

# Nickel-Catalyzed Decarbonylative Coupling of Aryl Esters and Arylboronic Acids

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A variety of functionalized biaryls can be accessed by coupling aryl and heteroaryl esters with boronic acids in Suzuki–Miyaura-type decarbonylative cross-coupling catalyzed by an affordable catalyst system composed of Ni(cod)<sub>2</sub> and PCy<sub>3</sub>. The methodology is tolerant of a variety of functional

groups and presents an attractive alternative to the use of palladium catalysis currently used in industry to acquire such bis(hetero)aryls, but also reveals challenges associated with nickel catalysis of esters in cross-coupling chemistry.

## Introduction

Situated just above palladium in the Periodic Table nickel is increasingly sought as an inexpensive alternative to palladium for use in cross-coupling methodologies. Nickel is able to access a variety of oxidation states, which allows for a diverse range of synthetically useful transformations.<sup>[1]</sup> The small atomic radius of nickel renders it more adept than palladium toward the activation of strong bonds, such as the C–O bonds of carboxylates,<sup>[2]</sup> carbamates,<sup>[3]</sup> and ethers.<sup>[4]</sup> Although the last decade has witnessed an increase in reports on nickel catalysis, to date catalysis with nickel remains much less studied than with palladium. Consequently, there lies great demand in further exploring the reactivity and catalytic potential of nickel.

Biaryls are considered “privileged structures” because of their prominence in pharmaceuticals.<sup>[5]</sup> In many cases, one or both of the aryl groups contain a heteroatom. Relevant examples include Gleevec, a tyrosine kinase inhibitor used to treat various types of cancers, as well as Atazanavir, an antiretroviral agent used to treat human immunodeficiency virus (HIV) (Figure 1).<sup>[6]</sup> Currently, the most common route to biaryls involves cross-coupling of aryl halides and organometallic reagents by using a palladium catalyst (Figure 2).<sup>[7,8]</sup> It is noteworthy that aryl chlorides, which are substantially less expensive than aryl bromides and iodides, tend to exhibit lower reactivity, presumably because of the stronger C–Cl bond relative to C–Br and C–I bonds. Biaryls may also be accessed by decarbonylative coupling with arenes.<sup>[9]</sup> Challenges associated with these methods include undesired homocoupling, sometimes use of toxic reagents

and or production of toxic by-products. Additionally, palladium is costly, and specialized ligands are required to circumvent low reactivity of aryl chlorides.<sup>[10]</sup> For heteroaryl compounds, the potential for catalyst poisoning by heteroatom binding presents an additional challenge in cross-coupling.

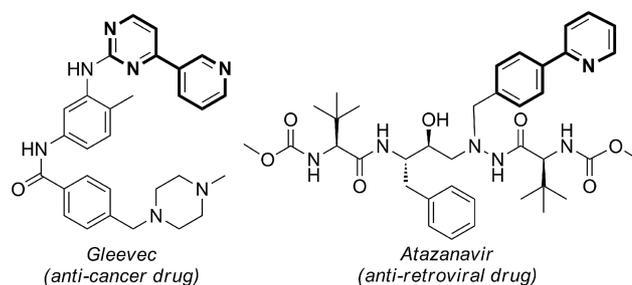
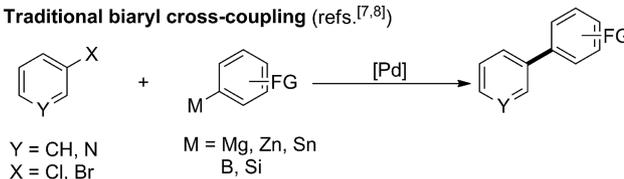
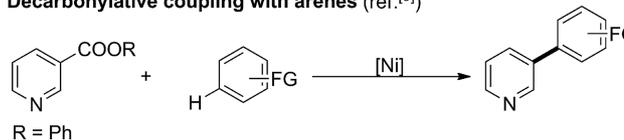


Figure 1. Examples of notable bis(hetero)aryls.

### Traditional biaryl cross-coupling (refs.<sup>[7,8]</sup>)



### Decarbonylative coupling with arenes (ref.<sup>[9]</sup>)



### This work

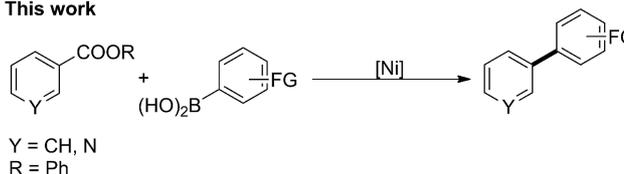


Figure 2. Cross-coupling routes to biaryls.

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Since Gooßen's report of a decarboxylative arylation process in 2006,<sup>[11]</sup> aryl compounds have received intensified interest as attractive cross-coupling partners in place of aryl halides due to their low cost, commercial availability and high thermal stability.<sup>[12]</sup> Several reports of cross-coupling using ethers,<sup>[4]</sup> aryl sulfonates,<sup>[13]</sup> phosphates,<sup>[14]</sup> carbamates,<sup>[3]</sup> and sulfamates have emerged in the last decade.<sup>[15]</sup> Notably in 2012, Itami et al. described an example decarbonylative coupling of aryl esters and azoles catalyzed by nickel and dcype [1,2-bis(dicyclohexylphosphino)ethane].<sup>[9]</sup> Although the method provided a route to bis(hetero)aryls, the azole scope was limited. Later in 2013, Itami and colleagues extended this work to the decarbonylative coupling of alkenyl esters and azoles also using nickel and dcype.<sup>[16]</sup>

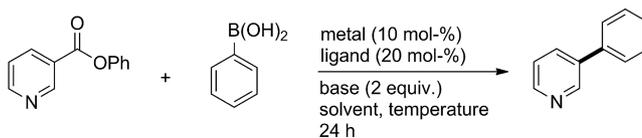
Despite these accounts, the use of esters as the electrophilic cross-coupling partner remains rare.<sup>[2,9,16]</sup> Owing to the ubiquitous nature of esters, their use in cross-coupling reactions would be highly advantageous for late-stage synthetic manipulation. Thus, given the small number of cross-coupling accounts using esters and our previous work in the field of nickel catalysis,<sup>[17]</sup> we sought to investigate nickel-catalyzed C–O activation<sup>[2–4,18]</sup> toward the preparation of biaryl scaffolds. Herein, we report that use of ArB(OH)<sub>2</sub> expands the scope of biaryls accessible by decarbonylative coupling of aryl esters.

## Results and Discussion

Our investigation began by identifying a suitable transmetallating reagent that could be coupled with phenyl nicotinate in the presence of Ni(cod)<sub>2</sub> (cod = 1,5-cyclooctadiene) and an appropriate phosphine ligand. Among those considered, including arylboronic acids, arylzinc reagents and amines, arylboronic acids afforded the best results (details provided in the Supporting Information). Markedly, arylboronic acids offer many advantages as cross-coupling partners since they are widely available, exhibit air and moisture stability and are affordable. Having established that nickel was necessary for catalysis (Table 1, Entry 1), our next task involved identifying the optimal combination of ligand, solvent and temperature (Table 1).

A selection of bidentate and monodentate phosphine ligands were screened in the presence of 10 mol-% Ni(cod)<sub>2</sub>. Of the bidentate ligands considered, only dcype generated the desired product, albeit in < 5% (Table 1, Entry 2). Interestingly, Itami et al. found dcype to be essential for nickel-catalyzed decarbonylative coupling of aryl esters and azoles to proceed.<sup>[9,16]</sup> The other bidentate phosphine ligands examined, including DIPHOS [1,2-bis(diphenylphosphino)ethane], dppb [1,2-bis(diphenylphosphino)butane], dppm [1,2-bis(diphenylphosphino)methane], and DPEPhos [oxybis(2,1-phenylene)bis(diphenylphosphine)], were all ineffective for the desired transformation (Table 1, Entries 3–6). The monodentate phosphine ligands PPh<sub>3</sub> and PCy<sub>3</sub> provided 3-phenylpyridine in 11% and 23% yield, respectively (Table 2, Entries 7 and 8). We selected PCy<sub>3</sub> for fur-

Table 1. Reaction condition optimizations. To a sealed tube was added phenyl nicotinate (0.5 mmol), phenylboronic acid (0.75 mmol), Ni(cod)<sub>2</sub> (0.05 mmol), ligand (0.1 mmol), base (1 mmol), and solvent (2 mL).



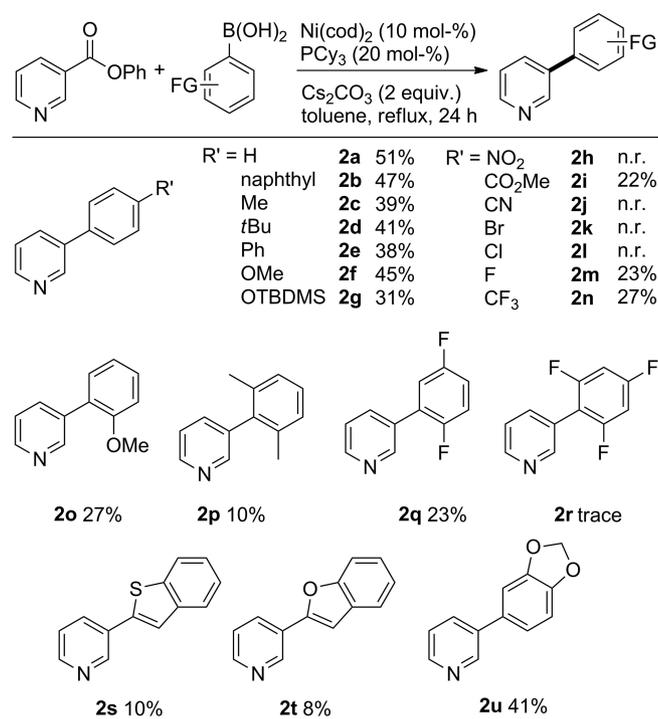
Entry	Metal	Ligand	Base	Solvent	T [°C]	Yield <sup>[a]</sup>
1	none	none	Cs <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	100	0%
2	Ni(cod) <sub>2</sub>	dcype	K <sub>3</sub> PO <sub>4</sub>	1,4-dioxane	100	<5%
3	Ni(cod) <sub>2</sub>	DIPHOS	K <sub>3</sub> PO <sub>4</sub>	1,4-dioxane	100	0%
4	Ni(cod) <sub>2</sub>	dppb	K <sub>3</sub> PO <sub>4</sub>	1,4-dioxane	100	0%
5	Ni(cod) <sub>2</sub>	dppm	K <sub>3</sub> PO <sub>4</sub>	1,4-dioxane	100	0%
6	Ni(cod) <sub>2</sub>	DPEPhos	K <sub>3</sub> PO <sub>4</sub>	1,4-dioxane	100	0%
7	Ni(cod) <sub>2</sub>	PPh <sub>3</sub>	K <sub>3</sub> PO <sub>4</sub>	1,4-dioxane	100	11%
8	Ni(cod) <sub>2</sub>	PCy <sub>3</sub>	K <sub>3</sub> PO <sub>4</sub>	1,4-dioxane	100	23%
9	Ni(cod) <sub>2</sub>	PCy <sub>3</sub>	K <sub>3</sub> PO <sub>4</sub>	1,4-dioxane	150	26%
10	Ni(cod) <sub>2</sub>	PCy <sub>3</sub>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	150	28%
11	Ni(cod) <sub>2</sub>	PCy <sub>3</sub>	Cs <sub>2</sub> CO <sub>3</sub>	toluene	150	31%
12 <sup>[b]</sup>	Ni(cod) <sub>2</sub>	PCy <sub>3</sub>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	150	27%
13 <sup>[c]</sup>	Ni(cod) <sub>2</sub>	PCy <sub>3</sub>	Cs <sub>2</sub> CO <sub>3</sub>	toluene	110	60%
14	Pd(OAc) <sub>2</sub>	PCy <sub>3</sub>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	100	0%
15	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl	none	K <sub>3</sub> PO <sub>4</sub>	1,4-dioxane	100	0%

[a] GC yield average based upon two runs by using *n*-dodecane as an internal standard. [b] Reaction mixture microwaved at 150 °C (400 W) for 45 min. [c] Reaction performed under a continuous flow of N<sub>2</sub>.

ther study and focused our attention on optimizing the solvent and the reaction temperature. When the reaction was performed in toluene at 150 °C, product conversion was found to increase slightly to 31% (Table 1, Entry 11). Microwaving the reaction mixture at 150 °C for 45 min gave the same result as conventional heating (Table 1, Entry 12). A variety of inorganic bases were additionally screened.<sup>[19]</sup> Of those considered, Cs<sub>2</sub>CO<sub>3</sub> gave the best result (28%; Table 1, Entry 10). Given these low yields, we wondered if CO poisoning of the Ni catalyst system might be the cause of the low turnover.

To test this hypothesis, the reaction was performed under a continuous flow of N<sub>2</sub> (Table 1, Entry 13), which gave a 60% GC yield, corresponding to a substantial improvement. Presumably, performing the reaction under a constant flow of N<sub>2</sub> facilitates removal of CO from the flask, thus mitigating catalyst poisoning. Photolysis using a broadband halogen lamp was also attempted; however, no improvement in yield was observed. Likewise, the addition of 10 mol-% of pyridine failed to provide any reaction enhancement. In accordance with these optimizations, the reaction conditions used were 10 mol-% of Ni(cod)<sub>2</sub> and

Table 2. Scope and limitation of boronic acids.



[a] Yields are reported for isolated products and are an average of two runs.

20 mol-% of PCy<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> (2 equiv.) in toluene at reflux for 24 h under a dynamic flow of N<sub>2</sub>.

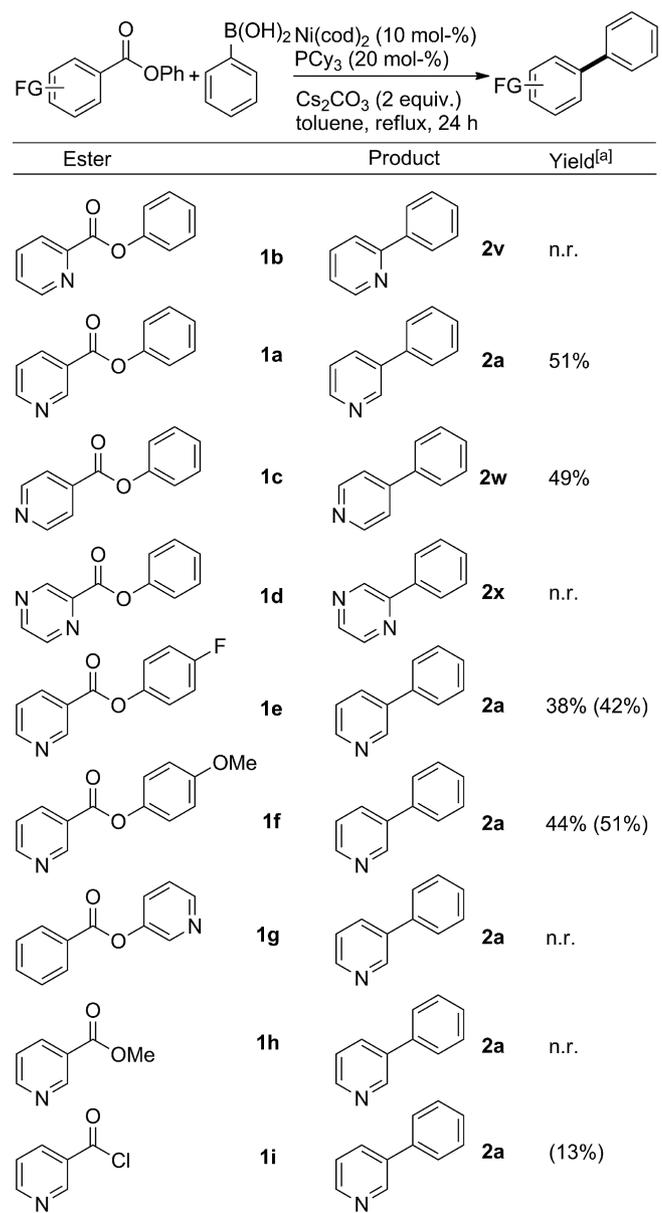
We next considered the scope of the reaction with respect to boronic acid and aryl ester. A variety of arylboronic acids possessing different electronic and steric properties were considered. Electron-rich and -neutral boronic acids gave the highest yields (Table 2; **2a–f**). Naphthyl- and biphenyl-based boronic acids were easily cross-coupled to phenyl nicotinate allowing for the generation of substituted polyarenes **2b** and **2e** in modest yields (Table 2). The reaction may also be performed on a gram scale; 3-phenylpyridine was obtained in 50% isolated yield. Mass balance is accounted for by unreacted starting material. Addition of a methyl or *tert*-butyl group in the *para* position of the aryl ring was also accommodated in the cases of **2c** and **2d** (Table 2). Aryl methyl ethers were tolerated in the reaction and were not susceptible to cleavage by nickel (Table 2; **2f** and **2o**), indicating a preference for cleavage of the weaker ester C–O bond. Methyl esters were also tolerated in the reaction, illustrating chemoselective preference for aryl ester activation (Table 2; **2i**). Use of a boronic acid bearing a butyldimethylsilyl-protected alcohol was also tolerated in the reaction, giving **2g** providing a site for further functional-group interconversion (Table 2).

*ortho*-Substituted arylboronic acids (Table 2; **2o** and **2p**) could also be used as nucleophilic partners; however, these substrates provided low yields, presumably because of a decrease in the efficacy of transmetalation due to steric congestion. Benzofuran and benzothiophene were also coupled to phenyl nicotinate (Table 2; **2s** and **2t**). Methyleneedioxy

acetal is additionally permitted (Table 2; **2u**), offering potential access to diol functionality that can be utilized in later transformations. A limitation of this methodology was observed for electron-deficient boronic acids. Boronic acids possessing fluorine substitution gave low yields (Table 2; **2m**, **2q**, **2r**), while the presence of a cyano, nitro, chloro, or bromo substituent was also found to be not compatible with this transformation (Table 2; **2h**, **2j**, **2k** and **2l**). These limitations are consistent with related methodologies, which do not tolerate electron-poor arylboronic acids.<sup>[2d,2g]</sup>

Next, the scope of the aryl ester was considered (Table 3). Substitution of the nitrogen atom on the aryl ring was not limited to the 3-position. Phenyl 4-pyridinecarboxylate can also be successfully cross-coupled to phenylboronic acid

Table 3. Scope and limitation of heteroaryl esters.



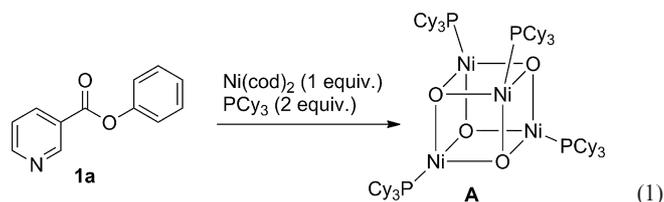
[a] Yields are reported for isolated products and are an average of two runs. [b] Numbers in parentheses represent GC yield averages based upon two runs by using *n*-dodecane as an internal standard.

giving 4-phenylpyridine in 49% isolated yield (Table 3; **2w**). Aryl 2-pyridinecarboxylates were unreactive (Table 3; **1b** and **1d**). The presence of nitrogen in this position likely shuts down reactivity due to presumed coordination to nickel (*vide infra*). Altering the electronics of the (O–Ar) fragment of the aryl ester influenced the reaction outcome. A fluorine atom in the *para* position resulted in lower product yield (Table 3; **1e**). The presence of a methoxy substituent in the *para* position, however, gave 51% – a similar yield obtained by using phenyl nicotinate (Table 3; **1f**). When methyl nicotinate (Table 3; **1h**) was treated with phenylboronic acid, no desired product was observed. Use of nicotinoyl chloride (Table 3; **1i**) instead of phenyl nicotinate resulted in only 13% GC yield of 3-phenylpyridine.

It is also possible to cross-couple non-heteroaryl esters, although a mixture of biaryl and ketone is produced (Table 4). The ketone product may arise from transmetalation with the boronic acid before CO has been extruded. The electronics of both aryl ester and boronic acid were considered. Both electron-rich and electron-deficient aryl esters were accommodated; however, differences in product selectivity were observed. Aryl esters possessing electron-neutral or -withdrawing substituents showed predominant formation for the biaryl product (Table 4, Entries 1 and 5–7). Interestingly, electron-rich aryl esters primarily formed the undesired ketone product (Table 4, Entries 2 and 3). Consistent with results obtained with heteroaryl esters, electron-deficient boronic acids resulted in lower yields than electron-rich ones (Table 4, Entries 3, 4, 6, and 7). At rationale for the formation of the ketone product only when non-heteroaryl esters are used is not known and warrants further investigation.

Attempts were made to identify relative catalytic species. The first step may involve oxidative addition of an aryl ester CO–OPh bond or Ar–CO bond. Efforts to identify such a species through stoichiometric reactivity were unsuccessful. Over a period of 4 h a [D<sub>8</sub>]toluene solution of Ni(cod)<sub>2</sub>,

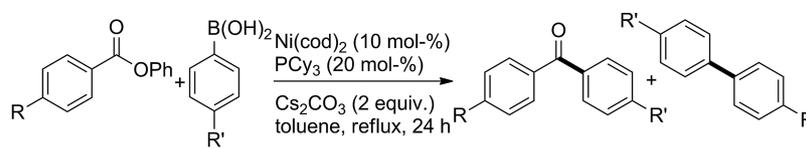
PCy<sub>3</sub>, and phenyl nicotinate was heated to 373 K giving a dark-red solution. NMR analysis showed a predominant signal at  $\delta = 42$  ppm [assignable to tetrameric aggregate **A**; Equation (1)], which grew in intensity as the reaction progressed. A series of transient phosphine-containing intermediates were also observed.<sup>[20]</sup> In 2010, Ogoshi et al. also encountered aggregate **A** in a report of nickel-catalyzed aldehyde coupling, where it was determined to be a catalytically ineffective off-cycle species.<sup>[21]</sup> We believe that **A** is likewise a decomposition product.



Another stoichiometric experiment was performed by using phenyl 2-pyridinecarboxylate (**1b**) in the hopes of observing the oxidative addition product [Equation (2)]. Instead, Ni(CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> (**B**; Figure 3) was isolated – an expected product of ester decarbonylation.<sup>[22]</sup> The presence of a nitrogen atom *ortho* to the ester group may play a critical role in facilitating Ni insertion into this bond. This result is consistent with the limitation of phenyl 2-pyridine- and 2-pyrazinecarboxylate substrates (Table 3; **1b** and **1d**) in the cross-coupling reaction. Such a species is proposed to be an off-cycle Ni(CO)-containing complex and lends support to the production of intermediate CO-containing species in this catalytic cycle. Crystallographic data for Ni(PCy<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub> (**B**) can be found in the Supporting Information.

Based on these results and literature reports, a possible mechanism for this methodology is presented in Figure 4,<sup>[8,23,24]</sup> although it should be noted that a detailed kinetic and mechanistic investigation has not yet been con-

Table 4. Scope and limitation of aryl esters.<sup>[a]</sup>



Entry			Ketone		Biaryl	
1	R = H	R' = OMe	<b>4a</b>	14%	<b>3a</b>	24%
2	R = Me	R' = OMe	<b>4b</b>	24%	<b>3b</b>	12%
3	R = OMe	R' = OMe	<b>4c</b>	33%	<b>3c</b>	0%
4	R = OMe	R' = CF <sub>3</sub>	<b>4d</b>	8%	<b>3d</b>	11%
5	R = F	R' = OMe	<b>4e</b>	12%	<b>3e</b>	25%
6	R = CO <sub>2</sub> Me	R' = OMe	<b>4f</b>	15%	<b>3f</b>	24%
7	R = CO <sub>2</sub> Me	R' = CF <sub>3</sub>	<b>4g</b>	0%	<b>3g</b>	34%

[a] Percentages represent <sup>1</sup>H NMR spectroscopy yields by using acetophenone as an internal standard.

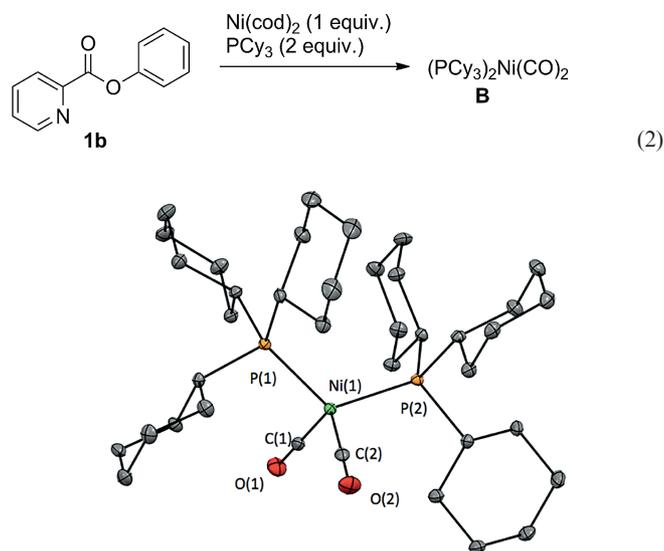


Figure 3. ORTEP depiction of the molecular structure of  $\text{Ni}(\text{PCy}_3)_2(\text{CO})_2$  (**B**) in the crystal (displacement ellipsoids are shown at the 50% probability level; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni(1)–P(1) 2.2503(8), Ni(1)–P(2) 2.2458(9), Ni(1)–C(1) 1.779(2), Ni(1)–C(2) 1.778(2), C(1)–O(1) 1.149(3), C(2)–O(2) 1.154(3); P(1)–Ni(1)–P(2) 120.35(3), P(1)–Ni(1)–C(1) 105.04(8), P(1)–Ni(1)–C(2) 105.51(8), P(2)–Ni(1)–C(2) 105.99(8).

ducted. The analysis presented is based on C–O cleavage, although C–C cleavage is also possible and cannot be excluded at this time (Figure 5). Following oxidative addition to give **I**, CO extrusion would give **II**, whereupon transmetalation would occur to give **III**. Confirmation that the aryl fragment bonded to the carbonyl group ( $\text{ArCO-R}$ ) is involved in the transmetalation was provided by substrate ester **1g**, because 3-phenylpyridine was not detected (Table 3). The CO extrusion and transmetalation steps likely occur at similar rates as evidenced by the products of reaction with phenyl benzoate (**1k**) to afford biaryl and ketone products in a 2:1 ratio (Table 4, Entry 1). Finally,

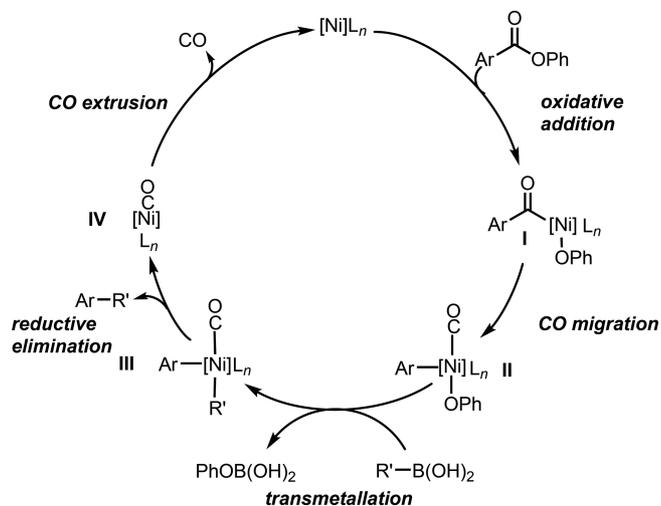


Figure 4. Possible reaction mechanism.

reductive elimination to yield the desired product followed by CO extrusion to reform the catalyst concludes the catalytic cycle. Notably, nickel can operate under various oxidation states;<sup>[1]</sup> however, the depiction in Figure 4 is consistent with the observed product distribution.

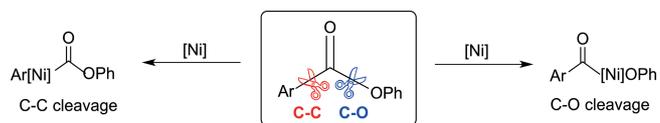


Figure 5. Possible bond cleavages for an aryl ester.

## Conclusions

We have reported an example of nickel-catalyzed decarbonylative Suzuki–Miyaura cross-coupling of aryl esters and boronic acids in modest yields. The method showcases a new economical route to biaryls, including heteroaryls, providing alternatives to commonly employed palladium catalysts and aryl halides. The reaction offers insight into the difficulties associated in cross-coupling esters by using nickel as a catalyst. Efforts to further expand the scope of this transformation and elucidate a better mechanistic understanding are currently underway in our laboratory.

## Experimental Section

**General Procedure for the Nickel-Catalyzed Decarbonylative Coupling of Heteroaryl Esters and Boronic Acids:** A 50 mL one-necked round-bottomed flask equipped with a Teflon stir bar was flame-dried and brought into the glovebox. Into this vessel were placed  $\text{Cs}_2\text{CO}_3$  (325.8 mg, 1 mmol, 2.0 equiv.), phenyl ester derivative (0.5 mmol, 1 equiv.), boronic acid (0.75 mmol, 1.5 equiv.),  $\text{Ni}(\text{cod})_2$  (13.5 mg, 0.05 mmol, 10 mol-%), tricyclohexylphosphine ( $\text{PCy}_3$ : 28.0 mg, 0.1 mmol, 20 mol-%) and toluene (4 mL). To the flask was attached a condenser equipped with an adapter for the attachment to an  $\text{N}_2$  line. The apparatus was removed from the glovebox and heated to reflux under a continuous flow of nitrogen for 24 h. After cooling of the vessel to room temperature, the crude reaction mixture was filtered through a small Celite plug with ethyl acetate and then concentrated in vacuo. Column chromatography was performed to afford the desired product. Yields are reported for isolated product and are an average of two runs.

**3-Phenylpyridine (2a) [1008-88-4]:**<sup>[25]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2a** as a colourless oil (39 mg, 51%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  = 8.89 (s, 1 H), 8.63 (s, 1 H), 7.92 (d,  $J$  = 7.9 Hz, 1 H), 7.60 (d,  $J$  = 6.8 Hz, 2 H), 7.49 (m, 4 H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz, 298 K):  $\delta$  = 148.62, 148.49, 138.01, 136.83, 134.51, 129.23, 128.25, 127.32, 123.72 ppm. HRMS (ESI): calcd. for  $\text{C}_{11}\text{H}_9\text{N}$  [ $\text{M} + \text{H}$ ]<sup>+</sup> 156.0735, found 156.0813.

**3-(1-Naphthyl)pyridine (2b) [189193-21-3]:**<sup>[26]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2b** as a white solid (47 mg, 47%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K):  $\delta$  = 8.77 (s, 1 H), 8.70 (d,  $J$  = 1.5 Hz, 1 H), 7.94–7.91 (t,  $J$  = 7.0 Hz, 2 H), 7.84–7.81 (m, 2 H), 7.61–7.42 (m, 5 H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 150 MHz, 298 K):  $\delta$  = 150.16, 148.15, 136.95, 135.98, 135.89, 133.37, 131.05, 128.11, 128.06, 126.98, 125.68 (2 C), 124.97,

124.87, 122.76 ppm. HRMS (ESI): calcd. for  $C_{15}H_{11}N [M + H]^+$  206.0891, found 206.0891.

**3-(4-Methyl)pyridine (2c)** [4423-09-0]:<sup>[27]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2c** as a colourless oil (33 mg, 39%).  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  = 8.84 (s, 1 H), 8.57 (s, 1 H), 7.87–7.85 (d,  $J$  = 8.4 Hz, 1 H), 7.49–7.47 (d,  $J$  = 7.6 Hz, 2 H), 7.35 (s, 1 H), 7.30–7.26 (d,  $J$  = 7.6 Hz, 2 H), 2.41 (s, 3 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz, 298 K):  $\delta$  = 148.04, 138.11, 136.70, 134.87, 134.29, 129.84 (2 C), 127.00, 123.63, 21.18 ppm. HRMS (ESI): calcd. for  $C_{12}H_{11}N [M + H]^+$  170.0891, found 170.0969.

**3-[4-(1,1-Dimethylethyl)pyridine] (2d)** [1110656-20-6]:<sup>[28]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2d** as a yellow oil (41 mg, 41%).  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  = 8.86 (s, 1 H), 8.57 (s, 1 H), 7.88–7.86 (d,  $J$  = 7.4 Hz, 1 H), 7.52–7.50 (m, 4 H), 7.35–7.33 (m, 1 H), 1.37 (s, 9 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 150 MHz, 298 K):  $\delta$  = 151.47, 148.38, 148.33, 136.71, 135.07, 134.43, 127.01, 126.27, 123.76, 34.82, 31.51 ppm. HRMS (ESI): calcd. for  $C_{15}H_{17}N [M + H]^+$  212.1361, found 212.1439.

**3-(1,1'-Biphenyl-4-yl)pyridine (2e)** [93324-68-6]:<sup>[29]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2e** as a white solid (38 mg, 33%).  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  = 8.92 (s, 1 H), 8.62 (m, 1 H), 7.94–7.92 (d,  $J$  = 7.7 Hz, 1 H), 7.75–7.73 (d,  $J$  = 7.7 Hz, 2 H), 7.68–7.64 (m, 4 H), 7.49–7.46 (m, 2 H), 7.40–7.36 (m, 2 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 150 MHz, 298 K):  $\delta$  = 148.16, 147.92, 141.42, 140.51, 136.60, 134.91, 129.11, 128.07, 127.85, 127.71, 127.44, 127.29, 123.99 ppm. HRMS (ESI): calcd. for  $C_{17}H_{13}N [M + H]^+$  232.1048, found 232.1126.

**3-(4-Methoxyphenyl)pyridine (2f)** [5958-02-1]:<sup>[29]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2f** as a white solid (42 mg, 45%).  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  = 8.82 (s, 1 H), 8.55 (s, 1 H), 7.84–7.82 (dt,  $J$  = 8.4, 2.1 Hz, 1 H), 7.54–7.50 (d,  $J$  = 8.8 Hz, 2 H), 7.35–7.32 (dd,  $J$  = 8.0, 4.0 Hz, 1 H), 7.03–7.00 (d,  $J$  = 7.9 Hz, 2 H), 3.86 (s, 3 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 150 MHz, 298 K):  $\delta$  = 160.00, 147.91, 147.78, 136.59, 132.76, 130.30, 128.42, 123.82, 114.77, 55.78 ppm. HRMS (ESI): calcd. for  $C_{12}H_{11}NO [M + H]^+$  186.0841, found 186.0919.

**3-(4-((1,1-Dimethylethyl)dimethylsilyloxy)phenyl)pyridine (2g)**: Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2g** as a yellow solid (44 mg, 31%).  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  = 8.83 (s, 1 H), 8.56 (s, 1 H), 7.86–7.84 (d,  $J$  = 8.0 Hz, 1 H), 7.47–7.45 (d,  $J$  = 8.9 Hz, 2 H), 7.35 (s, 1 H), 6.95–6.93 (d,  $J$  = 8.2 Hz, 2 H), 1.01 (s, 9 H), –0.24 (s, 6 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz, 298 K):  $\delta$  = 156.10, 147.75, 147.57, 134.09, 130.73, 128.21, 123.70, 120.75, 25.70, 18.27, –4.35 (2 C) ppm. HRMS (ESI): calcd. for  $C_{17}H_{23}NOSi [M + H]^+$  286.1549, found 286.1627.

**Methyl 4-(3-Pyridinyl)benzoate (2i)** [90395-47-4]:<sup>[30]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2i** as a white solid (25 mg, 22%).  $^1H$  NMR ( $CDCl_3$ , 600 MHz, 298 K):  $\delta$  = 8.91 (s, 1 H), 8.66 (s, 1 H), 8.15–8.14 (d,  $J$  = 7.3 Hz, 2 H), 7.93–7.92 (d,  $J$  = 7.8 Hz, 1 H), 7.67–7.65 (d,  $J$  = 7.8 Hz, 2 H), 7.42 (s, 1 H), 3.95 (s, 3 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 150 MHz, 298 K):  $\delta$  = 166.93, 149.26, 148.37, 142.33, 134.89, 130.58, 129.99, 127.32, 124.03 (2 C), 52.48 ppm. HRMS (ESI): calcd. for  $C_{13}H_{11}NO_2 [M + H]^+$  214.0790, found 214.0868.

**3-(4-Fluorophenyl)pyridine (2m)** [85589-65-7]:<sup>[29]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2m** as a colourless oil (20 mg, 23%).  $^1H$  NMR ( $CDCl_3$ , 300 MHz, 298 K):  $\delta$  = 8.82 (s, 1 H), 8.60 (s, 1 H), 7.85–7.83 (d,  $J$  = 6.8 Hz, 1 H), 7.55–

7.52 (t,  $J$  = 6.4 Hz, 2 H), 7.37 (s, 1 H), 7.20–7.14 (t,  $J$  = 8.0 Hz, 2 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz, 298 K):  $\delta$  = 162.95 (d,  $J_{C,F}$  = 266.2 Hz), 148.24, 147.91, 135.75, 134.46, 133.84 (d,  $J_{C,F}$  = 5.2 Hz), 128.82, 123.72, 116.24 (d,  $J_{C,F}$  = 17.6 Hz) ppm.  $^{19}F\{^1H\}$  NMR ( $CDCl_3$ , 282 MHz, 298 K):  $\delta$  = –114.64 ppm. HRMS (ESI): calcd. for  $C_{11}H_8FN [M + H]^+$  174.0641, found 174.0720.

**3-[4-(Trifluoromethyl)phenyl]pyridine (2n)** [426823-25-8]:<sup>[31]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2n** as a white solid (30 mg, 27%).  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  = 8.88 (s, 1 H), 8.67 (s, 1 H), 7.91–7.89 (d,  $J$  = 8.0 Hz, 1 H), 7.76–7.68 (m, 4 H), 7.42 (m, 1 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 150 MHz, 298 K):  $\delta$  = 148.88, 147.88, 141.26, 135.32, 133.91, 127.73, 126.32 (d,  $J_{C,F}$  = 3.7 Hz), 124.56 (d,  $J_{C,F}$  = 4.8 Hz), 124.23 (d,  $J_{C,F}$  = 271.2 Hz), 124.18 ppm.  $^{19}F\{^1H\}$  NMR ( $CDCl_3$ , 282 MHz, 298 K):  $\delta$  = –62.49 ppm. HRMS (ESI): calcd. for  $C_{12}H_8F_3N [M + H]^+$  224.0609, found 224.0687.

**3-(2-Methoxyphenyl)pyridine (2o)** [5958-01-0]:<sup>[32]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2o** as a white solid (25 mg, 27%).  $^1H$  NMR ( $CDCl_3$ , 300 MHz, 298 K):  $\delta$  = 8.78 (s, 1 H), 8.57 (s, 1 H), 7.87–7.84 (d,  $J$  = 8.0 Hz, 1 H), 7.37–7.31 (m, 3 H), 7.08–7.00 (m, 2 H), 3.82 (s, 3 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz, 298 K):  $\delta$  = 156.59, 150.30, 147.95, 136.79, 134.29, 130.68, 129.56, 127.09, 122.93, 121.07, 111.29, 55.54 ppm. HRMS (ESI): calcd. for  $C_{12}H_{11}NO [M + H]^+$  186.0841, found 186.0916.

**3-(2,6-Dimethylphenyl)pyridine (2p)** [157402-43-2]:<sup>[33]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2p** as a colourless oil (10 mg, 10%).  $^1H$  NMR ( $CDCl_3$ , 600 MHz, 298 K):  $\delta$  = 8.63 (s, 1 H), 8.46 (s, 1 H), 7.55–7.54 (d,  $J$  = 7.7 Hz, 1 H), 7.45–7.40 (dd,  $J$  = 7.7, 4.4 Hz, 1 H), 7.24–7.20 (t,  $J$  = 7.3 Hz, 1 H), 7.14–7.13 (d,  $J$  = 7.3 Hz, 2 H), 2.04 (s, 6 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 150 MHz, 298 K):  $\delta$  = 149.82, 147.90, 137.83, 137.40, 136.61, 136.49, 128.16, 127.79, 123.81, 21.13 ppm. HRMS (ESI): calcd. for  $C_{13}H_{13}N [M + H]^+$  184.1048, found 184.1126.

**3-(2,5-Difluorophenyl)pyridine (2q)** [426823-29-2]: Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2q** as a colourless oil (30 mg, 23%).  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  = 8.79 (s, 1 H), 8.65–8.63 (d,  $J$  = 3.4 Hz, 1 H), 7.87–7.85 (d,  $J$  = 6.0 Hz, 1 H), 7.41–7.37 (dd,  $J$  = 8.2, 3.4 Hz, 1 H), 7.20–7.04 (m, 3 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 150 MHz, 298 K):  $\delta$  = 158.44 (dd,  $J_{C,F}$  = 242.5, 3.3 Hz) 155.38 (dd,  $J_{C,F}$  = 243.7, 3.7 Hz), 149.09, 148.88, 135.77 (d,  $J_{C,F}$  = 4.1 Hz), 130.50, 126.49 (dd,  $J_{C,F}$  = 16.9, 8.0 Hz), 122.95, 117.04 (dd,  $J_{C,F}$  = 19.3, 8.4 Hz), 116.27 (dd,  $J_{C,F}$  = 24.4, 3.9 Hz), 115.83 (dd,  $J_{C,F}$  = 19.9, 7.2 Hz) ppm.  $^{19}F\{^1H\}$  NMR ( $CDCl_3$ , 282 MHz, 298 K):  $\delta$  = –118.30, –123.97 ppm. HRMS (ESI): calcd. for  $C_{11}H_7F_2N [M + H]^+$  192.0547, found 192.0625.

**3-(Benzo[*b*]thien-2-yl)pyridine (2s)** [936734-97-3]:<sup>[34]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2s** (10.2 mg, 10%) as a yellow solid.  $^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K):  $\delta$  = 9.00 (s, 1 H), 8.59–8.58 (d,  $J$  = 3.4 Hz, 1 H), 7.98–7.96 (d,  $J$  = 8.0 Hz, 1 H), 7.85–7.81 (d,  $J$  = 7.7 Hz, 2 H), 7.61 (s, 1 H), 7.39–7.34 (m, 3 H) ppm.  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 150 MHz, 298 K):  $\delta$  = 148.64, 148.60, 146.95, 139.95, 139.71, 139.23, 133.47, 128.43, 124.48, 124.40, 123.45, 121.94, 120.36 ppm. HRMS (ESI): calcd. for  $C_{13}H_9NS [M + H]^+$  212.0456, found 212.0534.

**3-(2-Benzofuranyl)pyridine (2t)** [7035-06-5]:<sup>[34]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2t** as a white solid (8 mg, 8%).  $^1H$  NMR ( $CDCl_3$ , 600 MHz, 298 K):  $\delta$  = 9.06 (s, 1 H), 8.53 (s, 1 H), 8.10–8.09 (d,  $J$  = 7.9 Hz, 1 H), 7.57–7.55 (d,  $J$  = 6.9 Hz, 1 H), 7.50–7.48 (d,  $J$  = 8.4 Hz, 1 H), 7.39 (s, 1 H), 7.29–

7.26 (t,  $J = 8.4$  Hz, 1 H), 7.21–7.17 (m, 1 H), 7.08 (s, 1 H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 150 MHz, 298 K):  $\delta = 154.67, 152.33, 148.55, 145.73, 131.66, 129.24, 128.29, 124.60, 123.30, 122.87, 120.82, 110.91, 102.46$  ppm. HRMS (ESI): calcd. for  $\text{C}_{13}\text{H}_9\text{NO}$  [ $\text{M} + \text{H}$ ] $^+$  196.0684, found 196.0762.

**3-(1,3-Benzodioxol-5-yl)pyridine (2u)** [869985-49-9]:<sup>[35]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2u** as a white solid (41 mg, 41%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, 298 K):  $\delta = 8.78$  (s, 1 H), 8.55 (s, 1 H), 7.83–7.80 (d,  $J = 5.9$  Hz, 1 H), 7.35 (s, 1 H), 7.04 (s, 2 H), 6.93 (d,  $J = 8.5$  Hz, 1 H), 6.02 (s, 2 H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz, 298 K):  $\delta = 148.62$  (2 C), 147.99 (2 C), 136.67, 134.34, 132.09, 123.73, 121.05, 109.07, 107.70, 101.53 ppm. HRMS (ESI): calcd. for  $\text{C}_{12}\text{H}_9\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$  200.0633, found 200.0712.

**4-Phenylpyridine (2w)** [939-23-1]:<sup>[36]</sup> Purification by column chromatography (hexane/EtOAc, 3:1) afforded **2w** (37 mg, 49%) as a white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz, 298 K):  $\delta = 8.67$  (s, 2 H), 7.65 (m, 2 H), 7.50 (m, 4 H), 7.45 (m, 1 H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 150 MHz, 298 K):  $\delta = 150.32, 148.68, 138.28, 129.33, 129.31, 127.20, 121.89$  ppm. HRMS (ESI): calcd. for  $\text{C}_{11}\text{H}_9\text{N}$  [ $\text{M} + \text{H}$ ] $^+$  156.0735, found 156.0813.

CCDC-1404055 (for **B**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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