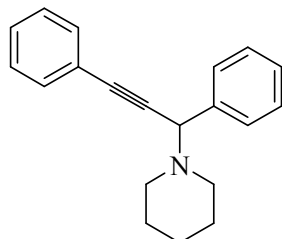


**Copper Nanoparticles Supported on Starch Micro Particles as a
Degradable Heterogeneous Catalyst for three-Component
Coupling Synthesis of Propargylamines**

Mohammad Gholinejad,^{*a} Fariba Saadati,^b Shahram Shaybanizadeh,^b Biji
Pullithadathil^c

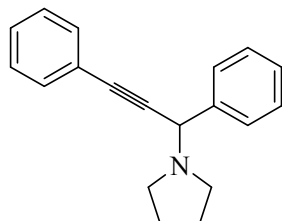
Characterizations of products:

1-(1, 3-diphenylprop-2-ynyl) piperidine (1a):¹



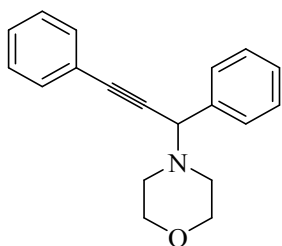
¹H NMR (CDCl₃, 250 MHz): δ 7.71-7.68 (m, 2H), 7.56 (d, 2H, *J*=5 Hz), 7.39-7.35 (m, 6H), 4.89 (s, 1H), 2.64 (br, 4H), 1.67-1.48 (m, 6H): ¹³CNMR (CDCl₃, 62.9 MHz): 138.0, 131.8, 128.7, 128.3, 128.1, 127.6, 123.20, 88.19, 85.64, 62.4, 50.68, 25.96, 24.32.

1-(1,3-diphenylprop-2-yn-1-yl) pyrrolidine (1b):²



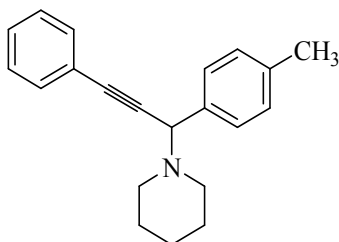
¹H NMR (CDCl₃, 250 MHz): δ 7.63-7.60 (m, 2H), 7.48 (m, 2H), 7.36-7.21 (m, 6H), 4.91 (s, 1H), 2.71 (br, 4H), 1.80 (br, 4H): ¹³C NMR (CDCl₃, 62.9 MHz): 139.25, 131.77, 128.30, 128.24, 128.1, 127.6, 123.08, 87, 86.49, 59.0, 50.20, 23.48.

4-(1, 3-diphenylprop-2-ynyl) morpholine (1c):¹



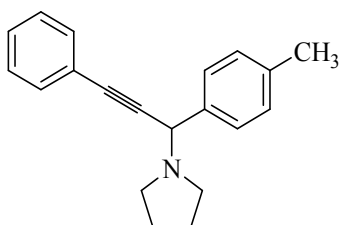
^1H NMR (CDCl_3 , 250 MHz): δ 7.65-7.62 (m, 2H), 7.51 (m, 2H), 7.37-7.26 (m, 6H), 4.80 (s, 1H), 3.74 (br, 4H), 2.64 (br, 4H), ^{13}C NMR (CDCl_3 , 62.9 MHz): 137.77, 131.79, 128.57, 128.21, 127.76, 122.97, 88.49, 85.03, 67.13, 62.03, 49.86.

1-(3-phenyl-1-(*p*-tolyl) prop-2-yn-1-yl) piperidine (1d):¹



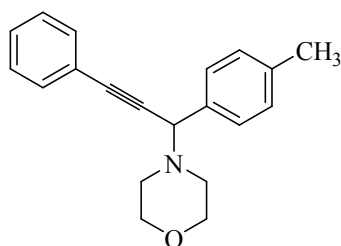
^1H NMR (CDCl_3 , 250 MHz): δ 7.53-7.50 (m, 4H), 7.34-7.16 (m, 5H), 4.77 (s, 1H), 2.59-2.55 (m, 4H), 2.36 (s, 3H), 1.61-1.44 (m, 6H). ^{13}C NMR (CDCl_3 , 62.9 MHz): 137.08, 131.79, 128.74, 128.47, 128.24, 127.98, 123.30, 87.59, 86.35, 62.11, 50.65, 26.15, 24.44, 21.10.

1-(3-phenyl-1-(*p*-tolyl)prop-2-yn-1-yl) pyrrolidine (1e):³



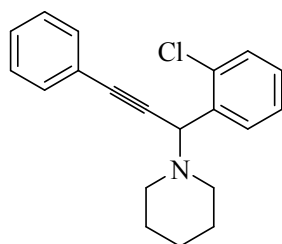
^1H NMR (CDCl_3 , 250 MHz): δ 7.48-7.42 (br, 4H), 7.31-7.15 (m, 5H), 4.89 (s, 1H), 2.72 (br, 4H), 2.35 (s, 3H), 1.81 (br, 4H). ^{13}C NMR (CDCl_3 , 62.9MHz): 137.3, 131.77, 128.95, 128.46, 128.24, 128.06, 123.41, 87.62, 86.71, 58.80, 50.22, 23.46, 21.10.

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



^1H NMR (CDCl_3 , 250 MHz): δ 7.52-7.49 (m, 4H), 7.34-7.16 (m, 5H), 4.75 (s, 1H), 3.73-3.71 (br, 4H), 2.63 (br, 4H), 2.36 (s, 3H). ^{13}NMR (CDCl_3 , 62.9 MHz): 137.47, 134.78, 131.78, 128.90, 128.50, 128.27, 128.18, 123.03, 88.23, 85.32, 67.15, 61.78, 49.86, 21.10.

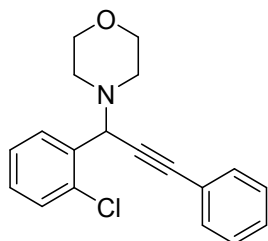
1-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) piperidine (1g):¹



^1H NMR (CDCl_3 , 250 MHz): δ 7.76-7.73 (m, 2H), 7.50-7.48 (m, 2H), 7.41-7.37 (m, 1H), 7.33-7.26 (m, 5H), 5.10 (s, 1H), 2.61 (br, 4H), 1.60-1.55 (m, 4H), 1.46-1.42 (M, 2H). $^{13}\text{CNMR}$ (CDCl_3 , 69.2 MHz): 136.39, 134.63,

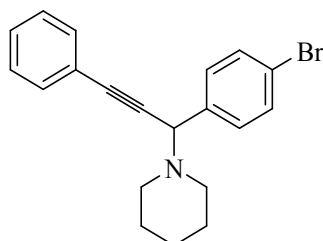
131.77, 130.55, 129.76, 128.74, 128.25, 128.10, 126.15, 123.05, 87.62, 85.80, 59.23, 50.73, 26.12, 24.43.

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



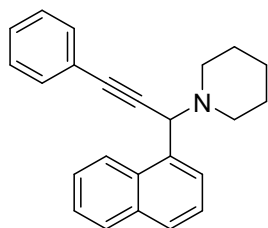
¹HNMR (CDCl₃, 250 MHz): δ 7.70 (br, 1H), 7.50-7.26 (m, 8H), 5.14 (s, 1H), 3.72 (br, 4H), 2.68 (br, 4H), ¹³NMR (CDCl₃, 62.9 MHz): 135.45, 134.63, 131.79, 130.57, 129.88, 129.67, 129.15, 128.30, 126.37, 122.75, 88.38, 84.38, 67.02, 58.92, 49.83.

1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl) piperidine (1i):⁴



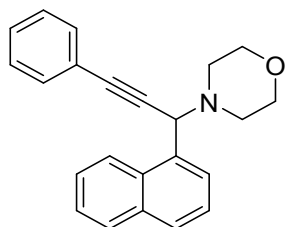
¹HNMR (CDCl₃, 250 MHz): δ 7.55-7.46 (m, 6H), 7.35-7.33 (m, 3H), 4.75 (s, 1H), 2.54-2.52 (br, 4H), 1.60-1.45 (m, 6H). ¹³C NMR (CDCl₃, 62.9 MHz): 145.41, 137.85, 131.80, 131.14, 130.18, 129.01, 128.51, 128.31, 128.21, 123.08, 121.36, 88.27, 85.27, 61.76, 50.63, 26.14, 24.36.

1-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl) piperidine (1j):¹



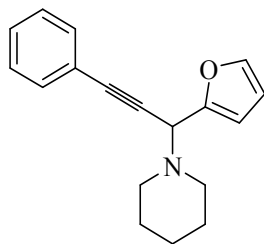
^1H NMR (CDCl_3 , 250 MHz): δ 8.49-8.46 (m, 1H), 8.02-7.84 (m, 3H), 7.762-7.38 (m, 8H), 5.51(s, 1H), 2.73 (br, 4H), 1.60-1.51 (m, 6H).
 ^{13}C NMR (CDCl_3 , 62.9 MHz): 134.08, 132.34, 131.88, 128.63, 128.44, 128.35, 128.10, 126.96, 125.81, 125.60, 125.04, 124.82, 123.47.

1-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl) piperidine (1k):¹



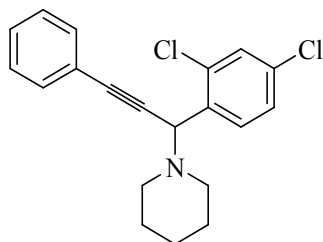
^1H NMR (CDCl_3 , 250 MHz): δ 8.41-8.38 (m, 1H), 7.95-7.82 (m, 3H), 7.56-7.26 (m, 8H), 5.45 (s, 1H), 3.74-3.68 (br, 4H), 2.73-2.71 (br, 4H). ^{13}C NMR (CDCl_3 , 62.9 MHz): 134.08, 133.18, 131.82, 128.90, 128.50, 128.33, 128.25, 127.11, 125.90, 125.69, 124.79, 123.05, 89.03, 84.98, 67.21, 60.17, 49.84.

1-(1-(furan-2-yl)-3-phenylprop-2-ynyl) piperidine (1l):¹



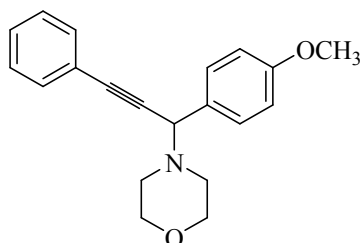
^1H NMR (CDCl_3 , 250 MHz): δ 7.52-7.43 (m, 3H), 7.34-7.26 (m, 3H), 6.49 (d, $J=2.5$ Hz, 1H), 6.36 (d, $J=2.5$ Hz, 1H), 4.87 (s, 1H), 2.59 (br, 4H), 1.70-1.42 (m, 6H). ^{13}C NMR (CDCl_3 , 62.9 MHz): 151.65, 142.53, 131.83, 128.25, 122.93, 109.94, 109.20, 86.36, 83.83, 56.55, 50.51, 25.94, 24.29.

1-(1-(2,4-dichlorophenyl)-3-phenylprop-2-yn-1-yl)piperidine (1m):⁵



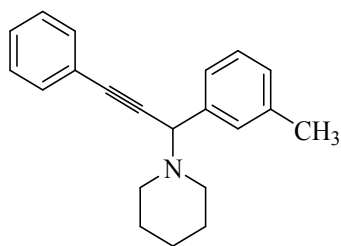
^1H NMR (CDCl_3 , 250 MHz): δ 7.73-7.70 (br, 1H), 7.49-7.25 (m, 7H), 5.04 (s, 1H), 2.60 (br, 4H), 1.57-1.43 (br, 6H). ^{13}C NMR (CDCl_3 , 62.9 MHz): 135.28, 133.96, 131.79, 131.44, 129.55, 128.31, 126.55, 122.81, 88.13, 84.97, 58.83, 50.74, 25.95, 24.29.

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



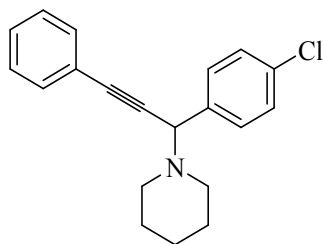
^1H NMR (CDCl_3 , 250 MHz): δ 7.55-7.52 (m, 4H), 7.33-7.26 (m, 3H), 6.92-6.8 (d, 2H), 4.74 (s, 2H), 3.82 (s, 3H), 3.73 (br, 4H), 2.62 (br, 4H). ^{13}C NMR (CDCl_3 , 62.9 MHz): 159.22, 131.77, 129.71, 128.27, 128.19, 123.01, 113.56, 88.26, 85.34, 67.13, 61.44, 55.27, 49.79.

1-(3-phenyl-1-(m-tolyl) prop-2-yn-1-yl) piperidine (1o):⁴



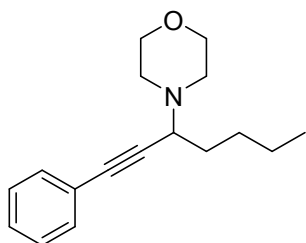
^1H NMR (CDCl_3 , 250 MHz): δ 7.52-7.25 (m, 8H), 7.12-7.09 (m, 1H), 4.75 (s, 1H), 2.57 (br, 4H), 2.38 (s, 3H), 1.59-1.44 (br, 6H). ^{13}C NMR (CDCl_3 , 62.9 MHz): 138.47, 137.63, 131.79, 129.21, 128.43, 128.23, 127.98, 127.90, 125.66, 123.42, 87.65, 86.30, 62.40, 50.74, 26.15, 24.43, 21.50.

1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl) piperidine (1p):⁴



^1H NMR (CDCl_3 , 250 MHz): δ 7.60-7.45 (m, 4H), 7.43-7.26 (m, 5H), 4.76 (s, 1H), 2.53 (br, 4H), 1.60-1.44 (m, 6H). ^{13}C NMR (CDCl_3 , 62.9 MHz): 137.29, 131.79, 129.79, 128.95, 128.50, 128.29, 128.17, 123.11, 87.81, 85.58, 61.69, 50.61, 26.13, 24.35.

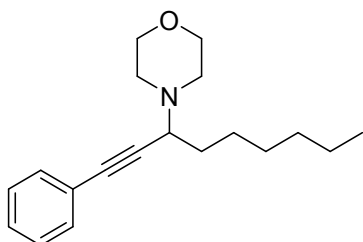
4-(1-phenylhept-1-yn-3-yl) morpholine (1q):⁶



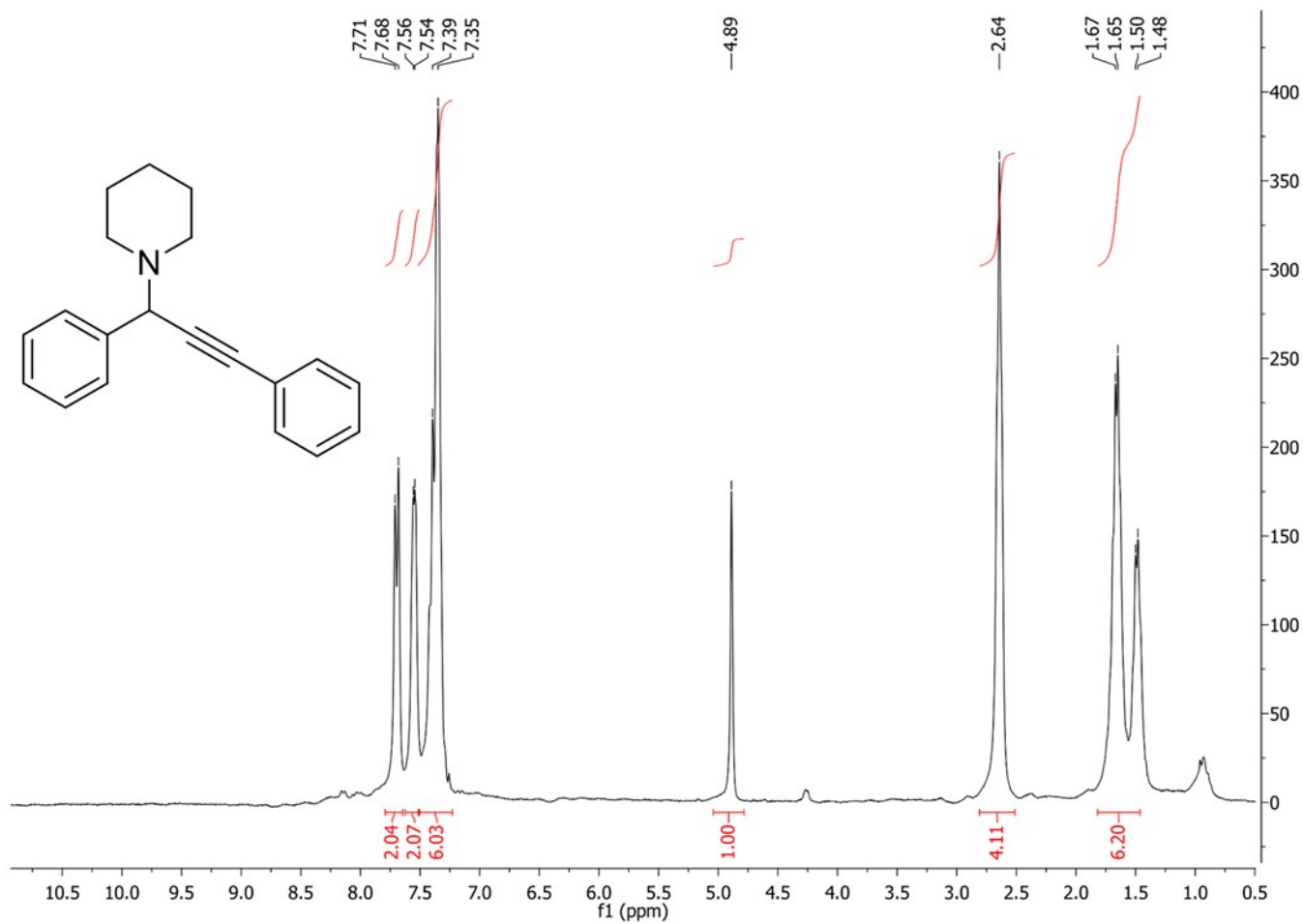
^1H NMR (CDCl_3 , 250 MHz): δ 7.42 (br, 2H), 7.29 (br, 3H), 3.75 (br, 4H), 3.48 (m, 1H), 2.72-2.59 (m, 4H), 1.72-1.67 (m, 3H), 1.50-1.31 (m, 4H), 0.89

(br, 3H). ^{13}C NMR (CDCl_3 , 62.9 MHz): 131.69, 131.31, 128.19, 127.90, 123.25, 87.19, 86.12, 67.12, 66.74, 58.12, 57.74, 49.71, 32.65, 32.30, 28.79, 28.42, 22.43, 14, 13.63.

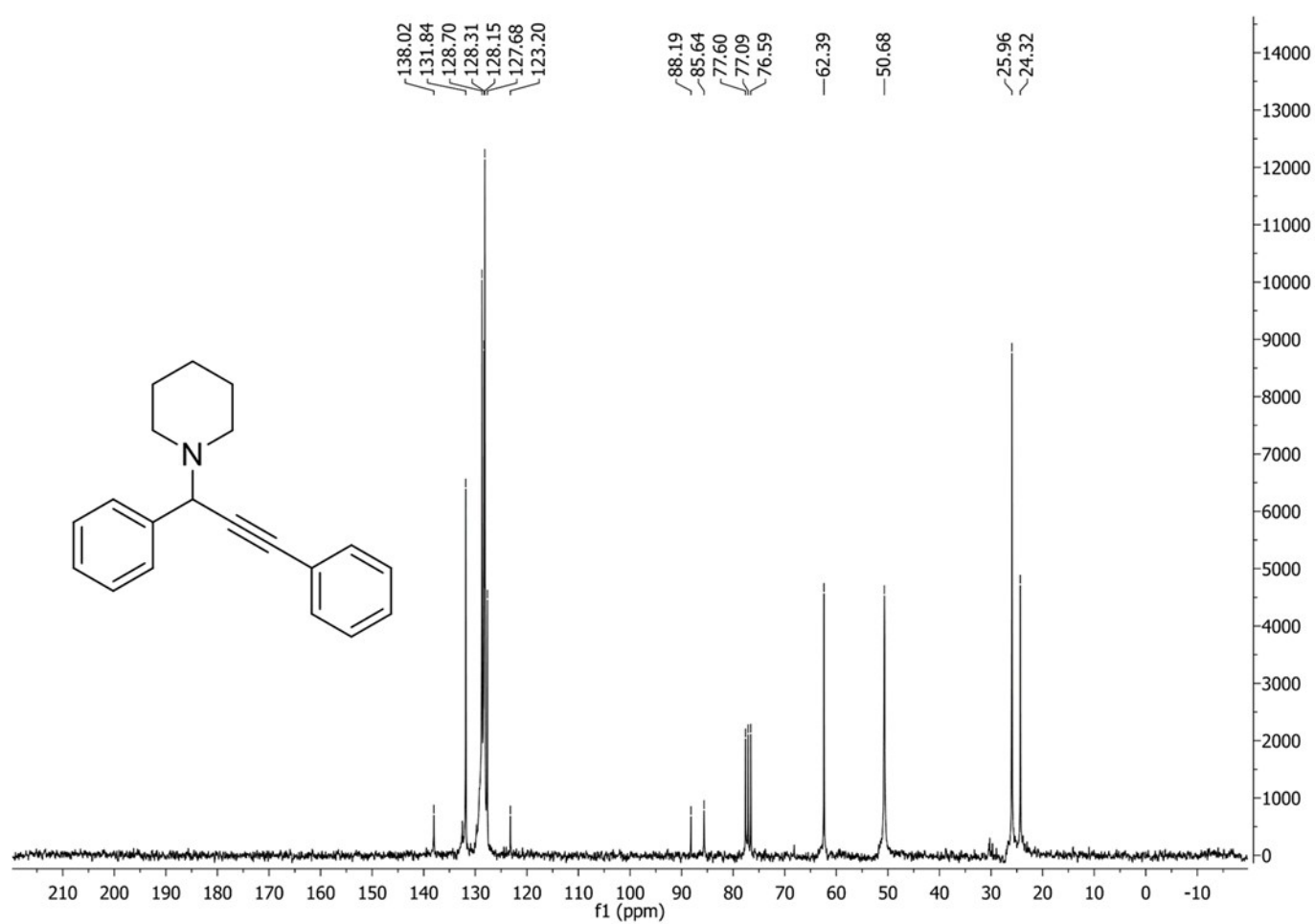
4-(1-phenylnon-1-yn-3-yl) morpholine (1r):¹



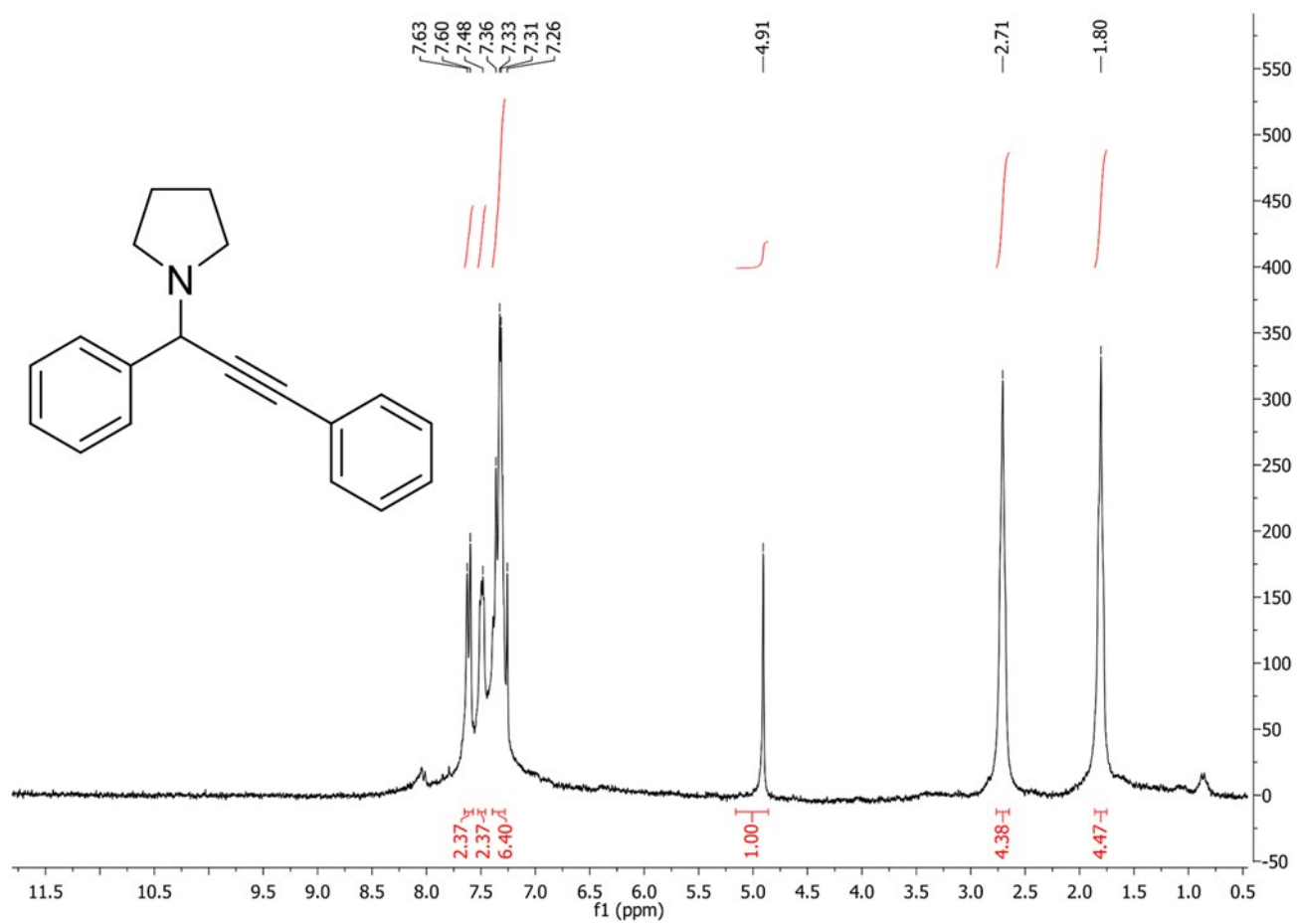
^1H NMR (CDCl_3 , 250 MHz): δ 7.42 (br, 2H), 7.29 (br, 3H), 3.75 (br, 4H), 3.48 (t, 1H, $J=7.2$ Hz), 2.72 (br, 2H), 2.59 (br, 2H), 1.72-1.67(m, 2H), 1.50-1.11(m, 9H), 0.89 (s, 1H). ^{13}C NMR (CDCl_3 , 62.9 MHz): 131.69, 128.19, 127.89, 123.25, 87.21, 86.12, 67.13, 58.13, 49.74, 32.93, 31.71, 29.65, 29.00, 26.53, 22.57, 14.02.



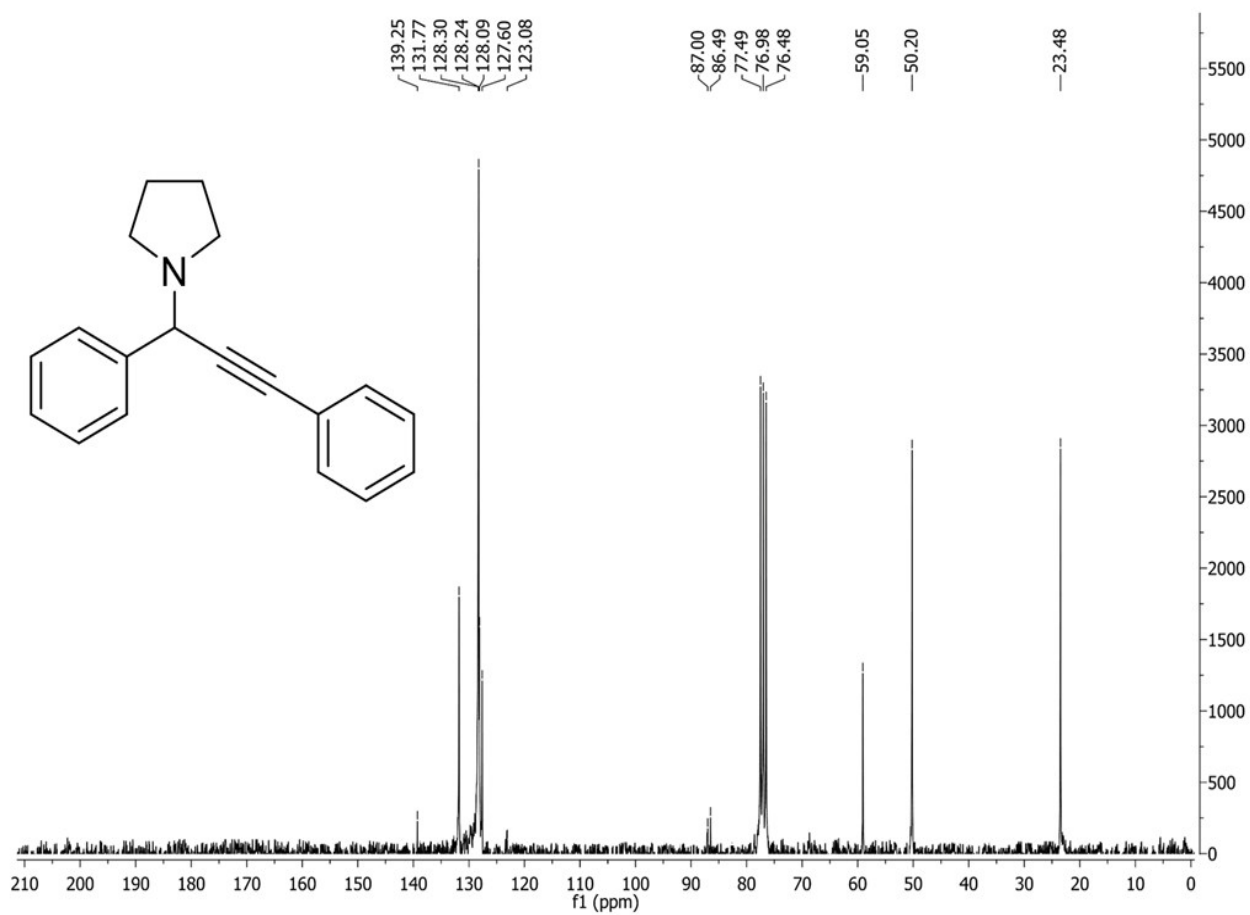
¹H NMR of: 1-(1, 3-diphenylprop-2-ynyl) piperidine (1a)



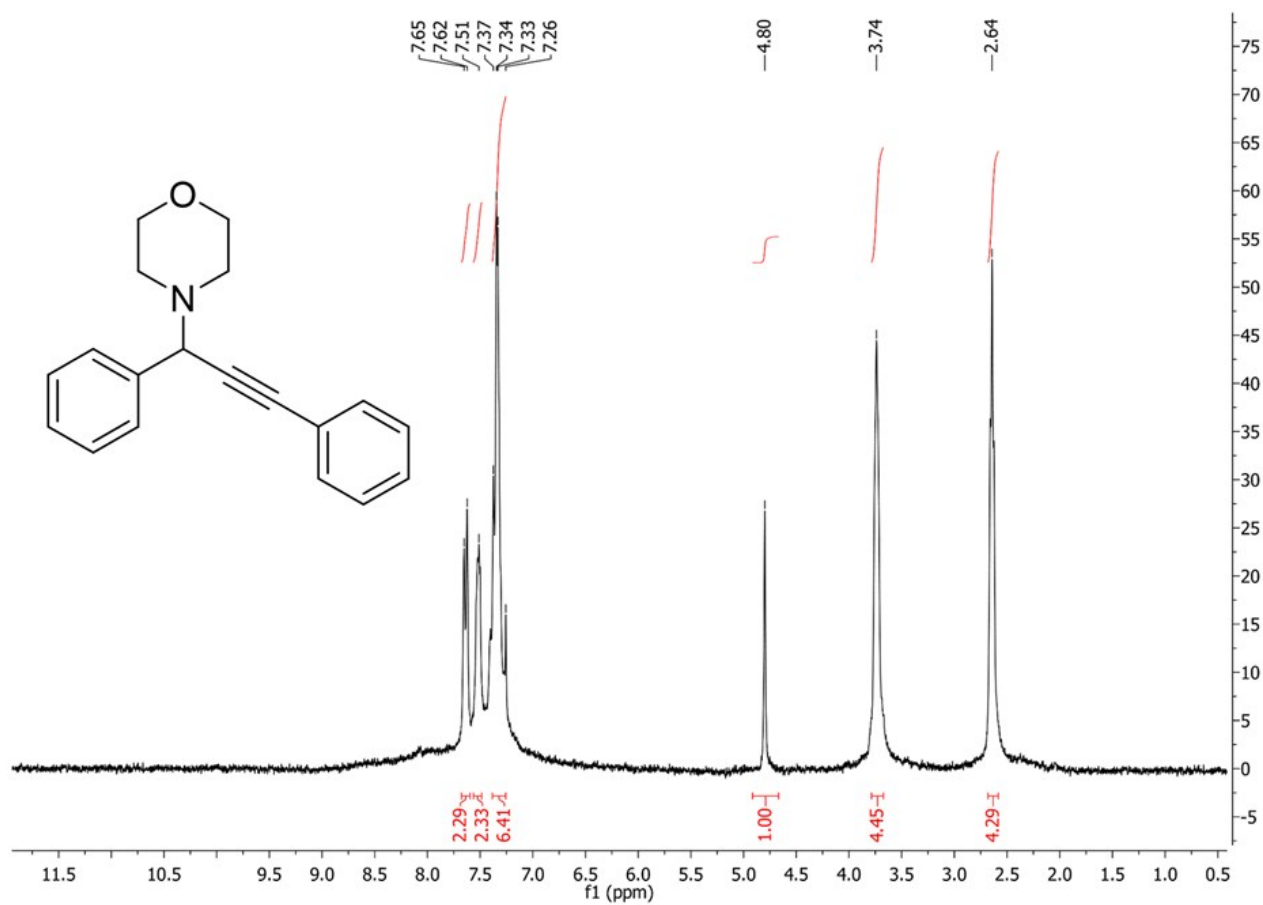
¹³C NMR of: 1-(1,3-diphenylprop-2-ynyl)piperidine (1a)



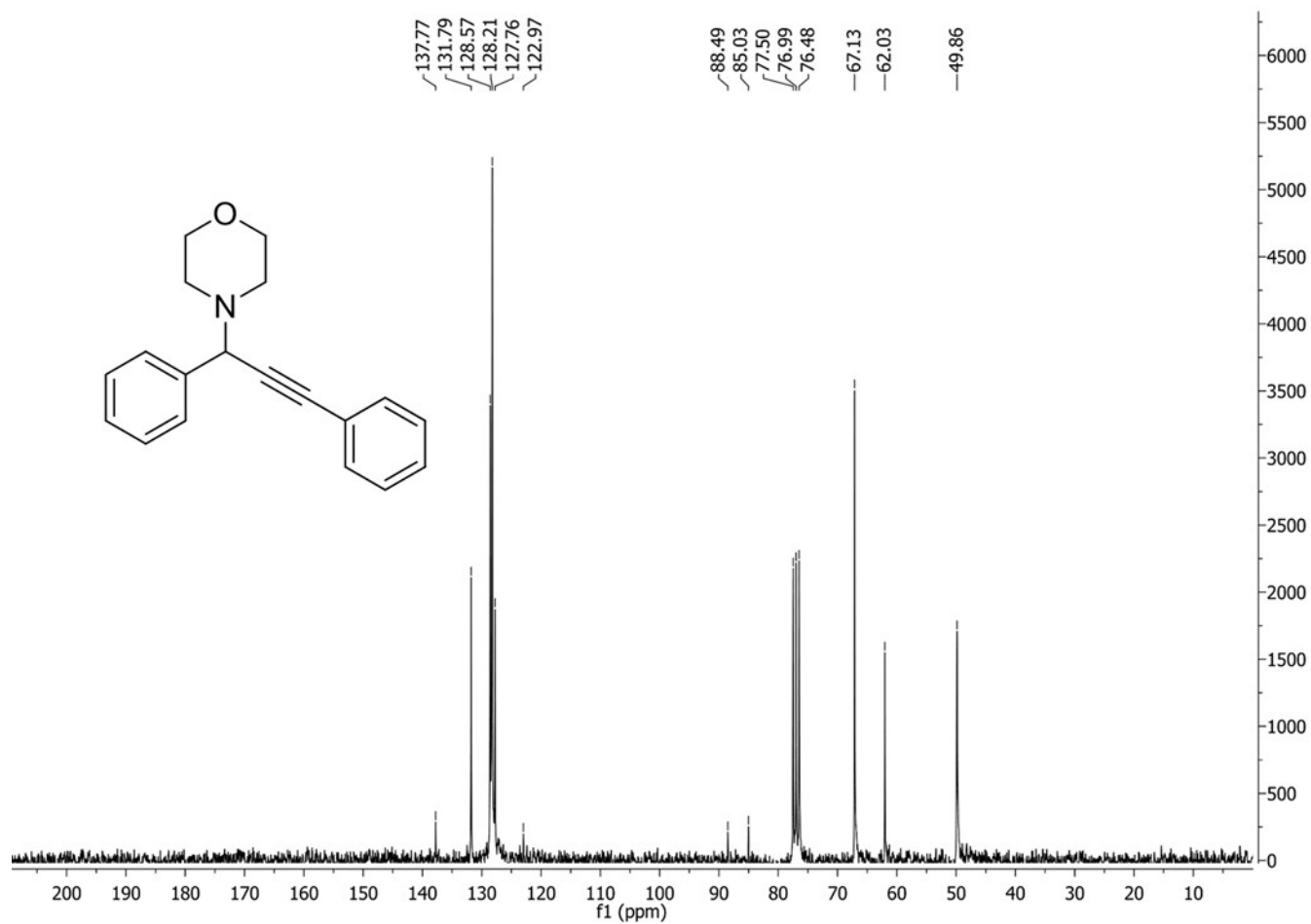
¹H NMR OF: 1-(1,3-diphenylprop-2-yn-1-yl)pyrrolidine (1b)



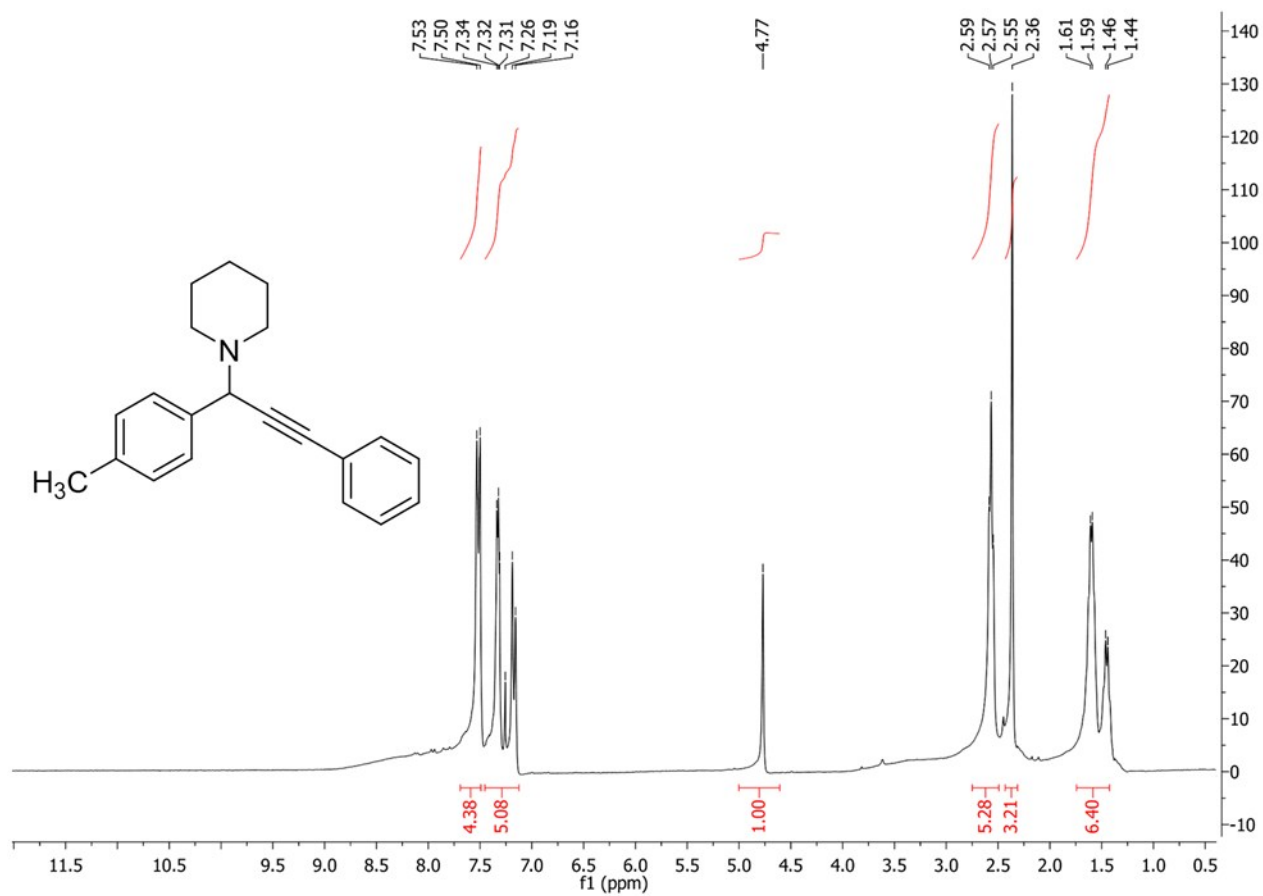
¹³C NMR: 1-(1,3-diphenylprop-2-yn-1-yl)pyrrolidine (1b)



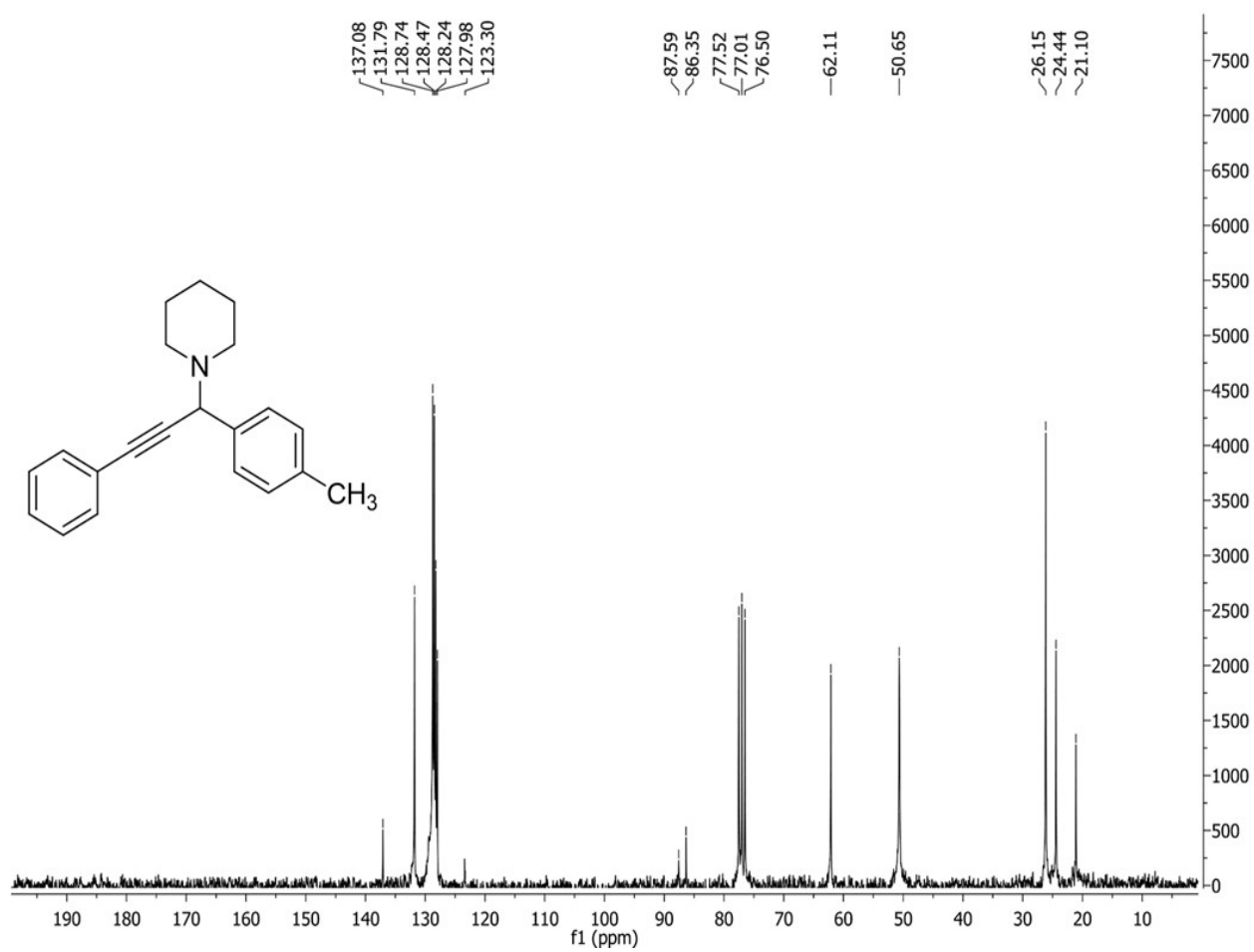
¹H NMR: 4-(1,3-diphenylprop-2-ynyl)morpholine (1c)



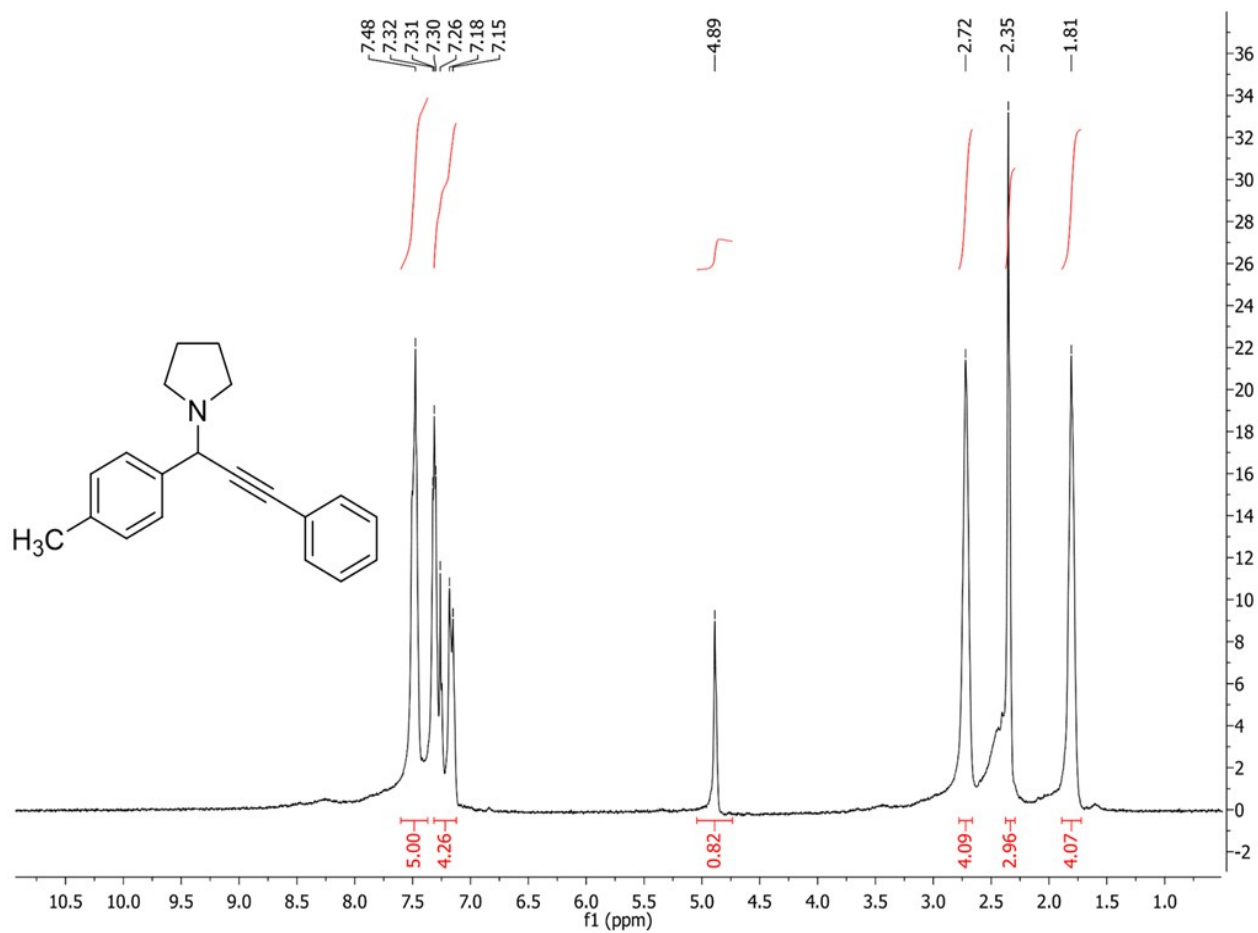
^{13}C NMR OF: 4-(1,3-diphenylprop-2-ynyl)morpholine (1c)



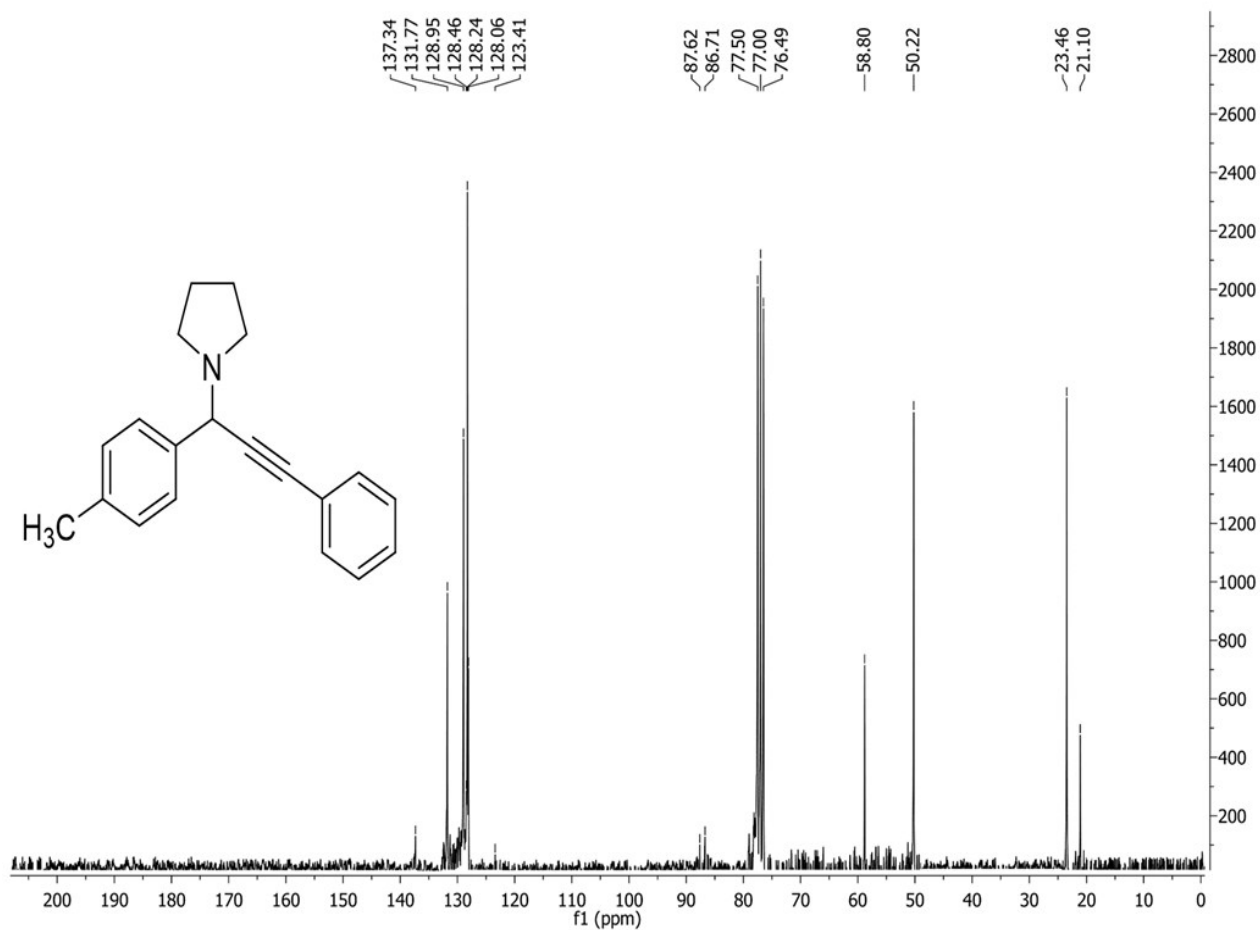
¹H NMR OF: 1-(3-phenyl-1-(p-tolyl) prop-2-yn-1-yl) piperidine (1d)



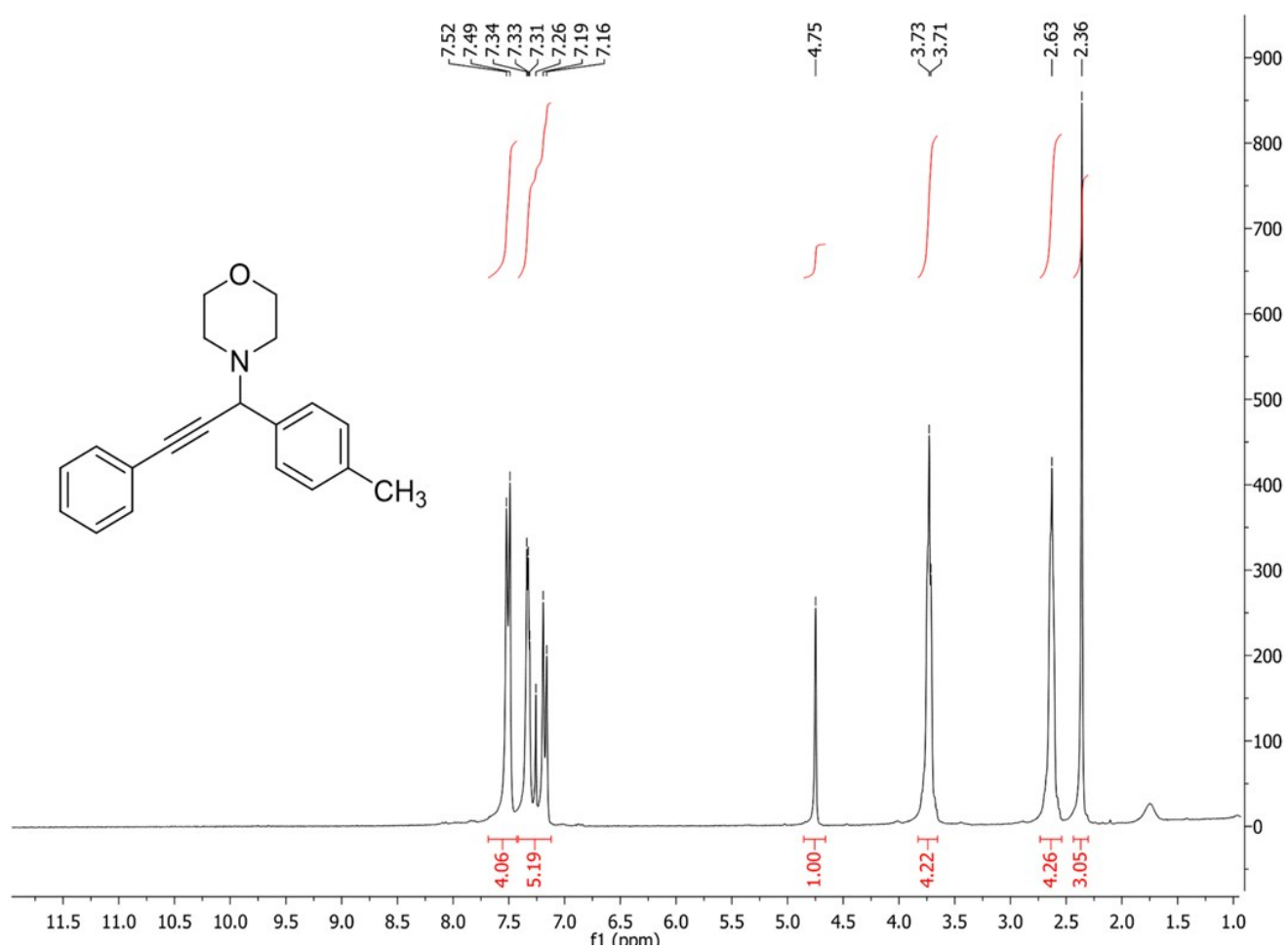
¹³C NMR OF: 1-(3-phenyl-1-(p-tolyl) prop-2-yn-1-yl) piperidine (1d)



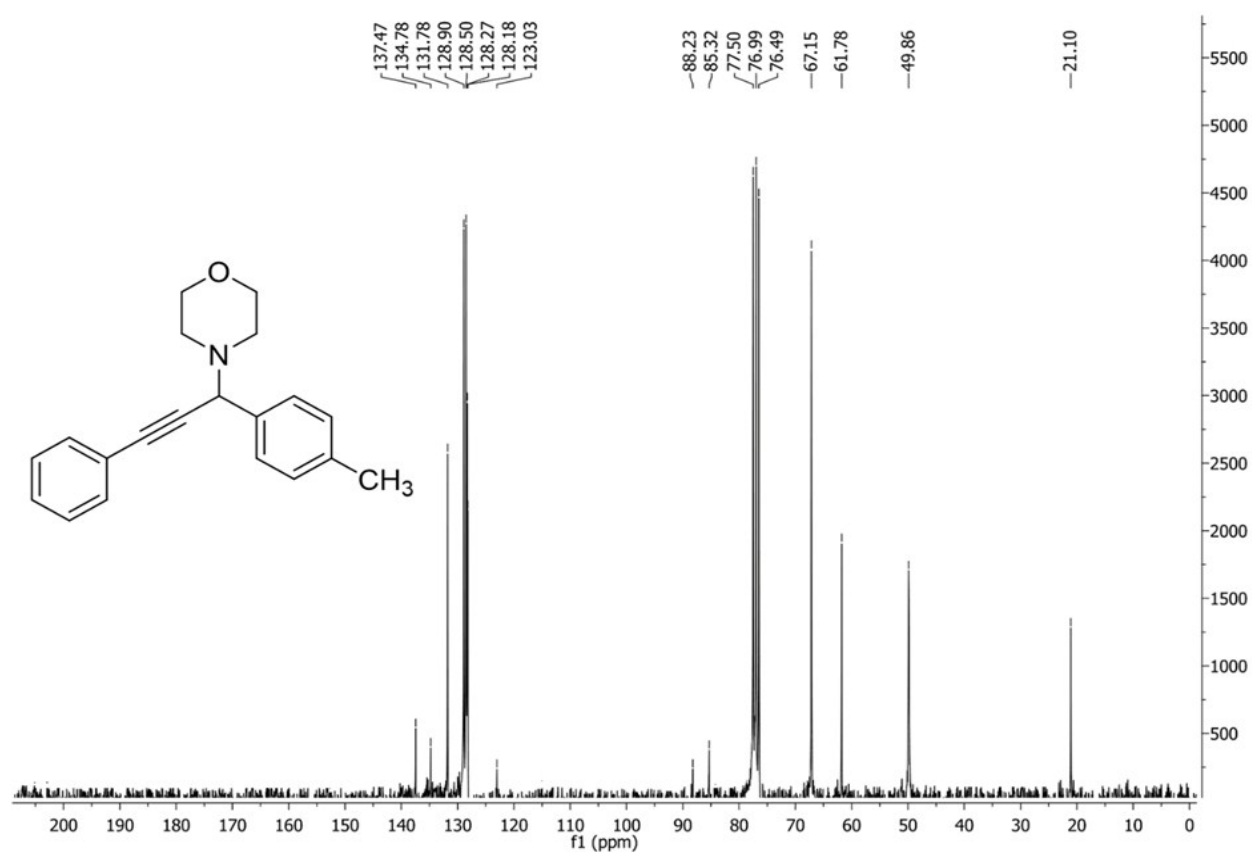
^1H NMR OF: 1-(3-phenyl-1-(p-tolyl) prop-2-yn-1-yl) pyrrolidine (1e)



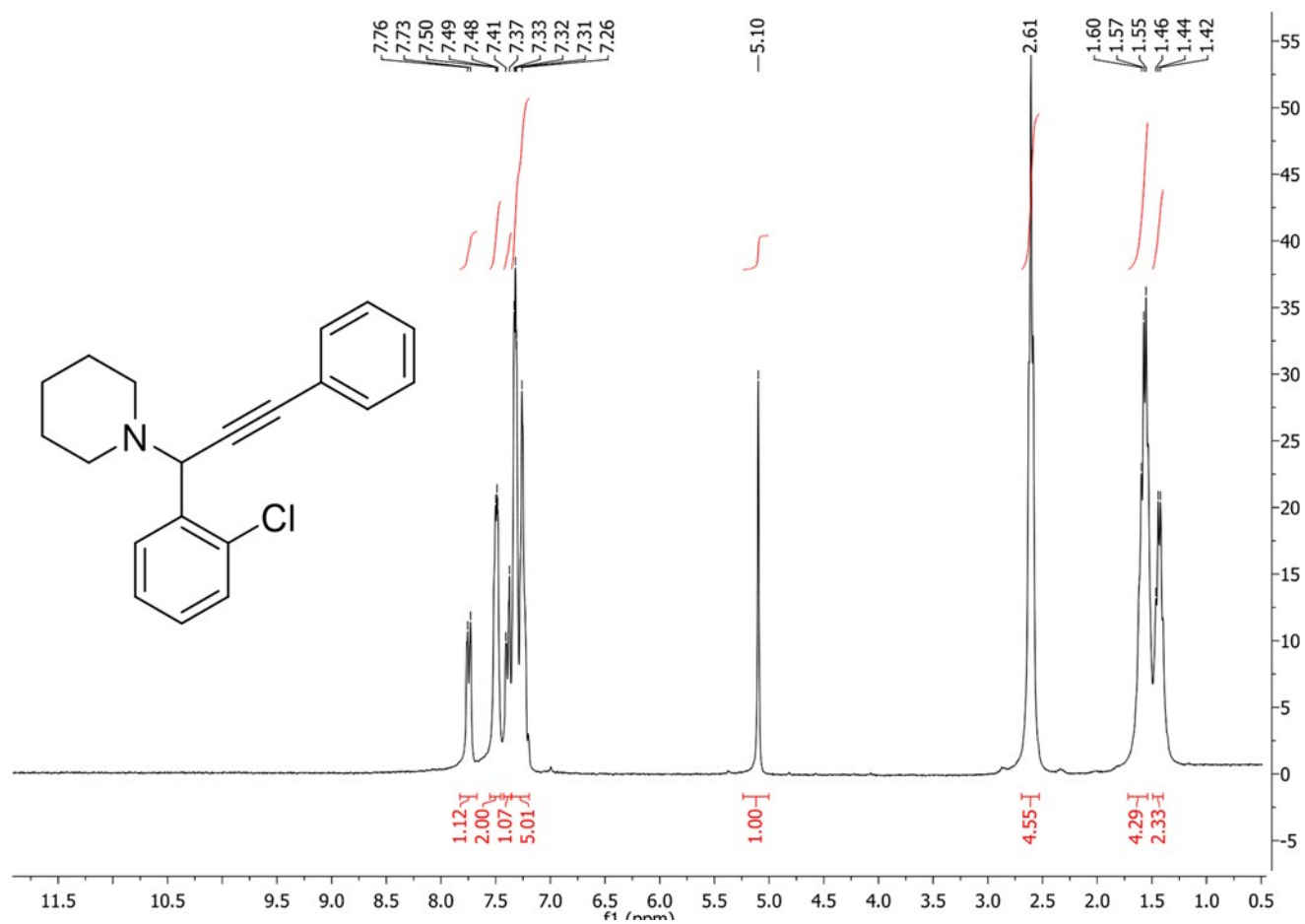
^{13}C NMR OF: 1-(3-phenyl-1-(p-tolyl) prop-2-yn-1-yl) pyrrolidine (1e)



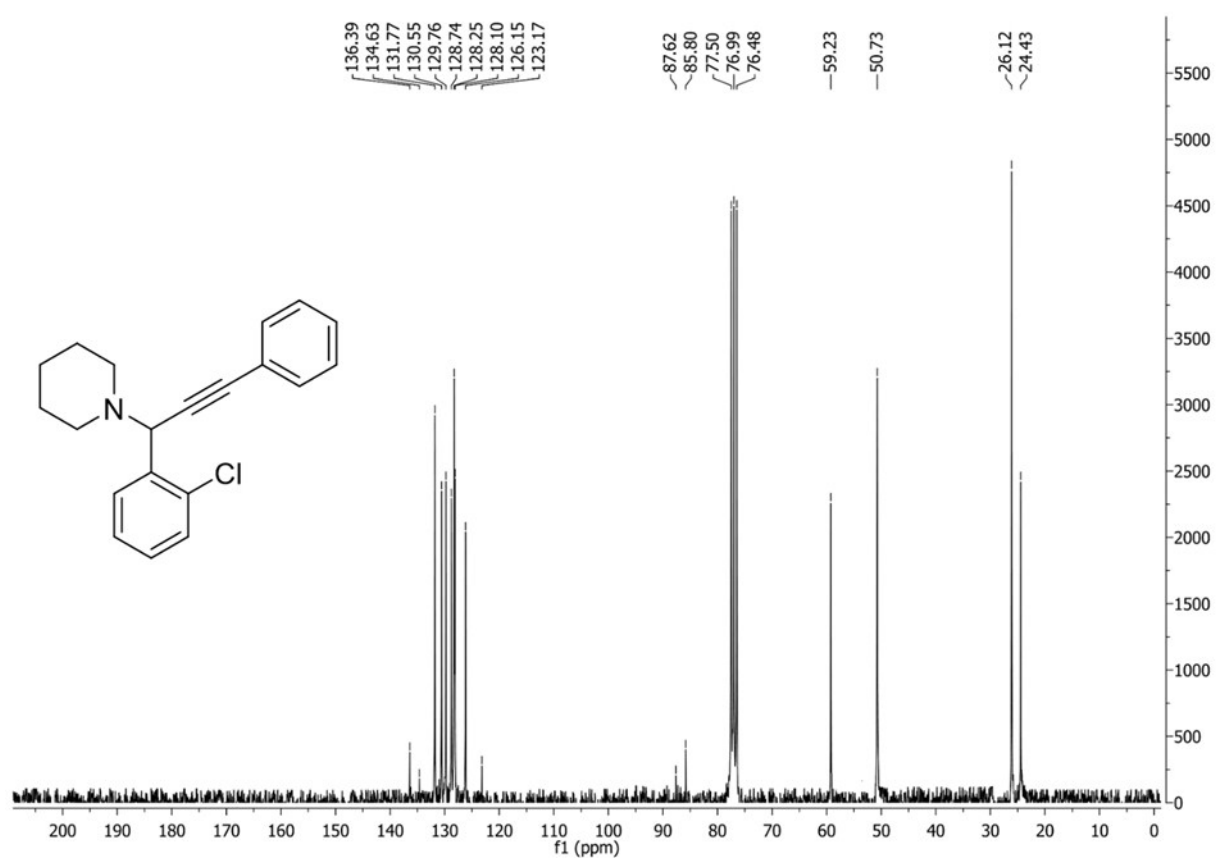
¹H NMR OF: 4-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)morpholine (1f)



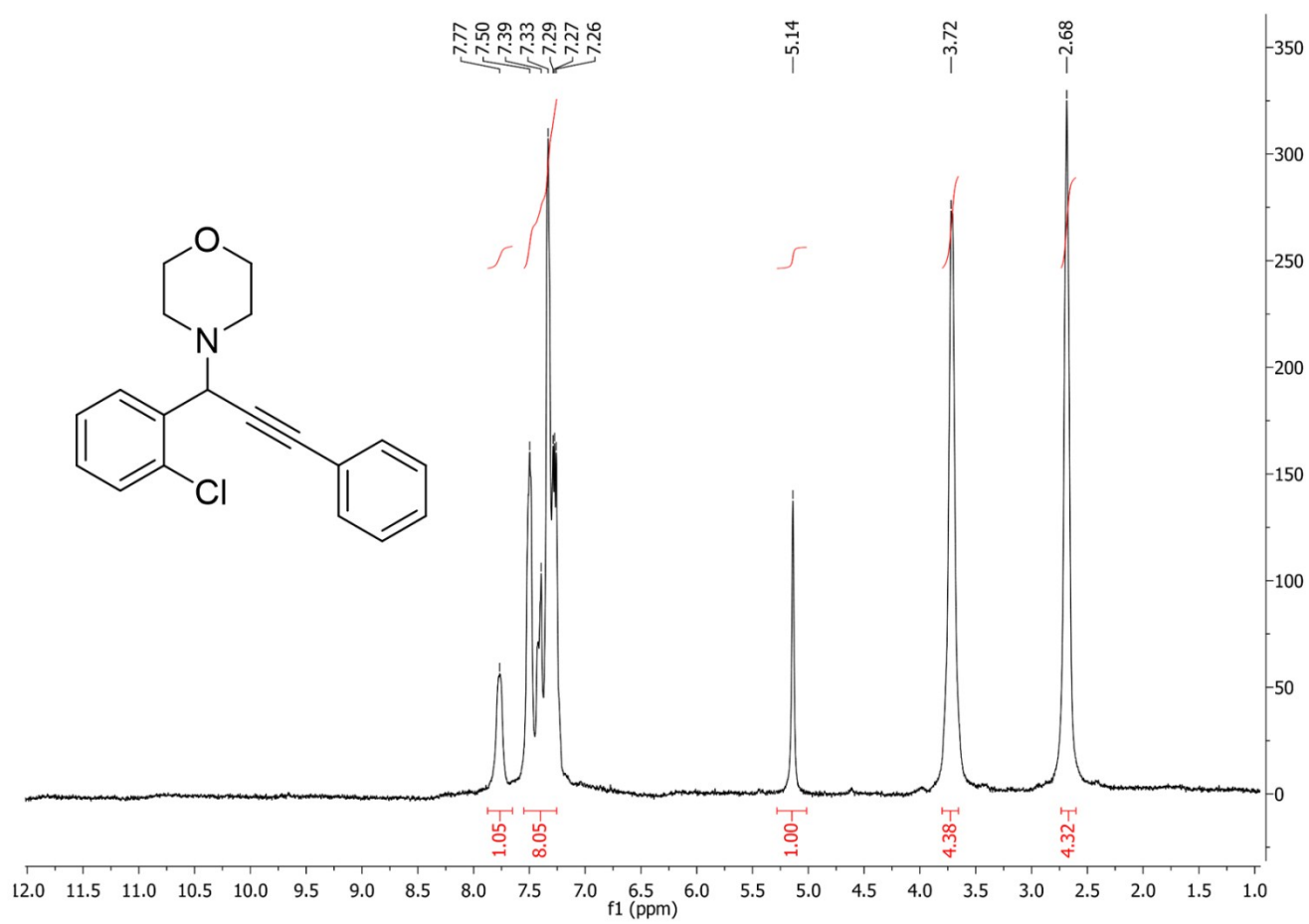
¹³C NMR OF: 4-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl) morpholine (1f)



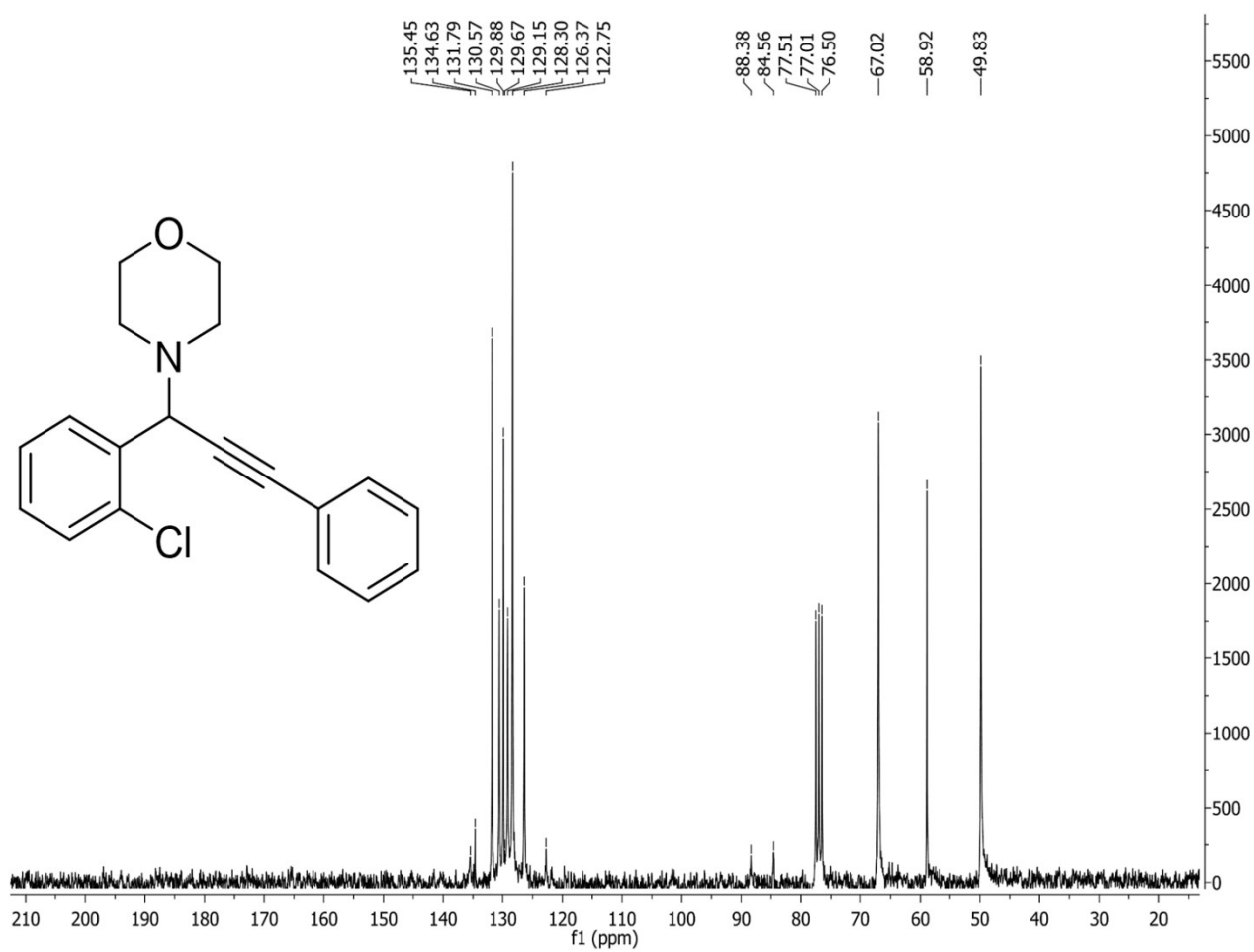
¹H NMR OF: 1-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) piperidine (1g)



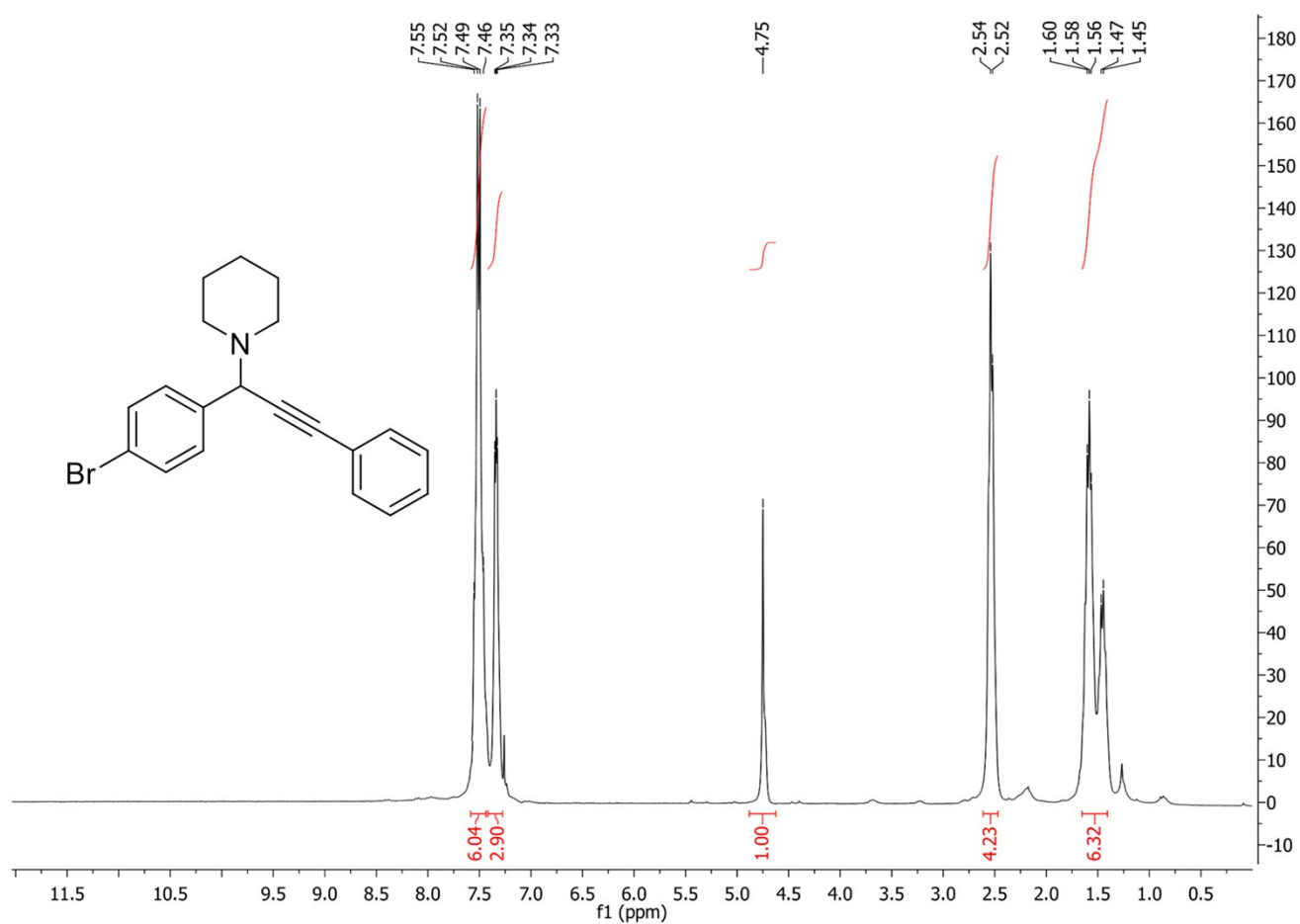
¹³C NMR OF: 1-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) piperidine (1g)



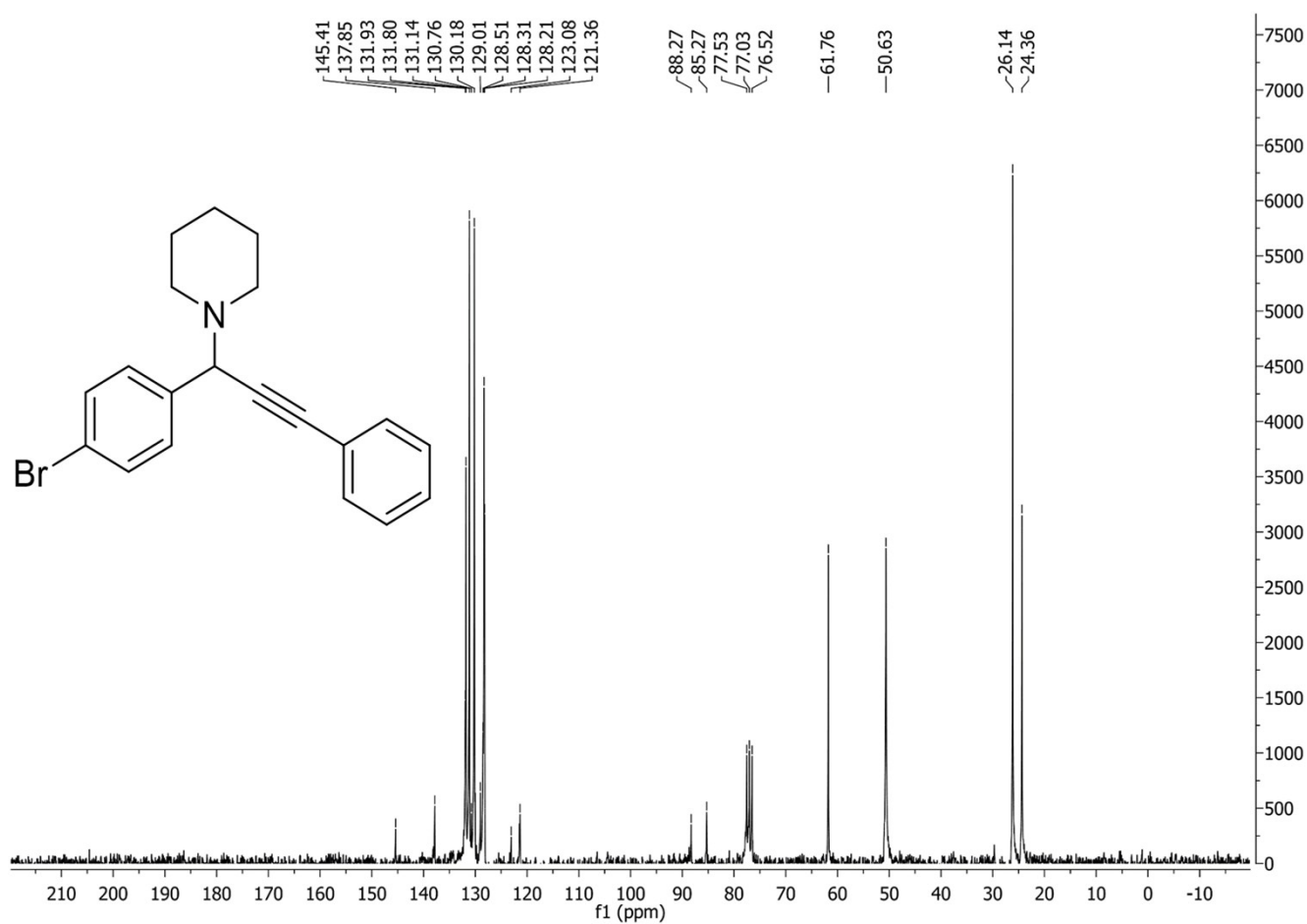
¹H NMR OF: 4-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) morpholine
(1h)



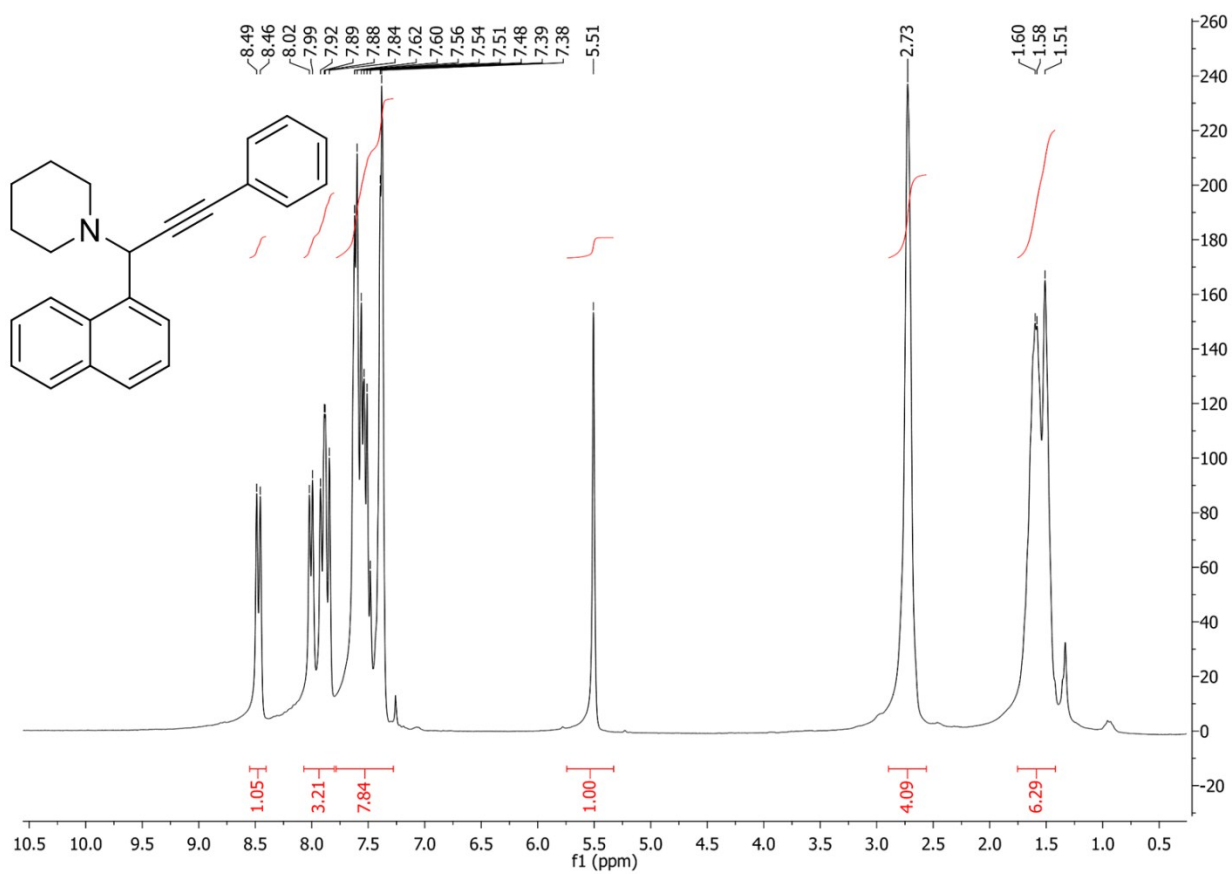
¹³C NMR OF: 4-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) morpholine
(1h)



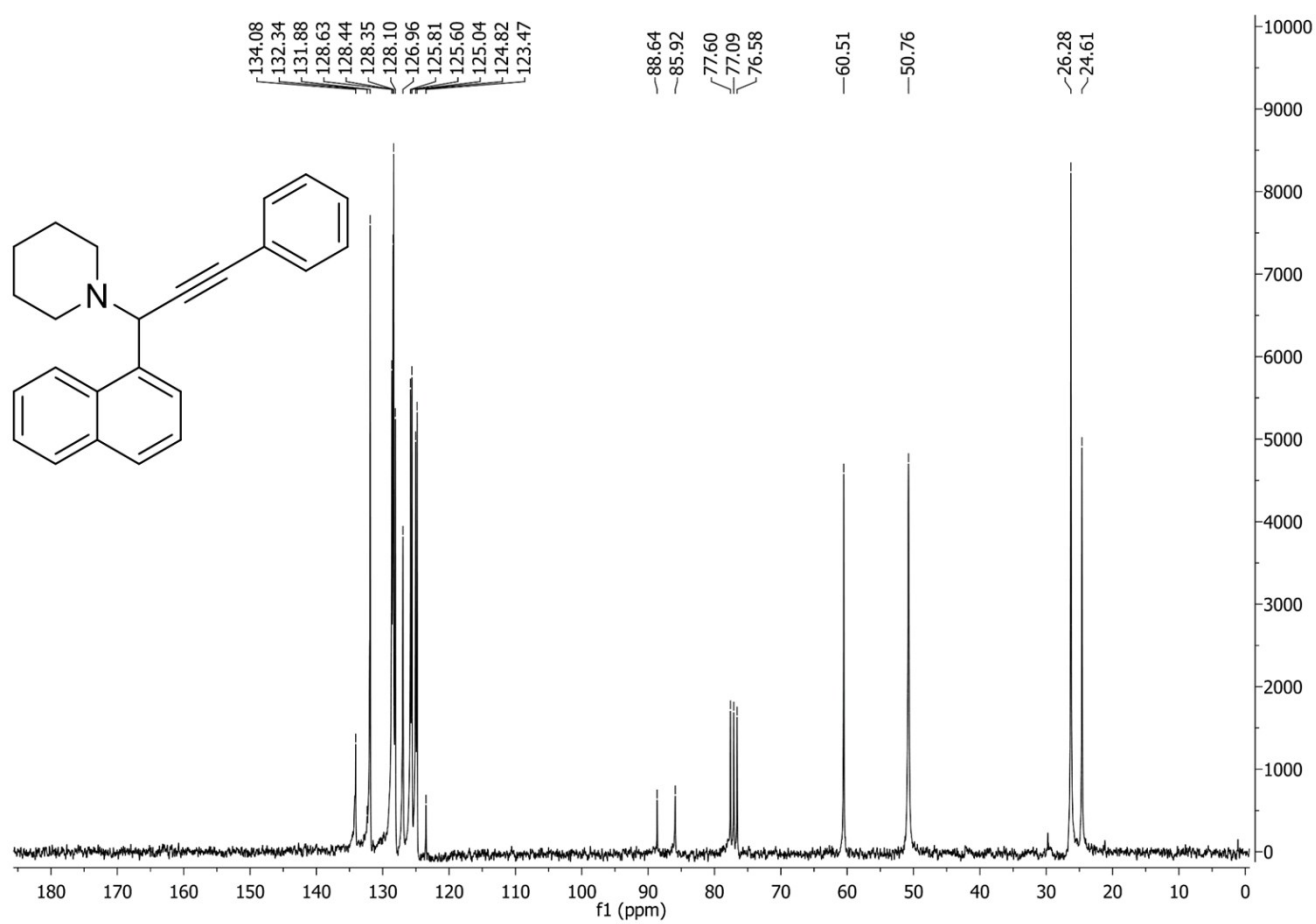
¹H NMR OF: 1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl) piperidine (1i)



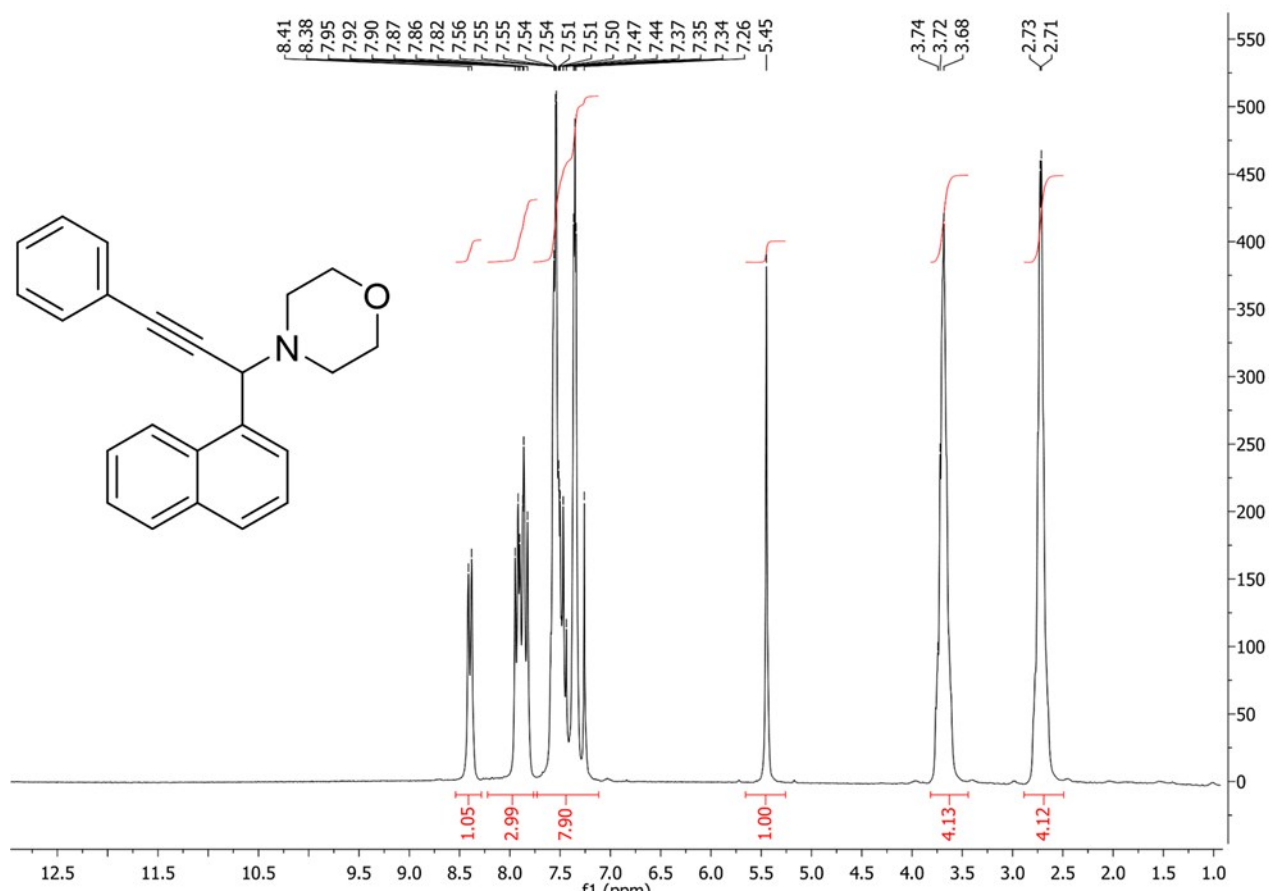
¹³C NMR OF: 1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl)
piperidine (1i)



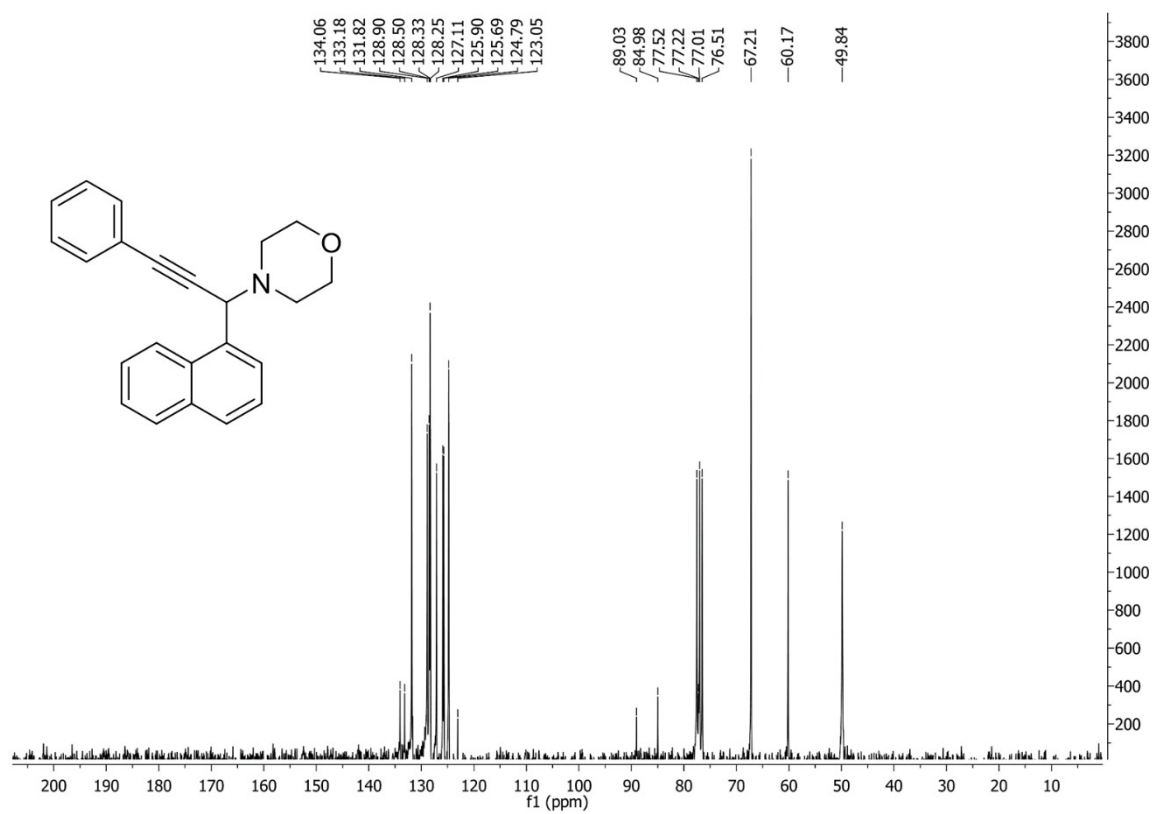
¹H NMR OF: 1-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl)piperidine (1j)



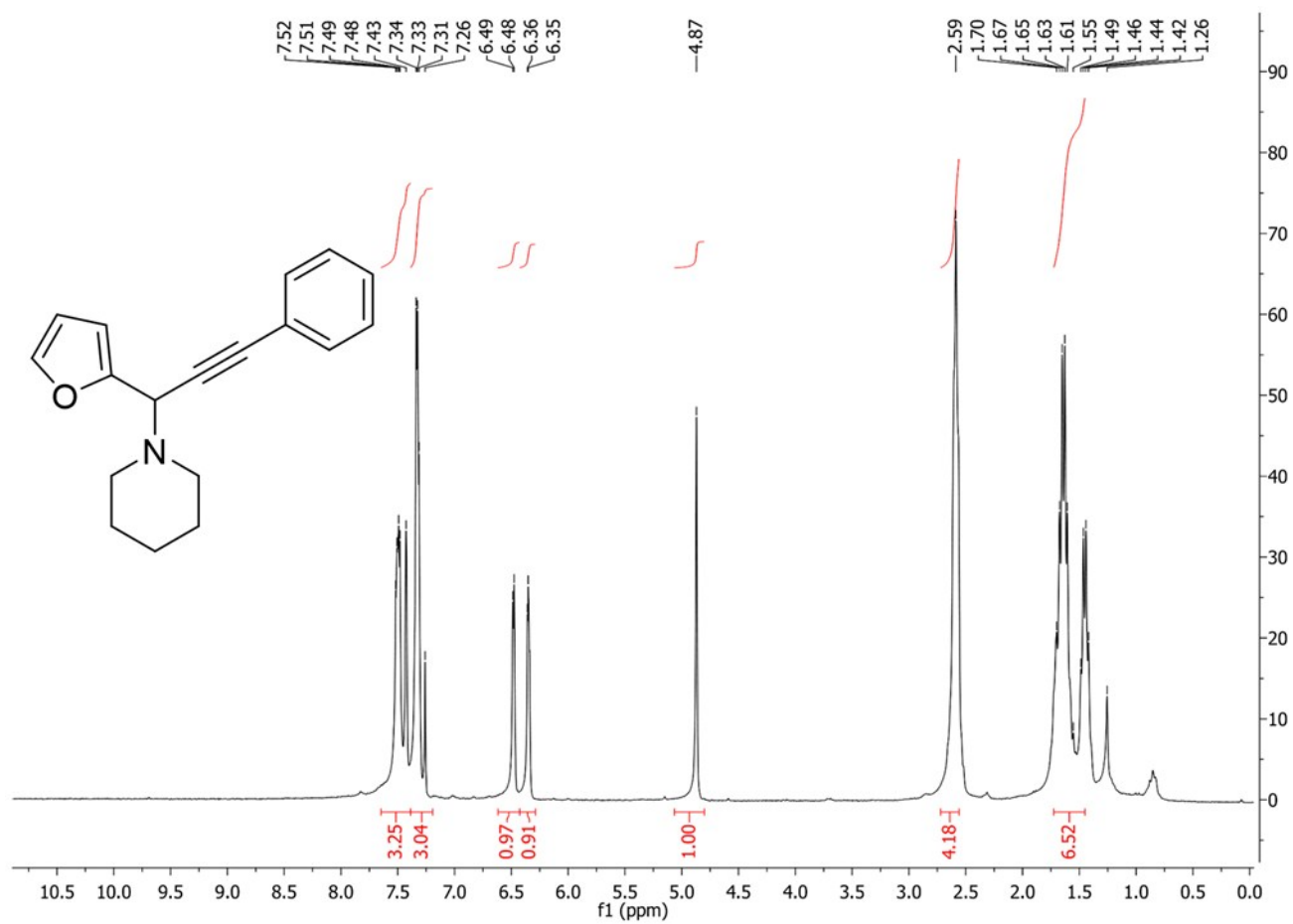
¹³C NMR OF: 1-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl) piperidine (1j)



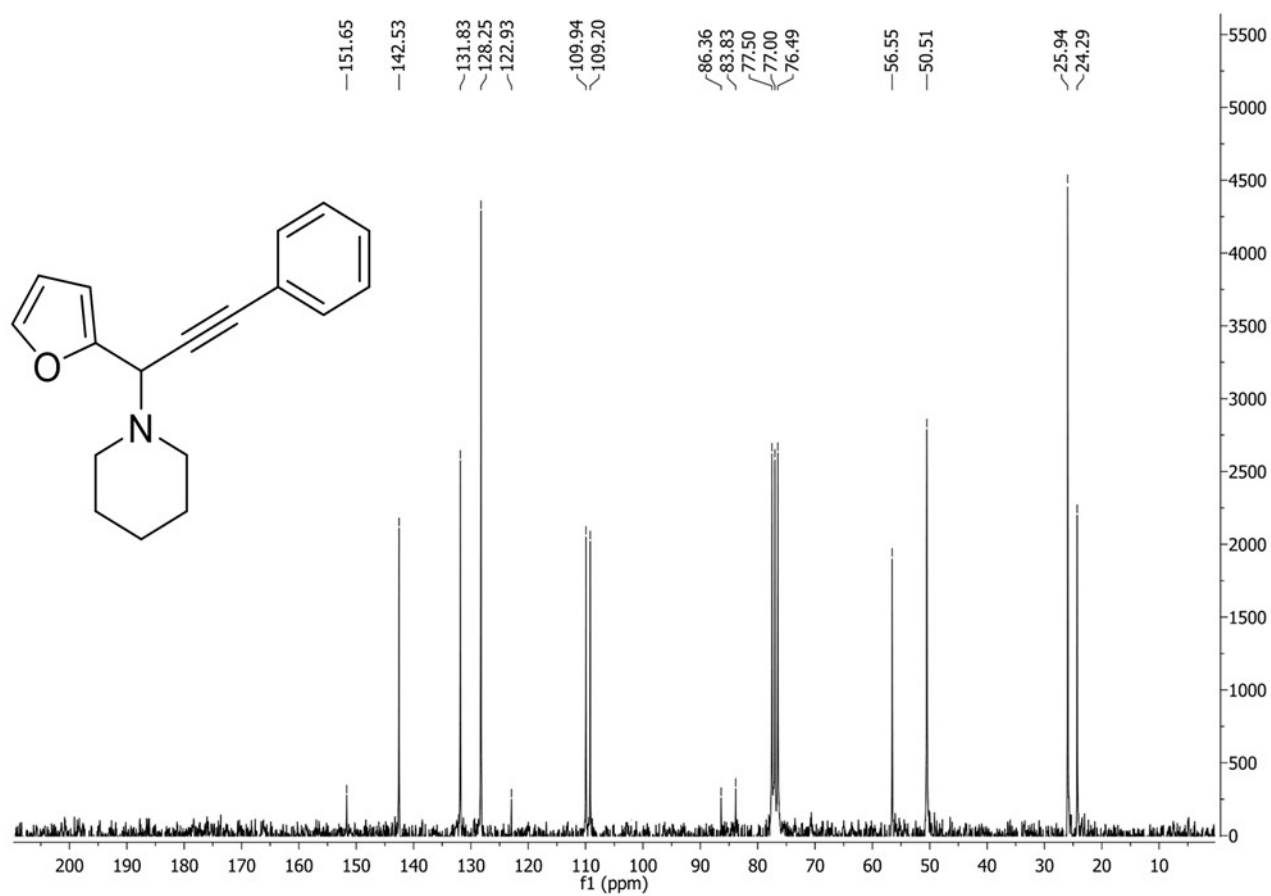
¹H NMR OF: 4-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl) morpholine (1k)



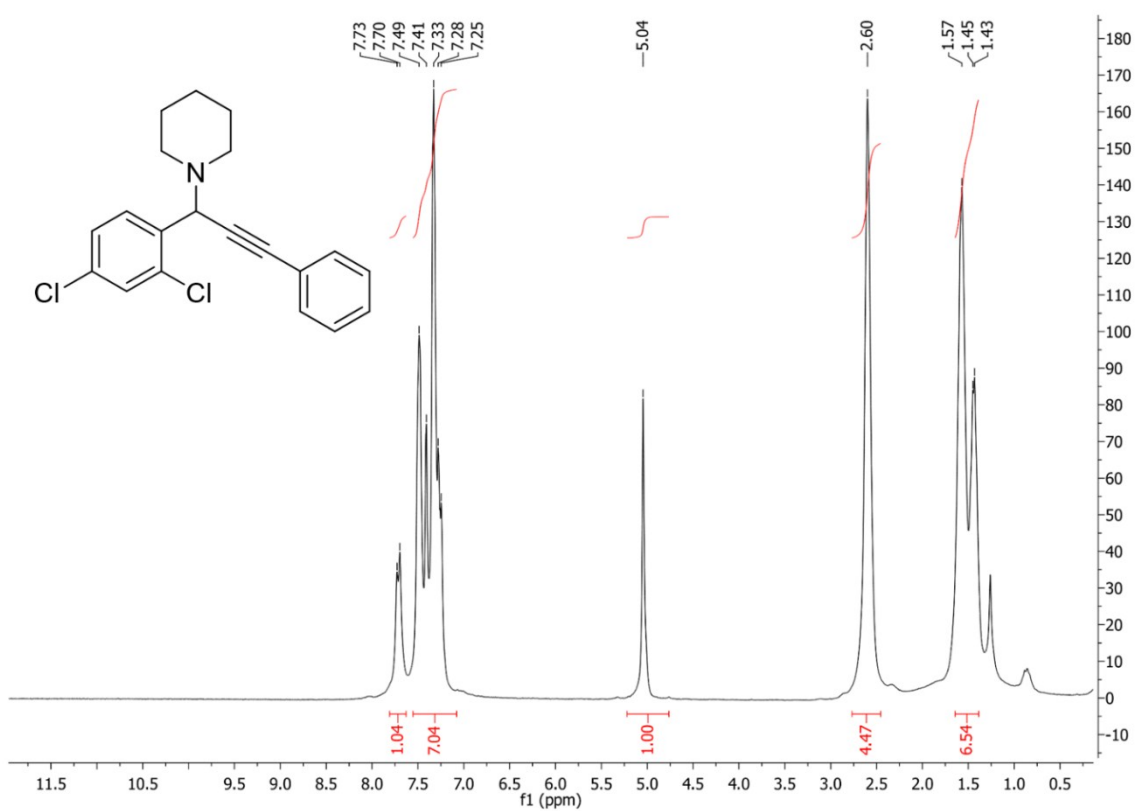
¹³C NMR OF: 4-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl) morpholine (1k)



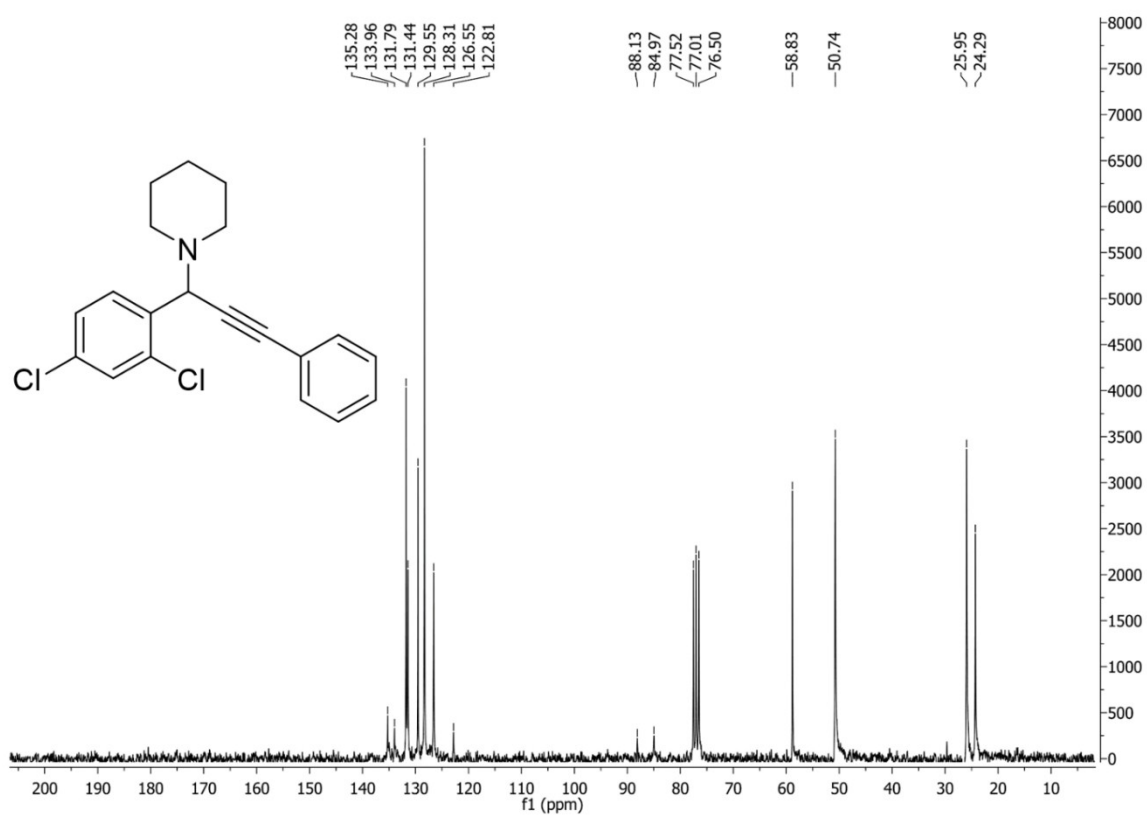
¹H NMR OF: 1-(1-(furan-2-yl)-3-phenylprop-2-ynyl) piperidine (II)



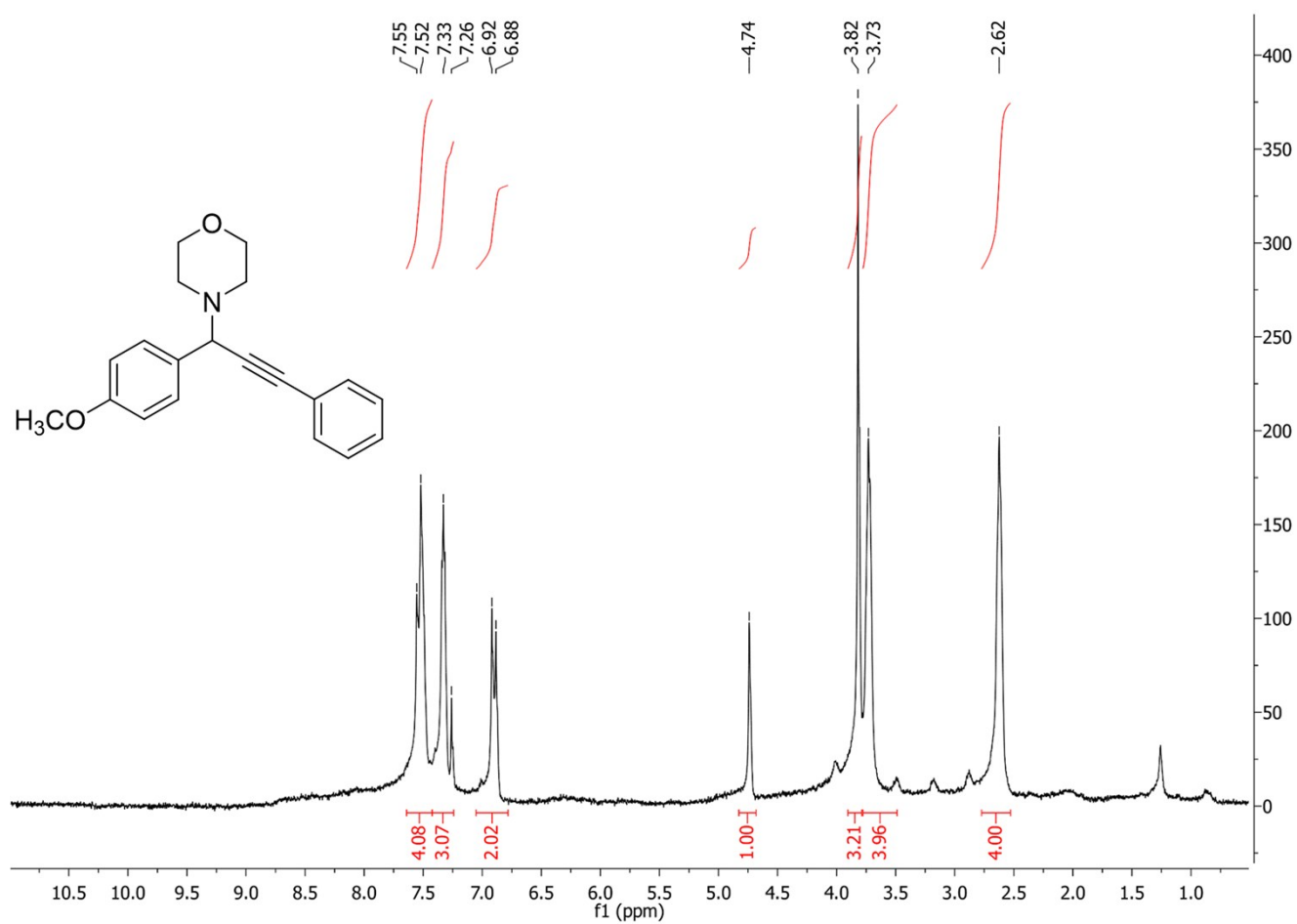
¹³C NMR OF: 1-(1-(furan-2-yl)-3-phenylprop-2-ynyl) piperidine (11)



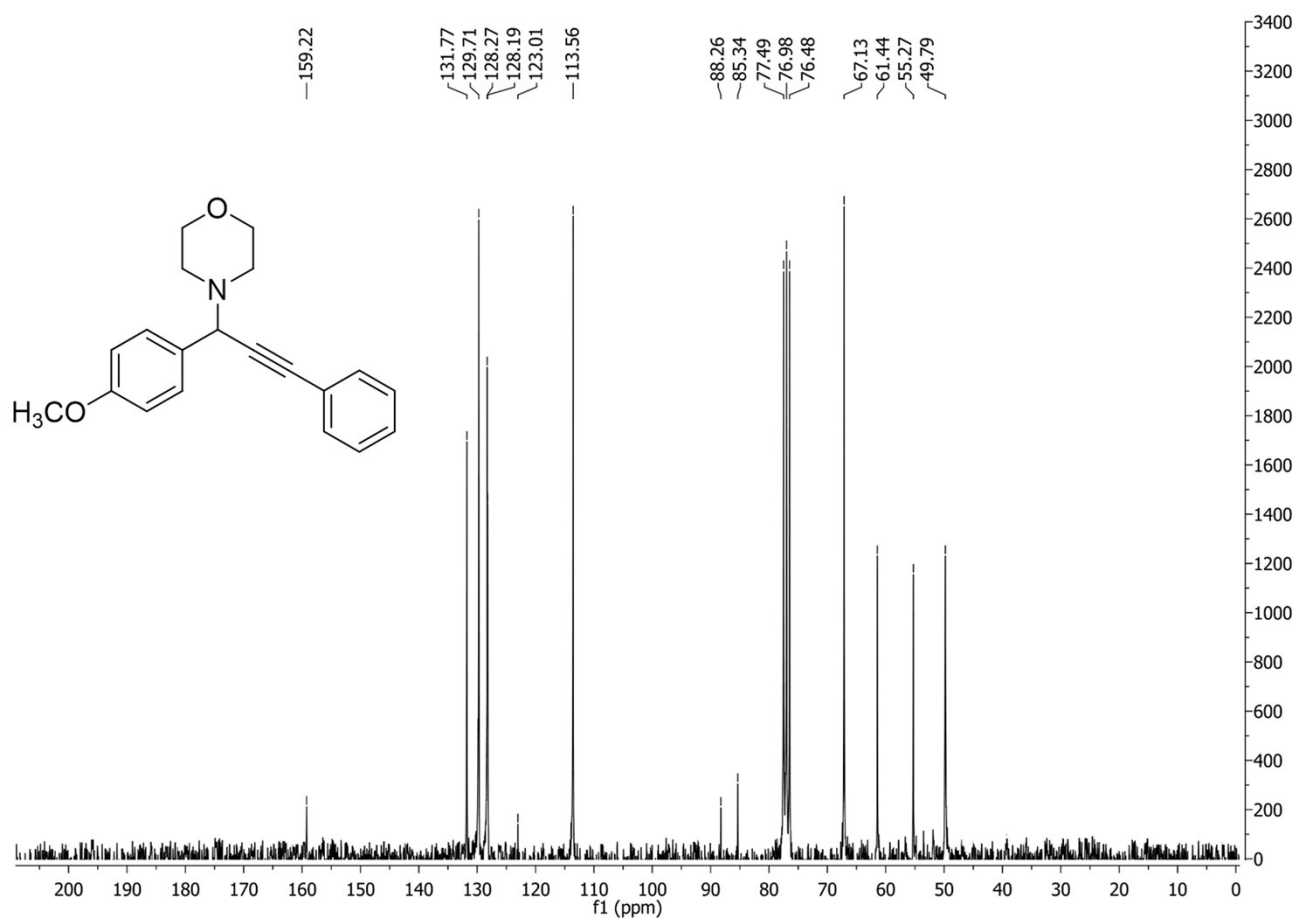
¹H NMR OF: 1-(1-(2,4-dichlorophenyl)-3-phenylprop-2-yn-1-yl)piperidine (1m)



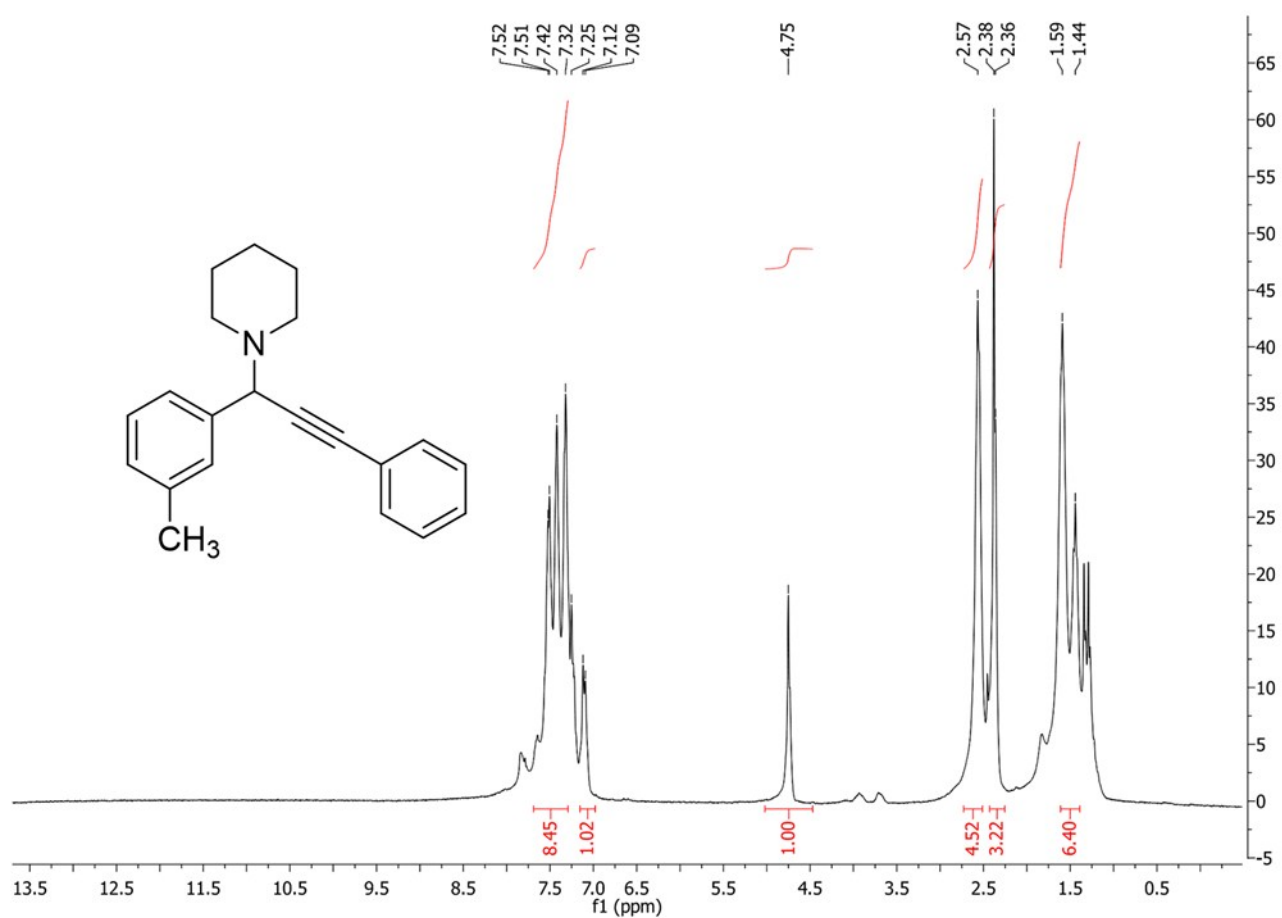
¹³C NMR OF: 1-(1-(2,4-dichlorophenyl)-3-phenylprop-2-yn-1-yl)piperidine (1m)



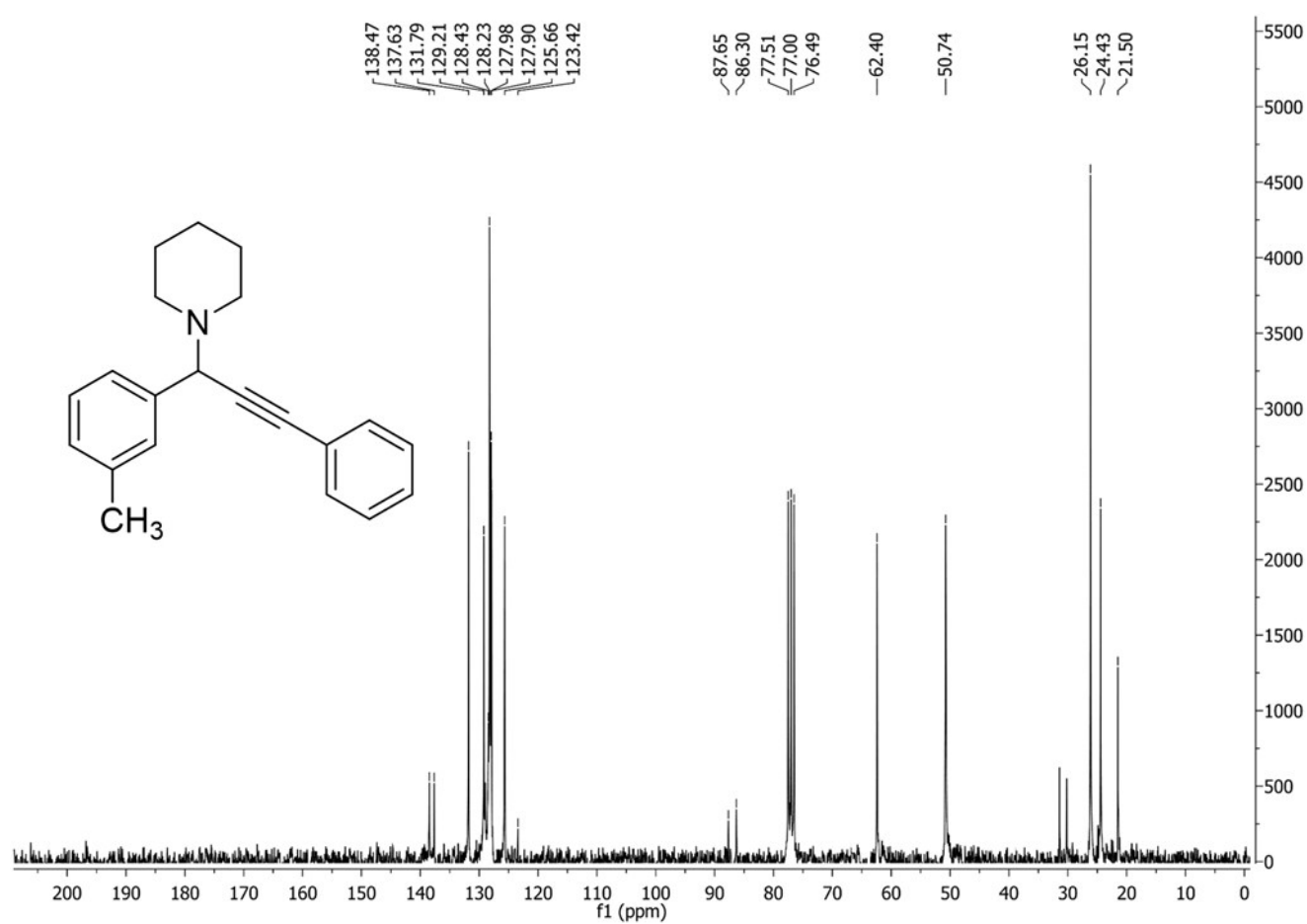
¹H NMR OF: 4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl) morpholine (1n)



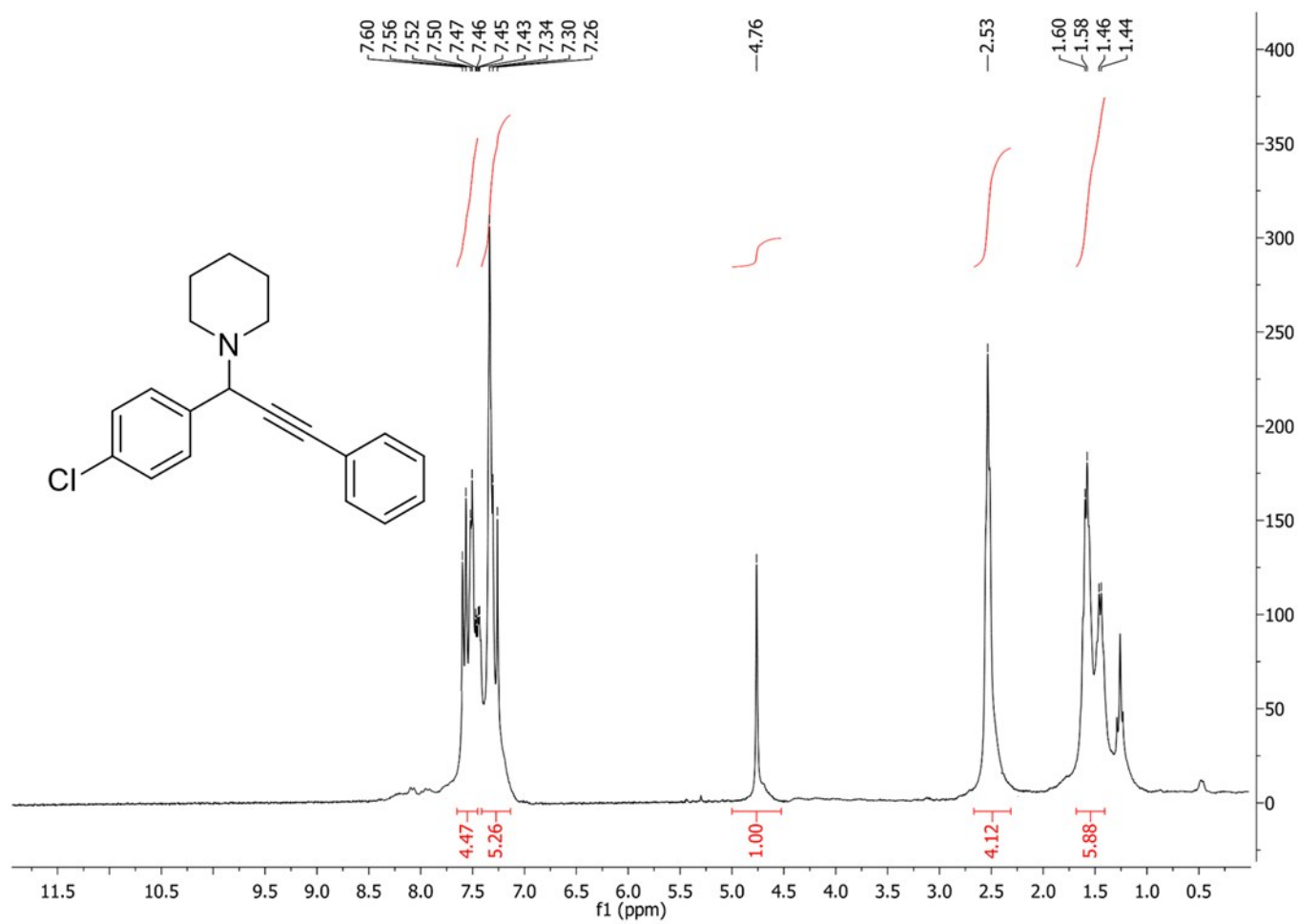
¹³C NMR OF: 4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl) morpholine (1n)



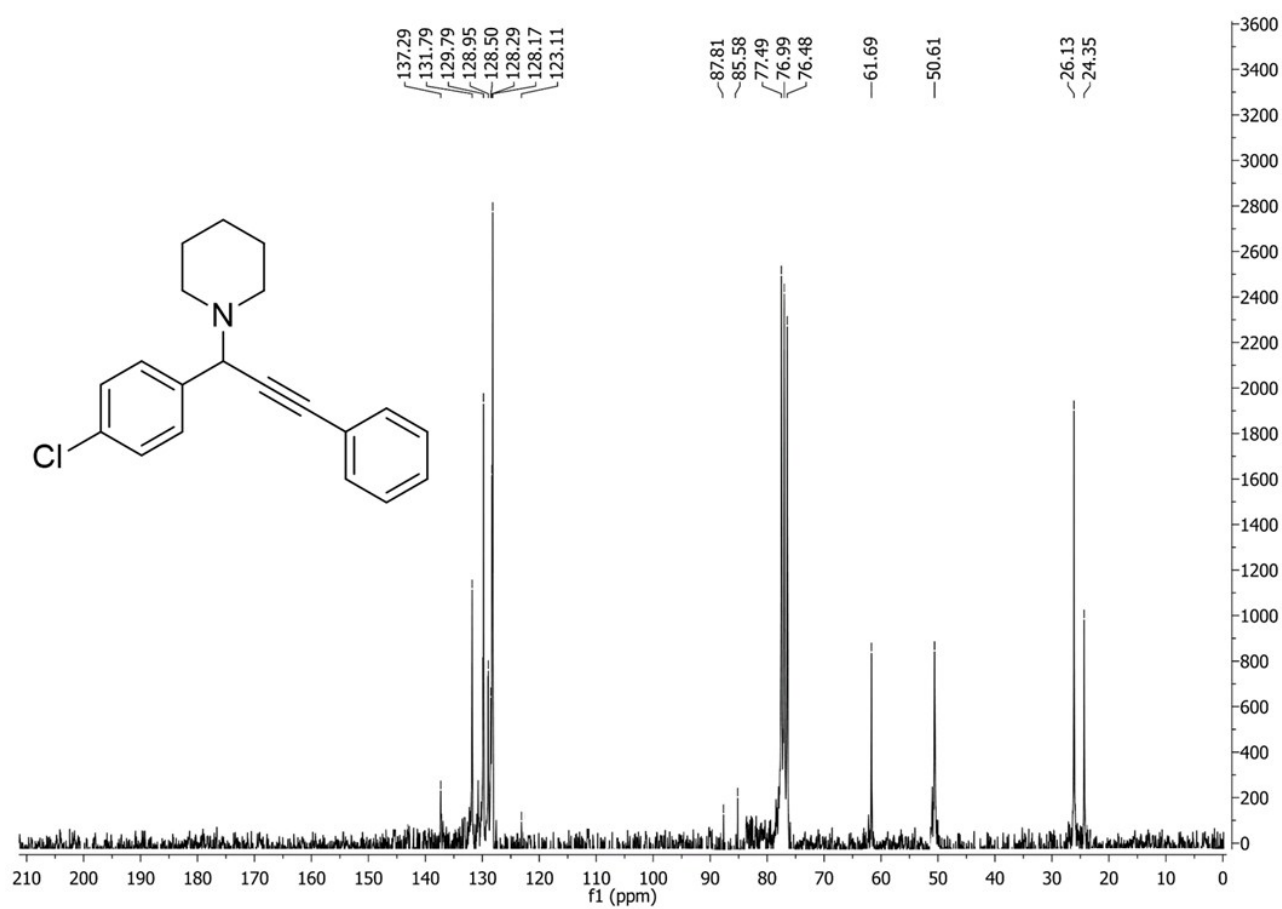
¹H NMR OF: 1-(3-phenyl-1-(m-tolyl) prop-2-yn-1-yl) piperidine (1o)



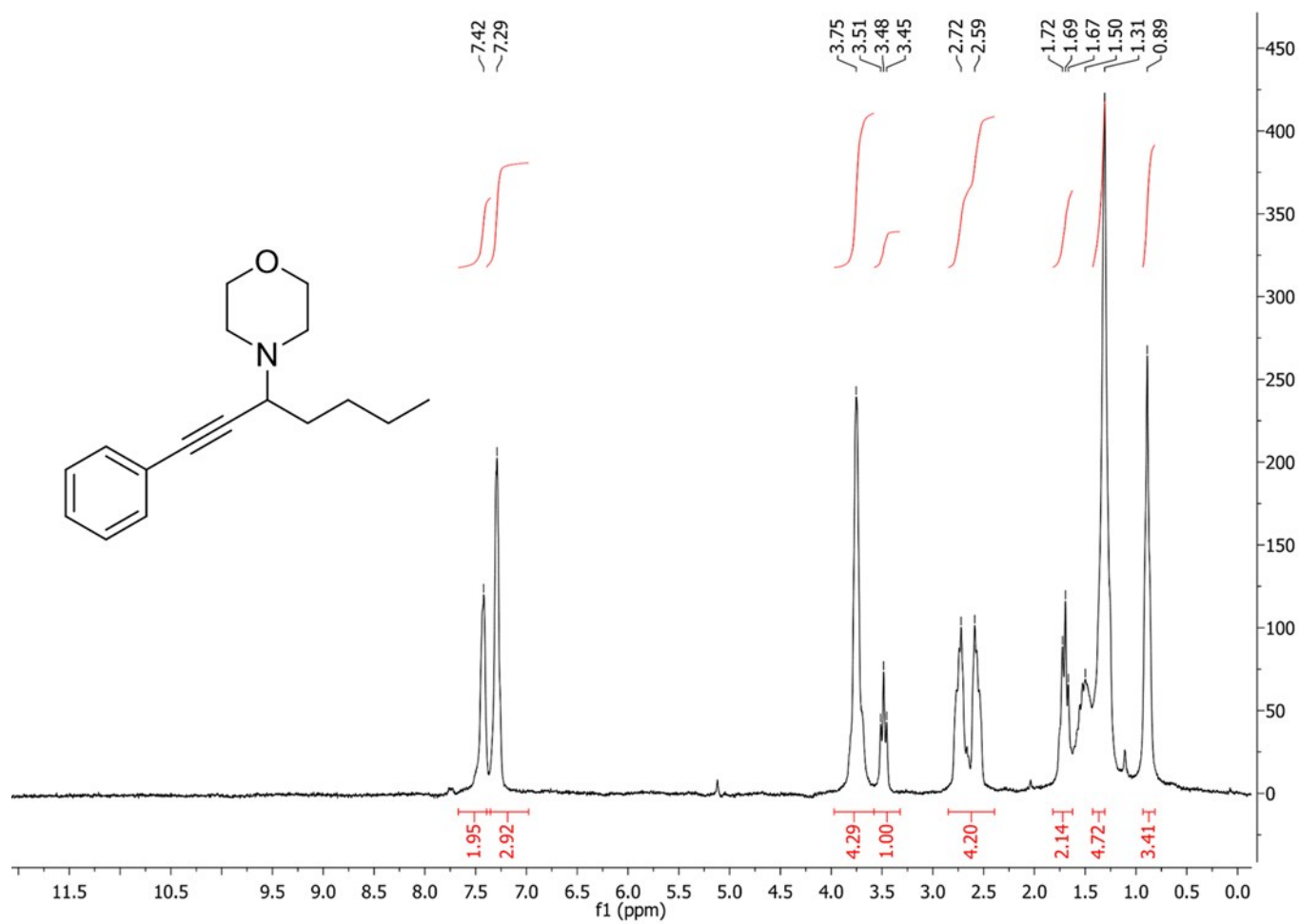
¹³C NMR OF: 1-(3-phenyl-1-(m-tolyl) prop-2-yn-1-yl) piperidine (1o)



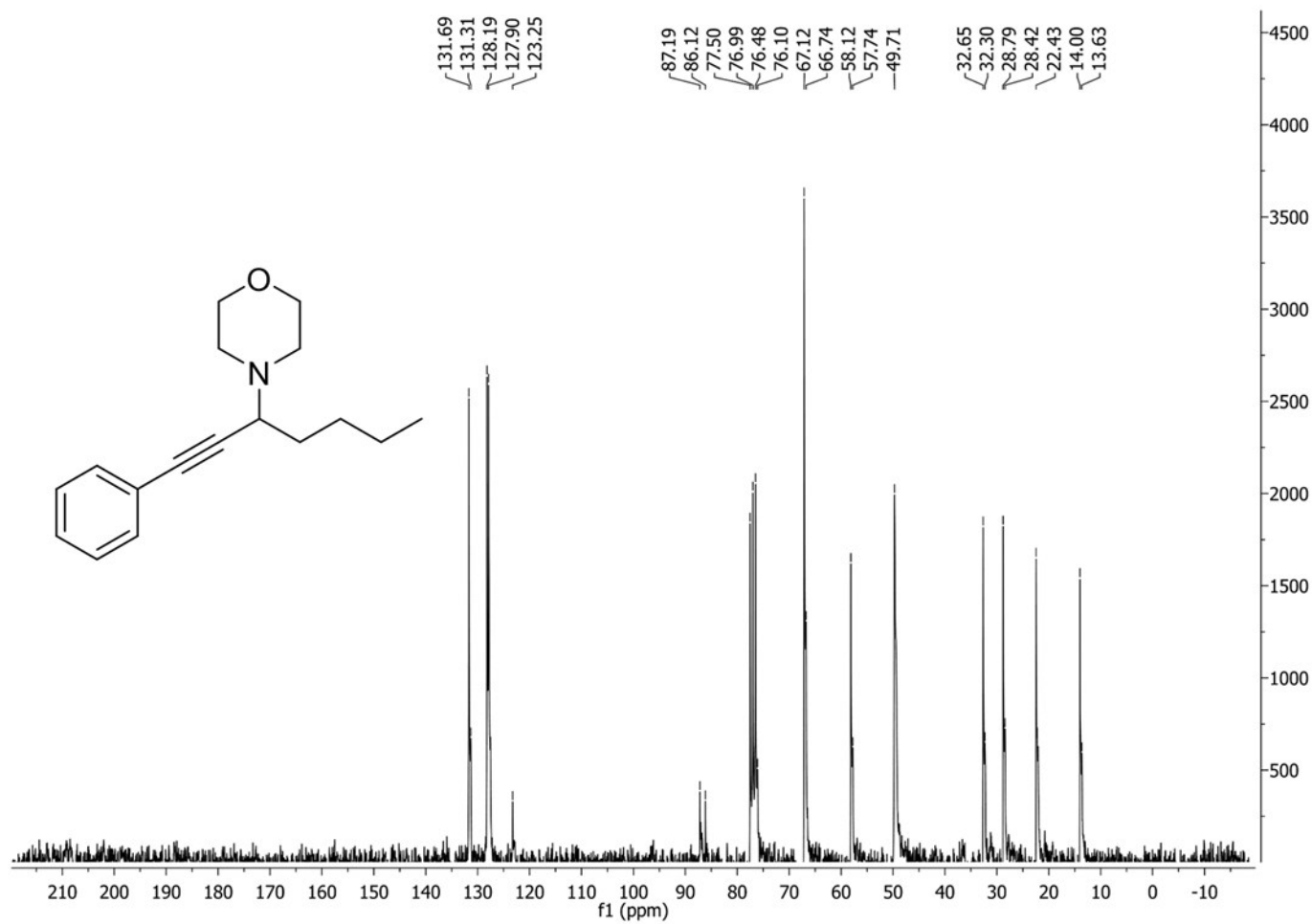
¹H NMR OF: 1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl) piperidine (1p)



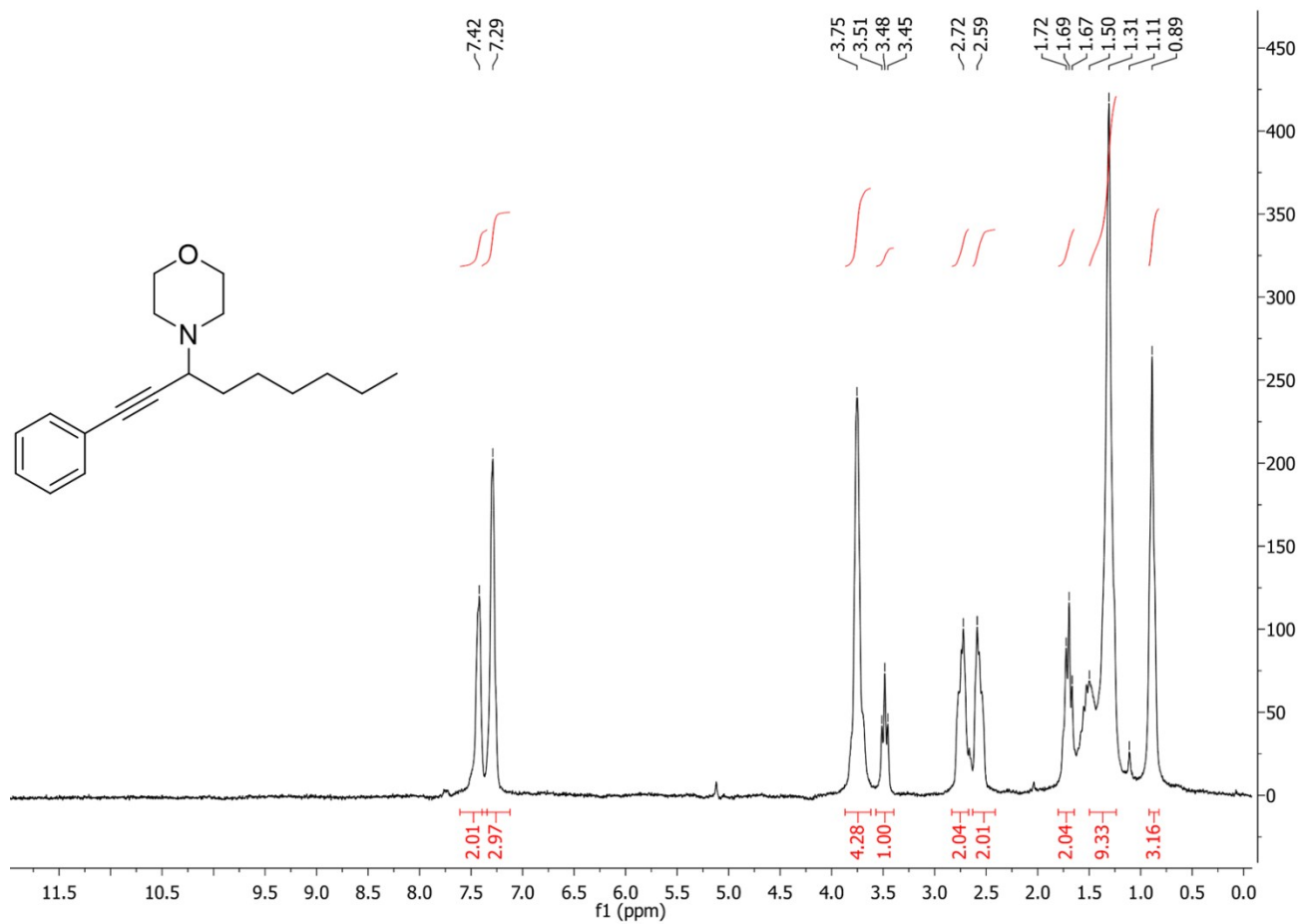
¹³C NMR OF: 1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl) piperidine
(1p)



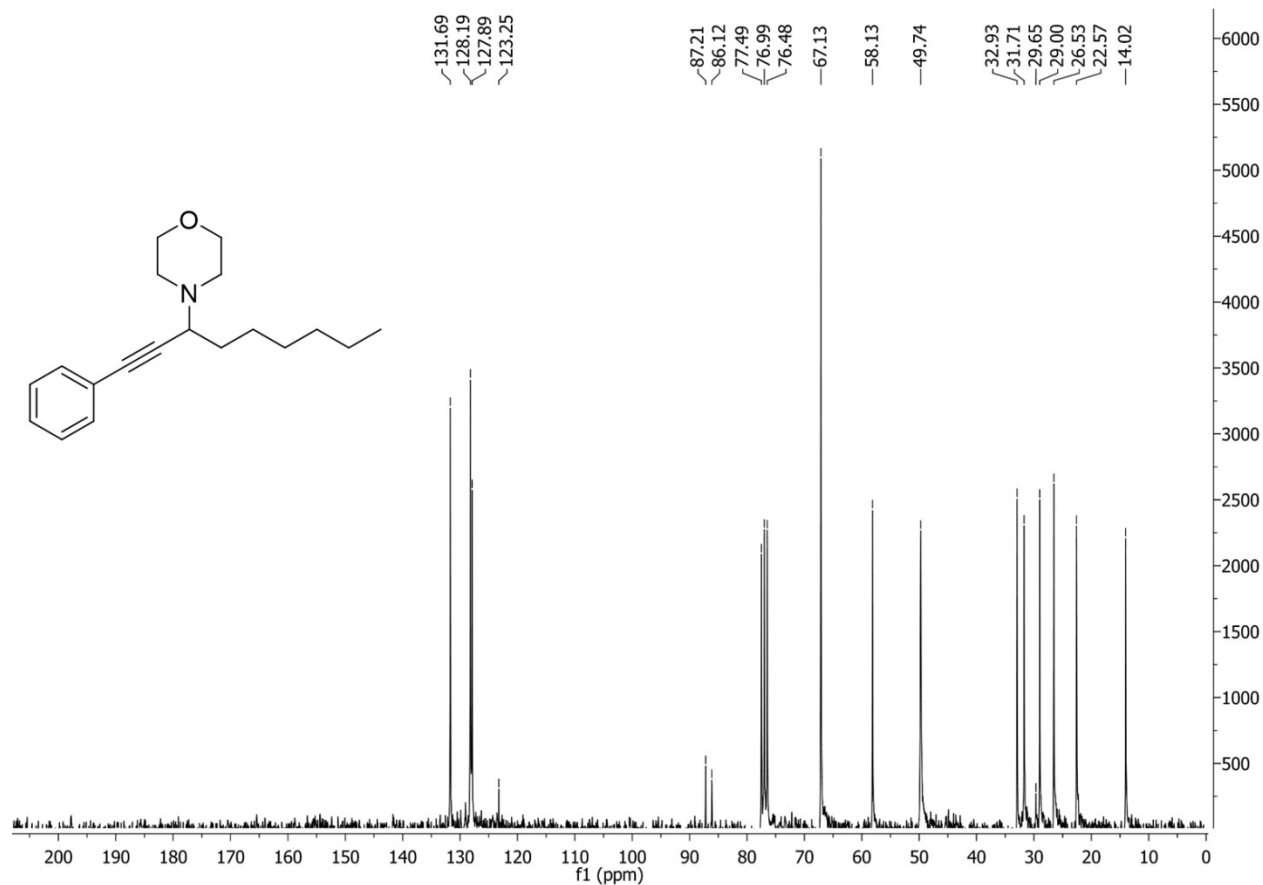
¹H NMR OF: 4-(1-phenylhept-1-yn-3-yl) morpholine (1q)



¹³C NMR OF: 4-(1-phenylhept-1-yn-3-yl) morpholine (1q)



¹H NMR OF: 4-(1-phenylnon-1-yn-3-yl) morpholine (1r)



¹³C NMR OF: 4-(1-phenylnon-1-yn-3-yl) morpholine (1r)

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