Electronic Supporting Information for

Iridium complexes of a chelating bis(iminoxolene): augmentation of metal-metal π bonding by metal-ligand π bonding

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I. ^{1}H NMR spectra

Figure S1. ^{1}H NMR spectrum of Egan (CD_2Cl_2, 400 MHz).

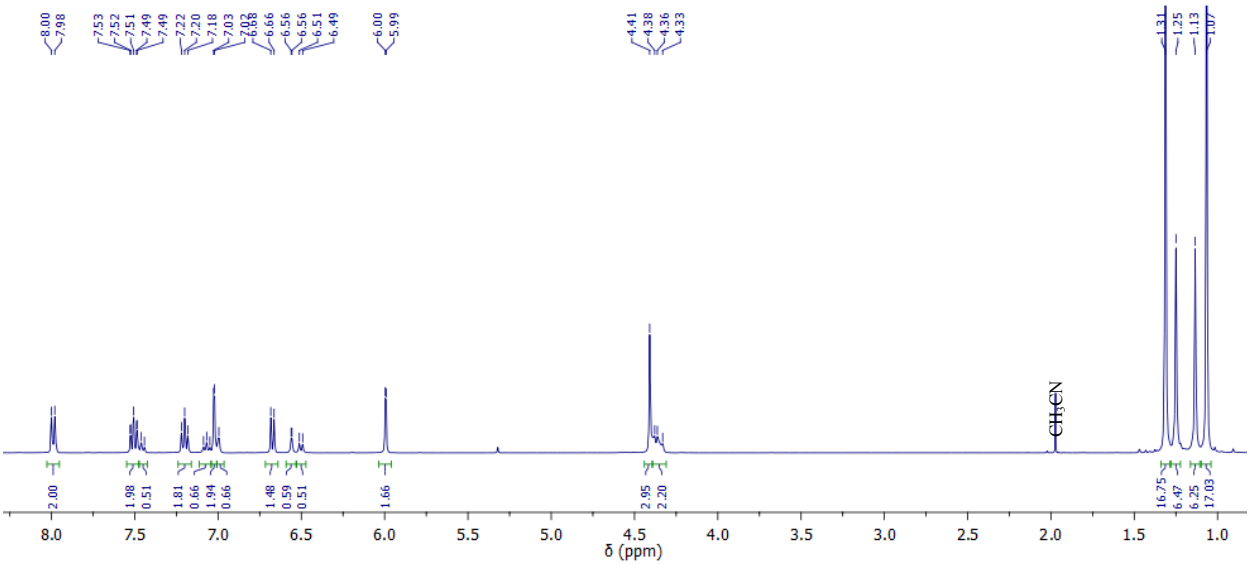


Figure S2. ^{1}H NMR spectrum of (Egan)$IrCl_2$ (C_6D_6, 500 MHz).

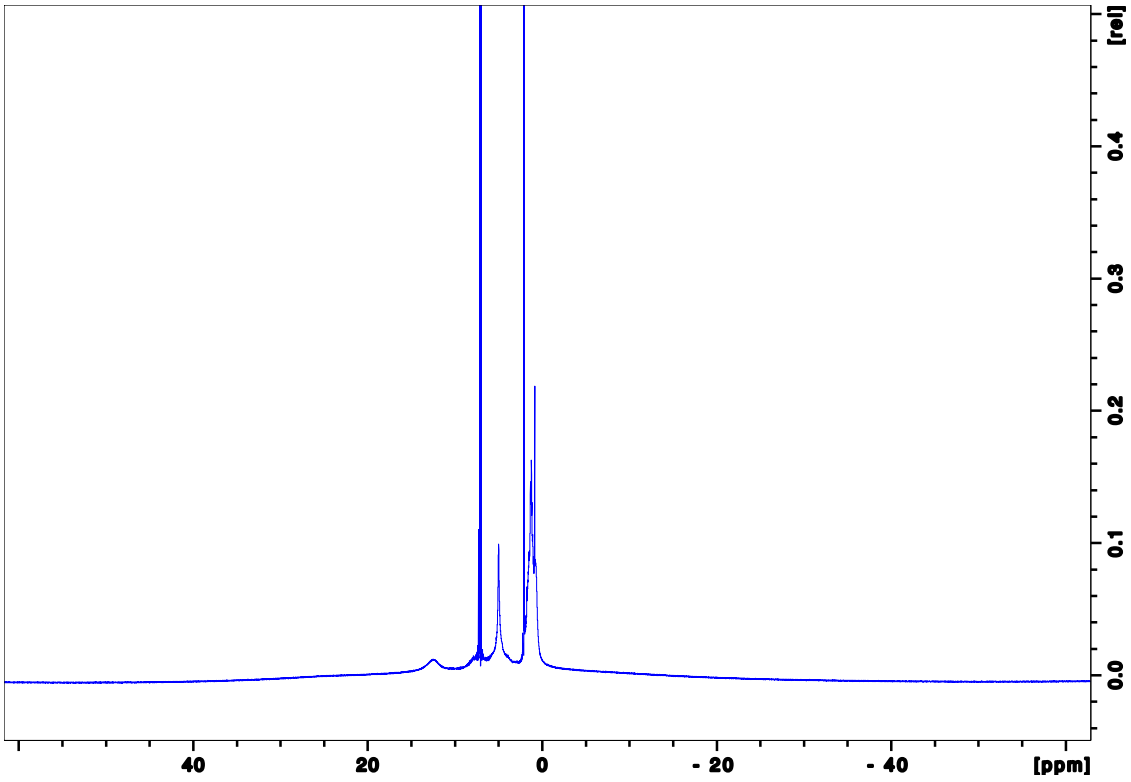


Figure S3. ^{1}H NMR spectrum of *cis*-α-(Egan)IrCl (C_6D_6, 400 MHz).

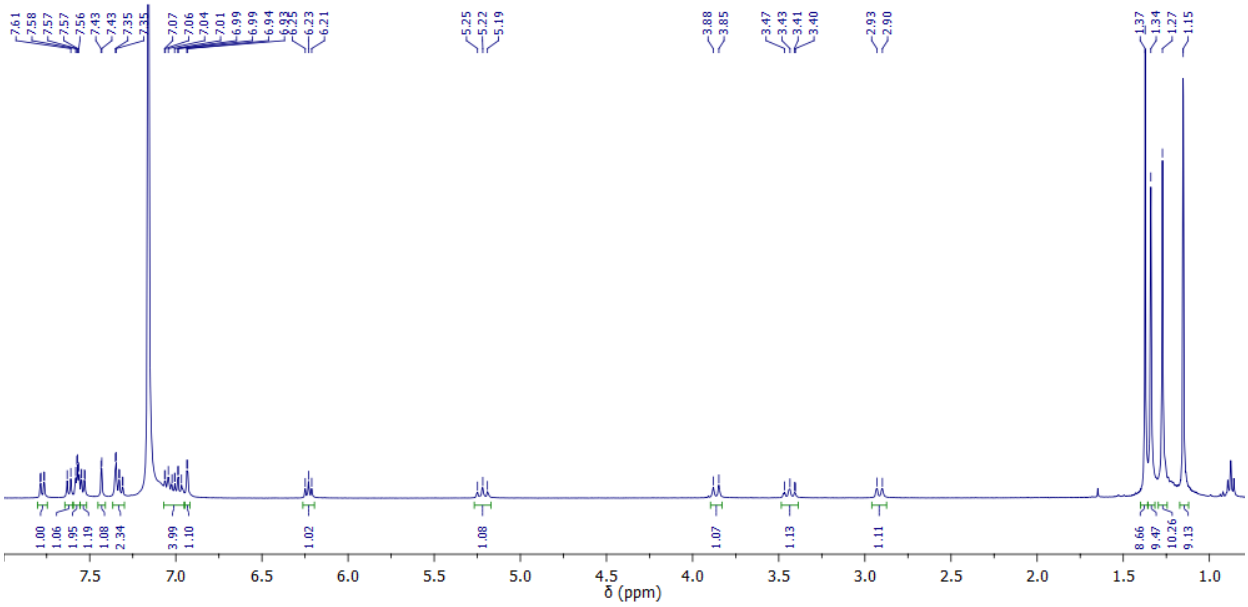


Figure S4. ^{1}H NMR spectrum of (*A*,*C*)-$(Egan)_2Ir_2$ (C_6D_6, 400 MHz).

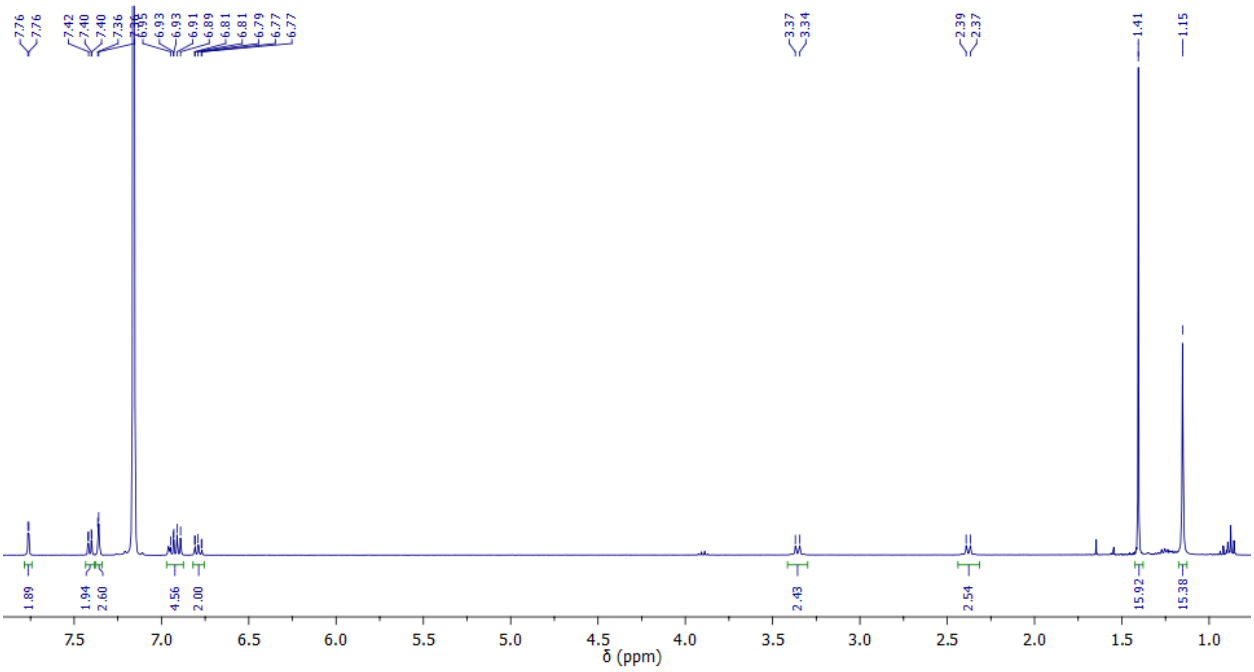


Figure S5. ^{1}H NMR spectrum of *cis*-β-(Egan)IrCl (C_6D_6, 400 MHz).

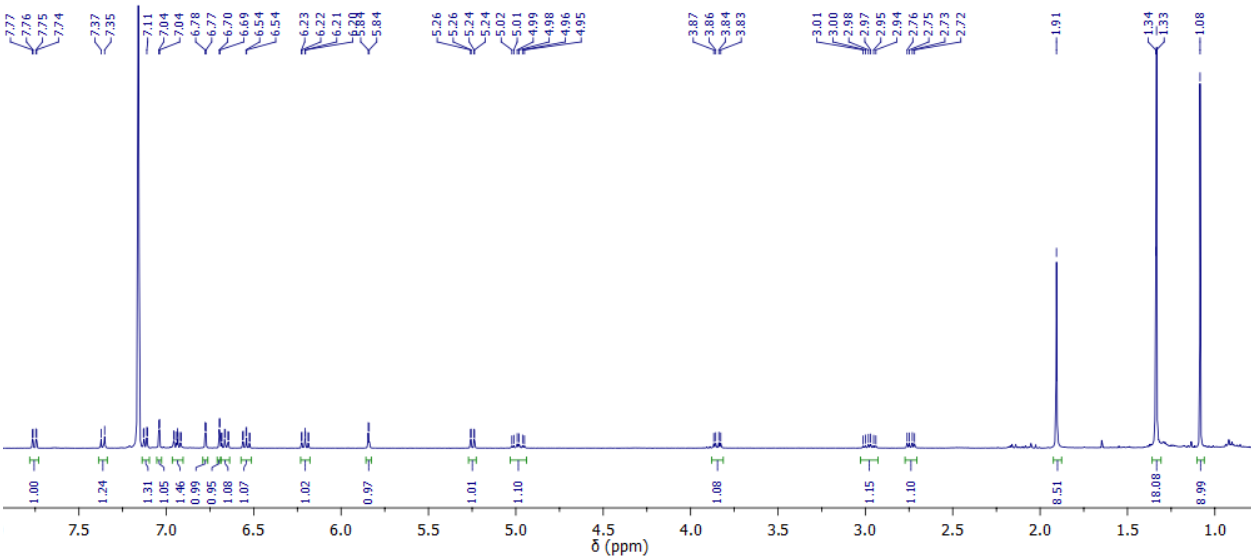


Figure S6. ^{1}H NMR spectrum of [Cp_2Co][(Egan)Ir] (acetone-d_6, 400 MHz).

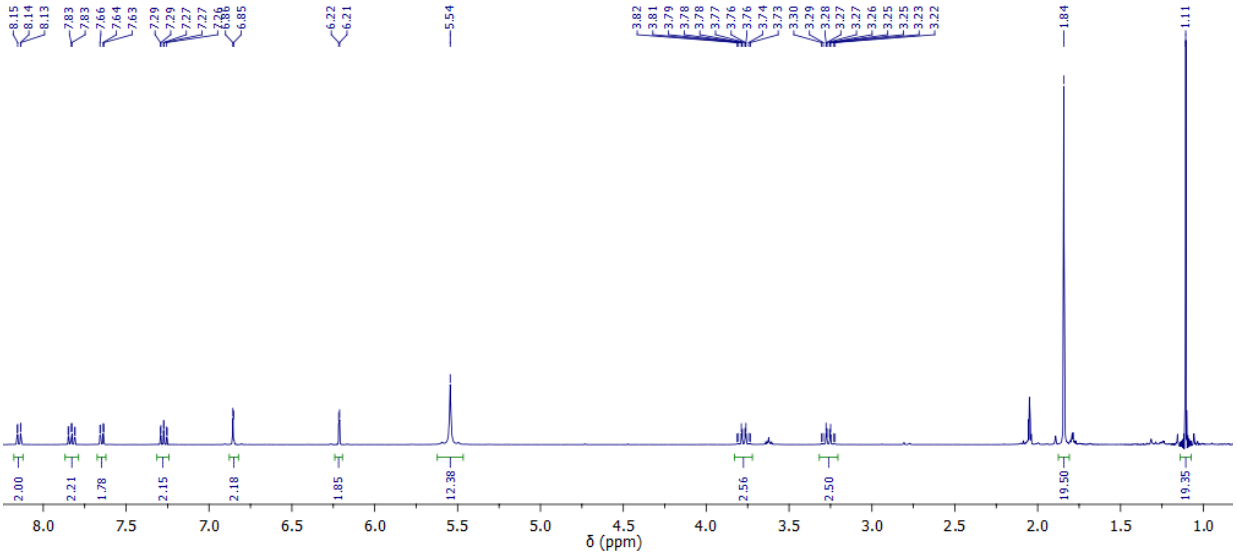
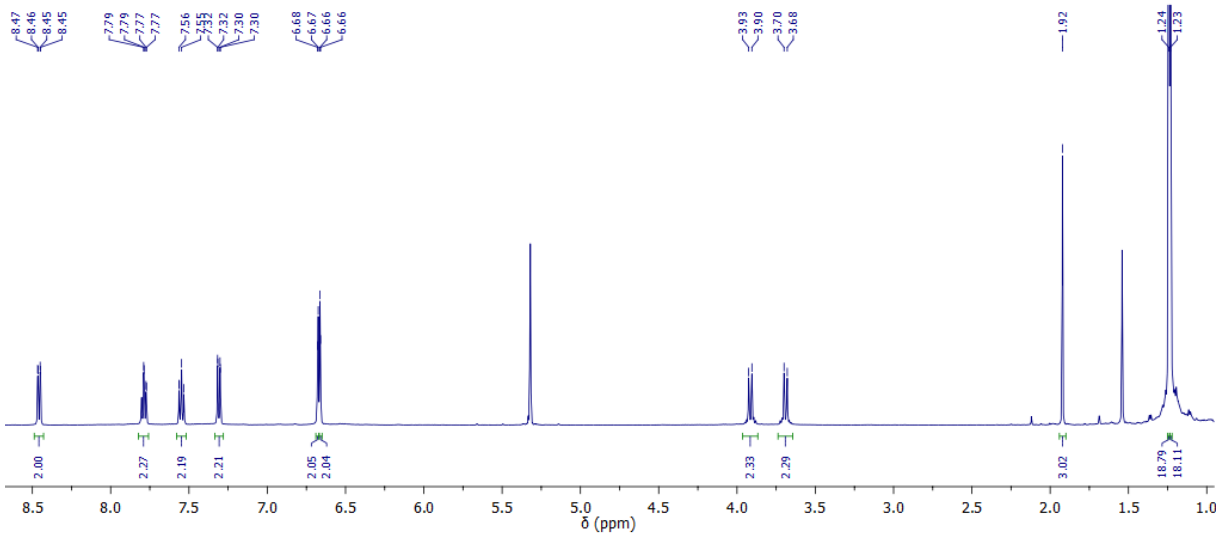


Figure S7. ^{1}H NMR spectrum of (Egan)IrCH$_3$ (CD_2Cl_2, 500 MHz).



II. $^{13}C\{^{1}H\}$ NMR spectra

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of Egan (CD_2Cl_2, 100.6 MHz)

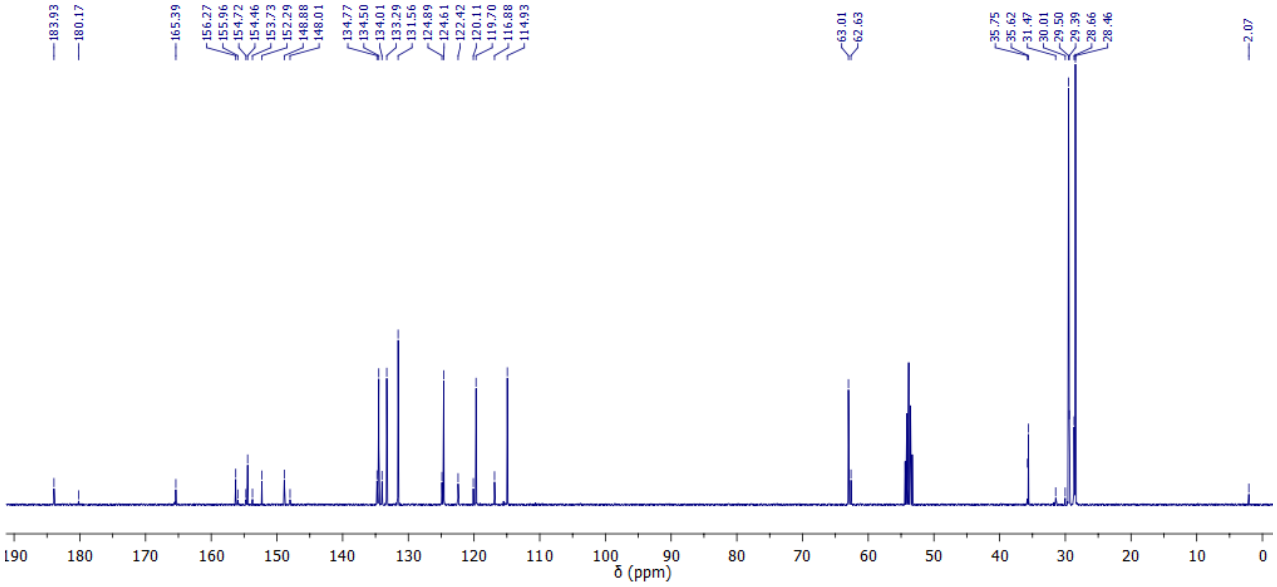


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of *cis*-α-(Egan)IrCl (CD_2Cl_2, 100.6 MHz)

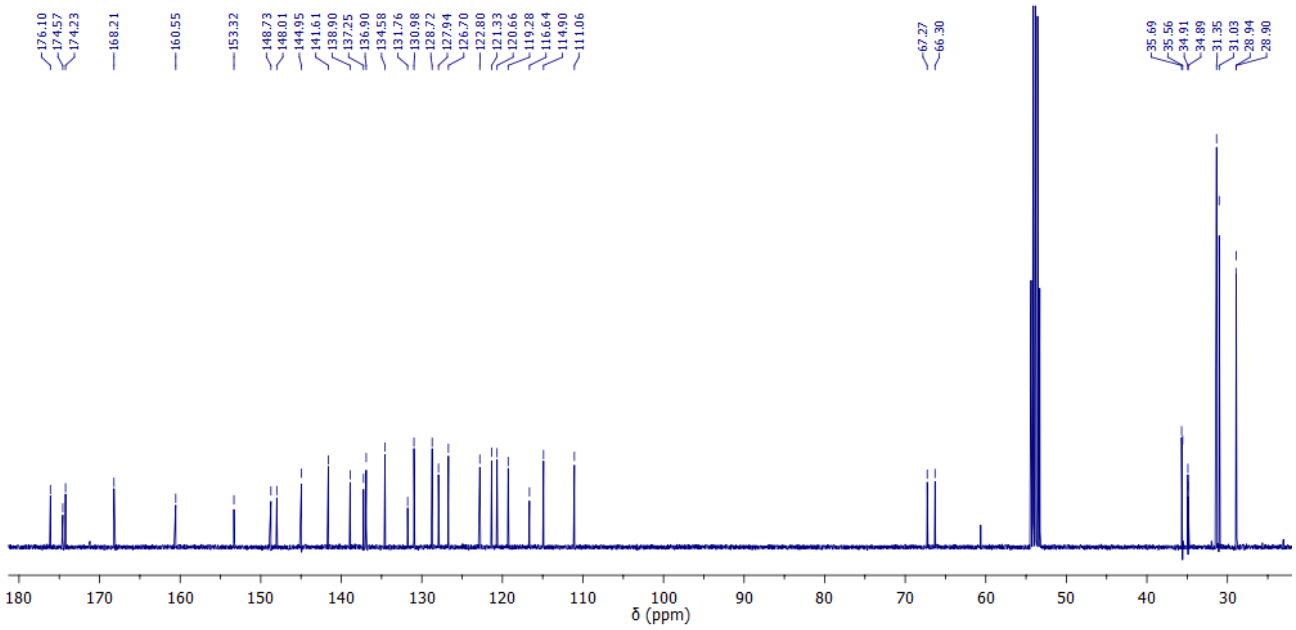


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of (*A*,*C*)-(Egan)$_2$Ir$_2$ (CD_2Cl_2, 150.9 MHz)

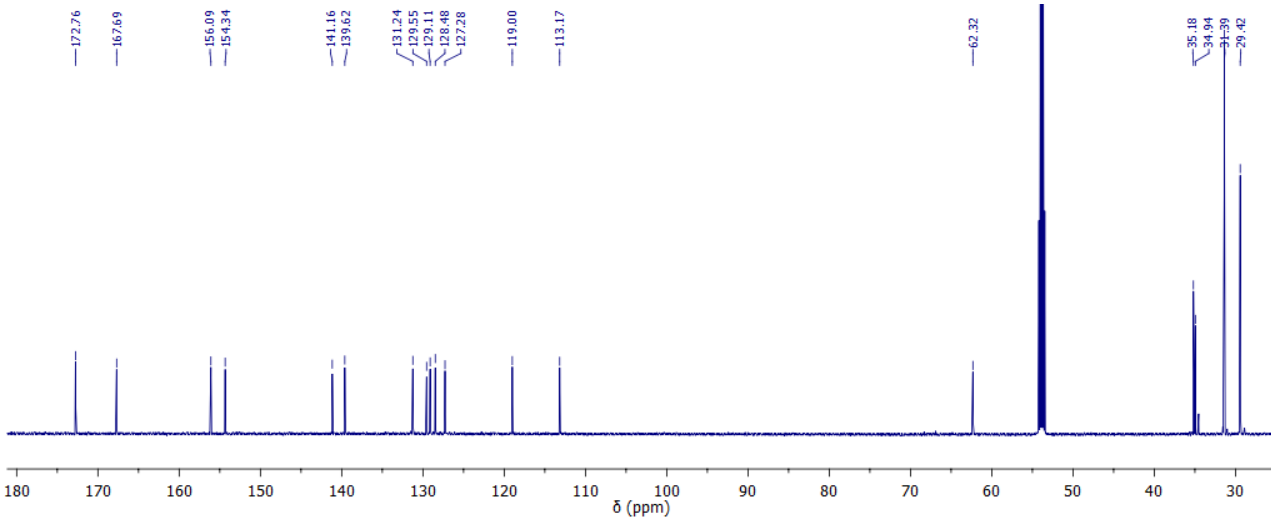


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of *cis*-β-(Egan)IrCl (CD_2Cl_2, 125.7 MHz)

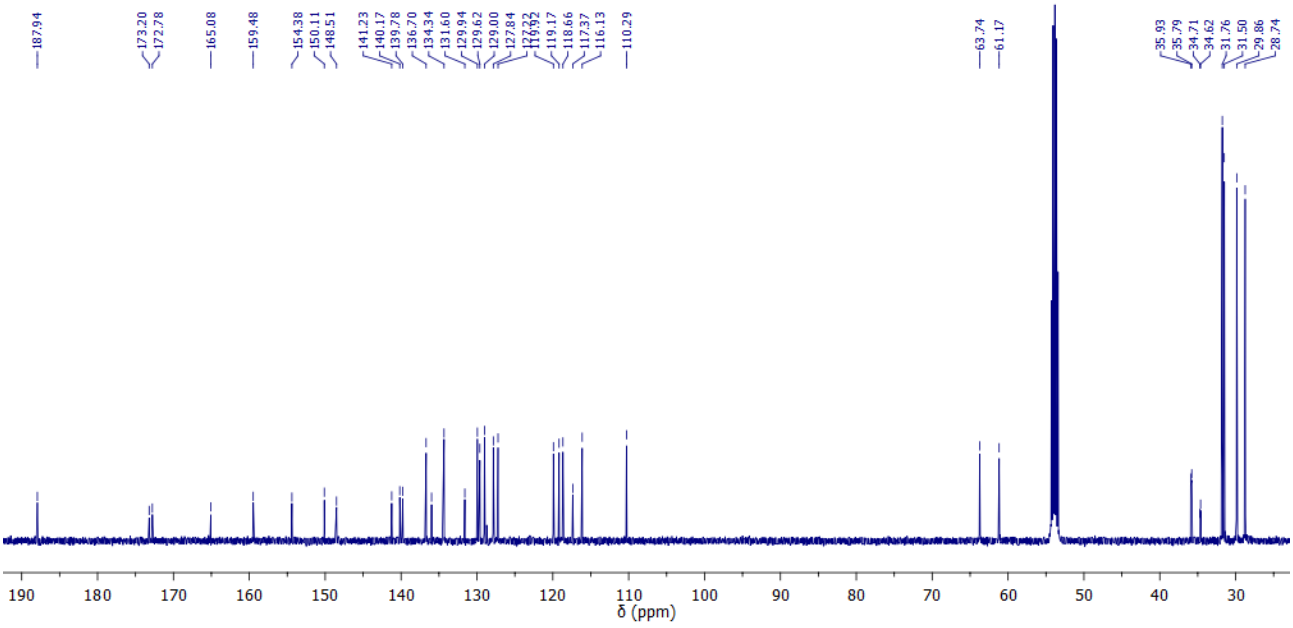


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of $[Cp_2Co][(Egan)Ir]$ (acetone-d_6, 100.6 MHz)

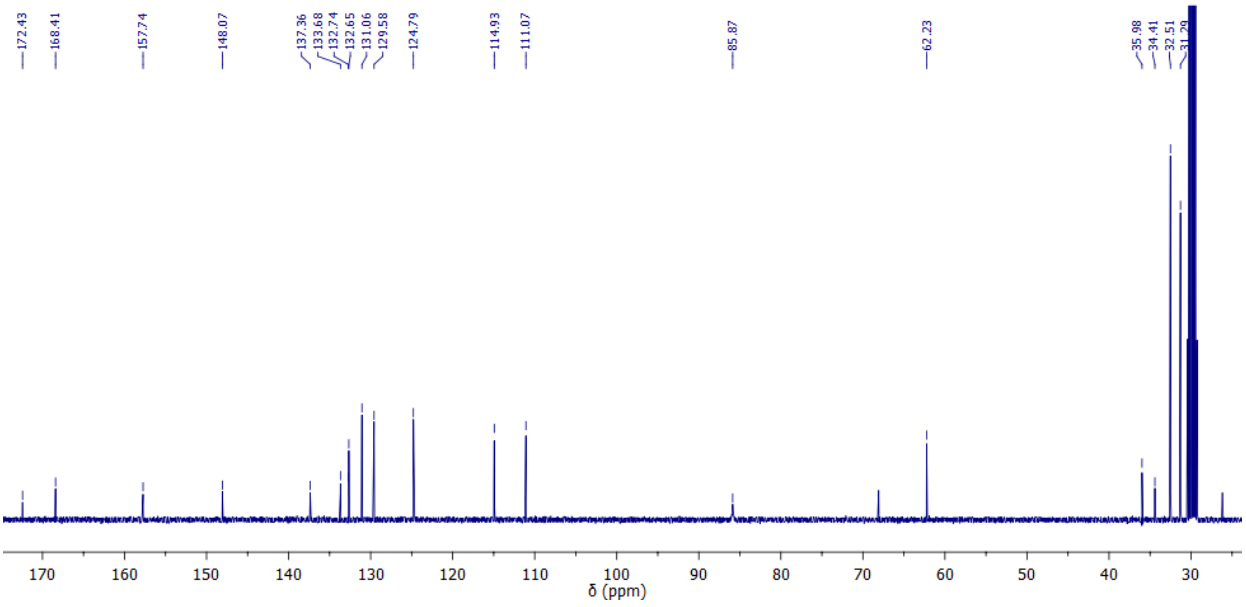
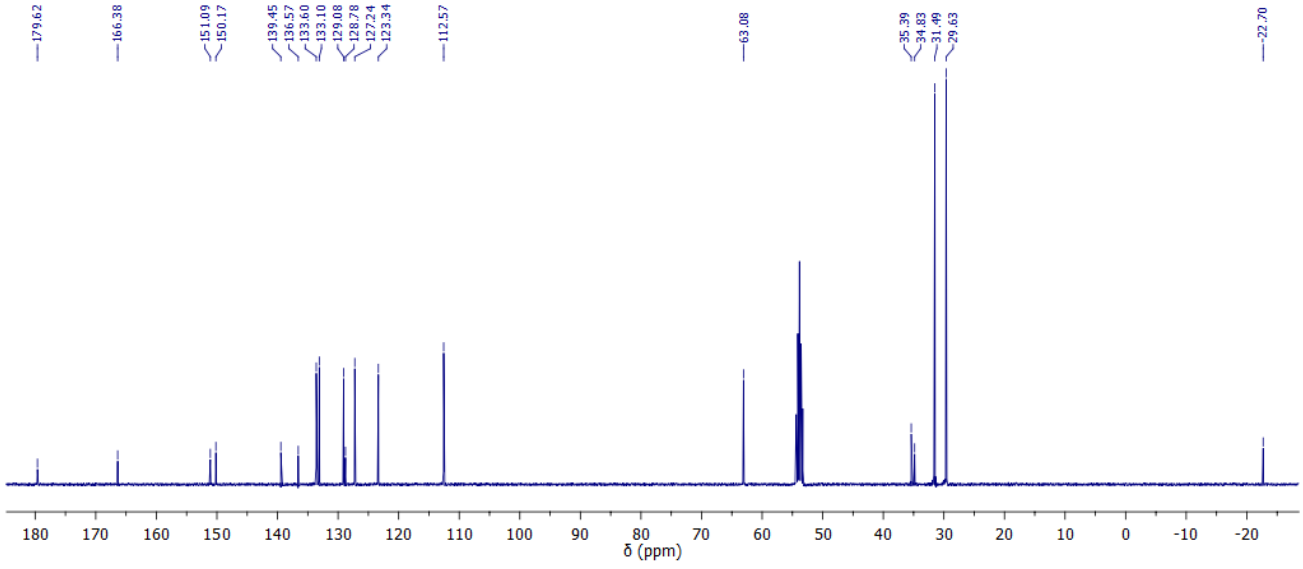


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of (Egan)$IrCH_3$ (CD_2Cl_2, 100.6 MHz)



III. IR spectra

Figure S14. IR spectrum of Egan (evaporated film)

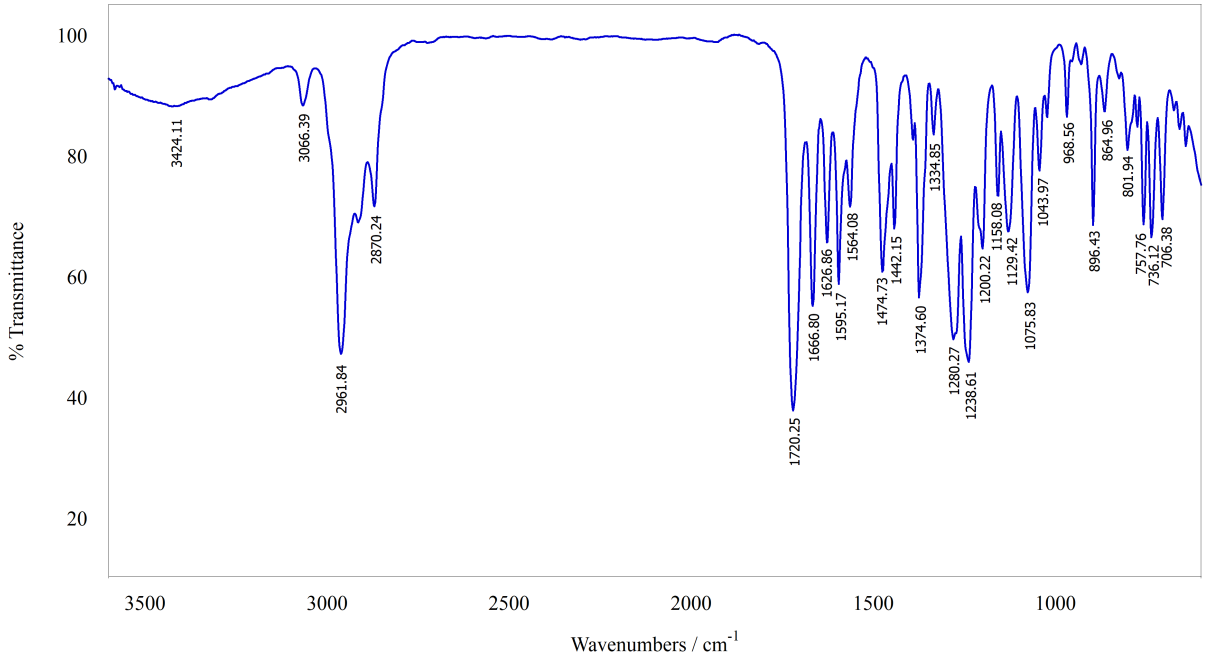


Figure S15. IR spectrum of (Egan)$IrCl_2$ (evaporated film)

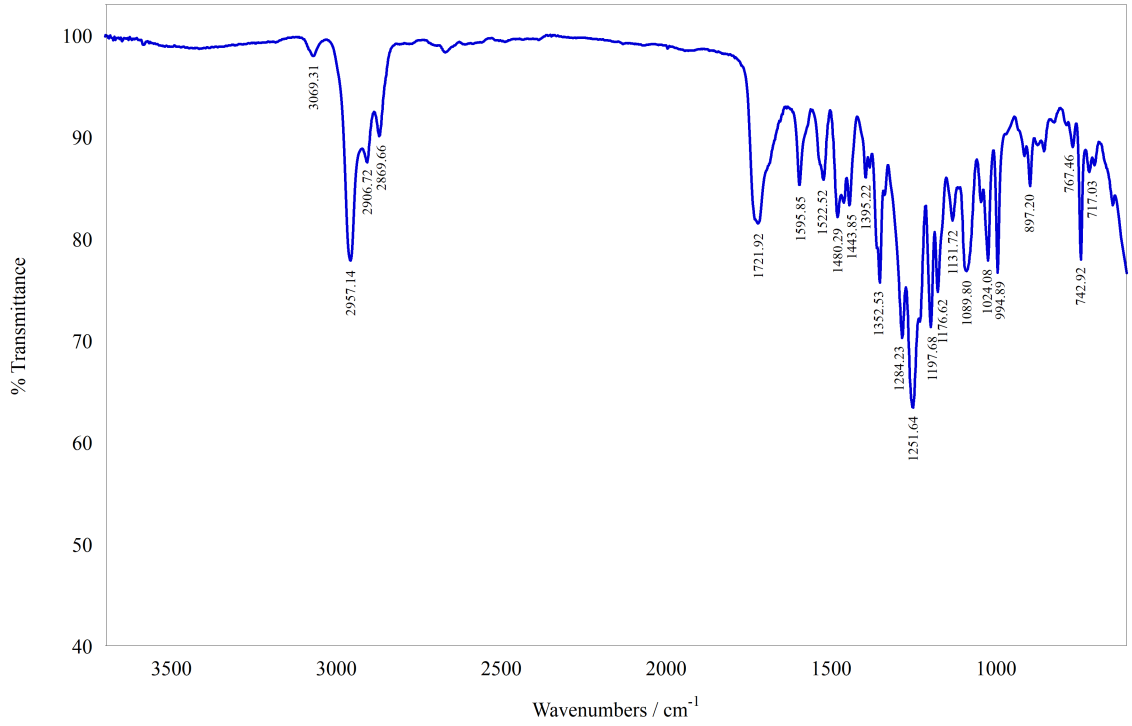


Figure S16. IR spectrum of *cis*-α-(Egan)IrCl (evaporated film)

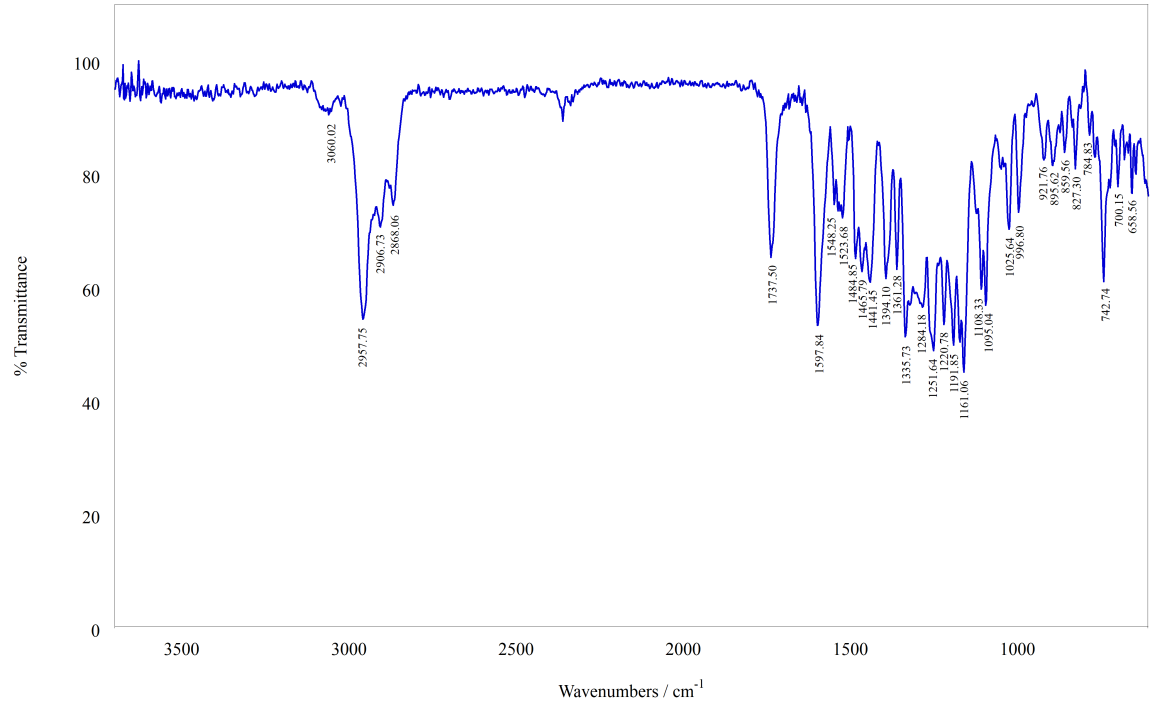


Figure S17. IR spectrum of (*A*,*C*)-$(Egan)_2Ir_2$ (evaporated film)

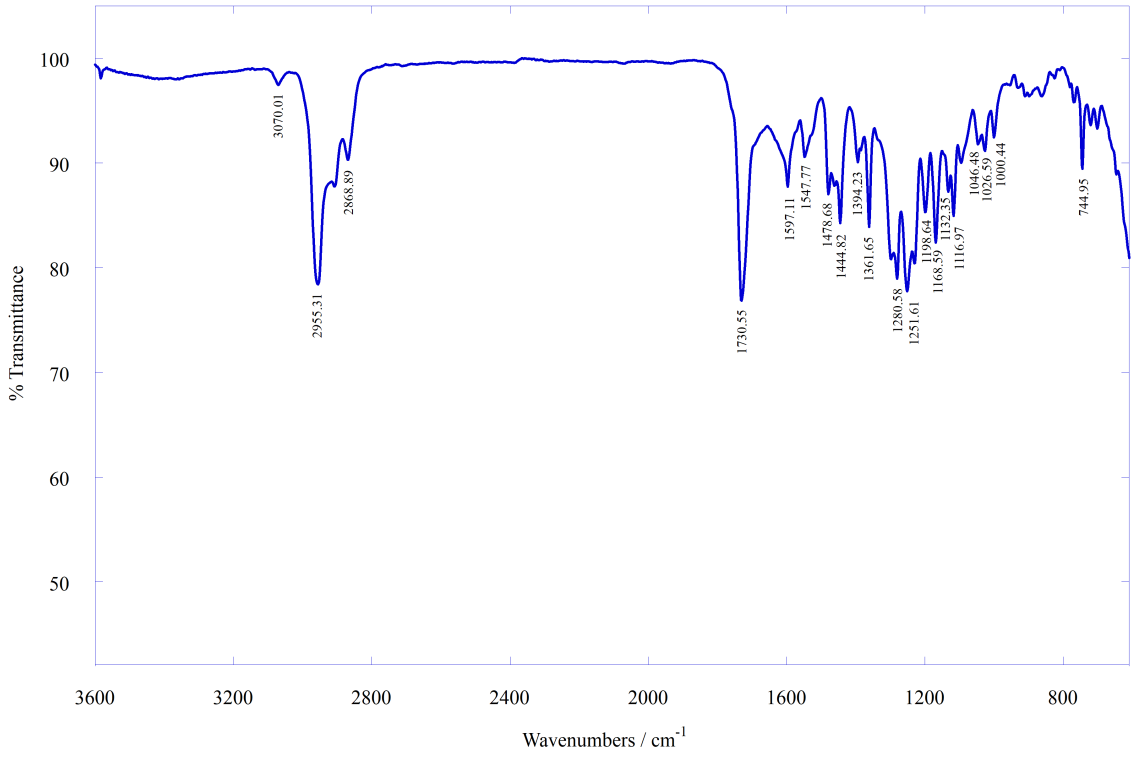


Figure S18. IR spectrum of *cis*-β-(Egan)IrCl (evaporated film)

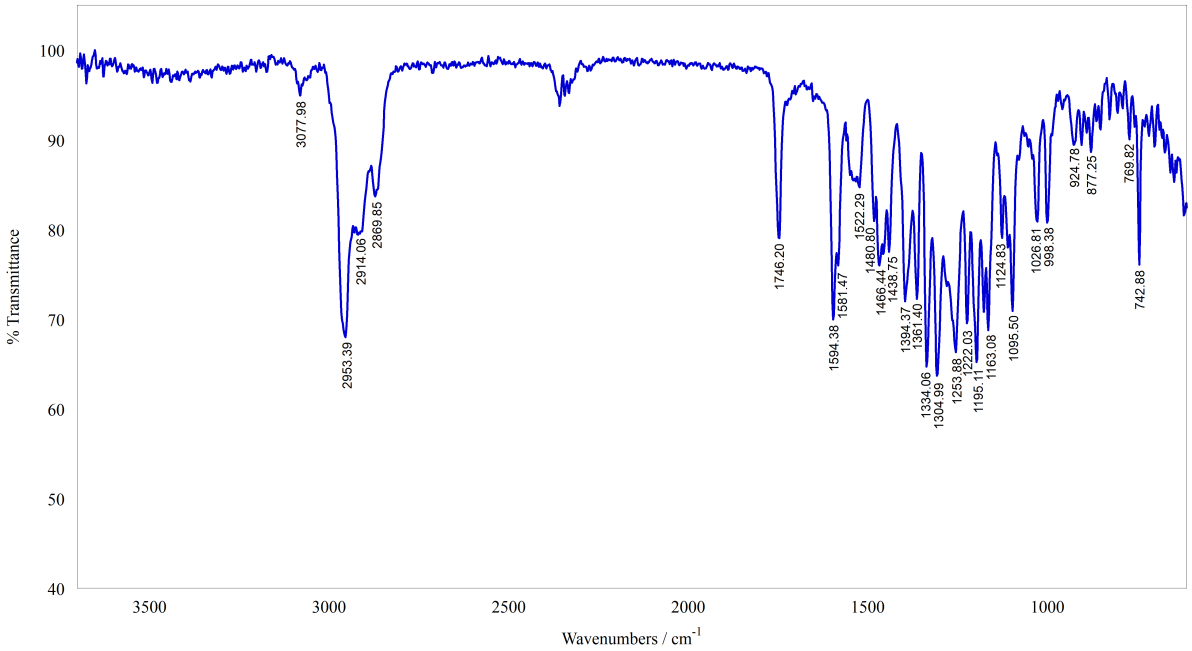


Figure S19. IR spectrum of $[Cp_2Co][(Egan)Ir]$ (ATR)

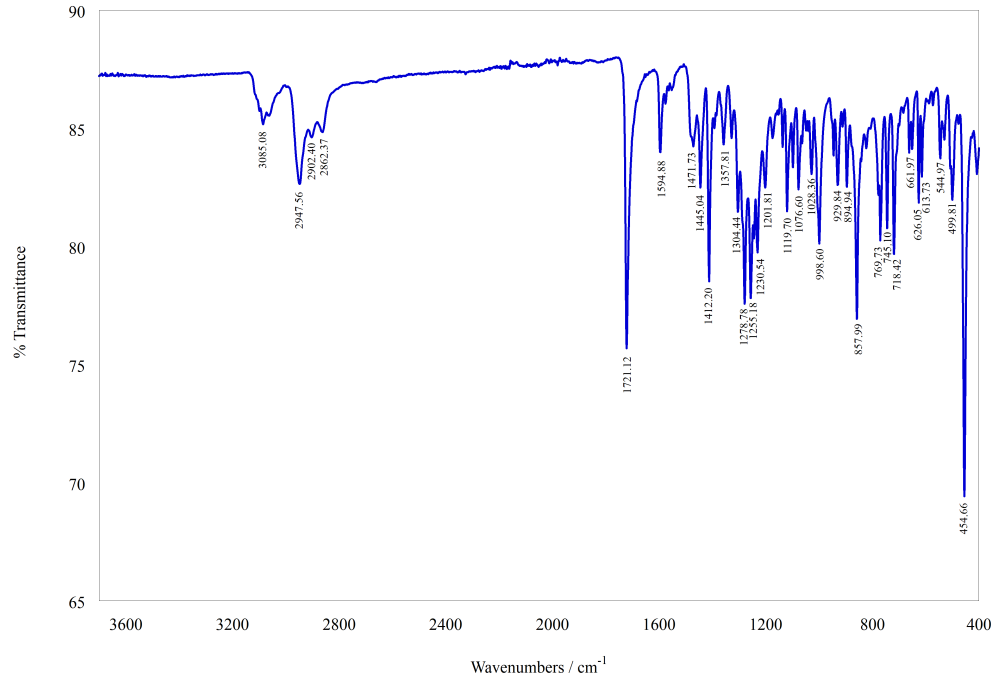
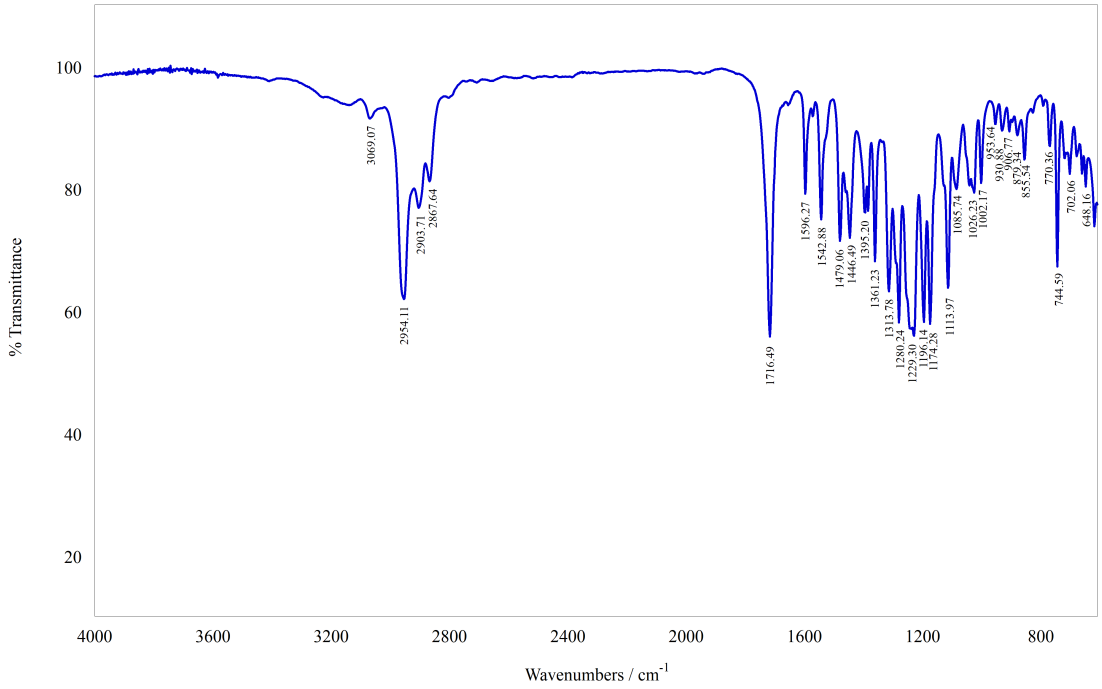


Figure S20. IR spectrum of (Egan)IrCH_3 (evaporated film)



IV. Optical Spectroscopy

Figure S21. Optical spectrum of Egan (CH_2Cl_2, 3.0×10^{-5} M).

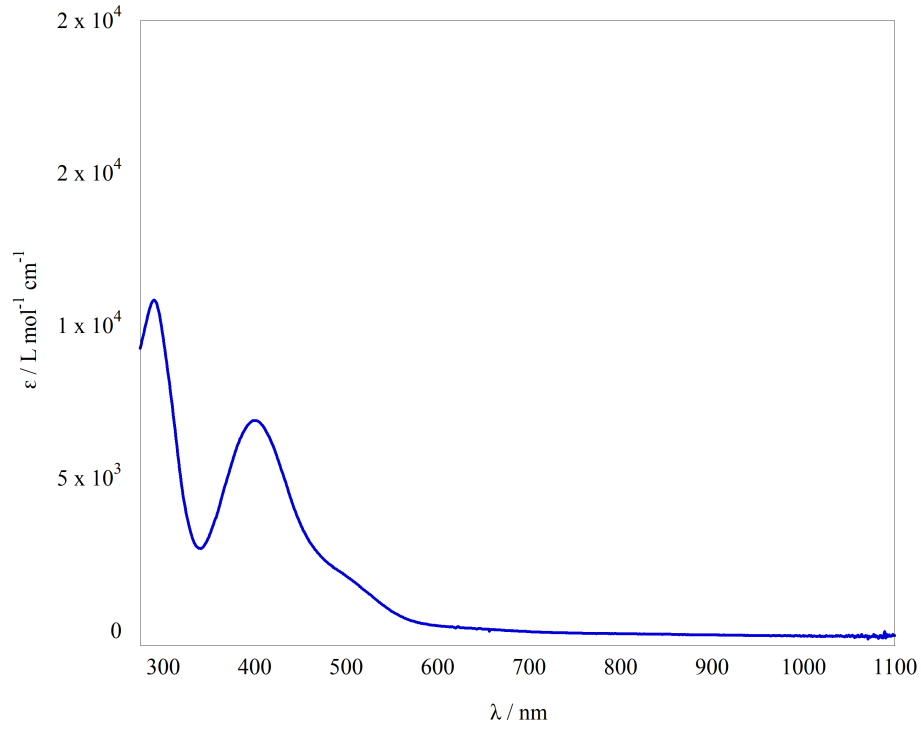


Figure S22. Optical spectrum of (Egan)$IrCl_2$ (CCl_4, 3.0×10^{-5} M).

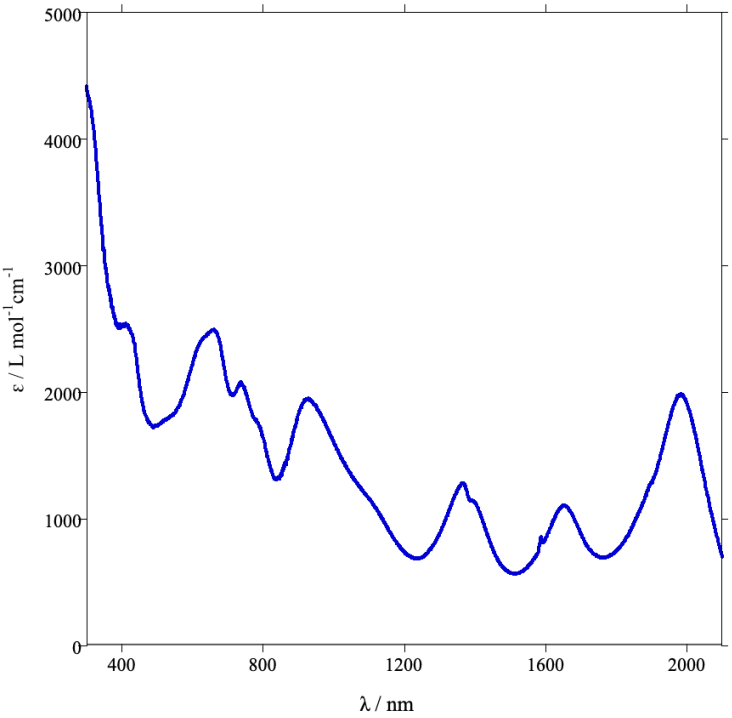


Figure S23. Optical spectrum of *cis*-α-(Egan)IrCl (CH_2Cl_2, 3.0×10^{-5} M)

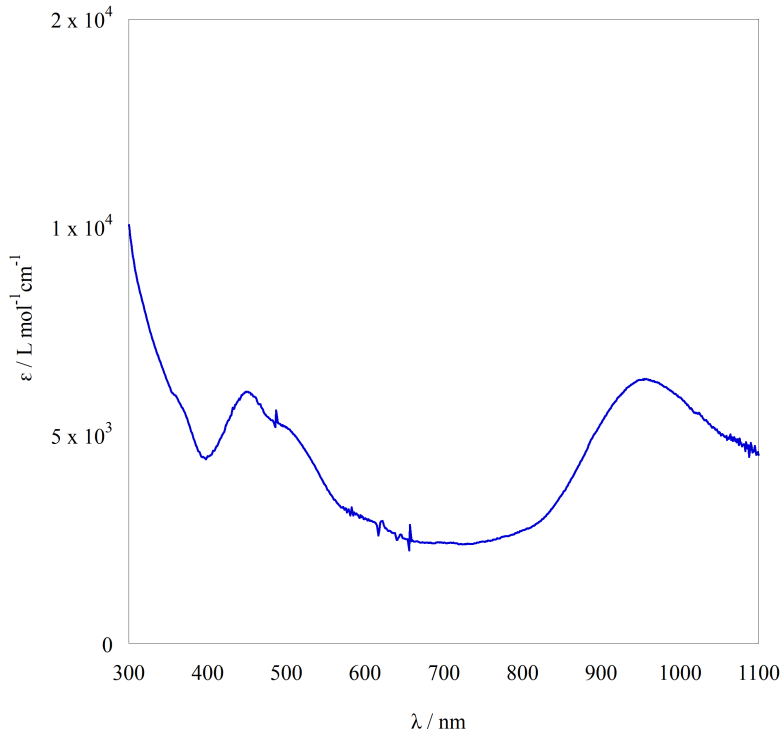


Figure S24. Optical spectrum of *cis*-β-(Egan)IrCl (CH_2Cl_2, 3.0×10^{-5} M)

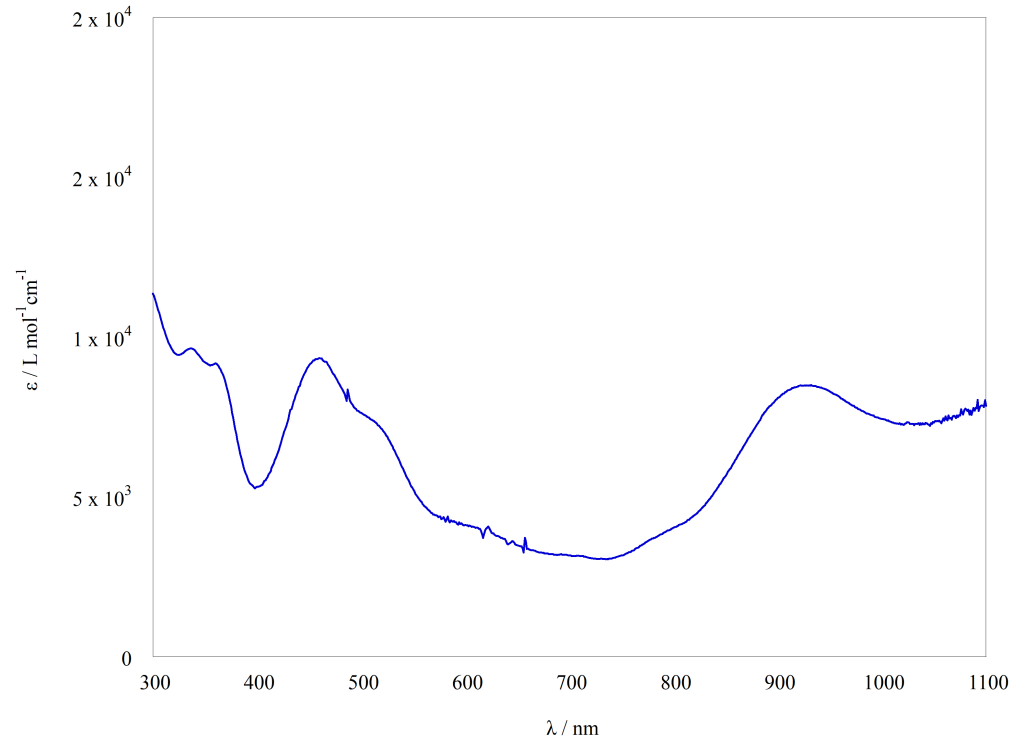
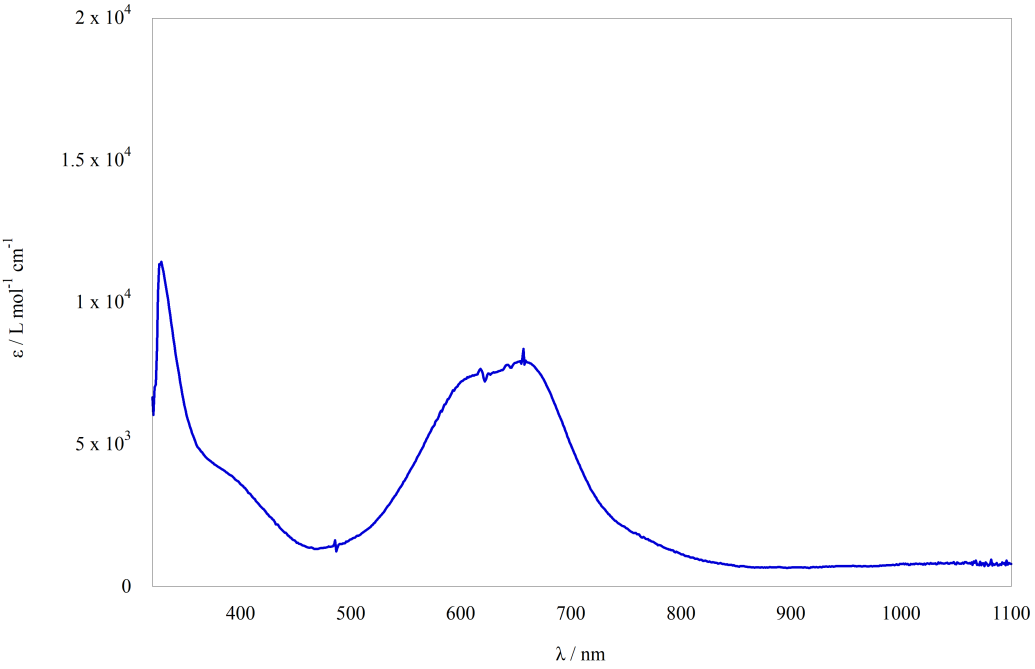


Figure S25. Optical spectrum of $[Cp_2Co][(Egan)Ir]$ (acetone, 3.0×10^{-5} M)



V. Electrochemistry

Figure S26. CV of *cis*-α-(Egan)IrCl (CH_2Cl_2, 100 mV s^{-1}, 0.1 M Bu_4NPF_6).

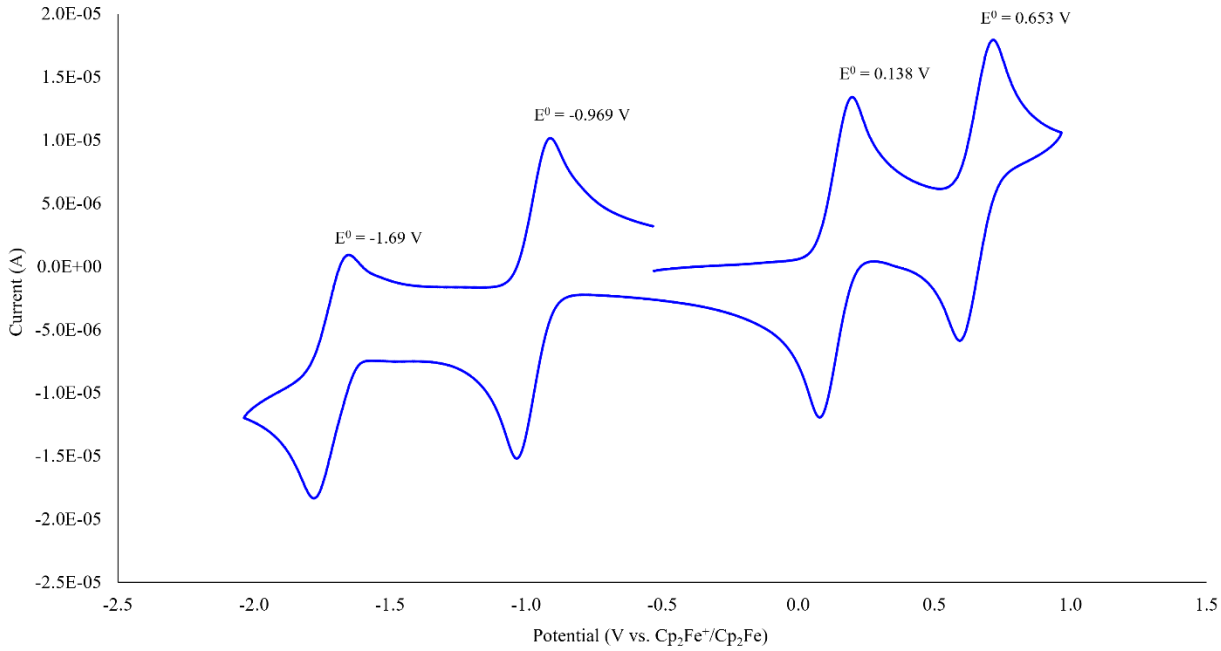


Figure S27. CV of *cis*-β-(Egan)IrCl (CH_2Cl_2, 100 mV s^{-1}, 0.1 M Bu_4NPF_6).

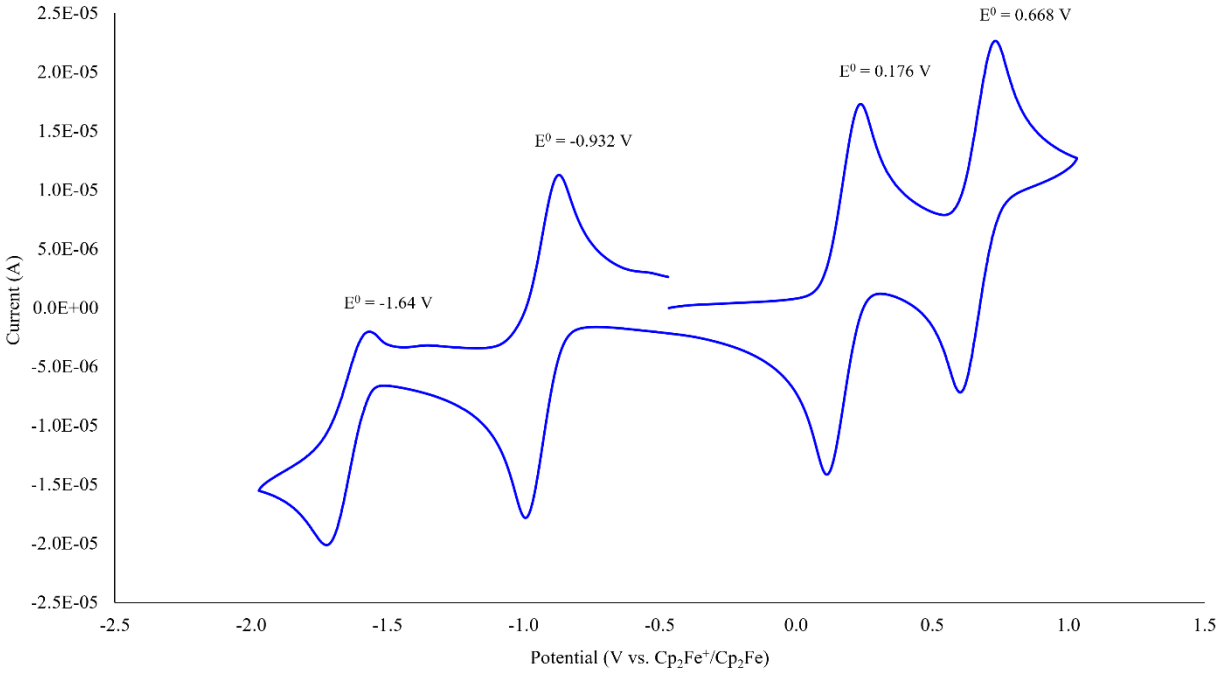


Figure S28. CV of $[Cp_2Co][(Egan)Ir]$ (THF, 100 mV s^{-1}, 0.1 M Bu_4NPF_6).

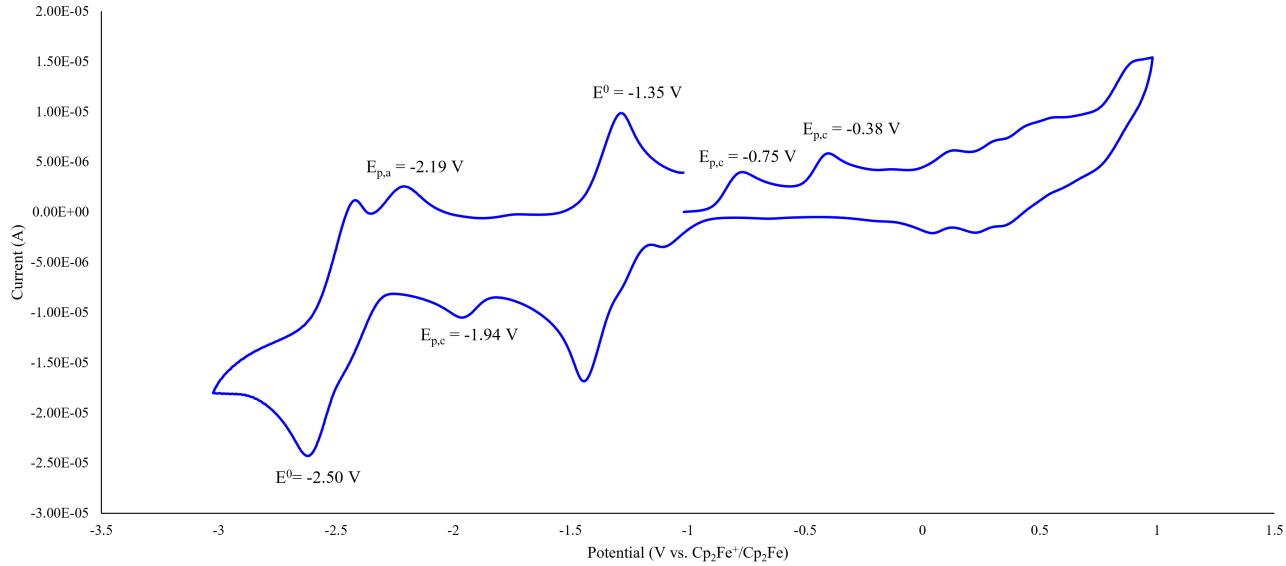
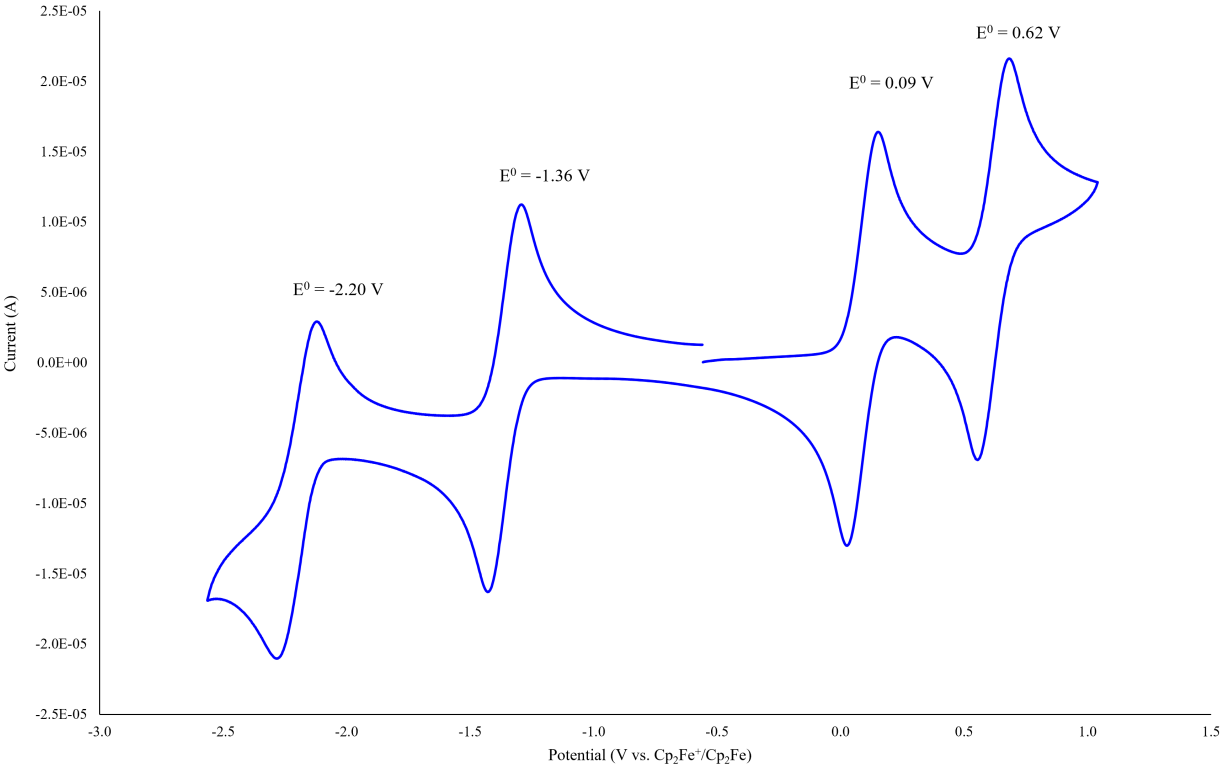
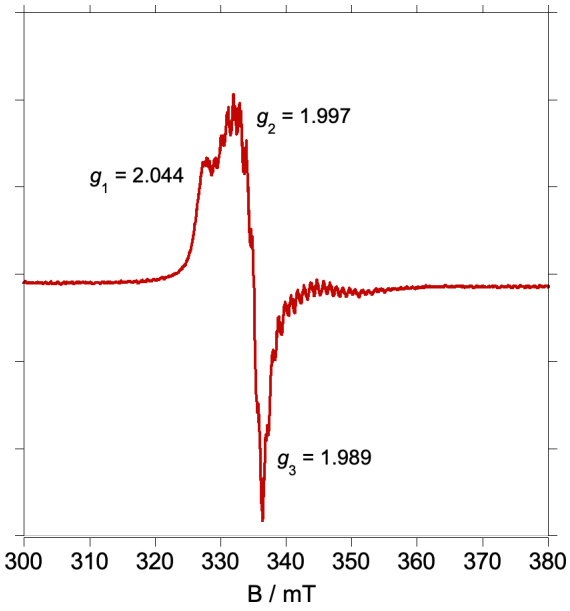


Figure S29. CV of (Egan)$IrCH_3$ (CH_2Cl_2, 100 mV s^{-1}, 0.1 M Bu_4NPF_6).



VI. EPR spectra

Figure S30. EPR spectrum of (Egan)$IrCl_2$ (13 K, CH_2Cl_2 glass).



VII. TDDFT analysis of the optical spectrum of (*A*,*C*)-(Egan)$_2$Ir$_2$

Table S1. Selected TDDFT calculated excitations for (*A*,*C*)-(Hap)$_4$Ir$_2$ and comparisons with experimentally observed bands in the optical spectrum of (*A*,*C*)-(Egan)$_2$Ir$_2$. Only excitations with calculated oscillator strengths greater than 0.015 and $E < 2.9$ eV are shown.

Excitn #	Sym-metry	Calc λ (cm^{-1})	Osc. strength (*f*)	Exptl λ (cm^{-1})	Exptl ε (L mol^{-1} cm^{-1})	Major component excitations	Coefficients
5	^1E	13100	0.0021	10600 (sh)	3300	128 → 130 129 → 130	0.48920 0.50370
6	^1E					128 → 131 129 → 131	–0.48920 0.50370
7	^1B	13300	0.0017	11200	3400	126 → 131 127 → 130 129 → 132	–0.27530 –0.27530 0.57821
9	^1B	16700	0.1705	13100 (sh)	10100	126 → 131 127 → 130 129 → 132	0.40036 0.40036 0.40589
10	^1E	16900	0.2923	14300	15800	123 → 132 125 → 131 127 → 132 128 → 130 128 → 131 129 → 130 129 → 131	–0.10926 0.10066 0.15513 –0.26341 0.37237 0.30634 0.34049
11	^1E					122 → 132 125 → 130 126 → 132 128 → 130 128 → 131 129 → 130 129 → 131	–0.10926 –0.10066 0.15513 0.37237 0.26341 –0.34049 0.30634
13	^1E	18600	0.0270	19500	7400	120 → 130 121 → 130 129 → 130	0.37999 0.56832 –0.11692
14	^1E					120 → 131 121 → 131 129 → 131	–0.37999 0.56832 –0.11692

23	^1B	23400	0.0268	20500	7200	122 → 130 123 → 131 125 → 132	–0.44436 0.44436 –0.30675
24	^1E	23400	0.0941			120 → 130 122 → 132 123 → 132 124 → 130 124 → 131 125 → 130 125 → 131	–0.18719 –0.31612 0.29598 0.34351 0.16947 –0.24278 –0.17796
25	^1E					120 → 131 122 → 132 123 → 132 124 → 130 124 → 131 125 → 130 125 → 131	–0.18719 –0.29598 –0.31612 –0.16947 0.34351 –0.17796 0.24278

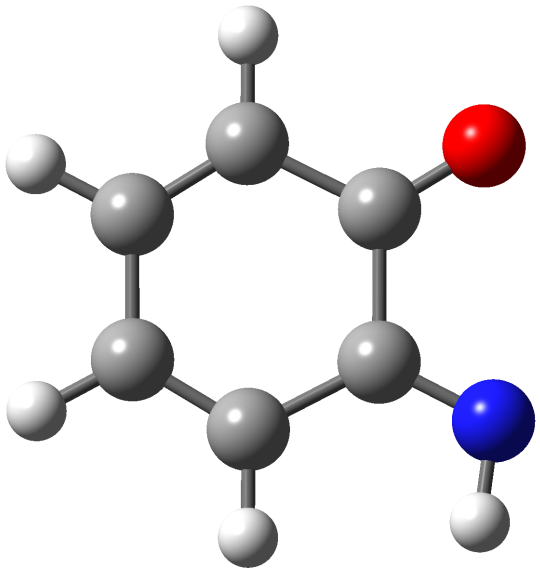
VIII. Comparison of experimental and calculated structural parameters for (*A*,*C*)-(Egan)$_2$Ir$_2$ and (*A*,*C*)-(Hap)$_2$Ir$_2$

Table S2. Selected distances, angles, and metrical oxidation states (MOS) of iminoxolene ligands in (*A*,*C*)-(Egan)$_2$Ir$_2$ (X-ray) and (*A*,*C*)-(Hap)$_4$Ir$_2$ (DFT)

	(*A*,*C*)-(Egan)$_2$Ir$_2$ *X-ray*	(*A*,*C*)-(Hap)$_4$Ir$_2$ *DFT* S_4 symmetry (minimum energy)	(*A*,*C*)-(Hap)$_4$Ir$_2$ *DFT* C_{2h} symmetry (transition state)
Distances / Å			
Ir–O	1.994(3)	2.043	2.051
Ir–N	1.938(3)	1.956	1.953
Ir–Ir	2.5584(4)	2.599	2.724
O1–C11	1.329(5)	1.317	1.310
N1–C12	1.394(5)	1.362	1.361
C11–C12	1.418(5)	1.432	1.435
C12–C13	1.388(6)	1.413	1.413
C13–C14	1.395(6)	1.383	1.382
C14–C15	1.400(6)	1.416	1.418
C15–C16	1.392(6)	1.386	1.384
C11–C16	1.402(6)	1.410	1.412
MOS	–1.66(9)	–1.27(4)	–1.20(4)
Angles / °			
O1–Ir–O1A	164.79(16)	170.60	169.77
N1–Ir–N1A	148.24(17)	164.87	161.24
O1–Ir–N1	81.23(13)	79.05	78.81

IX. Energies, Cartesian coordinates, and MOS values of calculated structures

A. Hap



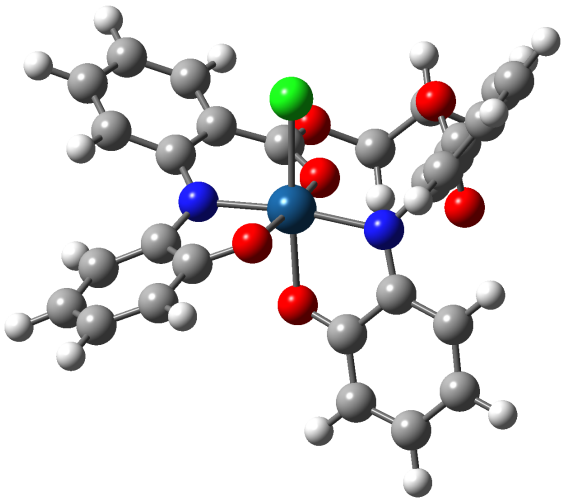
Energy of optimized structure = –361.564974878 a.u.

MOS = 0.27(10)

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-2.382255	2.166564	0.554457
2	7	0.062263	0.945926	0.118357
3	6	-2.345835	0.988312	0.239256
4	6	-1.016536	0.261467	-0.014203
5	6	-1.076340	-1.156993	-0.388541
6	1	-0.134064	-1.671375	-0.568361
7	6	-2.256550	-1.801240	-0.506435
8	1	-2.283216	-2.851342	-0.784767
9	6	-3.522281	-1.117763	-0.267278
10	1	-4.439714	-1.690899	-0.377943
11	6	-3.573774	0.186001	0.081539
12	1	-4.510743	0.703945	0.261629
13	1	0.878586	0.351086	-0.075372

B. *cis*-α-(egan)IrCl



Energy of optimized structure = –2204.52499146 a.u.

MOS = –1.49(9) (κ^3-iminoxolene)

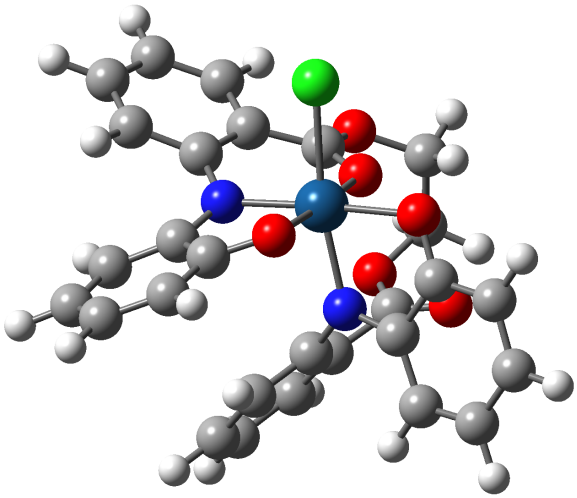
–1.05(7) (κ^2-iminoxolene)

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.087670	-1.590087	-1.610842
2	6	3.210425	-0.981979	-0.704998
3	6	2.712476	0.305562	-0.985282
4	6	3.120739	0.965148	-2.149502
5	6	4.022467	0.360998	-3.024517
6	6	4.504556	-0.921142	-2.759735
7	6	2.887312	-1.685434	0.574679
8	8	2.443318	-2.949372	0.348599
9	6	2.163991	-3.762822	1.497546
10	6	0.972733	-3.332808	2.347316
11	8	-0.307396	-3.408272	1.663391
12	6	-0.705970	-2.327194	0.986013
13	6	-2.067638	-2.387313	0.451523
14	6	-2.783712	-1.236488	-0.034617
15	6	-4.086632	-1.455160	-0.544527
16	6	-4.668160	-2.711667	-0.551754
17	6	-3.983480	-3.822216	-0.039908
18	6	-2.699929	-3.648576	0.448376
19	7	-2.217219	0.022214	-0.037315
20	6	-2.898319	1.229917	-0.158921
21	6	-2.114300	2.270056	-0.765952
22	6	-2.702601	3.523215	-1.022049
23	6	-4.006684	3.768413	-0.620513

24	6	-4.755202	2.774451	0.039651
25	6	-4.210541	1.519110	0.268540
26	8	-0.857371	2.016708	-1.116158
27	77	-0.248962	0.351493	-0.182987
28	8	0.102321	-1.379374	0.903959
29	7	1.699693	0.895680	-0.174444
30	6	1.954763	1.940785	0.647943
31	6	0.868938	2.237788	1.564271
32	6	1.039313	3.250360	2.538060
33	6	2.224858	3.953877	2.588465
34	6	3.294466	3.657352	1.700794
35	6	3.175147	2.663185	0.756082
36	8	-0.204007	1.493050	1.519927
37	17	-0.165399	-0.943823	-2.186934
38	8	3.041809	-1.219047	1.683586
39	1	3.038478	-3.781274	2.158897
40	1	2.000133	-4.761056	1.085747
41	1	-4.781351	0.764408	0.798959
42	1	-4.448017	4.745246	-0.798291
43	1	-2.101139	4.283808	-1.509732
44	1	-5.761787	2.993269	0.383765
45	1	3.994990	2.424906	0.087779
46	1	2.349030	4.744807	3.322937
47	1	4.219317	4.221835	1.774238
48	1	-4.615434	-0.618839	-0.983258
49	1	-5.660151	-2.832587	-0.978789
50	1	-4.439668	-4.806891	-0.044498
51	1	-2.146988	-4.499883	0.826322
52	1	2.691391	1.935809	-2.376199
53	1	4.327541	0.886018	-3.925277
54	1	5.193303	-1.402487	-3.447649
55	1	4.449874	-2.591378	-1.399715
56	1	0.870969	-4.047304	3.168511
57	1	1.114950	-2.329249	2.743296
58	1	0.219591	3.452124	3.219910

C. *cis*-β-(egan)IrCl



Energy of optimized structure = –2204.52269915 a.u.

MOS = –1.56(10) (κ^3-iminoxolene)

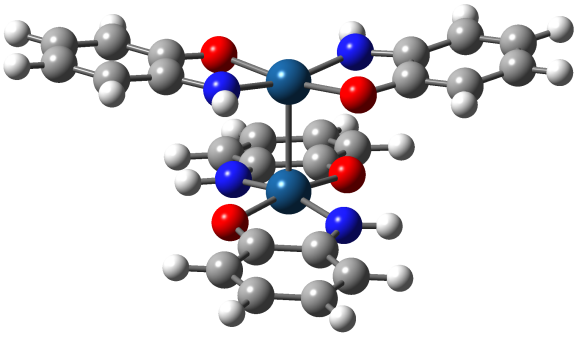
–0.94(6) (κ^2-iminoxolene)

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-4.141392	-1.451334	-0.290602
2	6	-2.832224	-0.923579	-0.299873
3	6	-2.631607	0.473518	-0.016080
4	6	-3.792680	1.261264	0.181596
5	6	-5.063933	0.714296	0.157594
6	6	-5.250933	-0.657323	-0.059557
7	6	-1.747622	-1.856599	-0.609910
8	8	-2.084448	-3.150813	-0.541311
9	6	-1.028076	-4.127561	-0.696283
10	6	-0.527828	-4.561544	0.682676
11	8	-0.301557	-3.433837	1.541406
12	6	0.843739	-2.718106	1.358861
13	6	0.848412	-1.529497	2.266358
14	6	1.211846	-0.249804	1.800201
15	6	1.221931	0.828947	2.694599
16	6	0.888011	0.642425	4.035210
17	6	0.513526	-0.620646	4.496117
18	6	0.479742	-1.693703	3.609421
19	7	1.505945	-0.002915	0.425657
20	6	2.785686	-0.009278	-0.010027
21	6	2.915016	-0.022451	-1.458283
22	6	4.208031	-0.064957	-2.043858
23	6	5.317387	-0.102743	-1.231176
24	6	5.190748	-0.120607	0.188082
25	6	3.956417	-0.091852	0.794373
26	8	1.830045	-0.090196	-2.161271
27	77	0.164315	0.377182	-1.057778
28	7	-1.370794	1.035872	0.037002
29	6	-1.065401	2.289470	0.575655
30	6	0.057757	2.926120	-0.046618
31	6	0.453437	4.210788	0.371444
32	6	-0.204471	4.827576	1.426480
33	6	-1.266515	4.179452	2.082999
34	6	-1.694000	2.925406	1.664767
35	1	6.087823	-0.156378	0.799294
36	1	4.279953	-0.068657	-3.126366
37	8	0.699075	2.297719	-1.028641
38	1	-1.752115	4.655042	2.930227
39	1	1.288779	4.681888	-0.137151
40	17	-1.148608	0.628597	-3.037932
41	8	-0.571258	-1.580225	-0.928427
42	8	1.713550	-3.031237	0.578508
43	1	0.387578	-5.150069	0.568258
44	1	-1.286268	-5.148166	1.204726
45	1	3.863624	-0.110569	1.874597
46	1	6.309427	-0.126115	-1.673257

47	1	-2.494114	2.419742	2.194331
48	1	0.115562	5.811718	1.757461
49	1	1.478279	1.813902	2.319156
50	1	0.906426	1.491274	4.712716
51	1	0.241206	-0.768295	5.536965
52	1	0.174769	-2.676909	3.952271
53	1	-3.676292	2.329494	0.307296
54	1	-5.922317	1.367550	0.290171
55	1	-6.246825	-1.088076	-0.075298
56	1	-4.268748	-2.507237	-0.494538
57	1	-0.226313	-3.710965	-1.302758
58	1	-1.485705	-4.976394	-1.210043

D. (*A*,*C*)-(Hap)$_4$Ir$_2$, minimum-energy structure, S_4-symmetric



Energy of optimized structure = –1655.38951132 a.u.

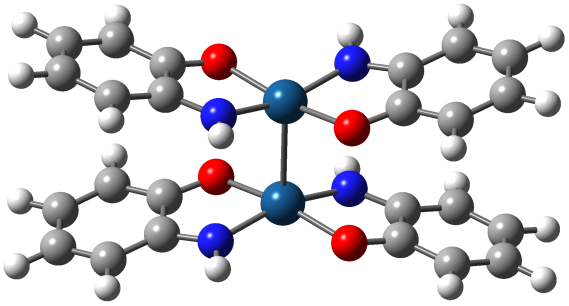
MOS = –1.27(4)

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	77	0.000000	0.000000	1.299539
2	77	0.000000	0.000000	-1.299539
3	8	0.640933	1.932855	1.466975
4	7	-1.699468	0.934139	1.557004
5	6	-0.332269	2.807902	1.614246
6	6	-1.665530	2.289634	1.681421
7	6	-2.762415	3.160237	1.866009
8	1	-3.769947	2.754413	1.918403
9	6	-2.531504	4.520173	1.967593
10	1	-3.365560	5.202171	2.103481
11	6	-1.214125	5.033664	1.895274
12	1	-1.057809	6.105540	1.981415
13	6	-0.121751	4.197995	1.720915
14	1	0.892473	4.582874	1.674385
15	8	-0.640933	-1.932855	1.466975
16	7	1.699468	-0.934139	1.557004

17	6	0.332269	-2.807902	1.614246
18	6	1.665530	-2.289634	1.681421
19	6	2.762415	-3.160237	1.866009
20	1	3.769947	-2.754413	1.918403
21	6	2.531504	-4.520173	1.967593
22	1	3.365560	-5.202171	2.103481
23	6	1.214125	-5.033664	1.895274
24	1	1.057809	-6.105540	1.981415
25	6	0.121751	-4.197995	1.720915
26	1	-0.892473	-4.582874	1.674385
27	8	1.932855	-0.640933	-1.466975
28	7	0.934139	1.699468	-1.557004
29	6	2.807902	0.332269	-1.614246
30	6	2.289634	1.665530	-1.681421
31	6	3.160237	2.762415	-1.866009
32	1	2.754413	3.769947	-1.918403
33	6	4.520173	2.531504	-1.967593
34	1	5.202171	3.365560	-2.103481
35	6	5.033664	1.214125	-1.895274
36	1	6.105540	1.057809	-1.981415
37	6	4.197995	0.121751	-1.720915
38	1	4.582874	-0.892473	-1.674385
39	8	-1.932855	0.640933	-1.466975
40	7	-0.934139	-1.699468	-1.557004
41	6	-2.807902	-0.332269	-1.614246
42	6	-2.289634	-1.665530	-1.681421
43	6	-3.160237	-2.762415	-1.866009
44	1	-2.754413	-3.769947	-1.918403
45	6	-4.520173	-2.531504	-1.967593
46	1	-5.202171	-3.365560	-2.103481
47	6	-5.033664	-1.214125	-1.895274
48	1	-6.105540	-1.057809	-1.981415
49	6	-4.197995	-0.121751	-1.720915
50	1	-4.582874	0.892473	-1.674385
51	1	2.616184	-0.492227	1.602711
52	1	-2.616184	0.492227	1.602711
53	1	0.492227	2.616184	-1.602711
54	1	-0.492227	-2.616184	-1.602711

E. (*A*,*C*)-(Hap)$_4$Ir$_2$, constrained to be C_{2h}-symmetric



Energy of optimized structure = –1655.37553652 a.u.

MOS = –1.20(4)

Single imaginary frequency: 17.1*i* cm^{-1}

Cartesian coordinates of optimized structure:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	77	0.000000	0.000000	1.361887
2	8	1.299132	1.576690	1.544737
3	7	-1.238283	1.476285	1.680231
4	1	-2.247676	1.381555	1.785858
5	6	0.713733	2.726668	1.770961
6	6	-0.717538	2.718998	1.874658
7	6	-1.423444	3.907748	2.167965
8	1	-2.507764	3.885446	2.252084
9	6	-0.715925	5.082163	2.338291
10	1	-1.243071	6.005607	2.558877
11	6	0.697538	5.094052	2.225538
12	1	1.229988	6.031118	2.364387
13	6	1.411461	3.942348	1.944867
14	1	2.493545	3.943826	1.860394
15	8	-1.299132	-1.576690	1.544737
16	7	1.238283	-1.476285	1.680231
17	1	2.247676	-1.381555	1.785858
18	6	-0.713733	-2.726668	1.770961
19	6	0.717538	-2.718998	1.874658
20	6	1.423444	-3.907748	2.167965
21	1	2.507764	-3.885446	2.252084
22	6	0.715925	-5.082163	2.338291
23	1	1.243071	-6.005607	2.558877
24	6	-0.697538	-5.094052	2.225538
25	1	-1.229988	-6.031118	2.364387
26	6	-1.411461	-3.942348	1.944867
27	1	-2.493545	-3.943826	1.860394
28	77	0.000000	0.000000	-1.361887
29	8	1.299132	1.576690	-1.544737
30	7	-1.238283	1.476285	-1.680231
31	1	-2.247676	1.381555	-1.785858
32	6	0.713733	2.726668	-1.770961
33	6	-0.717538	2.718998	-1.874658
34	6	-1.423444	3.907748	-2.167965
35	1	-2.507764	3.885446	-2.252084
36	6	-0.715925	5.082163	-2.338291
37	1	-1.243071	6.005607	-2.558877
38	6	0.697538	5.094052	-2.225538
39	1	1.229988	6.031118	-2.364387
40	6	1.411461	3.942348	-1.944867
41	1	2.493545	3.943826	-1.860394
42	8	-1.299132	-1.576690	-1.544737
43	7	1.238283	-1.476285	-1.680231
44	1	2.247676	-1.381555	-1.785858
45	6	-0.713733	-2.726668	-1.770961
46	6	0.717538	-2.718998	-1.874658

47	6	1.423444	-3.907748	-2.167965
48	1	2.507764	-3.885446	-2.252084
49	6	0.715925	-5.082163	-2.338291
50	1	1.243071	-6.005607	-2.558877
51	6	-0.697538	-5.094052	-2.225538
52	1	-1.229988	-6.031118	-2.364387
53	6	-1.411461	-3.942348	-1.944867
54	1	-2.493545	-3.943826	-1.860394