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Supporting Information

Copper Supported Hematite NPs as Magnetically Recoverable Nanocatalysts for One-Pot Synthesis of Aminioindolizines and Pyrrolo[1,2-a]quinolines

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1. General Remarks

Powder X-ray diffraction (PXRD) patterns were recorded on Rigaku Rotaflex spectrometer at 2θ range of 10–70° with Cu Kα radiation. TG-DTA analysis (Perkin Elmer, Pyris Diamond) with a heating rate of 10 °C/min in nitrogen atmosphere was used to study the thermal decomposition behavior of the as-prepared (dried) sample with respect to α-Al_2O_3 as the reference. The samples were degassed at 100 °C for 3 h prior to measurements. Fourier transform infrared (FT-IR) spectra were recorded on Perkin Elmer and the samples were prepared by mixing the powdered solids with KBr. Scanning electron microscopy (SEM) measurement was performed on a Philips XL30 electron micrograph. Transmission electron microscopy (TEM), SAED micrographs were obtained on a Joel JEM 2010 transmission electron microscope. The samples were supported on carbon-coated copper grids for the experiment. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was obtained from Perkin Elmer, Optima 2000. The elemental composition and electronic structure analysis of Cu@Fe_2O_3 was obtained from X-ray photoelectron spectra (XPS) of model SPECS and Omircon electron analyzer (EA125). The ^{1}H NMR and ^{13}C NMR spectra were measured on a BruckerAC-200 instrument using C_6D_6 as solvent. Mass spectral data were recorded on a Jeol-Accu TOF JMS-T100LC and micromass LCT Mass Spectrometer/Data system.

2. Characterization of fresh and recycled Cu@Fe_2O_3

2a. PXRD and TEM analysis of Cu@Fe_2O_3 catalyst:

The powder XRD of recycled catalyst was compared with its fresh sample. There was no change in the phases of XRD pattern observed as shown in Figure S1. However, slight change in the crystalinity and grain size of Fe_2O_3 was observed (Figure S1). Moreover, the internal morphology of recycled catalyst was analyzed by transmission electron microscopy (TEM) as shown in Figure S2. The results showed that there was no considerable change in the morphology.

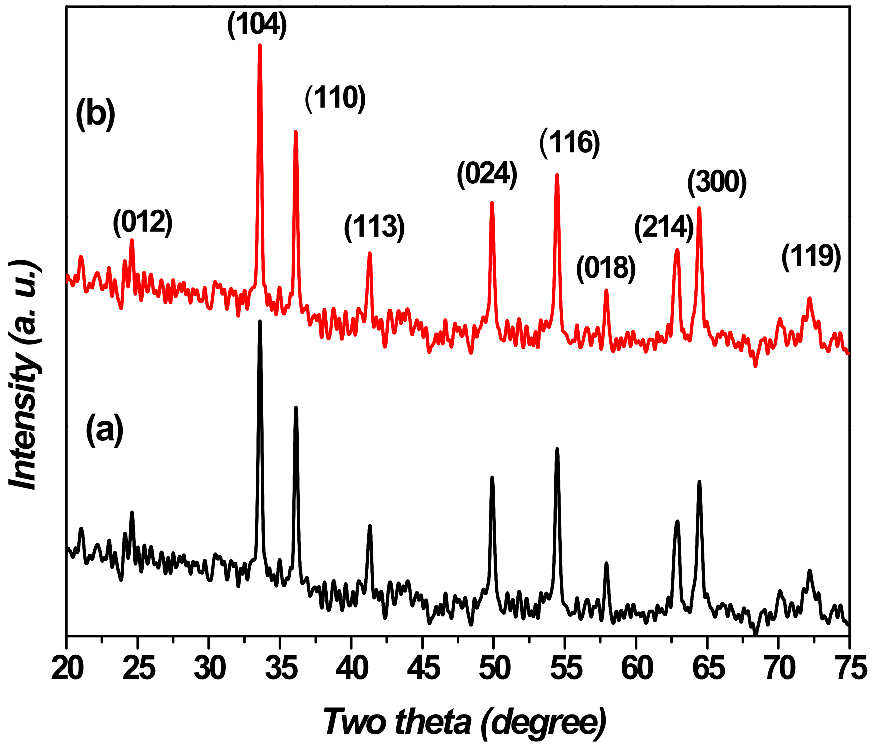


Figure S1: Comparison of PXRD of (a) fresh and (b) recycled Cu@Fe_2O_3 catalysts

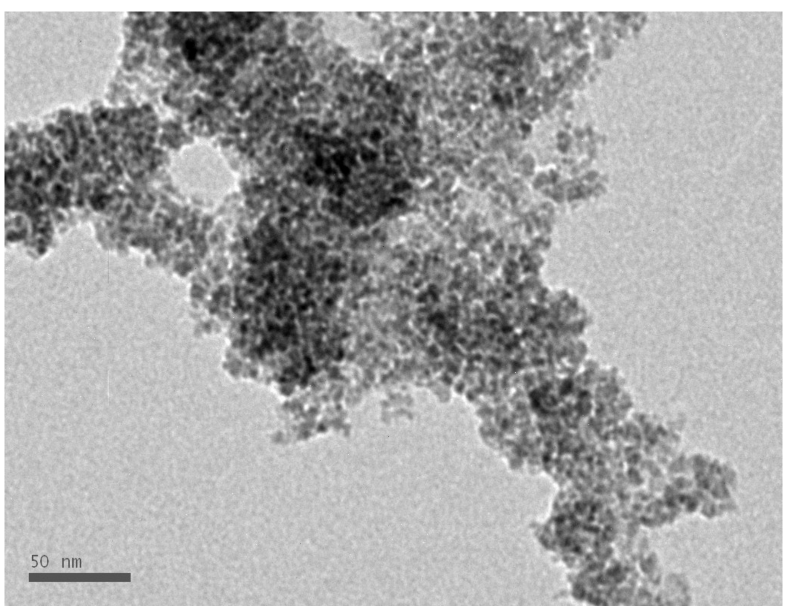


Figure S2: TEM image of recycled Cu@Fe_2O_3 catalyst

2b. High resolution XPS spectra of O1s and C1s region of fresh catalyst

The high resolution spectra of O1s and C1s regions showed the presence broad peaks with binding energies 530.3 and 285.7 eV respectively as shown in Figure S3.

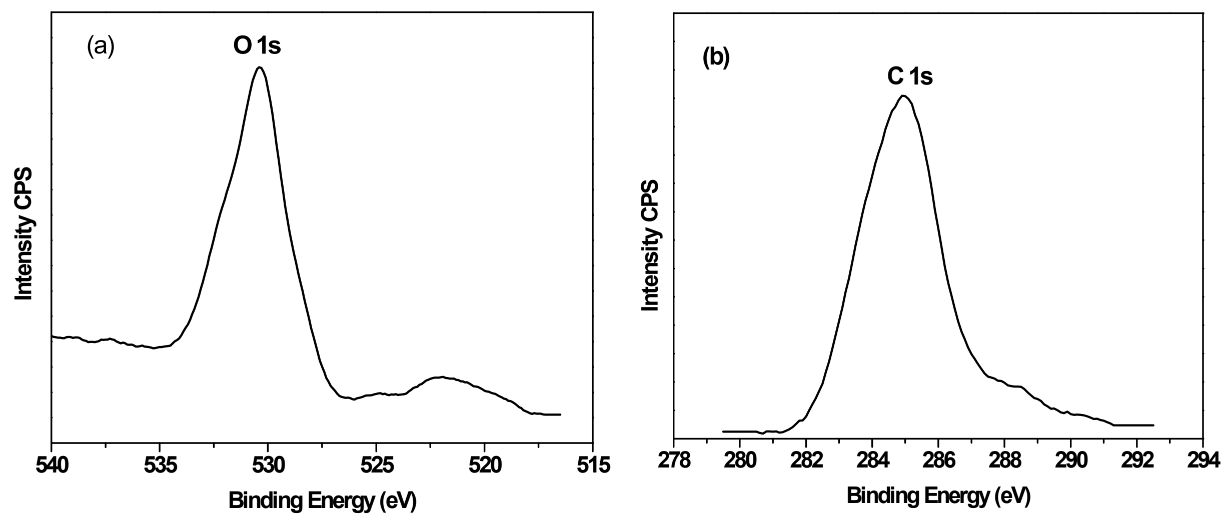


Figure S3: High resolution XPS spectra of (a) O1s and (b) C1s region of Cu@Fe_2O_3 catalyst

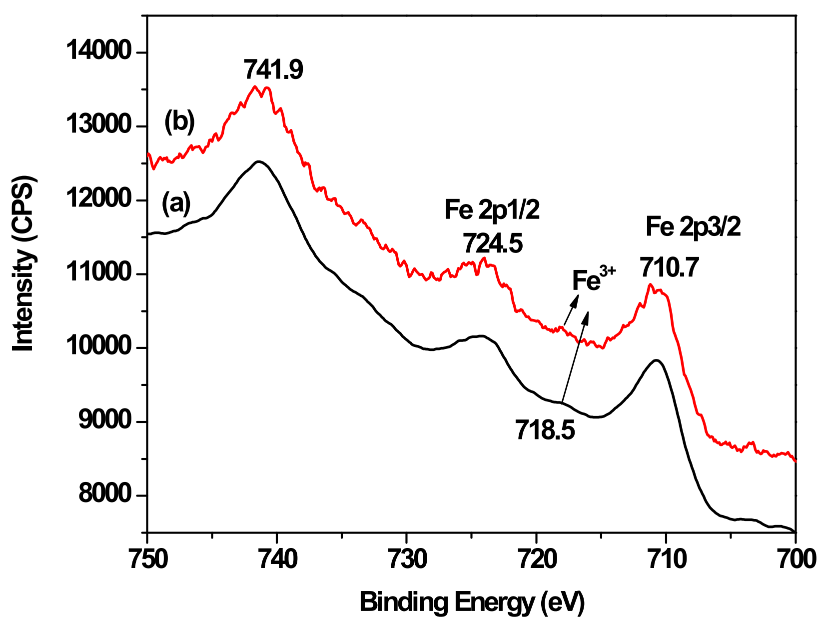


Figure S4: High resolution XPS spectra of Fe2p region of (a) fresh (b) recycled catalyst

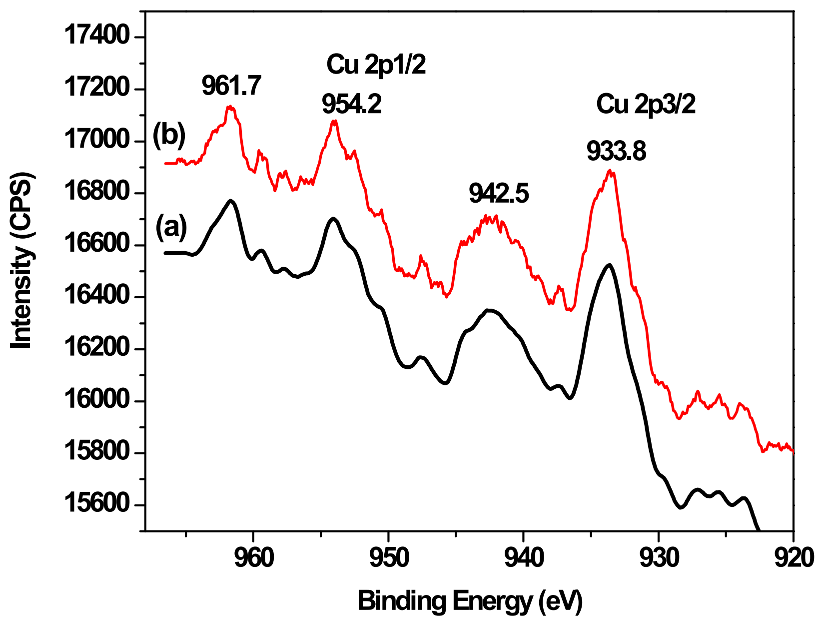
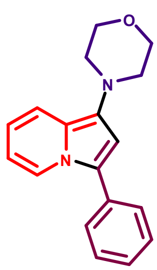


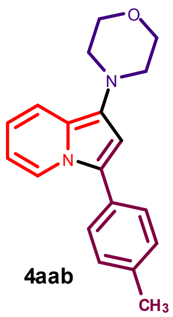
Figure S5: High resolution XPS spectra of Cu2p region of (a) fresh (b) recycled catalyst

3. Spectral data of known compounds



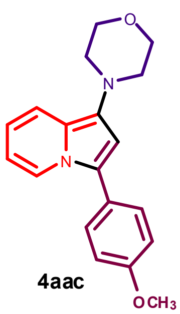
4aaa

4-(3-Phenylindolizin-1-yl)morpholine (**4aaa**) [Ref 1]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.91 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 9.1 Hz, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.20 (d, J = 6.8 Hz, 2H), 7.08 (t, J = 6.8 Hz, 1H), 6.66 (s, 1H), 6.35 (t, J = 7.6 Hz, 1H), 6.04 (t, J = 7.6 Hz, 1H), 3.75 (t, J = 4.5 Hz, 4H), 2.87 (t, J = 4.5 Hz, 4H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 133.07, 130.62, 129.19, 127.05, 126.12, 123.00, 121.86, 118.25, 114.95, 111.18, 106.56, 67.56, 54.69 ppm.



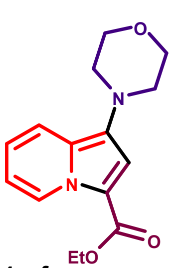
4aab

4-(3-p-tolylindolizin-1-yl)morpholine (**4aab**) [Ref 1]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.94 (d, J = 6.8 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.29 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 7.6 Hz, 2H), 6.67 (s, 1H), 6.35 (t, J = 7.6 Hz, 1H), 6.04 (t, J = 6.8 Hz, 1H), 3.75 (t, J = 4.5 Hz, 4H), 2.87 (t, J = 4.5 Hz, 4H), 2.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 136.60, 130.52, 130.19, 129.83, 125.70, 123.03, 121.85, 118.16, 114.66, 110.93, 106.16, 67.52, 54.66, 21.15 ppm.



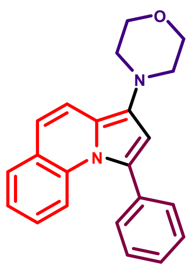
4aac

4-(3-(4-methoxyphenyl)indolizin-1-yl)morpholine (**4aac**) [Ref 1]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.90 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.28 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 8.3 Hz, 2H), 6.66 (s, 1H), 6.36 (t, J = 6.8 Hz, 1H), 6.08 (t, J = 6.8 Hz, 1H), 3.76 (t, J = 4.5 Hz, 4H), 3.34 (s, 3H), 2.90 (t, J = 4.5 Hz, 4H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 159.31, 130.38, 129.85, 125.55, 122.97, 121.83, 118.23, 114.75, 114.55, 110.93, 106.03, 67.62, 54.92, 54.77 ppm.



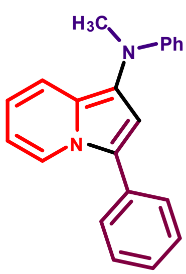
4aaf

Ethyl 1-morpholinoindolizine-3-carboxylate (**4aaf**) [Ref 1]: White solid. mp: 115-117 °C; ^{1}H NMR (400 MHz, C_6D_6) δ = 7.97 (d, J = 7.6 Hz, 1H), 7.03 (s, 1H), 7.02 (d, J = 8.3 Hz, 1H), 6.34 (t, J = 7.6 Hz, 1H), 6.18 (t, J = 6.8 Hz, 1H), 4.23 (q, J = 6.8 Hz, 2H), 3.90 (t, J = 11.4 Hz, 2H), 3.70 (d, J = 11.4 Hz, 2H), 3.47 (t, J = 11.4 Hz, 2H), 2.19 (d, 11.4 Hz, 2H), 1.12 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 164.74, 134.59, 121.93, 120.24, 118.10, 113.89, 111.42, 100.61, 68.14, 60.17, 49.91, 14.57 ppm;



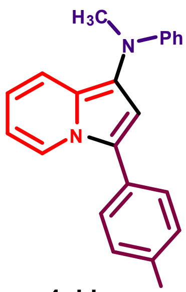
4baa

4-(1-phenylpyrrolo[1,2-a]quinolin-3-yl)morpholine (**4baa**) [Ref 2]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.58 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 9.2 Hz, 1H), 7.34 (d, *J* = 6.8 Hz, 3H), 7.13-7.09 (m, 3H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 9.9 Hz, 1H), 6.5 (s, 1H), 3.74 (t, *J* = 4.6 Hz, 4H), 2.87 (t, *J* = 4.6 Hz, 4H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ: 136.27, 134.64, 132.29, 129.55, 128.79, 128.70, 126.49, 124.88, 123.60, 118.15, 117.76, 117.21, 109.12, 67.50, 54.72 ppm.



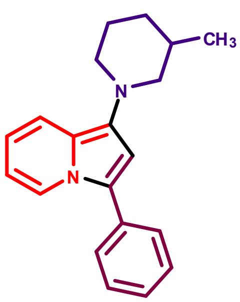
4aba

N-Methyl-*N*,3-diphenylindolizin-1-amine (**4aba**) [Ref 1]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.94 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 2H), 7.22-7.17 (m, 3H), 7.10 (t, J = 8.6 Hz, 2H), 6.84 (d, J = 9.1 Hz, 2H), 6.79 (d, J = 6.8 Hz, 1H), 6.69 (s, 1H), 6.28 (t, J = 7.6 Hz, 1H), 6.00 (t, J = 6.8 Hz, 1H), 3.12 (s, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 150.80, 132.71, 129.31, 129.23, 127.24, 124.17, 123.70, 122.30, 117.96, 117.52, 116.78, 113.74, 112.54, 111.20, 40.72 ppm.



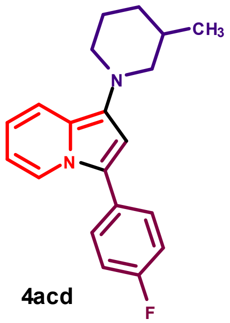
4abb

N-Methyl-*N*-phenyl-3-p-tolylindolizin-1-amine (**4abb**) [Ref 1]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.95 (d, J = 6.8 Hz, 1H), 7.29 (d, J = 7.6 Hz, 2H), 7.21 (t, J = 7.6 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 7.6 Hz, 2H), 6.80 (t, J = 7.6 Hz, 1H), 6.71 (s, 1H), 6.29 (t, J = 7.6 Hz, 1H), 6.02 (t, J = 6.8 Hz, 1H), 3.13 (s, 3H), 2.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 150.77, 136.88, 129.85, 129.23, 124.21, 123.53, 122.29, 117.88, 117.37, 116.45, 113.65, 113.38, 112.15, 110.98, 40.67, 21.18 ppm.



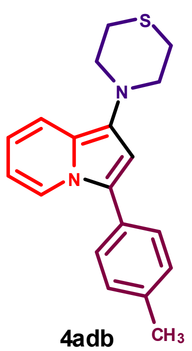
4aca

1-(3-Methylpiperidin-1-yl)-3-phenylindolizine (**4aca**) [Ref 1]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.94 (d, J = 6.8 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 7.6 Hz, 2H), 7.19 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 6.76 (s, 1H), 6.35 (t, J = 7.6 Hz, 1H), 6.04 (t, J = 6.8 Hz, 1H), 3.27-3.23 (m, 2H), 2.63 (t, J = 11.4 Hz, 1H), 2.37 (t, J = 10.6 Hz, 1H), 1.92-1.79 (m, 2H), 1.70-1.59 (m, 3H), 0.86 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 133.86, 130.36, 127.71, 125.37, 124.75, 120.32, 117.05, 113.19, 109.59, 105.30, 76.29, 61.61, 53.79, 31.91, 30.56, 25.16, 18.33 ppm.



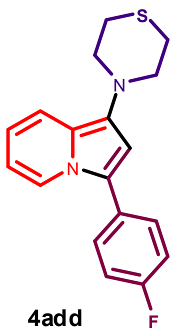
4acd

3-(4-Fluorophenyl)-1-(3-methylpiperidin-1-yl)indolizine (**4acd**) [Ref 1]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.74 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 8.3 Hz, 1H), 7.09 (t, J = 6.8 Hz, 2H), 6.83 (t, J = 8.3 Hz, 2H), 6.65 (s, 1H), 6.35 (t, J = 7.6 Hz, 1H), 6.05 (t, J = 7.6 Hz, 1H), 3.27-3.25 (m, 2H), 2.64 (t, J = 11.4 Hz, 1H), 2.38 (t, J = 10.6 Hz, 1H), 1.93-1.77 (m, 2H), 1.71-1.60 (m, 2H), 0.99-0.92 (m, 1H), 0.87 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 162.09 (d, $^{1}J_{C-F}$ = 245.3 Hz), 131.75, 129.92 (d, $^{3}J_{C-F}$ = 7.6 Hz), 129.30 (d, $^{4}J_{C-F}$ = 2.8 Hz), 126.03, 121.62, 121.51, 118.52, 116.06 (d, $^{2}J_{C-F}$ = 21.0 Hz), 114.61, 111.12, 106.71, 63.05, 55.29, 33.35, 32.02, 26.54, 19.78 ppm.



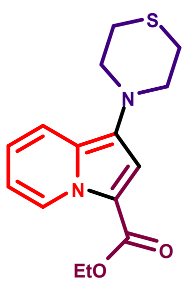
4adb

4-(3-p-Tolylindolizin-1-yl)thiomorpholine (**4adb**) [Ref 1]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.95 (d, J = 6.8 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 7.6 Hz, 2H), 6.68 (s, 1H), 6.35 (t, J = 7.6 Hz, 1H), 6.05 (t, J = 7.6 Hz, 1H), 3.14 (t, J = 4.5 Hz, 4H), 2.60 (t, J = 4.5 Hz, 4H), 2.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 136.67, 131.46, 130.19, 129.90, 126.20, 123.17, 121.90, 118.08, 114.94, 111.02, 107.04, 56.63, 28.84, 21.18 ppm.



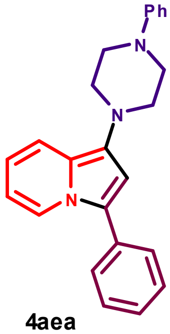
4add

4-(3-(4-Fluorophenyl)indolizin-1-yl)thiomorpholine (**4add**) [Ref 1]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.71 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.06 (dd, J = 8.3 Hz, J = 5.3 Hz, 2H), 6.83 (t, J = 8.3 Hz, 2H), 6.53 (s, 1H), 6.36 (t, J = 7.6 Hz, 1H), 6.05 (t, J = 6.8 Hz, 1H), 3.12 (t, J = 5.3 Hz, 4H), 2.60 (t, J = 4.5 Hz, 4H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 162.04 (d, $^1J_{C-F}$ = 247.2 Hz), 131.28, 129.90 (d, $^3J_{C-F}$ = 8.6 Hz), 128.93 (d, $^4J_{C-F}$ = 3.8 Hz), 126.14, 121.63, 121.51, 117.97, 116.02 (d, $^2J_{C-F}$ = 22.0 Hz), 115.10, 111.16, 107.14, 56.51, 28.74 ppm.



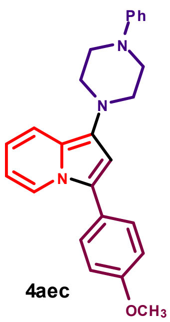
4adf

Ethyl 1-thiomorpholinoindolizine-3-carboxylate (**4adf**) [Ref 1]: White solid. m.p: 124-126 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.80 (d, J = 6.8 Hz, 1H), 7.01 (s, 1H), 7.00 (d, J = 8.3 Hz, 1H), 6.33 (t, J = 7.6 Hz, 1H), 6.16 (t, J = 6.8 Hz, 1H), 4.23 (q, J = 6.8 Hz, 2H), 3.83 (t, J = 11.4 Hz, 2H), 2.67 (t, J = 11.4 Hz, 2H), 2.57 (d, J = 11.4 Hz, 2H), 2.08 (d, J = 11.4 Hz, 2H), 1.13 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 164.34, 135.31, 121.55, 119.93, 117.72, 113.37, 111.12, 100.10, 59.84, 51.71, 29.00, 14.25 ppm.



4aea

3-Phenyl-1-(4-phenylpiperazin-1-yl)indolizine (**4aea**) [Ref 1]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.50-7.44 (m, 2H), 7.41-7.37 (m, 4H), 7.33 (d, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 3H), 6.93 (d, J = 7.6 Hz, 2H), 6.80 (t, J = 6.8 Hz, 1H), 6.65 (s, 1H), 3.33 (t, J = 4.5 Hz, 4H), 3.26-3.07 (m, 4H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 152.11, 133.03, 130.41, 129.34, 129.14, 128.92, 126.97, 126.19, 122.98, 121.83, 119.80, 118.22, 116.54, 114.95, 111.09, 106.56, 54.23, 49.88 ppm.

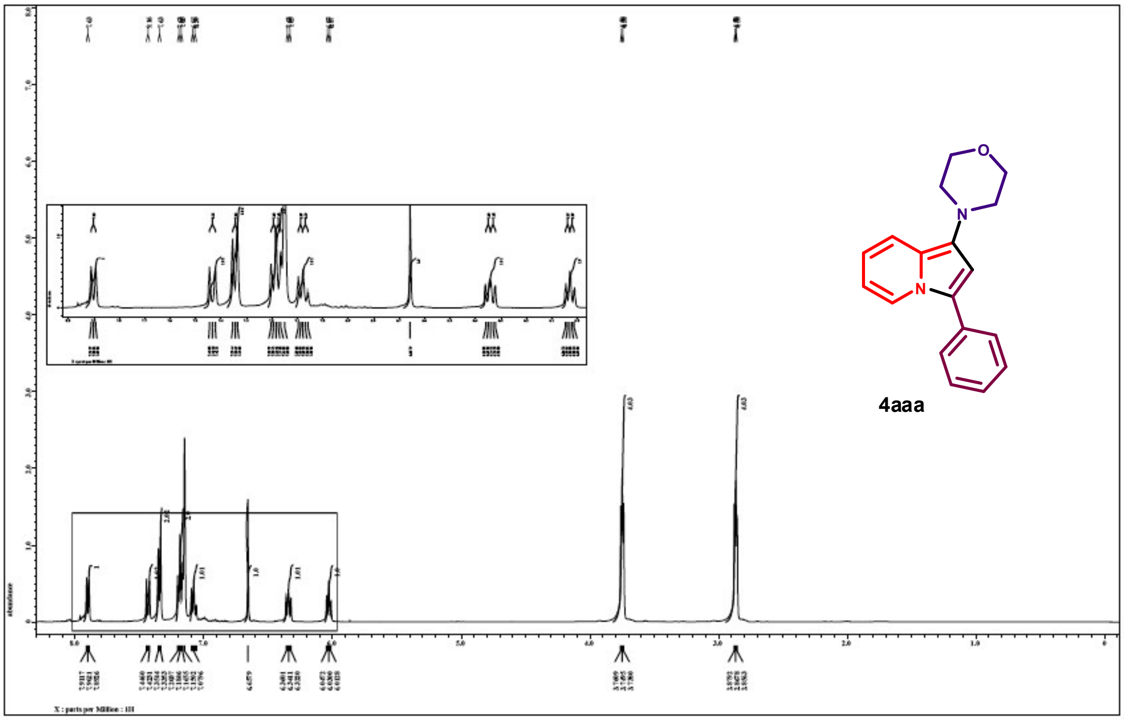


4aec

3-(4-Methoxyphenyl)-1-(4-phenylpiperazin-1-yl)indolizine **(4aec)** [Ref 1]: Yellow oil. ^{1}H NMR (400 MHz, C_6D_6) δ = 7.92 (d, J = 7.3 Hz, 1H), 7.55 (d, J = 8.7 Hz, 1H), 7.30 (d, J = 8.7 Hz, 2H), 7.25 (t, J = 7.3 Hz, 2H), 6.88 (d, J = 8.2 Hz, 3H), 6.83 (d, J = 8.7 Hz, 2H), 6.74 (s, 1H), 6.39 (t, J = 7.3 Hz, 1H), 6.10 (t, J = 6.8 Hz, 1H), 3.35 (s, 3H), 3.18-3.15 (m, 4H), 3.09-3.07 (m, 4H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 159.22, 152.12, 130.17, 129.79, 129.34, 125.63, 125.43, 122.88, 121.77, 119.75, 118.22, 116.52, 114.69, 114.52, 110.89, 106.12, 54.85, 54.30, 49.88 ppm.

References

1. U. C. RaJesh, G. Purohit, and D. S. Rawat, *ACS Sustainable Chem. Eng.* **2015, 3**, 2397.
2. S. Mishra, A. K. Bagdi, M. Ghosh, S. Sinha and A. HaJra, *RSC Adv.* **2014**, 4, 6672.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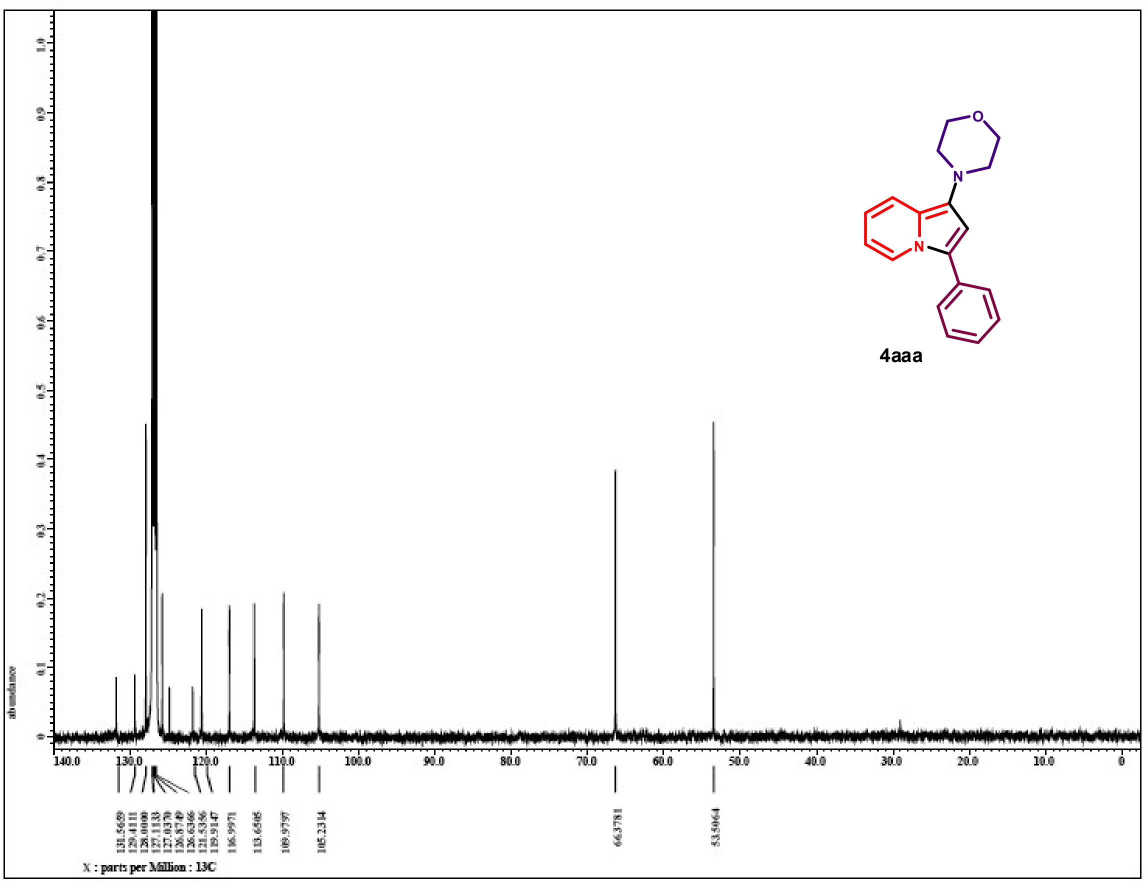
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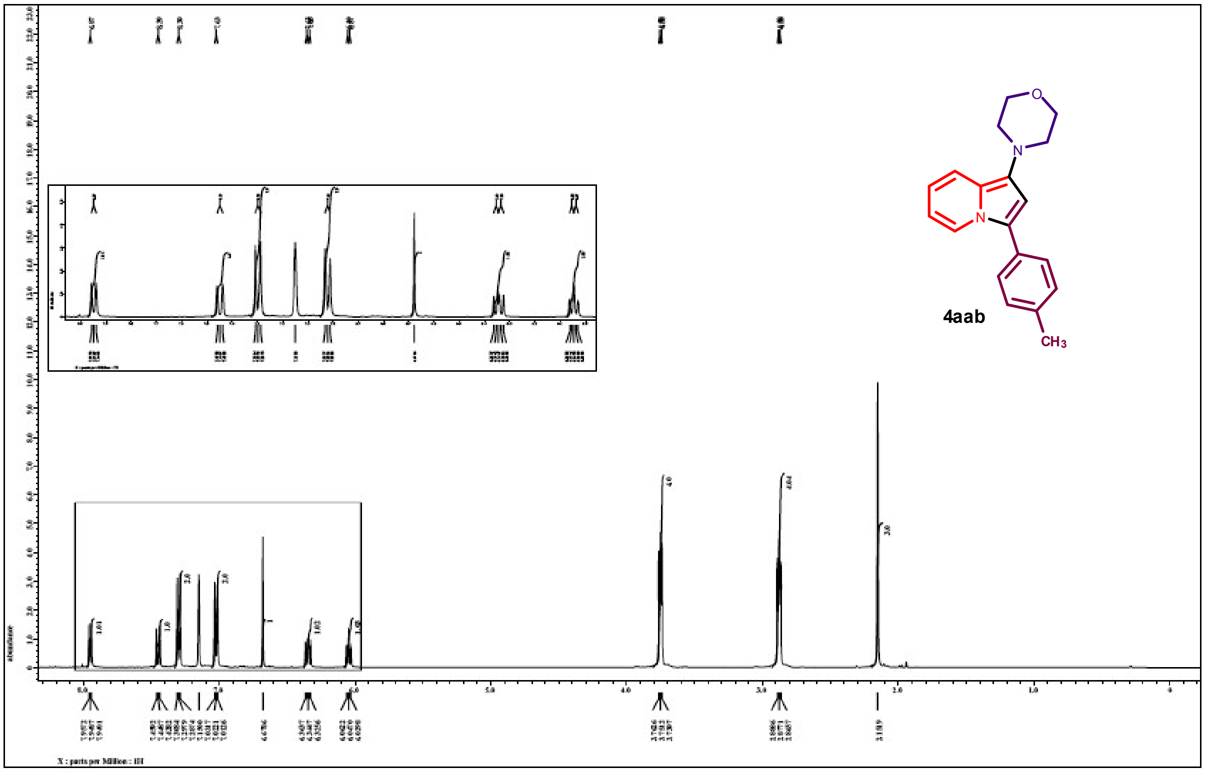
4aaa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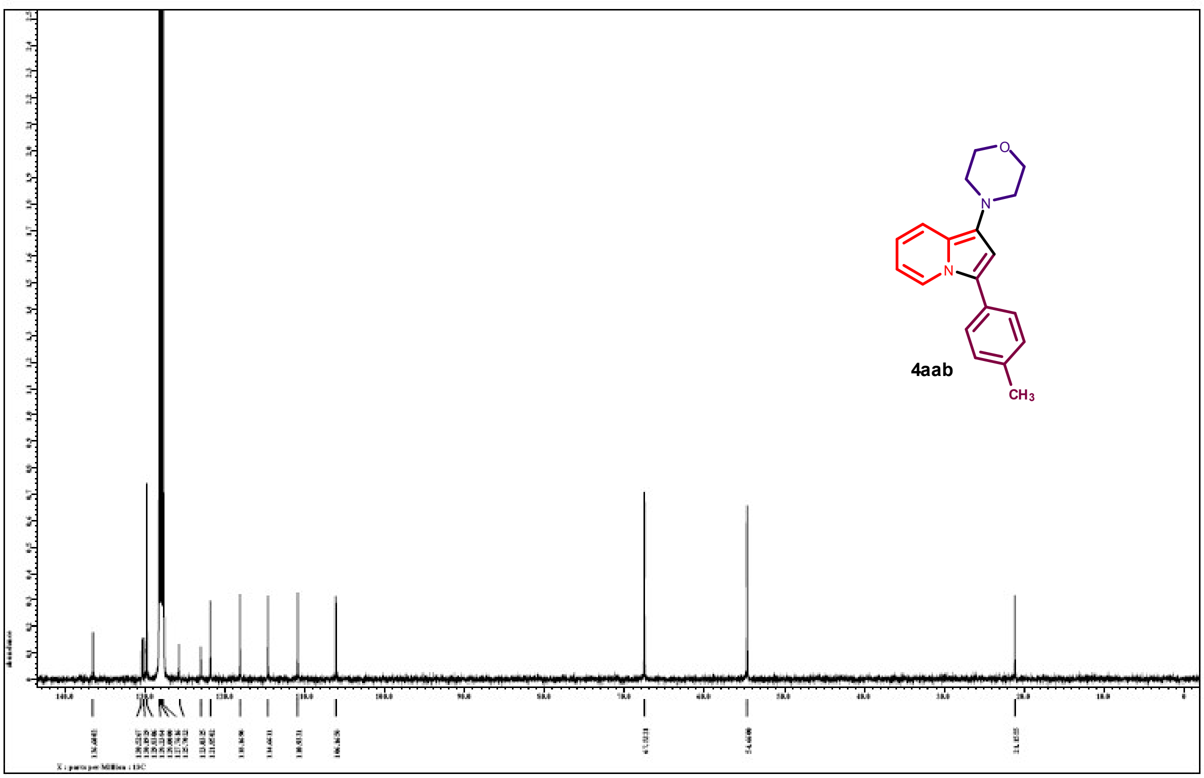
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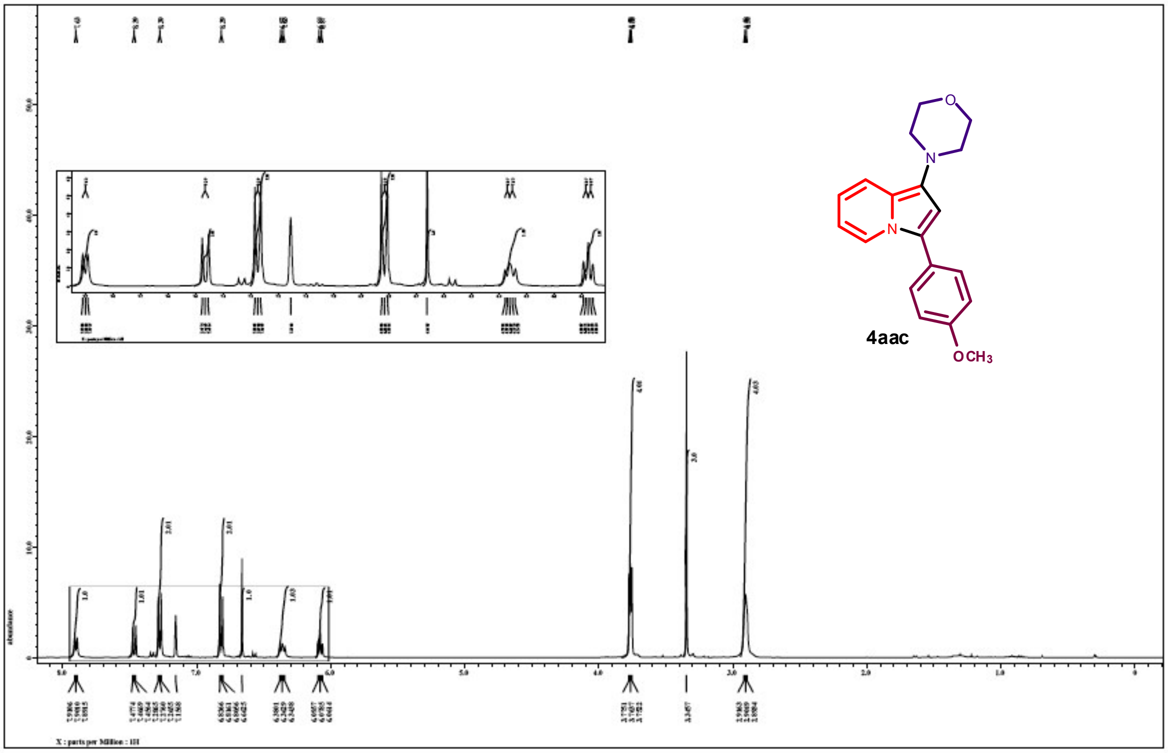
4aac
OCH3
X : parts per Million : 1H
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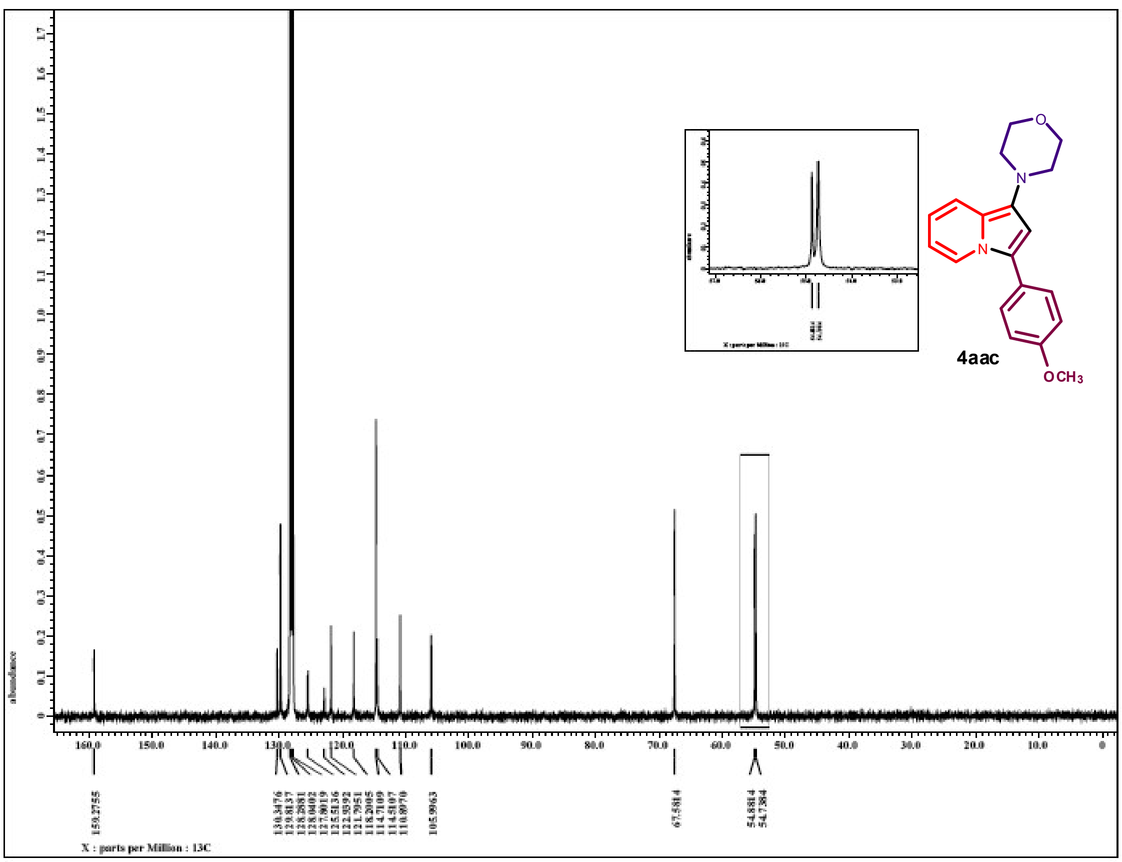
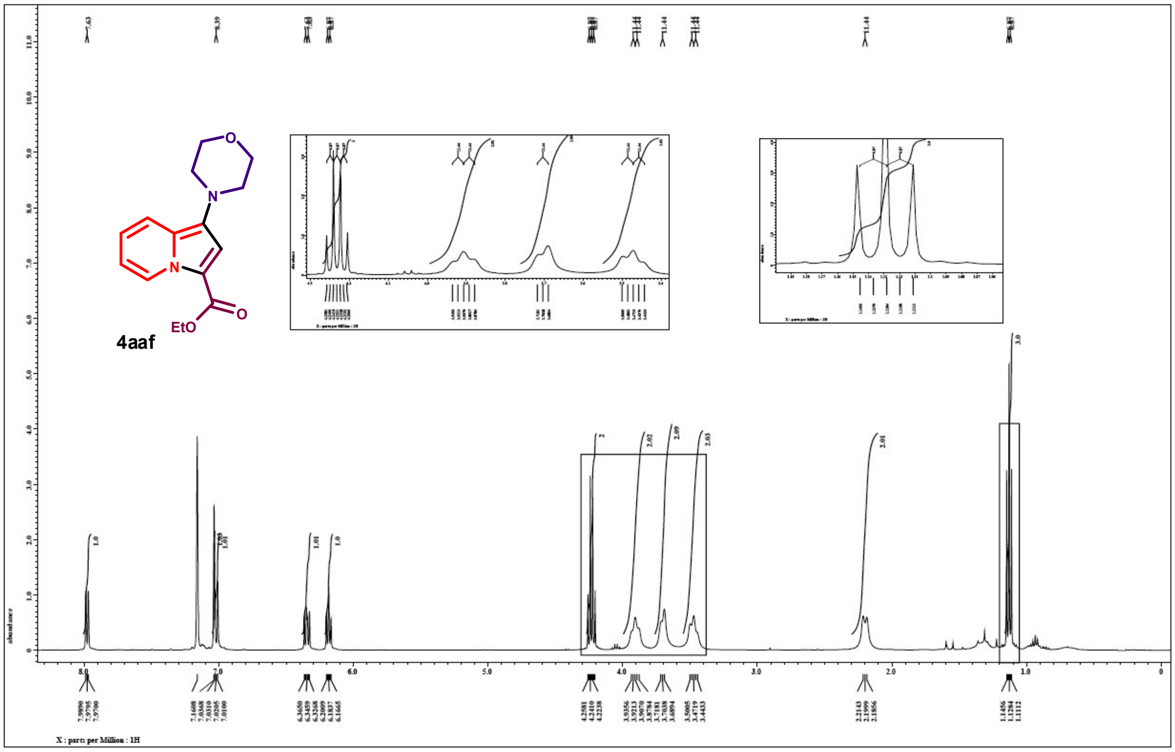
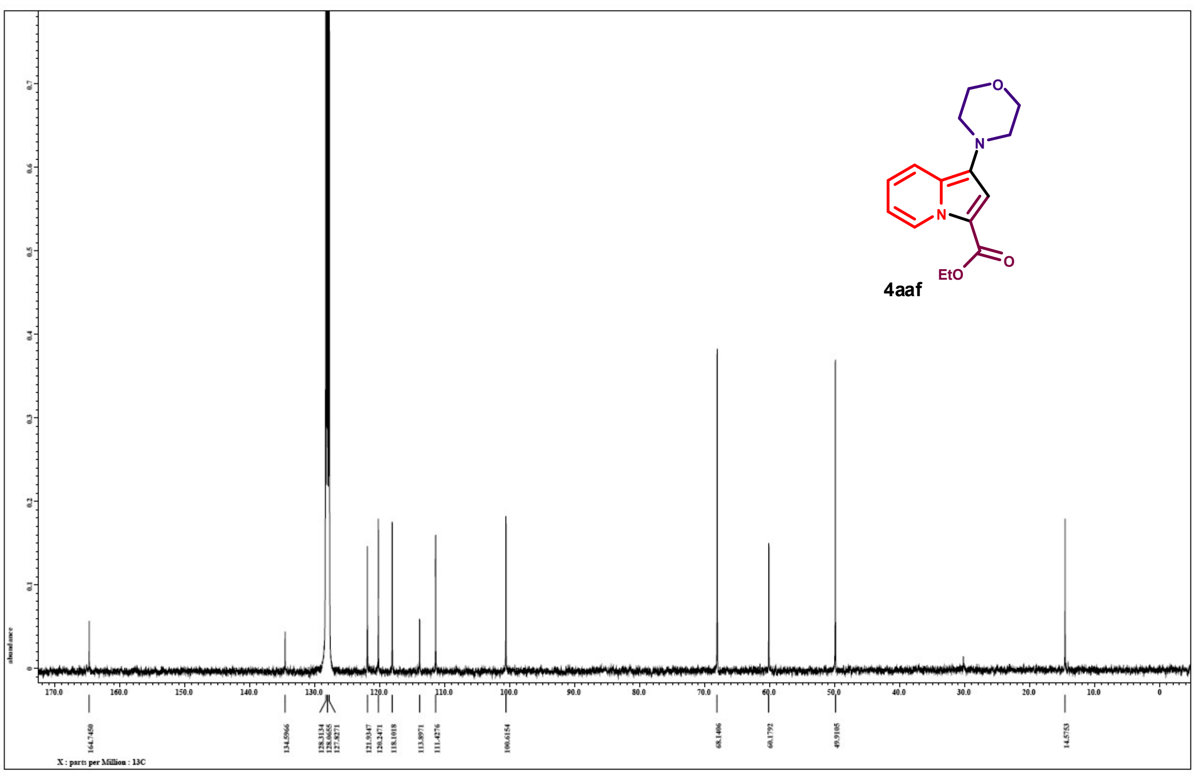
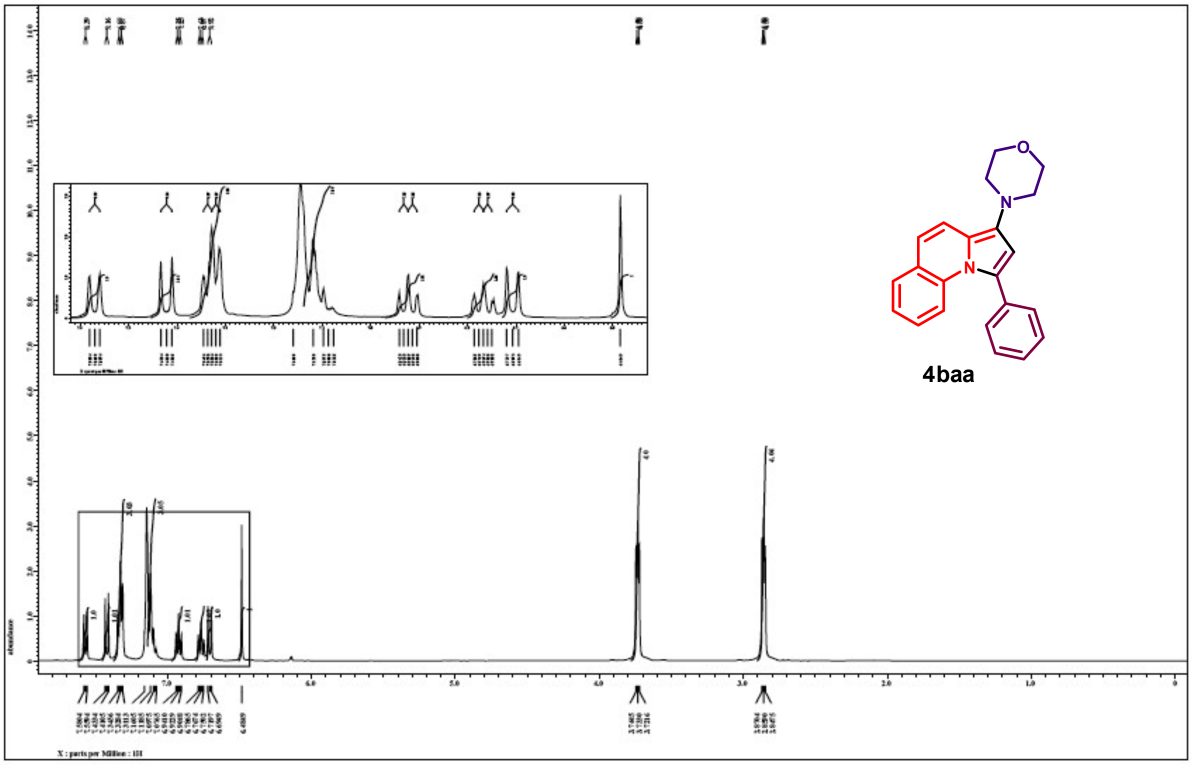
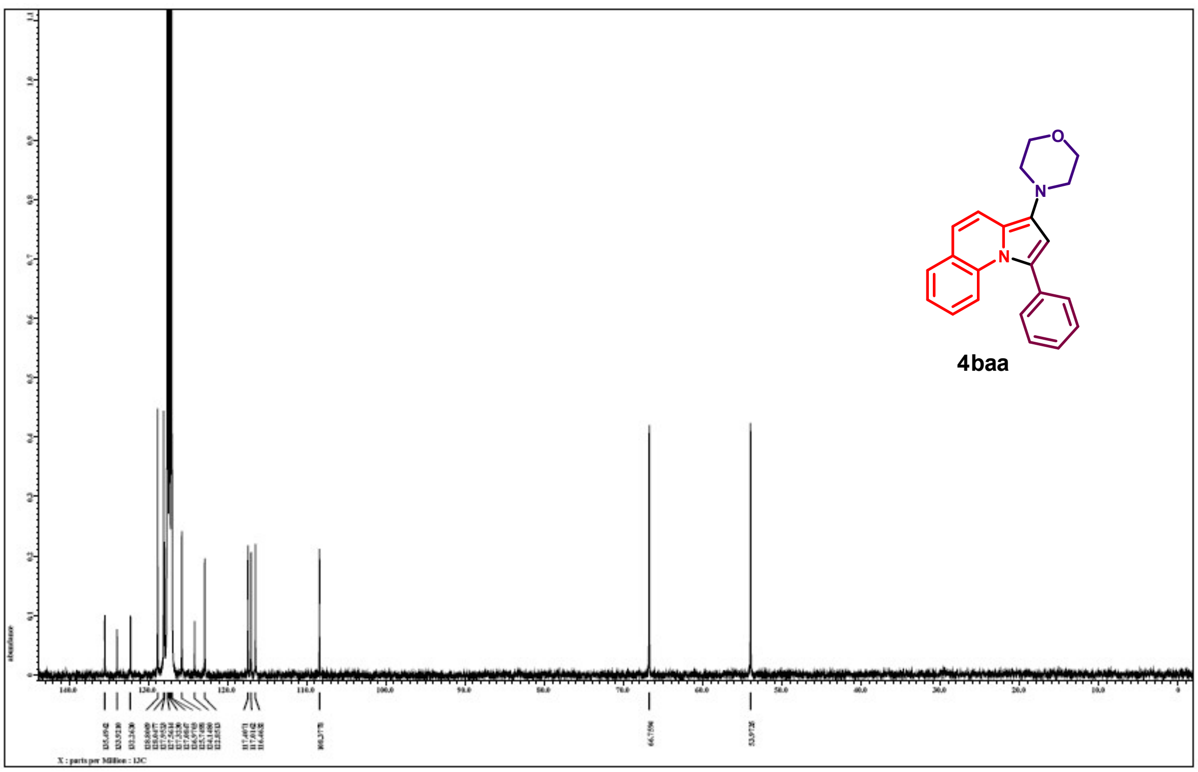
2.9089
2.8984

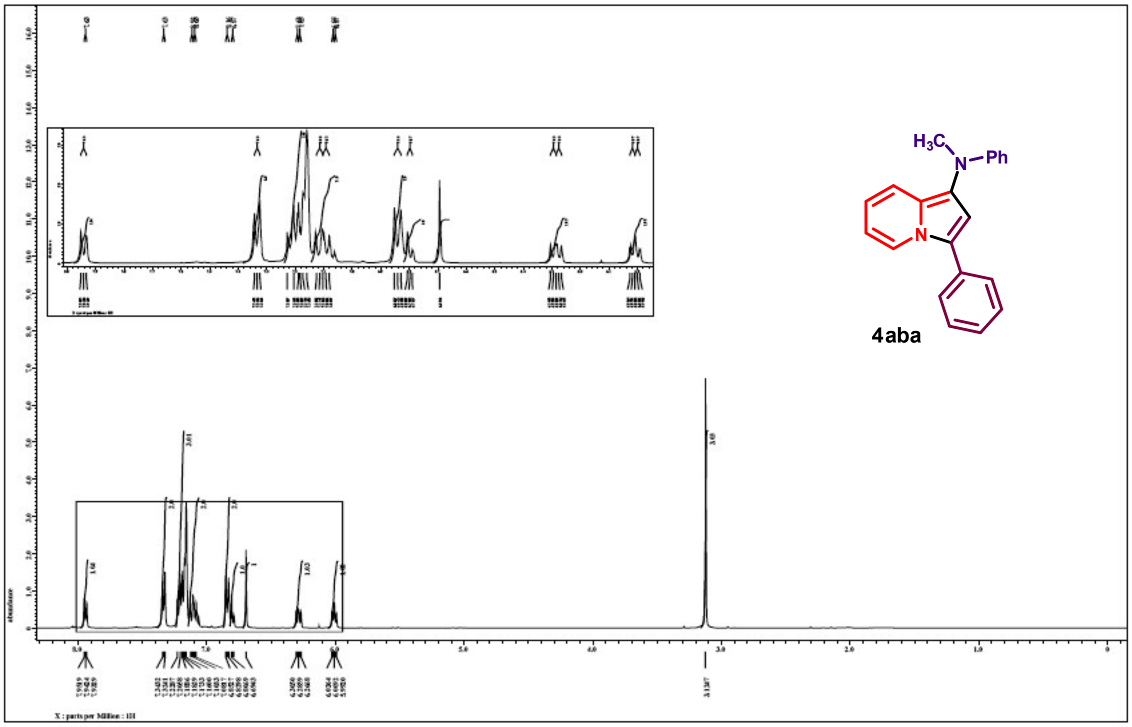

4aac
OCH3
X : parts per Million : 13C
abundance
159.2755
130.3476
129.8137
128.2581
128.0402
127.0019
125.5136
122.9392
121.7951
118.2005
114.7009
114.5107
110.8970
105.9963
67.5814
54.8814
54.7384


4aaf
EtO
X : parts per Million : 1H

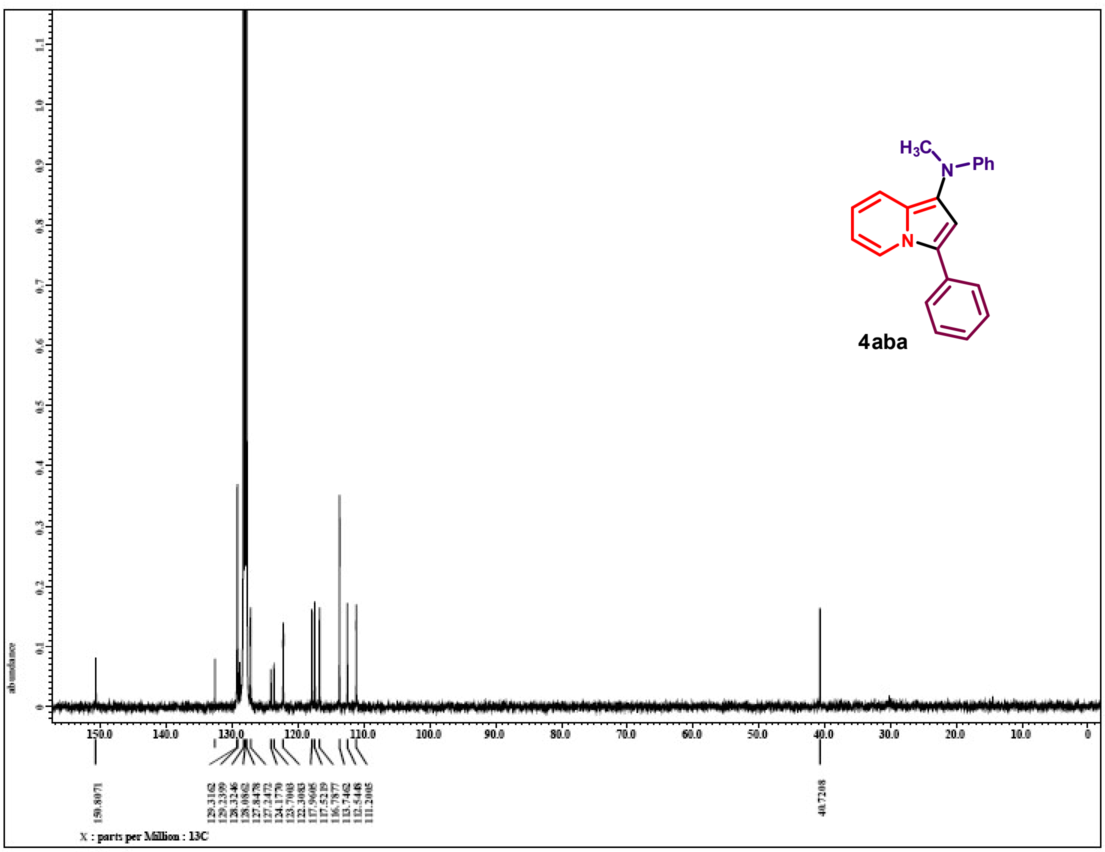

4aaf
EtO
164.7450
134.5966
128.3134
128.0655
127.8271
121.9347
120.2471
118.1018
113.8971
111.4276
100.6154
68.1406
60.1792
49.9105
14.5753
X : parts per Million : 13C


4baa
X : parts per Million : 1H

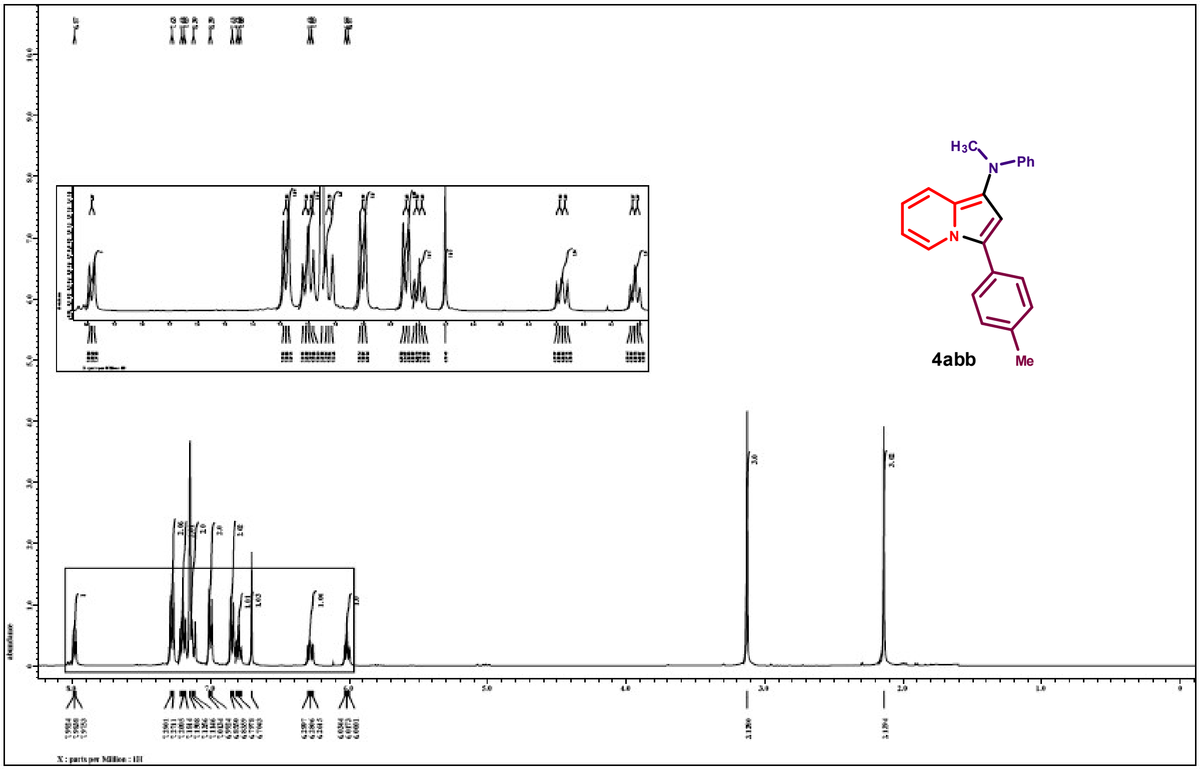

4baa
X : parts per Million : 13C



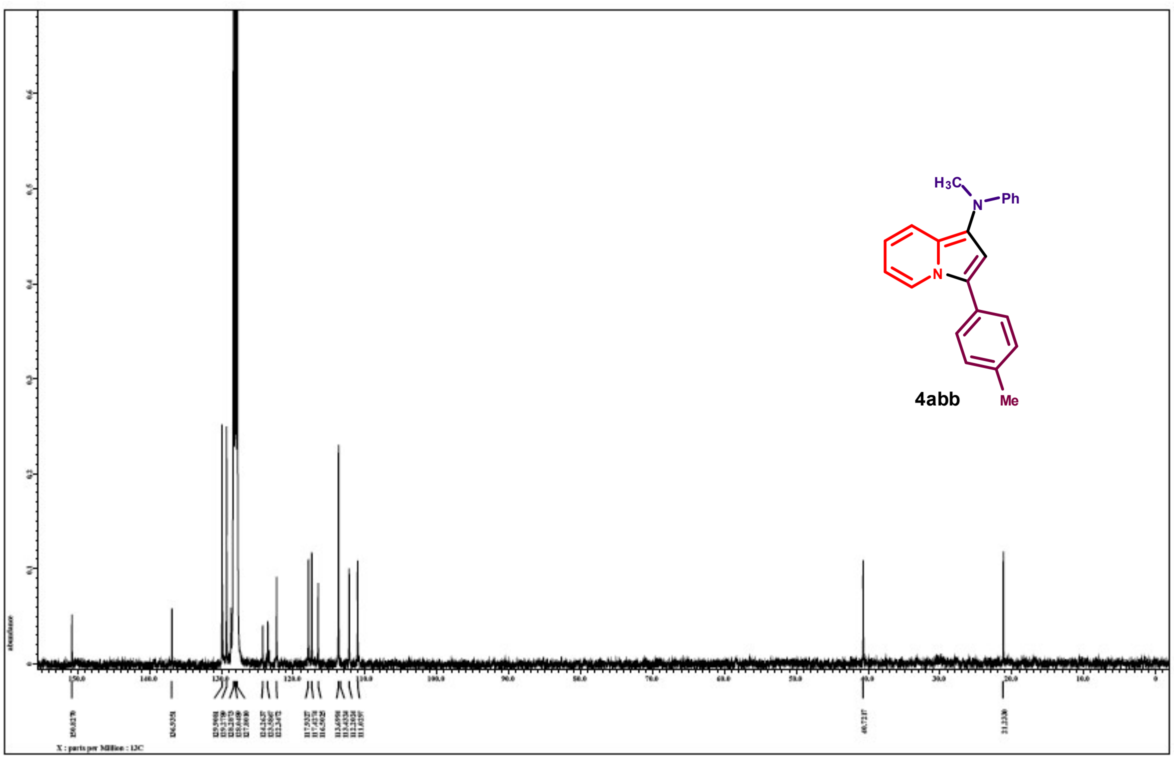
H3C
N
Ph
N
4aba
X : parts per Million : 1H
abundance



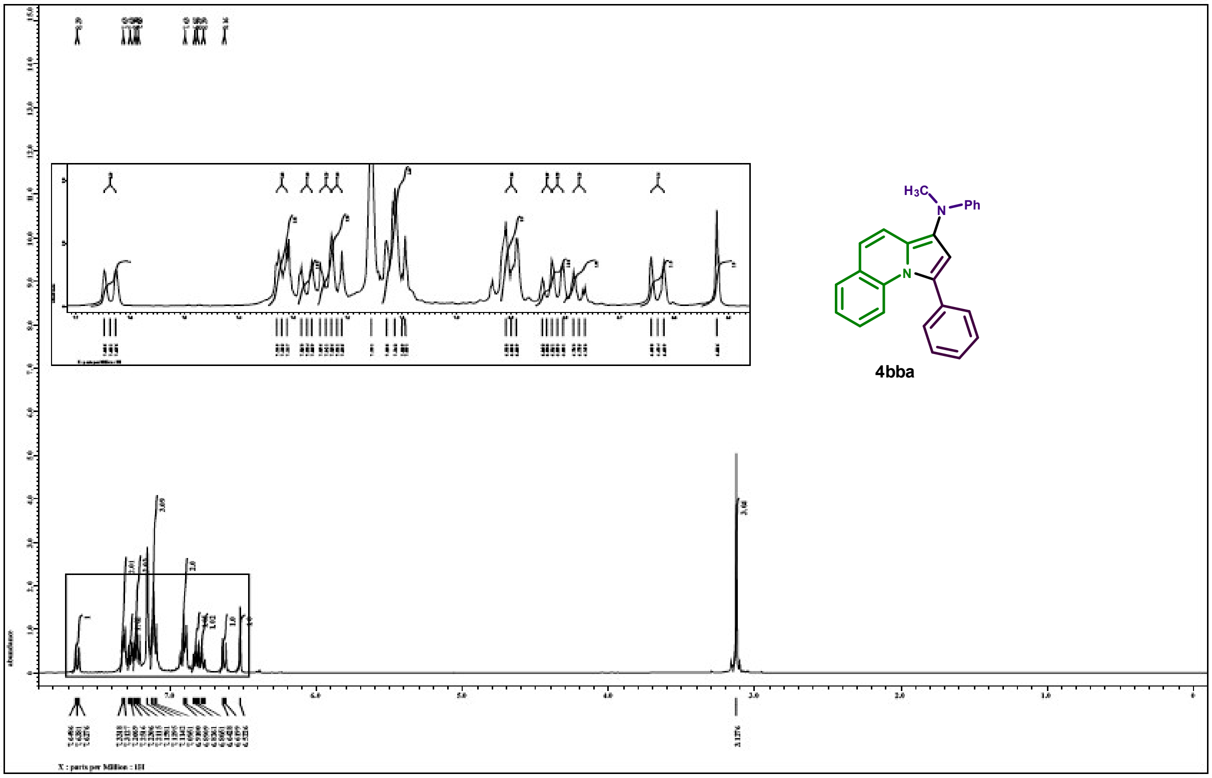
H3C
N
Ph
N
4aba
150.8071
129.3162
129.2399
128.3246
128.0862
127.8478
127.2472
124.1770
123.7083
122.3083
117.9605
117.5219
116.7877
113.7482
112.5448
111.2085
40.7208
X : parts per Million : 13C
abundance



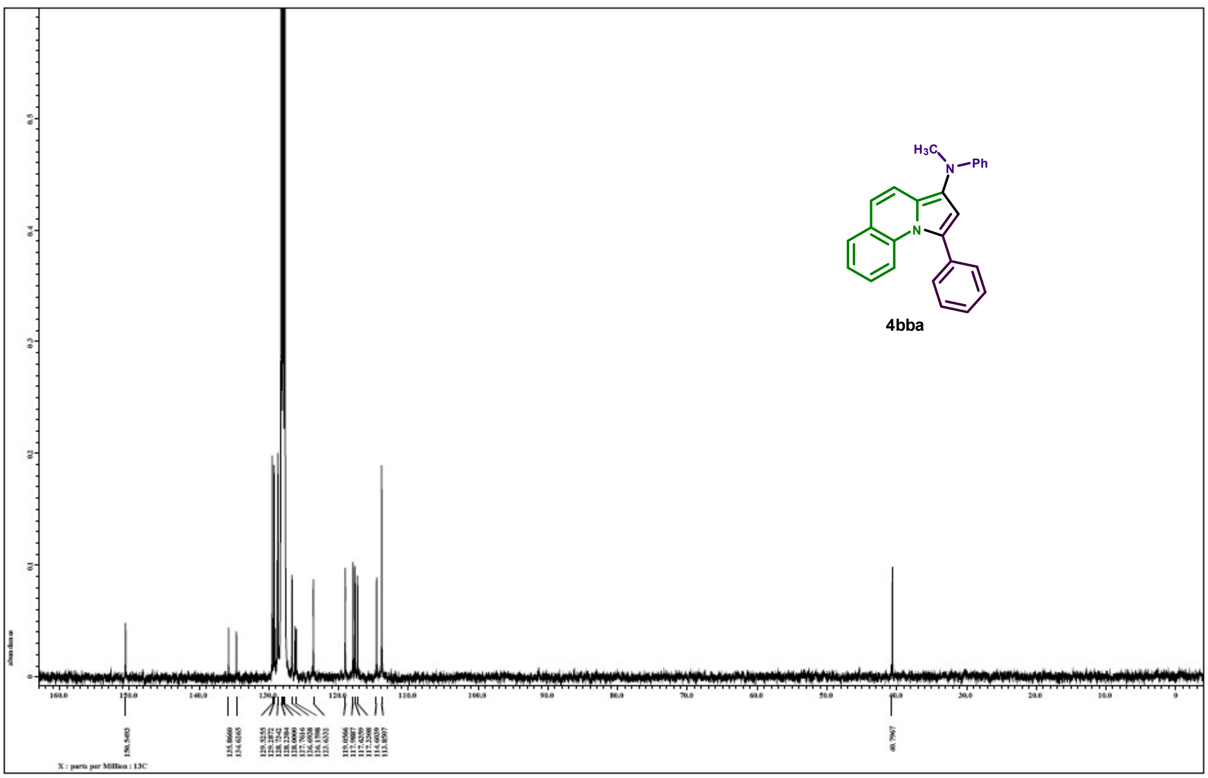
H3C
N
Ph
N
4abb
Me
X : parts per Million : 1H



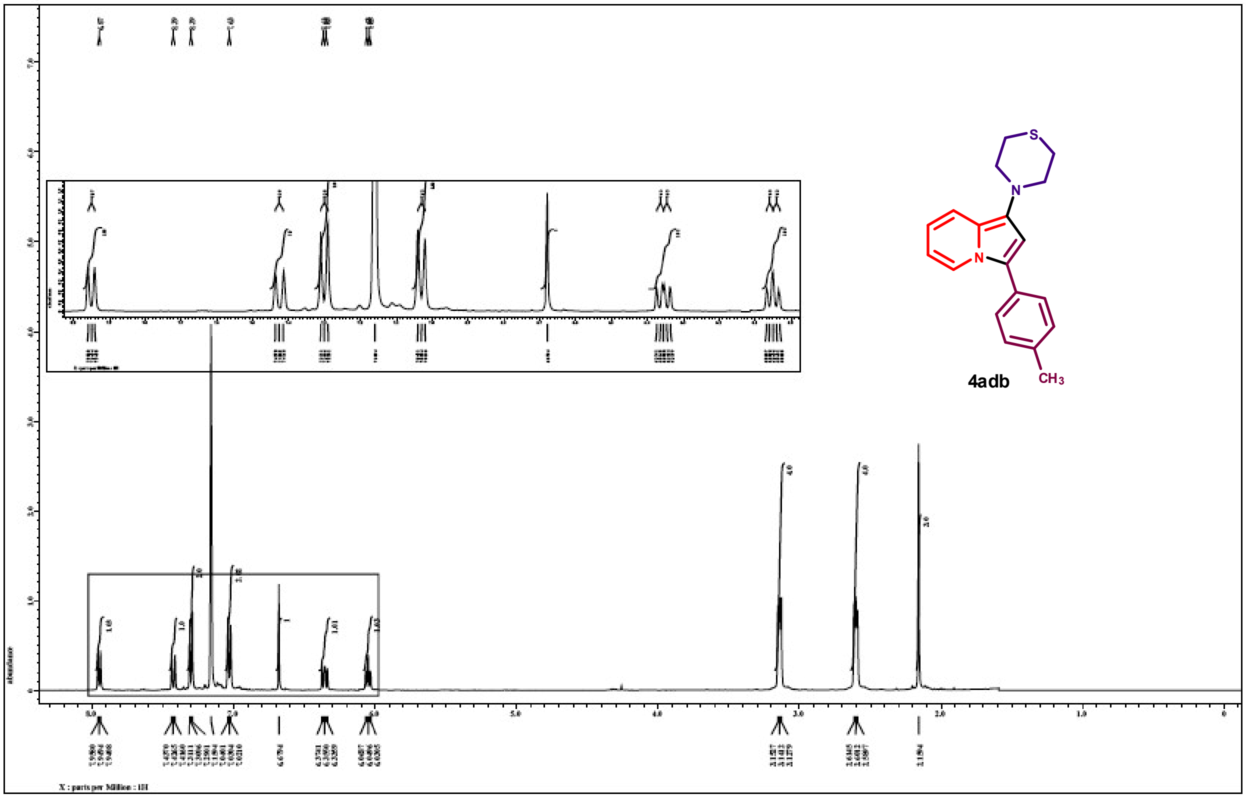
H3C
N
Ph
N
4abb
Me
X : parts per Million : 13C

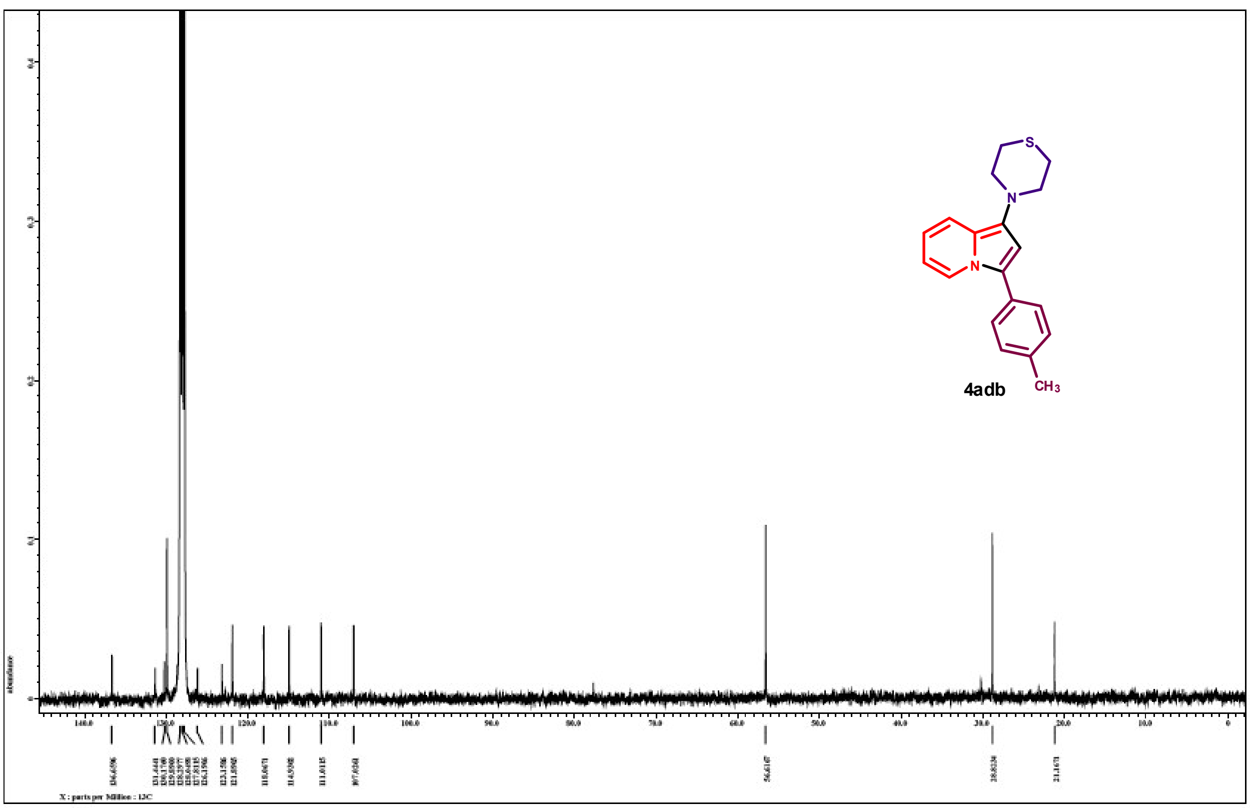

H3C
N
Ph
N
X : parts per Million : 1H
abundance
3.1276
3.68
3.09
2.0
1.02
1.0

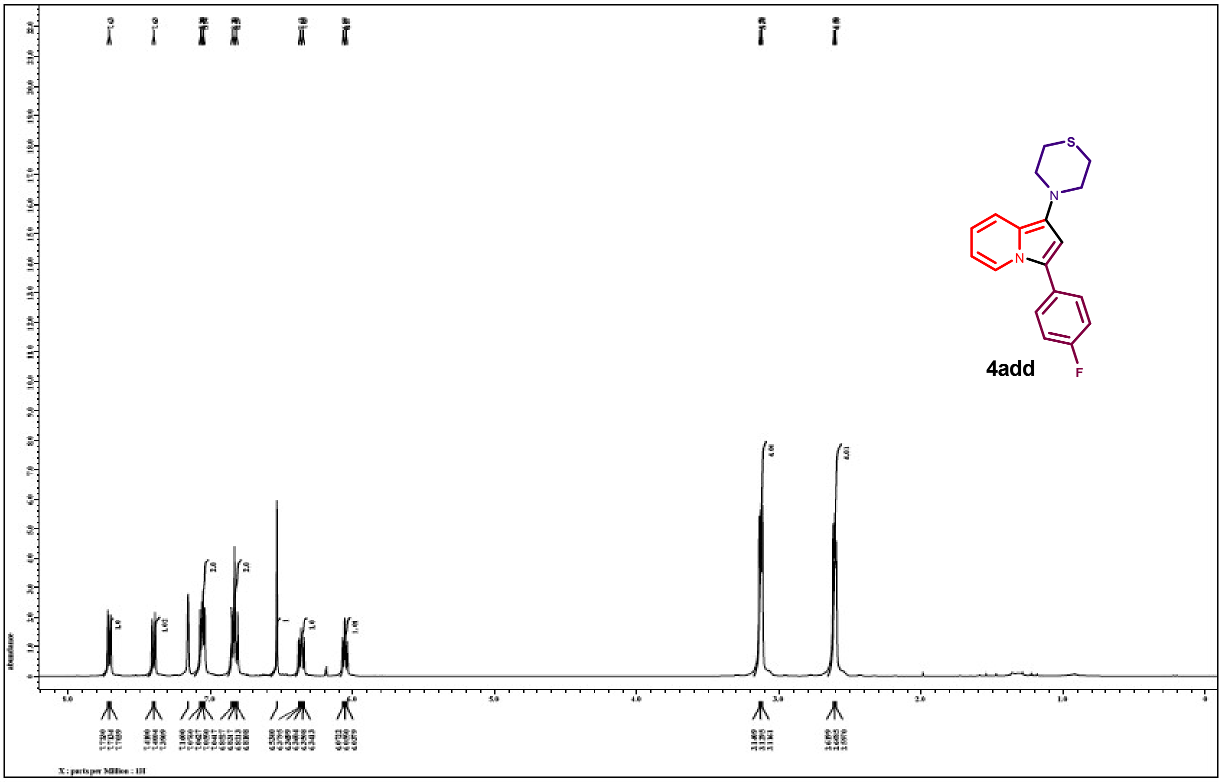
4bba

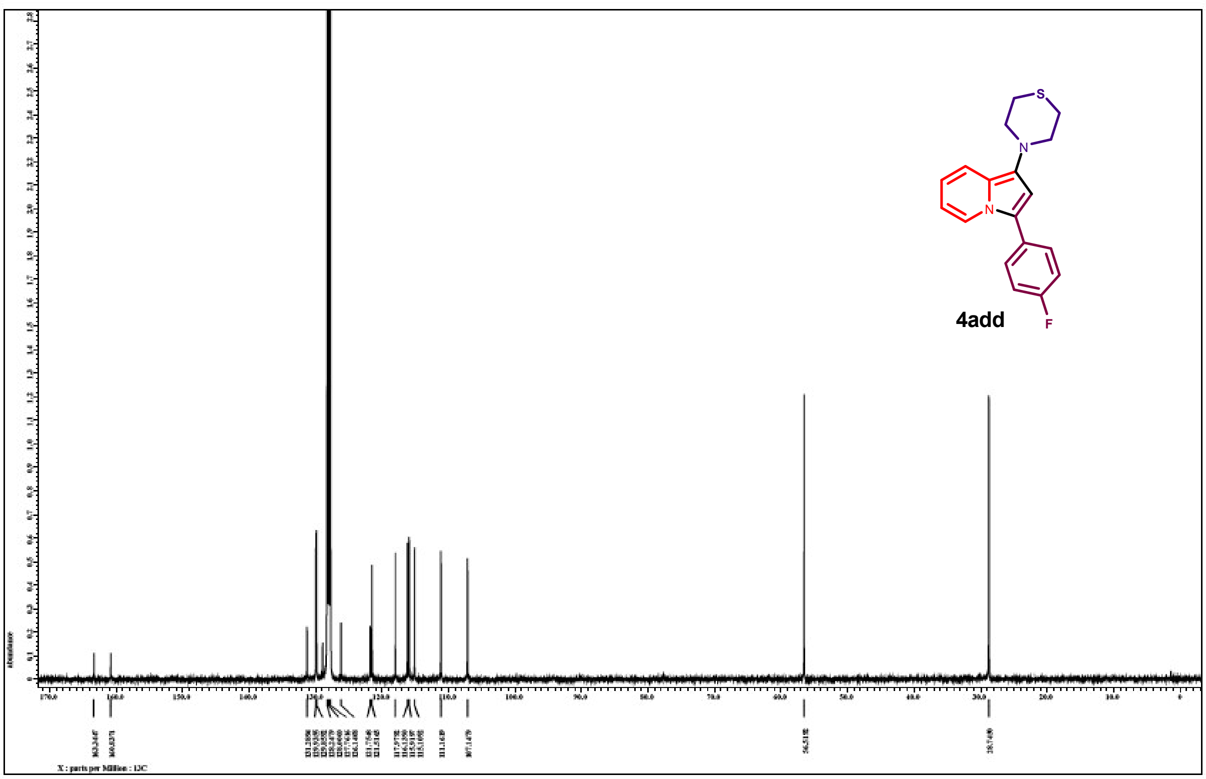

H3C
N
Ph
N
X : parts per Million : 13C
abundance
150.5403
135.8660
134.6265
40.7967

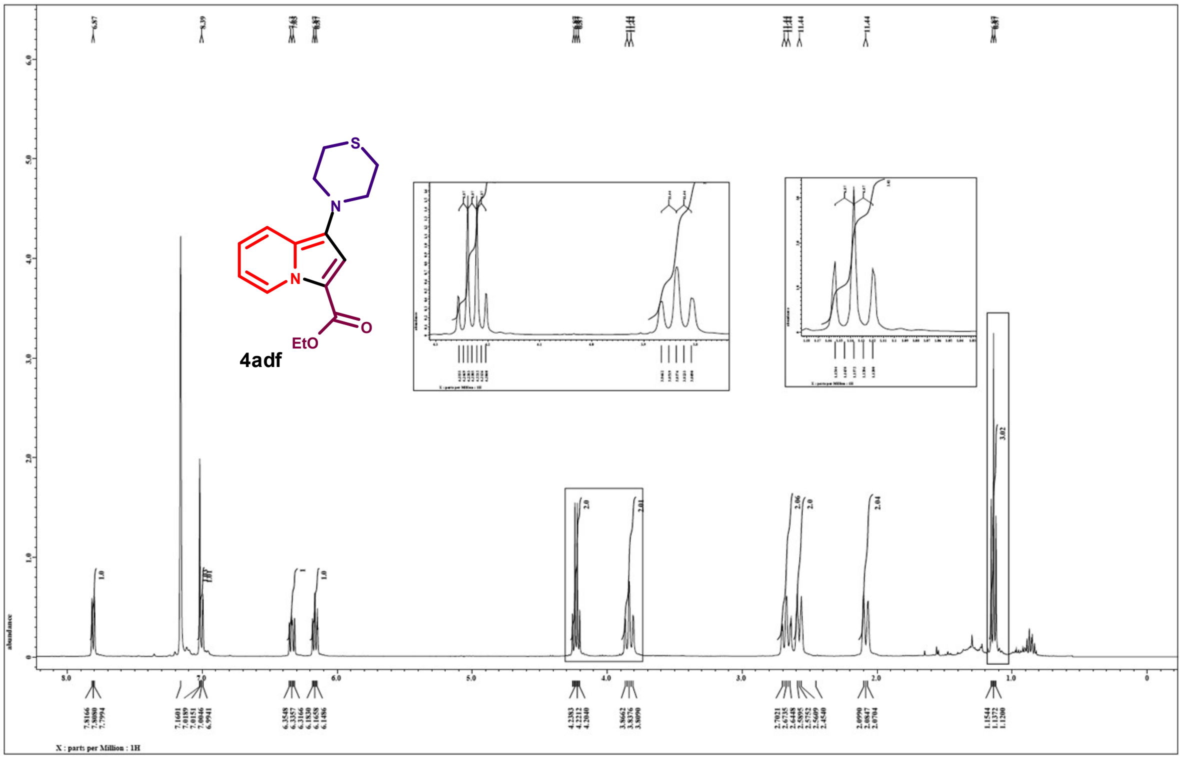
4bba


X : parts per Million : 1H
4adb

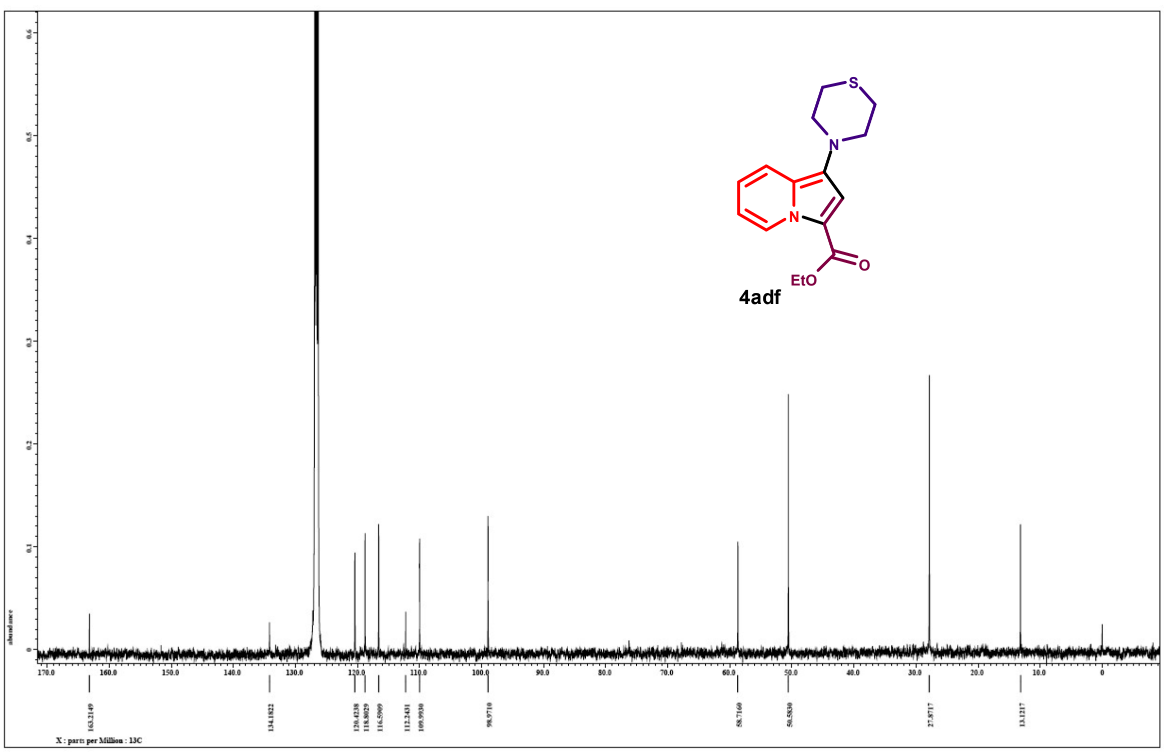

X : parts per Million : 13C
4adb


4add
abundance
X : parts per Million : 1H

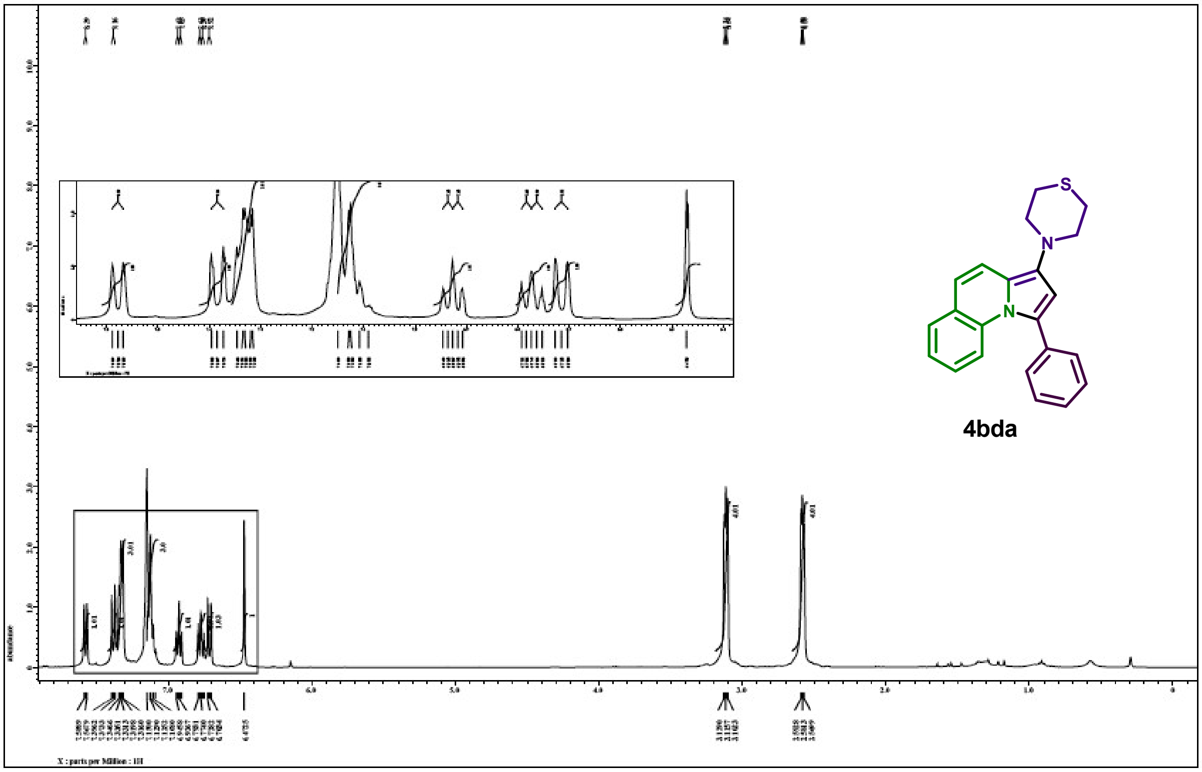

4add
abundance
X : parts per Million : 13C

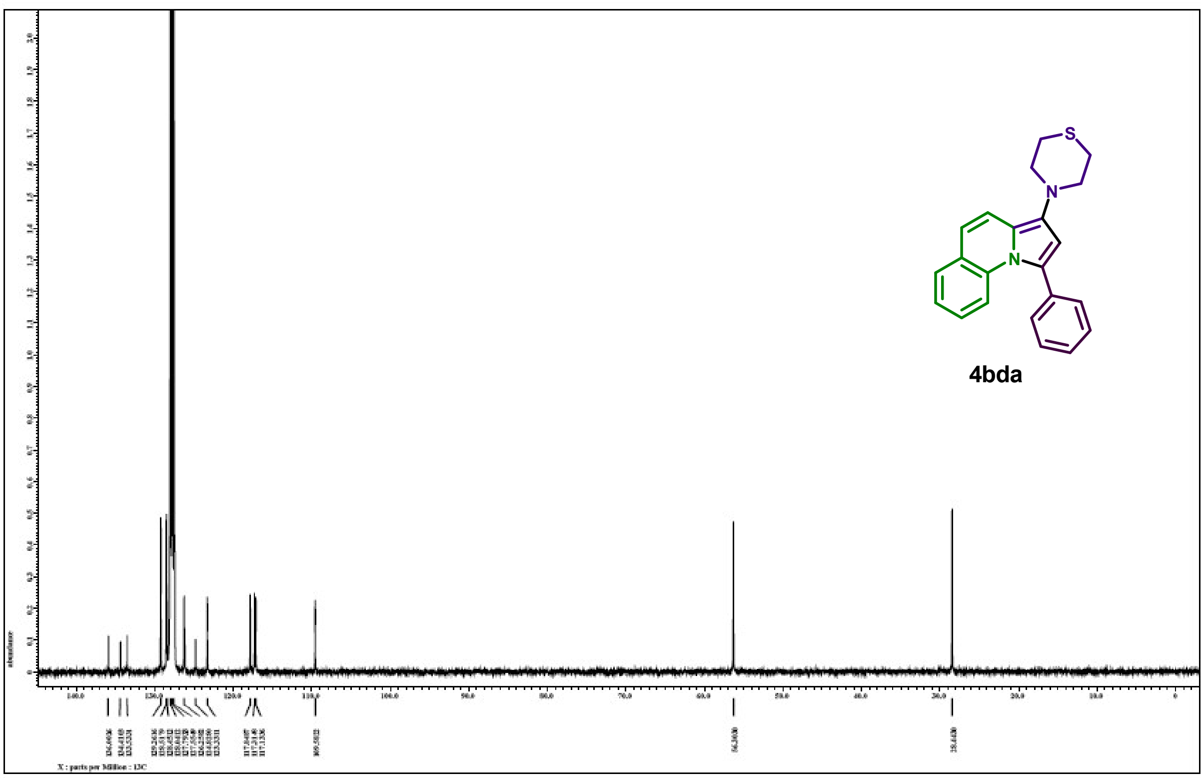


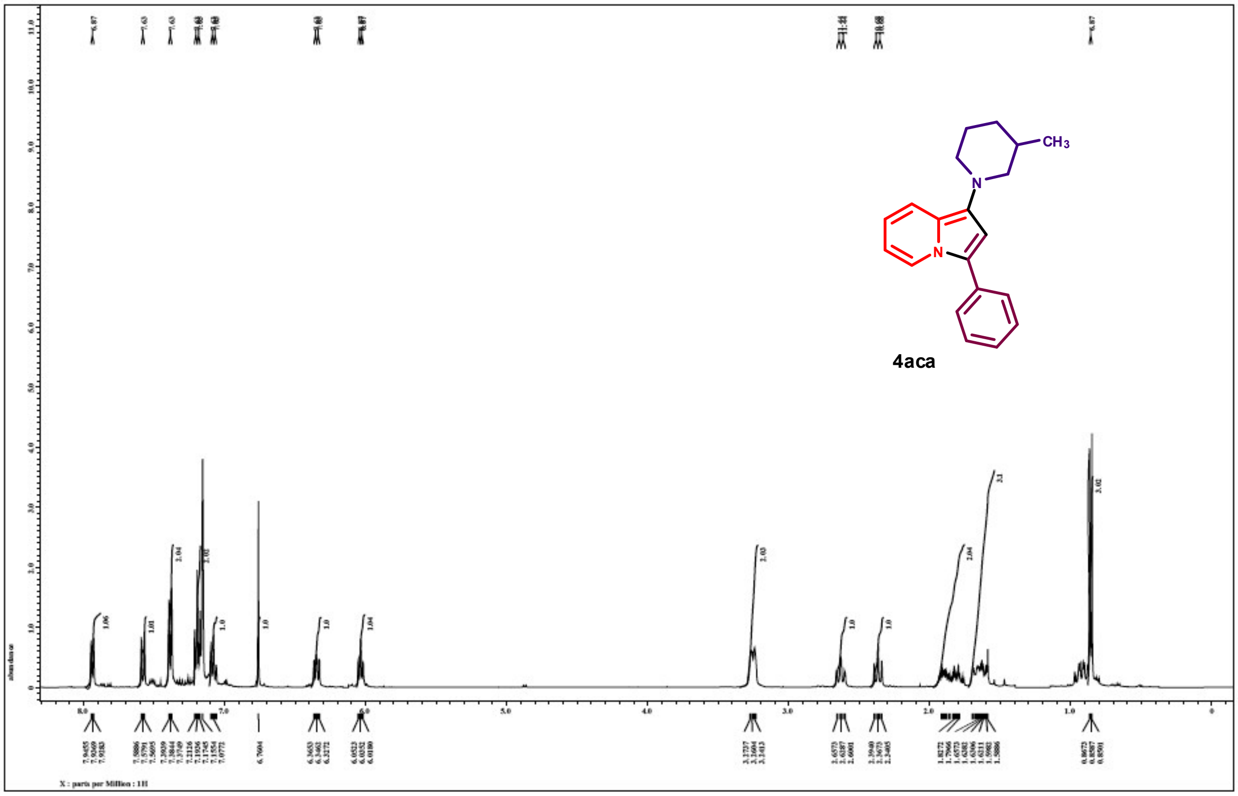
4adf
EtO
O
N
S
X : parts per Million : 1H
abundance

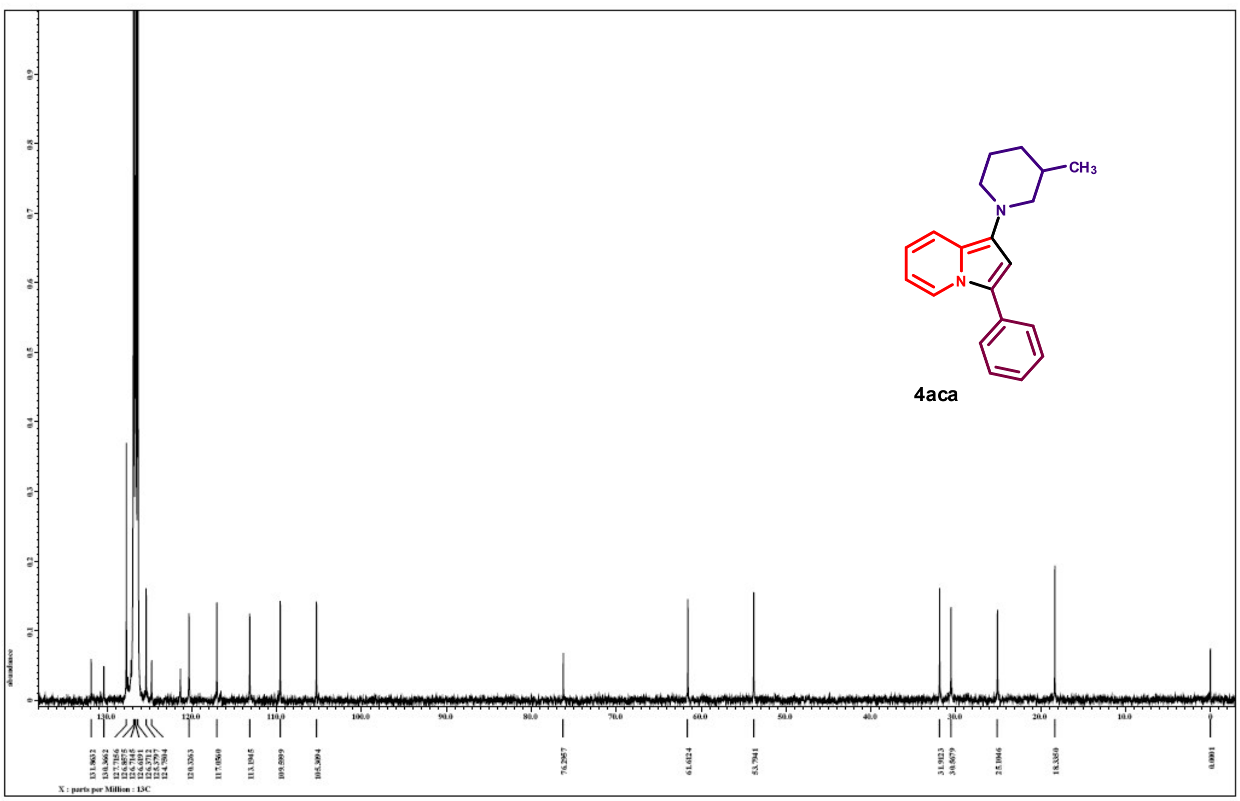


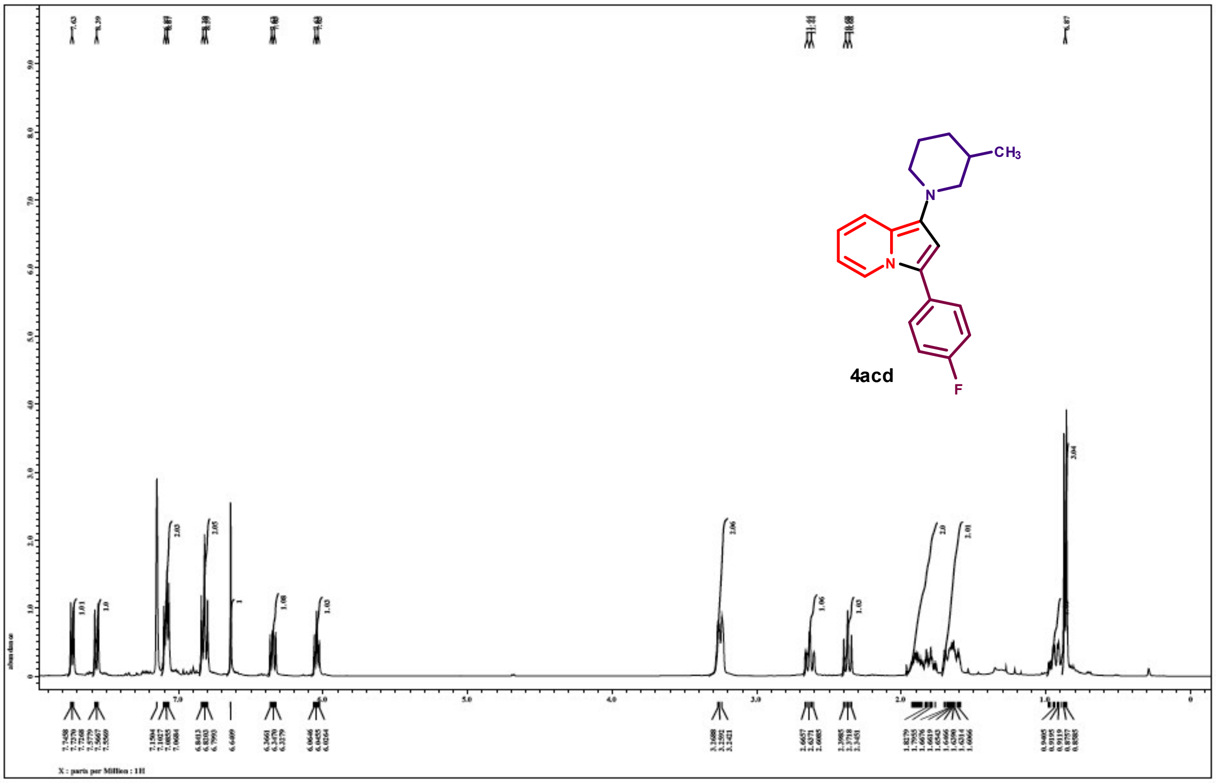
4adf
EtO
O
N
S
X : parts per Million : 13C
abundance
163.2149
134.1822
120.4238
118.8029
116.5909
112.2431
109.9930
98.9710
58.7160
50.5830
27.8717
13.1217

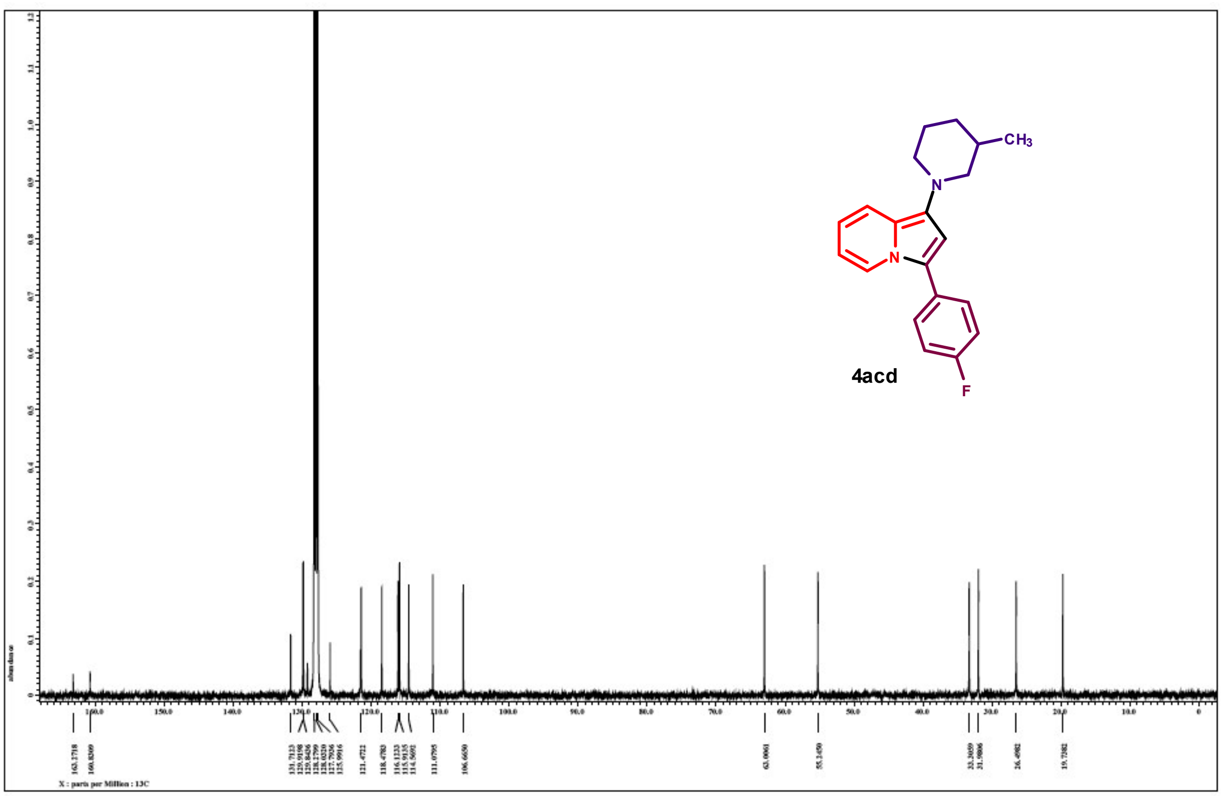

4bda
X : parts per Million : 1H

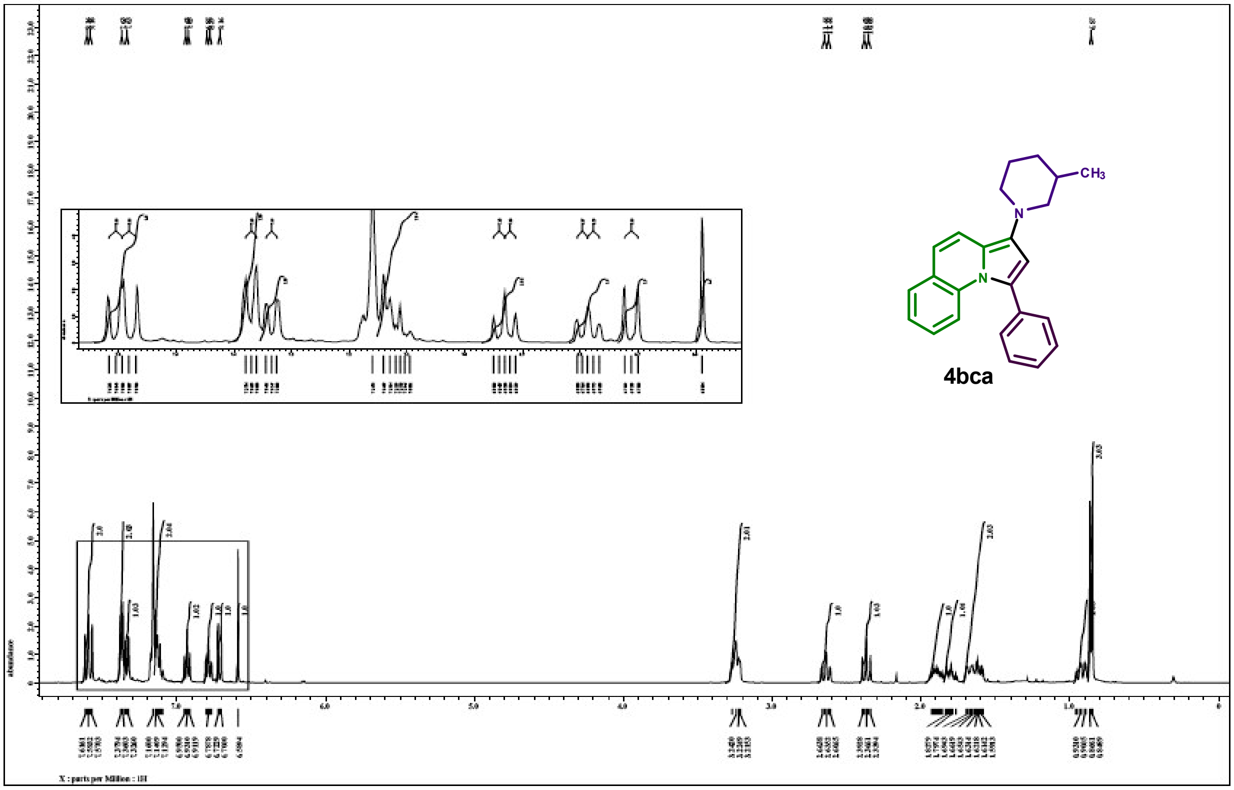

4bda
X : parts per Million : 13C

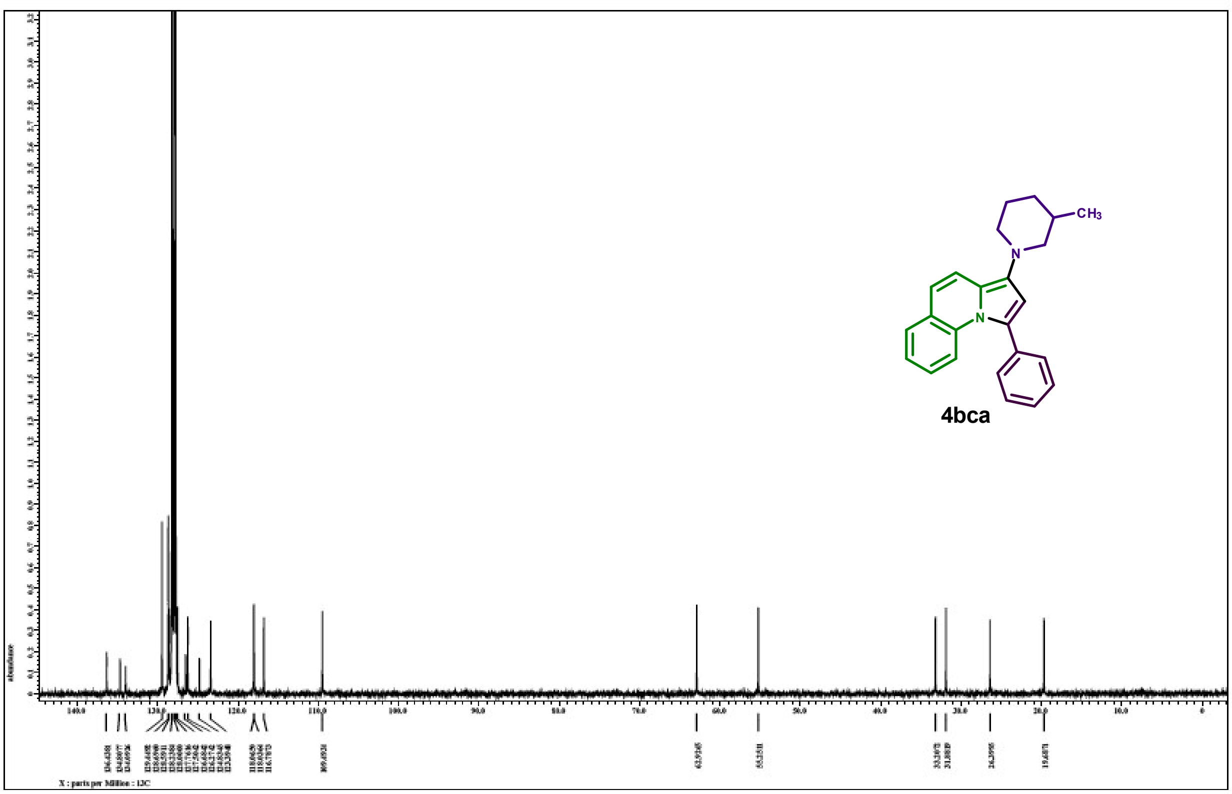


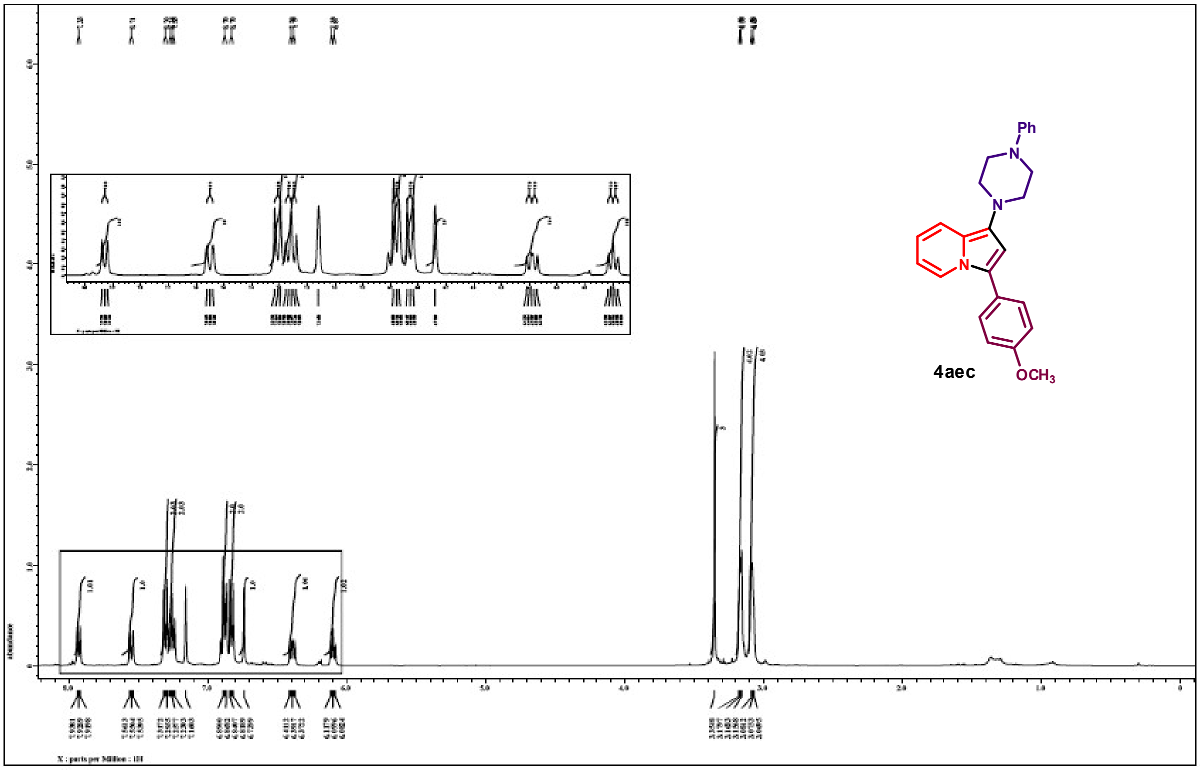


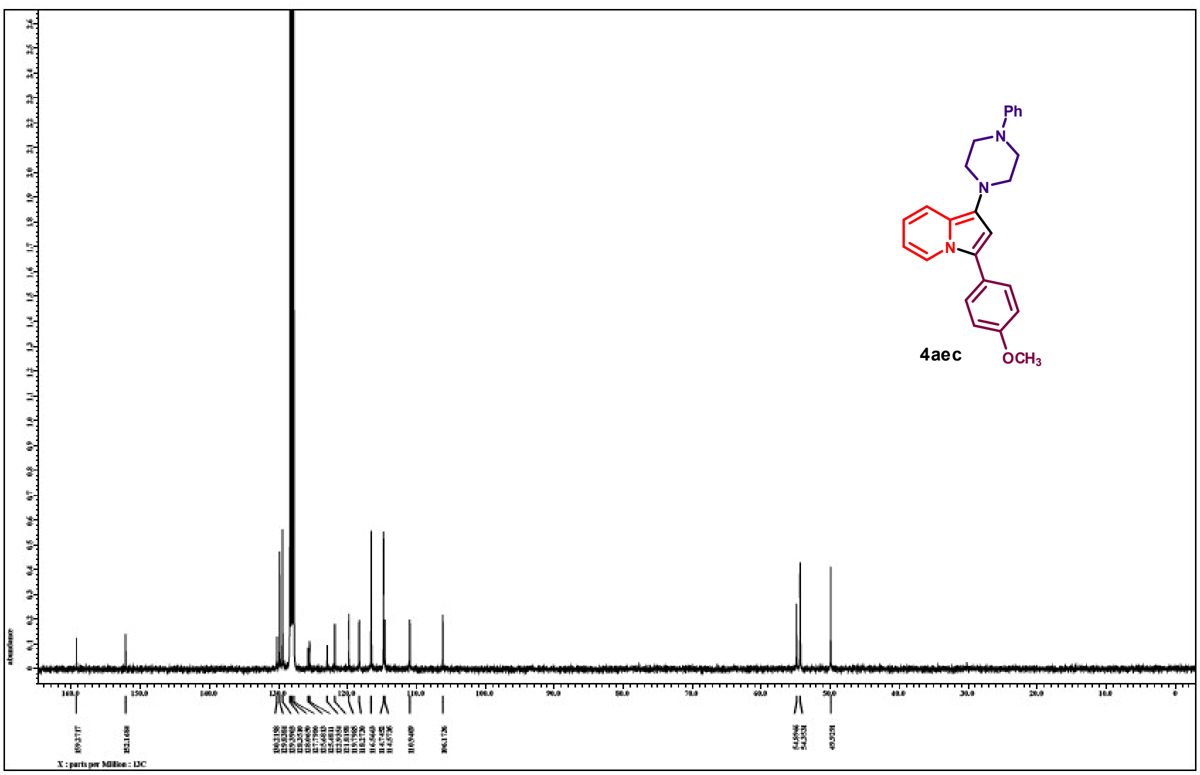

4acd
X : parts per Million : 1H

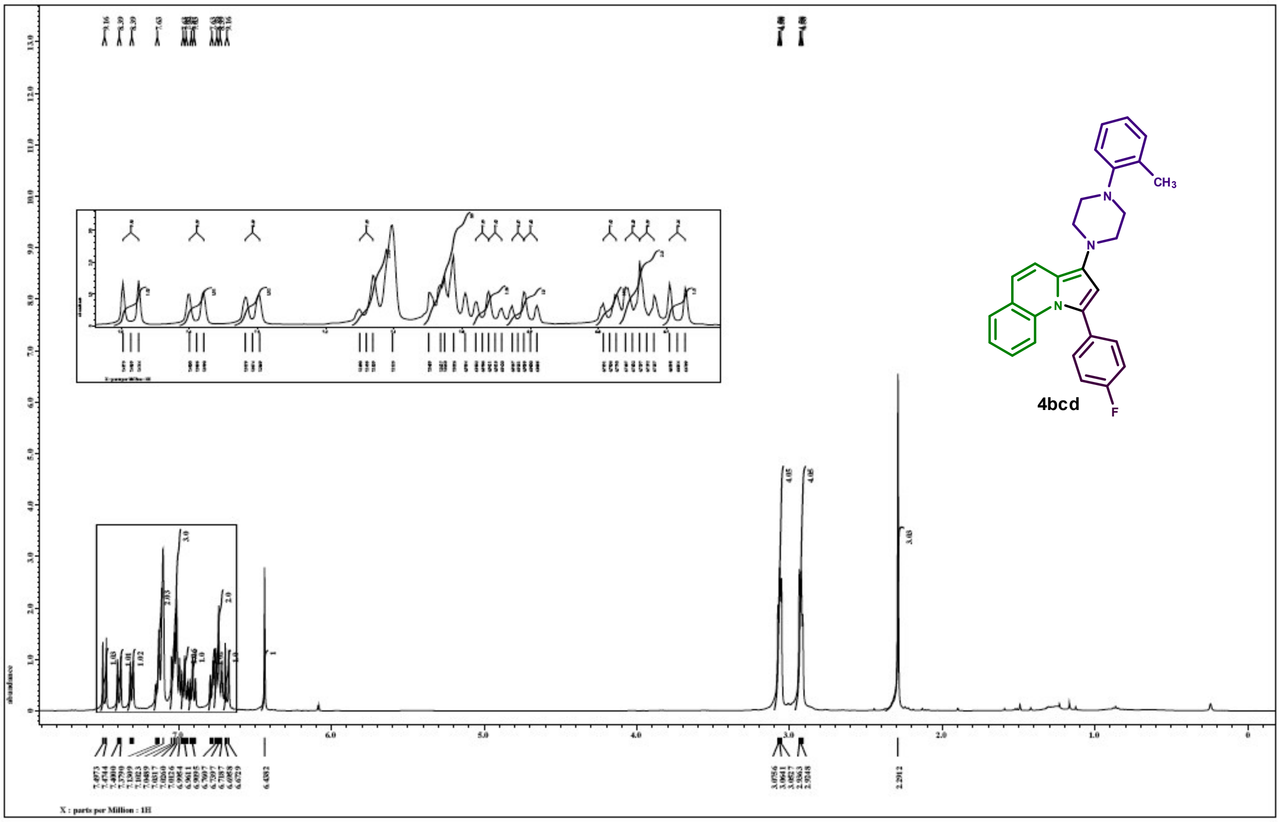

4acd
X : parts per Million : 13C

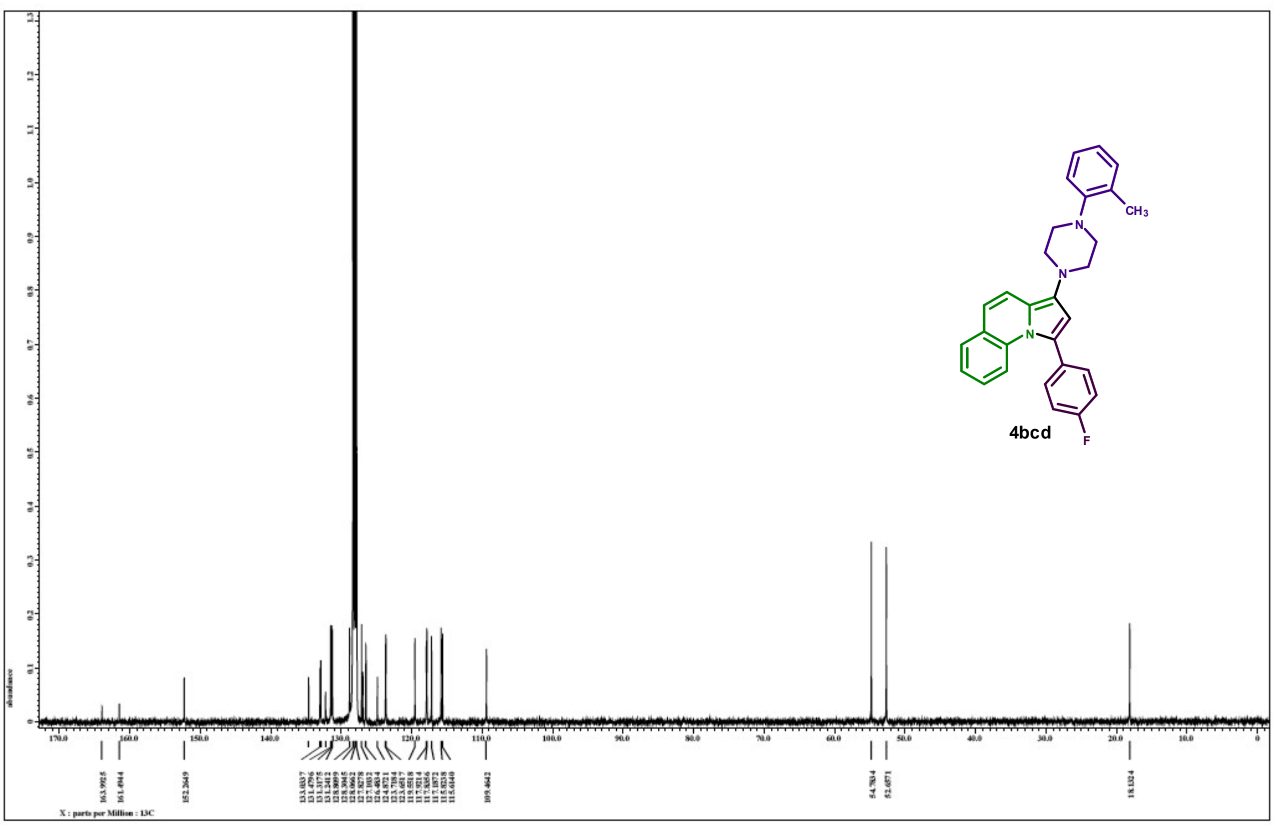

CH3
N
4bca
abundance
X : parts per Million : 1H

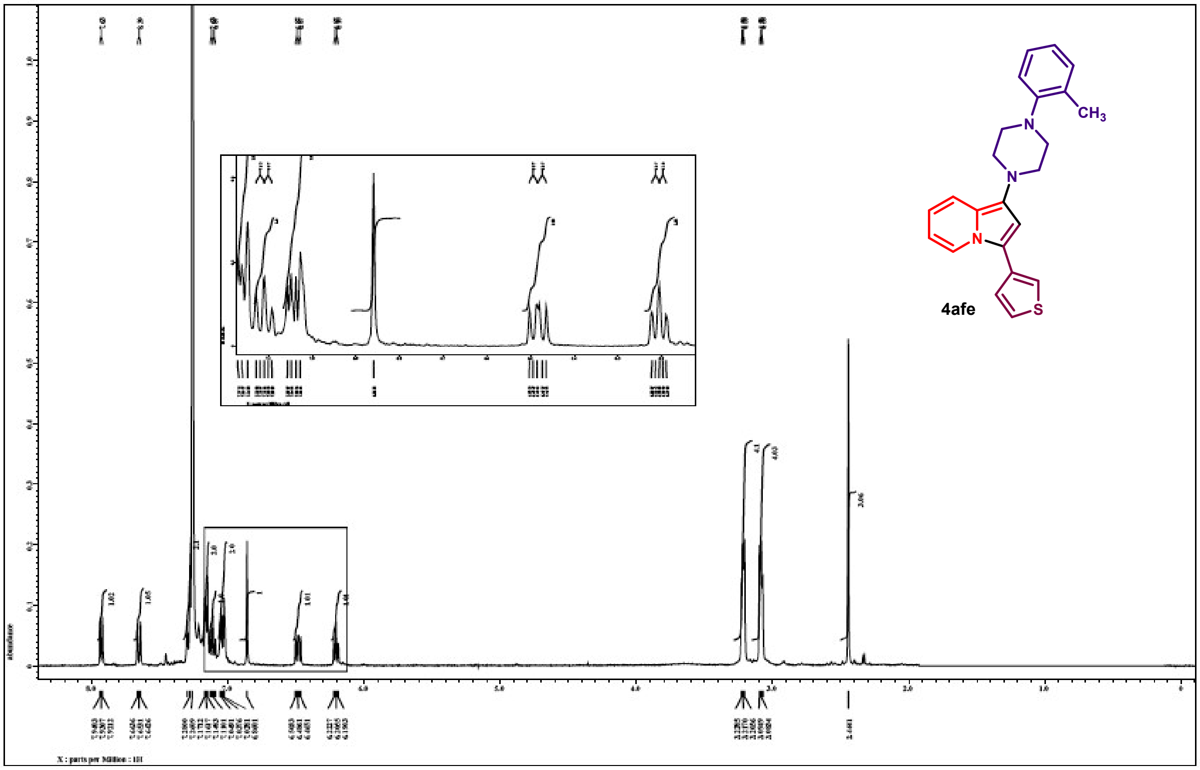

CH3
N
4bca
abundance
X : parts per Million : 13C


Ph
N
N
4aec
OCH3
abundance
X : parts per Million : 1H

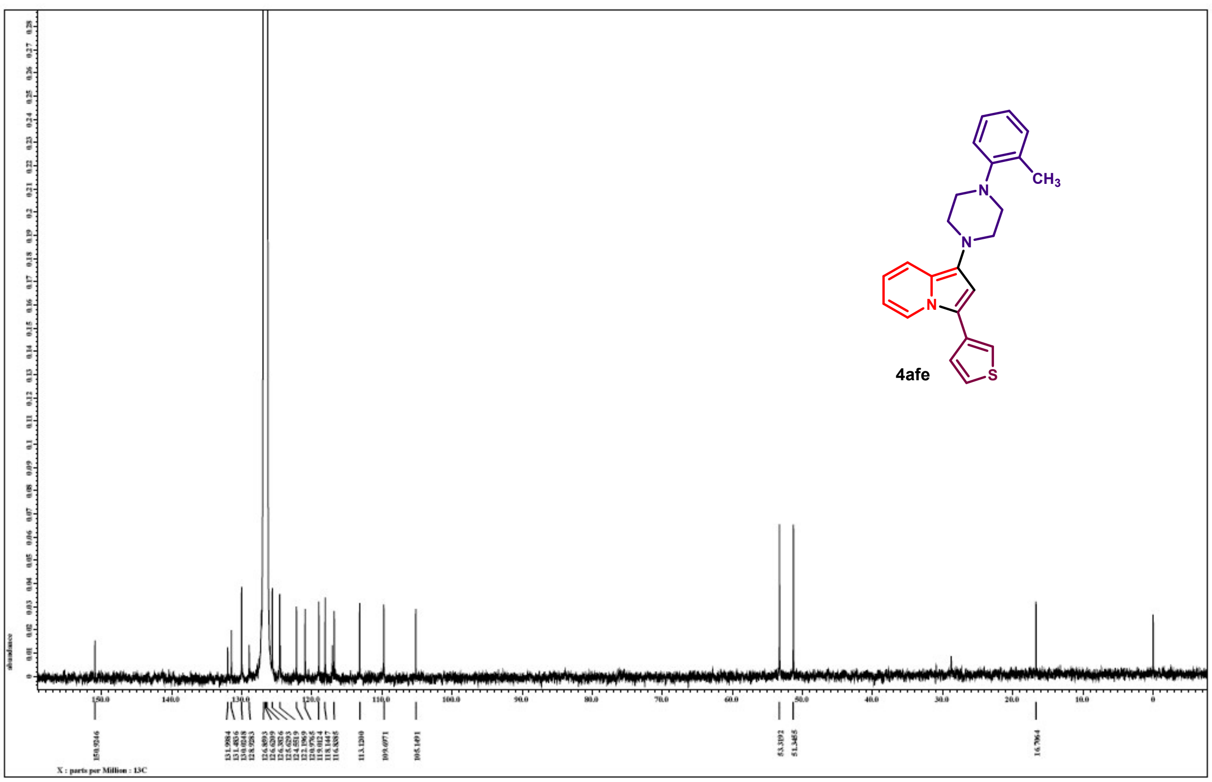

Ph
N
N
4aec
OCH3
abundance
X : parts per Million : 13C


4bcd
CH3
N
F
abundance
X : parts per Million : 1H

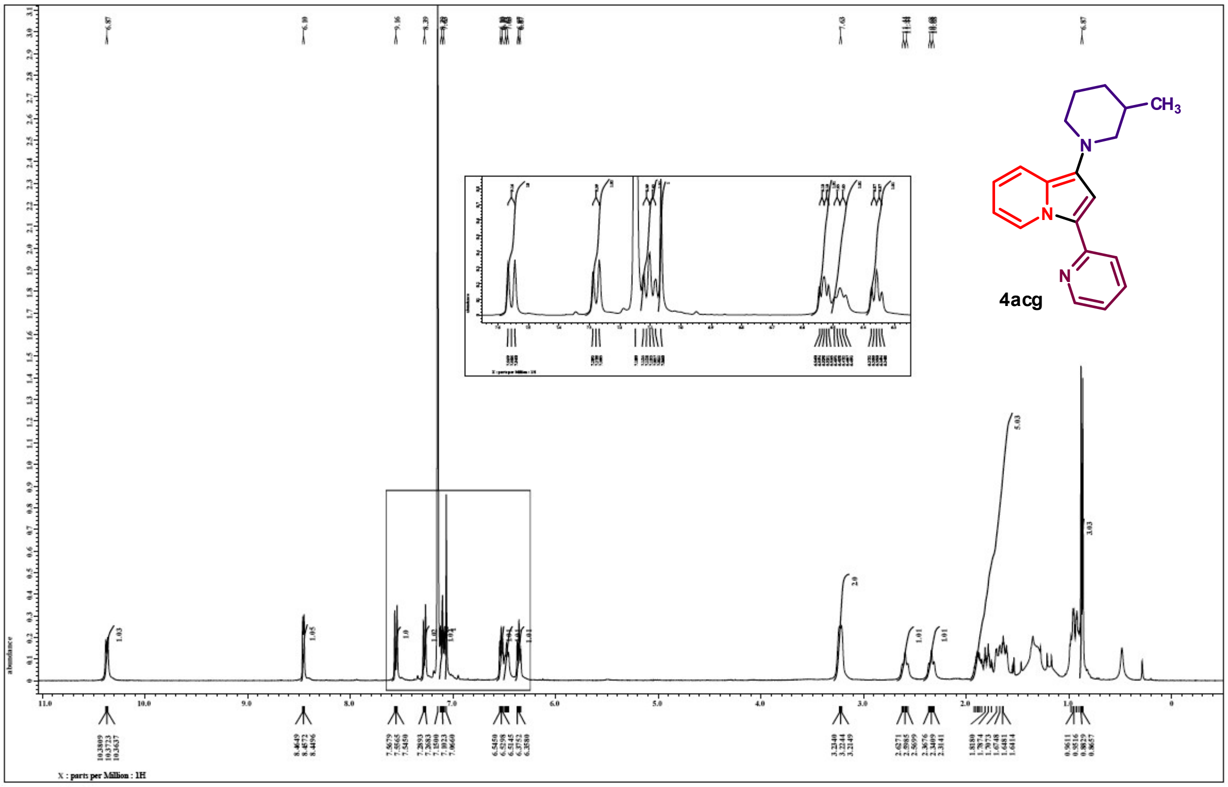

4bcd
CH3
N
F
abundance
X : parts per Million : 13C

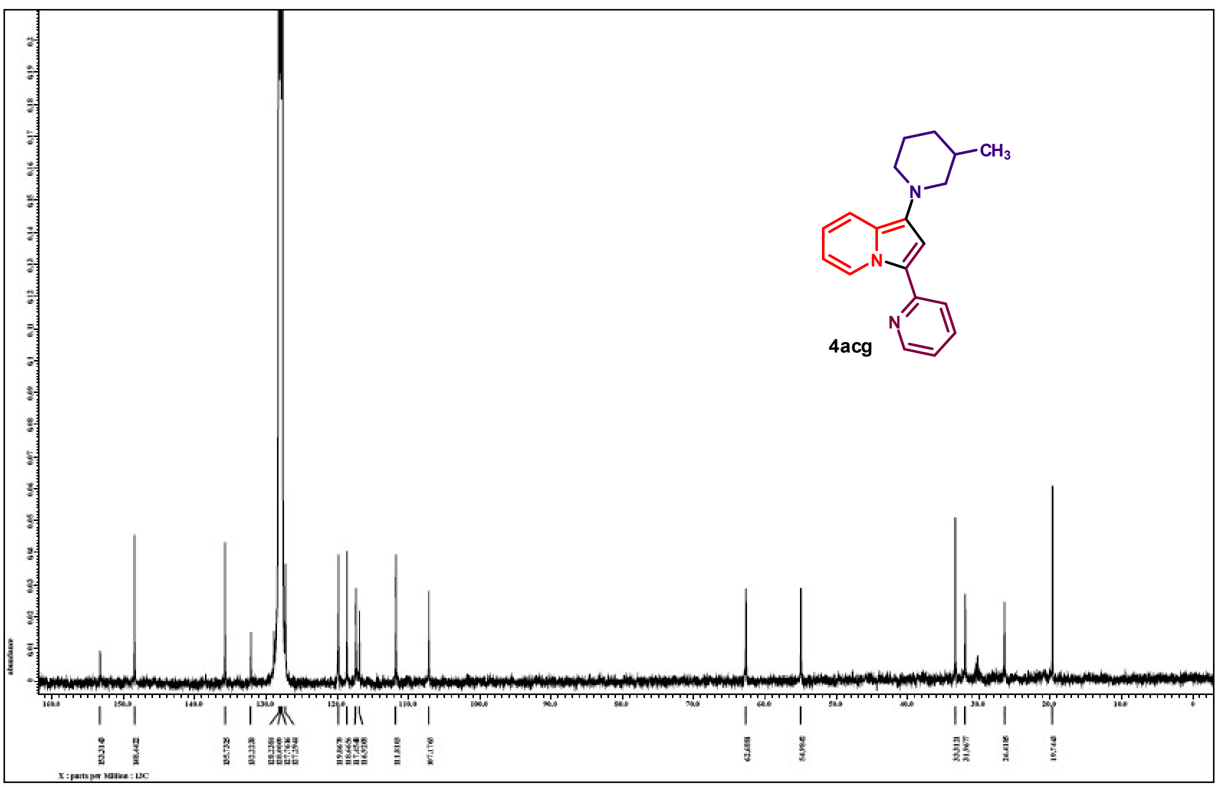


4afe
CH3
N
S
abundance
X : parts per Million : 1H



4afe
CH3
N
S
abundance
X : parts per Million : 13C


X : parts per Million : 1H
abundance
4acg
CH3
N


X : parts per Million : 13C
abundance
4acg
CH3
N