

*Supplementary Information*

A rare nitrene insertion followed by redox dimerization during the photolysis  
of ‘azido-*meta*-meconine’

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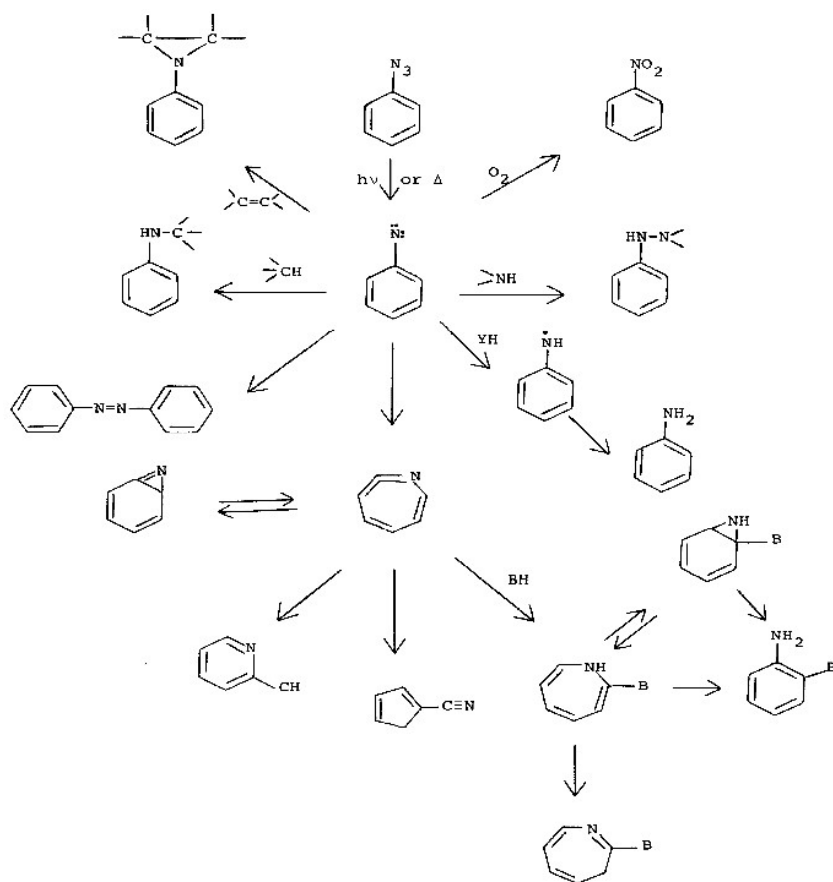
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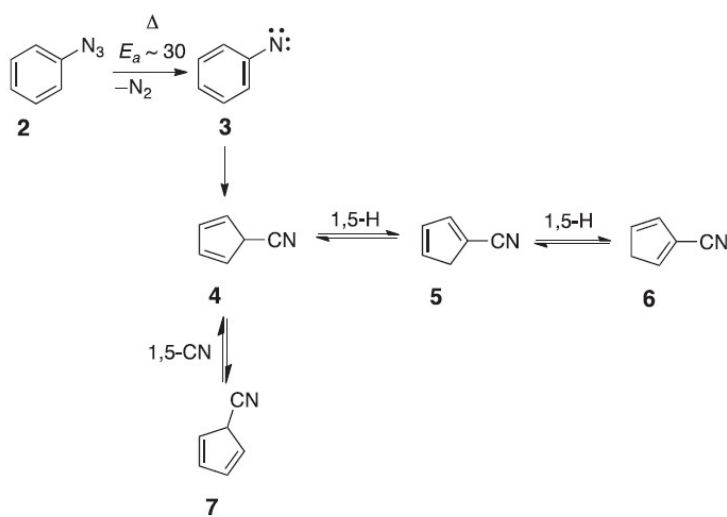
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E-mail: sv.eswaran@gmail.com

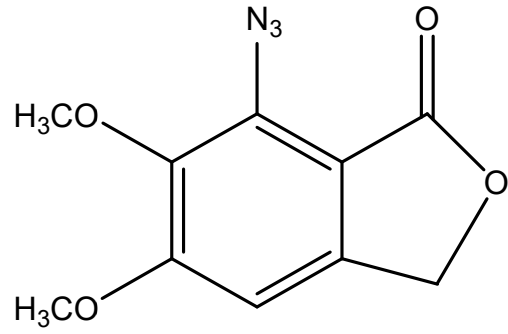
*Received 12 July 2025; accepted (revised) 15 May 2026*



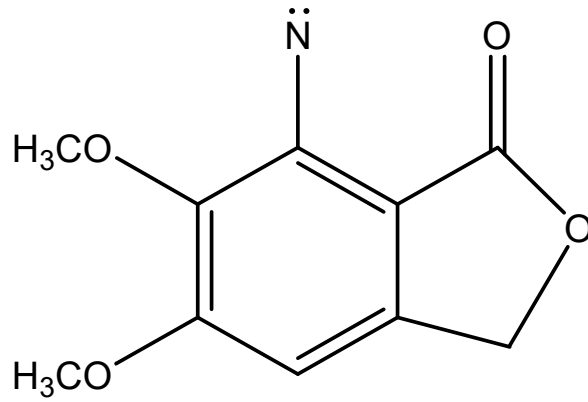
**SI-I:** General reaction pathways of aryl azides



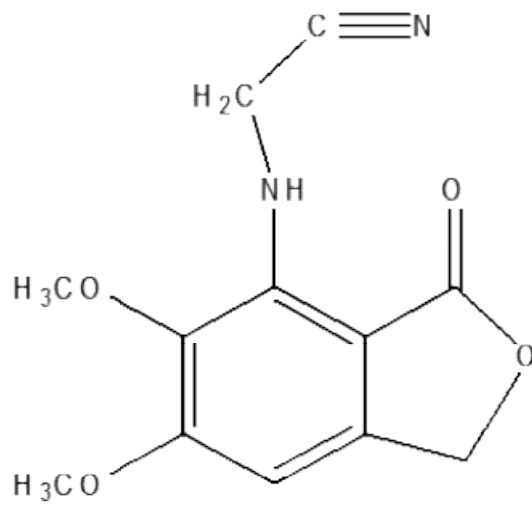
**SI-II:** Cycloperambulation in Cyclopentadiene nitrile



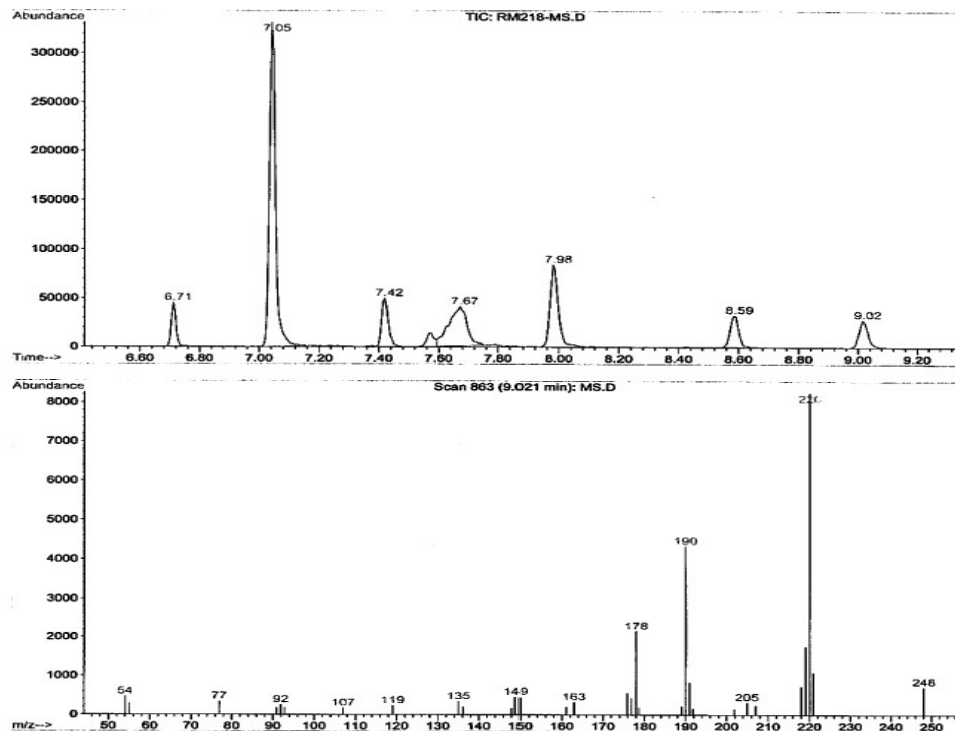
**SI-III:** Structure of 'Azido-meta-meconine'



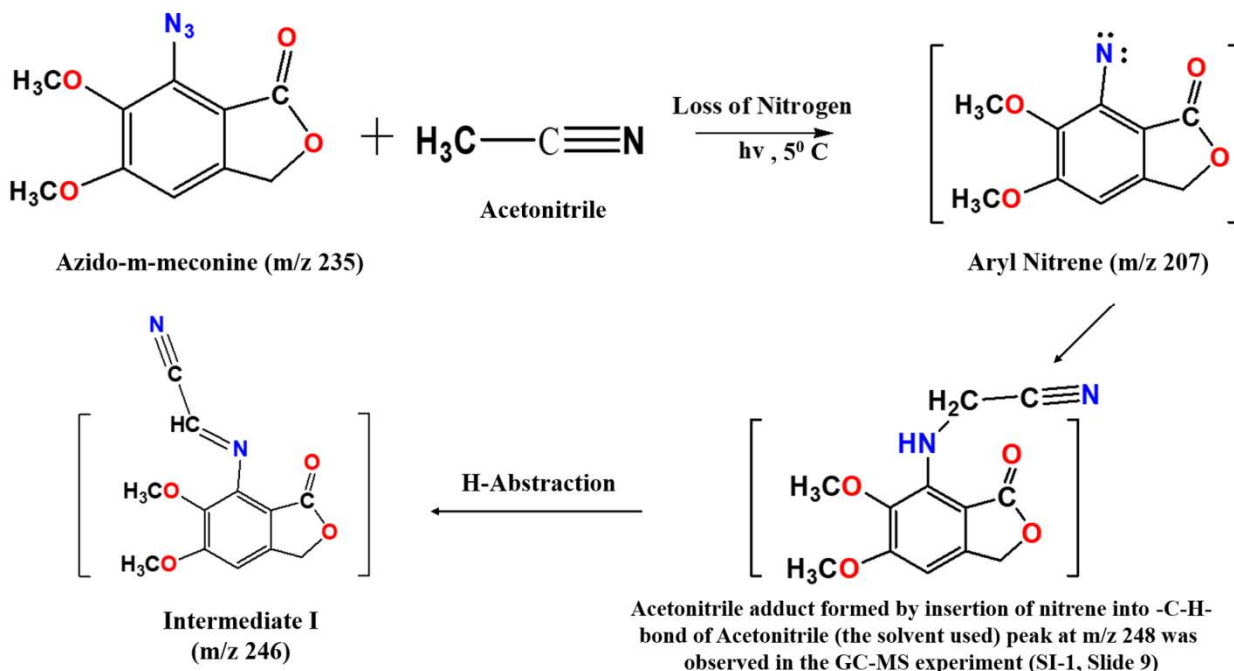
**SI-IV:** Structure of m/z 207



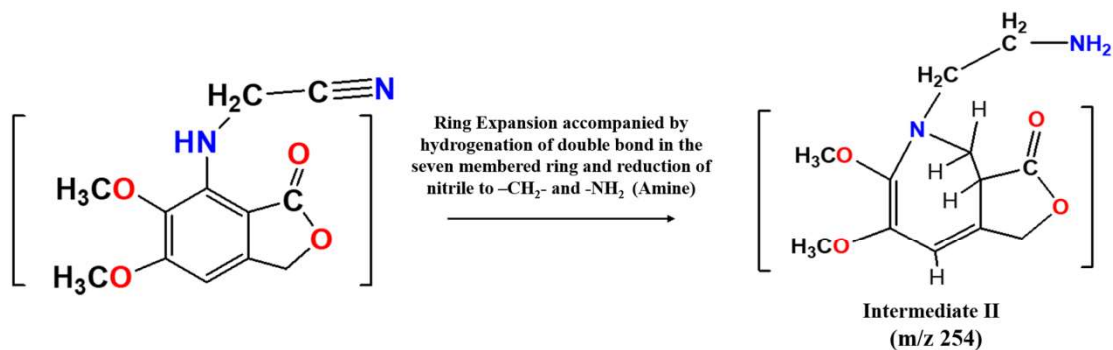
File : C:\HPCHEM\1\DATA\RYANM\RM218-MS.D  
 Operator : Ryan  
 Acquired : 8 Nov 06 3:43 pm using AcqMethod RYAN  
 Instrument : 5973D US7  
 Sample Name : a3mm t=70  
 Misc Info :  
 Vial Number : 1



### Proposed Pathway I



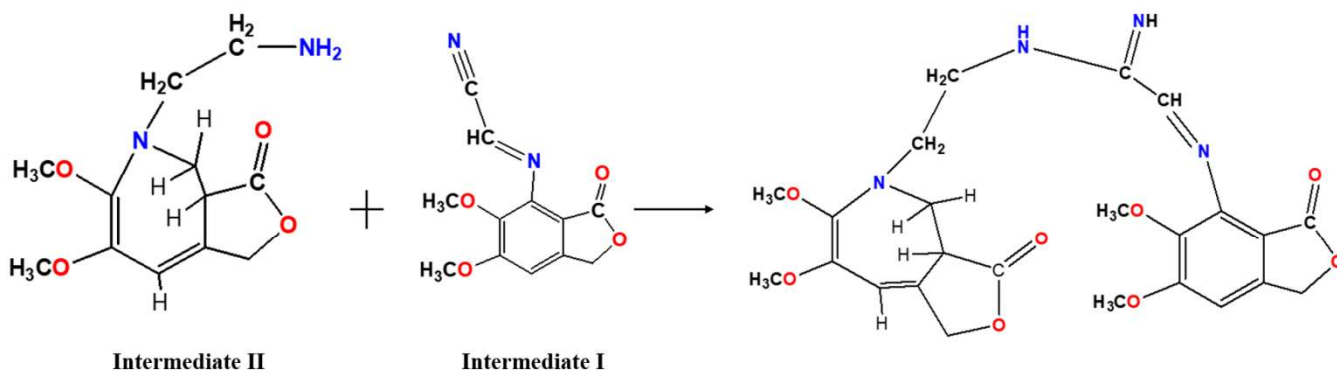
## Proposed Pathway II



In Pathway II, Acetonitrile adduct formed initially undergoes ring expansion via the corresponding heterocumulene, formed regiospecifically towards carbonyl side. Regiospecificity is known from previously work published in (J. Org. Chem. 2014). This is followed by reduction thereby leading to the amine intermediate II.

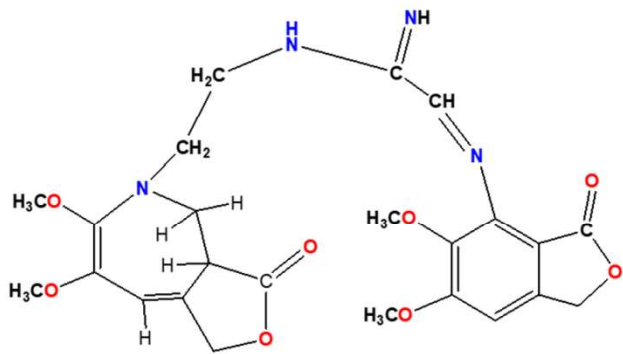
J. Org. Chem. 2014, 79, 3, 1199–1205, DOI: <https://doi.org/10.1021/jo402621w>

## Intermediate II + Intermediate I leading to m/z 500



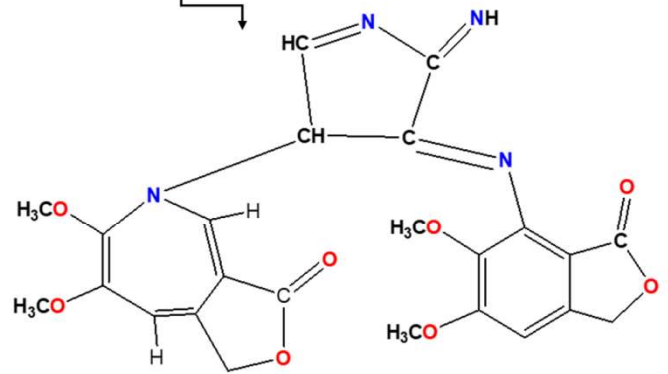
Nucleophilic addition of the amine to the carbon atom of the nitrile group yielding to the imine structure. This results in dimerization leading to amidine like structure.

## Proposed formation of m/z 494

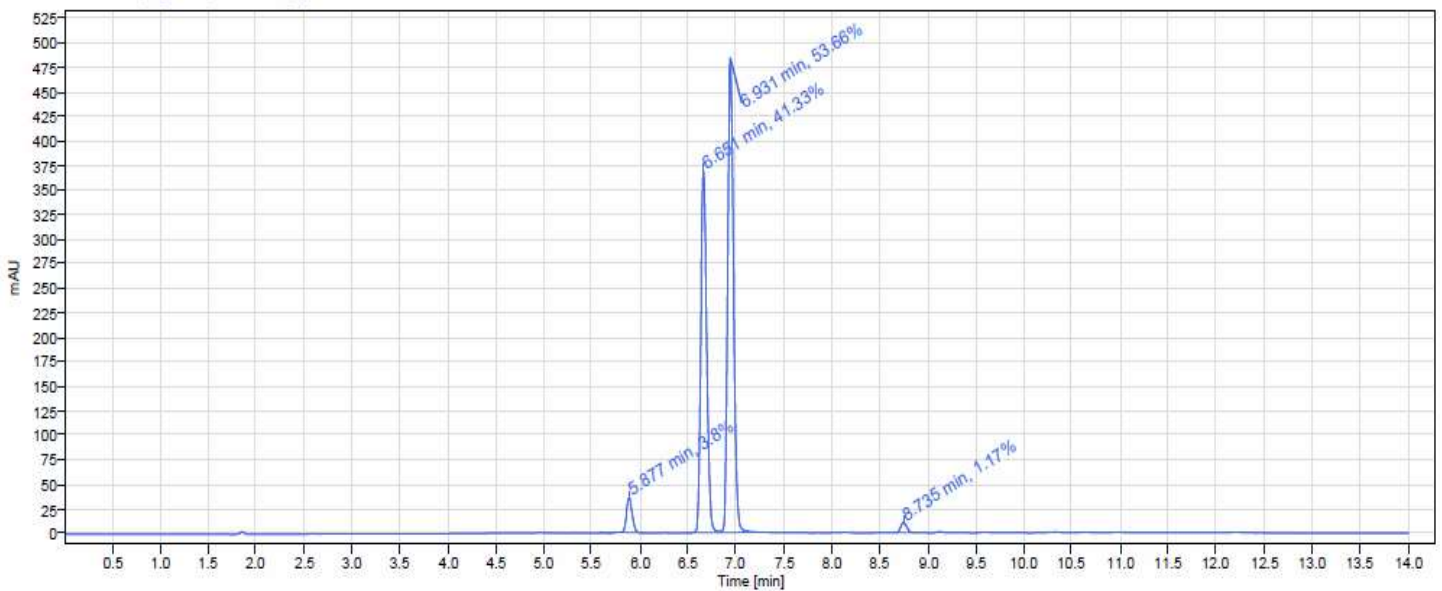


m/z 500  
C<sub>24</sub>H<sub>28</sub>N<sub>4</sub>O<sub>8</sub>

Two dehydrogenations : the first one forming the double bond in seven membered ring and the second one on the L.H.S of molecule between -CH- and -NH-. In, addition, -C-C- bond formation occurs leading to the five membered ring formation

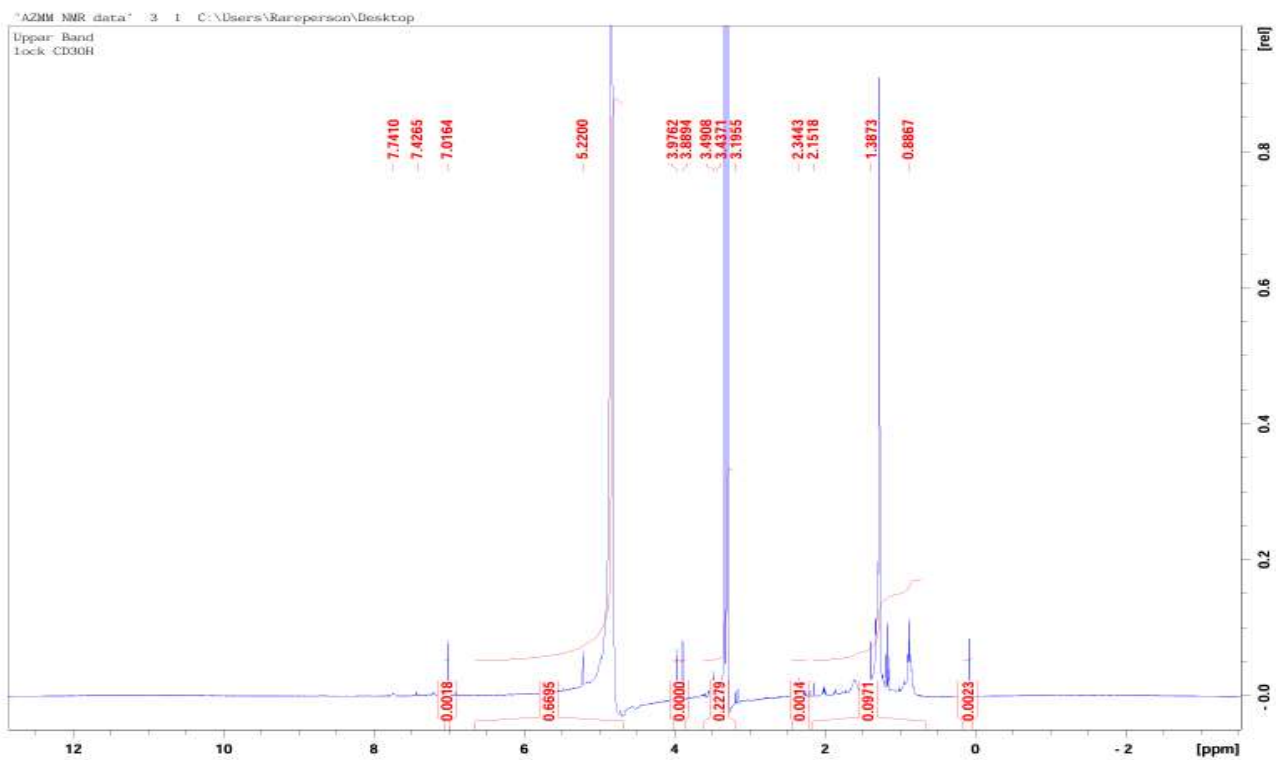
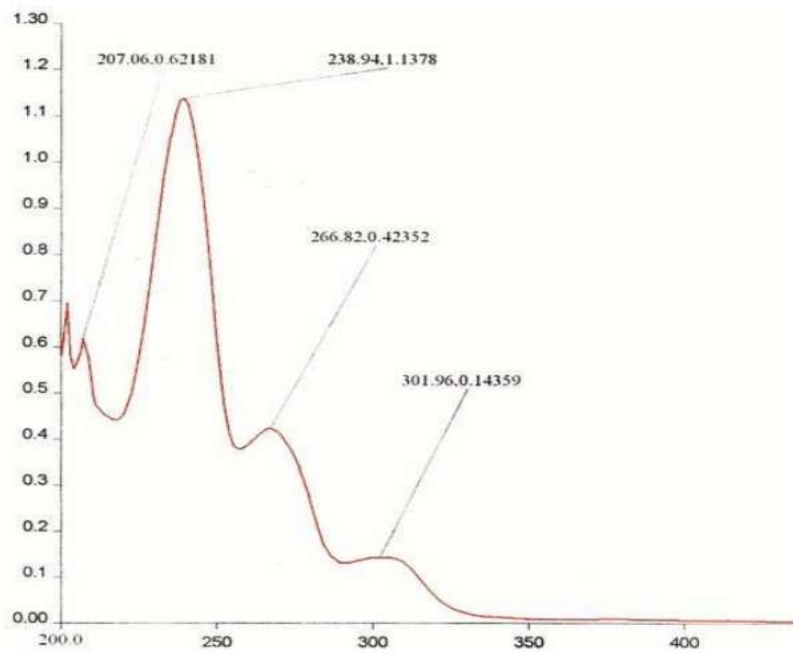


m/z 494  
C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>O<sub>8</sub>

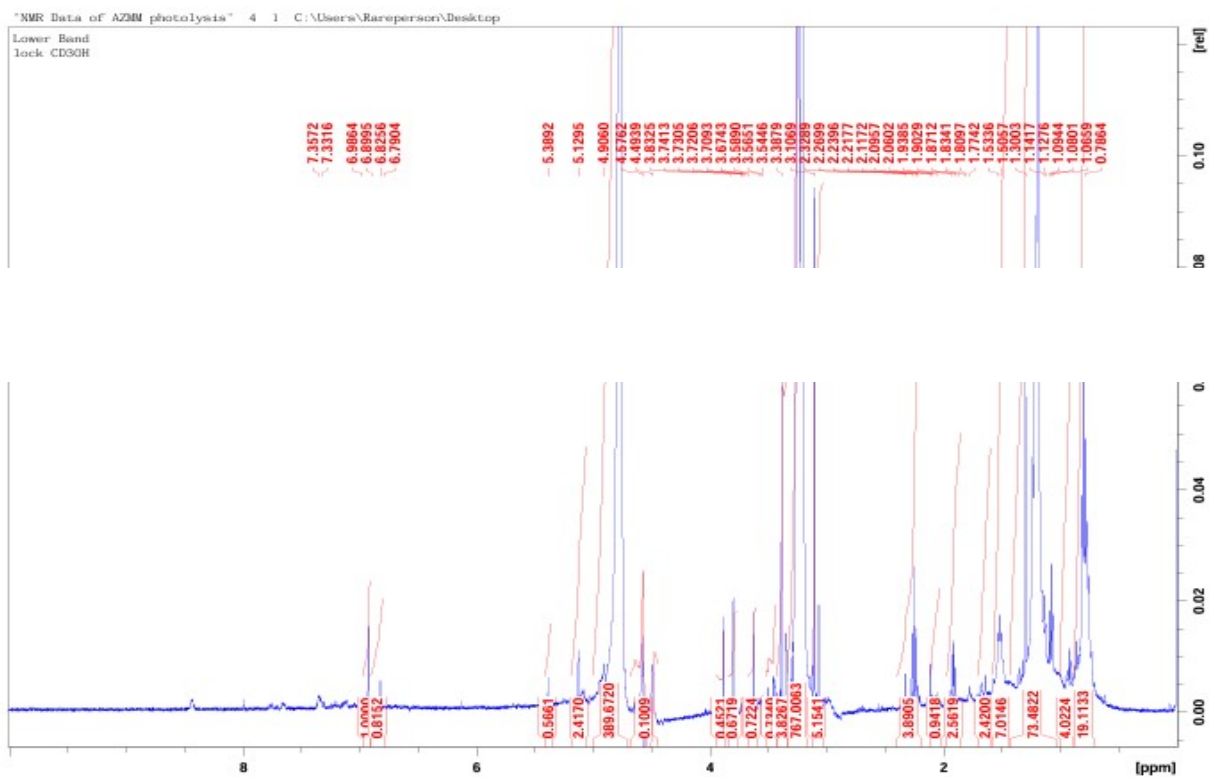


Sr. No	Fu
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ak Obtained



Sr. No	Functional Groups	Peaks Obtained
1.	-CH <sub>2</sub> present in lactone ring of azepine	4.76 (s)
2.	CH in azepine ring nearby CH <sub>2</sub> of the lactone	6.38 (s)
3.	-CH <sub>2</sub> present in lactone ring of aromatic ring	5.13 (s)
5.	CH of the five membered ring system	2.71 (s)
6.	-OCH <sub>3</sub> of aromatic ring	3.88(s)
7.	-OCH <sub>3</sub> of aromatic ring	3.80 (s)
8.	-OCH <sub>3</sub> of azepine	3.62(m)
9.	-OCH <sub>3</sub> of azepine	3.56(m)
10.	-CH of aromatic ring	6.82 (m)
11.	-CH in azepine ring nearby carbonyl of corresponding lactone ring	7.10 (m)
12.	-CH on -C=N- in the five membered ring	7.65(s)



1.	$\text{CH}_2$ in lactone of reduced azepine	5.13 (s)
2.	$\text{CH}_2$ in lactone aromatic	5.38 (t)
4.	asymmetric $-\text{CH}$ present in the reduced azepine system	2.71 (m)
5.	asymmetric $-\text{CH}$ present in the reduced azepine system	3.06 (m)
6.	$\text{O}-\text{CH}_3$ (Methoxy in aromatic System)	3.80 (s)
7.	$\text{O}-\text{CH}_3$ (Methoxy in aromatic System)	3.88 (s)
8.	$\text{O}-\text{CH}_3$ (Methoxy in reduced azepine ring)	3.50(s)
9.	$\text{O}-\text{CH}_3$ (Methoxy in reduced azepine ring)	3.51 (s)
10.	$\text{CH}$ present nearby methoxy group in the reduced azepine ring	6.1 (m)
11.	$-\text{CH}$ present next to the nitrogen outside the aromatic system	7.35 (m)
12.	$\text{CH}_2$ next to the nitrogen atom inside reduced azepine system	2.32 (m)
13.	$\text{CH}_2$ next to the nitrogen atom inside reduced azepine system	2.56 (m)
14.	$-\text{CH}$ present in the reduced azepine system nearby fused lactone ring	3.21 (m)
15.	$-\text{CH}$ present in the aromatic system	6.82 (m)

