Supporting Information

Spectroscopic and Quantum Chemical Studies on low-spin Fe^{IV}=O complexes: Fe-O bonding and its contributions to reactivity

Andrea Decker,[a] Jan-Uwe Rohde,[b] Eric J. Klinker,[b] Shaun D. Wong,[a] Lawrence Que, Jr.[b]* and Edward I. Solomon[a]*

Department of Chemistry, Stanford University, Stanford, California 94305, and Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, Minneapolis, Minnesota 55455

E-mail: Edward.Solomon@stanford.edu; que@chem.umn.edu

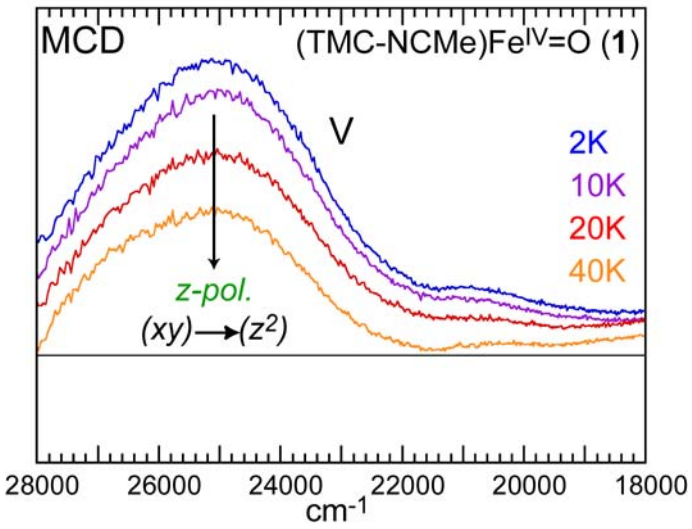

Figure SI-1: Variable-temperature MCD spectra at 7T of (TMC-NCMe)Fe^{IV}=O (**1**) in the energy region from 18,000-28,000 cm^{-1}.

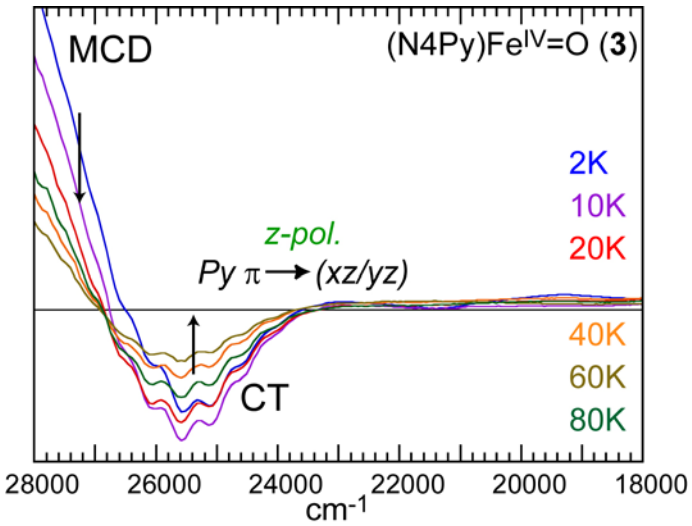

Figure SI-2: Variable-temperature MCD spectra at 7T of (N4Py)Fe^{IV}=O (**3**) in the energy region from 18,000-28,000 cm^{-1}.

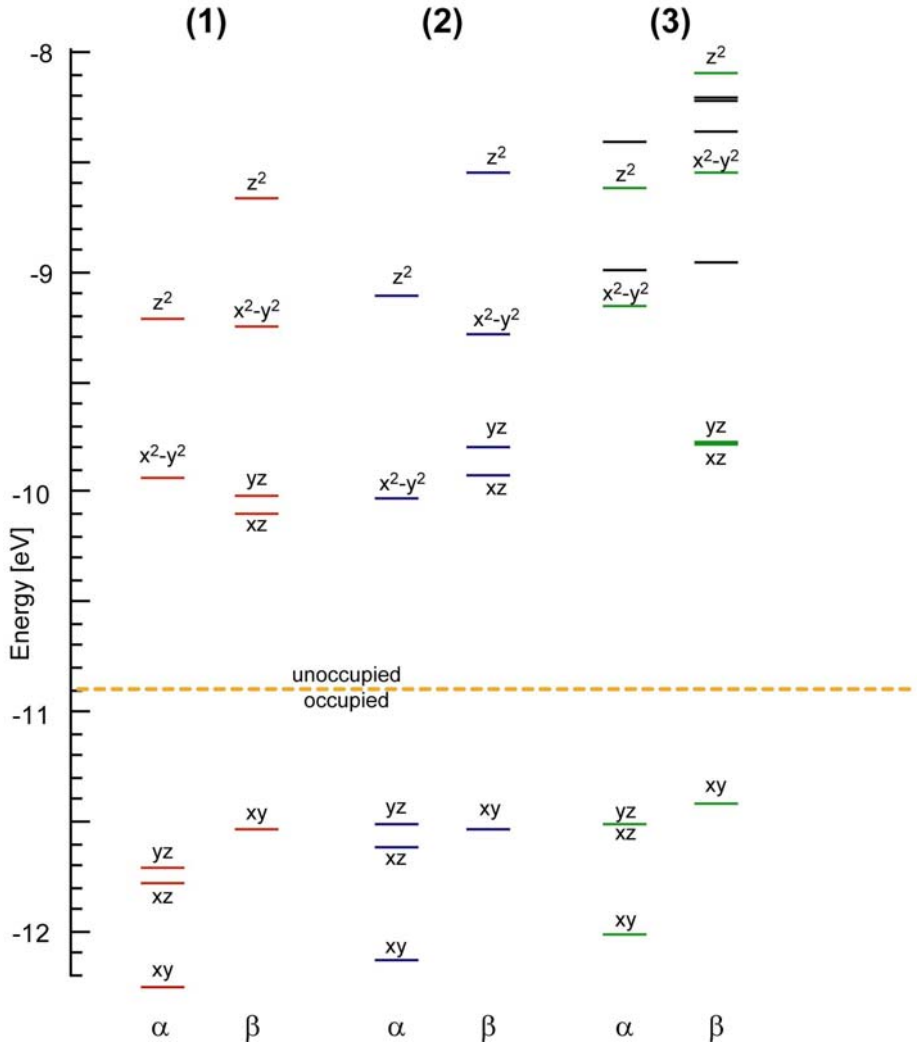

Figure SI-3: Energy level diagram of complexes **1, 2** and **3** (because of a different total charge, the levels of **2** were adjusted to the β-spin d(xy) MO of **1**. The black levels in **3** are pyridine π* orbitals and not involved in Fe-O interaction. (from Gaussian/BP86 calculations, for details see methodology section 2.4)

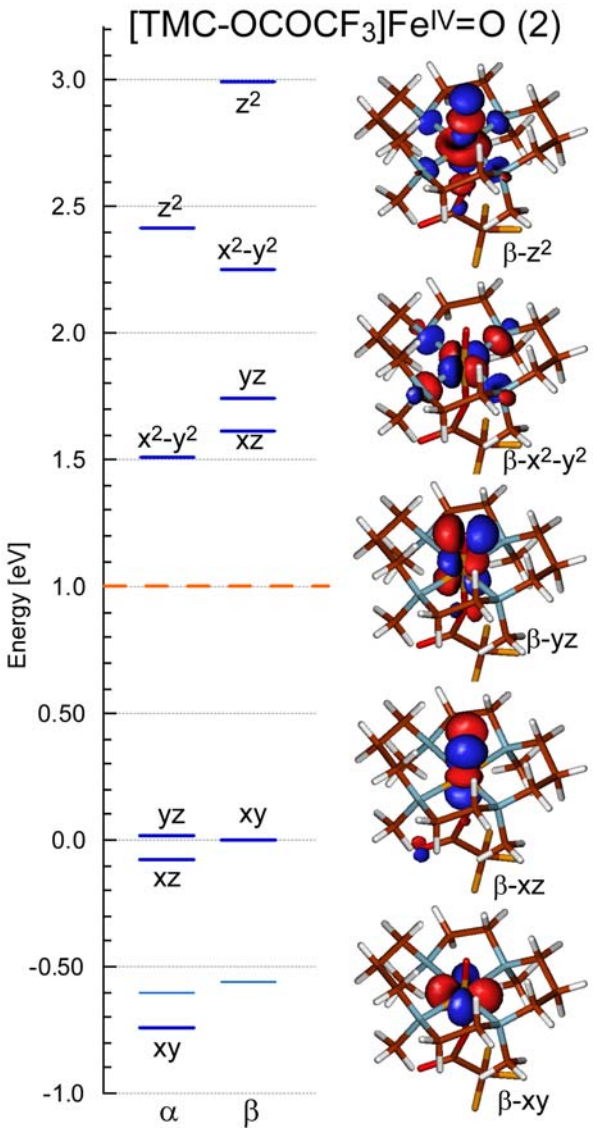

Figure SI-4: Energy level diagram and Fe-d based molecular orbitals of complex **2** (from Gaussian/BP86 calculations, for details see methodology section 2.4)

Table SI-1: Extended Table 3.3, including other functionals and methods applied

	1			**2**			**3**		
	G03/ BP86	G98/ B3LYP	ADF/ B88P86	G03/ BP86	G03/ B3LYP	ADF/ B88P86	G03/ BP86	G98/ B3LYP	ADF/ B88P86
r(Fe-O)	1.655	1.634	1.649	1.671	1.648	1.664	1.666	1.648	1.653
r(Fe-L_{ax})	2.123	2.162	2.112	1.977	1.976	1.994	2.071	2.073	2.086
r(Fe-N_{eq})	2.134	2.132	2.136	2.134	2.135	2.140	1.969	1.984	1.986
ν(Fe-O)	846	894	--	817	871	--	829	857	--

bond length in [Å], vibrational frequencies in [cm^{-1}]

Table SI-2: Functional dependence on spin state splitting: Energy difference ΔE between the S=1 ground state and the higher energy S=2 state (ΔE = E(S=2) – E(S=1)) of the Fe^{IV}=O complexes **1**, **2** and **3.**

Method	**1**	**2**	**3**
G03/B3LYP/triple-ξ	+4	+2	+9
G03/BP86/triple-ξ	+15	+12	+22
ADF/B88P86/triple-ξ	+13	+10	+20

all values in kcal/mol, for computational details see methodology section.

Table SI-3: Experimental (Abs) and calculated (TD-DFT) intensities of the ligand field transitions of complexes **1**, **2** and **3**.:

		Experimental (Abs)			**Computational (TD-DFT)[a]**		
d-d transitions		**1**	**2**	**3**	**1**	**2**	**3**
I	xy → x^2-y^2	~400[b]	~250[c] + shoulder	~400[d]	0	0	0
II	xy → xz/yz				0	37	0
III	xz/yz → x^2-y^2				415	138	485
IV	xz/yz → z^2				0	0	64[e]
V	xy → z^2				0	0	92[e]

all values in $M^{-1}cm^{-1}$; [a] using Gaussian/BP86/triple-ζ/solv, sum given for transitions into and out of d(xz/yz);[b] ref [1]; [c] ref [2]; [d] ref ; [e] intensity from mixed in MLCT and LMCT transitions

Table SI-4: Electronic structure parameters for complex **2** (for **1** and **3** given in main text)

	[TMC-OCOCF$_3$]Fe^{IV}=O (3)		
	Fe	**O**	**TMC+ax**
spin densities	1.39	0.67	-0.06
charges	1.40	-0.48	+0.08
α-MO [%]			
z^2	53	22	22
x^2-y^2	59	0	41
β-MO [%]			
z^2	56	21	21
x^2-y^2	69	0	31
yz	62	32	7
xz	58	33	10

from Gaussian/BP86 calculations, MO% given for unoccupied orbitals.

Table SI-5: Calculated Fe-O bond lengths, stretching frequencies and Fe-O bond orders of the Fe^{IV}=O reactants and Fe^{III}-OH products of an H-atom abstraction reaction

	Fe^{IV}=O				**Fe^{III}-OH**			
	1	**3**	**Δ**		**1**	**3**	**Δ**	
r(Fe-O) [Å]	1.66	1.67	+0.01		1.82	1.82	0.00	
ν(Fe-O)[cm^{-1}]	846	829	-17		615	647[a]	+32	
Bond order								
Fe-O σ+π	1.66	1.60	-0.06	-4%	0.80	0.82	-0.02	+3%
Fe-O σ	0.83	0.72	-0.11	-13%	0.53	0.50	-0.03	-6%
Fe-O π	0.83	0.87	+0.04	+5%	0.27	0.32	+0.05	+19%

all from Gaussian/BP86; [a] weighted average of three modes, Mayer'sche Bond Orders calculated using PyMOlize[3]

Table SI-6: Energy difference ΔE between the S=1/2 ground state and the higher energy S=5/2 state (ΔE = E(S=5/2) – E(S=1/2)) of the (N4Py)Fe^{III}-OH complex.

	lanl2dz-gas	lanl2dz-solv[b]	6-311G*-solv[c]
B3LYP/lanl2dz[a]	+4.2	+8.1	+3.3
BP86/lanl2dz[a]	+25.2	+29.1	+26.7

all values in kcal/mol, calculated with Gaussian, [a] geometry optimized with LanL2DZ in the gasphase, [b] solvent=acetonitrile, [c] single point with triple-ζ basis set 6-311G*

Table SI-7: Bond Order Analyis (Mayer) in Fe(IV)=O reactants and Fe(III)-OH products

	(TMC-NCMe)Fe^{IV}=O (1)				(N4Py)Fe^{IV}=O (3)			
	Fe-O	**Fe-L_{eq}**	**Fe-L_{ax}**	**Σ Fe**	**Fe-O**	**Fe-L_{eq}**	**Fe-L_{ax}**	**Σ Fe**
σ+π	1.66	1.71	0.26	3.63	1.60	2.19	0.33	4.12
σ	0.83	1.57	0.18		0.72	1.99	0.27	
π	0.83	0.14	0.08		0.87	0.20	0.03	

	(TMC-NCMe)Fe^{III}-OH					(N4Py)Fe^{III}-OH				
	Fe-O	**Fe-L_{eq}**	**Fe-L_{ax}**	**Σ Fe**	**O-H**	**Fe-O**	**Fe-L_{eq}**	**Fe-L_{ax}**	**Σ Fe**	**O-H**
σ+π	0.80	1.57	0.33	2.70	0.78	0.82	2.34	0.38	3.54	0.79
σ	0.53	1.48	0.21			0.50	2.05	0.33		
π	0.27	0.09	0.12			0.32	0.29	0.04		

Mayer'sche Bond Orders calculated using PyMolize[3]

References:

(1) Rohde, J.-U.; In, J.-H.; Lim, M. H.; Brennessel, W. W.; Bukowski, M. R.; Stubna, A.; Munck, E.; Nam, W.; Que, L., Jr. *Science* **2003**, *299*, 1037-1039.

(2) Rohde, J. U.; Que, L. *Angew. Chem. Int. Ed.* **2005**, *44*, 2255-2258.

(3) Tenderholt, A. L., PyMOlyze, Version 2.0. Stanford University, Stanford, CA, USA. http://pymolyze.sourceforge.net.

Full Reference 36 for the Gaussian 03 program package:

Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

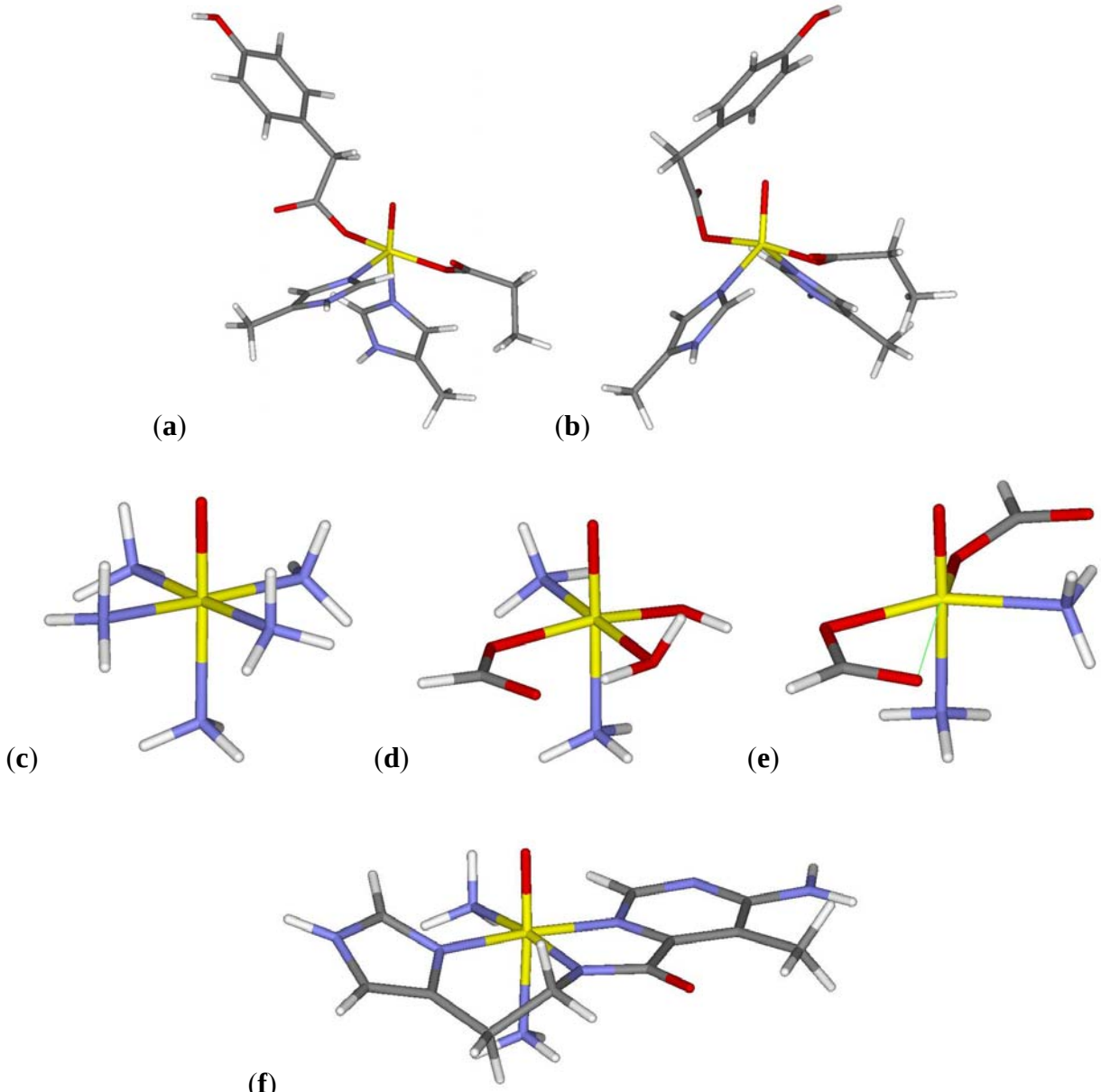

Figure SI-5: Structures of Fe^{IV}=O models, (**a**) 4-hydroxymandelate synthase (HmaS); (b) 4-hydroxypyruvate dioxygenase (HPPD); (c) non-heme iron model with five ammonias, $(NH_3)_5$; (d) model of phenylalanine hydroxylase; (e) Taurine:α-KG diogygenase; (f) bleomycin (BLM)

(TMC-NCMe)Fe(IV)=O S=1
ADF/B88P86

Fe	-0.02	0.00	-0.20
N	-1.42	1.59	-0.35
N	1.46	1.56	-0.17
N	1.46	-1.56	-0.17
N	-1.42	-1.59	-0.35
C	-0.62	2.64	-1.06
C	0.71	2.86	-0.39
C	2.38	1.31	-1.35
C	3.17	0.00	-1.30
C	2.38	-1.31	-1.35
C	0.71	-2.86	-0.39
C	-0.62	-2.64	-1.06
C	-2.60	-1.27	-1.22
C	-3.36	0.00	-0.86
C	-2.60	1.27	-1.22
C	-1.92	2.13	0.95
C	2.29	1.77	1.05
C	2.29	-1.77	1.05
C	-1.93	-2.12	0.95
N	-0.09	0.00	1.91
C	-0.13	0.00	3.07
C	-0.19	0.00	4.52
O	0.00	0.00	-1.85
H	-2.56	3.00	0.76
H	-2.51	1.36	1.47
H	-1.09	2.42	1.59
H	2.93	2.66	0.91
H	1.65	1.94	1.91
H	2.94	0.92	1.25
H	-2.57	-3.00	0.76
H	-1.10	-2.42	1.60
H	-2.51	-1.36	1.47
H	2.93	-2.66	0.91
H	2.94	-0.92	1.25
H	1.64	-1.94	1.92
H	-0.77	-0.86	4.88
H	0.83	-0.06	4.94
H	-0.66	0.92	4.88
H	-2.22	-1.17	-2.25
H	-3.28	-2.14	-1.19
H	-4.28	0.00	-1.46
H	-3.70	0.00	0.19
H	-3.28	2.14	-1.19
H	-2.22	1.18	-2.25
H	-1.19	3.59	-1.09
H	-0.48	2.29	-2.09
H	1.33	3.54	-0.98
H	0.57	3.32	0.59
H	1.77	1.35	-2.25
H	3.10	2.15	-1.38
H	3.81	0.00	-2.20
H	3.88	0.00	-0.46
H	3.10	-2.15	-1.38
H	1.77	-1.35	-2.25
H	1.33	-3.55	-0.98
H	0.57	-3.32	0.60
H	-1.19	-3.59	-1.09
H	-0.49	-2.30	-2.09

TMC-NCMe)Fe(IV)=O S=2
ADF/B88P86

Fe	-0.05	0.00	-0.18
N	-1.46	1.69	-0.36
N	1.52	1.63	-0.15
N	1.52	-1.63	-0.15
N	-1.45	-1.69	-0.37
C	-0.60	2.69	-1.09
C	0.75	2.90	-0.41
C	2.44	1.33	-1.31
C	3.21	0.00	-1.22
C	2.44	-1.32	-1.31
C	0.75	-2.90	-0.41
C	-0.60	-2.69	-1.09
C	-2.61	-1.29	-1.25
C	-3.33	0.00	-0.85
C	-2.61	1.30	-1.25
C	-1.98	2.28	0.90
C	2.32	1.85	1.08
C	2.33	-1.85	1.08
C	-1.98	-2.28	0.90
N	-0.15	0.00	1.90
C	-0.21	0.00	3.06
C	-0.28	0.00	4.50
O	0.00	0.00	-1.83
H	-2.59	3.17	0.68
H	-2.60	1.55	1.42
H	-1.15	2.56	1.56
H	3.00	2.71	0.95
H	1.66	2.05	1.93
H	2.93	0.97	1.32
H	-2.59	-3.17	0.68
H	-1.15	-2.57	1.56
H	-2.60	-1.55	1.42
H	3.00	-2.71	0.95
H	2.93	-0.98	1.32
H	1.66	-2.06	1.93
H	-0.74	-0.93	4.86
H	0.73	0.07	4.93
H	-0.88	0.85	4.85
H	-2.22	-1.19	-2.27
H	-3.33	-2.13	-1.25
H	-4.28	0.00	-1.40
H	-3.62	0.00	0.21
H	-3.33	2.13	-1.24
H	-2.22	1.19	-2.26
H	-1.12	3.66	-1.15
H	-0.46	2.31	-2.11
H	1.35	3.58	-1.02
H	0.60	3.39	0.56
H	1.83	1.34	-2.22
H	3.18	2.15	-1.37
H	3.89	0.00	-2.09
H	3.89	0.00	-0.35
H	3.17	-2.15	-1.37
H	1.83	-1.34	-2.22
H	1.35	-3.58	-1.02
H	0.60	-3.39	0.56
H	-1.12	-3.65	-1.16
H	-0.46	-2.31	-2.11

(TMC-NCMe)Fe(IV)=O S=1
excited state; ADF/B88P86

Fe	-0.03	0.00	-0.17
N	-1.44	1.64	-0.35
N	1.49	1.58	-0.16
N	1.49	-1.58	-0.16
N	-1.45	-1.64	-0.35
C	-0.61	2.65	-1.07
C	0.72	2.86	-0.38
C	2.38	1.31	-1.35
C	3.17	0.00	-1.30
C	2.38	-1.31	-1.35
C	0.72	-2.86	-0.38
C	-0.61	-2.65	-1.07
C	-2.61	-1.28	-1.23
C	-3.35	0.00	-0.86
C	-2.61	1.28	-1.23
C	-1.96	2.19	0.94
C	2.33	1.79	1.05
C	2.33	-1.80	1.05
C	-1.96	-2.19	0.94
N	-0.09	0.00	1.89
C	-0.14	0.00	3.06
C	-0.19	0.00	4.51
O	-0.06	0.00	-1.87
H	-2.58	3.07	0.74
H	-2.56	1.44	1.45
H	-1.13	2.48	1.59
H	2.97	2.68	0.90
H	1.69	1.97	1.92
H	2.97	0.94	1.25
H	-2.58	-3.07	0.74
H	-1.13	-2.48	1.59
H	-2.56	-1.44	1.45
H	2.97	-2.68	0.90
H	2.97	-0.94	1.25
H	1.69	-1.97	1.92
H	-0.76	-0.86	4.87
H	0.83	-0.06	4.92
H	-0.66	0.92	4.87
H	-2.21	-1.18	-2.25
H	-3.30	-2.13	-1.22
H	-4.28	0.00	-1.45
H	-3.68	0.00	0.19
H	-3.30	2.14	-1.22
H	-2.21	1.18	-2.25
H	-1.15	3.61	-1.12
H	-0.46	2.28	-2.09
H	1.34	3.56	-0.97
H	0.58	3.32	0.60
H	1.74	1.32	-2.24
H	3.10	2.15	-1.42
H	3.81	0.00	-2.21
H	3.89	0.00	-0.47
H	3.10	-2.15	-1.42
H	1.74	-1.33	-2.24
H	1.34	-3.56	-0.97
H	0.58	-3.32	0.61
H	-1.15	-3.61	-1.12
H	-0.46	-2.28	-2.09

(TMC-NCMe)Fe(IV)=O S=1
Gaussian/B3LYP

Fe	0.02	0.00	-0.22
N	1.42	-1.58	-0.35
N	-1.46	-1.56	-0.18
N	-1.46	1.56	-0.18
N	1.42	1.58	-0.35
C	0.63	-2.65	-1.08
C	-0.71	-2.87	-0.40
C	-2.40	-1.31	-1.36
C	-3.20	0.00	-1.31
C	-2.40	1.31	-1.36
C	-0.71	2.87	-0.40
C	0.63	2.65	-1.08
C	2.63	1.27	-1.22
C	3.40	0.00	-0.84
C	2.63	-1.27	-1.22
C	1.92	-2.11	0.97
C	-2.29	-1.77	1.06
C	-2.29	1.77	1.06
C	1.92	2.11	0.97
N	0.09	0.00	1.94
C	0.11	0.00	3.11
C	0.15	0.00	4.57
O	0.01	0.00	-1.86
H	2.56	-2.99	0.80
H	2.49	-1.35	1.49
H	1.08	-2.41	1.61
H	-2.93	-2.65	0.93
H	-1.64	-1.94	1.92
H	-2.93	-0.92	1.27
H	2.56	2.99	0.80
H	1.08	2.41	1.61
H	2.49	1.35	1.49
H	-2.93	2.65	0.93
H	-2.93	0.92	1.27
H	-1.64	1.94	1.92
H	0.67	0.89	4.94
H	-0.87	0.00	4.98
H	0.67	-0.89	4.94
H	2.27	1.17	-2.25
H	3.30	2.14	-1.18
H	4.33	0.00	-1.42
H	3.71	0.00	0.21
H	3.30	-2.14	-1.18
H	2.27	-1.17	-2.25
H	1.20	-3.59	-1.09
H	0.50	-2.32	-2.11
H	-1.33	-3.55	-1.01
H	-0.58	-3.35	0.57
H	-1.79	-1.35	-2.27
H	-3.11	-2.15	-1.39
H	-3.83	0.00	-2.20
H	-3.89	0.00	-0.46
H	-3.11	2.15	-1.39
H	-1.79	1.35	-2.27
H	-1.33	3.55	-1.01
H	-0.58	3.35	0.57
H	1.20	3.59	-1.09
H	0.50	2.32	-2.11

(TMC-NCMe)Fe(IV)=O S=1
Gaussian/BP86

Fe	-0.02	0.00	-0.21
N	-1.42	1.58	-0.35
N	1.46	1.56	-0.17
N	1.46	-1.56	-0.17
N	-1.42	-1.58	-0.35
C	-0.62	2.66	-1.08
C	0.71	2.88	-0.39
C	2.40	1.31	-1.36
C	3.20	0.00	-1.31
C	2.40	-1.32	-1.36
C	0.71	-2.88	-0.38
C	-0.62	-2.66	-1.08
C	-2.63	-1.27	-1.24
C	-3.40	0.00	-0.86
C	-2.63	1.27	-1.24
C	-1.92	2.11	0.97
C	2.30	1.77	1.08
C	2.30	-1.77	1.08
C	-1.93	-2.11	0.97
N	-0.09	0.00	1.92
C	-0.13	0.00	3.10
C	-0.19	0.00	4.56
O	0.00	0.00	-1.86
H	-2.57	2.99	0.80
H	-2.51	1.34	1.49
H	-1.09	2.41	1.61
H	2.94	2.66	0.94
H	1.65	1.93	1.94
H	2.95	0.91	1.27
H	-2.58	-2.99	0.80
H	-1.09	-2.41	1.62
H	-2.51	-1.34	1.49
H	2.94	-2.66	0.94
H	2.95	-0.91	1.27
H	1.65	-1.93	1.95
H	-0.77	-0.86	4.93
H	0.83	-0.06	4.99
H	-0.67	0.93	4.93
H	-2.25	-1.17	-2.27
H	-3.30	-2.15	-1.20
H	-4.34	0.00	-1.45
H	-3.73	0.00	0.20
H	-3.30	2.15	-1.20
H	-2.25	1.17	-2.27
H	-1.20	3.60	-1.11
H	-0.47	2.31	-2.12
H	1.34	3.57	-0.98
H	0.57	3.35	0.60
H	1.78	1.34	-2.27
H	3.11	2.16	-1.40
H	3.84	0.00	-2.21
H	3.91	0.00	-0.46
H	3.11	-2.17	-1.40
H	1.78	-1.34	-2.27
H	1.34	-3.57	-0.98
H	0.56	-3.35	0.60
H	-1.20	-3.60	-1.11
H	-0.48	-2.31	-2.12

(TMC-NCMe)Fe(IV)=O S=2
Gaussian/B3LYP

Fe	-0.03	0.00	-0.20
N	-1.46	1.68	-0.38
N	1.51	1.63	-0.14
N	1.52	-1.62	-0.15
N	-1.45	-1.68	-0.39
C	-0.60	2.70	-1.11
C	0.74	2.92	-0.41
C	2.47	1.34	-1.29
C	3.25	0.01	-1.19
C	2.48	-1.32	-1.30
C	0.76	-2.91	-0.42
C	-0.59	-2.69	-1.12
C	-2.62	-1.30	-1.28
C	-3.35	-0.01	-0.88
C	-2.63	1.29	-1.27
C	-1.98	2.25	0.91
C	2.30	1.84	1.13
C	2.31	-1.84	1.12
C	-1.97	-2.26	0.89
N	-0.17	-0.01	1.92
C	-0.24	-0.01	3.09
C	-0.33	-0.02	4.55
O	0.02	0.01	-1.84
H	-2.59	3.14	0.71
H	-2.60	1.51	1.42
H	-1.16	2.53	1.57
H	2.97	2.70	1.02
H	1.62	2.04	1.96
H	2.90	0.97	1.37
H	-2.58	-3.15	0.68
H	-1.15	-2.55	1.55
H	-2.59	-1.53	1.41
H	2.99	-2.69	1.00
H	2.91	-0.96	1.37
H	1.63	-2.05	1.95
H	-0.92	-0.88	4.89
H	0.67	-0.08	5.00
H	-0.82	0.90	4.91
H	-2.23	-1.18	-2.30
H	-3.32	-2.14	-1.28
H	-4.30	-0.01	-1.43
H	-3.63	-0.01	0.18
H	-3.34	2.13	-1.27
H	-2.24	1.19	-2.29
H	-1.13	3.66	-1.16
H	-0.45	2.34	-2.13
H	1.36	3.59	-1.02
H	0.59	3.42	0.55
H	1.88	1.35	-2.21
H	3.20	2.16	-1.33
H	3.94	0.02	-2.05
H	3.91	0.01	-0.31
H	3.21	-2.14	-1.35
H	1.89	-1.33	-2.22
H	1.38	-3.58	-1.04
H	0.61	-3.42	0.53
H	-1.11	-3.66	-1.19
H	-0.44	-2.32	-2.14

(TMC-NCMe)Fe(IV)=O S=2
Gaussian/BP86

Fe	-0.05	0.00	-0.19
N	-1.46	1.69	-0.37
N	1.52	1.63	-0.15
N	1.52	-1.63	-0.15
N	-1.46	-1.69	-0.37
C	-0.60	2.70	-1.11
C	0.75	2.92	-0.41
C	2.46	1.33	-1.32
C	3.24	0.00	-1.23
C	2.46	-1.33	-1.33
C	0.75	-2.92	-0.41
C	-0.60	-2.70	-1.11
C	-2.64	-1.30	-1.26
C	-3.37	0.00	-0.86
C	-2.64	1.30	-1.26
C	-1.98	2.27	0.92
C	2.33	1.84	1.11
C	2.33	-1.84	1.11
C	-1.98	-2.27	0.92
N	-0.15	0.00	1.90
C	-0.21	0.00	3.08
C	-0.28	0.00	4.54
O	0.00	0.00	-1.84
H	-2.59	3.17	0.72
H	-2.60	1.52	1.44
H	-1.15	2.55	1.58
H	3.01	2.71	0.99
H	1.66	2.04	1.96
H	2.94	0.96	1.34
H	-2.59	-3.17	0.72
H	-1.15	-2.55	1.58
H	-2.60	-1.53	1.44
H	3.01	-2.71	0.98
H	2.94	-0.96	1.34
H	1.66	-2.05	1.96
H	-0.75	-0.93	4.91
H	0.73	0.07	4.98
H	-0.88	0.85	4.90
H	-2.25	-1.19	-2.29
H	-3.35	-2.14	-1.26
H	-4.33	0.00	-1.39
H	-3.64	0.00	0.22
H	-3.35	2.15	-1.26
H	-2.25	1.19	-2.29
H	-1.13	3.67	-1.18
H	-0.45	2.32	-2.13
H	1.37	3.61	-1.02
H	0.59	3.42	0.57
H	1.84	1.34	-2.24
H	3.19	2.16	-1.39
H	3.93	0.00	-2.10
H	3.91	0.00	-0.35
H	3.19	-2.16	-1.39
H	1.84	-1.33	-2.24
H	1.37	-3.61	-1.02
H	0.59	-3.42	0.56
H	-1.13	-3.67	-1.18
H	-0.45	-2.32	-2.14

(TMC-NCMe)Fe(III)-OH S=1/2
ADF/B88P86

Fe	-0.03	0.01	-0.16
N	-1.40	-1.60	-0.37
N	1.47	-1.54	-0.22
N	1.42	1.59	-0.12
N	-1.43	1.60	-0.25
C	-0.60	-2.62	-1.14
C	0.74	-2.84	-0.49
C	2.40	-1.23	-1.38
C	3.17	0.08	-1.27
C	2.38	1.40	-1.27
C	0.68	2.90	-0.28
C	-0.69	2.72	-0.91
C	-2.64	1.29	-1.11
C	-3.36	-0.01	-0.78
C	-2.60	-1.25	-1.21
C	-1.88	-2.20	0.91
C	2.31	-1.80	0.99
C	2.24	1.76	1.12
C	-1.93	2.06	1.08
H	-0.49	-2.23	-2.16
H	-1.16	-3.57	-1.18
H	1.36	-3.49	-1.12
H	0.62	-3.35	0.47
H	1.79	-1.24	-2.29
H	3.13	-2.06	-1.44
H	3.82	0.12	-2.15
H	3.86	0.06	-0.42
H	1.82	1.49	-2.21
H	3.10	2.23	-1.25
H	0.57	3.35	0.71
H	1.28	3.60	-0.88
H	-0.62	2.50	-1.98
H	-1.26	3.65	-0.83
H	-3.33	2.15	-1.01
H	-2.30	1.25	-2.15
H	-4.30	0.00	-1.35
H	-3.67	-0.05	0.28
H	-2.24	-1.12	-2.24
H	-3.27	-2.13	-1.20
H	-2.48	-1.47	1.47
H	-2.52	-3.08	0.69
H	-1.04	-2.52	1.53
H	2.96	-2.66	0.80
H	1.67	-2.03	1.84
H	2.94	-0.94	1.23
H	2.86	0.88	1.32
H	1.58	1.93	1.98
H	2.90	2.63	1.01
H	-1.09	2.36	1.72
H	-2.48	1.26	1.58
H	-2.60	2.93	0.94
N	-0.07	-0.08	1.81
C	-0.09	-0.14	2.98
C	-0.12	-0.20	4.43
H	-0.67	-1.09	4.76
H	0.91	-0.27	4.82
H	-0.59	0.69	4.84
O	-0.05	-0.03	-1.97
H	-0.05	0.85	-2.40

(TMC-NCMe)Fe(III)-OH S=1/2
Gaussian/BP86

Fe	-0.02	0.01	-0.17
N	-1.40	-1.59	-0.37
N	1.47	-1.54	-0.22
N	1.42	1.59	-0.12
N	-1.44	1.59	-0.26
C	-0.60	-2.63	-1.15
C	0.74	-2.86	-0.49
C	2.41	-1.23	-1.39
C	3.20	0.09	-1.28
C	2.40	1.40	-1.29
C	0.68	2.93	-0.28
C	-0.69	2.74	-0.92
C	-2.66	1.29	-1.13
C	-3.40	-0.01	-0.78
C	-2.62	-1.25	-1.22
C	-1.89	-2.19	0.93
C	2.32	-1.80	1.02
C	2.25	1.75	1.15
C	-1.93	2.05	1.10
H	-0.47	-2.23	-2.17
H	-1.17	-3.58	-1.21
H	1.37	-3.51	-1.13
H	0.62	-3.39	0.48
H	1.78	-1.23	-2.30
H	3.13	-2.07	-1.47
H	3.86	0.12	-2.17
H	3.89	0.06	-0.42
H	1.83	1.50	-2.23
H	3.12	2.25	-1.26
H	0.57	3.38	0.72
H	1.29	3.62	-0.88
H	-0.61	2.53	-2.01
H	-1.28	3.68	-0.83
H	-3.35	2.16	-1.03
H	-2.33	1.25	-2.18
H	-4.35	0.00	-1.35
H	-3.70	-0.05	0.28
H	-2.26	-1.11	-2.25
H	-3.29	-2.14	-1.21
H	-2.48	-1.46	1.50
H	-2.53	-3.07	0.72
H	-1.04	-2.52	1.55
H	2.98	-2.67	0.83
H	1.67	-2.03	1.88
H	2.96	-0.94	1.26
H	2.87	0.87	1.34
H	1.58	1.92	2.01
H	2.92	2.63	1.05
H	-1.08	2.34	1.74
H	-2.48	1.24	1.59
H	-2.61	2.92	0.98
N	-0.06	-0.08	1.81
C	-0.09	-0.14	3.00
C	-0.11	-0.21	4.46
H	-0.67	-1.10	4.80
H	0.91	-0.28	4.86
H	-0.59	0.69	4.89
O	-0.05	-0.05	-1.99
H	-0.03	0.82	-2.47

(TMC-NCMe)Fe(III)-OH S=1/2
Gaussian/B3LYP

Fe	-0.01	0.00	-0.17
N	-1.42	-1.56	-0.37
N	1.46	-1.55	-0.14
N	1.48	1.54	-0.11
N	-1.40	1.59	-0.35
C	-0.61	-2.63	-1.09
C	0.71	-2.86	-0.38
C	2.44	-1.32	-1.29
C	3.24	-0.01	-1.22
C	2.48	1.32	-1.25
C	0.75	2.86	-0.34
C	-0.58	2.65	-1.06
C	-2.58	1.29	-1.26
C	-3.37	0.03	-0.90
C	-2.60	-1.24	-1.27
C	-1.96	-2.11	0.93
C	2.26	-1.78	1.13
C	2.27	1.74	1.17
C	-1.92	2.13	0.96
H	-0.45	-2.27	-2.10
H	-1.19	-3.56	-1.13
H	1.34	-3.54	-0.97
H	0.55	-3.34	0.59
H	1.87	-1.40	-2.22
H	3.16	-2.16	-1.28
H	3.90	-0.01	-2.10
H	3.93	-0.03	-0.36
H	1.94	1.46	-2.19
H	3.22	2.14	-1.20
H	0.59	3.33	0.64
H	1.38	3.54	-0.92
H	-0.42	2.30	-2.08
H	-1.14	3.59	-1.09
H	-3.24	2.17	-1.23
H	-2.19	1.18	-2.27
H	-4.29	0.04	-1.51
H	-3.71	0.02	0.14
H	-2.20	-1.12	-2.28
H	-3.27	-2.11	-1.26
H	-2.54	-1.35	1.44
H	-2.60	-2.97	0.73
H	-1.14	-2.43	1.59
H	2.88	-2.68	1.01
H	1.58	-1.93	1.97
H	2.92	-0.95	1.35
H	2.92	0.89	1.38
H	1.59	1.88	2.01
H	2.90	2.63	1.07
H	-1.11	2.42	1.62
H	-2.53	1.37	1.46
H	-2.55	3.00	0.77
N	-0.14	-0.01	1.91
C	-0.23	-0.03	3.08
C	-0.34	-0.04	4.54
H	-0.94	-0.90	4.86
H	0.65	-0.11	5.00
H	-0.83	0.87	4.89
O	-0.11	-0.02	-2.06
H	0.69	0.15	-2.59

(TMC-NMCe)Fe(III)-OH S=5/2
Gaussian/B3LYP

Fe	0.02	0.00	-0.30
N	1.45	1.69	-0.37
N	-1.51	1.64	-0.11
N	-1.51	-1.64	-0.12
N	1.45	-1.69	-0.37
C	0.60	2.72	-1.10
C	-0.76	2.93	-0.42
C	-2.54	1.34	-1.20
C	-3.30	0.00	-1.05
C	-2.54	-1.33	-1.21
C	-0.76	-2.93	-0.44
C	0.61	-2.71	-1.11
C	2.65	-1.30	-1.23
C	3.36	0.00	-0.82
C	2.64	1.31	-1.23
C	1.94	2.26	0.93
C	-2.23	1.85	1.20
C	-2.23	-1.86	1.19
C	1.95	-2.26	0.92
H	0.47	2.36	-2.12
H	1.13	3.68	-1.14
H	-1.38	3.57	-1.07
H	-0.62	3.47	0.52
H	-2.01	1.36	-2.15
H	-3.28	2.15	-1.20
H	-4.05	0.00	-1.87
H	-3.90	0.00	-0.13
H	-2.01	-1.36	-2.16
H	-3.28	-2.15	-1.21
H	-0.62	-3.47	0.50
H	-1.37	-3.57	-1.08
H	0.48	-2.35	-2.13
H	1.13	-3.67	-1.16
H	3.37	-2.13	-1.20
H	2.29	-1.21	-2.26
H	4.32	0.01	-1.34
H	3.61	0.00	0.25
H	2.29	1.22	-2.26
H	3.36	2.14	-1.19
H	2.56	1.53	1.45
H	2.55	3.16	0.75
H	1.10	2.53	1.58
H	-2.93	2.70	1.11
H	-1.51	2.08	1.99
H	-2.80	0.97	1.49
H	-2.80	-0.98	1.48
H	-1.51	-2.09	1.98
H	-2.93	-2.71	1.10
H	1.11	-2.54	1.57
H	2.56	-1.53	1.45
H	2.55	-3.16	0.73
N	0.19	-0.01	2.00
C	0.27	-0.01	3.17
C	0.37	-0.01	4.63
H	0.82	0.92	4.98
H	-0.62	-0.12	5.08
H	1.00	-0.84	4.96
O	-0.03	0.01	-2.11
H	-0.41	-0.35	-2.88

(TMC-OCOCF3)Fe(IV)=O S=1
ADF/B88P86

Fe	0.09	0.00	-0.34
N	1.52	-1.61	-0.33
N	-1.37	-1.56	-0.37
N	-1.27	1.63	-0.19
N	1.61	1.51	-0.16
C	0.72	-2.88	-0.25
C	-0.65	-2.66	0.35
C	-2.59	-1.24	0.44
C	-3.28	0.07	0.07
C	-2.52	1.29	0.57
C	-0.50	2.60	0.64
C	0.88	2.81	0.08
C	2.42	1.17	1.06
C	3.18	-0.16	0.99
C	2.35	-1.45	0.91
C	2.42	-1.77	-1.51
C	-1.79	-2.02	-1.72
C	-1.66	2.25	-1.50
C	2.53	1.78	-1.30
H	1.28	-3.63	0.34
H	0.63	-3.28	-1.26
H	-0.57	-2.36	1.40
H	-1.24	-3.60	0.29
H	-2.28	-1.19	1.49
H	-3.29	-2.08	0.33
H	-4.26	0.07	0.59
H	-3.51	0.13	-1.00
H	-2.22	1.13	1.61
H	-3.17	2.18	0.54
H	-1.04	3.57	0.68
H	-0.45	2.19	1.65
H	0.82	3.33	-0.89
H	1.47	3.45	0.75
H	3.16	1.98	1.20
H	1.74	1.16	1.92
H	3.93	-0.14	0.19
H	3.76	-0.23	1.92
H	3.04	-2.31	0.95
H	1.67	-1.50	1.76
H	3.05	-2.67	-1.36
H	1.83	-1.90	-2.42
H	3.06	-0.91	-1.65
H	-2.47	-2.88	-1.62
H	-0.92	-2.31	-2.32
H	-2.30	-1.21	-2.25
H	-2.21	1.53	-2.11
H	-2.29	3.13	-1.31
H	-0.77	2.55	-2.06
H	1.96	2.00	-2.20
H	3.18	2.63	-1.05
H	3.15	0.91	-1.52
O	-0.01	-0.09	1.32
O	-0.04	0.10	-2.33
C	0.55	0.15	-3.48
O	1.74	0.18	-3.78
C	-0.45	0.17	-4.70
F	-1.77	0.15	-4.33
F	-0.26	1.28	-5.45
F	-0.24	-0.92	-5.49

(TMC-OCOCF3)Fe(IV)=O S=1
Gaussian/B3LYP

Fe	0.74	0.22	0.06
N	1.10	-1.22	1.60
N	0.05	1.45	1.65
N	0.49	1.64	-1.50
N	1.56	-1.03	-1.50
C	0.85	-0.53	2.93
C	0.91	0.99	2.80
C	0.33	2.92	1.44
C	-0.20	3.50	0.13
C	0.66	3.08	-1.07
C	1.66	1.32	-2.41
C	1.68	-0.16	-2.75
C	2.96	-1.44	-1.06
C	3.01	-2.30	0.22
C	2.57	-1.62	1.53
C	0.25	-2.47	1.61
C	-1.41	1.28	1.99
C	-0.81	1.51	-2.25
C	0.79	-2.25	-1.92
H	1.58	-0.87	3.67
H	-0.14	-0.83	3.29
H	1.93	1.32	2.60
H	0.57	1.46	3.73
H	1.42	3.06	1.48
H	-0.11	3.46	2.30
H	-0.13	4.60	0.20
H	-1.26	3.28	-0.03
H	1.72	3.22	-0.81
H	0.44	3.71	-1.94
H	1.58	1.91	-3.34
H	2.57	1.61	-1.89
H	0.84	-0.42	-3.41
H	2.60	-0.41	-3.29
H	3.40	-2.02	-1.88
H	3.54	-0.53	-0.91
H	2.48	-3.25	0.08
H	4.06	-2.57	0.36
H	2.76	-2.31	2.36
H	3.16	-0.71	1.68
H	0.54	-3.10	2.45
H	-0.80	-2.20	1.71
H	0.35	-3.03	0.69
H	-1.64	1.88	2.89
H	-1.65	0.24	2.19
H	-2.03	1.61	1.17
H	-1.64	1.74	-1.59
H	-0.81	2.20	-3.11
H	-0.95	0.49	-2.61
H	-0.21	-1.97	-2.24
H	1.31	-2.74	-2.75
H	0.68	-2.96	-1.10
O	2.23	0.88	0.31
O	-1.11	-0.42	-0.23
C	-2.07	-1.30	-0.40
O	-1.99	-2.52	-0.64
C	-3.49	-0.67	-0.23
F	-3.55	0.68	-0.64
F	-4.47	-1.35	-0.93
F	-3.85	-0.68	1.13

(TMC-OCOCF3)Fe(IV)=O S=1
Gaussian/BP86

Fe	0.74	0.22	0.05
N	1.08	-1.16	1.64
N	0.06	1.51	1.59
N	0.51	1.58	-1.56
N	1.57	-1.11	-1.45
C	0.82	-0.43	2.95
C	0.92	1.08	2.77
C	0.37	2.98	1.34
C	-0.15	3.52	0.00
C	0.71	3.04	-1.17
C	1.68	1.21	-2.46
C	1.66	-0.29	-2.74
C	2.97	-1.49	-0.99
C	3.02	-2.29	0.32
C	2.56	-1.56	1.60
C	0.22	-2.41	1.66
C	-1.40	1.37	1.94
C	-0.80	1.44	-2.30
C	0.82	-2.37	-1.83
H	1.54	-0.77	3.72
H	-0.19	-0.71	3.31
H	1.96	1.38	2.54
H	0.59	1.60	3.69
H	1.46	3.10	1.38
H	-0.07	3.56	2.18
H	-0.07	4.62	0.03
H	-1.22	3.31	-0.15
H	1.78	3.16	-0.91
H	0.51	3.65	-2.08
H	1.61	1.77	-3.41
H	2.60	1.50	-1.94
H	0.80	-0.56	-3.37
H	2.57	-0.58	-3.30
H	3.43	-2.09	-1.80
H	3.54	-0.55	-0.87
H	2.51	-3.26	0.22
H	4.09	-2.55	0.49
H	2.74	-2.22	2.47
H	3.14	-0.63	1.73
H	0.52	-3.05	2.51
H	-0.84	-2.12	1.79
H	0.29	-2.98	0.73
H	-1.62	1.99	2.83
H	-1.66	0.33	2.15
H	-2.02	1.71	1.10
H	-1.63	1.70	-1.64
H	-0.80	2.11	-3.18
H	-0.95	0.40	-2.62
H	-0.23	-2.13	-2.07
H	1.31	-2.83	-2.71
H	0.81	-3.10	-1.02
O	2.25	0.89	0.28
O	-1.12	-0.41	-0.21
C	-2.09	-1.29	-0.39
O	-2.02	-2.52	-0.65
C	-3.52	-0.66	-0.20
F	-3.59	0.70	-0.62
F	-4.51	-1.35	-0.90
F	-3.87	-0.67	1.18

(TMC-OCOCF3)Fe(IV)=O S=2
Gaussian/BP86

Fe	0.68	0.27	0.04
N	1.16	-1.03	1.79
N	-0.06	1.67	1.61
N	0.43	1.48	-1.77
N	1.67	-1.20	-1.43
C	0.86	-0.18	3.03
C	0.86	1.33	2.75
C	0.18	3.10	1.15
C	-0.37	3.43	-0.25
C	0.53	2.96	-1.42
C	1.65	1.09	-2.58
C	1.74	-0.43	-2.75
C	3.07	-1.42	-0.89
C	3.14	-2.11	0.50
C	2.66	-1.31	1.73
C	0.37	-2.31	1.90
C	-1.51	1.50	2.01
C	-0.84	1.22	-2.53
C	1.02	-2.53	-1.74
H	1.59	-0.41	3.82
H	-0.13	-0.49	3.41
H	1.87	1.67	2.47
H	0.55	1.86	3.67
H	1.27	3.27	1.17
H	-0.28	3.78	1.90
H	-0.43	4.54	-0.32
H	-1.41	3.08	-0.38
H	1.58	3.17	-1.16
H	0.28	3.54	-2.33
H	1.61	1.57	-3.58
H	2.54	1.47	-2.04
H	0.91	-0.79	-3.38
H	2.68	-0.68	-3.28
H	3.63	-2.05	-1.62
H	3.56	-0.43	-0.83
H	2.67	-3.11	0.46
H	4.22	-2.31	0.68
H	2.93	-1.89	2.64
H	3.17	-0.34	1.76
H	0.70	-2.89	2.79
H	-0.70	-2.08	2.00
H	0.50	-2.93	1.01
H	-1.74	2.17	2.86
H	-1.71	0.46	2.29
H	-2.16	1.74	1.16
H	-1.71	1.53	-1.94
H	-0.83	1.78	-3.49
H	-0.94	0.14	-2.74
H	-0.01	-2.39	-2.09
H	1.61	-3.06	-2.52
H	0.98	-3.17	-0.85
O	2.15	1.04	0.22
O	-1.15	-0.37	-0.14
C	-2.02	-1.36	-0.31
O	-1.81	-2.58	-0.51
C	-3.50	-0.84	-0.18
F	-3.67	0.46	-0.72
F	-4.42	-1.67	-0.82
F	-3.86	-0.76	1.19

(N4Py)Fe(IV)=OS=1
ADF/B88P86

Fe	-0.07	0.00	0.53
N	-1.45	-1.35	0.11
N	-1.42	1.42	0.21
N	1.38	1.35	0.44
N	1.37	-1.35	0.33
N	0.13	0.08	-1.54
C	-2.31	-1.87	1.02
C	-3.30	-2.78	0.65
C	-3.42	-3.14	-0.69
C	-2.54	-2.60	-1.63
C	-1.56	-1.71	-1.20
C	-0.50	-1.14	-2.13
C	-2.26	1.90	1.16
C	-3.22	2.85	0.86
C	-3.33	3.33	-0.44
C	-2.47	2.84	-1.42
C	-1.51	1.88	-1.06
C	-0.49	1.35	-2.04
C	1.70	2.30	1.35
C	2.74	3.20	1.12
C	3.47	3.11	-0.06
C	3.14	2.13	-1.00
C	2.09	1.26	-0.71
C	1.65	0.08	-1.56
C	1.68	-2.37	1.16
C	2.72	-3.25	0.86
C	3.45	-3.07	-0.32
C	3.13	-2.01	-1.17
C	2.08	-1.17	-0.81
H	-2.17	-1.54	2.04
H	-3.97	-3.18	1.41
H	-4.20	-3.84	-1.01
H	-2.61	-2.87	-2.68
H	0.28	-1.90	-2.27
H	-0.92	-0.92	-3.11
H	-2.12	1.49	2.16
H	-3.87	3.22	1.66
H	-4.08	4.08	-0.70
H	-2.52	3.19	-2.45
H	-0.93	1.20	-3.03
H	0.31	2.11	-2.16
H	1.10	2.30	2.26
H	2.98	3.94	1.88
H	4.29	3.80	-0.26
H	3.70	2.03	-1.94
H	2.06	0.12	-2.58
H	1.08	-2.46	2.06
H	2.95	-4.06	1.55
H	4.27	-3.75	-0.57
H	3.68	-1.84	-2.10
O	-0.25	-0.05	2.18

(N4Py)Fe(IV)=O S=1
excited state; ADF/B88P86

Fe	-0.08	0.01	0.51
N	-1.45	-1.38	0.11
N	-1.43	1.44	0.21
N	1.41	1.35	0.45
N	1.39	-1.35	0.33
N	0.13	0.09	-1.56
C	-2.29	-1.90	1.03
C	-3.30	-2.79	0.66
C	-3.44	-3.12	-0.69
C	-2.56	-2.58	-1.63
C	-1.56	-1.70	-1.20
C	-0.51	-1.14	-2.13
C	-2.26	1.92	1.17
C	-3.23	2.86	0.87
C	-3.35	3.32	-0.45
C	-2.49	2.82	-1.43
C	-1.52	1.88	-1.07
C	-0.49	1.36	-2.05
C	1.72	2.27	1.37
C	2.76	3.17	1.15
C	3.48	3.10	-0.05
C	3.15	2.13	-1.00
C	2.10	1.26	-0.72
C	1.65	0.08	-1.57
C	1.71	-2.35	1.17
C	2.74	-3.24	0.88
C	3.46	-3.07	-0.31
C	3.13	-2.02	-1.18
C	2.09	-1.17	-0.82
H	-2.10	-1.58	2.06
H	-3.96	-3.20	1.42
H	-4.23	-3.81	-1.01
H	-2.65	-2.83	-2.69
H	0.27	-1.90	-2.28
H	-0.94	-0.92	-3.12
H	-2.09	1.51	2.16
H	-3.89	3.22	1.66
H	-4.12	4.05	-0.71
H	-2.56	3.17	-2.46
H	-0.93	1.22	-3.04
H	0.31	2.12	-2.15
H	1.13	2.26	2.28
H	3.01	3.92	1.90
H	4.30	3.79	-0.24
H	3.70	2.04	-1.94
H	2.07	0.12	-2.59
H	1.11	-2.41	2.09
H	2.98	-4.04	1.57
H	4.28	-3.75	-0.56
H	3.68	-1.86	-2.11
O	-0.32	-0.04	2.22

(N4Py)Fe(IV)=O S=1
Gaussian/B3LYP

Fe	0.08	0.00	-0.63
N	1.44	-1.39	-0.31
N	1.44	1.39	-0.31
N	-1.37	1.36	-0.49
N	-1.37	-1.36	-0.49
N	-0.10	0.00	1.43
C	2.27	-1.89	-1.27
C	3.25	-2.84	-0.96
C	3.39	-3.27	0.37
C	2.53	-2.76	1.36
C	1.56	-1.82	0.99
C	0.54	-1.26	1.97
C	2.27	1.89	-1.27
C	3.25	2.84	-0.96
C	3.39	3.27	0.37
C	2.53	2.75	1.36
C	1.56	1.81	0.99
C	0.54	1.26	1.97
C	-1.69	2.32	-1.38
C	-2.75	3.21	-1.13
C	-3.47	3.10	0.07
C	-3.14	2.08	0.99
C	-2.08	1.22	0.68
C	-1.63	0.00	1.48
C	-1.69	-2.32	-1.38
C	-2.75	-3.21	-1.13
C	-3.48	-3.09	0.07
C	-3.14	-2.08	0.99
C	-2.08	-1.22	0.68
H	2.12	-1.51	-2.27
H	3.90	-3.21	-1.75
H	4.15	-4.00	0.63
H	2.61	-3.08	2.39
H	-0.24	-2.01	2.14
H	1.01	-1.07	2.94
H	2.12	1.51	-2.27
H	3.89	3.22	-1.75
H	4.15	4.00	0.63
H	2.61	3.08	2.39
H	1.01	1.06	2.94
H	-0.24	2.01	2.14
H	-1.10	2.36	-2.29
H	-2.99	3.98	-1.86
H	-4.29	3.78	0.29
H	-3.69	1.96	1.92
H	-2.03	0.00	2.50
H	-1.10	-2.36	-2.29
H	-3.00	-3.97	-1.86
H	-4.29	-3.77	0.28
H	-3.69	-1.96	1.92
O	0.21	0.00	-2.28

(N4Py)Fe(IV)=O S=1
Gaussian/BP86

Fe	0.07	0.00	-0.62
N	1.43	-1.38	-0.30
N	1.43	1.38	-0.30
N	-1.36	1.35	-0.48
N	-1.37	-1.35	-0.48
N	-0.10	0.00	1.45
C	2.26	-1.87	-1.28
C	3.25	-2.82	-0.98
C	3.40	-3.27	0.35
C	2.54	-2.76	1.35
C	1.56	-1.81	1.00
C	0.54	-1.27	1.99
C	2.26	1.87	-1.28
C	3.25	2.83	-0.98
C	3.40	3.27	0.35
C	2.55	2.76	1.36
C	1.56	1.81	1.00
C	0.54	1.27	1.99
C	-1.68	2.31	-1.39
C	-2.74	3.21	-1.15
C	-3.48	3.11	0.05
C	-3.14	2.09	0.99
C	-2.09	1.22	0.69
C	-1.64	0.00	1.50
C	-1.68	-2.31	-1.39
C	-2.74	-3.21	-1.15
C	-3.48	-3.11	0.05
C	-3.15	-2.09	0.99
C	-2.09	-1.22	0.69
H	2.09	-1.48	-2.29
H	3.90	-3.20	-1.78
H	4.17	-4.00	0.61
H	2.64	-3.09	2.39
H	-0.25	-2.02	2.15
H	1.00	-1.08	2.97
H	2.09	1.48	-2.29
H	3.89	3.20	-1.78
H	4.17	4.00	0.61
H	2.64	3.09	2.39
H	1.01	1.07	2.97
H	-0.25	2.02	2.15
H	-1.08	2.33	-2.31
H	-2.98	3.97	-1.90
H	-4.30	3.80	0.26
H	-3.70	1.99	1.93
H	-2.05	0.00	2.52
H	-1.08	-2.33	-2.31
H	-2.98	-3.97	-1.90
H	-4.30	-3.80	0.26
H	-3.70	-1.99	1.93
O	0.21	0.00	-2.28

(N4Py)Fe(IV)=O S=2
Gaussian/B3LYP

Fe	0.12	0.00	-0.76
N	1.52	-1.48	-0.35
N	1.52	1.48	-0.35
N	-1.47	1.41	-0.52
N	-1.47	-1.41	-0.52
N	-0.08	0.00	1.33
C	2.38	-2.01	-1.26
C	3.37	-2.93	-0.89
C	3.47	-3.29	0.47
C	2.59	-2.74	1.41
C	1.61	-1.83	0.97
C	0.55	-1.26	1.90
C	2.38	2.01	-1.26
C	3.37	2.93	-0.89
C	3.47	3.30	0.47
C	2.59	2.74	1.41
C	1.61	1.83	0.97
C	0.55	1.26	1.90
C	-1.86	2.39	-1.37
C	-2.93	3.25	-1.04
C	-3.59	3.07	0.18
C	-3.18	2.04	1.06
C	-2.11	1.23	0.67
C	-1.61	0.00	1.43
C	-1.86	-2.39	-1.37
C	-2.93	-3.25	-1.04
C	-3.59	-3.07	0.18
C	-3.18	-2.04	1.06
C	-2.11	-1.23	0.67
H	2.25	-1.68	-2.29
H	4.03	-3.34	-1.64
H	4.24	-4.00	0.79
H	2.65	-3.01	2.46
H	-0.23	-2.01	2.04
H	0.98	-1.06	2.89
H	2.25	1.68	-2.29
H	4.03	3.34	-1.64
H	4.24	4.00	0.79
H	2.65	3.01	2.46
H	0.98	1.06	2.89
H	-0.23	2.01	2.04
H	-1.31	2.48	-2.30
H	-3.23	4.02	-1.74
H	-4.42	3.72	0.46
H	-3.68	1.89	2.01
H	-1.95	0.00	2.47
H	-1.31	-2.48	-2.30
H	-3.23	-4.02	-1.74
H	-4.42	-3.72	0.46
H	-3.68	-1.89	2.01
O	0.27	0.00	-2.39

(N4Py)Fe(IV)=O S=2
Gaussian/BP86

Fe	0.12	0.00	-0.75
N	1.52	-1.48	-0.35
N	1.52	1.48	-0.35
N	-1.47	1.41	-0.52
N	-1.47	-1.41	-0.52
N	-0.08	0.00	1.34
C	2.38	-2.01	-1.27
C	3.38	-2.92	-0.90
C	3.50	-3.29	0.46
C	2.61	-2.73	1.41
C	1.62	-1.83	0.98
C	0.55	-1.27	1.91
C	2.38	2.01	-1.27
C	3.38	2.92	-0.90
C	3.50	3.29	0.46
C	2.61	2.73	1.41
C	1.62	1.83	0.98
C	0.55	1.27	1.91
C	-1.86	2.39	-1.38
C	-2.94	3.25	-1.06
C	-3.61	3.08	0.18
C	-3.19	2.05	1.07
C	-2.12	1.23	0.68
C	-1.62	0.00	1.44
C	-1.86	-2.39	-1.38
C	-2.94	-3.25	-1.06
C	-3.61	-3.08	0.18
C	-3.19	-2.05	1.07
C	-2.12	-1.23	0.68
H	2.23	-1.68	-2.31
H	4.05	-3.34	-1.66
H	4.28	-3.99	0.78
H	2.69	-3.01	2.47
H	-0.24	-2.02	2.03
H	0.97	-1.07	2.91
H	2.23	1.68	-2.31
H	4.05	3.34	-1.66
H	4.28	3.99	0.78
H	2.69	3.01	2.47
H	0.97	1.07	2.91
H	-0.24	2.02	2.03
H	-1.31	2.47	-2.32
H	-3.25	4.03	-1.76
H	-4.44	3.74	0.45
H	-3.70	1.90	2.03
H	-1.96	0.00	2.49
H	-1.31	-2.47	-2.32
H	-3.25	-4.03	-1.76
H	-4.44	-3.74	0.45
H	-3.70	-1.90	2.03
O	0.28	0.00	-2.40

(N4Py)Fe(III)-OH S=1/2
Gaussian/B3LYP

Fe	0.06	0.00	-0.60
N	1.45	-1.37	-0.28
N	1.45	1.37	-0.28
N	-1.40	1.36	-0.49
N	-1.39	-1.36	-0.49
C	2.30	-1.83	-1.24
C	3.30	-2.76	-0.93
C	3.43	-3.21	0.41
C	2.54	-2.71	1.39
C	1.55	-1.79	1.01
C	2.30	1.83	-1.24
C	3.30	2.77	-0.93
C	3.42	3.21	0.40
C	2.54	2.72	1.39
C	1.55	1.80	1.01
C	-1.68	2.36	-1.36
C	-2.73	3.27	-1.10
C	-3.48	3.13	0.09
C	-3.16	2.09	0.99
C	-2.12	1.22	0.66
C	-1.68	-2.37	-1.36
C	-2.72	-3.27	-1.10
C	-3.47	-3.13	0.09
C	-3.16	-2.09	0.99
C	-2.11	-1.22	0.66
H	2.14	-1.44	-2.24
H	3.96	-3.12	-1.70
H	4.20	-3.92	0.68
H	2.62	-3.04	2.42
H	2.14	1.44	-2.24
H	3.96	3.13	-1.70
H	4.19	3.92	0.68
H	2.62	3.05	2.42
H	-1.07	2.44	-2.25
H	-2.95	4.05	-1.81
H	-4.29	3.82	0.31
H	-3.72	1.97	1.91
H	-1.06	-2.44	-2.25
H	-2.94	-4.06	-1.81
H	-4.28	-3.82	0.31
H	-3.72	-1.97	1.91
N	-0.14	0.00	1.42
C	0.51	-1.26	1.97
C	0.51	1.26	1.97
C	-1.67	0.00	1.47
H	-0.27	-2.02	2.12
H	0.95	-1.06	2.96
H	0.95	1.07	2.96
H	-0.27	2.02	2.12
H	-2.07	0.00	2.48
O	0.31	0.00	-2.40
H	-0.48	0.00	-2.98

(N4Py)Fe(III)-OH S=5/2
Gaussian/B3LYP

Fe	0.11	0.00	0.88
N	1.53	1.48	0.32
N	1.53	-1.48	0.32
N	-1.49	-1.43	0.51
N	-1.49	1.43	0.51
C	2.42	2.02	1.21
C	3.41	2.92	0.81
C	3.49	3.27	-0.56
C	2.58	2.71	-1.47
C	1.60	1.82	-1.00
C	2.42	-2.01	1.21
C	3.41	-2.92	0.81
C	3.49	-3.27	-0.56
C	2.58	-2.71	-1.47
C	1.60	-1.82	-1.00
C	-1.87	-2.44	1.32
C	-2.93	-3.30	0.97
C	-3.59	-3.10	-0.26
C	-3.18	-2.05	-1.10
C	-2.12	-1.23	-0.68
C	-1.88	2.44	1.32
C	-2.93	3.30	0.97
C	-3.59	3.10	-0.26
C	-3.18	2.05	-1.10
C	-2.12	1.23	-0.68
H	2.31	1.70	2.24
H	4.10	3.33	1.54
H	4.26	3.96	-0.90
H	2.63	2.96	-2.52
H	2.31	-1.70	2.24
H	4.10	-3.33	1.54
H	4.26	-3.96	-0.90
H	2.63	-2.96	-2.52
H	-1.34	-2.56	2.26
H	-3.23	-4.10	1.64
H	-4.41	-3.75	-0.55
H	-3.67	-1.88	-2.05
H	-1.34	2.56	2.26
H	-3.23	4.10	1.64
H	-4.41	3.75	-0.55
H	-3.67	1.87	-2.05
N	-0.10	0.00	-1.38
C	0.53	1.25	-1.92
C	0.53	-1.25	-1.92
C	-1.62	0.00	-1.44
H	-0.25	2.01	-2.05
H	0.95	1.07	-2.92
H	0.95	-1.07	-2.92
H	-0.25	-2.02	-2.05
H	-2.00	0.00	-2.47
O	0.26	0.00	2.67
H	0.15	0.00	3.63

(N4Py)Fe(III)-OH S=1/2
Gaussian/BP86

Fe	0.05	0.00	-0.58
N	1.43	-1.35	-0.28
N	1.43	1.35	-0.28
N	-1.38	1.35	-0.49
N	-1.38	-1.35	-0.49
C	2.28	-1.82	-1.25
C	3.29	-2.75	-0.94
C	3.43	-3.21	0.39
C	2.55	-2.72	1.39
C	1.55	-1.80	1.02
C	2.28	1.82	-1.25
C	3.29	2.75	-0.94
C	3.43	3.21	0.39
C	2.55	2.72	1.39
C	1.55	1.80	1.02
C	-1.64	2.37	-1.36
C	-2.69	3.28	-1.12
C	-3.46	3.15	0.06
C	-3.17	2.11	0.98
C	-2.12	1.22	0.67
C	-1.64	-2.37	-1.36
C	-2.69	-3.28	-1.12
C	-3.46	-3.15	0.06
C	-3.17	-2.11	0.98
C	-2.12	-1.22	0.67
H	2.12	-1.42	-2.25
H	3.96	-3.10	-1.73
H	4.22	-3.92	0.66
H	2.63	-3.06	2.42
H	2.12	1.42	-2.25
H	3.96	3.11	-1.73
H	4.21	3.92	0.66
H	2.63	3.06	2.42
H	-1.01	2.43	-2.25
H	-2.89	4.08	-1.84
H	-4.28	3.86	0.27
H	-3.74	1.99	1.90
H	-1.01	-2.43	-2.25
H	-2.89	-4.08	-1.84
H	-4.27	-3.86	0.27
H	-3.74	-1.99	1.90
N	-0.14	0.00	1.43
C	0.50	-1.27	1.99
C	0.50	1.27	1.99
C	-1.69	0.00	1.48
H	-0.29	-2.03	2.12
H	0.93	-1.08	2.98
H	0.93	1.08	2.98
H	-0.29	2.03	2.12
H	-2.10	0.00	2.50
O	0.28	0.00	-2.38
H	-0.55	0.00	-2.93

(N4Py)Fe(III)-OH S=5/2
Gaussian/BP86

Fe	0.11	0.00	0.89
C	-2.13	1.23	-0.69
N	-1.49	1.44	0.51
C	-1.89	2.46	1.33
C	-2.95	3.32	0.97
C	-3.61	3.11	-0.26
C	-3.20	2.06	-1.11
C	-1.63	0.00	-1.45
N	-0.11	0.00	-1.38
C	0.52	-1.26	-1.92
C	1.61	-1.81	-1.00
N	1.53	-1.48	0.32
C	2.43	-2.01	1.22
C	3.44	-2.90	0.81
C	3.53	-3.24	-0.56
C	2.61	-2.69	-1.48
N	1.53	1.48	0.32
C	2.43	2.01	1.22
C	3.44	2.90	0.81
C	3.53	3.25	-0.56
C	2.61	2.69	-1.48
C	1.61	1.81	-1.00
C	0.52	1.26	-1.92
N	-1.49	-1.44	0.51
C	-1.89	-2.46	1.33
C	-2.95	-3.32	0.97
C	-3.61	-3.11	-0.26
C	-3.20	-2.06	-1.11
C	-2.13	-1.23	-0.69
H	2.31	1.70	2.26
H	4.13	3.31	1.55
H	4.31	3.93	-0.91
H	2.66	2.94	-2.54
H	2.31	-1.70	2.26
H	4.13	-3.31	1.55
H	4.31	-3.93	-0.91
H	2.66	-2.94	-2.54
H	-1.34	-2.57	2.27
H	-3.25	-4.12	1.65
H	-4.44	-3.77	-0.56
H	-3.69	-1.88	-2.07
H	-1.34	2.57	2.27
H	-3.25	4.12	1.65
H	-4.44	3.77	-0.56
H	-3.69	1.88	-2.07
H	-0.26	2.03	-2.04
H	0.94	1.08	-2.94
H	0.94	-1.08	-2.94
H	-0.26	-2.03	-2.04
H	-2.01	0.00	-2.49
O	0.24	0.00	2.68
H	-0.07	0.00	3.62