

## *ESI for*

# **A simple and efficient approach for the palladium-catalyzed ligand-free Suzuki reaction in water**

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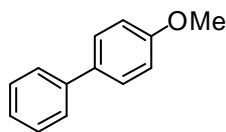
### **Materials and Methods**

Aryl halides and arylboronic acids were purchased from Alfa Aesar. Other chemicals were obtained commercially and used without purification. <sup>1</sup>H NMR spectra were recorded on a Bruker AvanceII 400 spectrometer using TMS as internal standard. All products were isolated by short chromatography on a silica gel (200-300 mesh) column using petroleum ether (60-90 °C), unless otherwise noted.

### **General Procedure for the Suzuki Reaction**

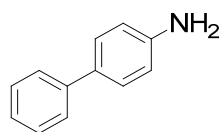
All Suzuki reactions were carried out under air. A mixture of aryl halide (0.5 mmol), arylboronic acid (0.75 mmol), (*i*-Pr)<sub>2</sub>NH (1.0 mmol), Pd(OAc)<sub>2</sub> (0.25 mol%, 0.28 mg), H<sub>2</sub>O (1.0 ml) was allowed to react in a sealed tube at 100 °C. The reaction mixture was added to brine (10 mL) and extracted with ethyl acetate (3×10 mL). The solvent was concentrated under vacuum and the product was isolated by short chromatography on a silica gel (200–300 mesh) column.

## Characterization Data of Products



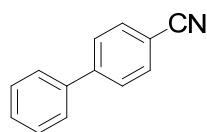
**4-methoxybiphenyl<sup>1</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.56-7.51 (m, 4H, Ar-H), 7.41 (t, *J* = 8.0 Hz, 2H, Ar-H), 7.32-7.28 (m, 1H, Ar-H), 7.00-6.96 (m, 2H, Ar-H), 3.85 (s, 3H, OCH<sub>3</sub>), ppm.



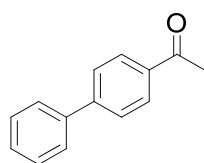
**4-Aminobiphenyl<sup>2</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.53 (d, *J* = 7.1 Hz, 2H, Ar-H), 7.40 (m, *J* = 13.4, 8.2 Hz, 4H, Ar-H), 7.27 (d, *J* = 7.3 Hz, 1H, Ar-H), 6.75 (d, *J* = 8.6 Hz, 2H, Ar-H), 3.71 (s, 2H, NH<sub>2</sub>), ppm.



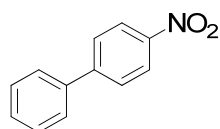
**biphenyl-4-carbonitrile<sup>3</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.73 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.68 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.59 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.48 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.42 (t, *J* = 7.2 Hz, 1H, Ar-H), ppm.



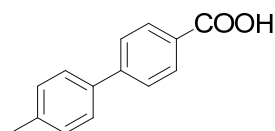
**4-acetylbiphenyl<sup>4</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.03 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.68 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.63 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.47 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.40 (t, *J* = 7.2 Hz, 1H, Ar-H), 2.64 (s, 3H, O=CCH<sub>3</sub>), ppm.



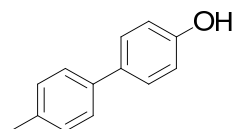
**4-nitrobiphenyl<sup>1</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.30 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.74 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.63 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.52-7.43 (m, 3H, Ar-H), ppm.



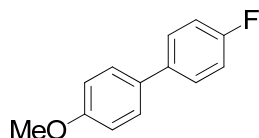
**4'-methylbiphenyl-4-carboxylic acid<sup>5</sup>**

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  12.90 (br, 1H, COOH), 8.01 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.78 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.64 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.31 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 2.36 (s, 3H, CH<sub>3</sub>), ppm.



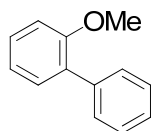
**4'-methylbiphenyl-4-ol<sup>6</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.74 (t, *J* = 8.0 Hz, 4H, Ar-*H*), 7.22 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.89 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 4.82 (s, 1H, OH), 2.38 (s, 3H, CH<sub>3</sub>), ppm.



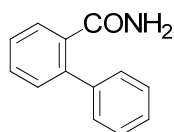
**4-methoxy-4'-fluorobiphenyl<sup>7</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.48 (dd, *J* = 11.3, 8.9 Hz, 4H, Ar-*H*), 7.10 (t, *J* = 8.7 Hz, 2H, Ar-*H*), 6.97 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 3.85 (s, 3H, CH<sub>3</sub>), ppm.



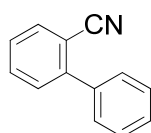
**2-methoxybiphenyl<sup>7</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 7.4 (m, 2H, Ar-*H*), 7.31 (m, 3H, Ar-*H*), 7.07-6.94 (m, 2H, Ar-*H*), 3.80 (s, 3H, OCH<sub>3</sub>), ppm.



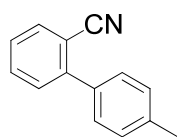
**2-Phenylbenzamide<sup>8</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : 7.80 (dd, 1H, Ar-*H*), 7.51 (dd, 1H, Ar-*H*), 7.45 (m, 6H, Ar-*H*), 7.36 (t, 1H, Ar-*H*), 5.52 (bs, 1H, N-*H*),  $\delta$  5.24 (bs, 1H, N-*H*), ppm.



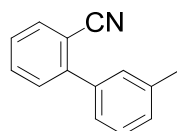
**biphenyl-2-carbonitrile<sup>9</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.63 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 7.55 (d, *J* = 6.7 Hz, 2H, Ar-*H*), 7.49 (m, *J* = 12.4, 7.6 Hz, 3H, Ar-*H*), 7.43 (m, *J* = 10.4, 7.3 Hz, 2H, Ar-*H*), ppm.



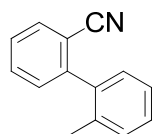
**4'-methylbiphenyl-2-carbonitrile<sup>10</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.74 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.62 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.50 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.46 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.41 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.30 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 2.42 (s, 3H, CH<sub>3</sub>), ppm.



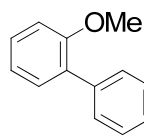
**3'-methylbiphenyl-2-carbonitrile<sup>11</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.73 (dd, *J* = 7.8, 1.0 Hz, 1H, Ar-*H*), 7.61 (m, *J* = 7.7, 1.4 Hz, 1H, Ar-*H*), 7.50 - 7.47 (m, 1H, Ar-*H*), 7.43 - 7.34 (m, 4H, Ar-*H*), 7.26 - 7.22 (m, 1H, Ar-*H*), 2.42 (s, 3H, CH<sub>3</sub>), ppm.



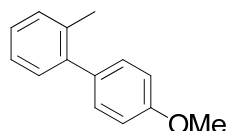
**2'-methylbiphenyl-2-carbonitrile<sup>12</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.71 (d, *J* = 8.7 Hz, 1H, Ar-*H*), 7.59 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 7.41 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 7.36 - 7.23 (m, 4H, Ar-*H*), 7.18 (d, *J* = 7.3 Hz, 1H, Ar-*H*), 2.18 (s, 3H, CH<sub>3</sub>), ppm.



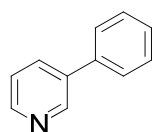
**2,4'-dimethoxybiphenyl<sup>7</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.47 (d, *J* = 9.2 Hz, 2H, Ar-*H*), 7.29 (t, *J* = 3.2 Hz, 2H, Ar-*H*), 6.93 - 7.03 (m, 4H, Ar-*H*), 3.84 (s, 3H, OCH<sub>3</sub>), 3.81 (s, 3H, OCH<sub>3</sub>), ppm.



**4-methoxy-2'-methyl-1,1'-biphenyl<sup>9</sup>**

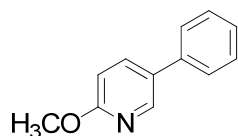
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.19-7.23 (m, 6H, Ar-*H*), 6.92 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 3.80 (s, 3H, OCH<sub>3</sub>), 2.26 (s, 3H, CH<sub>3</sub>), ppm.



**3-phenylpyridine<sup>13</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.85 (d, *J* = 0.8 Hz, 1H, Py), 8.60 (d, *J* = 4.8 Hz,

1H, Py), 7.87 (d,  $J = 8.0$  Hz, 1H, Py), 7.58 (d,  $J = 8.0$  Hz, 2H, Ph), 7.48 (t,  $J = 8.0$  Hz, 2H, Ph), 7.40 (t,  $J = 7.6$  Hz, 1H, Py), 7.37-7.34 (m, 1H, Ph), ppm.



**2-methoxyl-5-phenylpyridine<sup>14</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  8.39 (s, 1H, Py), 7.78 (dd,  $J = 8.4$  Hz,  $J = 2.4$  Hz, 1H), 7.53-7.51 (d,  $J = 7.6$  Hz, 2H, Py), 7.43 (t,  $J = 7.2$  Hz, 2H, Ph), 7.34 (t,  $J = 7.2$  Hz, 1H, Ph), 6.81 (d,  $J = 8.4$  Hz, 1H, Ph), 3.98 (s, 3H, OCH<sub>3</sub>), ppm.

## Reference

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### <sup>1</sup>H NMR Spectra for all Products

