Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Zn (II) anchored onto the magnetic natural hydroxyapatite (Zn^{II}/HAP/Fe_3O_4): as a novel, green and recyclable catalyst for A^3-coupling reaction towards propargylamines synthesis under solvent-free conditions

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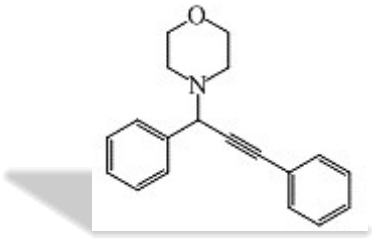
Experimental

General

All chemical reagents and solvents were purchased from Merck and Sigma-Aldrich chemical companies and were used as received without further purification. The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The FT-IR spectra were obtained using an AVATAR 370 FT-IR spectrometer (Therma Nicolet spectrometer, USA) using liquid films (neat) on NaCl Plates at room temperature in the range between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}. The NMR spectra were obtained in Brucker Avance 300 MHz instruments in $CDCl_3$. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization, in *m/z* (rel %). Elemental analysis was performed using a Thermo Finnigan Flash EA 1112 Series instrument. All yields refer to isolated products after purification by thin layer chromatography.

4-(1,3-diphenylprop-2-yn-1-yl)morpholine (**4a**).[1] Oily light liquid; isolated yield: 95%; FT-IR (neat): ν_{max}/cm^{-1} 3084, 3060, 3030, 2956, 2924, 2853, 2821, 2222, 2107, 1598, 1490, 1450, 1002, 915, 756; ^1H NMR (300 MHz, $CDCl_3$): δ 7.55-7.52 (2H, m, Ph), 7.43-7.40 (2H, m, Ph), 7.29-7.20 (6H, m, Ph), 4.69 (1H, s, CH), 3.62 (4H, br, $2CH_2$), 2.53 (4H, br, $2CH_2$);^{13}C NMR (75 MHz, $CDCl_3$): δ 137.8, 131.8, 128.6, 128.3, 128.2, 127.8, 123.0, 88.5, 85.1, 67.2, 62.0, 49.9, 29.7; MS, *m/z* (%): 277(7%, M^+), 191(74 %, M^+-morpholine), 86(78%, morpholine).



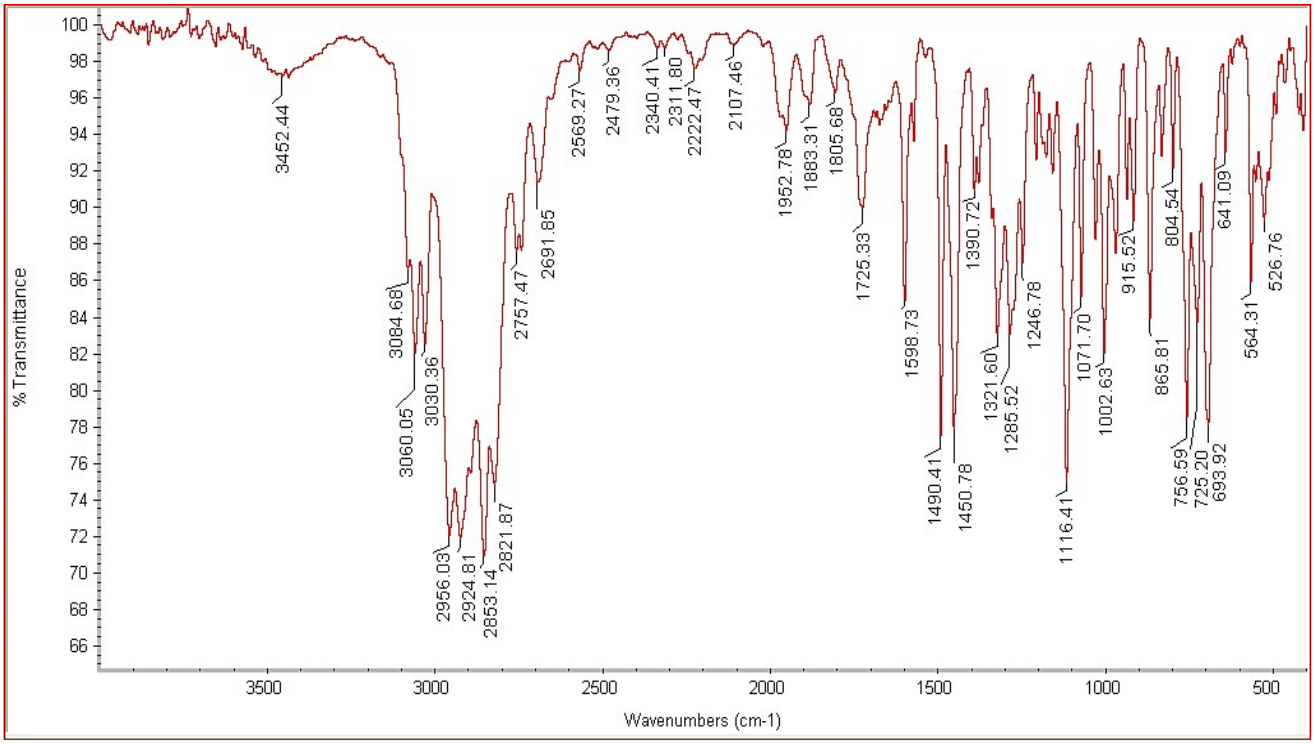


Figure 1: FT-IR (neat) spectrum 4-(1, 3-diphenylprop-2-yn-1-yl) morpholine (**4a**).

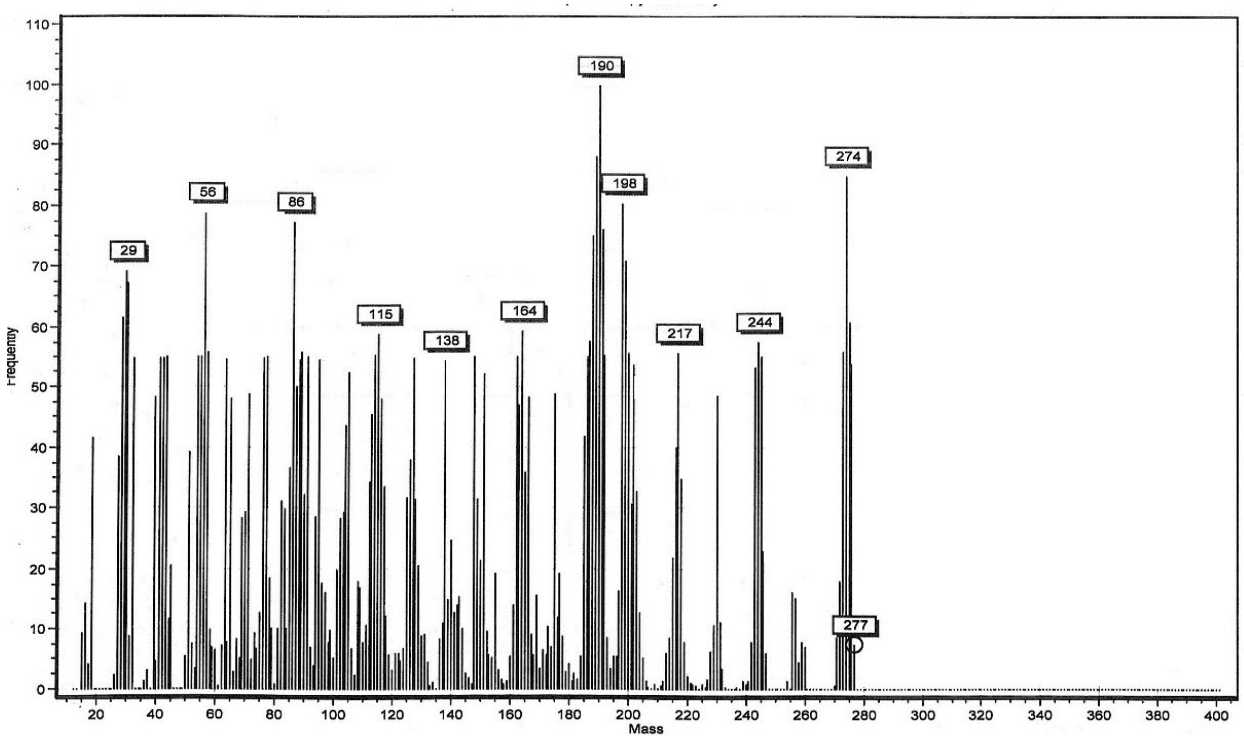


Figure 2: Mass spectrum of 4-(1, 3-diphenylprop-2-yn-1-yl) morpholine (**4a**).

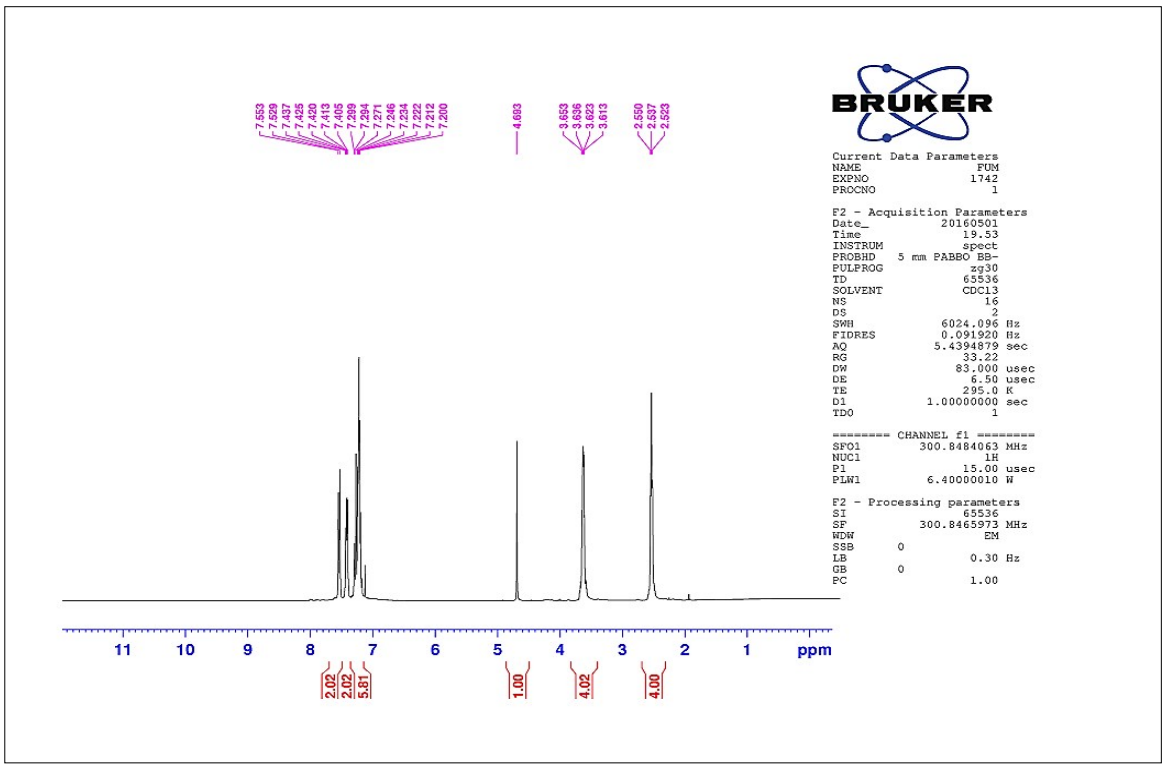


Figure 3: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-(1, 3-diphenylprop-2-yn-1-yl) morpholine(**4a**).

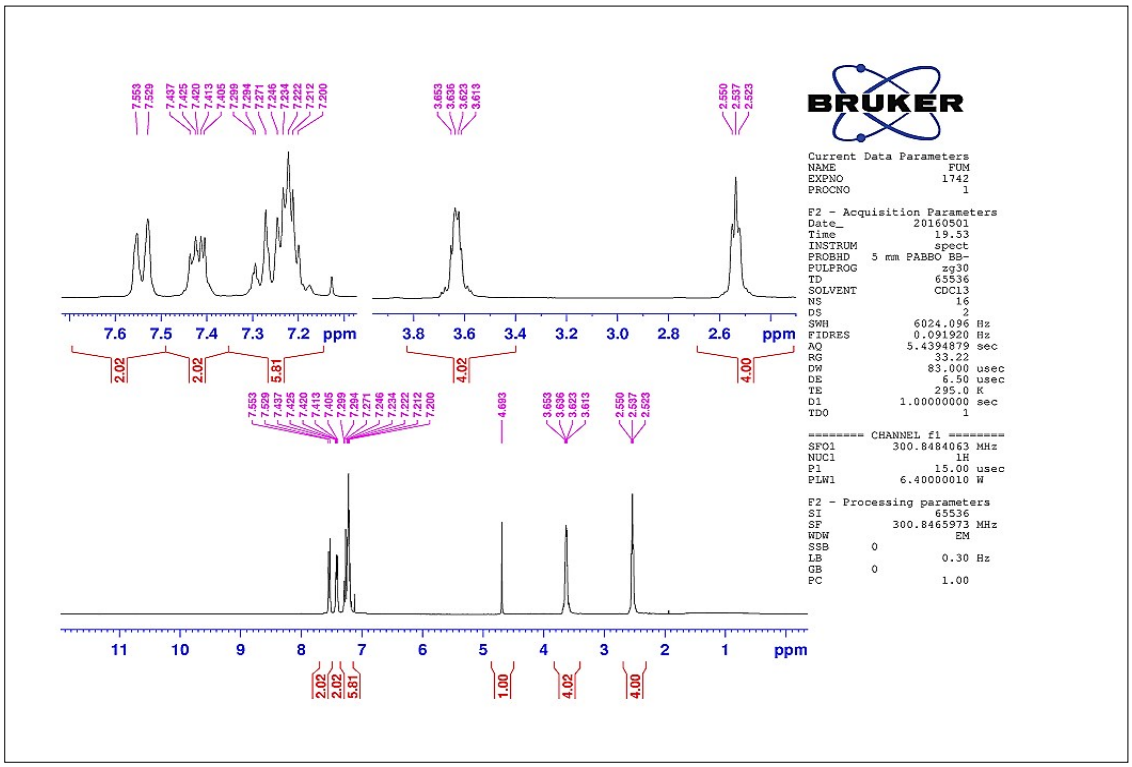


Figure 4: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-(1, 3-diphenylprop-2-yn-1-yl) morpholine (**4a**) expanded.

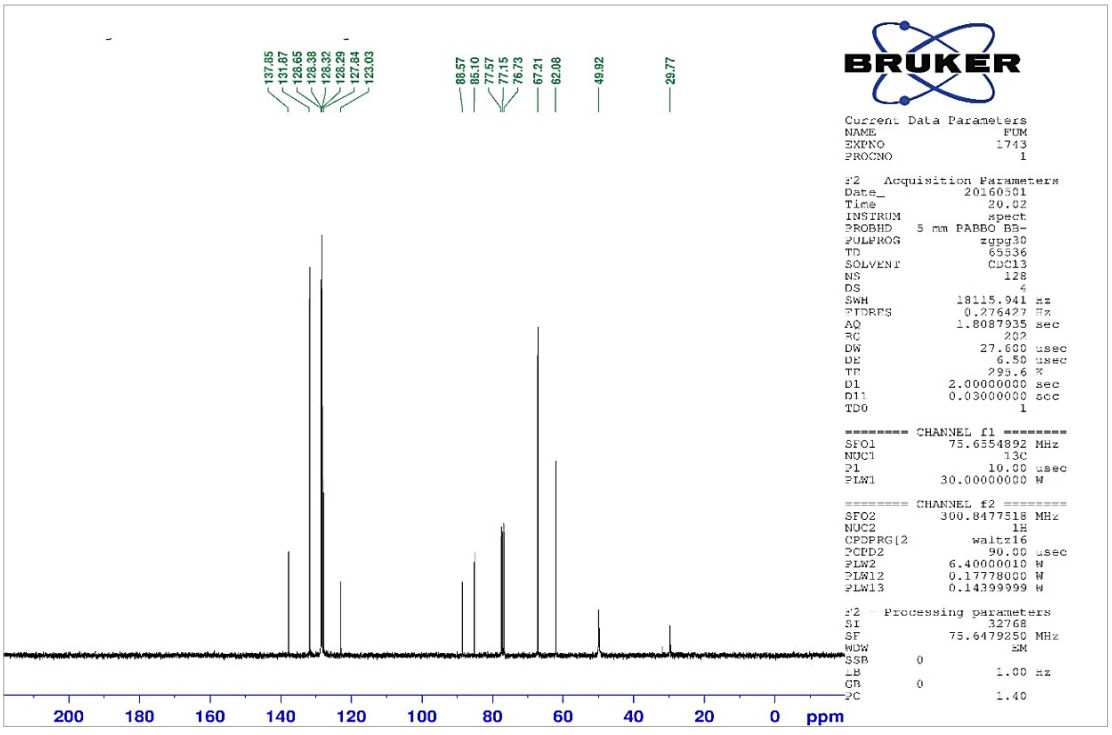
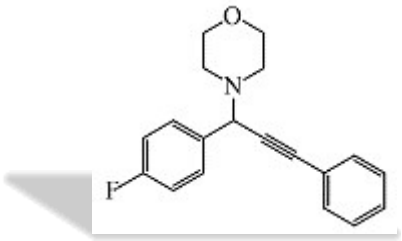


Figure 5: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 4-(1, 3-diphenylprop-2-yn-1-yl)morpholine (**4a**).

4-(1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl)morpholine (**4b**).[2a] Oily brown liquid; isolated yield: 80%; MS, *m/z* (%): 295(7%, M^+), 209(68%, M^+-morpholine), 86(65%, morpholine).



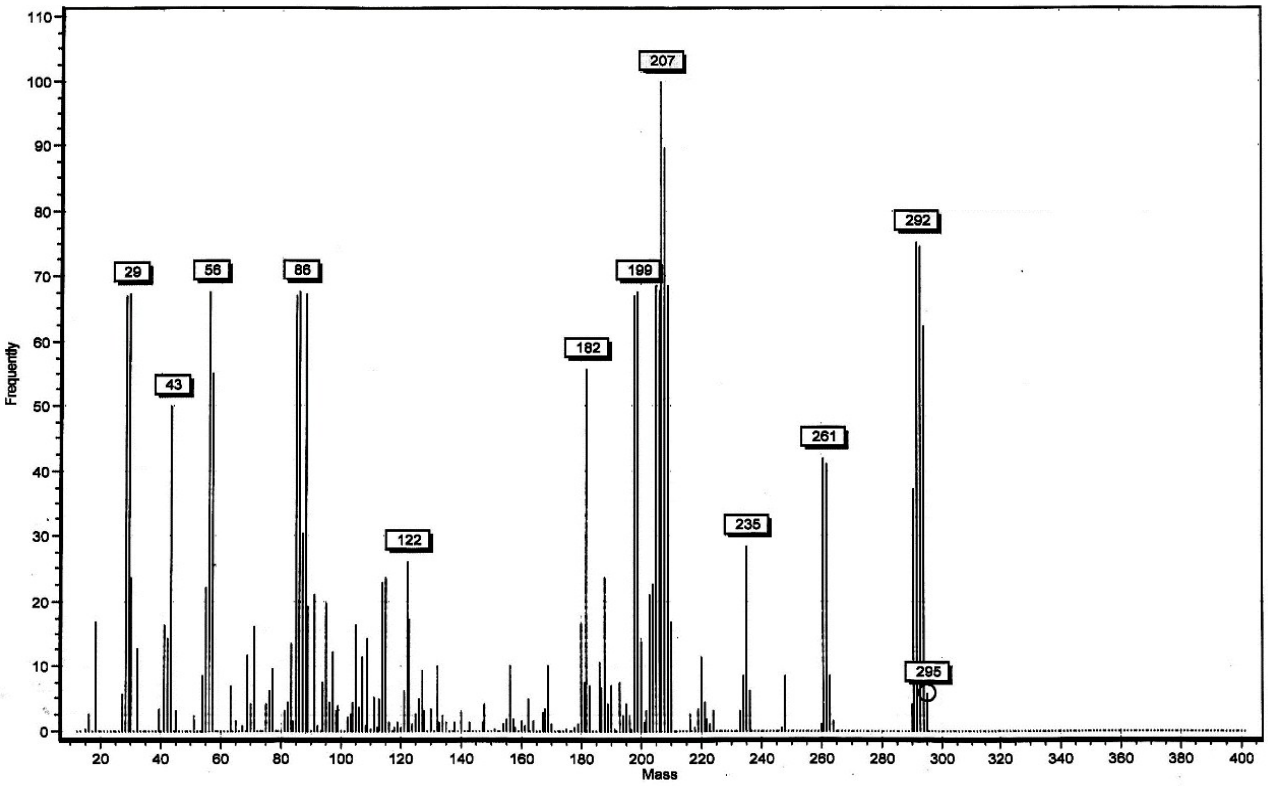
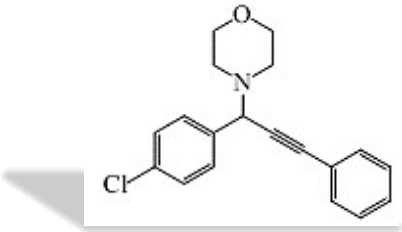


Figure 6: Mass spectrum of 4-(1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl) morpholine (**4b**).

4-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)morpholine (**4c**).[2b] Oily light liquid; isolated yield: 90 %; MS, *m/z* (%): 312(7%, M^+), 226(72%, M^+-morpholine), 111(74%, C_6H_4Cl).



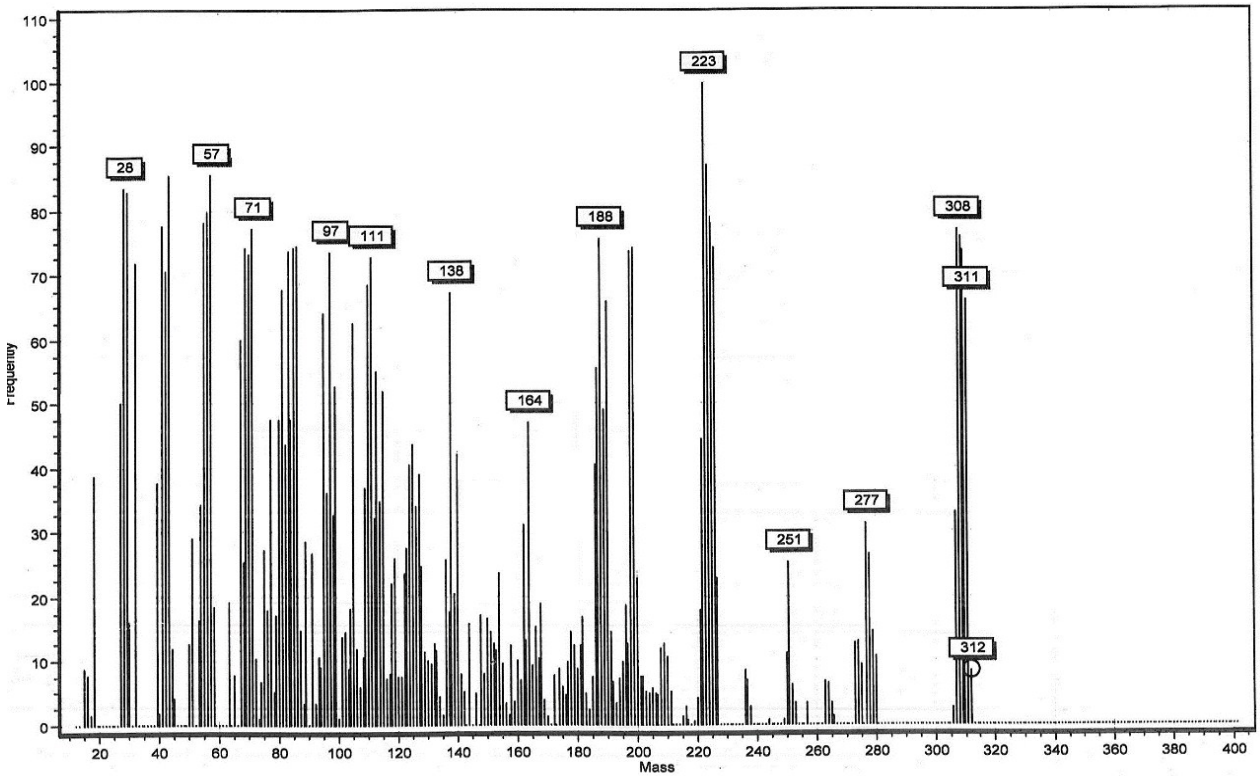
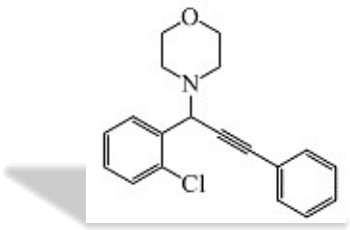


Figure 7: Mass spectrum of 4-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl) morpholine (**4c**).

4-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl)morpholine (**4d**).[2b] Oily light liquid; isolated yield: 90 %; MS, *m/z* (%): 312(4%, M^+), 226(28%, M^+-morpholine), 111(54%, C_6H_4Cl), 58(22%, C_3H_6O).



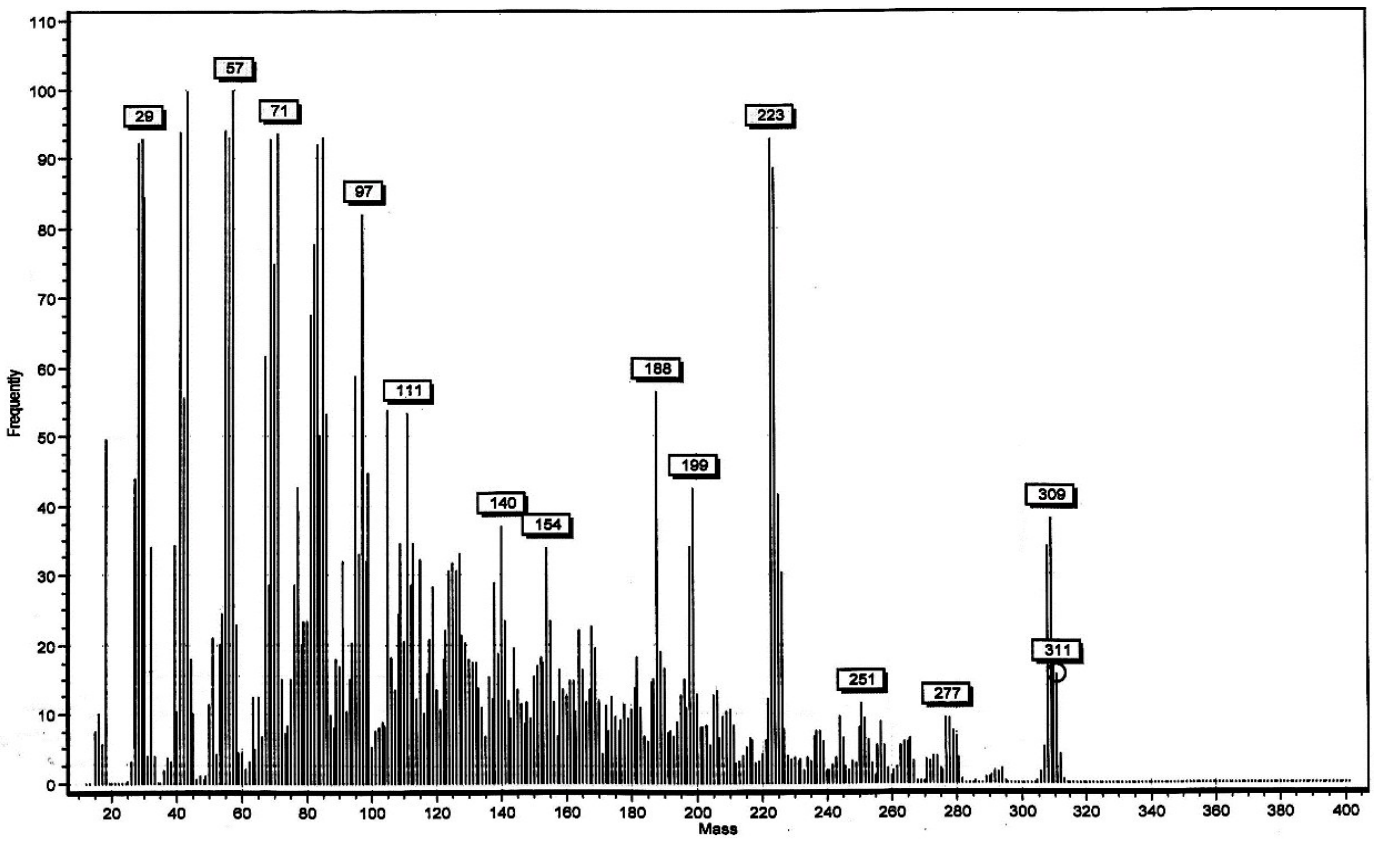
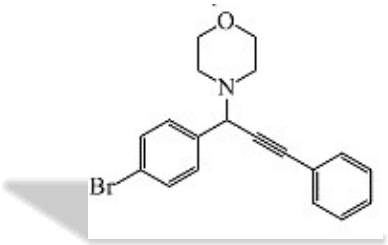


Figure 8: Mass spectrum of 4-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) morpholine (**4d**).

4-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl)morpholine (**4e**).[2b] Oily yellow liquid; isolated yield: 90 %; FT-IR (neat): ν_{max}/cm^{-1} 3056, 2953, 2923, 2853, 2197, 2103, 1598, 1487, 1453, 1005, 971, 756; MS, *m/z* (%): 355(22%, M^+), 269(62%, M^+-morpholine), 28(100%, C_2H_4).



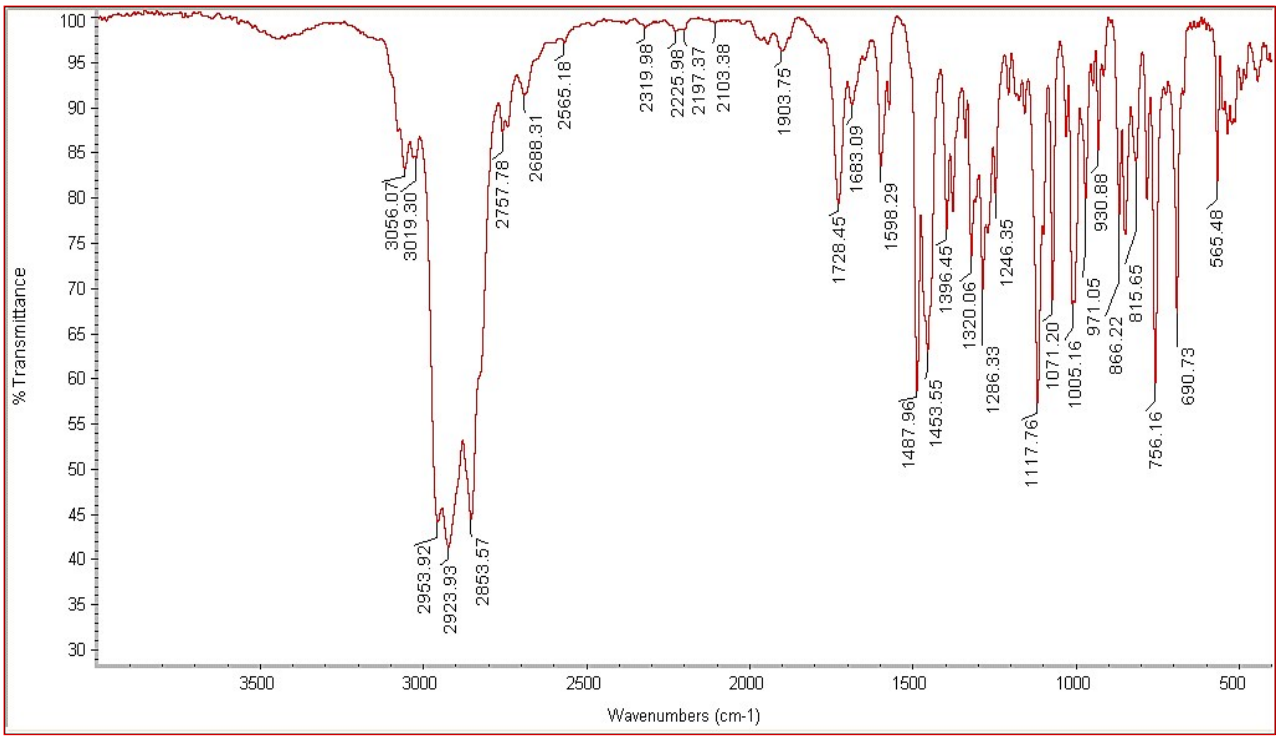


Figure 9: FT-IR (neat) spectrum of 4-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl) morpholine (**4e**).

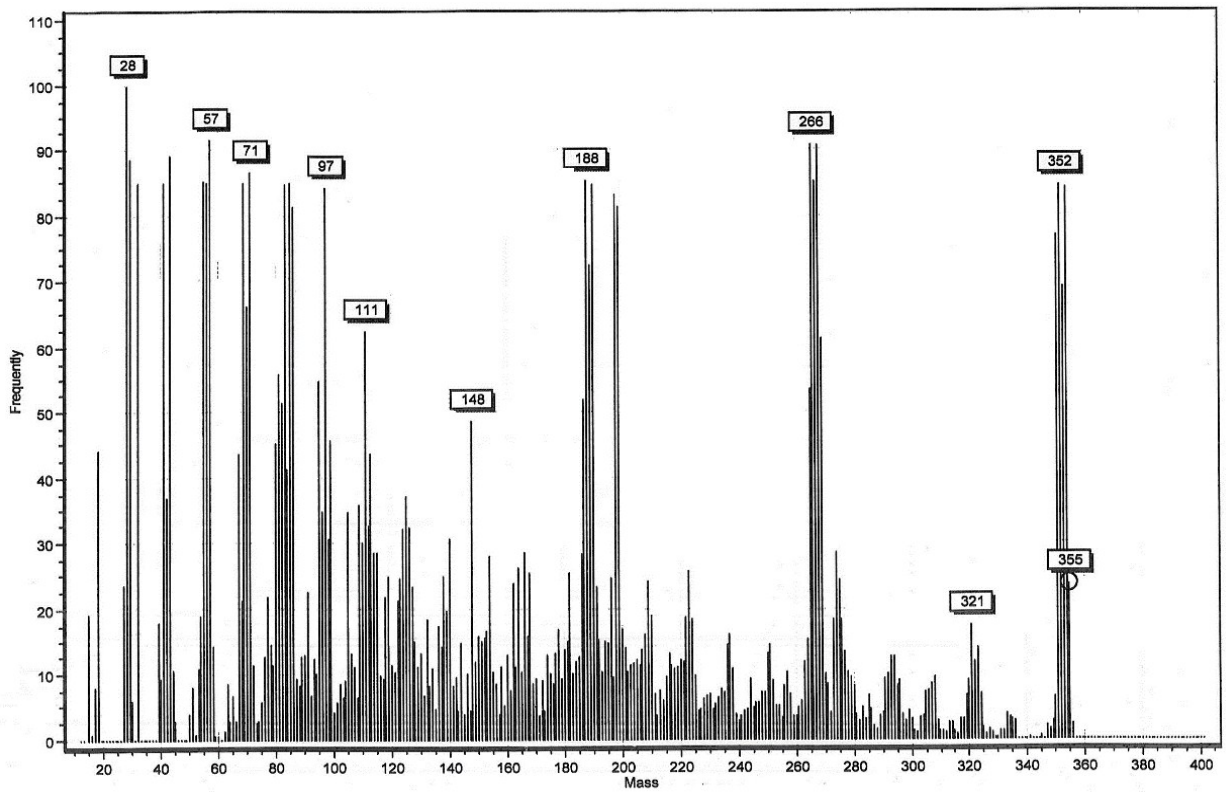
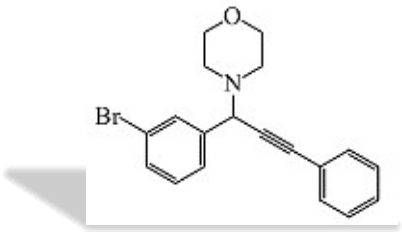


Figure 10: Mass spectrum of 4-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl) morpholine (**4e**).

4-(1-(3-bromophenyl)-3-phenylprop-2-yn-1-yl)morpholine (**4f**).[2a] Oily light liquid; isolated yield: 85 %; MS, *m/z* (%): 355(54%, M^+), 270(98%, M^+-morpholine), 201(8%, M^+-C_6H_4Br), 86(95%, morpholine).



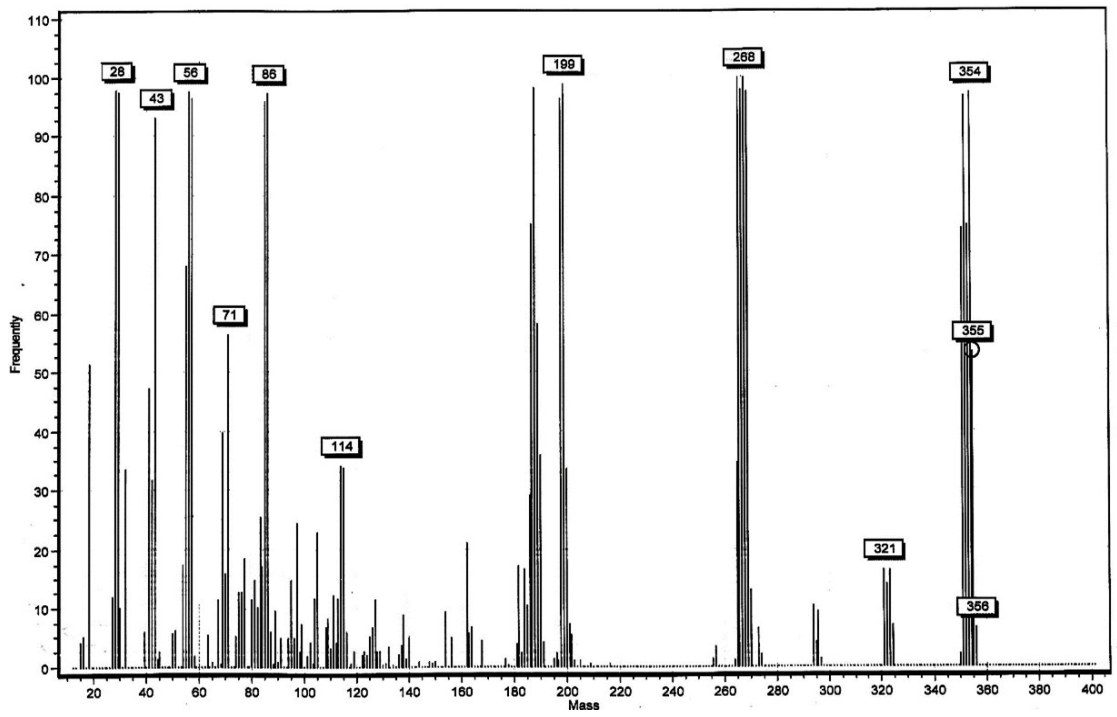
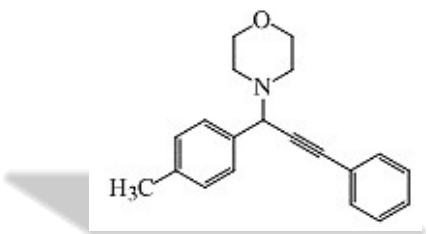


Figure 11: Mass spectrum of 4-(1-(3-bromophenyl)-3-phenylprop-2-yn-1-yl) morpholine (**4f**).

4-(3-phenyl-1-(*p*-tolyl)prop-2-yn-1-yl)morpholine (**4g**).[2b] Oily light liquid; isolated yield: 97%; MS, *m/z* (%): 291(8%, M^+), 205(68%, M^+-morpholine), 86(64%, morpholine).



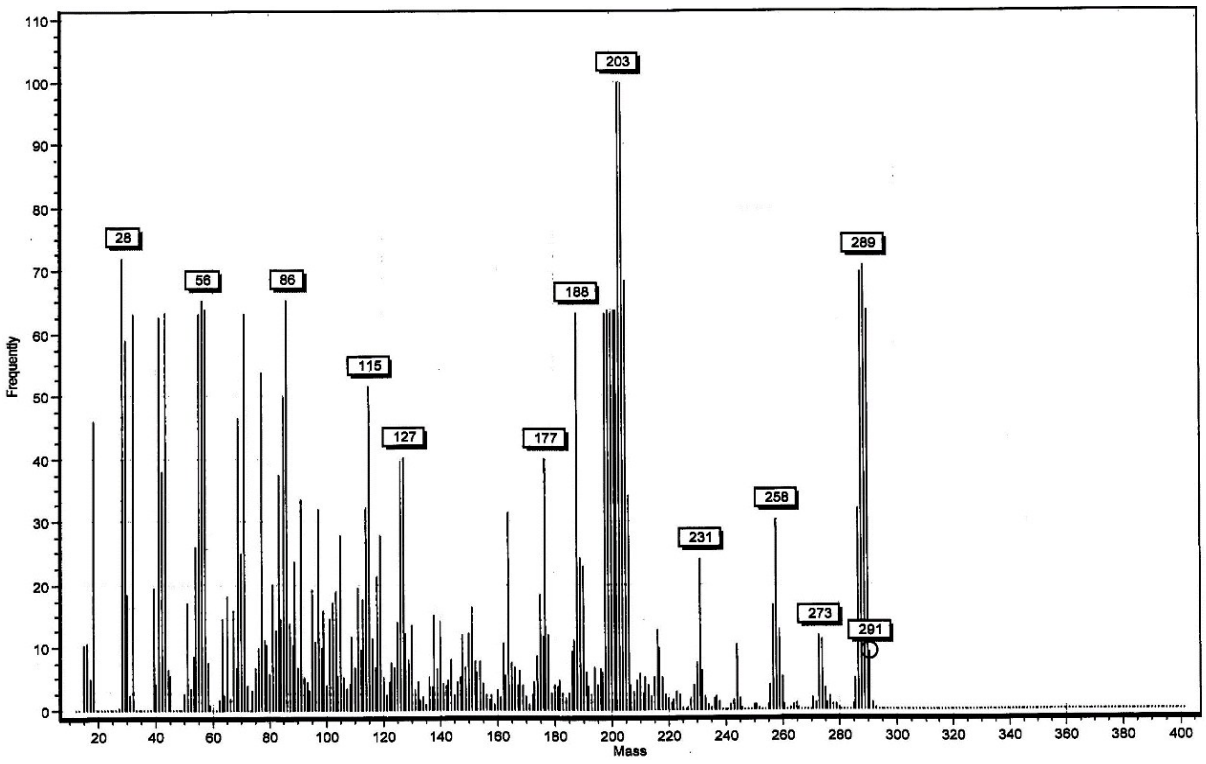
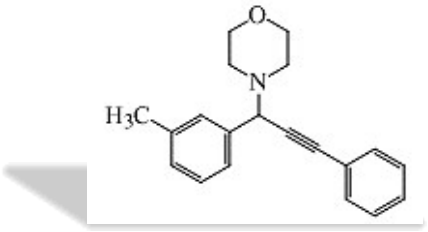


Figure 12: Mass spectrum of 4-(3-phenyl-1-(*p*-tolyl) prop-2-yn-1-yl) morpholine (**4g**).

4-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1-yl)morpholine (**4h**). Oily yellow liquid; isolated yield: 95%; FT-IR (neat): ν_{max}/cm^{-1} 3053, 3023, 2958, 2924, 2853, 2819, 2226, 1598, 1489, 1452, 1001, 756; ^1H NMR (300 MHz, $CDCl_3$): δ 7.69-7.49 (4H, m, Ph), 7.39-7.37 (3H, m, Ph), 7.30 (1H, t, *J*= 7.5 Hz, Ph), 7.19-7.16 (1H, m, Ph), 4.80 (1H, s, CH), 3.81 (4H, br, $2CH_2$), 2.76-2.64 (4H, m, $2CH_2$), 2.44 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9, 137.7, 131.8, 129.3, 128.6, 128.3, 128.2, 128.1, 125.7, 123.1, 88.3, 85.3, 67.1, 62.1, 50.0, 21.5; MS, *m/z* (%): 291(3%, M^+), 205(85%, M^+-morpholine), 200(60%, M^+- C_7H_7), 86(68%, morpholine); Anal. Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81, Found: C, 81.45; H, 7.32; N, 3.89 %.



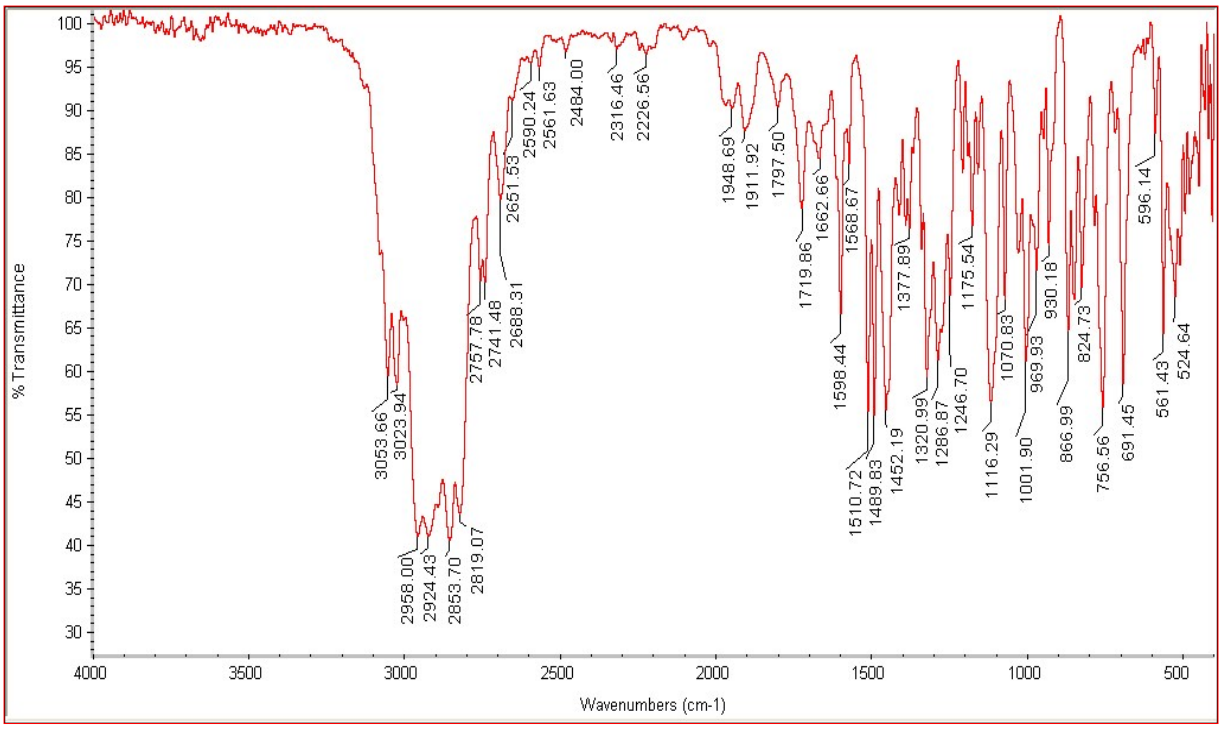


Figure 13: FT-IR (neat) spectrum of 4-(3-phenyl-1-(*m*-tolyl)prop-2-yn-1-yl)morpholine (**4h**).

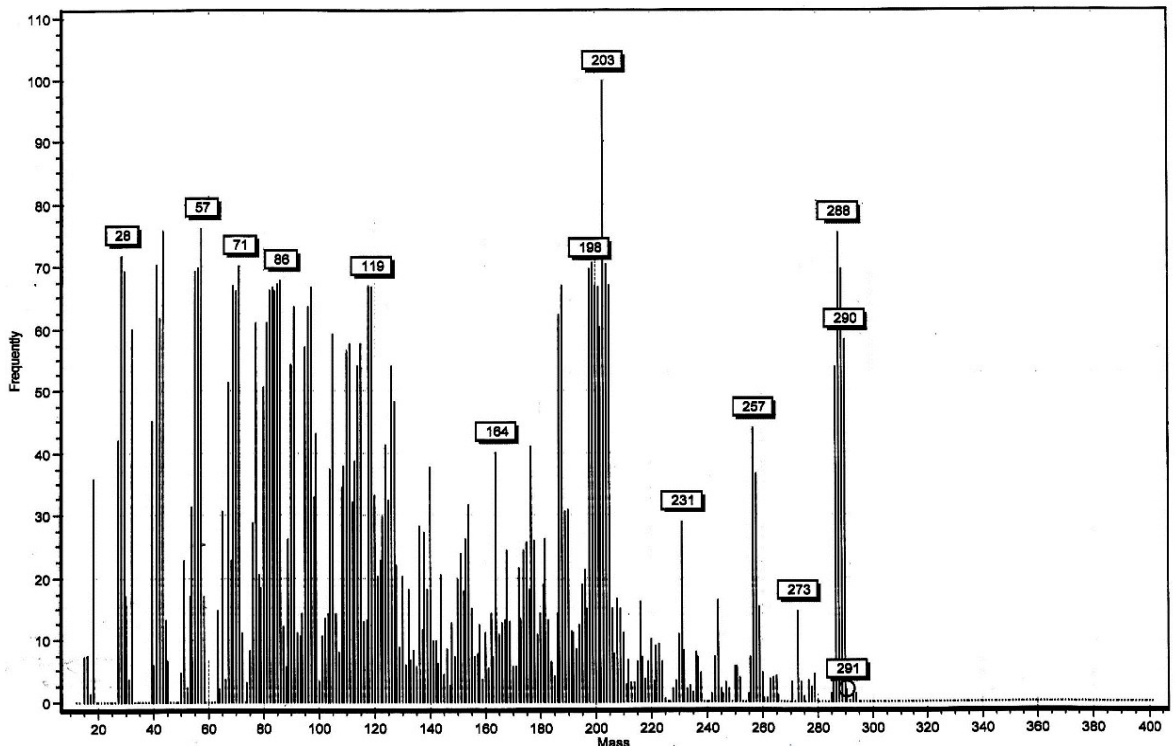


Figure 14: Mass spectrum of 4-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1-yl) morpholine (**4h**).

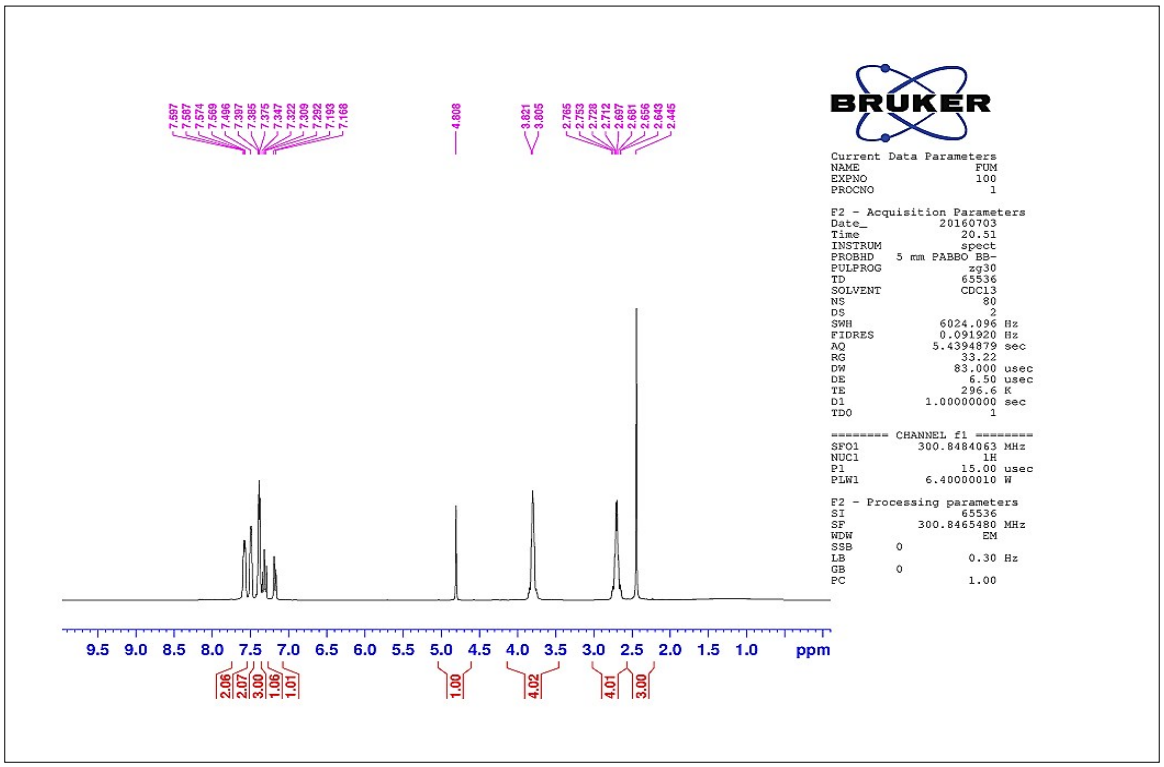


Figure 15: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1-yl) morpholine (**4h**).

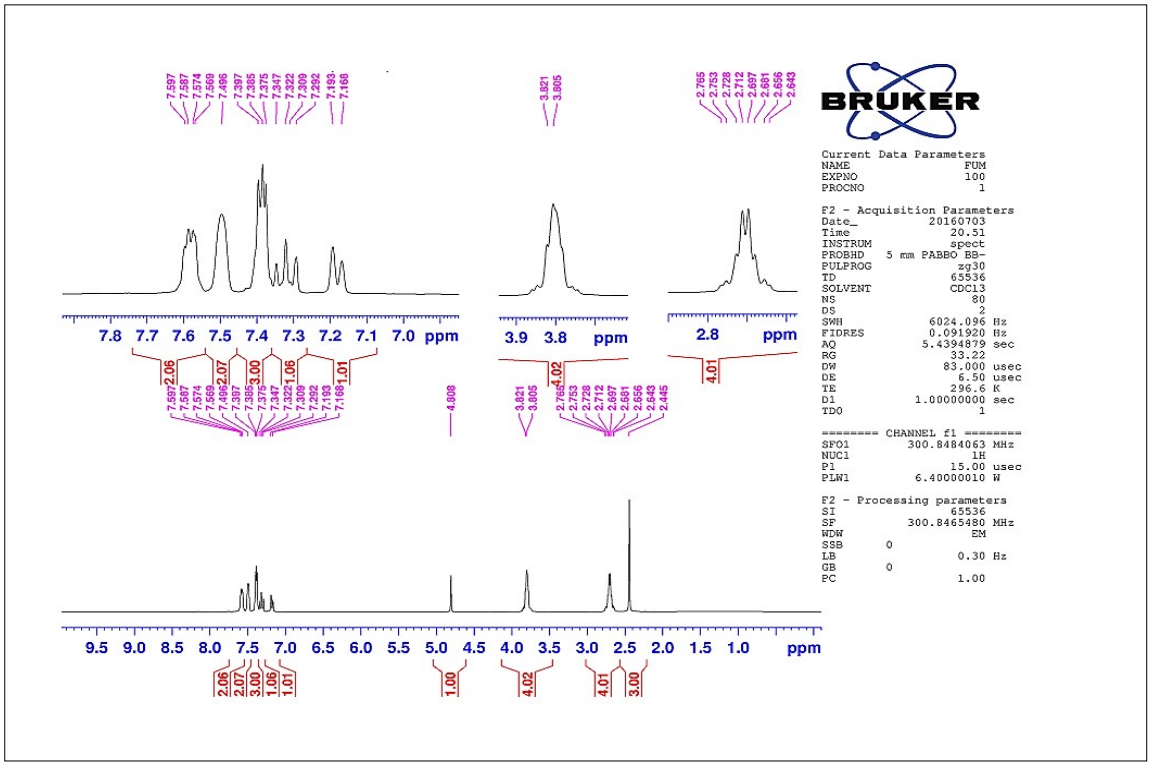


Figure 16: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1 yl)morpholine (**4h**) expanded.

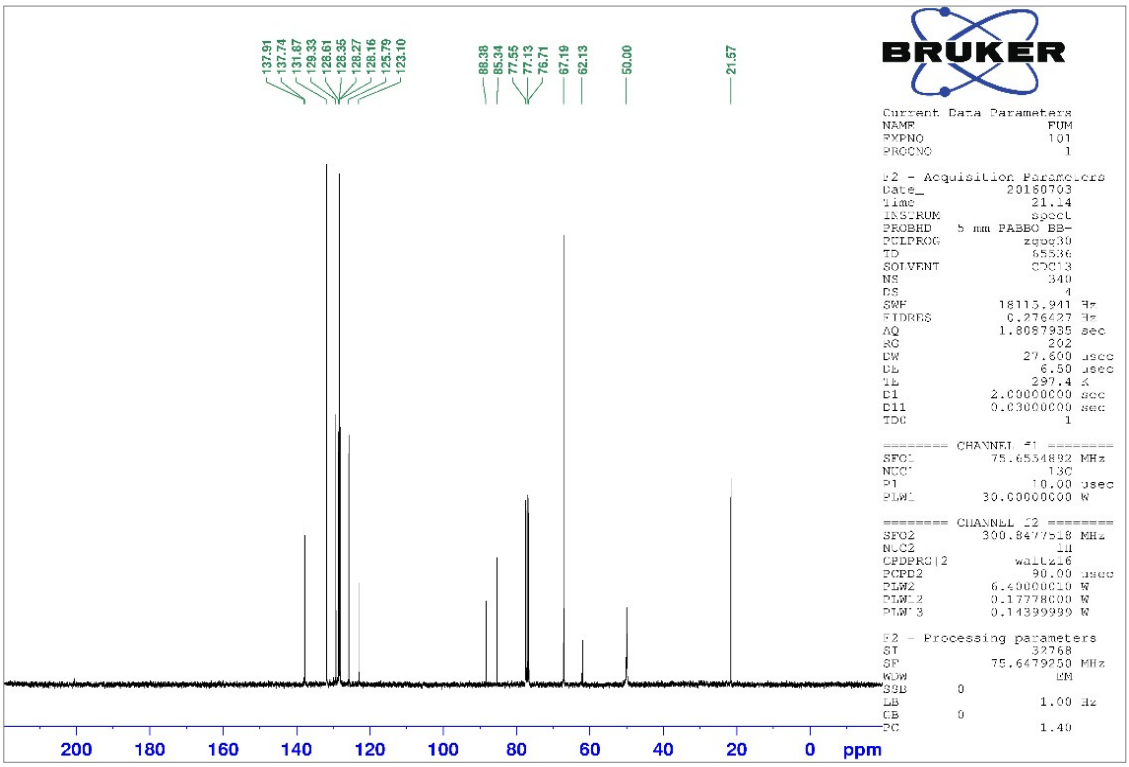
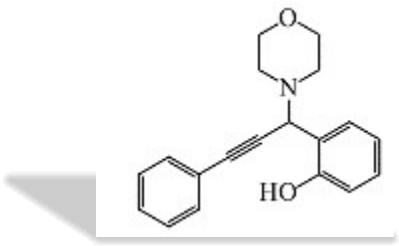


Figure 17: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 4-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1-yl) morpholine (**4h**).

2-(1-morpholino-3-phenylprop-2-yn-1-yl)phenol (**4i**).[2c] Oily light liquid; isolated yield: 90%; ^1H NMR (300 MHz, $CDCl_3$): δ 10.78 (1H, s, OH), 7.49-7.44 (3H, m, Ph), 7.29-7.25 (3H, m, Ph), 7.13 (1H, t, J = 7.2 Hz, Ph), 6.81-6.77 (2H, m, Ph), 4.99 (1H, s, CH), 3.70 (4H, br, $2CH_2$), 2.68 (4H, br, $2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.0, 131.9, 129.8, 128.8, 128.4, 122.3, 120.5, 119.4, 116.5, 90.4, 81.6, 66.9, 60.7; MS, *m/z* (%): 294(4%, M^+), 208(20%, M^+-morpholine), 86(80%, morpholine).



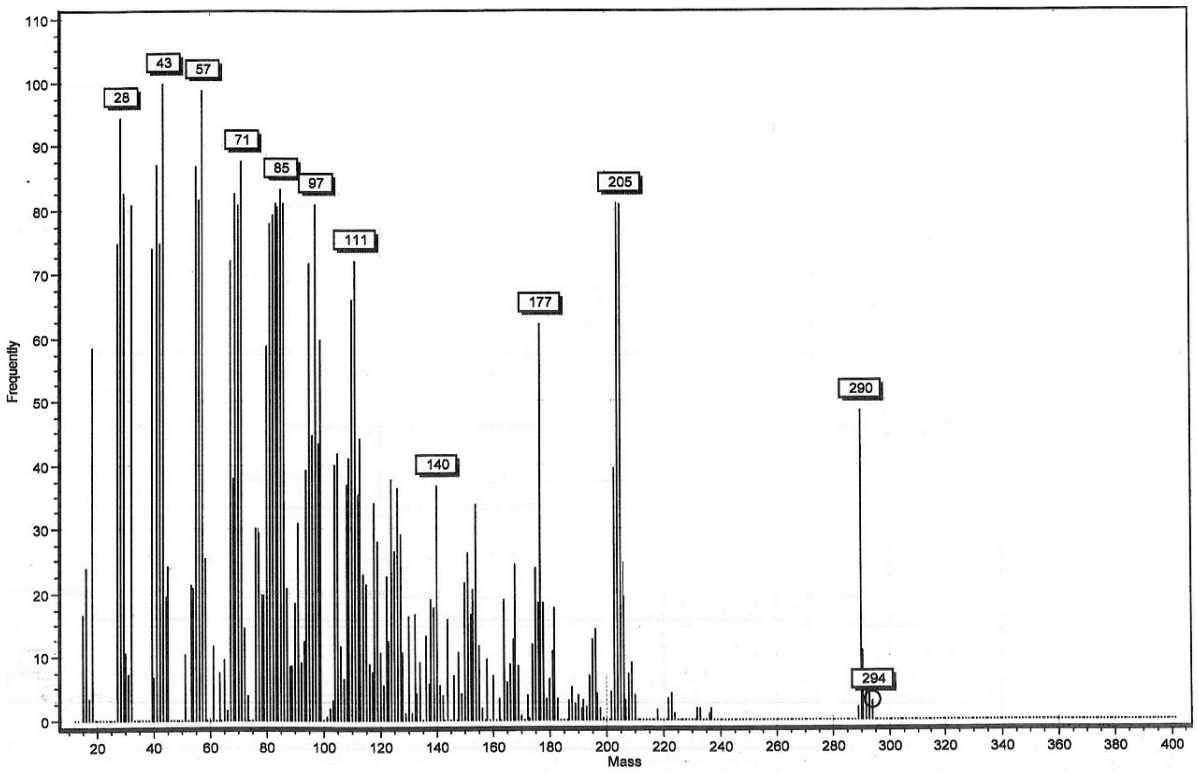


Figure 18: Mass spectrum of 2-(1-morpholino-3-phenylprop-2-yn-1-yl) phenol (**4i**).

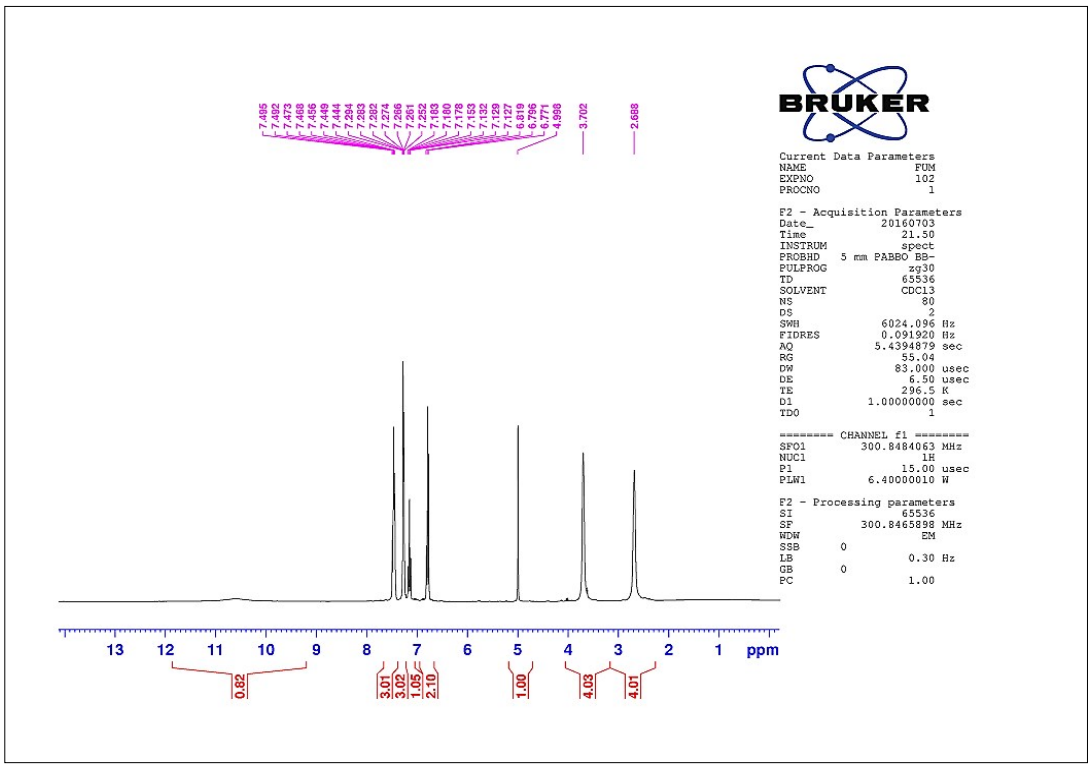


Figure 19: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 2-(1-morpholino-3-phenylprop-2-yn-1yl)phenol (**4i**).

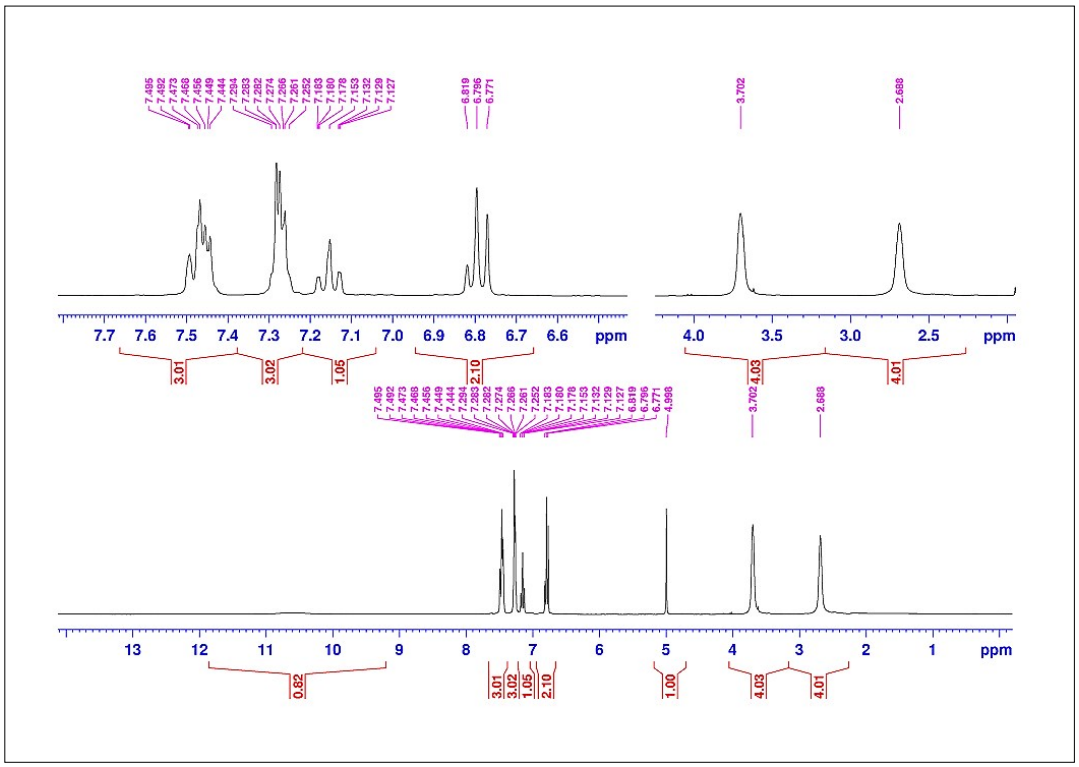


Figure 20: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 2-(1-morpholino-3-phenylprop-2-yn-1-yl) phenol (**4i**) expanded.

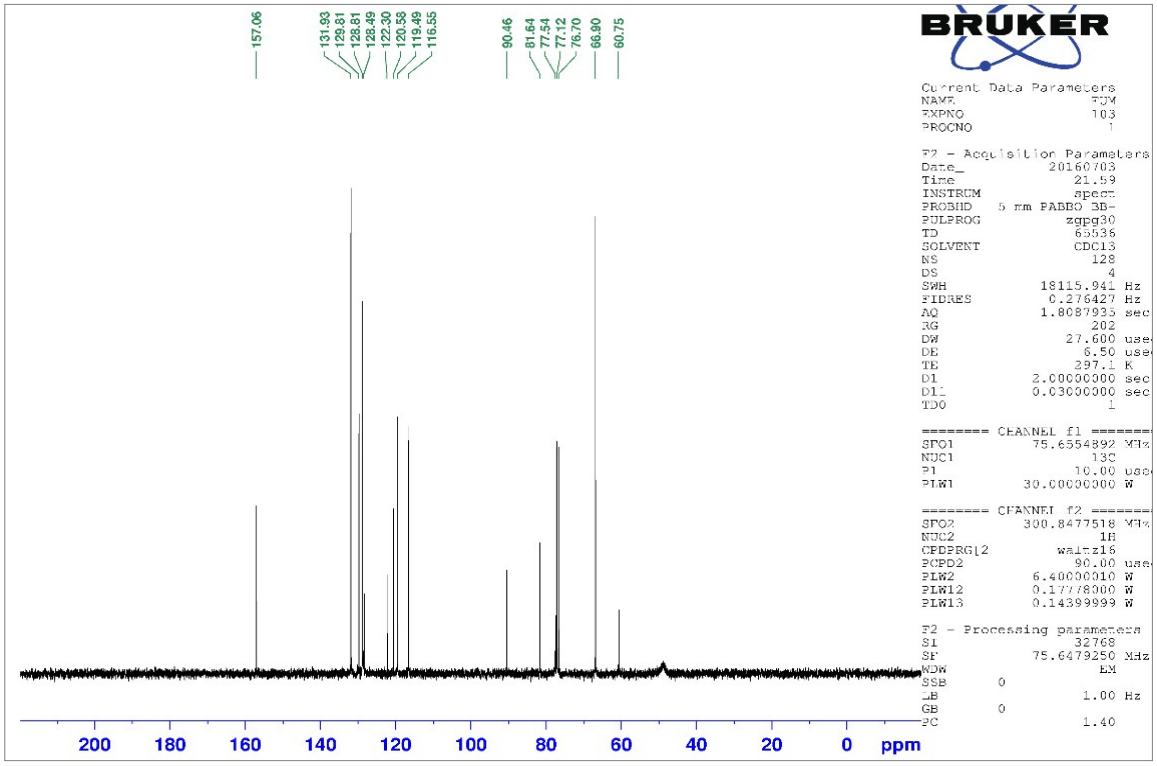


Figure 21: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 2-(1-morpholino-3-phenylprop-2-yn-1-yl) phenol (**4i**).

4-(1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-yl)morpholine (**4j**).[2b] Oily light liquid; isolated yield: 95 %; MS, *m/z* (%): 307(4%, M^+), 221(78%, M^+-morpholine), 86(23%, morpholine).

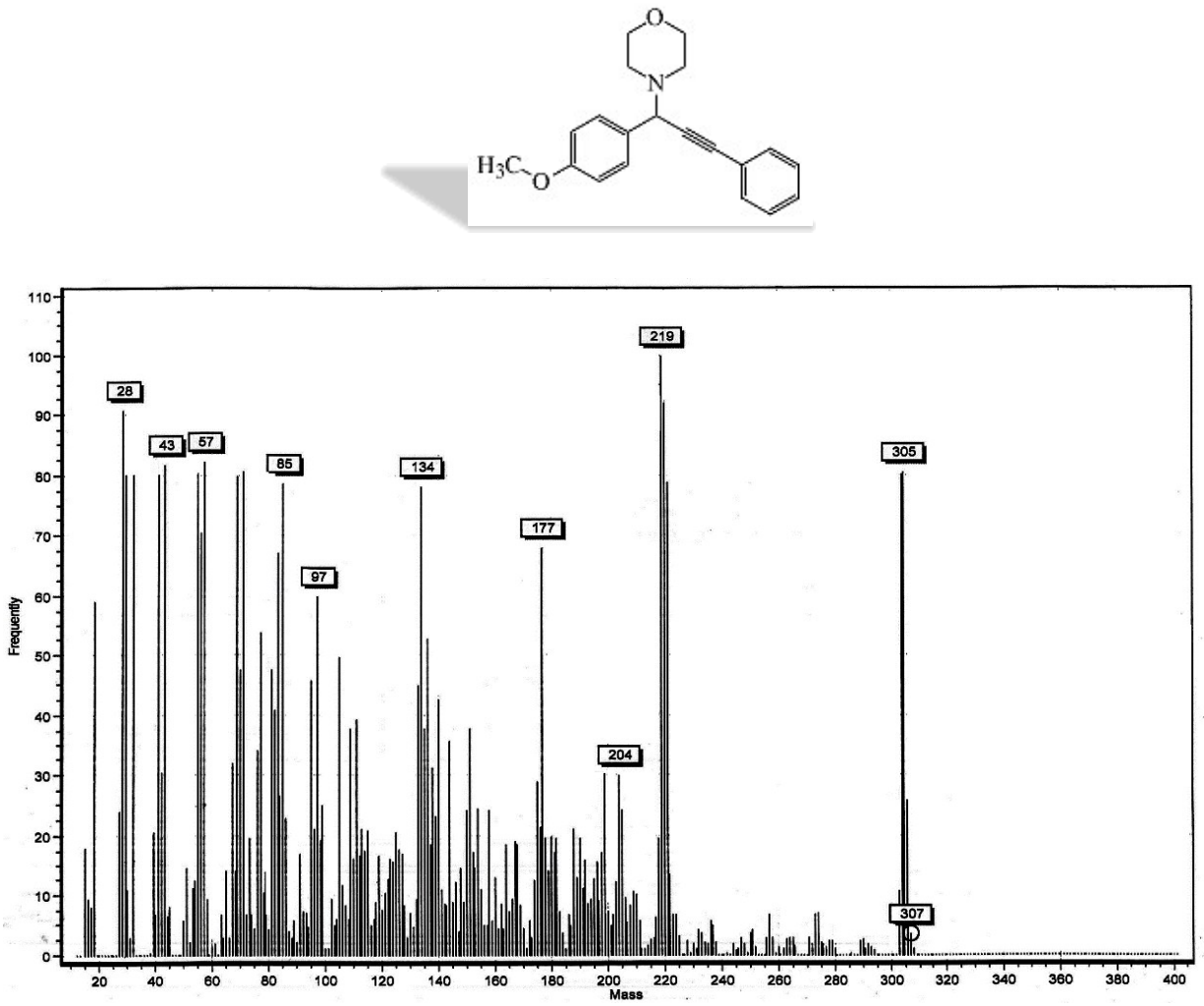


Figure 22: Mass spectrum of 4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl) morpholine (**4j**).

4-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl)morpholine (**4k**).[3a] Oily light liquid; isolated yield: 65 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (1H, d, *J* = 8.1 Hz, Ph), 7.83-7.71 (3H, m, Ph), 7.47-7.33 (5H, m, Ph), 7.24-7.21 (3H, m, Ph), 5.34 (1H, s, CH), 3.63-3.51 (4H, m, $2CH_2$), 2.64-2.56 (4H, m, $2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.1, 133.2, 131.8, 131.7, 128.9, 128.5, 128.3, 128.2, 127.1, 125.9, 125.7, 124.8, 124.7, 123.0, 89.0, 85.0, 67.2, 60.1, 29.7; MS, *m/z* (%): 327(8%, M^+), 241(68%, M^+- morpholine), 200(19%, M^+-naphthalene), 86(68%, morpholine).

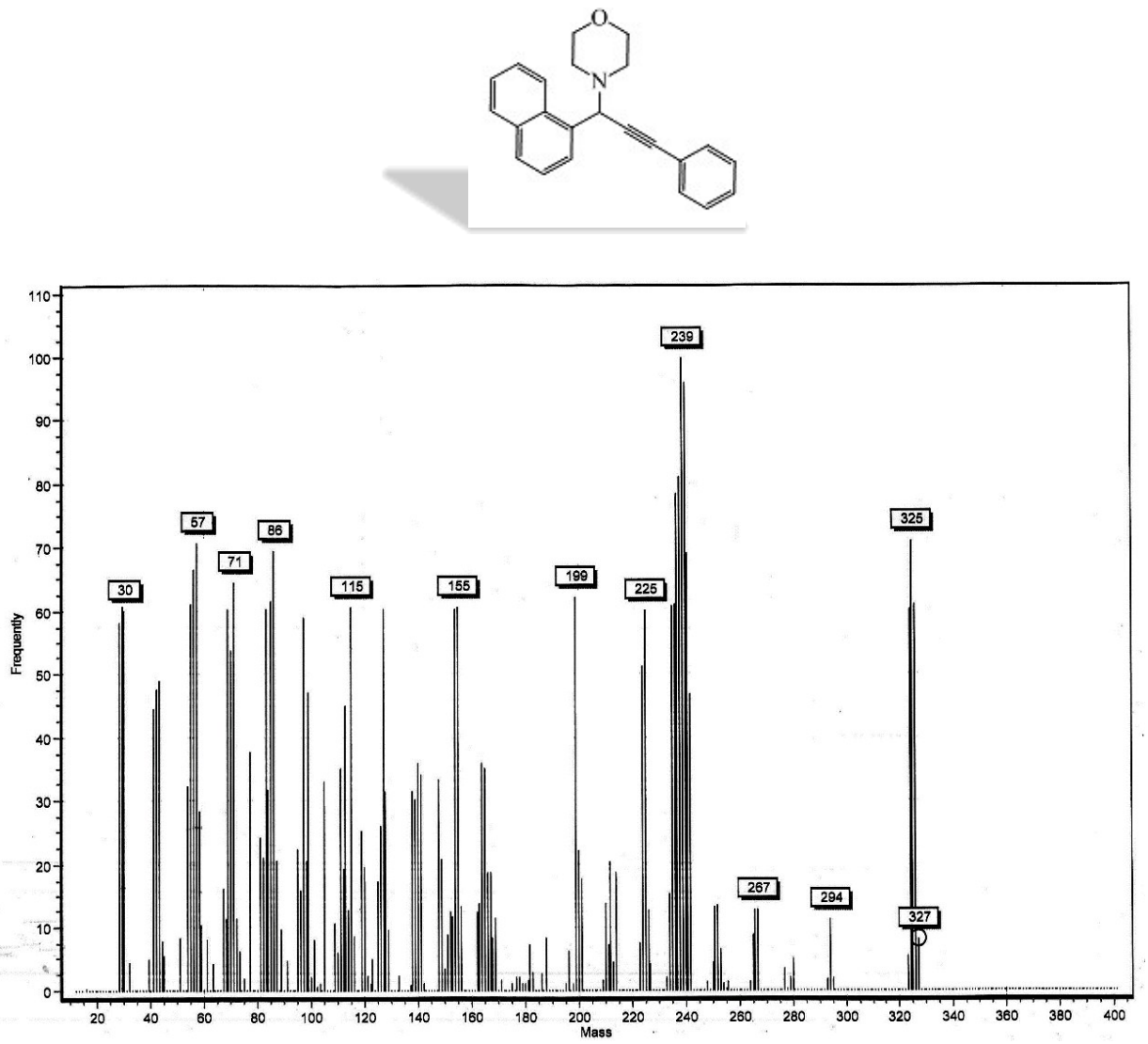


Figure 23: Mass spectrum of 4-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl) morpholine (**4k**).

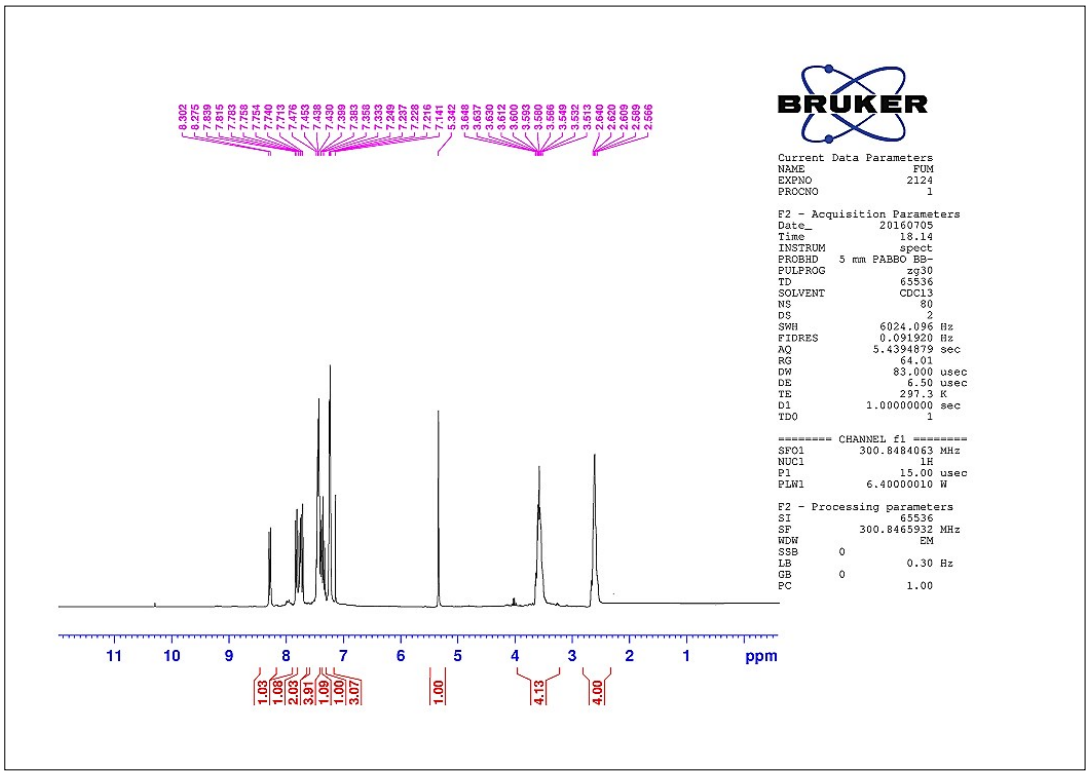


Figure 24: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl) morpholine (**4k**).

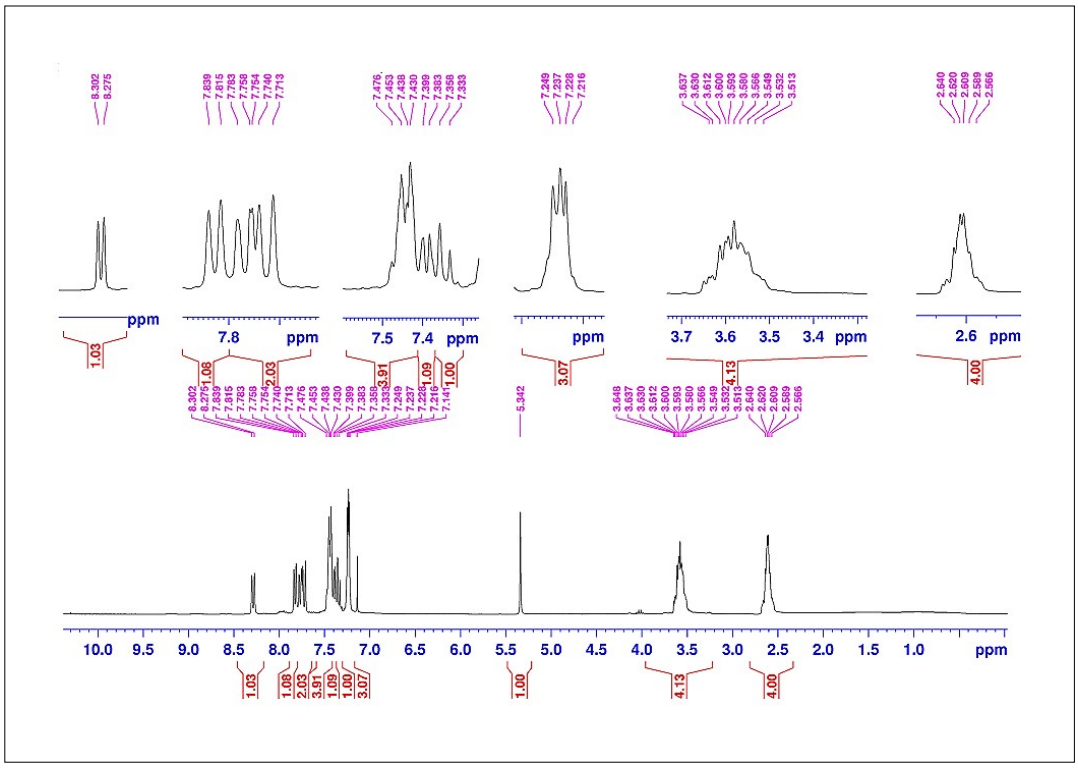
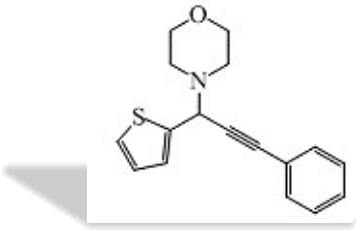


Figure 25: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl) morpholine (**4k**) expanded.

4-(3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-yl)morpholine (**4l**).[3b] Oily brown liquid; isolated yield: 80%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.37 (2H, m, thiophen), 7.33-7.29 (5H, m, Ph), 7.00 (1H, d, *J*= 3.9 Hz, thiophen), 5.03 (1H, s, CH), 3.79 (4H, br, $2CH_2$), 2.72(4H, br, $2CH_2$);^{13}C NMR (75 MHz, $CDCl_3$): δ 142.7, 131.8, 128.4, 128.3, 126.4, 126.3, 125.8, 122.6, 87.6, 84.2, 67.1, 57.8, 49.6; MS, *m/z* (%): 283(11%, M^+), 197(85%, M^+-morpholine), 86(34%, morpholine).



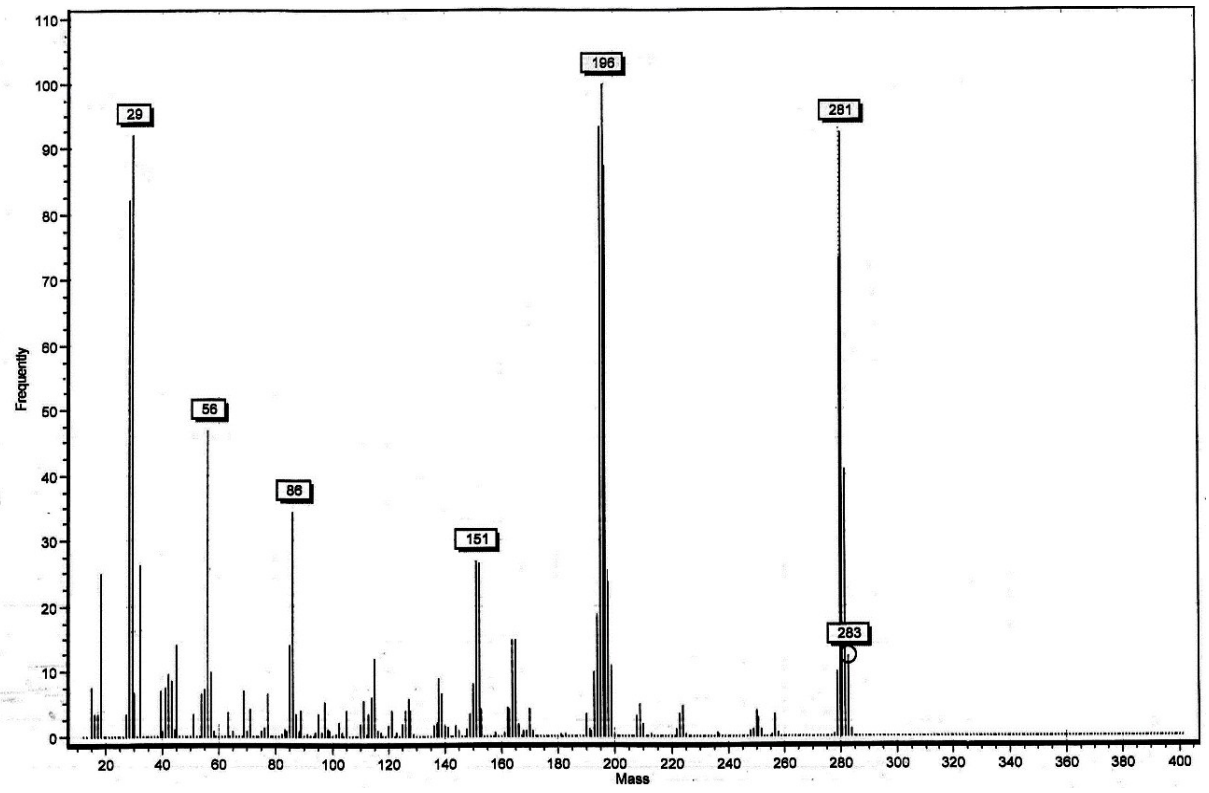


Figure 26: Mass spectrum of 4-(3-phenyl-1-(thiophen-2-yl) prop-2-yn-1-yl) morpholine (**4l**).

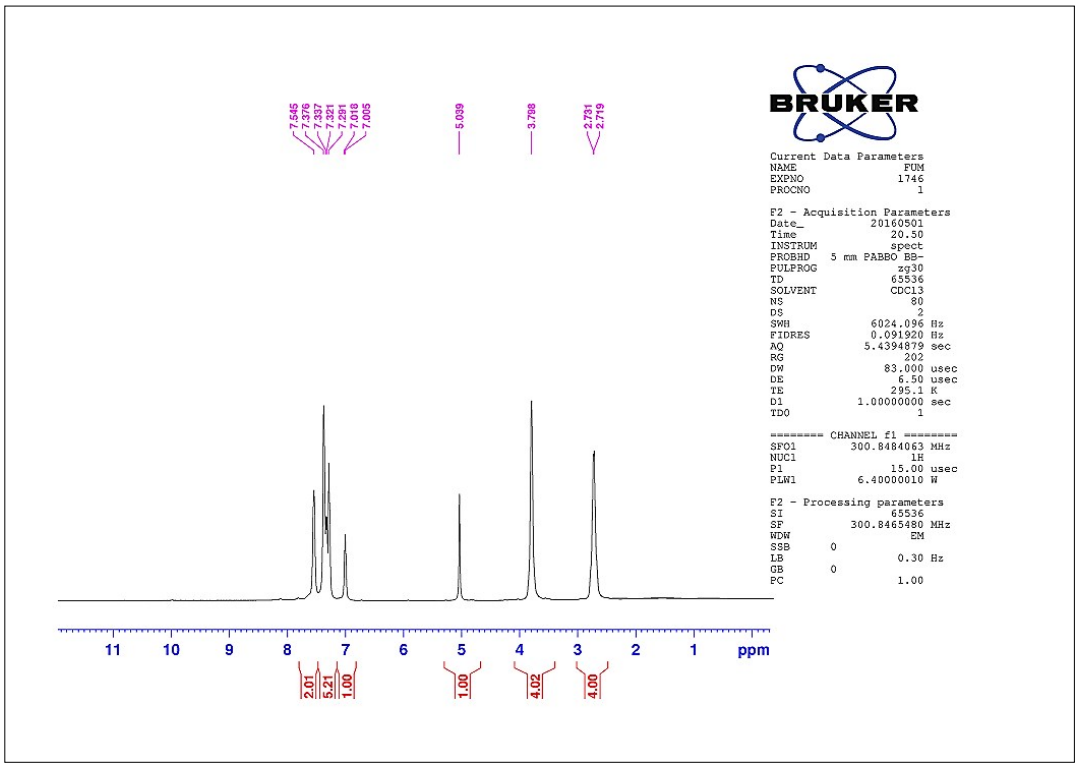


Figure 27: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-(3-phenyl-1-(thiophen-2-yl) prop-2-yn-1-yl) morpholine (**4l**).

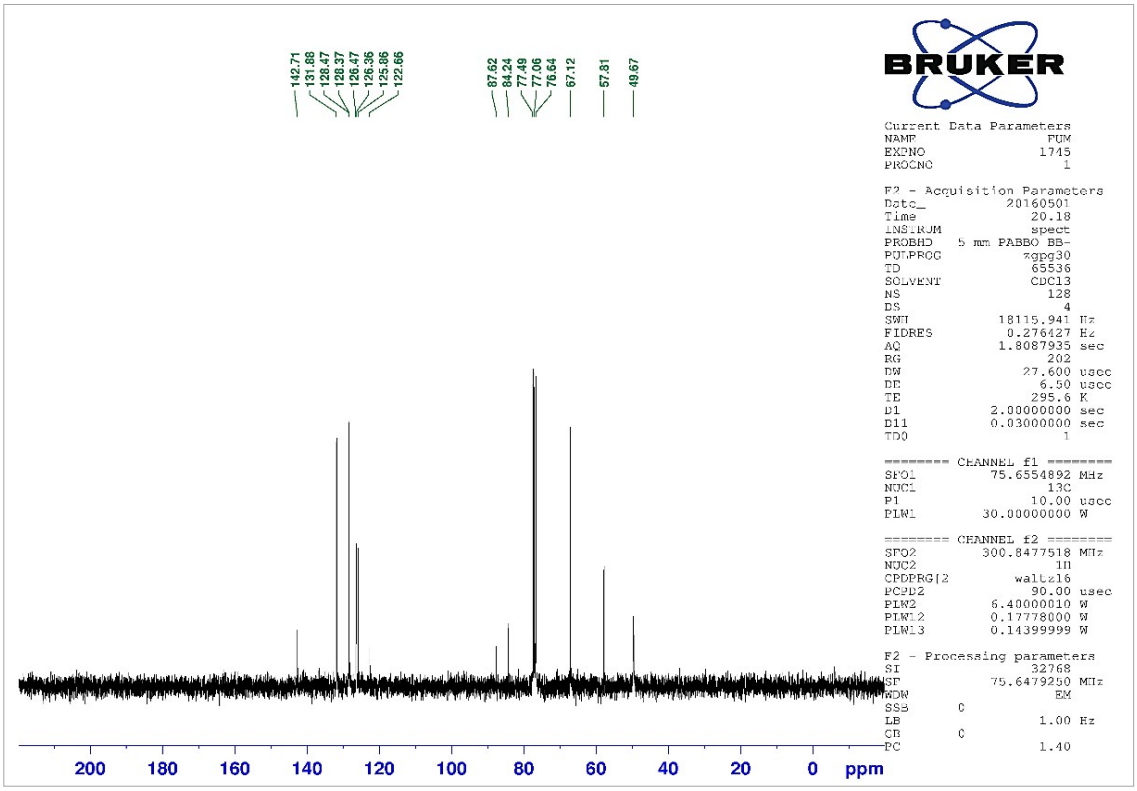
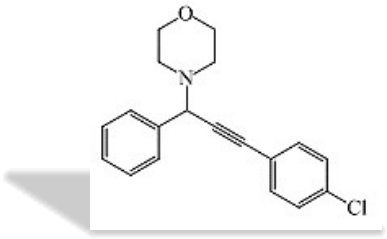


Figure 28: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 4-(3-phenyl-1-(thiophen-2-yl) prop-2-yn-1-yl) morpholine (**4l**).

4-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)morpholine (**4m**). Oily yellow liquid; isolated yield: 70 %; FT-IR (neat): ν_{max}/cm^{-1} 3076, 3039, 2969, 2927, 2880, 2852, 2816, 2202, 1597, 1488, 1447, 1072, 776; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66-7.63 (2H, m, Ph), 7.49-7.45 (2H, m, Ph), 7.44-7.38 (2H, m, Ph), 7.37-7.33 (3H, m, Ph), 4.81 (1H, s, CH), 3.79-3.76 (4H, m, $2CH_2$), 2.67-2.64 (4H, m, $2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.5, 134.3, 133.0, 128.6, 128.5, 128.3, 127.9, 121.4, 87.3, 86.1, 67.1, 62.0; MS, *m/z* (%): 311(8%, M^+), 225(18%, M^+-morpholine), 111(75%, C_6H_4Cl); Anal. Calcd for $C_{19}H_{18}ClNO$: C, 73.19; H, 5.82; N, 4.49, Found: C, 72.20; H, 5.79; N, 4.47 %.



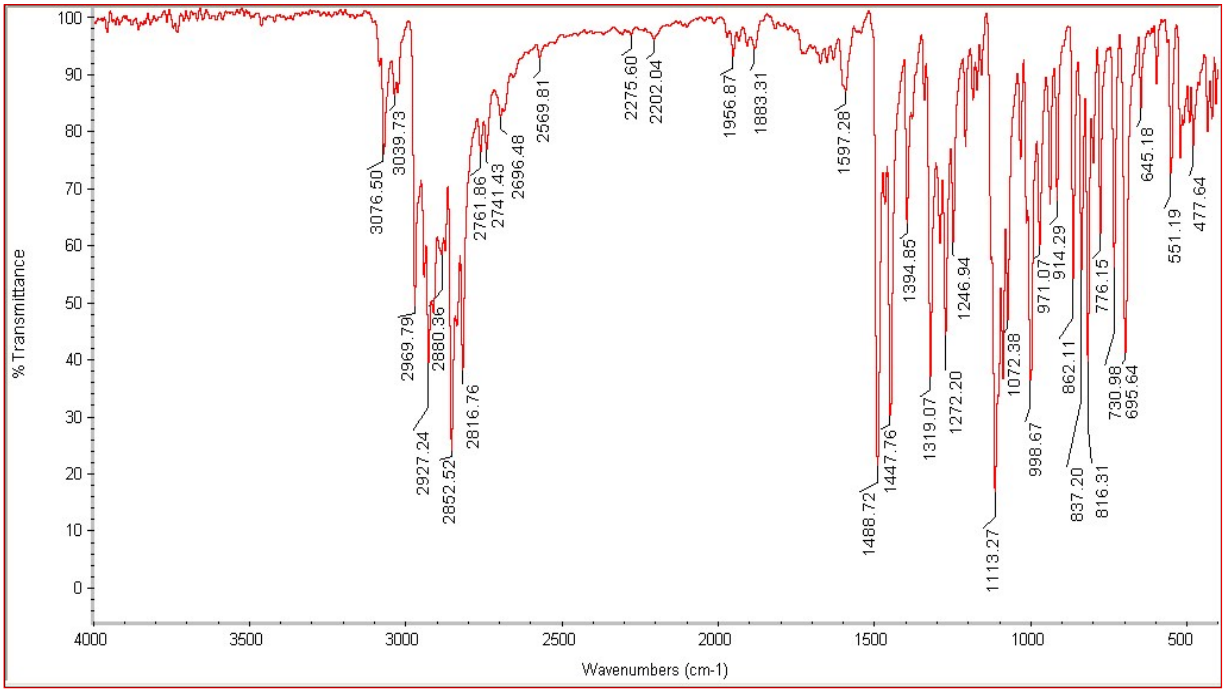


Figure 29: FT-IR (neat) spectrum of 4-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)morpholine (**4m**).

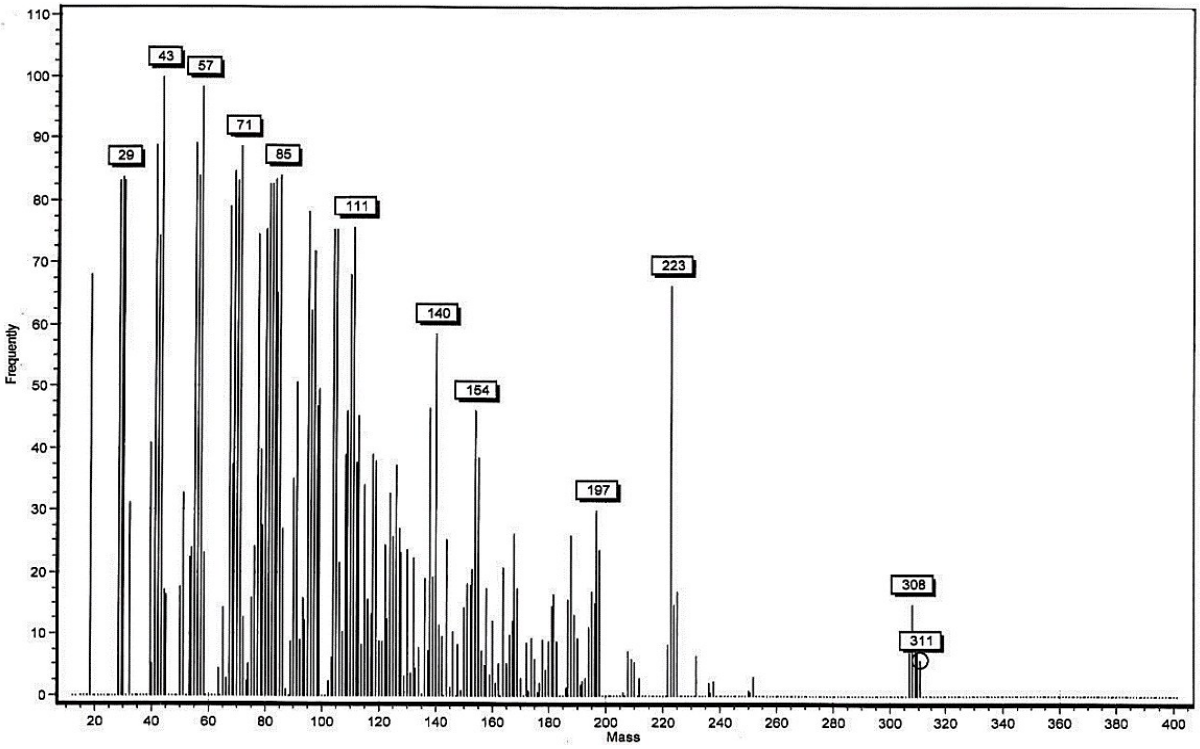


Figure 30: Mass spectrum of 4-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)morpholine (**4m**).

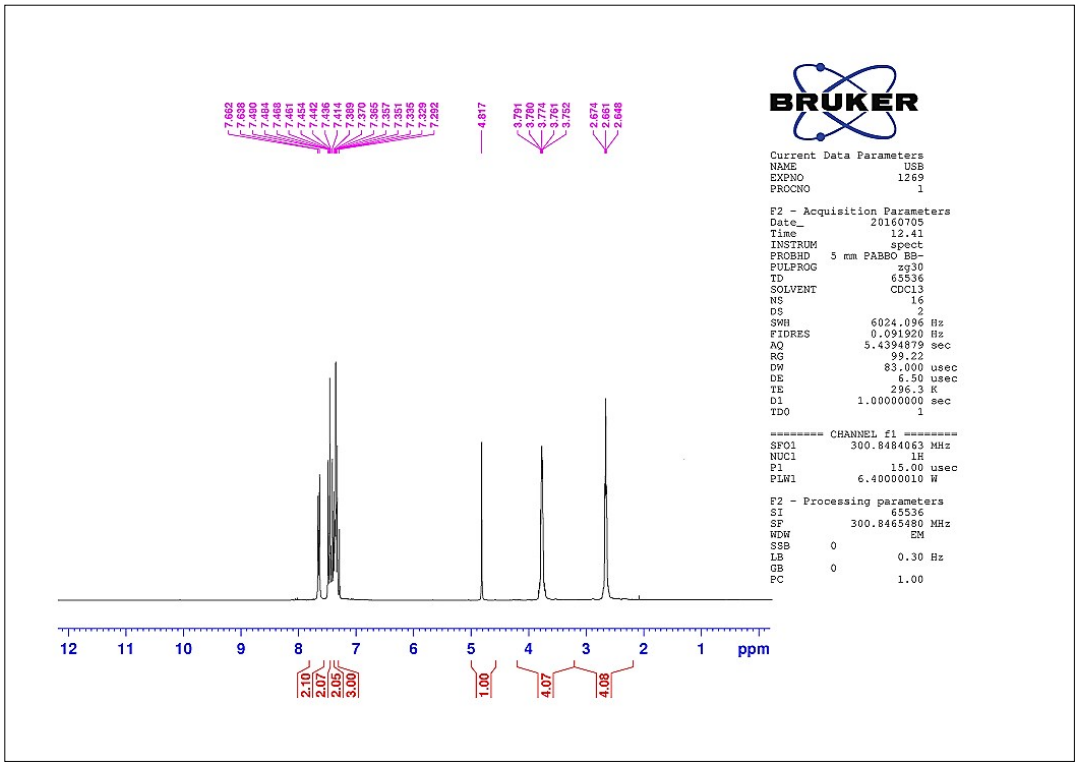


Figure 31: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)morpholine (**4m**).

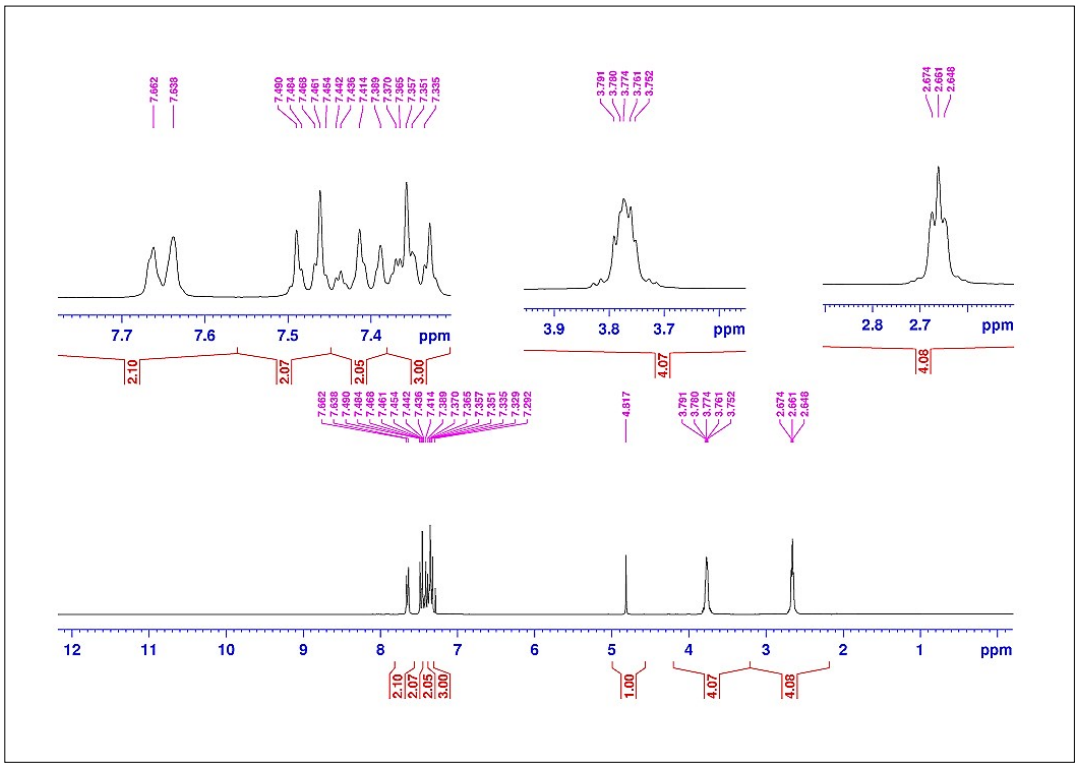


Figure 32: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)morpholine (**4m**) expanded.

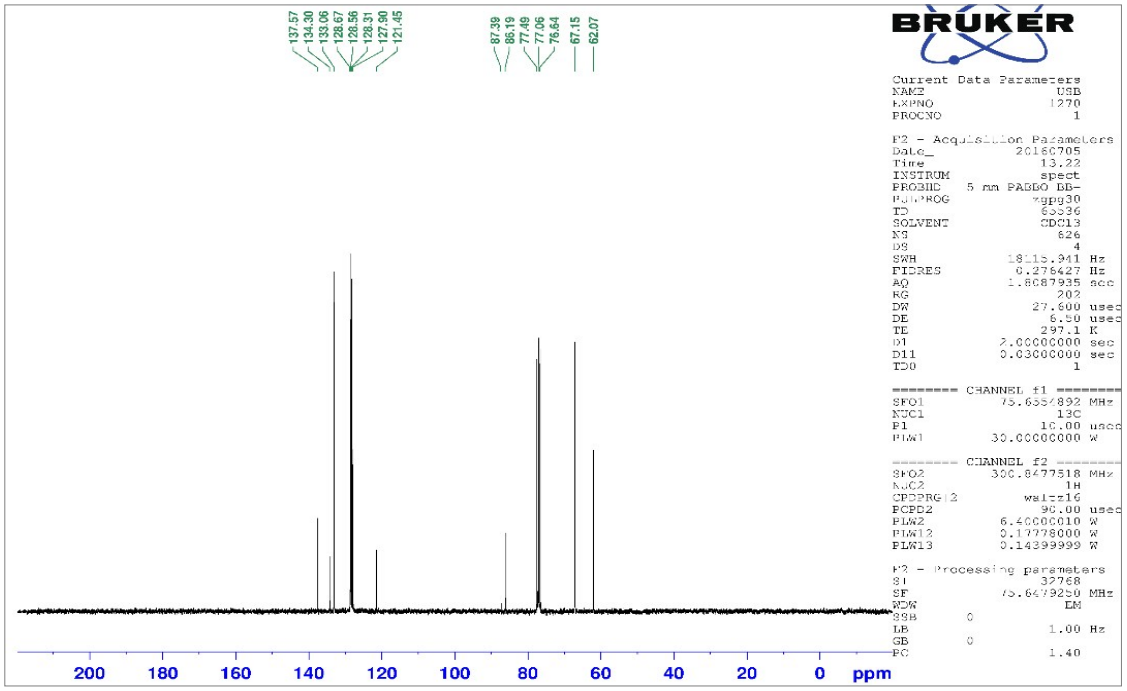
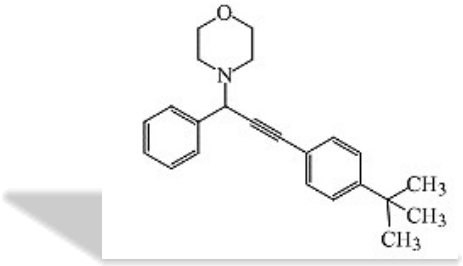


Figure 33: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 4-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)morpholine (**4m**).

4-(3-(4-(*tert*-butyl) phenyl)-1-phenylprop-2-yn-1-yl)morpholine (**4n**). Oily yellow liquid; isolated yield: 95%; FT-IR (neat): ν_{max}/cm^{-1} 3084, 3061, 3031, 2956, 2925, 2854, 2827, 2210, 1504, 1451, 1392, 1003, 777, 737; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (2H, d, J = 6.9 Hz, Ph), 7.40-7.38 (2H, m, Ph), 7.32-7.16 (5H, m, Ph), 4.72 (1H, s, CH), 3.67-3.63 (4H, m, $2CH_2$), 2.55 (4H, br, $2CH_2$), 1.23 (9H, s, $3CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.5, 137.7, 131.5, 128.7, 128.2, 127.8, 125.3, 119.9, 88.6, 84.2, 67.1, 62.0, 31.2; MS, *m/z* (%): 333(6%, M^+), 247(19%, M^+-morpholine), 57(92%, $C(CH_3)_3$); Anal. Calcd for $C_{23}H_{27}NO$: C, 82.84; H, 8.16; N, 4.20, Found: C, 81.78; H, 8.17; N, 3.97 %.



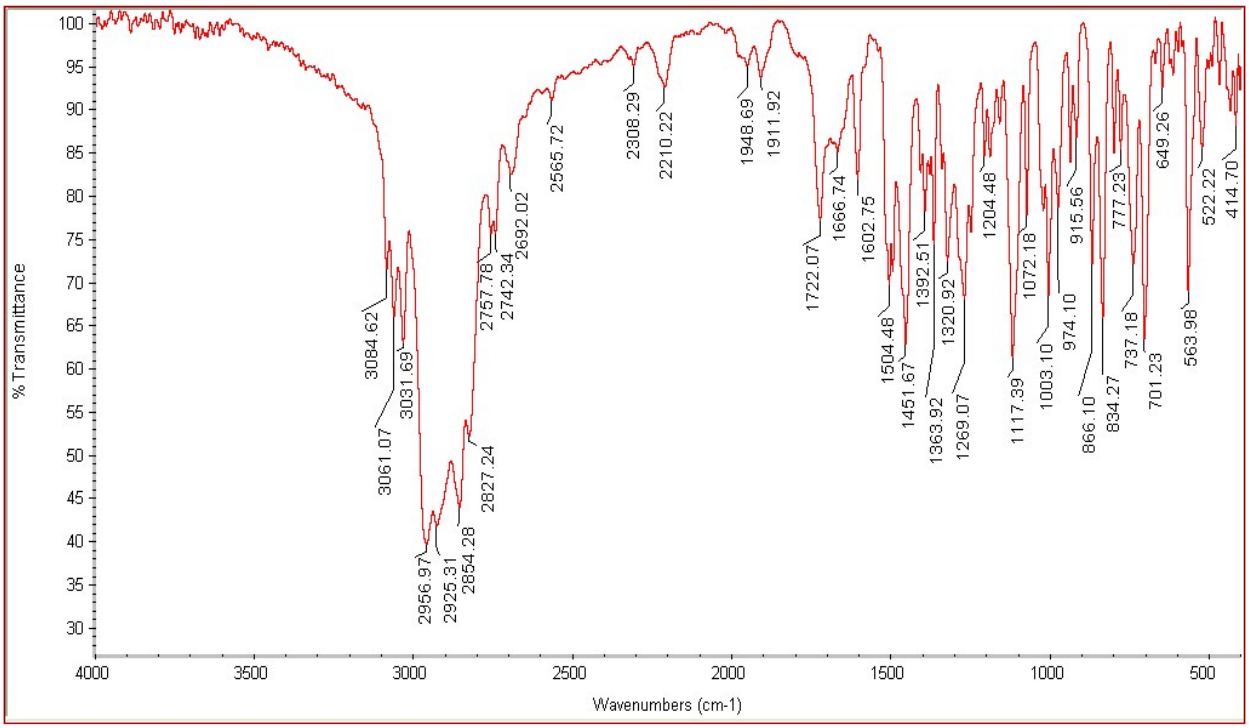


Figure 34: FT-IR (neat) spectrum of 4-(3-(4-(*tert*-butyl) phenyl)-1-phenylprop-2-yn-1-yl) morpholine (**4n**).

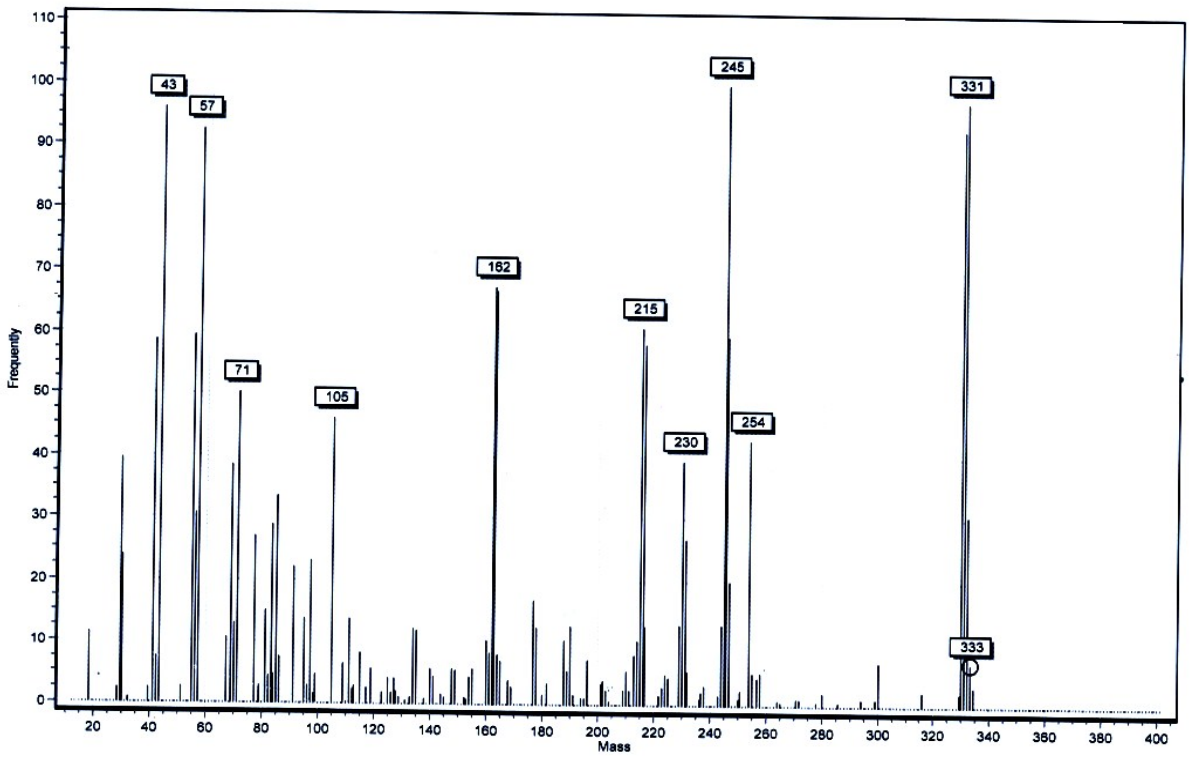


Figure 35: Mass spectrum of 4-(3-(4-(*tert*-butyl) phenyl)-1-phenylprop-2-yn-1-yl)morpholine (**4n**).

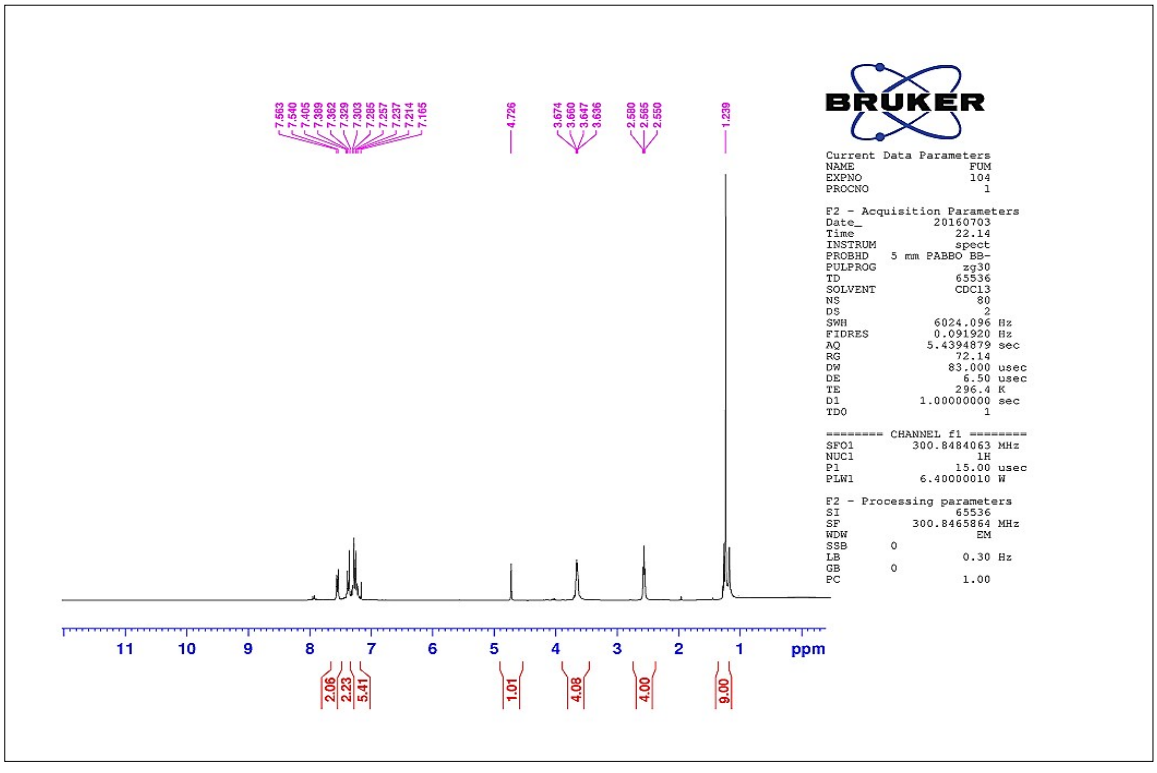


Figure 36: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-(3-(4-(*tert*-butyl) phenyl)-1-phenylprop-2-yn-1-yl)morpholine (**4n**).

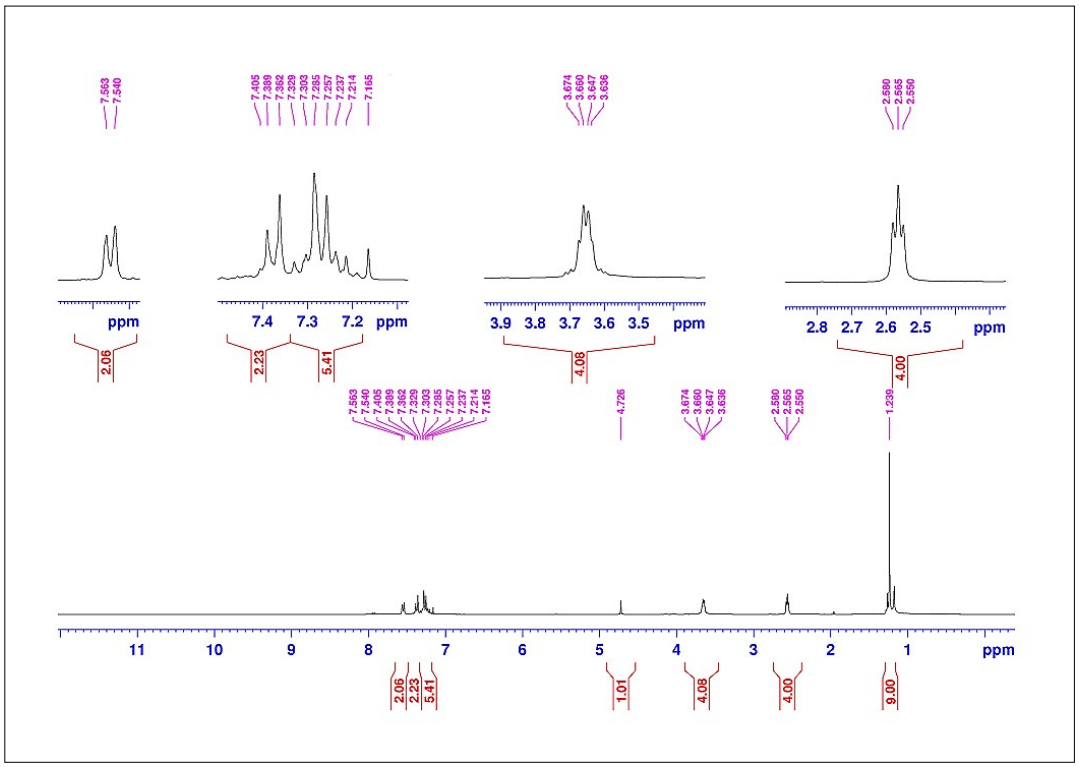


Figure 37: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-(3-(4-(*tert*-butyl) phenyl)-1 phenylpr op-2-yn-1-yl)morpholine (**4n**) expanded.

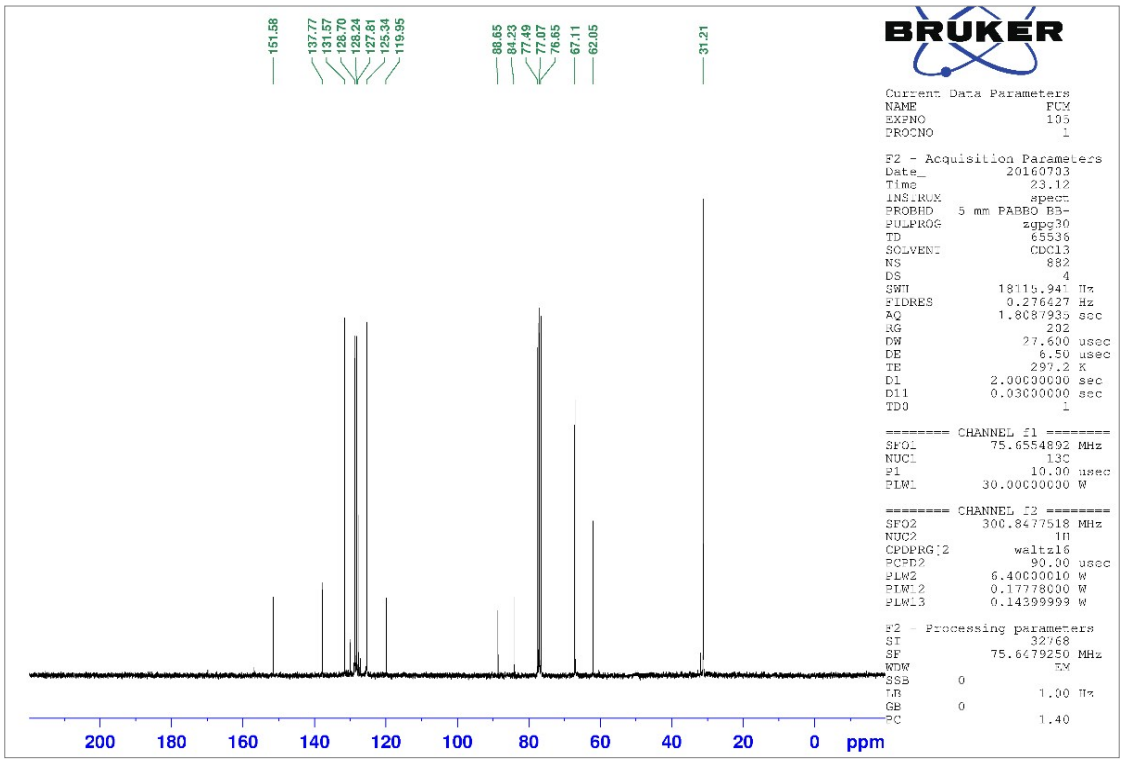
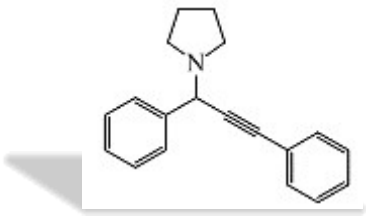


Figure 38: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 4-(3-(4-(*tert*-butyl) phenyl)-1-phenylprop-2-yn-1-yl)morpholine (**4n**).

1-(1,3-diphenylprop-2-yn-1-yl)pyrrolidine (**4o**).[4] Oily light liquid; isolated yield: 90%; MS, *m/z* (%): 261(2%, M^+), 190(100%, M^+-pyrrollidine), 184(29%, M^+-C_6H_5), 71(51%, pyrrolidine).



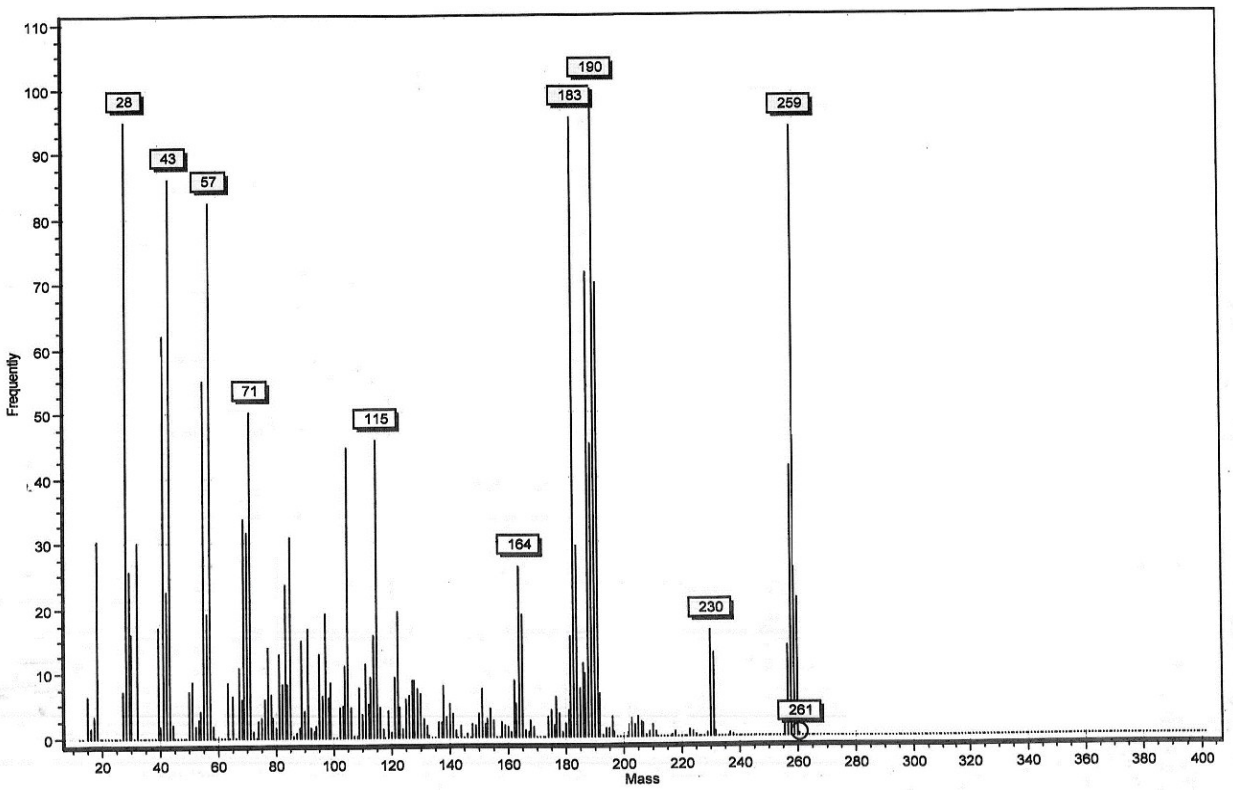
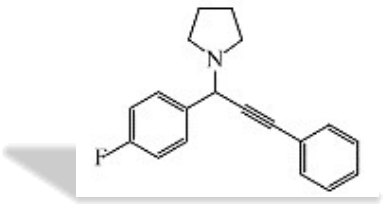


Figure 39: Mass spectrum of 1-(1, 3-diphenylprop-2-yn-1-yl) pyrrolidine (**4o**).

1-(1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (**4p**).[5] Oily light liquid; isolated yield: 60%; MS, *m/z* (%): 280(2%, M^+), 209(65%, M^+-pyrrollidine), 77(82%, C_6H_5), 57(85%, C_4H_8).



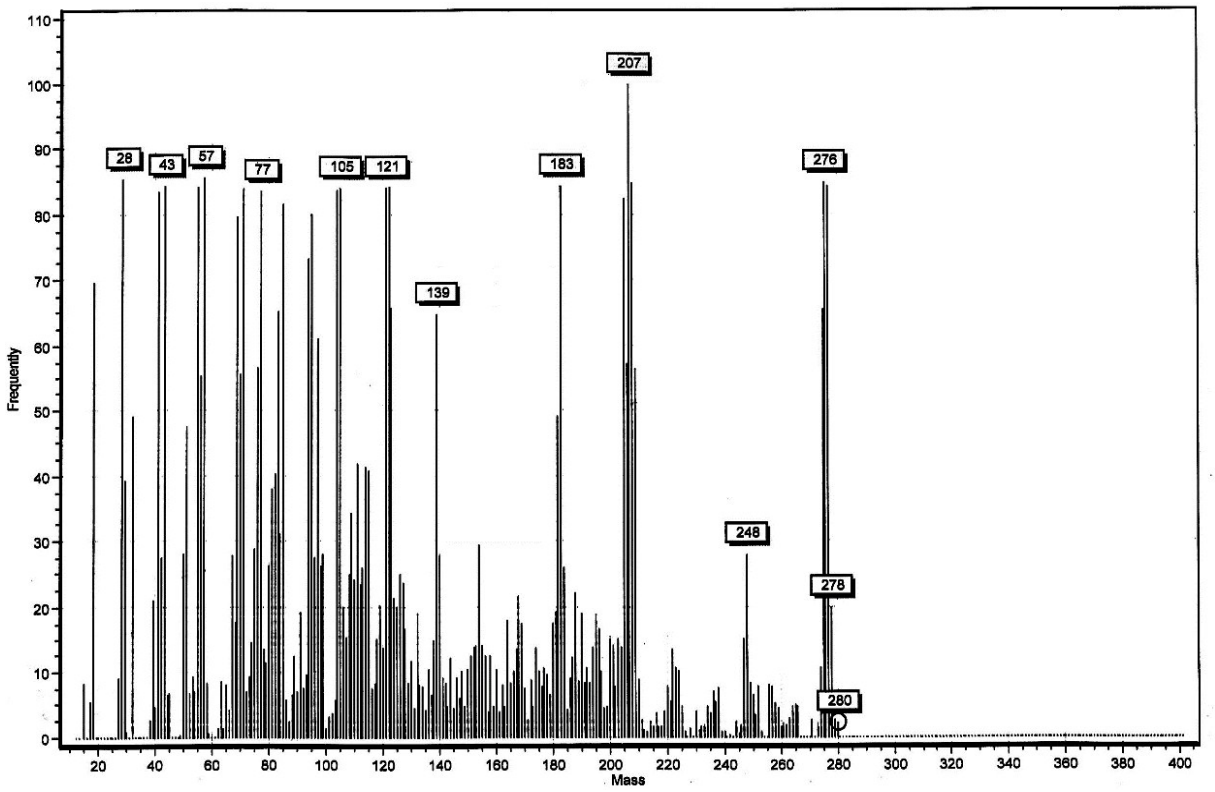
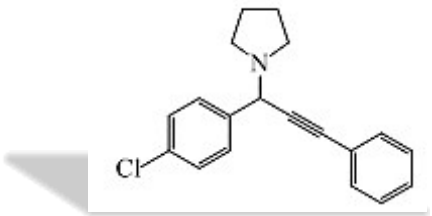


Figure 40: Mass spectrum of 1-(1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4p**).

1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (**4q**).[5] Oily light liquid; isolated yield: 80%; MS, *m/z* (%): 295(14%, M^+), 225(59%, M^+-pyrrollidine), 71(70%, pyrrolidine).



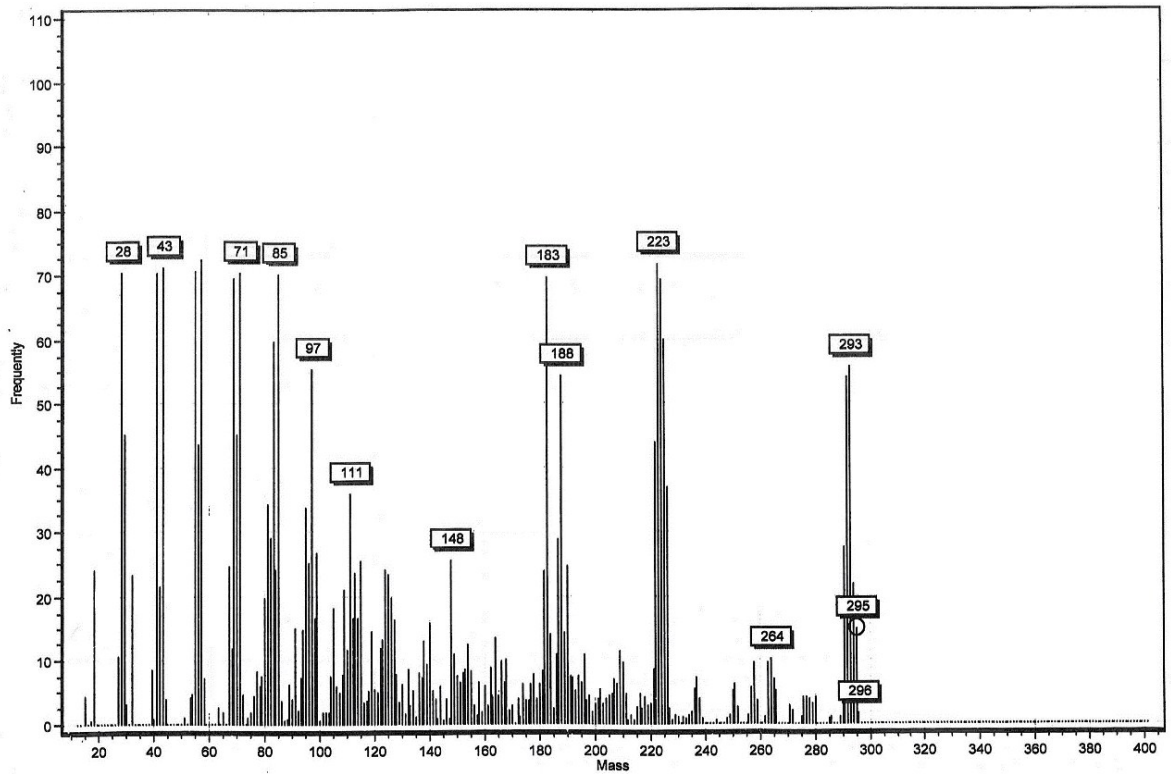
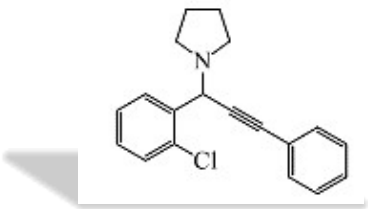


Figure 41 Mass spectrum of 1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4q**).

1-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (**4r**). Oily yellow liquid; isolated yield: 80%; FT-IR (neat): ν_{max}/cm^{-1} 3059, 3031, 2956, 2925, 2854, 2819, 2226, 2103, 1597, 1489, 1471, 1442, 1001, 752; ^1H NMR (300 MHz, $CDCl_3$): δ 7.72 (1H, dd, *J*= 7.5 Hz, *J* = 1.8 Hz, Ph), 7.41-7.38 (2H, m, Ph), 7.37 (1H, dd, *J* = 7.5 Hz, *J* = 1.5 Hz, Ph), 7.26-7.20 (5H, m, Ph), 5.24 (1H, s, CH), 2.69 (4H, br, $2CH_2$), 1.73 (4H, br, $2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.9, 133.8, 131.8, 130.2, 129.6, 128.9, 128.2, 128.2, 126.7, 123.0, 86.5, 86.3, 55.5, 50.4, 29.7, 23.4; MS, *m/z* (%): 295(37%, M^+), 224(74%, M^+-pyrrollidine), 184(72%, M^+-C_6H_4Cl), 71(72%, pyrrolidine); Anal. Calcd for $C_{19}H_{18}ClN$: C, 77.15; H, 6.13; N, 4.74, Found: C, 76.12; H, 5.18; N, 4.77 %.



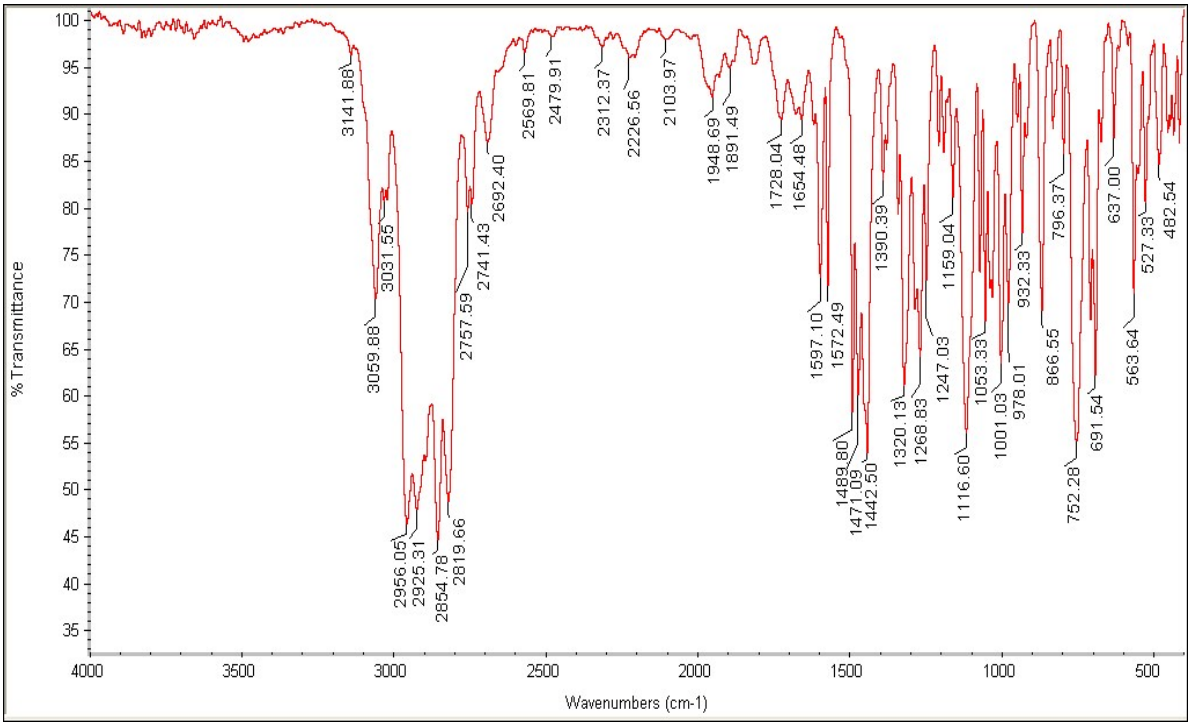


Figure 42: FT-IR (neat) spectrum of 1-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (**4r**).

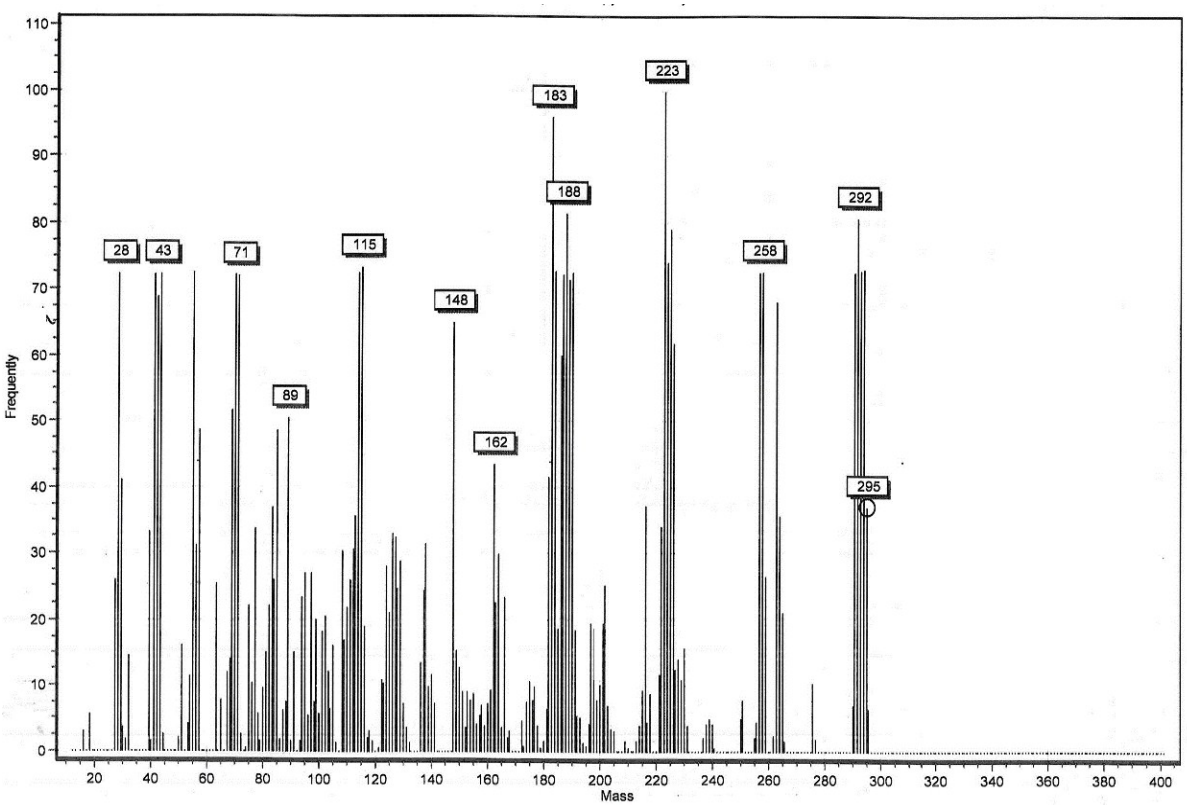


Figure 43: Mass spectrum of 1-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4r**).

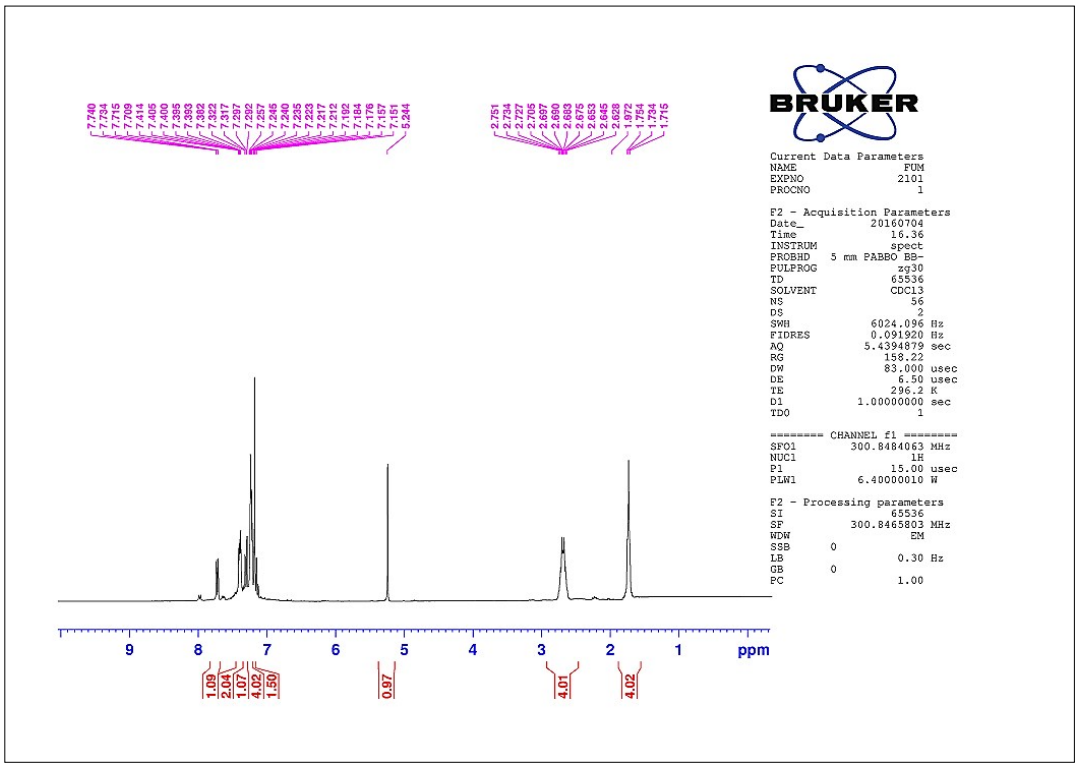


Figure 44: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 1-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4r**).

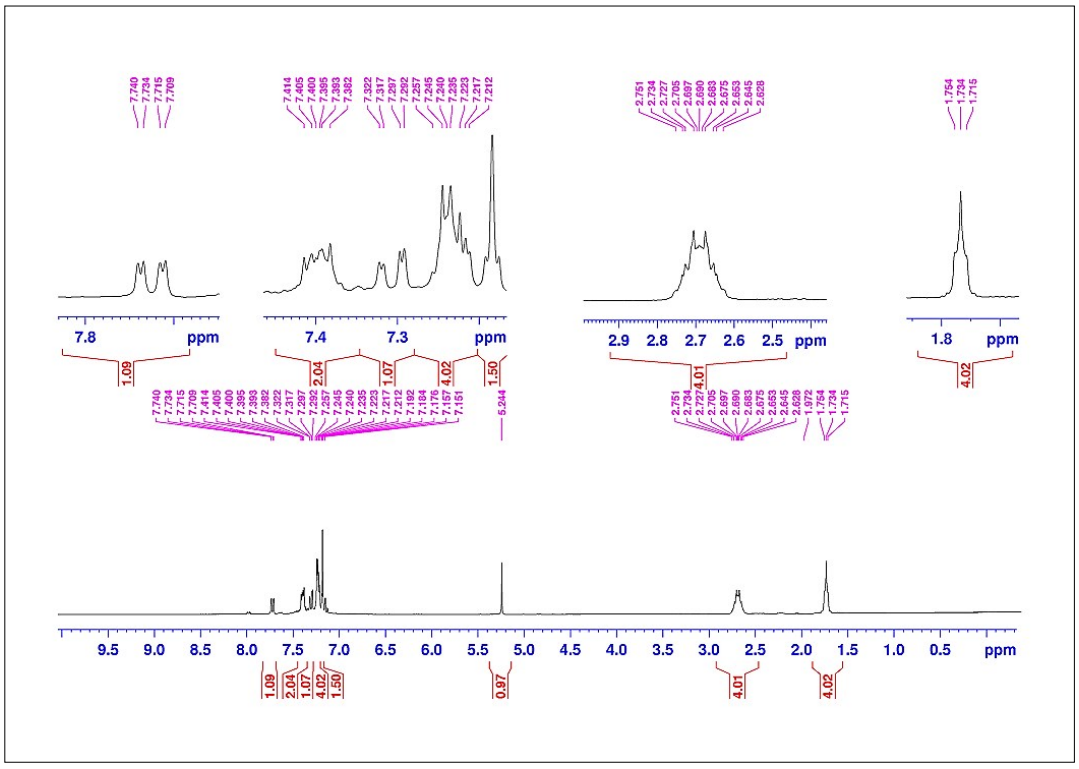


Figure 45: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 1-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4r**) expanded.

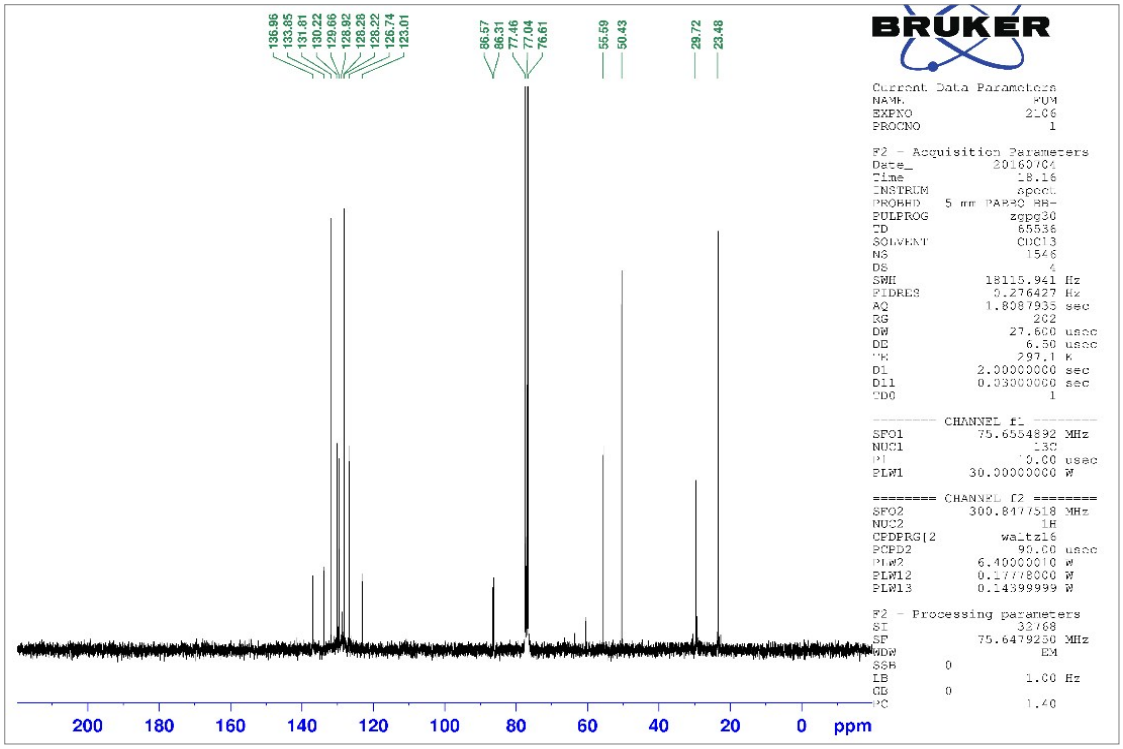
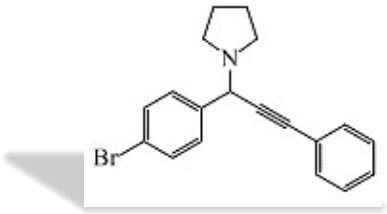


Figure 46: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 1-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4r**).

1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (**4s**).[5] Oily yellow liquid; isolated yield: 85 %; FT-IR (neat): ν_{max}/cm^{-1} 3058, 2958, 2924, 2853, 2230, 2197, 1595, 1486, 1458, 1011, 755; MS, *m/z* (%): 339(44%, M^+), 184(52%, M^+-C_6H_4Br), 71(91%, pyrrollidine), 57(100%, C_4H_8).



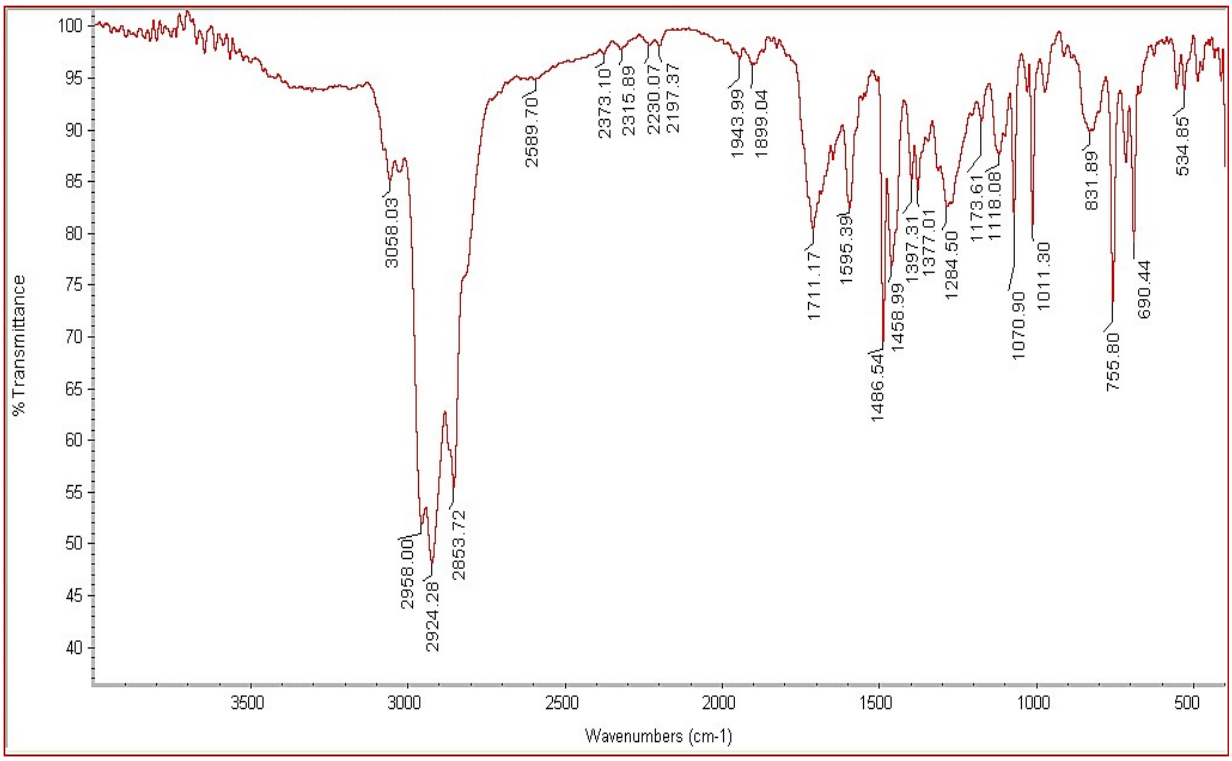


Figure 47: FT-IR (neat) spectrum of 1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4s**).

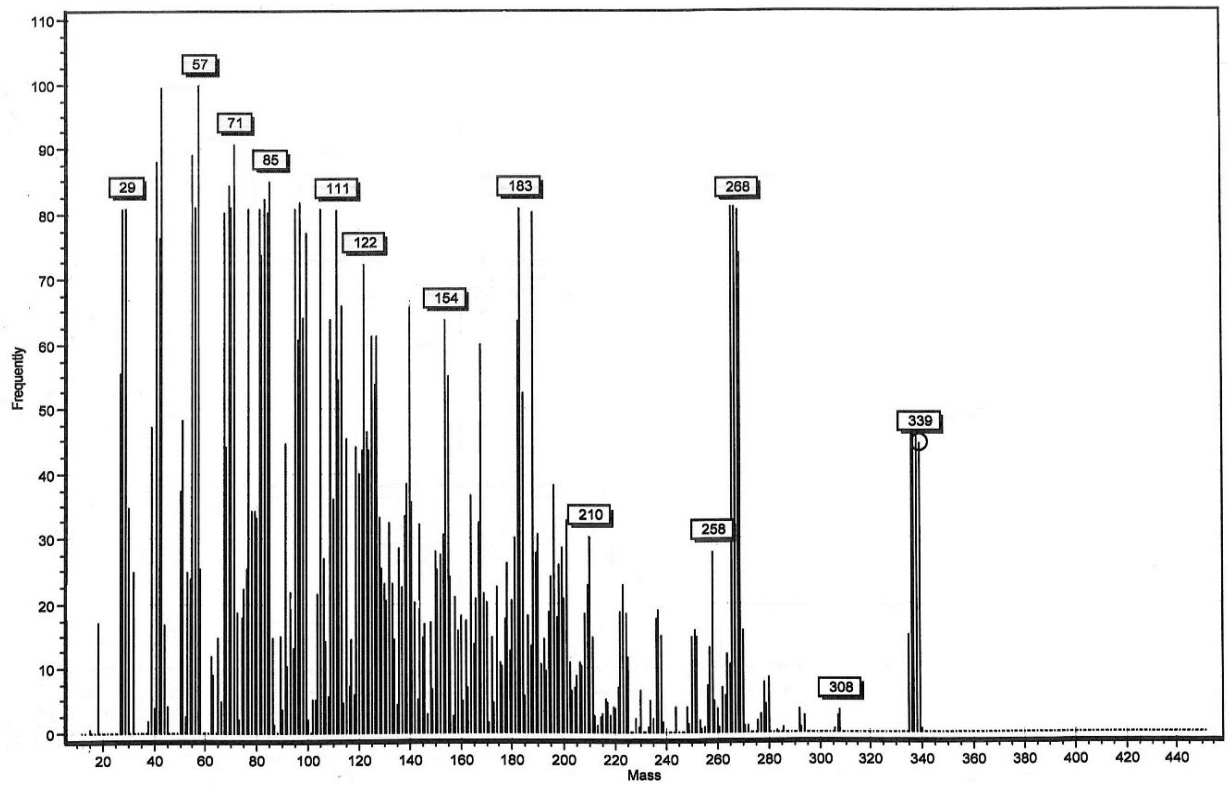
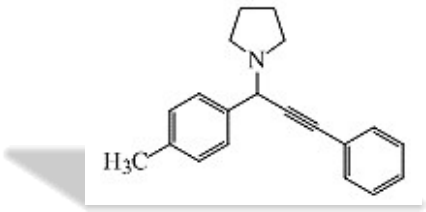


Figure 48: Mass spectrum of 1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4s**).

1-(3-phenyl-1-(*p*-tolyl)prop-2-yn-1-yl)pyrrolidine (**4t**).[5] Oily light liquid; isolated yield: 95 %; MS, *m/z* (%): 275(2%, M^+), 204(84%, M^+-pyrrollidine), 71(98%, pyrrollidine).



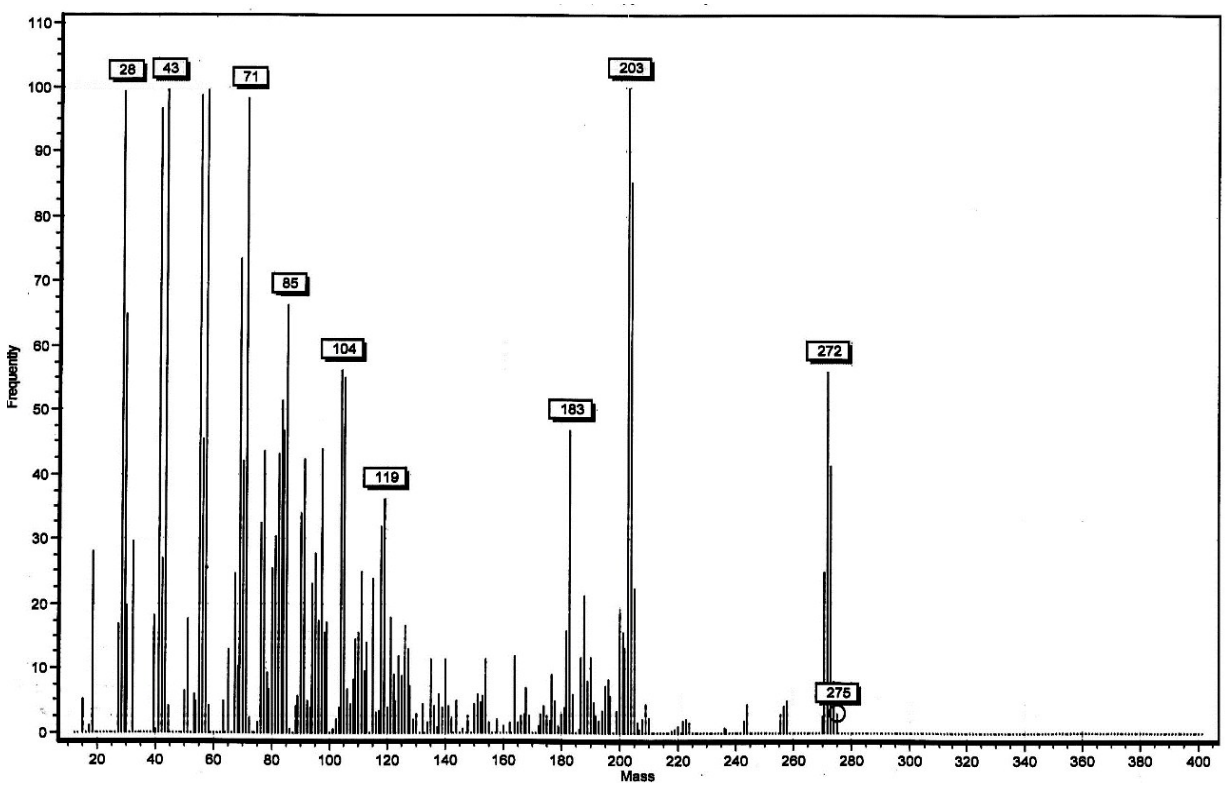


Figure 49: Mass spectrum of 1-(3-phenyl-1-(*p*-tolyl) prop-2-yn-1-yl) pyrrolidine (**4t**).

1-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1-yl) pyrrolidine (**4u**).[5] Oily light liquid; isolated yield: 90 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.37 (2H, m, Ph), 7.33-7.31 (2H, m, Ph), 7.24-7.22 (3H, m, Ph), 7.19-7.11 (1H, m, Ph), 7.04-7.01 (1H, m, Ph), 4.78 (1H, s, CH), 2.63 (4H, br, $2CH_2$), 2.28 (3H, s, CH_3), 1.73 (4H, br, $2CH_2$);^{13}C NMR (75 MHz, $CDCl_3$): δ 139.1, 137.9, 131.8, 131.7, 129.0, 128.4, 128.2, 128.1, 125.4, 123.2, 86.8, 86.7, 59.2, 50.3, 29.7, 23.5, 21.5, 14.1; MS, *m/z* (%): 275(3%, M^+), 204(98%, M^+-pyrrollidine), 184(12%, M^+-C_7H_7), 71(83%, pyrrollidine).

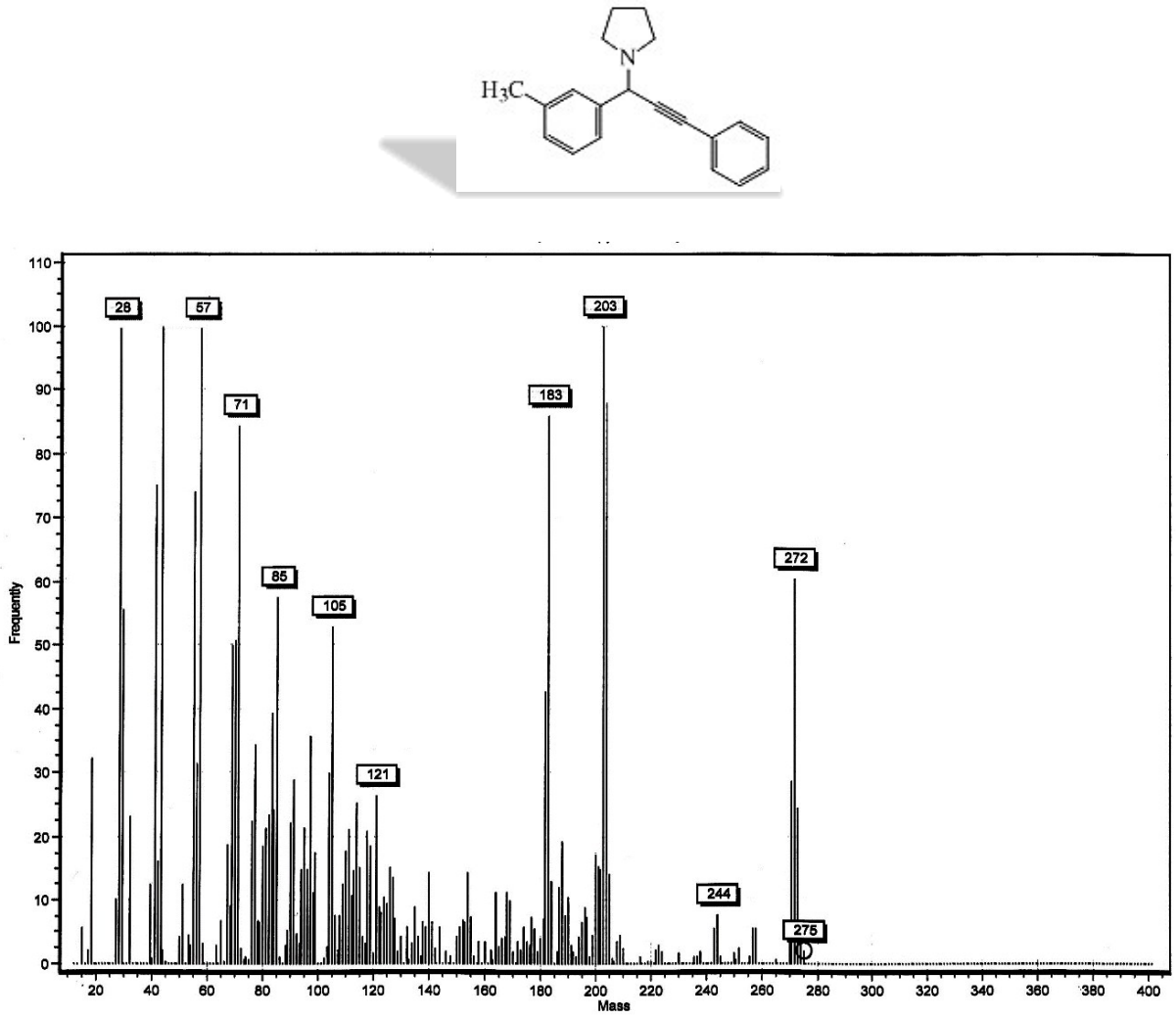


Figure 50: Mass spectrum of 1-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1-yl) pyrrolidine (**4u**).

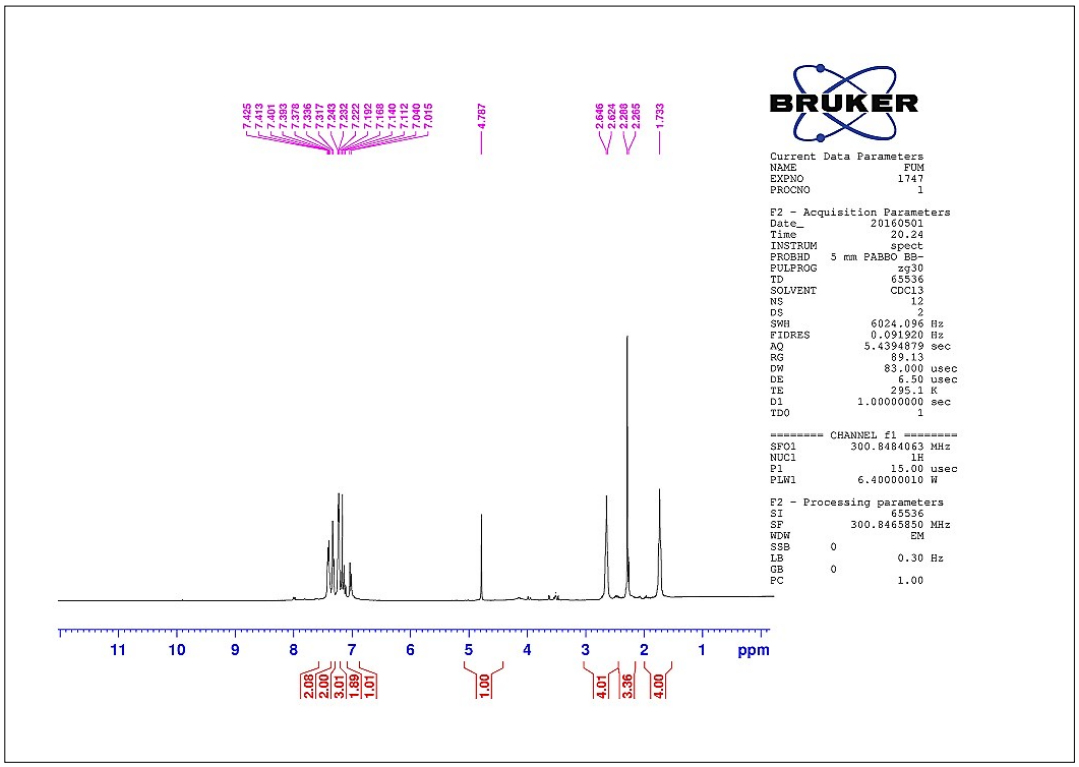


Figure 51: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 1-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1-yl) pyrrolidine (**4u**).

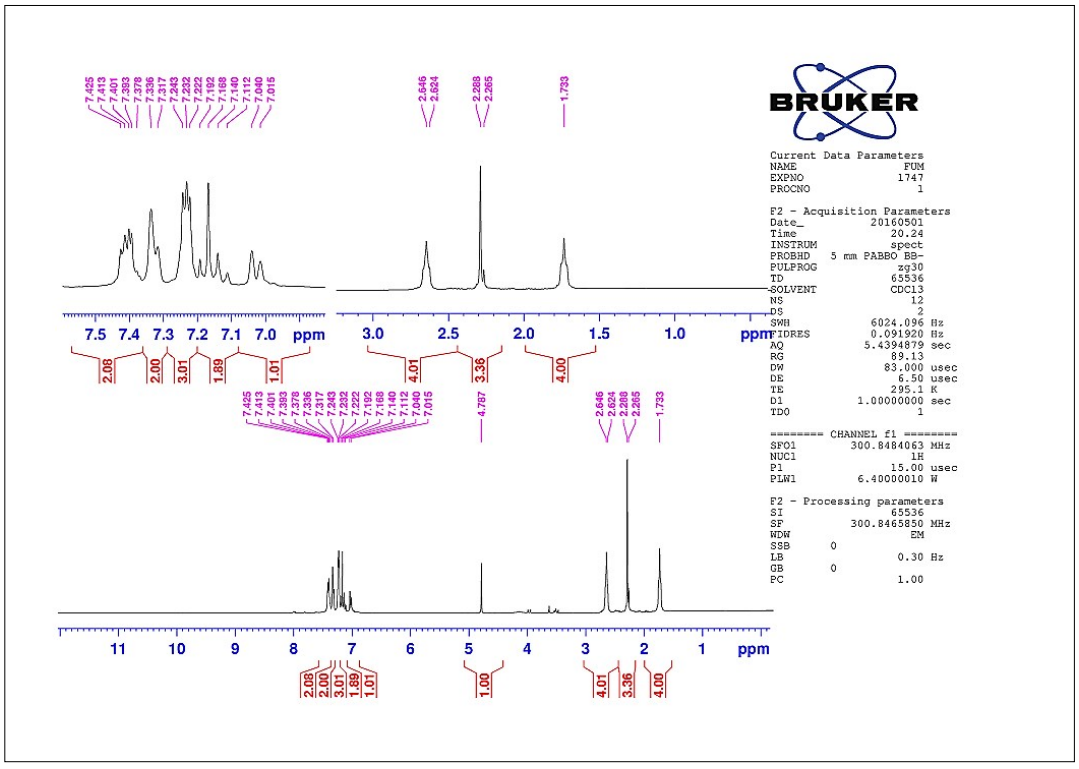


Figure 52: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 1-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1-yl) pyrrolidine (**4u**) expanded.

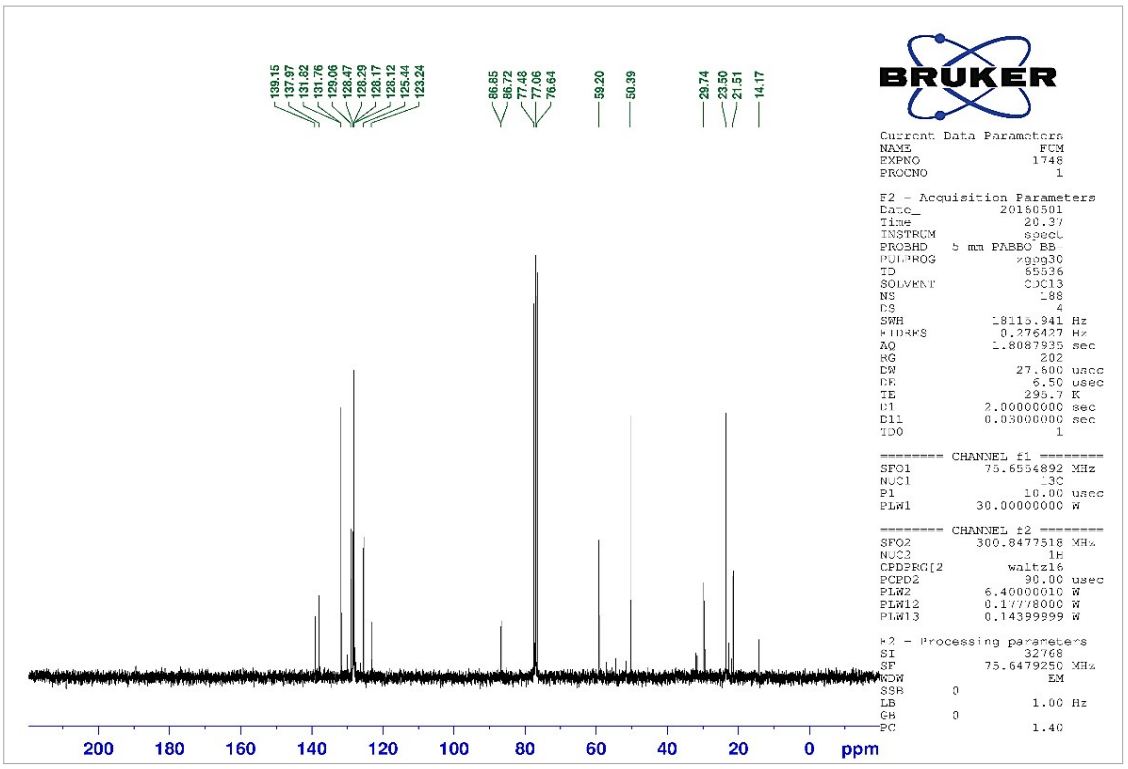


Figure 53: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 1-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1-yl) pyrrolidine (**4u**).

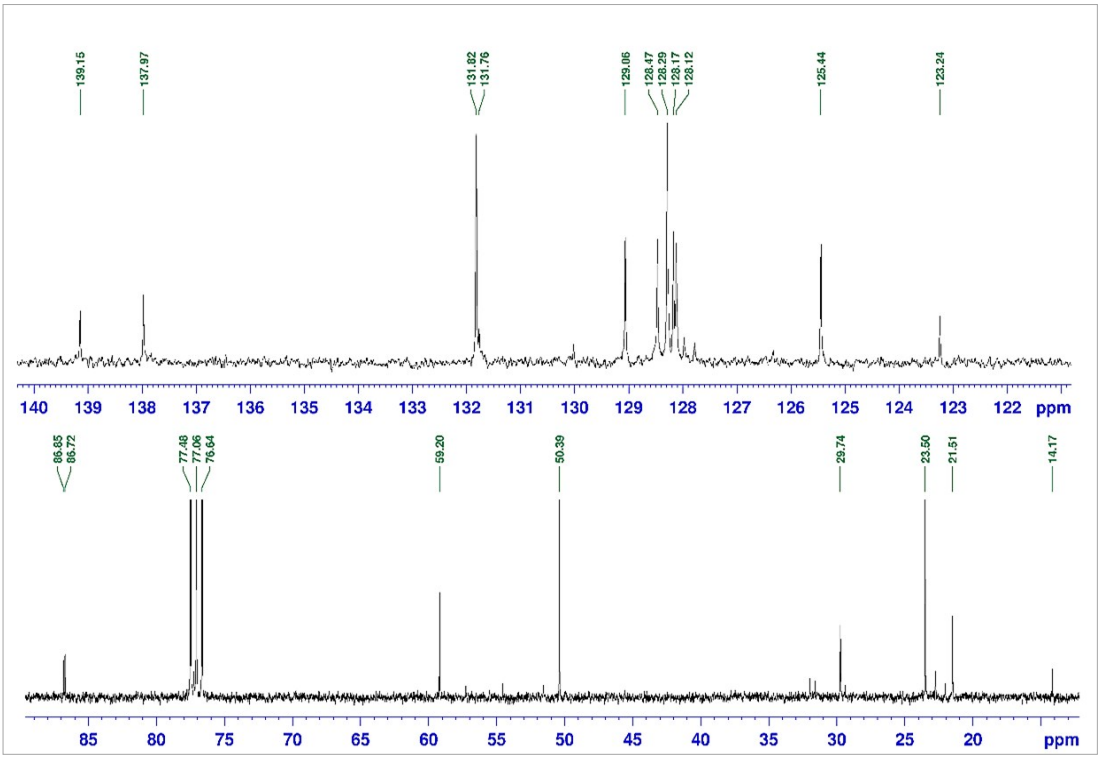


Figure 54: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 1-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1-yl) pyrrolidine (**4u**) expanded.

1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (**4v**).[5] Oily brown liquid; isolated yield: 95%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57-7.50 (4H, m, Ph), 7.35-7.33 (3H, m, Ph), 6.83-6.91 (2H, m, Ph), 4.92 (1H, s, CH), 3.84 (3H, s, OCH_3), 2.75 (4H, br, $2CH_2$), 1.85 (4H, br, $2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 131.7, 131.3, 129.5, 128.2, 128.1, 113.6, 86.8, 86.7, 58.4, 55.3, 50.2, 29.7, 23.4; MS, *m/z* (%): 291(2%, M^+), 220(98%, M^+-pyrrollidine), 71(94%, pyrrollidine).

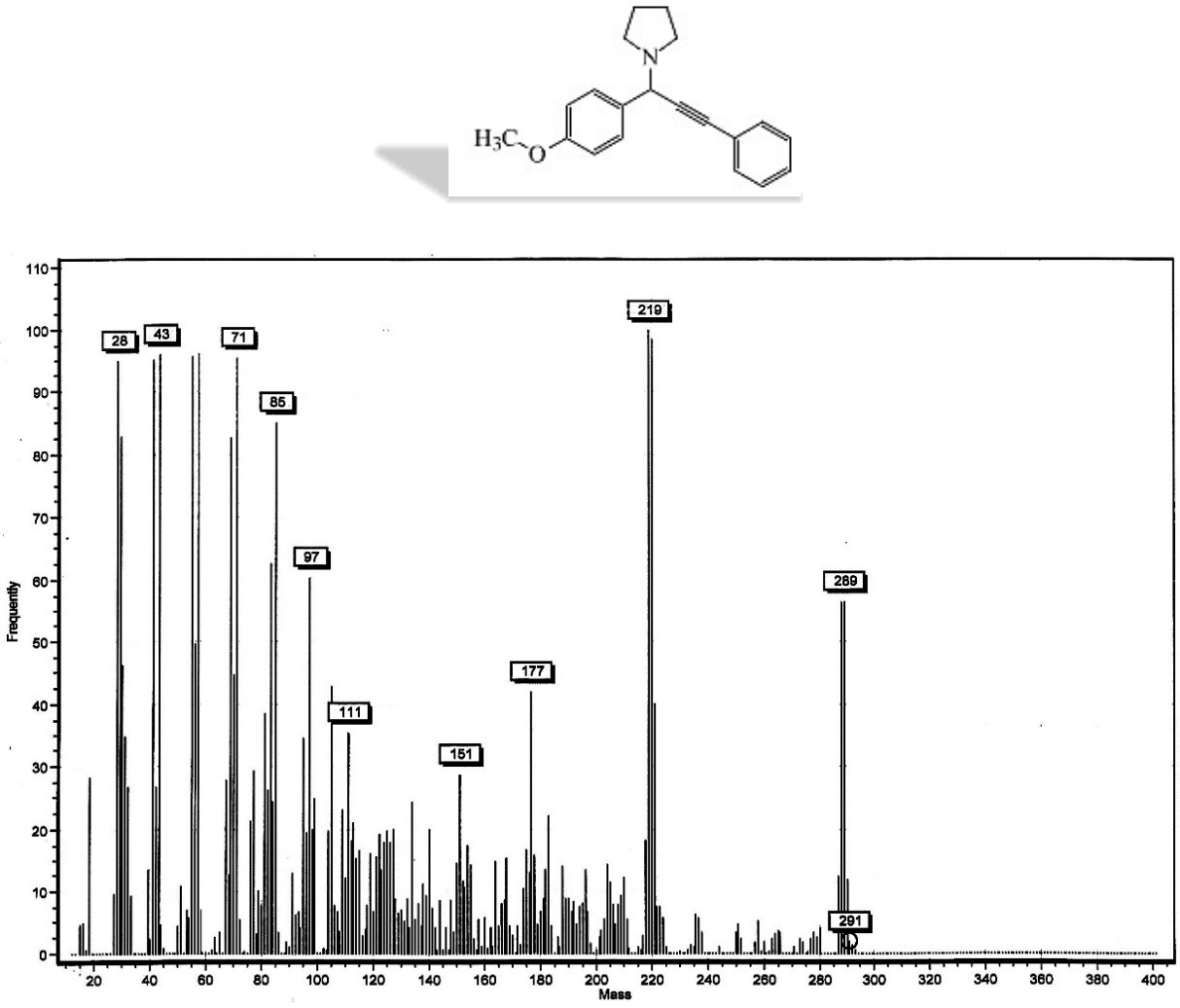


Figure 55: Mass spectrum of 1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4v**).

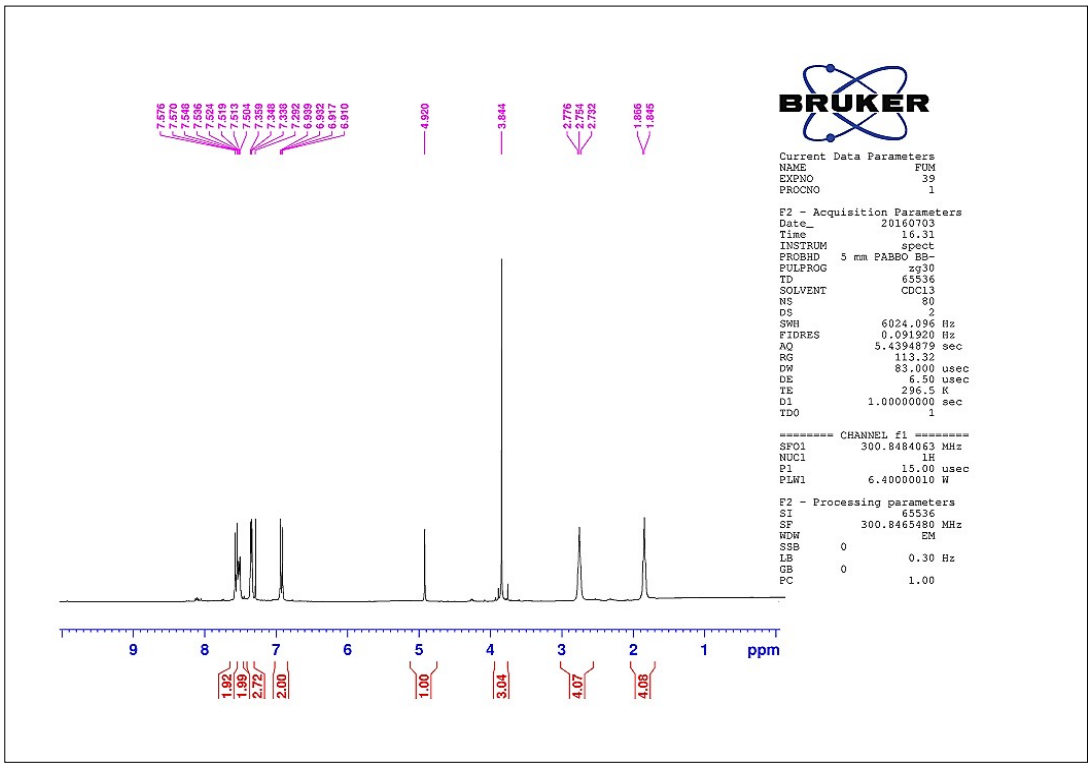


Figure 56: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4v**).

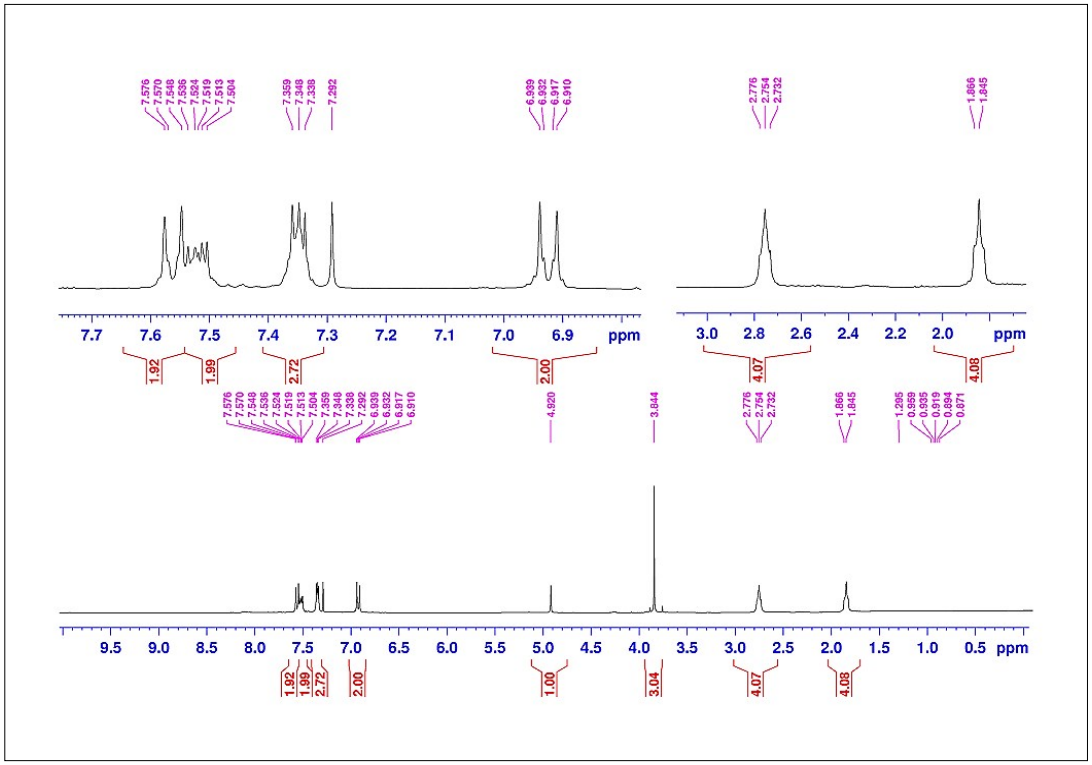


Figure 57: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4v**) expanded.

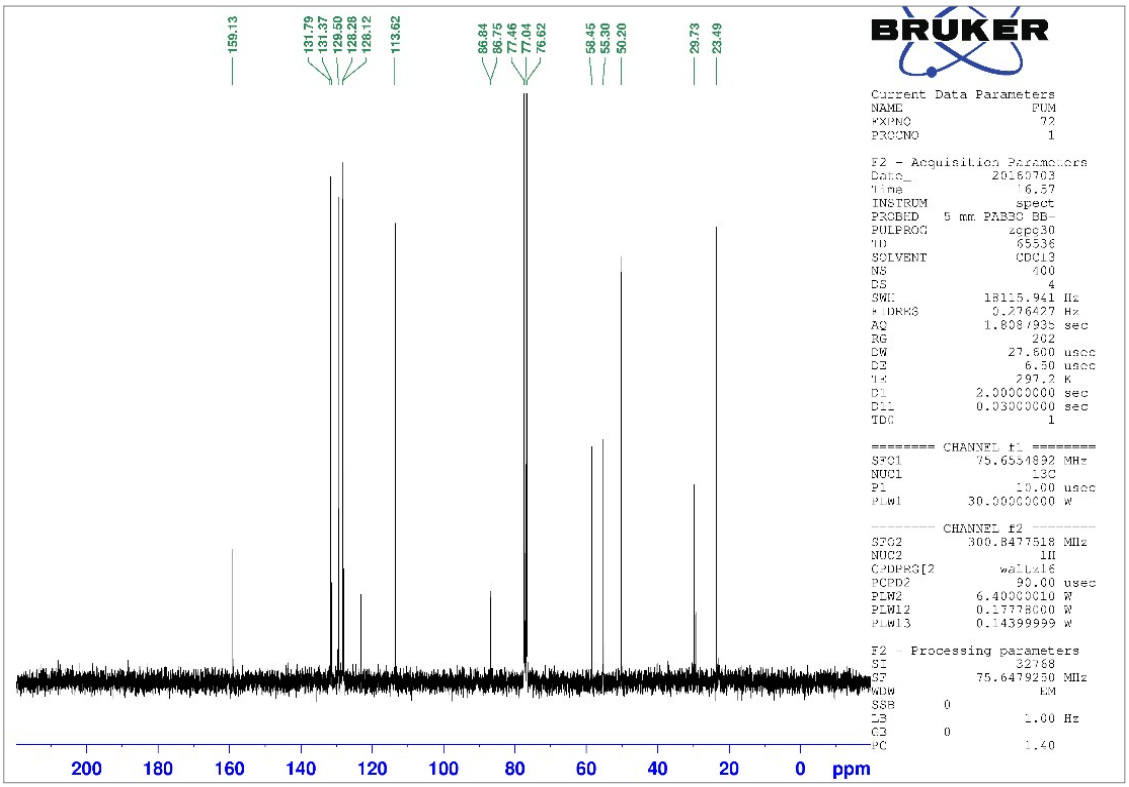
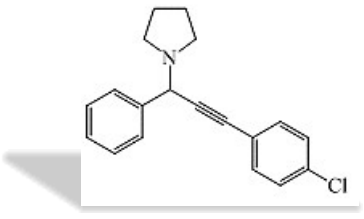


Figure 58: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl) pyrrolidine (**4v**).

1-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4w**). Oily brown liquid; isolated yield: 60 %; FT-IR (neat): ν_{max}/cm^{-1} 3080, 3061, 3029, 2962, 2924, 2872, 2853, 2814, 2197, 1599, 1489, 1452, 1014, 749; ^1H NMR (300 MHz, $CDCl_3$): δ 7.64-7.61 (2H, m, Ph), 7.45-7.42 (3H, m, Ph), 7.37-7.29 (4H, m, Ph), 4.96 (1H, s, CH), 2.76 (4H, br, $2CH_2$), 1.86 (4H, br, $2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.7, 134.2, 133.0, 128.6, 128.4, 128.3, 127.8, 126.4, 121.5, 87.5, 85.9, 59.1, 50.3; MS, *m/z* (%): 295(8%, M^+), 224(48%, M^+-pyrrollidine), 71(96%, pyrrollidine), 43(100%, C_3H_6); Anal. Calcd for $C_{19}H_{18}ClN$: C, 77.15; H, 6.13; N, 4.74, Found: C, 76.13; H, 5.17; N, 4.79 %.



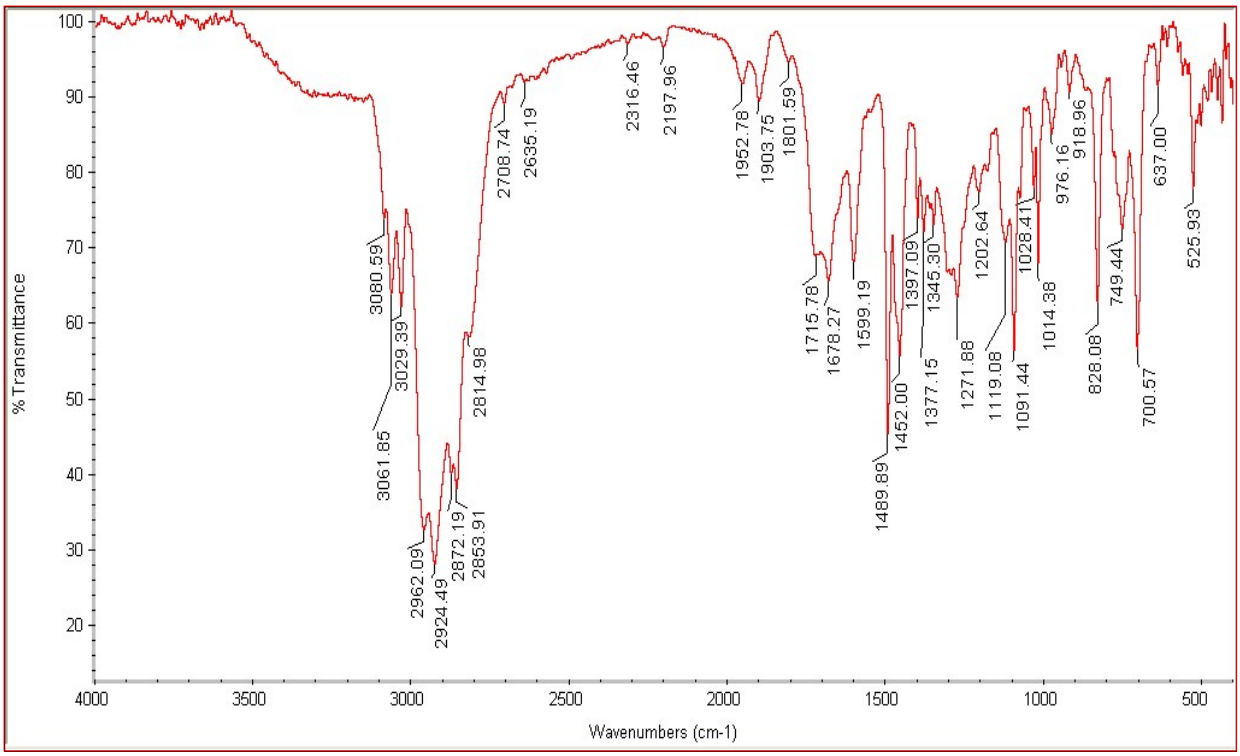


Figure 59: FT-IR (neat) spectrum of 1-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4w**).

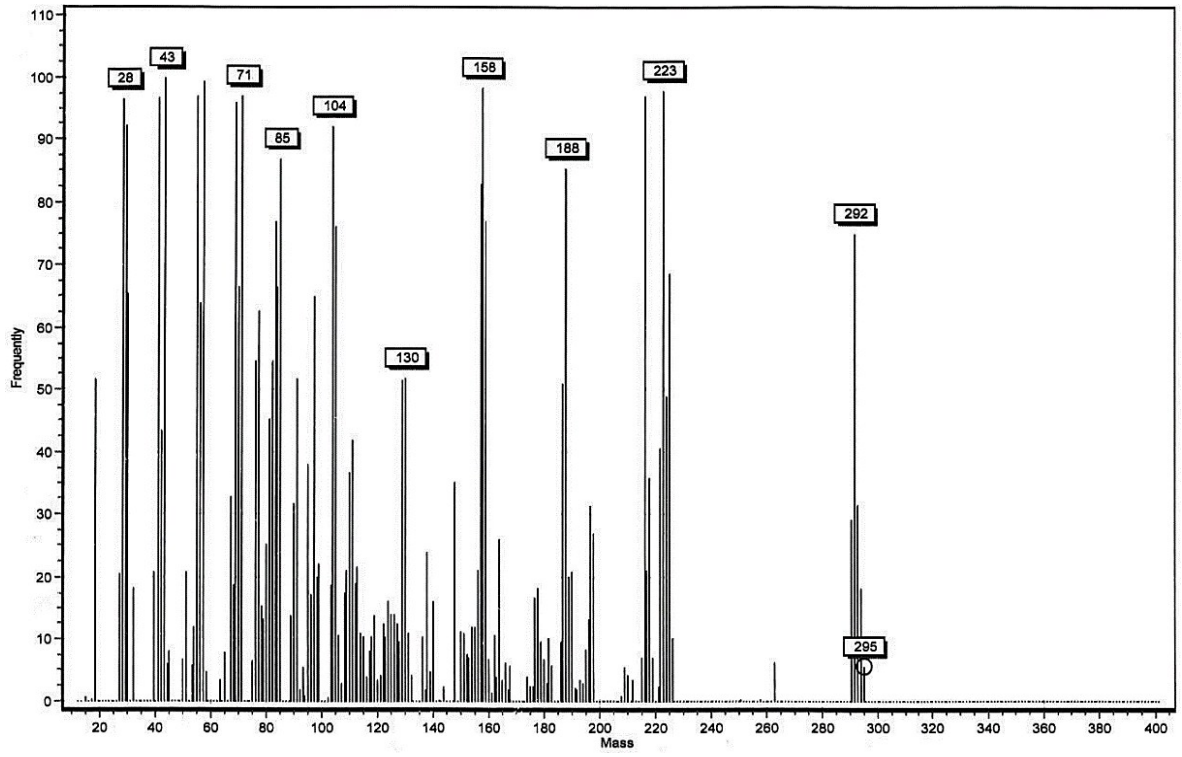


Figure 60: Mass spectrum of 1-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4w**).

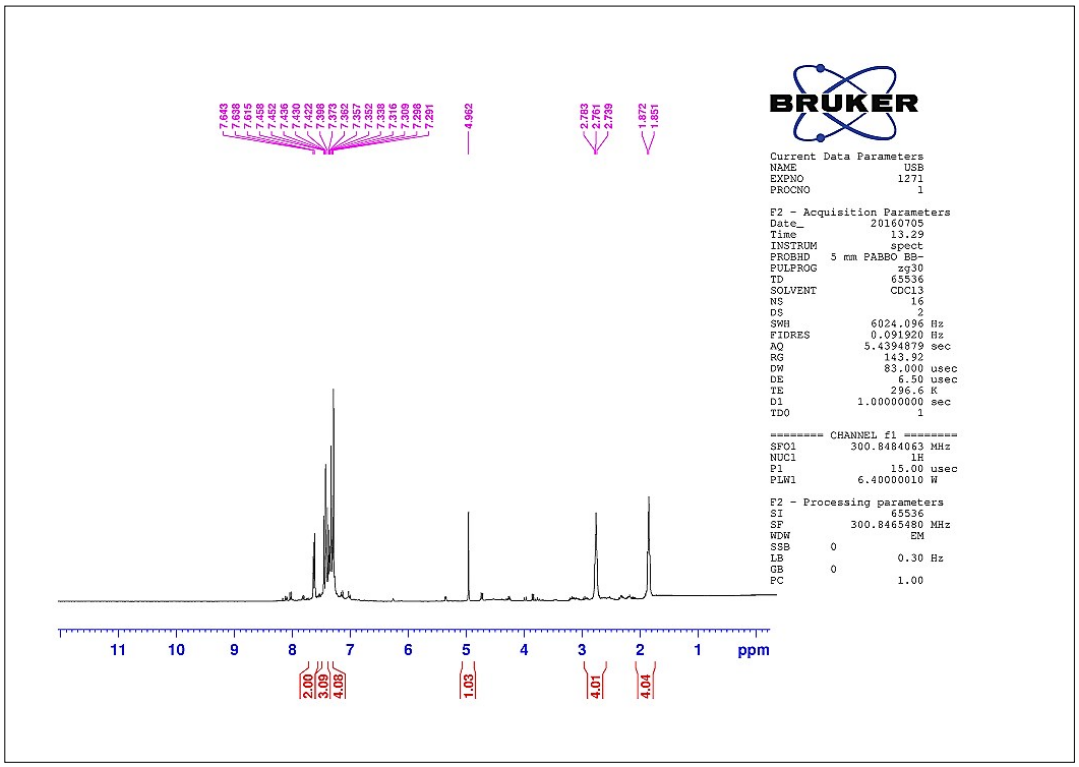


Figure 61: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 1-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4w**).

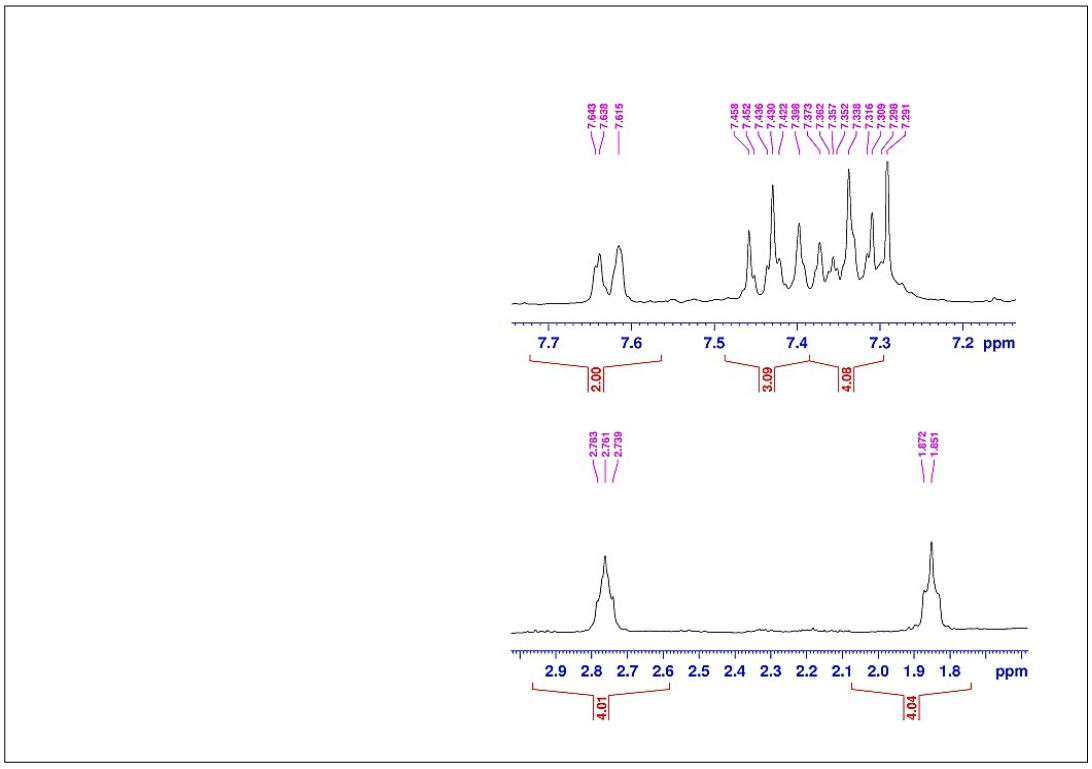


Figure 62: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 1-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4w**) expanded.

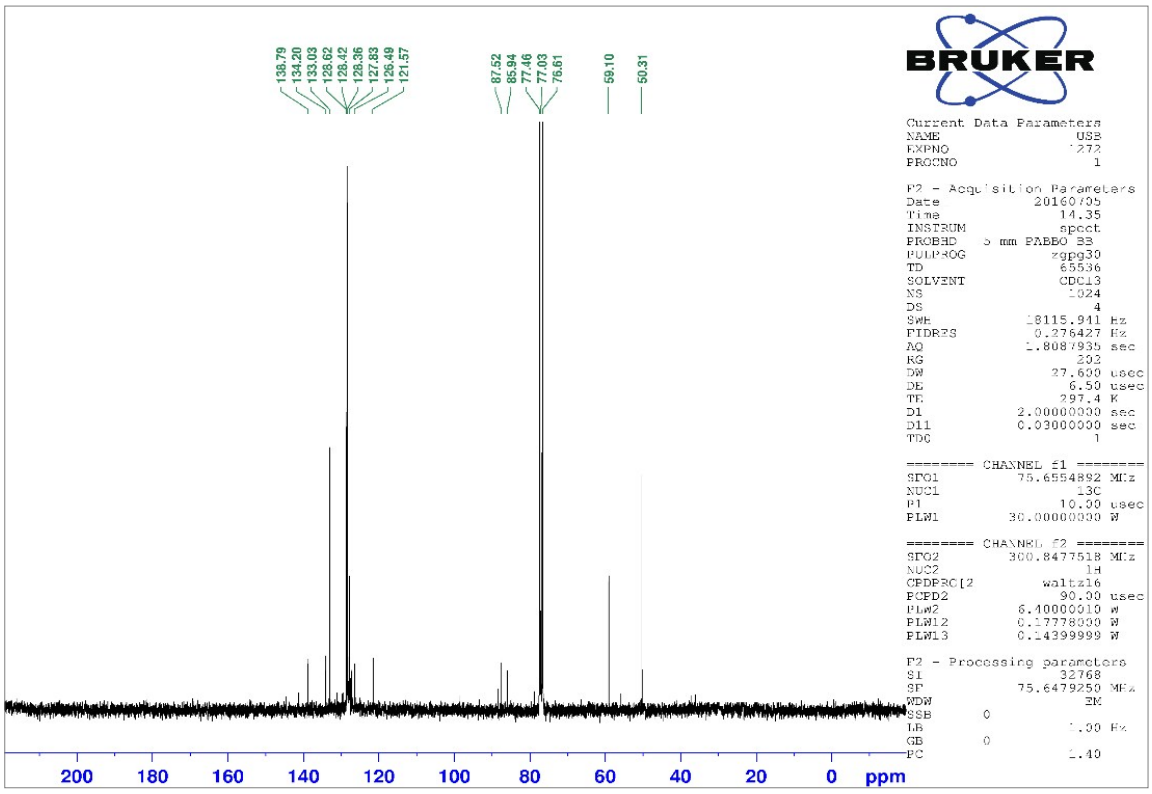
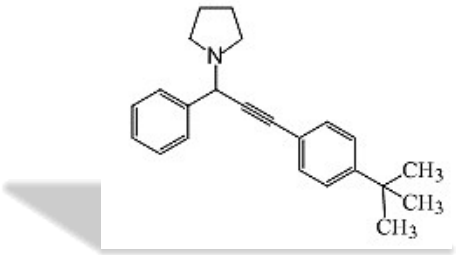


Figure 63: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 1-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4w**).

1-(3-(4-(*tert*-butyl) phenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4x**). Oily brown liquid; isolated yield: 90 %; FT-IR (neat): ν_{max}/cm^{-1} 3084, 3060, 3030, 2960, 2925, 2869, 2806, 2230, 2193, 1502, 1452, 1406, 1027, 737; ^1H NMR (300 MHz, $CDCl_3$): δ 7.53 (2H, d, J = 7.2 Hz, Ph), 7.37-7.34 (2H, m, Ph), 7.29-7.17 (5H, m, Ph), 4.87 (1H, s, CH), 2.65 (4H, br, $2CH_2$), 1.72 (4H, br, $2CH_2$), 1.23 (9H, s, $3CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.4, 139.2, 131.5, 128.4, 128.2, 127.6, 125.2, 120.1, 87.1, 85.6, 59.0, 50.1, 31.2, 29.7, 23.5; MS, *m/z* (%): 317(4%, M^+), 246(84%, M^+- pyrrollidine), 71(84%, pyrrollidine), 57(92%, $C(CH_3)_3$); Anal. Calcd for $C_{23}H_{27}N$: C, 87.02; H, 8.57; N, 4.41, Found: C, 86.06; H, 8.50; N, 3.94 %.



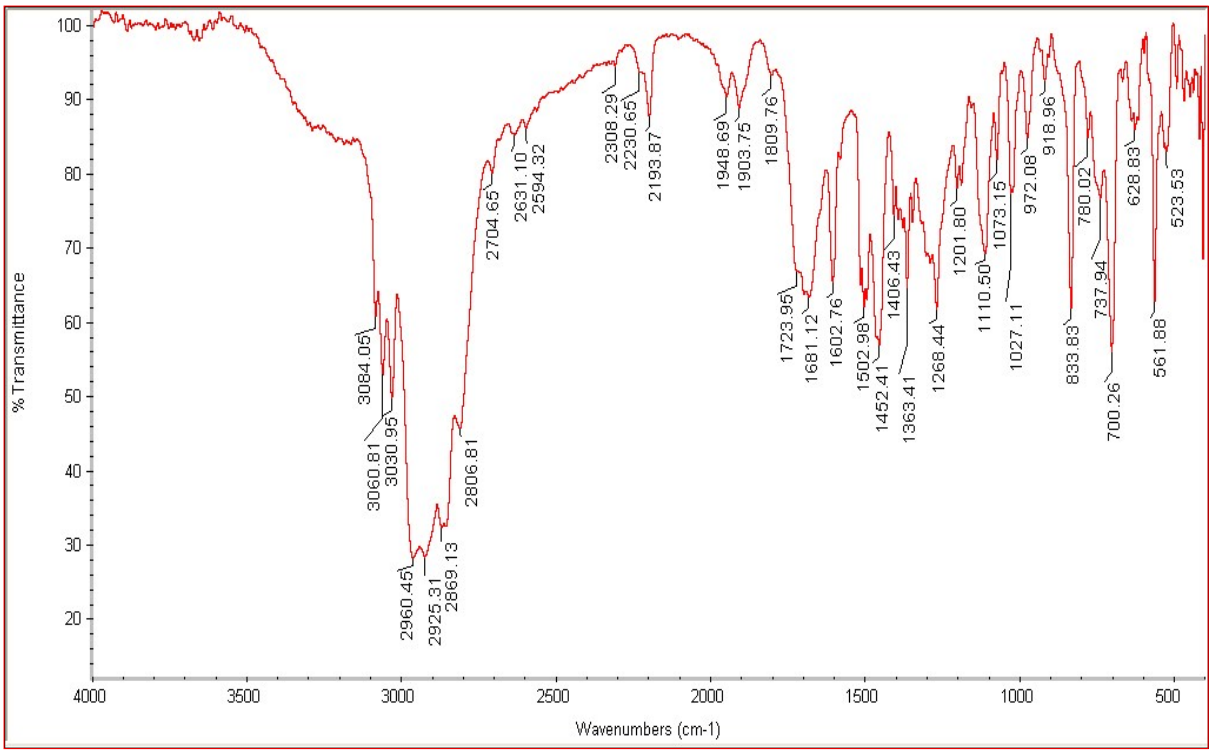


Figure 64: FT-IR (neat) spectrum of 1-(3-(4-(*tert*-butyl) phenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4x**).

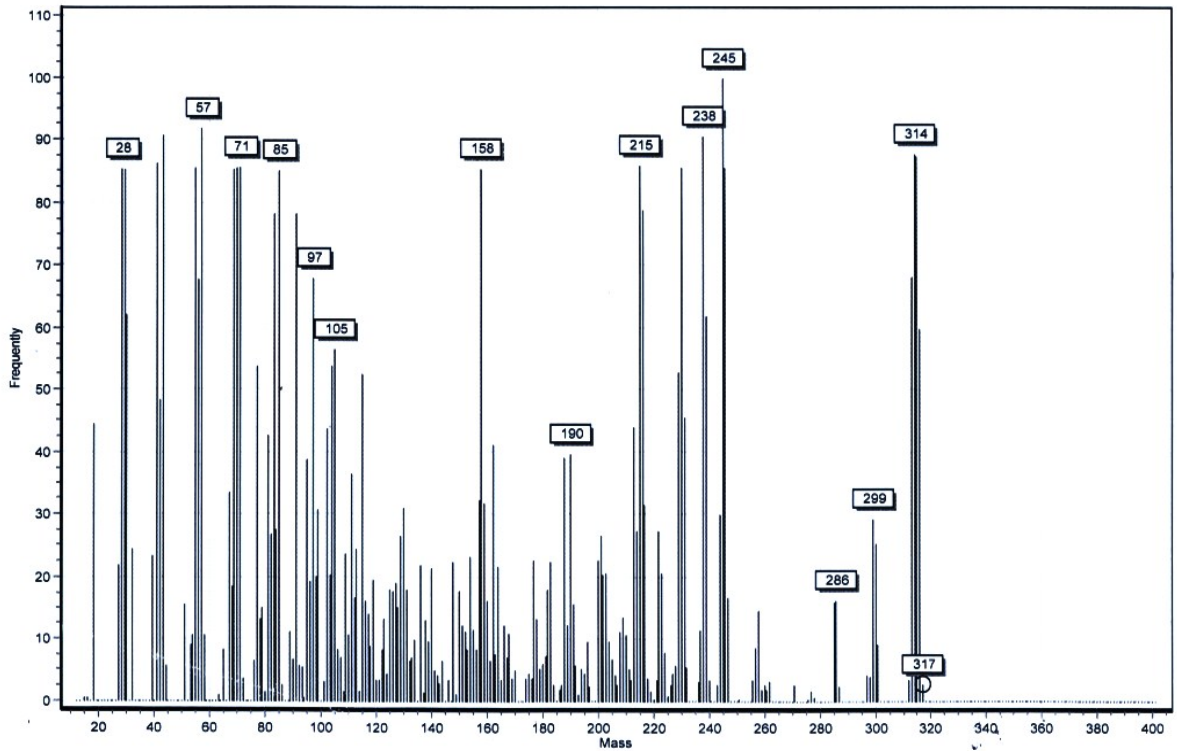


Figure 65: Mass spectrum of 1-(3-(4-(*tert*-butyl) phenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4x**).

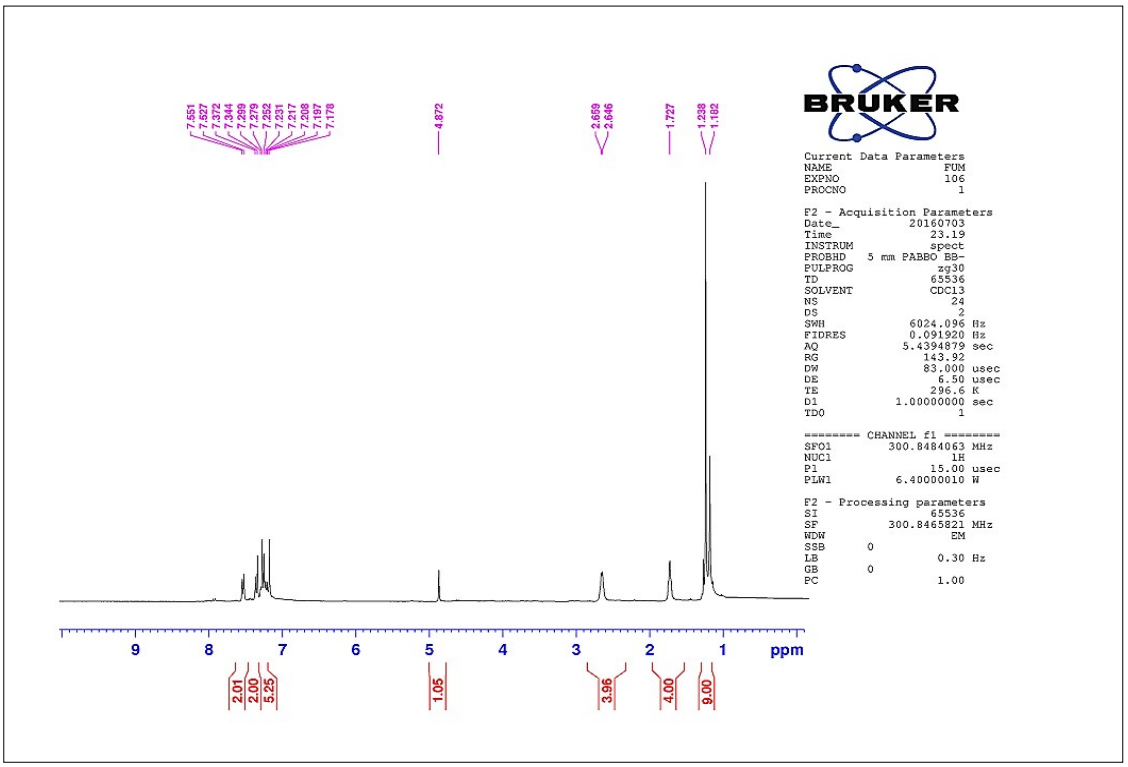


Figure 66: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 1-(3-(4-(*tert*-butyl) phenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4x**).

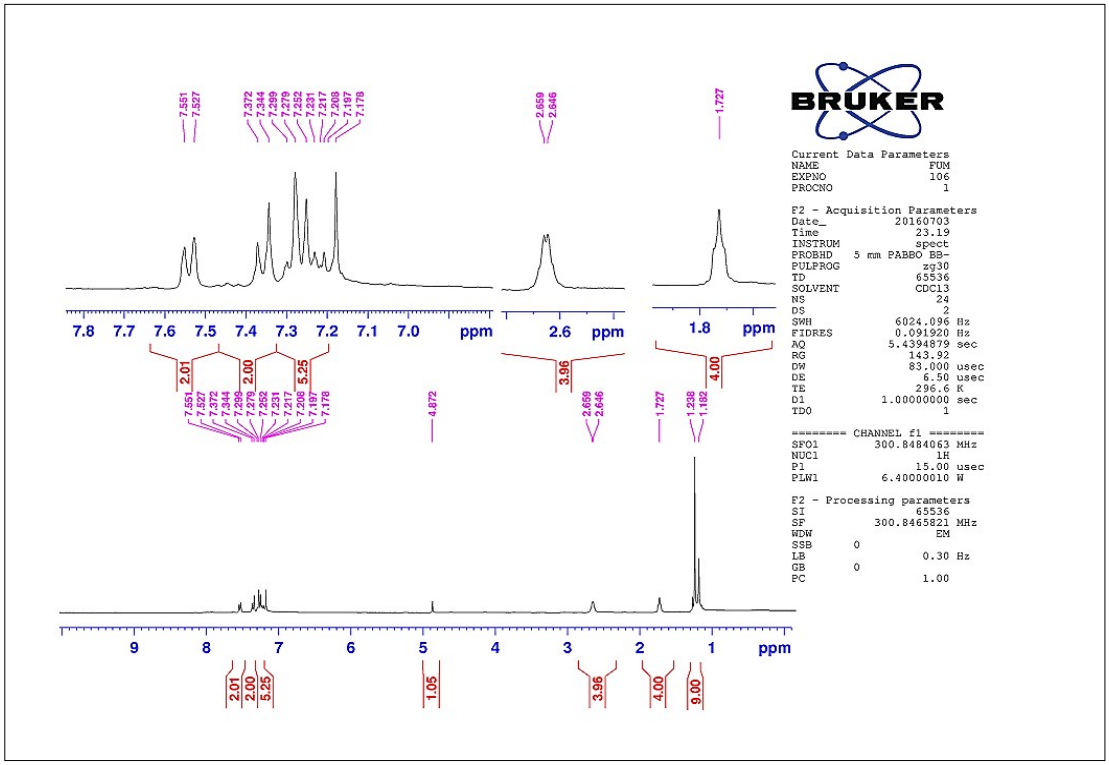


Figure 67: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 1-(3-(4-(*tert*-butyl) phenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4x**) expanded.

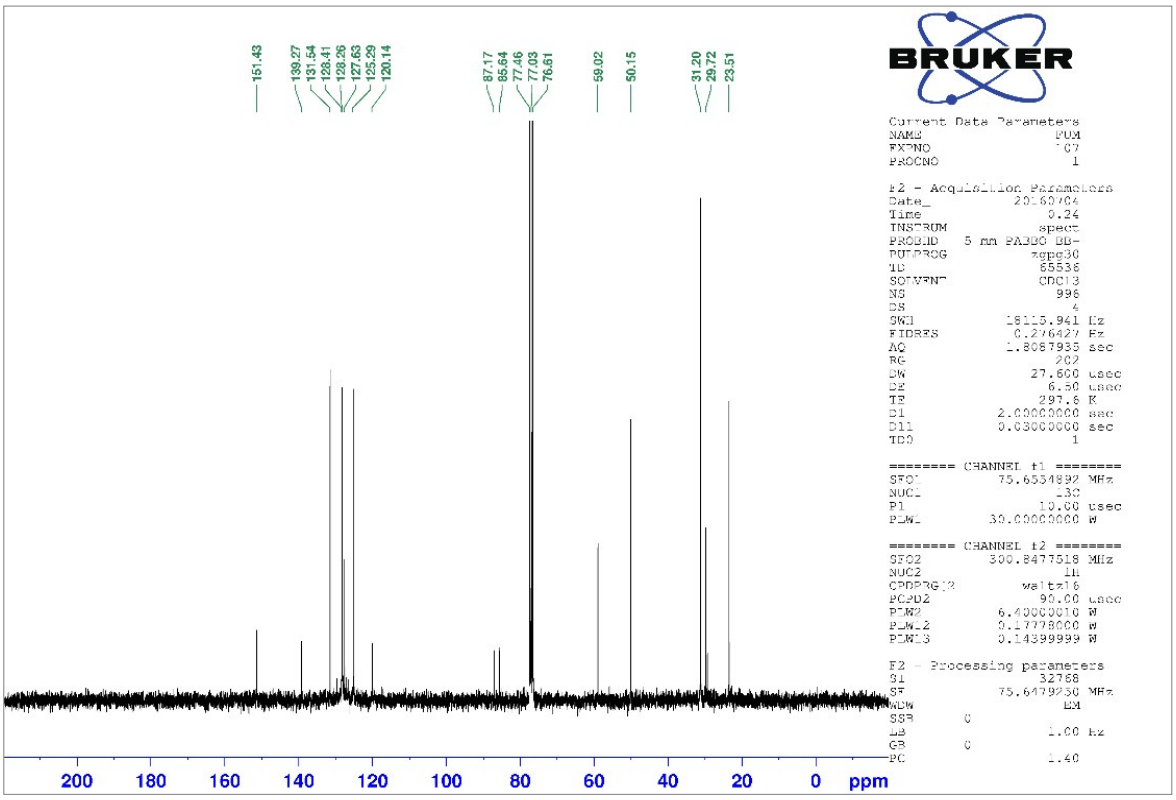


Figure 68: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 1-(3-(4-(*tert*-butyl) phenyl)-1-phenylprop-2-yn-1-yl)pyrrolidine (**4x**).

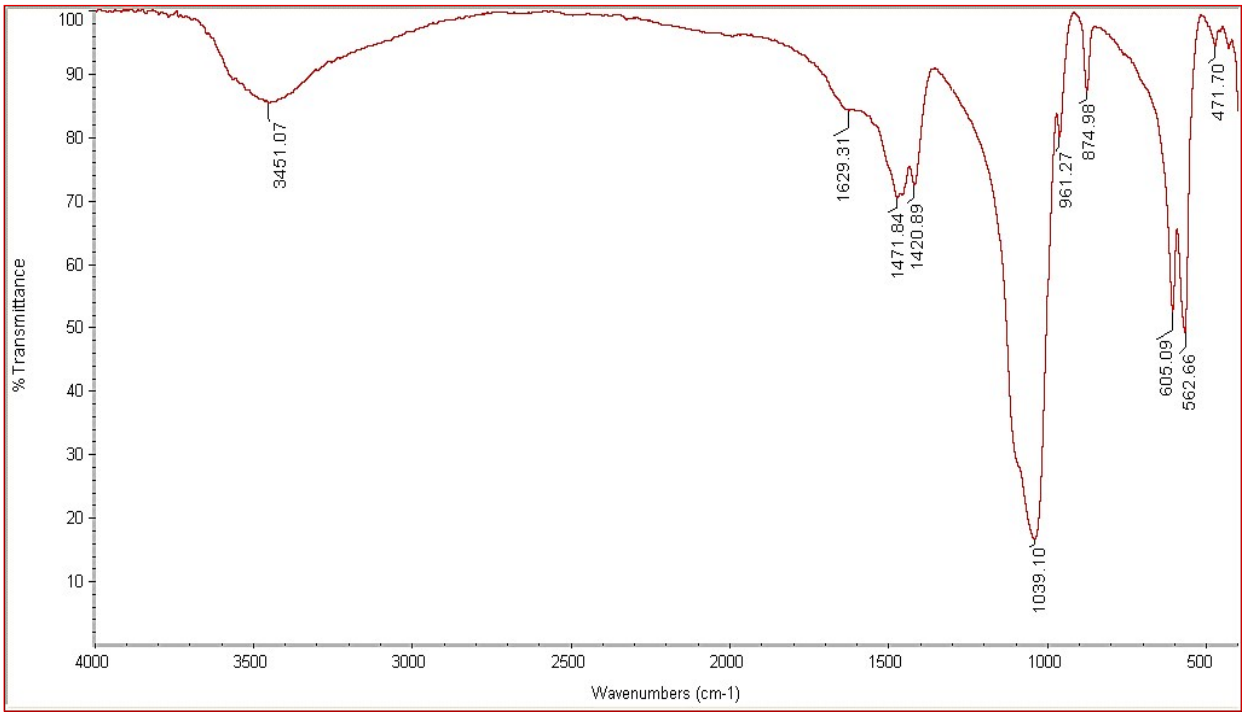


Figure 69: FT-IR spectrum of the bone ash (**I**).

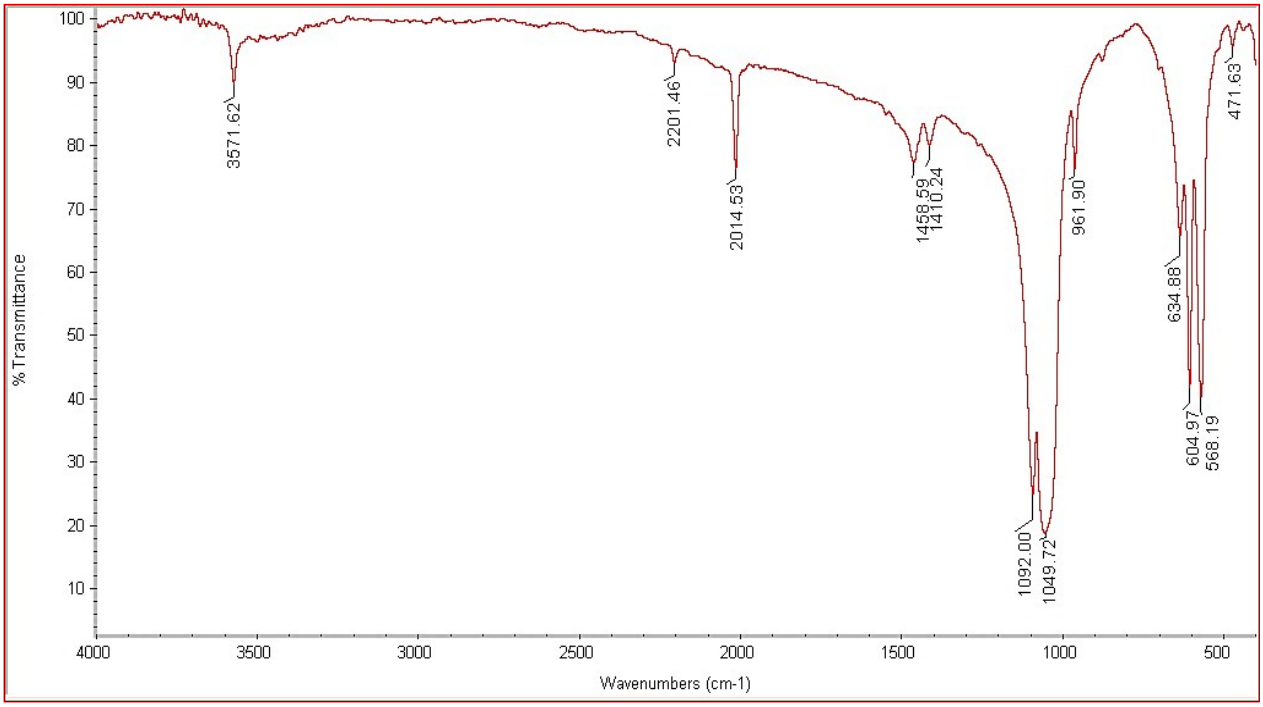


Figure 70: FT-IR spectrum of HAP (**II**).

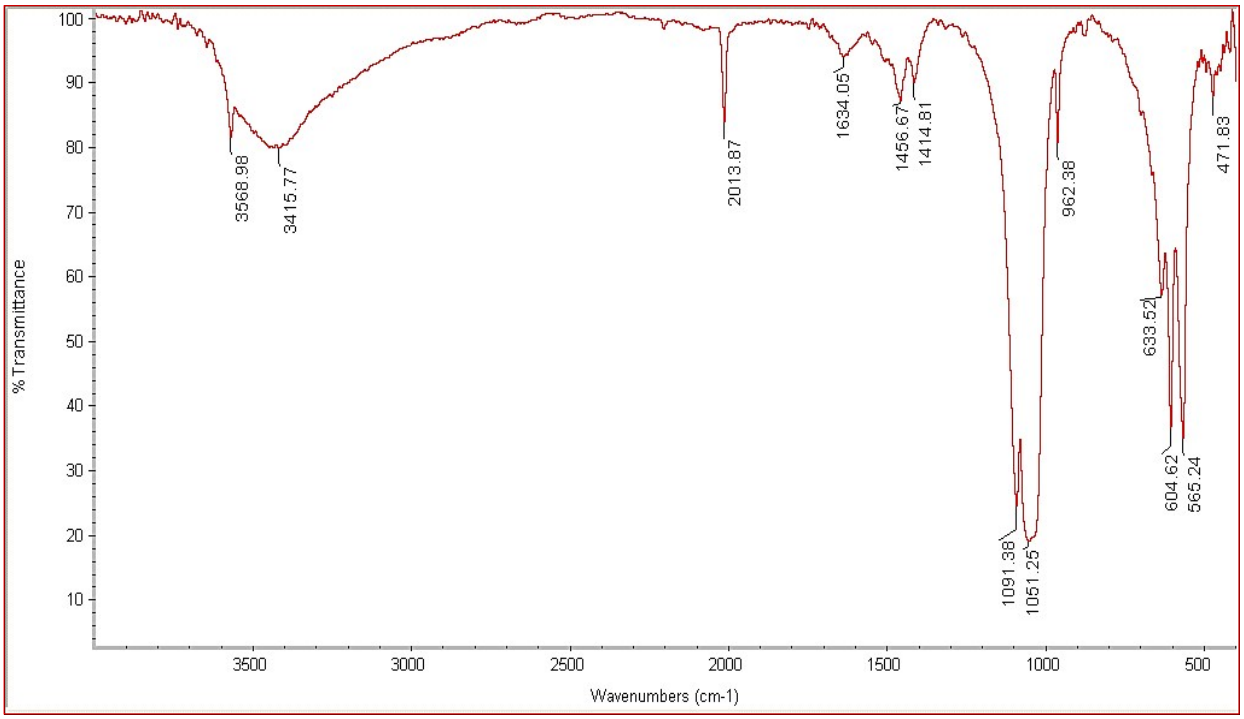


Figure 71: FT-IR spectrum of HAP/Fe_3O_4 (**III**).

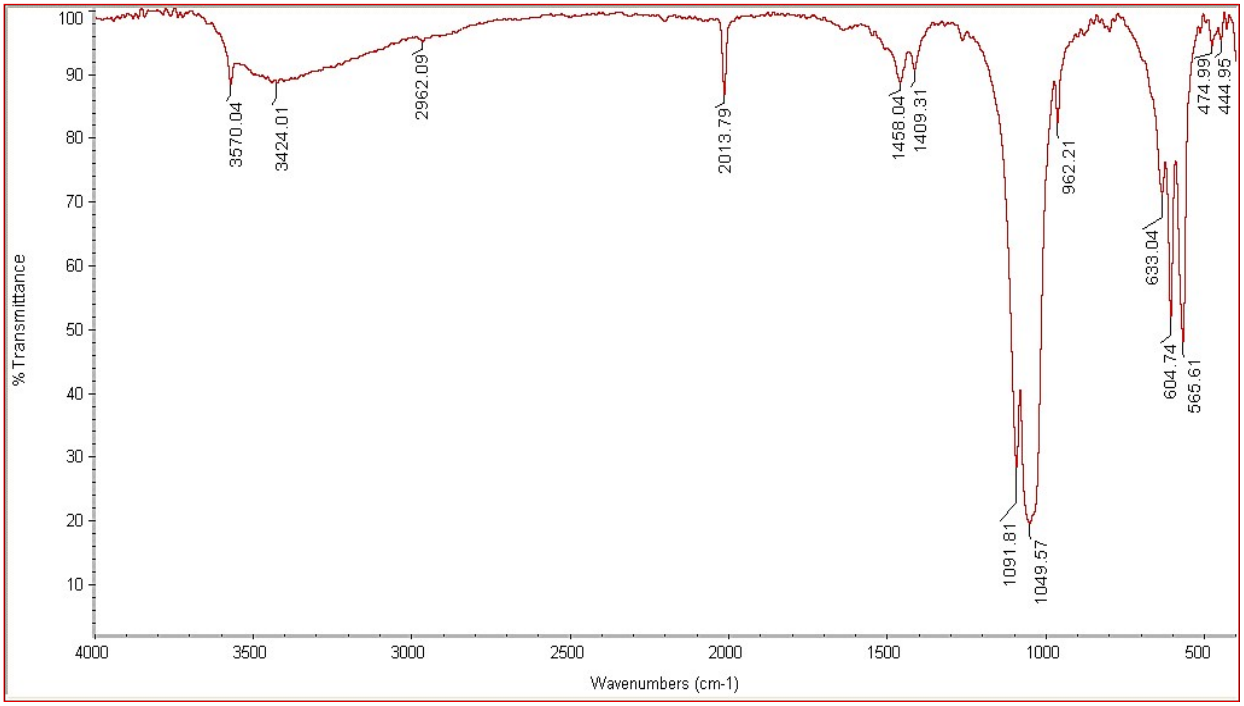


Figure 72: FT-IR spectrum of $Zn^{II}/HAP/Fe_3O_4$ (**IV**).

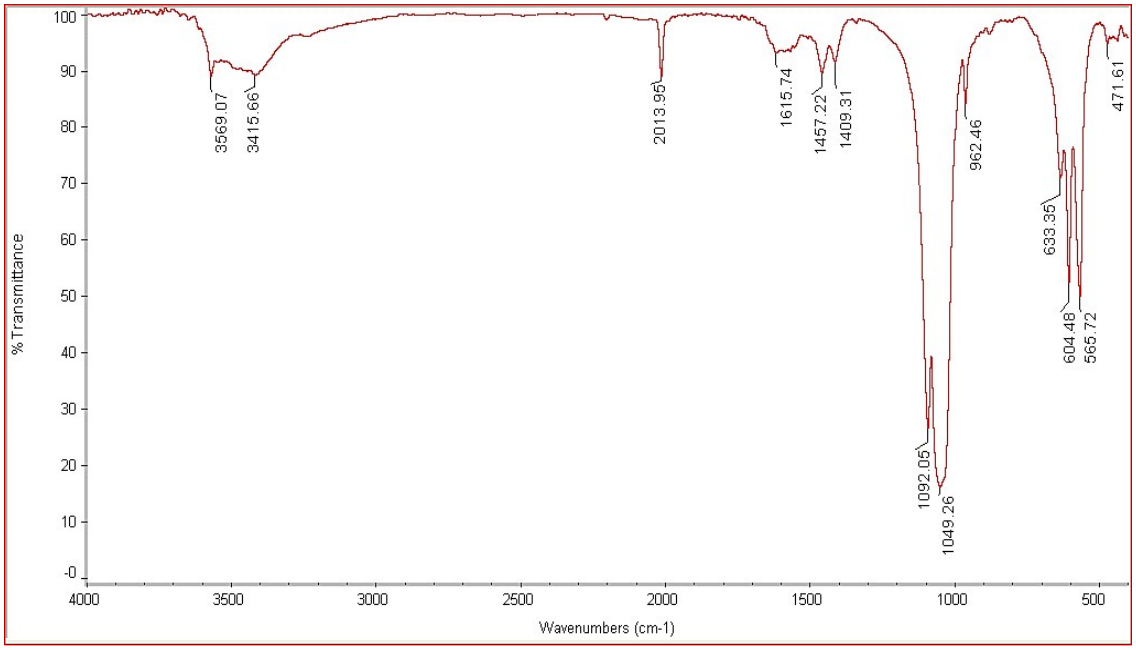


Figure 73: FT-IR spectrum of 7th reused $Zn^{II}/HAP/Fe_3O_4$ (**IV**).

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