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Supplementary Information

Magnetic nanoparticles modified with copper (I) complex as a novel and efficient reusable catalyst for A^3 coupling C-N bond formation

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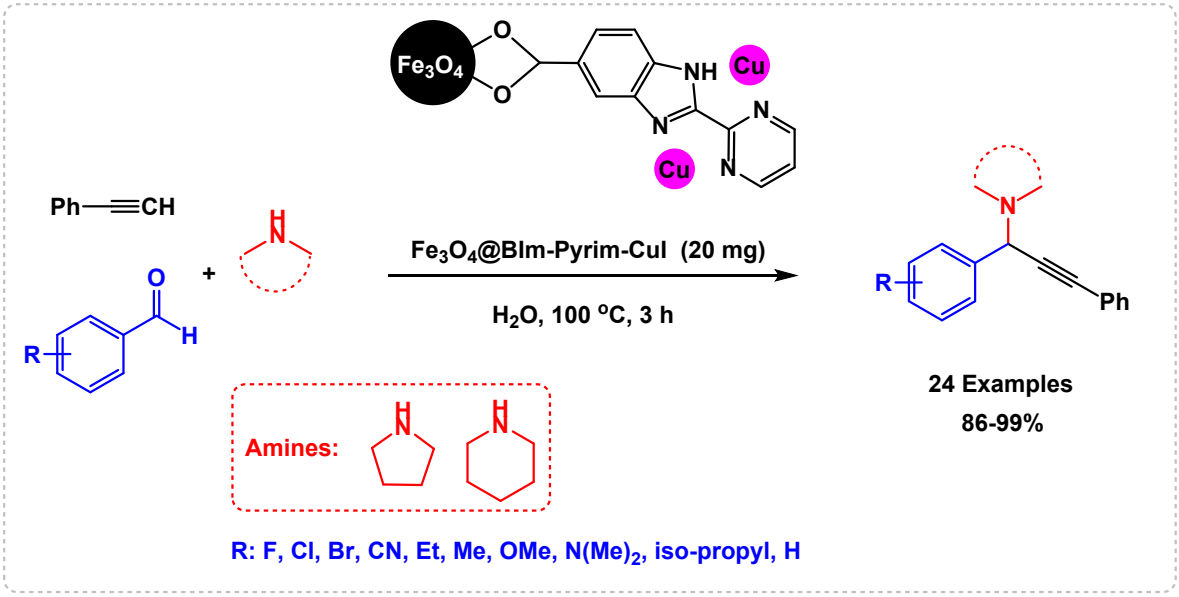
Abstract

Propargylamines are an important and valuable family of nitrogen-containing compounds with many applications in the fields of medicinal, industrial and chemical processes. One-pot multicomponent A^3 coupling reactions of aldehydes, amines, and alkynes in the presence of transition metals as the catalyst is an efficient strategy to prepare propargylamines. In the research work, we fabricated a novel magnetically reusable copper nanocatalyst [Fe_3O_4-BIm-Pyrim-CuI] through the immobilization of copper (I) complex on the surface of magnetic nanoparticles modified with benzimidazole-pyrimidine Ligand and evaluated its catalytic activity in the preparation of the propargylamines through one-pot multicomponent A^3 coupling reactions of aldehydes, amines, and alkynes. Under this catalytic system, aryl substrates with both electron-donating and electron-withdrawing substituents also gave the desired products in excellent yields under the standardized conditions. The Fe_3O_4-BIm-Pyrim-CuI catalyst was easily separated by an external magnet and the recovered catalyst was reused in 8 cycles without significant loss of activity.



Keywords: Fe_3O_4@BIm-Pyrim-CuI, Propargylamines, A^3 coupling reactions, Water, Magnetic separation.

Supplementary Information

Experimental

Materials

All reagents and solvents used in this work were purchased from Sigma-Aldrich, Fluka or Merck Chemical Companies and used without further purification.

General procedure for the synthesis of propargylamines catalyzed by Fe_3O_4@BIm-Pyrim-CuI nanocomposite

In a 10 mL round bottomed flask, a mixture of aldehyde (1 mmol), amine (1 mmol) and Fe_3O_4@BIm-Pyrim-CuI catalyst (20 mg) was stirred for 10 min. Phenylacetylene (1 mmol), and 3 mL water were added to the above mixture and allowed to stir under reflux conditions for 3 h. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the catalyst was separated using magnetic stirring bar. After evaporation of the solvent, the desired product was isolated by silica gel flash column chromatography with a mixture of petroleum ether/ethyl acetate as eluent. All products are well-known and identified by 1HNMR and 13CNMR spectroscopy. The products are well-known and characterized by 1HNMR and 13CNMR spectroscopy.

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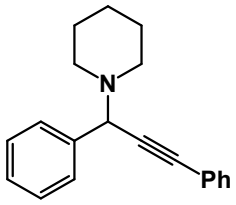
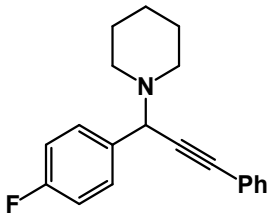
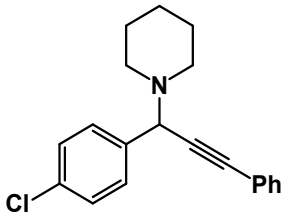
NMR data for propargylamines:



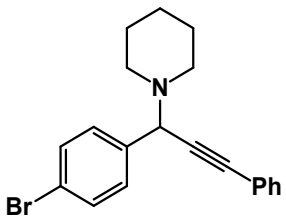
1-(1,3-diphenylprop-2-yn-1-yl)piperidine: (4a), yield 98%;^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.68 − 7.63 (m, 2H), 7.58 − 7.52 (m, 2H), 7.46− 7.29 (m, 6H), 4.83 (s, 1H), 2.60 − 2.58 (m, 4H), 1.66 − 1.60 (m, 4H), 1.56 − 1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 141.18, 132.11, 131.52, 130.67, 129.78, 128.64, 127.98, 126.50, 123.08, 122.43, 89.36, 86.41, 62.12, 50.36, 26.57, 24.36.



1-(1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl)piperidine: (4b), yield 93%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.63-7.55(m, 2H), 7.54-7.51(m, 2H), 7.41-7.32 (m, 5H), 4.83(s, 1H), 2.59(d, 4H), 1.67-1.61(m, 4H), 1.53-1.46(m, 2H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 137.12, 133.37, 132.41, 130.87, 129.12, 128.14, 123.43, 86.36, 85.21, 62.34, 51.24, 26.64, 25.37.



1-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]piperidine: (4c), yield 99%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.64-7.58(m, 2H), 7.56-7.51(m, 2H), 7.40-7.29 (m, 5H), 4.80(s, 1H), 2.58(d, 4H), 1.66-1.60(m, 4H), 1.50-1.47(m, 2H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 138.02, 134.12, 132.36, 130.41, 129.35, 128.68, 127.11, 123.18, 88.29, 86.32, 62.37, 50.23, 26.30, 25.31.



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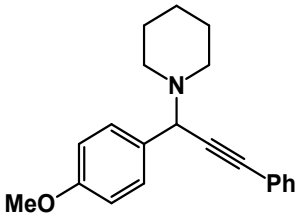
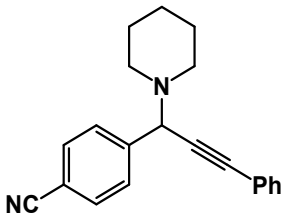
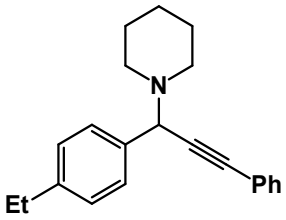
1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl)piperidine: (4d), yield 99%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.65-7.60(m, 2H), 7.57-7.55(m, 2H), 7.41-7.32 (m, 5H), 4.79(s, 1H), 2.61(t, 4H), 1.64-1.60(m, 4H), 1.59-1.46(m, 2H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 140.23, 132.38, 131.84, 130.36, 129.14, 128.54, 127.02, 126.31, 87.23, 86.30, 61.34, 51.21, 26.27, 25.39.



1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)piperidine: (4e), yield 96%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.61-7.57(m, 2H), 7.56-7.40(m, 2H), 7.40- 7.37(m, 2H), 7.36-7.33(m, 3H), 4.83(s, 1H), 3.95(s,3H), 2.58(m, 4H), 1.60-1.55(m, 4H), 1.49-1.45(m, 2H); ^{13}C-NMR ($CDCl_3$,100MHz): δ= 159.34, 138.13, 136.25, 134.12, 132.61, 131.96, 126.64, 122.71, 87.32, 86.74, 60.01, 56.36, 51.12, 27.87, 23.71.



1-[1-(4-Cyanophenyl)-3-phenyl-2-propynyl]piperidine: (4f), yield 90%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.68-7.57(m, 2H), 7.56-7.52(m, 2H), 7.39-7.35(m, 2H), 7.34-7.28(m, 3H), 4.83(s, 1H), 2.60 (m, 4H), 1.65-1.48(m, 4H), 1.47-1.28(m, 2H); ^{13}C-NMR ($CDCl_3$,100MHz): δ= 143.85, 132.12, 129.64, 128.37, 128.03, 127.56, 117.97, 112.53, 88.98, 85.32, 63.28, 51.39, 27.36, 24.75.



1-(1-(4-ethylphenyl)-3-phenylprop-2-yn-1-yl)piperidine: (4g), yield 97%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.63-7.61(m, 2H), 7.58-7.55(m, 2H), 7.38- 7.35(m, 2H), 7.35-7.29(m, 3H), 4.84(s, 1H), 2.59(m, 6H), 2.44(d,3 H), 1.62-1.55(m, 4H), 1.54-1.44(m, 2H); ^{13}C-NMR ($CDCl_3$,100MHz): δ= 137.09, 133.89, 129.13, 128.54, 127.97, 125.76, 87.89, 86.47, 59.38, 50.23, 26.89, 24.56, 21.54, 19.36.

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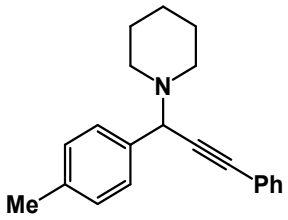
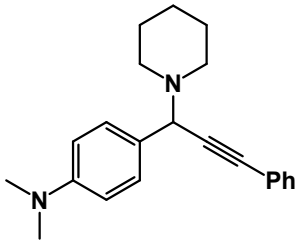
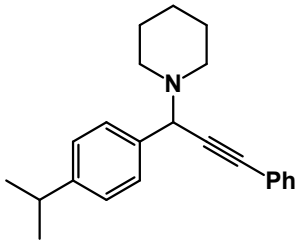


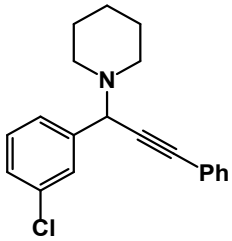
1-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)piperidine: (4h), yield 96%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.63-7.55(m, 2H), 7.54-7.51(m, 2H), 7.39- 7.36(m, 2H), 7.35-7.06(m, 3H), 4.85(s, 1H), 2.59(m, 4H), 1.62-1.57(m, 4H), 1.56-1.46(m, 2H); ^{13}C-NMR ($CDCl_3$,100MHz): δ= 138.34, 137.11, 134.02, 132.26, 131.76, 129.24, 128.37, 127.96, 126.31, 123.87, 88.16, 85.97, 59.87, 50.57, 27.55, 24.32, 21.37.



N,N-dimethyl-4-(3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)aniline: (4i), yield 92%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.60-7.57(m, 2H), 7.55-7.40(m, 2H), 7.39- 7.36(m, 2H), 7.36-7.31(m, 3H), 4.82(s, 1H), 3.89(s, 6H), 2.57(m, 4H), 1.58-1.48(m, 4H), 1.47-1.41(m, 2H); ^{13}C-NMR ($CDCl_3$,100MHz): δ= 138.32, 137.30, 133.98, 131.51, 130.02, 129.64, 128.76, 127.13, 125.76, 123.58, 88.32, 86.94, 59.96, 50.24, 26.64, 24.37, 21.14, 19.07.



1-(1-(4-isopropylphenyl)-3-phenylprop-2-yn-1-yl)piperidine: (4j), yield 88%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.62-7.59(m, 2H), 7.58-7.50(m, 2H), 7.48- 7.38(m, 2H), 7.36-7.26(m, 3H), 4.80(s, 1H), 2.60(m, 4H), 2.35(m, 1H), 1.67-1.60(m, 4H), 1.55-1.50(m, 2H), 1.19(s, 6 H); ^{13}C-NMR ($CDCl_3$,100MHz): δ= 147.23, 138.54, 129.52, 128.36, 127.02, 125.91, 88.02, 85.27, 61.22, 50.54, 36.26, 26.19, 24.62, 19.85.



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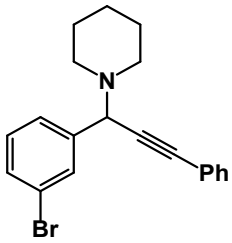
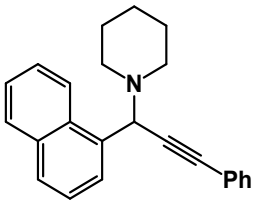
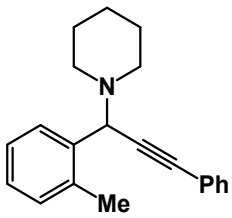
1-(1-(3-chlorophenyl)-3-phenylprop-2-yn-1-yl)piperidine: (4k), yield 94%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.65-7.62(m, 1H), 7.61-7.58(m, 1H), 7.57-7.7.52(m, 2H), 7.51-7.45(m, 1H), 7.44-7.35(m, 3H), 7.33-7.29(m, 1H), 4.81(s, 1H), 2.59(m, 4H), 1.66-1.60(m, 4H), 1.59-1.52(m, 2H); ^{13}C-NMR ($CDCl_3$,100MHz): δ= 142.12, 133.65, 132.71, 131.36, 130.73, 129.23, 128.68, 127.34, 124.06, 123.16, 87.96, 86.36, 61.85, 50.67, 26.72, 24.10.



1-(1-(3-Bromophenyl)-3-phenyl-2-propynyl])piperidine (4l), yield 95%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.83-7.61(m, 1H), 7.60-7.55(m, 1H), 7.54-7.51(m, 2H), 7.50-7.43(m, 1H), 7.38-7.32(m, 3H), 7.29-7.23(m, 1H), 4.79(s, 1H), 2.60-2.57(m, 4H), 1.67-1.63(m, 4H), 1.62-1.50(m, 2H); ^{13}C-NMR ($CDCl_3$,100MHz): δ= 141.20, 132.23, 131.46, 130.98, 129.64, 128.38, 128.21, 127.37, 123.78, 122.64, 88.47, 85.12, 62.03, 50.36, 26.97, 24.16.

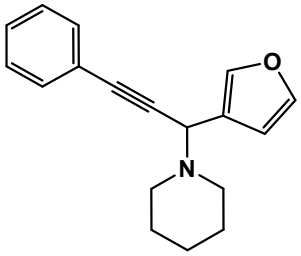


1-(1-(1-Naphathyl)- 3-phenyl-2-propynyl)piperidine. (4m), yield 97%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 8.10(s, 1H), 7.90 − 7.85(m, 3H), 7.81-7.75(m, 1H), 7.64-7.55(m, 2H), 7.53-7.46(m, 2H), 7.44-7.31(m, 3H), 4.97(s, 1H), 2.68-2.61(m, 4H), 1.721.54(m, 4H), 1.54-1.40(m, 2H); 13C-NMR (CDCl3, 100MHz): δ= 136.22, 133.08, 132.96, 131.87, 128.33, 128.13, 127.76, 127.58, 127.29, 126.71, 125.95, 125.86, 123.35, 88.13, 86.02, 62.53, 50.84, 26.19, 24.46.

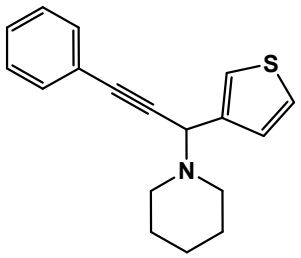


1-(3-phenyl-1-(o-tolyl)prop-2-yn-1-yl)piperidine: (4n), yield 89%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.63-7.60(m, 1H), 7.59-7.55(m, 1H), 7.53-7.50(m, 2H), 7.48-7.43(m, 1H), 7.38-7.34(m, 3H), 7.33-7.26(m, 1H), 4.80(s, 1H), 2.61(m, 4H), 2.35(s, 3H), 1.68-1.61(m, 4H), 1.60-1.50(m, 2H); ^{13}C-NMR ($CDCl_3$,100MHz): δ= 142.18, 132.03, 131.65, 130.85, 129.74, 128.36, 127.45, 125.32, 88.41, 85.16, 62.21, 50.95, 26.17, 24.83, 19.75.

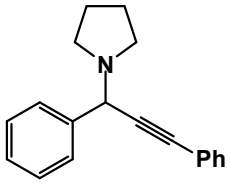
Supplementary Information



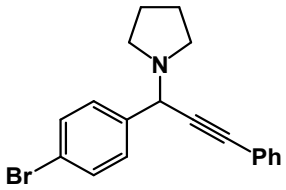
1 -[1-(2-furfuryl)-3-phenyl-prop-2-ynyl)-piperidine (4o), yield 90%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ=7.55-7.50 (m, 2H), 7.49-7.40(m, 1H), 7.37-7.32(m, 3H), 6.51-6.49(m,1H), 6.39-6.35 (m, 1H), 4.90 (s, 1H), 2.62-2.58 (m, 4H), 1.76-1.65 (m, 4H), 1.63-1.45 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 152.32, 141.26, 132.02, 129.11, 122.98, 109.98, 109.15, 86.40, 83.20, 56.64, 50.82, 29.87, 25.97.



1-(3-phenyl-1-(thiophen-3-yl)prop-2-yn-1-yl)piperidine (4p), yield 92%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ=7.53-7.50 (m, 2H), 7.49-7.40(m, 1H), 7.37-7.29(m, 3H), 6.52-6.49(m,1H), 6.39-6.33 (m, 1H), 4.85 (s, 1H), 2.60-2.53 (m, 4H), 1.72-1.60 (m, 4H), 1.58-1.40 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 151.64, 140.95, 131.05, 128.64, 121.61, 109.34, 109.04, 85.37, 83.19, 55.16, 50.74, 29.23, 25.68.

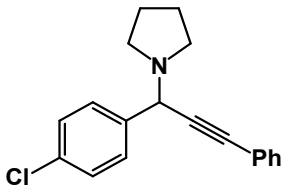


1-(1,3-diphenylprop-2-yn-1-yl)pyrrolidine: (4q), yield 95%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.67-7.54(m, 2H), 7.54-7.50(m, 2H), 7.39-7.30(m, 6H), 4.82(s, 1H), 2.80-2.74(m, 4H), 1.49-1.40(m, 4H); ^{13}C-NMR ($CDCl_3$, 100MHz):δ= 139.65, 129.36, 128.67, 127.41, 122.95, 88.50, 84.36, 67.18, 61.85, 23.12.

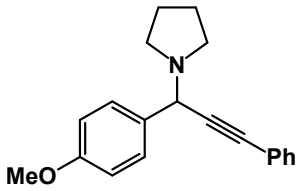


1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine: (4r), yield 97%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ=7.83-7.80(m, 2H), 7.71-7.56(m, 2H), 7.54-7.40(m, 2H), 7.37-7.30(m,3H),

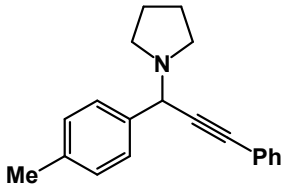
4.85(s, 1H), 2.78-2.74(m, 4H), 1.70-1.63(m, 4H); ^{13}C-NMR ($CDCl_3$, 100MHz):δ= 142.98, 131.65, 129.03, 128.64, 127.11, 122.61, 88.64, 85.37, 66.38, 61.25, 24.19.



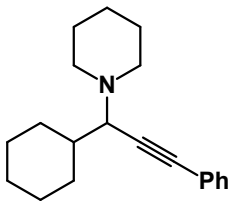
1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine: (4s), yield 96%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ=7.84-7.80(m, 2H), 7.67-7.55(m, 2H), 7.54-7.40(m, 2H), 7.39-7.31(m,3H), 4.85(s, 1H), 2.81-2.72(m, 4H), 1.89-1.84(m, 4H); ^{13}C-NMR ($CDCl_3$, 100MHz):δ= 1420.1, 131.20, 128.76, 125.36, 122.81, 87.32, 84.95, 63.02, 59.51, 24.94.



1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine: (4t), yield 90%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ=7.55-7.49(m, 2H), 7.45-7.41(m, 2H), 7.38-7.31(m, 2H), 7.27-7.22(m,3H), 4.83(s, 1H), 3.67(s, 3H), 2.79-2.73(m, 4H), 1.93-1.89(m, 4H); ^{13}C-NMR ($CDCl_3$, 100MHz):δ= 156.38, 131.82, 129.49, 128.33, 122.87, 121.26, 115.73, 88.50, 85.21, 61.12, 57.36, 55.95, 21.54.



1-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)pyrrolidine: (4u), yield 90%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ=7.57-7.54(m, 2H), 7.48-7.41(m, 2H), 7.38-7.31(m, 2H), 7.27-7.20(m,3H), 4.81(s, 1H), 2.78-2.75(m, 4H), 2.69(s, 3H), 1.91-1.88(m, 4H); ^{13}C-NMR ($CDCl_3$, 100MHz):δ= 156.38, 131.82, 129.49, 128.33, 122.87, 121.26, 115.73, 88.50, 85.21, 61.12, 57.36, 55.95, 21.54.



1-(1-cyclohexyl-3-phenylprop-2-yn-1-yl)piperidine: (4v), yield 86%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ=7.47-7.40(m, 2H), 7.35-7.27(m, 3H), 3.82-3.72(m, 4H), 3.06(d, 1H), 3.01-370(m, 2H), 2.69(m, 2H), 2.57(m, 1H), 1.99(t, 3H) ; ^{13}C-NMR ($CDCl_3$, 100MHz):δ= 131.70, 128.26, 127.96, 87.12, 86.51, 66.35, 57.15, 35.09, 26.12, 20.01, 15.56.

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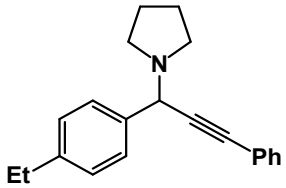
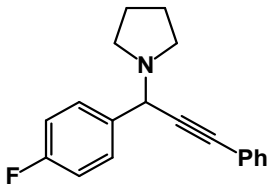


1-(1-(4-ethylphenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine: (4w), yield 90%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ=7.65-7.60 (m, 2H), 7.56-7.51 (m, 2H) , 7.38 − 7.31 (m, 2H),7.28-7.26(m, 3H), 4.82 (s, 1H), 2.80 − 2.71(m, 6H), 1.59-1.47 (m, 7H); ^{13}C-NMR ($CDCl_3$, 100MHz):δ= 138.23, 131.81, 128.50, 128.21, 127.89, 123.02, 88.50, 85.23, 61.23, 58.12, 23.56, 20.13, 19.02.



1-(1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine: (4x), yield 92%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= δ 7.85 (d, J=8.3Hz, 2H), 7.64 (d, J=8Hz, 2H) , 7.57 − 7.52 (m, 2H),7.38-7.32(m, 3H), 5.09 (s, 1H), 2.65 − 2.53 (m, 4H), 1.14 (t, J = 3.3 Hz, 6H); ^{13}C-NMR ($CDCl_3$, 100MHz, ppm): δ 154.13, 151.25, 135.64, 132.84, 131.50, 129.45, 128.74, 127.31, 124.39, 118.82, 118.23, 79.24, 73.61, 45.85, 44.09, 14.89.

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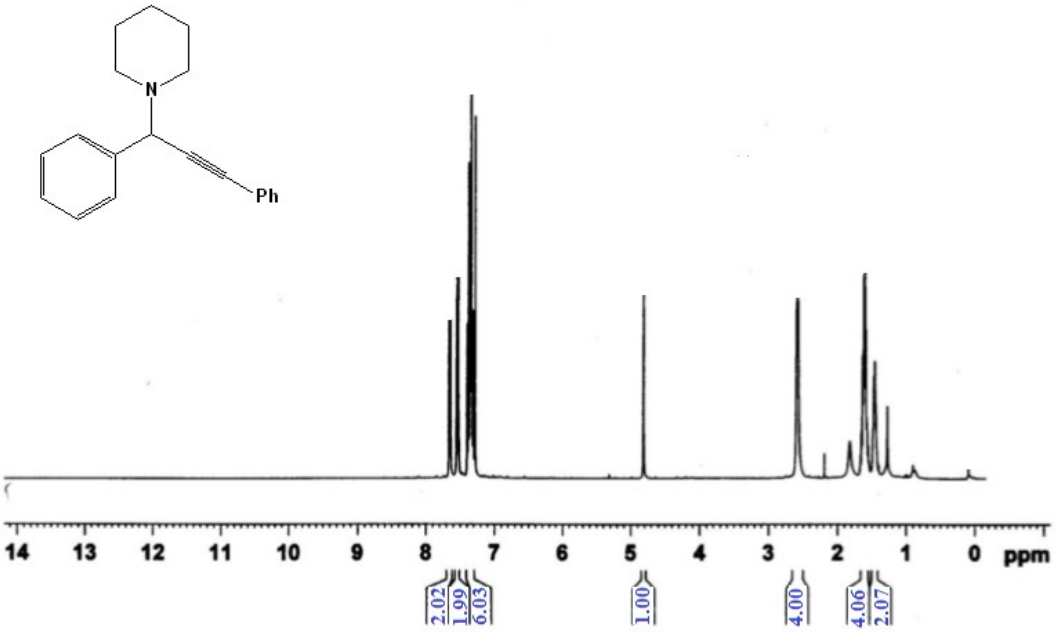

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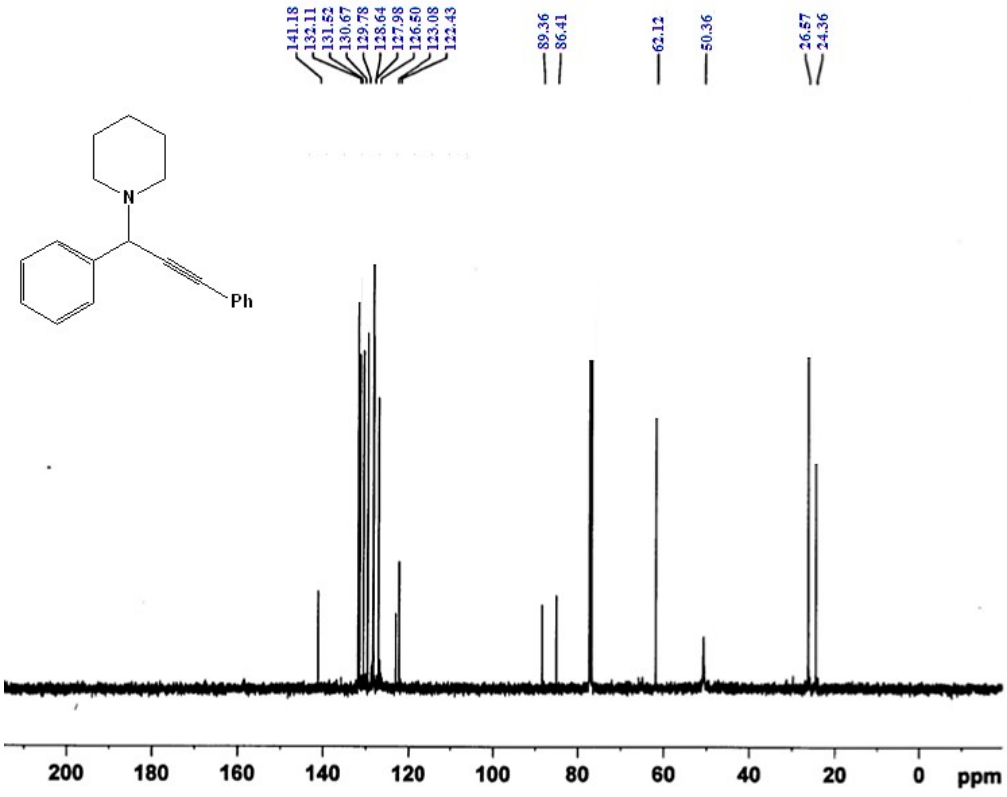

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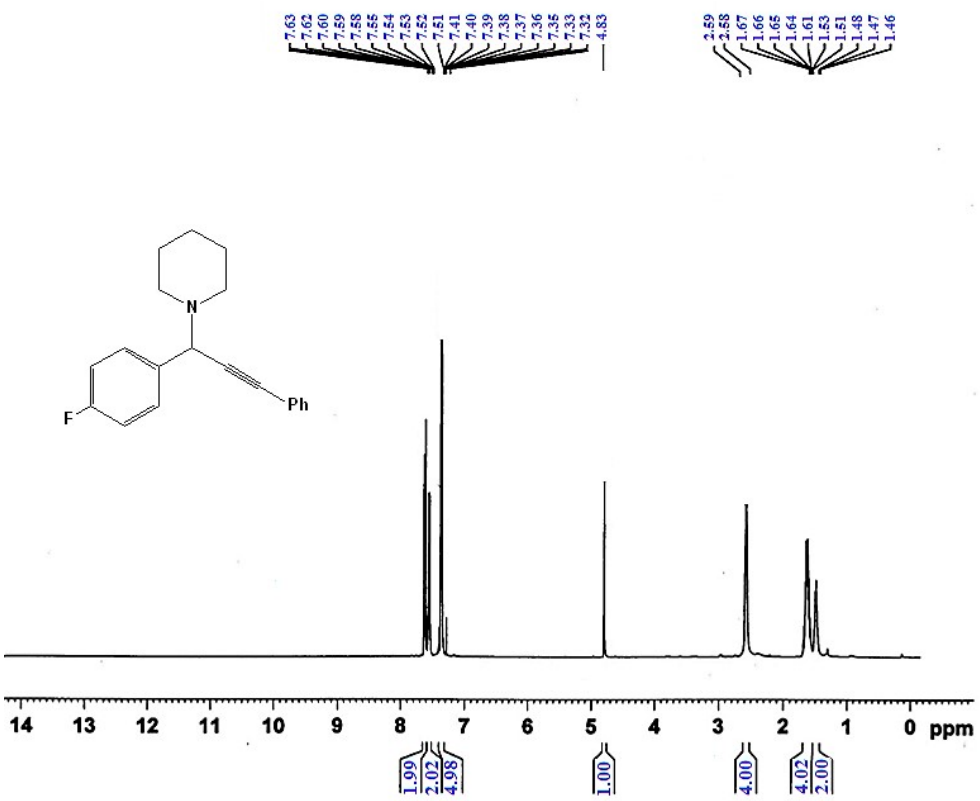

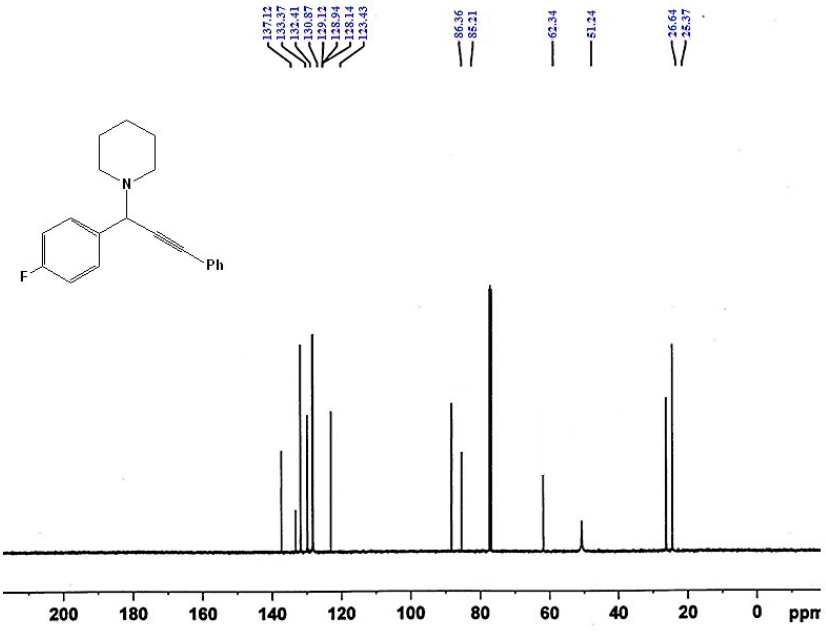

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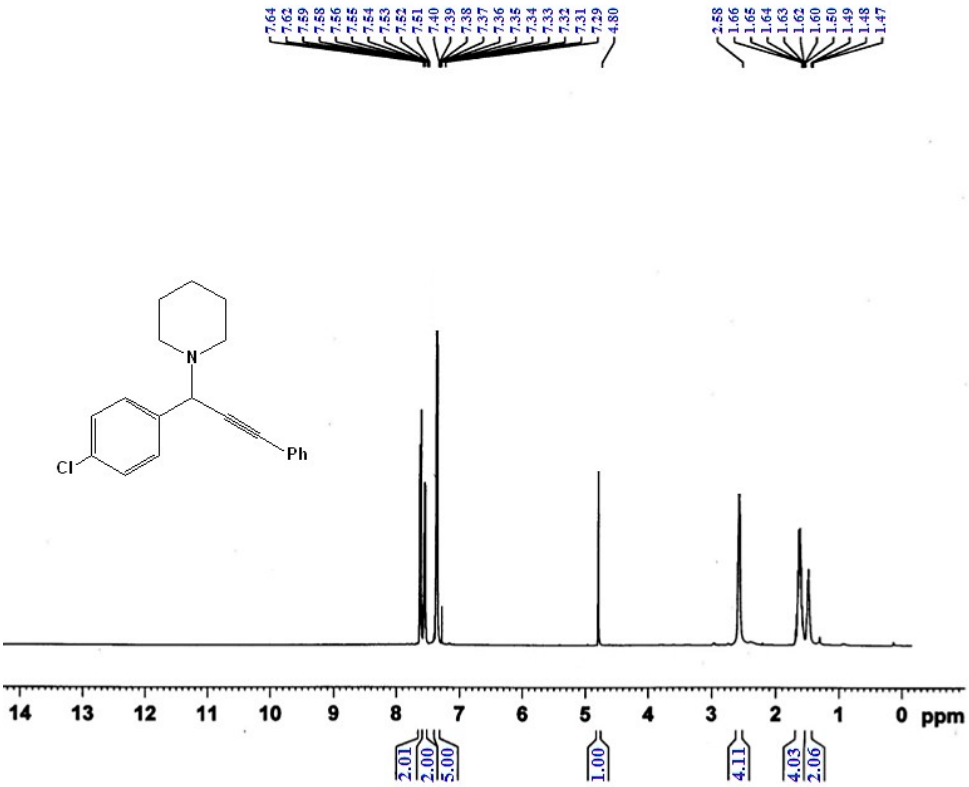

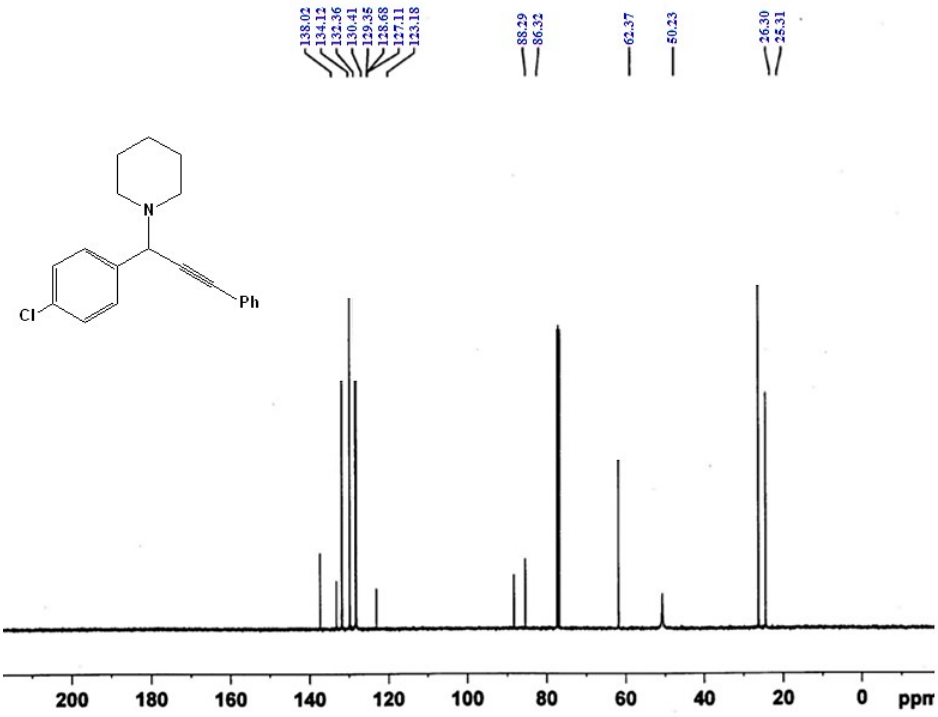

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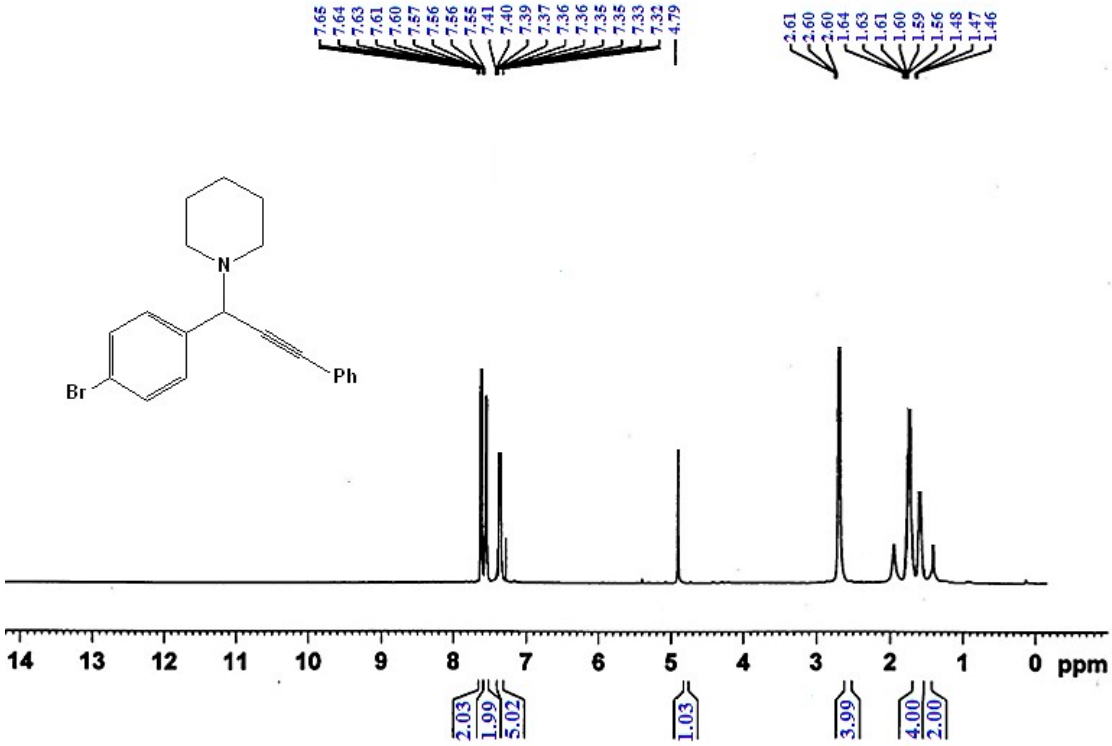

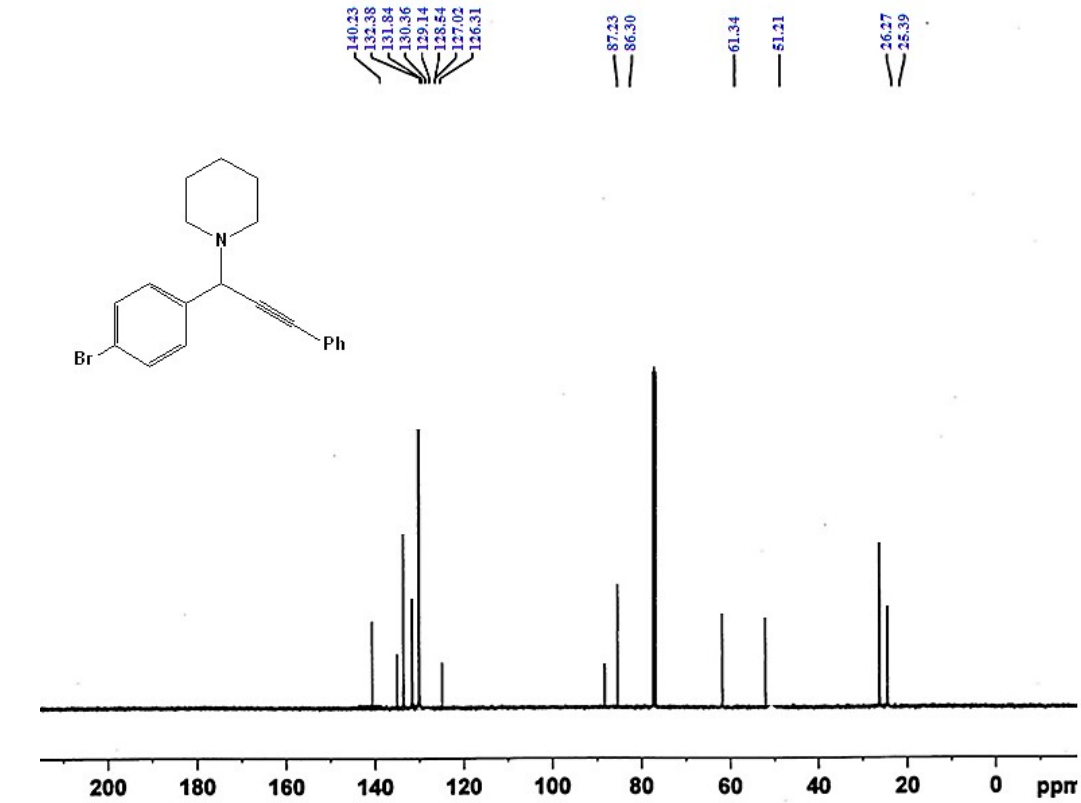

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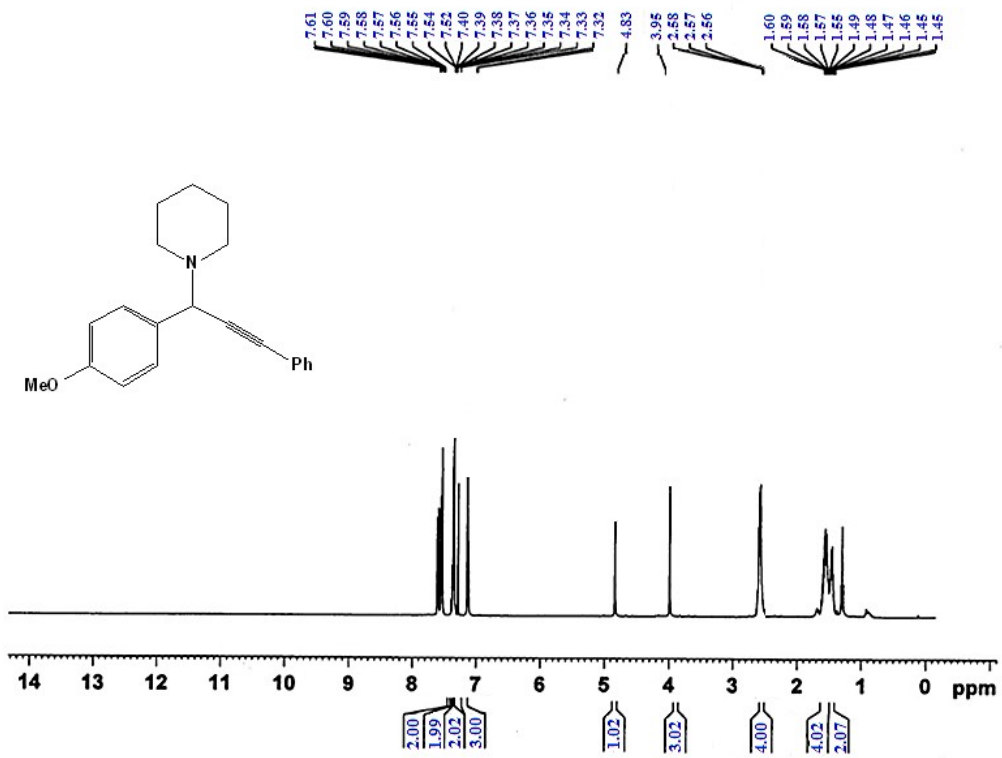

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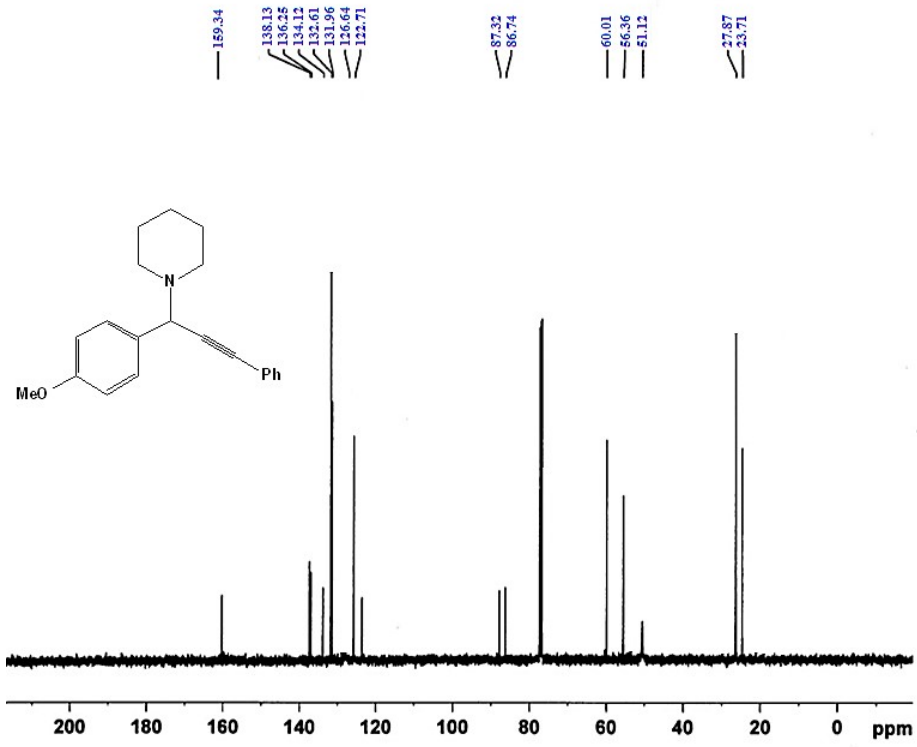

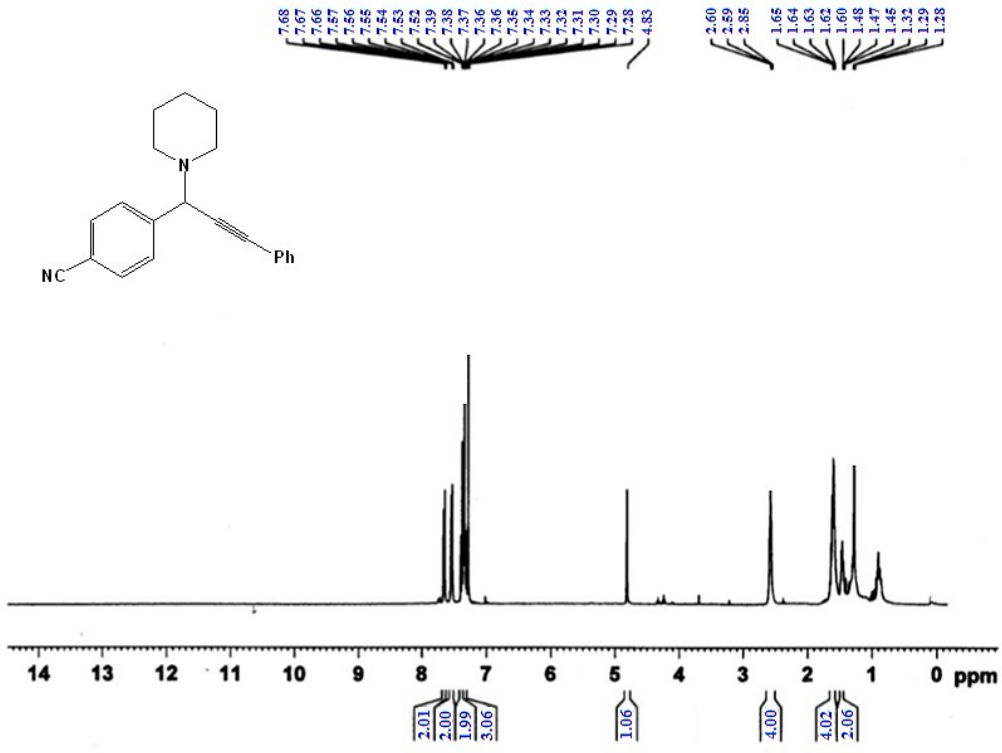

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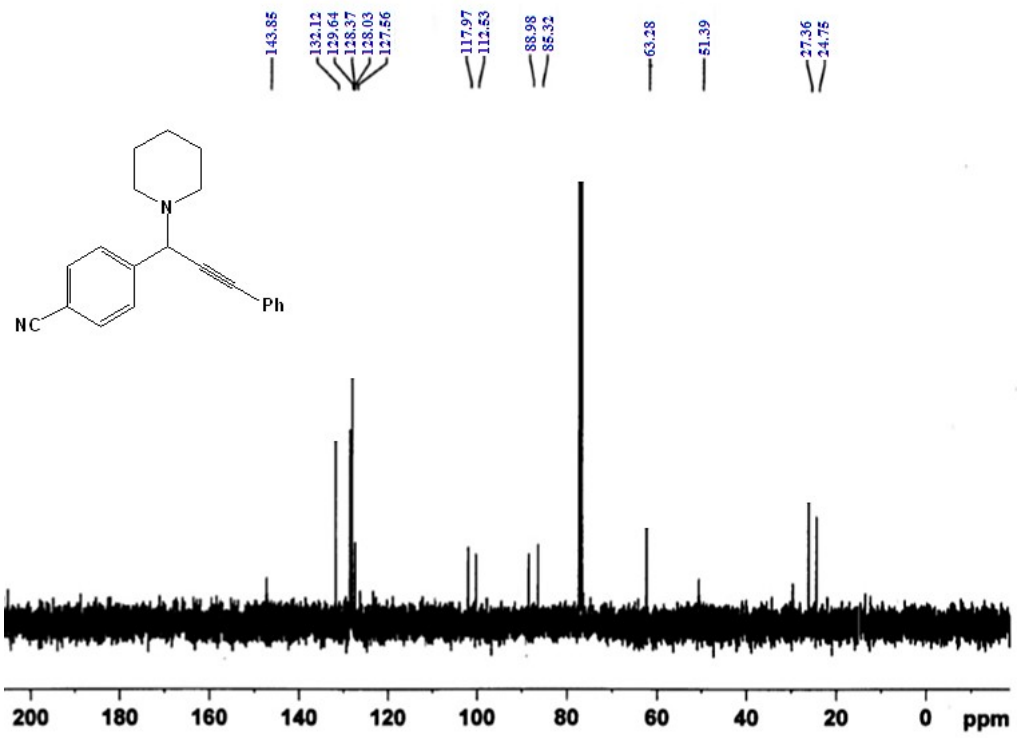

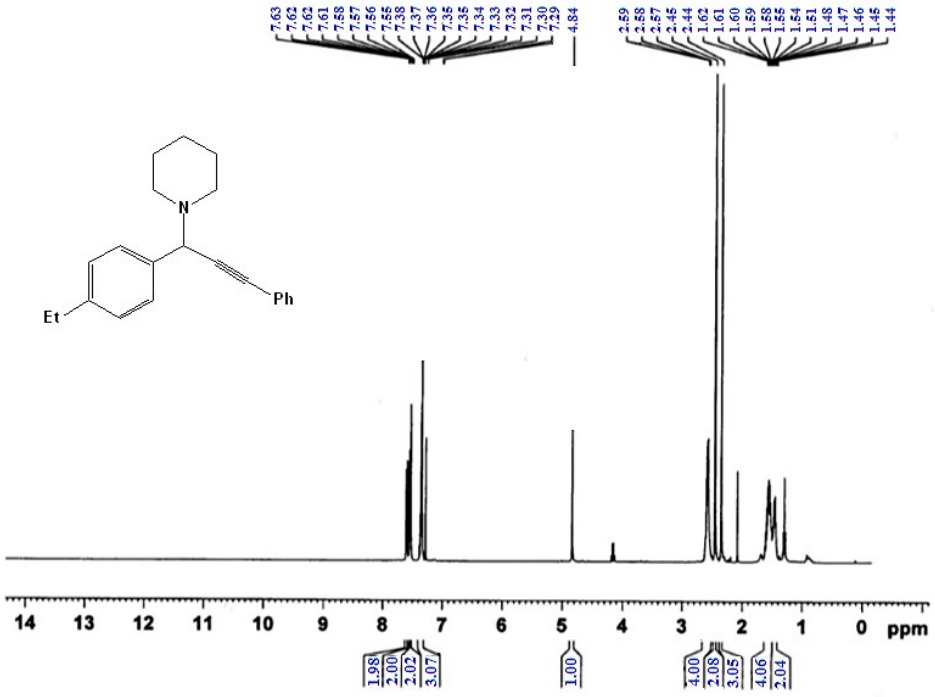

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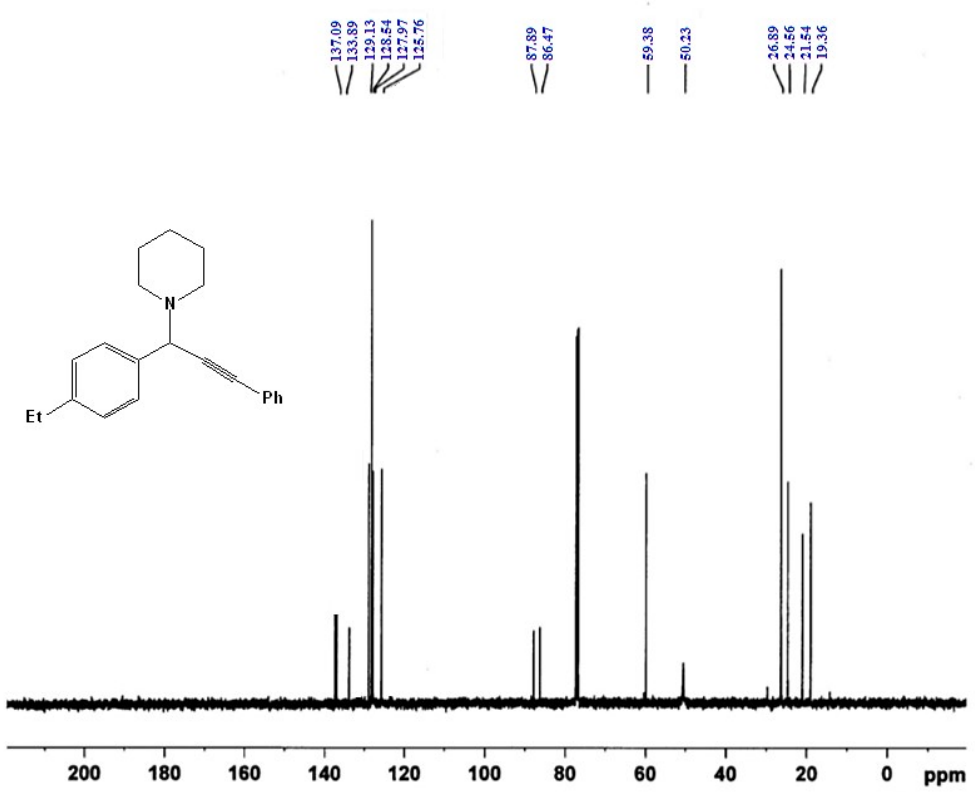

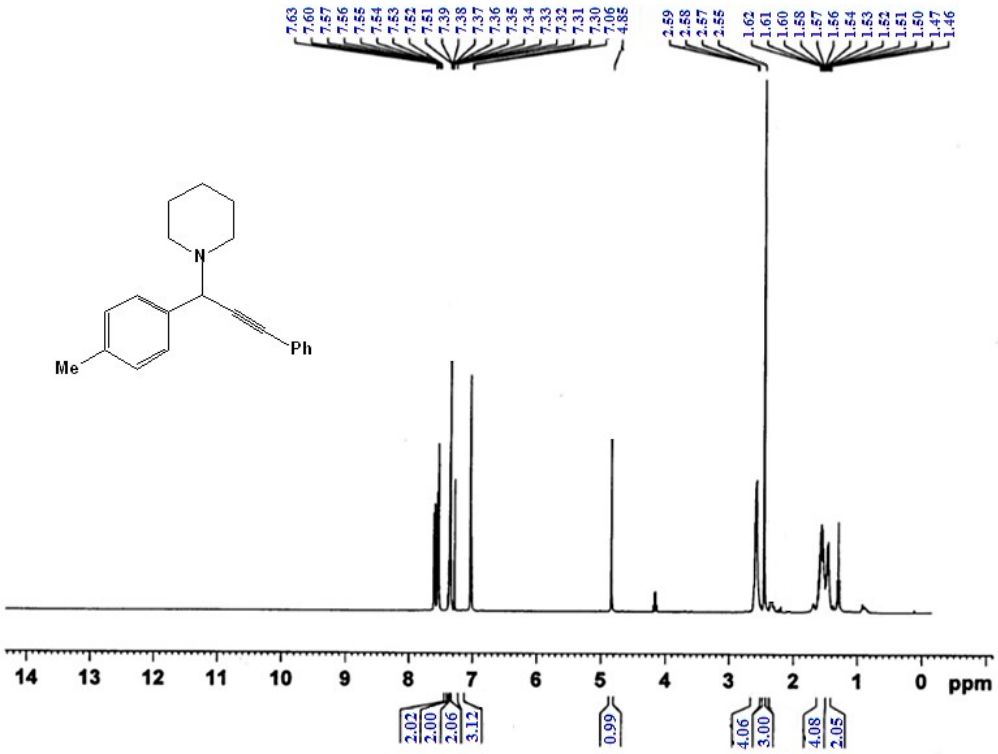

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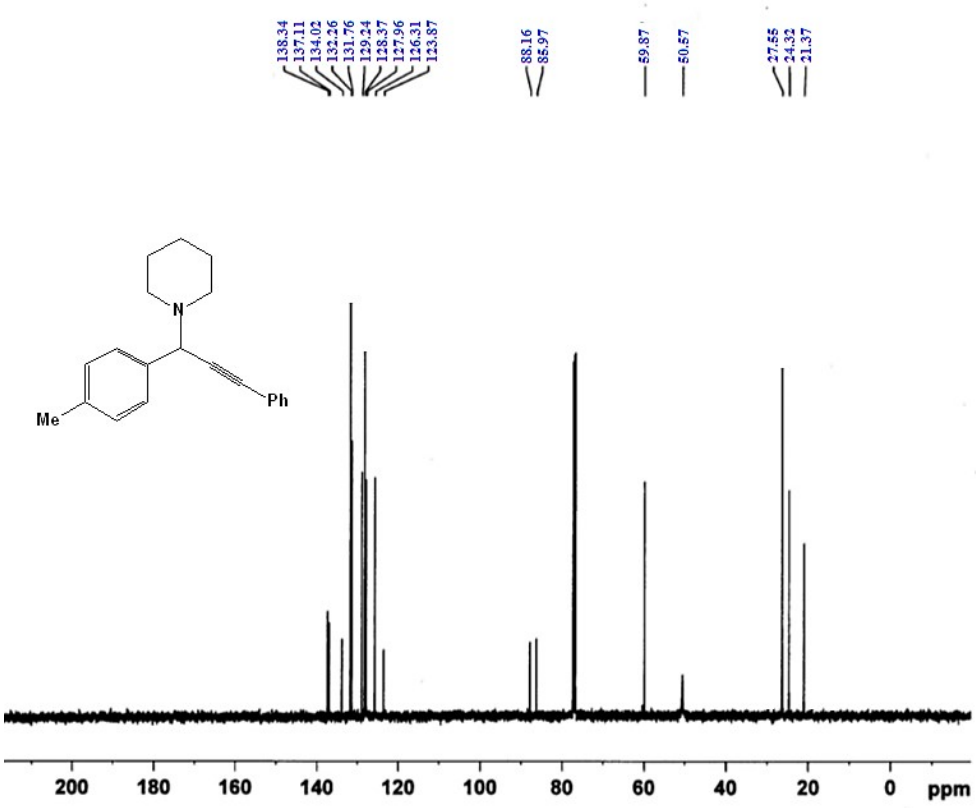

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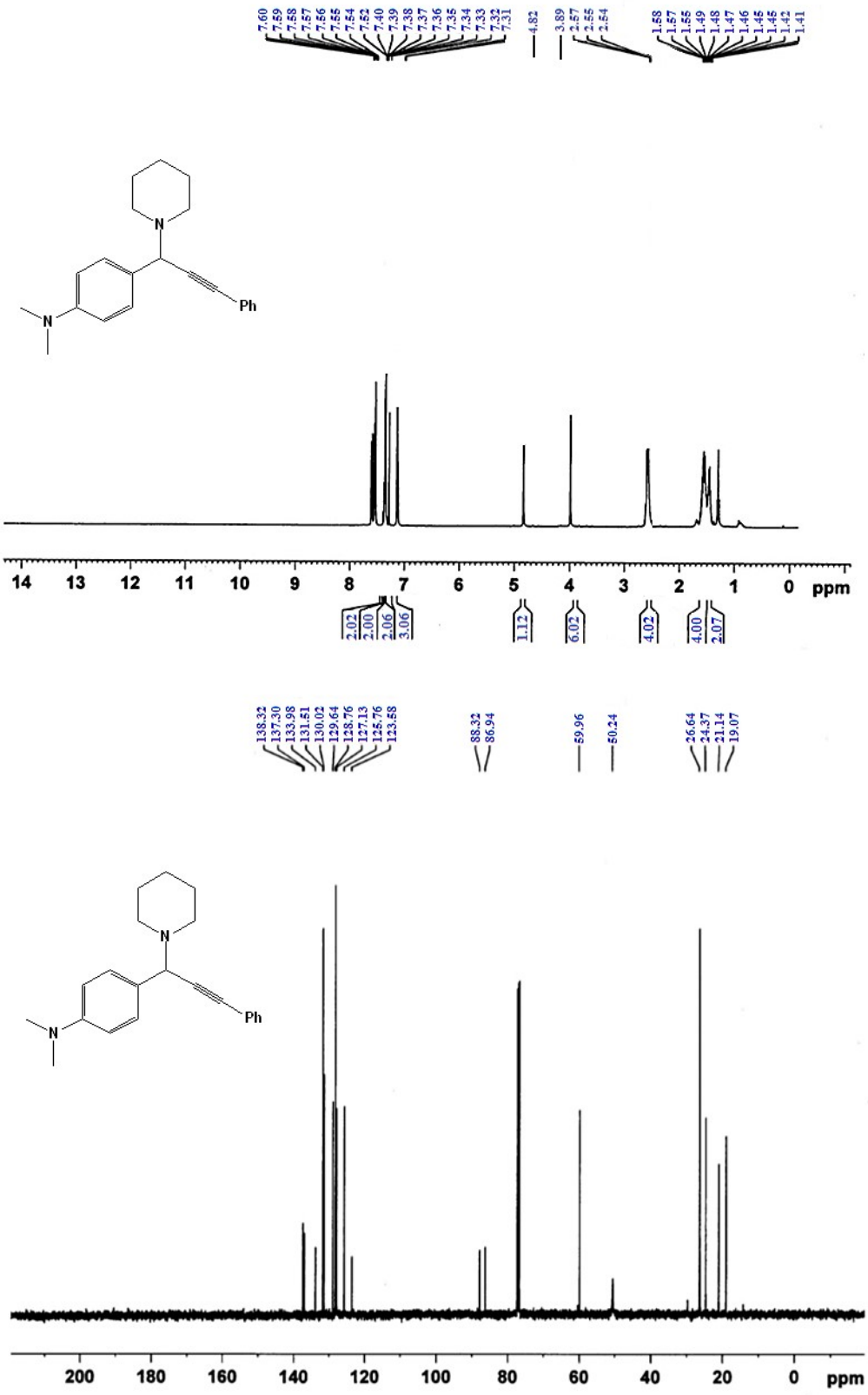

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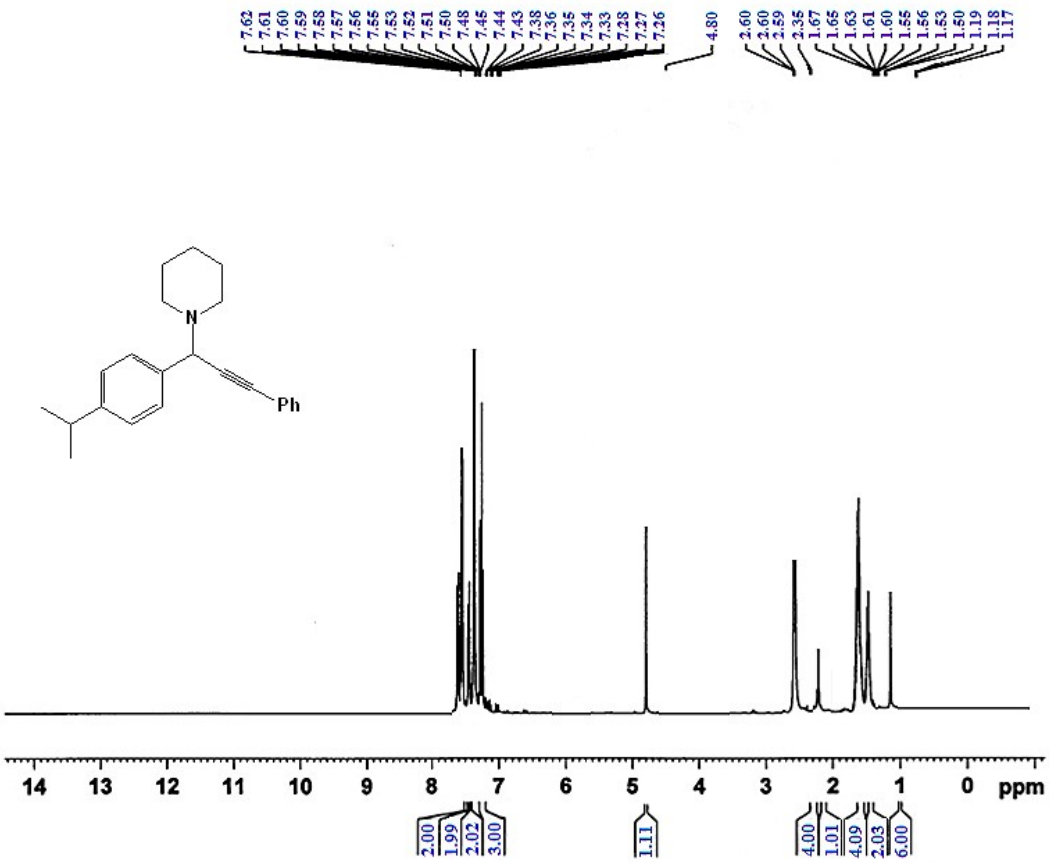

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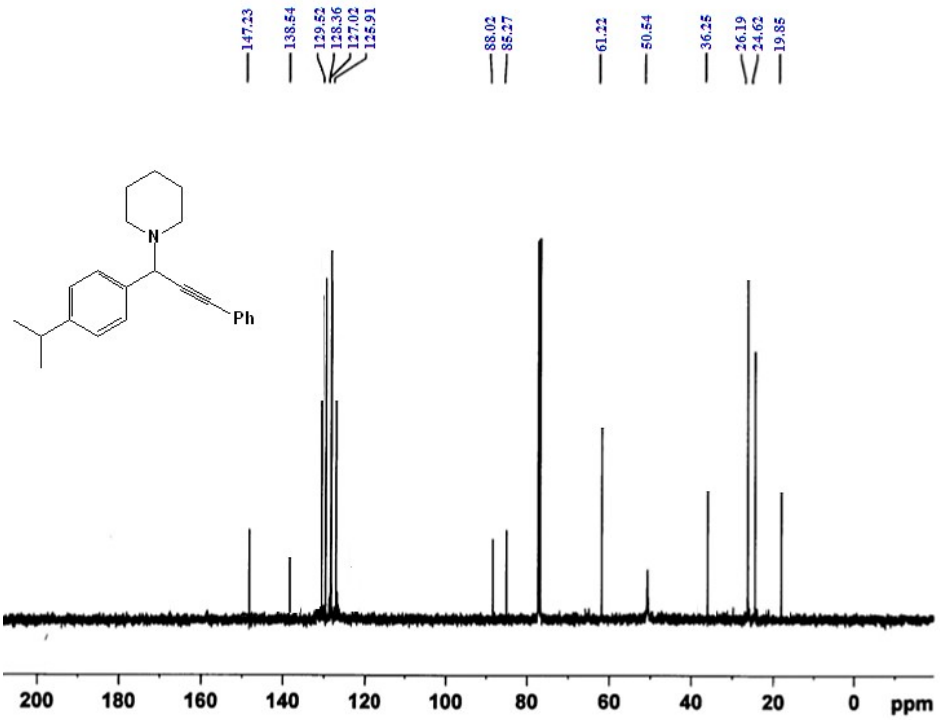

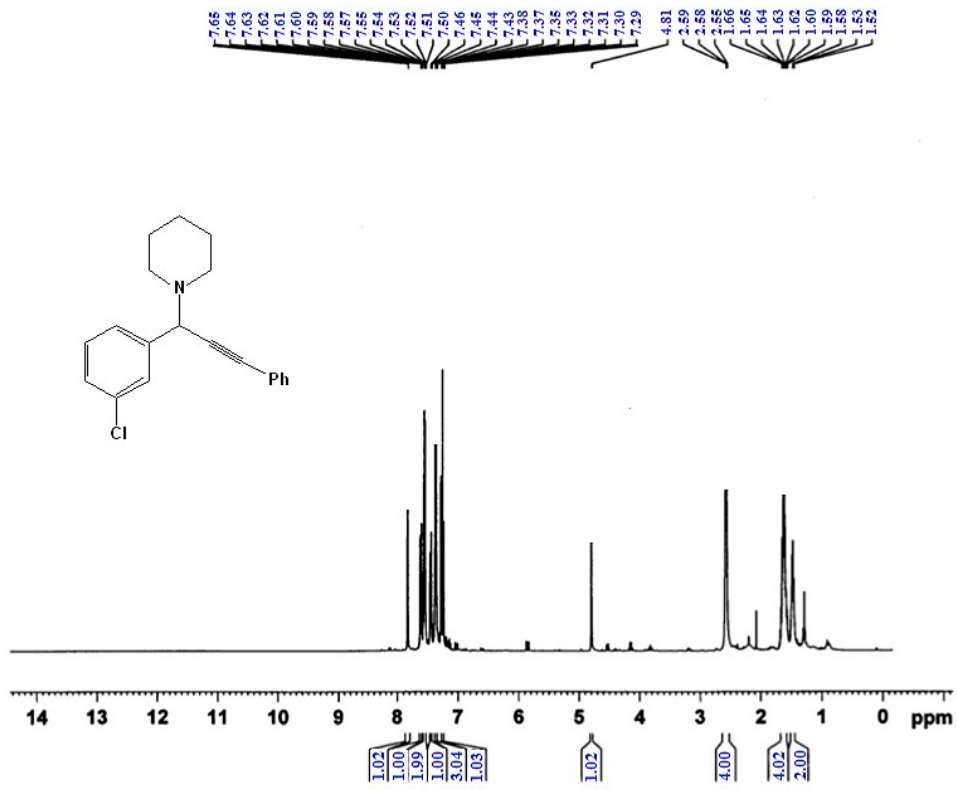

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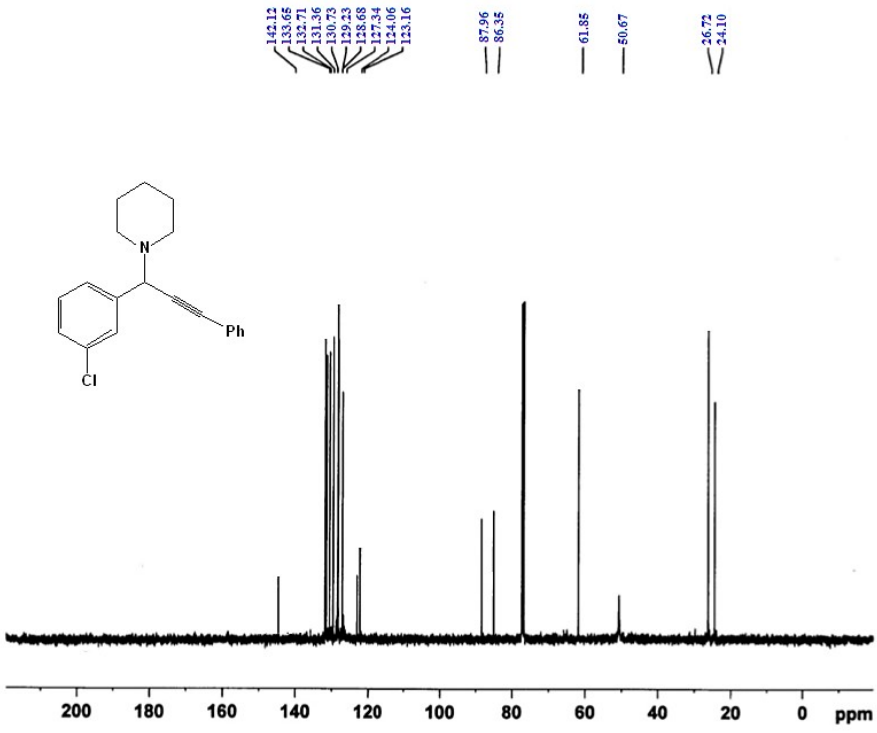

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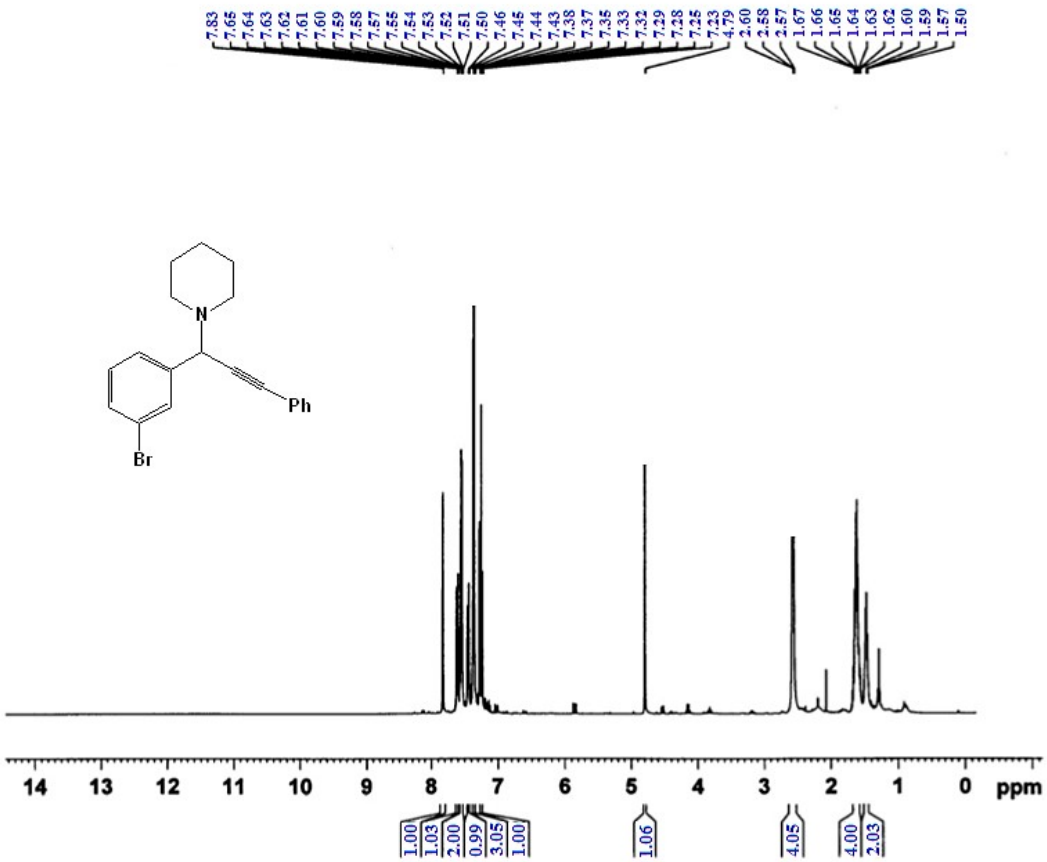

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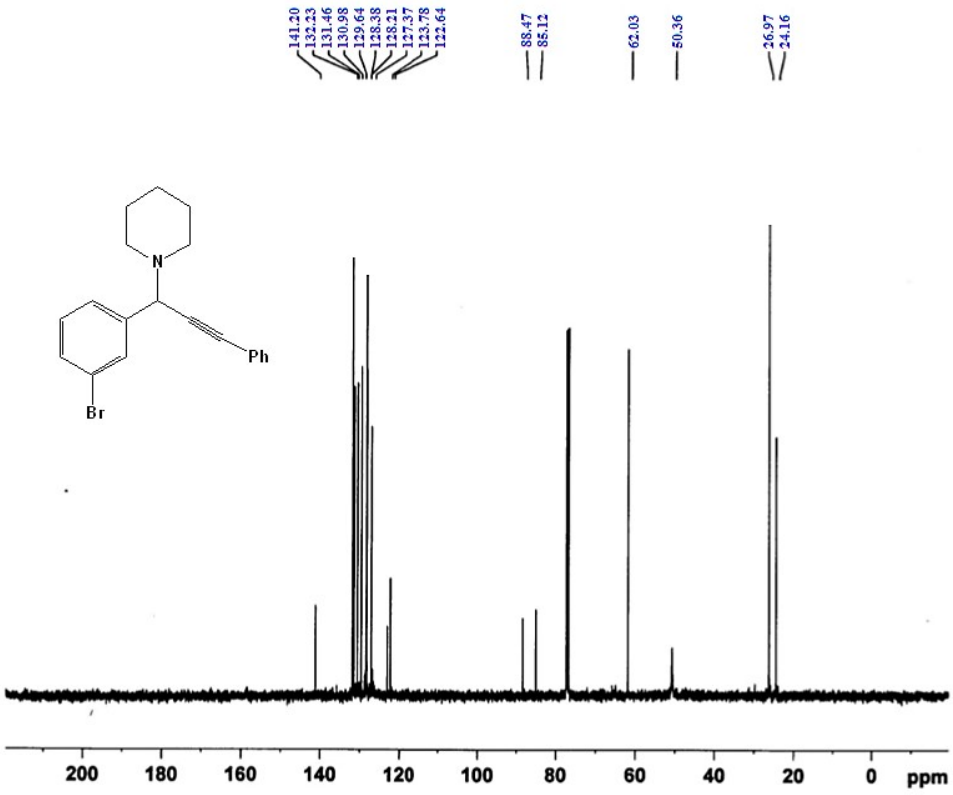

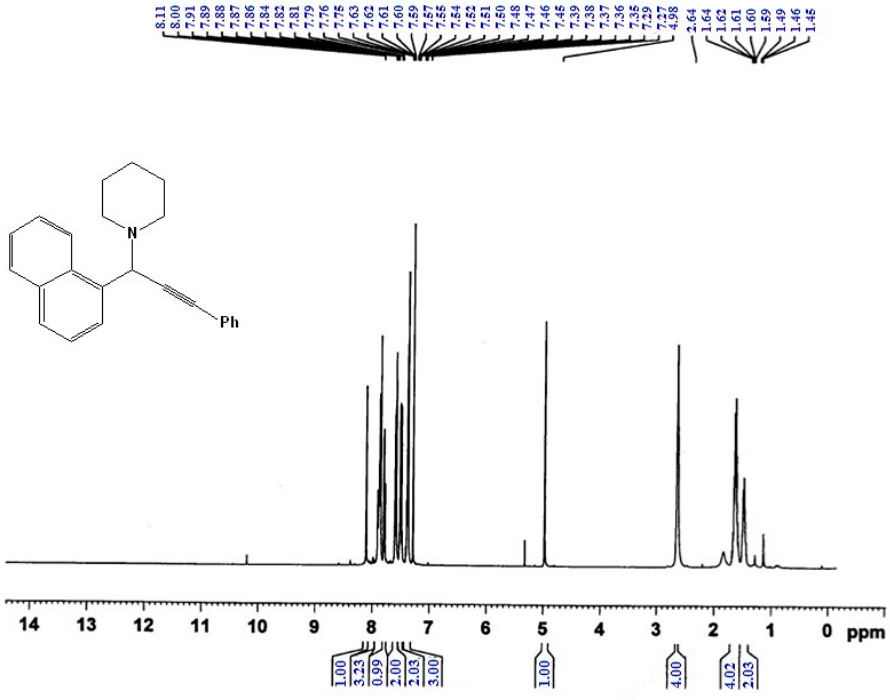

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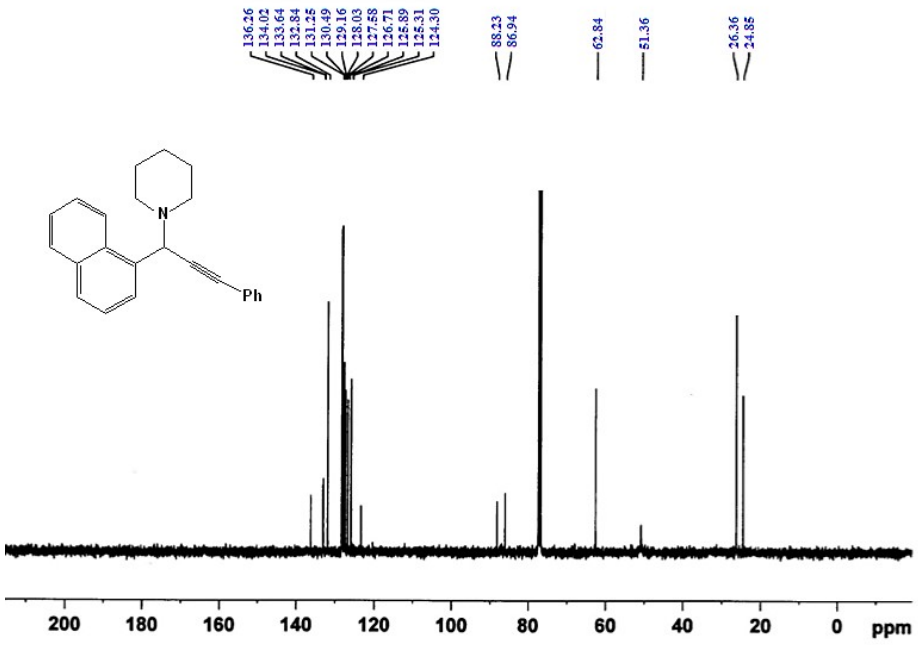

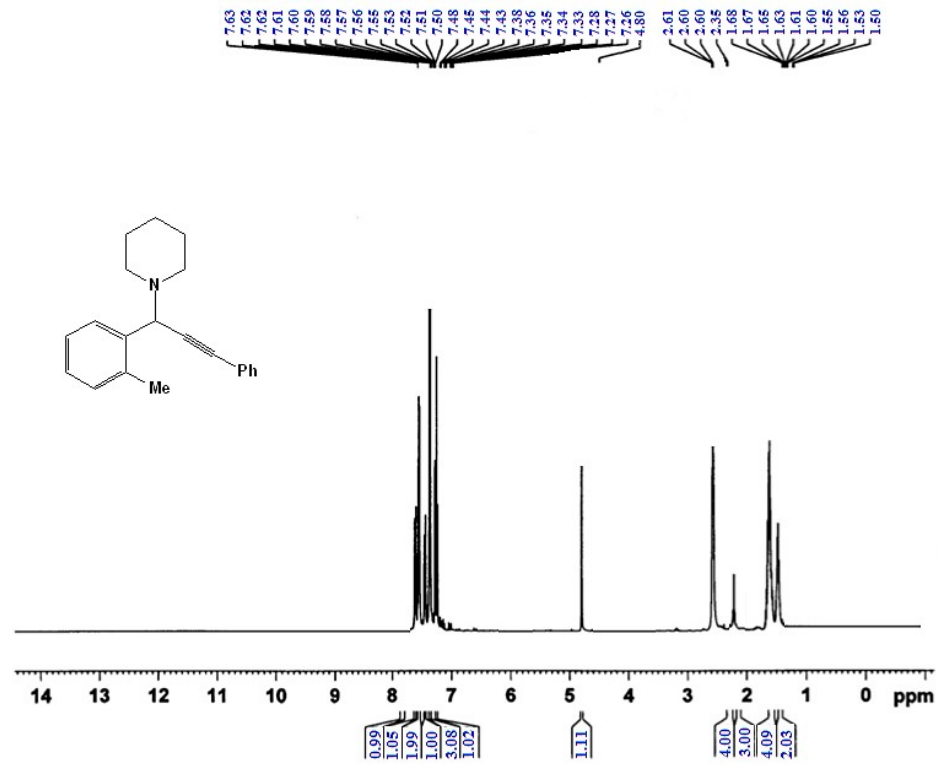

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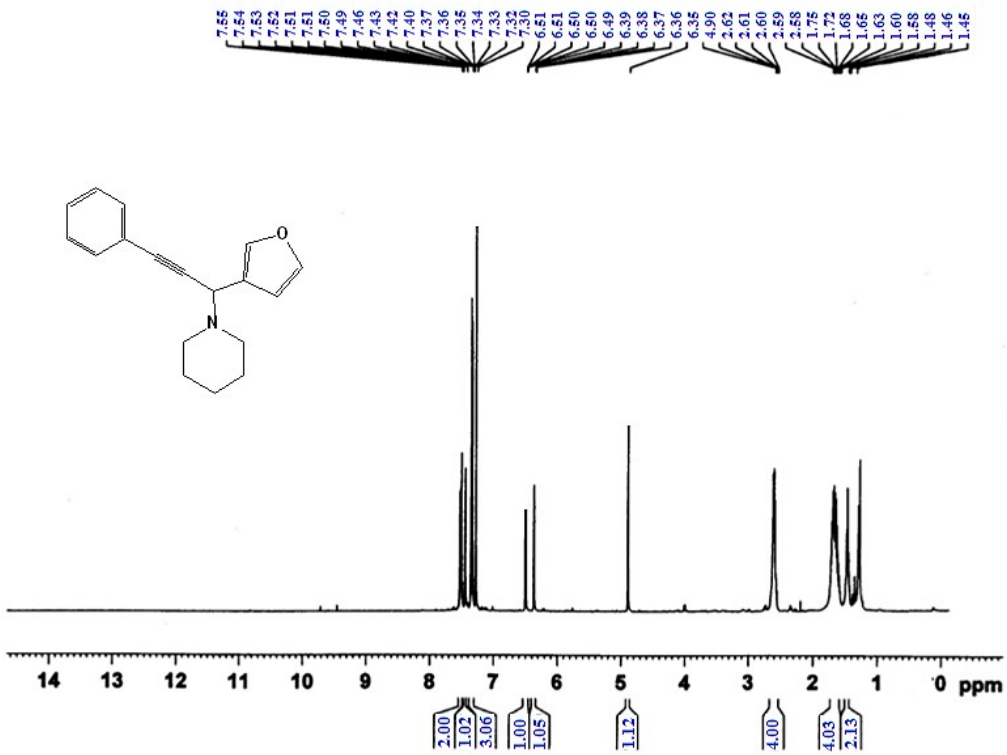

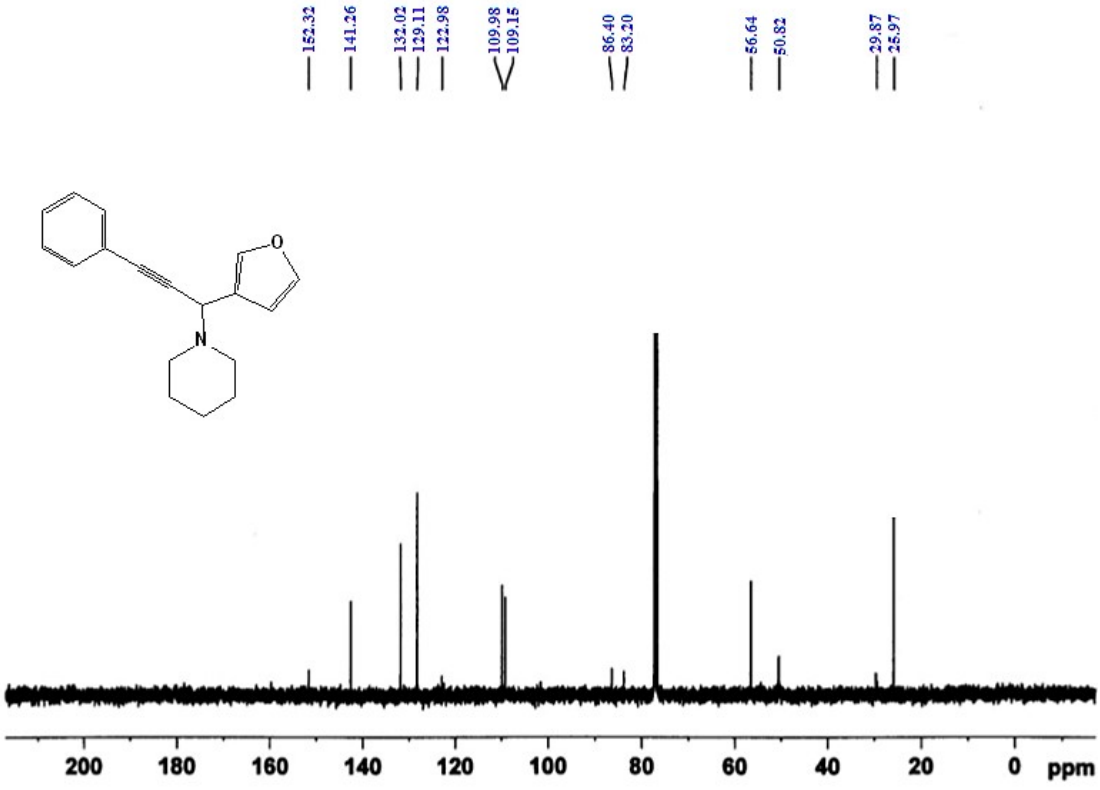

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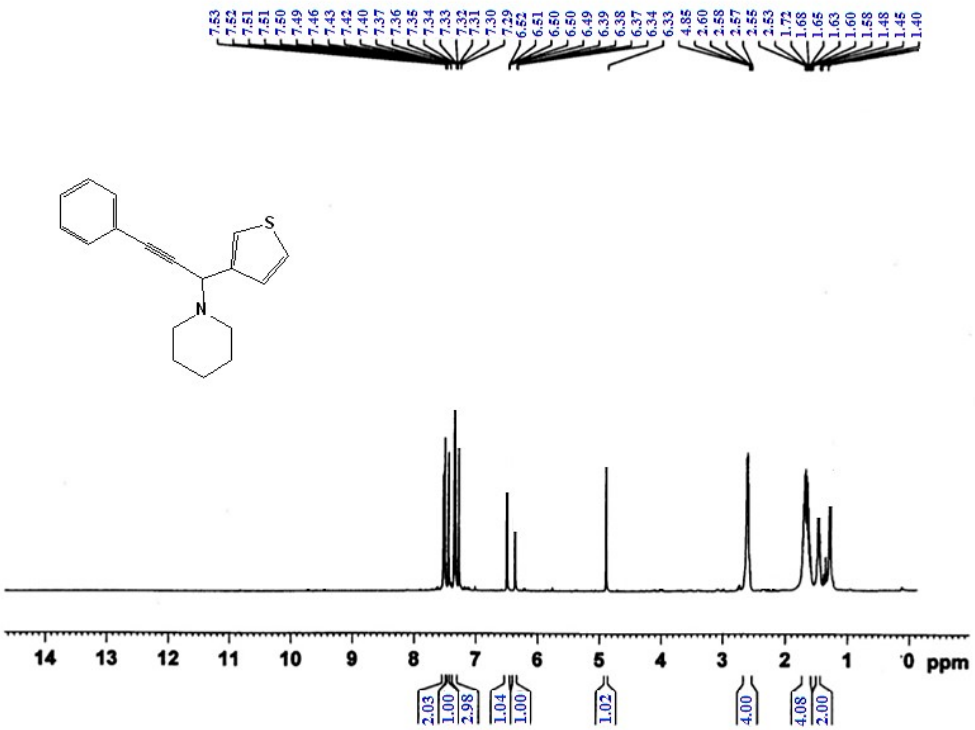

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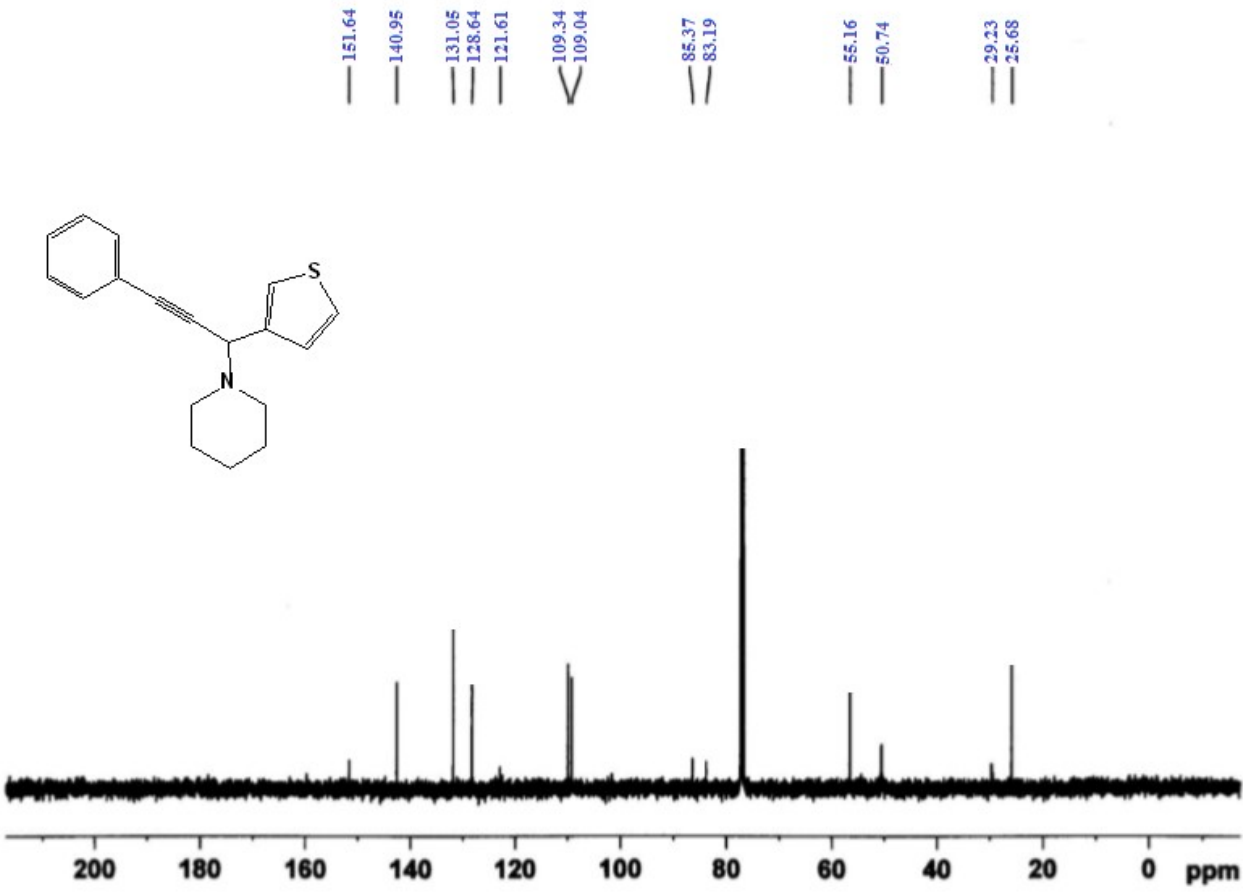

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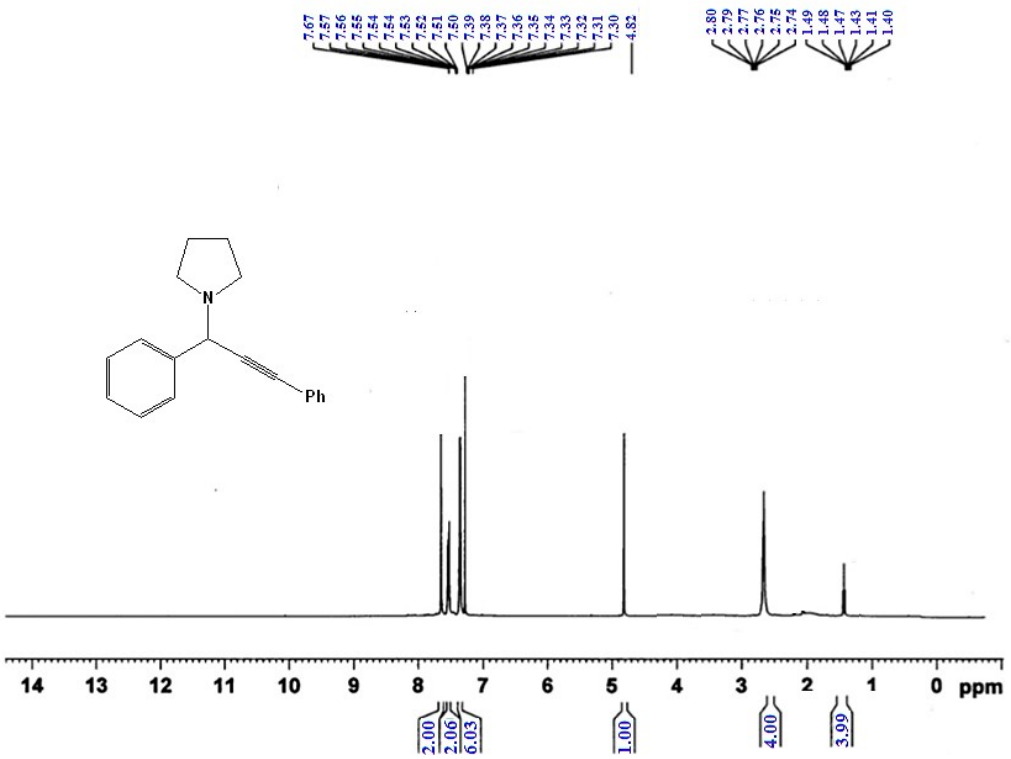

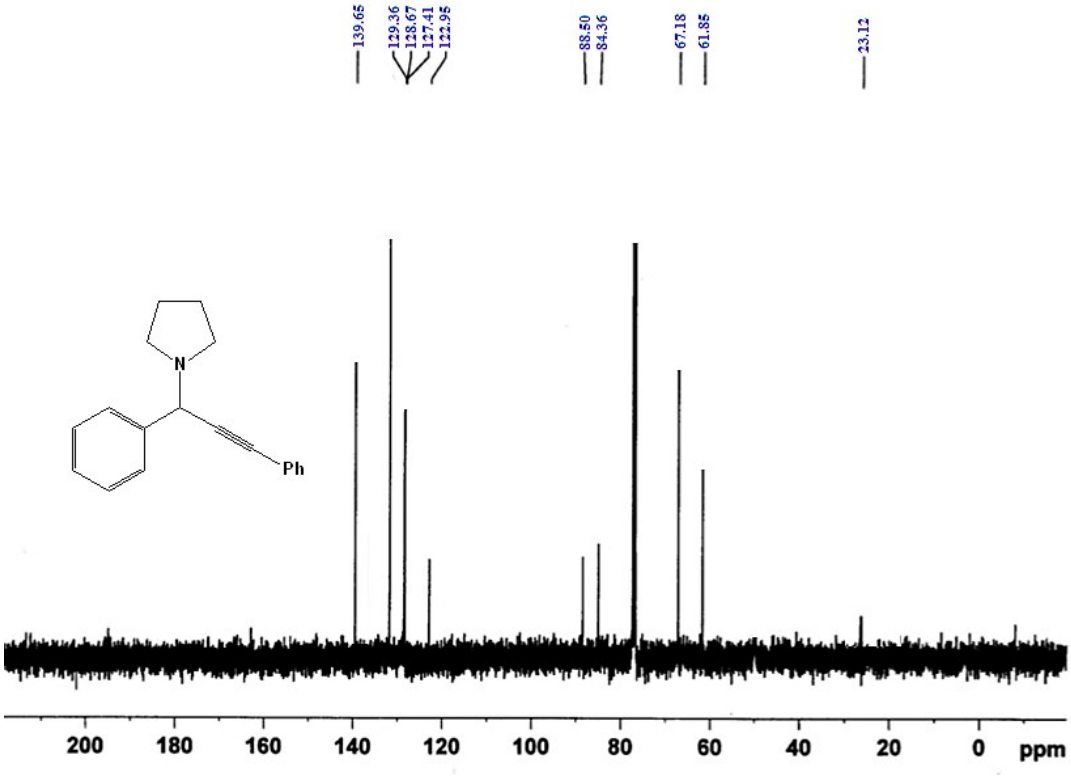

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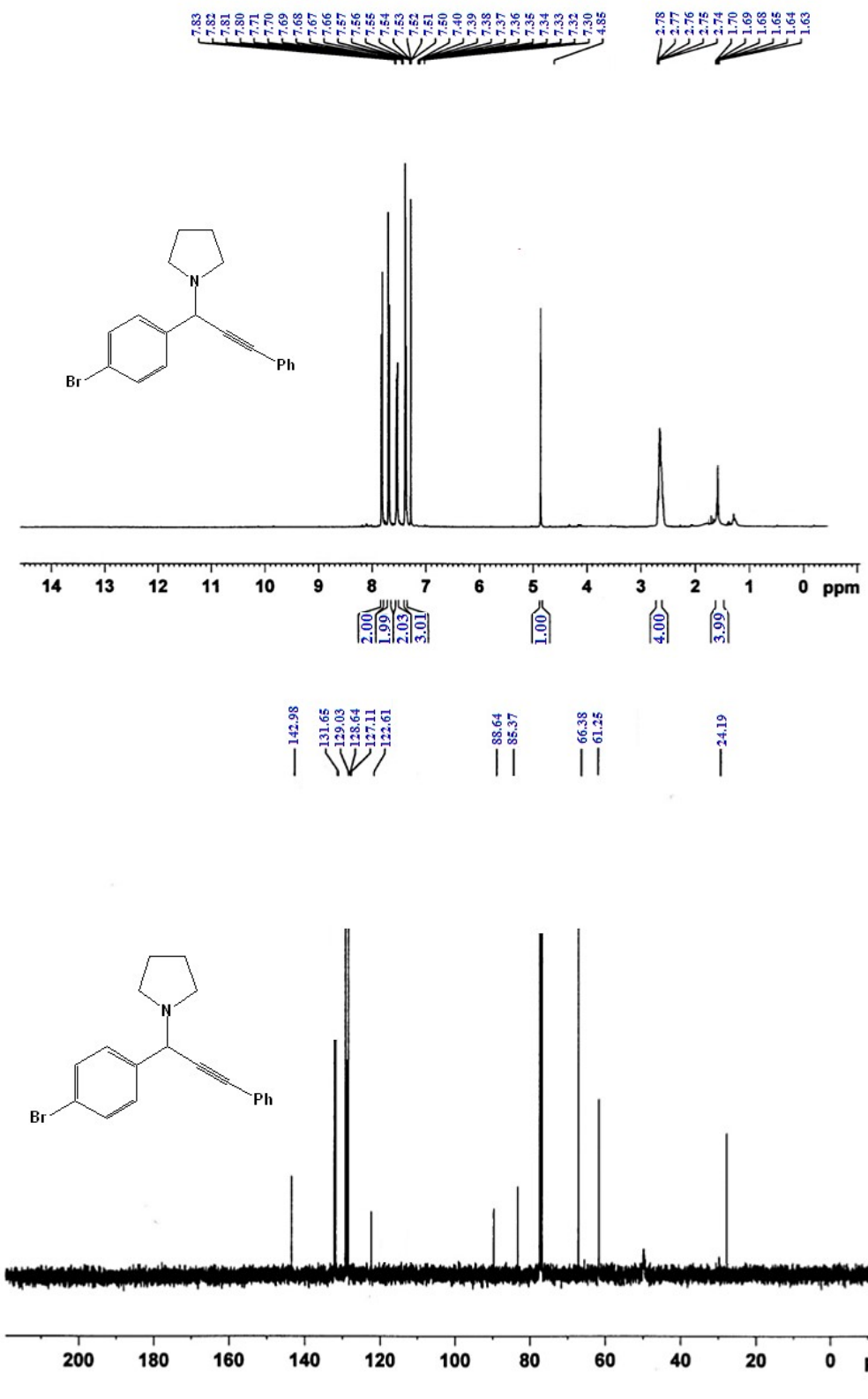

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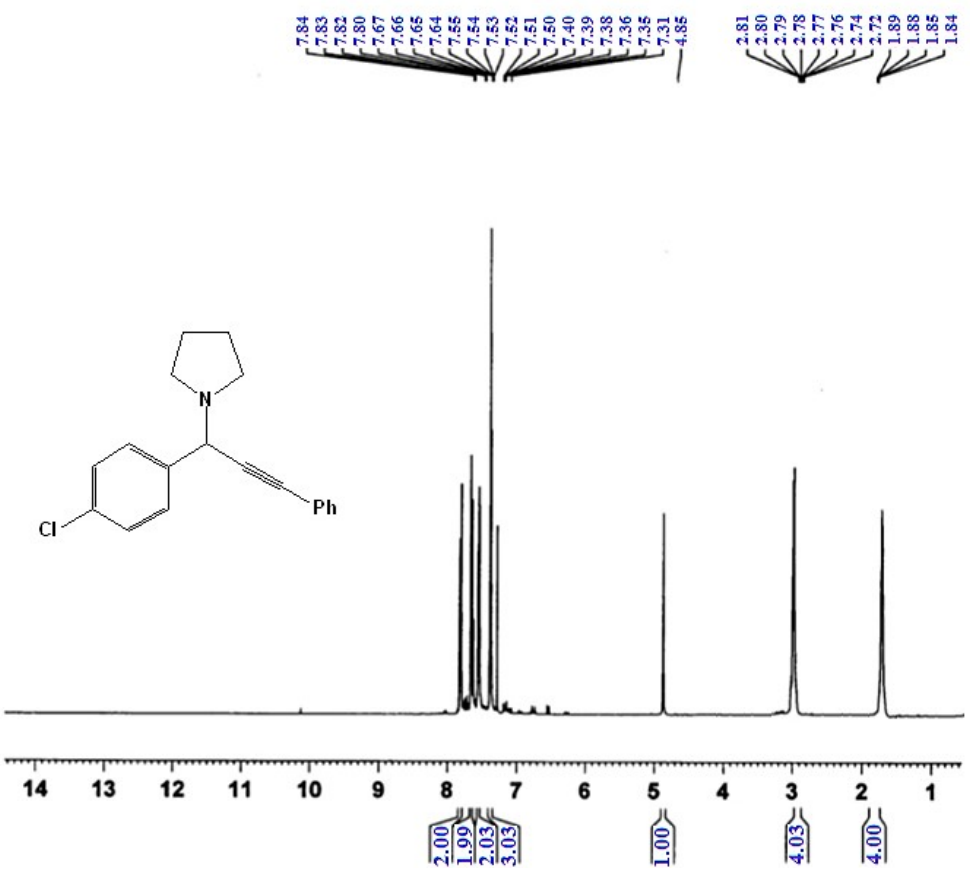

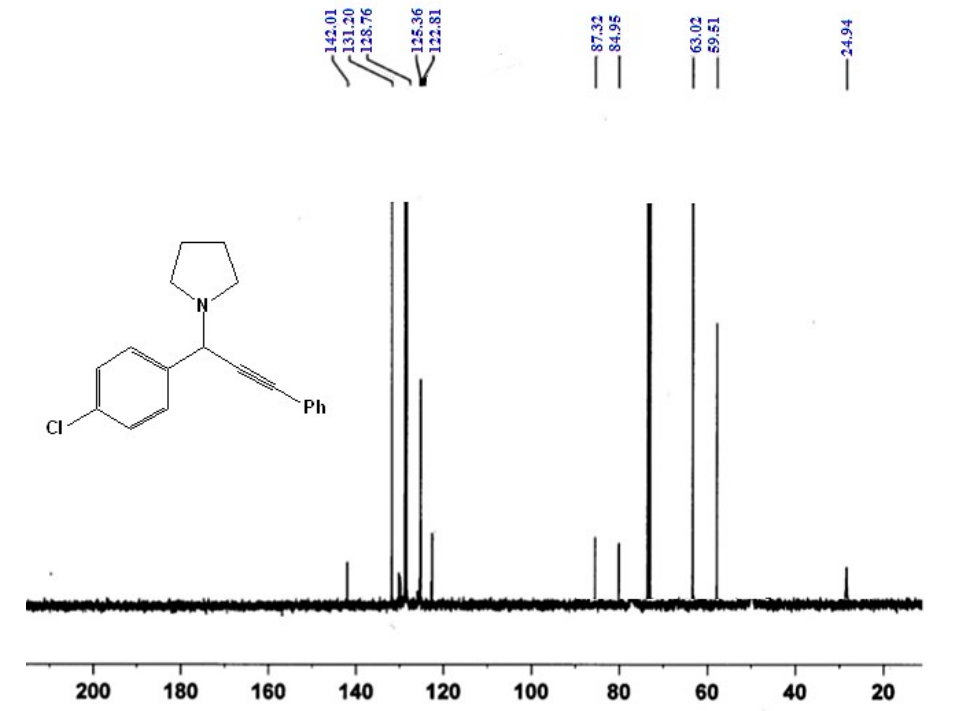

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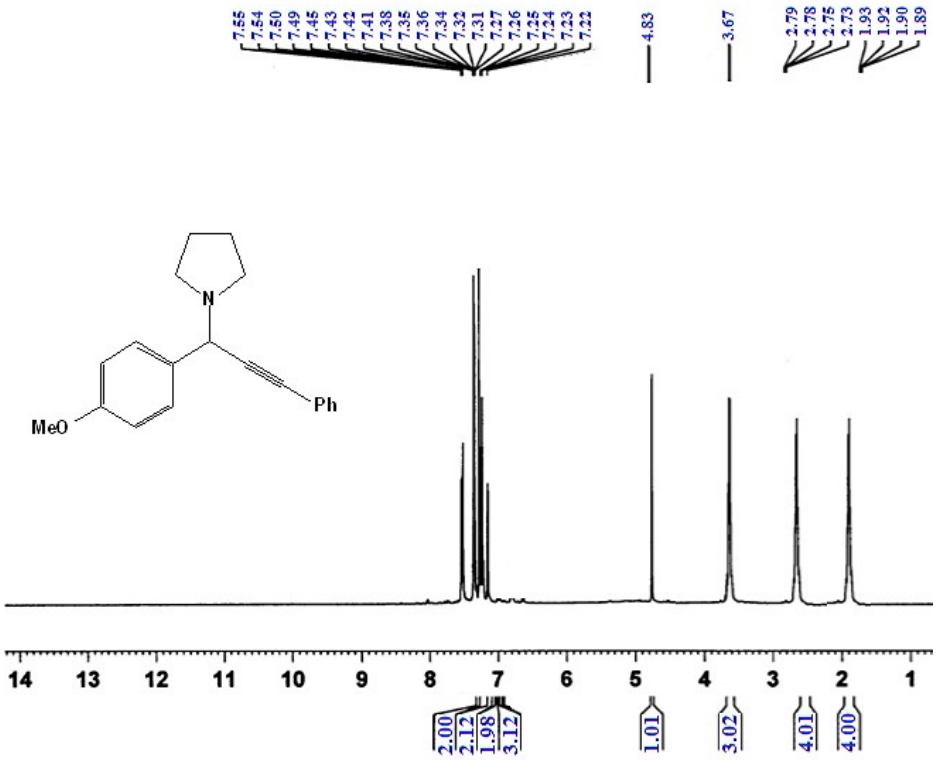

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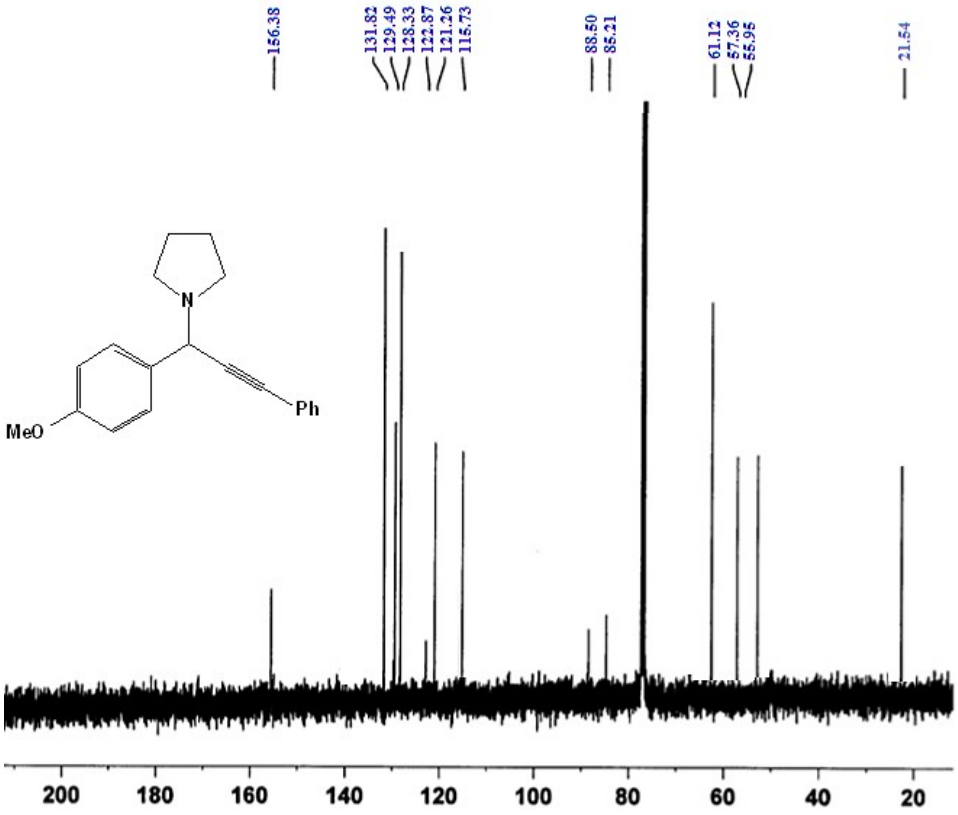

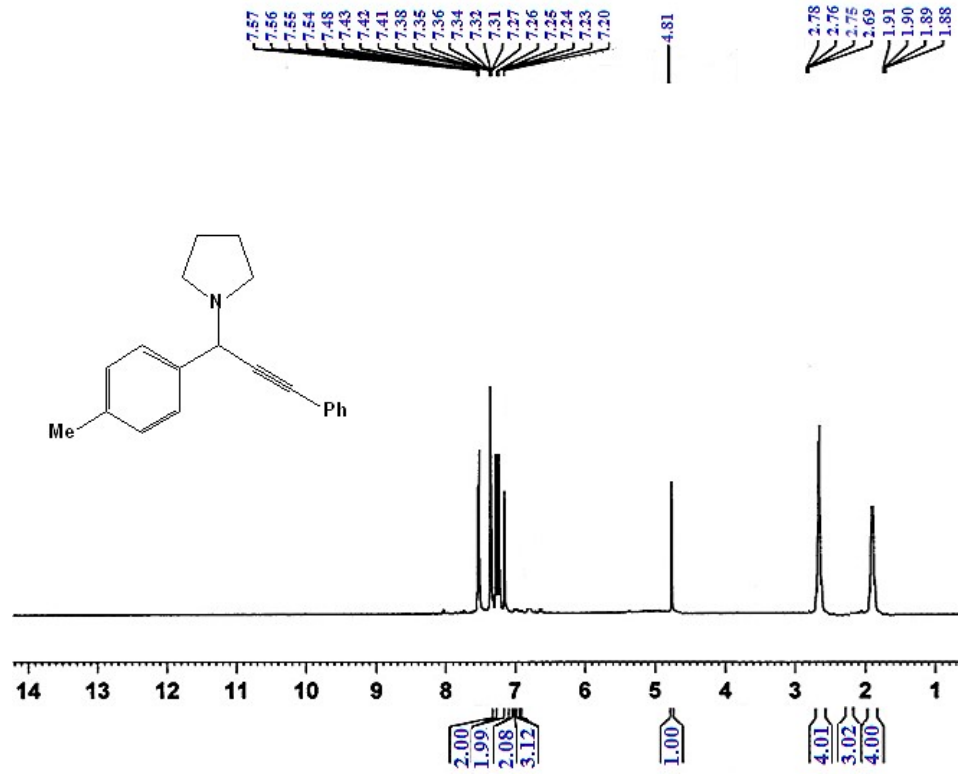

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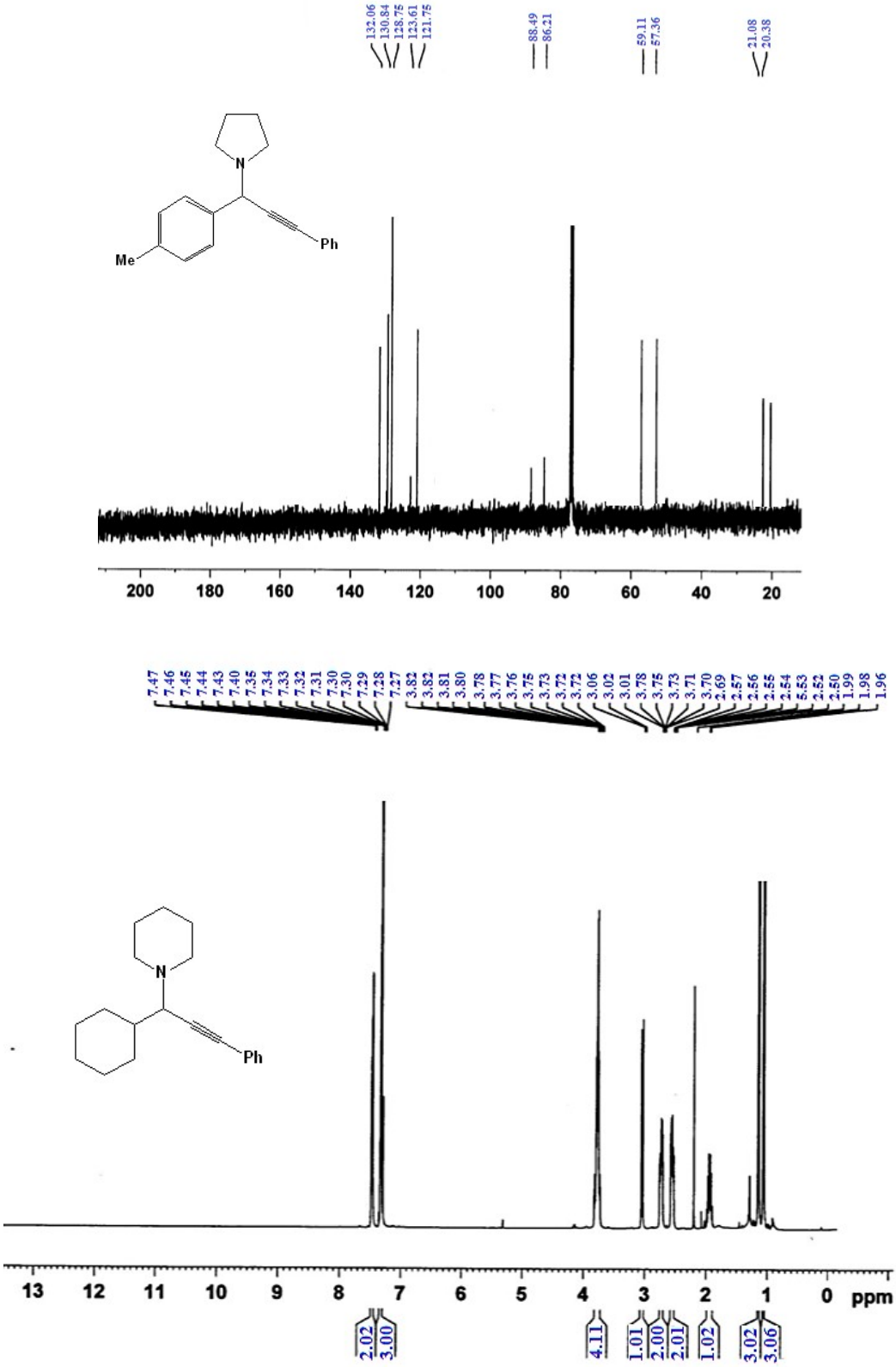

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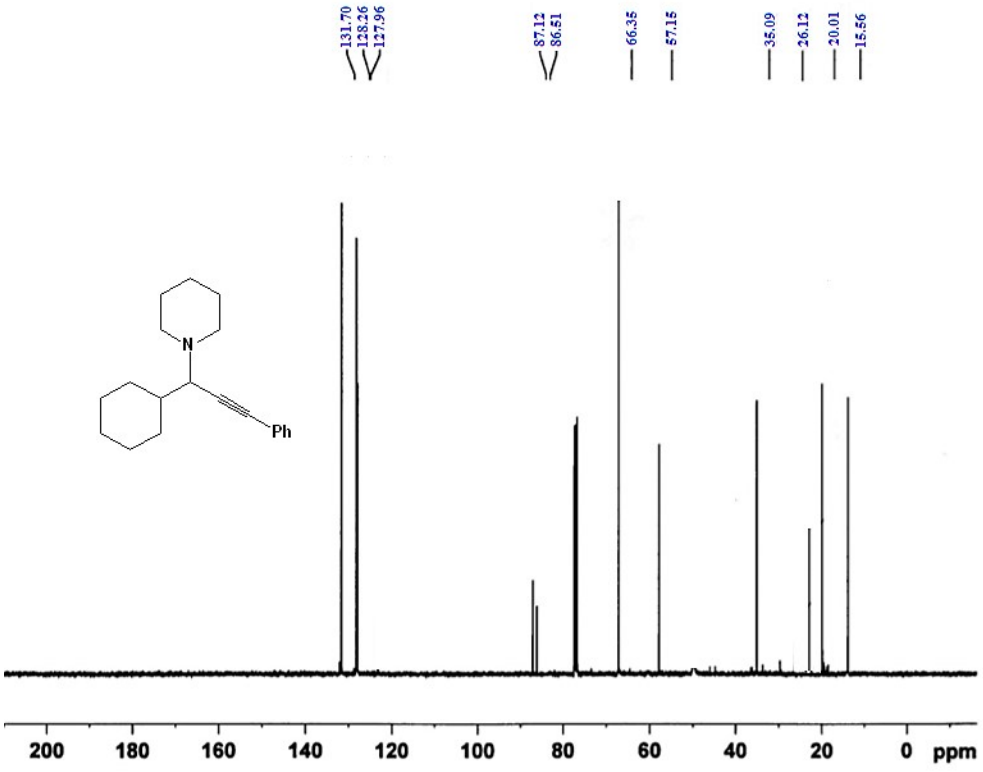

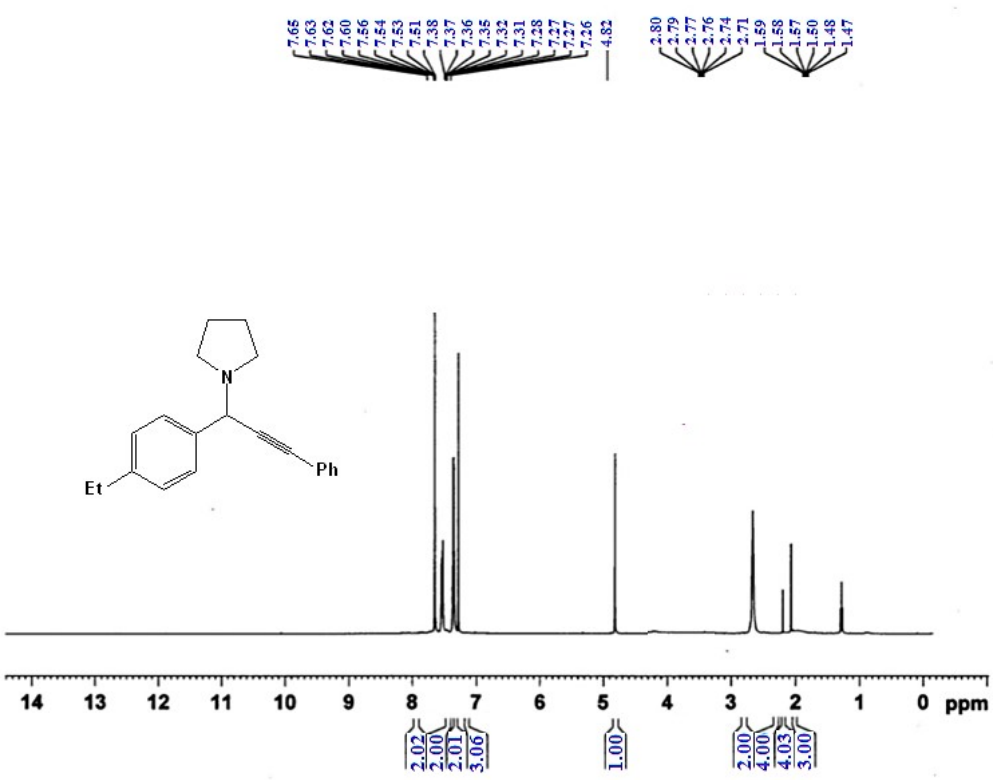

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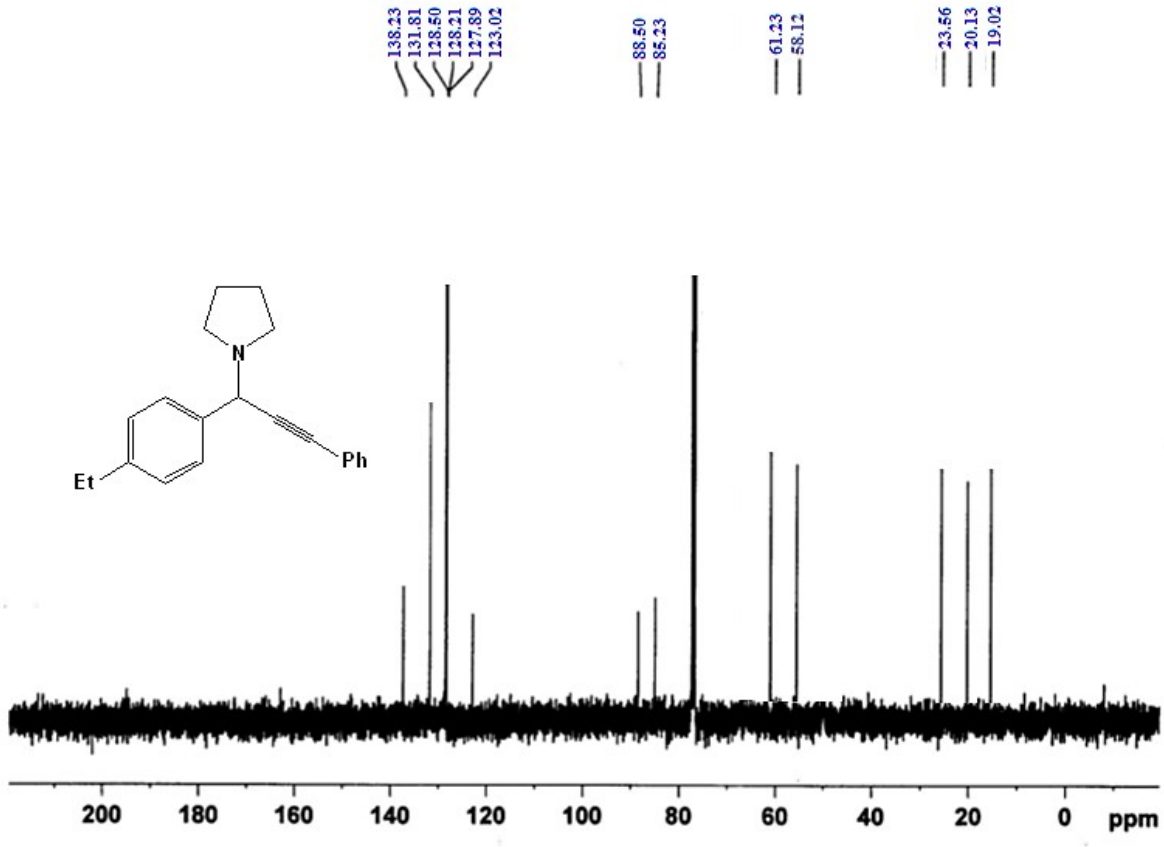

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