Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Nonheme Iron-Thiolate Complexes as Structural Models of Sulfoxide Synthase Active Sites

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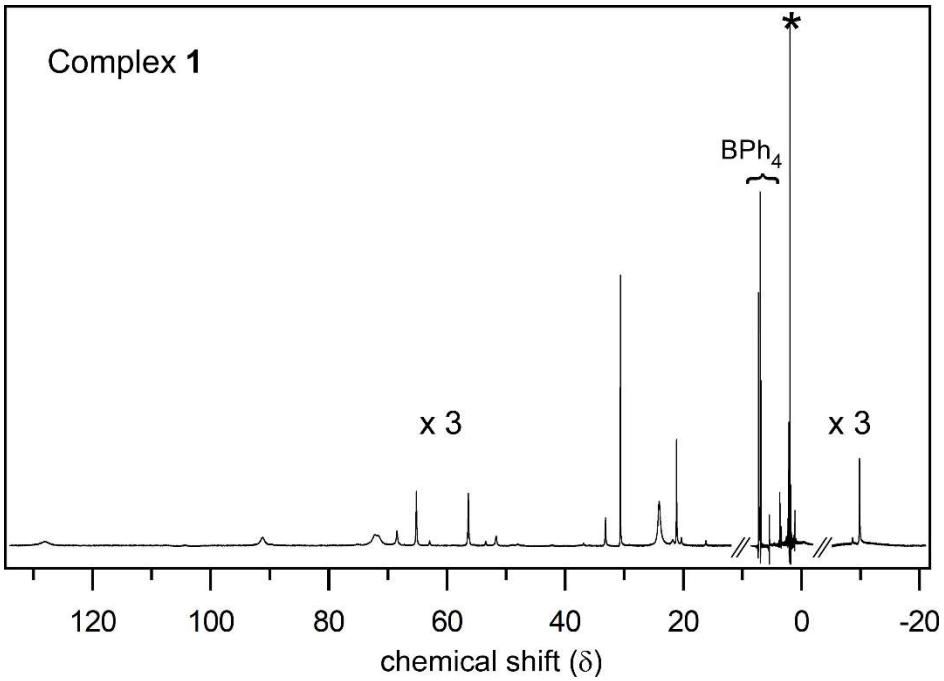

Figure S1. ^{1}H NMR spectrum of [Fe^{II}(**L**^{A})(SAr^{Me3})]BPh_4 (**1**) in CD_3CN at room temperature. The residual CH_3CN peak is labeled with an asterisk (*). The intensities of peaks outside the diamagnetic region were increased three-fold for the sake of clarity.

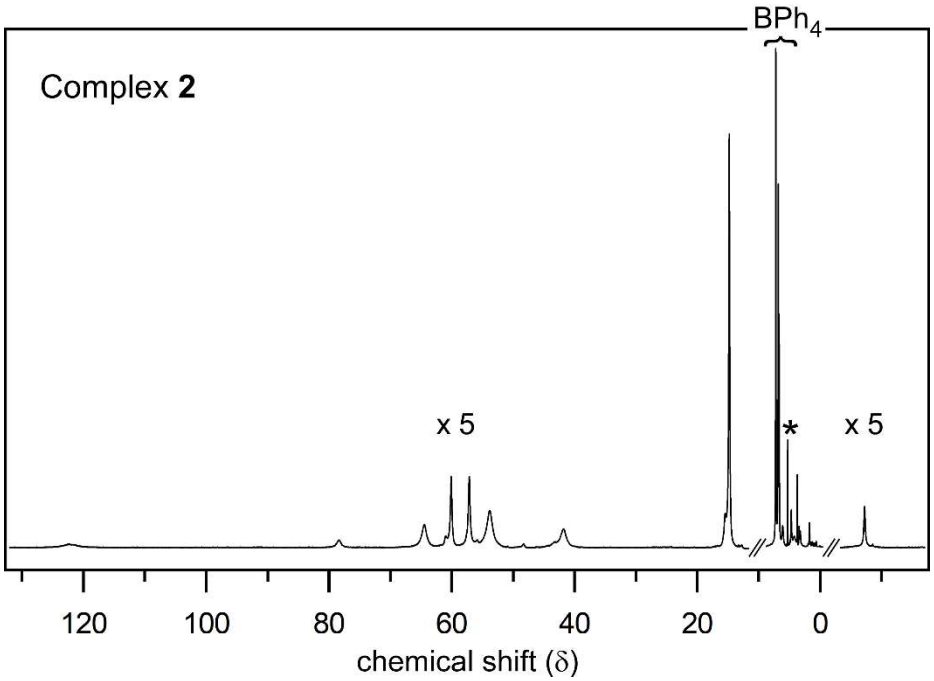

Figure S2. ^{1}H NMR spectrum of [Fe^{II}(**L**^{B})(SCy)]BPh_4 (**2**) in CD_2Cl_2 at room temperature. The residual CH_2Cl_2 peak is labeled with an asterisk (*). The intensities of peaks outside the diamagnetic region have been increased five-fold for the sake of clarity.

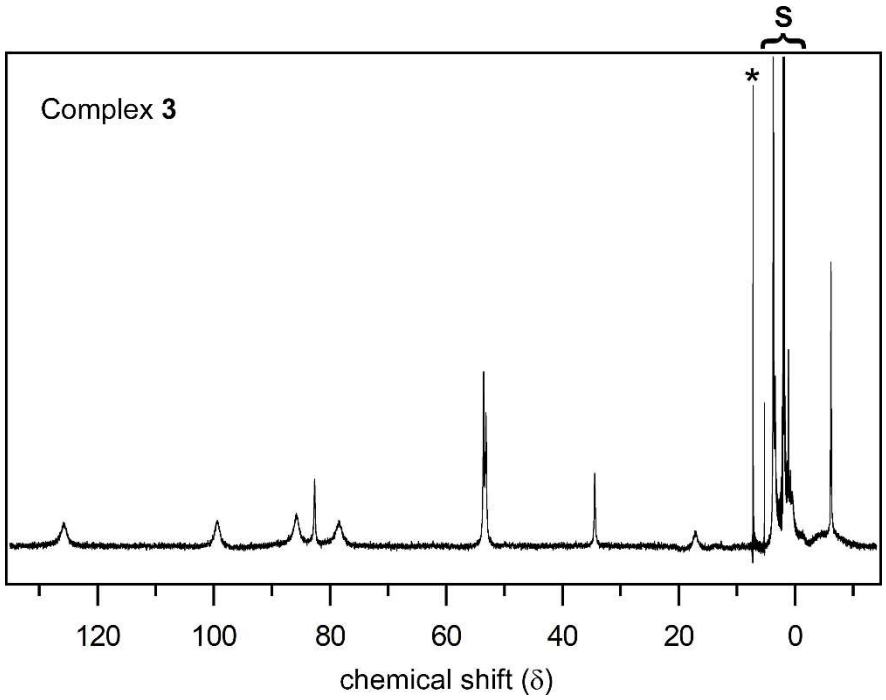

Figure S3. ^{1}H NMR spectrum of $[Fe^{II}(\mathbf{L^{A}})(CH_3CN)_2](OTf)_2$ (**3**) in $CDCl_3$ at room temperature. The residual $CHCl_3$ peak is labeled with an asterisk (*); peaks due to solvent are marked with "S".

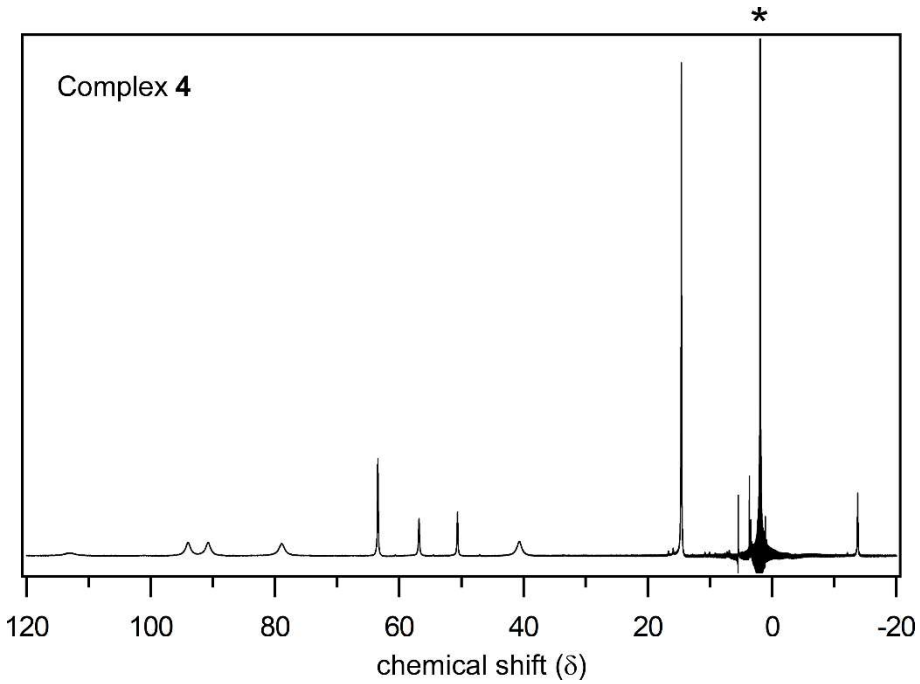

Figure S4. ^{1}H NMR spectrum of $[Fe^{II}(\mathbf{L^{B}})(OTf)_2]$ (**4**) in CD_3CN at room temperature. The residual CH_3CN peak is labeled with an asterisk (*).

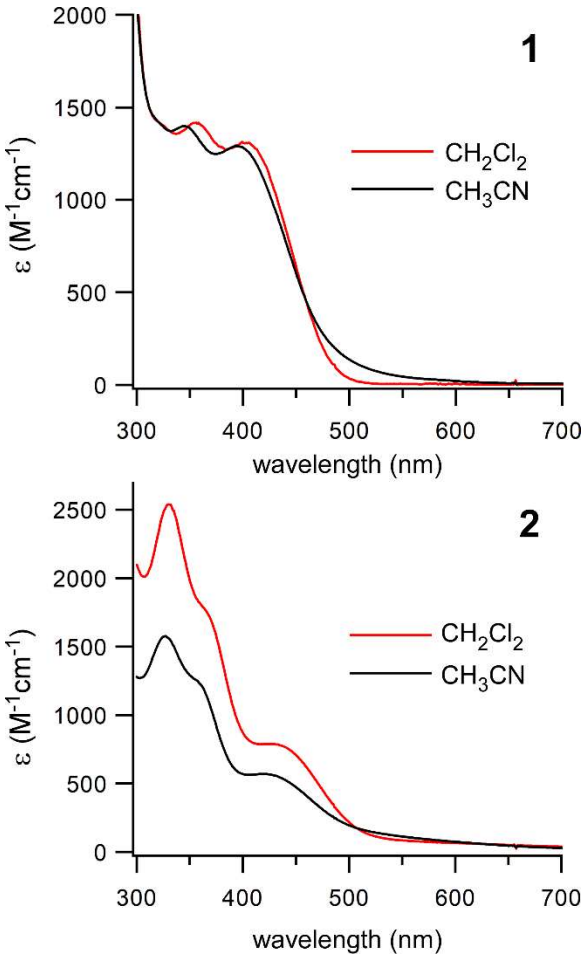

Figure S5. Comparison of UV-vis absorption spectra measured at room temperature for **1** (top) and **2** (bottom) in CH_2Cl_2 (red lines) and CH_3CN (black lines).

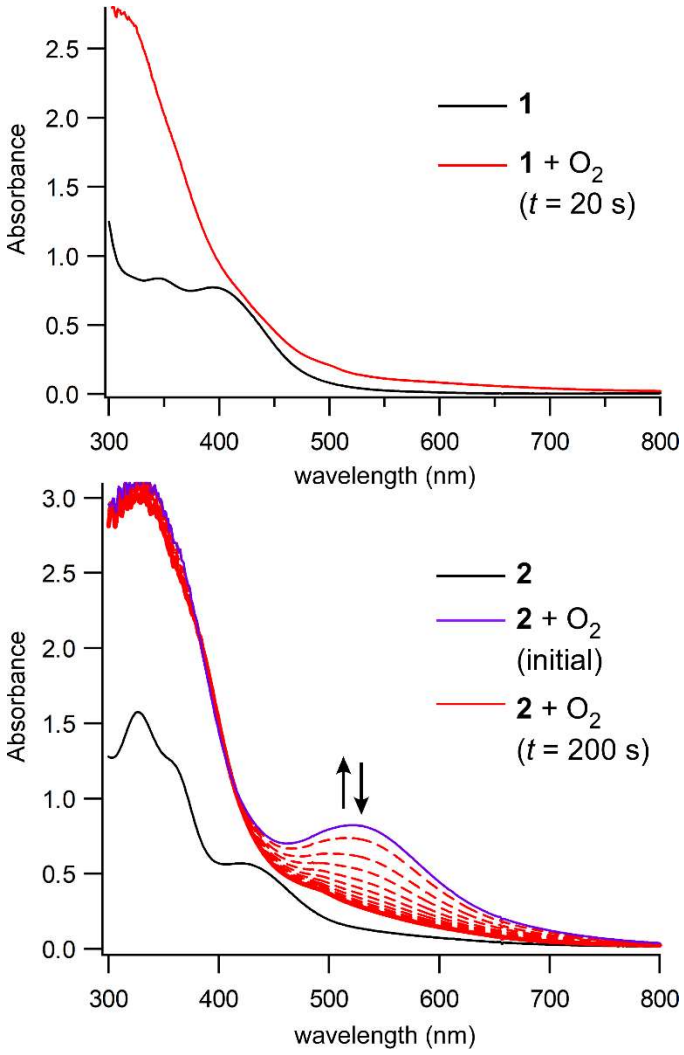

Figure S6. Reaction of complexes **1** (top) and **2** (bottom) with O_2 at room temperature in CH_3CN. ([**1**] = 0.6 mM; [**2**] = 1.0 mM). Exposure of **2** to O_2 initially generates an intermediate (purple line; λ_{max} = 520 nm) that decays over the course of 200 s.

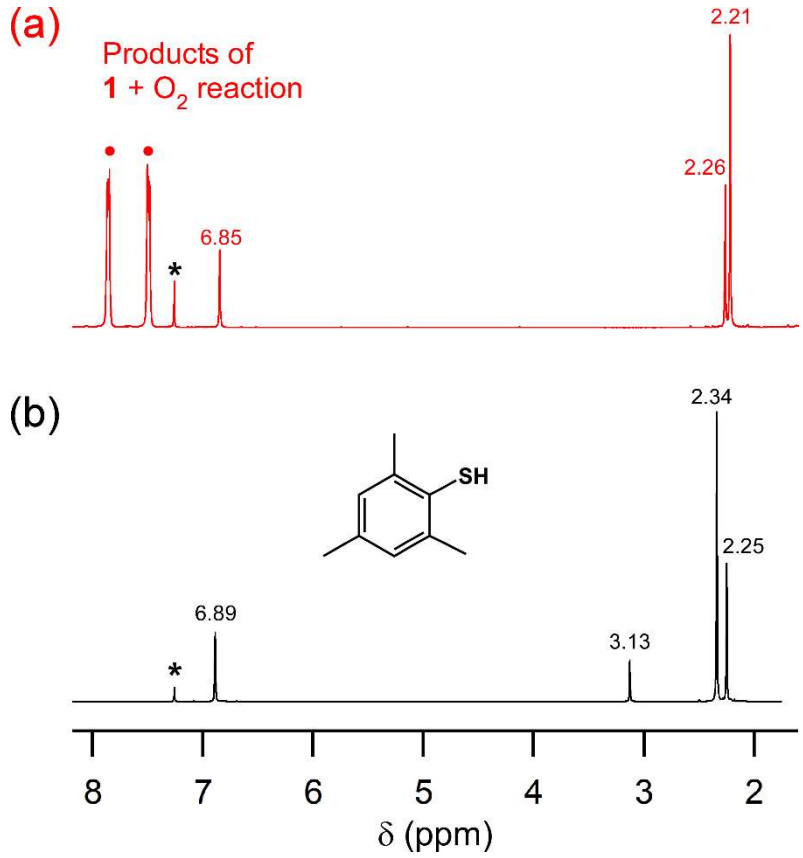

Figure S7. ^{1}H NMR spectra of (a) products isolated from the reaction of **1** with O_2 at room temperature and (b) the spectrum of commercial-available 2,4,6-trimethylthiophenol. Both spectra were measured in $CDCl_3$ solvent (features indicated by asterisks (*) are due to residual $CHCl_3$). The peaks marked with red dots in the top spectrum arise from naphthalene added as an internal standard. Comparison of the two spectra indicate that the disulfide (MesS−SMes) peaks in (a) are modestly shifted with respect to the those of the thiol precursor in (b), and the former spectrum lacks the peak at 3.13 pm arising from the thiol (S*H*) moiety.

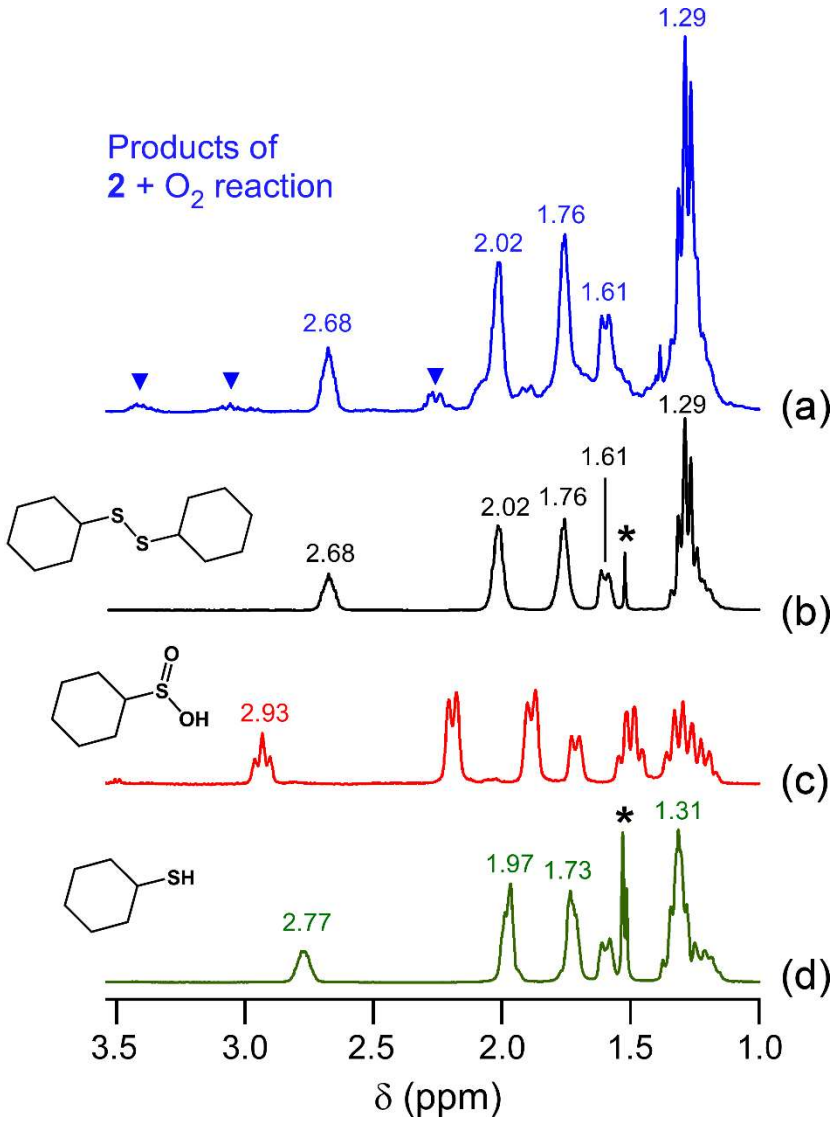

Figure S8. ^{1}H NMR spectrum of the products isolated from the reaction of **2** with O_2 at room temperature (a, blue line). Based on literature data (Luu *et al., J. Sulfur Chem.* **2015**, *36*, 340-350), the peaks labeled with a triangle (▼) are assigned dicyclohexyl thiosulfonate (CyS-S(O)$_2$Cy). The spectra of commercially-available dicyclohexyldisulfide (b, black), cyclohexanesulfinic acid (c, red line), and cyclohexanethiol (d, green) are provided for the sake of comparison. Peaks in the 2.5–3.5 ppm region arise from -SC*H* of the cyclohexyl rings. All spectra were measured at room temperature in CD_2Cl_2 solvent. Peaks labeled with an asterisk (*) are due to trace water in the solvent.

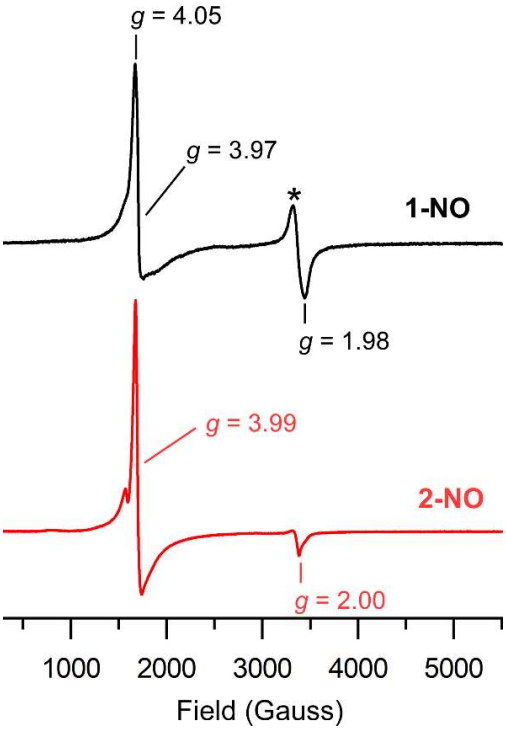

Figure S9. X-band EPR spectra of **1-NO** (top) and **2-NO** (bottom) in frozen CH_2Cl_2. Samples were prepared by addition of NO gas to solutions of the precursor complexes (**1-OTf** and **2**, respectively) at room temperature. EPR data collection: frequency = 9.47 GHz; power = 2.08 mW; T = 10 K. The feature marked with an asterisk (*) arises from a dinitrosyl iron complex.

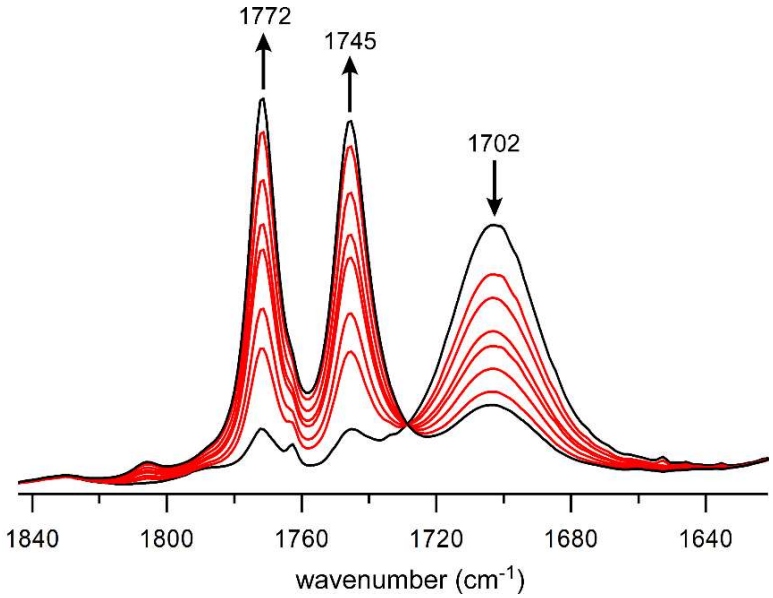

Figure S10. Time-resolved IR spectra for the decay of **2-NO** (ν(NO) = 1702 cm^{-1}) at room temperature in CH_2Cl_2. After the initial spectrum (t = 0), spectra were collected at t = 3, 5, 10, 15, 20, 25, and 30 minutes.

Mössbauer Data Analysis

For the sake of clarity, the MB spectra of **1** and **2** shown in Figure 4 were generated by removing contributions from minor species. The MB parameters and percent contribution of these minor species are provided here:

Spectrum A (complex 1, solid): $\delta = 0.45$ and $\Delta E_Q = 0.27$ mm/s (17 %); $\delta = 1.13$ and $\Delta E_Q = 2.75$ mm/s (10 %).

Spectrum B (complex 1, solution): $\delta = 0.5$ and $\Delta E_Q = 1.4$ mm/s (5 %); $\delta = 0.1$ and $\Delta E_Q = 0.8$ mm/s (5 %).

Spectrum C (complex 2, solid): $\delta = 0.39$ and $\Delta E_Q = 1.19$ mm/s (4 %).

Spectrum D (complex 2, solution): $\delta = 0.76$ and $\Delta E_Q = 2.83$ mm/s (13 %); $\delta = 0.35$ and $\Delta E_Q = 1.0$ mm/s (3 %)

Table S1. Summary of X-ray Crystallographic Data Collection and Structure Refinement

	1-OTf	**2** • 0.5 $C_2H_4Cl_2$	**3**	**4**
empirical formula	$C_{25}H_{28}F_3FeN_5O_3S_2$	$C_{47}H_{53}BClFeN_6S$	$C_{22}H_{23}F_6FeN_7O_6S_2$	$C_{20}H_{23}F_6FeN_7O_6S_2$
formula weight	635.50	836.12	715.44	691.42
crystal system	triclinic	triclinic	monoclinic	triclinic
space group	*P*-1	*P*-1	$P2_1/c$	*P*-1
a [Å]	9.0531(4)	10.5475(2)	18.4245(3)	9.5013(3)
b [Å]	12.0362(5)	14.1880(3)	10.08864(8)	11.2872(3)
c [Å]	13.5471(6)	14.5112(4)	16.8017(3)	13.9411(4)
α [°]	75.960(4)	78.014(2)	90.00	108.709(2)
β [°]	80.757(4)	89.101(2)	109.9733	90.333(2)
γ [°]	78.901(3)	86.0173(19)	90.00	104.242(2)
Volume [Å^3]	1395.18(10)	2119.09(9)	2935.24(7)	1366.65(6)
Z	2	2	4	2
ρ_{calc} [g/cm^3]	1.513	1.310	1.619	1.680
λ (Å)	1.5418	1.5418	1.5418	0.7107
T (K)	100.00(10)	100.00(10)	100.00(10)	100.00(10)
μ [mm^{-1}]	6.245	4.205	6.263	0.796
2Θ range [°]	7.7 to 141.4	7.9 to 141.2	10.1 to 148	6.6 to 59.2
reflections collected	25108	37008	29012	30626
independent reflections (R_{int})	5286 [R_{int} = 0.0558]	8011 [R_{int} = 0.0324]	5864 [R_{int} = 0.0375]	6978 [R_{int} = 0.0356]
Data/restraints/parameters	5286 / 0 / 368	8011 / 0 / 563	5864 / 0 / 399	6978 / 12 / 437
Goodness-of-fit (GOF) on F^2	1.045	1.067	1.084	1.050
*R*1/*wR*2 indexes [I >2σ(I)]	0.0443 / 0.1158	0.0472 / 0.1301	0.0654 / 0.1401	0.0419 / 0.0922
*R*1/*wR*2 indexes [all data]	0.0507 / 0.1220	0.0512 / 0.1340	0.0691 / 0.1423	0.0564 / 0.1012

Table S2. Summary of ^{19}F NMR data for $[NBu_4]OTf$ and Complexes **1-OTf**, **3**, and **4**.

Compound	^{19}F NMR Shift (ppm) [a]	Sample peak FWHM (Hz) [b]	$PhCF_3$ peak FWHM (Hz) [b]
$[NBu_4]OTf$	-79.8	5.6	5.2
Complex **1-OTf**	-78.7	17	4.4
Complex **3**	-76.6	101	6.1
Complex **4**	-77.9	20	5.8

[a] Chemical shift of the triflate anion referenced to trifluorotolunene ($PhCF_3$) as an internal standard (δ = –63.7 ppm). [b] FWHM = full width at half maximum

Table S3. DFT-computed bond distances (Å) for complexes [**1**$(CH_3CN)]^+$ and [**2**$(CH_3CN)]^+$ (*S* = 0 and 2). Metric parameters of the five-coordinate XRD structures are provided for comparison.

	[**1**$(CH_3CN)]^+$ (*S* = 2)	[**1**$(CH_3CN)]^+$ (*S* = 0)	**1-OTf** (XRD)
Fe–S1	2.424	2.451	2.3616(7)
Fe–N1 (amino)	2.393	2.084	2.312(2)
Fe–N2 (pyr)	2.252	2.036	2.133(2)
Fe–N3 (pyr)	2.242	2.030	2.150(2)
Fe–N5 (imid)	2.185	1.985	2.098(2)
Fe–N6 (CH_3CN)	2.213	1.924	—
Fe–S/N [ave]	2.285	2.085	2.211

	[**2**$(CH_3CN)]^+$ (*S* = 2)	[**2**$(CH_3CN)]^+$ (*S* = 0)	**2** (XRD)
Fe–S1	2.387	2.413	2.3048(7)
Fe–N1 (amino)	2.515	2.136	2.389(2)
Fe–N2 (pyr)	2.272	2.024	2.134(2)
Fe–N4 (imid)	2.185	2.036	2.101(2)
Fe–N6 (imid)	2.184	2.024	2.094(2)
Fe–N7 (CH_3CN)	2.323	1.936	—
Fe–S/N [ave]	2.311	2.095	2.205

Table S4. Cartesian Coordinates (Å) of the DFT-Optimized Model of [**1**(CH_3CN)]$^+$ (S = 2)

Fe	-0.028459000000	-0.048487000000	0.071954000000
S	-0.582014000000	-0.163281000000	2.429359000000
N	0.127777000000	-0.048055000000	-2.316039000000
N	-0.412257000000	2.071821000000	-0.583433000000
N	0.406292000000	-2.160056000000	-0.542898000000
N	-4.268773000000	-0.340524000000	-0.877118000000
H	-5.264802000000	-0.340604000000	-0.673496000000
N	-2.098027000000	-0.360297000000	-0.553999000000
C	0.640646000000	1.295357000000	-2.625761000000
H	0.616915000000	1.511955000000	-3.708940000000
H	1.696465000000	1.335145000000	-2.311014000000
C	-0.119511000000	2.358068000000	-1.866286000000
C	-0.497434000000	3.570125000000	-2.452248000000
H	-0.239830000000	3.774609000000	-3.493637000000
C	-1.213991000000	4.496240000000	-1.690578000000
H	-1.532653000000	5.444440000000	-2.130814000000
C	-1.533677000000	4.181291000000	-0.367669000000
H	-2.104653000000	4.869224000000	0.258990000000
C	-1.110366000000	2.954938000000	0.146019000000
H	-1.345467000000	2.649653000000	1.168508000000
C	1.089307000000	-1.114390000000	-2.627300000000
H	2.096446000000	-0.755749000000	-2.361715000000
H	1.112638000000	-1.360899000000	-3.704067000000
C	0.804792000000	-2.357005000000	-1.814042000000
C	0.984124000000	-3.643334000000	-2.331597000000
H	1.298209000000	-3.773002000000	-3.369360000000
C	0.764685000000	-4.745067000000	-1.502029000000
H	0.903185000000	-5.758775000000	-1.887089000000
C	0.362144000000	-4.529323000000	-0.182102000000
H	0.171585000000	-5.360712000000	0.498432000000
C	0.188223000000	-3.215345000000	0.253807000000
H	-0.144003000000	-2.981585000000	1.269281000000
C	-1.207522000000	-0.316839000000	-2.912167000000
H	-1.179282000000	-1.306762000000	-3.394889000000
H	-1.414237000000	0.401462000000	-3.723984000000
C	-2.334272000000	-0.298623000000	-1.910709000000
C	-3.694778000000	-0.283814000000	-2.127934000000
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H	-3.457033000000	-0.410701000000	1.116172000000
C	0.630066000000	0.070234000000	3.730361000000
C	1.299065000000	1.311052000000	3.917830000000
C	2.141605000000	1.486836000000	5.026151000000
H	2.639384000000	2.454783000000	5.152592000000
C	2.349629000000	0.484252000000	5.981795000000
C	1.709227000000	-0.743959000000	5.769284000000
H	1.866875000000	-1.556539000000	6.487643000000
C	0.863496000000	-0.973265000000	4.670298000000
C	1.108029000000	2.464448000000	2.967666000000

H	0.067832000000	2.832481000000	2.992287000000
H	1.771308000000	3.303253000000	3.227744000000
H	1.308715000000	2.166902000000	1.927568000000
C	3.196764000000	0.741091000000	7.206784000000
H	4.034038000000	1.422487000000	6.986144000000
H	2.601091000000	1.215345000000	8.008556000000
H	3.612808000000	-0.190626000000	7.621895000000
C	0.227748000000	-2.334646000000	4.516724000000
H	0.544199000000	-3.011106000000	5.325763000000
H	-0.873758000000	-2.274410000000	4.517875000000
H	0.506837000000	-2.797045000000	3.555052000000
N	2.165481000000	0.170664000000	0.258225000000
C	3.311263000000	0.043927000000	0.365195000000
C	4.748296000000	-0.136600000000	0.470575000000
H	5.014144000000	-0.470241000000	1.485039000000
H	5.074724000000	-0.895375000000	-0.256286000000
H	5.259228000000	0.812934000000	0.250272000000

Table S5. Cartesian Coordinates (Å) of the DFT-Optimized Model of [**1**(CH_3CN)]$^+$ (S = 0)

Fe	-0.024371000000	-0.068468000000	-0.192501000000
S	-0.572880000000	-0.134470000000	2.195823000000
N	0.191913000000	-0.075877000000	-2.264483000000
N	-0.389874000000	1.903974000000	-0.541400000000
N	0.290063000000	-2.056148000000	-0.460379000000
N	-4.119753000000	-0.462152000000	-0.827109000000
H	-5.102217000000	-0.513982000000	-0.572187000000
N	-1.943552000000	-0.346980000000	-0.615750000000
C	0.727415000000	1.270519000000	-2.582397000000
H	0.680668000000	1.489355000000	-3.661571000000
H	1.788269000000	1.290642000000	-2.290017000000
C	-0.025508000000	2.302261000000	-1.781409000000
C	-0.338400000000	3.571023000000	-2.272917000000
H	-0.025504000000	3.855827000000	-3.279426000000
C	-1.065411000000	4.449130000000	-1.464846000000
H	-1.335680000000	5.442538000000	-1.831035000000
C	-1.459996000000	4.022850000000	-0.195004000000
H	-2.041834000000	4.668310000000	0.466218000000
C	-1.102525000000	2.742272000000	0.228102000000
H	-1.387509000000	2.351781000000	1.207314000000
C	1.153100000000	-1.169962000000	-2.535322000000
H	2.157629000000	-0.820915000000	-2.255227000000
H	1.187304000000	-1.439720000000	-3.603650000000
C	0.791023000000	-2.358504000000	-1.680300000000
C	0.968223000000	-3.678675000000	-2.097241000000
H	1.365610000000	-3.885726000000	-3.092739000000
C	0.628570000000	-4.716204000000	-1.225481000000
H	0.760305000000	-5.757305000000	-1.531433000000
C	0.109946000000	-4.395848000000	0.030582000000
H	-0.181685000000	-5.171929000000	0.740025000000
C	-0.048575000000	-3.052187000000	0.371871000000

H	-0.458311000000	-2.732939000000	1.332690000000
C	-1.123207000000	-0.334228000000	-2.949264000000
H	-1.061754000000	-1.297247000000	-3.478272000000
H	-1.296270000000	0.428854000000	-3.724380000000
C	-2.247977000000	-0.364319000000	-1.959303000000
C	-3.614799000000	-0.436333000000	-2.107791000000
H	-4.252867000000	-0.472365000000	-2.986687000000
C	-3.091136000000	-0.405207000000	0.045544000000
H	-3.204675000000	-0.397693000000	1.128185000000
C	0.660925000000	0.047380000000	3.486777000000
C	1.387065000000	1.257314000000	3.677663000000
C	2.250402000000	1.390099000000	4.776846000000
H	2.793283000000	2.334156000000	4.899319000000
C	2.413082000000	0.382393000000	5.734868000000
C	1.699907000000	-0.806968000000	5.535473000000
H	1.809223000000	-1.619892000000	6.262632000000
C	0.841093000000	-0.998392000000	4.439782000000
C	1.216108000000	2.443156000000	2.763542000000
H	0.216341000000	2.894422000000	2.891947000000
H	1.963915000000	3.220913000000	2.982401000000
H	1.292333000000	2.159066000000	1.705884000000
C	3.280113000000	0.596694000000	6.954011000000
H	4.134338000000	1.256999000000	6.734406000000
H	2.706902000000	1.074681000000	7.769820000000
H	3.673971000000	-0.352407000000	7.351368000000
C	0.124778000000	-2.323678000000	4.323443000000
H	0.401305000000	-2.991608000000	5.154183000000
H	-0.970941000000	-2.198298000000	4.323705000000
H	0.376163000000	-2.835625000000	3.380161000000
N	1.853654000000	0.176777000000	0.144083000000
C	2.982811000000	0.265340000000	0.386535000000
C	4.400116000000	0.377874000000	0.686056000000
H	4.583487000000	0.126009000000	1.741723000000
H	4.974111000000	-0.312056000000	0.050194000000
H	4.741344000000	1.406529000000	0.492088000000

Table S6. Cartesian Coordinates (Å) of the DFT-Optimized Model of $[\mathbf{2}(CH_3CN)]^+$ ($S = 2$)

Fe	0.645977000000	-0.740881000000	0.018207000000
S	0.271056000000	-0.771553000000	2.374983000000
N	0.485812000000	-0.651299000000	-2.490562000000
N	-1.081810000000	0.659377000000	-0.445380000000
N	-1.339265000000	-3.823597000000	-2.154942000000
N	-0.509717000000	-2.488099000000	-0.600696000000
N	3.009656000000	2.055053000000	-2.167304000000
N	1.907082000000	0.925418000000	-0.619430000000
C	-0.721338000000	0.122211000000	-2.835617000000
H	-1.490925000000	-0.575233000000	-3.206032000000
H	-0.514785000000	0.798525000000	-3.682985000000
C	-1.376272000000	0.926827000000	-1.725735000000
C	-2.337840000000	1.889865000000	-2.072647000000

H	-2.553608000000	2.091527000000	-3.124871000000
C	-3.014403000000	2.573467000000	-1.064648000000
H	-3.770683000000	3.321912000000	-1.316339000000
C	-2.704058000000	2.284509000000	0.268349000000
H	-3.205420000000	2.794195000000	1.093303000000
C	-1.726488000000	1.326744000000	0.529350000000
H	-1.422507000000	1.069065000000	1.548719000000
C	0.359170000000	-2.063461000000	-2.887878000000
H	1.361122000000	-2.521596000000	-2.877888000000
H	-0.035310000000	-2.180857000000	-3.913360000000
C	-0.508097000000	-2.782313000000	-1.896852000000
C	-1.892950000000	-4.213179000000	-0.948864000000
H	-2.598445000000	-5.038357000000	-0.881611000000
C	-1.369627000000	-3.373963000000	0.005259000000
H	-1.560415000000	-3.347593000000	1.076565000000
C	-1.597128000000	-4.433930000000	-3.456896000000
H	-1.976421000000	-3.682312000000	-4.164665000000
H	-2.354317000000	-5.217212000000	-3.332149000000
H	-0.680410000000	-4.885321000000	-3.863873000000
C	1.736611000000	-0.013952000000	-2.924143000000
H	1.641703000000	0.454573000000	-3.920745000000
H	2.510605000000	-0.792219000000	-3.024221000000
C	2.198766000000	0.995600000000	-1.912989000000
C	3.237697000000	2.693273000000	-0.961512000000
H	3.852451000000	3.587470000000	-0.891841000000
C	2.541814000000	1.984169000000	-0.013259000000
H	2.449856000000	2.179248000000	1.053342000000
C	3.556602000000	2.444924000000	-3.463762000000
H	4.237422000000	1.671165000000	-3.847483000000
H	4.114564000000	3.381282000000	-3.342129000000
H	2.746727000000	2.610291000000	-4.188900000000
C	1.710244000000	-0.580186000000	3.534382000000
H	1.549089000000	-1.331494000000	4.329513000000
C	3.072730000000	-0.864986000000	2.891972000000
C	4.239387000000	-0.677721000000	3.876605000000
H	4.180537000000	-1.450386000000	4.666495000000
C	4.213573000000	0.709197000000	4.534233000000
H	5.026913000000	0.807147000000	5.274656000000
H	4.401173000000	1.480986000000	3.764120000000
C	2.855046000000	0.977774000000	5.196752000000
H	2.832394000000	1.990461000000	5.635687000000
H	2.716505000000	0.272329000000	6.038075000000
C	1.697085000000	0.806094000000	4.200566000000
H	1.767000000000	1.575285000000	3.409070000000
H	0.727289000000	0.966964000000	4.701853000000
H	3.079940000000	-1.886895000000	2.482482000000
H	3.205242000000	-0.188869000000	2.029377000000
H	5.197245000000	-0.843089000000	3.350965000000
N	2.546642000000	-2.037551000000	-0.298245000000
C	3.575274000000	-2.531578000000	-0.496599000000
C	4.879906000000	-3.126048000000	-0.746976000000

H	5.312898000000	-3.492580000000	0.196220000000
H	4.781483000000	-3.968888000000	-1.447313000000
H	5.549662000000	-2.369185000000	-1.183398000000

Table S7. Cartesian Coordinates (Å) of the DFT-Optimized Model of $[\mathbf{2}(CH_3CN)]^+$ ($S = 0$)

Fe	0.709241000000	-0.781139000000	-0.296501000000
S	0.511747000000	-1.174572000000	2.076471000000
N	0.625809000000	-0.636427000000	-2.426335000000
N	-0.898137000000	0.445275000000	-0.393359000000
N	-1.444737000000	-3.678726000000	-2.165889000000
N	-0.526240000000	-2.343108000000	-0.657830000000
N	3.142978000000	2.004128000000	-1.992323000000
N	1.924504000000	0.831786000000	-0.560999000000
C	-0.469810000000	0.305068000000	-2.799484000000
H	-1.150183000000	-0.178717000000	-3.518175000000
H	-0.042218000000	1.166561000000	-3.335619000000
C	-1.271387000000	0.821573000000	-1.629622000000
C	-2.351943000000	1.685507000000	-1.848839000000
H	-2.625533000000	1.965191000000	-2.868910000000
C	-3.059606000000	2.179945000000	-0.755149000000
H	-3.904870000000	2.856765000000	-0.903661000000
C	-2.666996000000	1.785882000000	0.527906000000
H	-3.191565000000	2.143916000000	1.416076000000
C	-1.586755000000	0.917830000000	0.664399000000
H	-1.229941000000	0.555896000000	1.633766000000
C	0.355411000000	-2.011008000000	-2.926113000000
H	1.309315000000	-2.558912000000	-2.974651000000
H	-0.065773000000	-2.004156000000	-3.945155000000
C	-0.555841000000	-2.677636000000	-1.943759000000
C	-2.008926000000	-3.993347000000	-0.943598000000
H	-2.759834000000	-4.774035000000	-0.843919000000
C	-1.431513000000	-3.154305000000	-0.017536000000
H	-1.608521000000	-3.082792000000	1.053766000000
C	-1.737448000000	-4.313959000000	-3.447475000000
H	-2.116778000000	-3.572607000000	-4.166573000000
H	-2.504707000000	-5.081952000000	-3.291819000000
H	-0.835675000000	-4.790644000000	-3.859764000000
C	1.949602000000	-0.101530000000	-2.839763000000
H	1.928372000000	0.317619000000	-3.859576000000
H	2.673939000000	-0.929784000000	-2.845151000000
C	2.346650000000	0.919970000000	-1.819698000000
C	3.224344000000	2.642741000000	-0.770240000000
H	3.802654000000	3.553257000000	-0.635398000000
C	2.458087000000	1.907982000000	0.104906000000
H	2.257724000000	2.096037000000	1.155768000000
C	3.796837000000	2.411717000000	-3.232135000000
H	4.516789000000	1.647768000000	-3.559386000000
H	4.331834000000	3.352648000000	-3.055346000000
H	3.050797000000	2.572865000000	-4.024053000000
C	1.837291000000	-0.638599000000	3.260026000000

H	1.738421000000	-1.348016000000	4.103419000000
C	3.262739000000	-0.786820000000	2.708641000000
C	4.336991000000	-0.364769000000	3.724399000000
H	4.341264000000	-1.075579000000	4.572410000000
C	4.088856000000	1.050098000000	4.266159000000
H	4.847801000000	1.313539000000	5.023211000000
H	4.204263000000	1.781368000000	3.443849000000
C	2.677737000000	1.169780000000	4.857844000000
H	2.493170000000	2.194700000000	5.224654000000
H	2.601460000000	0.507587000000	5.741070000000
C	1.600782000000	0.770077000000	3.834735000000
H	1.586192000000	1.499472000000	3.005960000000
H	0.599115000000	0.812443000000	4.295578000000
H	3.425794000000	-1.831662000000	2.397243000000
H	3.354601000000	-0.176755000000	1.795362000000
H	5.336359000000	-0.432359000000	3.257662000000
N	2.279410000000	-1.910576000000	-0.384823000000
C	3.251437000000	-2.535212000000	-0.467559000000
C	4.486063000000	-3.295514000000	-0.588273000000
H	4.830764000000	-3.625347000000	0.403844000000
H	4.323381000000	-4.180586000000	-1.221702000000
H	5.264121000000	-2.665302000000	-1.046608000000

Table S8. Cartesian Coordinates (Å) of the DFT-Optimized Model of [**1**-NO]$^+$ (S = 3/2)

Fe	0.040914000000	0.000430000000	0.106542000000
N	1.755544000000	0.237597000000	0.559059000000
O	2.723503000000	0.308569000000	1.201954000000
S	-0.721397000000	-0.026931000000	2.360715000000
N	0.290787000000	-0.056004000000	-2.245161000000
N	-0.364945000000	2.088725000000	-0.639176000000
N	0.274198000000	-2.151909000000	-0.477898000000
N	-4.171137000000	-0.307668000000	-1.032010000000
H	-5.175810000000	-0.317076000000	-0.876704000000
N	-2.020304000000	-0.288222000000	-0.602657000000
C	0.859454000000	1.265624000000	-2.559841000000
H	0.915432000000	1.444639000000	-3.647876000000
H	1.892869000000	1.288958000000	-2.176102000000
C	0.068047000000	2.360982000000	-1.884218000000
C	-0.202783000000	3.585081000000	-2.502721000000
H	0.163478000000	3.776881000000	-3.513383000000
C	-0.954271000000	4.539236000000	-1.813128000000
H	-1.189640000000	5.499175000000	-2.279236000000
C	-1.418656000000	4.238205000000	-0.530570000000
H	-2.022940000000	4.948422000000	0.036862000000
C	-1.100427000000	2.996096000000	0.019297000000
H	-1.449134000000	2.703132000000	1.011821000000
C	1.247873000000	-1.155438000000	-2.457570000000
H	2.228630000000	-0.835367000000	-2.069741000000
H	1.386473000000	-1.391432000000	-3.527343000000
C	0.798204000000	-2.381024000000	-1.697475000000

C	0.909642000000	-3.674225000000	-2.214282000000
H	1.333395000000	-3.827294000000	-3.208608000000
C	0.463807000000	-4.752699000000	-1.446408000000
H	0.537891000000	-5.772171000000	-1.834051000000
C	-0.090873000000	-4.503315000000	-0.189332000000
H	-0.469118000000	-5.311625000000	0.438451000000
C	-0.168363000000	-3.182868000000	0.255210000000
H	-0.605367000000	-2.929146000000	1.223458000000
C	-1.013784000000	-0.308707000000	-2.915995000000
H	-0.971326000000	-1.293178000000	-3.408518000000
H	-1.167882000000	0.421096000000	-3.727950000000
C	-2.189162000000	-0.281251000000	-1.971081000000
C	-3.537237000000	-0.291532000000	-2.254130000000
H	-4.083862000000	-0.293595000000	-3.193693000000
C	-3.231441000000	-0.301758000000	-0.064393000000
H	-3.460760000000	-0.298373000000	1.000027000000
C	0.569492000000	0.202179000000	3.588744000000
C	0.991583000000	1.507621000000	3.960615000000
C	1.940852000000	1.654920000000	4.980576000000
H	2.256562000000	2.665742000000	5.260278000000
C	2.496156000000	0.558899000000	5.654252000000
C	2.071526000000	-0.717798000000	5.270821000000
H	2.489365000000	-1.591180000000	5.782047000000
C	1.120395000000	-0.921755000000	4.255879000000
C	0.447514000000	2.746594000000	3.295004000000
H	-0.653371000000	2.781520000000	3.343421000000
H	0.848922000000	3.651953000000	3.773164000000
H	0.721153000000	2.778481000000	2.227870000000
C	3.504952000000	0.769811000000	6.757841000000
H	4.360040000000	1.371598000000	6.406582000000
H	3.057009000000	1.317383000000	7.605227000000
H	3.896531000000	-0.183451000000	7.144186000000
C	0.712822000000	-2.334153000000	3.913719000000
H	1.198745000000	-3.055099000000	4.586750000000
H	-0.379095000000	-2.470214000000	3.984865000000
H	0.996989000000	-2.592785000000	2.881013000000

Table S9. Cartesian Coordinates (Å) of the DFT-Optimized Model of [**2**-NO]$^+$ (S = 3/2)

Fe	0.161323000000	0.360138000000	-0.134511000000
N	1.496575000000	-0.840561000000	0.109780000000
O	2.021777000000	-1.740337000000	0.643418000000
S	-0.060203000000	0.934583000000	2.114212000000
N	-0.291314000000	0.108657000000	-2.563720000000
N	-1.567752000000	1.841414000000	-0.650756000000
N	-1.759345000000	-3.123530000000	-1.583269000000
N	-1.191379000000	-1.328344000000	-0.430553000000
N	2.132104000000	2.921824000000	-2.905952000000
N	1.333491000000	1.889513000000	-1.126347000000
C	-1.618525000000	0.698113000000	-2.822975000000
H	-2.374128000000	-0.089573000000	-2.671532000000

H	-1.708615000000	1.012770000000	-3.877453000000
C	-2.015527000000	1.841298000000	-1.917944000000
C	-2.914266000000	2.808829000000	-2.385629000000
H	-3.250017000000	2.778431000000	-3.424522000000
C	-3.380915000000	3.788805000000	-1.509903000000
H	-4.091844000000	4.545280000000	-1.852073000000
C	-2.915459000000	3.782474000000	-0.192791000000
H	-3.245508000000	4.525701000000	0.535334000000
C	-2.001670000000	2.798777000000	0.186019000000
H	-1.594905000000	2.774179000000	1.200330000000
C	-0.324367000000	-1.353098000000	-2.749493000000
H	0.710338000000	-1.734221000000	-2.740463000000
H	-0.766931000000	-1.647458000000	-3.719479000000
C	-1.096484000000	-1.942115000000	-1.605119000000
C	-2.297572000000	-3.266561000000	-0.317269000000
H	-2.876163000000	-4.144070000000	-0.038472000000
C	-1.936241000000	-2.143258000000	0.387947000000
H	-2.164869000000	-1.869891000000	1.415683000000
C	-1.863306000000	-4.078337000000	-2.682573000000
H	-2.422330000000	-3.641966000000	-3.523283000000
H	-2.393778000000	-4.968848000000	-2.325272000000
H	-0.862812000000	-4.375772000000	-3.028125000000
C	0.798751000000	0.782168000000	-3.290770000000
H	0.455780000000	1.174742000000	-4.264071000000
H	1.586011000000	0.043895000000	-3.514650000000
C	1.394285000000	1.877212000000	-2.452239000000
C	2.564744000000	3.629488000000	-1.798578000000
H	3.172387000000	4.526135000000	-1.893012000000
C	2.054941000000	2.981062000000	-0.701041000000
H	2.154275000000	3.234133000000	0.352260000000
C	2.450065000000	3.229157000000	-4.297046000000
H	3.078406000000	2.440402000000	-4.736210000000
H	2.997473000000	4.178840000000	-4.328268000000
H	1.528799000000	3.333127000000	-4.888144000000
C	1.261887000000	0.221351000000	3.202726000000
H	1.340026000000	-0.853280000000	2.964609000000
C	2.631349000000	0.877100000000	2.974817000000
C	3.698239000000	0.325268000000	3.934692000000
H	3.874001000000	-0.742815000000	3.707537000000
C	3.270939000000	0.470793000000	5.400421000000
H	4.019839000000	0.010144000000	6.067052000000
H	3.238926000000	1.544815000000	5.663645000000
C	1.891506000000	-0.155003000000	5.648922000000
H	1.562937000000	0.044999000000	6.684020000000
H	1.969392000000	-1.254302000000	5.553049000000
C	0.824503000000	0.364043000000	4.670613000000
H	0.625554000000	1.431797000000	4.875676000000
H	-0.127505000000	-0.169460000000	4.827827000000
H	2.948276000000	0.733621000000	1.929296000000
H	2.526769000000	1.967311000000	3.126855000000
H	4.657173000000	0.842996000000	3.761127000000