Supporting Information:

Computational Aspects:

(1) Calculations of Mössbauer properties

The Mössbauer technique is a powerful probe to investigate iron-containing systems. The ^{57}Fe quadrupole splitting (ΔE_Q) arises from the non-spherical nuclear charge distribution in the I*=3/2 excited state in the presence of an electric field gradient at the ^{57}Fe nucleus, while the isomer shift (δ_{Fe}) arises from differences in the electron density at the nucleus between the absorber (the molecule or system of interest) and a reference compound (usually α-Fe at 300K). The former effect is related to the components of the electric field gradient (EFG) tensor at the nucleus as follows:[1]

$$\Delta E_Q = \frac{1}{2} eQV_{zz}\left(1+\frac{\eta^2}{3}\right)^{1/2} \quad (1)$$

where *e* is the electron charge, *Q* is the quadrupole moment of the E*=14.4 keV excited state, and the principal components of the EFG tensor are labeled according to the convention:

$$|V_{zz}|>|V_{yy}|>|V_{xx}| \quad (2)$$

with the asymmetry parameter being given by:

$$\eta = \frac{V_{xx}-V_{yy}}{V_{zz}} \quad (3)$$

The isomer shift in ^{57}Fe Mössbauer spectroscopy is given by:[2]

$$\delta_{Fe}=E_A-E_{Fe}=\frac{2\pi}{3}Ze^2\left(<R^2>^*-<R^2>\right)\left(|\psi(0)|^2_A-|\psi(0)|^2_{Fe}\right) \quad (4)$$

where Z represents the atomic number of the nucleus of interest (iron) and R, R* are average nuclear radii of the ground and excited states of ^{57}Fe. Since $|\psi(0)|^2_{Fe}$ is a constant, the isomer shift (from Fe) can be written as:

$$\delta_{Fe} = \alpha\,[\,\rho(0) - c\,] \quad (5)$$

where α is the so-called calibration constant and $\rho(0)$ is the computed charge density at the iron nucleus. Both α and c can be obtained from the correlation between experimental δ_{Fe} values and the corresponding computed $\rho(0)$ data in a training set. Then, one can use equation (5) to predict δ_{Fe} for a new molecule from its computed $\rho(0)$, basically as described in detail elsewhere for a wide variety of heme and other model systems.[2] The computational methods and protocol used here are from previous methodological studies based on X-ray structures of mostly small iron-containing compounds.[1,2] Specifically, the hybrid functional B3LYP[3] with a Wachter's basis for Fe,[4] 6-311G* for all the other heavy atoms and 6-31G* for hydrogens was used to predict Mössbauer quadrupole splittings and isomer shifts. The same approach was used in the previous work for various iron-containing proteins and models with experiment-versus-theory linear correlation coefficients R^2=0.98 and 0.97, respectively,[1,2,5-14] covering a broad range of iron systems, including all iron spin states and all coordination states. To calculate ΔE_Q, we first evaluated the principal components of the electric field gradient tensor at the ^{57}Fe nucleus (V_{ii}), then we used equation (1) to deduce ΔE_Q, using Q = 0.16 (±5%) x 10^{-28}m^2,[15] a value previously found to permit excellent accord between theory and experiment in a broad range of systems.[1,2,5-14] To calculate δ_{Fe} values, we read the Kohn-Sham orbitals from the *Gaussian 09*[16] results into

the AIM 2000 program,[17] to evaluate the charge density at the iron nucleus, ρ(0). Then, we evaluated the isomer shifts by using the equation derived previously:[2]

$$\delta_{Fe} = -0.404\ [\rho(0) - 11614.16] \quad (6)$$

All the quantum chemical calculations were performed using *Gaussian 09*.[16]

(2) Geometry optimizations of IPC complexes

An appropriate level of theory for the geometry optimization of IPC complexes is critical for not only investigating structural properties of IPC complexes, but also building a solid basis for subsequent mechanistic investigations of relevant species along the reaction pathways. There are no prior reports of the geometry optimizations of the X-ray structures of IPC complexes. So, a methodological study was carried out, evaluating a number of DFT methods and basis set schemes. The methods studied here include the commonly used hybrid HF-DFT method B3LYP,[3] and another hybrid HF-DFT mPW1PW91 method[18] which was found to yield excellent predictions of various geometric, electronic, and mechanistic properties of metal complexes.[19-23] In addition, several recently developed DFT methods: M06,[24] B97D,[25] and ωB97XD,[26] were also investigated.

All three available X-ray structures of IPC complexes **3-5**[27,28] were used for comparison, using a commonly used simplification, i.e., with the *meso*-substituents of porphyrins replaced by hydrogens, to facilitate the calculations. We first evaluated the performance of these DFT methods with a double-zeta basis set 6-31G(d) for all atoms, designated as BS1. As shown by some key geometric parameters around the carbene center: the (average) lengths of the iron and porphyrin nitrogen bond (R_{FeN}), the iron and carbene bond length (R_{FeC}), and the carbene carbon and its neighboring carbon bond length (R_{CC}), in Table S1, the overall predictions are good with the mean absolute deviations (MADs) around 0.02 Å or less, and the mean percentage deviations (MPDs) around 1% or less. The best method here is mPW1PW91, with a MAD of only 0.011 Å and MPD of only 0.63%.

To facilitate future mechanistic studies of IPC complexes, which generally need a higher level of basis set for a more accurate description of energies, we then examined the use of a triple-zeta basis set for non-metal atoms while using the effective core potential basis LanL2DZ[29] for Fe, which also includes relativistic effect. In this case, we studied two basis set schemes. We first used 6-311G(d) just for the first coordination shell atoms while treating other non-metal atoms with 6-31G(d) (hereafter called BS2) to facilitate the comparison, then used the best DFT method from this comparison to evaluate the use of 6-311G(d) for all non-metal atoms, designated as BS3. As shown in Table S2, although MADs from using the triple-zeta basis set BS2 have slight improvement or deterioration depending on individual methods, the best method is still mPW1PW91. When the uniform triple-zeta basis 6-311G(d) was used for all non-metal atoms (i.e. BS3), the MAD and MPD are the same as when using BS2, for mPW1PW91. So, overall, among the methods studied here, the mPW1PW91 method with BS3 was found to give the best performance with a MAD of only 0.012 Å and MPD of only 0.65%. This also provides a good basis for subsequent calculations of the NMR spectroscopic properties discussed below. This method was then used to obtain the S=1 and S=2 optimized structures for the three IPC complexes.

(3) Calculations of NMR properties

There are also no prior reports of quantum chemical calculations of the ^{13}C NMR chemical shifts of the carbene carbons in IPC complexes, so we first performed another

methodological study, evaluating again the above five DFT methods and a few basis set schemes, plus solvent effects.

We first investigated the use of a locally dense basis set scheme to calculate chemical shieldings using the default gauge-independent atomic orbital (GIAO) method implemented in *Gaussian 09*,[16] i.e., LanL2DZ for iron, 6-311++G(2d,2p) for first coordination shell atoms, and 6-31G(d) for the rest, hereafter called BS4, which is basically the same basis set and NMR calculation method for previous predictions of ligand NMR chemical shifts in metalloporphyrins.[30,31] As shown in Table S3, experimental shifts of the selected compounds basically cover the whole range of known solution ^{13}C NMR chemical shifts of carbene carbons in IPC complexes,[27,32,33] and the five DFT methods all give good predictions, since the theory-versus-experiment linear correlation coefficients (R^2's) are all around 0.95 or higher. The best method is B97D, with R^2=0.9815. To see if the correlation could be further improved, we also investigated the use of a uniform basis set of 6-311++G(2d,2p) for all non-metal atoms, designated as BS5. As seen from Table S4, the R^2 values basically do not improve, indicating that BS4 is appropriate for the NMR shielding calculations. NPA charges of the carbene carbons in these IPC complexes using BS4 are all positive, consistent with the experimental observation of electrophilic reactivities. Moreover, the charges have excellent correlations with the experimental ^{13}C NMR shifts with R^2 values of ca. 0.95, and the best correlation is again from using the best NMR computational method B97D, see Table S5. Next, we evaluated solvent effects using the PCM method.[34-38] Results are shown in Table S6. Based on these results, it can be seen that solvent effects give no improvements for the NMR shift predictions or charge correlations, consistent with the fact that the experimentally used solvent, chloroform, is of low polarity (dielectric constant=4.7). Overall, these results show that the B97D calculations with BS4 and no solvent effects can yield excellent predictions of the experimental ^{13}C NMR properties in IPC complexes. This method was then used to obtain the ^{13}C NMR chemical shieldings (σ^{calc}'s) in the IPC complexes of interest.

The predicted ^{13}C NMR chemical shifts (δ^{pred}'s) for the singlet systems are based on the regression line in Figure 2A in the Text, using the calculated chemical shieldings:

$$\delta^{pred}\ (ppm) = 82.33 - 1.498\ \sigma^{calc} \qquad (7)$$

The mean absolute deviation is 6.71 ppm and the mean absolute percentage deviation is 2.43%. For S=1 and S=2 states, the total predicted chemical shift (δ^{pred}) includes both a diamagnetic or orbital contribution (δ_{dia}) from paired electrons and a hyperfine contribution (δ_{hf}) from unpaired electrons. δ_{dia} is calculated in the same way as for the diamagnetic singlet state, using equation (7). δ_{hf} is calculated using the same approach as described in previous reports,[10,39,40] with the spin densities calculated by using B3LYP[3] with a Wachter's basis for Fe,[4] 6-311G* for all the other heavy atoms and 6-31G* for hydrogens. This approach was previously found to enable accurate predictions of solution NMR hyperfine shifts with a theory-versus-experiment correlation coefficient R^2=0.99 in various heme and non-heme systems.[10,39,40]

(4) Coordinates of IPC complexes

The coordinates of the optimized structures of IPC complexes in this work (**3-11**) obtained by using the mPW1PW91/BS3 method are listed in Tables S7-15.

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Table S1. X-ray and Computed Geometric Parameters Obtained by Using BS1

Compound		X-ray	B3LYP	mPW1PW91	M06	B97D	WB97XD
4	R_{FeN}(Å)	1.973	2.015	1.991	2.001	1.999	2.006
	R_{FeC}(Å)	1.827	1.798	1.811	1.789	1.820	1.771
	R_{CC}(Å)	1.495	1.493	1.482	1.476	1.480	1.484
3	R_{FeN}(Å)	1.967	2.002	1.983	1.985	1.986	1.995
	R_{FeC}(Å)	1.767	1.766	1.757	1.746	1.776	1.723
	R_{CC}(Å)	1.483	1.489	1.481	1.475	1.479	1.484
5	R_{FeN}(Å)	1.985	2.001	1.986	1.983	1.997	1.989
	R_{FeC}(Å)	1.690	1.680	1.668	1.674	1.650	1.668
	R_{CC}(Å)	1.487	1.491	1.484	1.479	1.485	1.485
	MAD(Å)		0.016	0.011	0.018	0.015	0.023
	MPD(%)		0.87	0.63	1.0	0.84	1.2

Table S2. X-ray and Computed Geometric Parameters Obtained by Using BS2 and BS3

			BS2					BS3
Compound		X-ray	B3LYP	mPW1PW91	M06	B97D	WB97XD	mPW1PW91
4	R_{FeN}(Å)	1.973	2.021	2.003	1.990	2.007	2.012	2.002
	R_{FeC}(Å)	1.827	1.843	1.828	1.807	1.724	1.818	1.828
	R_{CC}(Å)	1.495	0.670	1.479	1.473	1.480	1.479	1.478
3	R_{FeN}(Å)	1.967	2.016	1.992	1.991	1.998	2.005	1.991
	R_{FeC}(Å)	1.767	1.786	1.765	1.741	1.773	1.732	1.764
	R_{CC}(Å)	1.483	1.484	1.478	1.473	1.477	1.482	1.478
5	R_{FeN}(Å)	1.985	2.001	1.994	1.985	2.006	2.000	1.992
	R_{FeC}(Å)	1.690	1.692	1.676	1.665	1.652	1.683	1.675
	R_{CC}(Å)	1.487	1.493	1.485	1.480	1.486	1.487	1.484
	MAD(Å)		0.020	0.012	0.017	0.018	0.018	0.012
	MPD(%)		1.1	0.65	0.98	0.98	0.98	0.65

Table S3. Experimental ^{13}C NMR Chemical Shifts and Computed Chemical Shieldings Obtained by Using BS4 (unit: ppm)

	Expt	B3LYP	mPW1PW91	M06	B97D	wB97XD
4	385.44[a)]	-309.82	-333.69	-485.33	-198.88	-351.86
3	358.98[a)]	-294.14	-322.58	-477.13	-178.38	-345.01
6	224.70[b)]	-214.91	-235.19	-362.44	-97.29	-255.00
7	302.70[b)]	-275.58	-299.05	-442.14	-155.77	-316.23
8	324.00[c)]	-289.43	-313.45	-466.79	-165.80	-332.66
9	312.00[b)]	-272.37	-295.31	-428.15	-155.75	-312.32
10	210.00[b)]	-187.85	-213.48	-332.59	-77.57	-240.00
11	327.47[a)]	-273.28	-300.32	-440.30	-163.06	-320.57
R^2		0.9457	0.9591	0.9434	0.9815	0.9691

[a)] Ref.27. [b)] Ref.32 [c)] Ref.33

Table S4. Experimental ^{13}C NMR Chemical Shifts and Computed Chemical Shieldings Obtained by Using BS5 (unit: ppm)

	Expt	B3LYP	mPW1PW91	M06	B97D	wB97XD
4	385.44[a)]	-331.28	-307.53	-486.33	-197.52	-349.61
3	358.98[a)]	-324.79	-296.27	-481.44	-180.59	-347.00
6	224.70[b)]	-238.45	-218.85	-369.93	-100.46	-257.91
7	302.70[b)]	-301.33	-278.35	-448.85	-158.22	-318.58
8	324.00[c)]	-315.30	-291.79	-474.84	-167.44	-334.78
9	312.00[b)]	-298.46	-275.93	-435.76	-158.50	-315.71
10	210.00[b)]	-216.59	-191.62	-340.95	-80.58	-243.03
11	327.47[a)]	-303.47	-276.42	-445.40	-165.99	-323.77
R^2		0.9502	0.9353	0.9296	0.9783	0.9600

[a)] Ref.27. [b)] Ref.32 [c)] Ref.33

Table S5. Experimental ^{13}C NMR Chemical Shifts and Computed Charges Obtained by Using BS4 (unit: ppm)

	Expt	B3LYP	mPW1PW91	M06	B97D	wB97XD
4	385.44[a)]	0.343	0.331	0.364	0.324	0.370
3	358.98[a)]	0.336	0.326	0.365	0.326	0.358
6	224.70[b)]	0.072	0.063	0.096	0.053	0.093
7	302.70[b)]	0.222	0.210	0.246	0.200	0.238
8	324.00[c)]	0.295	0.284	0.322	0.275	0.314
9	312.00[b)]	0.262	0.251	0.288	0.241	0.279
10	210.00[b)]	0.067	0.057	0.094	0.056	0.085
11	327.47[a)]	0.237	0.228	0.260	0.229	0.253
R^2		0.9549	0.9556	0.9457	0.9580	0.9580

[a)] Ref.27. [b)] Ref.32 [c)] Ref.33

Table S6. Computed Chemical Shieldings and Charges Obtained by Using B97D/BS4 with Solvent Effects

	σ^{calc} (ppm)	Q_C (e)
4	-197.93	0.317
3	-178.13	0.323
6	-94.43	0.049
7	-153.80	0.196
8	-165.04	0.274
9	-153.51	0.235
10	-71.90	0.045
11	-161.75	0.222
R^2	0.9798	0.9540

Table S7: Optimized Structure of **3**

Fe	0.094751	0.25031	-0.82309
N	-0.862723	-1.320874	-1.56831
N	-1.611772	1.285879	-0.873096
N	1.079	1.972513	-0.683113
N	1.821011	-0.667635	-1.217271
C	0.981696	-2.923386	-1.578379
C	-0.348553	-2.579474	-1.731904
C	-1.371912	-3.487908	-2.166602
C	-2.510415	-2.761654	-2.287239
C	-2.188359	-1.420272	-1.889972
C	-3.121934	-0.41125	-1.749827
C	-2.850252	0.841413	-1.23764
C	-3.843169	1.855009	-1.004091
C	-3.192008	2.92104	-0.483478
C	-1.799962	2.563602	-0.431218
C	-0.784748	3.442285	-0.105894
C	0.558382	3.179887	-0.29978
C	1.587965	4.178129	-0.239097
C	2.737873	3.575052	-0.627457
C	2.416238	2.199639	-0.883866
C	3.35205	1.228047	-1.183176
C	3.070457	-0.120663	-1.290377
C	4.061959	-1.143372	-1.486413
C	3.398566	-2.32267	-1.525269
C	2.001405	-2.010183	-1.391499
H	1.253288	-3.962167	-1.725265
H	-4.147621	-0.635095	-2.018158
H	-1.062174	4.441036	0.210565
H	4.3844	1.539342	-1.291582
C	-0.037821	-0.237623	0.866484
C	1.071895	-0.539025	1.782716
C	0.966357	-1.640881	2.65265
C	2.001955	-1.976021	3.508448
C	3.14613	-1.187222	3.563094
C	3.24879	-0.070765	2.742832
C	2.23484	0.238445	1.849273
C	-1.363667	-0.41703	1.511109
C	-1.772813	0.541635	2.447311
C	-2.982069	0.411579	3.112096
C	-3.789574	-0.698095	2.887642
C	-3.378851	-1.668063	1.984206
C	-2.183229	-1.525472	1.289442
H	0.067342	-2.244595	2.638731
H	1.908502	-2.845705	4.149605
H	3.948931	-1.437654	4.248066

H	4.12831	0.561891	2.791539
H	2.317924	1.11285	1.223796
H	-1.13541	1.396537	2.643792
H	-3.28868	1.174245	3.819833
H	-4.728773	-0.807087	3.418717
H	-3.993654	-2.54452	1.809106
H	-1.874128	-2.291749	0.590441
H	-1.218499	-4.536836	-2.376326
H	-3.488074	-3.093	-2.606752
H	-4.89685	1.749161	-1.218746
H	-3.59671	3.878538	-0.188398
H	1.43065	5.211913	0.033403
H	3.722834	4.007837	-0.729102
H	5.123171	-0.965119	-1.584825
H	3.799736	-3.315464	-1.67031

Table S8: Optimized Structure of **4**

Fe	0.315639	-0.050898	0.112592
N	0.167682	-0.984823	-1.649716
N	-0.082498	-1.765334	1.06715
N	0.775041	0.79114	1.870573
N	0.933844	1.600797	-0.836708
N	2.366518	-0.677821	0.081884
N	4.411247	-1.052853	-0.637905
C	0.452395	0.934451	-3.131364
C	0.197186	-0.407166	-2.88366
C	0.010149	-1.40727	-3.902996
C	-0.107754	-2.59675	-3.26108
C	-0.023594	-2.316707	-1.851732
C	-0.210494	-3.260306	-0.853574
C	-0.277877	-2.98739	0.501541
C	-0.59487	-3.9627	1.514532
C	-0.59784	-3.304809	2.697711
C	-0.254531	-1.935091	2.405636
C	-0.02169	-0.963337	3.367062
C	0.522183	0.286289	3.10994
C	1.021133	1.179216	4.124365
C	1.618501	2.207862	3.474906
C	1.450329	1.959941	2.066008
C	1.831831	2.838417	1.064326
C	1.539398	2.686307	-0.282899
C	1.81776	3.674029	-1.29456
C	1.365678	3.166552	-2.466602
C	0.843409	1.855941	-2.171262
H	0.435989	1.263798	-4.164216

H	-0.37693	-4.285336	-1.164329
H	-0.178662	-1.236712	4.404445
H	2.343242	3.745921	1.364935
C	-1.447304	0.423077	0.024804
C	-2.508198	-0.614033	-0.075272
C	-3.211974	-0.953854	1.086324
C	-4.238881	-1.885003	1.047738
C	-4.606439	-2.477807	-0.154845
C	-3.930218	-2.130983	-1.315718
C	-2.885313	-1.214897	-1.278996
C	-2.023689	1.77363	-0.032781
C	-3.134445	2.047078	-0.856153
C	-3.667512	3.321827	-0.941296
C	-3.149571	4.349123	-0.159509
C	-2.084226	4.090554	0.693675
C	-1.514245	2.828005	0.73917
C	3.067191	-1.319369	1.066189
C	4.339552	-1.56094	0.638053
C	3.197581	-0.533274	-0.92313
C	5.560777	-1.077289	-1.510761
H	-0.007658	-1.213261	-4.96631
H	-0.252035	-3.578355	-3.690012
H	-0.794005	-5.008299	1.327311
H	-0.791278	-3.69917	3.685304
H	0.942545	1.013006	5.189493
H	2.121458	3.066334	3.897304
H	2.291898	4.628707	-1.115288
H	1.398754	3.614713	-3.449684
H	-2.940525	-0.487155	2.02648
H	-4.759721	-2.142623	1.963878
H	-5.415581	-3.199346	-0.185467
H	-4.209245	-2.578635	-2.263915
H	-2.369998	-0.95549	-2.195374
H	-3.568882	1.250047	-1.445871
H	-4.504516	3.511042	-1.604642
H	-3.580979	5.343249	-0.209516
H	-1.684832	4.879442	1.321746
H	-0.695303	2.634189	1.411883
H	2.610647	-1.562639	2.011041
H	5.18309	-2.036596	1.109983
H	2.962793	-0.064548	-1.865134
H	5.855152	-2.104046	-1.732415
H	6.401565	-0.553446	-1.054273
H	5.307241	-0.579137	-2.444412

Table S9: Optimized Structure of **5**

Fe	-0.183232	4.833553	2.84716
N	-0.608128	4.868404	0.897341
C	-1.834429	5.032398	0.316388
C	-1.75327	4.856394	-1.106789
C	-0.457962	4.585231	-1.388846
C	0.245632	4.60096	-0.136962
C	1.607486	4.420914	-0.015802
C	2.305298	4.498004	1.171627
C	3.728186	4.347988	1.272442
C	4.03908	4.462776	2.585769
C	2.804351	4.678859	3.283768
N	1.752702	4.716313	2.406506
C	2.707278	4.798132	4.65494
C	1.527933	5.002601	5.339893
C	1.442225	5.150893	6.76597
C	0.137811	5.366725	7.053804
C	-0.565502	5.353017	5.801717
N	0.294568	5.123416	4.76349
C	-1.917665	5.592276	5.674353
C	-2.593556	5.645744	4.473188
C	-3.992976	5.938249	4.357771
C	-4.294572	5.880914	3.038632
C	-3.078828	5.549094	2.352571
N	-2.041384	5.425183	3.238578
C	-2.994444	5.354525	0.989221
H	2.172837	4.225839	-0.91912
H	3.622235	4.733781	5.231652
H	-2.486123	5.770388	6.579182
H	-3.901135	5.469666	0.407377
C	-0.454048	3.18964	3.021046
C	-0.67135	1.896862	3.165503
C	0.225871	0.917123	2.506872
C	-0.30754	-0.238742	1.928346
C	0.507985	-1.156709	1.285504
C	1.873401	-0.917757	1.210602
C	2.428123	0.219599	1.777533
C	1.604795	1.126741	2.428221
Cl	2.90323	-2.06691	0.40168
C	-1.821512	1.44971	3.990803
C	-3.066252	2.07658	3.905078
C	-4.125133	1.671755	4.705239
C	-3.94459	0.620846	5.591133
C	-2.72029	-0.027284	5.687683
C	-1.666113	0.39186	4.891793
Cl	-5.272569	0.099755	6.591239
H	-2.587131	4.944667	-1.788151

H	-0.001331	4.40287	-2.350849
H	4.390581	4.183028	0.435006
H	5.011117	4.411965	3.054817
H	2.283029	5.104885	7.442952
H	-0.321072	5.535464	8.017222
H	-4.645394	6.163485	5.18898
H	-5.247216	6.049217	2.557338
H	-1.375151	-0.419085	1.976681
H	0.088057	-2.04911	0.838647
H	3.49571	0.390498	1.721492
H	2.040544	2.003446	2.89134
H	-3.211182	2.882727	3.196475
H	-5.086831	2.163497	4.632602
H	-2.593629	-0.846573	6.384187
H	-0.706523	-0.105286	4.974169

Table S10: Optimized Structure of **6**

Fe	0.000352	0.000146	-0.271046
N	1.411124	1.389783	-0.488195
N	1.390886	-1.409116	-0.490219
N	-1.410646	-1.389342	-0.488881
N	-1.390274	1.409439	-0.490722
C	0.024517	3.394823	-0.364502
C	1.240851	2.746521	-0.425537
C	2.505773	3.421479	-0.491685
C	3.451823	2.460047	-0.606107
C	2.762101	1.201327	-0.592947
C	3.393082	-0.023782	-0.653577
C	2.744442	-1.239836	-0.595167
C	3.416077	-2.508151	-0.609723
C	2.456479	-3.456129	-0.495126
C	1.201327	-2.763383	-0.42777
C	-0.023998	-3.3945	-0.365612
C	-1.240293	-2.746061	-0.426222
C	-2.50525	-3.421025	-0.492553
C	-3.451313	-2.459617	-0.606645
C	-2.761586	-1.200873	-0.593777
C	-3.392592	0.024246	-0.654472
C	-2.743875	1.240231	-0.595836
C	-3.415504	2.50857	-0.609764
C	-2.455968	3.456465	-0.494465
C	-1.200792	2.763672	-0.427215
H	0.032115	4.477275	-0.318617
H	4.473534	-0.031659	-0.734164
H	-0.031481	-4.476976	-0.320274

H	-4.47302	0.032035	-0.735015
C	-0.000394	-0.000294	1.446744
H	2.634526	4.493989	-0.468694
H	4.522488	2.575673	-0.693759
H	4.484942	-2.638765	-0.698443
H	2.570036	-4.530373	-0.472705
H	-2.634032	-4.493512	-0.469466
H	-4.521998	-2.575218	-0.694095
H	-4.484378	2.63918	-0.698389
H	-2.569497	4.530688	-0.471428
Cl	1.420555	-0.00348	2.413852
Cl	-1.423464	0.001489	2.410861

Table S11: Optimized Structure of **7**

Fe	-0.010703	0.005222	-0.314599
N	-1.399228	-1.411133	-0.534468
N	-1.435308	1.388522	-0.513949
N	1.371336	1.423426	-0.518239
N	1.405021	-1.377448	-0.536621
C	0.02748	-3.388838	-0.425411
C	-1.20204	-2.764706	-0.48427
C	-2.453174	-3.464287	-0.563385
C	-3.418211	-2.521694	-0.676415
C	-2.754004	-1.248809	-0.650199
C	-3.408881	-0.034402	-0.707978
C	-2.785321	1.195192	-0.637924
C	-3.478845	2.451547	-0.656609
C	-2.536911	3.416667	-0.53071
C	-1.269935	2.746943	-0.451729
C	-0.054993	3.399373	-0.38302
C	1.174498	2.775359	-0.445343
C	2.427273	3.475606	-0.501738
C	3.391487	2.533159	-0.619302
C	2.724795	1.260856	-0.61891
C	3.378813	0.047509	-0.68749
C	2.75406	-1.181715	-0.639189
C	3.451127	-2.437533	-0.660105
C	2.509983	-3.403867	-0.552129
C	1.241056	-2.734175	-0.482402
H	0.0406	-4.471575	-0.387493
H	-4.488476	-0.047894	-0.799564
H	-0.068095	4.481873	-0.335472
H	4.459475	0.061215	-0.765032
C	-0.0347	0.010223	1.405758

H	-2.560857	-4.539256	-0.549221
H	-4.485665	-2.658814	-0.771979
H	-4.548627	2.564189	-0.758417
H	-2.670516	4.488749	-0.511744
H	2.535939	4.550165	-0.470327
H	4.460129	2.669696	-0.701754
H	4.522497	-2.547199	-0.747235
H	2.643738	-4.475885	-0.534921
Cl	1.421762	-0.02927	2.345945
C	-1.267233	0.147457	2.258148
H	-1.52435	1.219616	2.203907
H	-2.080373	-0.387787	1.768881
O	-1.21161	-0.318032	3.574324
H	-0.524888	0.156251	4.049319

Table S12: Optimized Structure of **8**

Fe	-0.058736	-0.000108	-0.394578
N	-1.460557	-1.407047	-0.551137
N	-1.471091	1.39751	-0.549449
N	1.330227	1.407801	-0.686361
N	1.341067	-1.398504	-0.685068
C	-0.048894	-3.39809	-0.515746
C	-1.273677	-2.761259	-0.508951
C	-2.534495	-3.449995	-0.515946
C	-3.494127	-2.497594	-0.573318
C	-2.815534	-1.231383	-0.586493
C	-3.460993	-0.011887	-0.60932
C	-2.82472	1.212415	-0.583022
C	-3.512244	2.473756	-0.565646
C	-2.559186	3.432743	-0.507611
C	-1.293513	2.75286	-0.504746
C	-0.073177	3.397983	-0.51401
C	1.147023	2.763368	-0.635223
C	2.398039	3.451701	-0.786549
C	3.347463	2.49922	-0.945173
C	2.674252	1.232657	-0.875877
C	3.313892	0.01176	-0.966433
C	2.683902	-1.213935	-0.872866
C	3.366478	-2.475641	-0.938796
C	2.423622	-3.434782	-0.781283
C	1.167336	-2.755228	-0.633332
C	0.048567	-0.000564	1.325276
H	-2.651389	-4.523992	-0.495208
H	-4.566797	-2.623134	-0.606855
H	-4.585813	2.591968	-0.596908

H	-2.683647	4.50583	-0.484378
H	2.51523	4.525886	-0.789333
H	4.408918	2.626319	-1.102737
H	4.429204	-2.595132	-1.093614
H	2.548551	-4.508087	-0.782438
Cl	-1.392869	-0.00354	2.304047
H	-4.544283	-0.015957	-0.633331
H	4.38746	0.015905	-1.113851
H	-0.044777	-4.481278	-0.485123
H	-0.075891	4.48112	-0.481786
C	1.304699	0.001054	2.148136
H	2.126742	-0.002393	1.431973
C	1.42416	1.272136	2.995973
H	0.653849	1.312078	3.767657
H	2.399553	1.285644	3.487752
H	1.344249	2.16984	2.381138
C	1.421246	-1.264401	3.004725
H	2.402534	-1.284923	3.48444
H	0.660417	-1.290555	3.786416
H	1.323577	-2.165828	2.397907

Table S13: Optimized Structure of **9**

Fe	-0.052247	0.008471	-0.385735
N	1.068981	1.628707	-0.668615
N	1.562246	-1.116902	-0.694948
N	-1.186177	-1.61044	-0.579105
N	-1.676519	1.135382	-0.559353
C	-0.651371	3.351667	-0.46703
C	0.659812	2.936052	-0.585897
C	1.773367	3.834055	-0.71137
C	2.874254	3.063198	-0.885762
C	2.428082	1.698332	-0.848779
C	3.272233	0.609975	-0.955697
C	2.859519	-0.706548	-0.87748
C	3.749365	-1.830359	-0.954214
C	2.984604	-2.940733	-0.805921
C	1.630491	-2.488381	-0.654505
C	0.544804	-3.335152	-0.54107
C	-0.771548	-2.917711	-0.534529
C	-1.89304	-3.815147	-0.551689
C	-3.004414	-3.042193	-0.617465
C	-2.554495	-1.678009	-0.624262
C	-3.403344	-0.589221	-0.654398
C	-2.983839	0.725188	-0.61306
C	-3.878722	1.848741	-0.589348

C	-3.104184	2.95712	-0.499982
C	-1.74106	2.503596	-0.487141
H	-0.84071	4.417657	-0.40877
H	4.33037	0.8015	-1.095425
H	0.737161	-4.402017	-0.513619
H	-4.47017	-0.779657	-0.690552
C	0.034586	0.018614	1.318229
C	1.268471	0.202586	2.184608
H	1.699594	4.912434	-0.682182
H	3.901187	3.370667	-1.027746
H	4.817571	-1.759245	-1.106873
H	3.289261	-3.978326	-0.814655
H	-1.818157	-4.893755	-0.531811
H	-4.040757	-3.348017	-0.659669
H	-4.956751	1.776964	-0.634638
H	-3.407385	3.99432	-0.459788
Cl	-1.389428	-0.202765	2.326926
O	1.106954	1.236485	3.130771
H	0.385938	0.975903	3.721841
C	1.684924	-1.113911	2.839147
H	2.601098	-0.943015	3.410505
H	0.908224	-1.470767	3.522586
H	1.870711	-1.890319	2.093249
H	2.065173	0.542746	1.522607

Table S14: Optimized Structure of **10**

Fe	-0.00042	0.000517	-0.235365
N	1.397873	1.401477	-0.458392
N	1.409825	-1.389306	-0.457662
N	-1.39115	-1.400896	-0.457097
N	-1.403072	1.389703	-0.45691
C	-0.010258	3.391095	-0.321503
C	1.212198	2.757487	-0.388289
C	2.468603	3.446339	-0.455214
C	3.425392	2.496757	-0.575184
C	2.751963	1.230359	-0.565532
C	3.398254	0.014421	-0.626814
C	2.762327	-1.20696	-0.565253
C	3.446368	-2.467675	-0.574929
C	2.497569	-3.425176	-0.454692
C	1.235414	-2.74677	-0.387594
C	0.018301	-3.390599	-0.321685
C	-1.204736	-2.75586	-0.386691
C	-2.460588	-3.445655	-0.449636
C	-3.418748	-2.496484	-0.568399

C	-2.745708	-1.230171	-0.560471
C	-3.392196	-0.01391	-0.619747
C	-2.756236	1.207852	-0.558989
C	-3.439904	2.468395	-0.564803
C	-2.489599	3.42547	-0.446315
C	-1.227964	2.746167	-0.385355
H	-0.015033	4.473148	-0.26921
H	4.478673	0.019105	-0.701883
H	0.022498	-4.47267	-0.269741
H	-4.472715	-0.018473	-0.697443
C	0.010802	-0.000516	1.477729
C	1.220164	-0.000308	2.217416
H	2.584848	4.519987	-0.425604
H	4.49465	2.624467	-0.660669
H	4.516604	-2.586486	-0.66082
H	2.622691	-4.497828	-0.425091
H	-2.575906	-4.519465	-0.420706
H	-4.488024	-2.62521	-0.654019
H	-4.510271	2.588438	-0.649182
H	-2.613892	4.498251	-0.416243
Cl	-1.384558	-0.002798	2.481722
N	2.22878	-0.000217	2.783279

Table S15: Optimized Structure of **11**

Fe	-0.028591	0.076534	-0.851832
N	-0.314725	-1.844575	-1.255632
N	-1.986103	0.385009	-1.092636
N	0.267523	2.032374	-1.00356
N	1.9427	-0.205595	-1.056065
C	1.986851	-2.641248	-1.046254
C	0.629736	-2.836668	-1.207446
C	0.032711	-4.116166	-1.460854
C	-1.282549	-3.892238	-1.696834
C	-1.492285	-2.480006	-1.55423
C	-2.729076	-1.869804	-1.640116
C	-2.956144	-0.531086	-1.390831
C	-4.255245	0.082829	-1.385164
C	-4.065212	1.385316	-1.068541
C	-2.647956	1.566334	-0.915154
C	-2.038767	2.793656	-0.741037
C	-0.678672	3.007654	-0.838655
C	-0.072414	4.309406	-0.857271
C	1.253173	4.116584	-1.045561
C	1.457988	2.696926	-1.111883
C	2.69999	2.105221	-1.208455

C	2.921646	0.743124	-1.161225
C	4.220376	0.130517	-1.191543
C	4.020155	-1.206481	-1.093627
C	2.599306	-1.404155	-1.028868
H	2.621668	-3.519376	-1.029587
H	-3.582842	-2.493068	-1.878957
H	-2.67626	3.660312	-0.612278
H	3.562922	2.755727	-1.285455
C	-0.025009	0.088891	0.898633
C	1.226119	0.520188	1.599971
C	3.167555	-0.235936	2.689209
C	3.766868	-1.546738	3.128168
C	-1.130649	-0.134685	1.828558
C	-1.304558	0.715904	2.936124
C	-2.351476	0.515497	3.820252
C	-3.216966	-0.559752	3.648735
C	-3.037018	-1.425421	2.576349
C	-2.017703	-1.206396	1.663614
H	3.825422	0.30916	2.010065
H	4.701502	-1.368544	3.664362
H	-0.631195	1.552951	3.075656
H	-2.487388	1.196323	4.653259
H	-4.026467	-0.72398	4.351544
H	-3.70066	-2.272624	2.443363
H	-1.87408	-1.88516	0.836158
H	0.569053	-5.054002	-1.481511
H	-2.053318	-4.608206	-1.943778
H	-5.181856	-0.429632	-1.600707
H	-4.802417	2.1699	-0.976174
H	-0.609861	5.24111	-0.754837
H	2.037043	4.856084	-1.12241
H	5.154155	0.666174	-1.286366
H	4.755466	-1.998488	-1.098913
O	1.943594	-0.531791	1.995057
O	1.516552	1.667588	1.825845
H	2.942819	0.417832	3.534011
H	3.087927	-2.083117	3.792989
H	3.980152	-2.183742	2.268849