

## Supporting Information

### ***In situ* generated nickel nanoparticles for carbonylative Suzuki reactions of aryl iodides with arylboronic acids at ambient CO pressure in poly(ethylene glycol)**

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## 1. General Information

**Reagent Information.** All the aryl halides and the arylboronic acids were purchased from Alfa Aesar and Accela ChemBio Co., Ltd. and were used as received. PEG-400 (bought from Acros) was pre-dried (toluene azeotrope) and pre-deoxygenated. The following **nickel catalyst**, bases, and *t*BuCOOH were used: NiCl<sub>2</sub> (98%, Alfa Aesar), K<sub>3</sub>PO<sub>4</sub> (99%, Alfa Aesar), and *t*BuCOOH (99%, Alfa Aesar).

**Analytical methods.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of solutions in CDCl<sub>3</sub> were recorded on a Bruker Avance 400 instrument. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvent signals (CDCl<sub>3</sub>: H 7.24 and C 77.0 ppm). The signals of water were observed at about 1.58 ppm in CDCl<sub>3</sub>, respectively. Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; ddd, doublet of doublet of doublets; tdd, doublet of doublet of triplets. Coupling constants, *J*, were reported in hertz unit (Hz).

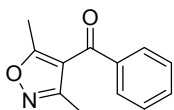
## 2. General Procedures for Ni-Catalyzed Carbonylative Suzuki Reactions

*General Procedure:* A 25 mL Schlenk flask was charged with arylboronic acid (0.75 mmol), NiCl<sub>2</sub> (0.01 mmol, 1.4 mg), K<sub>3</sub>PO<sub>4</sub> (1.0 mmol, 218.8 mg), PivOH (0.25 mmol, 25.8 mg), and PEG-400 (2.0 mL) before standard cycles of evacuation and back-filling with dry and pure carbon monoxide. Corresponding aryl iodide (0.5 mmol) was added successively. The mixture was stirred at 80 °C for the indicated time. At the end of the reaction, the reaction mixture was poured into a saturated aqueous NaCl solution (15 mL) and extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel (petroleum ether: diethyl ether = 25 : 1).

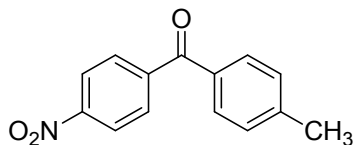
In the recycling experiment, the reaction mixture was extracted with ethyl acetate (3 × 15 mL), and the residue was subjected to a second run by charging it with the same substrates as mentioned above without further addition of **NiCl<sub>2</sub>** and PEG 400 1 atm of carbon monoxide.

### 3. Analytical Data of Products

The products, **3aa–3ka**, **3ab–3ad**, **3af**, **3ak**, **3cc**, **3dg**, **3ec**, **3ee**, **3gc**, **3ge**, **3gi**, **3ic**, **3ie**, **3ig**, **3ih**, and **3ma** were identified by comparison of their spectral data with those of our previous reports.<sup>[S1-S2]</sup>

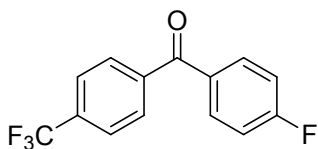


**(3,5-Dimethylisoxazol-4-yl)(phenyl)methanone (31a):** Following *general procedure*, **31a** was isolated as a colorless liquid (90 mg, 90%). Known compound; the NMR spectroscopic data agree with those described in ref..<sup>[S3]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.70–7.68 (m, 2 H), 7.59 (tt, *J*=8.0, 1.2 Hz, 1H), 7.50–7.46 (m, 2 H), 2.31 (s, 3 H), 2.28 ppm (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 190.4, 172.3, 159.6, 138.4, 133.2, 128.9, 128.7, 116.4, 13.3, 11.3 ppm.

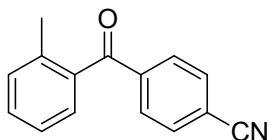


**(4-Nitrophenyl)(*p*-tolyl)methanone (3ae):** Following *general procedure*, **3ae** was isolated as a white solid (108 mg, 90%). Known compound; the NMR spectroscopic data agree with those described in ref..<sup>[S4]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.31 (d, *J* = 8.9 Hz, 2H), 7.89 (d, *J* = 8.9 Hz, 2 H), 7.69 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 2.44 ppm (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 194.5, 149.7, 144.6, 143.3, 133.6, 130.5,

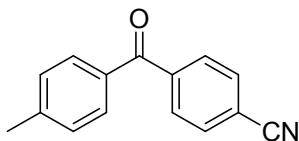
130.3, 129.4, 123.5, 21.7 ppm; mp 123.9–124.4 °C.



**(4-Fluorophenyl)(4'-(trifluoromethyl)phenyl)methanone (3mc):** Following *general procedure*, **3mc** was isolated as a white solid (95 mg, 71%). Known compound; the NMR spectroscopic data agree with those described in ref.<sup>[S5]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.87–7.80 (m, 4H), 7.74 (m, 2H), 7.20–7.13 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 194.0, 165.7 (d, <sup>1</sup>J<sub>CF</sub> = 254 Hz), 140.6, 133.8 (q, <sup>2</sup>J<sub>CF</sub> = 32), 132.9 (d, <sup>4</sup>J=3), 132.8 (d, <sup>3</sup>J<sub>CF</sub> = 9), 129.9, 125.4 (q, <sup>3</sup>J<sub>CF</sub> = 4), 123.6 (q, <sup>1</sup>J<sub>CF</sub> = 272 Hz), 115.8 (d, <sup>2</sup>J<sub>CF</sub>=22) ppm; mp 96.9–97.6 °C.

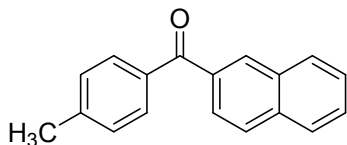


**4-(2-Methylbenzoyl)benzonitrile (3eh):** Following *general procedure*, **3eh** was isolated as a colorless liquid (96 mg, 87%). Known compound (CAS: 913485-57-1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.86 (d, *J*=8.0 Hz, 2 H), 7.74 (d, *J*=8.0 Hz, 2 H), 7.44–7.40 (m, 1 H), 7.31–7.23 (m, 3 H), 2.34 ppm (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 196.8, 141.1, 137.5, 136.9, 132.3, 131.4, 131.2, 130.3, 128.9, 125.4, 117.9, 116.2, 20.1 ppm.



**4-(4-Methylbenzoyl)benzonitrile (3gh):** Following *general procedure*, **3gh** was isolated as a white solid (101 mg, 92%). Known compound; the NMR spectroscopic data agree with those described in ref.<sup>[S6]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.83 (d, *J*=8.0 Hz, 2 H),

7.76 (d,  $J=8.0$  Hz, 2 H), 7.67 (d,  $J=8.0$  Hz, 2 H), 7.29 (d,  $J=8.0$  Hz, 2 H), 2.43 ppm (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.8, 144.4, 141.6, 133.6, 132.1, 130.3, 130.1, 129.3, 118.0, 115.3, 21.7 ppm.



**Naphthalen-2-yl(p-tolyl)methanone (3gj):** Following *general procedure*, **3gj** was isolated as a white solid (92 mg, 75%). Known compound; the NMR spectroscopic data agree with those described in ref.<sup>[S7]</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.23 (s, 1H), 7.94–7.88 (m, 4 H), 7.76 (d,  $J=8.0$  Hz, 2H), 7.62–7.51 (m, 2H), 7.30 (d,  $J=8.0$  Hz, 2 H), 2.45 (s, 3 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.5, 143.2, 135.2, 132.3, 131.6, 130.4, 129.3, 129.0, 128.2, 128.1, 127.8, 126.7, 125.8, 21.7 ppm; mp 81.6–82.2 °C.

#### 4. Hg(0) Poisoning Test

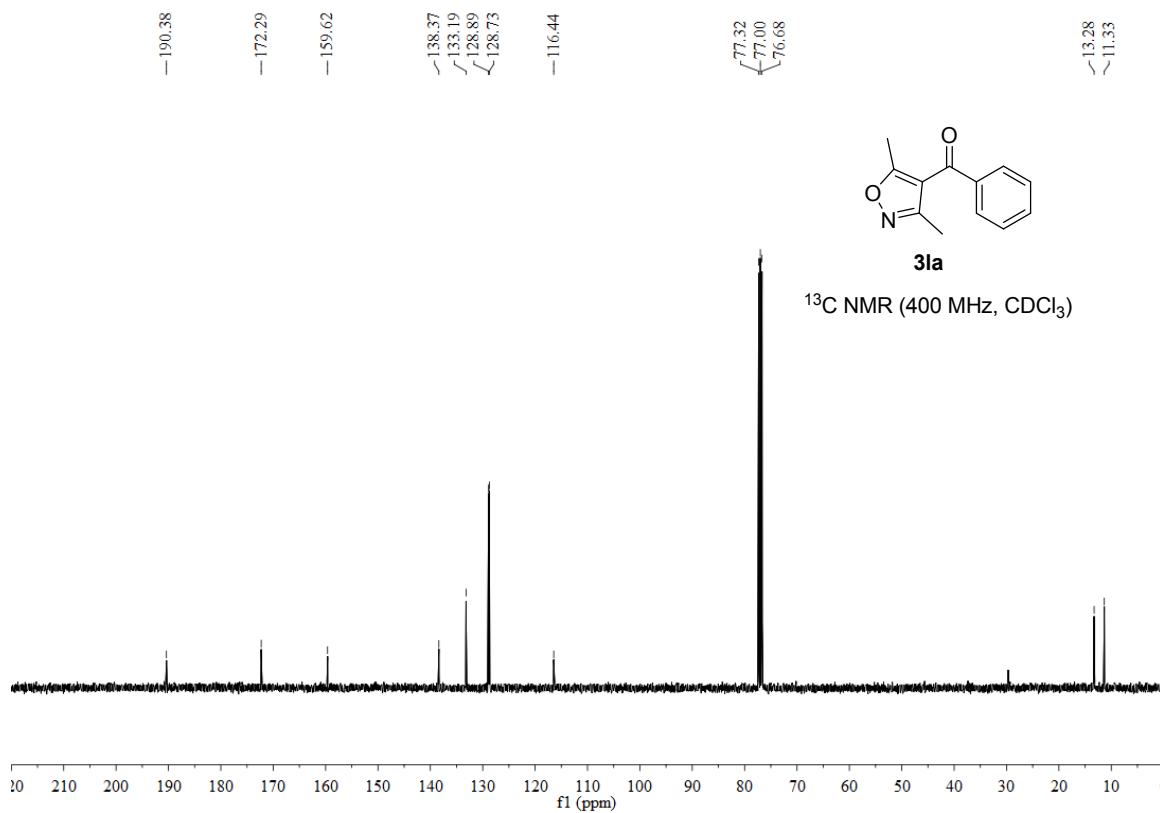
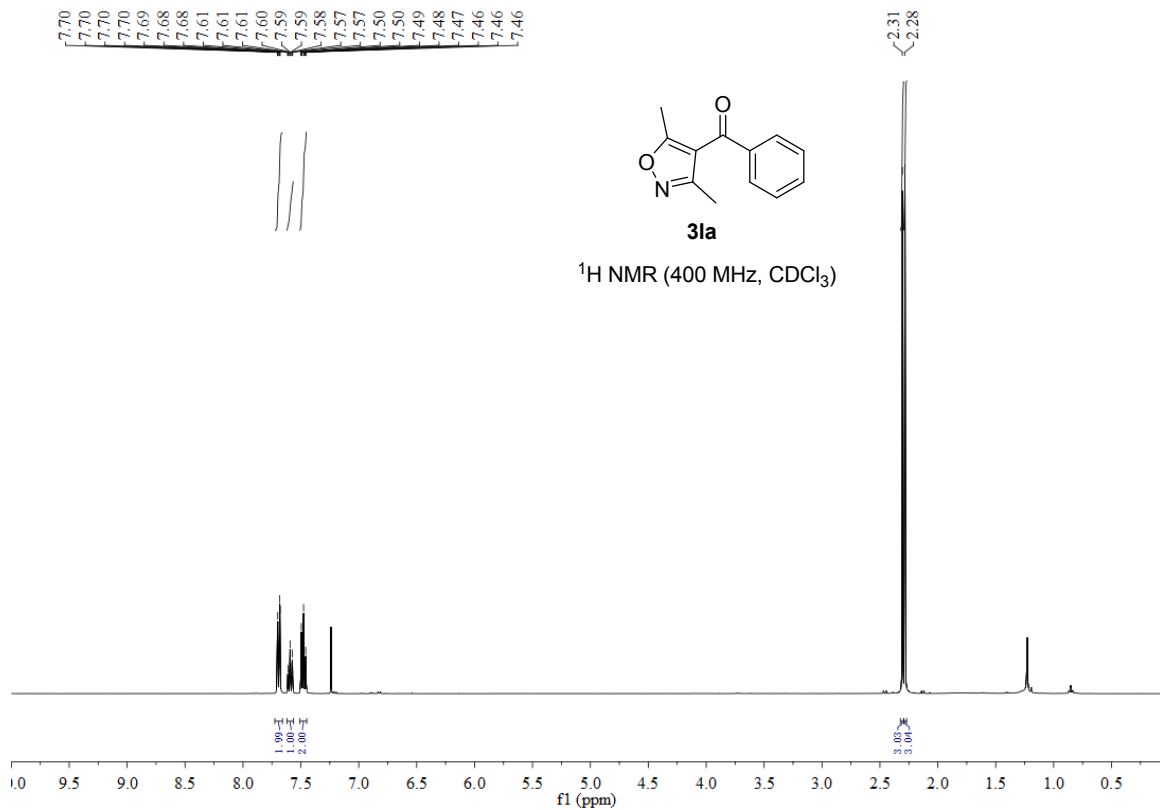
As *general procedure*, a reactions of 1-iodo-4-nitrobenzene **1a** (0.5 mmol, 127.0 mg), phenylboronic acid **2a** (0.75 mmol, 92.4 mg),  $\text{NiCl}_2$  (0.01 mmol, 1.4 mg),  $\text{K}_3\text{PO}_4$  (1.0 mmol, 218.8 mg), and  $t\text{BuCO}_2\text{H}$  (0.25 mmol, 25.8 mg) in PEG-400 (2.0 mL), with the addition of Elemental mercury (2mmol, 100eq, 401.2 mg) (relative to **nickel**) was conducted. Following the reaction for 3 h at 80 °C, the isolated yield of the desired product **3aa** was trace, suggesting that the reaction is completely inhibited by the introduction of Hg(0).



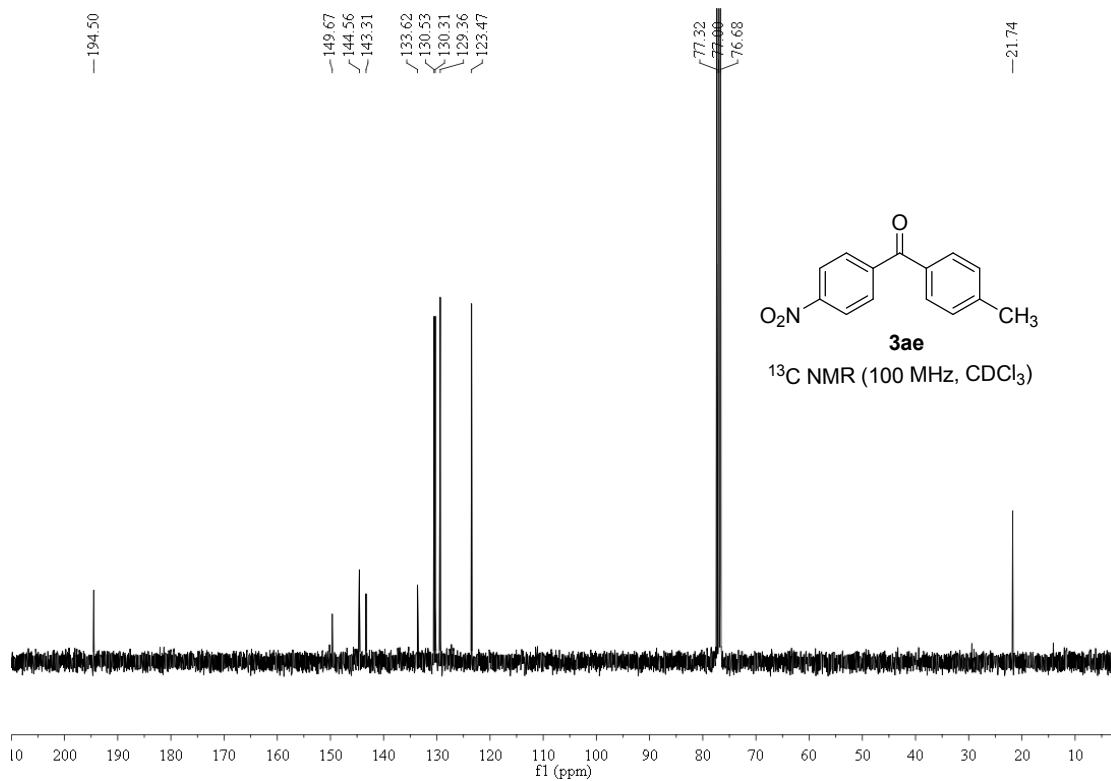
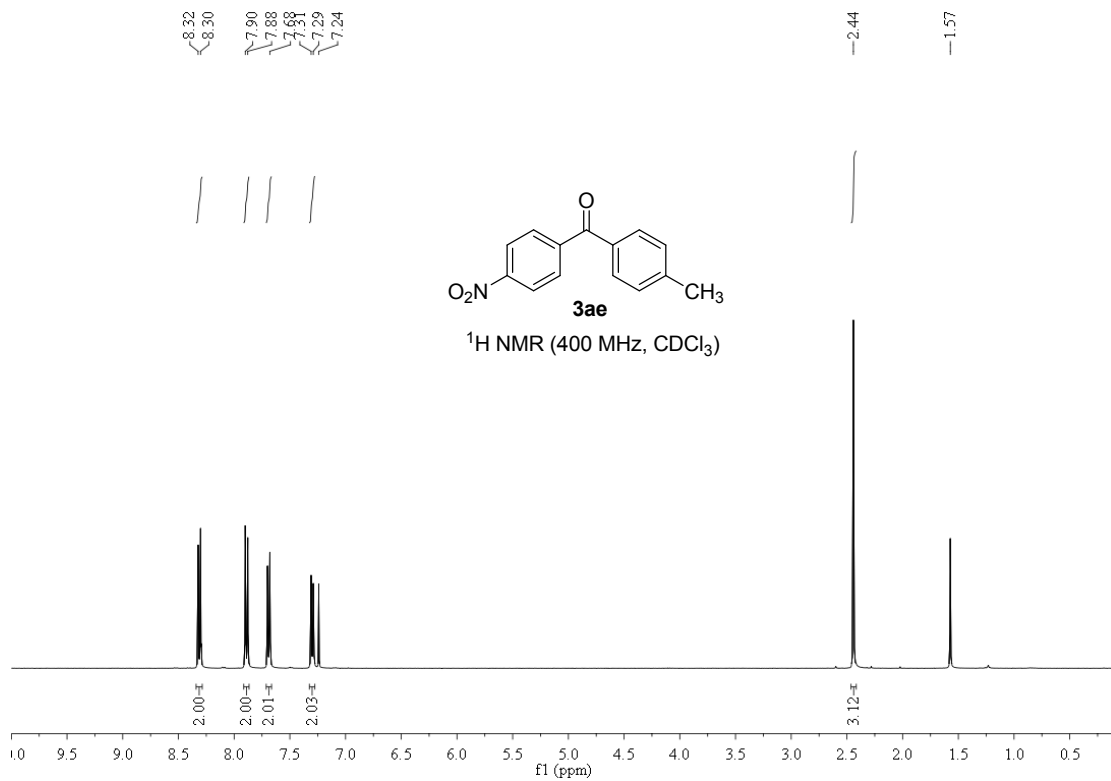
## 6. References

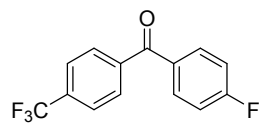
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## 7. NMR Spectra of Products









**3mc**

<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>)

