Electronic Supplementary Information

Microwave assisted one pot three component synthesis of propargylamine, tetra substituted propargylamine and pyrrolo[1,2-a]quinolines using CuNPs@ZnO-PTh as a heterogeneous catalyst

Akshara P. Shah[a], Anuj S. Sharma[b], Shilpa Jain[a]and Navinchandra G Shimpi [a,*]

[a]Department of Chemistry University of Mumbai, Santacruz (East), Mumbai-400098, India

[b]Department of Chemistry, School of Sciences, Gujarat University, Ahmedabad-380009, India

---

Table of Contents

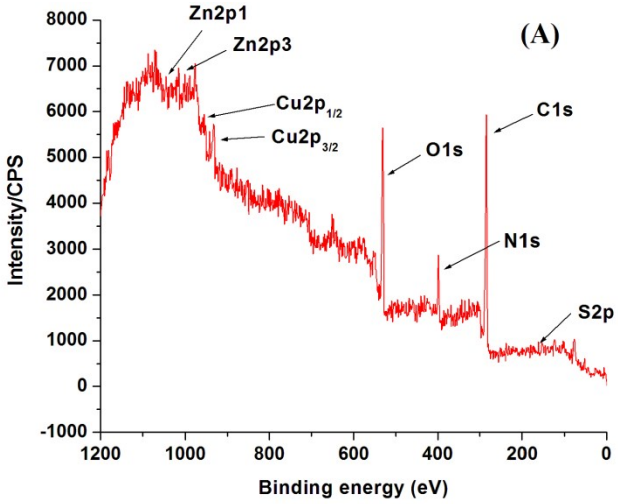


Figure S1 XPS Survey spectrum of Cu NPs/ZnO-PTh.

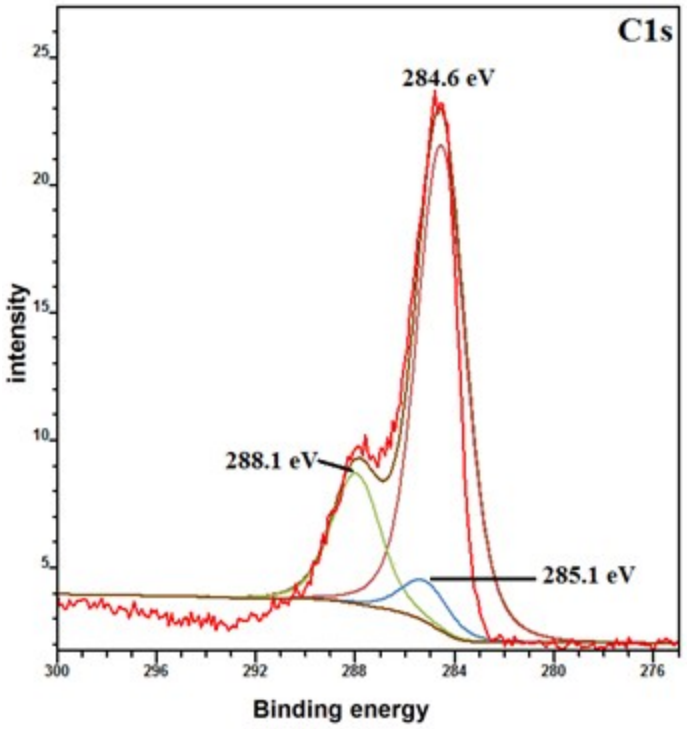


Figure S2 Deconvoluted spectrum of C1s.

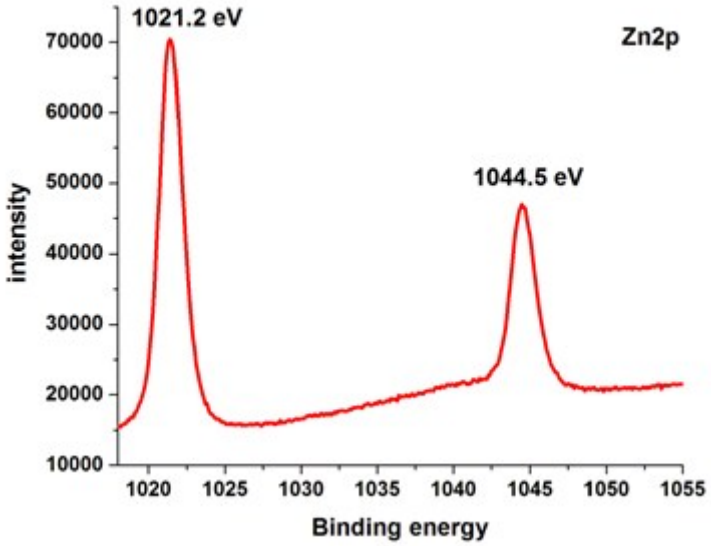


Figure S3 Deconvoluted spectrum of Zn2p.

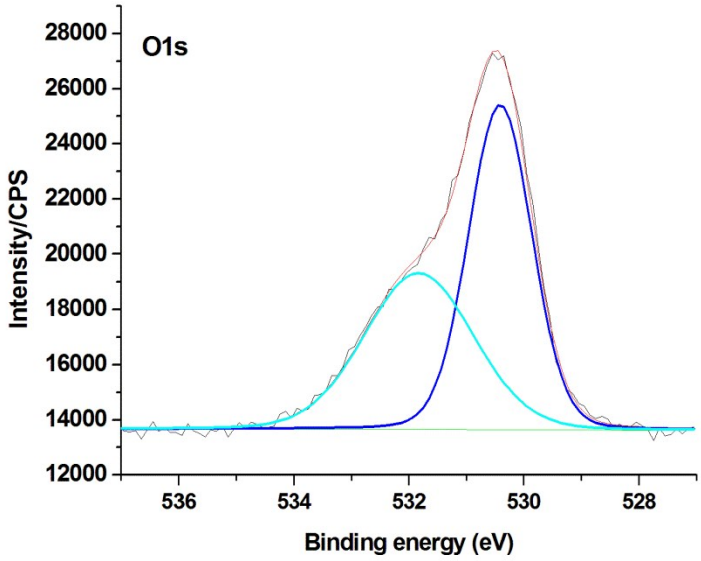


Figure S4 Deconvoluted spectrum of O1s.

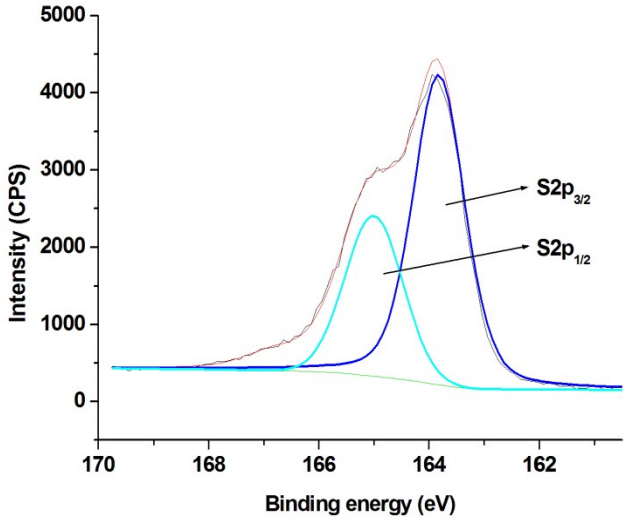


Figure S5 Deconvoluted spectrum of S2p.

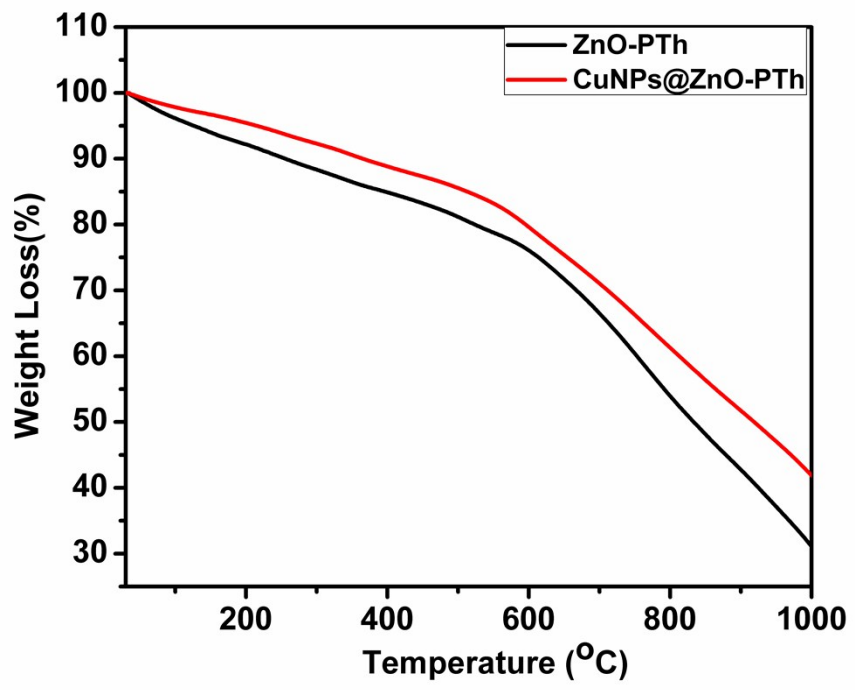
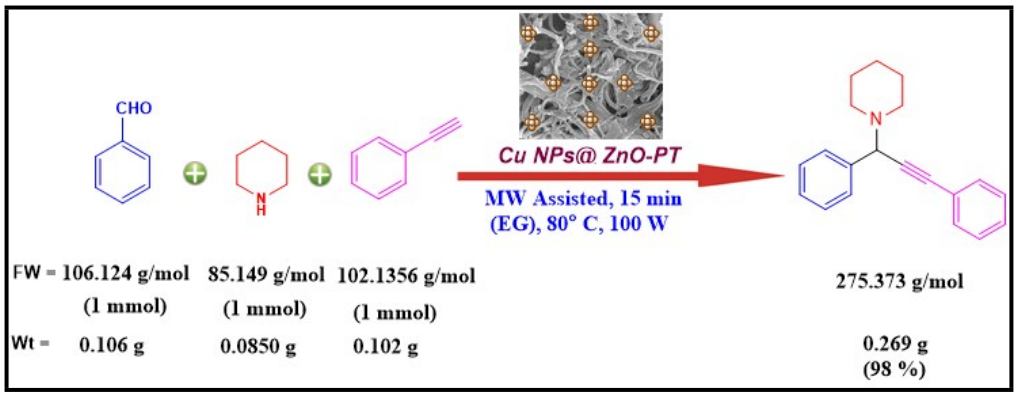


Figure S6. TGA of ZnO-PTh and CuNPs@ZnO-PTh

TGA studies for ZnO-PTh and CuNPs@ZnO-PTh were carried out and the graph of the percentage weight loss versus temperature is shown in Figure S6. The shape of the graph is typical of any grafted polymer. Initial weight loss of 5% was observed at 126°C for ZnO-PTh which increased to 215°C for CuNPs@ZnO-PTh. At 1000°C 31% residue was obtained for ZnO-PTh, which increase to 42% for CuNPs. Increase in temperature indicates the increase in thermal stability with incorporation of CuNPs in ZnO-PTh. This large increase in the

amount of residue was mainly attributed to oxidation of copper nanoparticles to copper oxide. A DSC study shows that Tg temperature increases from 273°C for ZnO-PTh to 316°C for CuNPs@ZnO-PTh respectively.

Calculation of E-factor and atom economy (AE) for 1-(1,3-diphenylprop-2-yn-1-yl) piperidine



E-Factor: The E factor of organic reaction can be calculated as the following equation. Total mass of starting raw materials–the total mass of product/the total mass of product. The ideal value of E-factor is zero.

E-factor for 1-(1, 3-diphenylprop-2-yn-1-yl) piperidine =

[0.106+0.0850+0.102-0.269]/ 0.269

***E-factor* = 0.0892**

Atom economy (AE): Atom economy (atom efficiency) is the conversion efficiency of a chemical reaction in terms of how many atoms from the starting materials reside within the product. AE has an ideal value of 100 %, i.e., all atoms from the starting materials reside in the product.

AE = [MW of product] / ∑ (MW of Stoichiometric reactants)× 100

AE of 1-(1, 3-diphenylprop-2-yn-1-yl) piperidine = [275.373 / 293.408] × 100

AE = 94 %

Process mass intensity (PMI): PMI is defined as the total mass used in a process divided by the mass of the product.

$$\text{PMI} = \frac{\sum[Mass\ of\ stoichiometric\ reactants]}{[Mass\ of\ Product]}$$

$$\text{PMI} = \frac{[0.106\ g + 0.085\ g + 0.102\ g\ ]}{[0.269\ g]}$$

PMI = 1.089

Reaction mass efficiency (RME):Reaction mass efficiency is defined as the mass of product divided by the sum of total mass of stoichiometric reactants.

$$\text{RME} = \frac{[Mass\ of\ product]}{\sum[Mass\ of\ Stoichiometric\ reactants]} \times 100$$

$$\text{RME} = \frac{[0.269\ g]}{[0.106\ g + 0.085\ g + 0.102\ g]} \times 100$$

RME =92 %

Carbon efficiency (CE):CE is defined is the percentage of carbon in the reactants that remain in the final product.

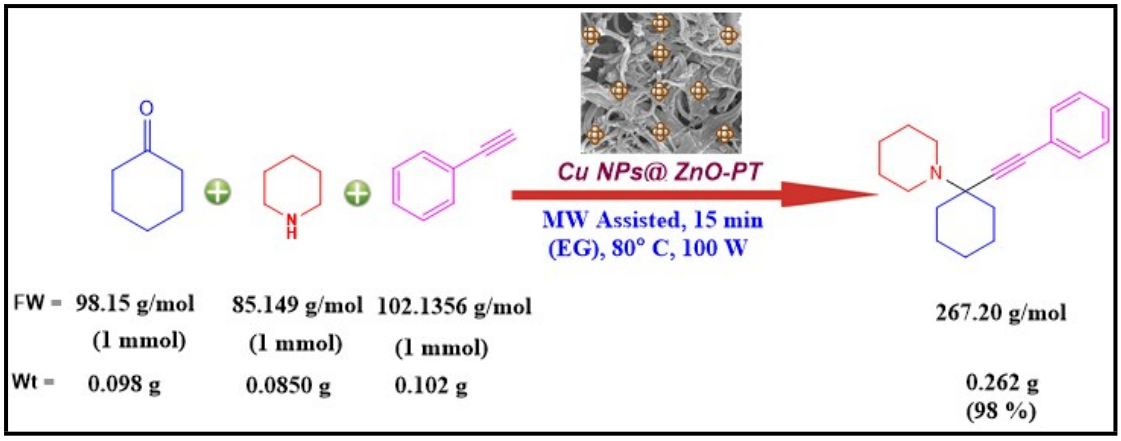
$$\text{CE} = \frac{[Amount\ of\ carbon\ in\ product]}{[Total\ carbon\ present\ in\ reactants]} \times 100$$

CE=

$$\frac{[moles\ of\ product\ \times carbons\ in\ produ}{[(moles\ of\ 1a\ \times carbon\ in\ 1a) + (moles\ of\ 2a\ \times carbon\ in\ 2a) + \times 100}$$

$$\text{CE} = \frac{[0.98\ \times 20]}{[(1 \times 7) + (1 \times 5) + (1 \times 8)]} \times 100$$

CE = 98 %



E-factor for 1-(1, 3-diphenylprop-2-yn-1-yl) piperidine =

[0.098+0.0850+0.102-0.262] / 0.262

E-factor **= 0.087**

Atom economy (AE)

AE = [MW of product] / ∑ (MW of Stoichiometric reactants)× 100

AE of 1-(1, 3-diphenylprop-2-yn-1-yl) piperidine = [267.20 / 285.43] × 100

AE = 94 %

Process mass intensity (PMI): PMI is defined as the total mass used in a process divided by the mass of the product.

$$\text{PMI} = \frac{\sum[Mass\ of\ stoichiometric\ reactants]}{[Mass\ of\ Product]}$$

$$\text{PMI} = \frac{[0.098\ g + 0.085\ g + 0.102\ g\ ]}{[0.262\ g]}$$

PMI = 1.087

Reaction mass efficiency (RME):Reaction mass efficiency is defined as the mass of product divided by the sum of total mass of stoichiometric reactants.

$$\text{RME} = \frac{[Mass\ of\ product]}{\sum[Mass\ of\ Stoichiometric\ reactants]} \times 100$$

$$\text{RME} = \frac{[0.262\ g]}{[0.098\ g + 0.085\ g + 0.102\ g]} \times 100$$

RME =92 %

Carbon efficiency (CE):CE is defined is the percentage of carbon in the reactants that remain in the final product.

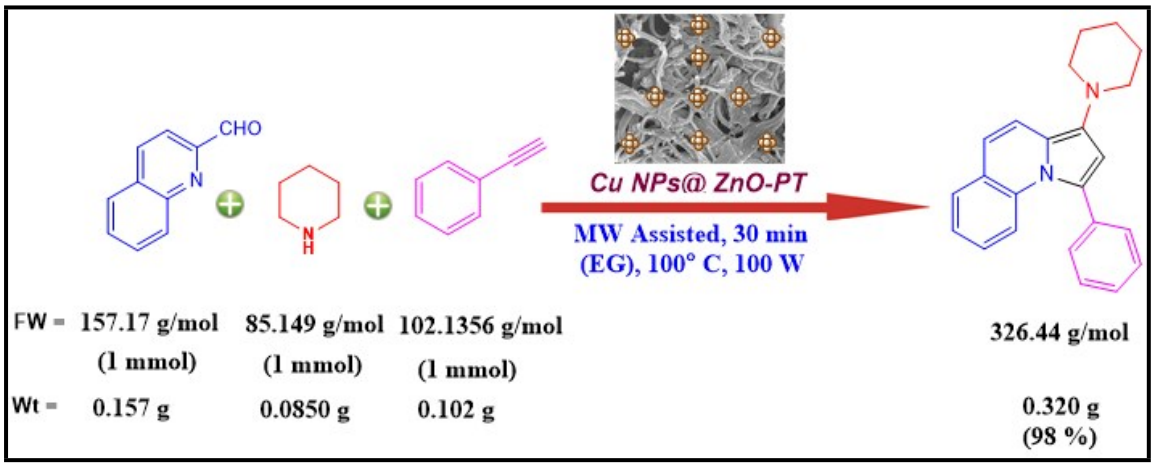
$$CE = \frac{[Amount\ of\ carbon\ in\ product]}{[Total\ carbon\ present\ in\ reactants]} \times 100$$

CE=

$$\frac{[moles\ of\ product\ \times carbons\ in\ produ}{[(moles\ of\ 1a\ \times carbon\ in\ 1a) + (moles\ of\ 2a\ \times carbon\ in\ 2a) + \times 100}$$

$$CE = \frac{[0.98\ \times 19]}{[(1 \times 6) + (1 \times 5) + (1 \times 8)]} \times 100$$

CE = 98 %



E-factor: The E factor of the organic conversion can be calculated as the total mass of raw materials minus the total mass of products, all divided by the total mass of product. The ideal value of E-factor is considered as zero.

E-factor =

$$\frac{[Total\ mass\ of\ raw\ materials - The\ total\ mass\ of\ product]}{[Mass\ of\ Product]}$$

$$\textit{E-factor} = \frac{[0.157\ g + 0.085\ g + 0.102\ g - 0.320\ g]}{[0.320\ g]}$$

E-factor = 0.075

Process mass intensity (PMI): PMI is defined as the total mass used in a process divided by the mass of the product.

$$\text{PMI} = \frac{\sum[Mass\ of\ stoichiometric\ reactants]}{[Mass\ of\ Product]}$$

$$\text{PMI} = \frac{[0.157\ g + 0.085\ g + 0.102\ g\ ]}{[0.320\ g]}$$

PMI = 1.075

Reaction mass efficiency (RME):Reaction mass efficiency is defined as the mass of product divided by the sum of total mass of stoichiometric reactants.

$$\text{RME} = \frac{[Mass\ of\ product]}{\sum[Mass\ of\ Stoichiometric\ reactants]} \times 100$$

$$\text{RME} = \frac{[0.320\ g]}{[0.157\ g + 0.085\ g + 0.102\ g]} \times 100$$

RME =93 %

Atom economy (AE):Atom economy (atom efficiency) is the conversion efficiency of a chemical reaction in terms of how many atoms from the starting materials reside within the product. AE has an ideal value of 100 %, i.e. all atoms from the starting materials reside in the product.

$$\text{AE} = \frac{[Molecular\ Wt\ of\ product]}{\sum[Molecular\ of\ Stoichiometric\ reactants]} \times 100$$

$$\text{AE} = \frac{[326.44\ ]}{[344.45]} \times 100$$

AE = 95 %

Carbon efficiency (CE):CE is defined is the percentage of carbon in the reactants that remain in the final product.

$$\text{CE} = \frac{[Amount\ of\ carbon\ in\ product]}{[Total\ carbon\ present\ in\ reactants]} \times 100$$

CE=

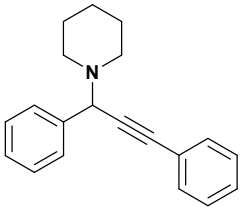
$$\frac{[moles\ of\ product\ \times carbons\ in\ produ}{[(moles\ of\ 1a\ \times carbon\ in\ 1a) + (moles\ of\ 2a\ \times carbon\ in\ 2a) + \times 100}$$

$$\text{CE} = \frac{[0.98\ \times 23]}{[(1 \times 10) + (1 \times 5) + (1 \times 8)]} \times 100$$

CE = 98 %

Propargylamine (A^3 coupling)

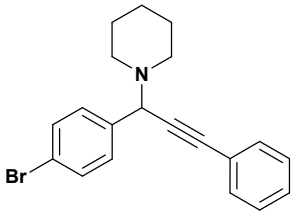
1. 1-(1, 3-diphenyl prop-2-ynyl) piperidine (Table 1, Entry 1)



Pale yellow oily liquid

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.6-1.66 (m, 6H), δ 2.36-2.71 (m, 4H), δ 4.86 (s, 1H), δ 7.22-7.23 (m, 3H), δ 7.29 (m, 4H), 7.31 (s, 1H), 7.51 (m, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** 24.18, 26.29, 51.06, 62.56, 86.01, 97.17, 123.99, 126.44, 127.13, 128.20, 129.92, 131.35, 132.01, 136.60 ppm.

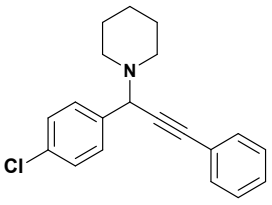
2. 1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl) piperidine (Table 1, Entry 2)



Dark brown oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.60-1.66 (m, 6H), δ 2.37-2.70 (m, 4H), δ 4.85 (s, 1H), δ 7.19-7.23 (m, 4H), 7.31 (s, 1H), 7.47-7.50 (m, 4H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** 23.49, 26.65, 51.44, 63.99, 85.60, 97.87, 119.48, 127.52, 128.20, 128.58, 128.68, 131.35, 132.60 ppm

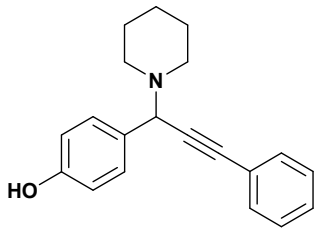
3. 1-(1-(4-Chlorophenyl)-3-Phenylprop-2-ynyl) piperidine (Table 1, Entry 3)



Yellow oily liquid

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.60-165 (m, 6H), δ 2.37-2.70 (m, 4H), δ 4. (s, 1H), δ 7.24 (m, 5H), 7.31 (m, 3H), δ 7.50 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** 23.50, 24.91, 51.75, 63.30, 85.33, 97.20, 125.31, 128.31, 128.68, 129.84, 130.01, 132.13, 134.08, 134.75.

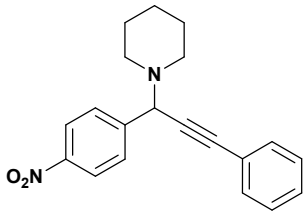
4. 4-(3-phenyl-1-(piperidin-1-yl) prop-2-yn-1-yl) phenol (Table 1, Entry 4)



Dark brown oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.56-1.67 (m, 6H), δ 2.37-2.67 (m, 4H), δ 5.23 (s, 1H), δ 6.88 (m, 2H), δ 7.19-7.23 (m, 4H), δ 7.31 (s, 1H), δ 7.51 (m, 2H).

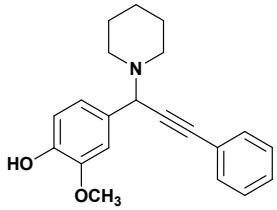
5. 1-(1-(4-nitrophenyl)-3-phenylprop-2-yn-1-yl) piperidine (Table 1, Entry 5)



Dark brown oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.57-1.62 (m, 6H), δ 2.31-2.37 (m, 4H), δ 4.83 (s, 1H), δ 7.20-7.31 (m, 4H), δ 7.29-7.53 (m, 6H).

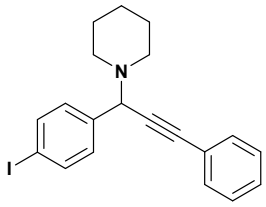
6. 2-methoxy-4-(3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)phenol (Table 1, Entry 6)



Dark brown oily liquid

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.6-2.73 (m, 4H), δ 3.52-3.67 (m, 4H), δ 3.88 (s, 3H), δ 4.78 (s, 1H), δ 4.86 (s, 1H), δ 7.20-7.31 (m, 3H), δ 7.29-7.53 (m, 5H).

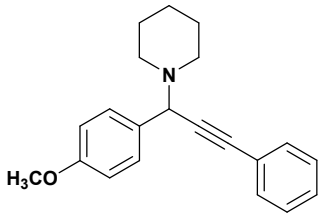
7. 1-(1-(4-iodophenyl)-3-phenylprop-2-yn-1-yl) piperidine (Table 1, Entry 7)



Yellow oily liquid

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.59-1.66 (m, 6H), δ 2.36-2.70 (m, 4H), δ 4.84 (s, 1H), δ 7.05-7.23 (m, 4H), 7.31 (s, 1H), 7.49-7.68 (m, 4H).

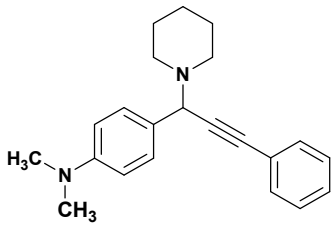
8. 1-(1-(4-Methoxyphenyl)-3-Phenylprop-2-ynyl) piperidine (Table 1, Entry 8)



Yellow oily liquid

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.61-1.64 (m, 6H), δ 2.43-2.68 (m, 4H), δ 3.80 (s, 3H), δ 5.24 (s, 1H), δ 7.02-7.23 (m, 4H), δ 7.31 (s, 1H), δ 7.33-7.50 (m, 2H).**^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 23.85, 25.91, 51.44, 56.32, 62.55, 85.32, 97.51, 113.95, 123.69, 123.98, 128.18, 128.80, 129.92, 131.34, 162.09 ppm.

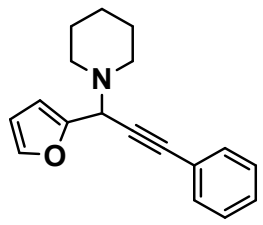
9. N,N-dimethyl-4-(3-phenyl-1-(piperidin-1-yl) prop-2-yn-1-yl) aniline (Table 1, Entry 9)



Dark brown oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.56-1.65 (m, 6H), δ 2.37-2.69 (m, 4H), δ 2.92 (s, 6H), δ 5.21 (s, 1H), δ 6.79 (s, 2H), δ 7.19-7.26 (m, 5H), δ 7.45 (m, 2H).

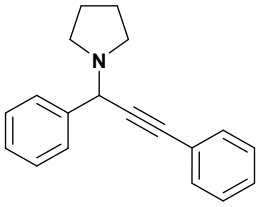
10. 1-(1-(furan-2-yl)-3-phenylprop-2-yn-1-yl) piperidine (Table 1, Entry 10)



Dark brown oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.42-1.70 (m, 6H), δ 2.59 (br, 4H), δ 4.87 (s, 1H), δ 6.36 (d, J = 2.5 Hz, 1H), δ 6.49 (d, J= 2.5 Hz, 1H), δ 7.34-7.26 (m, 3H), δ 7.52-7.43 (m, 3H).

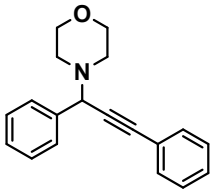
11. 1-(1, 3-diphenylprop-2-yn-1-yl) pyrrolidine (Table 1, Entry 11)



Dark brown oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.69 (m, 4H), δ 2.42 (m, 4H), δ 4.95 (s, 1H), δ7.23 (m, J = 2.5 Hz, 3H), δ 7.29-7.30 (m, J= 2.5 Hz, 5H), δ 7.48 (m, 2H). **MS**: 261.13, 191.07, 189.06, 176.05, 165.06, 152.20.

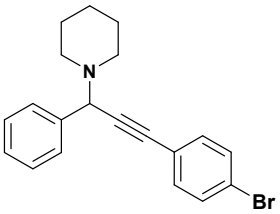
12. 4-(1, 3-diphenylprop-2-yn-1-yl) morpholine (Table 1, Entry 12)



Yellow Solid (MP = 51-53˚ C)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.60-1.66 (m, J= 4.7 Hz, 6H), δ 2.36-2.37 (m, J= 4.1 Hz, 4H), δ 4.86 (s, 1H), δ 7.22-7.29 (m, J= 15.0, 6.1 Hz, 5H), δ 7.31 (s, 1H), δ 7.51 (m, J = 7.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** 50.36, 63.77, 67.13, 85.23, 97.34, 123.87, 128.43, 128.75, 128.80, 129.24, 129.76, 131.23, 134.44, **MS**: 278.15, 192.08, 191.07, 189.06, 176.05, 165.06.

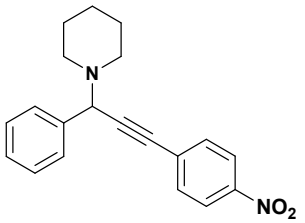
13. 1-(3-(4-bromophenyl)-1-phenylprop-2-yn-1-yl) piperidine (Table 1, Entry 13)



Dark yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.61-1.64 (m, 6H), δ 2.46-2.67 (m, 4H), δ 4.87 (s, 1H), δ 7.23-7.30 (m, 6H), δ 7.37-7.41 (m, 4H).

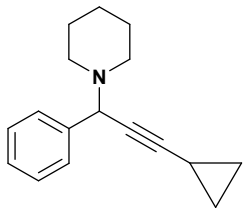
14. 1-(3-(4-nitrophenyl)-1-phenylprop-2-yn-1-yl) piperidine (Table 1, Entry 14)



Dark brown oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.60-1.66 (m, 6H), δ 2.36-2.71 (br, 4H), δ 4.86 (s, 1H), δ 7.23 (s, 1H), δ 7.29 (m, 4H), δ 7.70-8.12 (m, 4H).

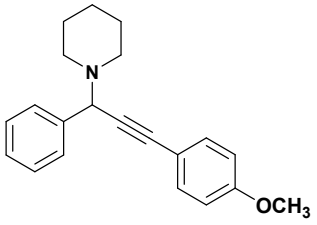
15. 1-(3-cyclopropyl-1-phenylprop-2-yn-1-yl) piperidine (Table 1, Entry 15)



Dark yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.82 (q, 4H), δ 1.26 (s, 1H), δ 1.60 (m, 6H), δ 2.41-2.63 (m, 4H), δ 4.79 (s, 1H), δ 7.22 (s, 1H), δ 7.27-7.29 (m, 4H).**^{13}C NMR (100 MHz, $CDCl_3$, ppm):**15.47, 28.00, 29.41, 51.42, 62.91, 74.12, 96.13, 128.18, 128.80, 131.36, 134.10 ppm.

16. 1-(3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-yl) piperidine (Table 1, Entry 16)

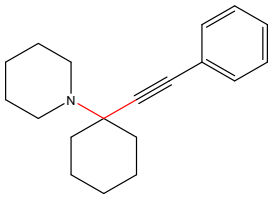


Light yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.60-1.66 (m, 6H), δ 2.36-2.71 (m, 4H), δ 3.80 (s, 3H), δ 4.86 (s, 1H), δ 6.85 (m, 2H), δ 7.22-7.29 (m, 5H), 7.48 (m, 2H).

Tetrasubstituted Propargylamine (KA^2 coupling)

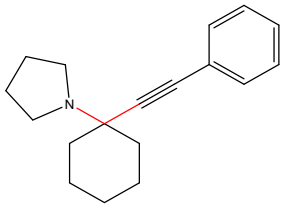
17. 1-(1-(phenylethynyl) cyclohexyl) piperidine (Table 4, Entry 1)



Yellow Solid (M.P = 51-54˚C)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.61-1.70 (m, 14H), δ 1.91 (m, 2H), δ 2.46-2.64 (m, 4H), δ 7.23 (m, 2H), δ 7.30 (s, 1H), δ 7.49 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** 22.07, 22.84, 25.62, 29.71, 39.19, 40.34, 65.72, 73.92, 79.92, 81.55. 121.82, 128.45, 129.21, 132.51 ppm.

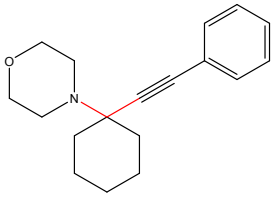
18. 1-(1-(phenylethynyl) cyclohexyl) pyrrolidine (Table 4, Entry 2)



Light yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.39-1.91 (m, 14H), δ 2.44-2.96 (m, 4H), δ 7.24-7.25 (m, 3H), δ 7.44 (m, 2H) **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 24.92, 26.27, 27.71, 35.36, 51.43, 62.56, 76.60, 94.33, 123.68, 128.24, 128.59, 131.72 ppm. **MS**: 255.15, 169.09, 165.06, 153.05, 152.05, 141.06, 128.05, 115.04.

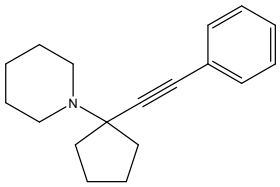
19. 4-(1-(phenylethynyl) cyclohexyl) morpholine (Table 4, Entry 3)



Pale yellow solid (MP = 93-95˚ C)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.59-1.83 (m, 10H), δ 2.54-2.81 (m, 4H), δ 3.78 (m, 4H), δ 7.24-7.25 (m, 3H), δ 7.44 (m, 2H). **MS**: 269.17, 205.12, 191.10, 189.09, 165.08, 153.08, 152.07, 141.0, 128.0, 115.0.

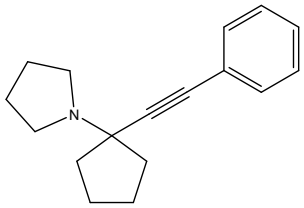
20. 1-(1-(phenylethynyl) cyclopentyl) piperidine (Table 4, Entry 4)



Yellow Solid (MP = 78-80˚ C)

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.59-1.76 (m, 12H), δ 1.98 (m, 2H), δ 2.36-2.69 (m, 4H), δ 7.23 (m, 2H), 7.30 (s, 1H), δ 7.46 (m, 2H).

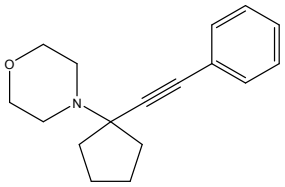
21. 1-(1-(phenylethynyl) cyclopentyl) pyrrolidine (Table 4, Entry 5)



Light yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ1.60-1.77 (m, 10H), δ 1.98 (m, 2H), δ 2.46-2.94 (m, 4H), δ 7.22 (m, 1H), δ 7.30 (s, 1H), δ 7.46 (m, 2H).

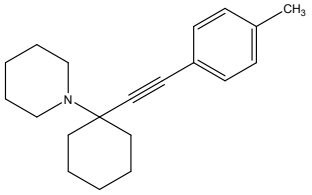
22. 4-(1-(phenylethynyl) cyclopentyl) morpholine (Table 4, Entry 6)



Light yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.60-1.98 (m, 8H), δ 2.56-2.78 (m, 4H), δ 3.78 (m, 4H), δ 7.23 (m, 2H), δ 7.30 (s, 1H), δ 7.46 (m, 2H).

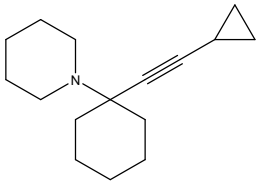
23. 1-(1-(p-tolyl ethynyl) cyclohexyl) piperidine (Table 4, Entry 8)



Light yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.59-1.65 (m, 14H), δ 1.87 (m, 4H), δ 2.33 (s, 3H), δ 2.43-2.83 (m, 4H), δ 7.11-7.39 (m, 4H).

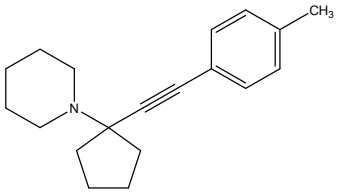
24. 1-(1-(cyclopropyl ethynyl) cyclohexyl) piperidine (Table 4, Entry 9)



Light yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.67-0.78 (m, 4H), δ 1.26 (s, 1H), δ 1.61 (m, 5H), δ 2.33-2.60 (m, 4H).

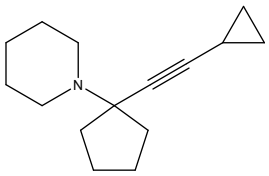
25. 1-(1-(p-tolyl ethynyl) cyclopentyl) piperidine (Table 4, Entry 10)



Light yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.59-1.75 (m, 12H), δ 1.93 (m, 4H), δ 2.34 (s, 3H), δ 2.55-2.74 (m, 4H), δ 7.30-7.41 (m, 4H).

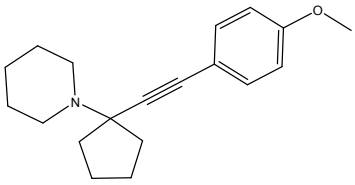
26. 1-(1-(cyclopropyl ethynyl) cyclopentyl) piperidine (Table 4, Entry 11)



Light yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.58-0.77 (m, 4H), δ 1.26 (s, 1H), δ 1.58-1.72 (m, 6H), δ 2.52-2.71 (m, 4H).

27.1-(1-((4-methoxyphenyl) ethynyl) cyclopentyl) piperidine (Table 4, Entry 12)

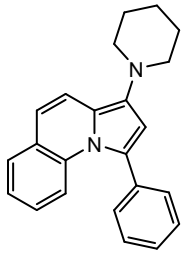


Light yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.59-1.75 (m, 12H), δ 1.93 (m, 4H), δ 2.55-2.74 (m, 4H), δ 3.80 (s, 3H), δ 6.84 (m, 2H), δ 7.44 (m, 2H).

Pyrrolo quinoline [1, 2-a] quinoline

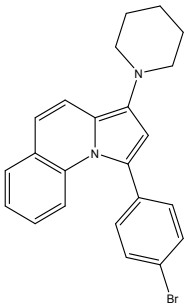
28.*1-Phenyl-3-piperidin-1yl-pyrrolo [1, 2-a] quinoline*(Table 6, Entry 1)



Brown oil

^{1}H NMR (300 MHz, $CDCl_3$):δ = 7.89 (s, J= 9.2 Hz, 1H), 7.73 (s, J = 9.2 Hz, 1H), 7.66-7.67 (m, J = 7.6 Hz, 3H), 7.37-7.49 (m, 6H), 6.74 (s, 1H), 3.13-4.31 (m, J = 5.3 Hz, 4H), 1.66-1.72 (m, 6H).

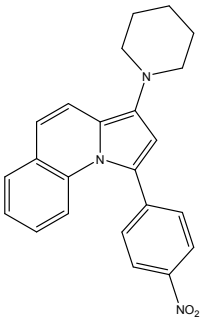
29. ***1-(4-Bromo-phenyl)-3-piperidin-1-yl-pyrrolo [1, 2a] quinoline*** **(Table 6, Entry 2)**



Yellow Solid

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (s, J = 8.4 Hz, 1H), 7.73 (s, 1H), 7.63-7.64 (m, 3H), 7.55 (dd, J = 6.8 Hz, 2H), 7.49 (dd, J= 8.4 Hz, 1H), 7.44 (d, J = 9.2 Hz, 1H), 7.32 (s, 1H), 6.71 (s,1H), 3.15-4.31 (m, 4H), 1.65-1.72 (m, 6H).

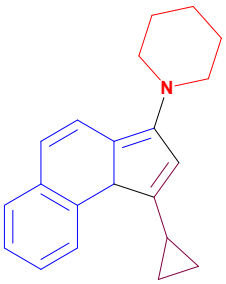
30. ***1-(4-nitrophenyl)-3-(piperidin-1-yl) pyrrolo [1, 2-a] quinoline*** **(Table 6, Entry 3)**



Yellow oil

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (m, 2H), 7.99 (s, 1H), 7.92 (m, 2H), 7.72 (d, J = 6.8 Hz, 2H), 7.52 (s, 1H), 7.43-7.45 (d, J = 9.2 Hz, 2H), 6.81 (s, 1H), 3.68-4.12 (m, 4H), 1.74-1.75 (m, 6H).

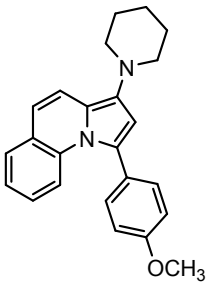
31. 1-cyclopropyl-3-(piperidin-1-yl) pyrrolo [1, 2-a] quinoline (Table 6, Entry 4)



Yellow oil

^{1}H NMR (300 MHz, $CDCl_3$): 7.91-7.92 (d, 2H), 7.72 (s, 1H), 7.56 (s,1H), 7.45 (s, 1H), 7.35 (s, 1H), 6.25 (s, 1H), 3.46-3.74 (m, 4H), 1.50-1.72 (m, 6H), 1.50 (s, 1H), 0.92-1.04 (m, 4H).

32. ***1-(4-methoxy-phenyl)-3-piperidin-1-yl)-pyrrolo [1, 2-a] quinoline*(Table 6, Entry 5)**



Brown oil

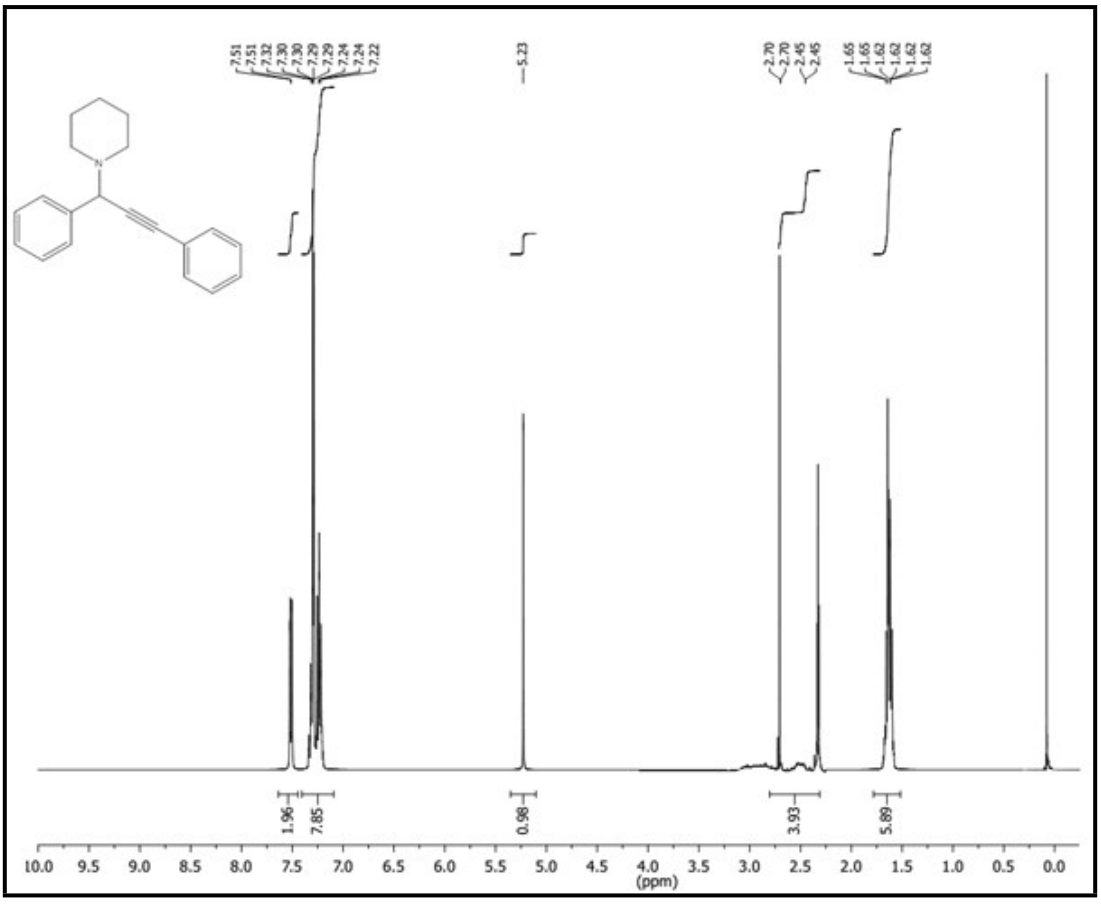
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.63-7.66 (dd, 3H), (d, J = 9.2 Hz, 2H), 7.46-7.48 (d, J = 7.6 Hz, 2H), 7.44 (d, 1H), 7.37 (s, 1H), 7.07 (m, J = 9.2 Hz, 2H), 6.71 (s, 1H), 4.32 (m, 2H), 3.83 (s, 1H), 3.11 (m, 4H), 1.65-1.72 (m, 6H) ppm**.**

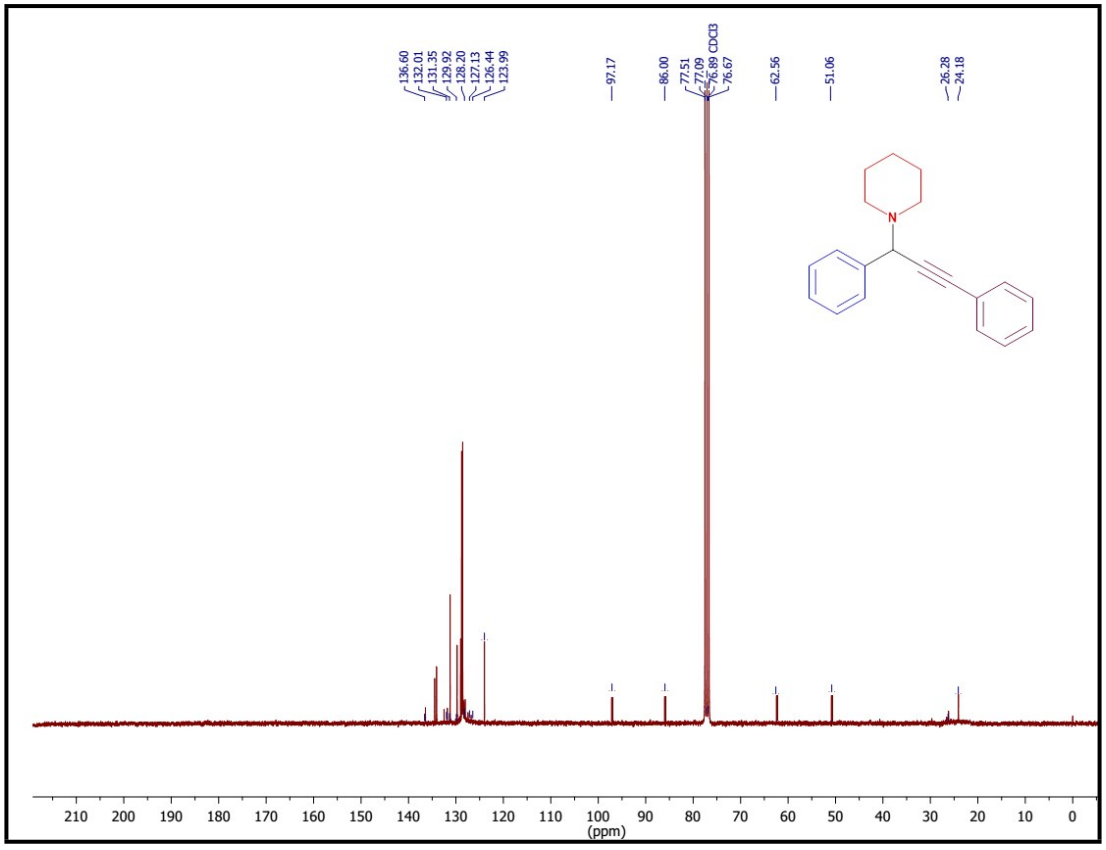
33. ***1-phenyl-3-(pyrrolidin-1-yl) pyrrolo [1, 2-a] quinoline*(Table 6, Entry 7)**

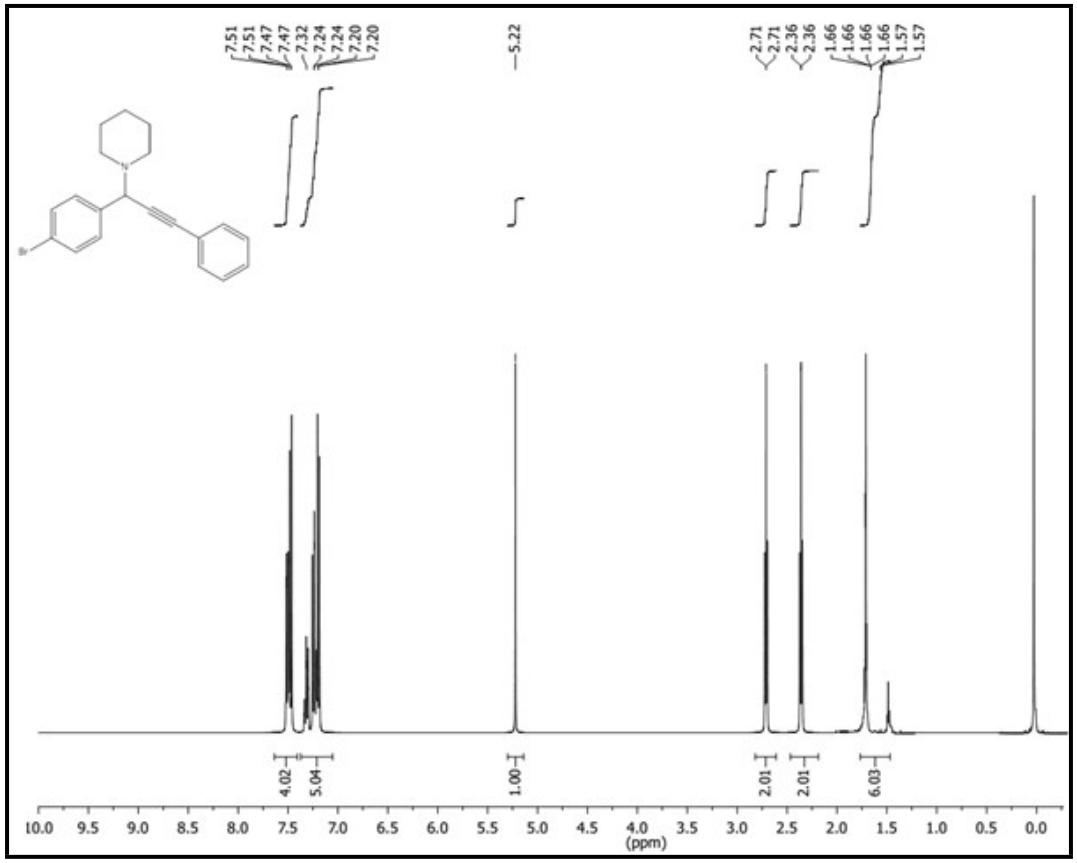
s

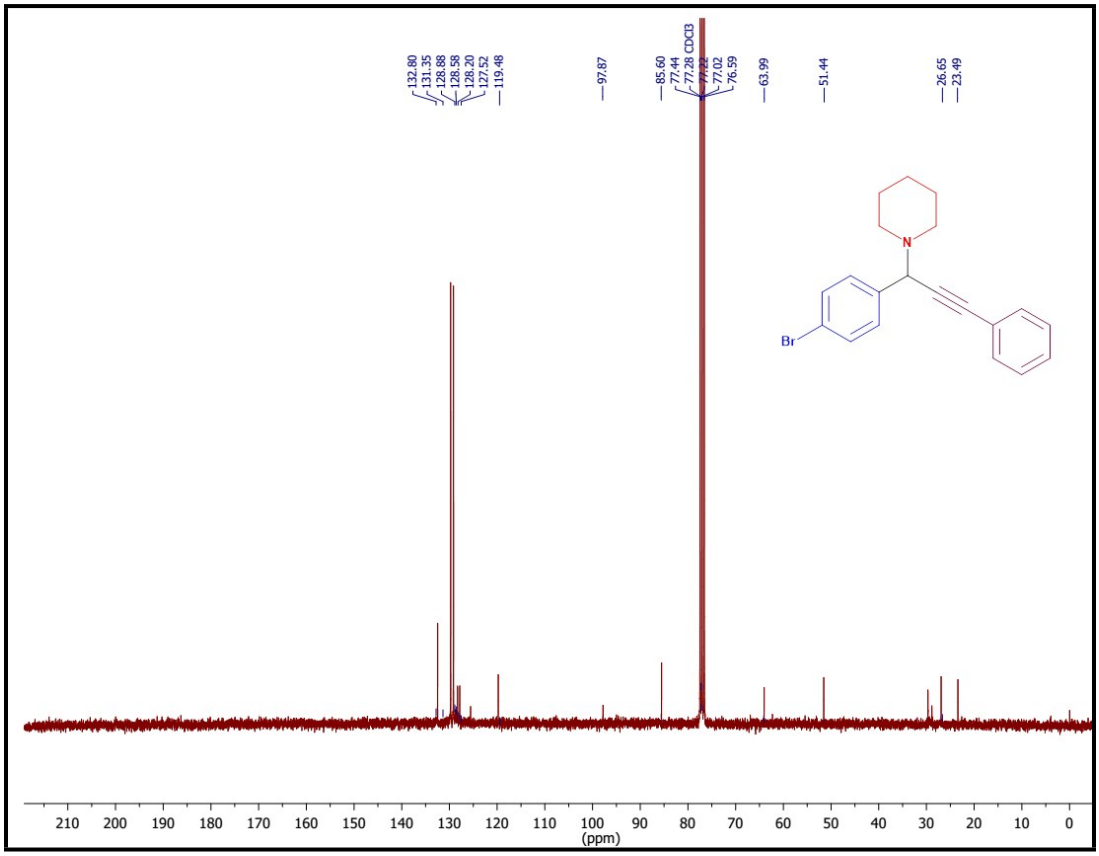
Brown oil

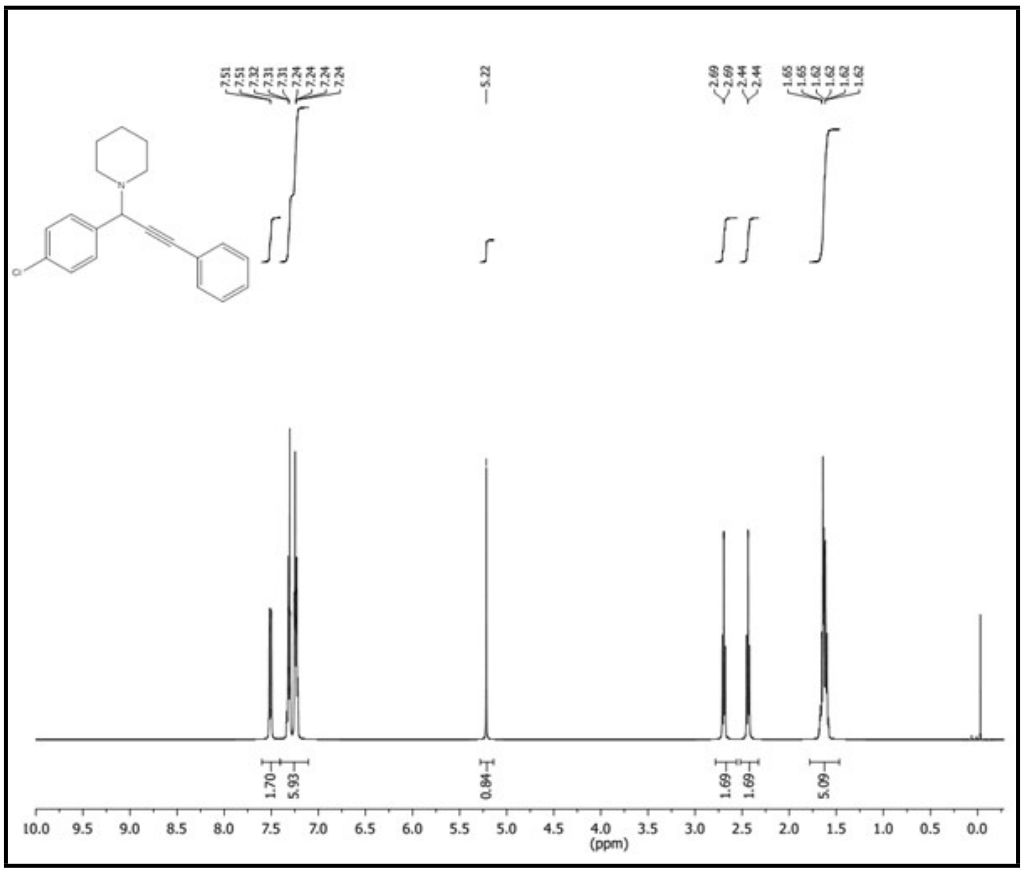
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.45 (m, 5H), 7.66-7.72 (m, 5H), 6.52 (s, 1H), 3.71-4.16 (m, J = 5.3 Hz, 4H), 1.70 (m, 4H). **^{13}C (100 MHz, $CDCl_3$):** δ 22.69, 26.91, 28.87, 31.92, 55.46, 109.75, 116.13, 119.52, 123.53, 124.82, 125.63, 127.22, 128.02, 129.32, 135.14, 135.42, 136.72, 139.41, 150.22 ppm. **MS:** 312.17, 311.16, 284.13, 283.13, 230.10, 191.08, 189.07, 165.07.

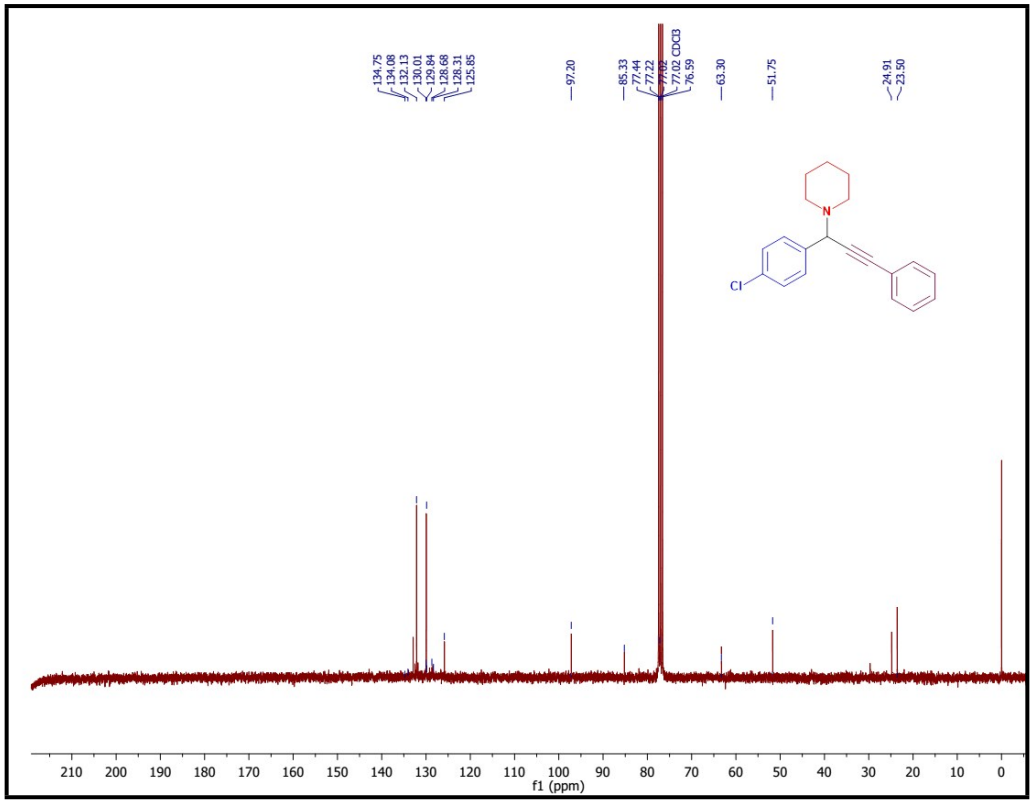

7.51
7.51
7.32
7.30
7.30
7.29
7.29
7.24
7.24
7.22
5.23
2.70
2.70
2.45
2.45
1.65
1.65
1.62
1.62
1.62
1.62
1.96
7.85
0.98
3.93
5.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

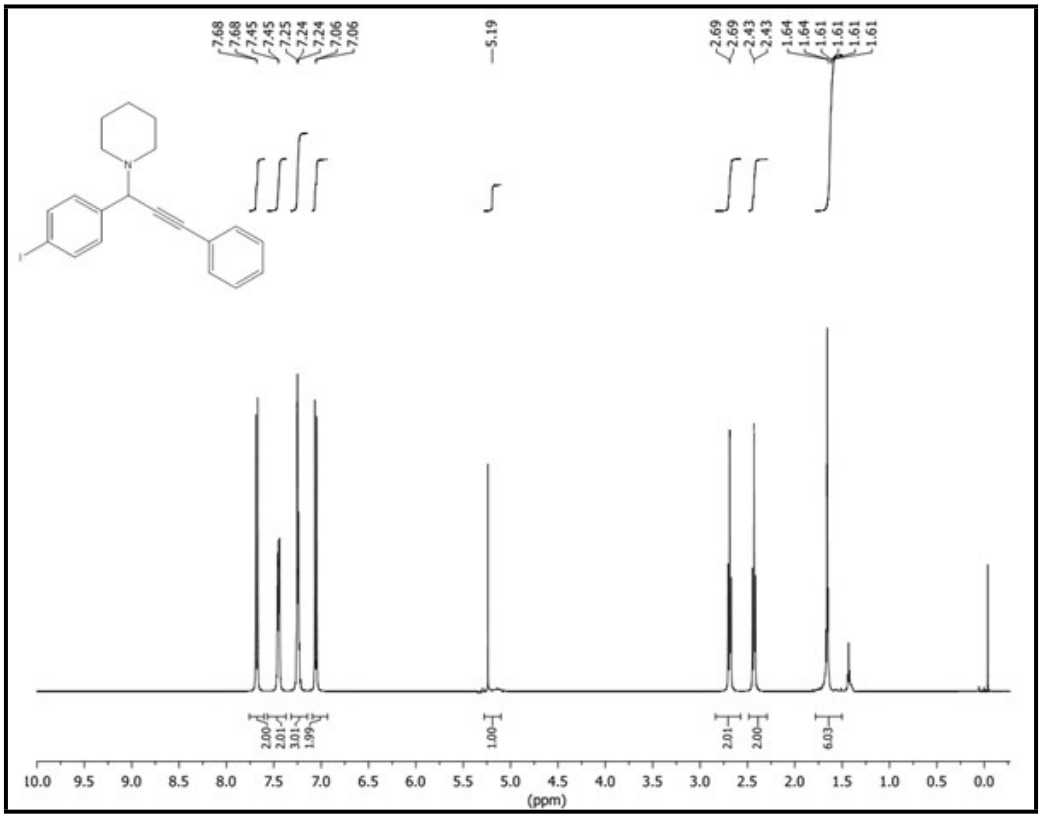

136.60
132.01
131.35
129.92
128.20
127.13
126.44
123.99
97.17
86.00
77.51
77.09
76.89
CDCl3
76.67
62.56
51.06
26.28
24.18
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

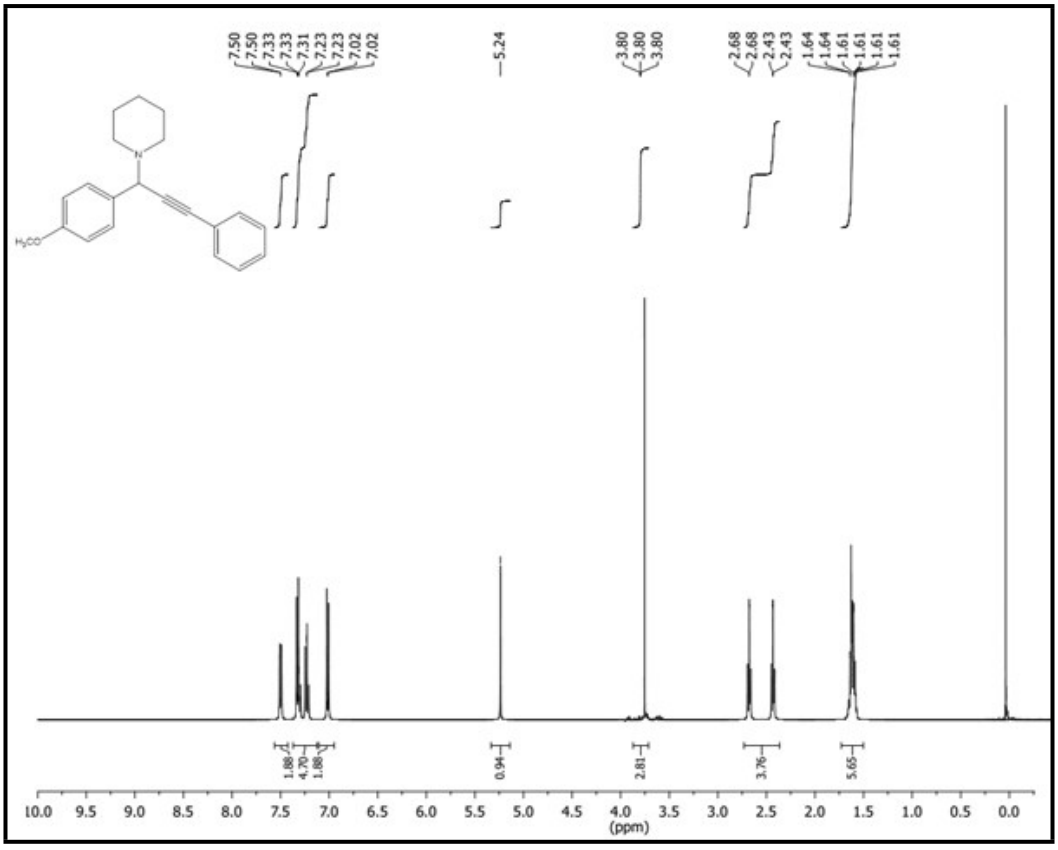

7.51
7.51
7.47
7.47
7.32
7.24
7.24
7.20
7.20
5.22
2.71
2.71
2.36
2.36
1.66
1.66
1.66
1.66
1.57
1.57
N
Br
4.02
5.04
1.00
2.01
2.01
6.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

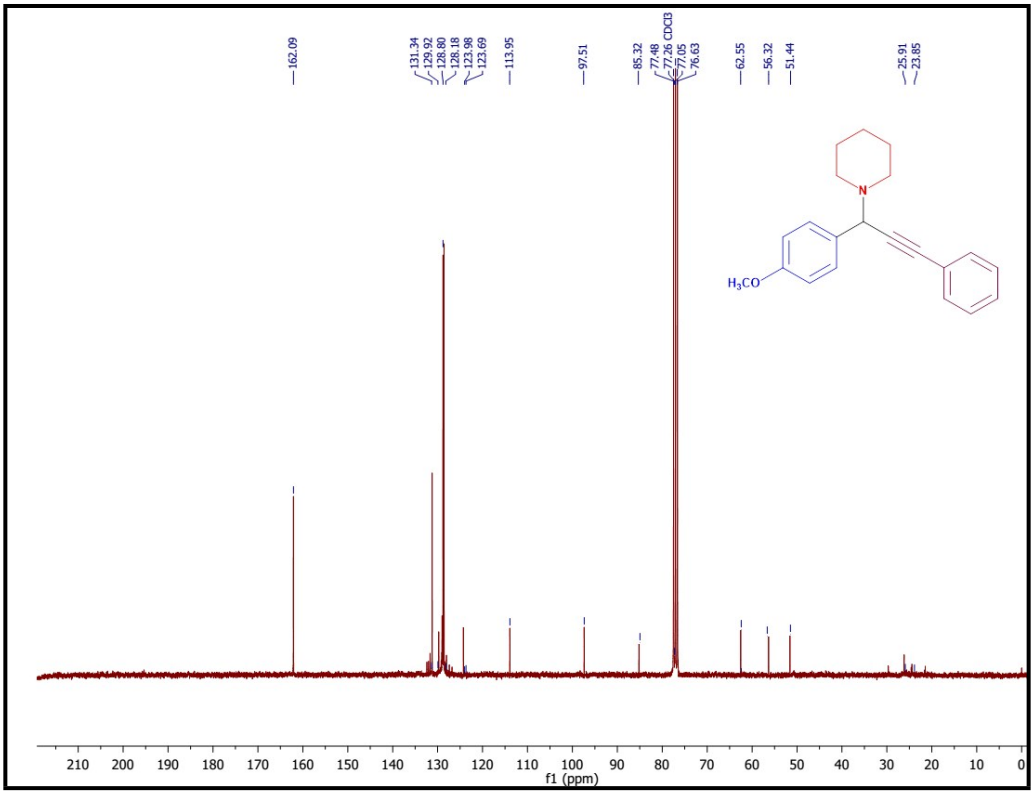

132.80
131.35
128.88
128.58
128.30
127.52
119.48
97.87
85.60
77.44
77.28 CDCl3
77.02
76.59
63.99
51.44
26.65
23.49
N
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

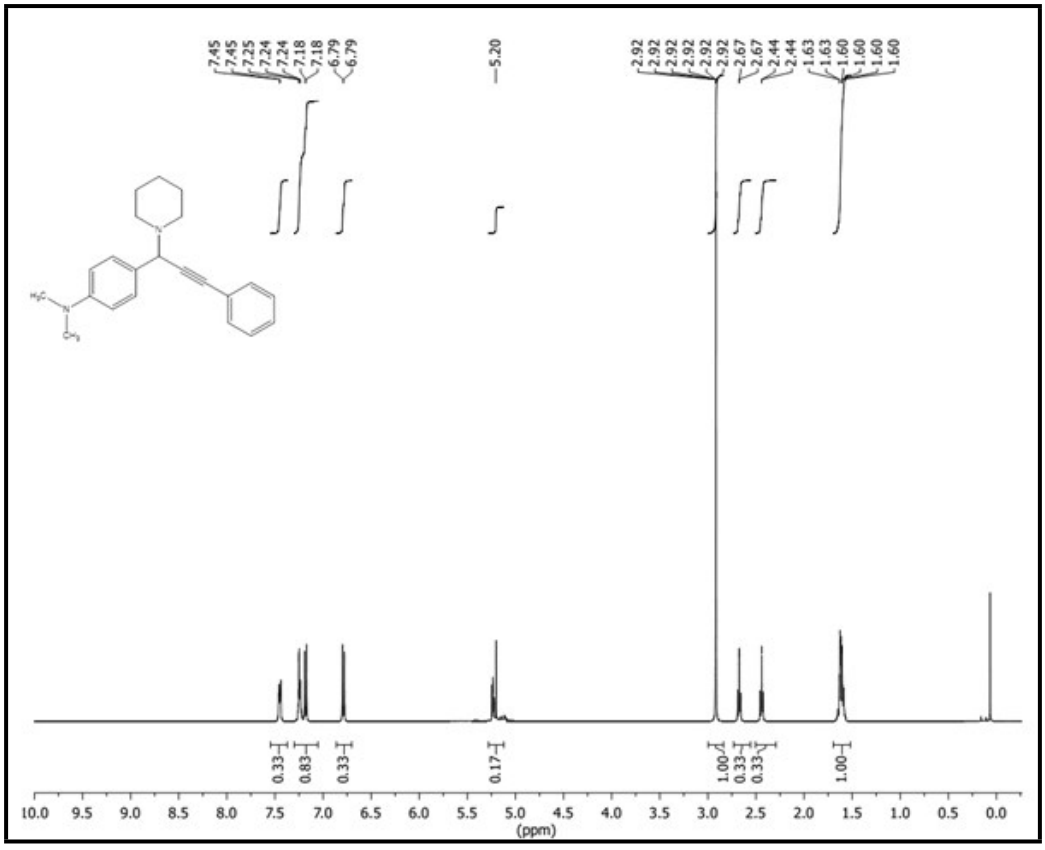

7.51
7.51
7.32
7.31
7.31
7.24
7.24
7.24
7.24
5.22
2.69
2.69
2.44
2.44
1.65
1.65
1.62
1.62
1.62
1.62
N
Cl
1.70
5.93
0.84
1.69
1.69
5.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

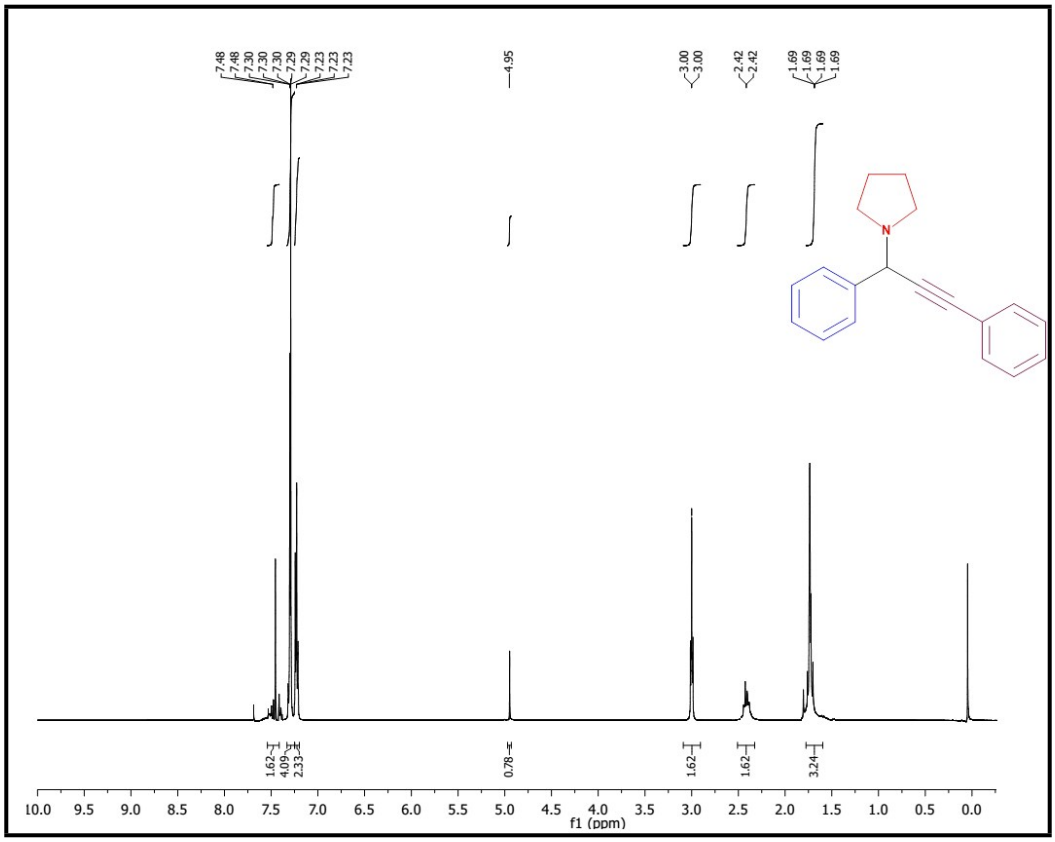

134.75
134.08
132.13
130.01
129.84
128.68
128.31
125.85
97.20
85.33
77.44
77.22
77.02 CDCl3
76.59
63.30
51.75
24.91
23.50
N
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

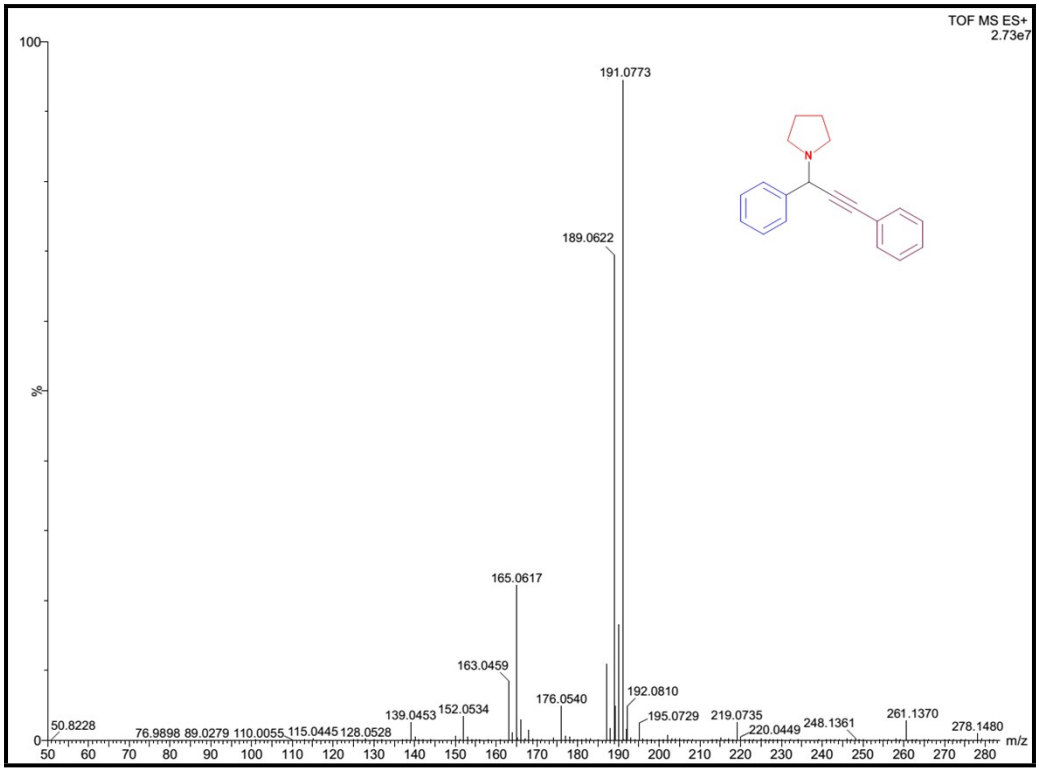

7.68
7.68
7.45
7.45
7.25
7.24
7.24
7.06
7.06
5.19
2.69
2.69
2.43
2.43
1.64
1.64
1.61
1.61
1.61
1.61
N
2.00
2.01
3.01
1.99
1.00
2.01
2.00
6.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

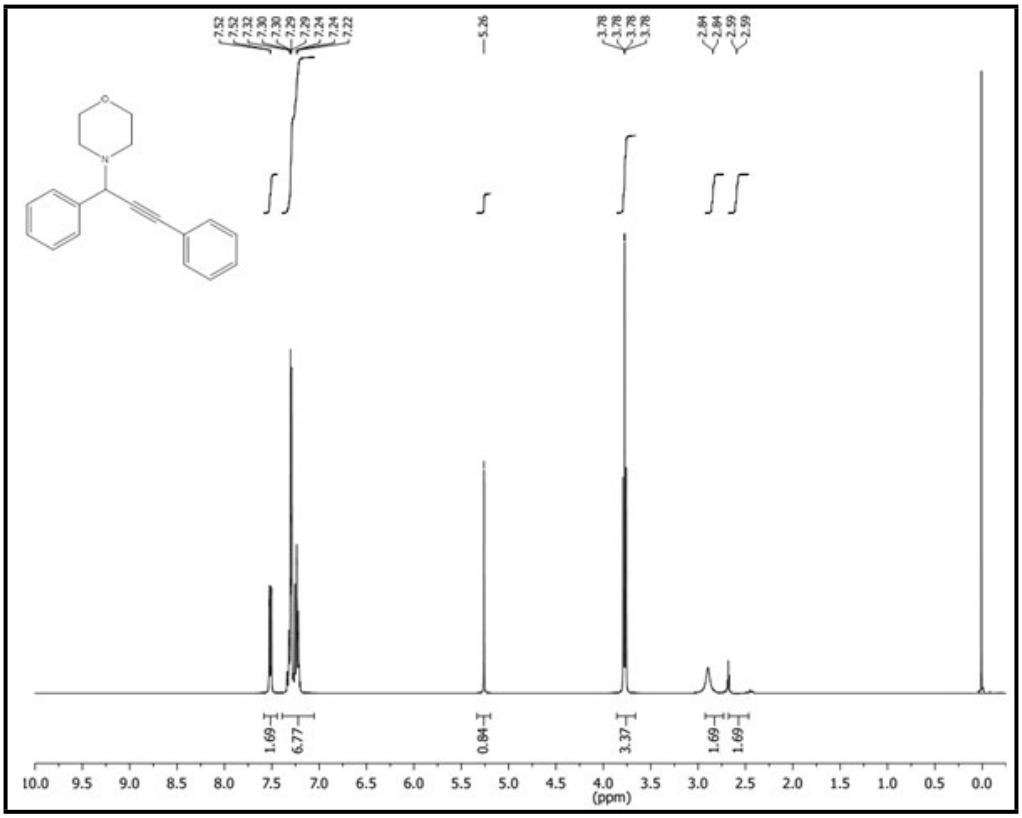

7.50
7.50
7.33
7.33
7.31
7.23
7.23
7.02
7.02
5.24
3.80
3.80
3.80
2.68
2.68
2.43
2.43
1.64
1.64
1.61
1.61
1.61
1.61
1.88
4.70
1.88
0.94
2.81
3.76
5.65
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

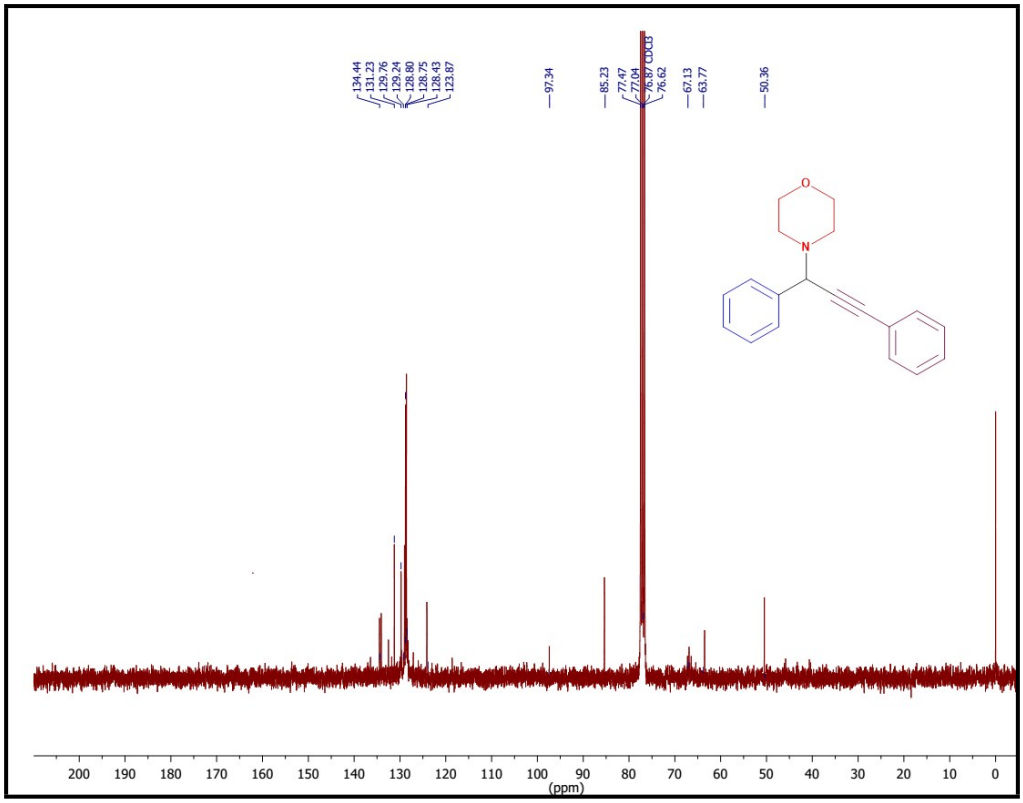

162.09
131.34
129.92
128.80
128.18
123.98
123.69
113.95
97.51
85.32
77.48
77.26 CDCl3
77.05
76.63
62.55
56.32
51.44
25.91
23.85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

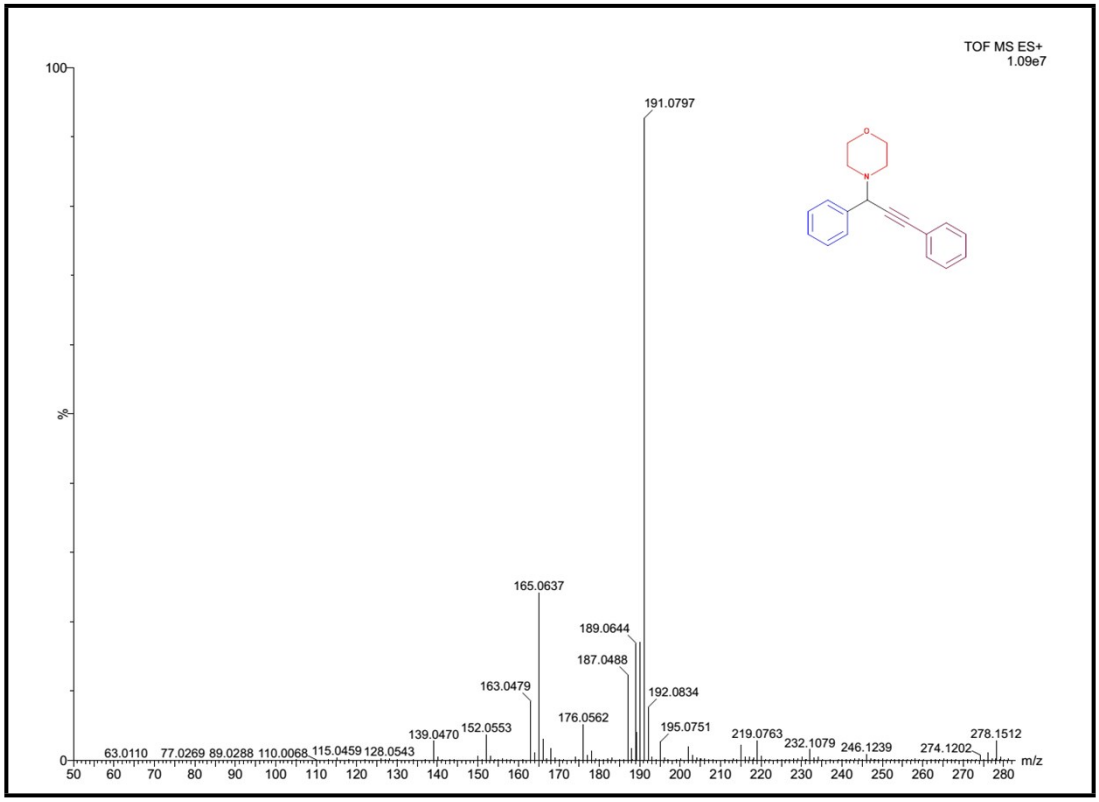

7.45
7.45
7.25
7.24
7.24
7.18
7.18
6.79
6.79
5.20
2.92
2.92
2.92
2.92
2.92
2.92
2.67
2.67
2.44
2.44
1.63
1.63
1.60
1.60
1.60
1.60
0.33
0.83
0.33
0.17
1.00
0.33
0.33
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

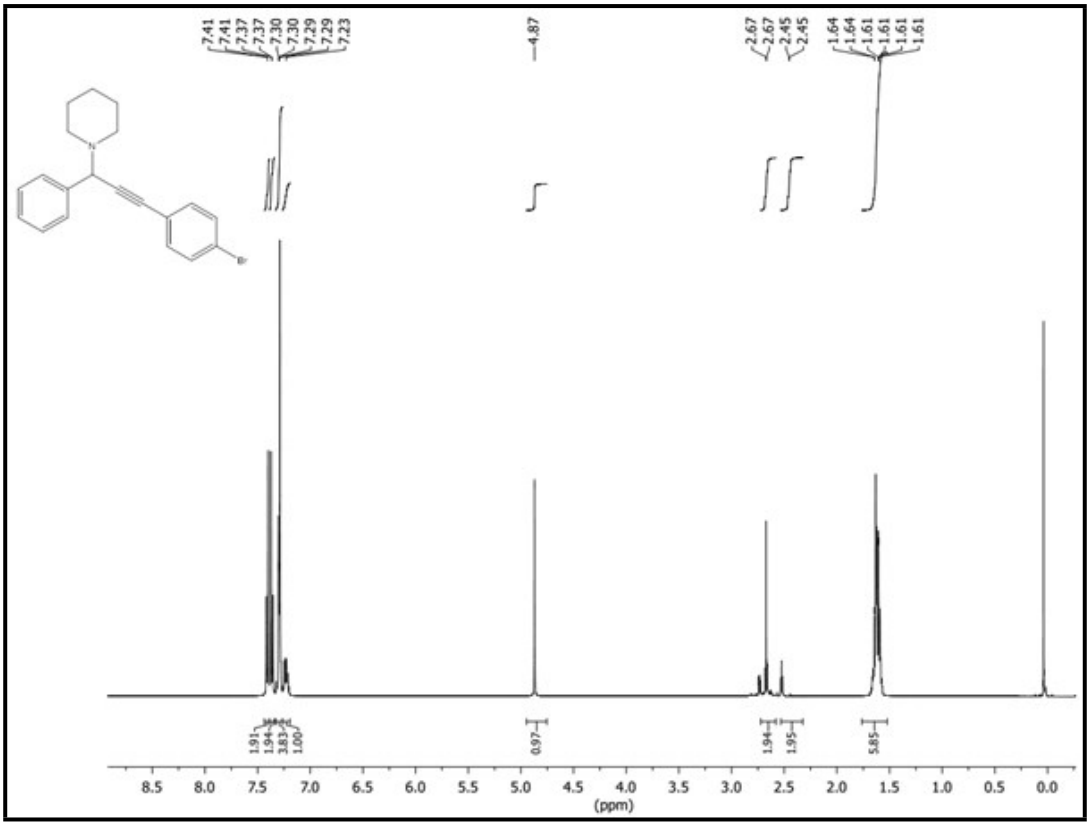

7.48
7.48
7.30
7.30
7.30
7.29
7.29
7.23
7.23
7.23
4.95
3.00
3.00
2.42
2.42
1.69
1.69
1.69
1.69
N
1.62
4.09
2.33
0.78
1.62
1.62
3.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

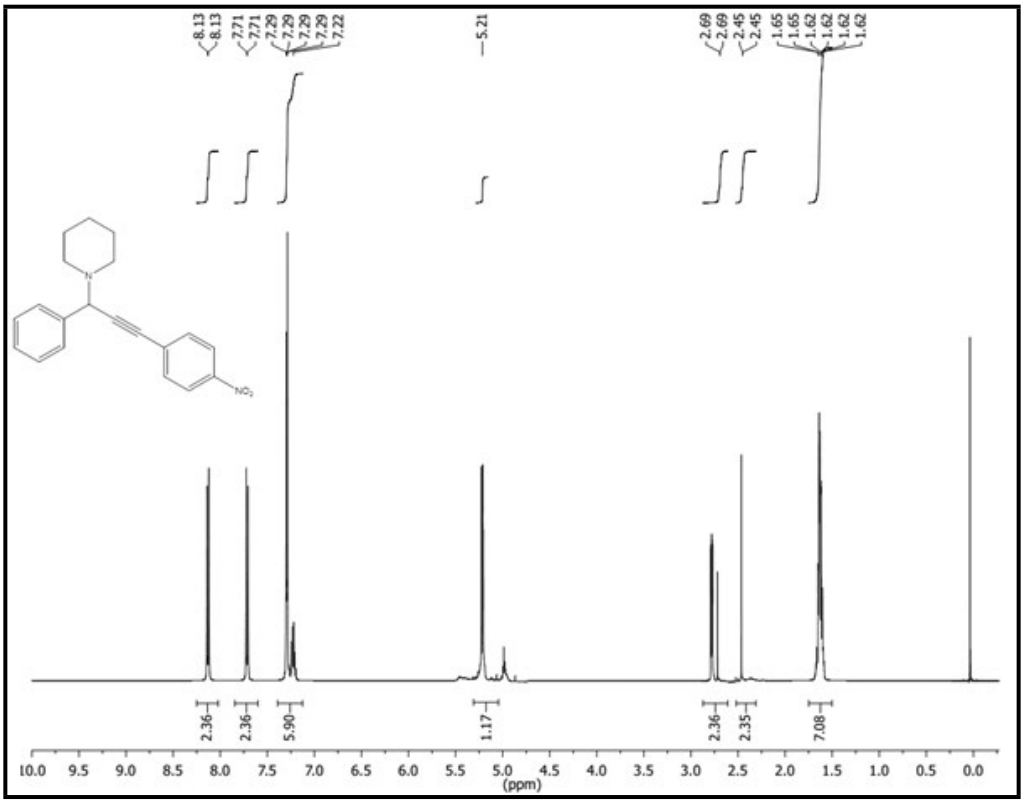

TOF MS ES+
2.73e7
100
%
0
191.0773
189.0622
165.0617
163.0459
176.0540
192.0810
139.0453
152.0534
195.0729
219.0735
220.0449
248.1361
261.1370
278.1480
50.8228
76.9898
89.0279
110.0055
115.0445
128.0528
m/z
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280

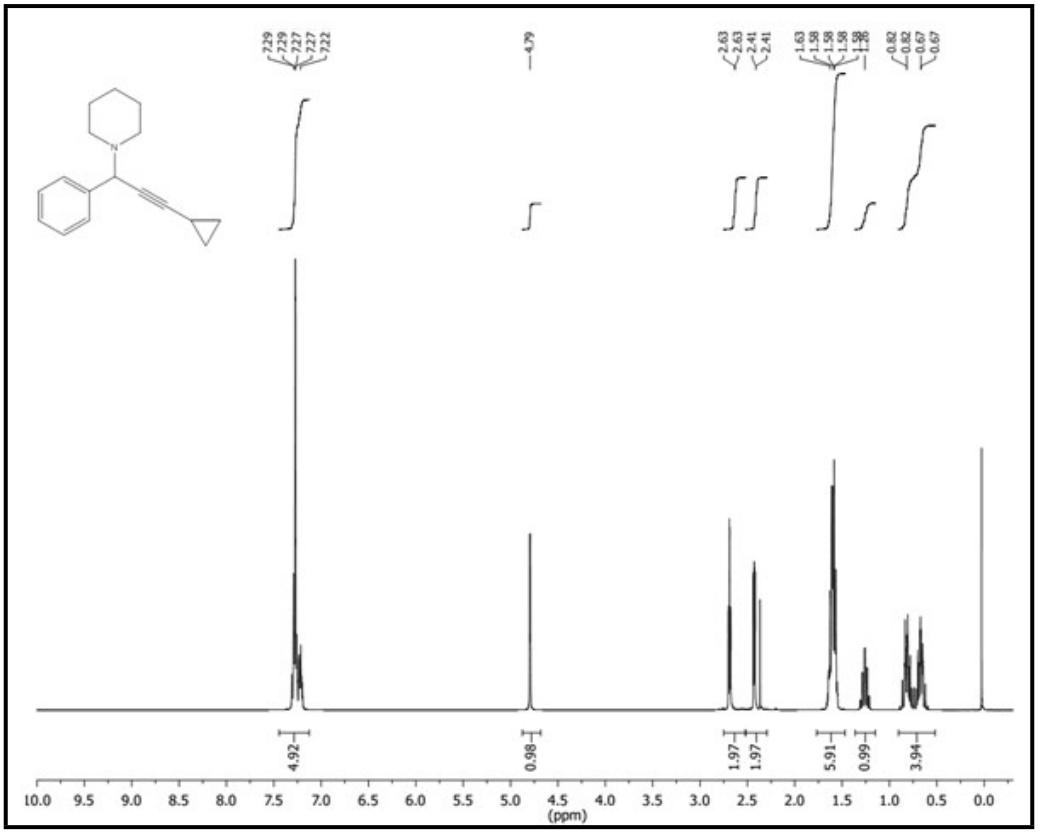

7.52
7.52
7.32
7.30
7.30
7.29
7.29
7.24
7.24
7.22
5.26
3.78
3.78
3.78
3.78
2.84
2.84
2.59
2.59
1.69
6.77
0.84
3.37
1.69
1.69
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

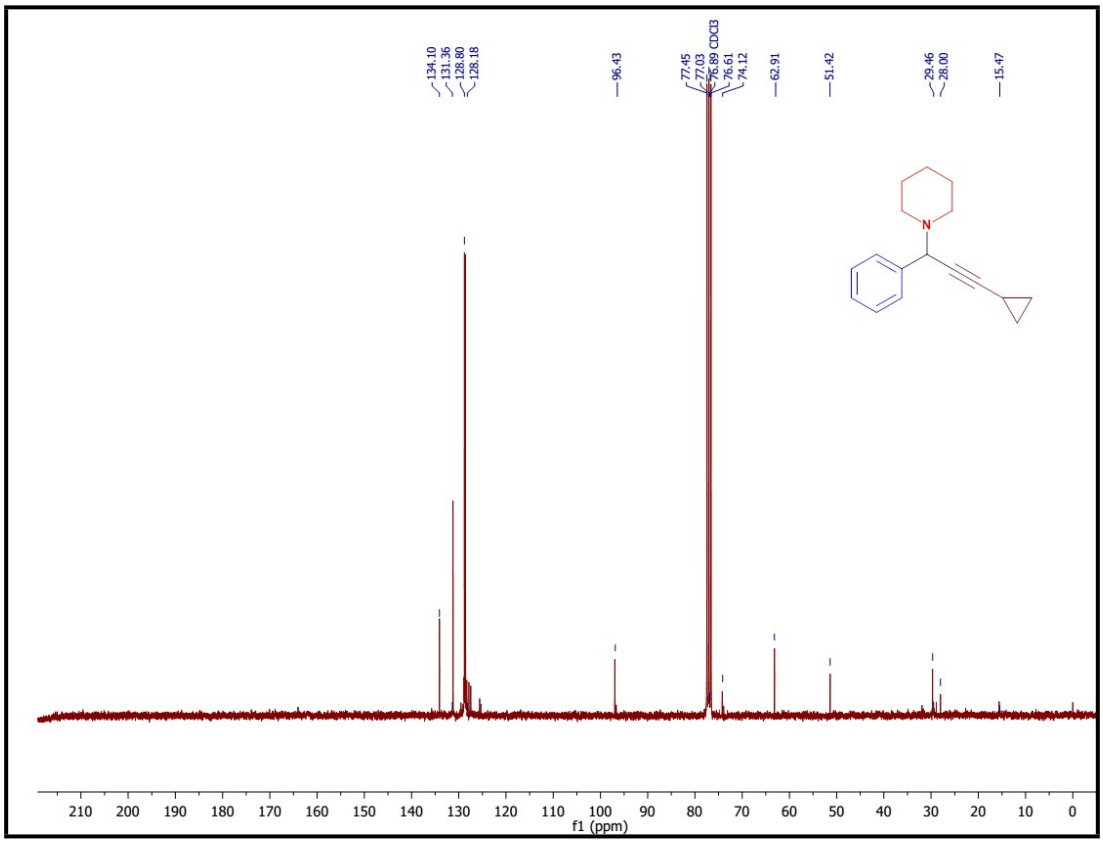

134.44
131.23
129.76
129.24
128.80
128.75
128.43
123.87
97.34
85.23
77.47
77.04
76.87 CDCl3
76.62
67.13
63.77
50.36
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

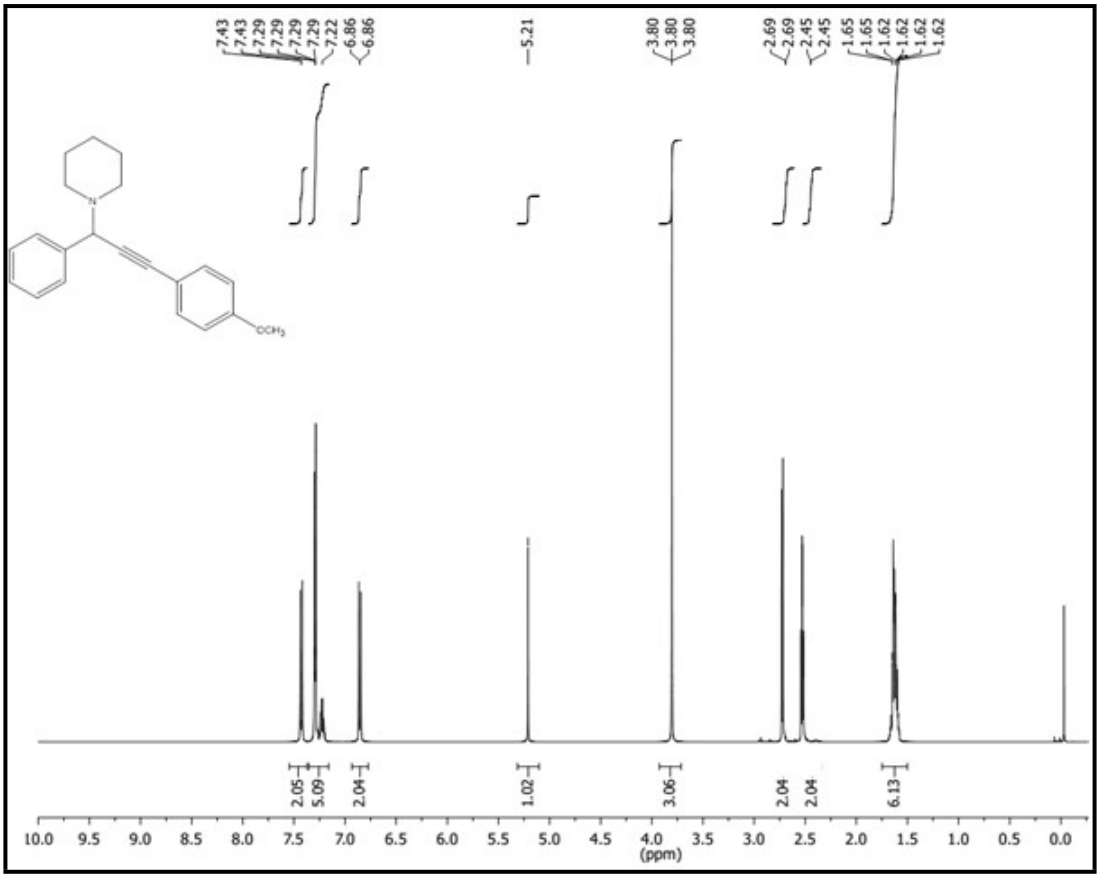

TOF MS ES+
1.09e7
100
%
0
191.0797
165.0637
189.0644
187.0488
163.0479
192.0834
176.0562
195.0751
139.0470
152.0553
219.0763
232.1079
246.1239
278.1512
274.1202
63.0110
77.0269
89.0288
110.0068
115.0459
128.0543
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280
m/z

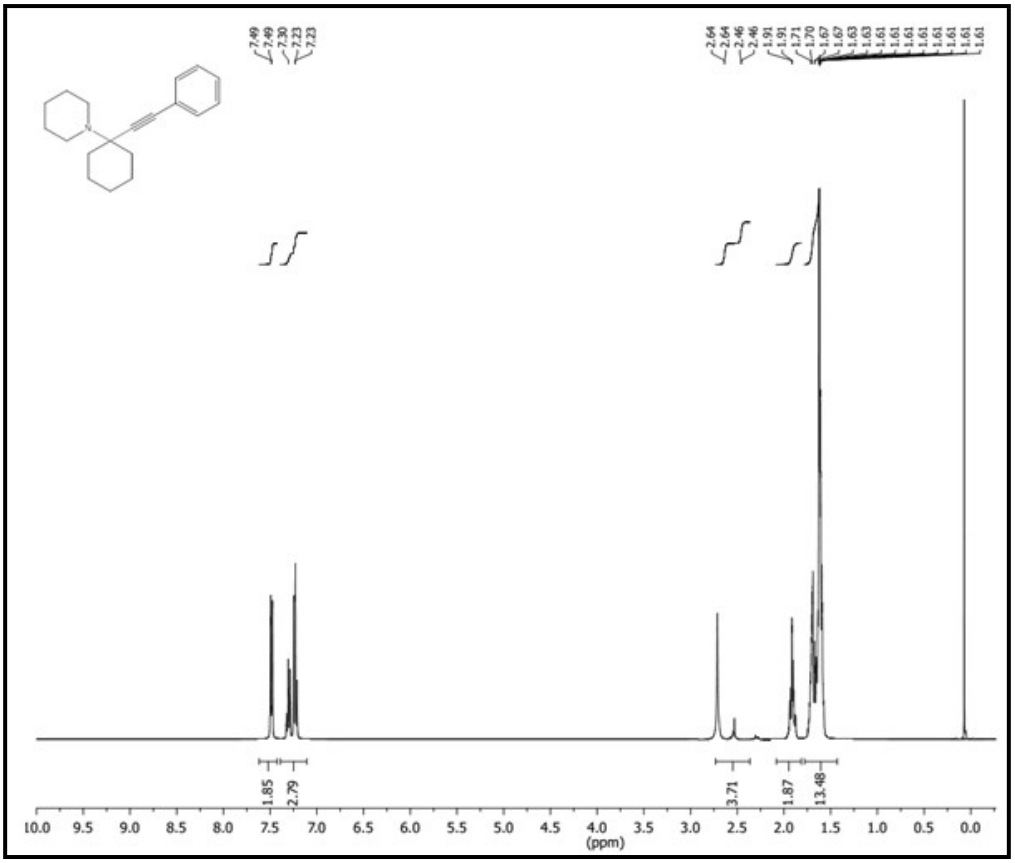

7.41
7.41
7.37
7.37
7.30
7.30
7.29
7.29
7.23
4.87
2.67
2.67
2.45
2.45
1.64
1.64
1.61
1.61
1.61
1.91
1.94
1.83
1.00
0.97
1.94
1.95
5.85
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

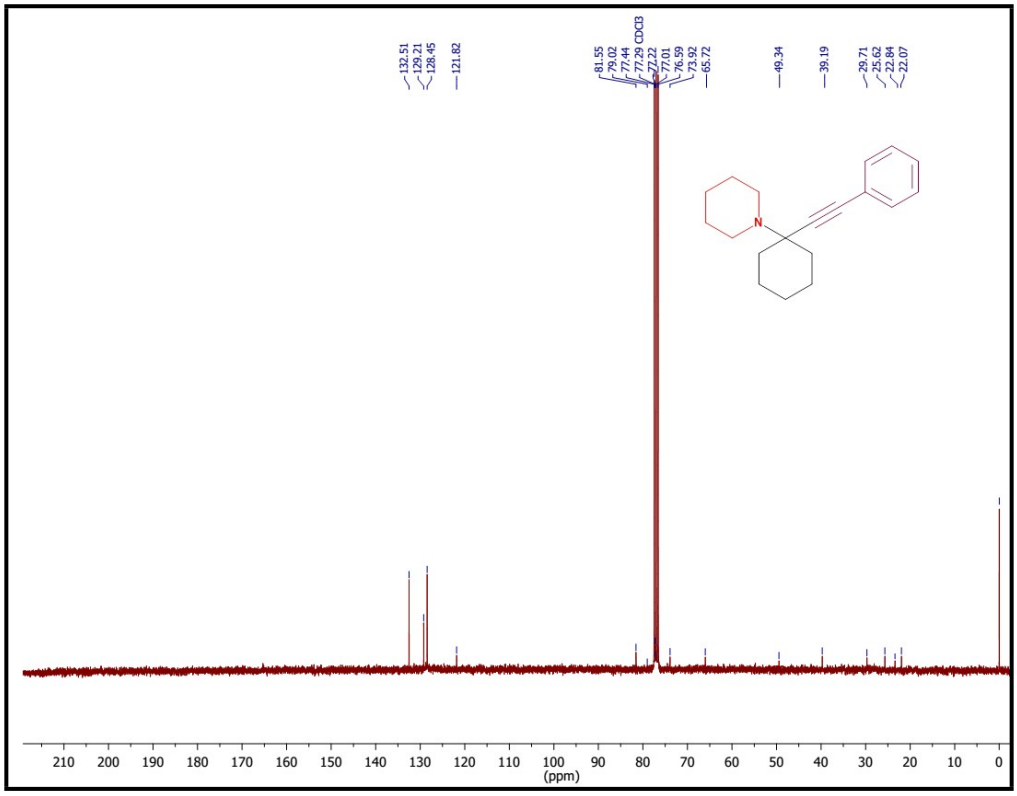

8.13
8.13
7.71
7.71
7.29
7.29
7.29
7.29
7.22
5.21
2.69
2.69
2.45
2.45
1.65
1.65
1.62
1.62
1.62
1.62
2.36
2.36
5.90
1.17
2.36
2.35
7.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

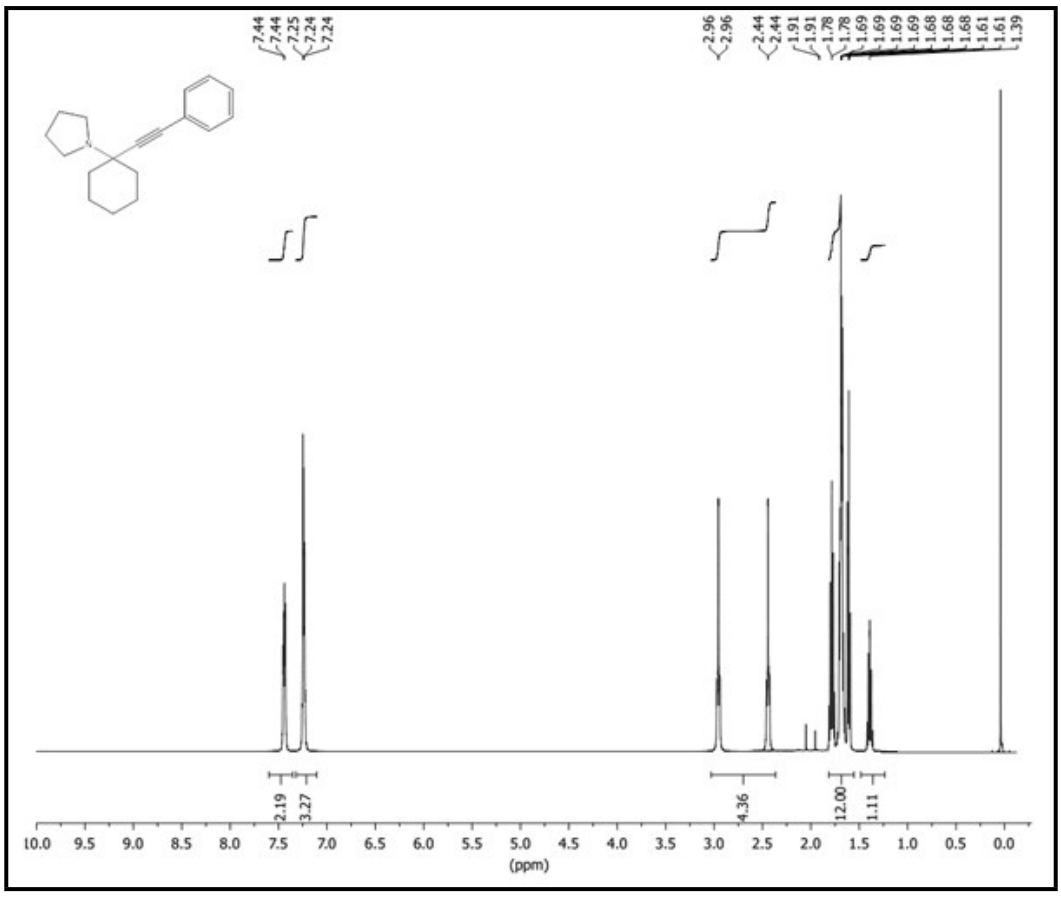

7.29
7.29
7.27
7.27
7.22
4.79
2.63
2.63
2.41
2.41
1.63
1.58
1.58
1.58
1.38
0.82
0.82
0.67
0.67
4.92
0.98
1.97
1.97
5.91
0.99
3.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

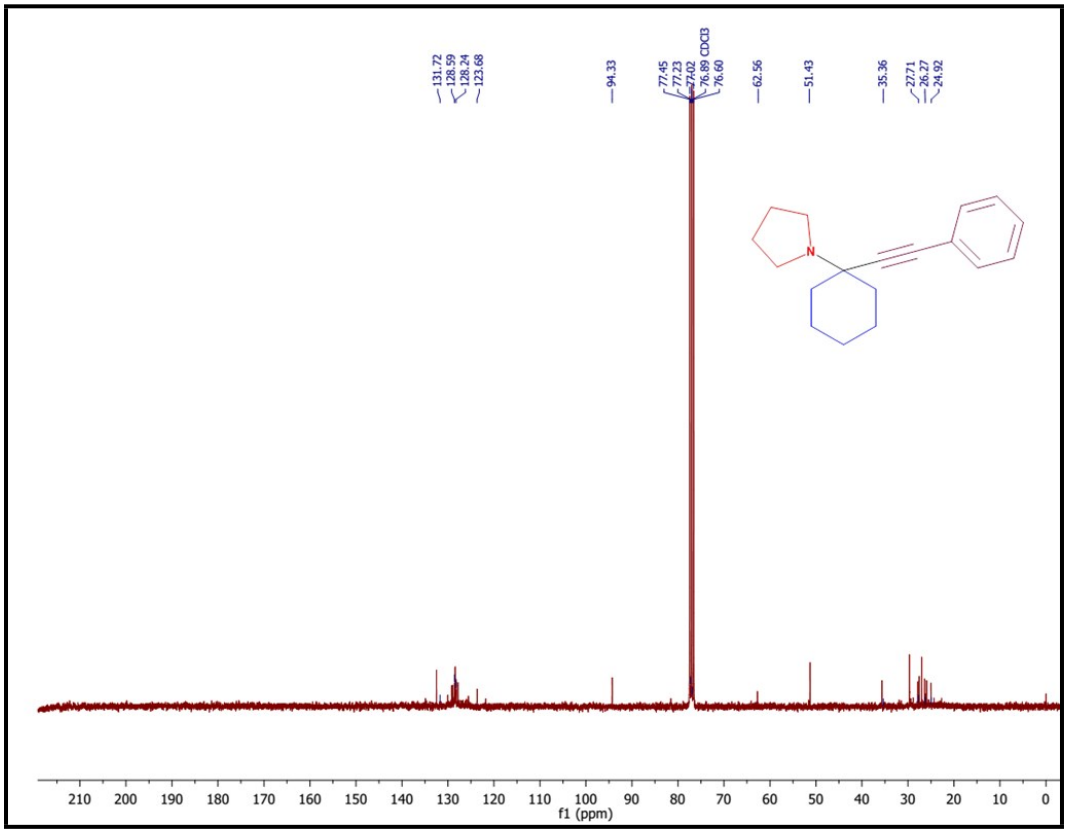

134.10
131.36
128.80
128.18
96.43
77.45
77.03
76.89 CDCl3
76.61
74.12
62.91
51.42
29.46
28.00
15.47
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

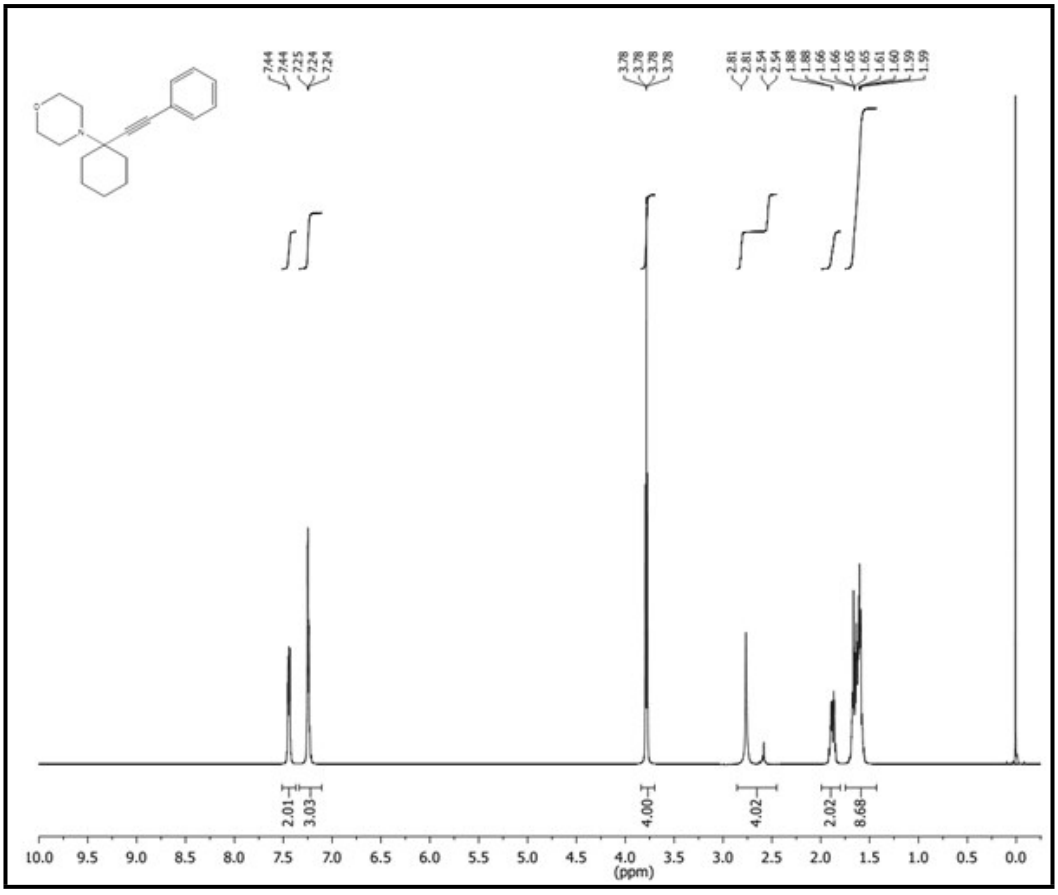

7.43
7.43
7.29
7.29
7.29
7.29
7.22
6.86
6.86
5.21
3.80
3.80
3.80
2.69
2.69
2.45
2.45
1.65
1.65
1.62
1.62
1.62
1.62
OCH3
2.05
5.09
2.04
1.02
3.06
2.04
2.04
6.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

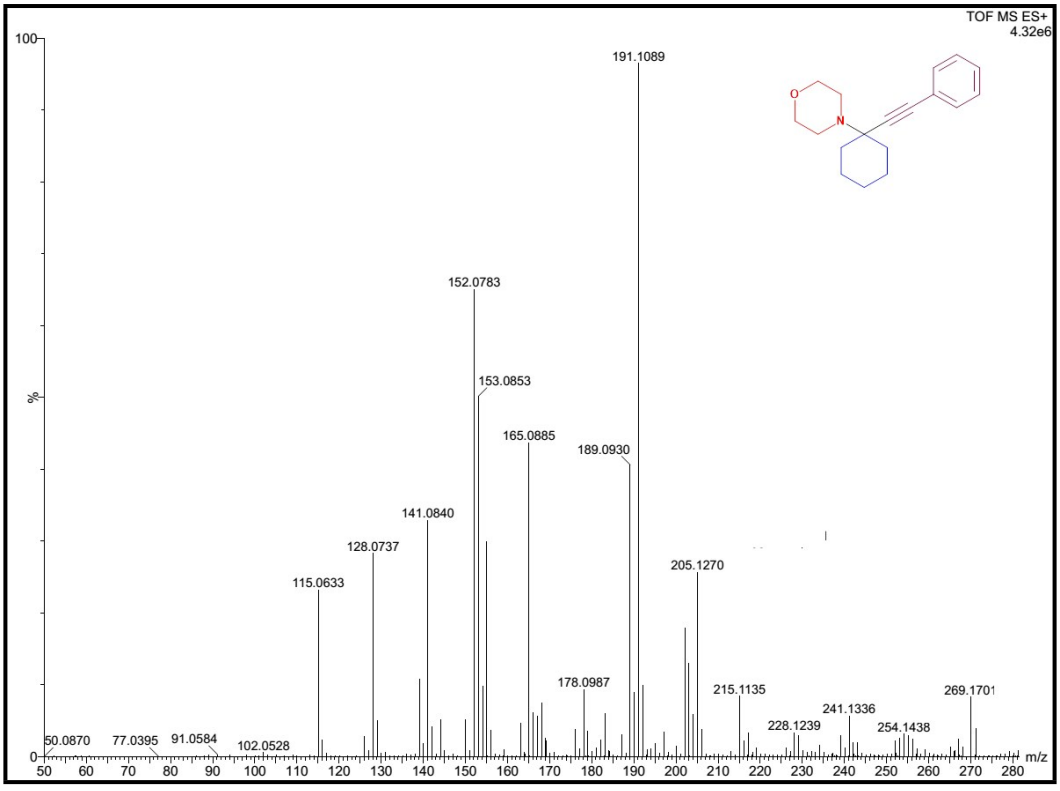

7.49
7.49
7.30
7.23
7.23
2.64
2.64
2.46
2.46
1.91
1.91
1.71
1.70
1.67
1.67
1.63
1.61
1.61
1.61
1.61
1.61
1.61
1.61
1.85
2.79
3.71
1.87
13.48
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

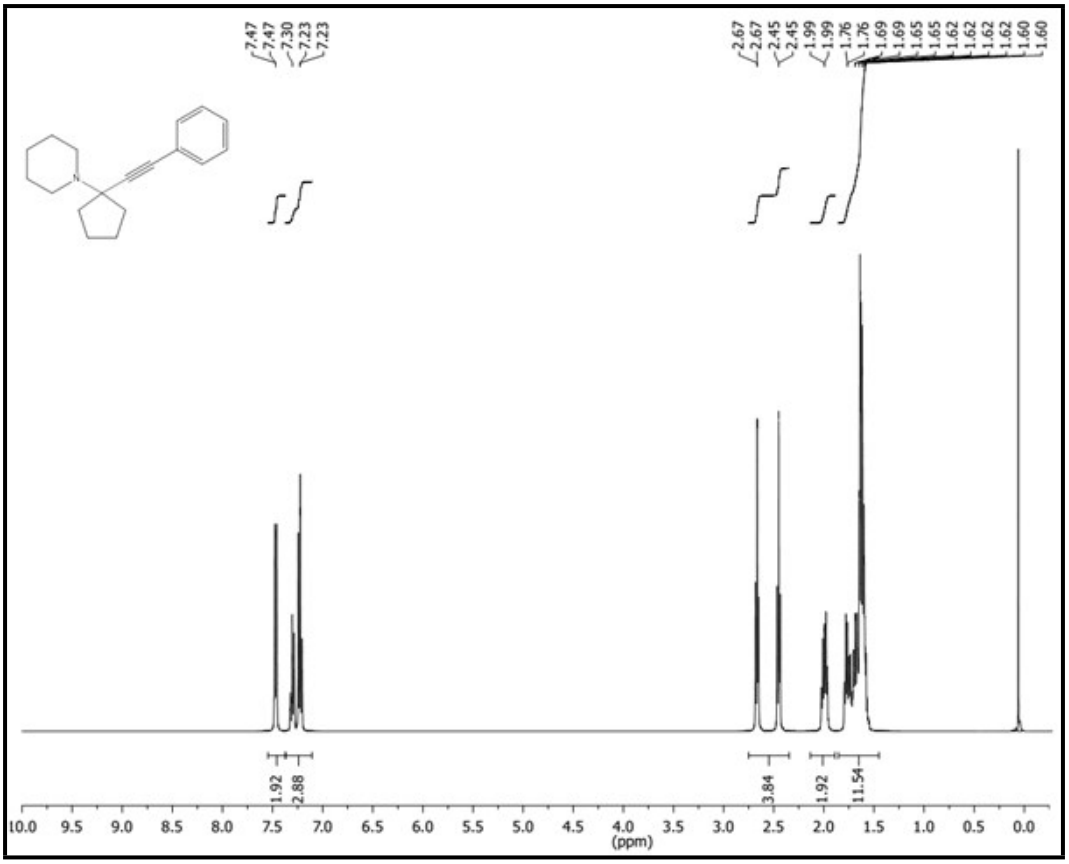

132.51
129.21
128.45
121.82
81.55
79.02
77.44
77.23
CDCl3
77.01
76.59
73.92
65.72
49.34
39.19
29.71
25.62
22.84
22.07
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

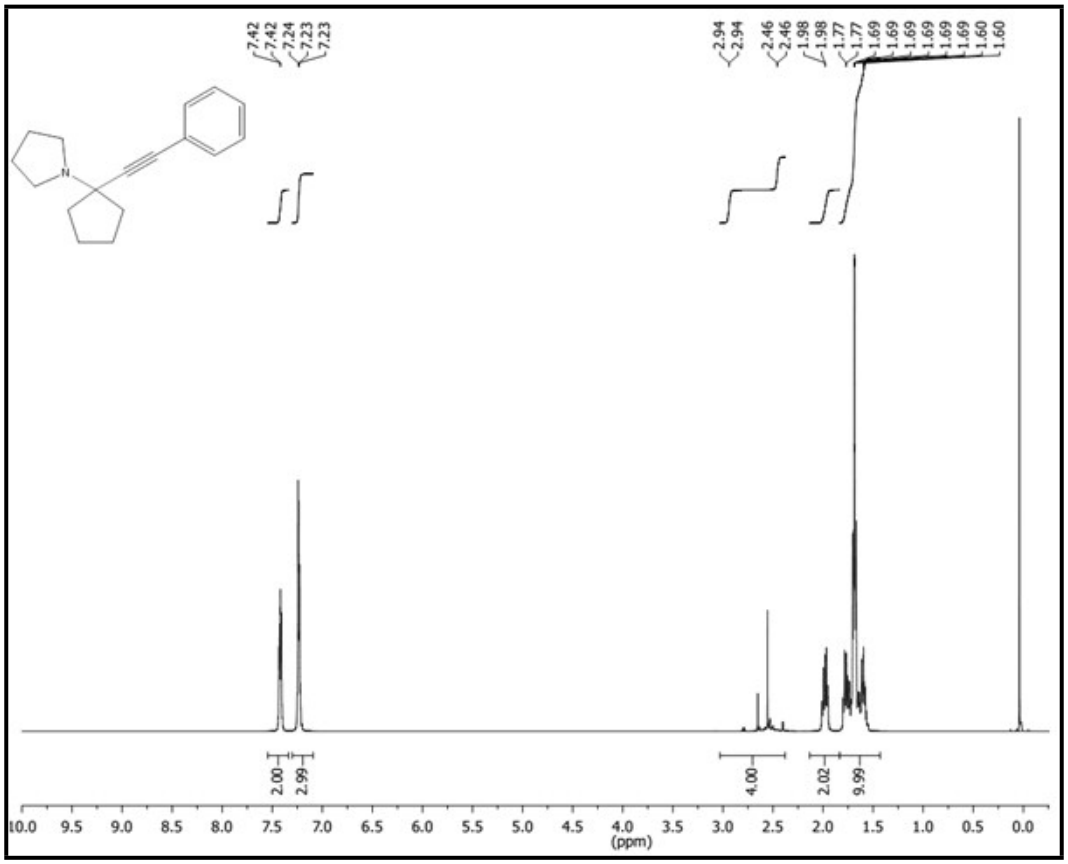

7.44
7.44
7.25
7.24
7.24
2.96
2.96
2.44
2.44
1.91
1.91
1.78
1.78
1.69
1.69
1.69
1.69
1.68
1.68
1.68
1.61
1.61
1.39
2.19
3.27
4.36
12.00
1.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

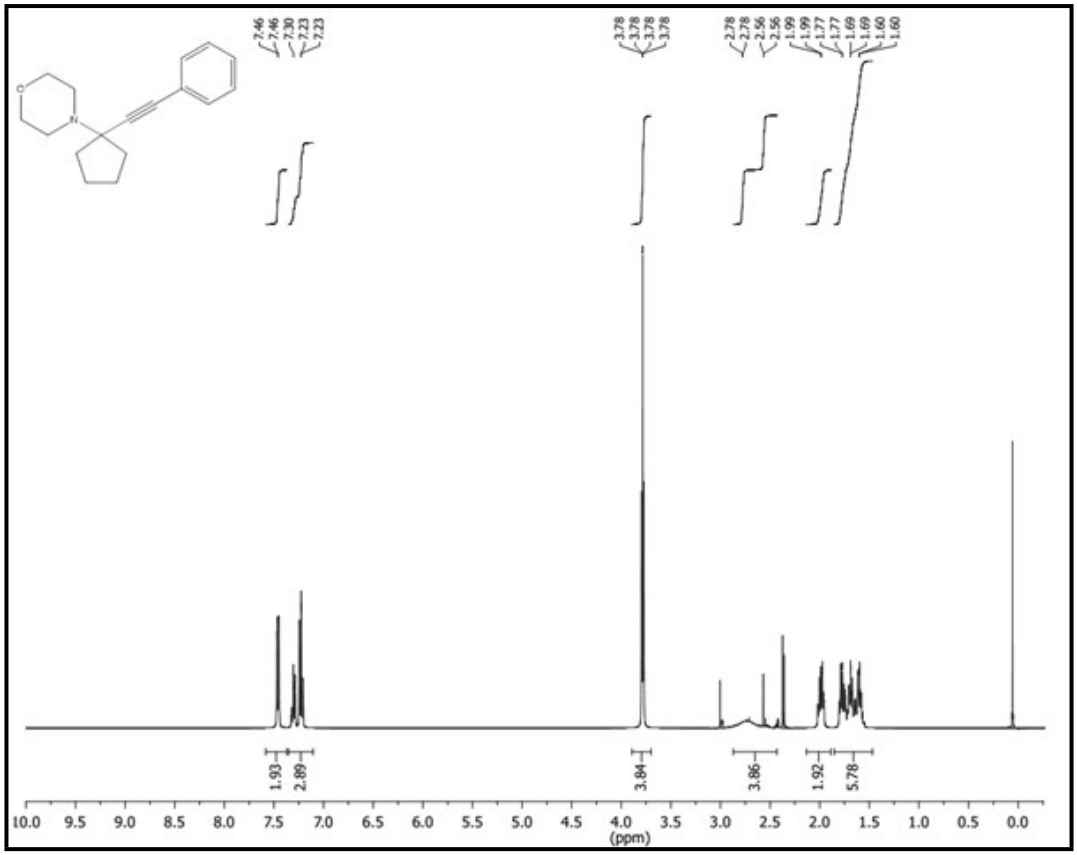

131.72
128.59
128.24
123.68
94.33
77.45
77.23
77.02
76.89
76.60
CDCl3
62.56
51.43
35.36
27.71
26.27
24.92
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

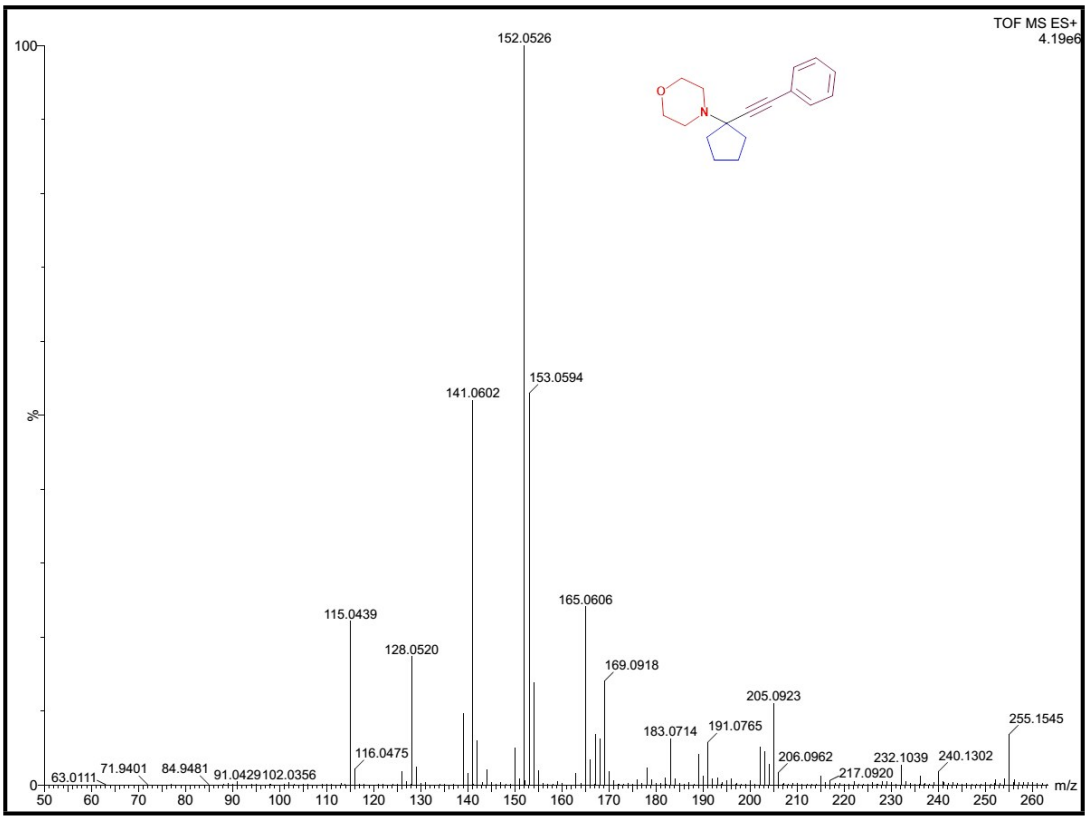

7.44
7.44
7.25
7.24
7.24
3.78
3.78
3.78
3.78
2.81
2.81
2.54
2.54
1.88
1.66
1.66
1.65
1.65
1.61
1.60
1.59
1.59
2.01
3.03
4.00
4.02
2.02
8.68
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

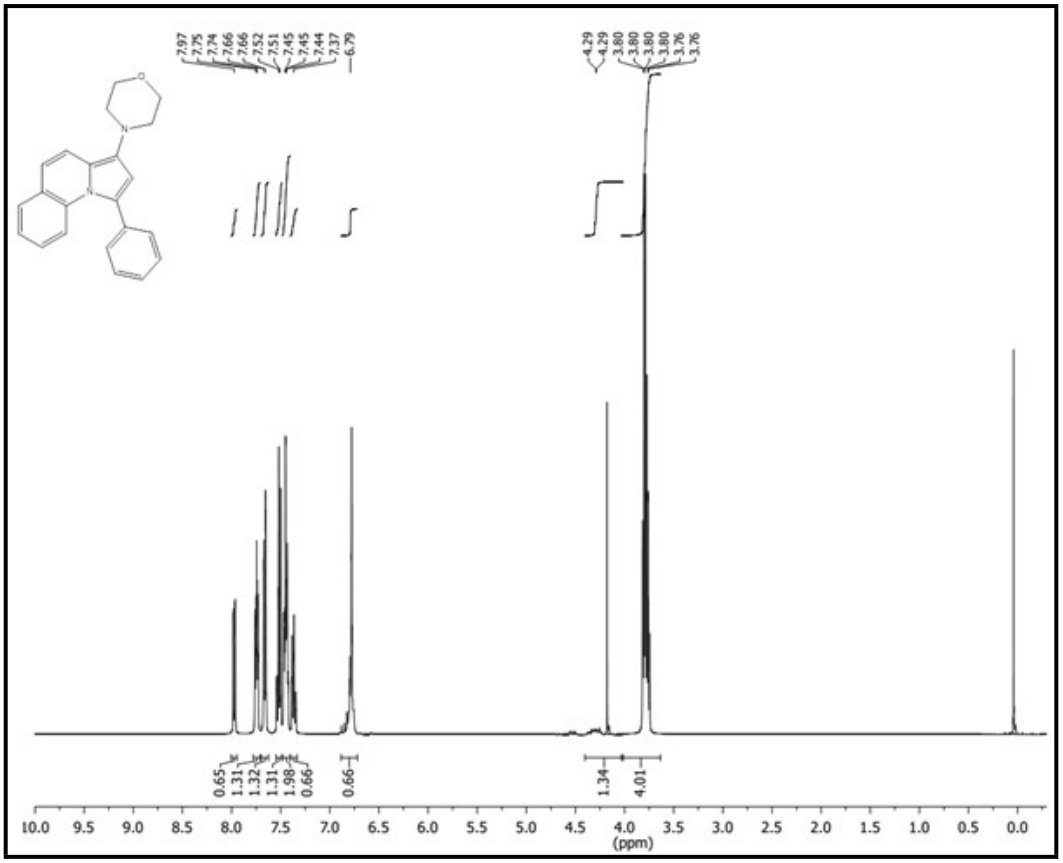

TOF MS ES+
4.32e6
100
%
0
191.1089
152.0783
153.0853
165.0885
189.0930
141.0840
128.0737
115.0633
205.1270
178.0987
215.1135
269.1701
241.1336
228.1239
254.1438
50.0870
77.0395
91.0584
102.0528
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280
m/z

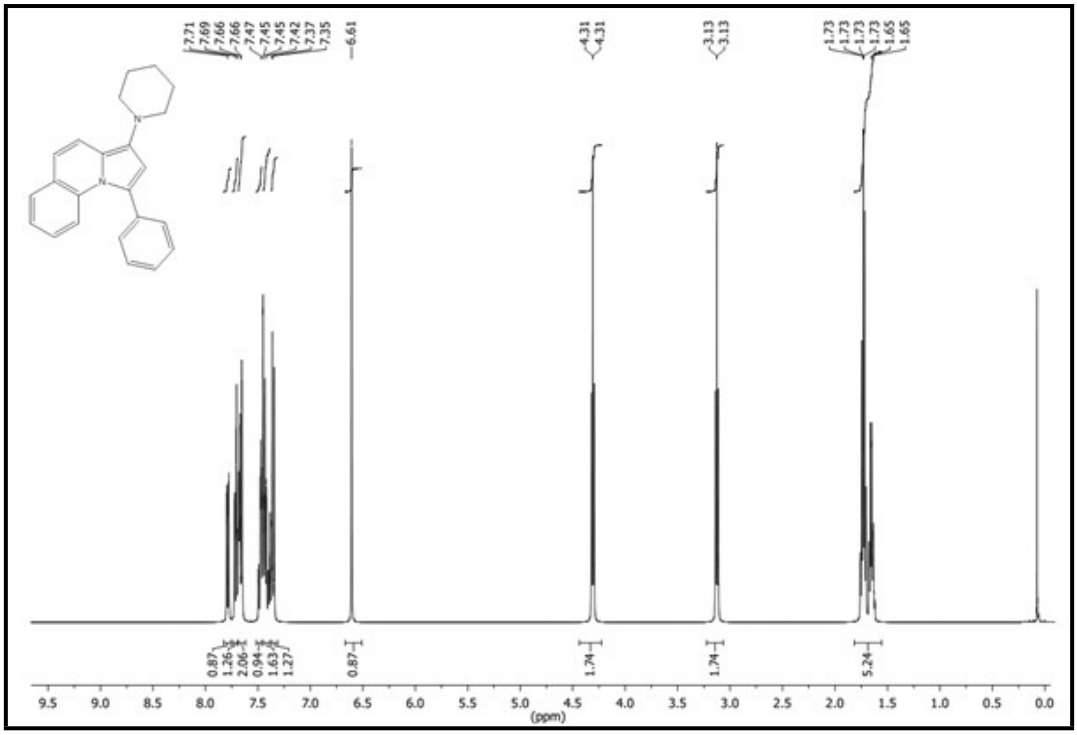

7.47
7.47
7.30
7.23
7.23
2.67
2.67
2.45
2.45
1.99
1.99
1.76
1.76
1.69
1.69
1.65
1.65
1.62
1.62
1.62
1.62
1.60
1.60
1.92
2.88
3.84
1.92
11.54
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

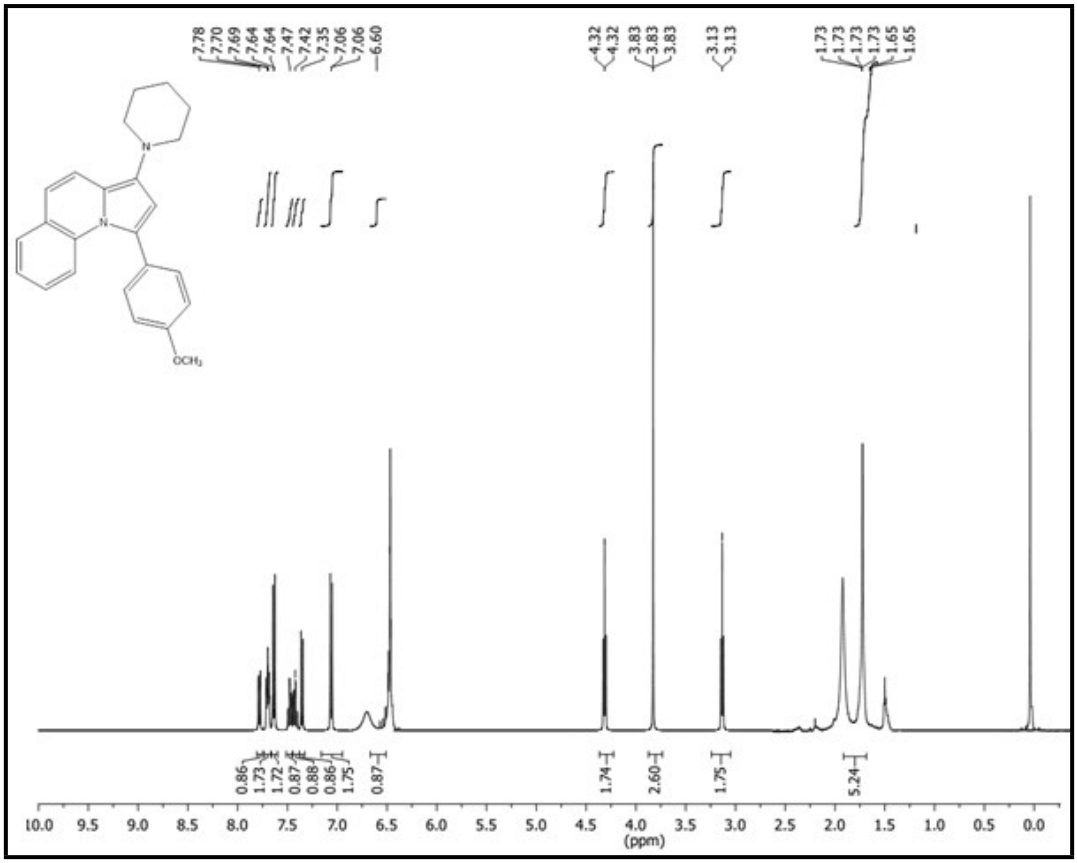

7.42
7.42
7.24
7.23
7.23
2.94
2.94
2.46
2.46
1.98
1.98
1.77
1.77
1.69
1.69
1.69
1.69
1.69
1.69
1.60
1.60
2.00
2.99
4.00
2.02
9.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

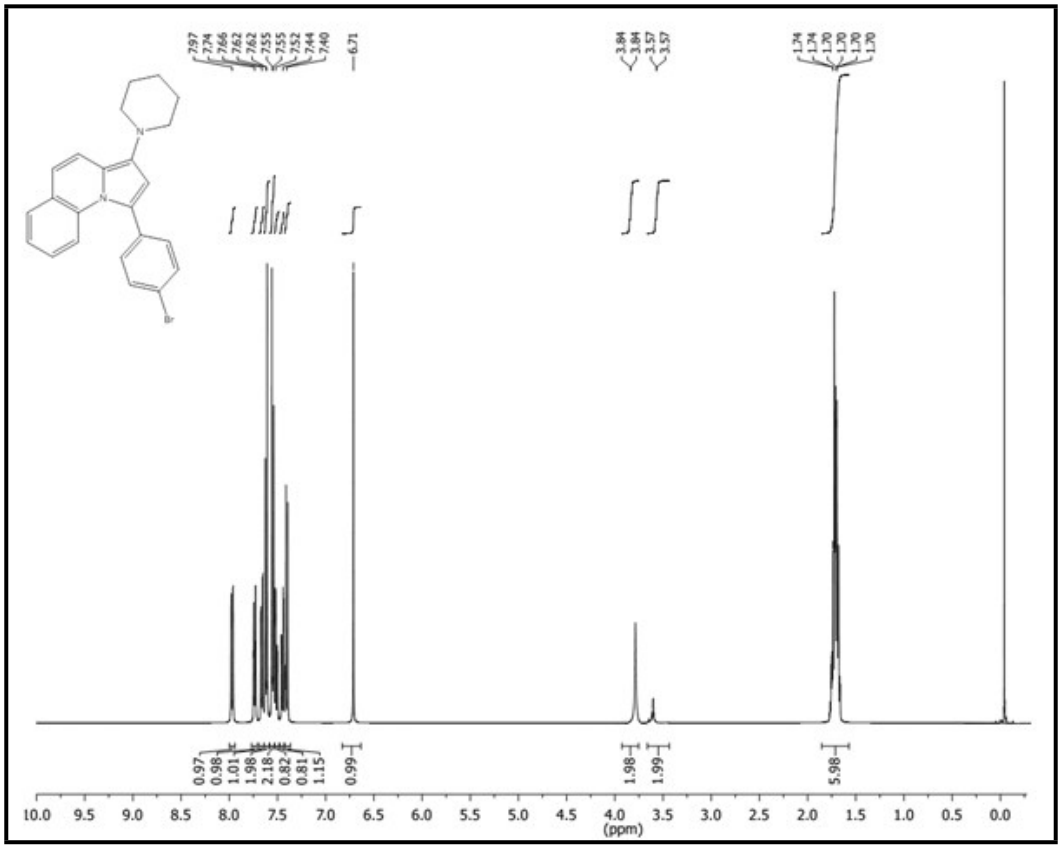

7.46
7.46
7.30
7.23
7.23
3.78
3.78
3.78
3.78
2.78
2.78
2.56
2.56
1.99
1.99
1.77
1.77
1.69
1.69
1.60
1.60
1.93
2.89
3.94
3.86
1.92
5.78
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

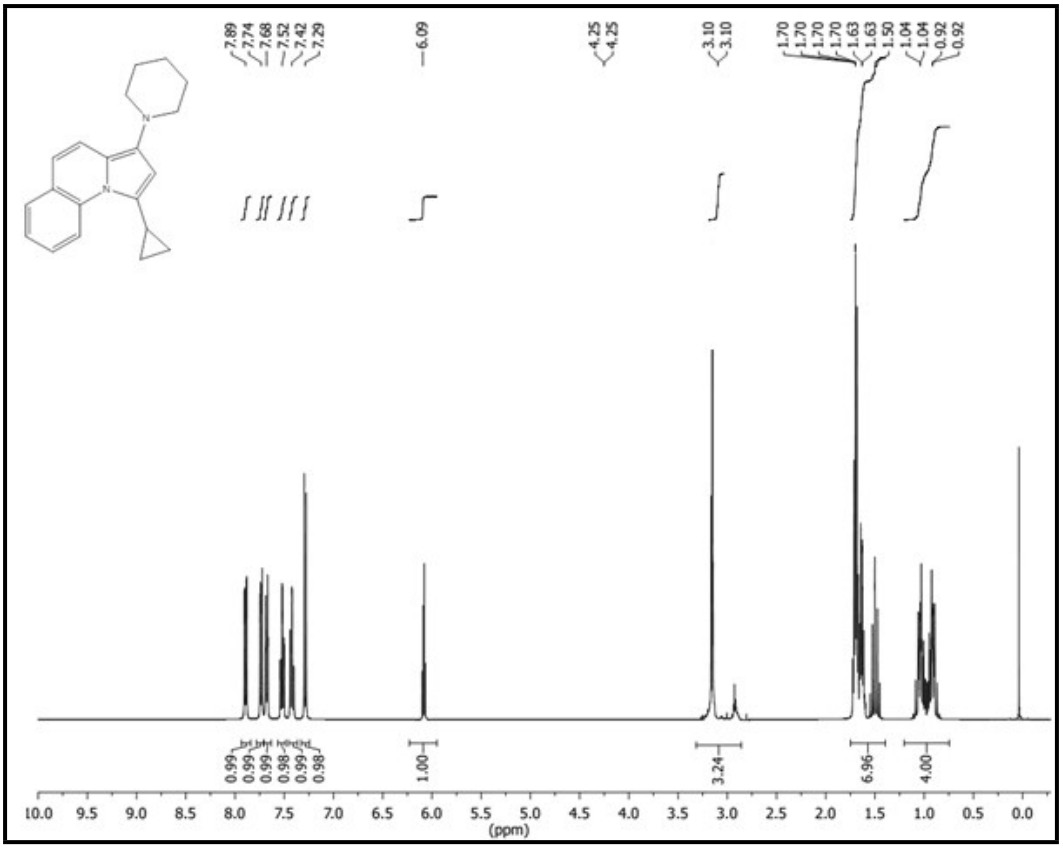

TOF MS ES+
4.19e6
100
%
0
152.0526
153.0594
141.0602
165.0606
115.0439
128.0520
169.0918
205.0923
183.0714
191.0765
255.1545
116.0475
206.0962
232.1039
240.1302
217.0920
63.0111
71.9401
84.9481
91.0429
102.0356
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260
m/z

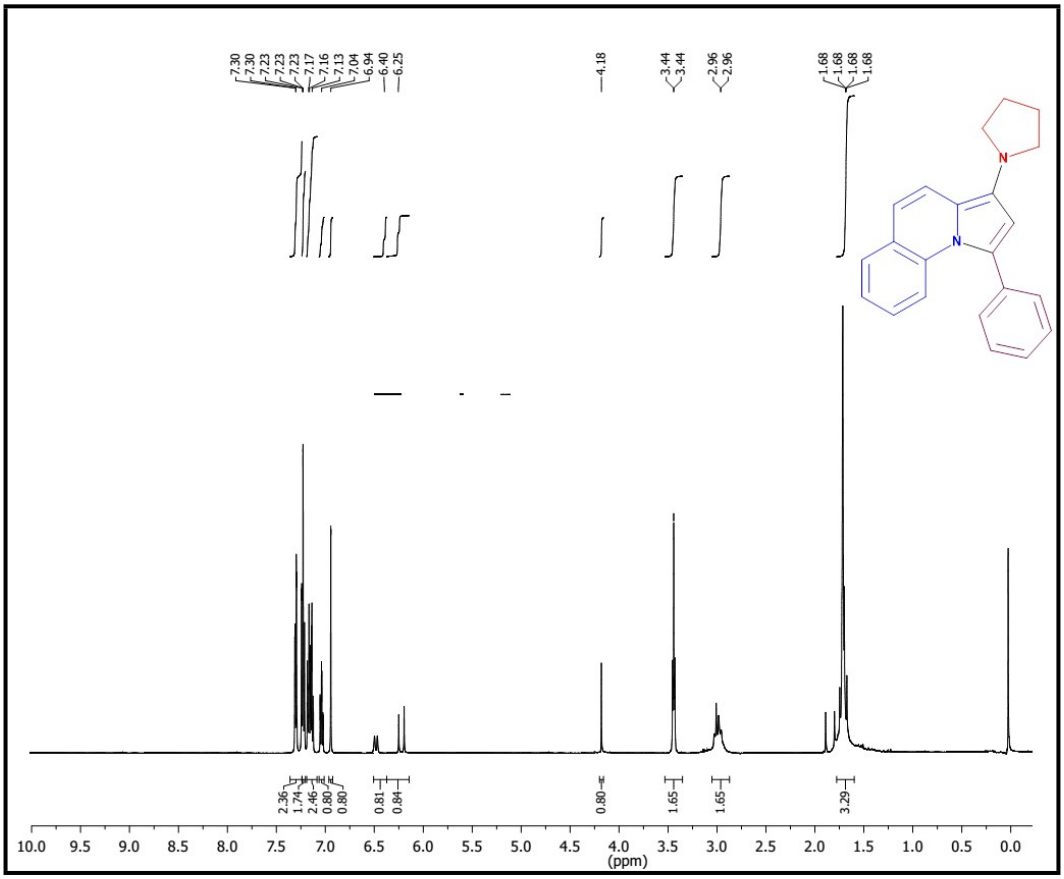

7.97
7.75
7.74
7.66
7.66
7.52
7.51
7.45
7.45
7.44
7.37
6.79
4.29
4.29
3.80
3.80
3.80
3.80
3.76
3.76
0.65
1.31
1.32
1.31
1.98
0.66
0.66
1.34
4.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

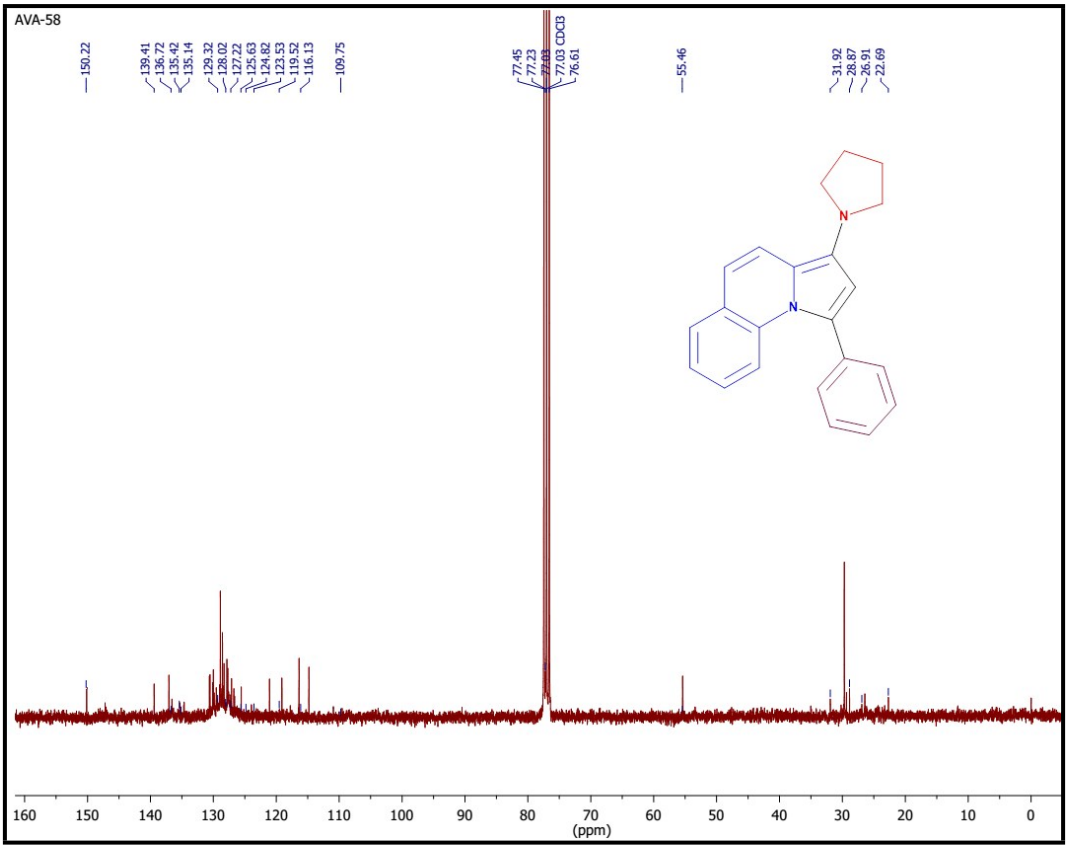

7.71
7.69
7.66
7.66
7.47
7.45
7.45
7.42
7.37
7.35
6.61
4.31
4.31
3.13
3.13
1.73
1.73
1.73
1.73
1.65
1.65
0.87
1.26
2.06
0.94
1.63
1.27
0.87
1.74
1.74
5.24
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

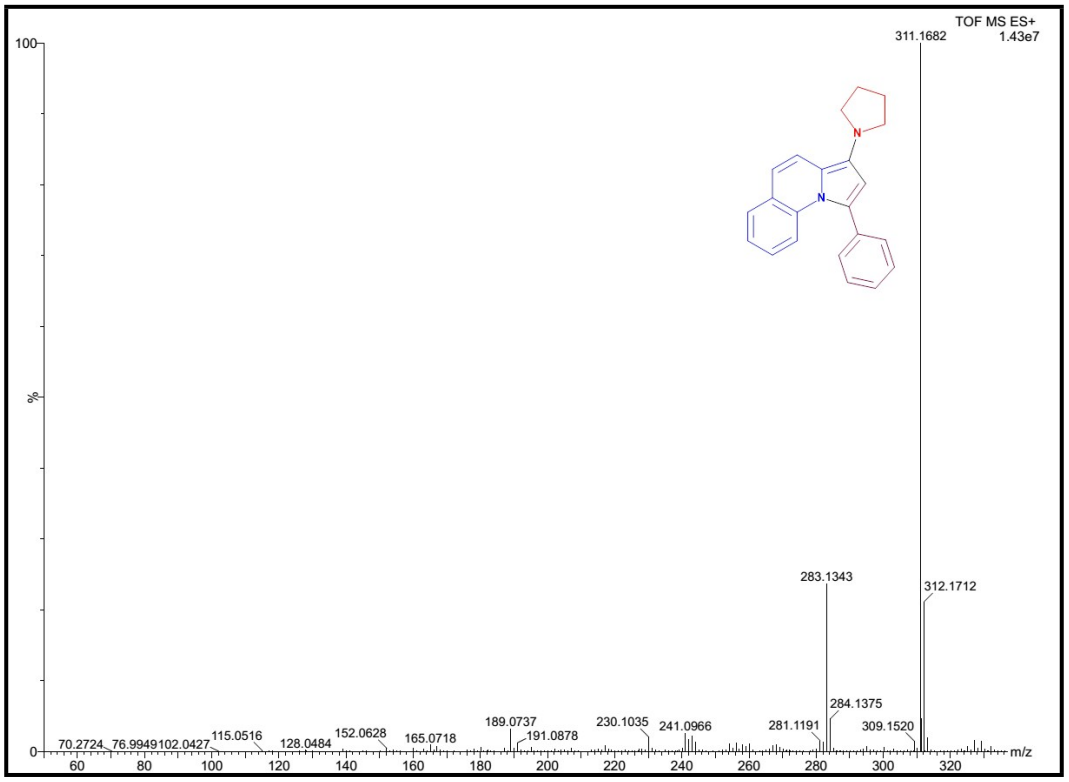

7.78
7.70
7.69
7.64
7.64
7.47
7.42
7.35
7.06
7.06
6.60
4.32
4.32
3.83
3.83
3.83
3.13
3.13
1.73
1.73
1.73
1.73
1.65
1.65
OCH3
0.86
1.73
1.72
0.87
0.88
0.86
1.75
0.87
1.74
2.60
1.75
5.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


7.97
7.74
7.66
7.62
7.62
7.55
7.55
7.52
7.44
7.40
6.71
3.84
3.84
3.57
3.57
1.74
1.74
1.70
1.70
1.70
1.70
Br
0.97
0.98
1.01
1.98
2.18
0.82
0.81
1.15
0.99
1.98
1.99
5.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


7.89
7.74
7.68
7.52
7.42
7.29
6.09
4.25
4.25
3.10
3.10
1.70
1.70
1.70
1.70
1.63
1.63
1.50
1.04
1.04
0.92
0.92
0.99
0.99
0.99
0.98
0.99
0.98
1.00
3.24
6.96
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


7.30
7.30
7.23
7.23
7.23
7.17
7.16
7.13
7.04
6.94
6.40
6.25
4.18
3.44
3.44
2.96
2.96
1.68
1.68
1.68
1.68
2.36
1.74
2.46
0.80
0.80
0.81
0.84
0.80
1.65
1.65
3.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


AVA-58
150.22
139.41
136.72
135.42
135.14
129.32
128.02
127.22
125.63
124.82
123.53
119.52
116.13
109.75
77.45
77.23
77.03
77.03 CDCl3
76.61
55.46
31.92
28.87
26.91
22.69
N
N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


TOF MS ES+
1.43e7
311.1682
100
%
0
N
N
283.1343
312.1712
284.1375
189.0737
230.1035
241.0966
281.1191
309.1520
191.0878
70.2724
76.9949
102.0427
115.0516
128.0484
152.0628
165.0718
60 80 100 120 140 160 180 200 220 240 260 280 300 320
m/z