy-3,5-dimethylphenyl)naphthalene (3q). Yellow oil (24 mg, 45%). EtOAc/petroleum ether = 1:80. ^1H NMR (400 MHz, CDCl_3): δ 7.98 (s, 1H), 7.91–7.82 (m, 3H), 7.70 (d, J = 8.4 Hz, 1H), 7.53–7.42 (m, 2H), 7.37 (s, 2H), 3.78 (s, 3H), 2.38 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 156.7 (s), 138.3 (s), 136.6 (s), 133.7 (s), 132.4 (s), 131.2 (s), 128.2 (s), 128.1 (s), 127.8 (s), 127.6 (s), 126.2 (s), 125.7 (s), 125.6 (s), 125.4 (s), 59.8 (s), 16.3 (s). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 163.6 (s), 145.2 (s), 137.7 (s), 135.2 (s), 133.7 (s), 132.5 (s), 130.0 (s), 128.7 (s), 128.1 (s), 127.7 (s), 126.5 (s), 126.0 (s), 125.2 (s), 125.0 (s), 110.9 (s), 53.6 (s). HRMS (APCI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{O}$, 263.1436; found, 263.1433.

2-Methoxy-5-(naphthalen-2-yl)pyridine (3r). White solid (25 mg, 53%); mp 106.2–107.1 °C. EtOAc/petroleum ether = 1:40. ^1H NMR (400 MHz, CDCl_3): δ 8.52 (s, 1H), 7.99–7.83 (m, 5H), 7.67 (d, J = 8.4 Hz, 1H), 7.55–7.45 (m, 2H), 6.88 (d, J = 8.5 Hz, 1H), 4.02 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 163.6 (s), 145.2 (s), 137.7 (s), 128.7 (s), 128.1 (s), 127.7 (s), 126.5 (s), 126.0 (s), 125.2 (s), 125.0 (s), 110.9 (s), 53.6 (s). HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{NO}$, 236.1075; found, 236.1073.

2-(3-Chloro-4-methoxyphenyl)naphthalene (3s). (34 mg, 63%); mp 139.1–140.3 °C. EtOAc/petroleum ether = 1:80. ^1H NMR (400 MHz, CDCl_3): δ 7.97 (d, J = 1.5 Hz, 1H), 7.93–7.84 (m, 3H), 7.75 (d, J = 2.3 Hz, 1H), 7.68 (dd, J = 8.5, 1.8 Hz, 1H), 7.58 (dd, J = 8.5, 2.3 Hz, 1H), 7.54–7.44 (m, 2H), 7.04 (d, J = 8.5 Hz, 1H), 3.97 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 154.5 (s), 136.8 (s), 134.6 (s), 133.6 (s), 132.5 (s), 129.1 (s), 128.5 (s), 128.1 (s), 127.6 (s), 126.5 (s), 126.4 (s), 126.0 (s), 125.3 (s), 125.1 (s), 122.9 (s), 112.3 (s), 56.3 (s). HRMS (APCI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{13}\text{ClO}$, 268.0655; found, 268.0653.

2-(4-Chlorophenyl)naphthalene (3t).²² White solid (21 mg, 44%); mp 130.3–131.4 °C. Petroleum ether. ^1H NMR (400 MHz, CDCl_3): δ 8.00 (s, 1H), 7.95–7.83 (m, 3H), 7.69 (d, J = 8.5 Hz, 1H), 7.64 (d, J = 8.3 Hz, 2H), 7.55–7.48 (m, 2H), 7.45 (d, J = 8.3 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 139.6 (s), 137.3 (s), 133.6 (s), 133.5 (s), 132.7 (s), 129.0 (s), 128.6 (s), 128.6 (s), 128.2 (s), 127.7 (s), 126.5 (s), 126.1 (s), 125.7 (s), 125.2 (s).

2-(3,5-Difluorophenyl)naphthalene (3u).²⁵ White solid (36 mg, 75%); mp 118.5–119.6 °C. Petroleum ether. ^1H NMR (400 MHz, CDCl_3): δ 8.01 (s, 1H), 7.97–7.82 (m, 3H), 7.66 (d, J = 8.4 Hz, 1H), 7.59–7.46 (m, 2H), 7.25–7.19 (m, 2H), 6.82 (t, J = 8.7 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 163.4 (dd, $J_{\text{C-F}}$ = 13.2, 248.9 Hz), 144.5 (t, $J_{\text{C-F}}$ = 9.5 Hz), 136.2 (t, $J_{\text{C-F}}$ = 2.6 Hz), 133.5 (s), 133.1 (s), 128.8 (s), 128.3 (s), 127.7 (s), 126.7 (s), 126.6 (s), 126.1 (s), 124.8 (s), 110.2 (dd, $J_{\text{C-F}}$ = 7.1, 18.8 Hz), 102.6 (t, $J_{\text{C-F}}$ = 25.6 Hz).

2-(3-Fluorophenyl)naphthalene (3v).²⁶ White solid (28 mg, 63%); mp 79.4–81.0 °C. Petroleum ether. ^1H NMR (400 MHz, CDCl_3): δ 8.03 (s, 1H), 7.97–7.82 (m, 3H), 7.71 (d, J = 8.4 Hz, 1H), 7.56–7.47 (m, 3H), 7.47–7.39 (m, 2H), 7.07 (t, J = 8.1 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 163.3 (d, $J_{\text{C-F}}$ = 246.5 Hz), 143.4 (d, $J_{\text{C-F}}$ = 7.8 Hz), 137.2 (d, $J_{\text{C-F}}$ = 2.2 Hz), 133.6 (s), 132.8 (s), 130.3 (d, $J_{\text{C-F}}$ = 8.4 Hz), 128.6 (s), 128.2 (s), 127.7 (s), 126.5 (s), 126.2 (s), 126.0 (s), 125.2 (s), 123.0 (d, $J_{\text{C-F}}$ = 2.7 Hz), 114.2 (dd, $J_{\text{C-F}}$ = 13.6, 22.1 Hz).

2-(3-(Trifluoromethyl)phenyl)naphthalene (3w). White solid (40 mg, 74%); mp 59.2–60.1 °C. Petroleum ether. ^1H NMR (400 MHz, CDCl_3): δ 8.05 (s, 1H), 8.01–7.84 (m, 5H), 7.73 (d, J = 8.3 Hz, 1H), 7.67–7.56 (m, 2H), 7.57–7.45 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, CDCl_3): δ 141.9 (s), 137.0 (s), 133.6 (s), 132.9 (s), 130.7 (s), 129.3 (s), 128.8 (s), 128.3 (s), 127.7 (s), 126.6 (s), 126.4 (s), 126.2 (s), 125.2 (s), 124.2 (q, $J_{\text{C-F}}$ = 3.8 Hz), 124.0 (q, $J_{\text{C-F}}$ = 3.8 Hz), 122.9 (q, $J_{\text{C-F}}$ = 273.4 Hz). HRMS (APCI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{17}\text{H}_{11}\text{F}_3$, 272.0813; found, 272.0813.

2-(3-Chlorophenyl)naphthalene (3x).²⁷ White solid (41 mg, 86%); mp 67.8–69.1 °C. Petroleum ether. ¹H NMR (400 MHz, CDCl₃): δ 8.01 (s, 1H), 7.89 (m, 3H), 7.69 (d, *J* = 7.7 Hz, 2H), 7.63–7.56 (m, 1H), 7.50 (d, *J* = 3.8 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H). ¹³C{¹H} (101 MHz, CDCl₃): δ 143.0 (s), 137.1 (s), 134.7 (s), 133.6 (s), 132.8 (s), 130.1 (s), 128.6 (s), 128.2 (s), 127.7 (s), 127.5 (s), 127.3 (s), 126.5 (s), 126.3 (s), 126.0 (s), 125.5 (s), 125.2 (s).

1-(4-Methoxyphenyl)naphthalene (4a).²⁸ White solid (21 mg, 45%); mp 113.7–114.6 °C. EtOAc/petroleum ether = 1:80. ¹H NMR (400 MHz, CDCl₃): δ 7.91 (t, *J* = 9.1 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.54–7.46 (m, 2H), 7.42 (t, *J* = 8.2 Hz, 4H), 7.03 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H). ¹³C{¹H} (101 MHz, CDCl₃): δ 158.9 (s), 139.9 (s), 133.8 (s), 133.1 (s), 131.8 (s), 131.1 (s), 128.2 (s), 127.3 (s), 126.9 (s), 126.1 (s), 125.9 (s), 125.7 (s), 125.4 (s), 113.7 (s), 55.4 (s).

4-Methoxy-1,1'-biphenyl (4b).²⁹ White solid (24 mg, 65%); mp 95.5–96.7 °C. EtOAc/petroleum ether = 1:100. ¹H NMR (400 MHz, CDCl₃): δ 7.54 (t, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 1H). ¹³C{¹H} (101 MHz, CDCl₃): δ 159.1 (s), 140.8 (s), 133.8 (s), 128.7 (s), 128.1 (s), 126.7 (s), 126.6 (s), 114.2 (s), 55.3 (s).

4'-Methoxy-2-methyl-1,1'-biphenyl (4c).³⁰ Colorless oil (22 mg, 55%). EtOAc/petroleum ether = 1:100. ¹H NMR (400 MHz, CDCl₃): δ 7.28–7.24 (m, 4H), 7.23–7.20 (m, 2H), 6.97–6.95 (m, 1H), 6.95–6.93 (m, 1H), 3.85 (s, 3H), 2.28 (s, 3H). ¹³C{¹H} (101 MHz, CDCl₃): δ 158.5 (s), 141.5 (s), 135.5 (s), 134.3 (s), 130.3 (s), 130.2 (s), 129.9 (s), 127.0 (s), 125.7 (s), 113.5 (s), 55.3 (s).

4'-Methoxy-3-methyl-1,1'-biphenyl (4d).²⁹ White solid (22 mg, 55%); mp 51.5–52.8 °C. EtOAc/petroleum ether = 1:100. ¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.39–7.28 (m, 3H), 7.12 (d, *J* = 6.9 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 3.85 (s, 3H), 2.41 (s, 3H). ¹³C{¹H} (101 MHz, CDCl₃): δ 159.1 (s), 140.8 (s), 138.3 (s), 133.9 (s), 128.6 (s), 128.1 (s), 127.6 (s), 127.4 (s), 123.8 (s), 114.1 (s), 55.3 (s), 21.5 (s).

4-Methoxy-4'-methyl-1,1'-biphenyl (4e).²⁹ White solid (27 mg, 68%); mp 88.4–89.5 °C. EtOAc/petroleum ether = 1:100. ¹H NMR (400 MHz, CDCl₃): δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.26–7.21 (m, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 3.84 (s, 3H), 2.38 (s, 3H). ¹³C{¹H} (101 MHz, CDCl₃): δ 158.9 (s), 138.0 (s), 136.3 (s), 133.7 (s), 129.4 (s), 127.9 (s), 126.6 (s), 114.1 (s), 55.3 (s), 21.0 (s).

4-Chloro-4'-methoxy-1,1'-biphenyl (4f).³¹ White solid (25 mg, 57%); mp 110.1–112.4 °C. EtOAc/petroleum ether = 1:100. ¹H NMR (400 MHz, CDCl₃): δ 7.57–7.42 (m, 4H), 7.37 (d, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H). ¹³C{¹H} (101 MHz, CDCl₃): δ 159.3 (s), 139.3 (s), 132.6 (s), 132.5 (s), 128.8 (s), 128.0 (s), 127.9 (s), 114.3 (s), 55.4 (s).

3,5-Difluoro-4'-methoxy-1,1'-biphenyl (4g).³² White solid (23 mg, 52%); mp 73.2–75.9 °C. EtOAc/petroleum ether = 1:100. ¹H NMR (400 MHz, CDCl₃): δ 7.51–7.46 (m, 2H), 7.09–7.02 (m, 2H), 7.01–6.95 (m, 2H), 6.77–6.69 (m, 1H), 3.86 (s, 3H). ¹³C{¹H} (101 MHz, CDCl₃): δ 164.5 (d, *J* = 13.2 Hz), 162.1 (d, *J* = 13.3 Hz), 160.0 (s), 144.1 (t), 131.3 (t), 128.1 (s), 114.4 (s), 109.4 (d, *J* = 7.0 Hz), 109.3 (d, *J* = 7.0 Hz), 101.8 (t), 55.4 (s).

(E)-1-Methoxy-4-styrylbenzene (4h).³¹ White solid (18 mg, 43%); mp 134.5–135.8 °C. EtOAc/petroleum ether = 1:100. ¹H NMR (400 MHz, CDCl₃): δ 7.52–7.43 (m, 4H), 7.37–7.31 (m, 2H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.10–6.94 (m, 2H), 6.92–6.87 (m, 2H), 3.83 (s, 3H). ¹³C{¹H} (101 MHz, CDCl₃): δ 159.3 (s), 137.6 (s), 130.1 (s), 128.6 (s), 128.2 (s), 127.7 (s), 127.2 (s), 126.6 (s), 126.2 (s), 114.1 (s), 55.3 (s).

4-Methoxy-1,1':4',1''-Terphenyl (4i).³³ White solid (26 mg, 50%); mp 225.3–225.8 °C. EtOAc/petroleum ether = 1:100. ¹H NMR (400 MHz, CDCl₃): δ 7.70–7.60 (m, 6H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 2H), 3.86 (s, 3H). ¹³C{¹H} (101 MHz, CDCl₃): δ 159.2 (s), 140.8 (s), 139.7 (s), 139.5 (s), 133.2 (s), 128.8 (s), 128.0 (s), 127.4 (s), 127.2 (s), 127.03 (s), 126.98 (s), 114.3 (s), 55.4 (s).

4,4'-Dimethoxy-1,1'-biphenyl (4j).³² White solid (23 mg, 54%); mp 171–172 °C. EtOAc/petroleum ether = 1:40. ¹H NMR (400 MHz, CDCl₃): δ 7.50–7.47 (m, 2H), 7.47–7.44 (m, 2H), 6.98–6.96 (m, 2H), 6.95–6.93 (m, 2H), 3.84 (s, 6H). ¹³C{¹H} (101 MHz, CDCl₃): δ 158.7 (s), 133.5 (s), 127.7 (s), 114.1 (s), 55.3 (s).

4'-(tert-Butyl)-3-methoxy-1,1'-biphenyl (4k).³⁴ Yellow oil (24 mg, 50%). EtOAc/petroleum ether = 1:100. ¹H NMR (400 MHz, CDCl₃): δ 7.56–7.51 (m, 2H), 7.49–7.43 (m, 2H), 7.37–7.31 (m, 1H), 7.21–7.15 (m, 1H), 7.14–7.10 (m, 1H), 6.90–6.85 (m, 1H), 3.86 (s, 3H), 1.36 (s, 9H). ¹³C{¹H} (101 MHz, CDCl₃): δ 159.9 (s), 150.4 (s), 142.6 (s), 138.2 (s), 129.7 (s), 126.8 (s), 125.7 (s), 119.6 (s), 112.7 (s), 112.4 (s), 55.3 (s), 34.5 (s), 31.4 (s).

4-Isopropyl-1,1'-biphenyl (4l).³⁵ Colorless Oil (20 mg, 48%) petroleum ether. ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.33–7.28 (m, 3H), 3.02–2.89 (m, 1H), 1.29 (d, *J* = 6.8 Hz, 8H). ¹³C{¹H} (101 MHz, CDCl₃): δ 148.0 (s), 141.2 (s), 138.7 (s), 128.7 (s), 127.1 (s), 127.0 (s), 126.9 (s), 126.8 (s), 33.8 (s), 24.0 (s).

2-(3-Chlorophenyl)-6-methoxynaphthalene (4m). (36 mg, 67%); mp 99.6–100.6 °C. EtOAc/petroleum ether = 1:100. ¹H NMR (400 MHz, CDCl₃): δ 7.93 (s, 1H), 7.78 (t, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 9.8 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 12.4 Hz, 2H), 3.93 (s, 3H). ¹³C{¹H} (101 MHz, CDCl₃): δ 158.0 (s), 143.1 (s), 134.9 (s), 134.7 (s), 134.1 (s), 130.0 (s), 129.8 (s), 129.1 (s), 127.4 (s), 127.3 (s), 127.0 (s), 125.8 (s), 125.7 (s), 125.3 (s), 119.4 (s), 105.6 (s), 55.4 (s). HRMS (APCI-TOF) *m/z*: [M]⁺ calcd for C₁₇H₁₃ClO, 268.0655; found, 268.0654.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.0c02266>.

¹H NMR and ¹³C NMR spectra and HRMS spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Yong-Ming Zhu – College of Pharmaceutical Sciences, Soochow University, Suzhou 215123, China; orcid.org/0000-0002-7078-7908; Email: zhuyongming@suda.edu.cn

Authors

Jing-Ya Zhou – College of Pharmaceutical Sciences, Soochow University, Suzhou 215123, China

Rui-Qing Liu – College of Pharmaceutical Sciences, Soochow University, Suzhou 215123, China

Cheng-Yi Wang – College of Pharmaceutical Sciences, Soochow University, Suzhou 215123, China

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.joc.0c02266>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the financial support by PAPD (A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions).

■ REFERENCES

(1) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. Aryl–aryl bond formation one century after the discovery of the Ullmann reaction. *Chem. Rev.* **2002**, *102*, 1359–1470.

- (2) (a) De Meijere, A.; Bräse, S.; Oestreich, M. *Metal Catalyzed Cross-Coupling Reactions and More*; John Wiley & Sons, 2013. (b) Miyaura, N.; Suzuki, A. Palladium-catalyzed cross-coupling reactions of organoboron compounds. *Chem. Rev.* **1995**, *95*, 2457–2483.
- (3) (a) Suzuki, A. Cross-coupling reactions of organoboranes: an easy way to construct C–C bonds (Nobel Lecture). *Angew. Chem., Int. Ed.* **2011**, *50*, 6722–6737. (b) Blakemore, D. C.; Castro, L.; Churcher, I.; Rees, D. C.; Thomas, A. W.; Wilson, D. M.; Wood, A. Organic synthesis provides opportunities to transform drug discovery. *Nat. Chem.* **2018**, *10*, 383–394.
- (4) (a) Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. Palladium-catalyzed borylation of aryl halides or triflates with dialkoxyborane: A novel and facile synthetic route to arylboronates. *J. Org. Chem.* **2000**, *65*, 164–168. (b) Ishiyama, T.; Murata, M.; Miyaura, N. Palladium (0)-catalyzed cross-coupling reaction of alkoxydiboron with haloarenes: a direct procedure for arylboronic esters. *J. Org. Chem.* **1995**, *60*, 7508–7510.
- (5) De Meijere, A.; Bräse, S.; Oestreich, M. *Metal Catalyzed Cross-Coupling Reactions and More*; John Wiley & Sons, 2013.
- (6) (a) Goossen, L. J.; Rodríguez, N.; Goossen, K. Carboxylic acids as substrates in homogeneous catalysis. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100–3120. (b) Dzik, W. I.; Lange, P. P.; Goossen, L. J. Carboxylates as sources of carbon nucleophiles and electrophiles: comparison of decarboxylative and decarbonylative pathways. *Chem. Sci.* **2012**, *3*, 2671–2678.
- (7) (a) Frost, C. G.; Wadsworth, K. J. Rhodium catalyzed addition of boronic acids to anhydrides: a new method for the synthesis of ketones. *Chem. Commun.* **2001**, 2316–2317. (b) Oguma, K.; Miura, M.; Satoh, T.; Nomura, M. Rhodium-catalyzed coupling of sodium tetraphenylborate with acid anhydrides in the presence or absence of norbornene. *J. Organomet. Chem.* **2002**, *648*, 297–301.
- (8) Muto, K.; Yamaguchi, J.; Musaev, D. G.; Itami, K. Decarbonylative organoboron cross-coupling of esters by nickel catalysis. *Nat. Commun.* **2015**, *6*, 7508.
- (9) (a) Shi, S.; Meng, G.; Szostak, M. Synthesis of Biaryls through Nickel-Catalyzed Suzuki–Miyaura coupling of amides by carbon–nitrogen bond cleavage. *Angew. Chem., Int. Ed.* **2016**, *55*, 6959–6963. (b) Zhou, T.; Ji, C.-L.; Hong, X.; Szostak, M. Palladium-catalyzed decarbonylative Suzuki–Miyaura cross-coupling of amides by carbon–nitrogen bond activation. *Chem. Sci.* **2019**, *10*, 9865–9871.
- (10) Liu, C.; Ji, C.-L.; Qin, Z.-X.; Hong, X.; Szostak, M. Synthesis of Biaryls via Decarbonylative Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling of Carboxylic Acids. *iScience* **2019**, *19*, 749–759.
- (11) Malapit, C. A.; Bour, J. R.; Brigham, C. E.; Sanford, M. S. Base-free nickel-catalyzed decarbonylative Suzuki–Miyaura coupling of acid fluorides. *Nature* **2018**, *563*, 100–104.
- (12) Gooßen, L. J.; Paetzold, J. New Synthesis of Biaryls via Rh-Catalyzed Decarbonylative Suzuki-Coupling of Carboxylic Anhydrides with Arylboroxines. *Adv. Synth. Catal.* **2004**, *346*, 1665–1668.
- (13) Guo, L.; Srimontree, W.; Zhu, C.; Maity, B.; Liu, X. Q.; Cavallo, L.; Rueping, M. Nickel-catalyzed Suzuki–Miyaura cross-couplings of aldehydes. *Nat. Commun.* **2019**, *10*, 1957.
- (14) Zhou, J.-Y.; Tao, S.-W.; Liu, R.-Q.; Zhu, Y.-M. Forging C–S Bonds through Nickel-Catalyzed Aryl Anhydrides with Thiophenols: Decarbonylation or Decarbonylation Accompanied by Decarboxylation. *J. Org. Chem.* **2019**, *84*, 11891–11901.
- (15) (a) Spránitz, P.; Sőregi, P.; Botlik, B.; Berta, M.; Soós, T. Organocatalytic Desymmetrisation of Fittig’s Lactones: Deuterium as a Reporter Tag for Hidden Racemisation. *Synthesis* **2019**, *51*, 1263–1272. (b) Phakhodee, W.; Duangkamol, C.; Wangngae, S.; Pattarawarapan, M. Acid anhydrides and the unexpected N, N-diethylamides derived from the reaction of carboxylic acids with $\text{Ph}_3\text{P}/\text{I}_2/\text{Et}_3\text{N}$. *Tetrahedron Lett.* **2016**, *57*, 325–328. (c) Burton, S. G.; Kaye, P. T. A convenient preparation of carboxylic acid anhydrides using a “supported” phosphorus pentoxide reagent. *Synth. Commun.* **1989**, *19*, 3331–3335.
- (16) Yamaguchi, J.; Muto, K.; Itami, K. Recent Progress in Nickel-Catalyzed Biaryl Coupling. *Eur. J. Org. Chem.* **2013**, *2013*, 19–30.
- (17) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. Recent advances in homogeneous nickel catalysis. *Nature* **2014**, *509*, 299–309.
- (18) Partyka, D. V. Transmetalation of unsaturated carbon nucleophiles from boron-containing species to the mid to late d-block metals of relevance to catalytic C–X coupling reactions (X = C, F, N, O, Pb, S, Se, Te). *Chem. Rev.* **2011**, *111*, 1529–1595.
- (19) Cao, Z.-C.; Luo, Q.-Y.; Shi, Z.-J. Practical cross-coupling between O-based electrophiles and aryl bromides via Ni catalysis. *Org. Lett.* **2016**, *18*, 5978–5981.
- (20) Chung, K. H.; So, C. M.; Wong, S. M.; Luk, C. H.; Zhou, Z.; Lau, C. P.; Kwong, F. Y. An efficient palladium–benzimidazolyl phosphine complex for the Suzuki–Miyaura coupling of aryl mesylates: facile ligand synthesis and metal complex characterization. *Chem. Commun.* **2012**, *48*, 1967–1969.
- (21) Cao, Z.-C.; Xie, S.-J.; Fang, H.; Shi, Z.-J. Ni-catalyzed cross-coupling of dimethyl aryl amines with arylboronic esters under reductive conditions. *J. Am. Chem. Soc.* **2018**, *140*, 13575–13579.
- (22) Minami, H.; Saito, T.; Wang, C.; Uchiyama, M. Organoaluminum-Mediated Direct Cross-Coupling Reactions. *Angew. Chem., Int. Ed.* **2015**, *54*, 4665–4668.
- (23) Zhang, Z.-B.; Ji, C.-L.; Yang, C.; Chen, J.; Hong, X.; Xia, J.-B. Nickel-Catalyzed Kumada Coupling of Boc-Activated Aromatic Amines via Nondirected Selective Aryl C–N Bond Cleavage. *Org. Lett.* **2019**, *21*, 1226–1231.
- (24) Petronzi, C.; Filosa, R.; Peduto, A.; Monti, M. C.; Margarucci, L.; Massa, A.; Ercolino, S. F.; Bizzarro, V.; Parente, L.; Riccio, R.; de Caprariis, P. Structure-based design, synthesis and preliminary anti-inflammatory activity of bolinaquinone analogues. *Eur. J. Med. Chem.* **2011**, *46*, 488–496.
- (25) Wu, G.-J.; Han, F.-S.; Zhao, Y.-L. Palladacycles derived from arylphosphinamides for mild Suzuki–Miyaura cross-couplings. *RSC Adv.* **2015**, *5*, 69776–69781.
- (26) Li, B.-J.; Li, Y.-Z.; Lu, X.-Y.; Liu, J.; Guan, B.-T.; Shi, Z.-J. Cross-Coupling of Aryl/Alkenyl Pivalates with Organozinc Reagents through Nickel-Catalyzed C–O Bond Activation under Mild Reaction Conditions. *Angew. Chem., Int. Ed.* **2008**, *47*, 10124–10127.
- (27) Zhou, H.; Li, J.; Yang, H.; Xia, C.; Jiang, G. Triarylphosphines as Aryl Donors for Pd(II)-Catalyzed Aromatic Coupling of Oxabenzonorbornadienes. *Org. Lett.* **2015**, *17*, 4628–4631.
- (28) Wei, J.; Liu, K.-M.; Duan, X.-F. Cobalt-Catalyzed Biaryl Couplings via C–F Bond Activation in the Absence of Phosphine or NHC Ligands. *J. Org. Chem.* **2017**, *82*, 1291–1300.
- (29) Ghosh, R.; Sarkar, A. Bidentate P, N–P Ligand for Nickel-Catalyzed Cross-Coupling of Aryl or Benzyl Chlorides with ArMgX . *J. Org. Chem.* **2010**, *75*, 8283–8286.
- (30) Chen, K.; Chen, W.; Yi, X.; Chen, W.; Liu, M.; Wu, H. Sterically hindered N-heterocyclic carbene/palladium (ii) catalyzed Suzuki–Miyaura coupling of nitrobenzenes. *Chem. Commun.* **2019**, *55*, 9287–9290.
- (31) Quibell, J. M.; Duan, G.; Perry, G. J. P.; Larrosa, I. Decarboxylative Suzuki–Miyaura coupling of (hetero)aromatic carboxylic acids using iodine as the terminal oxidant. *Chem. Commun.* **2019**, *55*, 6445–6448.
- (32) Salemi, H.; Kaboudin, B.; Kazemi, F.; Yokomatsu, T. Highly water-dispersible magnetite nanoparticle supported-palladium- β -cyclodextrin as an efficient catalyst for Suzuki–Miyaura and Sonogashira coupling reactions. *RSC Adv.* **2016**, *6*, S2656–S2664.
- (33) Seo, T.; Ishiyama, T.; Kubota, K.; Ito, H. Solid-state Suzuki–Miyaura cross-coupling reactions: olefin-accelerated C–C coupling using mechanochemistry. *Chem. Sci.* **2019**, *10*, 8202–8210.
- (34) Lee, H. W.; So, C. M.; Yuen, O. Y.; Wong, W.; Kwong, F. Y. Palladium-catalyzed cross-coupling of (hetero)aryl or alkenyl sulfonates with aryl titanium as the multi-functional reagent. *Org. Chem. Front.* **2020**, *7*, 926.
- (35) Schmidt, A.; Rahimi, A. A versatile catalyst system for Suzuki–Miyaura syntheses of sterically hindered biaryls employing a cyclobutene-1, 2-bis(imidazolium) salt. *Chem. Commun.* **2010**, *46*, 2995–2997.