

Supplementary Information

Zinc Iodide: a mild and efficient catalyst for one-pot synthesis of aminoindolizines via sequential A³ coupling/cycloisomerization

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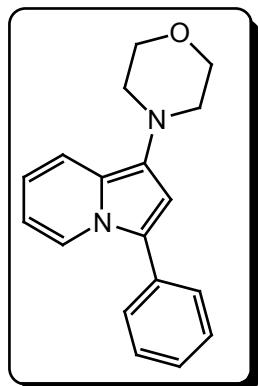
I. General information:

¹H NMR spectra were determined on a Bruker 400 (400 MHz) spectrometer as solutions in C₆D₆. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants J were given in Hz.. ¹³C NMR spectra were recorded at 100 MHz in C₆D₆ solution. Chemical shifts are expressed in parts per million (δ) and are referenced to C₆D₆ (δ = 128.06) as internal standard. TLC was done on silica gel coated glass slide (Merck, Silica gel G for TLC). Silica gel (60-120 mesh, SRL, India) was used for column chromatography. Petroleum ether refers to the fraction boiling in the range of 60-80 °C unless otherwise mentioned. All solvents were dried and distilled before use. Commercially available substrates were freshly distilled before the reaction. Solvents, reagents and chemicals were purchased from Aldrich and Merck Chemicals. All reactions involving moisture sensitive reactants were executed using oven dried glassware.

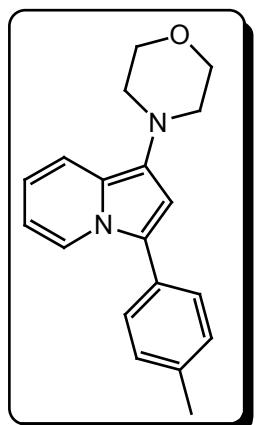
II. General experimental procedure for the synthesis of aminoindolizines (4):

To a solution of ZnI₂ (32mg, 10 mol%) in toluene (3 mL) taken in a reaction tube, pyridine-2-carboxaldehyde/ quinoline-2 carboxaldehyde (1.0 mmol), amine (1.1 mmol), and alkyne (1.2 mmol) were added sequentially. The resulting reaction mixture was then stirred at 100 °C in oil bath for 1 h. After completion of the reaction (TLC) the reaction mixture was cooled to RT and concentrated under vacuum to get a crude residue which was purified by column chromatography on silica gel column (60–120 mesh) using ethyl acetate-petroleum ether as an eluent to afford the pure aminoindolizine product (4) as yellow oil / gummy mass.

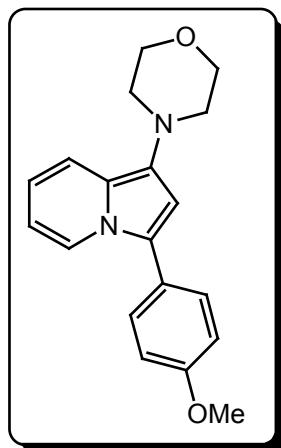
III. Characterization data for the products:



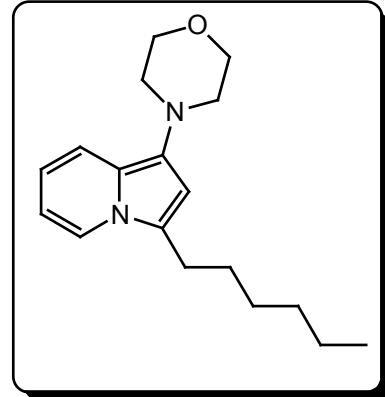
1-Morpholin-4-yl-3-phenyl-indolizine (4aaa):^a 255 mg, 92% yield; Yellow oil; ¹H NMR (C₆D₆, 400 MHz) δ : 7.90 (s, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.20-7.14 (m, 2H), 7.09-7.04 (m, 1H), 6.64 (s, 7H), 6.34 (s, 1H), 6.03 (s, 1H), 3.74 (s, 4H), 2.86 (s, 4H) ; ¹³C NMR (C₆D₆, 100 MHz) δ : 133.1, 130.6, 129.1, 128.9, 127.0, 126.5, 122.8, 121.8, 118.2, 114.9, 111.1, 106.4.



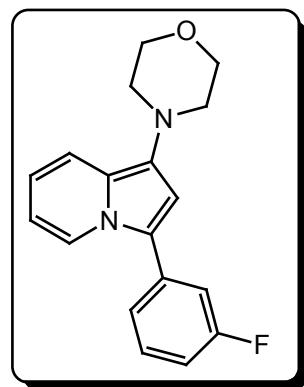
1-Morpholin-4-yl-3-p-tolyl-indolizine (4aab):^b 248 mg, 85% yield; Yellow oil; ¹H NMR (C₆D₆, 400 MHz) δ : 7.94 (d, *J* = 6.8 Hz, 1H), 7.43 (d, *J* = 9.2 Hz, 1H), 7.33-7.28 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.67 (s, 1H), 6.36-6.32 (m, 1H), 6.05 (t, *J* = 6.8 Hz, 1H), 3.74 (t, *J* = 4.8 Hz, 4H), 2.87 (t, *J* = 4.8 Hz, 4H), 2.15 (s, 3H) ; ¹³C NMR (C₆D₆, 100 MHz) δ : 136.6, 130.4, 130.2, 129.8, 129.0, 125.9, 122.8, 121.9, 118.2, 114.7, 110.9, 106.2, 67.5, 54.7, 21.2.



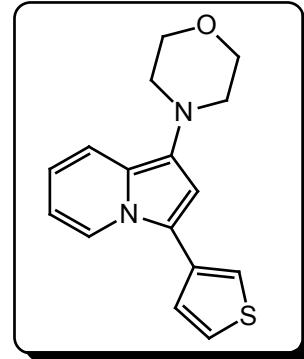
3-(4-Methoxy-phenyl)-1-morpholin-4-yl-indolizine(4aac):^b 267 mg, 87% yield; Yellow oil; ¹H NMR (C₆D₆, 400 MHz) δ : 7.89 (d, *J* = 6.8 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.83-6.79 (m, 2H), 6.64 (s, 1H), 6.35 (t, *J* = 7.6 Hz, 1H), 6.07 (t, *J* = 6.8 Hz, 1H), 3.75 (t, *J* = 4.8 Hz, 4H), 3.35 (s, 3H), 2.89 (s, 4H) ; ¹³C NMR (C₆D₆, 100 MHz) δ : 159.3, 130.2, 129.8, 125.5, 125.4, 122.9, 121.8, 118.2, 114.7, 114.5, 110.9, 106.0, 67.5, 54.9, 54.7.



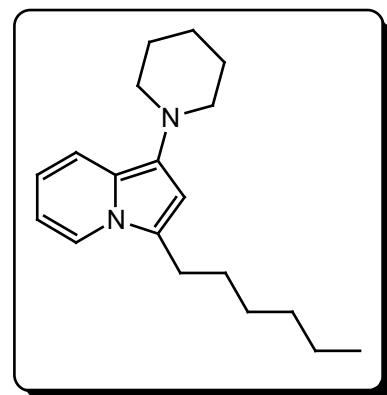
3-Hexyl-1-morpholin-4-yl-indolizine (4aad):^c 211 mg, 74% yield; Yellow oil; ^1H NMR (C_6D_6 , 400 MHz) δ : 7.46 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 7.2 Hz, 1H), 6.43 (s, 1H), 6.37-6.33 (m, 1H), 6.17 (t, J = 7.6 Hz, 1H), 3.75 (t, J = 4.8 Hz, 4H), 2.90 (t, J = 4.8 Hz, 4H), 2.44 (t, J = 7.6 Hz, 2H), 1.55-1.50 (m, 2H), 1.27-1.16 (m, 6H), 0.90-0.85 (m, 3H); ^{13}C NMR (C_6D_6 , 100 MHz) δ : 129.1, 127.8, 121.9, 121.2, 118.1, 113.1, 110.2, 104.2, 67.6, 54.9, 32.0, 29.5, 27.6, 26.2, 23.0, 14.3.



3-(3-Fluoro-phenyl)-1-morpholin-4-yl-indolizine (4aae): 222 mg, 75% yield; Yellow oil; ^1H NMR (C_6D_6 , 400 MHz) δ : 7.77 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 9.2 Hz, 1H), 7.07-6.90 (m, 3H), 6.77-6.72 (m, 1H), 6.54 (s, 1H), 6.35-6.31 (m, 1H), 6.02-5.98 (m, 1H), 3.75 (t, J = 4.8 Hz, 4H), 2.83 (t, J = 4.4 Hz, 4H), 2.15 (s, 3H); ^{13}C NMR (C_6D_6 , 100 MHz) δ : 163.7 (d, $^1J_{C-F}$ = 244 Hz), 135.1 (d, $^3J_{C-F}$ = 8 Hz), 130.7 (d, $^3J_{C-F}$ = 8 Hz), 127.9, 126.6, 123.3, 121.8, 121.6, 118.2, 115.4, 114.7 (d, $^2J_{C-F}$ = 22 Hz), 113.6 (d, $^2J_{C-F}$ = 21 Hz), 111.4, 106.8, 67.4, 54.6; Anal. Calcd. For (%) $\text{C}_{18}\text{H}_{17}\text{FN}_2\text{O}$: C, 72.95; H, 5.78; N, 9.45. Found C, 72.90; H, 5.75; N, 9.40.

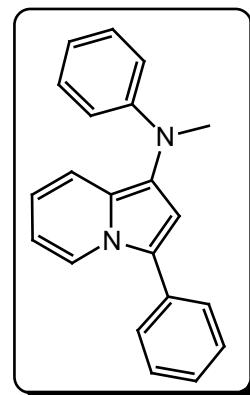


1-Morpholin-4-yl-3-thiophen-3-yl-indolizine (4aaaf): 201 mg, 71% yield; Yellow oil; ^1H NMR (C_6D_6 , 400 MHz) δ : 7.99 (d, J = 7.2 Hz, 1H), 7.64 (d, J = 9.2 Hz, 1H), 7.21 (d, J = 4.8 Hz, 1H), 7.13 (t, J = 4.8 Hz, 1H), 7.09 (s, 1H), 6.85 (s, 1H), 6.55 (t, J = 8.0 Hz, 1H), 6.28 (t, J = 6.8 Hz, 1H), 3.95 (t, J = 4.8 Hz, 4H), 3.06 (s, 4H); ^{13}C NMR (C_6D_6 , 100 MHz) δ : 133.6, 130.6, 128.1, 126.3, 126.0, 123.1, 122.6, 120.9, 118.4, 115.0, 111.4, 106.6, 67.8, 55.0; Anal. Calcd. For (%) $\text{C}_{16}\text{H}_{16}\text{N}_2\text{OS}$: C, 67.58; H, 5.67; N, 9.85. Found C, 67.53; H, 5.70; N, 9.79.

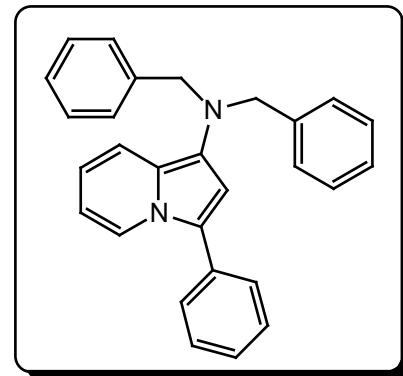


3-Hexyl-1-piperidin-1-yl-indolizine (4abd):^a 190 mg, 67% yield; Yellow oil; ^1H NMR (C_6D_6 , 400 MHz) δ : 7.64 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 6.8 Hz, 1H), 6.50 (s, 1H), 6.37-6.33 (m, 1H), 6.16 (t, J = 6.8 Hz, 1H), 2.99 (t, J = 4.8 Hz, 4H), 2.45 (t, J = 6.8 Hz, 2H), 1.70 (t, J = 5.2 Hz, 4H), 1.59-1.51 (m, 2H), 1.45-1.39 (m, 2H), 1.28-1.19 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (C_6D_6 , 100 MHz) δ : 128.1, 124.3, 121.7, 121.1, 118.4, 112.9, 110.1, 104.3, 56.1, 32.0, 29.6, 27.6, 26.9, 26.2, 24.7, 23.0,

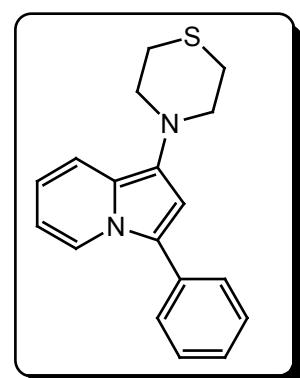
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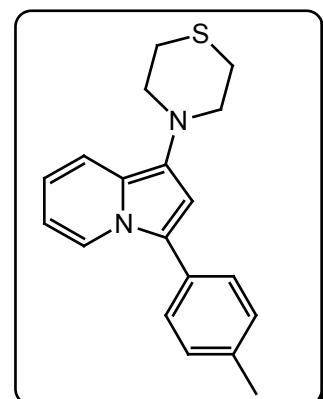
Methyl-phenyl-(3-phenyl-indolizin-1-yl)-amine (4aca):^a 202 mg, 68% yield; Yellow oil; ^1H NMR (C_6D_6 , 400 MHz) δ : 7.93 (d, J = 6.0 Hz, 1H), 7.32 (d, J = 6.8 Hz, 2H), 7.21-7.05 (m, 7H), 6.84-6.77 (m, 3H), 6.68 (s, 1H), 6.27 (s, 1H), 6.01 (t, J = 6.4 Hz, 1H), 3.12 (s, 1H); ^{13}C NMR (C_6D_6 , 100 MHz) δ : 150.7, 132.6, 129.2, 129.2, 128.9, 128.1, 127.2, 124.1, 123.7, 122.3, 117.9, 117.5, 116.7, 113.7, 112.5, 111.1, 40.6.



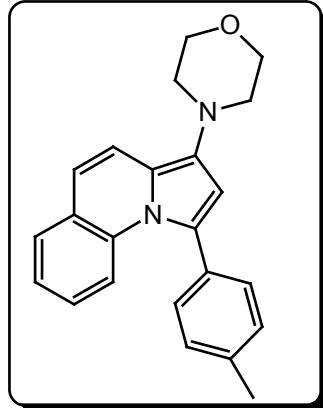
Dibenzyl-(3-phenyl-indolizin-1-yl)-amine (4ada):^a 349 mg, 90% yield; Yellow oil; ¹H NMR (C₆D₆, 400 MHz) δ : 7.80 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 4H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.15-7.10 (m, 7H), 7.04-7.02 (m, 3H), 6.70 (s, 1H), 6.33-6.29 (m, 2H), 5.95 (t, *J* = 7.2 Hz, 1H), 4.16 (s, 4H); ¹³C NMR (C₆D₆, 100 MHz) δ : 139.5, 132.5, 128.6, 127.6, 127.3, 127.0, 126.7, 126.4, 122.6, 121.4, 117.7, 114.7, 110.5, 108.3.



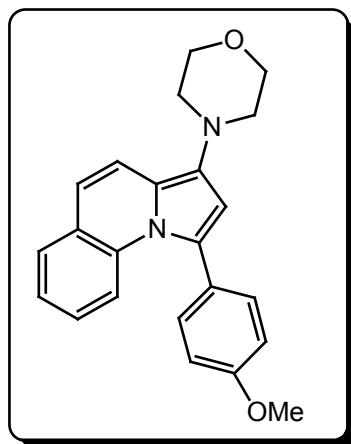
3-Phenyl-1-thiomorpholin-4-yl-indolizine (4aea): 258 mg, 88% yield; Yellow oil; ¹H NMR (C₆D₆, 400 MHz) δ : 7.89 (d, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 9.2 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.20-7.14 (m, 2H), 7.09-7.05 (m, 1H), 6.64 (s, 1H), 6.36-6.32 (m, 1H), 6.02 (t, *J* = 6.4 Hz, 1H), 3.11 (t, *J* = 5.2 Hz, 4H), 2.58 (t, *J* = 4.8 Hz, 4H); ¹³C NMR (C₆D₆, 100 MHz) δ : 133.0, 131.4, 129.1, 128.2, 127.0, 126.3, 123.0, 121.8, 118.0, 115.1, 111.1, 107.2, 56.5, 28.8; Anal. Calcd. For (%) C₁₈H₁₈N₂S: C, 73.43; H, 6.16; N, 9.51. Found C, 73.39; H, 6.10; N, 9.46.



1-Thiomorpholin-4-yl-3-p-tolyl-indolizine (4aeb): 255 mg, 83% yield; Yellow oil; ¹H NMR (C₆D₆, 400 MHz) δ : 8.14 (d, *J* = 6.8 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 1H), 6.55 (t, *J* = 6.8 Hz, 1H), 6.25 (t, *J* = 6.8 Hz, 1H), 3.34 (s, 4H), 2.80 (t, *J* = 4.8 Hz, 4H), 2.36 (s, 3H); ¹³C NMR (C₆D₆, 100 MHz) δ : 136.9, 132.4, 131.5, 130.5, 130.2, 126.4, 123.4, 122.2, 118.3, 115.2, 111.3, 107.3, 56.9, 29.1, 21.5; Anal. Calcd. For (%) C₁₉H₂₀N₂S: C, 73.99; H, 6.54; N, 9.08. Found C, 73.95; H, 6.50; N, 9.02.

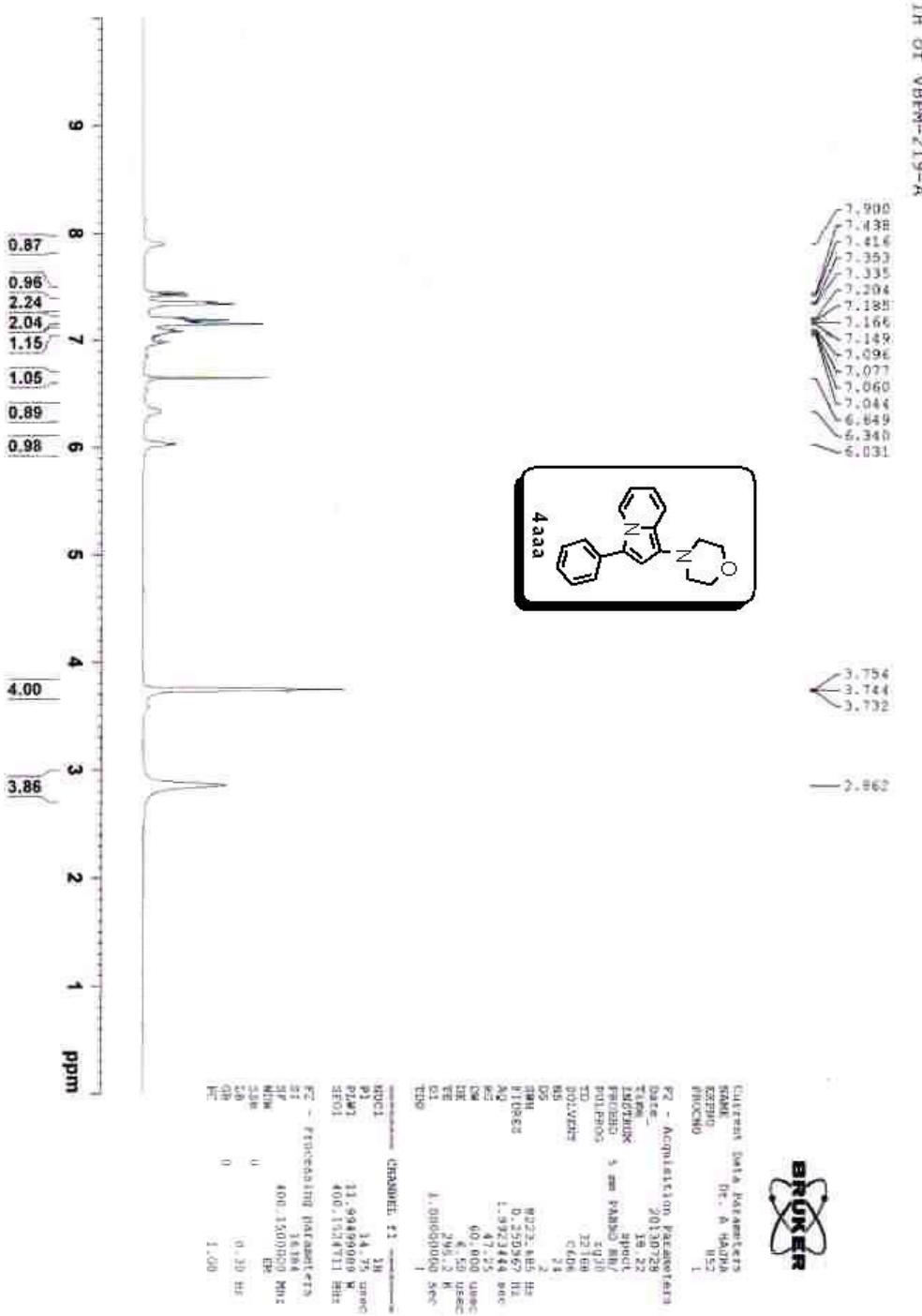


3-Morpholin-4-yl-1-p-tolyl-pyrrolo[1,2-a]quinoline (4bab):^c 290 mg, 85% yield; Yellow gummy mass; ¹H NMR (C₆D₆, 400 MHz) δ : 7.65 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 9.2 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.99-6.91 (m, 3H), 6.82-6.78 (m, 1H), 6.71 (d, *J* = 5.2 Hz, 1H), 6.51 (s, 1H), 3.74 (t, *J* = 4.8 Hz, 4H), 2.87 (t, *J* = 4.8 Hz, 4H), 2.12 (s, 3H); ¹³C NMR (C₆D₆, 100 MHz) δ : 137.4, 137.0, 134.8, 133.4, 132.8, 129.6, 129.5, 128.6, 126.5, 126.3, 124.7, 123.5, 118.1, 117.8, 117.0, 108.8, 67.5, 54.7, 21.2.



1-(4-Methoxy-phenyl)-3-morpholin-4-yl-pyrrolo[1,2-a]quinoline (4bac): 315 mg, 88% yield; Yellow gummy mass; ¹H NMR (C₆D₆, 400 MHz) δ : 7.65 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 9.2 Hz, 1H), 7.35 (d, *J* = 9.2 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.85-6.70 (m, 4H), 6.51 (s, 1H), 3.75 (t, *J* = 4.4 Hz, 4H), 3.29 (s, 3H), 2.89 (t, *J* = 4.8 Hz, 4H); ¹³C NMR (C₆D₆, 100 MHz) δ : 159.8, 134.9, 132.7, 131.0, 128.7, 128.6, 128.2, 126.5, 126.4, 124.5, 123.5, 117.9, 117.8, 116.9, 114.3, 108.7, 67.5, 54.8, 54.7; Anal. Calcd. For (%) C₂₃H₂₂N₂O₂: C, 77.07; H, 6.19; N, 7.82. Found C, 77.03; H, 6.12; N, 7.75.

IV. NMR Spectra:

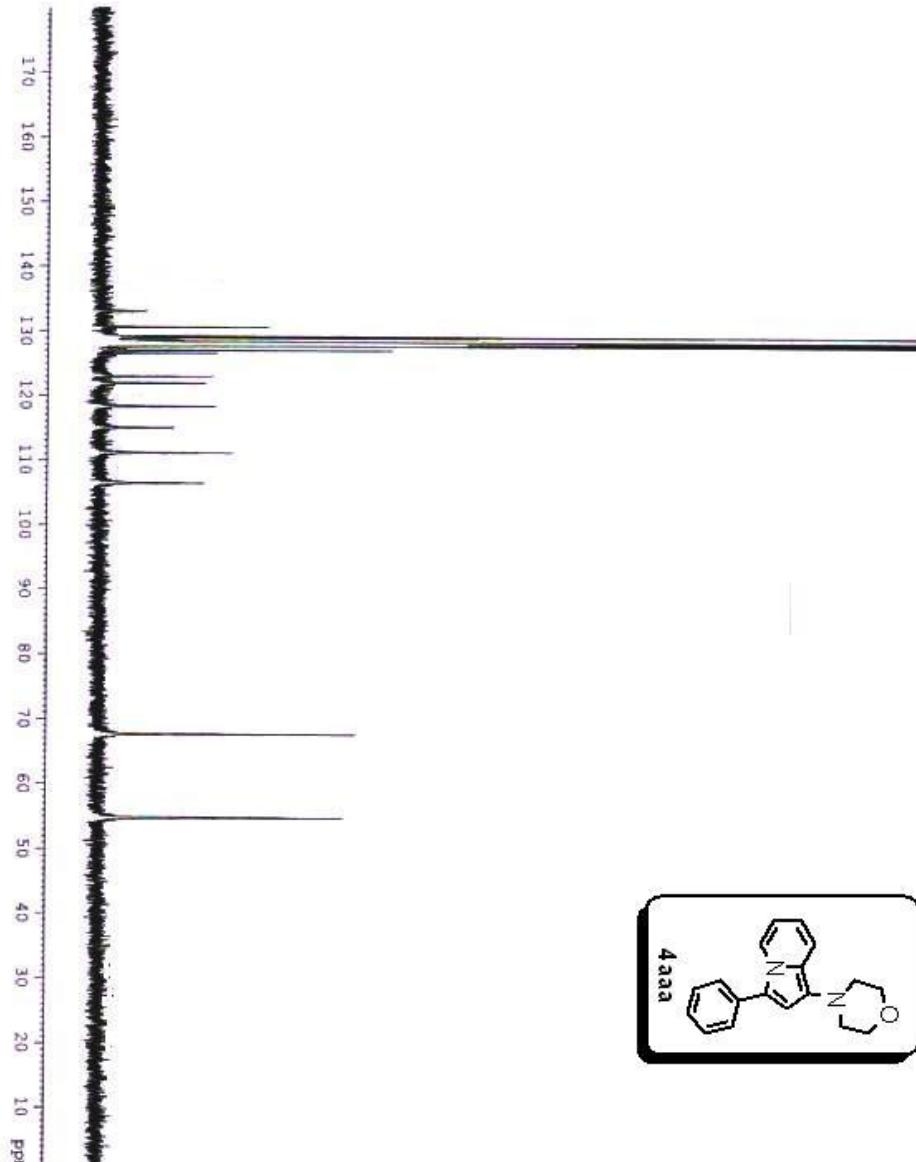
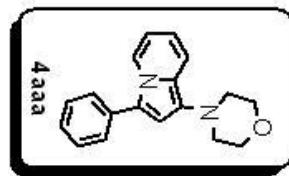


¹³C OF VBPM_219-A



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— 54.70



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CHANNEL: g2

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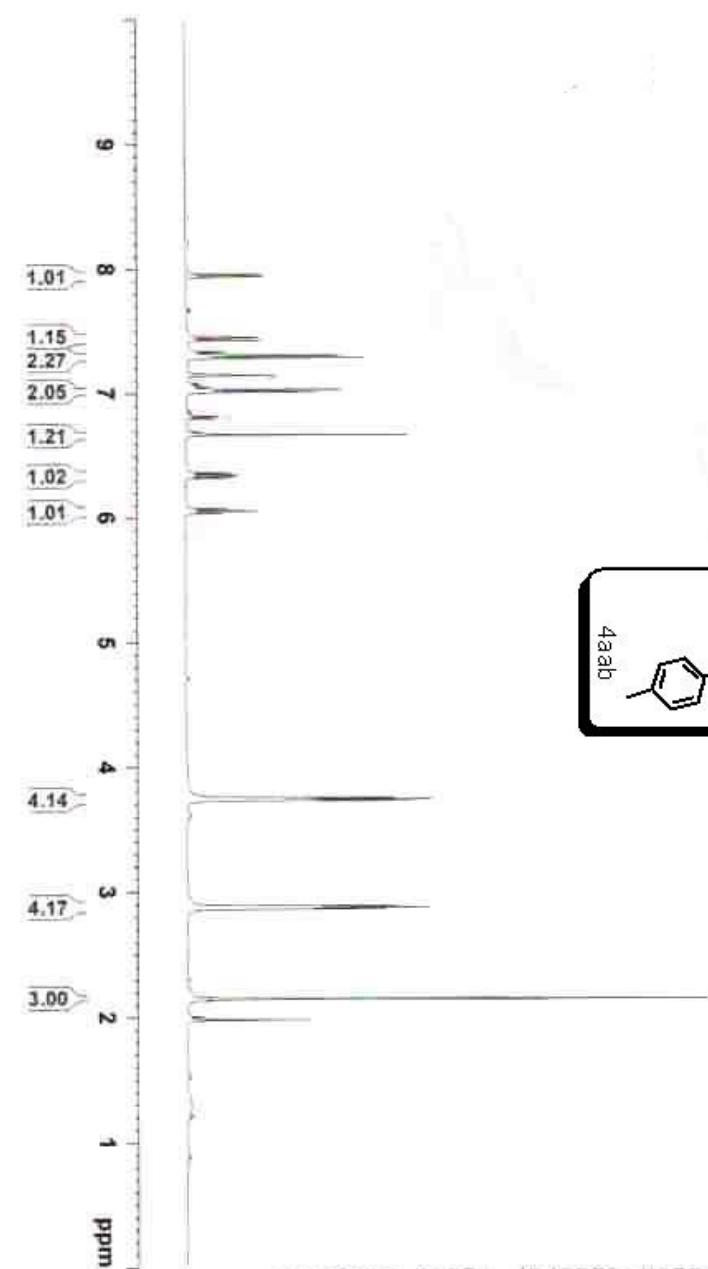
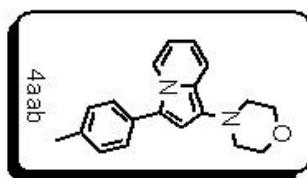
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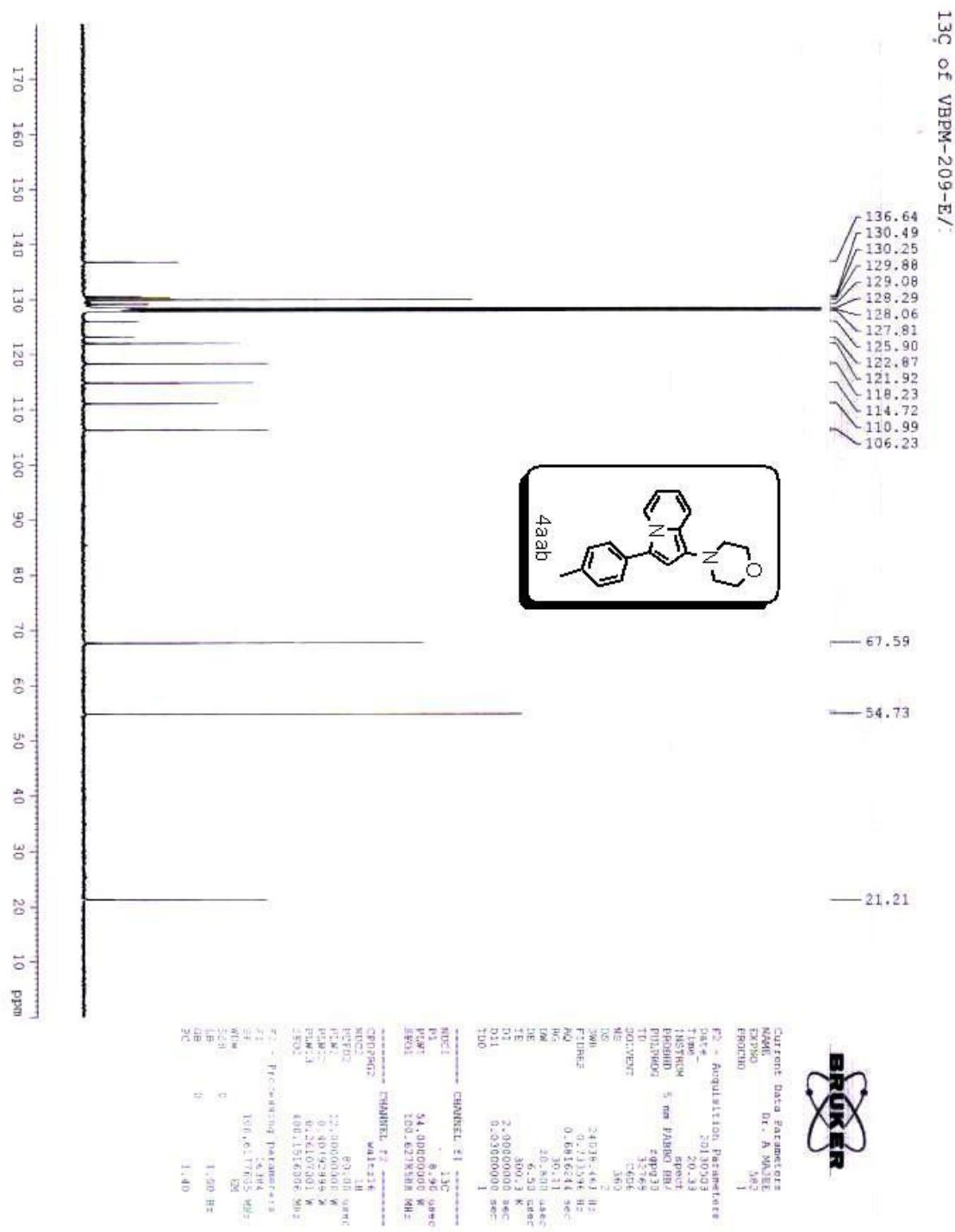
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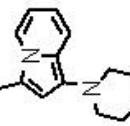


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4aac



Current para. parameterz
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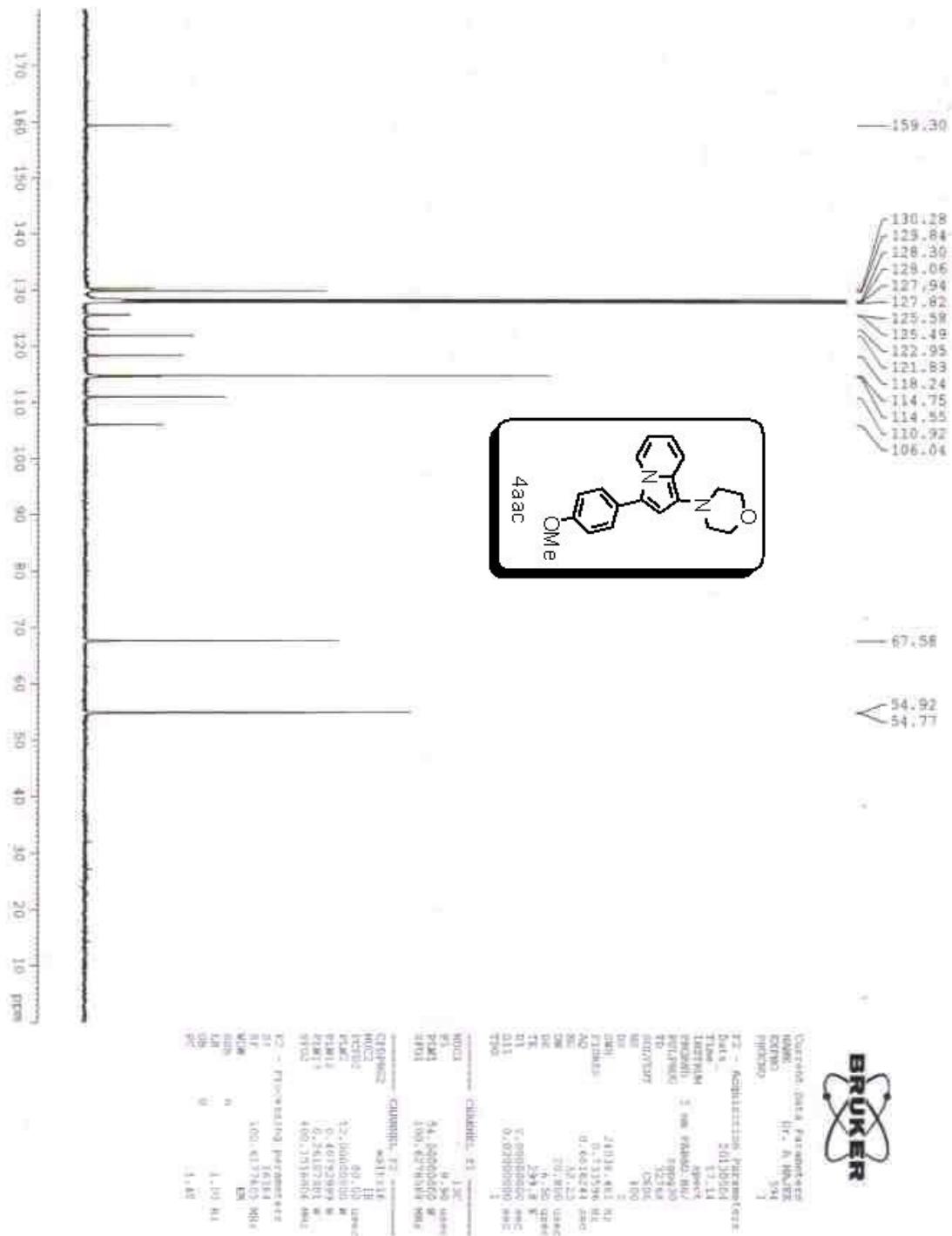
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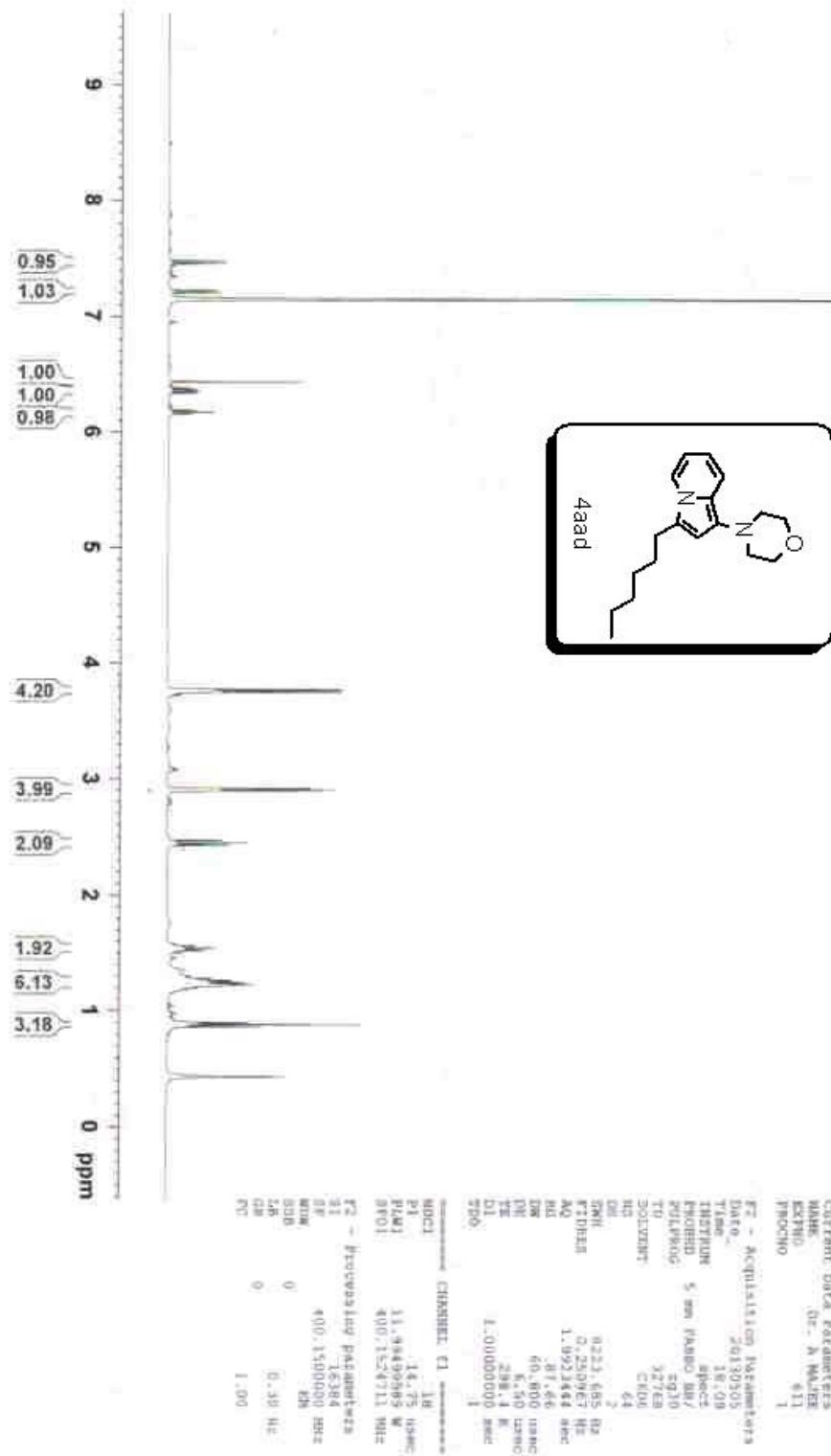
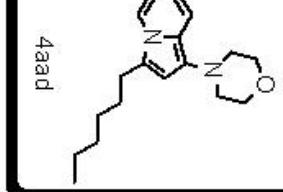
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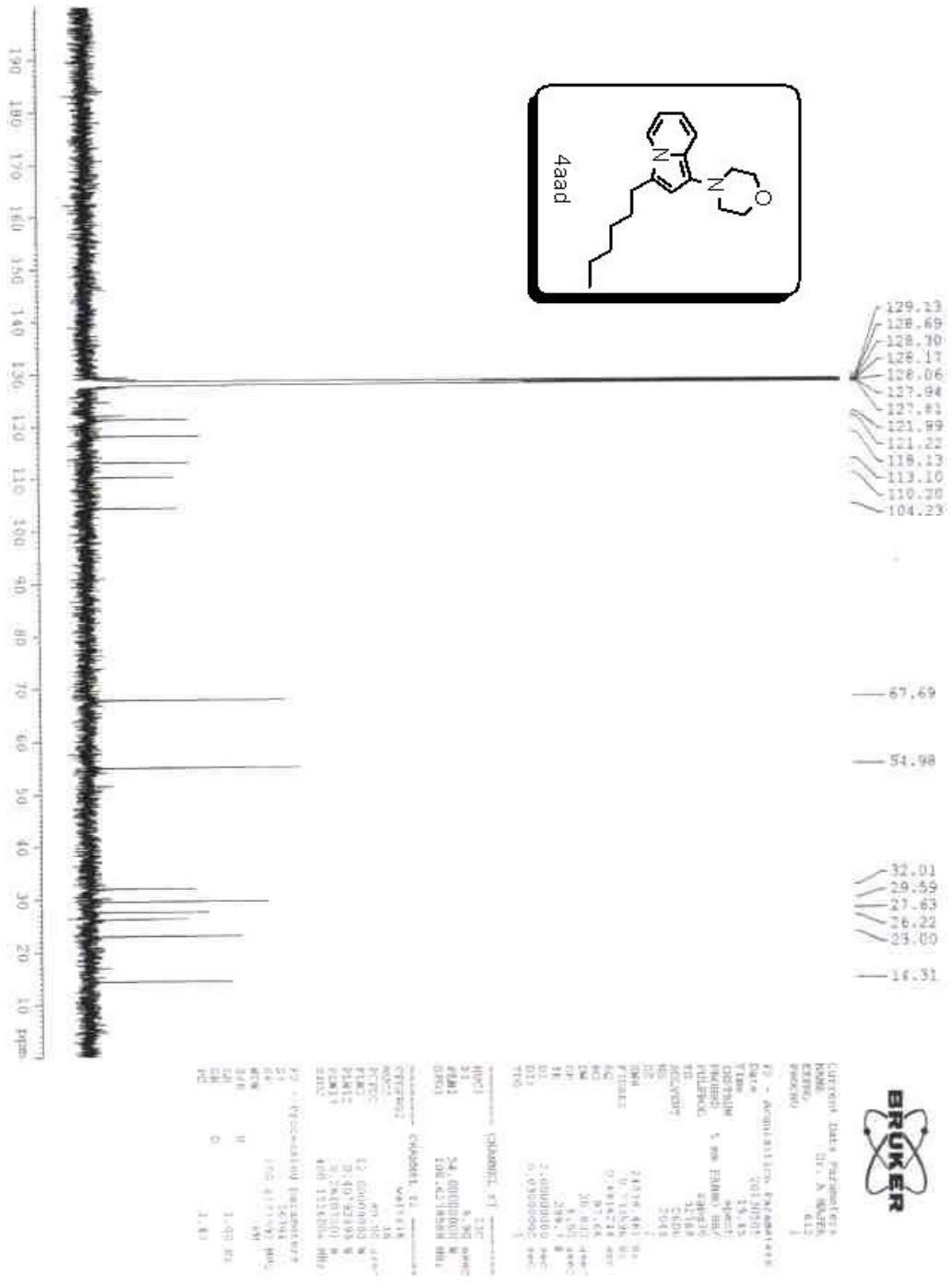
1H of VEPN-209-G/13

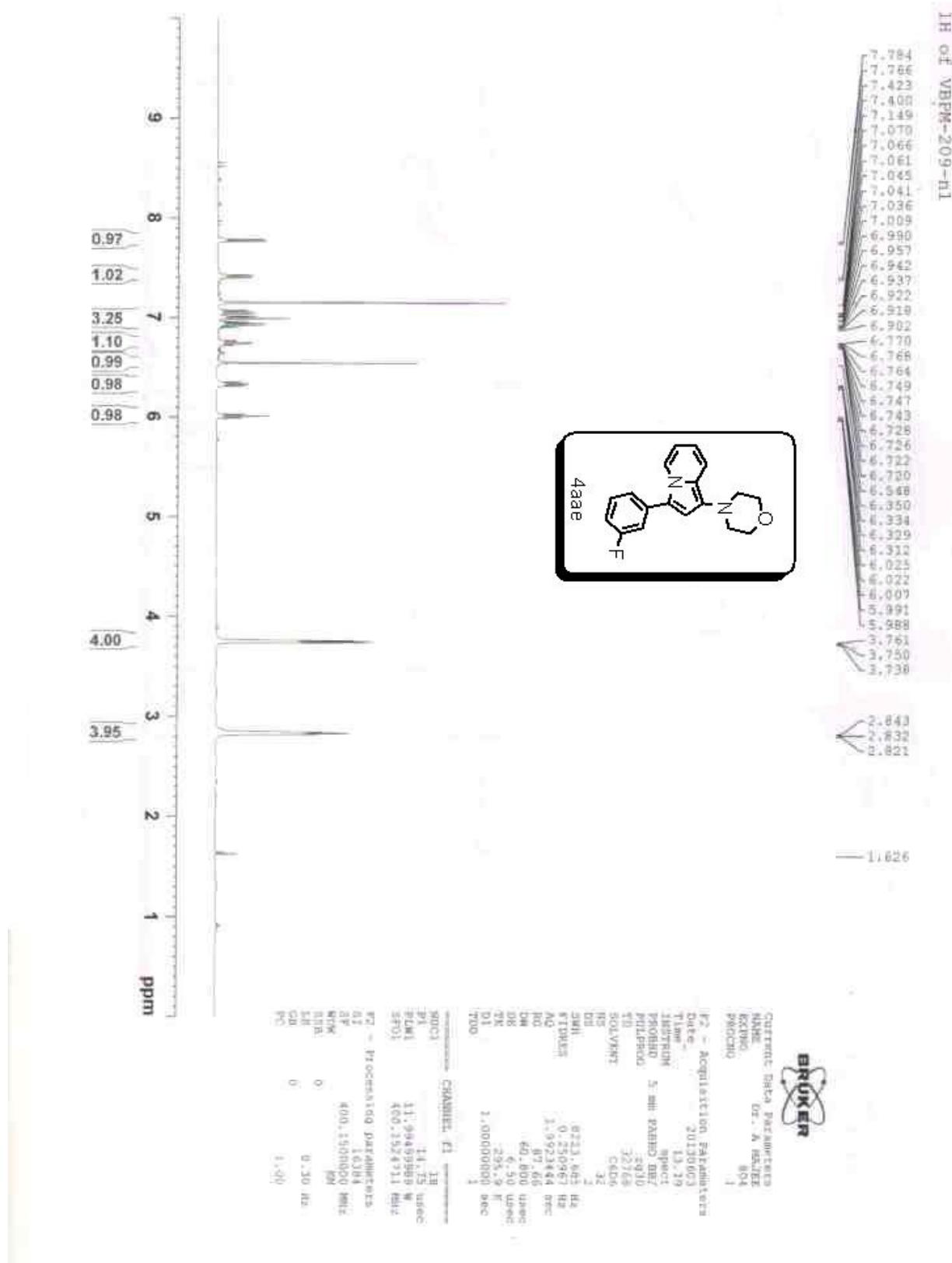
7.479
7.457
7.223
7.205
7.149
6.432
6.378
6.376
6.361
6.355
6.339
6.189
6.186
6.171
6.155
6.152

3.770
3.759
3.754
3.747
2.915
2.908
2.904
2.900
2.692
2.464
2.445
2.426
1.558
1.541
1.522
1.503
1.279
1.260
1.241
1.221
1.211
1.200
1.193
1.183
1.172
1.163
0.900
0.883
0.865
0.854
0.438



13C of vBPM-209-G/

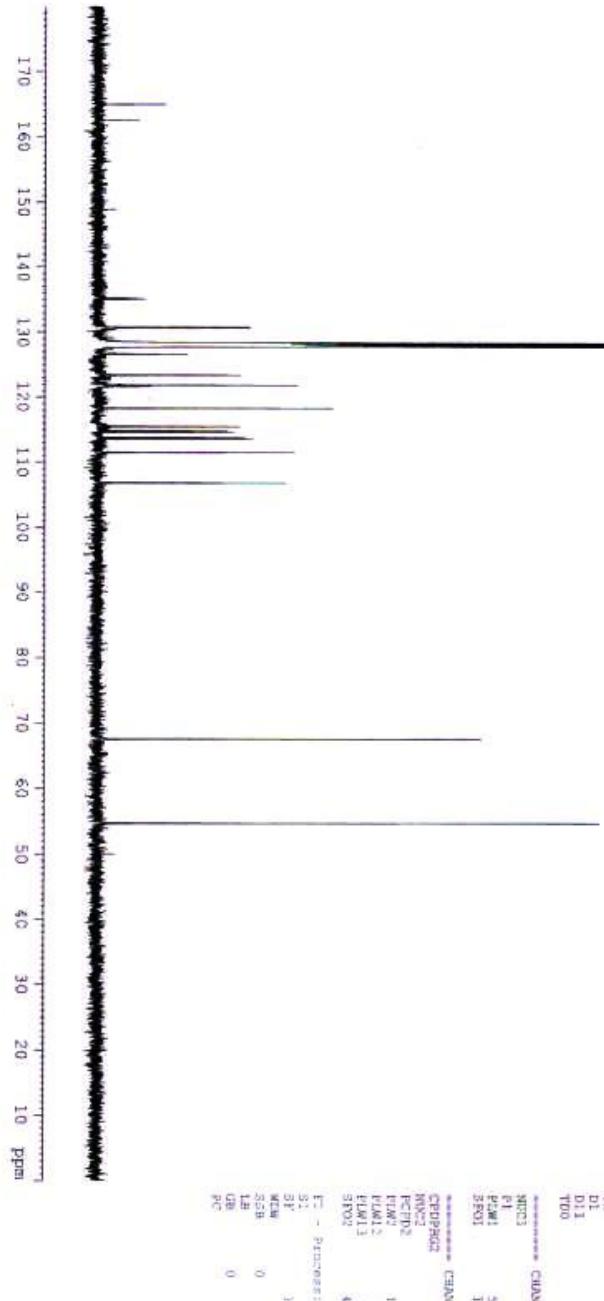
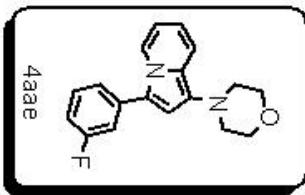




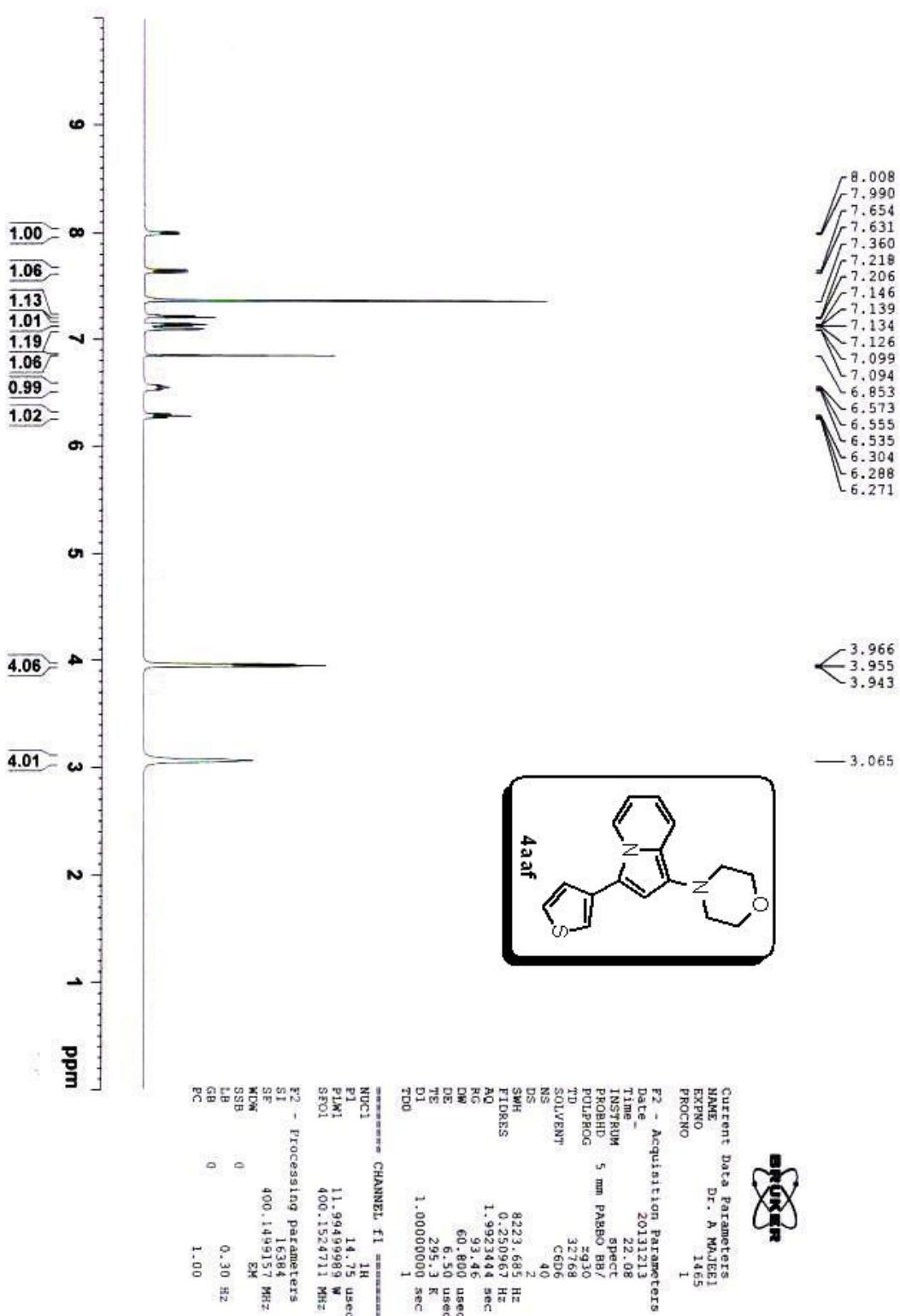
13C of VBPM-209-n1

164.92
162.48
135.15
135.07
130.72
130.64
128.30
128.18
128.06
127.94
127.82
126.61
123.39
121.80
121.65
118.24
115.44
114.80
114.58
113.72
113.51
111.48
106.81

67.48
54.63



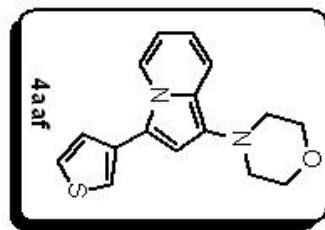
1H of VBPM-209-m



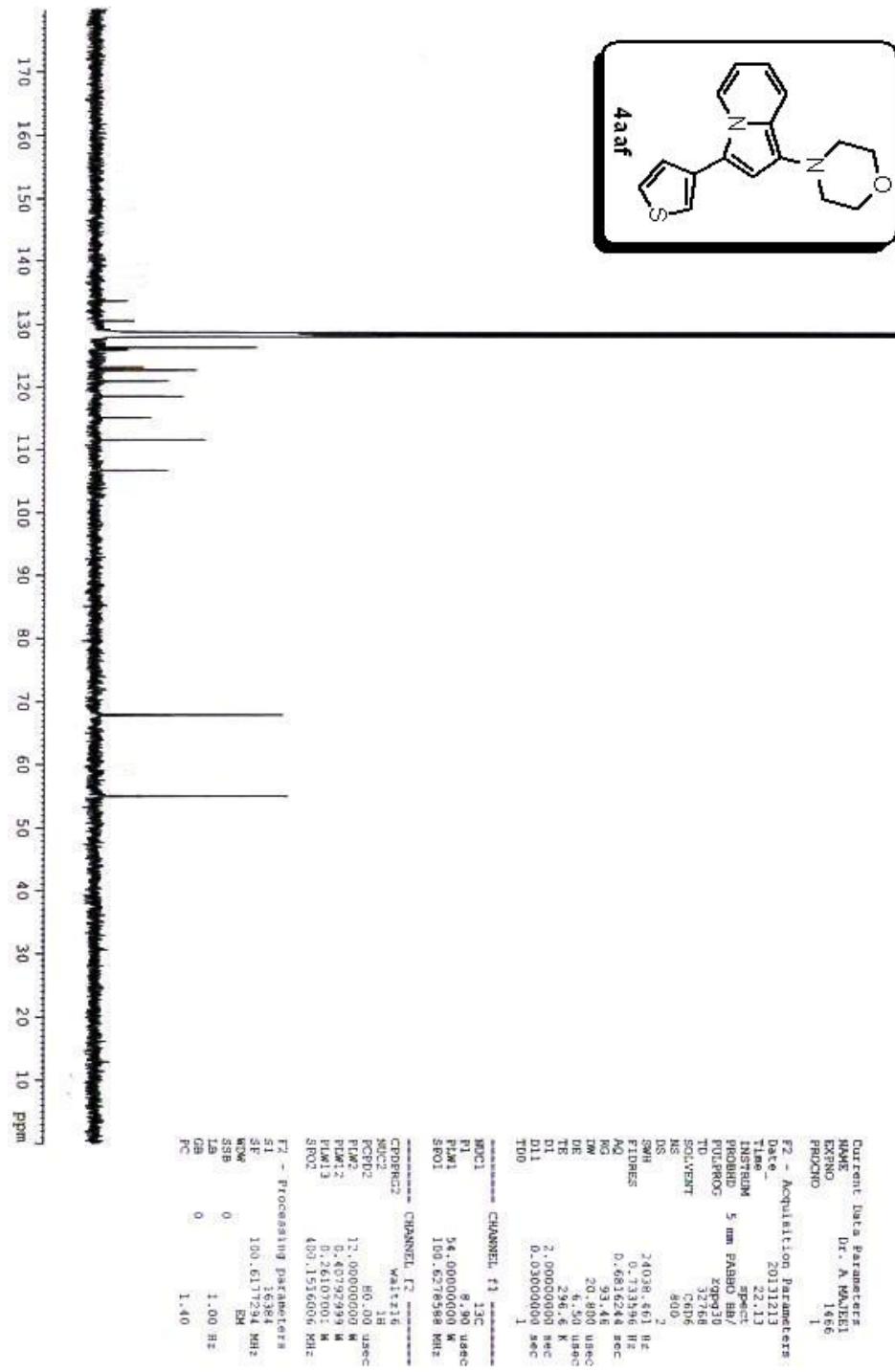
13C of VBPM-209-m

133.62
130.60
128.61
128.37
128.25
128.12
126.35
126.08
123.14
122.68
120.91
118.40
115.02
111.48
106.61

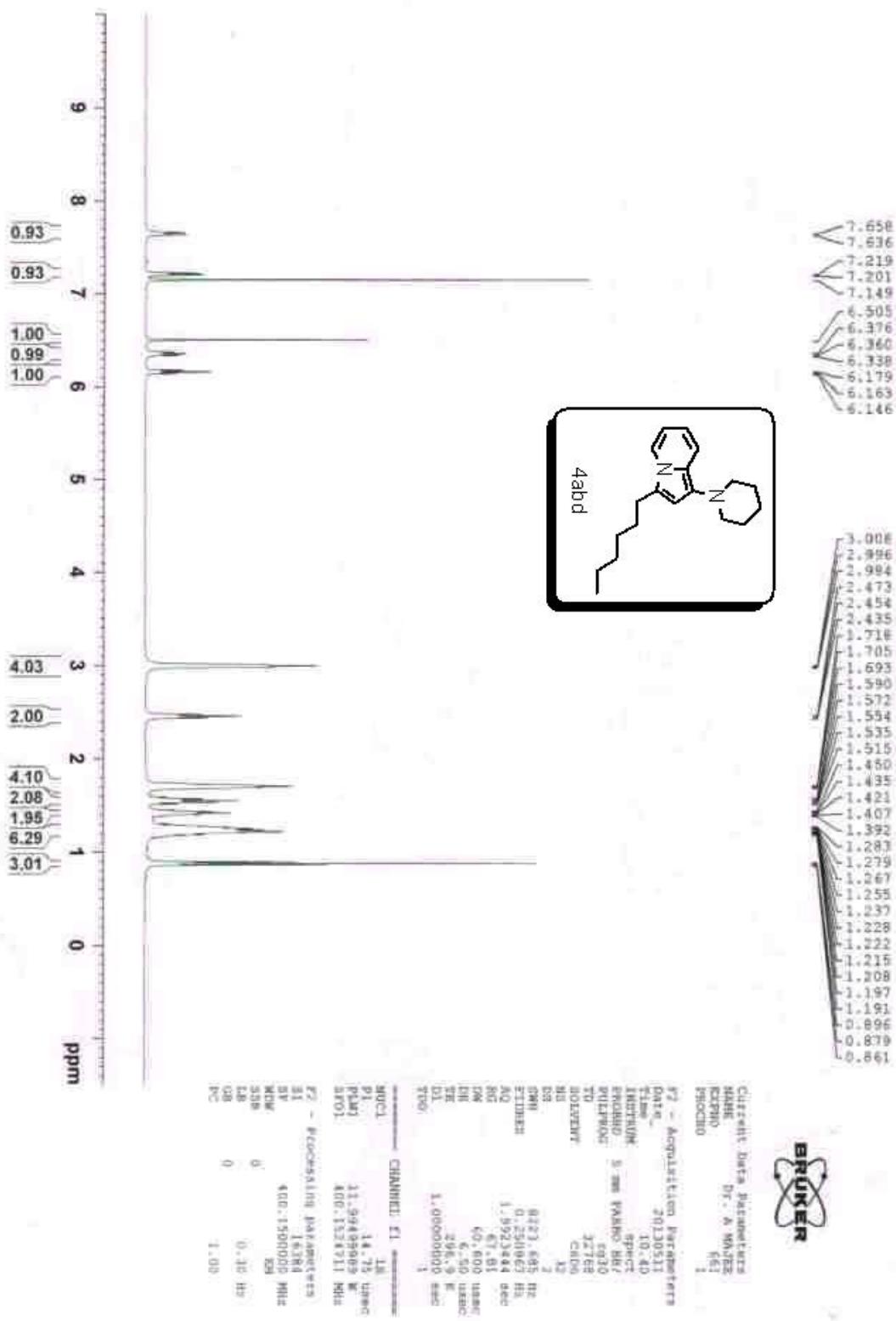
— 67.87
— 55.00

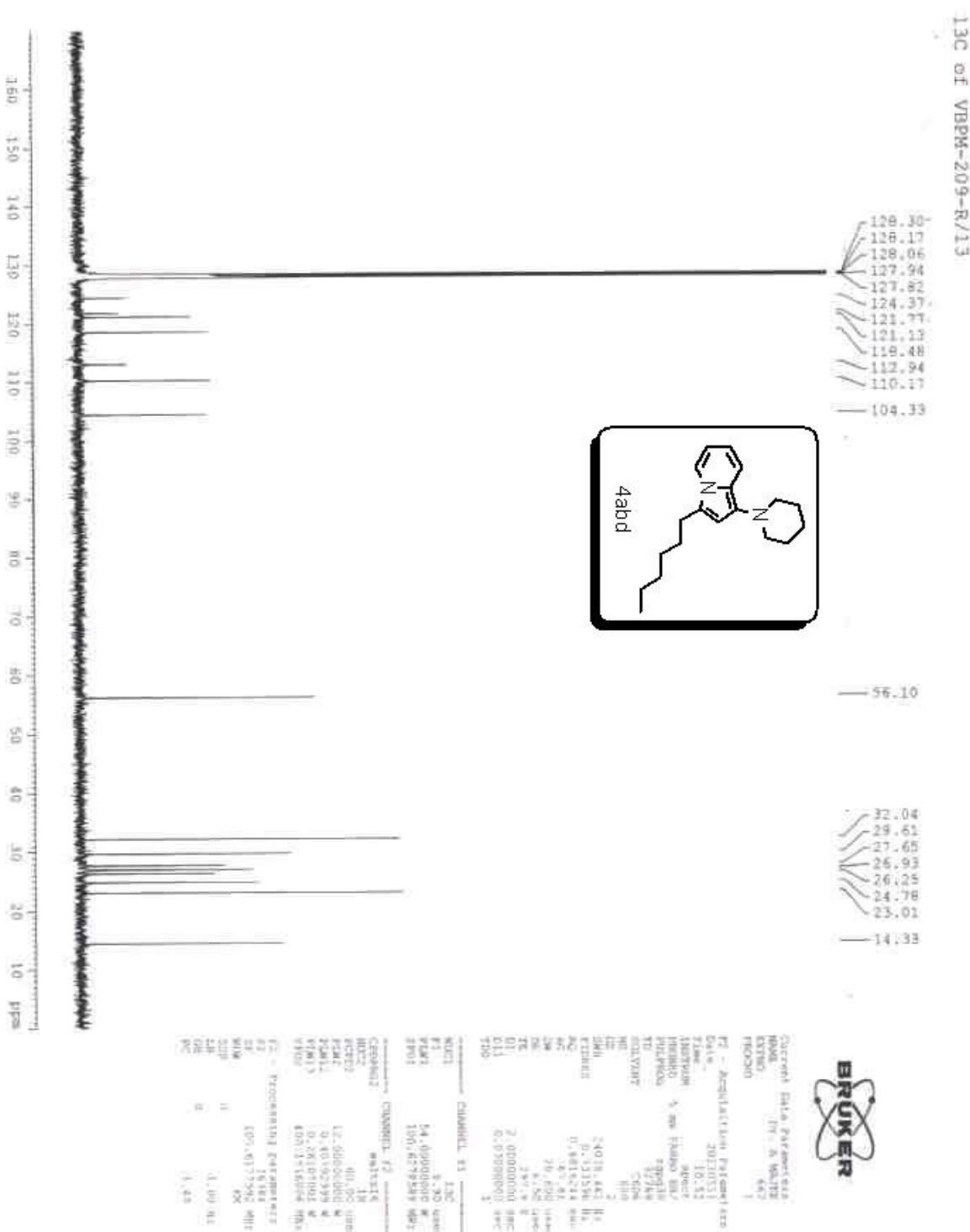


4aaf

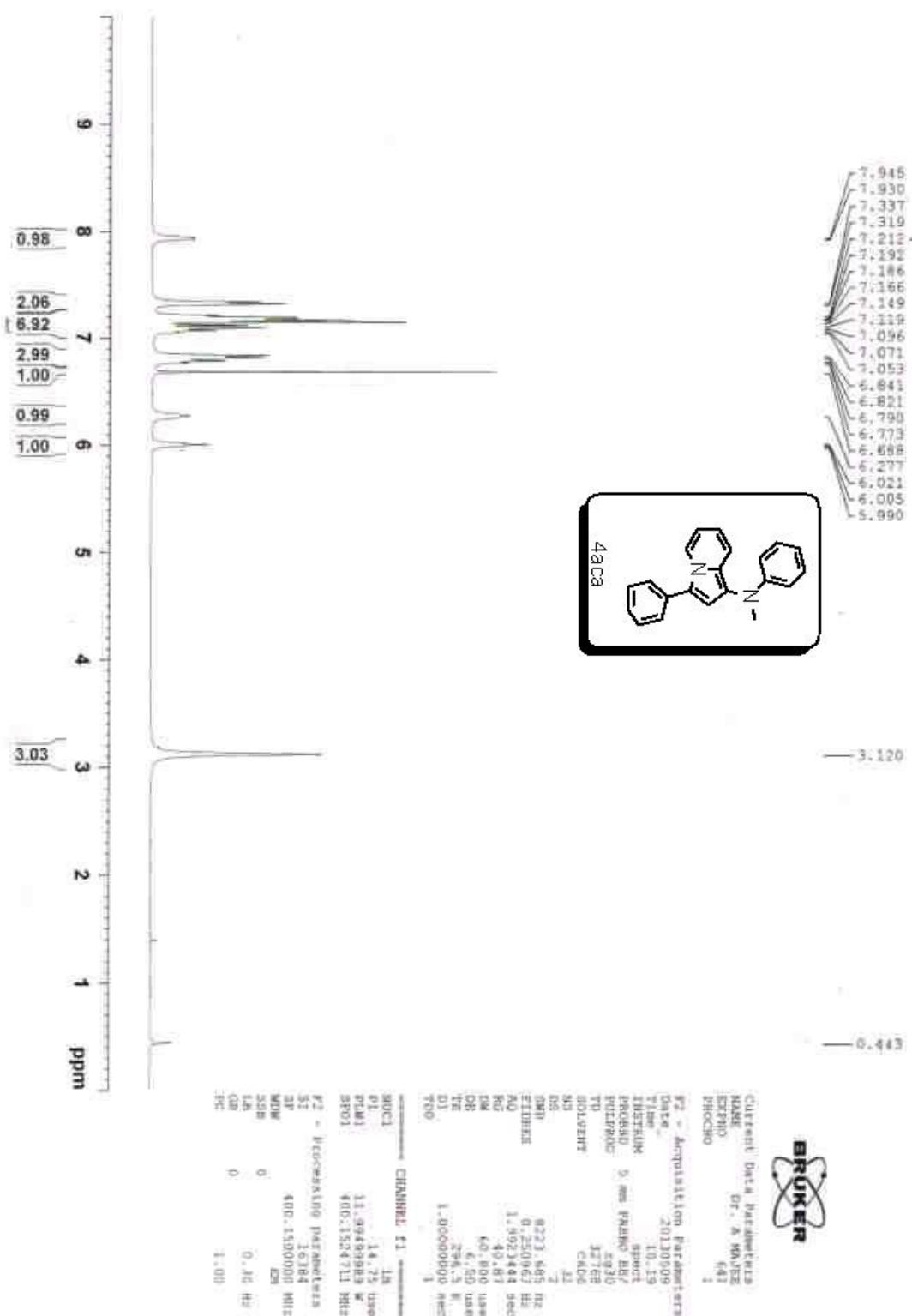


1H off VBPM-R/13



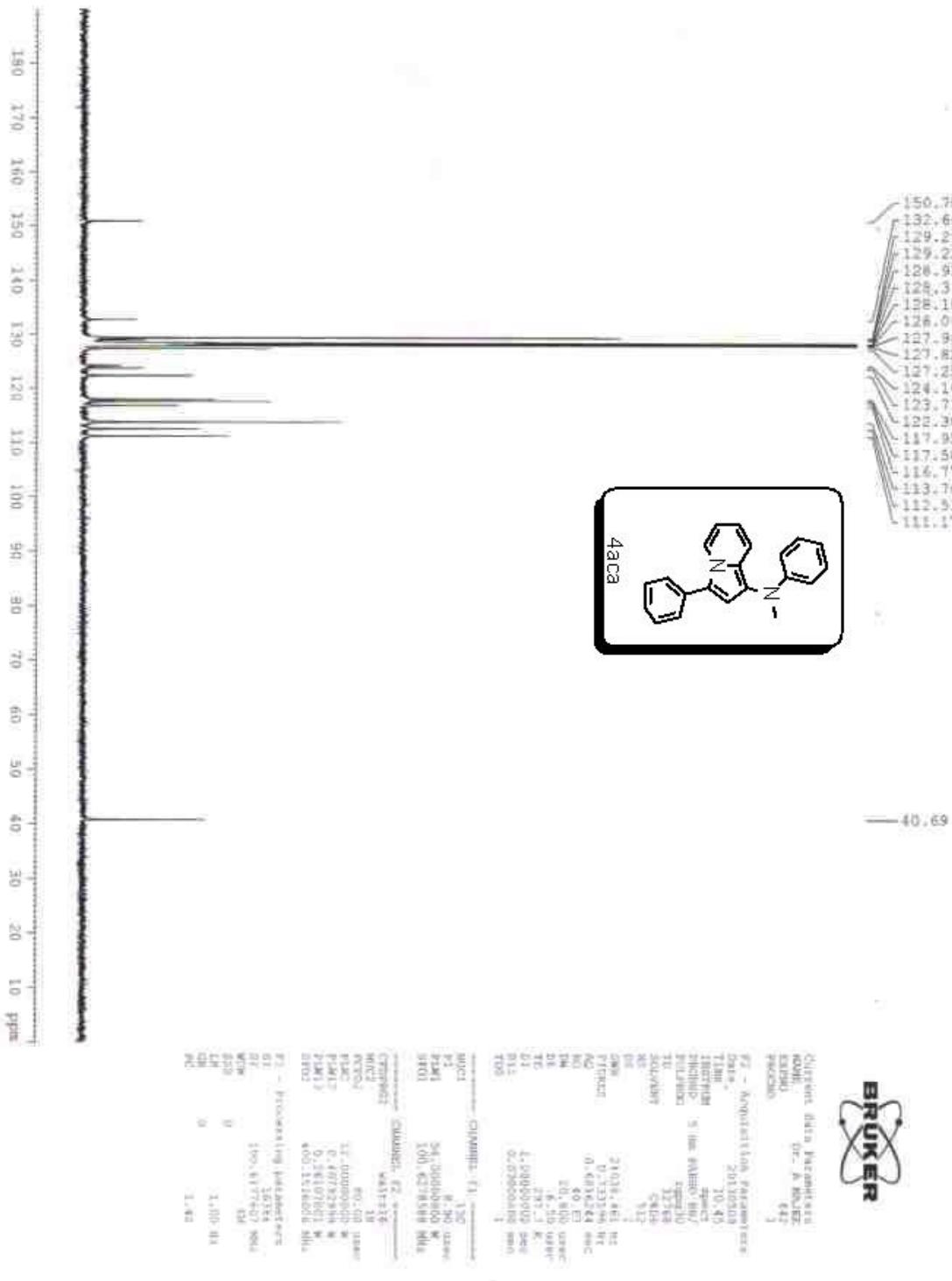
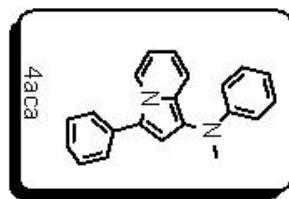


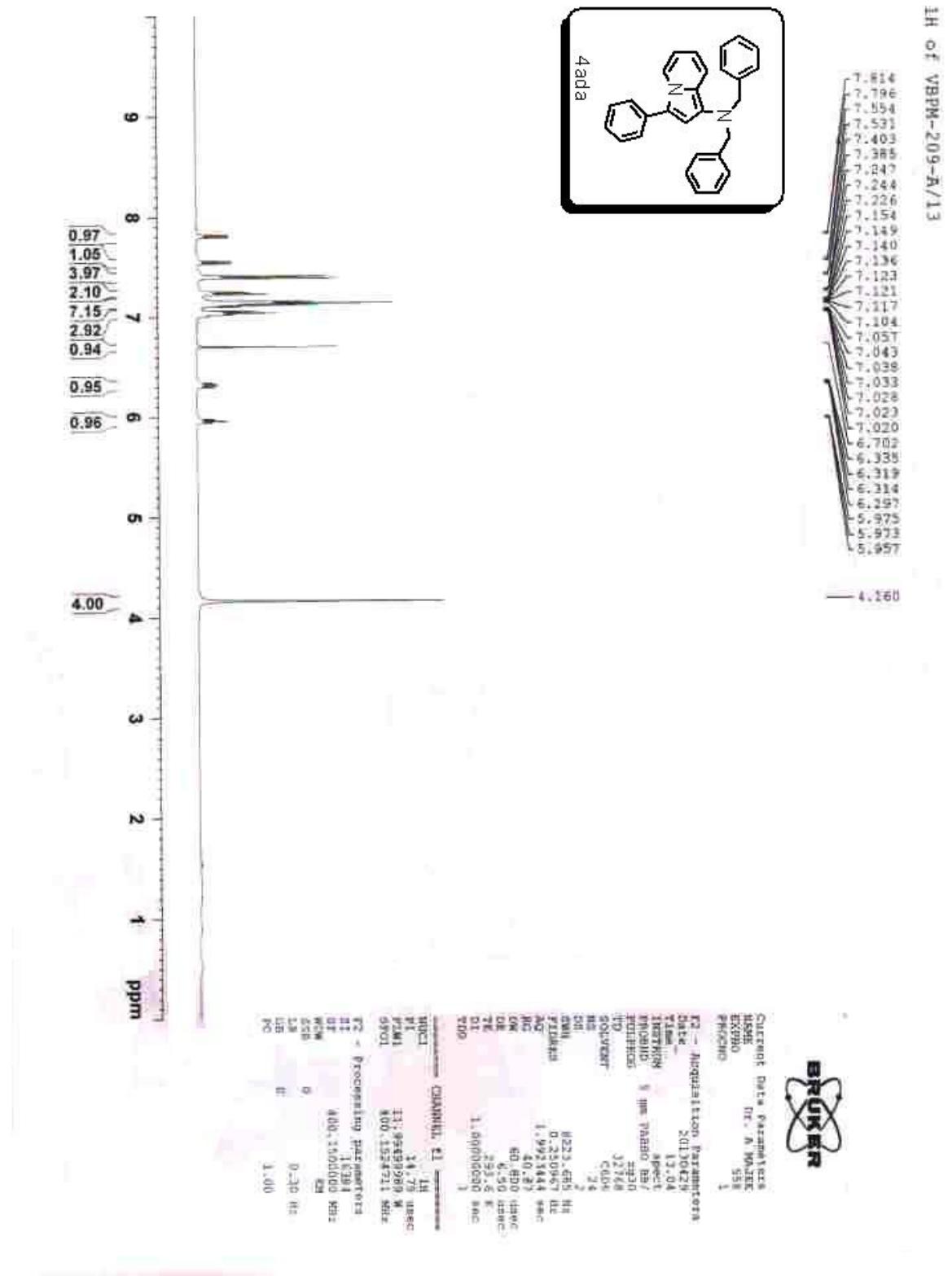
1H off VBRPM-209-O/13



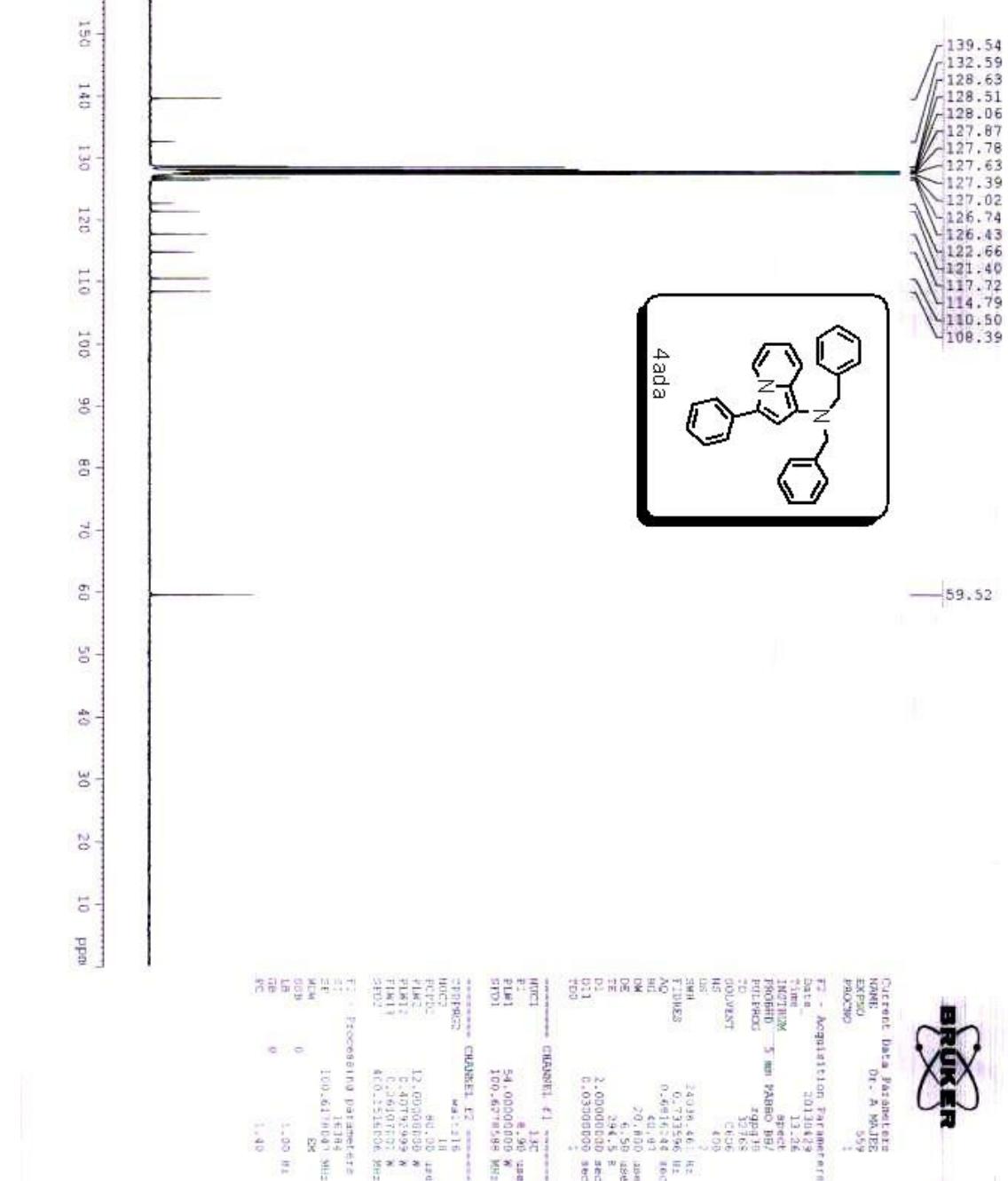
13C of VPPM-209-0/13

150.78
132.66
129.29
129.22
129.91
128.31
128.18
128.06
127.94
127.82
127.25
124.16
123.71
122.30
117.92
117.50
116.77
113.76
112.91
111.17

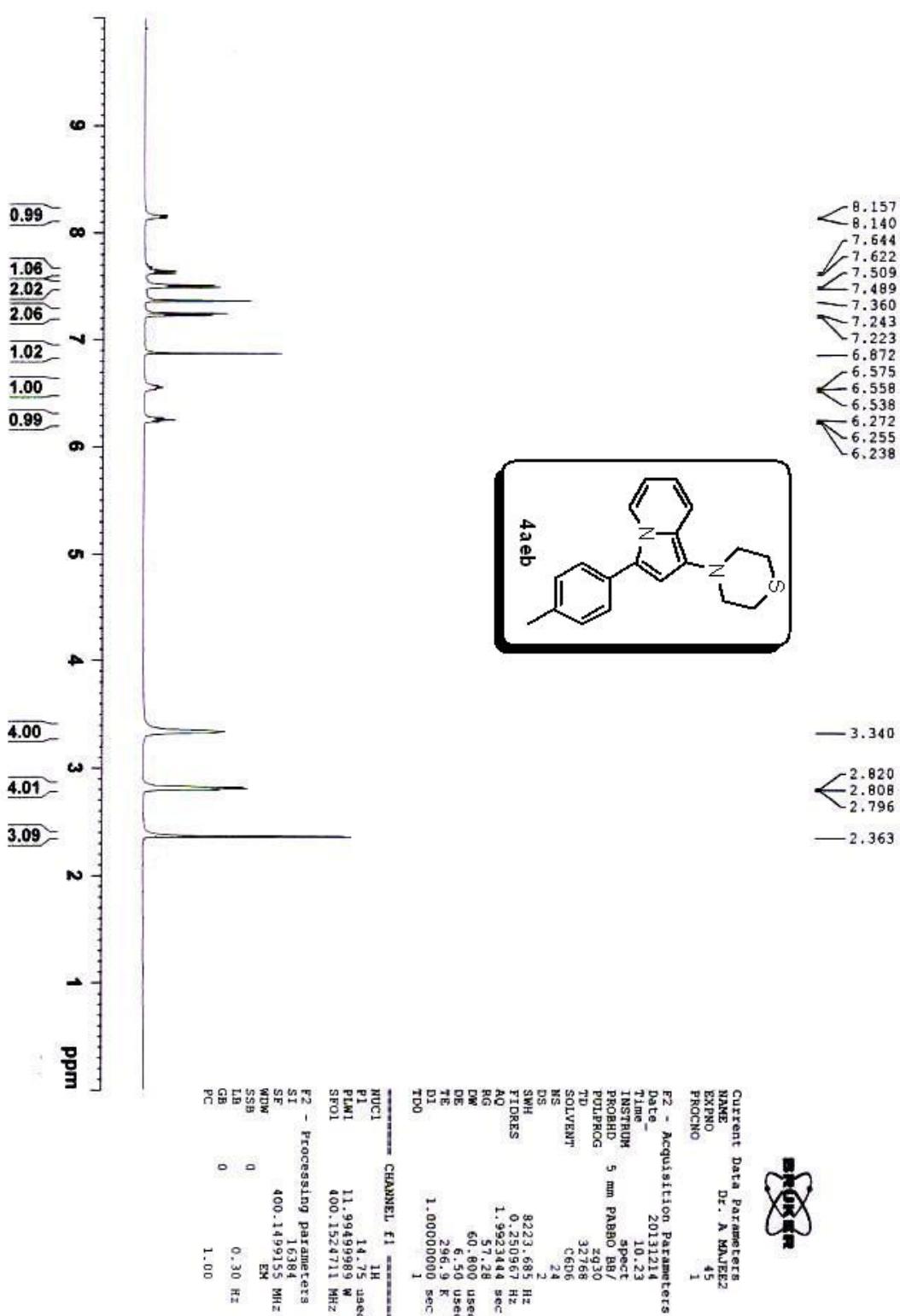




13C of VBPM-209-A/



1H of VBPM-210-C



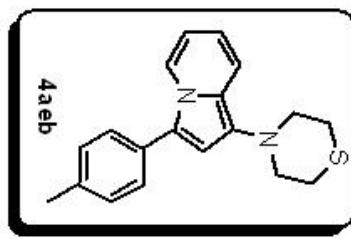
13C of VBPM-210-C

136.98
132.48
131.58
130.52
130.20
128.61
128.37
128.13
126.48
123.49
122.22
118.37
115.28
111.33
107.34

— 56.92

— 29.11

— 21.52



Current Data Parameters
NAME: Dr. A. MAJERZ
EXPNO: 45
PROCNO: 1

F2 - Acquisition Parameters
TD: 32768
TMS: 2013124
TIME: 10.28
INSTRUM: 5 mm PARROT BBR
PROBHD: zspgr10
PULPROG: zg3d6
SOLVENT: CDCl3
NS: 400
DS: 2
TE: 24038.461 Hz
SWH: 7335.96 Hz
ETR: 0.733596 sec
AQC: 0.681624 sec
RG: 57.8
DW: 20.800 usec
DPG: 6.50 usec
TEG: 298.1 K
D1: 2.000000 sec
D11: 0.0300000 sec
TD0: 1

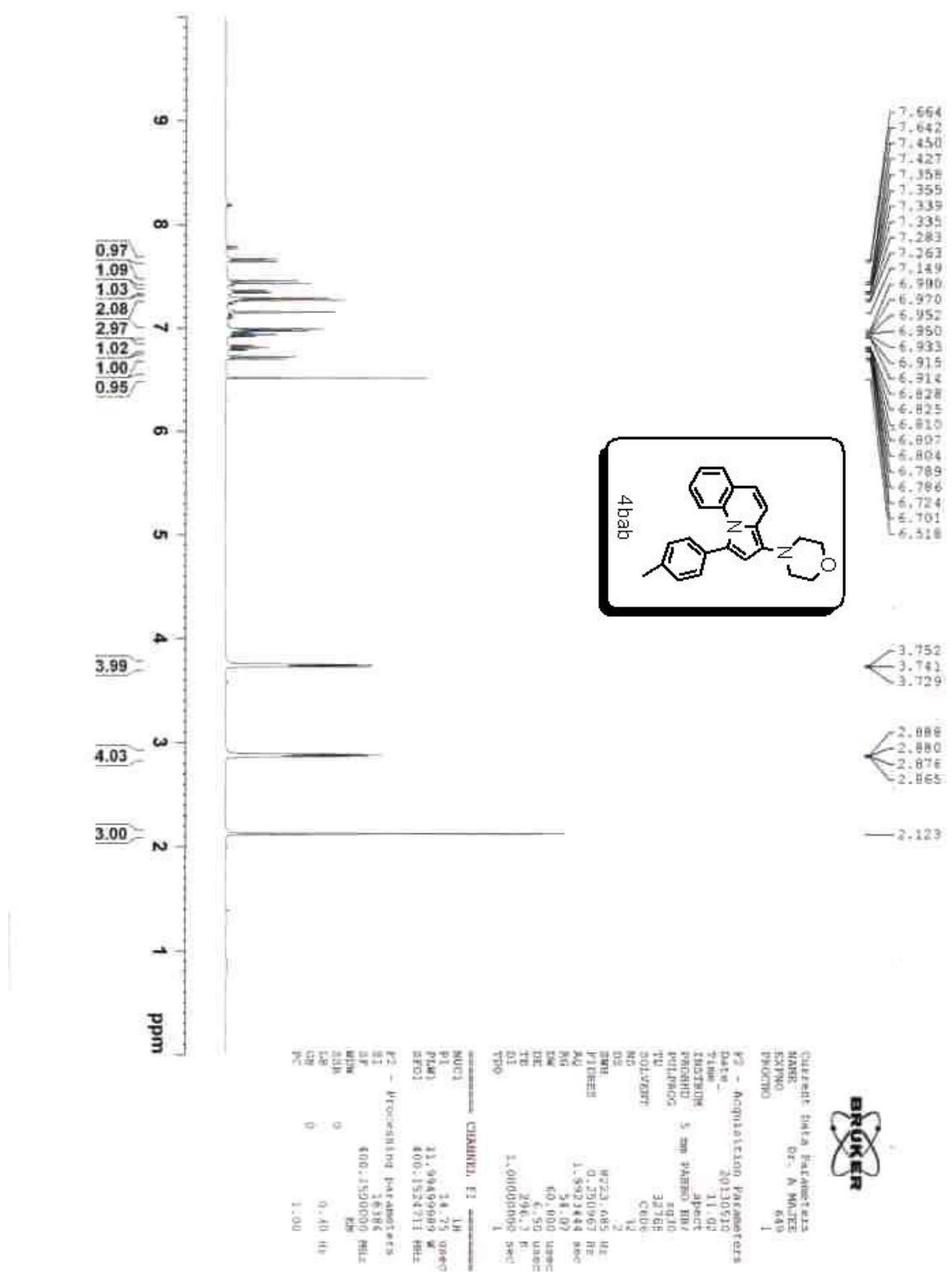
CHANNEL F1
MOC1: 13C
P1: 8.90 usec
P1M1: 54.0000000 MHz
SIPO1: 100.6278500 MHz

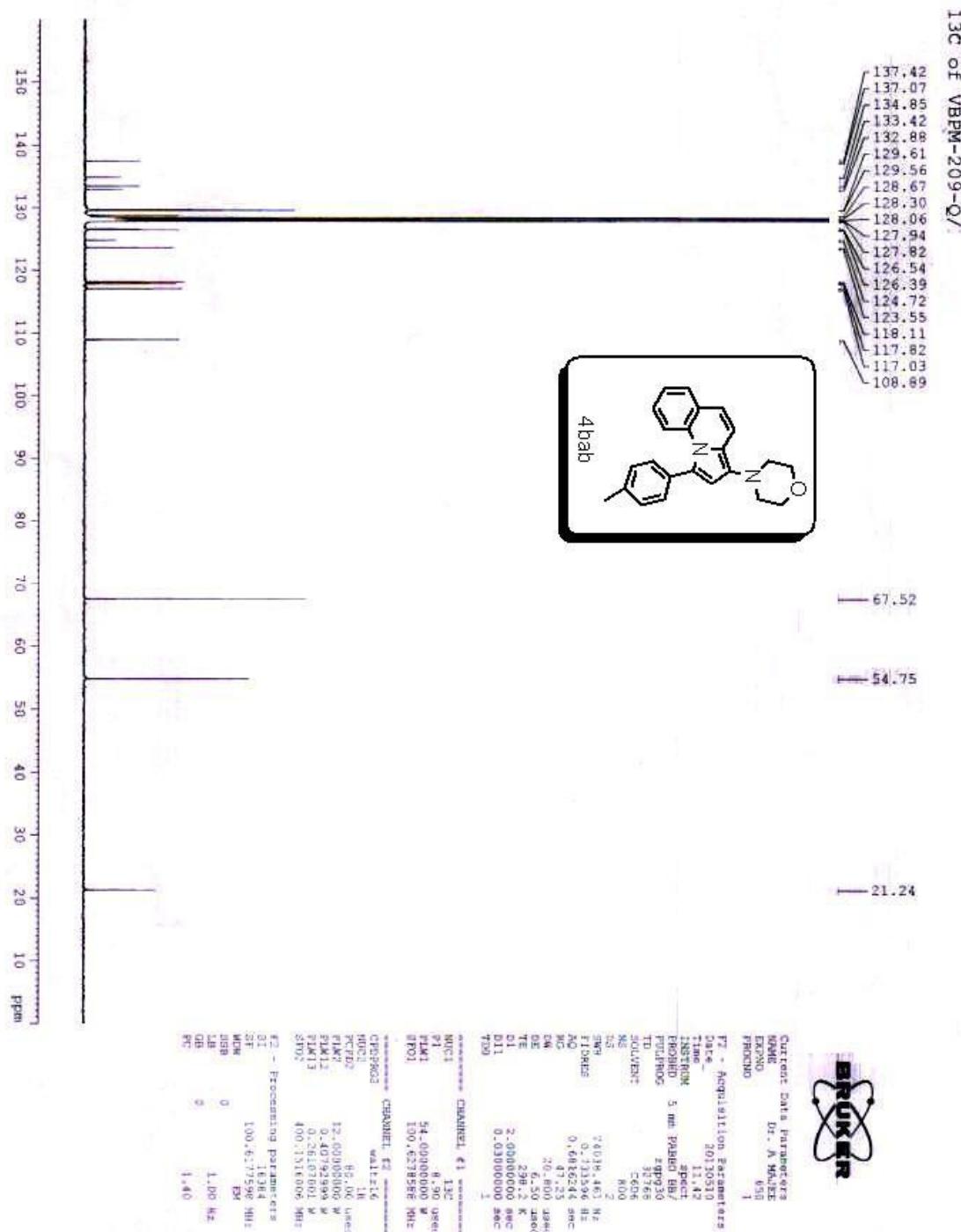
CHANNEL F2
CPDRG2: 13C13C
NSC1: 80.00 usec
CPDQ2: 10.0000000 W
P1W2: 0.40792499 W
P1W12: 0.24101091 W
P1W13: 0.24101091 W
EW02: 400.1516006 MHz

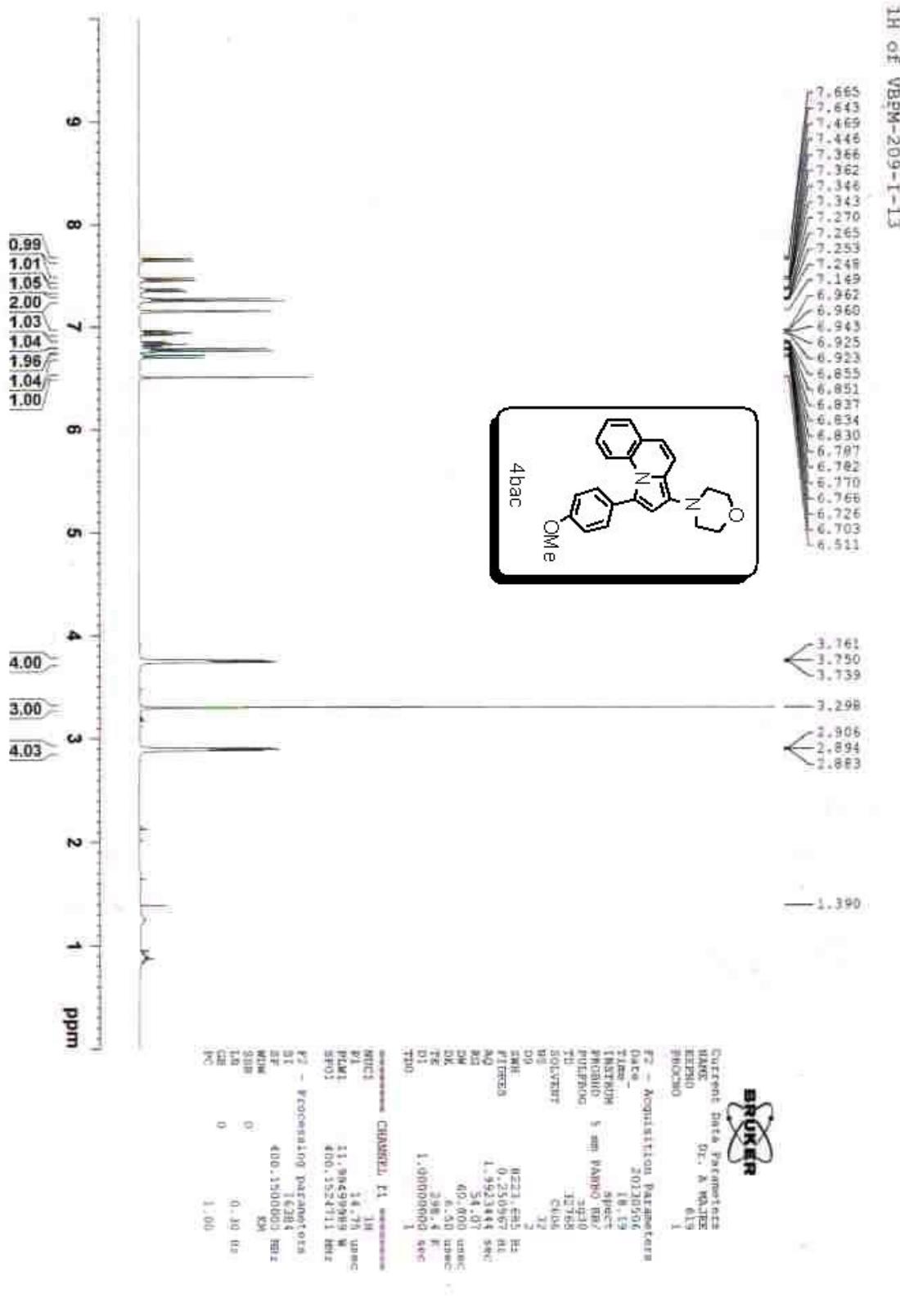
F2 - Processing parameters
ST: 16.384
SF: 100.617724 MHz
WM: 324
SSB: 0
LB: 1.00 Hz
PC: 1.40

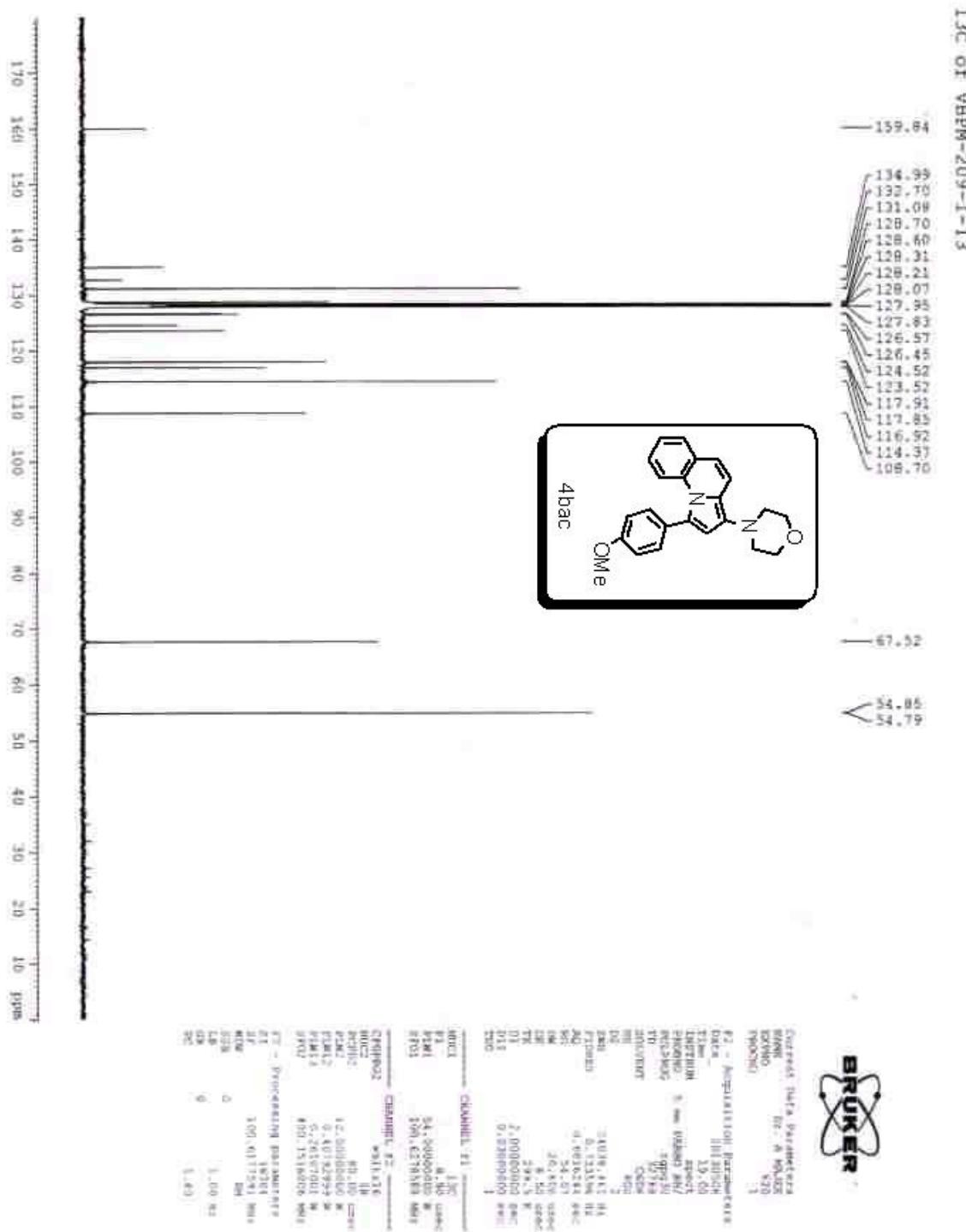


1H off VBRPM-209-Q/13









V. Photophysical studies:

Spectroscopic apparatus:

The steady state electronic absorption spectra of all the samples were recorded at the ambient temperature (300 K) using 1 cm pathlength rectangular quartz cuvette by Kozima, by means of JASCO V-650 absorption spectrophotometer. Steady state fluorescence spectra of all the samples were recorded by JASCO FP-6500 fluorescence spectrometer at 300 K. Emission was detected at right angles to the direction of excitation light in order to avoid stray light.

Quantum Yield Determination:

To calculate Fluorescence quantum yield (ϕ_f), we used the following formula^d,

$$\varphi_f = \frac{I_f}{I_f^R} \frac{A^R}{A} \left(\frac{n}{n^R} \right)^2 \varphi_f^R$$

Here, φ_f^R is the known fluorescence quantum yield of the reference sample (referred by the superscript 'R'); I_f and I_f^R are the integrated fluorescence intensities of the unknown sample and reference sample, respectively; A and A^R are the absorbances of the unknown sample and reference sample, respectively; n and n^R are the refractive indices of the solvents for the unknown sample and reference sample, respectively. The unknown sample and reference sample are excited at the same wavelength for measuring I_f and I_f^R , respectively. The fluorescence quantum yield of the samples are measured at 300 K relative to that of ZnTPhP in benzene solution ($\varphi_f^R = 0.033$ at 30° C)^e.

Photophysical study of **4bac** in various solvents:

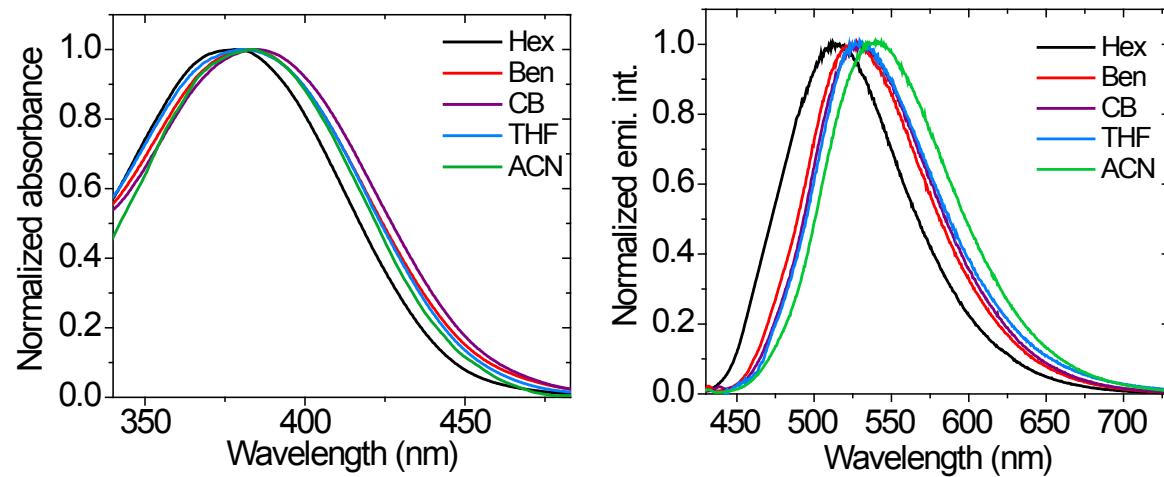
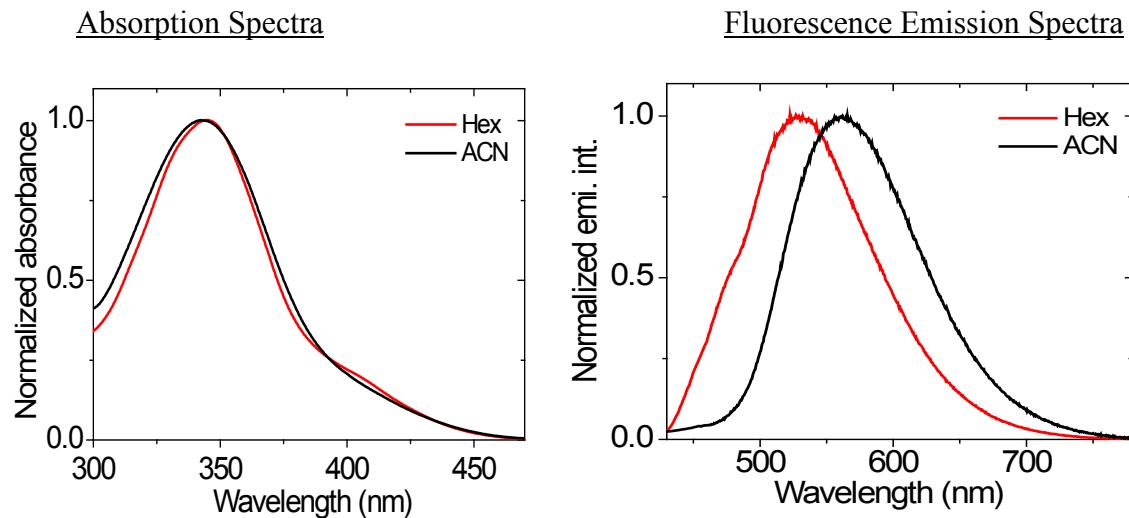


Fig 2 Absorbance and fluorescence emission spectra of **4bac** in various solvents (Concentration $\sim 10^{-4}$ mol L $^{-1}$). Hex= Hexane, Ben= Benzene, CB= Chlorobenzene, ACN= Acetonitrile.

Solvent	$\lambda_{\text{max}}(\text{nm})$	$\lambda_{\text{emi}}(\text{nm})^*$	ϕ_f	$\epsilon \text{ at } \lambda_{\text{max}}$ (cm $^{-1}$ M $^{-1}$)	$\bar{\nu}_a - \bar{\nu}_f$ (cm $^{-1}$)
Acetonitrile	384	541	0.40	4675	7557
Tetrahydrofuran	382	531	0.34	6005	7277
Chlorobenzene	385	529	0.47	4943	7070
Benzene	382	526	0.44	4733	7166
Hexane	379	514	0.34	3899	7070

* Excitation wavelength was chosen corresponding to their λ_{max} value. (Concentration $\sim 10^{-4}$ mol L $^{-1}$)

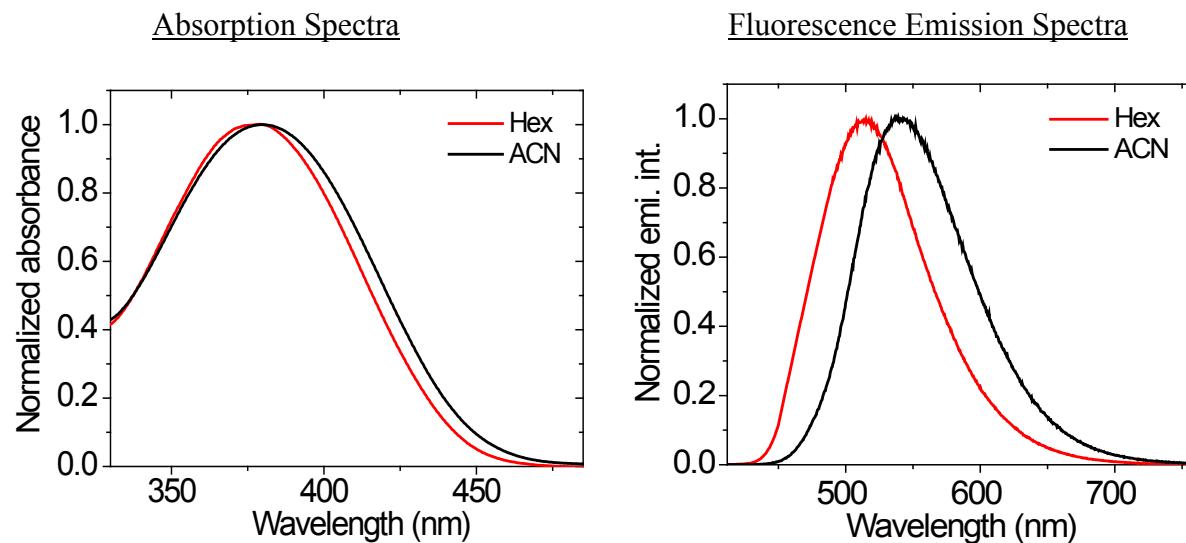
Absorbance and fluorescence emission spectra of **4aaa**.



Solvent	$\lambda_{\text{max}}(\text{nm})$	$\lambda_{\text{emi}} \text{ (nm)}^*$	ϕ_f	$\epsilon \text{ at } \lambda_{\text{max}}$ $(\text{cm}^{-1}\text{M}^{-1})$	$\bar{\nu}_a - \bar{\nu}_f$ (cm^{-1})
Acetonitrile	344	562	0.006	6423	11329
Hexane	345	529	0.035	9653	10082

* Excitation wavelength was chosen corresponding to their λ_{max} value. (Concentration $\sim 10^{-4}$ mol L⁻¹)

Absorbance and fluorescence emission spectra of **4bab**.



Solvent	$\lambda_{\text{max}}(\text{nm})$	$\lambda_{\text{emi}} \text{ (nm)}^*$	ϕ_f	$\epsilon \text{ at } \lambda_{\text{max}}$ $(\text{cm}^{-1}\text{M}^{-1})$	$\bar{\nu}_a - \bar{\nu}_f$ (cm^{-1})
Acetonitrile	381	543	0.50	5567	7831
Hexane	378	515	0.75	3914	7038

* Excitation wavelength was chosen corresponding to their λ_{max} value. (Concentration $\sim 10^{-4}$ mol L $^{-1}$)

VII. References:

- (a) B. Yan and Y. Liu, *Org. Lett.*, 2007, **9**, 4323.
- (b) Y. Bai, J. Zeng, J. Ma, B. K. Gorityala, and X.-W. Liu, *J. Comb. Chem.* 2010, **12**, 696.
- (c) S. Mishra, B. Naskar and R. Ghosh, *Tetrahedron Lett.*, 2012, **53**, 5483.
- (d) J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, second ed., Kluwer Academic/ Plenum Publishers, New York, 1999.
- (e) M. Ghosh, A. K. Mora, S. Nath, A. K. Chandra, A. Hajra and S. Sinha, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* 2013, **116**, 466.