Supporting Information for:

$[Ir(N^N^N)(C^N)L]^+$: A New Family of Luminophores Combining Tunability and Enhanced Photostability

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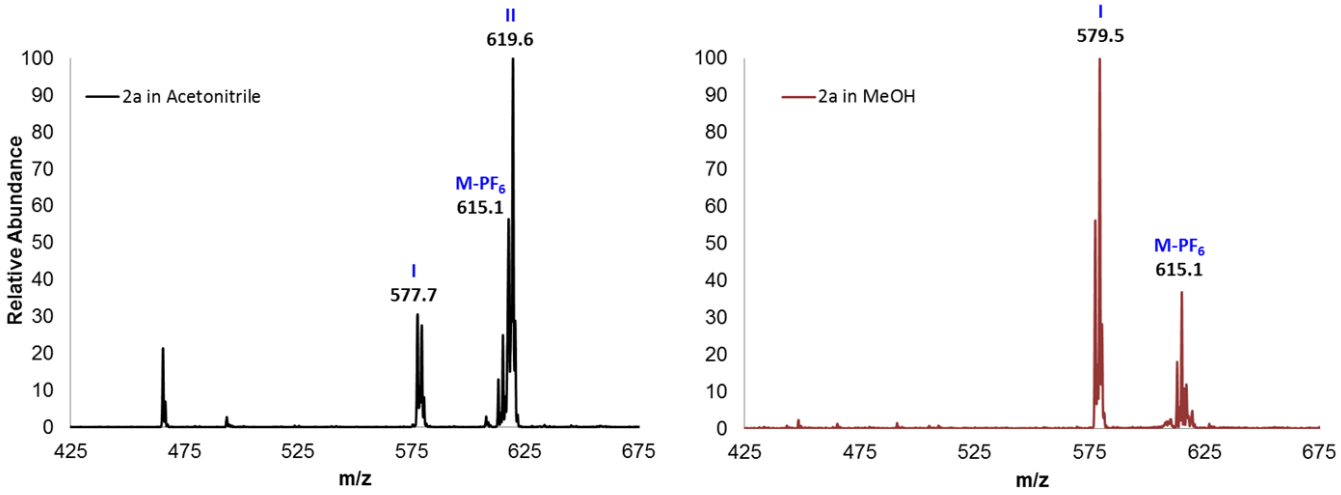


Figure S1. Electrospray ionization mass spectra collected for **2a** in acetonitrile (left) and methanol (right). Peak m/z values are given with black labels while assignments are made in blue. Spectra were collected with 50-60 µM solutions.

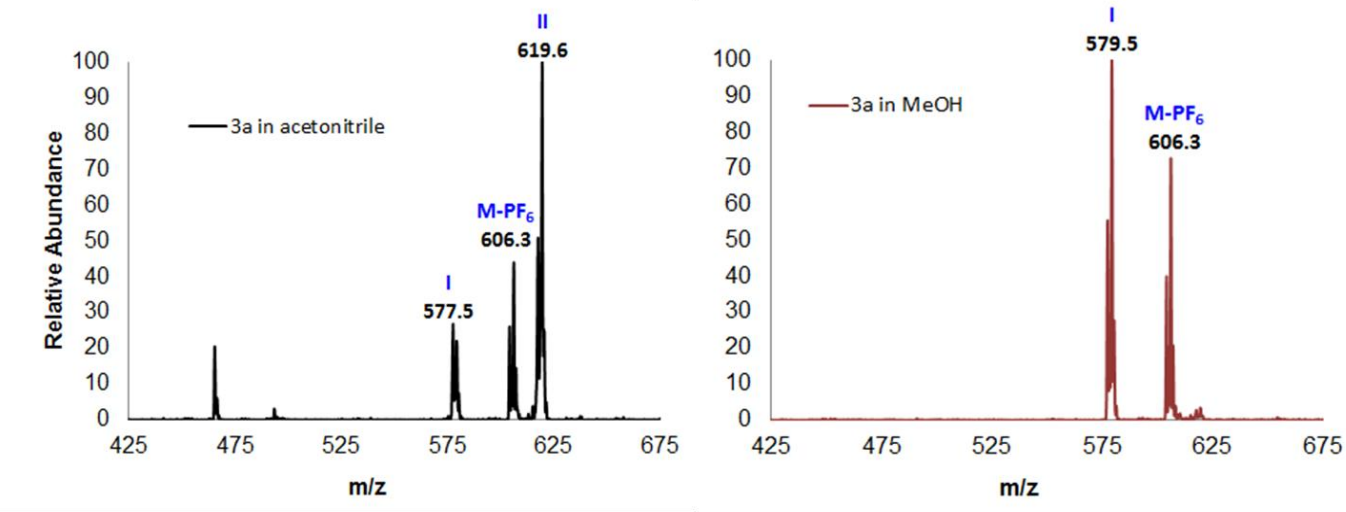


Figure S2. Electrospray ionization mass spectra collected for **3a** in acetonitrile (left) and methanol (right). Peak m/z values are given with black labels while assignments are made in blue. Spectra were collected with 50-60 µM solutions.

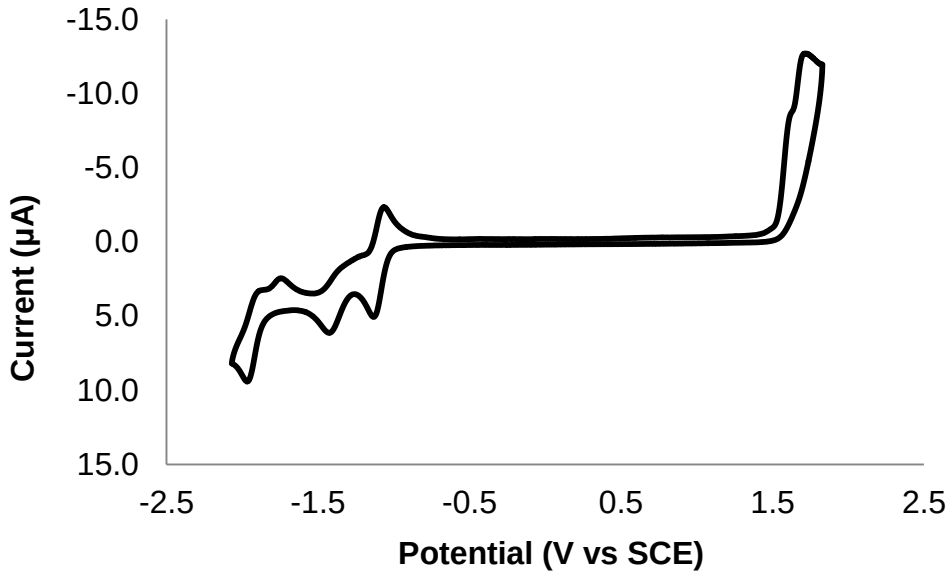


Figure S3: Cyclic voltammogram of **2g** showing its unique oxidation processes. The voltammogram was collected at 0.10 V/s using a three electrode system in a 0.10 M N(*n*-Bu)$_4$PF$_6$ (MeCN) solution. Potentials are referenced to SCE via a ferrocene internal standard.

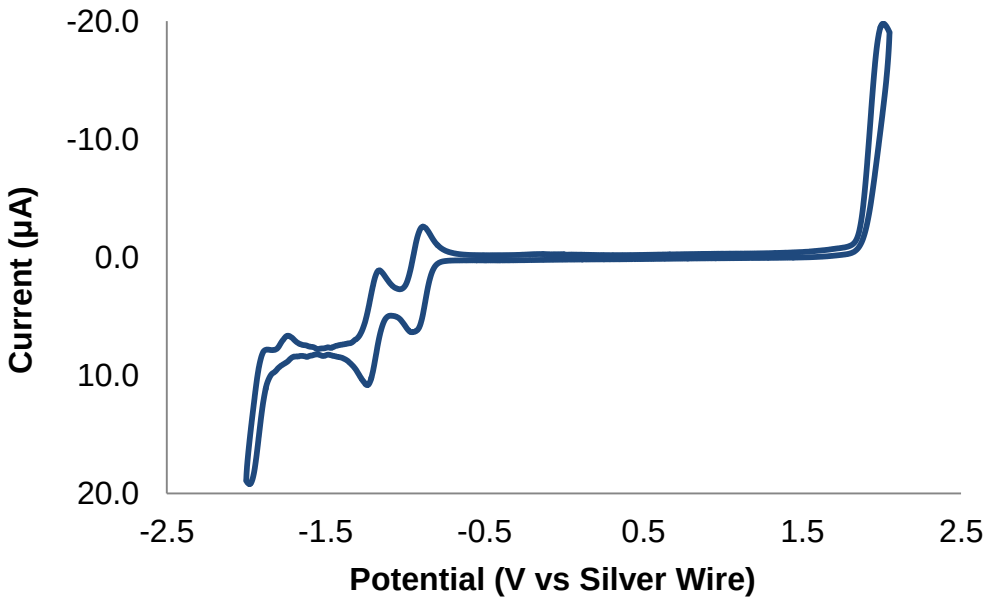


Figure S4: Cyclic voltammogram of model compound [Ir(tpy)(ppy)(py)](PF$_6$)$_2$ where py is pyridine. The second reduction which is reversible here is irreversible in all chloro compounds suggesting that the chloride may be causing the irreversibility by dissociating before or during the reduction process. A third reduction is visible for the pyridine complex as in the chlorides. The voltammogram was collected at 0.10 V/s using a three electrode system in a 0.10 M N(*n*-Bu)$_4$PF$_6$ (MeCN) solution. Potentials are referenced to a silver wire pseudoreference.

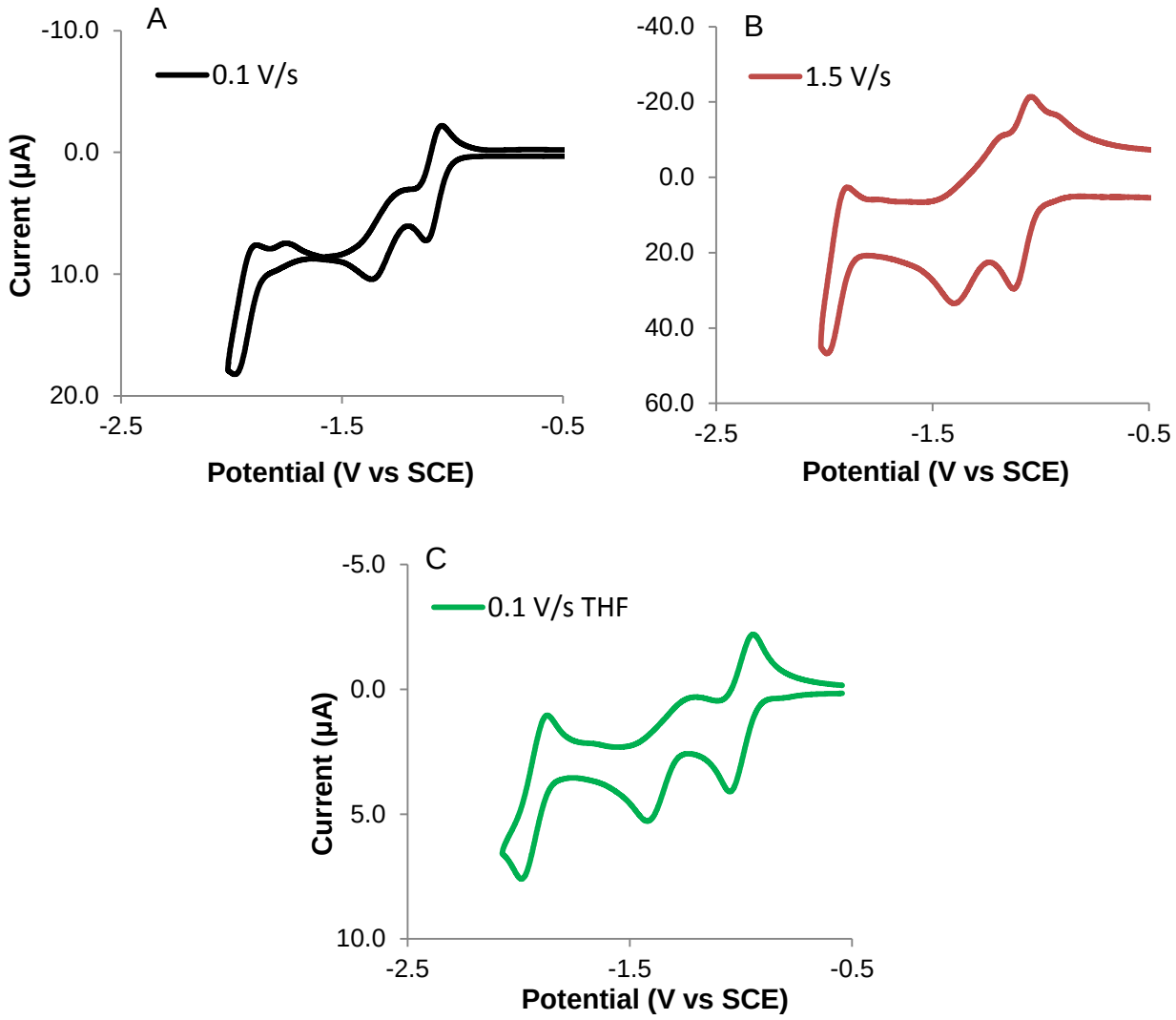


Figure S5: Scan rate and solvent dependence of reductions in **2a**. Cyclic voltammograms collected at (A) 0.10 V/s in MeCN, (B) 1.5 V/s in MeCN, and (C) 0.10 V/s in THF. Potentials are referenced to a ferrocene internal standard. All voltammograms were measured using 0.10 M $N(n\text{-}Bu)_4PF_6$ as electrolyte and a three electrode system.

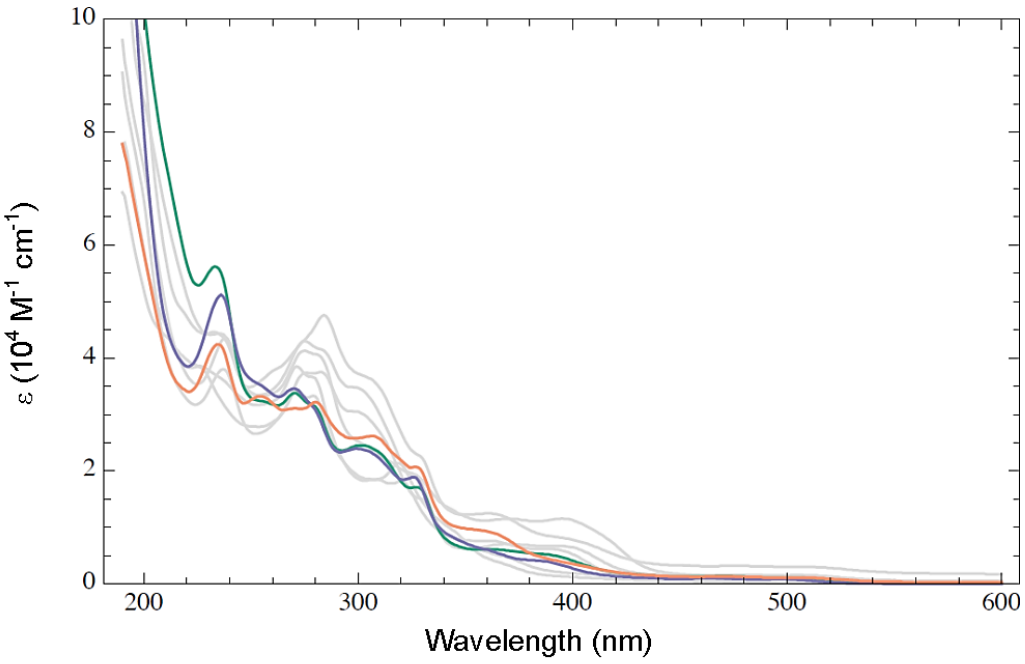


Figure S6: UV-vis absorption spectra for the tpy subset of compounds including **2a** (green), **2b** (purple), and **2c** (orange). UV-vis absorption spectra for all other members of the luminophore family are shown in the background in gray. All spectra were collected at room temperature in 10μM acetonitrile solutions.

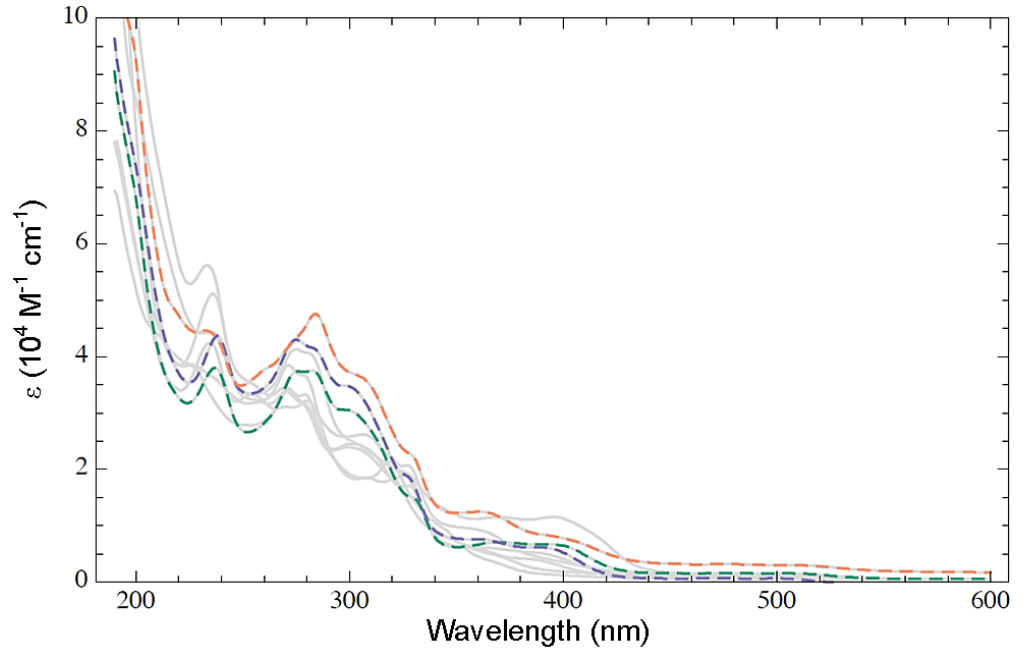


Figure S7: UV-vis absorption spectra for the phenylterpyridine subset of chloro compounds including **2d** (green dashes), **2e** (purple dashes), and **2f** (orange dashes). UV-vis absorption spectra for all other

members of the luminophore family are shown in the background in gray. All spectra were collected at room temperature in 10µM acetonitrile solutions.

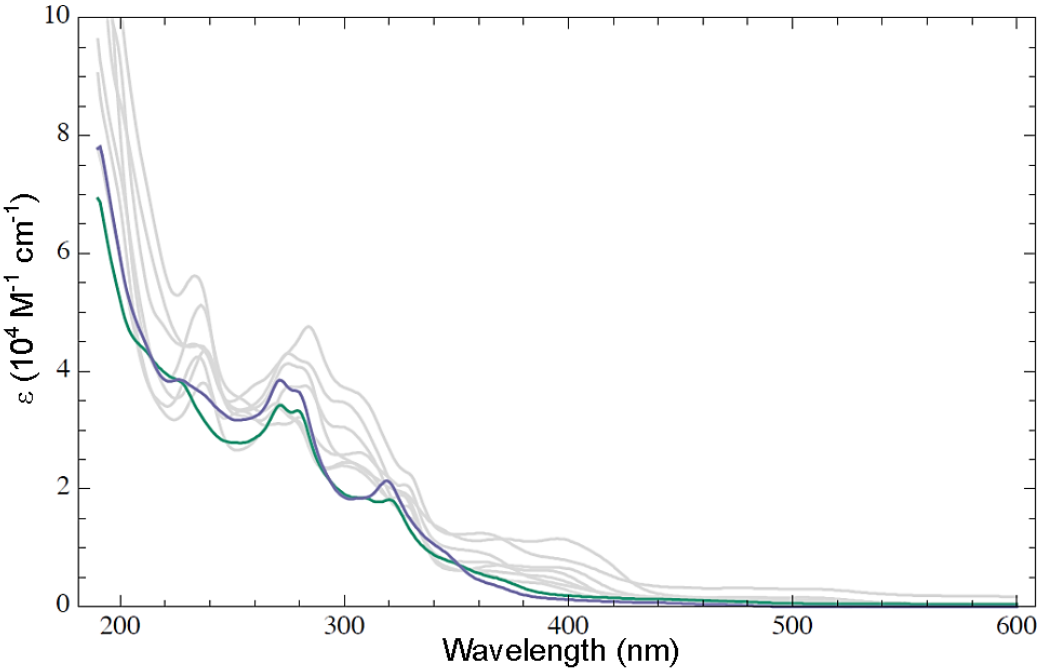


Figure S8: UV-vis absorption spectra for the cyano subset of compounds including **3a** (green) and **3b** (purple). UV-Vis absorption spectra for all other members of the luminophore family are shown in the background in gray. All spectra were collected at room temperature for 10µM acetonitrile solutions.

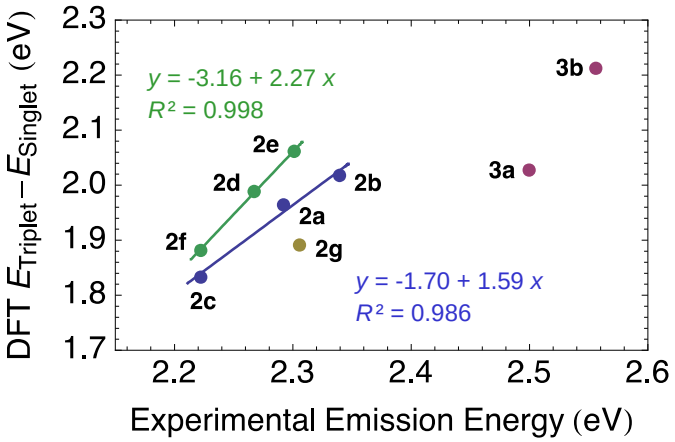


Figure S9: Comparison between experimental emission energy and a standard computational predictor of trends in emission: the difference in SCF energies for the triplet excited and singlet ground states calculated at the optimized triplet geometry. Linear correlations are identified for subsets of the luminophore family (green=[Ir(phtpy)(C^N)Cl](PF_6) and blue=[Ir(tpy)(C^N)Cl](PF_6)).

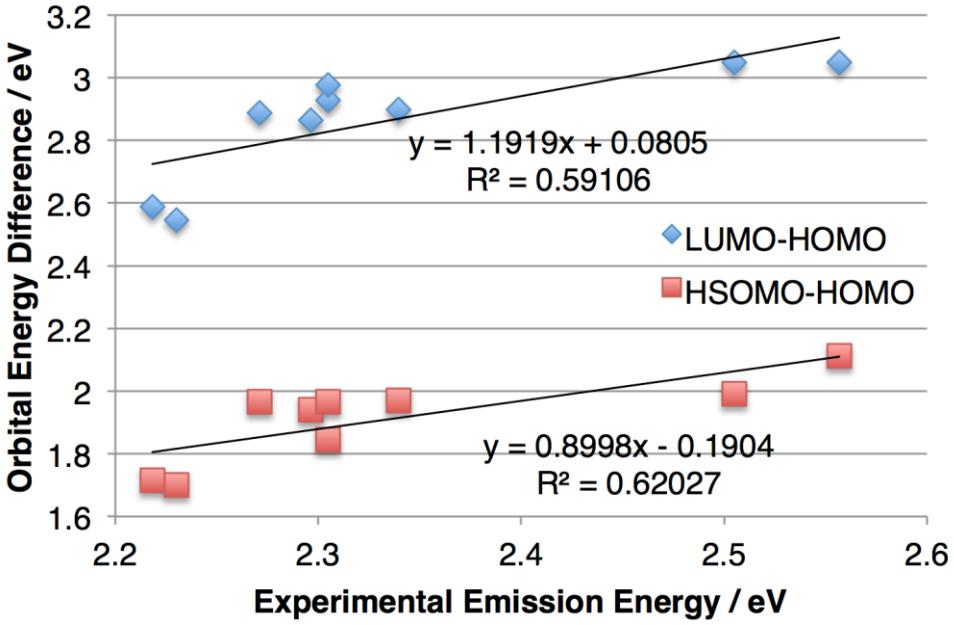
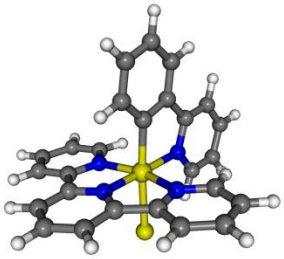
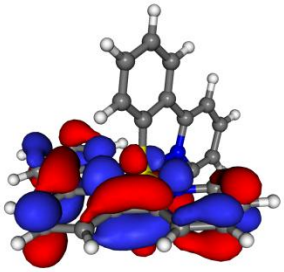
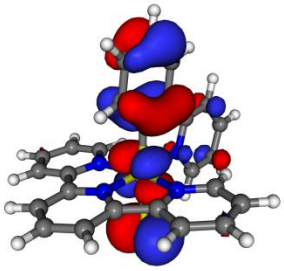
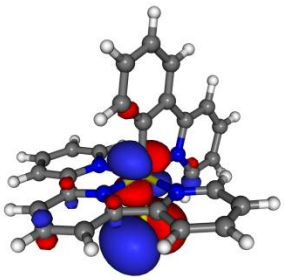


Figure S10: Correlations between experimental emission energy and two common computational predictors which model trends in emission by taking the difference between energies calculated for particular orbitals. The LUMO-HOMO model represented in blue diamonds involves subtracting the energies of the HOMO and LUMO calculated at the optimized singlet geometry. The HSOMO-HOMO model shown with red squares is based on the difference in the energies of the HOMO at the optimized singlet geometry and the HSOMO at the optimized triplet excited state geometry.

DFT Results for **2a**

SCF Energy: -1340.6604412 a.u.	

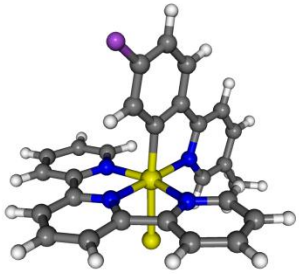
Frontier Orbitals:

Orbital	Energy / eV	
LUMO	-8.463	
HOMO	-5.579	
HOMO-1	-5.365	

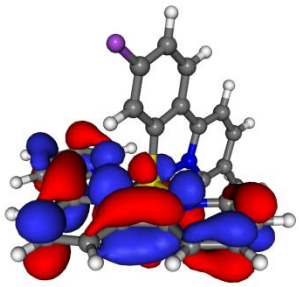
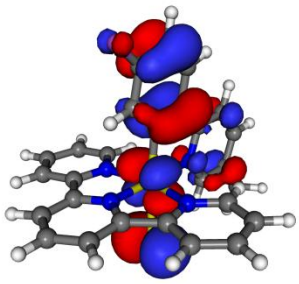
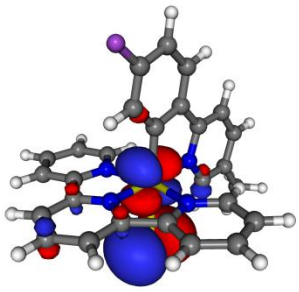
Singlet Optimized Coordinates for **2a**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.323019	0.014371	0.000000
2	17	0	2.758799	-0.697009	0.000000
3	7	0	0.267699	-0.322806	2.030730
4	7	0	0.267699	-0.322806	-2.030730
5	7	0	-0.127601	-1.904499	0.000000
6	7	0	0.753159	2.057221	0.000000
7	6	0	-1.572371	0.775021	0.000000
8	6	0	-0.347361	2.897471	0.000000
9	6	0	-0.155451	4.295311	0.000000
10	6	0	1.141449	4.826391	0.000000
11	6	0	2.247369	3.950971	0.000000
12	6	0	2.017809	2.571161	0.000000
13	6	0	-0.596081	-4.611479	0.000000
14	6	0	-4.078461	2.121381	0.000000
15	6	0	-2.889371	2.864691	0.000000
16	6	0	-1.640361	2.200711	0.000000
17	6	0	-2.779181	0.046961	0.000000
18	6	0	-4.021821	0.711761	0.000000
19	6	0	0.466039	0.215193	4.371820
20	6	0	0.466039	0.215193	-4.371820
21	6	0	0.496849	0.576993	3.017651
22	6	0	0.496849	0.576993	-3.017651
23	6	0	-0.008001	-1.642306	2.355000
24	6	0	-0.008001	-1.642306	-2.355000
25	6	0	-0.052971	-2.052387	3.695299
26	6	0	-0.052971	-2.052387	-3.695299
27	6	0	-0.466491	-3.926006	1.223298
28	6	0	-0.466491	-3.926006	-1.223298
29	6	0	-0.220481	-2.543206	1.202199
30	6	0	-0.220481	-2.543206	-1.202199
31	6	0	0.186319	-1.118607	4.717400
32	6	0	0.186319	-1.118607	-4.717400
33	1	0	3.265959	4.323141	0.000000
34	1	0	-5.039221	2.628421	0.000000
35	1	0	-2.943261	3.950611	0.000000
36	1	0	-2.767661	-1.040849	0.000000
37	1	0	-4.944001	0.135131	0.000000
38	1	0	2.820849	1.841991	0.000000
39	1	0	1.291259	5.902111	0.000000
40	1	0	-1.015721	4.954931	0.000000
41	1	0	-0.782961	-5.680579	0.000000
42	1	0	-0.543501	-4.464506	2.160798
43	1	0	-0.543501	-4.464506	-2.160798
44	1	0	0.659819	0.966692	5.130051
45	1	0	0.659819	0.966692	-5.130051
46	1	0	0.713699	1.590694	2.705601
47	1	0	0.713699	1.590694	-2.705601
48	1	0	-0.266051	-3.086997	3.940399
49	1	0	-0.266051	-3.086997	-3.940399
50	1	0	0.157889	-1.426008	5.757995
51	1	0	0.157889	-1.426008	-5.757995

DFT Results for **2b**

SCF Energy: -1479.2182244 a.u.	

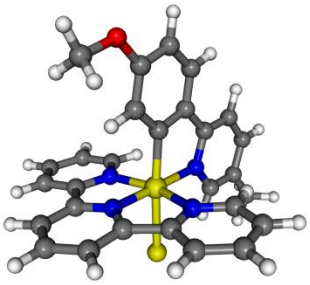
Frontier Orbitals:

Orbital	Energy / eV	
LUMO	-8.544	
HOMO	-5.645	
HOMO-1	-5.425	

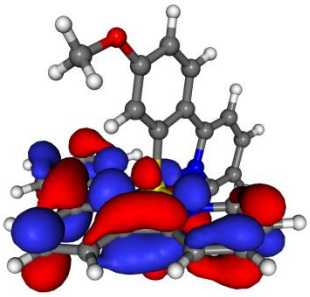
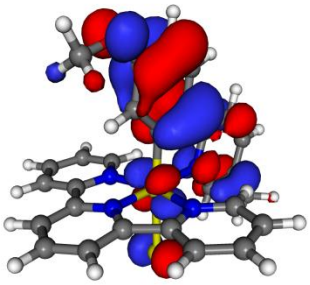
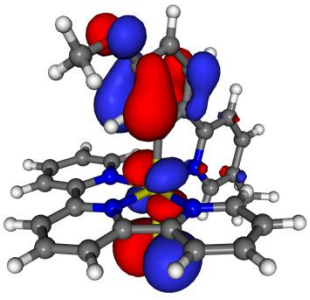
Singlet Optimized Coordinates for **2b**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.004266	0.000095	-0.373745
2	17	0	0.049025	0.000944	-2.907398
3	7	0	0.345297	2.032042	-0.406634
4	7	0	0.345123	-2.031893	-0.407614
5	7	0	1.975222	0.000035	-0.439287
6	6	0	-0.233159	-0.000427	1.651610
7	6	0	-0.224897	-4.373336	-0.446441
8	6	0	-0.224600	4.373530	-0.444574
9	6	0	-0.582874	3.019005	-0.389677
10	6	0	-0.583099	-3.018812	-0.391051
11	6	0	1.691306	-2.355696	-0.480537
12	6	0	1.691495	2.355795	-0.479447
13	6	0	2.099815	3.696088	-0.533536
14	6	0	2.099554	-3.695992	-0.535124
15	6	0	4.015861	-1.223411	-0.628789
16	6	0	4.015967	1.223396	-0.628175
17	6	0	2.616370	1.202438	-0.511478
18	6	0	2.616266	-1.202388	-0.512064
19	6	0	1.136256	4.718563	-0.516307
20	6	0	1.135939	-4.718423	-0.518289
21	7	0	-2.082503	0.000129	-0.252266
22	6	0	-2.602597	-0.000252	1.026949
23	6	0	-4.002642	-0.000490	1.198851
24	6	0	-4.847170	-0.000314	0.083156
25	6	0	-4.306639	0.000204	-1.226086
26	6	0	-2.907768	0.000304	-1.340288
27	6	0	4.711454	-0.000025	-0.679121
28	6	0	-0.883245	-0.000974	4.432802
29	6	0	-1.904764	-0.000763	3.472343
30	6	0	-1.592575	-0.000507	2.093194
31	6	0	0.789835	-0.000653	2.619040
32	6	0	0.440372	-0.000922	3.974600
33	1	0	4.556843	2.160729	-0.689187
34	1	0	4.556651	-2.160762	-0.690265
35	1	0	1.441153	-5.759032	-0.562633
36	1	0	1.441528	5.759172	-0.560272
37	1	0	-0.999278	5.132330	-0.432154
38	1	0	-0.999620	-5.132094	-0.434302
39	1	0	-1.618008	-2.705916	-0.339281
40	1	0	-1.617795	2.706132	-0.338009
41	1	0	3.154374	3.941423	-0.592476
42	1	0	3.154102	-3.941355	-0.594137
43	1	0	-4.420890	-0.000928	2.199047
44	1	0	-5.925635	-0.000613	0.221613
45	6	0	-5.187253	0.001176	-2.456825
46	1	0	-1.091324	-0.001152	5.497404
47	1	0	-2.937457	-0.000768	3.810401
48	1	0	1.842929	-0.000609	2.353803
49	9	0	1.470833	-0.001129	4.921170
50	1	0	-2.405781	0.000494	-2.302233
51	1	0	5.792875	-0.000048	-0.770554
52	1	0	-4.592090	-0.008977	-3.375423
53	1	0	-5.830704	0.890177	-2.482617
54	1	0	-5.846521	-0.876290	-2.472897

DFT Results for **2c**

SCF Energy: -1494.4837194 a.u.	

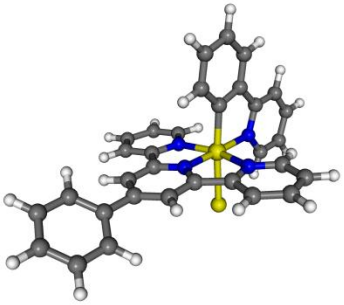
Frontier Orbitals:

Orbital	Energy / eV	
LUMO	-8.111	
HOMO	-5.565	
HOMO-1	-5.359	

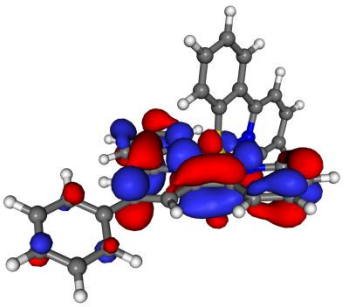
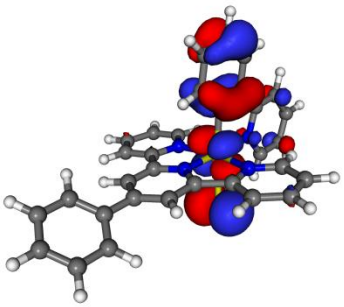
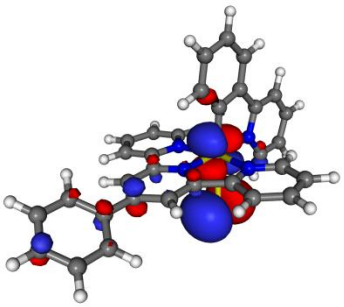
Singlet Optimized Coordinates for **2c**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.165772	0.064751	-0.451457
2	17	0	-0.623029	0.413365	-2.926493
3	7	0	0.162119	2.088131	-0.267272
4	7	0	0.158411	-1.931935	-0.832415
5	7	0	1.745484	0.130394	-0.931589
6	6	0	0.005920	-0.223388	1.565159
7	6	0	-0.409283	-4.262726	-1.064534
8	6	0	-0.400366	4.393792	0.152330
9	6	0	-0.737077	3.033749	0.098118
10	6	0	-0.743881	-2.939158	-0.744674
11	6	0	1.454257	-2.204129	-1.243566
12	6	0	1.457085	2.461216	-0.593420
13	6	0	1.842242	3.808862	-0.552998
14	6	0	1.837557	-3.512262	-1.572207
15	6	0	3.684647	-0.991244	-1.756475
16	6	0	3.685780	1.432615	-1.420522
17	6	0	2.351826	1.351835	-0.987556
18	6	0	2.350841	-1.030441	-1.317967
19	6	0	0.907666	4.788848	-0.178340
20	6	0	0.899982	-4.555100	-1.484668
21	7	0	-2.184831	-0.008911	0.074913
22	6	0	-2.437517	-0.203289	1.419770
23	6	0	-3.777508	-0.266612	1.862318
24	6	0	-4.826500	-0.133683	0.947855
25	6	0	-4.558826	0.065854	-0.429815
26	6	0	-3.212153	0.121100	-0.816915
27	6	0	4.350200	0.249324	-1.796968
28	6	0	-0.075498	-0.624075	4.375300
29	6	0	-1.263744	-0.523741	3.654206
30	6	0	-1.239844	-0.323015	2.250884
31	6	0	1.204644	-0.325862	2.297856
32	6	0	1.163794	-0.524621	3.697650
33	1	0	4.195736	2.387214	-1.481102
34	1	0	4.193775	-1.893621	-2.075223
35	1	0	1.185042	-5.570613	-1.740521
36	1	0	1.193875	5.835326	-0.147762
37	1	0	-1.151494	5.119064	0.445478
38	1	0	-1.162790	-5.038648	-0.984946
39	1	0	-1.740082	-2.666675	-0.420707
40	1	0	-1.732579	2.683609	0.339122
41	1	0	2.855425	4.093013	-0.815005
42	1	0	2.851718	-3.716801	-1.897256
43	1	0	-3.986865	-0.418651	2.915147
44	1	0	-5.855755	-0.183092	1.295222
45	6	0	-5.668598	0.215069	-1.448338
46	1	0	-0.067242	-0.776674	5.449438
47	1	0	-2.207164	-0.602066	4.188712
48	1	0	2.162162	-0.252042	1.791071
49	8	0	2.283134	-0.635999	4.509730
50	1	0	-2.915098	0.270793	-1.849677
51	1	0	5.379231	0.296107	-2.138841
52	1	0	-5.269153	0.358668	-2.457442
53	1	0	-6.308357	1.075923	-1.214398
54	1	0	-6.313679	-0.673011	-1.465450
55	6	0	3.614494	-0.547380	3.920855
56	1	0	4.304687	-0.662450	4.757891
57	1	0	3.771423	0.429569	3.443341
58	1	0	3.778977	-1.352942	3.192141

DFT Results for **2d**

SCF Energy: -1571.6851054 a.u.	

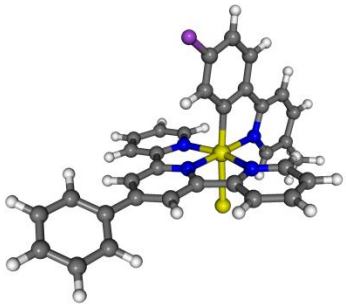
Frontier Orbitals:

Orbital	Energy / eV	
LUMO	-8.319	
HOMO	-5.432	
HOMO-1	-5.198	

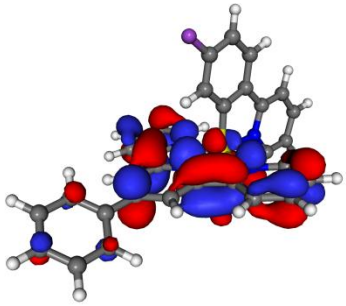
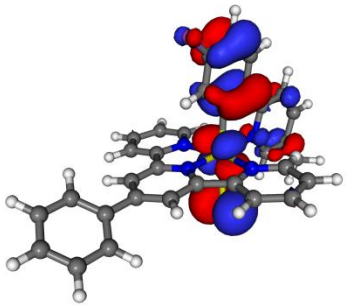
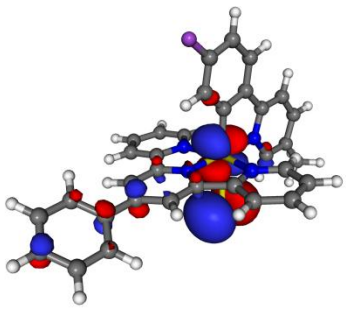
Singlet Optimized Coordinates for **2d**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.967082	0.017545	-0.355673
2	17	0	-0.558923	0.142599	-2.859644
3	7	0	-0.620833	2.045020	-0.234140
4	7	0	-0.619257	-2.011334	-0.440470
5	7	0	0.989664	0.007458	-0.131323
6	6	0	-1.496655	-0.081384	1.612718
7	6	0	-1.173052	-4.343924	-0.692933
8	6	0	-1.178847	4.390104	-0.236426
9	6	0	-1.541519	3.037433	-0.298170
10	6	0	-1.537650	-2.992538	-0.615324
11	6	0	0.724036	-2.338659	-0.331613
12	6	0	0.722715	2.361393	-0.100689
13	6	0	1.134265	3.700096	-0.032000
14	6	0	1.137292	-3.676705	-0.401226
15	6	0	3.038444	-1.214041	-0.073579
16	6	0	3.038637	1.218305	0.037595
17	6	0	1.641686	1.202399	-0.056638
18	6	0	1.641525	-1.189816	-0.162578
19	6	0	0.179007	4.727909	-0.100780
20	6	0	0.184376	-4.692618	-0.584076
21	7	0	-3.047250	0.028408	-0.539743
22	6	0	-3.750513	-0.030582	0.651439
23	6	0	-5.161423	-0.028042	0.628088
24	6	0	-5.843323	0.032697	-0.594662
25	6	0	-5.105945	0.090798	-1.795608
26	6	0	-3.708603	0.086884	-1.732659
27	6	0	3.765763	-0.000317	0.037409
28	6	0	-2.535743	-0.212071	4.258836
29	6	0	-3.415066	-0.157578	3.167922
30	6	0	-2.904330	-0.092218	1.850398
31	6	0	-0.630541	-0.135876	2.723657
32	6	0	-1.142804	-0.200743	4.034809
33	1	0	3.569031	2.158925	0.128034
34	1	0	3.573164	-2.154928	-0.128332
35	1	0	0.495363	-5.730818	-0.643332
36	1	0	0.488224	5.767165	-0.051605
37	1	0	-1.947478	5.152862	-0.295686
38	1	0	-1.939899	-5.096957	-0.837841
39	1	0	-2.569713	-2.677408	-0.700555
40	1	0	-2.573730	2.730388	-0.407474
41	1	0	2.186814	3.939746	0.069992
42	1	0	2.189798	-3.924634	-0.320677
43	1	0	-5.713486	-0.074086	1.559897
44	1	0	-6.929257	0.034581	-0.615261
45	1	0	-5.597112	0.138387	-2.761324
46	1	0	-2.924800	-0.262308	5.271916
47	1	0	-4.486968	-0.166029	3.349941
48	1	0	0.448056	-0.127636	2.582121
49	1	0	-0.460474	-0.241999	4.880835
50	1	0	-3.080435	0.129241	-2.616216
51	1	0	7.820024	-1.855688	1.458740
52	6	0	7.319777	-1.055626	0.920028
53	6	0	5.919044	-1.049417	0.821840
54	1	0	5.350138	-1.837368	1.310097
55	6	0	5.247334	-0.006603	0.137918
56	6	0	6.017138	1.027705	-0.448237
57	1	0	5.529872	1.818200	-1.013974
58	6	0	7.418172	1.018096	-0.354184
59	1	0	7.995899	1.810665	-0.821656
60	6	0	8.074929	-0.022356	0.331663
61	1	0	9.158956	-0.028507	0.405248

DFT Results for **2e**

SCF Energy: -1710.242878 a.u.	

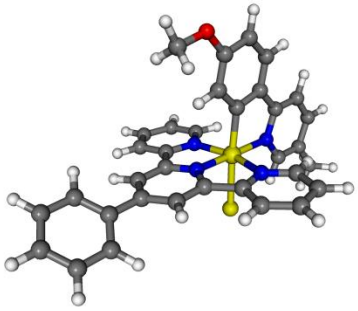
Frontier Orbitals:

Orbital	Energy / eV	
LUMO	-8.411	
HOMO	-5.482	
HOMO-1	-5.241	

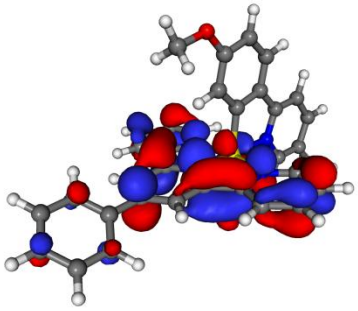
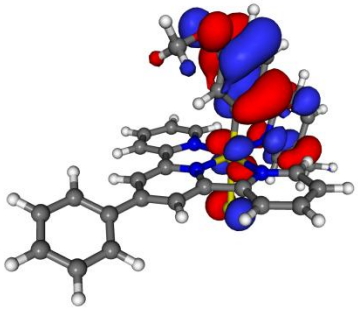
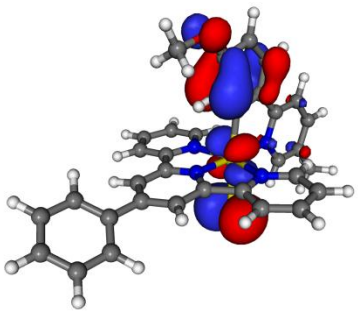
Singlet Optimized Coordinates for **2e**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.846958	0.036707	-0.347257
2	17	0	-0.557021	0.315393	-2.850122
3	7	0	-0.503110	2.056208	-0.114552
4	7	0	-0.495159	-1.981128	-0.577494
5	7	0	1.119434	0.026806	-0.221953
6	6	0	-1.275023	-0.189171	1.632417
7	6	0	-1.050710	-4.297243	-0.947981
8	6	0	-1.070072	4.392005	0.063362
9	6	0	-1.429938	3.043721	-0.070562
10	6	0	-1.417023	-2.956253	-0.766438
11	6	0	0.853417	-2.303821	-0.559244
12	6	0	0.844082	2.372229	-0.024468
13	6	0	1.253036	3.706253	0.113736
14	6	0	1.268705	-3.631438	-0.734762
15	6	0	3.173369	-1.179801	-0.353763
16	6	0	3.168813	1.240155	-0.082962
17	6	0	1.769045	1.219408	-0.103131
18	6	0	1.773649	-1.160707	-0.365456
19	6	0	0.291299	4.729468	0.158259
20	6	0	0.312128	-4.641336	-0.931695
21	7	0	-2.936364	0.047386	-0.423900
22	6	0	-3.574707	-0.078340	0.794485
23	6	0	-4.984603	-0.074163	0.834944
24	6	0	-5.721181	0.052841	-0.347894
25	6	0	-5.060297	0.176155	-1.594415
26	6	0	-3.656702	0.167863	-1.577847
27	6	0	3.900411	0.029990	-0.203473
28	6	0	-2.184034	-0.484099	4.324195
29	6	0	-3.110736	-0.357403	3.279523
30	6	0	-2.669908	-0.211395	1.943834
31	6	0	-0.347411	-0.316842	2.684368
32	6	0	-0.823155	-0.460287	3.992849
33	1	0	3.699408	2.176725	0.041294
34	1	0	3.708348	-2.110927	-0.498449
35	1	0	0.624361	-5.671330	-1.071876
36	1	0	0.598414	5.765221	0.262855
37	1	0	-1.843449	5.151743	0.090873
38	1	0	-1.820496	-5.045865	-1.099991
39	1	0	-2.453432	-2.643981	-0.777644
40	1	0	-2.464672	2.736262	-0.151620
41	1	0	2.308148	3.946177	0.183094
42	1	0	2.325054	-3.875657	-0.724149
43	1	0	-5.495147	-0.171341	1.786485
44	1	0	-6.807864	0.055428	-0.310326
45	6	0	-5.821276	0.312172	-2.895490
46	1	0	-2.491391	-0.597506	5.358294
47	1	0	-4.170713	-0.374325	3.518087
48	1	0	0.725859	-0.306742	2.518387
49	9	0	0.113668	-0.586218	5.025315
50	1	0	-3.068438	0.257786	-2.485307
51	1	0	8.039186	-1.883130	0.849159
52	6	0	7.504366	-1.052729	0.396544
53	6	0	6.100343	-1.051991	0.381386
54	1	0	5.564952	-1.875773	0.847858
55	6	0	5.384964	0.029594	-0.188500
56	6	0	6.113977	1.108768	-0.745534
57	1	0	5.590341	1.932569	-1.224838
58	6	0	7.518022	1.104648	-0.734970
59	1	0	8.063621	1.932567	-1.179150
60	6	0	8.218665	0.024905	-0.162626
61	1	0	9.305152	0.022999	-0.153142
62	1	0	-5.142105	0.396371	-3.749776
63	1	0	-6.463953	1.202067	-2.887347
64	1	0	-6.471731	-0.555338	-3.066644

DFT Results for **2f**

SCF Energy: -1725.5080149 a.u.	

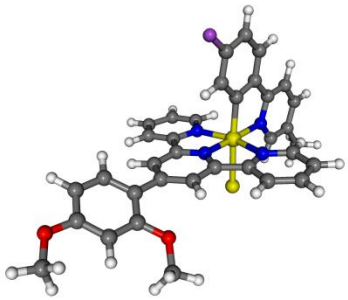
Frontier Orbitals:

Orbital	Energy / eV	
LUMO	-8.004	
HOMO	-5.417	
HOMO-1	-5.187	

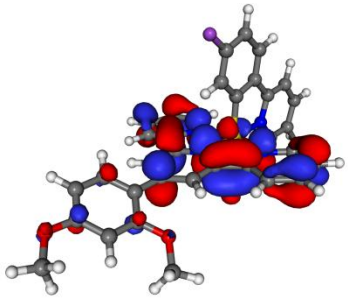
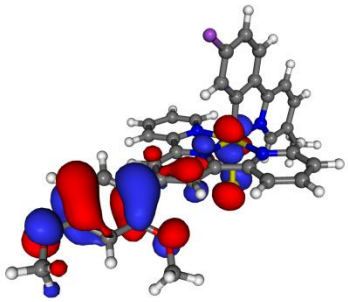
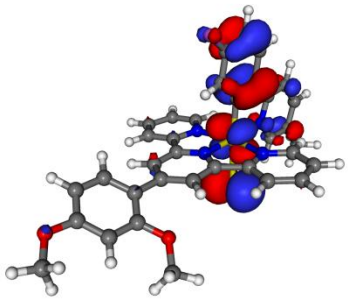
Singlet Optimized Coordinates for **2f**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.885980	-0.364259	0.228202
2	17	0	-0.601675	-2.496844	1.581130
3	7	0	-0.538555	-1.446124	-1.488666
4	7	0	-0.542125	0.717611	1.945719
5	7	0	1.081636	-0.279544	0.176595
6	6	0	-1.310420	1.324996	-0.839598
7	6	0	-1.110044	1.896904	3.969635
8	6	0	-1.102813	-2.752320	-3.434376
9	6	0	-1.464890	-2.009251	-2.301966
10	6	0	-1.469958	1.200618	2.807184
11	6	0	0.806095	0.914353	2.205229
12	6	0	0.810097	-1.597075	-1.774219
13	6	0	1.221190	-2.329947	-2.896698
14	6	0	1.214950	1.605484	3.354651
15	6	0	3.131706	0.321013	1.239639
16	6	0	3.133611	-0.981507	-0.818034
17	6	0	1.733685	-0.951904	-0.814391
18	6	0	1.731919	0.334214	1.206321
19	6	0	0.260140	-2.915927	-3.737524
20	6	0	0.252213	2.102525	4.249181
21	7	0	-2.973640	-0.427045	0.271357
22	6	0	-3.607595	0.616239	-0.376906
23	6	0	-5.019706	0.654828	-0.392711
24	6	0	-5.757103	-0.351030	0.238809
25	6	0	-5.099034	-1.418222	0.900122
26	6	0	-3.696696	-1.409360	0.886872
27	6	0	3.861646	-0.335368	0.214503
28	6	0	-2.209277	3.604215	-2.276380
29	6	0	-3.136168	2.729292	-1.712866
30	6	0	-2.703422	1.587084	-0.993185
31	6	0	-0.377057	2.211866	-1.411748
32	6	0	-0.825059	3.346250	-2.127245
33	1	0	3.667140	-1.487744	-1.613741
34	1	0	3.662708	0.772987	2.069012
35	1	0	0.559169	2.635262	5.143642
36	1	0	0.568731	-3.487623	-4.607033
37	1	0	-1.876229	-3.189340	-4.056442
38	1	0	-1.884571	2.263221	4.634504
39	1	0	-2.505513	1.013585	2.553555
40	1	0	-2.501119	-1.860801	-2.026381
41	1	0	2.277557	-2.446321	-3.112114
42	1	0	2.270887	1.749837	3.554716
43	1	0	-5.527405	1.468983	-0.897586
44	1	0	-6.843884	-0.315265	0.222811
45	6	0	-5.864649	-2.524374	1.593891
46	1	0	-2.515130	4.484728	-2.831608
47	1	0	-4.195517	2.939924	-1.836573
48	1	0	0.687602	2.026065	-1.306101
49	8	0	0.010025	4.278630	-2.727335
50	1	0	-3.109326	-2.184864	1.367375
51	1	0	8.035598	1.574852	1.130987
52	6	0	7.485674	0.717484	0.752726
53	6	0	6.081712	0.740519	0.735935
54	1	0	5.562631	1.631171	1.082711
55	6	0	5.346688	-0.360885	0.232824
56	6	0	6.056929	-1.487661	-0.249311
57	1	0	5.518019	-2.363544	-0.602663
58	6	0	7.460758	-1.512098	-0.227597
59	1	0	7.990770	-2.389755	-0.587131
60	6	0	8.180823	-0.409204	0.271663
61	1	0	9.267076	-0.428264	0.287329
62	1	0	-5.187968	-3.256912	2.045637
63	1	0	-6.516400	-3.057914	0.889813
64	1	0	-6.506123	-2.124034	2.389785
65	6	0	1.456238	4.114773	-2.637407
66	1	0	1.873829	4.963239	-3.181487
67	1	0	1.778752	3.177045	-3.110320
68	1	0	1.793138	4.143316	-1.592005

DFT Results for **2g**

SCF Energy: -1939.2625681 a.u.	

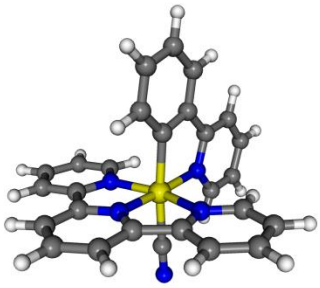
Frontier Orbitals:

Orbital	Energy / eV	
LUMO	-8.197	
HOMO	-5.220	
HOMO-1	-4.932	

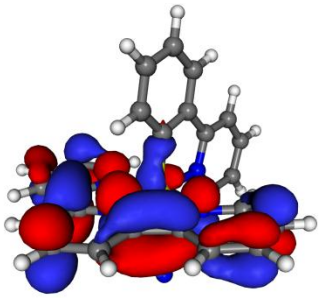
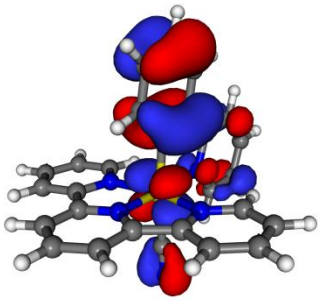
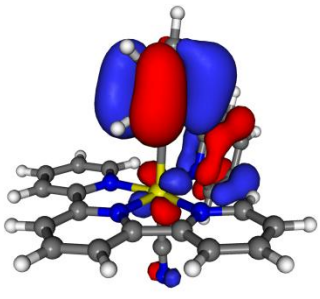
Singlet Optimized Coordinates for **2g**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-1.517043	0.089705	-0.319201
2	17	0	-1.140440	0.927413	-2.683876
3	7	0	-1.067722	1.976335	0.381818
4	7	0	-1.265350	-1.836427	-1.011122
5	7	0	0.441121	-0.069813	-0.161919
6	6	0	-2.012355	-0.568080	1.543451
7	6	0	-1.933816	-3.965416	-1.923196
8	6	0	-1.506030	4.239291	1.087885
9	6	0	-1.937291	2.984474	0.636380
10	6	0	-2.232160	-2.684173	-1.439657
11	6	0	0.062727	-2.234943	-1.042801
12	6	0	0.291824	2.177224	0.568464
13	6	0	0.771072	3.414912	1.021161
14	6	0	0.410191	-3.508283	-1.516481
15	6	0	2.430609	-1.331482	-0.529101
16	6	0	2.549889	0.955024	0.297218
17	6	0	1.153994	1.018553	0.244576
18	6	0	1.036238	-1.226312	-0.566248
19	6	0	-0.131281	4.458423	1.284984
20	6	0	-0.592627	-4.384979	-1.962450
21	7	0	-3.599626	0.238952	-0.424808
22	6	0	-4.279408	-0.147300	0.713700
23	6	0	-5.688288	-0.078579	0.729256
24	6	0	-6.381915	0.377402	-0.397214
25	6	0	-5.678251	0.773799	-1.560574
26	6	0	-4.277979	0.684641	-1.522707
27	6	0	3.225113	-0.239014	-0.079925
28	6	0	-3.015093	-1.453015	4.068211
29	6	0	-3.903431	-1.037765	3.065970
30	6	0	-3.416228	-0.598369	1.813198
31	6	0	-1.123605	-0.985875	2.553404
32	6	0	-1.644820	-1.413996	3.779442
33	1	0	3.131636	1.810455	0.608039
34	1	0	2.912501	-2.234360	-0.884104
35	1	0	-0.332299	-5.371236	-2.333528
36	1	0	0.230460	5.420215	1.634809
37	1	0	-2.235529	5.019136	1.277182
38	1	0	-2.737818	-4.610604	-2.259985
39	1	0	-3.249443	-2.316573	-1.395851
40	1	0	-2.985042	2.772112	0.466231
41	1	0	1.835884	3.561607	1.162623
42	1	0	1.450892	-3.811391	-1.542141
43	1	0	-6.231121	-0.380179	1.618039
44	1	0	-7.467956	0.428140	-0.379531
45	6	0	-6.391579	1.273293	-2.798417
46	1	0	-3.357993	-1.795565	5.038686
47	1	0	-4.970078	-1.061034	3.272397
48	1	0	-0.046541	-0.988190	2.414642
49	9	0	-0.746266	-1.826205	4.771394
50	1	0	-3.657389	0.966149	-2.367318
51	1	0	7.061869	-2.830595	0.579988
52	6	0	6.641203	-1.859812	0.342937
53	6	0	5.266551	-1.649046	0.279880
54	1	0	4.608556	-2.485961	0.497114
55	6	0	4.695407	-0.379376	-0.007341
56	6	0	5.602604	0.698276	-0.225200
57	8	0	5.046861	1.945926	-0.509271
58	6	0	6.997053	0.503707	-0.178169
59	1	0	7.666330	1.335636	-0.357639
60	6	0	7.515893	-0.775842	0.106285
61	8	0	8.863138	-1.069435	0.183619
62	1	0	-5.682527	1.534612	-3.590423
63	1	0	-6.992805	2.164735	-2.577240
64	1	0	-7.074939	0.511978	-3.196572
65	6	0	9.852404	-0.015439	-0.035847
66	1	0	10.819336	-0.505222	0.084400
67	1	0	9.746635	0.783957	0.709391
68	1	0	9.769230	0.396168	-1.050373
69	6	0	5.906434	3.033912	-0.977663
70	1	0	5.223669	3.844726	-1.237296
71	1	0	6.472320	2.728680	-1.866389
72	1	0	6.591112	3.364920	-0.186327

DFT Results for **3a**

SCF Energy: -1418.4928692 a.u.	

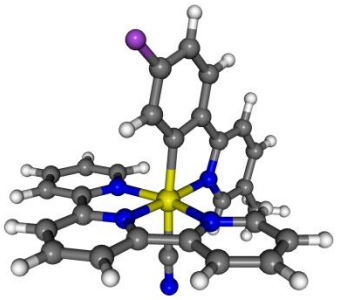
Frontier Orbitals:

Orbital	Energy / eV	
LUMO	-8.691	
HOMO	-5.642	
HOMO-1	-5.499	

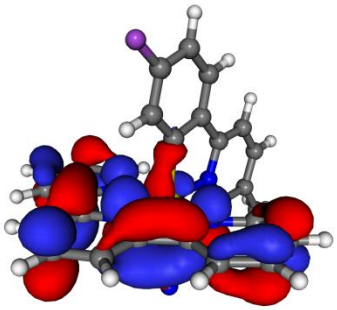
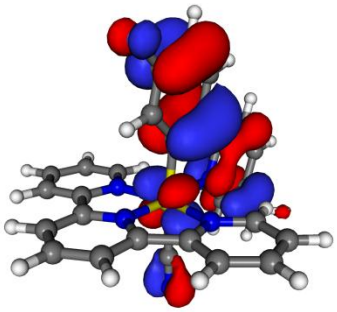
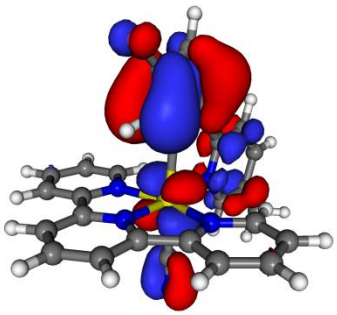
Singlet Optimized Coordinates for **3a**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.402989	0.009000	0.000000
2	6	0	2.436729	-0.407822	0.000000
3	7	0	3.608687	-0.609905	0.000000
4	7	0	0.329179	-0.330872	2.037168
5	7	0	0.329179	-0.330872	-2.037168
6	7	0	-0.021746	-1.919142	0.000000
7	7	0	0.721022	2.079489	0.000000
8	6	0	-1.561742	0.689276	0.000000
9	6	0	-0.423562	2.861209	0.000000
10	6	0	-0.303376	4.268404	0.000000
11	6	0	0.960900	4.870156	0.000000
12	6	0	2.112343	4.055645	0.000000
13	6	0	1.955883	2.666929	0.000000
14	6	0	-0.539421	-4.617774	0.000000
15	6	0	-4.120816	1.947552	0.000000
16	6	0	-2.958818	2.732225	0.000000
17	6	0	-1.687067	2.110654	0.000000
18	6	0	-2.746177	-0.076357	0.000000
19	6	0	-4.013402	0.541115	0.000000
20	6	0	0.479241	0.210955	4.380584
21	6	0	0.479241	0.210955	-4.380584
22	6	0	0.533984	0.571738	3.027009
23	6	0	0.533984	0.571738	-3.027009
24	6	0	0.055477	-1.651882	2.357293
25	6	0	0.055477	-1.651882	-2.357293
26	6	0	-0.010053	-2.061023	3.697568
27	6	0	-0.010053	-2.061023	-3.697568
28	6	0	-0.405983	-3.932892	1.223203
29	6	0	-0.405983	-3.932892	-1.223203
30	6	0	-0.140007	-2.553664	1.203008
31	6	0	-0.140007	-2.553664	-1.203008
32	6	0	0.203605	-1.124716	4.722640
33	6	0	0.203605	-1.124716	-4.722640
34	1	0	3.110131	4.480218	0.000000
35	1	0	-5.099045	2.420247	0.000000
36	1	0	-3.053793	3.815297	0.000000
37	1	0	-2.699636	-1.164125	0.000000
38	1	0	-4.914561	-0.068036	0.000000
39	1	0	2.806201	1.995976	0.000000
40	1	0	1.051855	5.952402	0.000000
41	1	0	-1.197761	4.880407	0.000000
42	1	0	-0.740976	-5.684139	0.000000
43	1	0	-0.500854	-4.468304	2.160832
44	1	0	-0.500854	-4.468304	-2.160832
45	1	0	0.653206	0.963945	5.141378
46	1	0	0.653206	0.963945	-5.141378
47	1	0	0.749009	1.586634	2.718095
48	1	0	0.749009	1.586634	-2.718095
49	1	0	-0.220561	-3.096724	3.939912
50	1	0	-0.220561	-3.096724	-3.939912
51	1	0	0.158804	-1.431331	5.762780
52	1	0	0.158804	-1.431331	-5.762780

DFT Results for **3b**

SCF Energy: -1557.0511812 a.u.	

Frontier Orbitals:

Orbital	Energy / eV	
LUMO	-8.750	
HOMO	-5.702	
HOMO-1	-5.548	

Singlet Optimized Coordinates for **3b**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.010660	0.000497	-0.453245
2	6	0	0.129447	0.002521	-2.523793
3	7	0	-0.338064	-2.037895	-0.472250
4	7	0	-0.335688	2.039222	-0.467695
5	7	0	-1.962256	0.001699	-0.546234
6	6	0	0.157209	-0.002263	1.617529
7	6	0	0.227700	4.381992	-0.460772
8	6	0	0.222552	-4.381335	-0.470107
9	6	0	0.586221	-3.027764	-0.434680
10	6	0	0.589778	3.027936	-0.428039
11	6	0	-1.682585	2.359591	-0.543799
12	6	0	-1.685340	-2.356519	-0.548918
13	6	0	-2.098449	-3.696471	-0.586616
14	6	0	-2.094101	3.700109	-0.578811
15	6	0	-4.005973	1.226345	-0.692703
16	6	0	-4.007398	-1.220249	-0.695430
17	6	0	-2.606289	-1.201069	-0.595986
18	6	0	-2.604884	1.205326	-0.593335
19	6	0	-1.139293	-4.722133	-0.546967
20	6	0	-1.133742	4.724547	-0.537045
21	7	0	2.094686	-0.000594	-0.221917
22	6	0	2.549801	-0.002441	1.083223
23	6	0	3.941021	-0.003245	1.323671
24	6	0	4.843162	-0.002121	0.255687
25	6	0	4.371197	-0.000095	-1.079830
26	6	0	2.980984	0.000607	-1.264267
27	6	0	-4.702477	0.003509	-0.742200
28	6	0	0.713824	-0.006004	4.424871
29	6	0	1.766988	-0.005154	3.499445
30	6	0	1.498221	-0.003354	2.110026
31	6	0	-0.894748	-0.003220	2.554552
32	6	0	-0.593178	-0.005043	3.921655
33	1	0	-4.550382	-2.157199	-0.741318
34	1	0	-4.547870	2.164026	-0.736494
35	1	0	-1.441473	5.764916	-0.565947
36	1	0	-1.448257	-5.762077	-0.577918
37	1	0	0.994068	-5.142843	-0.440757
38	1	0	1.000096	5.142545	-0.429846
39	1	0	1.625114	2.716738	-0.375152
40	1	0	1.621934	-2.717892	-0.381289
41	1	0	-3.153467	-3.938721	-0.649280
42	1	0	-3.148825	3.943742	-0.641074
43	1	0	4.307166	-0.004710	2.343855
44	1	0	5.912837	-0.002786	0.450369
45	6	0	5.313122	0.001236	-2.264154
46	1	0	0.885578	-0.007360	5.496006
47	1	0	2.786973	-0.005879	3.873858
48	1	0	-1.940223	-0.002531	2.257329
49	9	0	-1.655121	-0.005907	4.833960
50	1	0	2.545163	0.002162	-2.256348
51	1	0	-5.784769	0.004226	-0.821406
52	1	0	4.766518	0.003033	-3.212540
53	1	0	5.964193	-0.882403	-2.252759
54	1	0	5.965250	0.884048	-2.249976
55	7	0	0.235469	0.003634	-3.708237

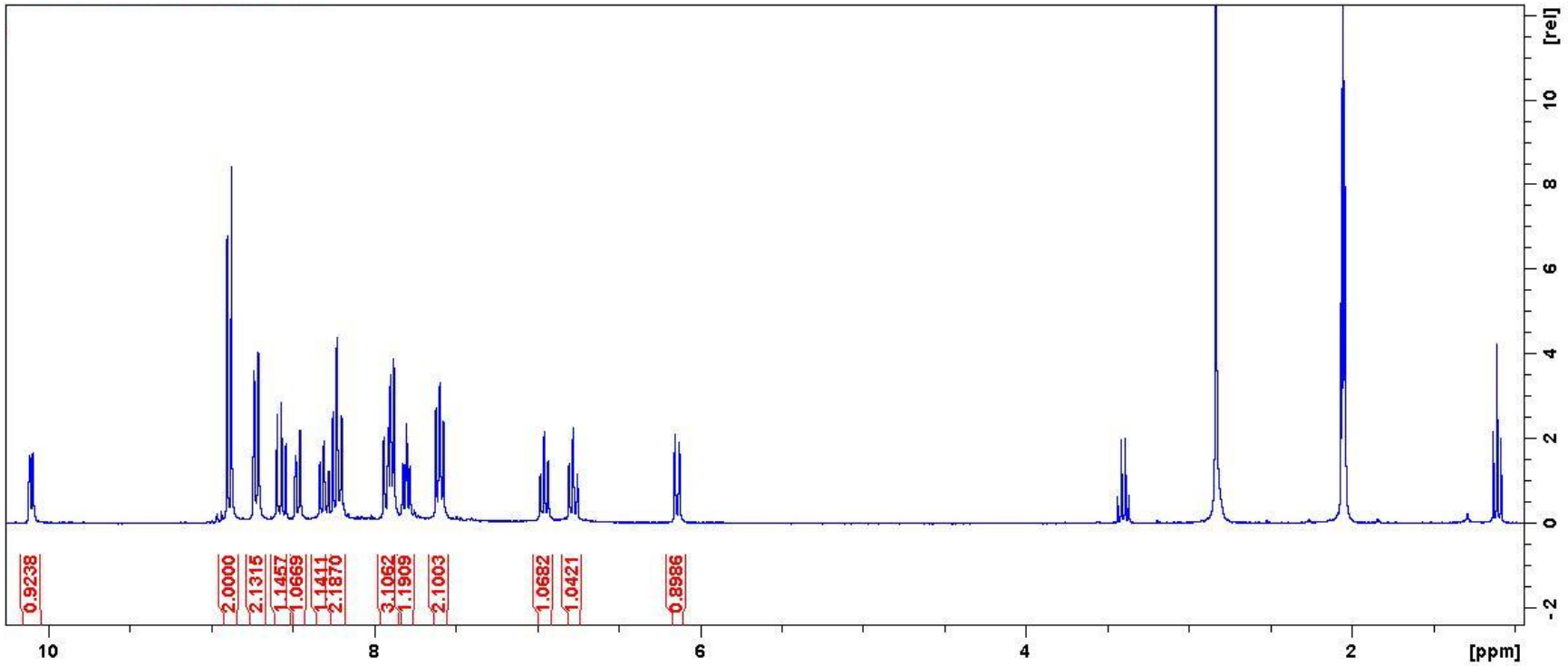


Figure S11: ^{1}H NMR spectrum collected for **2a** in acetone-d^{6} using a 300 MHz spectrometer. Residual solvent peaks are visible at 3.4 and 1.1 ppm.

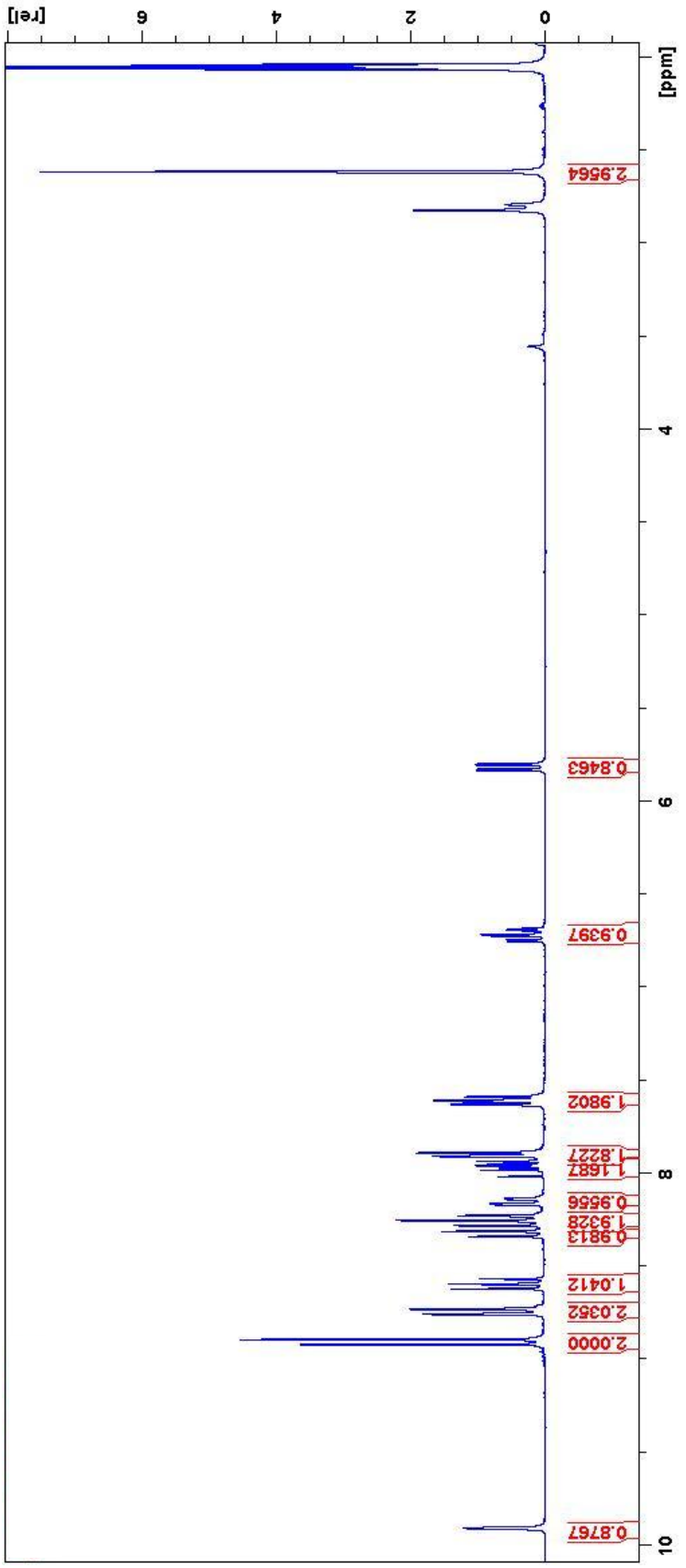


Figure S12: ^{1}H NMR spectrum collected for **2b** in acetone-d^{6} using a 300 MHz spectrometer.

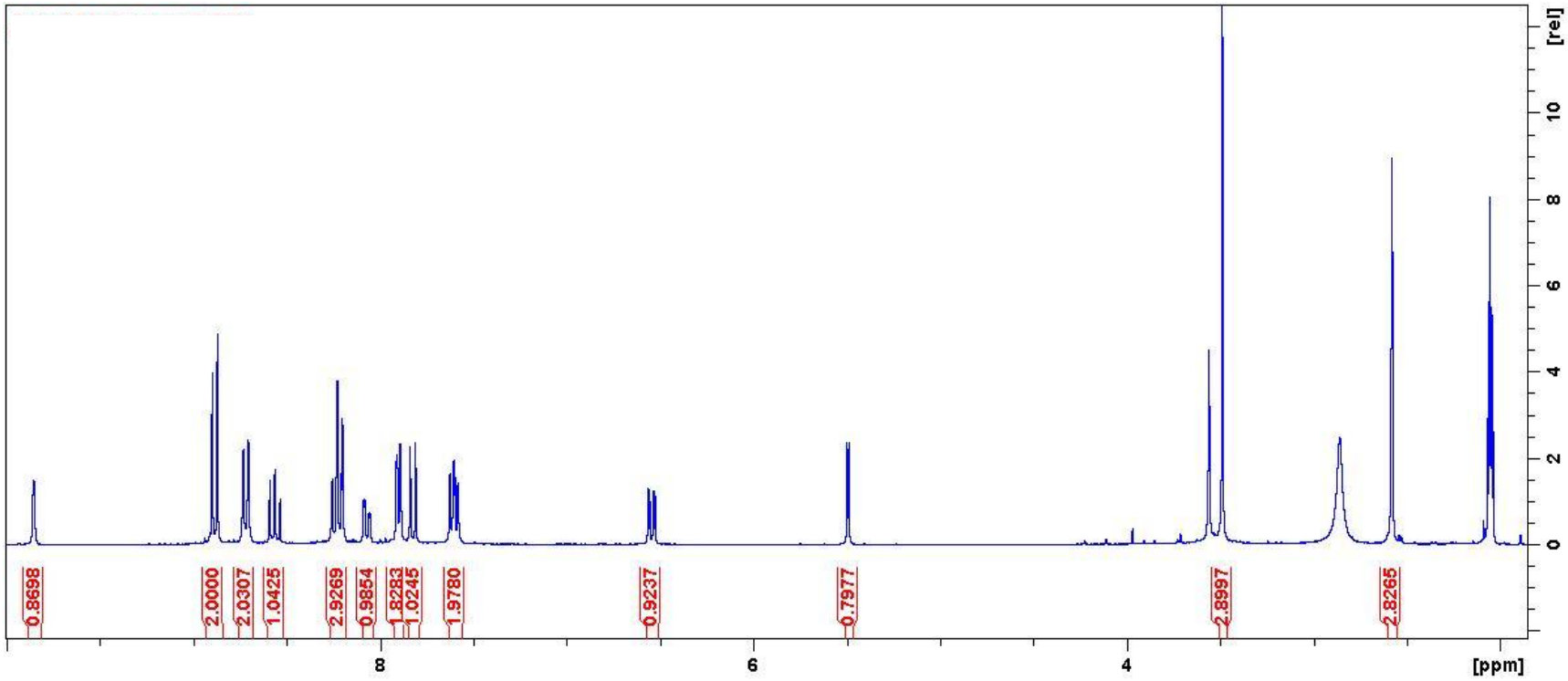


Figure S13: ^{1}H NMR spectrum collected for **2c** in acetone-d^{6} using a 300 MHz spectrometer.

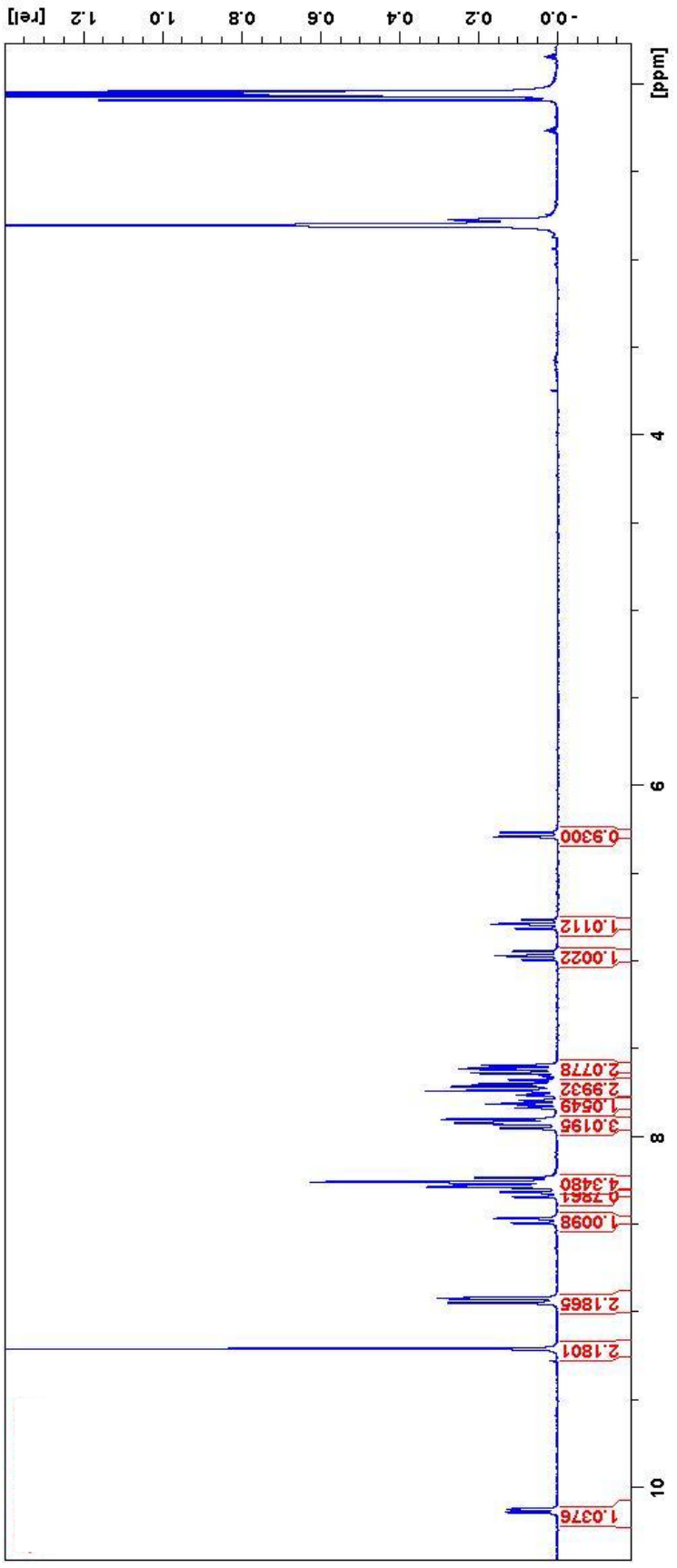


Figure S14: ^{1}H NMR spectrum collected for **2d** in acetone-d^{6} using a 300MHz spectrometer.

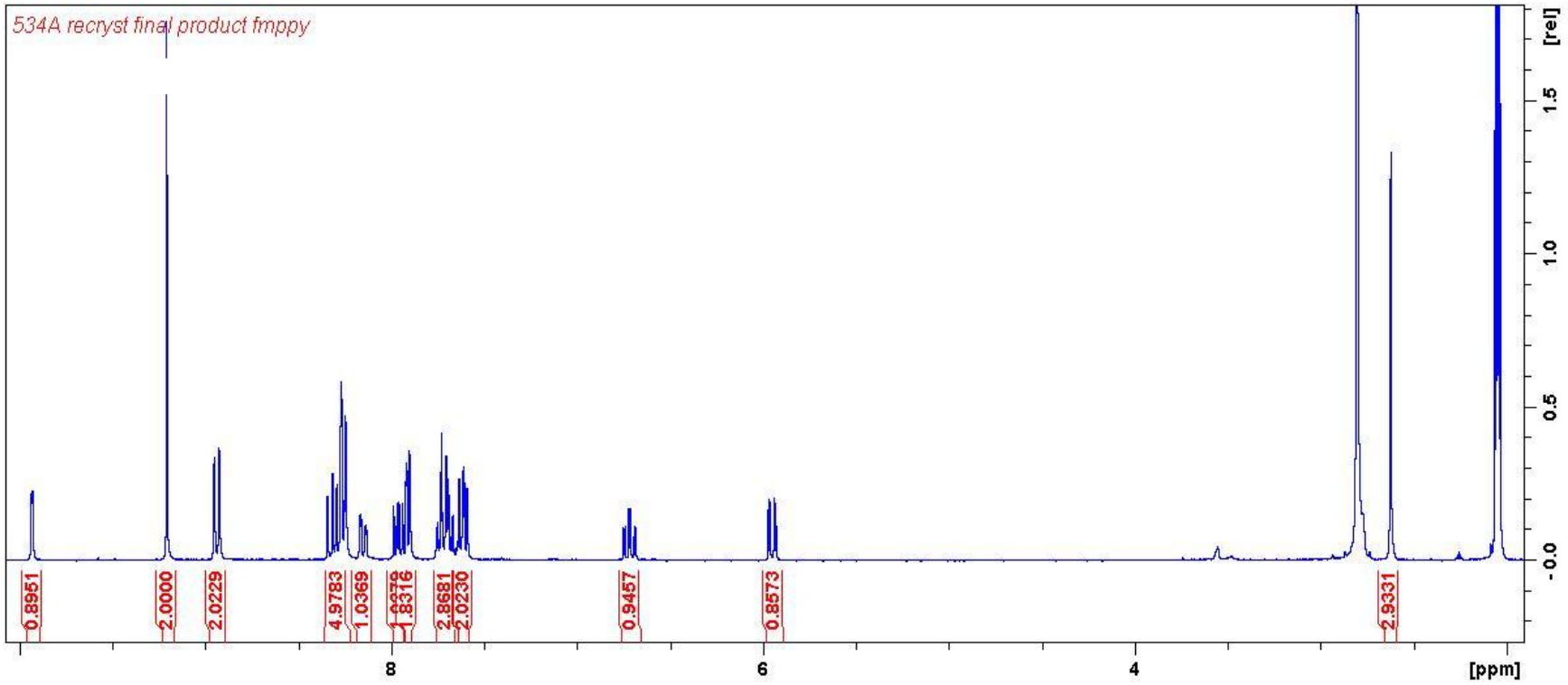


Figure S15: ^{1}H NMR Spectrum for **2e** collected in acetone-d^{6} using a 300 MHz spectrometer.

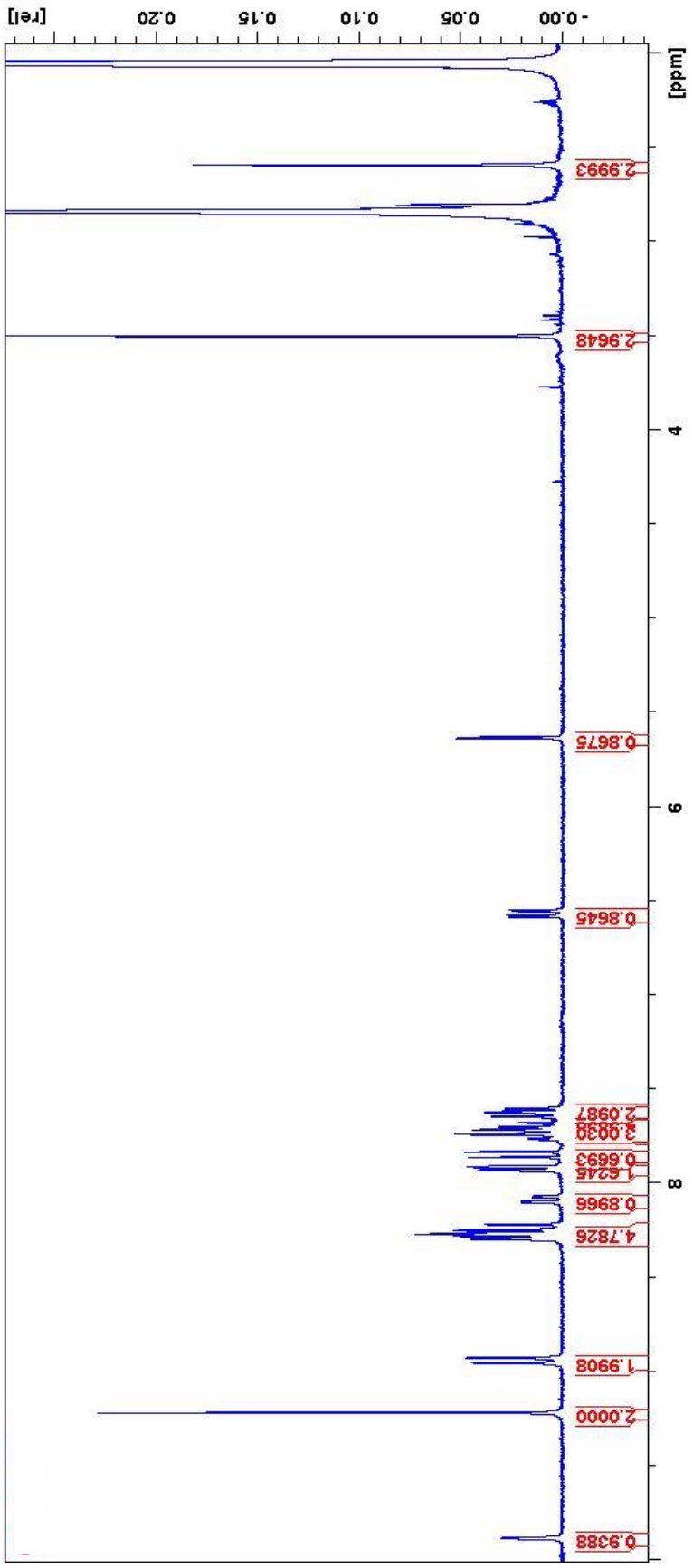


Figure S16: ^{1}H NMR spectrum collected for **2f** in acetone-d^{6} using a 300MHz spectrometer.

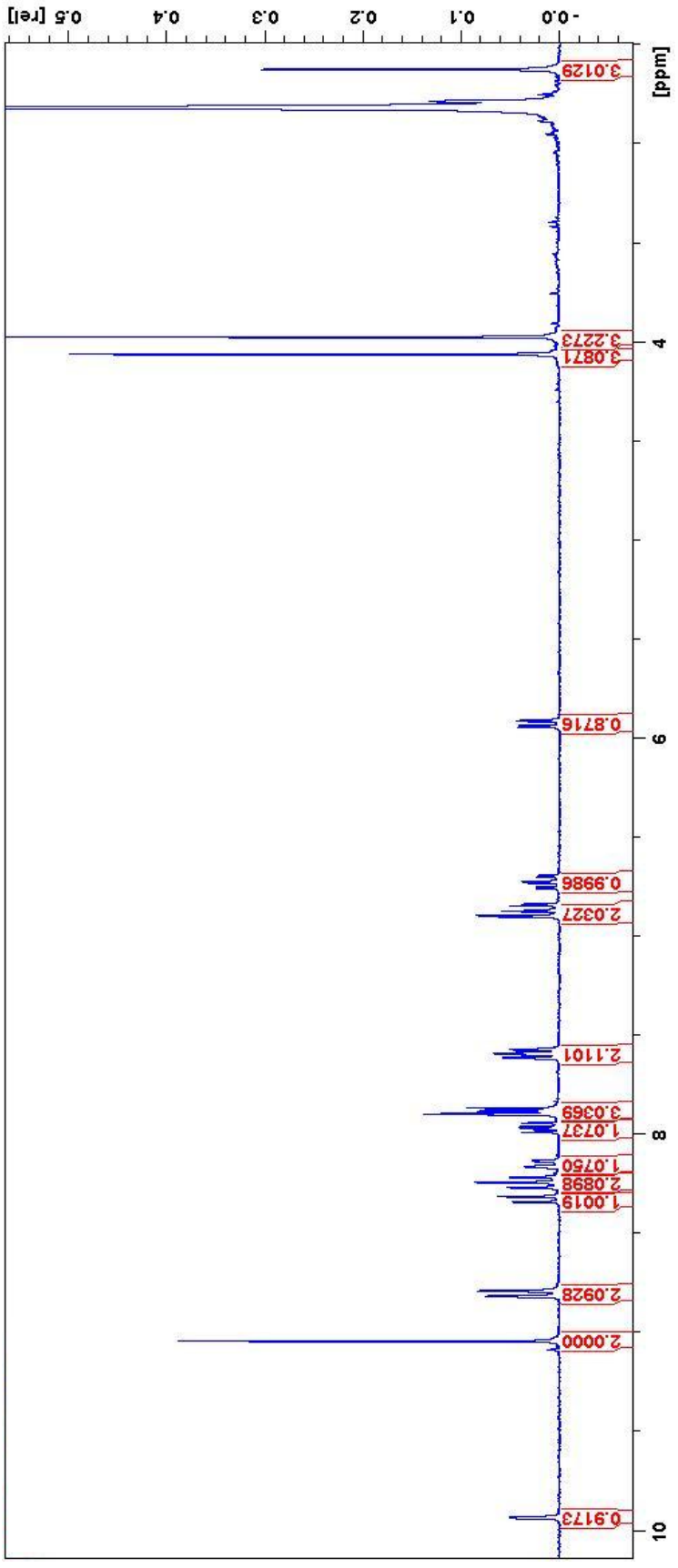


Figure S17: ^{1}H NMR spectrum of **2g** collected in acetone-d^{6} using a 300 MHz spectrometer.

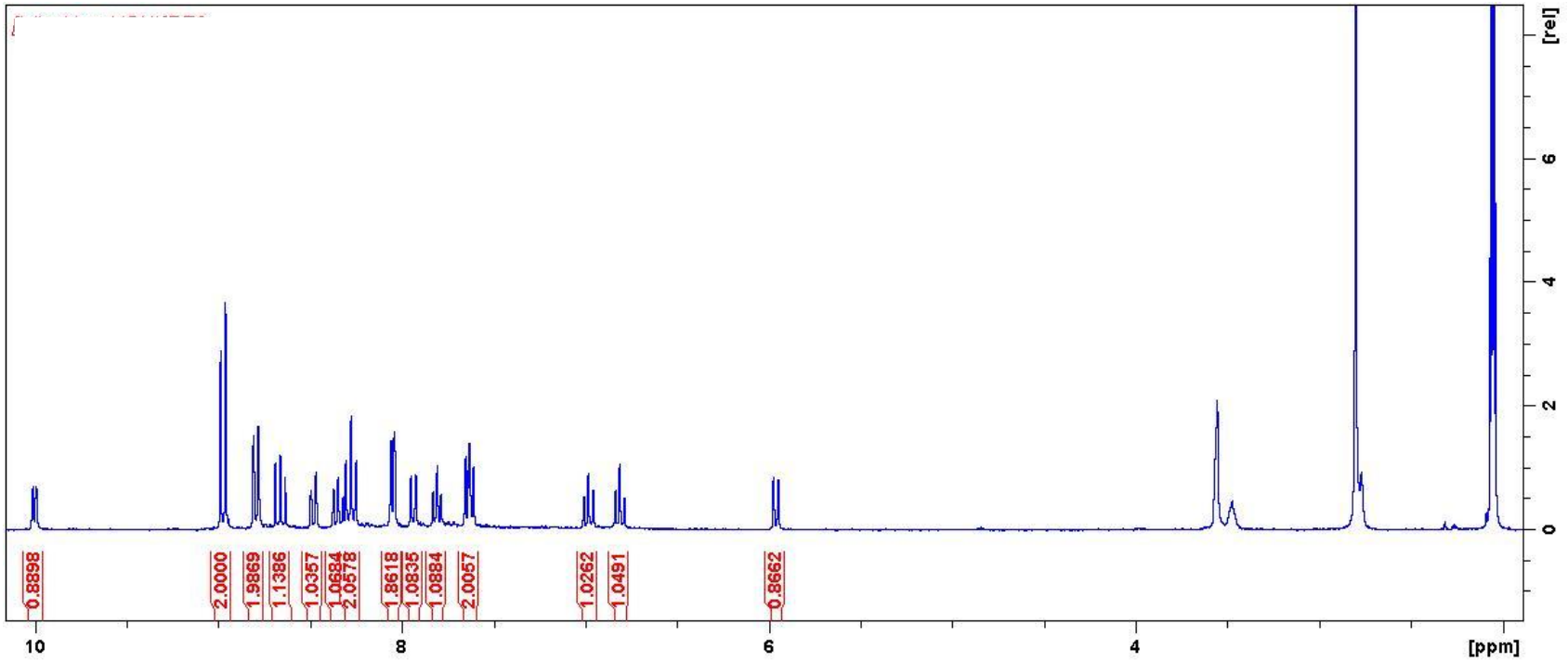


Figure S18: ^{1}H NMR spectrum collected for **3a** in acetone-d^{6} using a 300 MHz spectrometer.

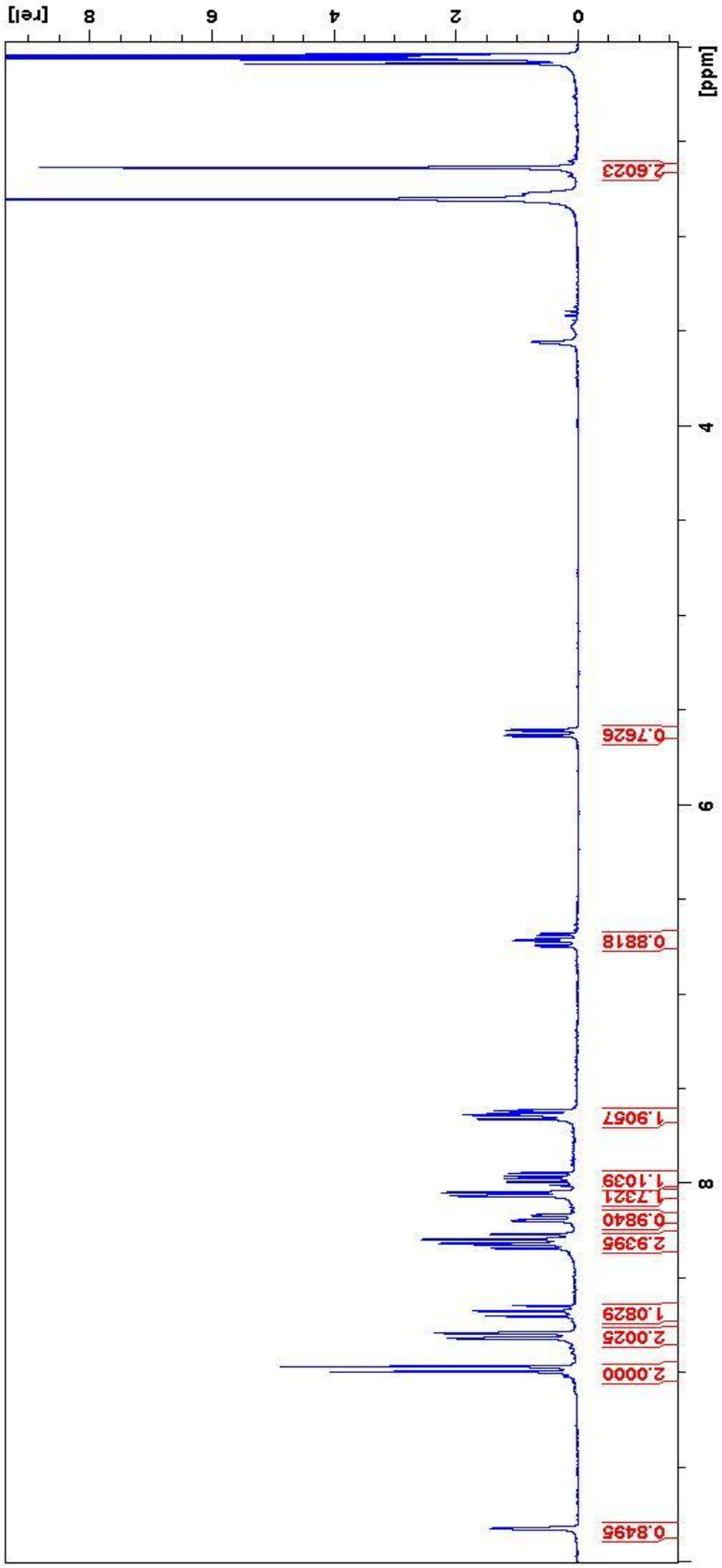


Figure S19: ^{1}H NMR spectrum collected for **3b** in acetone-d^{6} using a 300 MHz spectrometer.

Table S1. X-ray Crystallographic Data and Parameters for [Ir(tpy)(MeO-mppy)Cl](PF_6)

	[Ir(tpy)(MeO-mppy)Cl](PF_6)
Formula	$C_{28}H_{23}ClF_6IrN_4OP$
Color	Yellow
Shape	Plates
Formula Weight	850.17
Crystal System	Triclinic
Space Group	P-1
Temp (K)	150
Cell Constants	
a, Å	8.0342 (2)
b, Å	15.3470 (4)
c, Å	16.4079 (4)
α, deg	112.8650 (10)
β, deg	98.1830 (10)
γ, deg	101.1700 (10)
V, $Å^3$	1775.04 (8)
Formula units/unit cell	2
Dcal'd, gcm^{-3}	1.697
Absorption coefficient, mm^{-1}	3.96
F(000)	832
Diffractometer	Bruker Smart ApexII
Radiation, graphite monochr.	Mo K ʎ (ʎ =0.71073 Å)
Crystal size, mm	0.34 x 0.22 x 0.11
θ range, deg	1.5< θ <32.7
Range of h,k,l	±12, ±23, ±24
Reflections collected/unique	31772/12005
Rint	0.026
Refinement Method	Full Matrix Least-Squares on F2
Data/Restraints/Parameters	12005/0/446
GOF on F^2	0.780
Final R indices [I>2σ(I)]	R1=0.025 wR2=0.089
R indices (all data)	R1=0.027 wR2=0.0.92
Max. Resid. Peaks ($e*Å^{-3}$)	2.32 and -2.01

Table S2: Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Displacement Parameters ($Å^2$) for [Ir(tpy)(MeO-mppy)Cl](PF_6).

	x	y	z	$U_{iso}*/U_{eq}$
Ir1	0.73898 (2)	0.95219 (2)	0.69820 (2)	0.01539 (4)
Cl1	0.92263 (9)	0.99697 (5)	0.60610 (5)	0.02654 (12)
P1	0.78638 (12)	0.48543 (5)	0.81568 (5)	0.03212 (16)
N3	0.6113 (3)	1.04780 (16)	0.69887 (15)	0.0180 (4)
N1	0.8552 (3)	0.84505 (15)	0.70409 (14)	0.0177 (4)
F1	0.6905 (3)	0.57089 (14)	0.84775 (16)	0.0437 (5)

C7	0.7905 (3)	0.79767 (17)	0.75251 (16)	0.0198 (4)
N2	0.5471 (3)	0.86800 (16)	0.58190 (13)	0.0191 (4)
F2	0.6019 (3)	0.40453 (14)	0.77127 (15)	0.0456 (5)
C2	0.4705 (4)	0.9420 (2)	0.81275 (17)	0.0242 (5)
H2	0.4352	0.9915	0.8017	0.029*
C18	0.4312 (3)	0.91679 (19)	0.56450 (16)	0.0223 (4)
C14	0.5340 (4)	0.7766 (2)	0.52093 (17)	0.0266 (5)
H14	0.6142	0.7440	0.5326	0.032*
C17	0.2962 (4)	0.8714 (2)	0.48590 (19)	0.0318 (6)
H17	0.2153	0.9040	0.4752	0.038*
C15	0.4028 (4)	0.7296 (2)	0.44068 (19)	0.0352 (7)
H15	0.3963	0.6665	0.3989	0.042*
C16	0.2840 (4)	0.7766 (3)	0.4236 (2)	0.0376 (7)
H16	0.1951	0.7453	0.3705	0.045*
C23	0.6672 (3)	1.13860 (18)	0.76812 (17)	0.0229 (4)
C19	0.4642 (3)	1.01843 (18)	0.63277 (17)	0.0210 (4)
C21	0.4168 (4)	1.1765 (2)	0.7079 (3)	0.0360 (7)
H21	0.3506	1.2206	0.7112	0.043*
C20	0.3621 (4)	1.0831 (2)	0.6354 (2)	0.0287 (5)
H20	0.2609	1.0645	0.5902	0.034*
C22	0.5677 (4)	1.2048 (2)	0.7749 (2)	0.0309 (6)
H22	0.6020	1.2668	0.8235	0.037*
C6	0.6524 (3)	0.83168 (18)	0.79360 (16)	0.0197 (4)
C3	0.3896 (4)	0.9039 (2)	0.86691 (18)	0.0264 (5)
C5	0.5695 (4)	0.7935 (2)	0.84665 (18)	0.0250 (5)
H5	0.6025	0.7431	0.8569	0.030*
C4	0.4394 (4)	0.8291 (2)	0.88424 (18)	0.0273 (5)
H4	0.3863	0.8040	0.9202	0.033*
C1	0.6015 (3)	0.90743 (18)	0.77554 (15)	0.0178 (4)
C10	1.0524 (4)	0.7435 (2)	0.6675 (2)	0.0269 (5)
O1	0.2627 (3)	0.9445 (2)	0.90026 (17)	0.0398 (5)
C9	0.9853 (4)	0.6957 (2)	0.7168 (2)	0.0330 (6)
H9	1.0283	0.6453	0.7213	0.040*
C11	0.9825 (3)	0.81744 (18)	0.66221 (17)	0.0217 (4)
H11	1.0247	0.8496	0.6285	0.026*
C8	0.8555 (4)	0.7224 (2)	0.7593 (2)	0.0311 (6)
H8	0.8111	0.6902	0.7925	0.037*
C13	1.1909 (4)	0.7153 (2)	0.6189 (3)	0.0361 (6)
H13A	1.2831	0.7098	0.6593	0.054*
H13B	1.2371	0.7646	0.5996	0.054*
H13C	1.1415	0.6532	0.5666	0.054*
C12	0.1877 (5)	0.9144 (3)	0.9617 (2)	0.0453 (9)
H12A	0.1258	0.8459	0.9308	0.068*
H12B	0.1081	0.9521	0.9839	0.068*
H12C	0.2787	0.9249	1.0121	0.068*
F6	0.9704 (3)	0.56715 (17)	0.8582 (2)	0.0627 (7)

F3	0.7807 (5)	0.49325 (18)	0.72156 (16)	0.0636 (8)
F5	0.8815 (4)	0.39984 (17)	0.7838 (2)	0.0665 (8)
F4	0.7916 (5)	0.4775 (2)	0.90950 (16)	0.0689 (8)
N4	0.8942 (3)	1.07218 (15)	0.80993 (13)	0.0198 (4)
C24	0.8326 (4)	1.15369 (18)	0.82948 (17)	0.0237 (5)
C26	1.0888 (5)	1.2507 (2)	0.9508 (2)	0.0402 (7)
H26	1.1535	1.3100	0.9990	0.048*
C28	1.0503 (4)	1.0797 (2)	0.85837 (17)	0.0265 (5)
H28	1.0915	1.0243	0.8446	0.032*
C25	0.9294 (4)	1.2438 (2)	0.9008 (2)	0.0343 (6)
H25	0.8868	1.2988	0.9146	0.041*
C27	1.1516 (4)	1.1688 (2)	0.9287 (2)	0.0364 (7)
H27	1.2607	1.1731	0.9605	0.044*
C30	0.6256 (6)	0.4071 (4)	0.0453 (3)	0.0515 (9)
C29	0.6882 (7)	0.5149 (4)	0.0940 (4)	0.0735 (16)
H29A	0.6784	0.5429	0.0510	0.110*
H29B	0.8083	0.5337	0.1262	0.110*
H29C	0.6189	0.5385	0.1366	0.110*
N5	0.5749 (6)	0.3247 (3)	0.0067 (3)	0.0590 (9)
O2	0.6749 (17)	0.5622 (8)	0.4335 (11)	0.320 (9)
H2A	0.6127	0.5886	0.4124	0.480*
C38	0.5534 (17)	0.4878 (7)	0.4686 (11)	0.189 (7)
H38A	0.4766	0.4344	0.4134	0.227*
H38B	0.6342	0.4593	0.4928	0.227*

Table S3: Atomic Displacement Parameters ($Å^2$) for [Ir(tpy)(MeO-mppy)Cl](PF_6).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir1	0.01571 (5)	0.01694 (5)	0.01661 (5)	0.00606 (3)	0.00422 (3)	0.00947 (4)
Cl1	0.0215 (3)	0.0378 (3)	0.0329 (3)	0.0096 (2)	0.0109 (2)	0.0257 (3)
P1	0.0435 (4)	0.0208 (3)	0.0292 (3)	0.0072 (3)	0.0117 (3)	0.0076 (2)
N3	0.0176 (9)	0.0193 (9)	0.0228 (9)	0.0083 (7)	0.0058 (7)	0.0131 (7)
N1	0.0177 (9)	0.0181 (8)	0.0200 (8)	0.0062 (7)	0.0052 (7)	0.0099 (7)
F1	0.0513 (13)	0.0232 (8)	0.0501 (12)	0.0125 (8)	0.0144 (10)	0.0071 (8)
C7	0.0205 (10)	0.0203 (10)	0.0243 (10)	0.0089 (8)	0.0094 (8)	0.0125 (8)
N2	0.0180 (9)	0.0233 (9)	0.0175 (8)	0.0041 (7)	0.0052 (7)	0.0105 (7)
F2	0.0490 (12)	0.0241 (8)	0.0536 (12)	0.0004 (8)	0.0098 (10)	0.0116 (8)
C2	0.0271 (12)	0.0306 (12)	0.0259 (10)	0.0171 (10)	0.0108 (9)	0.0176 (9)
C18	0.0184 (10)	0.0281 (11)	0.0243 (10)	0.0024 (8)	0.0025 (8)	0.0177 (9)
C14	0.0270 (12)	0.0277 (12)	0.0214 (10)	0.0046 (10)	0.0067 (9)	0.0078 (9)
C17	0.0255 (13)	0.0384 (14)	0.0307 (12)	0.0007 (11)	−0.0048 (10)	0.0217 (11)
C15	0.0358 (16)	0.0369 (15)	0.0206 (11)	−0.0006 (12)	0.0038 (10)	0.0058 (10)
C16	0.0343 (16)	0.0432 (16)	0.0253 (12)	−0.0042 (13)	−0.0037 (11)	0.0152 (12)
C23	0.0250 (12)	0.0201 (10)	0.0281 (11)	0.0090 (8)	0.0073 (9)	0.0134 (9)
C19	0.0166 (10)	0.0253 (11)	0.0286 (11)	0.0066 (8)	0.0063 (8)	0.0186 (9)
C21	0.0282 (14)	0.0333 (14)	0.060 (2)	0.0167 (11)	0.0131 (13)	0.0286 (14)

C20	0.0197 (11)	0.0335 (13)	0.0453 (15)	0.0095 (10)	0.0083 (10)	0.0283 (12)
C22	0.0343 (14)	0.0247 (12)	0.0418 (14)	0.0148 (10)	0.0121 (12)	0.0183 (11)
C6	0.0194 (10)	0.0226 (10)	0.0238 (10)	0.0097 (8)	0.0085 (8)	0.0139 (8)
C3	0.0269 (12)	0.0377 (14)	0.0262 (11)	0.0183 (10)	0.0134 (9)	0.0184 (10)
C5	0.0266 (12)	0.0307 (12)	0.0316 (11)	0.0142 (10)	0.0139 (10)	0.0223 (10)
C4	0.0277 (13)	0.0399 (14)	0.0304 (12)	0.0175 (11)	0.0161 (10)	0.0245 (11)
C1	0.0185 (10)	0.0197 (9)	0.0169 (9)	0.0074 (8)	0.0042 (8)	0.0086 (8)
C10	0.0263 (13)	0.0245 (12)	0.0349 (13)	0.0114 (10)	0.0151 (10)	0.0133 (10)
O1	0.0458 (13)	0.0619 (15)	0.0460 (12)	0.0387 (12)	0.0344 (11)	0.0391 (12)
C9	0.0372 (15)	0.0313 (13)	0.0537 (17)	0.0243 (12)	0.0280 (14)	0.0289 (13)
C11	0.0222 (11)	0.0212 (10)	0.0255 (10)	0.0078 (8)	0.0101 (8)	0.0116 (8)
C8	0.0351 (15)	0.0308 (13)	0.0486 (16)	0.0193 (11)	0.0242 (13)	0.0289 (12)
C13	0.0346 (15)	0.0342 (14)	0.0546 (18)	0.0215 (12)	0.0272 (14)	0.0231 (13)
C12	0.0466 (19)	0.075 (3)	0.0430 (17)	0.0347 (18)	0.0324 (15)	0.0385 (18)
F6	0.0470 (13)	0.0348 (11)	0.0782 (18)	−0.0006 (10)	0.0097 (12)	0.0028 (11)
F3	0.114 (2)	0.0345 (11)	0.0354 (11)	0.0041 (13)	0.0294 (13)	0.0111 (9)
F5	0.0607 (16)	0.0337 (11)	0.094 (2)	0.0207 (11)	0.0252 (14)	0.0105 (12)
F4	0.113 (2)	0.0593 (15)	0.0388 (11)	0.0240 (15)	0.0114 (13)	0.0282 (11)
N4	0.0213 (9)	0.0193 (9)	0.0201 (8)	0.0074 (7)	0.0032 (7)	0.0096 (7)
C24	0.0278 (12)	0.0191 (10)	0.0247 (10)	0.0065 (9)	0.0055 (9)	0.0100 (8)
C26	0.0436 (18)	0.0287 (14)	0.0310 (13)	−0.0009 (12)	−0.0014 (12)	0.0037 (11)
C28	0.0245 (12)	0.0281 (12)	0.0236 (10)	0.0063 (9)	0.0001 (9)	0.0101 (9)
C25	0.0395 (16)	0.0220 (12)	0.0328 (13)	0.0069 (11)	0.0059 (12)	0.0047 (10)
C27	0.0321 (15)	0.0364 (15)	0.0282 (13)	0.0021 (12)	−0.0054 (11)	0.0088 (11)
C30	0.041 (2)	0.063 (3)	0.050 (2)	0.0128 (18)	0.0122 (16)	0.0240 (19)
C29	0.052 (3)	0.063 (3)	0.076 (3)	0.012 (2)	0.019 (2)	0.000 (2)
N5	0.059 (2)	0.060 (2)	0.058 (2)	0.0090 (18)	0.0100 (17)	0.0301 (18)
O2	0.277 (14)	0.182 (9)	0.44 (2)	0.022 (9)	−0.126 (14)	0.166 (12)
C38	0.207 (13)	0.101 (6)	0.37 (2)	0.089 (7)	0.189 (13)	0.151 (10)

Table S4: Bond Lengths in [Ir(tpy)(MeO-mppy)Cl](PF_6) (Å)*

Ir1—N3	1.944 (2)	C6—C1	1.423 (3)
Ir1—C1	2.021 (2)	C3—O1	1.366 (3)
Ir1—N4	2.035 (2)	C3—C4	1.399 (4)
Ir1—N2	2.040 (2)	C5—C4	1.384 (4)
Ir1—N1	2.068 (2)	C5—H5	0.9300
Ir1—Cl1	2.4457 (6)	C4—H4	0.9300
P1—F4	1.586 (2)	C10—C9	1.385 (4)
P1—F3	1.590 (2)	C10—C11	1.385 (4)
P1—F2	1.595 (2)	C10—C13	1.494 (4)
P1—F5	1.598 (3)	O1—C12	1.422 (4)
P1—F6	1.598 (3)	C9—C8	1.375 (4)
P1—F1	1.601 (2)	C9—H9	0.9300
N3—C23	1.348 (3)	C11—H11	0.9300

N3—C19	1.351 (3)	C8—H8	0.9300
N1—C11	1.357 (3)	C13—H13A	0.9600
N1—C7	1.360 (3)	C13—H13B	0.9600
C7—C8	1.392 (4)	C13—H13C	0.9600
C7—C6	1.456 (3)	C12—H12A	0.9600
N2—C14	1.342 (3)	C12—H12B	0.9600
N2—C18	1.368 (3)	C12—H12C	0.9600
C2—C1	1.382 (3)	N4—C28	1.344 (3)
C2—C3	1.405 (4)	N4—C24	1.373 (3)
C2—H2	0.9300	C24—C25	1.398 (4)
C18—C17	1.392 (3)	C26—C25	1.380 (5)
C18—C19	1.468 (4)	C26—C27	1.381 (5)
C14—C15	1.392 (4)	C26—H26	0.9300
C14—H14	0.9300	C28—C27	1.392 (4)
C17—C16	1.390 (5)	C28—H28	0.9300
C17—H17	0.9300	C25—H25	0.9300
C15—C16	1.363 (5)	C27—H27	0.9300
C15—H15	0.9300	C30—N5	1.128 (6)
C16—H16	0.9300	C30—C29	1.472 (7)
C23—C22	1.391 (4)	C29—H29A	0.9600
C23—C24	1.467 (4)	C29—H29B	0.9600
C19—C20	1.397 (4)	C29—H29C	0.9600
C21—C22	1.383 (5)	O2—C38	1.682 (16)
C21—C20	1.394 (5)	O2—H2A	0.8200
C21—H21	0.9300	C38—C38^{i}	1.42 (2)
C20—H20	0.9300	C38—H38A	0.9700
C22—H22	0.9300	C38—H38B	0.9700
C6—C5	1.398 (3)		
* All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.			

Table S5: Bond Angles in [Ir(tpy)(MeO-mppy)Cl](PF_6) (°)*

N3—Ir1—C1	93.17 (9)	C23—C22—H22	120.7
N3—Ir1—N4	80.29 (9)	C5—C6—C1	120.2 (2)
C1—Ir1—N4	91.56 (9)	C5—C6—C7	124.0 (2)
N3—Ir1—N2	80.38 (9)	C1—C6—C7	115.7 (2)
C1—Ir1—N2	92.88 (9)	O1—C3—C4	123.6 (2)
N4—Ir1—N2	160.37 (10)	O1—C3—C2	115.8 (2)
N3—Ir1—N1	173.78 (8)	C4—C3—C2	120.6 (2)
C1—Ir1—N1	80.69 (9)	C4—C5—C6	121.4 (2)
N4—Ir1—N1	100.70 (8)	C4—C5—H5	119.3

N2—Ir1—N1	98.89 (9)	C6—C5—H5	119.3
N3—Ir1—Cl1	92.04 (7)	C5—C4—C3	118.5 (2)
C1—Ir1—Cl1	174.75 (7)	C5—C4—H4	120.7
N4—Ir1—Cl1	88.64 (6)	C3—C4—H4	120.7
N2—Ir1—Cl1	88.67 (6)	C2—C1—C6	118.0 (2)
N1—Ir1—Cl1	94.12 (6)	C2—C1—Ir1	128.36 (18)
F4—P1—F3	179.9 (2)	C6—C1—Ir1	113.65 (17)
F4—P1—F2	90.49 (15)	C9—C10—C11	117.4 (3)
F3—P1—F2	89.40 (15)	C9—C10—C13	122.0 (3)
F4—P1—F5	89.74 (18)	C11—C10—C13	120.6 (3)
F3—P1—F5	90.31 (17)	C3—O1—C12	117.8 (2)
F2—P1—F5	89.32 (14)	C8—C9—C10	120.4 (3)
F4—P1—F6	90.83 (17)	C8—C9—H9	119.8
F3—P1—F6	89.28 (17)	C10—C9—H9	119.8
F2—P1—F6	178.64 (16)	N1—C11—C10	122.9 (2)
F5—P1—F6	91.03 (15)	N1—C11—H11	118.5
F4—P1—F1	90.10 (15)	C10—C11—H11	118.5
F3—P1—F1	89.85 (14)	C9—C8—C7	119.9 (2)
F2—P1—F1	90.50 (13)	C9—C8—H8	120.0
F5—P1—F1	179.75 (16)	C7—C8—H8	120.0
F6—P1—F1	89.15 (13)	C10—C13—H13A	109.5
C23—N3—C19	122.8 (2)	C10—C13—H13B	109.5
C23—N3—Ir1	118.67 (17)	H13A—C13—H13B	109.5
C19—N3—Ir1	118.40 (17)	C10—C13—H13C	109.5
C11—N1—C7	119.1 (2)	H13A—C13—H13C	109.5
C11—N1—Ir1	125.83 (17)	H13B—C13—H13C	109.5
C7—N1—Ir1	115.02 (17)	O1—C12—H12A	109.5
N1—C7—C8	120.2 (2)	O1—C12—H12B	109.5
N1—C7—C6	114.9 (2)	H12A—C12—H12B	109.5
C8—C7—C6	124.9 (2)	O1—C12—H12C	109.5
C14—N2—C18	119.6 (2)	H12A—C12—H12C	109.5
C14—N2—Ir1	127.01 (19)	H12B—C12—H12C	109.5
C18—N2—Ir1	113.21 (16)	C28—N4—C24	119.7 (2)
C1—C2—C3	121.3 (2)	C28—N4—Ir1	126.81 (18)
C1—C2—H2	119.4	C24—N4—Ir1	113.19 (16)
C3—C2—H2	119.4	N4—C24—C25	120.4 (3)
N2—C18—C17	120.7 (3)	N4—C24—C23	115.0 (2)
N2—C18—C19	115.1 (2)	C25—C24—C23	124.5 (3)
C17—C18—C19	124.2 (2)	C25—C26—C27	119.6 (3)
N2—C14—C15	121.3 (3)	C25—C26—H26	120.2
N2—C14—H14	119.3	C27—C26—H26	120.2
C15—C14—H14	119.3	N4—C28—C27	121.4 (3)
C16—C17—C18	119.0 (3)	N4—C28—H28	119.3
C16—C17—H17	120.5	C27—C28—H28	119.3
C18—C17—H17	120.5	C26—C25—C24	119.5 (3)
C16—C15—C14	119.6 (3)	C26—C25—H25	120.3

C16—C15—H15	120.2	C24—C25—H25	120.3
C14—C15—H15	120.2	C26—C27—C28	119.4 (3)
C15—C16—C17	119.7 (3)	C26—C27—H27	120.3
C15—C16—H16	120.1	C28—C27—H27	120.3
C17—C16—H16	120.1	N5—C30—C29	178.5 (5)
N3—C23—C22	119.5 (2)	C30—C29—H29A	109.5
N3—C23—C24	112.6 (2)	C30—C29—H29B	109.5
C22—C23—C24	127.9 (2)	H29A—C29—H29B	109.5
N3—C19—C20	119.8 (2)	C30—C29—H29C	109.5
N3—C19—C18	112.8 (2)	H29A—C29—H29C	109.5
C20—C19—C18	127.4 (2)	H29B—C29—H29C	109.5
C22—C21—C20	121.3 (3)	C38—O2—H2A	109.5
C22—C21—H21	119.3	C38^{i}—C38—O2	128.1 (11)
C20—C21—H21	119.3	C38^{i}—C38—H38A	105.3
C21—C20—C19	117.8 (3)	O2—C38—H38A	105.3
C21—C20—H20	121.1	C38^{i}—C38—H38B	105.3
C19—C20—H20	121.1	O2—C38—H38B	105.3
C21—C22—C23	118.7 (3)	H38A—C38—H38B	106.0
C21—C22—H22	120.7		

* All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes. ^{i} Symmetry code: −x+1, −y+1, −z+1.