

Supplementary Information: Development of a New Arylation Reaction Catalyzed by Polymer Bound 1,3-(Bisbenzimidazolyl) Benzene Co(Ii) Complex and Generation of Bioactive Adamanate Amines

Baburajeev Chumadathil Pookunoth^{1,†}, Shilpa Eshwar Rao^{1,2,†}, Suresha Nayakanahundi Deveshegowda³, Prashant Kashinath Metri³, Kashifa Fazl-Ur-Rahman¹, Ganga Periyasamy¹, Gayathri Virupaiah^{1,4}, Babu Shubha Priya³, Vijay Kumar Pandey⁵, Peter Edward Lobie^{5,6,*}, Rangappa Knchugarakoppal Subbegowda^{7,*} and Basappa^{1,3,*}

¹ Department of Chemistry, Central College Campus, Bangalore University, Bangalore-560001, India; baburajeevnambiar@gmail.com (B.C.P.); shilpa.gaikwad1989@gmail.com (S.E.R.); kashifaf07@gmail.com (K.F.-U.R.); ganga.periyasamy@gmail.com (G.P.); gayathritvr@yahoo.co.in (G.V.)

² Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, Karnataka, India;

³ Laboratory of Chemical Biology, Department of Studies in Organic Chemistry, University of Mysore, Manasagangotri, Mysore, 570006 Karnataka, India; sureshand92@gmail.com (S.N.D.); prashant.metri@gmail.com (P.K.M.); priyabs_chem@yahoo.com (B.S.P.)

⁴ Department of Chemistry, Bengaluru City University, Bangalore-560001, India

⁵ Tsinghua Berkeley Shenzhen Institute, Tsinghua Shenzhen International Graduate School, Shenzhen 518055, China; vijay.pandey@sz.tsinghua.edu.cn

⁶ Shenzhen Bay Laboratory, Shenzhen 518055, China

⁷ Institution of Excellence, Vijnana Bhavan, University of Mysore, Mysore 570005, India

* Correspondence: pelobie@sz.tsinghua.edu.cn (P.E.L.); rangappaks@chemistry.uni-mysore.ac.in (R.K.S.); salundibasappa@gmail.com (B.); Tel.: +91-9481200076 (B.); +91-821-241-9428 (R.K.S.)

† These authors contributed equally.

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SI-01

Experimental Section

Materials and Method

All organic chemicals used were purchased from Sigma-Aldrich. ^1H and ^{13}C NMR spectra were recorded on a Bruker WH-200 (400MZ) and JEOLJSM-ECS(400MHz) spectrometer in CDCl_3 or DMSO-d_6 as solvent, using TMS as an internal standard and chemical shifts are expressed as ppm. High resolution mass spectra were determined on a Bruker Daltonics instrument. Mass spectra were determined on a Agilent LC-MS and the elemental analyses were carried out using an Elemental Vario Cube CHNS rapid Analyzer. The progress of the reaction was monitored by TLC pre-coated silica gel G plates.

SI-02

Elemental analysis

Elemental analysis of the catalyst and chemical composition confirmed the purity and stoichiometry of the complex. Physical properties and analytical data are given in table 1.

Table S1. –Physical properties and analytical data.

Parameters	Colour	C%	H%	N%	Co%
Chloromethylated PS-DVB	White	73.9	6.3	----	----
Functionalized beads with BBZN	Yellow	67.8	8.4	4.5	----
PS-Co(BBZN)Cl ₂	Blue	61.3	7.2	6.8	12.4

Calculated values are in parenthesis.

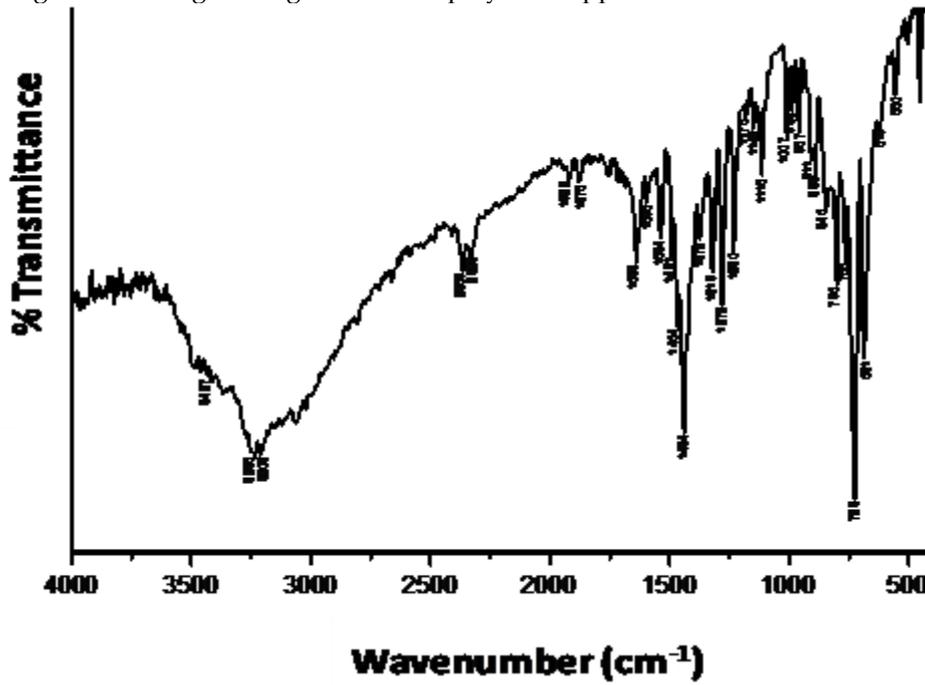
FT-IR spectral studies

The IR spectra the polymer support, ligand, functionalized beads, PS-Co(BBZN)Cl₂ was recorded in the region between 4000–400 cm^{-1} . The IR spectrum of pure chloromethylated polystyrene beads exhibited peaks at 1265 cm^{-1} due to $\text{CH}_2\text{-Cl}$ group and at 815 cm^{-1} due to C-Cl group. The decrease in the intensities of these peaks on reacting with BBZNH_2 is attributed to the functionalization of BBZN ligand on to the polymer support. The free BBZNH_2 ligand exhibited peak around 3427 cm^{-1} which is absent in the functionalized polymer support indicating that the N-heterocyclic ligand has been attached through the nitrogen on to the polymer support. The IR spectra of the ligand, polymer beads, functionalized, anchored beads and unsupported complex are depicted in Figure 1a–e.

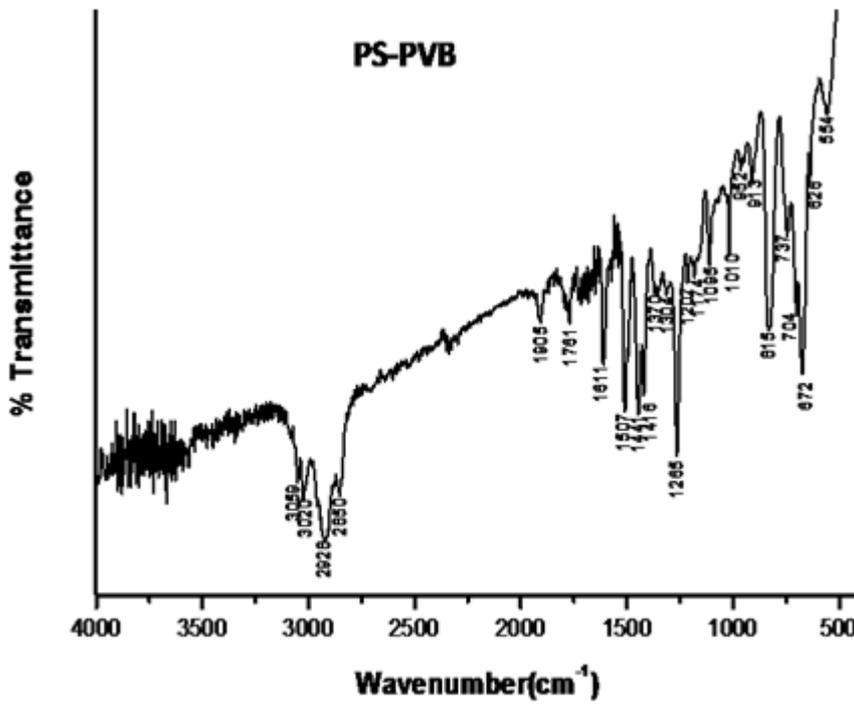
The $\nu_{\text{C=N}}$ peak for the functionalized beads exhibited at 1657 cm^{-1} is shifted to 1632 cm^{-1} in the anchored beads indicating that the ligand is coordinated to cobalt. BBZNH_2 ligand exhibited peak at

3229 cm^{-1} which was absent in the polymer supported copper complex confirmed that bonding of the BBZN ligand is through nitrogen on to the polymer support.

(a)



(b)



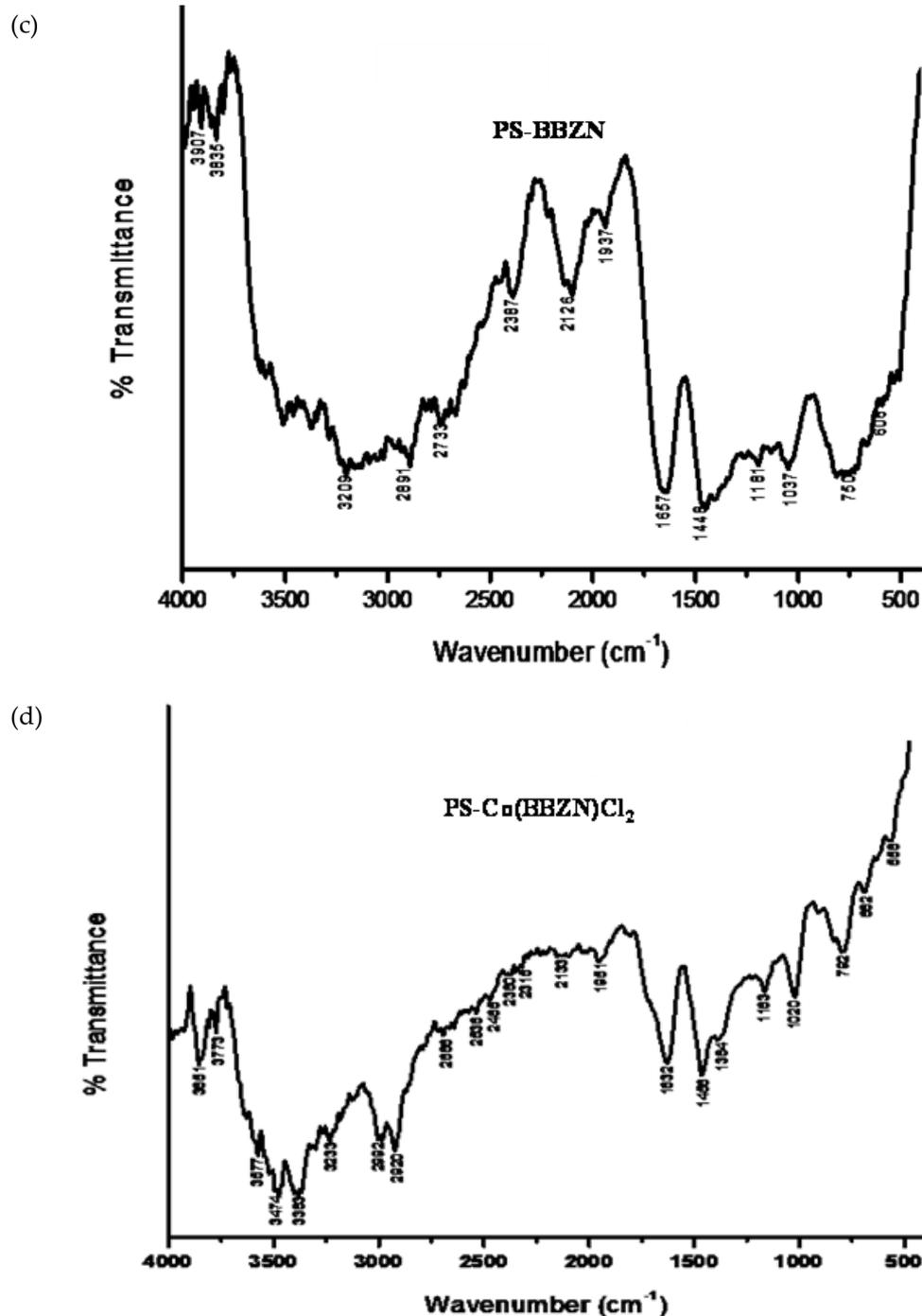


Figure S1. (a) IR spectrum of BBZN ligand. (b) IR spectrum of chloromethylated polystyrene cross-linked with 6.5% divinylbenzene. (c) IR spectrum of functionalized polymer. (d) IR spectrum of PS-Co(BBZN)Cl₂

UV-vis/DRS spectral studies

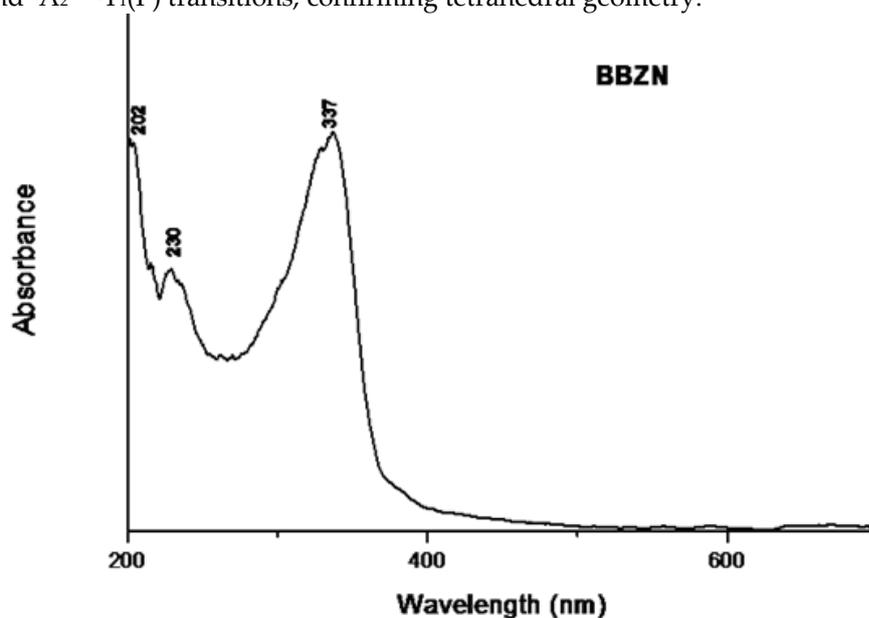
The electronic spectra of the complexes and ligand are presented in the Figure 2 and spectral data are compiled in Table 1. BBZNH₂ showed bands at 211, 235, 297 and 311 nm due to $\varphi \rightarrow \varphi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively. Upon immobilization on the polymer, the PS-BBZNH exhibited these bands at 212, 236, 298 and 316 nm.

Table S1. UV-Vis/DRS spectra data of ligand, polymer functionalized ligand and catalysts (nm).

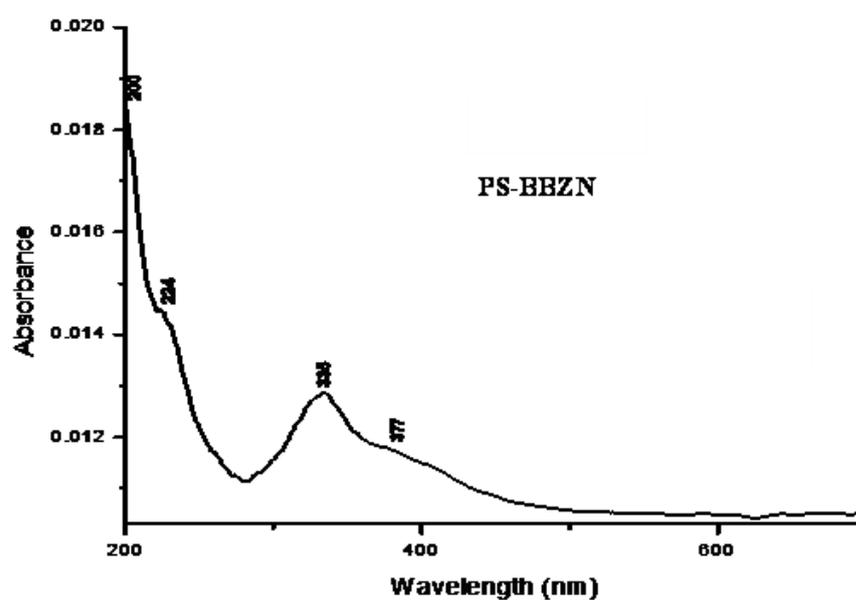
Sample	$\varphi \rightarrow \varphi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	CT	d-d transitions	structure assigned
BBZN	211	235	297, 311	-	-	-
PS-BBZNH	212	236	298, 316	-	-	-
PS-(Co(II)BBZN)Cl ₂		228	304	395	435, 606	tetrahedral

The electronic spectrum of the polymer support BBZN catalyst was recorded in the diffuse reflectance mode as BaSO₄ disk. In the spectrum of BBZN ligand, bands observed at 230 and 337 nm were assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The spectrum of PS-Co(BBZN)Cl₂ exhibited intra-ligand transition bands at 228, 304 and 395 nm and d-d transitions at 435 and 606 nm assigned to ${}^4A_2 \rightarrow {}^4T_1(F)$ and ${}^4A_2 \rightarrow {}^4T_1(P)$ transitions, confirming tetrahedral geometry.

(a)



(b)



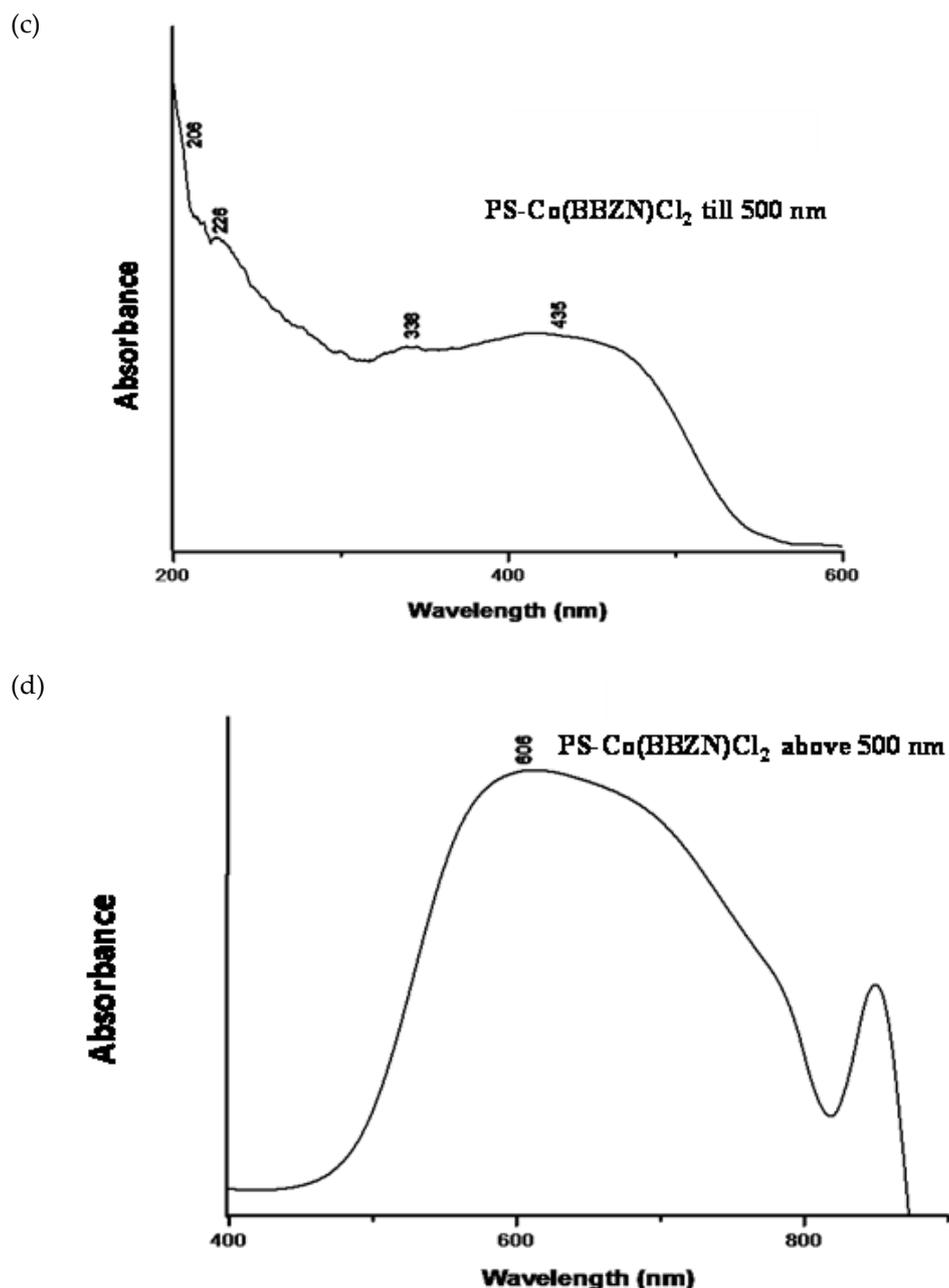
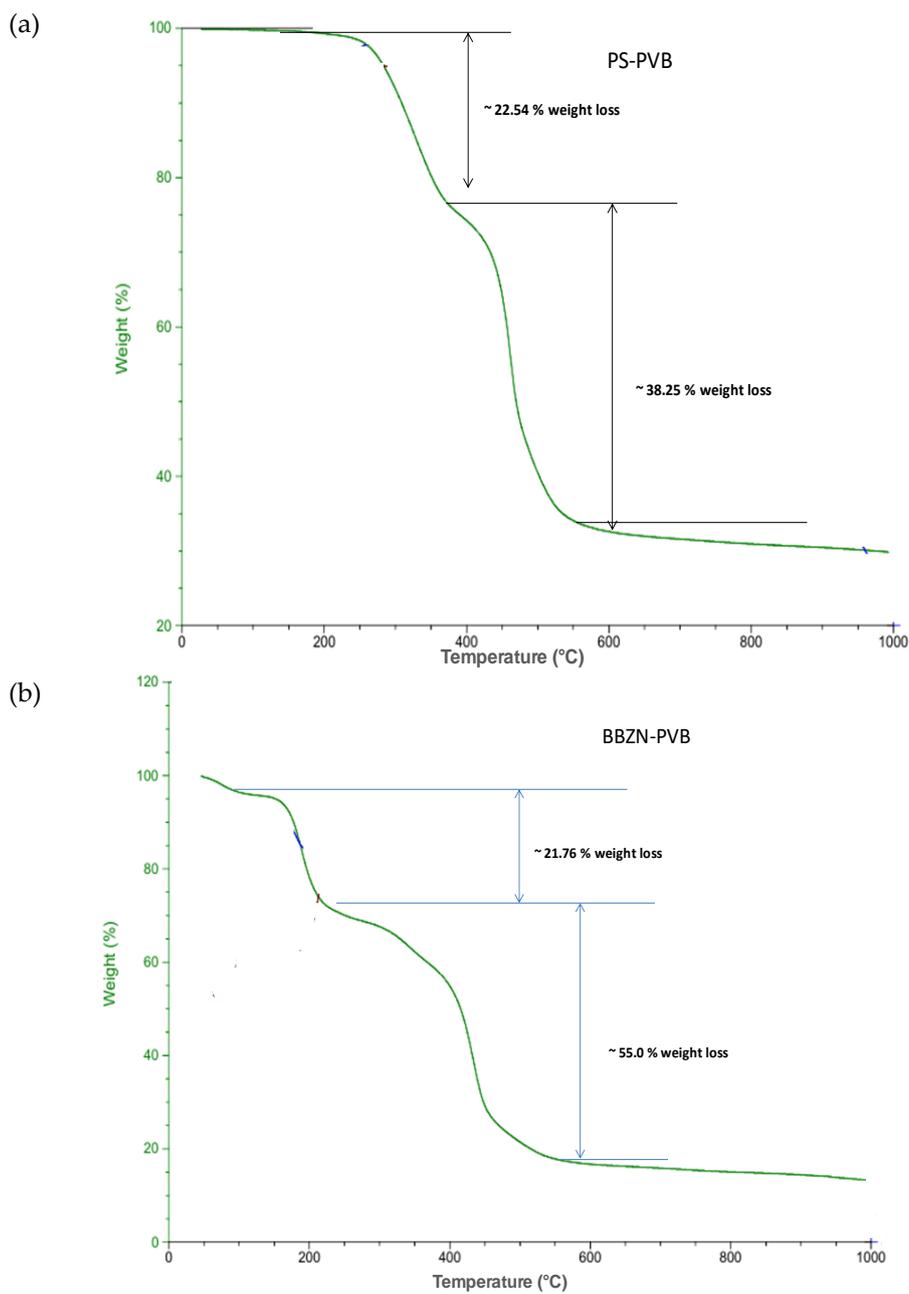


Figure S2. (a) Electronic spectrum of BBZN in methanol. (b) Electronic spectrum of functionalized polymer. (c) Electronic spectrum of PS-Co(BBZN)Cl₂ till 500 nm. (d) Electronic spectrum of PS-Co(BBZN)Cl₂ above 500 nm.

Thermal Analysis

The thermal stability of the polymer support and the PS-Co(II)BBZNCl₂ catalyst were studied in nitrogen atmosphere with a heating rate of 10 °C/min upto 1000 °C. The Thermograms are depicted in Fig 3a–b. The thermogram of PS-PVB depicts that the polymer is stable upto 210 °C and in the range of 210 to 390 °C, there is weight loss of 22.54% indicating the loss of chloride ions in the polymer support. The thermogram of unbound complex depicts that one chloride ion is lost around 210 °C. Another chloride ion and one benzimidazole group of ligand is lost in the range 210 to 420 °C. In the functionalized polymer, the ligand is lost in the first stage (25%) in the range 100–210 °C (Figure 3S b). After 210 °C, the polymer decomposed.

In the polymer supported Co complex in the first stage chloride is lost below 200°C. In the second stage 37 % weight loss is due to decomposition of the ligand in the range 200–400°C (Figure 3S d).



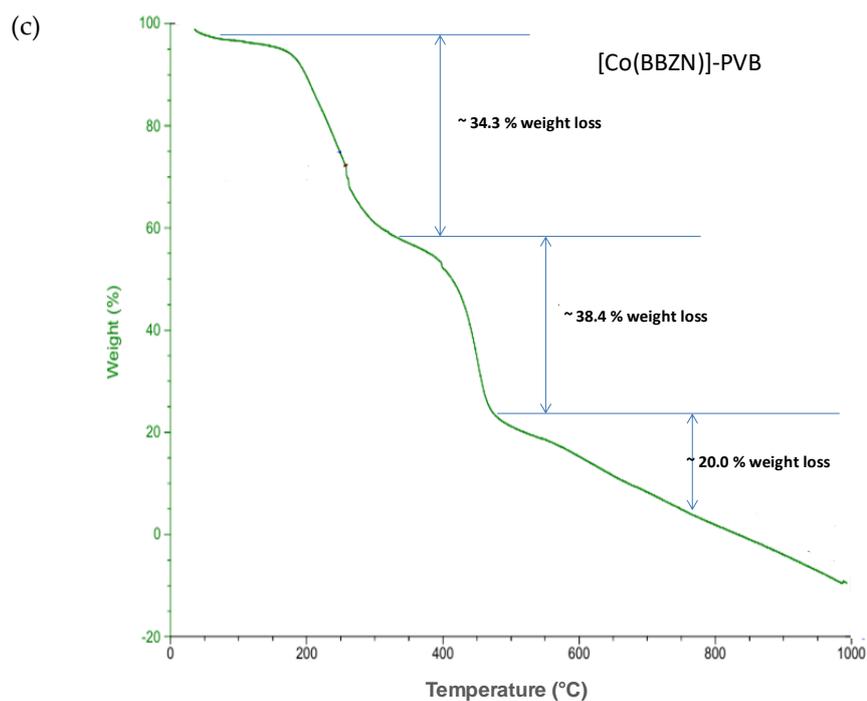
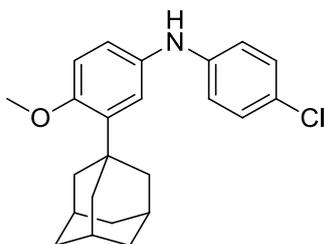


Figure 3S. (a) Thermogram of Polymer support. (b) Thermogram of BBZN-PVB. (c) Thermogram of PS-Co(BBZN)Cl₂.

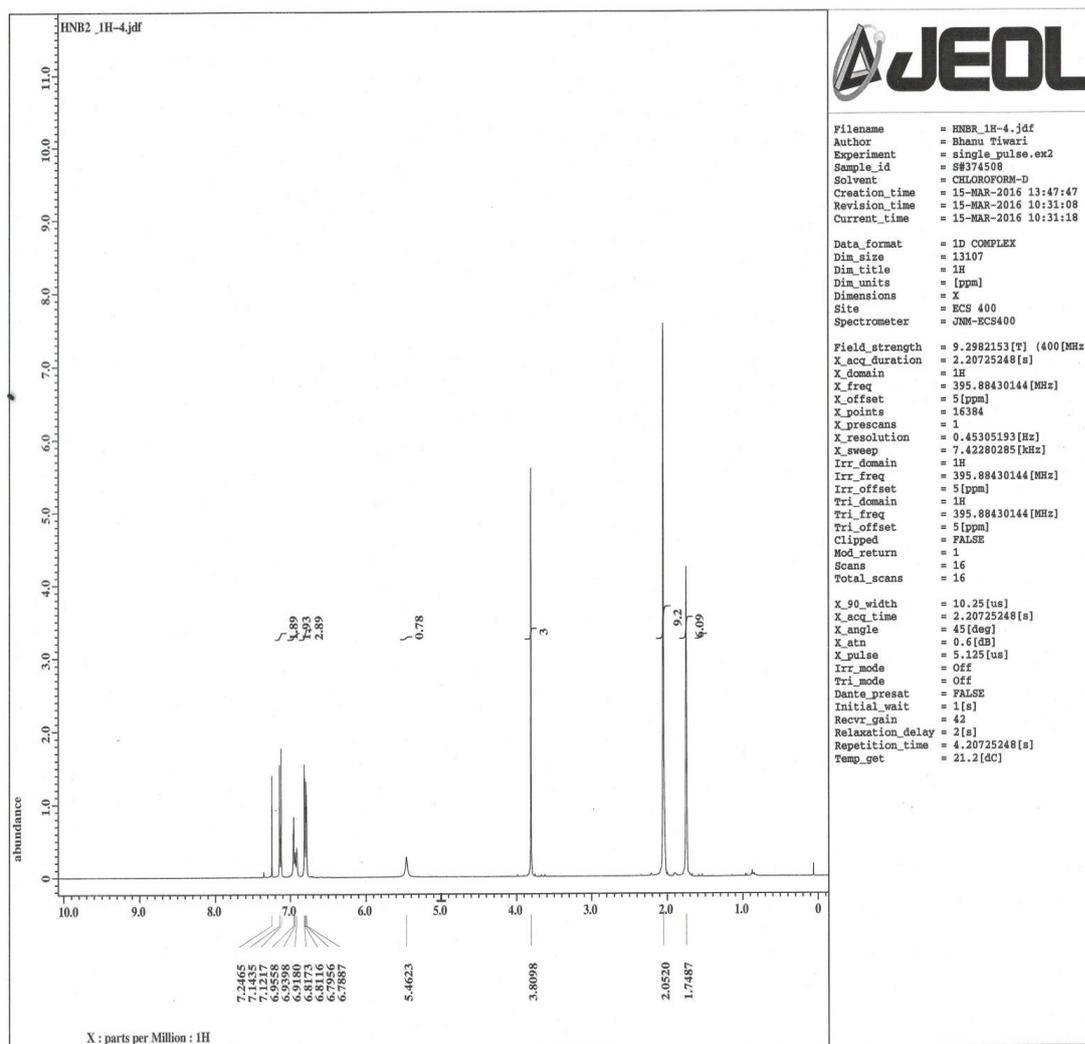
Hence, based on the above spectroscopic data, the structure of the polymer bound copper complex is assigned as follows:

Stereochemistry – IR spectral results indicate that BBZNH₂ is co-ordinated to Co(II) through tertiary N of benzimidazole. Hence the ligand acts as a chelating bidentate ligand. Based on elemental and TGA analysis, ESR and electronic spectral results, tetrahedral geometry is assigned to polymer bound complex.

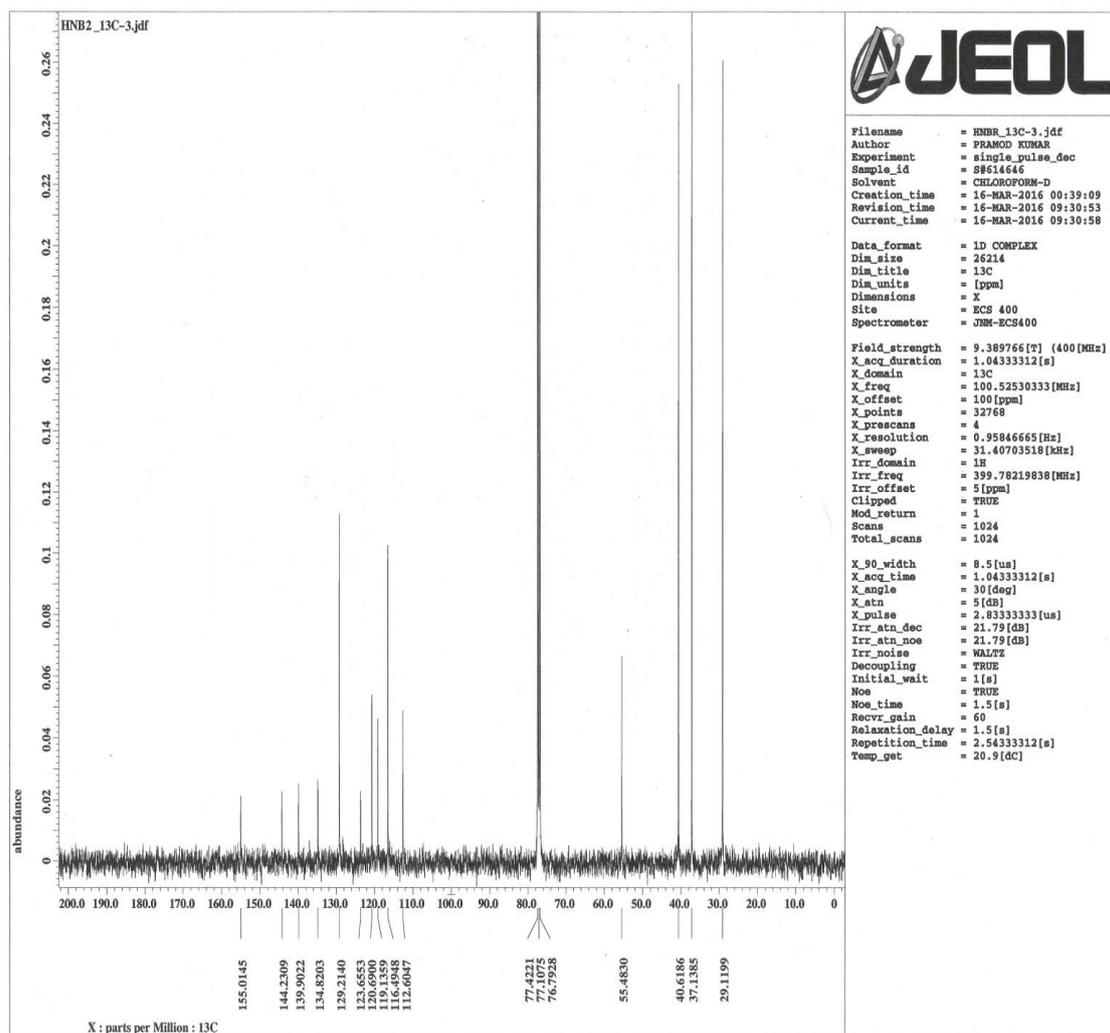
SI-03



3-(adamantan-1-yl)-N-(4-chlorophenyl)-4-methoxyaniline(3a).



¹H NMR spectra of 3-(adamantan-1-yl)-N-(4-chlorophenyl)-4-methoxyaniline(3a).



^{13}C NMR spectra of 3-(adamantan-1-yl)-N-(4-chlorophenyl)-4-methoxyaniline (3a).

LC-MS REPORT

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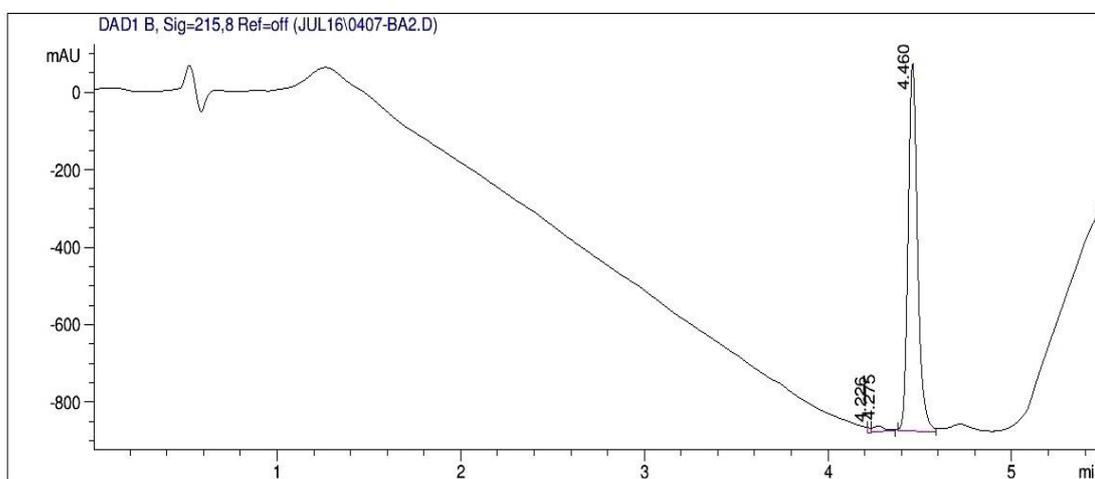
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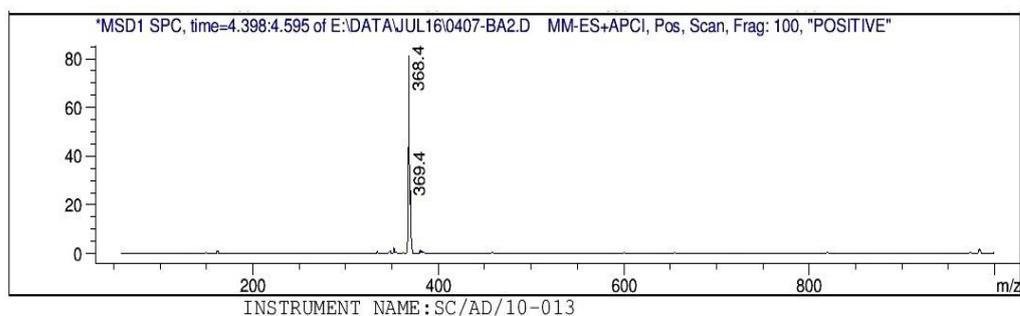
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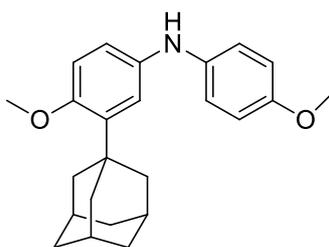


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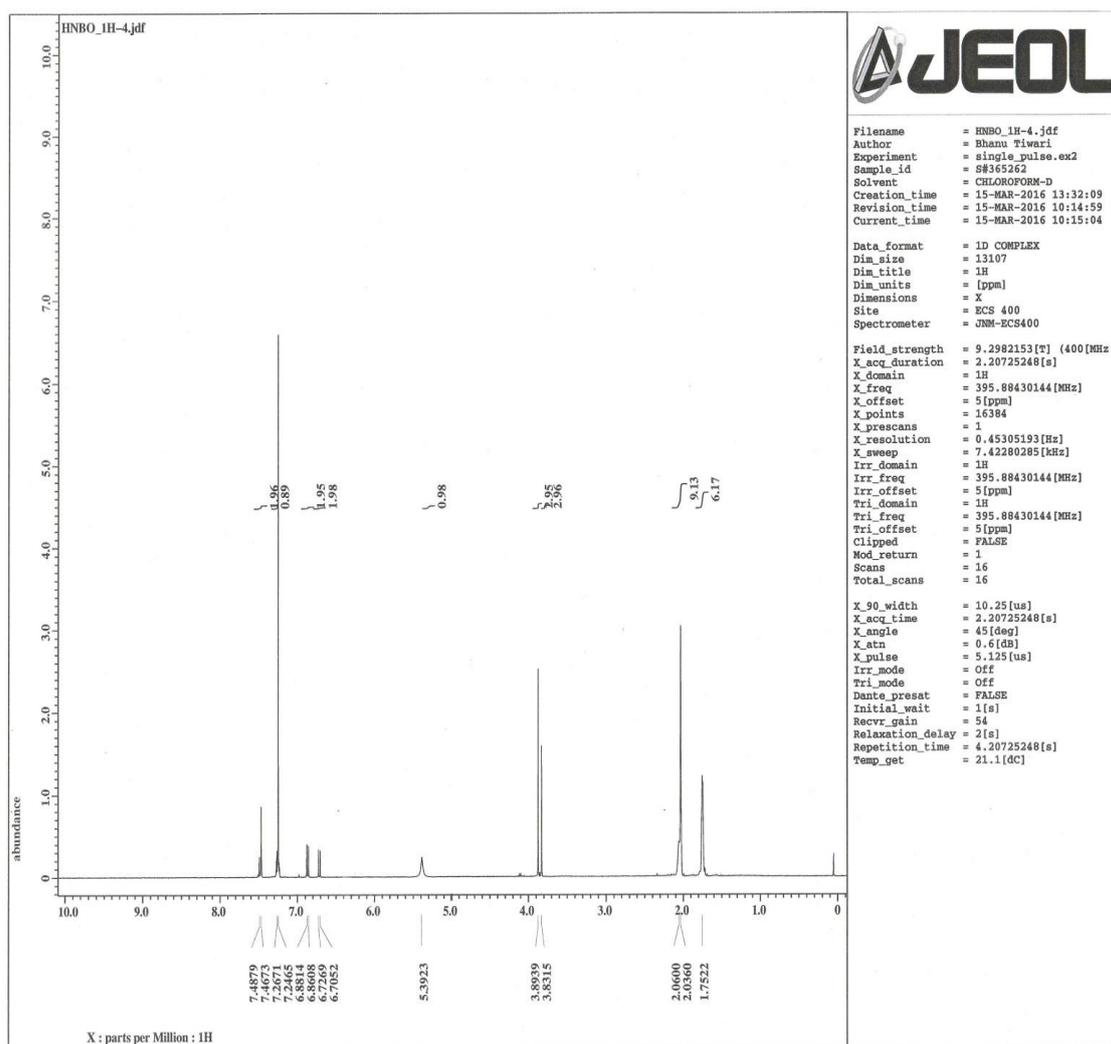


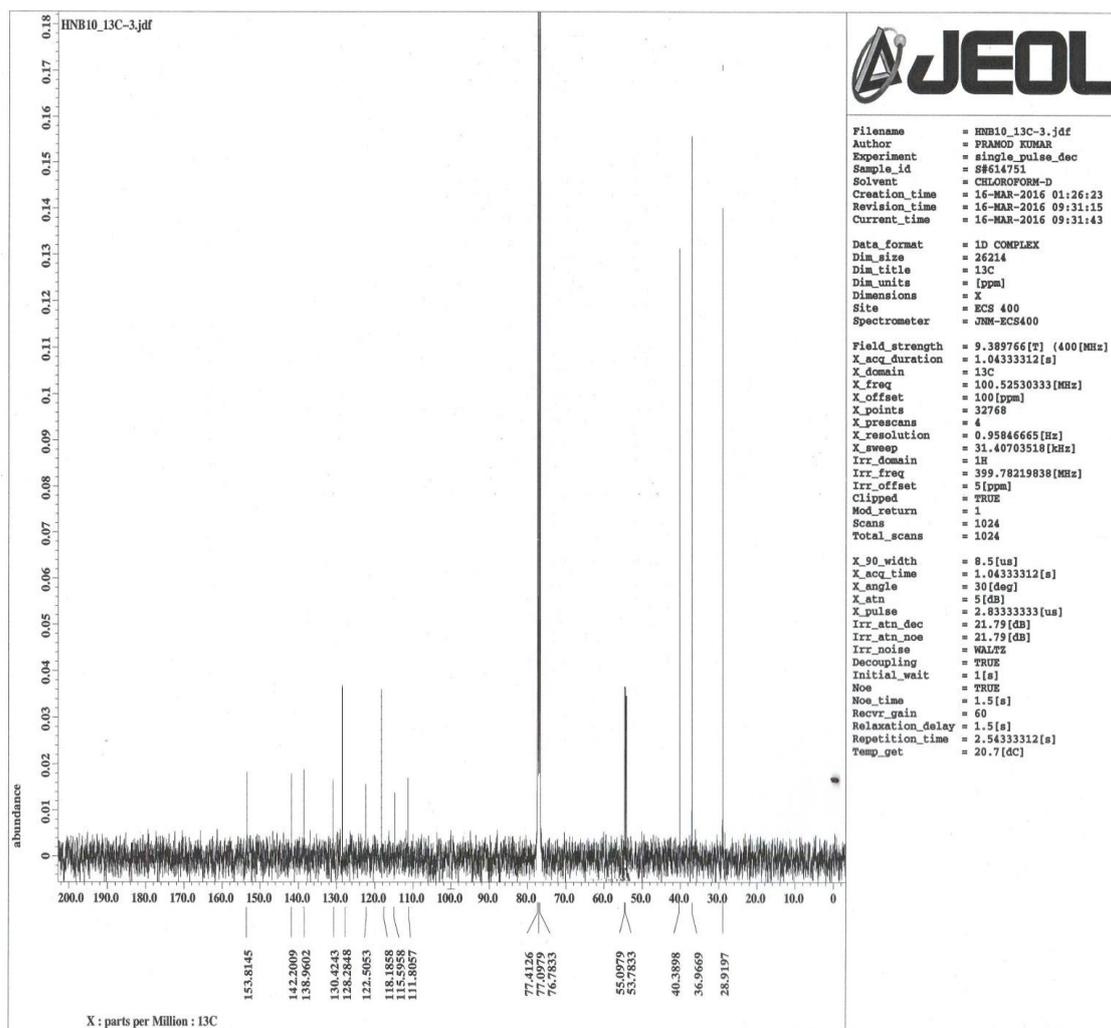
Mass spectra of 3-(adamantan-1-yl)-N-(4-chlorophenyl)-4-methoxyaniline (3a).

SI-04



3-(adamantan-1-yl)-4-methoxy-N-(4-methoxyphenyl)aniline (3b).

¹H NMR spectra of 3-(adamantan-1-yl)-4-methoxy-N-(4-methoxyphenyl)aniline (3b).



¹³C NMR spectra of 3-(adamantan-1-yl)-4-methoxy-N-(4-methoxyphenyl)aniline (3b).

LC-MS REPORT

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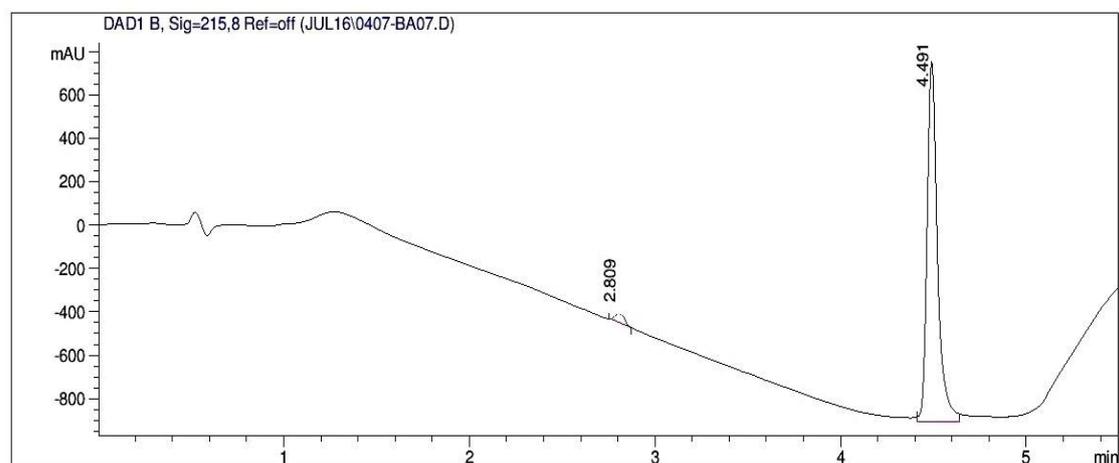
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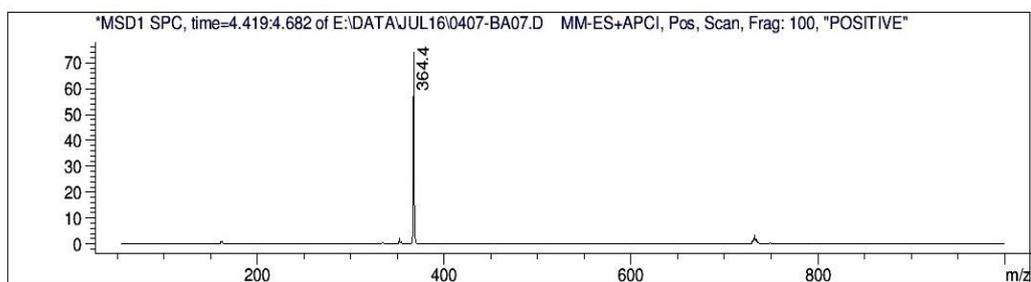
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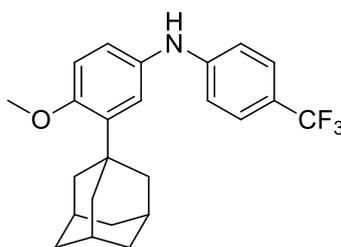
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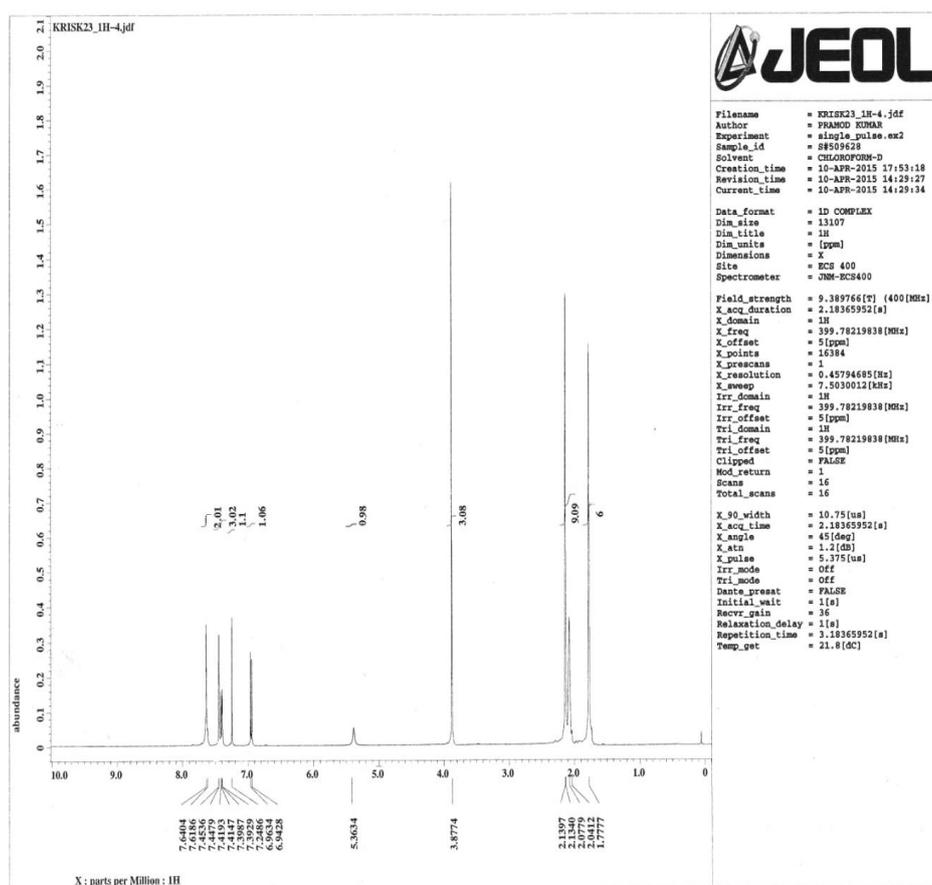
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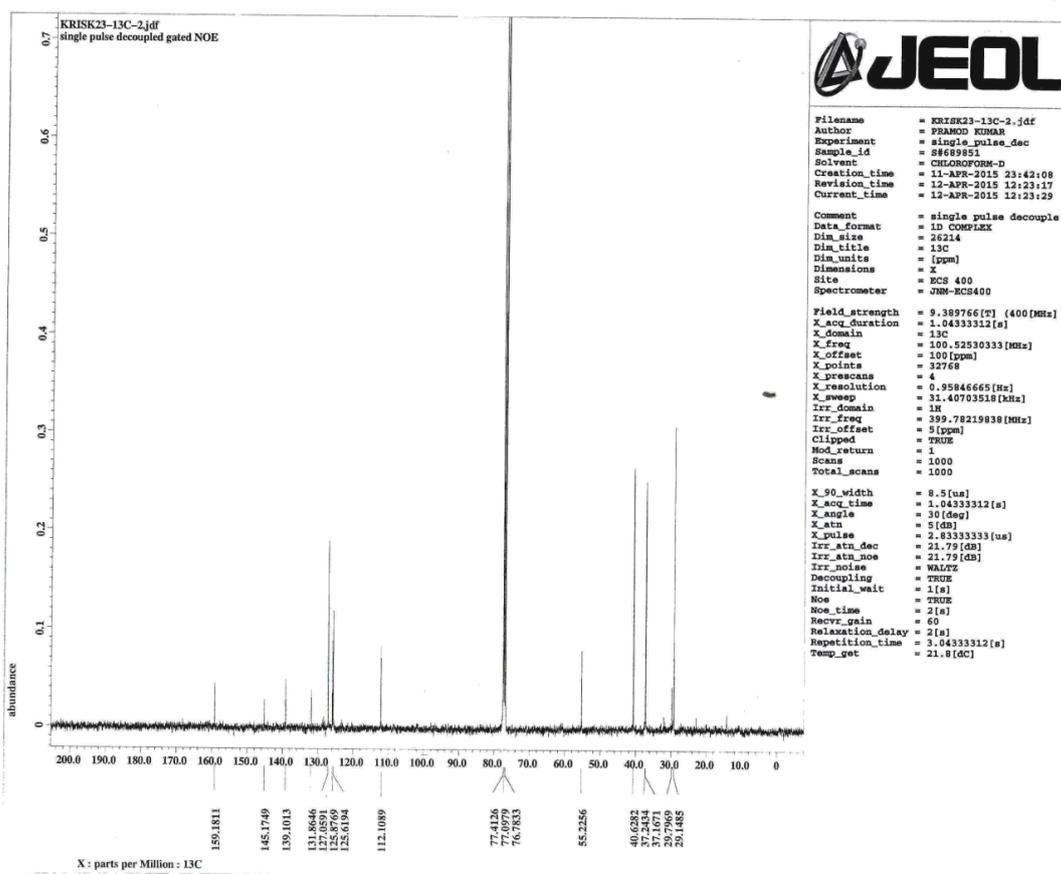
Mass spectra of 3-(adamantan-1-yl)-4-methoxy-N-(4-methoxyphenyl)aniline (3b).

SI-05



3-(adamantan-1-yl)-4-methoxy-N-(4-(trifluoromethyl)phenyl)aniline (3c).

¹H NMR 3-(adamantan-1-yl)-4-methoxy-N-(4-(trifluoromethyl)phenyl)aniline (3c).



¹³C NMR spectra of 3-(adamantan-1-yl)-4-methoxy-N-(4-(trifluoromethyl)phenyl)aniline(3c).

LC-MS REPORT

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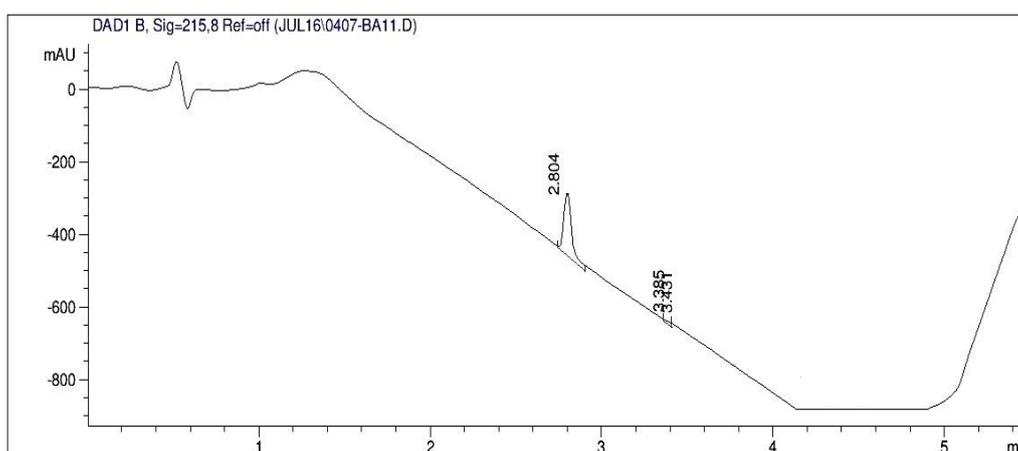
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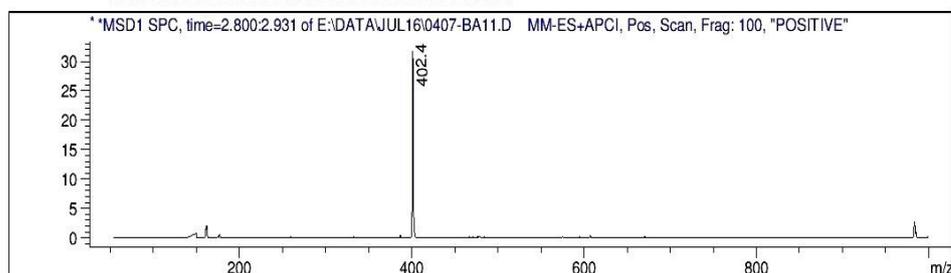
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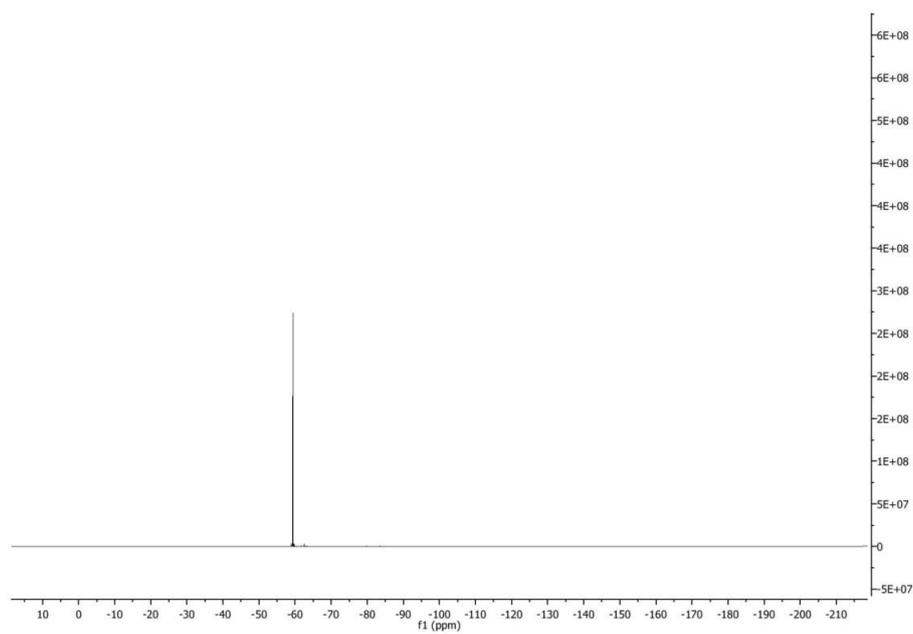


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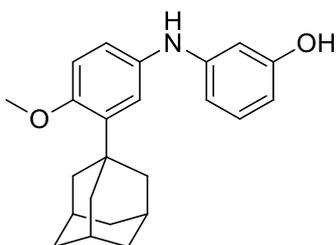
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Mass spectra of 3-(adamantan-1-yl)-4-methoxy-N-(4-(trifluoromethyl)phenyl)aniline (3c).

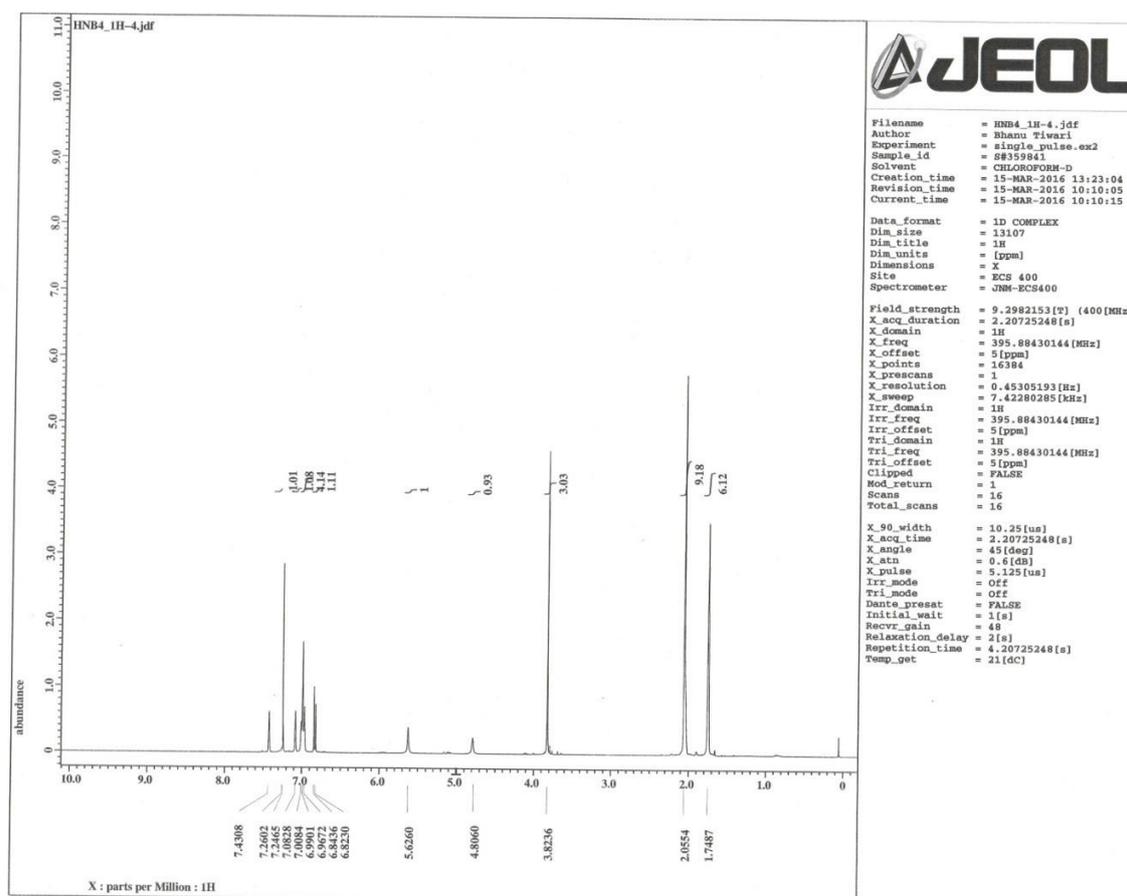


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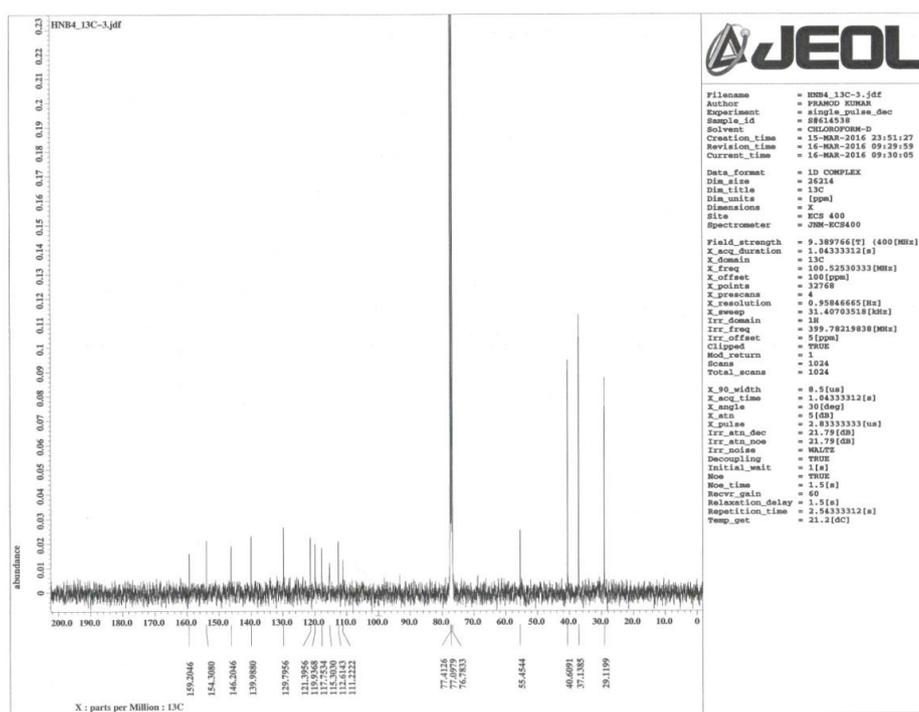
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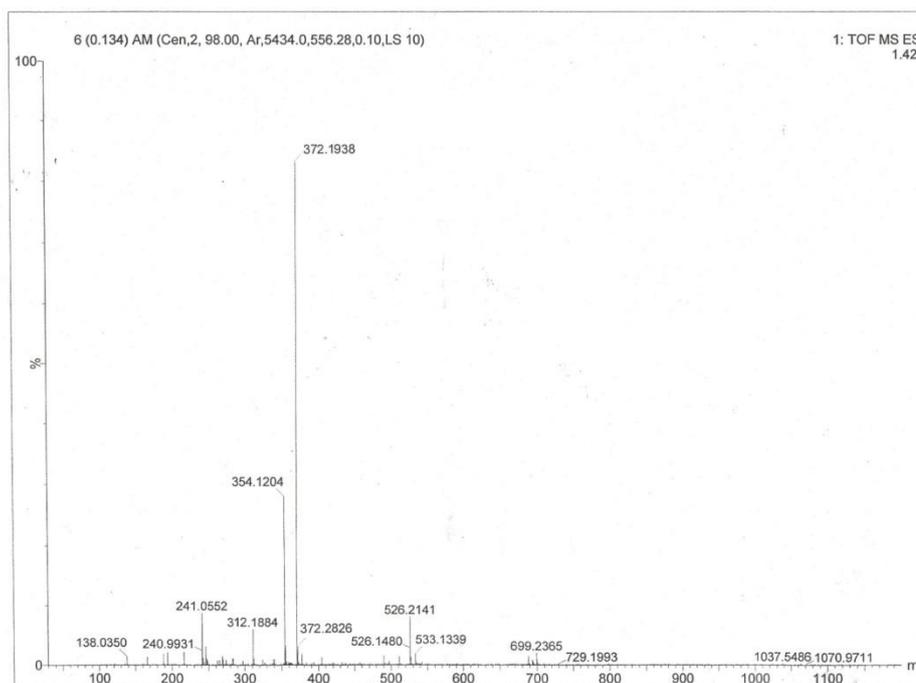
3-((3-(adamantan-1-yl)-4-methoxyphenyl)amino)phenol(3d).



¹H NMR spectra of 3-((3-(adamantan-1-yl)-4-methoxyphenyl)amino)phenol (3d).

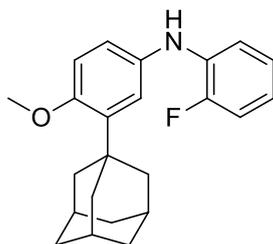


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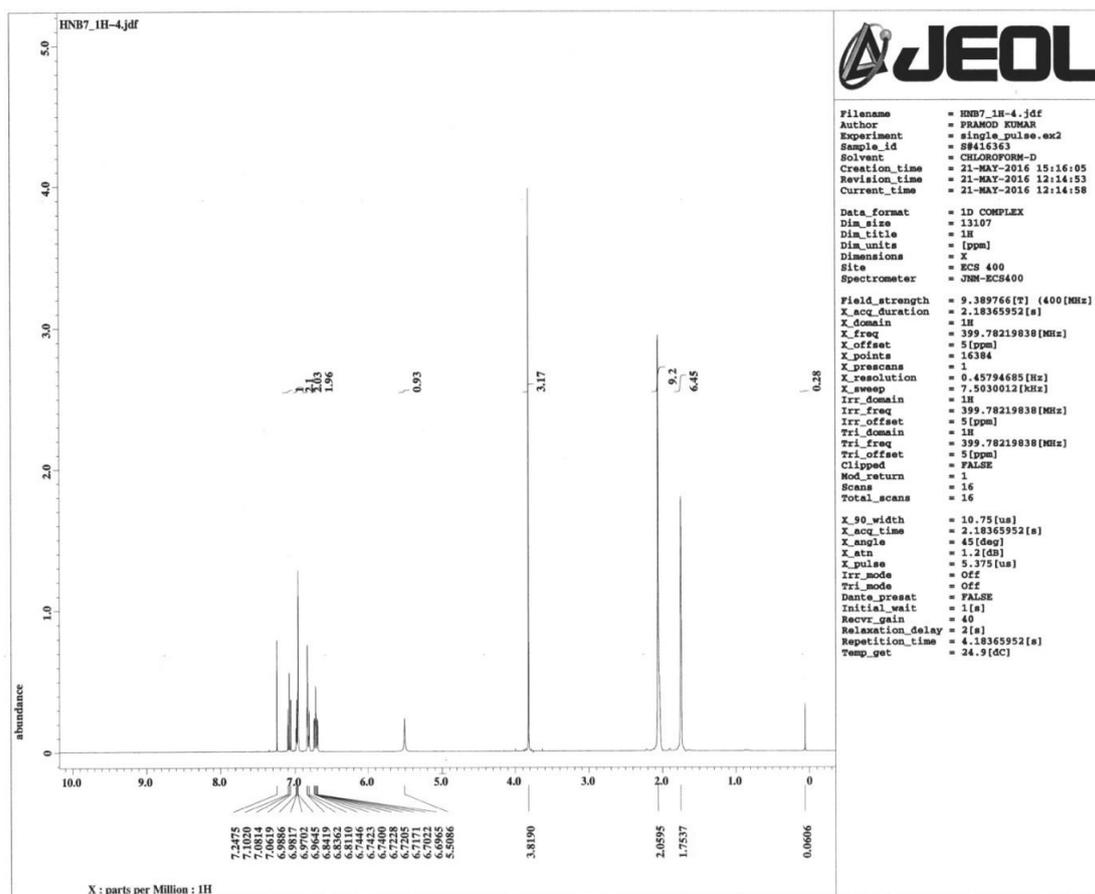


Mass spectra of 3-((3-(adamantan-1-yl)-4-methoxyphenyl)amino)phenol (3d).

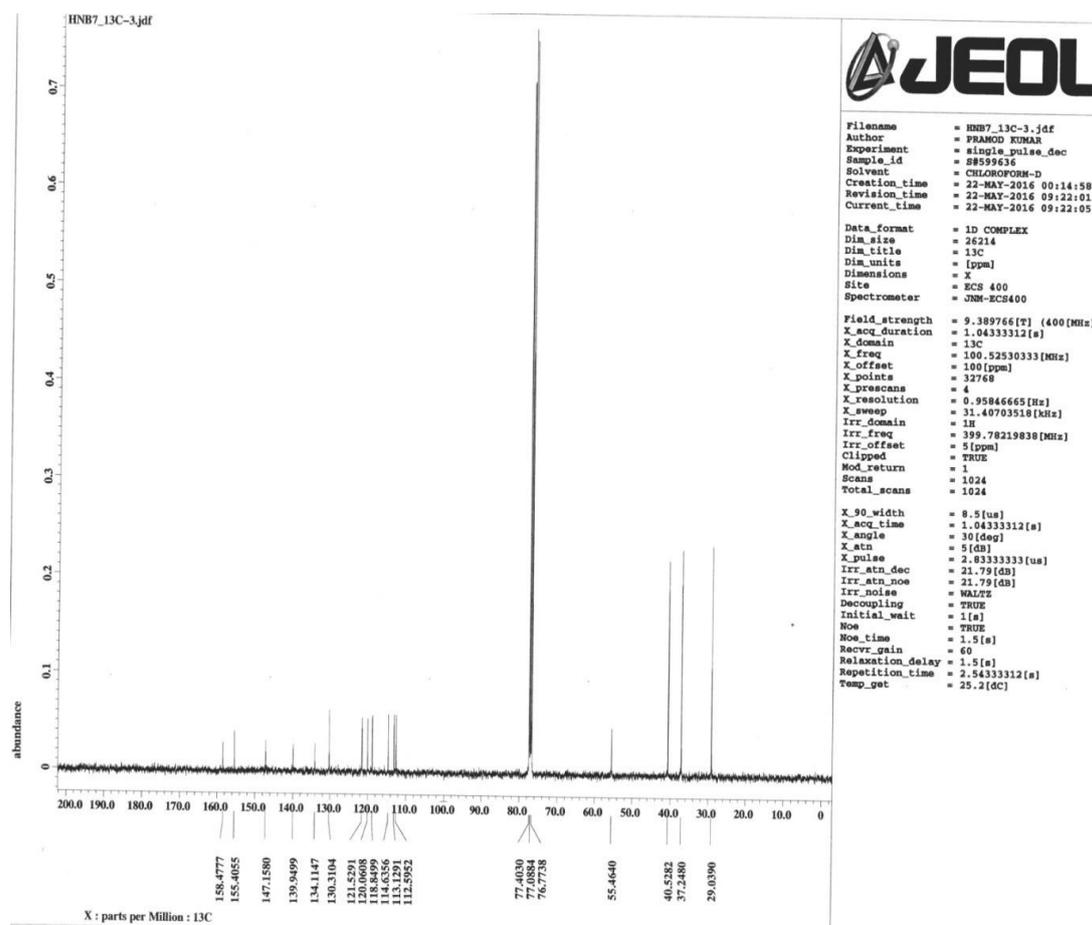
SI-07



3-(adamantan-1-yl)-N-(2-fluorophenyl)-4-methoxyaniline (3e).



¹H NMR spectra of 3-(adamantan-1-yl)-N-(2-fluorophenyl)-4-methoxyaniline (3e).



^{13}C NMR of spectra 3-(adamantan-1-yl)-N-(2-fluorophenyl)-4-methoxyaniline (3e).

LC-MS REPORT

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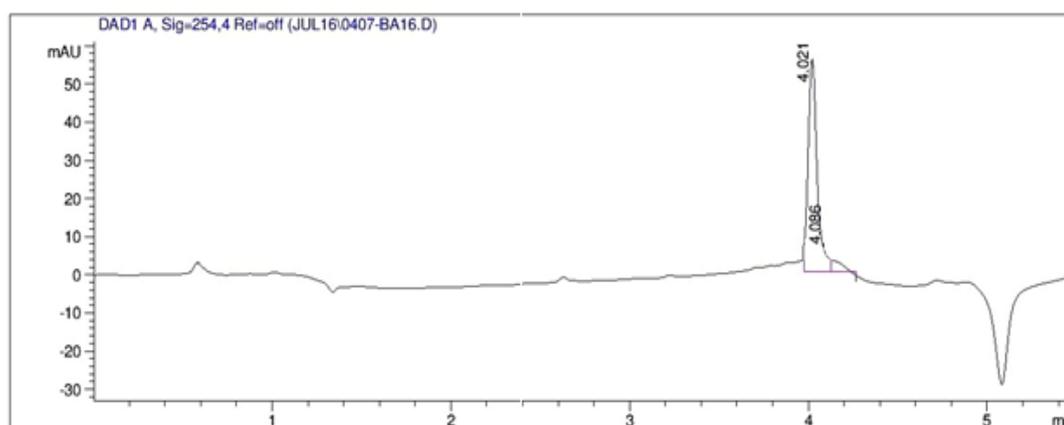
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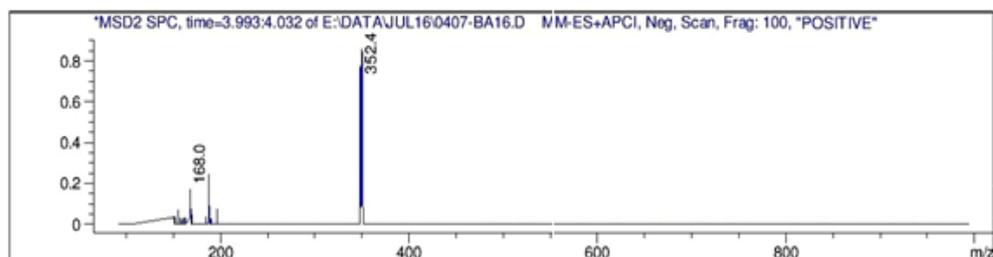
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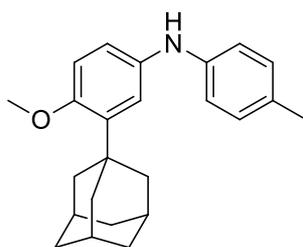
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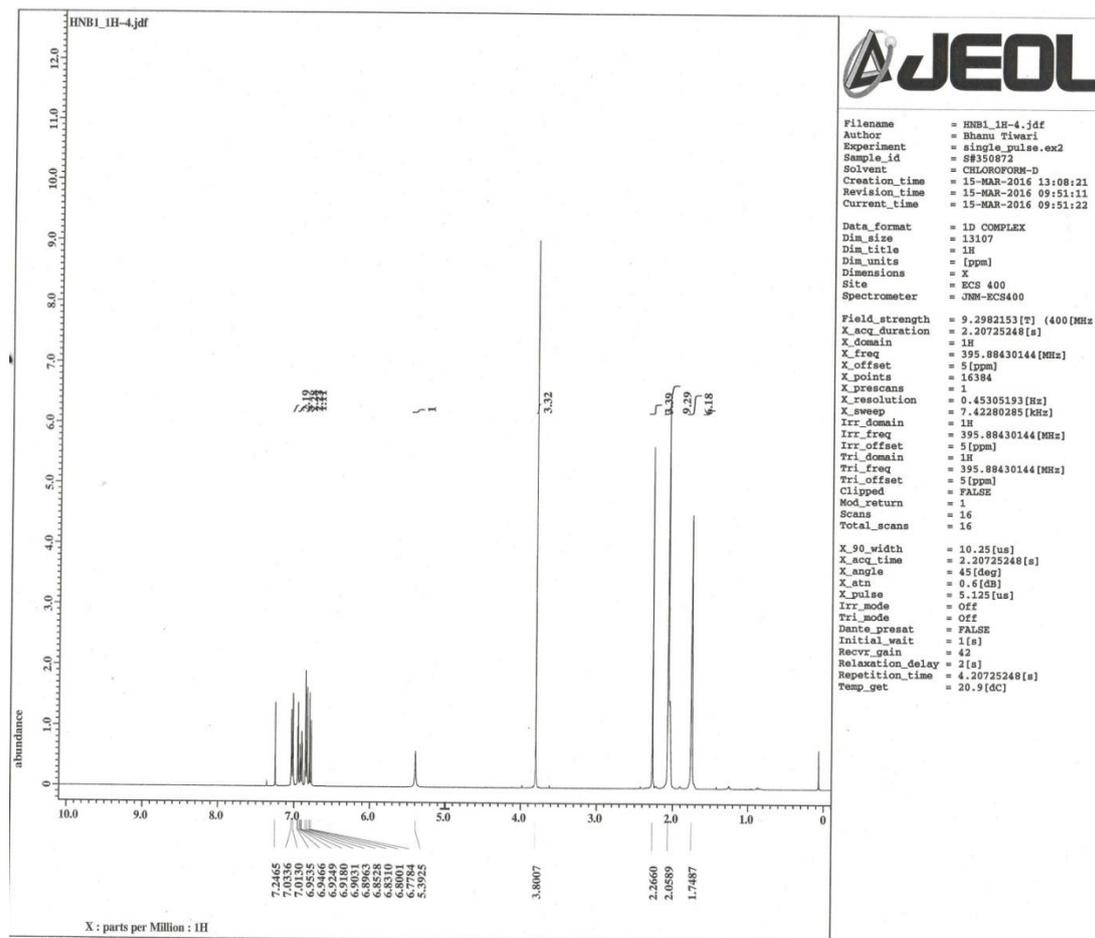
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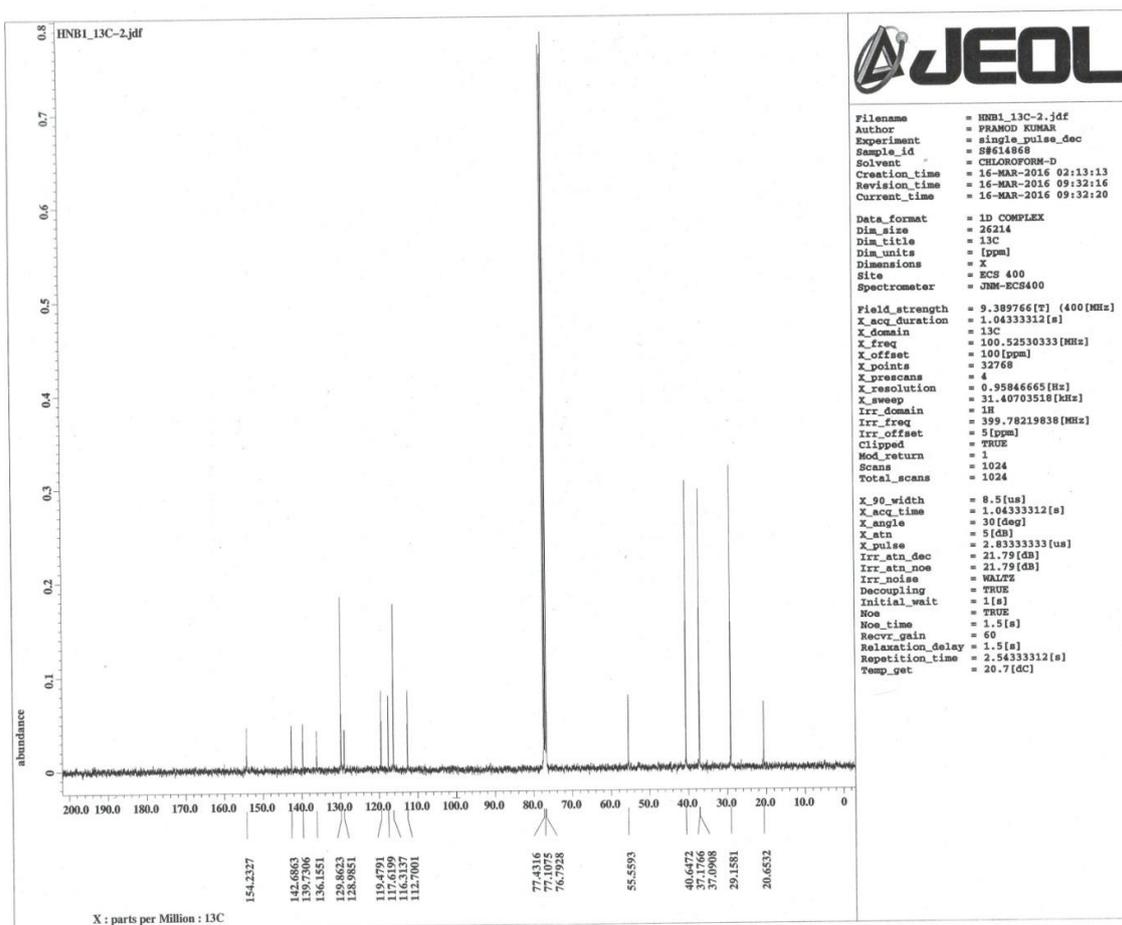
Mass spectra of 3-(adamantan-1-yl)-N-(2-fluorophenyl)-4-methoxyaniline (3e).

SI-08



3-(adamantan-1-yl)-4-methoxy-N-(p-tolyl)aniline (3f).

¹H NMR spectra of 3-(adamantan-1-yl)-4-methoxy-N-(p-tolyl)aniline (3f).



^{13}C NMR spectra of 3-(adamantan-1-yl)-4-methoxy-N-(p-tolyl)aniline (3f).

LC-MS REPORT

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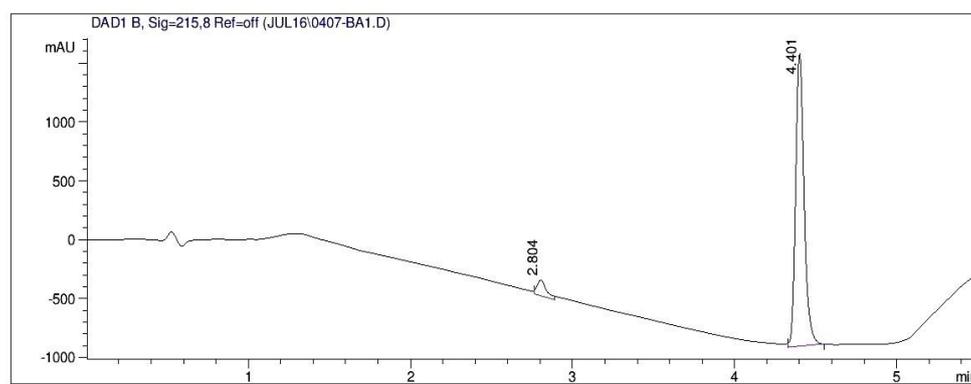
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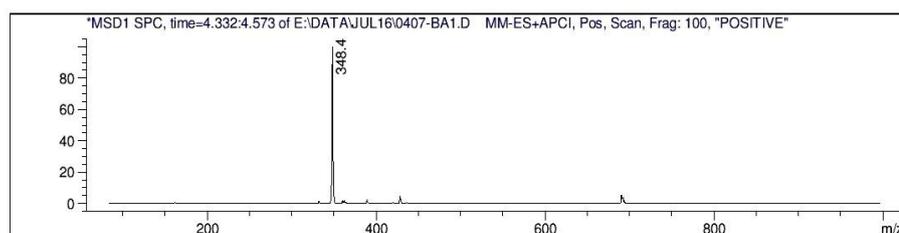
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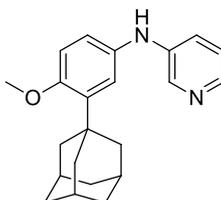
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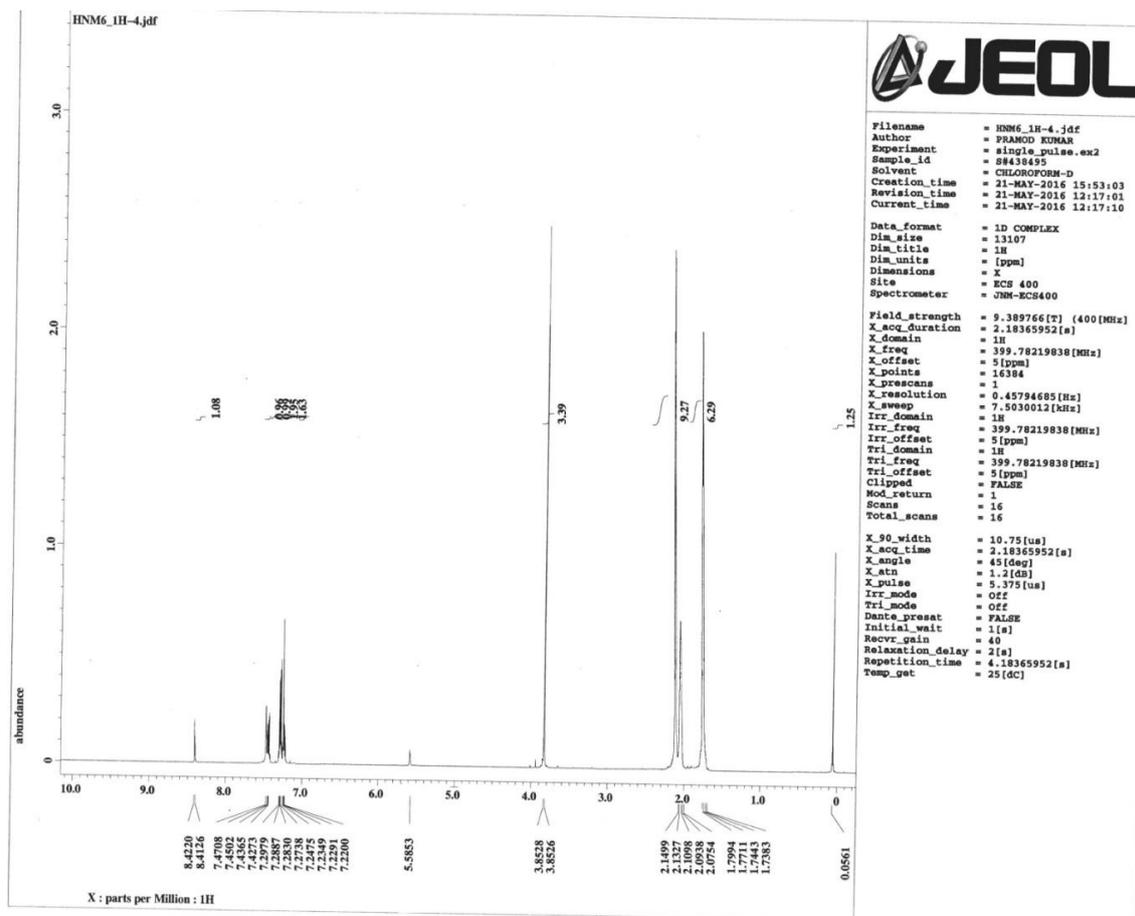
INSTRUMENT NAME: SC/AD/10-013

Mass spectra of 3-(adamantan-1-yl)-4-methoxy-N-(p-tolyl)aniline (3f).

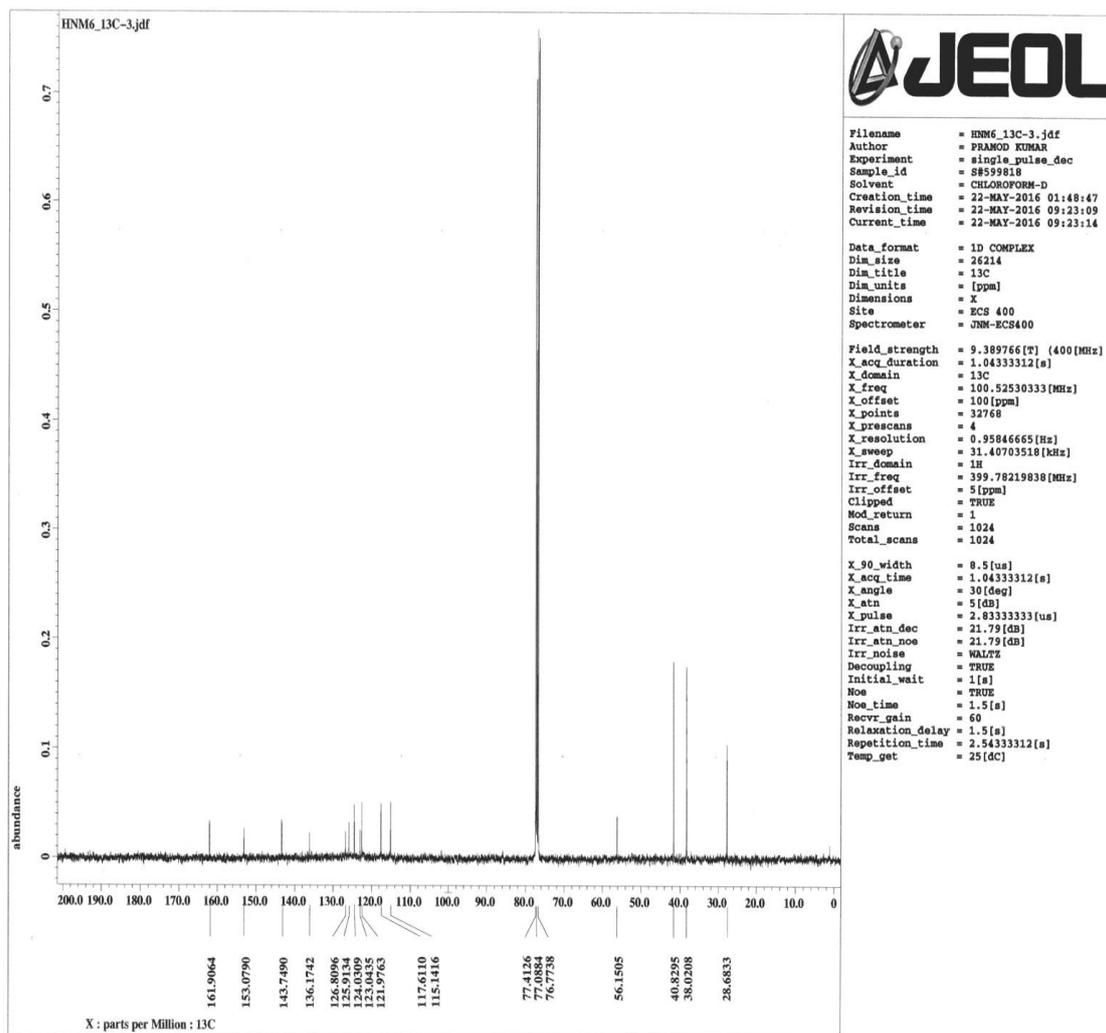
SI-09



N-(3-adamantan-1-yl)-4-methoxyphenylpyridin-3-amine (3g).



¹H NMR spectra of N-(3-adamantan-1-yl)-4-methoxyphenylpyridin-3-amine (3g).



^{13}C NMR spectra of N-(3-adamantan-1-yl)-4-methoxyphenylpyridin-3-amine (3g).

LC-MS REPORT

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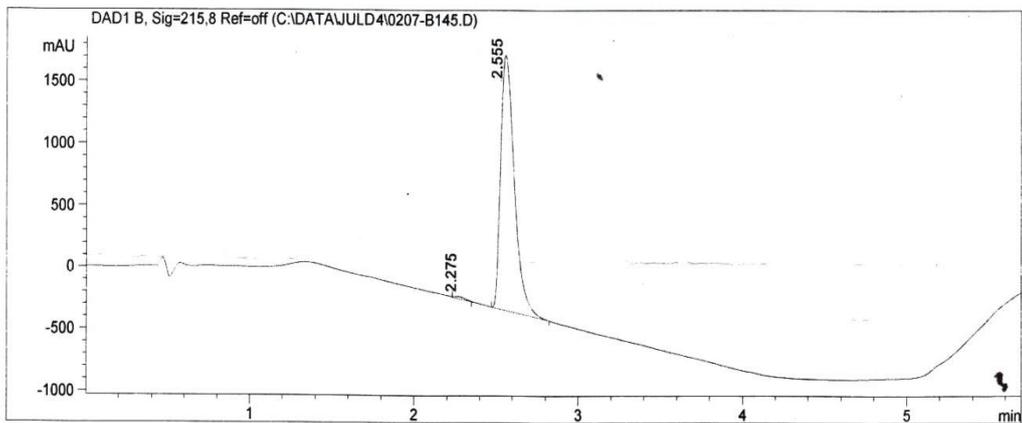
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Sample Name    :
Acq Method     : C:\CHEM32\1\METHODS\AT_595FAD.M
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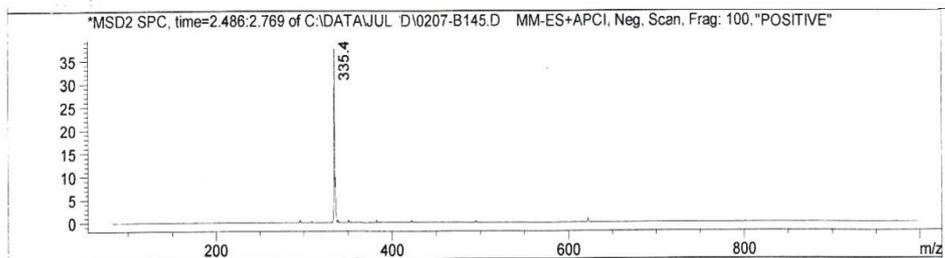
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                        %B      5-95      95      95-5      5

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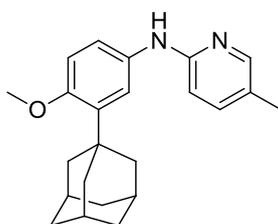
Peak No	RT min	Area	Area %
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2	2.555	1.200e+004	99.201



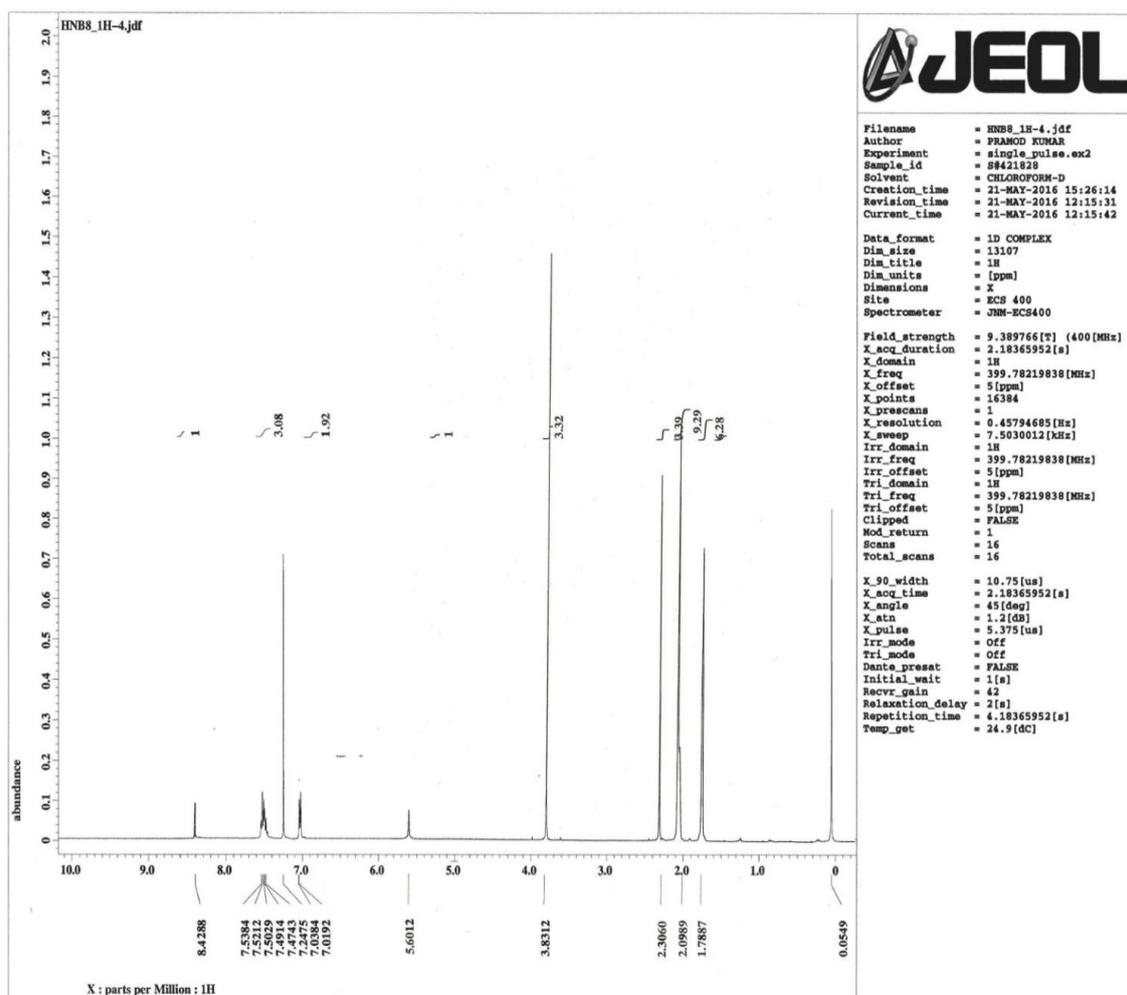
INSTRUMENT NAME: SC/AD/10-013

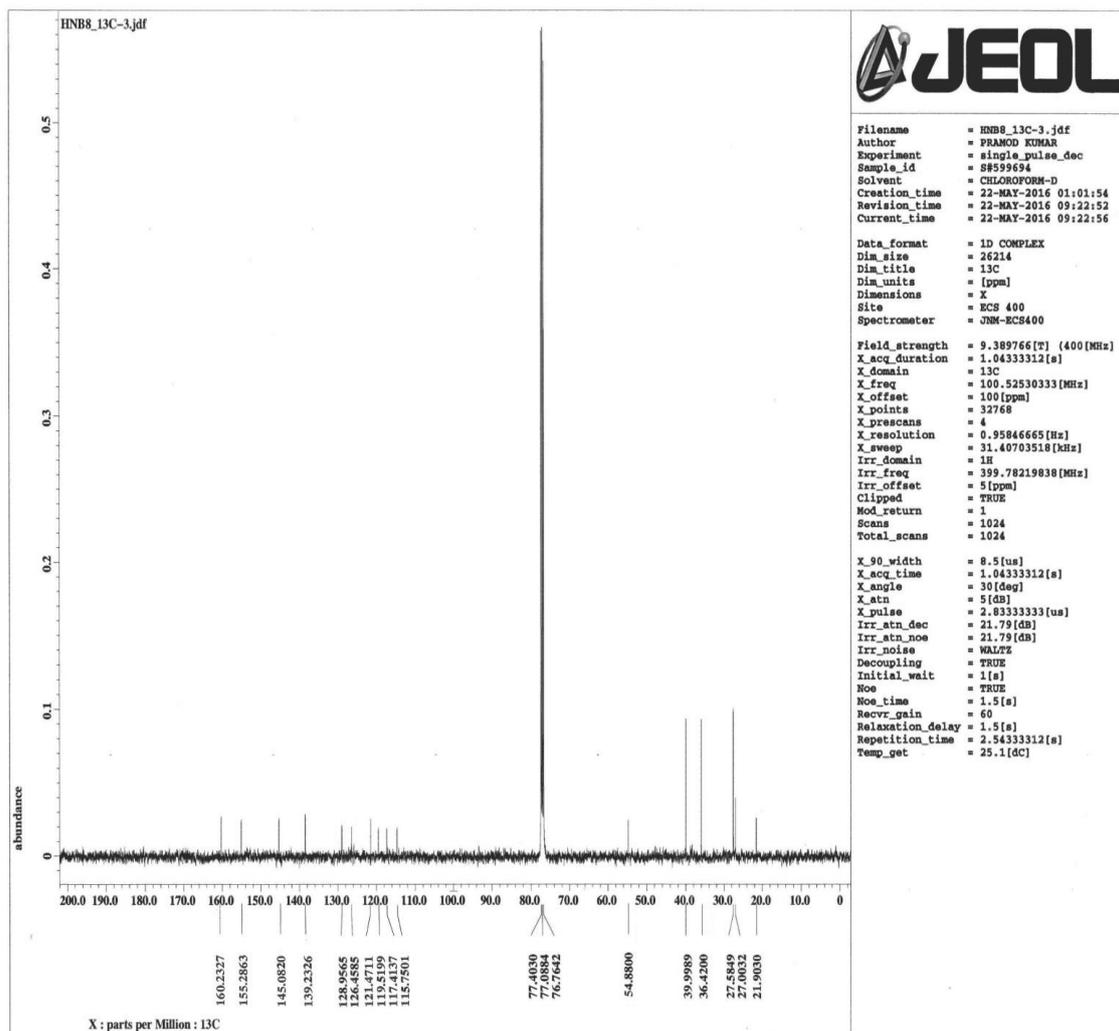
Mass spectra of N-(3-adamantan-1-yl)-4-methoxyphenylpyridin-3-amine (3g).

SI-10

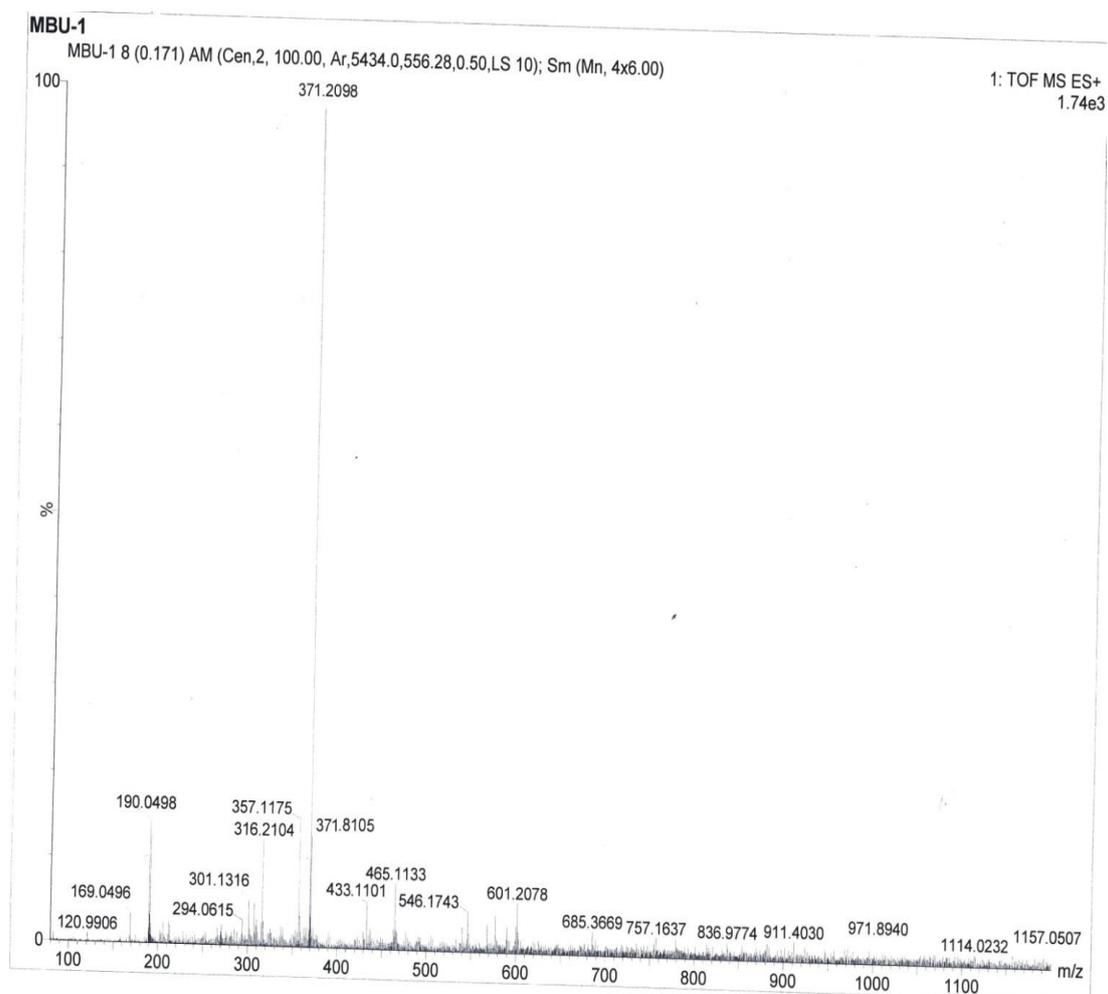


N-(3-adamantan-1-yl)-4-methoxyphenyl)-5-methylpyridin-2-amine (3h).

¹H NMR spectra of N-(3-adamantan-1-yl)-4-methoxyphenyl)-5-methylpyridin-2-amine (3h).

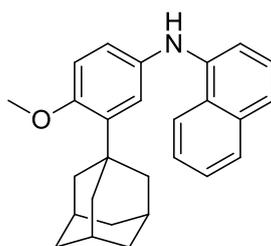


¹³C NMR spectra of N-(3-adamantan-1-yl)-4-methoxyphenyl)-5-methylpyridin-2-amine (3h).

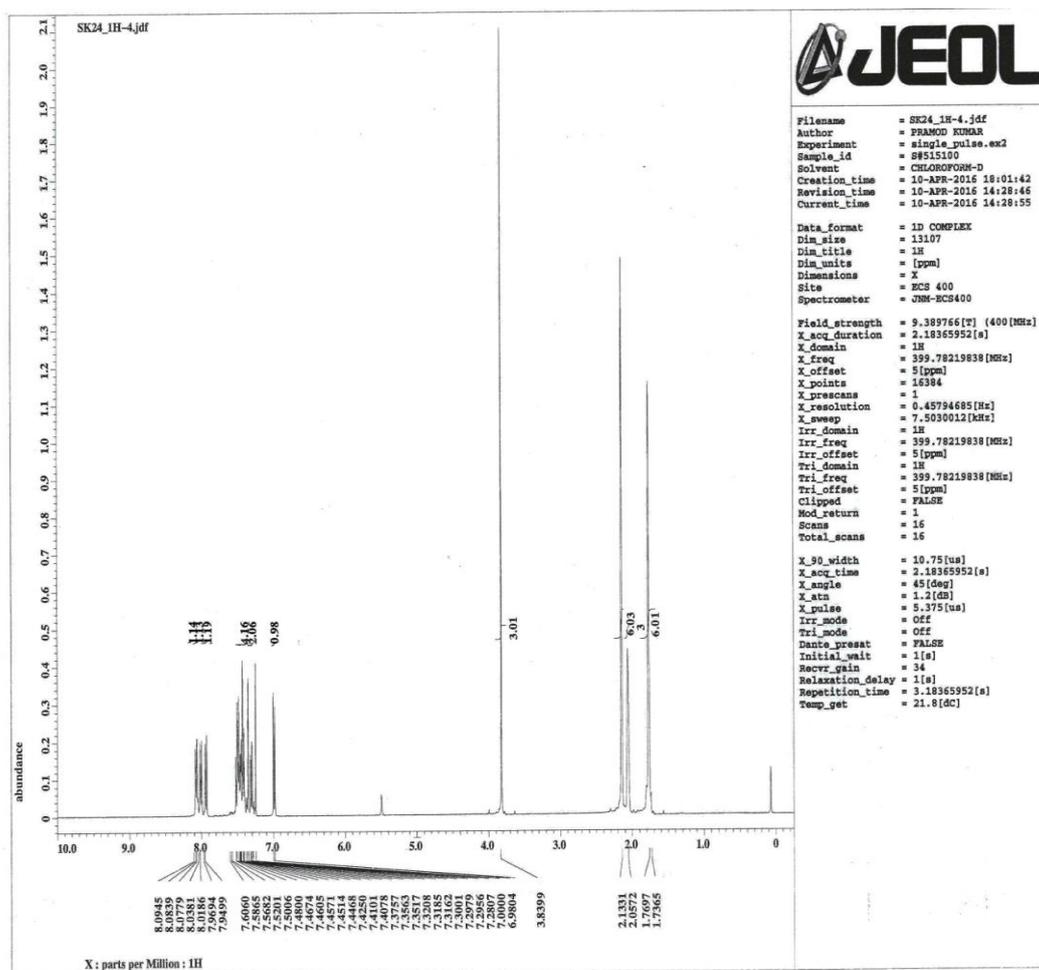


Mass spectra of N-(3-adamantan-1-yl)-4-methoxyphenyl)-5-methylpyridin-2-amine (3h).

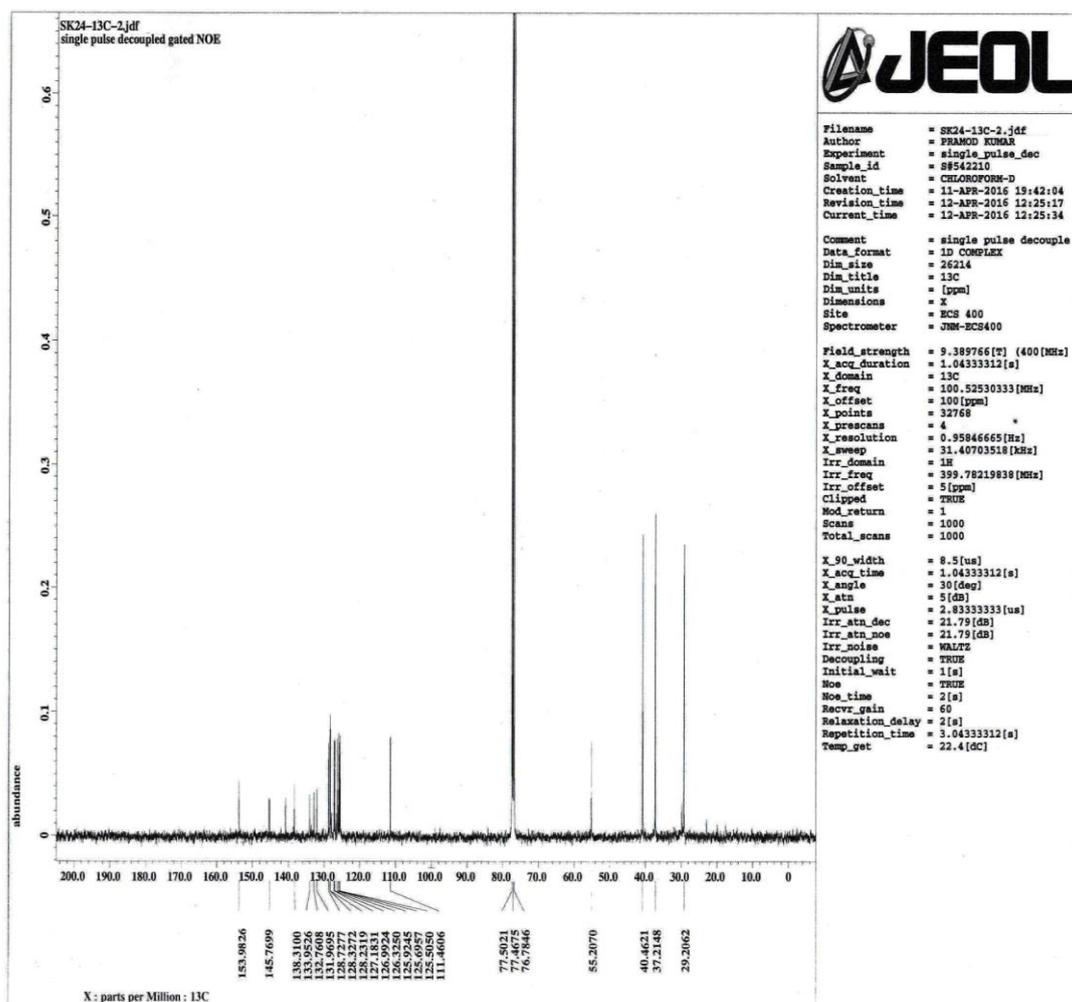
SI-11



N-(3-adamantan-1-yl)-4-methoxyphenyl)naphthalen-1-amine (3i).



¹H NMR spectra of N-(3-adamantan-1-yl)-4-methoxyphenyl)naphthalen-1-amine (3i).



^{13}C NMR spectra of N-(3-adamantan-1-yl)-4-methoxyphenyl)naphthalen-1-amine (3i).

LC-MS REPORT

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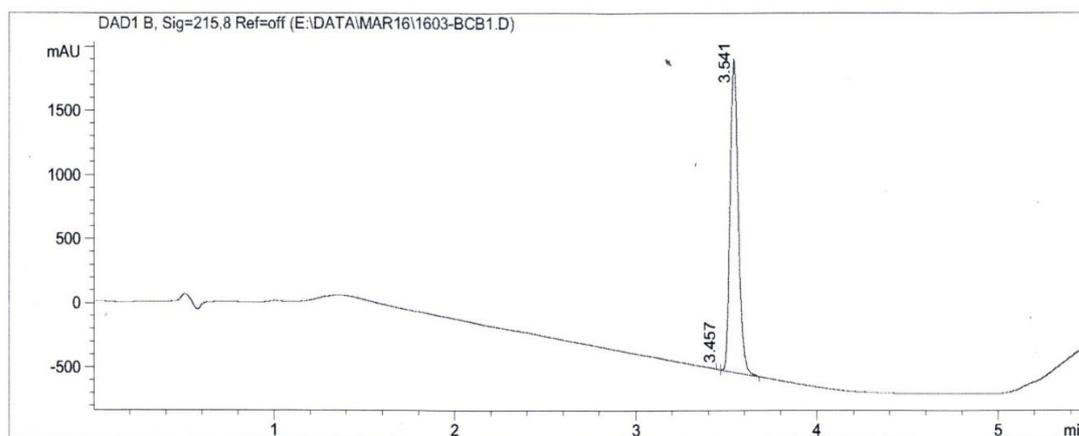
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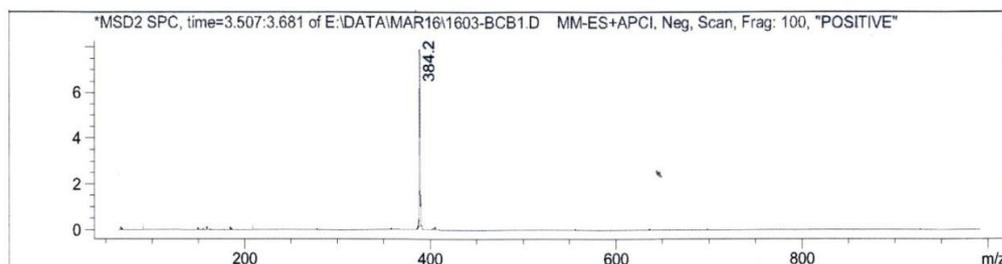
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                       %B      5-95    95      95-5    5
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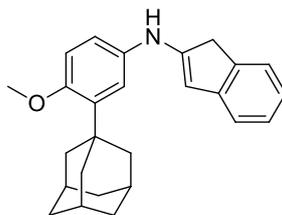
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2	3.541	7.666e+003	99.983



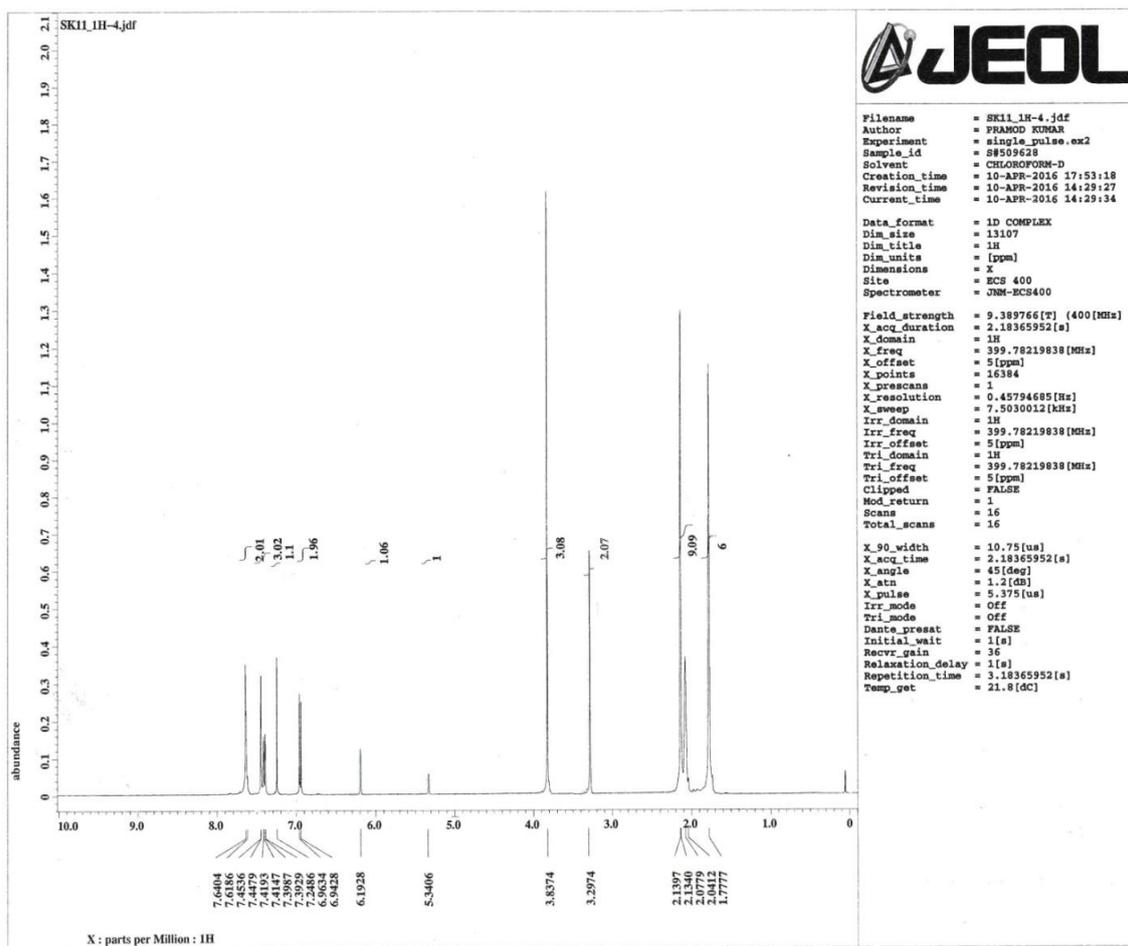
INSTRUMENT NAME:SC/AD/10-013

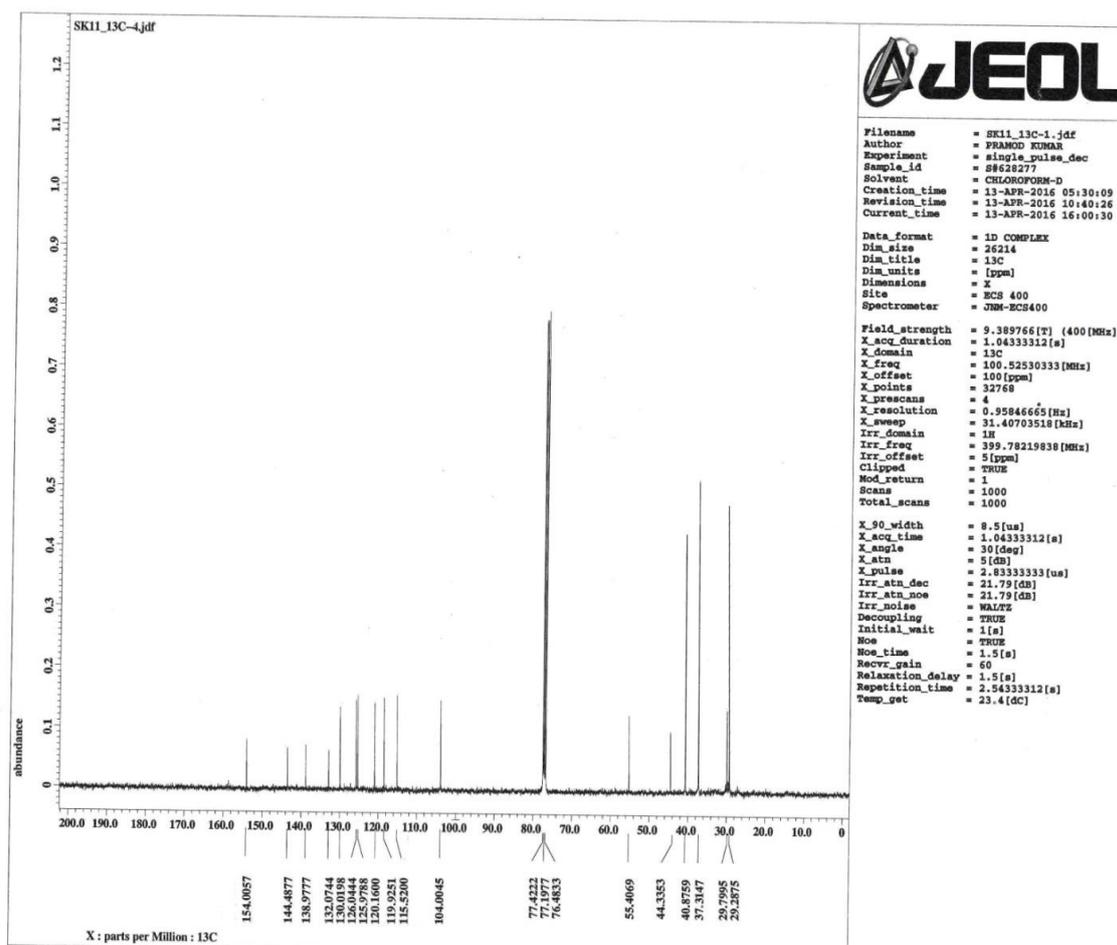
Mass spectra of N-(3-adamantan-1-yl)-4-methoxyphenyl)naphthalen-1-amine (3i).

SI-12



N-(3-adamantan-1-yl)-4-methoxyphenyl)-1H-inden-2-amine (3j).

¹H NMR spectra of N-(3-adamantan-1-yl)-4-methoxyphenyl)-1H-inden-2-amine (3j).



^{13}C NMR spectra of N-(3-adamantan-1-yl)-4-methoxyphenyl)-1H-inden-2-amine (3j).

LC/MS REPORT

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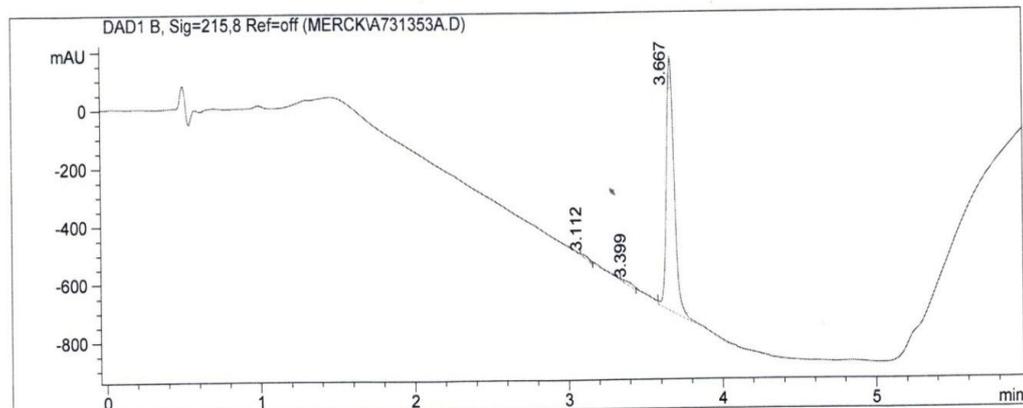
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Vial No.       : P2-F-02
Injection Date  : 11- Jul- 2016           6:15:07 PM
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Acq Method     : C:\CHEM32\1\METHODS\AT_595FAD.M
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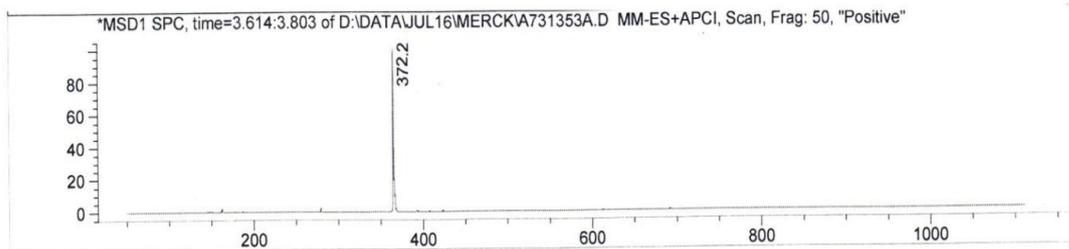
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Method info :A-0.1%HCOOH;B-ACN Flow: 1.5ml/min,
             Column-ATLANTIS dC18 (50X4.6mm-5µm, ) DUAL MODE
             TIME (MIN) : 0--3      3--4      4--4.5  4.5-6
                       %B          5-95      95      95-5    5
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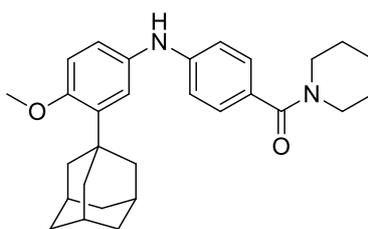
Peak No	RT min	Area	Area %
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2	3.399	5.734e+001	0.882
3	3.667	3.041e+003	98.208



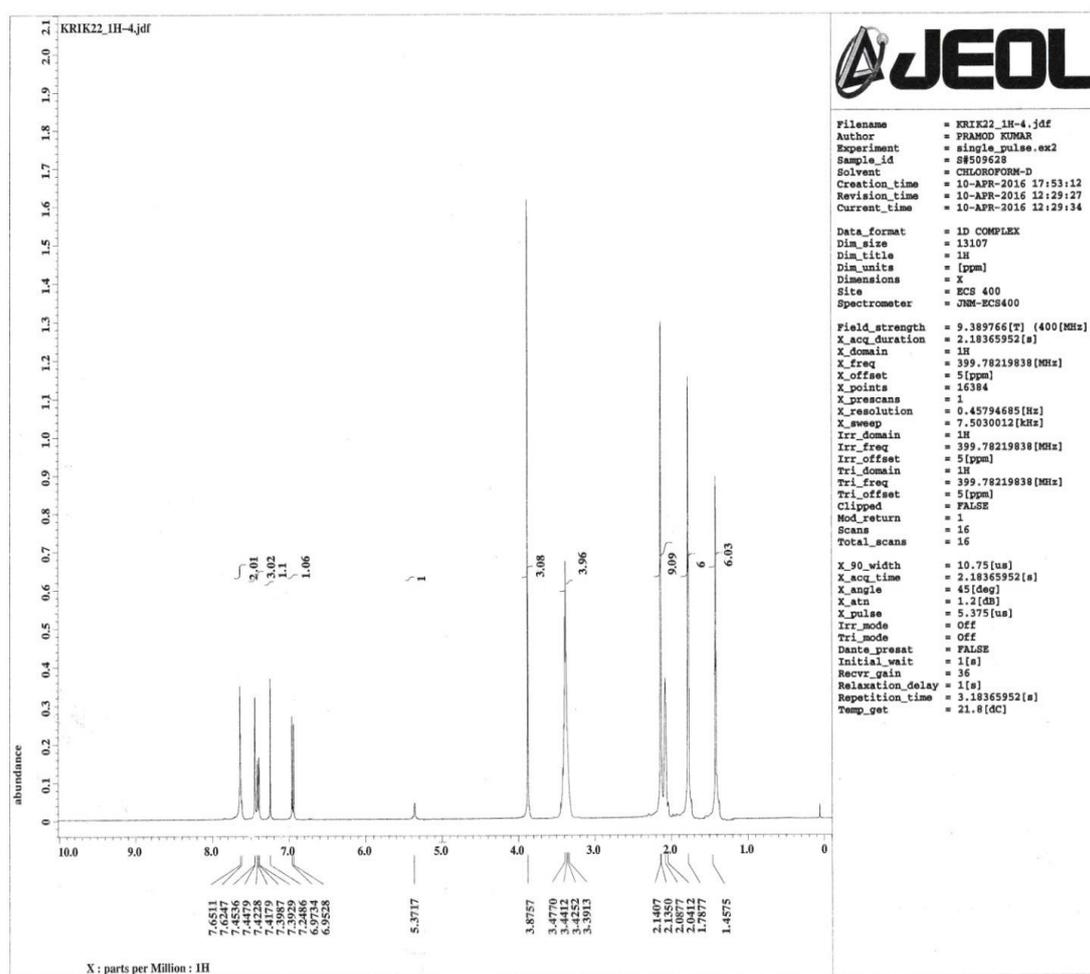
Instrument Code : SC/AD/10-010

Mass spectra of N-(3-adamantan-1-yl)-4-methoxyphenyl)-1H-inden-2-amine (3j).

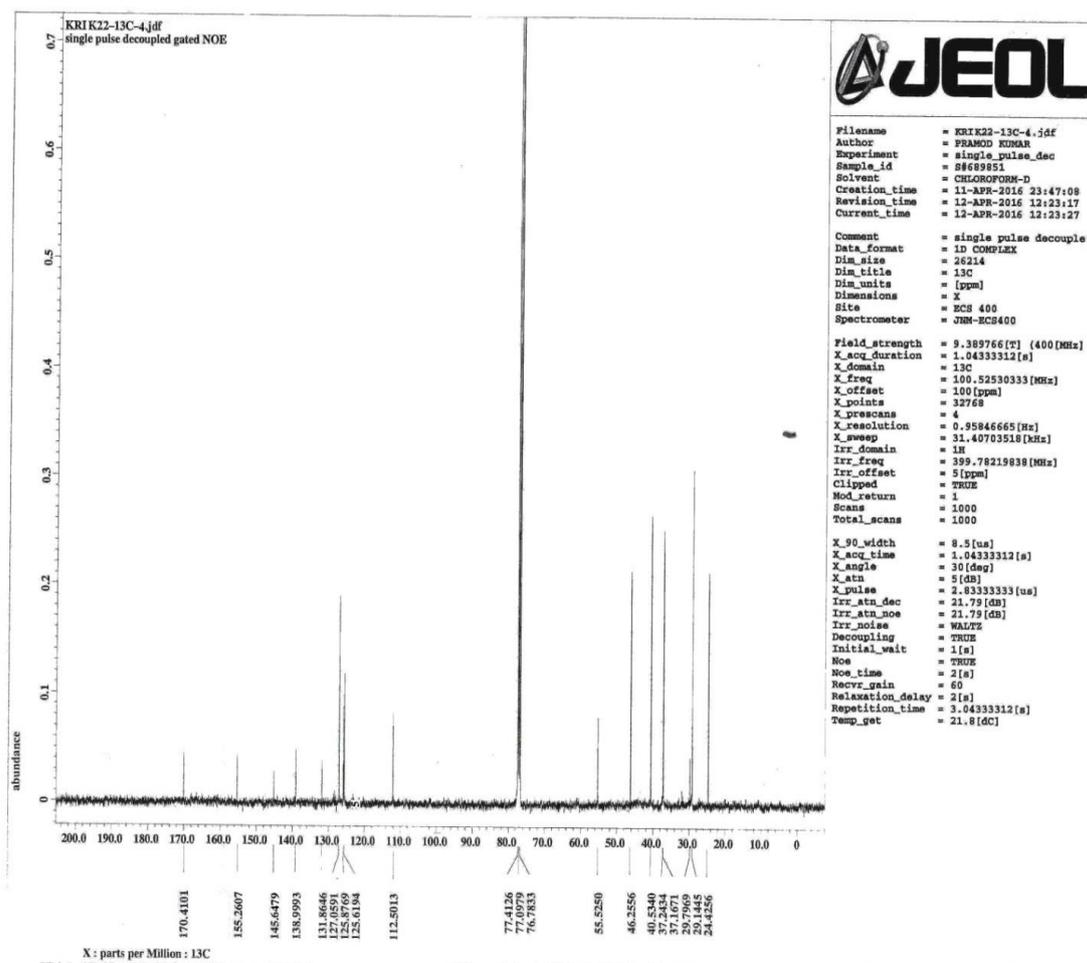
SI-13



(4-((3-(adamantan-1-yl)-4-methoxyphenyl)amino)phenyl)(piperidin-1-yl)methanone (3k)



^1H NMR spectra of 4-((3-(adamantan-1-yl)-4-methoxyphenyl)amino)phenyl(piperidin-1-yl)methanone (3k).



¹³C NMR spectra of 4-((3-(adamantan-1-yl)-4-methoxyphenyl)amino)phenyl(piperidin-1-yl)methanone(3k).

LC-MS REPORT

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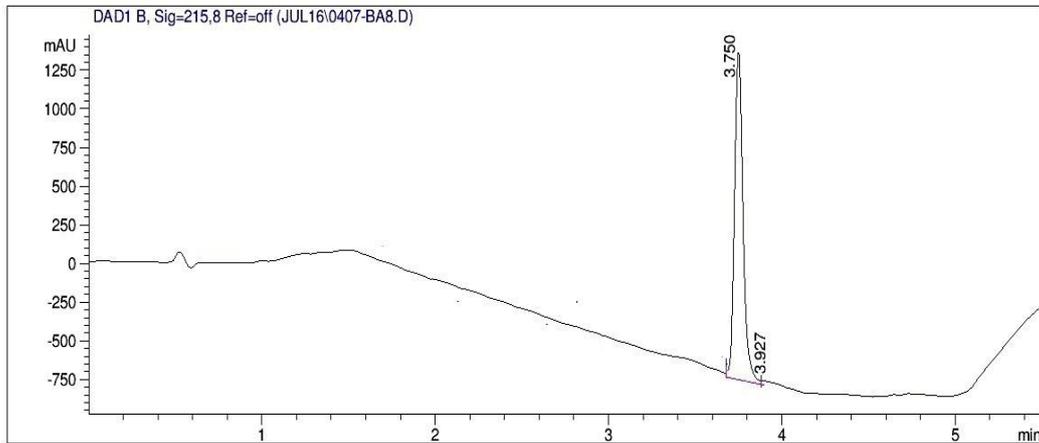
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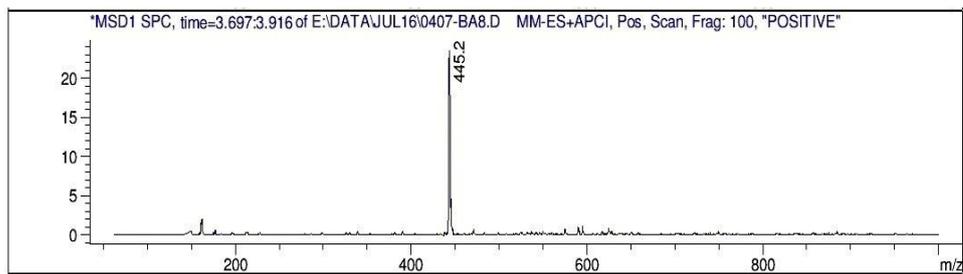
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Method info :MOBILE PHASE:A-10mM Ammonium acetate in water ;B-Acetonitrile,
Flow: 1.2ml/min,
COLUMN:ZORBAX XDB C18 (50X4.6mm-5µm, )
TIME (MIN)  : 0--2.5    2.5--4.0    4.0--4.5    4.5--6.0
              %B        10-95       95         95-10       10

```

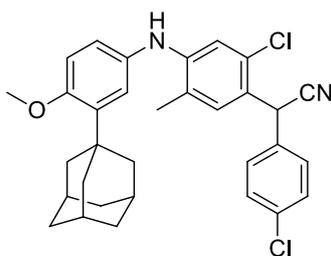


Peak No	RT min	Area	Area %
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2	3.927	1.033e+002	10.225

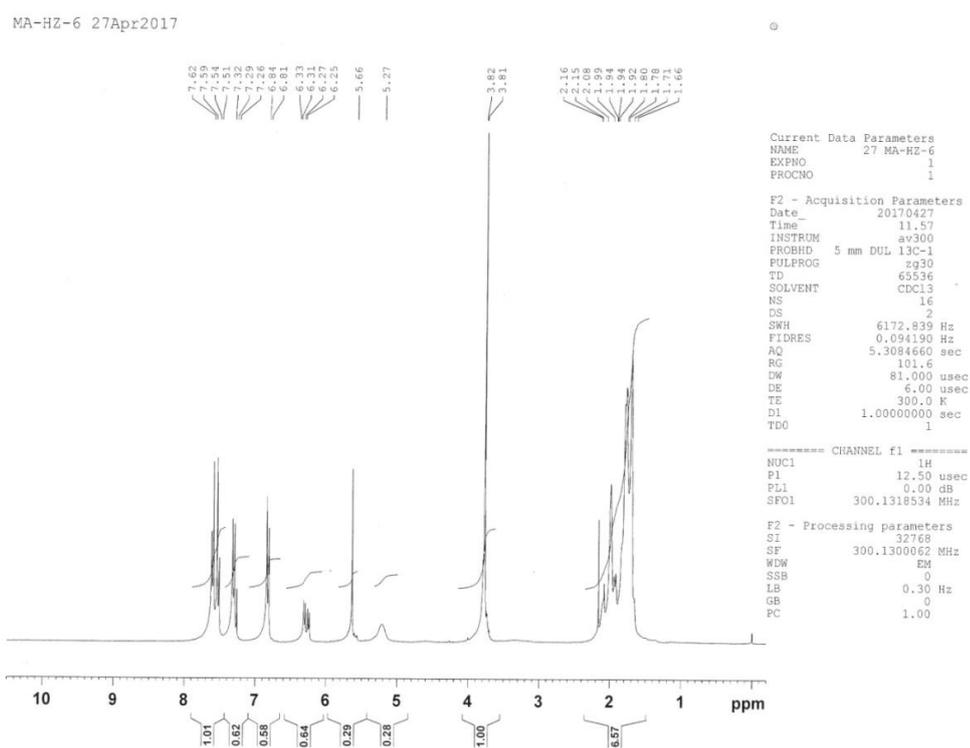


INSTRUMENT NAME:SC/AD/10-013

Mass spectra of (4-((3-(adamantan-1-yl)-4-methoxyphenyl)amino)phenyl)(piperidin-1-yl)methanone (3k).

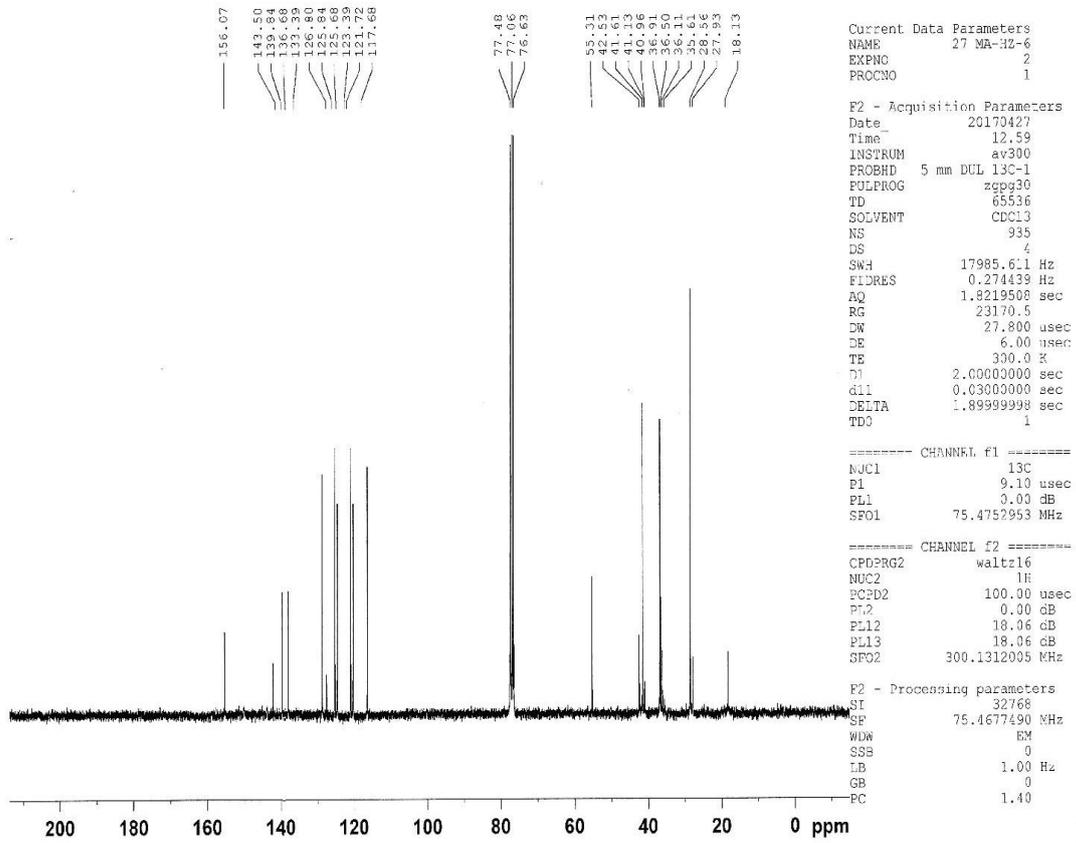


2-(4-((3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)amino)-2-chloro-5-methylphenyl)-2-(4-chlorophenyl)acetonitrile (3l).

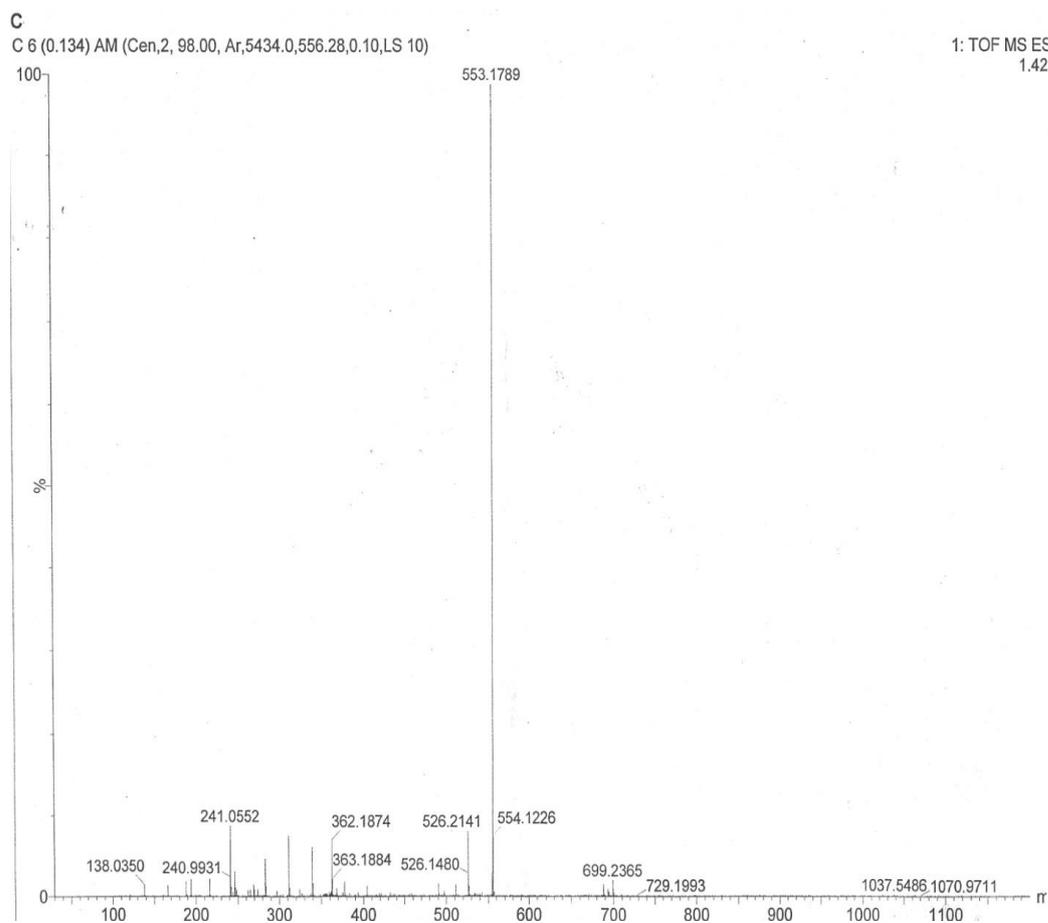


^1H NMR spectra of 2-(4-((3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)amino)-2-chloro-5-methylphenyl)-2-(4-chlorophenyl)acetonitrile (3l).

MA-HZ-6 27Apr2017

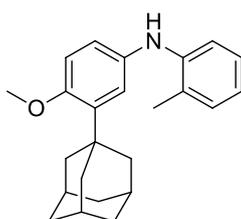


¹³C NMR spectra of 2-(4-((3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)amino)-2-chloro-5-methylphenyl)-2-(4-chlorophenyl)acetonitrile (3l).

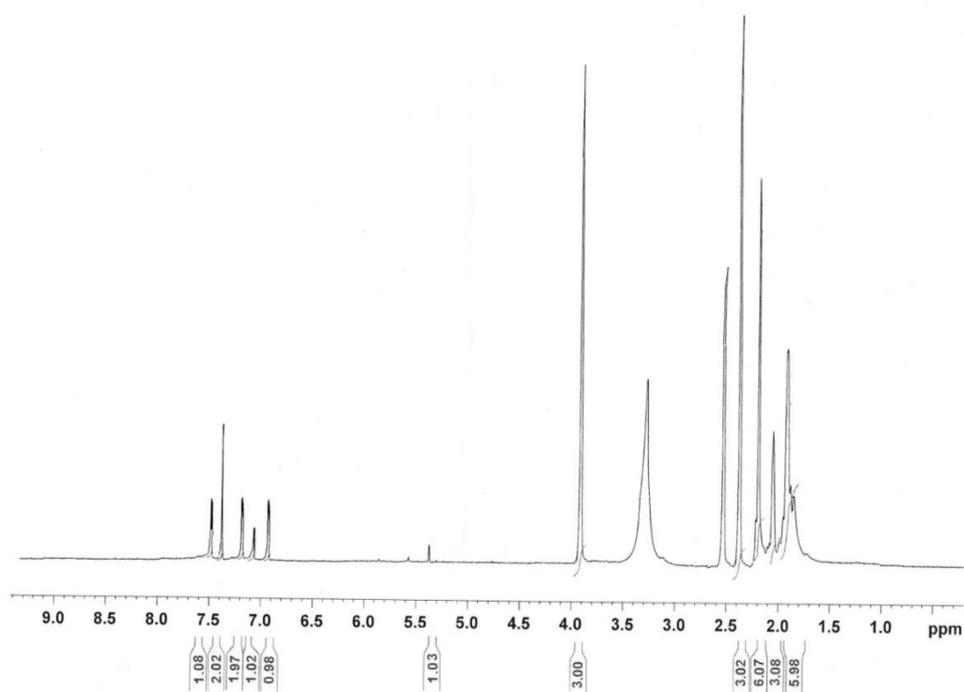


Mass spectra of 2-(4-((3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)amino)-2-chloro-5-methylphenyl)-2-(4-chlorophenyl)acetonitrile (3l).

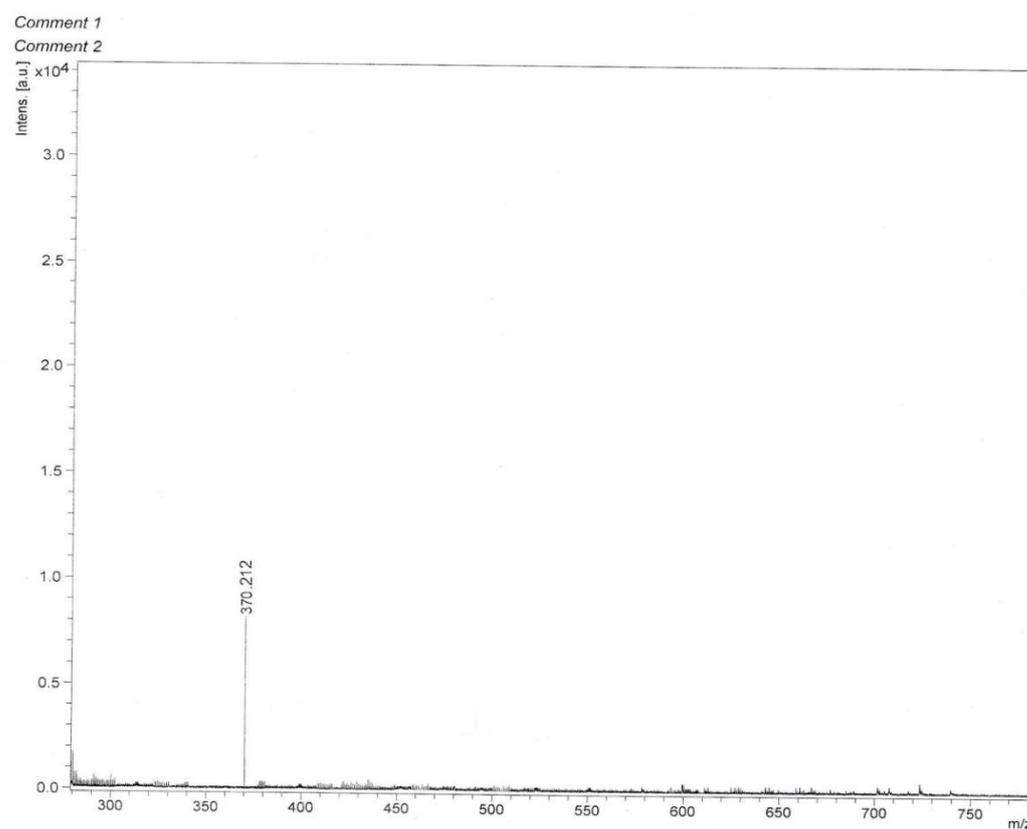
SI-15



Off white colored solid; mp 118-120 °C 3-(adamantan-1-yl)-4-methoxy-N-(o-tolyl)aniline (3m): ¹HNMR (400 MHz, CDCl₃) 7.40(s, 1H), 7.36(d, 1H), 7.17- 7.10(m, 4H), 6.94(d, 1H), 5.37(s, 1H), 3.87(s, 3H), 2.41(s, 3H), 2.14(m, 6H), 2.06(m, 3H), 1.77(m, 6H); HRMS Calcd 370.214 .Found: 370.212 (M+Na⁺).



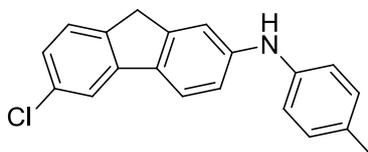
^1H NMR spectra of 3-(adamantan-1-yl)-4-methoxy-N-(o-tolyl)aniline (3m).

**Acquisition Parameter**

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Acquisition operation mode	Reflector
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Number of shots	200
Name of spectrum used for calibration	
Calibration reference list used	

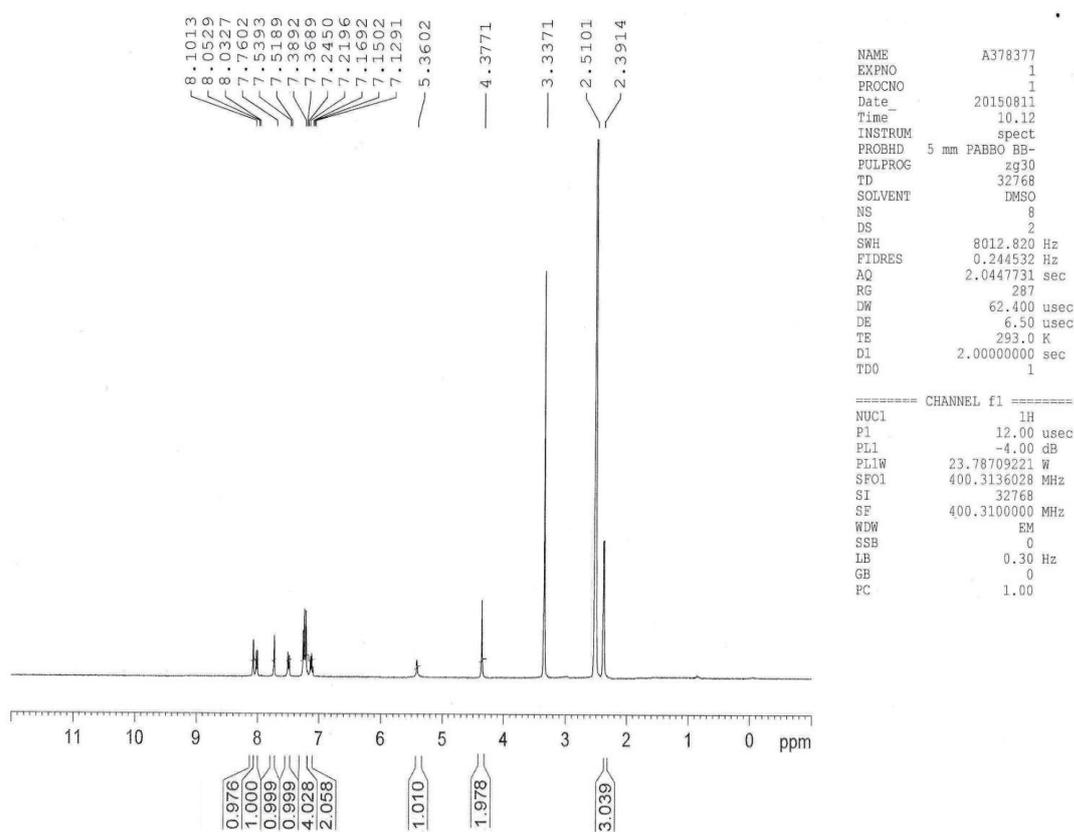
Bruker Daltonics flexAnalysis

Mass spectra of 3-(adamantan-1-yl)-4-methoxy-N-(o-tolyl)aniline (3m).

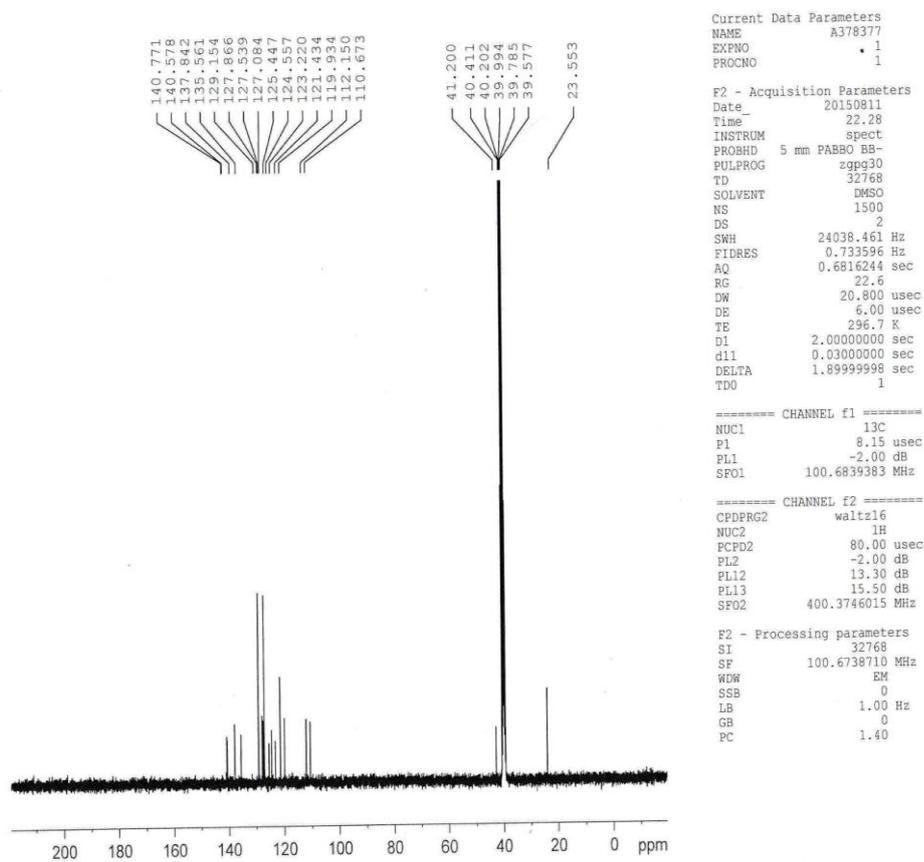
SI-16

6-chloro-N-(p-tolyl)-9H-fluoren-2-amine (5b).

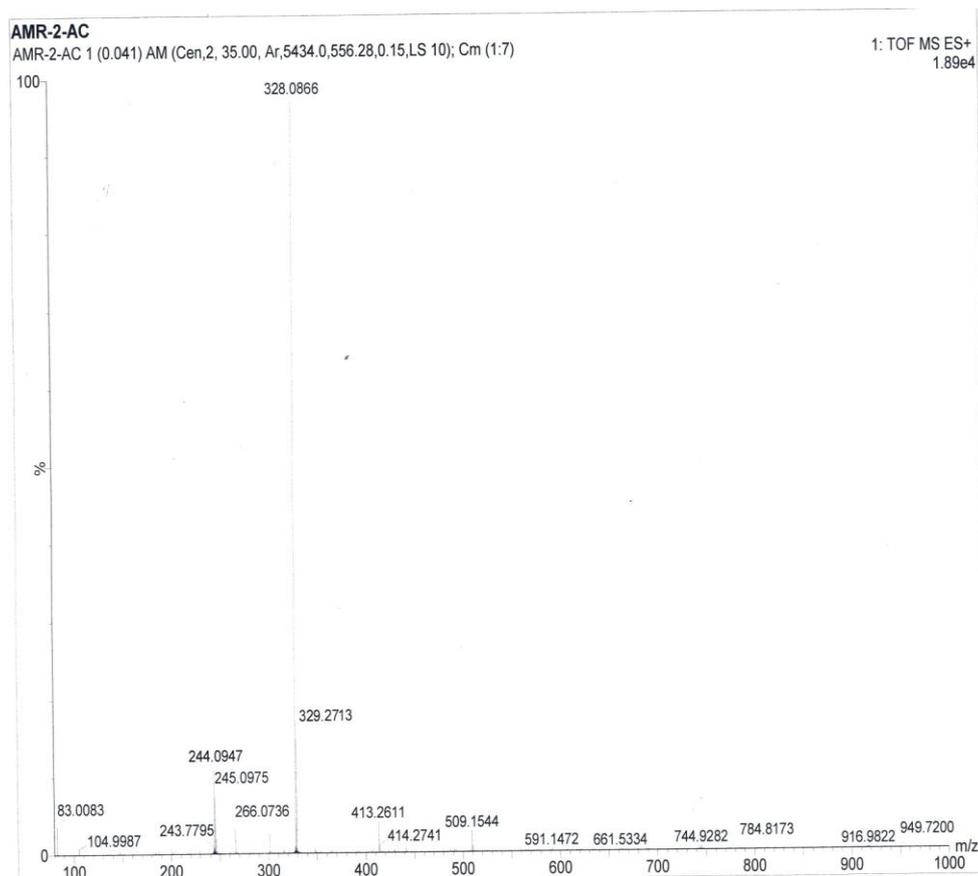
Yellow colored solid; mp 131-132 °C ¹H NMR (400 MHz, DMSO-d₆); 8.10 (s, 1H), 8.05-8.03 (d, J=8Hz, 1H), 7.76 (s, 1H), 7.53- 7.51 (d, J=8.0Hz, 1H), 7.38-7.21 (m, 4H), 7.16-7.12 (m, 2H), 5.36 (s, 1H), 4,37 (s, 2H), 2.39 (s, 3H) ; ¹³C NMR (100 MHz, DMSO-d₆); 140.7, 140.5, 137.8, 135.5, 129.1, 127.8, 127.5, 127.0, 125.4, 123.2, 121.4, 119.9, 112.1, 110.6, 41.20, 23.5; HRMS Calcd 328.0863; Found: 328.0866 (M+Na)⁺; Anal.Calcd for C₂₀H₁₆ClN: C, 78.55; H, 5.27; N, 4.58; Found: C, 78.58; H, 5.21; N, 4.55.



¹H NMR spectra of 6-chloro-N-(p-tolyl)-9H-fluoren-2-amine (5b).

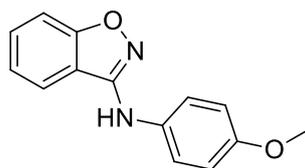


¹³C NMR spectra of 6-chloro-N-(p-tolyl)-9H-fluoren-2-amine (5b).



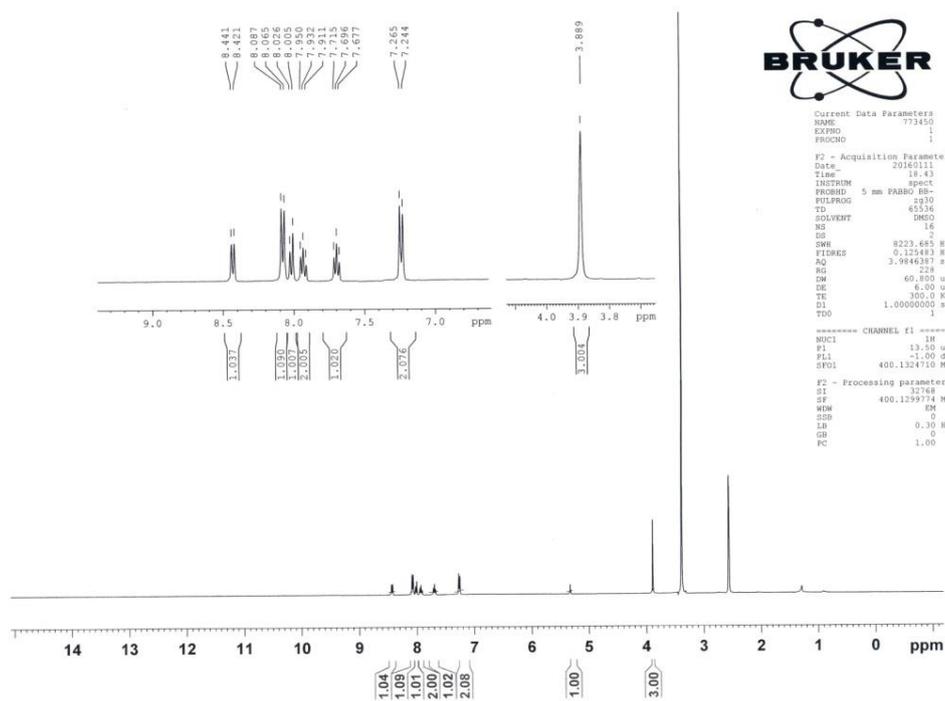
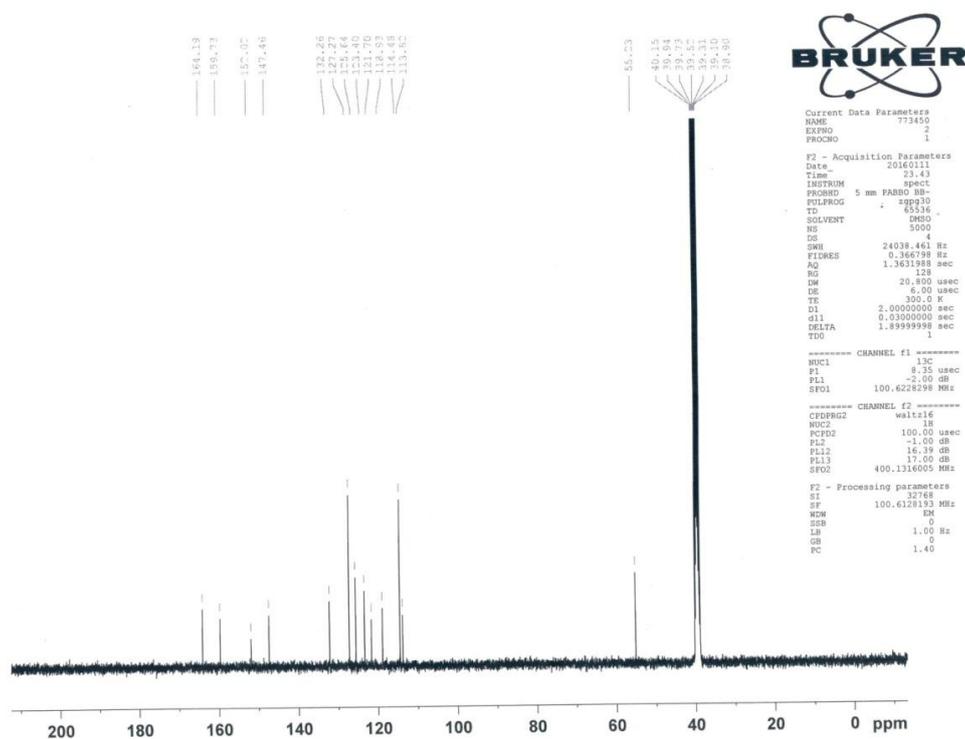
Mass spectra of 6-chloro-N-(p-tolyl)-9H-fluoren-2-amine (5b).

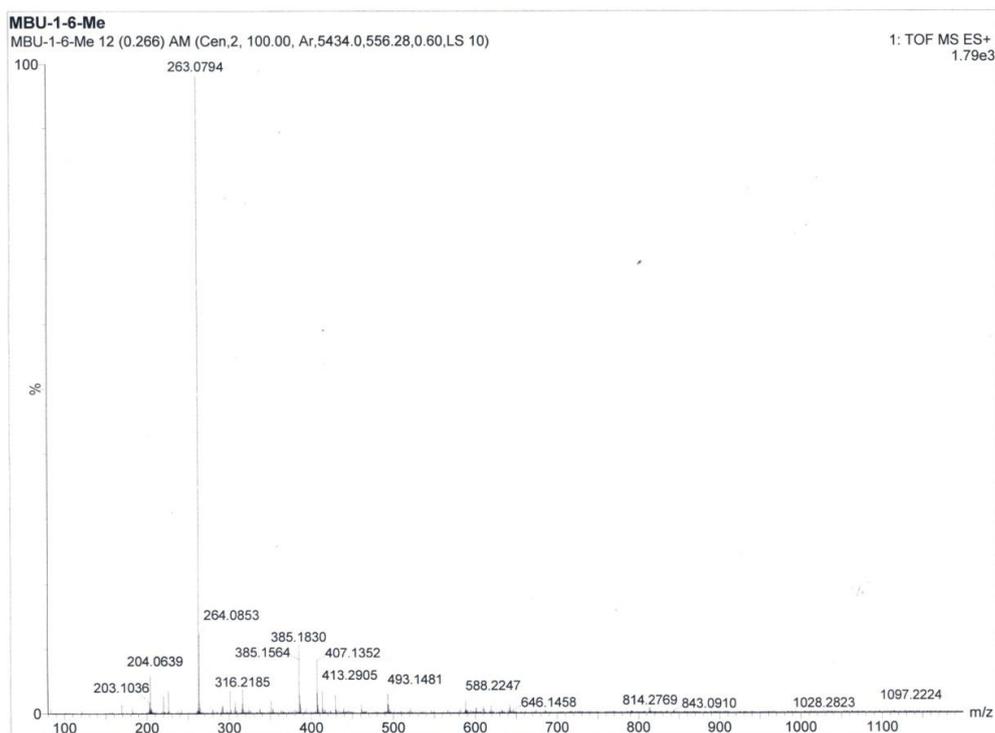
SI-17



N-(4-methoxyphenyl)benzo[d]isoxazol-3-amine (5c).

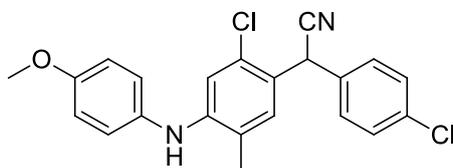
White colored solid; mp 98-100°C; ^1H NMR (400 MHz, DMSO- d_6); 8.44-8.42 (d, $J=8.0\text{Hz}$, 1H), 8.08-8.06 (d, $J=8.0\text{Hz}$, 1H), 8.02-8.00 (d, $J=8.0\text{Hz}$, 1H), 7.95-7.91 (m, $J=8.0\text{Hz}$, 2H), 7.71-7.67 (m, 1H), 7.26-7.24 (d, $J=8.0\text{Hz}$, 2H), 5.32 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6); 164.1, 159.7, 152.0, 147.4, 132.2, 127.2, 125.6, 123.4, 121.7, 118.9, 114.4, 113.8, 55.2; HRMS Calcd 263.0791; Found: 263.0794 ($\text{M}+\text{Na}^+$); Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$: C, 69.99; H, 5.03; N, 11.66; Found: C, 70.05; H, 5.08; N, 11.59.

¹H NMR spectra of N-(4-methoxyphenyl)benzo[d]isoxazol-3-amine (5c).¹³C NMR spectra of N-(4-methoxyphenyl)benzo[d]isoxazol-3-amine (5c).



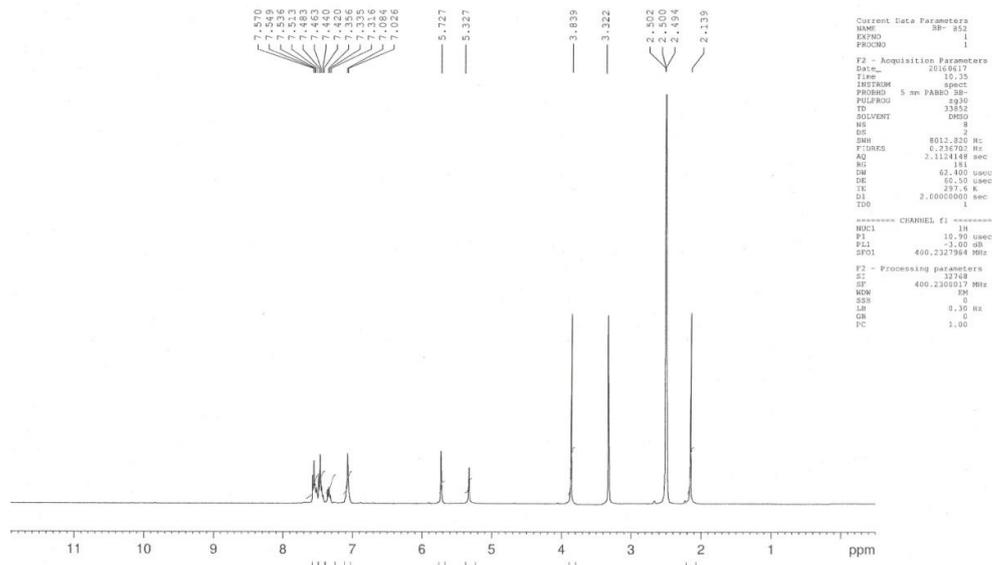
Mass spectra of N-(4-methoxyphenyl)benzo[d]isoxazol-3-amine (5c).

SI-18

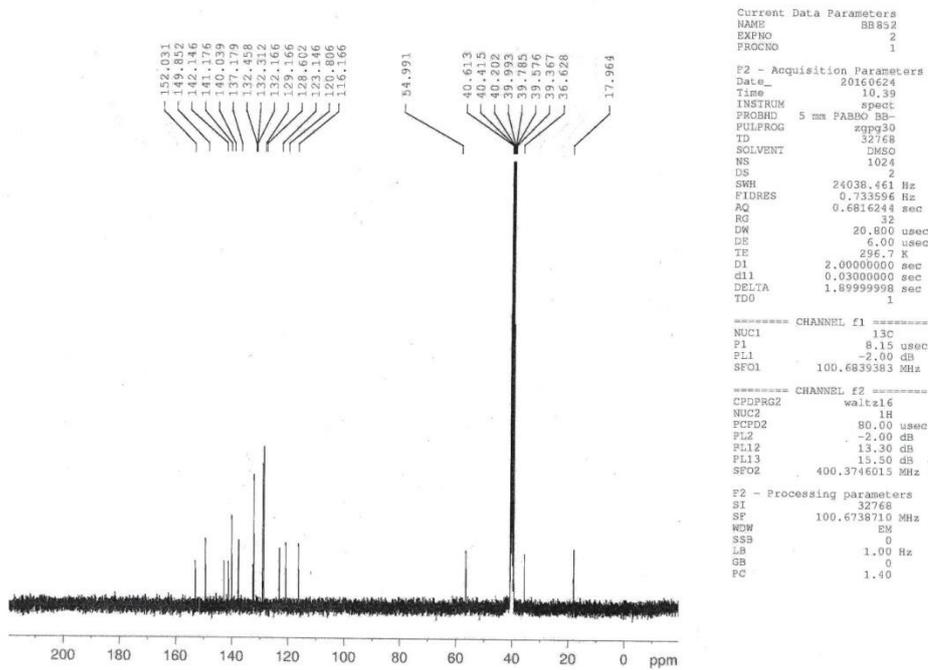


2-(2-chloro-4-((4-methoxyphenyl)amino)-5-methylphenyl)-2-(4-chlorophenyl)acetonitrile (5e).

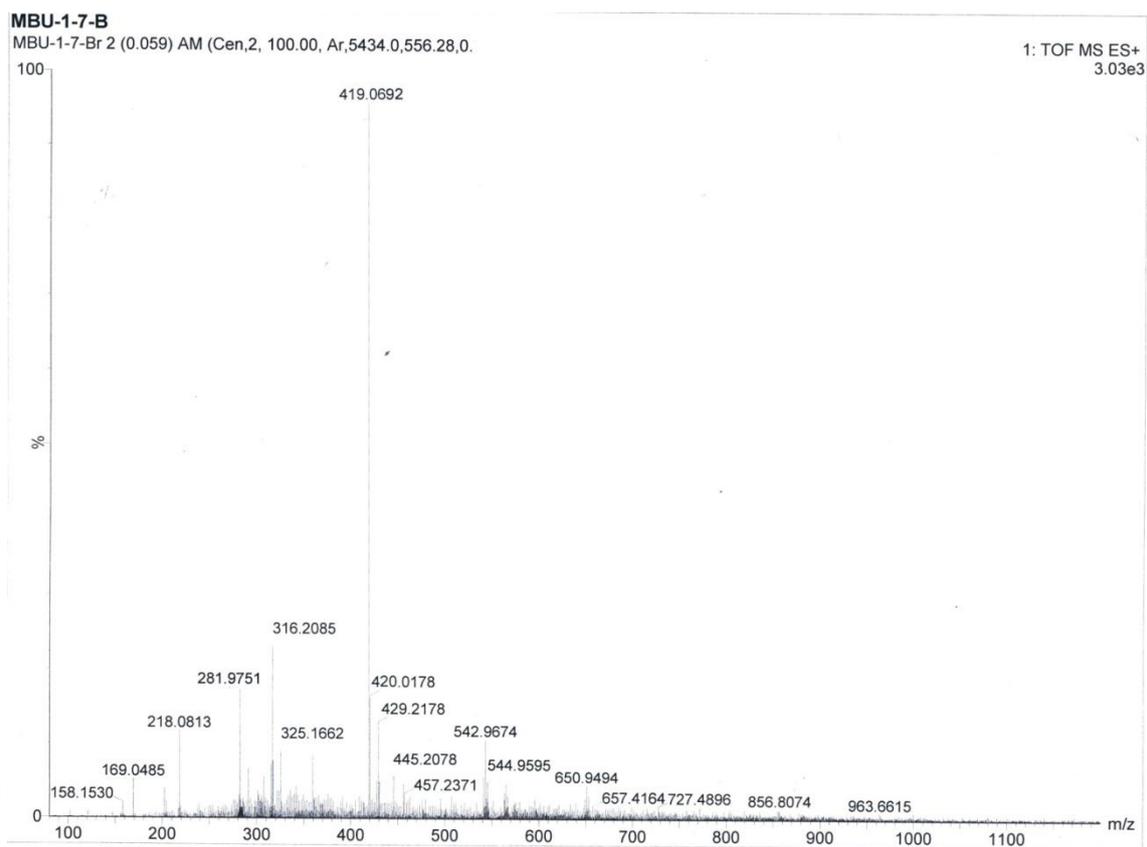
Off-white colored solid; mp 111-112 °C: ^1H NMR (400 MHz, DMSO-d_6); 7.57-7.53 (m, 3H), 7.51-7.42 (m, 3H), 7.35-7.31 (m, 2H), 7.08-7.02 (m, 2H), 5.72 (s, 1H), 5.32 (s, 1H), 3.83 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6); 152.0, 149.8, 141.1, 140.0, 137.1, 132.4, 132.3, 132.1, 129.1, 128.6, 123.1, 120.8, 116.1, 54.99, 36.6, 17.9; HRMS Calcd 419.0688; Found: 419.0692 ($\text{M}+\text{Na}$) $^+$; Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}$: C, 66.51; H, 4.57; N, 7.05; Found: C, 66.59; H, 4.52; N, 7.11.



¹H NMR spectra of 2-(2-chloro-4-((4-methoxyphenyl)amino)-5-methylphenyl)-2-(4-chlorophenyl)acetonitrile (5e).



¹³C NMR spectra of 2-(2-chloro-4-((4-methoxyphenyl)amino)-5-methylphenyl)-2-(4-chlorophenyl)acetonitrile (5e).



Mass spectra of
2-(2-chloro-4-((4-methoxyphenyl)amino)-5-methylphenyl)-2-(4-chlorophenyl)acetonitrile (5e).



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