Supporting Information Available

A General Method for the Suzuki-Miyaura Cross-Coupling of Sterically Hindered Aryl Chlorides: Synthesis of Di- and Tri-*ortho*-substituted Biaryls in Isopropanol at Room Temperature

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General Information

- All aryl halides and boronic acids were used as received (Aldrich, Acros, Combi-Blocks). Technical grade isopropanol was used to carry out catalytic reactions. (Mallinckrodt Chemicals). Sodium *tert*-butoxide (Acros) was stored under argon in a MBraun glovebox.
- Palladacycle **1** was prepared according to the reported procedure.[1]
- All reactions were carried out under an atmosphere of argon in screw cap vials.
- Flash chromatography was performed on silica gel 60 (230-400 mesh) (Natland International Corporation) using mixtures hexanes:ethylacetate (10:1), unless otherwise noted.
- ^{1}H nuclear magnetic resonance spectra were recorded on a Varian-300 or Varian-400 MHz spectrometer at ambient temperature in $CDCl_3$ (Cambridge Isotope Laboratories, Inc).

Catalytic Dehalogenation of 2-chloro-*m*-xylene. *Procedure:* In a glovebox, **1** (2 mol %, 14.6 mg) and sodium *tert*-butoxide (1.2 mmol, 115 mg) were added in turn to a vial equipped with a magnetic bar, and closed with a screw cap fitted with a septum. Outside the glovebox, technical grade isopropanol (1.5 mL) and 2-chloro-*m*-xylene (1 mmol, 132

μL) were injected in that order through the septum. The reaction was monitored by gas chromatography, affording >99% of *m*-xylene in 20 min.

Suzuki-Miyaura Cross-Coupling of Aryl Chlorides with Phenylboronic Acid. *General Procedure*: In a glovebox, **1** (2 mol %, 14.6 mg), sodium *tert*-butoxide (1.2 mmol, 115 mg) and phenylboronic acid (1.4 mmol, 171 mg) were added in turn to a vial equipped with a magnetic bar, and sealed with a screw cap fitted with a septum. Outside the glovebox, technical grade isopropanol (1.5 mL) was injected into the vial and the mixture stirred on a stirring plate at room temperature for 15 min. Aryl chloride (1 mmol) was then injected at a rate of 20 μl/30 sec. The reaction was monitored by gas chromatography. When finished, a small amount of silica gel was added to the vial, the solvent was evaporated *in vacuo* and the product isolated by flash chromatography. The amount of product shown is the average of two runs:

Biphenyl (Table 1, entry 1).[2] The procedure afforded 294 mg (95 %) of the title compound.

4-Methylbiphenyl (Table 1, entry 2).[3] The procedure afforded 286 mg (85 %) of the title compound.

2-Methylbiphenyl (Table 1, entry 3).[4] The procedure afforded 291 mg (87 %) of the title compound.

4-Methoxybiphenyl (Table 1, entry 4).[3] The procedure afforded 309 mg (84%) of the title compound.

3-Methoxybiphenyl (Table 1, entry 5).[5] The procedure afforded 346 mg (94 %) of the title compound.

2-Methoxybiphenyl (Table 1, entry 5).[6] The procedure afforded 343 mg (93 %) of the title compound.

4-Acetylbiphenyl (Table 1, entry 7).[7] The procedure afforded 372 mg (95 %) of the title compound.

Suzuki-Miyaura Cross-Coupling of Sterically Hinderd Aryl Chlorides with Sterically Hindered Boronic Acids. *General Procedure*: In a glovebox, **1** (2 mol %, 7.3 mg), sodium *tert*-butoxide (0.6 mmol, 58 mg) and boronic acid (0.7 mmol,) were added in turn to a vial equipped with a magnetic bar, and sealed with a screw cap fitted with a septum. Outside the glovebox, technical grade isopropanol (1 mL) was injected into the vial and the mixture stirred on a stirring plate at room temperature for 15 min. The aryl chloride (0.5 mmol) was then injected at a rate of 10 μl/30 sec. The reaction was monitored by gas chromatography. When reaction reached completion, a small amount of silica gel was added to the vial, the solvent was evaporated *in vacuo* and the product isolated by flash chromatography. The reported yields are the average of two runs:

2,2'-Dimethylbiphenyl (Table 2, entry 1).[4] The procedure afforded 140 mg (77 %) of the title compound.

1-*o*-Tolyl-naphtalene (Table 2, entry 2).[8] The procedure afforded 184 mg (85 %) of the title compound.

2,6-Dimethylbiphenyl (Table 2, entry 3).[9] The procedure afforded 160 mg (88 %) of the title compound.

2,2',4-Trimethylbiphenyl (Table 2, entry 4).[10] The procedure afforded 166 mg (85 %) of the title compound.

1-(2,6-Dimethyl-phenyl)-naphtalene (Table 2, entry 5).[11] The procedure afforded 201 mg (87 %) of the title compound.

Large Scale Suzuki-Miyaura Cross-Coupling of 2,6-Dimethylphenyl Chloride with 2-Methylphenyl Boronic Acid. *Procedure:* In a glovebox, **1** (2 mol %, 36.5 mg), sodium *tert*-butoxide (3 mmol, 288 mg) and 2-methylphenylboronic acid (3.2 mmol, 428 mg) were added in turn to a vial equipped with a magnetic bar, and closed with a screw cap fitted with a septum. Outside the glovebox, technical grade isopropanol (4 mL) was injected into the vial and the mixture stirred on a stirring plate at room temperature for 15 min. 2,6-Dimethylphenyl chloride (2.5 mmol, 330 μL) was then injected at a rate of 20 μl/30 sec. The reaction was monitored by gas chromatography. When the reaction reached completion, silica gel was added to the vial, the solvent was evaporated *in vacuo* and the product isolated by flash chromatography. The procedure afforded 429 mg (87%) of the desired product.[10]

Isolation of 2-Methylamino-biphenyl: *Procedure:* In a glovebox, **1** (0.2 mmol, 146 mg) and sodium *tert*-butoxide (0.2 mmol, 19.2 mg) were added in turn to a vial equipped with a magnetic bar, and closed with a screw cap fitted with a septum. Outside the glovebox, technical grade isopropanol (1 mL) was injected into the vial and the mixture stirred at room temperature for 5 min. The mixture was concentrated *in vacuo* and the product isolated by flash chromatography using an ethyl ether/hexanes (1:10) mixture. The procedure afforded 37 mg of the title compound. The biphenyl was unequivocally identified by comparison with an authentic sample. ^{1}H NMR (δ, 400 MHz, $CDCl_3$): 7.568 (d, 2H, J= 7.6 Hz), 7.382 (t, 2H, J= 7.6 Hz), 7.278 (t, 2H, J= 7.2 Hz), 7.215 (dd, 4H, J= 1.6, 7.2 Hz), 7.019 (m, 2H, J= 6.8 Hz), 2.534 (s, 6H). In a similar experiment without adding sodium *tert*-butoxide, **1** was recovered quantitatively.

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