An investigation of steric influence on the reactivity of $Fe^{V}(O)(OH)$ tautomers in stereospecific C-H hydroxylation

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Supporting Information

Table 1. Crystal data for $\mathbf{1}^{\mathbf{OTf}}$

Empirical formula	$C_{17}\,H_{29}\,F_6\,Fe\,N_5\,O_6\,S_2.C_4H_{10}O$
Formula weight	707.54
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.9370(17) Å
	b = 16.024(3) Å
	c = 19.794(4) Å
	α = 90˚
	β = 92.782(3)˚
	γ = 90˚
Volume	2831.29 $Å^3$
Z	4
Density (calculated)	1.660 Mg/m^3
Absorption coefficient	0.771 mm^{-1}
F(000)	1472
Crystal size	0.30 x 0.15 x 0.15 mm^3
Theta range for data collection	1.636 to 28.083 °
Index ranges	-11<=h<=7, -20<=k<=18, -25<=l<=24
Reflections collected	16414
Independent reflections	6388
Completeness	99.8% (theta = 25.242)
Absorption correction	Empirical
Max. and min. transmission	1.0 and 0.707660
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6388/0/338
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0576, wR2 = 0.1346
R indices (all data)	R1 = 0.0976, wR2 = 0.1493
Largest diff. peak and hole	0.571 and -0.768 $e.Å^{-3}$

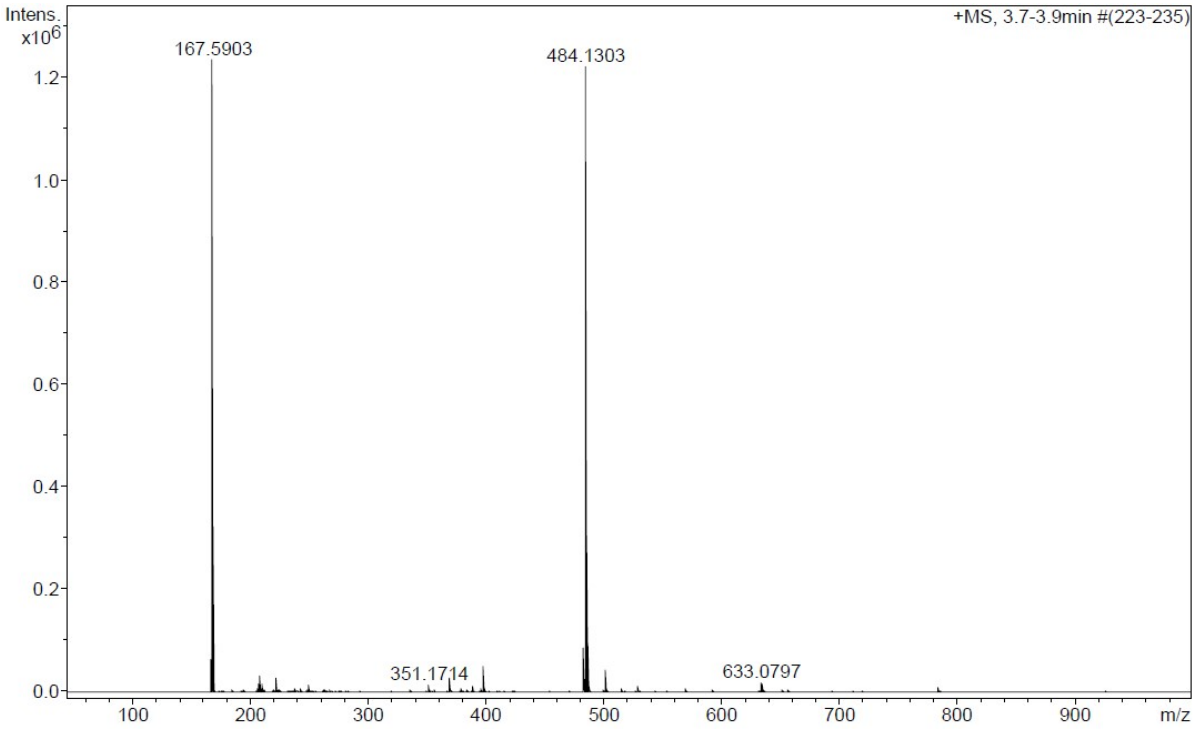

Figure S1. The high resolution mass spectrum (HRMS) of $[Fe^{II}(^{Me2,Me2}PyzTACN)]^{2+}$ (**1**^{Pz}) in CH_3CN.

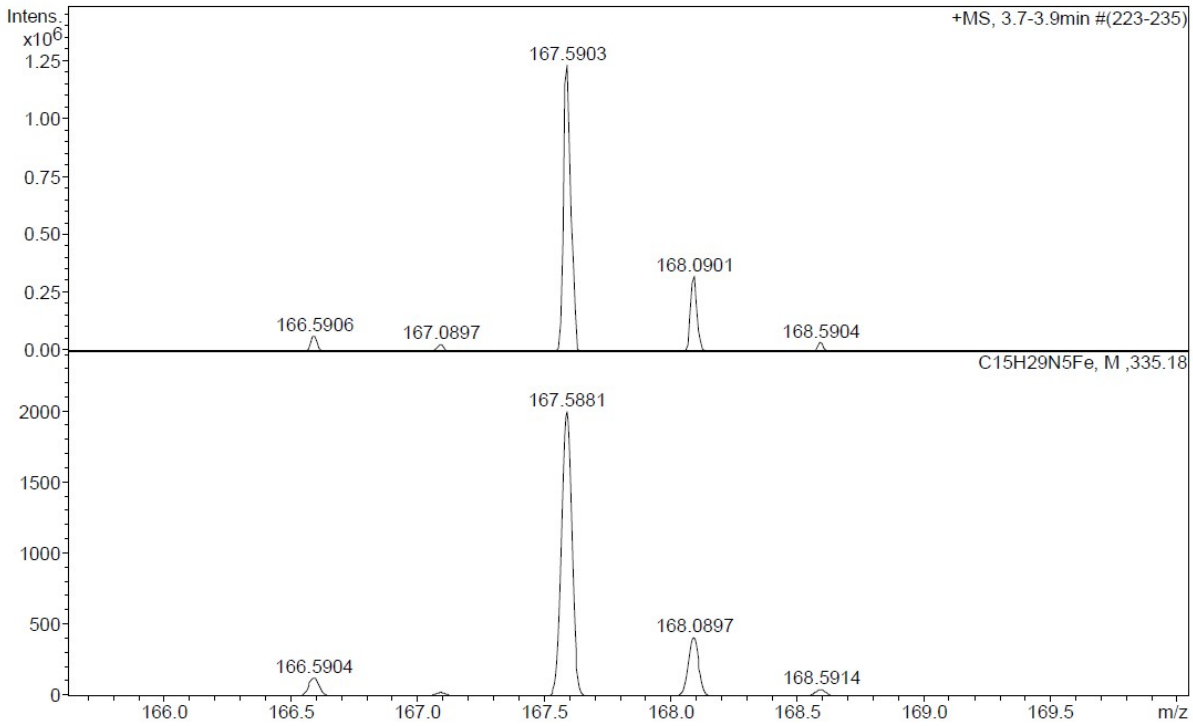

Figure S2. The experimental (top) and simulated (bottom) isotopic distribution patters for $[Fe^{II}(^{Me2,Me2}PyzTACN)]^{2+}$.

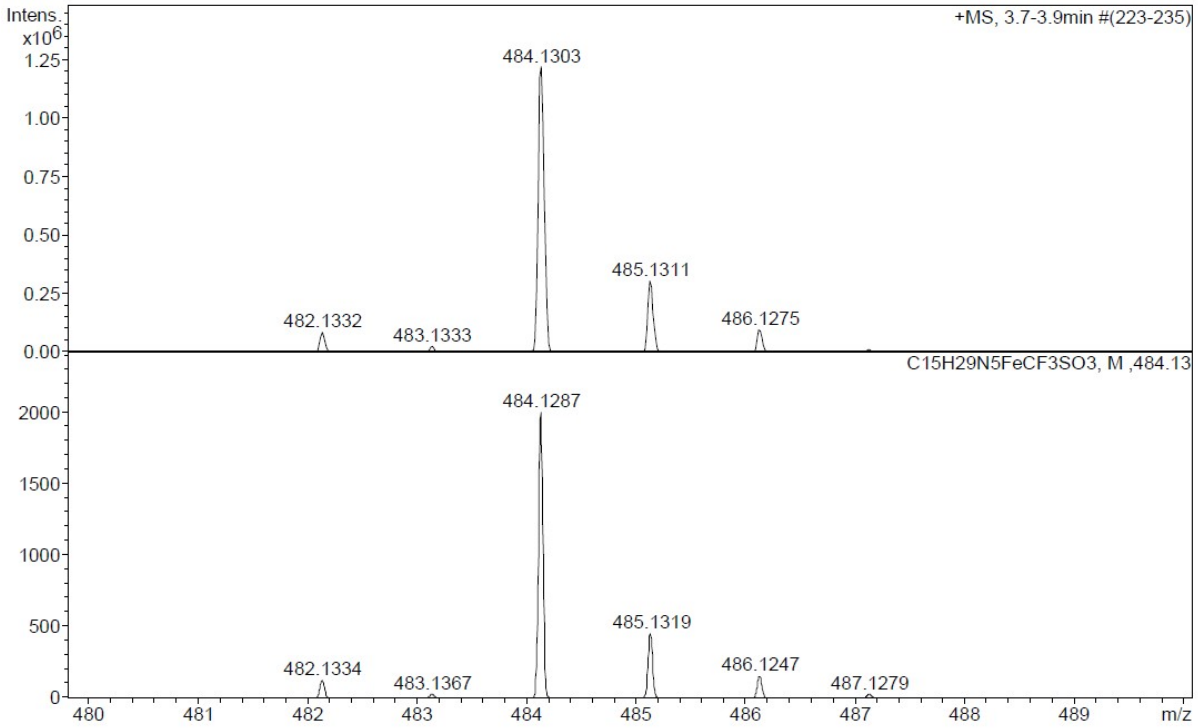

Figure S3. The experimental (top) and simulated (bottom) isotopic distribution patters for $[Fe^{II}(^{Me2,Me2}PyzTACN)(CF_3SO_3)]^+$.

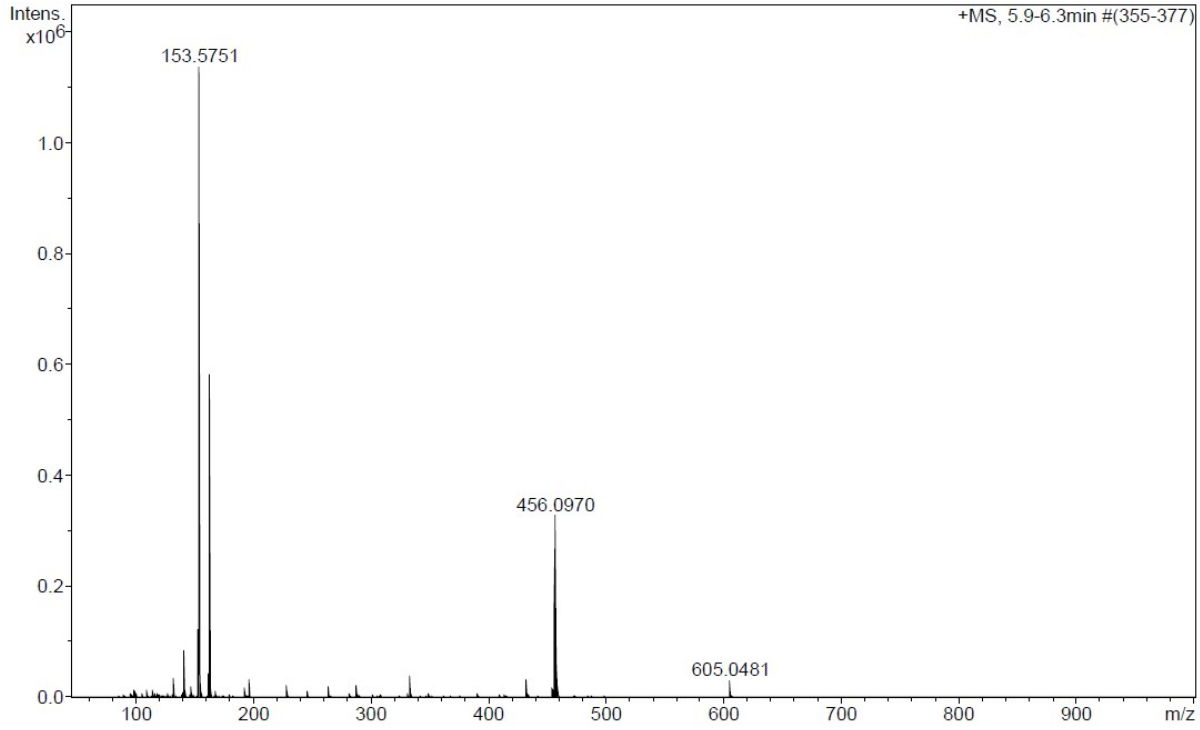

Figure S4. The HRMS of $[Fe^{II}(^{Me2,Me}ImTACN)]^{2+}$ (**1**$^{\mathbf{Im}}$) in CH_3CN.

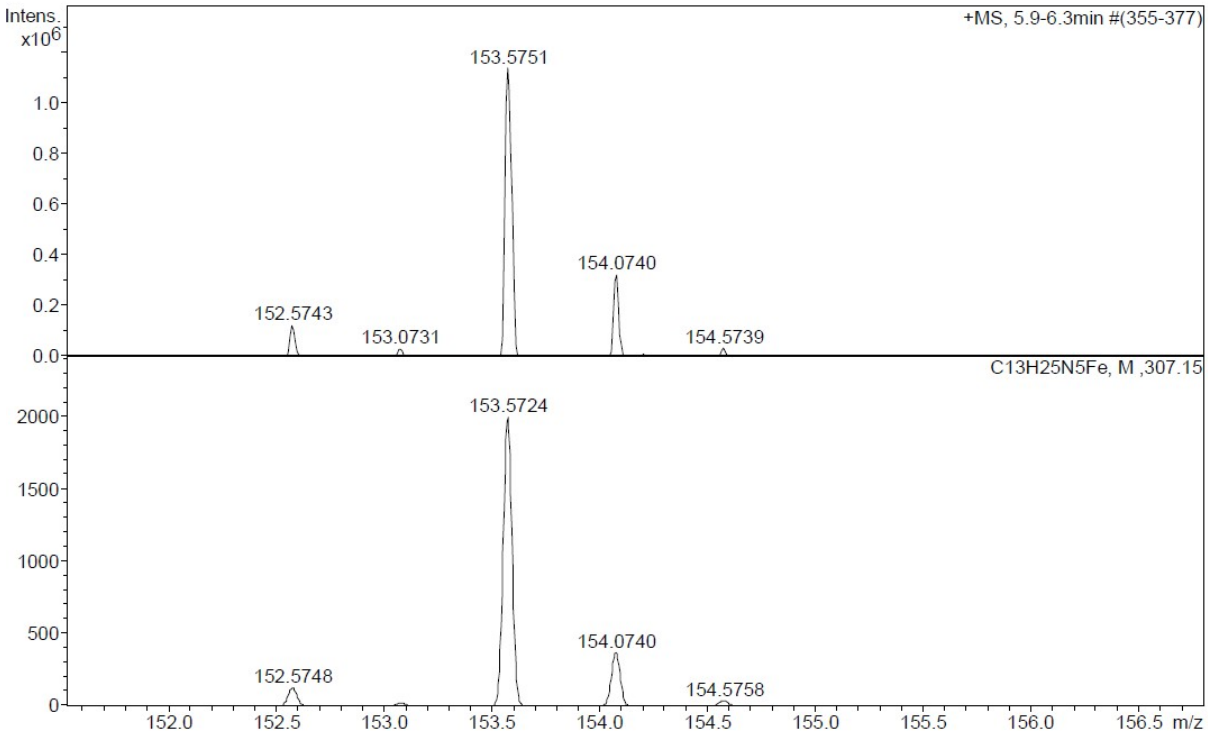

Figure S5. The experimental (top) and simulated (bottom) isotopic distribution patters for $[Fe^{II}(^{Me2,Me}ImTACN)]^{2+}$.

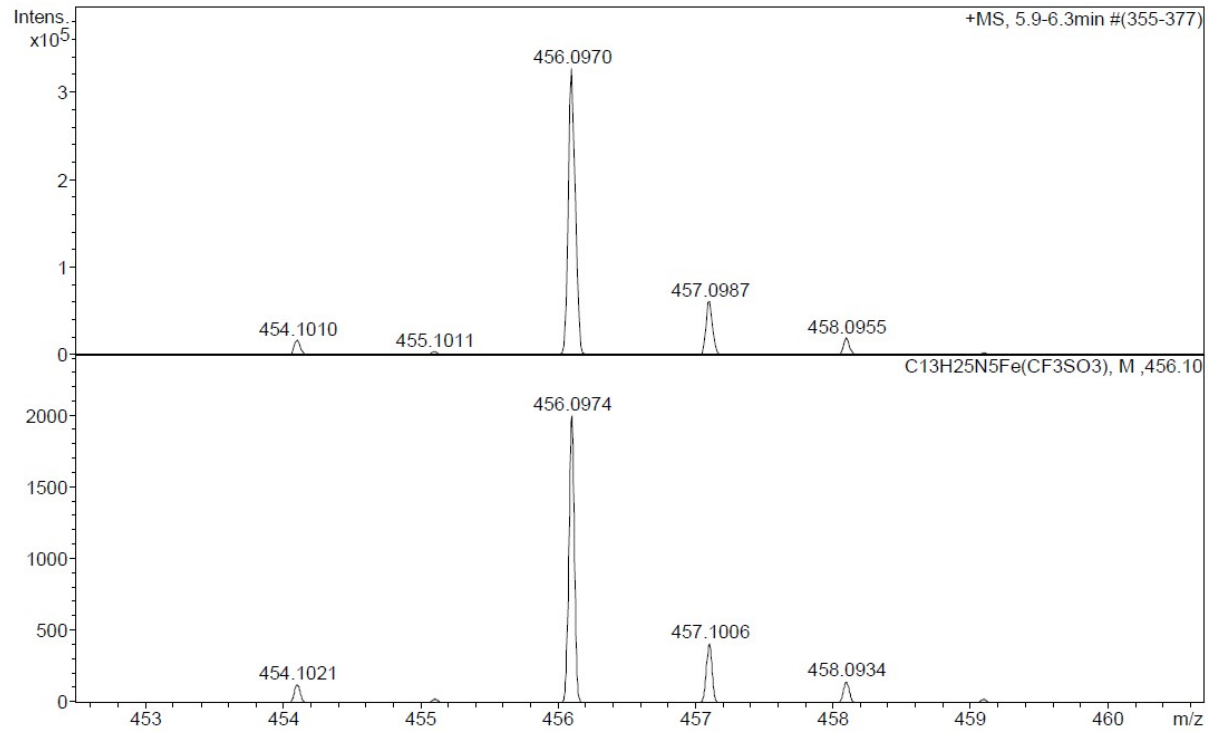

Figure S6. The experimental (top) and simulated (bottom) isotopic distribution patters for $[Fe^{II}(^{Me2,Me}ImTACN)(CF_3SO_3)]^{+}$.

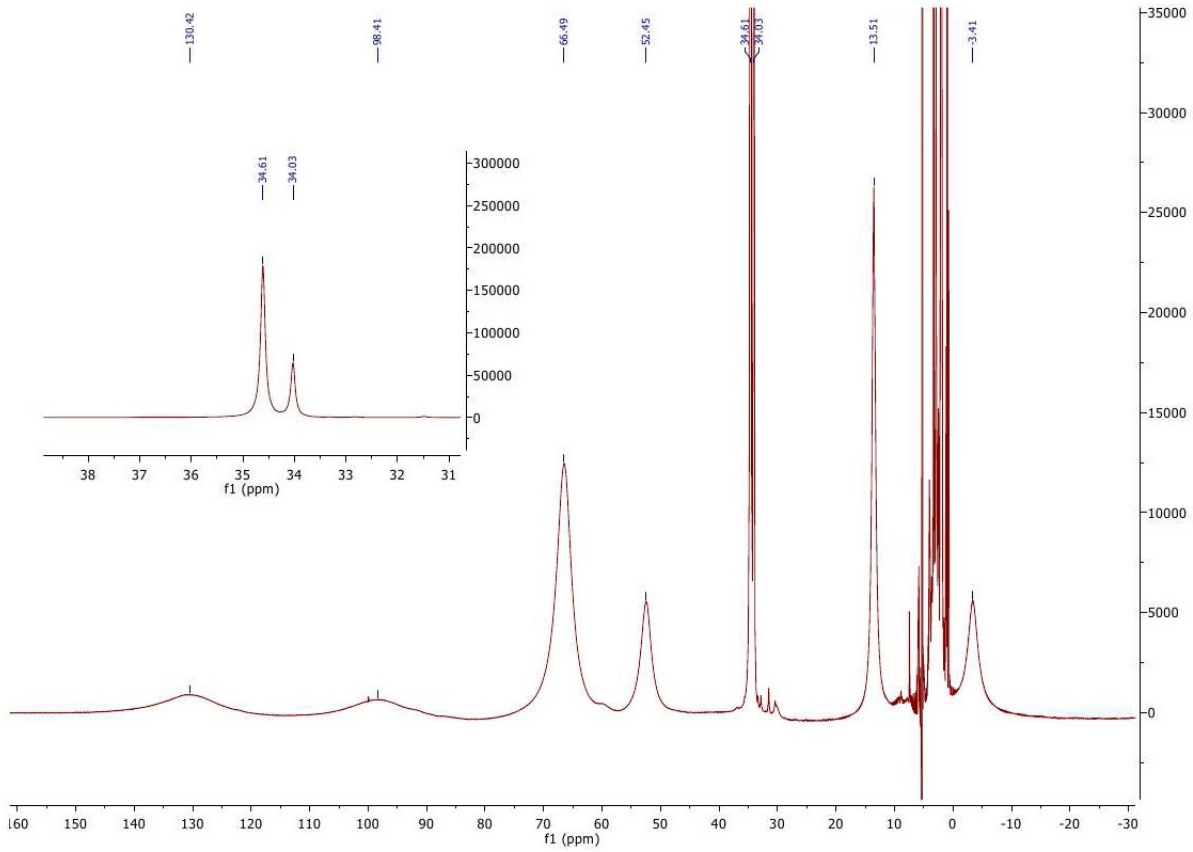

Figure S7. The ^{1}H NMR spectrum of complex $\mathbf{1}^{\mathbf{Pz}}$ in CD_3CN.

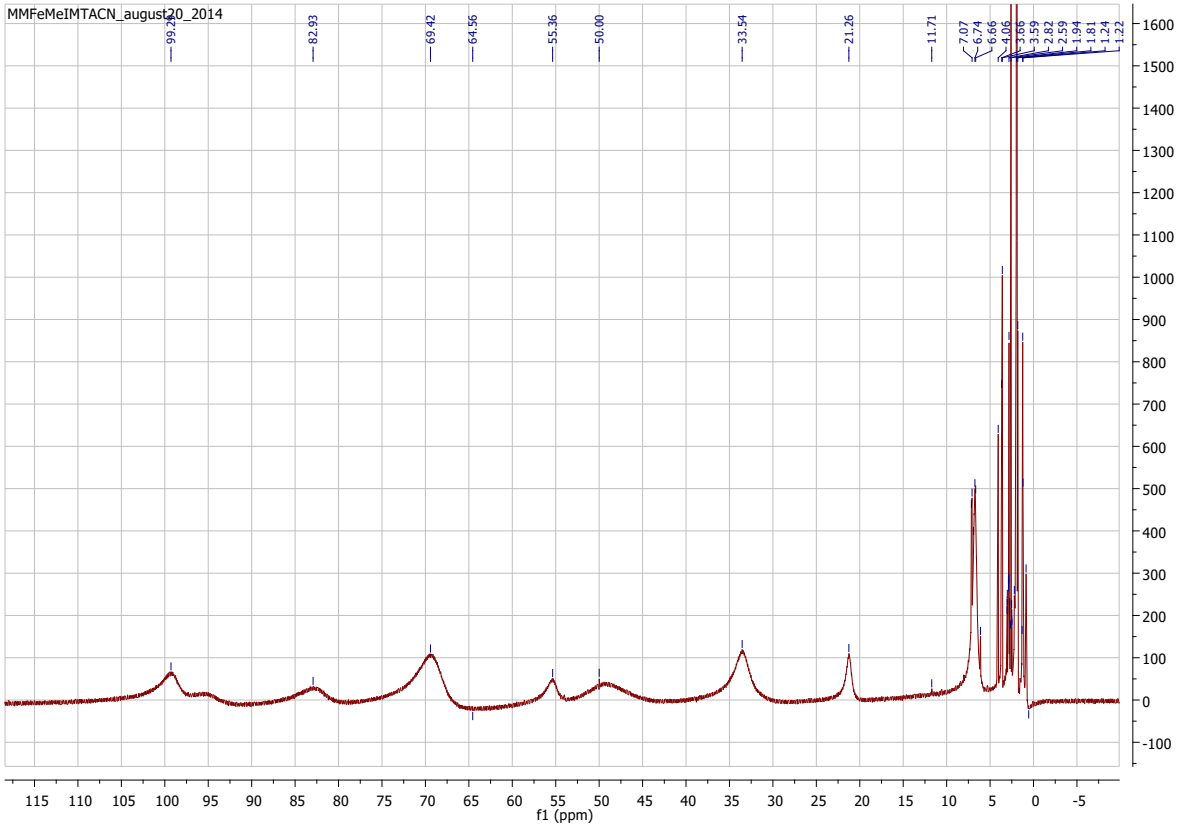

Figure S8. The ^{1}H NMR spectrum of complex $\mathbf{1}^{\mathbf{Im}}$ in CD_3CN.

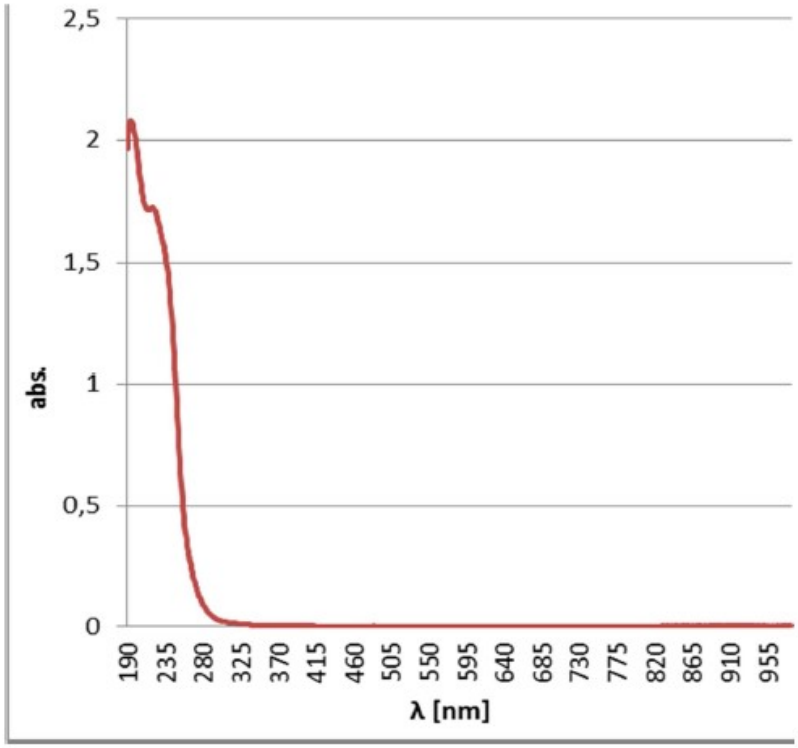

Figure S9. The UV/Vis spectrum of complex $\mathbf{1}^{\mathbf{Pz}}$ in CD_3CN.

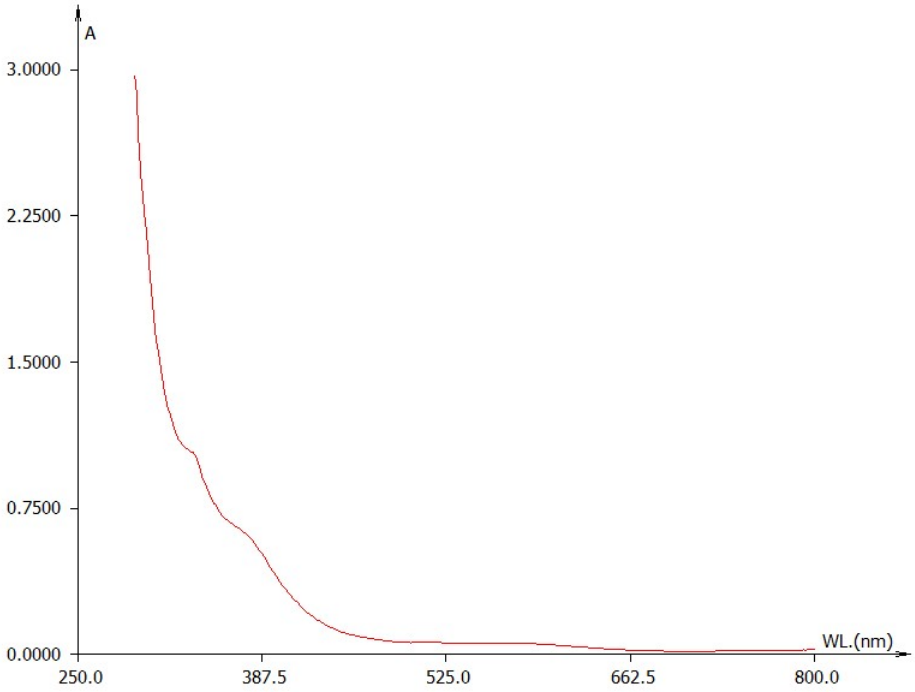

Figure S10. The UV/Vis spectrum of complex $\mathbf{1}^{\mathbf{Im}}$ in CD_3CN.

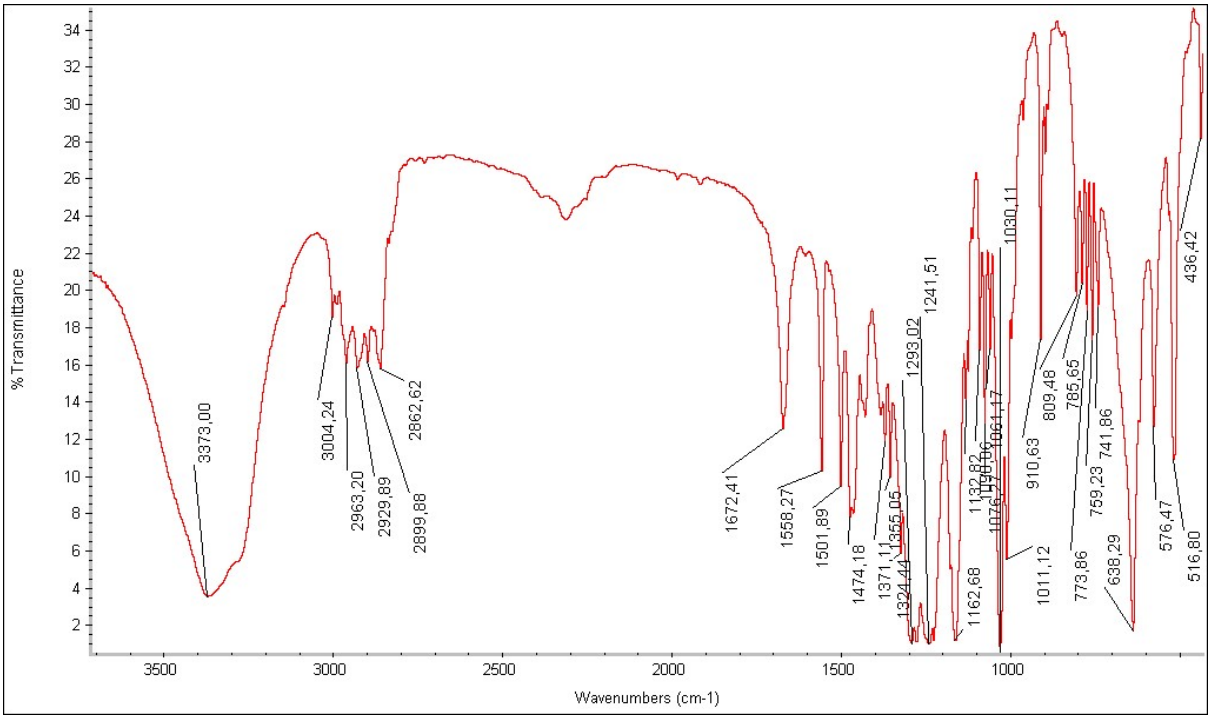

Figure S11. The FT-IR spectrum of complex $\mathbf{1}^{\mathbf{Pz}}$.

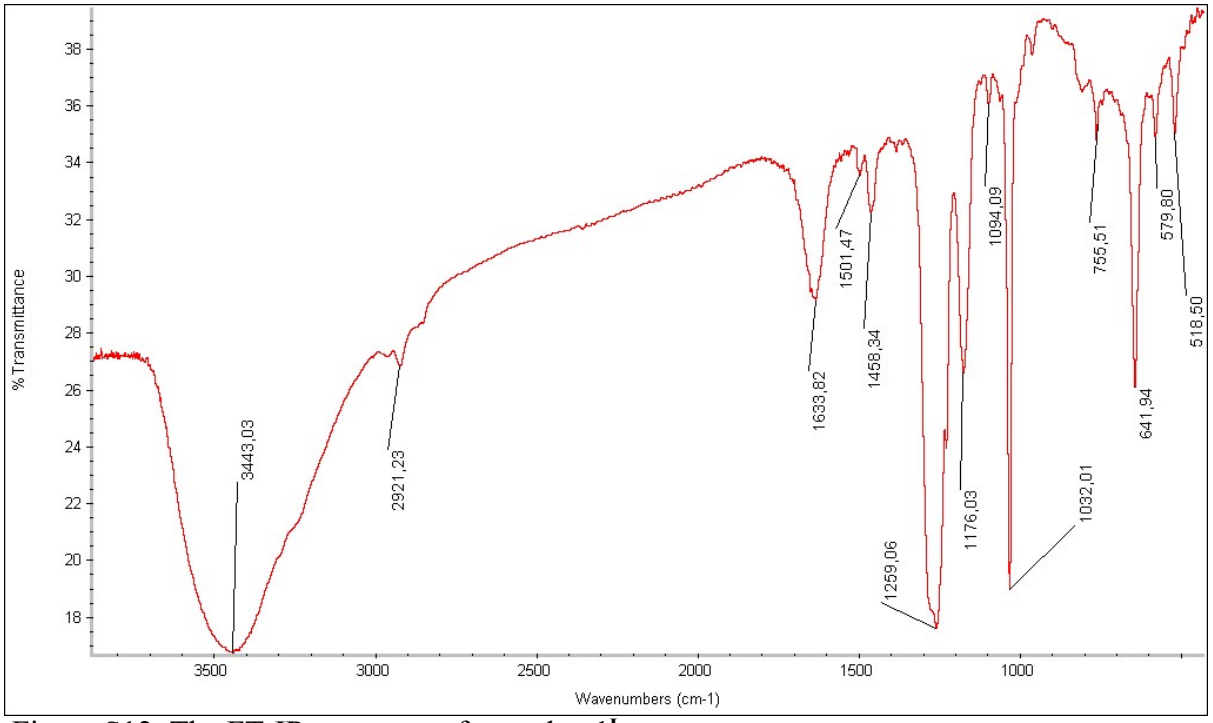

Figure S12. The FT-IR spectrum of complex $\mathbf{1}^{\mathbf{Im}}$.

DFT Data

Species ^{4}A (O_a)
HF energy= -1212.25121978
No Imaginary frequency
Zero-point correction= 0.460418 (Hartree/Particle)
Thermal correction to Energy= 0.483084
Thermal correction to Enthalpy= 0.484028
Thermal correction to Gibbs Free Energy= 0.411269
Sum of electronic and zero-point Energies= -1211.790801
Sum of electronic and thermal Energies= -1211.768136
Sum of electronic and thermal Enthalpies= -1211.767192
Sum of electronic and thermal Free Energies= -1211.839951

Coordinates: **A (O_a)**

Fe	-7.10440000	-0.01020000	-4.24610000
N	-5.97490000	-0.48270000	-5.74440000
C	-5.51410000	-1.66430000	-6.33440000
N	-4.23450000	0.07070000	-7.00790000
C	-5.94080000	-2.99360000	-6.23440000
H	-6.75860000	-3.27980000	-5.58000000
N	-6.69790000	1.94770000	-4.95980000
C	-5.24710000	-3.93790000	-6.98900000
H	-5.54220000	-4.98210000	-6.93140000
N	-8.83300000	0.19990000	-5.49830000
C	-4.16750000	-3.57590000	-7.82090000
H	-3.65720000	-4.34570000	-8.39320000
C	-3.73150000	-2.25550000	-7.92010000
H	-2.89410000	-1.98420000	-8.55670000
N	-8.29790000	0.94040000	-2.84110000
C	-4.42110000	-1.31330000	-7.15460000
C	-3.17260000	0.84160000	-7.66480000
H	-2.19640000	0.48500000	-7.32050000
H	-3.27420000	1.90040000	-7.41980000
H	-3.24870000	0.71460000	-8.74920000
C	-5.16720000	0.51370000	-6.15180000
C	-5.31770000	1.87220000	-5.52980000
H	-4.59920000	1.95860000	-4.70580000
H	-5.13110000	2.69440000	-6.23150000
C	-7.70940000	2.35760000	-5.99820000
H	-7.22070000	2.91990000	-6.80220000
H	-8.41310000	3.05130000	-5.53210000
C	-8.44150000	1.14910000	-6.58260000
H	-9.33140000	1.47860000	-7.13720000
H	-7.80540000	0.60210000	-7.28170000
C	-9.23950000	-1.11020000	-6.09170000
H	-10.08070000	-0.95630000	-6.77980000

H	-9.53690000	-1.79330000	-5.29330000
H	-8.39900000	-1.54340000	-6.63660000
C	-9.96430000	0.75600000	-4.66770000
H	-10.08240000	1.81750000	-4.89890000
H	-10.90310000	0.26920000	-4.95450000
C	-9.70110000	0.54040000	-3.18620000
H	-9.80110000	-0.51640000	-2.92190000
H	-10.41460000	1.11100000	-2.57580000
C	-7.98960000	0.48240000	-1.45000000
H	-8.71630000	0.92710000	-0.75820000
H	-6.98080000	0.79830000	-1.18080000
H	-8.05870000	-0.60700000	-1.40340000
C	-8.07430000	2.43830000	-2.96010000
H	-8.02610000	2.87060000	-1.95480000
H	-8.94920000	2.87920000	-3.44400000
C	-6.78640000	2.78050000	-3.71700000
H	-5.91510000	2.54130000	-3.10460000
H	-6.76450000	3.85330000	-3.95370000
O	-5.69800000	0.20100000	-3.16380000
H	-5.44180000	-0.64040000	-2.74960000
O	-7.52180000	-1.51350000	-3.79660000

Species ^{4}TS^{4}A^{4}B

HF energy= -1212.19319961

One imaginary frequency (2256 *i*)

Zero-point correction= 0.454222 (Hartree/Particle)

Thermal correction to Energy= 0.476940

Thermal correction to Enthalpy= 0.477884

Thermal correction to Gibbs Free Energy= 0.404655

Sum of electronic and zero-point Energies= -1211.738977

Sum of electronic and thermal Energies= -1211.716260

Sum of electronic and thermal Enthalpies= -1211.715316

Sum of electronic and thermal Free Energies= -1211.788545

Coordinates: **^{4}TS^{4}A^{4}B**

Fe	-7.12690000	0.00790000	-4.25670000
N	-5.99060000	-0.47240000	-5.77580000
C	-5.53900000	-1.65480000	-6.36790000
N	-4.22050000	0.06460000	-7.00540000
C	-5.98590000	-2.97920000	-6.28360000
H	-6.81770000	-3.25880000	-5.64390000
N	-6.70100000	1.92750000	-4.95710000
C	-5.29270000	-3.92770000	-7.03170000
H	-5.60210000	-4.96840000	-6.98540000
N	-8.85110000	0.18590000	-5.48980000
C	-4.19490000	-3.57490000	-7.84500000
H	-3.68660000	-4.34850000	-8.41410000
C	-3.73910000	-2.26130000	-7.92880000
H	-2.88790000	-1.99760000	-8.55020000
N	-8.30980000	0.95360000	-2.84380000
C	-4.42660000	-1.31320000	-7.16720000

C	-3.14000000	0.82830000	-7.63970000
H	-2.17300000	0.45530000	-7.28690000
H	-3.23060000	1.88560000	-7.38300000
H	-3.20310000	0.71640000	-8.72650000
C	-5.16200000	0.51040000	-6.15730000
C	-5.31100000	1.85940000	-5.51770000
H	-4.60070000	1.94040000	-4.68530000
H	-5.12500000	2.69550000	-6.20260000
C	-7.71240000	2.33320000	-6.00680000
H	-7.21100000	2.87940000	-6.81340000
H	-8.40730000	3.04010000	-5.54770000
C	-8.45880000	1.12530000	-6.58250000
H	-9.34630000	1.46320000	-7.13560000
H	-7.82850000	0.57120000	-7.28060000
C	-9.24630000	-1.13970000	-6.05730000
H	-10.10640000	-1.01340000	-6.72740000
H	-9.50970000	-1.81810000	-5.24260000
H	-8.40980000	-1.56290000	-6.61570000
C	-9.98240000	0.74740000	-4.66440000
H	-10.10490000	1.80650000	-4.90580000
H	-10.92160000	0.25600000	-4.94220000
C	-9.71370000	0.54600000	-3.18110000
H	-9.80750000	-0.50940000	-2.90830000
H	-10.42740000	1.11830000	-2.57230000
C	-7.99430000	0.51640000	-1.44660000
H	-8.68880000	1.00610000	-0.75240000
H	-6.96640000	0.79220000	-1.19960000
H	-8.10860000	-0.56720000	-1.36830000
C	-8.08790000	2.44970000	-2.97520000
H	-8.05480000	2.89710000	-1.97590000
H	-8.95170000	2.88670000	-3.48150000
C	-6.78660000	2.76360000	-3.71320000
H	-5.92720000	2.50140000	-3.09030000
H	-6.72830000	3.83430000	-3.95230000
O	-5.79940000	-0.06900000	-3.14990000
H	-6.36870000	-1.20200000	-3.05090000
O	-7.41730000	-1.57740000	-3.65180000

Species ^{4}B (O_b)

HF energy= -1212.24702836

No Imaginary frequency

Zero-point correction= 0.460302 (Hartree/Particle)

Thermal correction to Energy= 0.483071

Thermal correction to Enthalpy= 0.484015

Thermal correction to Gibbs Free Energy= 0.410869

Sum of electronic and zero-point Energies= -1211.786727

Sum of electronic and thermal Energies= -1211.763958

Sum of electronic and thermal Enthalpies= -1211.763013

Sum of electronic and thermal Free Energies= -1211.836159

Coordinates: **^{4}B (O_b)**

Fe	-7.08070000	0.00770000	-4.20510000
N	-5.94470000	-0.46700000	-5.74020000

C	-5.49360000	-1.64780000	-6.33770000
N	-4.20070000	0.08210000	-7.00100000
C	-5.93530000	-2.97440000	-6.26000000
H	-6.76830000	-3.25770000	-5.62440000
N	-6.69710000	1.92650000	-4.95760000
C	-5.24740000	-3.91590000	-7.02100000
H	-5.55600000	-4.95710000	-6.98100000
N	-8.84390000	0.16920000	-5.47310000
C	-4.15770000	-3.55560000	-7.84220000
H	-3.65240000	-4.32430000	-8.42050000
C	-3.71100000	-2.23970000	-7.92590000
H	-2.87100000	-1.96760000	-8.55900000
N	-8.27690000	0.98760000	-2.82550000
C	-4.39430000	-1.29770000	-7.15230000
C	-3.14400000	0.85610000	-7.66190000
H	-2.16500000	0.49450000	-7.33100000
H	-3.23970000	1.91280000	-7.40440000
H	-3.23080000	0.74180000	-8.74690000
C	-5.13570000	0.52150000	-6.14150000
C	-5.30540000	1.87500000	-5.52060000
H	-4.59510000	1.98350000	-4.69160000
H	-5.13940000	2.70460000	-6.21810000
C	-7.71330000	2.31120000	-6.01130000
H	-7.21480000	2.85240000	-6.82290000
H	-8.41180000	3.01840000	-5.55840000
C	-8.45270000	1.09550000	-6.57140000
H	-9.33560000	1.42880000	-7.13560000
H	-7.81740000	0.53630000	-7.26140000
C	-9.26410000	-1.14300000	-6.04760000
H	-10.11640000	-0.99770000	-6.72430000
H	-9.54490000	-1.81910000	-5.23840000
H	-8.43220000	-1.58300000	-6.60080000
C	-9.96130000	0.74280000	-4.64280000
H	-10.09260000	1.79810000	-4.89740000
H	-10.90610000	0.24800000	-4.89520000
C	-9.67910000	0.56490000	-3.15720000
H	-9.76420000	-0.48660000	-2.87080000
H	-10.39050000	1.14360000	-2.55180000
C	-7.95000000	0.56960000	-1.42580000
H	-8.65170000	1.05330000	-0.73460000
H	-6.92660000	0.86340000	-1.18360000
H	-8.04670000	-0.51410000	-1.33840000
C	-8.07290000	2.48350000	-2.97990000
H	-8.03440000	2.94520000	-1.98730000
H	-8.94720000	2.90200000	-3.48340000
C	-6.78540000	2.79880000	-3.73810000
H	-5.91490000	2.57550000	-3.11640000
H	-6.75020000	3.86120000	-4.01590000
O	-5.79720000	0.09240000	-3.20520000
O	-7.62450000	-1.60630000	-3.75590000
H	-7.00740000	-2.04400000	-3.14250000

Species C

HF energy= -40.5168640094

No Imaginary frequency

Zero-point correction= 0.045075 (Hartree/Particle)
Thermal correction to Energy= 0.047941
Thermal correction to Enthalpy= 0.048885
Thermal correction to Gibbs Free Energy= 0.025402
Sum of electronic and zero-point Energies= -40.471789
Sum of electronic and thermal Energies= -40.468923
Sum of electronic and thermal Enthalpies= -40.467979
Sum of electronic and thermal Free Energies= -40.491462

Coordinates: **C**

C	0.00740000	0.33430000	-0.00440000
H	0.37240000	-0.69790000	-0.00440000
H	0.37240000	0.85040000	0.88950000
H	0.37240000	0.85040000	-0.89830000
H	-1.08740000	0.33430000	-0.00440000

Species ^{4}TS^{4}AC^{6}D
HF energy= -1252.73959494
One imaginary frequency (1635 *i*)
Zero-point correction= 0.499767 (Hartree/Particle)
Thermal correction to Energy= 0.526042
Thermal correction to Enthalpy= 0.526986
Thermal correction to Gibbs Free Energy= 0.445242
Sum of electronic and zero-point Energies= -1252.239828
Sum of electronic and thermal Energies= -1252.213553
Sum of electronic and thermal Enthalpies= -1252.212609
Sum of electronic and thermal Free Energies= -1252.294353

Coordinates: **^{4}TS^{4}AC^{6}D**

Fe	-7.28600000	-0.00430000	-4.31640000
N	-6.06510000	-0.47970000	-5.76250000
C	-5.66340000	-1.63750000	-6.43700000
N	-4.21400000	0.03490000	-6.88060000
C	-6.20450000	-2.92790000	-6.49900000
H	-7.09650000	-3.19290000	-5.94030000
N	-6.70230000	1.91950000	-4.88170000
C	-5.54240000	-3.85590000	-7.29950000
H	-5.93160000	-4.86810000	-7.37060000
N	-8.90530000	0.32980000	-5.66620000
C	-4.37860000	-3.51780000	-8.02170000
H	-3.89600000	-4.27380000	-8.63500000
C	-3.83140000	-2.23820000	-7.96490000
H	-2.93360000	-1.98320000	-8.52080000
N	-8.51030000	0.95160000	-2.94660000
C	-4.49440000	-1.31090000	-7.15720000
C	-3.06040000	0.77250000	-7.40660000
H	-2.13530000	0.31360000	-7.04300000
H	-3.09870000	1.81110000	-7.07240000
H	-3.07750000	0.74630000	-8.50060000
C	-5.16790000	0.47670000	-6.04380000
C	-5.28500000	1.79880000	-5.34570000
H	-4.63500000	1.79090000	-4.46290000

H	-4.99990000	2.65110000	-5.97470000
C	-7.60760000	2.43590000	-5.97170000
H	-7.02410000	2.99560000	-6.71150000
H	-8.29860000	3.15480000	-5.52550000
C	-8.37370000	1.30580000	-6.66590000
H	-9.19440000	1.72540000	-7.26470000
H	-7.72240000	0.75290000	-7.34590000
C	-9.35790000	-0.90960000	-6.36320000
H	-10.14630000	-0.66210000	-7.08600000
H	-9.73830000	-1.61890000	-5.62590000
H	-8.51450000	-1.36270000	-6.88710000
C	-10.05390000	0.92600000	-4.88970000
H	-10.09610000	2.00050000	-5.08730000
H	-11.00010000	0.50900000	-5.25240000
C	-9.90500000	0.64440000	-3.40290000
H	-10.07400000	-0.41530000	-3.19410000
H	-10.62950000	1.22970000	-2.81970000
C	-8.32490000	0.43290000	-1.55730000
H	-9.05730000	0.91080000	-0.89420000
H	-7.31190000	0.65740000	-1.22080000
H	-8.48080000	-0.64750000	-1.55480000
C	-8.19960000	2.43500000	-2.98570000
H	-8.21810000	2.83400000	-1.96570000
H	-8.99800000	2.94360000	-3.53120000
C	-6.83180000	2.70620000	-3.61180000
H	-6.03940000	2.36510000	-2.94280000
H	-6.70010000	3.78120000	-3.79670000
O	-5.95350000	0.00290000	-3.12030000
H	-5.69370000	-0.88990000	-2.84130000
O	-7.90180000	-1.59390000	-3.96880000
C	-6.61300000	-3.34220000	-2.62520000
H	-7.25630000	-2.36860000	-3.33020000
H	-5.70310000	-3.53990000	-3.19530000
H	-6.46040000	-2.92830000	-1.62600000
H	-7.35970000	-4.13730000	-2.67090000

Species ^{6}D

HF energy= -1252.85697547

No Imaginary frequency

Zero-point correction= 0.507674 (Hartree/Particle)

Thermal correction to Energy= 0.535001

Thermal correction to Enthalpy= 0.535945

Thermal correction to Gibbs Free Energy= 0.451537

Sum of electronic and zero-point Energies= -1252.349302

Sum of electronic and thermal Energies= -1252.321975

Sum of electronic and thermal Enthalpies= -1252.321030

Sum of electronic and thermal Free Energies= -1252.405439

Coordinates: **^{6}D**

Fe	-7.16820000	-0.12250000	-4.21490000
N	-5.89130000	-0.52790000	-5.85090000
C	-5.44790000	-1.61320000	-6.61300000
N	-4.14850000	0.16250000	-7.06450000

C	-5.90740000	-2.93360000	-6.70740000
H	-6.74650000	-3.28730000	-6.11420000
N	-6.64110000	1.92420000	-4.94790000
C	-5.24050000	-3.78500000	-7.58380000
H	-5.56880000	-4.81650000	-7.67950000
N	-8.98330000	0.31900000	-5.61500000
C	-4.14280000	-3.34190000	-8.35180000
H	-3.65000000	-4.03950000	-9.02360000
C	-3.67460000	-2.03310000	-8.26790000
H	-2.82780000	-1.69850000	-8.86040000
N	-8.47090000	1.11520000	-2.87940000
C	-4.34890000	-1.18480000	-7.38540000
C	-3.08160000	0.99790000	-7.62300000
H	-2.10720000	0.56750000	-7.36930000
H	-3.13980000	2.00660000	-7.21030000
H	-3.18540000	1.04870000	-8.71160000
C	-5.08640000	0.49720000	-6.15260000
C	-5.24290000	1.81590000	-5.44420000
H	-4.56710000	1.84480000	-4.58010000
H	-4.98580000	2.66790000	-6.08750000
C	-7.58420000	2.37050000	-6.02700000
H	-7.02860000	2.87600000	-6.82640000
H	-8.25090000	3.12650000	-5.60510000
C	-8.39500000	1.22370000	-6.64440000
H	-9.18640000	1.65110000	-7.27900000
H	-7.75890000	0.61030000	-7.28730000
C	-9.54380000	-0.87620000	-6.29830000
H	-10.26270000	-0.58880000	-7.07870000
H	-10.08160000	-1.49960000	-5.57460000
H	-8.73770000	-1.45280000	-6.76460000
C	-10.05420000	1.01460000	-4.82310000
H	-10.06110000	2.07590000	-5.08610000
H	-11.04180000	0.63320000	-5.10910000
C	-9.86760000	0.83000000	-3.31700000
H	-10.08120000	-0.20700000	-3.03460000
H	-10.58310000	1.46610000	-2.77450000
C	-8.29660000	0.69240000	-1.45840000
H	-8.98910000	1.24710000	-0.81080000
H	-7.26580000	0.87290000	-1.14990000
H	-8.50340000	-0.37730000	-1.36560000
C	-8.10630000	2.56540000	-3.03360000
H	-8.07760000	3.04610000	-2.04870000
H	-8.89530000	3.07450000	-3.59340000
C	-6.74370000	2.75490000	-3.70850000
H	-5.95010000	2.42100000	-3.03440000
H	-6.58370000	3.82030000	-3.93040000
O	-5.89590000	-0.23330000	-2.90500000
H	-5.02940000	-0.65960000	-2.95770000
H	-8.61020000	-2.45940000	-4.42500000
O	-7.98510000	-2.03670000	-3.82010000
C	-7.50820000	-3.01490000	-2.83630000
H	-8.36880000	-3.44320000	-2.31470000
H	-6.93290000	-3.79380000	-3.34540000
H	-6.87520000	-2.46090000	-2.14450000

Species ^{4}TS^{4}BC^{6}E
HF energy= -1252.74011685
One imaginary frequency (1582 *i*)
Zero-point correction= 0.500130 (Hartree/Particle)
Thermal correction to Energy= 0.526268
Thermal correction to Enthalpy= 0.527212
Thermal correction to Gibbs Free Energy= 0.445990
Sum of electronic and zero-point Energies= -1252.239987
Sum of electronic and thermal Energies= -1252.213849
Sum of electronic and thermal Enthalpies= -1252.212905
Sum of electronic and thermal Free Energies= -1252.294127

Coordinates: **^{4}TS^{4}BC^{6}E**

Fe	-7.14130000	0.12180000	-4.18130000
N	-6.22210000	-0.50490000	-5.80880000
C	-6.15940000	-1.67000000	-6.57740000
N	-4.59860000	-0.20850000	-7.29990000
C	-6.88930000	-2.86590000	-6.53530000
H	-7.67050000	-3.02410000	-5.79820000
N	-6.35280000	1.94220000	-4.84840000
C	-6.56120000	-3.84090000	-7.47350000
H	-7.10330000	-4.78290000	-7.47100000
N	-8.87680000	0.75490000	-5.26820000
C	-5.54130000	-3.64060000	-8.42900000
H	-5.32110000	-4.42960000	-9.14280000
C	-4.80750000	-2.45850000	-8.47630000
H	-4.02070000	-2.31120000	-9.21070000
N	-7.94090000	1.23850000	-2.63620000
C	-5.13410000	-1.48210000	-7.53060000
C	-3.49430000	0.38550000	-8.06030000
H	-2.59430000	-0.22630000	-7.94080000
H	-3.28940000	1.39340000	-7.69410000
H	-3.76390000	0.43640000	-9.12000000
C	-5.27520000	0.32220000	-6.26300000
C	-5.06350000	1.61890000	-5.54210000
H	-4.28920000	1.48760000	-4.77720000
H	-4.75690000	2.44160000	-6.19900000
C	-7.32600000	2.62690000	-5.78090000
H	-6.78030000	3.10530000	-6.60170000
H	-7.81030000	3.43460000	-5.22780000
C	-8.36220000	1.65240000	-6.34270000
H	-9.18600000	2.21310000	-6.80710000
H	-7.92350000	1.01800000	-7.11590000
C	-9.63300000	-0.37750000	-5.87780000
H	-10.47440000	0.01120000	-6.46640000
H	-10.00310000	-1.03120000	-5.08630000
H	-8.96950000	-0.95190000	-6.52680000
C	-9.76590000	1.50780000	-4.31090000
H	-9.67060000	2.58020000	-4.50270000
H	-10.81450000	1.25480000	-4.50340000
C	-9.42300000	1.17520000	-2.86450000
H	-9.73220000	0.15530000	-2.62300000
H	-9.93640000	1.86200000	-2.17740000
C	-7.62670000	0.67210000	-1.28850000

H	-8.14130000	1.26420000	-0.52110000
H	-6.54860000	0.69630000	-1.12550000
H	-7.97640000	-0.36090000	-1.23890000
C	-7.40700000	2.65420000	-2.73170000
H	-7.19010000	3.02760000	-1.72510000
H	-8.19210000	3.29690000	-3.13720000
C	-6.13910000	2.71330000	-3.57930000
H	-5.31300000	2.23330000	-3.04990000
H	-5.86320000	3.75460000	-3.79560000
O	-5.71550000	-0.15830000	-3.19810000
O	-8.00260000	-1.35340000	-3.74700000
H	-7.49510000	-1.90650000	-3.12930000
C	-4.29600000	-2.26060000	-3.38100000
H	-5.06720000	-1.16330000	-3.35460000
H	-4.39420000	-2.64380000	-2.36340000
H	-4.73100000	-2.89210000	-4.15760000
H	-3.30720000	-1.86070000	-3.61300000

Species ^{6}E

HF energy= -1252.86026806

No Imaginary frequency

Zero-point correction= 0.506982 (Hartree/Particle)

Thermal correction to Energy= 0.534811

Thermal correction to Enthalpy= 0.535755

Thermal correction to Gibbs Free Energy= 0.449891

Sum of electronic and zero-point Energies= -1252.353286

Sum of electronic and thermal Energies= -1252.325457

Sum of electronic and thermal Enthalpies= -1252.324513

Sum of electronic and thermal Free Energies= -1252.410377

Coordinates: **^{6}E**

Fe	-7.43650000	-0.25080000	-4.31950000
N	-5.98050000	-0.59820000	-5.75850000
C	-5.55970000	-1.68990000	-6.52650000
N	-4.20030000	0.05300000	-6.93390000
C	-6.06650000	-2.99070000	-6.63890000
H	-6.93560000	-3.30800000	-6.06890000
N	-6.70010000	1.87050000	-4.88720000
C	-5.40790000	-3.85520000	-7.50980000
H	-5.76920000	-4.87380000	-7.62380000
N	-9.04100000	0.36890000	-5.71490000
C	-4.28030000	-3.44210000	-8.25120000
H	-3.79760000	-4.15000000	-8.91950000
C	-3.76980000	-2.14960000	-8.14890000
H	-2.90170000	-1.83920000	-8.72350000
N	-8.62570000	1.05690000	-2.91510000
C	-4.43380000	-1.28750000	-7.27250000
C	-3.10570000	0.86350000	-7.47540000
H	-2.14550000	0.40960000	-7.20940000
H	-3.14630000	1.87320000	-7.06290000
H	-3.19330000	0.91660000	-8.56540000
C	-5.14300000	0.40880000	-6.03710000
C	-5.28800000	1.72520000	-5.32240000

H	-4.64720000	1.72170000	-4.43160000
H	-4.97050000	2.57240000	-5.94540000
C	-7.57310000	2.38810000	-5.99460000
H	-6.96340000	2.90110000	-6.74890000
H	-8.23370000	3.15350000	-5.57990000
C	-8.39530000	1.29310000	-6.68850000
H	-9.15320000	1.76540000	-7.33140000
H	-7.75810000	0.68380000	-7.33460000
C	-9.57610000	-0.82830000	-6.42780000
H	-10.31810000	-0.52370000	-7.17820000
H	-10.03440000	-1.50400000	-5.70320000
H	-8.75620000	-1.35430000	-6.92510000
C	-10.13080000	1.04670000	-4.93350000
H	-10.11610000	2.11710000	-5.15740000
H	-11.10780000	0.68150000	-5.27100000
C	-10.00980000	0.79800000	-3.43000000
H	-10.23600000	-0.24870000	-3.20360000
H	-10.73850000	1.42450000	-2.89430000
C	-8.56480000	0.61100000	-1.49580000
H	-9.35250000	1.09480000	-0.90170000
H	-7.60410000	0.89830000	-1.05270000
H	-8.69590000	-0.47350000	-1.44270000
C	-8.23070000	2.50180000	-3.02600000
H	-8.24230000	2.97150000	-2.03520000
H	-8.98220000	3.03390000	-3.61420000
C	-6.83590000	2.67340000	-3.63980000
H	-6.07320000	2.31440000	-2.94130000
H	-6.64280000	3.74170000	-3.81990000
O	-8.17510000	-1.83410000	-3.87660000
H	-7.96790000	-2.68250000	-3.46820000
H	-6.12950000	-0.18660000	-1.89410000
O	-5.80260000	-0.32100000	-2.79490000
C	-4.78950000	-1.37130000	-2.74610000
H	-3.94830000	-1.02990000	-2.13540000
H	-5.21440000	-2.29160000	-2.33200000
H	-4.46550000	-1.54230000	-3.77220000

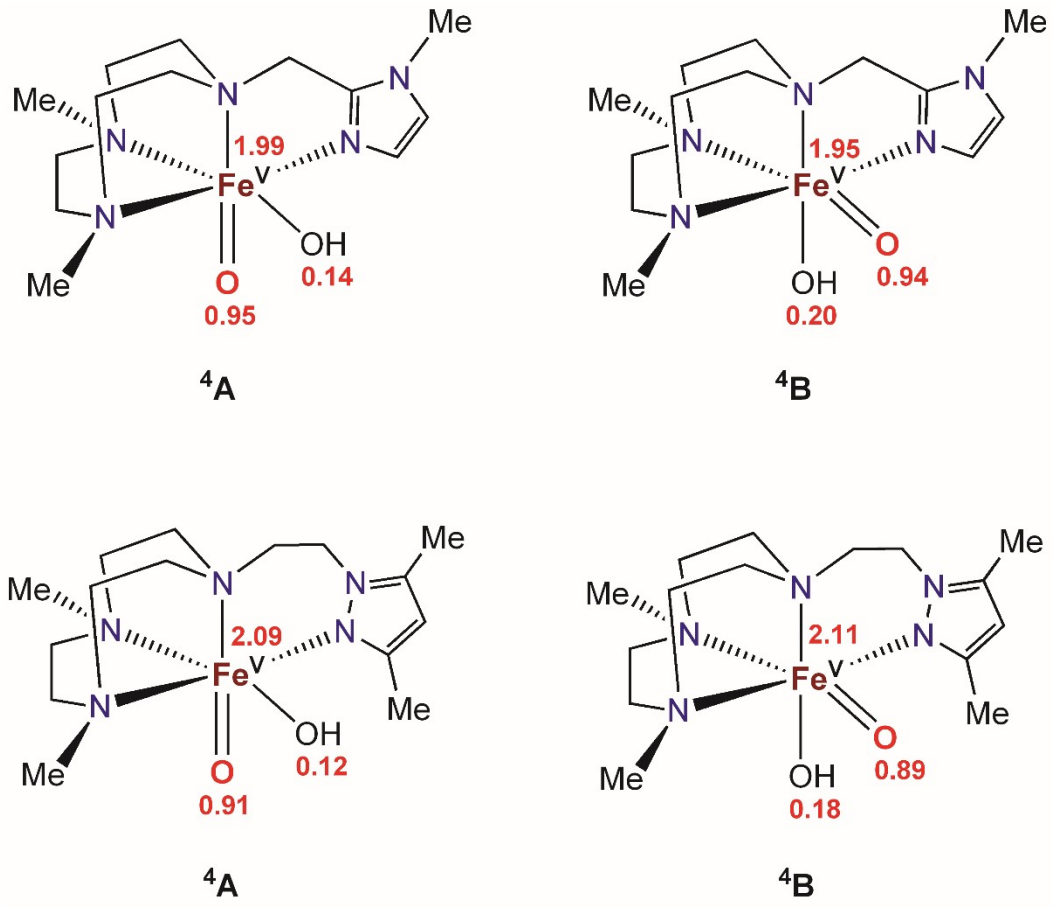

Figure S13. Spin densities for the two tautomers of $[Fe^{IV}(O)(^{Me2,Me}ImTACN)]^{2+}$ (**2**^{Im}, top) and $[Fe^{IV}(O)(^{Me2,Me2}PyzTACN)]^{2+}$ (**2**^{Pz}, bottom); $^4A = O_A$, $^4B = O_B$.

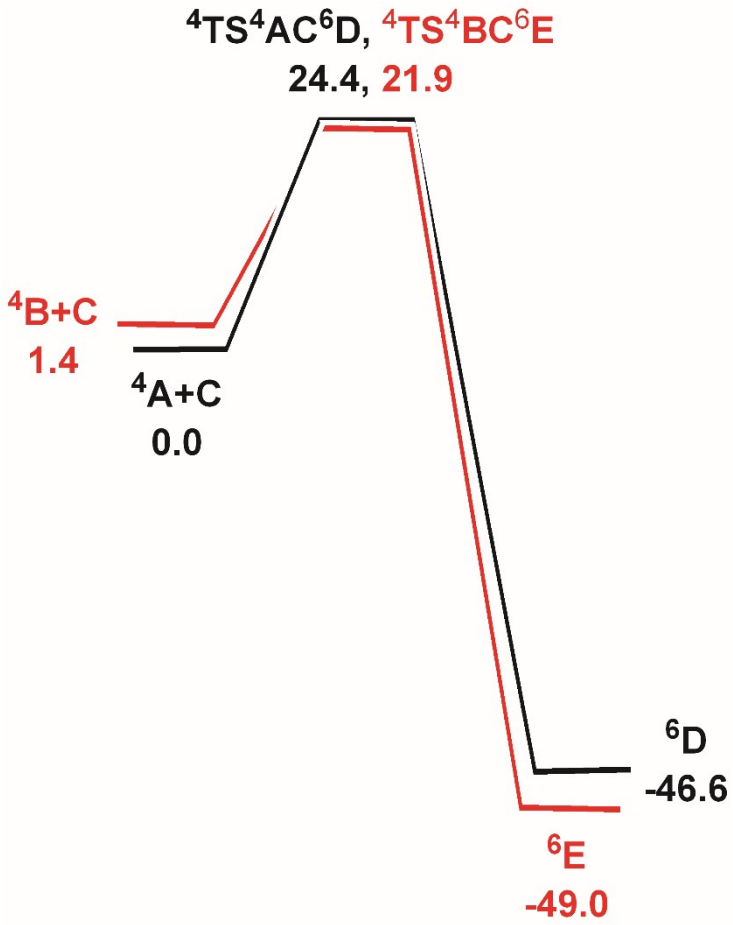

Figure S14. Potential energy profiles for C-H activation of methane by the two tautomers of $[Fe^{IV}(O)(^{Me2,Me}ImTACN)]^{2+}$ (**2**^{im}).

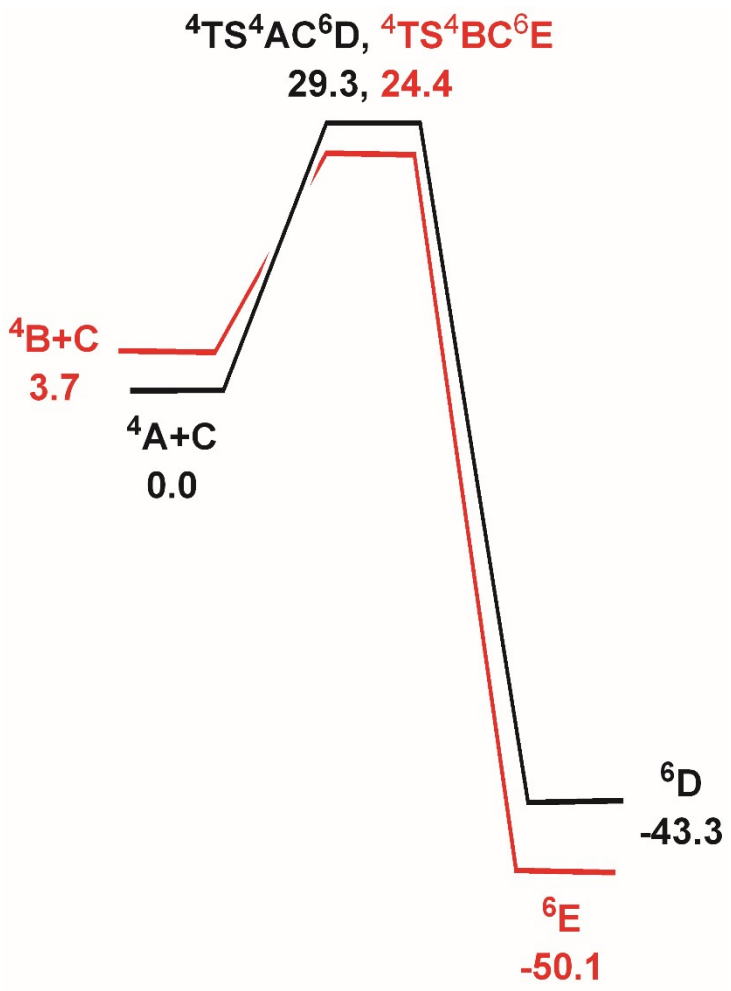

Figure S15. Potential energy profiles for C-H activation of methane by the two tautomers of $[Fe^{IV}(O)(^{Me2,Me2}PyzTACN)]^{2+}$ (**2**^{Pz}).