Supplementary Information (SI)

for

An iron(IV)-oxo intermediate on a carbanionic ligand framework: reactivity and decay pathways

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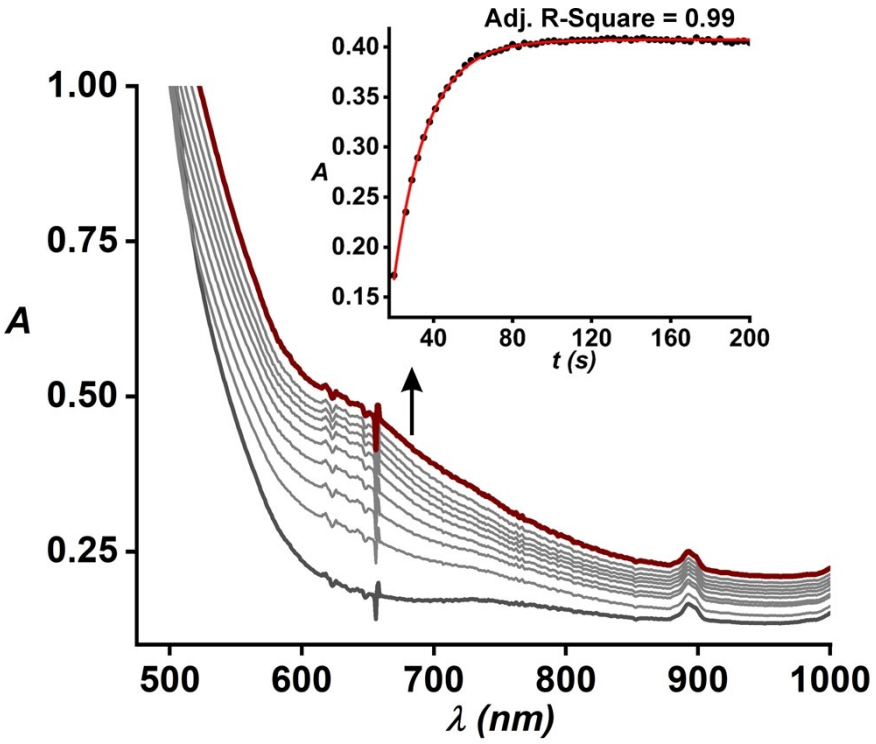


Fig. S1 *Generation of iron(IV)-oxo from complex* ***1*** *(1 mM) using IBX ester (3 equiv.) at 253 K. Inset: Time trace for the formation of the 700 nm band.*

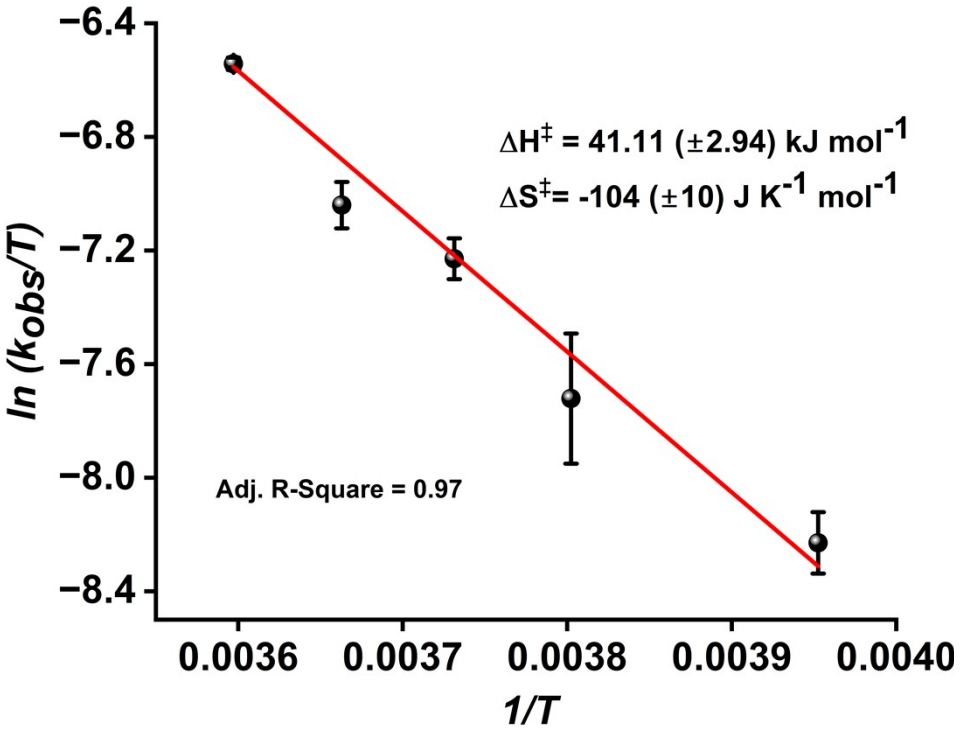


Fig. S2 *Eyring plot from temperature-dependent UV–vis kinetic data for the formation of iron(IV)-oxo species* ***2*** *displaying a broad band at 700 nm. Activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) were obtained from the linear fit of the experimental data.*

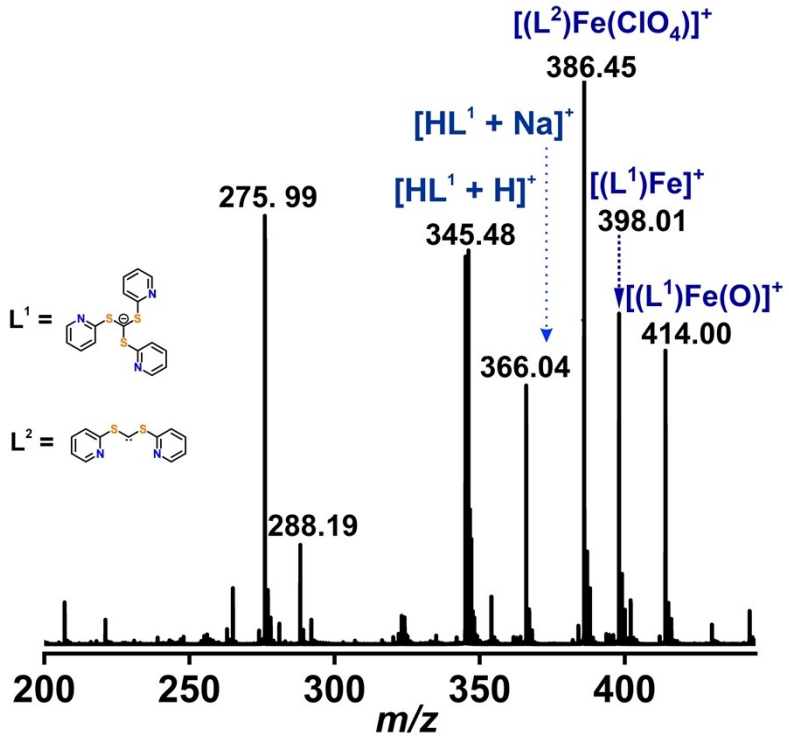


Fig. S3 *ESI-MS (positive ion mode, CH_3CN) spectrum of* ***2****, generated in the reaction of* ***1*** *with IBX ester (3 equiv.) in CH_3CN at 298 K.*

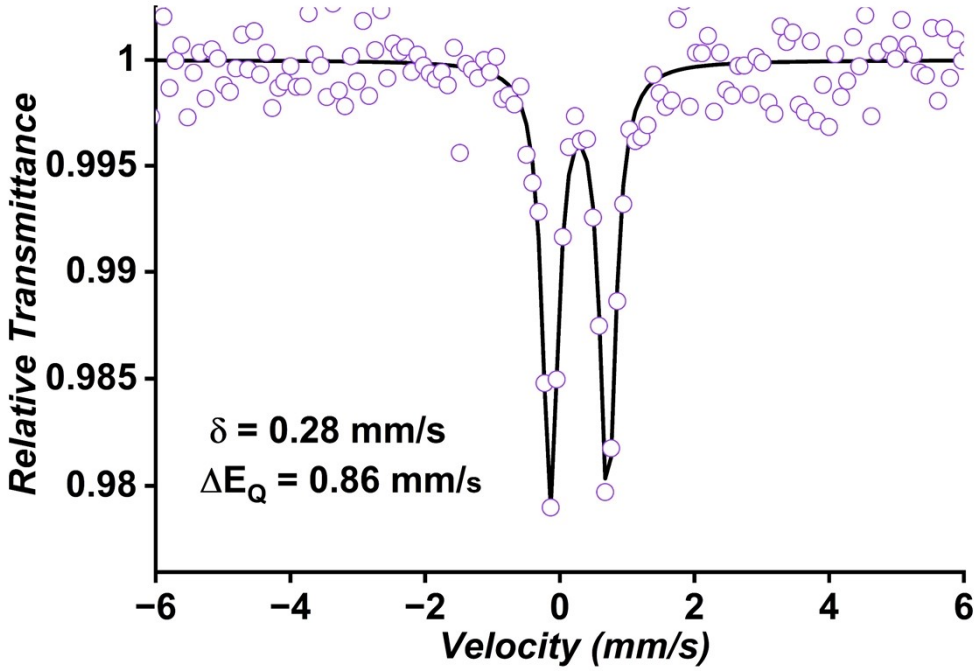


Fig. S4 *Zero-field ^{57}Fe (100% enriched) Mössbauer spectrum of a frozen acetonitrile sample of complex* ***1*** *at 77 K.*

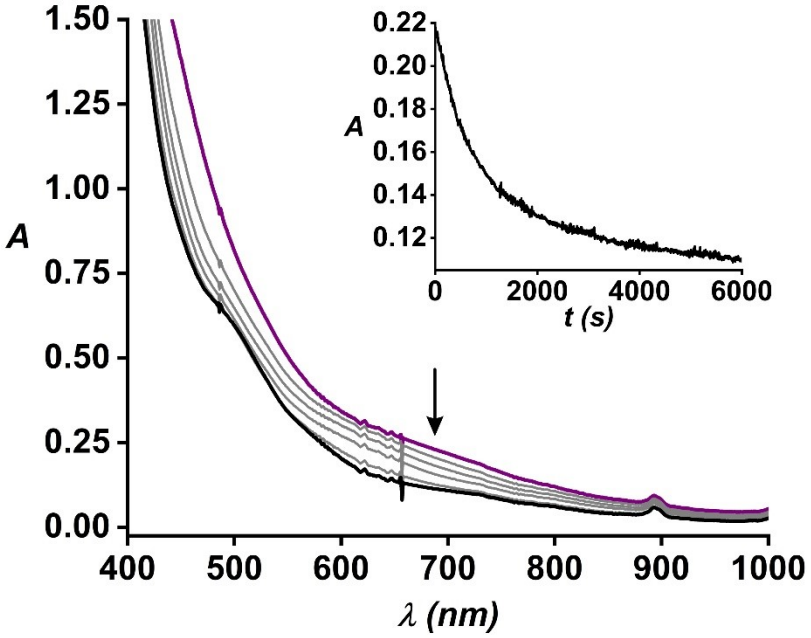


Fig. S5 *UV–vis spectra showing the decay of* ***2*** *at 278 K in acetonitrile. Inset: Decay of the 700 nm band.*

Table S1 *Computed parameters [Energy (E), Triplet – Quintet energy gap (ΔE_{TQ}) in kcal/mol, and Fe=O bond length (Å) for* ***2a****,* ***2b****, and* ***2c.*** *(For* ***2a,*** *the square pyramidal isomer was compared)*

Complex	**2a**	**2b**	**2c**
E (*S*=2) (Kcal/mol)	-2092406.897	-2175759.478	-2175762.579
E (*S*=0) (Kcal/mol)	-2092413.617	-2175769.447	-2175769.055
E (*S*=1) (Kcal/mol)	- 2092422.019	- 2175777.453	-2175776.892
ΔE_{TQ} (Kcal/mol)	15.1	17.9	14.3
Fe=O (Å)	1.613	1.643	1.660

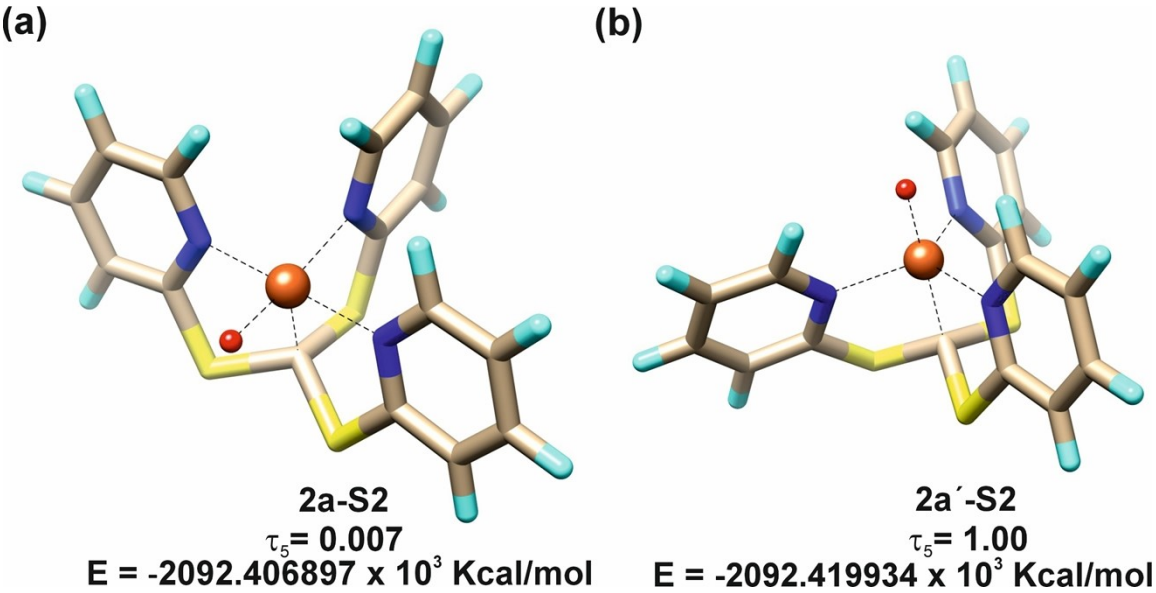


Fig. S6 *Optimised geometries of the two S = 2 isomers of* ***2a****, denoted as* ***2a-S2*** *and* ***2a'-S2****. The relative energies (in kcal mol⁻¹) and* τ_5 *values for each structure are indicated within the figure. The* ***2a'-S2*** *isomer is computed to be more stable than* ***2a-S2*** *by 13 kcal/mol.*

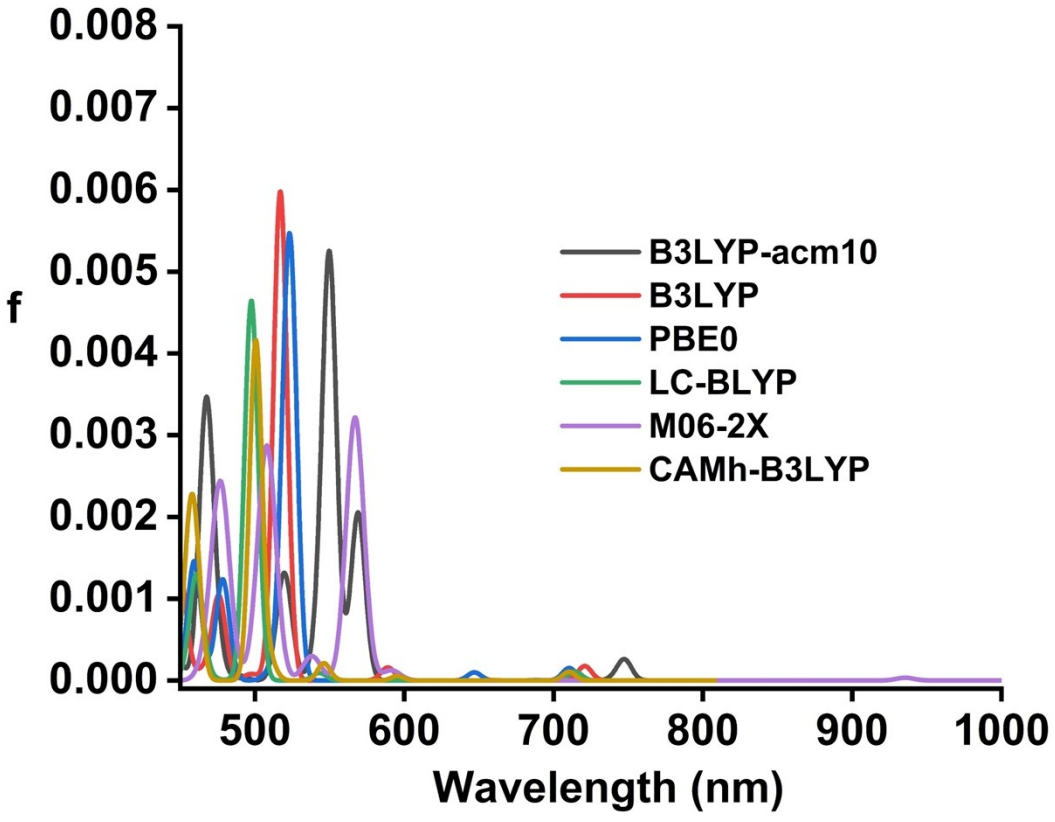


Fig. S7 *Comparison of TD-DFT absorption spectra of complex* ***2b*** *calculated using different functionals (B3LYP-acm10 (10% Hartree–Fock exchange), B3LYP (20% Fock exchange), PBE0, LC-BLYP, M06-2X, LACVP, CAMh-B3LYP(Kaila and coworker, J. Chem. Theory Comput.* **2020,** *16,* 587−600*). Functional labels are shown in the plot.*

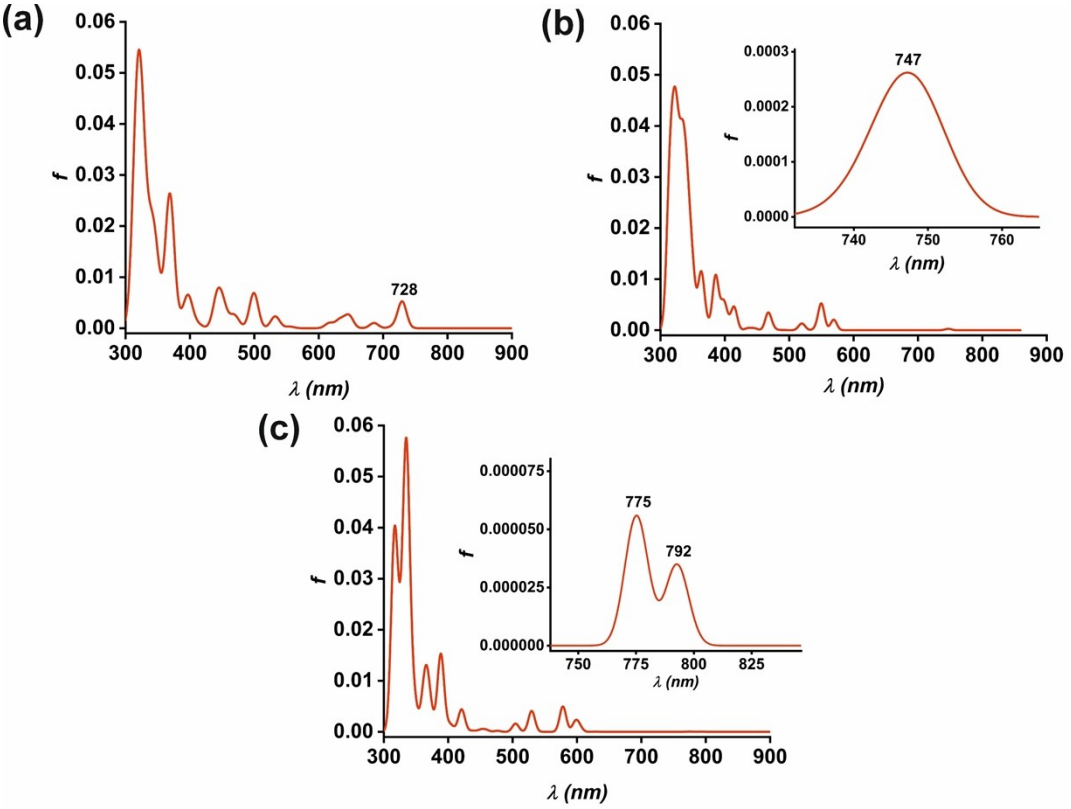


Fig. S8 *Time-dependent DFT (TD-DFT) calculated UV–vis absorption spectrum of (a)* ***2a-S1****, (b)* ***2b****, and (c)* ***2c****. Calculations were performed at the (B3LYP with 10% HF exchange) level of theory using the (CPCM) solvation model for acetonitrile.*

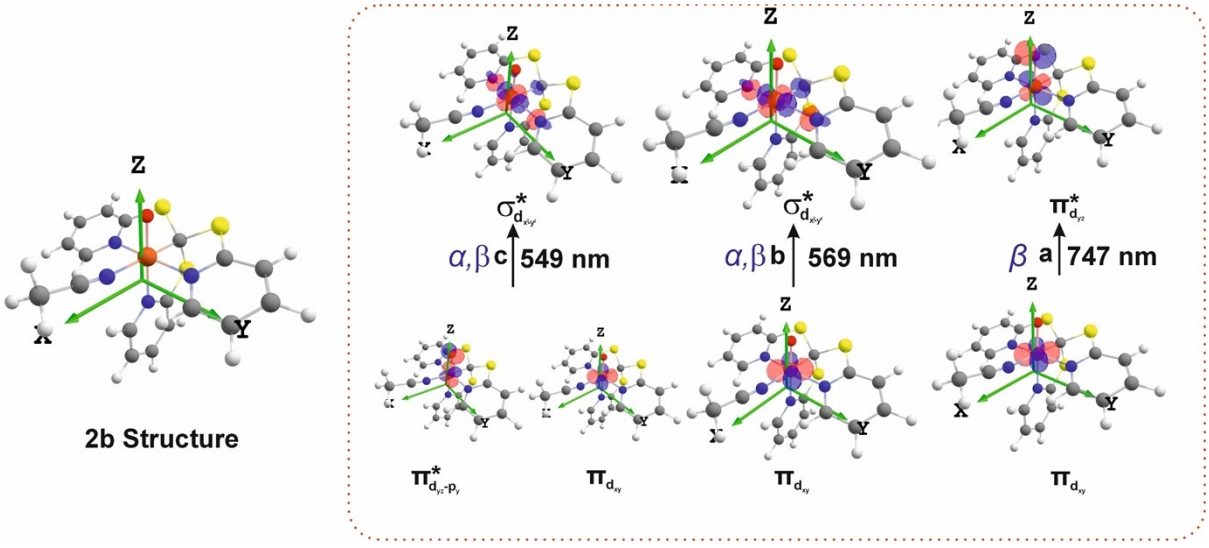


Fig. S9 *Optimised structure of* ***2b*** *with labelled axes. Selected electronic transitions at λ_{max} = 549 and 569 nm (α, β -spin) and 747 nm (β-spin) are shown, with the corresponding molecular orbitals.*

Table S2 *Comparison of predicted Mössbauer parameters for* ***2a-S1****,* ***2b****, and* ***2c*** *with experimentally obtained results.*

Complex	δ (mm/s)	$\lvert\Delta E_Q\rvert$ (mm/s)
Experimental	-0.06	1.67
2a-S1	0.15	3.39
2b	**-0.062**	**2.08**
2c	-0.04	0.452

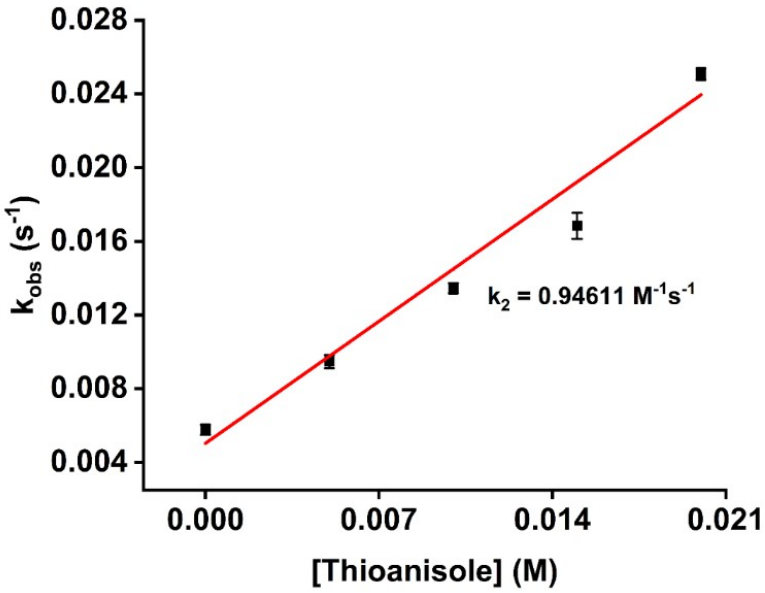


Fig. S10 *Plot of* k_{obs} *vs concentration of substrate for the reaction of the iron-oxo intermediate (****2****) with thioanisole.*

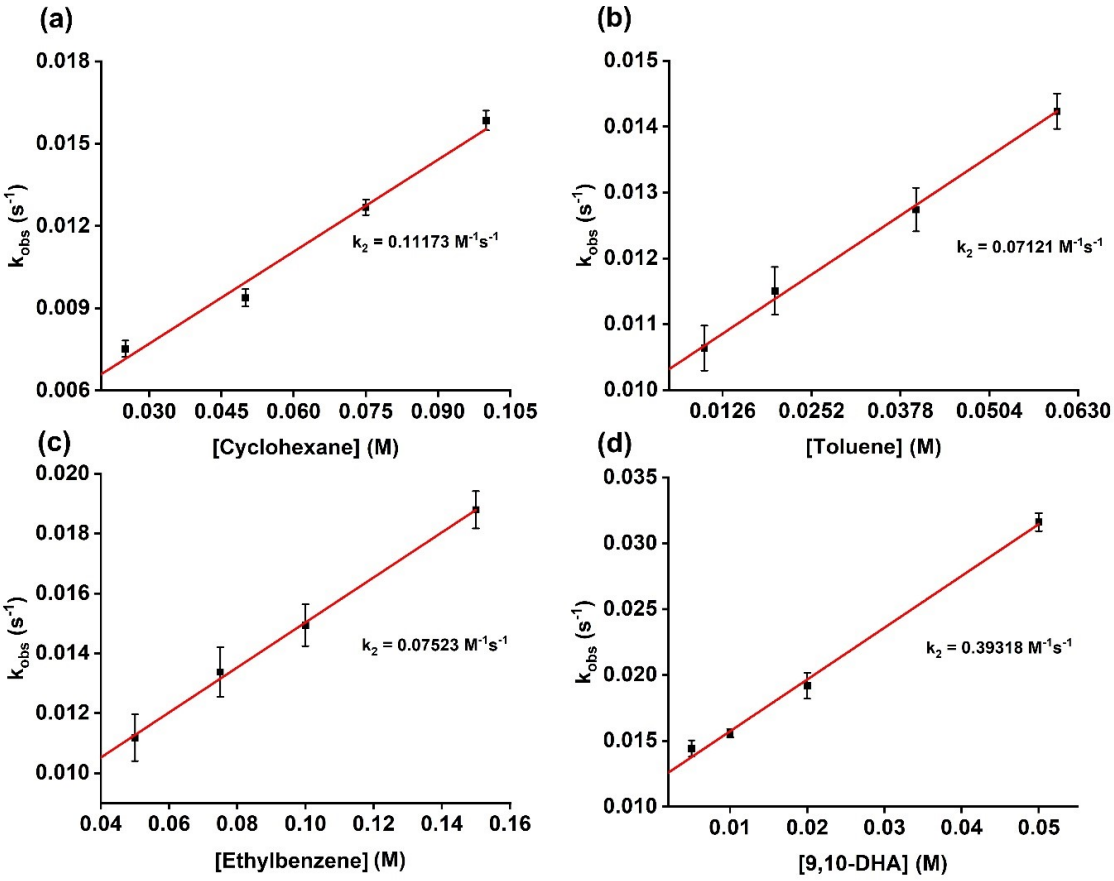


Fig. S11 *Plot of k_{obs} vs substrate concentration for the reaction of iron(IV)-oxo intermediate (**2**) with (a) cyclohexane, (b) toluene, (c) ethylbenzene, and (d) 9,10-dihydroanthracene (9,10-DHA) at 298 K.*

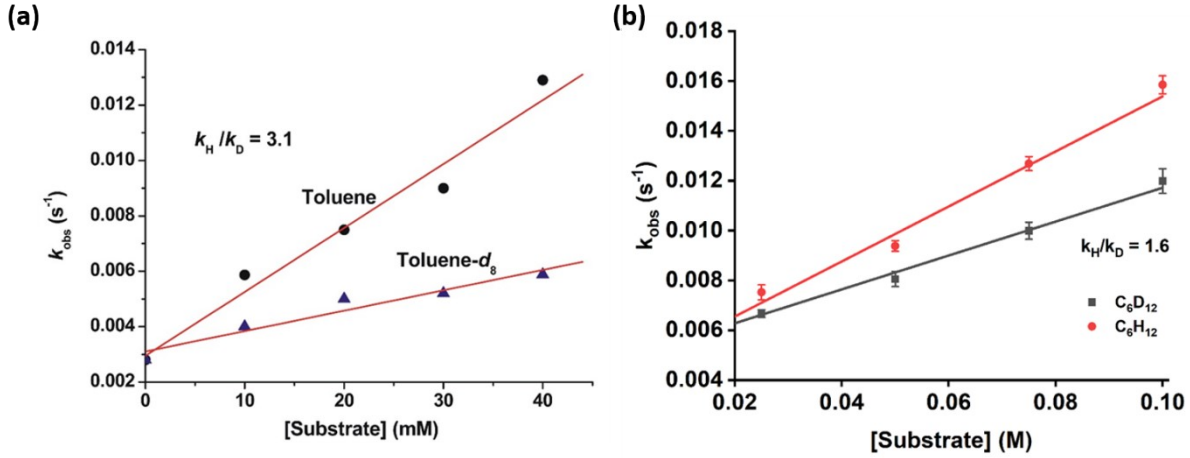


Fig. S12 *Kinetic isotope effect for the HAT reaction with (a) toluene and toluene-d_8, (b) cyclohexane and cyclohexane-d_{12}.*

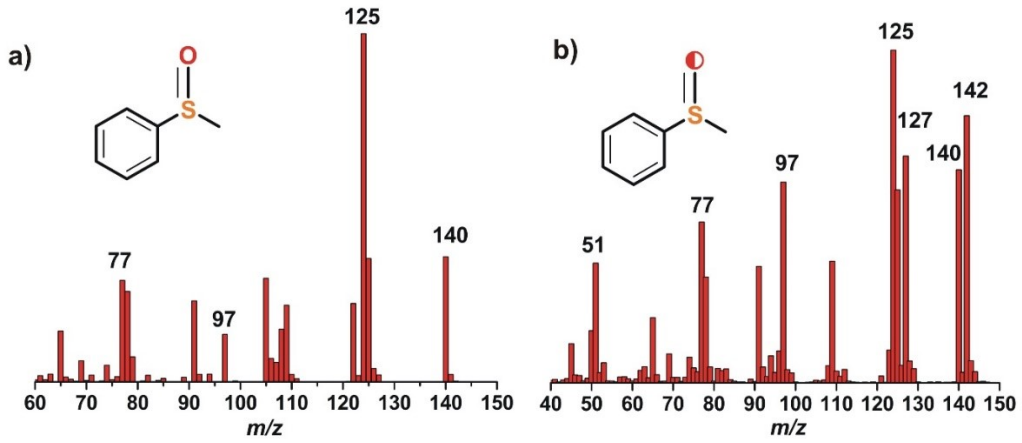


Fig. S13 *GC-MS spectra of the product derived from the reaction of (a) iron(IV)-oxo intermediate + thioanisole (50 equiv.) and (b) iron(IV)-oxo intermediate + thioanisole (50 equiv.) + 20 μL of* $H_2{}^{18}O$.

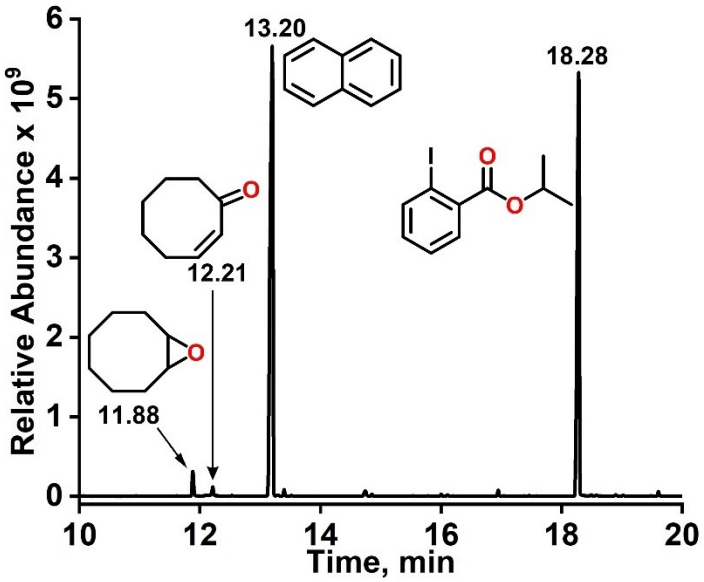


Fig. S14 *Gas chromatogram of the oxidised products formed in the reaction of* ***1*** *with cyclooctene (100 equiv.) in the presence of IBX ester (3.0 equiv.).*

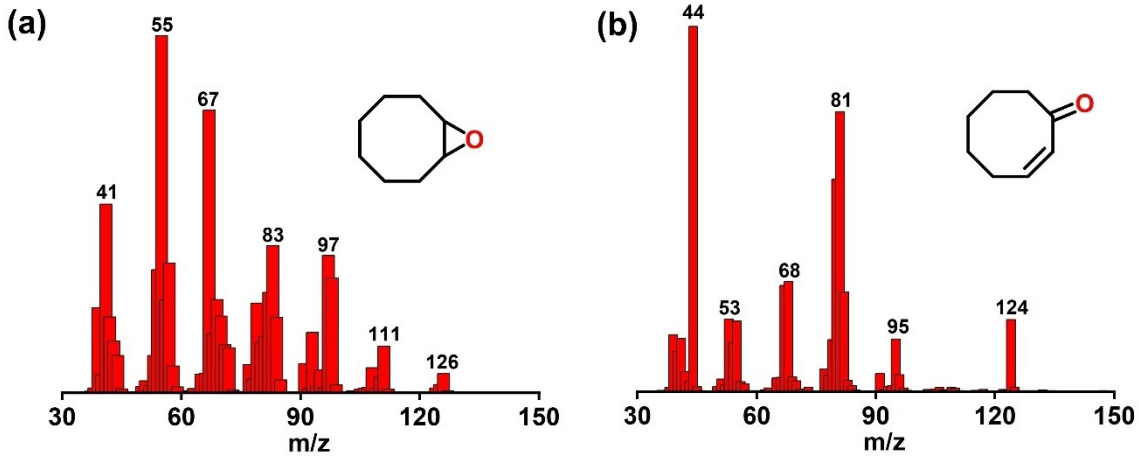


Fig. S15 *GC-MS spectra of (a) cyclooctene epoxide and (b) cyclooctene-2-one formed in the reaction of* ***1*** *with cyclooctene (100 equiv.) in the presence of IBX ester (3 equiv.).*

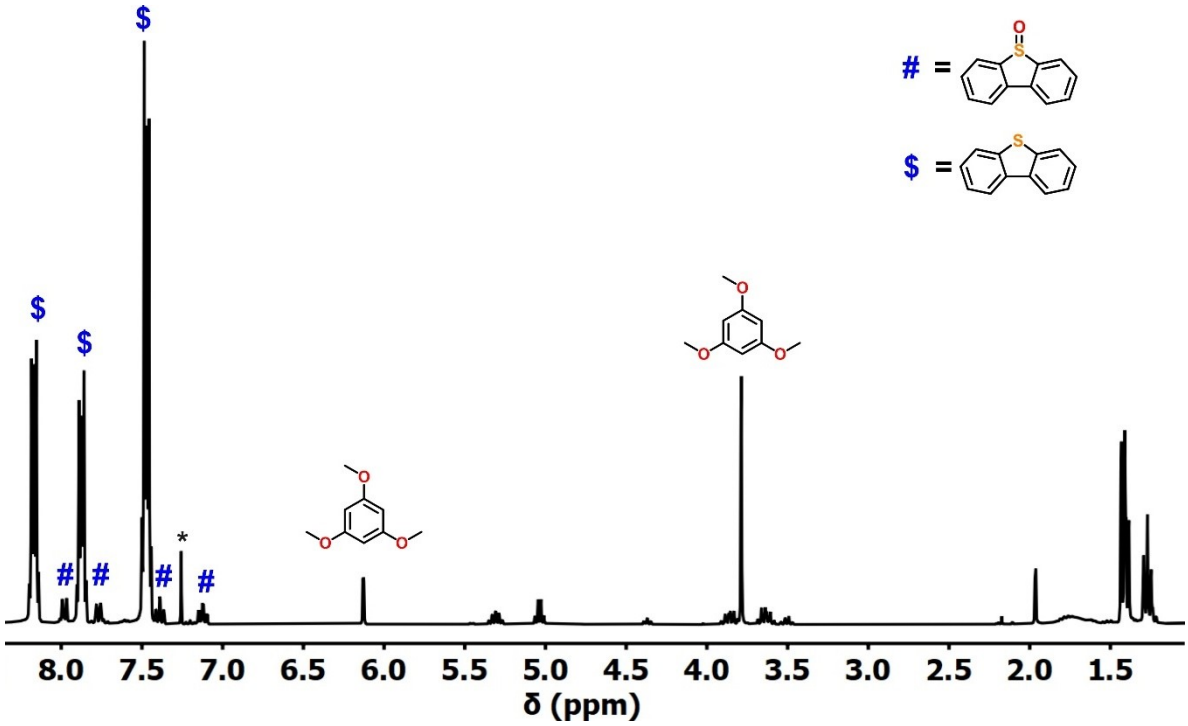
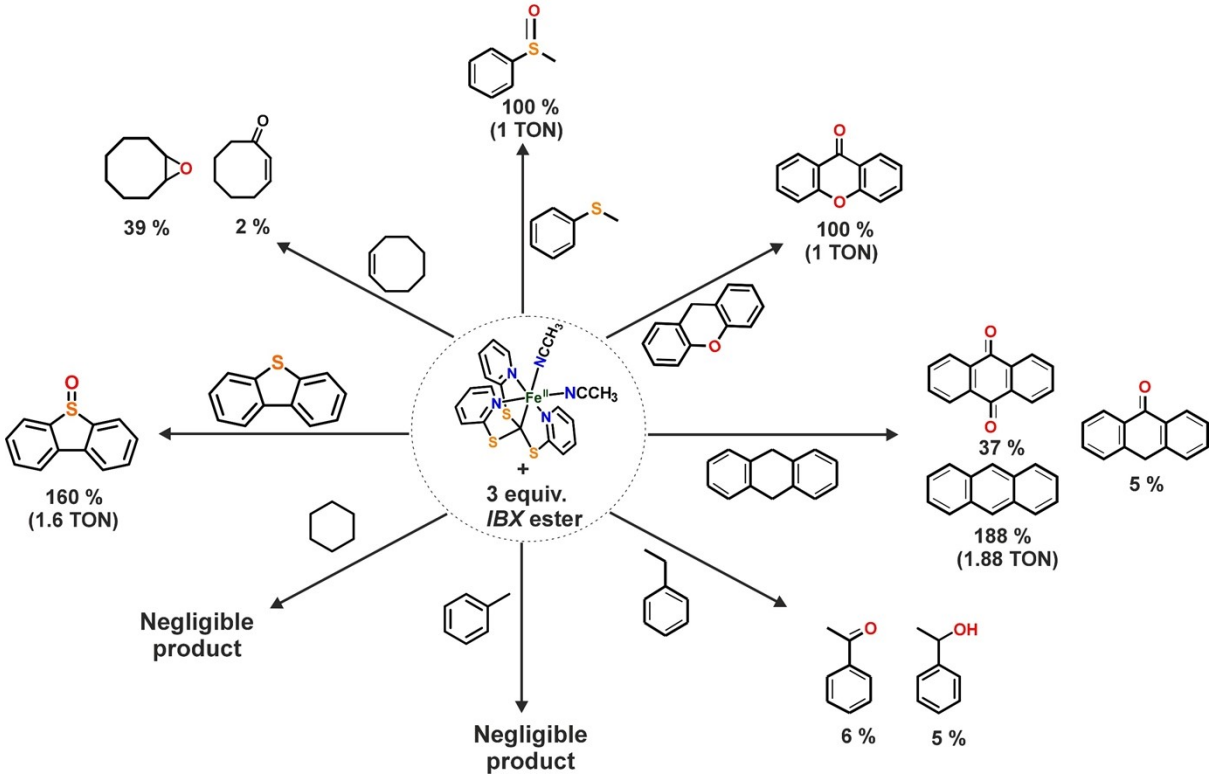


Fig. S16 *^{1}H NMR spectrum of the oxidised products formed in the reaction of* ***1*** *with dibenzothiophene (20 equiv.) in the presence of IBX ester (3.0 equiv.).*



Scheme S1 *Products derived from the reaction of the iron(IV)-oxo intermediate (**2**) with different substrates. Experimental conditions: Complex 0.002-0.005 mmol, 0.02 mmol (for solid substrates) / 0.2 mmol (for liquid substrates), CH_3CN solvent, 298 K., IBX Ester: 3 equiv.*

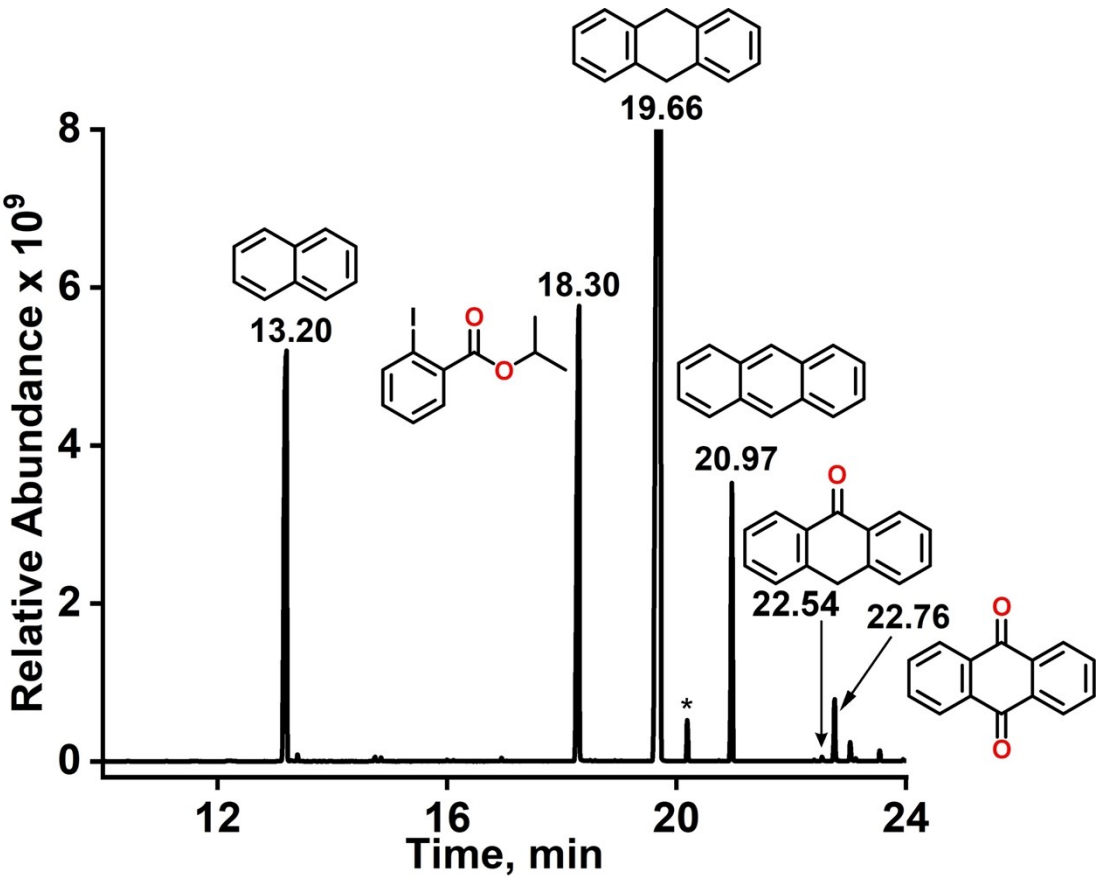


Fig. S17 *Gas chromatogram of the oxidised products formed in the reaction of* ***1*** *with 9,10-dihydroanthracene (10 equiv.) in the presence of IBX ester (3.0 equiv.).(*-marked peak at 20.18 originates from 2-iodobenzoic acid)*

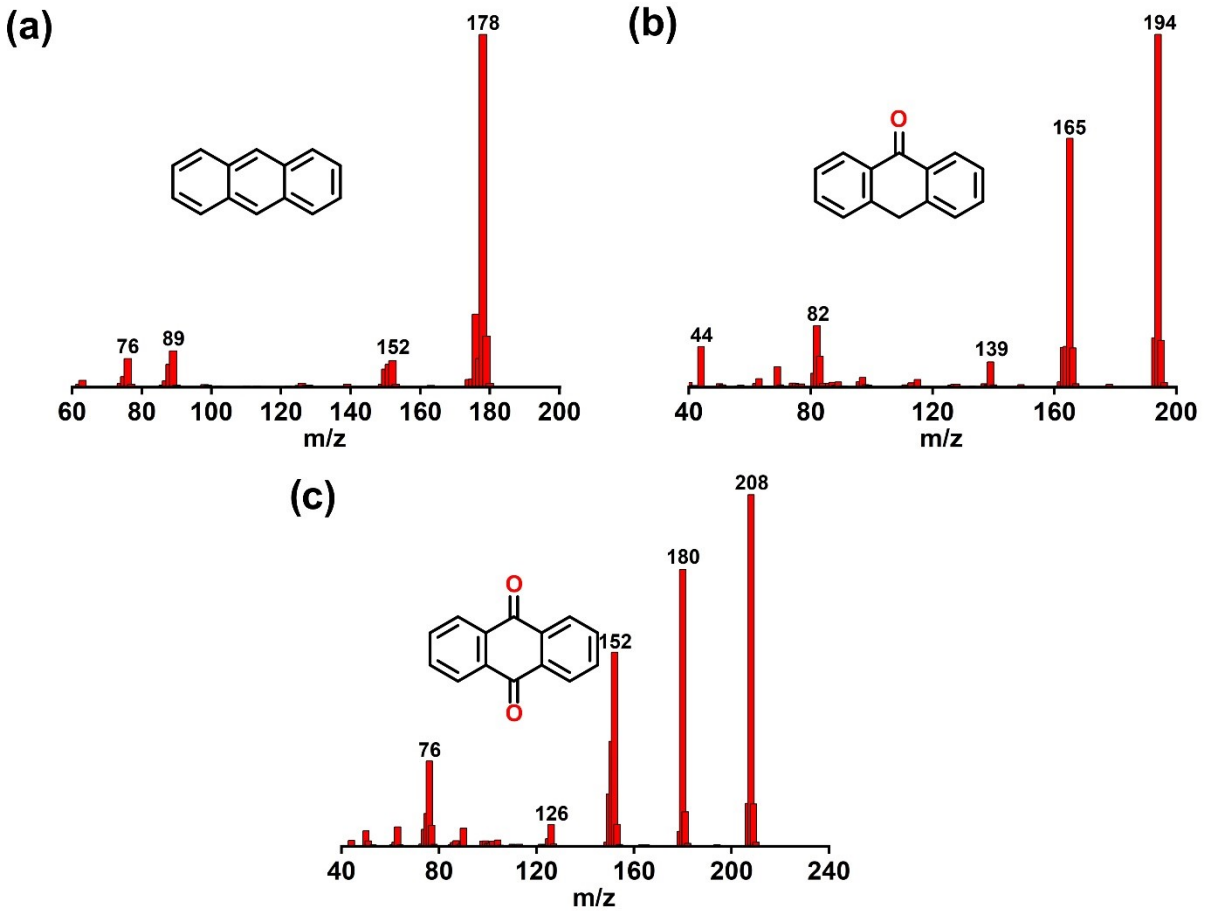


Fig. S18 *GC-MS spectra of (a) anthracene, (b) anthrone and (c) anthraquinone formed in the reaction of* ***1*** *with 9,10-dihydroanthracene (10 equiv.) and IBX ester (3 equiv.).*

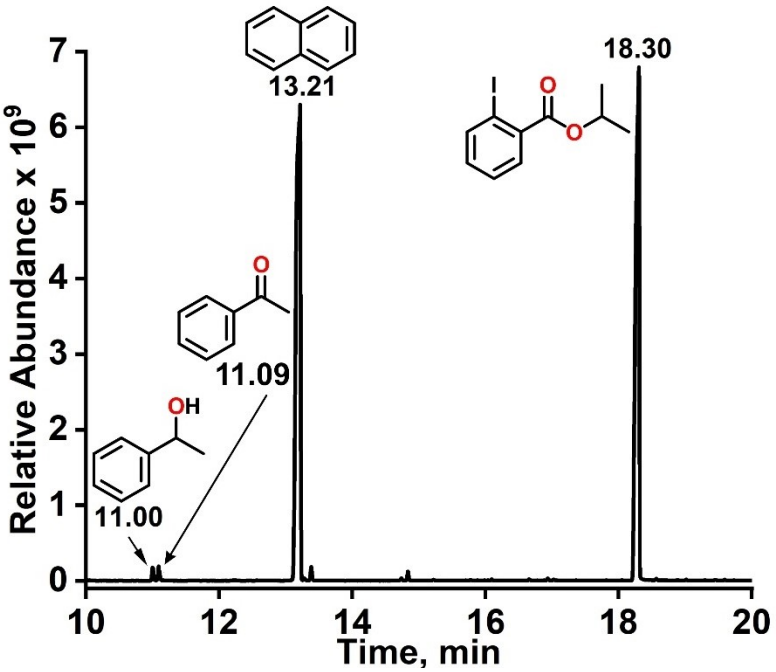


Fig. S19 *Gas chromatogram of the oxidised products formed in the reaction of* ***1*** *with ethylbenzene (100 equiv.) in the presence of IBX ester (3.0 equiv.).*

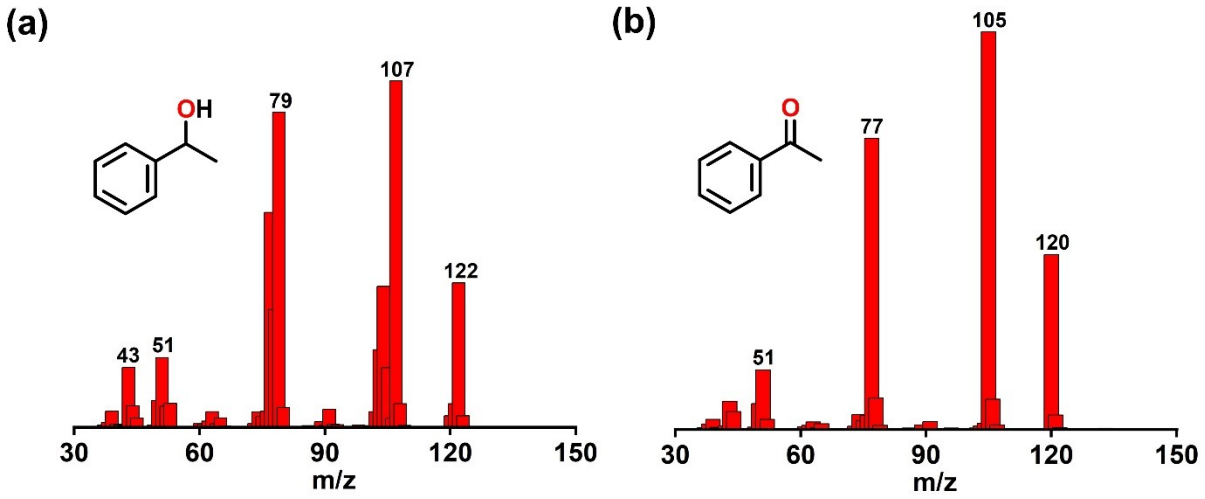


Fig. S20 *GC-MS spectra of (a) 1-phenylethan-1-ol and (b) acetophenone formed in the reaction of* ***1*** *with ethylbenzene (100 equiv.) and IBX ester (3 equiv.).*

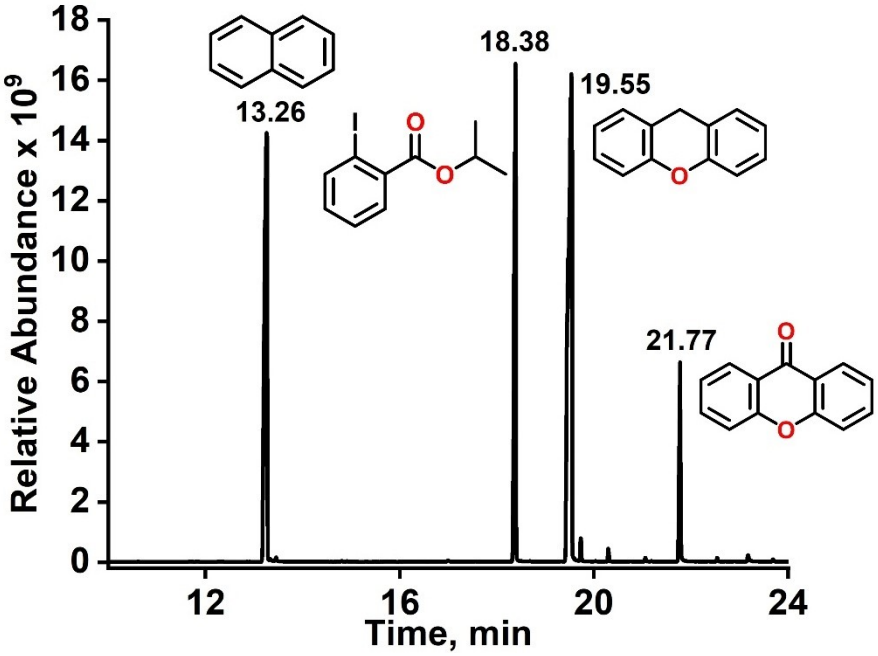


Fig. S21 *Gas chromatogram of the oxidised products formed in the reaction of iron(IV)-oxo intermediate with xanthene (10 equiv.) in the presence of IBX ester (3.0 equiv.).*

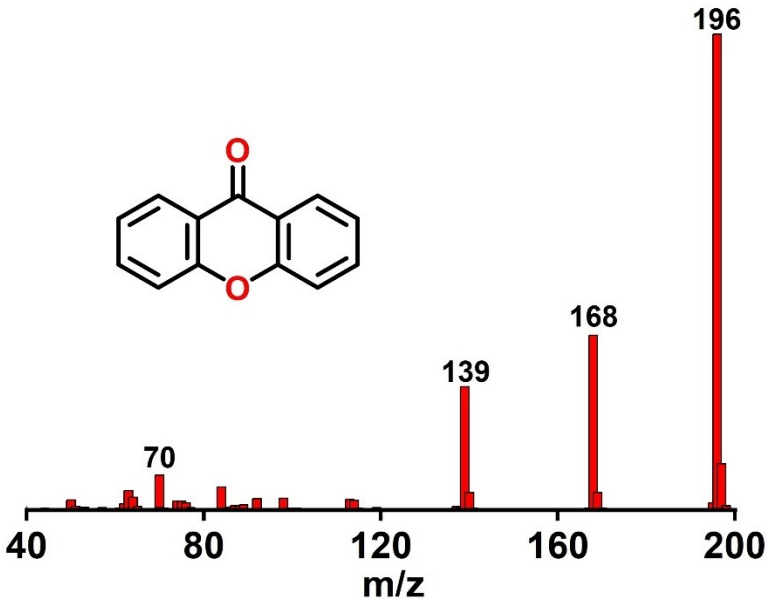


Fig. S22 *GC-MS spectra of xanthone formed in the reaction of* ***1*** *with xanthene (10 equiv.) and IBX ester (3 equiv.).*

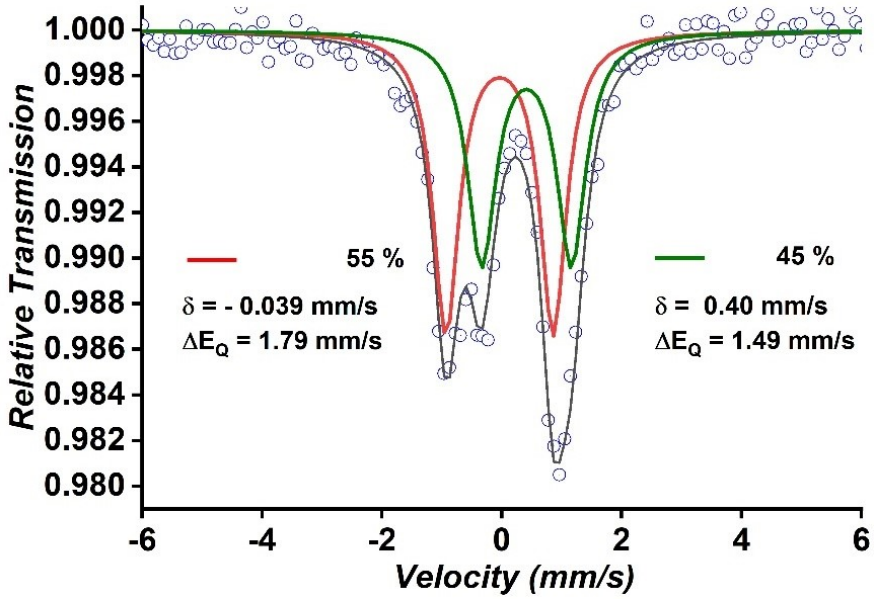


Fig. S23 *Zero-field* ^{57}*Fe (100% enriched) Mössbauer spectrum of the frozen acetonitrile (77 K) obtained from the reaction of complex* ***1*** *(2 mM) with IBX ester (3 equiv.) at 298 K.*

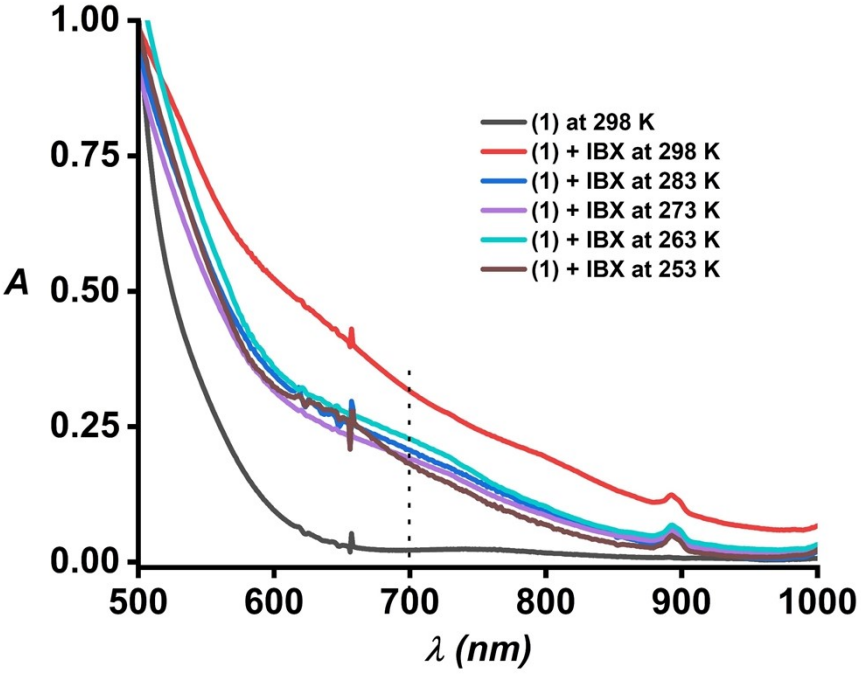


Fig. S24 *Generation of* ***2*** *in the reaction between* ***1*** *(1 mM) and IBX ester (3 equiv.) at different temperatures.*

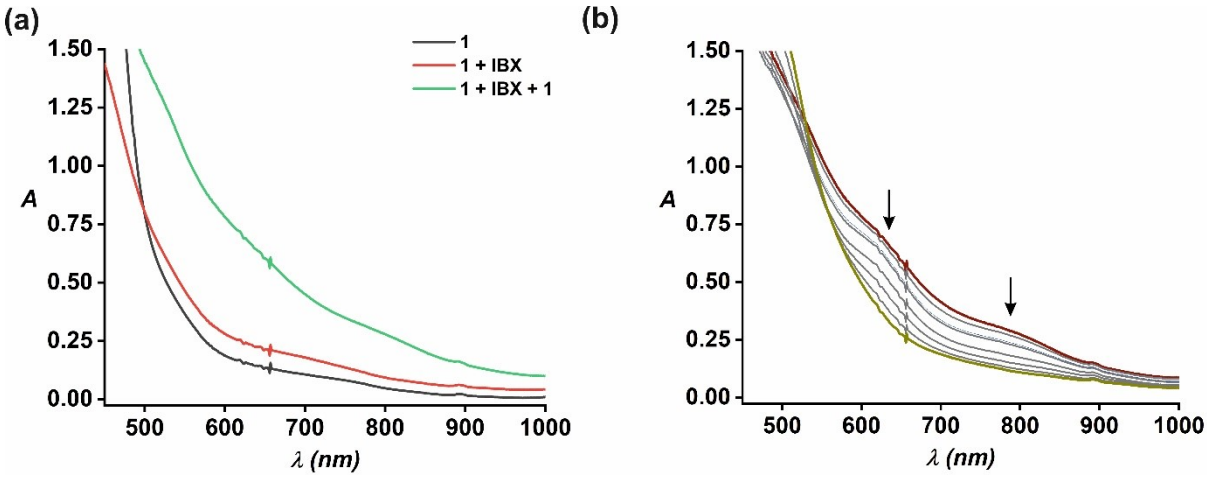


Fig. S25 *(a) Generation of iron-oxo from* ***1*** *(1mM) using IBX ester (3 equiv.) followed by addition of* ***1*** *(1 equiv) at 278 K in acetonitrile (b) Decay of the species (showing bands at 650 and 790 nm)at this temperature.*

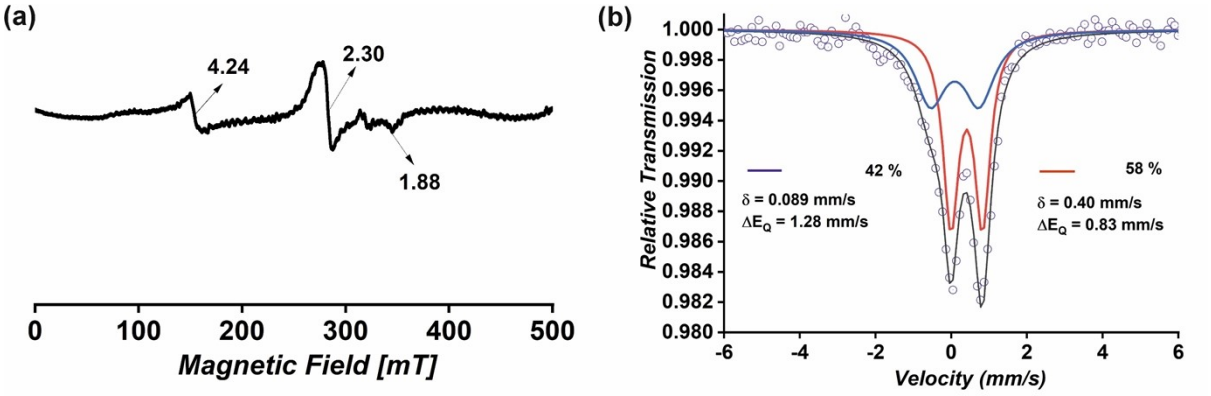


Fig. S26 *(a) X-band EPR of the decay product of* ***2*** *in a frozen acetonitrile glass at 77 K, (Experimental conditions for EPR: temperature = 77 K, microwave frequency = 9.026 GHz, microwave power = 3 mW, modulation amplitude = 100 kHz, modulation width = 1 mT, time constant = 0.05 s) (b) Zero-field* ^{57}*Fe Mössbauer of the decay product in a frozen acetonitrile at 77 K.*

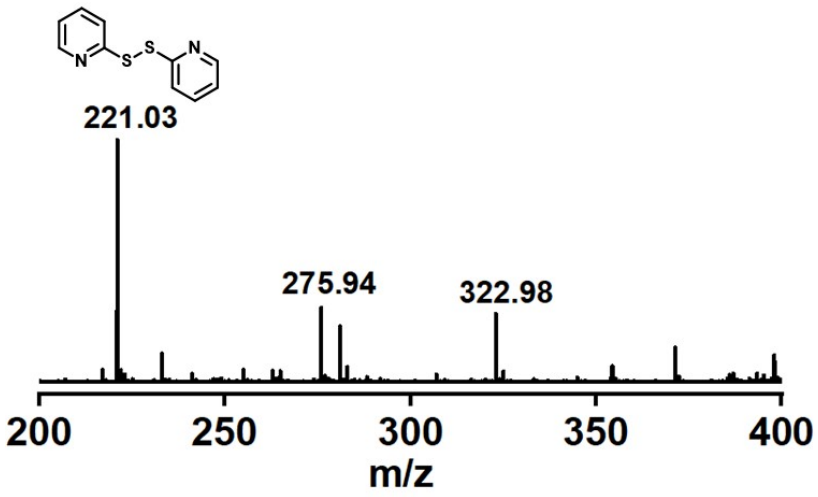


Fig. S27 *ESI-MS (positive ion mode in acetonitrile) of the decay product of* ***2****.*

Table S3 Cartesian coordinates for the optimised structure of the five-coordinate $[(L^1)Fe^{IV}(O)]^+$ species (2a-S1) in triplet spin state.

Atom Number	Coordinates (Angstroms) *X*	*Y*	*Z*
Fe	0.000000000	0.000000000	0.000000000
S	2.035422137	-0.079814927	-2.394219944
S	2.729811983	-1.456952612	0.165832323
S	2.723138873	1.496151002	0.082104768
O	0.000000000	0.000000000	1.606257940
N	-0.613276615	0.005260464	-2.007928250
N	0.134779878	-2.000636091	-0.125363408
N	0.107020665	1.999821822	-0.109301623
C	-1.901712784	0.039823375	-2.405739463
H	-2.646874306	0.059644040	-1.613450234
C	0.090622902	-0.005678392	-4.301625967
H	0.903246266	-0.021374993	-5.023155619
C	-2.259887522	0.049173225	-3.745936314
H	-3.308720848	0.075553746	-4.026671889
C	1.370860141	-2.546982871	-0.024512301
C	-1.239501834	0.026323544	-4.708519618
H	-1.480875490	0.035275093	-5.769085076
C	0.368914582	-0.017052980	-2.925779167
C	1.907754455	0.000000000	-0.551178867
C	-0.938259688	-2.803623283	-0.262293536
H	-1.902291793	-2.308713562	-0.345155221
C	-0.980816060	2.790729039	-0.190043752
H	-1.940979417	2.284365368	-0.238217719
C	1.338392775	2.560680454	-0.050565913
C	-0.826198850	-4.187750152	-0.280159761
H	-1.718485933	-4.798409857	-0.383130159

C	0.447114588	-4.760141379	-0.164699110
H	0.571815182	-5.840424600	-0.182070604
C	1.562025495	-3.933234982	-0.045948466
H	2.567368780	-4.340883937	0.018388579
C	-0.887695609	4.176041001	-0.194902593
H	-1.791328842	4.775831743	-0.252376252
C	1.510849544	3.950069243	-0.062803336
H	2.512758410	4.369833092	-0.031075674
C	0.382302551	4.763657409	-0.125836336
H	0.493078703	5.845547441	-0.133863136

Table S4 Cartesian coordinates for the optimised structure of the six-coordinate $[(L^1)Fe^{IV}(O)(CH_3CN)]^+$ species (2b) in triplet spin state.

Atom Number	Coordinates (Angstroms) *X*	*Y*	*Z*
Fe	0.000000000	0.000000000	0.000000000
S	0.877967578	-1.480321919	-2.553554309
S	0.940087278	1.449656537	-2.537759290
S	-1.684433009	0.058226079	-2.671103671
N	0.003466416	0.015094048	2.003958055
N	-0.086373917	-1.975311193	-0.125015639
O	1.643263263	0.000000000	0.016588616
N	-0.098001614	1.972758961	-0.149818590
N	-2.073470935	-0.013369733	-0.026785937
C	-0.528860246	-2.768376458	0.870075311
H	-0.897393886	-2.265126094	1.757053601
C	0.406088030	-3.932339122	-1.434803392
H	0.757780611	-4.351325257	-2.373866488
C	-0.508448502	-4.153690629	0.782439333
H	-0.868886291	-4.749777913	1.615859171

C	0.383129908	2.528682812	-1.286939881
C	-0.020289158	-4.746214867	-0.389808086
H	0.008810955	-5.828389255	-0.494884754
C	0.357620257	-2.540817875	-1.271708604
C	0.000000000	0.000000000	-1.970686307
C	-0.579219068	2.773126533	0.820833607
H	-0.978533221	2.276718068	1.698586605
C	-2.851346541	-0.045197263	1.076791988
H	-2.330448002	-0.058140839	2.027641192
C	-2.668783399	0.002953698	-1.234916834
C	0.216716477	0.020362651	3.135555794
C	-0.559031117	4.157737163	0.719599216
H	-0.950674323	4.761097236	1.533517257
C	-0.029680017	4.740429765	-0.439591808
H	0.000796505	5.821677849	-0.553269911
C	0.434491905	3.918053627	-1.462002453
H	0.815825557	4.328871937	-2.393075945
C	-4.237123031	-0.059779082	1.021331554
H	-4.812747280	-0.084050026	1.942126001
C	-4.066568252	-0.012513087	-1.379213769
H	-4.507454233	-0.000235691	-2.372634280
C	-4.856608037	-0.043488896	-0.236570379
H	-5.940834610	-0.055773384	-0.323319179
C	0.491552507	0.016277888	4.558869759
H	0.036855099	-0.869993789	5.014363073
H	0.073556589	0.919383005	5.016068423
H	1.575294641	-0.006041750	4.716784297

Table 5 Cartesian coordinates for the optimised structure of the six-coordinate [(L^1)Fe^{IV}(O)(CH_3CN)]$^+$ species (2c) in triplet spin state.

Atom Number	Coordinates (Angstroms) *X*	*Y*	*Z*
Fe	0.000000000	0.000000000	0.000000000
S	-1.458997486	-0.911728541	-2.638182909
S	1.479094305	-0.876590262	-2.639199624
S	-0.022172766	1.690567777	-2.729798988
O	0.001626552	-0.005633718	1.660443805
N	-1.966407872	-0.044298017	-0.167448112
N	0.020555846	-1.922779632	-0.044989953
N	1.967607945	0.000000000	-0.168112455
N	-0.023028536	1.965733152	-0.068749009
C	-2.761037973	0.308871130	0.862188424
H	-2.244850048	0.651995308	1.753094400
C	-3.911733181	-0.604726001	-1.459918745
H	-4.327029965	-0.950940493	-2.402754919
C	-4.144265710	0.215882541	0.793406180
H	-4.745399189	0.507780410	1.649802639
C	2.532526237	-0.427032931	-1.320026746
C	0.027084128	-3.071238320	-0.061964736
C	-4.729262913	-0.258640732	-0.388419857
H	-5.809949965	-0.343505397	-0.478023101
C	-2.522042459	-0.483992189	-1.319172819
C	0.000000000	0.000000000	-2.072560493
C	2.754628299	0.368886063	0.861858458
H	2.231052177	0.699164761	1.753355450
C	-0.029948982	2.690734232	1.072730602
H	-0.020192321	2.105331652	1.986905878
C	-0.033247265	2.610476944	-1.255412181

C	0.036549494	-4.519766016	-0.110774936
H	-0.807952128	-4.865917915	-0.716507766
H	-0.050740896	-4.922461990	0.903802485
H	0.974621483	-4.860482817	-0.561975332
C	4.139527481	0.305598738	0.792433282
H	4.734542230	0.609170930	1.649067926
C	4.734425920	-0.155691468	-0.389792973
H	5.816640272	-0.217941514	-0.479312472
C	3.924417715	-0.518438530	-1.461495651
H	4.346632979	-0.854958542	-2.404845853
C	-0.047552688	4.076362471	1.076263066
H	-0.051921889	4.609410998	2.022673313
C	-0.051415885	4.014144615	-1.328466183
H	-0.058818527	4.497735275	-2.301894607
C	-0.059156860	4.752535942	-0.152584213
H	-0.073313038	5.839508423	-0.190604926

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