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Supplementary Information

Cu-Ni bimetallic reusable catalyst for synthesis of propasrgylamines via multicomponent coupling reaction under solvent free conditions

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[A] Experimental Detail

Materials

All reagents were of analytical grade, purchased from M/S S. D. Fine Chemicals Pvt. Ltd. and used without further purification. All products were characterized IR, ^{1}HNMR, MS analysis.

Preparation of Cu-Ni bimetallic catalyst

An aqueous solution of Cu $(NO_3)_2.6H_2O$ (5 ml, 0.02M) and $Ni(NO_3)_2$ (5 ml, 0.02M) was stirred vigorously for 5 minutes to form homogonous solution and cooled to 10 °C. To this, an aqueous solution of $NaBH_4$ (1 ml, 4.0M) was added drop wise under inert atmosphere (by purging N_2 gas) with vigorous stirring. After completion of addition, the reaction mixture was stirred for another 5 min at 10 °C. The black precipitate formed was filtered and washed with deionized water, followed by ethanol and dried under vacuum at 100 °C.

Characterization of Cu-Ni bimetallic catalyst

The Cu-Ni catalyst was characterized by various techniques such as ICP, XRD, and SEM-EDAX. Isolated reaction products were characterized by ^{1}HNMR (400 MHz), and GC-MS techniques. Bulk composition of the catalyst was determined by ICP-AES (Varian AA240 analyzer). The shape and morphology were observed by Scanning Electron Microscopy (SEM). Surface composition was determined by energy dispersive X-ray analysis (EDAX). Both SEM and EDAX information were obtained using a FEI Quanta 200 ESEM FEG instrument. X-ray XRD patterns were recorded on a Bruker AXS diffractometer with Cu-Kα radiation (λ=1.540562A^0) over a 2ϴ range of 0-80 °C.

Inductive coupled plasma (ICP) analysis reveals the bulk composition of Cu-Ni was $Cu_{0.49}Ni_{0.51}$ which was also similar to that of precursor solution. Scanning electron microscopy (SEM) images fig-1(a) and (b) gives morphological information that the Cu/Ni present in the form of irregular, dense particles with extremely broad size distribution (<200 nm to >400 nm. (Figure 1(a) and 1(b)) The large particles are formed apparently due to agglomeration, as the reaction in between metallic ions and sodium borohydride is strongly exothermic.[1] Energy dispersive X-ray analysis (EDAX), (Figure 2) shows 48.5% of Cu and 51.5% of Ni as the surface composition, which is nearly the same as that of the bulk. XRD (Figure 3) pattern shows amorphous and random nature of the particles.[2] Recovered catalyst after fifth cycle was characterized by SEM, ICP ($Cu_{0.489}Ni_{0.511}$), EDAX (Cu-48.3% & Ni-51.7%) which is similar to freshly prepared catalyst and XRD shows no significant structural change and leaching of metals in catalyst. (Figure 6, 7, 8)

Figure. 1 (a) SEM images of Cu-Ni bimetallic catalyst

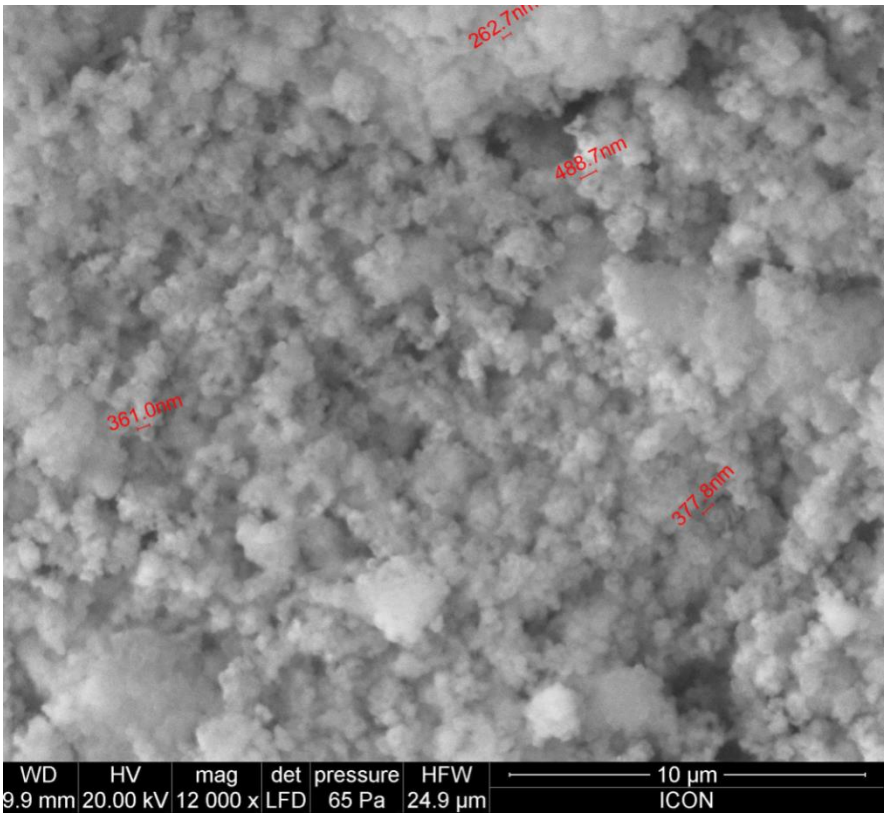


Figure 1(b) SEM images of Cu-Ni bimetallic catalyst

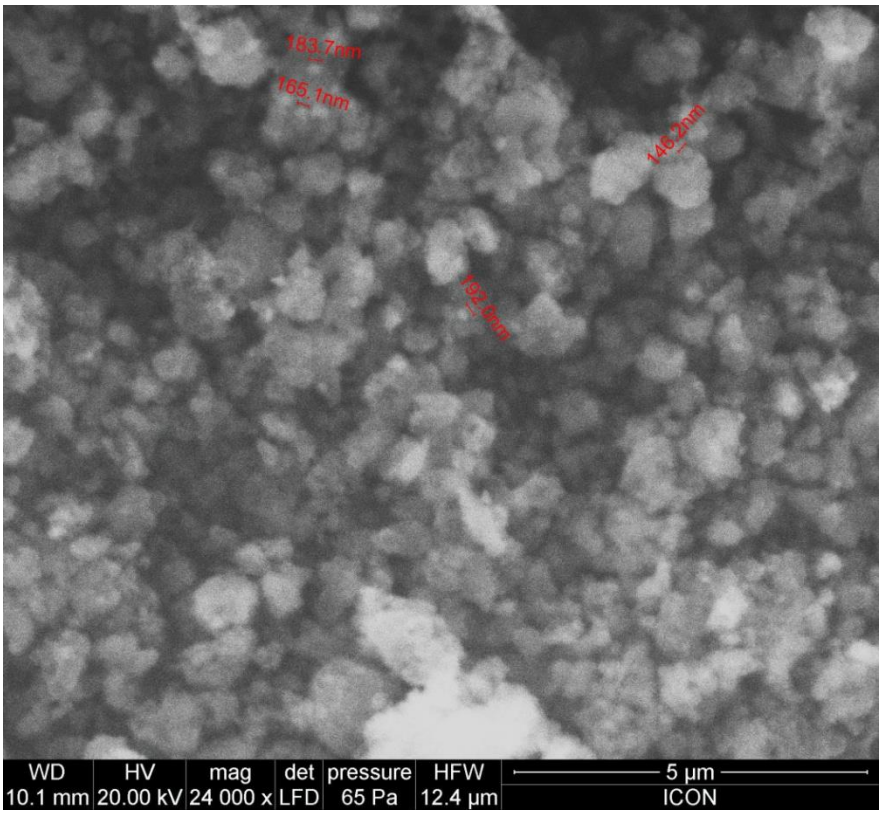


Figure 2. EDAX of Cu-Ni bimetallic catalyst

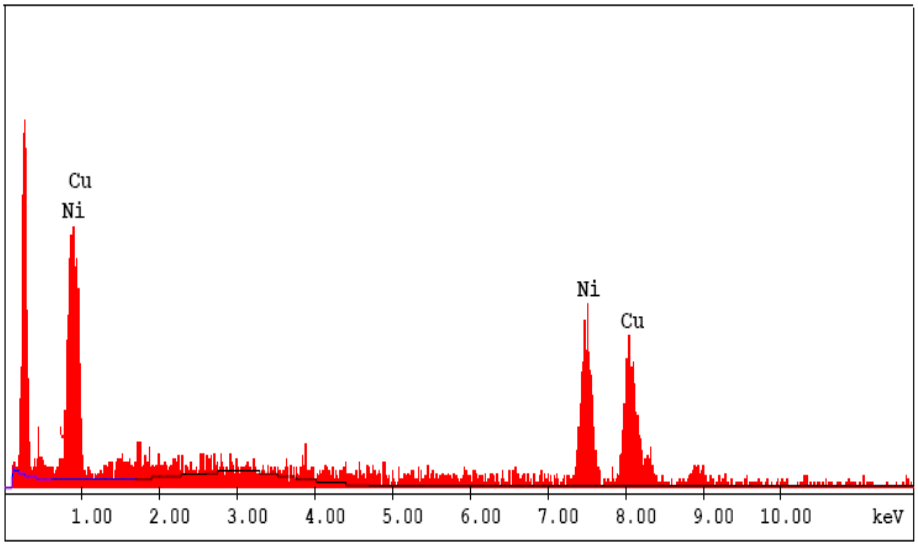


Figure 3. XRD of Cu-Ni bimetallic catalyst

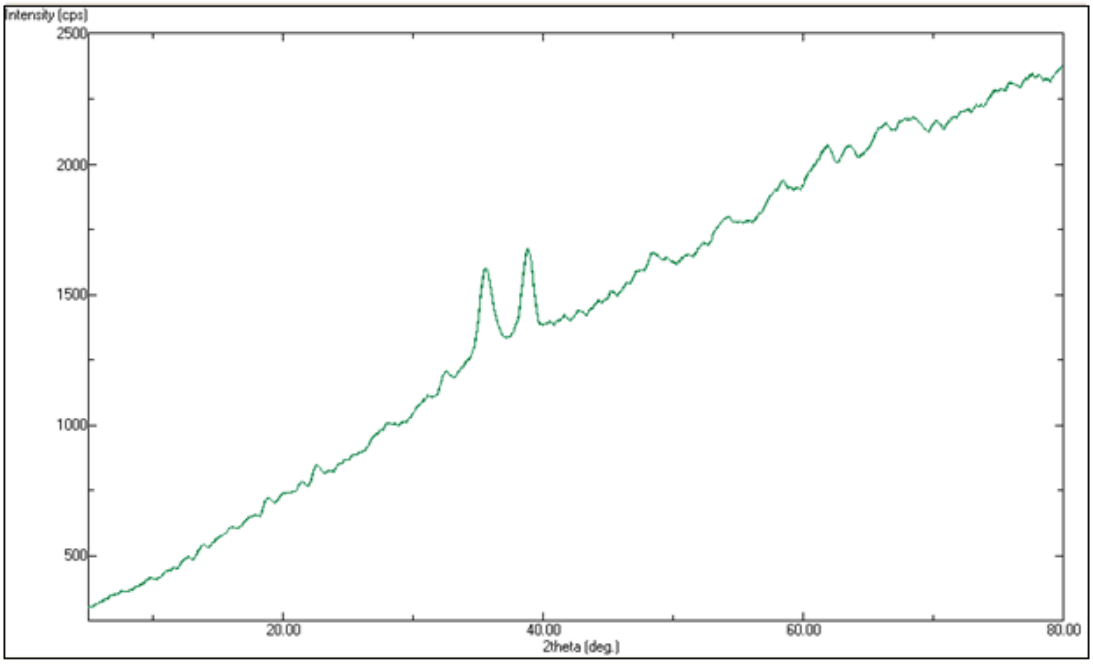


Figure. 5 a. Cu-Ni bimetallic catalyst suspended in ethyl acetate after reaction complettion; **5 b.** Cu-Ni bimetallic catalyst was collected by magnetic bar.

5a 5b

Figuer. 6 SEM image of recovered catalyst after 5th cycle

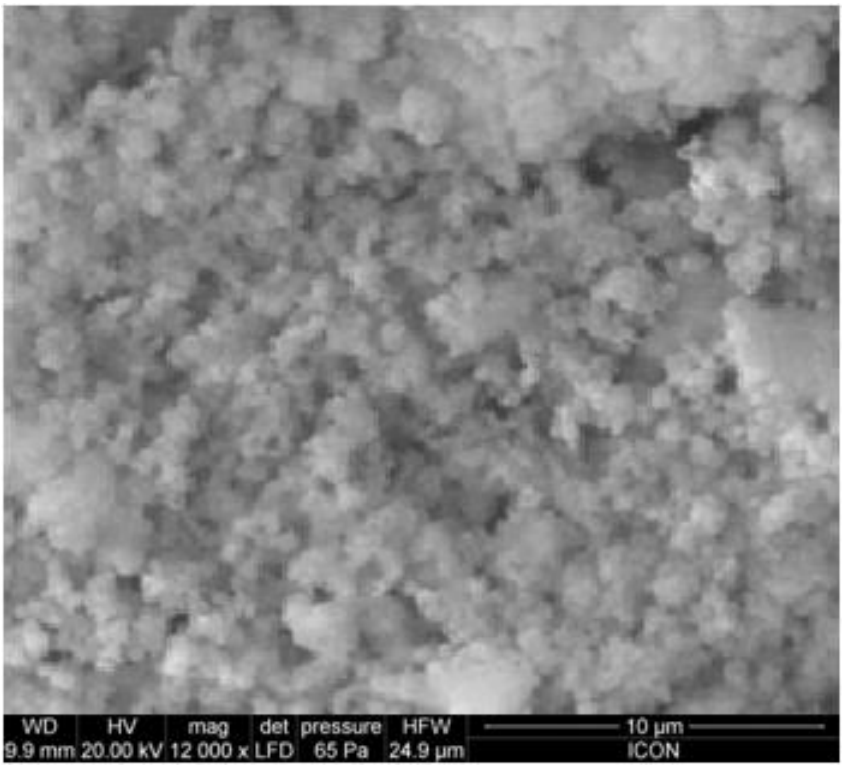


Figure. 7 EDAX of recovered catalyst after 5th cycle

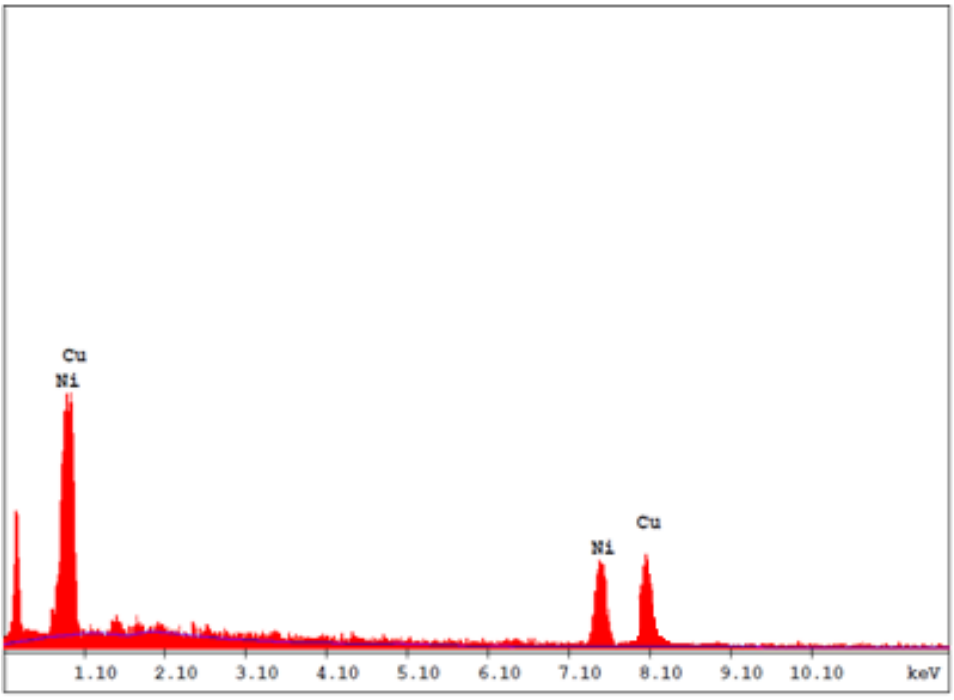
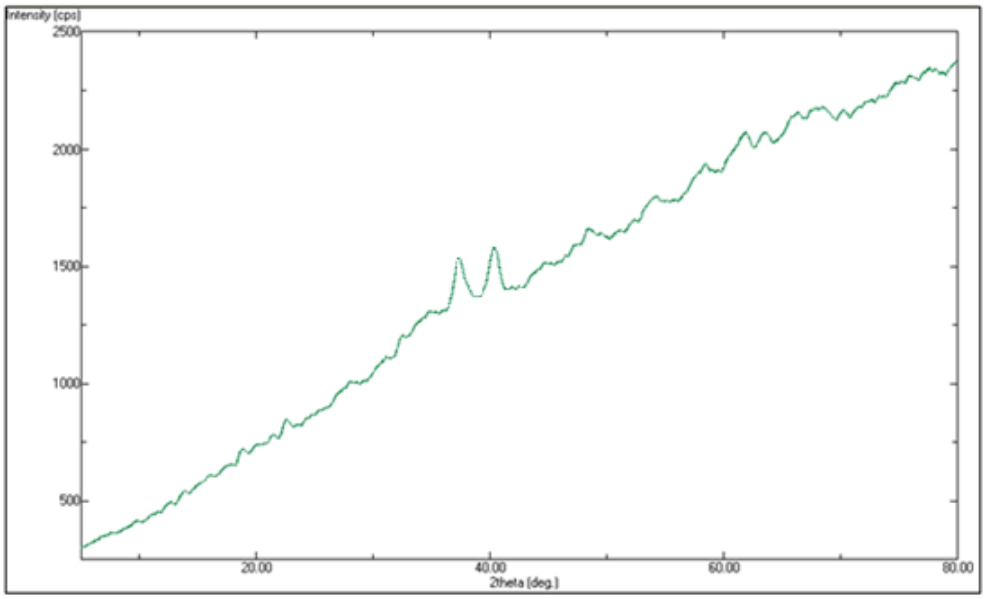


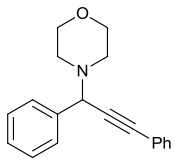
Figure. 8 XRD of recovered catalyst after 5th cycle



General process for the synthesis of 4-(1,3-diphenylprop-2-yn-1-yl)morpholine (1a).
In experiment, benzaldehyde (1.0 mmol), morpholine (1.1 mmol), phenylacetylene (1.2 mmol) and Cu-Ni (1:1) catalyst (20 wt%) was added and reaction was heated under stirring at 90 °C for 3h, reaction was monitored on GC (perkin elmer equipped with a 30 m capillary column). After complete reaction, reaction mass was diluted by ethyl acetate and catalyst was recovered by magnet and washed by ethyl acetate, product was concentrated under vacuum and purified by column chromatography, product was analyzed by IR,^{1}HNMR and GC-MS. For the recycling test, the recovered catalyst was further washed with ethanol followed by acetone.

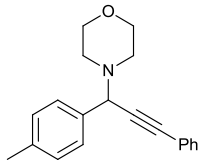
[B] Analytical Data

Entry 1) 4-(1,3-diphenylprop-2-yn-1-yl)morpholine



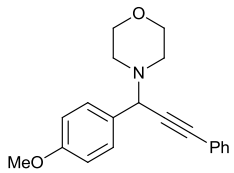
Yield: 93%, light yellow solid, Mp 51-53 °C (lit[3] 52-53 °C). **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.67-7.66 (d, J= 7.2 Hz, 2H), 7.56-7.53 (m, 2 H), 6.59-6.55 (m, 2 H), 5.89-5.75 (m, 1 H), 5.12-5.06 (m, 2 H), 3.36-3.34 (m, 1 H), 2.32-2.26 (m, 2H), 1.65-1.47 (m, 2H), 0.95-0.93 (t, 3 H). δ7.67 (d, J= 7.2 Hz, 2H), 7.56-7.54 (m, 2H), 7.42-7.32 (m, 6H), 4.83 (s. 1H), 3.87-3.73 (m, 4H), 2.67 (br, 4H); **MS** (m/z/rel.int.): 277(M^+): 56(22.4), 86(18.6), 191(100), 277(15.1).

Entry 2) 4-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)morpholine



Yield: 80%, yellow solid, Mp 80-81 °C (lit[3] 79-80 °C), **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.60-7.58 (m, 4H), 7.40-7.37 (m, 3H), 7.26-7.24 (d, *J*= 8 Hz, 2H), 4.82 (s,1H), 3.84-3.79 (m, 4H), 2.74-2.69 (m, 4H), 2.43 (s, 3H); **MS** (m/z/rel.int.): 292.17 (M^+) (21.9%), 56(22.4), 86(18.6), 191(100), 277(15.1).

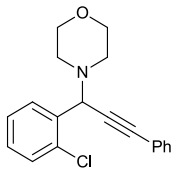
Entry 3) 4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)morpholine



Yield: 83%, yellow solid, Mp 87-89 °C (lit[4] 89-90 °C), **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.68-7.66 (d, J= 7.6 Hz, 2H), 7.50-7.48 (d, J= 8.8 Hz, 2H), 7.42-7.29 (m, 3H), 6.91-6.89

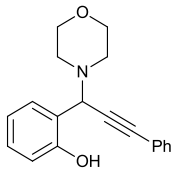
(d, J=8.8 Hz, 2H), 4.81 (s, 1H), 3.85 (s, 3H), 3.79-3.76 (m, 4H), 2.67 (s, 4H); **MS** (m/z/rel.int.): 307(M^+): 56(9.9), 86(14.4), 178(10.7), 200(24.6), 221(100), 307(7.3).

Entry 4) 4-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl)morpholine



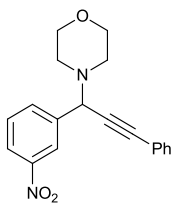
Yield: 85%, yellow solid, Mp 94-96 °C (lit[4] 95-97 °C), **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.82-7.80 (d, J= 7.6, 1H), 7.56-7.55 (m, 2H), 7.46-7.44 (d, J= 7.2 Hz, 1H),7.38-7.27 (m, 5H), 5.18 (s, 1H), 3.79-3.71 (m. 4H), 2.74-2.71 (t, 4H); **MS** (m/z/rel.int.): 311(M^+): 56(50.5), 86(32.9), 189(36.3), 200(57.8), 225(100), 311(14.7).

Entry 5) 2-(1-morpholino-3-phenylprop-2-yn-1-yl)phenol



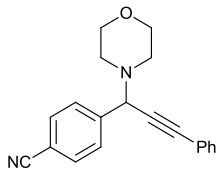
Yield: 78%, yellow solid, Mp 96-97 °C (lit[3] 96-98 °C), **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 10.80 (s, 1H), 7.57-7.53 (m, 3H), 7.37-7.35 (m, 3H), 7.26-7.21 (m, 1H), 6.85-6.90 (m, 2H), 5.08 (s, 1H), 3.79 (s, 4H), 2.78 (s, 4H); **MS** (m/z/rel.int.): 293(M^+): 77(13.5), 158(14.7), 178(10.7), 202(13.5), 234(84.5), 293(100).

Entry 6) 4-(1-(3-nitrophenyl)-3-phenylprop-2-yn-1-yl)morpholine



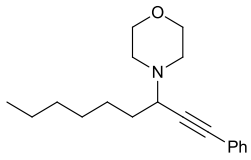
Yield: 85%, orange solid, Mp 101-103 °C (lit[3] 102-103 °C); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 8.56 ppm (s, 1H), 8.20-8.18 (d, J= 8.0 Hz, 1H), 8.03-8.06 (d, J= 8.0 Hz, 1H), 7.60-7.55 (m, 3H), 7.40-7.37 (m, 3H), 4.91 (s, 1H), 3.83-3.75 (m, 4H), 2.73-2.65 (m, 4H); **MS** (m/z/rel.int): 322(M^+): 56 (88.2), 86 (46.1), 189 (68.8), 200 (90.3), 236 (100), 264 (16.7), 291 (16.0), 322 (23.7).

Entry 7) 4-(1-morpholino-3-phenylprop-2-yn-1-yl)benzonitrile



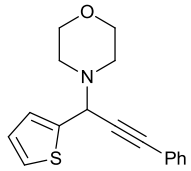
Yield: 90%, yellow solid, Mp 91-93 °C (lit[5] 94-95 °C); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.55-7.53 (d, J= 8.0 Hz, 2H), 7.50-7.48 (d, J= 8.0 Hz, 2H), 7.43-7.39 (m, 5H), 4.95 (s, 1H), 3.80-3.72 (m, 4H), 2.71-2.63 (m, 4H); **MS** (m/z/rel.int): 303(M^+): 56 (88.2), 86 (46.1), 189 (68.8), 200 (90.3), 236 (100), 264 (16.7), 291 (16.0), 322 (23.7).

Entry 8) 4-(1-phenylnon-1-yn-3-yl)morpholine



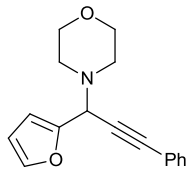
Yield: 78%, yellow solid, Mp 51-53 °C (lit[4] 52-53 °C), **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.46 (m, 2H), 7.32-7.29 (d, J= 11.6 Hz, 3H), 3.79 (brs, 4H), 3.53-3.50 (s, 1H), 2.77 (brs, 2H), 2.61 (brs, 2H), 1.75-1.73 (m, 2H), 1.58-1.51 (m, 2H), 1.34-1.29 (m, 6H), 0.92 (br, 3H); **MS** (m/z/rel.int): 286(M^+): 56 (88.2), 86 (46.1), 189 (68.8), 200 (90.3), 236 (100), 264 (16.7), 291 (16.0), 322 (23.7).

Entry 9) 4-(3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-yl)morpholine



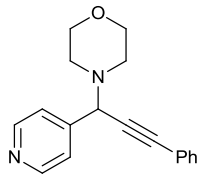
Yield: 95%, brown solid, Mp 74-76 °C (lit[6] 75-77 °C); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.57-7.54 (m, 2H), 7.38-7.37 (m, 3H), 7.33-7.32 (d, J= 5,2 Hz, 1H), 7.29-7.28 (d, J= 5,2 Hz, 1H), 7.02-7.00 (d, J=5.2 Hz, 1H), 5.04 (s, 1H), 3.84-3.75 (m, 4H), 2.78-2.67 (m, 4H); **MS** (m/z/rel.int): 283(M^+): 56(12.4), 86(9.7), 152(8.5), 197(100), 283(15.8).

Entry 10) 4-(1-(furan-2-yl)-3-phenylprop-2-yn-1-yl)morpholine



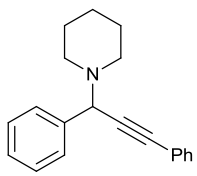
Yield: 93%, yellow solid, Mp 69-71 °C (lit[6] 72-73 °C); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.54-7.51 (m, 2H),7.43 (brs, 1H), 7.37-7.36 (m, 3H), 6.55-6.54 (d, J= 2.8 Hz, 1H), 6.40-6.38 (m, 1H), 4.91 (s, 1H), 3.85-3.76 (m, 4 H), 2.73-2.66 (m, 4H); 7**MS** (m/z/rel.int): 283(M^+): 56(12.4), 86(9.7), 152(8.5), 197(100), 283(15.8).

Entry 11) 4-(3-phenyl-1-(pyridin-4-yl)prop-2-yn-1-yl)morpholine



Yield: 90%, brown solid, Mp 86-88 °C (lit[4] 85-87 °C); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.70-7.68 (d, J=7.6 Hz, 2H), 7.58-7.56 (m, 2H), 7.43-7.29 (m, 6H), 4.85 (s, 1H), 2.63-2.61 (m, 4H), 1.69-1.63 (m, 4H), 1.51-1.48 (m, 2H); 7**MS** (m/z/rel.int): 279(M+): 51(48.9), 77(64.5), 103(87.1), 131(88.4), 208(100), 279(1.8).

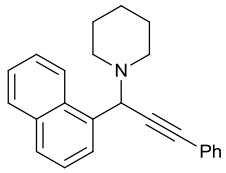
Entry 12) 1-(1,3-diphenylprop-2-yn-1-yl)piperidine



Yield: 90%, yellow solid, Mp 63-65 °C (lit[4] 64-65 °C); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.54-7.52 (d, J= 8.0 Hz, 2H), 7.63-7.57 (M, 2H), 7.43-7.40 (m, 3H), 7.30-7.28 (d, J= 8.0

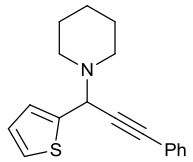
Hz, 1H), 4.31 (s, 1H), 3.80-3.73 (m, 4 H), 2.71-2.63 (m, 4H); **MS** (m/z/rel.int): 275(M^+): 115(16.5), 191(100), 198(84.9), 275(20.8).

Entry 13) 1-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl)piperidine



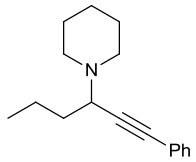
Yield: 82%, yellow solid, Mp 51-53 °C (lit[3] 52-53 °C); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 8.58-8.56 (d, J= 8.4 Hz, 1H), 8.12-8.10 (d, J= 7.2 Hz, 1H), 8.00-7.99 (d, J= 8 Hz, 1H), 7.95-7.93 (d, J= 8.4 Hz, 1H), 7.73-7.58 (m, 5H), 7.49-7.46 (m, 3H), 5.60 (s, 1H), 2.82-2.80 (m, 4H), 1.74-1.39 (m, 6H) **MS** (m/z/rel.int): 275(M^+): 115(16.5), 191(100), 198(84.9), 275(20.8).

Entry 14) 1-(3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-yl)piperidine



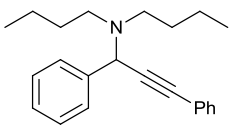
Yield: 88%, yellow solid, Mp 34-35 °C (lit[4] 52-53 °C), **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.58-7.55 (m, 2H), 7.38-7.37 (m, 3H), 7.33-7.27 (m, 2H), 7.02-7.00 (d, *J*=8.6 Hz, 1H), 5.03 (s, 1H), 2.72-2.65 (m, 4H), 1.73-1.62 (m, 4H), 1.53- 1.50 (m, 2H); **MS** (m/z/rel.int): 275(M^+): 115(16.5), 191(100), 198(84.9), 275(20.8).

Entry 15) 1-(1-phenylhex-1-yn-3-yl)piperidine



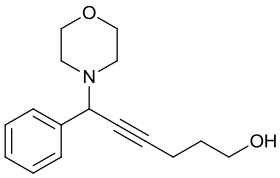
Yield: 85%, yellow solid, Mp 50-52 °C (lit[4] 52-53 °C); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.56-7.51 (m, 2H), 7.41-7.37 (m, 3H), 3.73 (m, 1H), 2.51-2.45 (m, 4H), 1.63-1.58 (m, 2H), 1.53- 1.47 (m, 6H), 0.95- 0.92 (m, 3H); **MS** (m/z/rel.int): 240(M^+): 115(17.3), 198(100), 240(2.1).

Entry 16) *N*-butyl-N-(1,3-diphenylprop-2-yn-1-yl)butan-1-amine



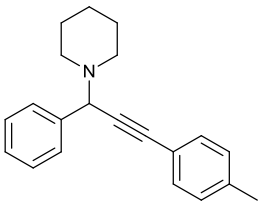
Yield: 85%, brown solid, Mp 57-58 °C (lit[7] 59-60 °C), **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.62-7.55 (m, 4H), 7.45-7.40 (m, 3H), 7.33-7.27 (m, 3H), 4.87 (m, 1H), 2.49-2.45 (m, 4H), 1.39-1.36 (m, 4H), 1.31- 1.27 (m, 4H), 0.93- 0.89 (m, 3H); **MS** (m/z/rel.int.): 276(M^+): 188(9.1), 191(100), 276(18.4).

Entry 17) 6-morpholino-6-phenylhex-4-yn-1-ol



Yield: 87%, yellow solid, Mp 46-47 °C (lit[8] 47-49 °C); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.58-7.52 (m, 2H), 7.33-7.26 (m, 3H), 4.92 (m, 1H), 3.94 (brs, 1H), 3.82-3.75 (m, 4H), 3.49-3.44 (m, 2H), 2.69-2.66 (m, 4H), 1.91- 1.85 (m, 4H), 1.63- 1.56 (m, 2H); **MS** (m/z/rel.int.): 259(M^+): 56(64.9), 86(57), 115(39..6), 129(47.7), 155(26.5), 182(100), 200(10.9), 259(16.9)**.**

Entry 18) 1-(1-phenyl-3-(*p*-tolyl)prop-2-yn-1-yl)piperidine

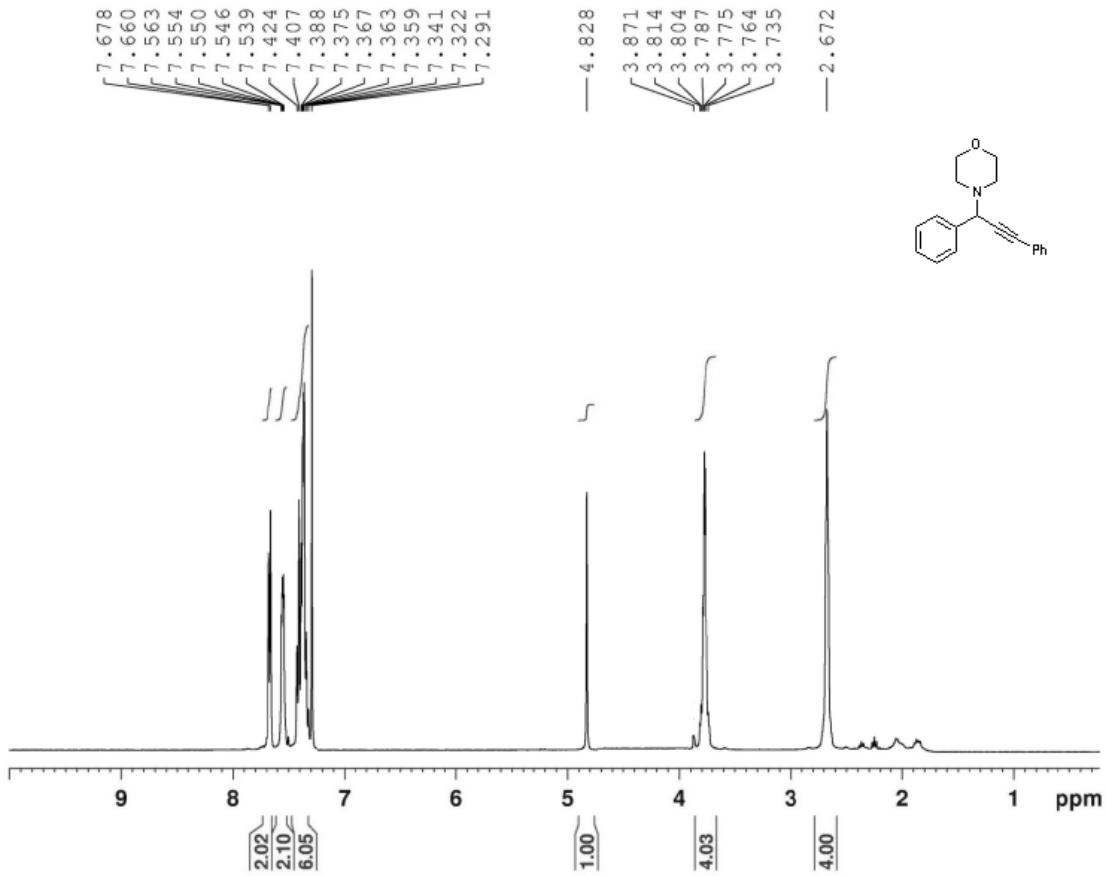


Yield: 85%, yellow solid, Mp 58-60 °C (lit[8] 47-49 °C); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si) δ= 7.63-7.61 (m, 2H), 7.53 (br, 2H), 7.43-7.40 (m, 3H), 7.35 (t, 1H), 7.20 (d, 1H), 4.85 (s, 1H), 2.69-2.66 (m, 4H), 2.48 (s, 3H), 1.72-1.68 (m, 4H), 1.56-1.37 (m, 2H); **MS** (m/z/rel.int.): 289(M^+): 128(16.5), 205(100), 212(84.9), 289(20.8)

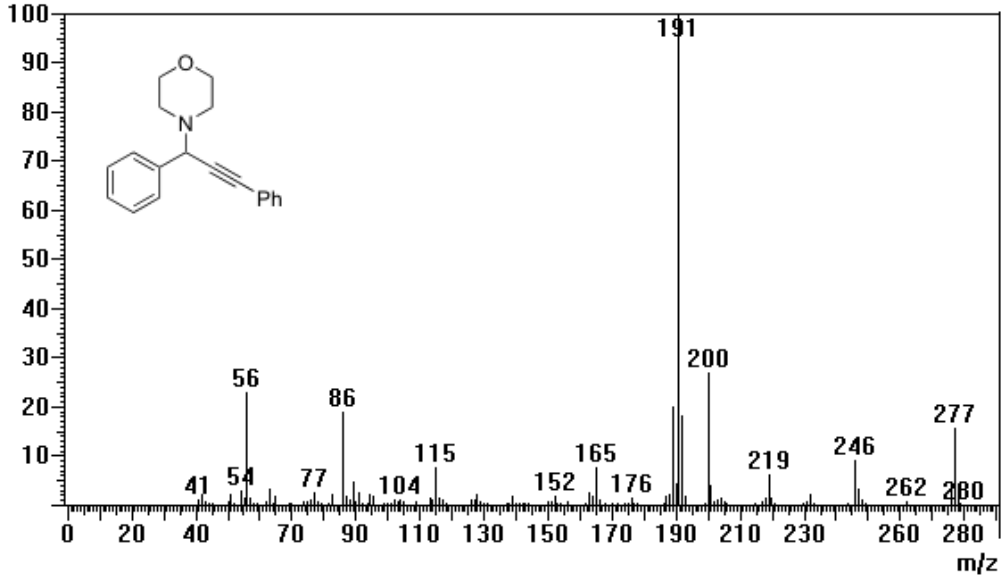
[C] Spectral Copies of ^{1}HNMR and MS

1. 4-(1,3-diphenylprop-2-yn-1-yl)morpholine

^{1}H NMR:

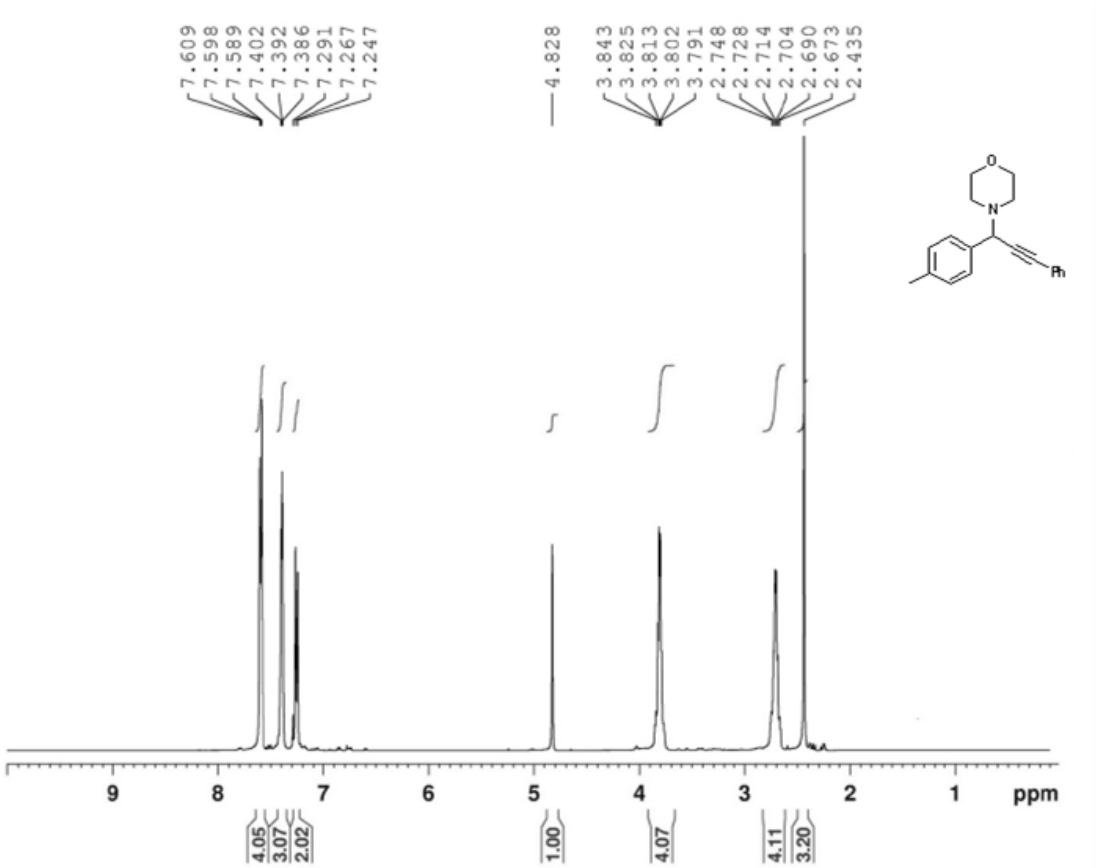


MS:



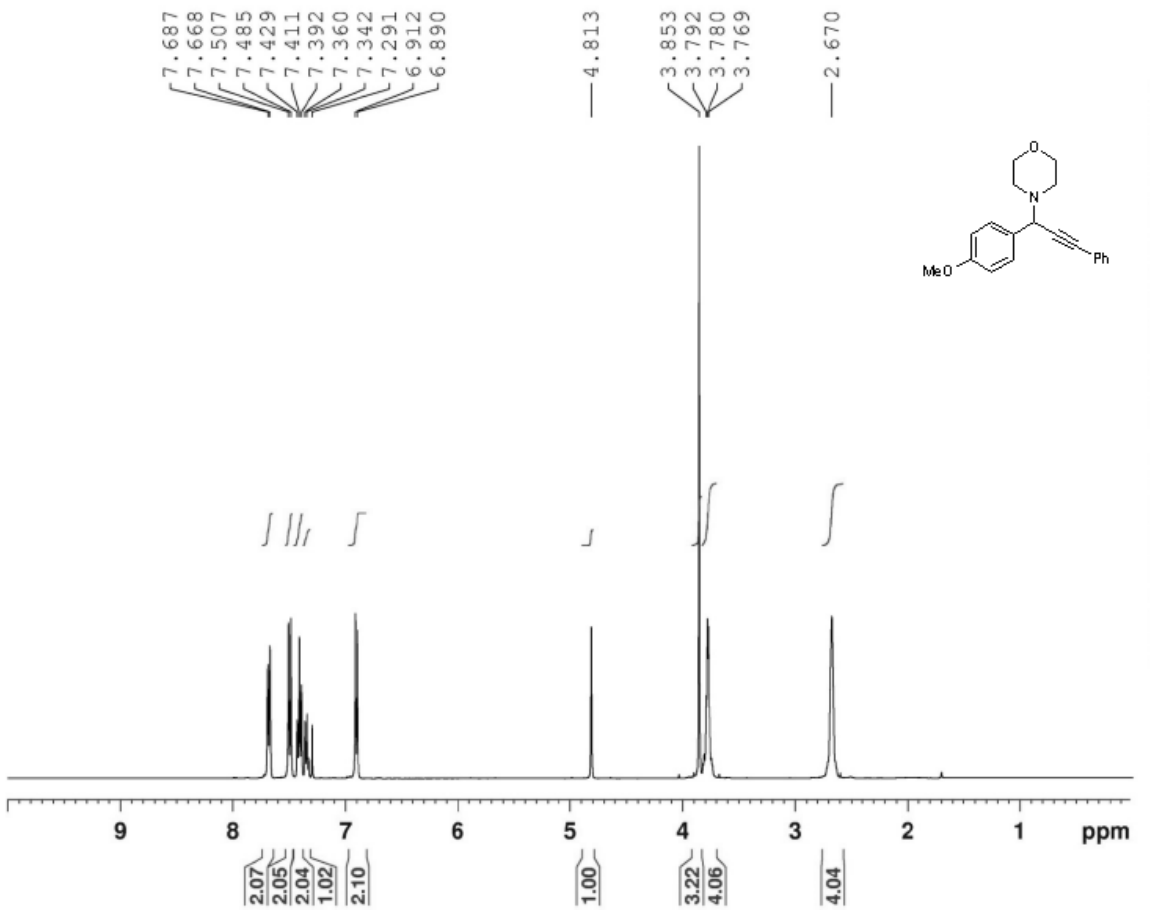
Entry 2) 4-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)morpholine

^{1}HNMR

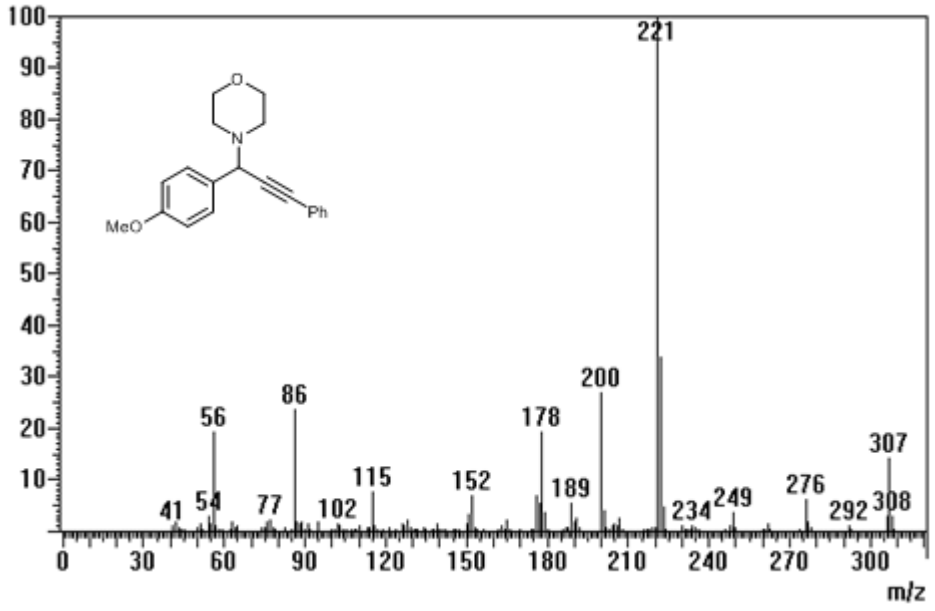


Entry 3) 4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)morpholine

^{1}HNMR



MS:



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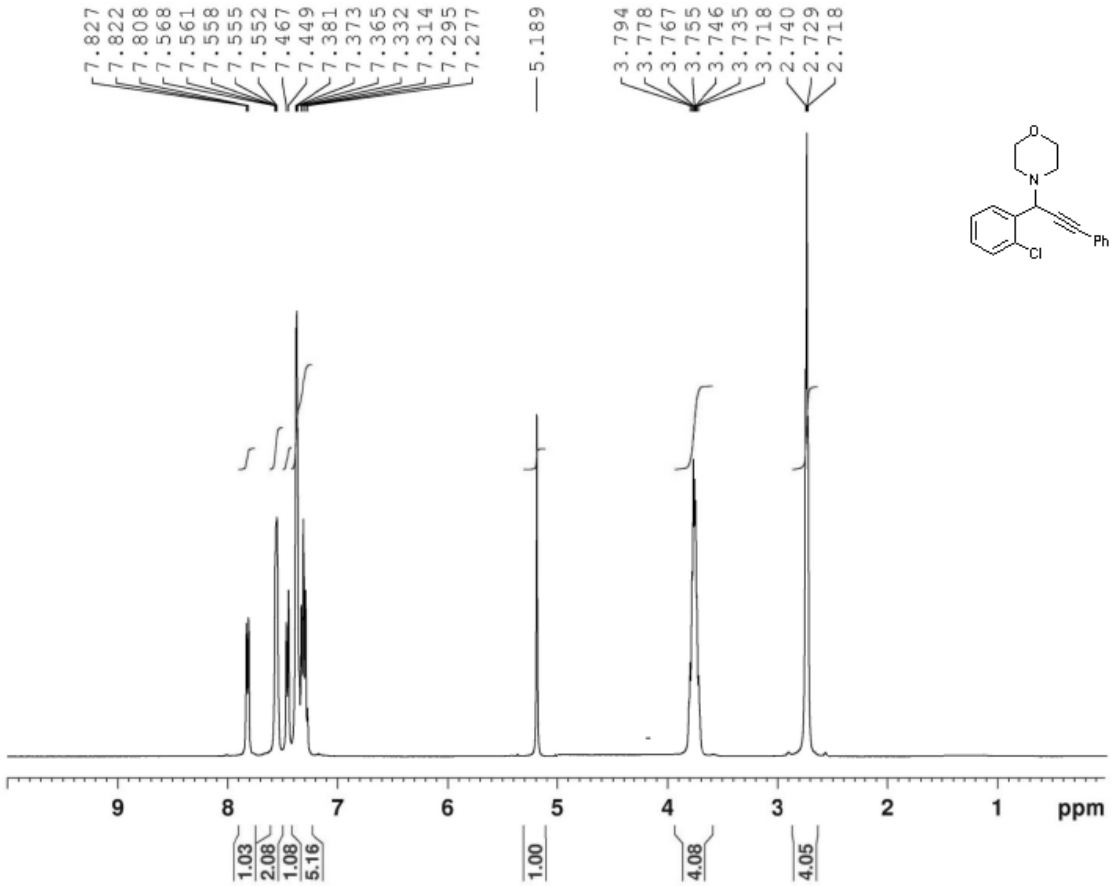
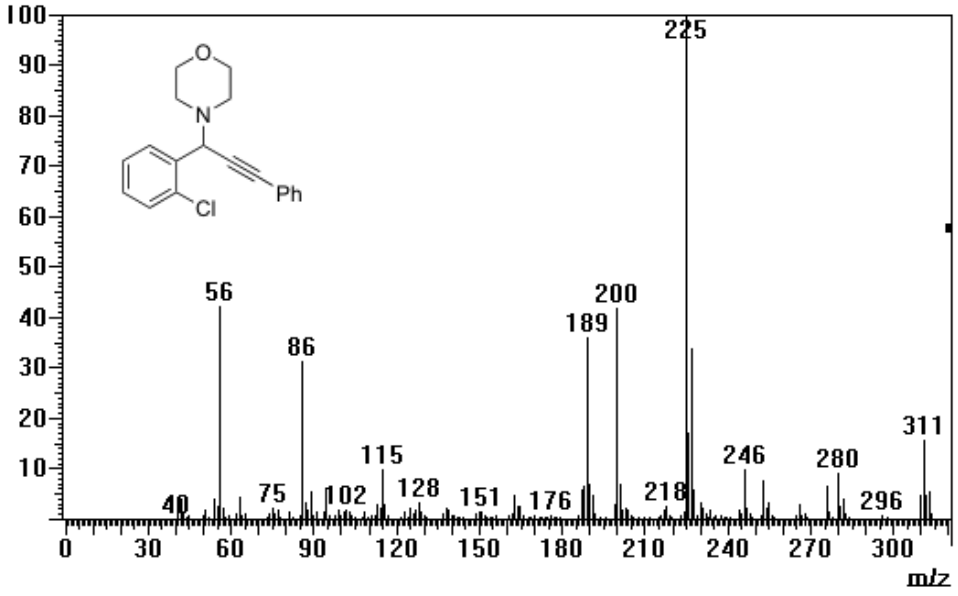
Entry 4) 4-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl)morpholine

^{1}HNMR

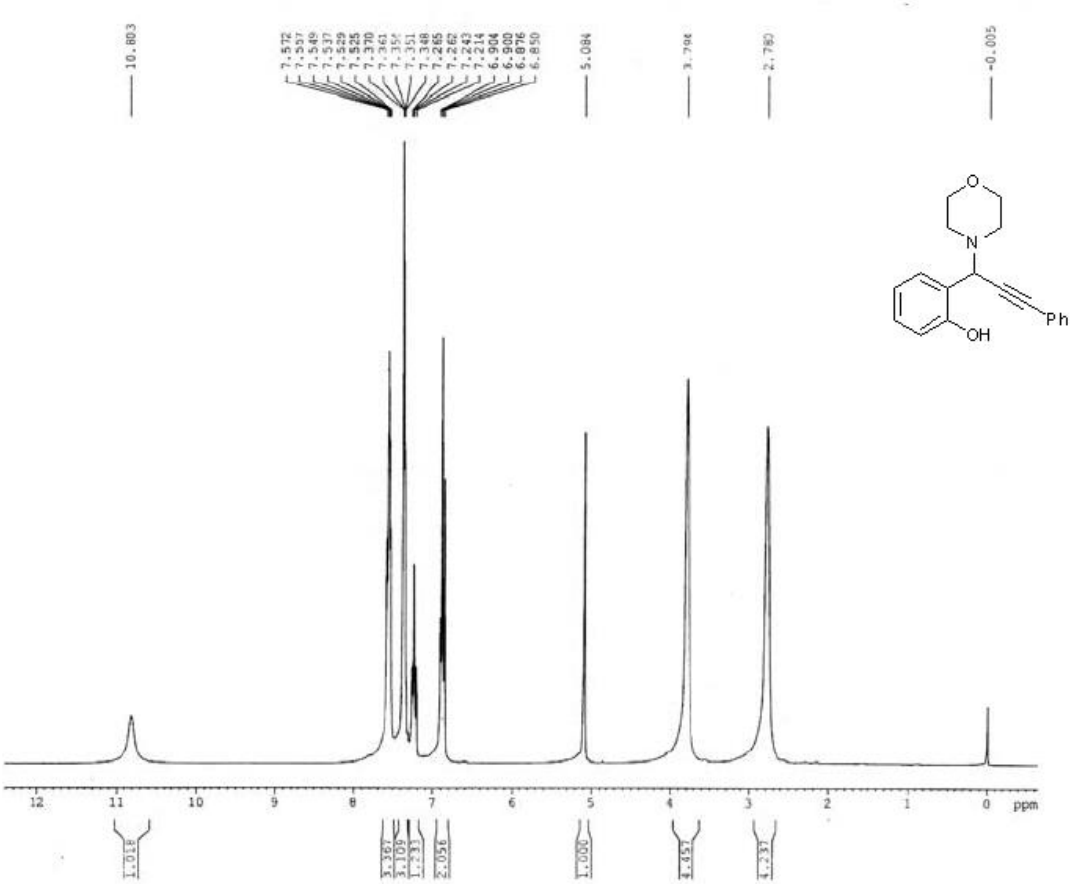


MS

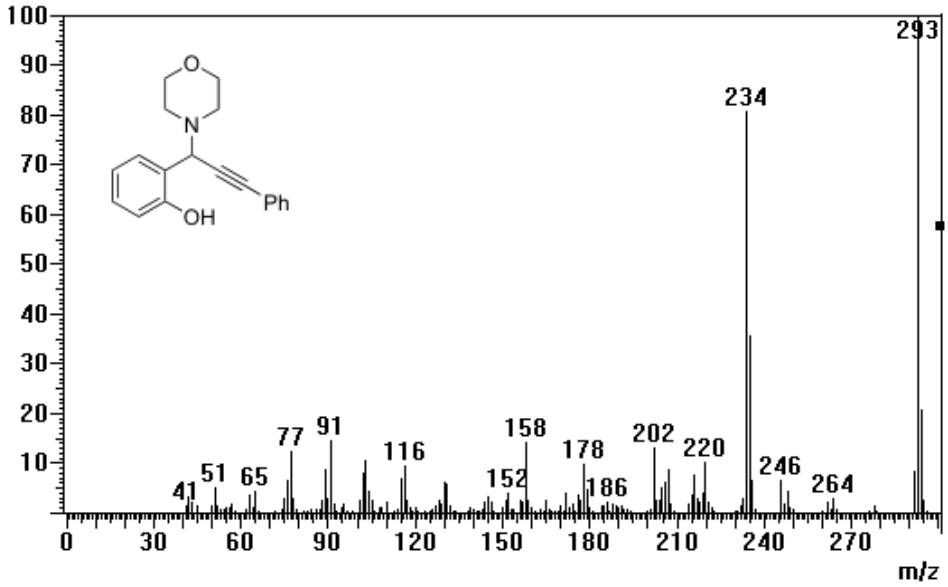


Entry 5) 2-(1-morpholino-3-phenylprop-2-yn-1-yl)phenol

[1]HNMR

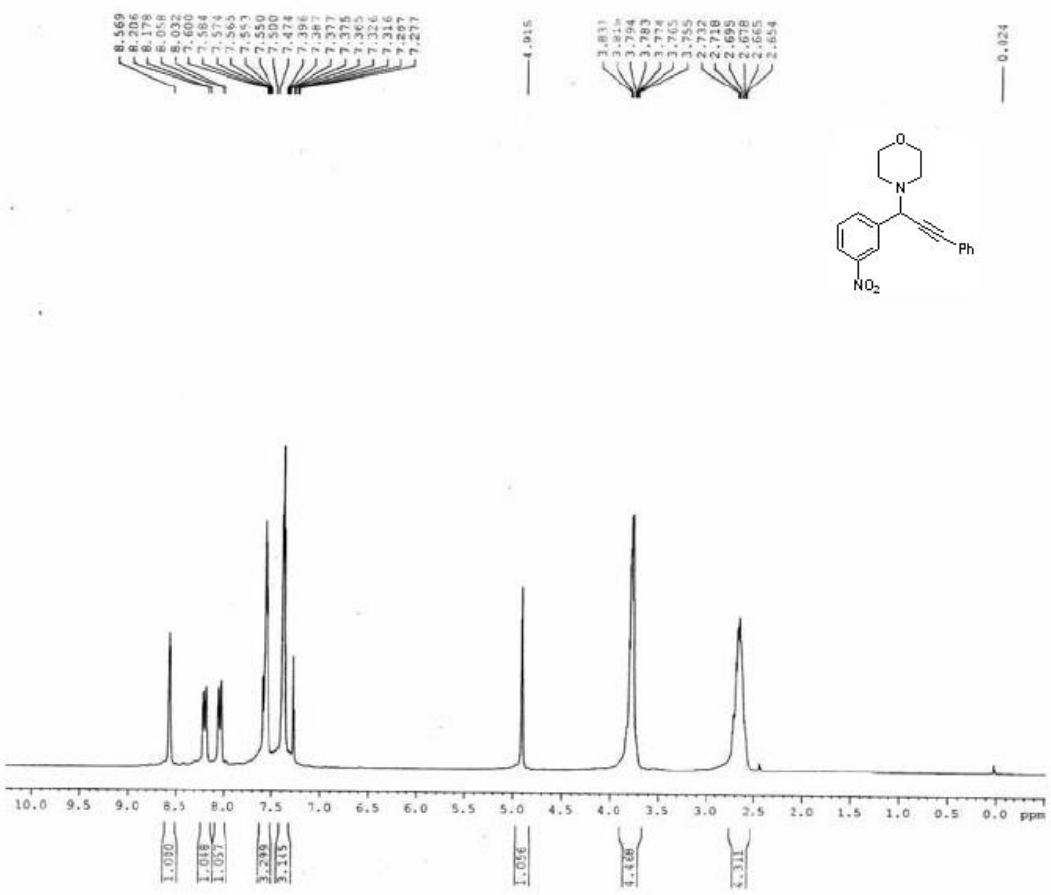


MS:

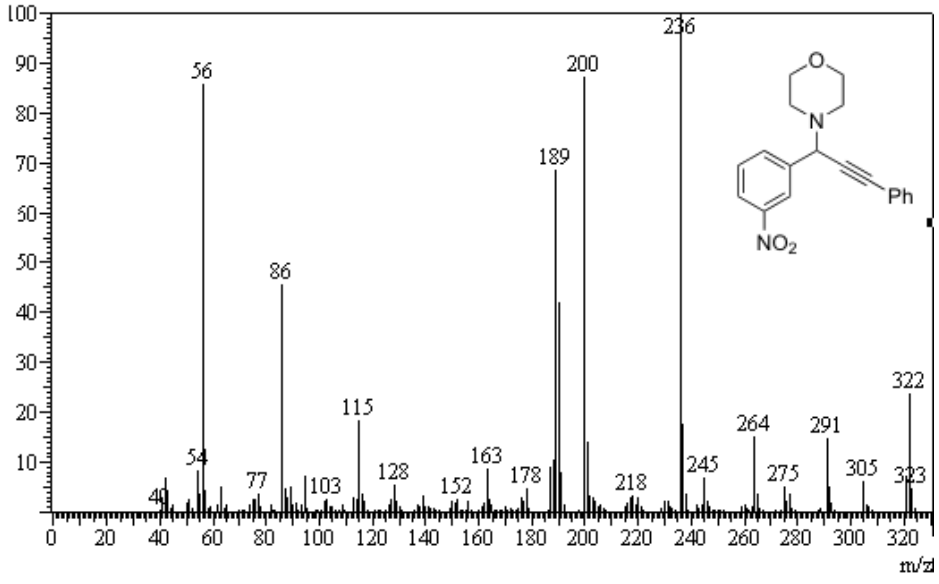


Entry 6) 4-(1-(3-nitrophenyl)-3-phenylprop-2-yn-1-yl)morpholine

^{1}HNMR

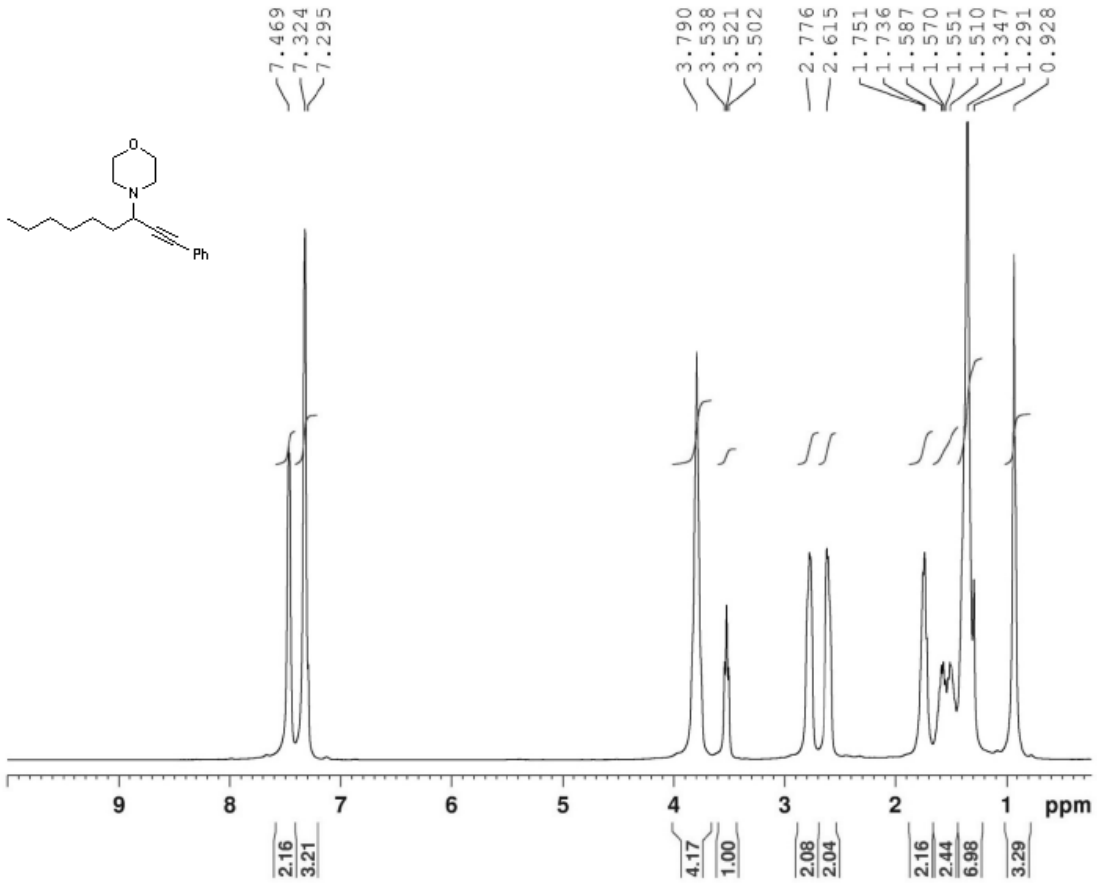


MS:



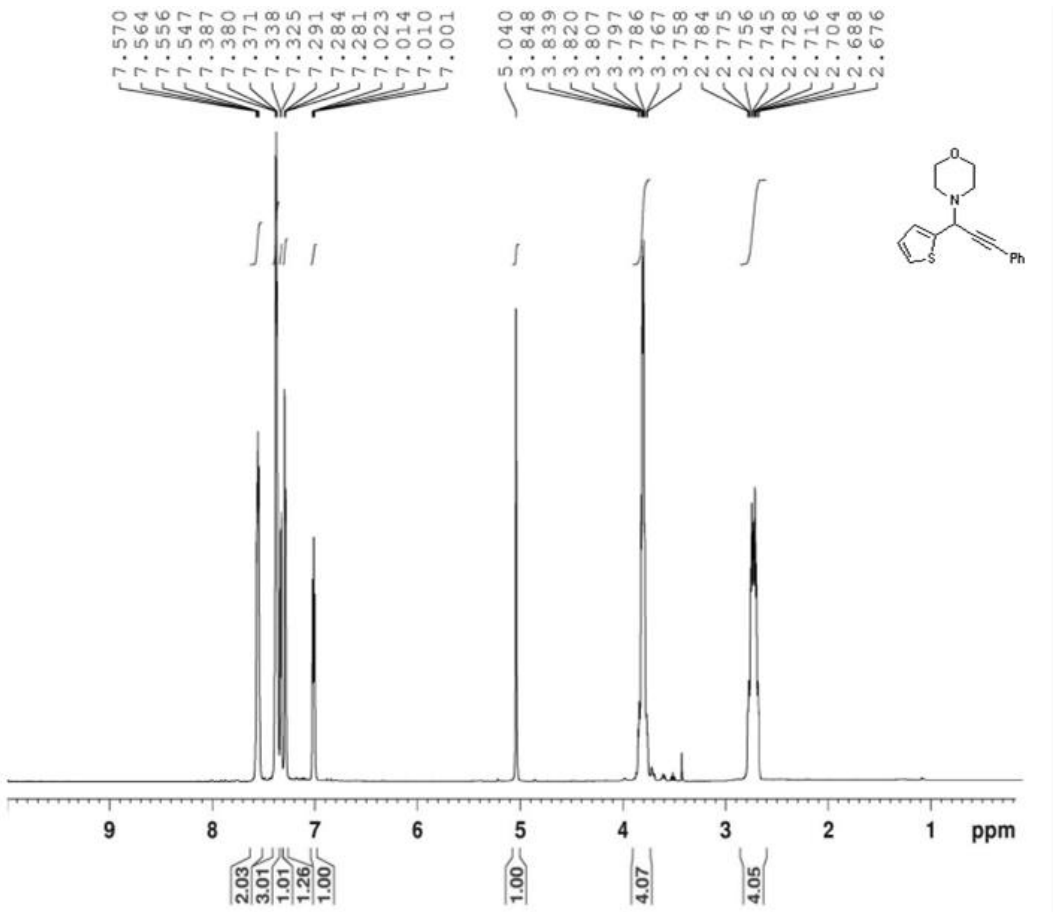
Entry 8) 4-(1-phenylnon-1-yn-3-yl)morpholine

^{1}HNMR

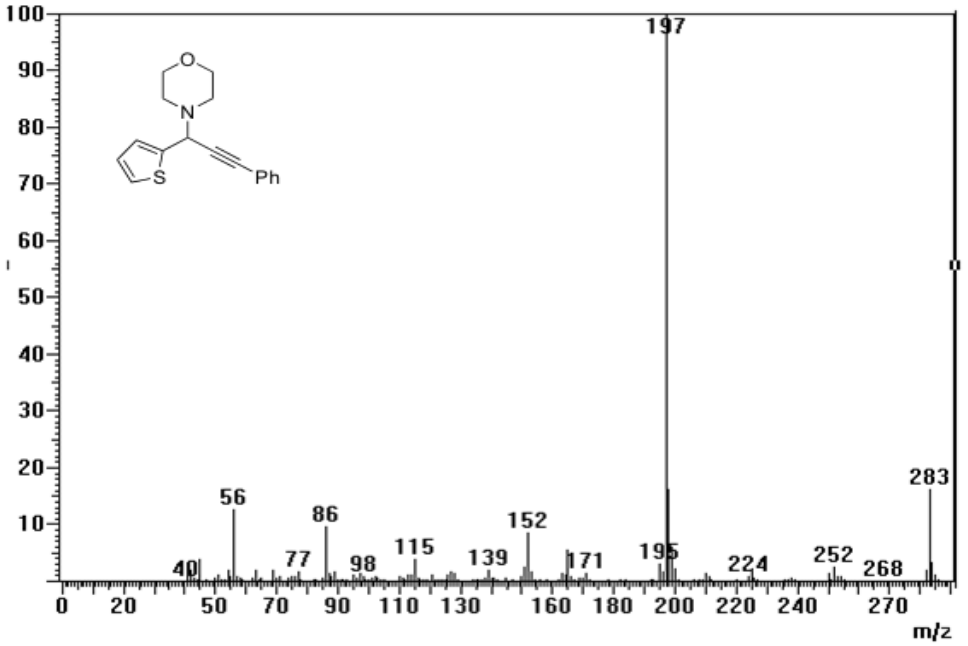


Entry 9) 4-(3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-yl)morpholine

^{1}HNMR

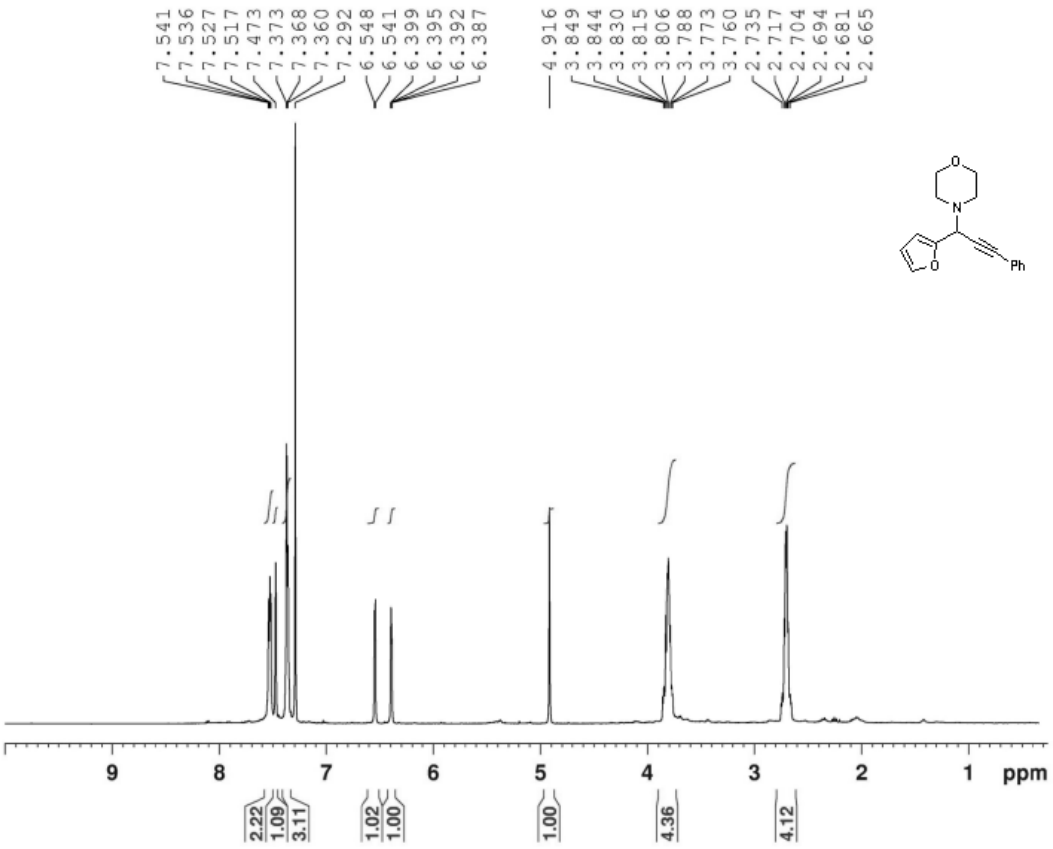


MS

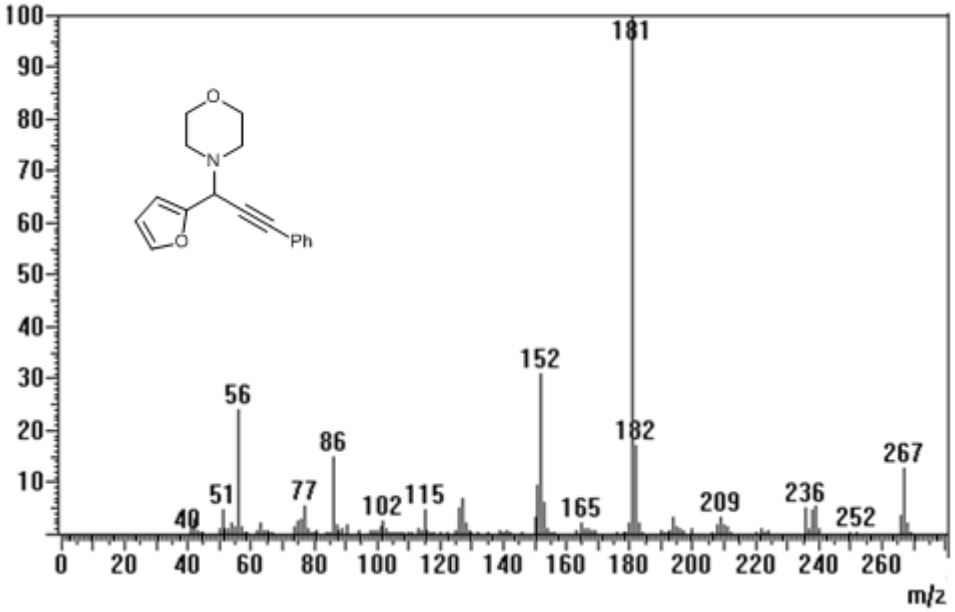


Entry 10) 4-(1-(furan-2-yl)-3-phenylprop-2-yn-1-yl)morpholine

[1]HNMR

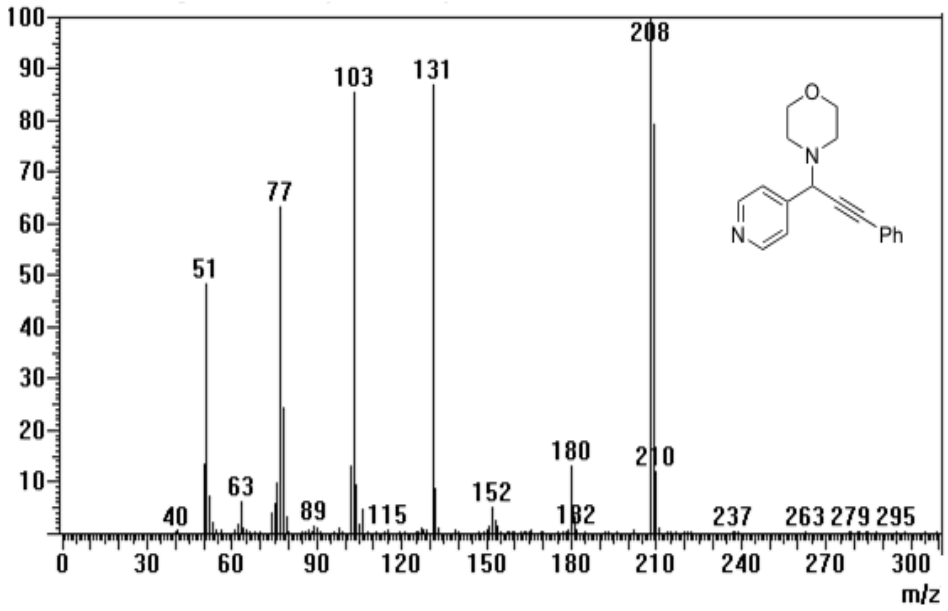


MS:



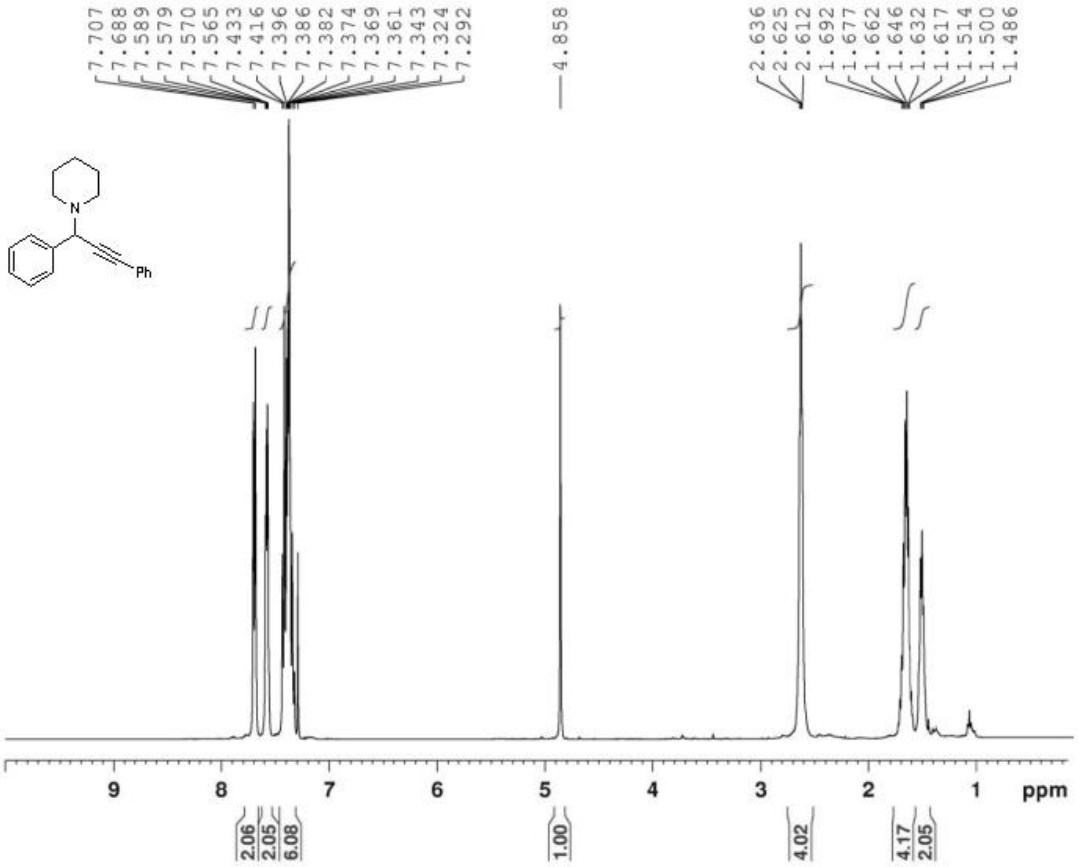
Entry 11) 4-(3-phenyl-1-(pyridin-4-yl)prop-2-yn-1-yl)morpholine

MS:

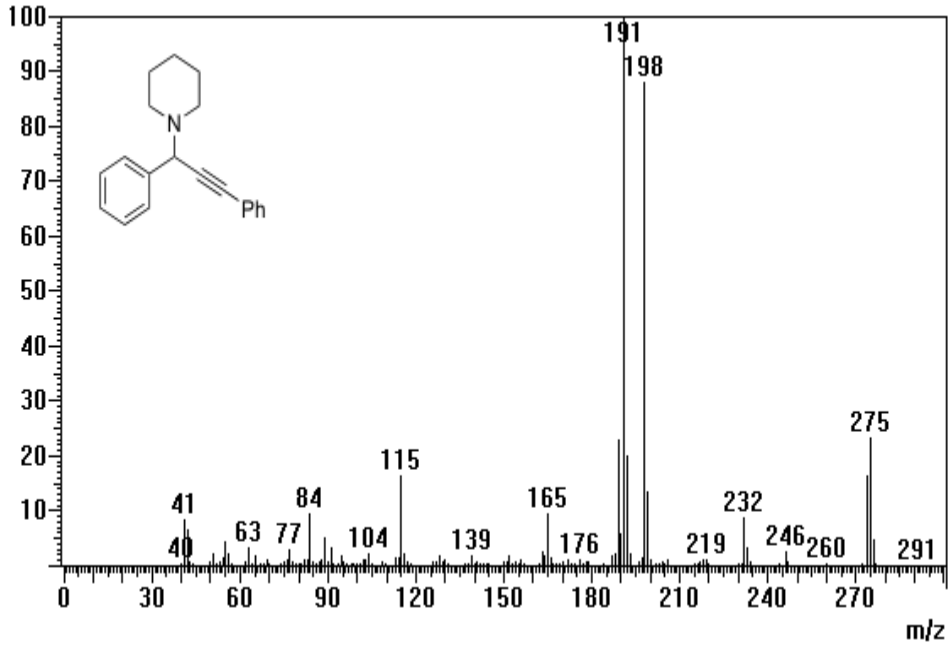


Entry 12) 1-(1,3-diphenylprop-2-yn-1-yl)piperidine

^{1}HNMR

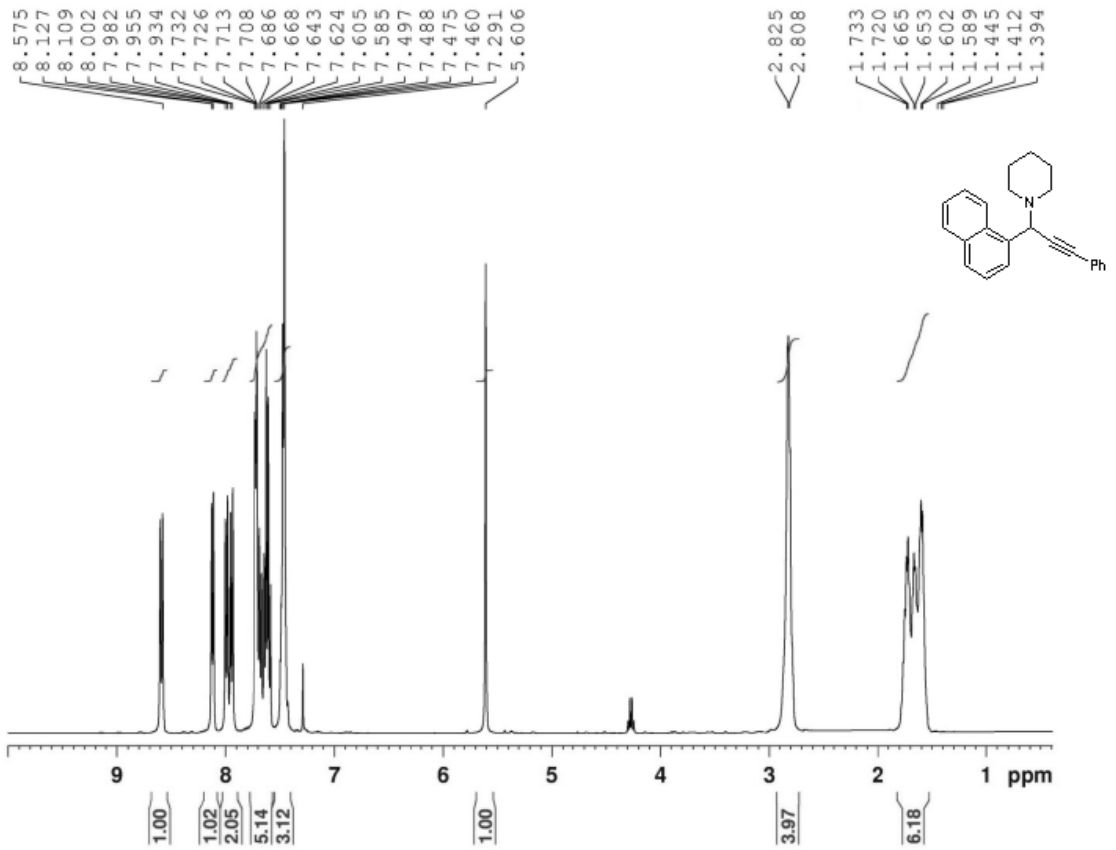


MS:



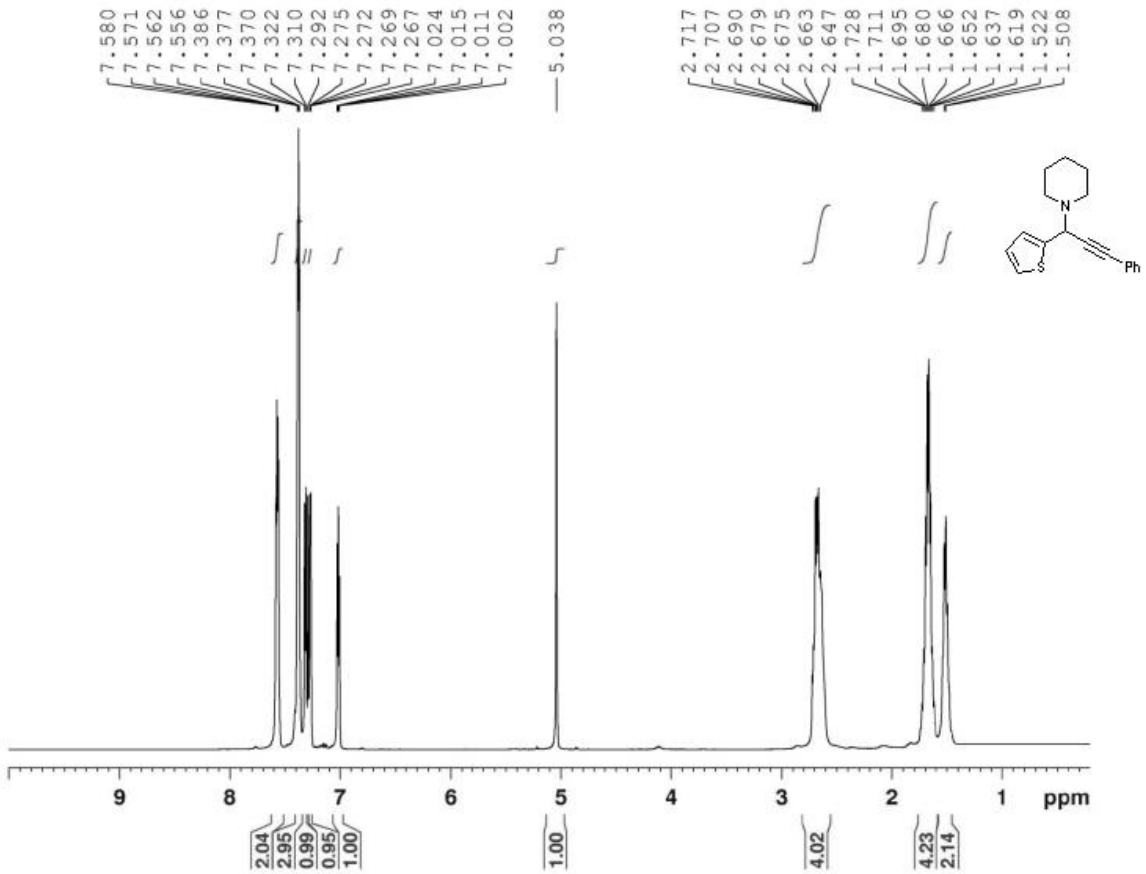
Entry 13) 1-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl)piperidine

^{1}HNMR



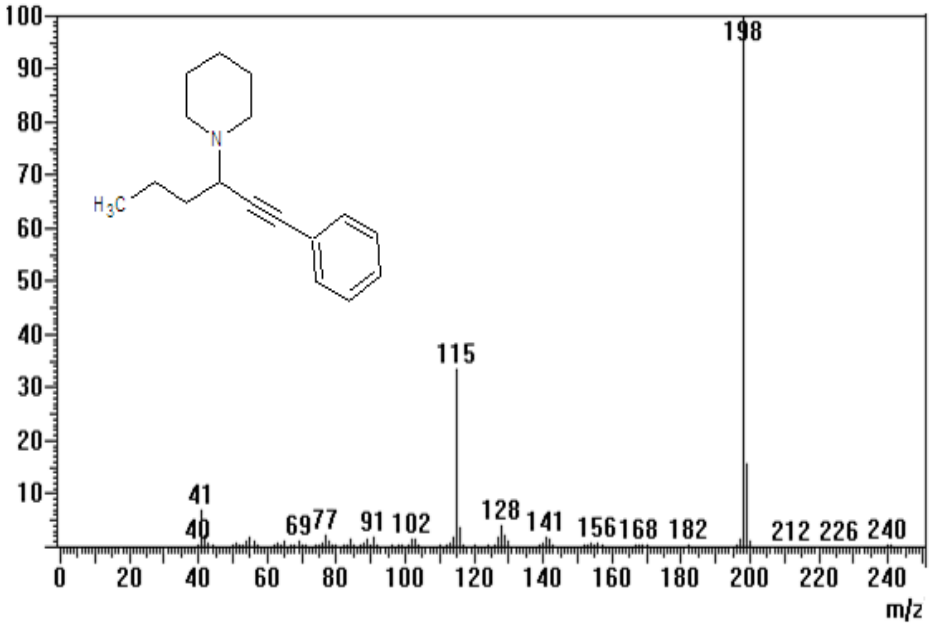
Entry 14) 1-(3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-yl)piperidine

^{1}HNMR

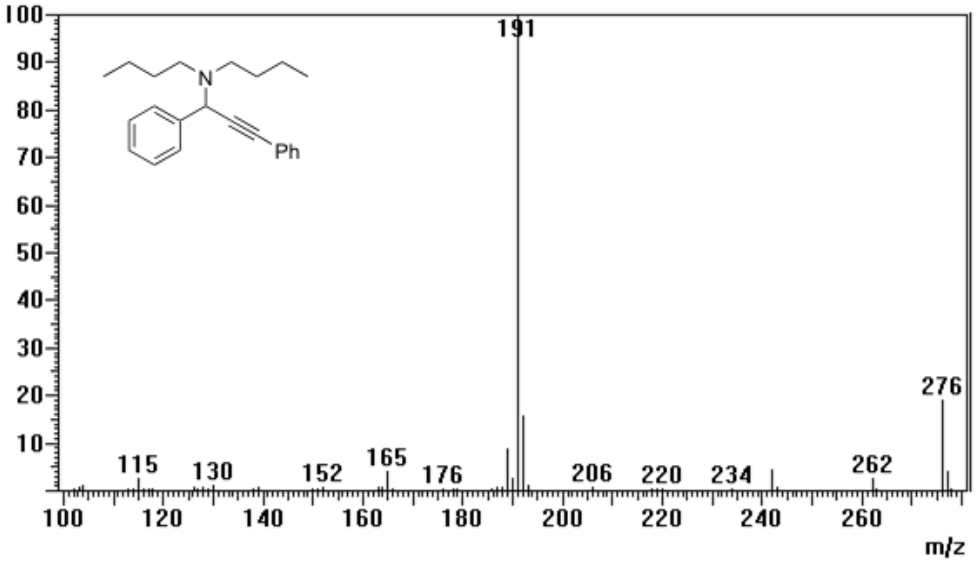


Entry 15) 1-(1-phenylhex-1-yn-3-yl)piperidine

MS:

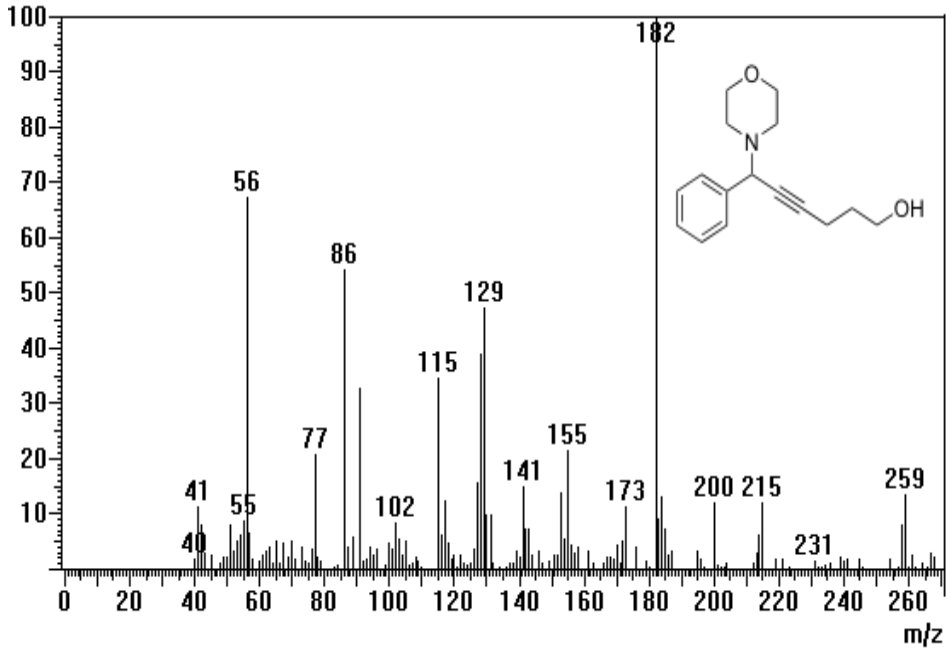


Entry 16) *N*-butyl-N-(1,3-diphenylprop-2-yn-1-yl)butan-1-amine



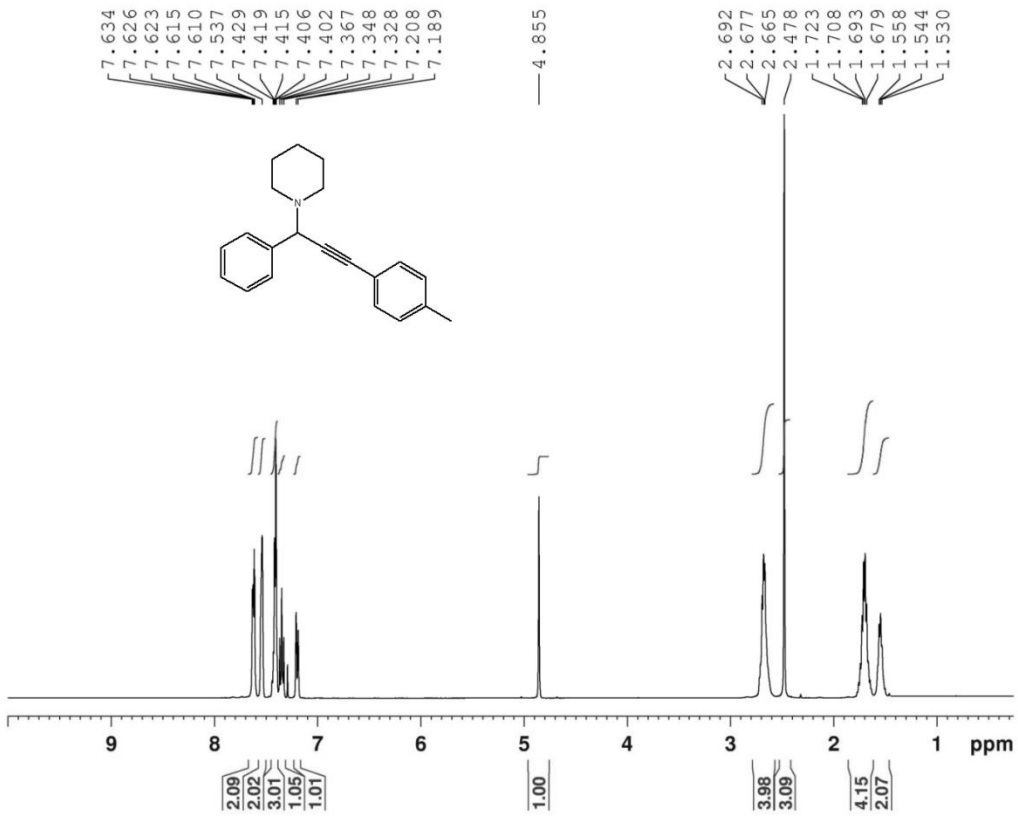
Entry 17) 6-morpholino-6-phenylhex-4-yn-1-ol

MS:



Entry 18) 1-(1-phenyl-3-(*p*-tolyl)prop-2-yn-1-yl)piperidine

[1]HNMR



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