

Supporting Information

Nanocrystalline magnesium oxide stabilized gold nanoparticles: an advanced nanotechnology based green, recyclable heterogeneous catalyst platform for the one-pot synthesis of propargylamines

**Keya Layek,^a Rajashree Chakravarti,^b M. Lakshmi Kantam,^{*a} H. Maheswaran^a and Ajayan
Vinu^b**

^aInorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad-500607, India.

^bWorld Premier International (WPI) Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1
Namiki, Tsukuba 305-0044, Japan.
Email: mlakshmi@iict.res.in

CONTENTS

General Remarks.....	S2
EDX and FT-IR characterization of NAP-Mg-Au(0) catalyst.....	S2
Screening of supported Au(0) catalysts for the one pot synthesis of propargylamines.....	S4
Screening of solvents for the one-pot synthesis of propargylamines.....	S4
Spectroscopic characterization of products.....	S4
¹ H-NMR spectra of the products.....	S9
¹³ C-NMR spectra of the products.....	S19
References.....	S28

General remarks

NAP-MgO (commercial name: NanoActive™ Magnesium Oxide Plus), was purchased from Nano Scale Materials, Inc. (Manhattan, USA). All chemicals were purchased from commercial sources, and were used as received. All solvents used for experiments were dried using standard procedures, and distilled prior to use. The particle size and morphology of the samples were studied using Philips TECNAI F12 FEI Transmission Electron Microscope (TEM). The X-ray powder diffraction (XRD) patterns were recorded on a Rigaku diffractometer with Cu K α radiation. X-ray Photoelectron Spectra (XPS) were obtained using a PHI Quantera SXM (ULVAC-PHI), which was equipped with a monochromatic Al K α X-ray source. The analysis area was defined by the X-ray beam, and the X-ray beam size was 1.5×0.1 mm at 60 W for both wide and high resolution spectra; the photoelectron take-off angle was 45 degrees. Wide spectra were obtained at a pass energy of 280 eV with 0.5 eV step and high resolution spectra were obtained at a pass energy of 26 eV with 0.1 eV step for C 1s and a pass energy of 55 eV with 0.1 eV step for N 1s and O 1s. The FT-IR spectra were recorded on a Perkin–Elmer spectrophotometer. Energy dispersive X-ray spectroscopy (EDX) was performed on a Hitachi SEM S-520, EDX-Horiba Link instrument. BET surface area was measured by a Nova Quantachrome 4000e instrument. ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectra were recorded on an Avance 300 and Inova 500 (300 MHz & 500 MHz for ¹H-NMR and 300 MHz for ¹³C-NMR) spectrometer in CDCl₃ using TMS as an internal standard. ACME SILICA GEL (100-200 mesh) was used for column chromatography purposes using ethyl acetate/hexanes as eluting agents, and thin layer chromatography was performed on Merck precoated silica-gel 60-F254 plates.

Characterization of NAP-Mg-Au (0) catalyst by Energy Dispersive X-ray (EDX) Studies:

The energy-dispersive X-ray (EDX) studies of NAP-Mg-Au (0) catalyst have been performed and the results from these studies reveal not only the presence of peaks that corresponds to Mg, O and Au(0) but also reveal the relative amounts of these elements present in the catalyst. (See Figure 1) It has been determined from these studies that there exists 68.88% atomic oxygen, 29.56% atomic magnesium and 1.55% atomic gold, respectively in NAP-Mg-Au (0) catalyst. Elemental mapping of NAP-Mg-Au (0) catalyst by using electron microprobe scanning (see inset Figure 1) shows that the Au(0) nanoparticles are uniformly distributed on to NAP-MgO support, and no agglomeration of Au(0) nanoparticles is discernable in the catalyst.

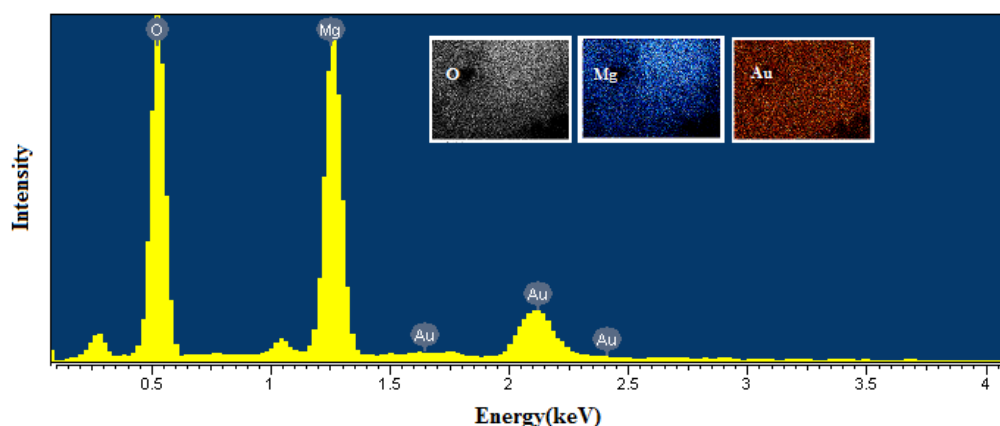


Figure 1. Energy-dispersive X-ray (EDX) pattern of NAP-Mg-Au (0) catalyst. The inset shows the elemental mapping of the catalyst.

FT-IR Characterization of NAP-Mg-Au (0) catalyst

The Fourier Transformation-Infra-Red (FT-IR) spectra of pristine NAP-MgO and those of fresh and spent NAP-Mg-Au (0) catalyst are shown in Figure 2. During the preparation of this catalyst, the surface of nanocrystalline MgO was hydroxylated as indicated by the presence of non-H-bonded OH groups at 3697 cm^{-1} in the FTIR spectra (Figure 2b). This is consistent with the reactive profile of NAP-MgO with water.

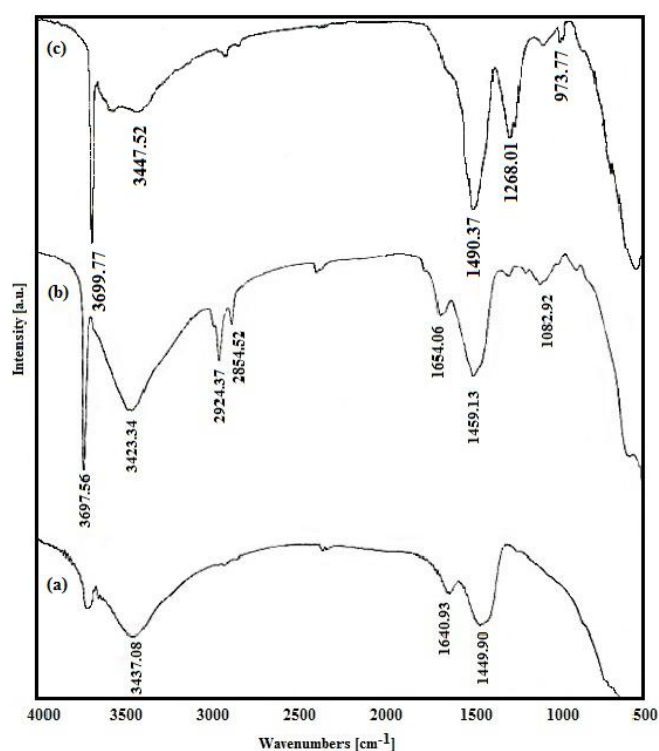


Figure 2. FTIR spectra of (a) pristine NAP-MgO, (b) fresh NAP-Mg-Au(0) and (c) spent NAP-Mg-Au(0) catalyst.

Table 1. Screening of supported Au(0) catalysts for the one pot synthesis of propargylamines^a

Catalyst	BET area of the support (m ² /g)	BET area of the Au(0) catalyst (m ² /g)	Au content (%)	Average particle size (± 2) nm	Yield(%) ^b
Nano HAP-Au(0) ¹	150	61	1.37	6	71
Meso CeO ₂ -Au(0) ²	120	105	1.50	11	84
NAP-Mg-Au(0)	183	143	1.55	10	96

^a Reaction conditions: benzaldehyde (1.0 mmol), piperidine (1.2 mmol), phenylacetylene (1.5 mmol), catalyst (30 mg) and toluene (2mL) stirred at 100°C for 24 hours.

^b Isolated yields based on benzaldehyde after silica-gel flash column chromatography.

Table 2. Screening of different solvents for the one-pot synthesis of propargylamines catalyzed by NAP-Mg-Au(0)^a

Entry	Solvent	Yield(%) ^b
1.	Water	21
2.	Toluene	96
3.	Methanol	54
4.	Ethanol	48
5.	Acetonitrile	66
6.	Tetrahydrofuran	no reaction

^a Reaction conditions: benzaldehyde(1.00 mmol), piperidine(1.2mmol), phenylacetylene(1.5mmol), NAP-Mg-Au (0) catalyst (30 mg) and solvent (2mL) stirred at 100°C till the completion of the reaction.

^b Isolated yields based on benzaldehyde after silica-gel flash column chromatography.

Spectroscopic characterization of the products

1-(1, 3-diphenylprop-2-ynyl) piperidine (Table 2, Entry 1): Pale yellow liquid, 96%. ¹H NMR (300 MHz, CDCl₃, ppm): δ 1.37-1.50 (m, 2H), 1.50-1.65 (m, 4H), 2.4-2.6 (m, 4H), 4.75 (s, 1H), 7.20-7.37 (m, 6H), 7.4-7.5 (m, 2H), 7.55-7.65 (m, 2H); ¹³C NMR (300 MHz,

CDCl₃ , ppm): δ 24.691, 26.444, 59.930, 62.888, 86.344, 88.432, 123.651, 127.886, 128.312, 128.675, 132.156, 138.914. ESI-MS: $m/z = 275$ (M⁺).

1-(1-naphthalen-2-yl)-3-phenylprop-2-ynyl piperidine (Table 2, Entry 2): Yellow liquid, 88%. ¹H NMR (300 MHz, CDCl₃, ppm): δ 1.4-1.6 (m, 2H), 1.6-1.8 (m, 4H), 2.4-2.6 (m, 4H), 4.7 (s, 1H), 7.27-7.40 (m, 5H), 7.4-7.6 (m, 7H); ¹³C NMR (300 MHz, CDCl₃ , ppm): δ 25.302, 25.816, 50.026, 51.284, 80.915, 86.852, 122.745, 125.118, 126.124, 127.685, 128.015, 128.418, 131.822, 133.704, 135.254. ESI-MS: $m/z = 326$ (M+H)⁺.

1-(1-(2-fluorophenyl)-3-phenylprop-2-ynyl) piperidine (Table 2, Entry 3): Yellow liquid, 87%. ¹H NMR (300 MHz, CDCl₃, ppm): δ 1.35-1.50 (m, 2H), 1.5-1.7 (m, 4H), 2.5-2.6 (m, 4H), 5.0 (s, 1H), 6.97-7.15 (m, 2H), 7.2-7.4 (m, 3H), 7.4-7.55 (m, 4H); ¹³C NMR (300 MHz, CDCl₃ , ppm): δ 25.322, 25.863, 44.102, 50.842, 80.905, 86.825, 115.224, 122.768, 124.106, 127.114, 128.414, 128.952, 130.404, 132.335, 161.328. ESI-MS: $m/z = 294$ (M+H)⁺.

1-(1-(3-fluorophenyl)-3-phenylprop-2-ynyl) piperidine (Table 2, Entry 4): Yellow liquid, 85%. ¹H NMR (300 MHz, CDCl₃, ppm): δ 1.35-1.50 (m, 2H), 1.50-1.65 (m, 4H), 2.45-2.55 (m, 4H), 4.70 (s, 1H), 7.27-7.35 (m, 4H), 7.4-7.5 (m, 2H), 7.5-7.6 (m, 3H); ¹³C NMR (300 MHz, CDCl₃ , ppm): δ 25.312, 25.814, 50.852, 80.961, 86.802, 114.052, 115.816, 122.748, 124.414, 128.548, 130.114, 132.306, 141.522, 162.656. ESI-MS: $m/z = 294$ (M+H)⁺.

1-(1-(4-fluorophenyl)-3-phenylprop-2-ynyl) piperidine (Table 2, Entry 5): Yellow liquid, 89%. ¹H NMR (300 MHz, CDCl₃, ppm): δ 1.4-1.5 (m, 2H), 1.5-1.7 (m, 4H), 2.4-2.6 (m, 4H), 4.75 (s, 1H), 7.05-7.15 (m, 5H), 7.22-7.35 (m, 2H), 7.4-7.5 (m, 2H); ¹³C NMR (300 MHz, CDCl₃ , ppm): δ 25.324, 25.842, 50.863, 80.985, 86.844, 115.625, 122.735, 129.112, 130.412, 131.206, 132.329, 135.916, 162.038. ESI-MS: $m/z = 294$ (M+H)⁺.

1-(1-(4-chlorophenyl)-3-phenylprop-2-ynyl) piperidine (Table 2, Entry 6): Yellow liquid, 88%. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 1.37-1.50 (m, 2H), 1.50-1.65 (m, 4H), 2.40-2.55 (m, 4H), 4.70 (s, 1H), 7.20-7.35 (m, 5H), 7.40-7.50 (m, 2H), 7.5-7.6 (m, 2H); ^{13}C NMR (300 MHz, CDCl_3 , ppm): δ 24.701, 26.489, 50.965, 61.984, 62.056, 85.658, 88.554, 123.656, 128.512, 128.724, 130.112, 132.225, 133.621, 137.851. ESI-MS: $m/z = 310$ (M) $^+$.

1-(1-(3-bromophenyl)-3-phenylprop-2-ynyl) piperidine (Table 2, Entry 7): Yellow liquid, 87%. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 1.4-1.5 (m, 2H), 1.5-1.7 (m, 4H), 2.4-2.6 (m, 4H), 4.7 (s, 1H), 7.27-7.37 (m, 3H), 7.40-7.57 (m, 6H); ^{13}C NMR (300 MHz, CDCl_3 , ppm): δ 24.662, 26.485, 50.995, 62.102, 62.198, 85.362, 87.774, 122.684, 123.445, 127.412, 128.662, 128.745, 129.946, 130.884, 131.712, 131.805, 132.346, 141.568. ESI-MS: $m/z = 355$ (M+H) $^+$.

1-(1-(4-bromophenyl)-3-phenylprop-2-ynyl) piperidine (Table 2, Entry 8): Yellow liquid, 86%. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 1.35-1.50 (m, 2H), 1.5-1.7 (m, 4H), 2.45-2.60 (m, 4H), 4.7 (s, 1H), 7.28-7.40 (m, 3H), 7.4-7.55 (m, 6H); ^{13}C NMR (300 MHz, CDCl_3 , ppm): δ 24.762, 26.542, 50.917, 62.058, 62.133, 85.628, 88.715, 121.889, 123.512, 128.675, 128.714, 130.104, 131.578, 138.216. ESI-MS: $m/z = 354$ (M) $^+$.

1-(1-(3-nitrophenyl)-3-phenylprop-2-ynyl) piperidine (Table 2, Entry 9): Yellow liquid, 74%. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 1.25-1.37 (m, 2H), 1.37-1.50 (m, 4H), 2.47-2.60 (m, 4H), 4.82 (s, 1H), 7.28-7.35 (m, 3H), 7.45-7.55 (m, 3H), 7.57-7.62 (m, 2H), 7.75-7.80 (m, 1H); ^{13}C NMR (300 MHz, CDCl_3 , ppm): δ 25.414, 25.806, 49.812, 50.845, 80.962, 86.824, 122.442, 125.308, 128.426, 128.625, 129.516, 132.308, 134.922, 140.807, 147.622. ESI-MS: $m/z = 321$ (M+H) $^+$.

1-(1-(4-nitrophenyl)-3-phenylprop-2-ynyl) piperidine (Table 2, Entry 10): Yellow liquid, 72%. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 1.30-1.50 (m, 2H), 1.5-1.7 (m, 4H), 2.4-2.6 (m,

4H), 4.85 (s, 1H), 7.3-7.4 (m, 2H), 7.40-7.57 (m, 4H), 8.0 (d, J=8.0Hz, 1H), 8.15 (d, J=7.8Hz, 1H), 8.5 (m, 1H); ^{13}C NMR (300 MHz, CDCl_3 , ppm): 25.362, 26.028, 50.854, 81.024, 86.745, 122.775, 123.952, 128.512, 129.266, 131.125, 133.624, 146.445. ESI-MS: $m/z = 321$ (M+H) $^+$.

1-(3-phenyl-1-(4-trifluoromethyl) phenyl) prop-2-ynyl) piperidine (Table 2, Entry 11):

Yellow liquid, 85%. ^1H NMR (500 MHz, CDCl_3 , ppm): δ 1.4-1.6 (m, 2H), 1.6-1.75 (m, 4H), 2.60-2.72 (m, 4H), 4.9 (s, 1H), 7.27-7.32 (m, 2H), 7.4-7.5 (m, 3H), 7.65 (d, J=8.0Hz, 2H), 7.8 (d, J=8.0Hz, 2H); ^{13}C NMR (300 MHz, CDCl_3 , ppm): δ 24.585, 26.512, 50.962, 62.195, 62.263, 85.172, 85.946, 124.520, 125.526, 128.332, 128.612, 129.905, 132.108, 143.202. ESI-MS: $m/z = 344$ (M+H) $^+$.

1-(3-phenyl-1-*p*-tolylprop-2-ynyl) piperidine (Table 2, Entry 12): Yellow liquid, 81%. ^1H

NMR (300 MHz, CDCl_3 , ppm): δ 1.35-1.50 (m, 2H), 1.5-1.7 (m, 4 H), 2.3 (m, 3 H), 2.4-2.6 (m, 4H), 4.7 (s, 1 H), 7.05-7.15 (m, 2H), 7.2-7.35 (m, 3H), 7.4-7.5 (m, 4H); ^{13}C NMR (300 MHz, CDCl_3 , ppm): δ 21.445, 24.812, 26.664, 51.105, 62.456, 62.512, 86.724, 88.012, 123.724, 128.312, 129.416, 132.124, 135.976, 137.365. ESI-MS: $m/z = 290$ (M+H) $^+$.

1-(1-(4-methoxyphenyl)-3-phenylprop-2-ynyl) piperidine (Table 2, Entry 13): Yellow

liquid, 79%. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 1.35-1.5 (m, 2H), 1.5-1.7 (m, 4H), 2.4-2.6 (m, 4 H), 3.9 (s, 3H), 4.7 (s, 1H), 6.95-7.10 (m, 2H), 7.2-7.35 (m, 3 H), 7.4-7.55 (m, 4H); ^{13}C NMR (300 MHz, CDCl_3 , ppm): δ 24.812, 26.425, 50.985, 55.624, 62.125, 86.812, 88.042, 113.718, 123.786, 128.354, 128.665, 129.981, 130.984, 132.116, 160.014. ESI-MS: $m/z = 305$ (M) $^+$.

1-(1-(2-methoxyphenyl)-3-phenylprop-2-ynyl) piperidine (Table 2, Entry 14): Yellow

liquid, 45%. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 1.35-1.50 (m, 2H), 1.5-1.67 (m, 4H), 2.4-2.6 (m, 4 H), 3.7 (s, 3H), 4.7 (s, 1H), 7.22-7.4 (m, 5H), 7.4-7.5 (m, 2H), 7.5-7.6 (m, 2H); ^{13}C

NMR (300 MHz, CDCl₃, ppm): δ 25.348, 25.844, 44.926, 50.817, 56.106, 80.923, 86.882, 114.026, 120.875, 122.742, 127.388, 128.495, 129.962, 132.414, 158.409. ESI-MS: $m/z = 305$ (M)⁺.

1-(1-phenylhept-1-yn-3-yl) piperidine (Table 2, Entry 16): Yellow liquid, 90%. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.9-1.0 (m, 3H), 1.20-1.35 (m, 3H), 1.40-1.55 (m, 3H), 1.60-1.75 (m, 6H), 2.6 (s, 2H), 2.8 (s, 2H), 3.6 (s, 1H), 7.2-7.3 (m, 3H), 7.3-7.4 (m, 2H); ¹³C NMR (300 MHz, CDCl₃, ppm): δ 14.102, 21.852, 25.324, 26.112, 33.105, 47.622, 51.225, 78.628, 89.426, 122.702, 128.472, 128.548, 132.306. ESI-MS: $m/z = 255$ (M)⁺.

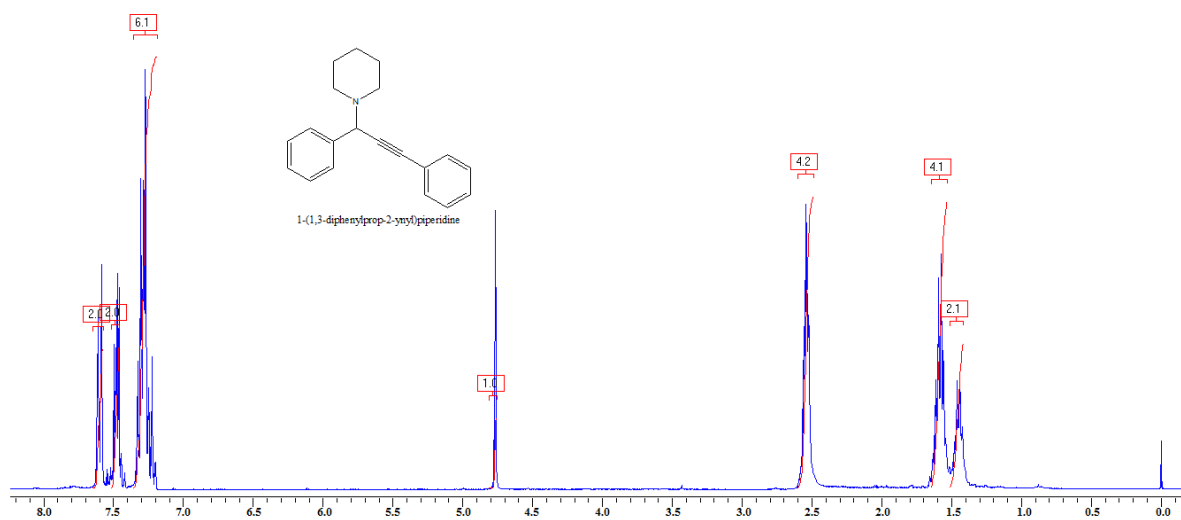
1-(1, 3-diphenylprop-2-ynyl) pyrrolidine (Table 3, Entry 1): Yellow liquid, 82%. ¹H NMR (300 MHz, CDCl₃, ppm): δ 1.40-1.65 (m, 4H), 2.4-2.6 (m, 4H), 4.7 (s, 1H), 6.9-7.1 (m, 6H), 7.27-7.40 (m, 2H), 7.4-7.6 (m, 2H); ¹³C NMR (300 MHz, CDCl₃, ppm): δ 25.325, 50.595, 54.462, 80.995, 86.842, 122.742, 127.302, 128.457, 128.882, 132.369, 140.012. ESI-MS: $m/z = 261$ (M)⁺.

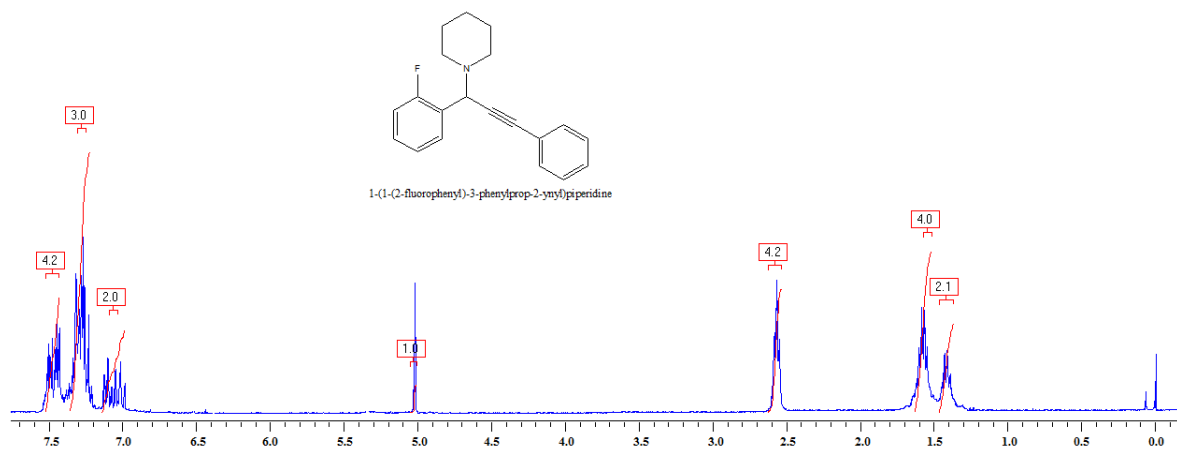
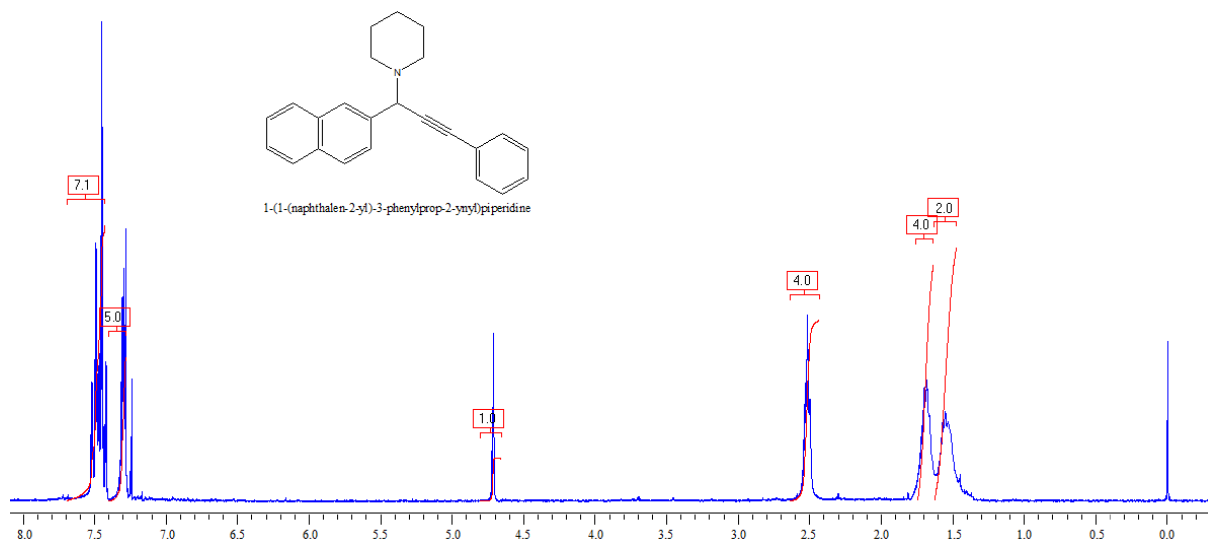
4-(1, 3 diphenylprop-2-ynyl) morpholine (Table 3, Entry 2): Yellow liquid, 91%. ¹H NMR (300 MHz, CDCl₃, ppm): δ 1.4-1.5 (m, 2H), 1.5-1.7 (m, 4H), 2.45-2.55 (m, 4H), 4.7 (s, 1H), 7.27-7.40 (m, 3H), 7.40-7.55 (m, 5H); ¹³C NMR (300 MHz, CDCl₃, ppm): δ 49.812, 61.404, 67.116, 84.365, 88.974, 121.841, 122.712, 128.415, 128.564, 130.366, 131.415, 137.106. ESI-MS: $m/z = 278$ (M+H)⁺.

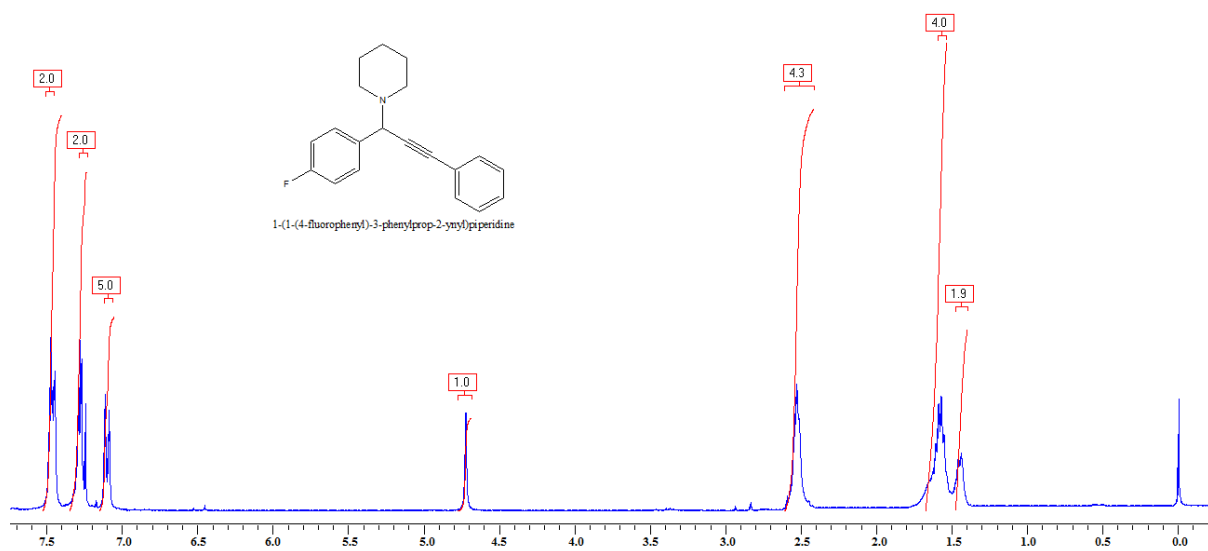
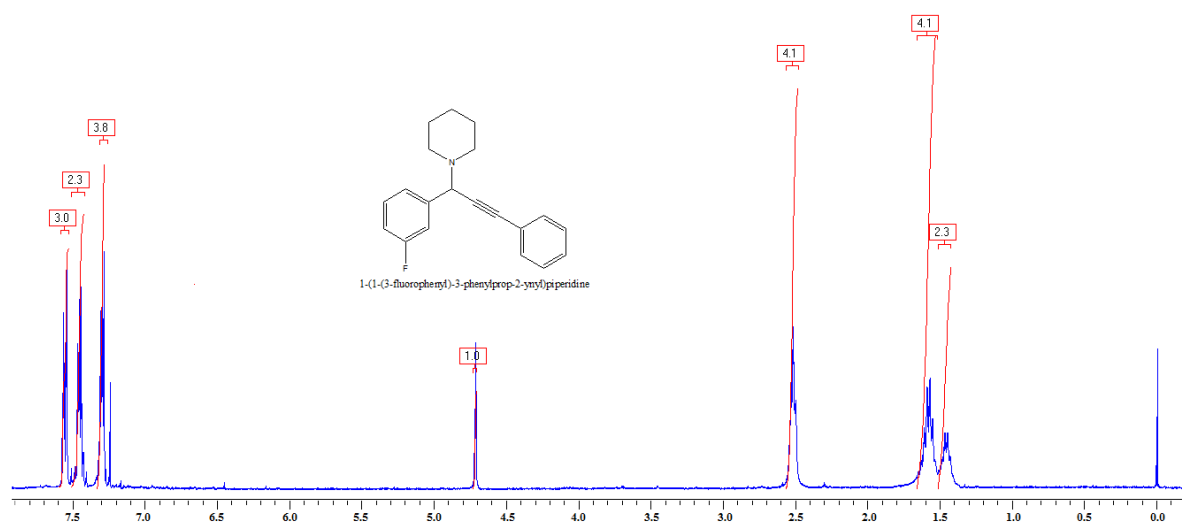
1-(1-phenyl-3-(trimethylsilyl)-prop-2-ynyl) piperidine (Table 3, Entry 3): Yellow liquid, 78%. ¹H NMR (300 MHz, CDCl₃, ppm): δ 0.1 (s, 9H), 1.4-1.5 (m, 2H), 1.50-1.67 (m, 4H), 4.8 (s, 1H), 7.22-7.40 (m, 5H), 7.4-7.6 (m, 4H); ¹³C NMR (300 MHz, CDCl₃, ppm): δ 0.000, 25.321, 25.845, 50.814, 54.462, 80.102, 99.312, 127.365, 128.522, 128.866, 140.102. ESI-MS: $m/z = 272$ (M+H)⁺.

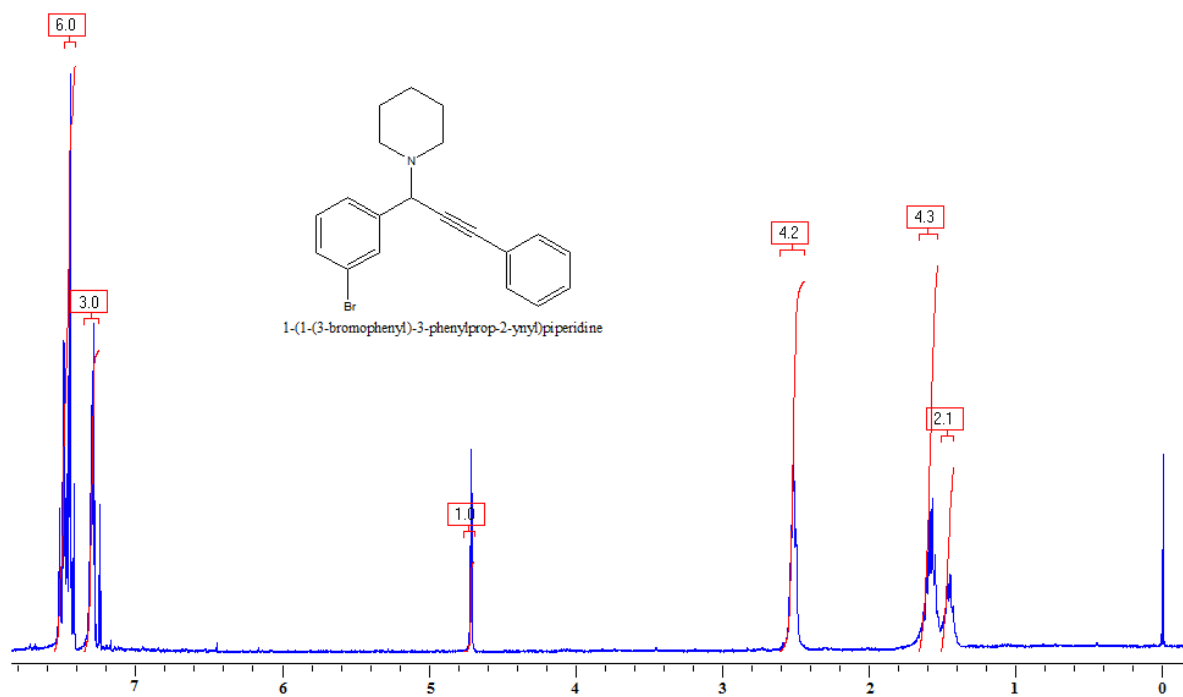
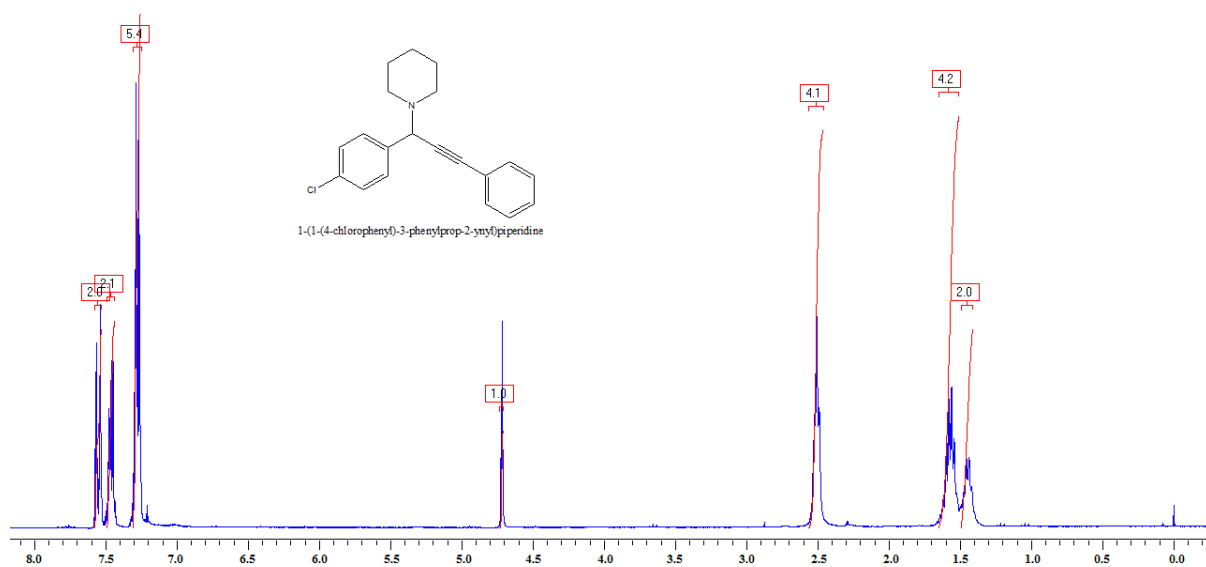
1-(1-phenylundec-2-ynyl) piperidine (Table 3, Entry 4): Yellow liquid, 83%. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 0.85-1.00 (m, 3H), 1.20-1.35 (m, 8H), 1.35-1.60 (m, 10H), 1.9-2.1 (m, 2H), 2.20-2.35 (m, 4H), 4.5(s, 1H), 7.10-7.27 (m, 2H), 7.27-7.37 (m, 1H), 7.4-7.5 (m, 2H); ^{13}C NMR (300 MHz, CDCl_3 , ppm): δ 14.106, 19.120, 22.725, 25.325, 25.842, 28.442, 28.764, 28.916, 29.335, 31.824, 50.818, 51.224, 74.554, 79.501, 79.712, 127.326, 128.542, 128.843, 139.905. ESI-MS: $m/z = 312$ ($\text{M}+\text{H}$) $^+$.

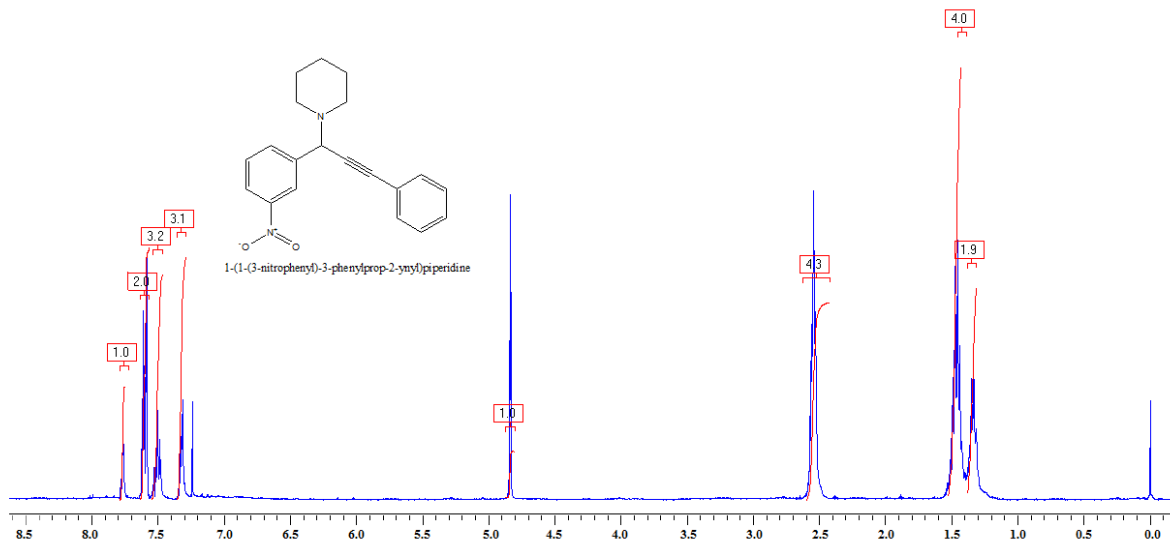
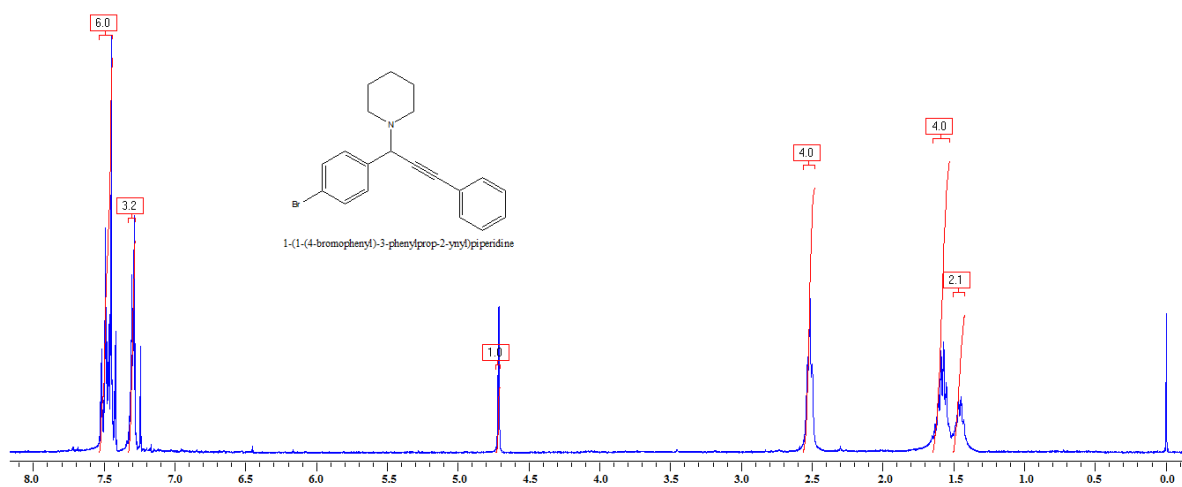
^1H NMR spectra of the products

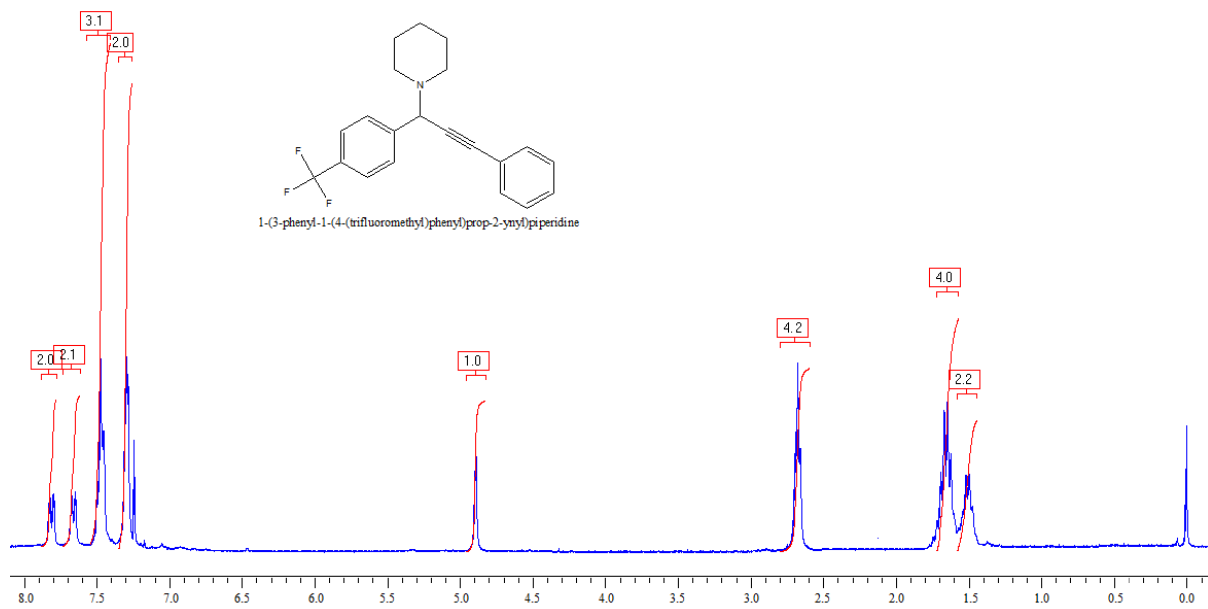
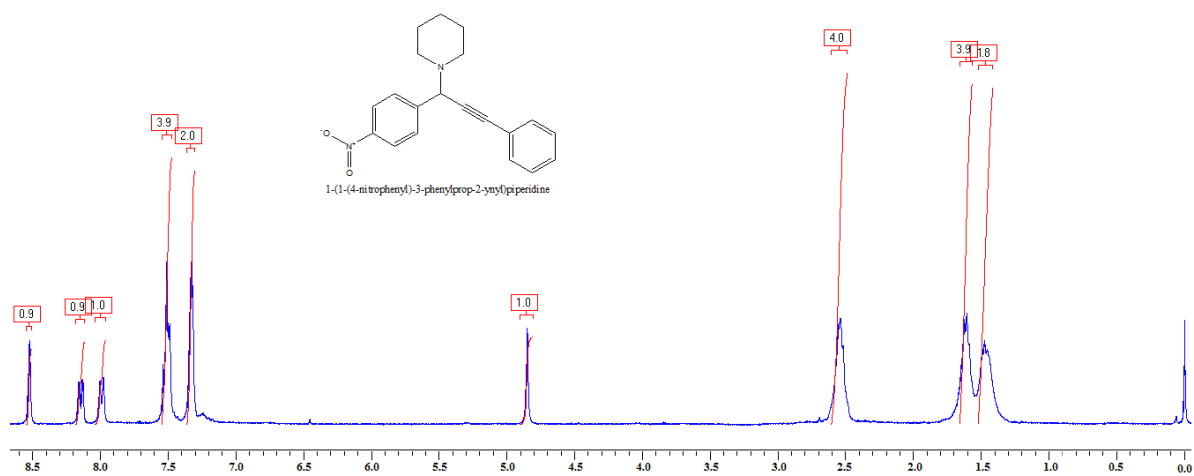


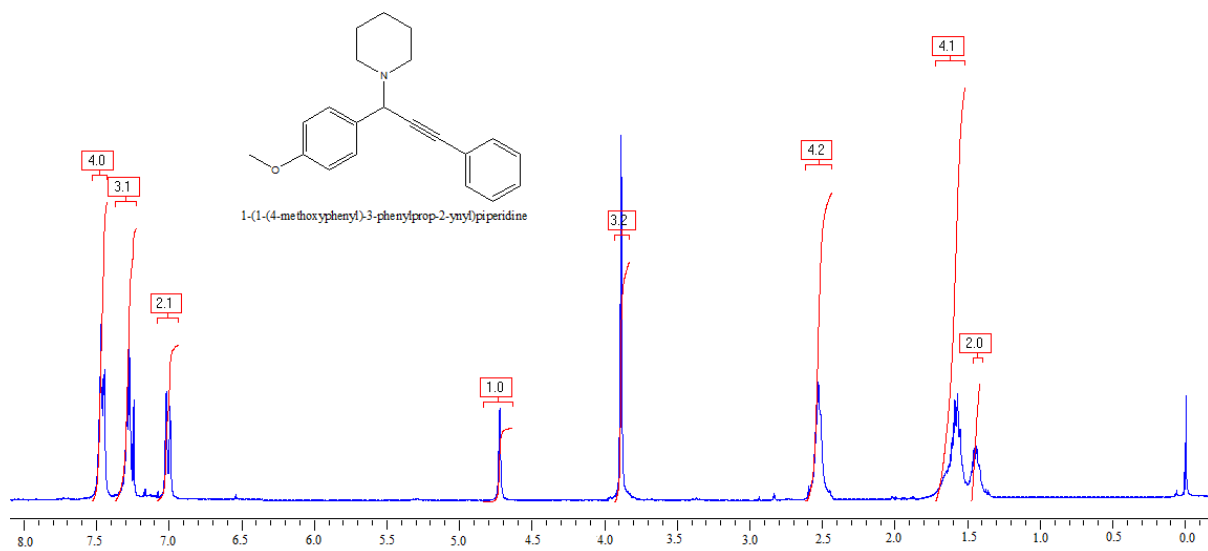
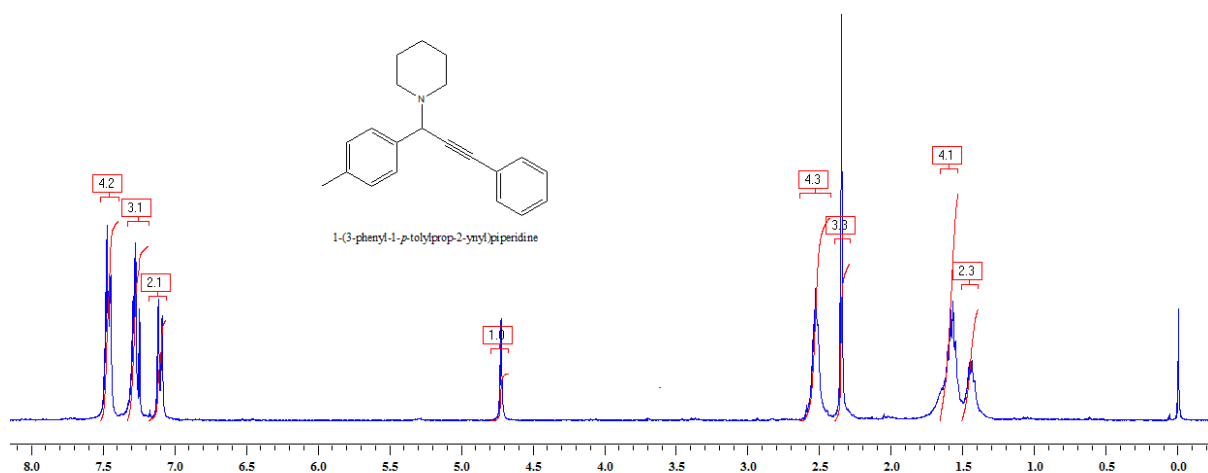


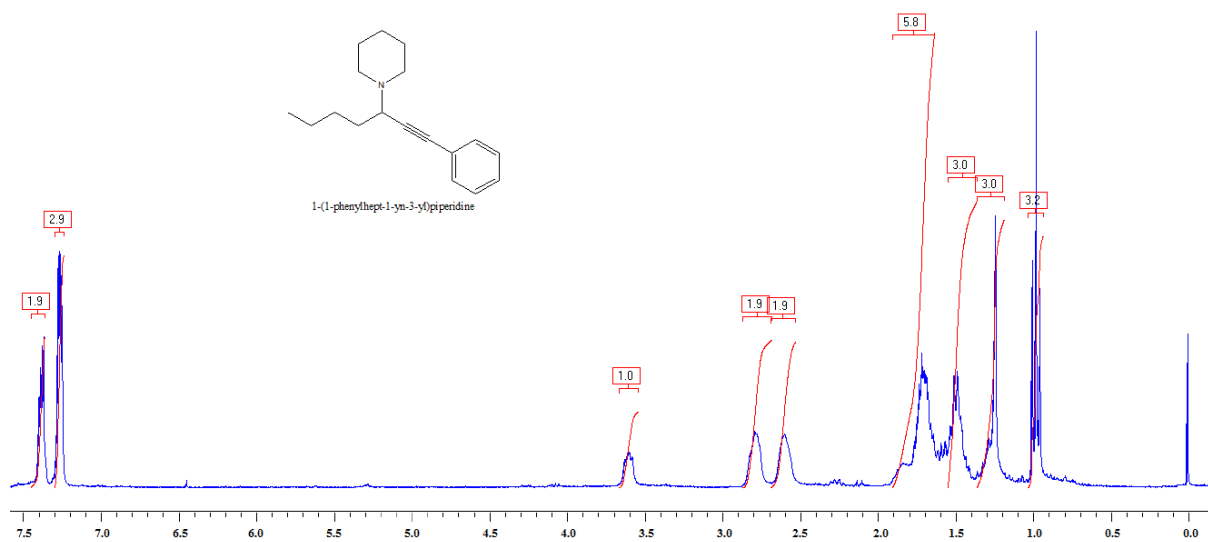
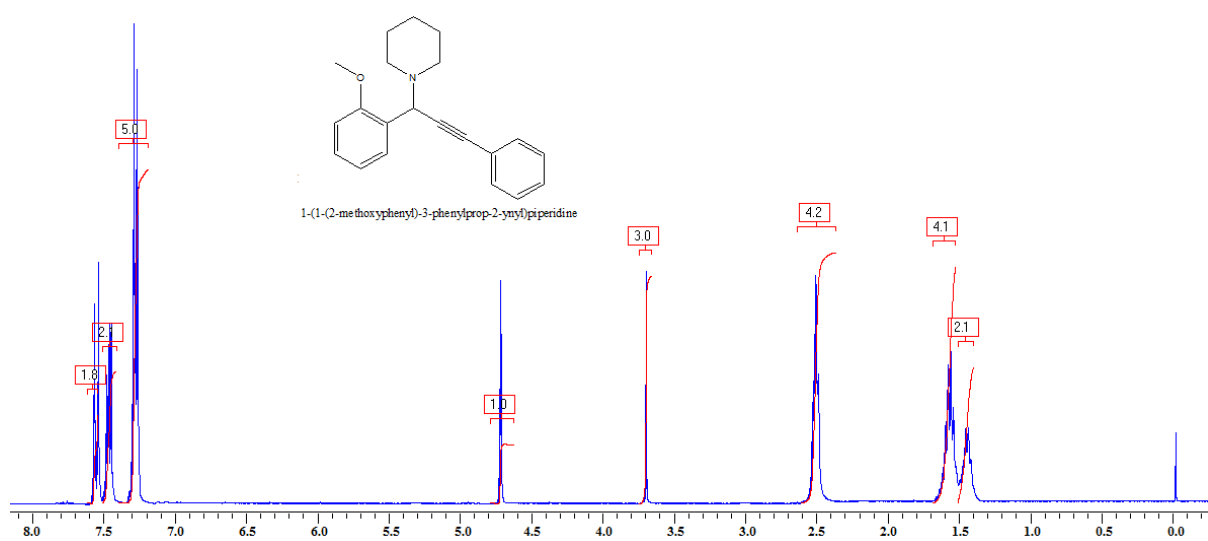


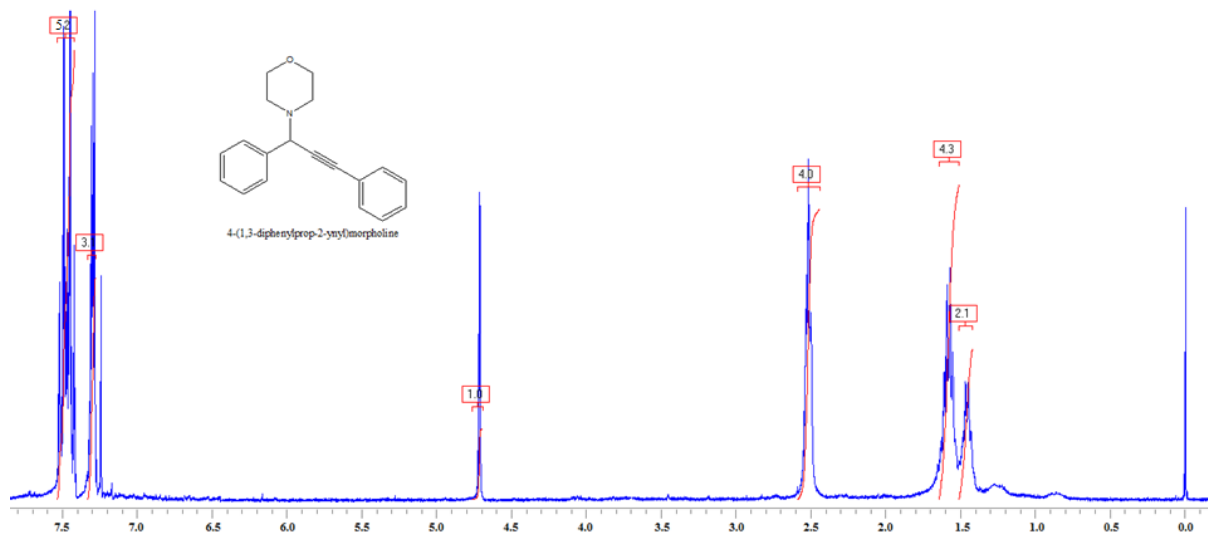
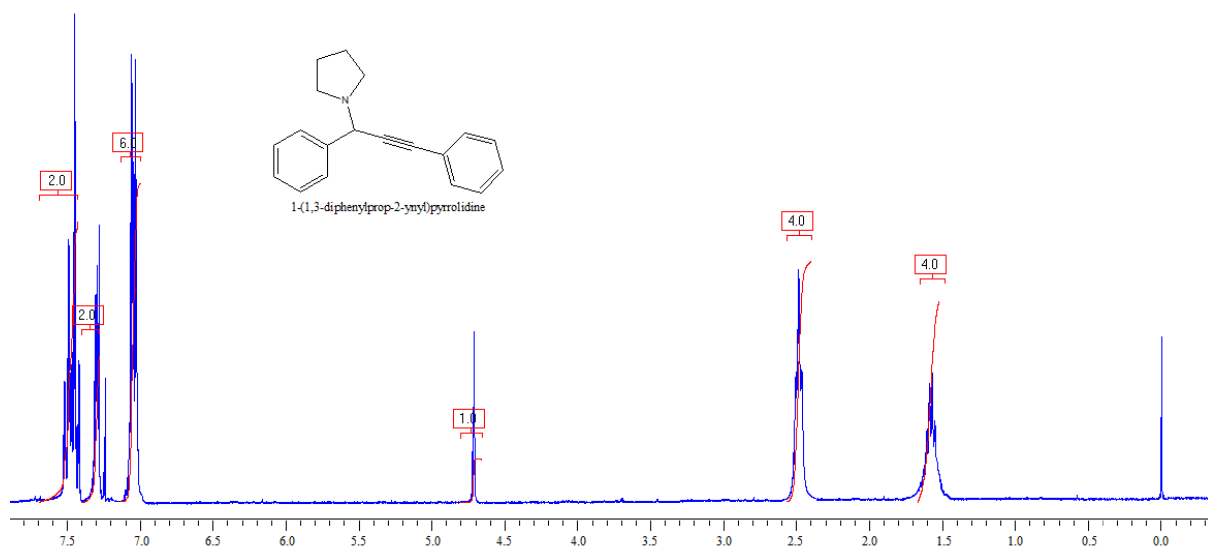


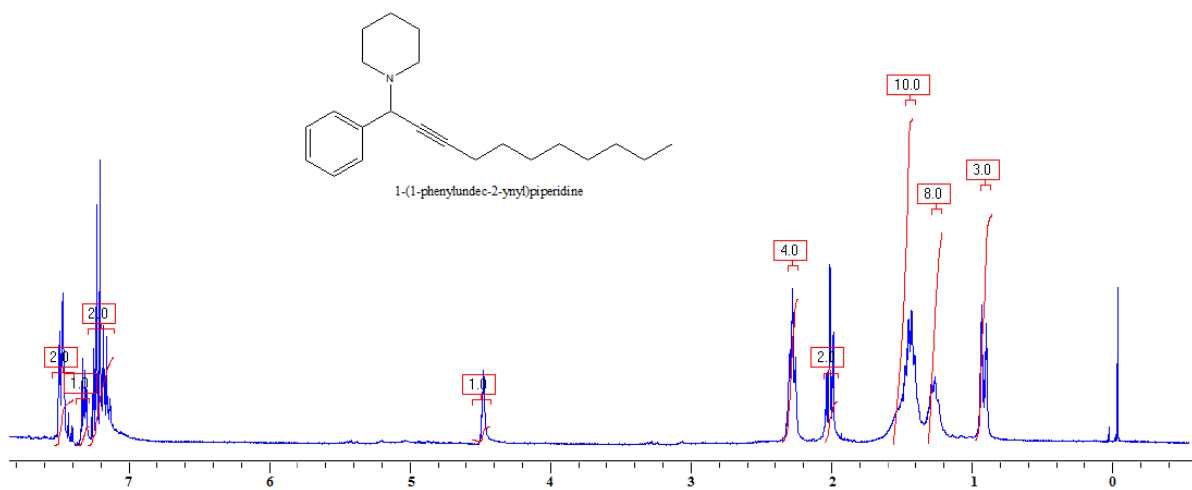
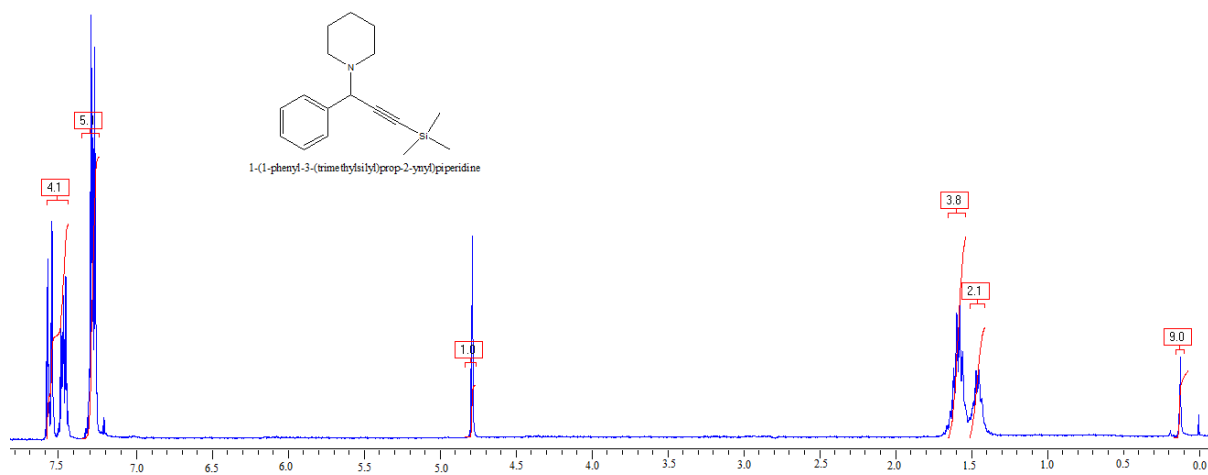




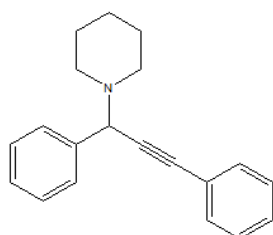




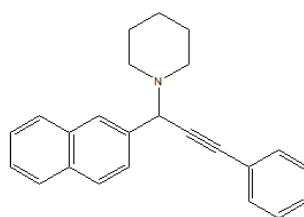
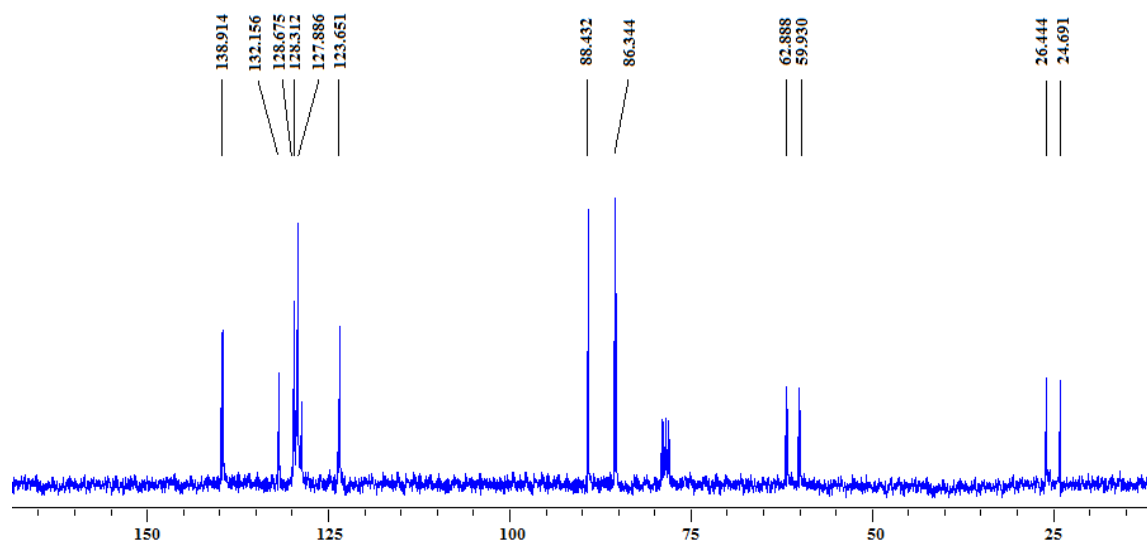




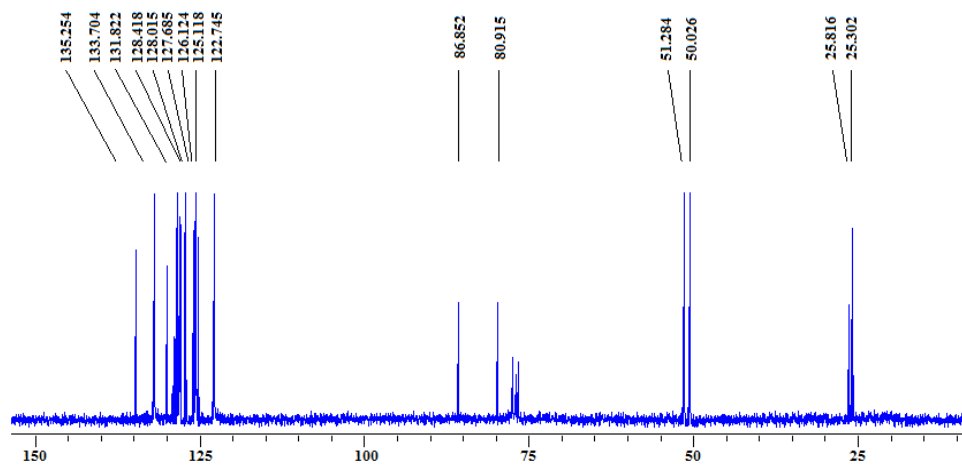
¹³C NMR spectra of the products

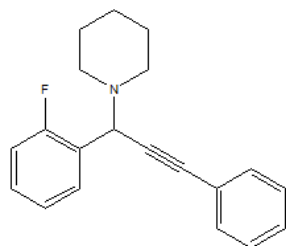


1-(1,3-diphenylprop-2-ynyl)piperidine

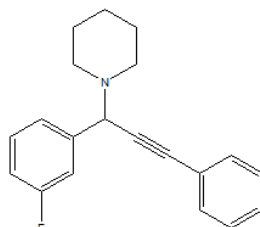
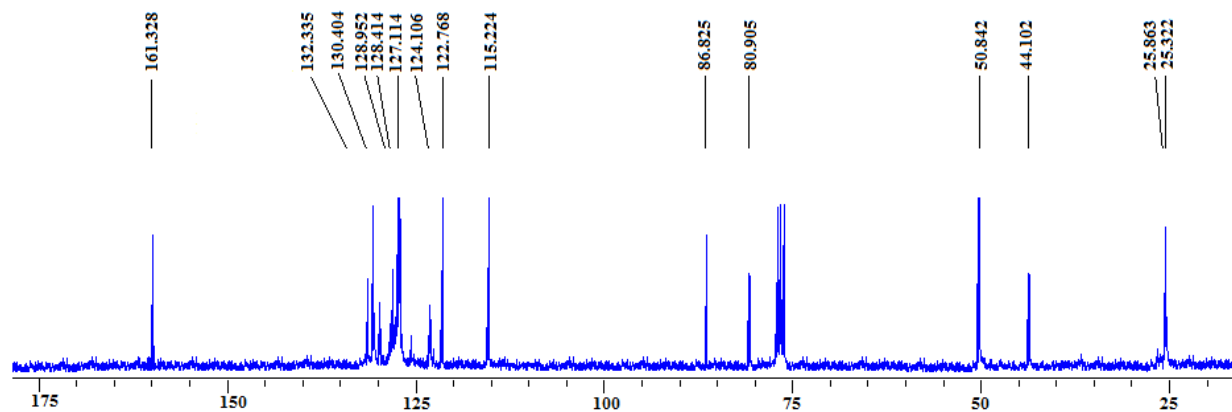


1-(1-(naphthalen-2-yl)-3-phenylprop-2-ynyl)piperidine

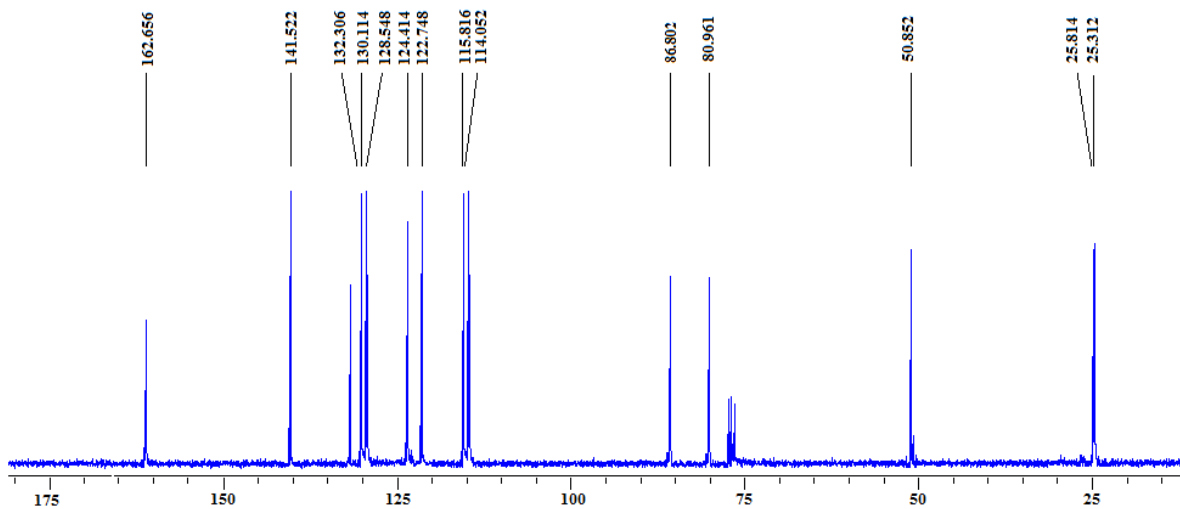


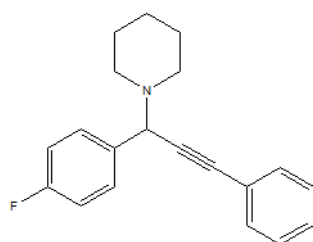


1-(1-(2-fluorophenyl)-3-phenylprop-2-ynyl)piperidine

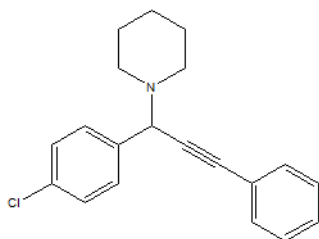
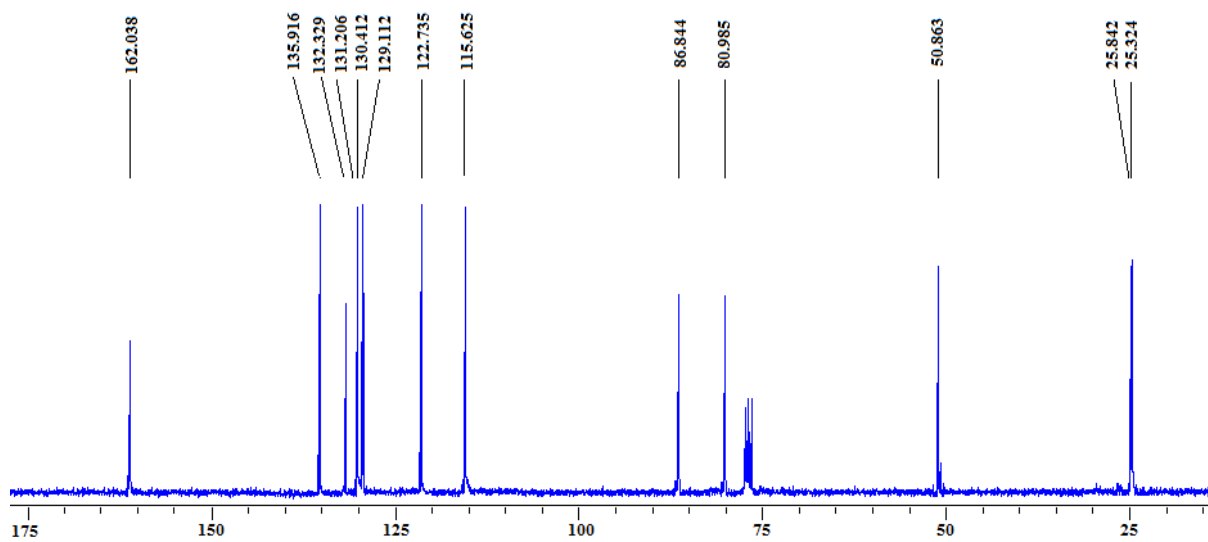


1-(1-(3-fluorophenyl)-3-phenylprop-2-ynyl)piperidine

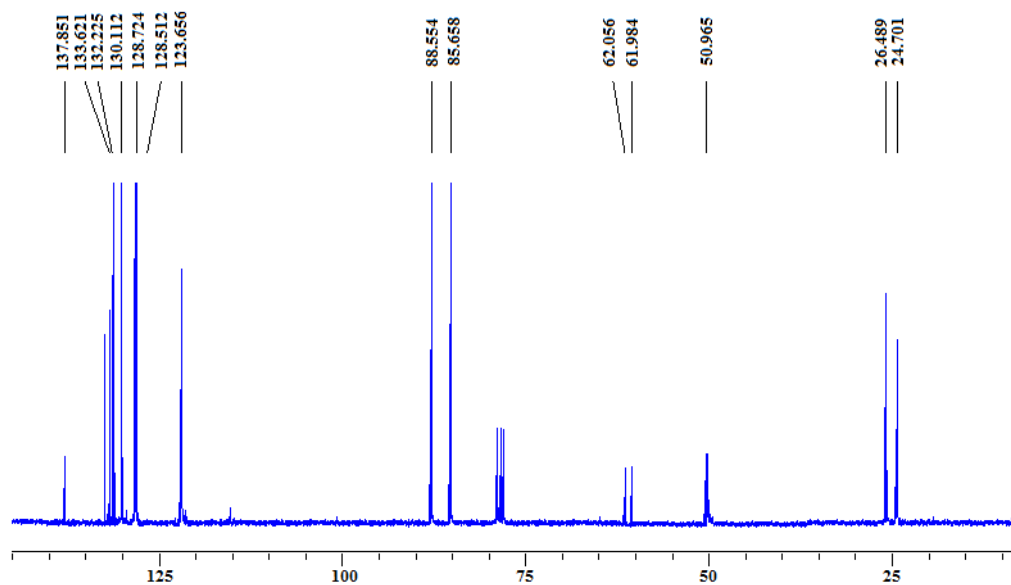


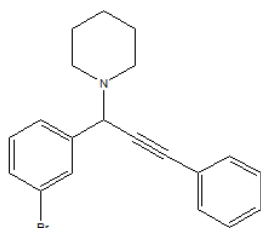


1-(1-(4-fluorophenyl)-3-phenylprop-2-ynyl)piperidine

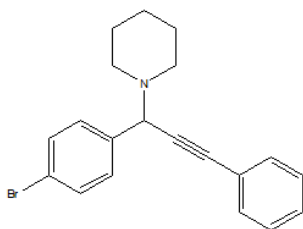
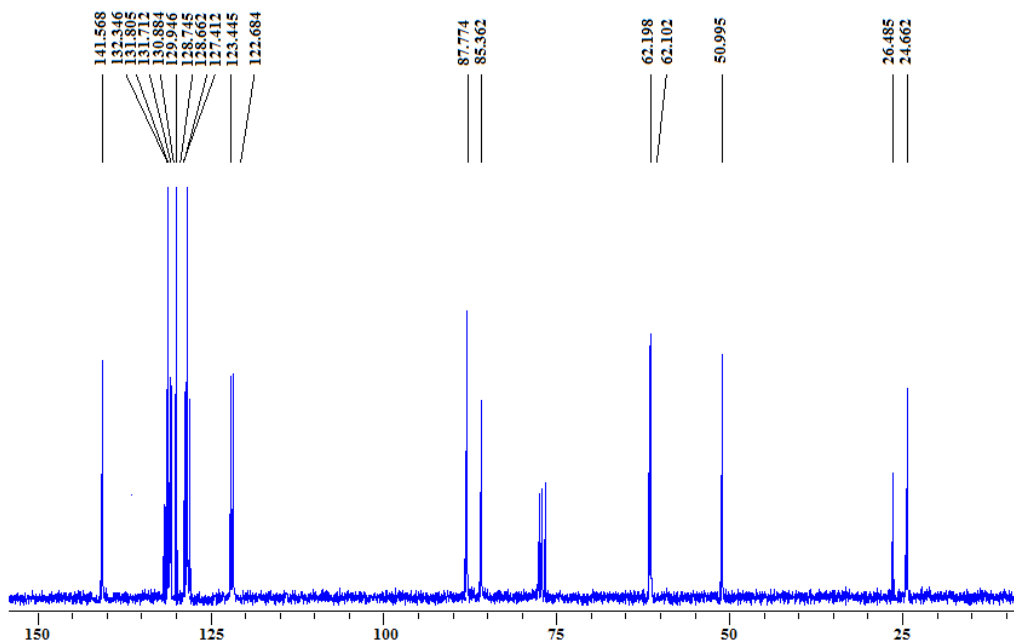


1-(1-(4-chlorophenyl)-3-phenylprop-2-ynyl)piperidine

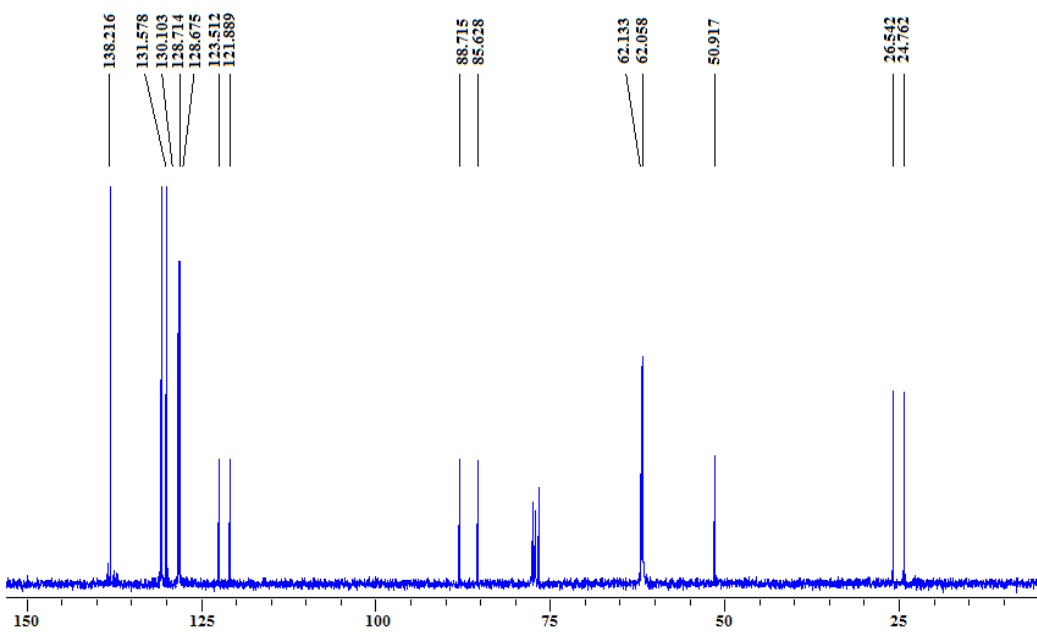


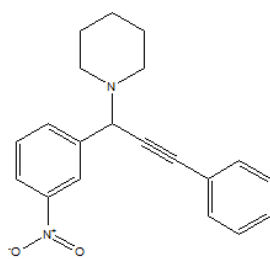


1-(1-(3-bromophenyl)-3-phenylprop-2-ynyl)piperidine

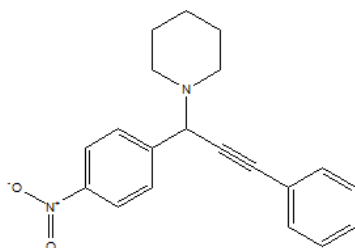
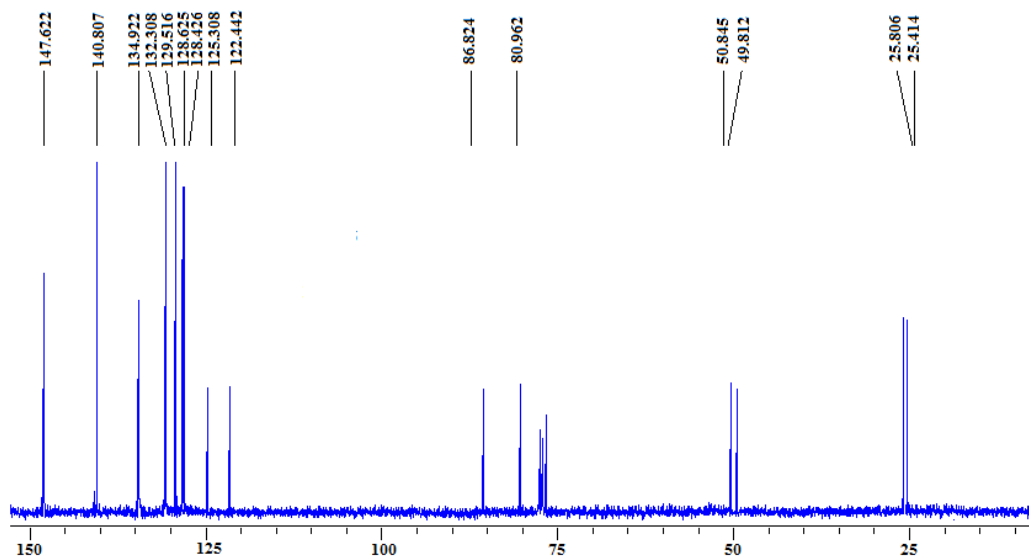


1-(1-(4-bromophenyl)-3-phenylprop-2-ynyl)piperidine

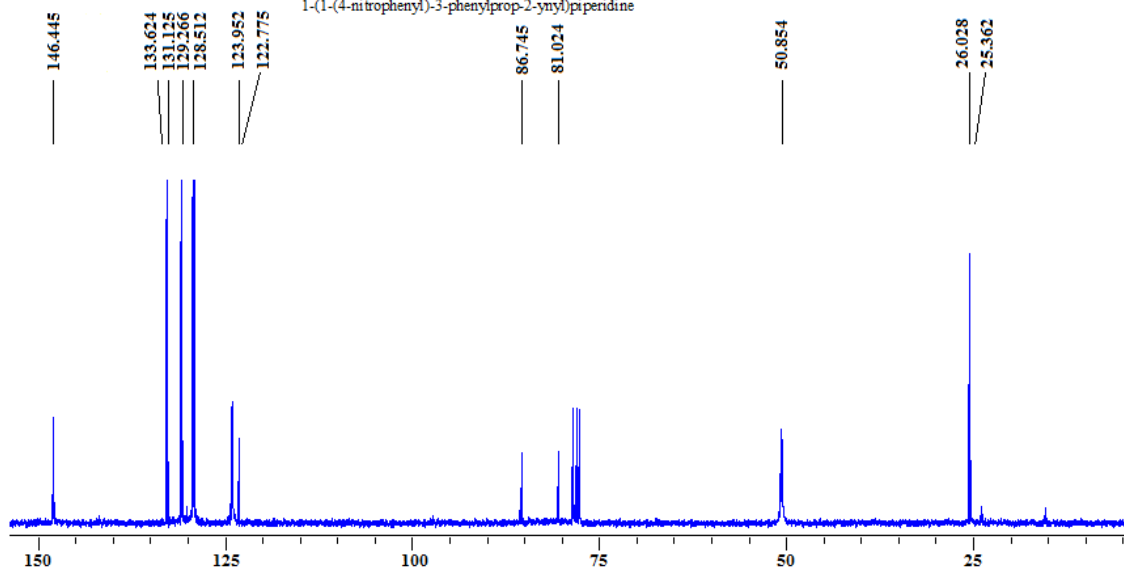


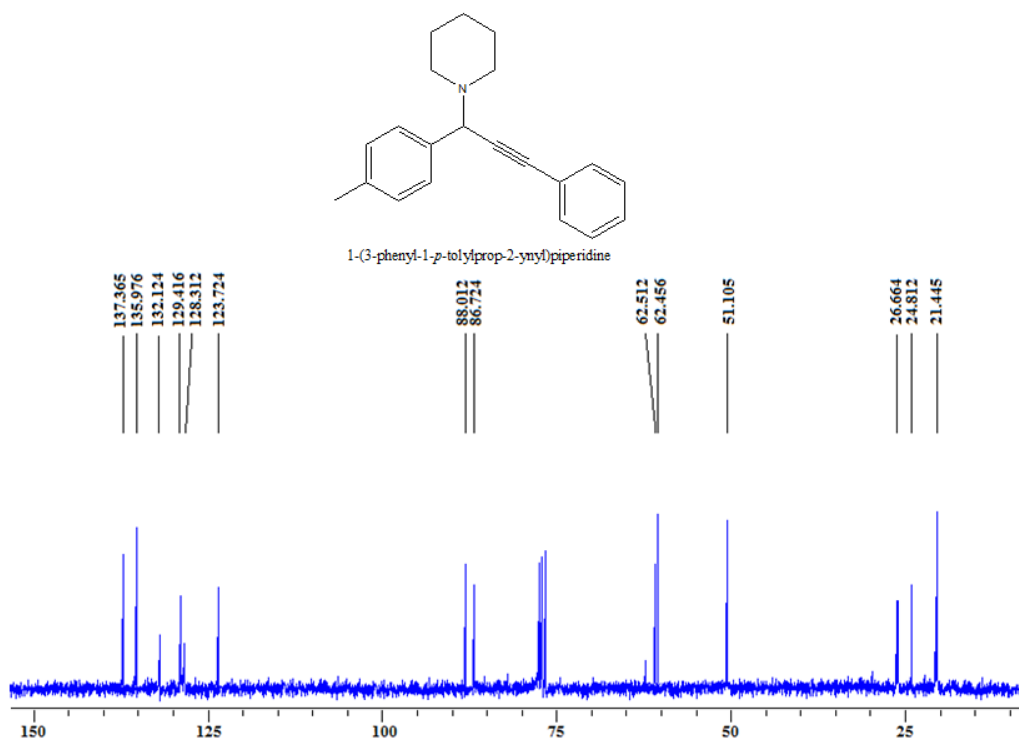
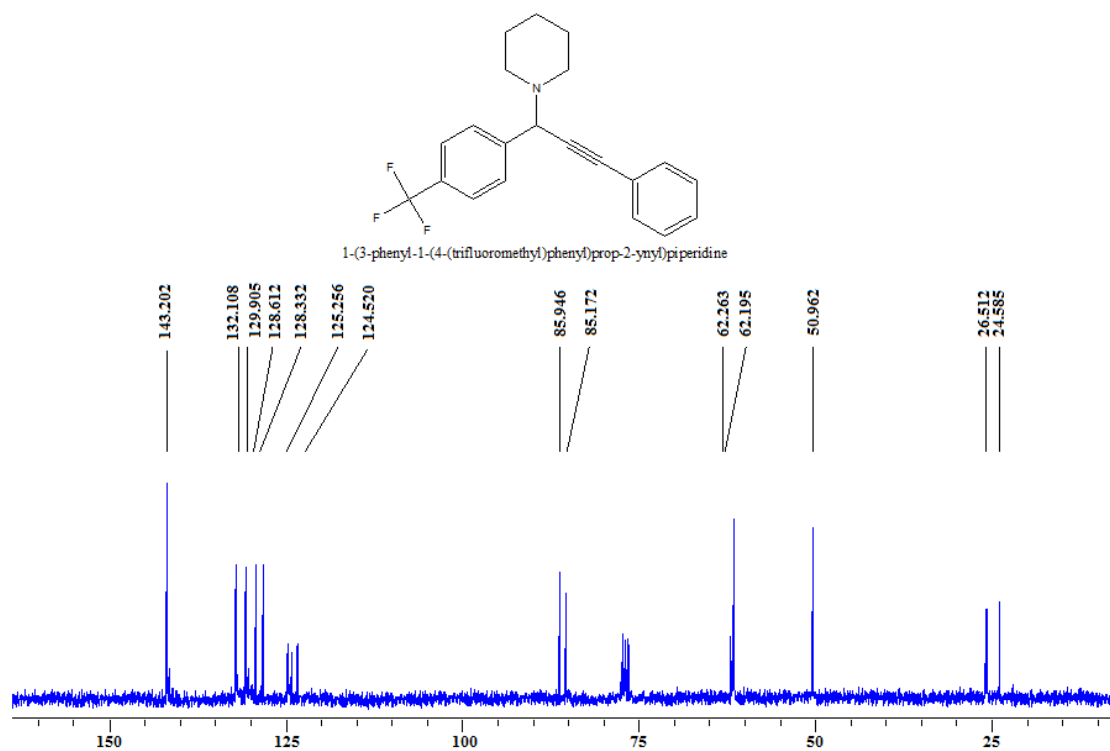


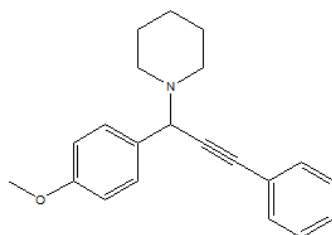
1-(1-(3-nitrophenyl)-3-phenylprop-2-ynyl)piperidine



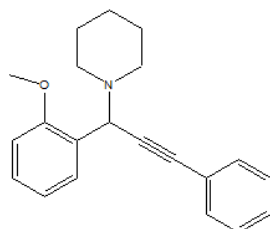
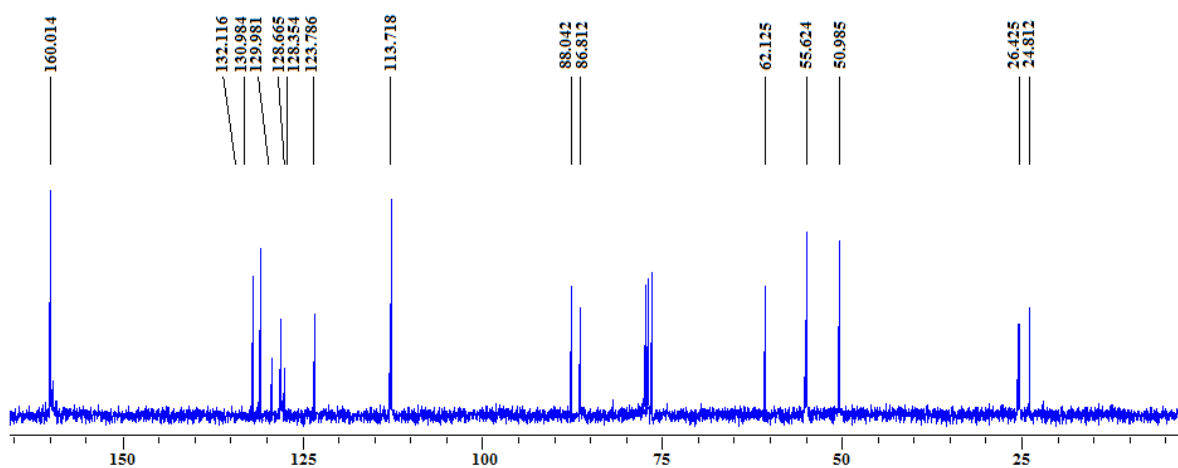
1-(1-(4-nitrophenyl)-3-phenylprop-2-ynyl)piperidine



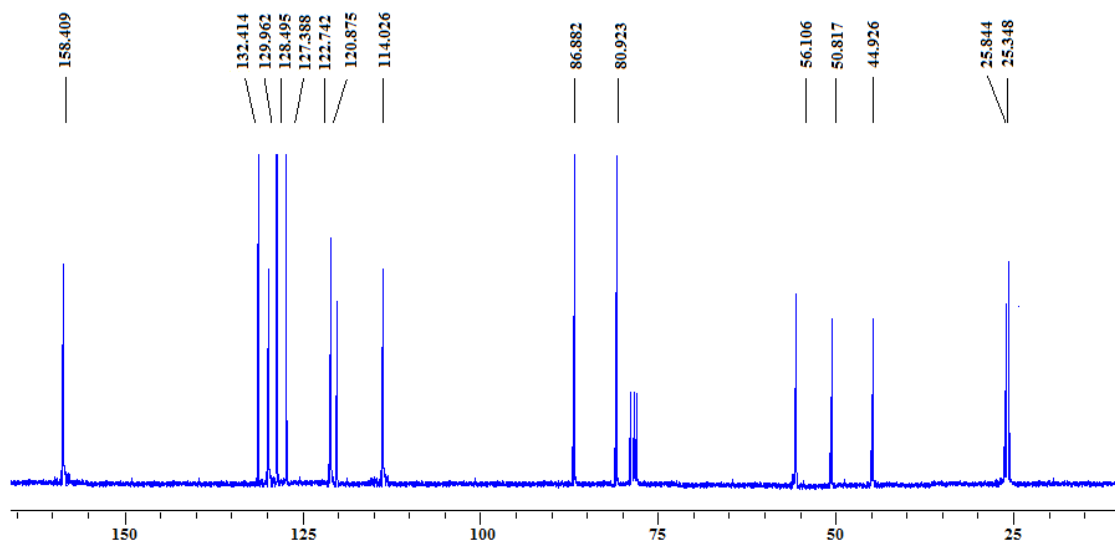


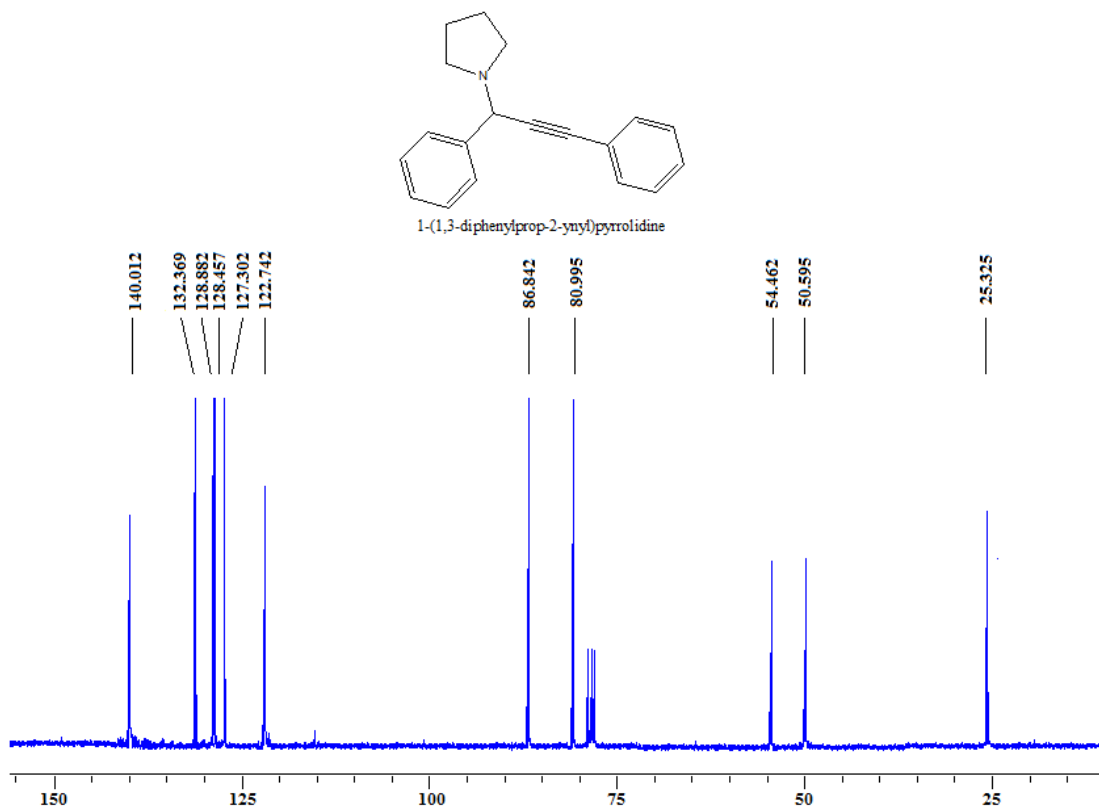
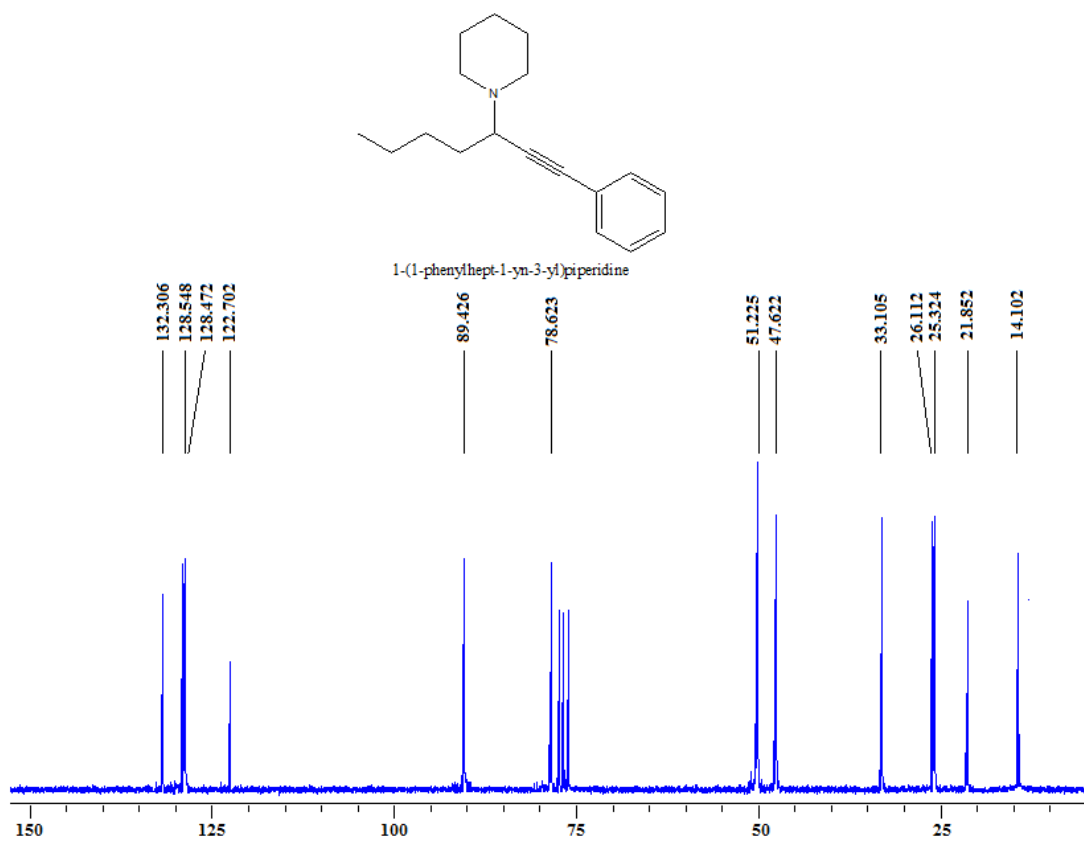


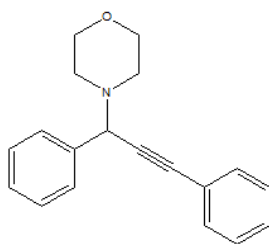
1-(1-(4-methoxyphenyl)-3-phenylprop-2-ynyl)piperidine



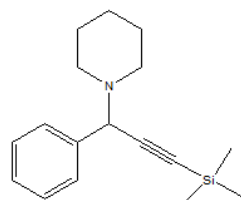
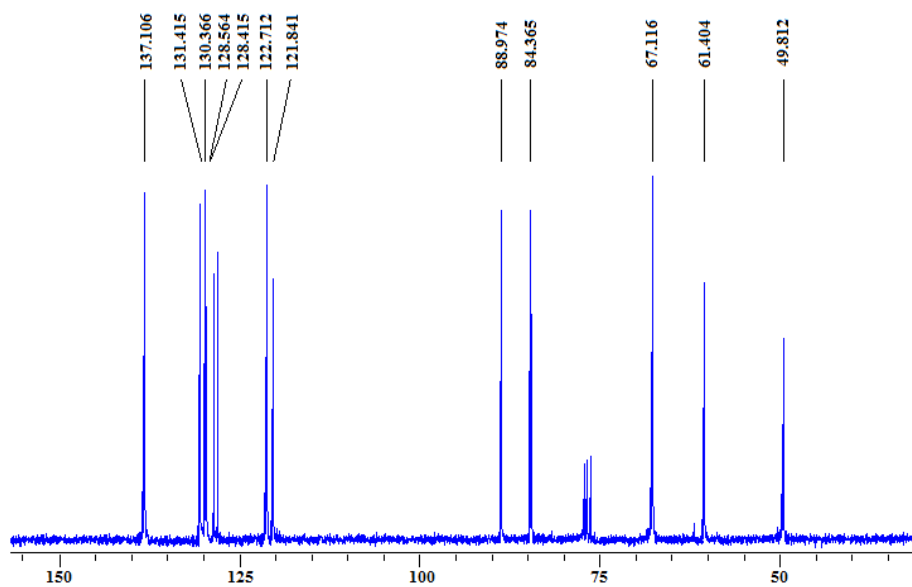
1-(1-(2-methoxyphenyl)-3-phenylprop-2-ynyl)piperidine



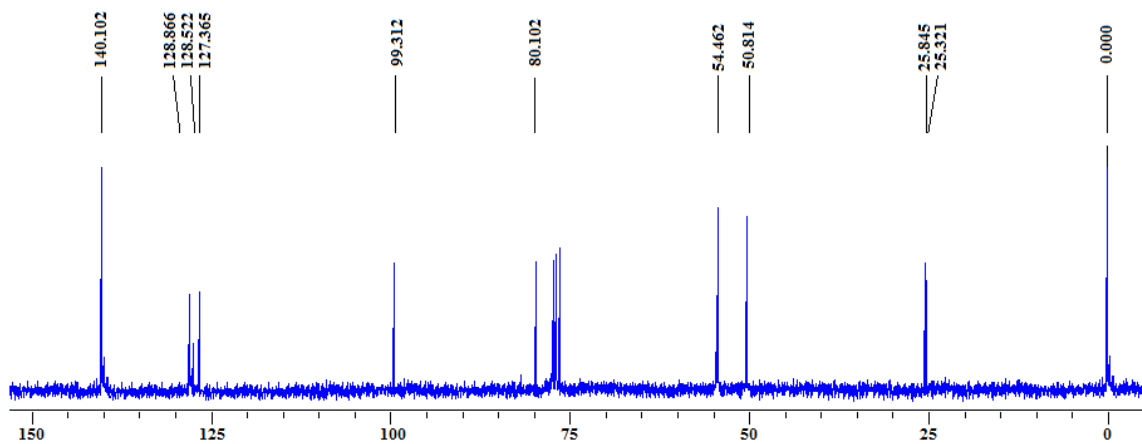


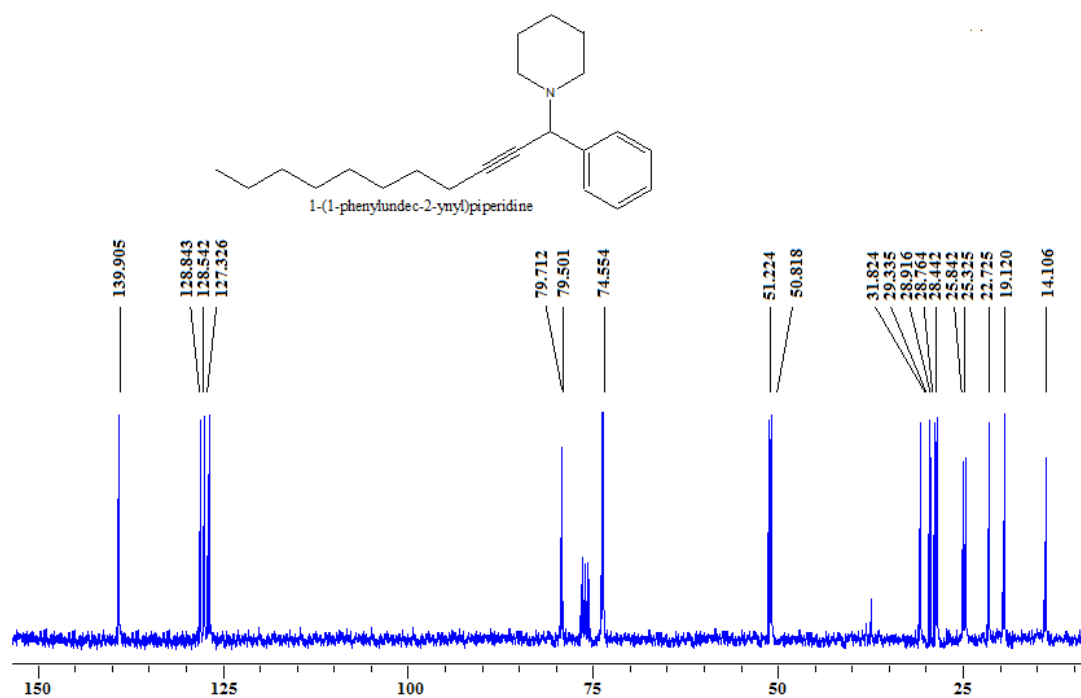


4-(1,3-diphenylprop-2-ynyl)morpholine



1-(1-phenyl-3-(trimethylsilyl)prop-2-ynyl)piperidine





References

1. For synthesis of nano hydroxyapatite see: W. Feng, Li Mu-sen, Lu Yu-Peng and Qi Yong-Xin, *Mater. Lett.*, 2005, **59**, 916.
2. For synthesis of meso-ceria see: Z-Y. Yuan, T-Z. Ren, A. Vantomme and B-Li.Su, *Chem. Mater.*, 2004, **16**, 5096.