Supporting information for

Catalyst-Free Activation of Methylene Chloride and Alkynes by Amines in a Three-Component Coupling Reaction to Propargylamines

Vikas S. Rawat, Thulasiram Bathini, S. Govardan and Bojja Sreedhar*

Inorganic & Physical Chemistry Division, Indian Institute of Chemical Technology (Council of Scientific & Industrial Research), Hyderabad 500607, India

Tel.: +91-40-27193510; fax: +91-40-27160921.

E-mail: sreedharb@iict.res.in

Table of content

Experimental Section

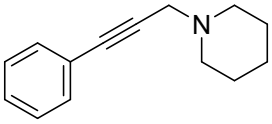
General information

All chemicals were purchased from Sigma-Aldrich and S.D Fine Chemicals, Pvt. Ltd. India and used as received. The IR spectra of all compounds were recorded on a Perkin-Elmer, Spectrum GX FTIR spectrometer. The IR values are reported in reciprocal centimeters (cm^{-1}). ESI mass spectra were recorded on a Finnigan LCQ Advantagemax spectrometer. High-resolution mass spectra (HRMS) were recorded on QSTAR XL Hybrid MS/MS mass spectrometer using ESI-QTOF mass spectrometry. All the glassware was dried before use. Ethyl acetate, hexane and acetone were distilled before use. Silica gel (100–200 mesh) was used for column chromatography and reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm silica gel coated glass plates $60F_{254}$ using UV light as visualizing agent and iodine or $KMnO_4$ solution followed by heating as developing agent. ^1H NMR spectra were recorded at 300 MHz. The chemical shifts are expressed (ppm), referenced to TMS (0.00 ppm) peak. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet. ^{13}C NMR spectra were recorded at 75 MHz. The chemical shifts are expressed (in ppm), reported from the central peak of deuterochloroform (77 ppm). The ^{13}C NMR spectra are proton decoupled.

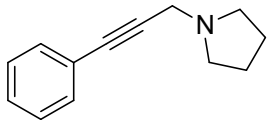
General procedure for the synthesis propargylamine: Alkynes (1.0 mmol) and amine (3.2 mmol) was added to 2 mL of dihalomethane in a pressure tube, and stirred at 70 °C for 12 hours. After completion of the reaction, the reaction mixture was diluted with H_2O (5 mL) and the aqueous layers were extracted with ethyl acetate (2X10 mL), then organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The crude product was loaded on a silica gel column and eluted with hexane and acetone as eluting mixture to afford the pure corresponding propargylamine product.

Characterization data of compounds

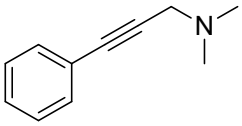
1. 1-(3-Phenylprop-2-yn-1-yl)piperidine (Table 2, Entry 1):[1] Light yellow liquid (145 mg, 72%); FT-IR (Neat): 405, 527, 692, 758, 858, 948, 994, 1034, 1068, 1109, 1155, 1274, 1341, 1445, 1489, 1599, 2512, 2637, 2752, 2797, 2853, 2933, 3055, 3405 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.41-1.51 (m, 2H), 1.61-1.69 (m, 4H), 2.58 (s, 4H), 3.49 (s, 2H), 7.28-7.30 (m, 3H), 7.42-7.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.8, 25.8, 48.4, 53.3, 84.8, 85.0, 123.1, 127.9, 128.1, 131.6; ESI-MS (*m/z*): 200 $(M+H)^+$; ESI-HRMS found: 200.1428 $(M+H)^+$ for $C_{14}H_{18}N$ requires 200.1433.



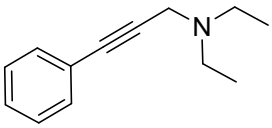
2. 1-(3-Phenylprop-2-yn-1-yl)pyrrolidine (Table 2, Entry 2):[1] Light yellow liquid (126 mg, 68%); FT-IR (Neat): 527, 692, 719, 757, 800, 1027, 1068, 1123, 1154, 1261, 1322, 1374, 1459, 1489, 1611, 1723, 2852, 2924, 2957, 3410 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.82-1.87 (m, 4H), 2.70-2.75 (m, 4H), 3.65 (s, 2 H), 7.28-7.30 (m, 3 H), 7.41-7.44 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.8, 29.6, 43.6, 52.4, 84.7, 128.0, 128.2, 131.6; ESI-MS (*m/z*): 186 $(M+H)^+$; ESI-HRMS found: 186.1276 $(M+H)^+$ for $C_{13}H_{16}N$ requires 186.1277.



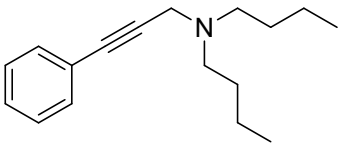
3. *N*,*N*-Dimethyl-3-phenylprop-2-yn-1-amine (Table 2, Entry 3):[2] Light yellow liquid (112 mg, 70%); FT-IR (Neat): 525, 596, 691, 756, 813, 837, 914, 948, 1034, 1071, 1155, 1260, 1323, 1359, 1460, 1489, 1599, 1646, 2775, 2823, 2856, 2929, 3058, 3446 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 6H), 3.53 (s, 2H), 7.29-7.31 (m, 3H), 7.42-7.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.1, 48.4, 84.3, 85.3, 128.0, 128.2, 131.6; ESI-MS (*m/z*): 160 $(M+H)^+$; ESI-HRMS found: 160.1122 $(M+H)^+$ for $C_{11}H_{14}N$ requires 160.1120 .



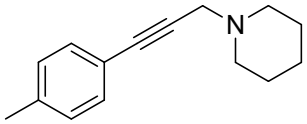
4. *N*,*N*-Diethyl-3-phenylprop-2-yn-1-amine (Table 2, Entry 4):[2] Light yellow liquid (121 mg, 65%); FT-IR (Neat): 524, 618, 690, 755, 913, 945, 980, 1028, 1065, 1089, 1123, 1155, 1200, 1252, 1288, 1320, 1378, 1459, 1489, 1598, 2818, 2930, 2970, 3057, 3447 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.12 (t, 6H, *J* = 7.1 Hz), 2.63 (q, 4H, *J* = 7.1, 14.3 Hz), 3.64 (s, 2H), 7.28- 7.29 (m, 3H), 7.41-7.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.5, 41.3, 47.2, 84.1, 84.8, 127.7, 128.0, 131.5; ESI-MS (*m/z*): 188 $(M+H)^+$; ESI-HRMS found: 188.1429 $(M+H)^+$ for $C_{13}H_{18}N$ requires 188.1433.



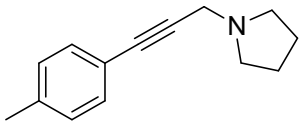
5. *N*-Butyl-*N*-(3-phenylprop-2-yn-1-yl)butan-1-amine (Table 2, Entry 5):[3] Light yellow liquid (151 mg, 62%); FT-IR (Neat): 525, 619, 691, 755, 801, 948, 106, 1259, 1320, 1375, 1461, 1489, 1600, 1729, 2865, 2928, 2956 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, 6H, *J* = 7.3 Hz), 1.31-1.38 (m, 4H), 1.45-1.51 (m, 4H), 2.53 (t, 4H, *J* = 7.6 Hz), 3.61 (s, 2H), 7.27-7.29 (m, 3H), 7.41-7.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 20.6, 29.6, 42.5, 53.5, 84.5, 84.9, 127.8, 128.1, 131.6; ESI-MS (*m/z*): 244 $(M+H)^+$; ESI-HRMS found: 244.2056 $(M+H)^+$ for $C_{17}H_{26}N$ requires 244.2060.



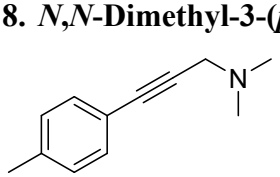
6. 1-(3-(*p*-Tolyl)prop-2-yn-1-yl)piperidine (Table 2, Entry 9):[4] Light yellow liquid (167 mg, 78%); FT-IR (Neat): 527, 758, 816, 858, 994, 1035, 1110, 1156, 1333, 1371, 1451, 1508, 1677, 1738, 2754, 2798, 2855, 2930, 3422 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.61-1.68 (m, 6H), 2.33 (s, 3H), 2.58 (br s, 4H), 3.47 (s, 2H), 7.10 (d, 2H, J = 7.9 Hz), 7.33 (d, 2H, J = 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 23.7, 25.6, 48.3, 53.2, 83.6, 85.3, 119.9, 128.9, 131.5, 138.1; ESI-MS (*m/z*): 214 $(M+H)^+$; ESI-HRMS found: 214.1594 $(M+H)^+$ for $C_{15}H_{20}N$ requires 214.1590.



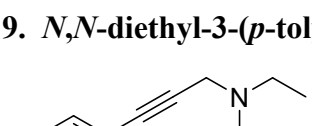
7. 1-(3-(*p*-Tolyl)prop-2-yn-1-yl)pyrrolidine (Table 2, Entry 10):[5] Light yellow liquid (144 mg, 72%); FT-IR (Neat): 527, 761, 816, 1124, 1256, 1323, 1373, 1459, 1508, 1639, 1678, 2854, 2924, 2956, 3448, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.82-1.85 (m, 4H), 2.33 (s, 3H), 2.70-2.73 (m, 4H), 3.63 (s, 2H), 7.10 (d, 2H, J = 7.7 Hz), 7.32 (d, 2H, J = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.8, 29.6, 43.7, 52.5, 81.9, 84.1, 119.0, 128.9, 131.5, 138.0; ESI-MS (*m/z*): 200 $(M+H)^+$; ESI-HRMS found: 200.1437 $(M+H)^+$ for $C_{14}H_{18}N$ requires 200.1433.



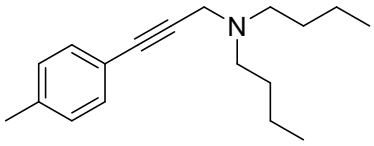
8. *N*,*N*-Dimethyl-3-(*p*-tolyl)prop-2-yn-1-amine (Table 2, Entry 11):[6] Light yellow liquid (118 mg, 68%); FT-IR (Neat): 411, 524, 569, 675, 770, 816, 949, 1035, 1100, 1155, 1177, 1260, 1325, 1359, 1461, 1509, 1608, 1680, 2775, 2861, 2927, 3028, 3422 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 2.36 (s, 6H), 3.46 (s, 2H), 7.11 (d, 2H, J = 7.7 Hz), 7.33 (d, 2H, J = 8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 44.0, 48.4, 83.4, 85.4, 120.0, 128.9, 131.5, 138.0; ESI-MS (*m/z*): 174 $(M+H)^+$; ESI-HRMS found: 174.1279 $(M+H)^+$ for $C_{12}H_{16}N$ requires 174.1277.



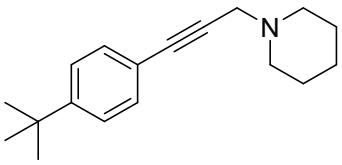
9. *N*,*N*-diethyl-3-(*p*-tolyl)prop-2-yn-1-amine (Table 2, Entry 12):[7] Light yellow liquid (133 mg, 66%); FT-IR (Neat): 414, 525, 568, 677, 758, 816, 893, 946, 978, 1021, 1063, 1089, 1121, 1154, 1200, 1255, 1289, 1321, 1379, 1458, 1509, 1643, 1902, 2819, 2927, 2970, 3449 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.11 (t, 6H, J = 7.1 Hz), 2.33 (s, 3H), 2.62 (q, 4H, J = 7.3, 7.1, 14.4, 14.3 Hz), 3.63 (s, 2H), 7.10 (d, 2H, J = 7.9 Hz), 7.32 (d, 2H, J = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.4, 21.2, 41.2, 47.1, 83.3, 84.9, 120.1, 128.8, 131.4, 137.7; ESI-MS (*m/z*): 202 $(M+H)^+$; ESI-HRMS found: 202.1587 $(M+H)^+$ for $C_{14}H_{20}N$ requires 202.1590.



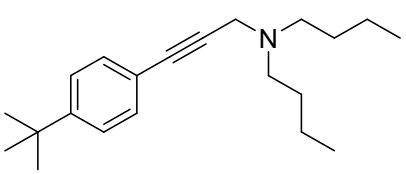
10. *N*-Butyl-*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)butan-1-amine (Table 2, Entry 13):[8] Light yellow liquid (160 mg, 62%) FT-IR (Neat): 415, 525, 676, 756, 815, 947, 1085, 1259, 1321, 1374, 1460, 1509, 1646, 1729, 2817, 2865, 2929, 2956, 3027, 3449 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, 6H, J = 7.1 Hz), 1.28-1.40 (m, 4H), 1.43-1.52 (m, 4H), 2.33 (s, 3H), 2.52 (t, 4H, J = 7.7, 7.1 Hz), 3.59 (s, 2H), 7.10 (d, 2H, J = 7.9 Hz), 7.31 (d, 2H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 20.6, 21.3, 29.6, 42.6, 53.5, 83.8, 84.9, 120.2, 128.9, 131.5, 137.8; ESI-MS (*m/z*): 258 $(M+H)^+$; ESI-HRMS found: 258.2201 $(M+H)^+$ for $C_{18}H_{28}N$ requires 258.2216.



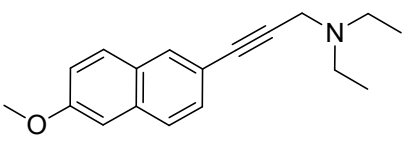
11. 1-(3-(4-(*tert*-Butyl)phenyl)prop-2-yn-1-yl)piperidine (Table 2, Entry 14): Light yellow liquid (212 mg, 83%); FT-IR (Neat): 561, 669, 762, 834, 993, 1020, 1108, 1156, 1269, 1341, 1364, 1459, 1507, 1609, 2753, 2798, 2859, 2933, 3446 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.30 (s, 9H), 1.61-1.68 (m, 4H), 2.59 (br s, 4H), 3.49 (s, 2H), 7.30-7.39 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6, 25.5, 31.1, 33.6, 48.2, 53.0, 83.3, 85.6, 119.9, 125.1, 131.4, 151.3; ESI-MS (*m/z*): 256 $(M+H)^+$; ESI-HRMS found: 256.2045 $(M+H)^+$ for $C_{18}H_{26}N$ requires 256.2059.



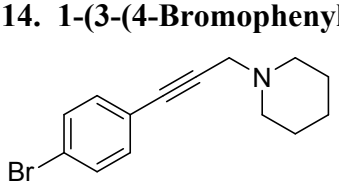
12. *N*-Butyl-*N*-(3-(4-(*tert*-butyl)phenyl)prop-2-yn-1-yl)butan-1-amine (Table 2, Entry 15): Light yellow liquid (210 mg, 70%); FT-IR (Neat): 561, 649, 756, 833, 949, 1019, 1090, 1268, 1321, 1364, 1463, 1505, 1683, 1727, 2817, 2867, 2931, 2958, 3449 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, 6H, *J* = 7.1 and 7.36 Hz), 1.30-1.53 (m, 17H), 2.53 (t, 4H, *J* = 7.7, 7.3 Hz), 3.61 (s, 2H), 7.30-7.37 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 20.6, 29.6, 31.1, 34.6, 42.5, 53.5, 83.7, 85.0, 120.3, 125.1, 131.3, 151.0; ESI-MS (*m/z*): 300 $(M+H)^+$; ESI-HRMS found: 300.2686 $(M+H)^+$ for $C_{21}H_{34}N$ requires 300.2685.



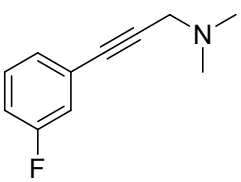
13. *N*,*N*-Diethyl-3-(6-methoxynaphthalen-2-yl)prop-2-yn-1-amine (Table 2, Entry 16):[9] Light yellow liquid (193 mg, 72%); FT-IR (Neat): 473, 507, 544, 664, 739, 808, 853, 890, 954, 985, 1032, 1063, 1088, 1122, 1161, 1198, 1243, 1269, 1322, 1387, 1460, 1482, 1601, 1628, 2820, 2932, 2969, 3058 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.14 (t, 6H, *J* = 7.1 Hz), 2.67 (q, 4H, *J* = 7.1 Hz), 3.68 (s, 2H), 3.91 (s, 3H), 7.08- 7.16 (m, 2H), 7.42-7.45 (m, 1H), 7.65 (t, 2H, *J* = 7.3, 8.4 Hz), 7.86 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.5, 41.3, 47.2, 55.1, 83.6, 85.3, 105.6, 118.1, 119.1, 126.5, 128.3, 129.0, 129.1, 131.0, 133.8, 158.0; ESI-MS (*m/z*): 268 $(M+H)^+$; ESI-HRMS found: 268.1680 $(M+H)^+$ for $C_{18}H_{22}ON$ requires 268.1695.



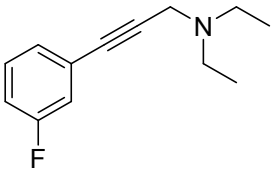
14. 1-(3-(4-Bromophenyl)prop-2-yn-1-yl)piperidine (Table 2, Entry 17): Light yellow liquid (181 mg, 65%); FT-IR (Neat): 521, 696, 760, 802, 822, 860, 1013, 1035, 1070, 1106, 1155, 1259, 1323, 1340, 1392, 1463, 1485, 1643, 1440, 2753, 2798, 2853, 2930, 3444 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.63-1.67 (m, 6H), 2.55-2.63 (m, 4H), 3.47 (s, 2H), 7.29 (d, 2H, *J* = 8.5 Hz), 7.43 (d, 2H, *J* = 8.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.7, 25.7, 48.3, 53.4, 84.1, 86.0, 122.15, 122.18, 131.4, 133.1; ESI-MS (*m/z*): 280 $(M+2)^+$; ESI-HRMS found: 278.0518 $(M)^+$ for $C_{14}H_{17}NBr$ requires 278.0538.



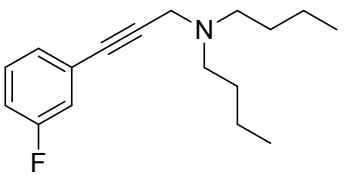
15. 3-(3-Fluorophenyl)-*N*,*N*-dimethylprop-2-yn-1-amine (Table 2, Entry 18): Light yellow liquid (101 mg, 57%); FT-IR (Neat): 521, 598, 681, 760, 784, 872, 989, 1036, 1077, 1150, 1170, 1277, 1322, 1359, 1463, 1483, 1581, 1610, 1647, 2776, 2855, 2925, 3446 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 6H), 3.49 (s, 2H), 6.99-7.03 (m, 1H), 7.11- 7.14 (m, 1H), 7.20-7.22 (m, 1H), 7.24-7.28 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.0, 48.3, 85.2, 86.4, 115.4 (d, *J* = 22 Hz), 118.4 (d, *J* = 22 Hz), 122.3, 127.4, 129.7 (d, *J* = 7 Hz), 162.6 (d, *J* = 246 Hz),; ESI-MS (*m/z*): 178 $(M+H)^+$; ESI-HRMS found: 178.1025 $(M+H)^+$ for $C_{11}H_{13}NF$ requires 178.1026.



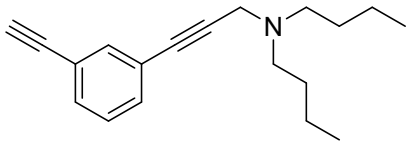
16. *N*,*N*-Diethyl-3-(3-fluorophenyl)prop-2-yn-1-amine (Table 2, Entry 19): Light yellow liquid (111 mg, 54 %); FT-IR (Neat): 462, 521, 617, 681, 782, 869, 988, 1066, 1123, 1147, 1201, 1275, 1321, 1379, 1432, 1479, 1579, 1608, 2819, 2933, 2971, 3448 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.12 (t, 6H, J = 7.3, 6.9 Hz), 2.62 (q, 4H, J = 7.1, 14.3 Hz), 3.64 (s, 2H), 6.96-7.03 (m, 1H), 7.09-7.12 (m, 1H), 7.18-7.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.4, 41.2, 47.2, 83.75, 83.79, 85.4, 115.1 (d, J = 20 Hz), 118.4 (d, J = 22 Hz), 125.1(d, J = 9 Hz), 127.4, 129.6 (d, J = 8 Hz), 162.2 (d, J = 245 Hz); ESI-MS (*m/z*): 206 $(M+H)^+$; ESI-HRMS found: 206.1334 $(M+H)^+$ for $C_{13}H_{17}N$ F requires 206.1339.



17. *N*-butyl-*N*-(3-(3-fluorophenyl)prop-2-yn-1-yl)butan-1-amine (Table 2, Entry 20): Light yellow liquid (131 mg, 50%); FT-IR (Neat): 460, 521, 622, 681, 740, 783, 870, 950, 988, 1080, 1126, 1148, 1169, 1279, 1321, 1375, 1433, 1464, 1483, 1579, 1608, 1685, 1728, 2817, 2866, 2931, 2957 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, 6H, J = 7.3 Hz), 1.31-1.38 (m, 4H), 1.44-1.520 (m, 4H), 2.51 (t, 4H, J = 7.6, 7.4 Hz), 3.60 (s, 2H), 6.94-7.01 (m, 1H), 7.10-7.12 (m, 1H), 7.18-7.20 (m, 1H), 7.22-7.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 20.6, 29.6, 42.5, 53.6, 83.7, 85.9, 115.1 (d, J = 20.8 Hz), 118.4 (d, J = 22.5 Hz), 125.2 (d, J = 9.3 Hz), 127.5, 129.7 (d, J = 8.7 Hz), 162.3 (d, J = 245.8 Hz); ESI-MS (*m/z*): 262 $(M+H)^+$; ESI-HRMS found: 262.1966 $(M+H)^+$ for $C_{17}H_{25}NF$ requires 262.1965.



18. *N*-Butyl-*N*-(3-(3-ethynylphenyl)prop-2-yn-1-yl)butan-1-amine (Table 2, Entry 21): Light yellow liquid (131 mg, 50%); FT-IR (Neat): 476, 568, 600, 622, 649, 686, 736,794, 896, 949, 984, 1090, 1124, 1179, 1321, 1376, 1406, 1471, 1572, 1594, 1688, 1726, 2817, 2862, 2929, 2956, 3062, 3305 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, 6H, J = 7.3, 7.4 Hz), 1.31-1.38 (m, 4H), 1.44-1.50 (m, 4H), 2.51 (t, 4H, J = 7.6, 7.3 Hz), 3.07 (s, 1H), 3.60 (s, 2H), 7.23-7.26 (m, 1H), 7.38-7.41 (m, 2H), 7.54 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 20.6, 29.6, 42.5, 53.5, 77.6, 82.7, 83.9, 85.6, 122.2, 123.7, 128.2, 131.3, 131.9, 135.1; ESI-MS (*m/z*): 268 $(M+H)^+$; ESI-HRMS found: 268.2041 $(M+H)^+$ for $C_{19}H_{26}N$ requires 268.2059.



References:

1. Y. Heo, S. Lee and K. Park, *Org. Lett*., 2013, **15**, 3322.

2. Y. Wei, H. Zhao and Y. Zhu, *Synthesis*, 2013, **45**, 952.

3. R. Khalifeh, Z. Rashidi and H. Sharghi, *Heteroat. Chem.*, 2013, **24**, 372.

4. X. -Y. Dou, J. Gao, L. -N. He, Q. -W. Song and Z. -Z. Yang*, Chem. Comm.*, 2012, **48**, 2024.

5. E. O. Chukhajian, L. V. Ayrapetyan, El. O. Chukhajian and H. A. Panosyan, *Chem. Heterocycl. Compd*., 2010, **46**, 151.

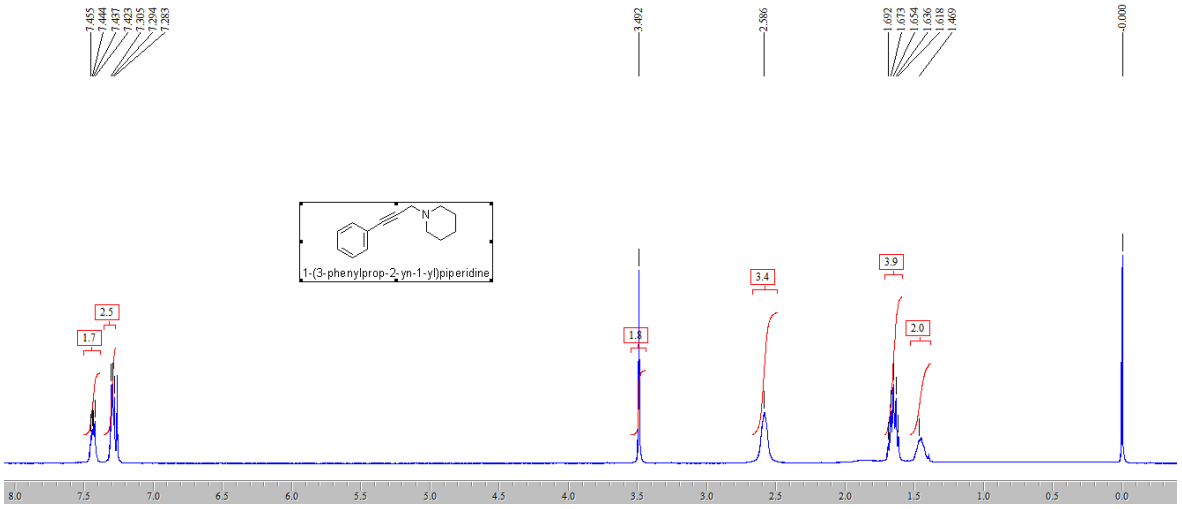
6. M. Bao, X. Feng, Z. Xu and X. Yu, *J. Org. Chem*., 2011, **76**, 6901.

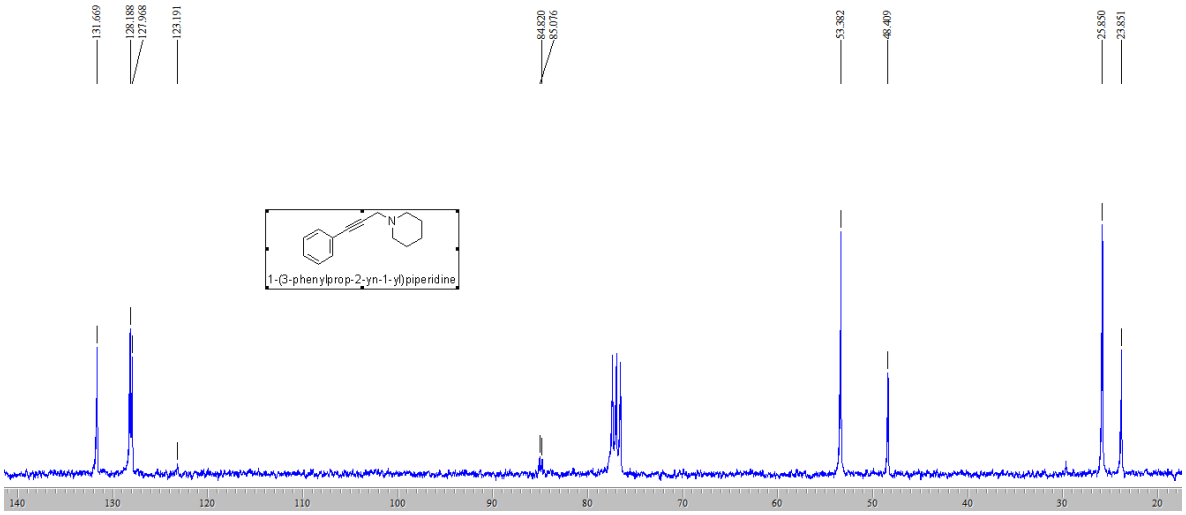
7. Y. Tang, T. Xiao and L. Zhou, *Tetrahedron Lett*., 2012, **53**, 6199.

8. A. Kr. Bagdi, A. Hajra, A. Majee and M. Rahman, *Tetrahedron Lett*., 2011, **52**, 4437.

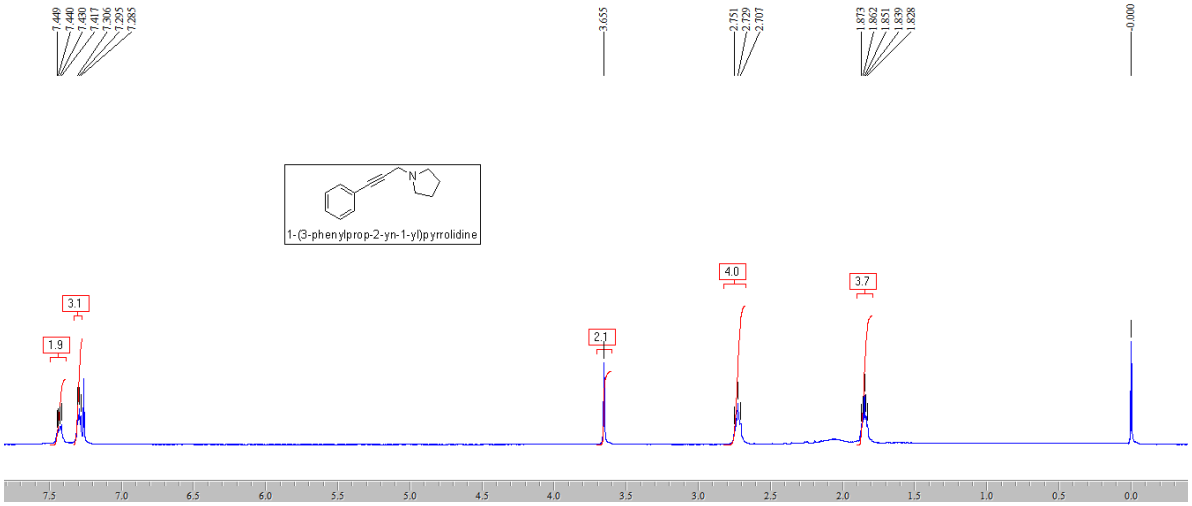
9. H. Doucet, M. Lemhadri and M. Santelli, *Synthesis*, 2005, **8**, 1359.

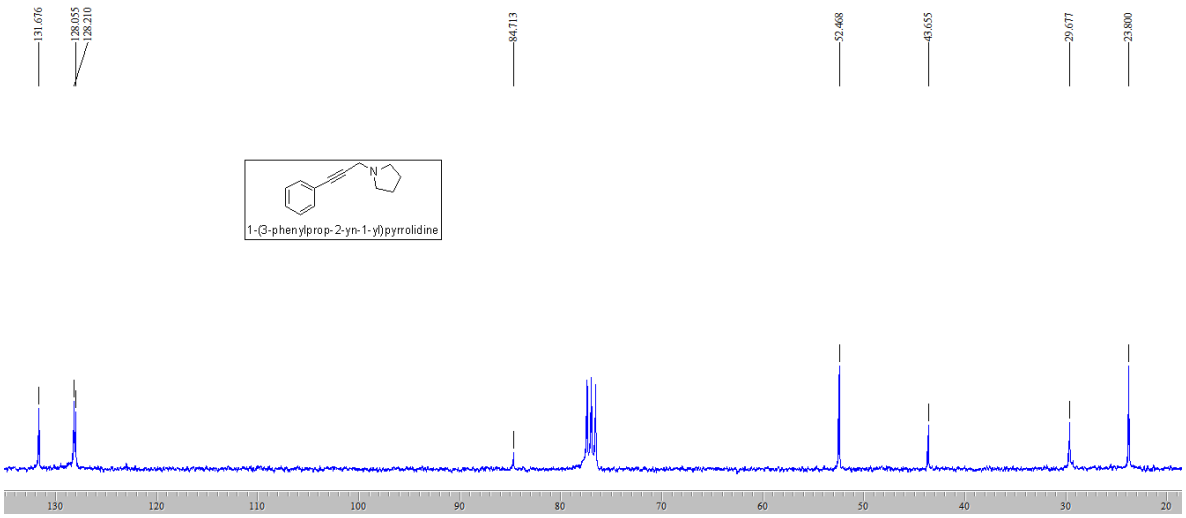
1. 1-(3-Phenylprop-2-yn-1-yl)piperidine:



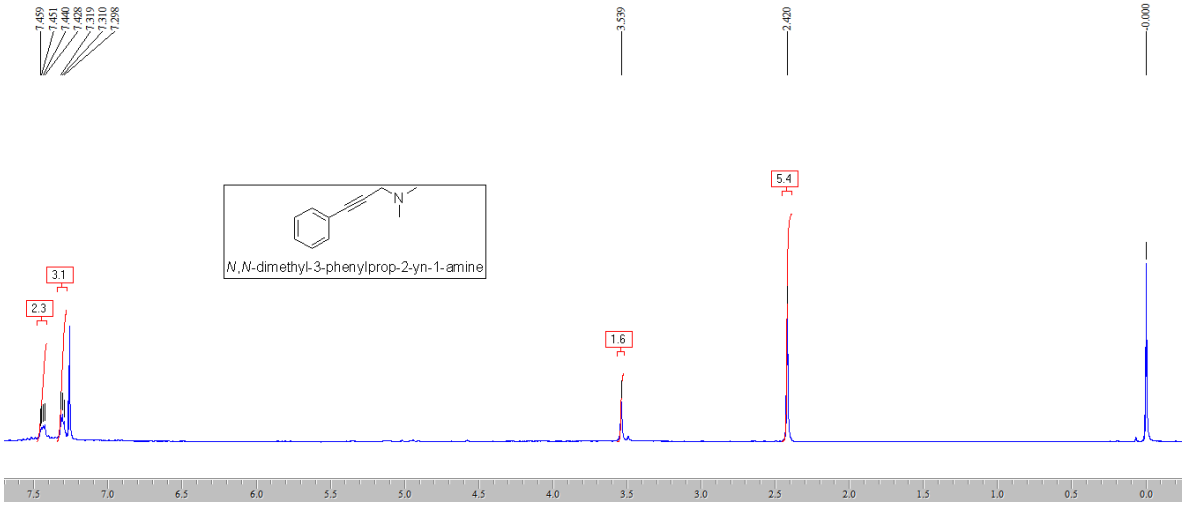


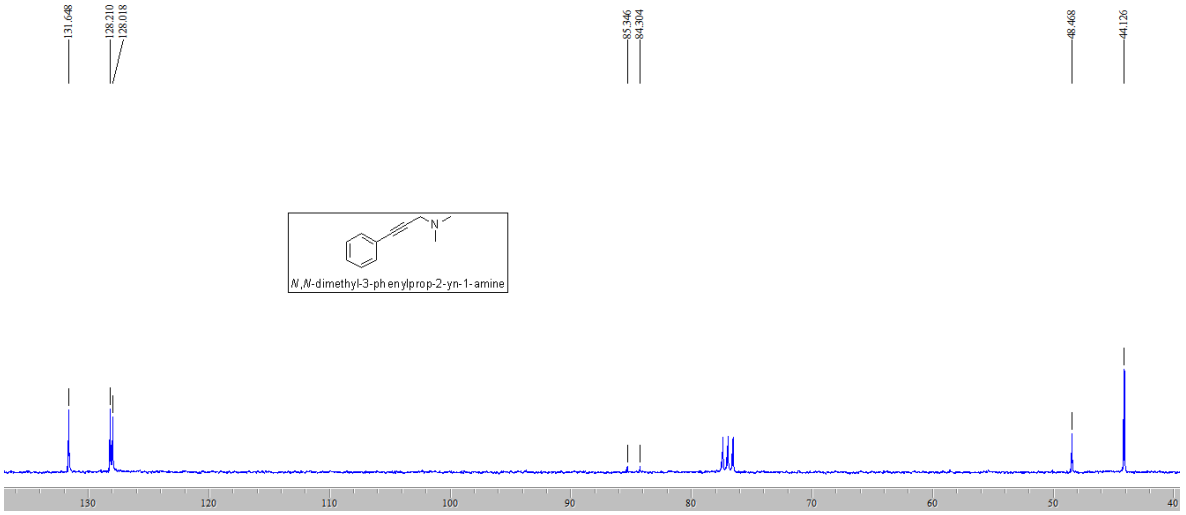
2. 1-(3-Phenylprop-2-yn-1-yl)pyrrolidine:



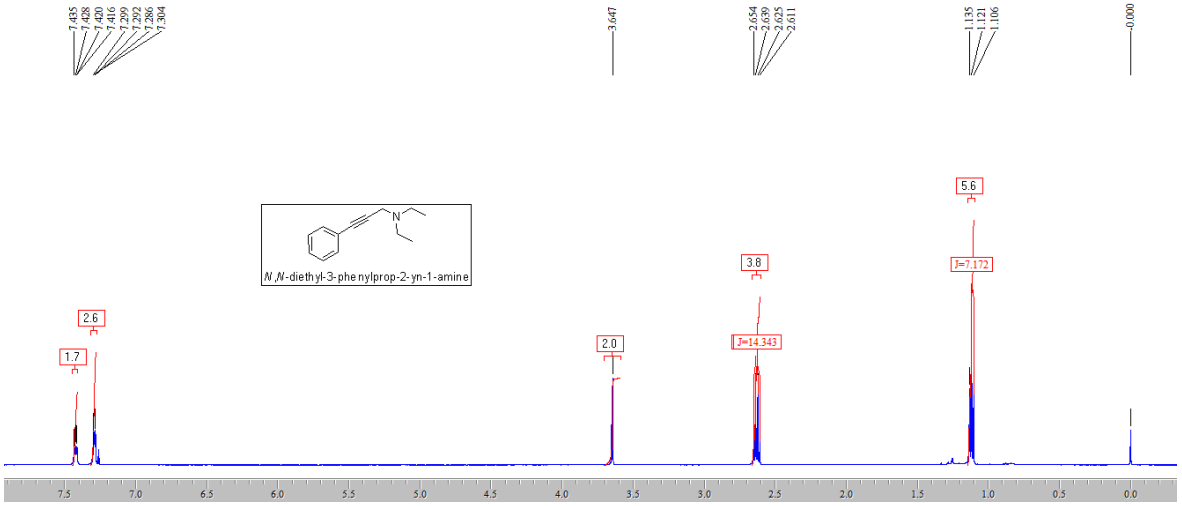


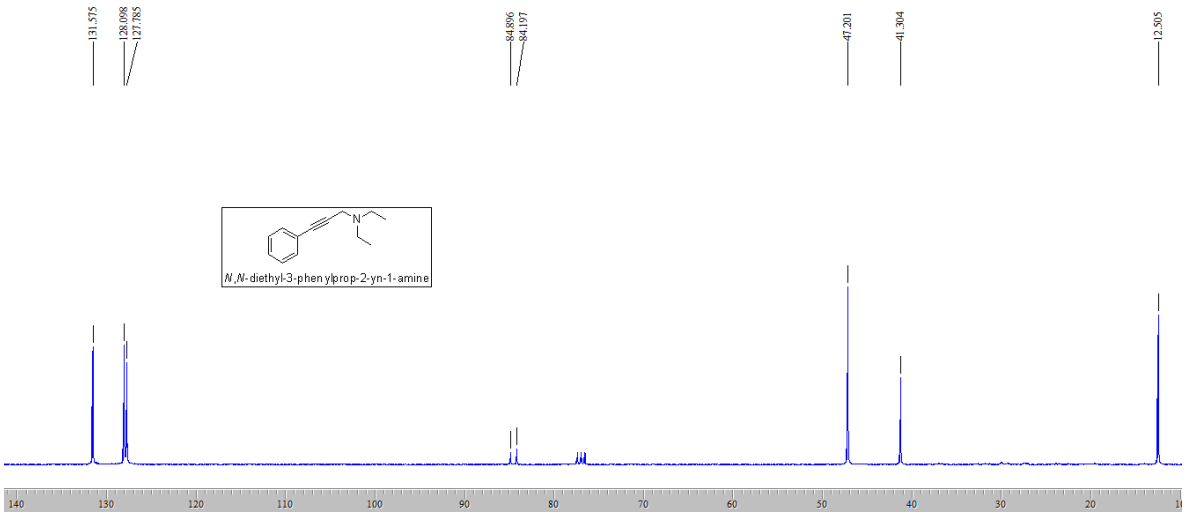
3. *N,N*-Dimethyl-3-phenylprop-2-yn-1-amine:



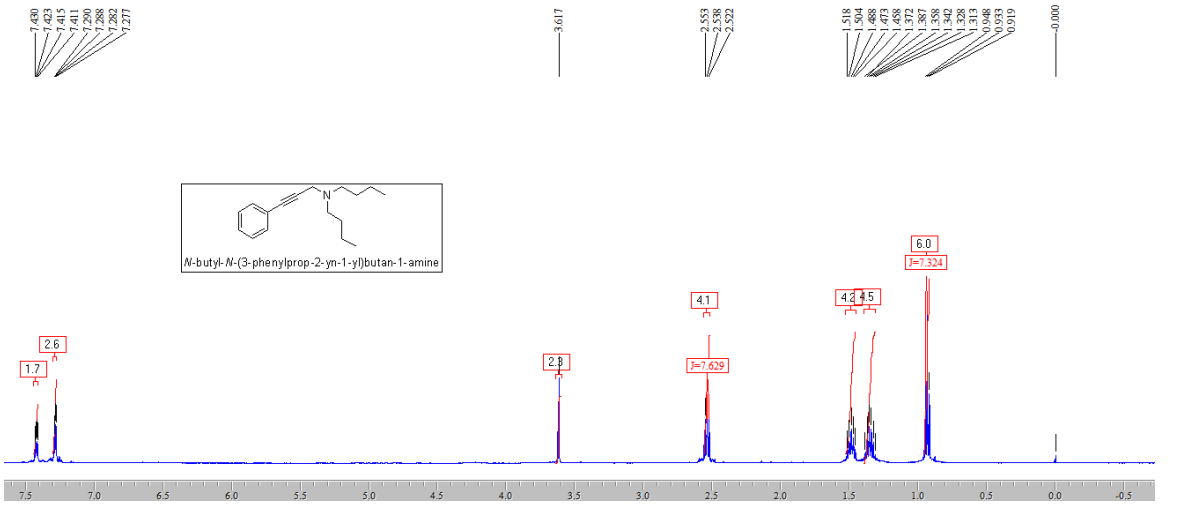


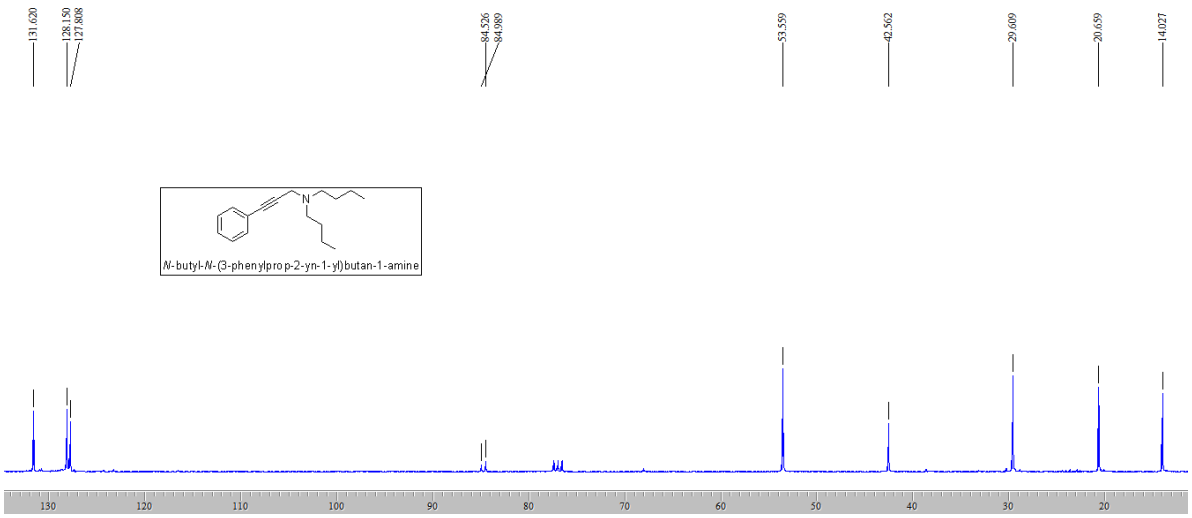
4. *N*,*N*-Diethyl-3-phenylprop-2-yn-1-amine:



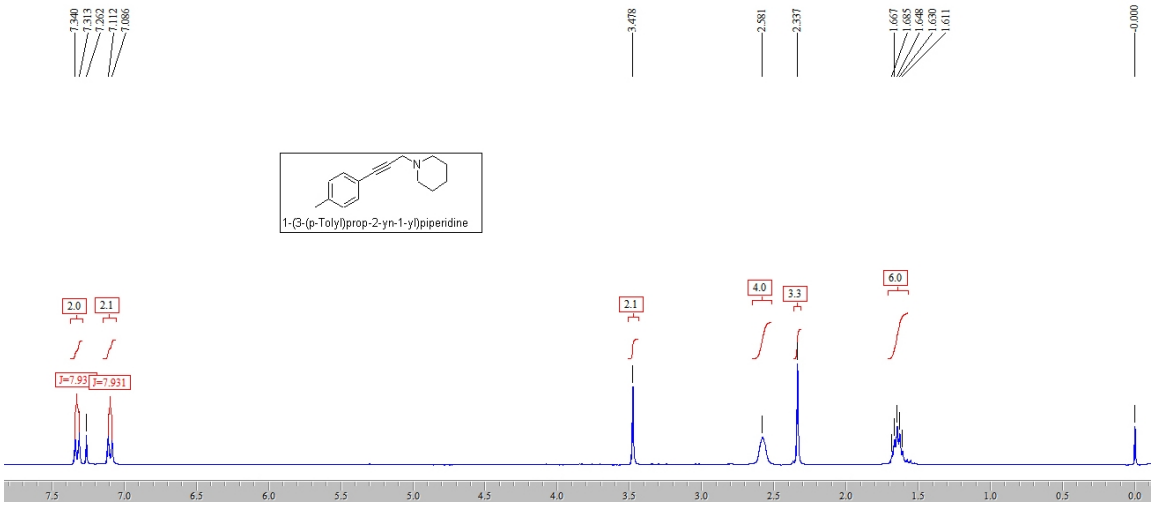


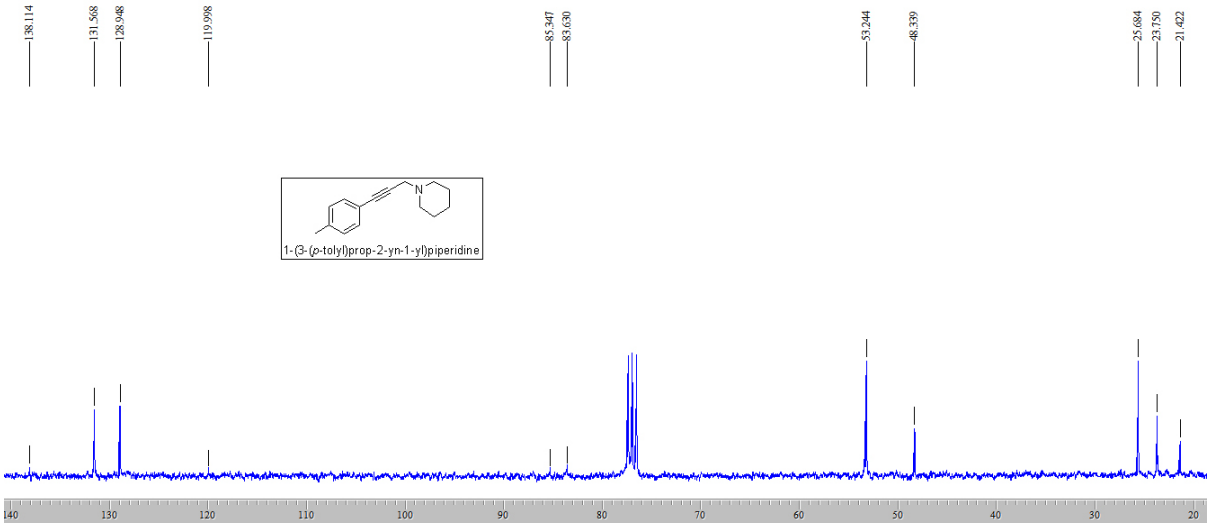
5. *N*-Butyl-*N*-(3-phenylprop-2-yn-1-yl)butan-1-amine:



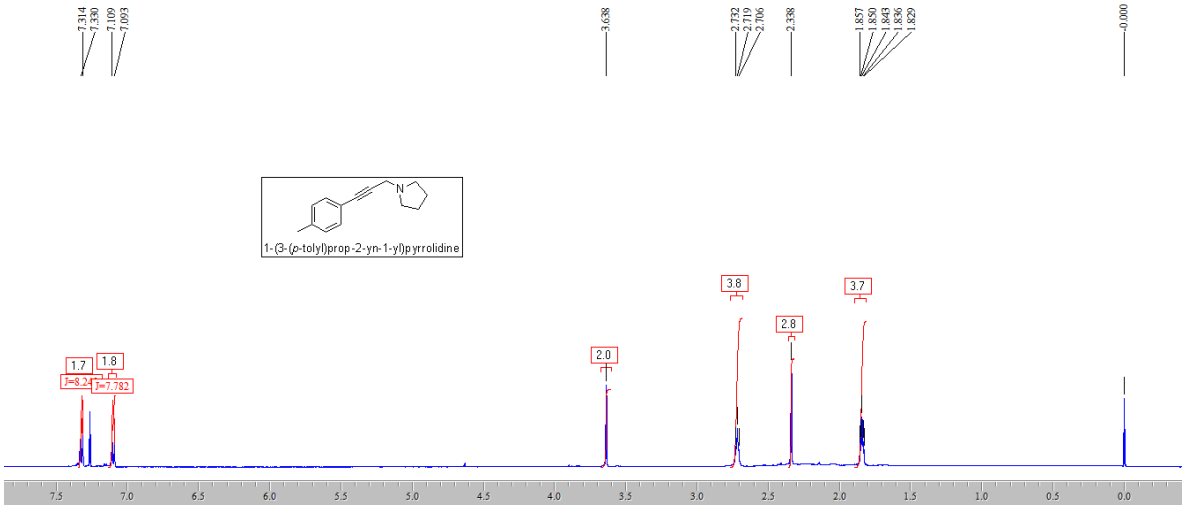


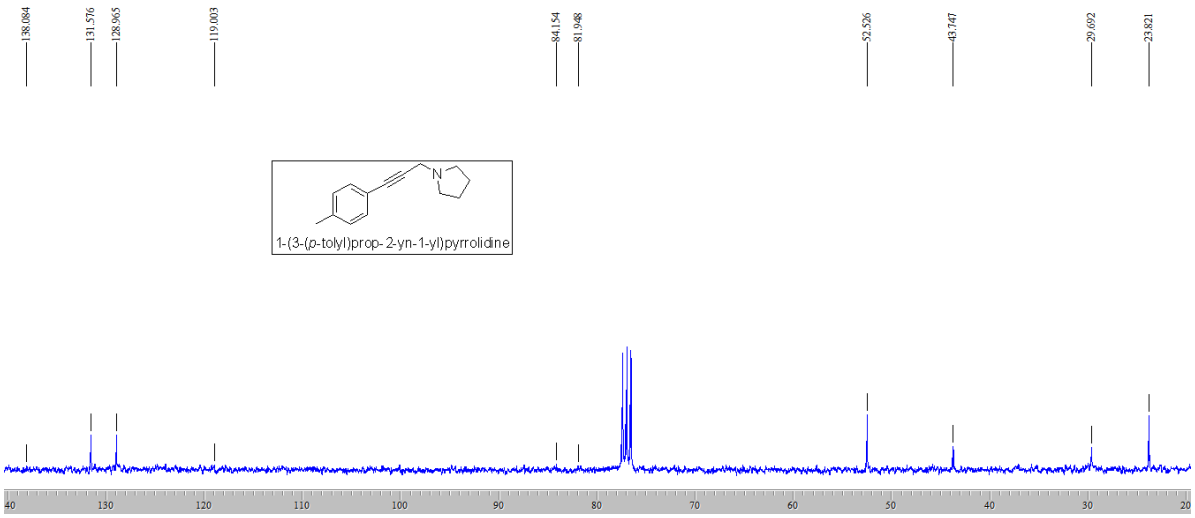
6. 1-(3-(*p*-Tolyl)prop-2-yn-1-yl)piperidine:



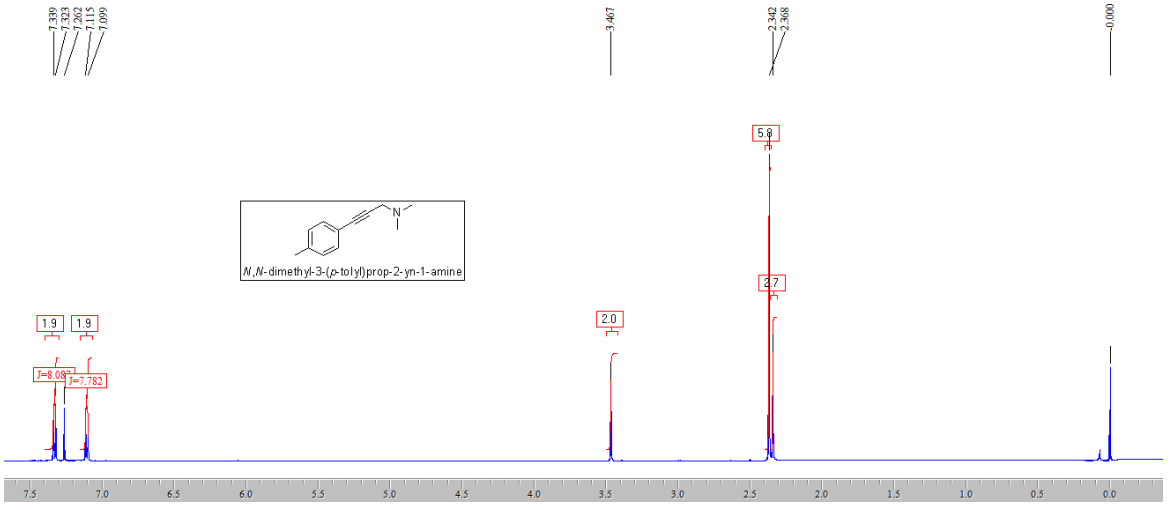


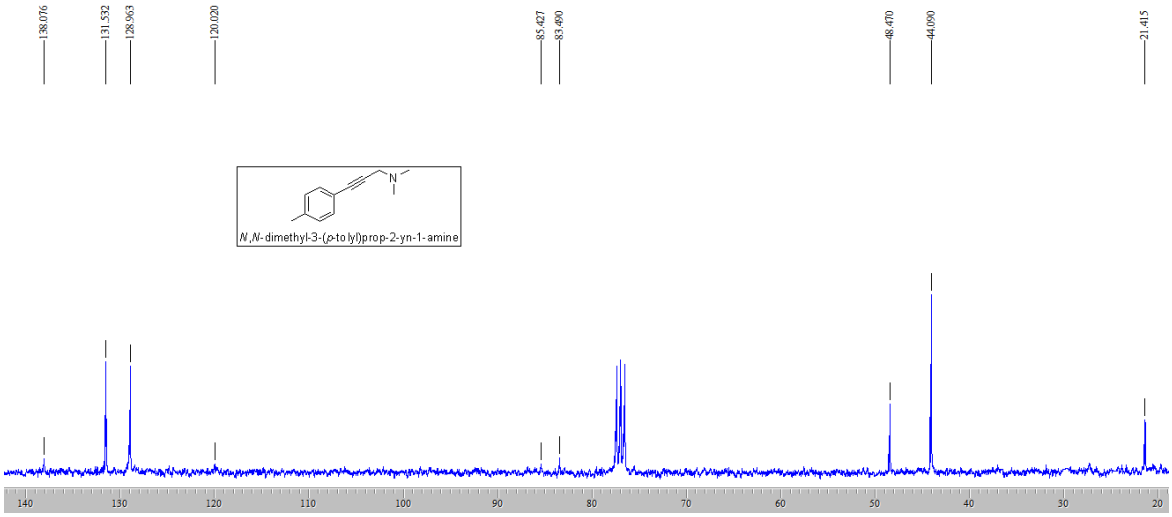
7. 1-(3-(*p*-Tolyl)prop-2-yn-1-yl)pyrrolidine:



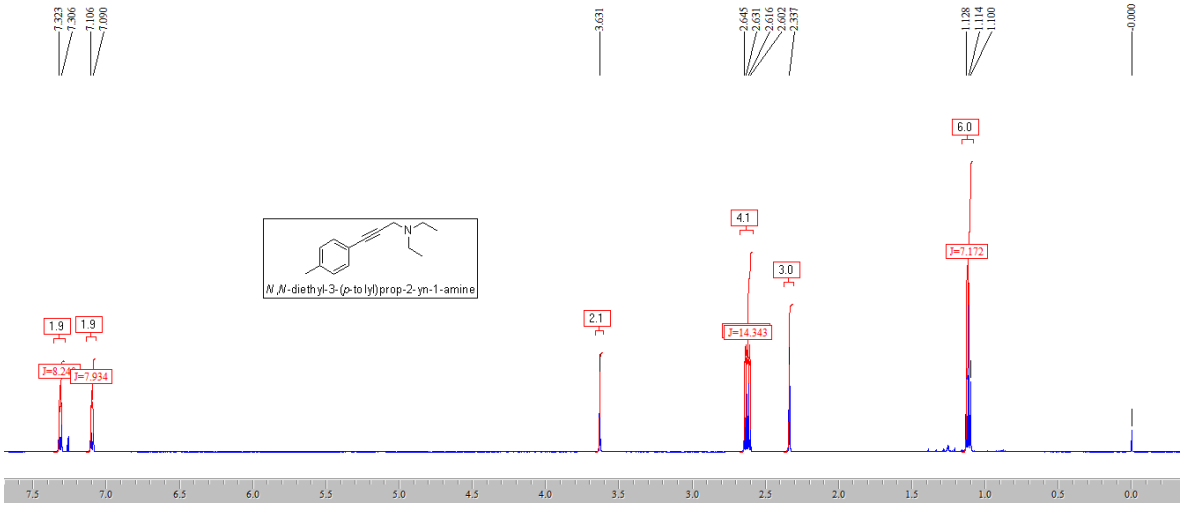


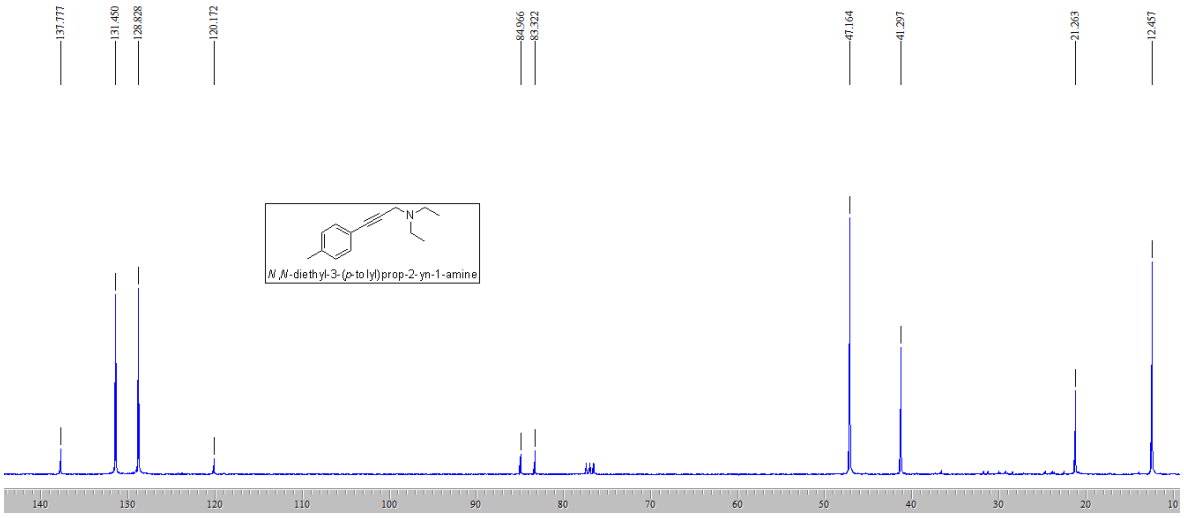
8. *N*,*N*-Dimethyl-3-(*p*-tolyl)prop-2-yn-1-amine:



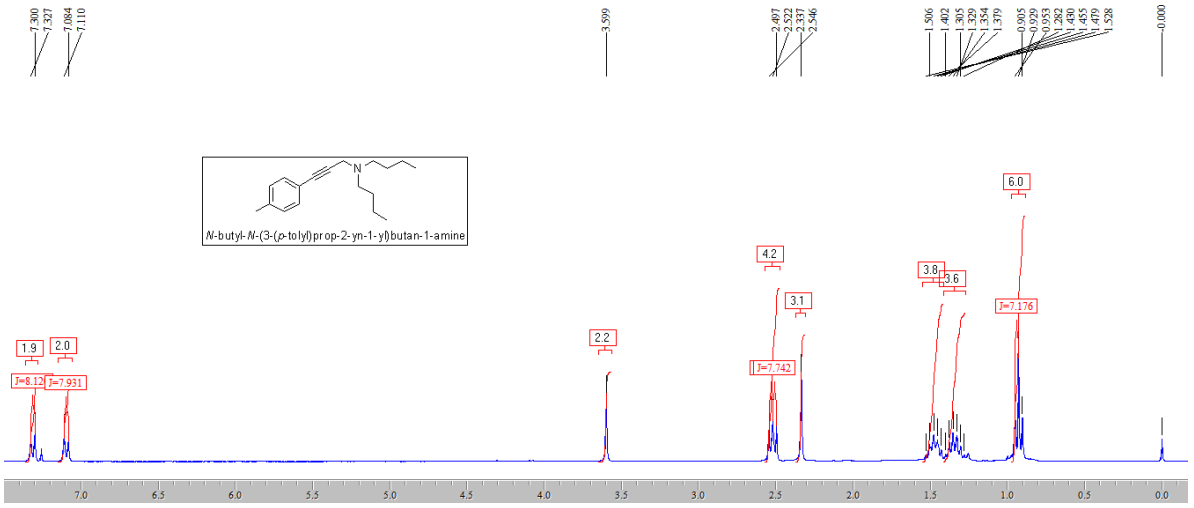


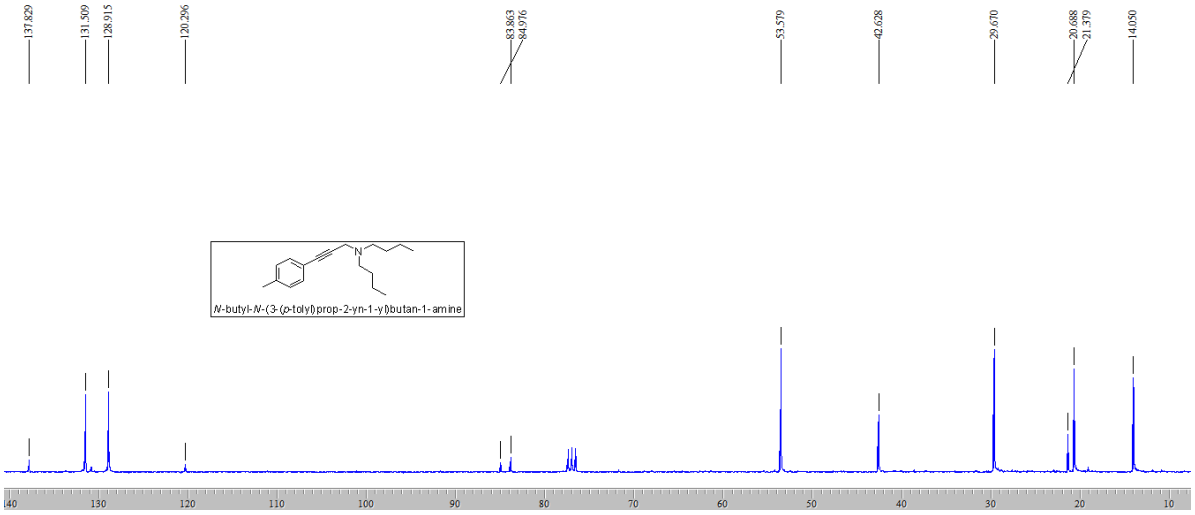
9. *N*, *N*-Diethyl-3-(*p*-tolyl)prop-2-yn-1-amine:



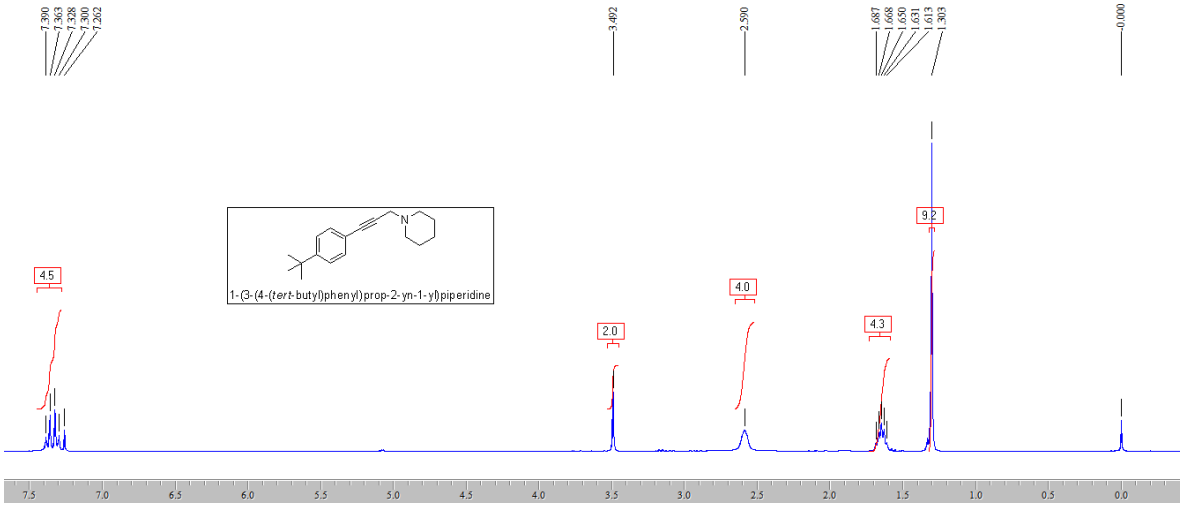


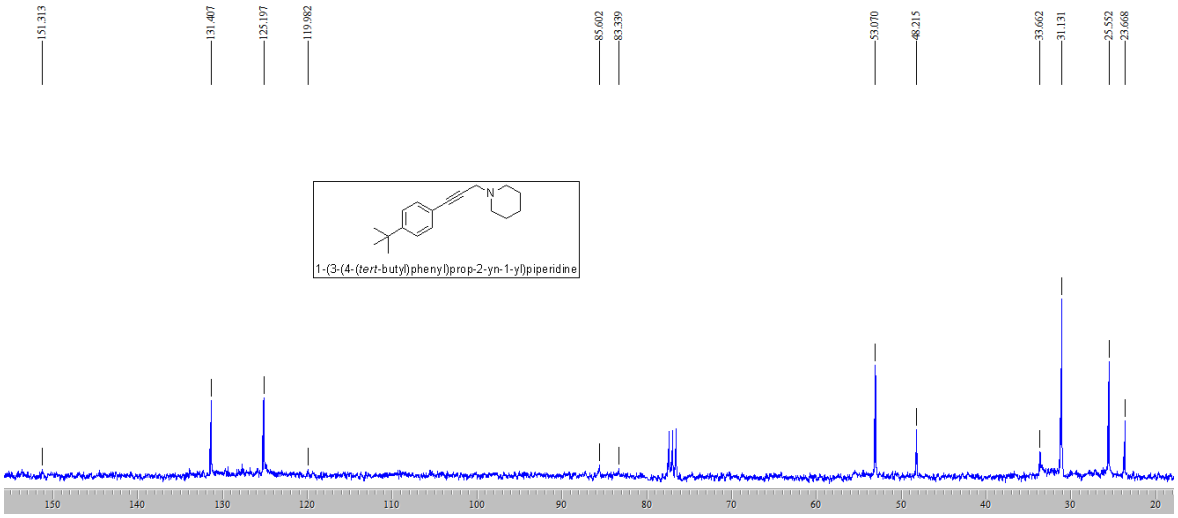
10. *N*-Butyl-*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)butan-1-amine:



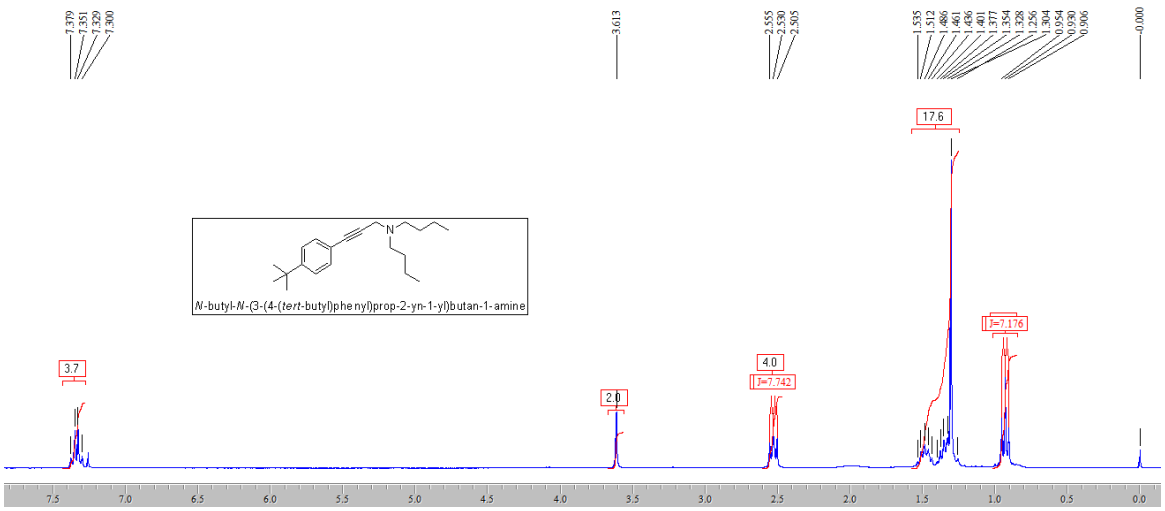


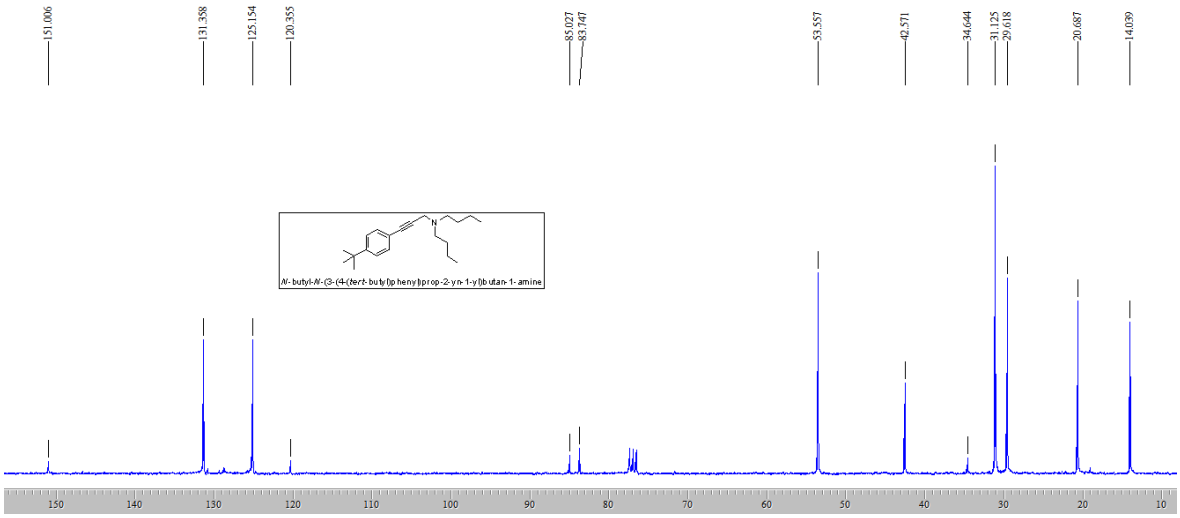
11. 1-(3-(4-(*tert*-Butyl)phenyl)prop-2-yn-1-yl)piperidine:



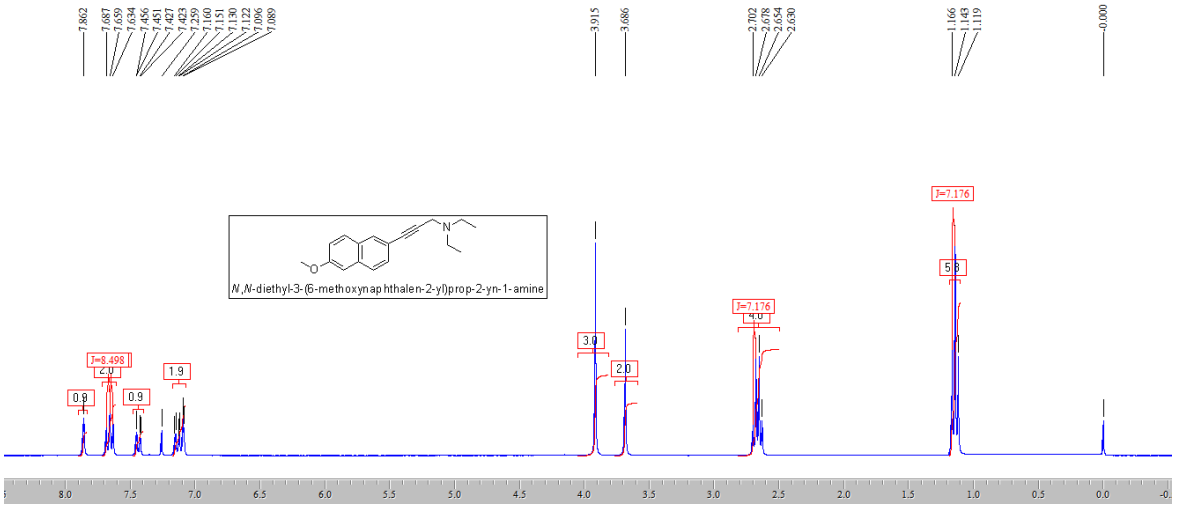


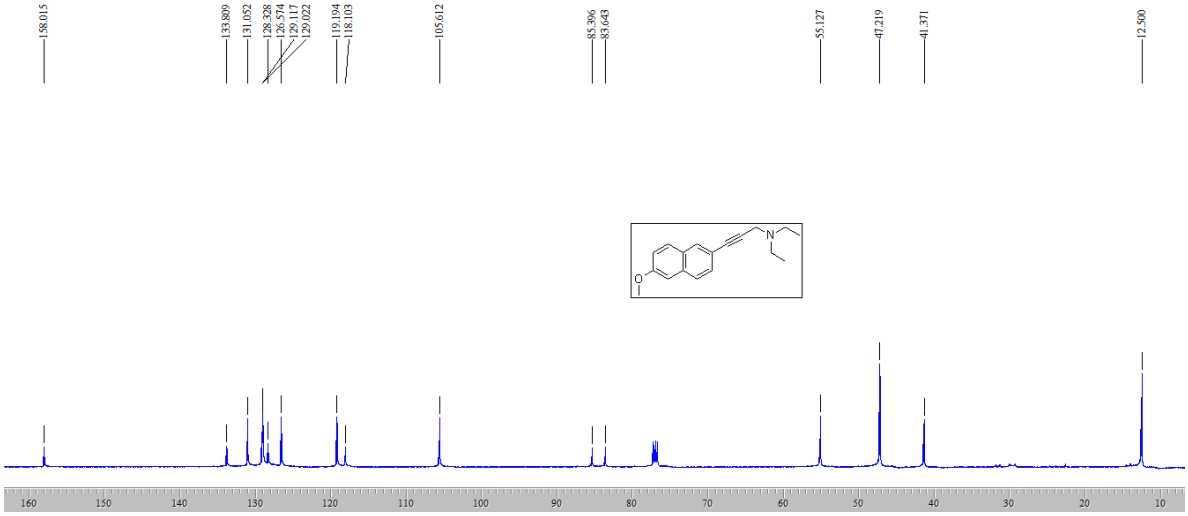
12. *N*-Butyl-*N*-(3-(4-(tert-butyl)phenyl)prop-2-yn-1-yl)butan-1-amine:



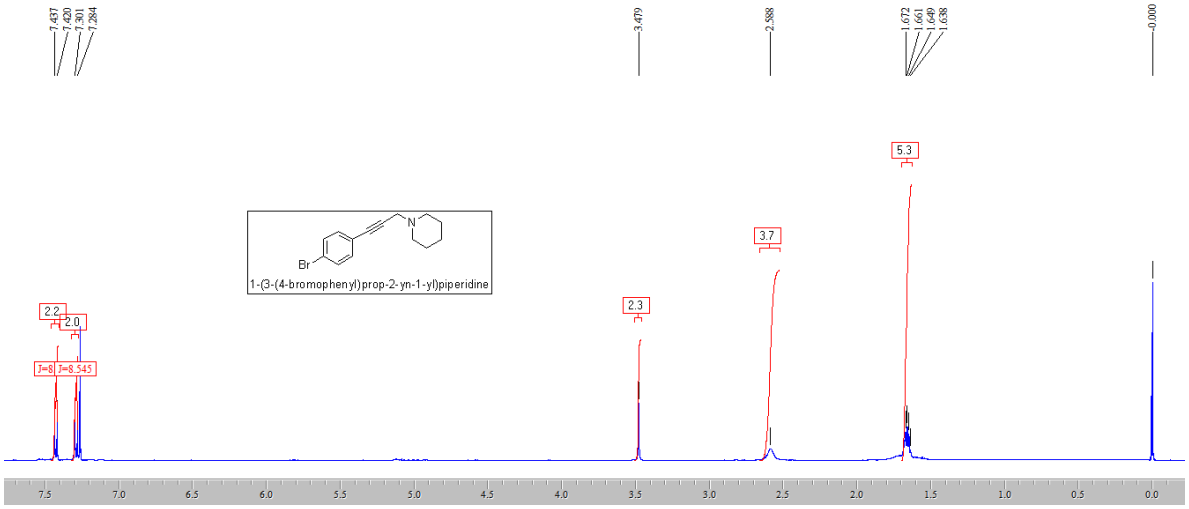


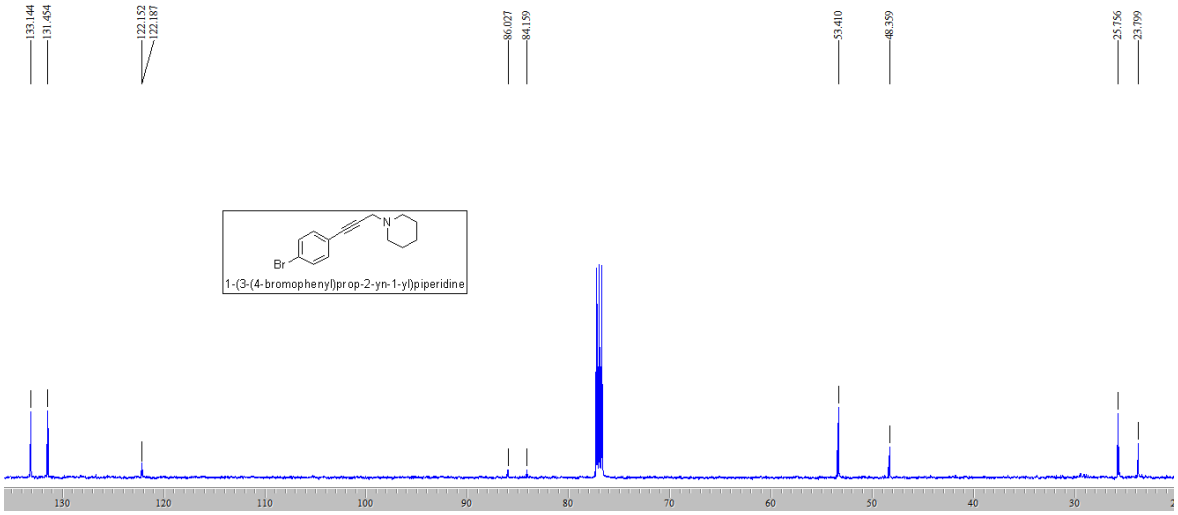
13. *N*,*N*-Diethyl-3-(6-methoxynaphthalen-2-yl)prop-2-yn-1-amine:



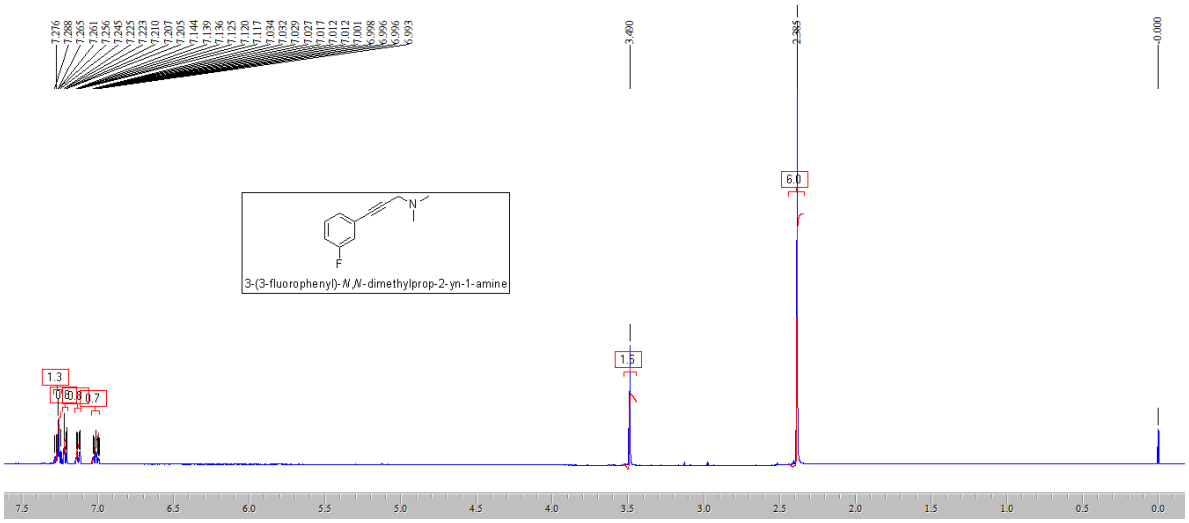


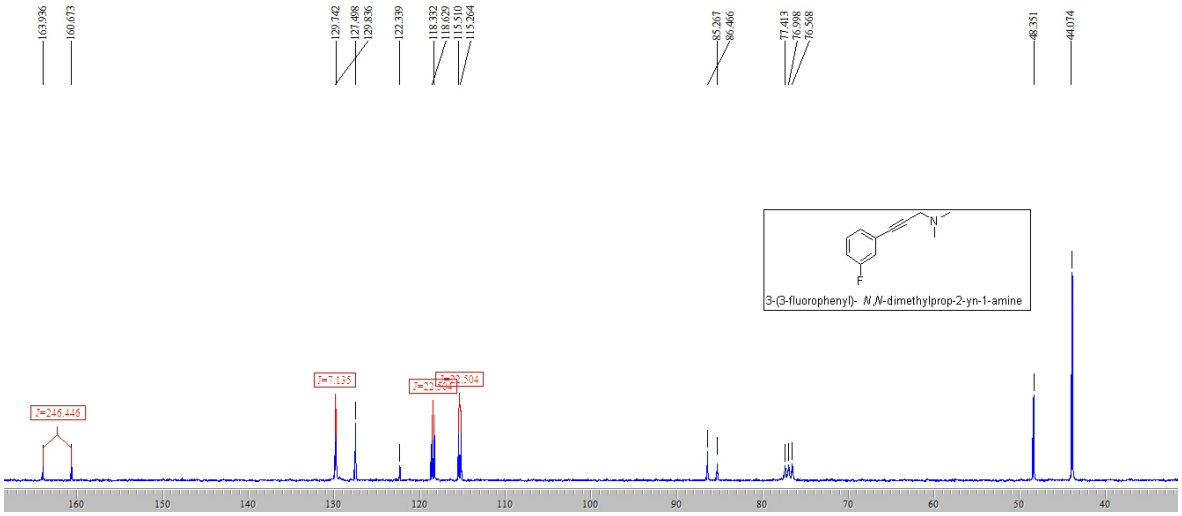
14. 1-(3-(4-Bromophenyl)prop-2-yn-1-yl)piperidine:



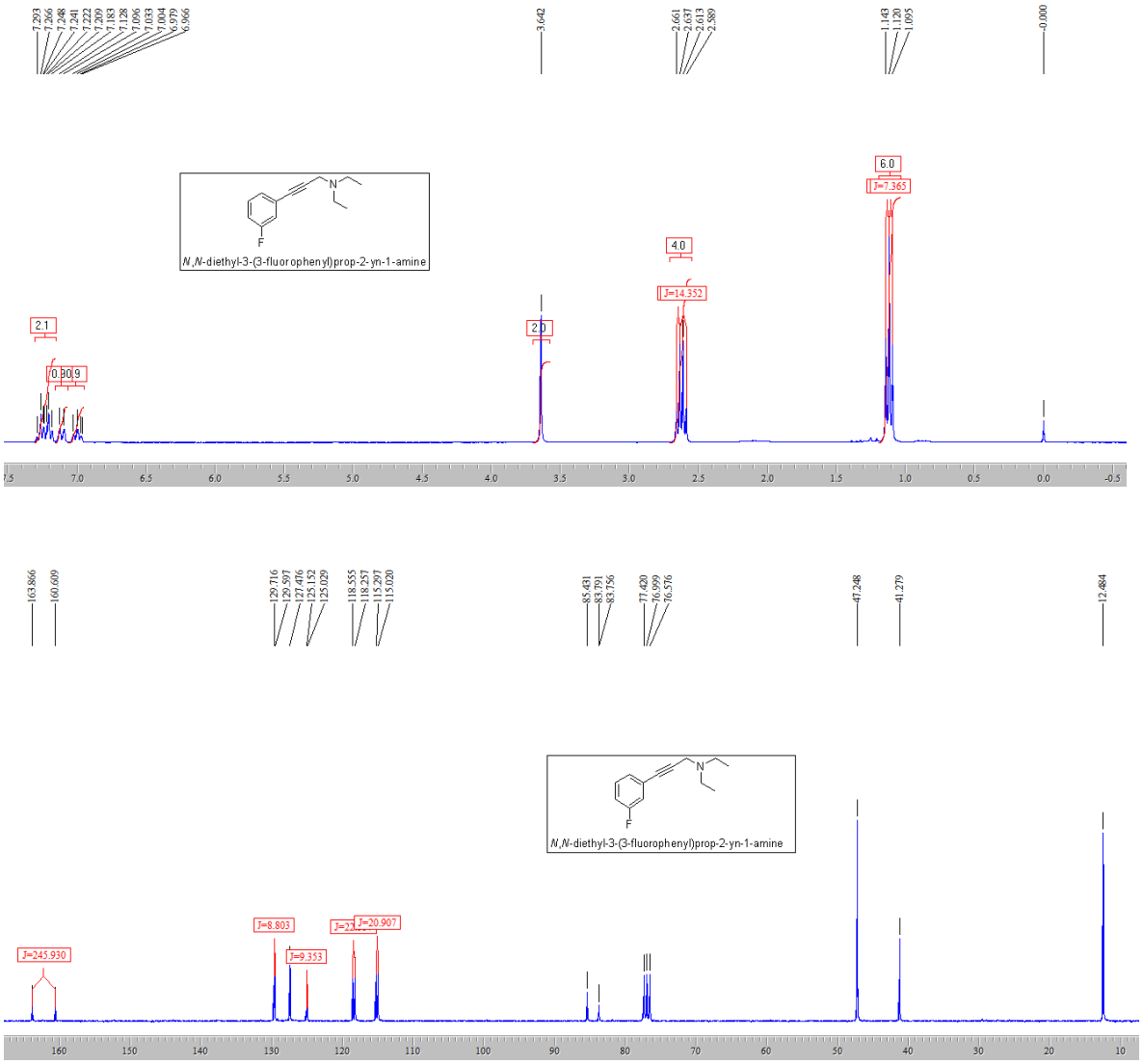


15. 3-(3-Fluorophenyl)-*N*,*N*-dimethylprop-2-yn-1-amine:

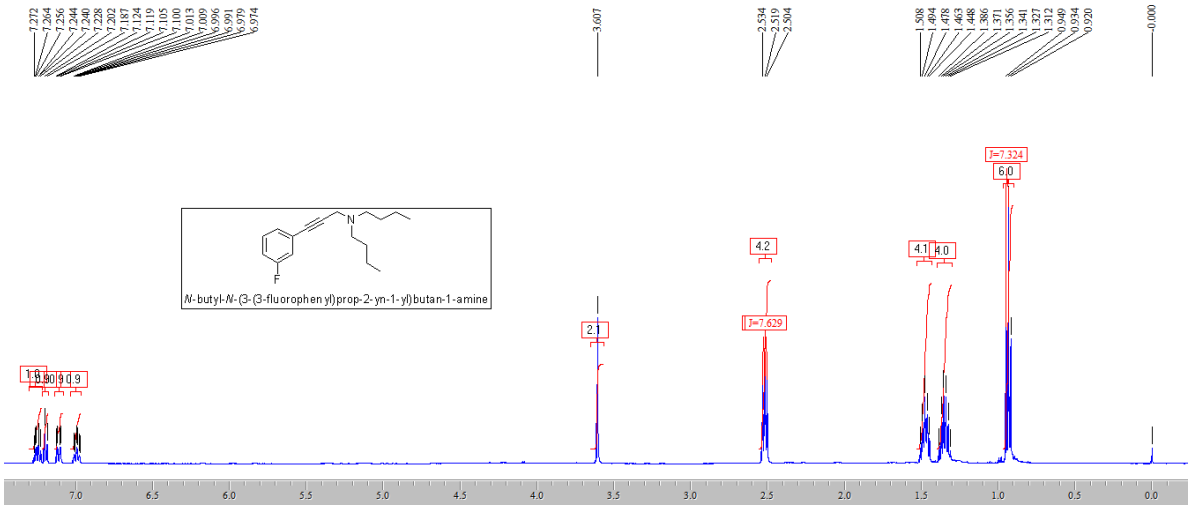


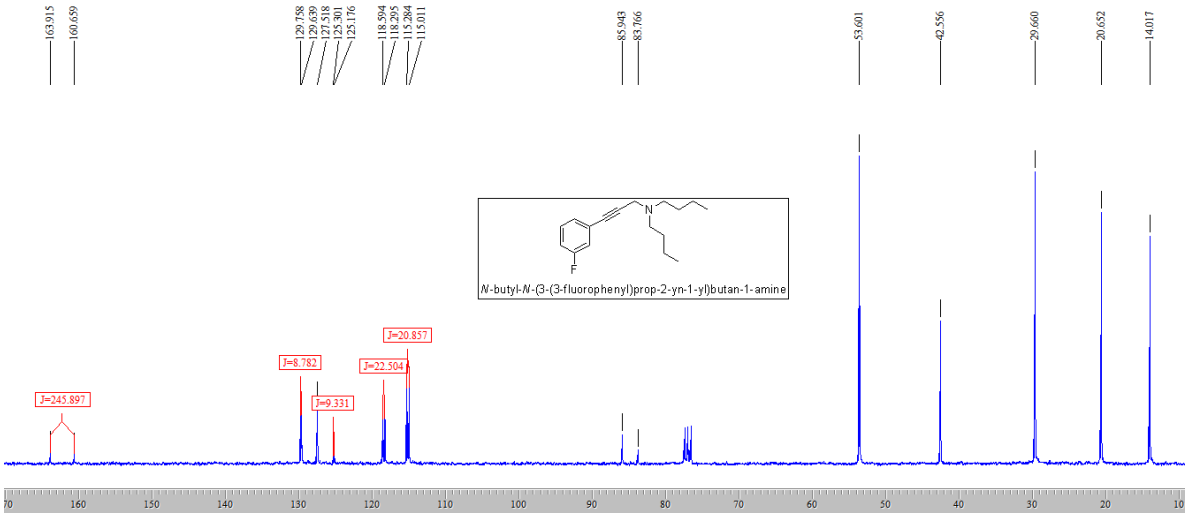


16. *N*,*N*-Diethyl-3-(3-fluorophenyl)prop-2-yn-1-amine:



17. *N*-Butyl-*N*-(3-(3-fluorophenyl)prop-2-yn-1-yl)butan-1-amine:





18. *N*-Butyl-*N*-(3-(3-ethynylphenyl)prop-2-yn-1-yl)butan-1-amine: