Chan–Evans–Lam Amination of Boronic Acid Pinacol (BPin) Esters:

Overcoming the Aryl Amine Problem

Supporting Information

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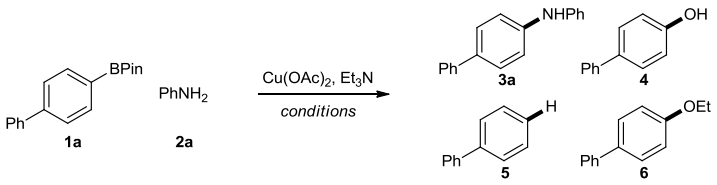
Contents

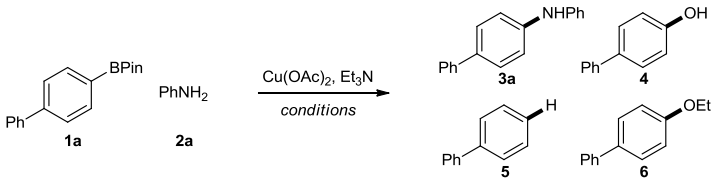
1. Data from solvent optimisation.



entry	reaction conditions	**3a**:**4**:**5**:**6** (%)[b]
1	CH_2Cl_2, 0.25 M, 40 °C	31:2:5:--
2	MeCN, 0.25 M, 60 °C	39:8:6:--
3	EtOH, 0.25 M, 60 °C	43:12:15:38
4	EtOAc, 0.25 M, 60 °C	3:1:0:--
5	Toluene, 0.25 M, 60 °C	2:7:12:--
6	DMSO, 0.25 M, 60 °C	7:4:5:--
7	Acetone, 0.25 M, 60 °C	5:6:3:--
8	DMF, 0.25 M, 60 °C	16:6:7:--
9	THF, 0.25 M, 60 °C	5:1:0:--
10	MeCN:EtOH (1:1), 0.25 M, 60 °C	47:14:12:20
11	MeCN:EtOH (2:1), 0.25 M, 60 °C	46:15:11:14
12	MeCN:EtOH (5:1), 0.25 M, 60 °C	46:14:13:12
13	MeCN:EtOH (10:1), 0.25 M, 60 °C	47:14:13:9
14	MeCN:EtOH (20:1), 0.25 M, 60 °C	45:13:10:1
15	MeCN:EtOH (30:1), 0.25 M, 60 °C	38:11:7:0

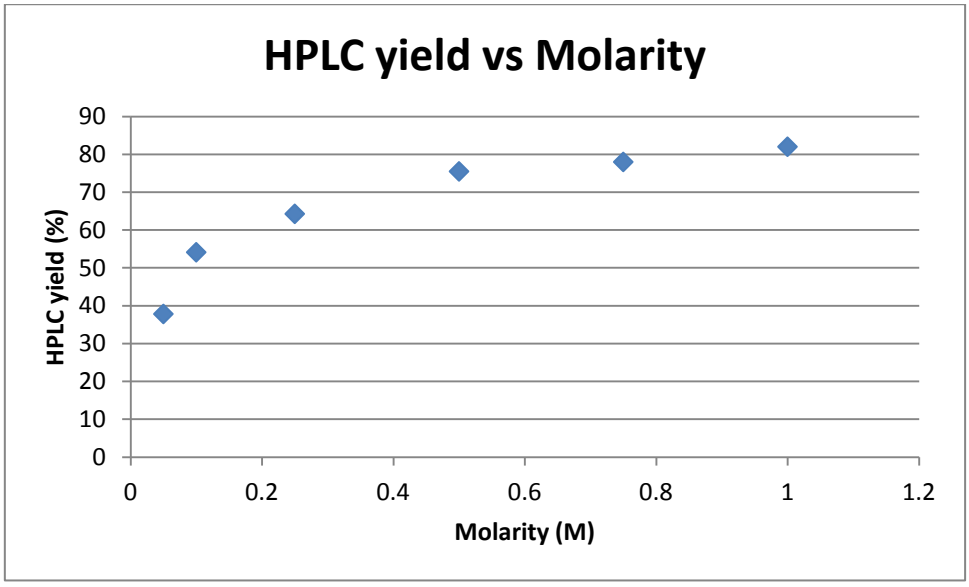
[a] **1a** (1.0 equiv, 0.3 mmol), **2a** (2 equiv, 0.6 mmol), $Cu(OAc)_2$ (1 equiv, 0.3 mmol), Et_3N (2 equiv, 0.6 mmol), solvent, air, 24 h. [b] Determined by HPLC analysis using an internal standard. Mass balance is returned starting material.

2. Data from concentration optimization.



entry	reaction conditions	**3a** (%)[b]
1	MeCN:EtOH (20:1), 1 M, 3 Å MS, 80 °C	82
2	MeCN:EtOH (20:1), 0.75 M, 3 Å MS, 80 °C	78
3	MeCN:EtOH (20:1), 0.5 M, 3 Å MS, 80 °C	75
4	MeCN:EtOH (20:1), 0.25 M, 3 Å MS, 80 °C	64
5	MeCN:EtOH (20:1), 0.1 M, 3 Å MS, 80 °C	54
6	MeCN:EtOH (20:1), 0.05 M, 3 Å MS, 80 °C	38

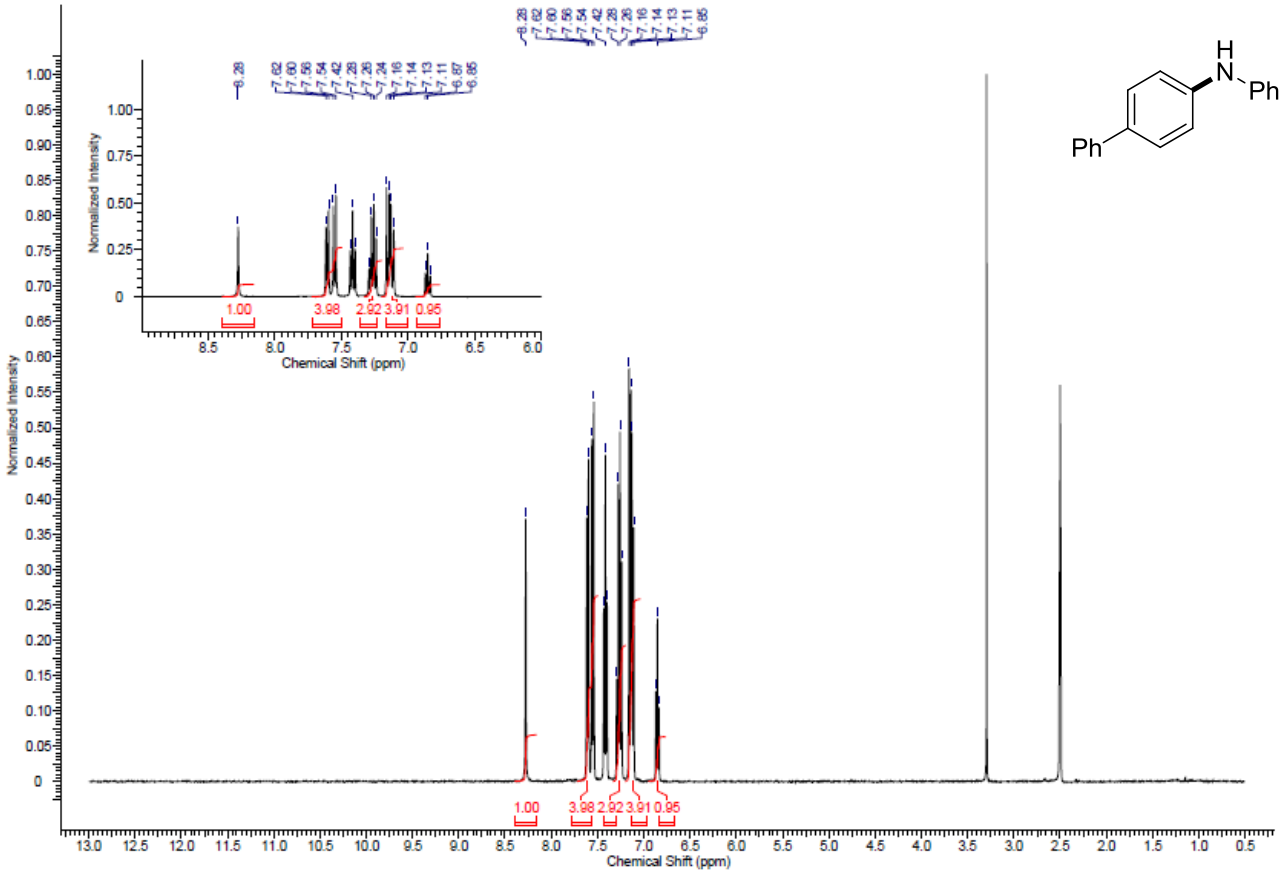
[a] **1a** (1.0 equiv, 0.3 mmol), **2a** (2 equiv, 0.6 mmol), $Cu(OAc)_2$ (1 equiv, 0.3 mmol), Et_3N (2 equiv, 0.6 mmol), 3 Å MS (75 mg), solvent, air, 24 h. [b] Determined by HPLC analysis using an internal standard. Mass balance is returned starting material.



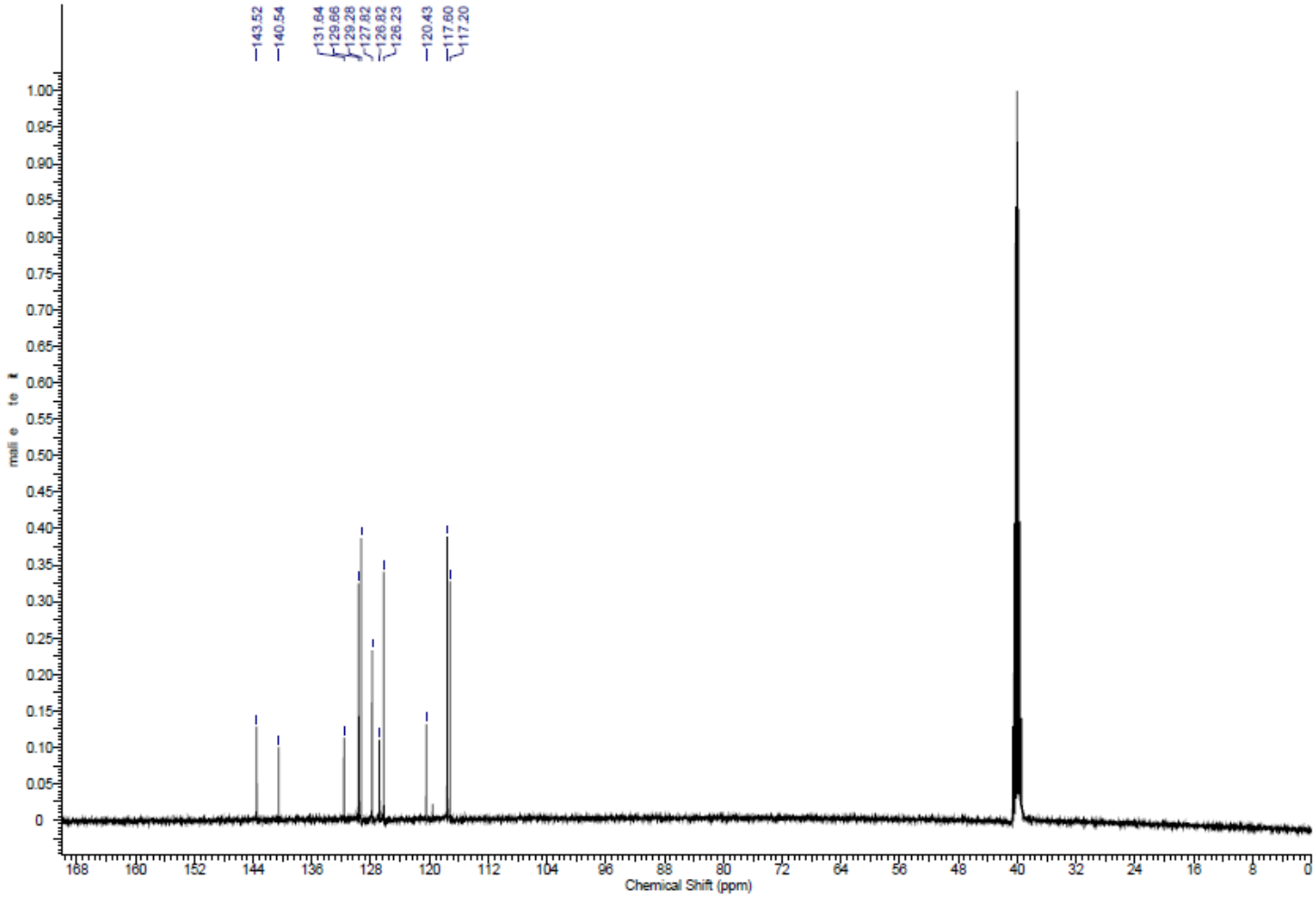
3. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, LCMS, HRMS, and IR spectra.

***N*-Phenyl-[1,1'-biphenyl]-4-amine (3a).**

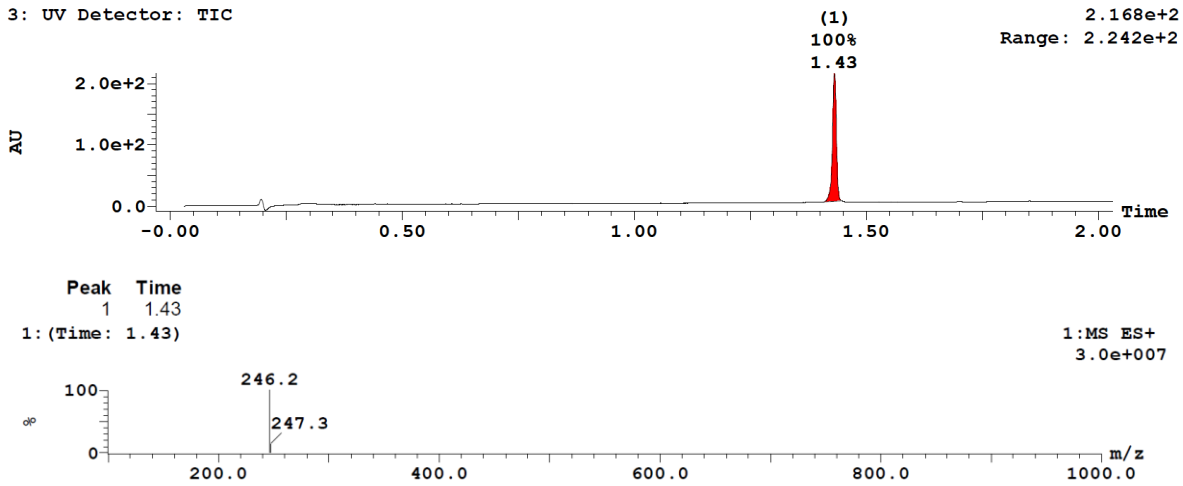
^{1}H-NMR Spectra



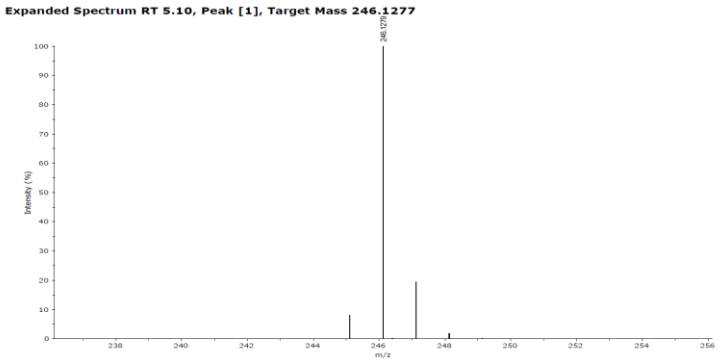
^{13}C-NMR Spectra



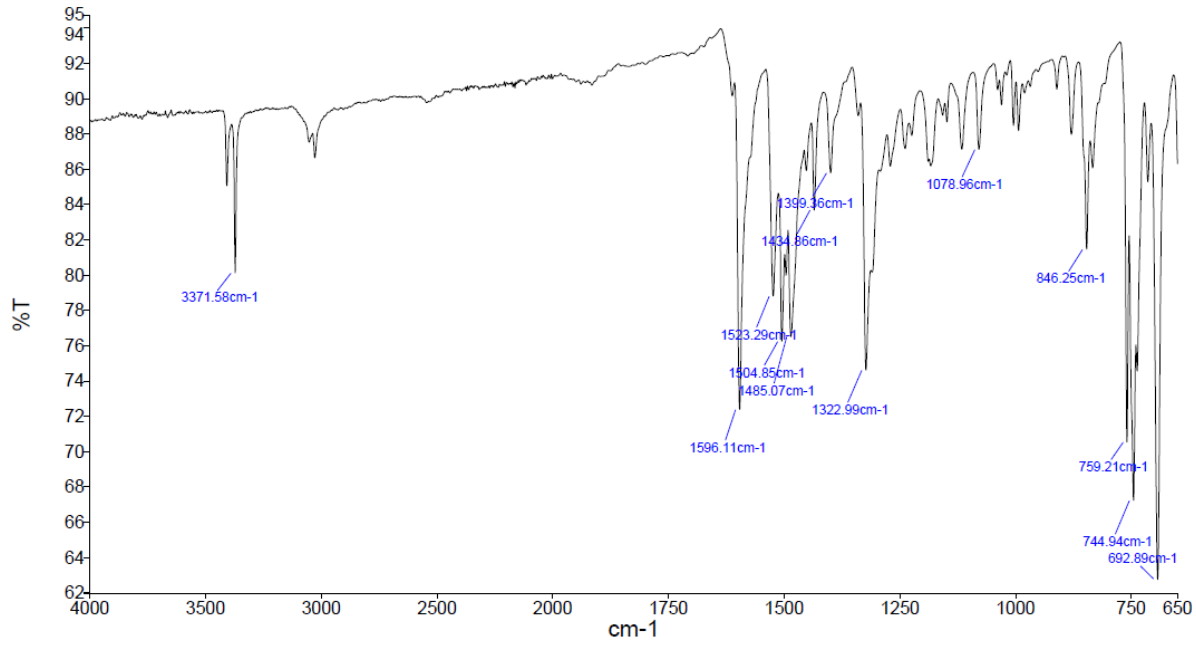
LCMS



HRMS

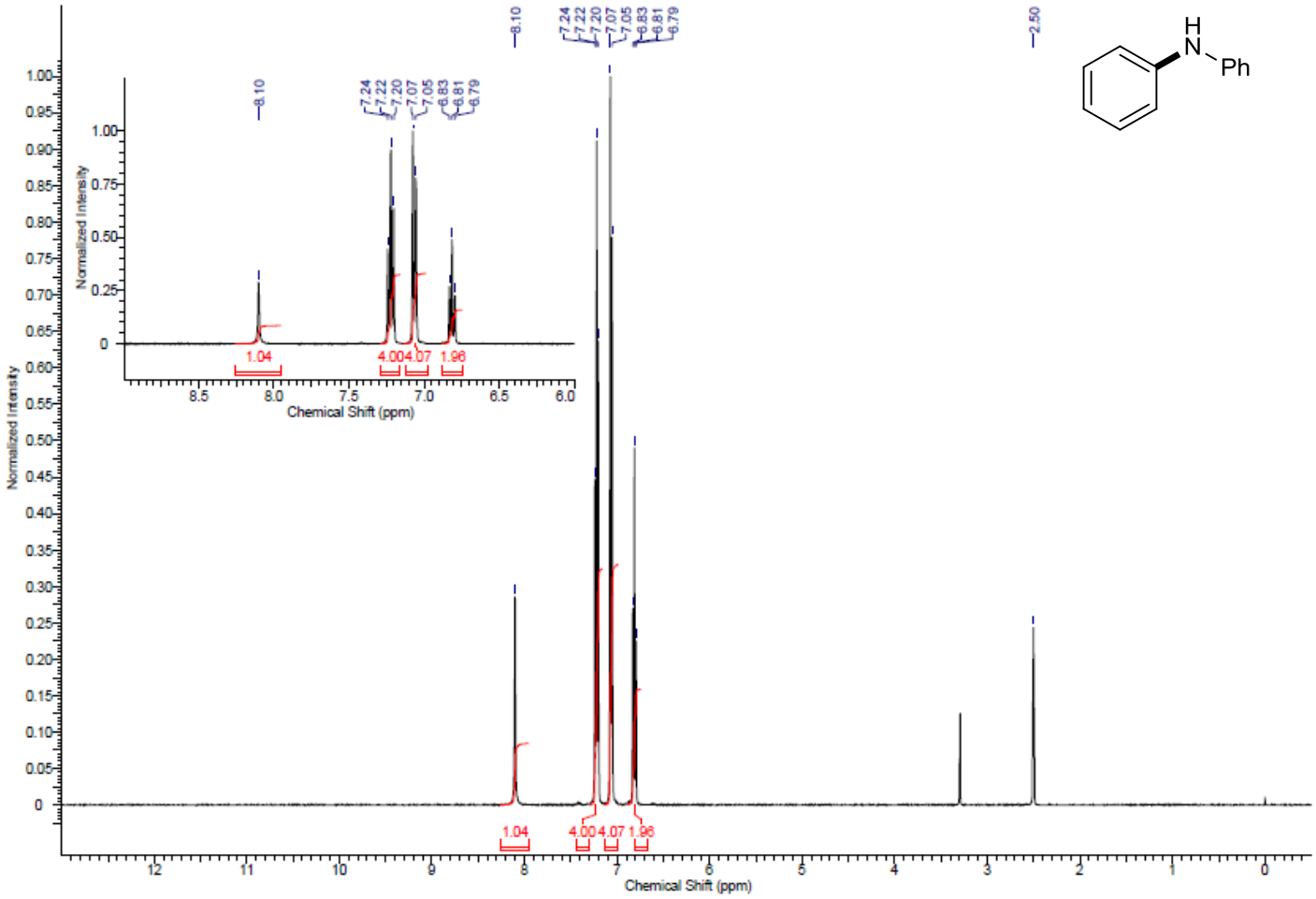


IR Spectra

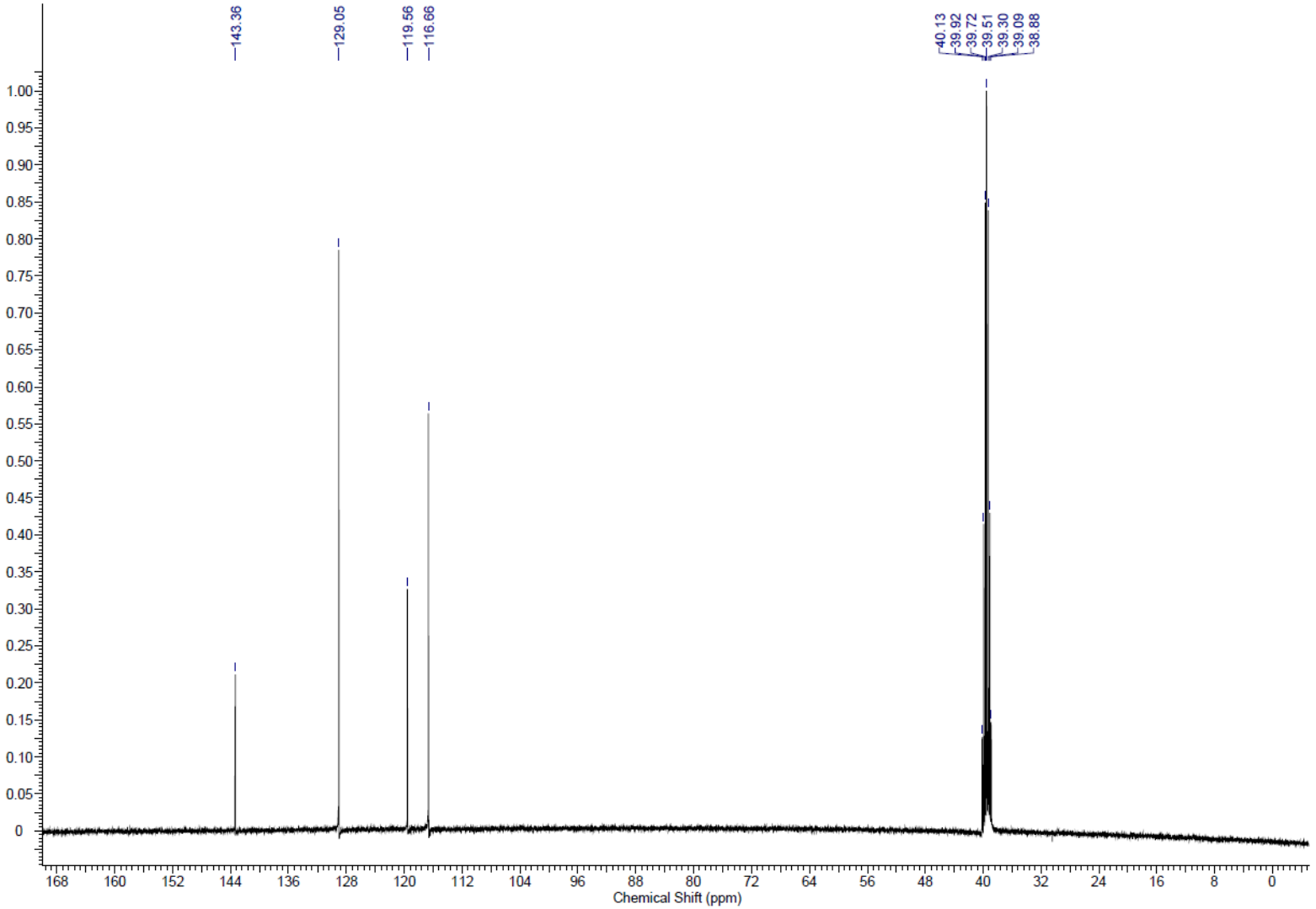


Diphenylamine (3b).

^{1}H-NMR Spectra



^{13}C-NMR Spectra



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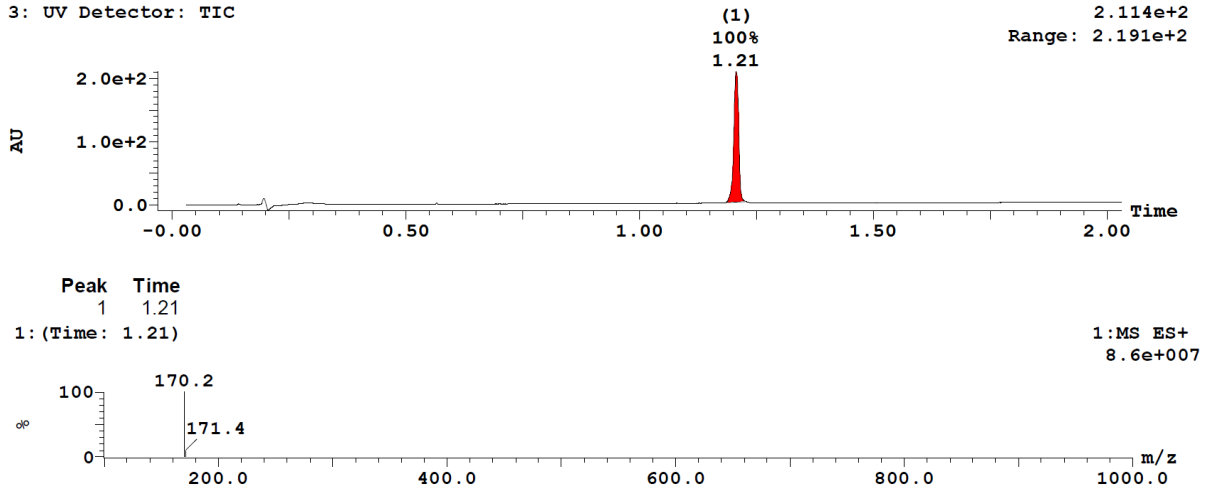

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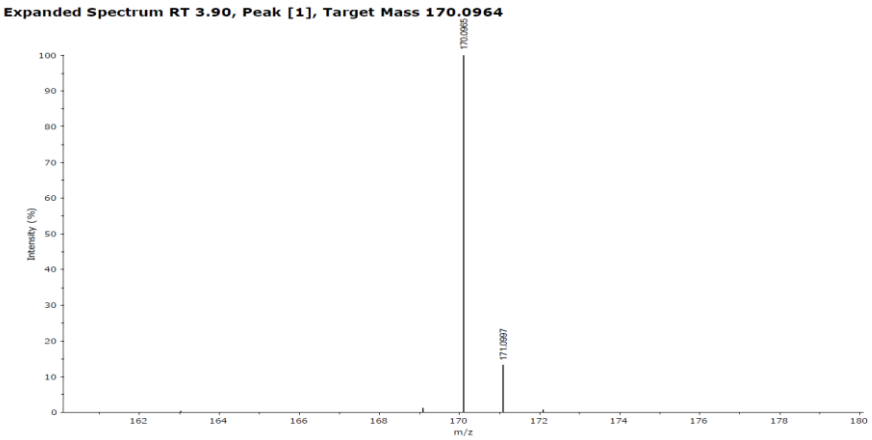
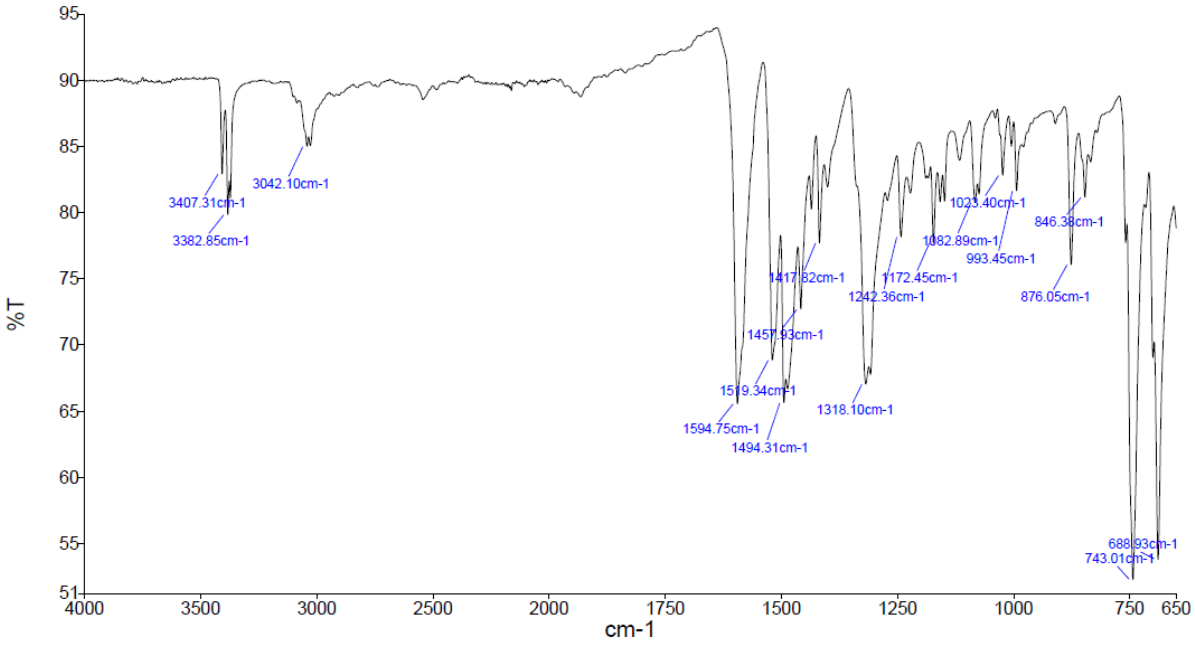
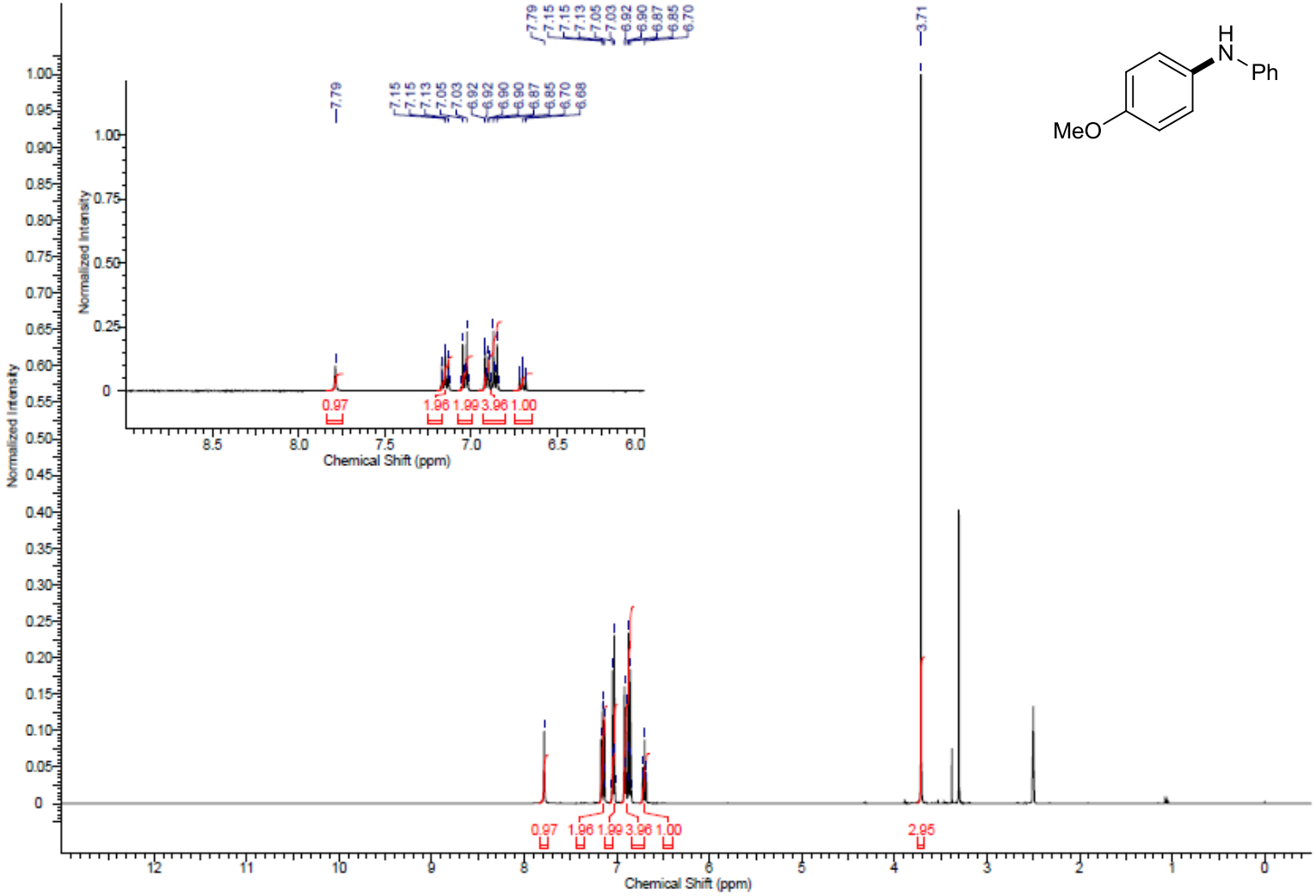


IR Spectra

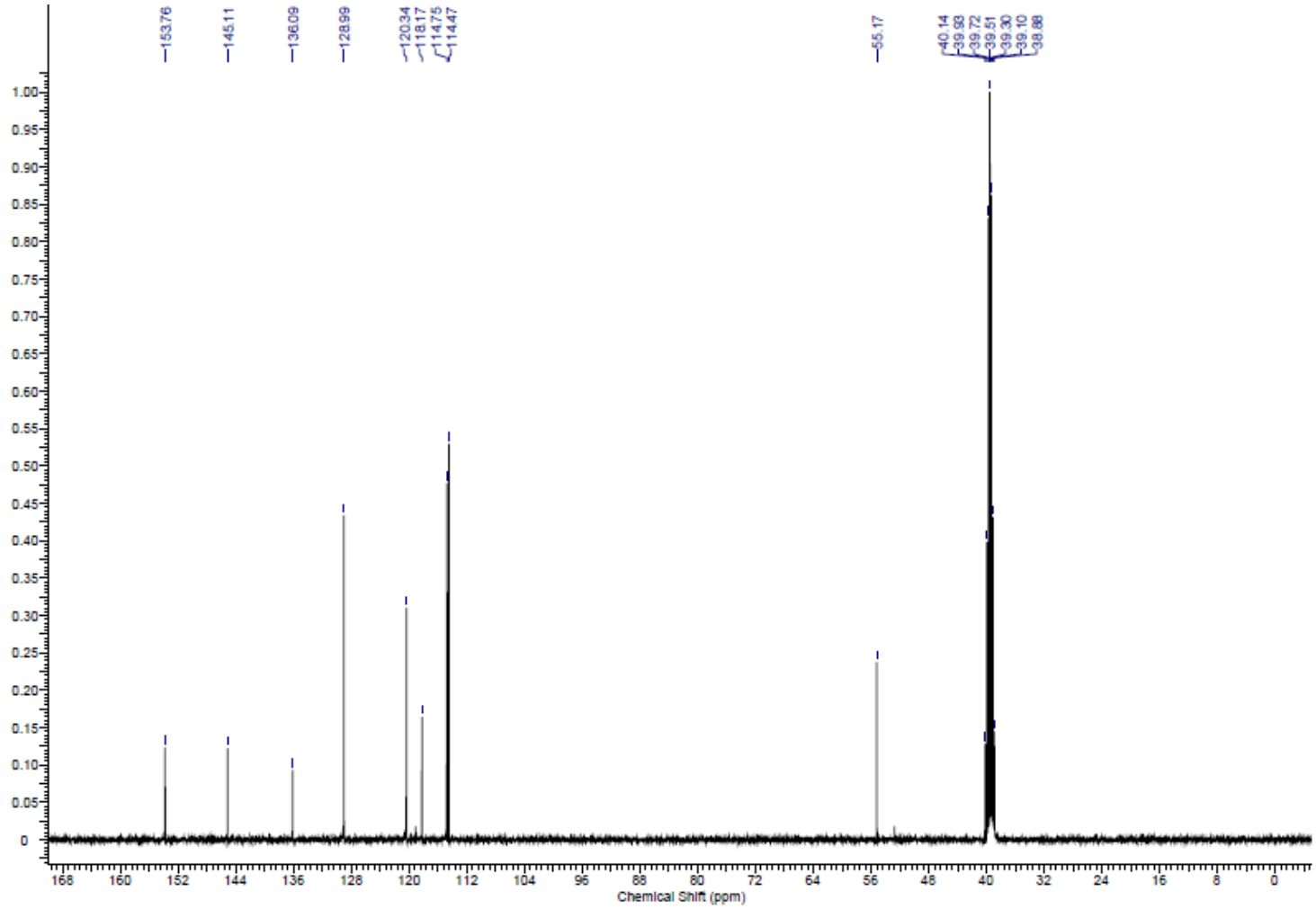


4-Methoxy-*N*-phenylaniline (3c).

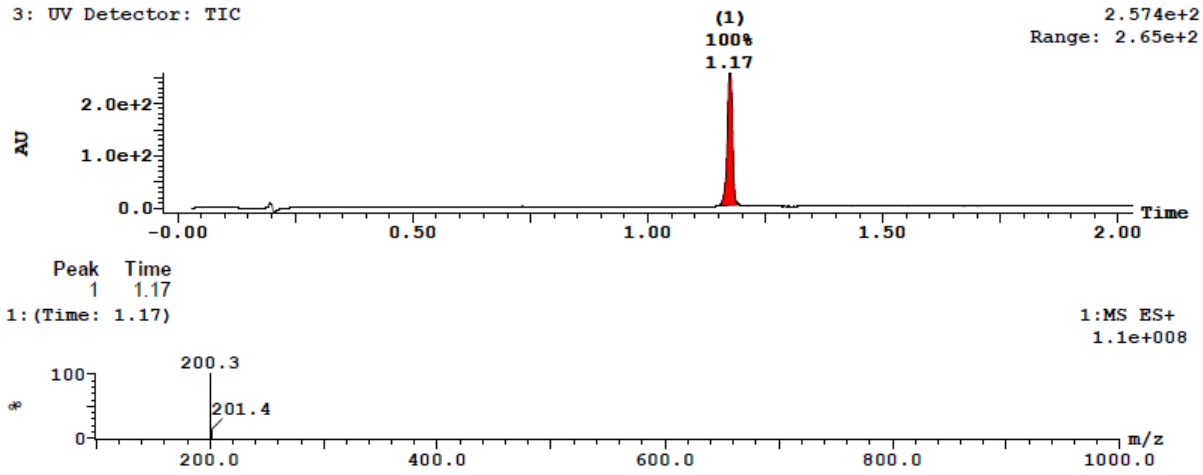
^{1}H NMR Spectra



^{13}C NMR Spectra



LCMS



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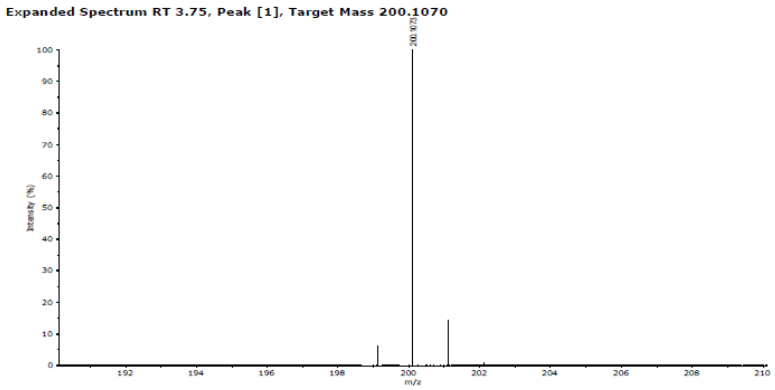
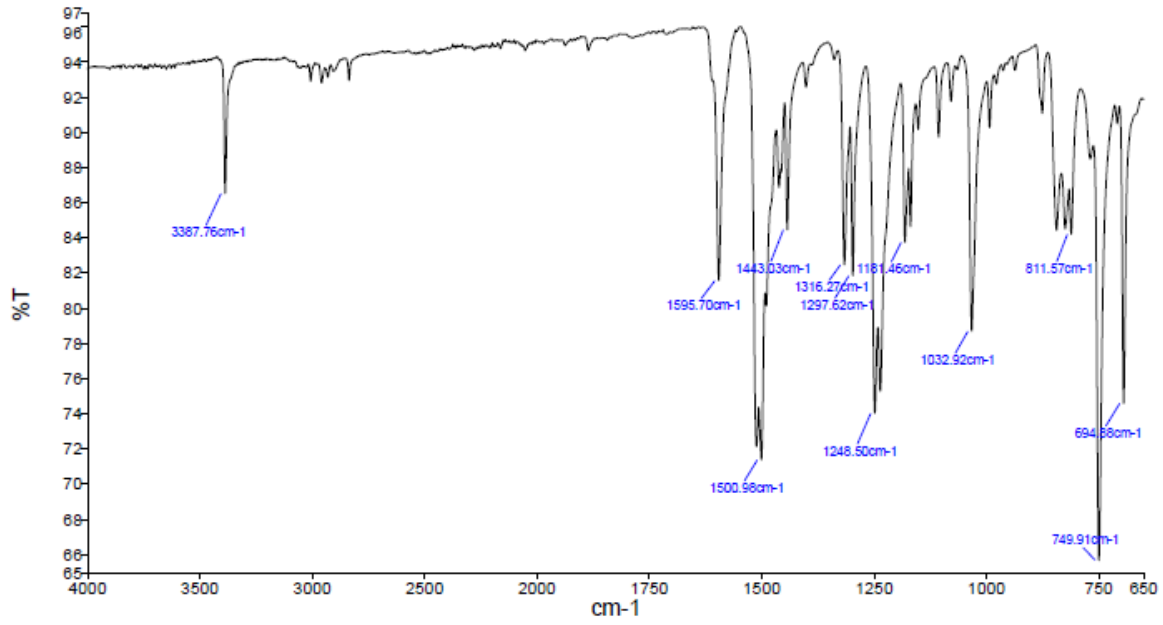
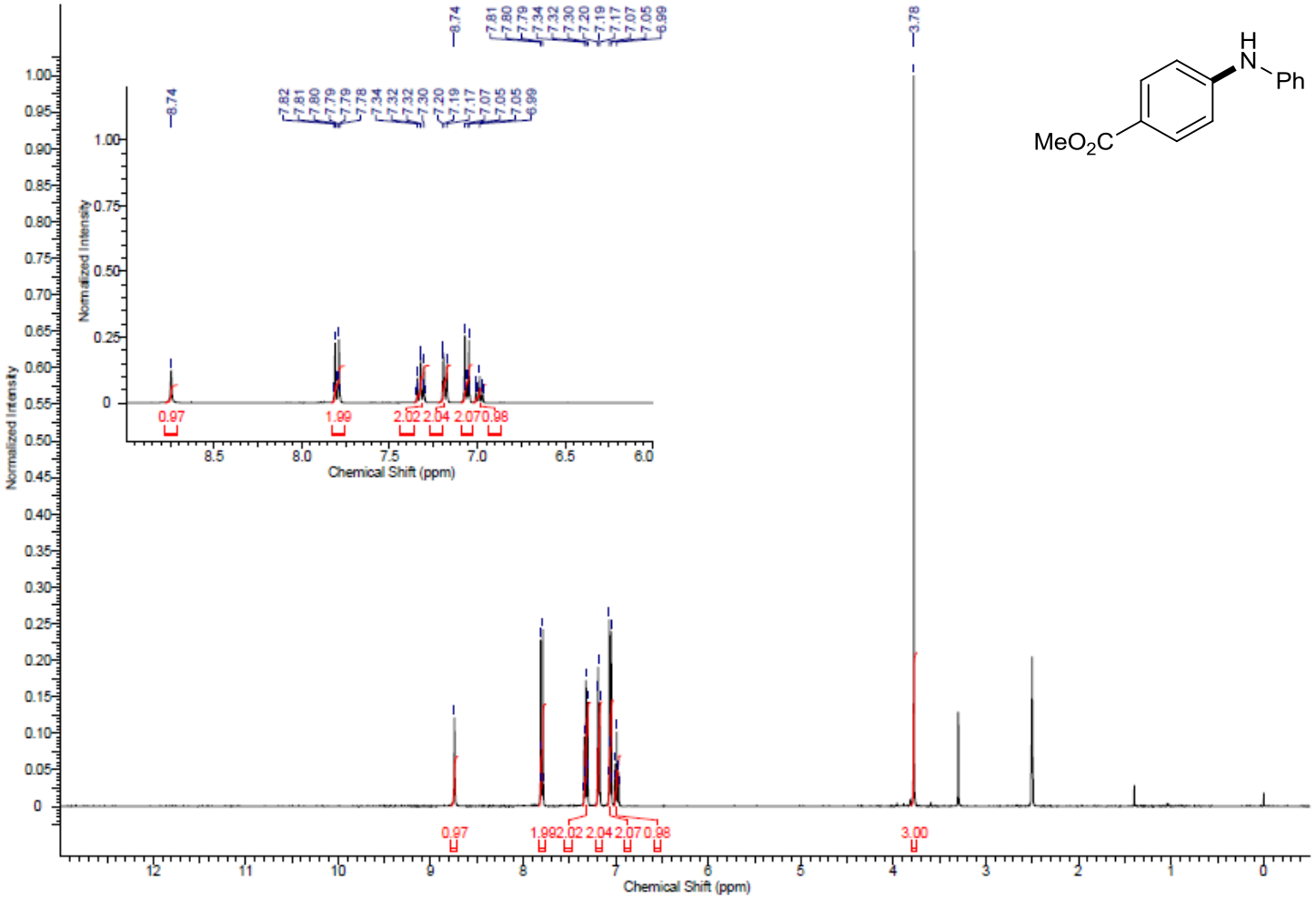


IR Spectra

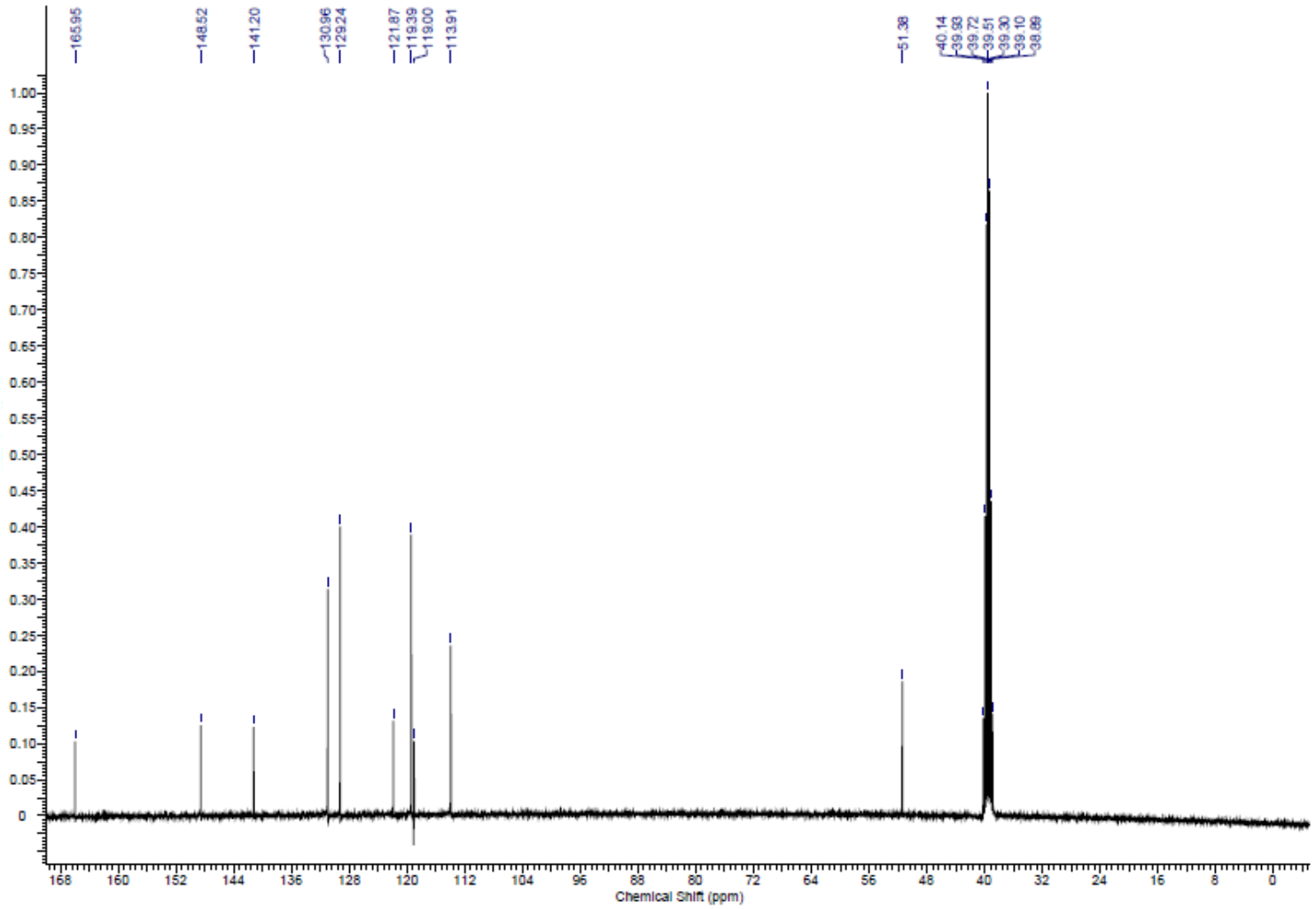


Methyl-4-(phenylamino)benzoate (3d).

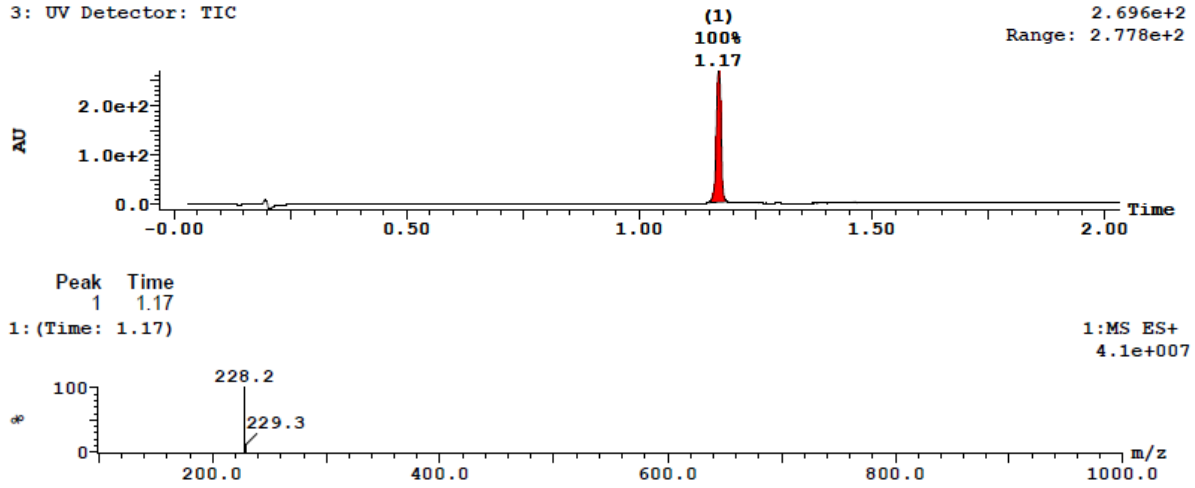
^{1}H NMR SPECTRA



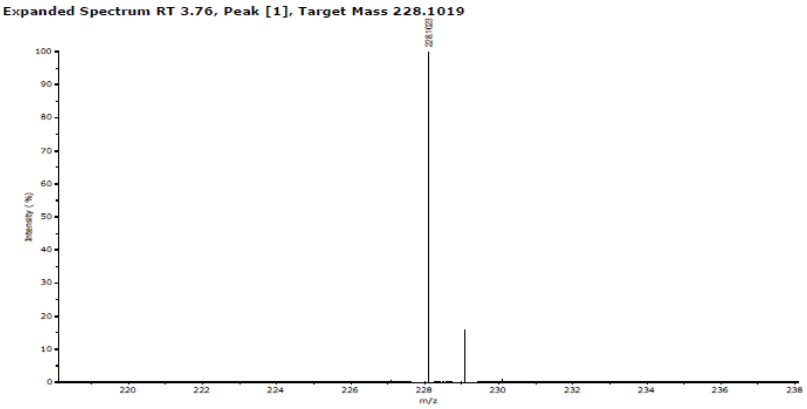
^{13}C NMR SPECTRA



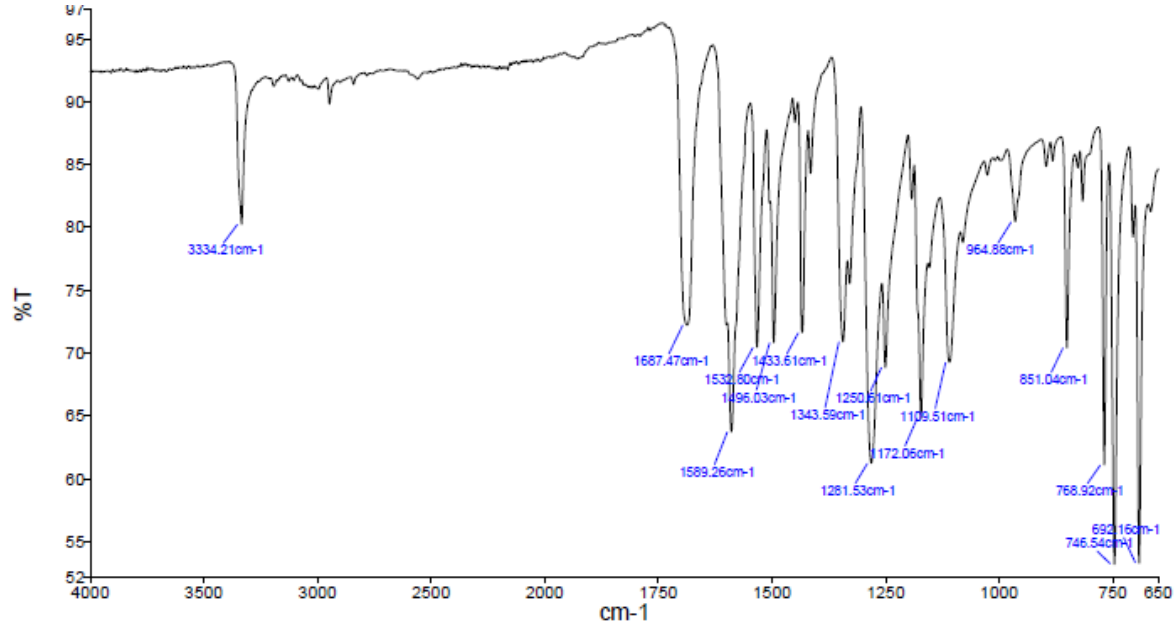
LCMS



HRMS

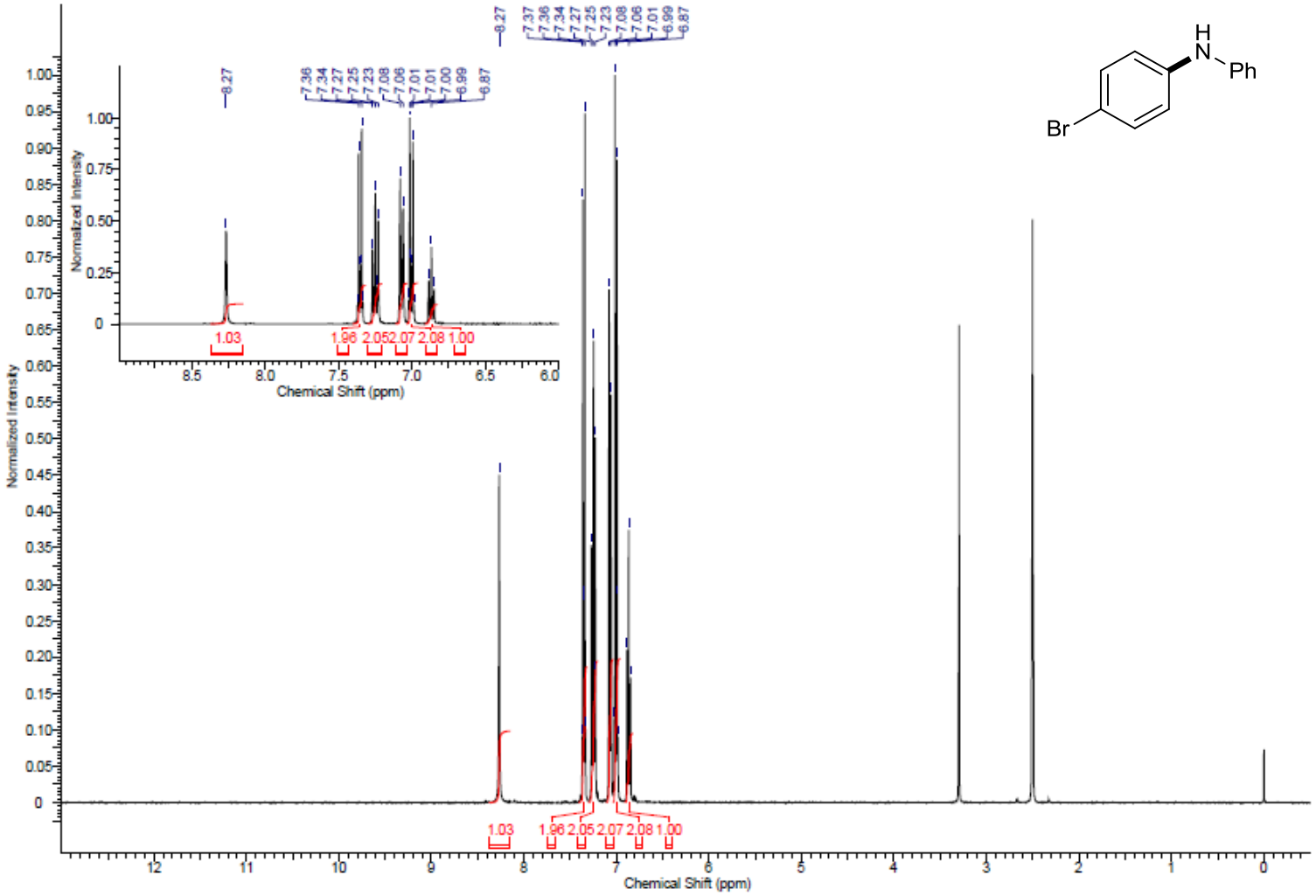


IR SPECTRA

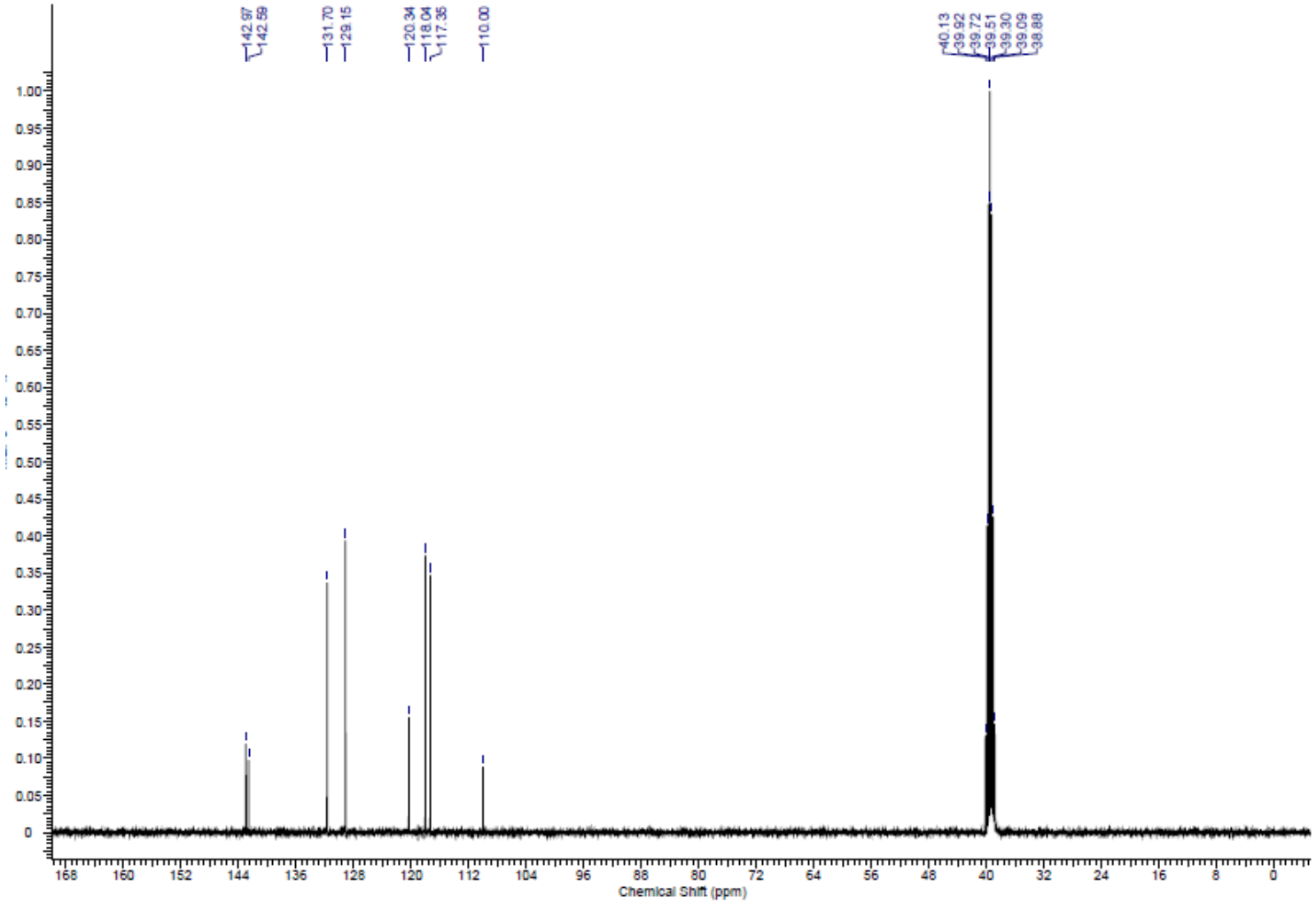


4-Bromo-*N*-phenylaniline (3e).

^{1}H NMR Spectra



^{13}C NMR Spectra



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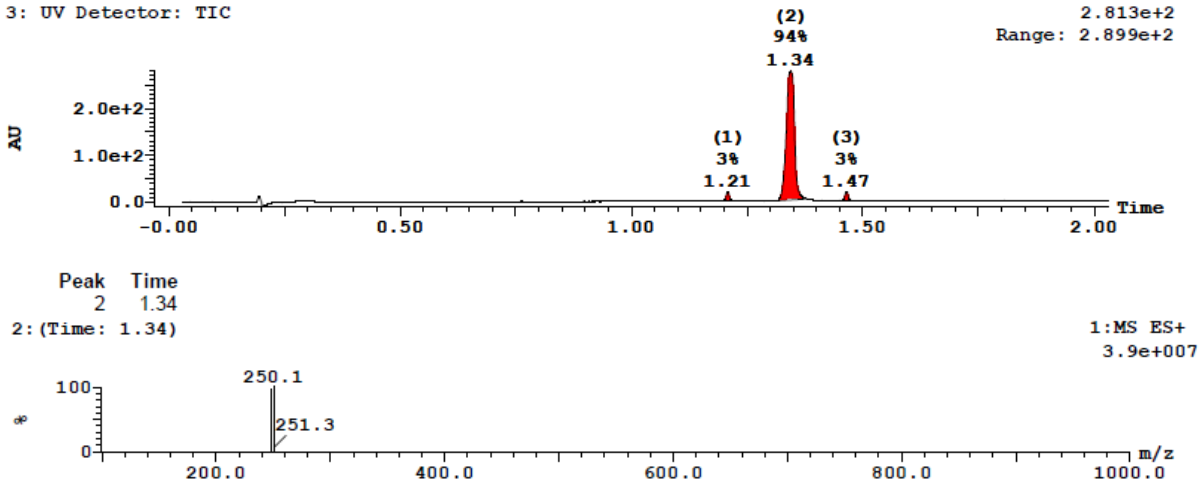

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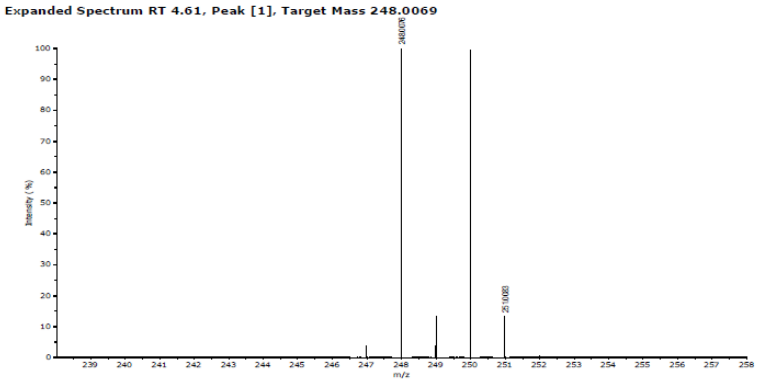
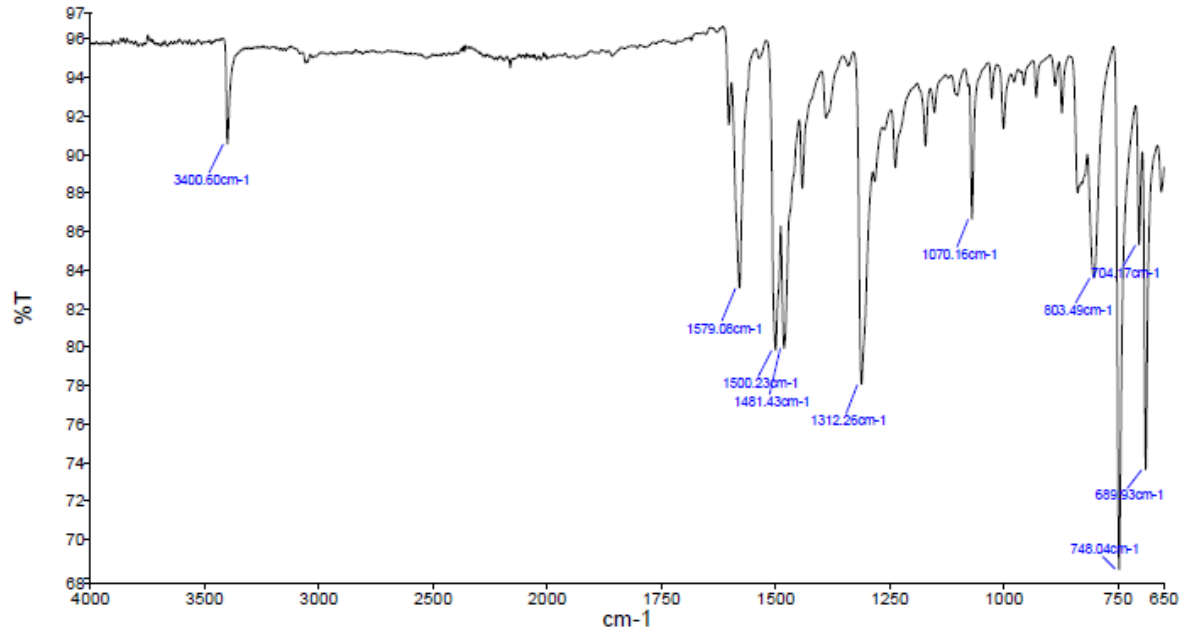
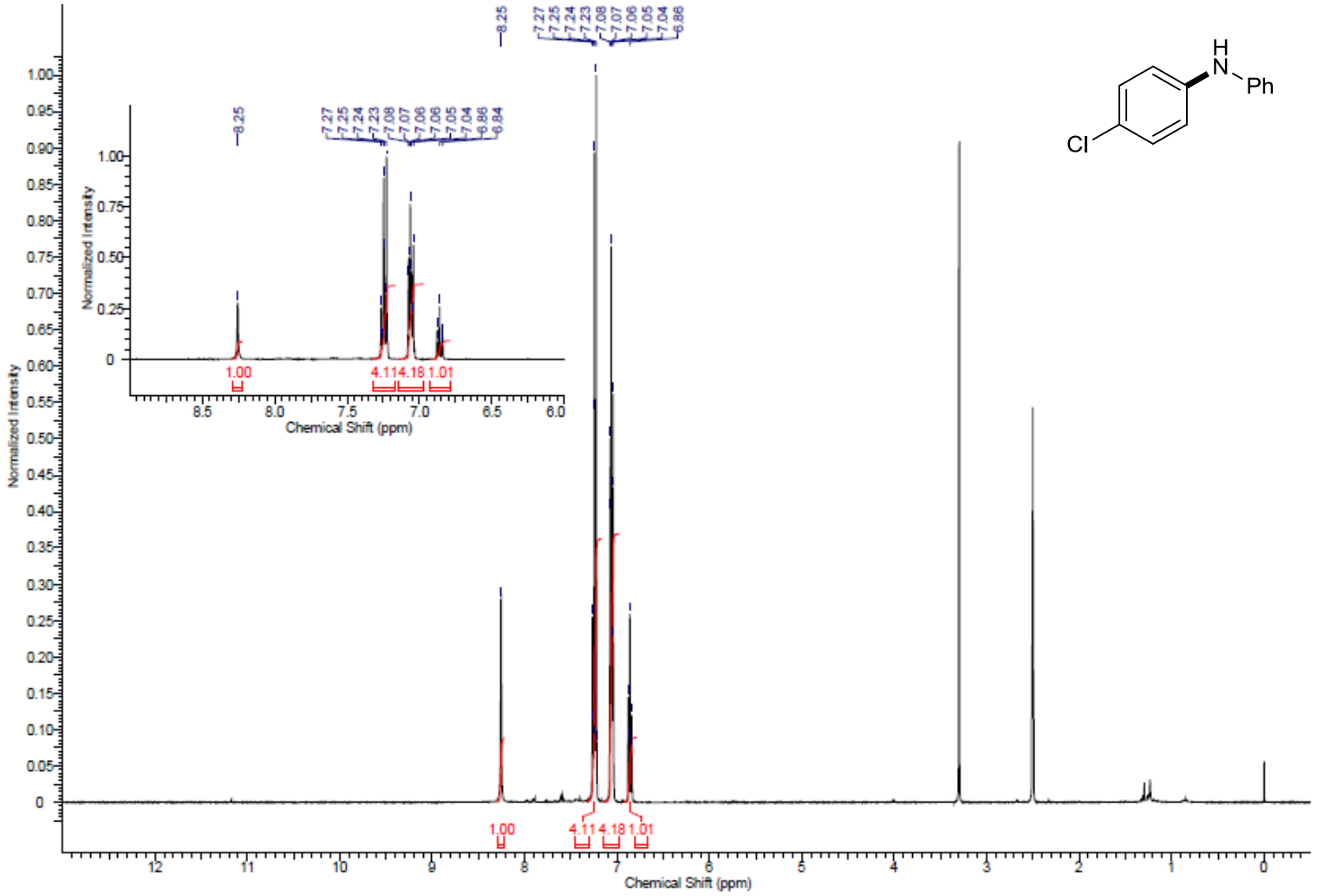


IR Spectra

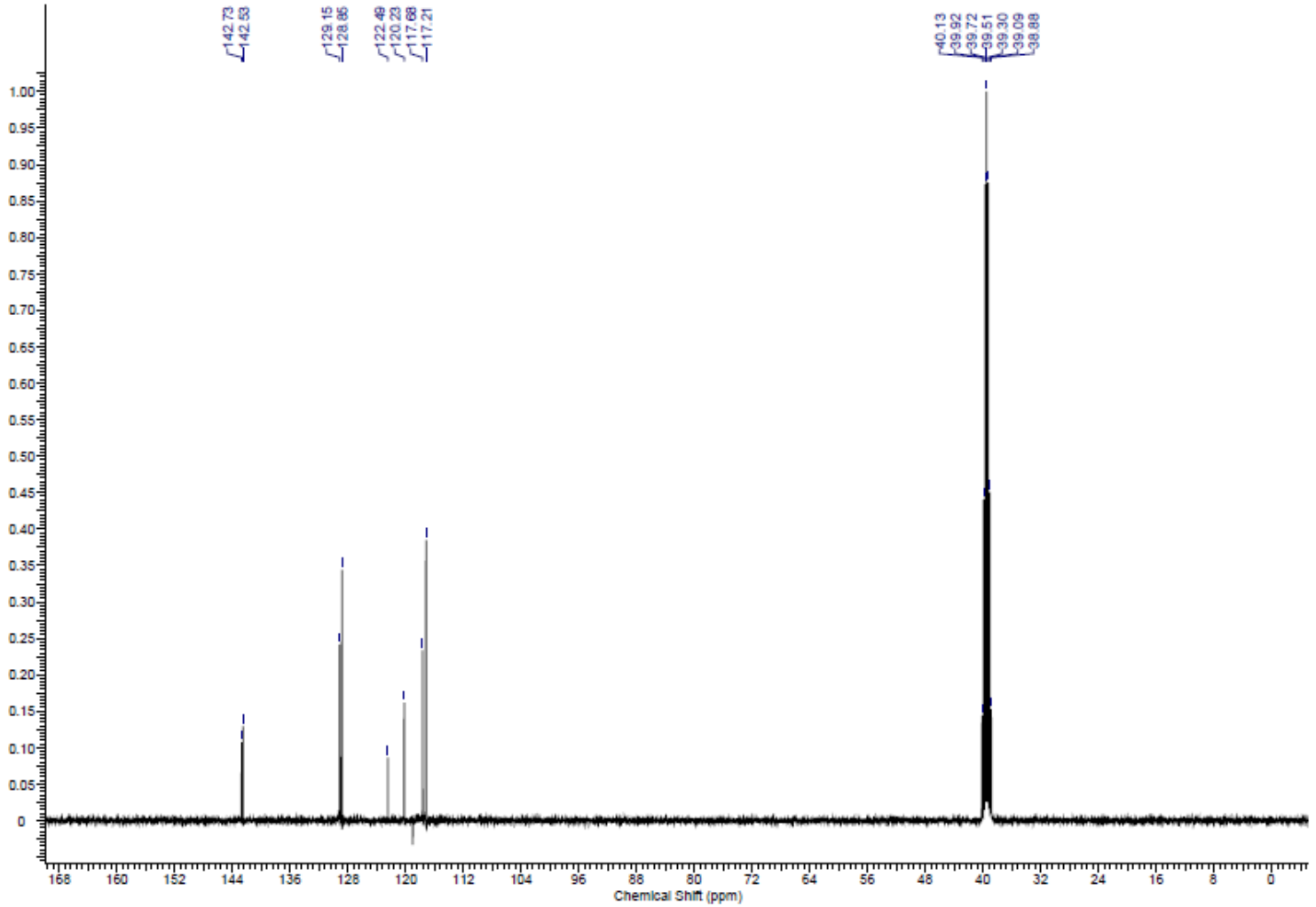


4-Chloro-*N*-phenylaniline (3f).

^{1}H NMR Spectra



^{13}C NMR Spectra



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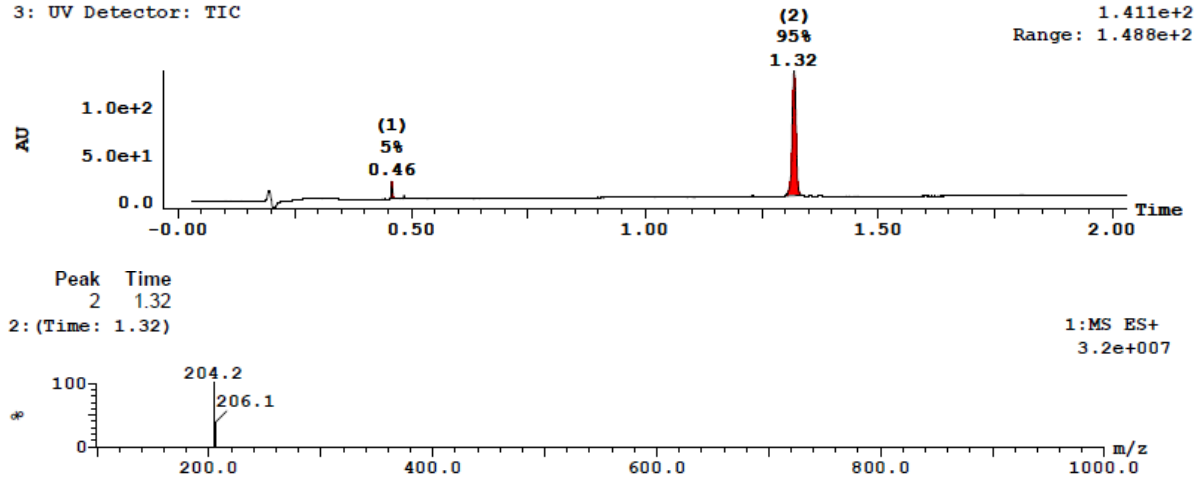

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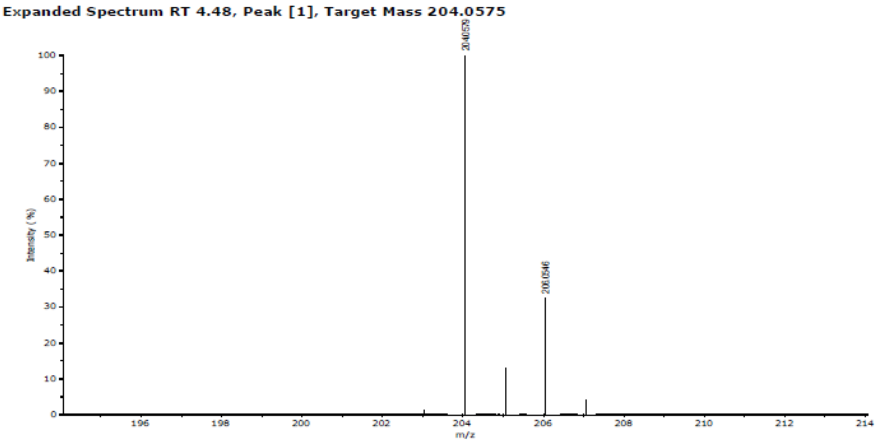

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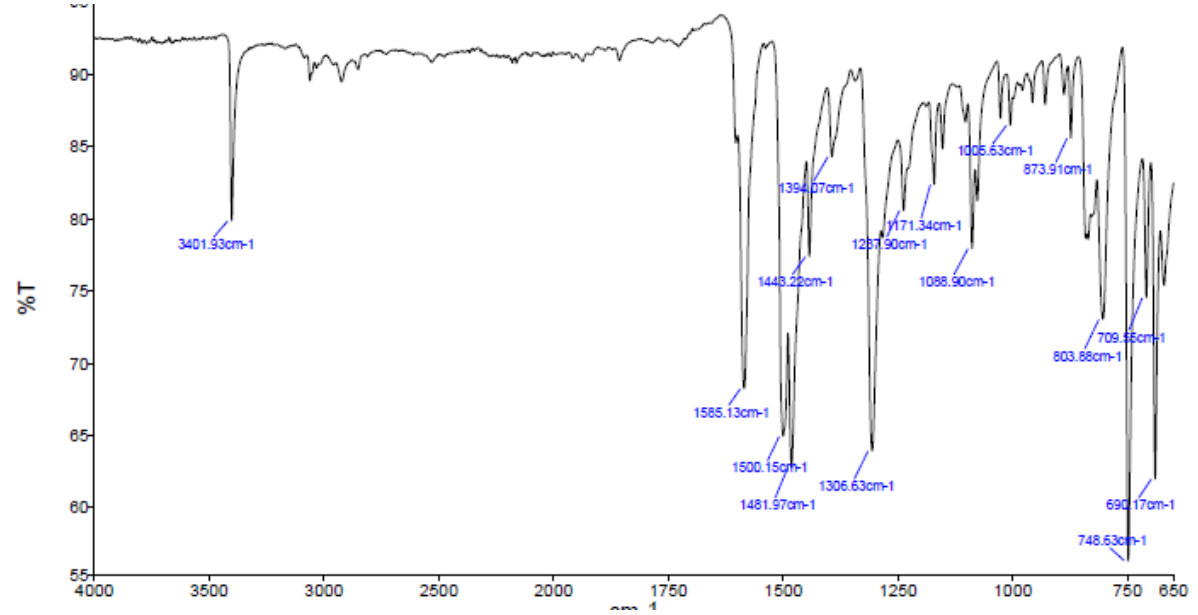
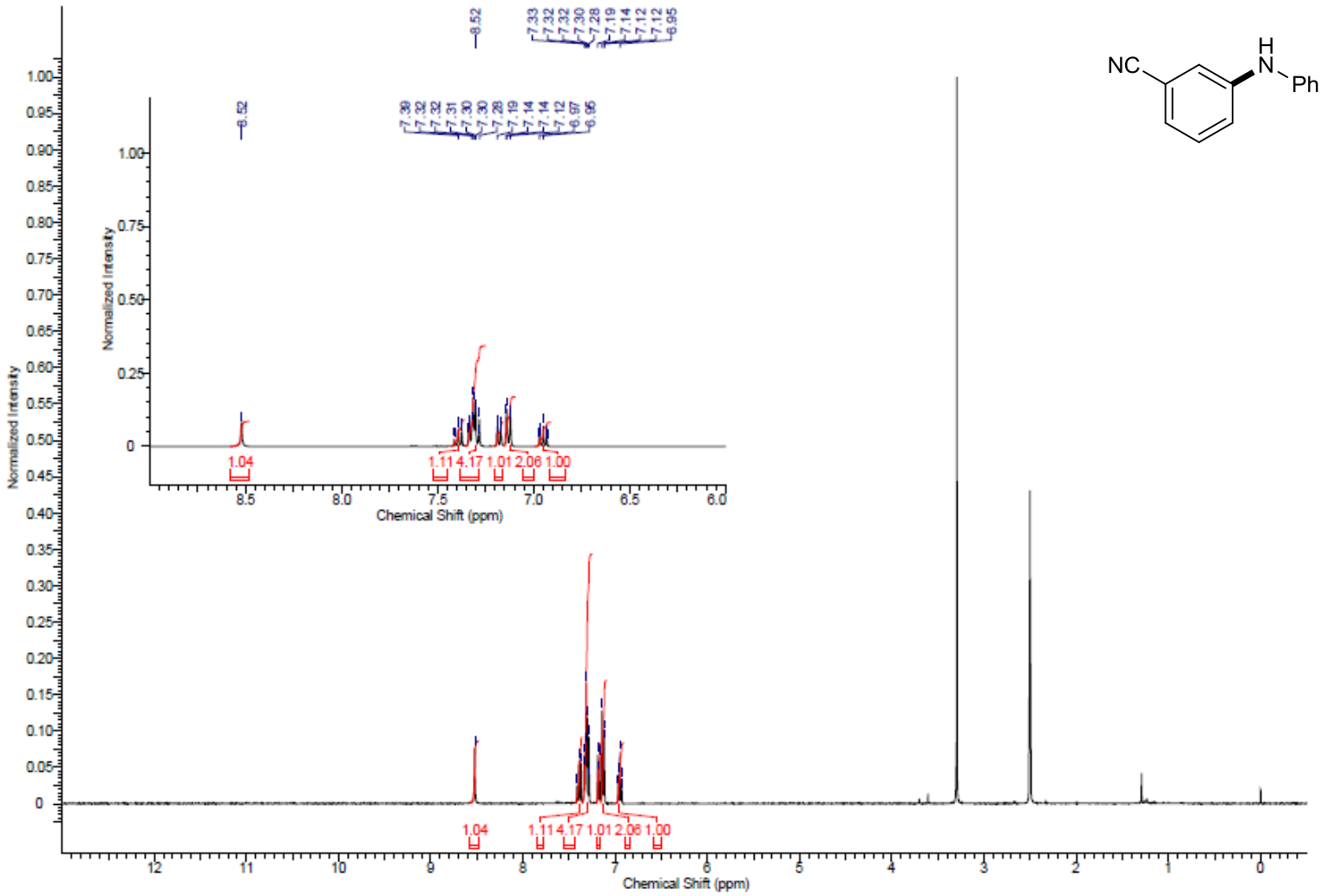
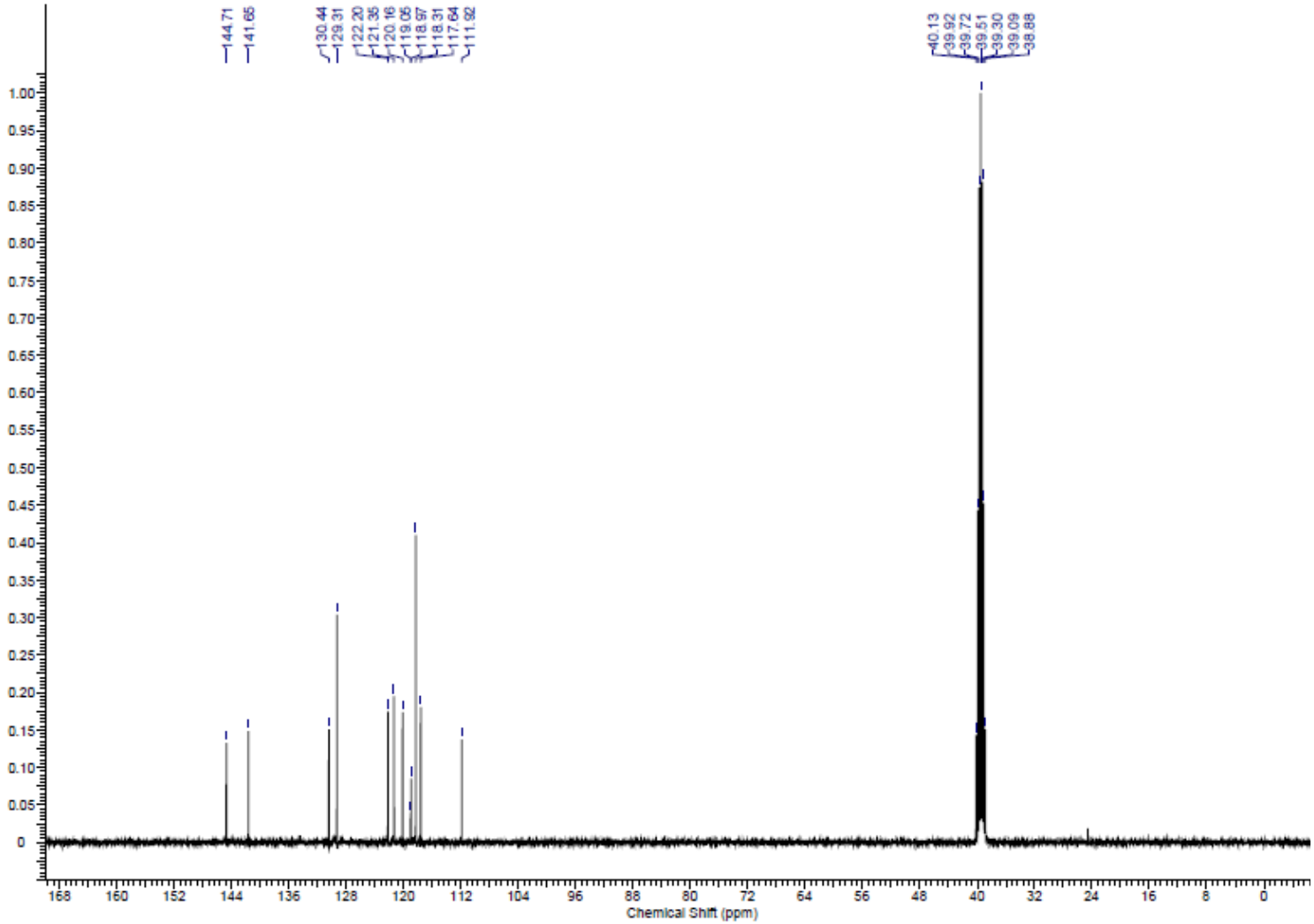


3-(Phenylamino)benzonitrile (3g).

^{1}H NMR Spectra



^{13}C NMR Spectra



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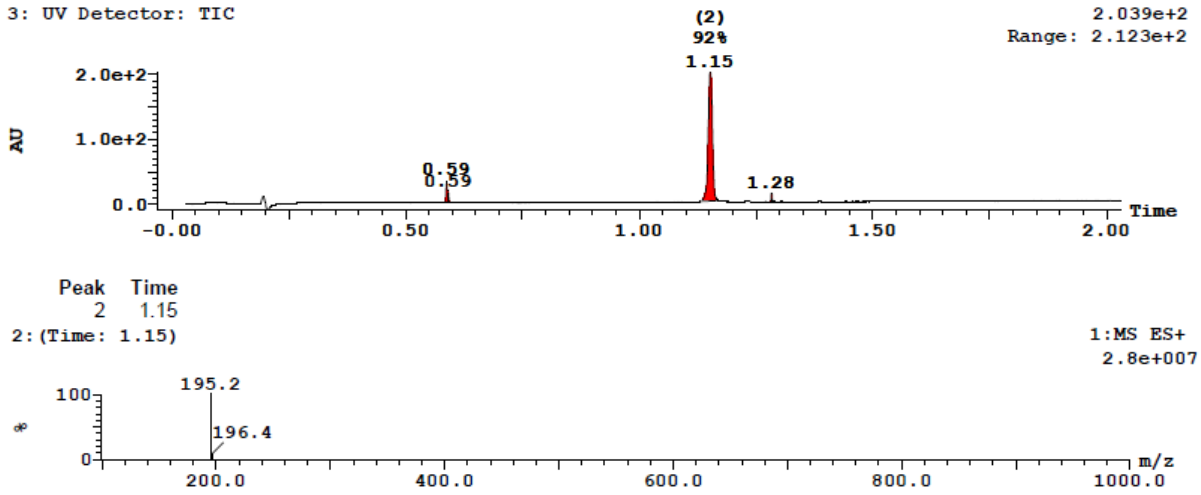

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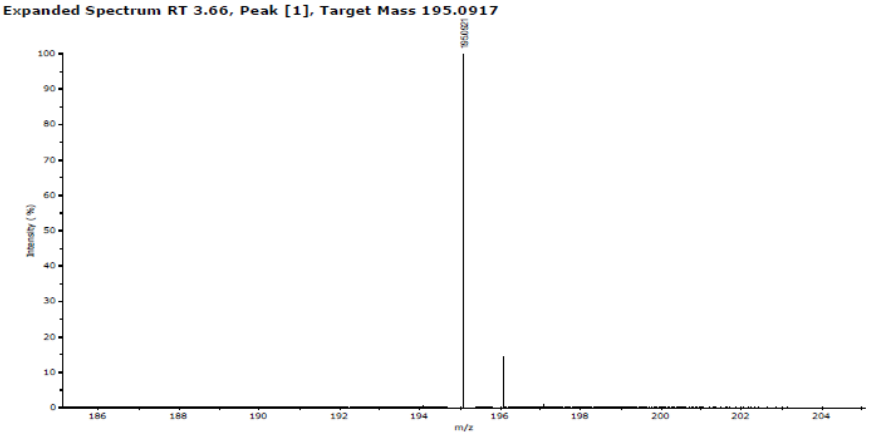
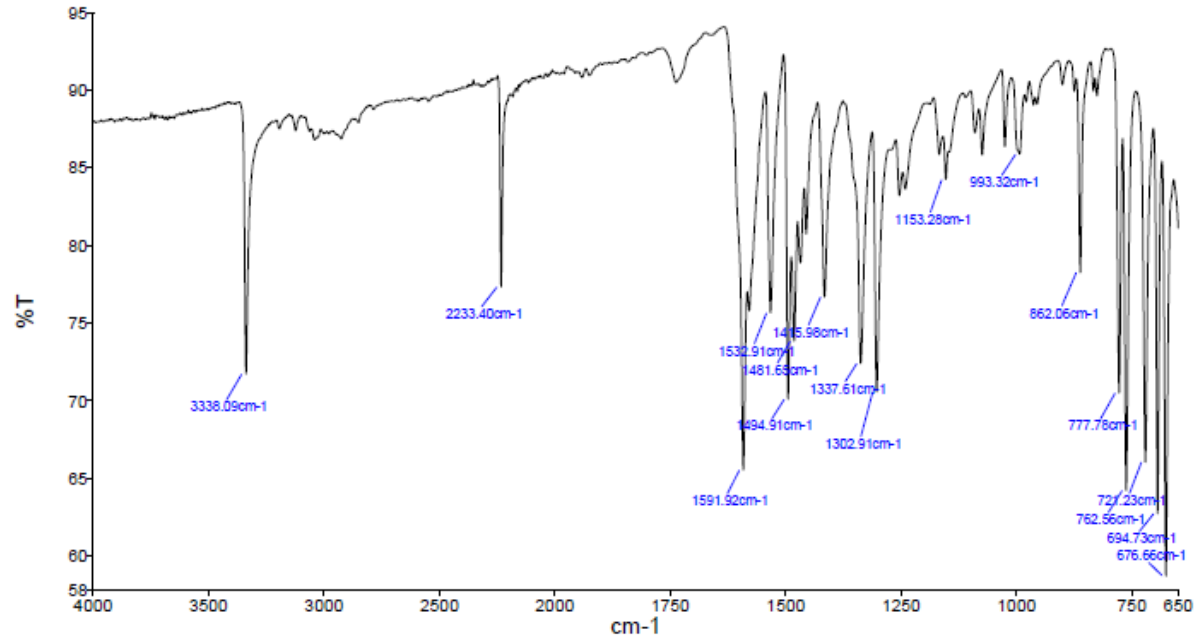
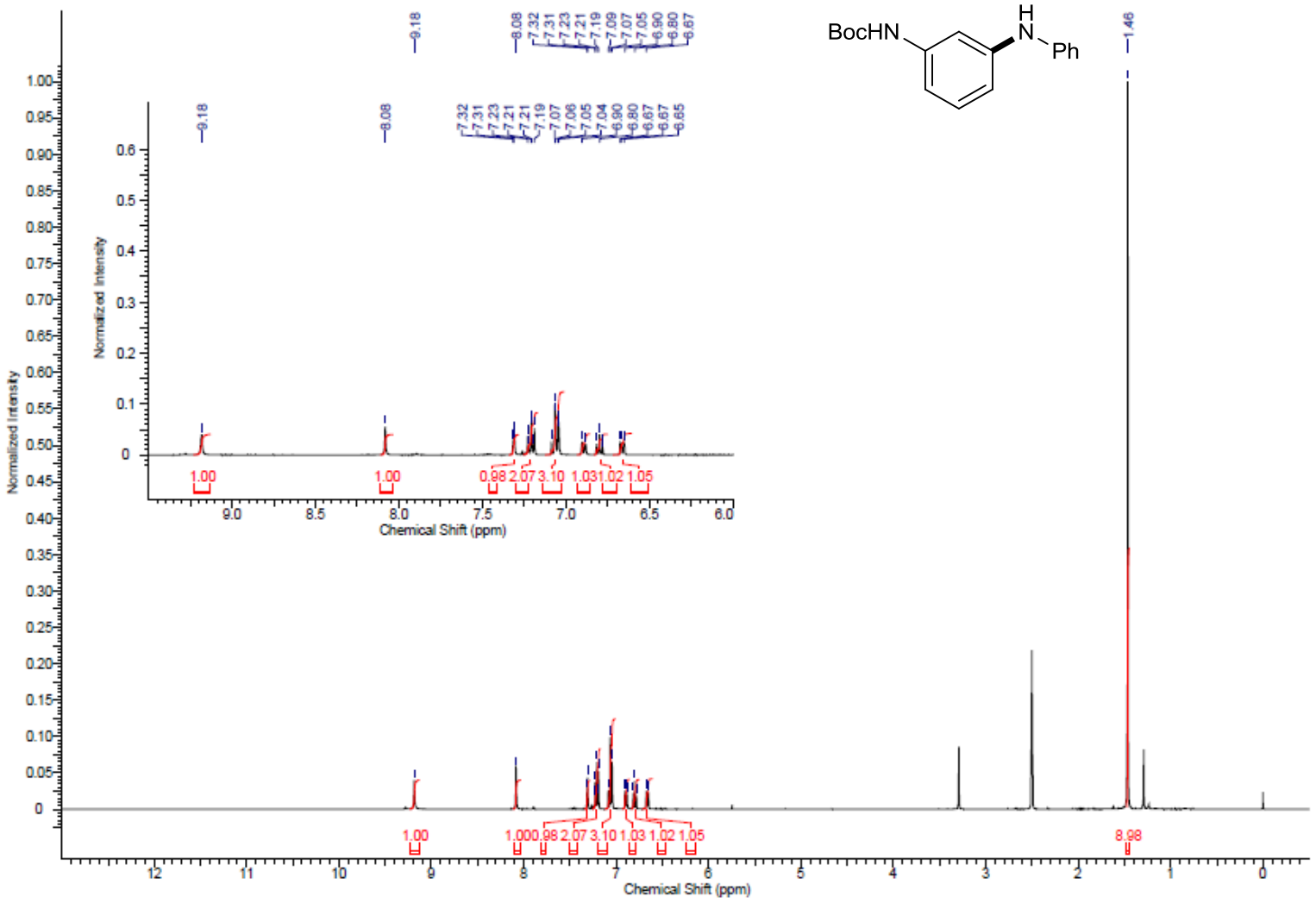


IR Spectra

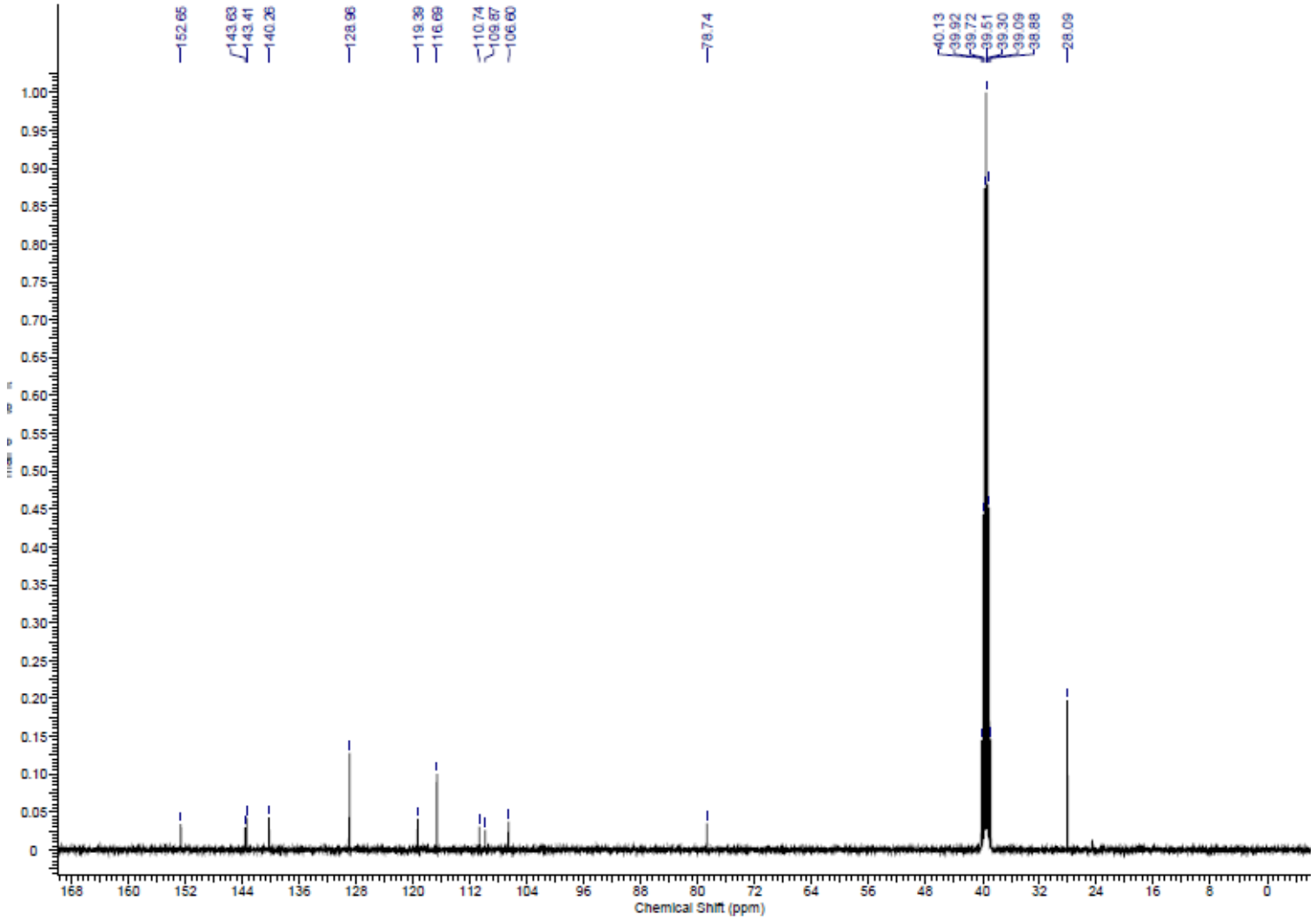


***tert*-Butyl-(3-(phenylamino)phenyl)carbamate (3h).**

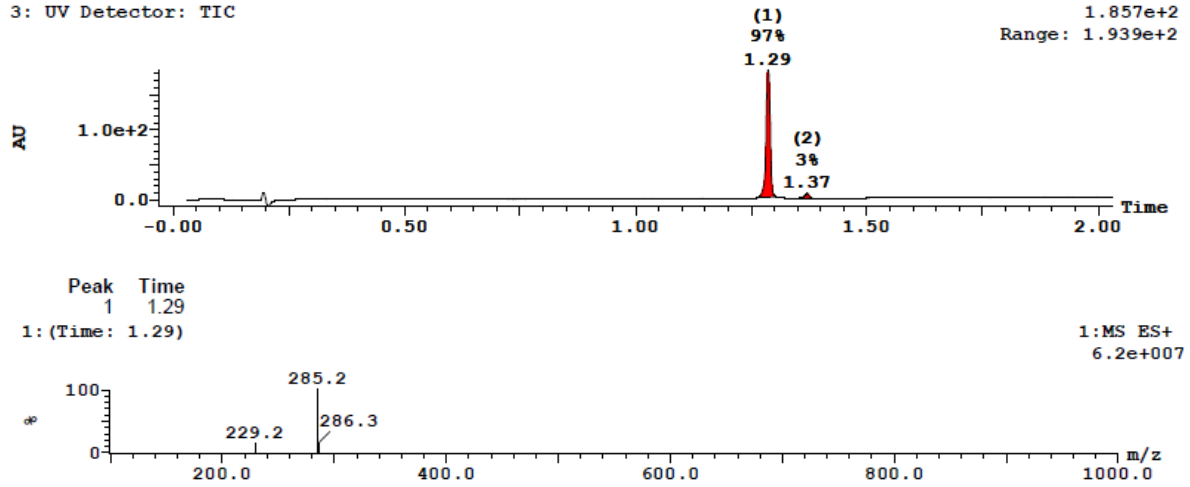
^{1}H NMR Spectra



^{13}C NMR Spectra



LCMS



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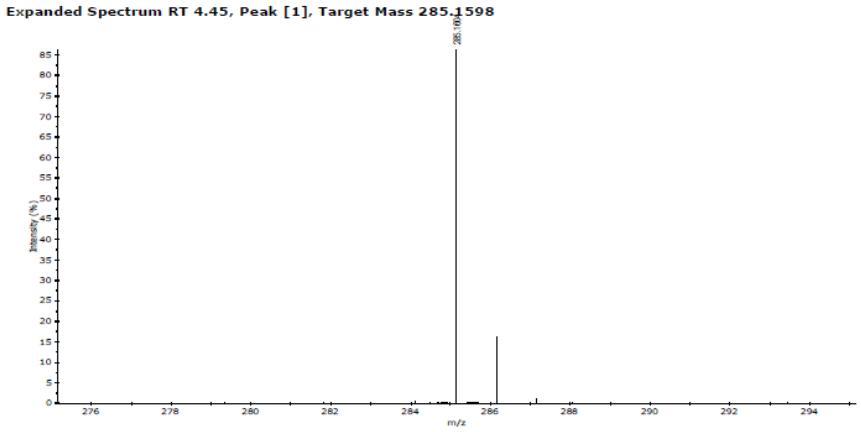
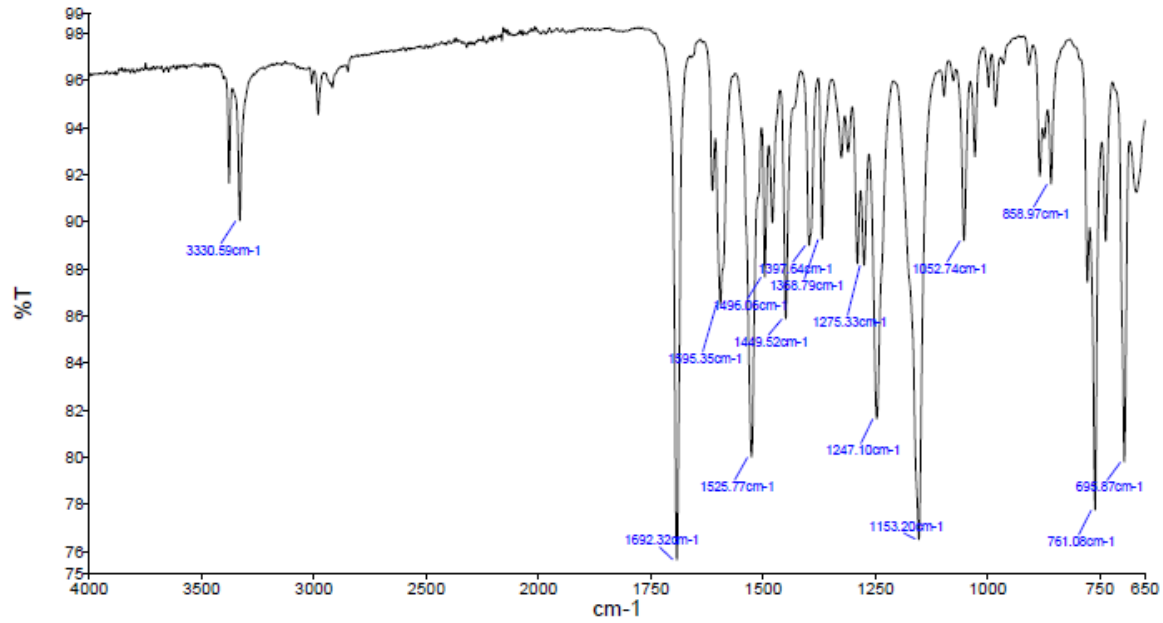
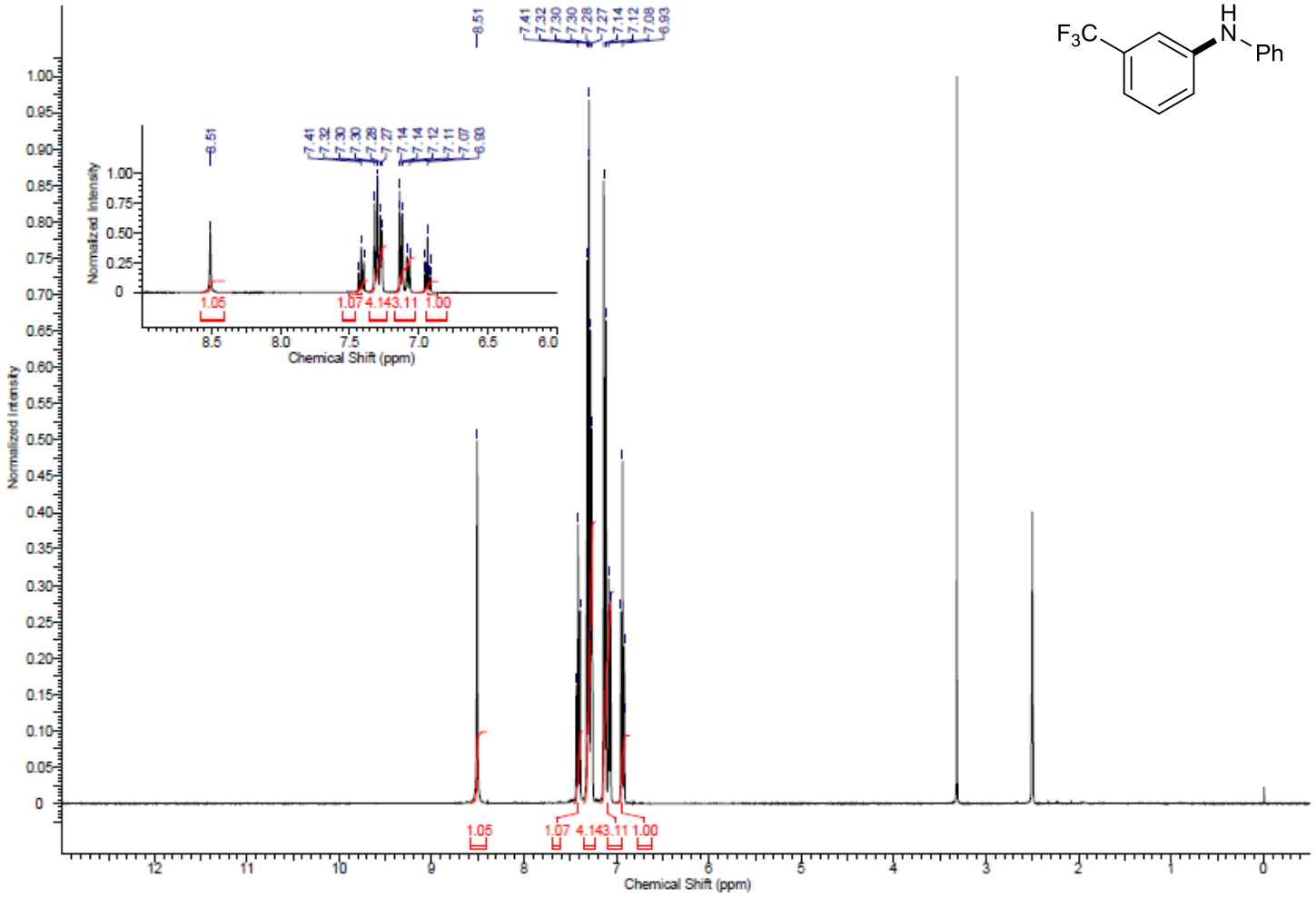


IR Spectra

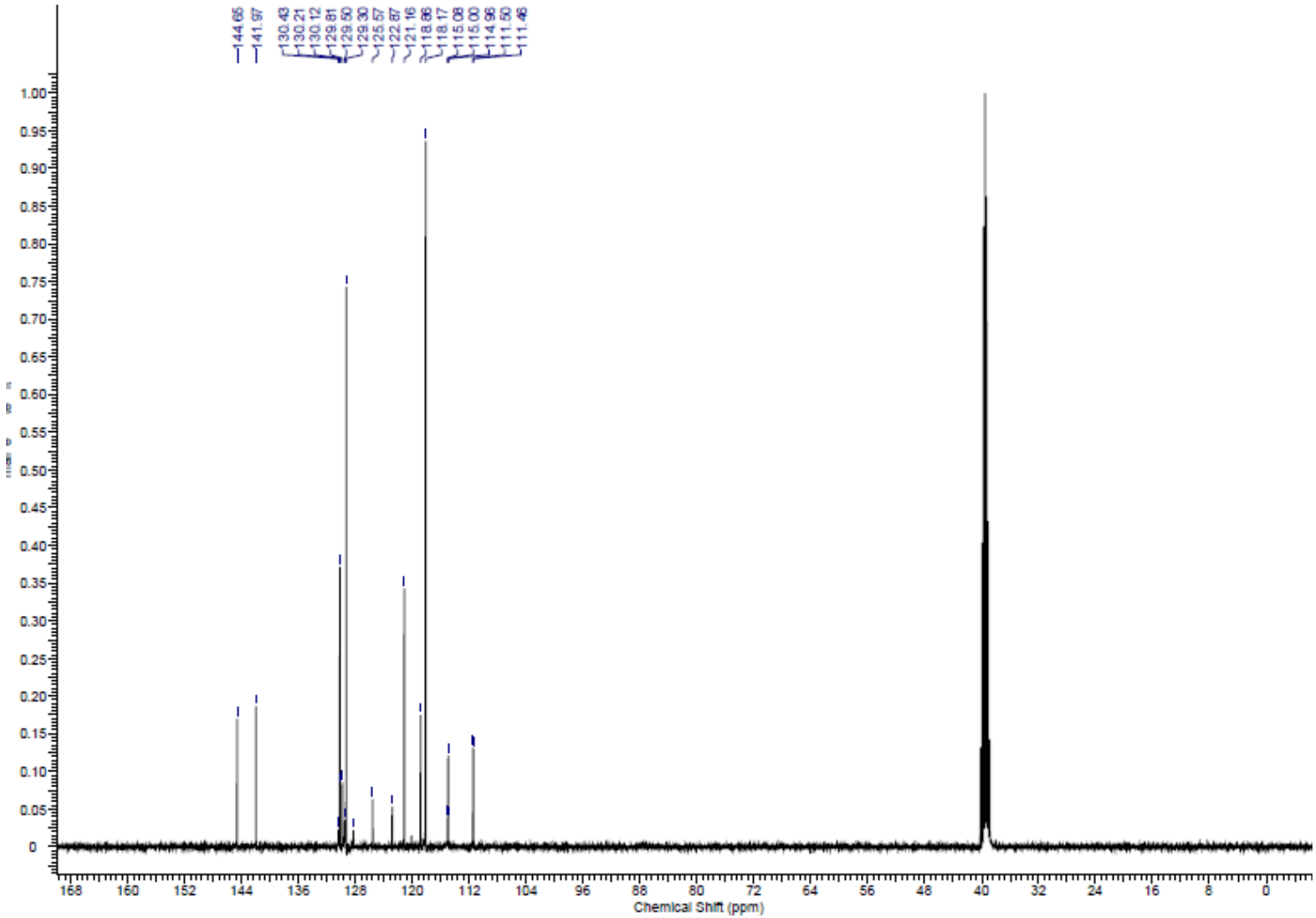


***N*-Phenyl-3-(trifluoromethyl)aniline (3i).**

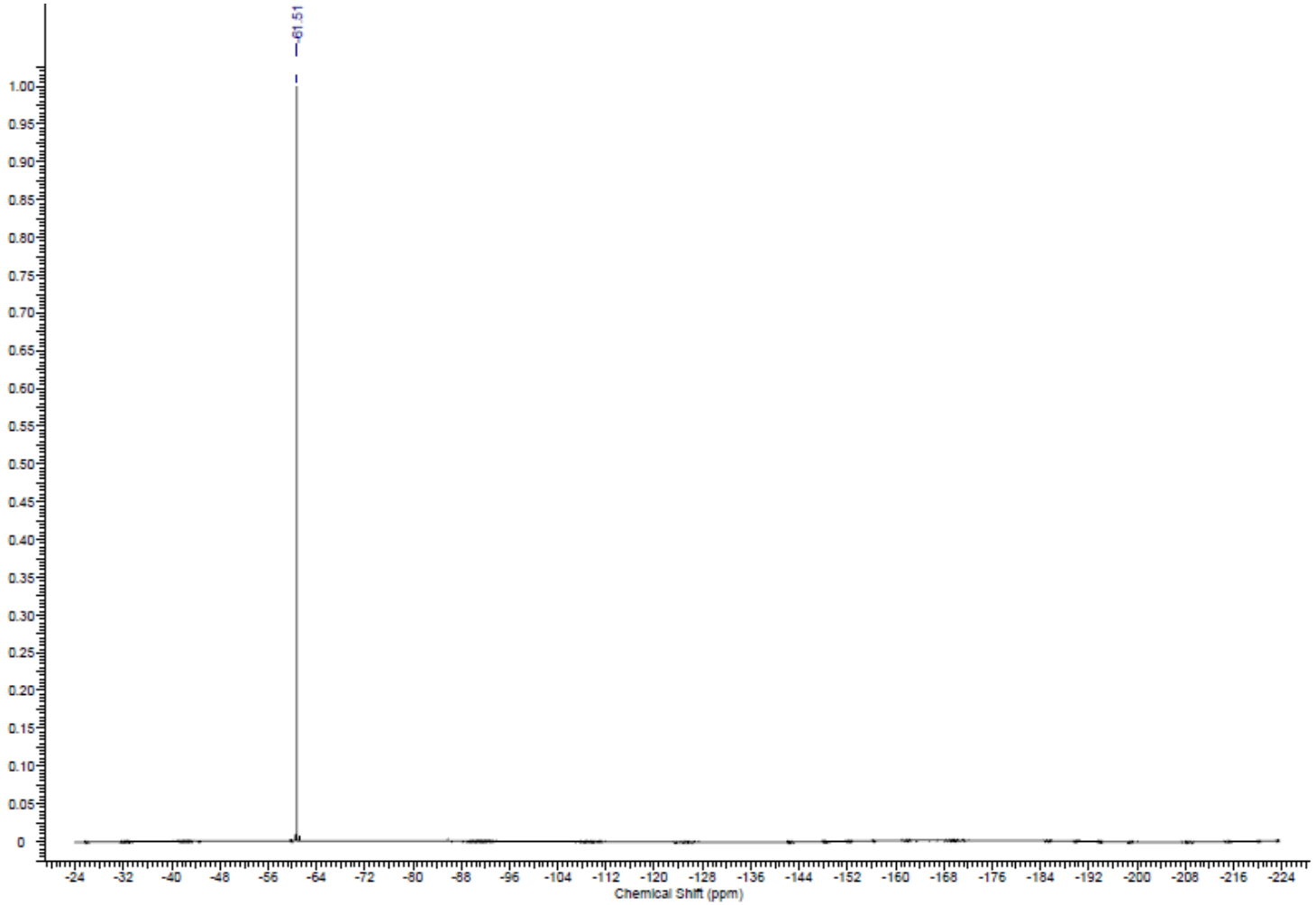
^{1}H NMR Spectra



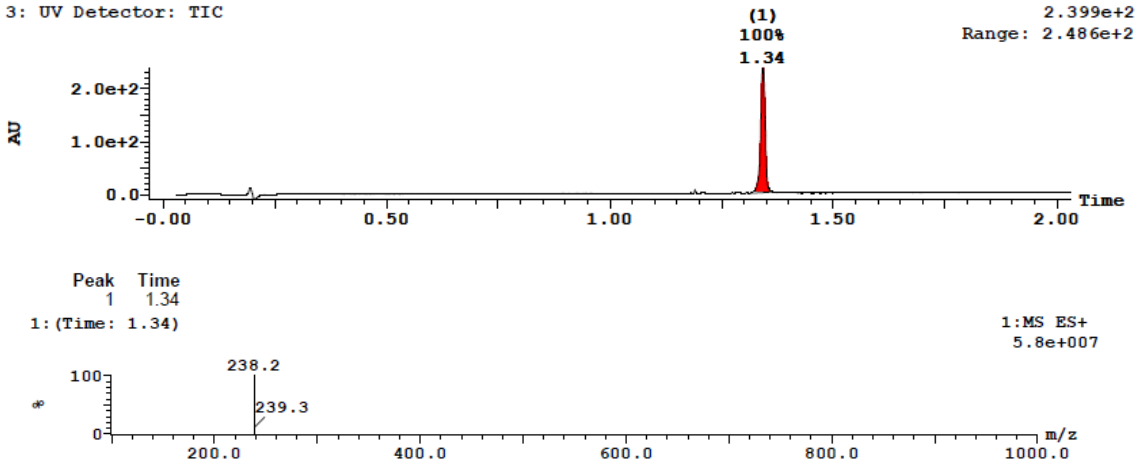
^{13}C NMR Spectra



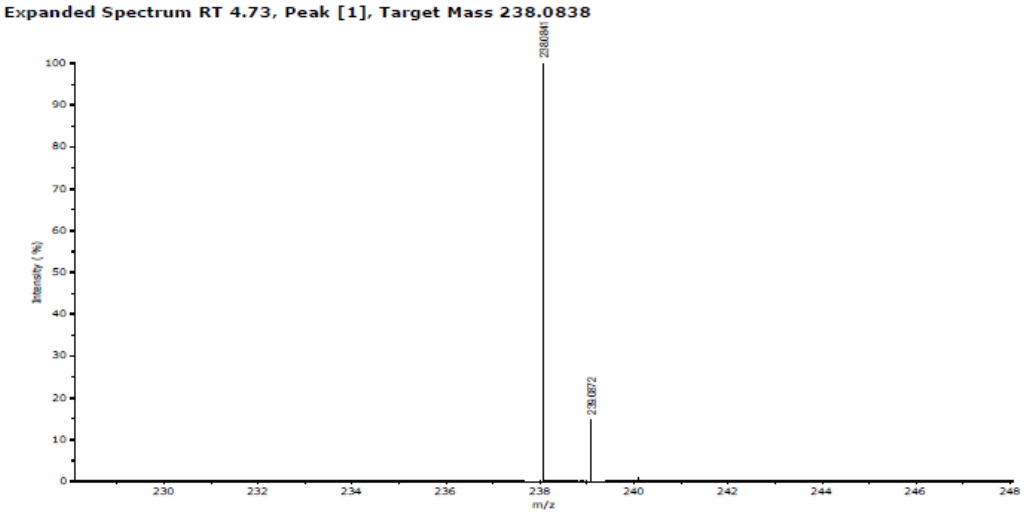
^{19}F NMR Spectra



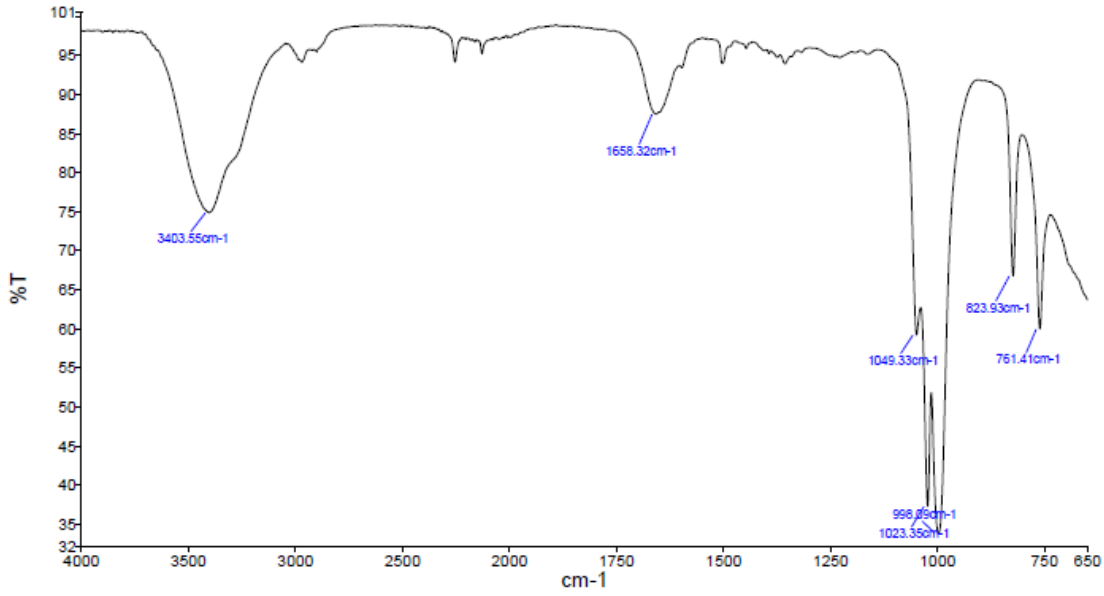
LCMS



HRMS

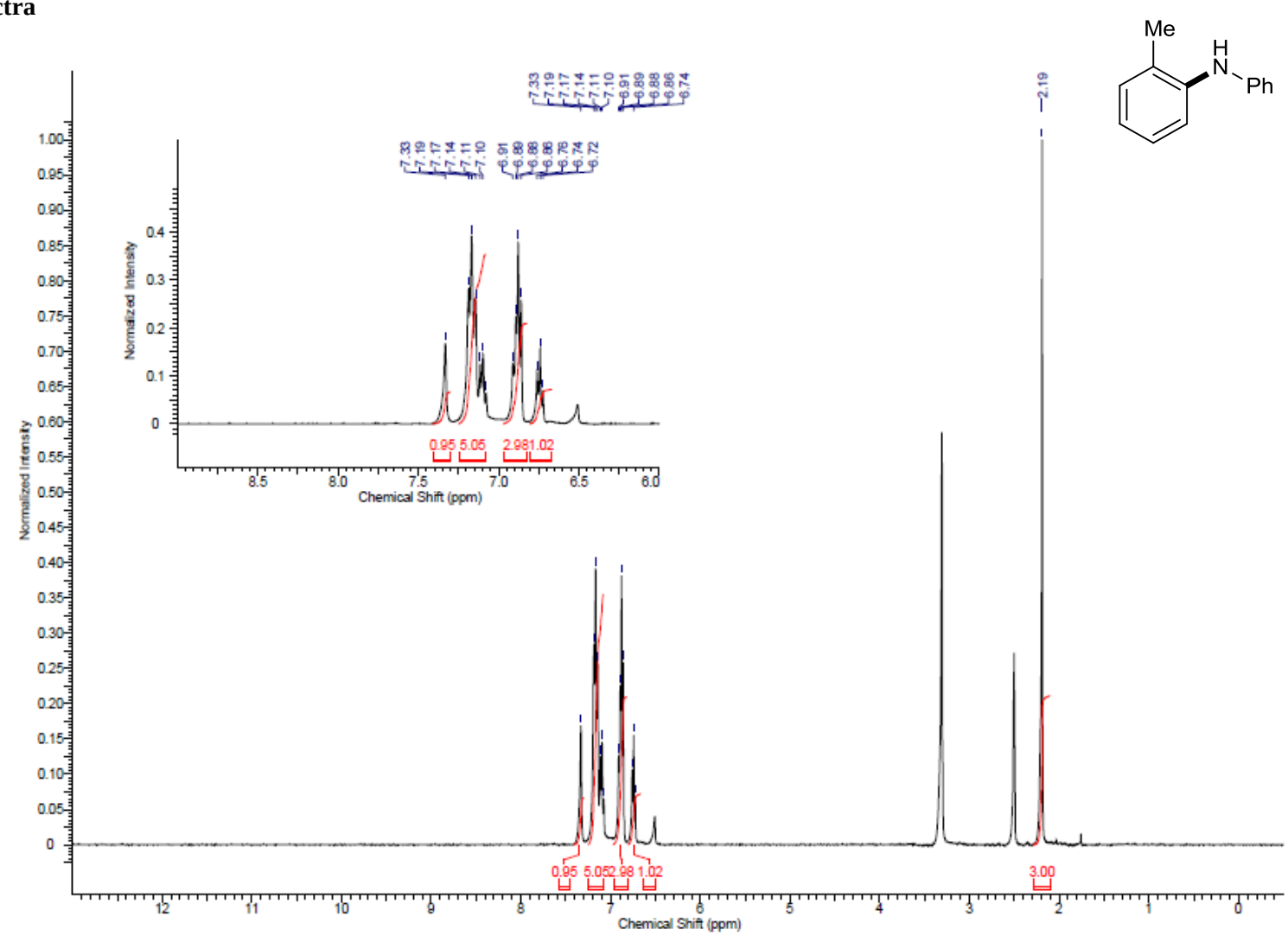


IR Spectra

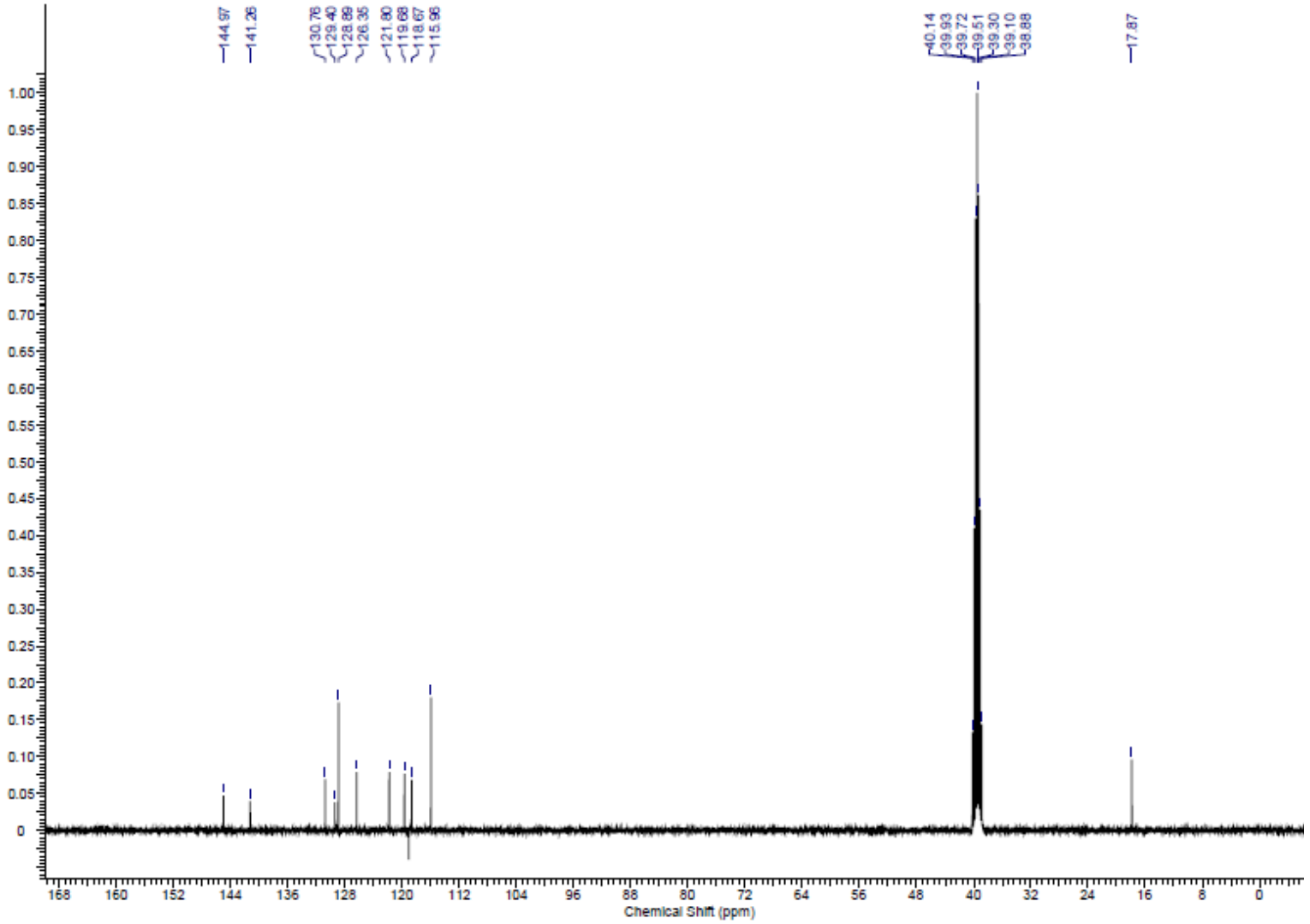


2-Methyl-*N*-phenylaniline (3j).

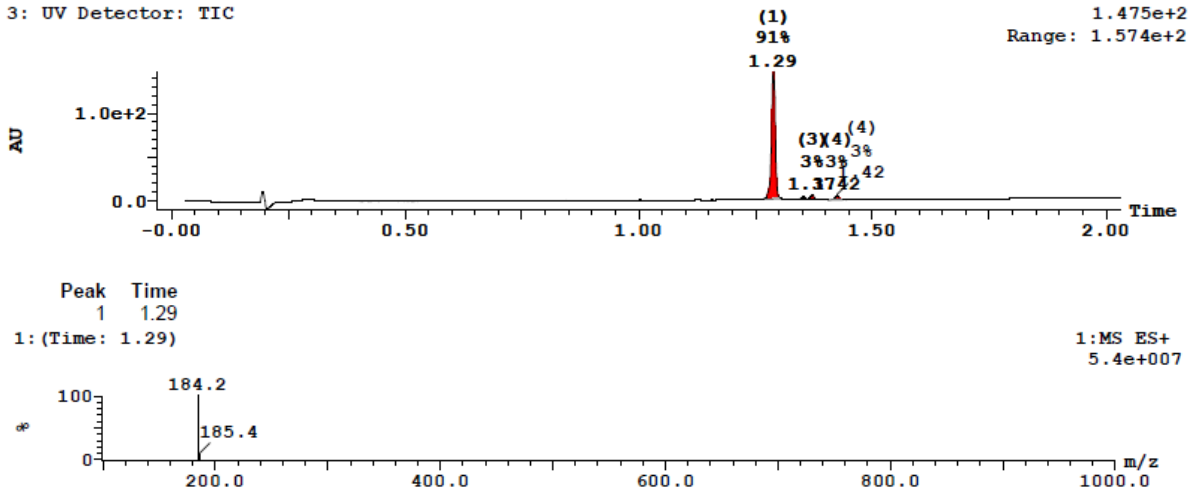
^{1}H NMR Spectra



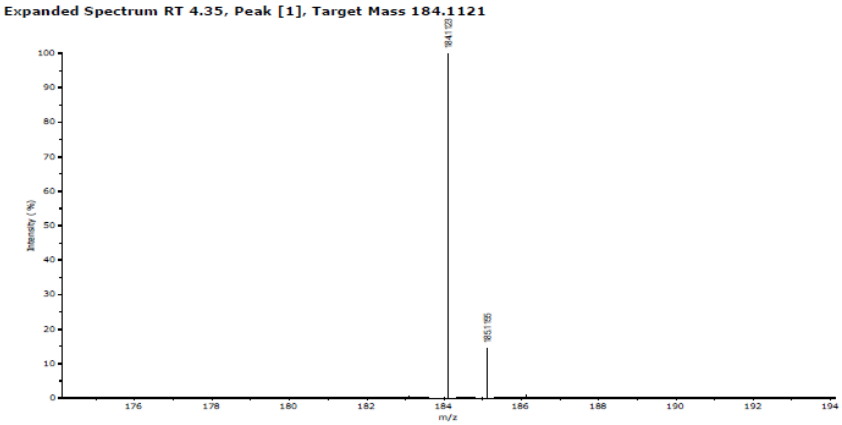
^{13}C NMR Spectra



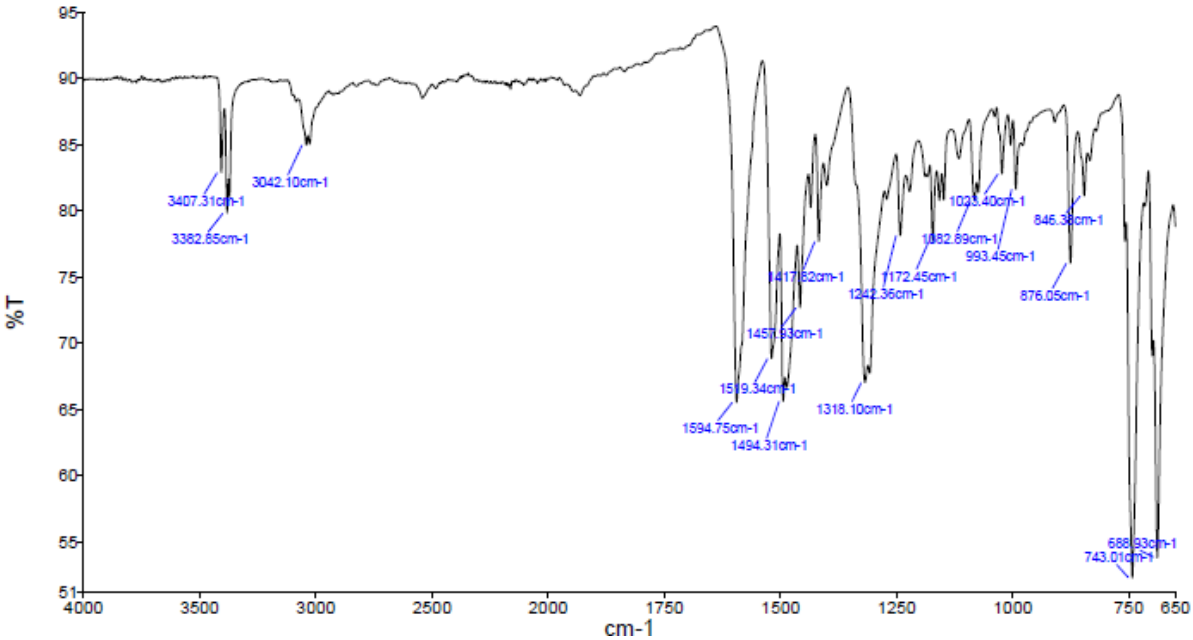
LCMS



HRMS

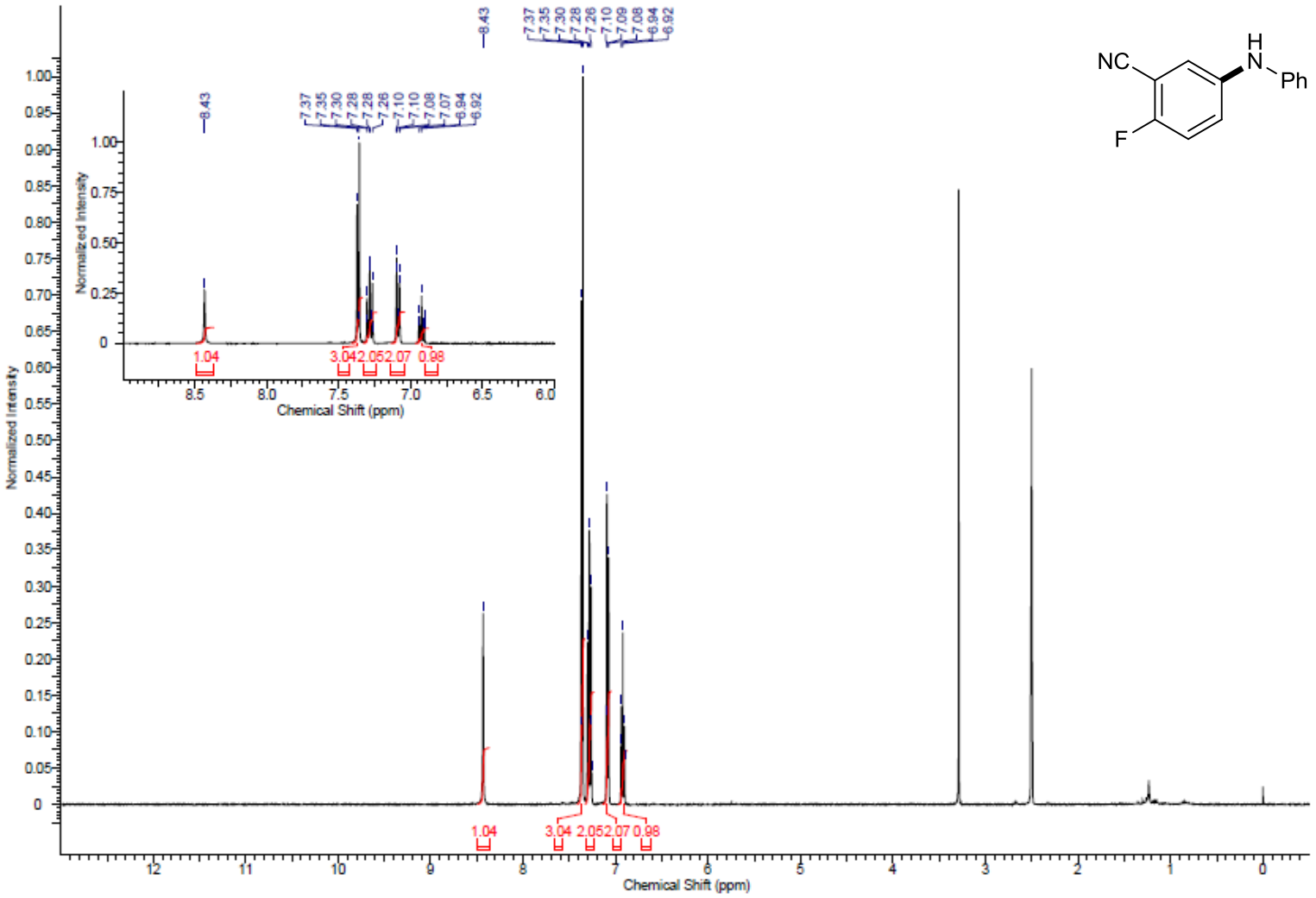


IR Spectra

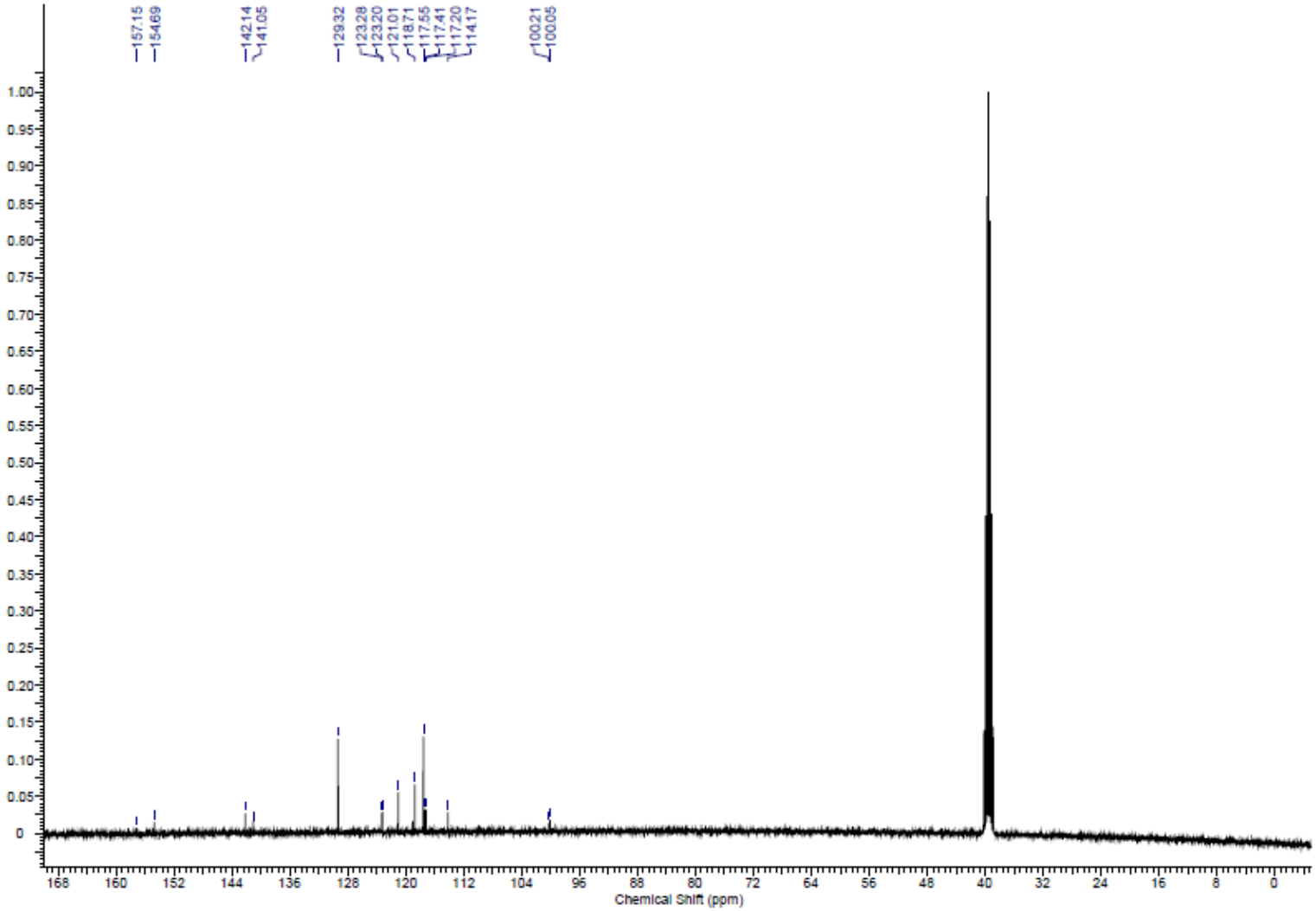


2-Fluoro-5-(phenylamino)benzonitrile (3k).

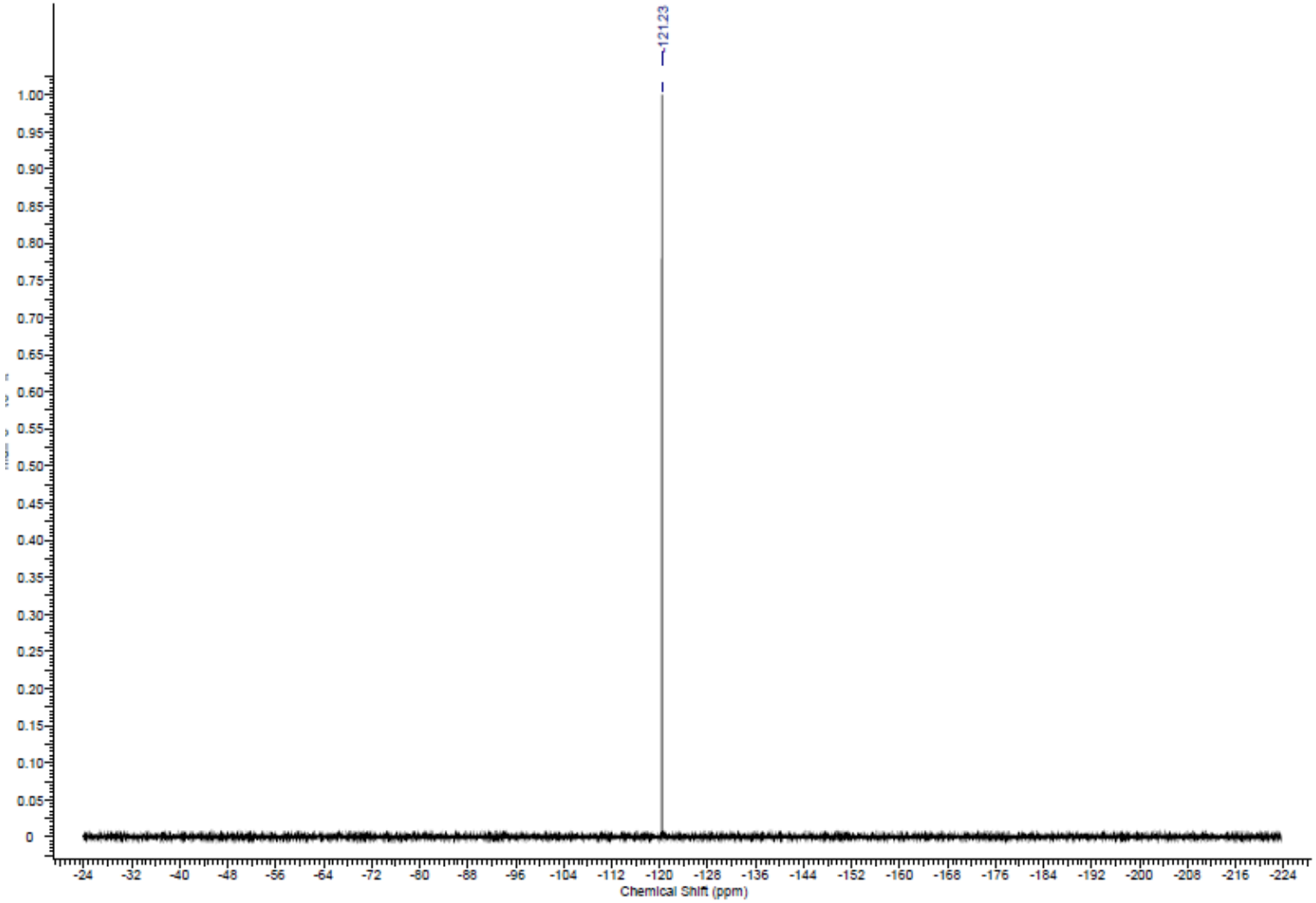
^{1}H NMR Spectra



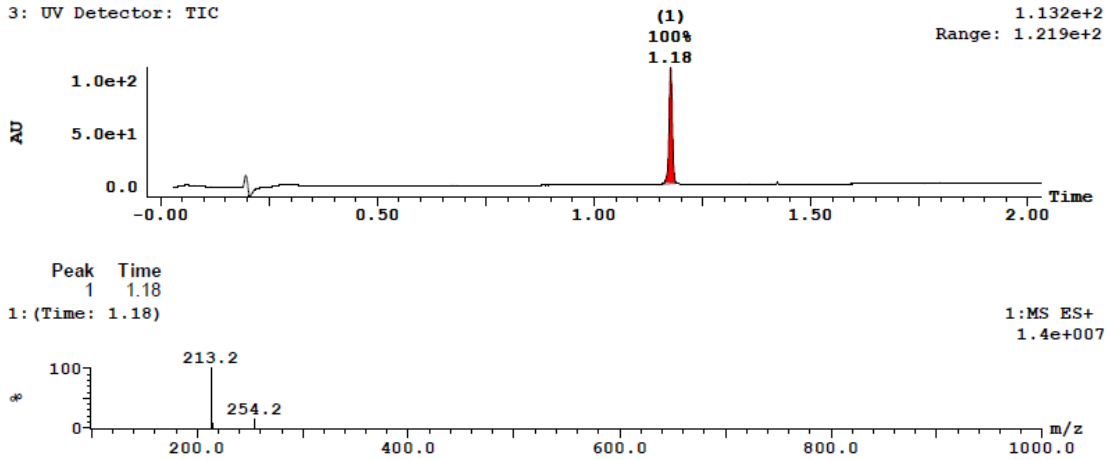
^{13}C NMR Spectra



^{19}F NMR Spectra



LCMS



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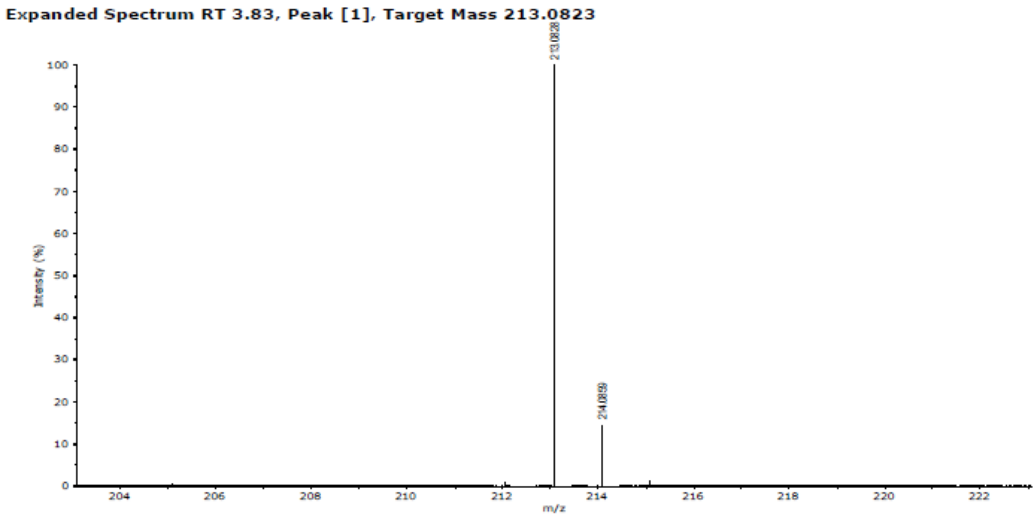
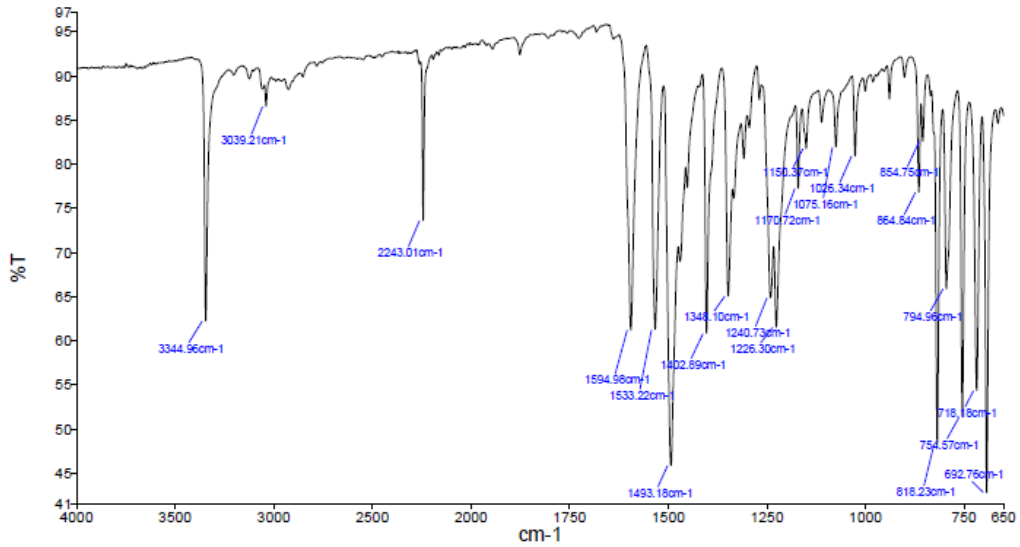
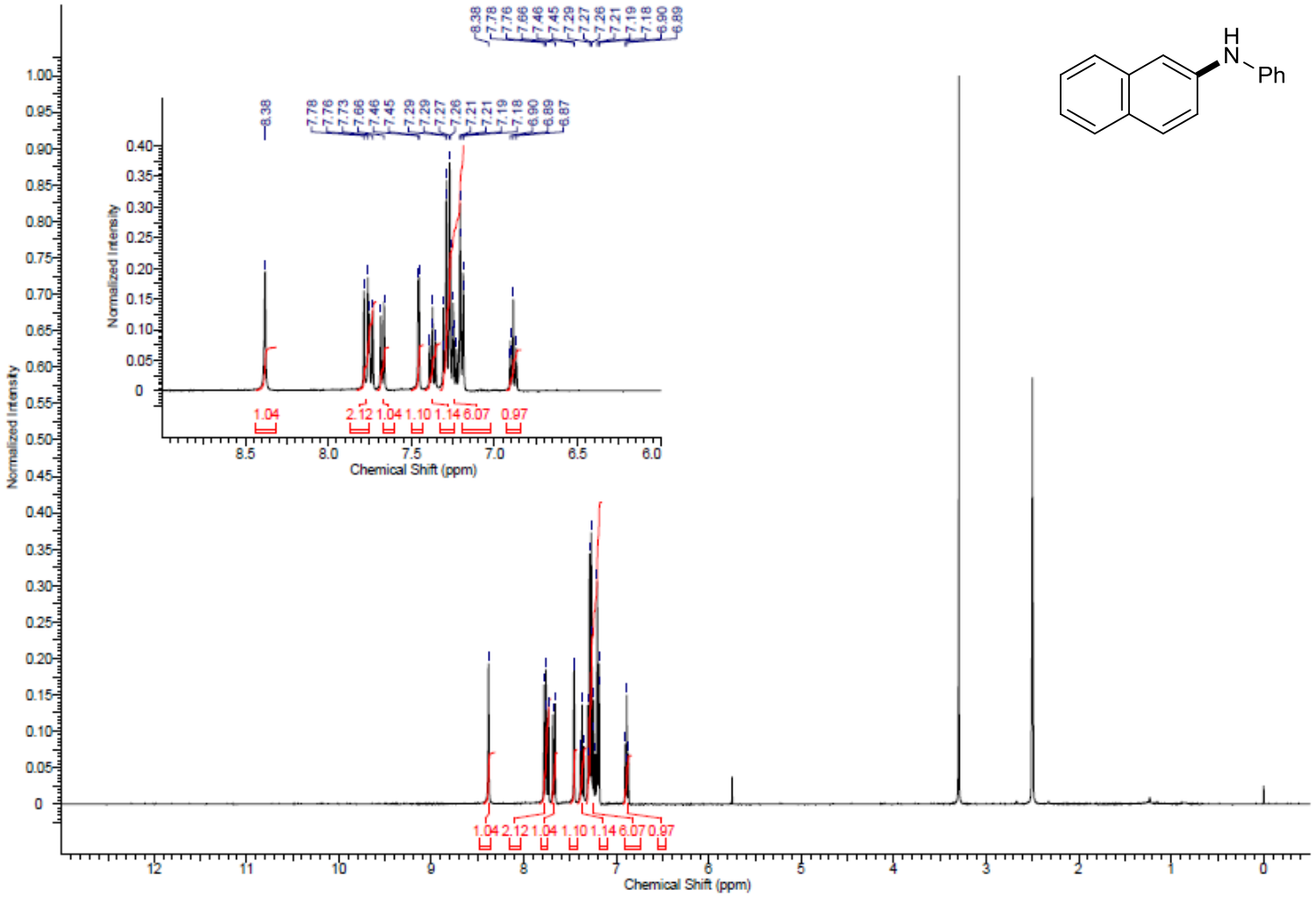


IR Spectra

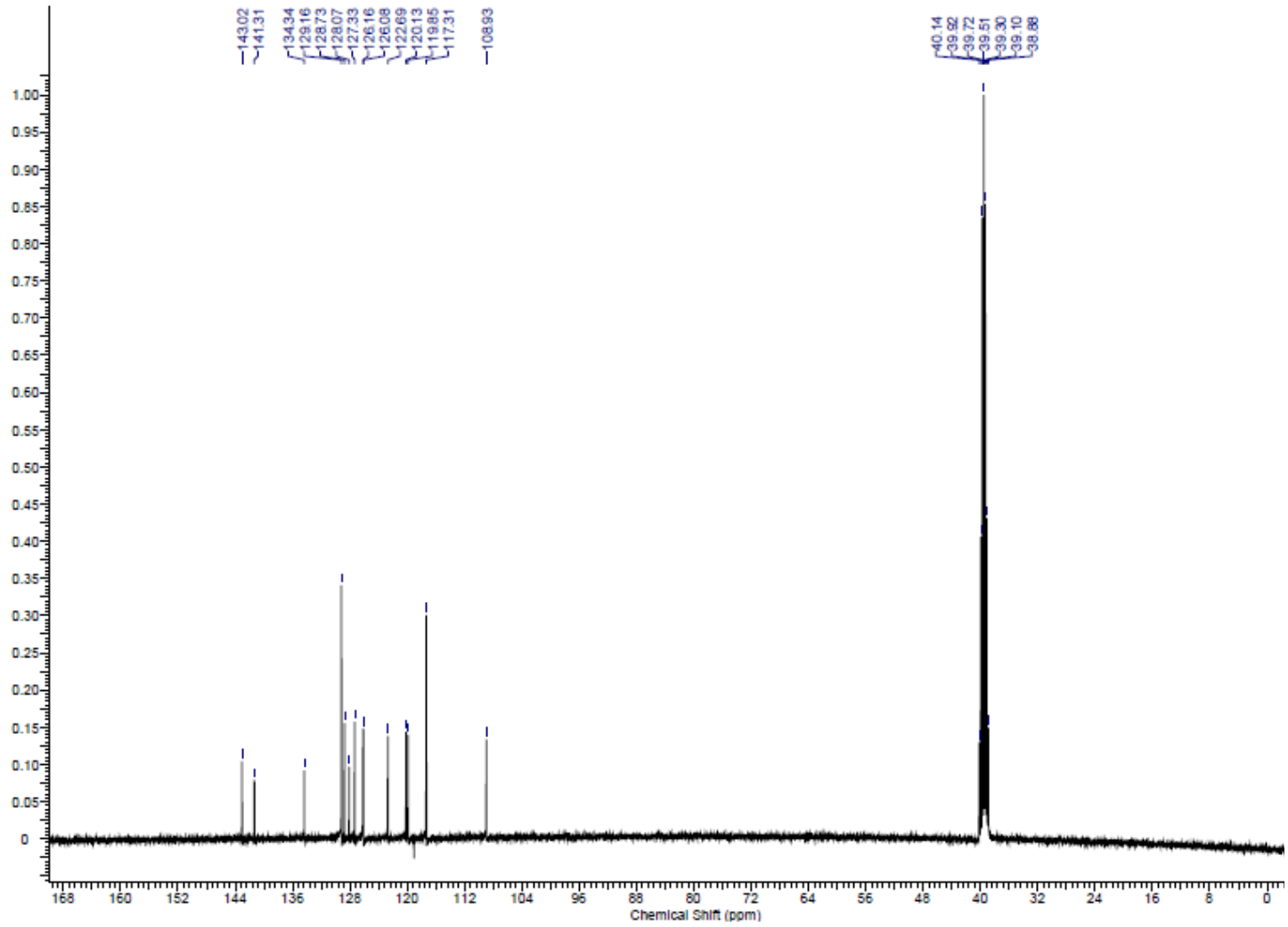


***N*-Phenylnaphthalen-2-amine (3l).**

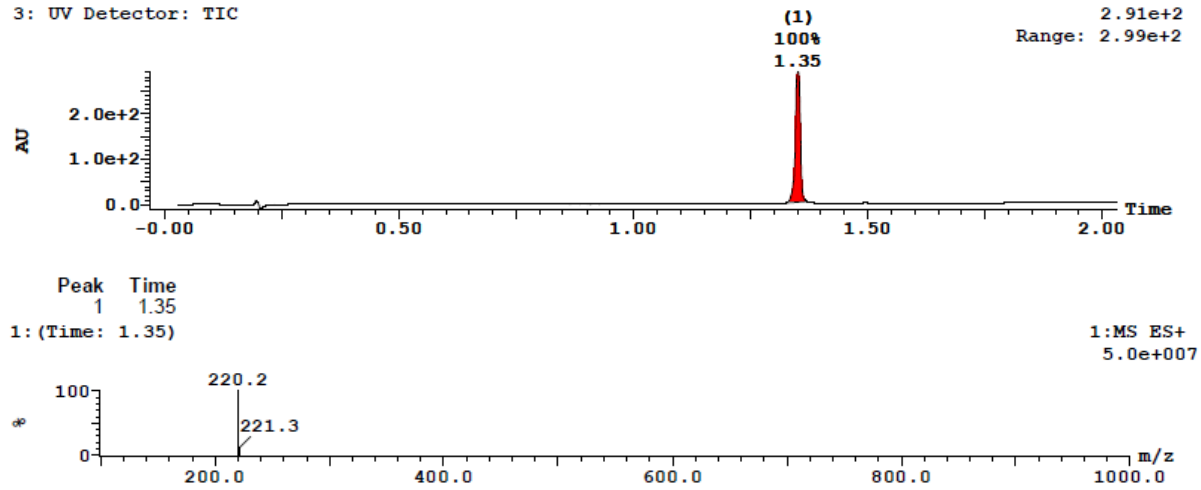
^{1}H NMR Spectra



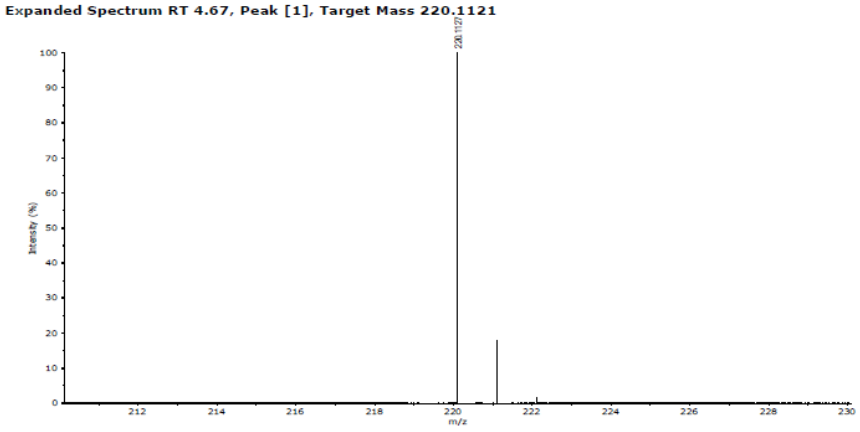
^{13}C NMR Spectra



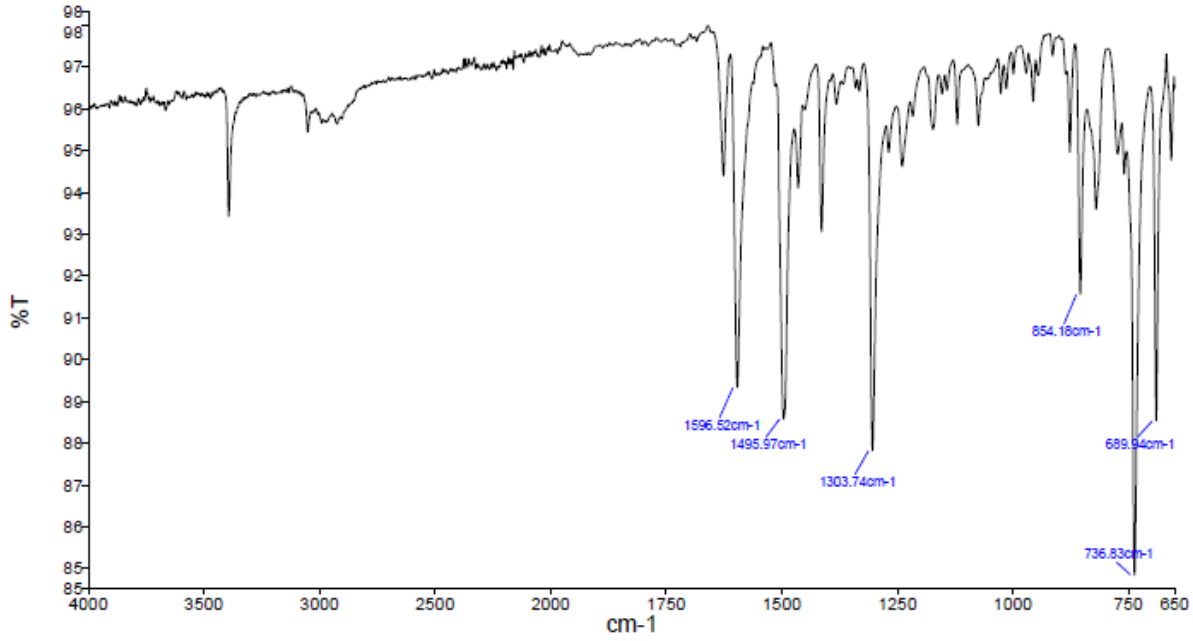
LCMS



HRMS

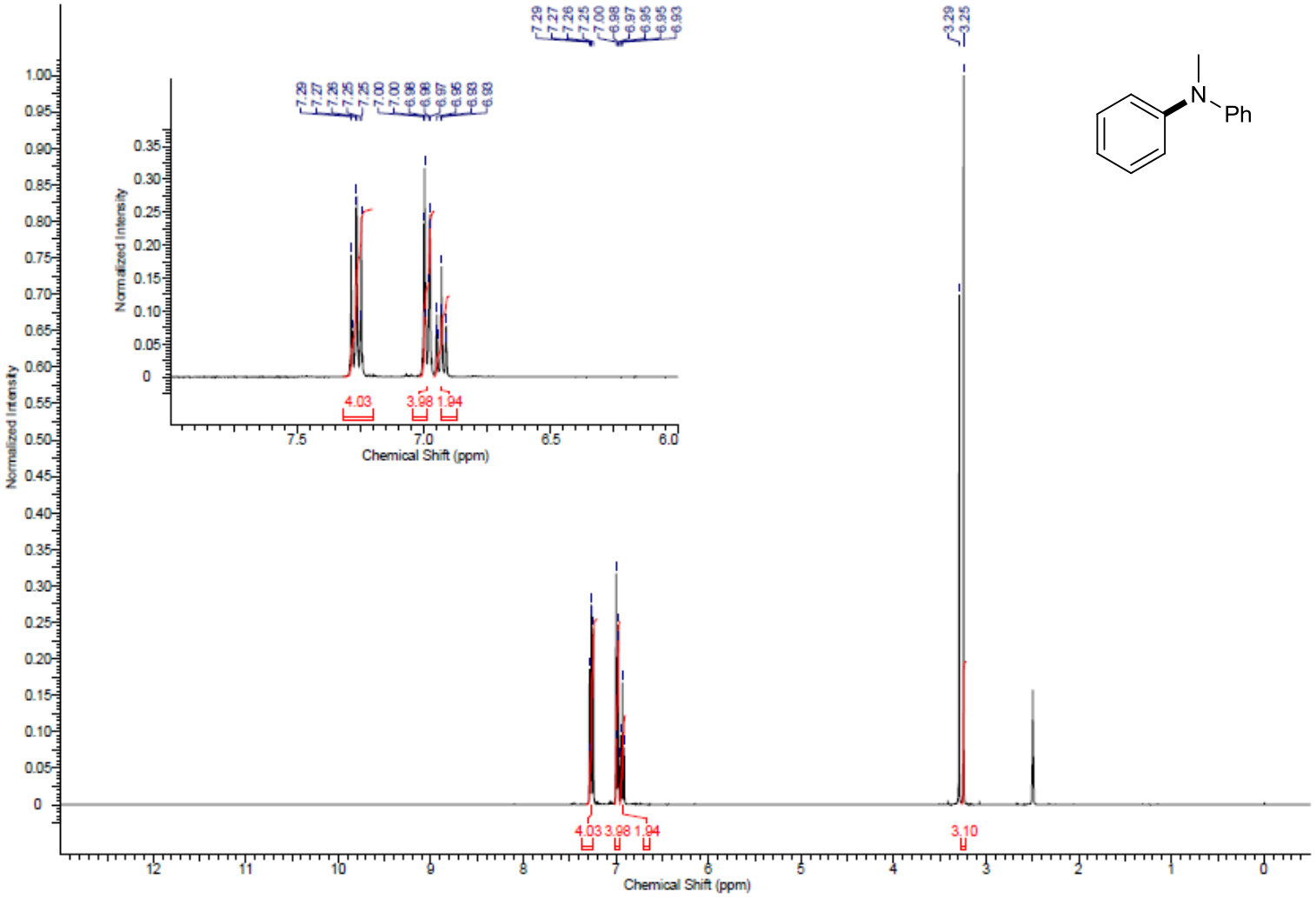


IR Spectra

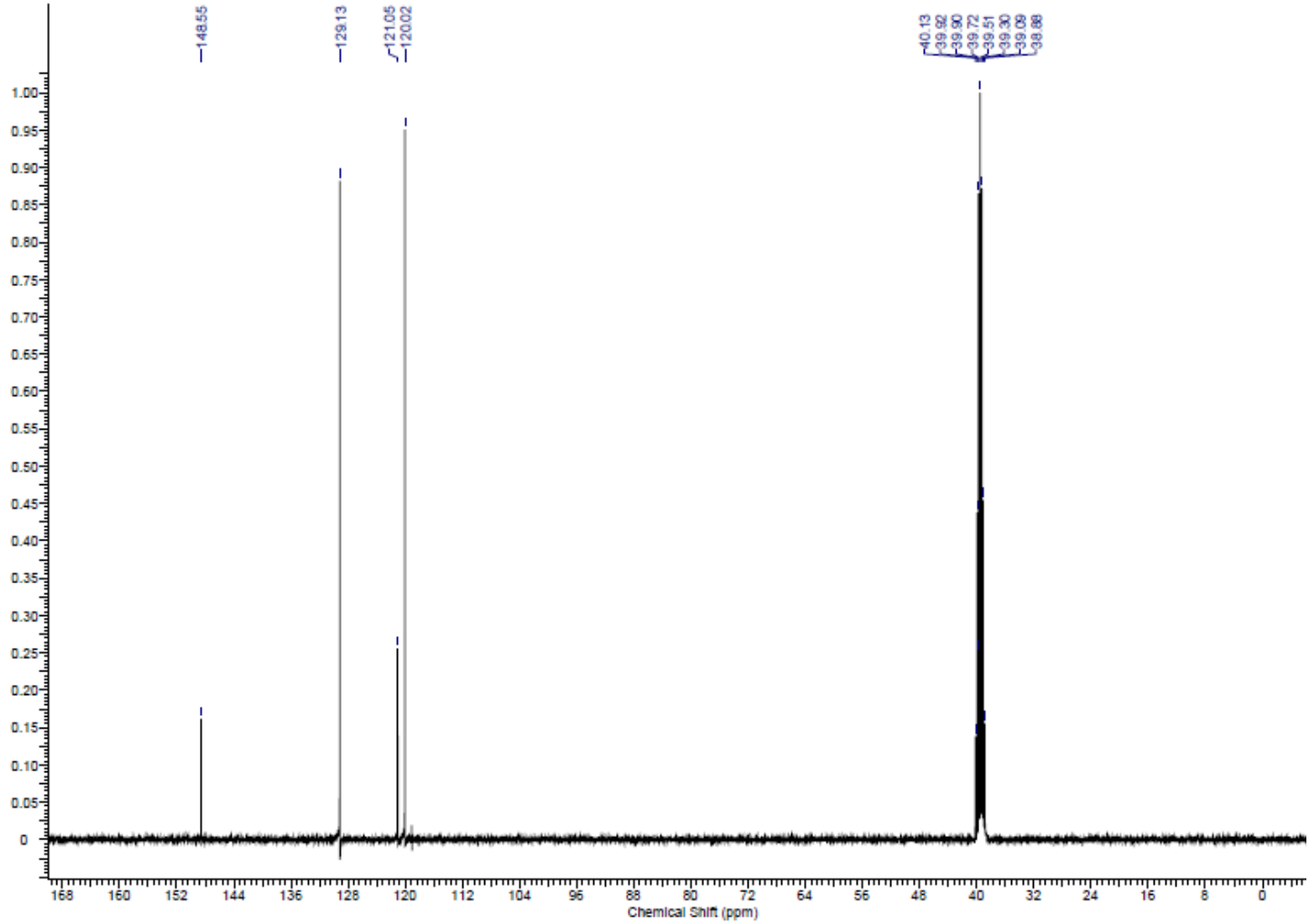


***N*-Methyl-*N*-phenylaniline (3m).**

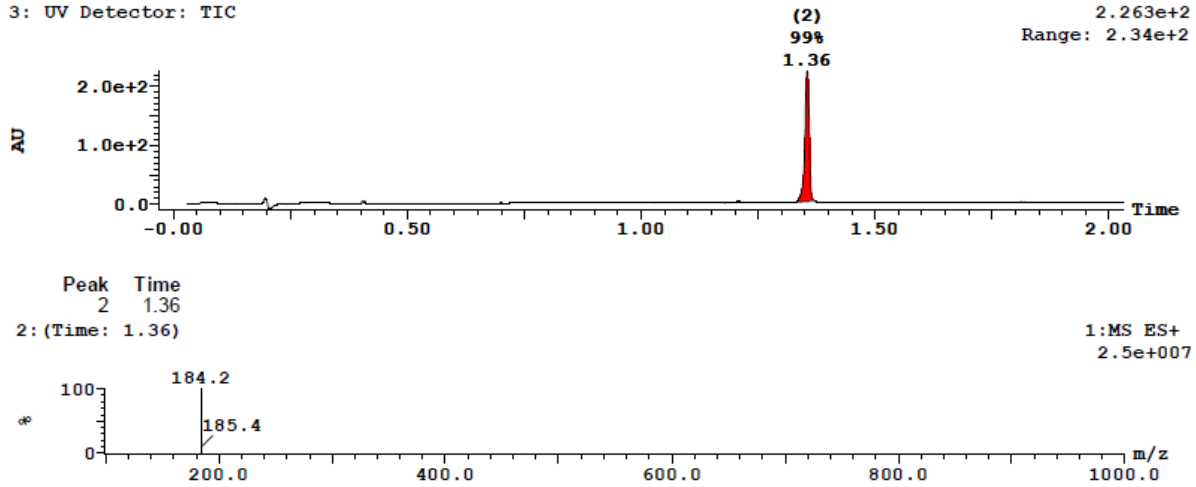
^{1}H NMR Spectra



^{13}C NMR Spectra



LCMS



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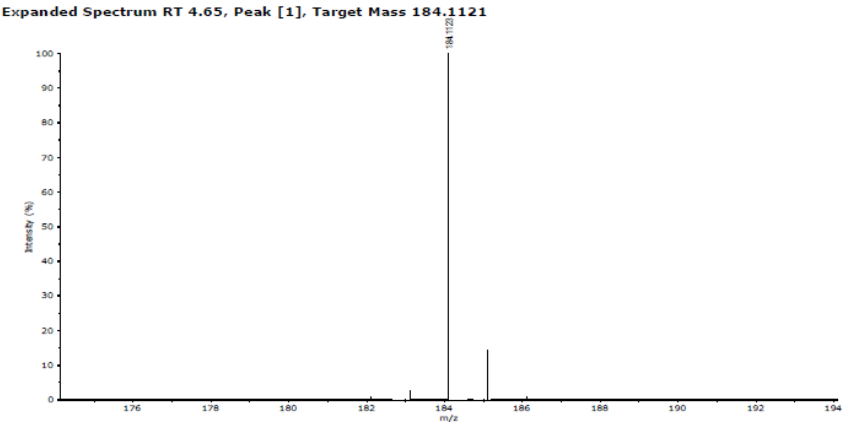
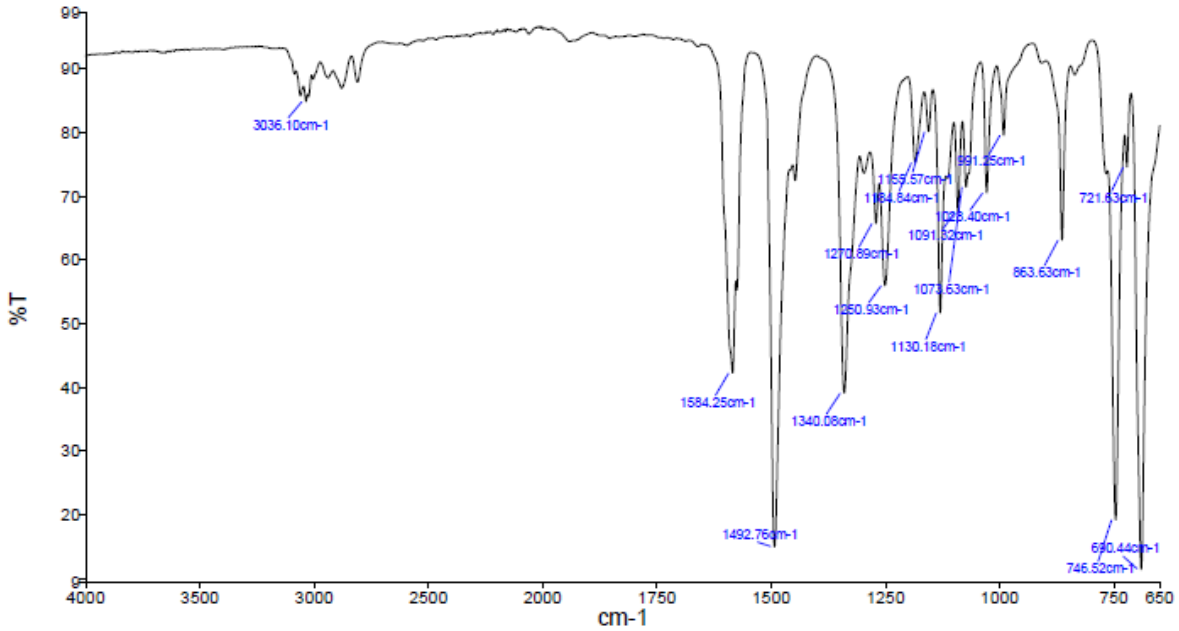
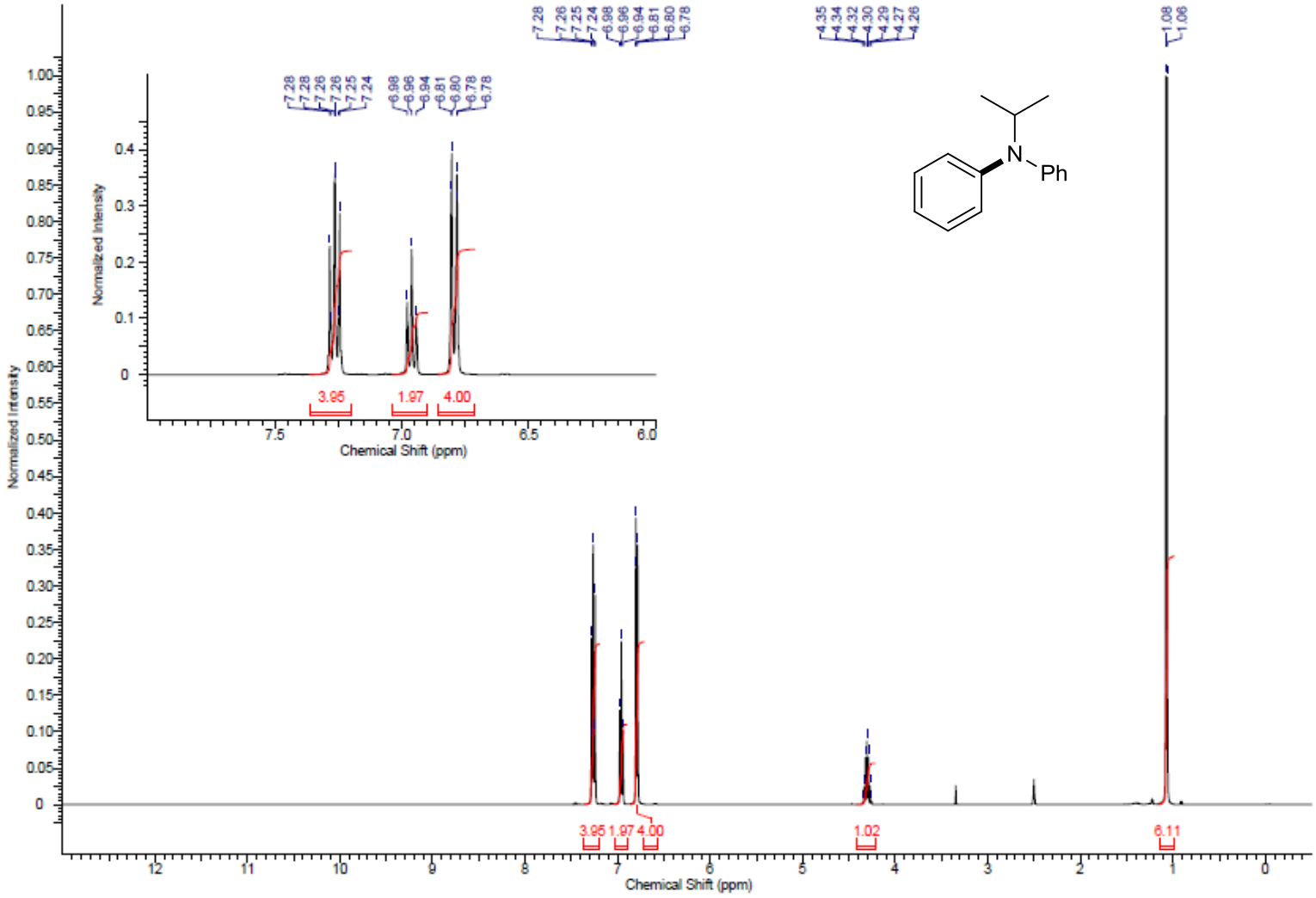


IR Spectra

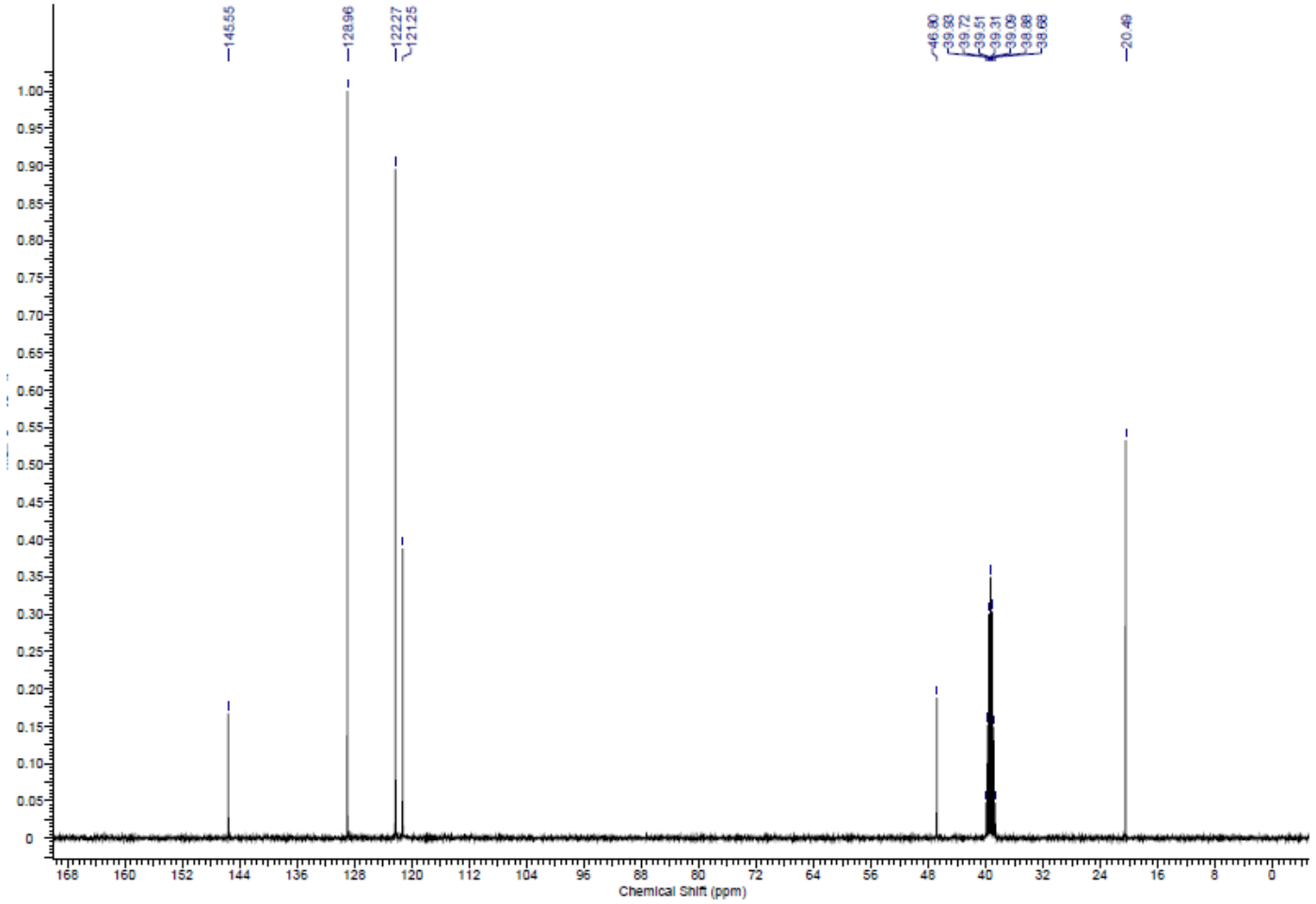


***N*-Isopropyl-*N*-phenylaniline (3n).**

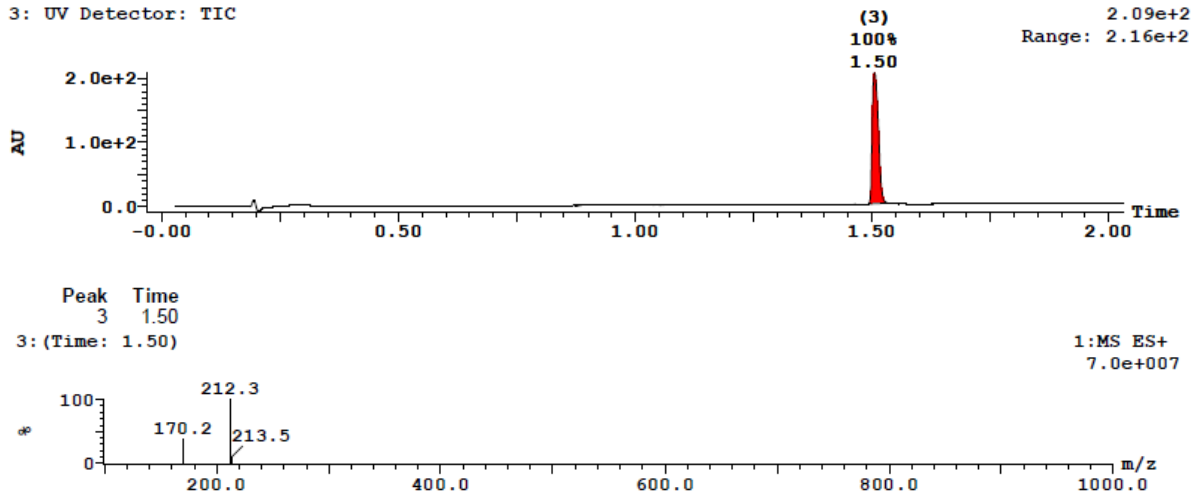
^{1}H NMR Spectra



^{13}C NMR Spectra



LCMS



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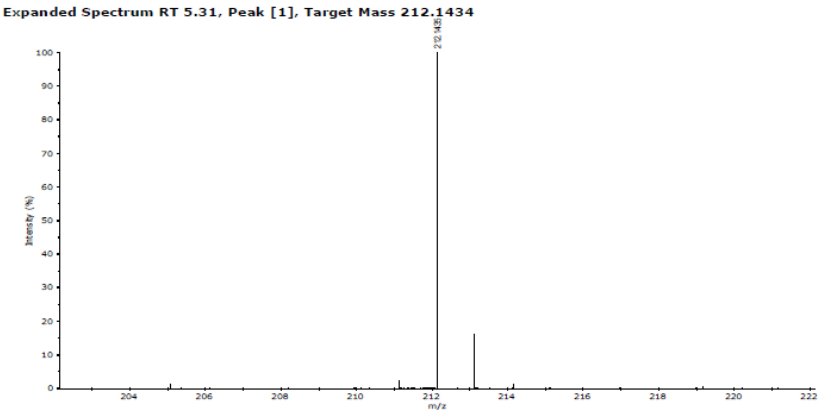
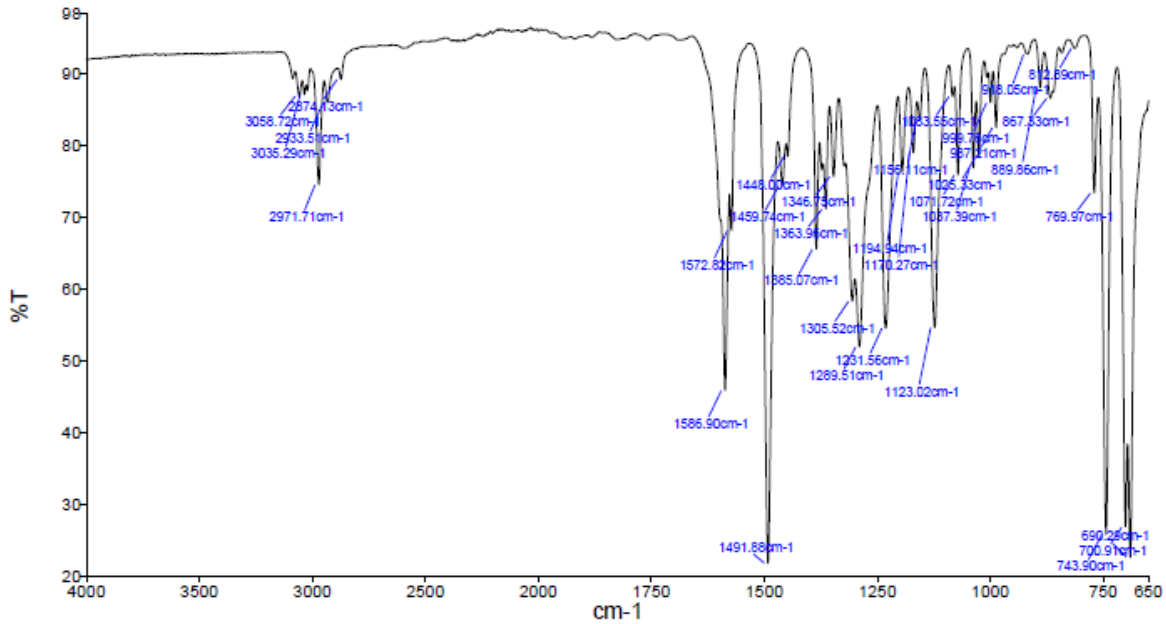
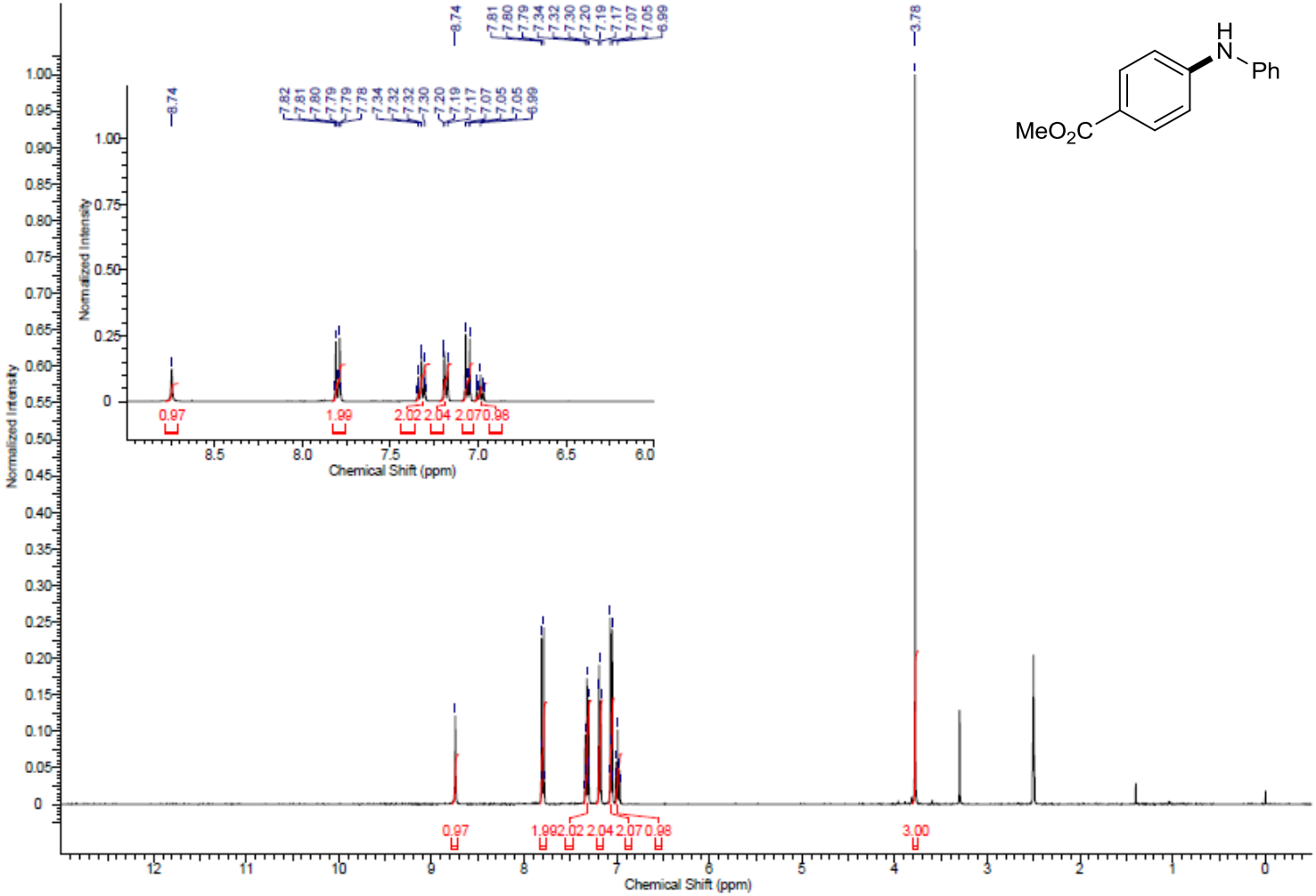


IR Spectra

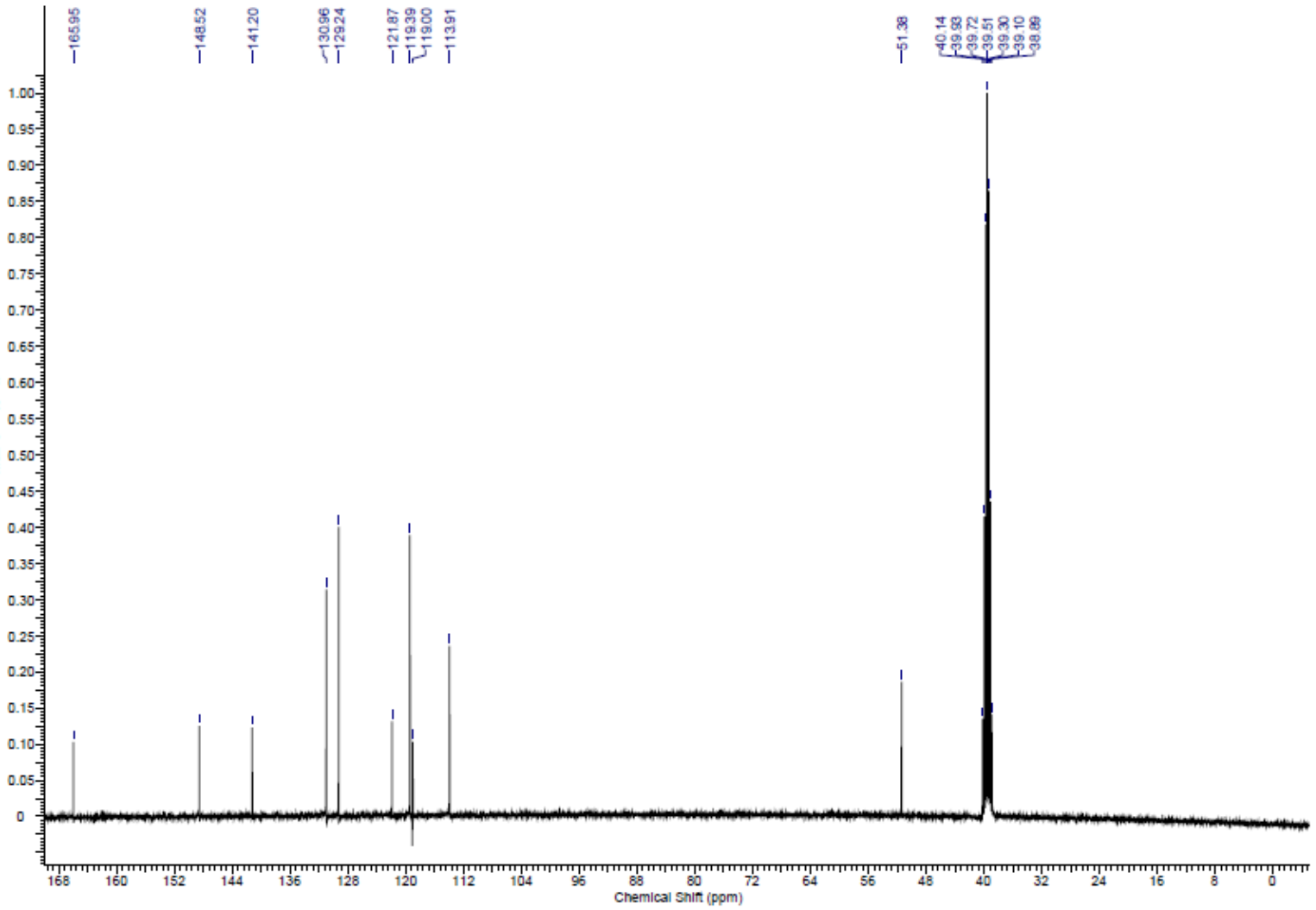


Methyl 4-(phenylamino)benzoate (3o).

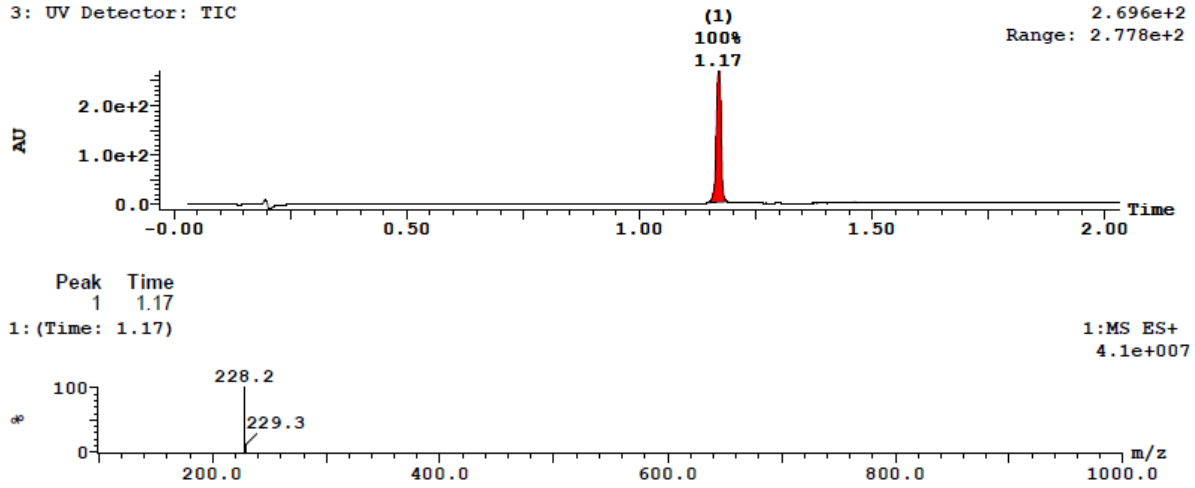
^{1}H NMR SPECTRA



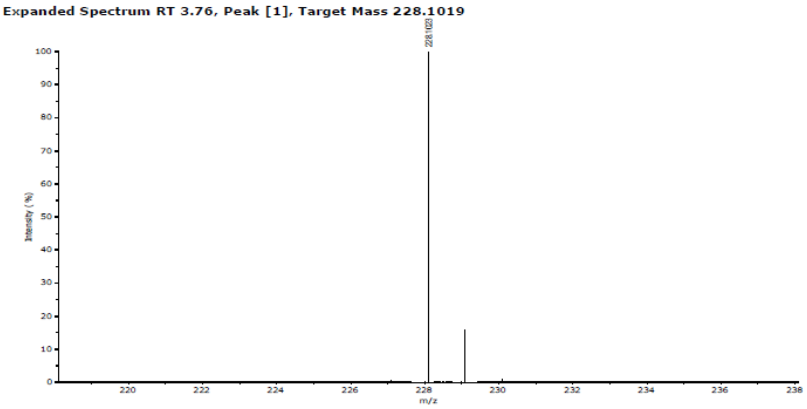
^{13}C NMR SPECTRA



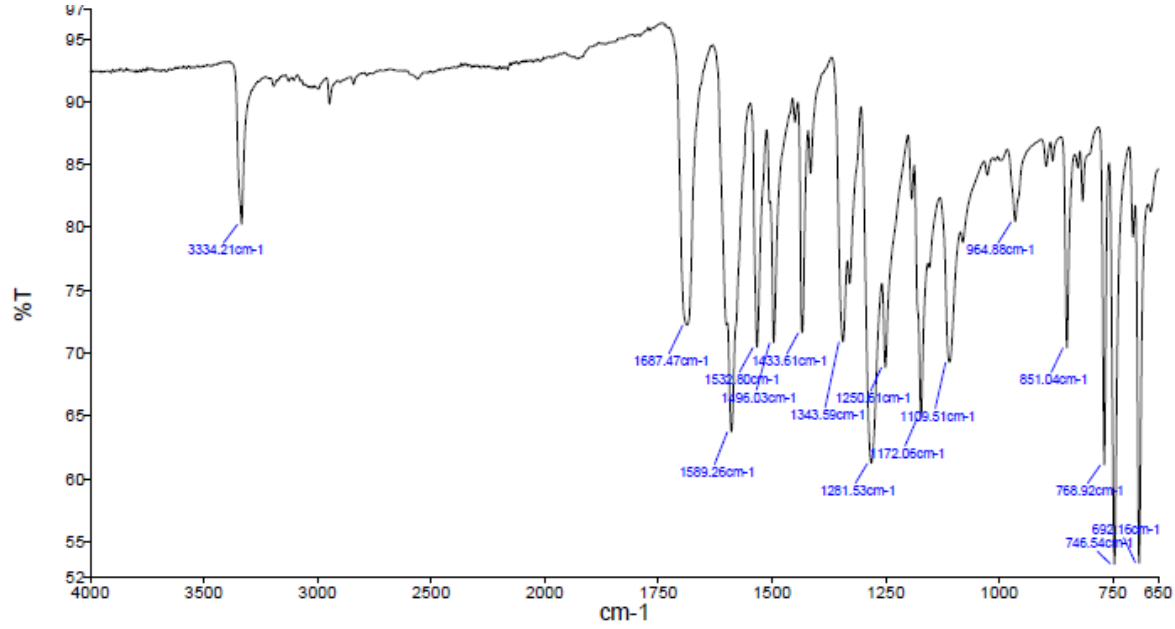
LCMS



HRMS

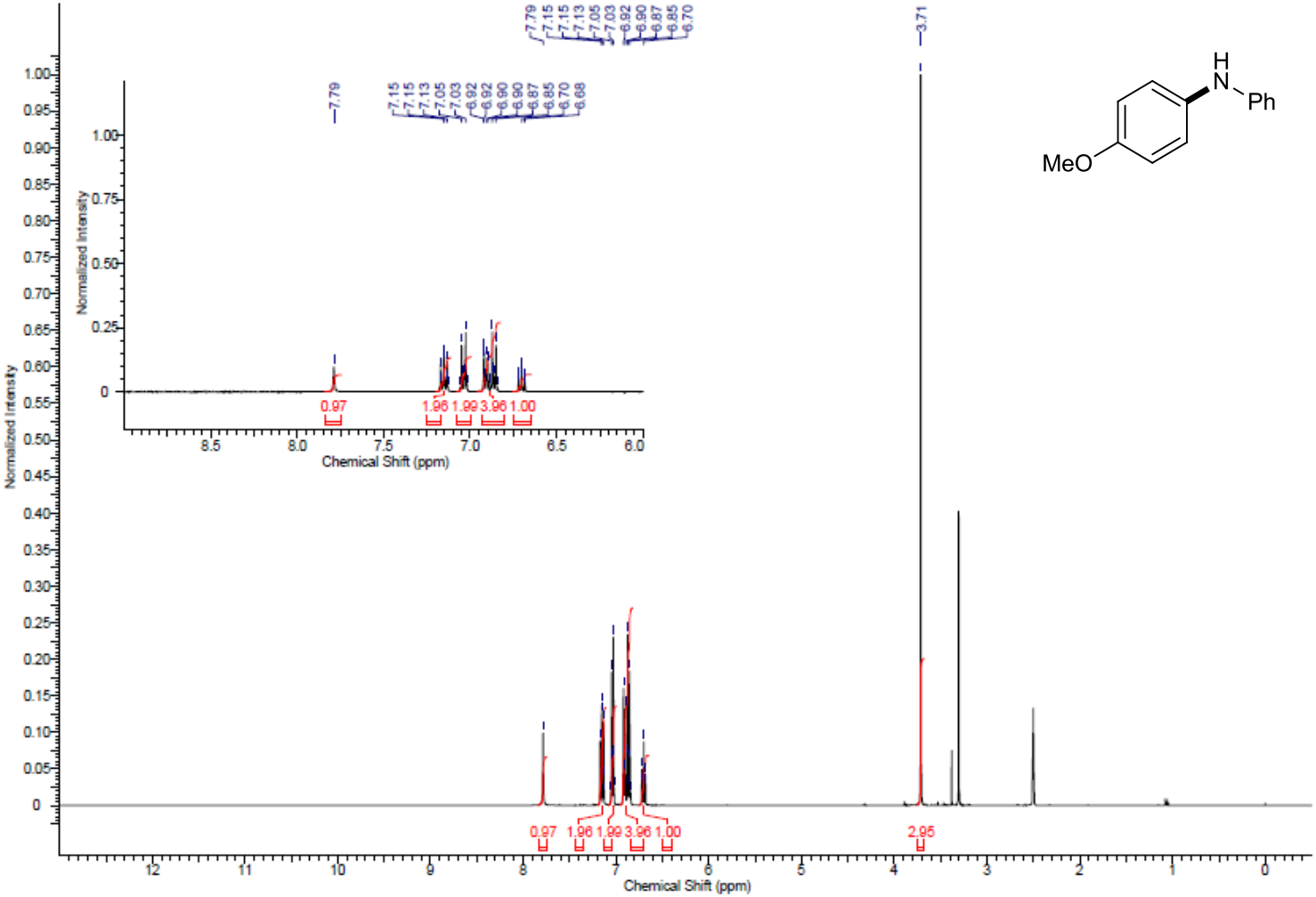


IR SPECTRA

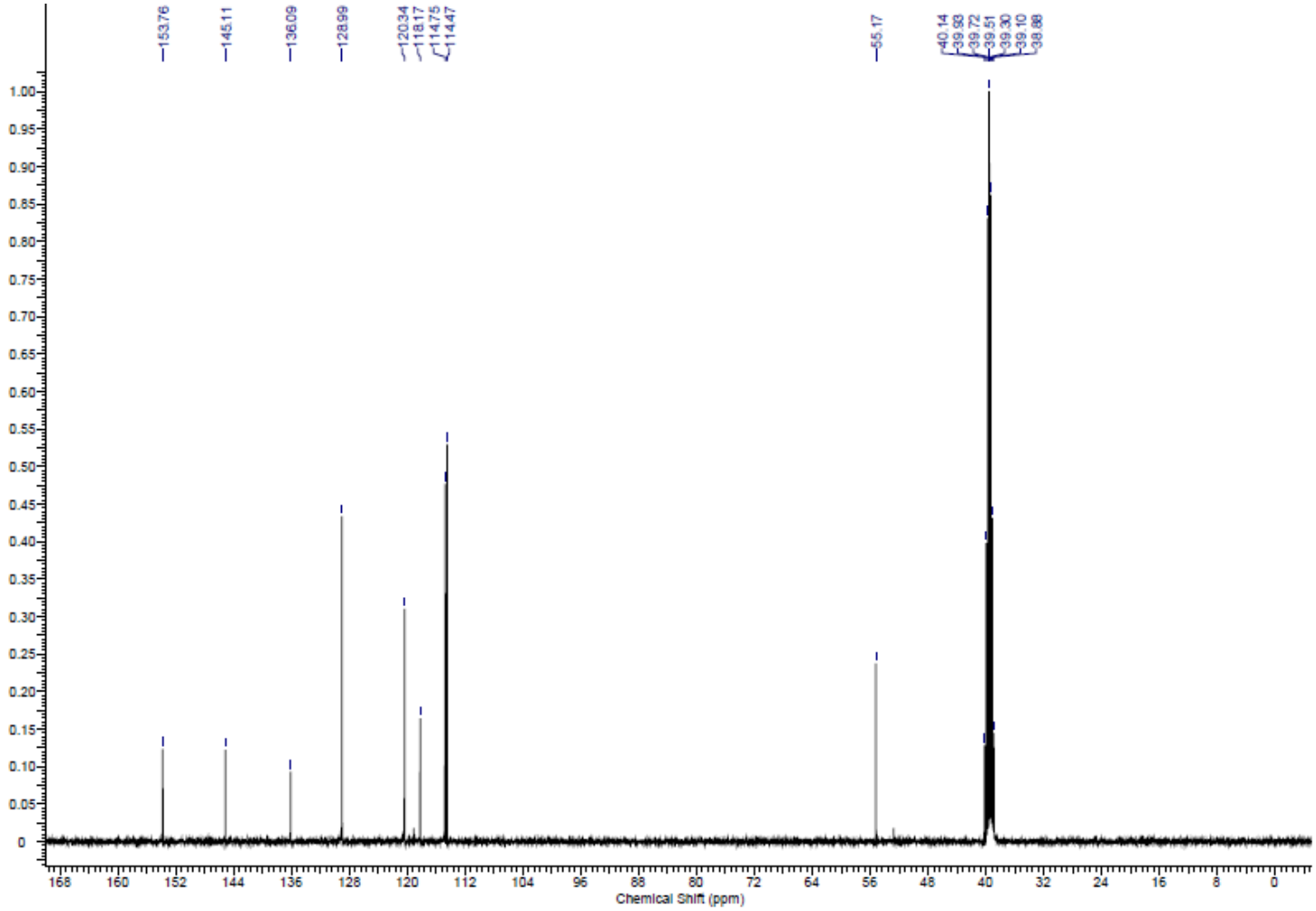


4-Methoxy-*N*-phenylaniline (3p).

^{1}H NMR Spectra



^{13}C NMR Spectra



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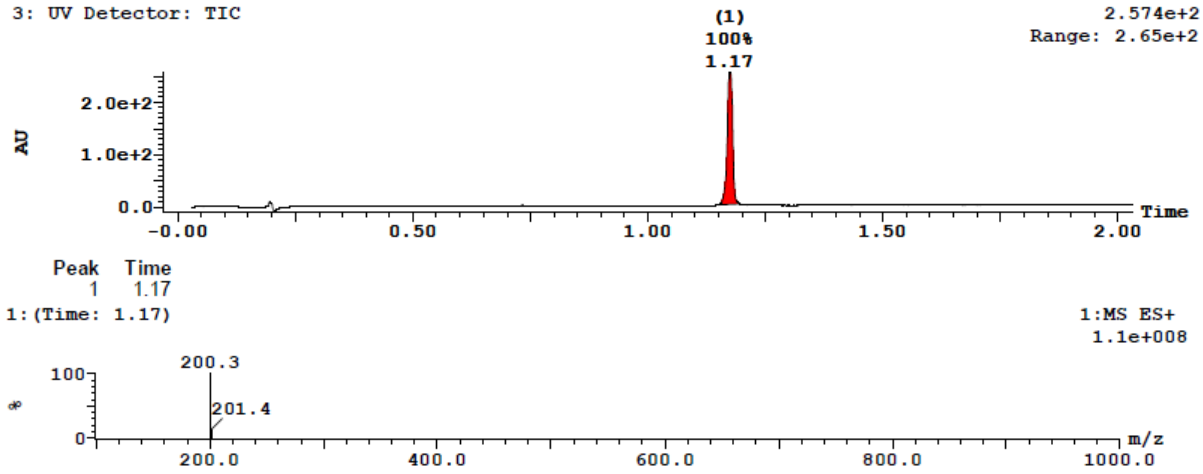

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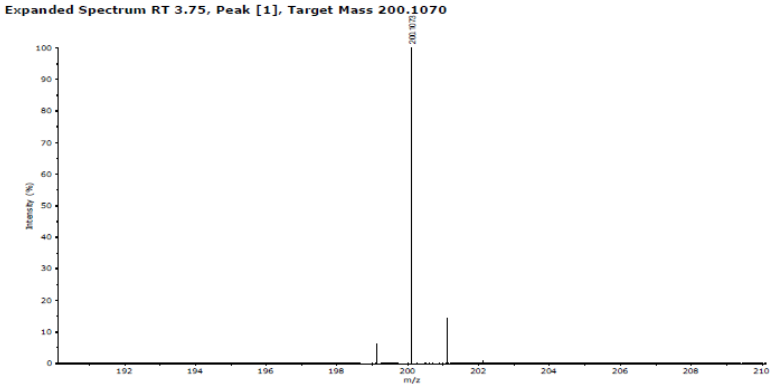
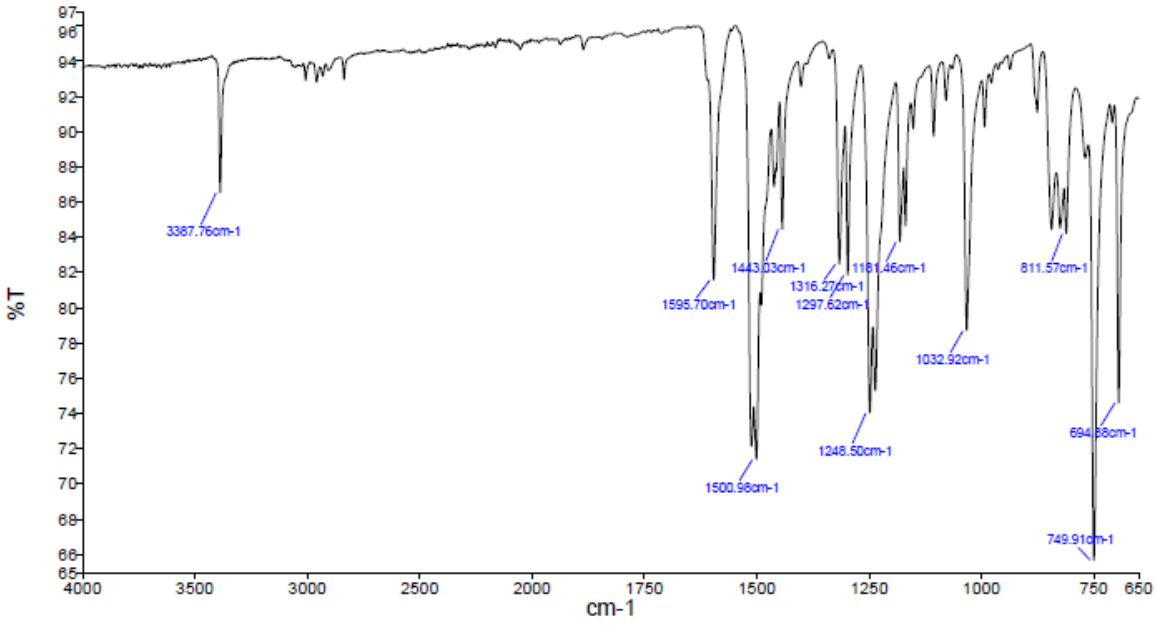
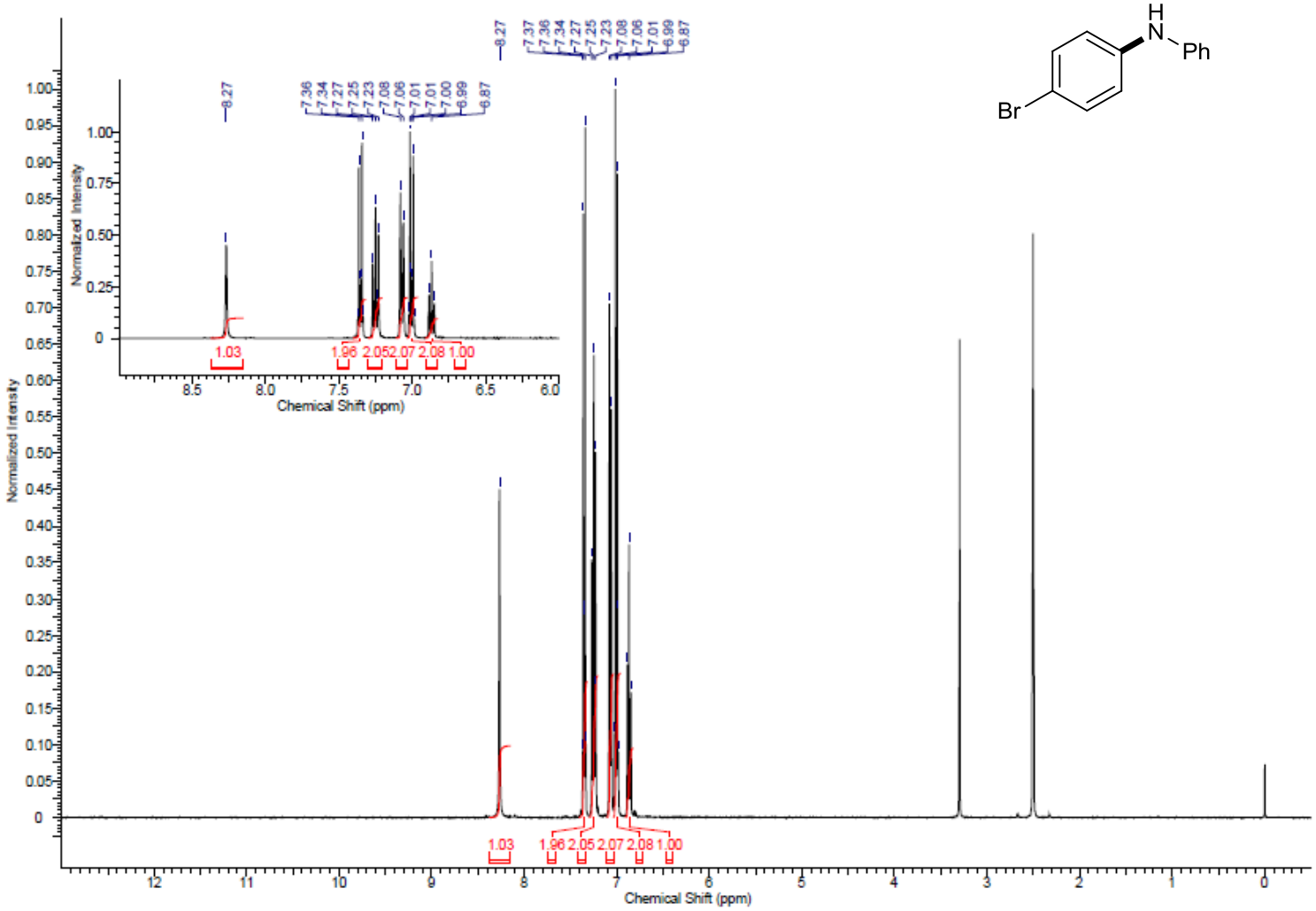


IR Spectra

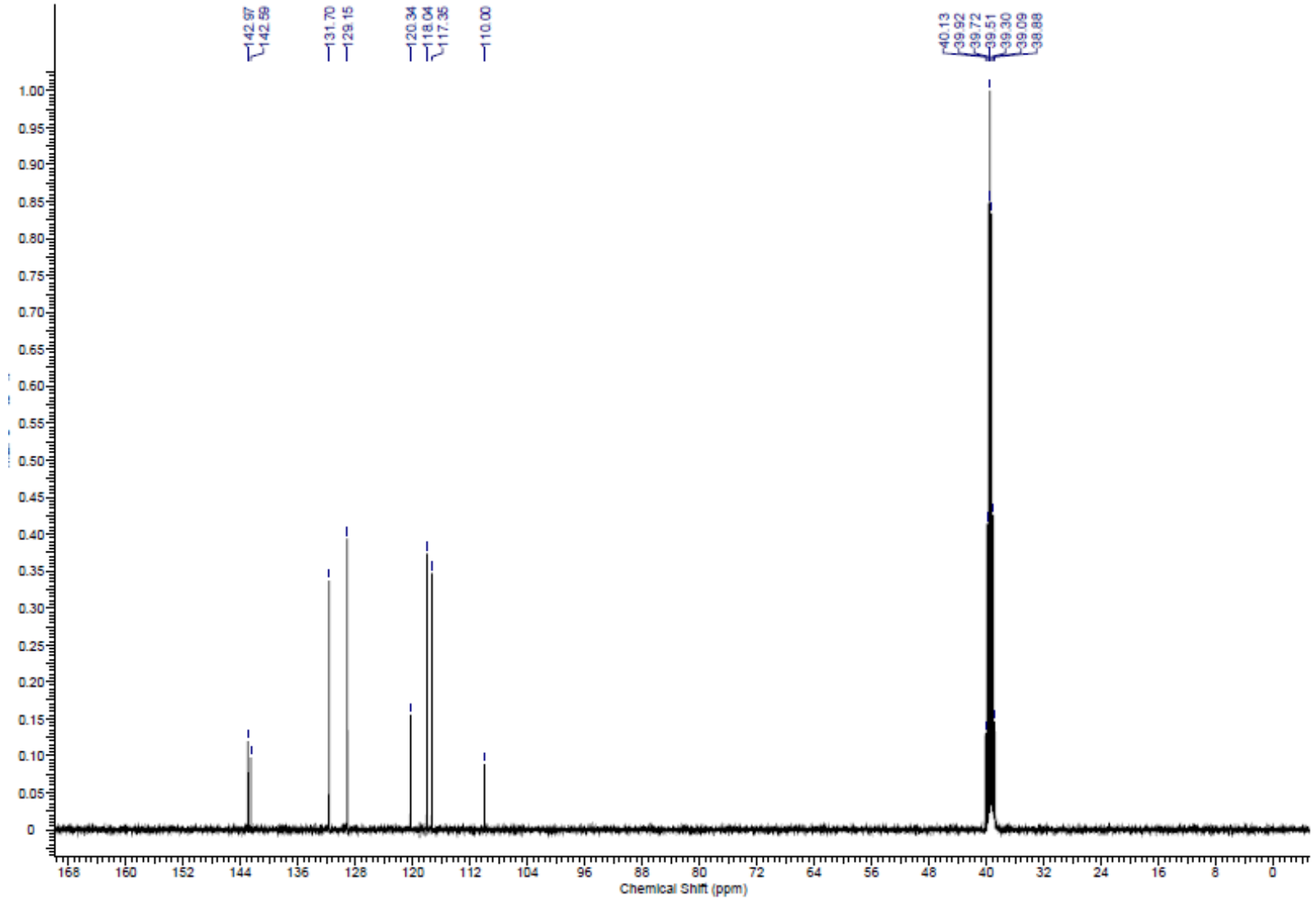


4-Bromo-*N*-phenylaniline (3q).

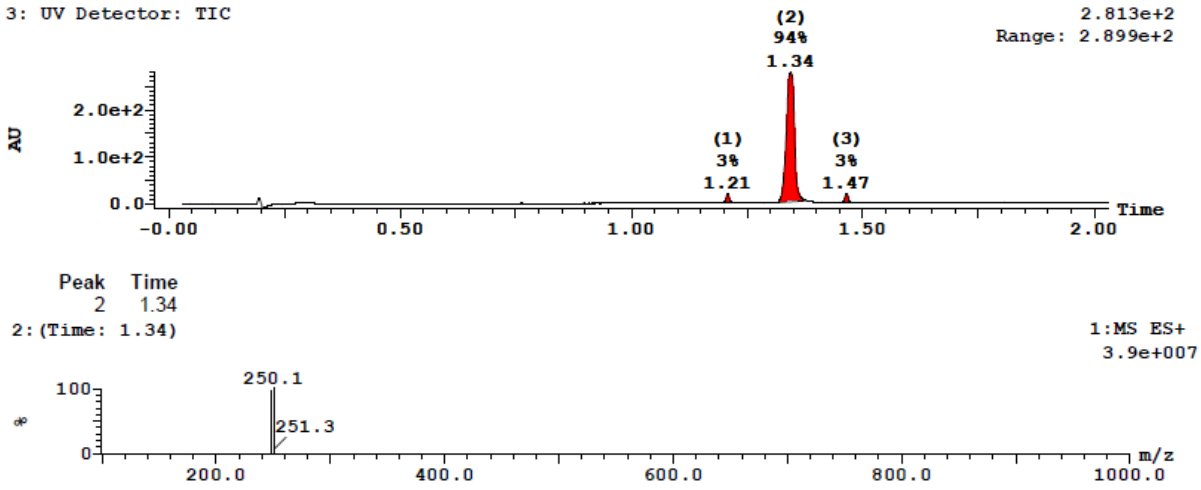
^{1}H NMR Spectra



^{13}C NMR Spectra



LCMS



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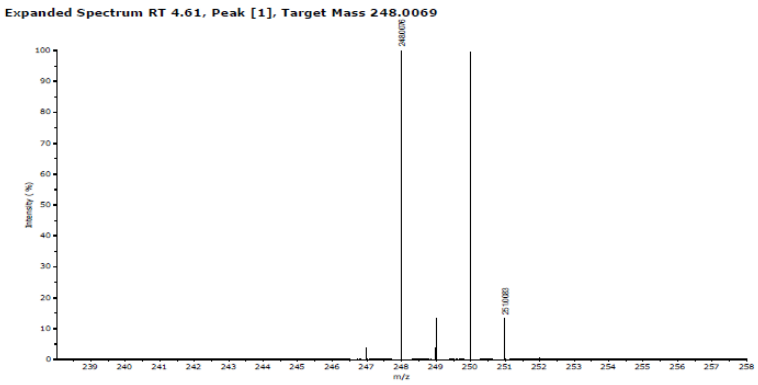
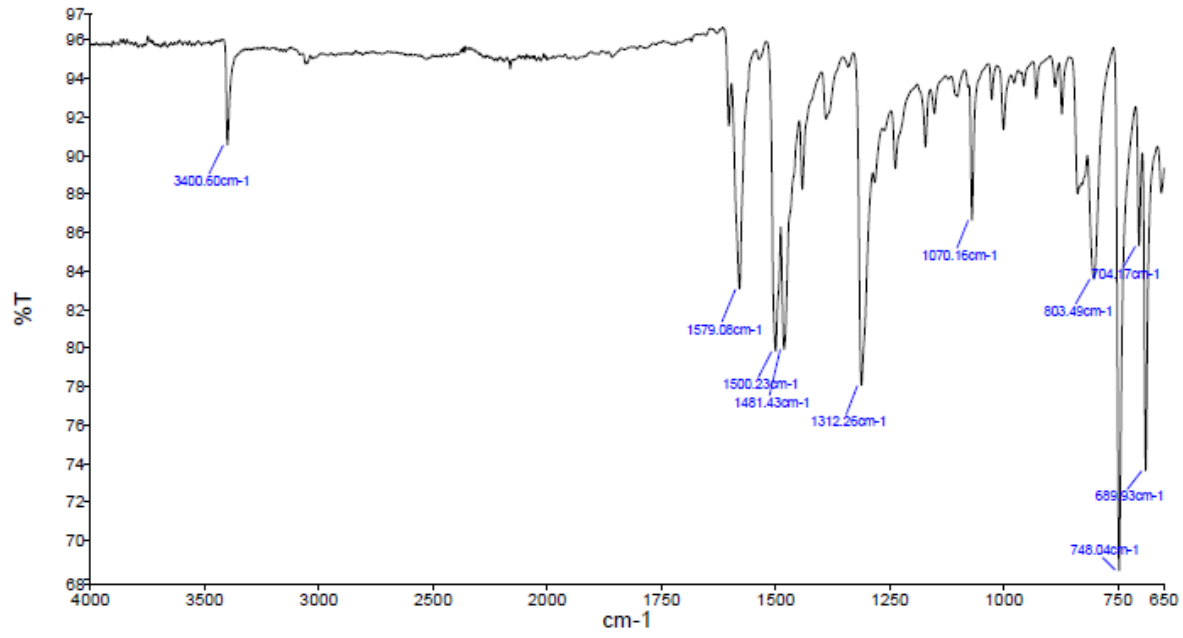
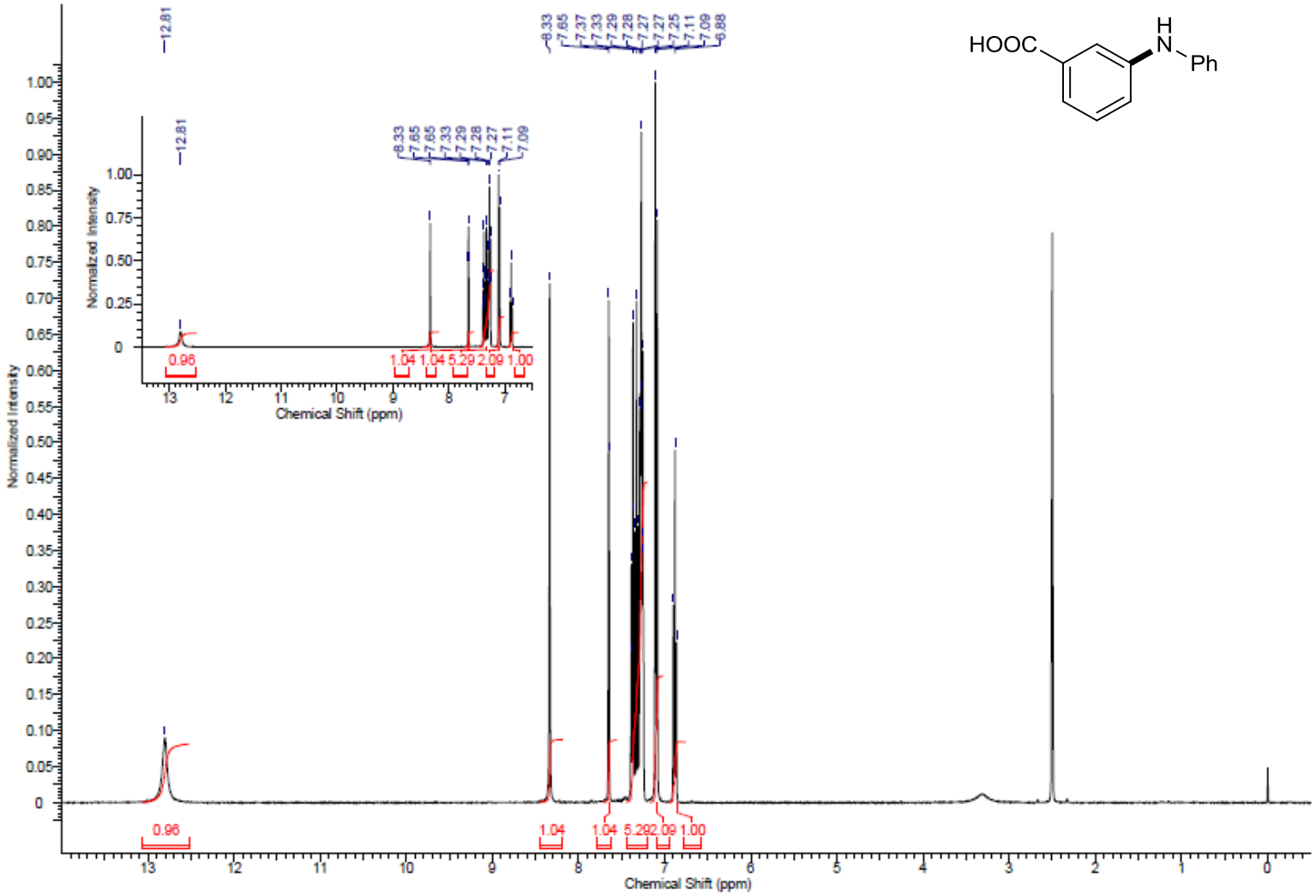


IR Spectra

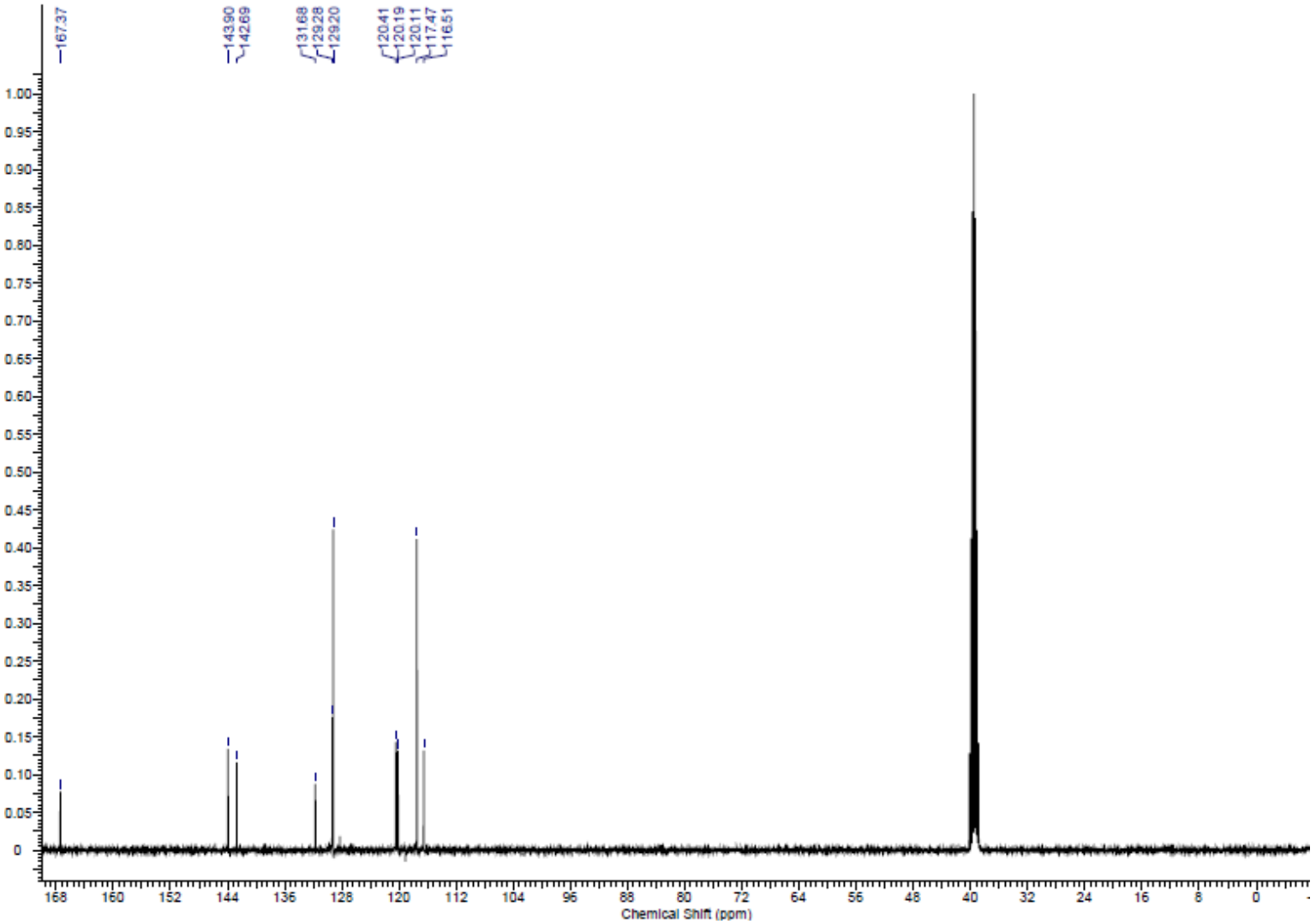


3-(Phenylamino)benzoic acid (3r).

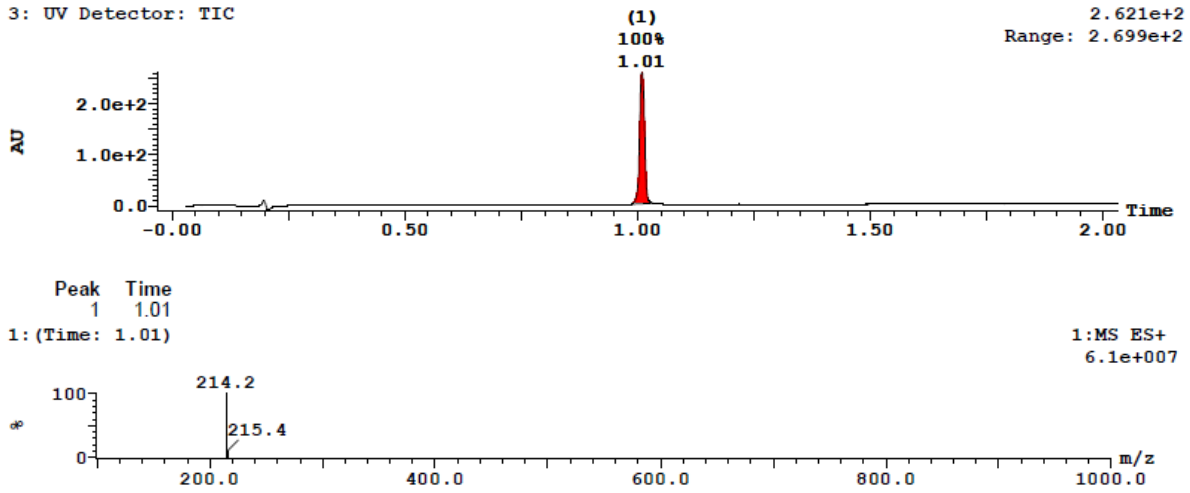
^{1}H NMR Spectra



^{13}C NMR Spectra



LCMS



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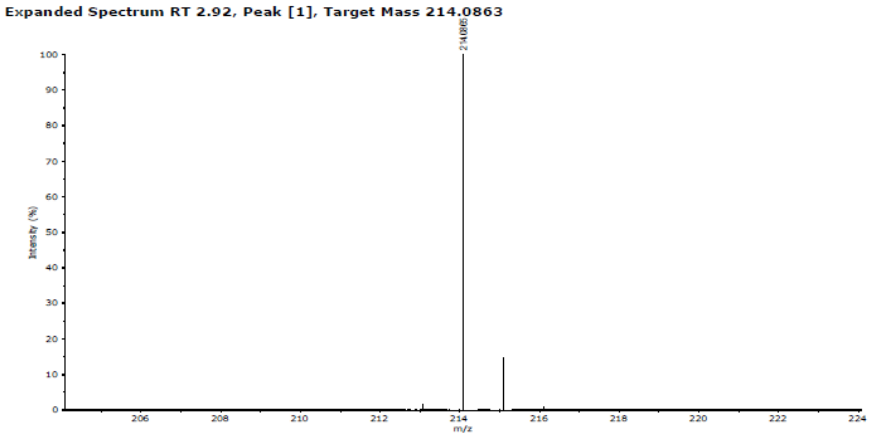
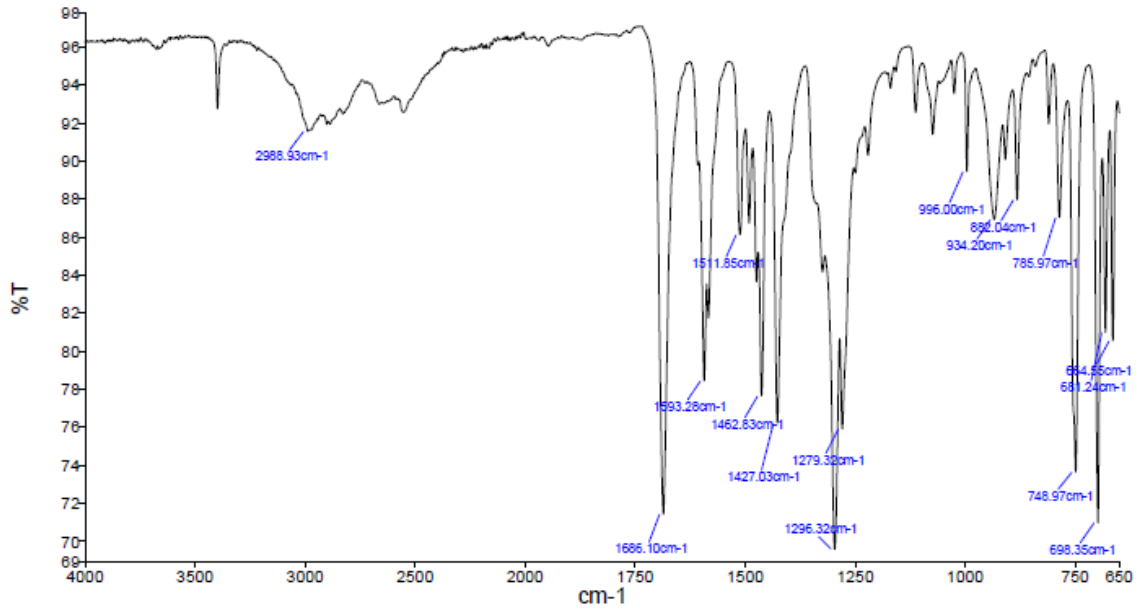
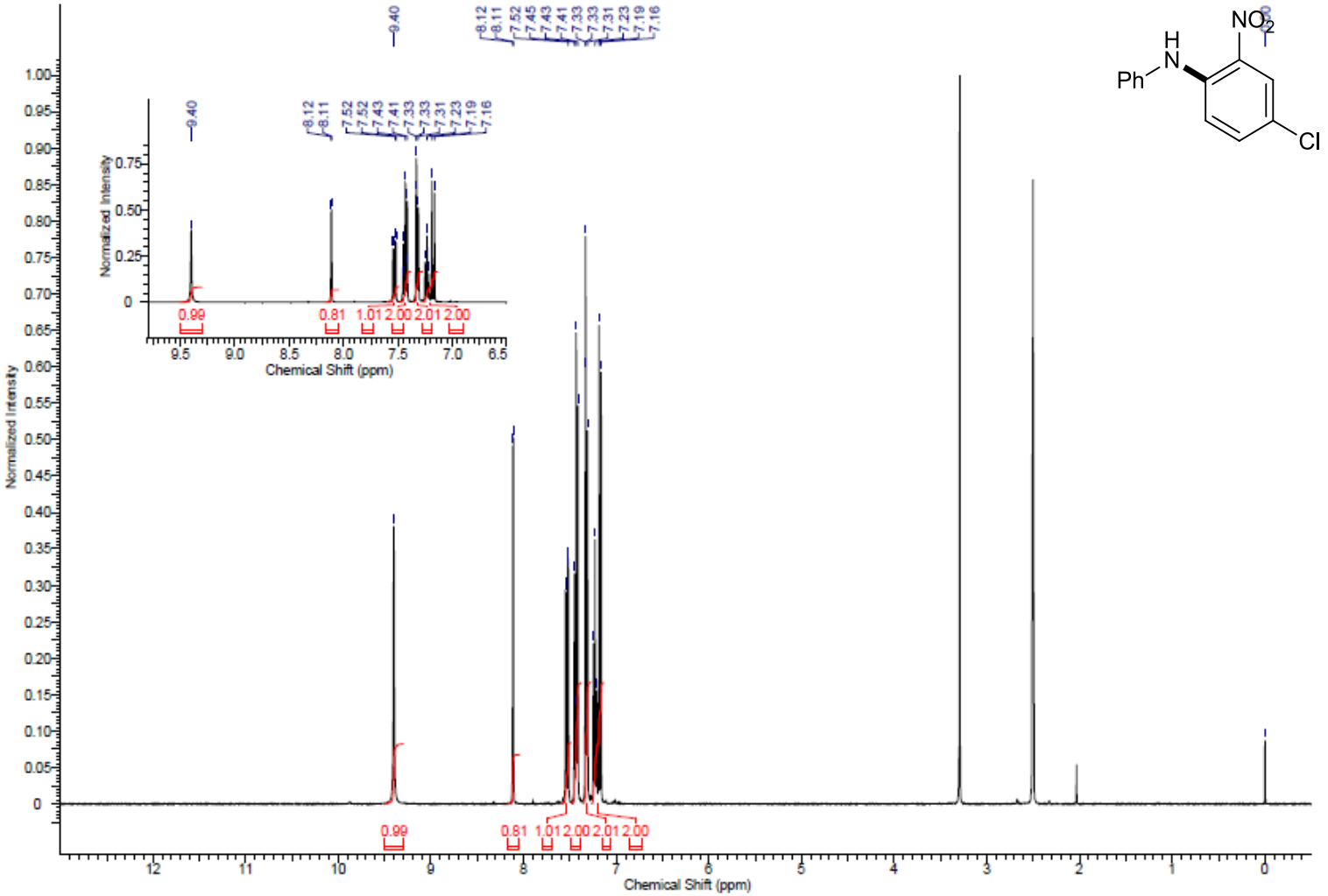


IR Spectra

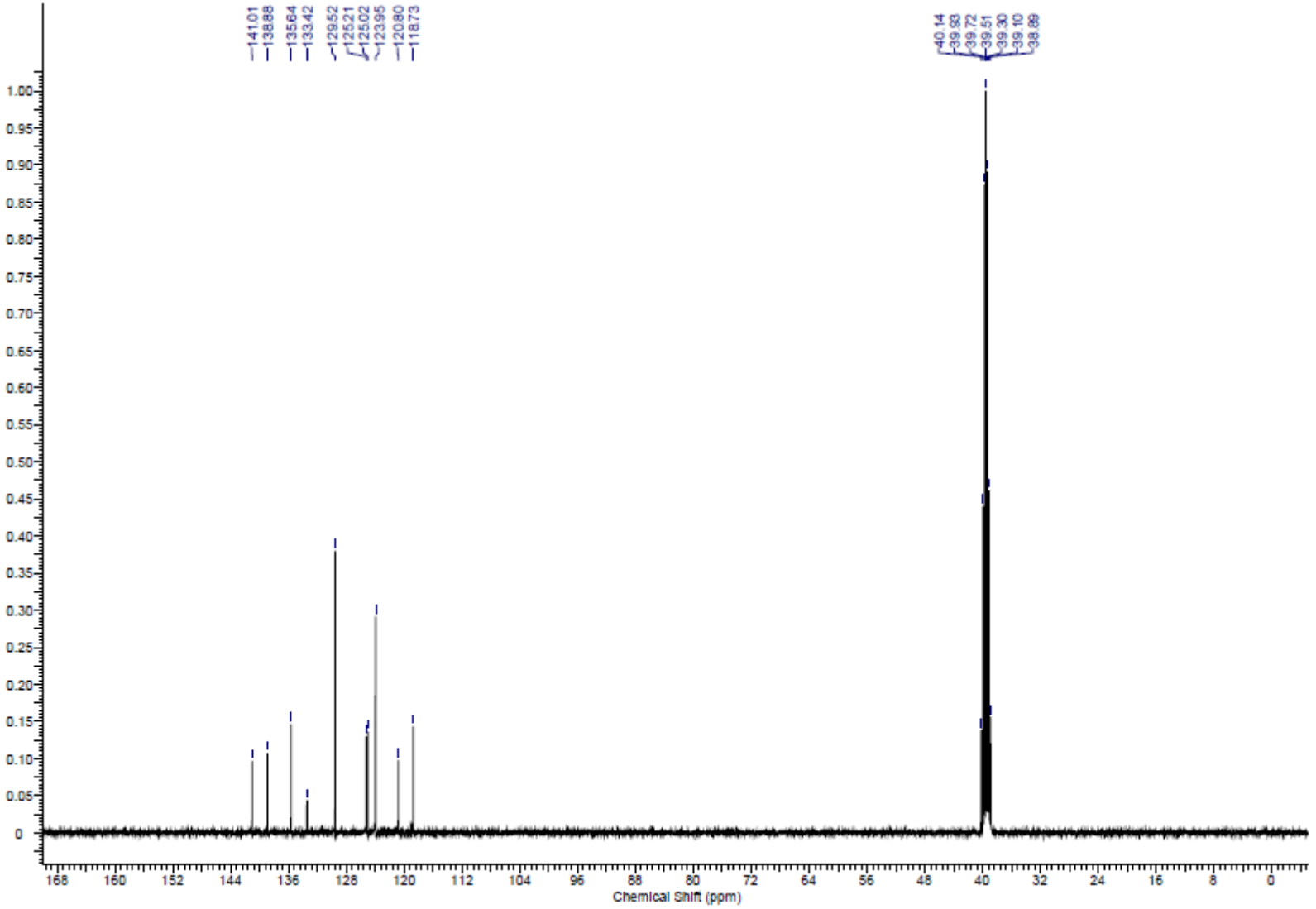


4-Chloro-2-nitro-*N*-phenylaniline (3s).

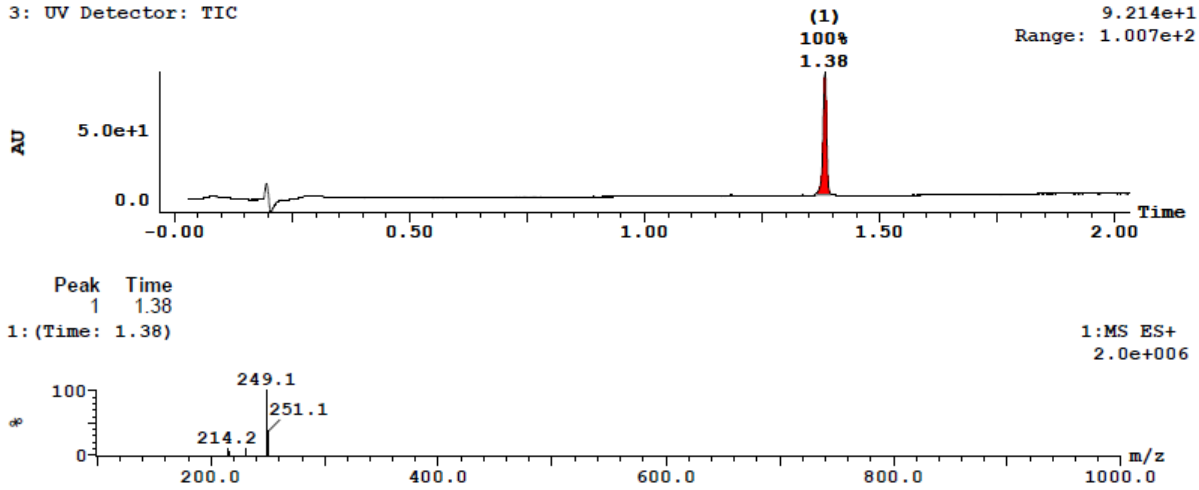
^{1}H NMR Spectra



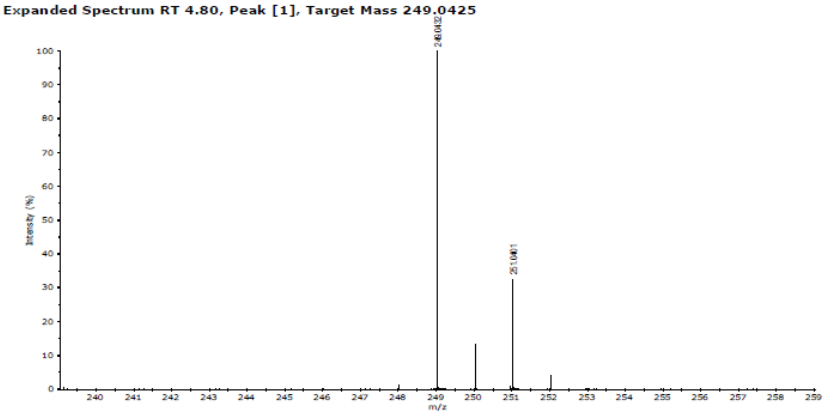
^{13}C NMR Spectra



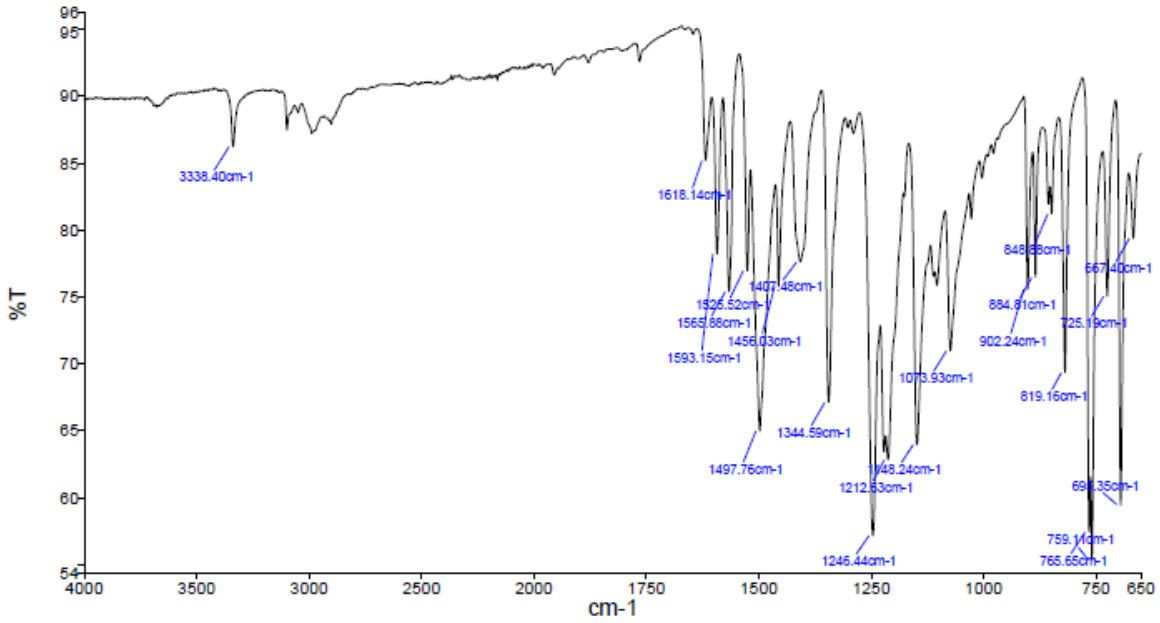
LCMS



HRMS

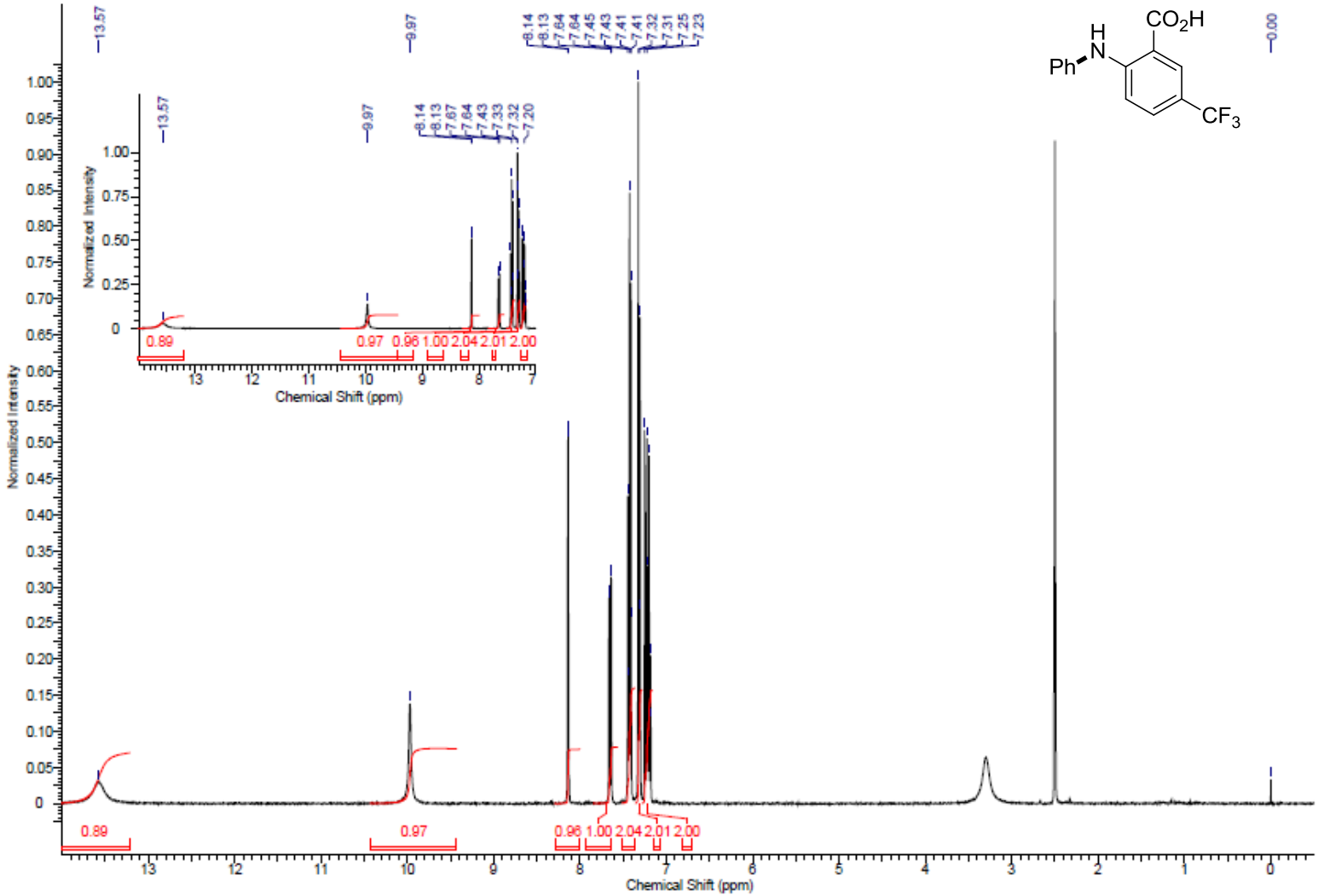


IR Spectra

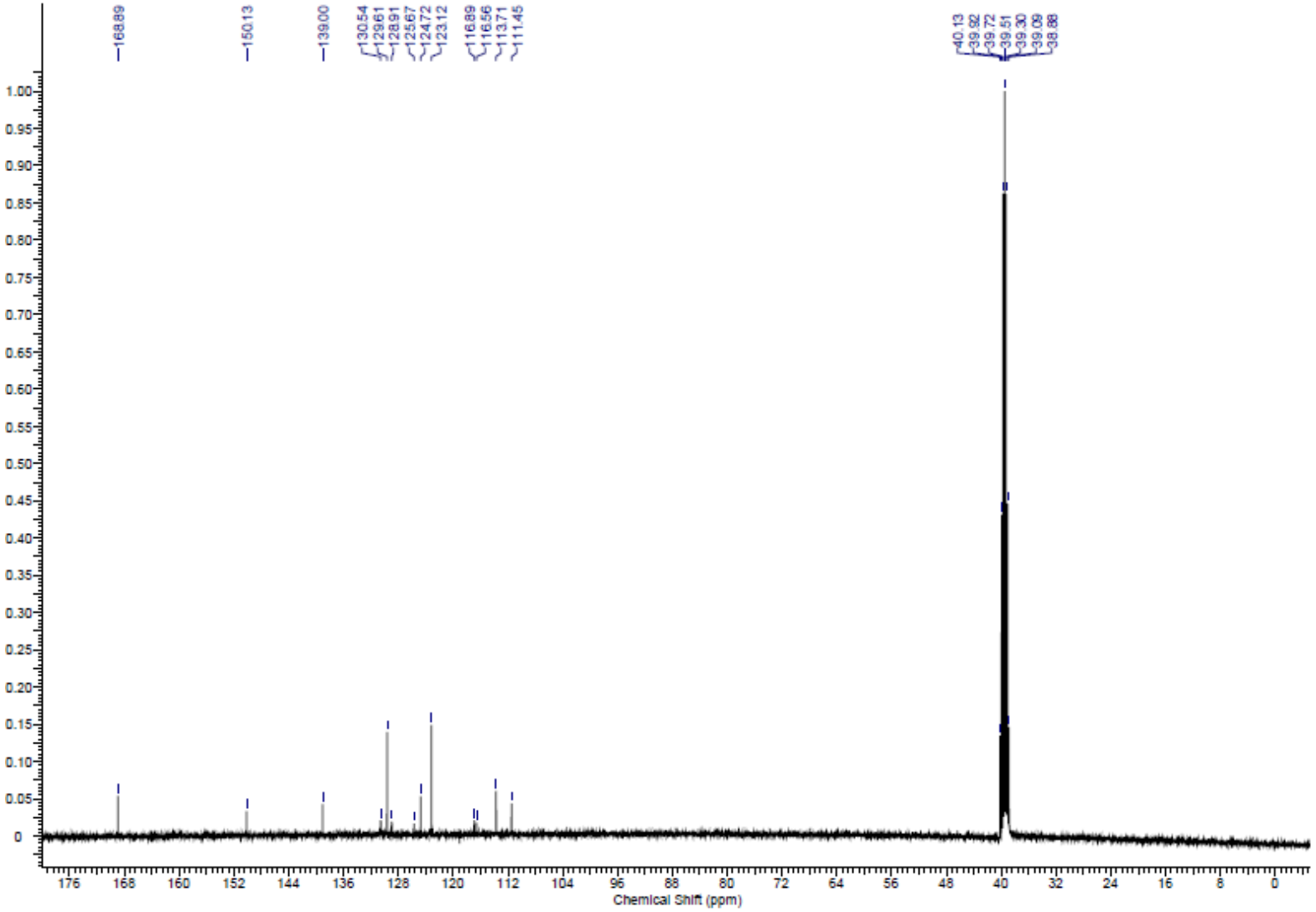


2-(Phenylamino)-5-(trifluoromethyl)benzoic acid (3t).

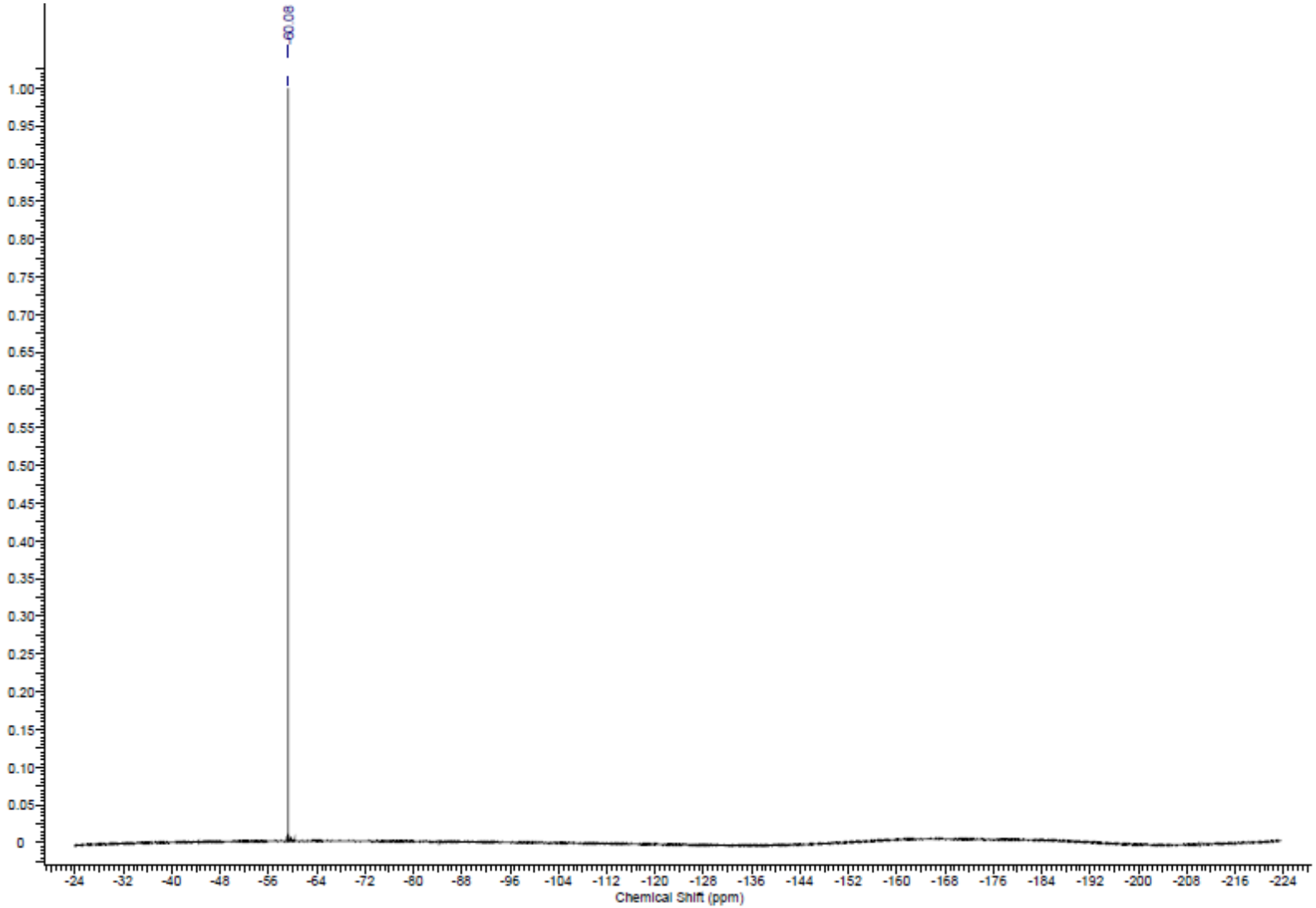
^{1}H NMR Spectra



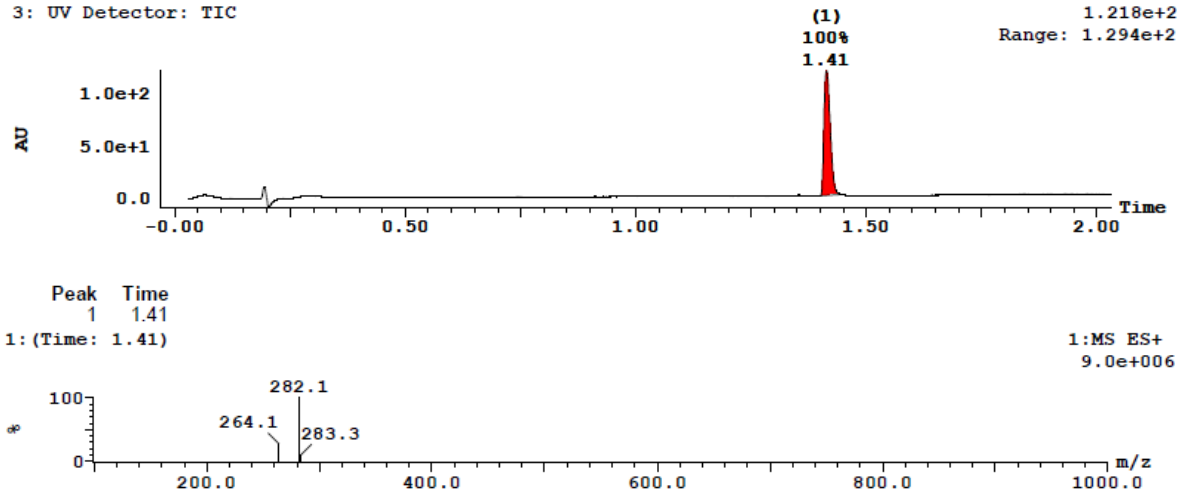
^{13}C NMR Spectra



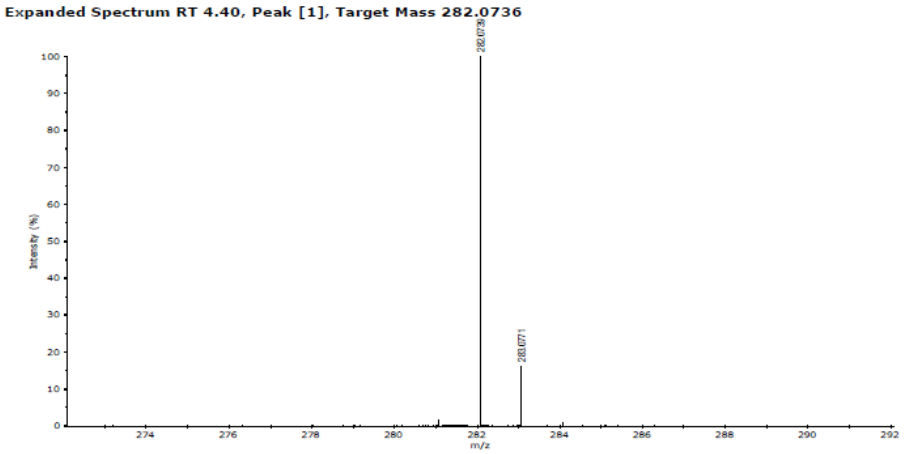
^{19}F NMR Spectra



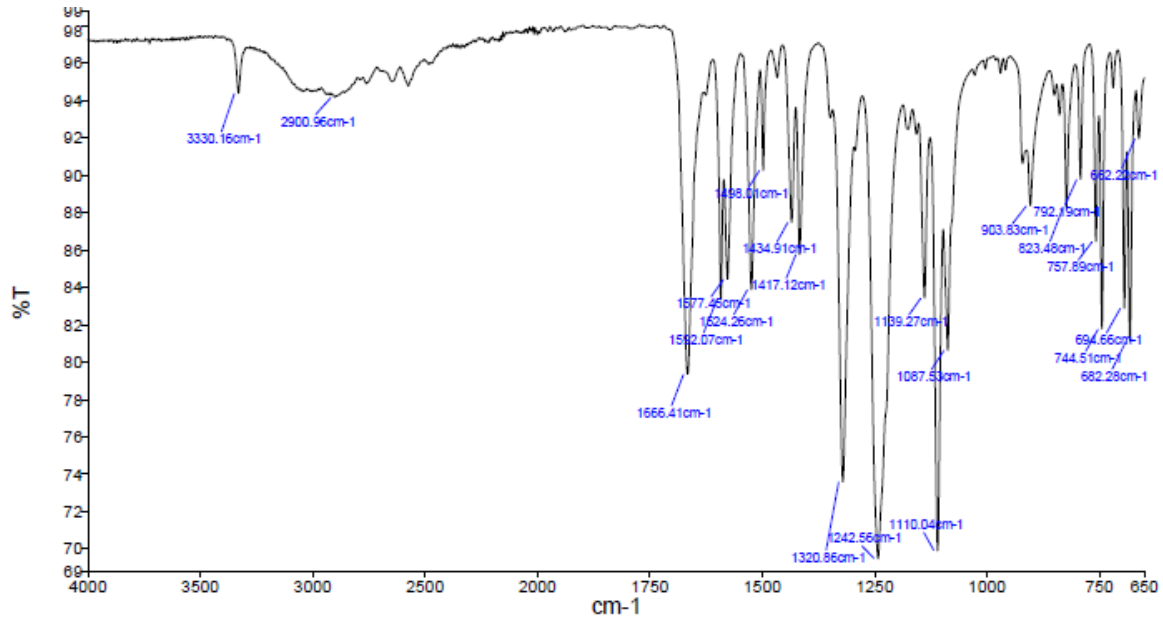
LCMS



HRMS

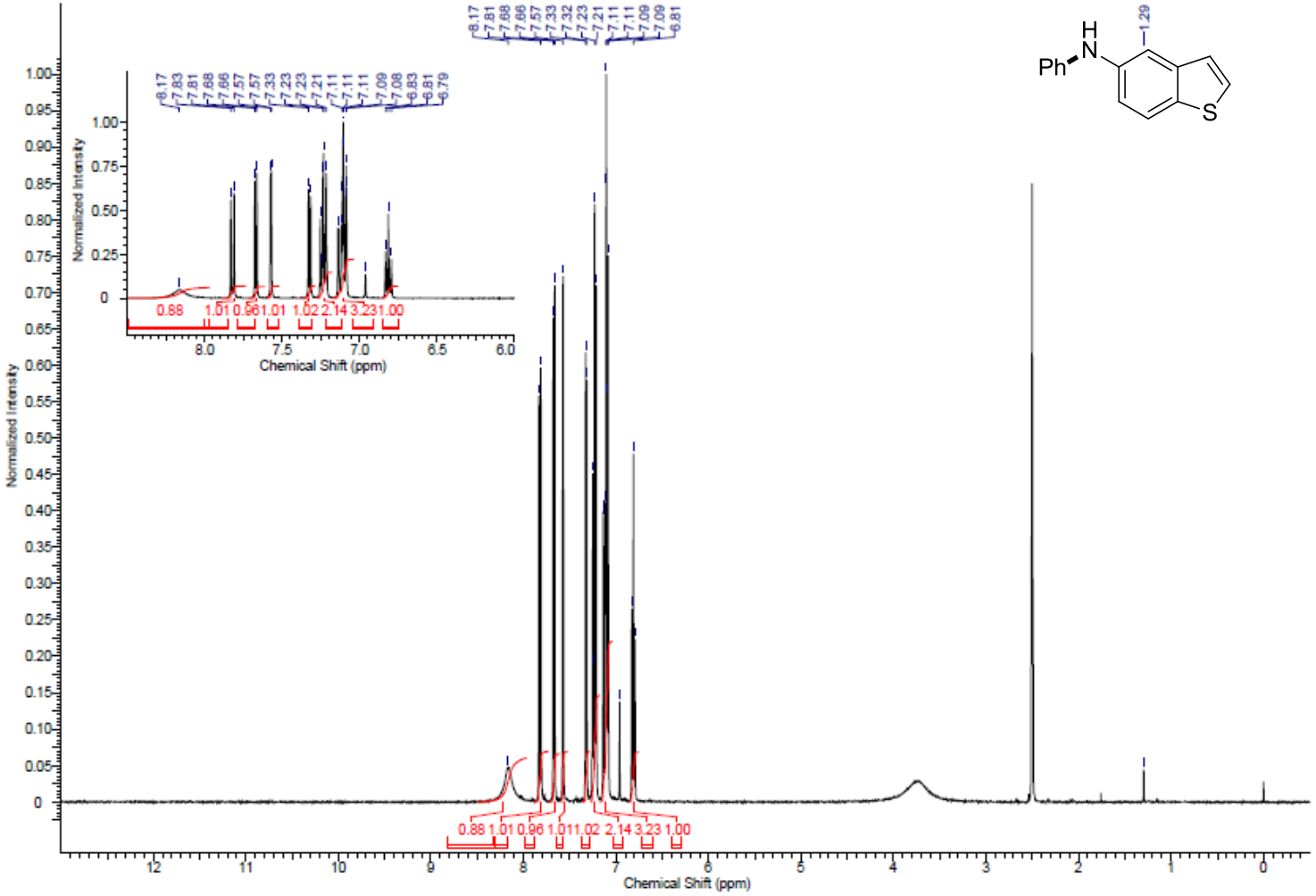


IR Spectra

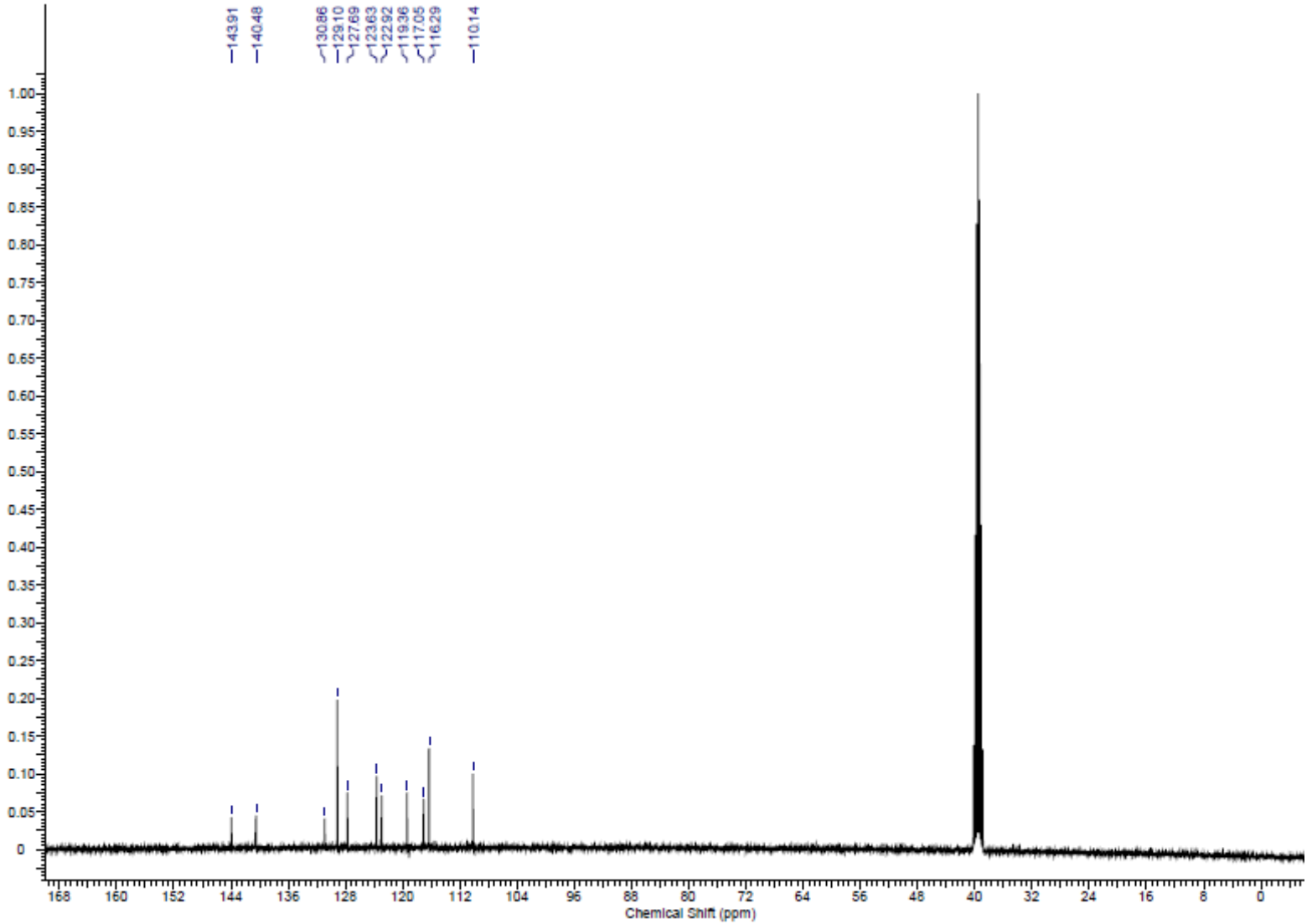


***N*-Phenylbenzo[b]thiophen-5-amine (3u).**

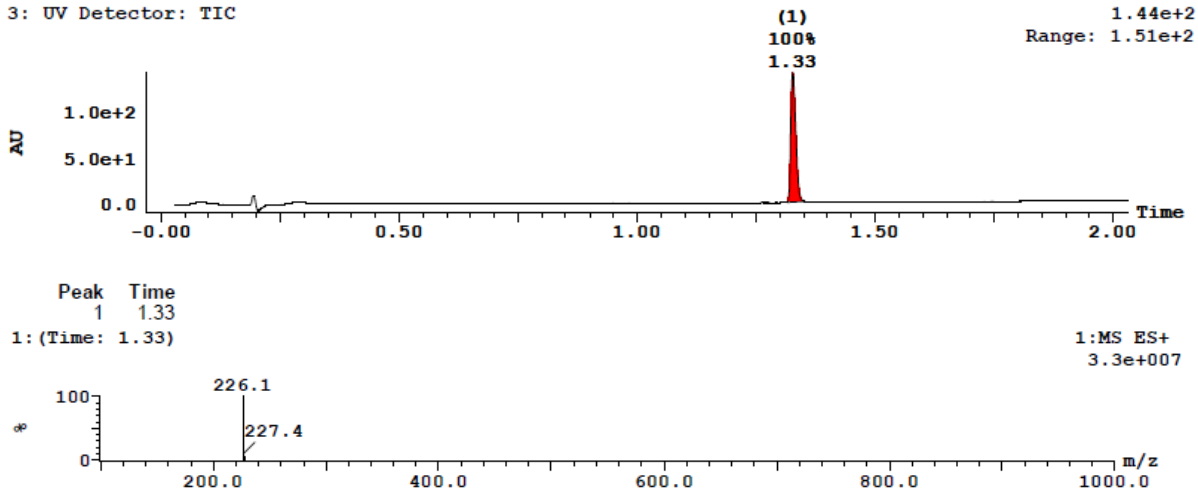
^{1}H NMR Spectra



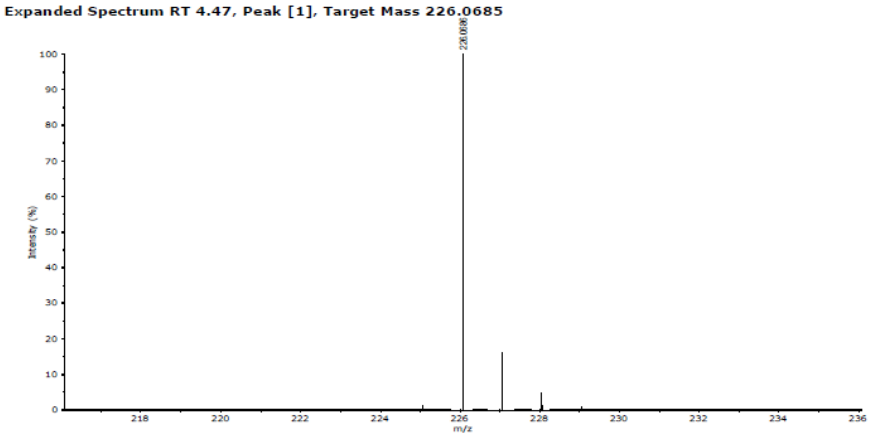
^{13}C NMR Spectra



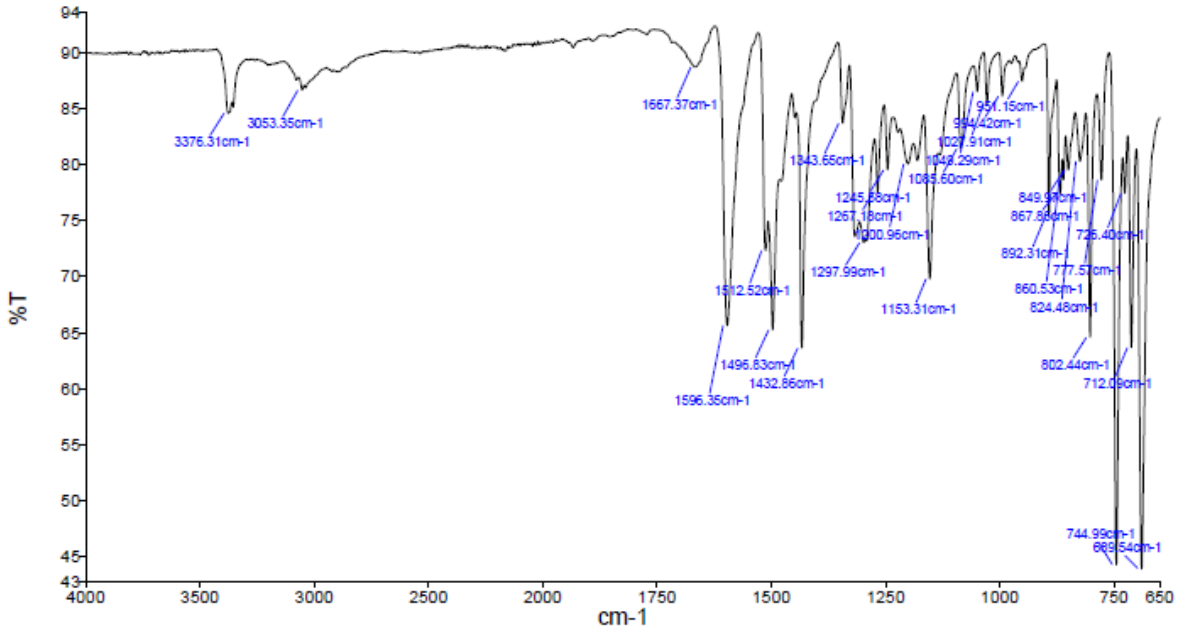
LCMS



HRMS

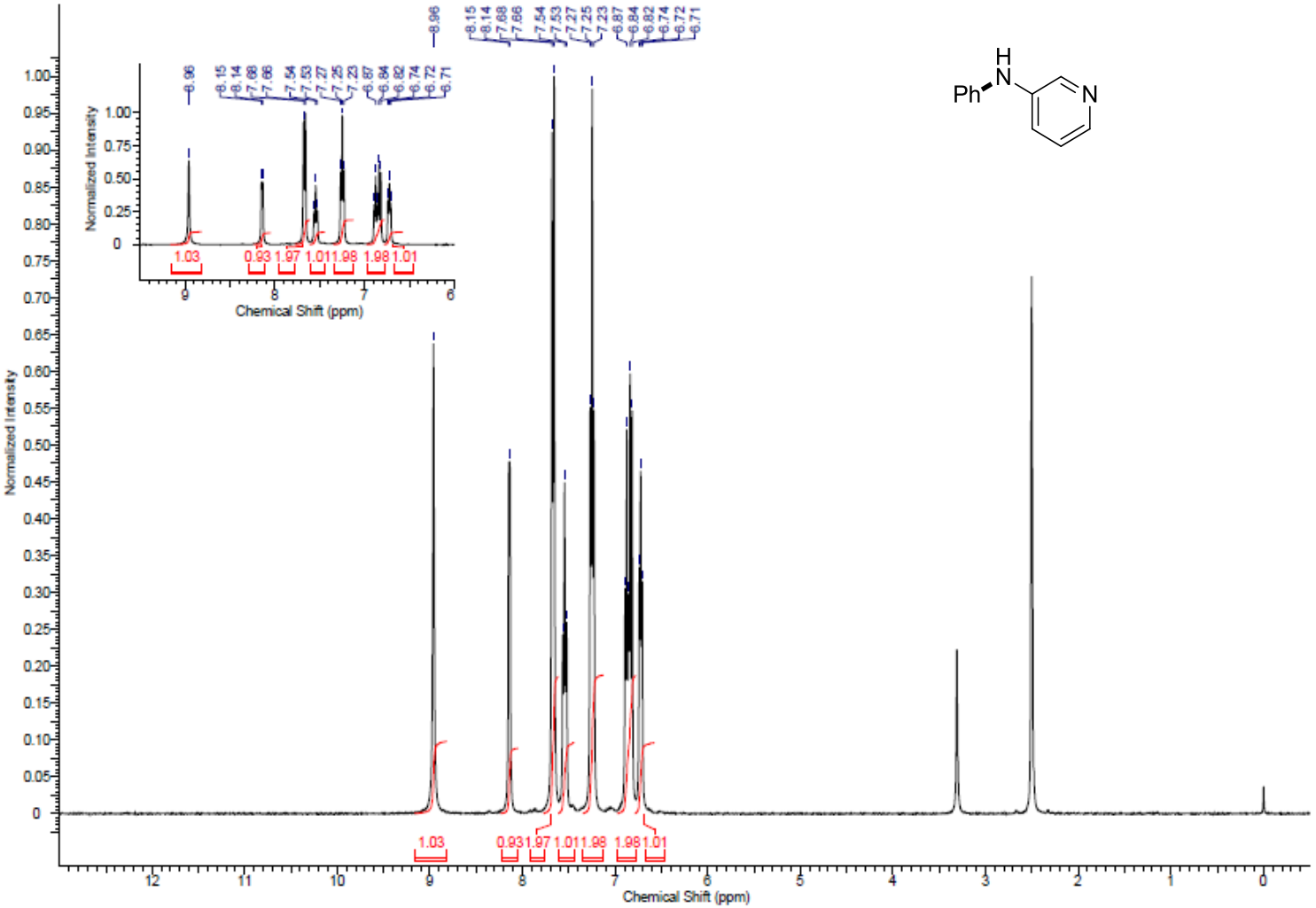


IR Spectra

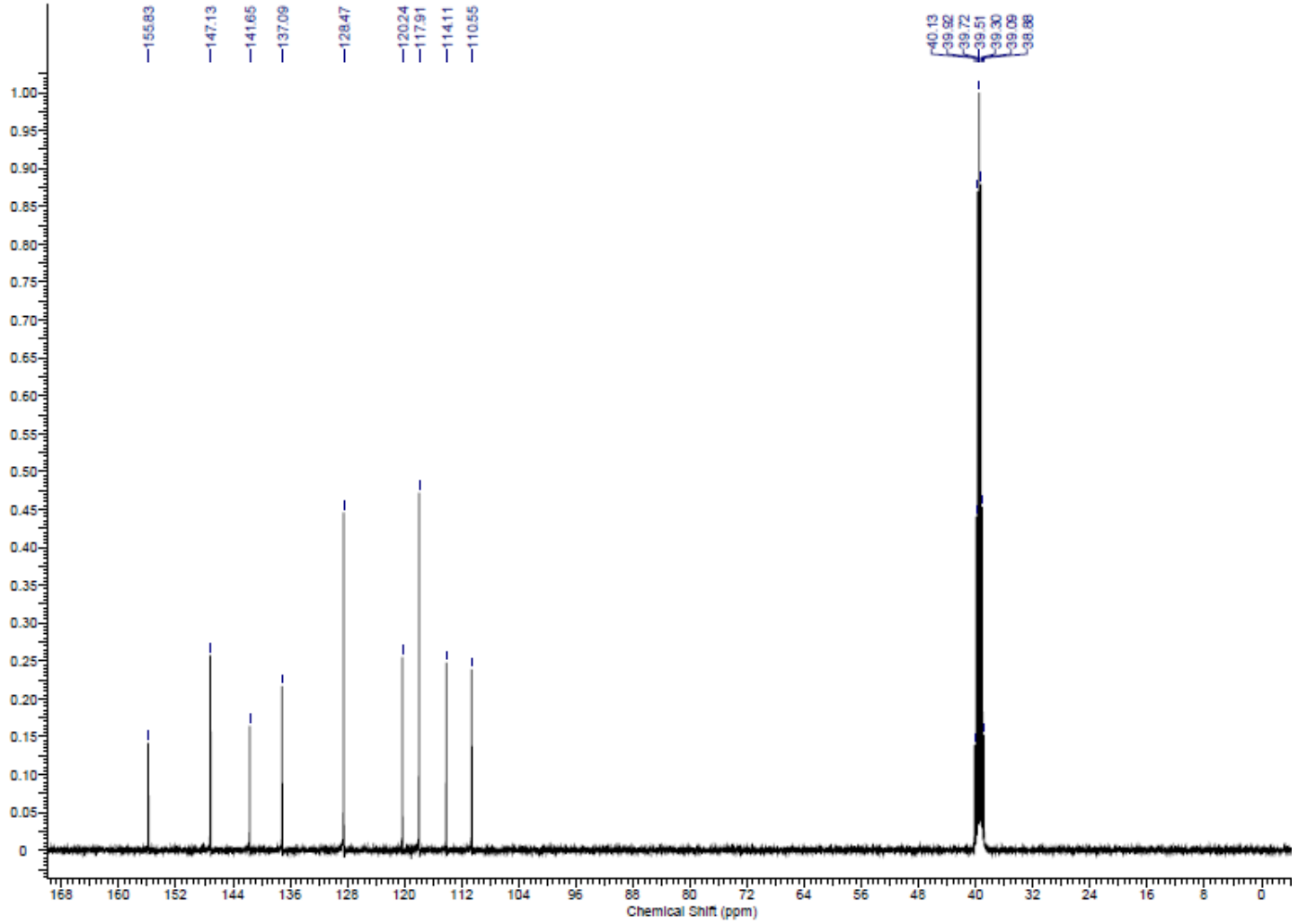


***N*-Phenylpyridin-3-amine (3v).**

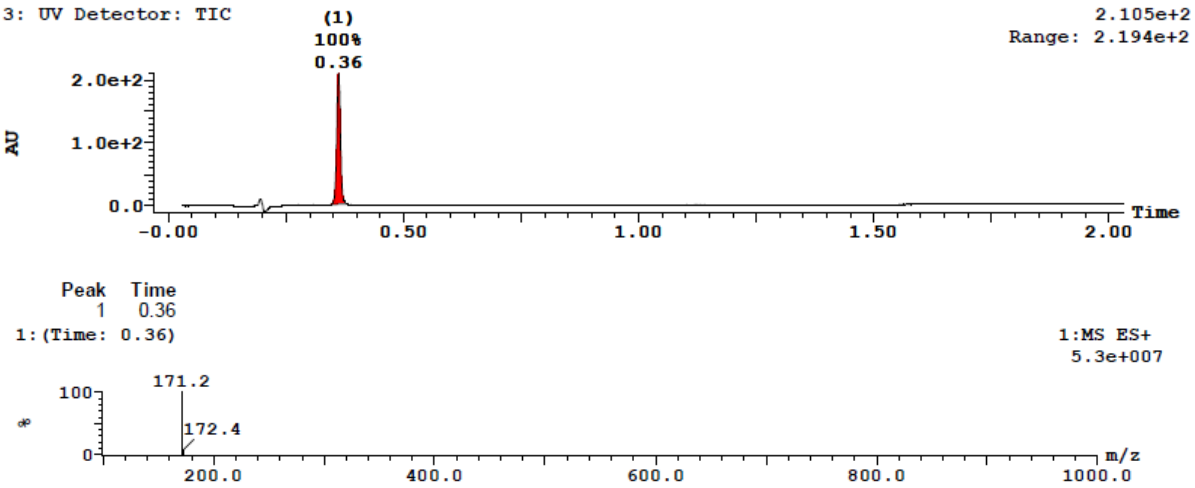
^{1}H NMR Spectra



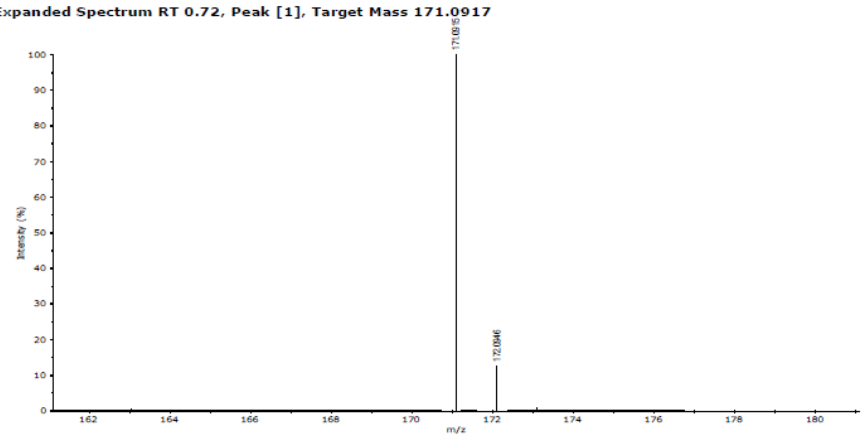
^{13}C NMR Spectra



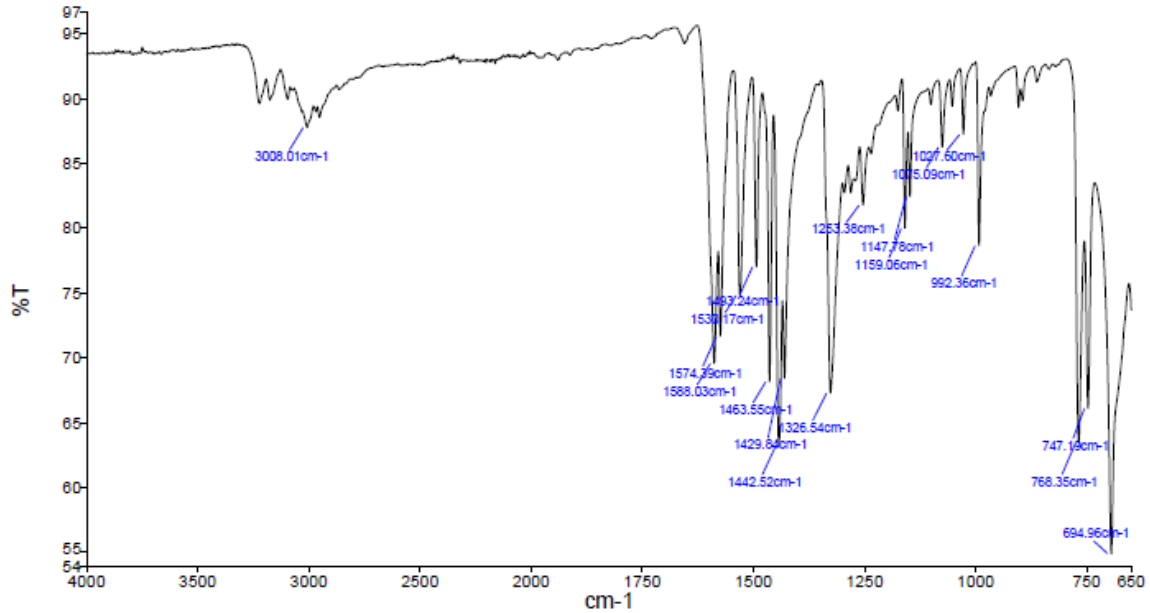
LCMS



HRMS

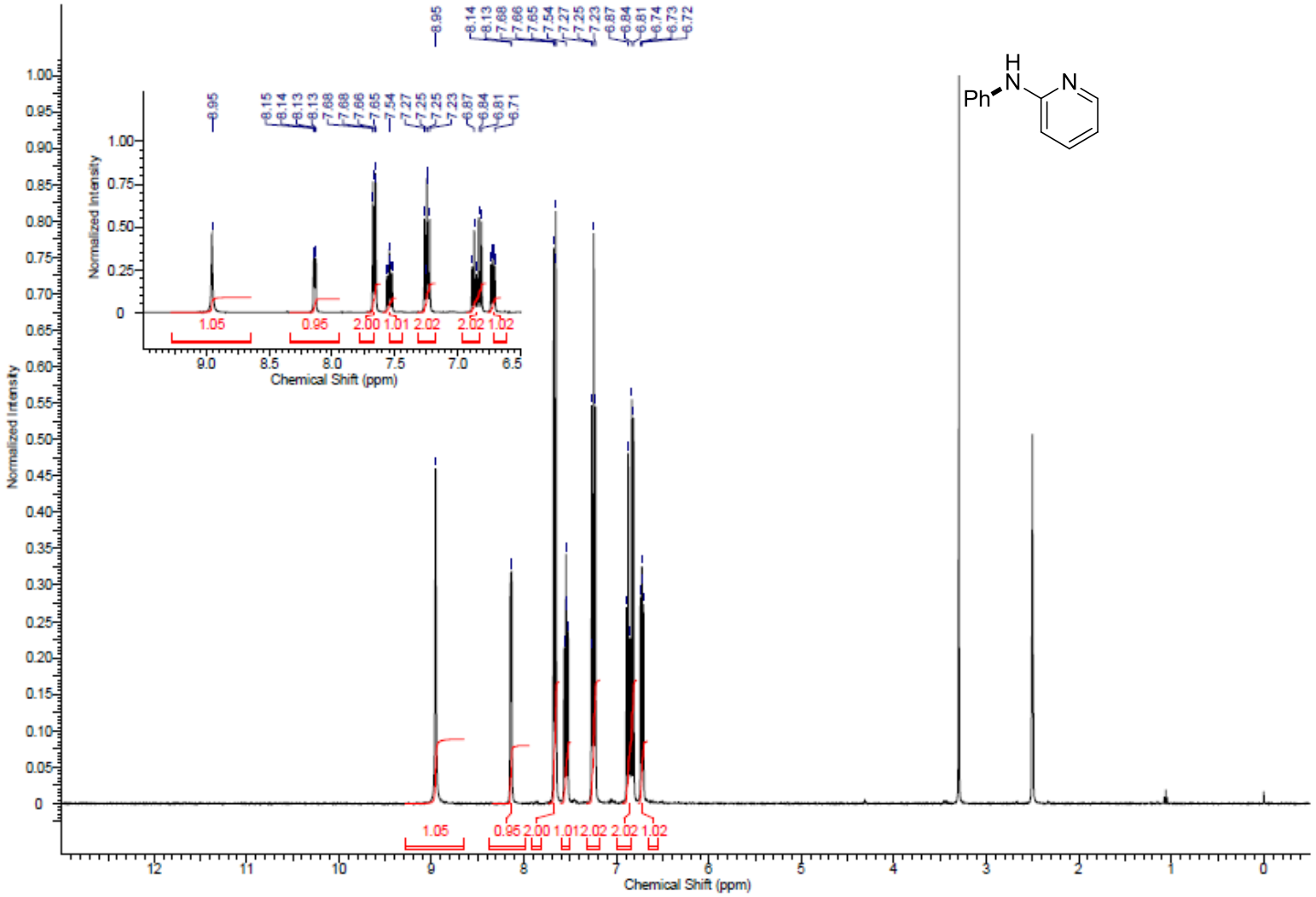


IR Spectra

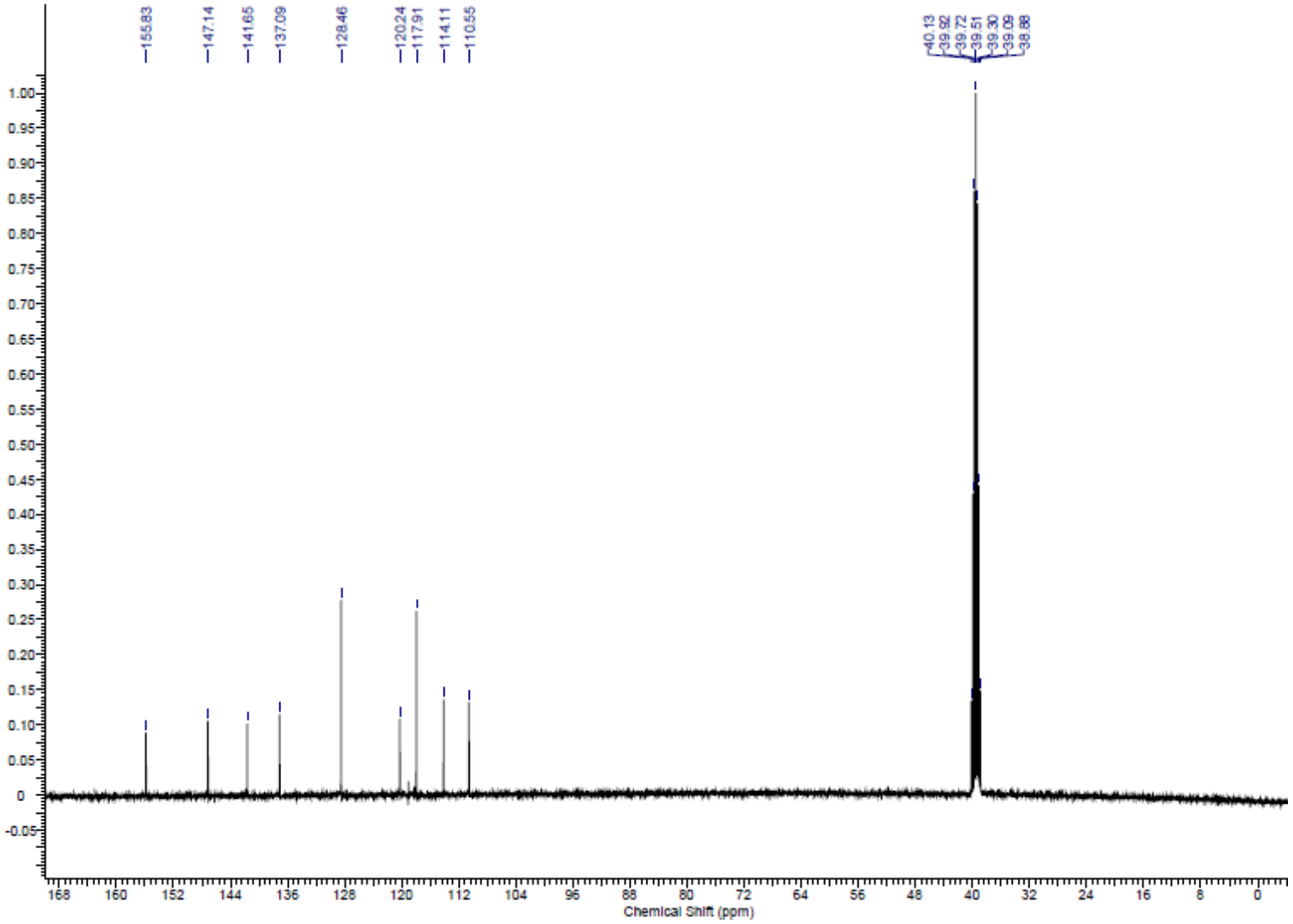


***N*-Phenylpyridin-2-amine (3w).**

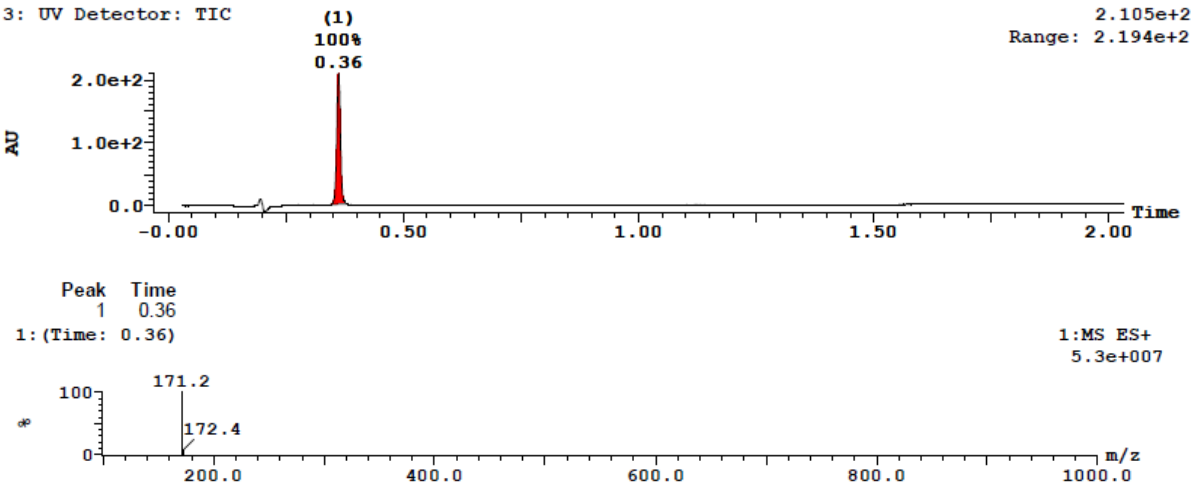
^{1}H NMR Spectra



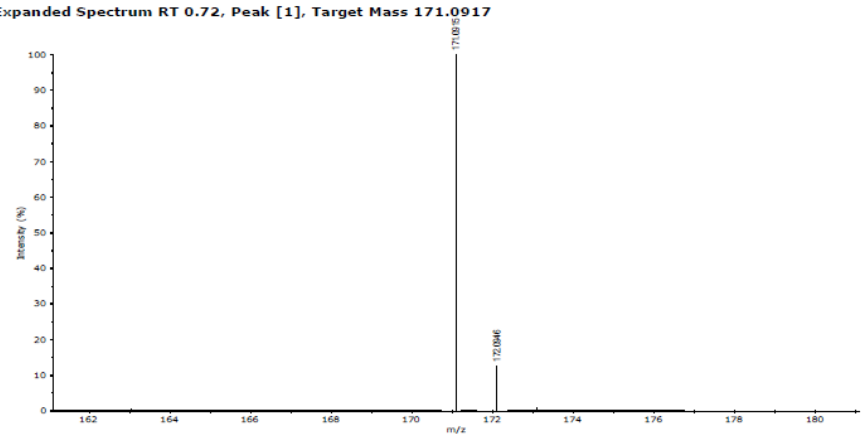
^{13}C NMR Spectra



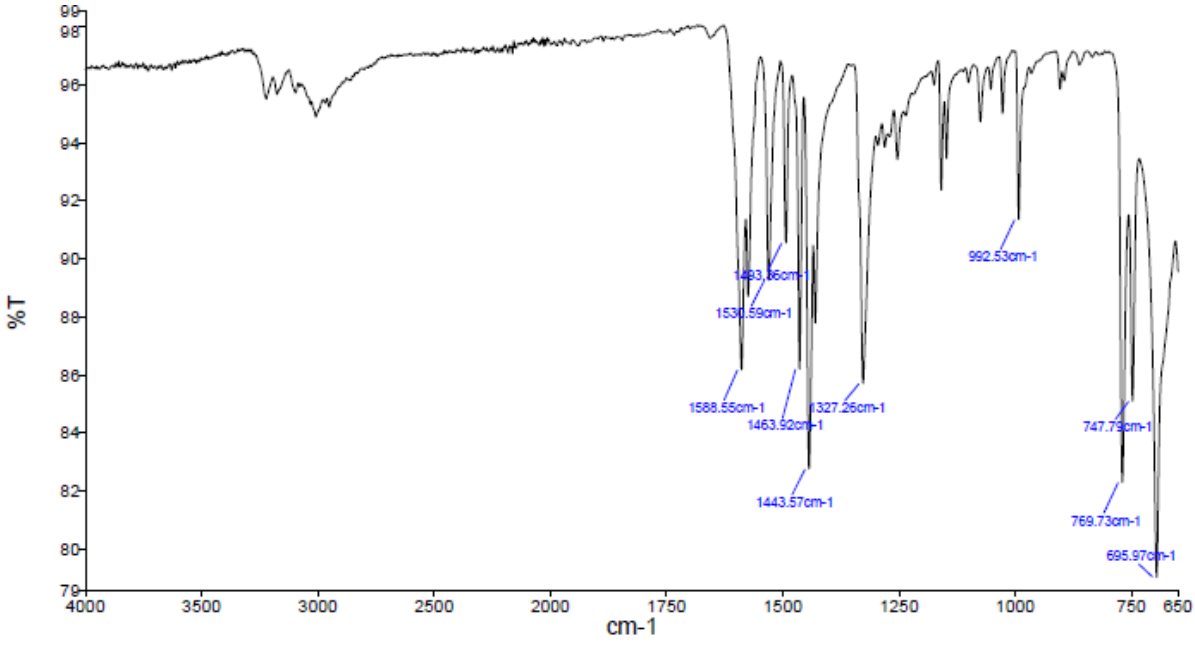
LCMS



HRMS

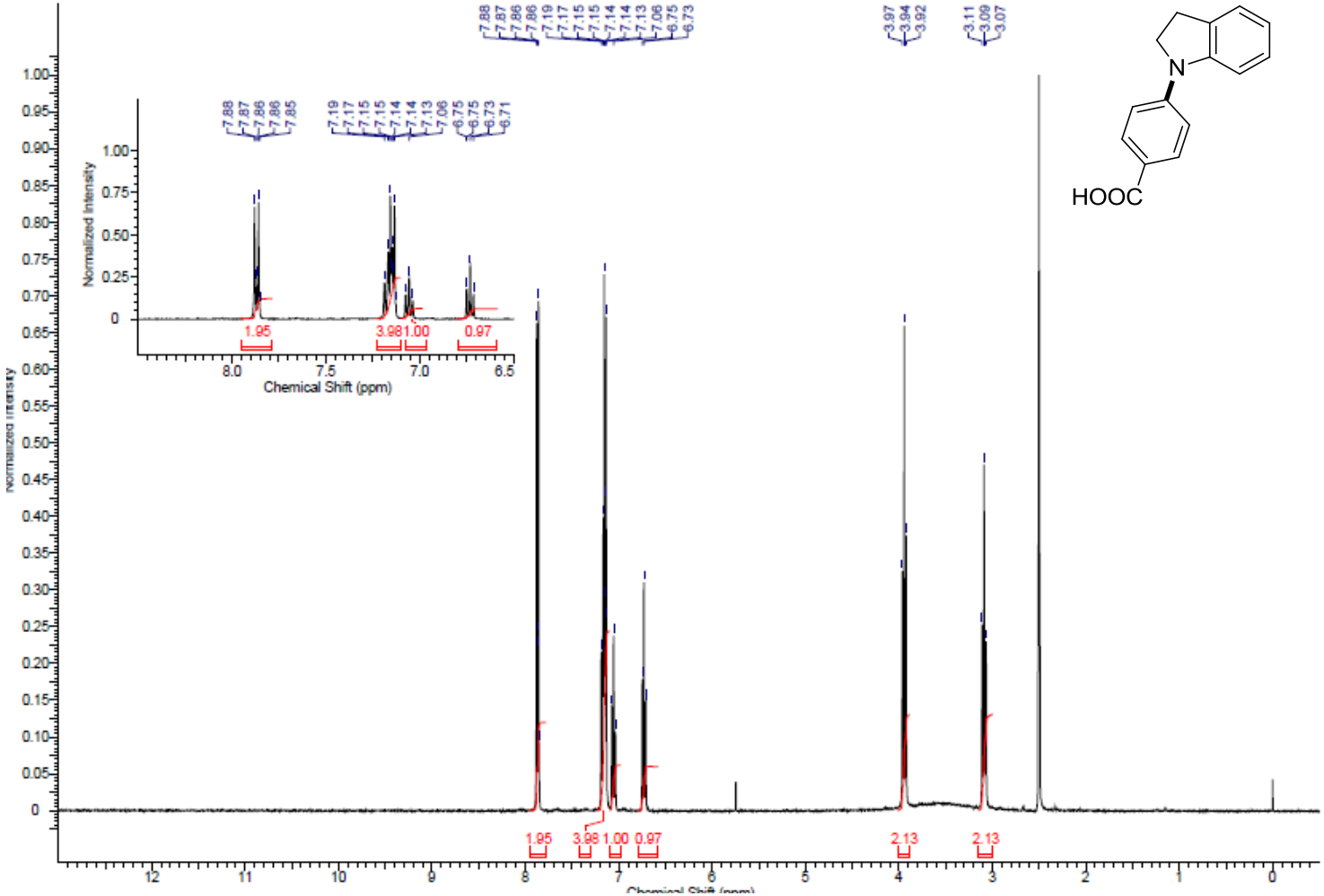


IR Spectra

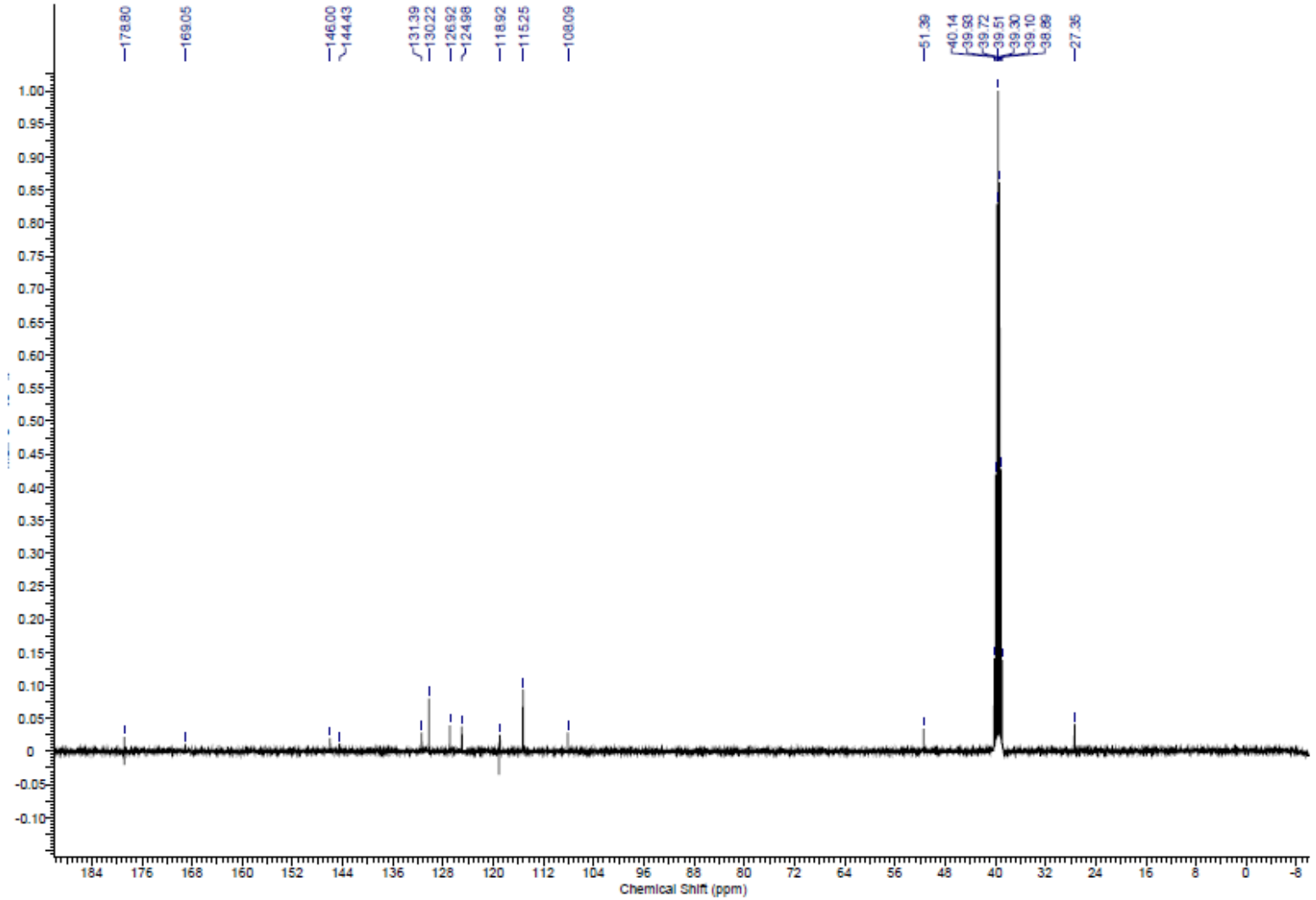


4-(indolin-1-yl)benzoic acid (3x).

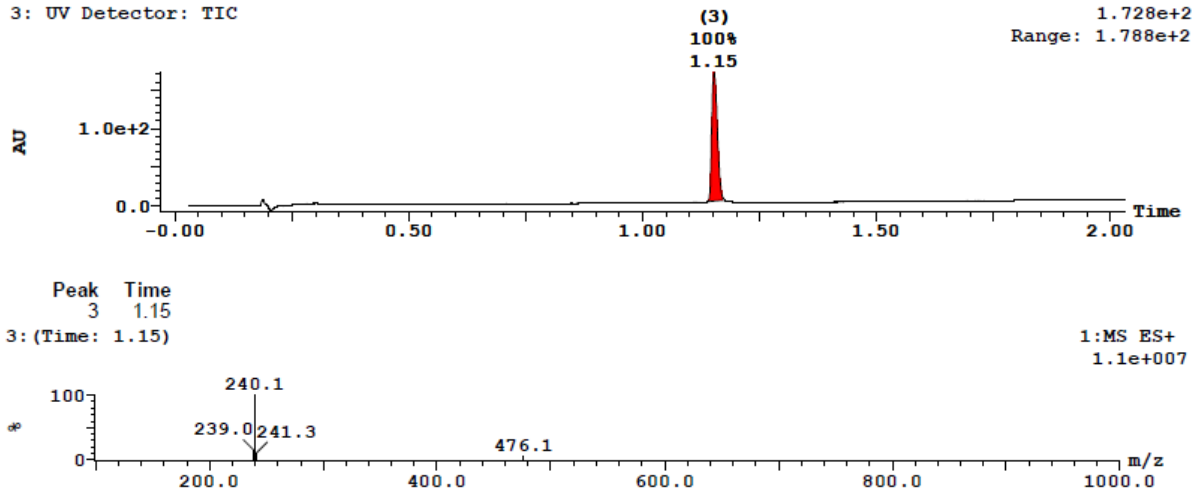
^{1}H NMR Spectra



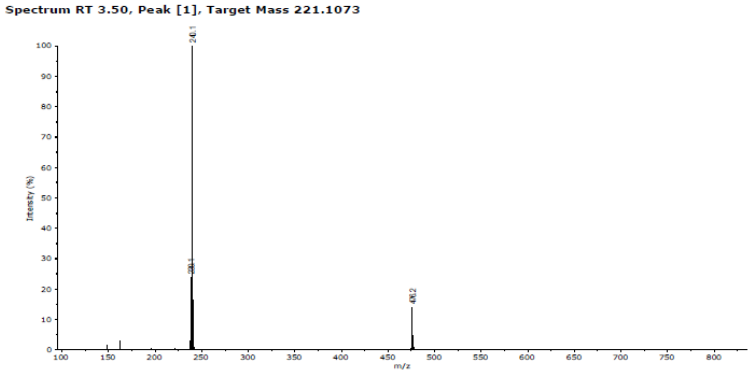
^{13}C NMR Spectra



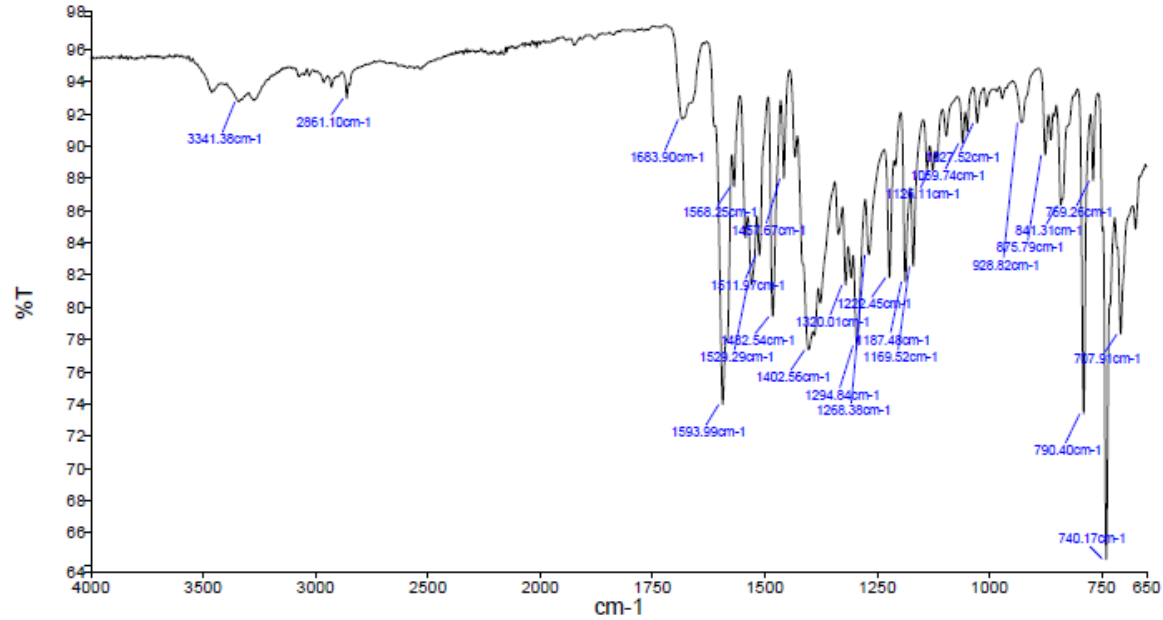
LCMS



HRMS

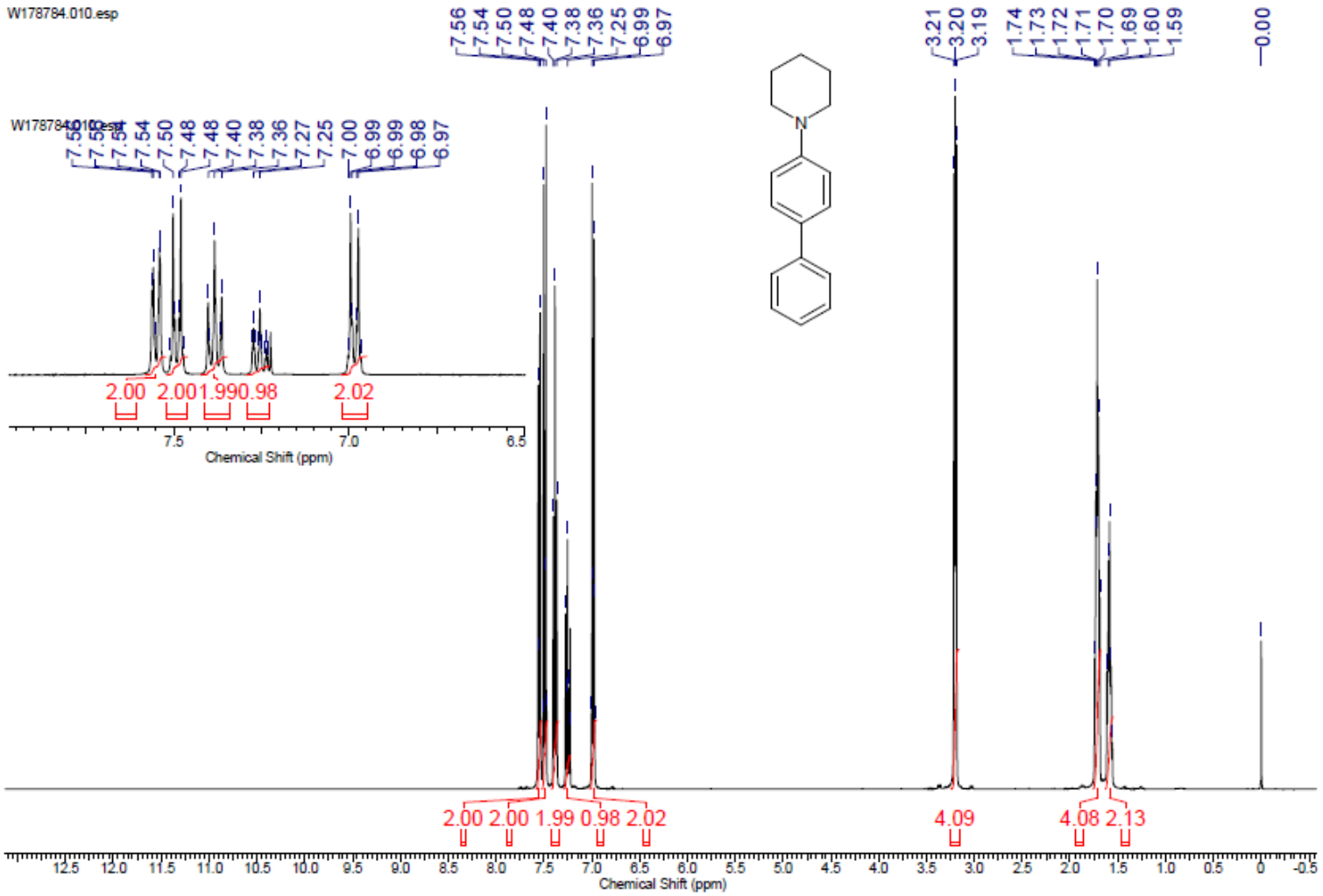


IR Spectra

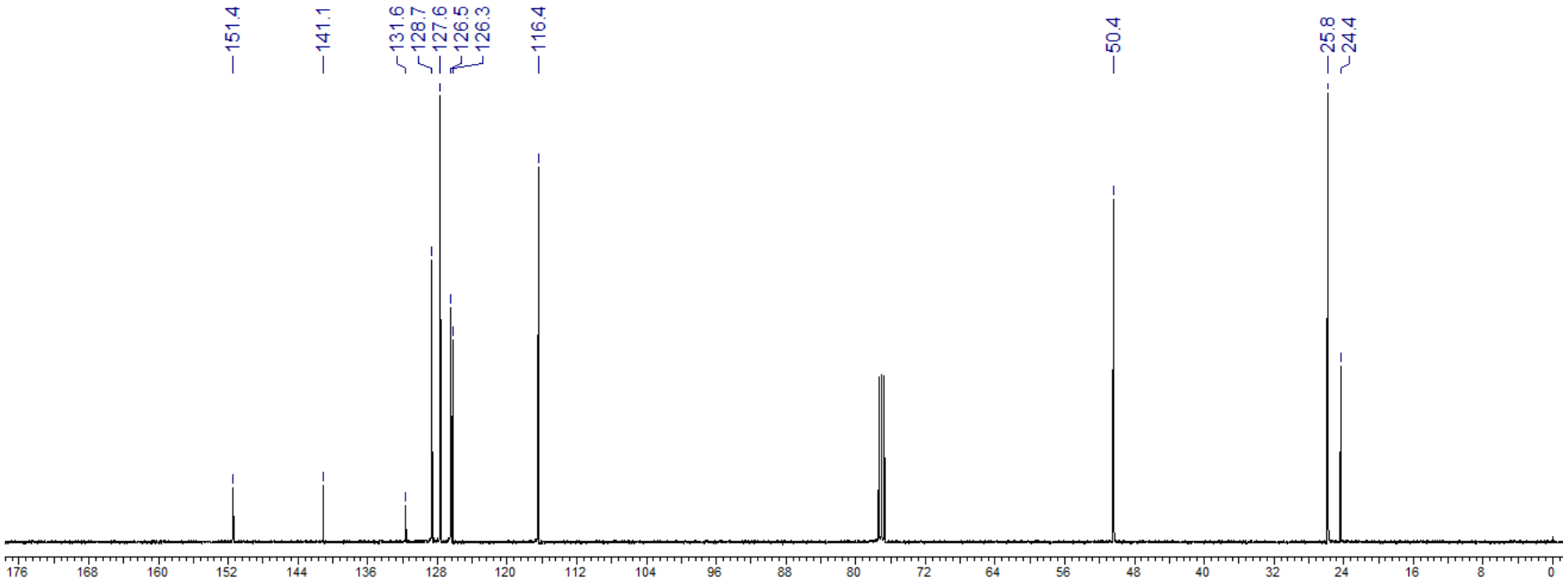


1-([1,1'-Biphenyl]-4-yl)piperidine (7a).

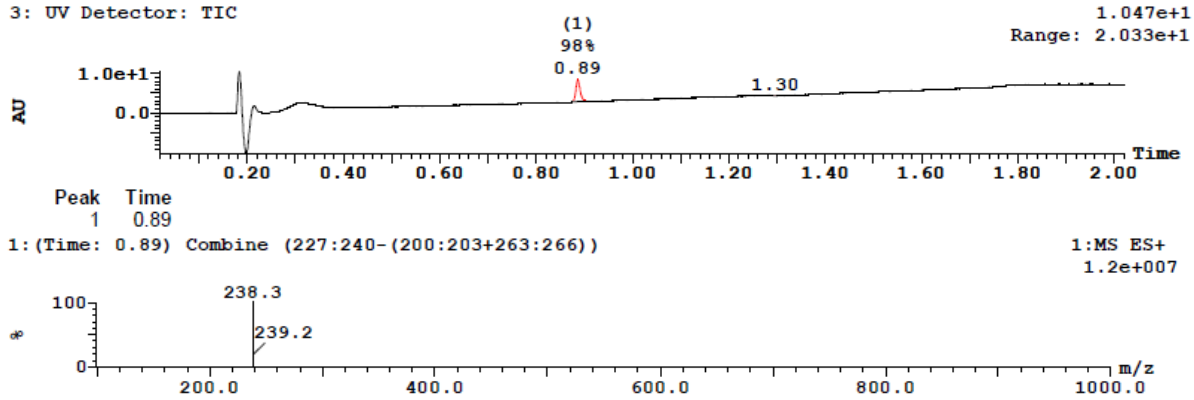
^{1}H NMR Spectra



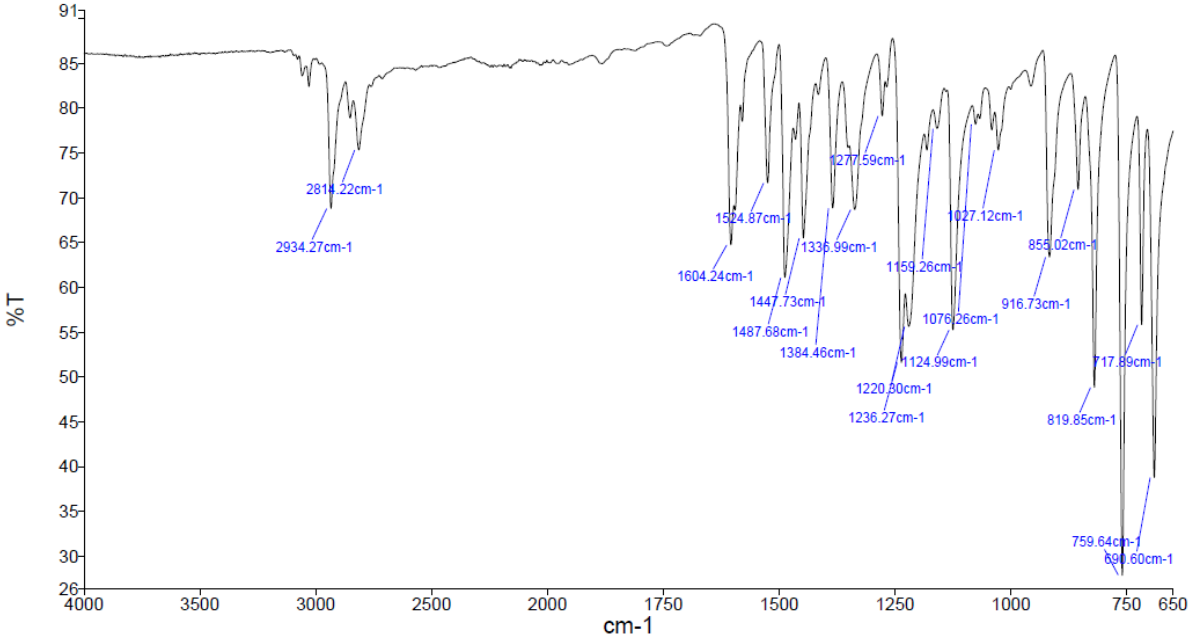
^{13}C NMR Spectra



LCMS

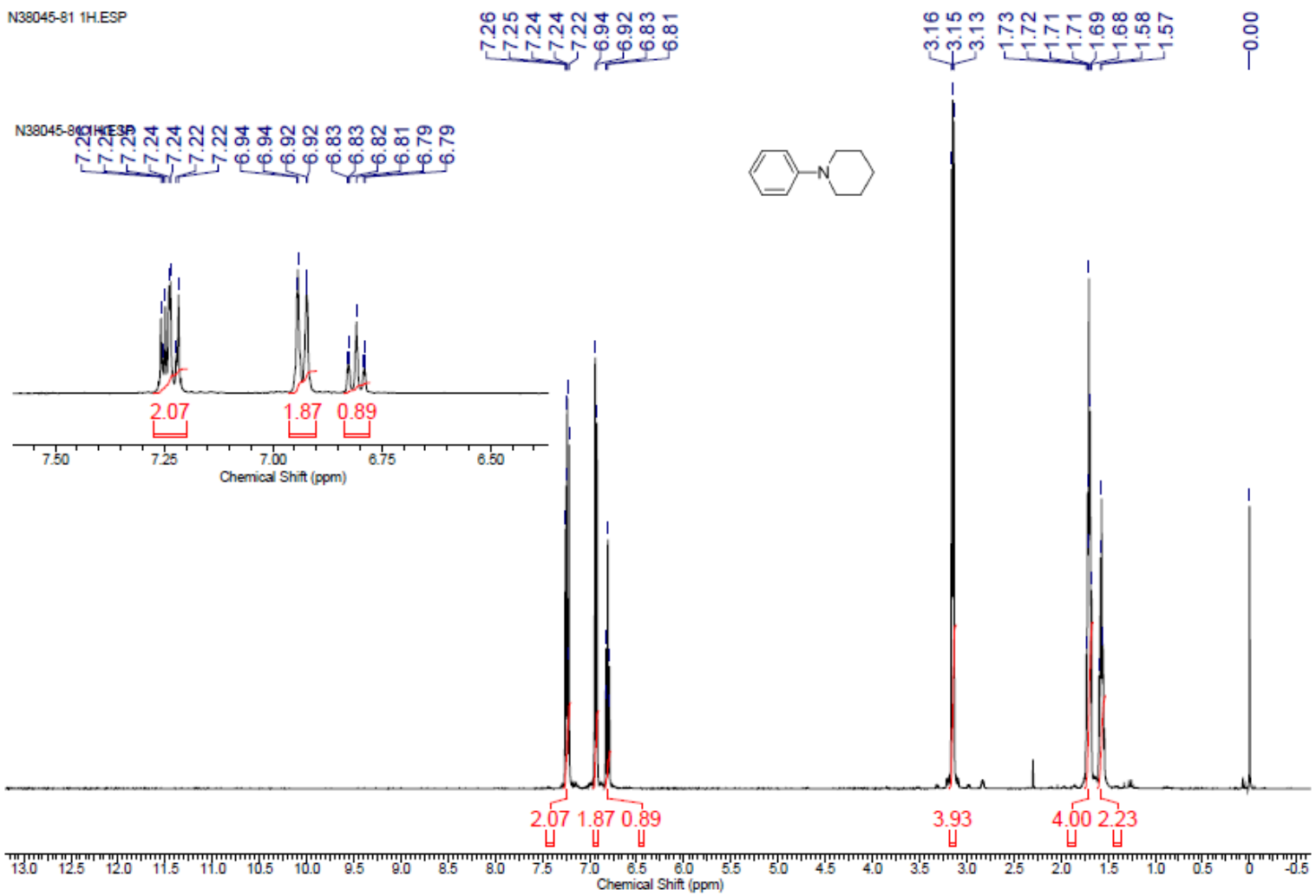


IR Spectra

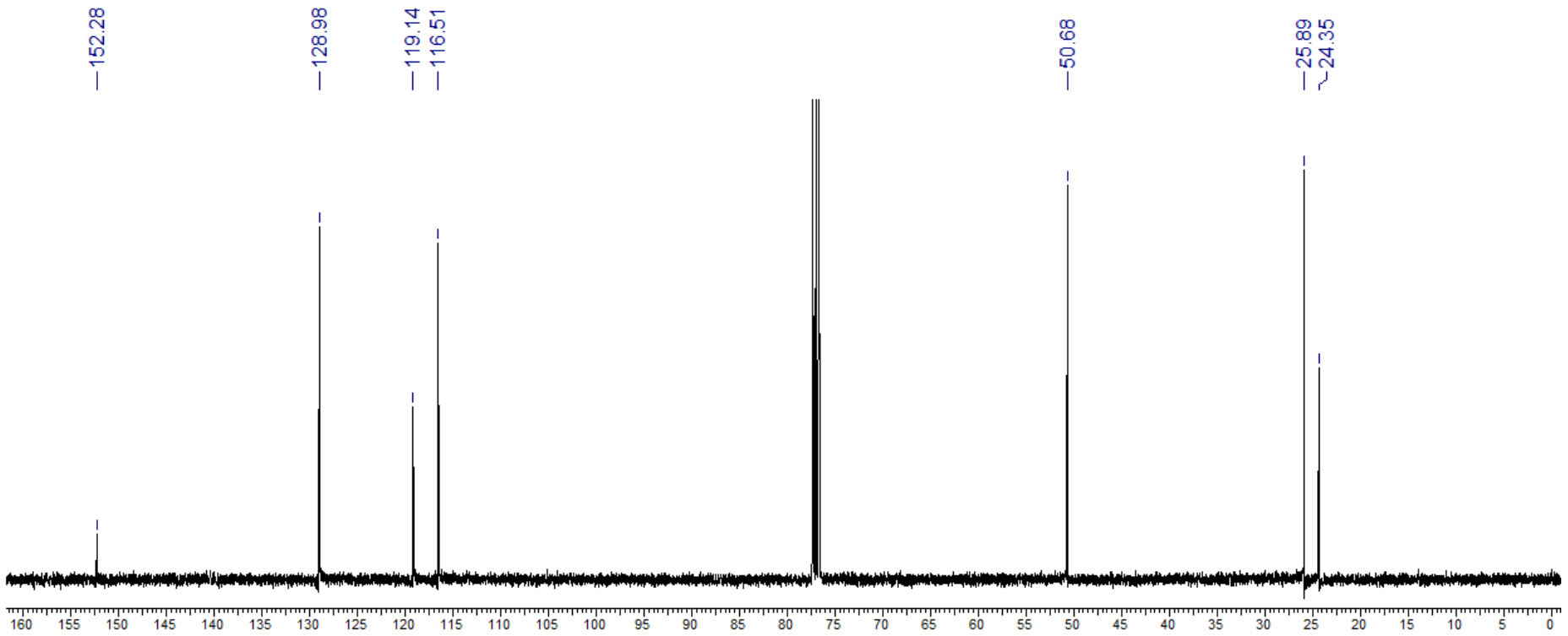


1-Phenylpiperidine (7b).

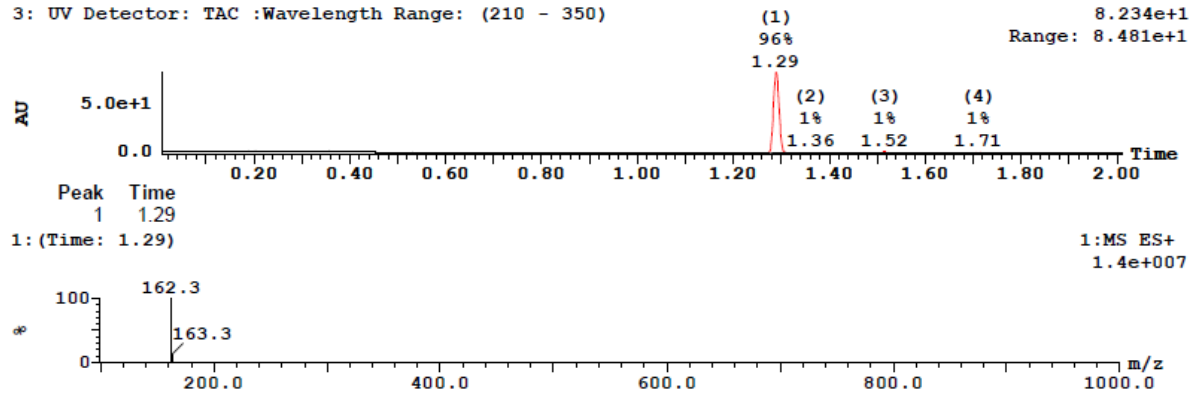
^{1}H NMR Spectra



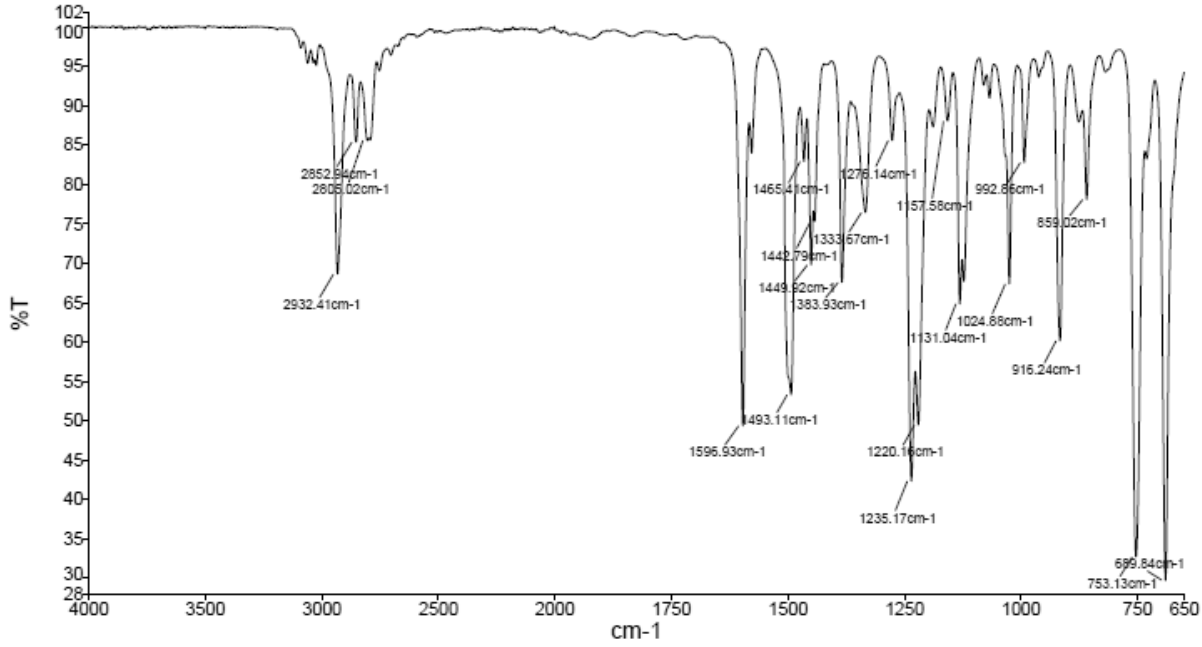
^{13}C NMR Spectra



LCMS

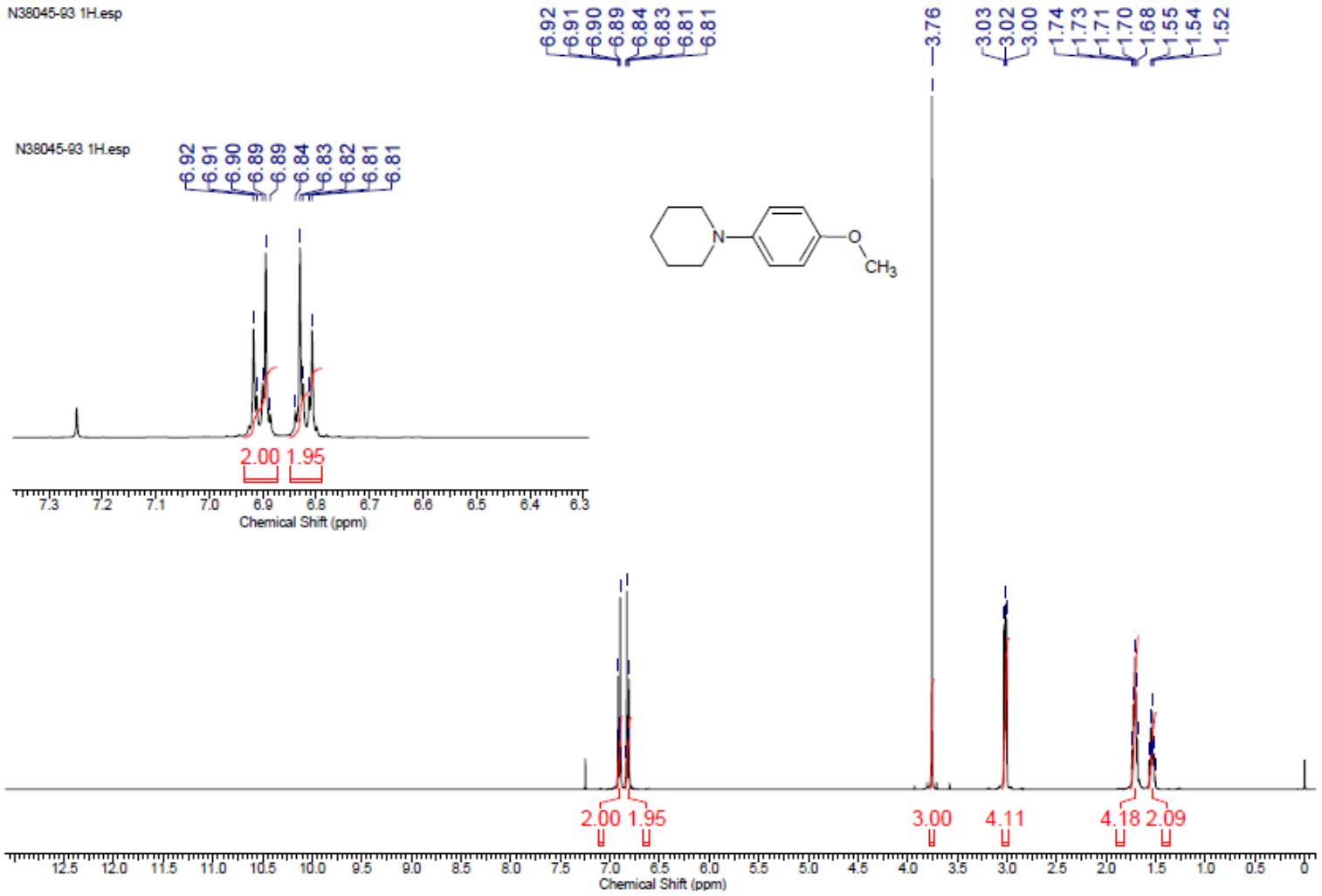


IR Spectra

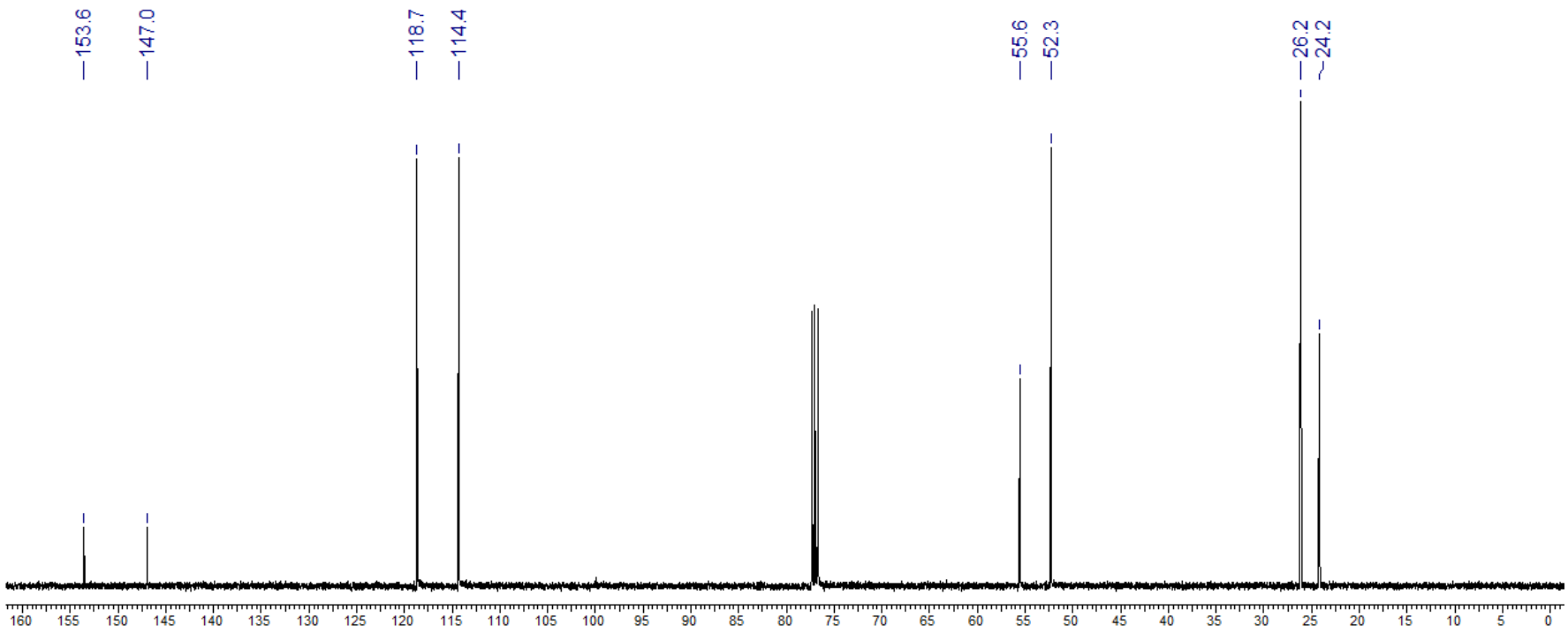


1-(4-Methoxyphenyl)piperidine (7c).

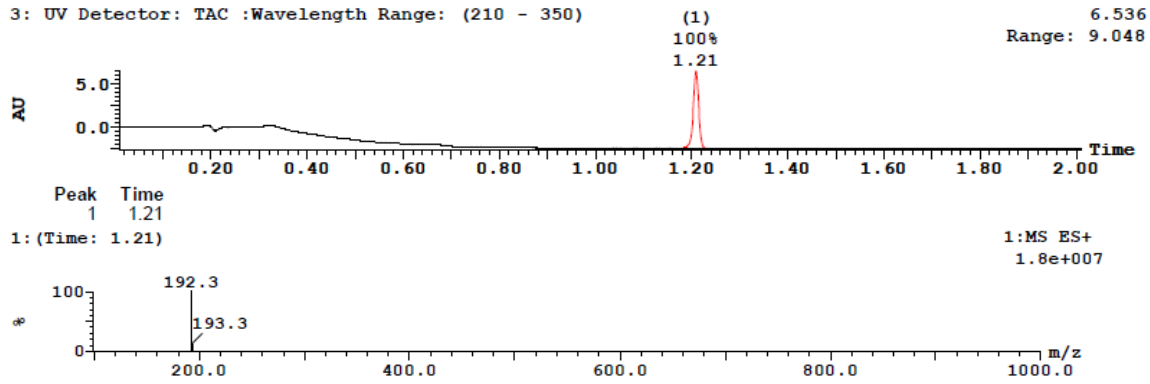
^{1}H NMR Spectra



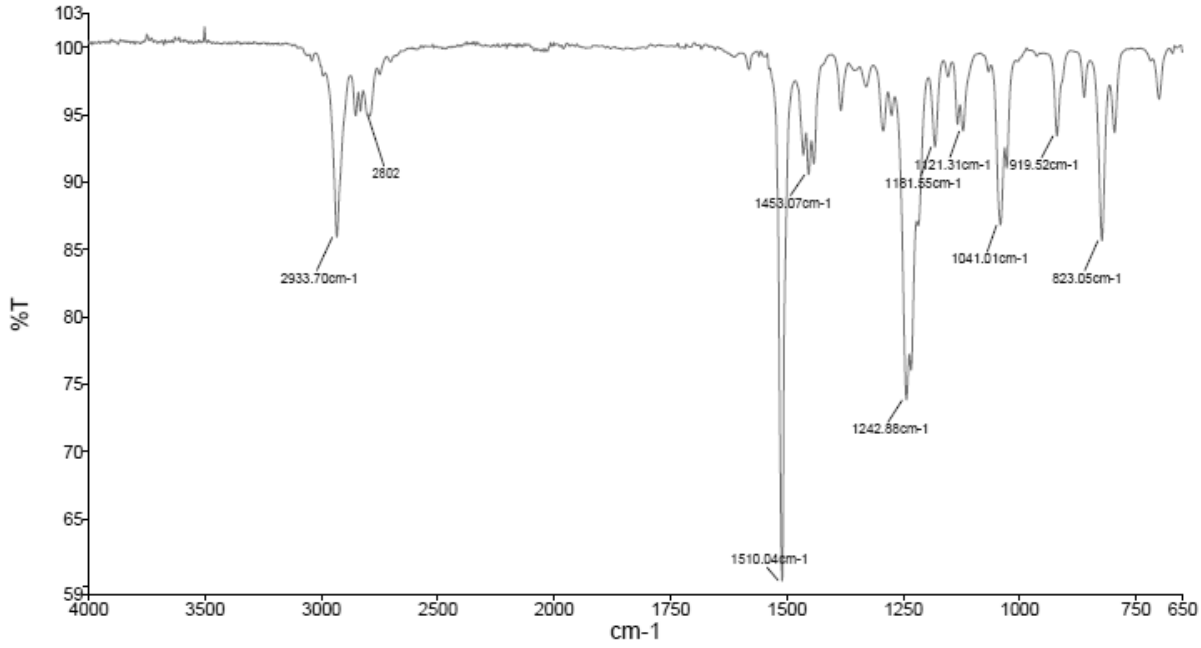
^{13}C NMR Spectra



LCMS

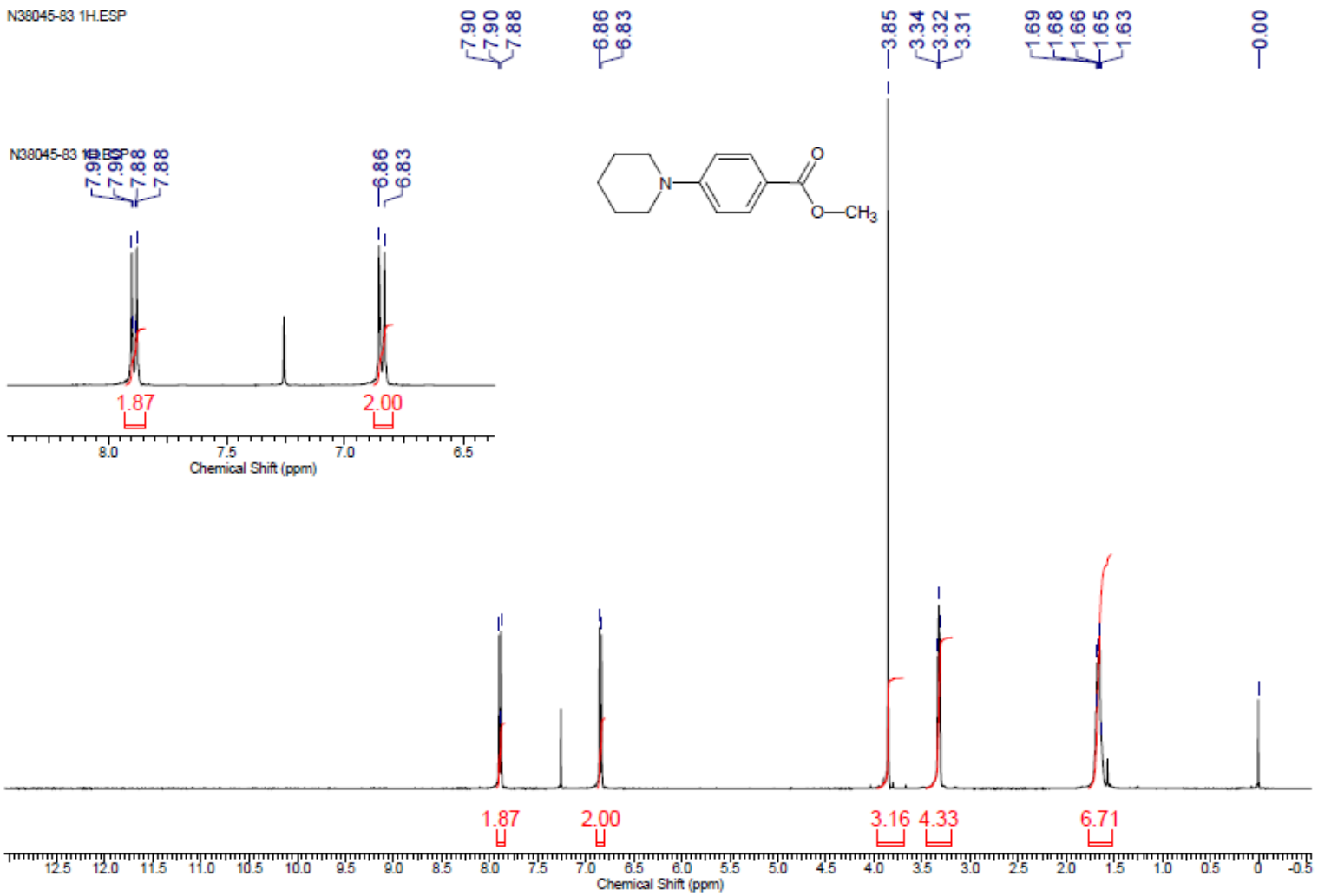


IR Spectra

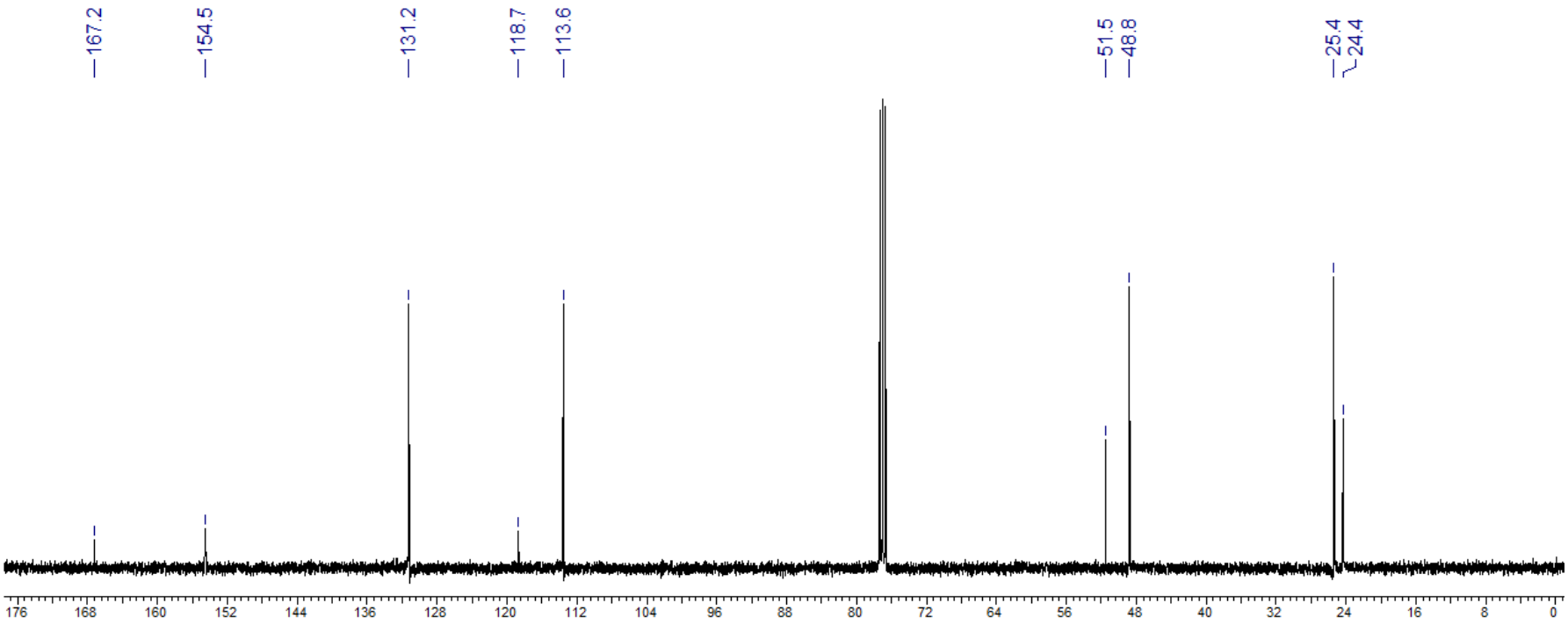


Methyl 4-(piperidin-1-yl)benzoate (7d).

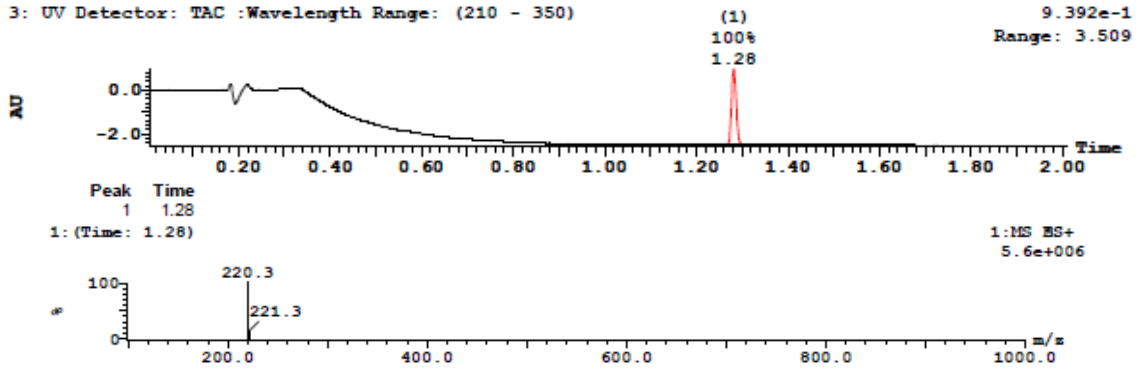
^{1}H NMR Spectra



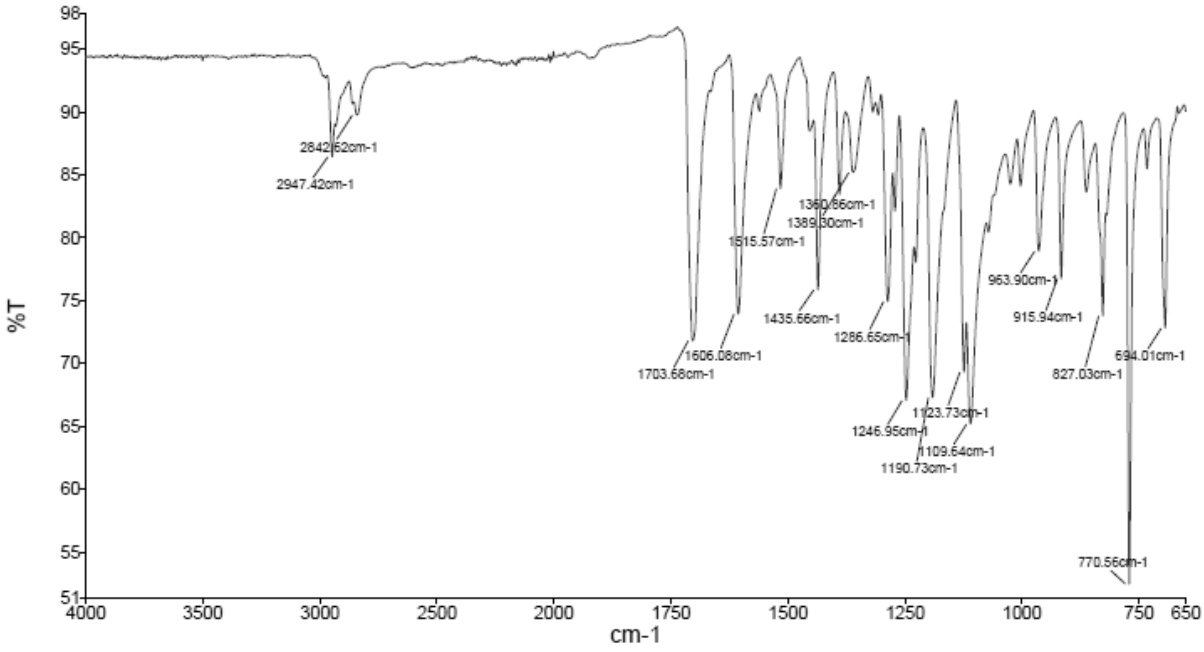
^{13}C NMR Spectra



LCMS

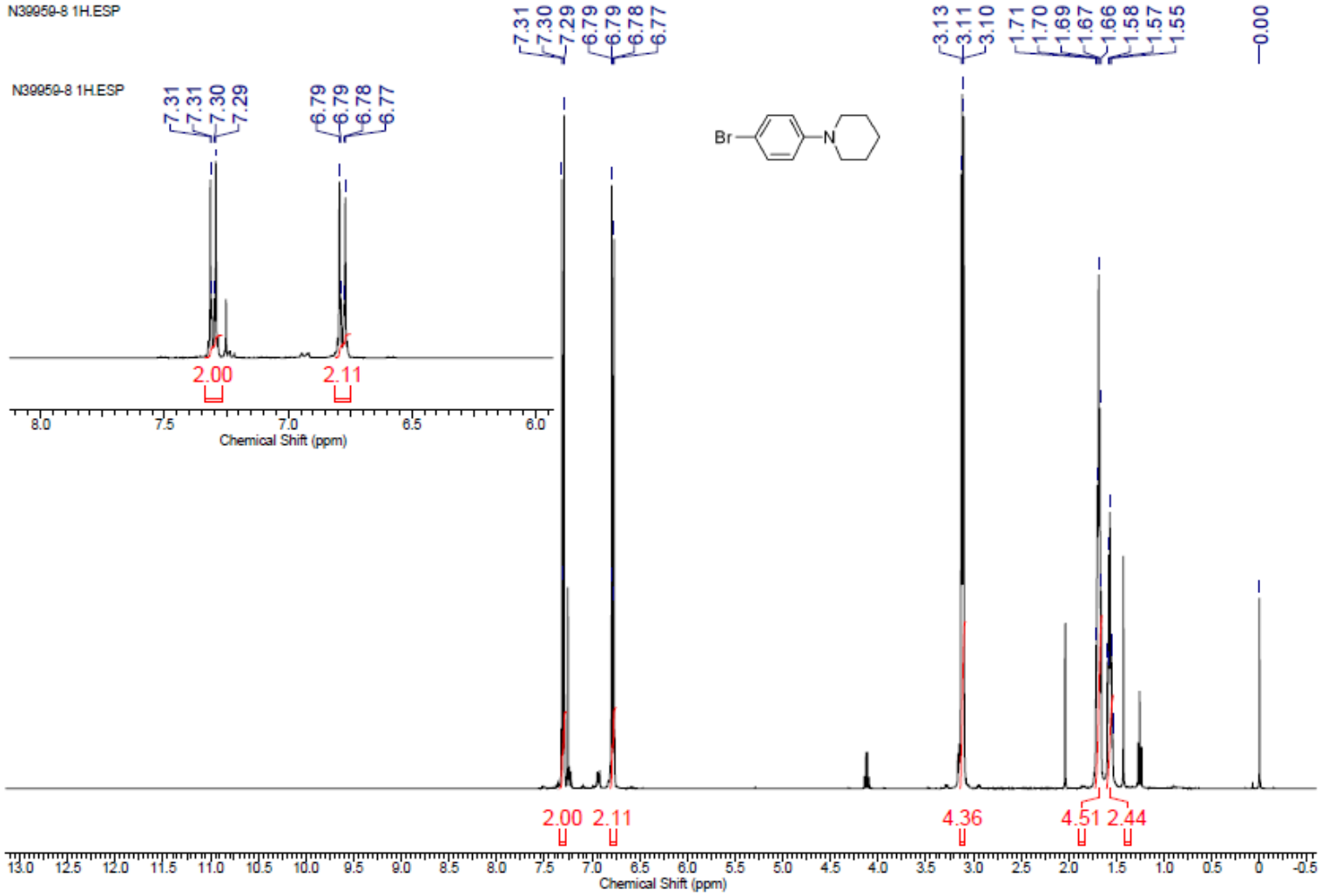


IR Spectra

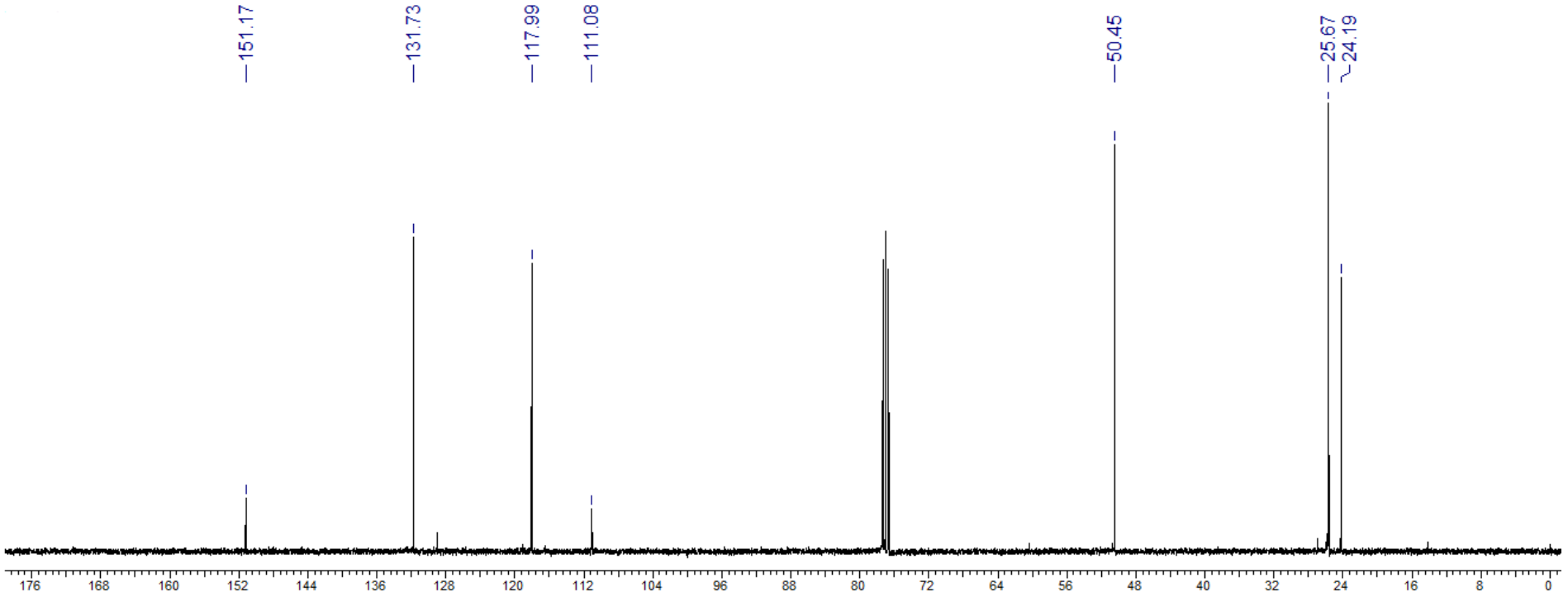


1-(4-Bromophenyl)piperidine (7e).

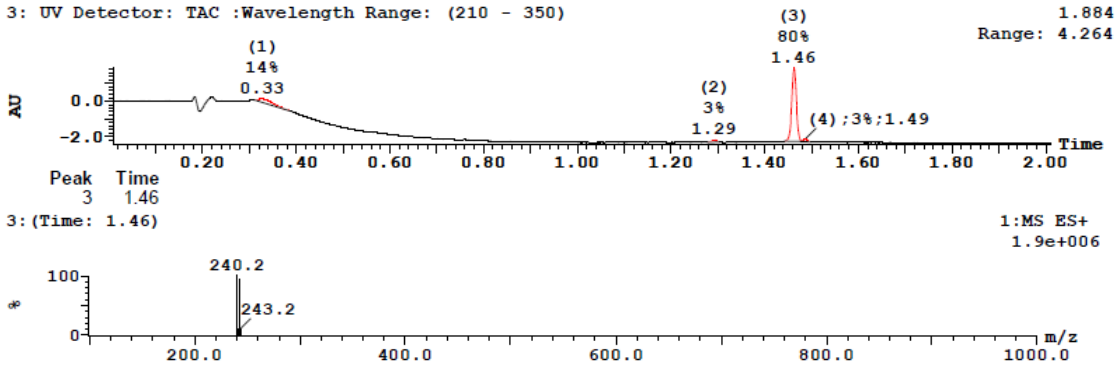
^{1}H NMR Spectra



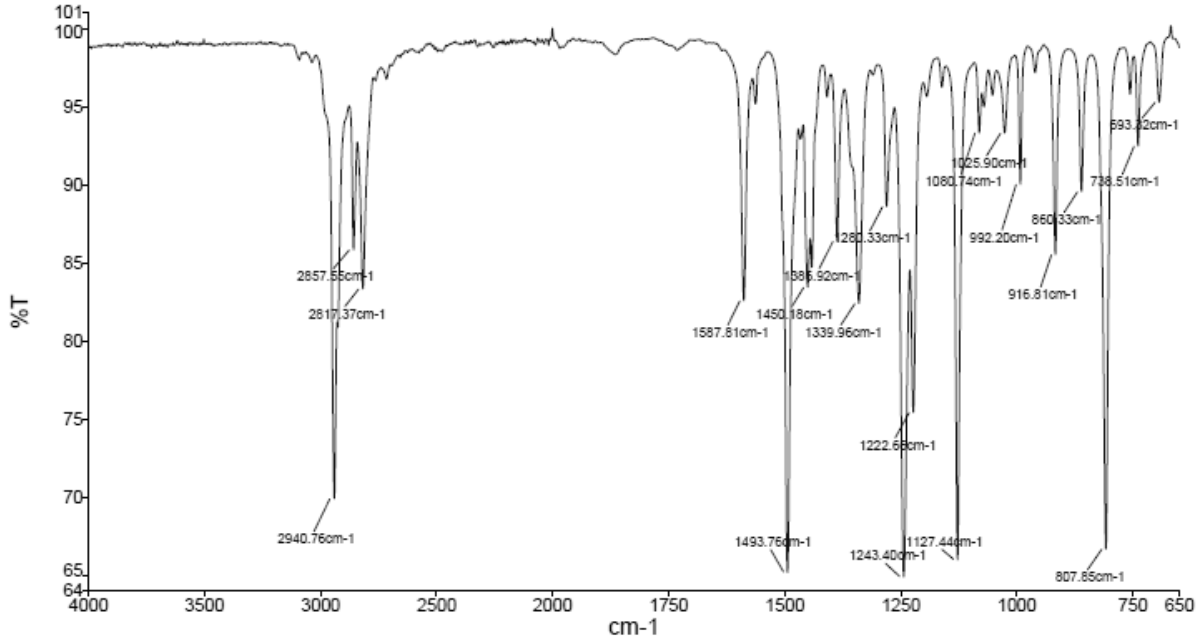
^{13}C NMR Spectra



LCMS

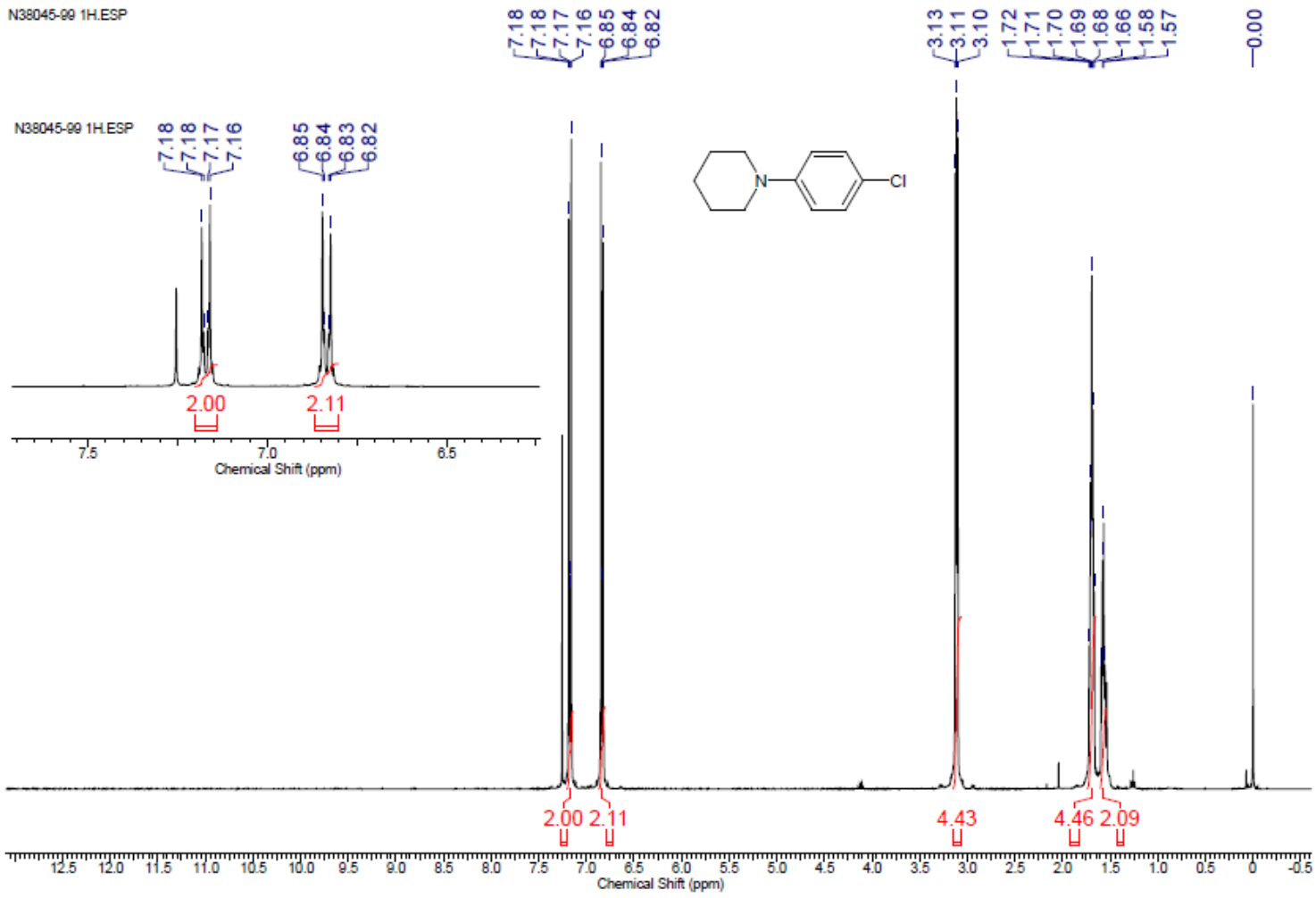


IR Spectra

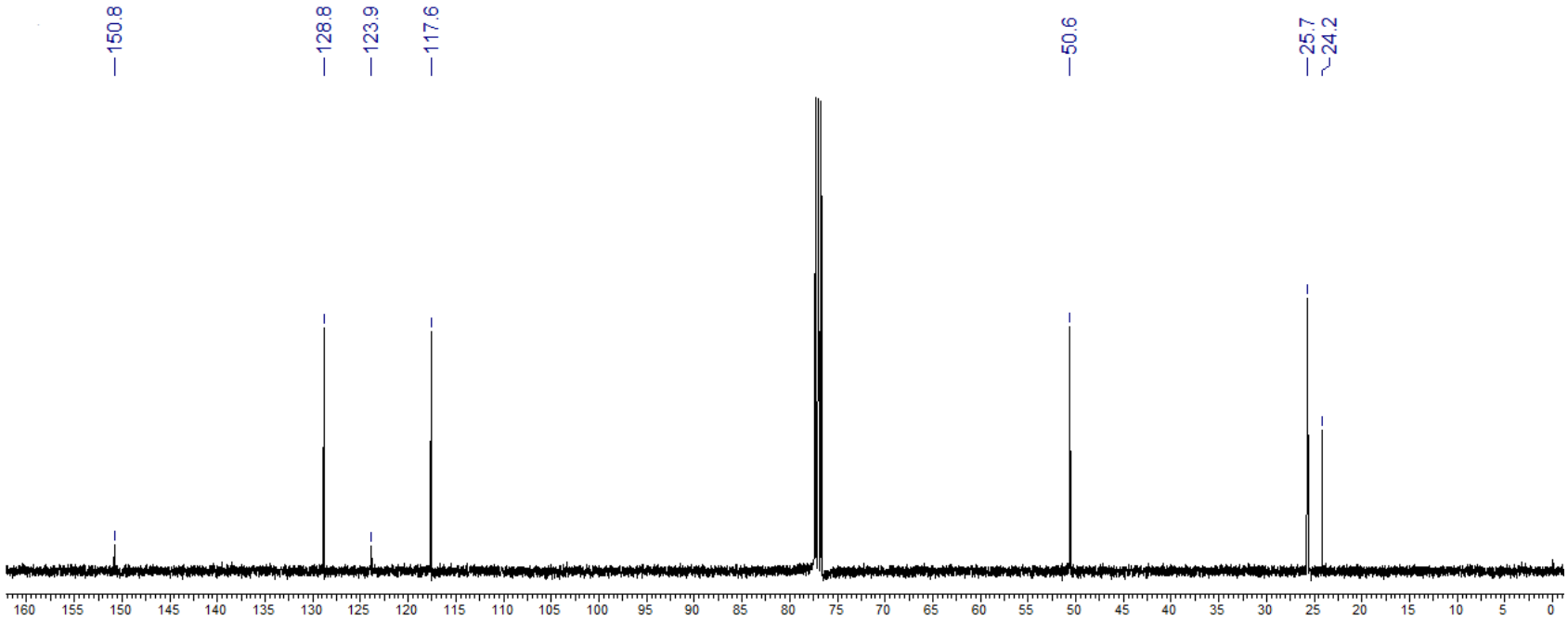


1-(4-Chlorophenyl)piperidine (7f).

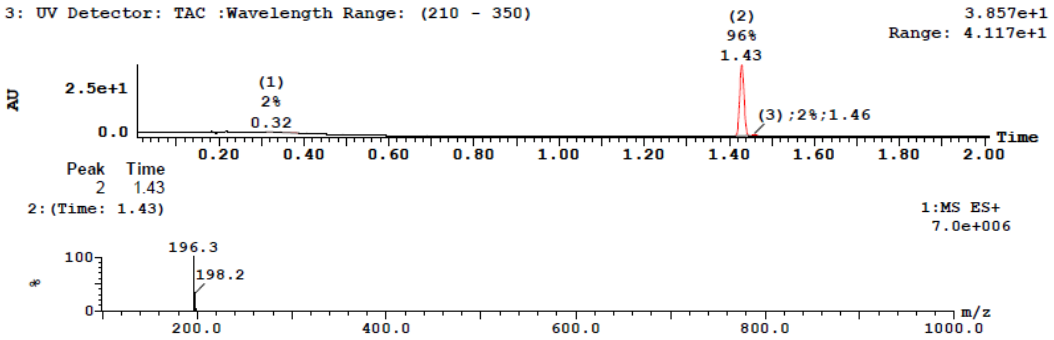
^{1}H NMR Spectra



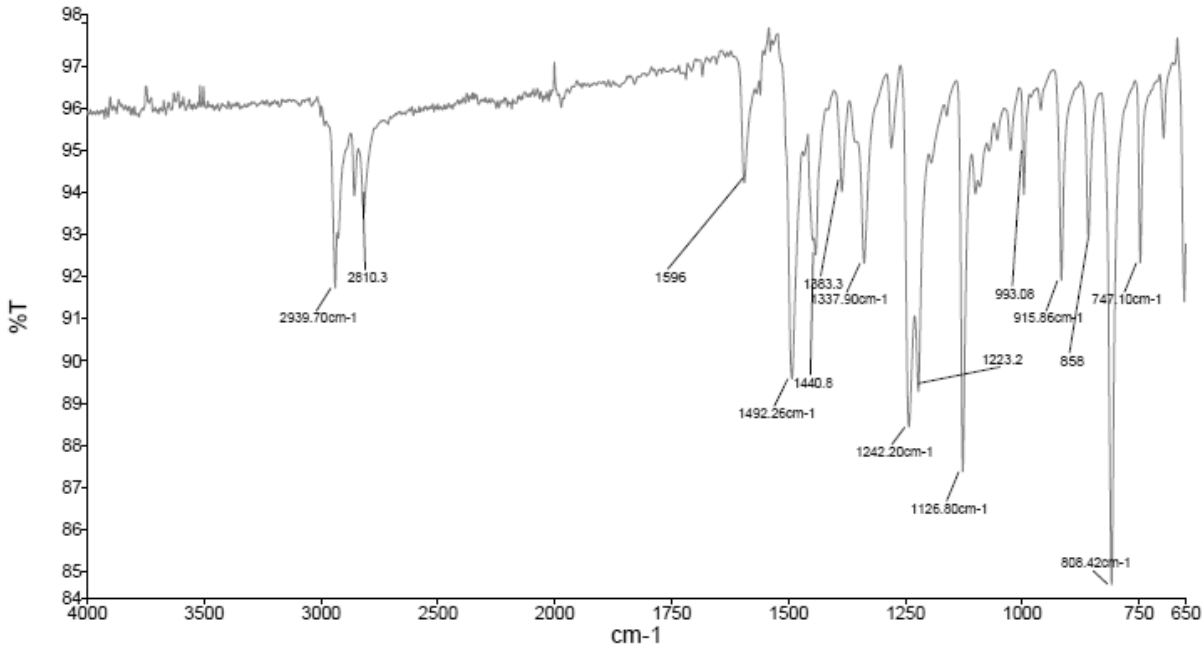
^{13}C NMR Spectra



LCMS

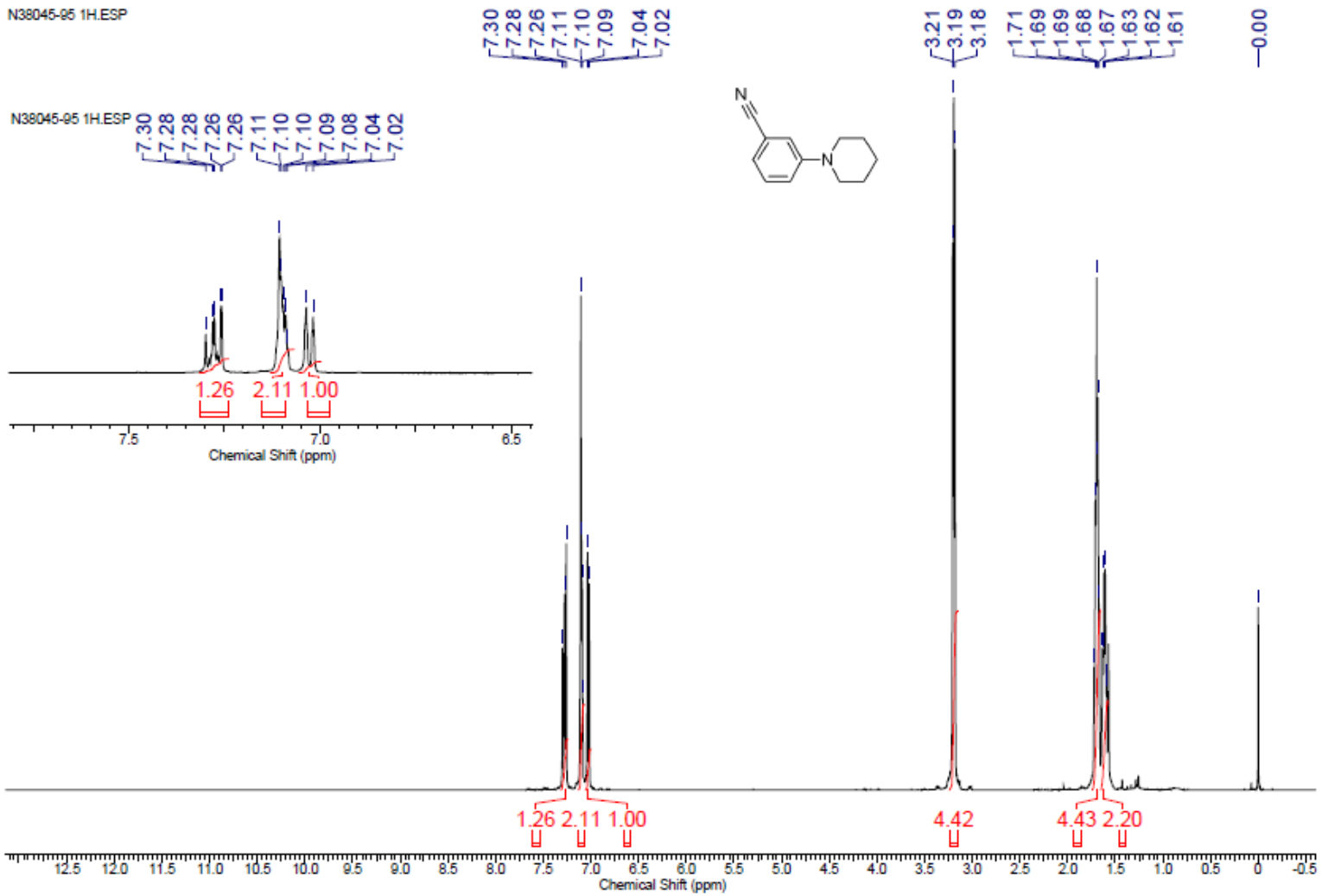


IR Spectra

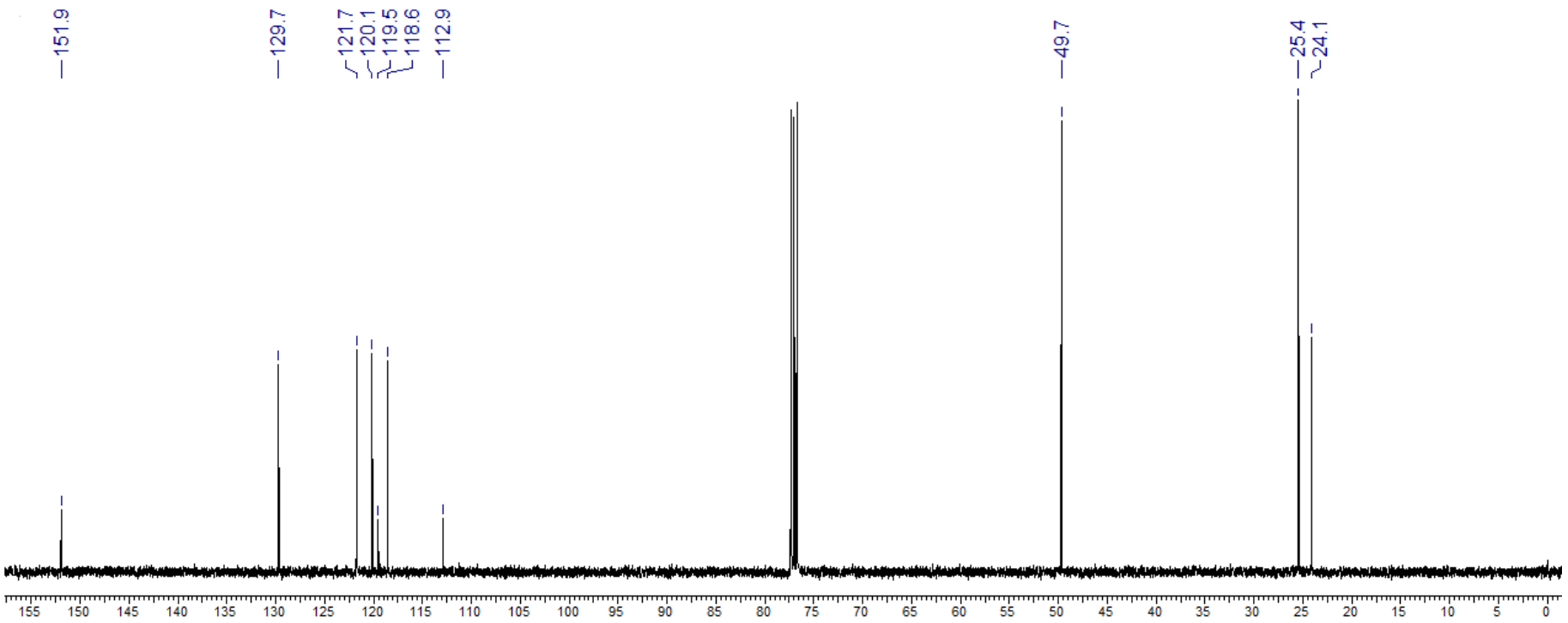


1-(3-Cyanophenyl)piperidine (7g).

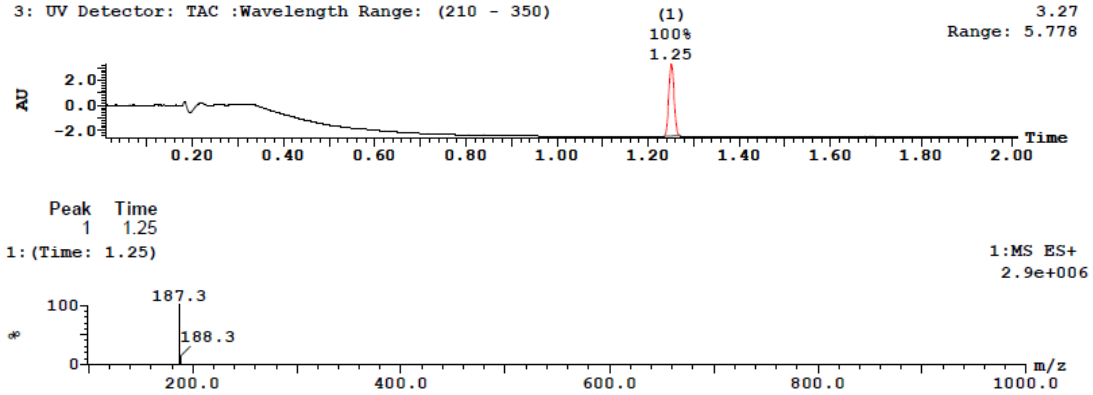
^{1}H NMR Spectra



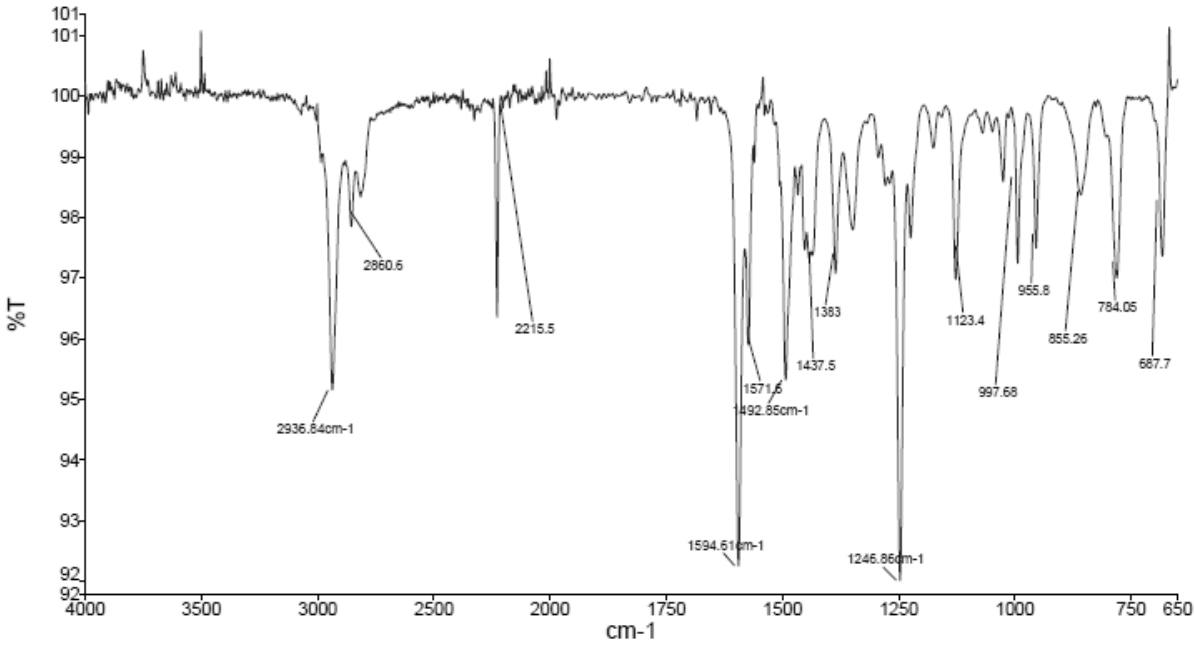
^{13}C NMR Spectra



LCMS

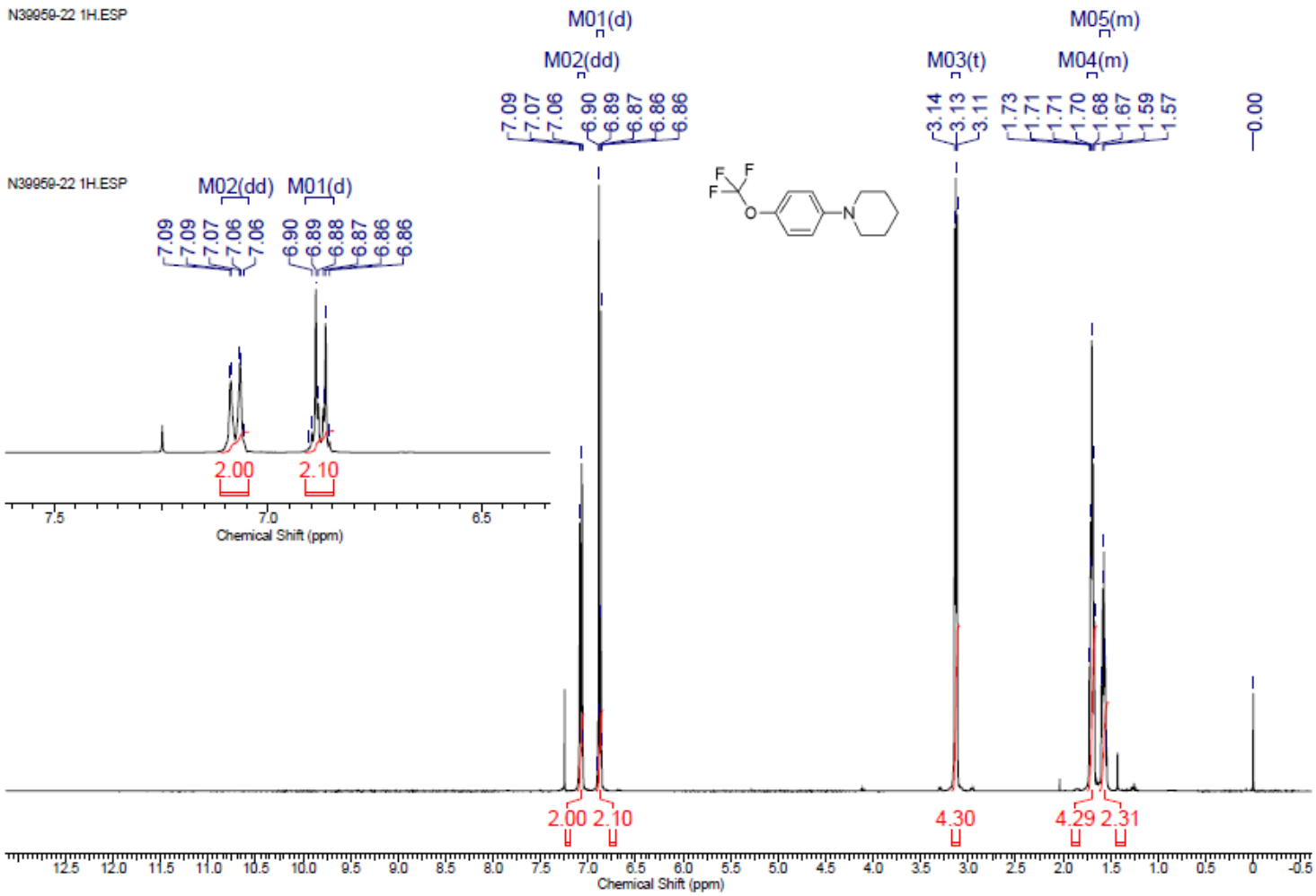


IR Spectra

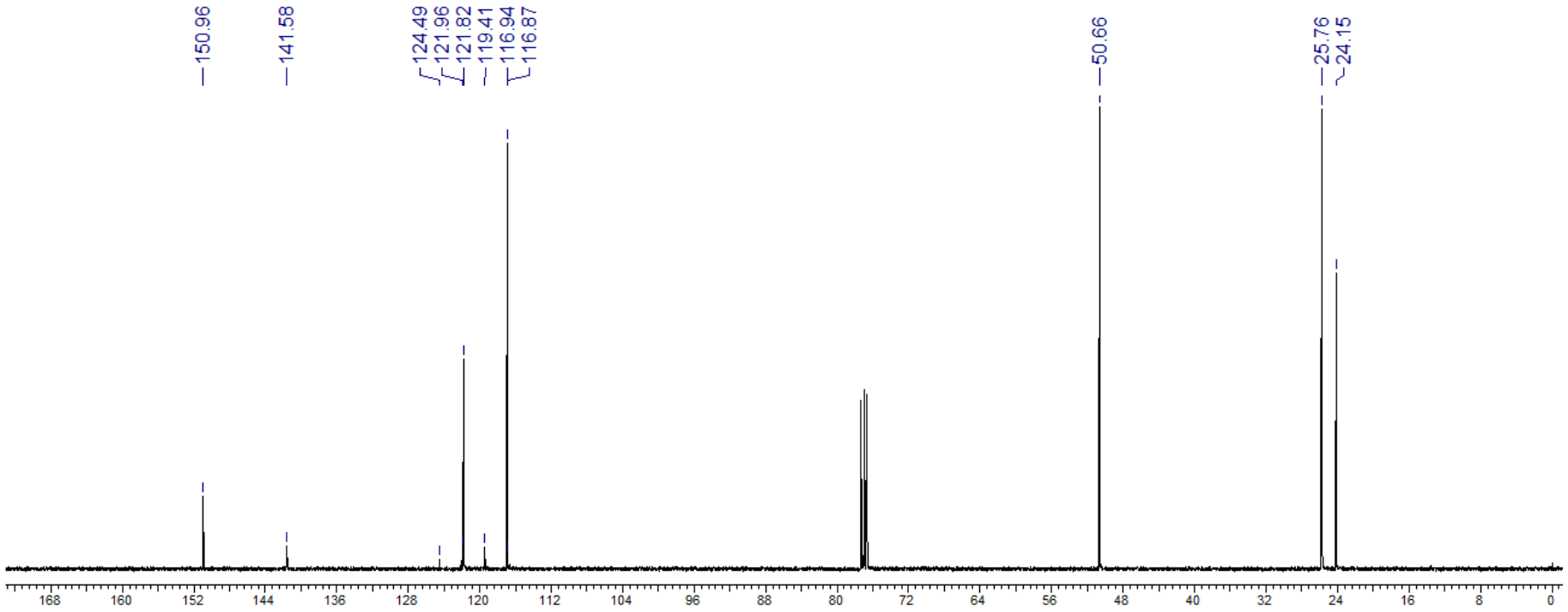


1-(4-(Trifluoromethoxy)phenyl)piperidine (7h).

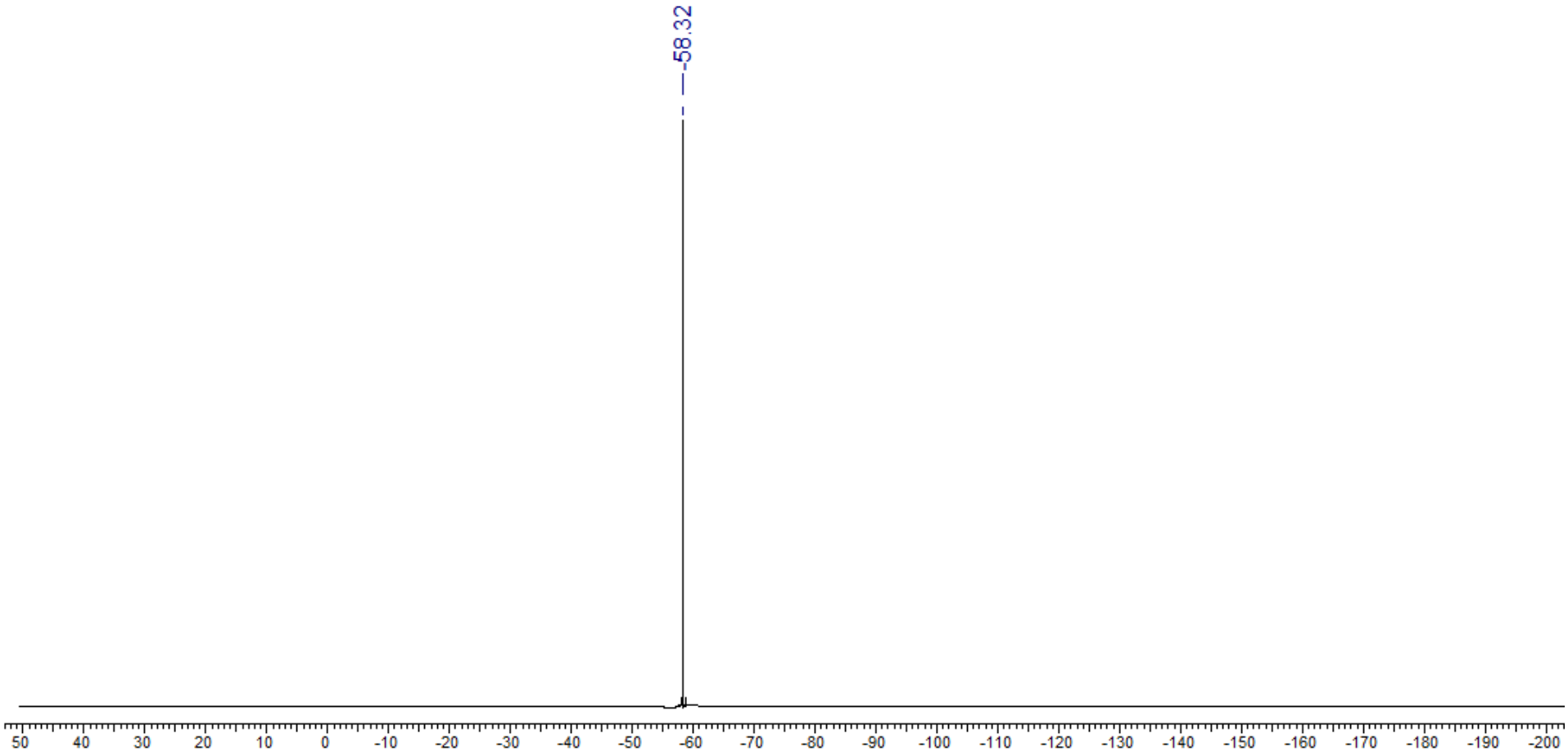
^{1}H NMR Spectra



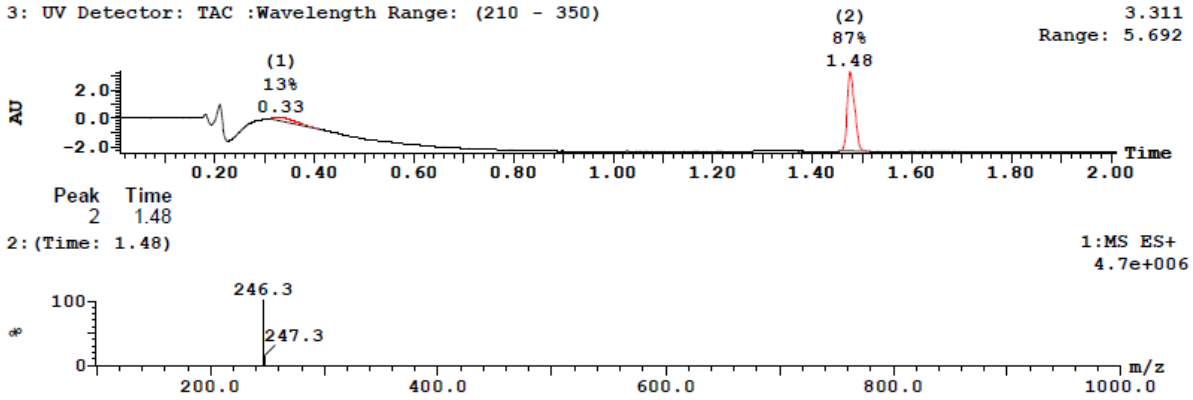
^{13}C NMR Spectra



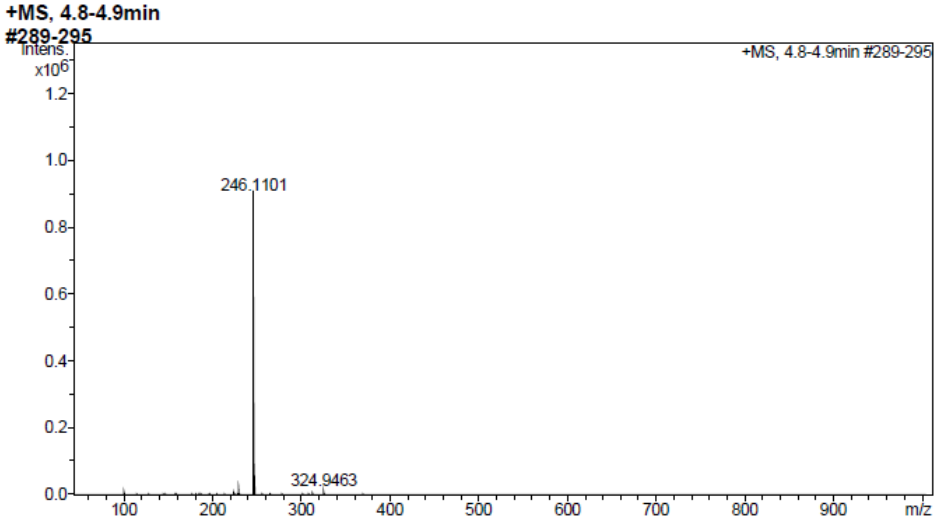
^{19}F NMR Spectra



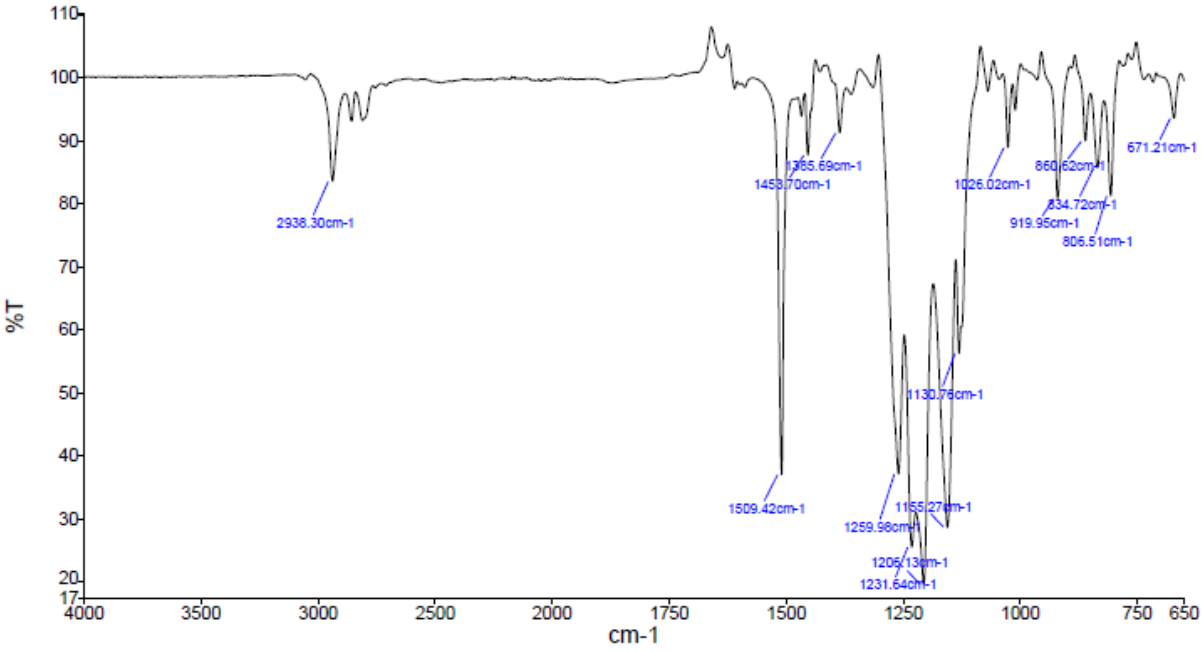
LCMS



HRMS

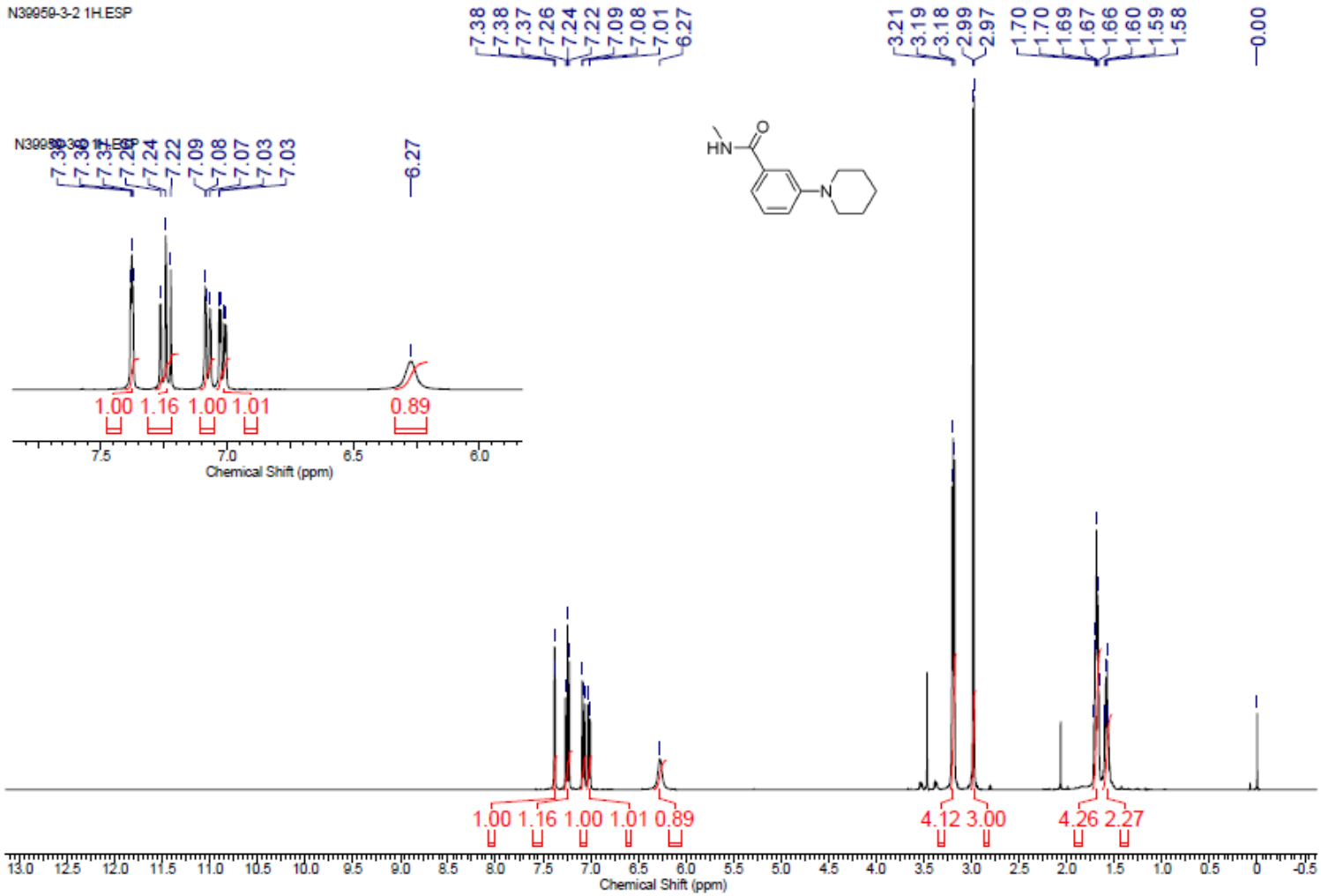


IR Spectra

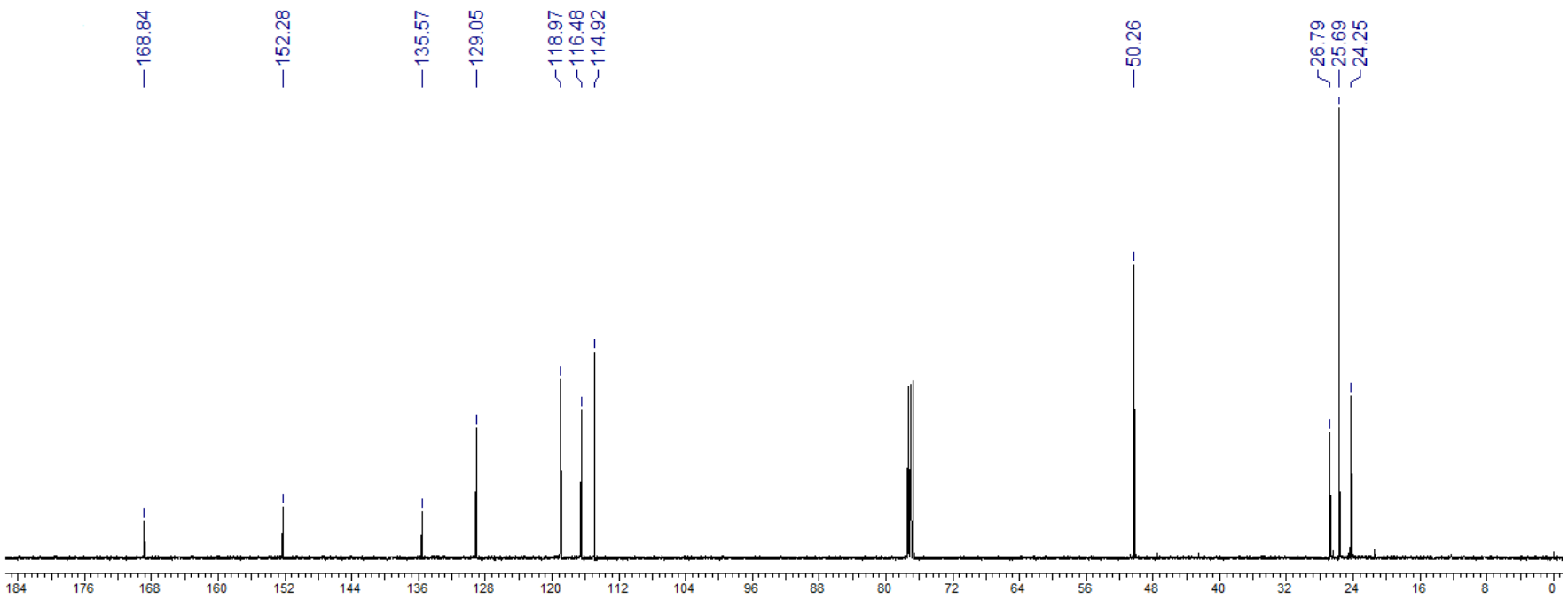


***N*-Methyl-3-(piperidin-1-yl)benzamide (7i).**

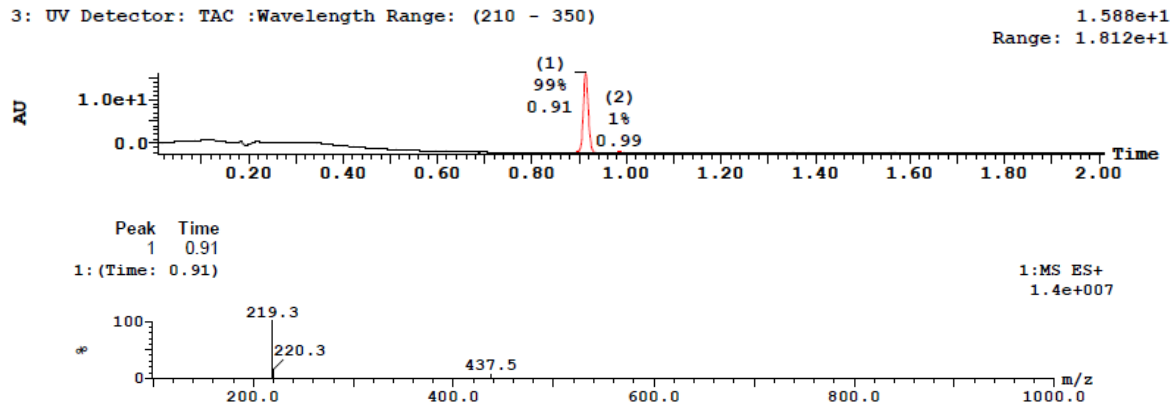
^{1}H NMR Spectra



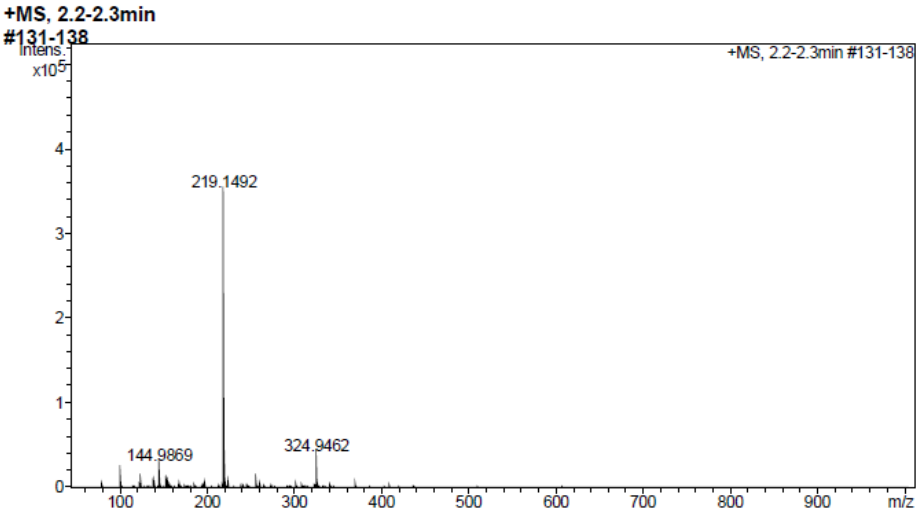
^{13}C NMR Spectra



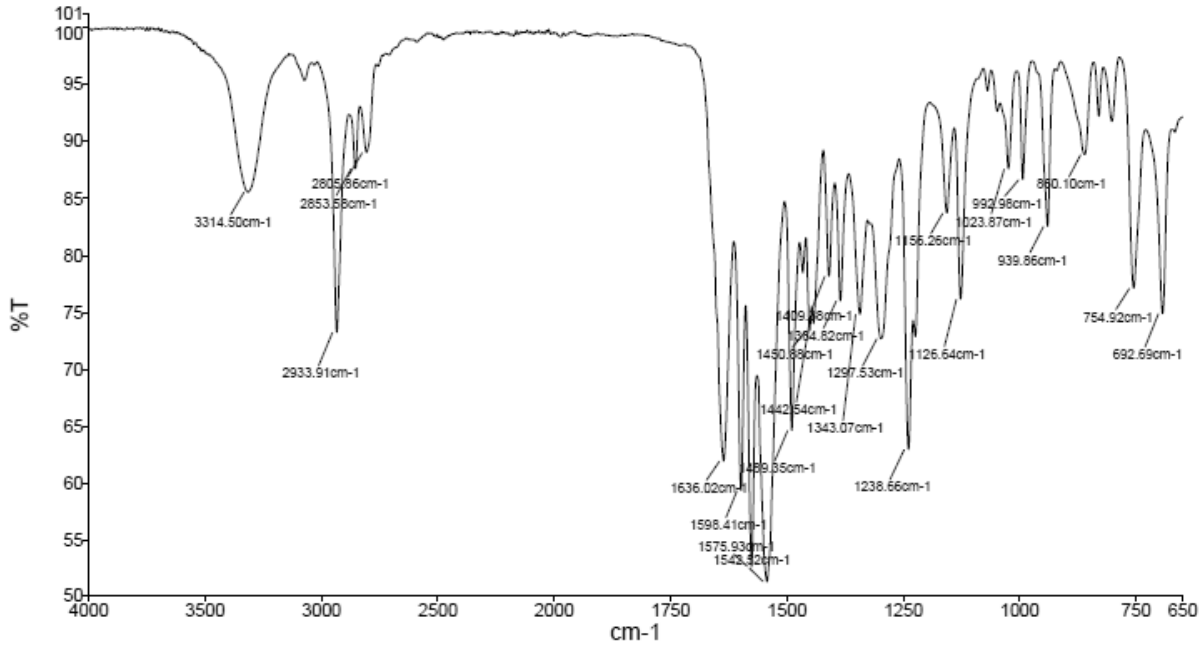
LCMS



HRMS

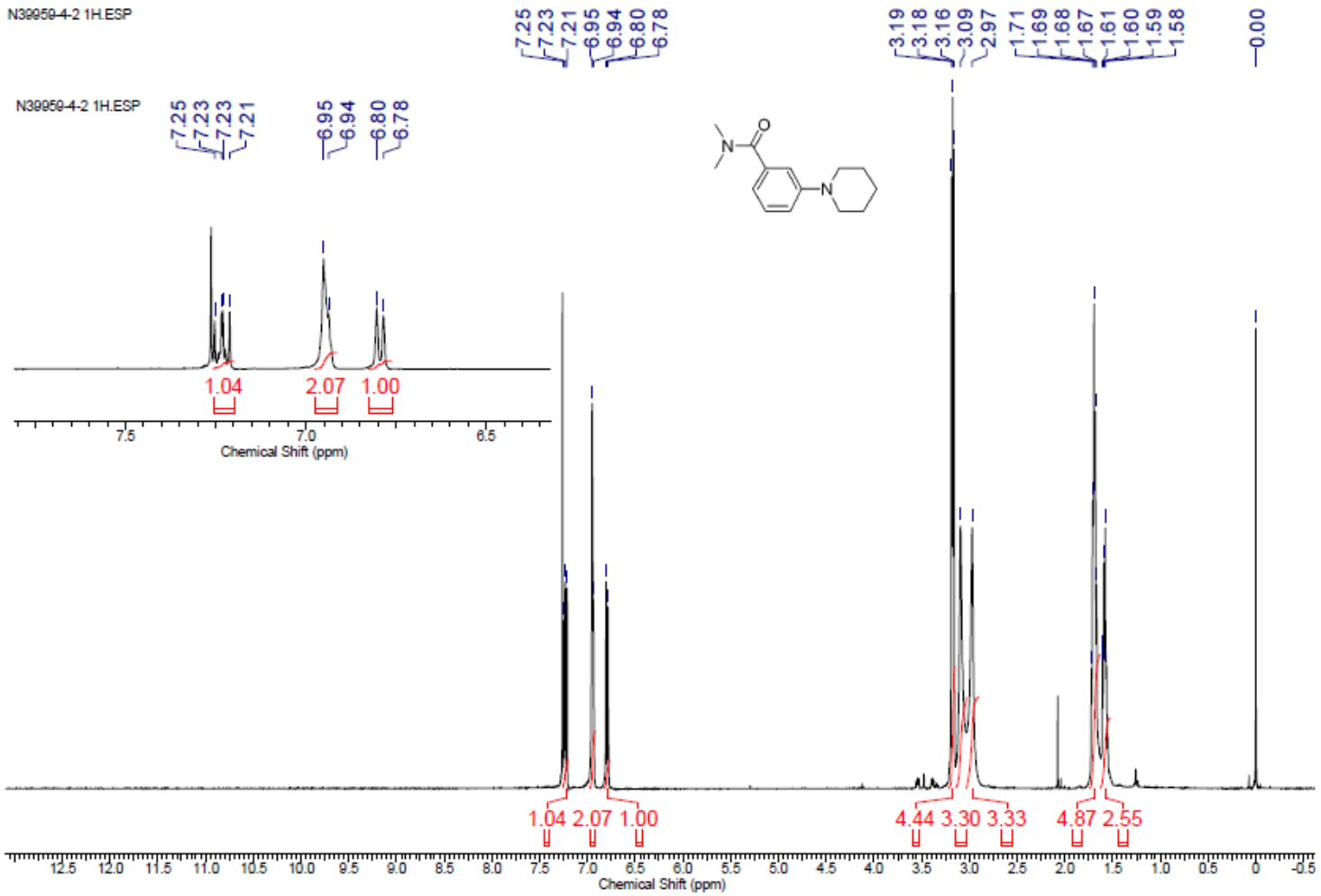


IR Spectra

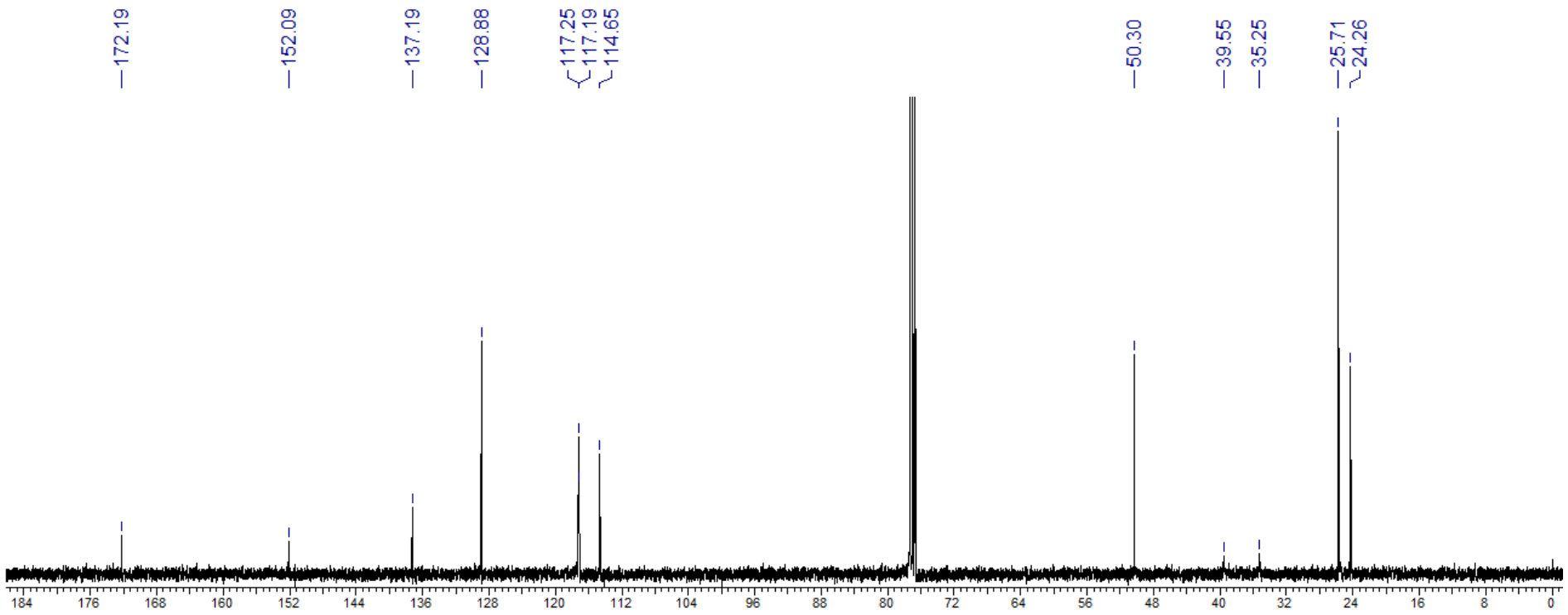


***N*,*N*-Dimethyl-3-(piperidin-1-yl)benzamide (7j).**

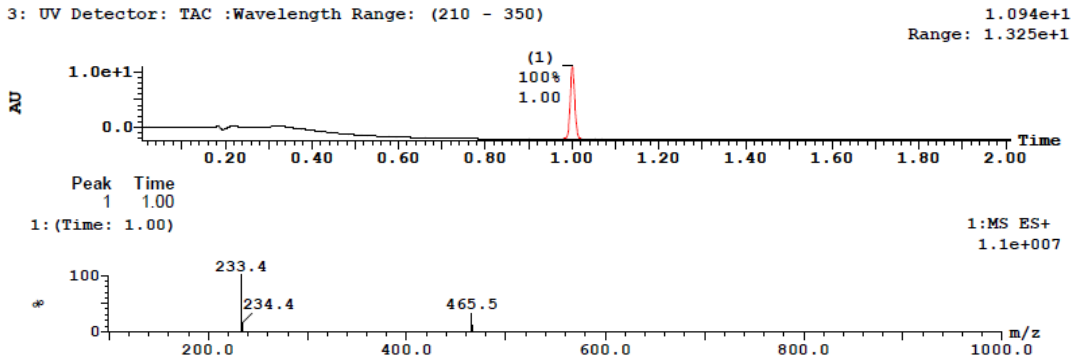
^{1}H NMR Spectra



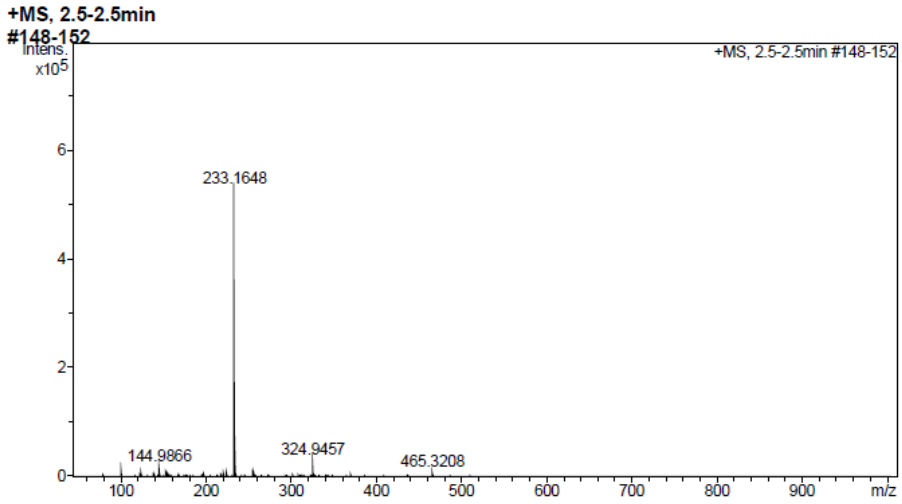
^{13}C NMR Spectra



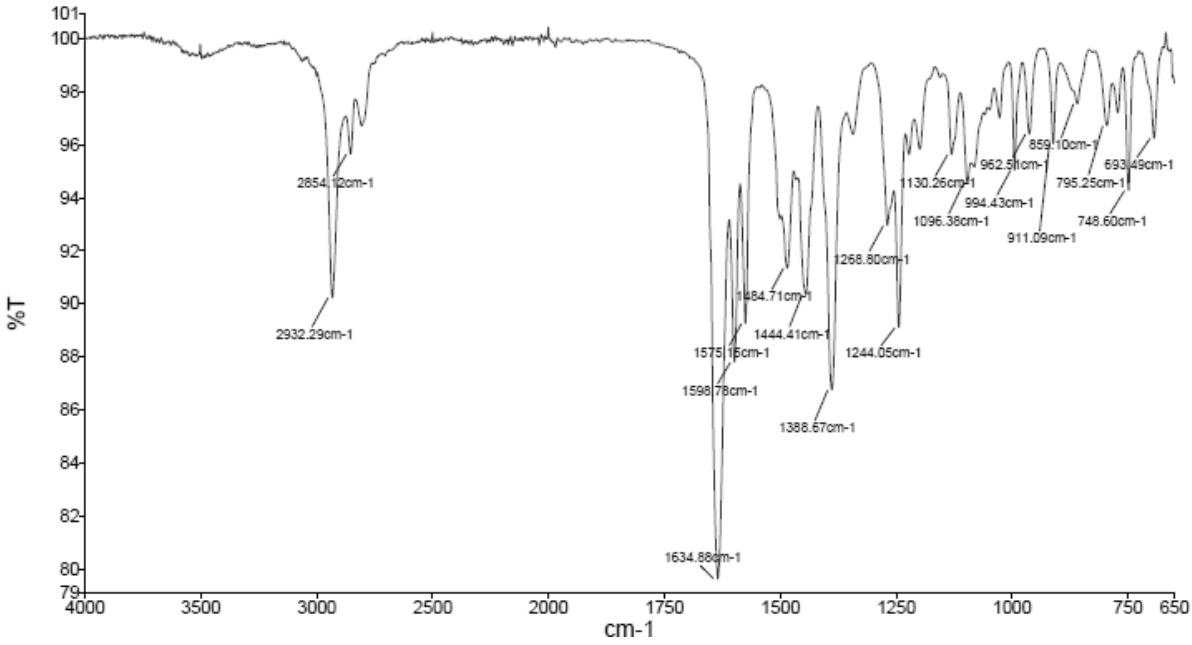
LCMS



HRMS

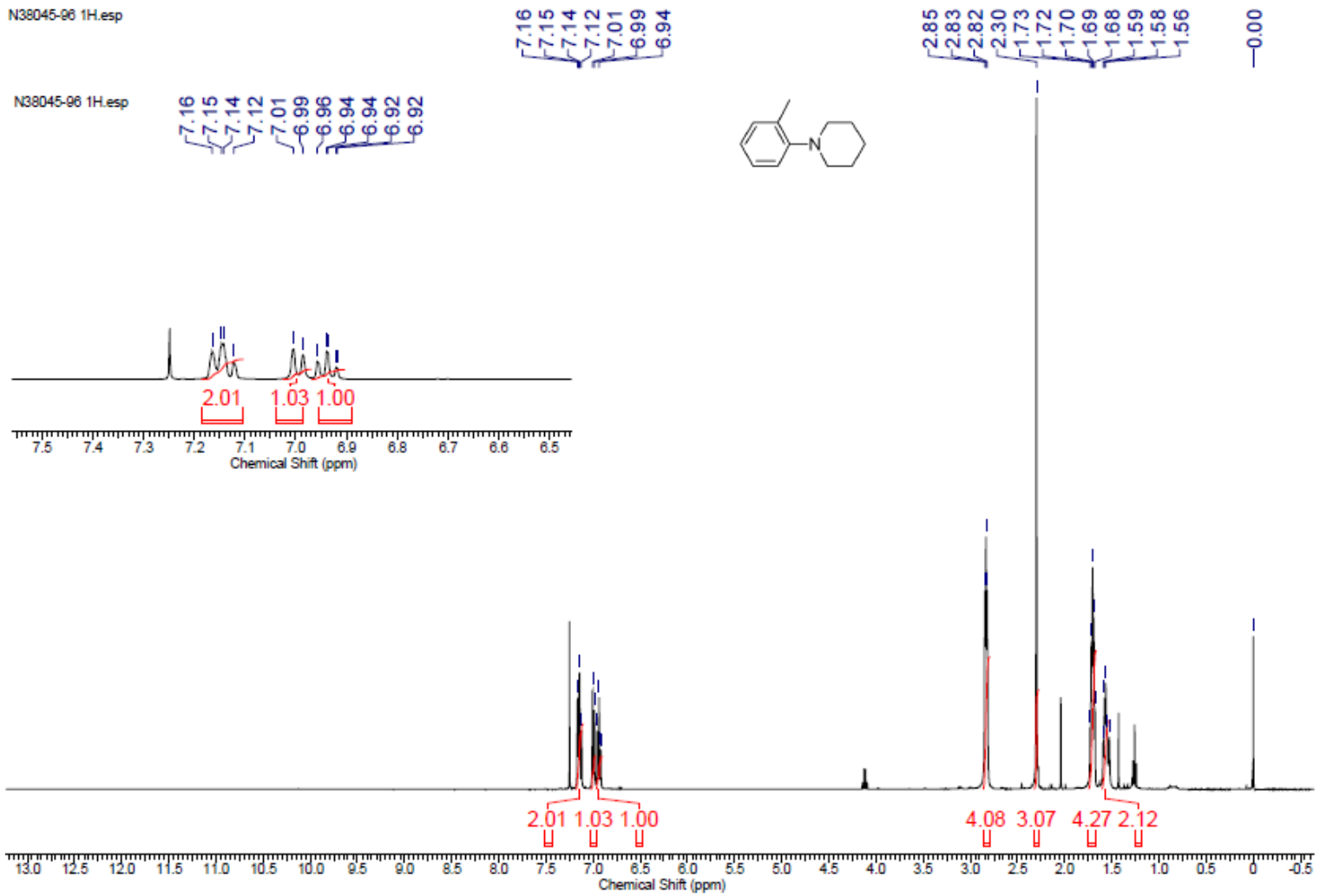


IR Spectra

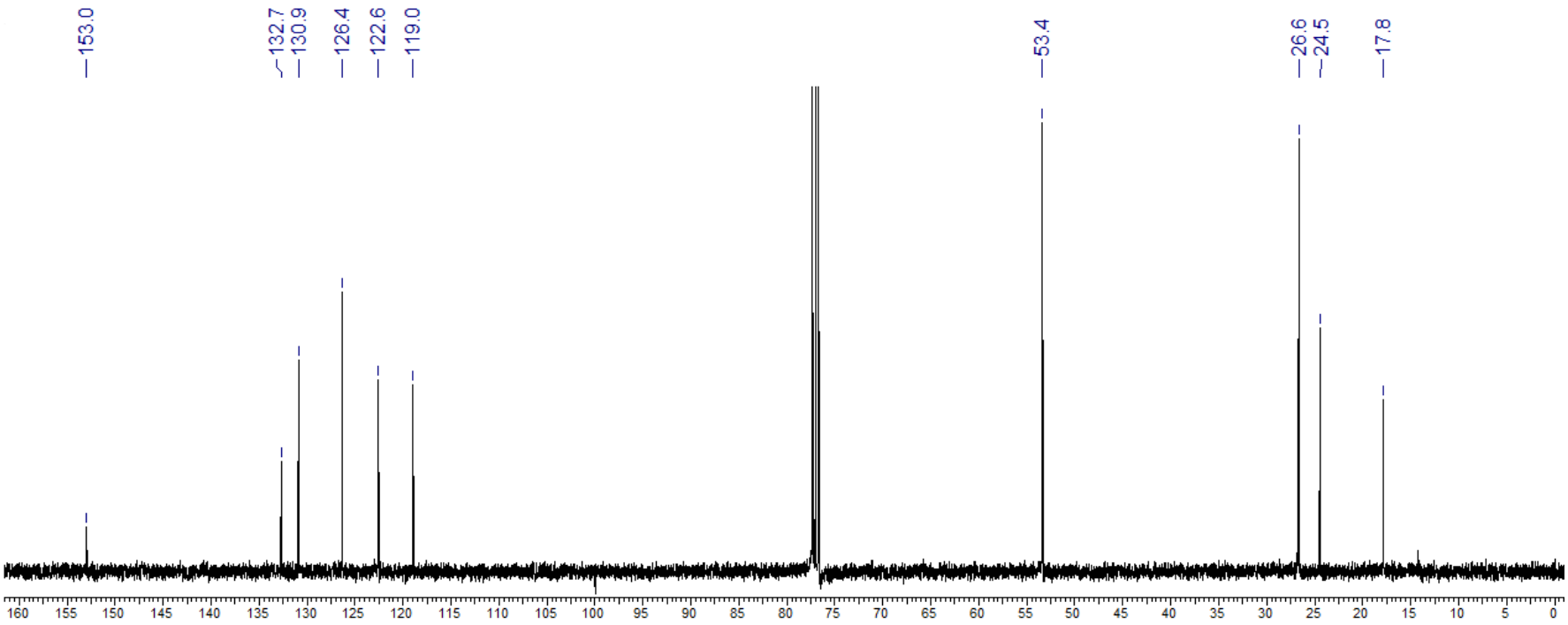


1-(*o*-Tolyl)piperidine (7k).

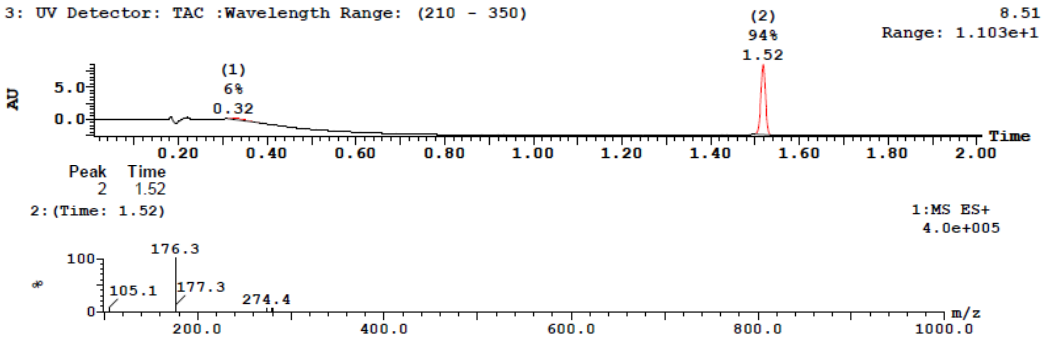
^{1}H NMR Spectra



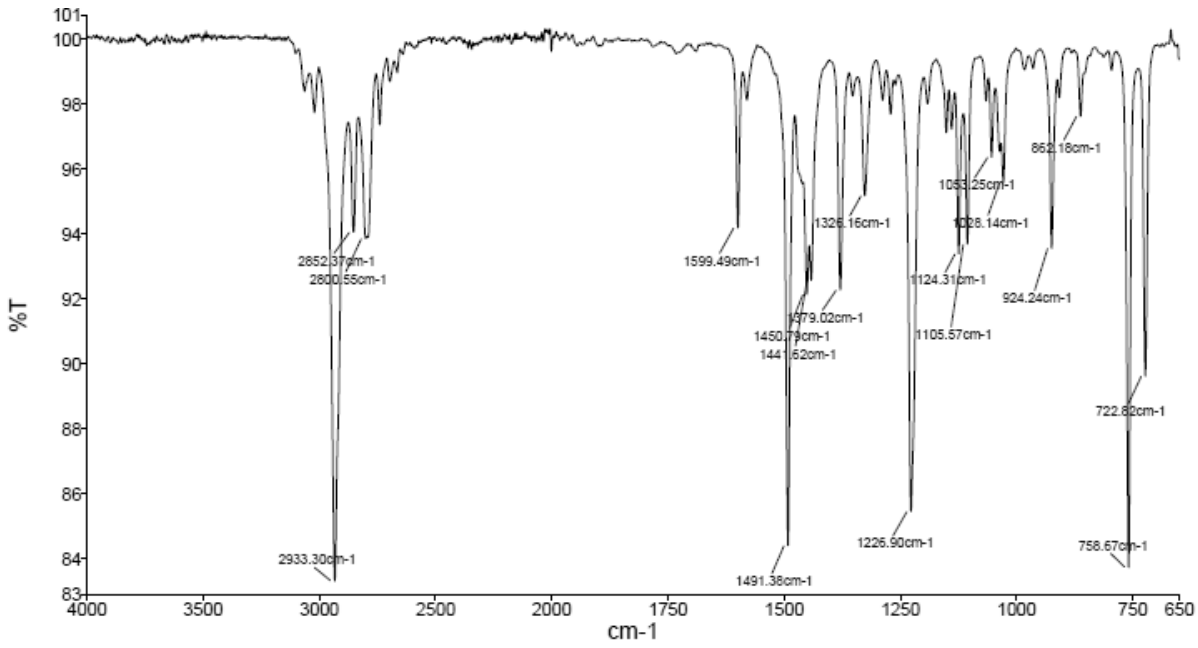
^{13}C NMR Spectra



LCMS

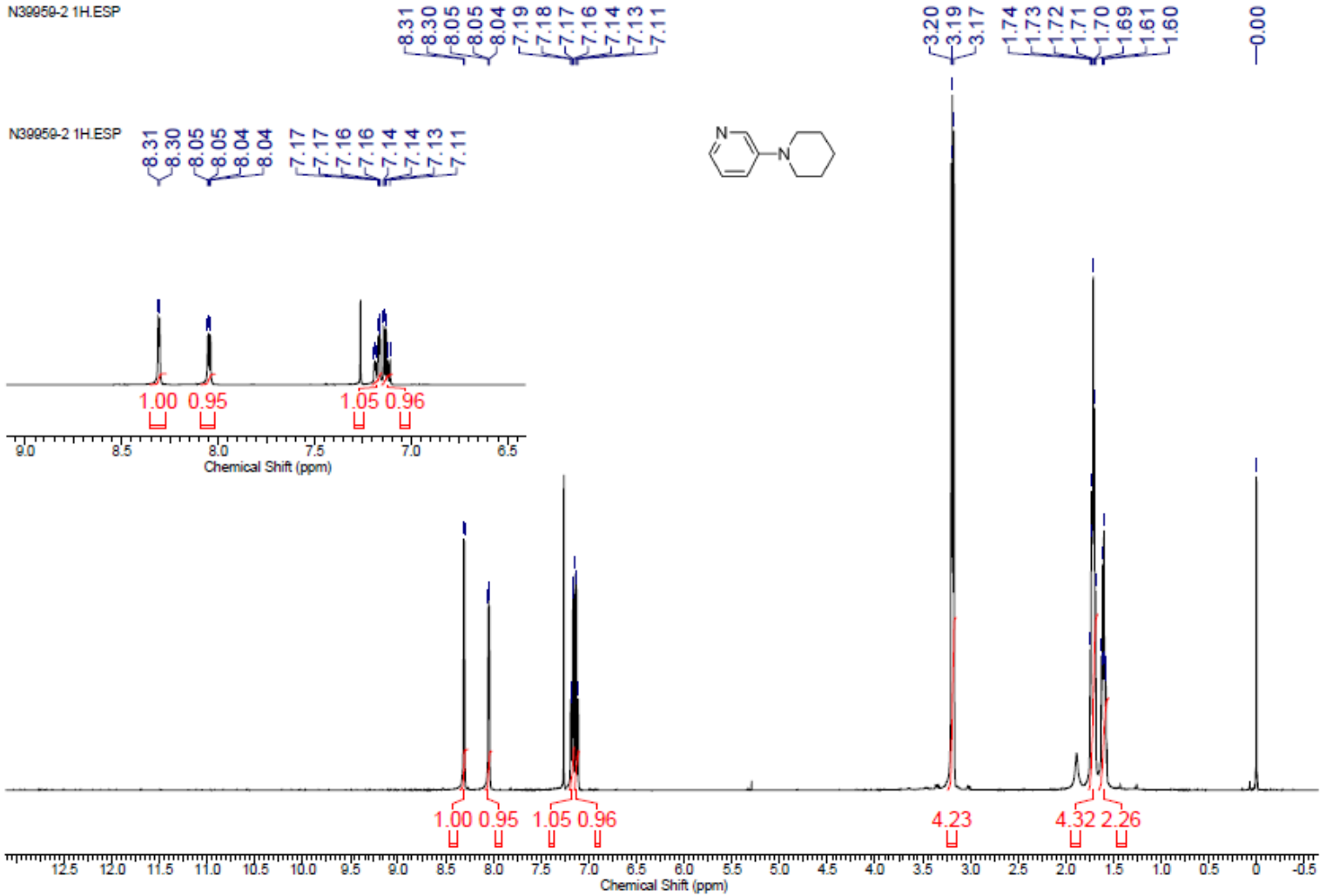


IR Spectra

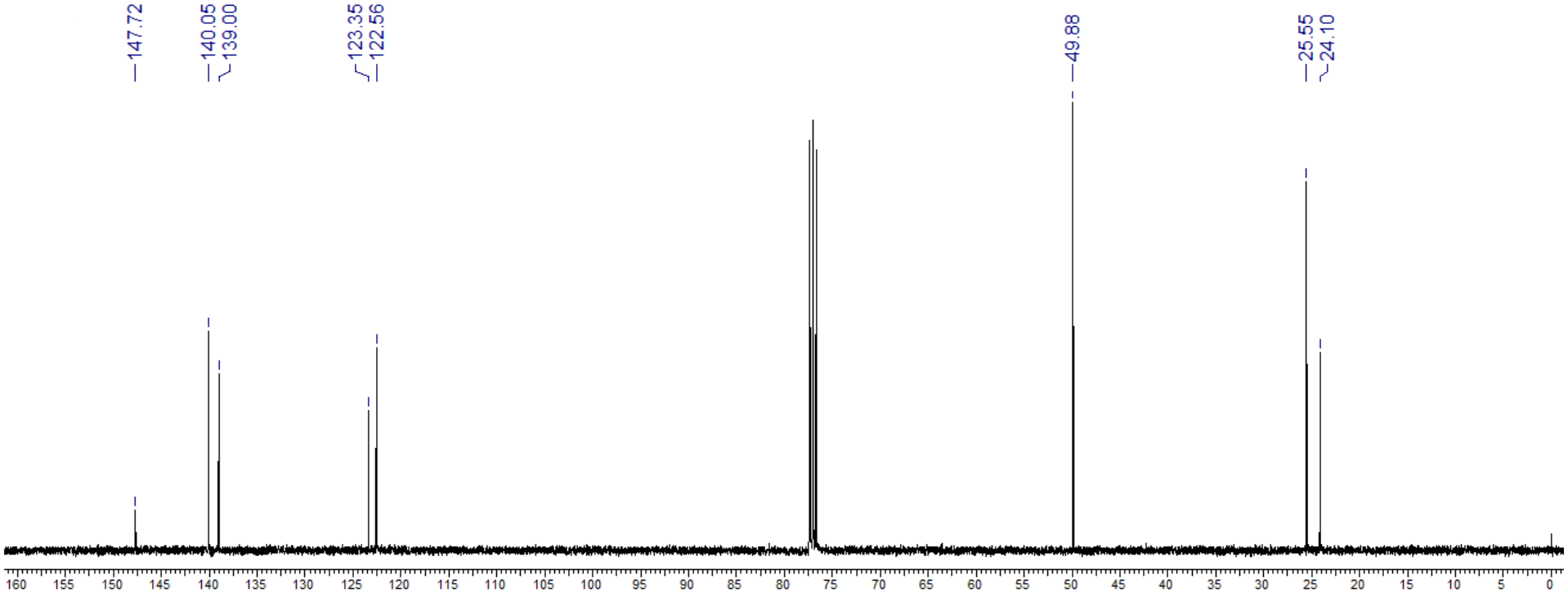


3-(Piperidin-1-yl)pyridine (7l).

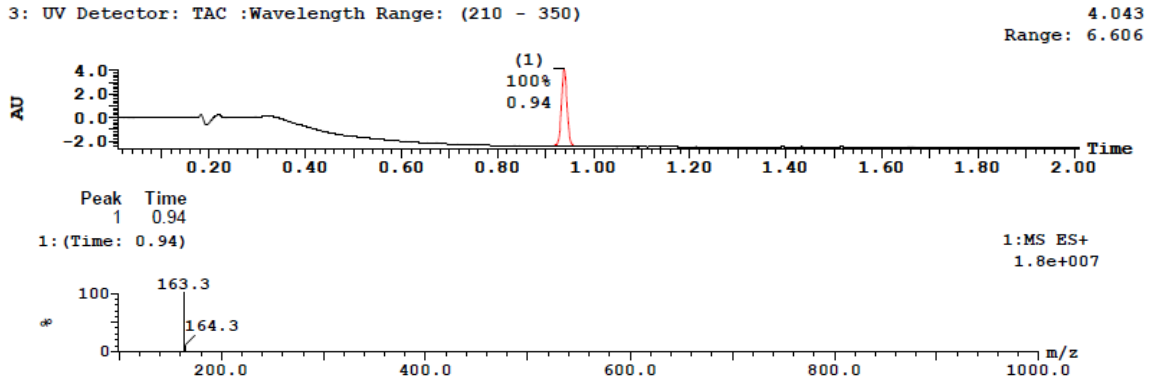
^{1}H NMR Spectra



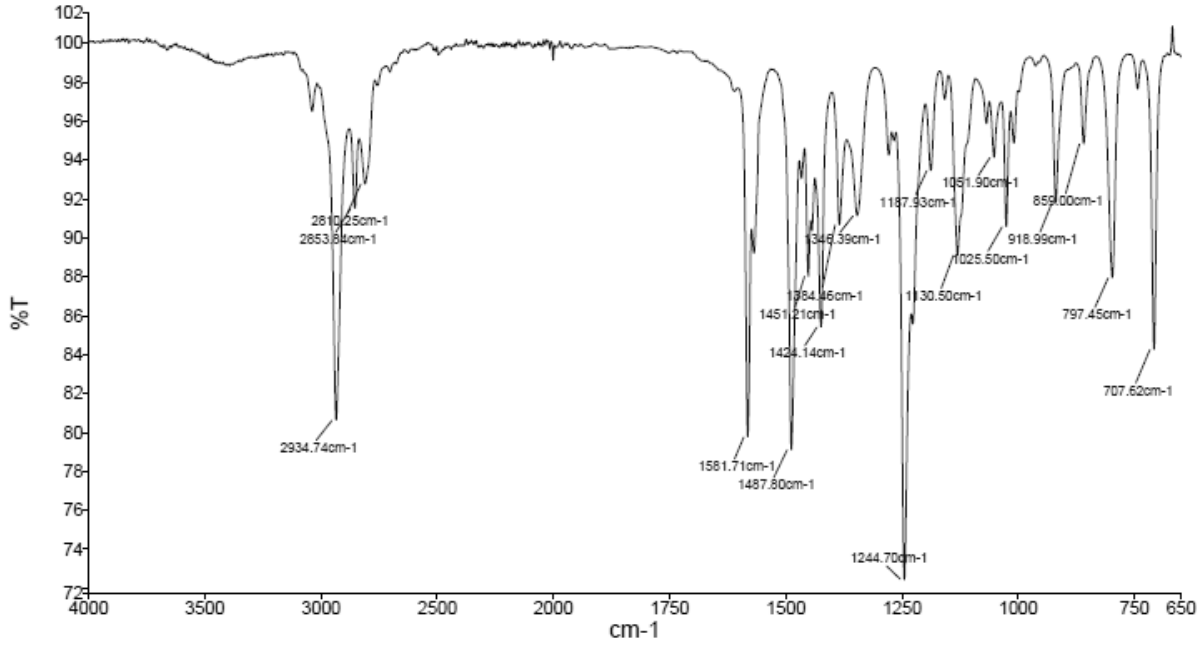
^{13}C NMR Spectra



LCMS

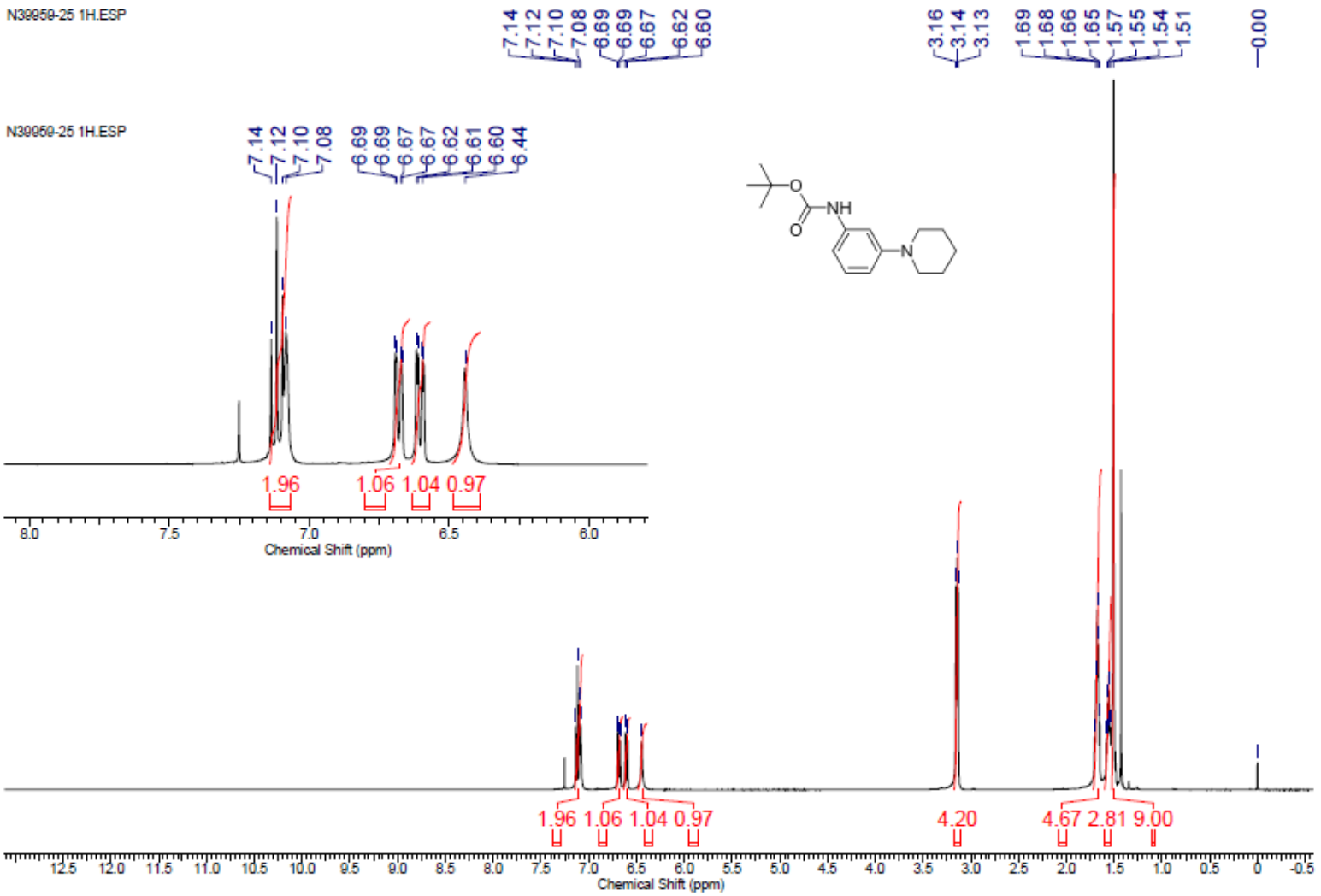


IR Spectra

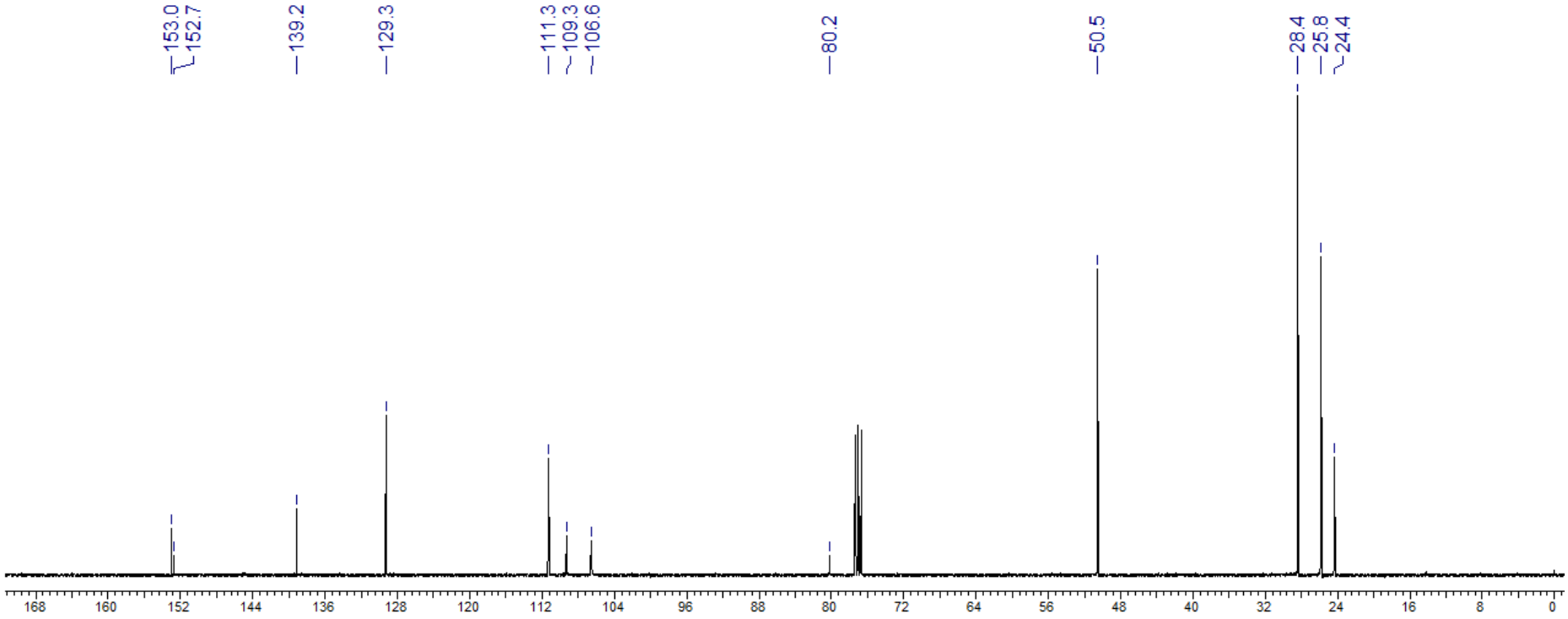


***tert*-Butyl (3-(piperidin-1-yl)phenyl)carbamate (7m).**

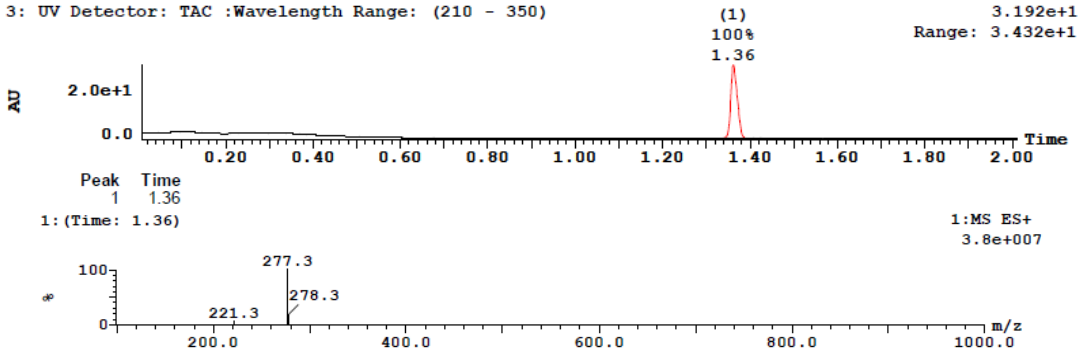
^{1}H NMR Spectra



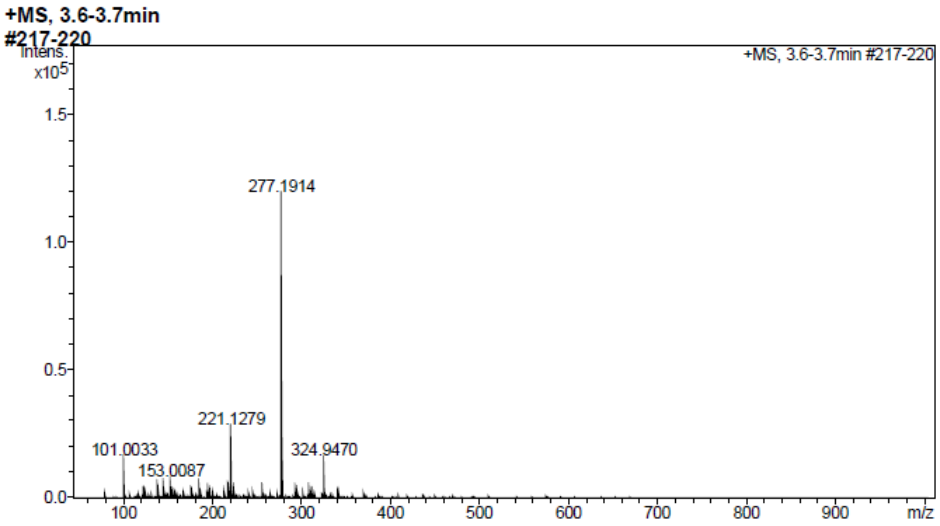
^{13}C NMR Spectra



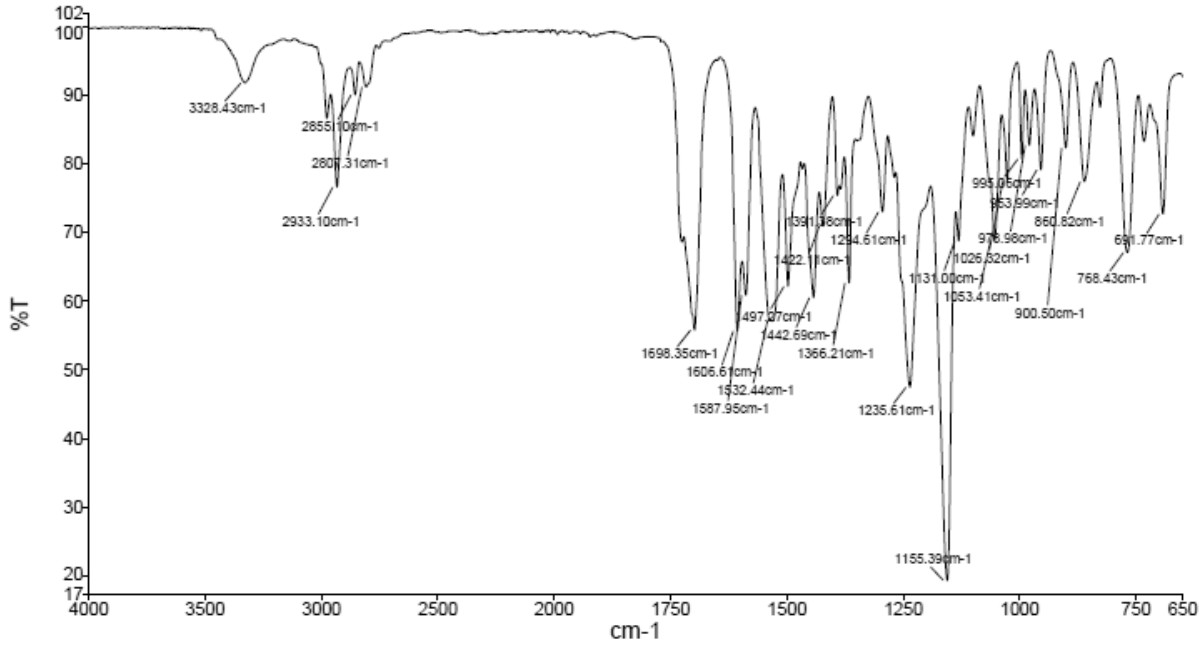
LCMS



HRMS

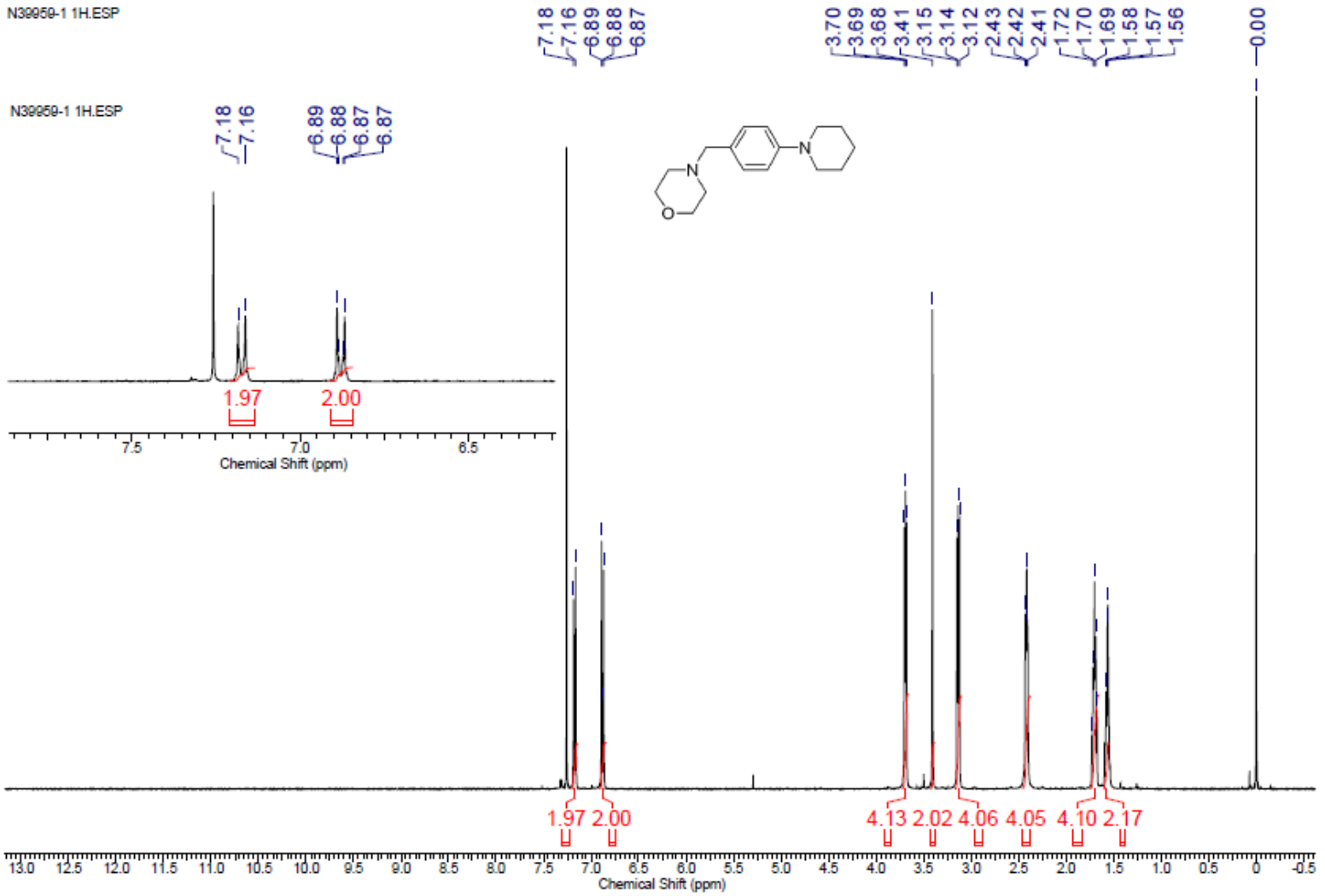


IR Spectra

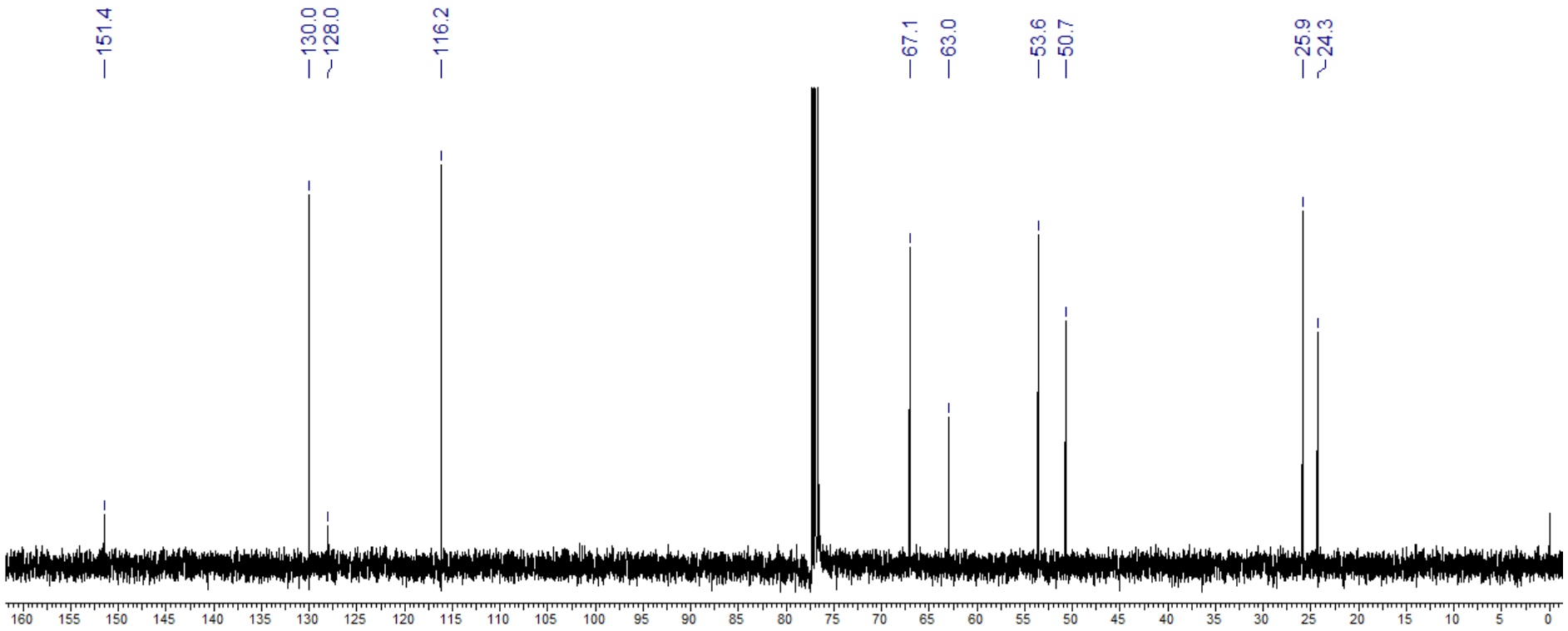


4-(4-(Piperidin-1-yl)benzyl)morpholine (7n).

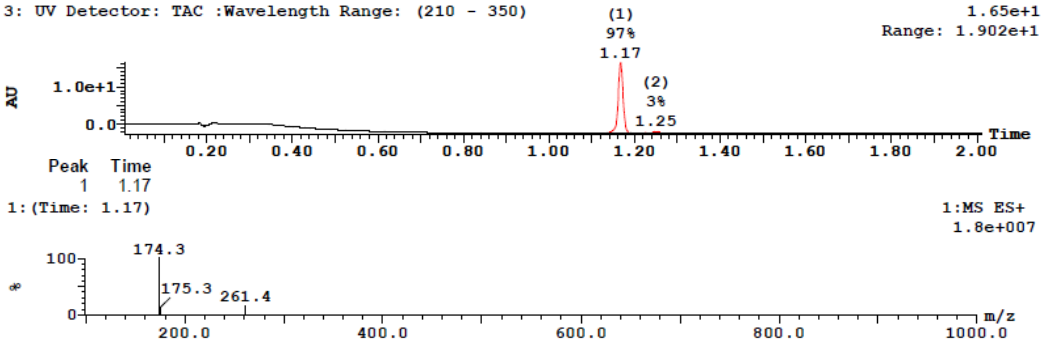
^{1}H NMR Spectra



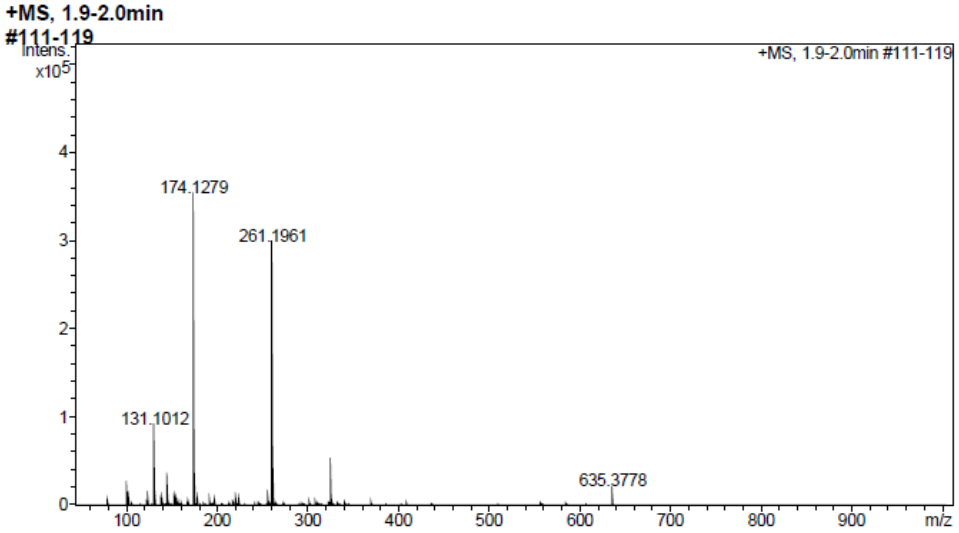
^{13}C NMR Spectra



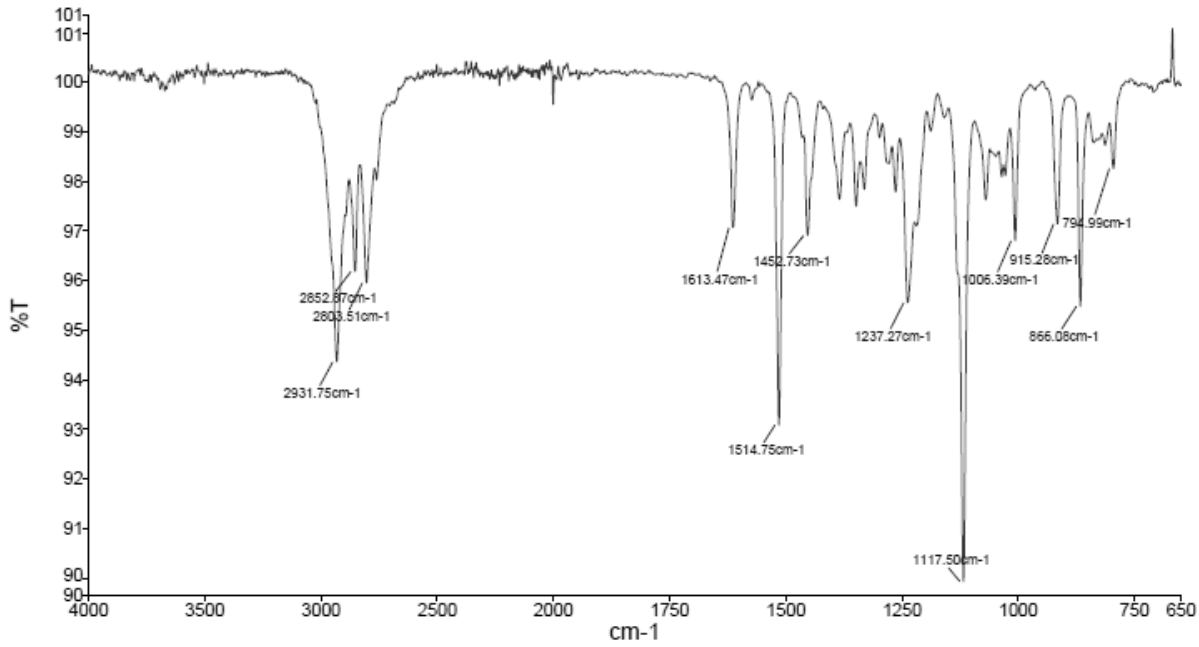
LCMS



HRMS

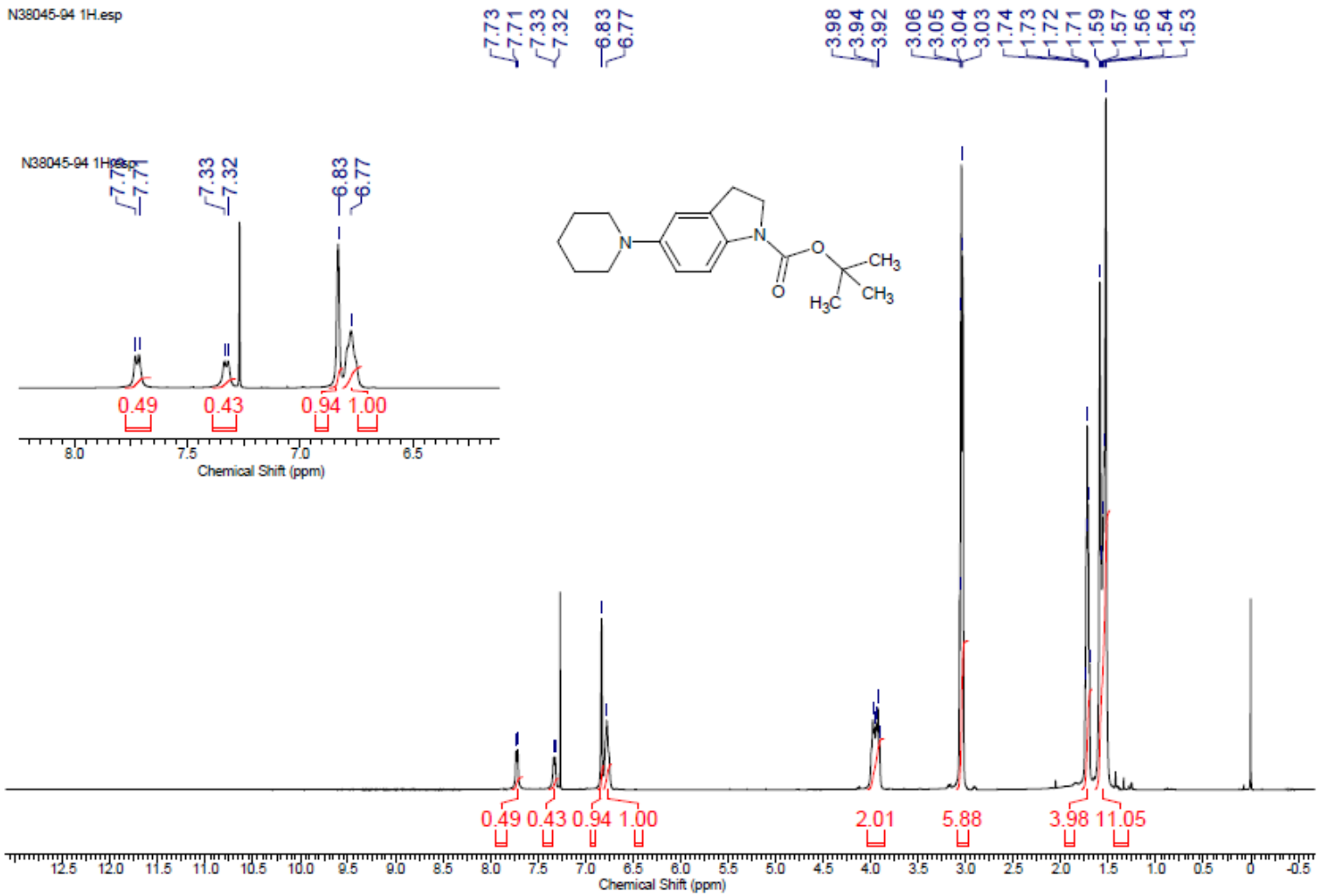


IR Spectra

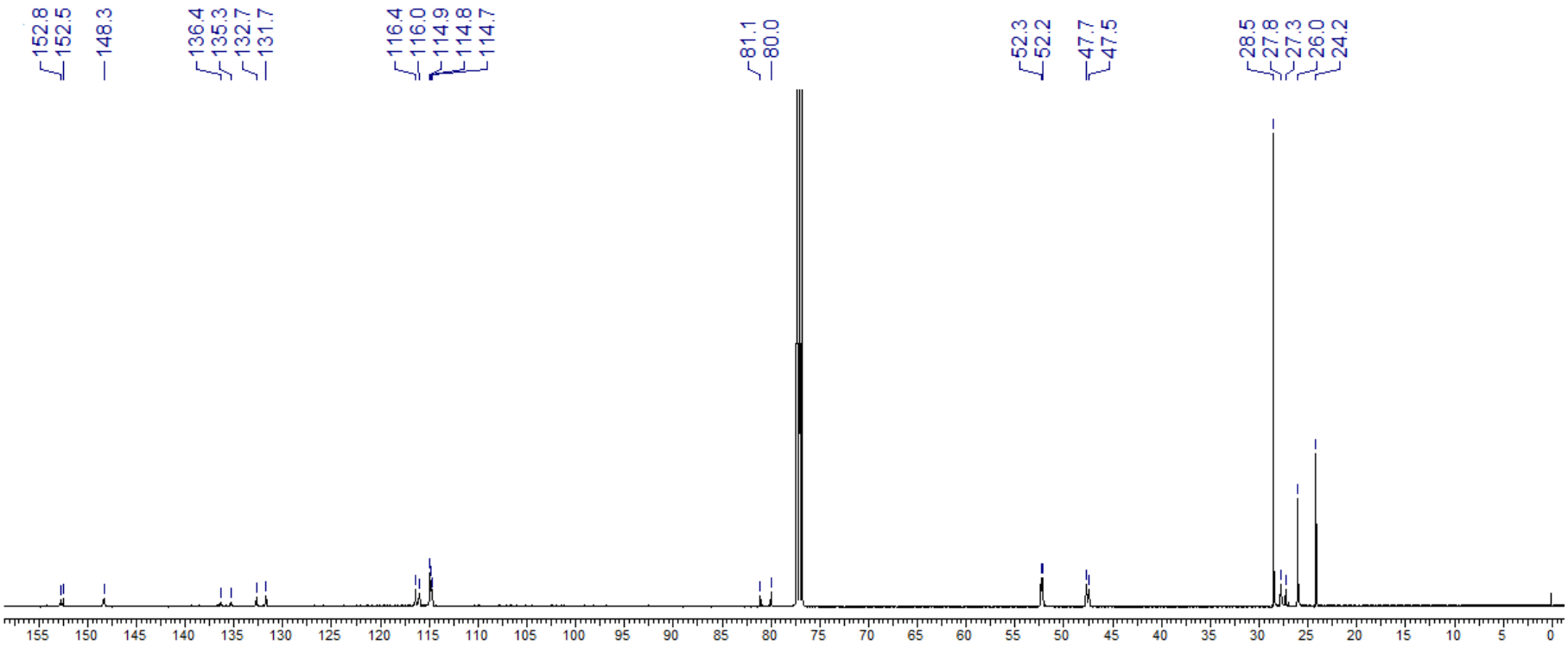


***tert*-Butyl 5-(piperidin-1-yl)indoline-1-carboxylate (7o).**

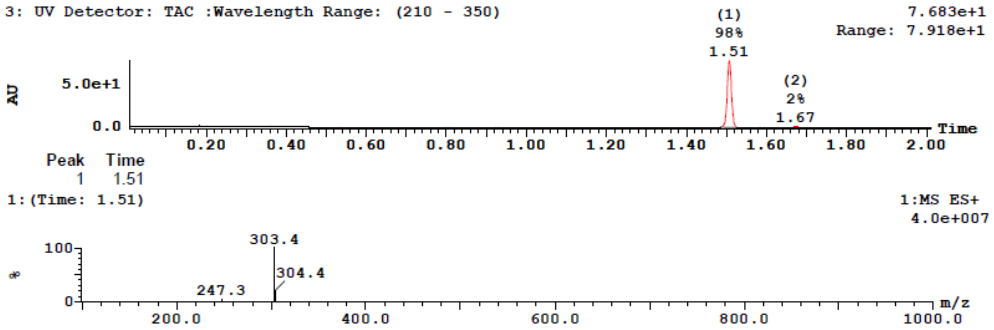
^{1}H NMR Spectra



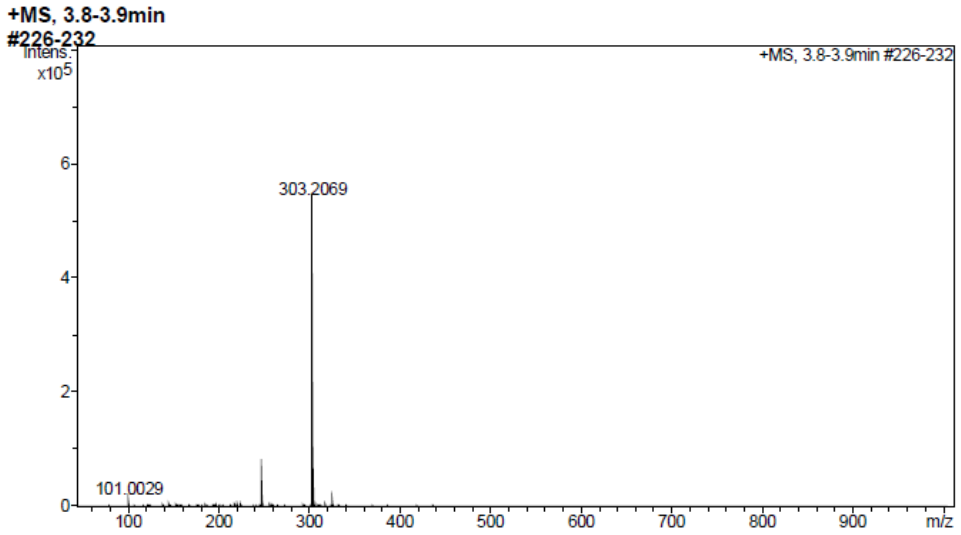
^{13}C NMR Spectra



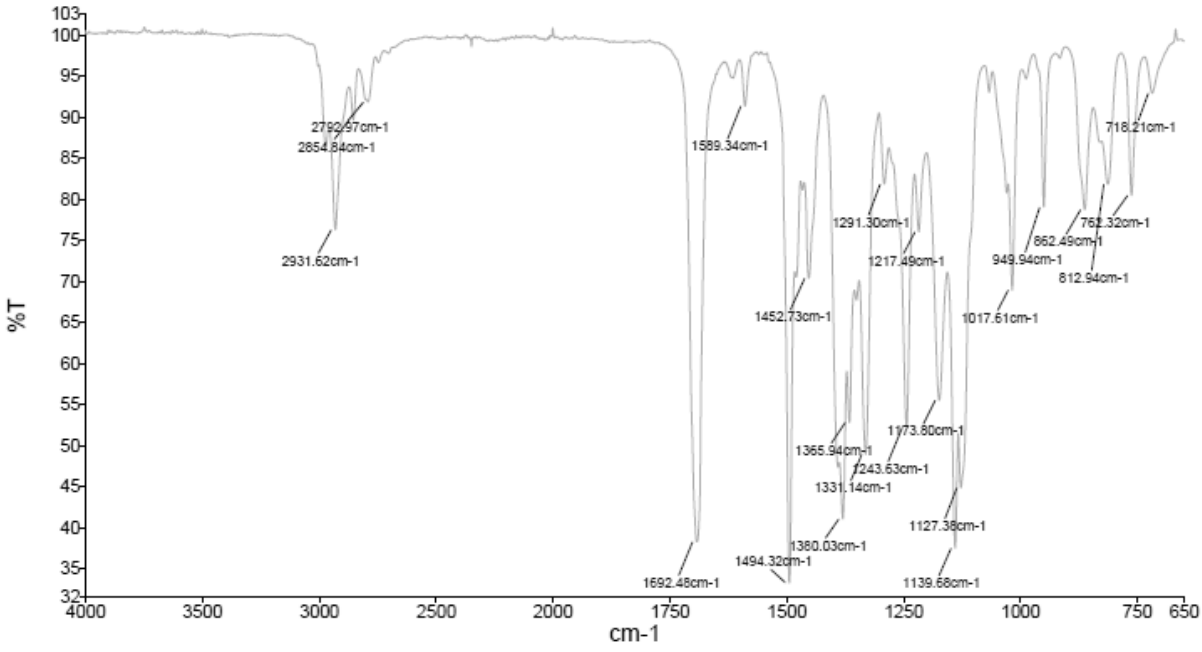
LCMS



HRMS

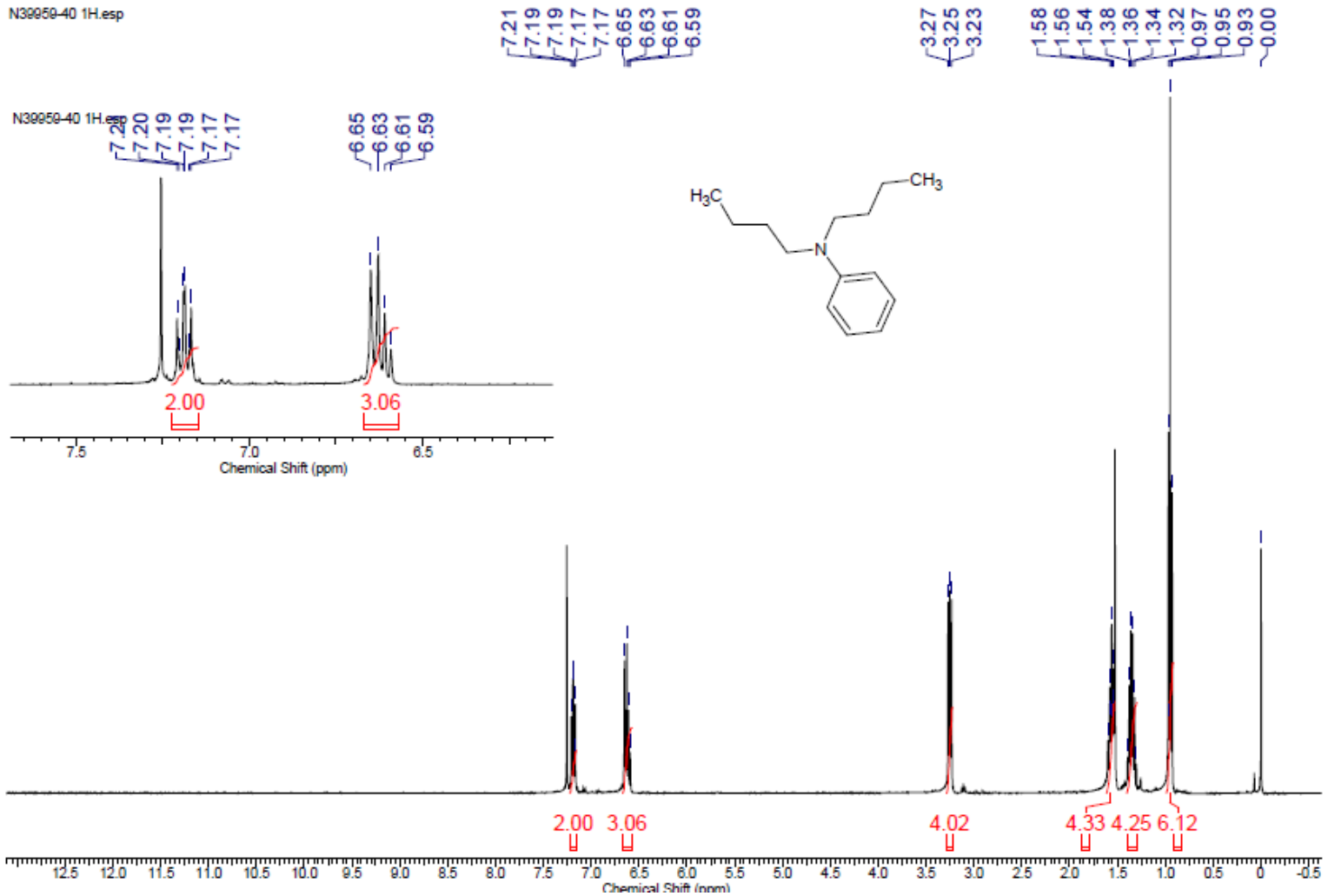


IR Spectra

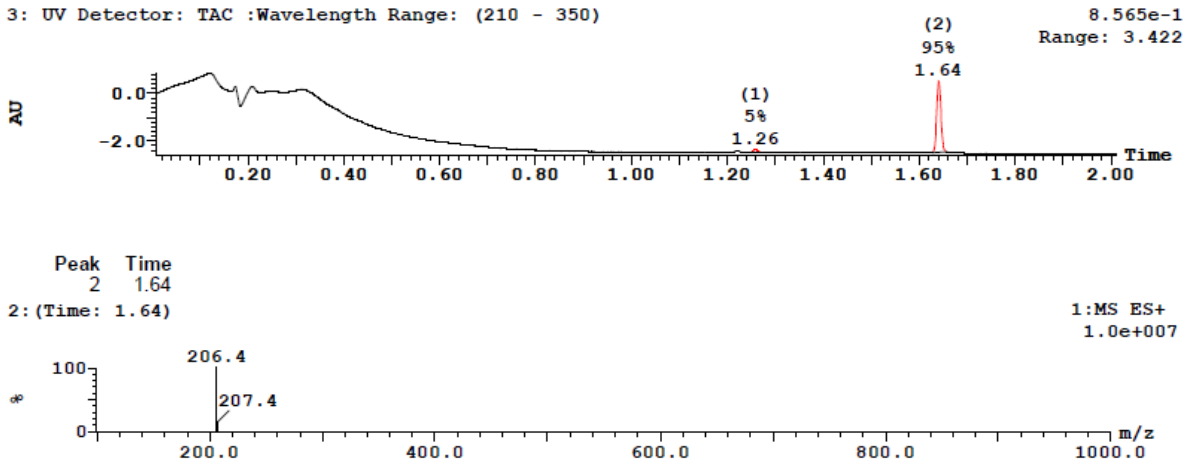


***N*,*N*-Dibutylaniline (7p).**

^{1}H NMR Spectra



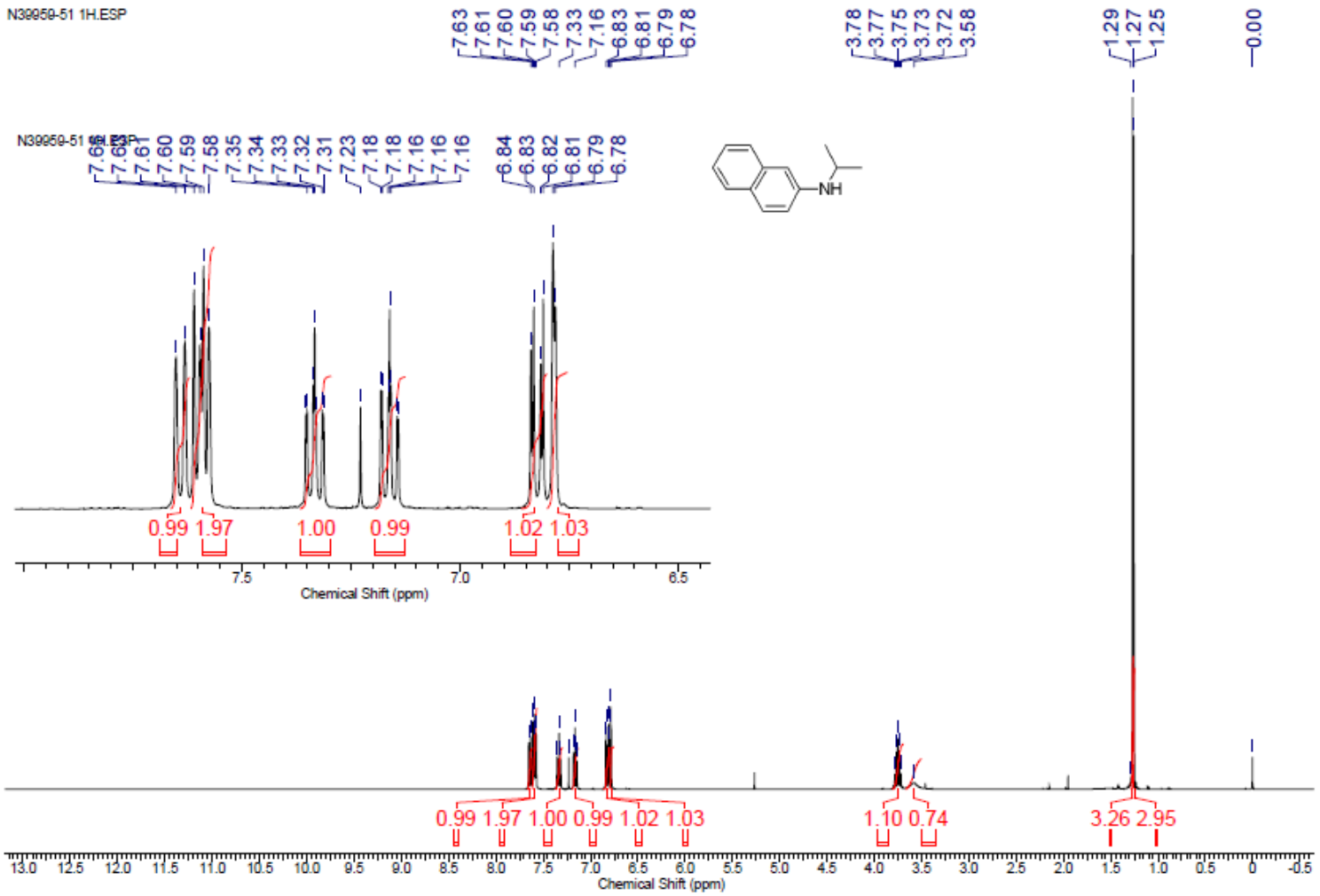
LCMS


3: UV Detector: TAC :Wavelength Range: (210 - 350)
8.565e-1
Range: 3.422
(2)
95%
1.64
(1)
5%
1.26
AU
0.0
-2.0
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
1.80
2.00
Time

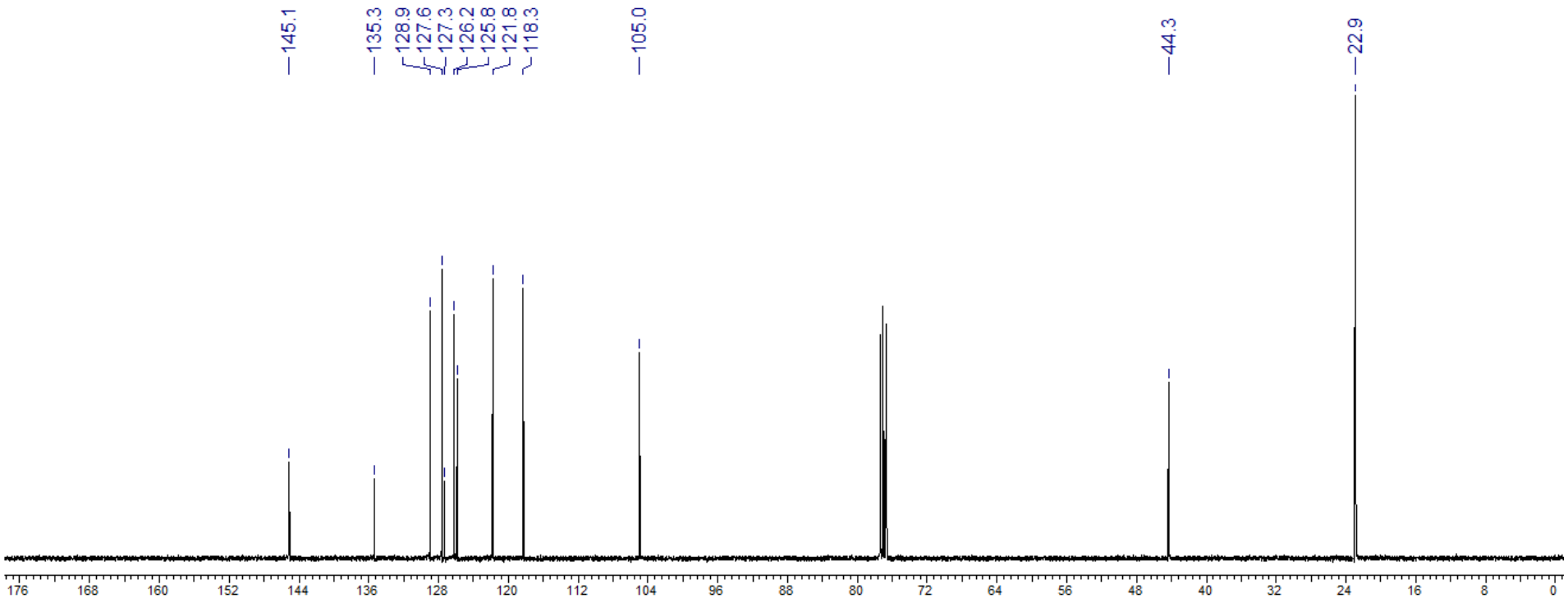
Peak Time
2 1.64
2:(Time: 1.64)
1:MS ES+
1.0e+007
206.4
207.4
100
%
0
200.0
400.0
600.0
800.0
1000.0
m/z

***N*-Isopropylnaphthalen-2-amine (7q).**

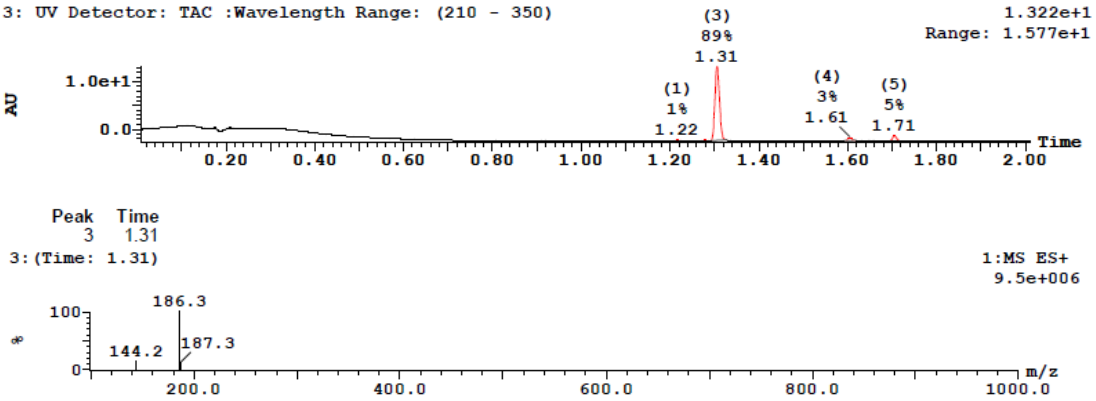
^{1}H NMR Spectra



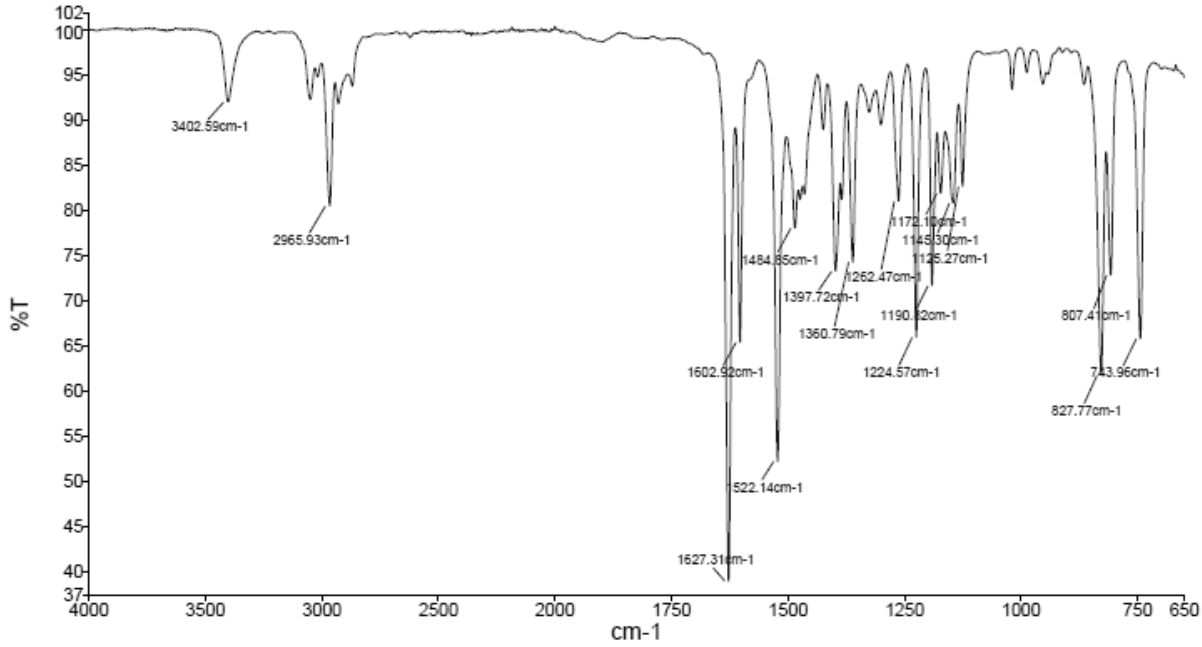
^{13}C NMR Spectra



LCMS

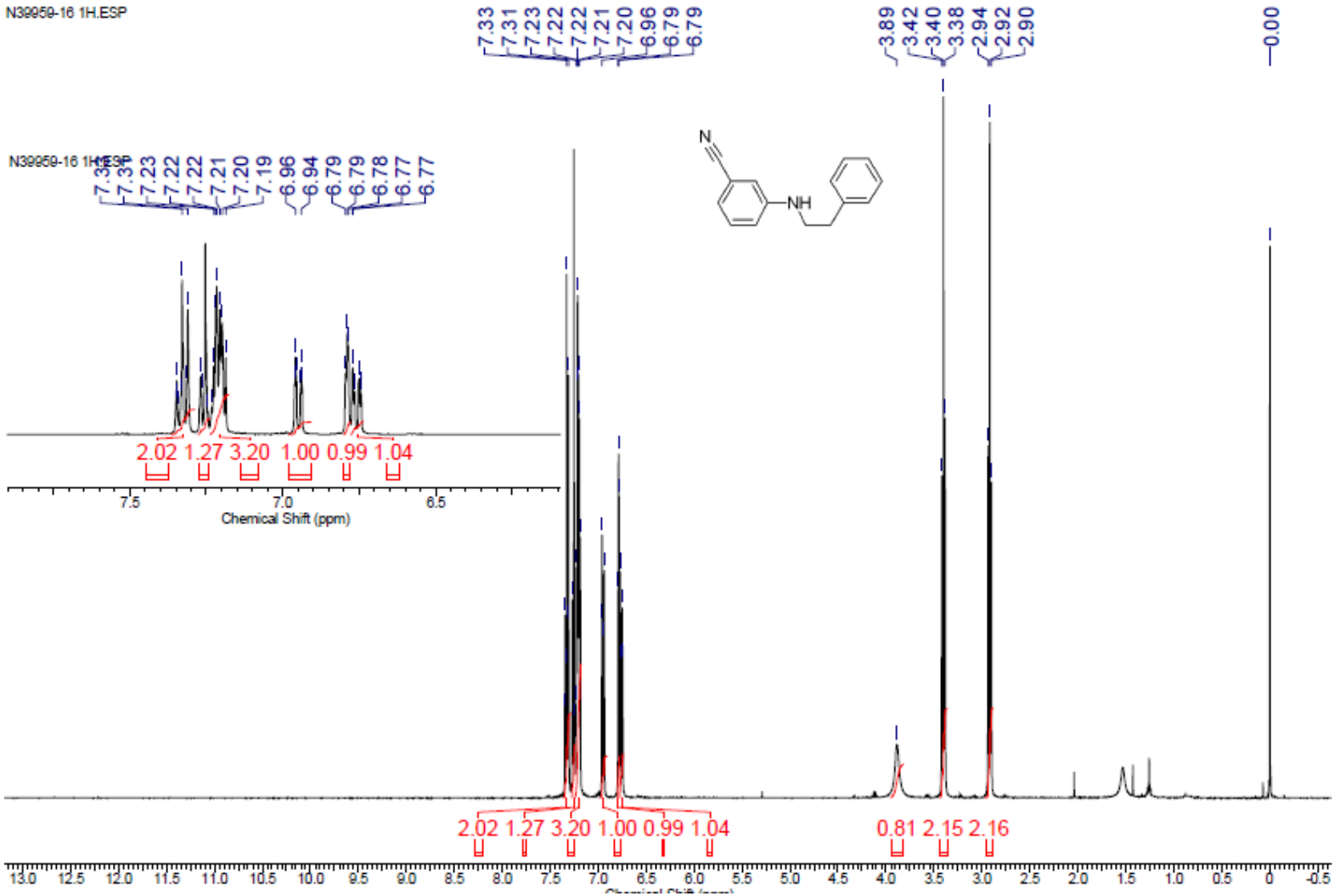


IR Spectra

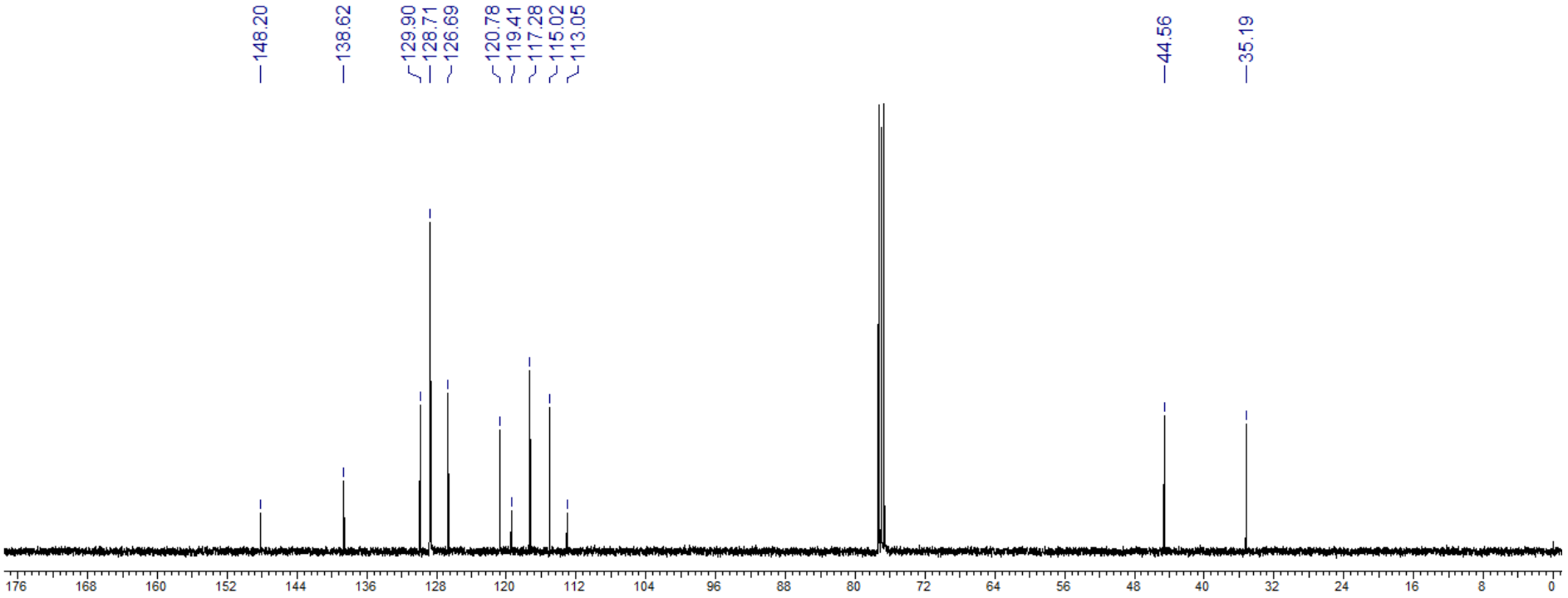


3-(Phenethylamino)benzonitrile (7r).

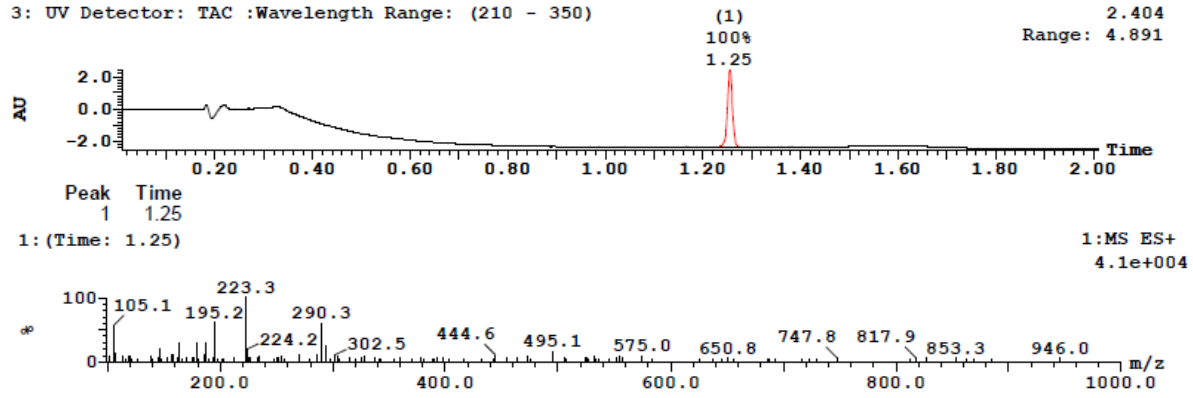
^{1}H NMR Spectra



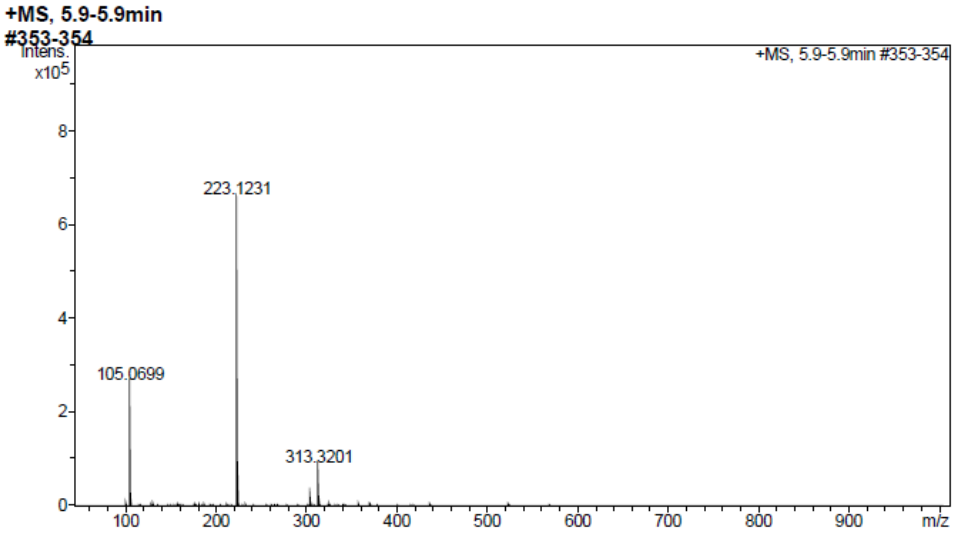
^{13}C NMR Spectra



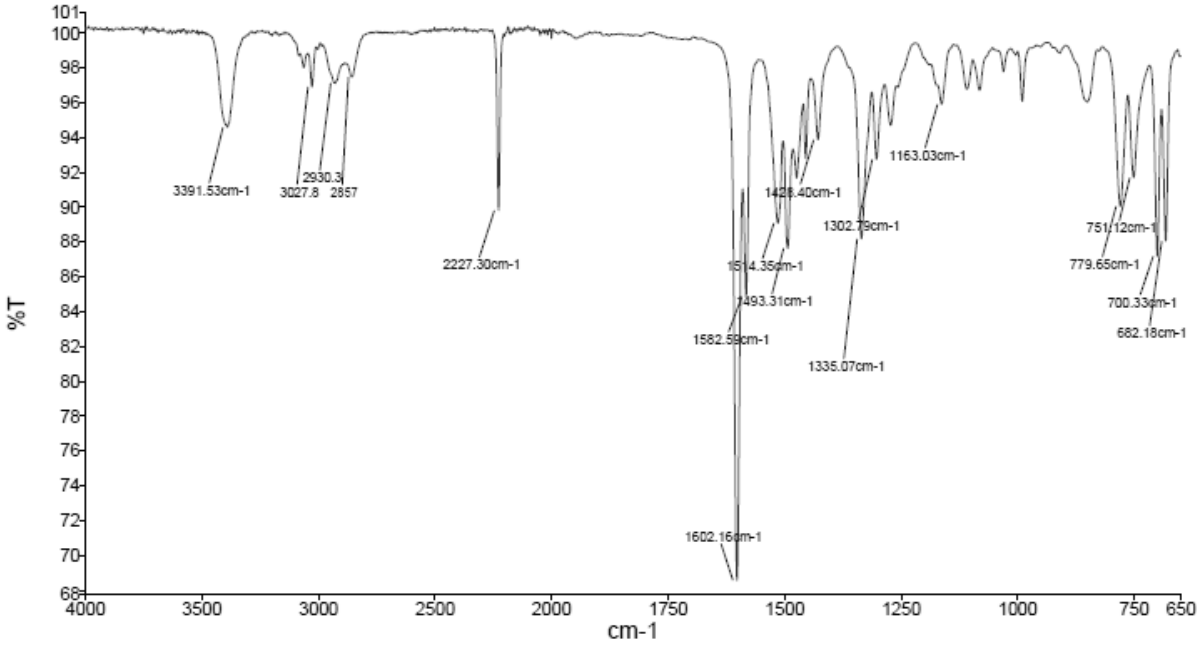
LCMS



HRMS

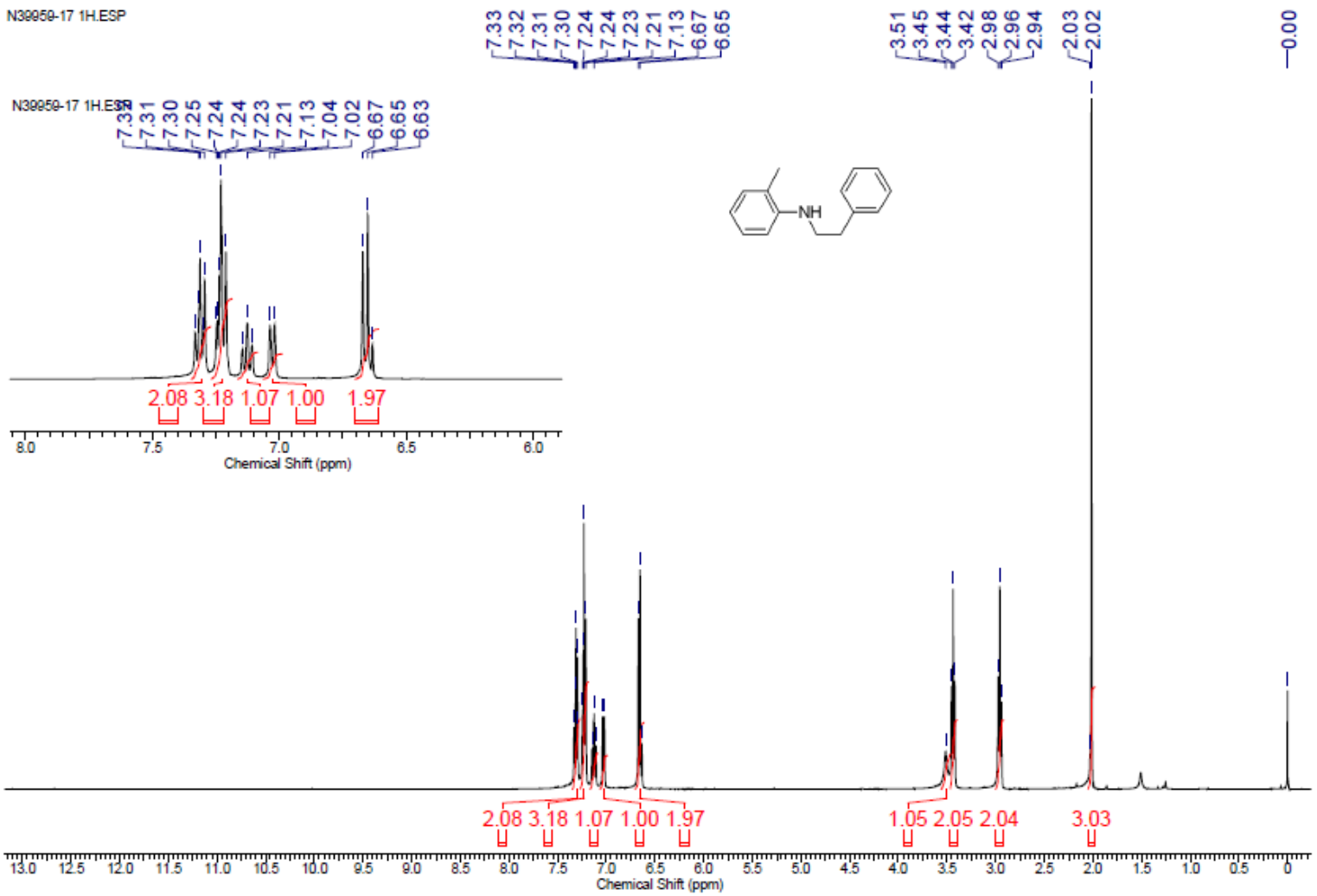


IR Spectra

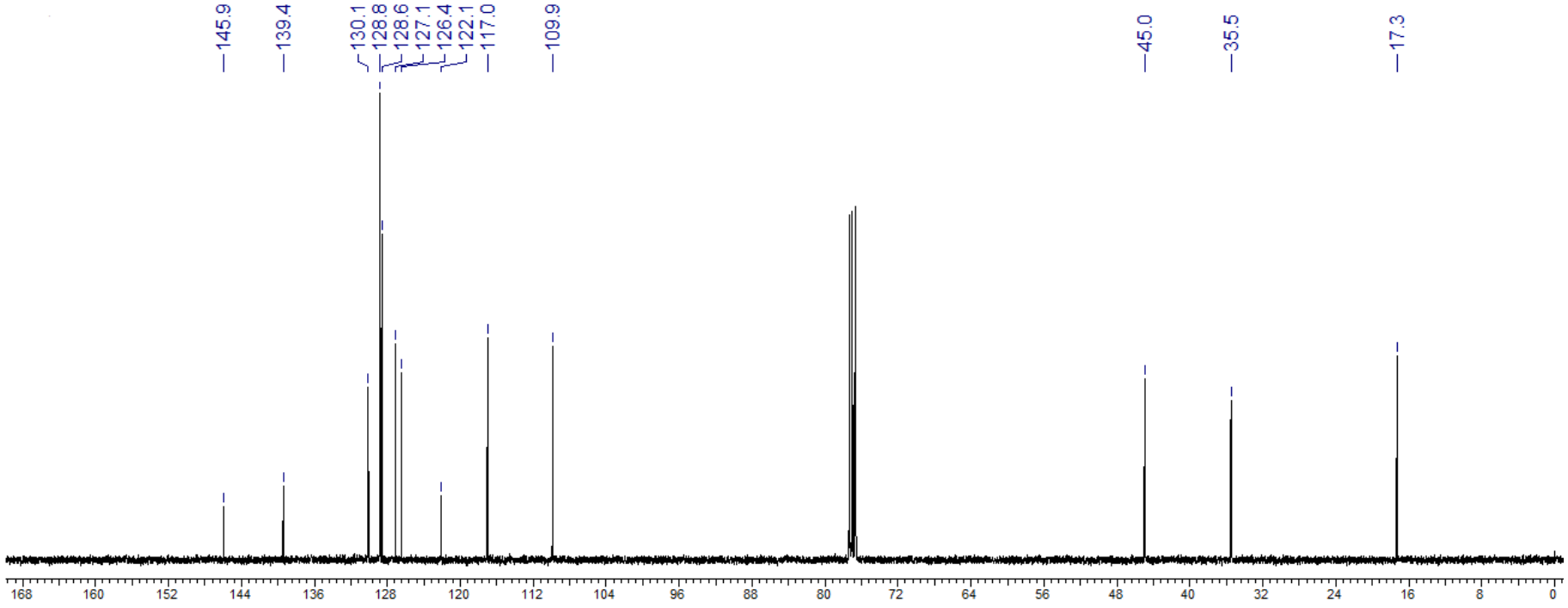


2-Methyl-*N*-phenethylaniline (7s).

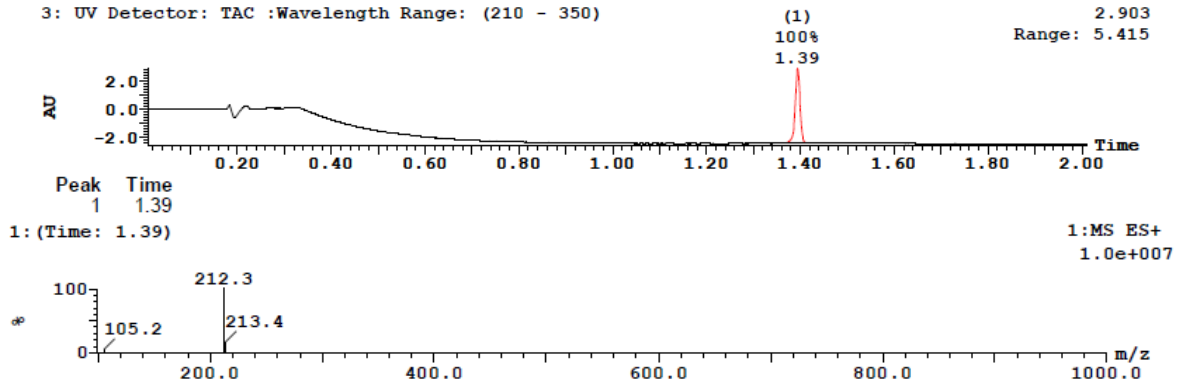
^{1}H NMR Spectra



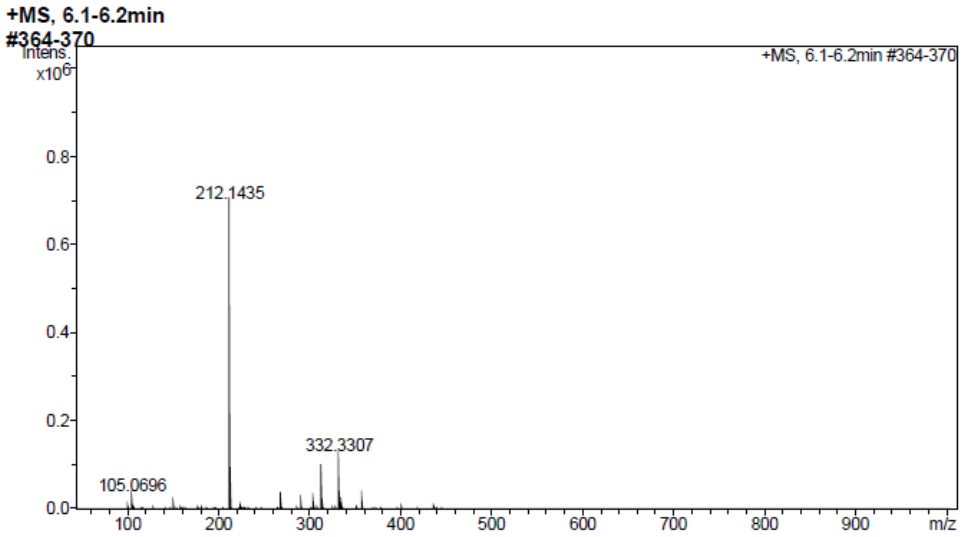
^{13}C NMR Spectra



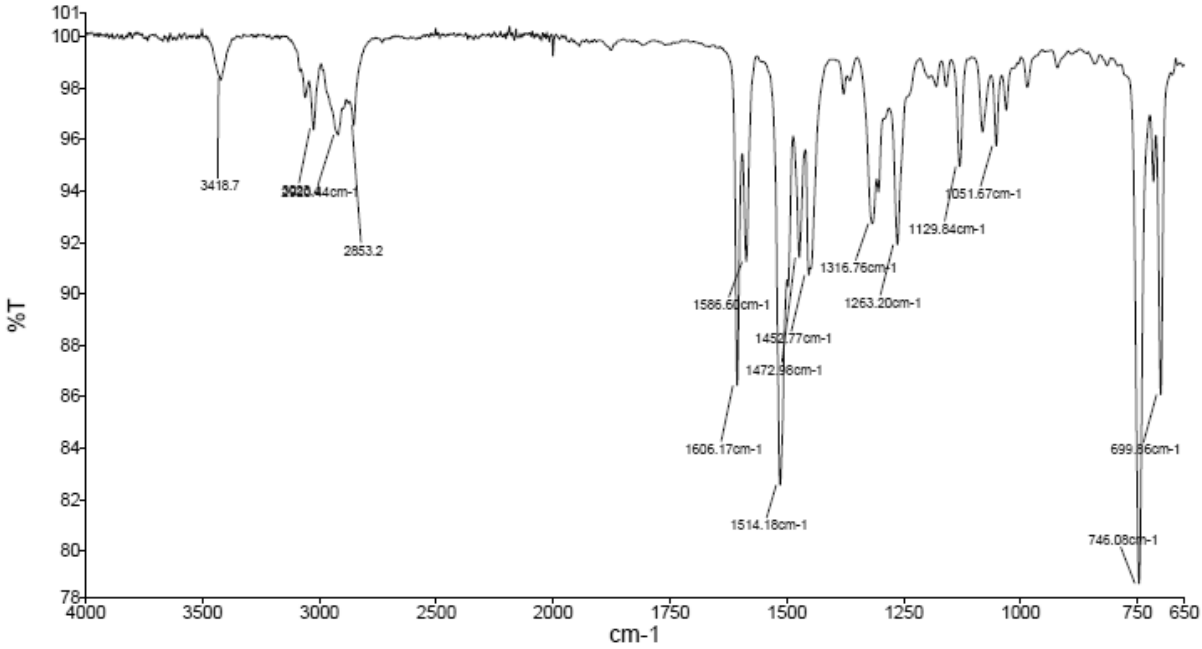
LCMS



HRMS

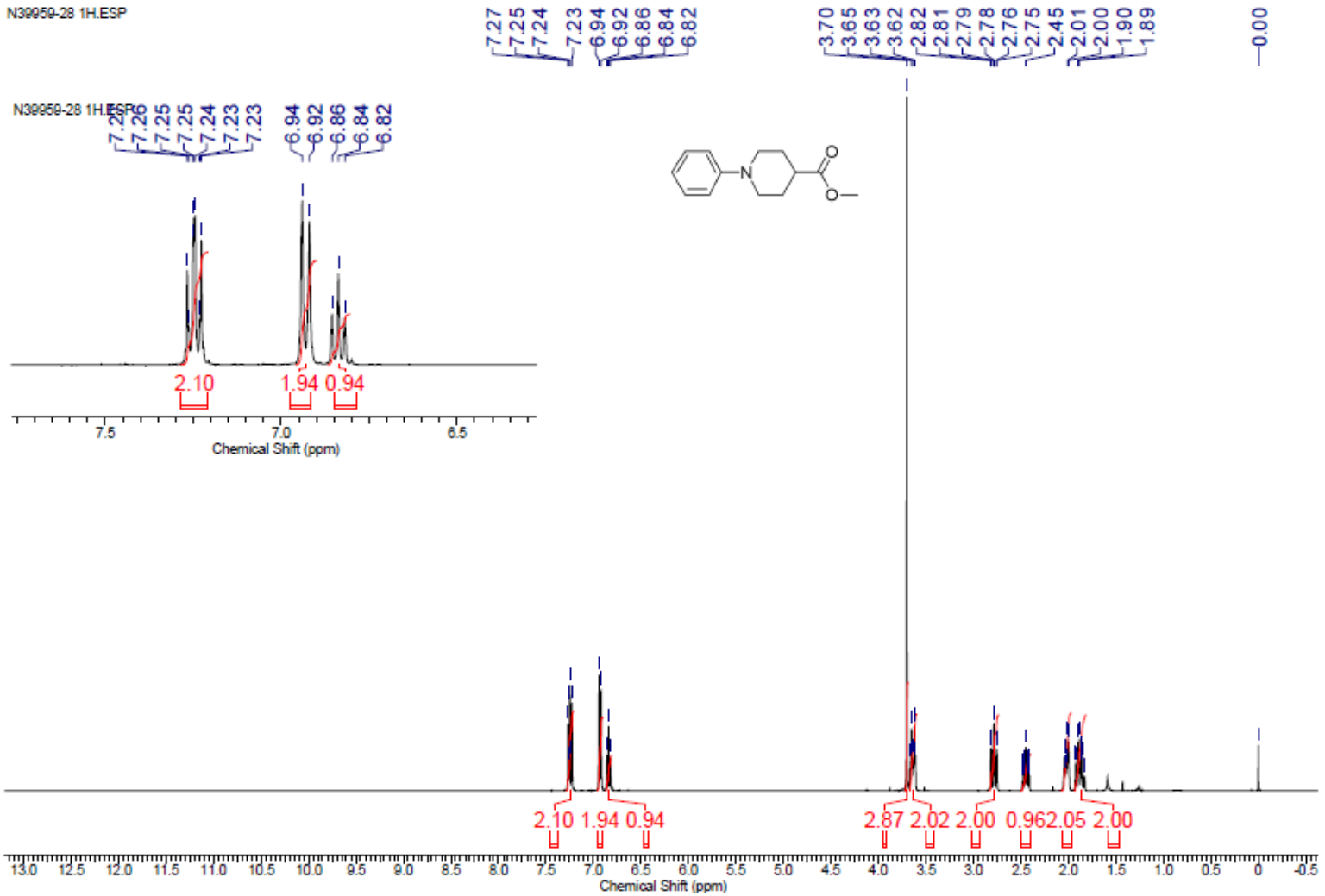


IR Spectra

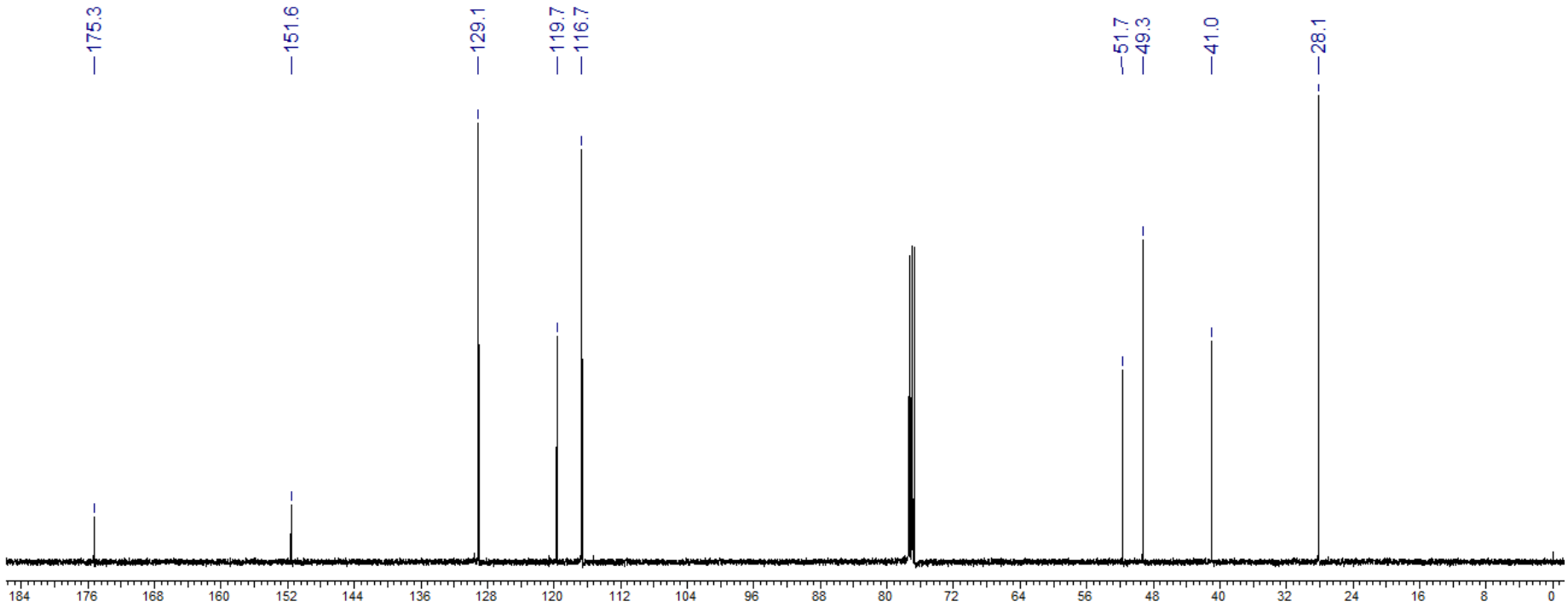


Methyl 1-phenylpiperidine-4-carboxylate (7t).

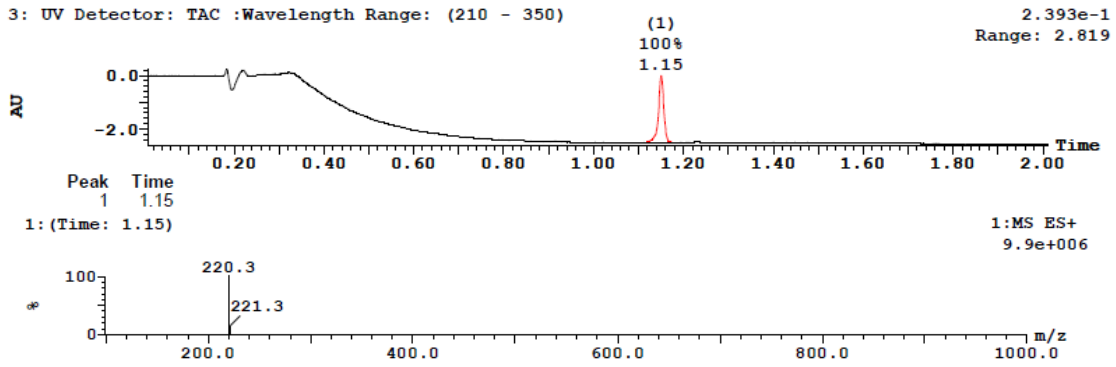
^{1}H NMR Spectra



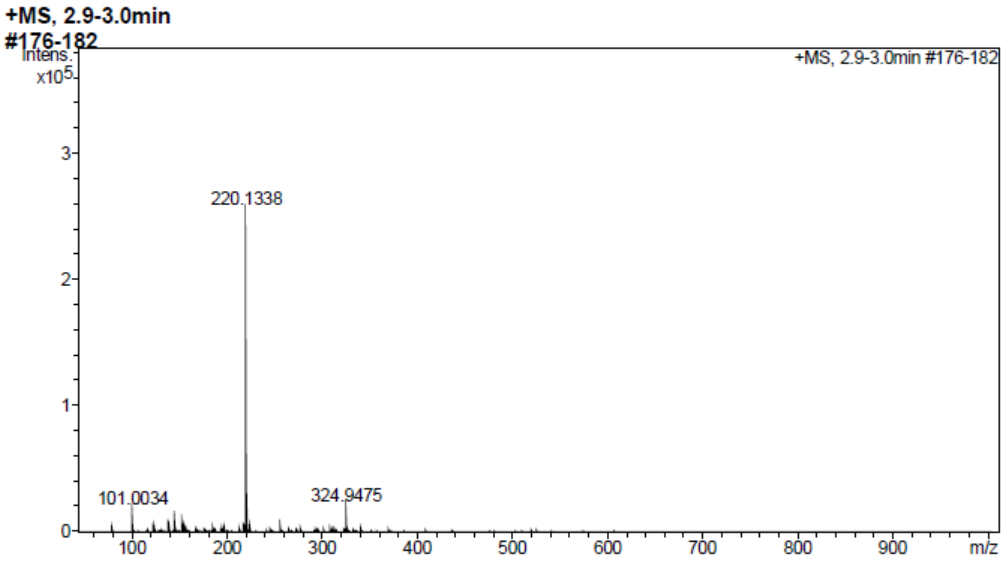
^{13}C NMR Spectra



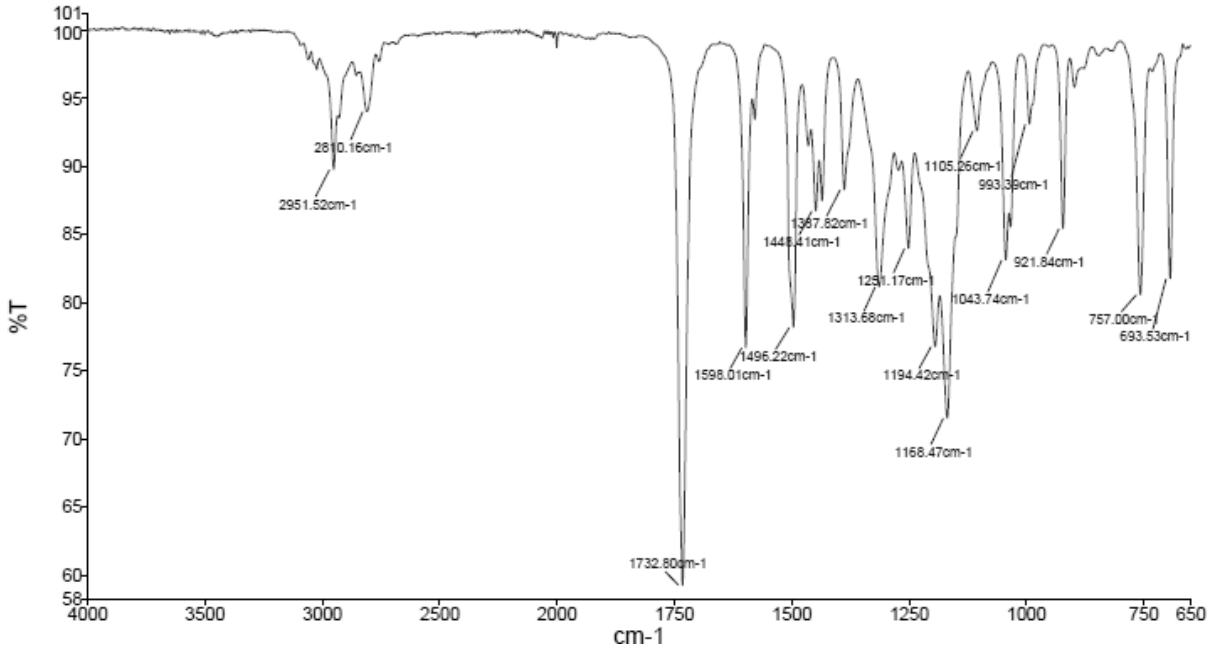
LCMS



HRMS

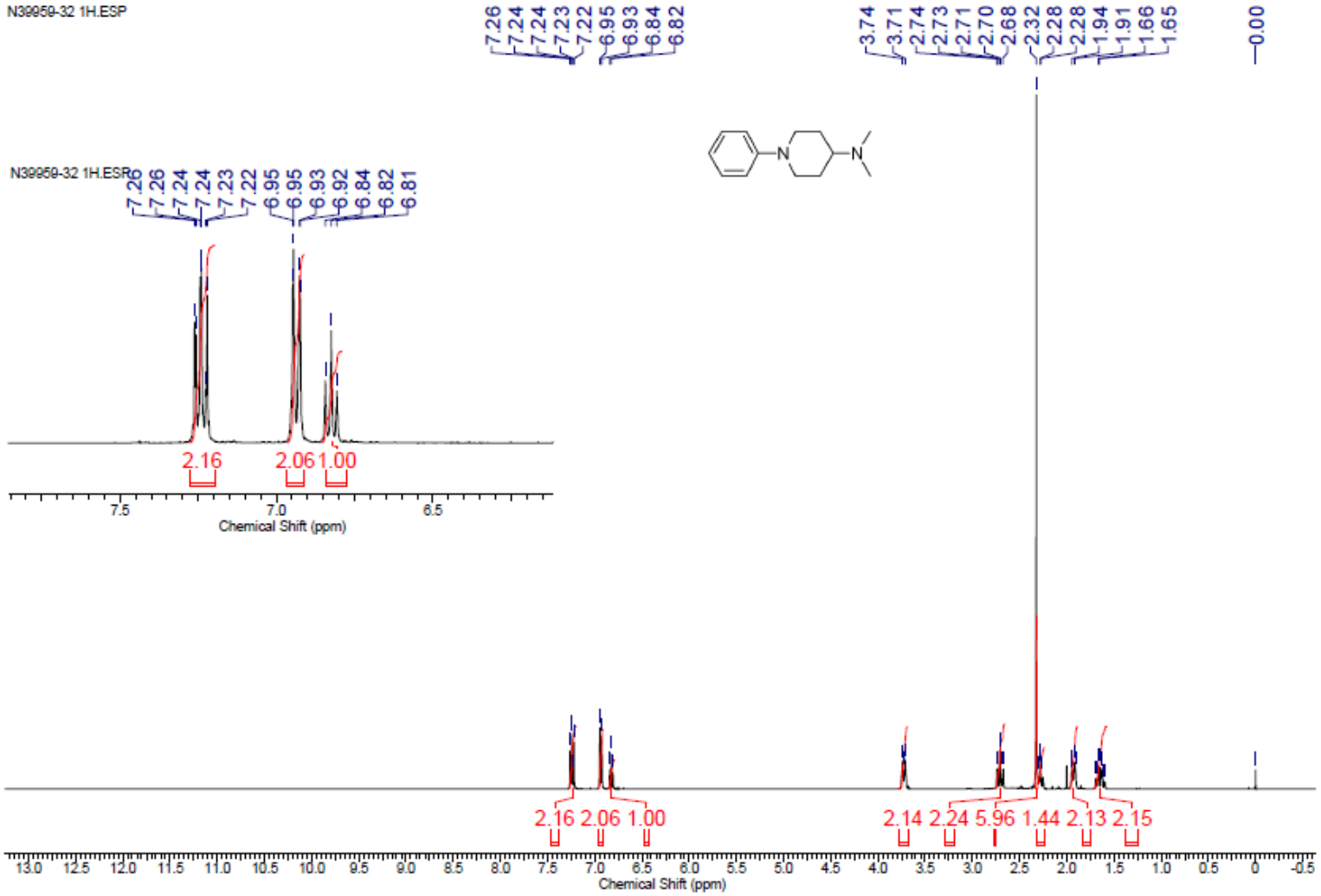


IR Spectra

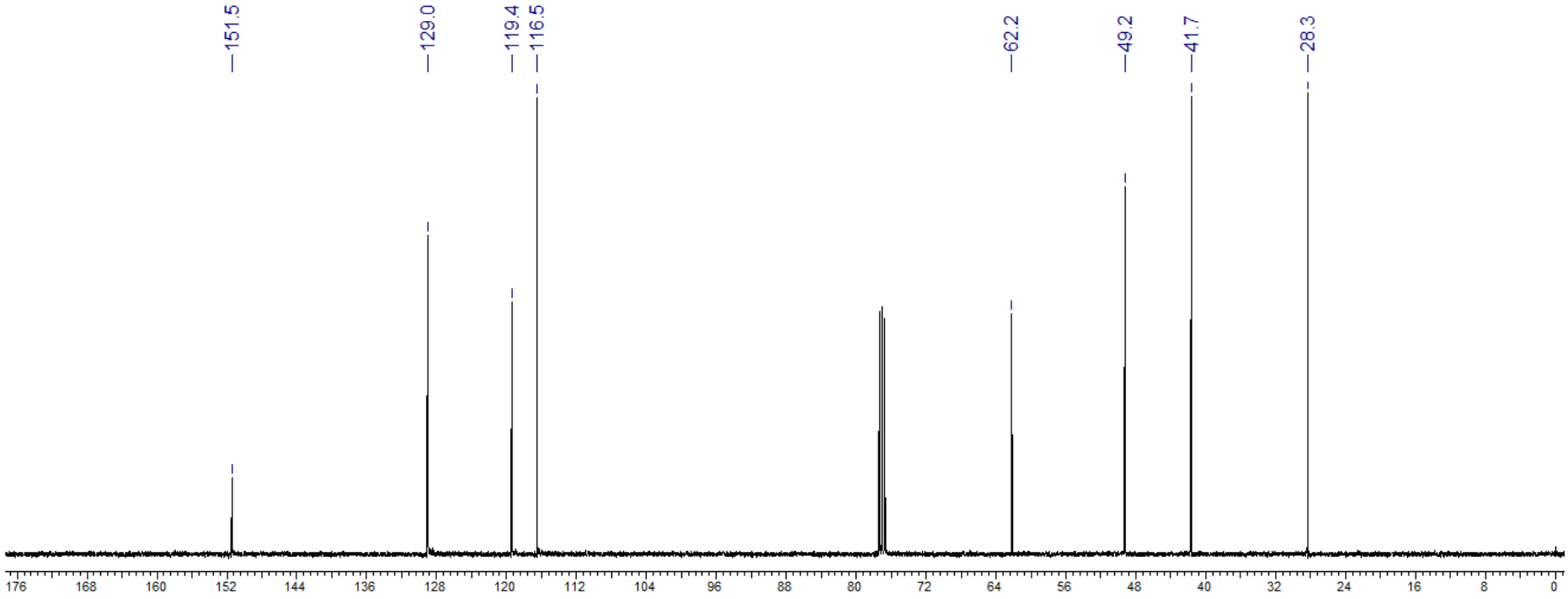


***N*,*N*-Dimethyl-1-phenylpiperidin-4-amine (7u).**

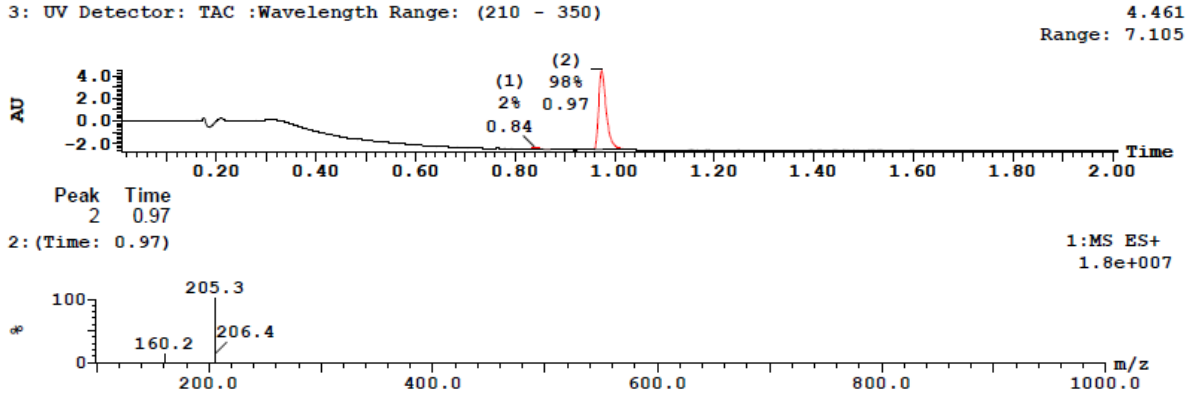
^{1}H NMR Spectra



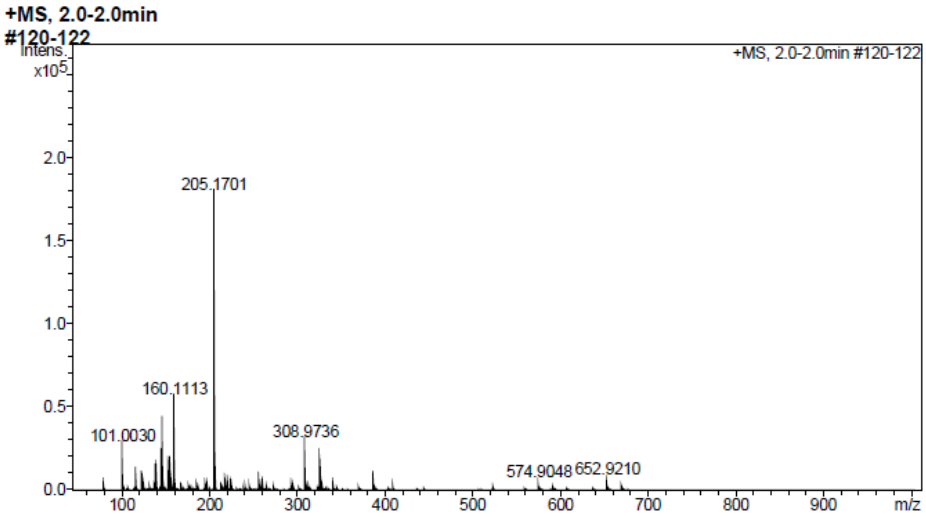
^{13}C NMR Spectra



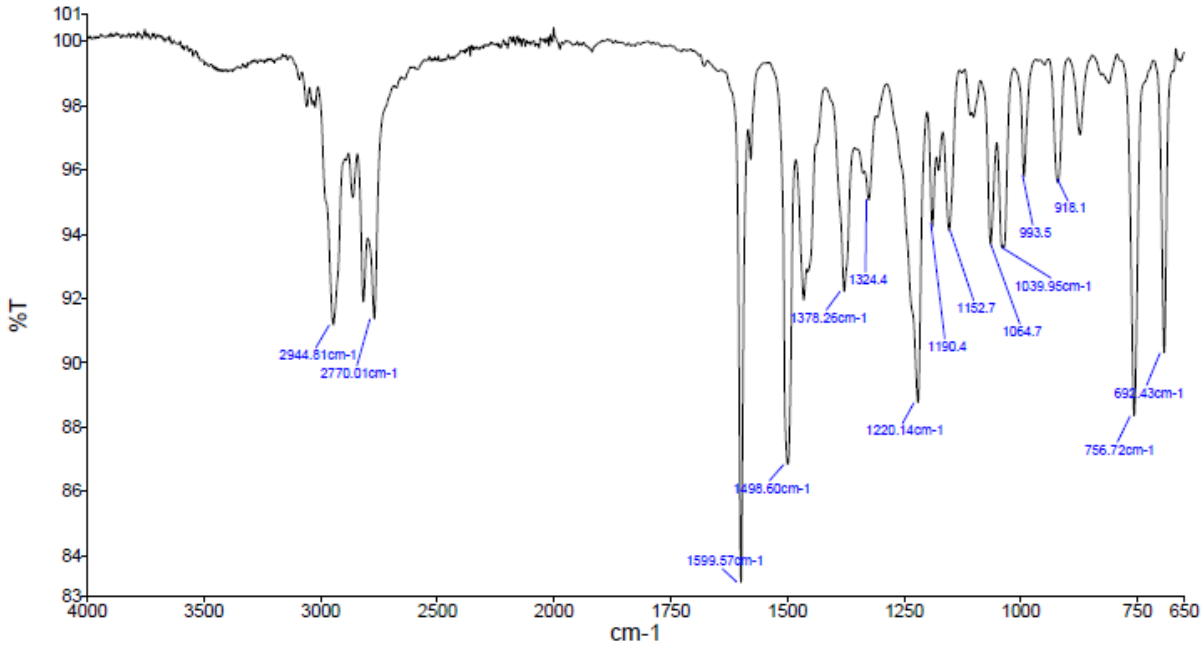
LCMS



HRMS

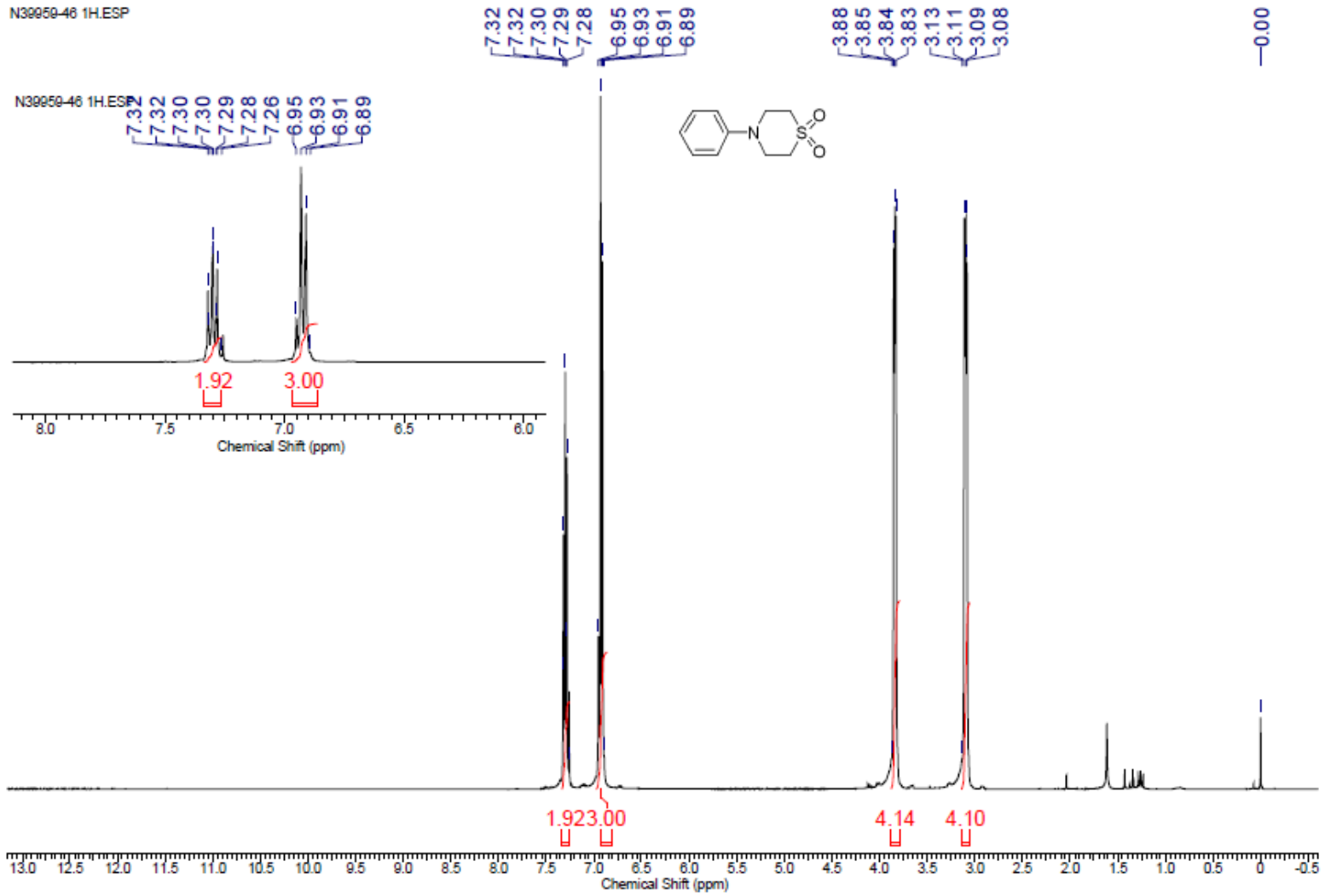


IR Spectra

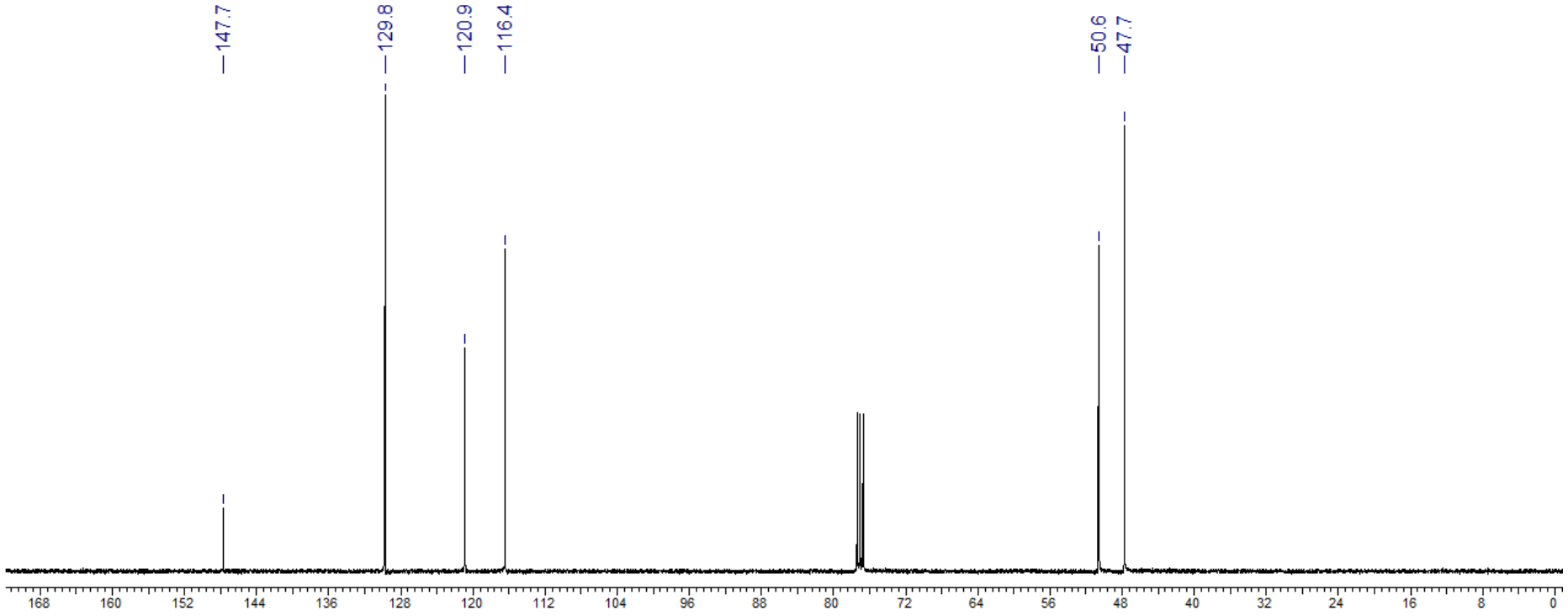


4-Phenylthiomorpholine 1,1-dioxide (7v).

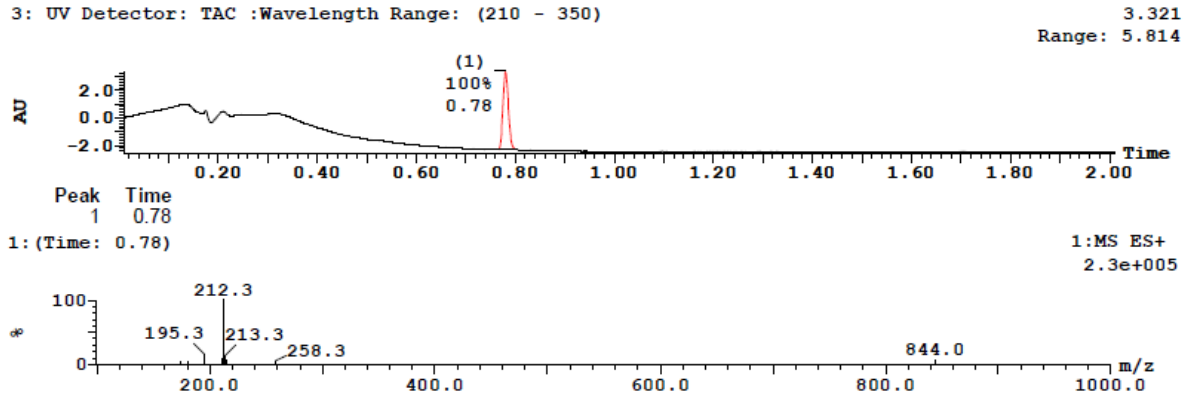
^{1}H NMR Spectra



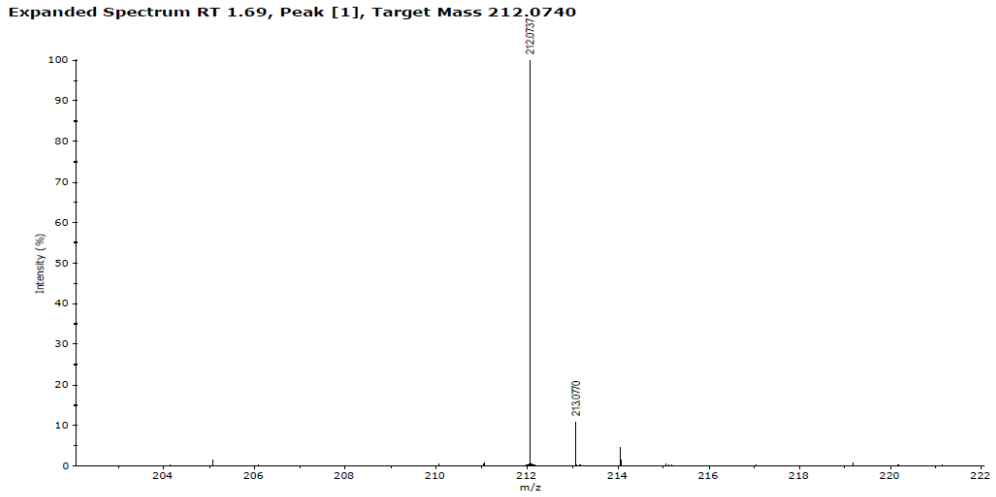
^{13}C NMR Spectra



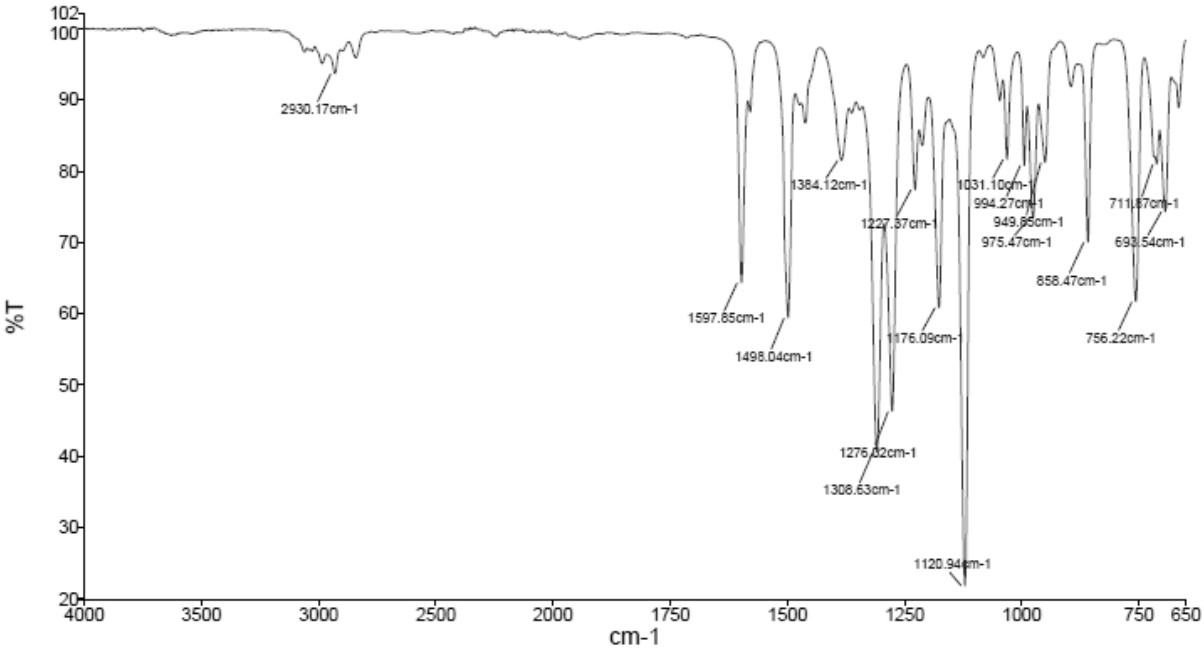
LCMS



HRMS

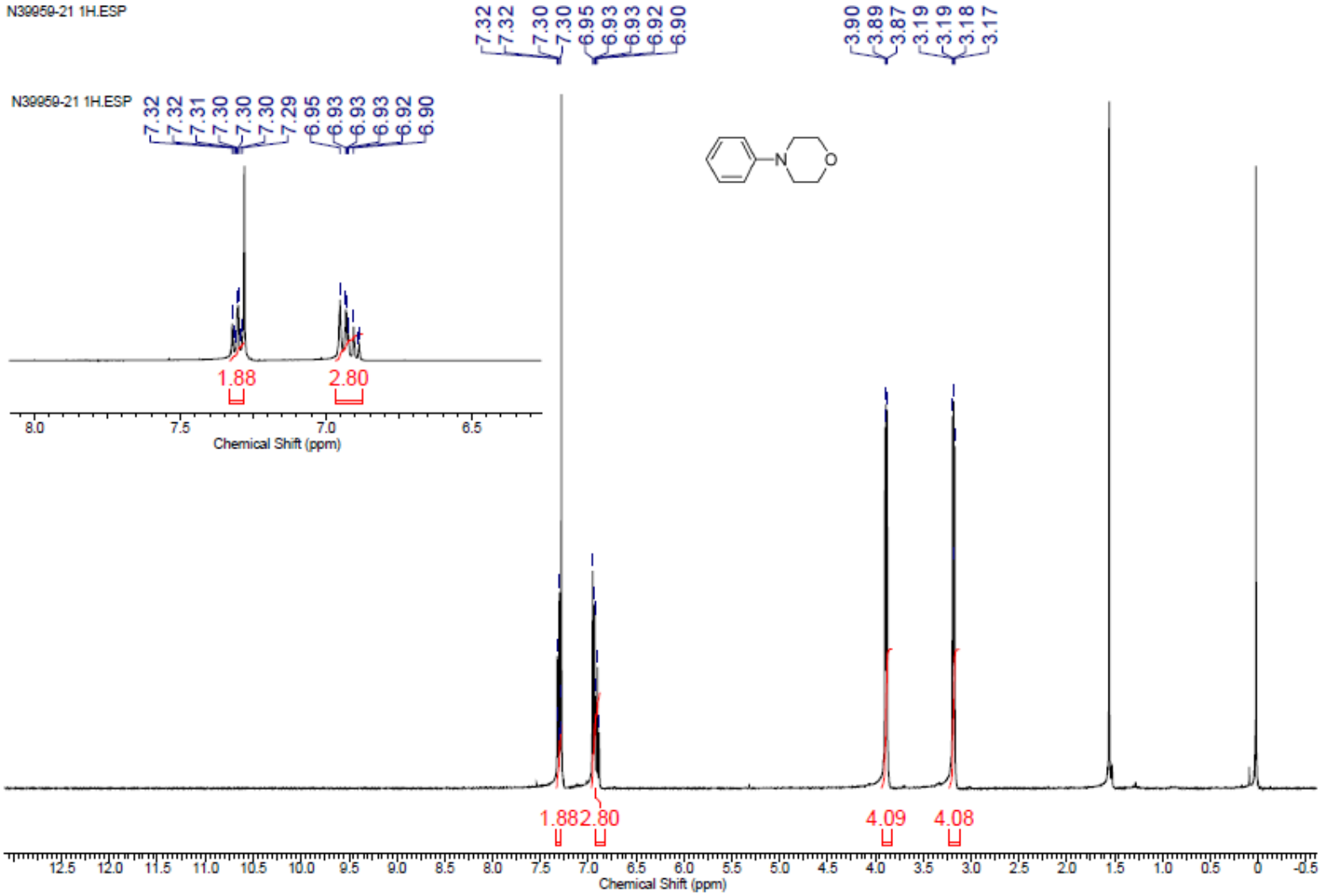


IR Spectra

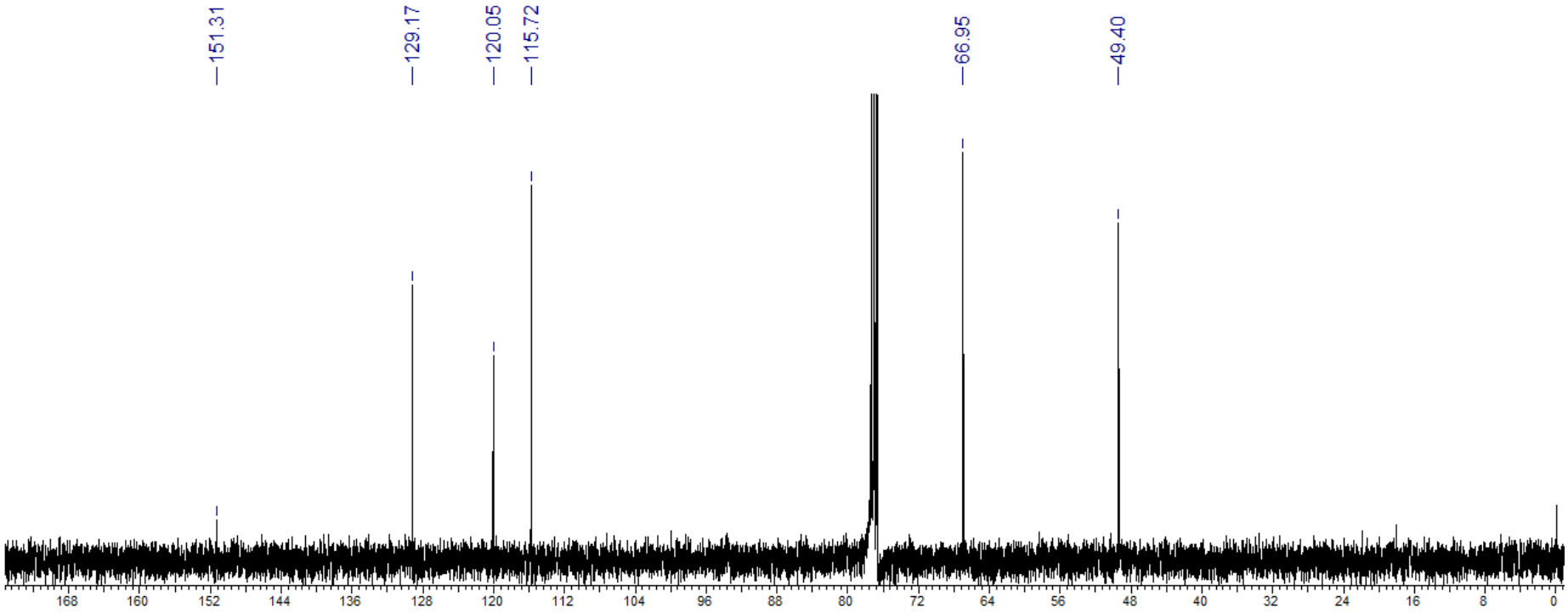


4-Phenylmorpholine (7w).

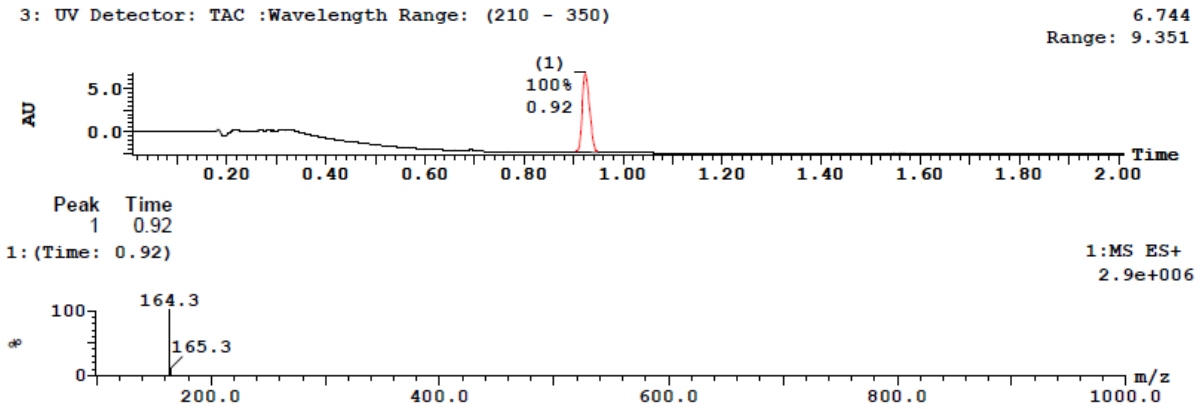
^{1}H NMR Spectra



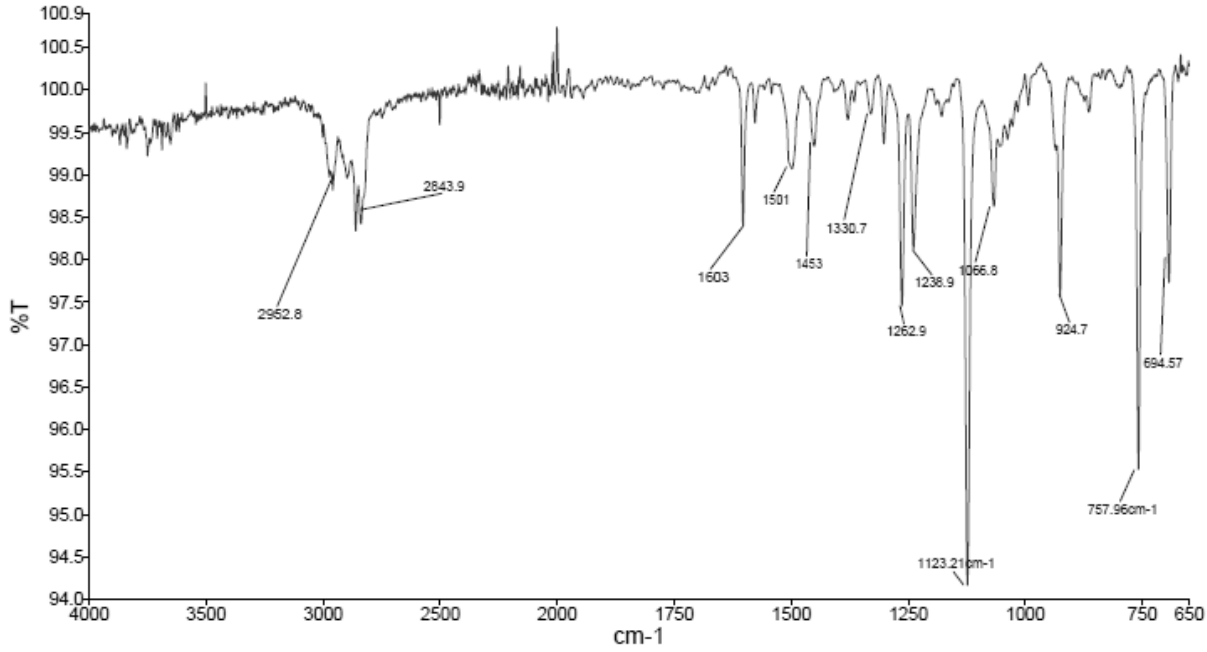
^{13}C NMR Spectra



LCMS

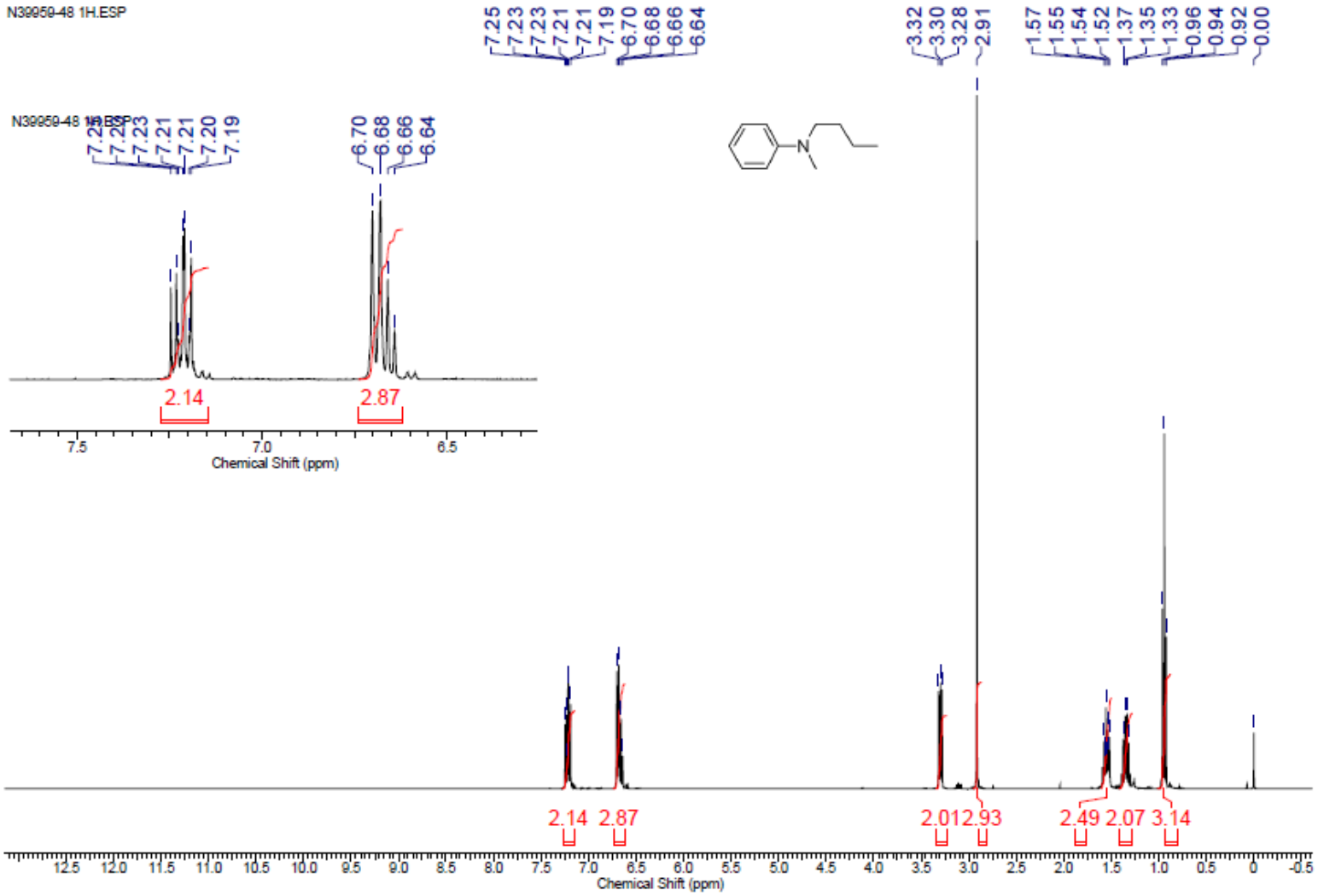


IR Spectra

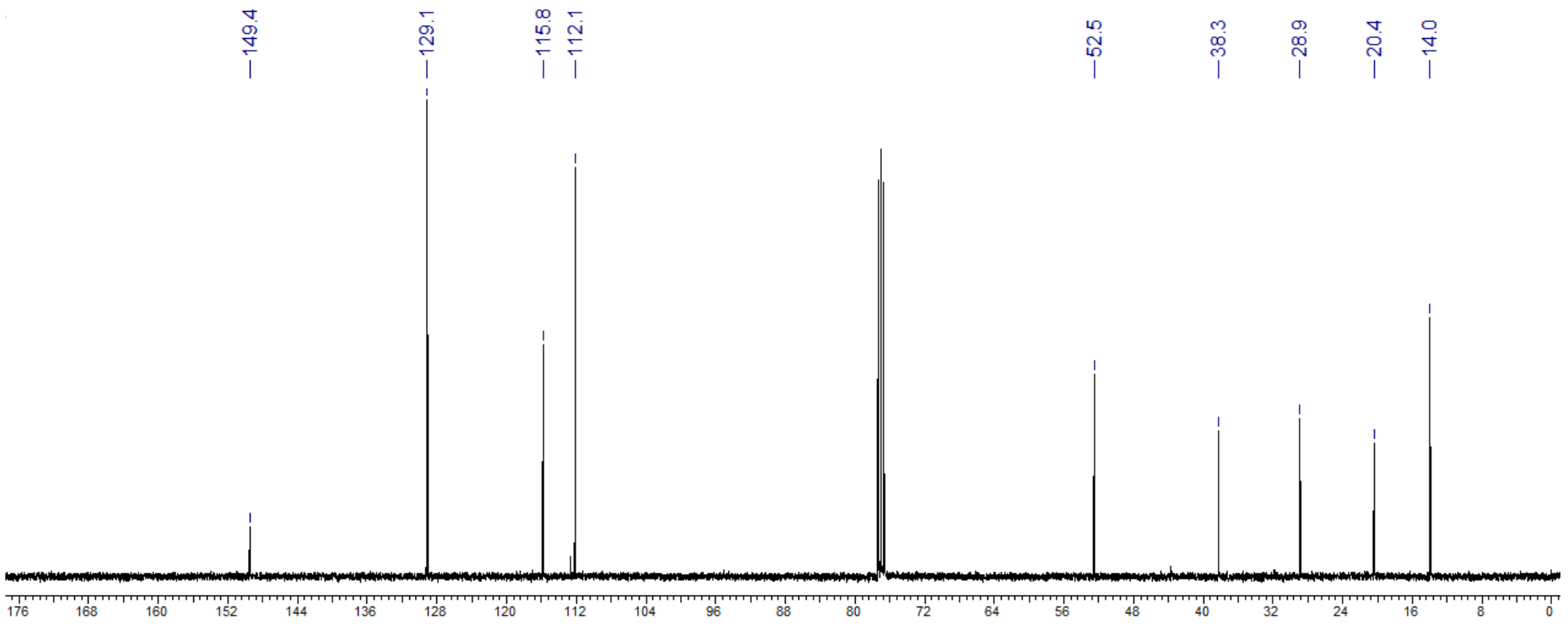


***N*-Butyl-*N*-methylaniline (7x).**

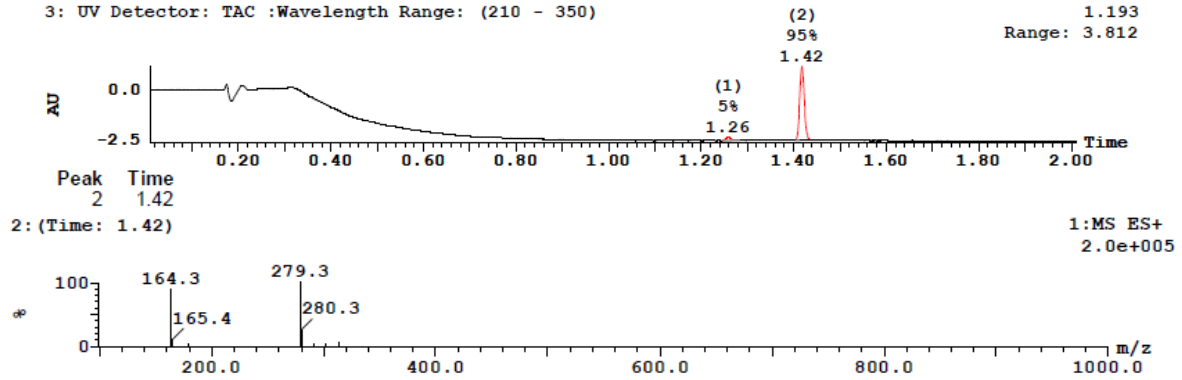
^{1}H NMR Spectra



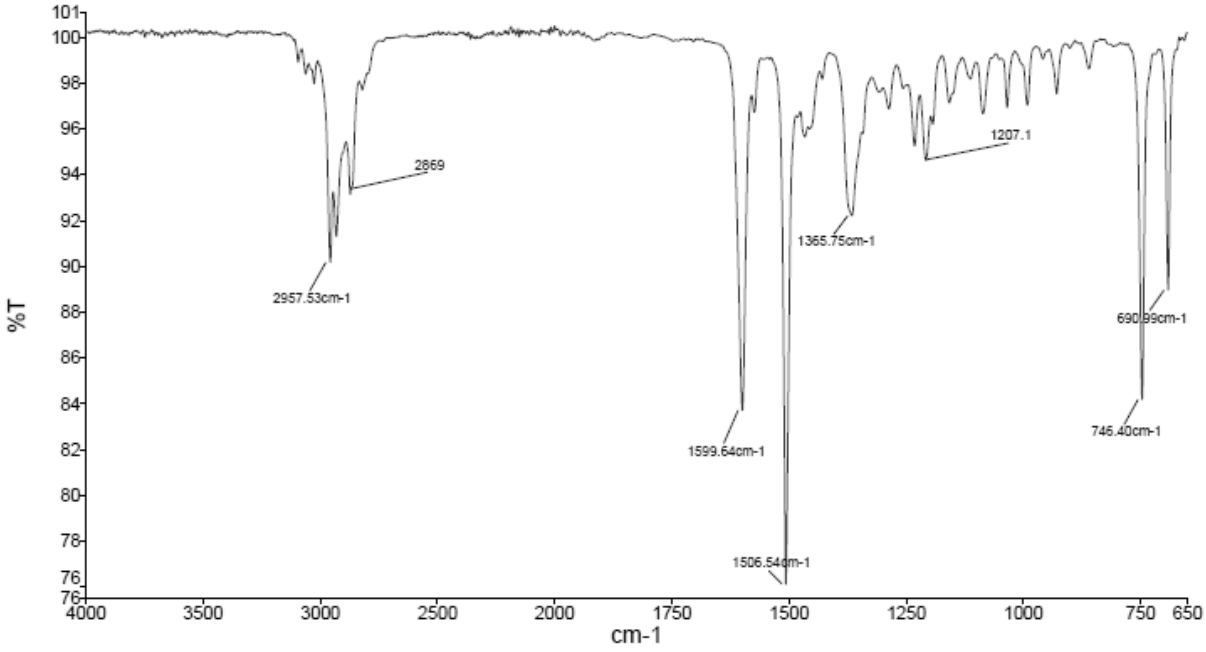
^{13}C NMR Spectra



LCMS

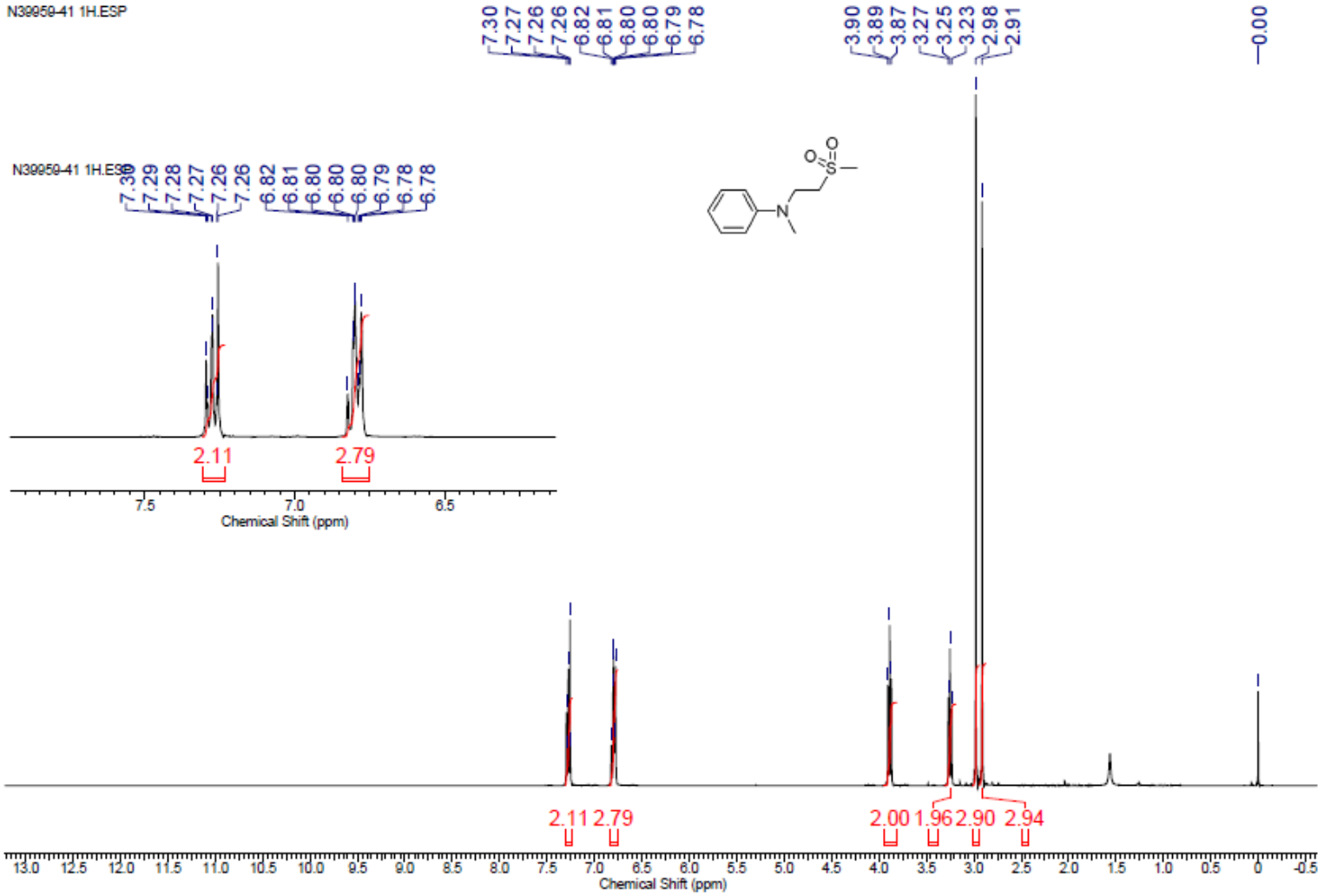


IR Spectra

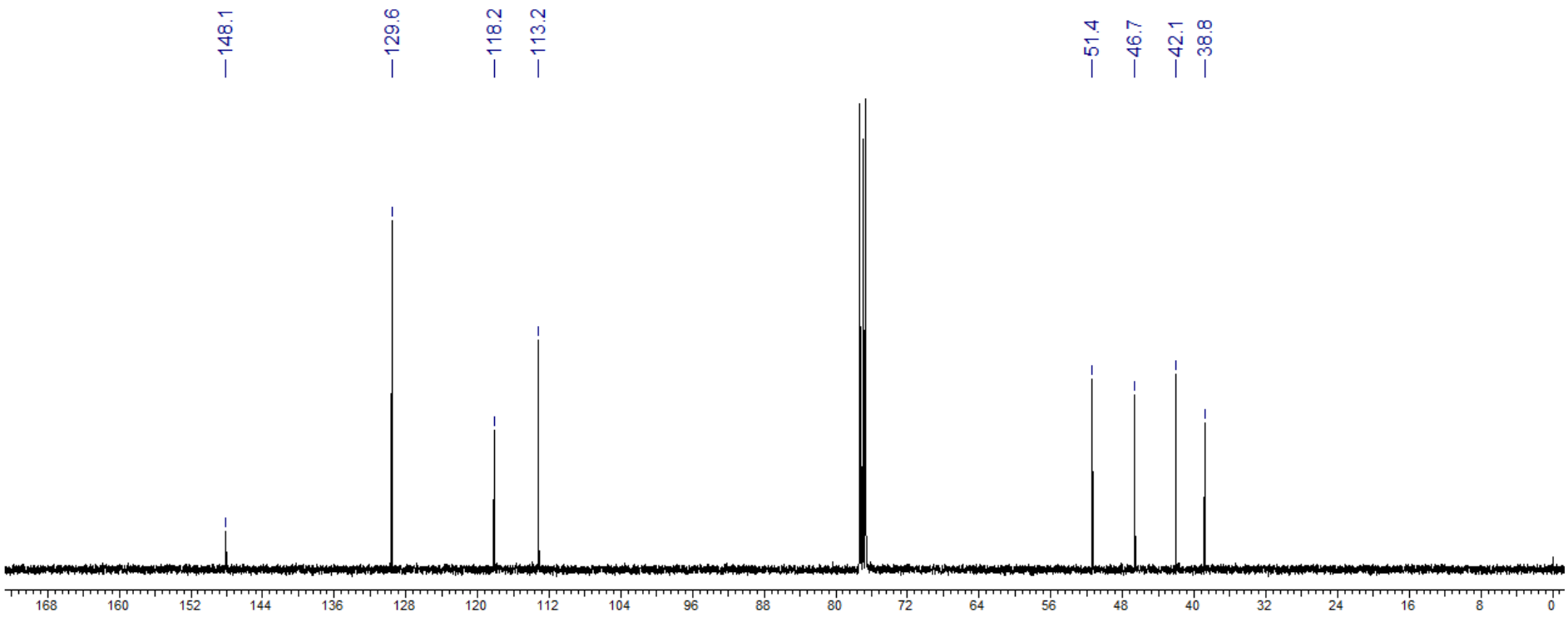


***N*-Methyl-*N*-(2-(methylsulfonyl)ethyl)aniline (7y).**

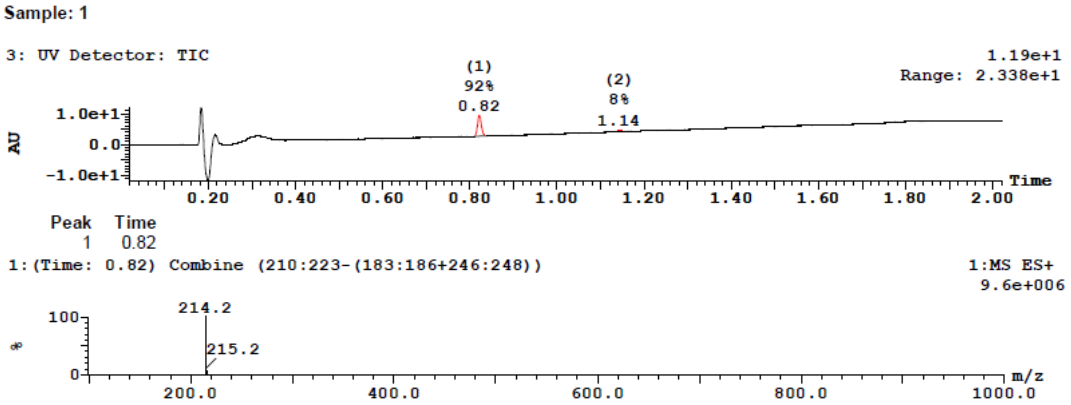
^{1}H NMR Spectra



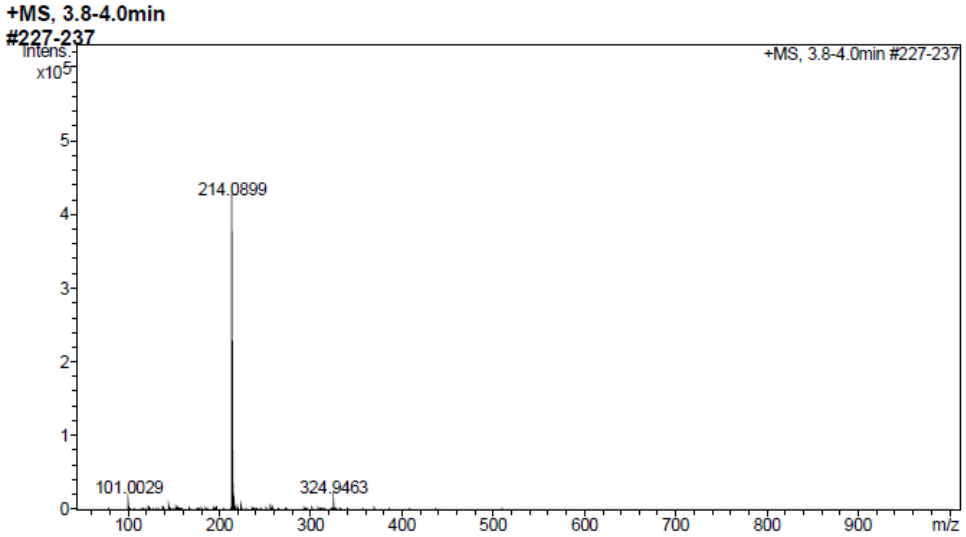
^{13}C NMR Spectra



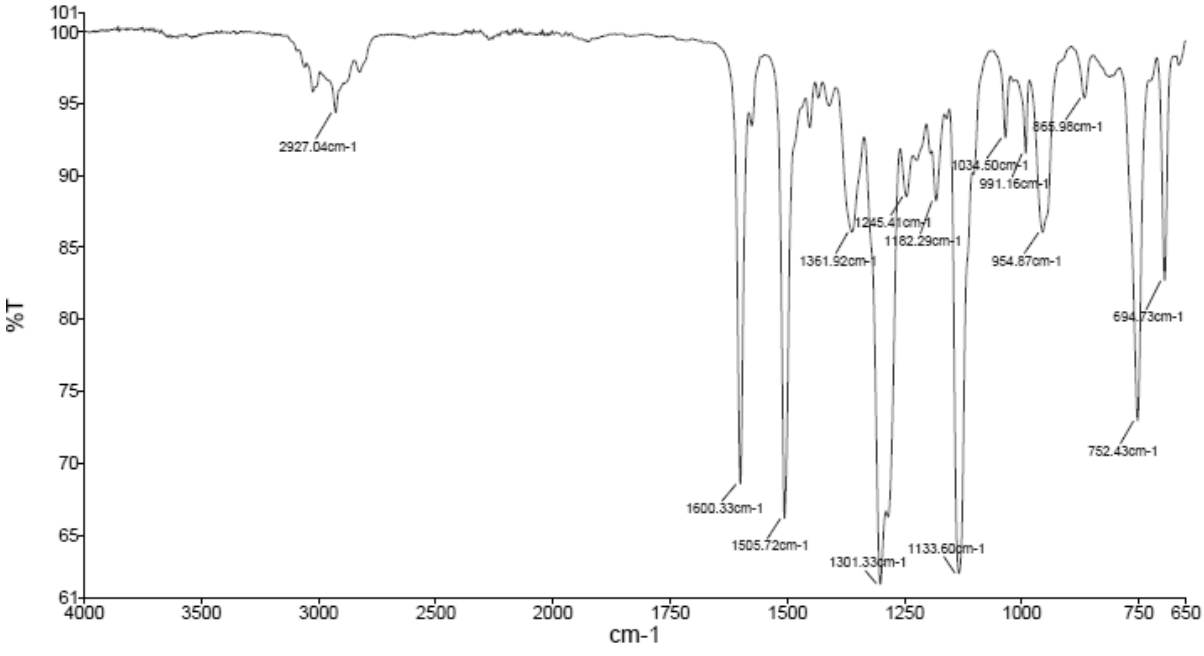
LCMS



HRMS

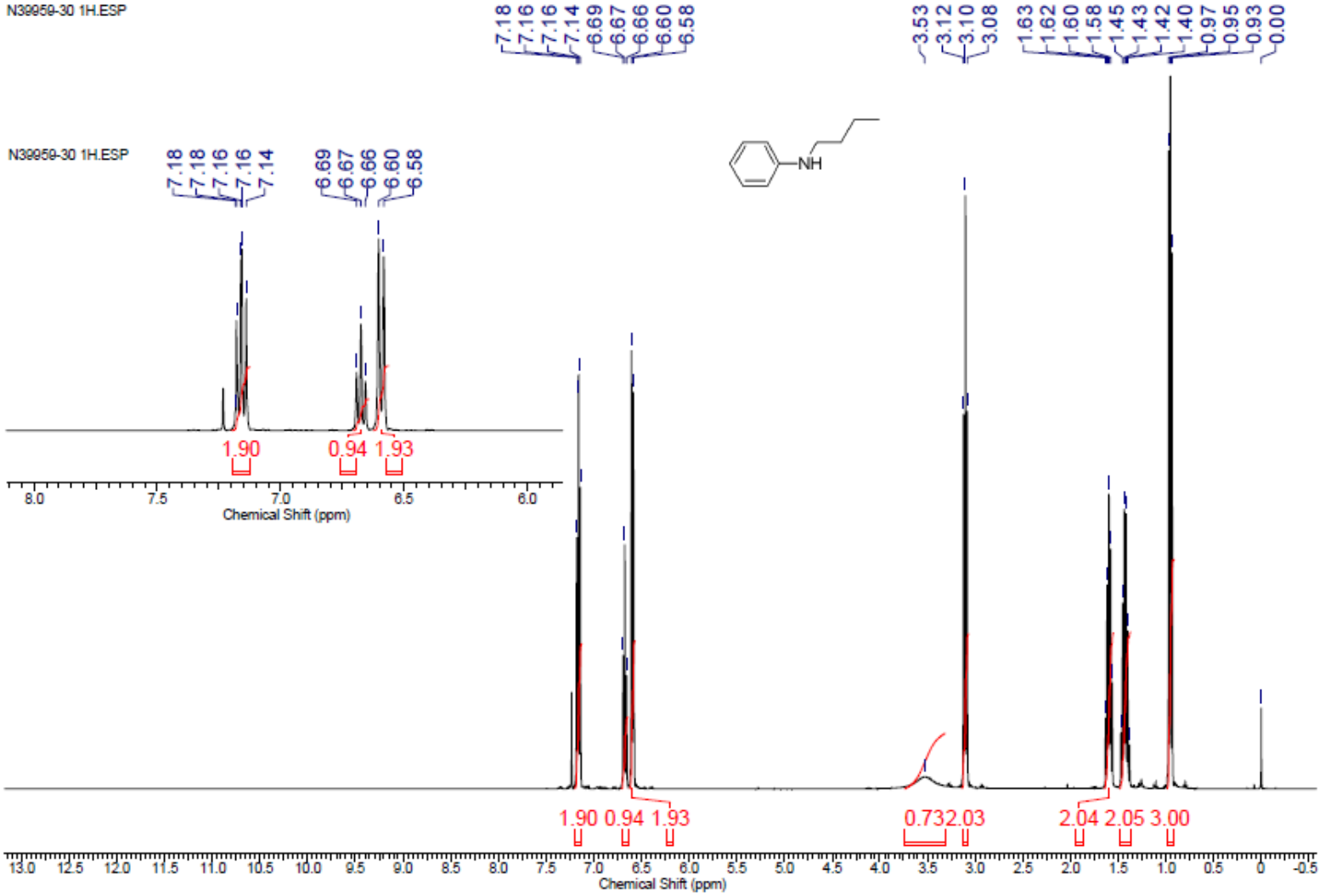


IR Spectra

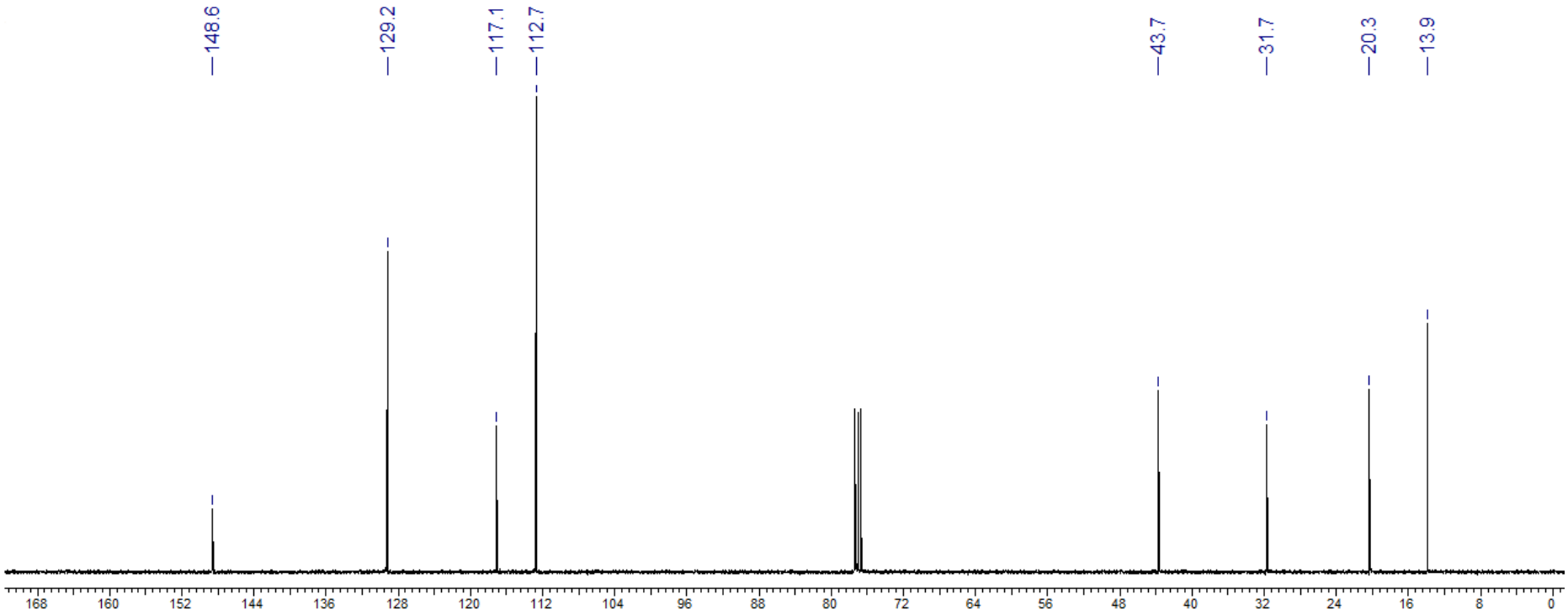


***N*-Butylaniline (7z).**

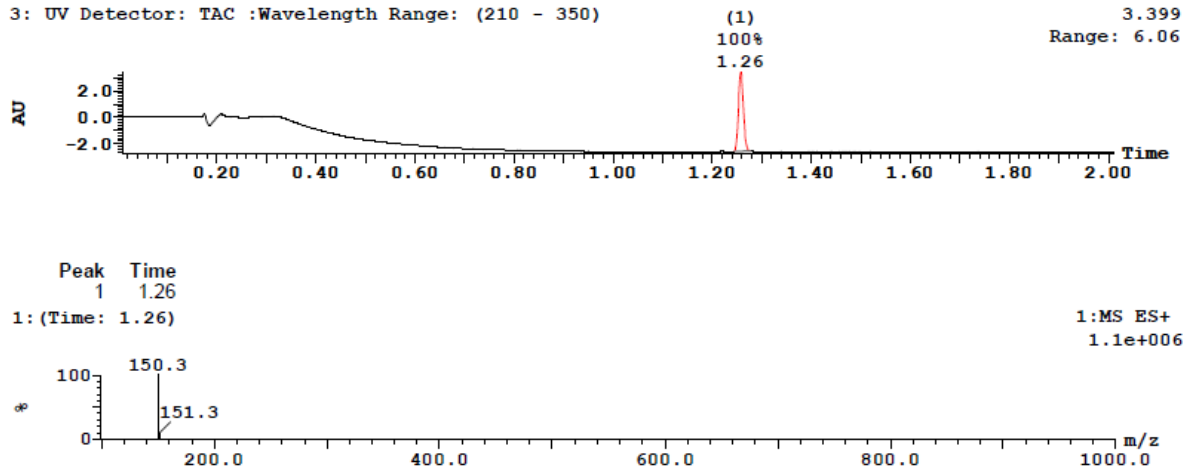
^{1}H NMR Spectra



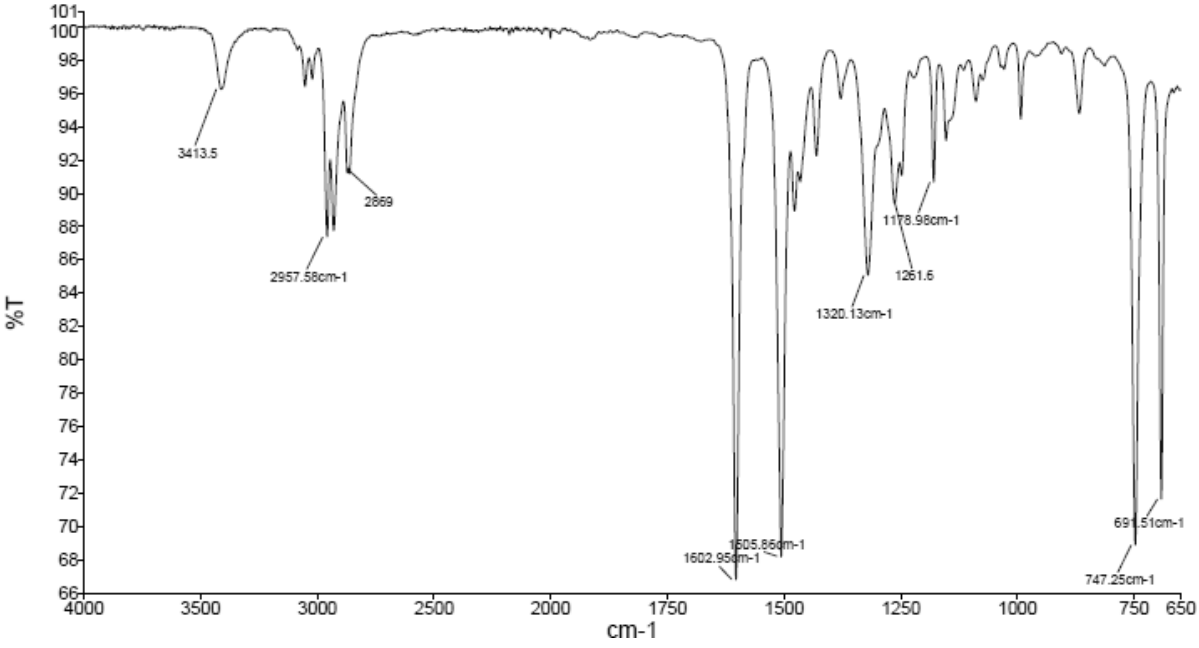
^{13}C NMR Spectra



LCMS

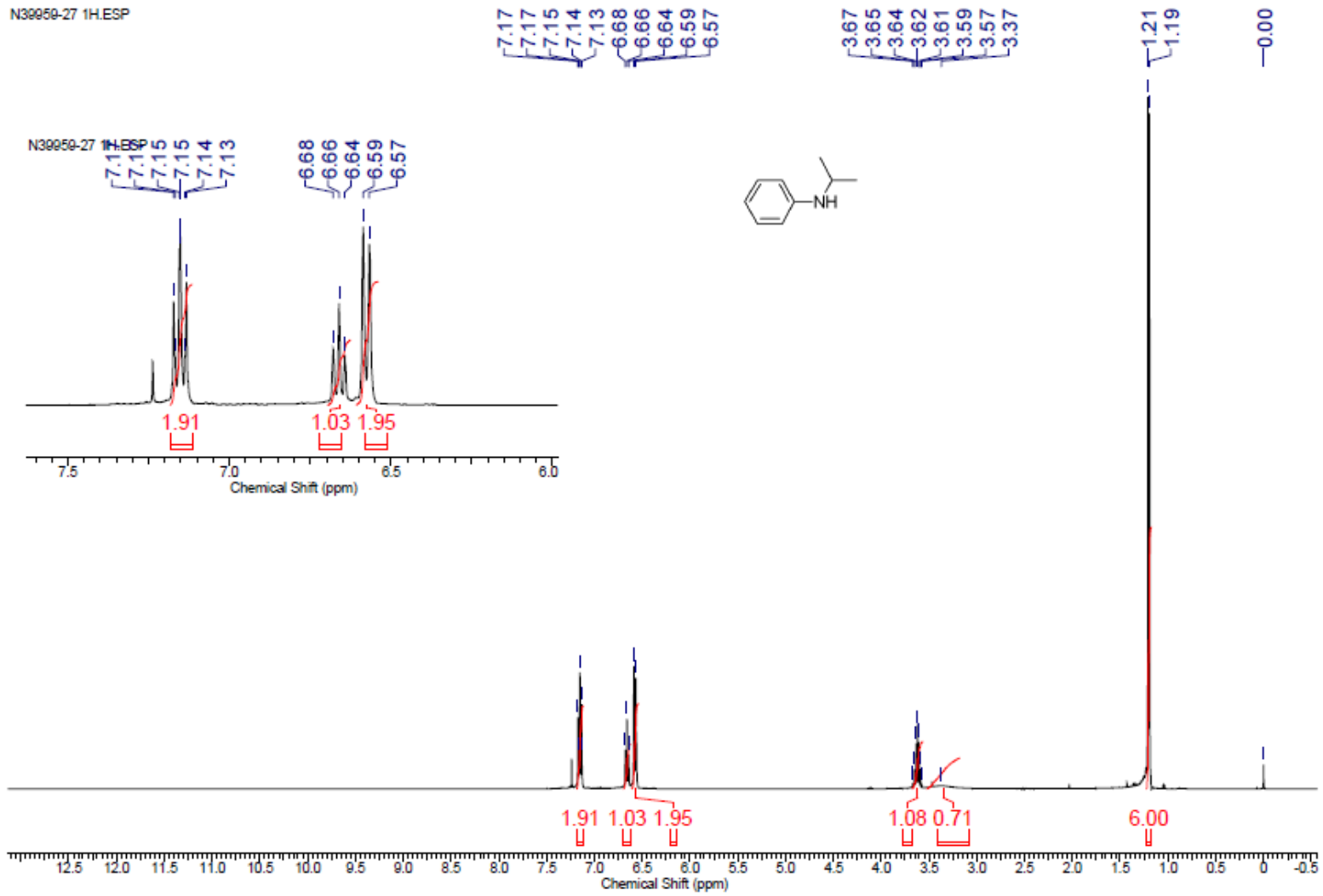


IR Spectra

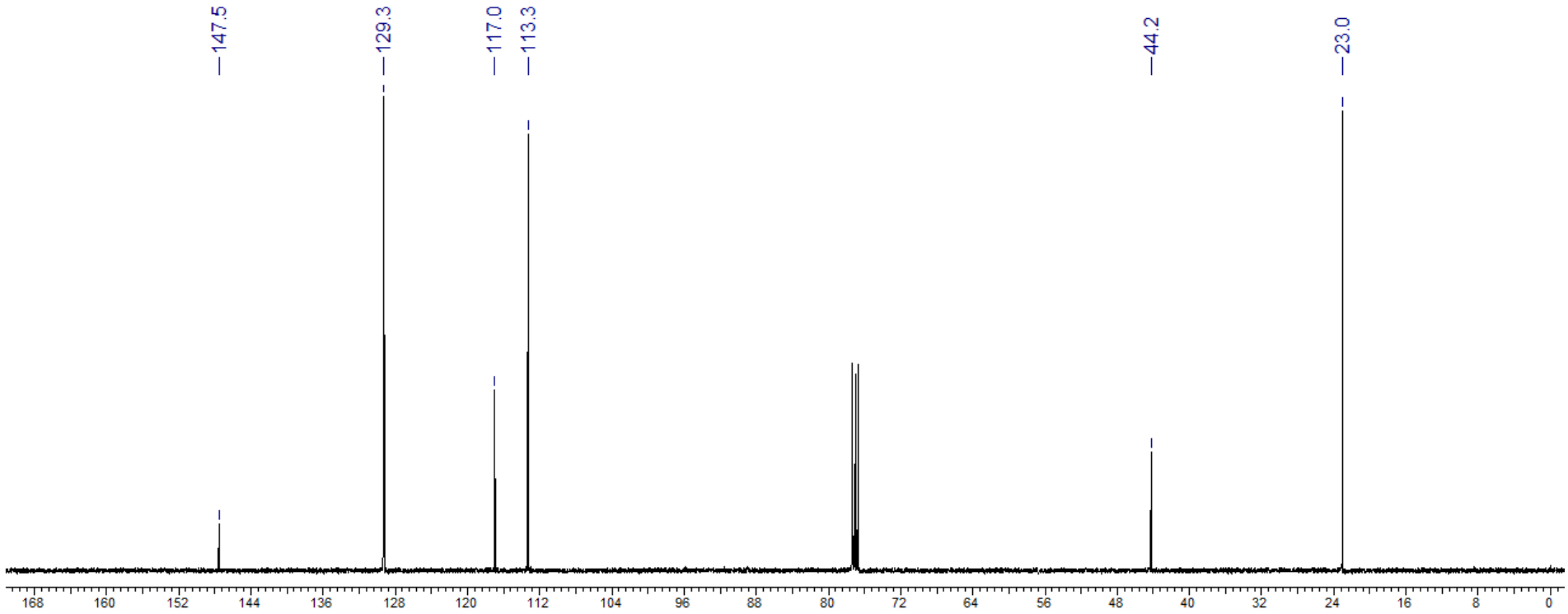


***N*-Isopropylaniline (7aa).**

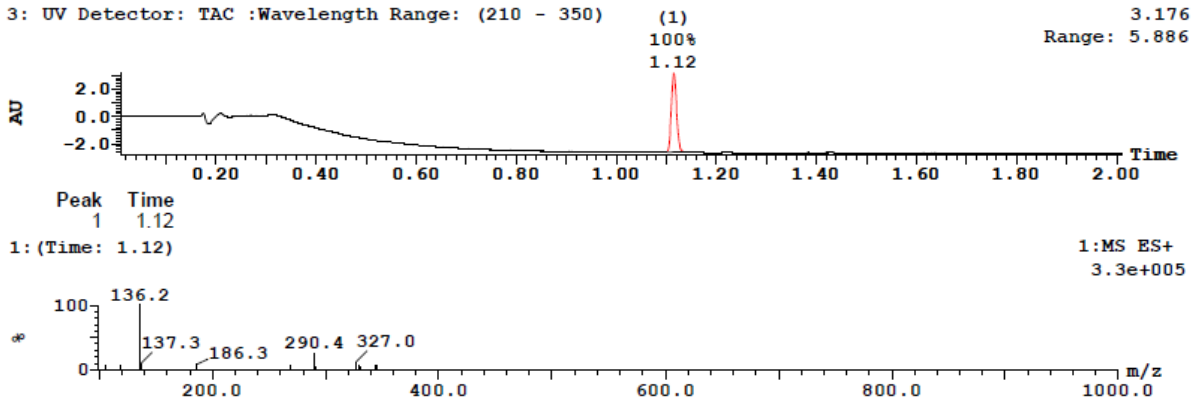
^{1}H NMR Spectra



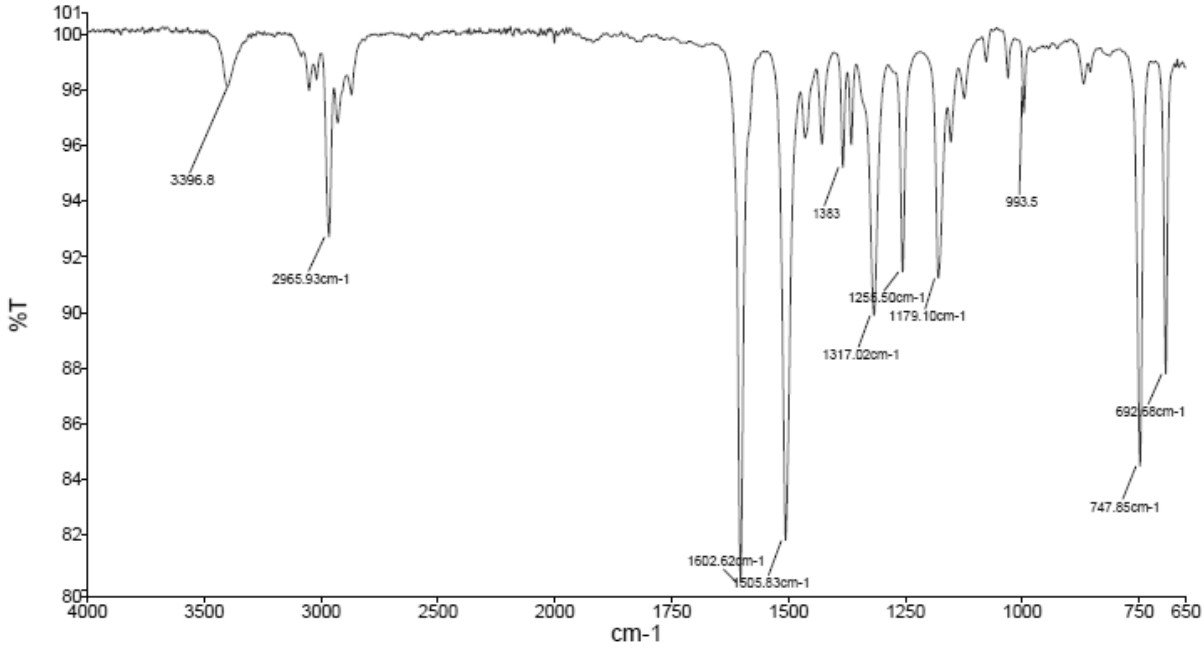
^{13}C NMR Spectra



LCMS

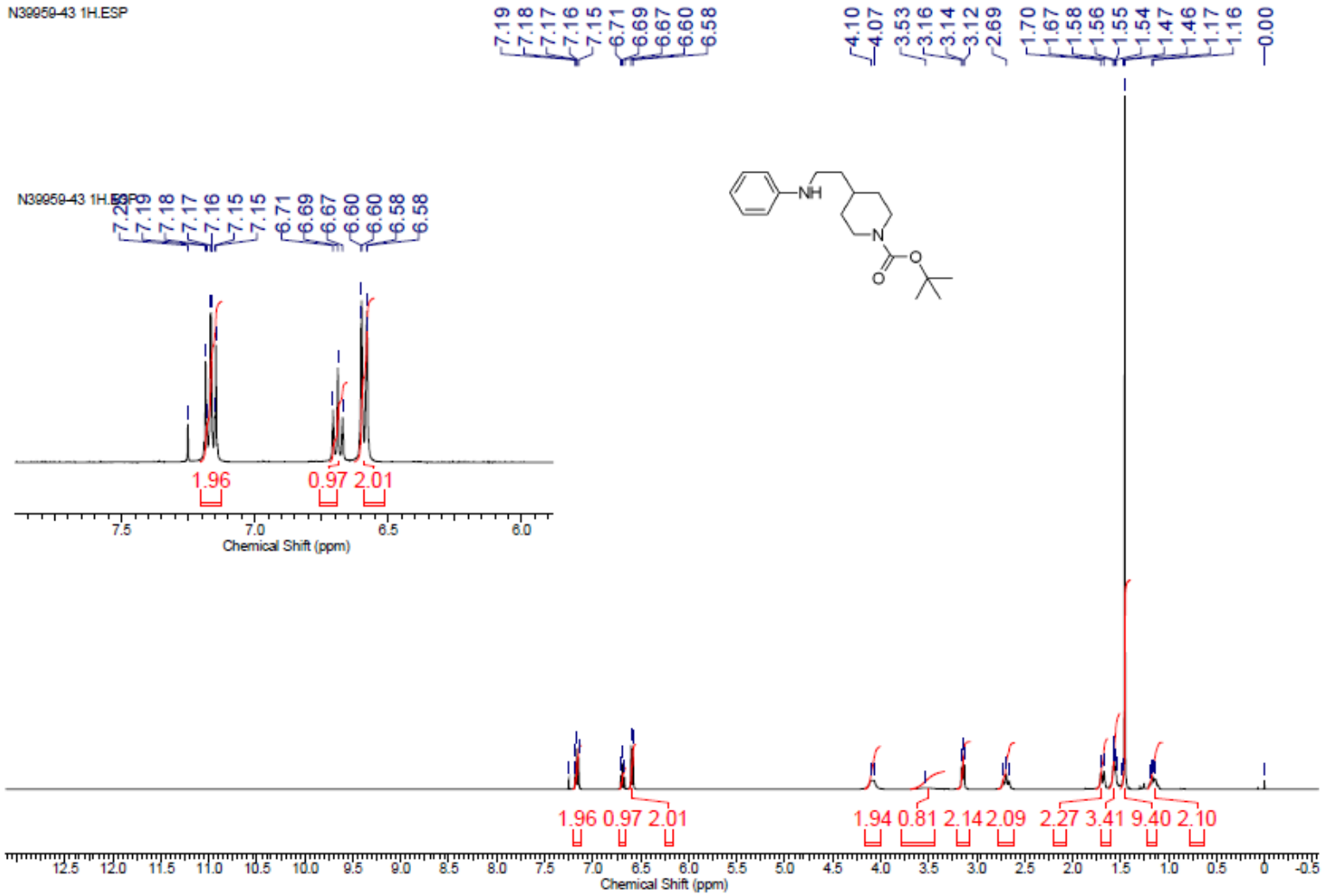


IR Spectra

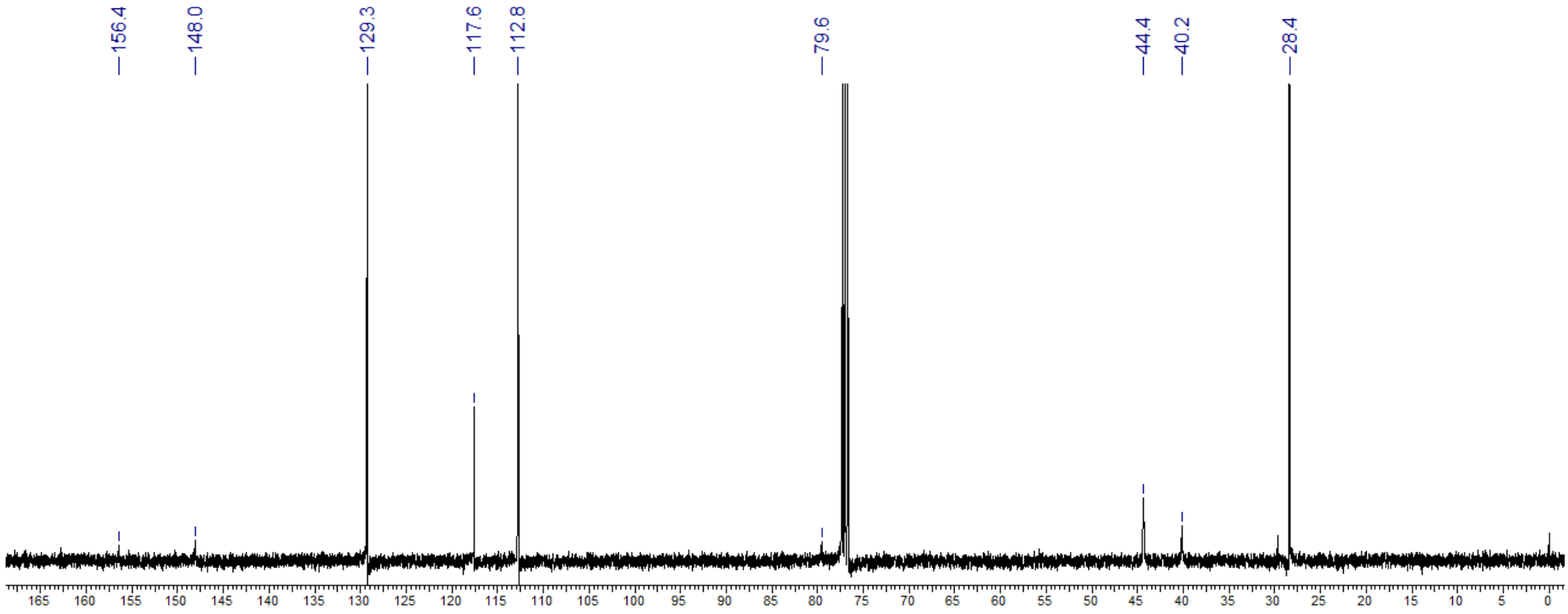


***tert*-Butyl 4-(2-(phenylamino)ethyl)piperidine-1-carboxylate (7ab).**

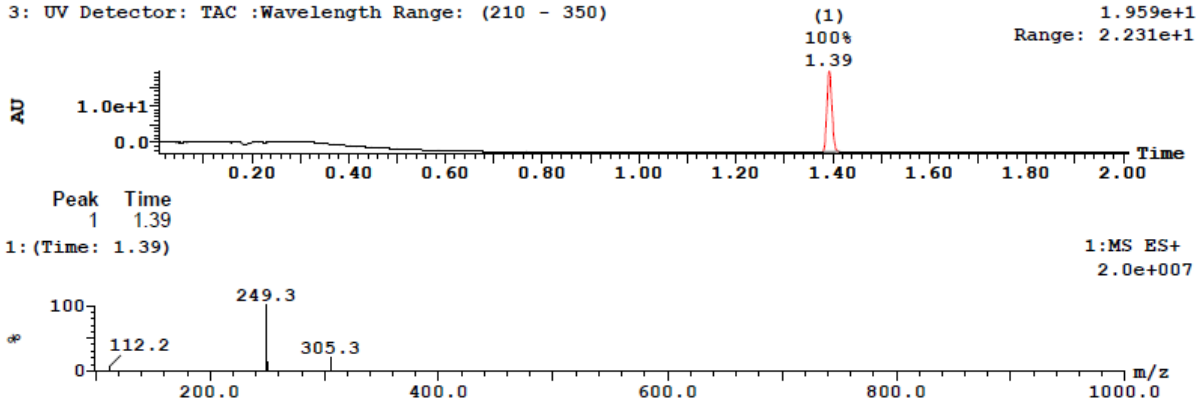
^{1}H NMR Spectra



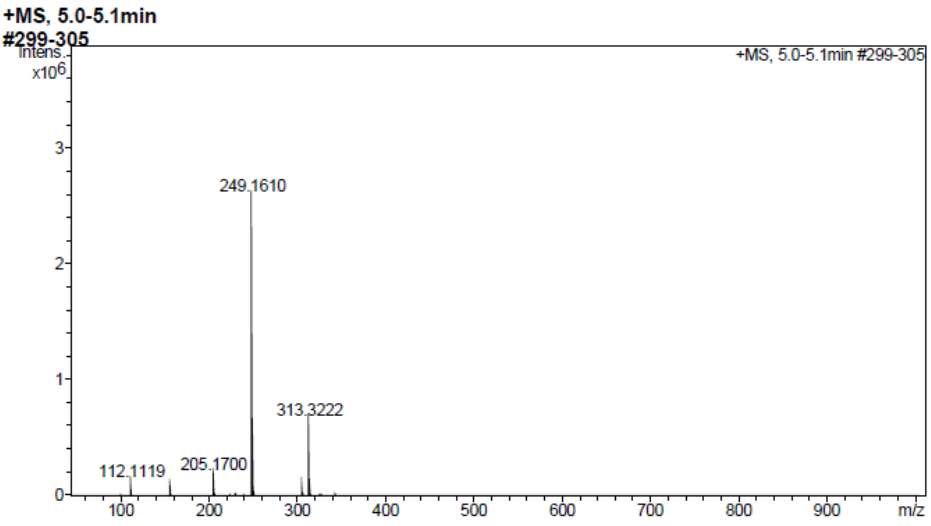
^{13}C NMR Spectra



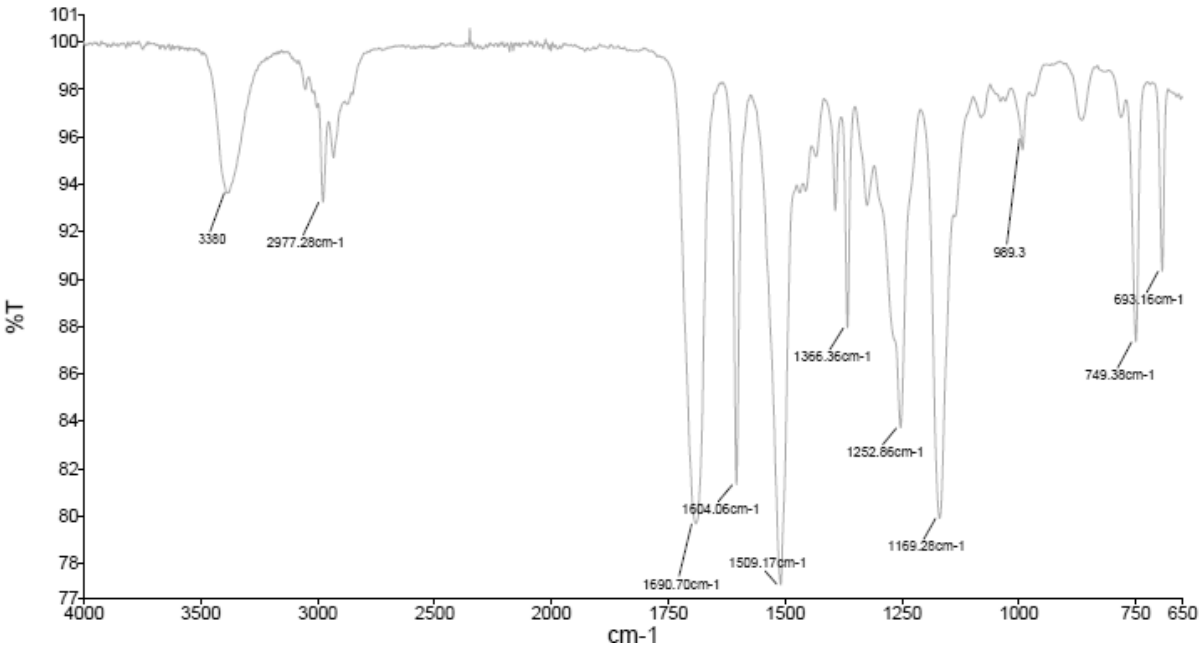
LCMS



HRMS

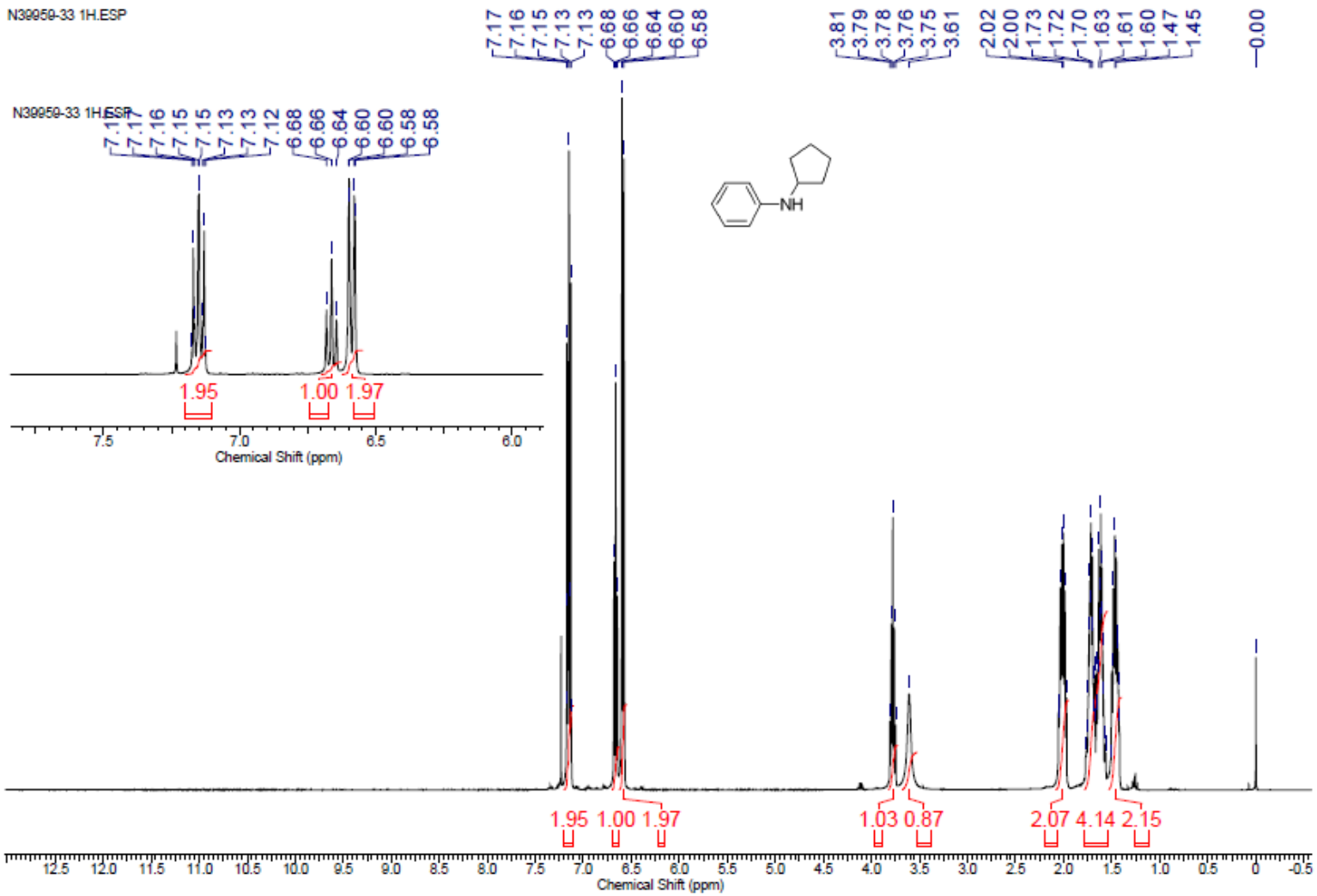


IR Spectra

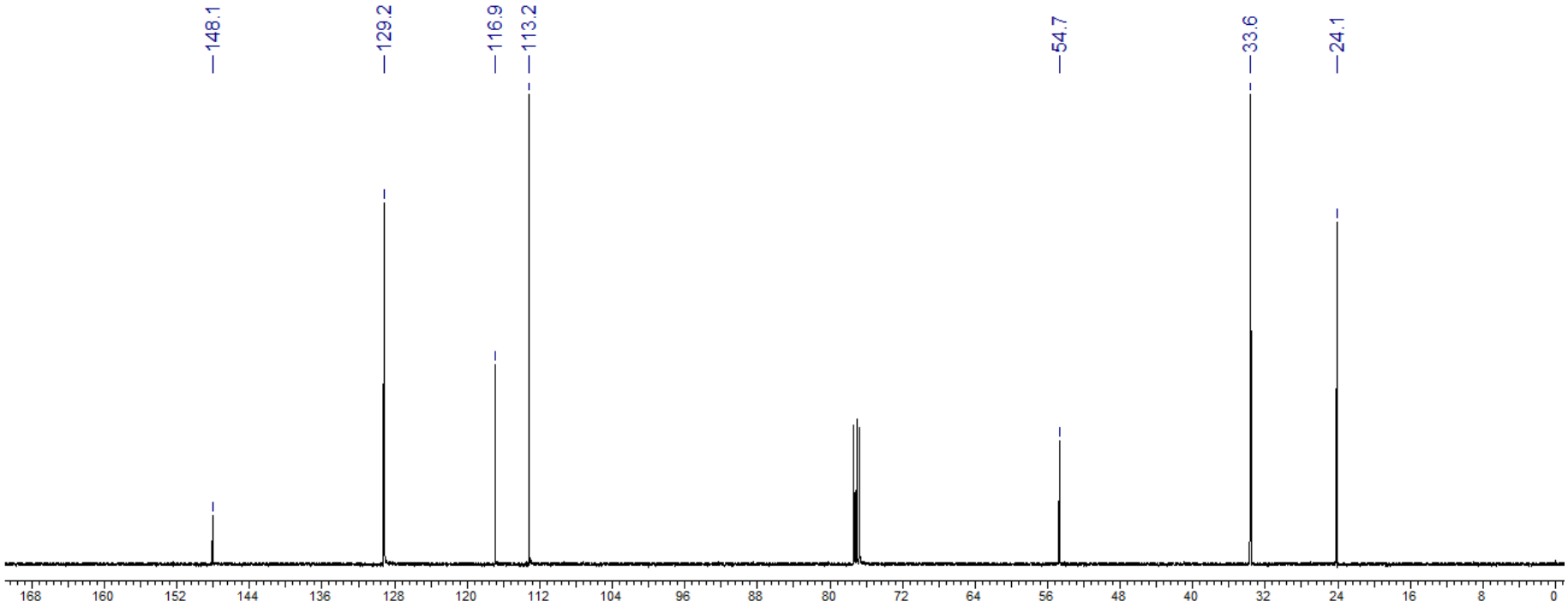


***N*-Cyclopentylaniline (7ac).**

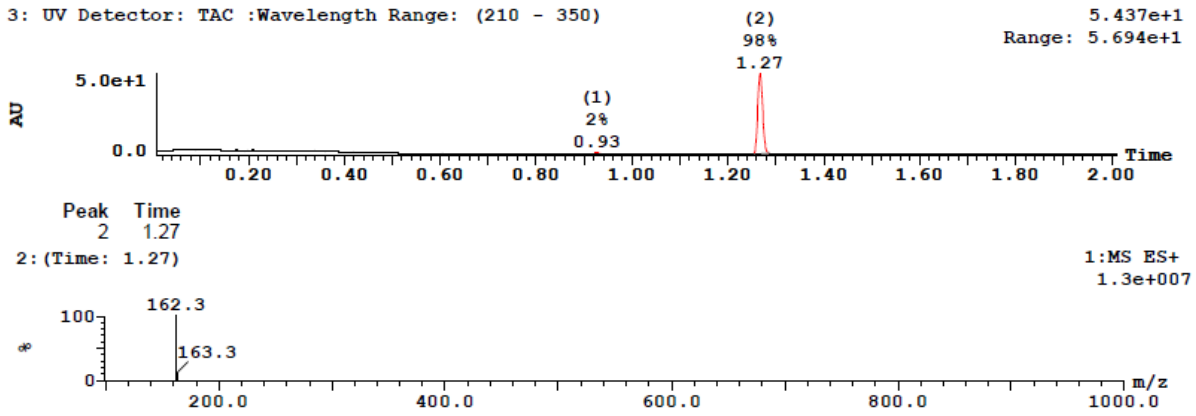
^{1}H NMR Spectra



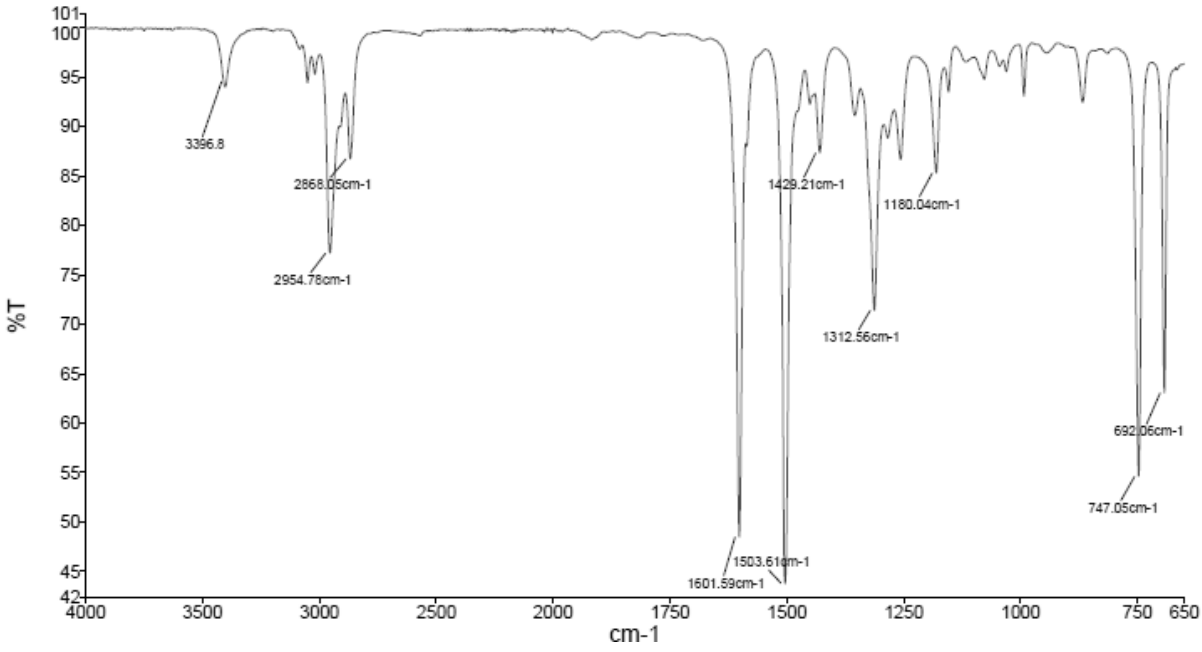
^{13}C NMR Spectra



LCMS

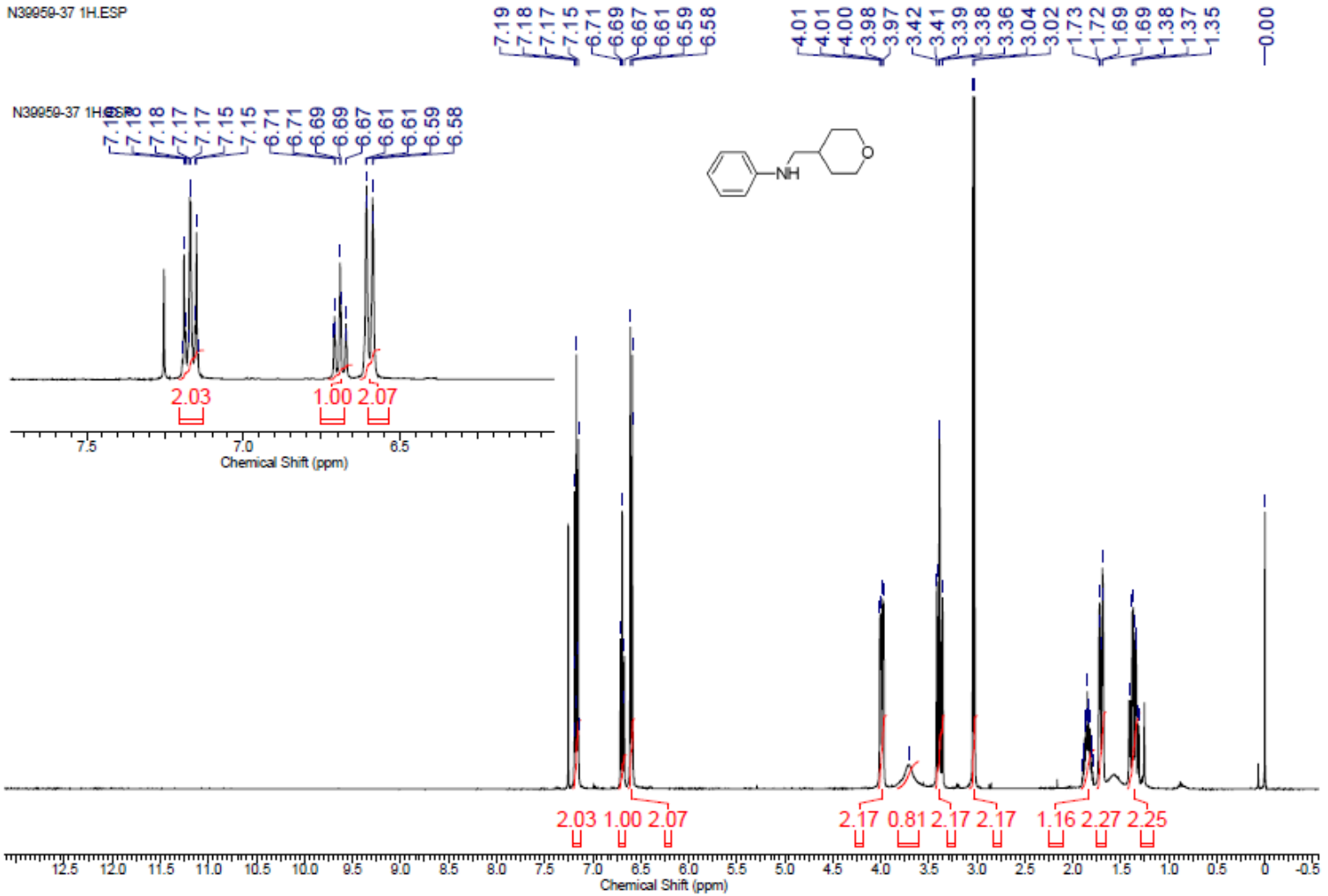


IR Spectra

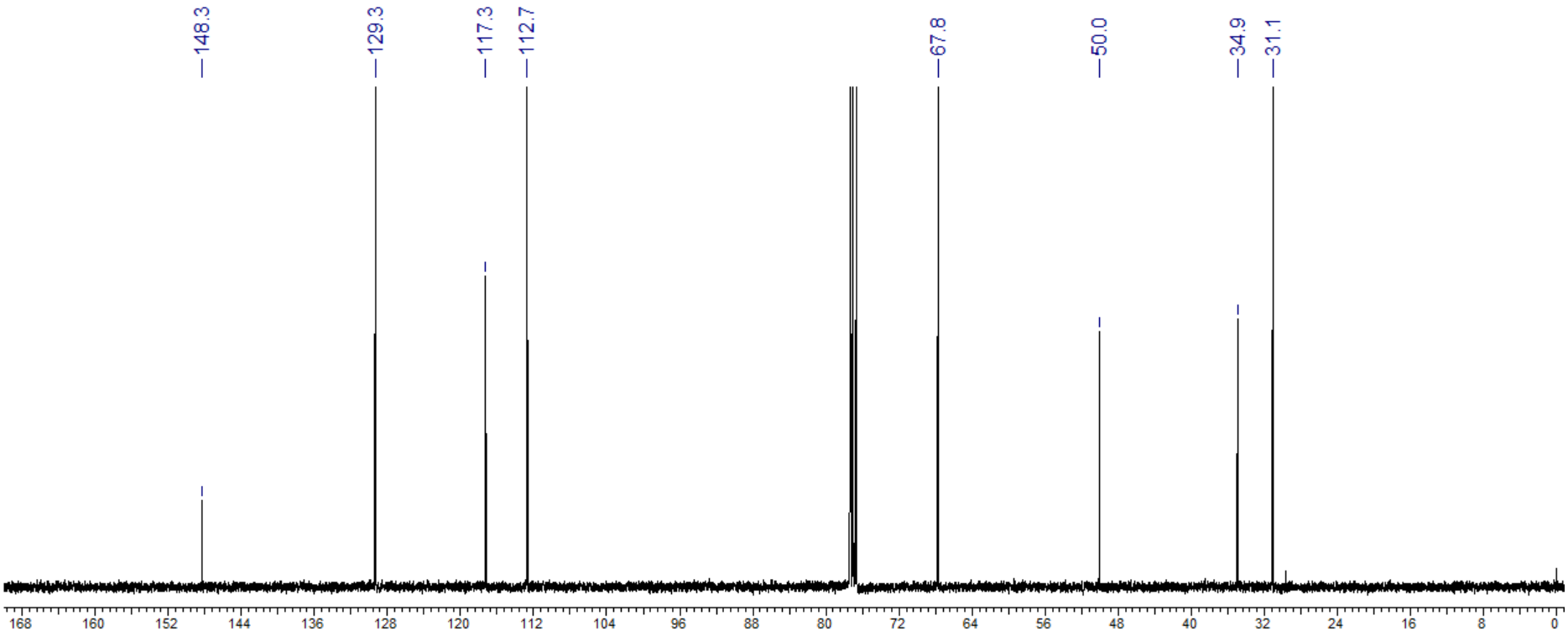


***N*-((Tetrahydro-2*H*-pyran-4-yl)methyl)aniline (7ad).**

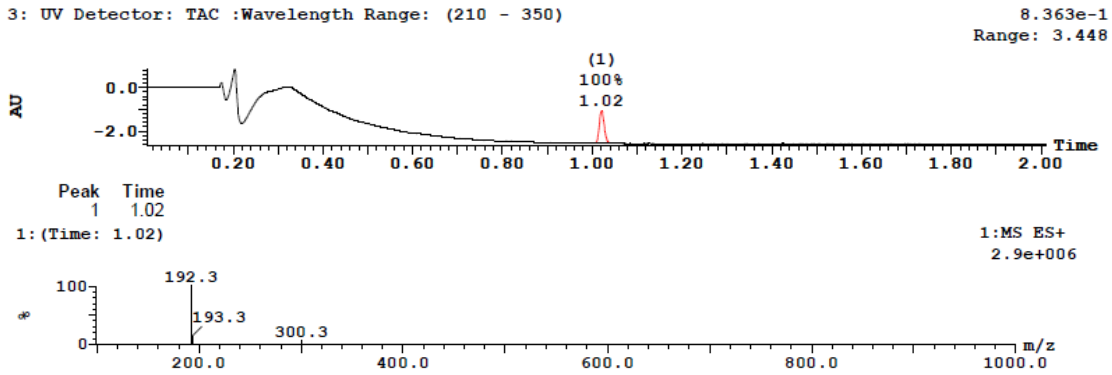
^{1}H NMR Spectra



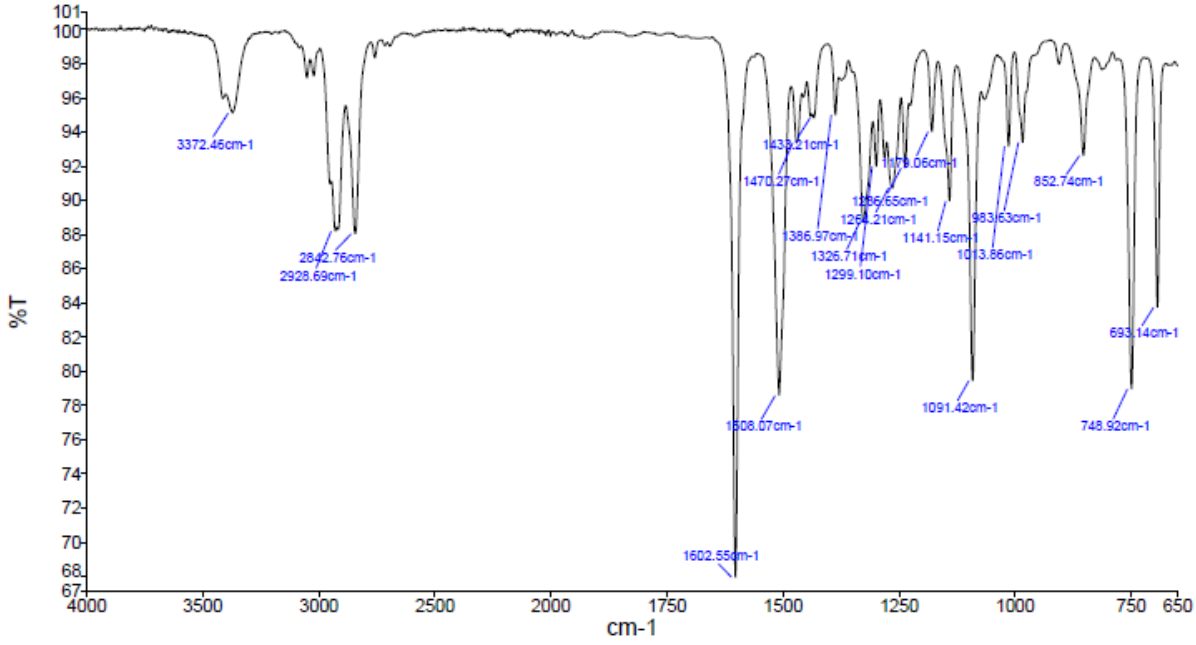
^{13}C NMR Spectra



LCMS

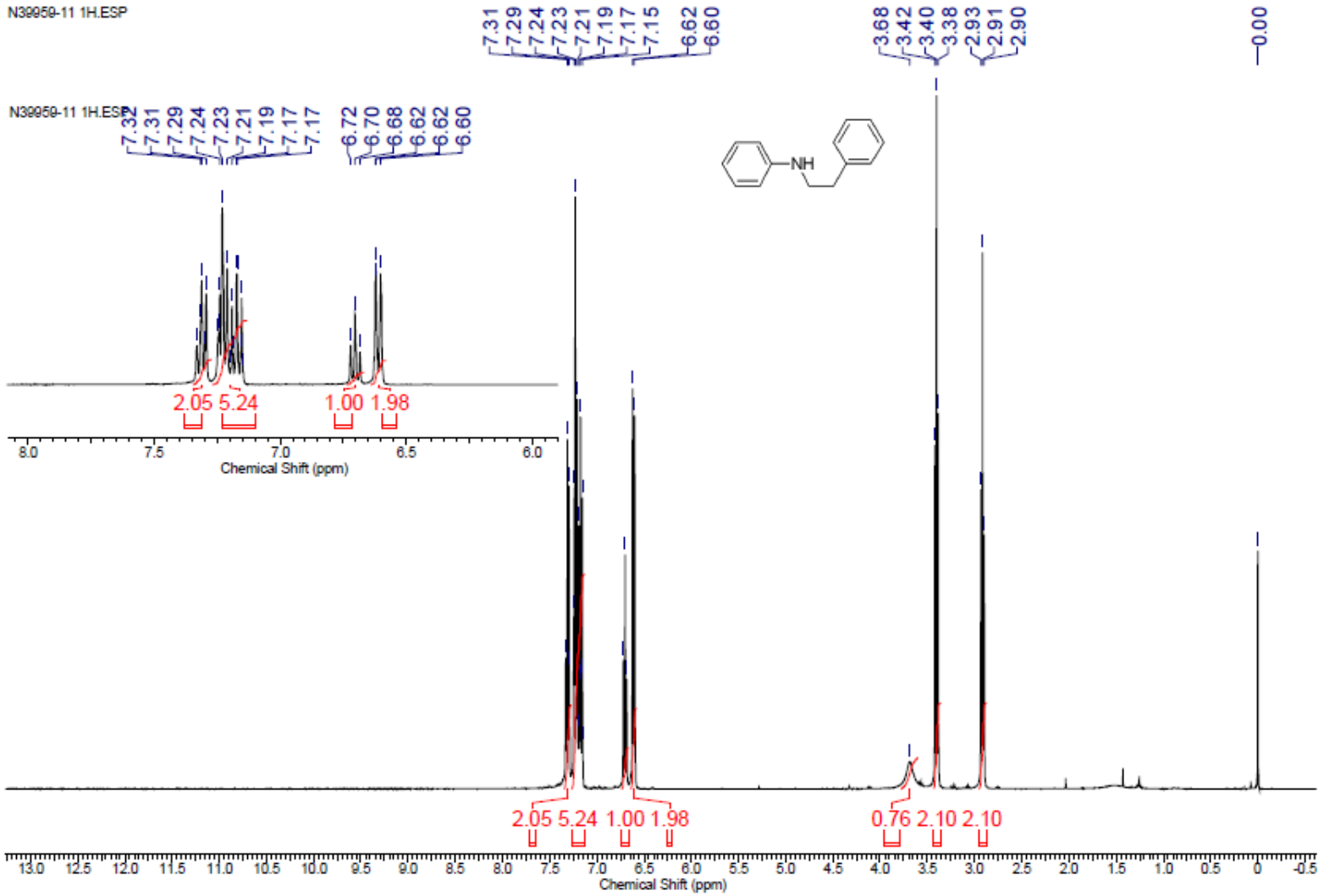


IR Spectra

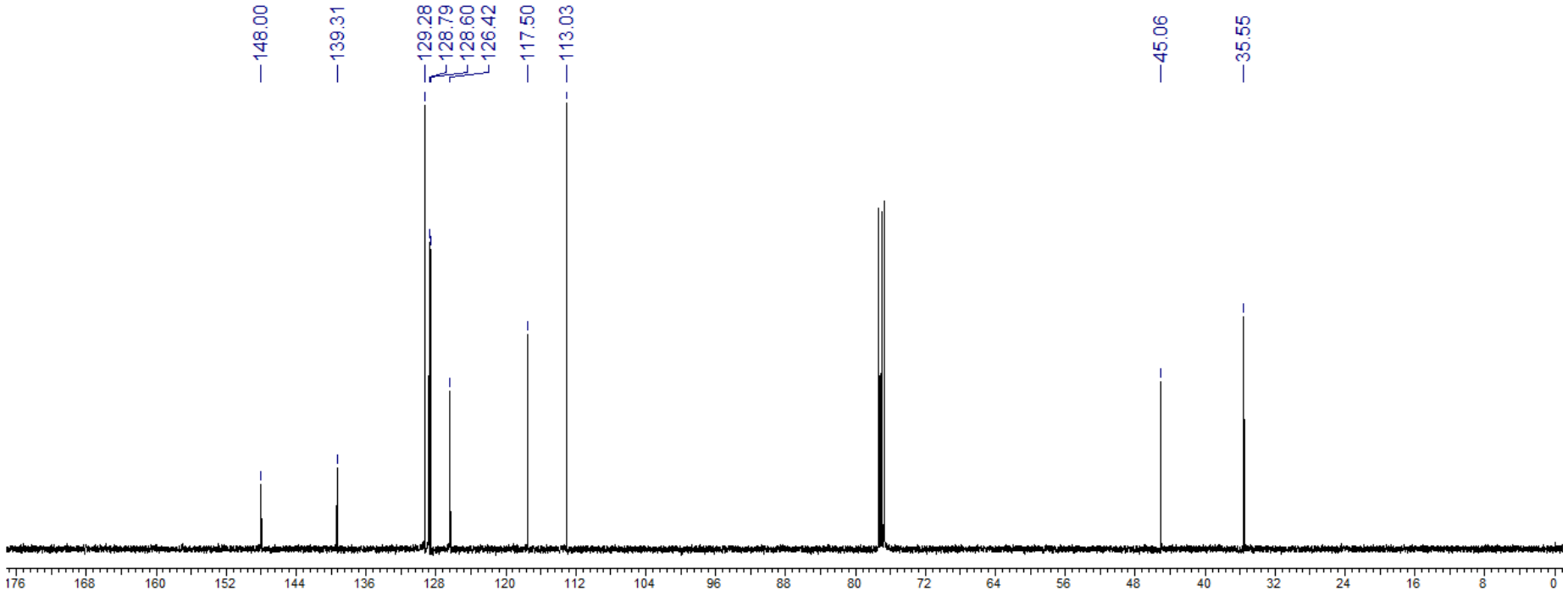


***N*-Phenethylaniline (7ae).**

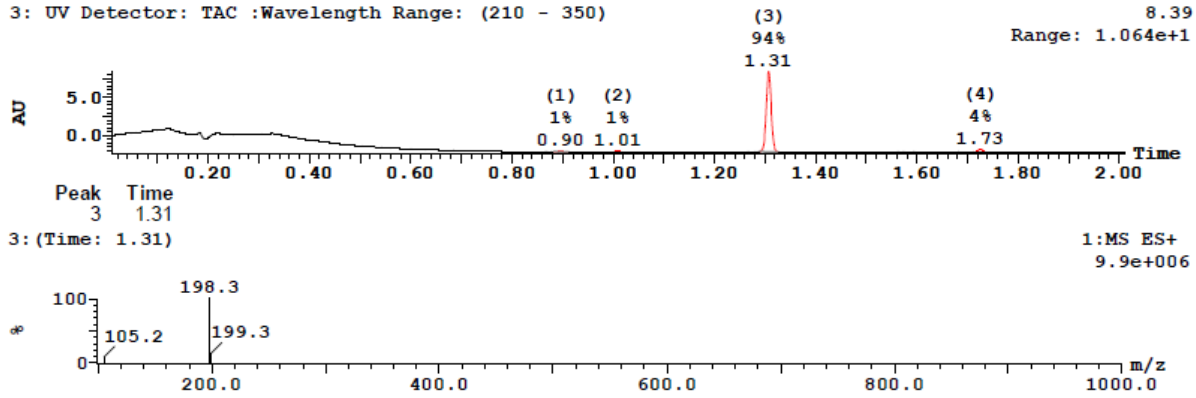
^{1}H NMR Spectra



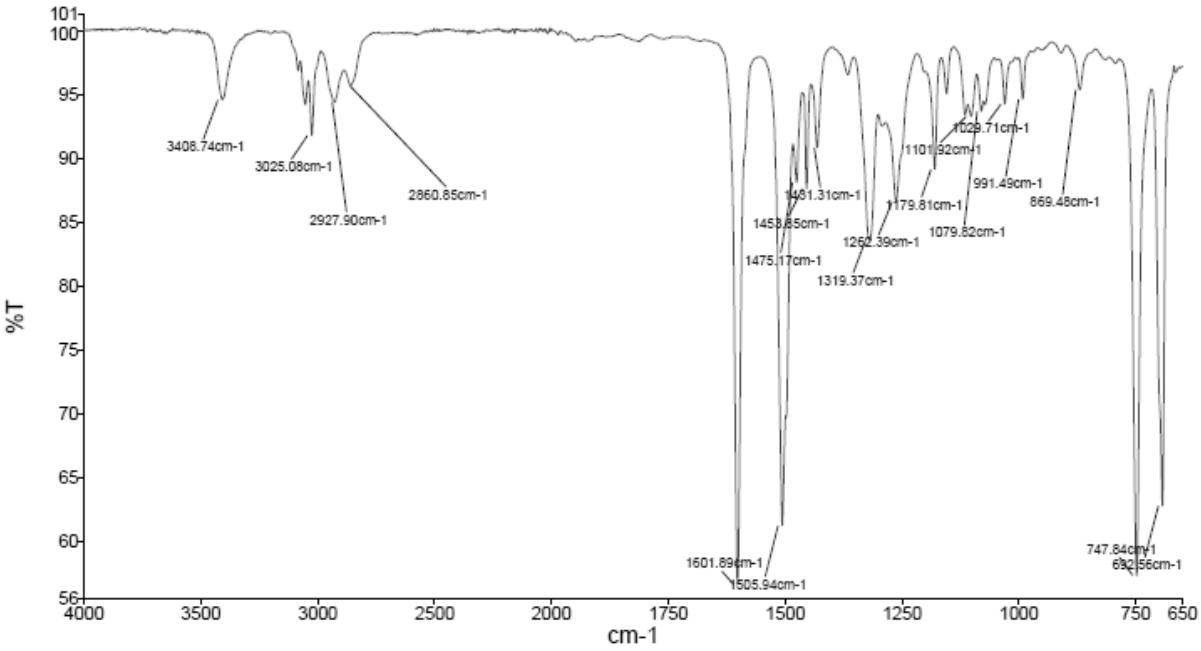
^{13}C NMR Spectra



LCMS

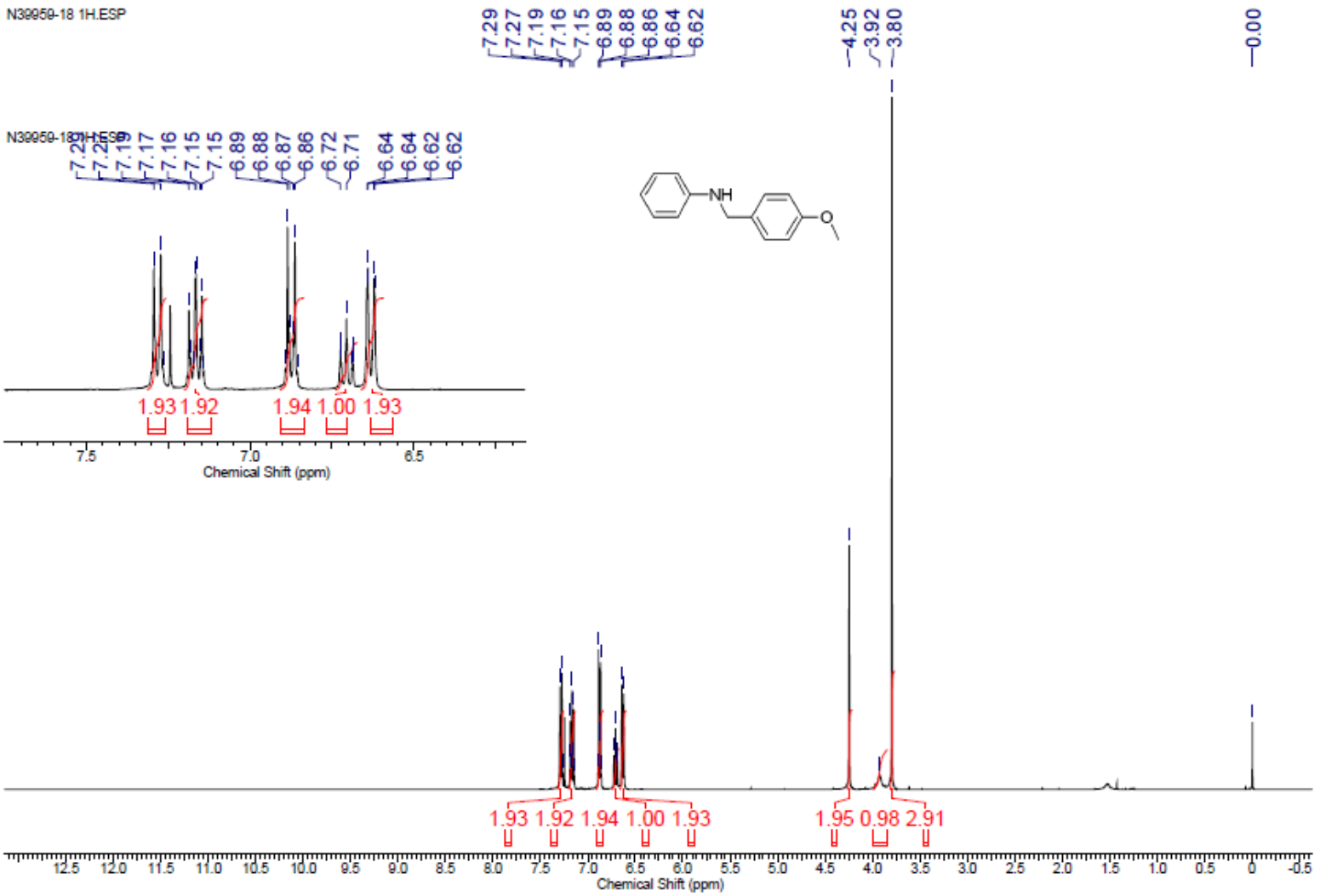


IR Spectra

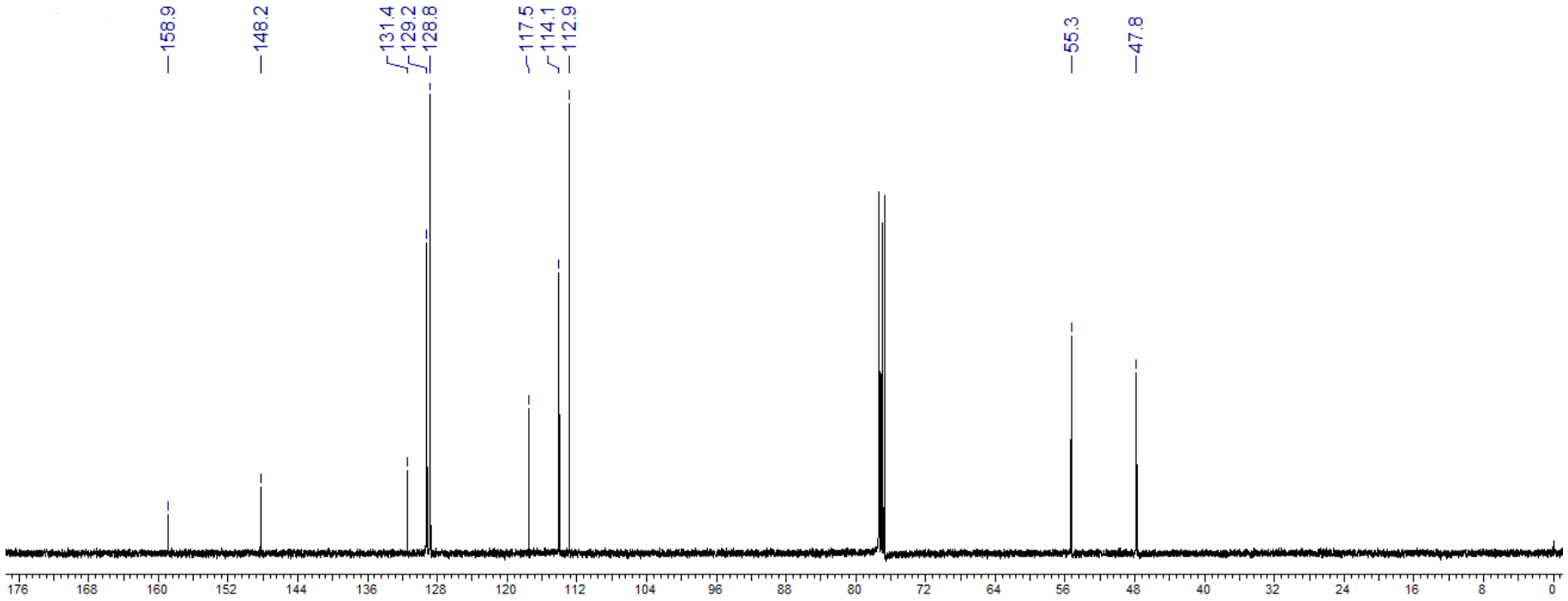


***N*-(4-Methoxybenzyl)aniline (7af).**

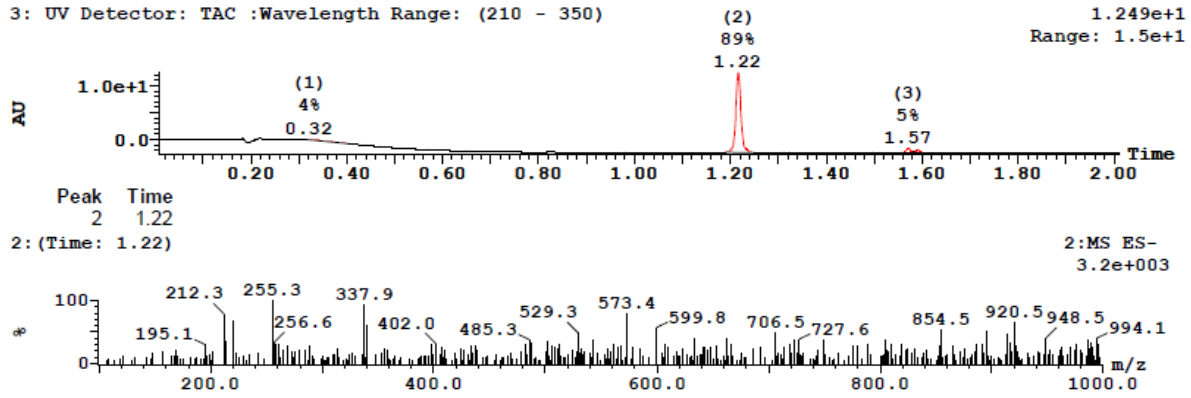
^{1}H NMR Spectra



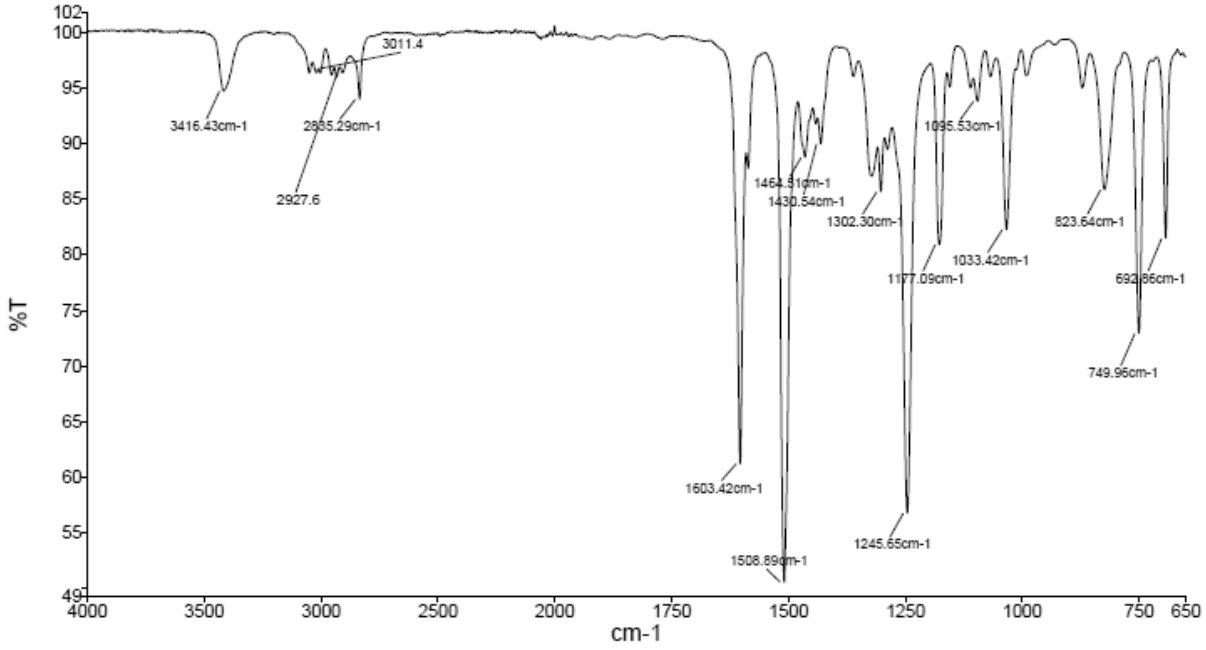
^{13}C NMR Spectra



LCMS

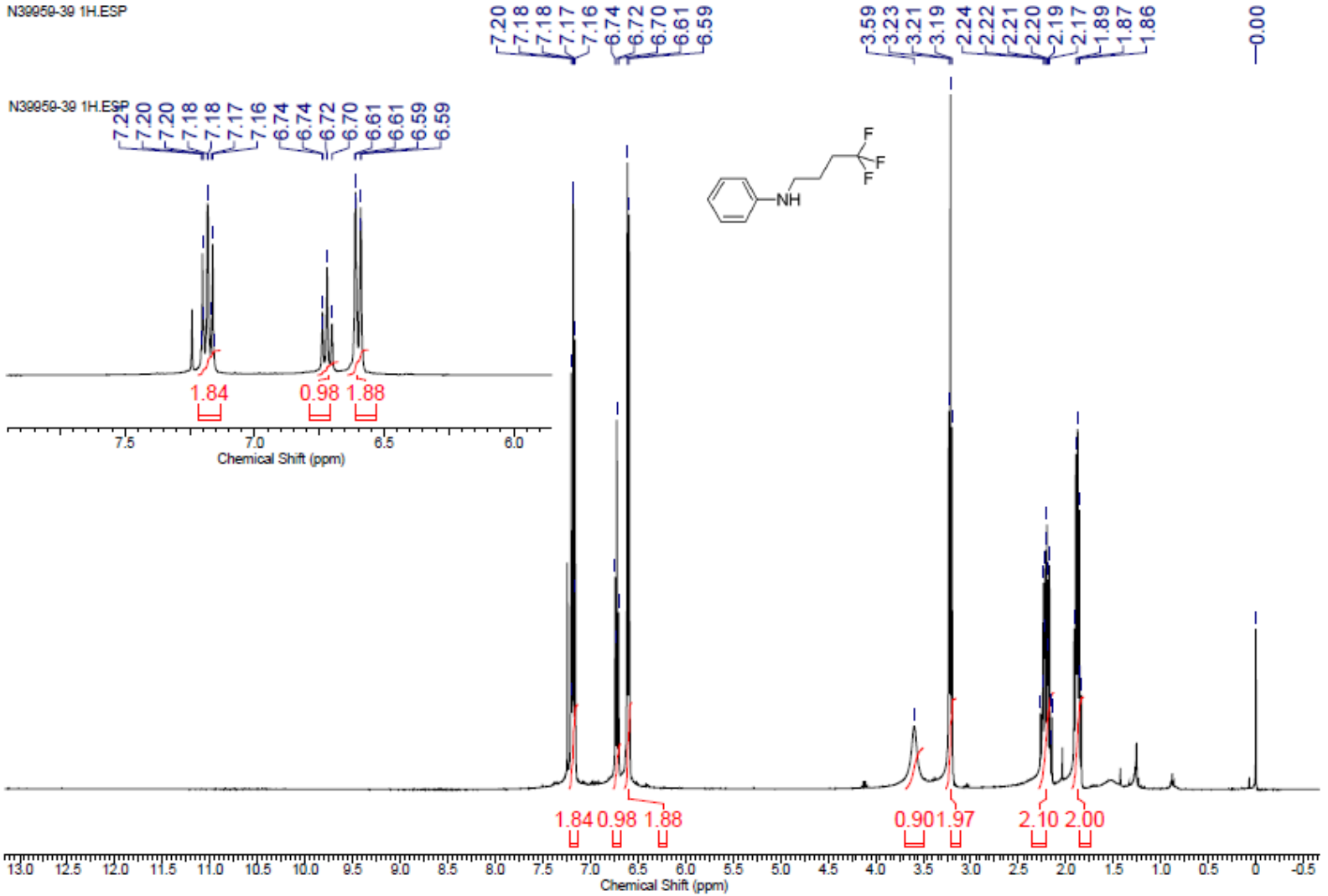


IR Spectra

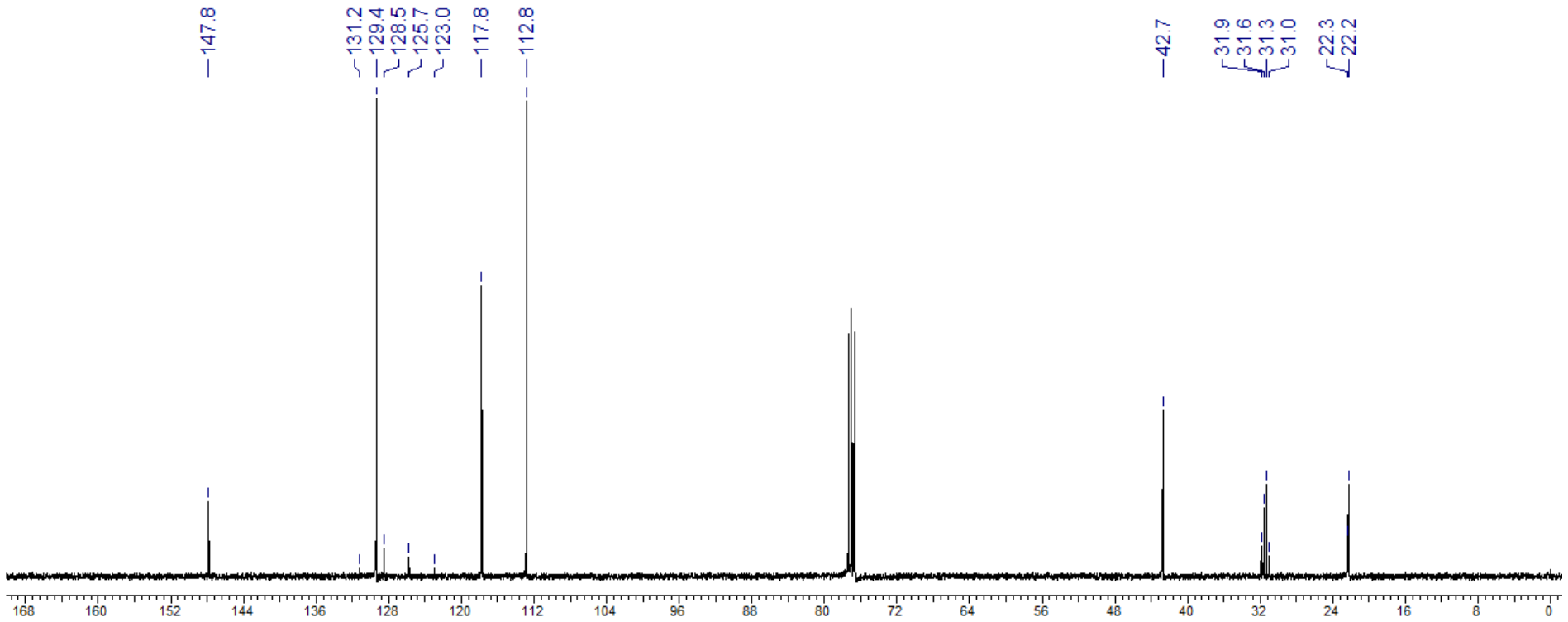


***N*-(4,4,4-Trifluorobutyl)aniline (7ag).**

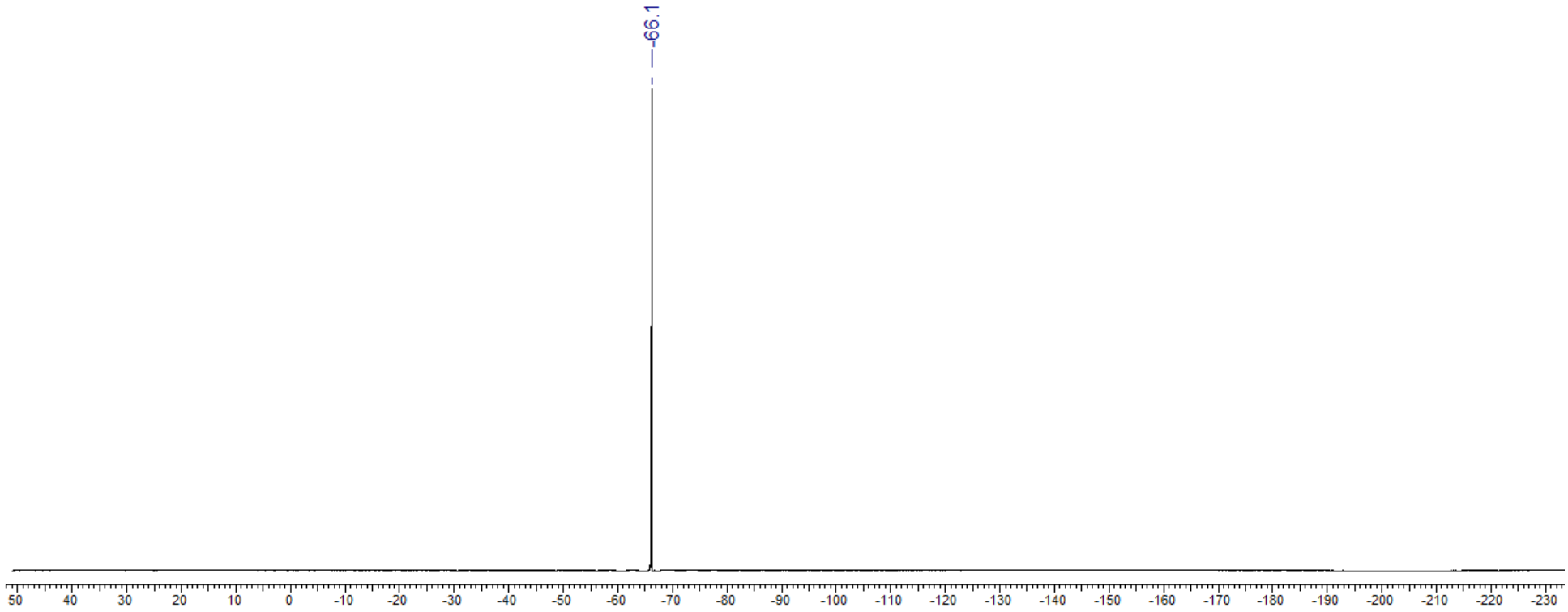
^{1}H NMR Spectra



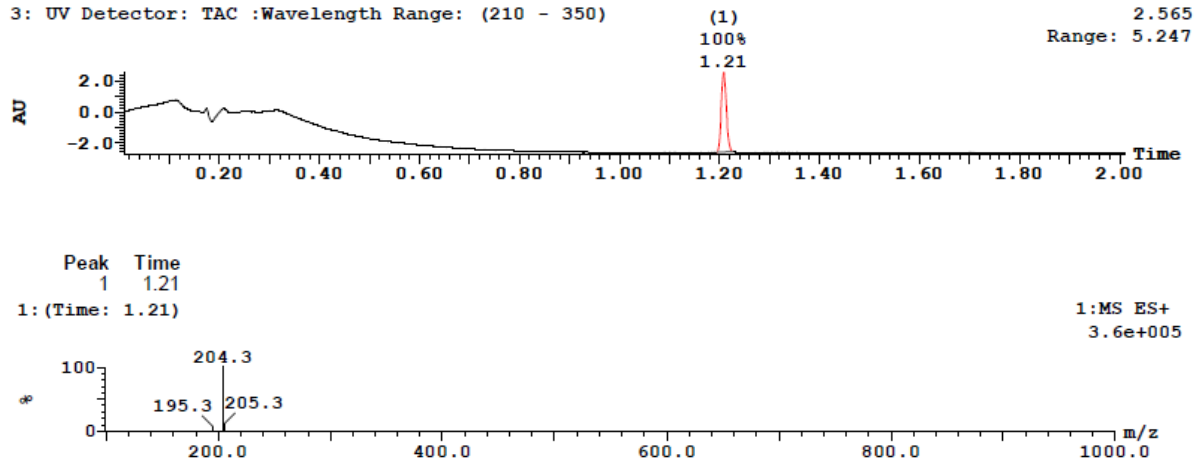
^{13}C NMR Spectra



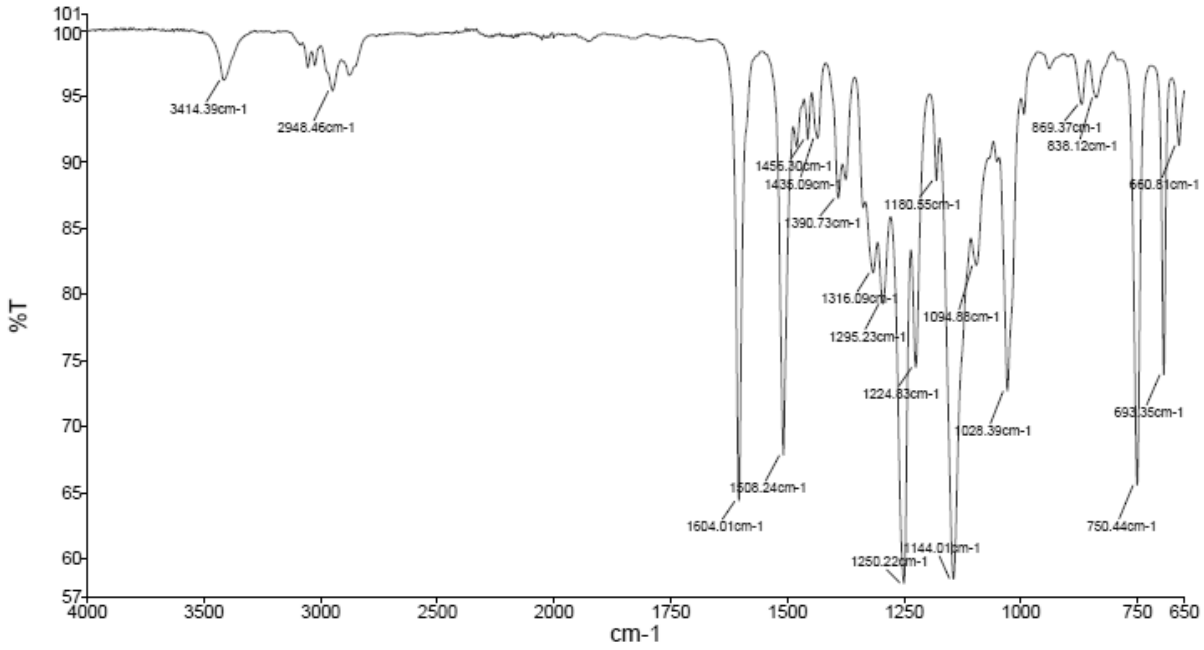
^{19}F NMR Spectra



LCMS

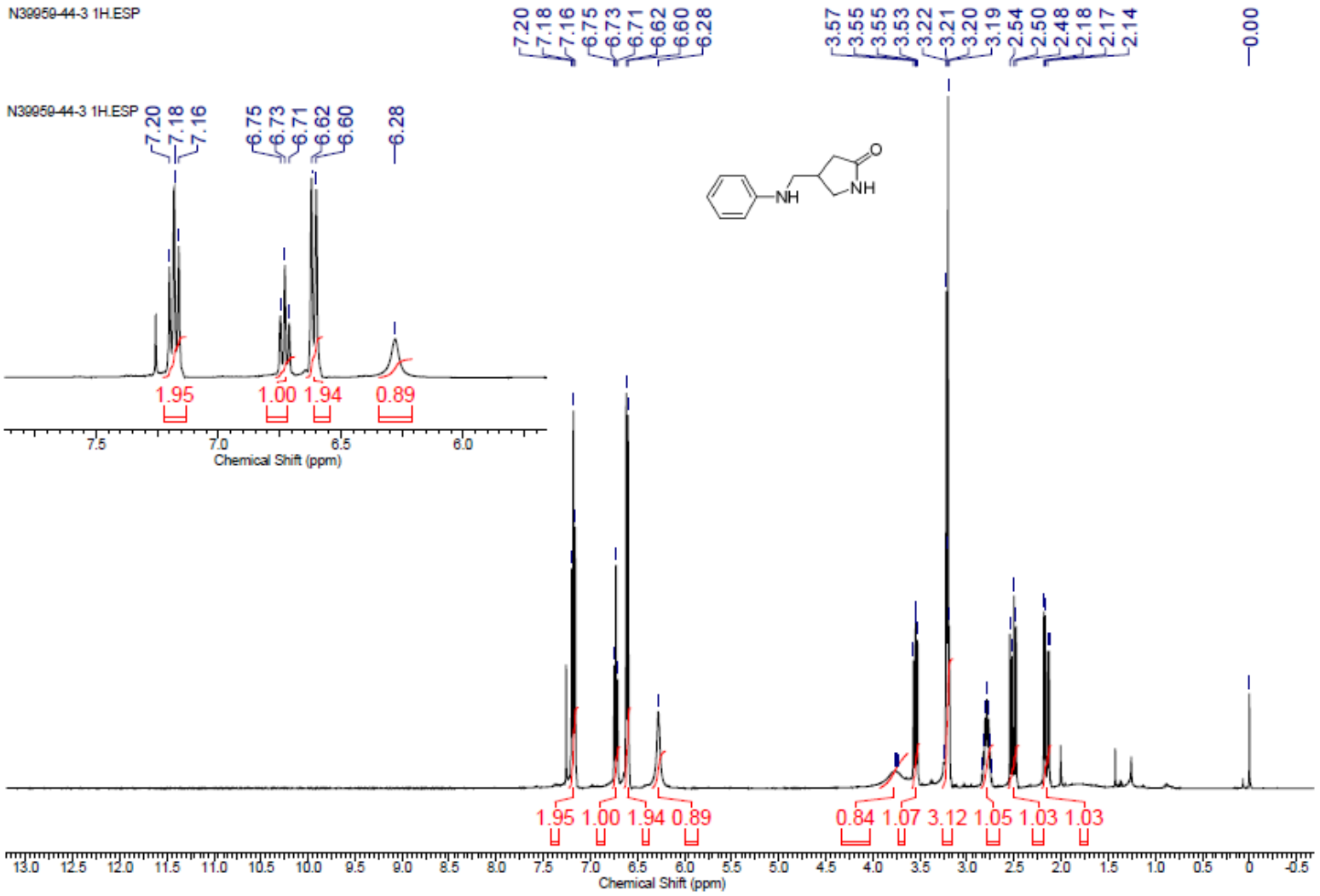


IR Spectra

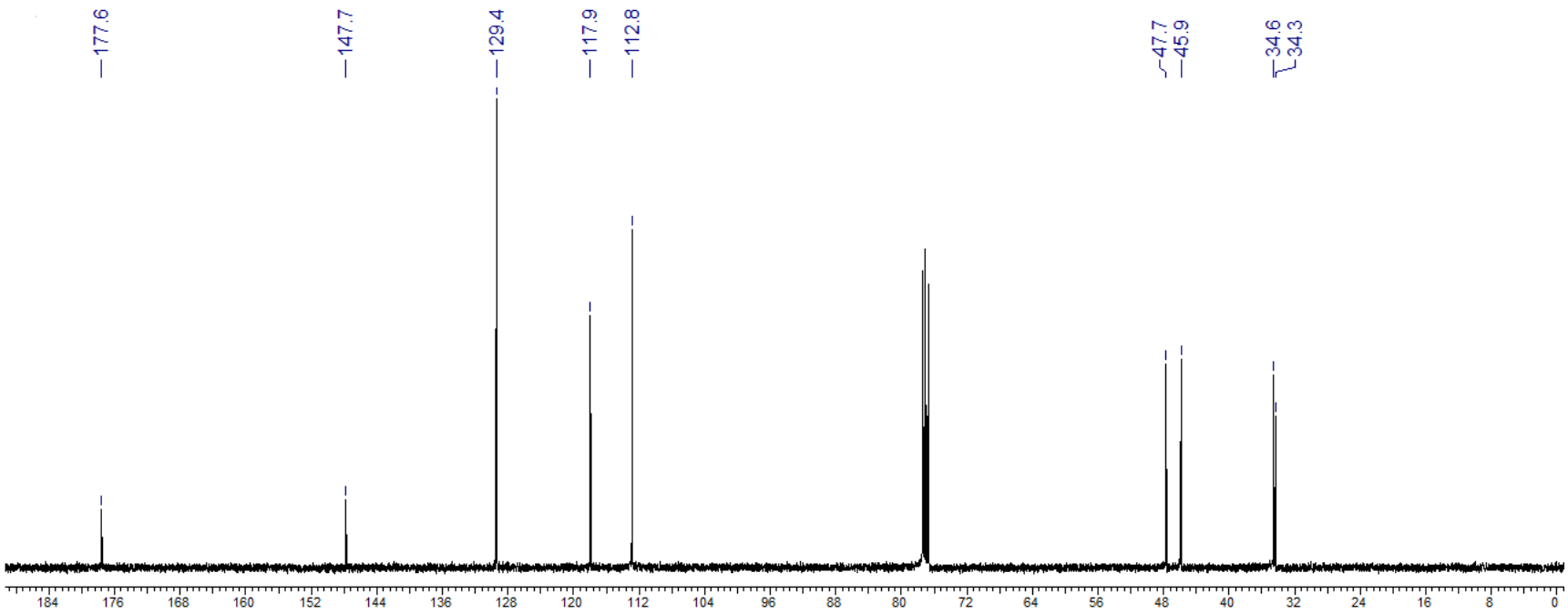


4-((Phenylamino)methyl)pyrrolidin-2-one (7ah).

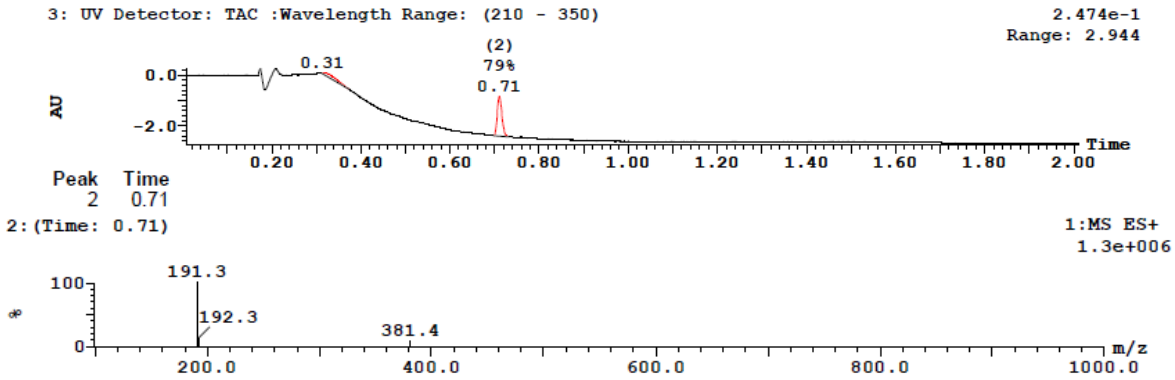
^{1}H NMR Spectra



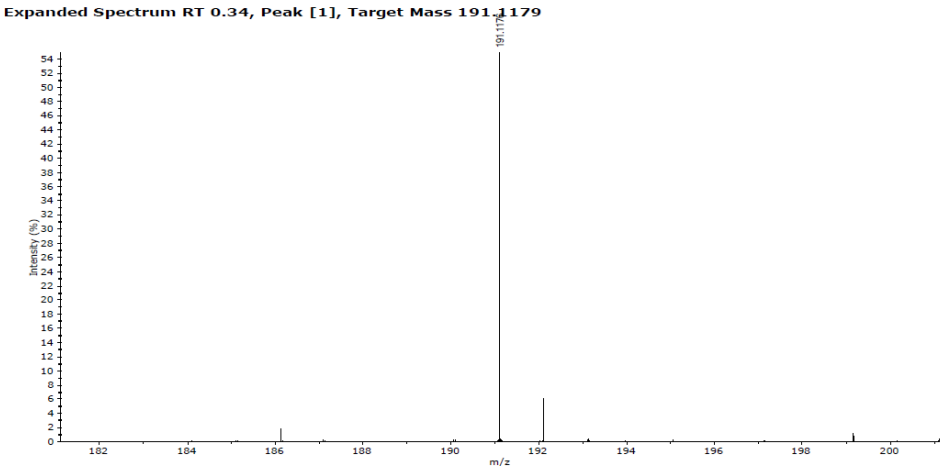
^{13}C NMR Spectra



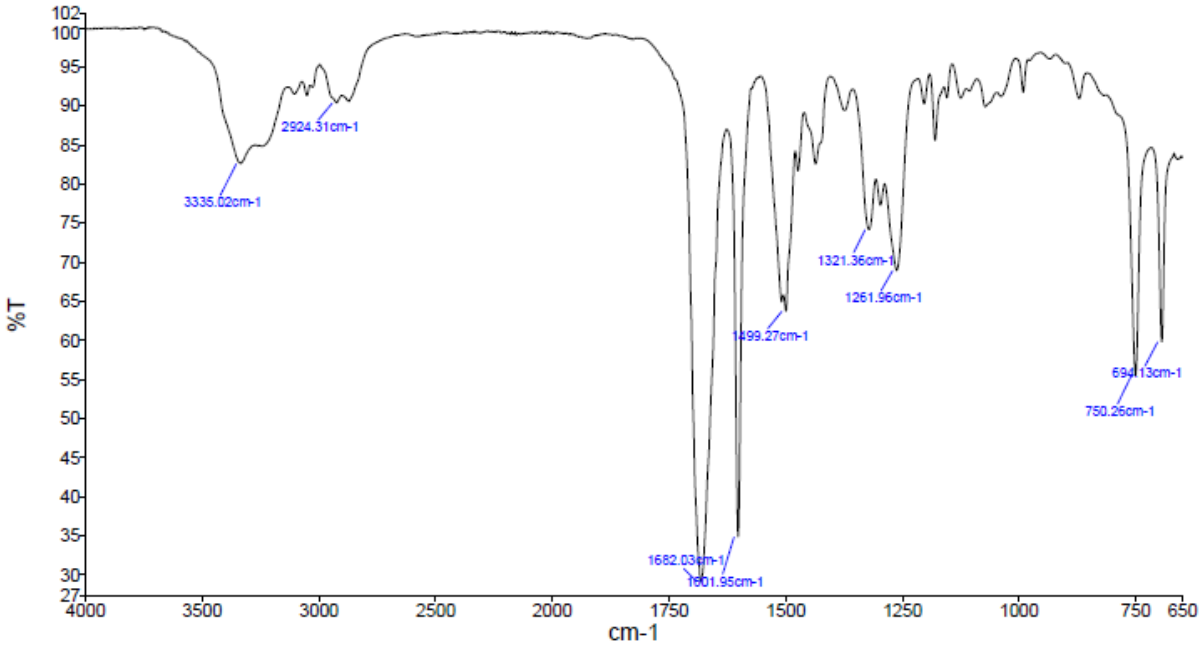
LCMS



HRMS

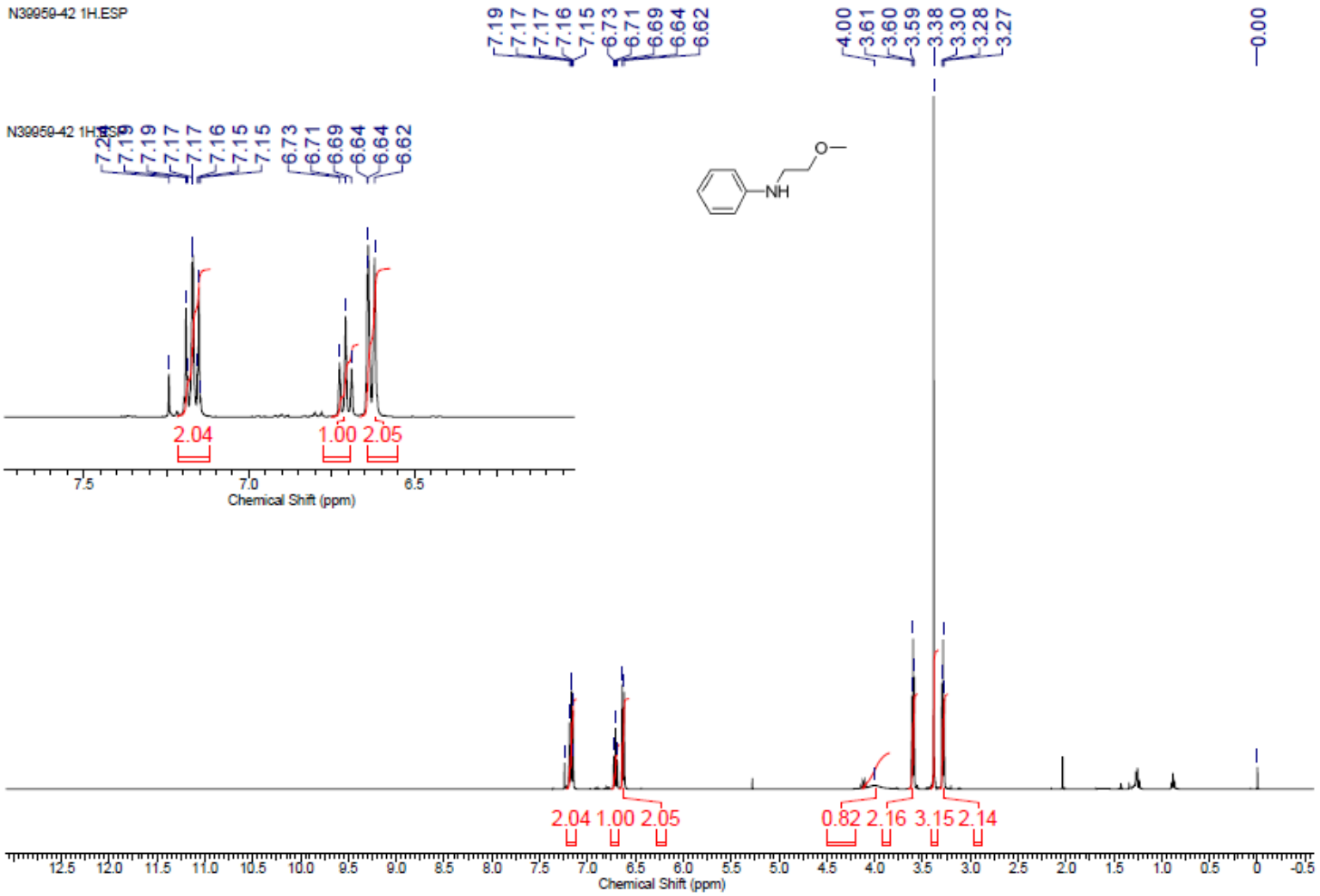


IR Spectra

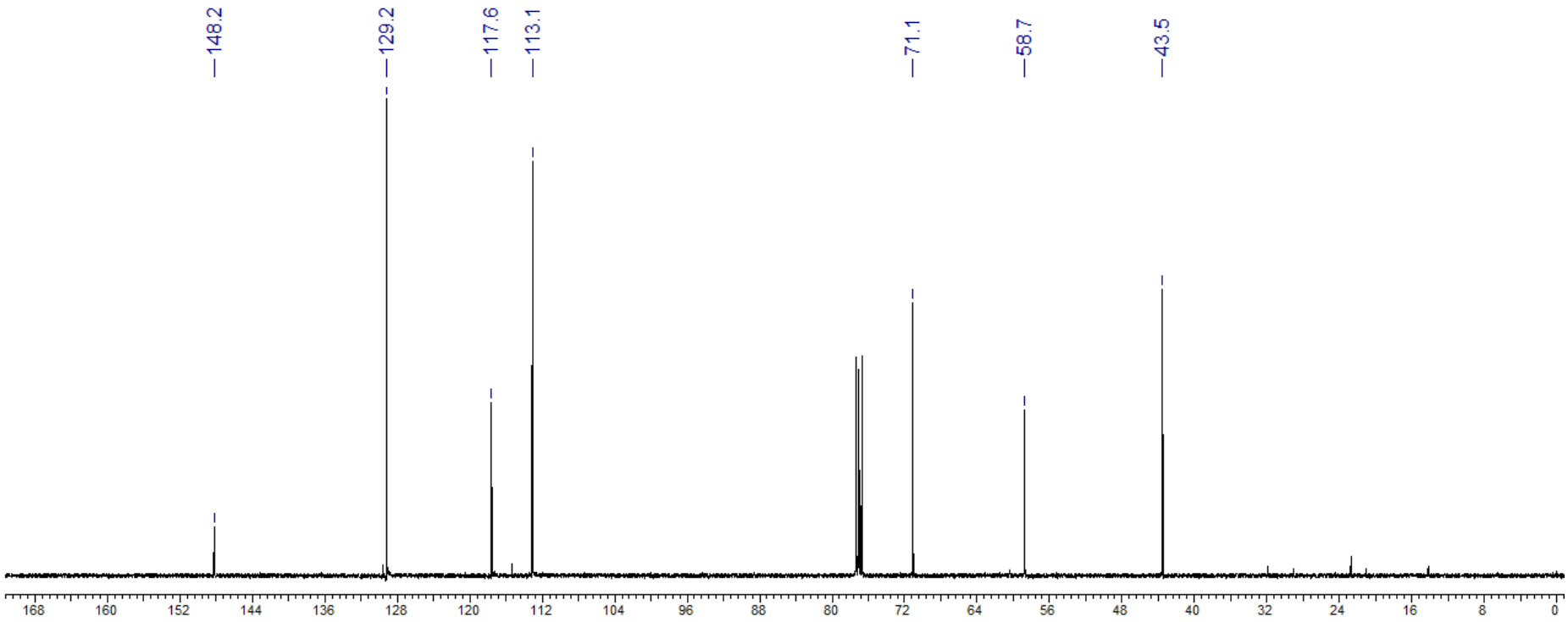


***N*-(2-Methoxyethyl)aniline (7ai).**

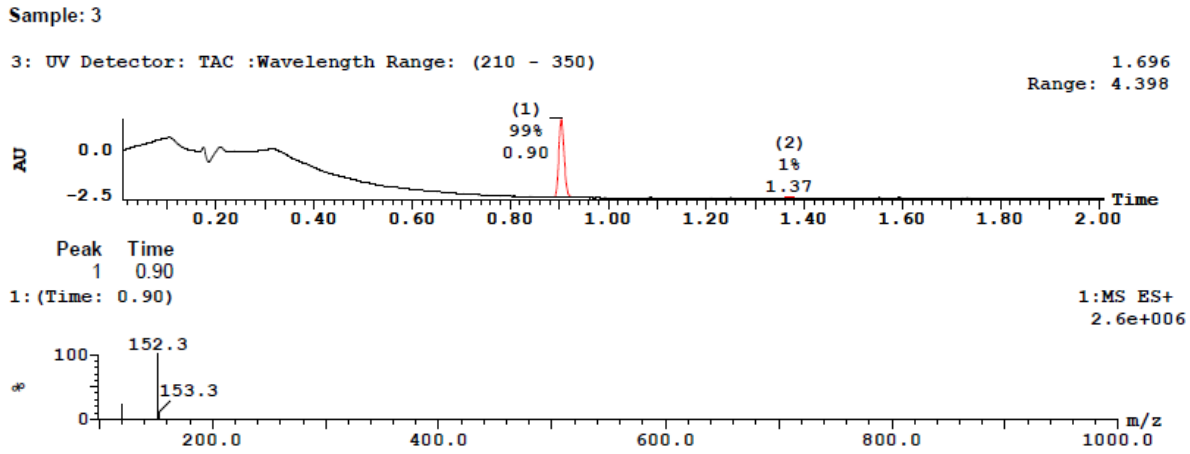
^{1}H NMR Spectra



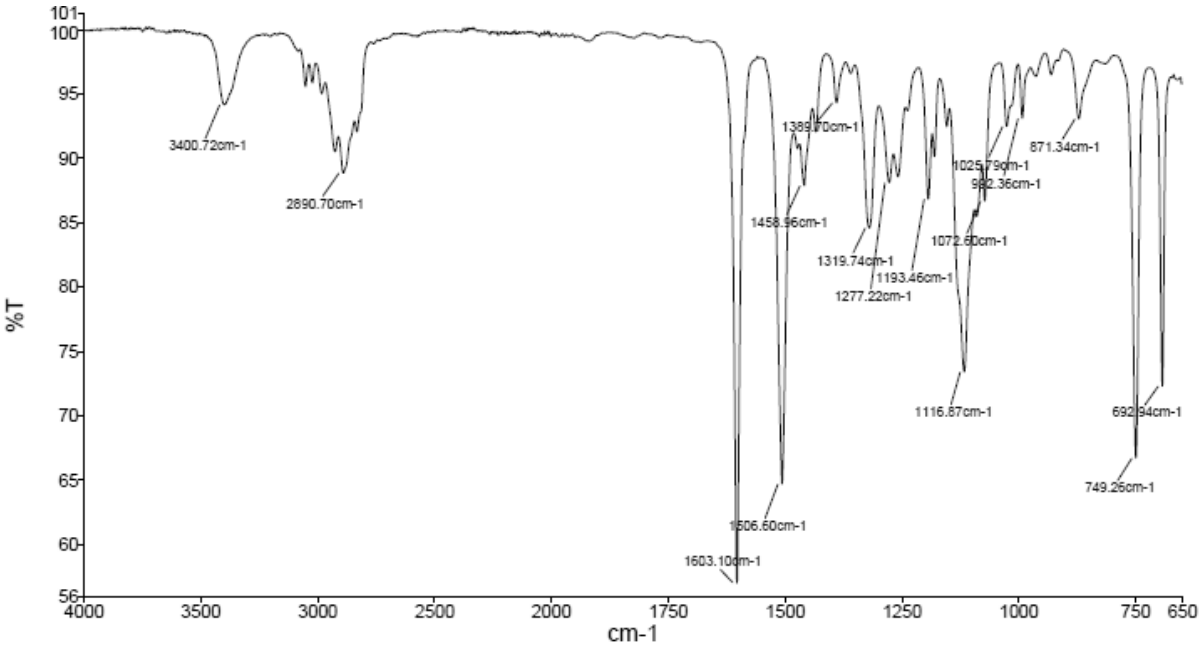
^{13}C NMR Spectra



LCMS

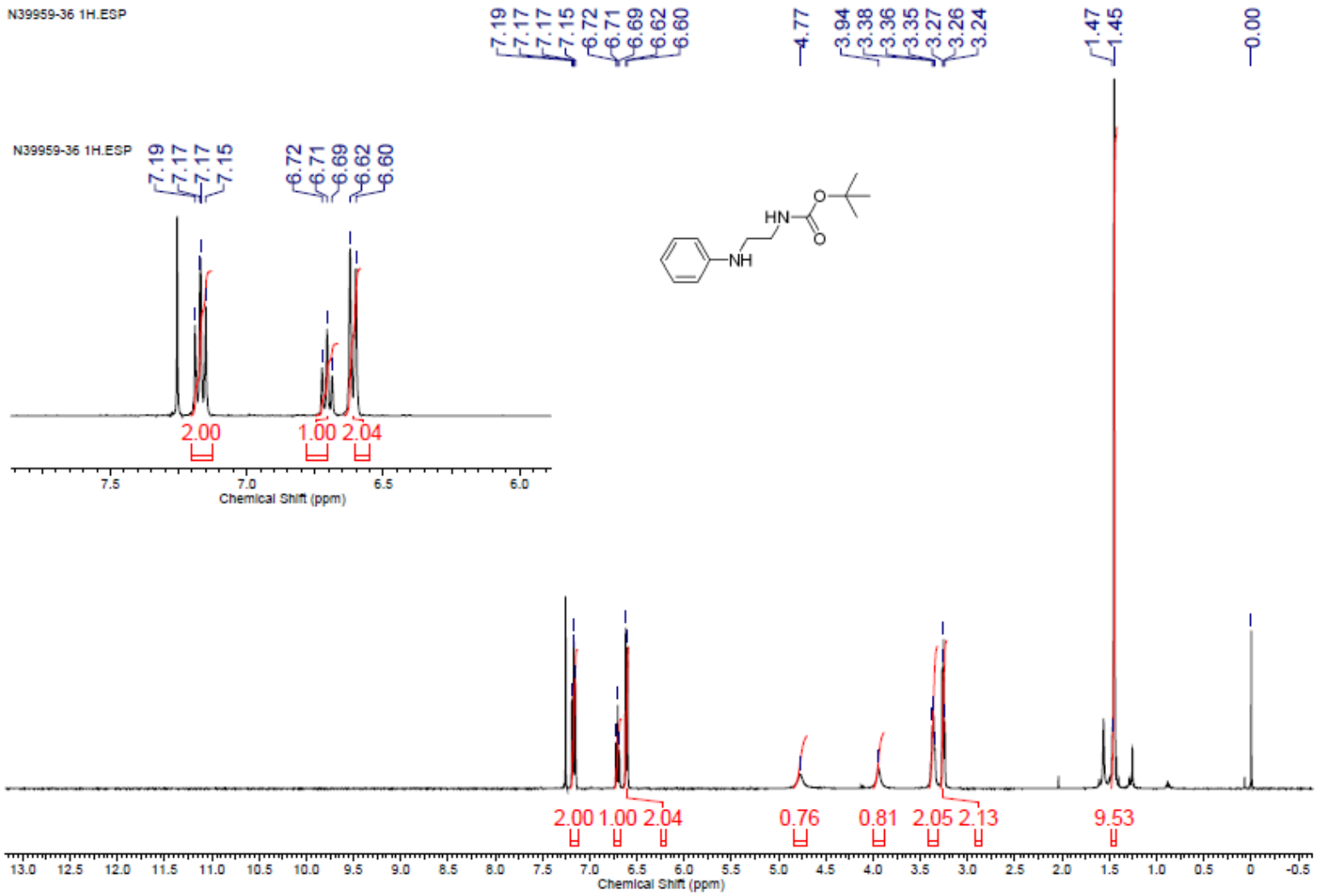


IR Spectra

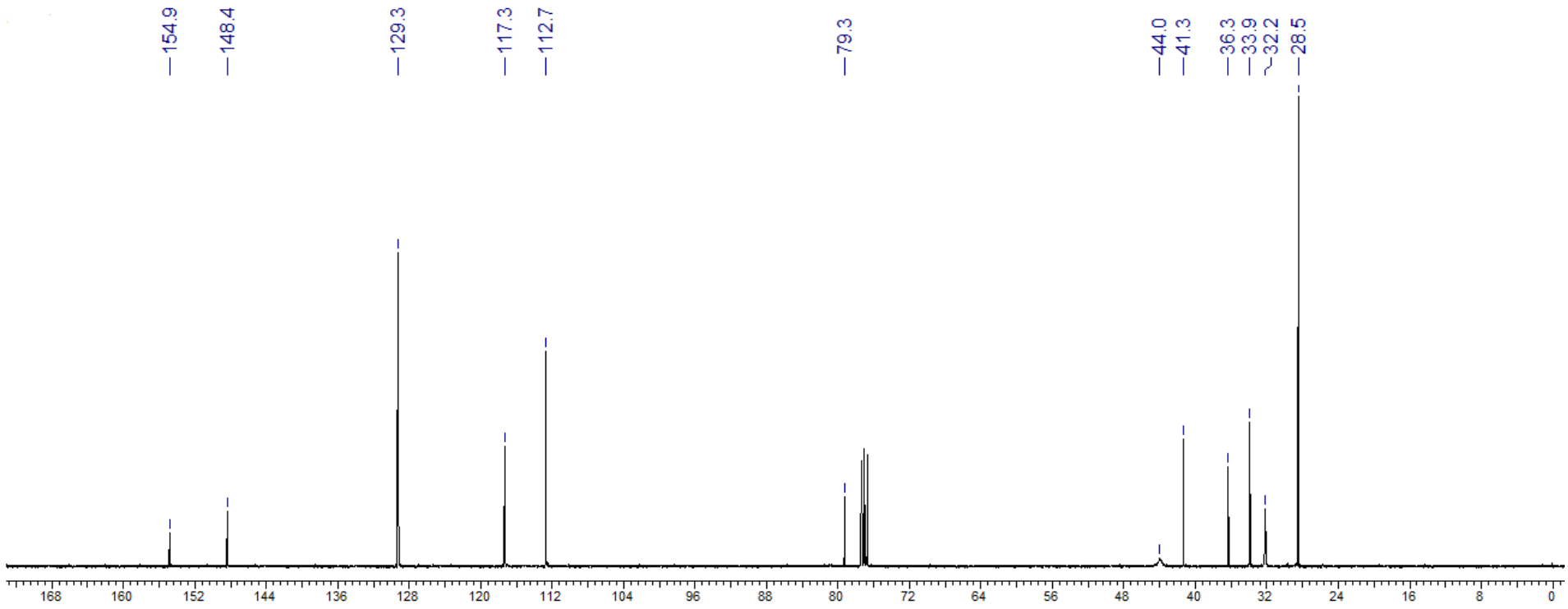


***tert*-Butyl (2-(phenylamino)ethyl)carbamate (7aj).**

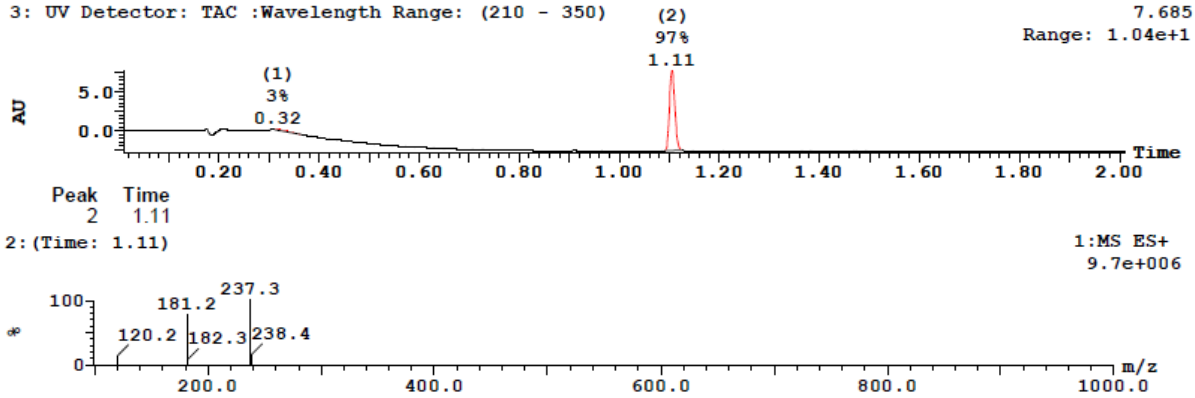
^{1}H NMR Spectra



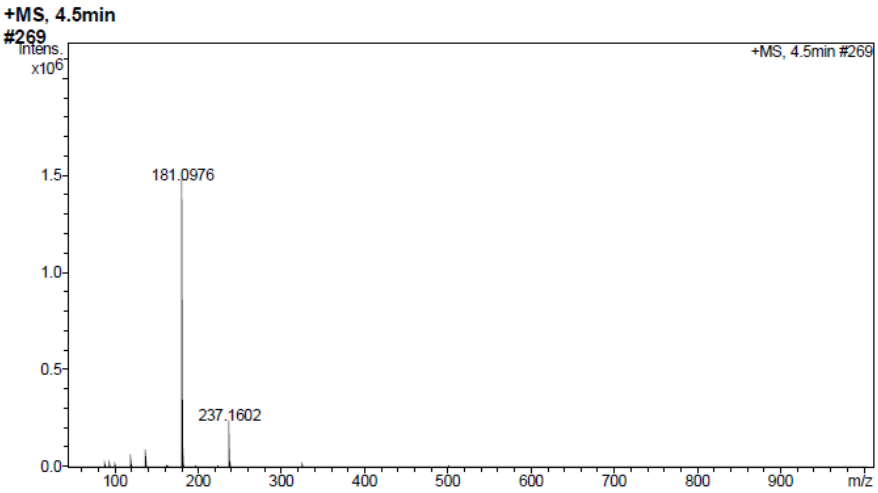
^{13}C NMR Spectra



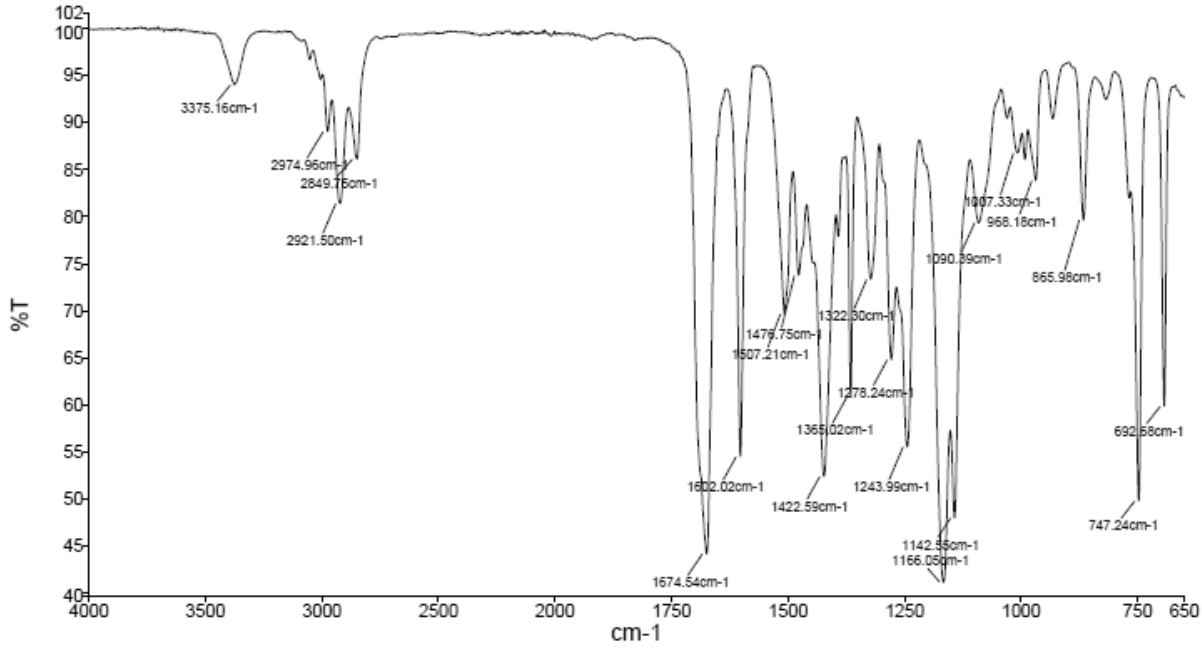
LCMS



HRMS

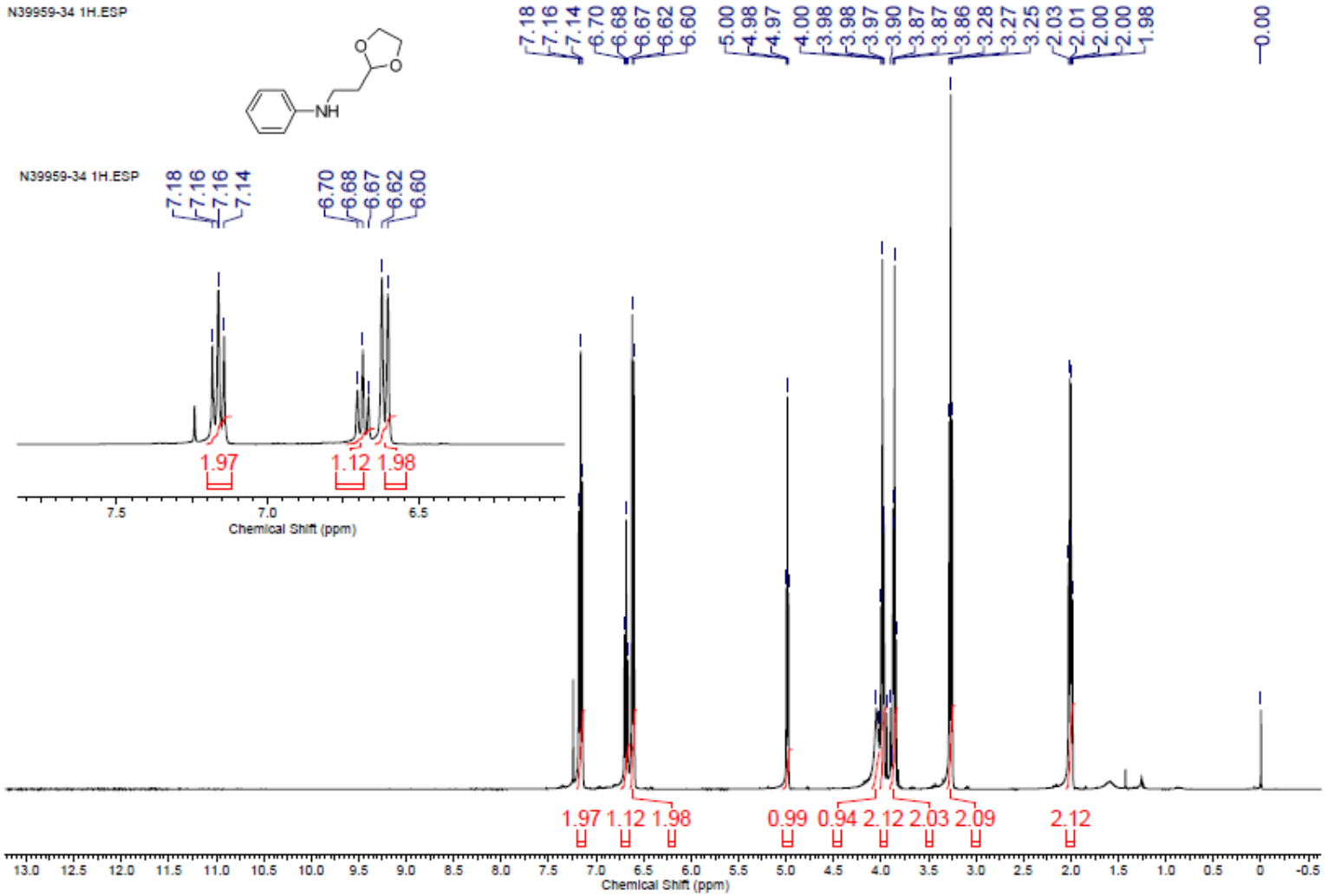


IR Spectra

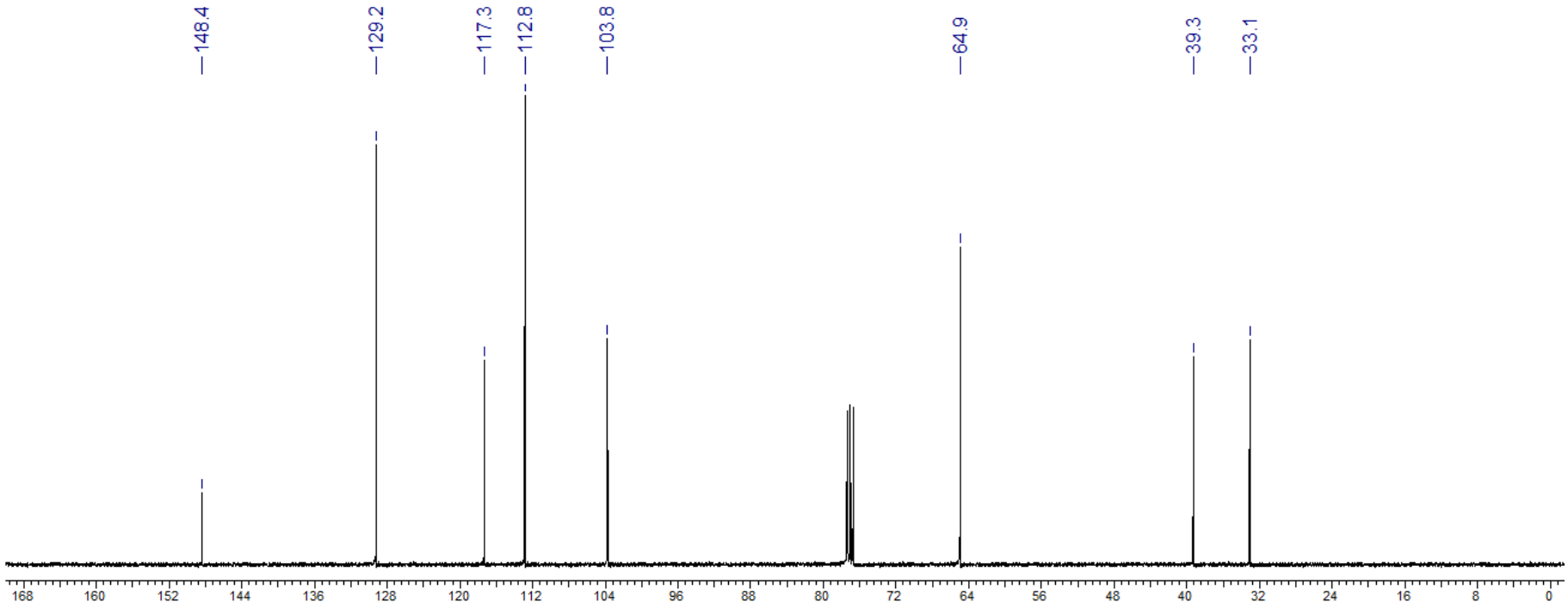


***N*-(2-(1,3-Dioxolan-2-yl)ethyl)aniline (7ak).**

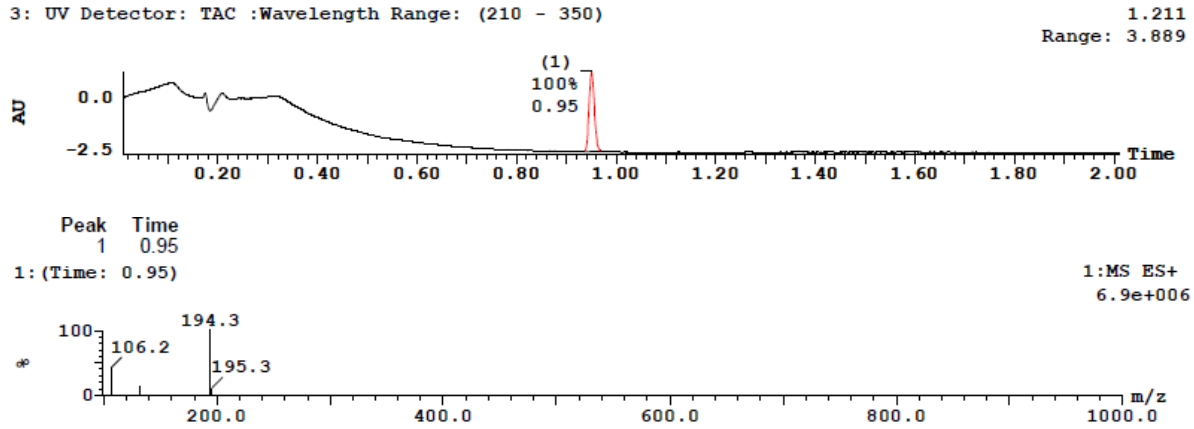
^{1}H NMR Spectra



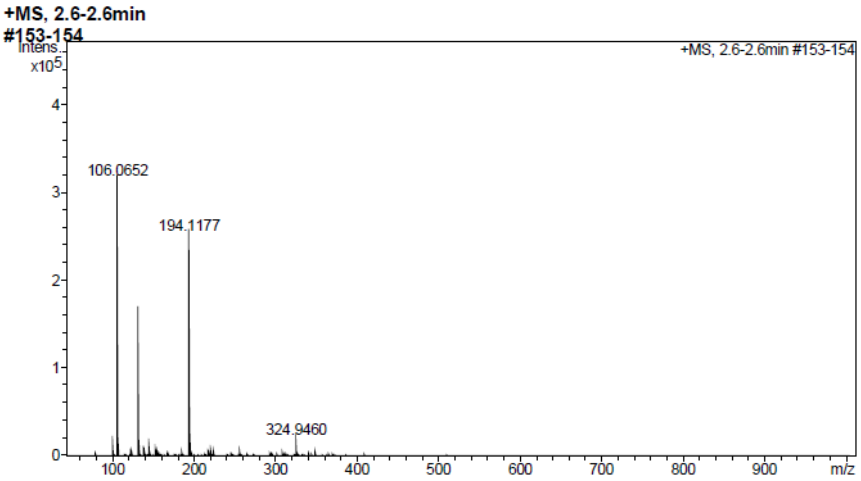
^{13}C NMR Spectra



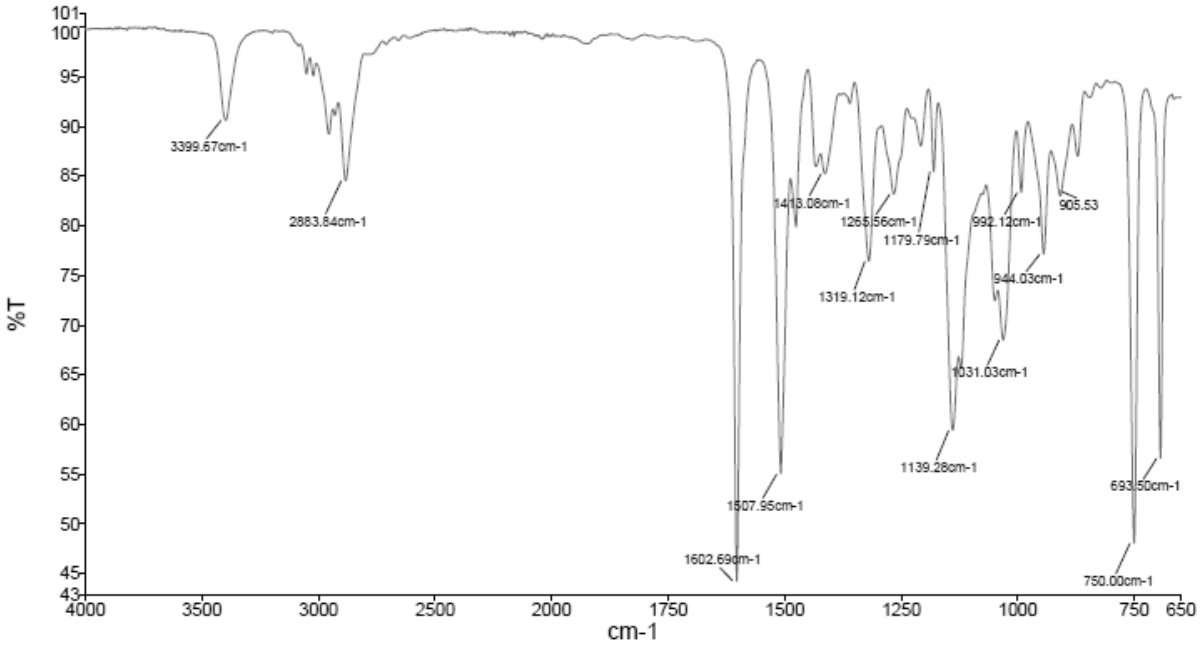
LCMS



HRMS

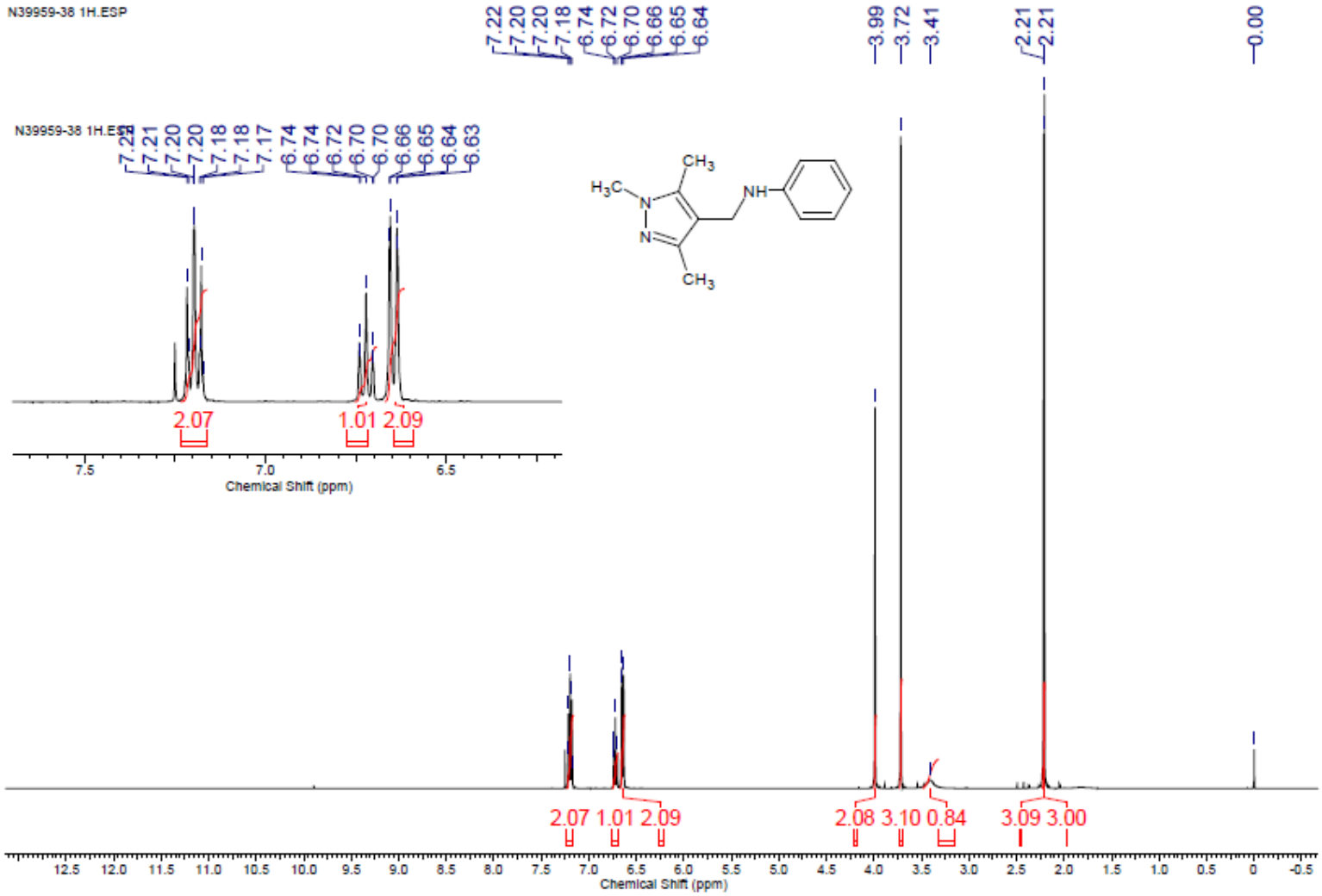


IR Spectra

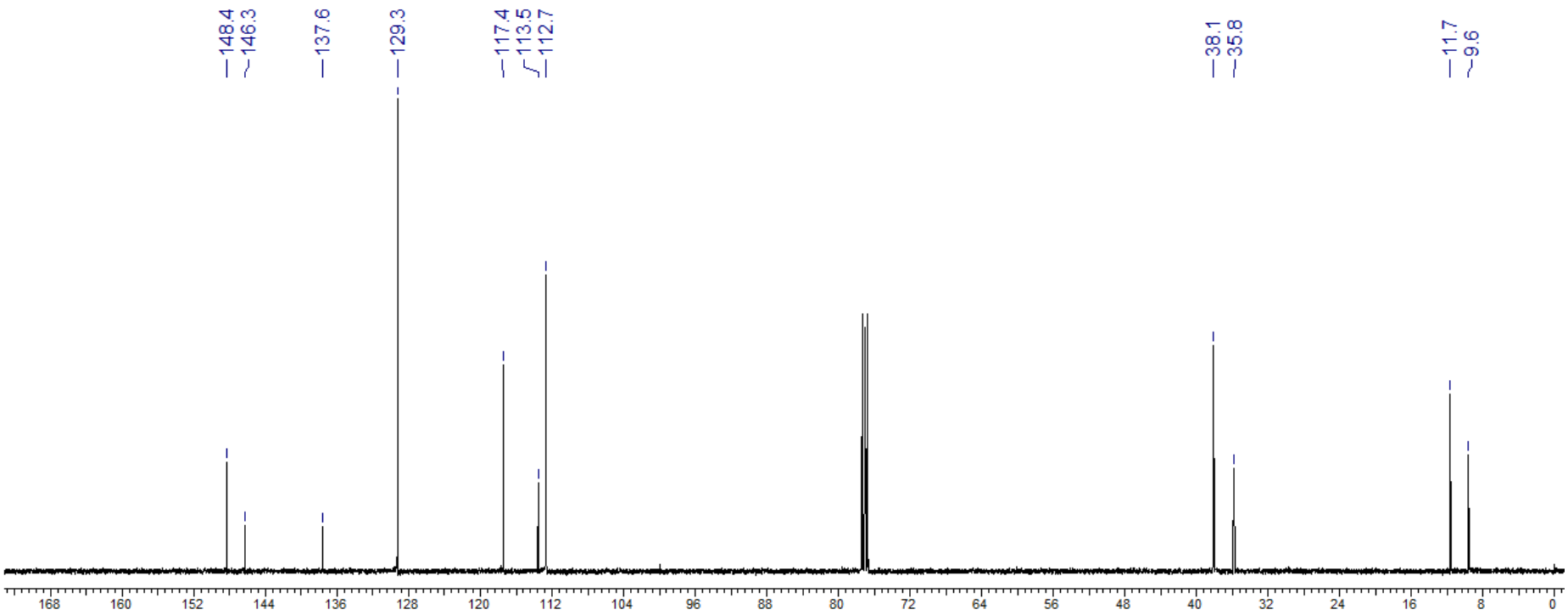


***N*-((1,3,5-Trimethyl-1*H*-pyrazol-4-yl)methyl)aniline (7al).**

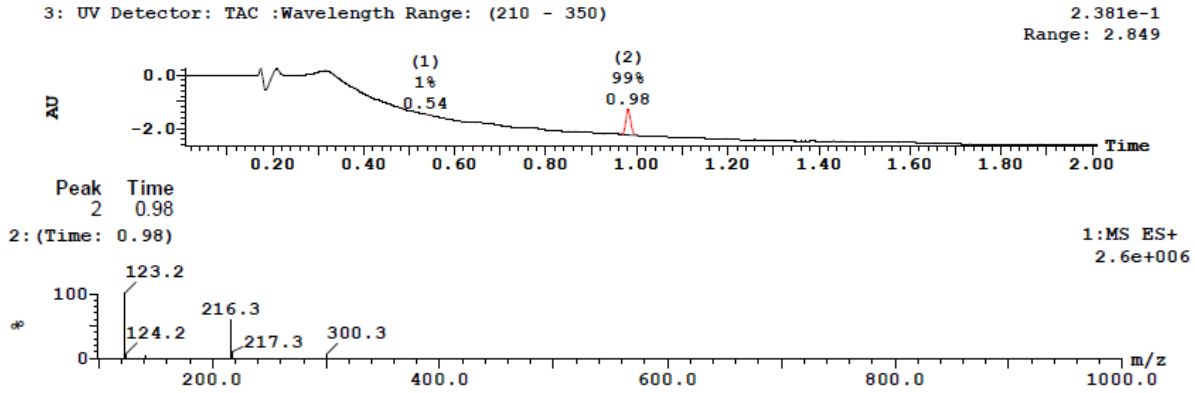
^{1}H NMR Spectra



^{13}C NMR Spectra



LCMS



IR Spectra