

ELECTRONIC SUPPLEMENTARY INFORMATION

A chelating diisocyanide ligand for cyclometalated Ir(III) complexes

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Table S1 Crystal data and collection details for complex **2**.

2	
CCDC number	1062816
Formula	C ₄₂ H ₂₃ N ₄ F ₄ Ir, BF ₄ , 2 CHCl ₃ , CH ₂ Cl ₂
F _w	1262.32
T, K	298
λ, Å	0.71073 (Mo-Kα)
Crystal system	Monoclinic
Space group	P ₂₁ /n
a, Å	9.2828(8)
b, Å	22.6451(19)
c, Å	24.351(2)
α, deg	90.000
β, deg	97.1920(10)
γ, deg	90.000
Cell volume, Å ³	5078.6(7)
Z	4
D _c , g cm ⁻³	1.651
μ, mm ⁻¹	3.115
F(000)	2460
h, k, l max	11,28,30
Crystal size, mm	0.20,0.16,0.11
θ limits, °	1.69 to 26.48
Reflections collected	52915
Independent reflections	10464
Data/restraints/parameters	10464/24/626
weight. Scheme ^a	0.071600 15.736697
GOF on F ²	1.131
R ₁ (I > 2σ(I))	0.0589
wR ₂ (all data)	0.1568
Peak/hole, e Å ⁻³	1.466 and -1.186
Notes:	The cell contains 2 molecules of CHCl ₃ and one molecule of CH ₂ Cl ₂ , disordered over two positions (58:42 ratio).

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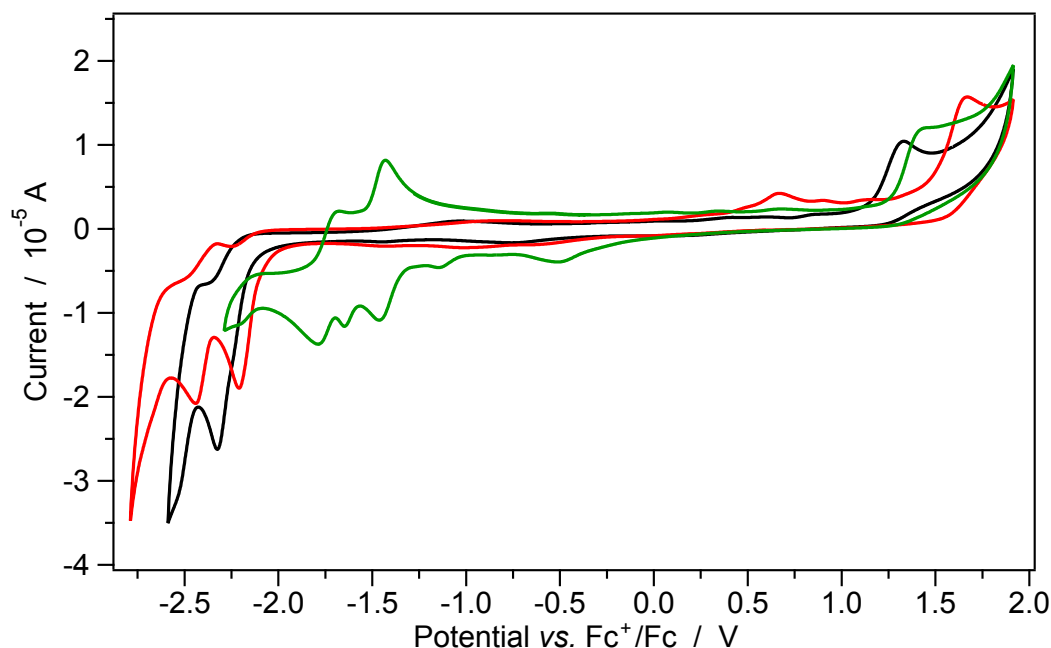


Fig. S1 Cyclic voltammograms of complexes **2–4** (approx. 1 mM) in room-temperature acetonitrile solution (with 0.1 M TBAPF₆) recorded at a scan rate of 100 mV s⁻¹.

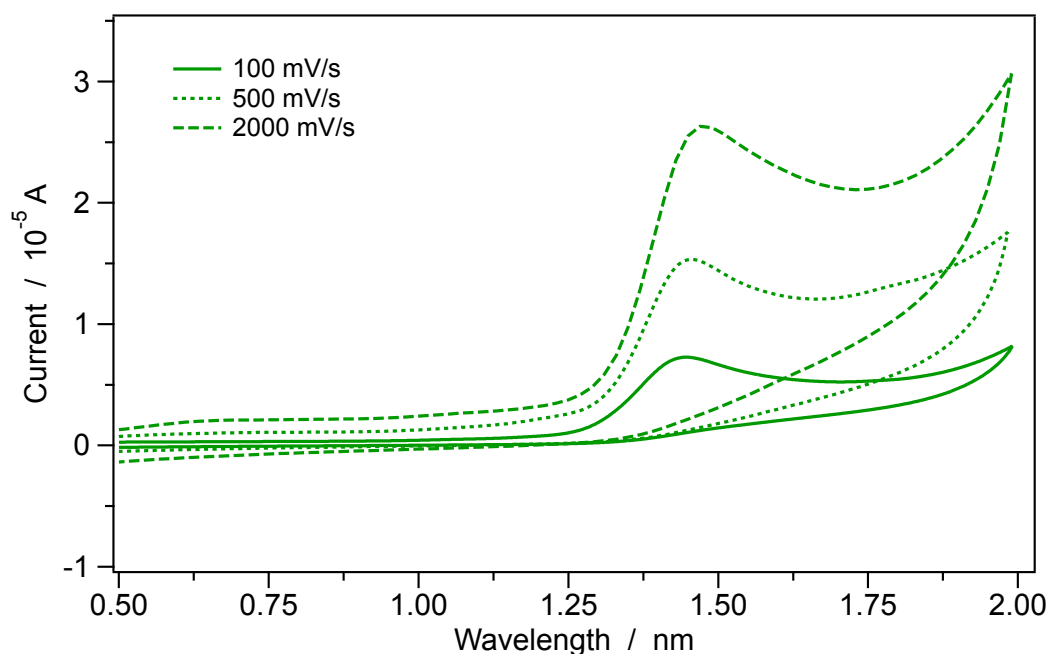


Fig. S2 Cyclic voltammograms of complex **4** (approx. 1 mM) in room-temperature acetonitrile solution (with 0.1 M TBAPF₆) recorded at different scan rates to evaluate the irreversibility of the oxidation processes.

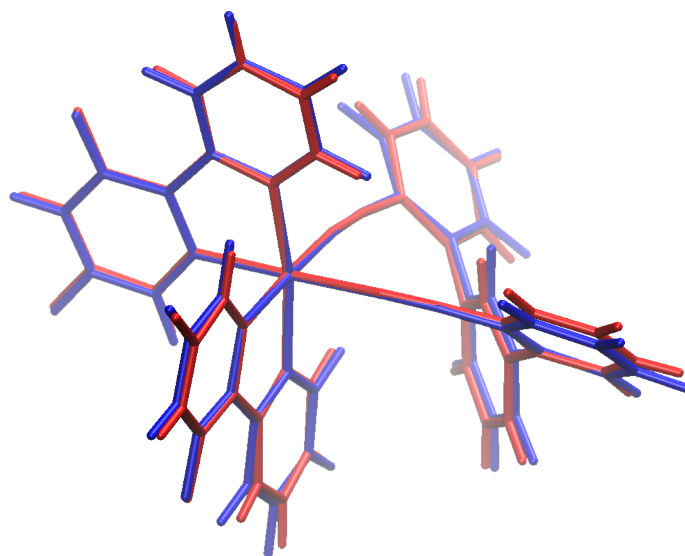


Fig. S3 Structural overlay between the experimental X-ray structure (reported in red) of the cationic part of complex **3** and the theoretically computed one (in blue). The structural overlay is calculated by minimizing the root-mean-square deviation (RMSD) of all the atomic positions, except hydrogen atoms: RMSD = 0.127 Å.

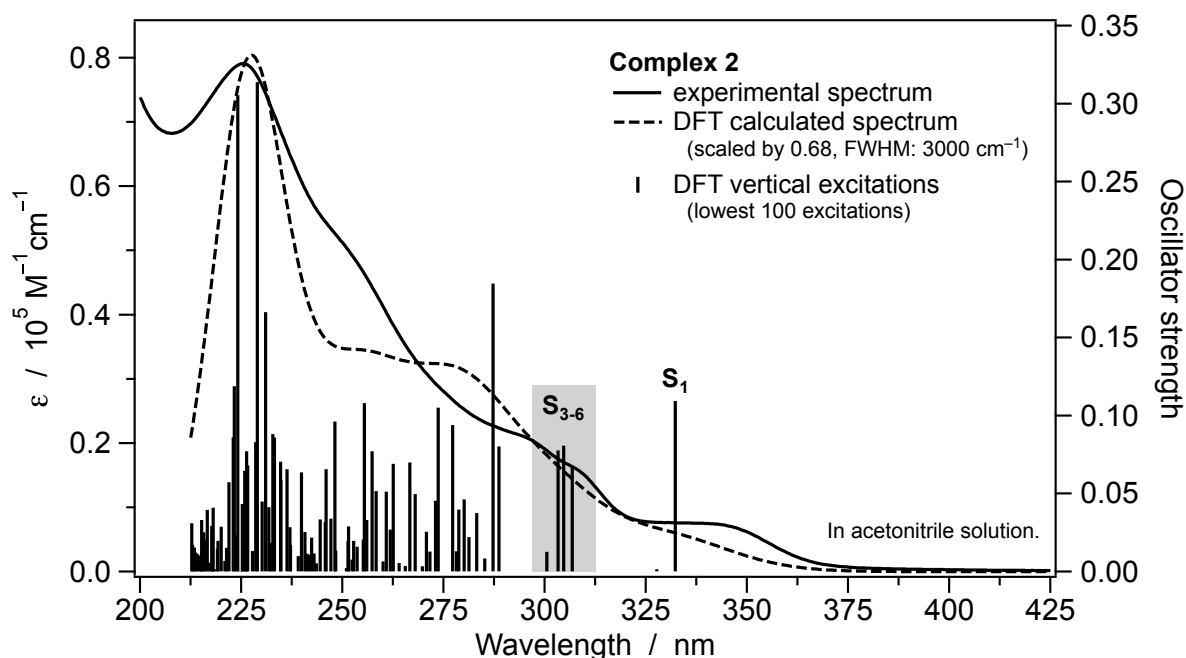


Fig. S4 Simulated absorption spectrum of complex **2** (dashed black line) obtained by convoluting the lowest 100 singlet vertical excitations (black bars) with Gaussian having FWHM of 3000 cm^{-1} . The simulated spectrum is compared with the room-temperature experimental absorption profile of **2** in acetonitrile (full black line).

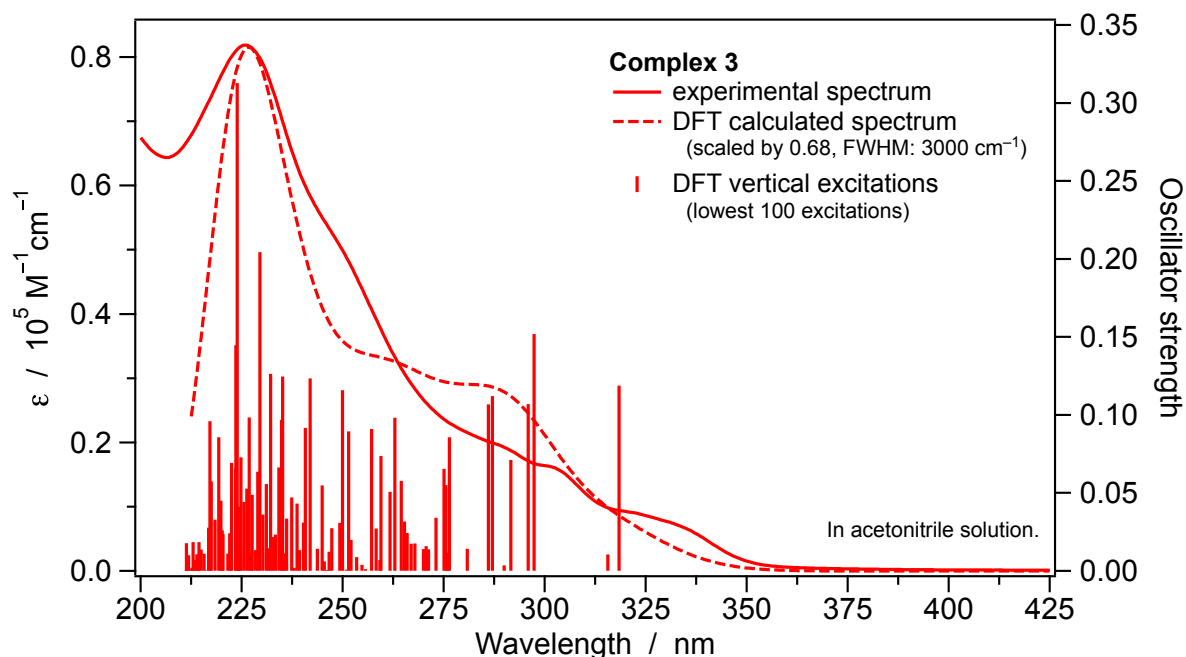


Fig. S5 Simulated absorption spectrum of complex **3** (dashed red line) obtained by convoluting the lowest 100 singlet vertical excitations (red bars) with Gaussian having FWHM of 3000 cm^{-1} . The simulated spectrum is compared with the room-temperature experimental absorption profile of **3** in acetonitrile (full red line).

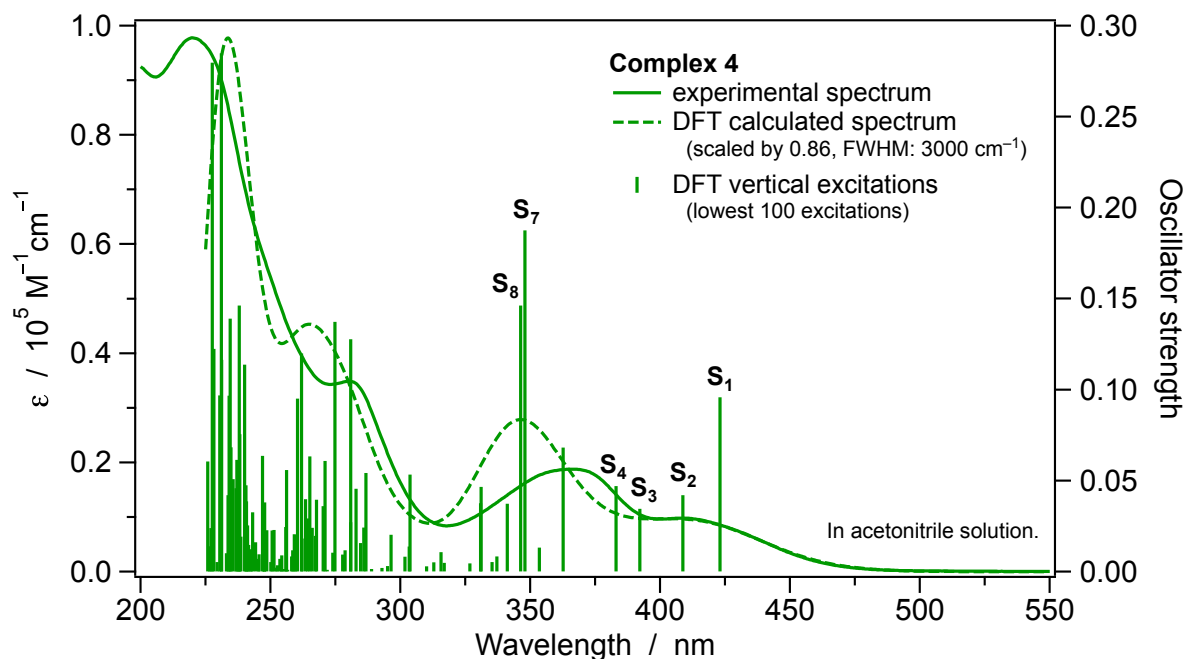


Fig. S6 Simulated absorption spectrum of complex **4** (dashed green line) obtained by convoluting the lowest 100 singlet vertical excitations (green bars) with Gaussian having FWHM of 3000 cm^{-1} . The simulated spectrum is compared with the room-temperature experimental absorption profile of **3** in acetonitrile (full green line).

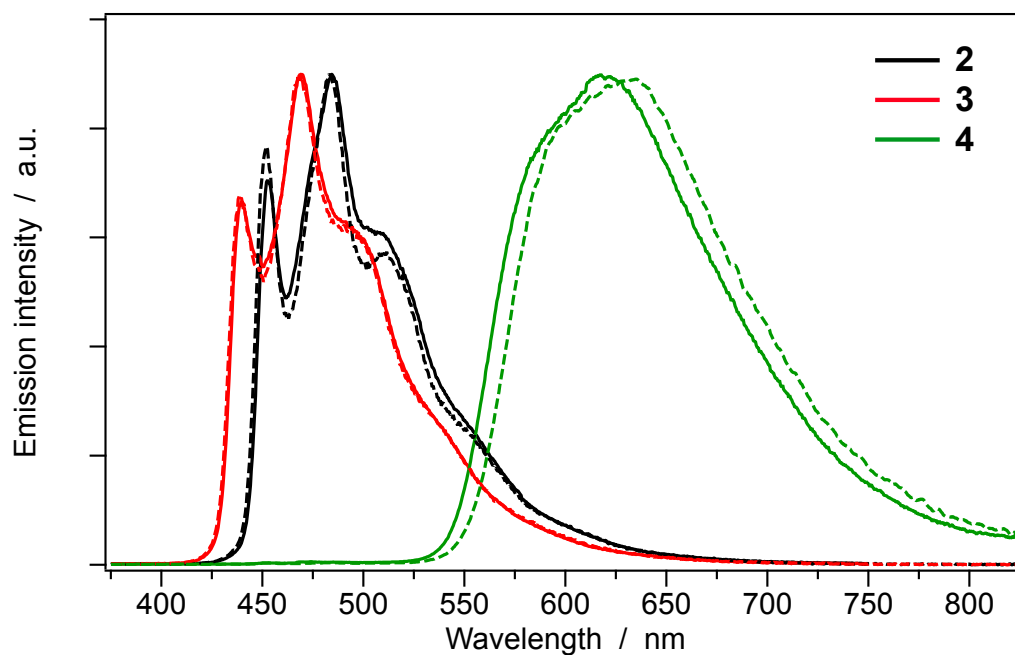


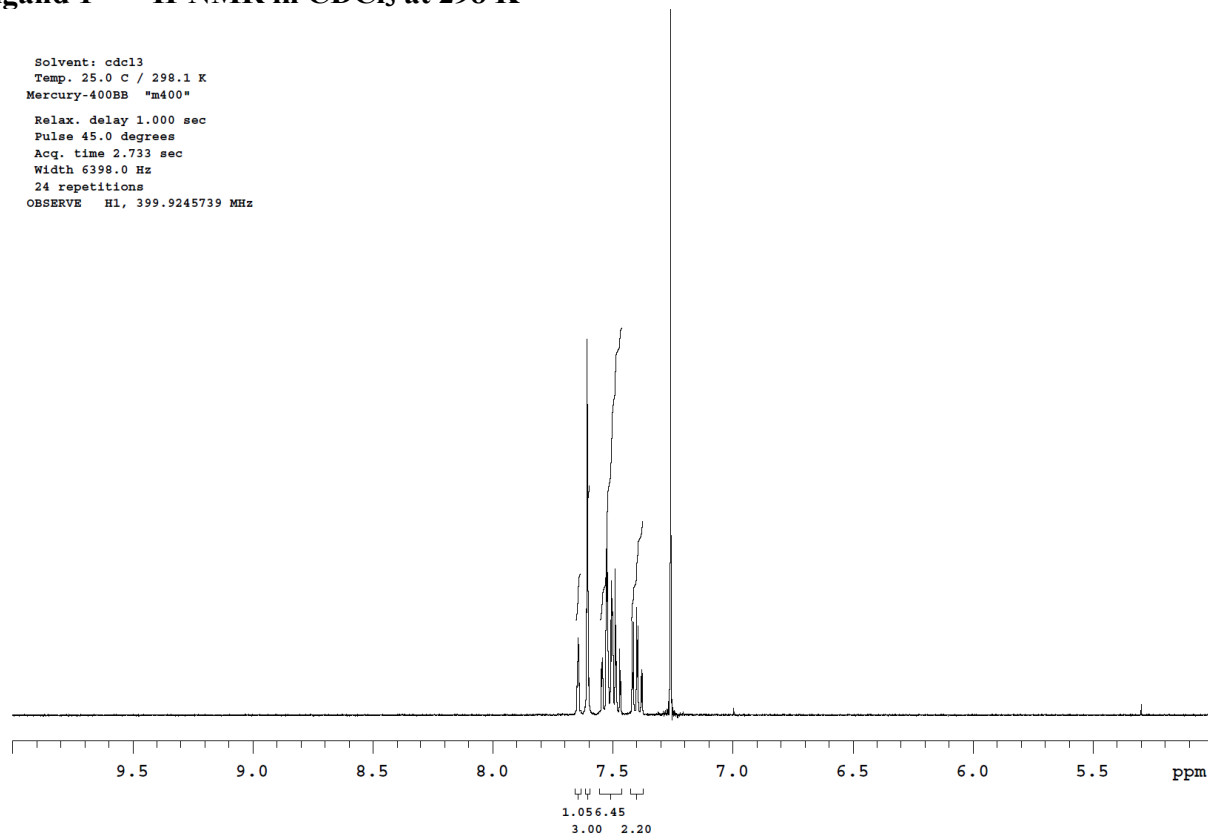
Fig. S7 Normalized emission spectra of **2–4** in PMMA matrix 1% w./w. at 298 K (full lines). The emission spectra in RT acetonitrile solution are also reported (dashed lines) for comparison.

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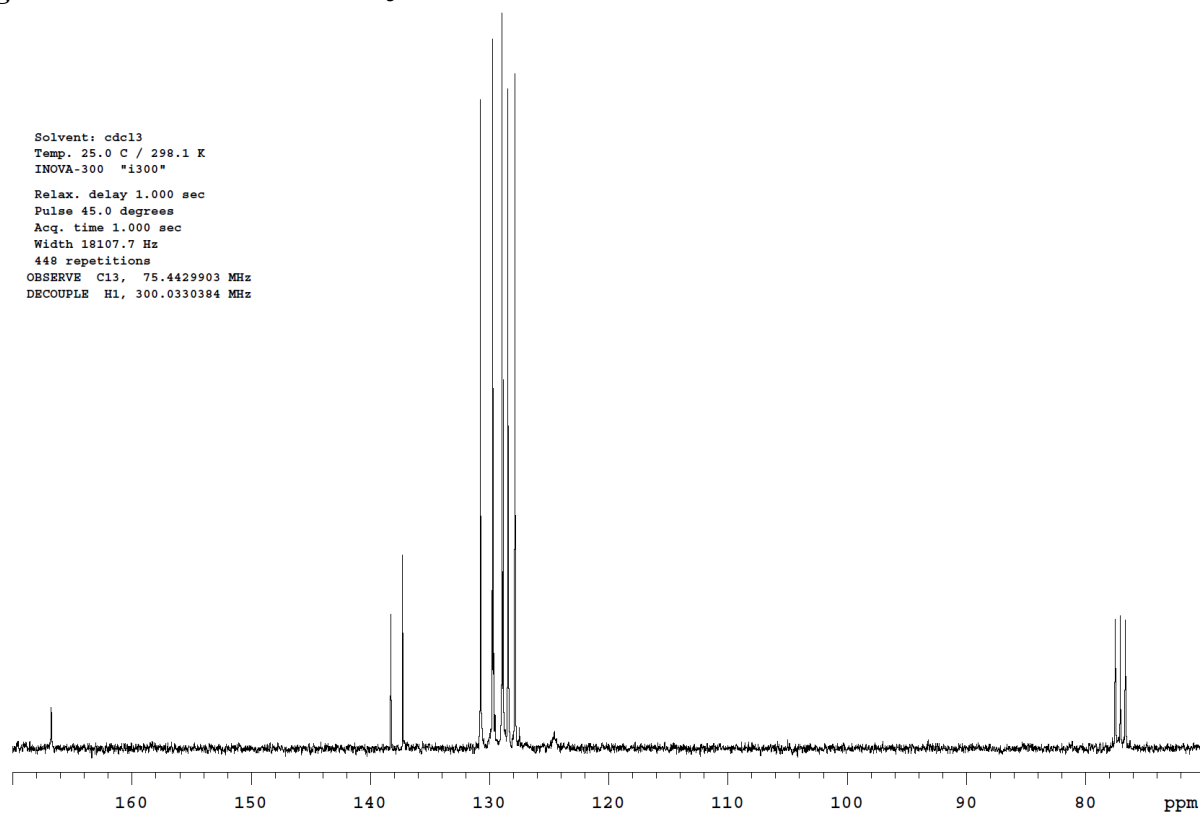
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NMR SPECTRA

Ligand 1 — ^1H -NMR in CDCl_3 at 298 K



Ligand 1 — ^{13}C -NMR in CDCl_3 at 298 K



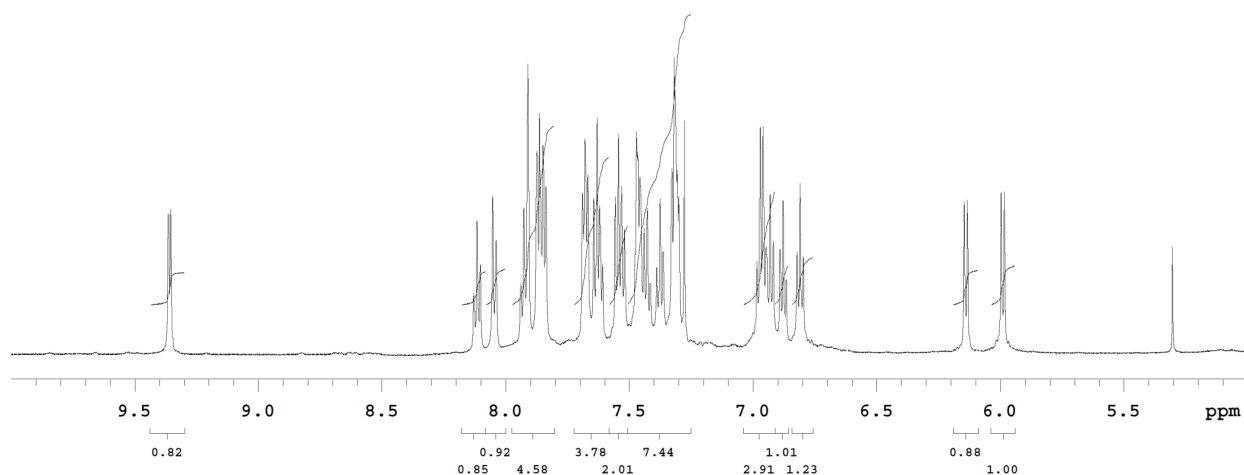
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Complex 2 — ^1H -NMR in CDCl_3 at 263 K

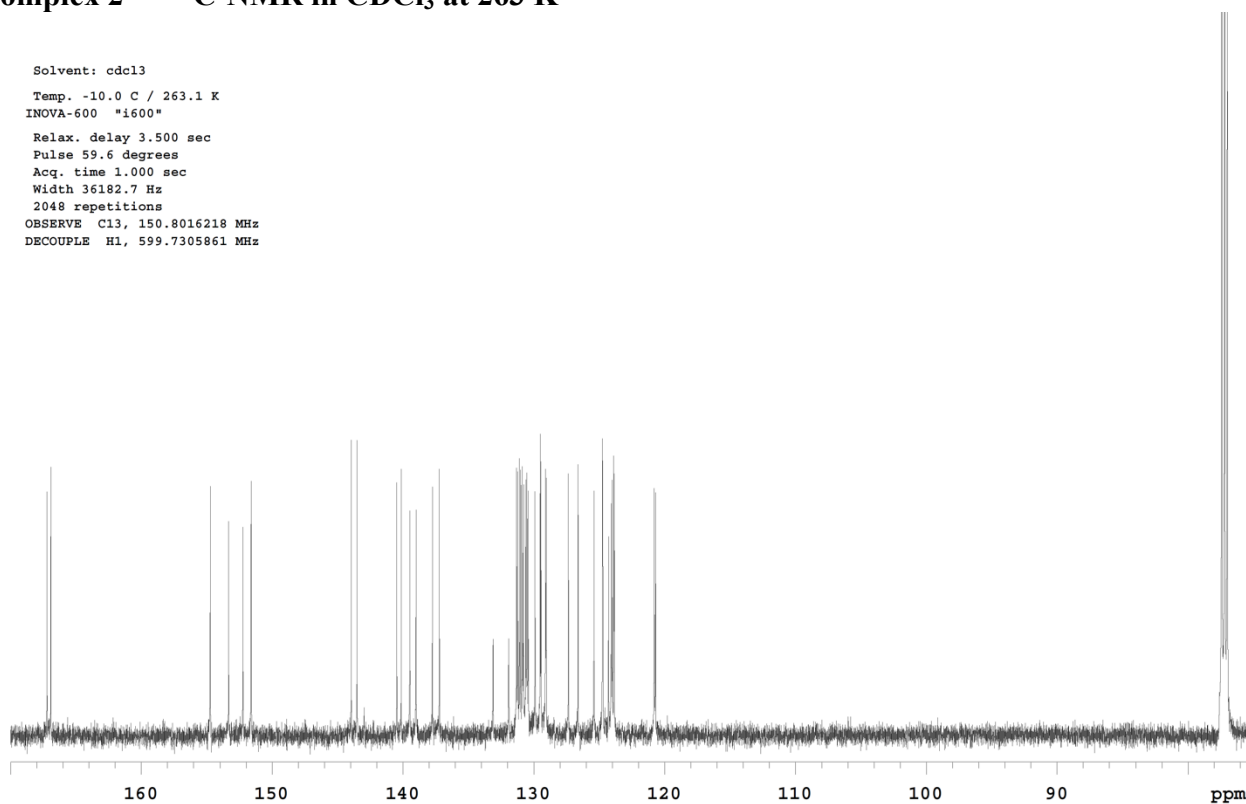
Solvent: cdcl_3
Temp. -10.0 C / 263.1 K
File: ME-335-protone-10C
INOVA-600 "1600"

OBSERVE H1, 599.7275759 MHz



Complex 2 — ^{13}C -NMR in CDCl_3 at 263 K

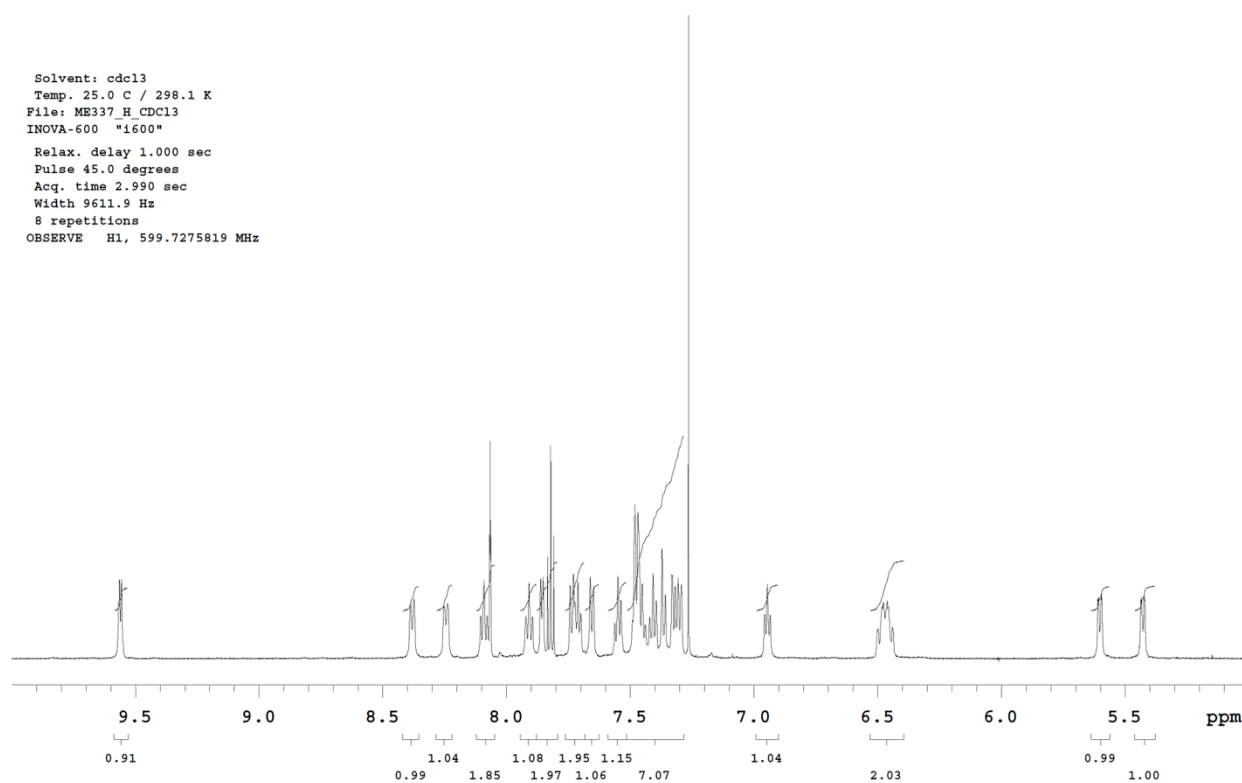
Solvent: cdcl_3
Temp. -10.0 C / 263.1 K
INOVA-600 "1600"
Relax. delay 3.500 sec
Pulse 59.6 degrees
Acq. time 1.000 sec
Width 36182.7 Hz
2048 repetitions
OBSERVE C13, 150.8016218 MHz
DECOUPLE H1, 599.7305861 MHz



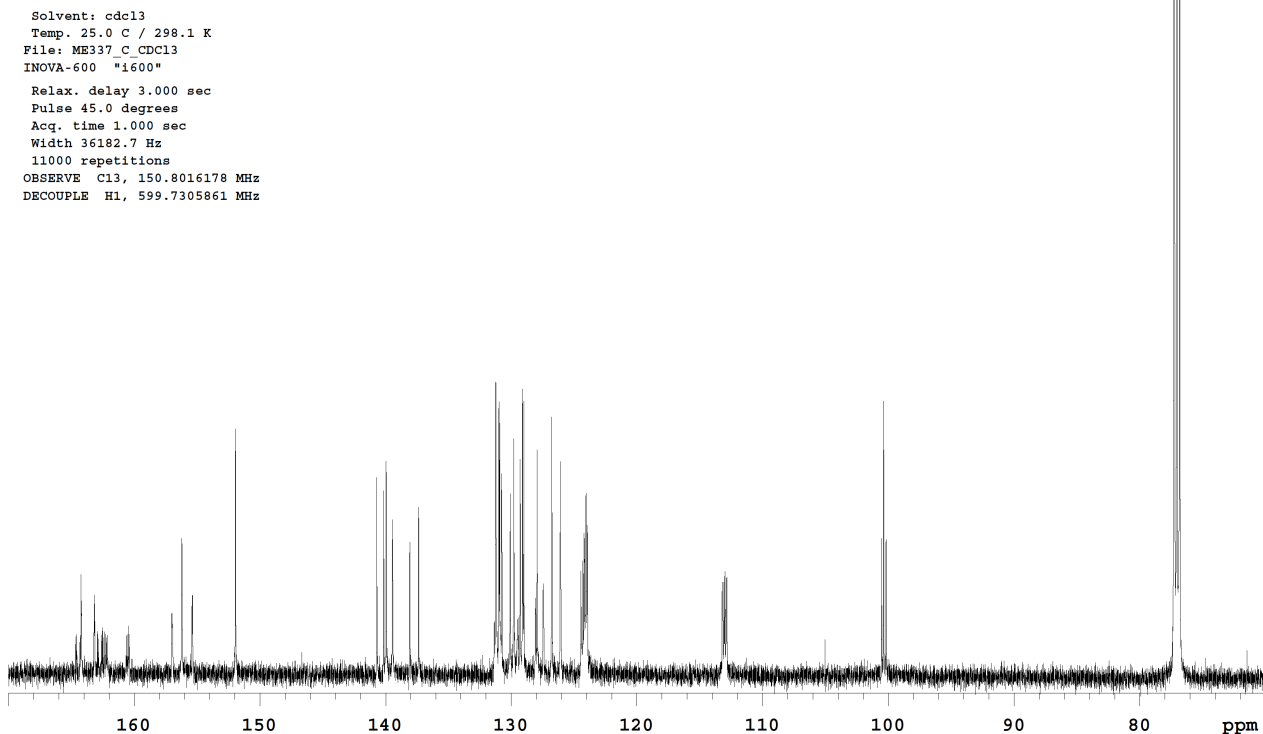
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Complex 3 — ^1H -NMR in CDCl_3 at 298 K



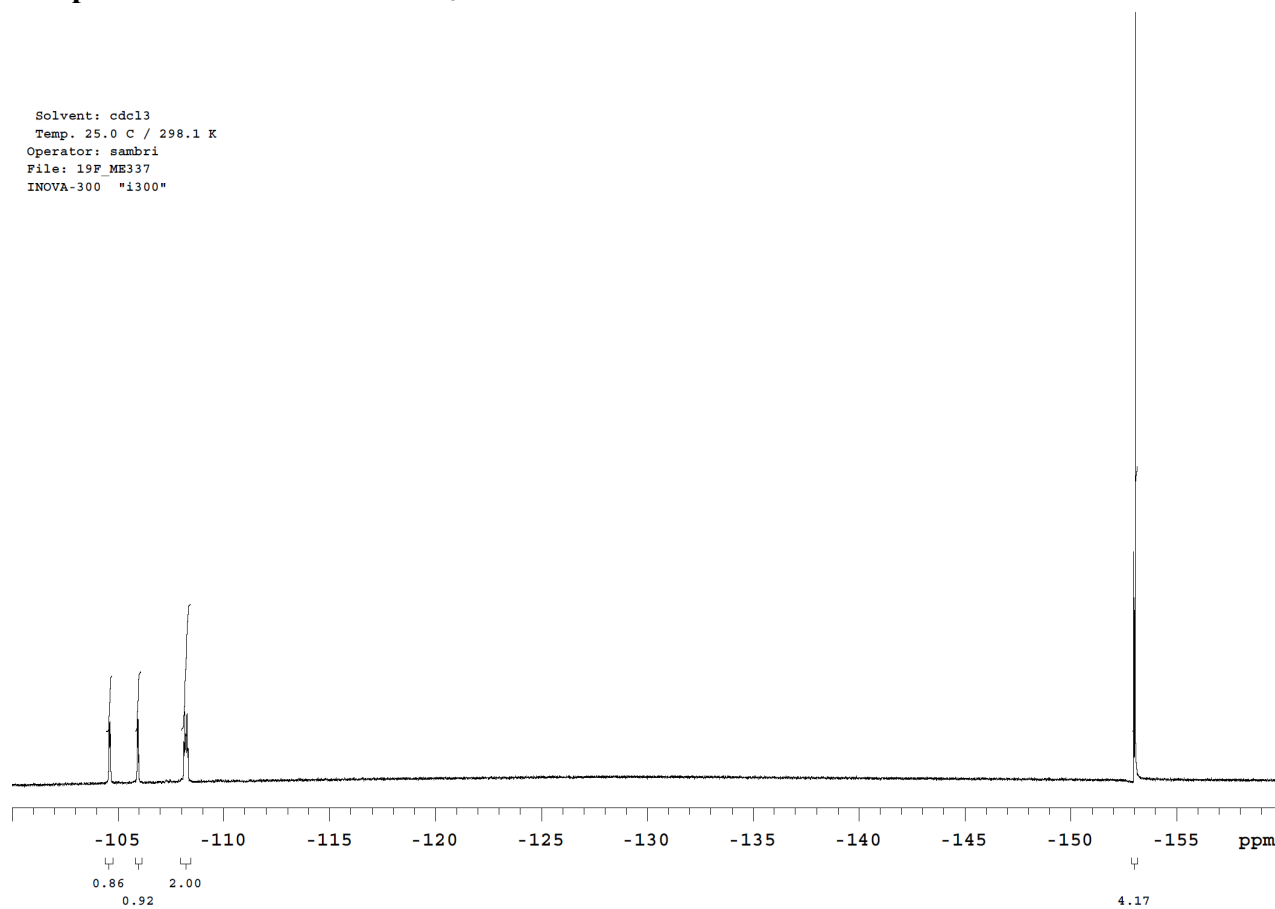
Complex 3 — ^{13}C -NMR in CDCl_3 at 298 K



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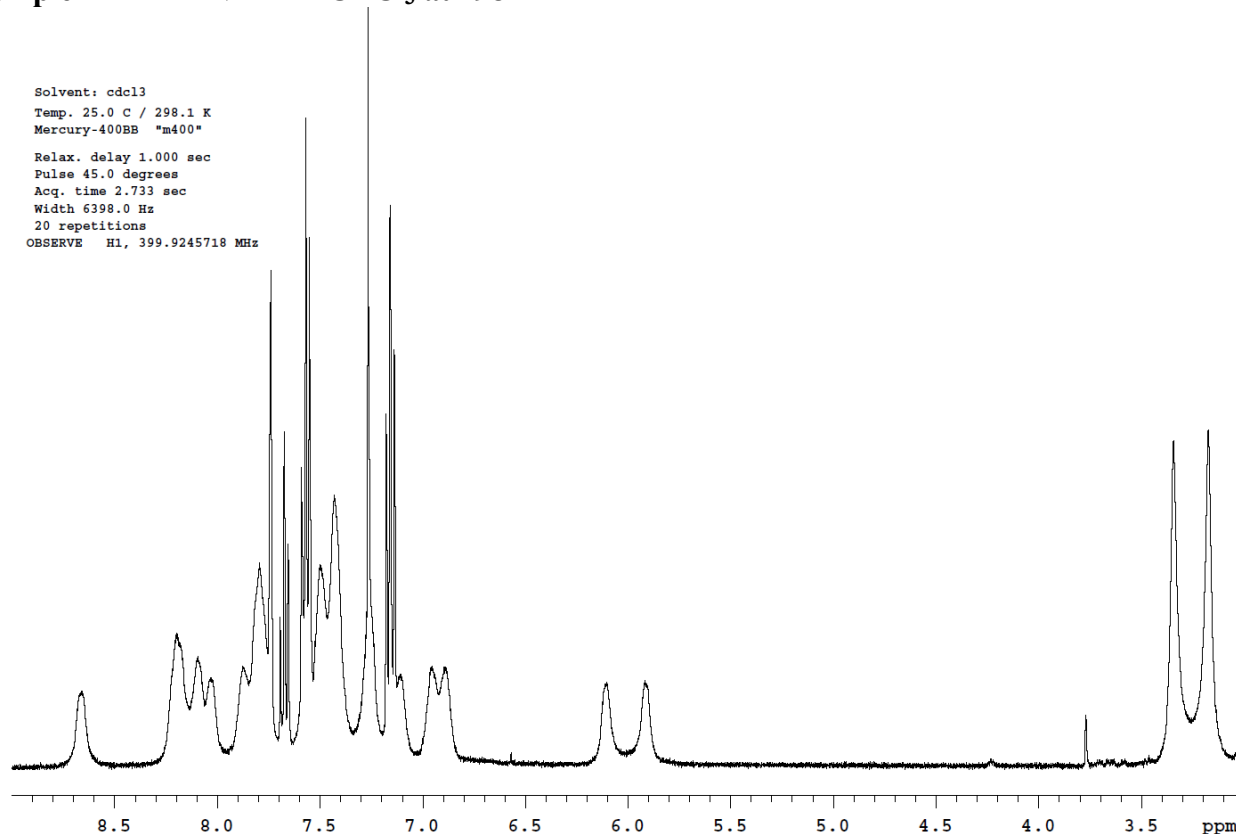
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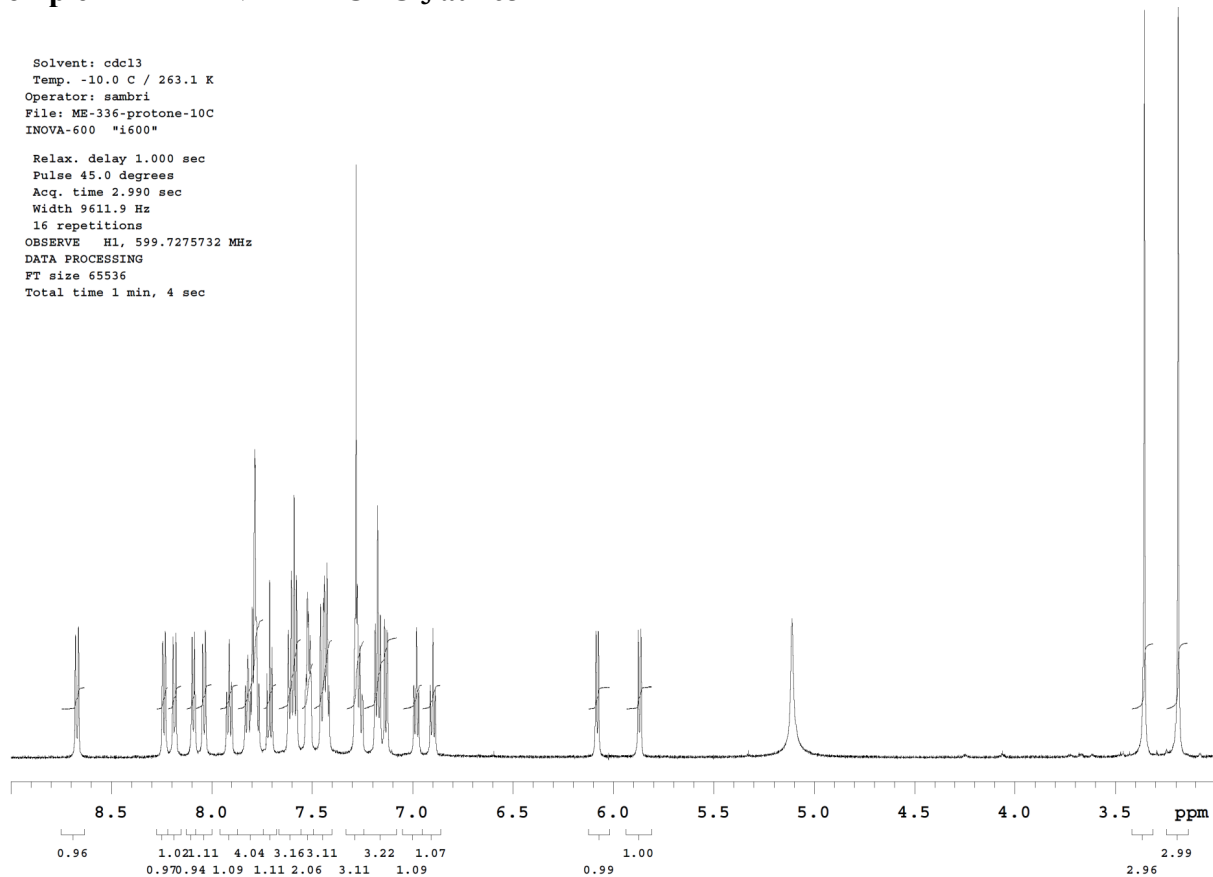
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Complex 4 — ^1H -NMR in CDCl_3 at 298 K



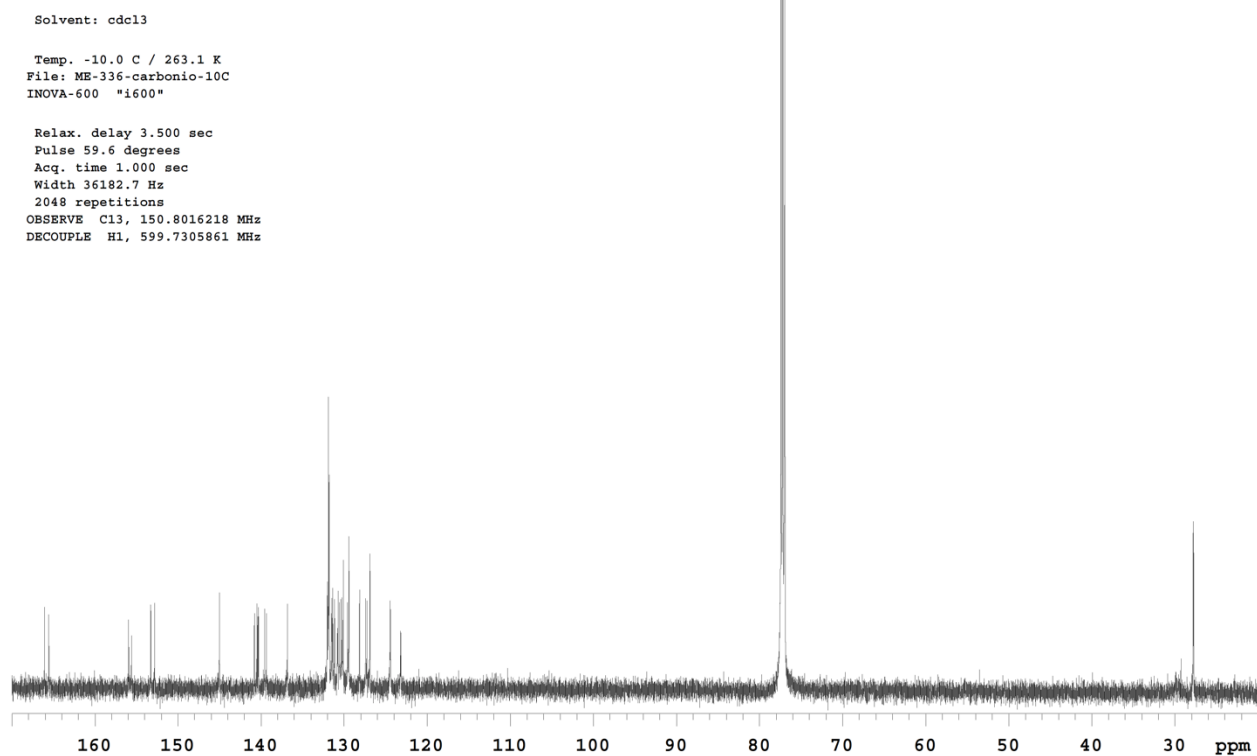
Complex 4 — ^1H -NMR in CDCl_3 at 263 K



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Complex 4 — ^{13}C -NMR in CDCl_3 at 263 K

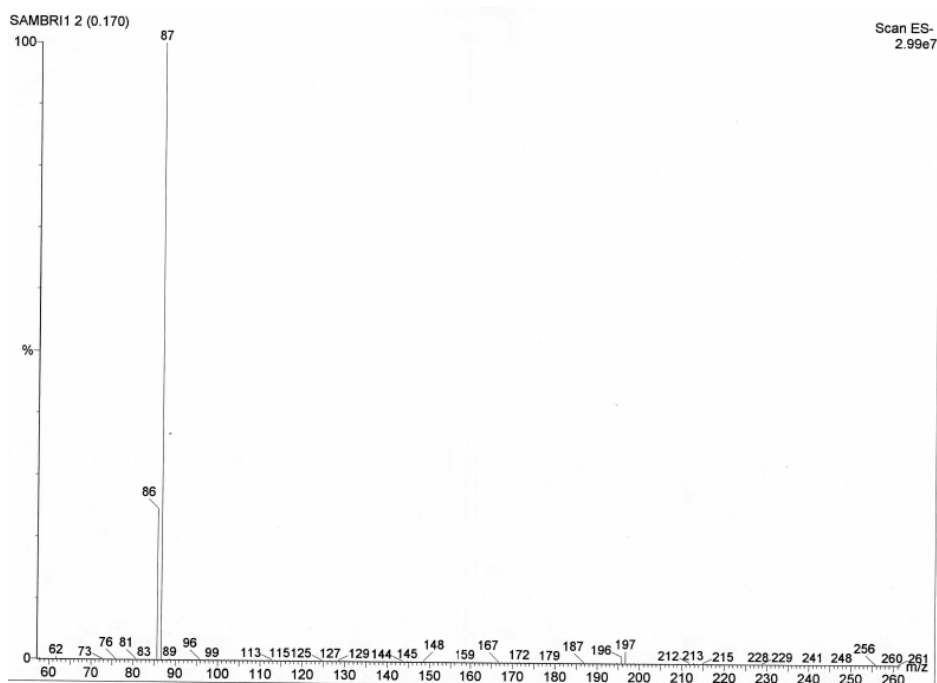
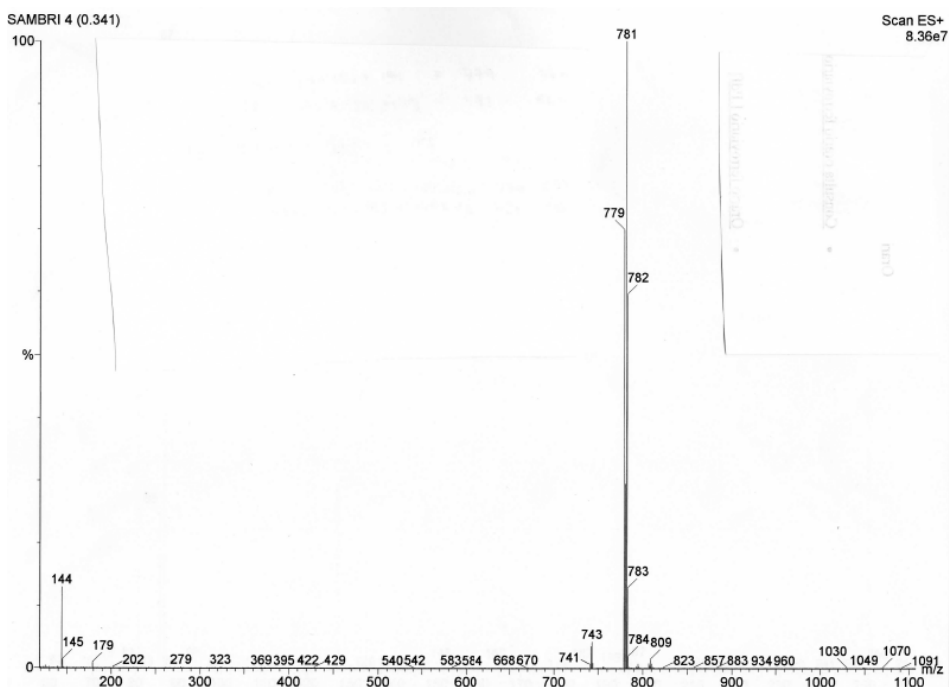


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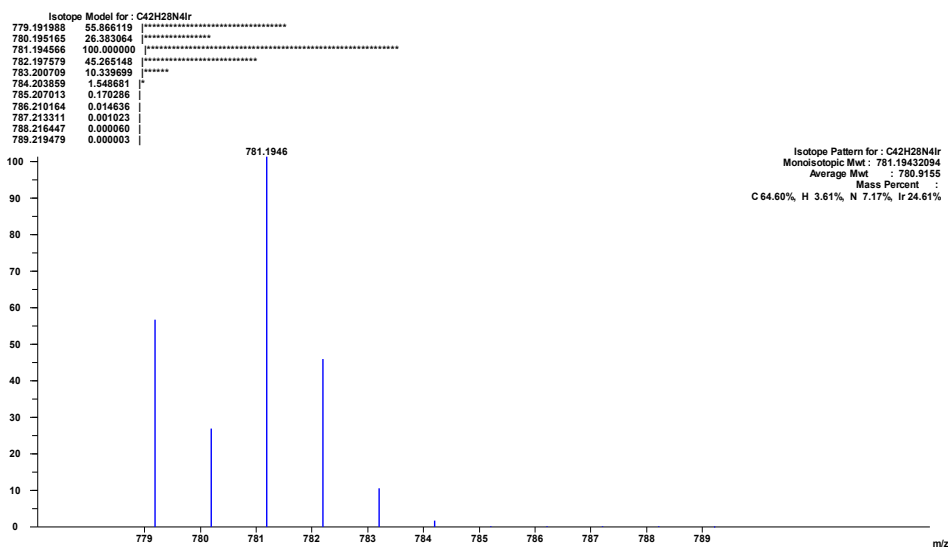
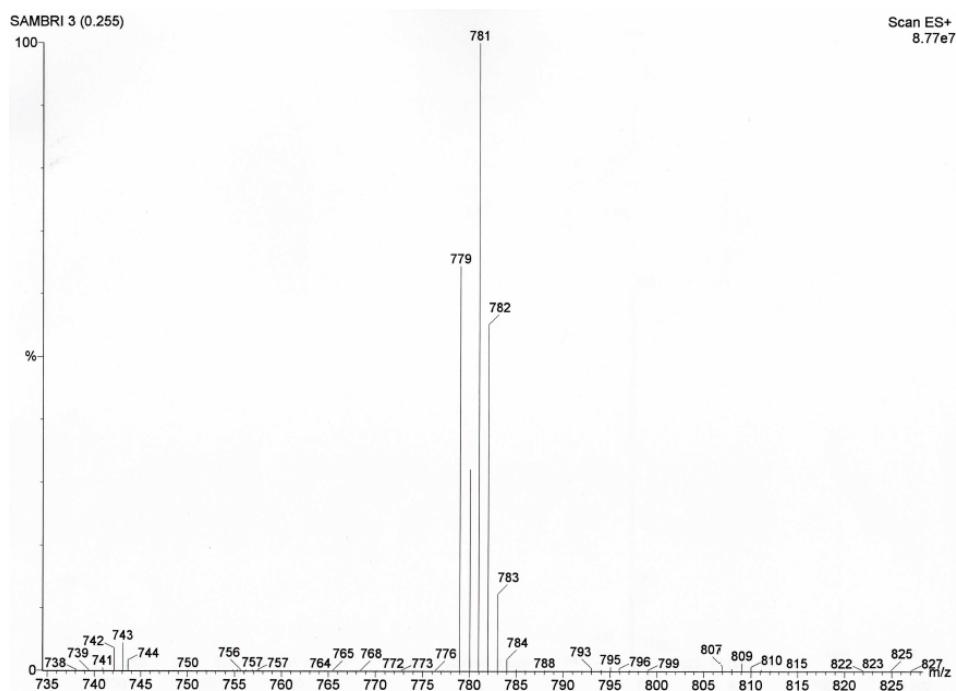
ESI-MS SPECTRA

Complex 2 — ESI-MS spectra in acetonitrile (cations and anions) and simulated isotopic pattern of the cationic molecular ion.



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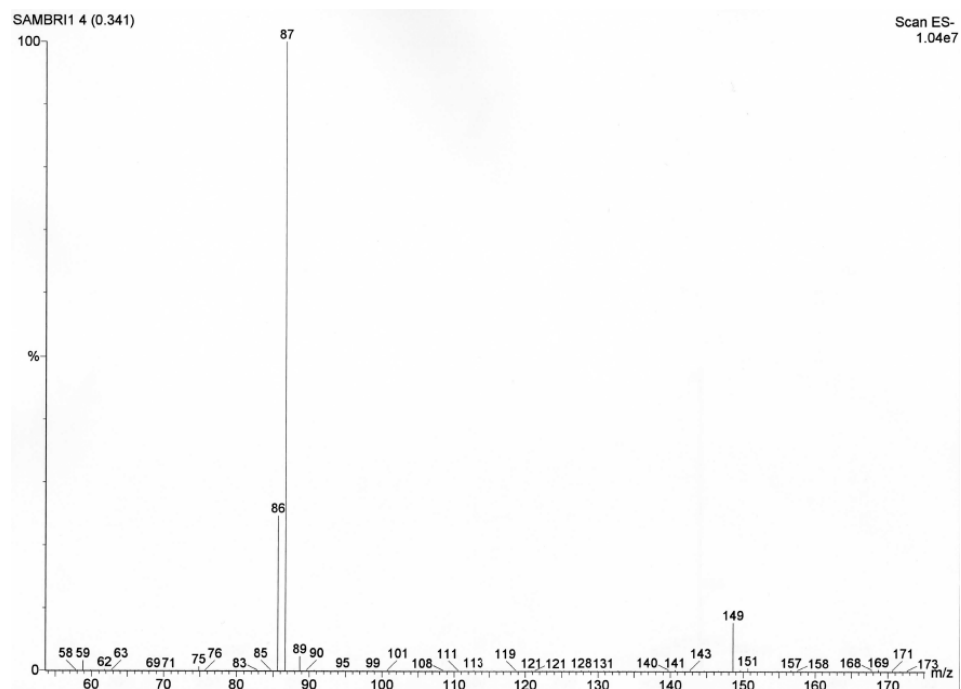
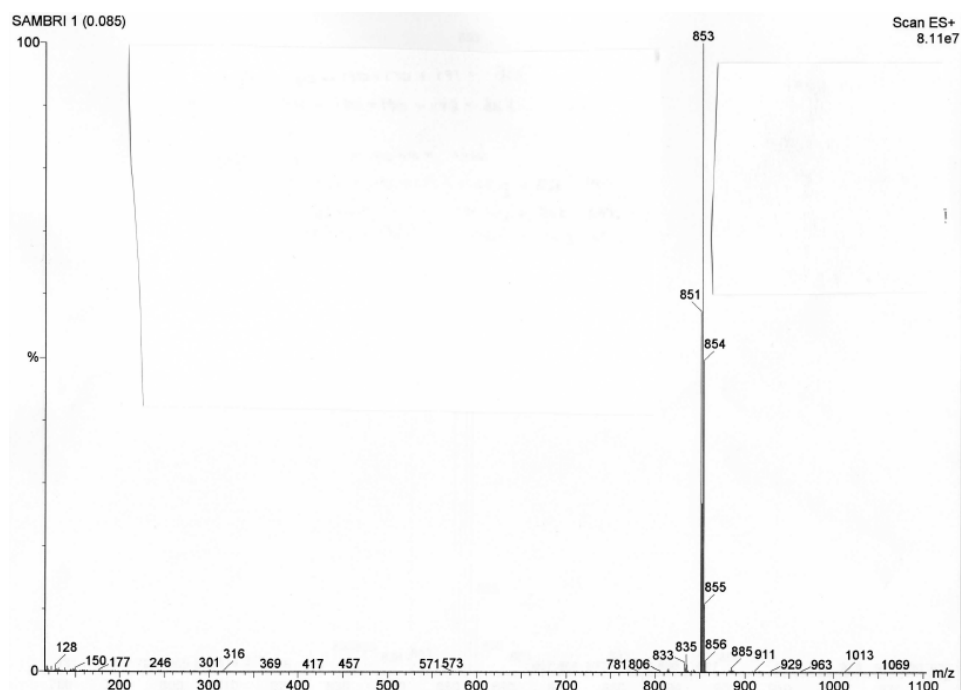
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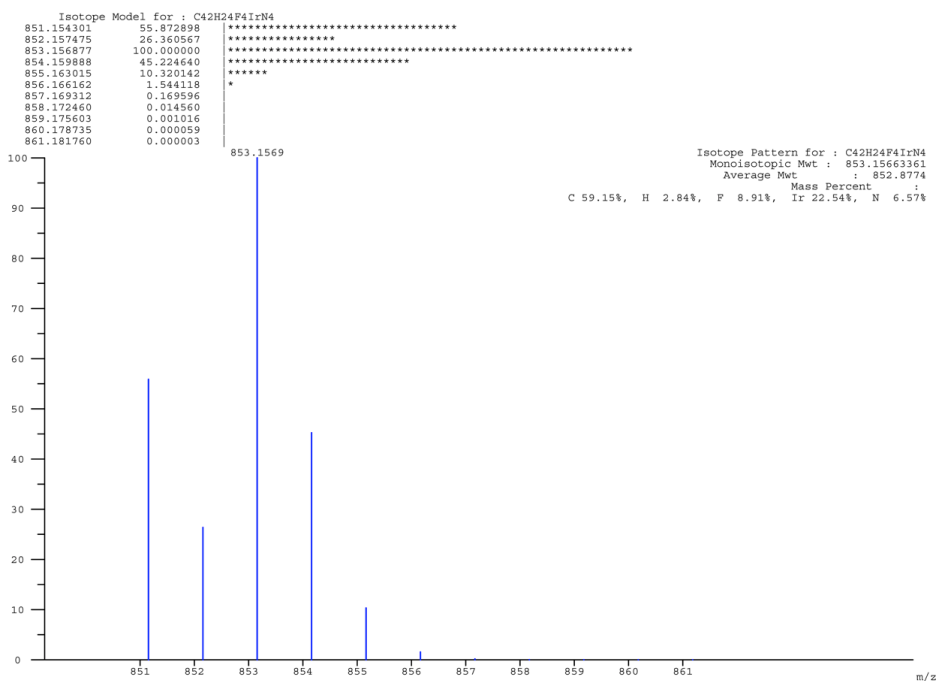
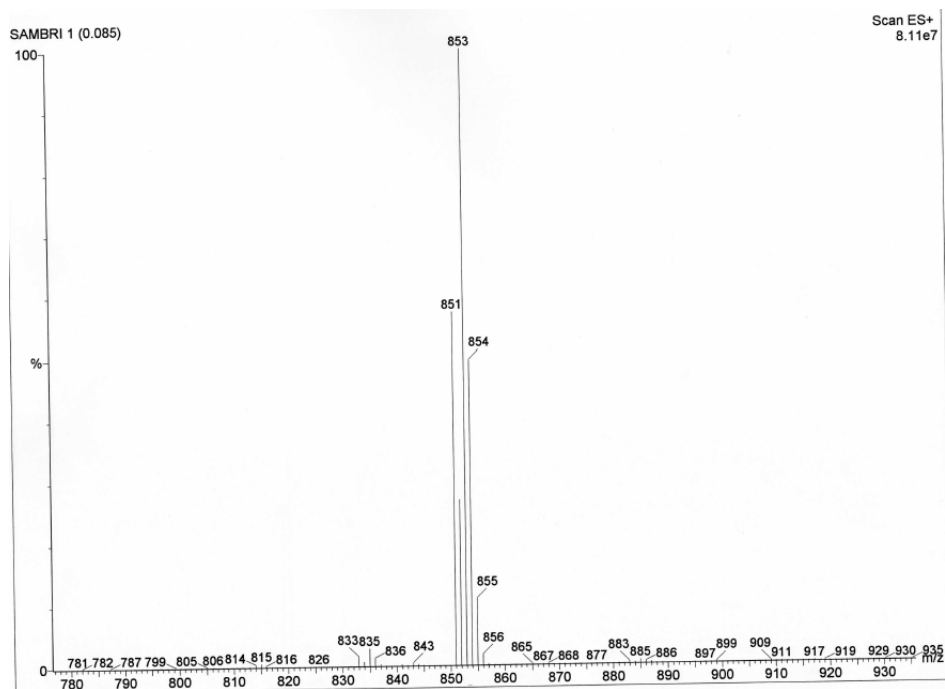
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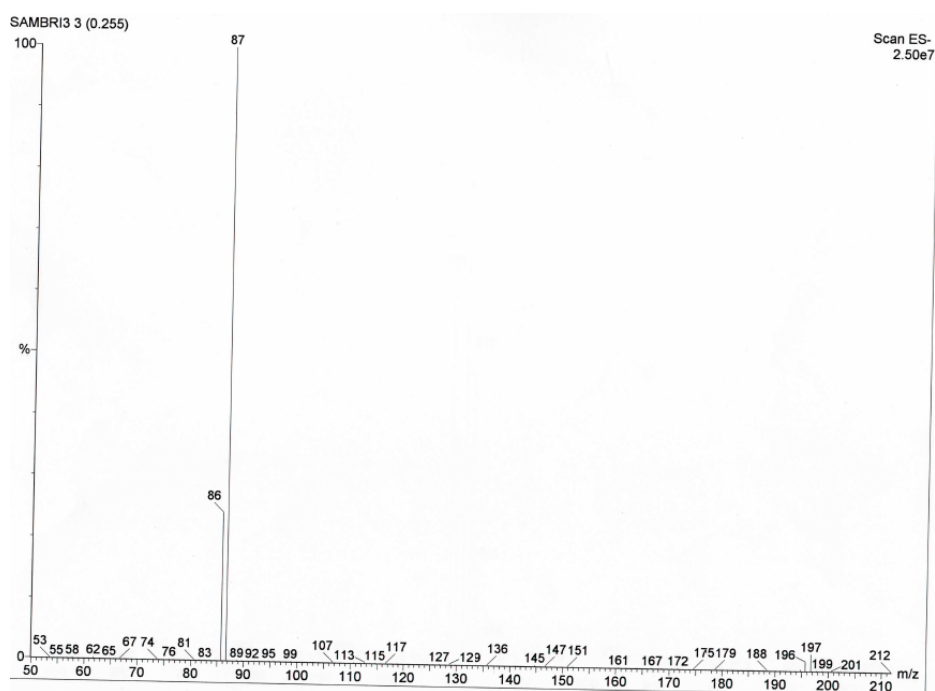
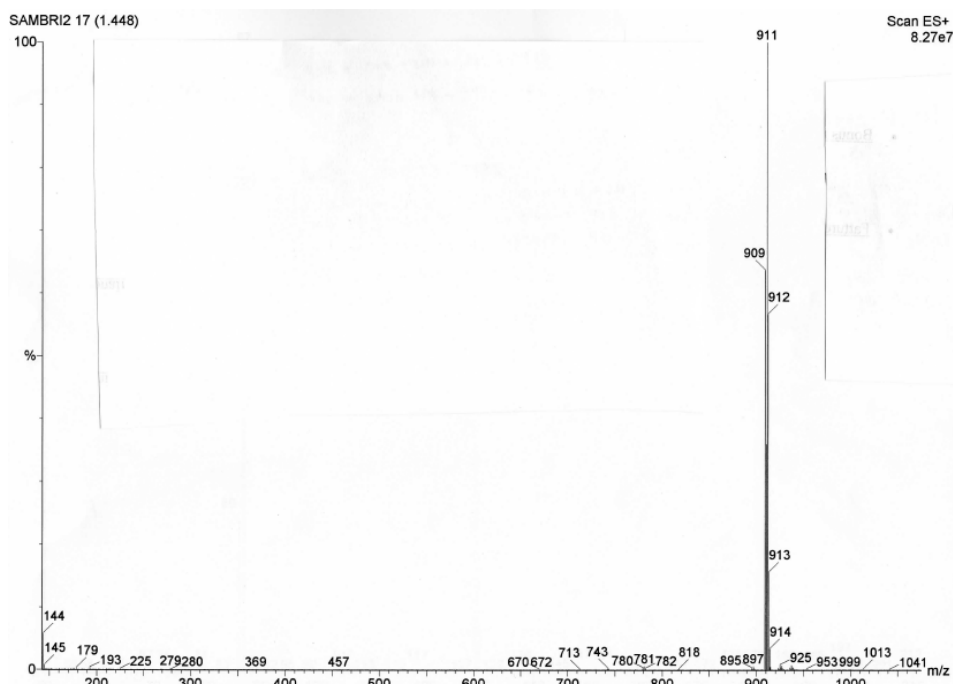
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