

Supporting Information

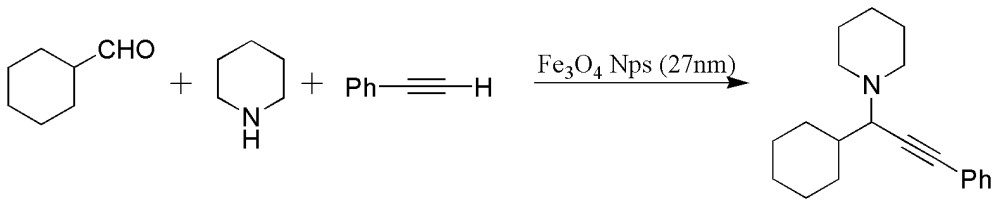
A One-Step Method to Produce Graphene@Fe₃O₄ composite and Its Excellent Catalytic Activity for Three-Component Coupling of Aldehyde, Alkyne and Amine

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Table S1. Three-component Coupling of Cyclohexanecarbaldehyde, Piperidine, and Phenylacetylene Catalyzed by Fe₃O₄ catalyst^a

		
entry	solvent	isolated yield(%) ^b
1	THF	50
2	CH ₃ CN	45
3	DMF	15
4	CH ₃ OCH ₃	48
5	CH ₂ Cl ₂	70
6	CH ₃ CH ₂ OH	57
7	H ₂ O	30
8	CH ₃ COOEt	60

^a For a detail experimental operation, see Supporting Information. All reactions were carried on a 1 mmol scale with aldehyde/amine/alkyne = 1:1.2:1.5, 5% catalyst. ^b Isolated yields based on the aldehyde

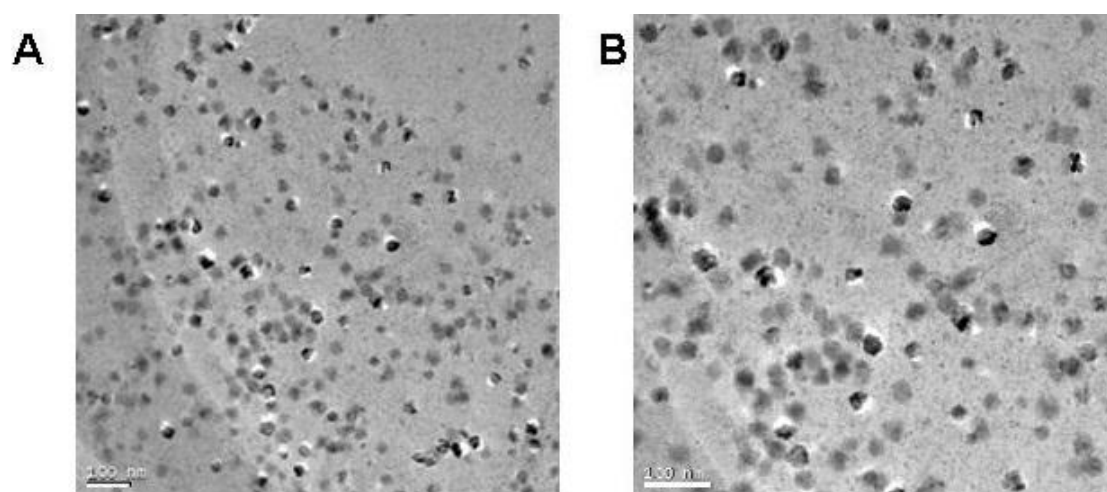


Figure S1. TEM images of graphene@Fe₃O₄ as-synthesized (A) and after the sixth catalytic cycle (B).

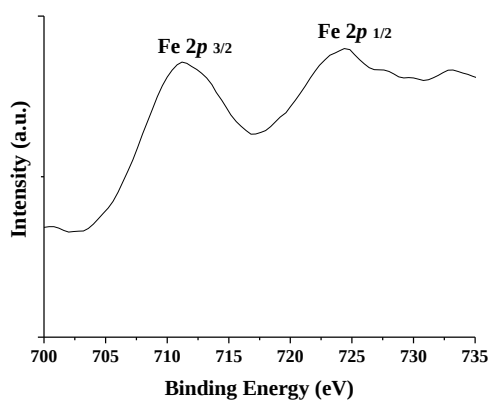
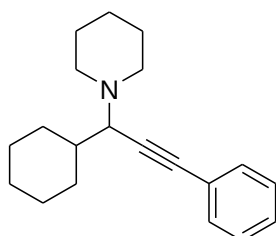


Figure S2. The Fe 2p high resolution XPS spectrum of graphene/Fe₃O₄.

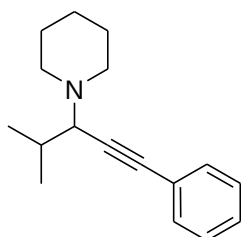
Characterization data for A³-coupling products



1-(1-Cyclohexyl-3-phenyl-2-propynyl)piperidine.

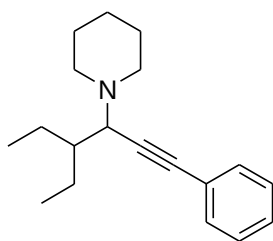
IR (neat, cm⁻¹): 3027, 2928, 2851, 2800, 1509, 1447, 1318, 1156, 1105, 996, 816, 734, 530; ¹H-NMR (CDCl₃, 400MHz, ppm): δ 7.45-7.43(m, 2H), 7.31-7.25(m, 3H), 3.10(d,

$J = 10.0\text{ Hz}$, 1H), 2.66-2.60(m, 2H), 2.42-2.39(m, 2H), 2.12-2.02(m, 2H), 1.78-1.68(m, 2H), 1.65-1.51(m, 6H), 1.46-1.42(m, 2H), 1.33-1.12(m, 3H), 1.07-0.88(m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 131.68, 128.15, 127.57, 123.79, 87.74, 86.12, 64.36, 50.77, 39.58, 31.31, 30.42, 26.78, 26.27, 26.25, 24.70; MS m/z (%) (relative intensity): 280[$\text{M}^+ - 1$], 0.01], 214(2), 212(100), 155(1), 129(23).



***N*-(1-Isopropyl-3-phenyl-2-propynyl)piperidine.**

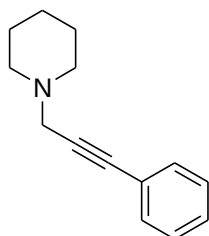
IR (neat, cm^{-1}): 3057, 2932, 2856, 2802, 1598, 1489, 1445, 1381, 1157, 1097, 1004, 754, 691; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.47–7.45 (m, 2H), 7.34–7.27 (m, 3H), 3.02 (d, $J = 10.0\text{ Hz}$, 1H), 2.69–2.63 (m, 2H), 2.44 (br, 2H), 1.97–1.91 (m, 1H), 1.68–1.55 (m, 4H), 1.49–1.45 (m, 2H), 1.12 (d, $J = 6.4\text{ Hz}$, 3H), 1.04 (d, $J = 6.4\text{ Hz}$, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 131.68, 128.16, 127.61, 123.77, 87.83, 86.01, 65.62, 50.83, 30.40, 26.27, 24.70, 20.65, 19.87; MS m/z (%) (relative intensity): 240[$\text{M}^+ - 1$], 0.24], 198(100), 141(4), 115(33).



1-[1-(1-Ethylpropyl)-3-phenyl-2-propynyl]piperidine.

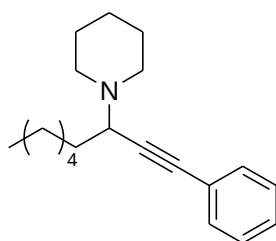
IR (neat, cm^{-1}): 3057, 2961, 2934, 2875, 2802, 1598, 1489, 1445, 1380, 1158, 1095, 910, 755, 691; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.44-7.42(m, 2H), 7.31-7.24(m, 3H), 3.22(d, $J = 9.6\text{ Hz}$, 1H), 2.65-2.60(m, 2H), 2.43-2.38(m, 2H), 1.78-1.68(m, 1H), 1.63-1.51(m, 6H), 1.50-1.39(m, 4H), 0.90(t, $J = 7.2\text{ Hz}$, 3H), 0.84(t, $J = 7.2\text{ Hz}$, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 131.68, 128.15, 127.53, 123.93, 88.10, 85.90, 61.52, 50.93, 41.62, 26.36, 24.76, 22.49, 20.95, 10.74, 9.84; HRMS calcd for $\text{C}_{19}\text{H}_{28}\text{N}$ ($\text{M}+1$)

270.2216, found 270.2216. MS m/z (%) (relative intensity): 268[(M^+ -1), 0.1], 212(1), 198(100), 141(2), 128(3), 115(24).



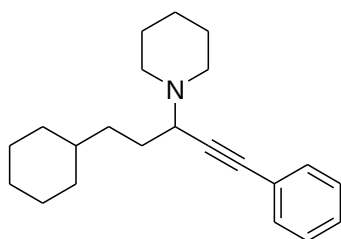
N-(3-Phenyl)-prop-2-ynyl)piperidine

IR (neat, cm^{-1}): 3056, 2935, 2854, 2798, 1598, 1489, 1445, 1341, 1155, 1110, 1035, 995, 756, 692, 527; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.45–7.43 (m, 2H), 7.30–7.29 (m, 3H), 3.48 (s, 2H), 2.58 (br, 4H), 1.68–1.62(m, 4H), 1.46 (br, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 131.66, 128.16, 127.90, 123.28, 85.06, 84.92, 53.43, 48.46, 25.93, 23.91. MS m/z (%) (relative intensity): 199[(M^+), 49], 198(92), 170(14), 157(47), 156(53), 143(11), 115(100), 89(12).



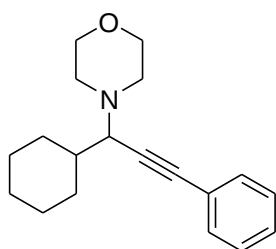
1-(1-phenylhept-1-yn-3-yl)piperidine

IR (neat, cm^{-1}): 3056, 2931, 2855, 2802, 1489, 1464, 1327, 1157, 1098, 755, 691; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.45–7.41 (m, 2H), 7.32–7.28 (m, 3H), 3.49–3.46 (dd, $J_1 = 7.2$ Hz, $J_2 = 6.0$ Hz, 1H), 2.71–2.66 (m, 2H), 2.51–2.47 (m, 2H), 1.76–1.61 (m, 7H), 1.60–1.52 (m, 3H), 1.50–1.26 (m, 7H), 0.90–0.87 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 131.71, 128.17, 127.70, 123.64, 88.24, 85.60, 58.63, 50.59, 33.48, 31.76, 29.08, 26.85, 26.20, 24.59, 22.61, 14.05; MS m/z (%) (relative intensity): 254[(M^+ -1), 0.1], 212(2), 198(100), 155(1), 141(2), 128(4), 115(17), 91(1).



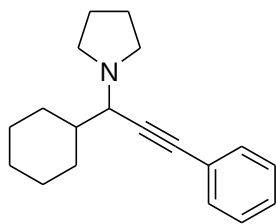
1-(5-cyclohexyl-1-phenylpent-1-yn-3-yl)piperidine

IR (neat, cm^{-1}): 3056, 2924, 2850, 2802, 1489, 1447, 1327, 1103, 990, 756, 691;
 ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.44–7.42 (m, 2H), 7.31–7.27 (m, 3H),
 3.49–3.46 (t, J = 7.6 Hz, 1H), 2.71–2.66 (m, 2H), 2.48 (br, 2H), 1.75–1.55 (m, 10H),
 1.50–1.41 (m, 3H), 1.37–1.09 (m, 6H), 0.97–0.86 (m, 3H); ^{13}C NMR (100 MHz,
 CDCl_3): δ 131.69, 128.14, 127.68, 123.61, 88.24, 85.58, 58.5, 50.56, 37.63, 34.62,
 33.39, 30.95, 26.67, 26.37, 26.16, 24.56;; MS m/z (%) (relative intensity): 310[(M^+ -1),
 0.2], 228(6), 198(100), 149(2), 128(3), 115(16), 95(1).



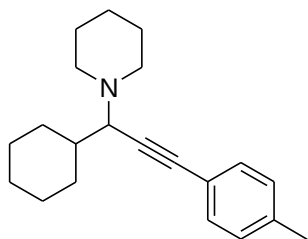
N-(1-isopropyl-3-phenyl-2-propynyl)morpholine

IR (neat, cm^{-1}): 3056, 2925, 2851, 2819, 1489, 1448, 1259, 1117, 1007, 863, 756, 691,
 566; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.44–7.43 (m, 2H), 7.31–7.28 (m, 3H),
 3.79–3.74 (m, 4H), 3.13 (d, J = 9.6 Hz, 1H), 2.73–2.68 (m, 2H), 2.54–2.49 (m, 2H),
 2.12–2.03 (m, 2H), 1.79–1.74 (m, 2H), 1.69–1.56 (m, 4H), 1.33–0.93 (m, 2H),
 1.23–1.26 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 131.69, 128.20, 127.82, 123.40,
 86.76, 86.63, 67.21, 63.95, 39.08, 30.98, 30.36, 26.71, 26.16, 26.00; MS m/z (%)
 (relative intensity): 282[(M^+ -1), 0.2], 212(3), 200(100), 165(1), 141(2), 129(2),
 115(21), 91(1).



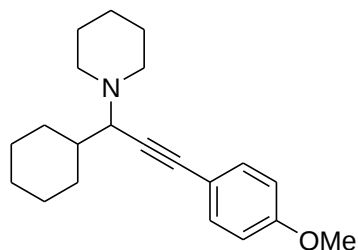
1-[1-Cyclohexyl-3-(4-methylphenyl)-2-propynyl]pyrrodine.

IR (neat, cm^{-1}): 3056, 2926, 2851, 2807, 1669, 1599, 1489, 1447, 1260, 1130, 1029, 755, 691; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.44-7.42(m, 2H), 7.31-7.25(m, 3H), 3.35(d, J = 8.4Hz, 1H), 2.74-2.72(m, 2H), 2.65-2.63(m, 2H), 2.09(d, J = 12.4 Hz, 1H), 1.95(d, J = 12.8 Hz, 1H), 1.78-1.75(m, 6H), 1.69-1.66(m, 1H), 1.62-1.53(m, 1H), 1.32- 1.05(m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ 131.71, 128.18, 127.68, 123.68, 87.94, 85.73, 61.24, 50.03, 41.35, 30.70, 30.29, 26.70, 26.23, 26.21, 23.53; MS m/z (%) (relative intensity): 267[(M^+), 0.1], 212(1), 184(100), 153(1), 141(1), 128(3), 115(22), 91(1).



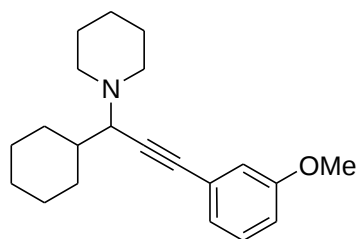
1-[1-Cyclohexyl-3-(4-methylphenyl)-2-propynyl]piperidine.

IR (neat, cm^{-1}): 3027, 2929, 2851, 2800, 1509, 1447, 1319, 1263, 1105, 996, 815, 734, 529; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.33(d, J =8.0Hz, 2H), 7.09(d, J = 8.0Hz, 2H), 3.08(d, J = 10.0Hz, 1H), 2.64-2.60(m, 2H), 2.39(br, 2H), 2.33(s, 3H), 2.12-2.01(m, 2H), 1.77-1.68(m, 2H), 1.65-1.54(m, 7H), 1.46-1.45(m, 3H), 1.32-1.15(m, 4H), 1.06-0.85(m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 137.53, 131.55, 128.88, 120.72, 86.92, 86.12, 64.38, 50.73, 39.60, 31.31, 30.44, 26.90, 26.80, 26.30, 26.26, 24.72, 21.38; MS m/z (%) (relative intensity): 294[($\text{M}^+ - 1$), 0.2], 212(100), 169(1), 155(1), 141(1), 129(24), 115(2), 91(1).



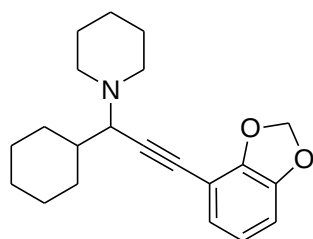
1-(1-cyclohexyl-3-(4-methoxyphenyl)prop-2-ynyl)piperidine

IR (neat, cm^{-1}): 3039, 2929, 2851, 2800, 1606, 1509, 1447, 1248, 1173, 1105, 1034, 832, 536; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.37(d, $J = 8.8\text{Hz}$, 2H), 6.81(d, $J = 8.8\text{Hz}$, 2H), 3.80(s, 3H), 3.08(d, $J = 9.6\text{Hz}$, 1H), 2.64-2.59(m, 2H), 2.39(br, 2H), 2.11-2.01(m, 2H), 1.77-1.55(m, 9H), 1.46-1.41(m, 2H), 1.32-1.02(m, 3H), 1.00-0.87(m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.09, 133.03, 116.00, 113.78, 86.11, 85.80, 64.39, 55.28, 55.26, 50.73, 39.63, 31.32, 30.45, 26.81, 26.30, 26.27, 26.11, 24.72; MS m/z (%) (relative intensity): 310[(M^+ -1), 0.2], 246(0.1), 228(100), 213(1), 198(2), 185(1), 158(1), 145(19), 135(2), 115(2), 91(1).



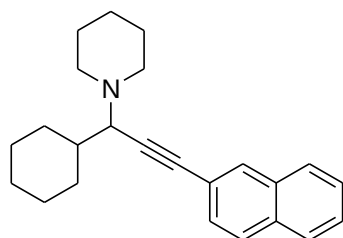
1-(1-cyclohexyl-3-(3-methoxyphenyl)prop-2-ynyl)piperidine

IR (neat, cm^{-1}): 3000, 2930, 2851, 2801, 1671, 1600, 1449, 1286, 1201, 1161, 1104, 1046, 996, 855, 780, 733, 687; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.22-7.18(m, 1H), 7.04 (d, $J = 7.6\text{Hz}$, 1H), 6.97 (d, $J = 2.0\text{Hz}$, 1H), 6.83-6.81(dd, $J_1 = 8.4\text{ Hz}$, $J_2 = 2.4\text{ Hz}$, 1H), 3.80(s, 3H), 3.10(d, $J = 10.0\text{Hz}$, 1H), 2.64-2.59(m, 2H), 2.39(br, 2H), 2.17(s, 1H), 2.11-2.01(m, 2H), 1.78-1.65(m, 2H), 1.61-1.54(m, 7H), 1.46-1.41(m, 2H), 1.32-1.02(m, 4H), 1.00-0.87(m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.37, 129.33, 124.77, 124.41 116.77, 114.23, 65.94, 64.45, 55.38, 55.36, 50.85, 39.63, 31.37, 30.57, 26.82, 26.32, 26.18, 24.68, 15.36; MS m/z (%) (relative intensity): 310[(M^+ -1), 0.2], 232(2), 228(100), 213(1), 185(1), 171(1), 159(1), 145(13), 128(1), 115(2).



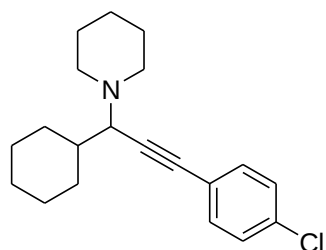
1-(3-(benzo[d][1,3]dioxol-4-yl)-1-cyclohexylprop-2-ynyl)piperidine

IR (neat, cm^{-1}): 2926, 2853, 2802, 1488, 1444, 1247, 1205, 1103, 1041, 1046, 940, 859, 810; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 6.97 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 6.90(d, $J = 1.2$ Hz, 1H), 6.74(d, $J = 8.4$ Hz, 1H), 5.96(s, 2H), 3.08(d, $J = 9.6$ Hz, 1H), 2.65-2.59(m, 2H), 2.41-2.37(m, 2H), 2.11-2.02(m, 2H), 1.79-1.76(br, 2H), 1.69-1.55(m, 6H), 1.47-1.43(m, 2H), 1.31-1.16(m, 4H), 1.06-1.03(m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.28, 147.26, 125.96, 117.07, 111.78, 108.23, 101.11, 85.96, 85.84, 64.32, 50.73, 39.58, 31.29, 30.41, 26.89, 26.78, 26.27, 26.24, 26.07, 24.70; MS m/z (%) (relative intensity): 324[(M^+ -1), 0.2], 292(0.1), 248(3), 242(100), 165(2), 159(22), 149(1), 135(2), 91(2).



1-[1-Cyclohexyl-3-(1-naphthyl)-2-propynyl]piperidine.

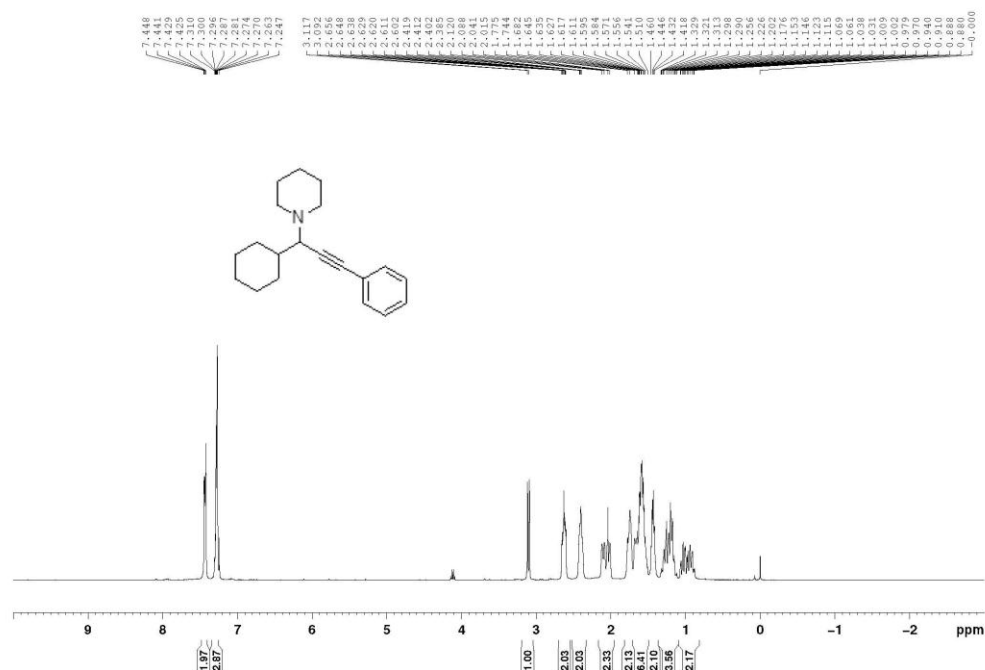
IR (neat, cm^{-1}): 3056, 2929, 2851, 2800, 2749, 1726, 1597, 1447, 1265, 1105, 995, 858, 816, 744, 474; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.94(s, 1H), 7.80-7.74(m, 3H), 7.50-7.45(m, 1H), 3.15(d, $J = 10.0$ Hz, 1H), 2.69-2.65(m, 2H), 2.46-2.43(m, 2H), 2.16(d, $J = 12.4$ Hz, 1H), 2.06(d, $J = 12.4$ Hz, 1H), 1.77-1.58(m, 9H), 1.47-1.44(m, 2H), 1.32-1.22(m, 4H), 1.20-1.04(m, 1H), 0.99-0.93(m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 133.04, 132.50, 131.11, 128.90, 128.34, 127.76, 127.69, 127.55, 126.37, 126.25, 121.10, 88.22, 86.46, 64.47, 39.61, 31.38, 30.45, 26.81, 26.31, 26.28, 26.11, 24.72; MS m/z (%) (relative intensity): 330[(M^+ -1), 0.2], 292(0.1), 279(0.1), 248(100), 215(1), 203(1), 191(2), 178(3), 165(25), 152(3), 124(2).

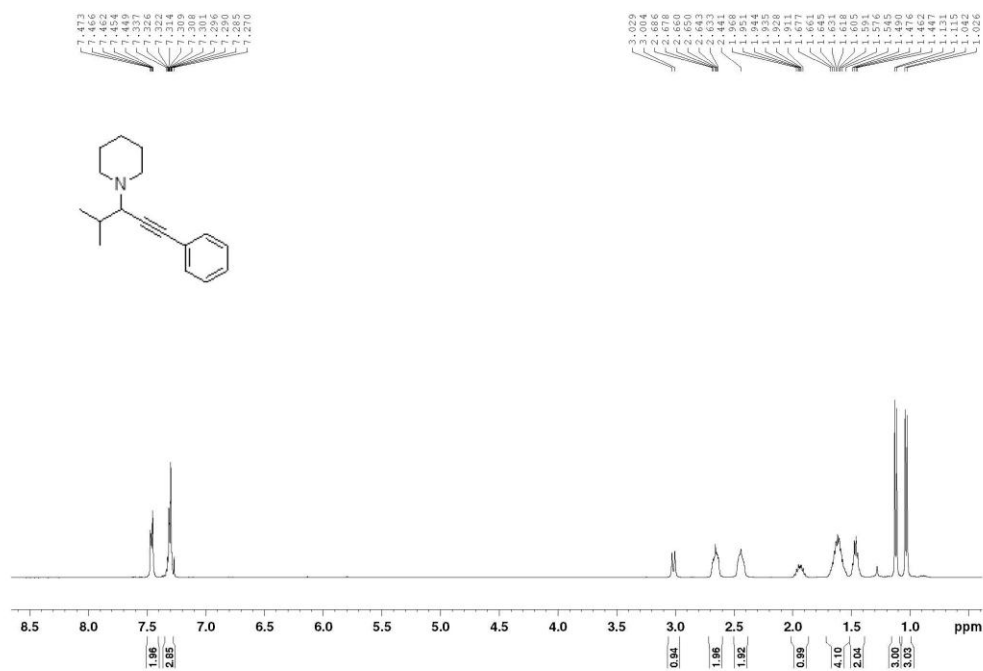
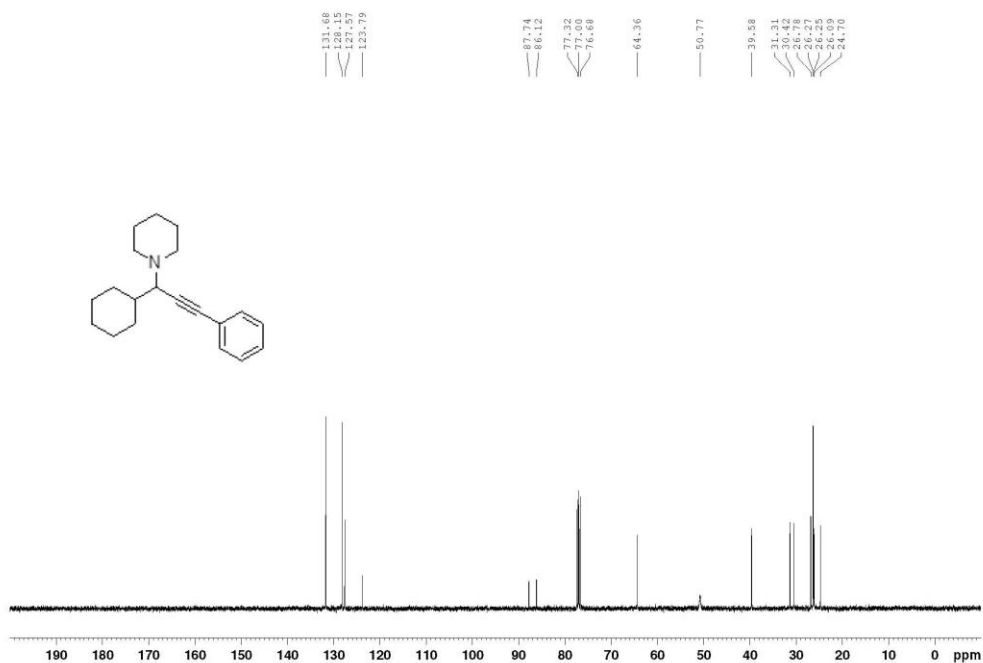


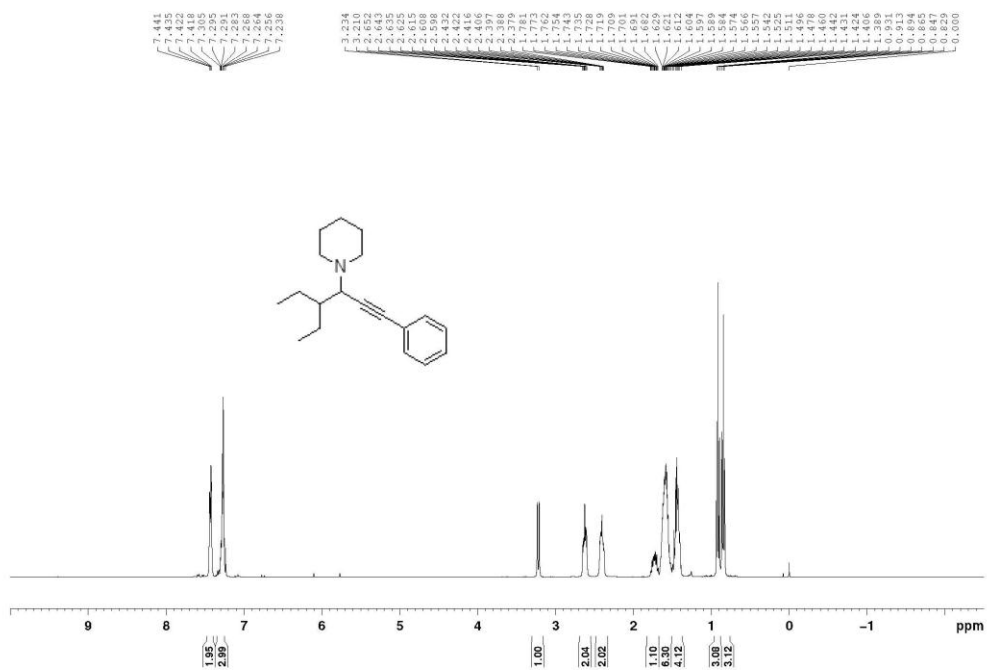
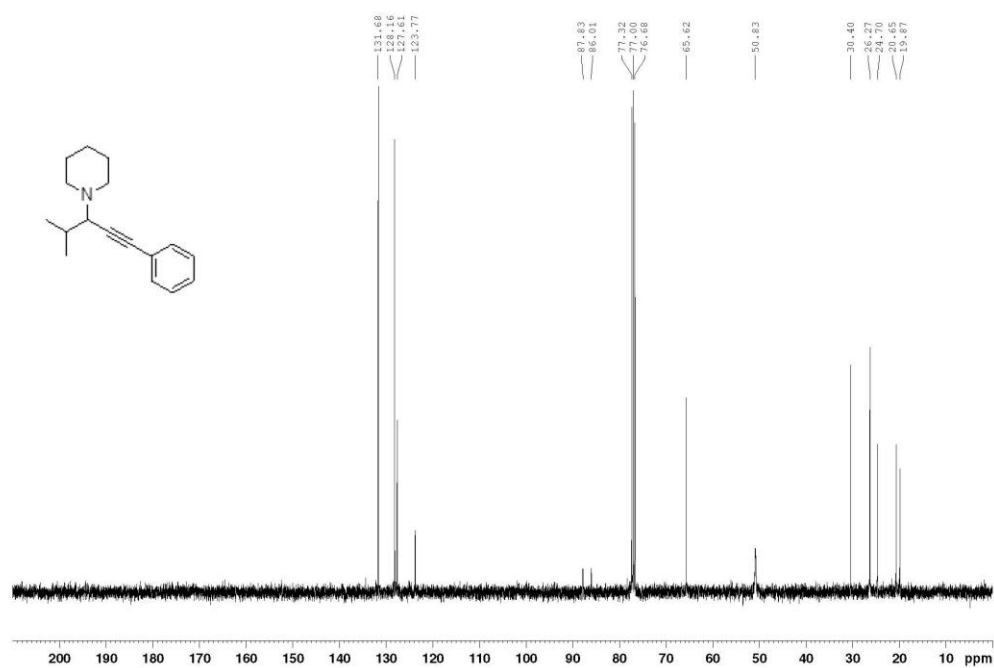
1-(3-(4-chlorophenyl)-1-cyclohexylprop-2-ynyl)piperidine

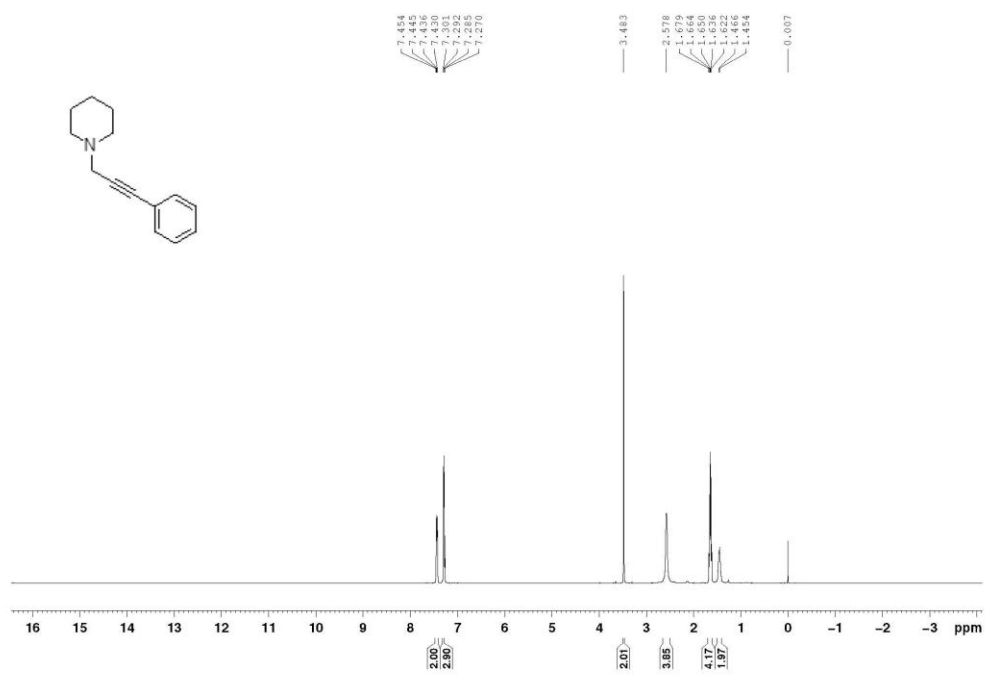
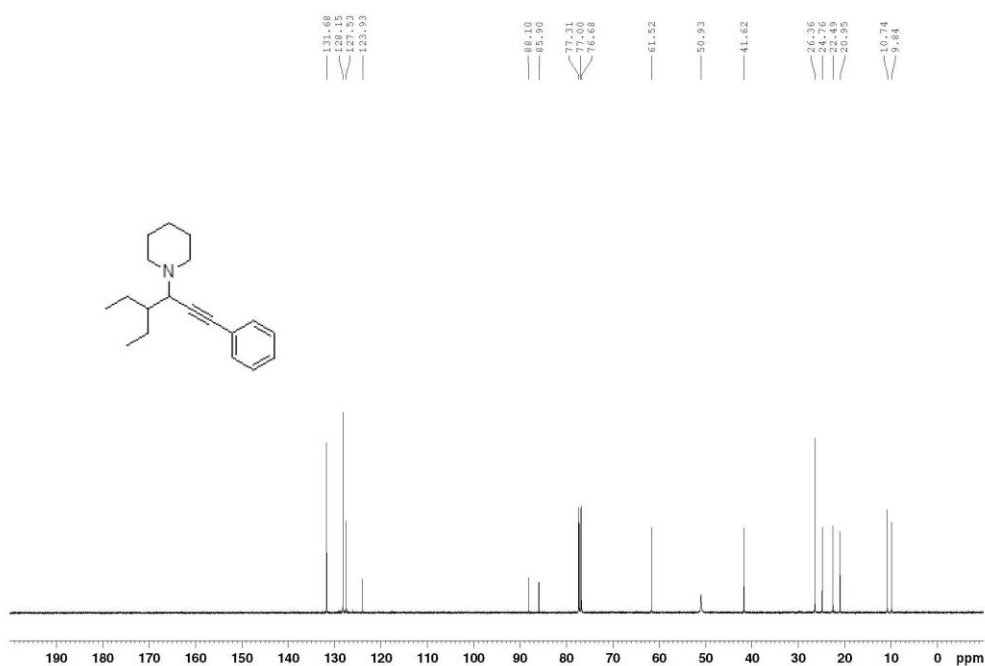
IR (neat, cm^{-1}): 2930, 2851, 2800, 2680, 1489, 1447, 1318, 1262, 1094, 1015, 827, 740, 526; ^1H -NMR (CDCl_3 , 400MHz, ppm): δ 7.35(d, $J = 8.4\text{Hz}$, 2H), 7.26(d, $J = 8.4\text{Hz}$, 2H), 3.09(d, $J = 10.0\text{Hz}$, 3H), 2.63-2.58(m, 2H), 2.38(br, 2H), 2.08-2.01(m, 2H), 1.85-1.74(m, 2H), 1.68-1.51(m, 6H), 1.46-1.42(m, 2H), 1.33-0.14(m, 3H), 1.05-0.87(m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 133.50, 132.91, 128.44, 122.25, 88.90, 85.05, 64.35, 50.73, 39.49, 31.30, 30.39, 26.76, 26.25, 26.22, 26.05, 24.68; MS m/z (%) (relative intensity): 314[M^+], 0.2], 234(35), 232(100), 197(1), 175(1), 151(7), 149(22), 127(1), 114 (2).

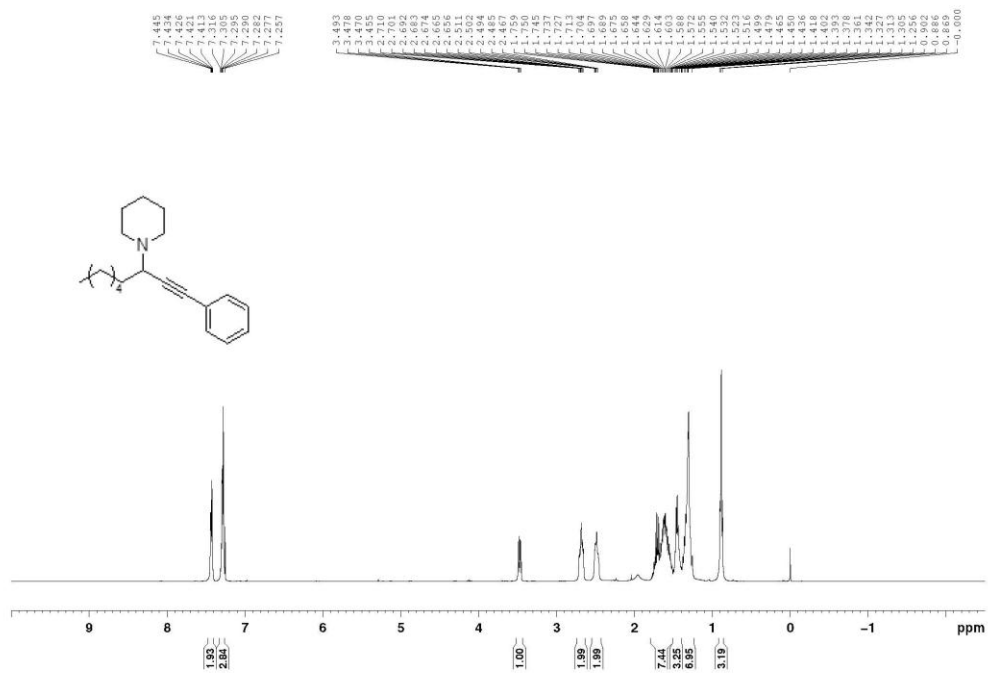
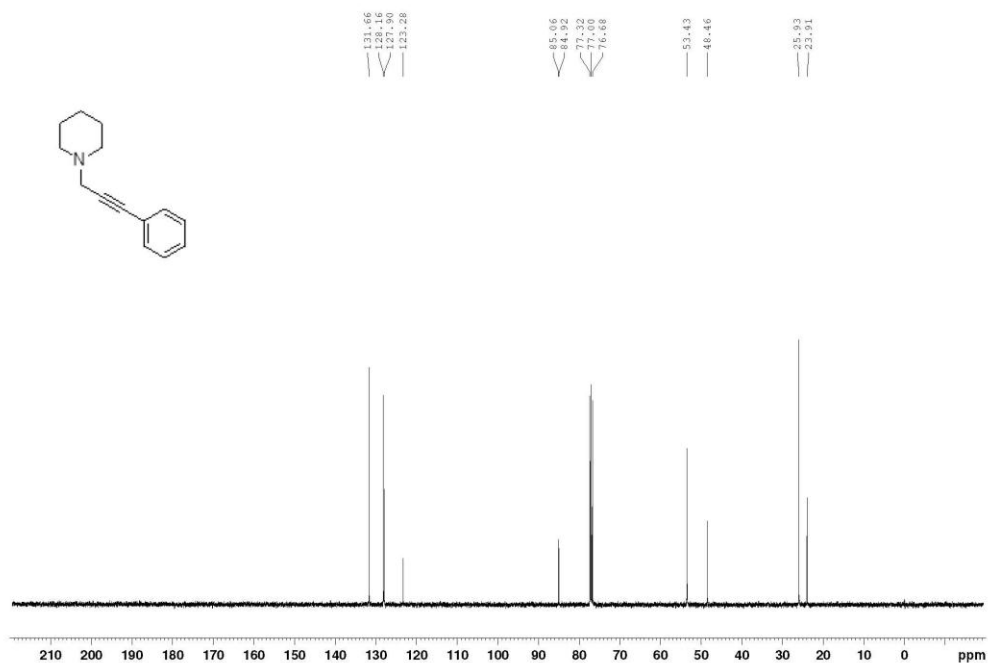
Copies of ^1H NMR, ^{13}C NMR

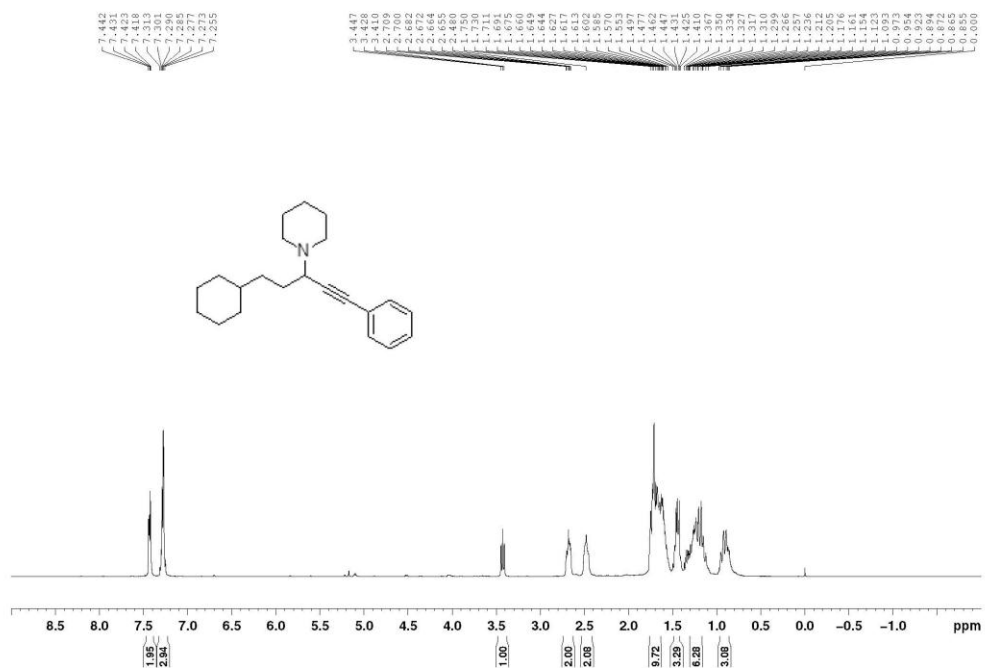
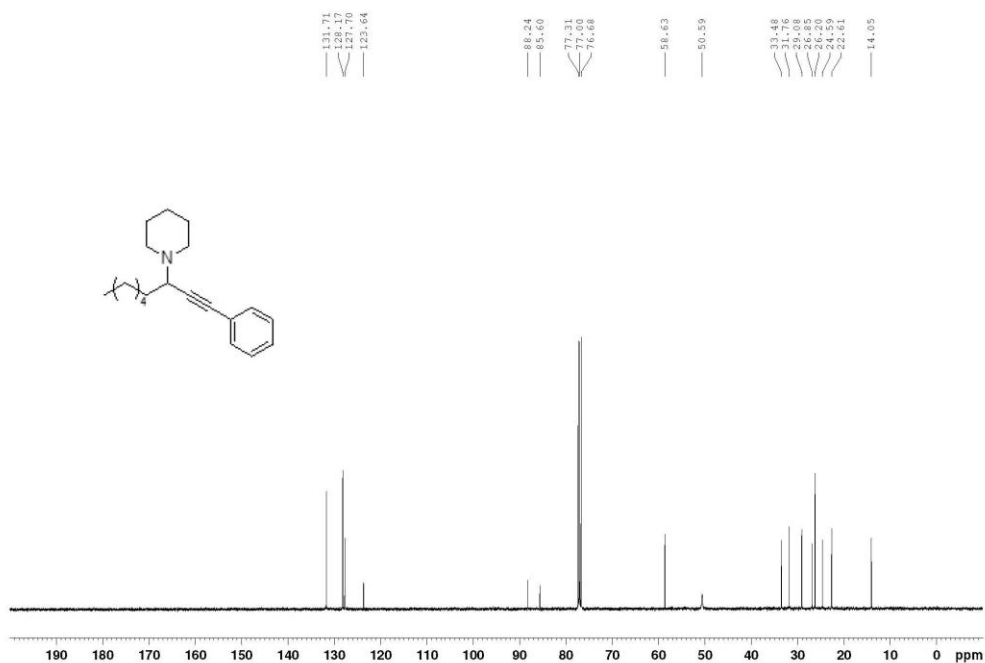


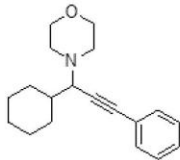
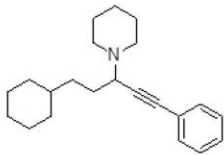


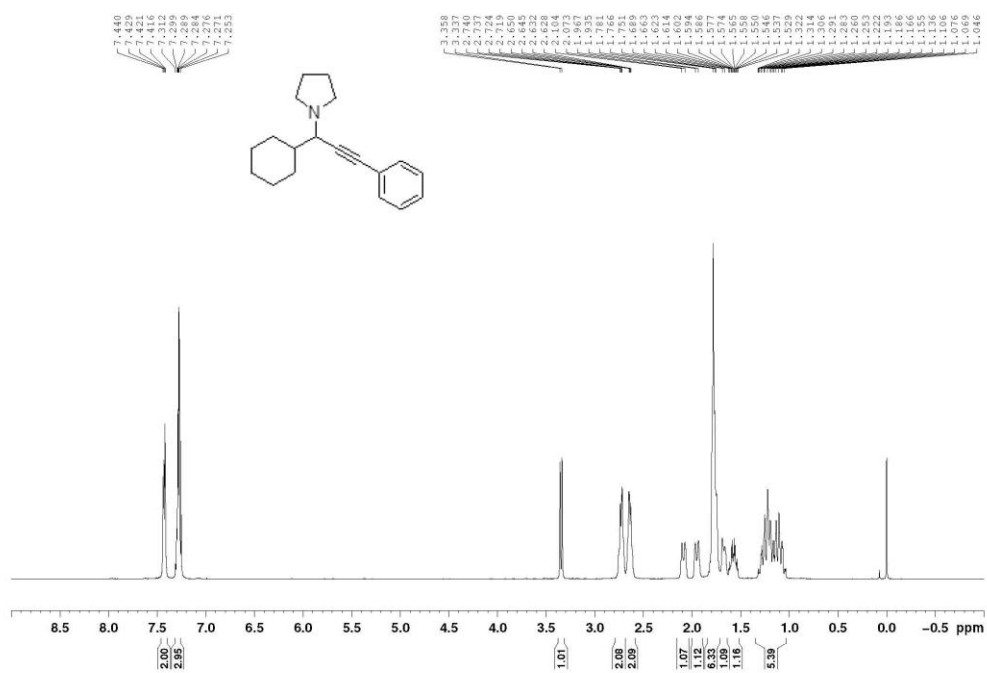
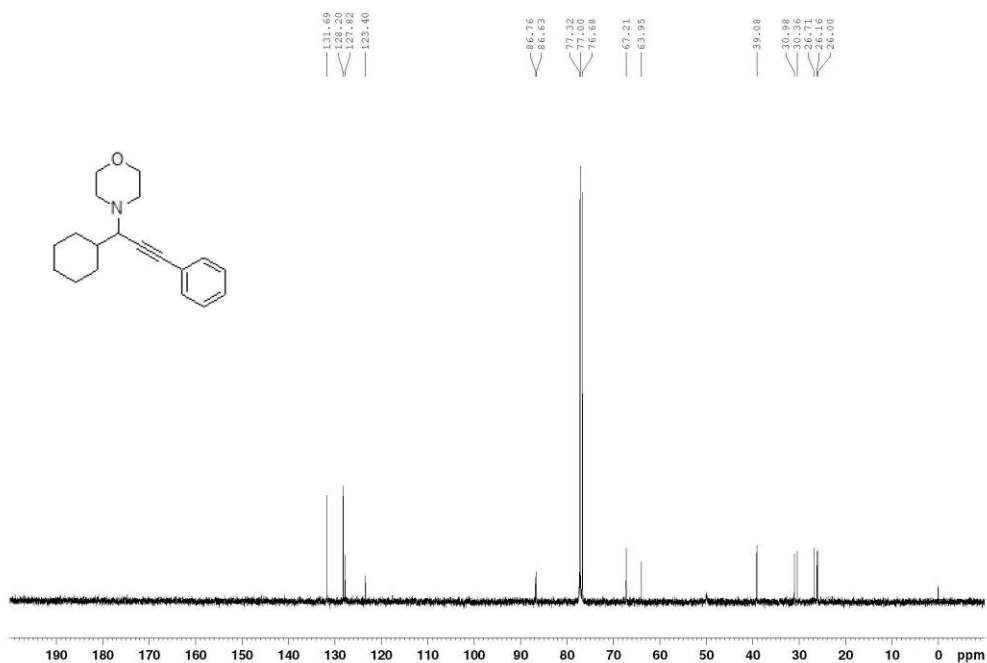












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