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	$C_{42}H_{23}N_4F_4Ir$, BF_4, 2 $CHCl_3$, CH_2Cl_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 ($I > 2\sigma(I)$)	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_2Cl_2, disordered over two positions (58:42 ratio).

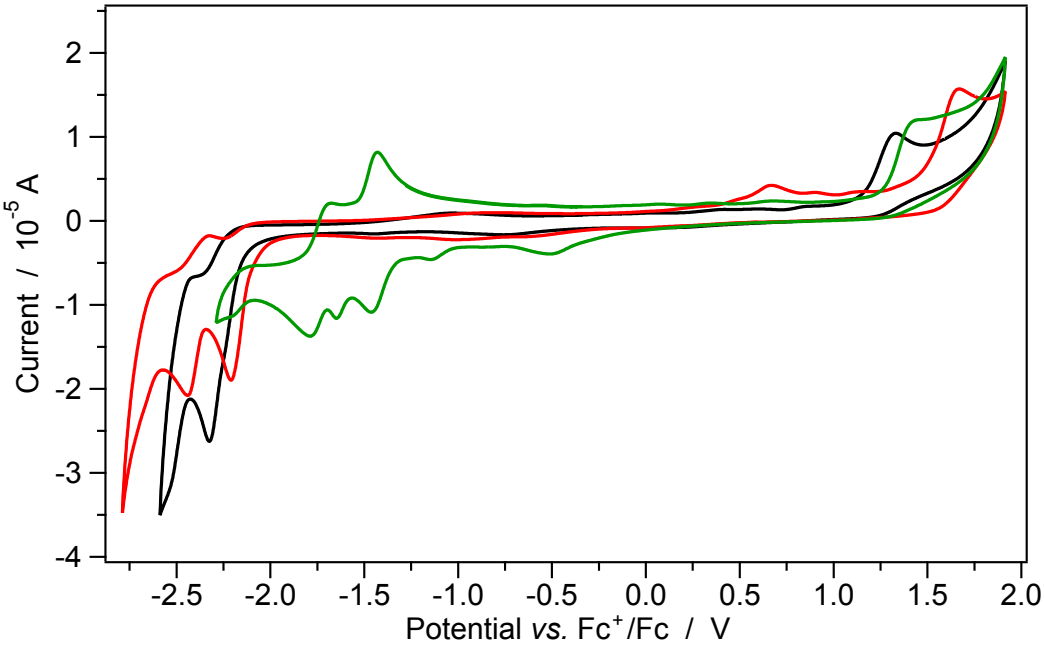


Fig. S1 Cyclic voltammograms of complexes **2–4** (approx. 1 mM) in room-temperature acetonitrile solution (with 0.1 M $TBAPF_6$) recorded at a scan rate of 100 mV s^{-1}.

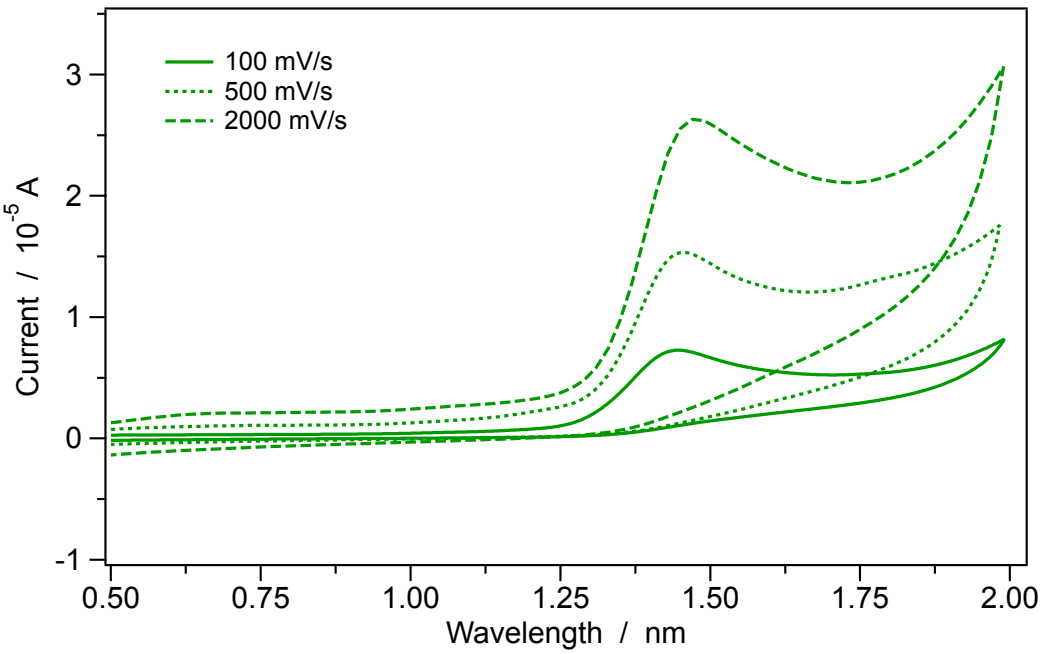


Fig. S2 Cyclic voltammograms of complexes **4** (approx. 1 mM) in room-temperature acetonitrile solution (with 0.1 M $TBAPF_6$) recorded at different scan rates to evaluate the irreversibility of the oxidation processes.

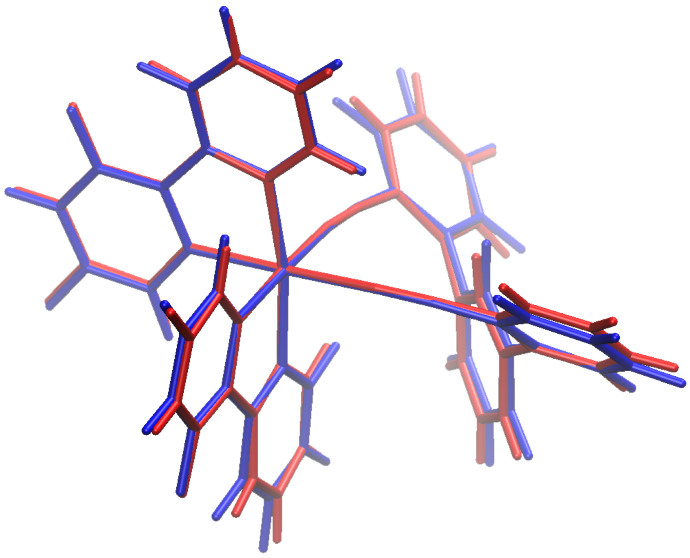


Fig. S3 Structural overlay between the experimental X-ray structure (reported in red) of the cationic part of complex **3** and the theoretically computed one (in blue). The structural overlay is calculated by minimizing the root-mean-square deviation (RMSD) of all the atomic positions, except hydrogen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

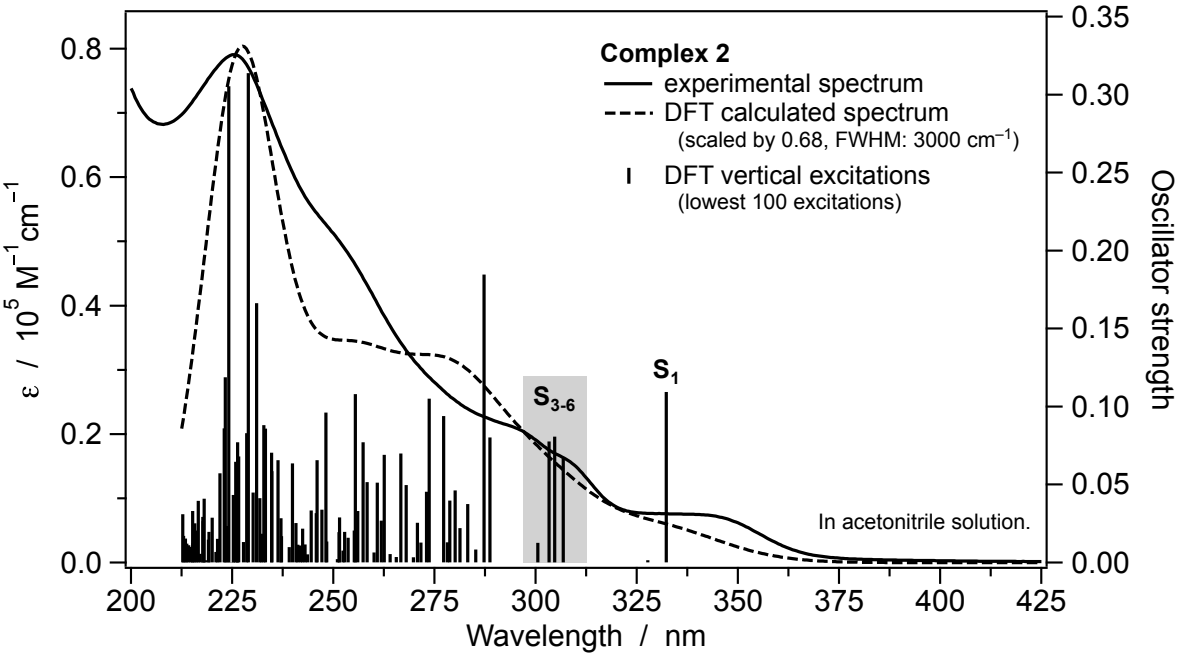


Fig. S4 Simulated absorption spectrum of complex **2** (dashed black line) obtained by convoluting the lowest 100 singlet vertical excitations (black bars) with Gaussian having FWHM of 3000 cm^{-1}. The simulated spectrum is compared with the room-temperature experimental absorption profile of **2**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

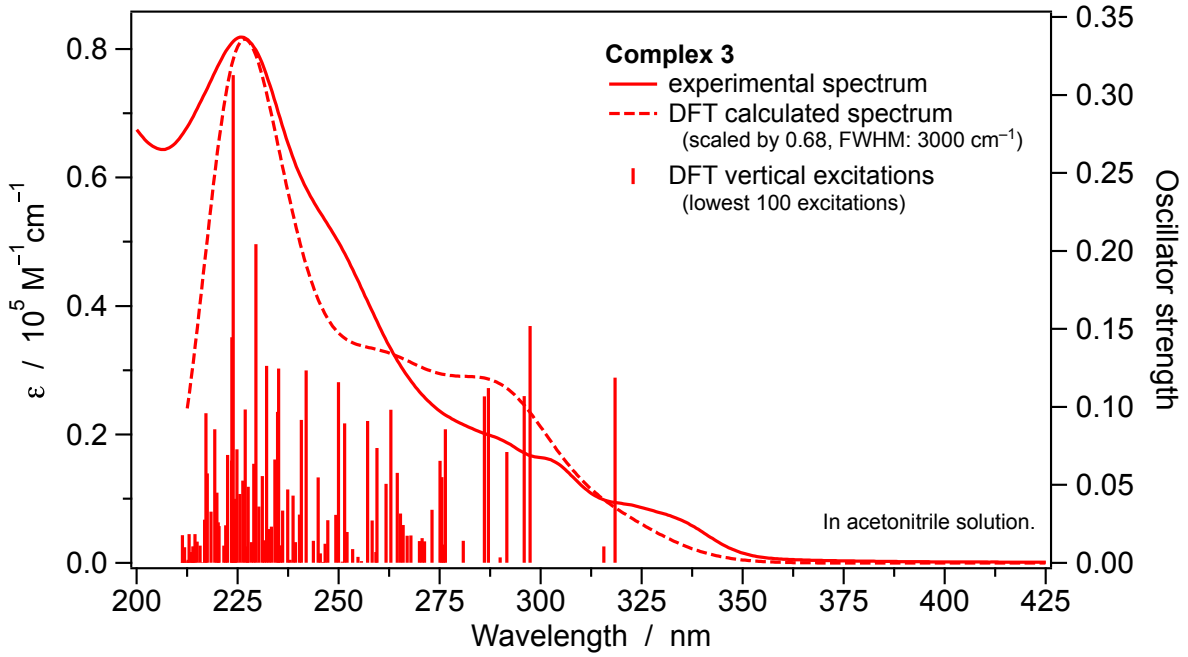


Fig. S5 Simulated absorption spectrum of complex **3** (dashed red line) obtained by convoluting the lowest 100 singlet vertical excitations (red bars) with Gaussian having FWHM of 3000 cm^{-1}. The simulated spectrum is compared with the room-temperature experimental absorption profile of **3** in acetonitrile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

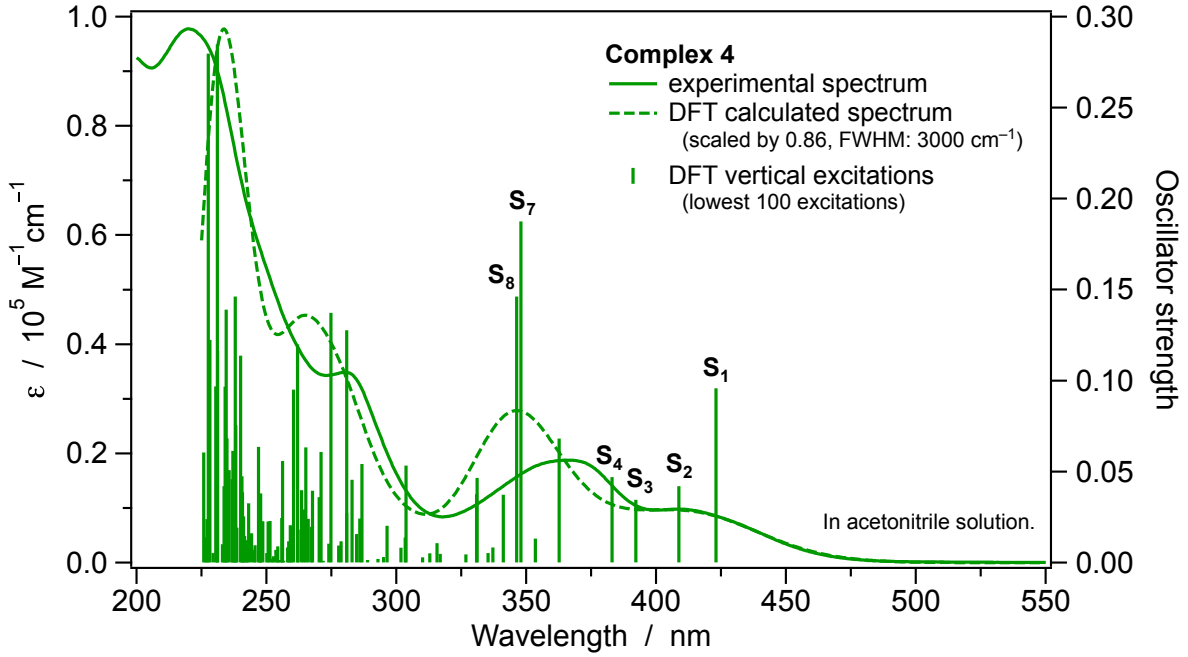


Fig. S6 Simulated absorption spectrum of complex **4** (dashed green line) obtained by convoluting the lowest 100 singlet vertical excitations (green bars) with Gaussian having FWHM of 3000 cm^{-1}. The simulated spectrum is compared with the room-temperature experimental absorption profile of **3**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

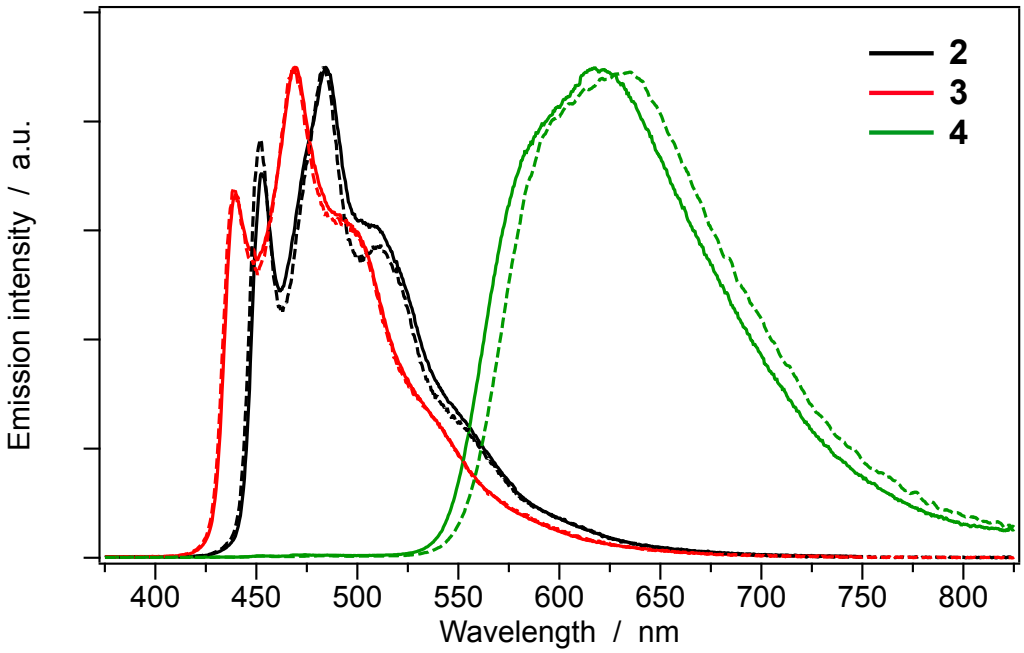
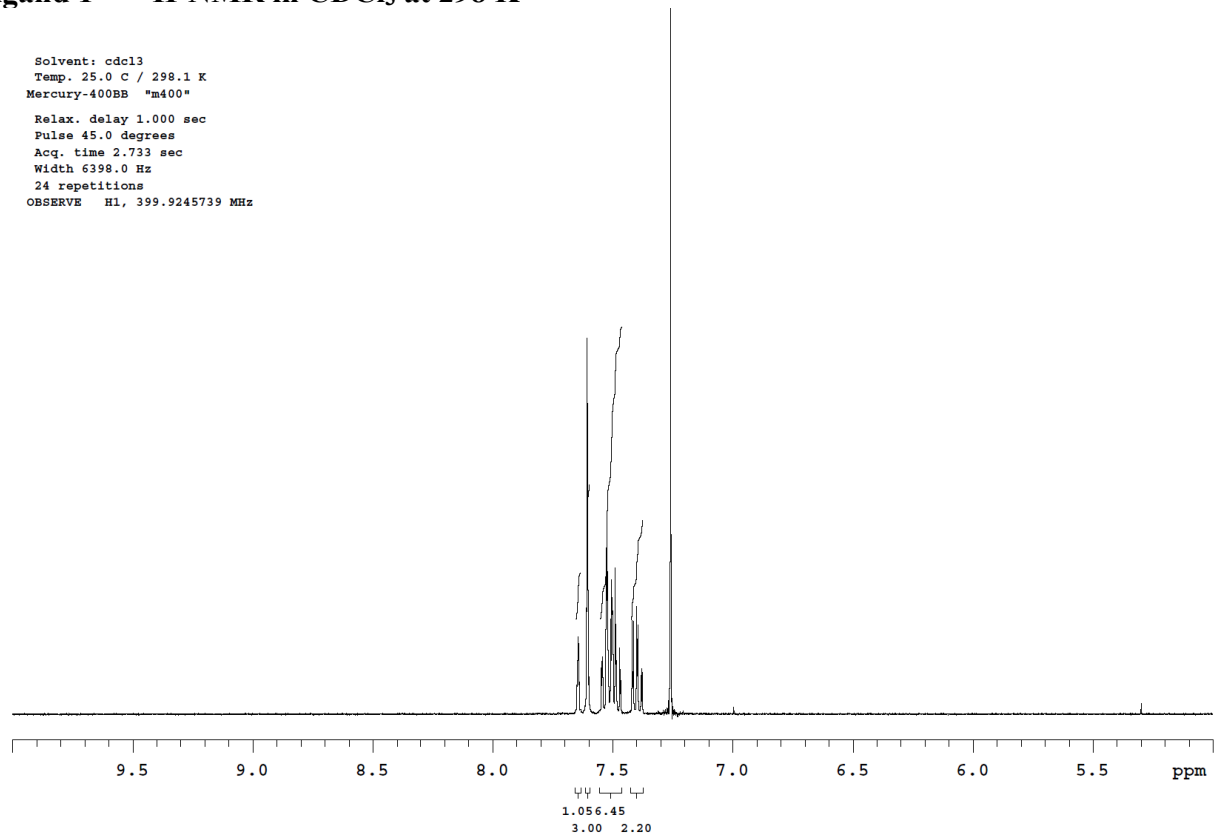


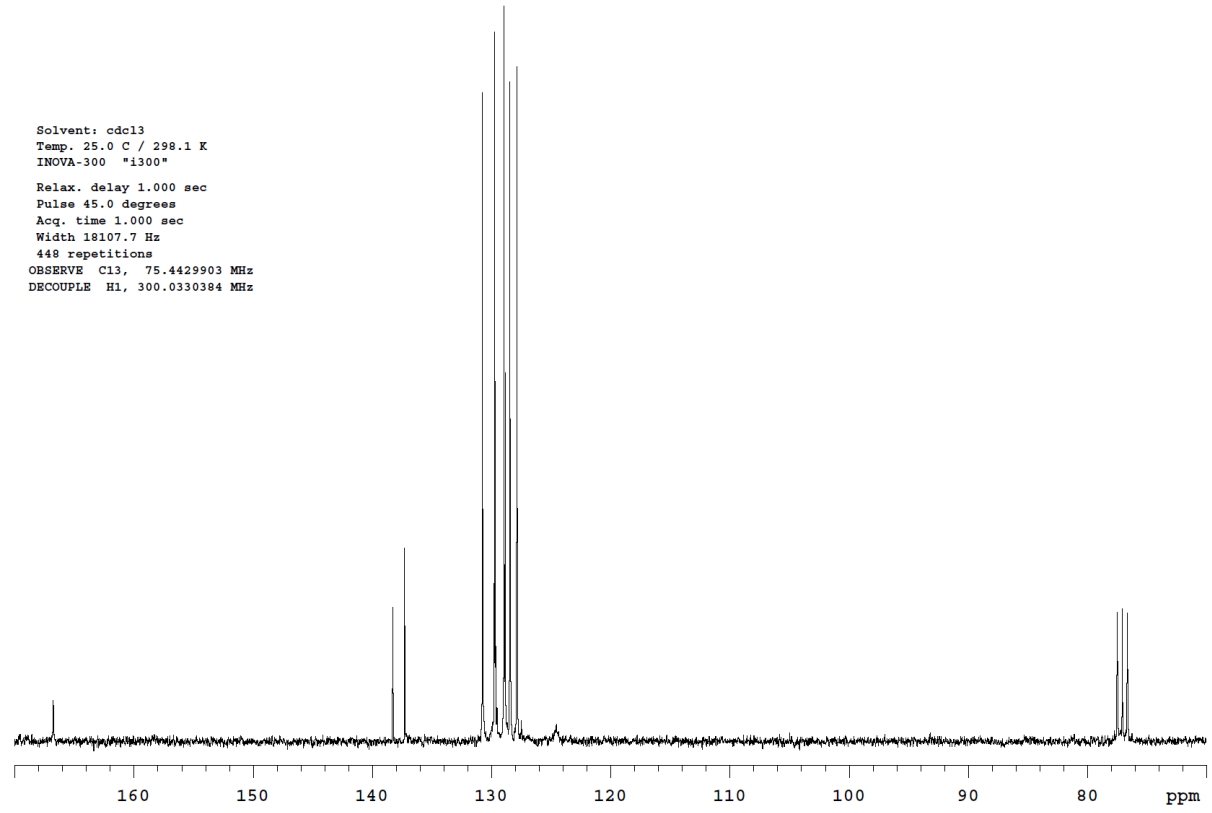
Fig. S7 Normalized emission spectra of **2–4** in PMMA matrix 1% w./w. at 298 K (full lines). The emission spectra in RT acetonitrile solution are also reported (dashed lines) for comparison.

NMR SPECTRA

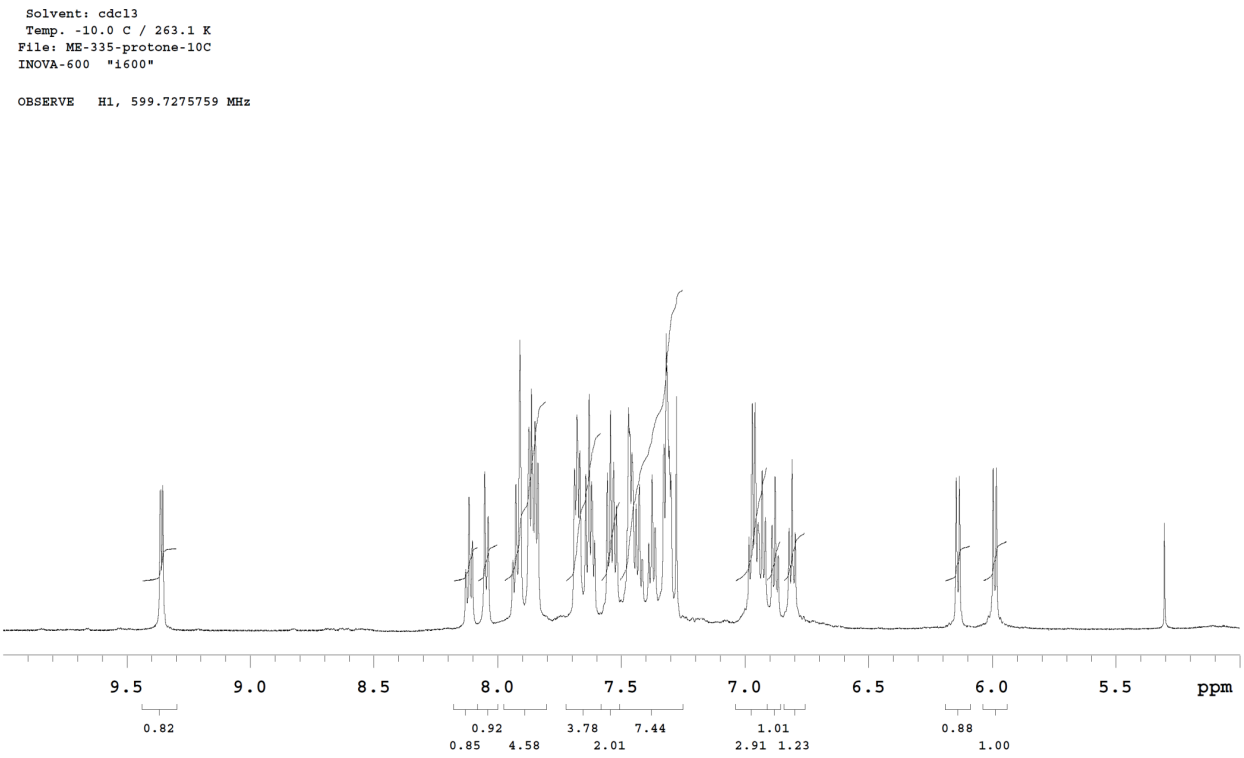
Ligand 1 — ^{1}H-NMR in $CDCl_3$ at 298 K



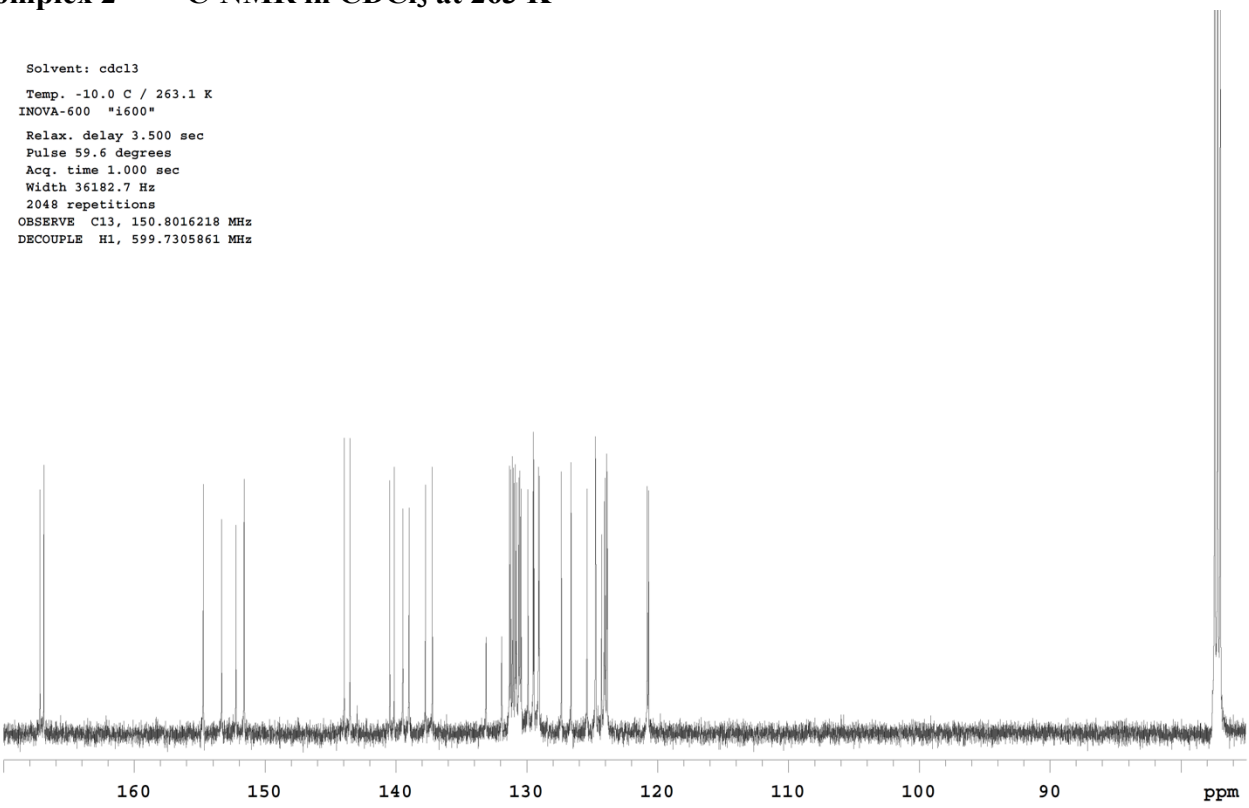
Ligand 1 — ^{13}C-NMR in $CDCl_3$ at 298 K



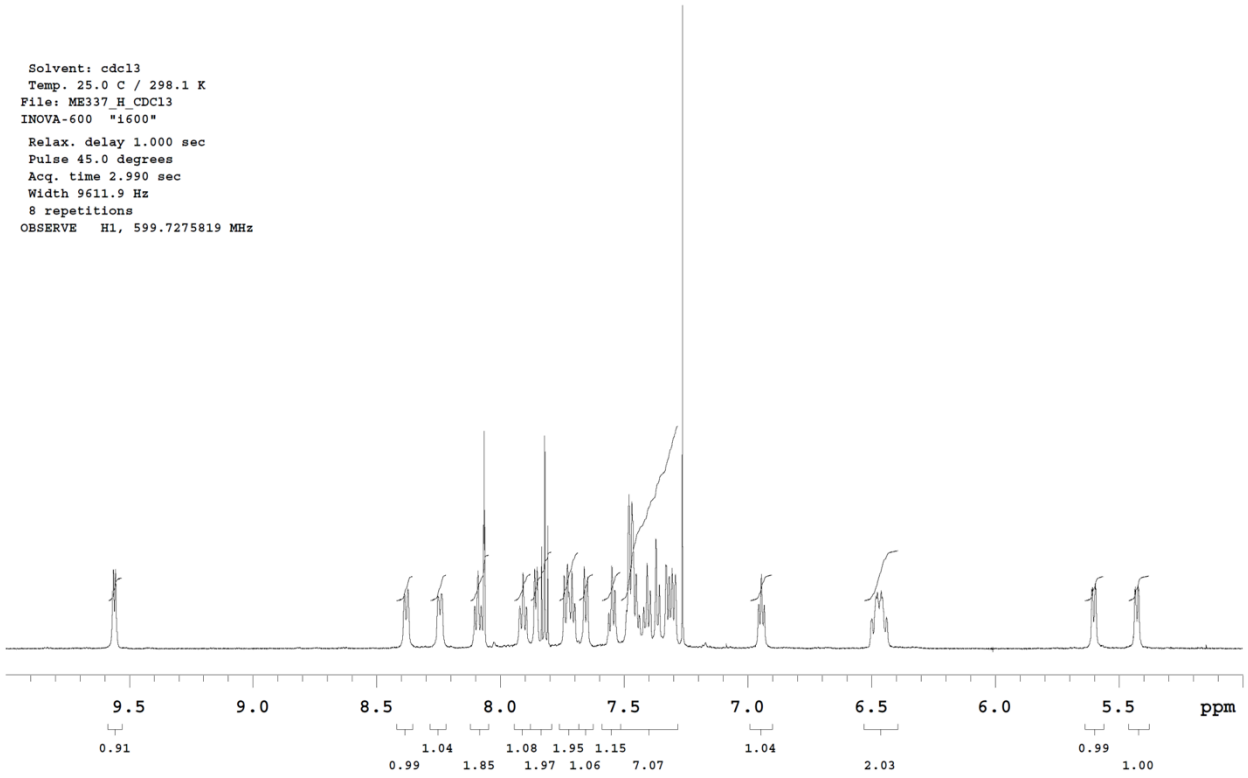
Complex 2 — ^{1}H-NMR in $CDCl_3$ at 263 K



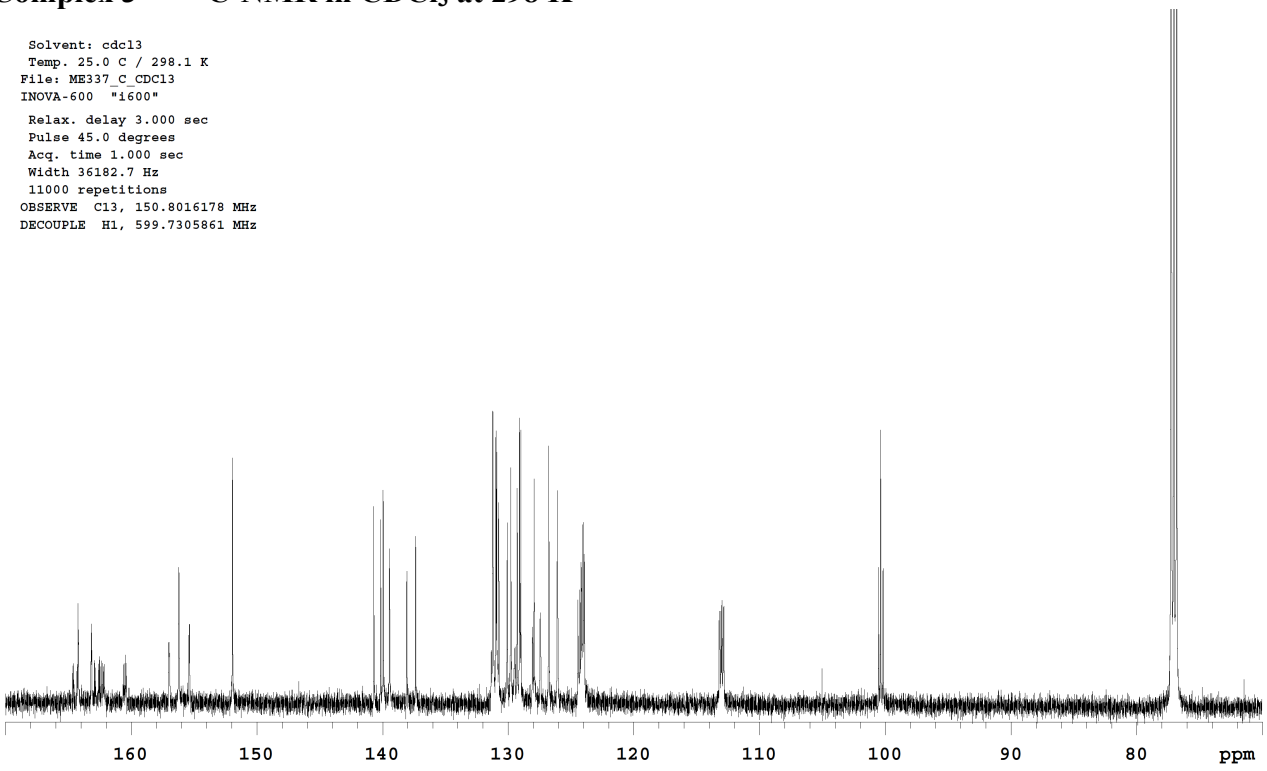
Complex 2 — ^{13}C-NMR in $CDCl_3$ at 263 K



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



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



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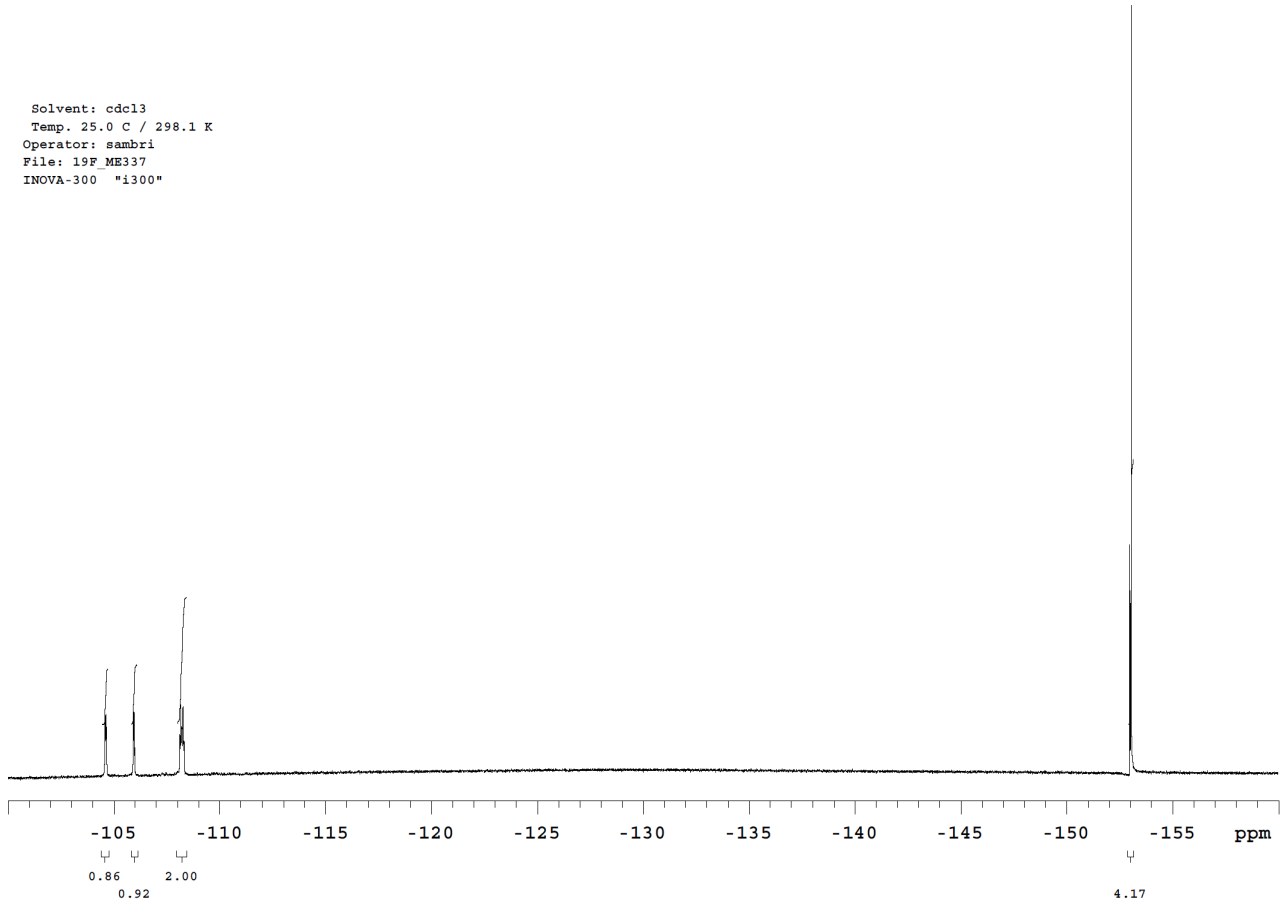
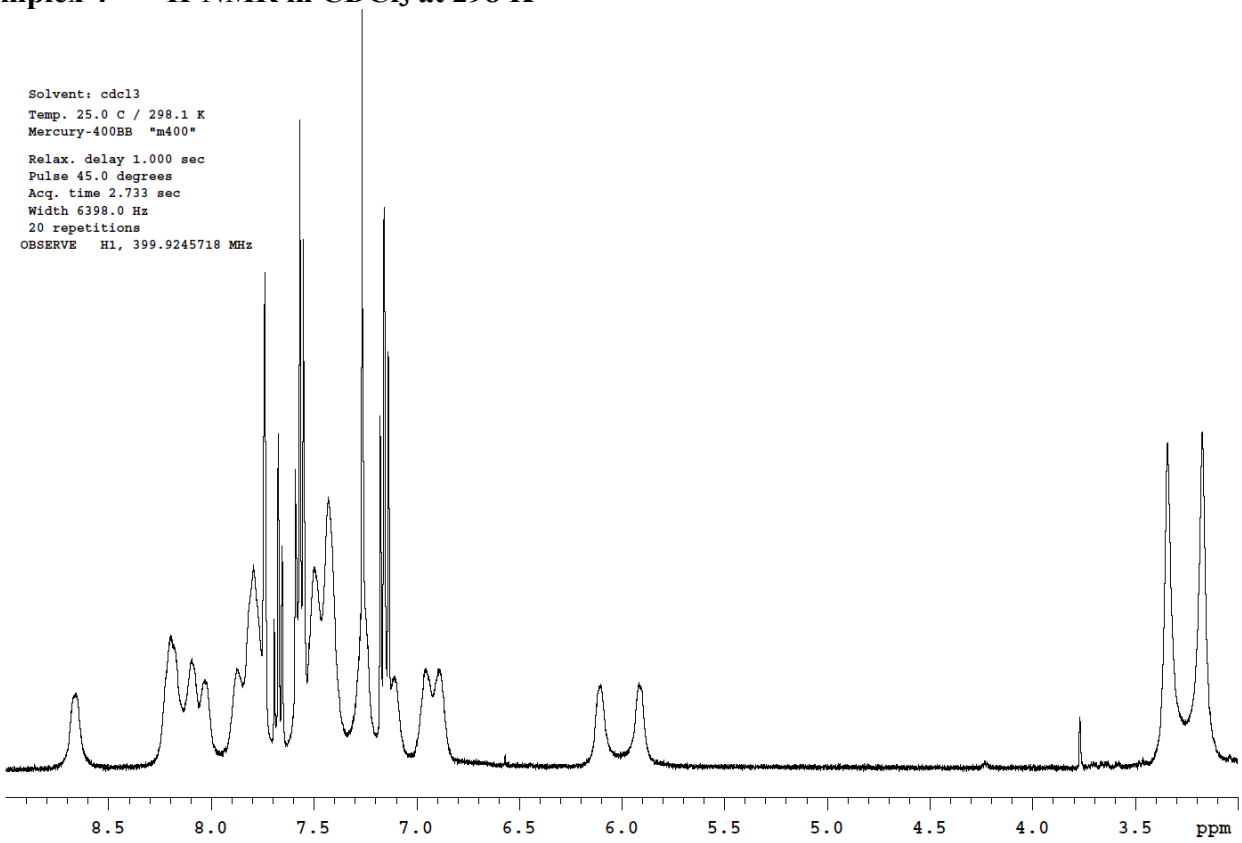
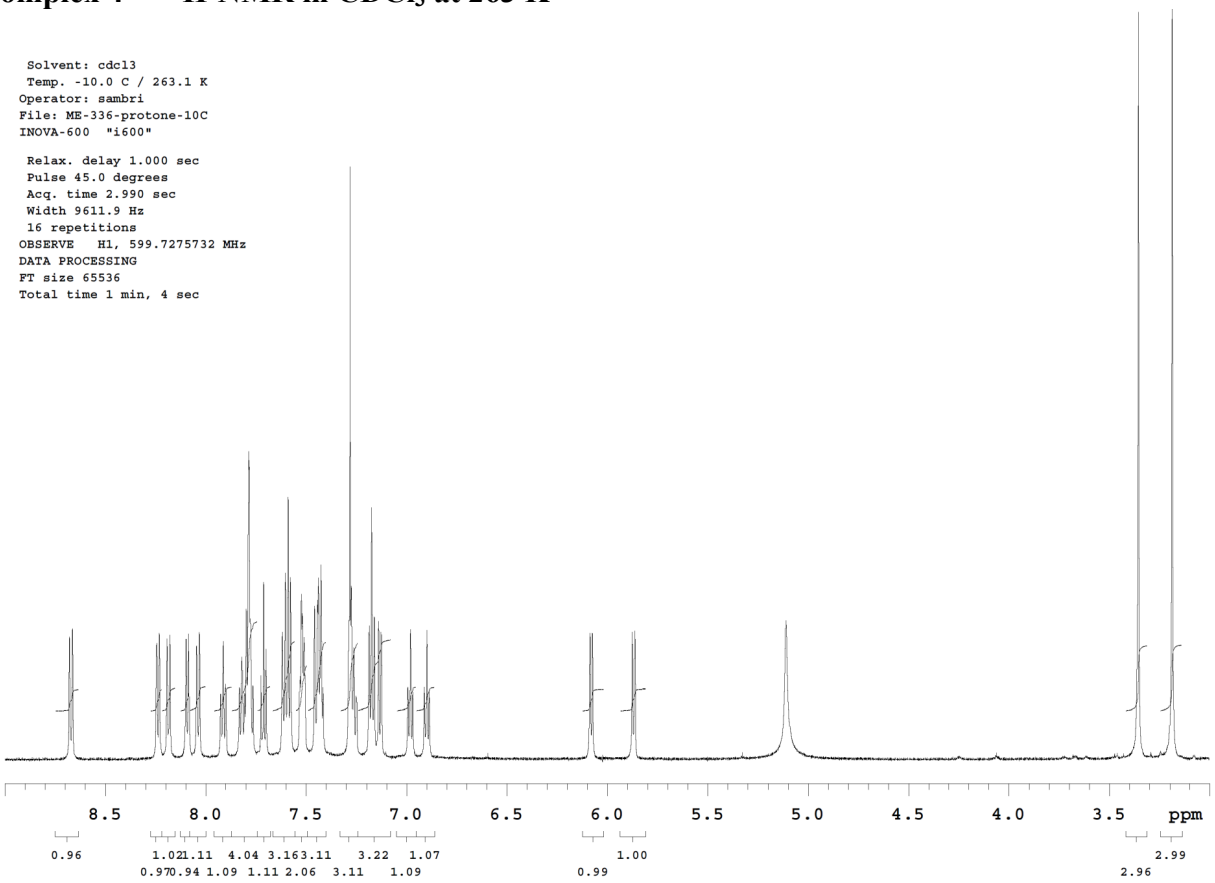


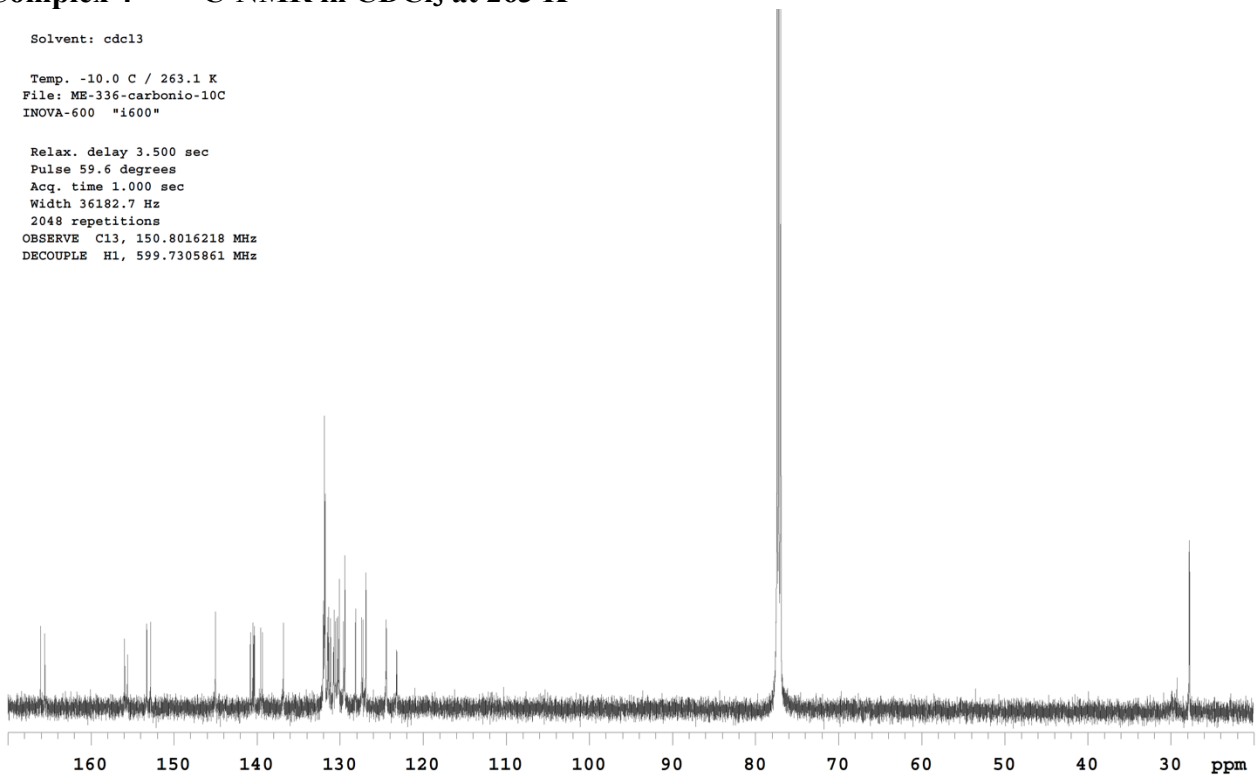
Complex 4 — ^{1}H-NMR in $CDCl_3$ at 298 K



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

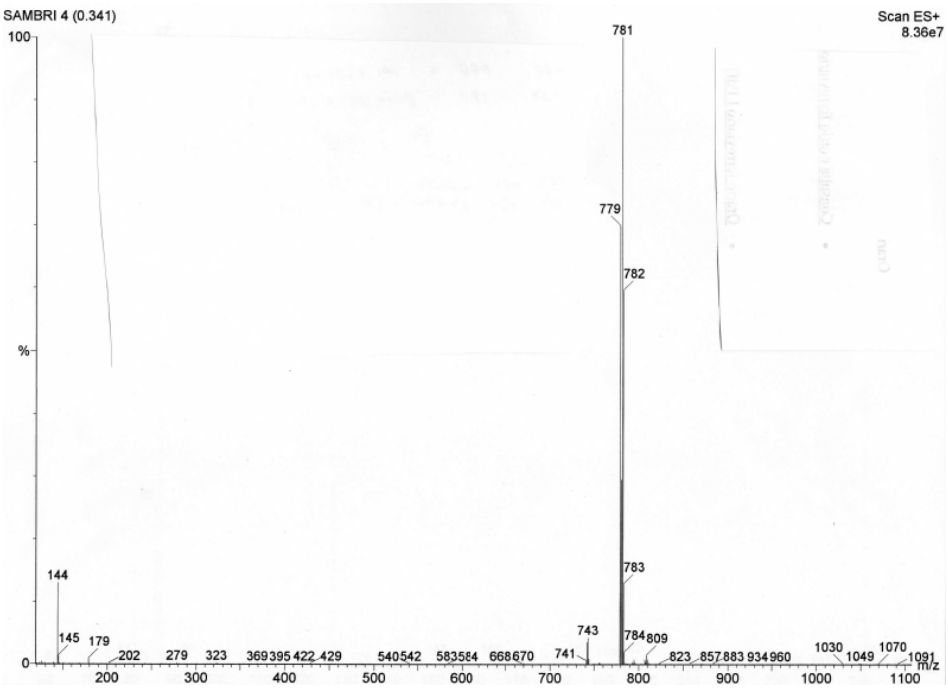


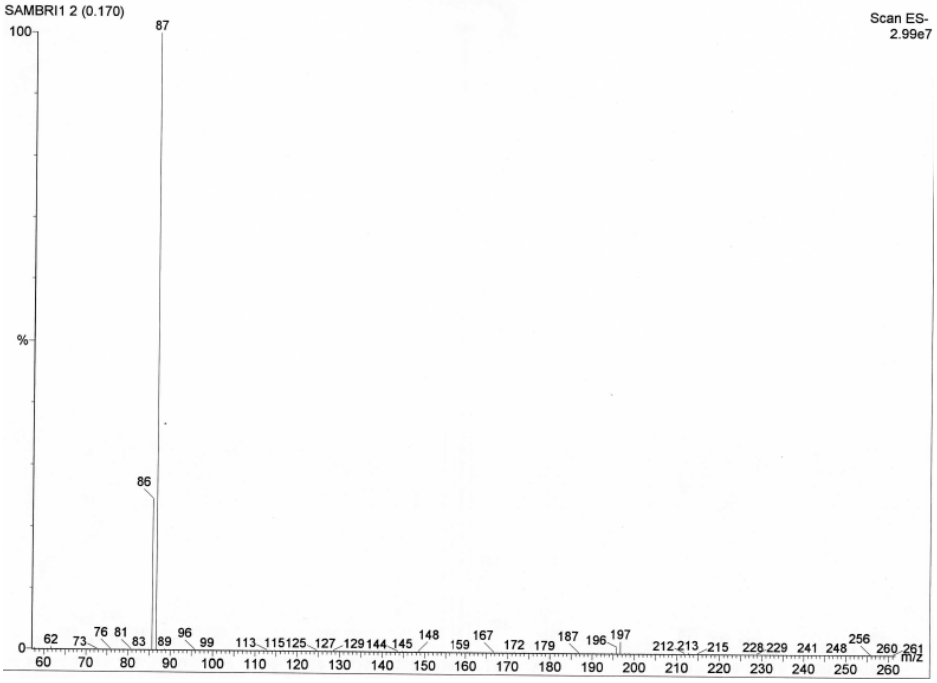
Complex 4 — ^{13}C-NMR in $CDCl_3$ at 263 K

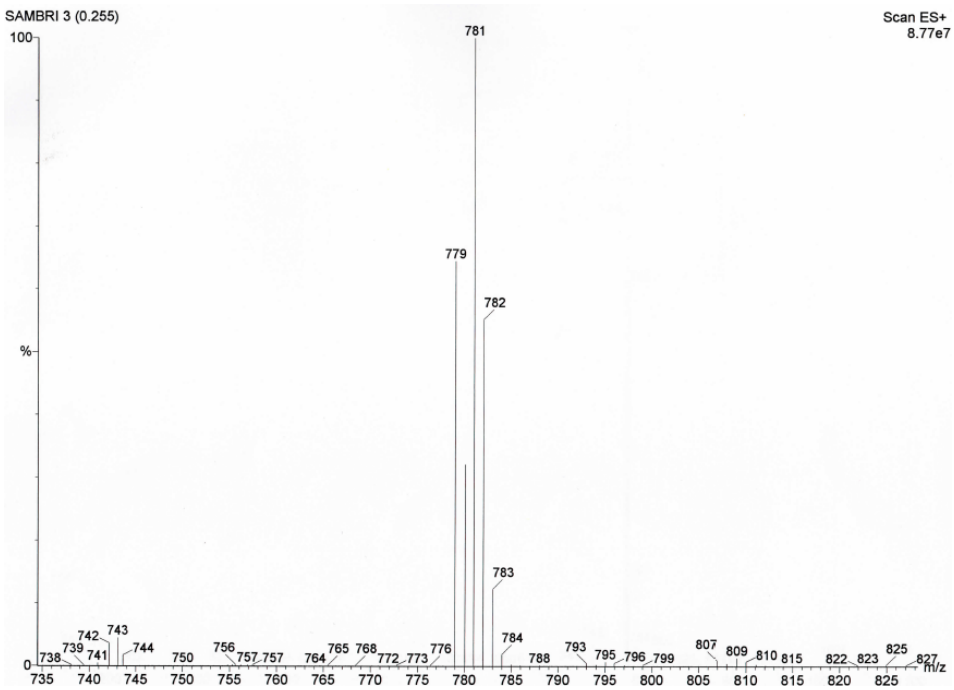


ESI–MS SPECTRA

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



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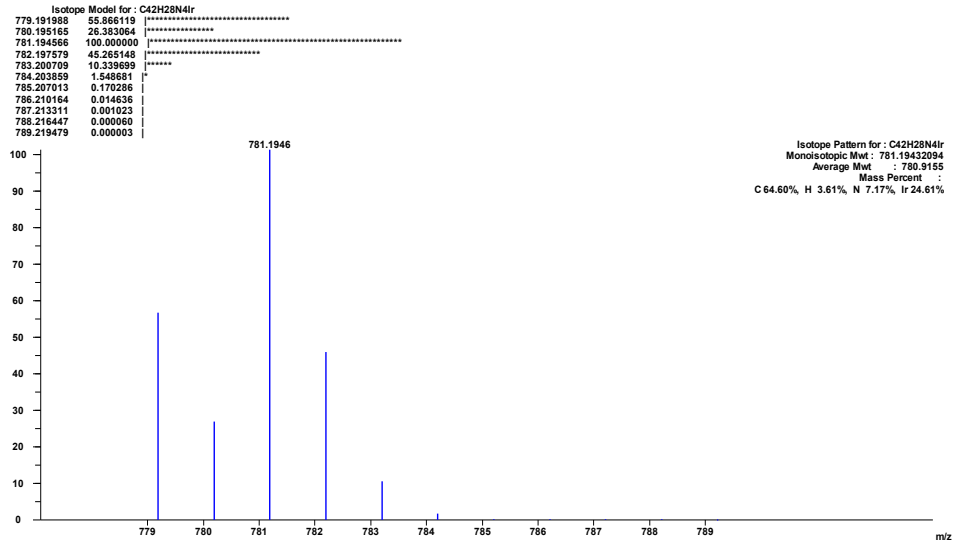
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Average Mwt : 780.9155
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80
70
60
50
40
30
20
10
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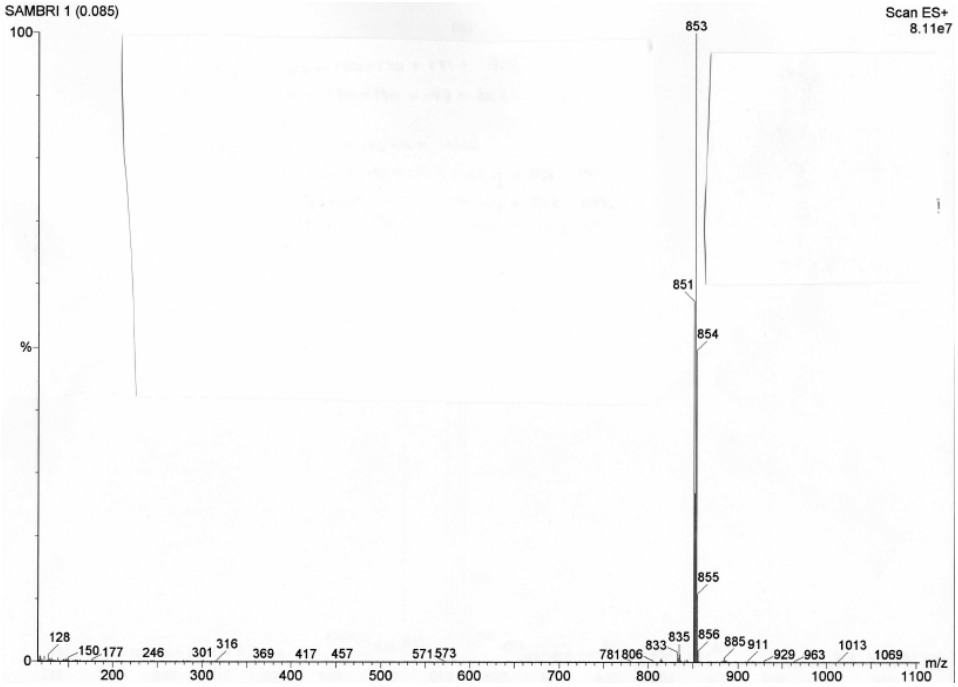
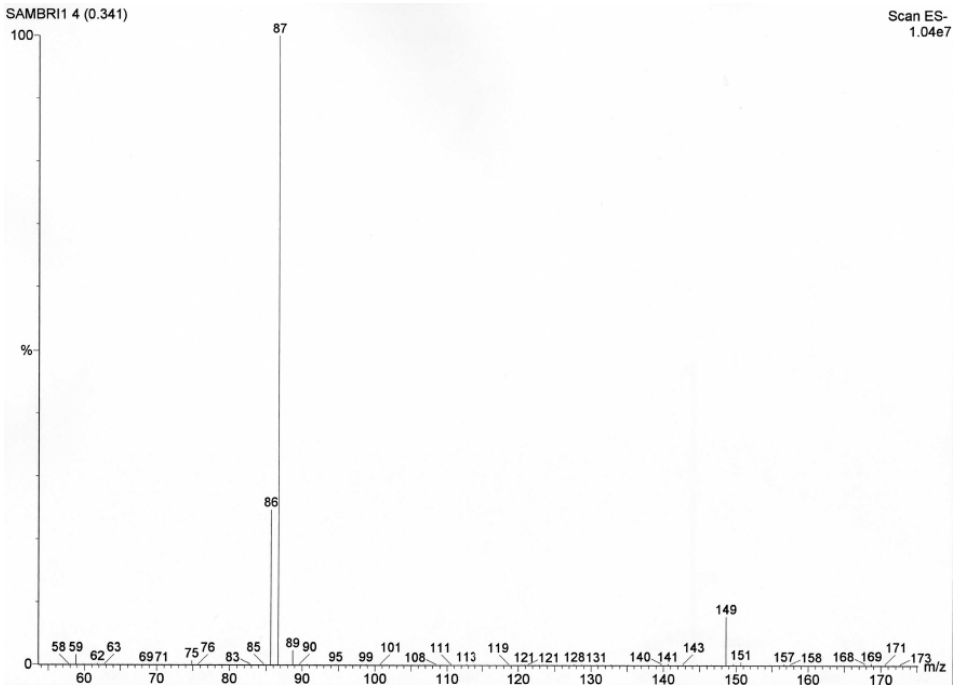
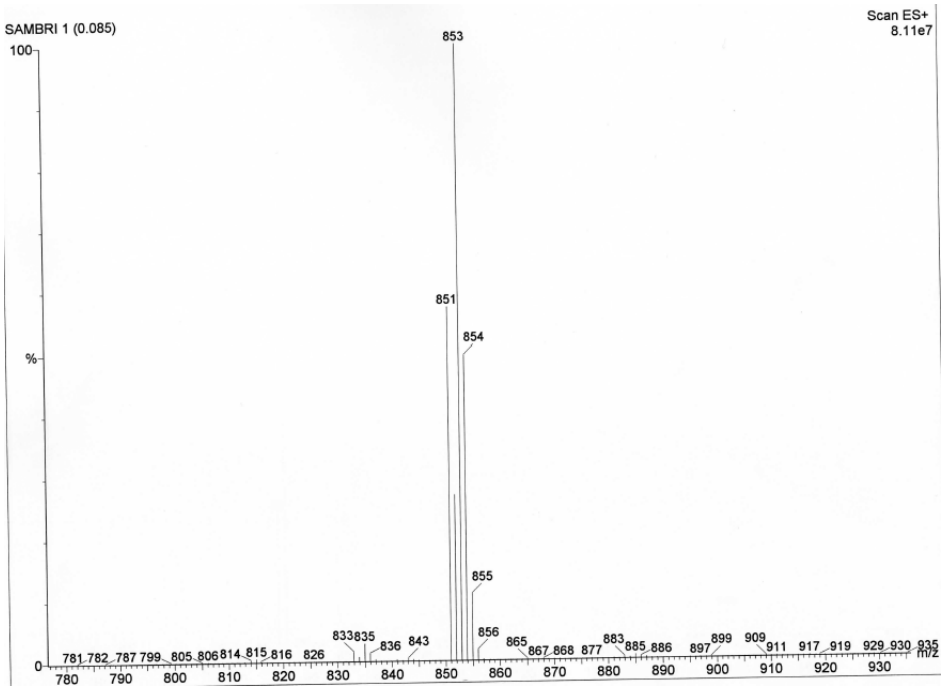
Complex 3 — ESI–MS spectra in acetonitrile (cations and anions) and simulated isotopic pattern of the cationic molecular ion.



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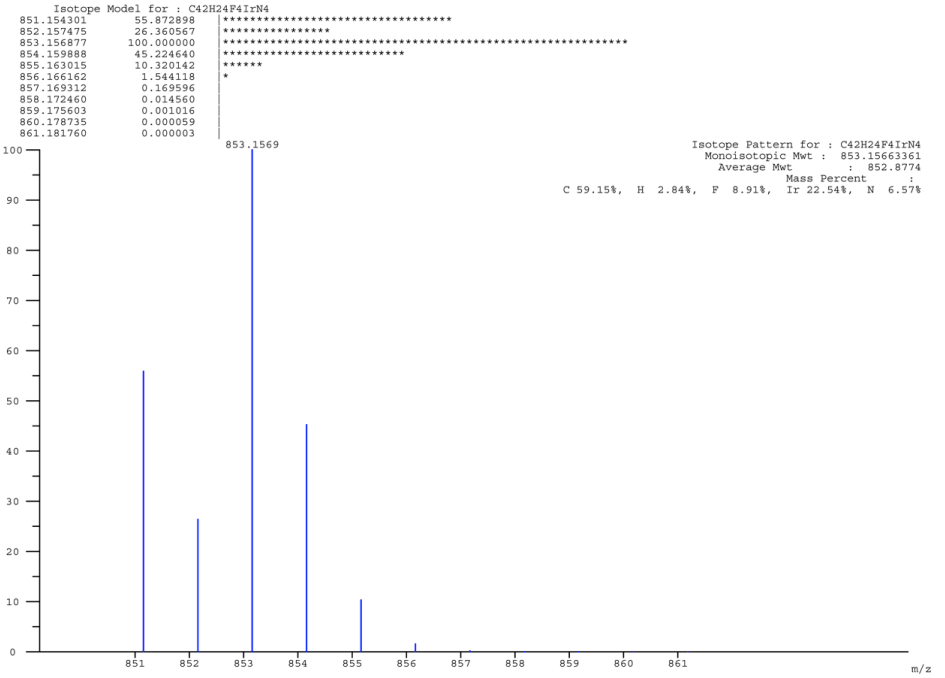
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80
70
60
50
40
30
20
10
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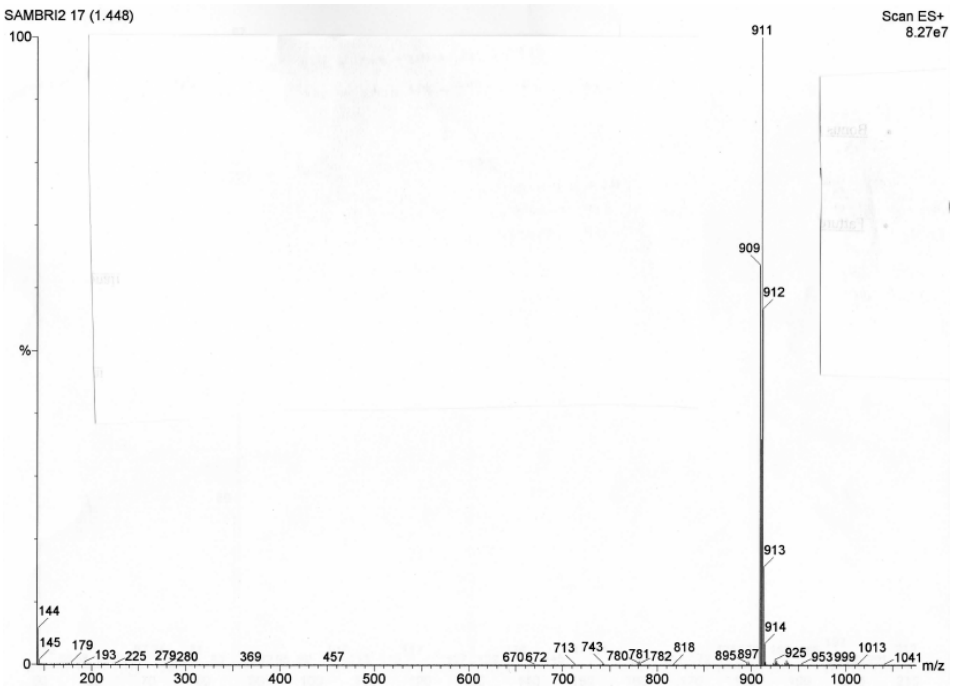
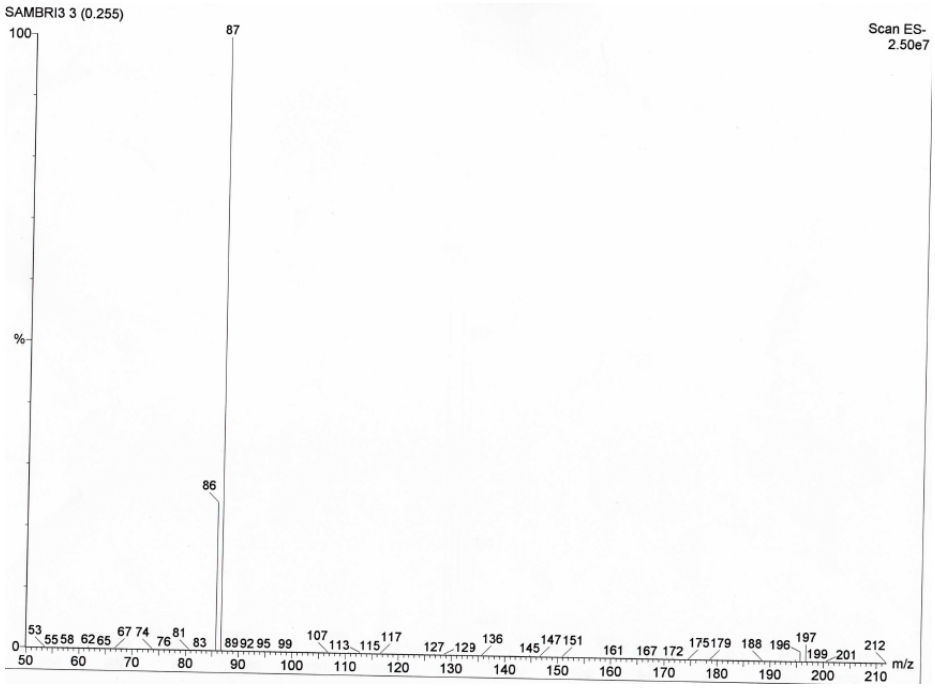
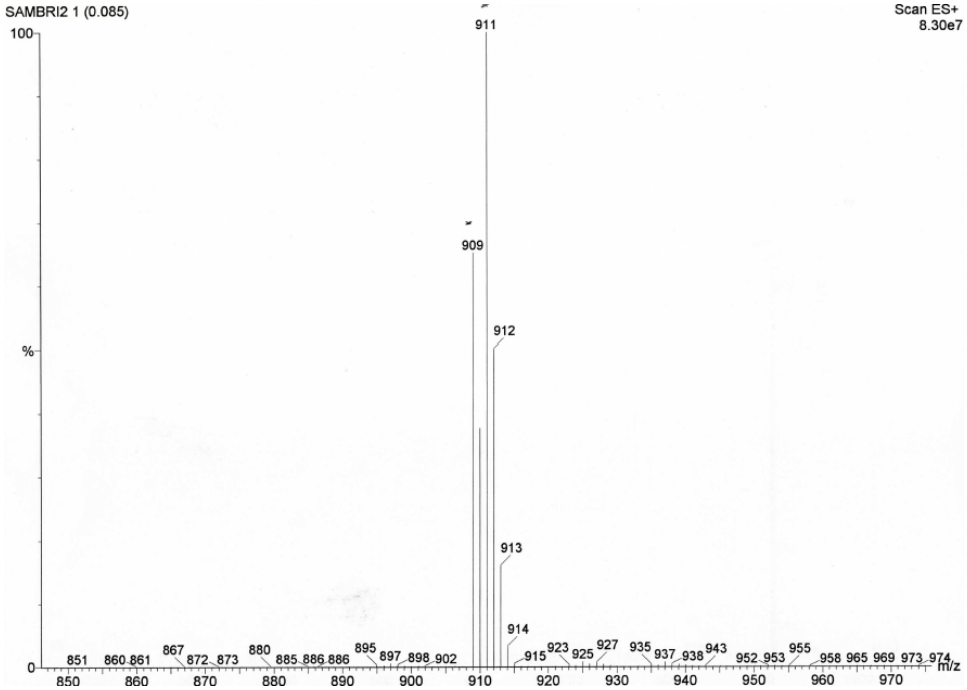
m/z

Complex 4 — ESI–MS spectra in acetonitrile (cations and anions) and simulated isotopic pattern of the cationic molecular ion.



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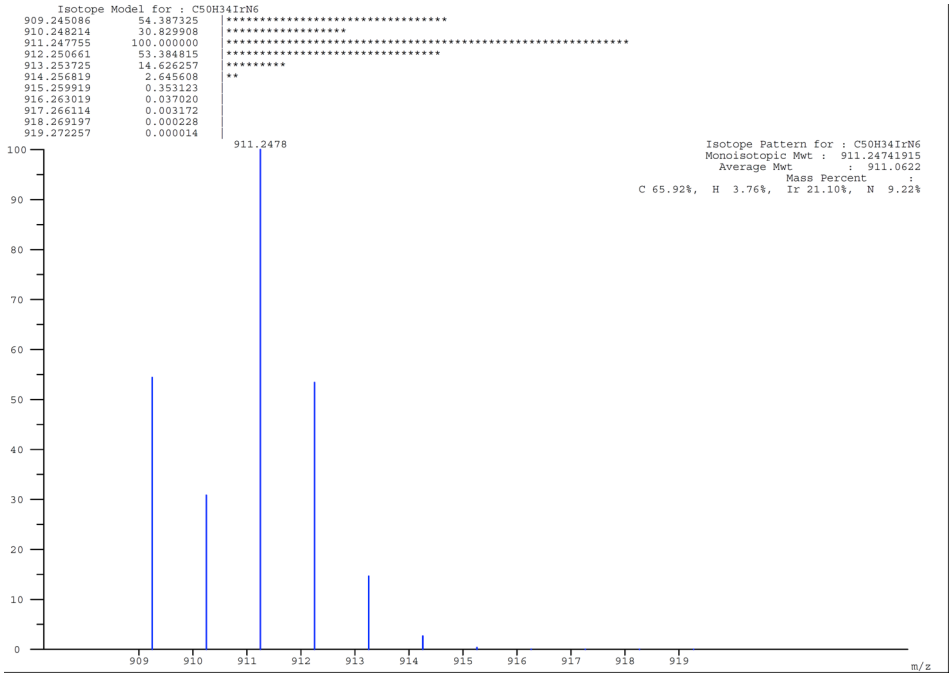
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914.256819 2.645608 **
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10
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m/z