Electronic Supplementary Material (ESI) for RSC Advances.

The Effect of Nitrido, Azide, and Nitrosyl Ligands on Magnetization Densities and Magnetic Properties of Iridium PNP Pincer-Type Complexes

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Supporting Information

Table S1. Complex **1** coordinates used in calculations.

Iridium Nitrido Complex—Coordinates

1.Ir	3.108815	4.144296	3.001956
2.P	4.907875	5.688703	3.153434
3.P	0.837854	3.435935	2.898634
4.N	2.034958	6.08844	2.938375
5.N	3.953393	2.625572	3.028754
6.C	2.732862	7.260266	2.990219
7.H	2.157012	8.195242	2.94871
8.C	4.095759	7.288678	3.091576
9.H	4.638609	8.232747	3.122954
10.C	0.672651	6.119803	2.857444
11.H	0.189638	7.106257	2.824084
12.C	-0.077561	4.978085	2.816741
13.H	-1.164744	5.020588	2.760415
14.C	6.082773	5.599712	1.633621
15.C	6.696363	4.194524	1.493714
16.H	7.217387	4.129755	0.5238
17.H	5.92251	3.412848	1.520225
18.H	7.43257	3.976937	2.278376
19.C	7.192912	6.664863	1.677479
20.H	7.713242	6.677831	0.705351
21.H	7.946563	6.447562	2.446021
22.H	6.79355	7.674833	1.850792
23.C	5.172167	5.864659	0.41603
24.H	4.740373	6.874886	0.4431
25.H	4.344934	5.140474	0.381232
26.H	5.769881	5.762693	-0.504911
27.C	5.840218	5.628166	4.83389
28.C	4.730726	5.57711	5.905234
29.H	5.198817	5.567565	6.903795
30.H	4.111117	4.676978	5.789816
31.H	4.070865	6.454484	5.84127
32.C	6.704526	4.36011	4.943983
33.H	7.59843	4.41094	4.307408
34.H	6.134109	3.456607	4.680655
35.H	7.049229	4.251288	5.985855
36.C	6.692157	6.88824	5.076328
37.H	6.087825	7.803841	5.003697
38.H	7.537988	6.971992	4.382768
39.H	7.105446	6.845406	6.097723
40.C	0.374881	2.465003	1.305396

41.C	1.090015	3.203375	0.154799
42.H	0.824936	2.718438	-0.799809
43.H	2.18089	3.174672	0.281309
44.H	0.781847	4.257831	0.103128
45.C	-1.141512	2.491646	1.031095
46.H	-1.335079	1.988537	0.069215
47.H	-1.515638	3.52165	0.946288
48.H	-1.725657	1.969874	1.799241
49.C	0.88527	1.015515	1.370455
50.H	0.31076	0.405411	2.081253
51.H	1.949527	0.971756	1.646718
52.H	0.775519	0.551425	0.376222
53.C	0.273835	2.527358	4.499664
54.C	-1.199804	2.086962	4.443571
55.H	-1.36157	1.264782	3.733411
56.H	-1.872115	2.917142	4.181141
57.H	-1.501135	1.721351	5.439415
58.C	1.180077	1.315937	4.791206
59.H	0.928236	0.918254	5.788727
60.H	2.242294	1.601245	4.790828
61.H	1.043814	0.502721	4.066804
62.C	0.452419	3.559863	5.631822
63.H	-0.209433	4.427204	5.500477
64.H	1.489646	3.923718	5.67005
65.H	0.212481	3.078225	6.594126

Table S2. Complex **2** coordinates used in calculations.

Iridium Azide Complex—Coordinates

1.Ir	-0.725591	-1.142321	0.171785
2.N	-1.596409	0.66319	0.270197
3.H	2.57813	2.385428	1.494469
4.N	0.021108	-3.01359	0.197165
5.C	3.290977	1.588543	1.242453
6.N	1.133967	-3.498873	0.206906
7.N	2.14359	-4.082492	0.233414
8.H	4.294082	-0.682728	0.078712
9.H	4.051771	1.560335	2.040472
10.P	-2.931613	-1.894404	0.436102
11.C	-2.963696	0.78611	0.484105
12.C	-3.775641	-0.294261	0.602397
13.C	-0.856023	1.830921	0.135208
14.C	0.481056	1.807818	-0.079744

15.P	1.218805	0.145882	-0.175521
16.H	3.802388	1.859681	0.310246
17.C	2.603834	0.211252	1.170472
18.C	1.870478	-0.039044	2.505062
19.H	2.594635	0.030951	3.33433
20.H	1.080602	0.707041	2.676631
21.H	1.4046	-1.033519	2.529626
22.C	3.666904	-0.88097	0.959087
23.H	3.232819	-1.884849	0.855142
24.H	4.334599	-0.899086	1.836782
25.H	-5.38919	-3.850228	-0.245978
26.C	-3.716956	-2.71368	-1.117321
27.C	-3.533237	-1.685064	-2.252773
28.H	-3.876546	-2.132152	-3.200274
29.H	-4.112281	-0.768245	-2.072902
30.H	-2.474925	-1.405357	-2.3612
31.C	-2.933661	-3.988562	-1.488221
32.H	-1.856155	-3.787034	-1.564231
33.H	-3.28911	-4.351515	-2.467419
34.H	-3.076784	-4.798885	-0.762496
35.C	-5.212992	-3.03324	-0.958617
36.H	-5.793892	-2.156056	-0.638187
37.H	-5.616668	-3.358015	-1.932498
38.H	-1.432292	-2.279891	2.922518
39.C	-3.368325	-2.840555	2.049724
40.C	-4.848581	-2.711779	2.453416
41.H	-5.000017	-3.229278	3.415598
42.H	-5.139464	-1.661398	2.596075
43.H	-5.531266	-3.165676	1.724572
44.C	-2.97677	-4.324597	1.926494
45.H	-3.657387	-4.876956	1.264012
46.H	-3.034715	-4.795201	2.92215
47.H	-1.949081	-4.442996	1.553644
48.C	-2.503337	-2.179591	3.144155
49.H	-2.729589	-1.107827	3.243562
50.H	-2.713812	-2.666339	4.11134
51.H	2.832391	2.085635	-1.939128
52.C	1.964549	0.063089	-1.947844
53.C	2.423618	-1.375508	-2.253976
54.H	2.783542	-1.42057	-3.295654
55.H	3.239959	-1.714432	-1.604119
56.H	1.589339	-2.084208	-2.156124
57.C	0.804458	0.412047	-2.902365
58.H	-0.060002	-0.245167	-2.726505

59.H	1.142233	0.274588	-3.942979
60.H	0.472658	1.452878	-2.781054
61.C	3.120608	1.050798	-2.175083
62.H	4.01226	0.7933	-1.587995
63.H	3.411136	1.024955	-3.238784
64.H	-3.352359	1.808333	0.551193
65.H	-4.84579	-0.167678	0.762483
66.H	1.038803	2.736689	-0.19137
67.H	-1.413742	2.770927	0.209667

Table S3. Complex **3** coordinates used in calculations.

Iridium Nitrosyl Complex—C oordinates

1.Ir	-0.597821	-1.341953	-0.273545
2.N	-0.386032	-1.479713	1.705612
3.H	1.467429	0.82764	-2.72398
4.C	4.03626	0.44091	0.669539
5.C	1.88837	1.663572	-2.147445
6.H	3.829682	1.014602	1.584736
7.H	4.976093	-0.10824	0.837759
8.H	2.915231	2.792648	0.219612
9.H	1.750757	2.578391	-2.744796
10.P	-2.823892	-1.900356	0.482293
11.C	-1.326574	-1.197163	2.671903
12.C	-2.749307	-1.102607	2.212186
13.C	0.015234	-0.486628	2.576981
14.C	0.668157	0.713124	1.95924
15.P	1.188499	0.20888	0.196461
16.H	2.96846	1.505244	-2.036901
17.C	1.18217	1.852918	-0.791105
18.C	-0.289765	2.236813	-1.03971
19.H	-0.313916	3.209249	-1.555923
20.H	-0.80519	1.502856	-1.670347
21.H	-0.859677	2.347721	-0.105981
22.C	1.859161	2.988737	0.005428
23.H	1.344083	3.199231	0.952957
24.H	1.809354	3.907709	-0.599554
25.H	-5.912782	-1.850517	0.840478
26.C	-4.277039	-0.998714	-0.386187
27.C	-3.792324	0.420541	-0.743321
28.H	-4.629989	0.969301	-1.201329
29.H	-3.472613	0.99067	0.140759

30.H	-2.962082	0.403804	-1.459145
31.C	-4.666402	-1.739235	-1.679661
32.H	-3.808881	-1.884846	-2.35169
33.H	-5.41069	-1.134028	-2.220333
34.H	-5.124467	-2.715881	-1.478599
35.C	-5.501174	-0.879248	0.545611
36.H	-5.280906	-0.303332	1.455037
37.H	-6.291759	-0.336334	0.00412
38.H	-3.553761	-4.245754	-1.365321
39.C	-3.143331	-3.772118	0.759755
40.C	-2.124382	-4.251736	1.814972
41.H	-2.24396	-5.339355	1.936433
42.H	-1.089037	-4.061267	1.502782
43.H	-2.281727	-3.791483	2.800715
44.C	-4.567906	-4.089112	1.250479
45.H	-4.827114	-3.550951	2.17389
46.H	-4.624637	-5.165405	1.477349
47.H	-5.332287	-3.87724	0.491841
48.C	-2.853119	-4.511978	-0.563896
49.H	-1.82984	-4.315783	-0.915768
50.H	-2.946237	-5.594862	-0.387462
51.H	4.214845	1.143049	-0.154908
52.C	2.929269	-0.579151	0.348101
53.C	2.857823	-1.624462	1.481415
54.H	3.832509	-2.132994	1.538764
55.H	2.662148	-1.175591	2.465537
56.H	2.092344	-2.387639	1.288547
57.C	3.237777	-1.318605	-0.971046
58.H	2.4603	-2.060872	-1.204031
59.H	4.19176	-1.856453	-0.856744
60.H	3.340268	-0.641337	-1.828097
61.N	-0.744076	-1.312009	-2.07069
62.O	-0.915646	-1.136567	-3.226822
63.H	-3.451294	-1.588174	2.90538
64.H	-3.064585	-0.049694	2.113461
65.H	-0.045026	1.55078	1.872428
66.H	1.527807	1.07463	2.541739

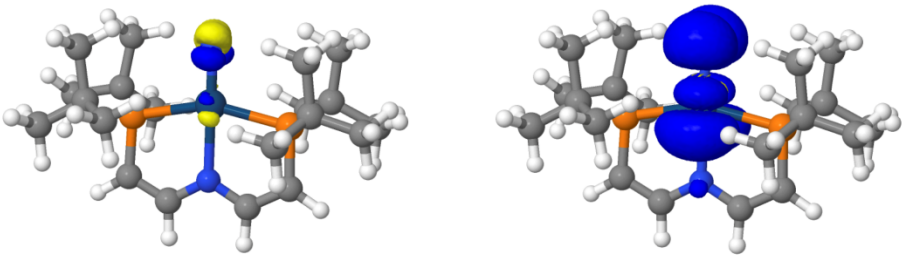


Figure S1. Complex **1** a) magnetization density difference plot between CAS(9,8) and CAS(9,10)SCF and b) magnetization density plot of CAS(9,10)SCF where blue is α-density and yellow is β-density.

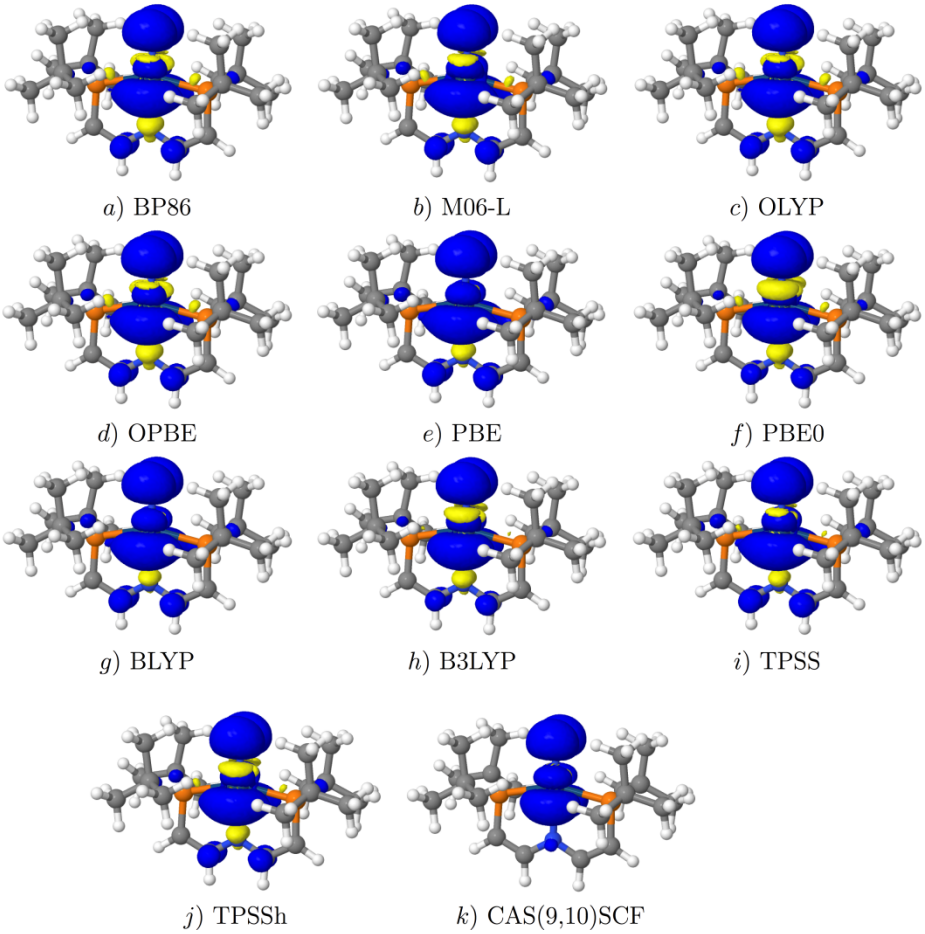


Figure S2. Complex **1** magnetization density plots of DFT and CASSCF methods where blue is α-density and yellow is β-density.

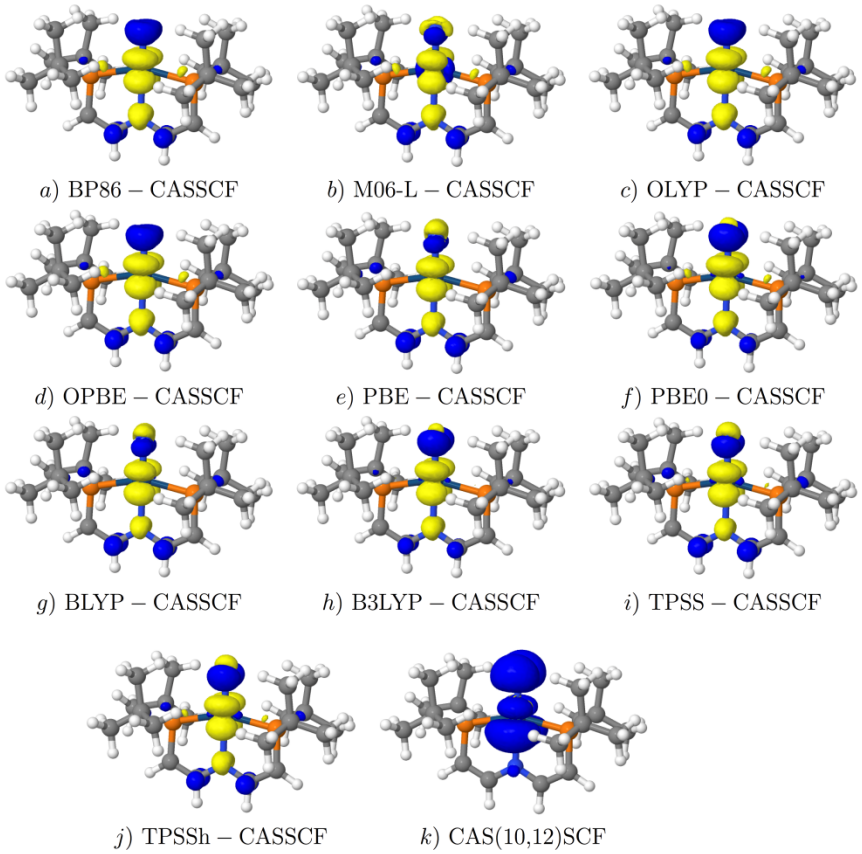


Figure S3. Complex **1** DFT-CASSCF magnetization density difference plots where blue is α-density and yellow is β-density.

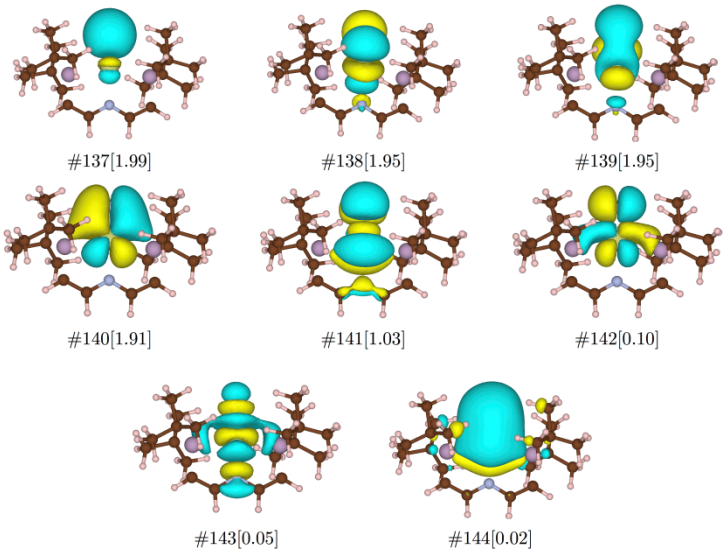


Figure S4. CAS(9,8)SCF orbitals and their natural occupation numbers for complex **1**.

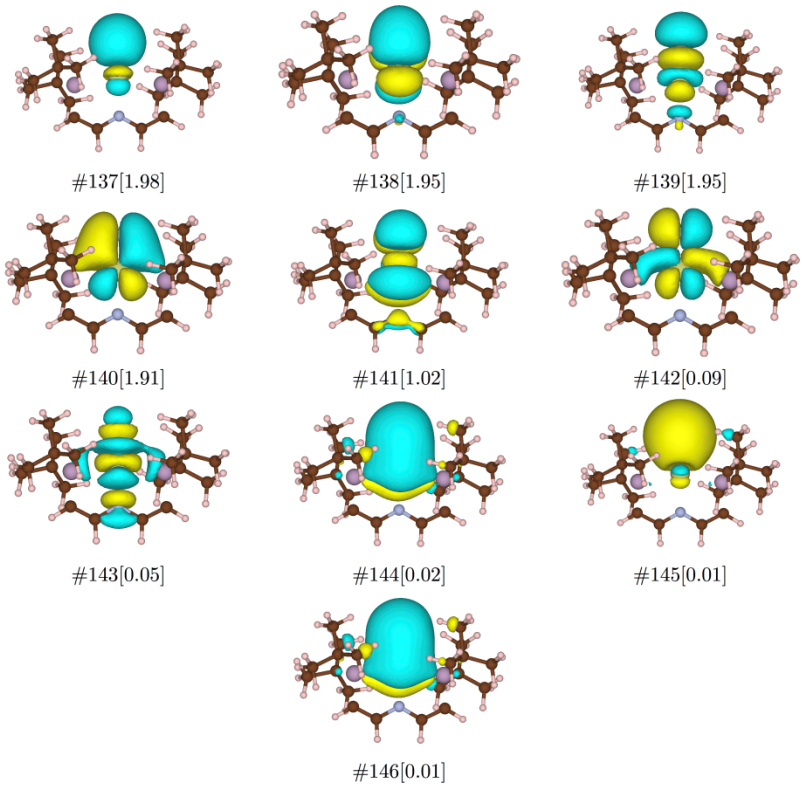


Figure S5. CAS(9,10)SCF orbitals and their natural occupation numbers for complex **1**.

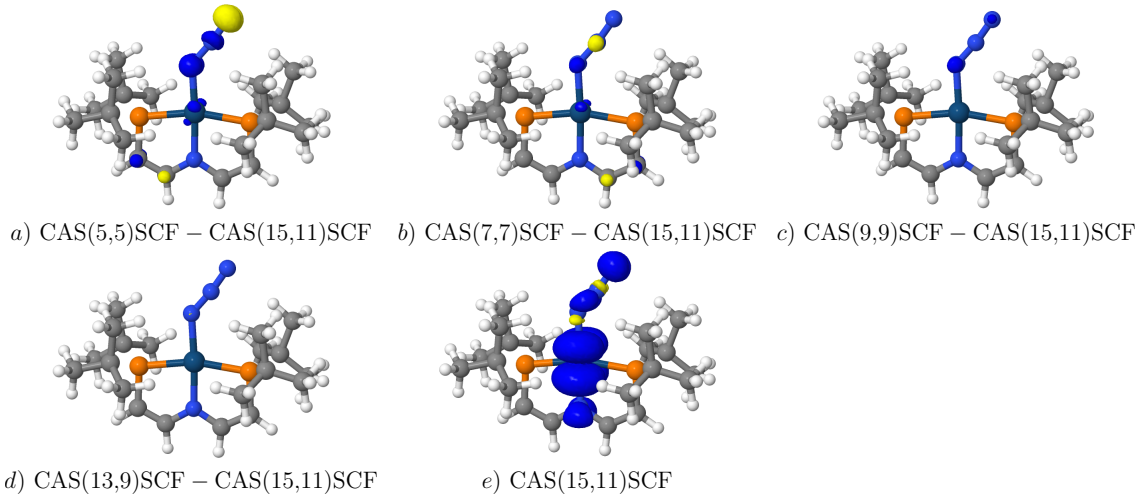


Figure S6. Complex **2** CASSCF-CASSCF magnetization density difference plots and magnetization density plot of CAS(15,11)SCF where blue is α-density and yellow is β-density.

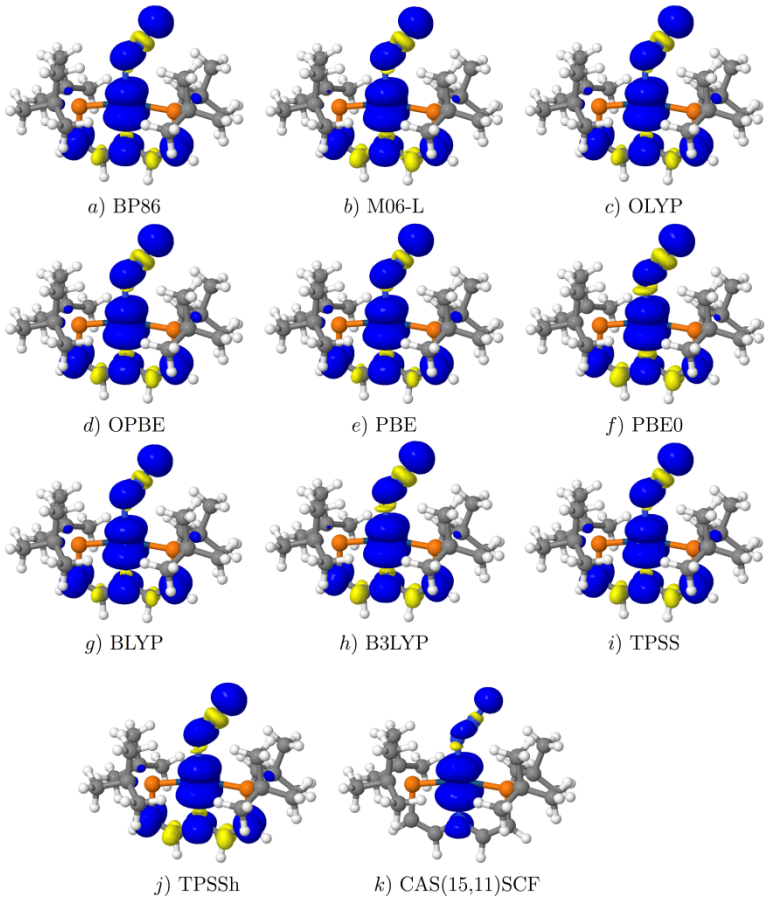


Figure S7. Complex **2** magnetization density plots of DFT and CASSCF methods where blue is α-density and yellow is β-density.

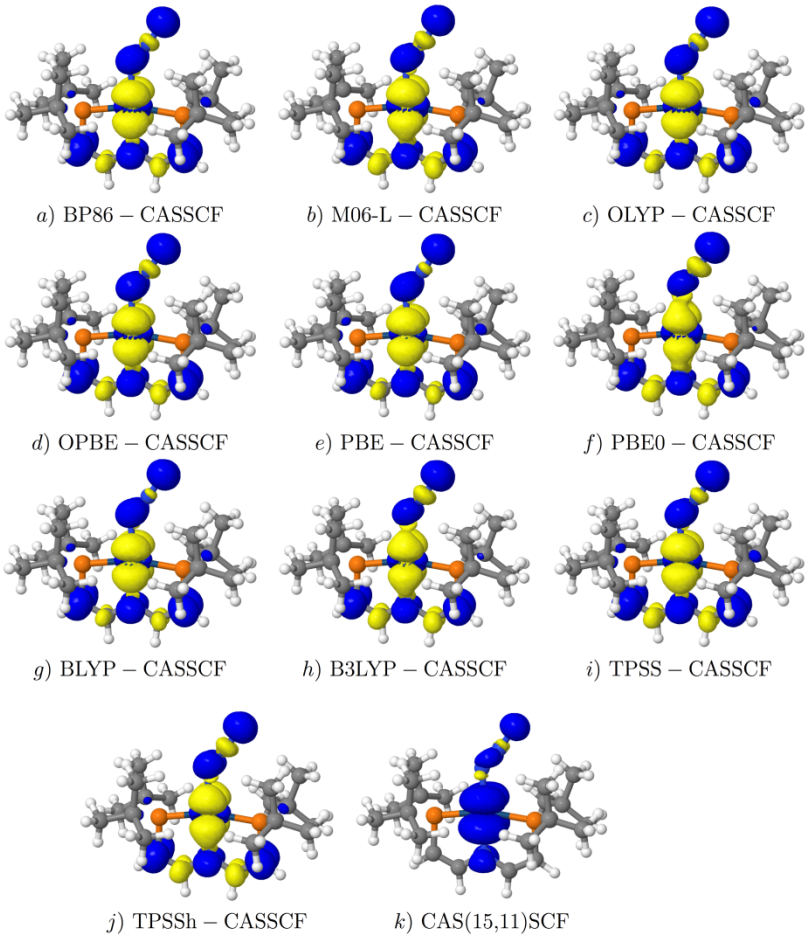


Figure S8. Complex **2** DFT-CASSCF magnetization density difference plots and CASSCF reference magnetization density where blue is α-density and yellow is β-density.

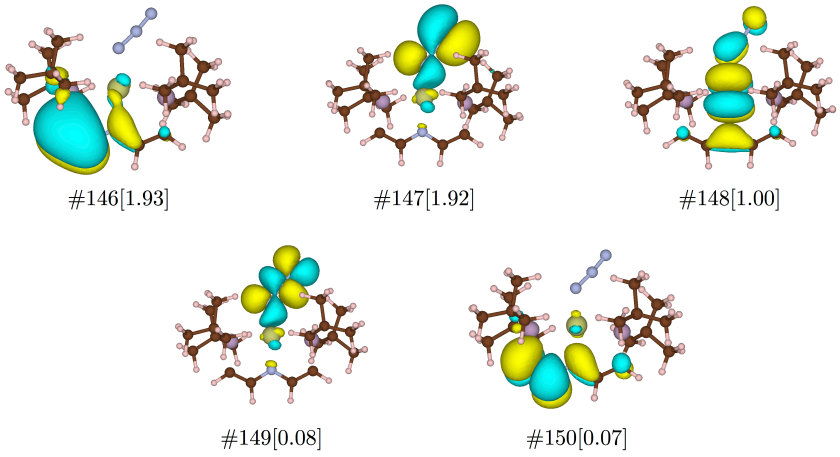


Figure S9. CAS(5,5)SCF orbitals and their natural occupation numbers for complex **2**.

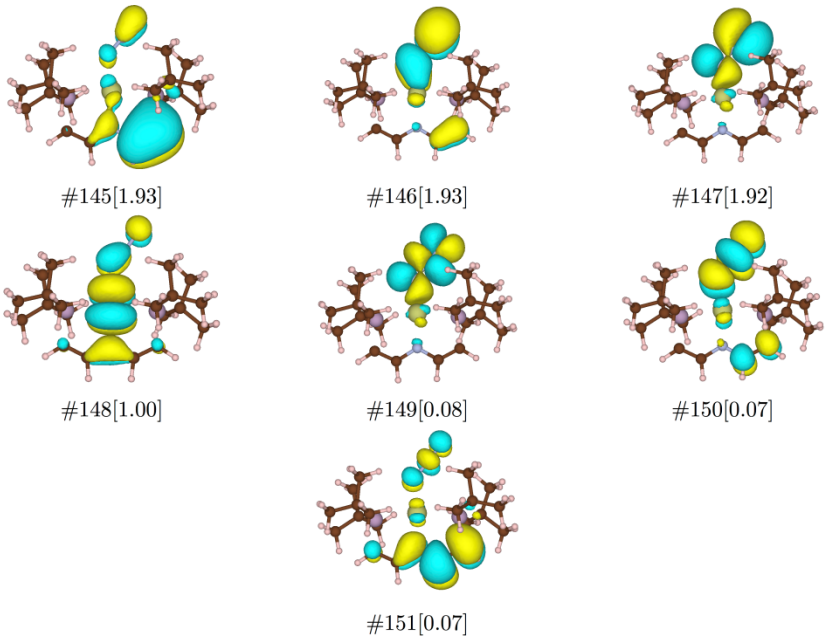


Figure S10. CAS(7,7)SCF orbitals and their natural occupation numbers for complex **2**.

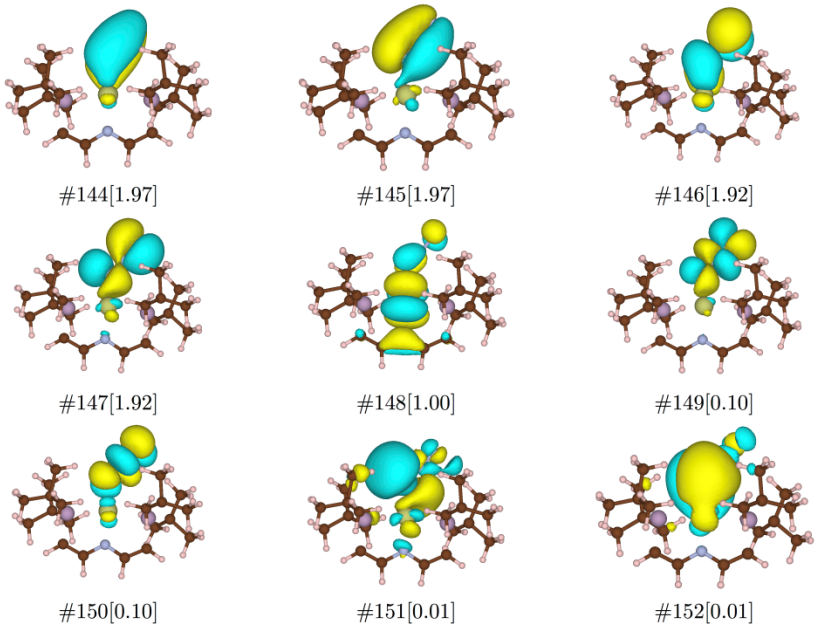


Figure S11. CAS(9,9)SCF orbitals and their natural occupation numbers for complex **2**.

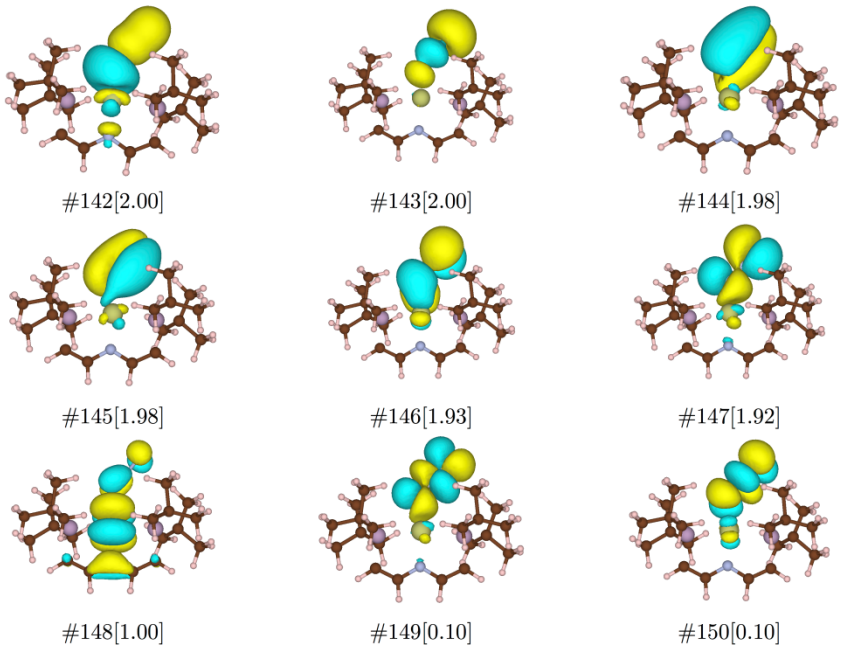


Figure S12. CAS(13,9)SCF orbitals and their natural occupation numbers for complex **2**.

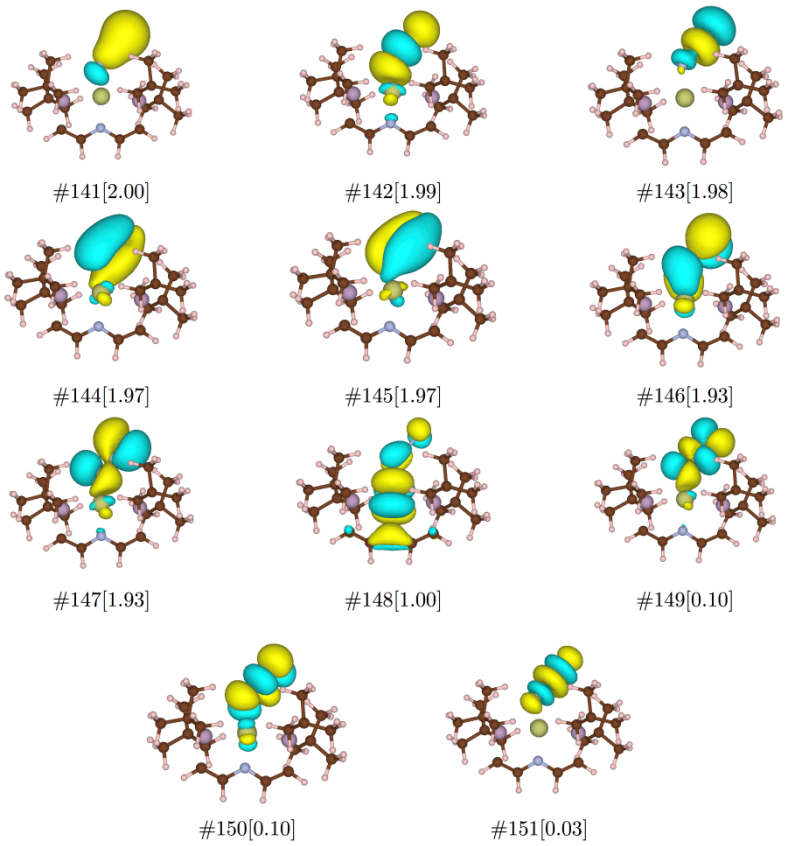
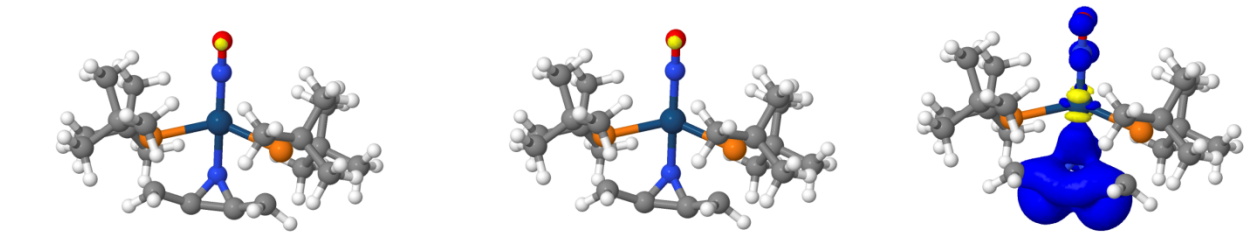
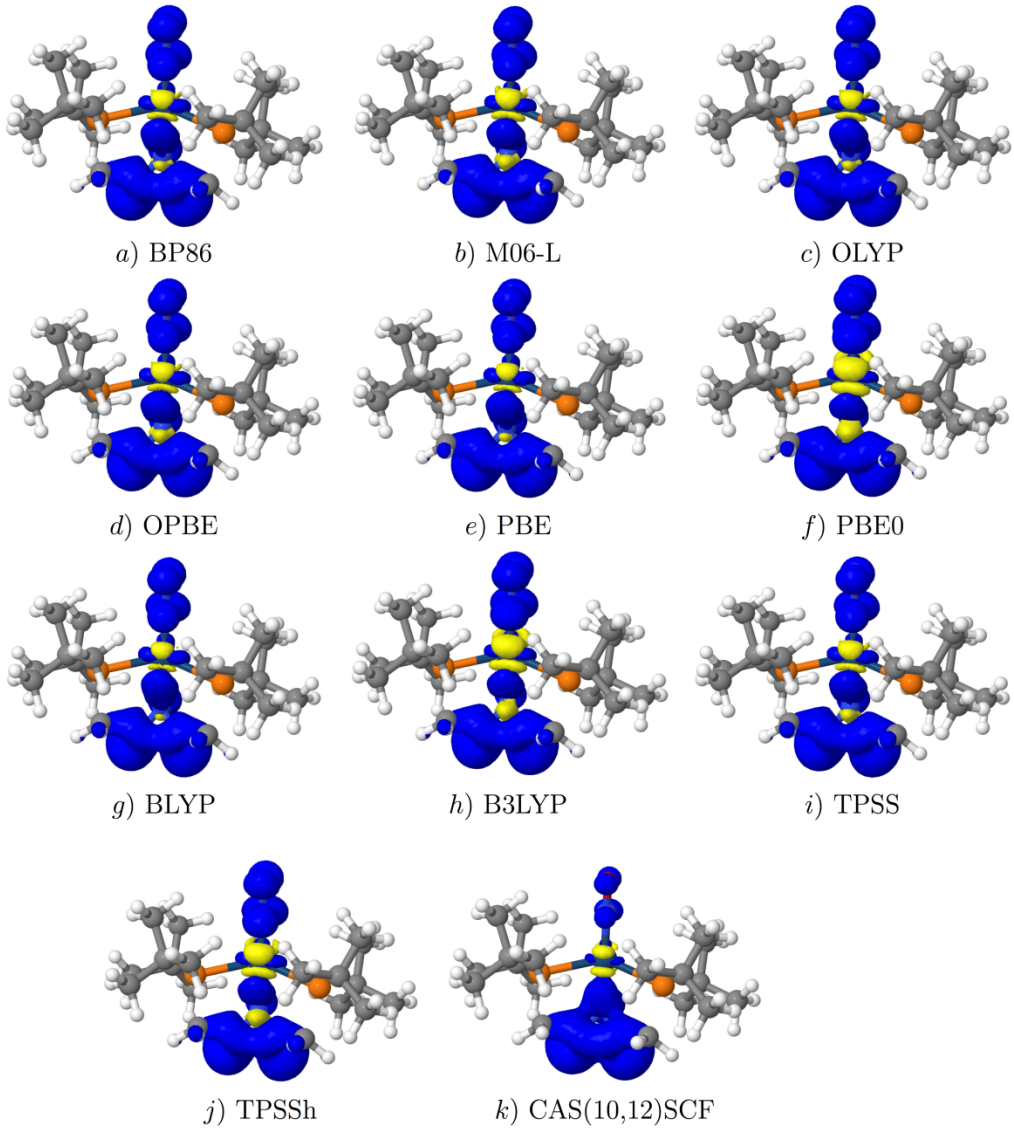


Figure S13. CAS(15,11)SCF orbitals and their natural occupation numbers for complex **2**.



a) CAS(6,6)SCF − CAS(10,12)SCF *b*) CAS(8,8)SCF − CAS(10,12)SCF *c*) CAS(10,12)SCF

Figure S14. Complex **3** CASSCF-CASSCF magnetization density difference plots and magnetization density plot of CAS(10,12)SCF where blue is α-density and yellow is β-density.



a) BP86 *b*) M06-L *c*) OLYP

d) OPBE *e*) PBE *f*) PBE0

g) BLYP *h*) B3LYP *i*) TPSS

j) TPSSh *k*) CAS(10,12)SCF

Figure S15. Complex **3** magnetization density plots of DFT and CASSCF methods where blue is α-density and yellow is β-density.

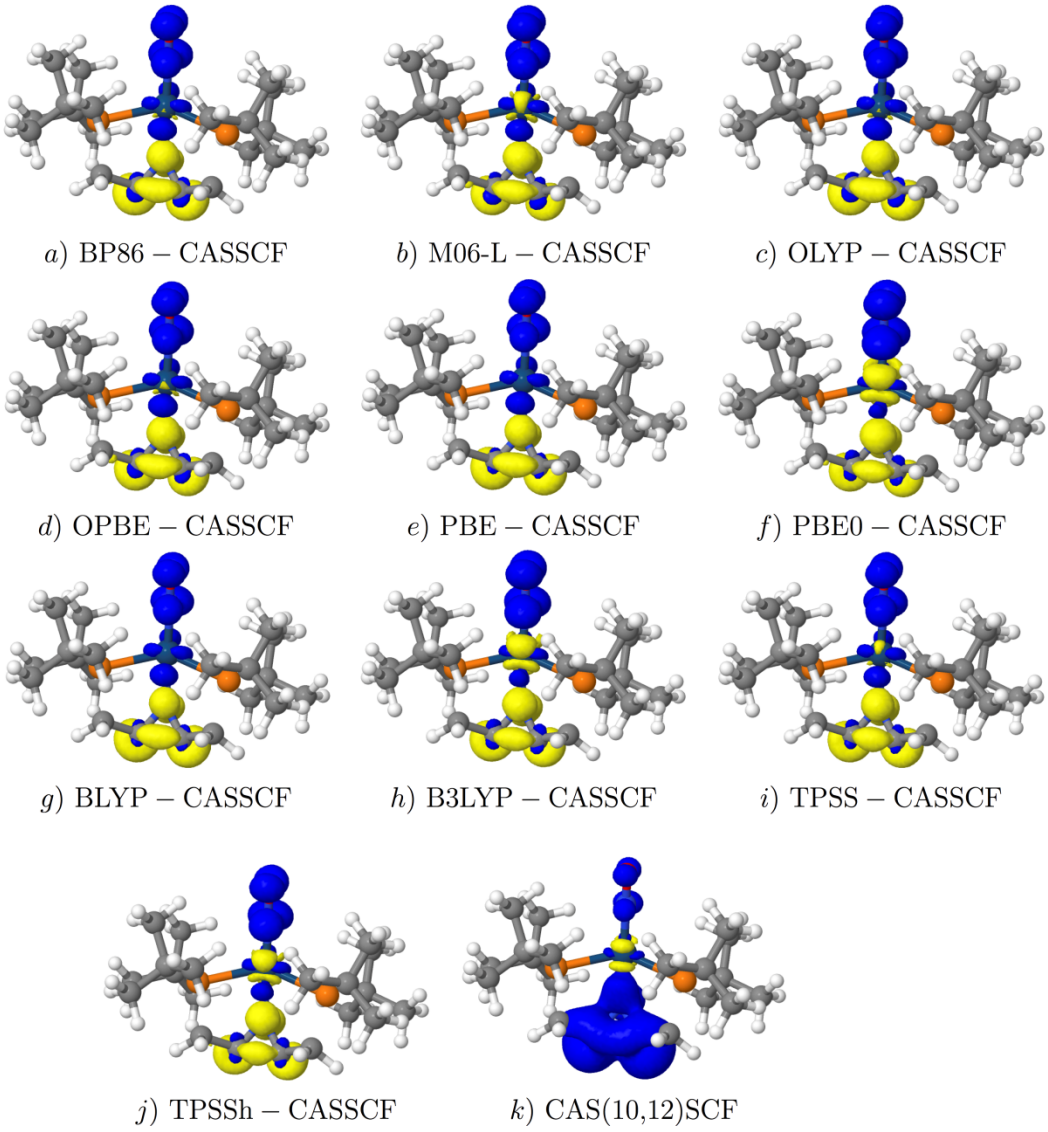


Figure S16. Complex **3** DFT-CASSCF magnetization density difference plots where blue is α-density and yellow is β-density.

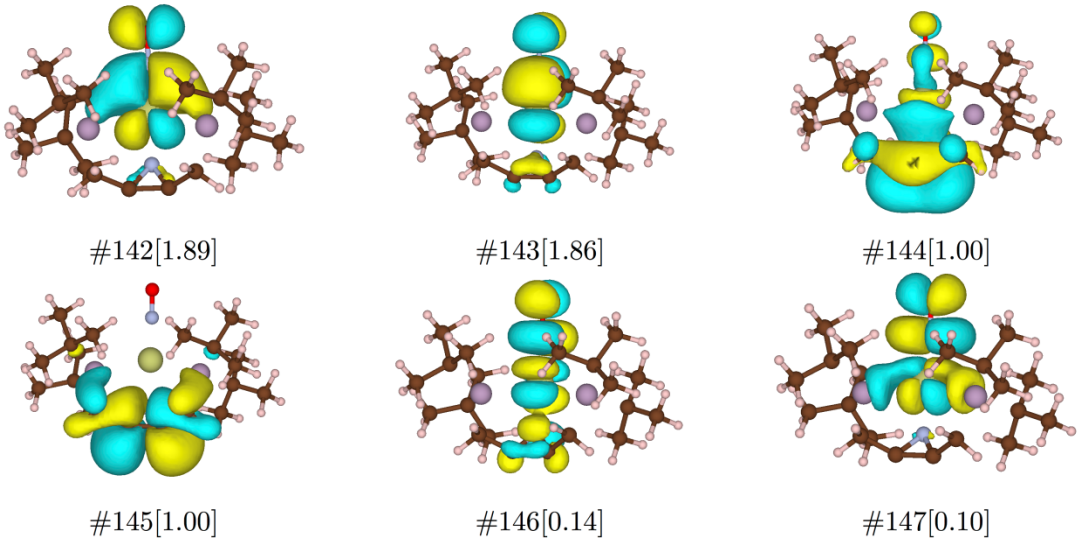


Figure S17. CAS(6,6)SCF orbitals and their natural occupation numbers for complex **3**.

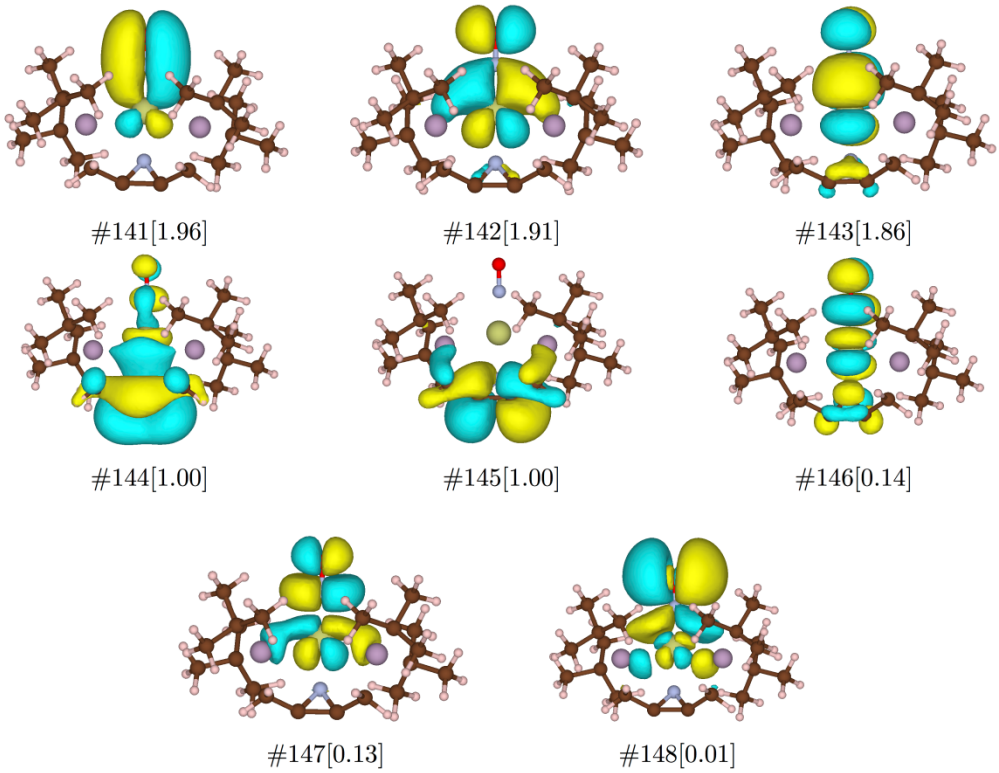


Figure S18. CAS(8,8)SCF orbitals and their natural occupation numbers for complex **3**.

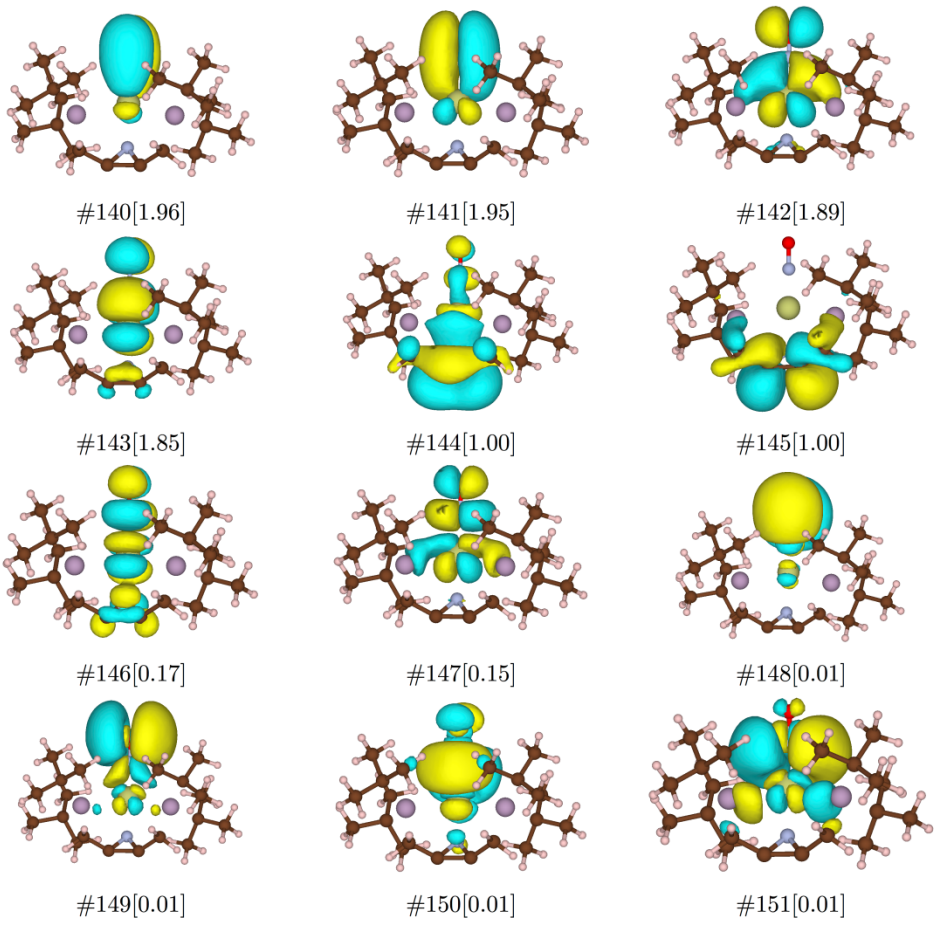


Figure S19. CAS(10,12)SCF orbitals and their natural occupation numbers for complex **3**.

Table S4: Total spin expectation values $\langle S^2 \rangle$ calculated for various exchange-correlation functionals and complexes 1, 2, and 3. The ideal value is also given.

Method	1		2		3	
	ideal $\langle S^2 \rangle$	$\langle S^2 \rangle$	ideal $\langle S^2 \rangle$	$\langle S^2 \rangle$	ideal $\langle S^2 \rangle$	$\langle S^2 \rangle$
B3LYP	0.7500	0.7580	0.7500	0.7586	2.0000	2.0549
BLYP	0.7500	0.7537	0.7500	0.7526	2.0000	2.0137
BP86	0.7500	0.7543	0.7500	0.7531	2.0000	2.0160
M06-L	0.7500	0.7554	0.7500	0.7573	2.0000	2.0277
OLYP	0.7500	0.7566	0.7500	0.7532	2.0000	2.0169
OPBE	0.7500	0.7576	0.7500	0.7536	2.0000	2.0195
PBE	0.7500	0.7539	0.7500	0.7528	2.0000	2.0148
PBE0	0.7500	0.7603	0.7500	0.7614	2.0000	2.0783
TPSSH	0.7500	0.7579	0.7500	0.7576	2.0000	2.0420
TPSS	0.7500	0.7555	0.7500	0.7544	2.0000	2.0229