Electronic Supplementary Information

DIFERROCENYLPYRYLIUM SALTS AND ELECTRON RICH BISPYRAN FROM OXIDATIVE COUPLING OF FERROCENYLPYRAN. EXAMPLE OF REDOX SYSTEMS SWITCHED BY PROTON TRANSFER

Fatou Ba,[1] Nolwenn Cabon,[1] Pascal Le Poul,[1] Samia Kahlal,[2] Jean- Yves Saillard,[2] Nicolas Le Poul,[3] Stephane Golhen,[2] Bertrand Caro∗,[1] Françoise Robin-Le Guen[1]

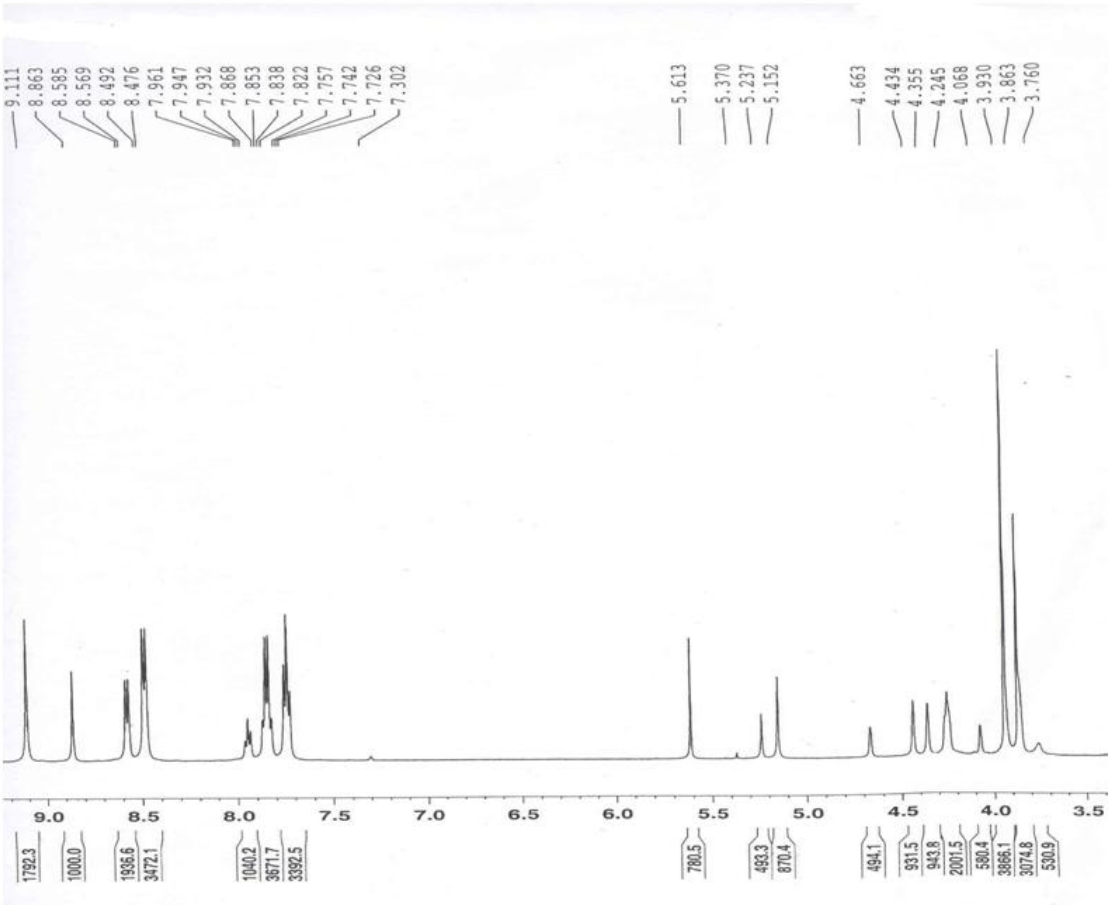
1) Institut Sciences Chimiques de Rennes, U.M.R. CNRS 6226, I.U.T. Lannion, B.P. 30219, rue E. Branly 22302 Lannion, France,

2) Institut Sciences Chimiques de Rennes, U.M.R. CNRS 6226, Université de Rennes 1, 263 avenue du Général Leclerc CS 74205 35042 Rennes Cedex, France

3) Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique, U.M.R. CNRS 6521, Université de Bretagne Occidentale, 6 avenue Victor Le Gorgeu CS 93837 29238 Brest Cedex 3, France.

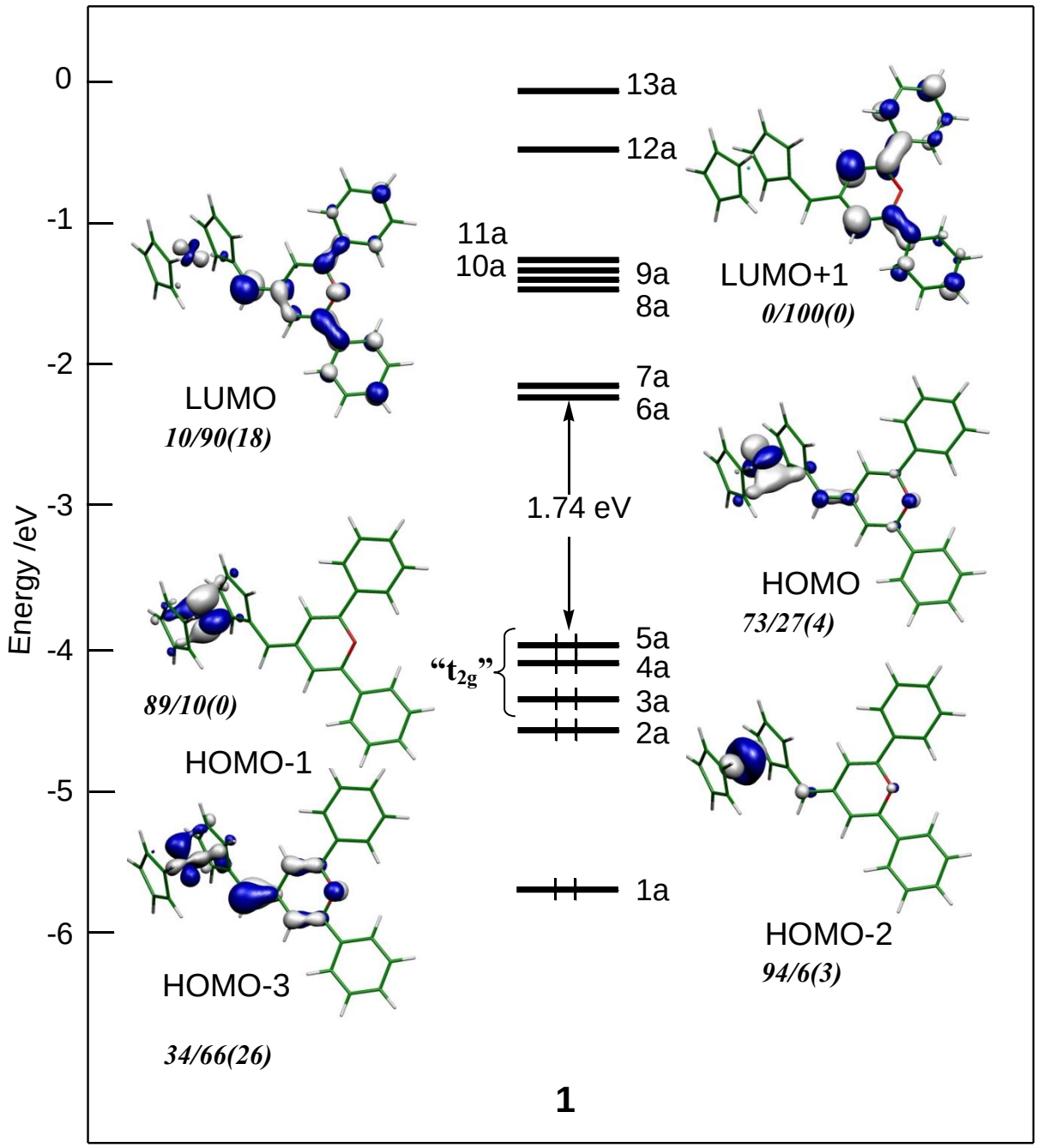
E- Mail: bertrand.caro@univ-rennes1.fr

ESI 01: ^{1}H NMR spectrum of 2^{2+}



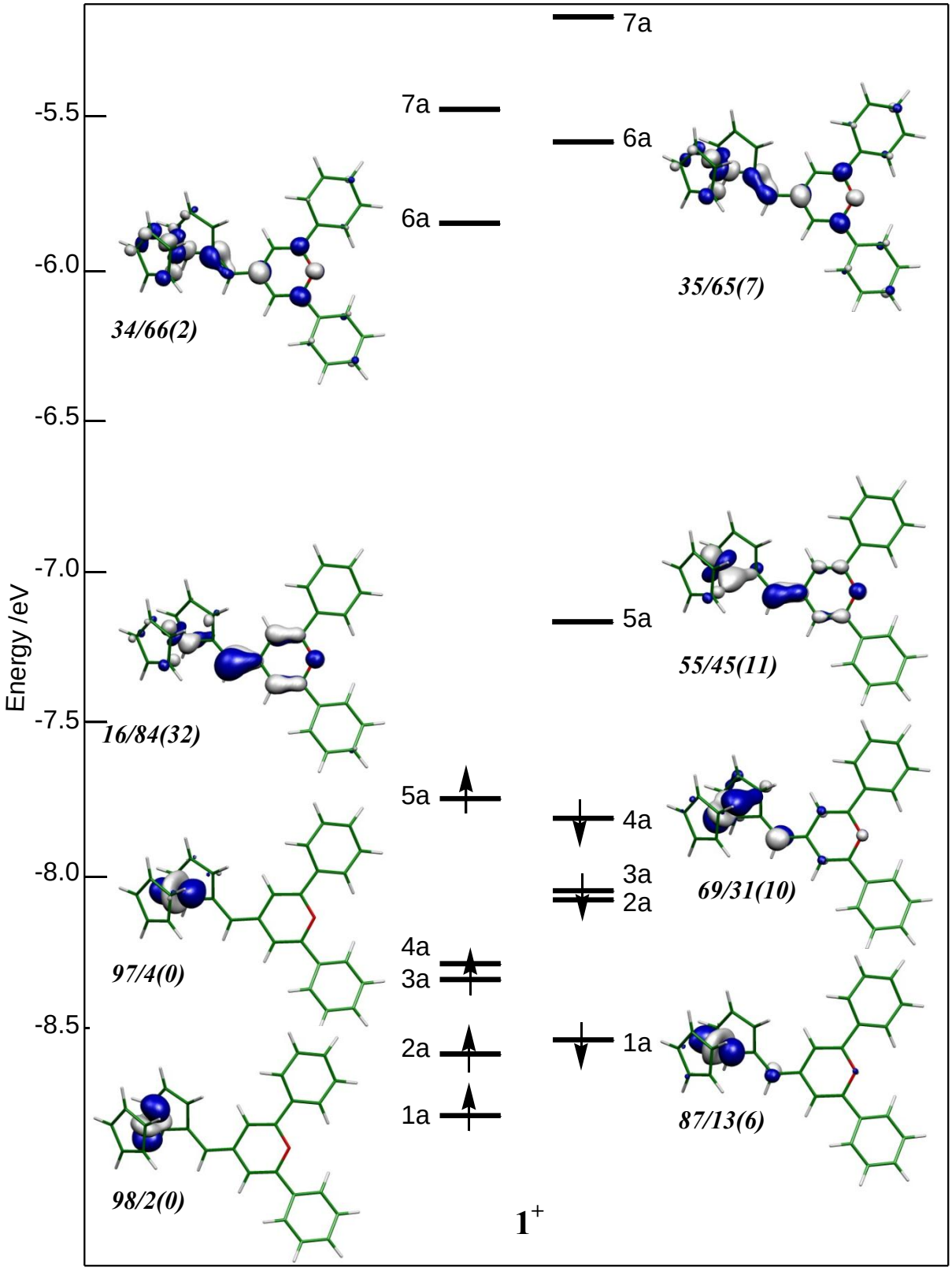
ESI 02: M.O. Diagrams

ESI 02-a) M.O. Diagram of **1**



MO diagram of **1**. The numerical values indicate the MO localization in (%) in the following order: Fe/ligand(C_α).

ESI 02-b) M.O. Diagram of **1**$^{+\cdot}$



MO diagram of $1^{+\cdot}$ The numerical values indicate the MO localization in (%) in the following order: Fe/ligand(C_2)

ESI 03: Spin density of $1^{+\cdot}$

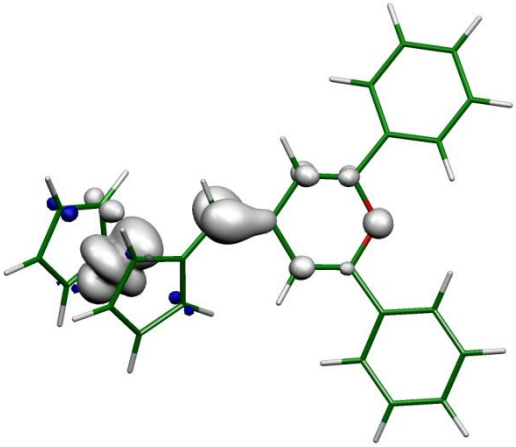


Figure : Plot of the total spin density for $\mathbf{1}^{+\bullet}$. The contour value is 0.003 [e/bohr^3].

ESI 04: Cartesian coordinates of the optimized geometries

1 C_1

Bonding Energy -340.14695689 eV

Atom	X	Y	Z (Angstrom)
1.C	3.165370	9.118214	8.351473
2.C	3.342416	7.702605	8.051352
3.C	3.439290	5.180775	5.327330
4.H	3.342224	7.011822	8.898075
5.C	3.504624	5.730624	6.565521
6.H	3.606485	5.065421	7.421525
7.C	3.384574	7.157413	6.788336
8.C	3.197993	7.920076	5.570830
9.H	3.026013	8.990533	5.639351
10.C	3.117245	7.334321	4.351850
11.C	3.503602	3.746277	5.007571
12.C	4.072986	2.822520	5.906577
13.H	4.520904	3.176285	6.835480
14.C	4.096891	1.461432	5.609628

15.H	4.548075	0.763856	6.316532
16.C	3.561334	0.989820	4.405098
17.H	3.583389	-0.075926	4.173351
18.C	3.007780	1.897671	3.498623
19.H	2.589601	1.542424	2.555635
20.C	2.981909	3.261505	3.792822
21.H	2.543246	3.962763	3.085995
22.C	2.829095	8.026682	3.085913
23.C	2.953039	9.427322	2.983322
24.H	3.316400	10.004074	3.833590
25.C	2.628612	10.087713	1.801410
26.H	2.731567	11.172294	1.745817
27.C	2.180405	9.366818	0.687782
28.H	1.924387	9.886613	-0.236600
29.C	2.071289	7.976545	0.770207
30.H	1.726556	7.403965	-0.092148
31.C	2.395527	7.311002	1.954095
32.H	2.301519	6.228631	2.013083
33.C	2.260074	9.658758	9.343633
34.H	1.632761	9.066988	10.005554
35.C	2.288509	11.089004	9.264071
36.H	1.702598	11.774280	9.871011
37.C	3.240441	11.457998	8.255783
38.H	3.512892	12.471300	7.971756
39.C	3.788359	10.252386	7.706379
40.H	4.567264	10.192039	6.950371
41.C	5.683071	9.281401	10.705854
42.H	5.954715	8.252621	10.483205
43.C	4.700812	9.708793	11.660642

44.H	4.100918	9.061743	12.295891
45.C	4.642561	11.143053	11.625144
46.H	3.987317	11.771172	12.223769
47.C	5.585481	11.600039	10.645068
48.H	5.771868	12.636208	10.373551
49.C	6.227420	10.449140	10.075967
50.H	6.989264	10.460427	9.300670
51.O	3.252508	5.961668	4.192541
52.Fe	4.162869	10.359825	9.753713

$[1]^+$ S=1/2 C_1

Bonding Energy -334.43373602 eV

Atom	**X**	**Y**	**Z (Angstrom)**
1.C	2.906295	9.125410	8.373447
2.C	3.045356	7.749198	8.030533
3.C	3.376964	5.221704	5.325621
4.H	2.883041	7.032135	8.838009
5.C	3.346622	5.792760	6.568832
6.H	3.382769	5.141482	7.439511
7.C	3.214156	7.207297	6.743123
8.C	3.114573	7.968097	5.535426
9.H	2.918088	9.034731	5.577517
10.C	3.105006	7.362691	4.307937
11.C	3.488526	3.792046	5.027769
12.C	4.043873	2.905754	5.973031
13.H	4.445668	3.287856	6.911626
14.C	4.119249	1.542412	5.700382
15.H	4.560729	0.868070	6.434200
16.C	3.642546	1.040493	4.484096

17.H	3.700522	-0.027906	4.274006
18.C	3.097642	1.912419	3.536354
19.H	2.723557	1.525054	2.588446
20.C	3.024782	3.278326	3.800639
21.H	2.589724	3.951027	3.064261
22.C	2.876592	8.027335	3.021696
23.C	3.012108	9.426024	2.904614
24.H	3.351178	10.018024	3.754443
25.C	2.736350	10.064225	1.699091
26.H	2.847689	11.145885	1.622127
27.C	2.322492	9.320626	0.588032
28.H	2.099872	9.823679	-0.353561
29.C	2.198386	7.931848	0.688344
30.H	1.876202	7.348473	-0.174376
31.C	2.476820	7.287065	1.892055
32.H	2.367733	6.207106	1.965951
33.C	2.211737	9.605028	9.558095
34.H	1.670470	8.976796	10.260297
35.C	2.245743	11.033834	9.561083
36.H	1.756770	11.678934	10.285358
37.C	3.049392	11.461578	8.454928
38.H	3.295747	12.488912	8.201434
39.C	3.489881	10.298140	7.751039
40.H	4.160117	10.296042	6.896391
41.C	5.865988	9.272401	10.632817
42.H	6.144123	8.242175	10.423299
43.C	4.951781	9.702695	11.643866
44.H	4.443587	9.066538	12.363578
45.C	4.844283	11.131975	11.557169

46.H	4.238366	11.766410	12.198560
47.C	5.679220	11.572013	10.478947
48.H	5.817466	12.600449	10.156561
49.C	6.304183	10.416976	9.903159
50.H	6.997241	10.414830	9.066308
51.O	3.260955	6.002835	4.200118
52.Fe	4.168123	10.284529	9.759991

$[1\text{-H}]^+$ C_1

Bonding Energy -338.26257419 eV

Atom	**X**	**Y**	**Z (Angstrom)**
1.C	7.855205	6.532827	1.323332
2.C	6.588781	7.172890	.793443
3.C	3.741737	4.644672	.911557
4.C	4.885047	5.313259	.515495
5.H	5.428732	4.958092	-.356169
6.C	5.341158	6.440760	1.221007
7.C	4.587640	6.873988	2.320093
8.H	4.894283	7.759868	2.869359
9.C	3.454782	6.190034	2.722324
10.C	3.146373	3.473977	.275898
11.C	3.646165	2.999751	-.957785
12.H	4.471383	3.507650	-1.455092
13.C	3.076751	1.887276	-1.567940
14.H	3.467706	1.536025	-2.522646
15.C	2.001069	1.226447	-.963397
16.H	1.554117	.357058	-1.446496
17.C	1.498714	1.684278	.259212
18.H	.662993	1.169389	.733025

19.C	2.062588	2.797587	.875761
20.H	1.670192	3.142754	1.829668
21.C	2.604582	6.498719	3.864832
22.C	2.913282	7.590688	4.708065
23.H	3.771448	8.227893	4.499546
24.C	2.128115	7.868200	5.821011
25.H	2.381955	8.710772	6.463997
26.C	1.018929	7.067023	6.117220
27.H	.408780	7.283353	6.994565
28.C	.695240	5.990285	5.285072
29.H	-.170663	5.367888	5.510593
30.C	1.475945	5.706771	4.167805
31.H	1.213795	4.869135	3.525455
32.C	8.272247	5.163638	1.165597
33.H	7.701253	4.360039	.706283
34.C	9.596585	5.036990	1.698872
35.H	10.186212	4.124318	1.725413
36.C	9.991840	6.314532	2.211346
37.H	10.934798	6.546885	2.698317
38.C	8.916659	7.234207	1.988001
39.H	8.908995	8.288150	2.256886
40.C	6.950783	6.058561	4.769992
41.H	6.198533	6.841872	4.792933
42.C	6.762915	4.709808	4.315452
43.H	5.846220	4.283000	3.915923
44.C	7.995675	4.007319	4.502492
45.H	8.184462	2.968006	4.245632
46.C	8.943564	4.919008	5.069650
47.H	9.978405	4.693025	5.313195

48.C	8.299267	6.186606	5.235162
49.H	8.756585	7.088272	5.634306
50.O	3.060723	5.087043	2.010767
51.Fe	8.291672	5.636518	3.206556
52.H	6.538351	8.209726	1.149591
53.H	6.630204	7.214936	-.306913

2^{2+} C_i

Bonding Energy -667.37639304 eV

Atom	**X**	**Y**	**Z (Angstrom)**
1.C	.643167	-1.709059	-.691845
2.C	-.318374	-.721276	-.063214
3.C	-3.082215	-.011661	-2.620487
4.C	-1.833262	-.084072	-2.031009
5.H	-.991804	.361209	-2.553150
6.C	-1.664096	-.679431	-.767487
7.C	-2.802742	-1.202197	-.137517
8.H	-2.717521	-1.669008	.840283
9.C	-4.049464	-1.134114	-.736625
10.C	-3.419510	.616922	-3.892862
11.C	-2.404966	1.136024	-4.729175
12.H	-1.355889	1.053823	-4.446940
13.C	-2.728885	1.749891	-5.934215
14.H	-1.937492	2.144774	-6.571010
15.C	-4.067119	1.856831	-6.332222
16.H	-4.318119	2.337398	-7.278243
17.C	-5.080916	1.345587	-5.515351
18.H	-6.123383	1.428316	-5.822533
19.C	-4.764496	.732296	-4.306421

20.H	-5.561096	.348624	-3.673350
21.C	-5.310446	-1.628947	-.202538
22.C	-5.370169	-2.175716	1.100308
23.H	-4.479042	-2.221852	1.724786
24.C	-6.572611	-2.651139	1.610715
25.H	-6.606139	-3.068241	2.616971
26.C	-7.738170	-2.591615	.837046
27.H	-8.679769	-2.965290	1.240304
28.C	-7.693526	-2.052297	-.453294
29.H	-8.599435	-2.007370	-1.057553
30.C	-6.493788	-1.574564	-.971709
31.H	-6.468081	-1.165841	-1.979213
32.C	1.402379	-2.677225	.059262
33.H	1.292850	-2.885773	1.121596
34.C	2.326128	-3.317271	-.827287
35.H	3.030910	-4.098182	-.555131
36.C	2.136674	-2.767631	-2.135905
37.H	2.674838	-3.055487	-3.034976
38.C	1.093613	-1.784523	-2.061971
39.H	.724658	-1.207804	-2.907032
40.C	-1.133307	-4.897290	-.695101
41.H	-1.547861	-4.850084	.308887
42.C	-1.627777	-4.209850	-1.852240
43.H	-2.486778	-3.544892	-1.883636
44.C	-.804531	-4.562711	-2.966933
45.H	-.917401	-4.203506	-3.986551
46.C	.198163	-5.473518	-2.503215
47.H	.982702	-5.922151	-3.107029
48.C	-.004771	-5.682126	-1.099844

49.H	.595665	-6.318967	-.455373
50.O	-4.156464	-.544209	-1.965684
51.Fe	.374718	-3.659085	-1.467439
52.H	-.519097	-1.070782	.959096
53.C	-.643167	1.709059	.691845
54.C	.318374	.721276	.063214
55.C	3.082215	.011661	2.620487
56.C	1.833262	.084072	2.031009
57.H	.991804	-.361209	2.553150
58.C	1.664096	.679431	.767487
59.C	2.802742	1.202197	.137517
60.H	2.717521	1.669008	-.840283
61.C	4.049464	1.134114	.736625
62.C	3.419510	-.616922	3.892862
63.C	2.404966	-1.136024	4.729175
64.H	1.355889	-1.053823	4.446940
65.C	2.728885	-1.749891	5.934215
66.H	1.937492	-2.144774	6.571010
67.C	4.067119	-1.856831	6.332222
68.H	4.318119	-2.337398	7.278243
69.C	5.080916	-1.345587	5.515351
70.H	6.123383	-1.428316	5.822533
71.C	4.764496	-.732296	4.306421
72.H	5.561096	-.348624	3.673350
73.C	5.310446	1.628947	.202538
74.C	5.370169	2.175716	-1.100308
75.H	4.479042	2.221852	-1.724786
76.C	6.572611	2.651139	-1.610715
77.H	6.606139	3.068241	-2.616971

78.C	7.738170	2.591615	-.837046
79.H	8.679769	2.965290	-1.240304
80.C	7.693526	2.052297	.453294
81.H	8.599435	2.007370	1.057553
82.C	6.493788	1.574564	.971709
83.H	6.468081	1.165841	1.979213
84.C	-1.402379	2.677225	-.059262
85.H	-1.292850	2.885773	-1.121596
86.C	-2.326128	3.317271	.827287
87.H	-3.030910	4.098182	.555131
88.C	-2.136674	2.767631	2.135905
89.H	-2.674838	3.055487	3.034976
90.C	-1.093613	1.784523	2.061971
91.H	-.724658	1.207804	2.907032
92.C	1.133307	4.897290	.695101
93.H	1.547861	4.850084	-.308887
94.C	1.627777	4.209850	1.852240
95.H	2.486778	3.544892	1.883636
96.C	.804531	4.562711	2.966933
97.H	.917401	4.203506	3.986551
98.C	-.198163	5.473518	2.503215
99.H	-.982702	5.922151	3.107029
100.C	.004771	5.682126	1.099844
101.H	-.595665	6.318967	.455373
102.O	4.156464	.544209	1.965684
103.Fe	-.374718	3.659085	1.467439
104.H	.519097	1.070782	-.959096

3 **C_1**

Bonding Energy -672.82466874 eV

Atom	X	Y	Z (Angstrom)
1.C	-1.318309	-1.555461	-6.969461
2.C	.909686	-.611111	-7.647383
3.C	1.782805	-1.575938	-6.969540
4.C	-.435944	-1.108242	-8.056706
5.Fe	3.589883	-2.507000	-7.605555
6.O	1.837703	3.515152	-8.106834
7.C	2.830945	2.603046	-7.794210
8.C	2.568792	1.276181	-7.667088
9.H	3.401309	.602507	-7.487248
10.C	1.242413	.727192	-7.849756
11.C	.263877	1.713036	-8.248040
12.H	-.763377	1.392693	-8.401885
13.C	.555097	3.034757	-8.351567
14.C	4.147119	3.242799	-7.645972
15.C	5.214139	2.573806	-7.011946
16.H	5.061364	1.575494	-6.601857
17.C	6.459035	3.183832	-6.877299
18.H	7.269225	2.650360	-6.378138
19.C	6.668180	4.480511	-7.363152
20.H	7.641997	4.959184	-7.250392
21.C	5.616299	5.157401	-7.985714
22.H	5.767081	6.168299	-8.367854
23.C	4.368102	4.548339	-8.126145
24.H	3.554799	5.076254	-8.620852
25.C	-.396698	4.112915	-8.651435
26.C	-1.662309	3.831199	-9.205385
27.H	-1.923929	2.805775	-9.462676

28.C	-2.578417	4.850977	-9.447857
29.H	-3.552992	4.607586	-9.872861
30.C	-2.250786	6.181033	-9.156616
31.H	-2.969927	6.978760	-9.348295
32.C	-.993572	6.476120	-8.623342
33.H	-.726136	7.508789	-8.393717
34.C	-.073947	5.455824	-8.372735
35.H	.897602	5.690861	-7.941817
36.C	1.637027	-3.011480	-7.079944
37.H	.918842	-3.511931	-7.724530
38.C	2.569046	-3.649162	-6.204405
39.H	2.688852	-4.720963	-6.071078
40.C	3.327493	-2.624841	-5.548997
41.H	4.120708	-2.777995	-4.821404
42.C	2.862369	-1.357018	-6.023798
43.H	3.217539	-.394201	-5.671026
44.C	4.157897	-1.792161	-9.492991
45.H	3.640761	-1.027068	-10.066038
46.C	3.914586	-3.205165	-9.542960
47.H	3.170219	-3.710531	-10.153696
48.C	4.819944	-3.842628	-8.628515
49.H	4.880581	-4.910138	-8.431031
50.C	5.617154	-2.823195	-8.009739
51.H	6.392607	-2.982589	-7.264541
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55.O	-1.452868	-1.083295	-12.192801
56.C	-2.416714	-1.328873	-11.228515

57.C	-2.115717	-1.383027	-9.904478
58.H	-2.931096	-1.513189	-9.198476
59.C	-.775518	-1.155990	-9.404962
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66.C	-6.043855	-2.320423	-11.663192
67.H	-6.813877	-2.859524	-11.109409
68.C	-6.327565	-1.803670	-12.933712
69.H	-7.319698	-1.928198	-13.368956
70.C	-5.323168	-1.139418	-13.644499
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73.H	-3.269135	-.477197	-13.653920
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75.C	.469383	-.169018	-14.069006
76.H	-.502148	.320473	-14.136671
77.C	1.373345	-.080601	-15.128309
78.H	1.102008	.478410	-16.024952
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86.H	-.538730	-.309450	-5.266220
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88.H	-2.277551	-1.692589	-3.718441
89.C	-2.835344	-2.742624	-5.631969
90.H	-3.603542	-3.444441	-5.316857
91.C	-2.354301	-2.571603	-6.970793
92.H	-2.669173	-3.159302	-7.827960
93.C	-3.893640	.732772	-7.504031
94.H	-3.453163	1.038524	-8.448992
95.C	-3.572419	1.257814	-6.209754
96.H	-2.841617	2.034161	-5.998089
97.C	-4.381846	.572879	-5.243065
98.H	-4.368800	.738662	-4.168558
99.C	-5.198349	-.379815	-5.939454
100.H	-5.915680	-1.059558	-5.486447
101.C	-4.893777	-.282521	-7.339131
102.H	-5.353117	-.862761	-8.135049

4^{2+} C_i

Bonding Energy -659.51152917 eV

Atom	**X**	**Y**	**Z (Angstrom)**
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2.C	2.111803	.773861	-2.001463
3.H	1.880044	-.100577	-2.604176
4.C	1.527166	.934587	-.732962
5.C	1.819765	2.106572	-.019213
6.H	1.389666	2.259384	.966889
7.C	2.708868	3.039987	-.521530

8.C	.665586	-.120545	-.117220
9.C	1.379104	-1.343070	.305690
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12.C	2.838011	-3.171372	.358952
13.H	3.610990	-3.881420	.080264
14.C	2.033094	-3.220116	1.541230
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19.H	3.320317	1.321255	2.302093
20.C	3.651594	-.622375	3.372899
21.H	2.995192	-.544209	4.235053
22.C	4.513658	-1.726145	3.070009
23.H	4.619018	-2.634881	3.659724
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25.H	5.935172	-2.068370	1.359867
26.C	4.776438	-.140868	1.401432
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28.C	3.205430	4.230052	.155602
29.C	2.609832	4.664953	1.360902
30.H	1.744024	4.145209	1.770579
31.C	4.304812	4.949119	-.360863
32.H	4.783685	4.622365	-1.281649
33.C	3.545274	1.768876	-3.854008
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36.C	4.402864	2.822492	-4.240998

37.H	4.624337	3.625659	-3.542292
38.C	4.962654	2.843174	-5.514449
39.H	5.624179	3.660538	-5.800774
40.C	3.107352	5.778348	2.028817
41.H	2.638946	6.107201	2.957018
42.C	4.203249	6.479112	1.510963
43.H	4.593909	7.348595	2.039700
44.C	4.796461	6.062149	.314384
45.H	5.651689	6.605581	-.089215
46.C	4.674939	1.821469	-6.426483
47.H	5.111366	1.843314	-7.425719
48.C	3.824369	.772706	-6.056899
49.H	3.595640	-.020900	-6.768334
50.Fe	3.145588	-1.467155	1.506269
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52.C	-2.941761	-1.749391	2.527561
53.C	-2.111803	-.773861	2.001463
54.H	-1.880044	.100577	2.604176
55.C	-1.527166	-.934587	.732962
56.C	-1.819765	-2.106572	.019213
57.H	-1.389666	-2.259384	-.966889
58.C	-2.708868	-3.039987	.521530
59.C	-.665586	.120545	.117220
60.C	-1.379104	1.343070	-.305690
61.C	-2.466922	2.006243	.387219
62.H	-2.914980	1.708865	1.330939
63.C	-2.838011	3.171372	-.358952
64.H	-3.610990	3.881420	-.080264
65.C	-2.033094	3.220116	-1.541230

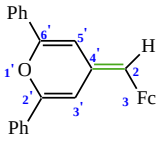
66.H	-2.091216	3.966972	-2.327730
67.C	-1.156094	2.089967	-1.527365
68.H	-.450274	1.837444	-2.314292
69.C	-3.820799	-.357540	-2.346561
70.H	-3.320317	-1.321255	-2.302093
71.C	-3.651594	.622375	-3.372899
72.H	-2.995192	.544209	-4.235053
73.C	-4.513658	1.726145	-3.070009
74.H	-4.619018	2.634881	-3.659724
75.C	-5.210723	1.428020	-1.854092
76.H	-5.935172	2.068370	-1.359867
77.C	-4.776438	.140868	-1.401432
78.H	-5.134767	-.372790	-.511314
79.C	-3.205430	-4.230052	-.155602
80.C	-2.609832	-4.664953	-1.360902
81.H	-1.744024	-4.145209	-1.770579
82.C	-4.304812	-4.949119	.360863
83.H	-4.783685	-4.622365	1.281649
84.C	-3.545274	-1.768876	3.854008
85.C	-3.265019	-.741562	4.784618
86.H	-2.600698	.080673	4.522257
87.C	-4.402864	-2.822492	4.240998
88.H	-4.624337	-3.625659	3.542292
89.C	-4.962654	-2.843174	5.514449
90.H	-5.624179	-3.660538	5.800774
91.C	-3.107352	-5.778348	-2.028817
92.H	-2.638946	-6.107201	-2.957018
93.C	-4.203249	-6.479112	-1.510963
94.H	-4.593909	-7.348595	-2.039700

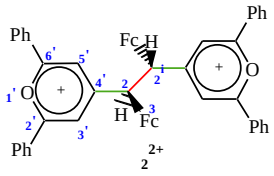
95.C	-4.796461	-6.062149	-.314384
96.H	-5.651689	-6.605581	.089215
97.C	-4.674939	-1.821469	6.426483
98.H	-5.111366	-1.843314	7.425719
99.C	-3.824369	-.772706	6.056899
100.H	-3.595640	.020900	6.768334
101.Fe	-3.145588	1.467155	-1.506269
102.O	-3.240920	-2.841351	1.767096

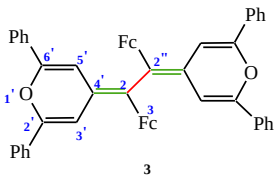
ESI 05: Table: Selected bond lengths for 1, $1^{+\cdot}$, $[1\text{-H}]^{+}$, 2^{2+}, 3 and 4^{2+} complexes. Experimental values are in brackets.

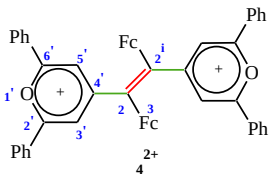
	1 *C1*	$1^{+\cdot}$ *C1*	$[1\text{-H}]^{+}$ *C1*	2^{2+} *Ci*	3 *C1*		4^{2+} *Ci*
HOMO-LUMO gap (eV)	1.74		0.23	0.23	1.33		0.24
C2-C2^{i} (Å)				1.582 [1.532]	[a]1.494 [1.514]		1.373 [1.268]
C2-C3 (Å)	1.458 [1.486]	1.425	1.515	1.515 [1.509]	1.469 [1.469]	1.471 [1.469]	1.477 [1.516]
C2-C4' (Å)	1.376 [1.384]	1.407	1.508	1.519 [1.534]	1.394 [1.361]	1.390 [1.366]	1.495 [1.507]
C4'-C5' (Å)	1.449 [1.445]	1.431	1.406	1.407 [1.390]	1.448 [1.464]	1.446 [1.450]	1.406 [1.461]
C5'-C6' (Å)	1.355 [1.337]	1.431	1.382	1.383 [1.386]	1.358 [1.333]	1.359 [1.326]	1.385 [1.363]
C6'-O1' (Å)	1.388 [1.374]	1.375	1.367	1.366 [1.336]	1.385 [1.368]	1.388 [1.378]	1.364 [1.386]
O1'-C2' (Å)	1.390 [1.365]	1.373	1.370	1.368 [1.341]	1.392 [1.391]	1.394 [1.392]	1.369 [1.358]
C2'-C3' (Å)	1.356 [1.342]	1.369	1.383	1.385 [1.383]	1.357 [1.343]	1.356 [1.323]	1.384 [1.383]
C3'-C4' (Å)	1.449 [1.440]	1.431	1.401	1.403 [1.382]	1.437 [1.451]	1.442 [1.451]	1.403 [1.418]
Fe-C(Cp') (Å) range average	2.069-2.122 [2.025-2.066] 2.084 [2.040]	2.073-2.204 2.112	2.082-2.131 2.099	2.082-2.115 [2.009-2.053] 2.092 [2.032]	2.075-2.132 [2.025-2.067]	2.074-2.133 [2.034-2.067]	2.076-2.139 [2.012-2.055]
Fe-C(Cp) (Å) range average	2.087-2.093 [2.028-2.046] 2.088 [2.038]	2.099-2.161 2.128		[1.984-2.011]	2.083-2.099	2.084-2.101	2.094-2.119 [2.036-2.106]

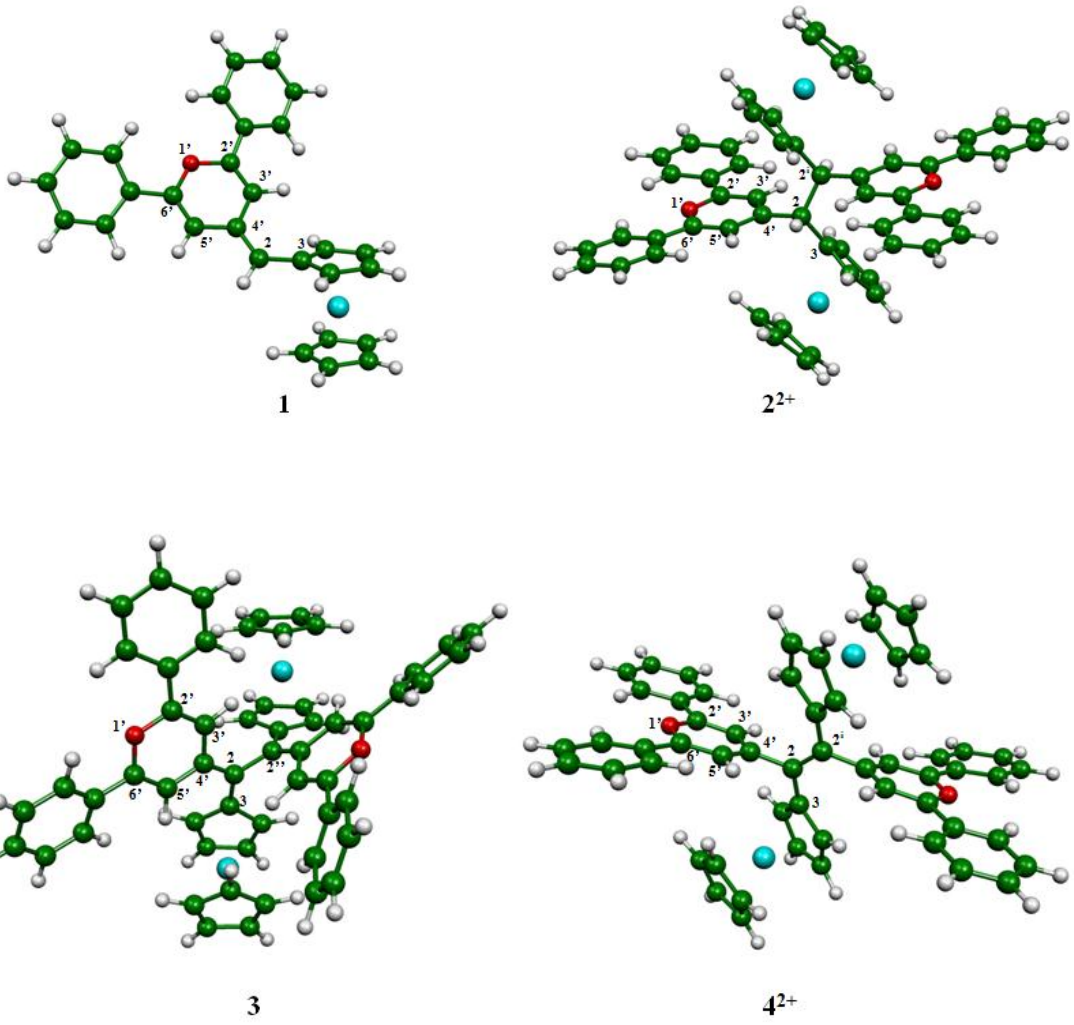
[a]C(2)-C(2'') distance.







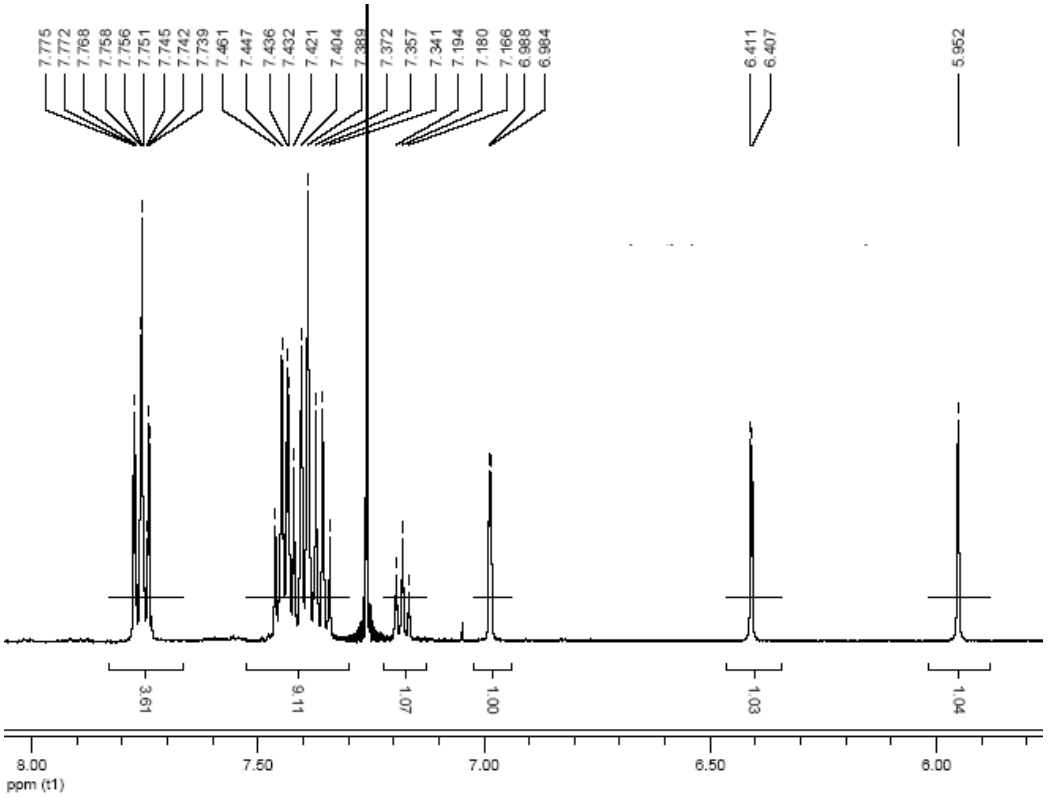




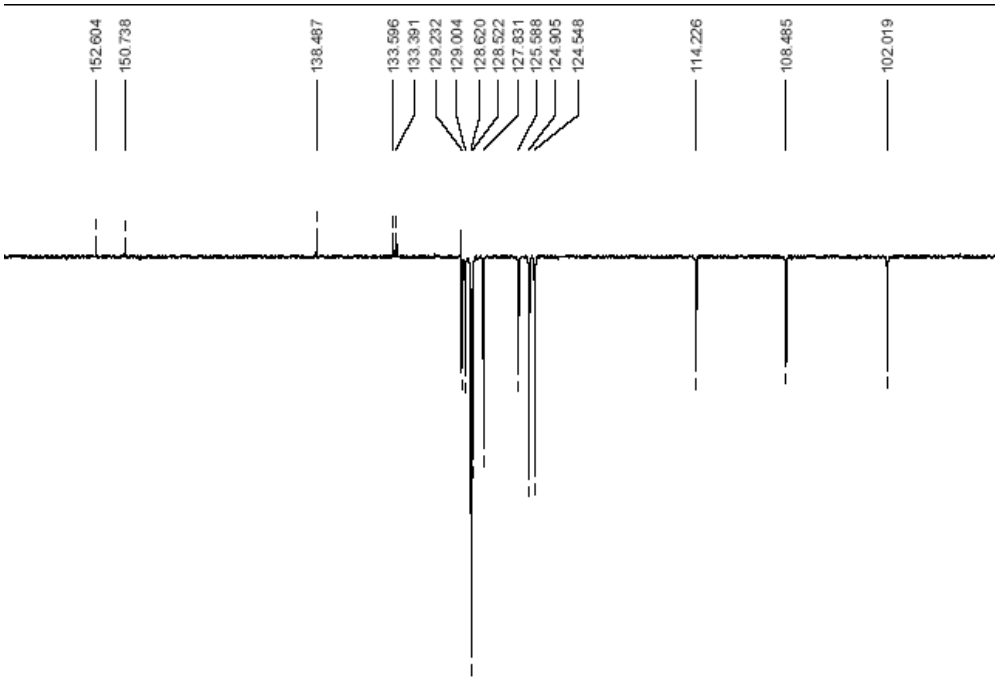
1 **2^{2+}** **3** **4^{2+}**

ESI 06: Compound phenylmethylenepyran [ref 19] : NMR ^{1}H, ^{13}C, UV-Vis spectra, Cyclic Voltammetry

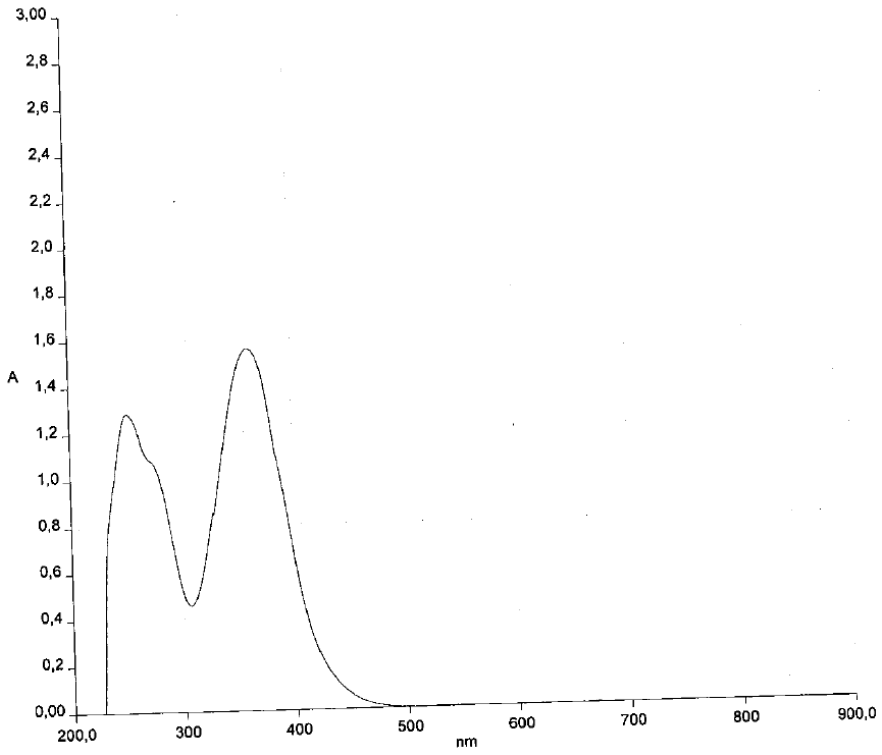
NMR ^{1}H ($CDCl_3$, 500 MHz, RT) of phenylmethylenepyran



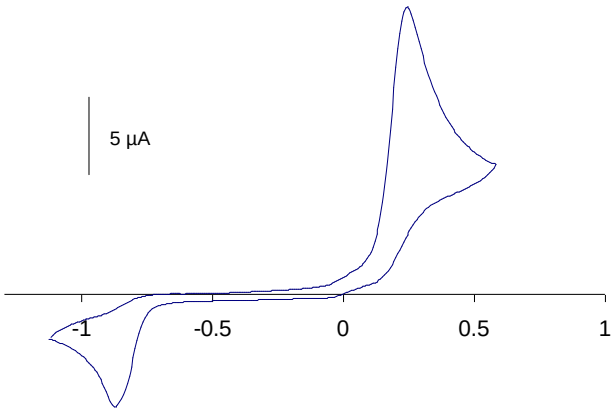
NMR ^{13}C ($CDCl_3$, 125 MHz, JMOD sequence, RT) of phenylmethylenepyran



UV-vis spectrum of phenylmethylenepyran (CH_2Cl_2, 6.6 10^{-5} M, RT)

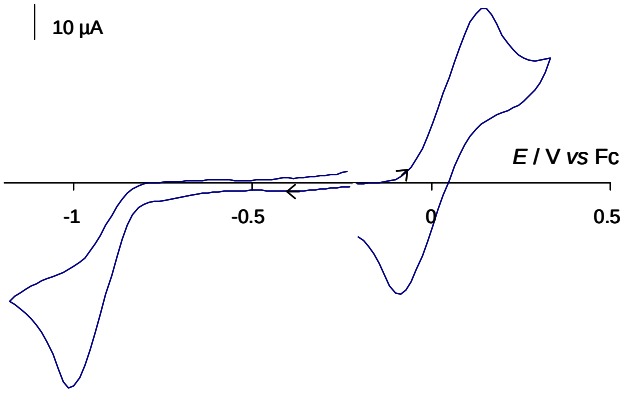


Cyclic Voltammetry of phenylmethylenepyran (C= 7.5 10^{-4} mol L^{-1}), in CH_2Cl_2–Bu_4NBF_4 (0.2 M) at a Pt electrode, v = 0.1 V s^{-1}, E/V *vs* Fc



ESI 07: Voltammogram of 1 + HBF_4

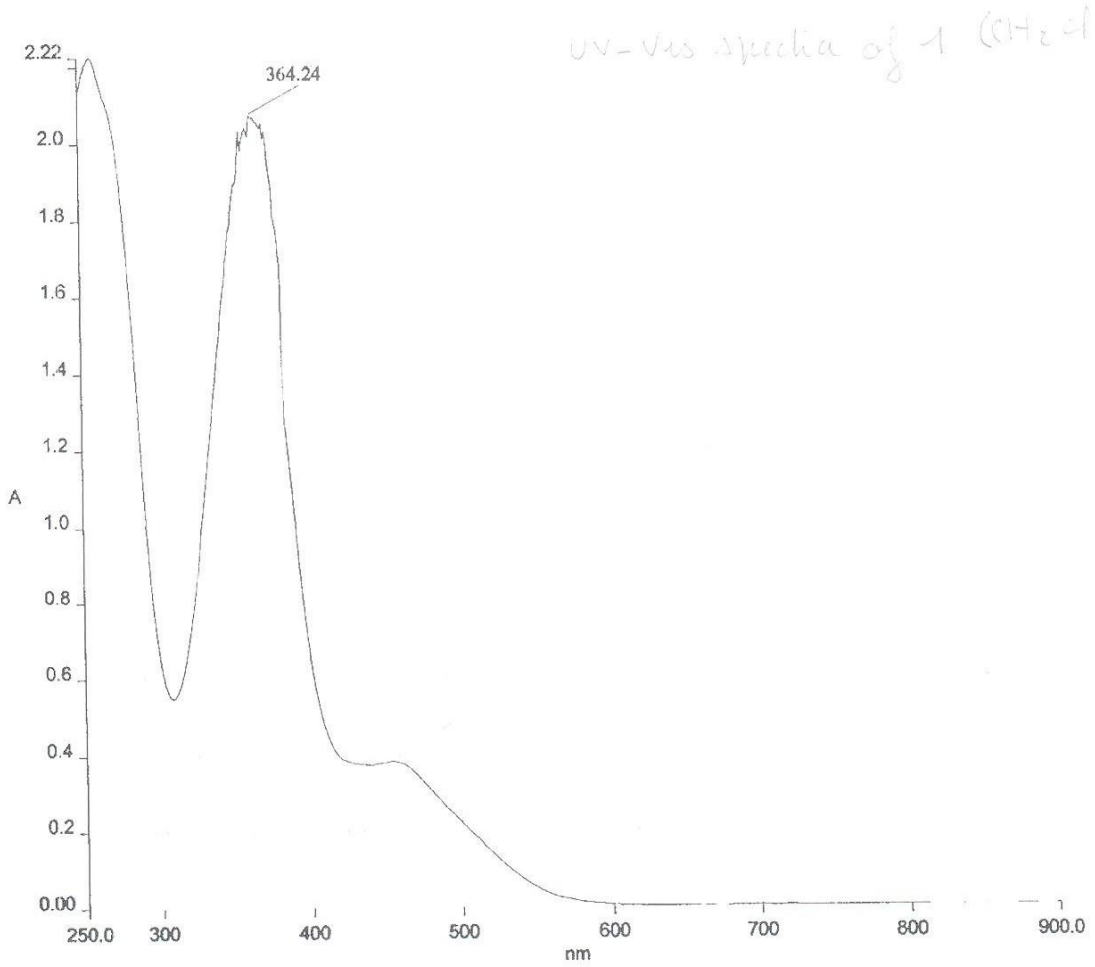
Cyclic Voltammetry of **1** ($7.2\ 10^{-3}$ M) + 1 eq of HBF_4, Et_2O in CH_2Cl_2–Bu_4NBF_4 (0.2 M) at a vitreous carbon electrode, $v = 0.2$ V s^{-1}, E/V *vs* Fc



ESI 08: 2^{2+} CIF

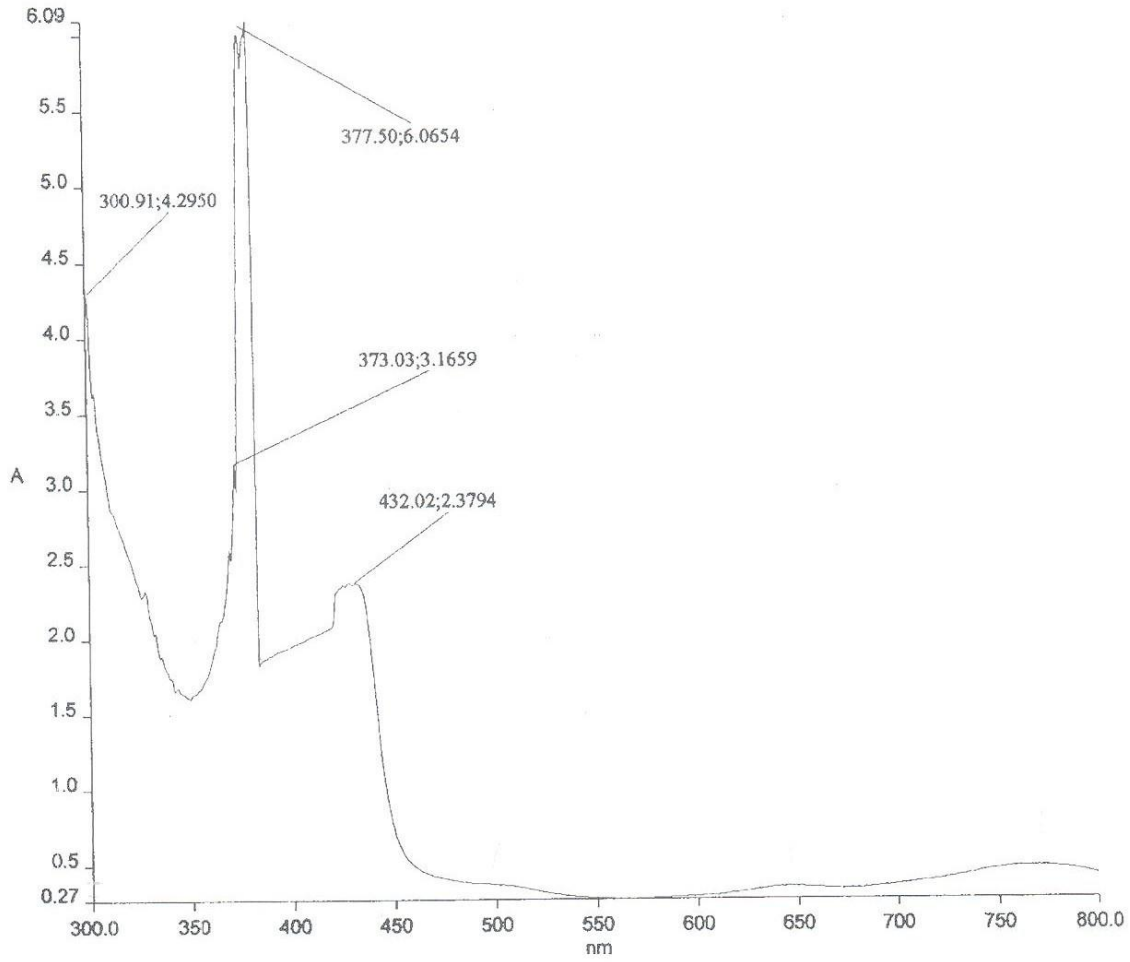
ESI 09: 3 CIF

ESI 10: UV-Vis spectrum of 1 (10^{-4} mol.L^{-1}, CH_2Cl_2)

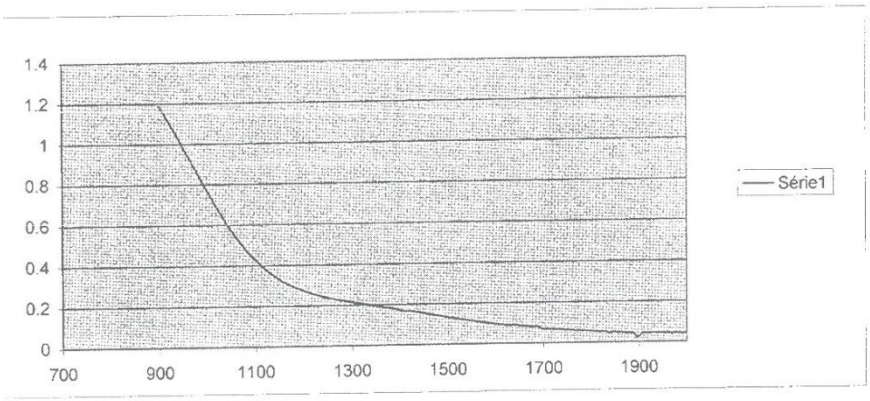


ESI 11: UV-Vis and NIR spectra of 2^{2+}

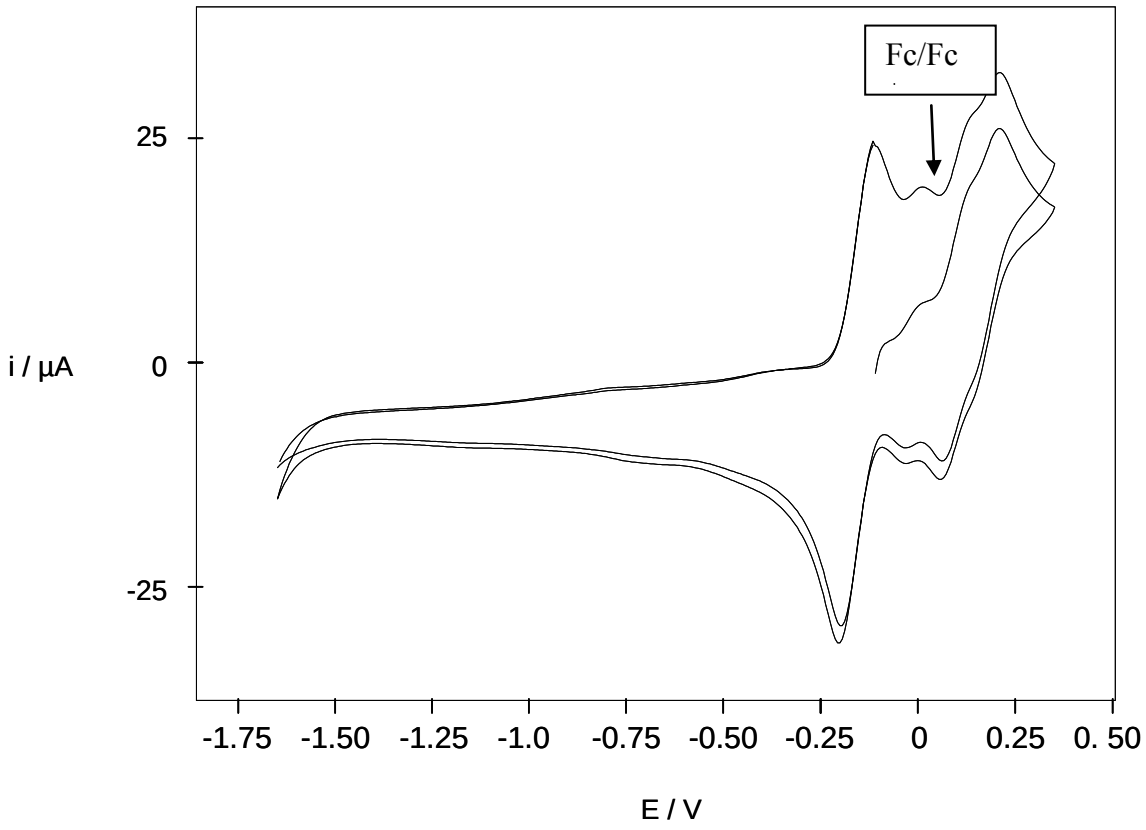
UV-Vis spectrum of 2^{2+} ($1.5\ 10^{-4}$ mol.L^{-1}, CH_2Cl_2)



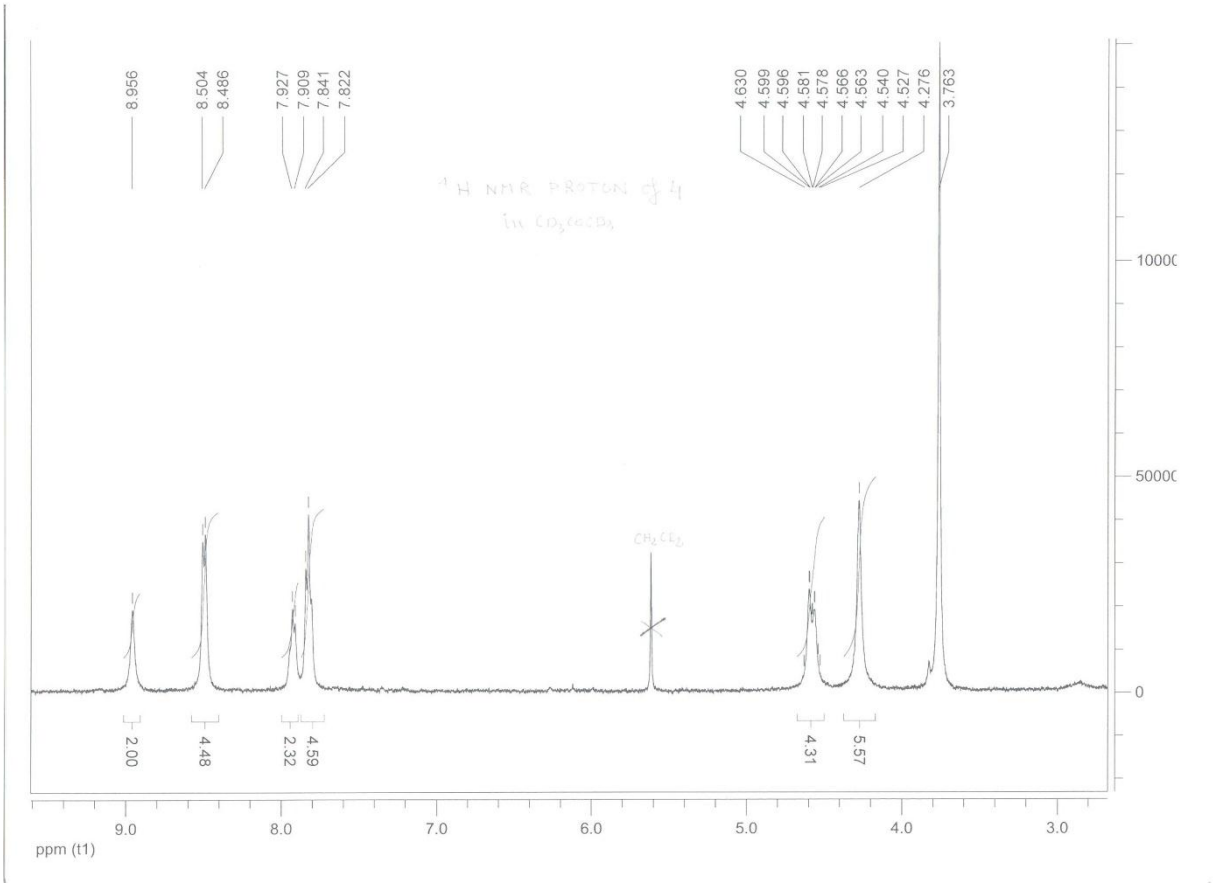
NIR spectrum of 2^{2+} ($3\ 10^{-4}$ mol.L^{-1}, CH_2Cl_2)



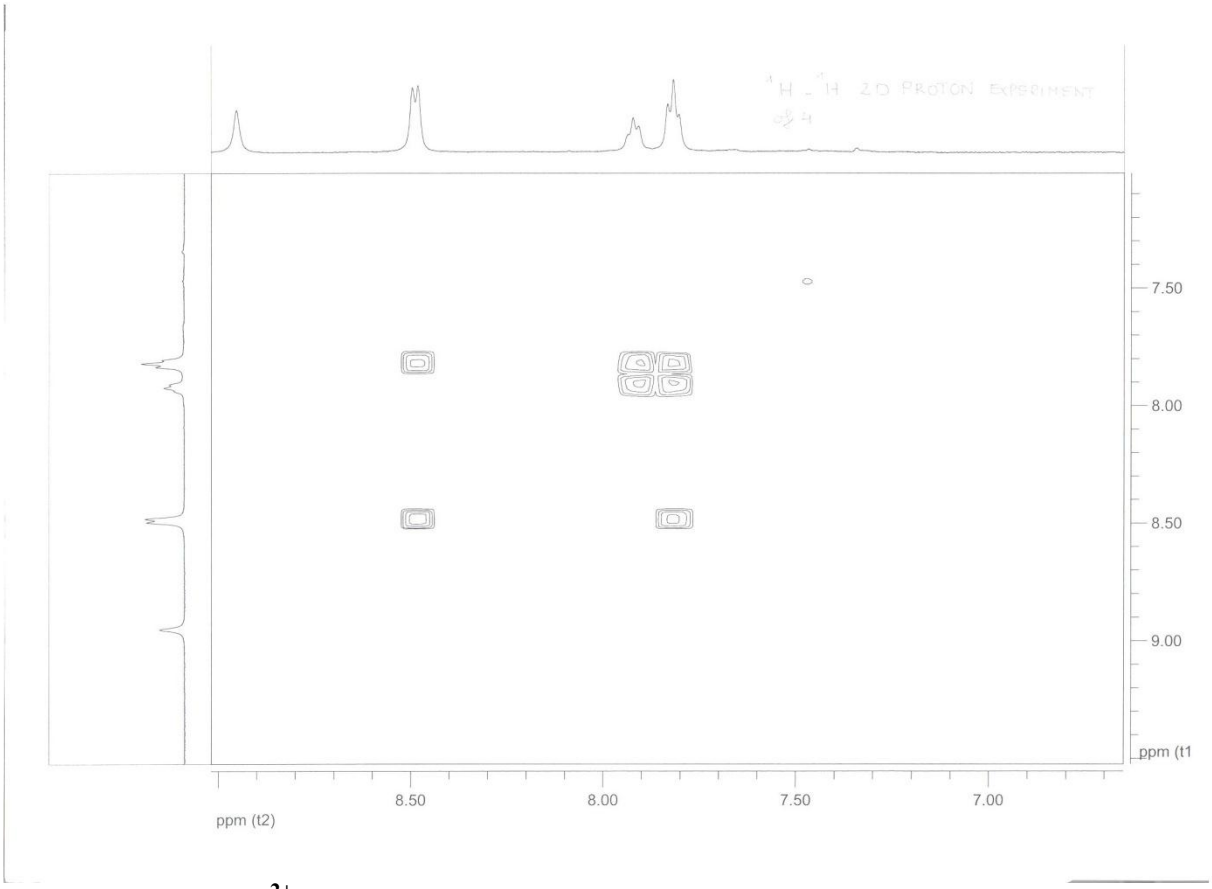
ESI 12: Cyclic voltammetry of $\mathbf{4}^{2+}$ (1,2 10^{-3} M) in CH_2Cl_2- $[NBu_4][BF_4]$ (0.2 M) at a Pt disk electrode, v = 0.2 $V.s^{-1}$, E/V *vs* $[FeCp_2]^{0/+}$



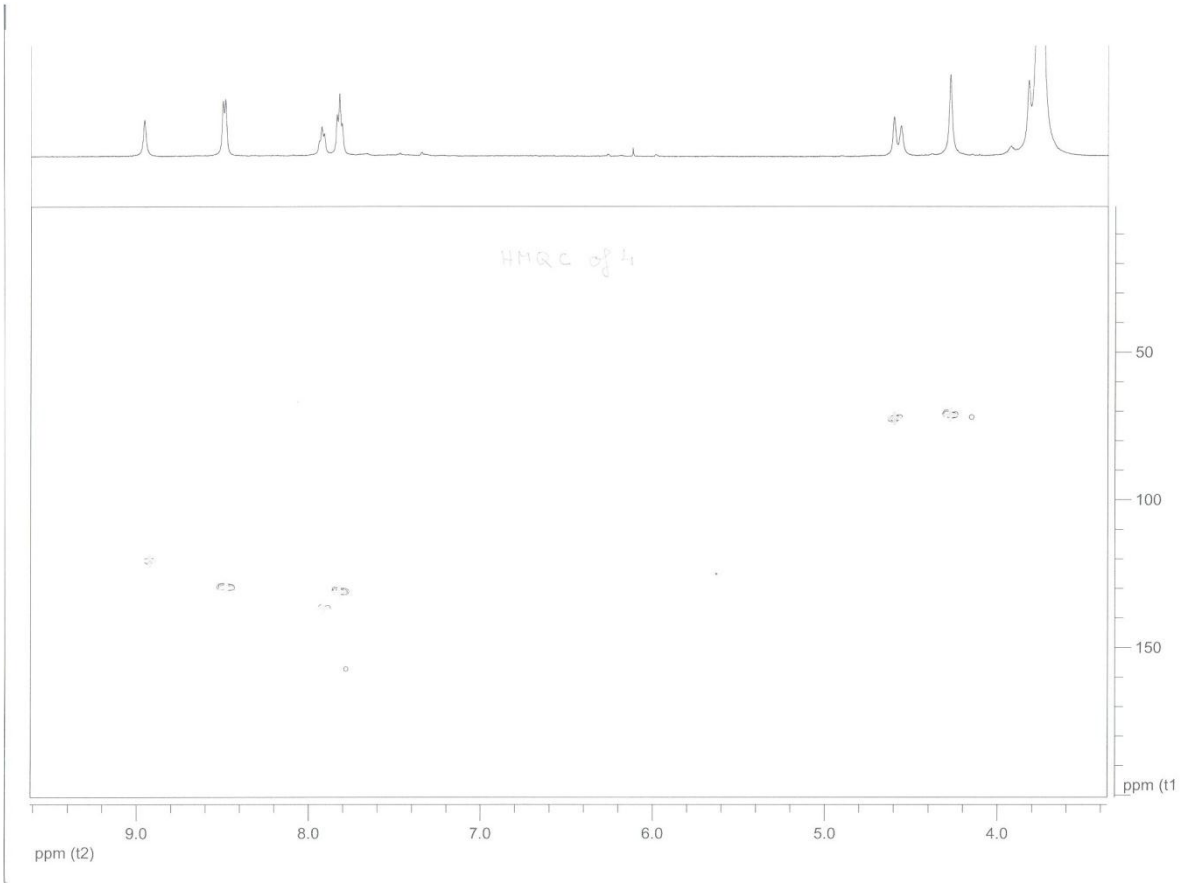
ESI 13: ^{1}**H NMR spectrum of** $\mathbf{4}^{2+}$



^{1}H NMR 2D spectrum of 4^{2+} (COSY)

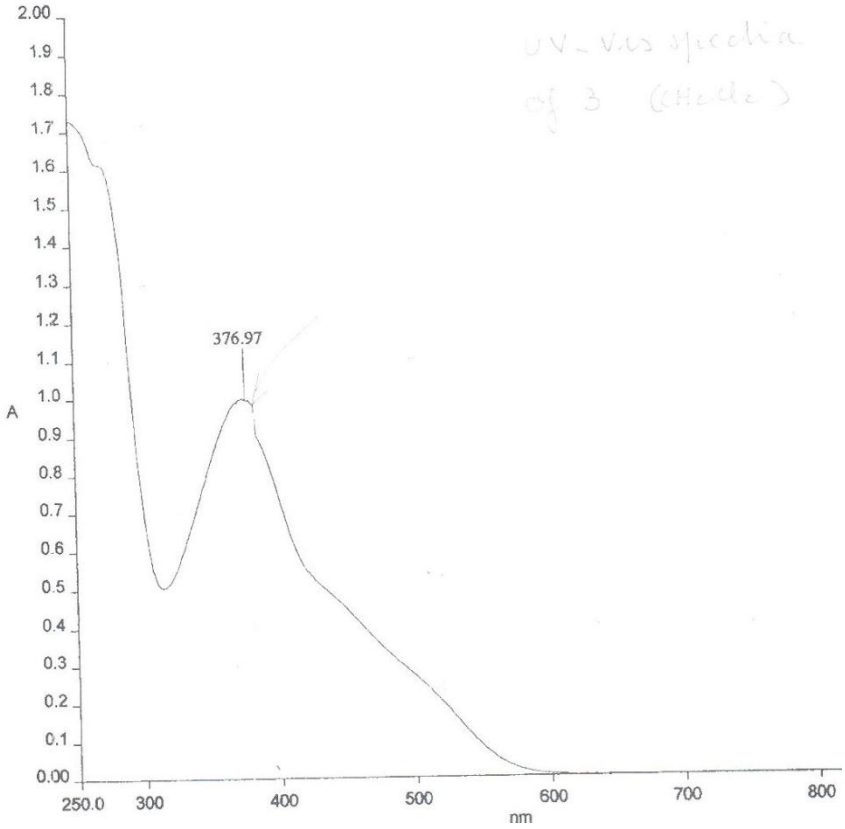


^{1}H NMR 2D spectrum of 4^{2+} (HMQC)



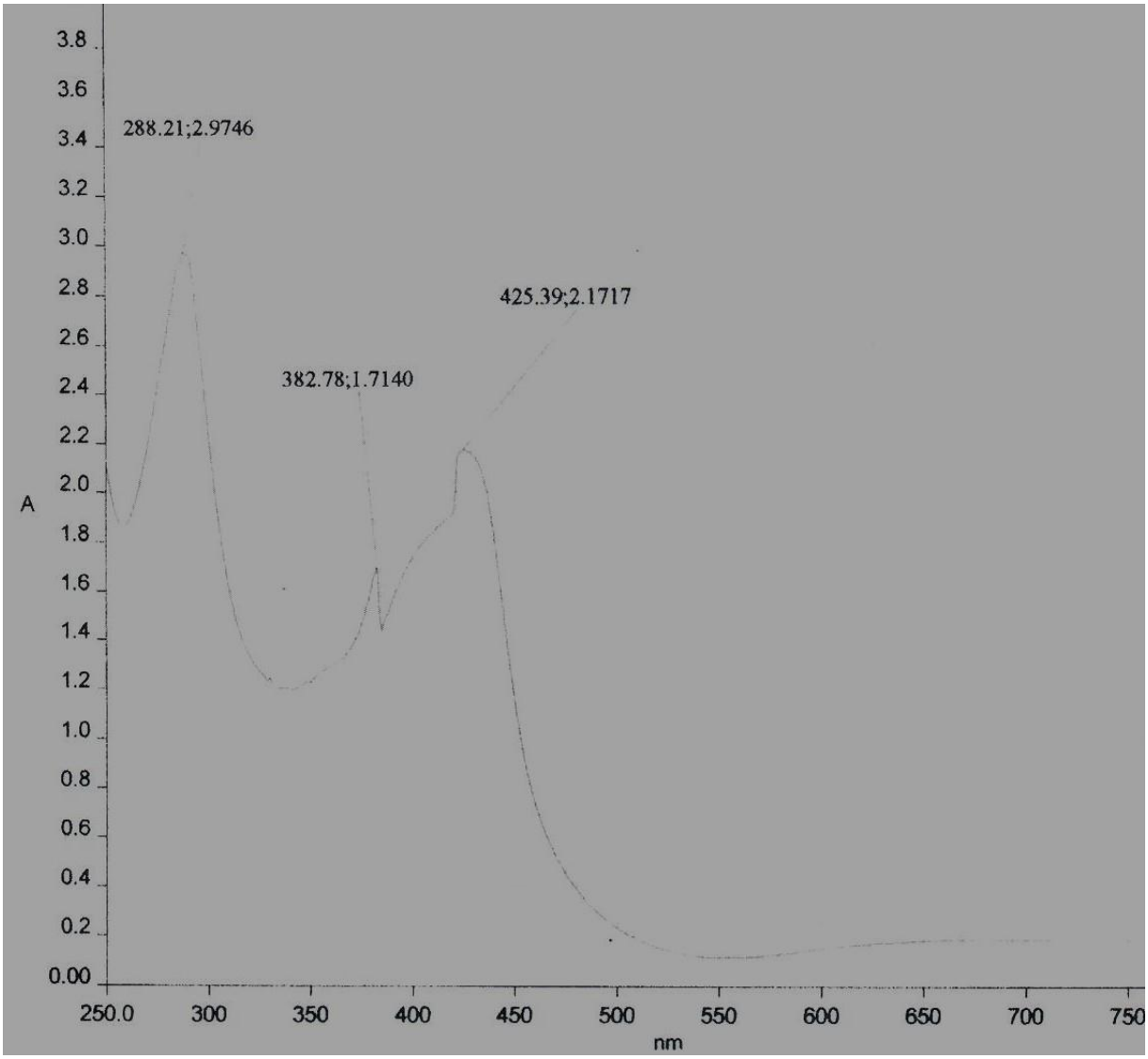
ESI 14: 4^{2+} CIF

ESI 15: UV-Vis spectrum of 3 (5 10^{-5} mol.L^{-1}, CH_2Cl_2)

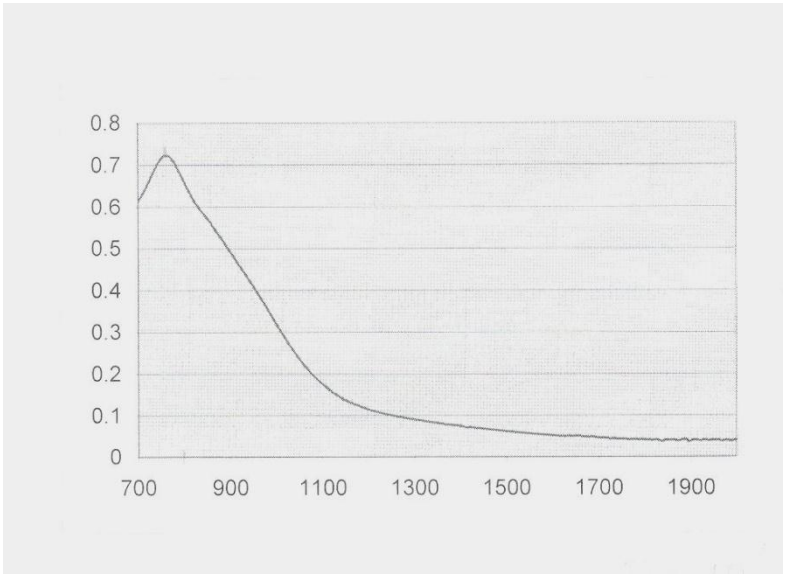


ESI 16: UV-Vis and NIR spectra of 4^{2+}

UV-Vis spectrum of 4^{2+} (10^{-4} mol.L^{-1}, CH_2Cl_2)

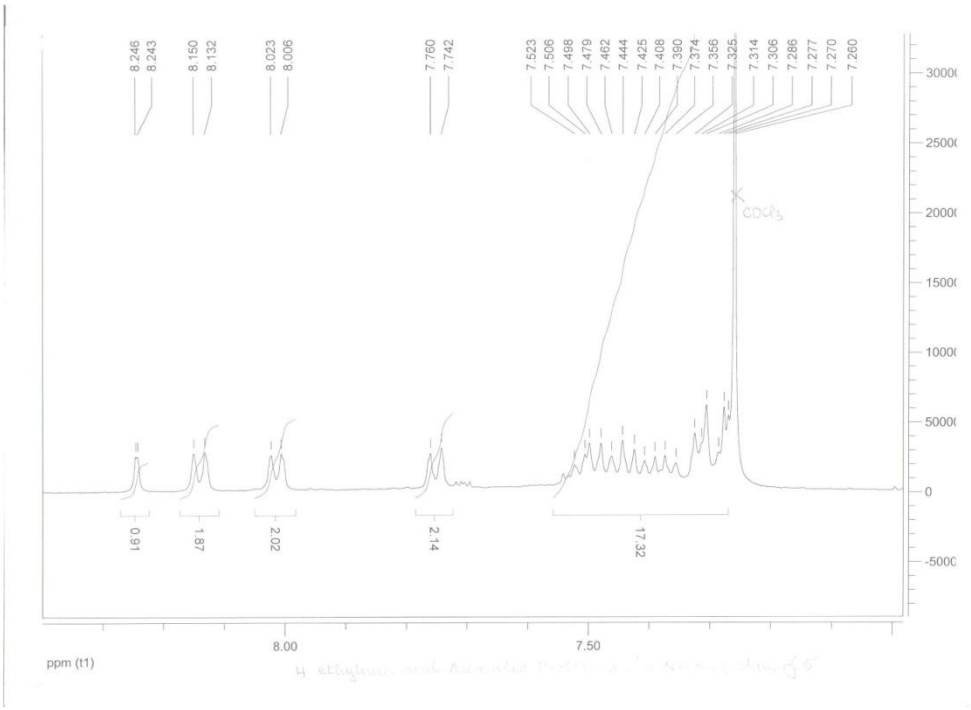


NIR spectrum of 4^{2+} 4 10^{-4} mol.L^{-1}, CH_2Cl_2)

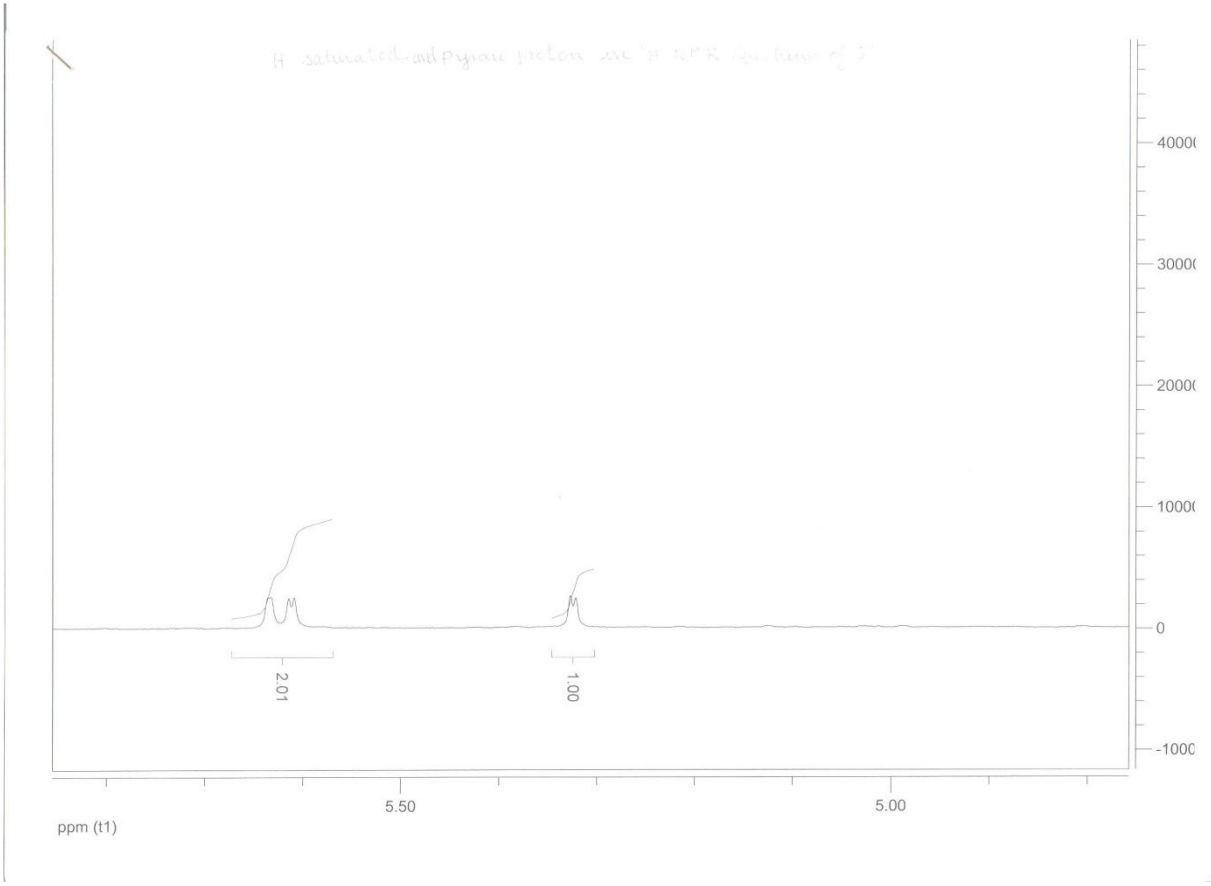


ESI 17: ^{1}H NMR spectra of 5

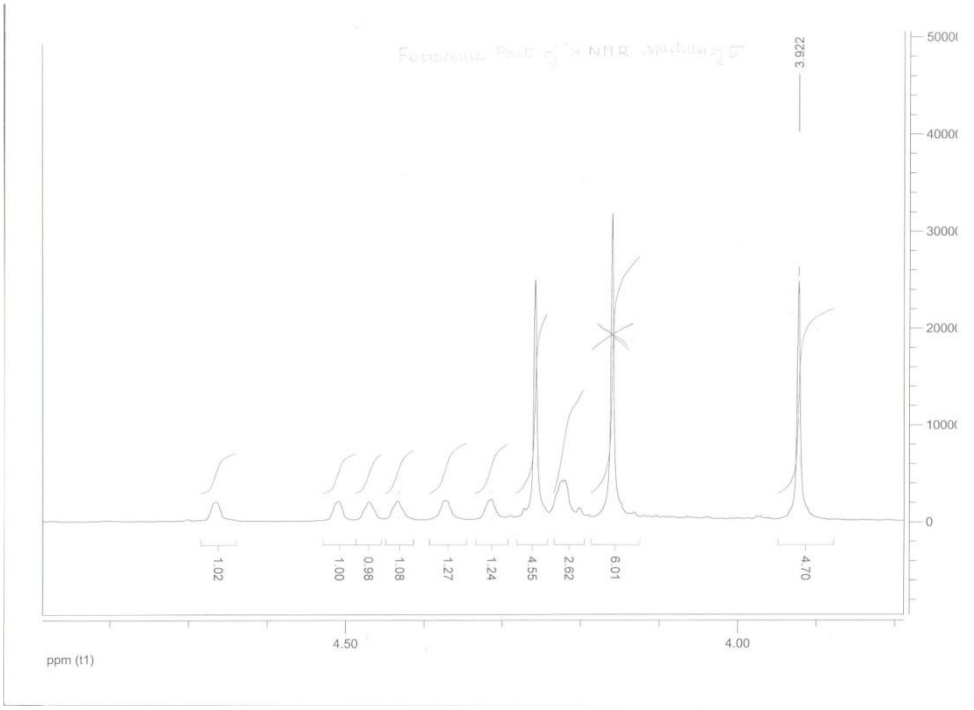
^{1}H NMR spectrum of 5 (7.5 ppm-8.5ppm)



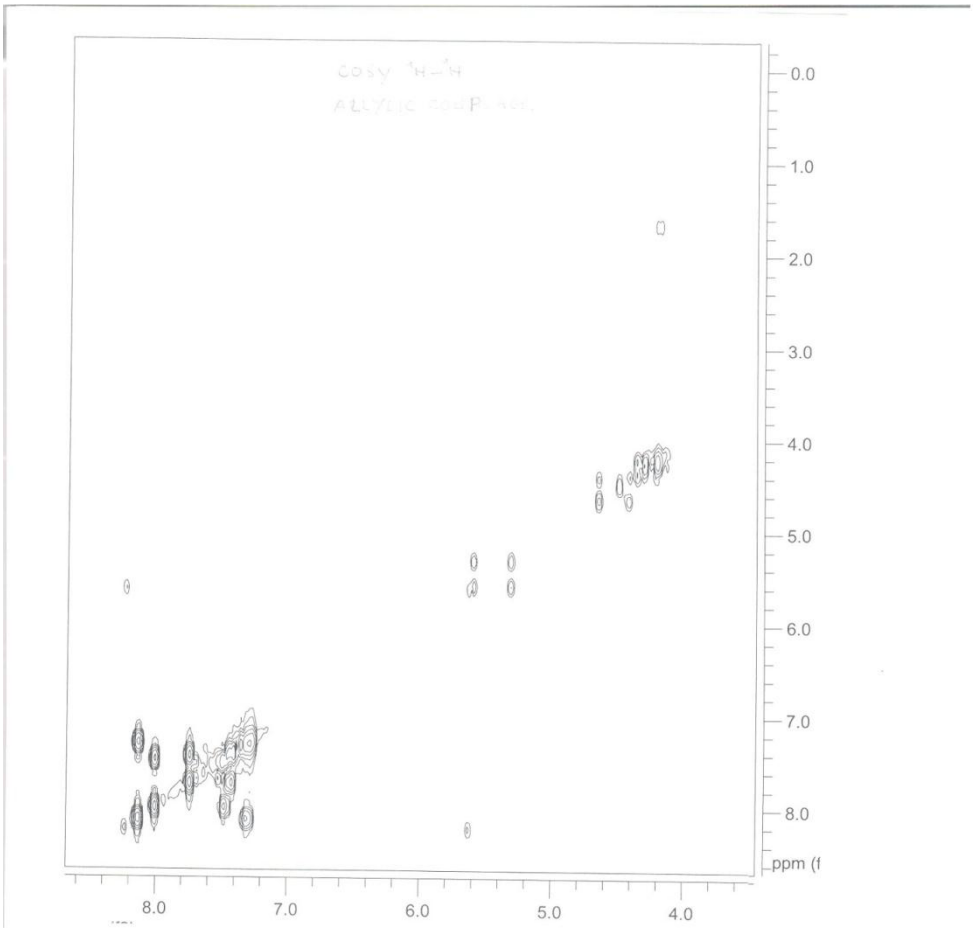
^{1}H NMR spectrum of 5 (5.0 ppm-6 ppm)



^{1}H NMR spectrum of 5 (3.8 ppm-5 ppm)



^{1}H NMR 2D spectrum of 5 (COSY)



ESI 18: IR spectrum of 5 (KBr)