# Efficient Ruthenium and Copper Cocatalzyed Five-Component Coupling to Form Dipropargyl Amines Under Mild Conditions in Water

**E. Ryan Bonfield and Chao-Jun Li***
**Department of Chemistry, McGill University, 801 Sherbrooke street West, Montreal, Quebec H3A 2K6 Canada**

## Supplementary Materials

## Experimental

### 3-Phenyl-N-(3-phenylprop-2-ynyl)-N-(3-phenylpropyl)prop-2-yn-1-amine (Table 2 entry 1)

Purification by column chromatography (0-5% EtOAc gradient, $R_f$=0.3 in 9:1 hexanes:EtOAc) gave a pale yellow oil; IR (neat) $\nu_{max}$ 3026, 2942, 1598, 1489, 1453, 1442, 1350, 1324cm$^{-1}$. $^1$H NMR (400MHz, $CDCl_3$) δ 7.42-7.40 (m, 4H), 7.27-7.13 (m, 11H), 3.71 (s, 4H), 2.72-2.67 (m, 4H), 1.89 (tt, J = 7.5, 7.5Hz, 2H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 141.9, 131.7, 128.3, 128.2, 128.1, 128.0, 125.7, 123.0, 85.1, 84.6, 52.3, 43.2, 33.4, 29.0; HRMS *m/z* calcd for $C_{27}H_{24}N$ (M-H$^+$) 362.1909, found 362.1901.

### N,N-Bis(3-phenylprop-2-ynyl)butan-1-amine (Table 2, entry 2)

Purification by column chromatography (99:1 hexanes:EtOAc, $R_f$=0.4 in 9:1 hexanes:EtOAc) gave a pale yellow oil; IR (neat) $\nu_{max}$ 3033, 2956, 2931, 1598, 1489, 1442, 1359, 1324cm$^{-1}$. $^1$H NMR (400MHz, $CDCl_3$) δ 7.49-7.44 (m, 4H), 7.32-7.29 (m, 6H), 3.74 (s, 4H), 2.70 (t, J = 7.4Hz, 2H), 1.62-1.54 (m, 2H), 1.43 (tt, J = 7.4, 7.4Hz 2H), 0.98 (t, J = 7.2Hz, 3H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 131.9, 128.3, 128.1, 123.3, 85.1, 84.9, 53.0, 43.4, 29.8, 20.7, 14.1; HRMS *m/z* calcd for $C_{22}H_{22}N$ (M-H$^+$) 300.1752, found 300.1750.

### N,N-Bis(3-phenylprop-2-ynyl)benzenamine (Table 2, entry 3)

Purification by column chromatography (0-1% EtOAc gradient, $R_f$ =0.5 in 9:1 hexanes:EtOAc) gave pale yellow oil; IR (neat) $\nu_{max}$ 3060, 1682, 1597, 1504, 1489, 1442, 1346, 1224cm$^{-1}$. $^1$H NMR (400MHz, $CDCl_3$) δ 7.40-7.36 (m, 4H), 7.33-7.20 (m, 8H), 7.07-7.04 (m, 2H), 6.88 (tt, J = 7.2, 1.0Hz, 1H), 4.38 (s, 4H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 148.3, 131.9, 129.2, 128.3, 128.3, 123.0, 119.6, 116.0, 85.2, 84.7, 41.5; HRMS *m/z* calcd for $C_{24}H_{18}N$ (M-H$^+$) 320.1439, found 320.1436.

### N,N-Di(hept-2-ynyl)benzenamine (Table 2, entry 4)

Purification by column chromatography (0-1% EtOAc gradient, $R_f$ =0.7 in 9:1 hexanes:EtOAc) gave a colourless oil; IR (neat) $\nu_{max}$ 2957, 2932, 1600, 1504, 1456, 1366, 1328, 1221cm$^{-1}$. $^1$H NMR (400MHz, $CDCl_3$) δ 7.27-7.23 (m, 2H), 6.95 (d, J = 6.6, 2H), 6.83 (t, J = 7.2Hz, 1H), 4.06 (t, J = 2.0Hz, 4H), 2.18-2.14 (m, 4H), 1.49-1.32 (m, 8H), 0.88 (t, J = 7.4Hz, 6H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 148.5, 128.9, 119.1, 115.8,

84.7, 75.5, 40.7, 30.8, 21.9, 18.4, 13.6; HRMS *m/z* calcd for $C_{20}H_{26}N$ (M-$H^+$) 280.2065, found 280.2063.

**4-Methoxy-N,N-bis(3-phenylprop-2-ynyl)benzenamine (Table 2, entry 5)**
Purification by column chromatography (0-2% EtOAc gradient, $R_f$ 0.3 in 9:1 hexanes:EtOAc) gave a pale yellow oil; IR (neat) $\nu_{max}$ 3055, 2932, 2833, 1735, 1598, 1511, 1489, 1442, 1246, 1028$cm^{-1}$. $^1$H NMR (400MHz, $CDCl_3$) δ 7.40-7.34 (m, 4H), 7.29-7.22 (m, 6H), 7.09-7.05 (m, 2H), 6.90-6.84 (m, 2H), 4.30 (s, 4H), 3.76 (s, 3H); $^{13}$C NMR (400MHz, $CDCl_3$) δ 154.2, 142.7, 131.8, 128.2, 128.1, 123.0, 119.3, 114.4, 85.1, 84.9, 55.6, 42.6; HRMS *m/z* calcd for $C_{25}H_{21}NO$ ($M^+$) 351.1623, found 351.1610, for $C_{25}H_{20}NO$ (M-$H^+$) 350.1545, found 350.1540.

**4-Methyl-N,N-bis(3-phenylprop-2-ynyl)benzenamine (Table 2, entry 6)**
Purification by column chromatography (0-1% EtOAc gradient, $R_f$=0.4 in 9:1 hexanes:EtOAc) gave a yellow oil; IR (neat) $\nu_{max}$ 3032, 2920, 1616, 1598, 1519, 1489, 1442, 1366, 1335, 1233, 1207, 1155, 1070, 1028$cm^{-1}$. $^1$H NMR (400MHz, $CDCl_3$) δ 7.39-7.34 (m, 4H), 7.26-7.20 (m, 6H), 7.11-7.08 (m, 2H), 6.98 (dt, J = 8.4, 2.2Hz, 2H), 4.34 (s, 4H), 2.27 (s, 3H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 146.1, 131.7, 129.6, 129.1, 128.1, 128.0, 123.0, 116.6, 85.1, 84.6, 41.7, 20.4; HRMS *m/z* calcd for $C_{25}H_{21}NO$ (M-$H^+$) 334.1596, found 334.1591.

**N,N-Bis(3-phenylprop-2-ynyl)cyclopentanamine (Table 2, entry 7)**
Purification by column chromatography (1-2% EtOAc gradient, $R_f$=0.3 in 9:1 hexanes:EtOAc) gave a colourless oil; IR (neat) $\nu_{max}$ 3055, 2956, 2869, 2805, 1598, 1489, 1442, 1349, 1324, $cm^{-1}$. $^1$H NMR (400MHz, $CDCl_3$) δ 7.43 (s, 4H), 7.28 (d, J = 2.8Hz, 6H), 3.82 (s, 4H), 3.03 (tt, J = 8.0, 8.0Hz, 1H), 2.04-1.93 (m, 2H), 1.8-1.72 (m, 2H), 1.66-1.44 (m, 4H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 131.7, 128.1, 127.9, 123.2, 84.9, 84.8, 62.9, 42.1, 31.4, 24.0; HRMS *m/z* calcd for $C_{23}H_{22}N$ (M-$H^+$) 312.1752, found 312.1750.

**N,N-Bis(3-phenylprop-2-ynyl)prop-2-en-1-amine (Table 2, entry 8)**
Purification by column chromatography (0-1% EtOAc gradient, $R_f$=0.2 in 9:1 hexanes:EtOAc) gave a colourless oil; IR (neat) $\nu_{max}$ 3079, 2918, 2813, 1598, 1489, 1442, 1363, 1326, 1252, 1108 $cm^{-1}$. $^1$H NMR (400MHz, $CDCl_3$) δ 7.47-7.42 (m, 4H), 7.30-7.27 (m, 6H), 5.92 (ddt, J = 17.2, 10.4, 6.8Hz, 1H), 5.35 (ddt, J = 17.2, 1.6, 1.6Hz, 1H), 5.22 (dm, J = 10.0Hz, 1H), 3.72 (s, 4H), 3.32 (dt, J = 6.8, 1.2Hz, 2H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 135.0, 131.8, 128.3, 128.1, 123.2, 118.8, 85.3, 84.6, 56.5, 42.9; HRMS *m/z* calcd for $C_{21}H_{18}N$ (M-$H^+$) 284.1439, found 284.1437.

**N-Methyl-3-phenyl-N-(3-phenylprop-2-ynyl)prop-2-yn-1-amine (Table 2, entry 9)**
Purification by column chromatography (0-5% EtOAc gradient, $R_f$ =0.5 in 7:3 hexanes:EtOAc) gave a orange oil; IR (neat) $\nu_{max}$ 3056, 2944, 2866, 2790, 1598, 1489, 1442, 1361, 1326 $cm^{-1}$. $^1$H NMR (400MHz, $CDCl_3$) δ 7.48-7.46 (m, 4H), 7.33-7.30 (m, 6H), 3.67 (s, 4H), 2.53 (s, 3H); $^{13}$C NMR (100MHz, $CDCl_3$) δ 131.8, 128.3, 128.1, 123.1, 85.3, 84.6, 45.6, 41.5; HRMS *m/z* calcd for $C_{19}H_{16}N$ (M-$H^+$) 258.1283, found 258.1285.