

**SUPPORTING INFORMATION**

**Title:** Facile Synthesis of Substituted Alkynes by Cyclopalladated Ferrocenylimine Catalyzed Cross-Coupling of Arylboronic Acids/Esters with Terminal Alkynes

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## Selected characterization data for cross-coupling reaction of arylboronic reagents and terminal alkynes products.

**Diphenylacetylene (3a).**<sup>[11]</sup> White solid, mp 58–61 °C (lit. 60–62 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.62–7.52 (m, 4H), 7.42–7.28 (m, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 132.0, 128.7, 128.6, 123.7, 89.7 ppm.

**(*p*-Hexylphenyl) phenylacetylene (3b).**<sup>[12]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.55–7.47 (m, 2H), 7.44 (d, *J* = 8.04 Hz, 2H), 7.40–7.30 (m, 3H), 7.15 (d, *J* = 7.04 Hz, 2H), 2.61 (t, *J* = 7.80 Hz, 2H), 1.65–1.52 (m, 2H), 1.36–1.26 (m, 4H), 0.89 (t, *J* = 6.40 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 143.4, 131.6, 131.5, 128.5, 128.3, 128.1, 123.5, 120.4, 89.6, 88.7, 35.9, 31.4, 31.0, 22.5, 14.0 ppm.

**(3-Phenylethynyl) pyridine (3c).**<sup>[13]</sup> Yellow solid, mp 48–49 °C (lit. 50–51 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.78 (s, 1H), 8.56 (s, 1H), 7.83 (d, *J* = 7.88 Hz, 1H), 7.60–7.49 (m, 2H), 7.45–7.35 (m, 3H), 7.35–7.27 (m, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 152.0, 148.3, 138.7, 131.7, 128.9, 128.5, 123.2, 122.5, 120.7, 92.9, 85.8 ppm.

**(*p*-Tolyl) phenylacetylene (3d).**<sup>[14]</sup> White solid, mp 71–72 °C (lit. 72–73 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.52 (d, *J* = 8.08 Hz, 2H), 7.42 (d, *J* = 8.08 Hz, 2H), 7.34–7.32 (m, 3H), 7.14 (d, *J* = 8.00 Hz, 2H), 2.36 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 138.4, 131.6, 131.5, 129.1, 128.3, 128.0, 123.5, 120.2, 89.6, 88.7, 21.5 ppm.

**3-(*p*-Tolyl) pyridine (3e).**<sup>[15]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.90–8.65 (m, 1H), 8.65–8.35 (m, 1H), 7.80 (d, *J* = 7.69 Hz, 1H), 7.44 (d, *J* = 8.04 Hz, 2H), 4.39–7.26 (m, 1H), 7.17 (d, *J* = 8.04 Hz, 2H), 2.38 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 152.1, 148.2, 139.1, 138.4, 131.6, 129.2, 123.1, 120.9, 119.4, 93.0, 85.3, 21.6 ppm.

**(3-Tolyl-phenyl) acetylene (3f).**<sup>[16]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.55–7.50 (m, 2H), 7.40–7.29 (m, 5H), 7.27–7.10 (m, 2H), 2.36 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 138.0, 132.2, 131.6, 129.2, 128.7, 128.3, 128.2, 128.1, 123.3, 123.0, 89.5, 89.0, 21.3 ppm.

**Phenyl [3-(trifluoromethyl) phenyl] ethyne (3g).**<sup>[17]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.76–7.72 (m, 1H), 7.72–7.62 (m, 1H), 7.61–7.50 (m, 3H), 7.49–7.41 (m, 1H), 7.40–7.30 (m, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 134.7, 131.7, 131.1 (q, <sup>2</sup>*J* (C, F) = 32 Hz), 129.6, 128.9, 128.4, 124.7, 124.3, 124.1, 123.8 (q, <sup>1</sup>*J* (C, F) = 270 Hz), 122.6, 90.9, 87.8 ppm.

**(*p*-Methoxyphenyl)phenylacetylene (3h).**<sup>[11]</sup> White solid, mp 59–60 °C (lit. 57–61 °C); <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.53–7.50 (m, 2H), 7.50–7.45 (m, 2H), 7.37–7.30 (m, 3H), 6.87 (d,  $J$  = 8.80 Hz, 2H), 3.83 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 159.6, 133.1, 131.5, 128.3, 128.0, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3 ppm.

**(2-Methoxyphenyl)phenylacetylene (3i).**<sup>[18]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.57–7.52 (m, 2H), 7.52–7.47 (m, 1H), 7.36–7.22 (m, 4H), 6.95–6.88 (m, 1H), 6.88–6.84 (m, 1H), 3.86 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 160.0, 133.6, 131.7, 129.9, 128.3, 128.2, 123.6, 120.5, 113.9, 112.4, 93.5, 85.8, 55.8 ppm.

**Ethyl phenylpropiolate (3j).**<sup>[19]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.59 (d,  $J$  = 7.40 Hz, 2H), 7.45 (t,  $J$  = 7.40, 1H), 7.38 (t,  $J$  = 7.40 Hz, 2H), 4.30 (q,  $J$  = 7.20 Hz, 2H), 1.36 (t,  $J$  = 7.20 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 154.0, 132.9, 130.5, 128.5, 119.5, 86.0, 80.6, 62.0, 14.0 ppm.

**1-Heptynylbenzene (3k).**<sup>[20]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.45–7.32 (m, 2H), 7.30–7.24 (m, 3H), 2.40 (t,  $J$  = 7.20 Hz, 2H), 1.65–1.52 (m, 2H), 1.48–1.28 (m, 4H), 0.92 (t,  $J$  = 7.20 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 131.6, 128.2, 127.5, 124.1, 90.5, 80.6, 31.2, 28.5, 22.3, 19.4, 14.0 ppm.

**1-Phenyl-1-octyne (3l).**<sup>[11]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40–7.37 (m, 2H), 7.30–7.22 (m, 3H), 2.40 (t,  $J$  = 7.08 Hz, 2H), 1.65–1.54 (m, 2H), 1.50–1.38 (m, 2H), 1.38–1.26 (m, 4H), 0.90 (t,  $J$  = 7.08 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 131.0, 127.6, 126.9, 123.6, 90.0, 90.0, 30.9, 28.2, 28.1, 22.1, 18.9, 13.5 ppm.

**1-Phenyl-1-decyne (3m).**<sup>[11]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40–7.36 (m, 2H), 7.29–7.23 (m, 3H), 2.40 (t,  $J$  = 7.20 Hz, 2H), 1.64–1.53 (m, 2H), 1.48–1.39 (m, 2H), 1.37–1.27 (m, 8H), 0.89 (t,  $J$  = 7.20 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 131.5, 128.2, 127.4, 124.1, 90.5, 80.5, 31.9, 29.2, 29.1, 29.0, 28.8, 22.7, 19.4, 14.1 ppm.

**1-(4-Methylphenyl)-1-heptyne (3n).**<sup>[21]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.28 (d,  $J$  = 8.00 Hz, 2H), 7.07 (d,  $J$  = 8.00 Hz, 2H), 2.38 (t,  $J$  = 7.20 Hz, 2H), 2.32 (s, 3H), 1.68–1.53 (m, 2H), 1.46–1.27 (m, 4H), 0.92 (t,  $J$  = 7.20 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 136.9, 130.9, 128.4, 120.5, 89.1, 80.0, 30.6, 28.0, 21.7, 20.9, 18.9, 13.5 ppm.

**1-(4-Methylphenyl)-1-octyne (3o).**<sup>[22]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.28 (d,  $J$  = 8.04 Hz, 2H), 7.07 (d,  $J$  = 8.04 Hz, 2H), 2.39 (t,  $J$  = 7.12 Hz, 2H), 2.32 (s, 3H), 1.68–1.53 (m, 2H), 1.48–1.39 (m, 2H), 1.37–1.26 (m, 4H), 0.90 (s,  $J$  = 6.88 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 137.4, 131.4, 128.9, 121.0, 89.7, 80.6, 31.4, 28.8, 28.6, 22.6, 21.4, 19.4, 14.1 ppm.

**1-(4-Methylphenyl)-1-decyne (3p).**<sup>[11]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.28 (d,  $J$  = 8.08 Hz, 2H), 7.07 (d,  $J$  = 8.08 Hz, 2H), 2.38 (t,  $J$  = 7.08 Hz, 2H), 2.32 (s, 3H), 1.68–1.53 (m, 2H), 1.48–1.39 (m, 2H), 1.37–1.26 (m, 8H), 0.88 (s,  $J$  = 6.88 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 137.4, 131.4, 129.0, 121.0, 89.6, 80.5, 31.8, 29.2, 29.1, 28.9, 28.8, 22.7, 21.4, 19.4, 14.1 ppm.

**1-(3-Methylphenyl)-1-heptyne (3q).**<sup>[23]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.24–7.13 (m, 3H), 7.06 (d,  $J$  = 7.20 Hz, 1H), 2.39 (t,  $J$  = 7.08 Hz, 2H), 2.30 (s, 3H), 1.68–1.53 (m, 2H), 1.46–1.28 (m, 4H), 0.92 (t,  $J$  = 7.20 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 137.8, 132.1, 128.6, 128.3, 128.0, 123.9, 90.1, 80.7, 31.1, 28.5, 22.2, 21.2, 19.4, 14.0 ppm.

**2-Methyl-4-(*p*-tolyl)-but-3-yn-2-ol (3r).**<sup>[13]</sup> Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.32 (d,  $J$  = 7.80 Hz, 2H), 7.11 (d,  $J$  = 7.80 Hz, 2H), 2.33 (s, 3H), 2.28 (s, br, 1H), 1.61 (s, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 138.3, 131.5, 129.0, 119.7, 93.1, 82.2, 65.7, 31.6, 21.5 ppm.