Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supporting Informations

Syntheses, Optical and Intramolecular Magnetic Properties of Mono- and Di-Nitronyl Nitroxide and Oxoverdazyl Radicals Appended to 2,6-Bispyrazolylpyridine Core

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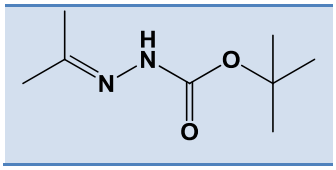
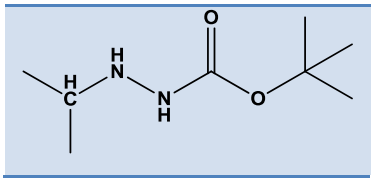
GENERAL EXPERIMENTAL PROCEDURES:

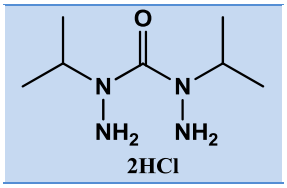
Synthesis of tert-Butyl-2-isopropenylhydrazenecarboxylate (16). Tert-butoxy carbazate (2.0 g, 15.1 mmol) was added to dry acetone (10 ml) at rt and stir for 12 h. The resulting mixture was evaporated to get white precipitate. Yield 2.0 g (73%). ^{1}H NMR (400MHz, $CDCl_3$ 27°C), δ_H = 1.38 (9H, s), 1.94 (6H, s), 7.0 (1H, s) ppm.



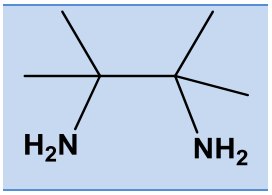
Synthesis of tert-Butyl-2-isopropylhydrazenecarboxylate (17). Sodium borohydride (1 g, 26.5 mmol) was added to (**16**) (1.5 g, 5.29 mmol) in ethanol (150 ml) and the mixture was refluxed for 6 h. The resulting mixture was evaporated, and 60 ml of water and 23.3 ml of 1 M HCl aq. was added to the residue. The crude product was extracted with dichloromethane and purified by recrystallization from dichloromethane/ hexane. Yield: 1.0 g (66%) ^{1}H NMR (400MHz, $CDCl_3$ 27°C), 1.07(6H, d, J=2.8), 1.38(9H, s,tert-butyl), 2.0(1H, t), 2.97(1H, sept), 1.0 (1H, d) ppm.



2,4-diisopropylcarbono-hydrazide bis-hydrochloride: Synthesized from **17** as per the reported procedure by Parè et al. [Ref.: Parè, E. C.; Brook, D. J. R.; Brieger, A.; Badik, M.; Schinke, M. *Org. Biomol. Chem.*, **2005**, *3*, 4258-4261.]



2,3-diamino-2,3-dimethylbutane: Synthesized from 2,3-dinitro-2,3-dimethylbutane as per the reported procedure by Ray et al. [Ref. Hirel, C.; Vostrikova, K. E.; Pècaut, J.; Ovcharenko, V. I.; Rey, P. *Chem. -Eur. J.* **200**1, *7*, 2008].



ESR Spectroscopic Analysis:

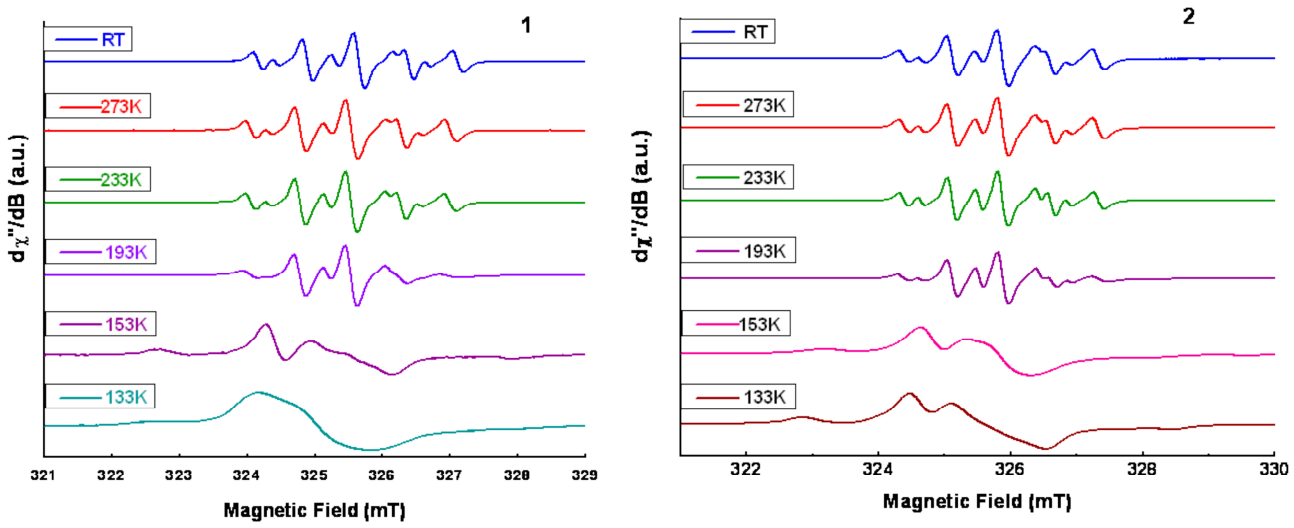


FIGURE S 1. ESR spectra (Δms = ± 1) of **1** and **2** at (c = 10^{-3} M in toluene) 298 – 133 K

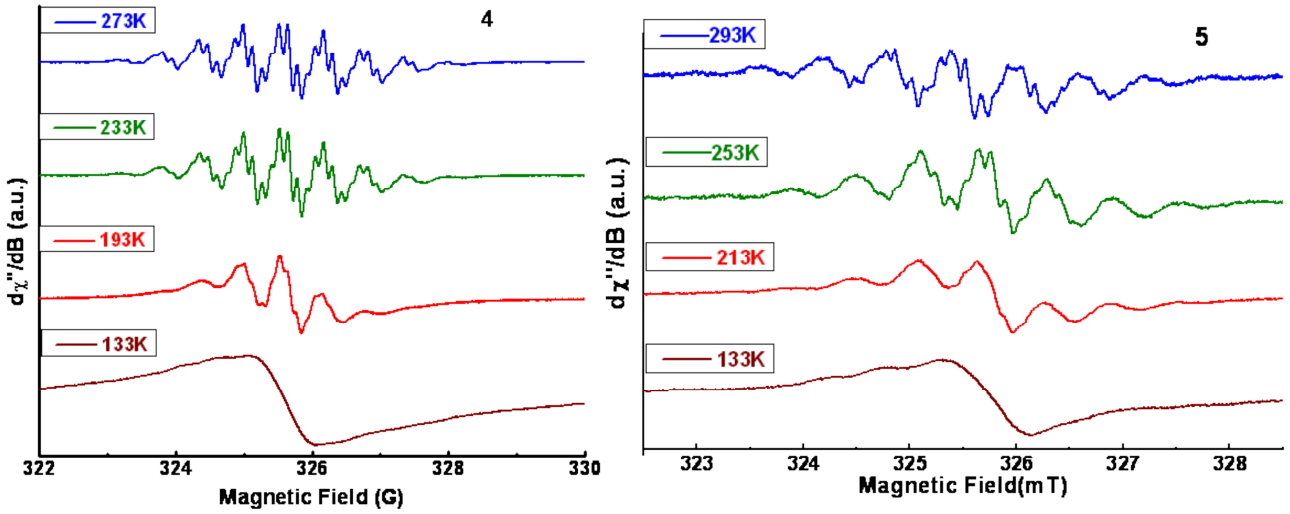


FIGURE S 2. ESR spectra (Δms = ± 1) of **4** and **5** at (c = 10^{-3} M in toluene) 273 – 133 K.

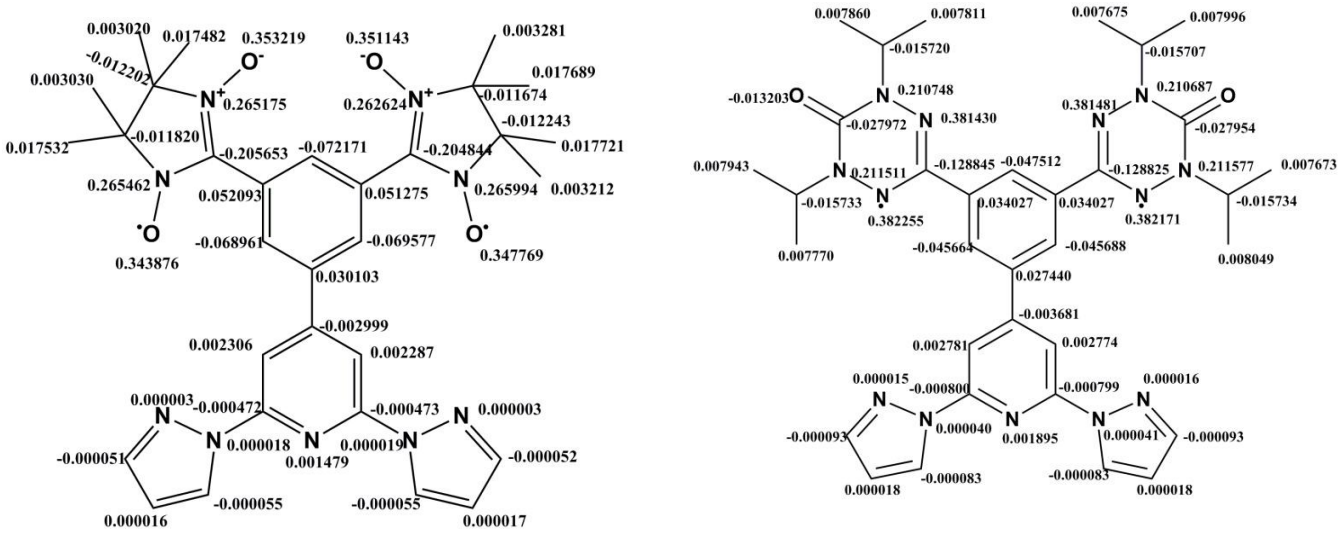


FIGURE S3. Atomic spin density distribution for biradicals **3** and **6** (DFT; B3LYP /6–31+G(d)).

TABLE S1. Singlet-Triplet splitting (ΔE_{ST}) (DFT; B3LYP /6–31+G(d); T*he* values are in kJ/mol.)

Molecule geometry	Compound 3	Compound 6
$\theta_1 = \theta_2 = 0°$	126.2135	110.8310
$\theta_1 = 0°$, $\theta_2 = -10$	123.0737	110.9310
$\theta_1 = 10°$, $\theta_2 = -10°$	120.5419	110.6955
$\theta_1 = 20°$, $\theta_2 = -20°$	120.9216	109.9480
$\theta_1 = 10°$, $\theta_2 = 0°$	120.7462	111.0150

Table S2. Crystal data and structure refinement for **1** (**CCDC**: 768145)

Empirical formula	$C_{24}H_{24}N_7O_2$
Formula weight	442.50
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 14.584(2) A alpha = 90 deg. b = 10.5609(14) A beta = 109.665(2) deg. c = 15.240(2) A gamma = 90 deg.
Volume	2210.4(5) $Å^3$
Z, Calculated density	4, 1.330 Mg/m^3
Absorption coefficient	0.089 mm^{-1}
F(000)	932
Crystal size	0.36 x 0.22 x 0.16 mm
Theta range for data collection	1.48 to 26.04 deg.
Limiting indices	-17<=h<=18, -12<=k<=13, -18<=l<=18
Reflections collected / unique	22106 / 4347 [R(int) = 0.0980]
Completeness to theta = 26.04	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9859 and 0.9686
Refinement method	Full-matrix least-squares on F_2
Data / restraints / parameters	4347 / 0 / 302
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0651, wR2 = 0.1373
R indices (all data)	R1 = 0.1084, wR2 = 0.1542
Largest diff. peak and hole	0.321 and -0.332 $e.Å^{-3}$

checkCIF/PLATON report

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No errors found in this datablock

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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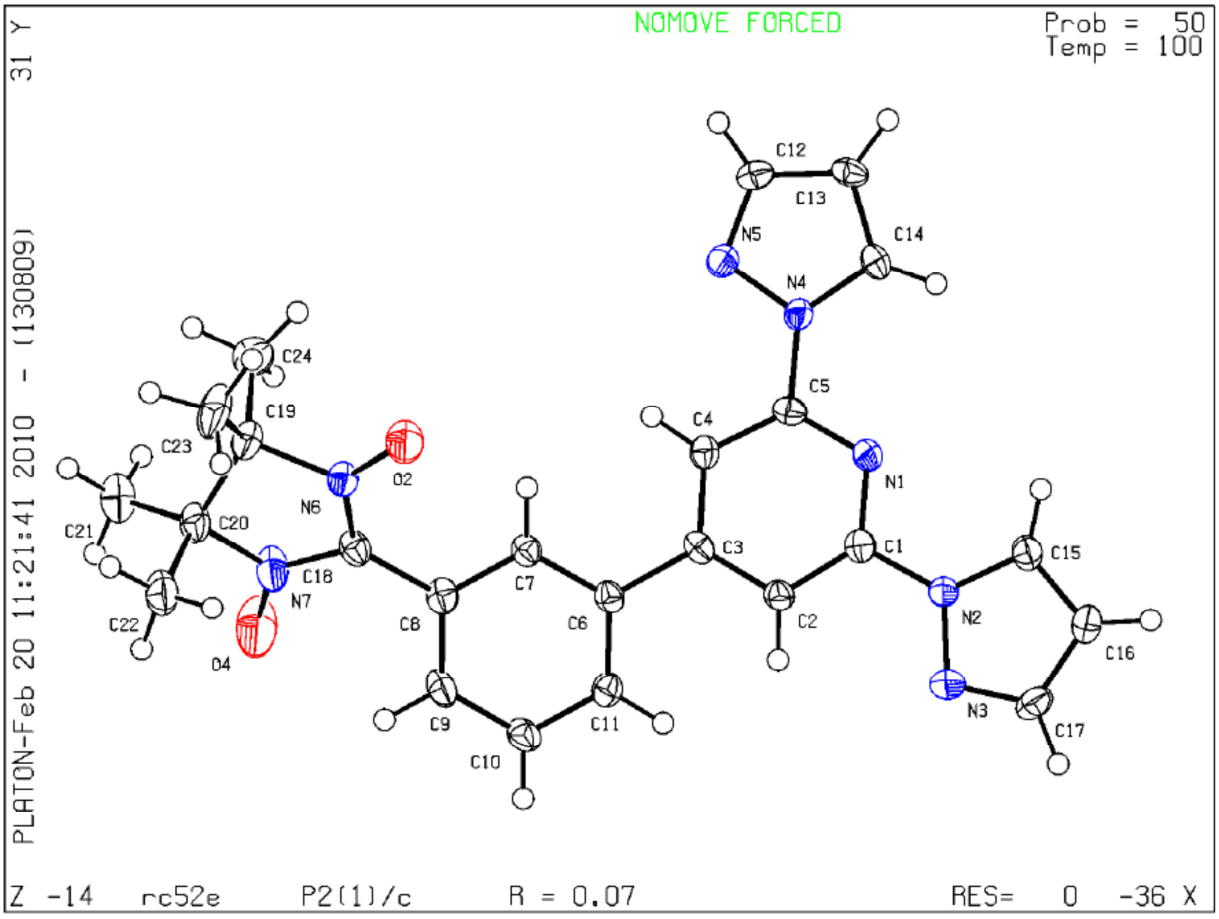


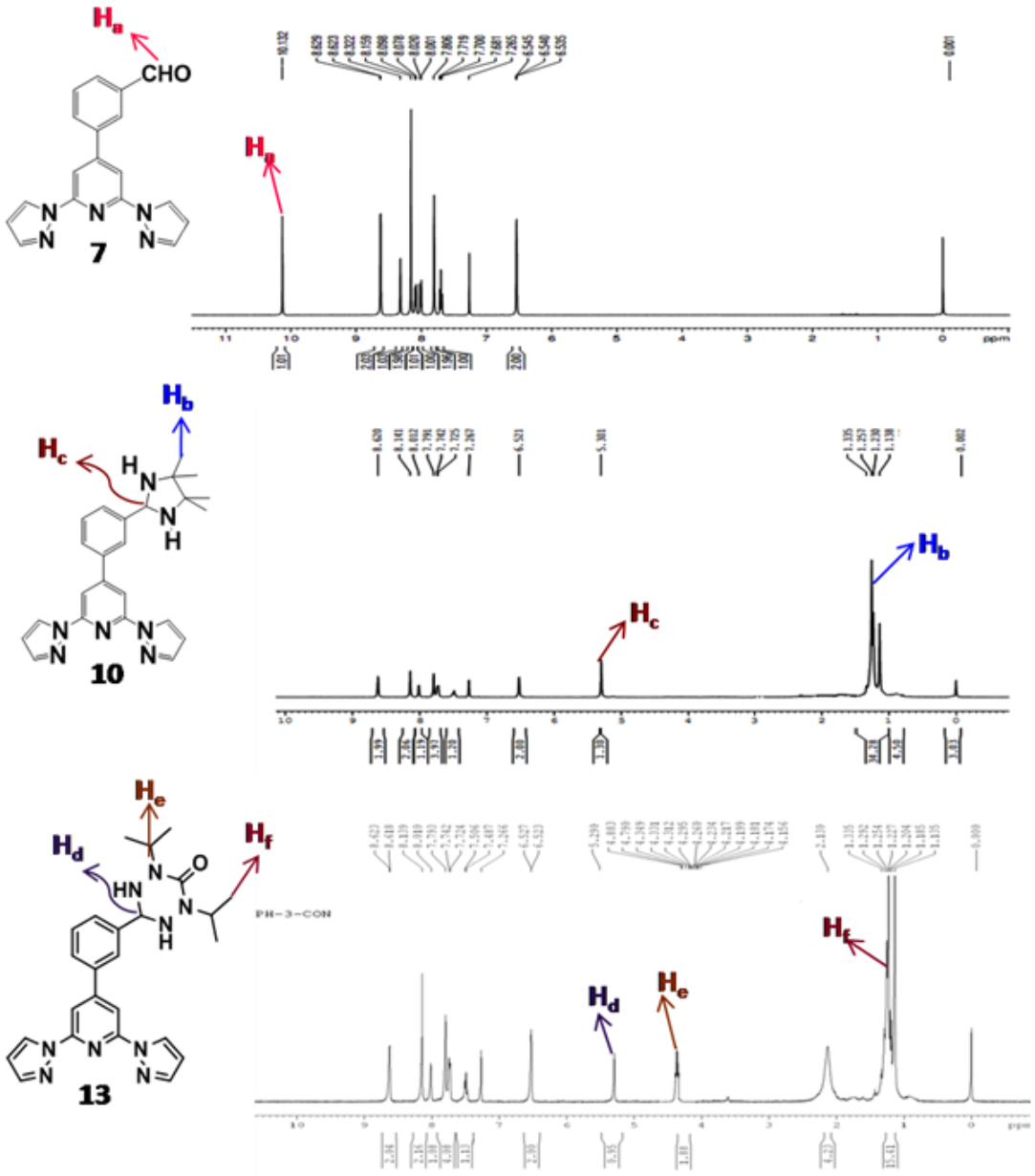


FIGURE S6: Comparative ^{1}H-NMR spectra of radical precursors **10** and **13** obtained from the corresponding aldehyde **7**.

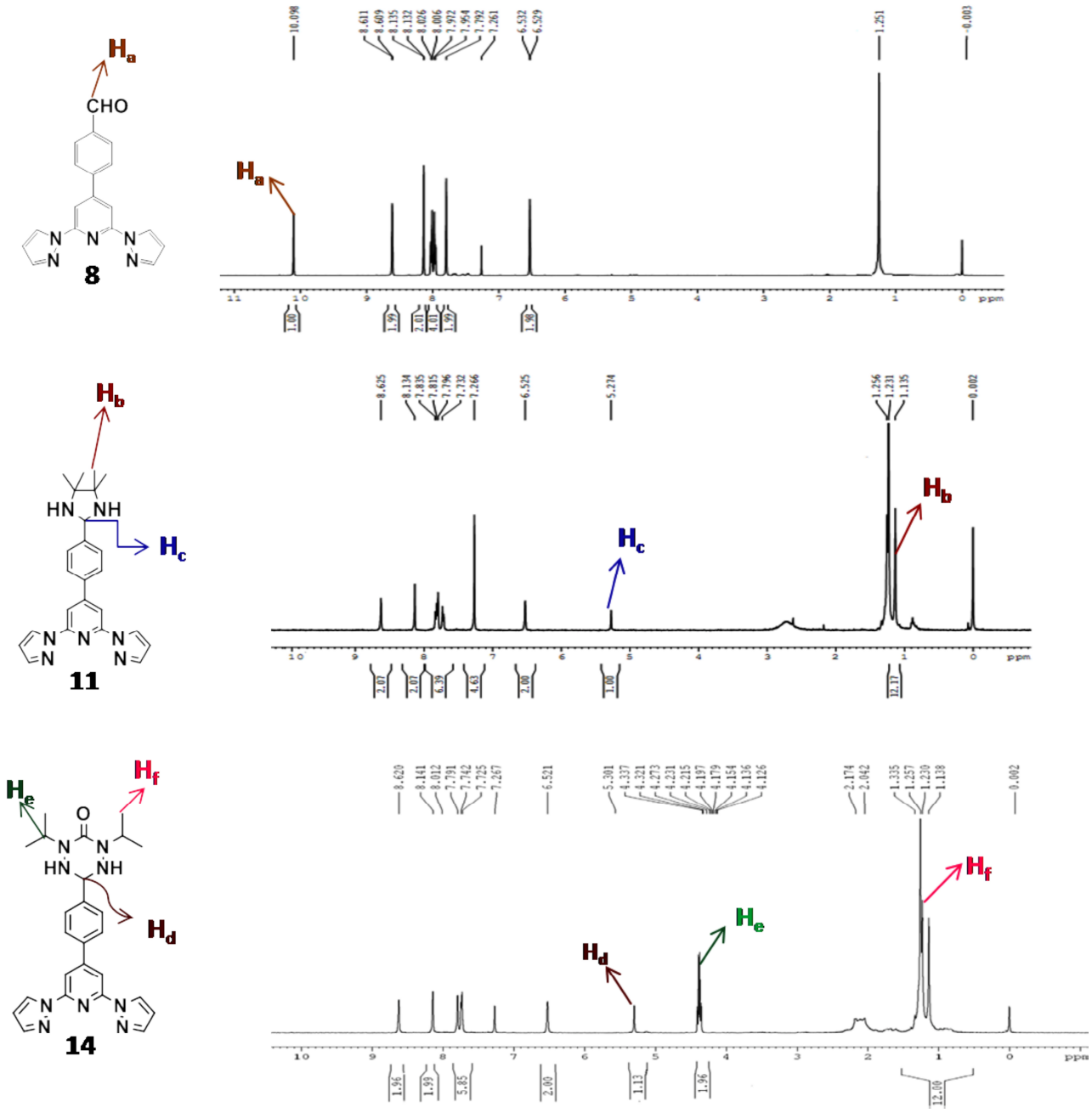
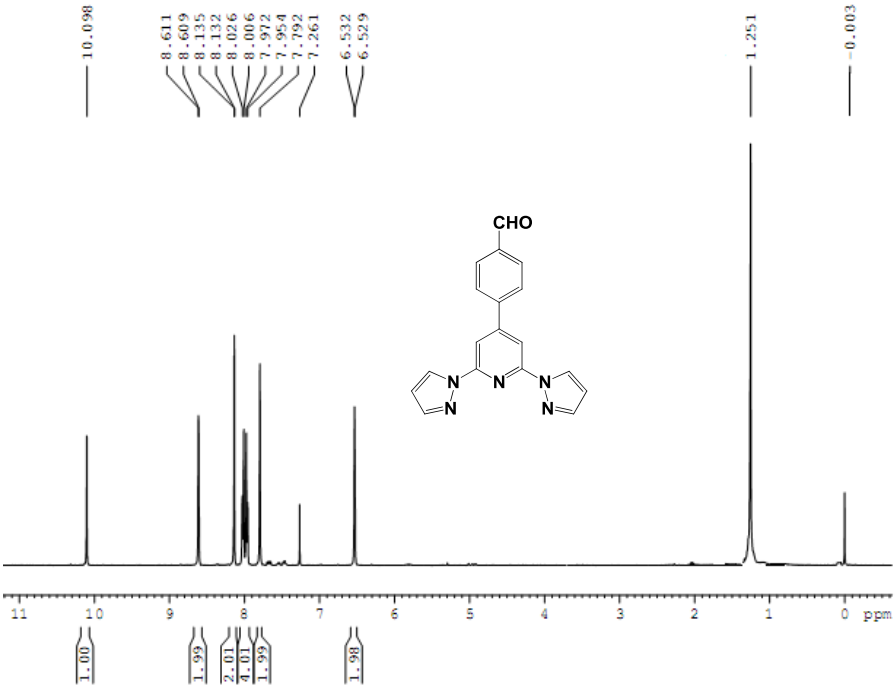
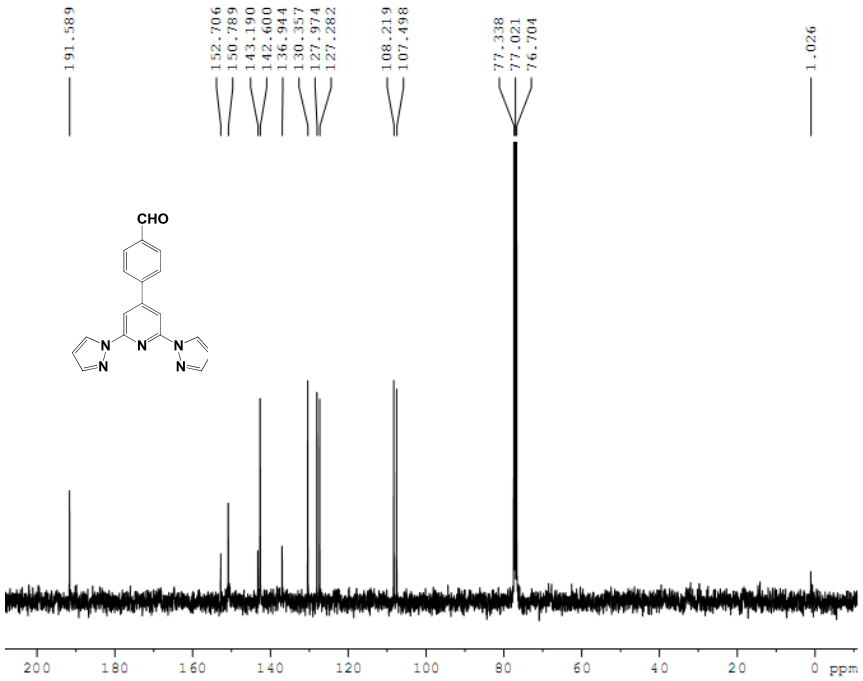
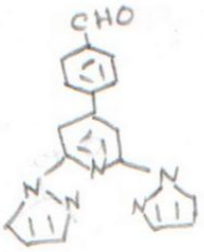


FIGURE S7: Comparative ^{1}H-NMR spectra of radical precursors **11** and **14** obtained from the corresponding aldehyde **8**.







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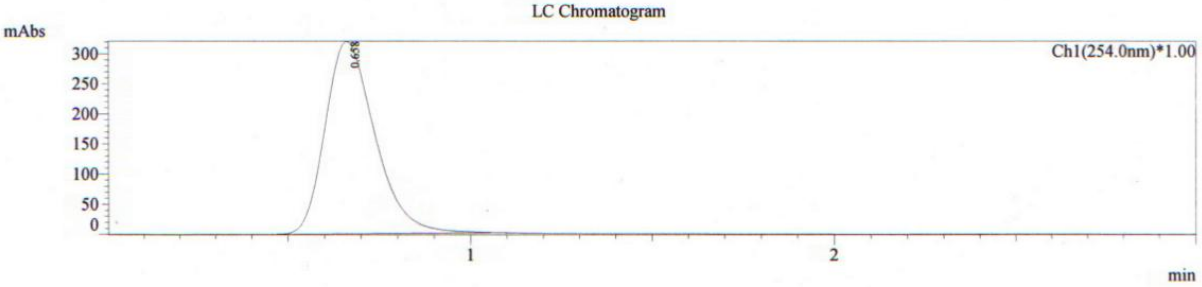

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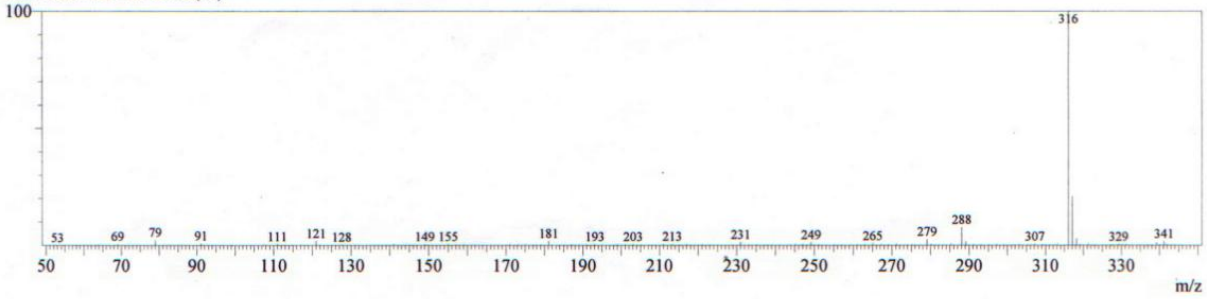

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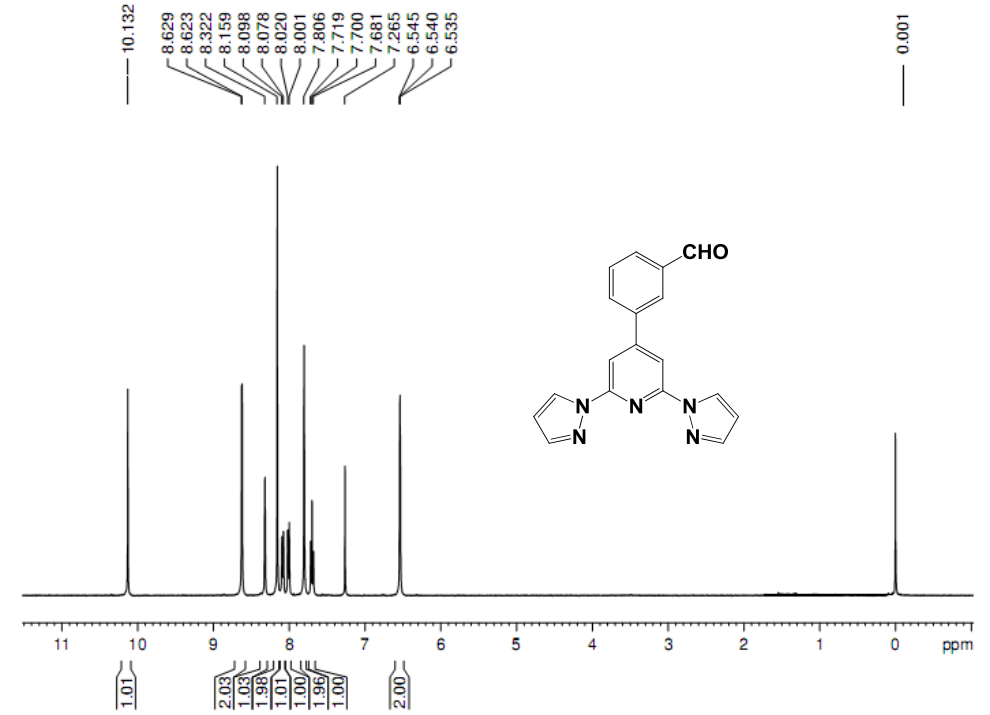
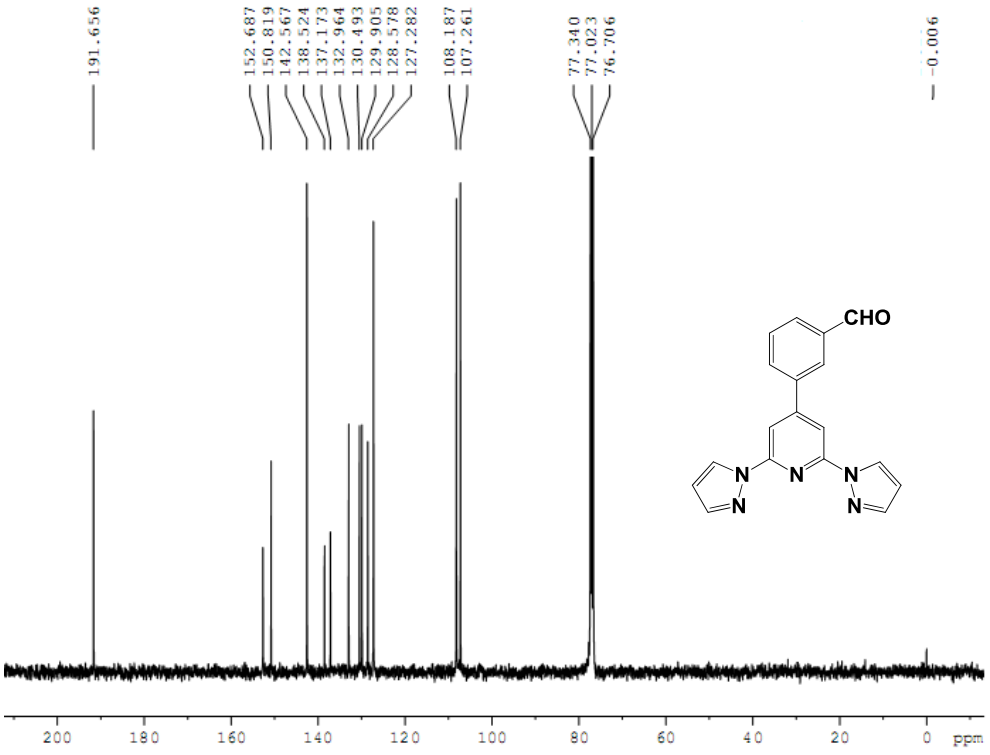
OPERATOR





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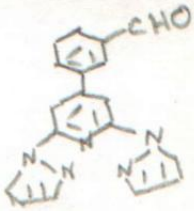

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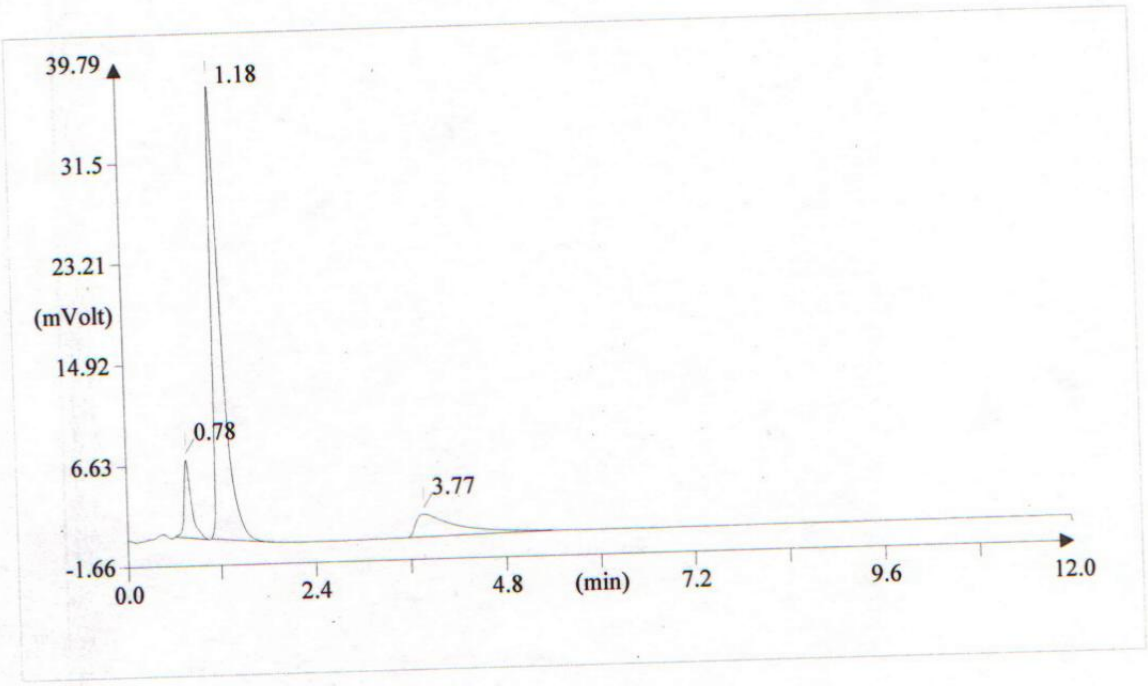

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Carbon	68. 65	1. 18
Hydrogen	4. 09	3. 77

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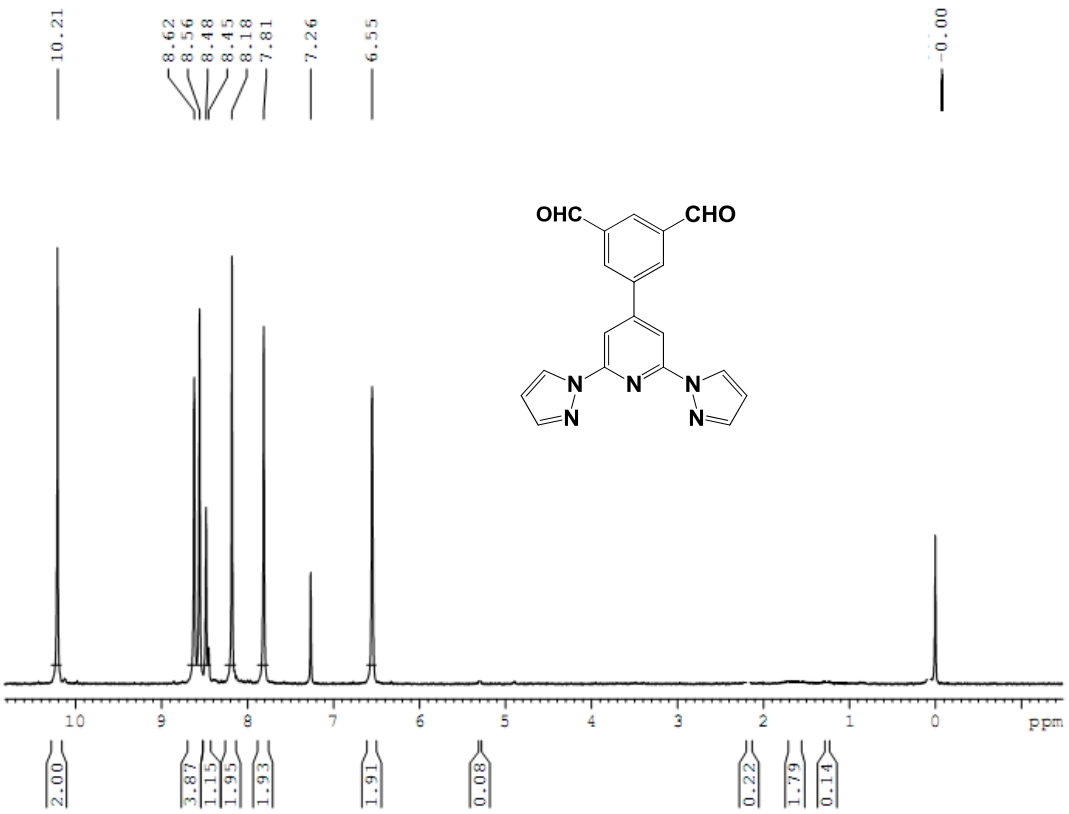

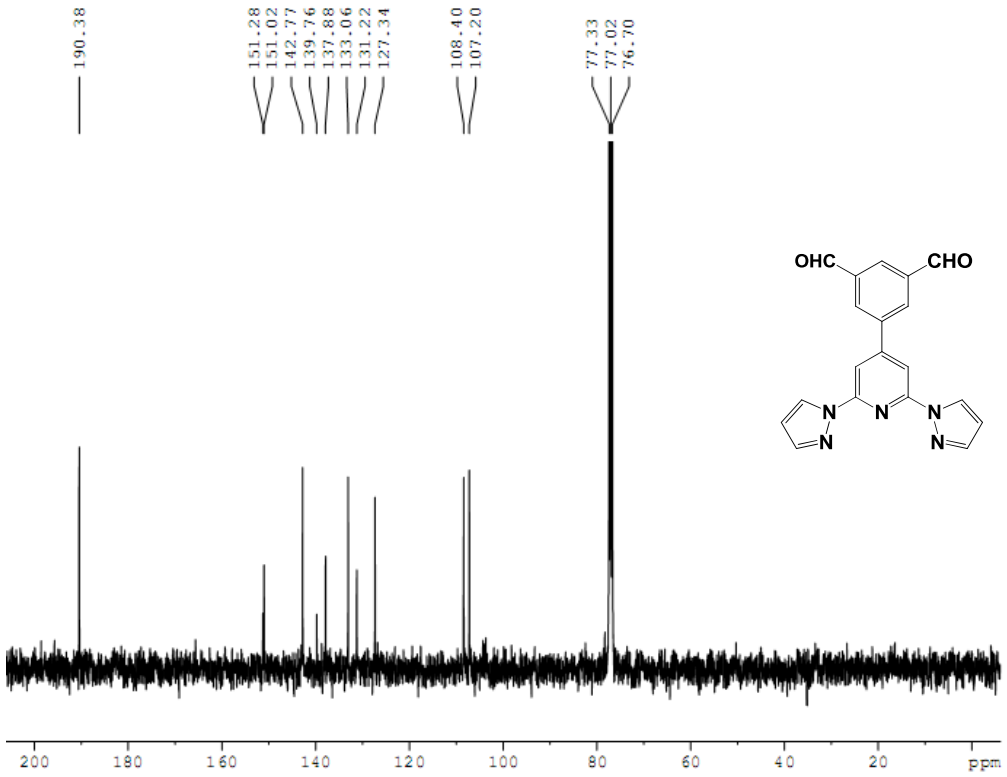

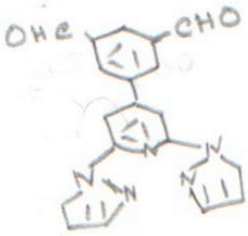

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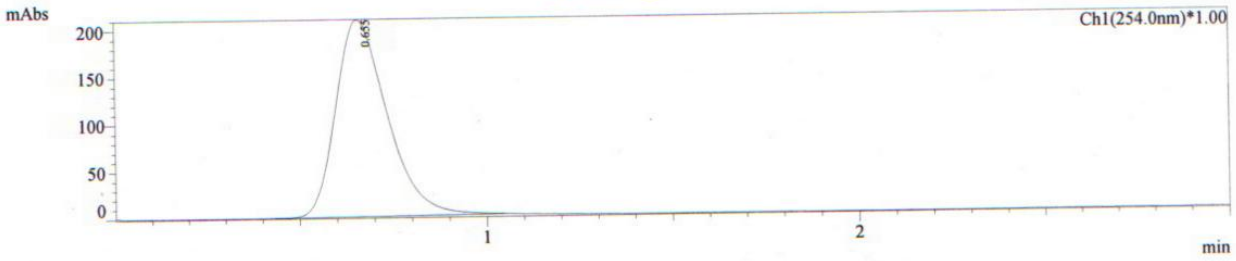

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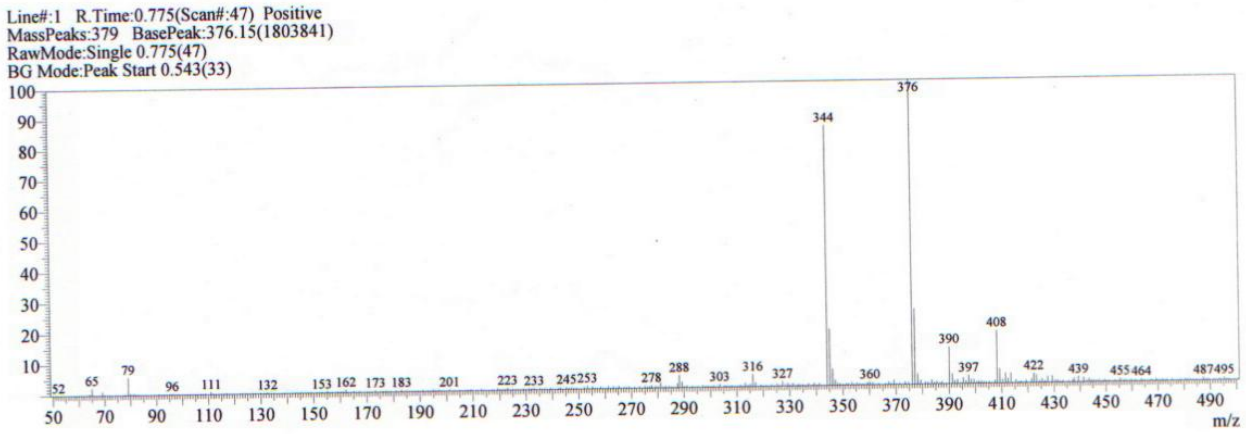

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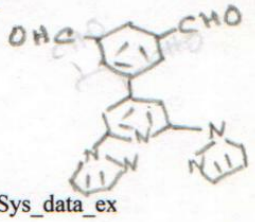

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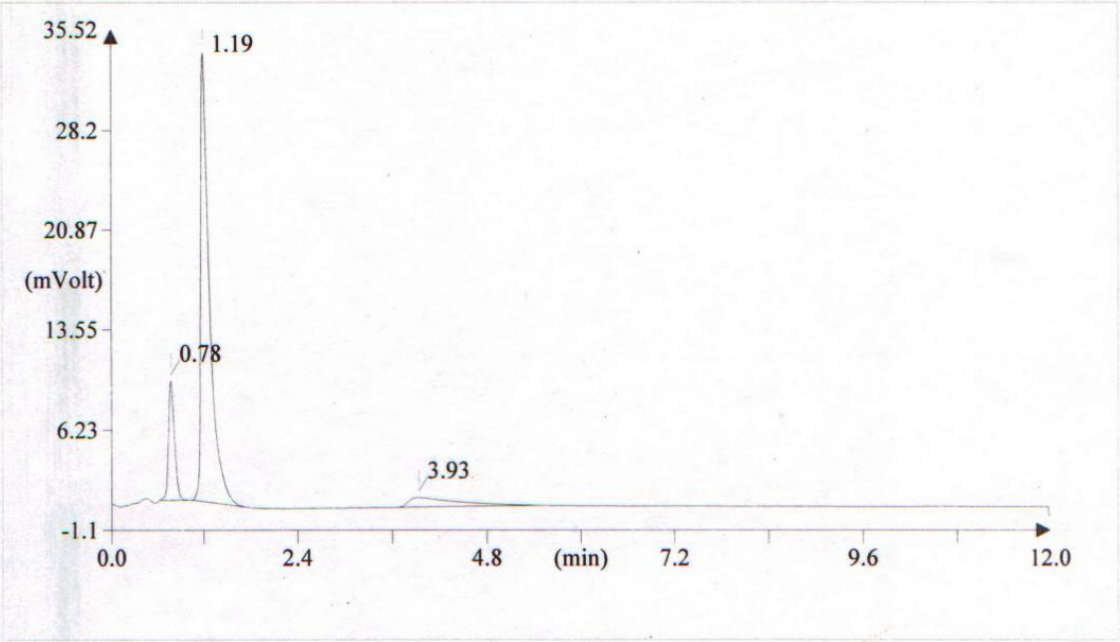

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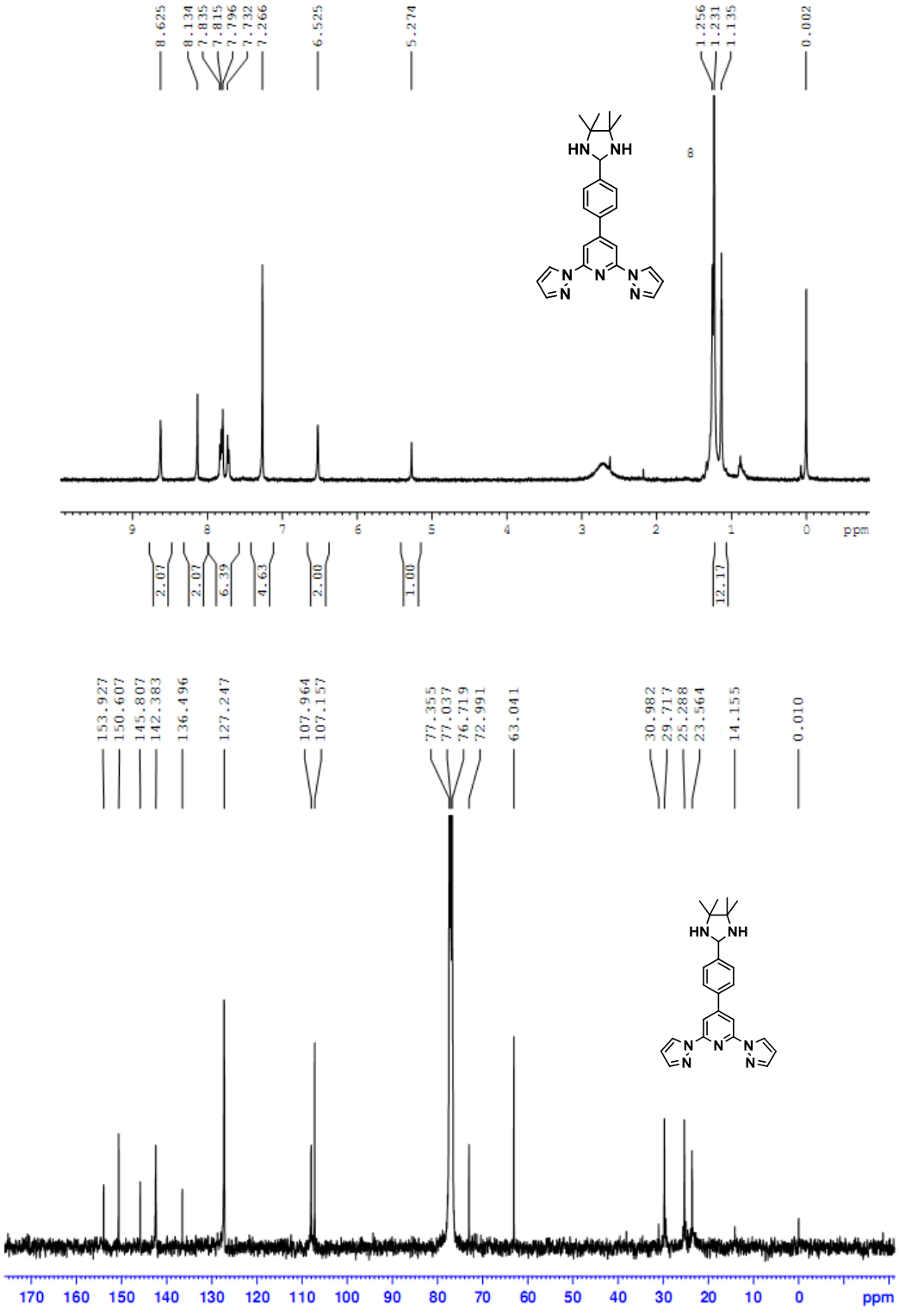
Carbon	66. 32	1. 19
Hydrogen	3. 88	3. 93



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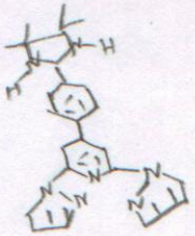

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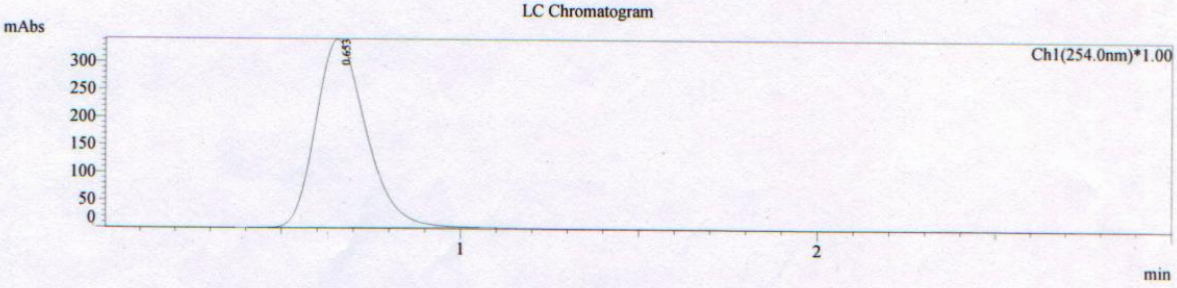

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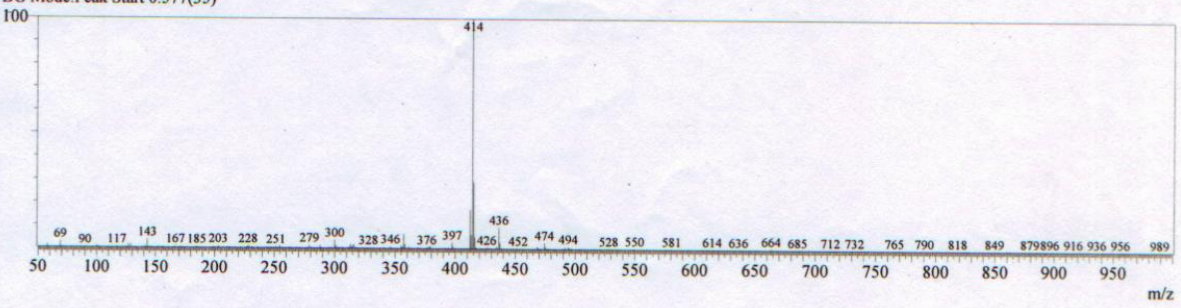

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OPERATOR

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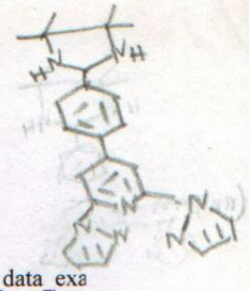

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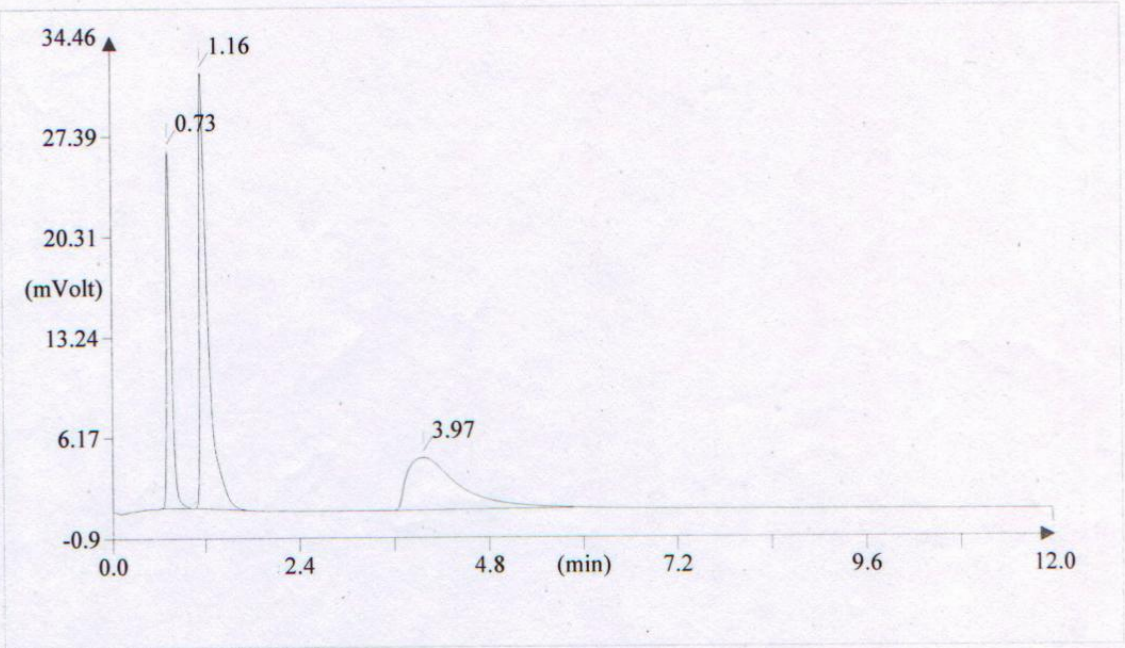

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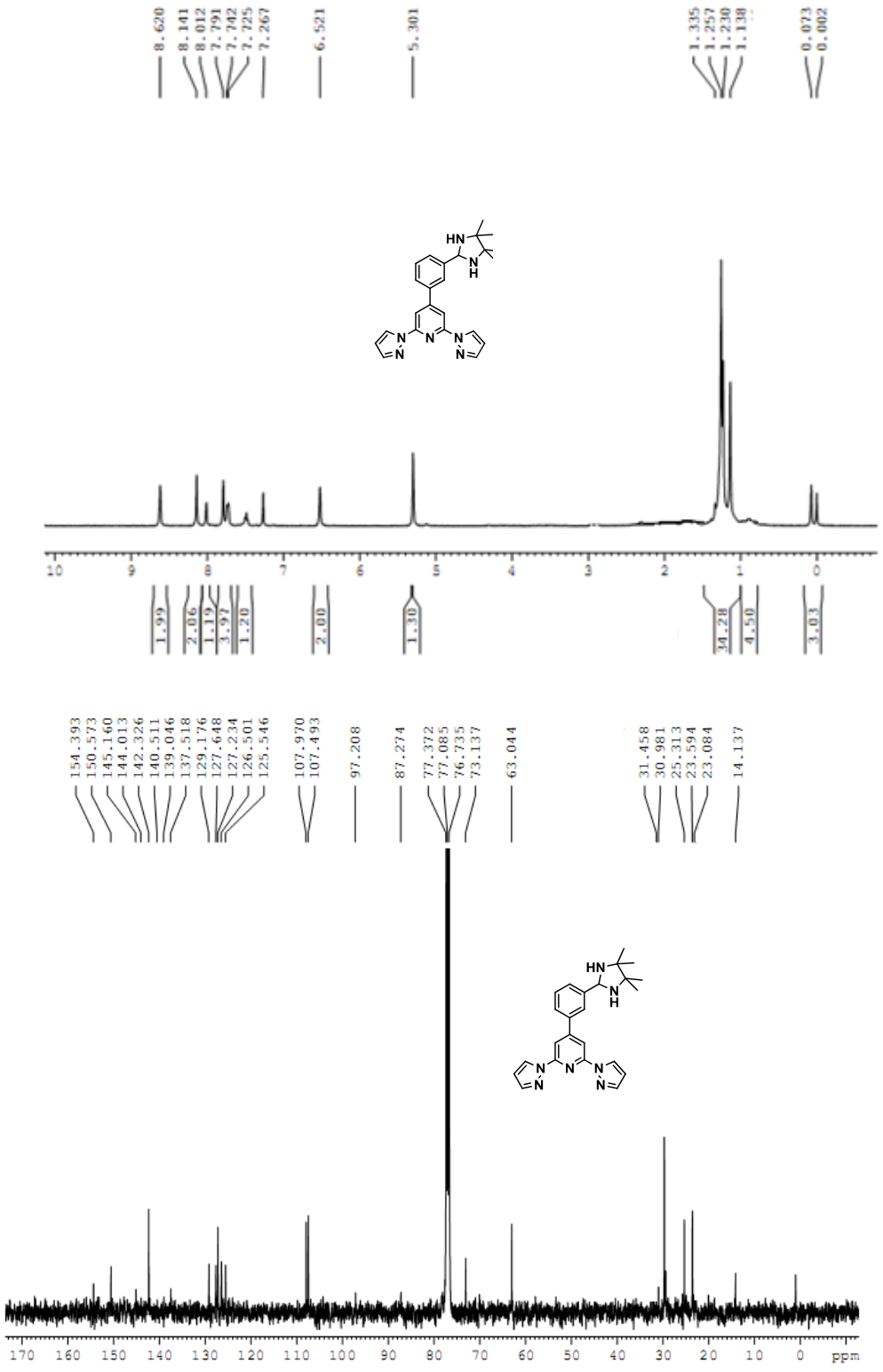

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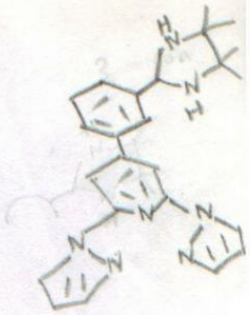

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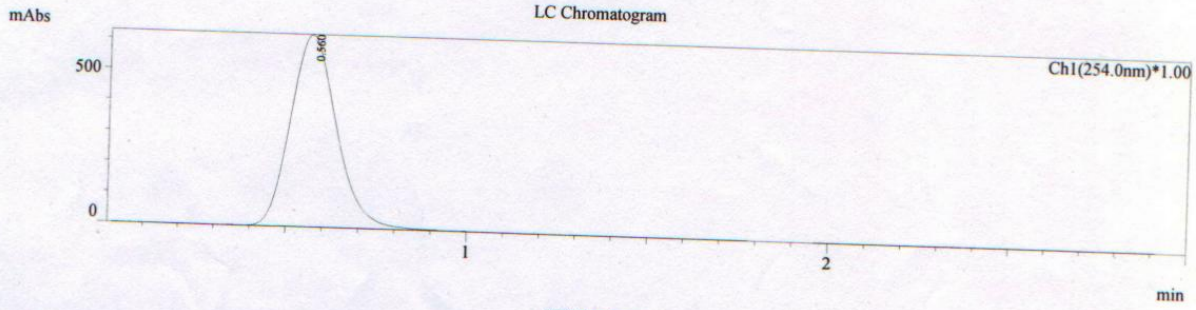

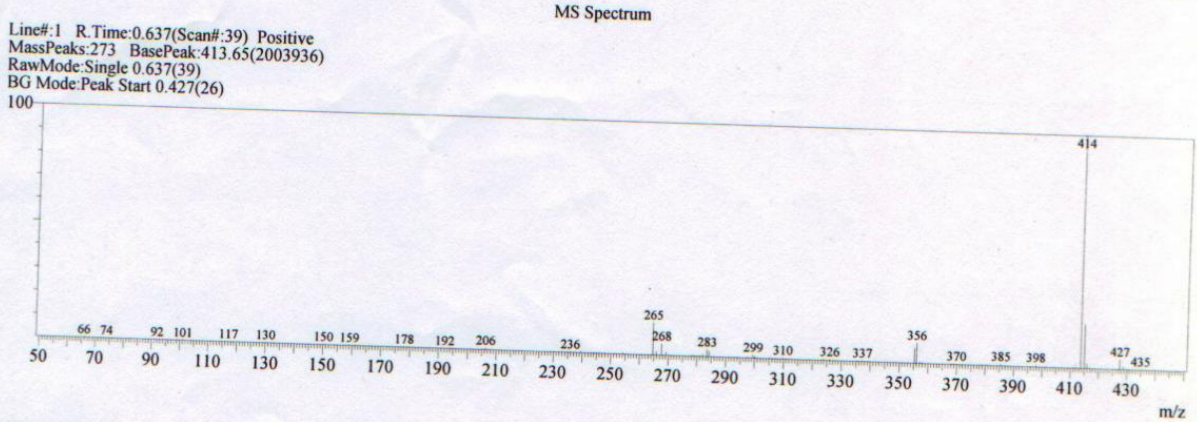

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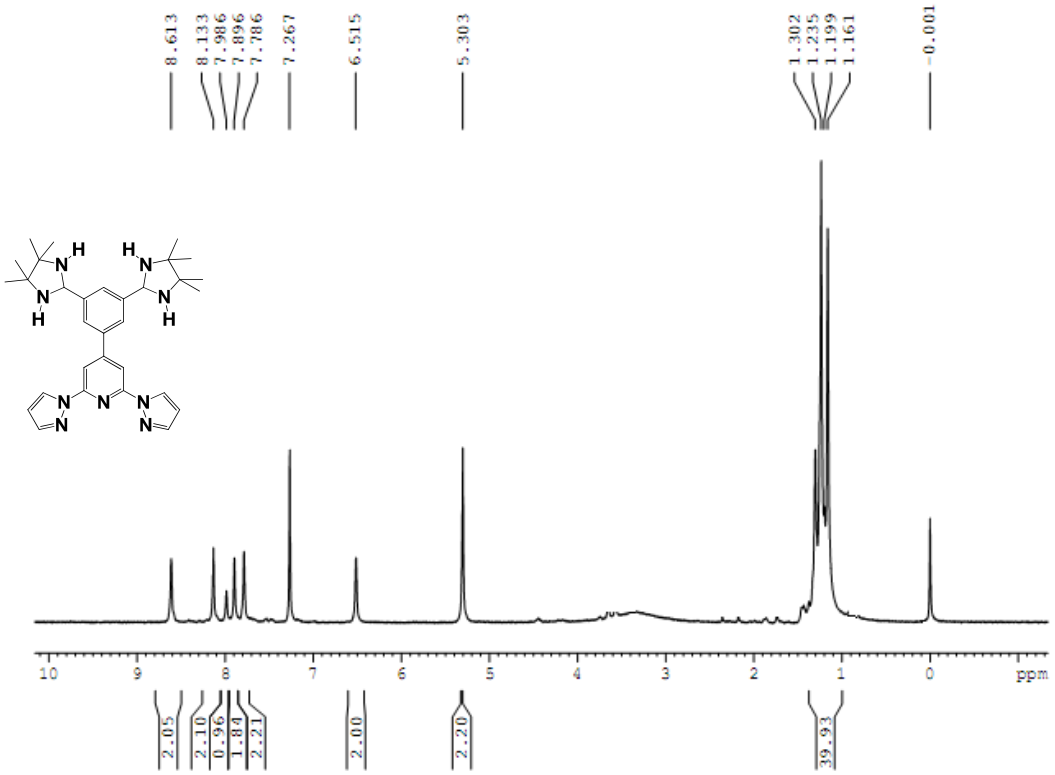
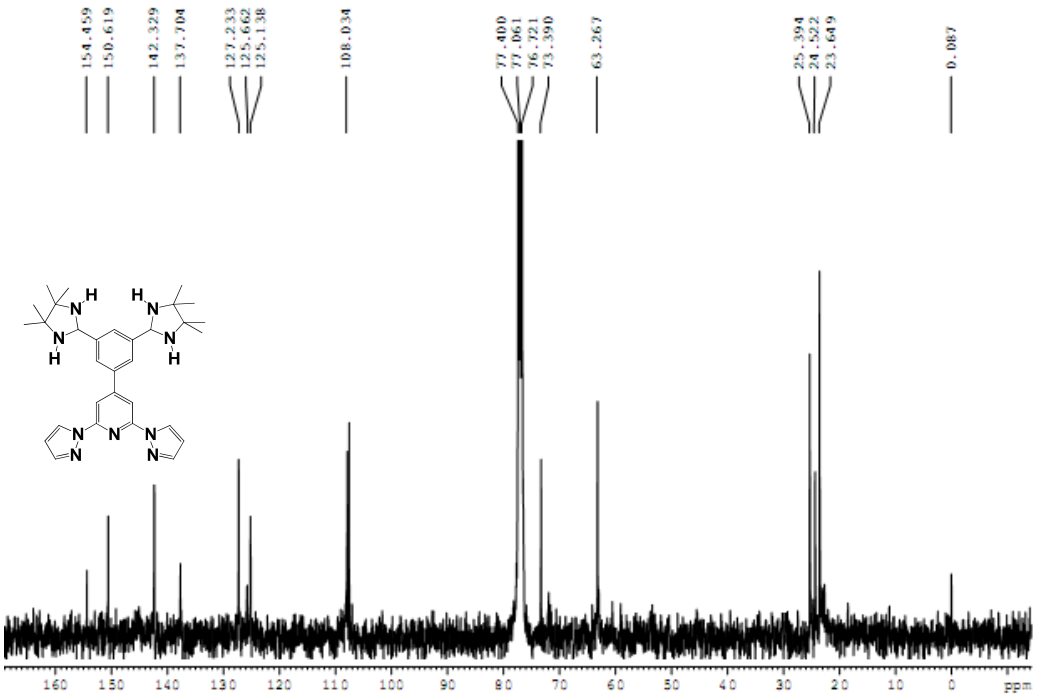
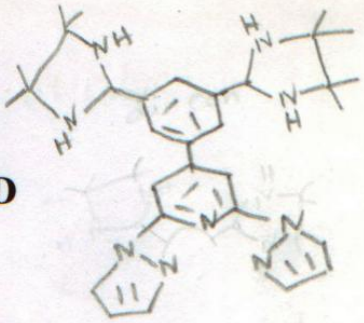
OPERATOR







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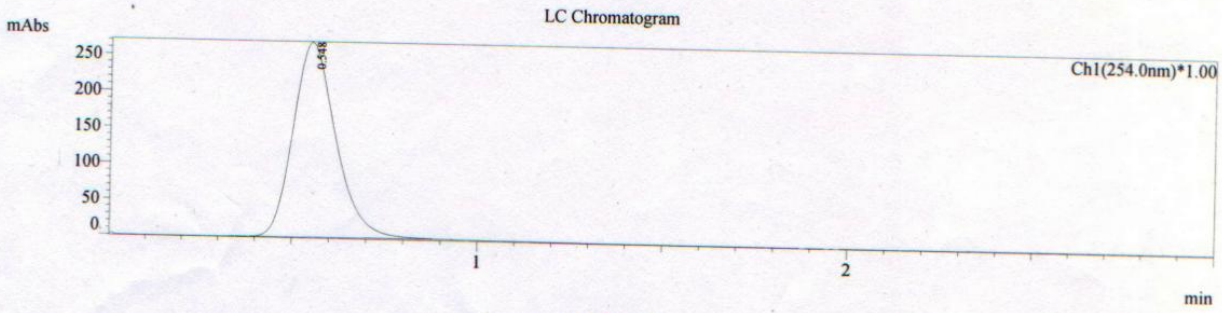
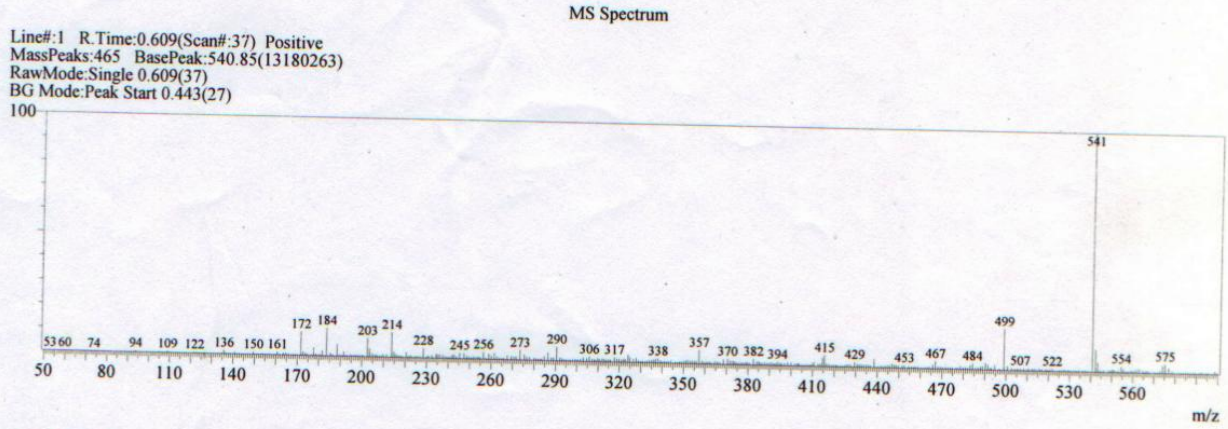
Method Name : C:\LCMSsolution\User\Method\Copy of JAY-4-APCI.qlm





MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name	Base m/z	Base Int.
1	0.609	0.443	0.843	863222857	88407493	9.76		100.00		540.85	13180263
				863222857	88407493			100.00			

OPERATOR

FLASH EA 1112 SERIES CHN REPORT
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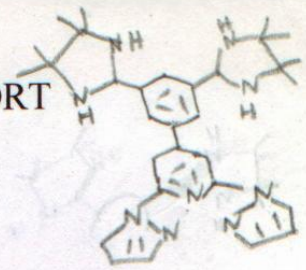
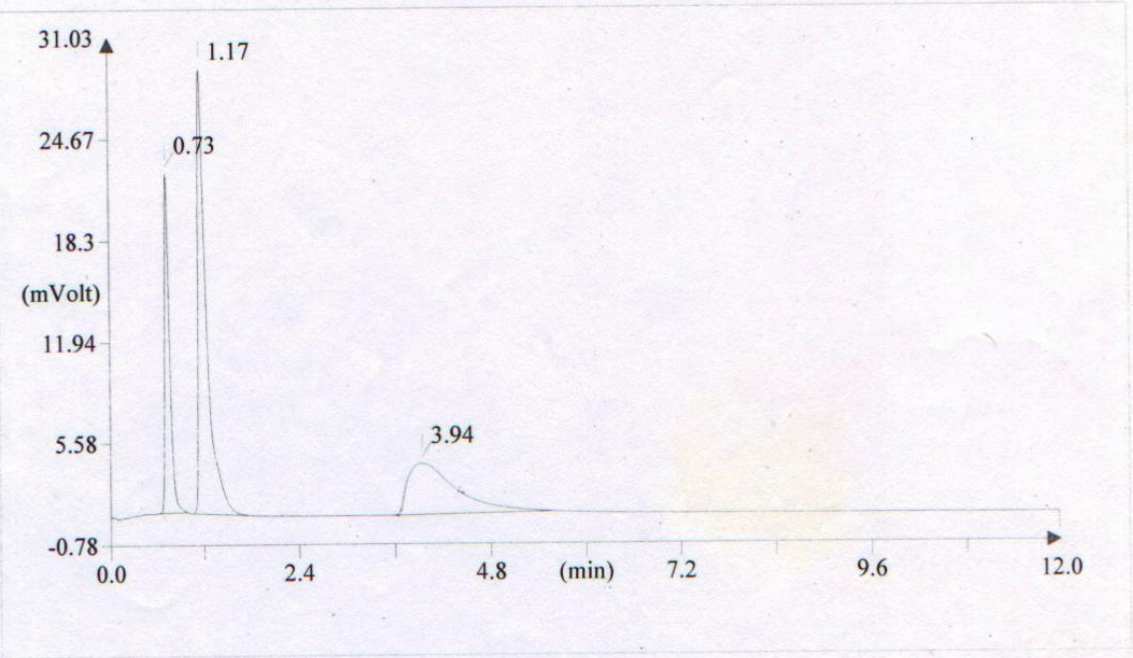
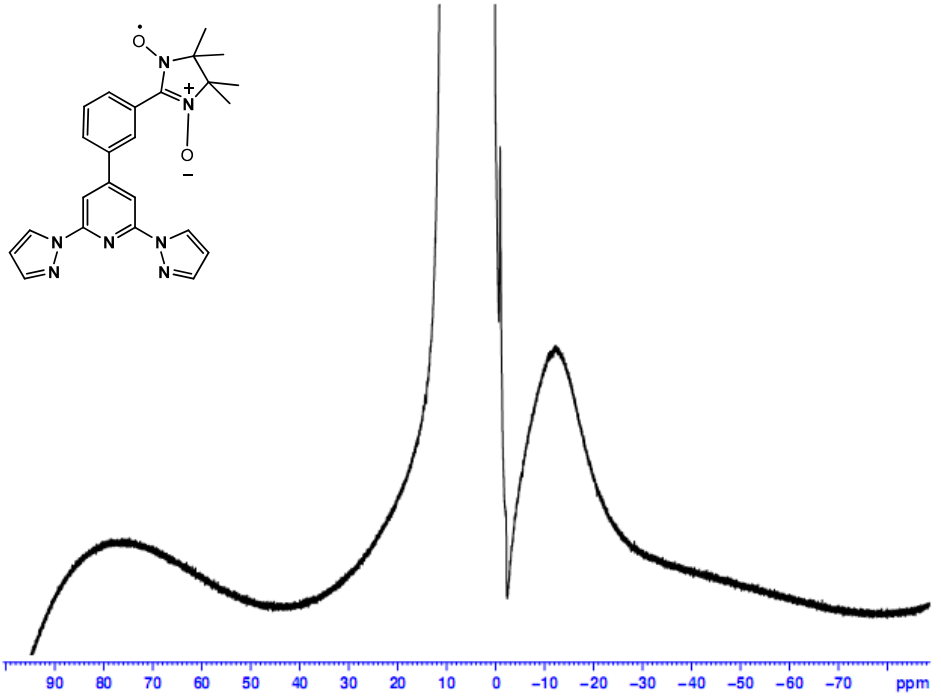
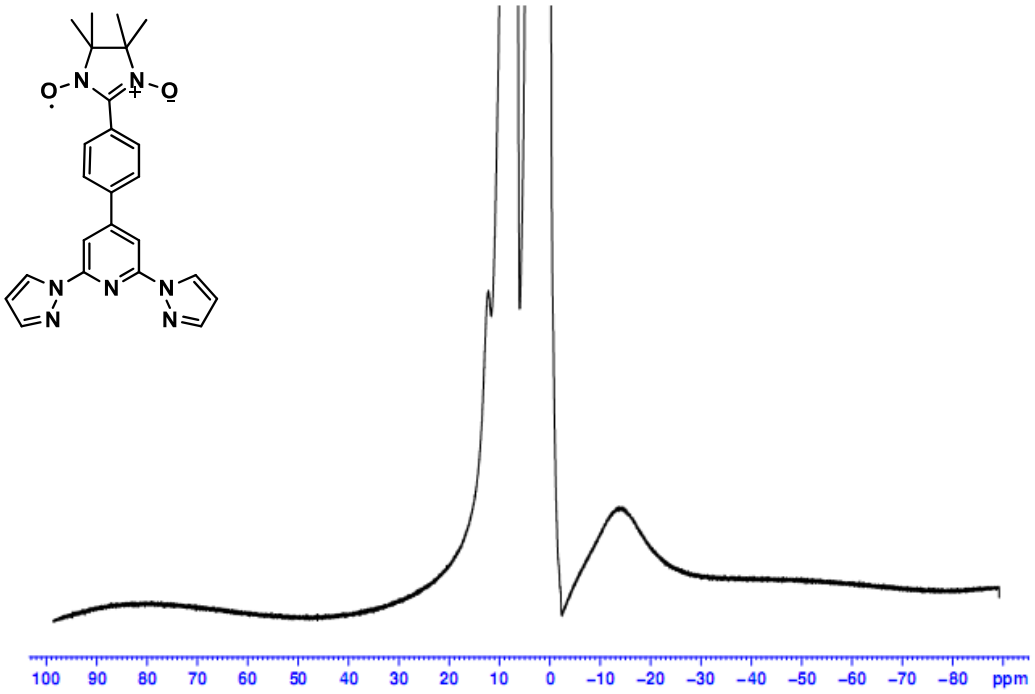


Method filename:	I:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_exa
Sample ID:	PHE-4 (# 47)
Analysis type:	UnkNown
Chromatogram filename:	UNK-29012010-1.dat
Sample weight:	.985

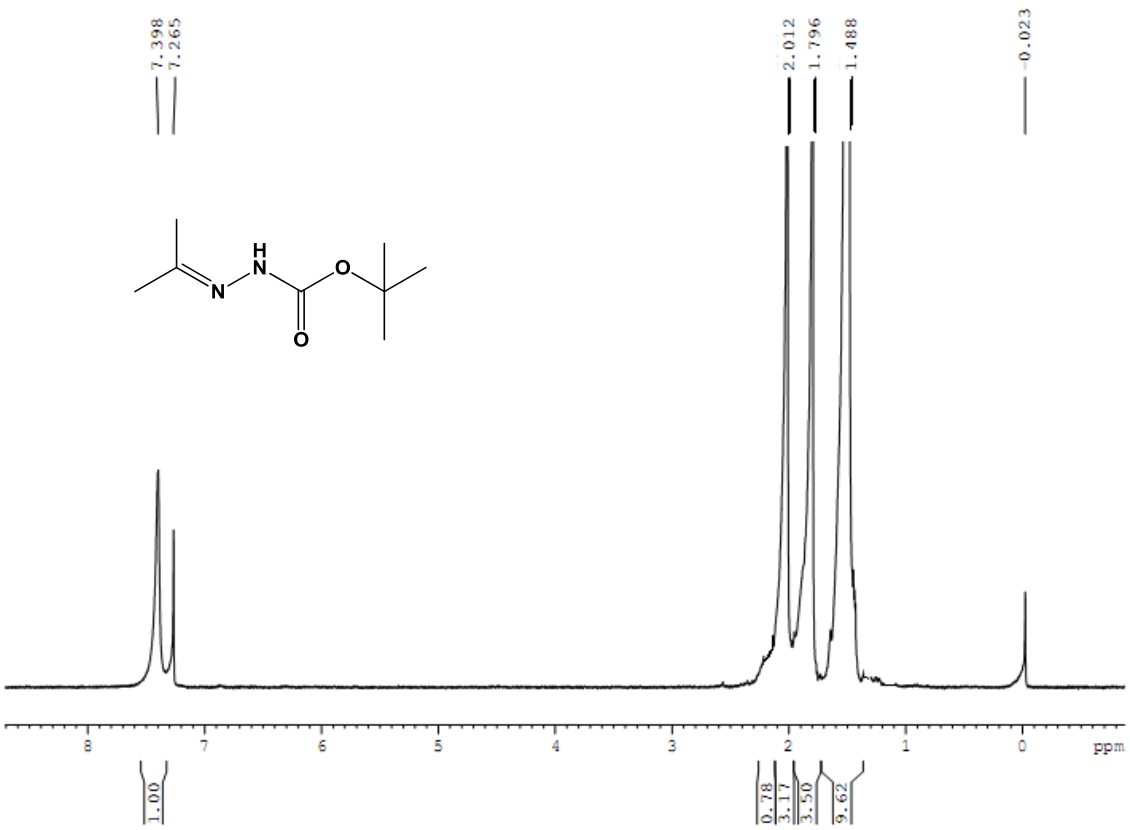


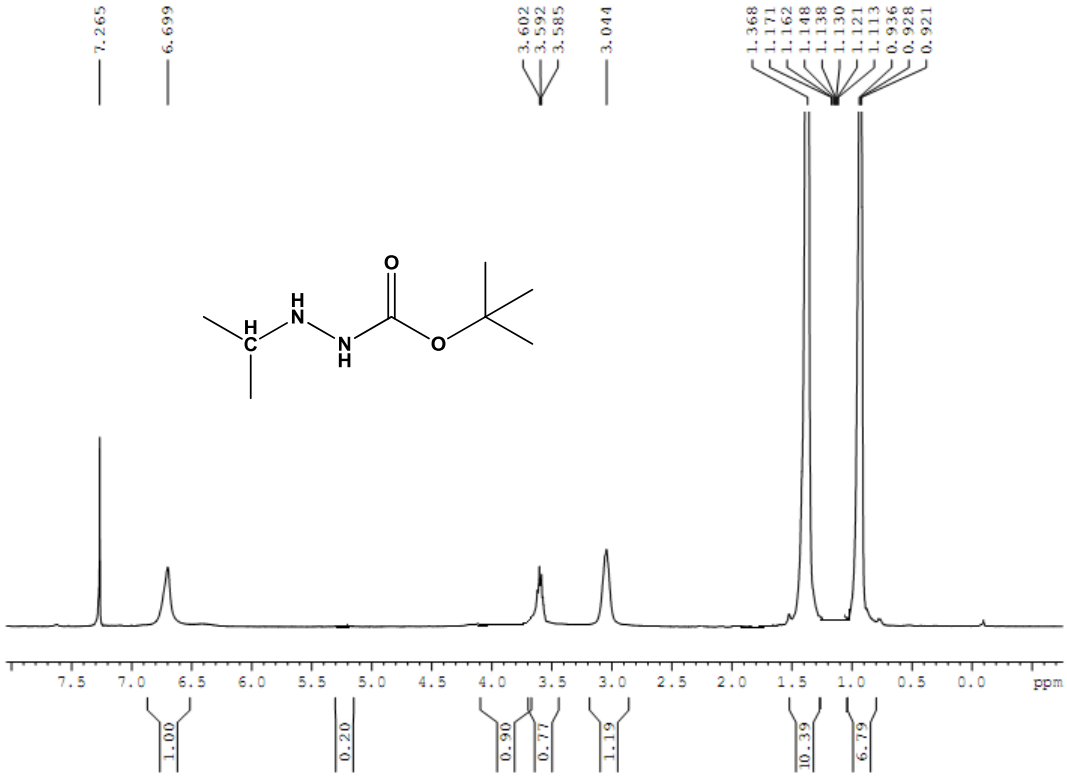
Element Name	Element %	Ret. Time
Nitrogen	24. 31	0. 73
Carbon	68. 81	1. 17
Hydrogen	7. 58	3. 94

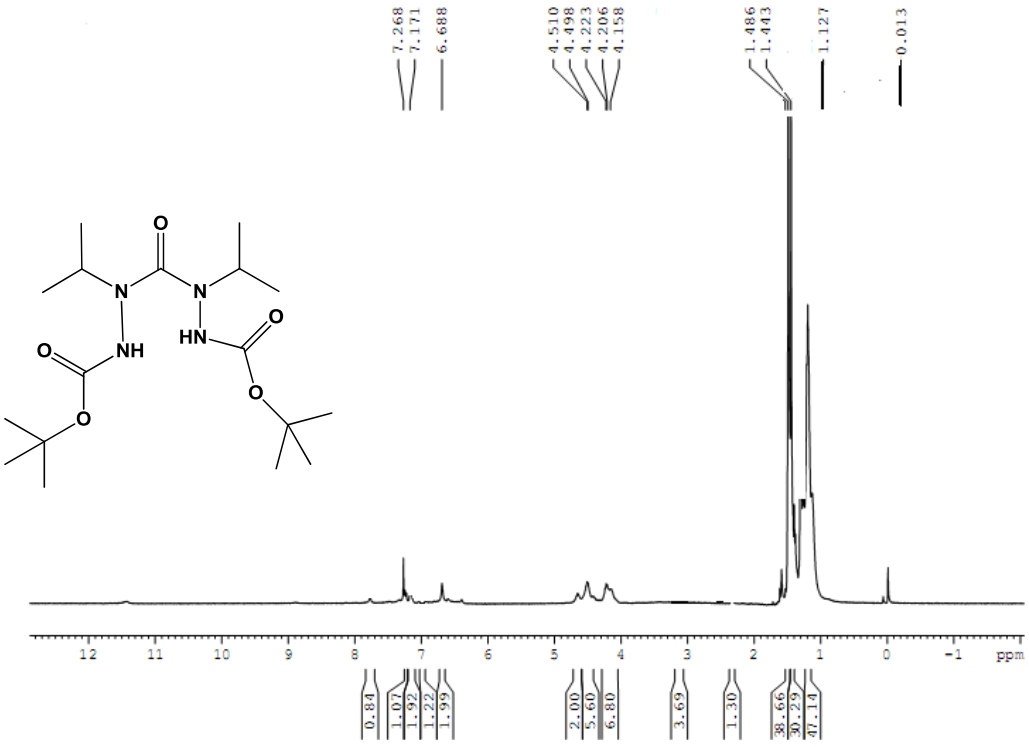


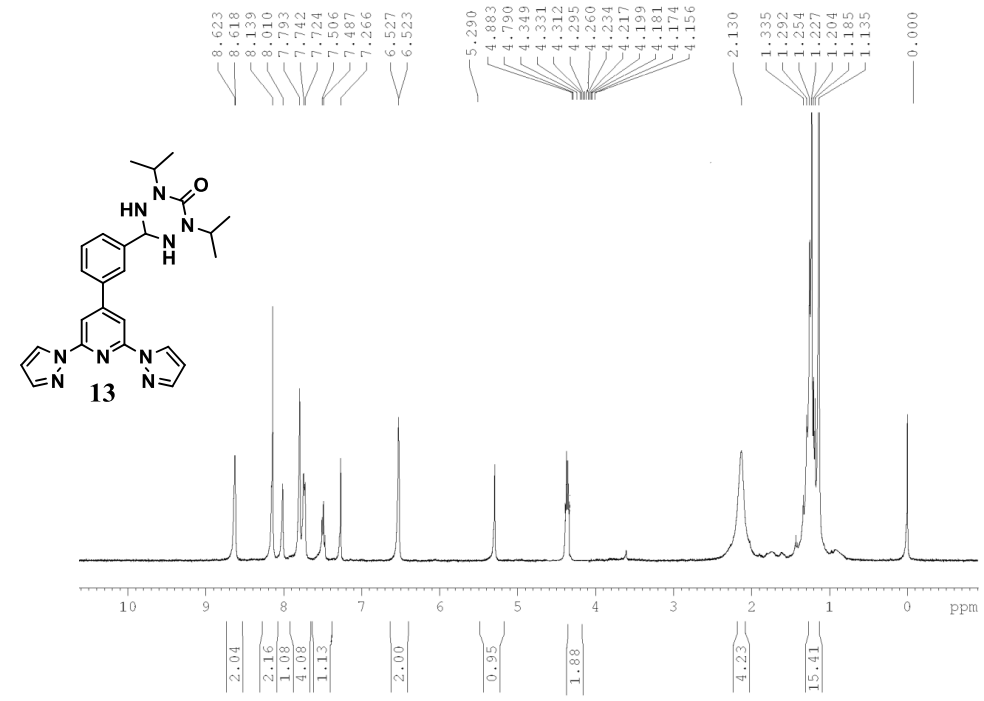


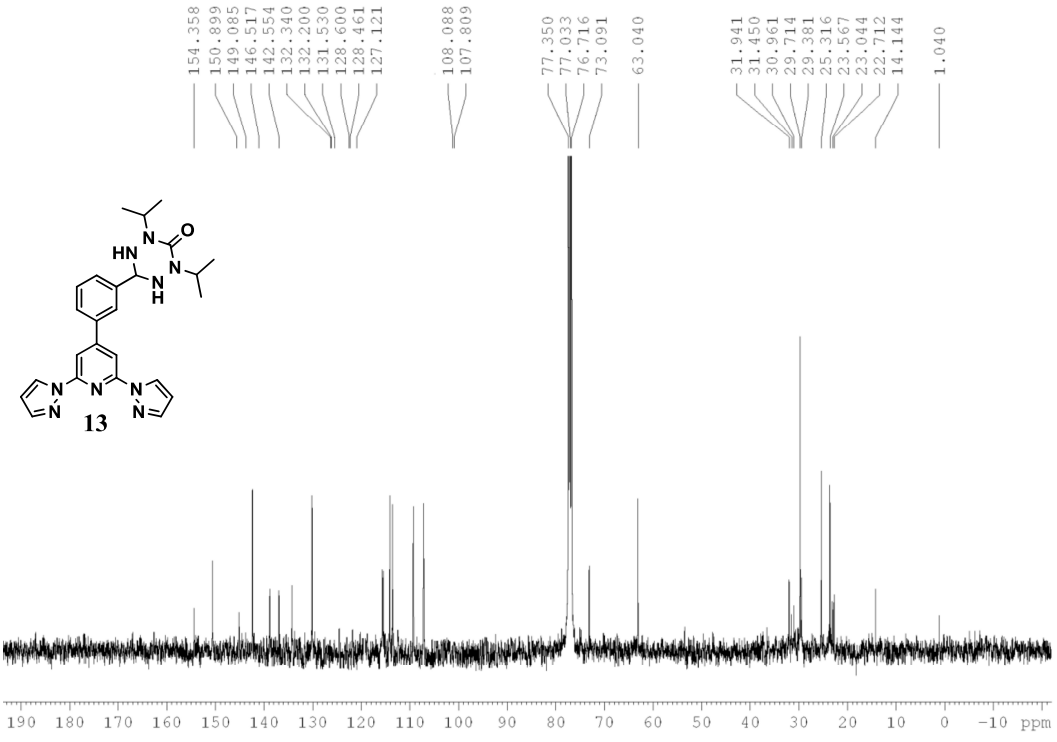
S26

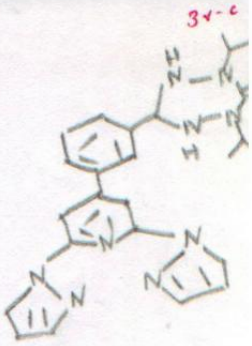








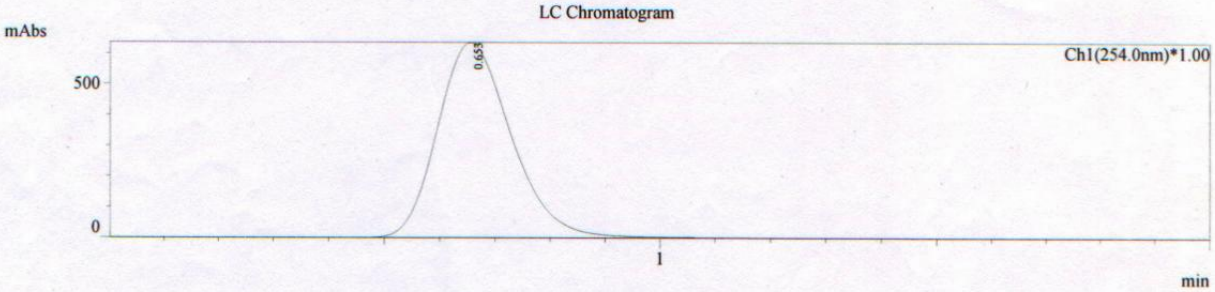




LCMS-2010A DATA REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

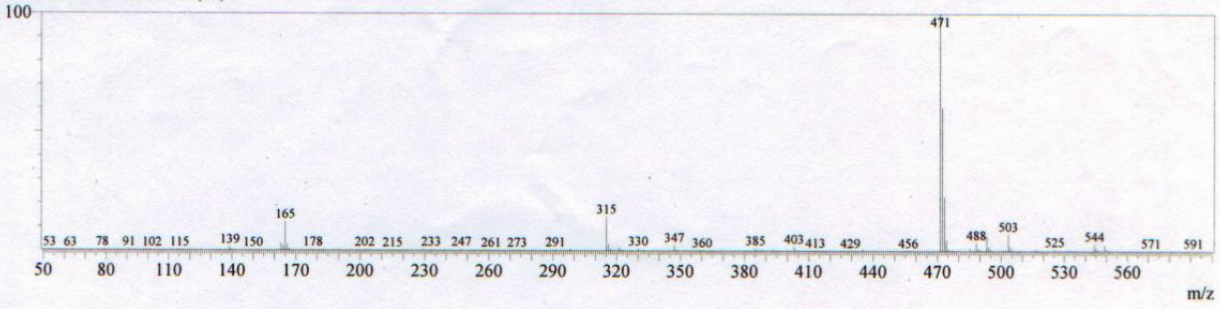
User : Admin
Sample : PHM29
Inj. Volume : 5.000
Data Name : C:\LCMSsolution\User\Data\PHM29-APCI-POS1.qld
Method Name : C:\LCMSsolution\User\Method\esi.qlm

LC Chromatogram



MS Spectrum

Line#:1 R.Time:0.765(Scan#:46) Positive
MassPeaks:370 BasePeak:471.30(15473457)
RawMode:Single 0.765(46)
BG Mode:Peak Start 0.560(34)



MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name	Base m/z	Base Int.
1	0.765	0.560	1.143	678285523	37263095	18.20		100.00		471.30	15473457
				678285523	37263095			100.00			

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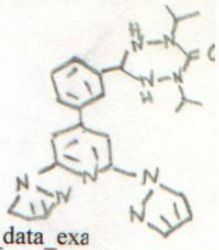
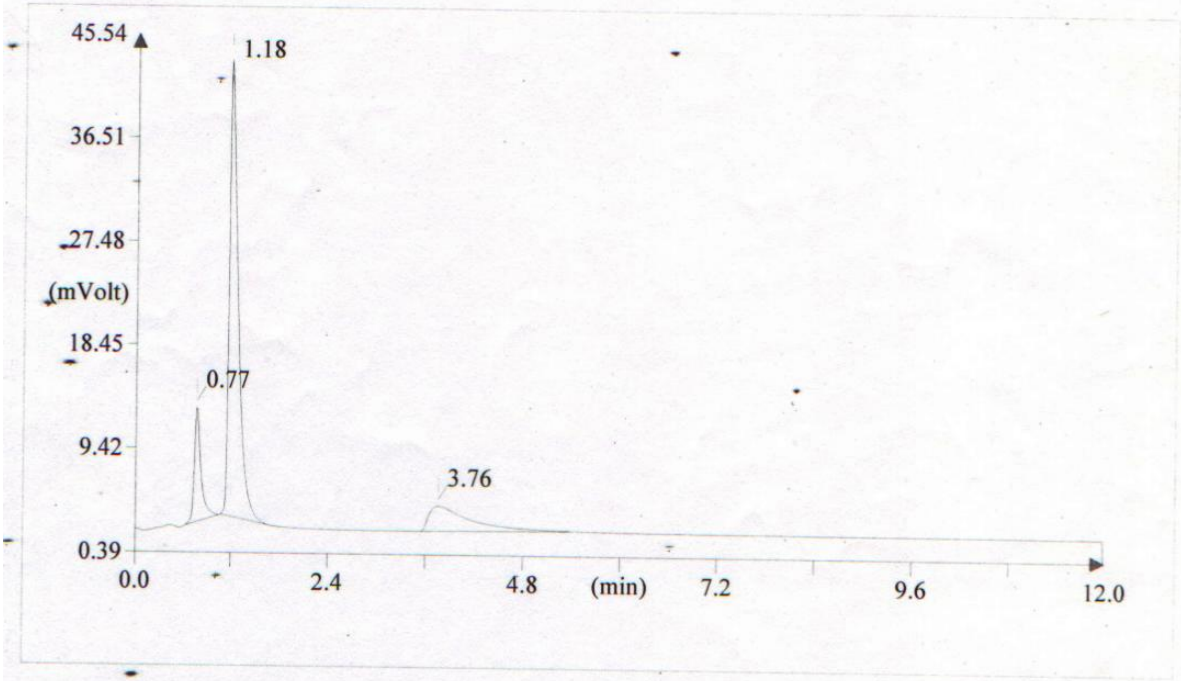
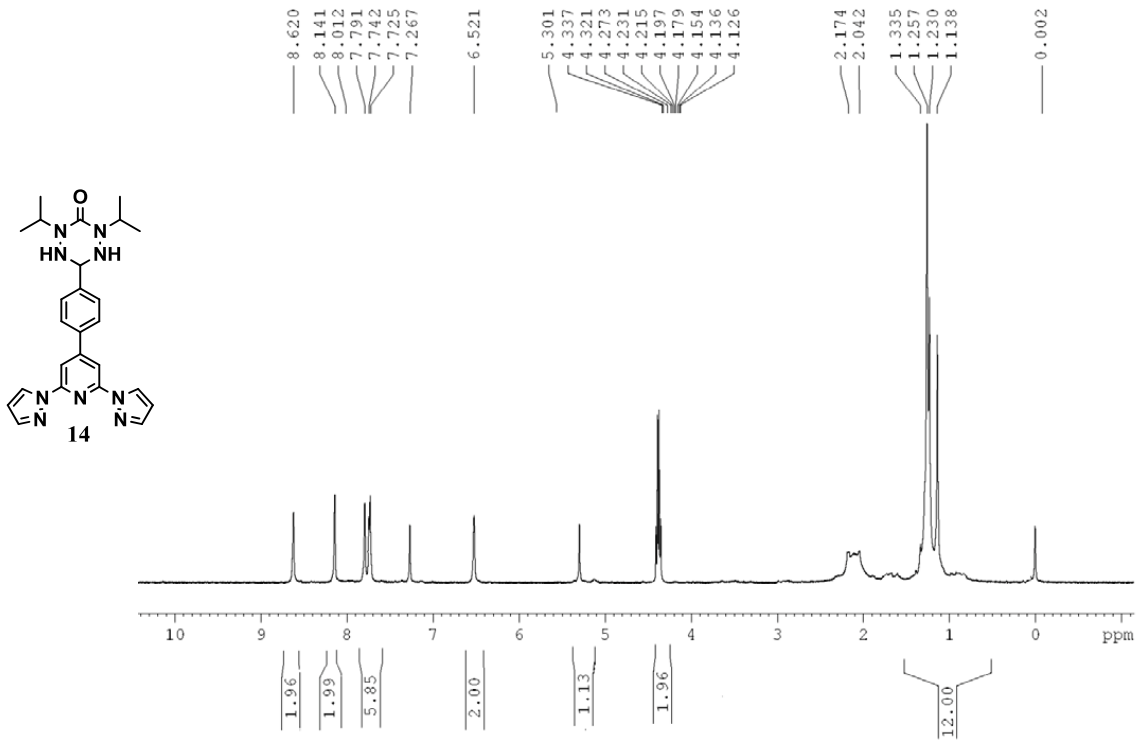
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

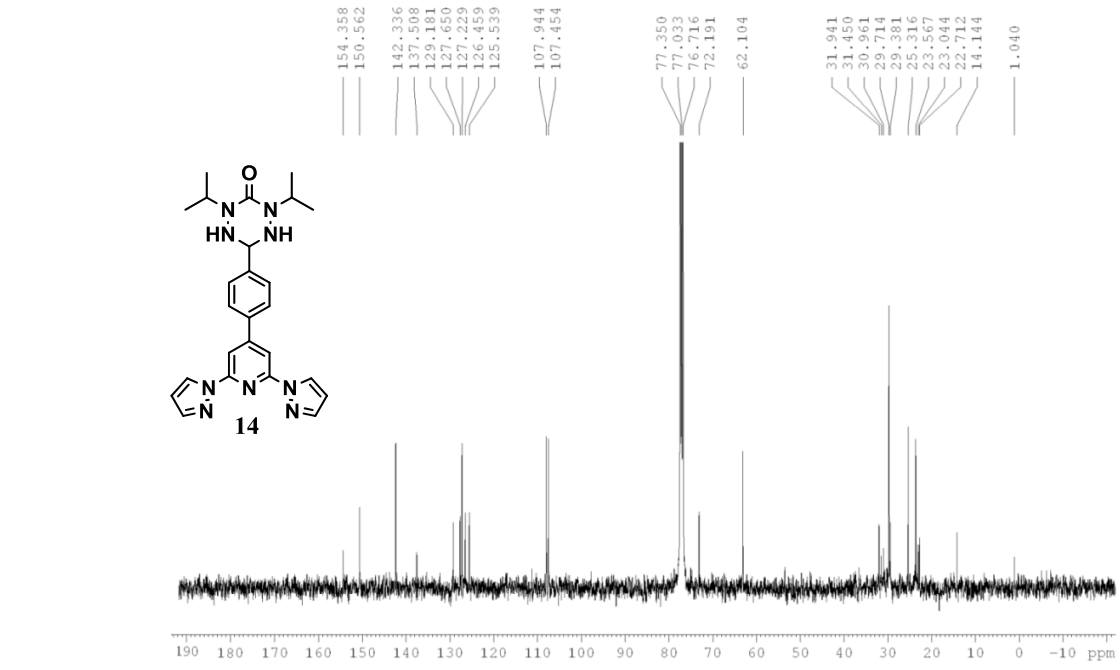


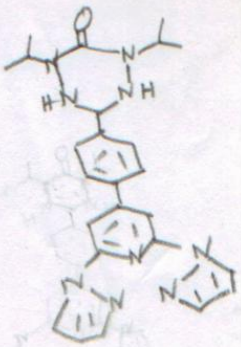
Method filename:	I:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_exa
Sample ID:	PHE-10 (# 5)
Analysis type:	UnkNown
Chromatogram filename:	UNK-14062010-5.dat
Sample weight:	1.138



Element Name	Element %	Ret. Time
Nitrogen	26. 59	0. 77
Carbon	63. 48	1. 18
Hydrogen	6. 25	3. 76



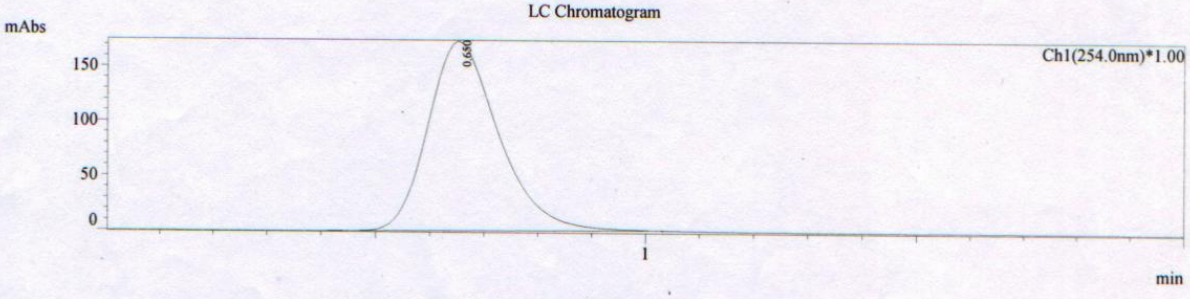




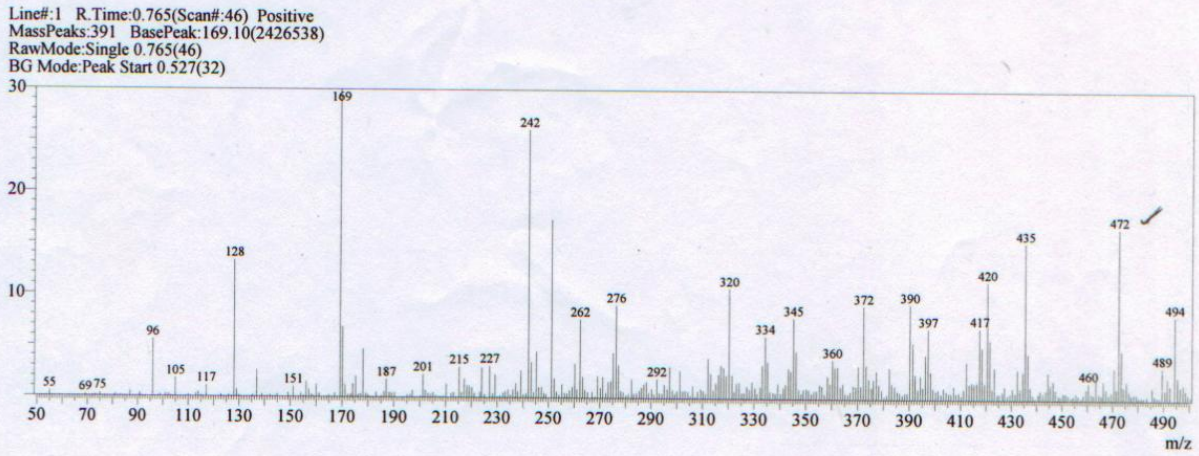
LCMS-2010A DATA REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

User	: Admin
Sample	: PHM23
Inj. Volume	: 5.000
Data Name	: C:\LCMSsolution\User\Data\PHM23-APCI-POS1.qld
Method Name	: C:\LCMSsolution\User\Method\esi.qlm

LC Chromatogram

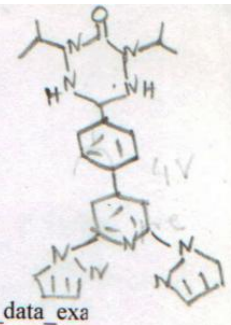


MS Spectrum

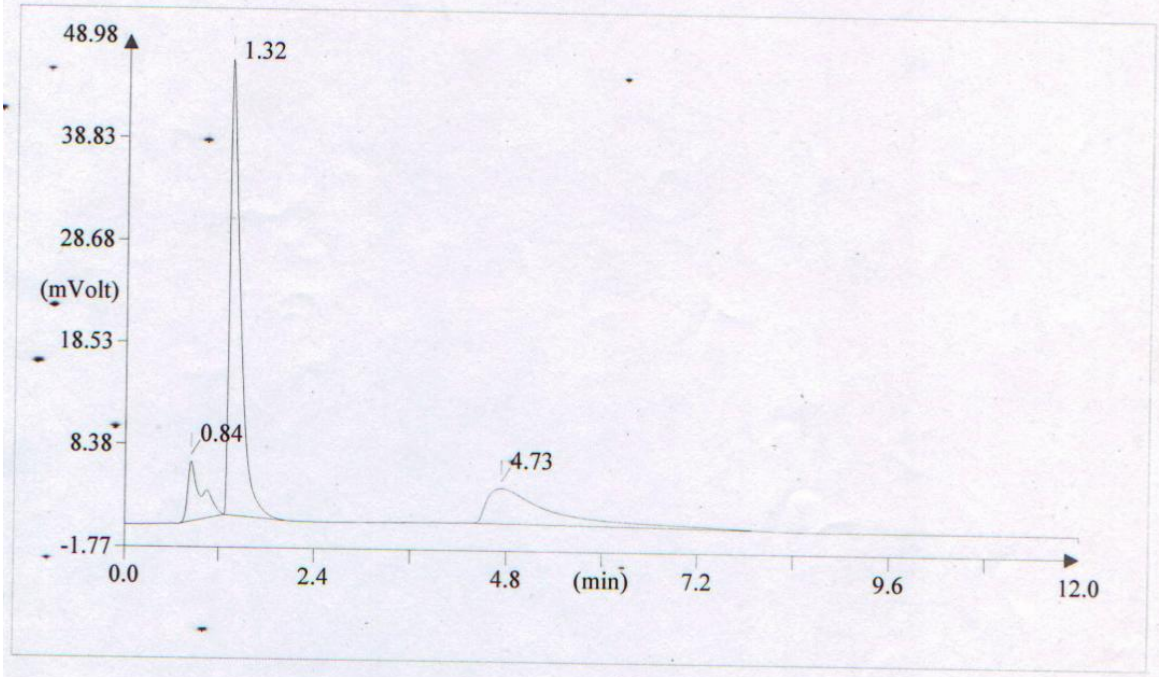


OPERATOR

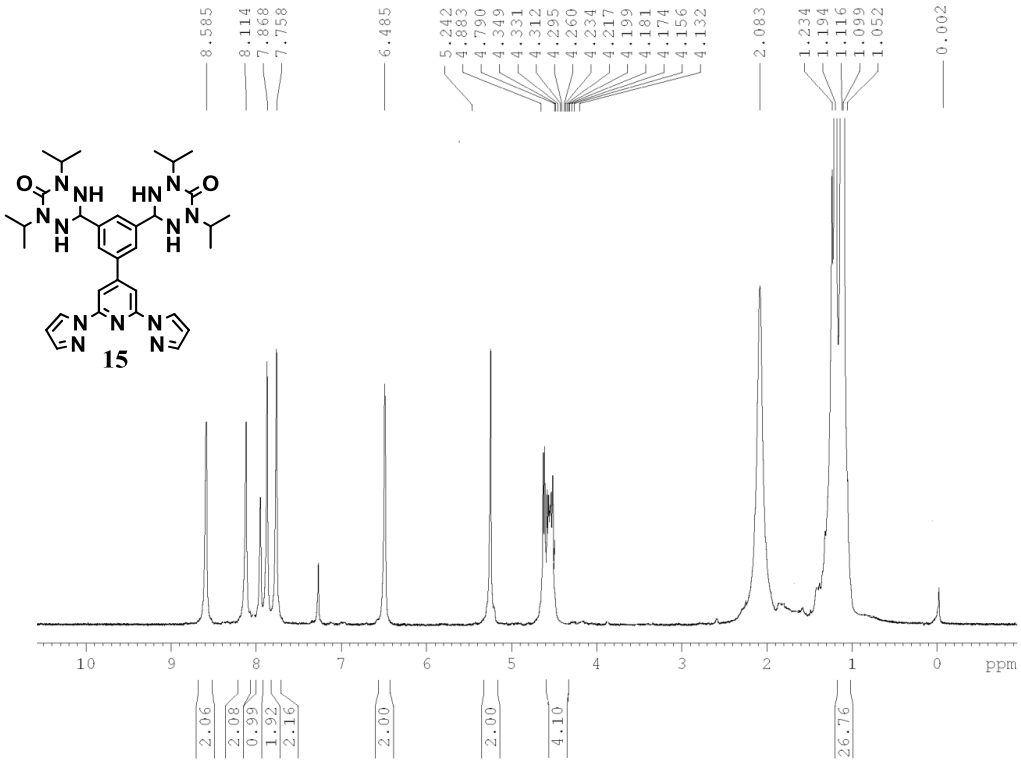
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

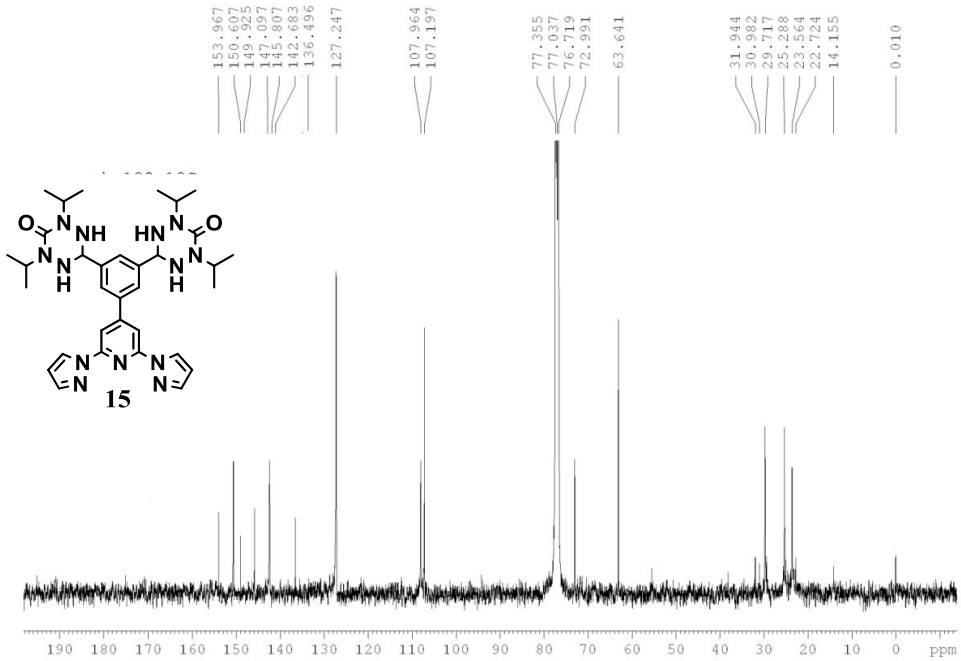


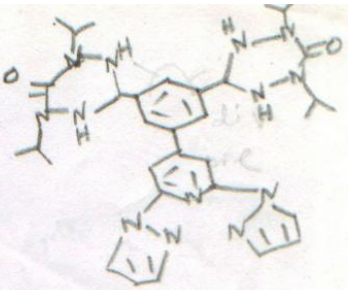
Method filename:	I:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_exa
Sample ID:	PHE-6 (# 82)
Analysis type:	UnkNown
Chromatogram filename:	UNK-14052010-6.dat
Sample weight:	1.68



Element Name	Element %	Ret. Time
Nitrogen	26. 45	0. 84
Carbon	63. 58	1. 32
Hydrogen	6. 25	4. 73



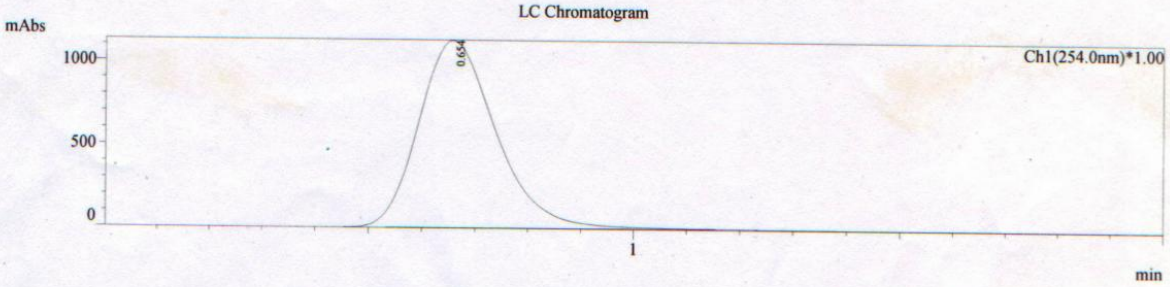




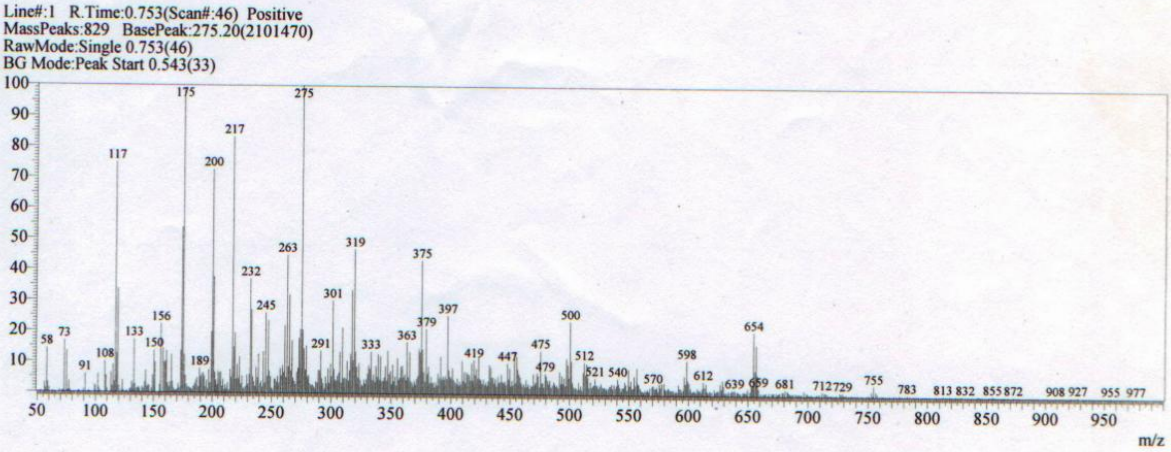
LCMS-2010A DATA REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

User	: Admin
Sample	: PHM-26
Inj. Volume	: 5.000
Data Name	: C:\LCMSsolution\User\Data\PHM-26-APCI-POS1.qld
Method Name	: C:\LCMSsolution\User\Method\esi.qlm

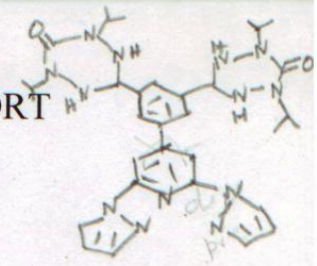
LC Chromatogram



MS Spectrum

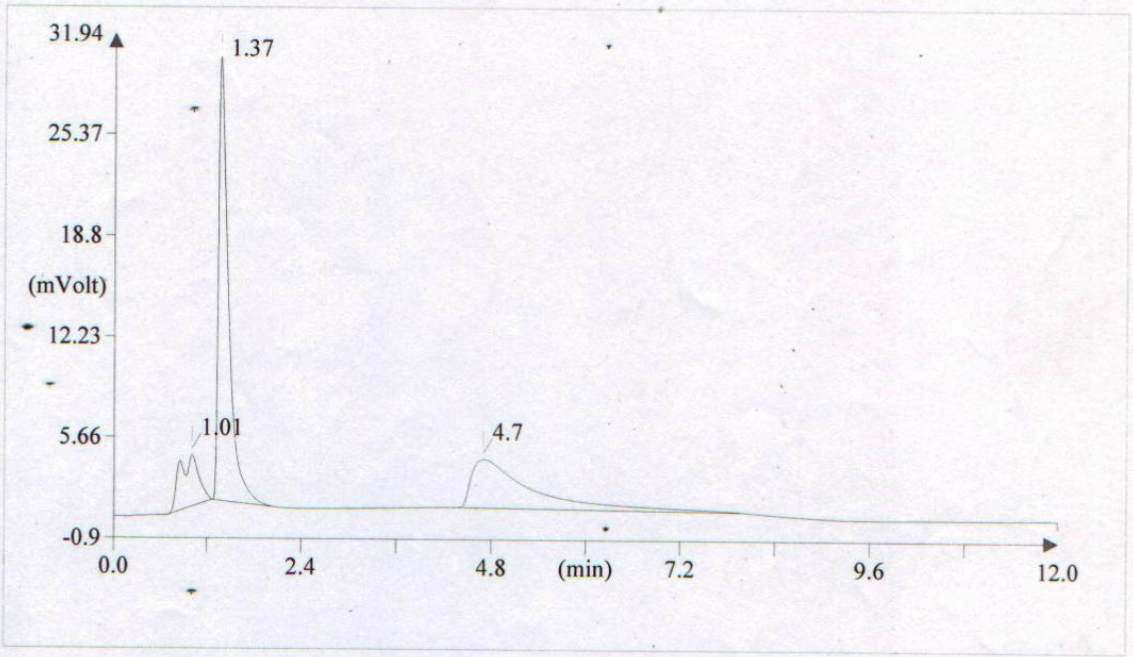


OPERATOR

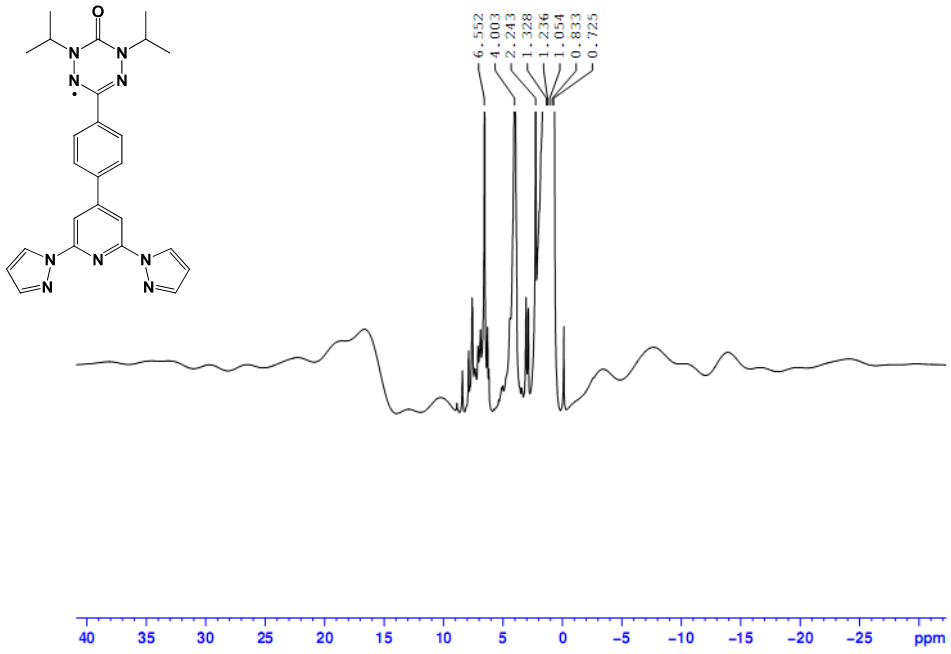


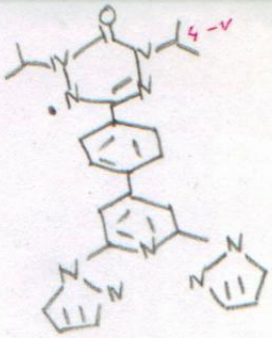
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename:	I:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_exa
Sample ID:	PHE-7 (# 83)
Analysis type:	UnkNown
Chromatogram filename:	UNK-14052010-7.dat
Sample weight:	1.392



Element Name	Element %	Ret. Time
Nitrogen	27. 45	1. 01
Carbon	60. 32	1. 37
Hydrogen	6. 85	4. 70

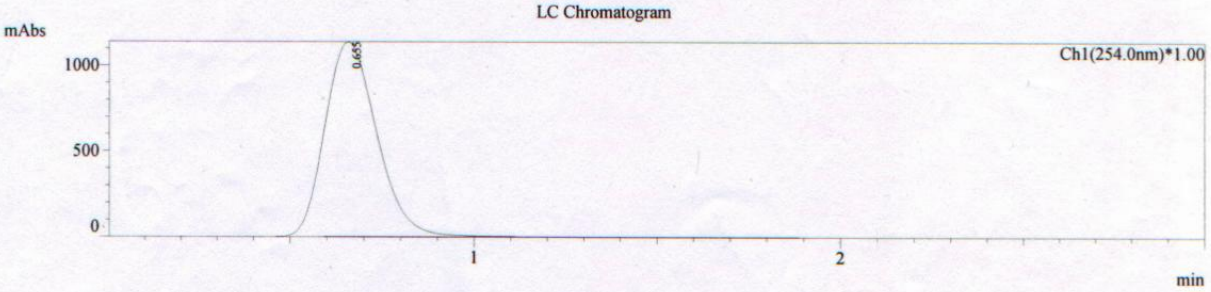




LCMS-2010A DATA REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

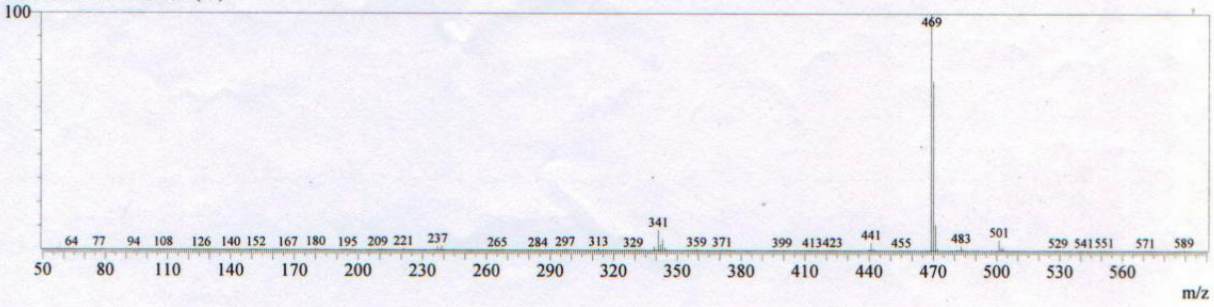
User	: Admin
Sample	: PHM27
Inj. Volume	: 5.000
Data Name	: C:\LCMSsolution\User\Data\PHM27-APCI-POS1.qld
Method Name	: C:\LCMSsolution\User\Method\esi.qlm

LC Chromatogram



MS Spectrum

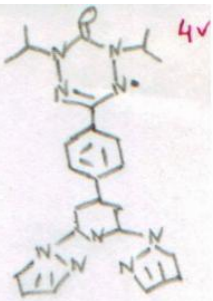
Line#:1 R.Time:0.750(Scan#:45) Positive
MassPeaks:462 BasePeak:469.05(14875317)
RawMode:Single 0.750(45)
BG Mode:Peak Start 0.527(32)



MS Peak Table

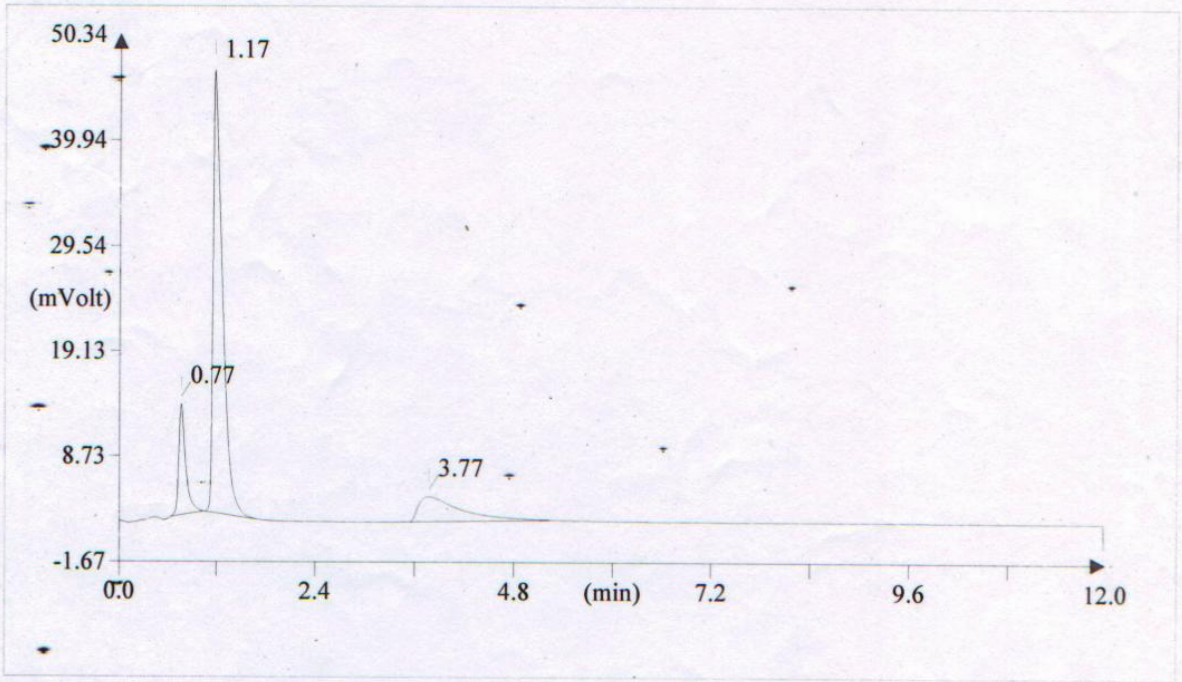
Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name	Base m/z	Base Int.
1	0.750	0.527	1.043	543292820	34651166	15.67		100.00		469.05	14875317
				543292820	34651166			100.00			

OPERATOR

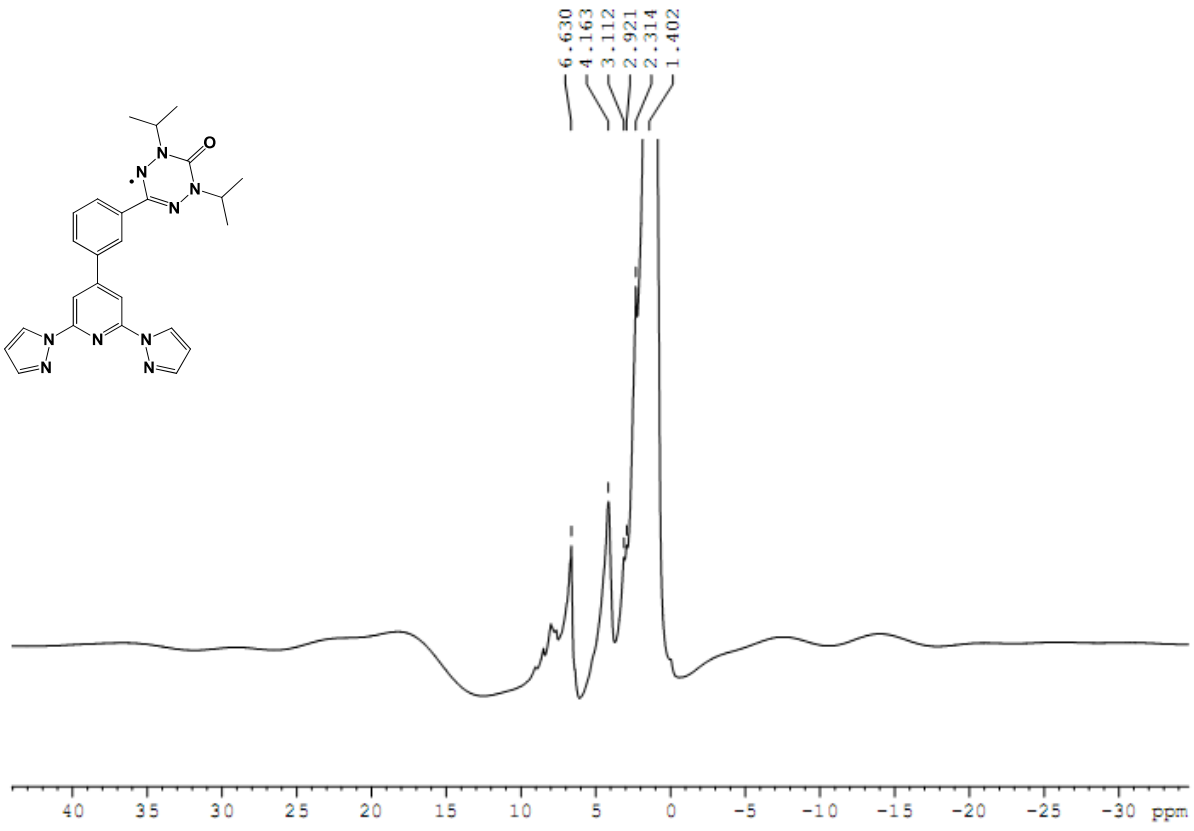


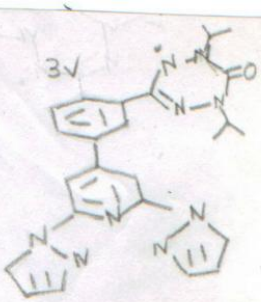
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename:	I:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_exa
Sample ID:	PHE-8 (# 6)
Analysis type:	UnkNown
Chromatogram filename:	UNK-14062010-6.dat
Sample weight:	1.145



Element Name	Element %	Ret. Time
Nitrogen	26. 78	0. 77
Carbon	64. 15	1. 17
Hydrogen	5. 48	3. 77

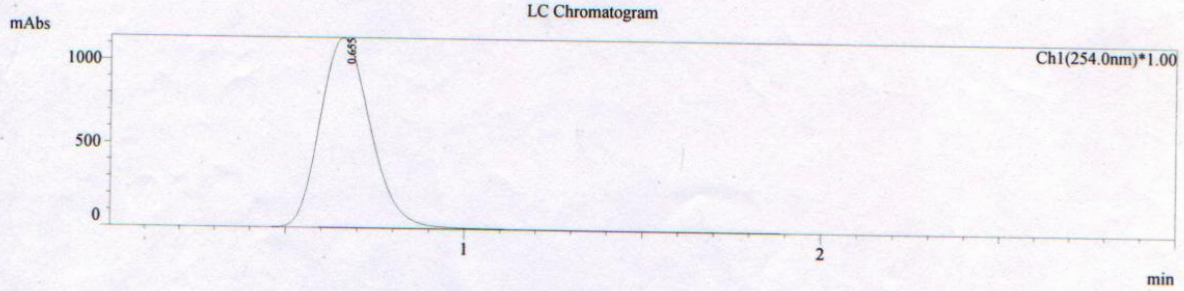




LCMS-2010A DATA REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

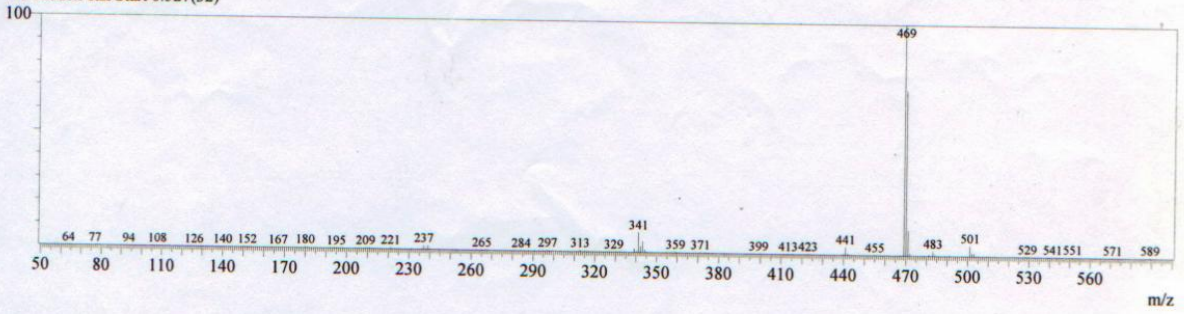
User	: Admin
Sample	: PHM28
Inj. Volume	: 5.000
Data Name	: C:\LCMSsolution\User\Data\PHM27-APCI-POS1.qld
Method Name	: C:\LCMSsolution\User\Method\esi.qlm

LC Chromatogram



MS Spectrum

Line#:1 R.Time:0.750(Scan#:45) Positive
MassPeaks:462 BasePeak:469.15(14875317)
RawMode:Single 0.750(45)
BG Mode:Peak Start 0.527(32)



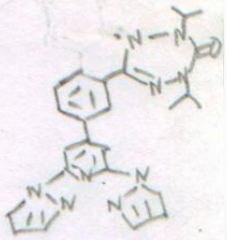
MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name
1	0.750	0.527	1.043	543292820	34651166	15.67		100.00	
				543292820	34651166			100.00	

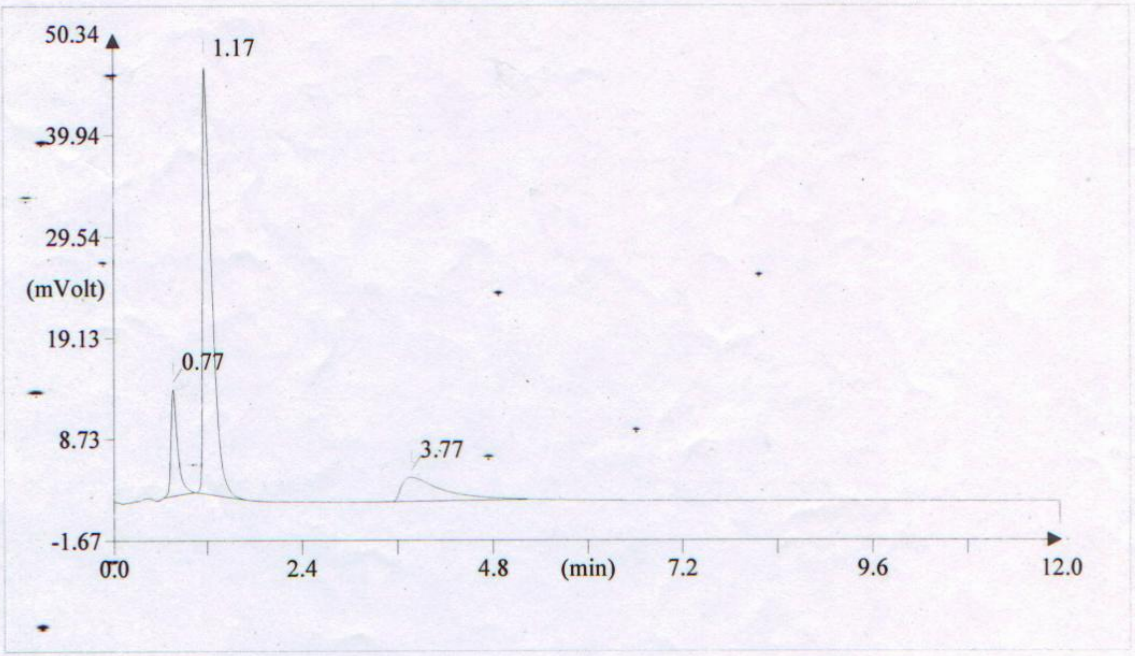
Base m/z	Base Int.
469.05	14875317

OPERATOR

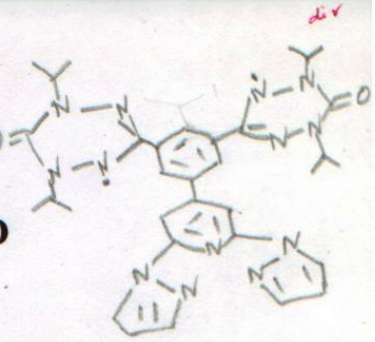
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD



Method filename:	I:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_exa
Sample ID:	PHE-18
Analysis type:	UnkNown
Chromatogram filename:	UNK-14062010-6.dat
Sample weight:	1.145



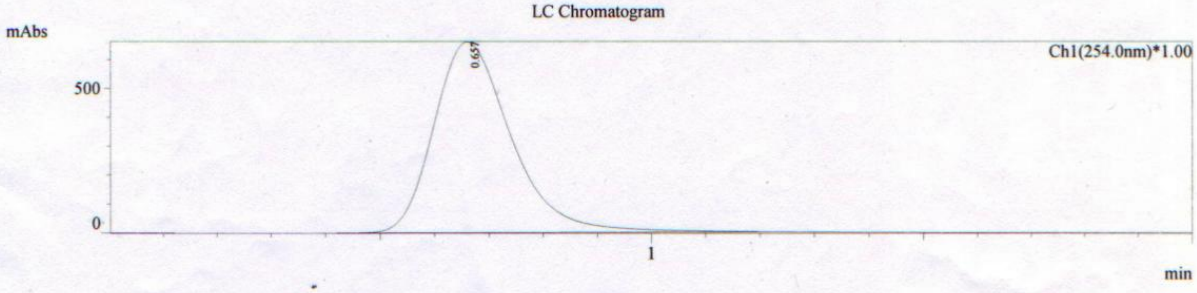
Element Name	Element %	Ret. Time
Nitrogen	26. 88	0. 77
Carbon	64. 17	1. 17
Hydrogen	5. 48	3. 77



LCMS-2010A DATA REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

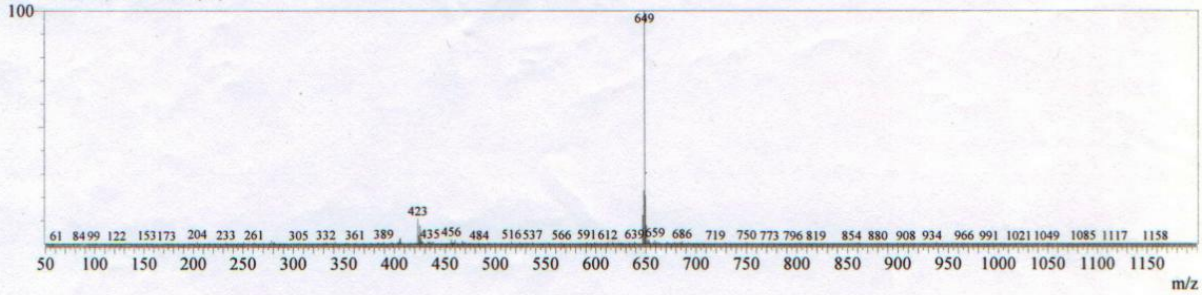
User	: Admin
Sample	: PHM-28
Inj. Volume	: 5.000
Data Name	: C:\LCMSsolution\User\Data\PHM-28-APCI-NEG1.qld
Method Name	: C:\LCMSsolution\User\Method\esi.qlm

LC Chromatogram



MS Spectrum

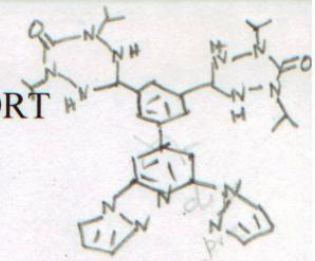
Line#:1 R.Time:0.674(Scan#:41) Negative
MassPeaks:595 BasePeak:648.75(579651)
RawMode:Single 0.674(41)
BG Mode:Peak Start 0.560(34)



MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name	Base m/z	Base Int.
1	0.674	0.560	1.093	19351102	1379892	14.02		100.00		648.75	579651
				19351102	1379892			100.00			

OPERATOR



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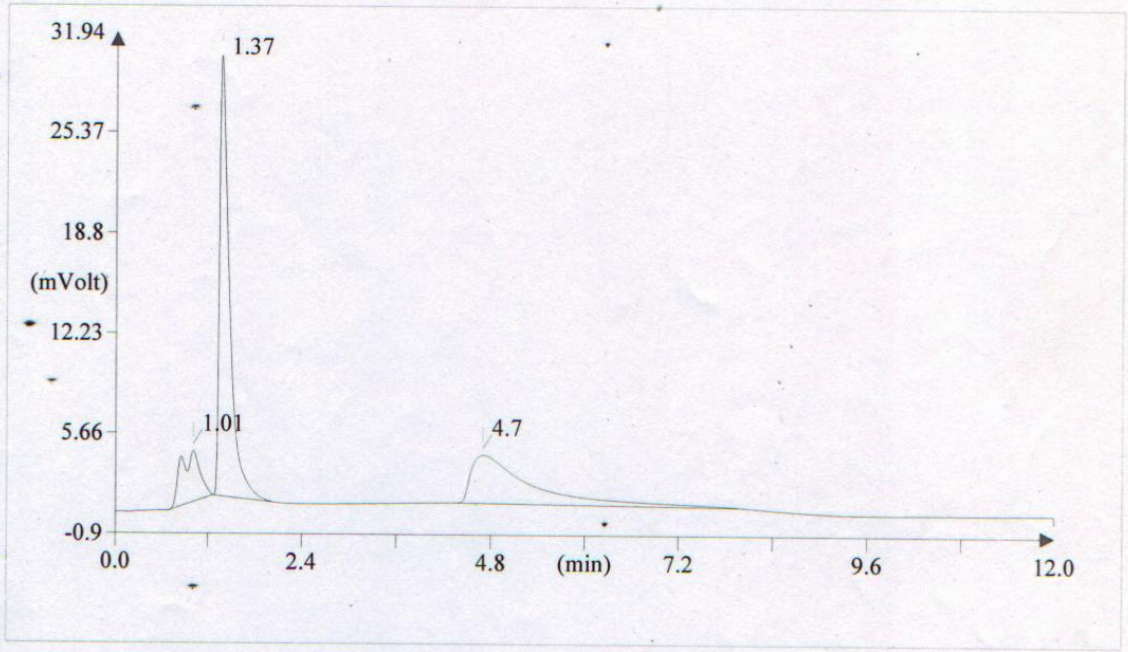
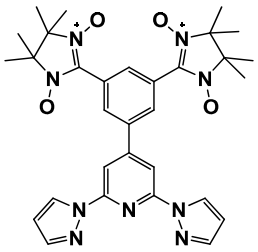
Method filename:	I:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_exa
Sample ID:	PHE-7 (# 83)
Analysis type:	UnkNown
Chromatogram filename:	UNK-14052010-7.dat
Sample weight:	1.392



Element Name	Element %	Ret. Time
Nitrogen	27. 45	1. 01
Carbon	66. 32	1. 37
Hydrogen	6. 85	4. 70



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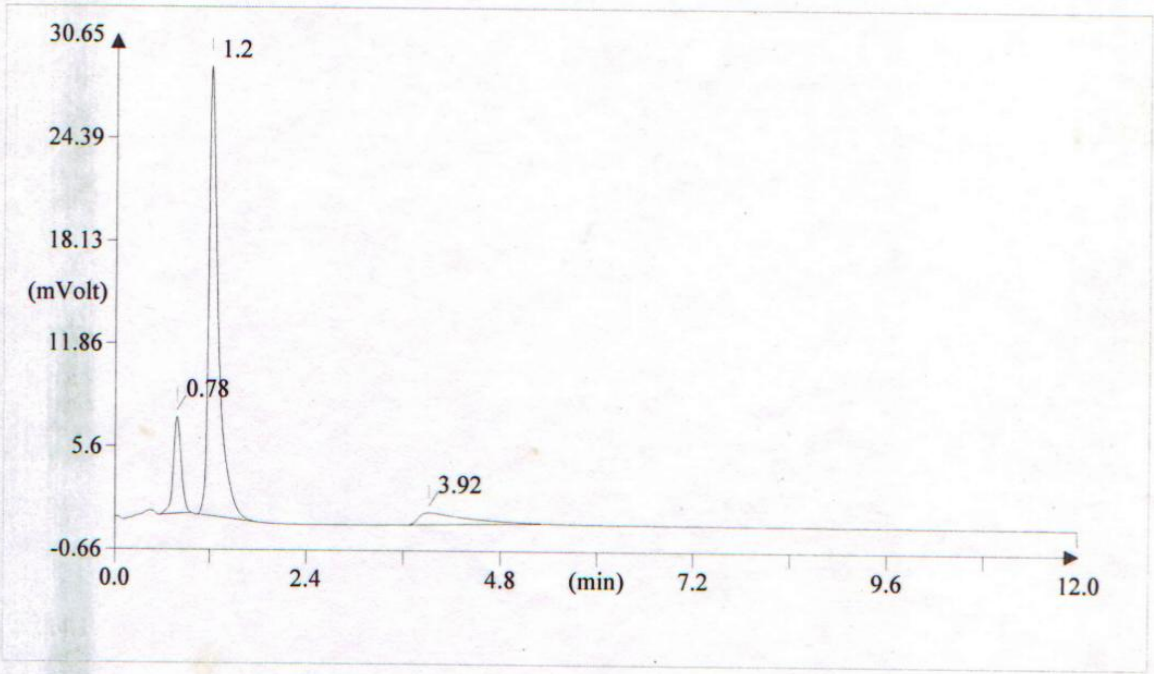
radical

Method filename:	D:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	PHE-3 (# 8)
Analysis type:	UnkNown
Chromatogram filename:	UNK-21062009-1.dat
Sample weight:	1.056



Element Name	Element %	Ret. Time
Nitrogen	21. 32	0. 79
Carbon	62. 15	1. 20
Hydrogen	5. 95	3. 92