Suzuki–Miyaura cross-couplings of arenediazonium tetrafluoroborate salts with arylboronic acids catalyzed by aluminum hydroxide-supported palladium nanoparticles

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Supporting Information

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All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. Deuterated solvents were purchased from aladdin. All chromatographically pure reagents were used as solvents. Column chromatography was performed on silica gel (200-300 mesh) with petroleum ether (solvent A)/ethyl acetate (solvent B) gradients, unless otherwise specified. All yields were referred to isolated yields (average of two runs) of compounds. The known compounds were partly characterized by melting points (for solid samples), IR, 1H NMR and 13C NMR, and compared to authentic samples or the literature data. Melting points were measured with a RD-II digital melting point apparatus and are uncorrected. IR spectra (KBr) were recorded on an FT-IR spectrophotometer. 1H NMR data were acquired at 300 K on a Bruker Advance 600 MHz spectrometer or Avarian Inova 500 MHz spectrometer using CDCl₃ as solvent. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃, δ = 7.26). Spectra are reported as follows: chemical shift (δ = ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. 13C NMR spectra were collected on commercial instruments (150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl₃, δ = 77.0). Mass spectroscopy data of the product was collected on an Agilent 6890-5973N GCMS-EI instrument.

Synthesis of the catalyst 1

A mixture of Pd (PPh₃)₄ (260 mg, 0.225 mmol), tetra (ethylene glycol) (418 mg, 2.20 mmol), 1-butanol (3 mL, 32.7 mmol), and aluminum tri-sec-butoxide (9.50 g, 38.5 mmol) was stirred at 110 °C for 10 h, and then the reaction mixture was further stirred at 110 °C for 0.5 h to form a black gel after water was added dropwise. Subsequently, filtering, washing with acetone, and drying the gel at room temperature in the air to give the catalyst 1 as dark greyish-green powder.

Characterization of the catalyst 1

The catalyst 1 was characterized by transmission electron microscopy (TEM). A distinct fibrous morphology is shown in the TEM image (Figure 1).

General procedure for Suzuki cross-coupling reactions

To a tube equipped with a magnetic stir bar were added arenediazonium tetrafluoroborate salt (0.3 mmol, 1.0 equiv.), arylboronic acid (0.36 mmol, 1.2 equiv.) and the catalyst 1 (11.2 mg, 0.3 mol% Pd) in turn. Subsequently, solvent (MeOH, 1.8 mL) was added under air atmosphere. The reaction mixture
was then stirred at the specified temperature\(^2\) (Digital display temperature control instrument was used in this process) until the arenediazonium tetrafluoroborate salt was completely consumed. After the solvent (chromatographically pure MeOH) was removed under reduced pressure, the residue was purified by silica gel column chromatography to afford the corresponding pure product.

### Screening of palladium catalysts

**Table 4** Palladium-Catalyzed Suzuki-Miyaura cross-coupling reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat*</th>
<th>t (h)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Cat* 1</td>
<td>4</td>
<td>92</td>
</tr>
<tr>
<td>2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Cat* 2</td>
<td>24</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>Pd (PPh(_3))(_4)</td>
<td>32</td>
<td>31</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), phenylboronic acid (43.9 mg, 1.2 equiv, 0.36 mmol), catalyst (0.3 mol% Pd), MeOH (1.8 mL), 25 °C. <sup>b</sup> Isolated yield. <sup>c</sup> In this process of the preparation of the catalyst 2, aluminium isopropoxide was used instead of aluminium tri-sec-butoxide.

### Some cross-couplings at 25 °C

**Table 5** Cross-Couplings of arenediazonium tetrafluoroborate salts and arylboronic acids catalyzed by the Palladium nanoparticles catalyst 1

<table>
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<th>Entry</th>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
<th>t (h)</th>
<th>Product</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
<tbody>
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<td>H</td>
<td>3</td>
<td><img src="image" alt="Product 1" /></td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>4-NO(_2)</td>
<td>H</td>
<td>1.5</td>
<td><img src="image" alt="Product 2" /></td>
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<tr>
<td>3</td>
<td>4-Br</td>
<td>4-CH(_3)</td>
<td>2</td>
<td><img src="image" alt="Product 3" /></td>
<td>54</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: arenediazonium tetrafluoroborate (0.3 mmol), arylboronic acid (0.36 mmol, 1.2 equiv), catalyst (0.3 mol% Pd, 11.2 mg), MeOH (1.8 mL), 25 °C. <sup>b</sup> Isolated yield.

### A typical recycling procedure for Suzuki cross-coupling reactions

The corresponding recycling reaction for 3-nitrobenzenediazonium tetrafluoroborate and phenylboronic acid was carried out with the recovered catalyst 1 that determined the amount of the substrate and reagent as reference in MeOH at 20 °C. Reaction times were 6, 22, and 28 h for cycles 1, 2, and 3, respectively. After the reaction was fully completed, the reaction solvent, MeOH, was concentrated in vacuum to obtain the precipitate. CH\(_2\)Cl\(_2\) (1.0 mL) was then added in order to dissolve and extract the coupling products and the remaining materials and to precipitate the catalyst 1. Subsequently, the resultant mixture was filtered and the filtrate was washed two times with CH\(_2\)Cl\(_2\) (0.5
× 2 mL). At last, the remaining precipitate was dried under vacuum to give the catalyst 1 and reused. After the two cycles, the TEM showed that the recycled catalyst 1 remain the same fibrous morphology (Figure 2).

**Figure 2.** The TEM images of the catalyst 1

Characterization data for Suzuki cross-coupling products

**Biphenyl**\[^{3, 5, 9, 13}\]

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 42.5 mg of the coupling product after purification by column chromatography of the crude product. Yield = 92%; \( R_f = 0.6 \) (Petroleum ether); White solid; M.p. = 65-66 °C; IR (cm\(^{-1}\), KBr) v: 3034, 1608, 1506, 1480, 1430 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.35-7.38 \) (t, \( J = 8.0 \) Hz, 2H), 7.44-7.47 (m, \( J = 8.0 \) Hz, 4H), 7.61-7.62 (d, 4H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \( \delta = 141.32, 128.82, 127.32, 127.24 \) ppm.

**2-Nitrobiphenyl**\[^{4, 5, 12, 13}\]

Following the general procedure using 2-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 56.1 mg of the coupling product after purification by column chromatography of the crude product. Yield = 94%; \( R_f = 0.2 \) (Petroleum ether/AcOEt = 50/1 v/v); Yellow oil; IR (cm\(^{-1}\), KBr) v: 3062, 3031, 2868, 1605, 1568, 1525, 1472, 1452, 1354, 1306, 1162, 1142, 1093, 1075, 917, 852, 782, 770, 740, 698, 666 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta = 7.33-7.35 \)
(m, 2H), 7.42-7.47 (m, 4H), 7.48-7.51 (m, 1H), 7.62-7.65 (m, 1H), 7.86-7.88 (q, 1H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 149.35, 137.45, 136.34, 132.00, 132.72, 128.72, 128.26, 128.22, 127.94, 124.08\) ppm MS (EI) \(m/z\) (%): 199 (M\(^+\), 18), 171 (60), 152 (100), 143 (32).

**3-Nitrobiphenyl** \(^{4,5,11,12}\)

Following the general procedure using 3-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 54.9 mg of the coupling product after purification by column chromatography of the crude product. Yield = 92%; R\(_f\) = 0.2 (Petroleum ether/AcOEt = 50/1 v/v); Pale yellow solid; M.p. = 57-59 °C; IR (cm\(^{-1}\), KBr): \(\nu = 3081, 2922, 2851, 1577, 1528, 1499, 1472, 1349, 1291, 1043, 993, 897, 873, 812, 767, 731, 695, 675\) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.43-7.46\) (m, 1H), 7.50-7.53 (m, 2H), 7.61-7.65 (m, 3H), 7.92-7.94 (m, 1H), 8.20-8.22 (m, 1H), 8.46-8.47 (t, 1H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 148.76, 142.89, 138.67, 133.04, 129.72, 129.18, 128.56, 127.17, 122.03, 121.95\) ppm.

**4-Nitrobiphenyl** \(^{3,4,5,13}\)

Following the general procedure using 4-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 57.9 mg of the coupling product after purification by column chromatography of the crude product. Yield = 97%; R\(_f\) = 0.2 (Petroleum ether/AcOEt = 50/1 v/v); Pale yellow solid; M.p. = 113-115 °C; IR (cm\(^{-1}\), KBr): \(\nu = 3077, 1598, 1515, 1345, 1105, 740, 697\) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.45-7.48\) (m, 1H), 7.50-7.53 (m, 2H), 7.63-7.65 (m, 2H), 7.74-7.76 (m, 2H), 8.30-8.32 (m, 2H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 147.63, 147.11, 138.77, 129.17, 128.94, 127.80, 127.39, 124.11\) ppm.

**4-Bromobiphenyl** \(^{6,12}\)

Following the general procedure using 4-bromobenzenediazonium tetrafluoroborate (82.4 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 51.2 mg of the coupling product after purification by column chromatography of the crude product. At the same time, using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 4-bromophenylboronic acid (72.3 mg, 0.36 mmol, 1.2 equiv) provided 54.8 mg of product. Yield = 73% and 78%, respectively; R\(_f\) = 0.7 (Petroleum ether); White solid; M.p. = 89-90 °C; IR (cm\(^{-1}\), KBr): \(\nu = 3128, 3031, 1668, 1587, 1477, 1449, 1393, 1366, 1310, 1275, 1108, 1080, 1003, 830, 767, 691\) cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.37-7.40\) (t, 1H), 7.45-7.49 (m, 4H), 7.57-7.60 (m, 2H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 140.16, 140.02, 132.04, 131.87, 128.91, 128.76, 128.52, 127.65, 126.95, 121.54\) ppm.

**3-Methyldiphenyl** \(^{10,12,13}\)
Following the general procedure using 3-methylbenzenediazonium tetrafluoroborate (61.8 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 22.7 mg of the coupling product after purification by column chromatography of the crude product. At the same time, using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 3-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 44.4 mg of product. Yield = 45% and 88%, respectively; \( R_f = 0.6 \) (Petroleum ether); Colourless liquid; IR (cm\(^{-1}\), KBr) \( \nu \): 3060, 3030, 2948, 2860, 1610, 1589, 1482, 1377, 1076, 1026, 882, 753, 727, 699, 617 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta = 7.66-7.65 \) (q, 2H), 7.50-7.46 (m, 4H), 7.41-7.38 (m, 2H), 7.24-7.22 (d, 1H), 2.49 (s, 3H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \( \delta = 141.50, 141.38, 138.43, 128.83, 128.80, 128.14, 128.11, 127.31, 127.29, 124.42, 21.67 \) ppm; MS (EI) \( m/z \) (\%) 168 (M\(^+\), 100), 152 (22).

4-Methylbiphenyl \([3, 5, 9, 10, 12]\)

Following the general procedure using 4-methylbenzenediazonium tetrafluoroborate (61.8 mg, 0.3 mmol), and phenylboronic acid (43.9 mg, 0.36 mmol, 1.2 equiv) provided 36.8 mg of the coupling product after purification by column chromatography of the crude product. At the same time, using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 4-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 37.3 mg of product. Yield = 73% and 74%, respectively; \( R_f = 0.5 \) (Petroleum ether); White solid; M.p. = 41-43 °C; IR (cm\(^{-1}\), KBr) \( \nu \): 3067, 3033, 2917, 2860, 1602, 1567, 1522, 1488, 1378, 1340, 1044, 823, 766, 706, 481 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta = 2.43 \) (s, 3H), 7.28-7.29 (d, \( J = 7.8 \) Hz, 2H), 7.34-7.37 (m, 1H), 7.44-7.47 (t, 2H), 7.52-7.54 (d, \( J = 7.8 \) Hz, 2H), 7.61-7.62 (q, 2H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \( \delta = 141.20, 138.40, 137.04, 129.51, 128.74, 127.02, 127.00, 21.12 \) ppm.

2-Methyldiphenyl \([9, 10, 12]\)

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 2-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 34.8 mg of the coupling product after purification by column chromatography of the crude product. Yield = 69%; \( R_f = 0.5 \) (Petroleum ether); Colourless liquid; IR (cm\(^{-1}\), KBr) \( \nu \): 3068, 3038, 2919, 2850, 1610, 1467, 1406, 1378, 1369, 1051, 848, 797, 721, 666 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta = 7.52-7.51 \) (m, 2H), 7.45-7.42 (t, 2H, \( J = 1.2 \) Hz), 7.37-7.35 (m, 2H), 7.34 (t, 2H, \( J = 1.2 \) Hz), 2.38 (s, 3H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \( \delta = 135.82, 135.36, 130.31, 129.80, 129.20, 128.07, 127.25, 127.15, 126.77, 125.76, 125.54, 20.47 \) ppm; MS (EI) \( m/z \) (\%) 168 (M\(^+\), 100), 152 (22).

2-Methoxylbiphenyl \([9, 10]\)

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 2-methoxylphenylboronic acid (55.8 mg, 0.36 mmol, 1.2 equiv) provided 53.5 mg of the coupling product after purification by column chromatography of the crude product. Yield = 58%; \( R_f = 0.5 \) (Petroleum ether); Colourless liquid; IR (cm\(^{-1}\), KBr) \( \nu \): 3068, 3038, 2919, 2850, 1610, 1467, 1406, 1378, 1369, 1051, 848, 797, 721, 666 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta = 7.52-7.51 \) (m, 2H), 7.45-7.42 (t, 2H, \( J = 1.2 \) Hz), 7.37-7.35 (m, 2H), 7.34 (t, 2H, \( J = 1.2 \) Hz), 2.38 (s, 3H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \( \delta = 135.82, 135.36, 130.31, 129.80, 129.20, 128.07, 127.25, 127.15, 126.77, 125.76, 125.54, 20.47 \) ppm; MS (EI) \( m/z \) (\%) 168 (M\(^+\), 100), 152 (22).
chromatography of the crude product. Yield = 97%; Rf = 0.2 (Petroleum ether); Yellow transparent liquid; IR (cm\(^{-1}\), KBr): v: 3059, 3025, 2955, 2833, 1597, 1584, 1504, 1483, 1463, 1430, 1260, 1236, 1180, 1123, 1056, 1028, 1009, 754, 732, 699 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 3.84\) (s, 3H), 7.02-7.03 (dd, J=8.4, 0.6 Hz, 1H), 7.06-7.08 (td, J=7.2, 0.6 Hz, 1H), 7.34-7.35 (d, J=1.8 Hz, 1H), 7.36 (q, J=1.2 Hz, 1H), 7.37 (t, J=1.8 Hz, 1H), 7.43-7.46 (dd, J=7.2, 1.8 Hz, 2H), 7.56-7.58 (dd, J=8.4, 1.2 Hz, 2H) ppm; \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 156.50, 138.58, 130.91, 130.77, 129.57, 128.62, 127.99, 126.92, 120.85, 111.27, 55.57\) ppm.

3-Methoxybiphenyl\(^9\)

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 3-methoxyphenylboronic acid (55.8 mg, 0.36 mmol, 1.2 equiv) provided 37 mg of the coupling product after purification by column chromatography of the crude product. Yield = 67%; Rf = 0.2 (Petroleum ether); Canary yellow liquid; IR (cm\(^{-1}\), KBr): v: 3064, 3033, 2957, 2940, 2833, 1604, 1569, 1480, 1424, 1293, 1214, 1176, 1058 1013, 786, 673 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 3.89\) (s, 3H), 6.92-6.94 (ddd, J=8.4, 3.0, 1.2 Hz, 1H), 7.16 (m, 1H), 7.21-7.22 (m, 1H), 7.36-7.39 (m, 2H), 7.45-7.48 (m, 2H), 7.61 (t, J=1.2 Hz, 1H), 7.62-7.63 (d, J=1.2 Hz, 1H) ppm; \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 159.97, 142.81, 141.14, 129.77, 128.76, 127.44, 127.22, 119.71, 112.93, 112.71, 55.32\) ppm; MS (EI) m/z (%) 184 (M\(^+\), 100), 169 (43), 77 (7).

3-chlorobiphenyl\(^12, 13\)

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 3-chlorophenylboronic acid (56.3 mg, 0.36 mmol, 1.2 equiv) provided 45.1 mg of the coupling product after purification by column chromatography of the crude product. Yield = 80%; Rf = 0.6 (Petroleum ether); Colorless transparent liquid; IR (cm\(^{-1}\), KBr): v: 3057, 3033, 2924, 1380, 1494, 1464, 1425, 1310, 1072, 1038, 1011, 771, 746, 697 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.34-7.41\) (m, 3H), 7.45-7.50 (m, 3H), 7.57-7.63 (m, 3H) ppm; \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 139.83, 134.67, 130.00, 128.91, 127.91, 127.88, 127.31, 127.28, 127.13, 125.31, 125.29\) ppm; MS (EI) m/z (%) 188 (M\(^+\), 100), 152 (47), 76 (11).

4-chlorobiphenyl\(^4, 5, 11, 12\)

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 4-chlorophenylboronic acid (56.3 mg, 0.36 mmol, 1.2 equiv) provided 47.9 mg of the coupling product after purification by column chromatography of the crude product. Yield = 85%; Rf = 0.6 (Petroleum ether); White solid; M.p. = 32 °C; IR (cm\(^{-1}\), KBr): v: 3065, 2922, 1656, 1586, 1473, 1393, 1095, 1002, 831, 756, 686, 618 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 7.37-7.40\) (ddd, J=8.4, 2.4, 1.2 Hz, 1H), 7.42 (t, J=1.8 Hz, 1H), 7.43 (t, J=1.8 Hz, 1H), 7.44-7.46 (m, 1H), 7.47-7.48 (dd, J=4.8, 1.8 Hz, 1H), 7.52-7.55 (dt, J=8.4, 2.4 Hz, 2H), 7.57-7.58 (m, 2H) ppm; \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 140.02, 139.69, 133.40, 129.06, 128.92, 128.90, 128.41, 127.60, 127.00\) ppm.
3,5-dimethylbiphenyl [9]

Following the general procedure using benzenediazonium tetrafluoroborate (57.6 mg, 0.3 mmol), and 3,5-dimethylphenylboronic acid (54.0 mg, 0.36 mmol, 1.2 equiv) provided 50.2 mg of the coupling product after purification by column chromatography of the crude product. Yield = 92%; Rf = 0.6 (Petroleum ether); Colorless transparent liquid; IR (cm\(^{-1}\), KBr): \(\nu\): 3068, 3038, 2919, 2850, 2837, 1610, 1583, 1467, 1406, 1378, 1369, 1051, 848, 797, 729, 673 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\): 2.41-2.42 (d, 6H), 7.01-7.04 (d, 1H), 7.23-7.25 (d, 2H), 7.35-7.37 (t, J=7.2 Hz, 1H), 7.44-7.47 (m, 2H), 7.61-7.62 (d, J=7.2 Hz, 2H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\): 141.50, 141.29, 138.26, 128.91, 128.65, 127.21, 127.09, 125.13, 21.42 ppm; MS (EI) \(m/z\) (%): 182 (M\(^+\), 100), 167 (79), 152 (14).

4-Methyl-2’-nitrobiphenyl [7]

Following the general procedure using 2-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and 4-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 50.5 mg of the coupling product after purification by column chromatography of the crude product. Yield = 79%; Rf = 0.6 (Petroleum ether); Yellow oily liquid; IR (cm\(^{-1}\), KBr): \(\nu\): 3027, 2921, 2867, 1613, 1566, 1525, 1475, 1355, 1305, 1283, 1041, 853, 819, 781, 749, 721, 704, 656, 639 cm\(^{-1}\); \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta\): 2.42 (s, 3H), 7.23-7.27 (m, 4H), 7.44-7.48 (m, 2H), 7.59-7.62 (m, 1H), 7.83-7.84 (q, 1H) ppm; \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)), \(\delta\): 149.2, 138.0, 136.0, 134.1, 132.1, 131.8, 129.3, 127.8, 127.6, 123.8, 21.1 ppm; MS (EI) \(m/z\) (%): 213 (M\(^+\), 42), 196 (48), 152 (82), 77 (68).

4-Methyl-3’-nitrobiphenyl [4]

Following the general procedure using 3-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and 4-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 52.4 mg of the coupling product after purification by column chromatography of the crude product. Yield = 82%; Rf = 0.6 (Petroleum ether); White solid; M.p. = 75-76 °C; IR (cm\(^{-1}\), KBr): \(\nu\): 3087, 3025, 2922, 2854, 1582, 1529, 1380, 1346, 1293, 1260, 1186, 1084, 1037, 967, 899, 874, 804, 739, 681 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\): 2.43 (s, 3H), 7.31-7.32 (d, 2H), 7.53-7.54 (q, 2H), 7.58-7.61 (t, 1H), 7.90-7.91 (m, 1H), 8.17-8.19 (m, 1H), 8.44-8.45 (t, 1H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\): 148.74, 142.77, 138.58, 135.72, 132.78, 129.90, 127.65, 126.95, 121.70, 121.62, 21.16 ppm.

4-Methyl-4’-nitrobiphenyl [8]

Following the general procedure using 4-nitrobenzenediazonium tetrafluoroborate (71.1 mg, 0.3 mmol), and 4-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2
equiv) provided 46.6 mg of the coupling product after purification by column chromatography of the crude product. Yield = 73%; R$_f$ = 0.1 (Petroleum ether); White solid; M.p. = 140-142 °C; IR (cm$^{-1}$, KBr) ν: 3078, 2924, 2852, 1595, 1513, 1483, 1397, 1338, 1294, 1189, 1107, 1004, 853, 824, 753, 720, 696 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$): δ = 2.44 (s, 3H), 7.31-7.32 (q, 2H), 7.53-7.55 (m, 2H), 7.71-7.74 (m, 2H), 8.27-8.30 (m, 2H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): δ = 149.35, 137.45, 136.34, 132.34, 132.00, 128.72, 128.26, 128.22, 127.94, 124.08, 21.21 ppm.

Following the general procedure using 4-bromobenzenediazonium tetrafluoroborate (82.4 mg, 0.3 mmol), and 4-methylphenylboronic acid (49.9 mg, 0.36 mmol, 1.2 equiv) provided 38.2 mg of the coupling product after purification by column chromatography of the crude product. Yield = 78%; R$_f$ = 0.6 (Petroleum ether); White solid; M.p. = 129-130 °C; IR (cm$^{-1}$, KBr) ν: 3022, 2915, 2848, 1476, 1388, 1071, 1001, 805, 720, 543, 501 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$): δ = 2.41 (s, 3H), 7.25-7.27 (t, 2H), 7.44-7.47 (m, 4H), 7.54-7.57 (m, 2H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$): δ = 140.10, 137.54, 137.15, 131.86, 129.68, 126.82, 121.24, 21.18 ppm.

**References:**

[2] Unless otherwise specified, digital display temperature control instrument was used in this process.
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