

Green synthesis of 2,3,4,9-tetrahydro-1*H*-carbazoles/ 2,3-dimethylindoles catalyzed by [bmim (BF₄)] ionic liquid in methanol

Tamatakallu O. ShrungheshKumar¹, Kittappa M. Mahadevan^{1*}

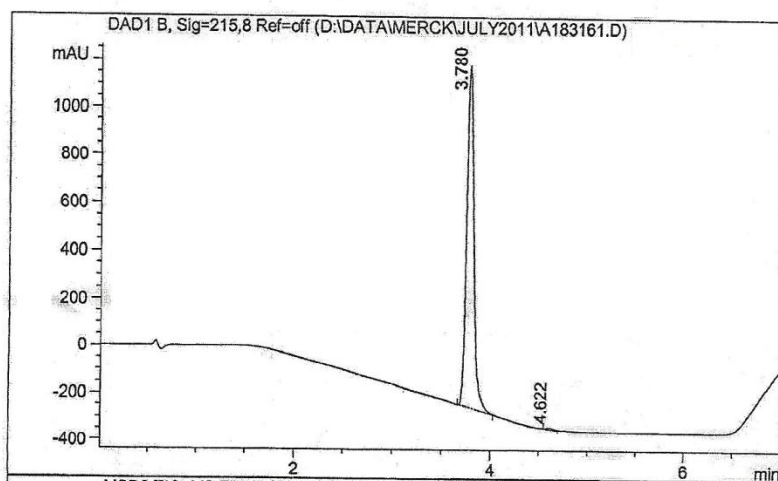
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University, Shankaraghatta, Karnataka, 577451, India*

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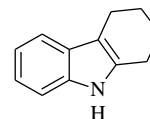
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Data file : D:\DATA\MERCK\JULY2011\A183161.D
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 Vial No. : P1-C-07
 Acq Method : D:\METHODS\AT_3070MFA.M
 Injection vol : 2.0ul

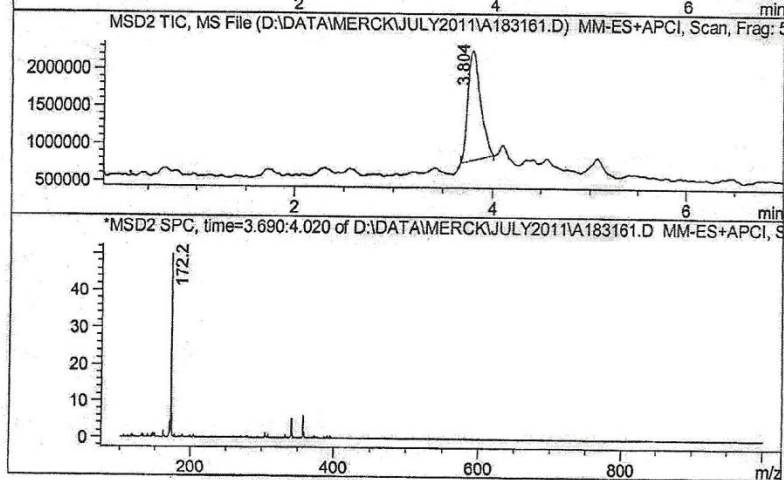
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 Column-Atlantis dC18 (50X4.6mm-5 μm ,) POSITIVE MODE
 TIME (MIN) : 0--3.0 3.0--5.0 5.0--5.5 5.5--7.0
 %B 30-95 95 95-30 30



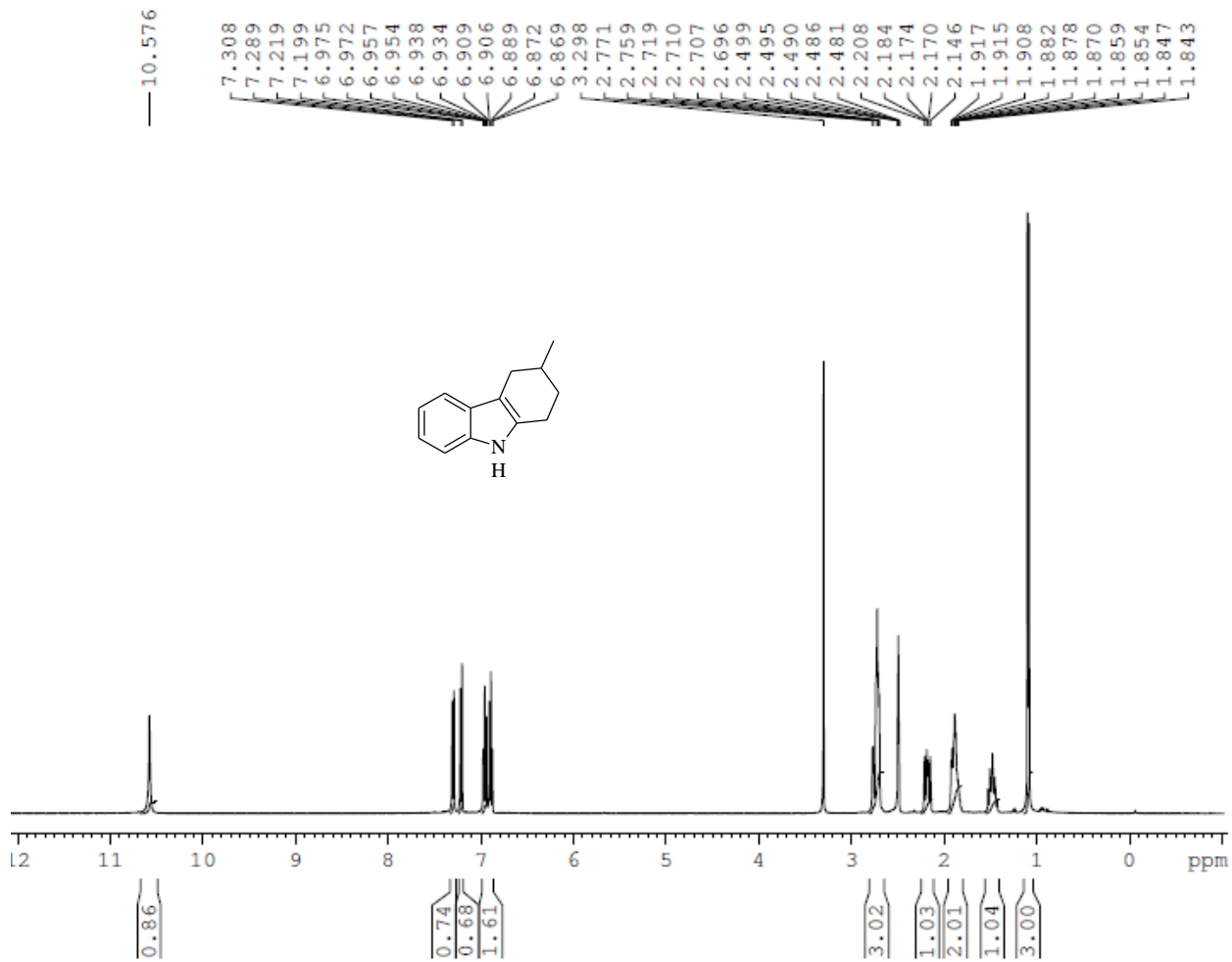
Peak No	RT min	Area	Area %
1	3.78	7357.81	99.34
2	4.62	48.90	0.66



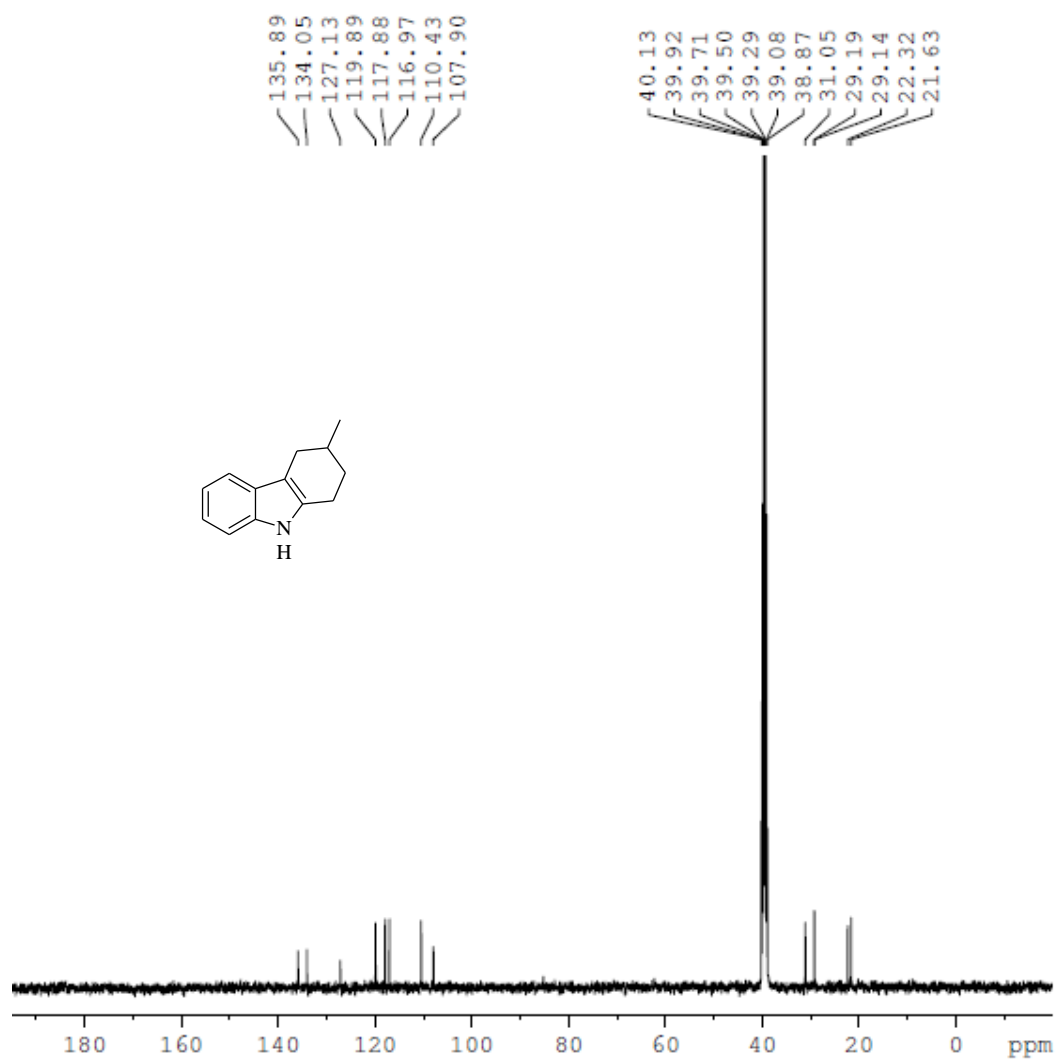
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Mass Spectrum of 2,3,4,9-tetrahydro-1H-carbazole (**3a**)



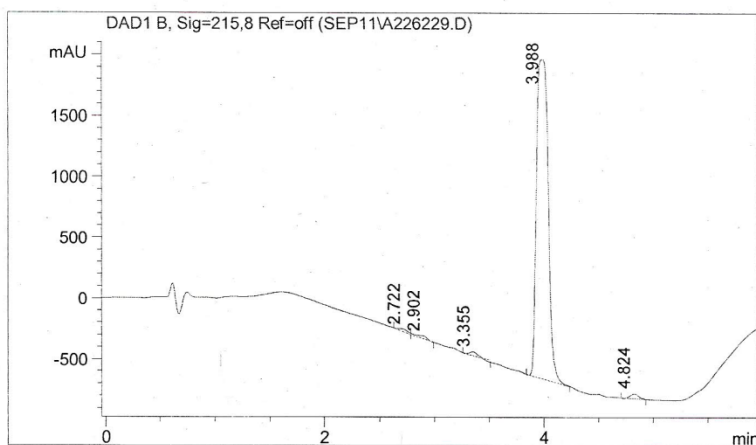
^1H NMR Spectrum of 3-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3b**)



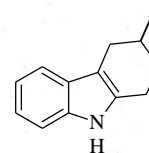
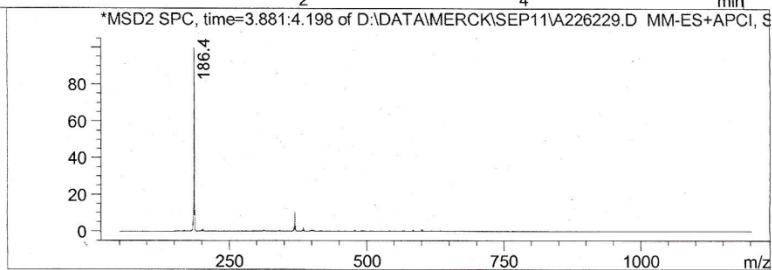
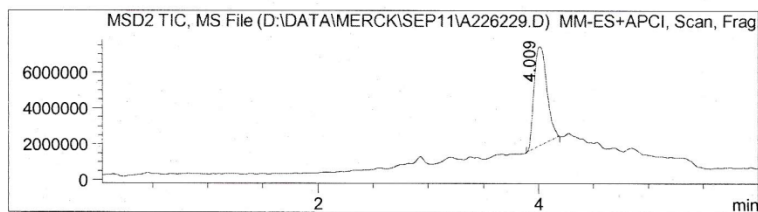
^{13}C NMR Spectrum of 3-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3b**)

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 Acq Method : C:\CHEM32\1\METHODS\AT_595FA1.M
 Injection vol : 2.0ul
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Method info : A-0.1%HCOOH;B-ACN Flow: 1.2ml/min,
 Column-ATLANTIS C18 (50X4.6mm-5µm,) POSITIVE MODE
 TIME (MIN) : 0--3 3--4 4--4.5 4.5-6
 %B : 5-95 95 95-5 5



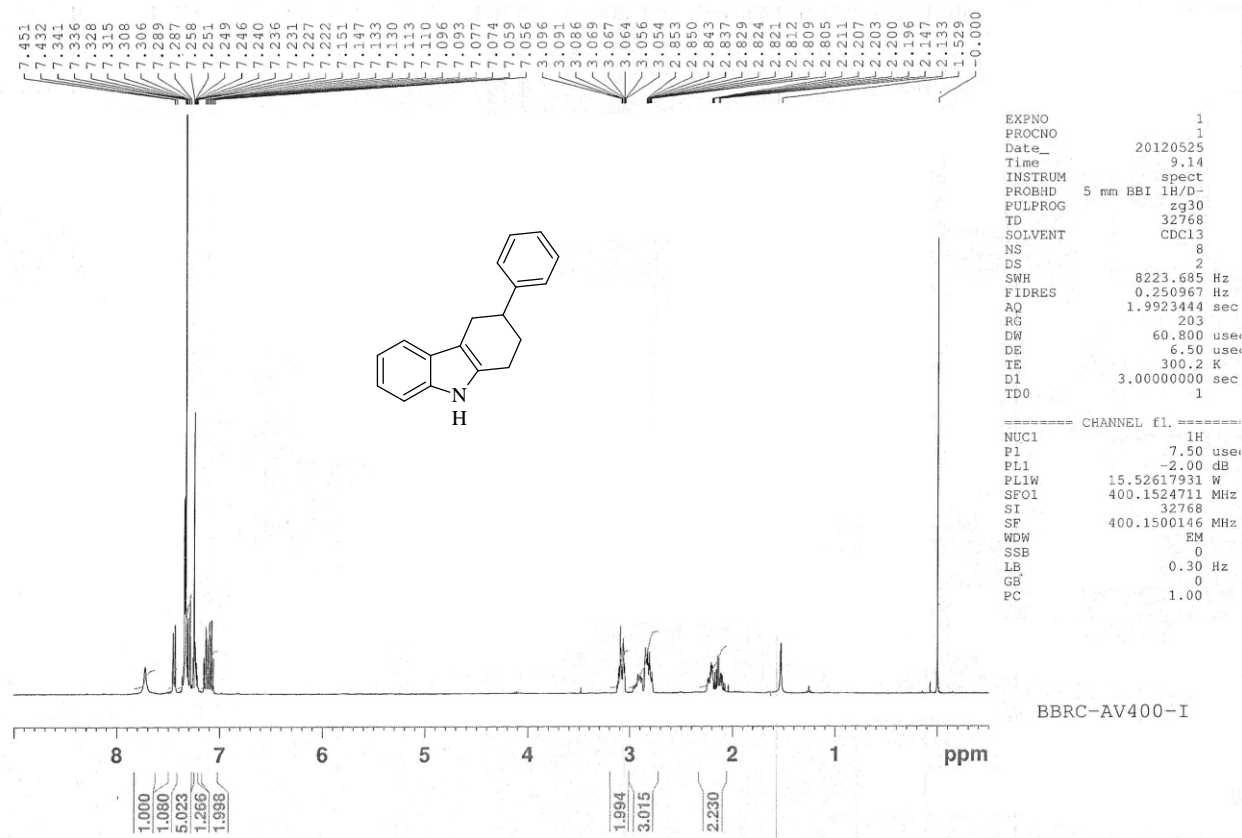
Peak No	RT min	Area	Area %
1	2.72	147.61	0.73
2	2.90	150.35	0.74
3	3.36	179.79	0.89
4	3.99	19500.65	96.55
5	4.82	219.26	1.09



Mass Calcd m/z = 185.2

Found m/z = 186.4(M+1)

Mass Spectrum of 3-methyl-2,3,4,9-tetrahydro-1H-carbazole (3b)

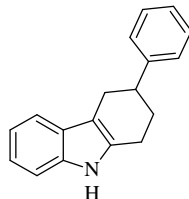


^1H NMR Spectrum of 3-phenyl-2,3,4,9-tetrahydro-1*H*-carbazole (**3c**)

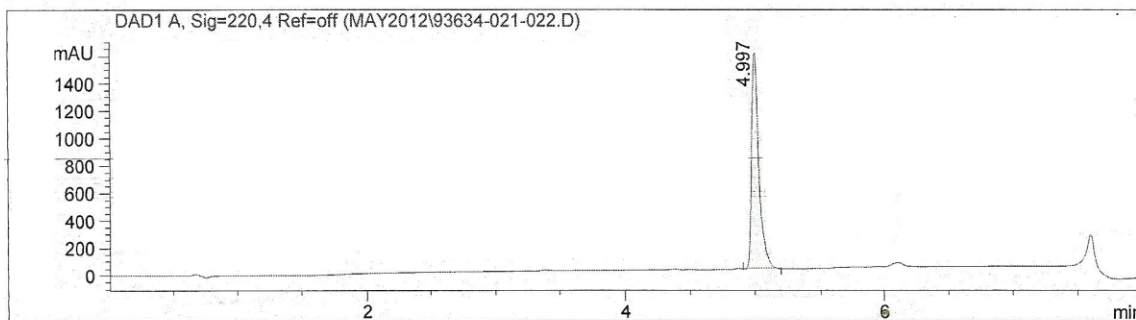
LC/MS REPORT

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 Injection vol : 3 µL
 Sample Name :
 Acq Method : C:\CHEM32\1\METHODS\BBRC-MS-04.M

Method info :

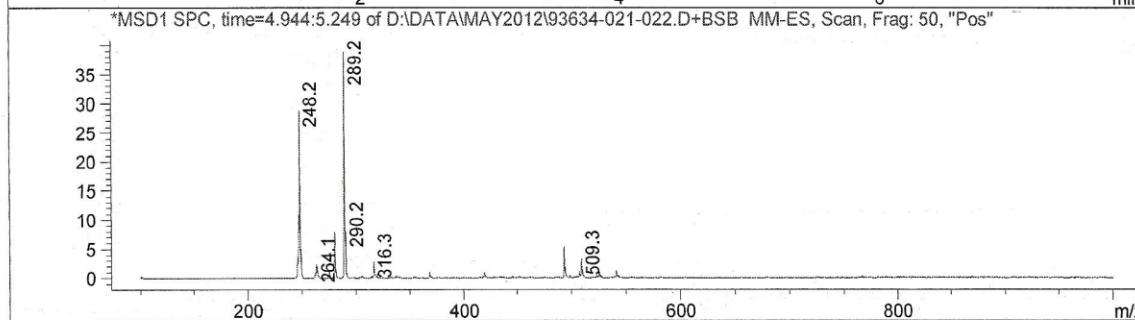
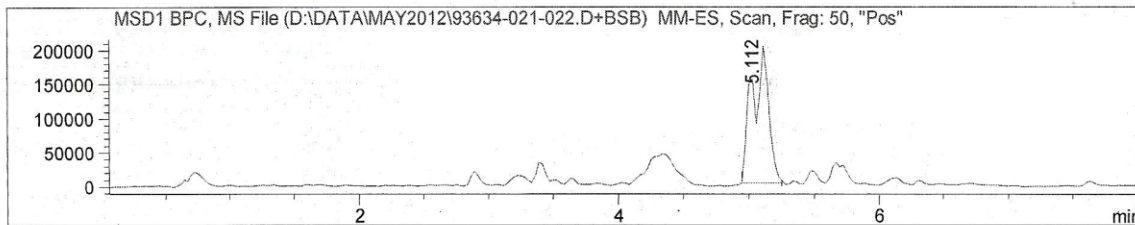


Mass Calcd m/z = 247.3
 Found m/z = 248.2(M+1)



DAD1 A, Sig=220,4 Ref=off

#	Meas. R	Area	Area %
1	4.997	5.985e3	100.000



Mass Spectrum of 3-phenyl-2,3,4,9-tetrahydro-1H-carbazole (3c)



¹H NMR Spectrum of 6-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3d**)

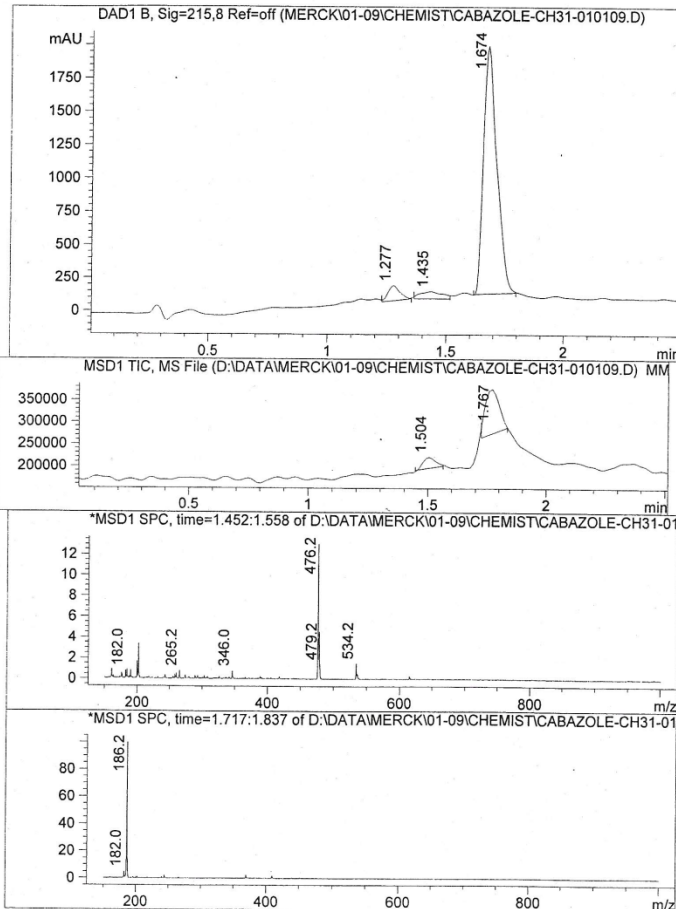
LC/MS REPORT

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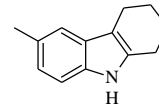
-09\CHEMIST\CABAZOLE-CH31-010109.D

AR.M

Method info :



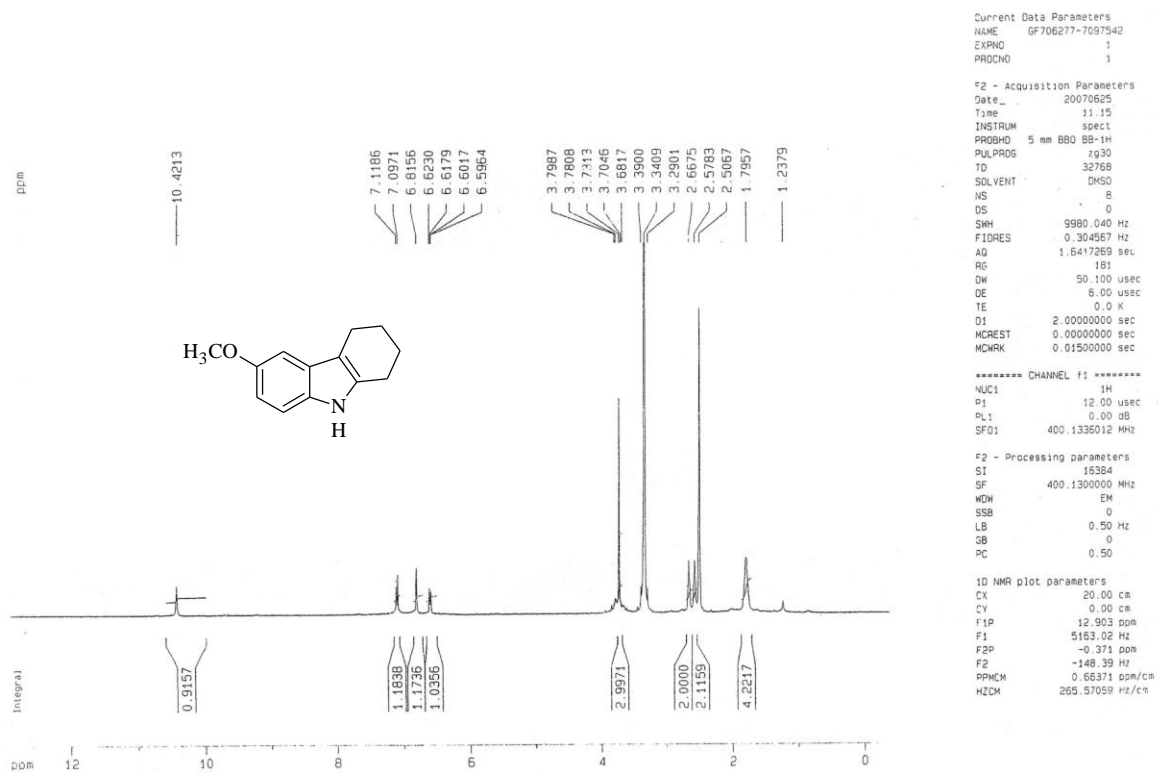
Peak No	RT min	Area	Area %
1	1.28	1394.04	4.84
2	1.44	1373.17	4.58
3	1.67	17371.82	90.57



Mass Calcd $m/z = 185.2$

Found $m/z = 186.2(M+1)$

Mass Spectrum of 6-methyl-2,3,4,9-tetrahydro-1H-carbazole (3d)

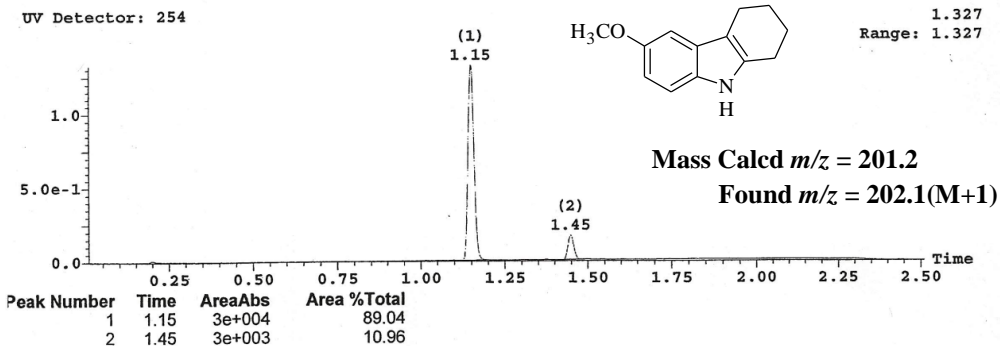


^1H NMR Spectrum of 6-methoxy-2,3,4,9-tetrahydro-1H-carbazole (**3f**)

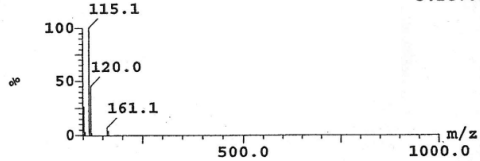
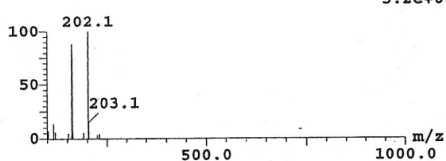
Mobile A: 0.1% HCOOH (Aq)
 Mobile B: 0.1% HCOOH in ACN
 %B: 0.0-0.2min=05% 1.5min=90% 2.0min=05%
 Column: BEH C18 (2.1x50)mm; 1.7µm

Vial: 1:A,2
 Flow Rate: 0.8 ml/min
 Dec-2008

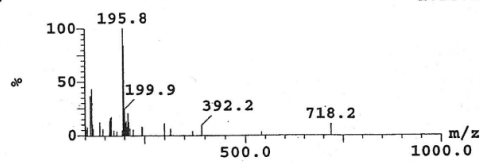
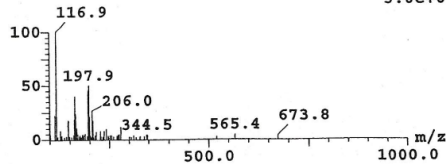
UPLC Report:



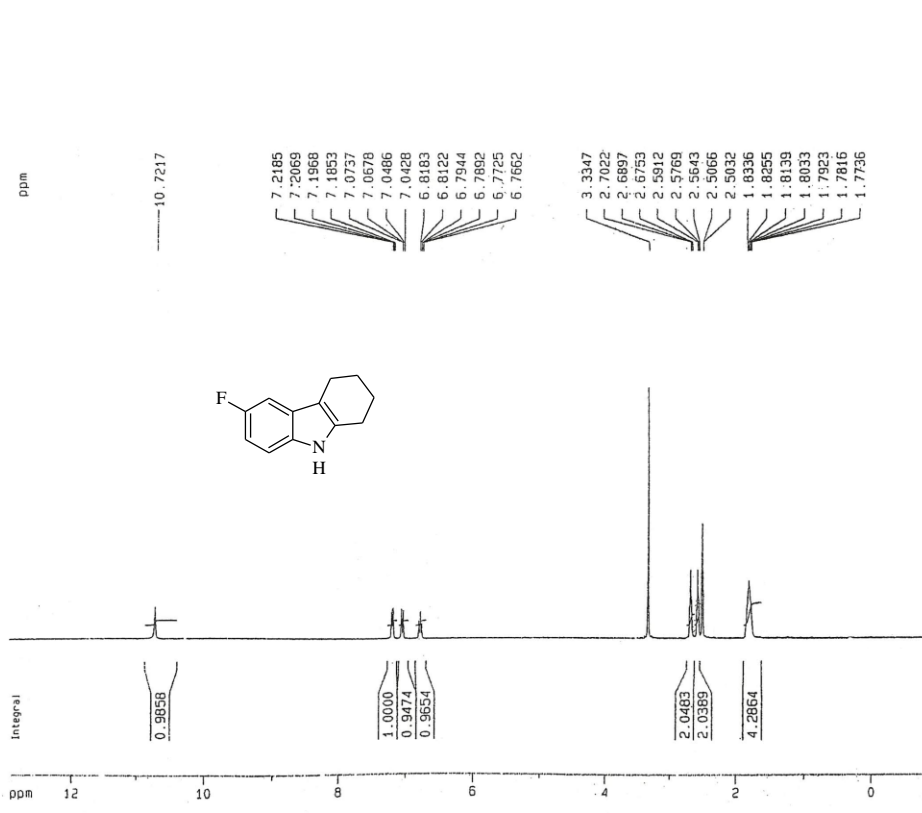
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1	1.15	2	1.45
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		1:MS ES+	2:MS ES+
		5.2e+007	3.2e+007



Peak ID	Time	Peak ID	Time
1	1.15	2	1.45
: (Time: 1.15)		: (Time: 1.45)	
		2:MS ES-	2:MS ES-
		3.0e+005	1.1e+005



Mass Spectrum of 6-methoxy-2,3,4,9-tetrahydro-1H-carbazole (3f)



```

Current Date Parameters
NAME GF706465-7096216
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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Time 15.56
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 8
DS 0
SWH 9980.040 Hz
FIDRES 0.304567 Hz
AQ 1.5417269 sec
RG 256
DM 50.100 usec
DE 6.00 usec
JE 0.0 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

***** CHANNEL f1 *****
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P1 12.00 usec
PL1 0.00 dB
SFO1 400.1336012 MHz

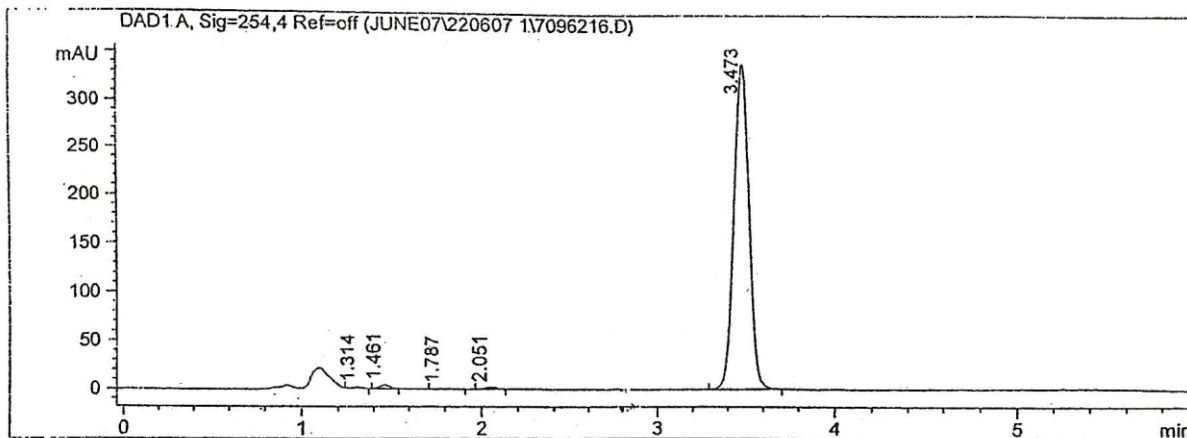
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LB 0.50 Hz
SB 0
PC 0.50

1D NMR plot parameters
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CY 0.00 cm
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F2P -0.794 ppb
F2 -317.54 Hz
PPMCM 0.68626 ppm/cm
HZCM 274.59207 Hz/cm

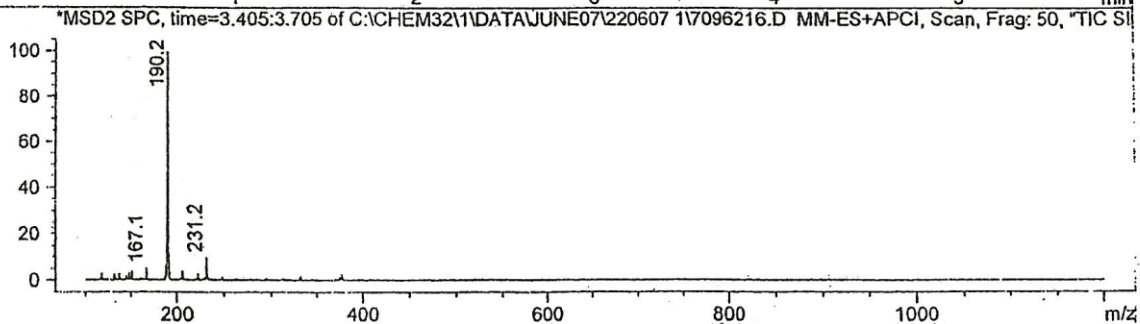
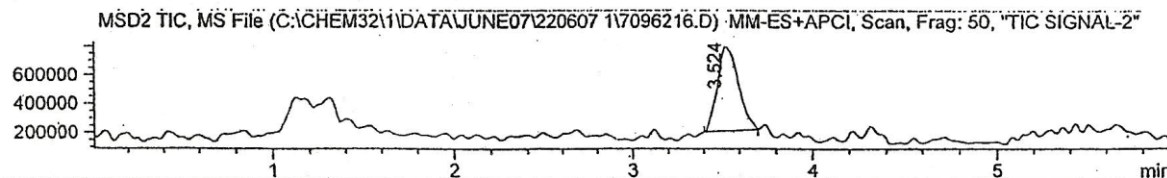
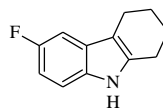
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¹H NMR Spectrum of 6-fluoro-2,3,4,9-tetrahydro-1H-carbazole (**3g**)

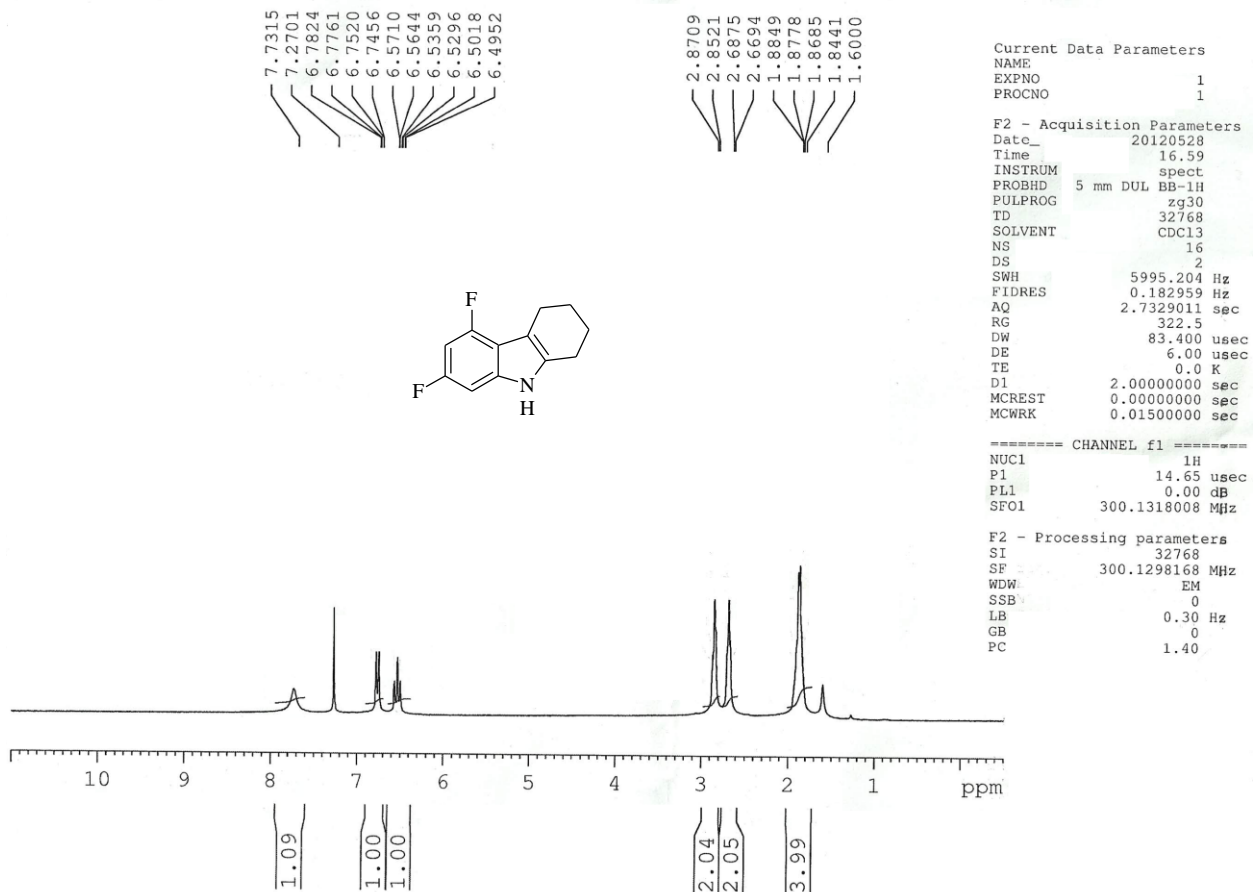
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 Column-Atlantis dC18 (75X4.6mm-5µm) Positive Mode
 Time (min.): 0--1.0 1.0--3.0 3.0--3.5 3.5--4.0 4.5--6.0
 % B : 70 70--95 95 95--70 70



Peak No	RT min	Area	Area %
1	1.314	5.230e+000	0.255
2	1.461	1.720e+001	0.839
3	1.787	8.143e+000	0.397
4	2.051	9.611e+000	0.469
5	3.473	2.009e+003	98.039



Mass Spectrum of 6-fluoro-2,3,4,9-tetrahydro-1H-carbazole (3g)



¹H NMR Spectrum of 5,7-difluoro-2,3,4,9-tetrahydro-1H-carbazole (**3h**)

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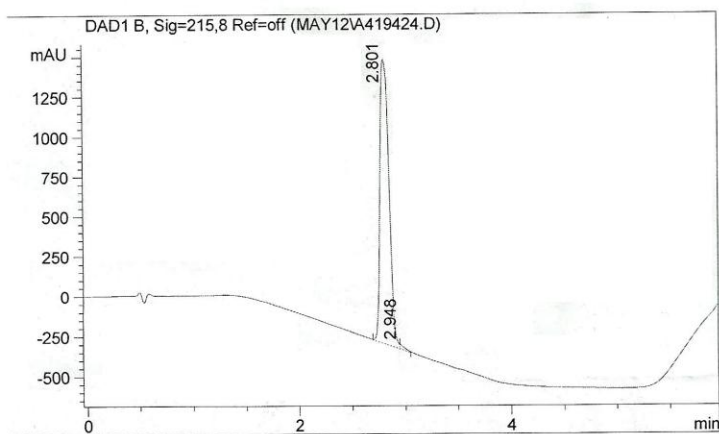
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Injection Date  : 24. May. 2012
Sample Name     : IS09361-38
Sample No.      : P1-E-07
Acq Method      : C:\CHEM32\1\METHODS\XT_3070FA.M
Injection vol   : 2.0ul
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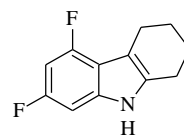
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                  Column-X-terra MS C8 (50X4.6mm-5µm, ) POSITIVE MODE
                  TIME (MIN) : 0--2.5  2.5--4.0  4.0--4.5  4.5--6.0
                               %B       30-95    95      95-30    30
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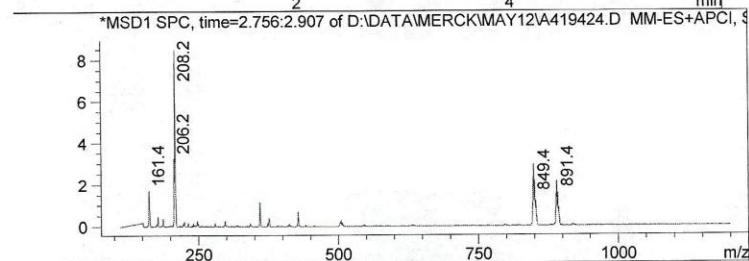
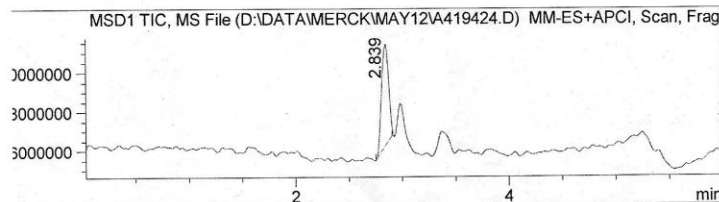


Peak No	RT min	Area	Area %
1	2.80	10671.08	99.09
2	2.95	98.14	0.91

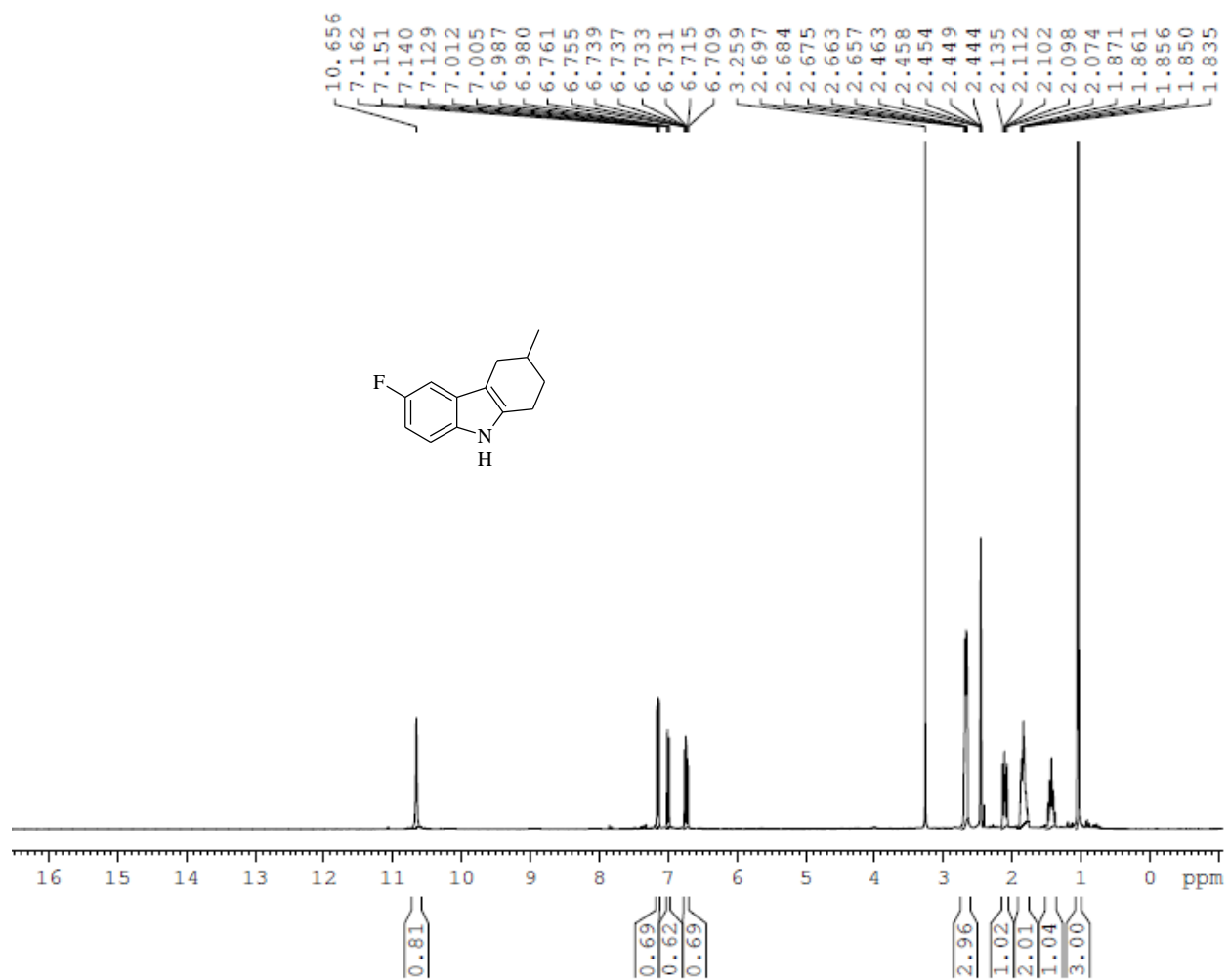


Mass Calcd $m/z = 207.2$

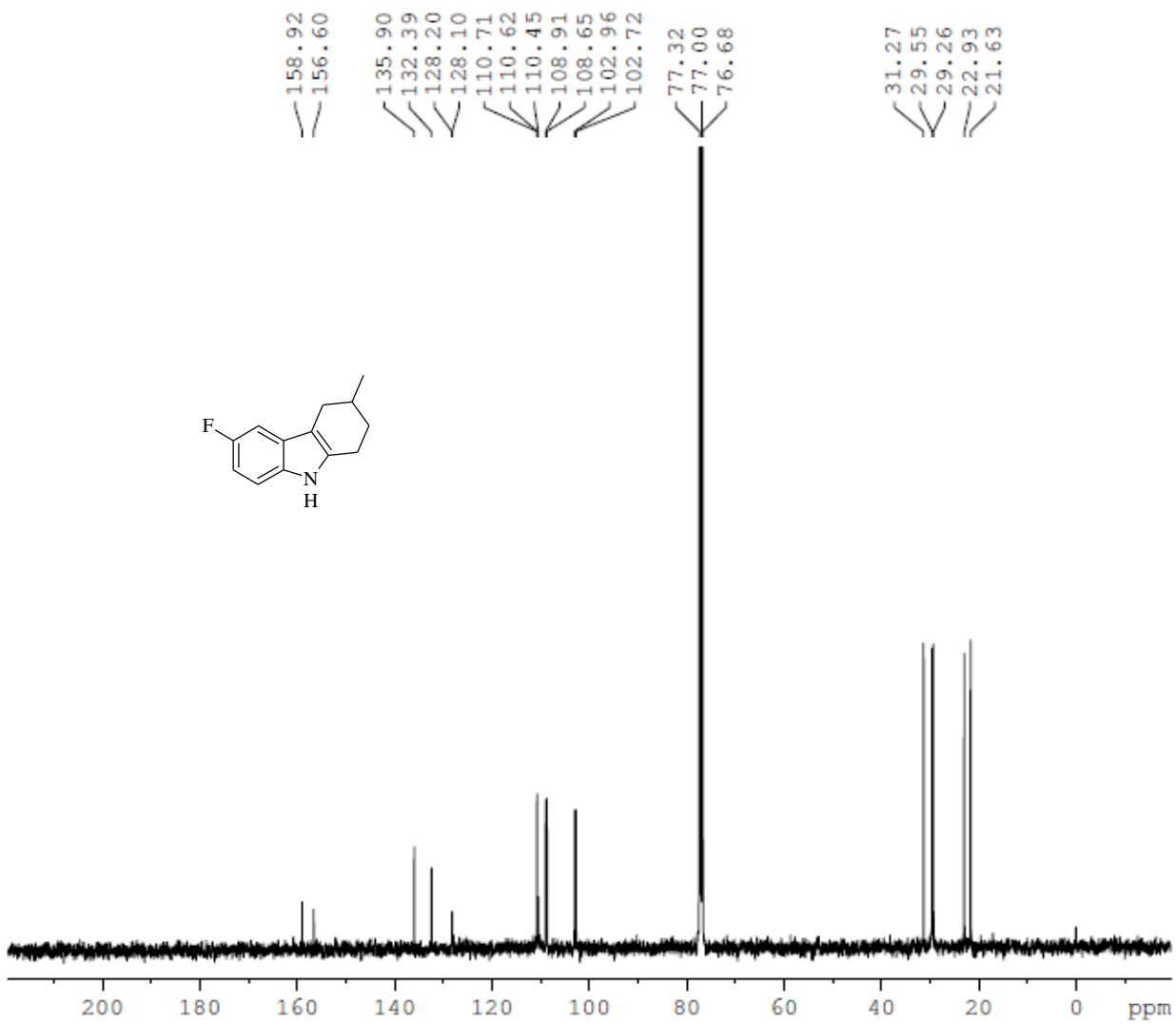
Found $m/z = 208.2(M+1)$



Mass Spectrum of 5,7-difluoro-2,3,4,9-tetrahydro-1H-carbazole (**3h**)



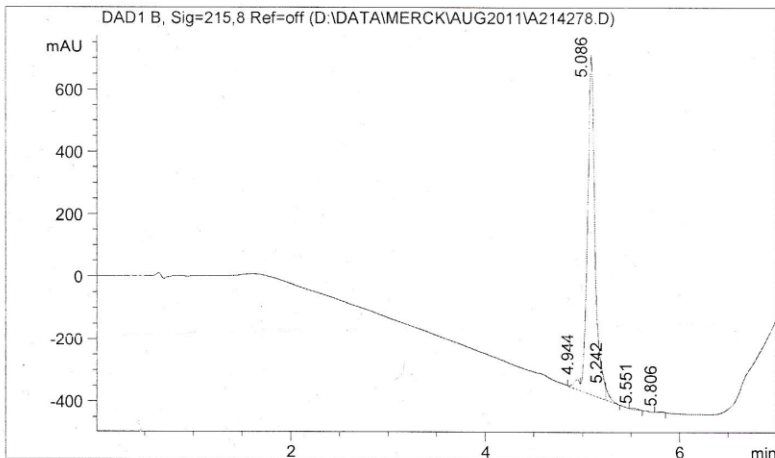
¹H NMR Spectrum of 6-fluoro-3-methyl-2,3,4,9-tetrahydro-1H-carbazole (**3j**)



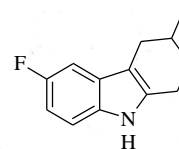
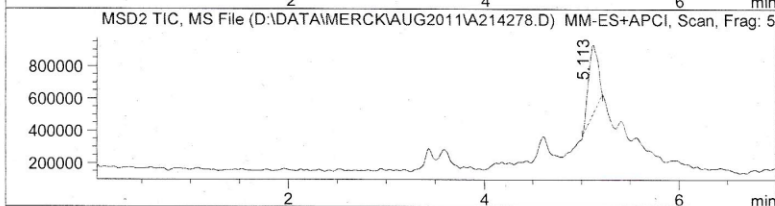
¹³C NMR Spectrum of 6-fluoro-3-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**3j**)

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 Injection Date : 8/29/2011
 Sample Name : IS08510-027
 Vial No. : P1-A-06
 Acq Method : D:\METHODS\AT_1090MFA.M
 Injection vol : 2.0

Method info : A-0.1%HCOOH;B-MEOH Flow: 1.2ml/min,
 Column-Atlantis dC18 (50X4.6mm-5µm,) POSITIVE MODE
 TIME (MIN) : 0--4.0 4.0--5.0 5.0--5.5 5.5-7.0
 %B 10-95 95 95-10 10

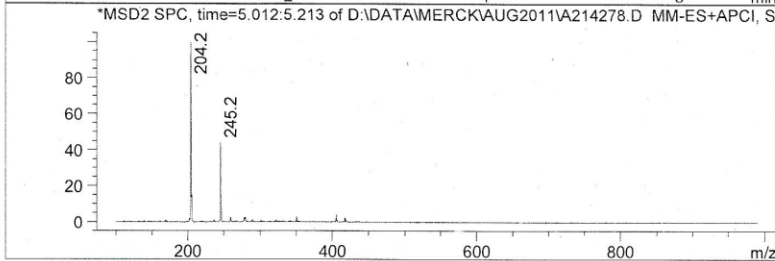


Peak No	RT min	Area	Area %
1	4.94	148.35	2.43
2	5.09	5812.48	95.40
3	5.24	80.88	1.33
4	5.55	27.86	0.46
5	5.81	23.40	0.38

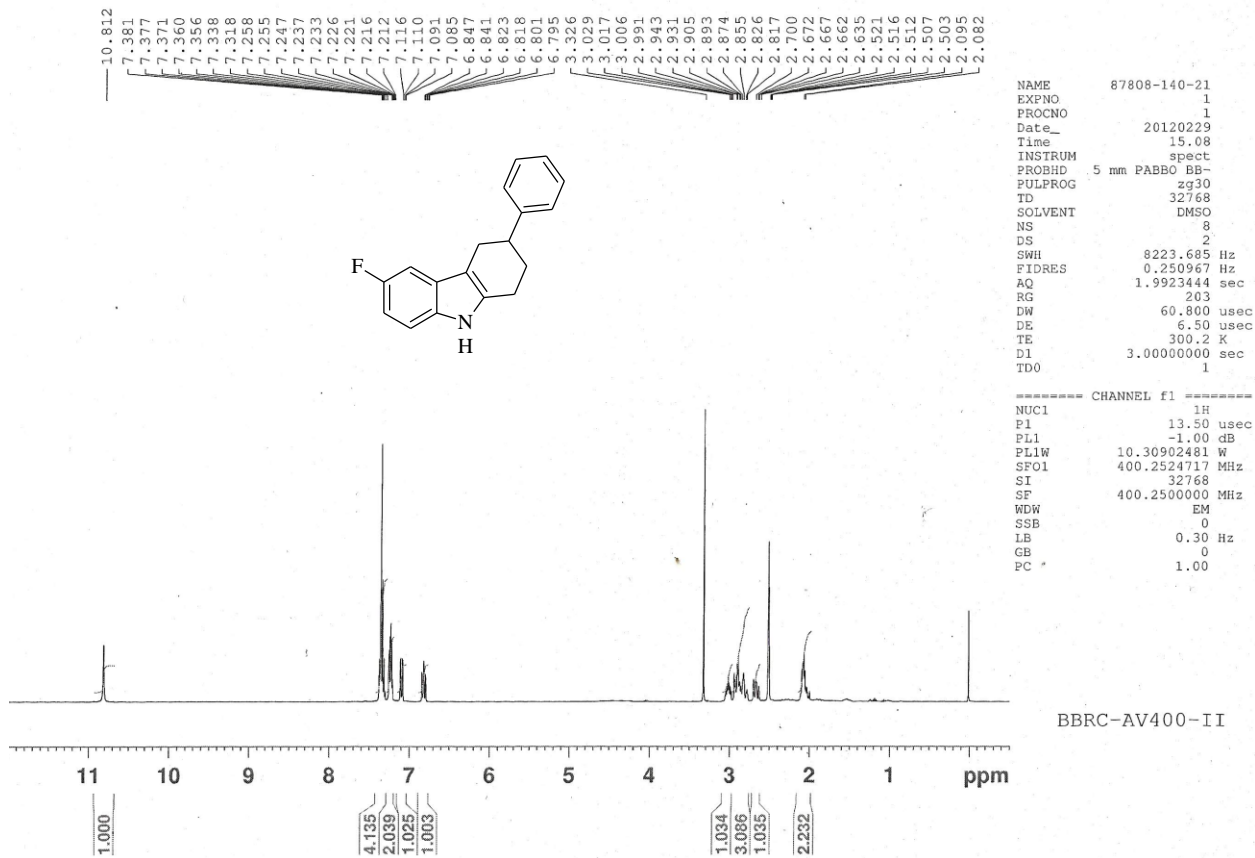


Mass Calcd $m/z = 203.2$

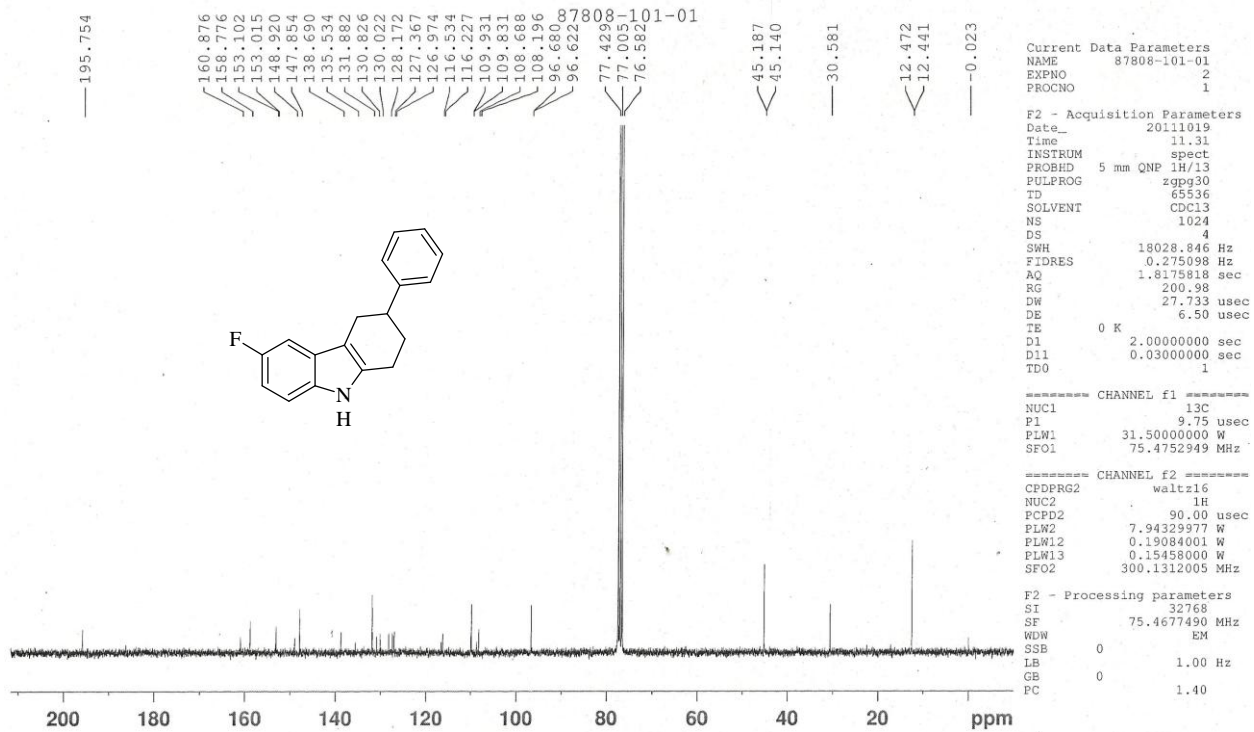
Found $m/z = 204.2(M+1)$



Mass Spectrum of 6-fluoro-3-methyl-2,3,4,9-tetrahydro-1H-carbazole (3j)



¹H NMR Spectrum of 6-fluoro-3-phenyl-2,3,4,9-tetrahydro-1H-carbazole (3k)

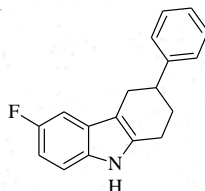


^{13}C NMR Spectrum of 6-fluoro-3-phenyl-2,3,4,9-tetrahydro-1H-carbazole (**3k**)

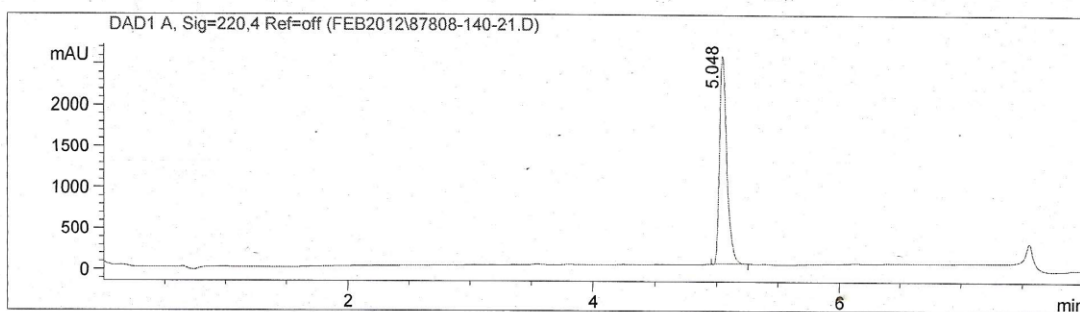
LC/MS REPORT

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 Injection Date : 29/02/2012
 Injection vol : 3 µL
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 Acq Method : C:\CHEM32\1\METHODS\BBRC-MS-04.M
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Method info :

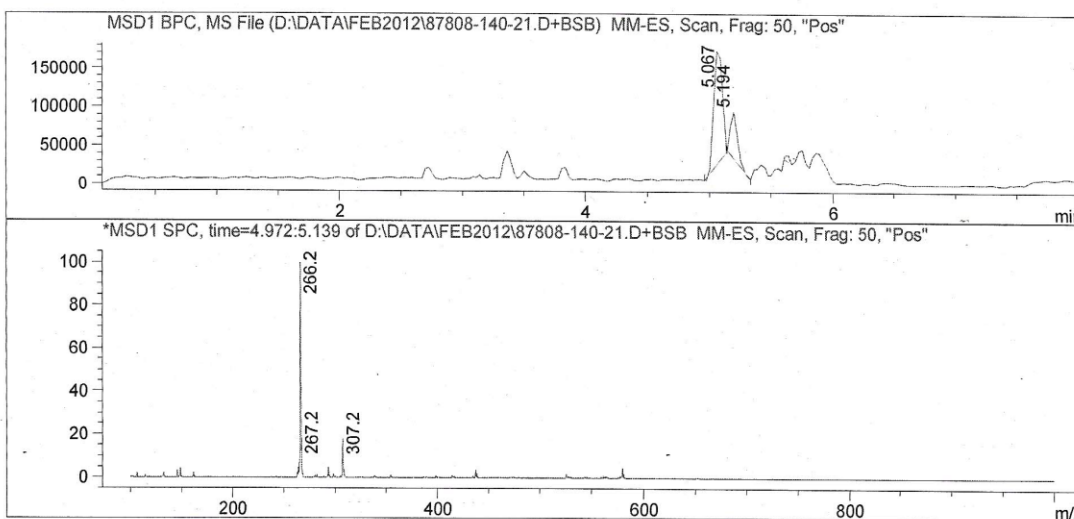


Mass Calcd $m/z = 265.3$
 Found $m/z = 266.2(M+1)$



DAD1 A, Sig=220,4 Ref=off

#	Meas. R	Area	Area %
1	5.048	1.058e4	100.000



Mass Spectrum of 6-fluoro-3-phenyl-2,3,4,9-tetrahydro-1H-carbazole (**3k**)