CuBr-Catalyzed Efficient Alkynylation of sp^3 C-H Bonds Adjacent to a Nitrogen Atom

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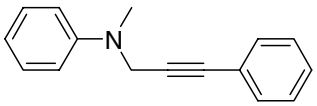
Supporting Materials

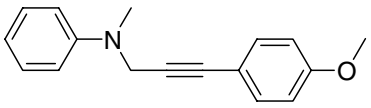
Experimental Section

General information: ^{1}H NMR spectra were recorded on Varian 400MHz spectrometer in $CDCl_3$ solution and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; dt, doublet of triplet; ddd, doublet of doublet of doublet; ddt, doublet of doublet of triplet; m, multiplet; q, quartet; and bs, broad singlet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals (central peak is 77.00 ppm). MS data were obtained by KRATOS MS25RFA Mass Spectrometer. HRMS were made by McGill University. IR spectra were recorded by an ABB Bomem MB100 instrument. Melting points were recorded by Melting Point Apparatus, Gallenkamp. Flash column chromatography was performed over SORBENT silica gel 30-60 μm. All reagents were weighed and handled in air, and backfilled under an inert atmosphere of nitrogen at room temperature. All reagents were purchased from Aldrich and used without further purification. 1-Phenyl-piperidine and 2-phenyl-1,2,3,4-tetrahydro-isoquinoline were prepared by the literature method[1].

General procedure: To a mixture of CuBr (14.0 mg, 0.1 mmol), *N*,*N*-dimethylaniline (0.508 mL, 4.0 mmol) and phenylacetylene (0.22 mL, 2.0 mmol) was added *tert*-butyl hydroperoxide (0.4 mL, 5–6M in decane) under nitrogen over 30 seconds at room temperature. The reaction temperature was raised to 100 ^{o}C over 15 min. The resulting mixture was stirred at the same temperature for 3 hr. The reaction mixture was cooled to room temperature; the resulting suspension was diluted with diethyl ether and filtrated through a short fluorisil column eluting with diethyl ether. Solvent was evaporated and the residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 95:5), and the fraction with an R_f=0.5 was collected and concentrated to give the desired product 3a.

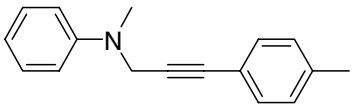


***N*-Methyl-*N*-(3-phenylprop-2-ynyl)benzenamine (3a).** Isolated yield is 74% as yellow oil by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.5). ^{1}H NMR (ppm) δ 7.35-7.33(m, 2H), 7.28-7.20(m, 5H), 6.89-6.87(m, 2H), 6.80-6.77(m, 1H), 4.22(s, 2H), 3.00(s, 3H); ^{13}C NMR (ppm) δ 149.03, 131.55, 128.90, 128.01, 127.91, 122.82, 117.97, 114.18, 84.92, 84.03, 43.29, 38.73; MS (EI) *m/z* (%) 221(M^+, 100), 220(77), 144(15), 116(10), 115(75), 104(12), 77(13).

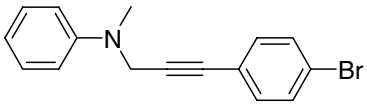


***N*-(3-(4-Methoxyphenyl)prop-2-ynyl)-*N*-methylbenzenamine (3b).** Isolated yield is 82% as white solid by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.25). Melting point is 72.0-73.0 ^{o}C. IR (KBr): ν_{max} 3065, 3006, 2969, 2818, 1604, 1508, 1251,

1030, 836, 756, 693 cm^{-1}; ^1H NMR (ppm) δ 7.29-7.23(m, 4H), 6.88(d, J = 8.0 Hz, 2H), 6.80-6.74(m, 3H), 4.22(s, 2H), 3.74(s, 3H), 3.00(s, 3H); ^{13}C NMR (ppm) δ 159.13, 149.08, 132.94, 128.87, 117.86, 114.94, 114.15, 113.63, 83.84, 83.39, 55.24, 43.30, 38.69; MS (EI) *m/z* (%) 251(M^+, 42), 250(14), 146(11), 145(100), 102(8), 77(6); HRMS calcd for $C_{17}H_{17}NO$: 251.1310; found: 251.1317.

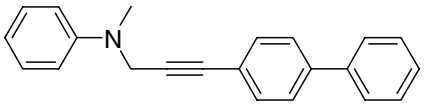


***N*-Methyl-*N*-(3-*p*-tolylprop-2-ynyl)benzenamine (3c).** Isolated yield is 74% as light yellow solid by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.5). IR (KBr): v_{max} 3056, 3023, 2990, 2962, 2884, 2223, 1598, 1353, 1234, 1201, 1110, 994, 923, 819, 759, 695, 529 cm^{-1}; ^1H NMR (ppm) δ 7.26-7.22(m, 4H), 7.02(d, J = 8.0 Hz, 2H), 6.87(d, J = 8.0 Hz, 2H), 6.77(dd, J = 7.2, 7.2 Hz, 1H), 4.21(s, 2H), 2.99(s, 3H), 2.28(s, 3H); ^{13}C NMR (ppm) δ 149.06, 137.90, 131.41, 128.87, 128.74, 119.74, 117.89, 114.15, 84.16, 84.10, 43.28, 38.67, 21.51; MS (EI) *m/z* (%) 236(M^++1, 17), 235(M^+, 94), 234(M^+-1, 60), 201(34), 200(34), 199(34), 198(32), 144(11), 130(12), 129(100), 128(21), 119(6), 106(16), 91(9), 77(20),63(5), 51(6); HRMS calcd for $C_{17}H_{17}N$: 235.1361; found: 235.1365.

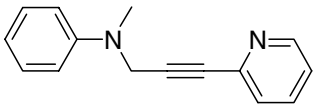


***N*-(3-(4-Bromophenyl)prop-2-ynyl)-*N*-methylbenzenamine (3d).** Isolated yield is 74% as light yellow solid by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.4). IR (KBr): v_{max} 3060, 3023, 2876, 2811, 1599, 1505, 1485, 1366, 1333, 1235, 1110, 1070, 1011, 826, 752, 689, 521 cm^{-1}; ^1H NMR (ppm) δ 7.33(d, J = 8.4 Hz, 2H), 7.24(dd, J = 8.0, 6.6 Hz, 2H), 7.17(d, J = 8.4 Hz, 2H), 6.85(d, J = 8.0 Hz, 2H), 6.78(dd, J = 6.6, 6.6 Hz, 1H), 4.20(s,

2H), 2.98(s, 3H); ^{13}C NMR (ppm) δ 148.91, 132.99, 131.23, 128.92, 122.12, 121.77, 118.06, 114.14, 86.24, 83.02, 43.28, 38.73; MS (EI) *m/z* (%) 302(M^++2, 16), 301(M^++1, 96), 300(M^+, 78), 299(M^+-1, 100), 298(66), 219(14), 196(12), 195(80), 193(81), 144(24), 115(10), 114(32), 113(12), 106(14), 104(22), 77(28); HRMS calcd for $C_{16}H_{14}BrN$: 299.0309; found: 299.0305.

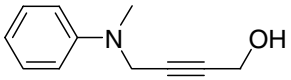


***N*-Methyl-*N*-(3-biphenylprop-2-ynyl)benzenamine (3e).** Isolated yield is 60% as white solid by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.3). Melting point is 83.0-84.5 ^{o}C. IR (KBr): ν_{max} 3060, 2815, 1596, 1505, 1485, 1370, 1109, 919, 841, 764, 750, 692, 503 cm^{-1}; ^{1}H NMR (ppm) δ 7.52(d, *J* = 8.0 Hz, 2H), 7.47(d, *J* = 8.0 Hz, 2H), 7.42-7.37(m, 4H), 7.31(d, *J* = 7.2 Hz, 1H), 7.26(dd, *J* = 8.0, 8.0 Hz, 2H), 6.90(d, *J* = 8.8 Hz, 2H), 6.79(dd, *J* = 7.2, 7.2 Hz, 1H), 4.25(s, 2H), 3.02(s, 3H); ^{13}C NMR (ppm) δ 149.05, 140.60, 140.12, 131.98, 128.93, 128.66, 127.41, 126.81, 126.71, 121.74, 118.00, 114.22, 85.63, 83.92, 43.38, 38.77; MS (EI) *m/z* (%) 298(M^++1, 18), 297(M^+, 77), 296(M^+-1, 35), 192(20), 191(100), 189(18), 129(16), 77(12); HRMS calcd for $C_{22}H_{19}N$: 297.1517; found: 297.1510.

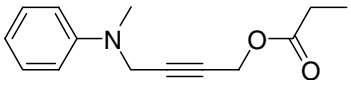


***N*-Methyl-*N*-(3-(pyridin-2-yl)prop-2-ynyl)benzenamine (3f).** Isolated yield is 36% as yellow oil by flash column chromatography (hexane/ethyl acetate = 10:1, R_f = 0.1). IR (neat liquid): ν_{max} 3061, 2880, 2819, 2236, 1599, 1581, 1505, 1464, 1427, 1342, 1200, 1114, 922, 778, 754, 692 cm^{-1}; ^{1}H NMR (ppm) δ 8.50(d, *J* = 4.4 Hz, 1H), 7.52(dd, *J* = 7.8, 7.8 Hz, 1H), 7.30-7.23(m, 3H), 7.14-7.11(m, 1H), 6.88(d, *J* = 8.4 Hz, 2H), 6.78(dd, *J* = 7.0, 7.0 Hz, 1H), 4.27(s, 2H), 3.02(s, 3H); ^{13}C NMR (ppm) δ 149.54, 148.75, 142.75, 135.74, 128.86, 126.95,

122.51, 117.94, 113.97, 85.18, 83.38, 43.02, 38.70; MS (EI) *m/z* (%) 222(M^+, 20), 221(M^+-1, 16), 207(12), 180(3), 144(12), 118(12), 117(100), 104(8), 89(9), 77(16), 63(5), 51(5); HRMS calcd for $C_{15}H_{14}N_2$: 222.1157; found: 222.1152.

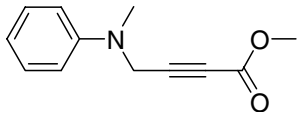


4-(*N*-Methyl-*N*-phenylamino)but-2-yn-1-ol (3g). Isolated yield is 40% as light yellow oil by flash column chromatography (hexane/ethyl acetate = 10:1, R_f = 0.1). IR (neat liquid): ν_{max} 3360, 3060, 2916, 2868, 1600, 1505, 1334, 1241, 1200, 1116, 1014, 924, 754, 692 cm^{-1}; ^1H NMR (ppm) δ 7.23(dd, J = 8.0, 7.2 Hz, 2H), 6.81(d, J = 9.2 Hz, 2H), 6.77(d, J = 7.2 Hz, 1H), 4.14(s, 2H), 4.04(s, 2H), 2.93(s, 3H), 2.02(bs, 1H); ^{13}C NMR ($CDCl_3$, ppm) δ 148.79, 128.93, 118.09, 114.09, 82.11, 81.08, 51.01, 42.71, 38.68; MS (EI) *m/z* (%) 176(M^++1, 12), 175(M^+, 100), 174(M^+-1, 38), 158(26), 144(22), 130(10), 115(8), 106(22), 104(16), 91(7), 77(38), 51(10), 39(6); HRMS calcd for $C_{11}H_{13}NO$: 175.0997; found: 175.0992.

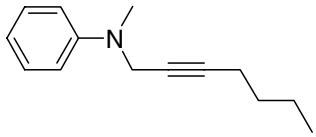


4-(*N*-Methyl-*N*-phenylamino)but-2-ynyl propiolate (3h). Isolated yield is 58% as light yellow oil by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.2). IR (neat liquid): ν_{max} 3060, 3029, 2982, 2943, 2880, 1745, 1600, 1505, 1342, 1174, 1128, 1082, 995, 754, 692 cm^{-1}; ^1H NMR (ppm) δ 7.23(dd, J = 9.2, 7.6 Hz, 2H), 6.80(d, J = 9.2 Hz, 2H), 6.76(d, J = 7.6 Hz, 1H), 4.62(t, J = 1.6 Hz, 2H), 4.05(t, J = 1.6 Hz, 2H), 2.93(s, 3H), 2.31(q, J = 7.4 Hz, 2H), 1.12(t, J = 7.4 Hz, 3H); ^{13}C NMR (ppm) δ 173.25, 148.73, 128.84, 117.97, 113.97, 82.21, 77.88, 52.19, 42.61, 38.56, 27.32, 9.00; MS (EI) *m/z* (%) 232(M^++1, 13), 231(M^+, 79), 230(M^+-1, 12), 174(13), 159(12), 158(100), 157(55), 156(39), 144(16), 143(20),

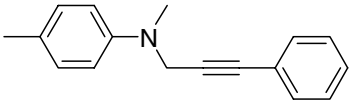
142(15), 120(13), 115(15), 107(11), 106(23), 105(17), 104(20), 78(11), 77(53), 57(73), 51(20), 42(11), 39(11); HRMS calcd for $C_{14}H_{17}NO_2$: 231.1259; found: 231.1253.



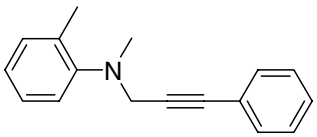
Methyl 4-(*N*-methyl-*N*-phenylamino)but-2-ynoate (3i). Isolated yield is 25% as light yellow oil by flash column chromatography (hexane/ethyl acetate = 10:1, R_f = 0.4). IR (neat liquid): ν_{max} 3033, 2953, 2892, 2232, 1716, 1600, 1505, 1435, 1254, 1202, 1057, 996, 922, 752, 692 cm^{-1}; ^1H NMR (ppm) δ 7.26-7.22(m, 2H), 6.82-6.78(m, 3H), 4.13(s, 2H), 3.68(s, 3H), 2.94(s, 3H); ^{13}C NMR (ppm) δ 153.33, 148.24, 128.95, 118.49, 113.99, 83.71, 75.58, 52.57, 42.42, 38.67; MS (EI) *m/z* (%) 204(M^++1, 13), 203(M^+, 100), 202(M^+-1, 35), 188(15), 172(46), 158(18), 146(10), 145(75), 144(91), 143(12), 120(40), 106(31), 105(17), 104(26), 91(7),63(5), 77(52), 51(12), 39(5); HRMS calcd for $C_{12}H_{13}NO_2$: 203.0946; found: 203.0941.



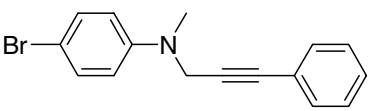
***N*-(hept-2-ynyl)-*N*-methylbenzenamine (3j).** Isolated yield is 12% as light yellow oil by flash column chromatography (hexane/ethyl acetate = 10:1, R_f = 0.8). IR (neat liquid): ν_{max} 3061, 2957, 2932, 2876, 2272, 1600, 1506, 1362, 1338, 1241, 1199, 1112, 995, 926, 752, 690 cm^{-1}; ^1H NMR (ppm) δ 7.22(ddt, J = 7.6, 7.2, 2.4 Hz, 2H), 6.82(dt, J = 7.6, 1.2 Hz, 2H), 6.75(ddt, J = 7.2, 7.2, 1.2 Hz, 1H), 3.98(t, J = 2.4 Hz, 2H), 2.93(s, 3H), 2.12(tt, J = 7.2, 2.4 Hz, 2H), 1.44-1.38(m, 2H), 1.37-1.30(m, 2H), 0.86(t, J = 7.2 Hz, 3H); ^{13}C NMR (ppm) δ 149.16, 128.78, 117.69, 114.10, 84.33, 75.21, 42.83, 38.52, 30.89, 21.92, 18.45, 13.68; MS (EI) *m/z* (%) 202(M^++1, 13), 201(M^+, 88), 200(M^+-1, 100), 158(40), 157(16), 144(46), 132(26), 106(17), 104(14), 77(26); HRMS calcd for $C_{14}H_{19}N$: 201.1517; found: 201.1514.



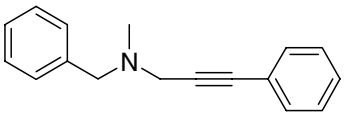
***N*,4-Dimethyl-*N*-(3-phenylprop-2-ynyl)benzenamine (3k).** Isolated yield is 73% as light yellow oil by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.6). IR (neat liquid): ν_{max} 3033, 2919, 2862, 2808, 1616, 1520, 1489, 1334, 1240, 1109, 922, 807, 756, 691 cm^{-1}; ^1H NMR (ppm) δ 7.34-7.31(m, 2H), 7.19-7.17(m, 3H), 7.04(d, J = 8.8 Hz, 2H), 6.79(d, J = 8.4 Hz, 2H), 4.15(s, 2H), 2.93(s, 3H), 2.24(s, 3H); ^{13}C NMR (ppm) δ 147.03, 131.49, 129.39, 127.94, 127.80, 127.35, 122.89, 114.72, 85.03, 84.13, 43.65, 38.90, 20.41; MS (EI) *m/z* (%) 236(M^++1, 18), 235(M^+, 100), 234(59), 220(12), 158(11), 120(27), 118(12), 115(40), 91(15); HRMS calcd for $C_{17}H_{17}N$: 235.1361; found: 253.1356.



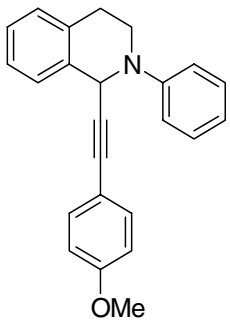
***N*,2-Dimethyl-*N*-(3-phenylprop-2-ynyl)benzenamine (3l).** Isolated yield is 53% as yellow oil by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.8). IR (neat liquid): ν_{max} 3059, 3020, 2946, 2869, 2792, 1598, 1490, 1442, 1351, 1329, 1223, 1091, 919, 756, 727, 691 cm^{-1}; ^1H NMR (ppm) δ 7.38-7.36(m, 2H), 7.23-7.12(m, 6H), 6.96(dd, J = 7.2, 7.2 Hz, 1H), 3.88(s, 2H), 2.84(s, 3H), 2.33(s, 3H); ^{13}C NMR (ppm) δ 150.23, 132.42, 131.45, 130.86, 128.02, 127.79, 126.07, 123.26, 123.03, 120.32, 85.38, 84.86, 46.21, 40.48, 18.28; MS (EI) *m/z* (%) 236(M^++1, 18), 235(M^+, 100), 234(46), 220(43), 158(13), 120(33), 118(20), 115(61), 91(20); HRMS calcd for $C_{17}H_{17}N$: 235.1361; found: 253.1355.



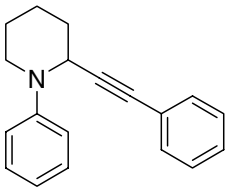
4-Bromo-*N*-methyl-*N*-(3-phenylprop-2-ynyl)benzenamine (3m). Isolated yield is 69% as yellow solid by flash column chromatography (hexane/ethyl acetate = 95:5, R_f = 0.4). IR (KBr): ν_{max} 3072, 2957, 2897, 2815, 1597, 1503, 1367, 1241, 1203, 1116, 1076, 921, 805, 760, 693, 496 cm^{-1}; ^1H NMR (ppm) δ 7.34-7.30(m, 4H), 7.23-7.22(m, 3H), 6.71(d, J = 9.2 Hz, 2H), 4.17(s, 2H), 2.96(s, 3H); ^{13}C NMR (ppm) δ 147.94, 131.56, 131.53, 128.04, 122.59, 115.66, 113.90, 110.01, 84.31, 84.28, 43.22, 38.77; MS (EI) *m/z* (%) 301(M^++1, 56), 300(M^+, 33), 299(M^+-1, 56), 298(24), 231(17), 220(16), 158(18), 157(10), 116(12), 115(100), 77(11); HRMS calcd for $C_{16}H_{14}BrN$: 299.0309; found: 299.0305.



***N*-Benzyl-*N*-methyl-3-phenylprop-2-yn-1-amine (5).** Isolated yield is 36% as yellow oil by flash column chromatography (hexane/ethyl acetate = 10:1, R_f = 0.4). IR (neat liquid): ν_{max} 3061, 3029, 2940, 2837, 2792, 2231, 1950, 1882, 1598, 1489, 1454, 1325, 1123, 1026, 756, 691 cm^{-1}; ^1H NMR (ppm) δ 7.45-7.43(m, 2H), 7.35-7.22(m, 8H), 3.61(s, 2H), 3.48(s, 2H), 2.38(s, 3H); ^{13}C NMR (ppm) δ 138.18, 131.47, 128.96, 128.07, 128.02, 127.76, 126.96, 123.06, 85.56, 84.31, 60.15, 45.68, 41.95; MS (EI) *m/z* (%) 236(M^++1, 13), 235(M^+, 73), 234(53), 191(21), 158(67), 144(37), 132(12), 118(12), 116(17), 115(100), 91(51), 89(10), 65(11); HRMS calcd for $C_{17}H_{17}N$: 235.1361; found: 235.1366.

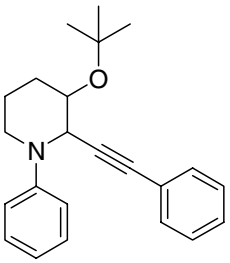


1-(4-Methoxy-phenylethynyl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline (7). Isolated yield is 74% as light yellow sticky oil by flash column chromatography (hexane/ethyl acetate = 20:1, R_f = 0.45). IR (neat liquid): ν_{max} 3061, 3025, 2932, 2836, 2206, 1600, 1499, 1374, 1246, 1172, 1106, 1033, 832, 756, 692 cm^{-1}; ^1H NMR (ppm) δ 7.34-7.31(m, 1H), 7.30-7.26(m, 2H), 7.21-7.16(m, 4H), 7.15-7.12(m, 1H), 7.08(d, *J* = 8.0 Hz, 2H), 6.84(dd, *J* = 7.6, 7.6 Hz, 1H), 6.69(dt, *J* = 8.8, 2.4 Hz, 2H), 5.60(s, 1H), 3.73-3.60(m, 2H), 3.68(s, 3H), 3.09(ddd, *J* = 16.0, 9.6, 6.0 Hz, 1H), 2.92(dt, *J* = 16.0, 4.0 Hz, 1H); ^{13}C NMR (ppm) δ 159.10, 149.32, 135.40, 134.14, 132.93, 128.92, 128.70, 127.23, 126.94, 126.04, 119.34, 116.46, 114.95, 113.54, 87.03, 84.52, 55.17, 52.25, 43.41, 28.95; MS (EI) *m/z* (%) 340(M^++1, 16), 339(M^+, 72), 338(M^+-1, 100), 324(5), 223(19), 220(10), 219(14), 208(15), 191(13), 189(12), 118(15), 104(10), 77(12); HRMS calcd for $C_{24}H_{20}NO$ (M-1): 338.1545; found: 338.1540; $C_{24}H_{21}NO$: 339.1623; found: 339.1604.



1-phenyl-2-(2-phenylethynyl)piperidine (9). Isolated yield is 12% as light yellow oil by flash column chromatography (methylene chloride/hexane/diethyl ether = 50:30:1, R_f = 0.6). IR (neat liquid): ν_{max} 3063, 3032, 2937, 2856, 2821, 1598, 1501, 1489, 1442, 1377, 1346, 1304, 1245, 1165, 1118, 1023, 914, 755, 691, 525 cm^{-1}; ^1H NMR (ppm) δ 7.33-7.31(m, 2H), 7.27-7.21(m, 5H), 7.03(d, *J* = 8.0 Hz, 2H), 6.85(dd, *J* = 7.2, 7.2 Hz, 1H), 4.72(dd, *J* = 4.0, 4.0 Hz, 1H), 3.41(d, *J* = 11.6 Hz, 1H), 3.19(ddd, *J* = 11.6, 11.6, 2.8 Hz, 1H), 1.99-1.96(m, 2H), 1.87-1.78(m, 2H), 1.73-1.65(m, 2H); ^{13}C NMR (ppm) δ 150.94, 131.55, 128.77, 127.97, 127.70, 123.12, 120.00, 117.65, 87.36, 85.76, 50.54, 45.79, 31.52, 26.02, 20.25; MS (EI) *m/z*

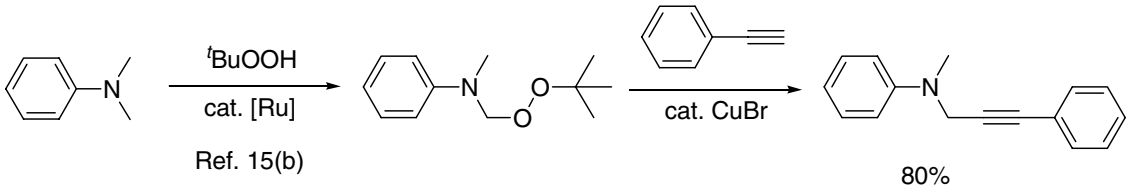
(%) 262(24), 261(M^+, 100), 260(96), 232(31), 205(10), 204(19), 106(11), 104(10), 77(14); HRMS calcd for $C_{19}H_{19}N$: 261.1517; found: 261.1520.



3-*tert*-Butoxy-1-phenyl-2-phenylethynyl-piperidine (10). Isolated yield is 12% as white solid by flash column chromatography (hexane/diethyl ether = 15:1, R_f = 0.4). IR (KBr): ν_{max} 3057, 2973, 2944, 1599, 1491, 1254, 1189, 1107, 1016, 915, 758, 690 cm^{-1}; ^1H NMR (ppm) δ 7.31-7.29(m, 2H), 7.26-7.22(m, 5H), 7.01(d, J = 7.6 Hz, 2H), 6.85(dd, J = 7.6, 7.6 Hz, 1H), 4.53(d, J = 2.4 Hz, 1H), 3.93(d, J = 2.4 Hz, 1H), 3.35(d, J = 11.6 Hz, 1H), 3.15(dt, J = 11.6, 2.4 Hz, 1H), 2.10-2.00(m, 2H), 1.66-1.60(m, 2H), 1.28(s, 9H); ^{13}C NMR (ppm) δ 151.42, 131.52, 128.60, 128.00, 127.86, 122.90, 120.01, 118.12, 86.57, 86.02, 74.24, 68.34, 57.70, 44.73, 28.42, 27.58, 20.70; MS (EI) *m/z* (%) 333(M^+, 11), 277(27), 276(100), 263(10), 206(38), 182(6), 160(8), 115(8), 105(9), 77(14), 71(7); HRMS calcd for $C_{23}H_{27}NO$: 333.2092; found: 333.2082.

Alternatively, it is possible that *tert*-butylperoxide products are involved as intermediates (Scheme 1). *tert*-Butylperoxymethyl-methyl-phenyl-amine was synthesized based on the literature method (15b). When *tert*-butylperoxymethyl-methyl-phenyl-amine was reacted with phenylacetylene in the presence of 5 mol % CuBr, the desired alkynylation product was obtained in 80 % yield.

Scheme 1. Formation of the product *via* a peroxide intermediate



Reference:

[1] Kwong, F. Y.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2002**, *4*, 581-584.