Supporting Information

Iron-Based Dehydration Catalyst for Selective Formation of Styrene

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PART I

1. Experimental Data for Section "Catalyst Design"

1.1 Magnetic Moment of $[Fe(OTf)_2(FOX)]$ - Evans' NMR Method[1-3]

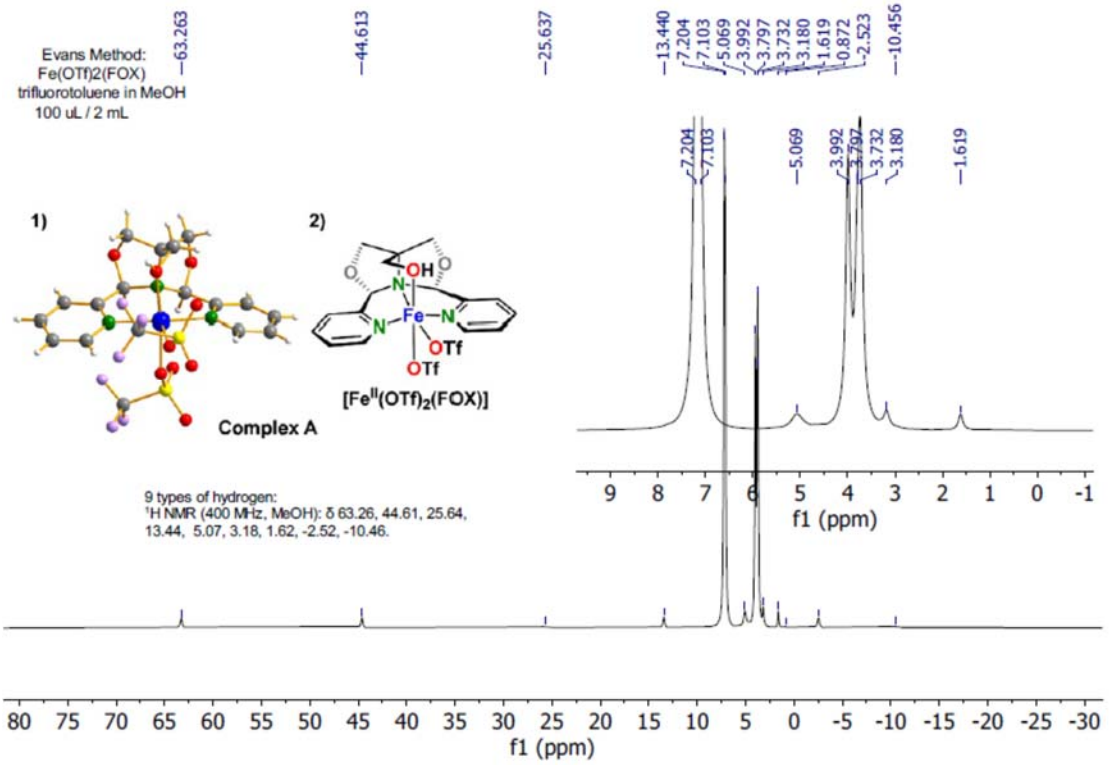


Figure S1. ^{1}H NMR spectrum of trifluorotoluene for Evans' Method. NMR tube: $[Fe(OTf)_2(FOX)]$ (**A**) and trifluorotoluene in methanol solvent.

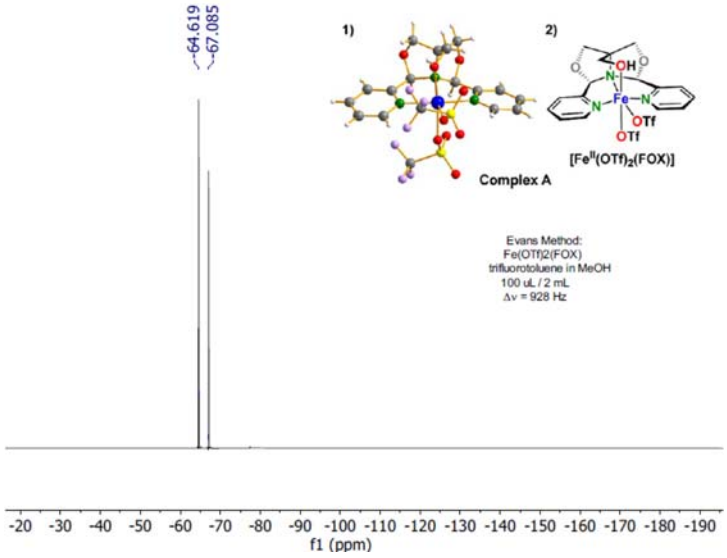


Figure S2. ^{19}F NMR spectrum of trifluorotoluene for Evans' Method. NMR tube: $[Fe(OTf)_2(FOX)]$ (**A**) and trifluorotoluene w/ capillary of trifluorotoluene, MeOH solvent.

Table S1. Data for determination of effective magnetic moment μ_{eff} of **A**.

Sample Mass [g]	0.0357	X_M [m^3/mol]	0.01077
Molar Mass [g/mol]	653.30	μ_{eff}(**A**)	5.05
Temperature [K]	296.2	μ_{eff}(HS Fe^{2+})	5.1-5.7
NMR Frequency [MHz]	376.46	μ_{eff}(LS Fe^{2+})	0
Total Volume [mL]	1.00		
Delta [ppm]	2.466		
Delta [Hz]	928.3		
Concentration [M]	0.0546		

(1) Evans, D. F. The determination of the paramagnetic susceptibility of substances in solution by nuclear magnetic resonance. *J. Chem. Soc.* **1959**, 2003-2005.

(2) Kettle, S. F. A. Magnetic properties of transition metal complexes. In:*Physical Inorganic Chemistry*; Springer: Berlin, Heidelberg, 1996, pp.185-210.

(3) Phillips, W. D.; Poe, M. Contact Shifts and Magnetic Susceptibilities in Iron-Sulfur Proteins as Determined from Nuclear Magnetic Resonance Spectra. *Meth. Enzymol.* **1972**, *24*, 304–317.

2. Experimental Data for Section "Reaction Optimization"

2.1 Kinetic NMR Studies

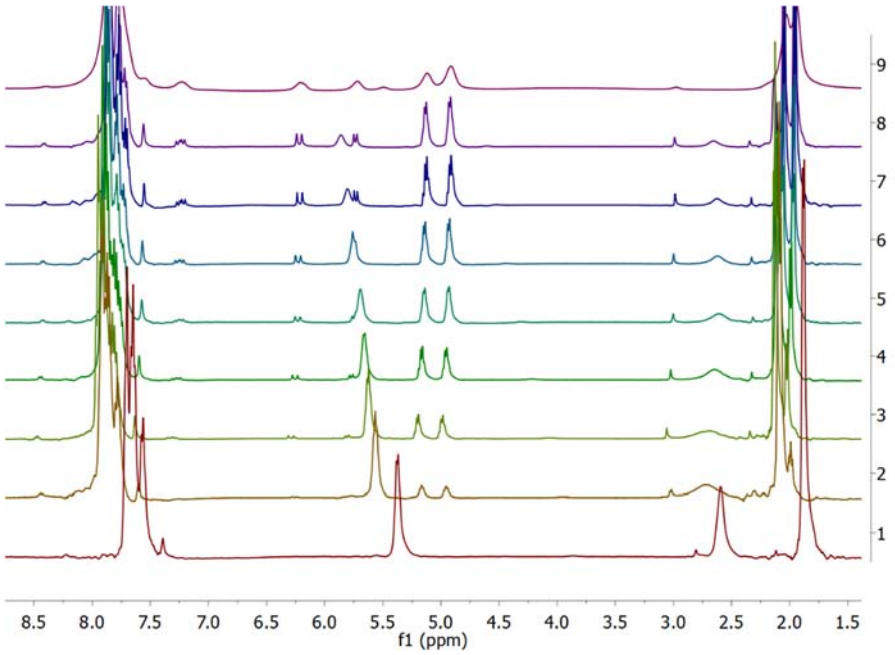


Figure S3. ^{1}H NMR spectra of 1.64 M solution of 1-phenylethanol in deuterated *o*-dichlorobenzene with 1 mol% [$Fe(OTf)_2$(FOX)] after heating at 100 °C for 0h, 2h, 4h, 6h, 8h, 10h, 12h, 14h, and 36h.

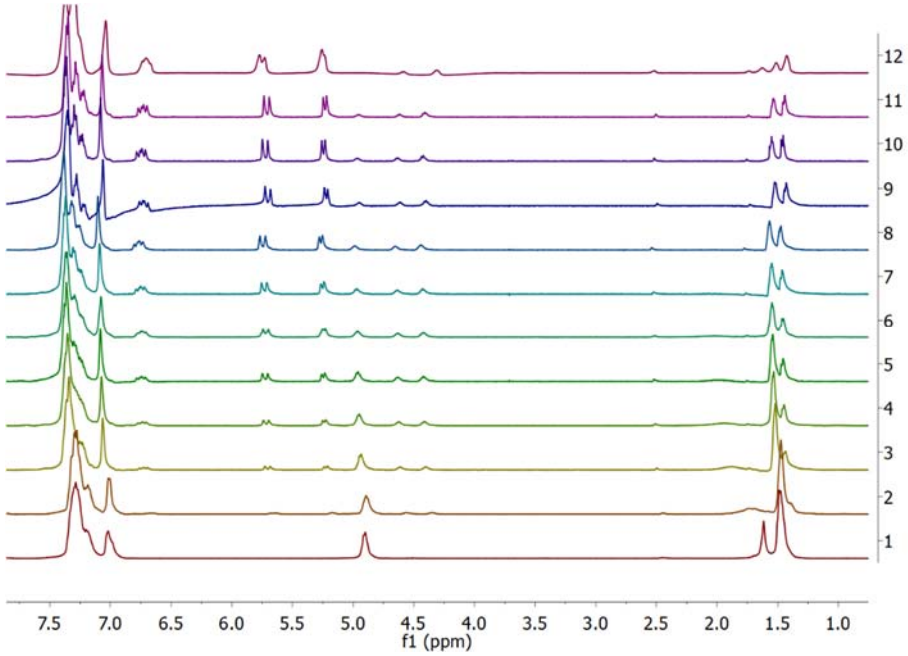


Figure S4. ^{1}H NMR spectra of 164 mM solution of 1-phenylethanol in deuterated *o*-dichlorobenzene with 1 mol% [Fe(OTf)$_2$(FOX)] after heating at 100 °C for 0h, 1h, 2h, 3h, 4h, 5h, 6h, 7h, 8h, 9h, 12h, and 24h.

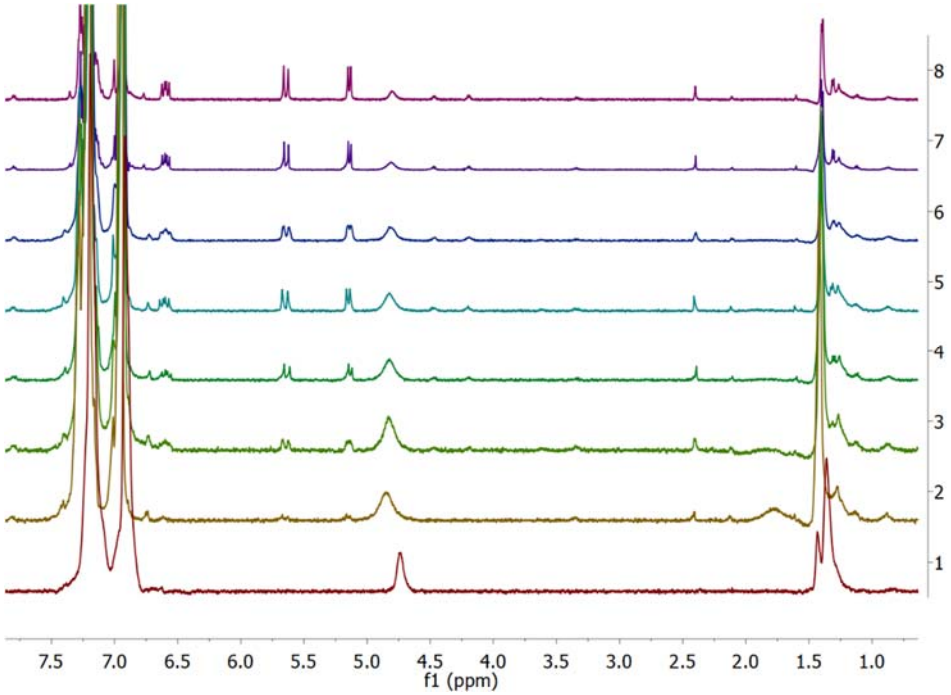


Figure S5. ^{1}H NMR spectra of 16.4 mM solution of 1-phenylethanol in deuterated *o*-dichlorobenzene with 1 mol% [Fe(OTf)$_2$(FOX)] after heating at 100 °C for 0h, 13h, 39h, 62, 87h, 112h, 136h, and 164h.

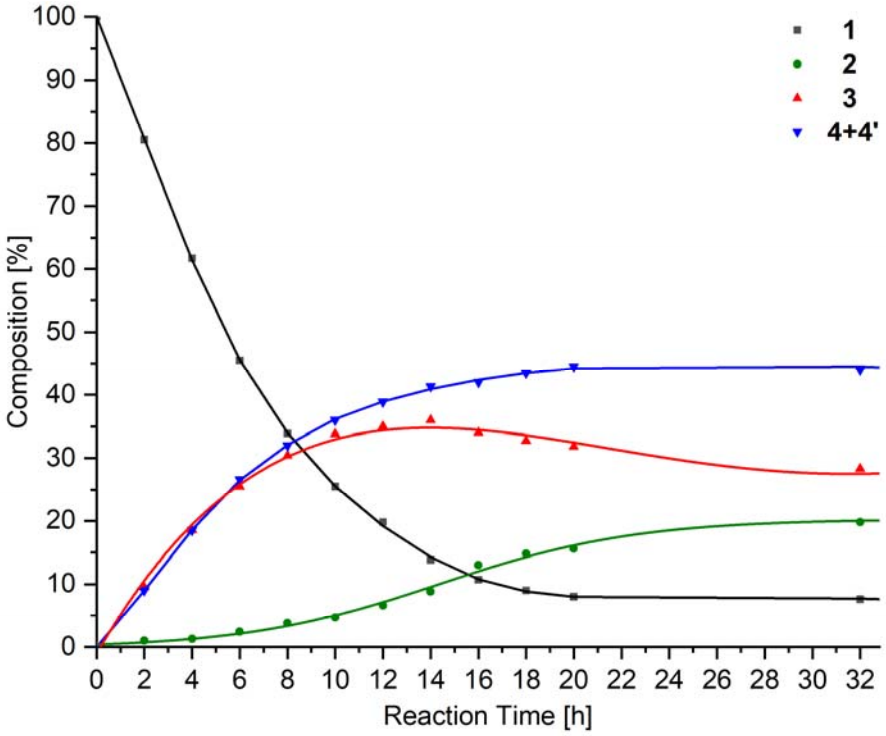


Figure S6. Reaction progress of 1.64 M solution of 1-phenylethanol in deuterated *o*-dichlorobenzene with 1 mol% $[Fe(OTf)_2(FOX)]$ at 100 °C.

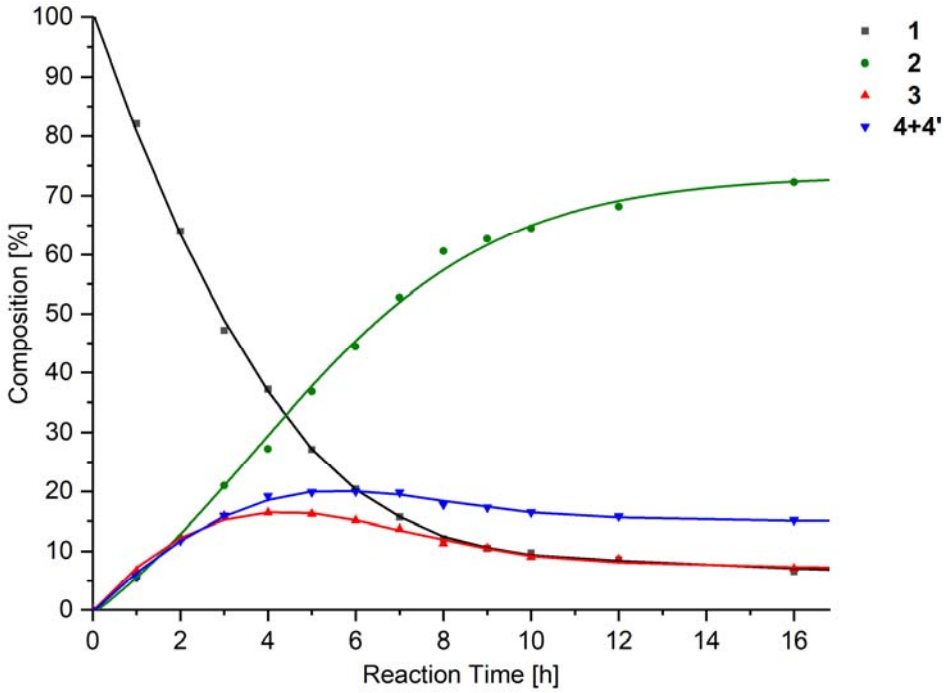


Figure S7. Reaction progress of 164 mM solution of 1-phenylethanol in deuterated *o*-dichlorobenzene with 1 mol% $[Fe(OTf)_2(FOX)]$ at 100 °C.

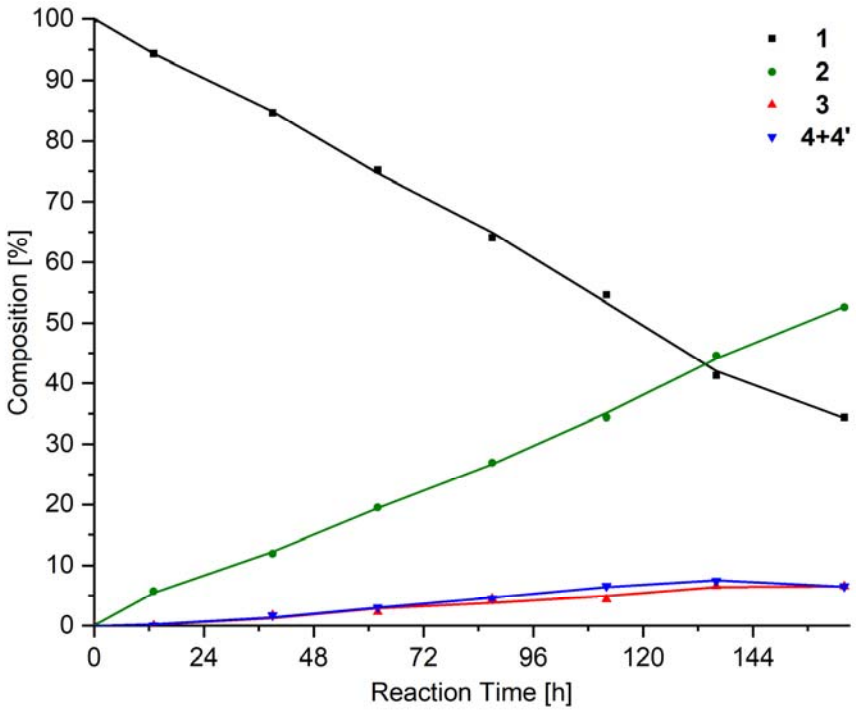
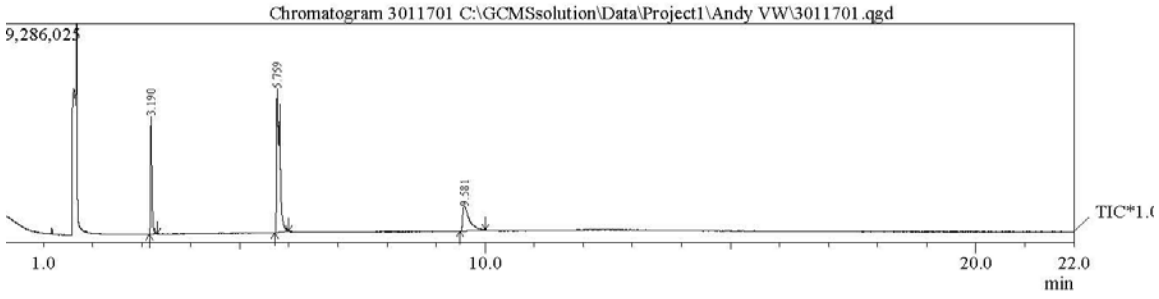


Figure S8. Reaction progress of 16.4 mM solution of 1-phenylethanol in deuterated *o*-dichlorobenzene with 1 mol% $[Fe(OTf)_2(FOX)]$ at 100 °C.

3. Experimental Data for Section “Mechanistic Investigations”

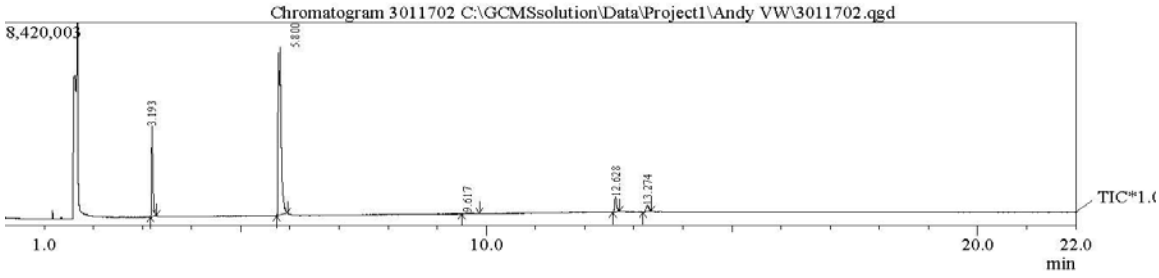
3.1 GC-MS Data for Experiments with Isotope Labels



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.190	3.158	3.317	48598533	19.95	26583668	41.22	1.82	MI	Styrene
2	5.759	5.717	6.000	143345667	58.84	32396895	50.23	4.42	MI	ODCB
3	9.581	9.492	10.008	51679499	21.21	5512353	8.55	9.37	MI	PhEtOH
				243623699	100.00	64492916	100.00			

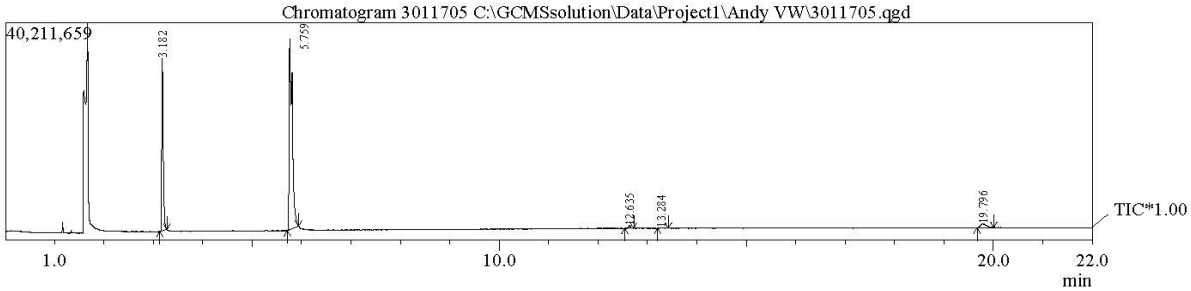
Figure S9. Gas chromatogram of mixture of 1-phenylethanol-d_5, styrene-d_0, and [Fe(OTf)$_2$(FOX)] in *o*-dichlorobenzene.



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.193	3.167	3.283	31665025	18.02	17079332	32.24	1.85	MI	Styrene
2	5.800	5.733	5.950	130972340	74.52	31677263	59.79	4.13	MI	ODCB
3	9.617	9.500	9.858	1672773	0.95	221575	0.42	7.52	MI	PhEtOH
4	12.628	12.575	12.717	7678451	4.37	2792293	5.27	2.74	MI	Rac-Ether
5	13.274	13.192	13.358	3760752	2.14	1212392	2.29	3.09	MI	Meso Ether
				175749341	100.00	52982855	100.00			

Figure S10. Gas chromatogram of mixture of 1-phenylethanol-d_5, styrene-d_0, and [Fe(OTf)$_2$(FOX)] in *o*-dichlorobenzene after heating at 120 °C for 1h.



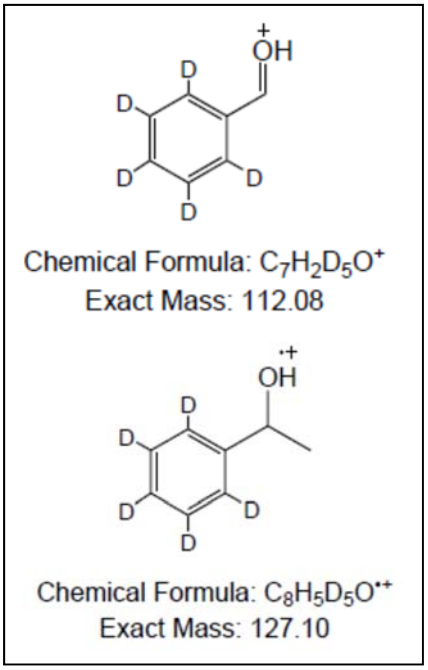
Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.182	3.133	3.275	64299441	28.61	32000370	46.64	2.00	MI	styrene
2	5.759	5.717	5.942	153214044	68.17	35315223	51.48	4.33	MI	ODCB
3	12.635	12.542	12.725	1151410	0.51	463587	0.68	2.48	MI	Rac Ether
4	13.284	13.208	13.425	414678	0.18	108647	0.16	3.82	MI	Meso Ether
5	19.796	19.675	20.008	5687634	2.53	718098	1.05	7.90	MI	Styrene dimer
				224767207	100.00	68605925	100.00			

Figure S11. Gas chromatogram of mixture of 1-phenylethanol-d_5, styrene-d_0, and [Fe(OTf)$_2$(FOX)] in *o*-dichlorobenzene after heating at 120 °C for 4h.

Table S2. Selected MS data for 1-phenylethanol fraction. (d_5, m/z = 127)

0h		1h		
m/z	Count	m/z	Count	
104	2	104	81	
105	203	105	43	
106	2622	106	122	
107	5967	107	412	
108	5258	108	195	
109	11242	109	88	
110	24351	110	1277	
111	18182	111	137	
112	213753	112	13023	M^+ – Me
113	16300	113	883	
114	933	114	132	
120	0	120	8	
121	16	121	25	
122	2	122	105	
123	72	123	24	
124	0	124	0	
125	6640	125	312	
126	8047	126	154	
127	56806	127	3012	M^+
128	5354	128	323	
129	391	129	45	



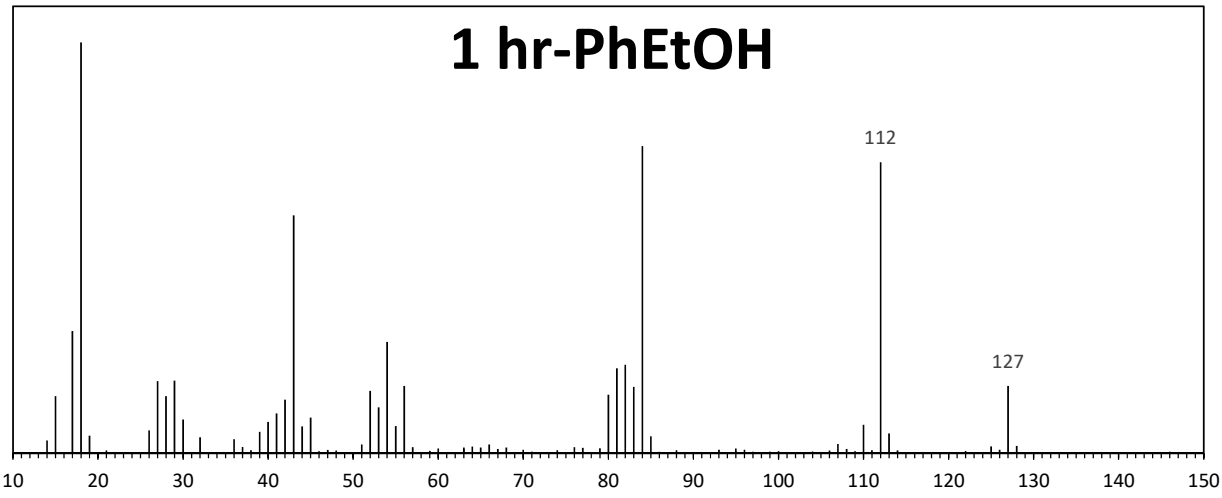
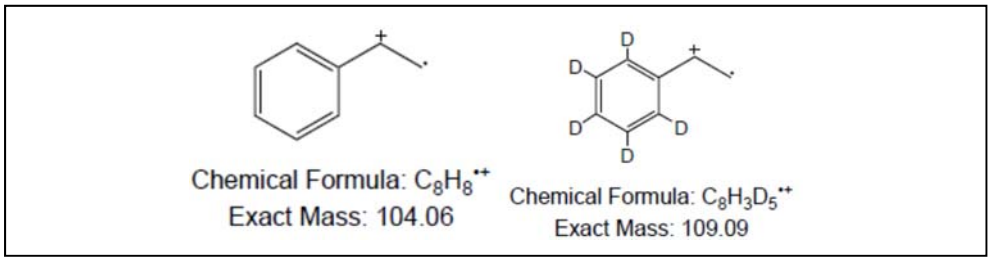


Figure S12. Mass spectrum of phenyethanol peak from mixture of 1-phenylethanol-d_5, styrene-d_0, and [Fe(OTf)$_2$(FOX)] in *o*-dichlorobenzene after heating at 120 °C for 1h.

Table S3. Selected MS data for styrene fraction. (d_0, m/z = 104)

0h		1h		4h		
m/z	Count	m/z	Count	m/z	Count	
102	84878	102	52237	102	66292	
103	459329	103	296529	103	353912	
104	1006683	104	642864	104	803269	M^+
105	85282	105	58646	105	77743	
106	3575	106	11827	106	33842	
107	805	107	52347	107	158618	
108	483	108	72101	108	220934	
109	6228	109	238097	109	733965	d_5-M^+
110	414	110	21817	110	71325	



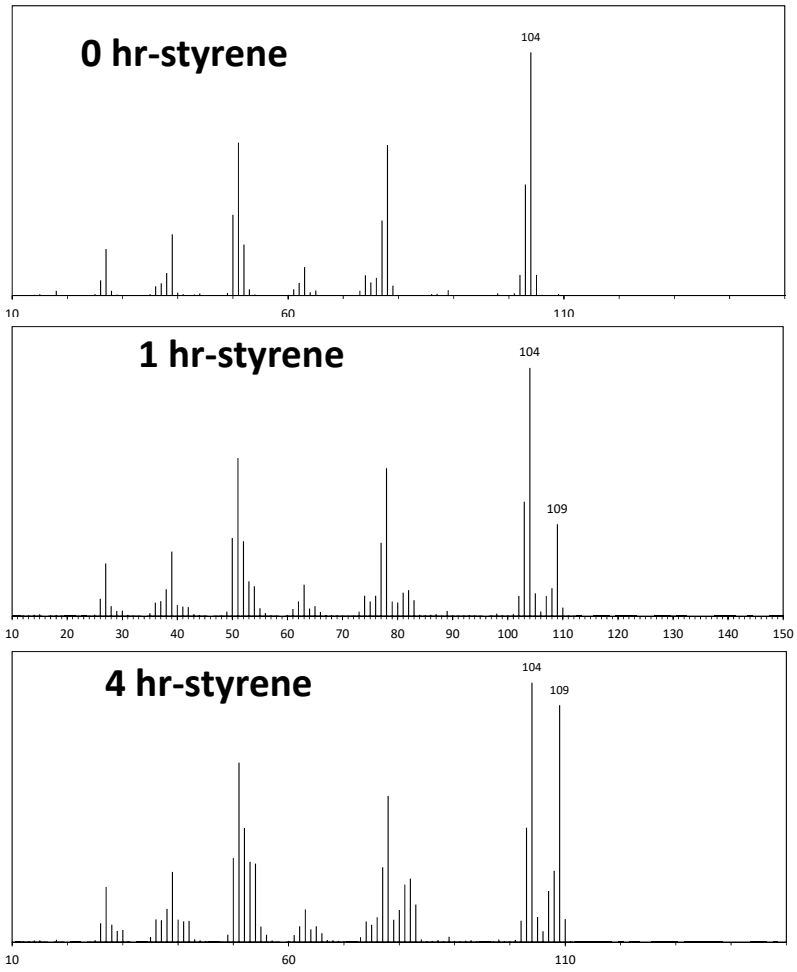
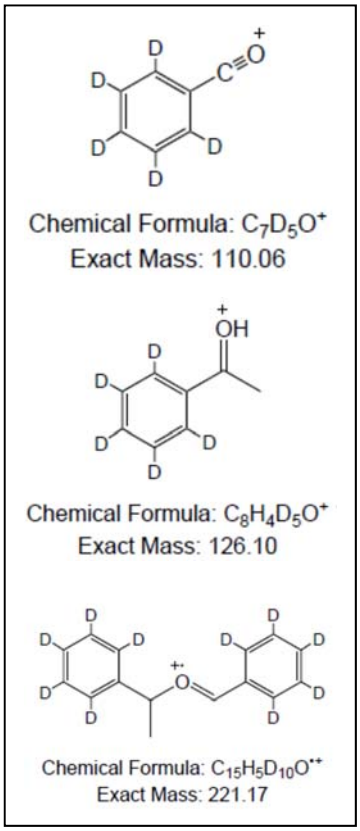


Figure S13. Mass spectra of styrene peak from mixture of 1-phenylethanol-d_5, styrene-d_0, and [Fe(OTf)$_2$(FOX)] in *o*-dichlorobenzene after heating at 120 °C for 0h, 1h, and 4h. Note growth of d_5.

Table S4. Selected MS data for meso α-methylbenzyl ether. (d_{10}, m/z = 236)

1h		4h		
m/z	Count	m/z	Count	
108	4495	108	66	
109	16511	109	267	
110	132251	110	5961	d_5-Ph-CO$^+$
111	34953	111	1434	
112	8301	112	194	
120	60	120	3	
121	489	121	150	
122	229	122	74	
123	0	123	27	
124	0	124	0	
125	1574	125	14	
126	20473	126	780	M$^+$ – PhCHCH$_3$
127	11503	127	443	
128	751	128	69	
129	122	129	0	
210	0	210	25	
211	56	211	0	
212	12	212	16	
213	0	213	0	
214	0	214	31	
215	0	215	0	
216	27	216	0	
217	16	217	8	
218	0	218	0	
219	10	219	17	
220	69	220	30	
221	670	221	28	d_{10}-M$^+$ – Me
222	163	222	45	
223	5	223	19	
236	0	236	1	no M$^+$



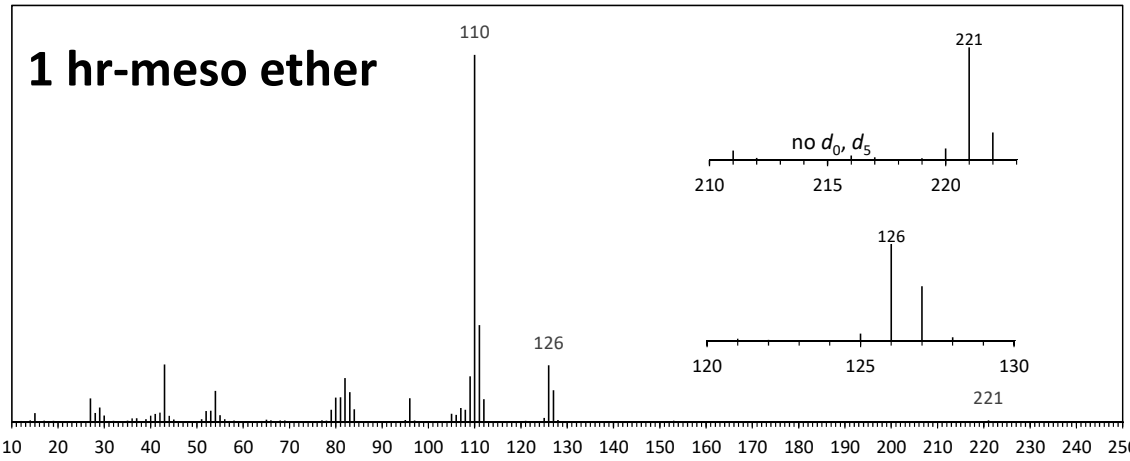
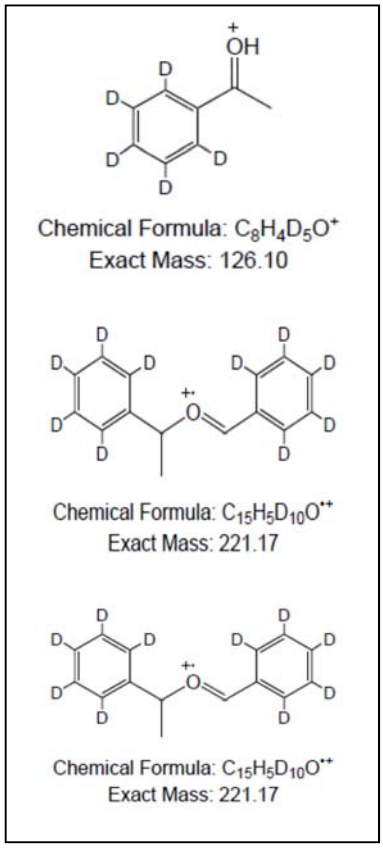


Figure S14. Mass spectrum of meso α-methylbenzyl ether from mixture of 1-phenylethanol-d_5, styrene-d_0, and [Fe(OTf)$_2$(FOX)] in *o*-dichlorobenzene after heating at 120 °C for 1h.

Table S5. Selected MS data for chiral α-methylbenzyl ethers. (d_{10}, m/z = 236)

1h		4h		
m/z	Count	m/z	Count	
108	10729	108	1112	
109	37658	109	5422	
110	335143	110	43205	d_5-Ph-CO$^+$
111	80521	111	10520	
112	18438	112	2334	
120	25	120	0	
121	677	121	579	
122	275	122	335	
123	193	123	89	
124	127	124	2	
125	2837	125	0	
126	43415	126	5645	M$^+$ – PhCHCH$_3$
127	22971	127	2709	
128	2196	128	227	
129	116	129	65	
210	0	210	15	
211	0	211	15	
212	29	212	0	
213	0	213	0	
214	32	214	3	
215	0	215	0	
216	119	216	177	
217	97	217	21	
218	13	218	65	
219	41	219	18	
220	0	220	139	
221	4049	221	230	d_{10}-M$^+$ – Me
222	772	222	146	
223	124	223	1	
236	19	236	22	trace M$^+$



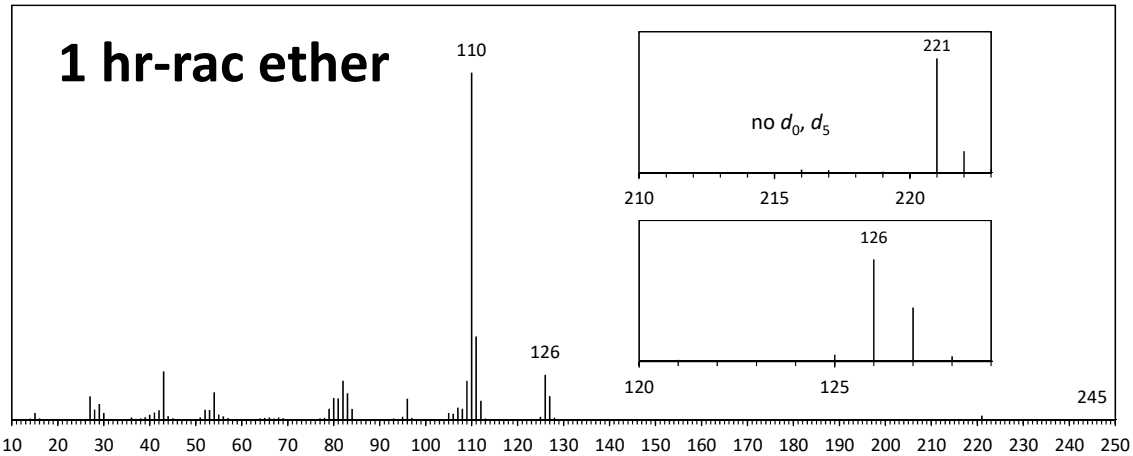
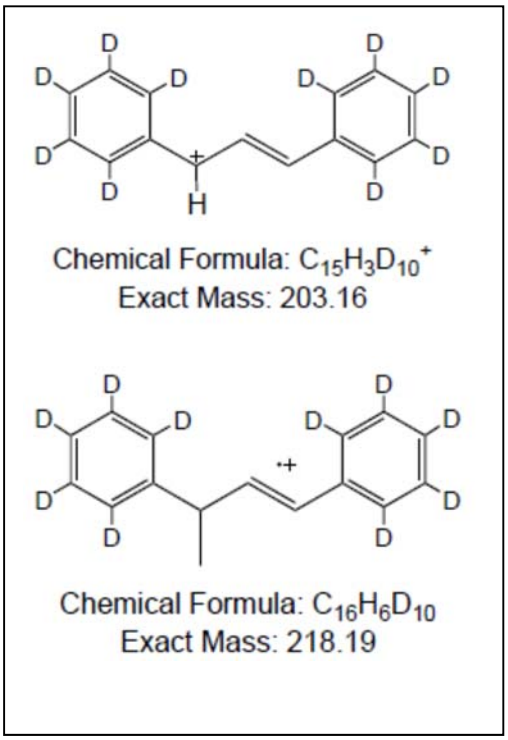


Figure S15. Mass spectrum of rac α-methylbenzyl ether from mixture of 1-phenylethanol-d_5, styrene-d_0, and [Fe(OTf)$_2$(FOX)] in *o*-dichlorobenzene after heating at 120 °C for 1h.

Table S6. Selected MS data for styrene dimer (d_{10}, m/z = 218; d_5, m/z = 213; d_0, m/z = 208).

m/z	4h Count	
192	74	
193	2529	d_0-M$^+$ – Me
194	841	
195	836	
196	1378	
197	2074	
198	19941	d_5-M$^+$ – Me
199	3443	
200	429	
201	137	
202	308	
203	7439	d_{10}-M$^+$ – Me
204	1212	
205	261	
206	247	
207	146	
208	1562	d_0-M$^+$
209	475	
210	121	
211	489	
212	1936	
213	16873	d_5-M$^+$
214	3250	
215	357	
216	268	
217	207	
218	5786	d_{10}-M$^+$
219		



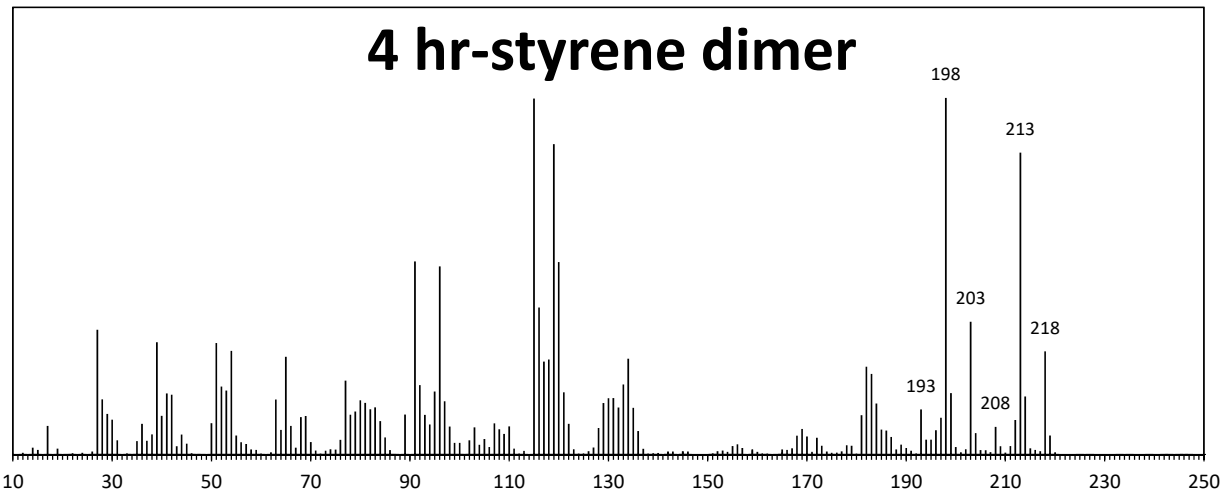


Figure S16. Mass spectrum of styrene dimer from mixture of 1-phenylethanol-d_5, styrene-d_0, and [Fe(OTf)$_2$(FOX)] in *o*-dichlorobenzene after heating at 120 °C for 4h.

Reference Mass Spectra (from SDBS):

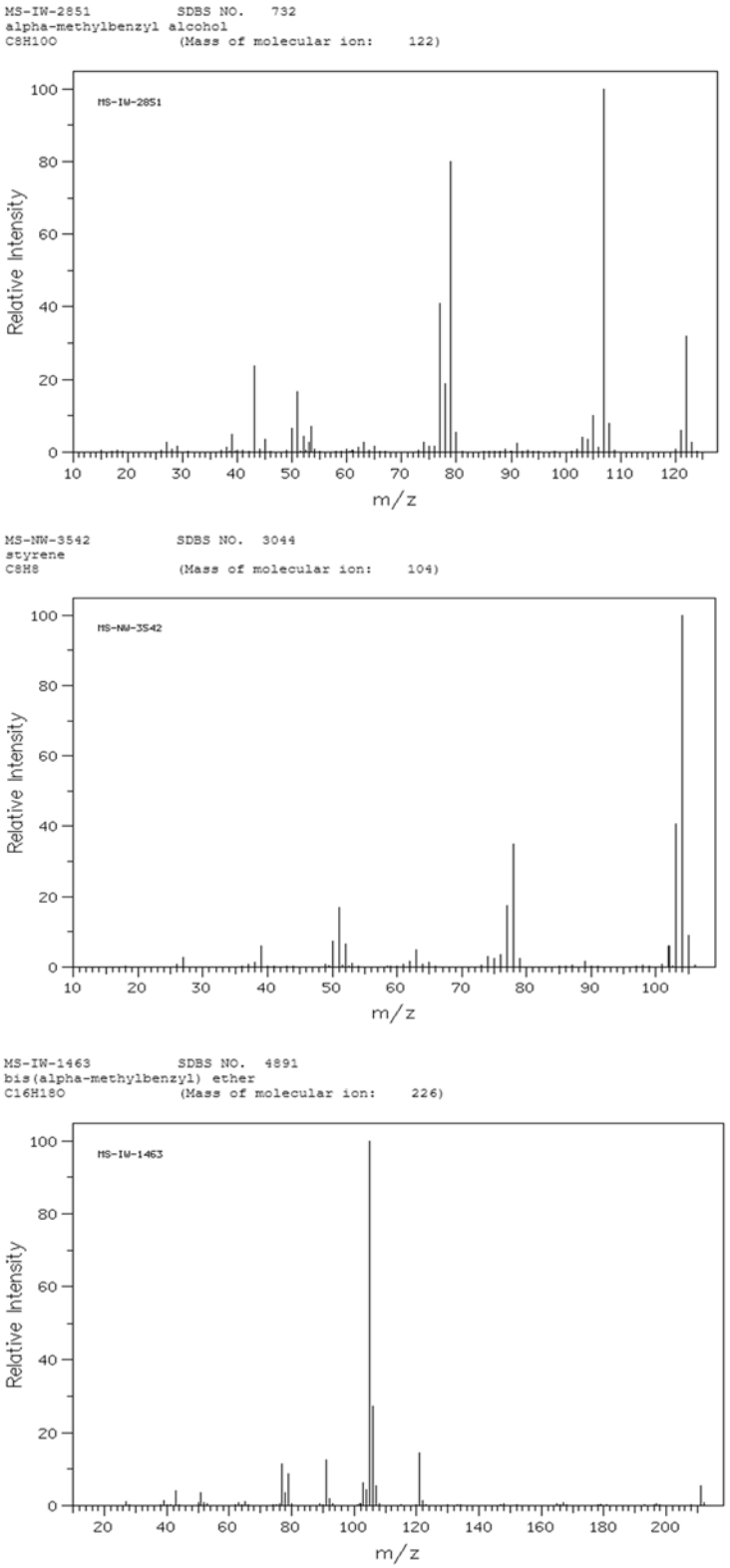


Figure S17. Standard mass spectra of 1-phenylethanol, styrene, and α-methylbenzyl ether from SDBS (URL https://sdbs.db.aist.go.jp)

3.2 NMR Spectra for Substrate Binding

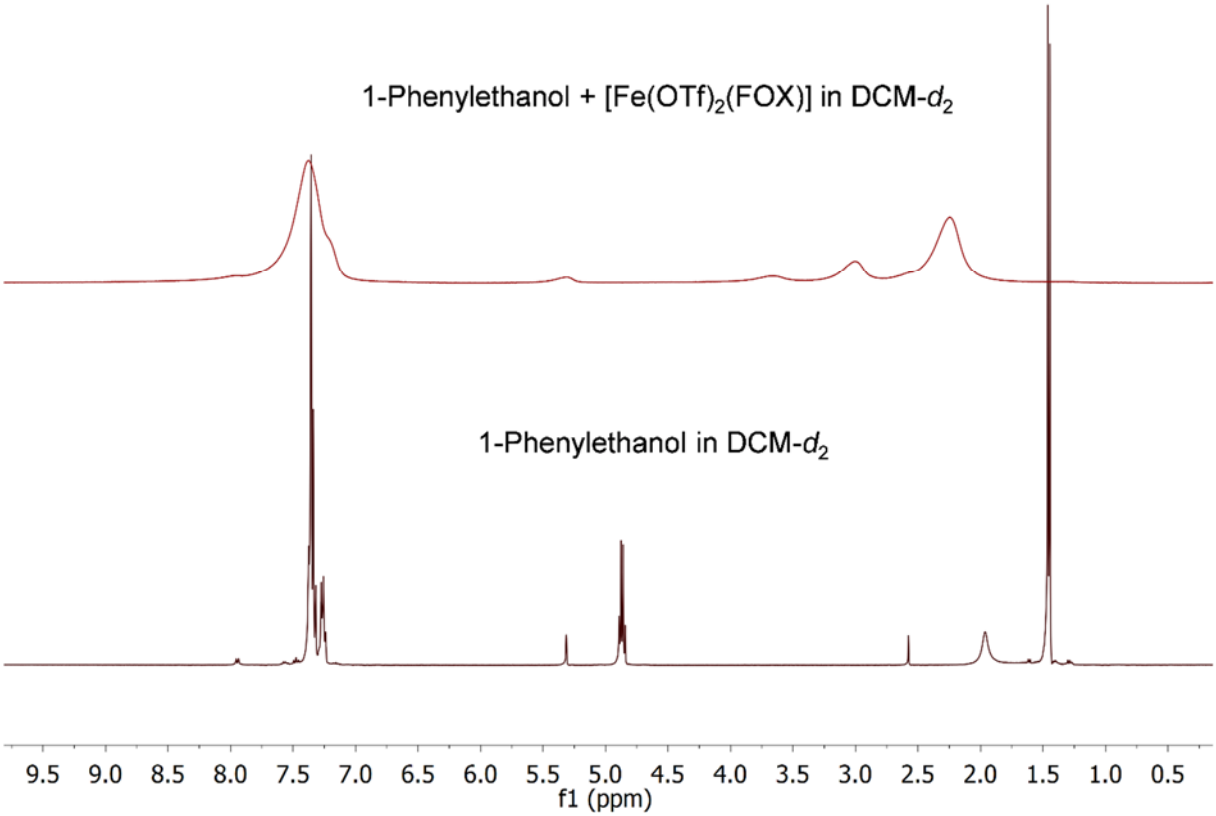


Figure S18. Comparison of ^{1}H NMR spectrum of 1-phenylethanol in presence of [Fe(OTf)$_2$(FOX)] in deuterated dichloromethane (DCM-d_2) (top) and ^{1}H NMR spectrum of pure 1-phenylethanol in DCM-d_2 (bottom).

4. Experimental Data for Section “Reaction Scale-up”

4.1 Reactive Distillation Setup

Figure S19. Picture of the reactive distillation setup. The syringe was recharged with 39 mL of 1-phenylethanol after the initial 60 mL were dispensed.

4.2 NMR Spectra of Reaction Mixture and Distillate

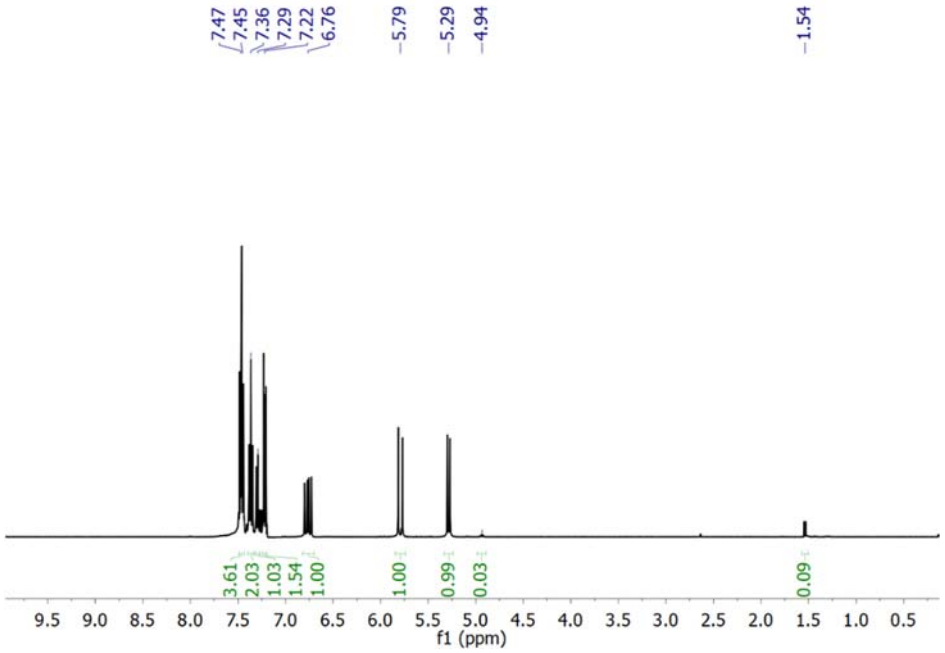


Figure S20. ^{1}H NMR spectrum of aliquot (approx. 100 µL) of distillate (115 g) in deuterated chloroform.

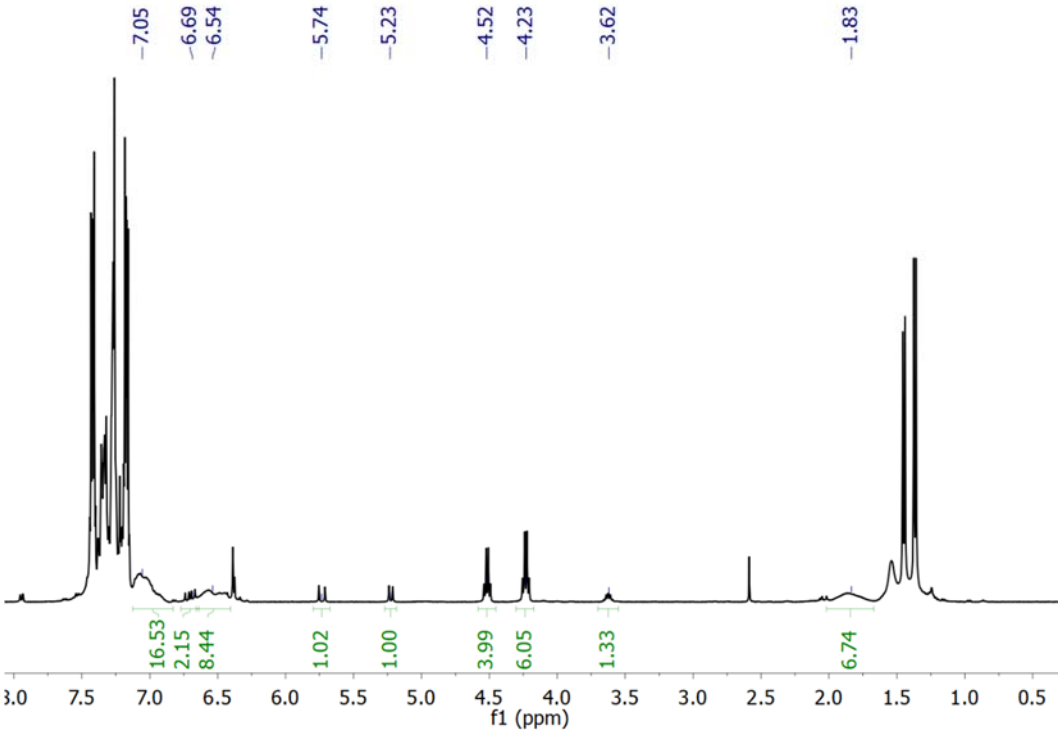


Figure S21. ^{1}H NMR spectrum of aliquot (approx. 100 µL) of residual reaction mixture in deuterated chloroform. The broad signals at 7.05, 6.54, and 1.83 ppm are indicative for the formation of polystyrenes (approx. 7% for total reaction).

Supporting Information – PART II

Iron-Based Dehydration Catalyst for Selective Formation of Styrene

Olaf Nachtigall*, Andrew I. VanderWeide, William. W. Brennessel, & William D. Jones*

5. X-ray Structure Details for **A-D**

REFERENCE NUMBER: jonon95

CRYSTAL STRUCTURE REPORT

C_{18} H_{17} F_6 Fe N_3 O_9 S_2

or

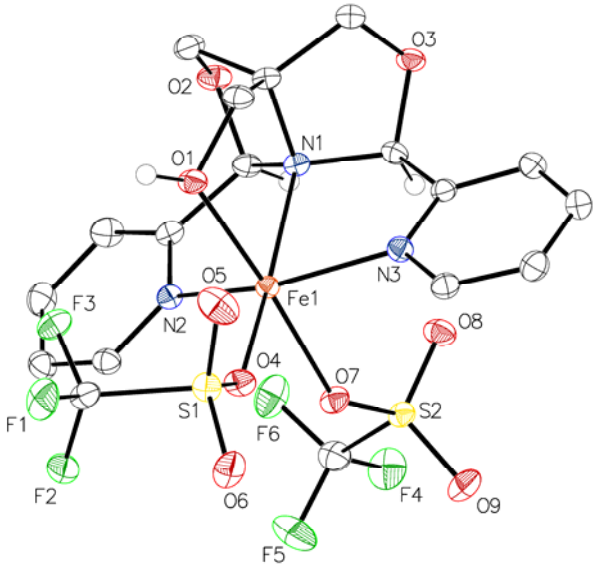
(κ^4-L)Fe(OTf)$_2$

A

Report prepared for:

Dr. O. Nachtigall, Prof. W. Jones

November 19, 2020



William W. Brennessel

X-ray Crystallographic Facility

Department of Chemistry, University of Rochester

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Rochester, NY 14627

Data collection

A crystal (0.221 x 0.184 x 0.142 mm^3) was placed onto a thin glass optical fiber or a nylon loop and mounted on a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.01(10) K. A preliminary set of cell constants and an orientation matrix were calculated from a small sampling of reflections.[1] A short pre-experiment was run, from which an optimal data collection strategy was determined. The full data collection was carried out using a PhotonJet (Cu) X-ray source with frame times of 0.05 and 0.16 seconds and a detector distance of 31.2 mm. Series of frames were collected in 0.50º steps in ω at different 2θ, κ, and ϕ settings. After the intensity data were corrected for absorption, the final cell constants were calculated from the xyz centroids of 27130 strong reflections from the actual data collection after integration.[1] See Table S7 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT[2] and refined using SHELXL.[3] The space group $P2_1/n$ was determined based on systematic absences. Most or all non-hydrogen atoms were assigned from the solution. Full-matrix least squares / difference Fourier cycles were performed which located any remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The O-H hydrogen atom was found from the difference Fourier map and refined freely. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0306$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.0812$ (F^2, all data).

Structure description

The structure is the one suggested. The asymmetric unit contains one molecule in a general position. Hydrogen bonding links molecules along [101] (see figure and Table S13).

Structure manipulation and figure generation were performed using Olex2.[4] Unless noted otherwise all structural diagrams containing anisotropic displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B04 Hutchison Hall, Department of Chemistry, University of Rochester. The instrument was purchased with funding from NSF MRI program grant CHE-1725028. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

[1] *CrysAlisPro*, version 171.40.84a; Rigaku Corporation: Oxford, UK, 2020.

[2] Sheldrick, G. M. *SHELXT*, version 2018/2; *Acta. Crystallogr.* **2015**, *A71*, 3-8.

[3] Sheldrick, G. M. *SHELXL*, version 2018/3; *Acta. Crystallogr.* **2015**, *C71*, 3-8.

[4] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Olex2*, version 1.3-ac4; *J. Appl. Cryst.* **2009**, *42*, 339-341.

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

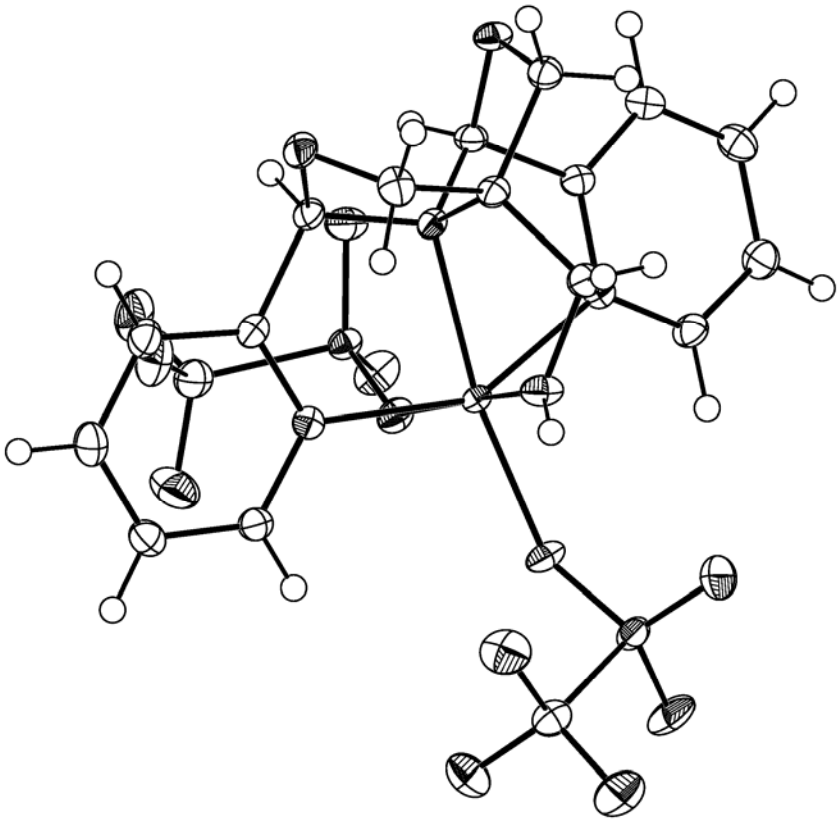
$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

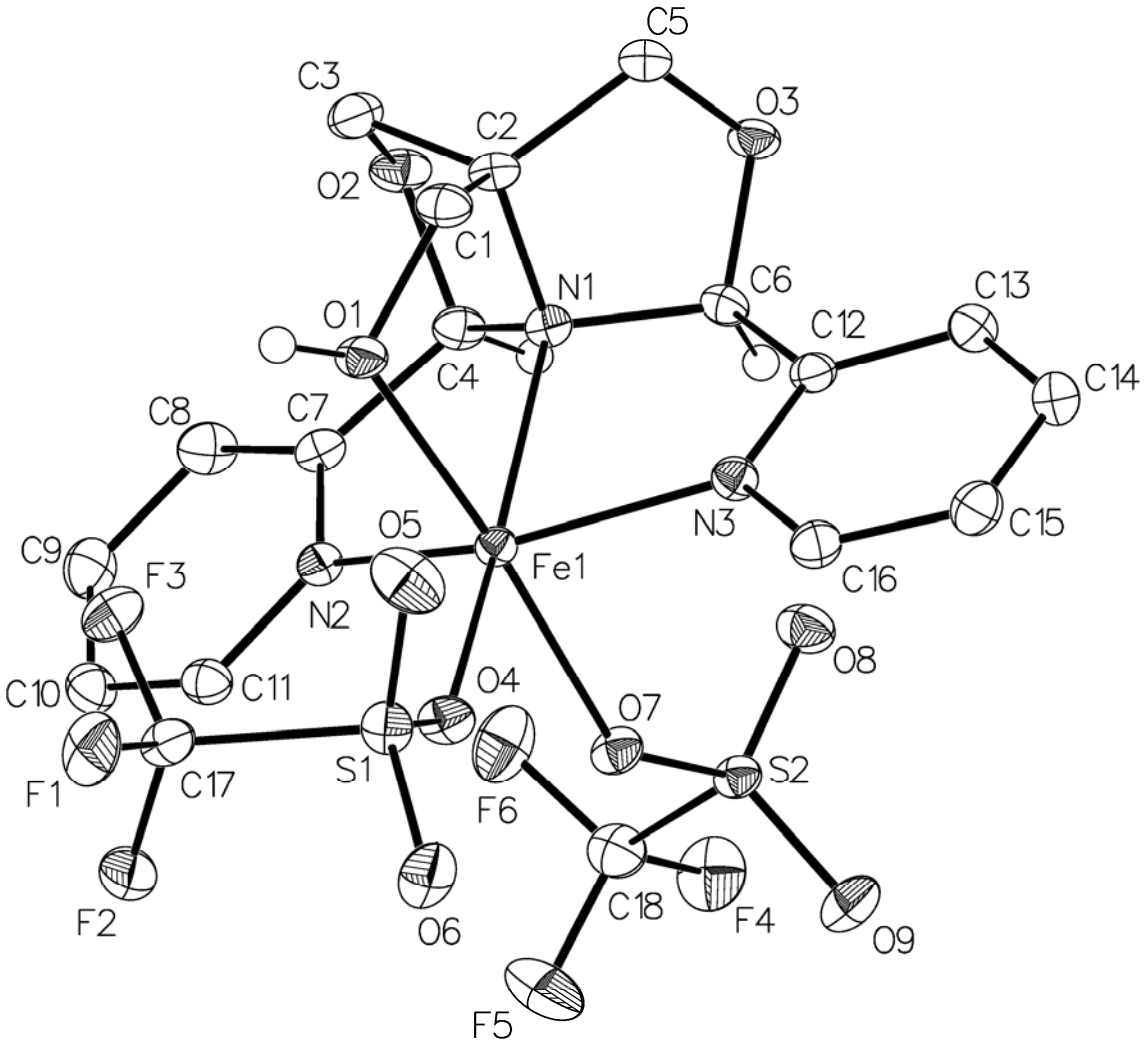
where $w = 1 \,/\, [\sigma^2 (F_o^2) + (aP)^2 + bP]$ and

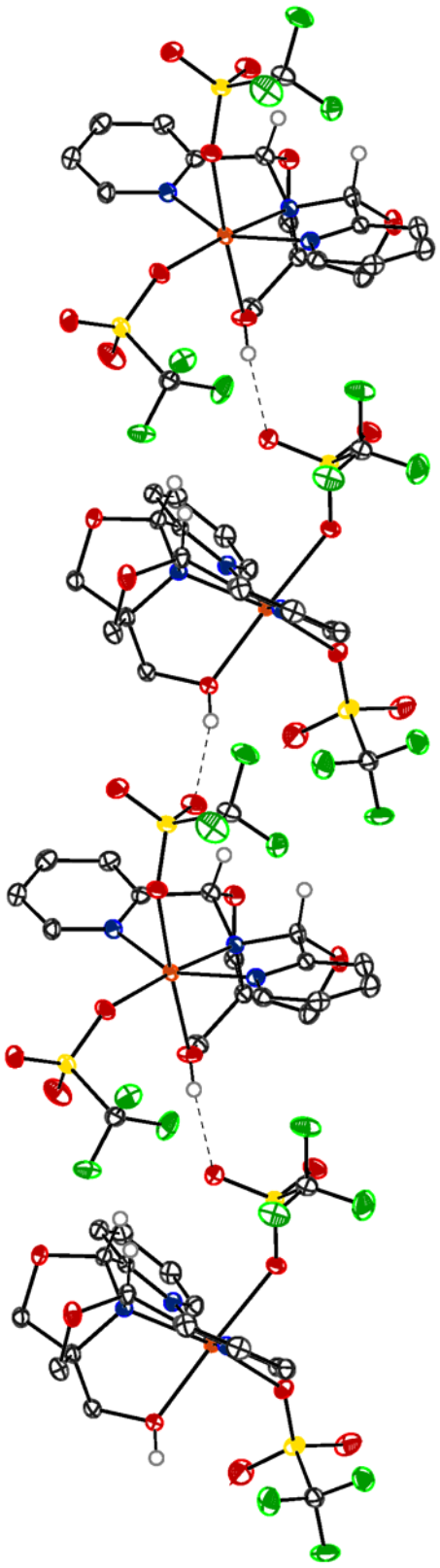
$$P = 1/3 \max (0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters




C5
C3
O3
C2
O2
C1
N1
C6
C13
O1
C12
C4
C14
C8
C7
N3
O5
C15
C9
F3
Fe1
C16
N2
O8
C10
C11
O4
O7
F1
C17
S1
S2
F6
C18
F2
O6
F4
O9
F5



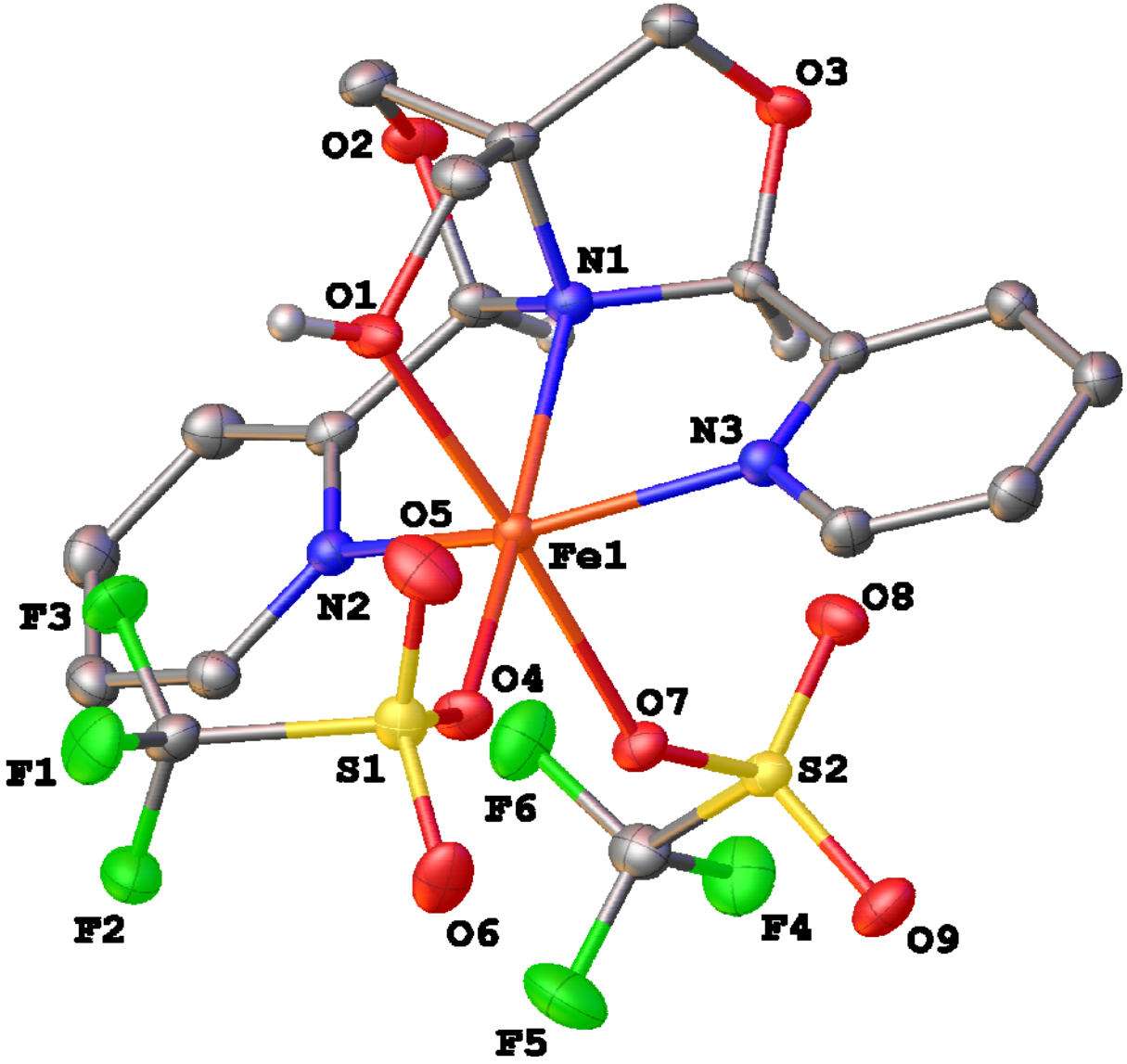

O3
O2
N1
O1
N3
O5
Fe1
N2
F3
O8
O4
O7
F1
S1
S2
F6
F2
O6
F4
O9
F5

Table S7. Crystal data and structure refinement for **A**.

Identification code	jonon95	
Empirical formula	C18 H17 F6 Fe N3 O9 S2	
Formula weight	653.32	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.99030(10) Å	α = 90°
	b = 15.5335(2) Å	β = 99.8240(10)°
	c = 14.0576(2) Å	γ = 90°
Volume	2364.69(5) Å^3	
Z	4	
Density (calculated)	1.835 Mg/m^3	
Absorption coefficient	7.749 mm^{-1}	
F(000)	1320	
Crystal color, morphology	light yellow, block	
Crystal size	0.221 x 0.184 x 0.142 mm^3	
Theta range for data collection	4.277 to 79.787°	
Index ranges	$-13 \le h \le 13$, $-19 \le k \le 19$, $-17 \le l \le 17$	
Reflections collected	40193	
Independent reflections	4997 [R(int) = 0.0647]	
Observed reflections	4757	
Completeness to theta = 74.504°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00000 and 0.69760	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4997 / 0 / 356	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0306, wR2 = 0.0795	
R indices (all data)	R1 = 0.0323, wR2 = 0.0812	
Largest diff. peak and hole	0.373 and -0.477 e.Å^{-3}	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **A**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Fe1	7270(1)	3097(1)	5155(1)	12(1)
S1	8483(1)	4712(1)	6529(1)	17(1)
S2	5740(1)	3674(1)	2873(1)	15(1)
F1	10754(1)	4800(1)	7439(1)	30(1)
F2	10598(1)	4777(1)	5895(1)	26(1)
F3	10311(1)	3615(1)	6654(1)	30(1)
F4	5982(1)	3262(1)	1116(1)	31(1)
F5	7460(1)	4051(1)	1859(1)	38(1)
F6	7360(1)	2710(1)	2219(1)	31(1)
O1	8019(1)	2427(1)	6456(1)	19(1)
O2	7283(1)	420(1)	4658(1)	20(1)
O3	4649(1)	1046(1)	4996(1)	17(1)
O4	7969(1)	4287(1)	5618(1)	18(1)
O5	8130(2)	4328(1)	7368(1)	30(1)
O6	8440(1)	5631(1)	6462(1)	27(1)
O7	6642(1)	3772(1)	3752(1)	17(1)
O8	4978(1)	2914(1)	2868(1)	21(1)
O9	5108(1)	4449(1)	2529(1)	24(1)
N1	6485(1)	1768(1)	4950(1)	13(1)
N2	8545(1)	2482(1)	4400(1)	14(1)
N3	5412(1)	3251(1)	5398(1)	15(1)
C1	7164(2)	1824(1)	6741(1)	17(1)
C2	6677(2)	1249(1)	5878(1)	15(1)
C3	7588(2)	559(1)	5678(1)	20(1)
C4	7101(2)	1257(1)	4273(1)	15(1)
C5	5376(2)	885(1)	5927(1)	16(1)
C6	5133(2)	1808(1)	4664(1)	14(1)
C7	8324(2)	1660(1)	4127(1)	15(1)
C8	9121(2)	1194(1)	3659(1)	21(1)
C9	10180(2)	1592(1)	3460(2)	22(1)
C10	10399(2)	2446(1)	3726(1)	19(1)

C11	9566(2)	2866(1)	4196(1)	17(1)
C12	4630(2)	2604(1)	5106(1)	14(1)
C13	3380(2)	2648(1)	5148(1)	18(1)
C14	2916(2)	3396(1)	5486(1)	21(1)
C15	3713(2)	4071(1)	5788(2)	21(1)
C16	4954(2)	3971(1)	5741(1)	17(1)
C17	10126(2)	4464(1)	6632(1)	19(1)
C18	6696(2)	3413(1)	1967(1)	22(1)

Table S9. Bond lengths [Å] and angles [°] for **A**.

Fe(1)-O(1)	2.1442(14)	C(1)-H(1B)	0.9700
Fe(1)-O(4)	2.0641(13)	C(1)-C(2)	1.528(2)
Fe(1)-O(7)	2.2359(13)	C(2)-C(3)	1.525(3)
Fe(1)-N(1)	2.2366(15)	C(2)-C(5)	1.551(2)
Fe(1)-N(2)	2.1233(15)	C(3)-H(3A)	0.9700
Fe(1)-N(3)	2.1404(16)	C(3)-H(3B)	0.9700
S(1)-O(4)	1.4655(13)	C(4)-H(4)	0.9800
S(1)-O(5)	1.4329(16)	C(4)-C(7)	1.528(2)
S(1)-O(6)	1.4297(15)	C(5)-H(5A)	0.9700
S(1)-C(17)	1.828(2)	C(5)-H(5B)	0.9700
S(2)-O(7)	1.4541(13)	C(6)-H(6)	0.9800
S(2)-O(8)	1.4476(14)	C(6)-C(12)	1.529(2)
S(2)-O(9)	1.4308(14)	C(7)-C(8)	1.386(3)
S(2)-C(18)	1.830(2)	C(8)-H(8)	0.9300
F(1)-C(17)	1.330(2)	C(8)-C(9)	1.388(3)
F(2)-C(17)	1.327(2)	C(9)-H(9)	0.9300
F(3)-C(17)	1.334(2)	C(9)-C(10)	1.388(3)
F(4)-C(18)	1.335(2)	C(10)-H(10)	0.9300
F(5)-C(18)	1.323(2)	C(10)-C(11)	1.381(3)
F(6)-C(18)	1.328(2)	C(11)-H(11)	0.9300
O(1)-H(1)	0.80(3)	C(12)-C(13)	1.387(3)
O(1)-C(1)	1.431(2)	C(13)-H(13)	0.9300
O(2)-C(3)	1.431(2)	C(13)-C(14)	1.386(3)
O(2)-C(4)	1.410(2)	C(14)-H(14)	0.9300
O(3)-C(5)	1.434(2)	C(14)-C(15)	1.385(3)
O(3)-C(6)	1.409(2)	C(15)-H(15)	0.9300
N(1)-C(2)	1.518(2)	C(15)-C(16)	1.385(3)
N(1)-C(4)	1.488(2)	C(16)-H(16)	0.9300
N(1)-C(6)	1.473(2)	O(1)-Fe(1)-O(7)	175.01(5)
N(2)-C(7)	1.345(2)	O(1)-Fe(1)-N(1)	75.24(5)
N(2)-C(11)	1.345(2)	O(4)-Fe(1)-O(1)	95.57(5)
N(3)-C(12)	1.341(2)	O(4)-Fe(1)-O(7)	84.31(5)
N(3)-C(16)	1.349(2)	O(4)-Fe(1)-N(1)	169.01(6)
C(1)-H(1A)	0.9700	O(4)-Fe(1)-N(2)	108.56(6)

O(4)-Fe(1)-N(3)	99.42(6)	C(11)-N(2)-C(7)	118.50(16)
O(7)-Fe(1)-N(1)	105.37(5)	C(12)-N(3)-Fe(1)	116.50(12)
N(2)-Fe(1)-O(1)	91.01(6)	C(12)-N(3)-C(16)	118.21(16)
N(2)-Fe(1)-O(7)	84.31(5)	C(16)-N(3)-Fe(1)	125.03(13)
N(2)-Fe(1)-N(1)	78.08(6)	O(1)-C(1)-H(1A)	110.0
N(2)-Fe(1)-N(3)	149.21(6)	O(1)-C(1)-H(1B)	110.0
N(3)-Fe(1)-O(1)	98.97(6)	O(1)-C(1)-C(2)	108.55(15)
N(3)-Fe(1)-O(7)	85.95(5)	H(1A)-C(1)-H(1B)	108.4
N(3)-Fe(1)-N(1)	76.50(6)	C(2)-C(1)-H(1A)	110.0
O(4)-S(1)-C(17)	101.66(8)	C(2)-C(1)-H(1B)	110.0
O(5)-S(1)-O(4)	114.40(9)	N(1)-C(2)-C(1)	110.50(14)
O(5)-S(1)-C(17)	104.44(9)	N(1)-C(2)-C(3)	102.38(14)
O(6)-S(1)-O(4)	112.88(9)	N(1)-C(2)-C(5)	103.77(14)
O(6)-S(1)-O(5)	117.36(10)	C(1)-C(2)-C(5)	112.20(15)
O(6)-S(1)-C(17)	103.68(9)	C(3)-C(2)-C(1)	113.94(16)
O(7)-S(2)-C(18)	103.02(8)	C(3)-C(2)-C(5)	113.07(15)
O(8)-S(2)-O(7)	113.51(8)	O(2)-C(3)-C(2)	104.00(15)
O(8)-S(2)-C(18)	102.48(9)	O(2)-C(3)-H(3A)	111.0
O(9)-S(2)-O(7)	114.89(8)	O(2)-C(3)-H(3B)	111.0
O(9)-S(2)-O(8)	115.94(9)	C(2)-C(3)-H(3A)	111.0
O(9)-S(2)-C(18)	104.75(9)	C(2)-C(3)-H(3B)	111.0
Fe(1)-O(1)-H(1)	139(2)	H(3A)-C(3)-H(3B)	109.0
C(1)-O(1)-Fe(1)	112.40(11)	O(2)-C(4)-N(1)	107.28(14)
C(1)-O(1)-H(1)	108(2)	O(2)-C(4)-H(4)	108.9
C(4)-O(2)-C(3)	103.85(13)	O(2)-C(4)-C(7)	111.00(15)
C(6)-O(3)-C(5)	105.38(13)	N(1)-C(4)-H(4)	108.9
S(1)-O(4)-Fe(1)	138.31(9)	N(1)-C(4)-C(7)	111.94(14)
S(2)-O(7)-Fe(1)	139.79(8)	C(7)-C(4)-H(4)	108.9
C(2)-N(1)-Fe(1)	112.70(10)	O(3)-C(5)-C(2)	105.66(14)
C(4)-N(1)-Fe(1)	111.58(11)	O(3)-C(5)-H(5A)	110.6
C(4)-N(1)-C(2)	104.73(13)	O(3)-C(5)-H(5B)	110.6
C(6)-N(1)-Fe(1)	110.22(10)	C(2)-C(5)-H(5A)	110.6
C(6)-N(1)-C(2)	104.02(13)	C(2)-C(5)-H(5B)	110.6
C(6)-N(1)-C(4)	113.30(14)	H(5A)-C(5)-H(5B)	108.7
C(7)-N(2)-Fe(1)	117.89(12)	O(3)-C(6)-N(1)	107.16(14)
C(11)-N(2)-Fe(1)	123.60(13)	O(3)-C(6)-H(6)	109.5

O(3)-C(6)-C(12)	111.22(14)	C(14)-C(13)-C(12)	118.75(18)
N(1)-C(6)-H(6)	109.5	C(14)-C(13)-H(13)	120.6
N(1)-C(6)-C(12)	109.92(14)	C(13)-C(14)-H(14)	120.3
C(12)-C(6)-H(6)	109.5	C(15)-C(14)-C(13)	119.33(18)
N(2)-C(7)-C(4)	118.09(16)	C(15)-C(14)-H(14)	120.3
N(2)-C(7)-C(8)	122.30(17)	C(14)-C(15)-H(15)	120.8
C(8)-C(7)-C(4)	119.43(17)	C(16)-C(15)-C(14)	118.47(18)
C(7)-C(8)-H(8)	120.6	C(16)-C(15)-H(15)	120.8
C(7)-C(8)-C(9)	118.85(18)	N(3)-C(16)-C(15)	122.72(18)
C(9)-C(8)-H(8)	120.6	N(3)-C(16)-H(16)	118.6
C(8)-C(9)-H(9)	120.5	C(15)-C(16)-H(16)	118.6
C(10)-C(9)-C(8)	118.95(18)	F(1)-C(17)-S(1)	110.29(13)
C(10)-C(9)-H(9)	120.5	F(1)-C(17)-F(3)	108.21(16)
C(9)-C(10)-H(10)	120.6	F(2)-C(17)-S(1)	111.93(13)
C(11)-C(10)-C(9)	118.84(18)	F(2)-C(17)-F(1)	107.89(16)
C(11)-C(10)-H(10)	120.6	F(2)-C(17)-F(3)	107.60(16)
N(2)-C(11)-C(10)	122.55(18)	F(3)-C(17)-S(1)	110.79(13)
N(2)-C(11)-H(11)	118.7	F(4)-C(18)-S(2)	110.08(14)
C(10)-C(11)-H(11)	118.7	F(5)-C(18)-S(2)	111.39(14)
N(3)-C(12)-C(6)	118.28(15)	F(5)-C(18)-F(4)	108.42(16)
N(3)-C(12)-C(13)	122.51(17)	F(5)-C(18)-F(6)	108.43(17)
C(13)-C(12)-C(6)	119.14(16)	F(6)-C(18)-S(2)	110.55(13)
C(12)-C(13)-H(13)	120.6	F(6)-C(18)-F(4)	107.87(17)

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **A**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	13(1)	9(1)	12(1)	-1(1)	1(1)	-1(1)
S1	18(1)	15(1)	17(1)	-5(1)	2(1)	-1(1)
S2	17(1)	14(1)	12(1)	0(1)	0(1)	-1(1)
F1	27(1)	36(1)	23(1)	-4(1)	-10(1)	0(1)
F2	23(1)	31(1)	26(1)	8(1)	7(1)	0(1)
F3	30(1)	16(1)	44(1)	6(1)	6(1)	6(1)
F4	35(1)	44(1)	13(1)	-4(1)	-1(1)	1(1)
F5	38(1)	43(1)	35(1)	2(1)	15(1)	-16(1)
F6	32(1)	35(1)	24(1)	-4(1)	4(1)	12(1)
O1	20(1)	19(1)	15(1)	5(1)	-3(1)	-6(1)
O2	28(1)	11(1)	22(1)	-1(1)	10(1)	0(1)
O3	19(1)	12(1)	18(1)	1(1)	1(1)	-4(1)
O4	23(1)	13(1)	18(1)	-3(1)	-1(1)	-4(1)
O5	35(1)	39(1)	20(1)	-5(1)	11(1)	-9(1)
O6	26(1)	15(1)	36(1)	-10(1)	-4(1)	3(1)
O7	20(1)	16(1)	13(1)	1(1)	-1(1)	0(1)
O8	23(1)	21(1)	19(1)	2(1)	0(1)	-7(1)
O9	28(1)	19(1)	22(1)	2(1)	-4(1)	5(1)
N1	16(1)	12(1)	11(1)	-1(1)	2(1)	-1(1)
N2	15(1)	14(1)	14(1)	1(1)	2(1)	1(1)
N3	15(1)	14(1)	15(1)	-1(1)	3(1)	-1(1)
C1	22(1)	17(1)	13(1)	2(1)	2(1)	-3(1)
C2	19(1)	11(1)	14(1)	1(1)	3(1)	-1(1)
C3	23(1)	16(1)	20(1)	4(1)	6(1)	3(1)
C4	20(1)	11(1)	16(1)	-2(1)	5(1)	-1(1)
C5	20(1)	13(1)	17(1)	1(1)	4(1)	-2(1)
C6	15(1)	13(1)	15(1)	0(1)	3(1)	-4(1)
C7	19(1)	12(1)	12(1)	0(1)	1(1)	1(1)
C8	26(1)	17(1)	21(1)	-2(1)	8(1)	1(1)
C9	22(1)	25(1)	22(1)	-2(1)	7(1)	5(1)
C10	18(1)	23(1)	18(1)	2(1)	4(1)	-1(1)

C11	18(1)	16(1)	15(1)	0(1)	2(1)	-2(1)
C12	16(1)	13(1)	14(1)	2(1)	1(1)	-1(1)
C13	17(1)	18(1)	21(1)	2(1)	2(1)	-2(1)
C14	16(1)	22(1)	24(1)	3(1)	4(1)	1(1)
C15	21(1)	17(1)	24(1)	-1(1)	5(1)	3(1)
C16	19(1)	12(1)	21(1)	-2(1)	3(1)	1(1)
C17	22(1)	15(1)	18(1)	2(1)	0(1)	0(1)
C18	24(1)	24(1)	16(1)	1(1)	1(1)	-3(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **A**.

	x	y	z	U(eq)
H1	8640(30)	2411(19)	6850(20)	33(7)
H1A	6485	2128	6950	21
H1B	7572	1477	7275	21
H3A	8433	757	5857	24
H3B	7484	35	6030	24
H4	6551	1225	3647	19
H5A	5419	273	6064	20
H5B	5021	1174	6428	20
H6	4920	1836	3959	17
H8	8949	624	3481	25
H9	10735	1291	3154	27
H10	11094	2731	3589	23
H11	9718	3437	4378	20
H13	2862	2184	4954	22
H14	2079	3445	5510	25
H15	3422	4579	6018	25
H16	5493	4419	5954	21

Table S12. Torsion angles [°] for **A**.

Fe1-O1-C1-C2	51.43(17)	O7-S2-C18-F6	57.95(15)
Fe1-N1-C2-C1	9.60(17)	O8-S2-O7-Fe1	0.47(16)
Fe1-N1-C2-C3	-112.12(13)	O8-S2-C18-F4	58.97(16)
Fe1-N1-C2-C5	130.06(12)	O8-S2-C18-F5	179.27(14)
Fe1-N1-C4-O2	138.62(11)	O8-S2-C18-F6	-60.11(15)
Fe1-N1-C4-C7	16.61(17)	O9-S2-O7-Fe1	137.16(12)
Fe1-N1-C6-O3	-151.71(11)	O9-S2-C18-F4	-62.47(16)
Fe1-N1-C6-C12	-30.73(16)	O9-S2-C18-F5	57.83(16)
Fe1-N2-C7-C4	7.0(2)	O9-S2-C18-F6	178.45(13)
Fe1-N2-C7-C8	-177.90(14)	N1-C2-C3-O2	-31.63(17)
Fe1-N2-C11-C10	178.31(14)	N1-C2-C5-O3	11.82(17)
Fe1-N3-C12-C6	2.2(2)	N1-C4-C7-N2	-16.1(2)
Fe1-N3-C12-C13	-174.72(14)	N1-C4-C7-C8	168.66(16)
Fe1-N3-C16-C15	172.89(14)	N1-C6-C12-N3	20.1(2)
O1-C1-C2-N1	-38.2(2)	N1-C6-C12-C13	-162.95(16)
O1-C1-C2-C3	76.40(19)	N2-C7-C8-C9	-0.4(3)
O1-C1-C2-C5	-153.50(15)	N3-C12-C13-C14	1.4(3)
O2-C4-C7-N2	-135.91(16)	C1-C2-C3-O2	-150.96(15)
O2-C4-C7-C8	48.8(2)	C1-C2-C5-O3	131.13(15)
O3-C6-C12-N3	138.57(16)	C2-N1-C4-O2	16.41(18)
O3-C6-C12-C13	-44.4(2)	C2-N1-C4-C7	-105.59(16)
O4-S1-C17-F1	-179.47(13)	C2-N1-C6-O3	-30.67(17)
O4-S1-C17-F2	60.41(15)	C2-N1-C6-C12	90.32(16)
O4-S1-C17-F3	-59.69(15)	C3-O2-C4-N1	-37.29(18)
O5-S1-O4-Fe1	-22.35(17)	C3-O2-C4-C7	85.30(17)
O5-S1-C17-F1	-60.22(15)	C3-C2-C5-O3	-98.32(17)
O5-S1-C17-F2	179.66(13)	C4-O2-C3-C2	42.90(17)
O5-S1-C17-F3	59.56(15)	C4-N1-C2-C1	131.07(15)
O6-S1-O4-Fe1	-160.01(12)	C4-N1-C2-C3	9.36(17)
O6-S1-C17-F1	63.22(15)	C4-N1-C2-C5	-108.47(15)
O6-S1-C17-F2	-56.90(16)	C4-N1-C6-O3	82.46(17)
O6-S1-C17-F3	-177.00(14)	C4-N1-C6-C12	-156.55(14)
O7-S2-C18-F4	177.03(14)	C4-C7-C8-C9	174.69(18)
O7-S2-C18-F5	-62.67(16)	C5-O3-C6-N1	39.32(17)

C5-O3-C6-C12	-80.84(17)	C9-C10-C11-N2	-0.6(3)
C5-C2-C3-O2	79.37(18)	C11-N2-C7-C4	-174.07(16)
C6-O3-C5-C2	-31.06(17)	C11-N2-C7-C8	1.1(3)
C6-N1-C2-C1	-109.77(16)	C12-N3-C16-C15	-1.0(3)
C6-N1-C2-C3	128.51(15)	C12-C13-C14-C15	-1.2(3)
C6-N1-C2-C5	10.69(17)	C13-C14-C15-C16	0.0(3)
C6-N1-C4-O2	-96.29(17)	C14-C15-C16-N3	1.2(3)
C6-N1-C4-C7	141.71(15)	C16-N3-C12-C6	176.59(16)
C6-C12-C13-C14	-175.46(17)	C16-N3-C12-C13	-0.3(3)
C7-N2-C11-C10	-0.6(3)	C17-S1-O4-Fe1	89.56(14)
C7-C8-C9-C10	-0.8(3)	C18-S2-O7-Fe1	-109.55(13)
C8-C9-C10-C11	1.2(3)		

Table S13. Hydrogen bonds and close contacts for **A** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1...O8#1	0.80(3)	1.94(3)	2.719(2)	165(3)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,z+1/2

REFERENCE NUMBER: jonon94

CRYSTAL STRUCTURE REPORT

$C_{30}\ H_{41}\ F_6\ Fe\ N_3\ O_{11}\ S_2$

or

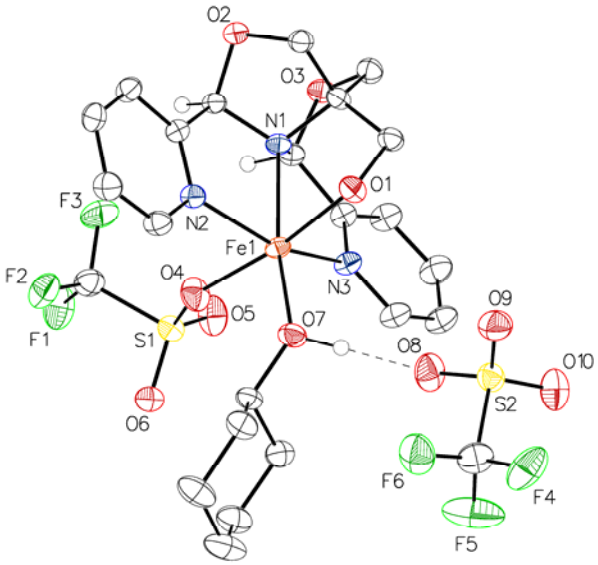
$[(\kappa^4\text{-L})Fe(OTf)(OHC_6H_{11})][OTf] \cdot C_6H_{11}OH$

B

Report prepared for:

Dr. O. Nachtigall, Prof. W. Jones

November 19, 2020



William W. Brennessel

X-ray Crystallographic Facility

Department of Chemistry, University of Rochester

120 Trustee Road

Rochester, NY 14627

Data collection

A crystal (0.237 x 0.135 x 0.0159 mm^3) was placed onto a thin glass optical fiber or a nylon loop and mounted on a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.00(13) K. A preliminary set of cell constants and an orientation matrix were calculated from a small sampling of reflections.[1] A short pre-experiment was run, from which an optimal data collection strategy was determined. The full data collection was carried out using a PhotonJet (Cu) X-ray source with frame times of 0.17 and 0.68 seconds and a detector distance of 31.2 mm. Series of frames were collected in 0.50º steps in ω at different 2θ, κ, and ϕ settings. After the intensity data were corrected for absorption, the final cell constants were calculated from the xyz centroids of 29439 strong reflections from the actual data collection after integration.[1] See Table S14 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT[2] and refined using SHELXL.[3] The space group *P*-1 was determined based on intensity statistics. Most or all non-hydrogen atoms were assigned from the solution. Full-matrix least squares / difference Fourier cycles were performed which located any remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The O-H hydrogen atoms were found from the difference Fourier map and refined freely. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0508$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.1472$ (F^2, all data).

Structure description

The structure is the one suggested. The asymmetric unit contains one monocationic iron complex, one triflate anion, and one cocrystallized cyclohexanol solvent molecule, all in general positions. Hydrogen bonding links the three species (see figures and Table S20).

Structure manipulation and figure generation were performed using Olex2.[4] Unless noted otherwise all structural diagrams containing anisotropic displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B04 Hutchison Hall, Department of Chemistry, University of Rochester. The instrument was purchased with funding from NSF MRI program grant CHE-1725028. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

[1] *CrysAlisPro*, version 171.40.84a; Rigaku Corporation: Oxford, UK, 2020.

[2] Sheldrick, G. M. *SHELXT*, version 2018/2; *Acta. Crystallogr.* **2015**, *A71*, 3-8.

[3] Sheldrick, G. M. *SHELXL*, version 2018/3; *Acta. Crystallogr.* **2015**, *C71*, 3-8.

[4] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Olex2*, version 1.3-ac4; *J. Appl. Cryst.* **2009**, *42*, 339-341.

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

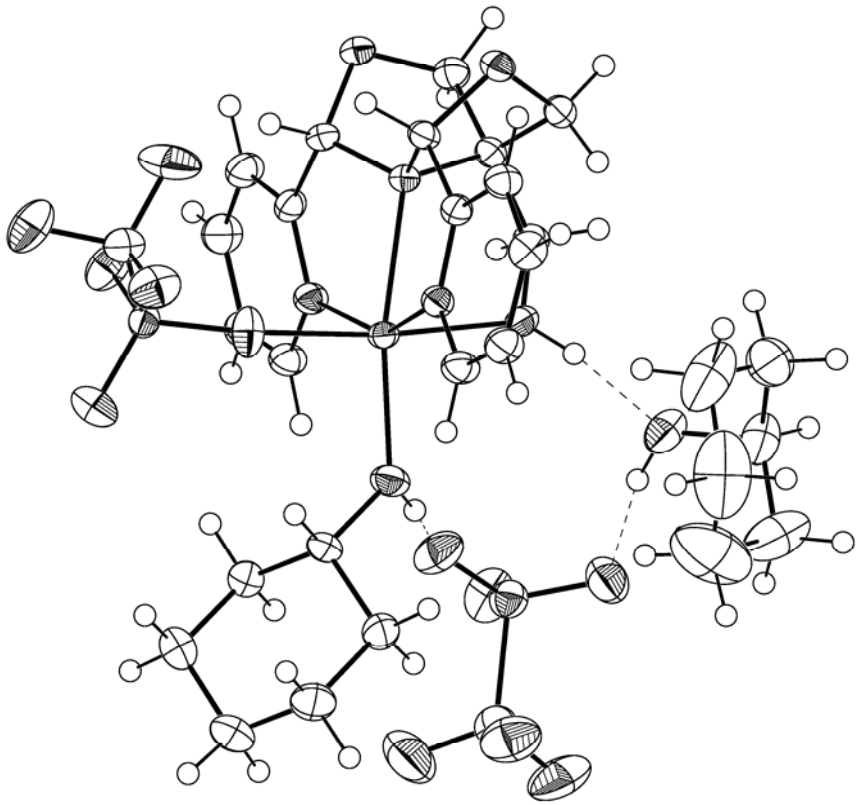
$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

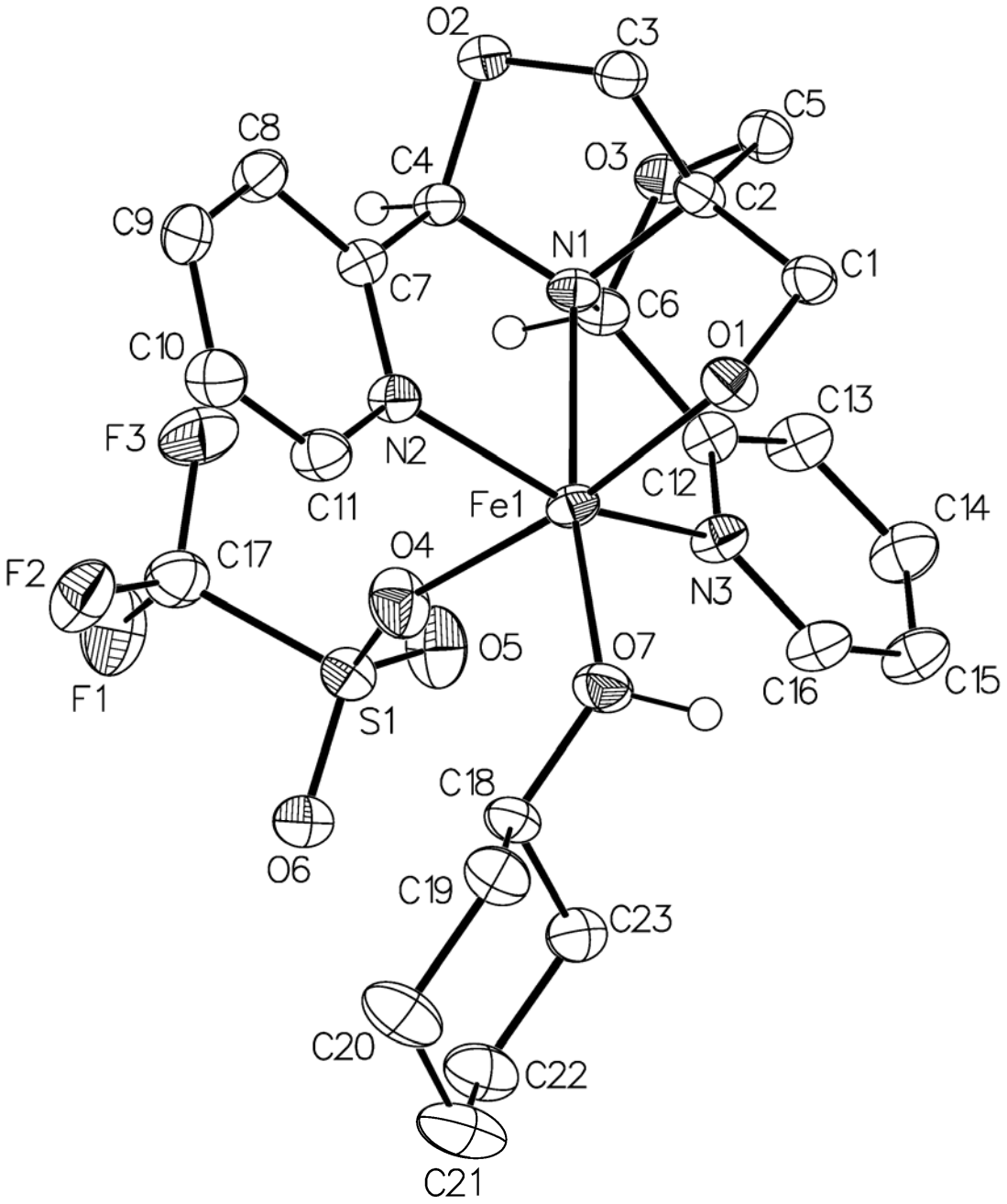
where $w = 1 \,/\, [\sigma^2 (F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max (0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

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C3
C5
C8
C4
O3
C2
C9
N1
C1
C7
C6
C10
O1
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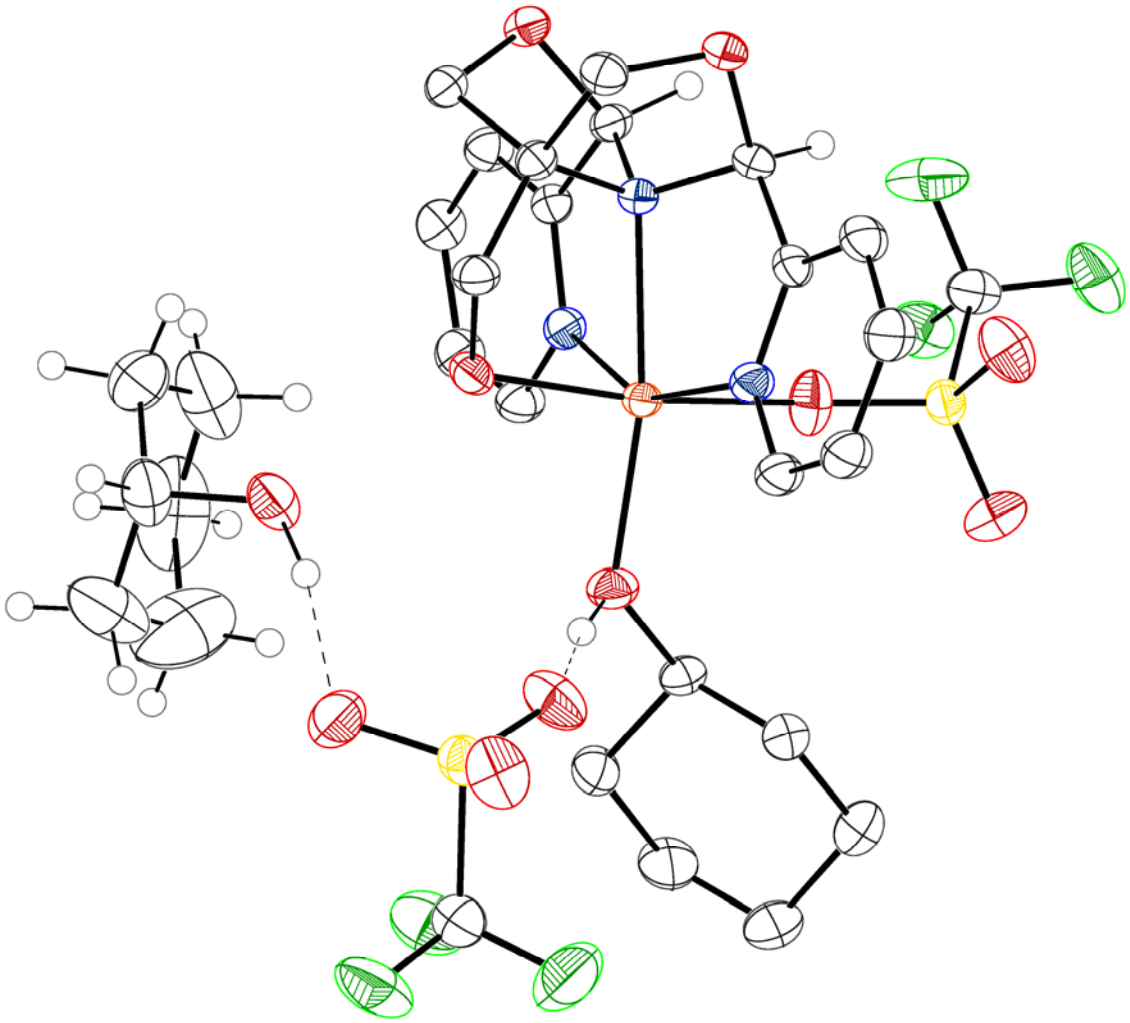
F3
N2
C12
C11
Fe1
C14
O4
C17
F2
N3
O5
O7
C16
C15
F1
S1
C18
O6
C19
C23
C20
C22
C21



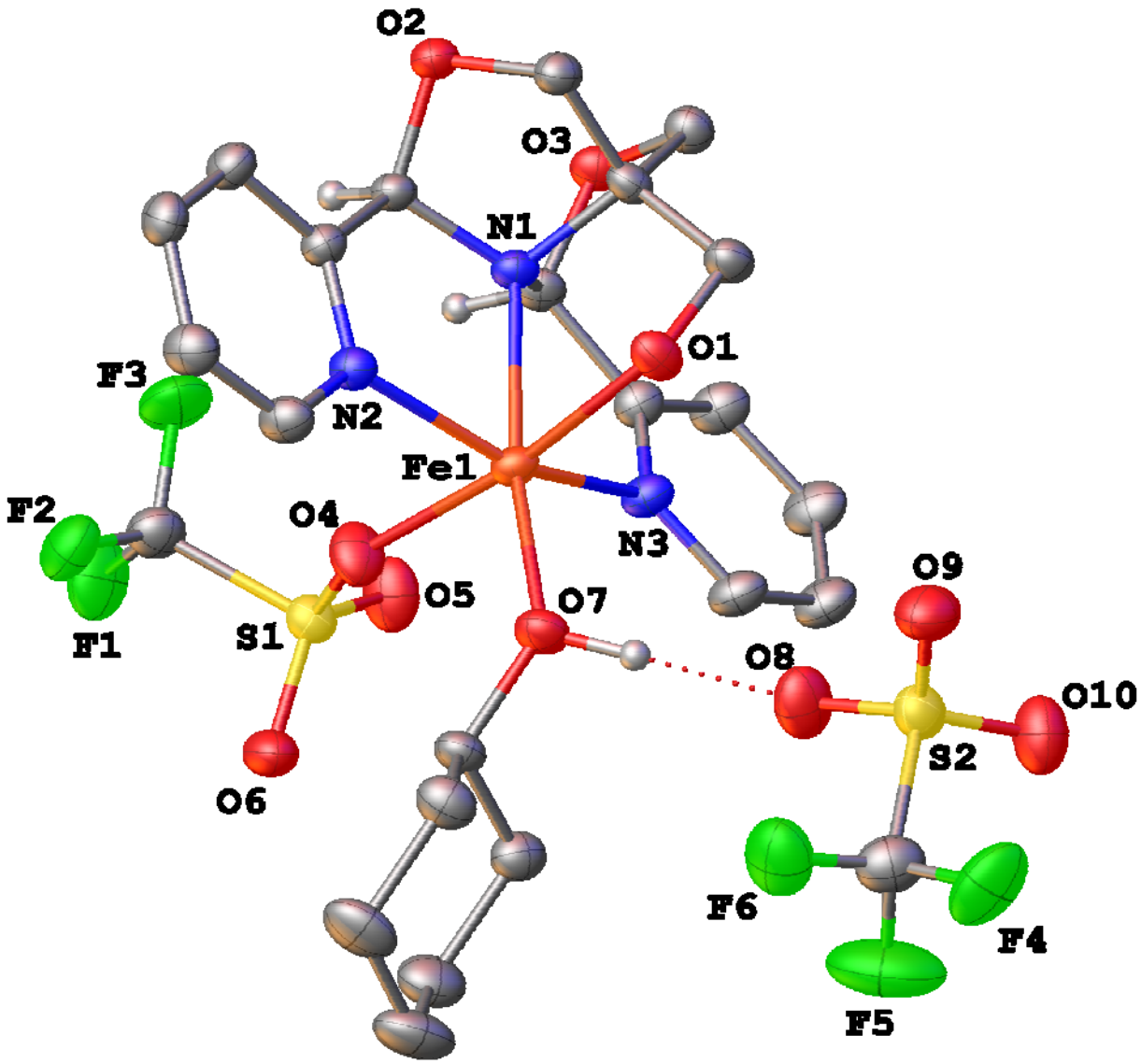

O2
O3
N1
O1
F3
N2
Fe1
F2
O4
N3
O9
O5
O7
F1
S1
O8
O10
S2
O6
F6
F4
F5

Table S14. Crystal data and structure refinement for **B**.

Identification code	jonon94	
Empirical formula	C30 H41 F6 Fe N3 O11 S2	
Formula weight	853.63	
Temperature	100.00(13) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 10.0940(2) Å	α = 77.548(2)°
	b = 13.5688(3) Å	β = 80.246(2)°
	c = 14.2285(2) Å	γ = 80.970(2)°
Volume	1860.70(6) Å^3	
Z	2	
Density (calculated)	1.524 Mg/m^3	
Absorption coefficient	5.107 mm^{-1}	
F(000)	884	
Crystal color, morphology	light yellow, block	
Crystal size	0.237 x 0.135 x 0.0159 mm^3	
Theta range for data collection	3.213 to 79.127°	
Index ranges	$-12 \le h \le 12$, $-17 \le k \le 16$, $-18 \le l \le 16$	
Reflections collected	46235	
Independent reflections	7836 [R(int) = 0.0710]	
Observed reflections	7318	
Completeness to theta = 74.504°	99.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00000 and 0.58008	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7836 / 0 / 490	
Goodness-of-fit on F^2	1.127	
Final R indices [I>2sigma(I)]	R1 = 0.0508, wR2 = 0.1407	
R indices (all data)	R1 = 0.0538, wR2 = 0.1472	
Largest diff. peak and hole	0.528 and -0.613 e.Å^{-3}	

Table S15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **B**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Fe1	3922(1)	2996(1)	3048(1)	19(1)
S1	1646(1)	2229(1)	5112(1)	23(1)
F1	1318(2)	1995(2)	6996(1)	49(1)
F2	3201(2)	1218(1)	6390(1)	42(1)
F3	2952(2)	2845(2)	6269(2)	55(1)
O1	5117(2)	3757(1)	1816(1)	25(1)
O2	6300(2)	4788(1)	3966(1)	23(1)
O3	3371(2)	5904(1)	3804(1)	23(1)
O4	2865(2)	2292(2)	4407(2)	37(1)
O5	723(2)	3148(2)	5067(2)	40(1)
O6	1070(2)	1311(2)	5203(2)	36(1)
O7	3711(2)	1877(1)	2342(2)	28(1)
N1	4382(2)	4328(2)	3537(1)	20(1)
N2	5657(2)	2374(2)	3747(2)	21(1)
N3	2156(2)	4080(2)	2827(2)	23(1)
C1	4929(3)	4845(2)	1720(2)	25(1)
C2	5002(2)	5093(2)	2709(2)	21(1)
C3	6450(2)	5005(2)	2924(2)	23(1)
C4	5399(2)	4036(2)	4224(2)	20(1)
C5	4176(3)	6123(2)	2869(2)	25(1)
C6	3102(2)	4890(2)	3909(2)	21(1)
C7	6194(2)	2992(2)	4156(2)	20(1)
C8	7417(3)	2702(2)	4526(2)	26(1)
C9	8083(3)	1729(2)	4495(2)	27(1)
C10	7488(3)	1073(2)	4111(2)	29(1)
C11	6296(3)	1427(2)	3736(2)	27(1)
C12	2003(2)	4855(2)	3299(2)	22(1)
C13	922(3)	5627(2)	3219(2)	30(1)
C14	-9(3)	5609(2)	2606(2)	33(1)
C15	155(3)	4818(2)	2107(2)	32(1)
C16	1244(3)	4057(2)	2246(2)	28(1)

C17	2314(3)	2063(2)	6249(2)	32(1)
C18	3165(3)	921(2)	2774(2)	24(1)
C19	3966(3)	77(2)	2297(2)	31(1)
C20	3411(4)	-936(2)	2745(3)	44(1)
C21	1906(4)	-852(3)	2696(3)	48(1)
C22	1112(3)	20(2)	3155(2)	39(1)
C23	1669(3)	1024(2)	2699(2)	29(1)
S2	3150(1)	2783(1)	-469(1)	30(1)
F4	3303(2)	1570(2)	-1686(2)	61(1)
F5	1746(3)	1331(2)	-474(3)	83(1)
F6	3837(3)	823(2)	-303(2)	56(1)
O8	2851(3)	2620(2)	573(2)	43(1)
O9	4543(2)	2907(2)	-852(2)	43(1)
O10	2183(3)	3482(2)	-977(2)	47(1)
C24	2999(3)	1550(3)	-741(2)	40(1)
O11	6354(2)	3376(2)	172(2)	38(1)
C25	7781(3)	3165(3)	-193(2)	45(1)
C26	8591(4)	3261(4)	568(3)	61(1)
C27	8461(4)	2462(5)	1442(3)	73(1)
C28	8773(5)	1408(5)	1202(4)	86(2)
C29	7909(7)	1313(4)	427(6)	103(2)
C30	8092(5)	2150(4)	-467(3)	68(1)

Table S16. Bond lengths [Å] and angles [°] for **B**.

Fe(1)-O(1)	2.1186(18)	C(3)-H(3B)	0.9700
Fe(1)-O(4)	2.1478(19)	C(4)-H(4)	0.9800
Fe(1)-O(7)	2.0478(18)	C(4)-C(7)	1.528(3)
Fe(1)-N(1)	2.2096(19)	C(5)-H(5A)	0.9700
Fe(1)-N(2)	2.129(2)	C(5)-H(5B)	0.9700
Fe(1)-N(3)	2.146(2)	C(6)-H(6)	0.9800
S(1)-O(4)	1.4504(19)	C(6)-C(12)	1.531(3)
S(1)-O(5)	1.431(2)	C(7)-C(8)	1.392(3)
S(1)-O(6)	1.428(2)	C(8)-H(8)	0.9300
S(1)-C(17)	1.814(3)	C(8)-C(9)	1.390(4)
F(1)-C(17)	1.331(3)	C(9)-H(9)	0.9300
F(2)-C(17)	1.340(3)	C(9)-C(10)	1.392(4)
F(3)-C(17)	1.332(3)	C(10)-H(10)	0.9300
O(1)-H(1)	0.92(4)	C(10)-C(11)	1.375(4)
O(1)-C(1)	1.438(3)	C(11)-H(11)	0.9300
O(2)-C(3)	1.435(3)	C(12)-C(13)	1.390(3)
O(2)-C(4)	1.421(3)	C(13)-H(13)	0.9300
O(3)-C(5)	1.435(3)	C(13)-C(14)	1.392(4)
O(3)-C(6)	1.417(3)	C(14)-H(14)	0.9300
O(7)-H(7)	0.95(6)	C(14)-C(15)	1.385(4)
O(7)-C(18)	1.460(3)	C(15)-H(15)	0.9300
N(1)-C(2)	1.511(3)	C(15)-C(16)	1.394(4)
N(1)-C(4)	1.487(3)	C(16)-H(16)	0.9300
N(1)-C(6)	1.471(3)	C(18)-H(18)	0.9800
N(2)-C(7)	1.340(3)	C(18)-C(19)	1.512(3)
N(2)-C(11)	1.345(3)	C(18)-C(23)	1.514(4)
N(3)-C(12)	1.342(3)	C(19)-H(19A)	0.9700
N(3)-C(16)	1.345(3)	C(19)-H(19B)	0.9700
C(1)-H(1A)	0.9700	C(19)-C(20)	1.534(4)
C(1)-H(1B)	0.9700	C(20)-H(20A)	0.9700
C(1)-C(2)	1.531(3)	C(20)-H(20B)	0.9700
C(2)-C(3)	1.526(3)	C(20)-C(21)	1.518(5)
C(2)-C(5)	1.552(3)	C(21)-H(21A)	0.9700
C(3)-H(3A)	0.9700	C(21)-H(21B)	0.9700

C(21)-C(22)	1.526(4)	O(4)-Fe(1)-N(1)	97.44(8)
C(22)-H(22A)	0.9700	O(7)-Fe(1)-O(1)	92.34(7)
C(22)-H(22B)	0.9700	O(7)-Fe(1)-O(4)	93.81(8)
C(22)-C(23)	1.527(4)	O(7)-Fe(1)-N(1)	168.73(8)
C(23)-H(23A)	0.9700	O(7)-Fe(1)-N(2)	102.64(8)
C(23)-H(23B)	0.9700	O(7)-Fe(1)-N(3)	103.98(8)
S(2)-O(8)	1.437(2)	N(2)-Fe(1)-O(4)	82.78(8)
S(2)-O(9)	1.441(2)	N(2)-Fe(1)-N(1)	78.25(8)
S(2)-O(10)	1.424(2)	N(2)-Fe(1)-N(3)	152.63(8)
S(2)-C(24)	1.831(3)	N(3)-Fe(1)-O(4)	89.23(8)
F(4)-C(24)	1.323(4)	N(3)-Fe(1)-N(1)	76.90(8)
F(5)-C(24)	1.319(4)	O(4)-S(1)-C(17)	102.00(13)
F(6)-C(24)	1.315(4)	O(5)-S(1)-O(4)	114.87(13)
O(11)-H(11A)	0.93(4)	O(5)-S(1)-C(17)	104.97(13)
O(11)-C(25)	1.452(4)	O(6)-S(1)-O(4)	112.82(13)
C(25)-H(25)	0.9800	O(6)-S(1)-O(5)	116.55(14)
C(25)-C(26)	1.500(5)	O(6)-S(1)-C(17)	103.36(13)
C(25)-C(30)	1.483(5)	Fe(1)-O(1)-H(1)	137(3)
C(26)-H(26A)	0.9700	C(1)-O(1)-Fe(1)	113.68(14)
C(26)-H(26B)	0.9700	C(1)-O(1)-H(1)	110(3)
C(26)-C(27)	1.465(7)	C(4)-O(2)-C(3)	103.12(17)
C(27)-H(27A)	0.9700	C(6)-O(3)-C(5)	105.11(17)
C(27)-H(27B)	0.9700	S(1)-O(4)-Fe(1)	150.30(14)
C(27)-C(28)	1.515(8)	Fe(1)-O(7)-H(7)	117(3)
C(28)-H(28A)	0.9700	C(18)-O(7)-Fe(1)	126.94(15)
C(28)-H(28B)	0.9700	C(18)-O(7)-H(7)	109(3)
C(28)-C(29)	1.555(9)	C(2)-N(1)-Fe(1)	112.46(13)
C(29)-H(29A)	0.9700	C(4)-N(1)-Fe(1)	111.82(13)
C(29)-H(29B)	0.9700	C(4)-N(1)-C(2)	104.85(17)
C(29)-C(30)	1.518(8)	C(6)-N(1)-Fe(1)	108.70(14)
C(30)-H(30A)	0.9700	C(6)-N(1)-C(2)	104.04(17)
C(30)-H(30B)	0.9700	C(6)-N(1)-C(4)	114.73(18)
O(1)-Fe(1)-O(4)	172.66(8)	C(7)-N(2)-Fe(1)	117.43(16)
O(1)-Fe(1)-N(1)	76.39(7)	C(7)-N(2)-C(11)	118.6(2)
O(1)-Fe(1)-N(2)	91.97(8)	C(11)-N(2)-Fe(1)	123.74(17)
O(1)-Fe(1)-N(3)	93.17(8)	C(12)-N(3)-Fe(1)	115.24(16)

C(12)-N(3)-C(16)	118.8(2)	N(1)-C(6)-C(12)	109.67(18)
C(16)-N(3)-Fe(1)	125.89(17)	C(12)-C(6)-H(6)	110.4
O(1)-C(1)-H(1A)	110.1	N(2)-C(7)-C(4)	117.7(2)
O(1)-C(1)-H(1B)	110.1	N(2)-C(7)-C(8)	122.1(2)
O(1)-C(1)-C(2)	108.18(19)	C(8)-C(7)-C(4)	120.2(2)
H(1A)-C(1)-H(1B)	108.4	C(7)-C(8)-H(8)	120.6
C(2)-C(1)-H(1A)	110.1	C(9)-C(8)-C(7)	118.8(2)
C(2)-C(1)-H(1B)	110.1	C(9)-C(8)-H(8)	120.6
N(1)-C(2)-C(1)	111.68(18)	C(8)-C(9)-H(9)	120.6
N(1)-C(2)-C(3)	102.40(19)	C(8)-C(9)-C(10)	118.8(2)
N(1)-C(2)-C(5)	103.50(18)	C(10)-C(9)-H(9)	120.6
C(1)-C(2)-C(5)	113.5(2)	C(9)-C(10)-H(10)	120.6
C(3)-C(2)-C(1)	113.0(2)	C(11)-C(10)-C(9)	118.8(2)
C(3)-C(2)-C(5)	111.81(19)	C(11)-C(10)-H(10)	120.6
O(2)-C(3)-C(2)	103.32(18)	N(2)-C(11)-C(10)	122.8(2)
O(2)-C(3)-H(3A)	111.1	N(2)-C(11)-H(11)	118.6
O(2)-C(3)-H(3B)	111.1	C(10)-C(11)-H(11)	118.6
C(2)-C(3)-H(3A)	111.1	N(3)-C(12)-C(6)	117.5(2)
C(2)-C(3)-H(3B)	111.1	N(3)-C(12)-C(13)	122.2(2)
H(3A)-C(3)-H(3B)	109.1	C(13)-C(12)-C(6)	120.2(2)
O(2)-C(4)-N(1)	106.78(18)	C(12)-C(13)-H(13)	120.6
O(2)-C(4)-H(4)	109.6	C(12)-C(13)-C(14)	118.8(2)
O(2)-C(4)-C(7)	109.62(18)	C(14)-C(13)-H(13)	120.6
N(1)-C(4)-H(4)	109.6	C(13)-C(14)-H(14)	120.4
N(1)-C(4)-C(7)	111.61(18)	C(15)-C(14)-C(13)	119.3(2)
C(7)-C(4)-H(4)	109.6	C(15)-C(14)-H(14)	120.4
O(3)-C(5)-C(2)	105.46(19)	C(14)-C(15)-H(15)	120.7
O(3)-C(5)-H(5A)	110.6	C(14)-C(15)-C(16)	118.6(3)
O(3)-C(5)-H(5B)	110.6	C(16)-C(15)-H(15)	120.7
C(2)-C(5)-H(5A)	110.6	N(3)-C(16)-C(15)	122.3(2)
C(2)-C(5)-H(5B)	110.6	N(3)-C(16)-H(16)	118.8
H(5A)-C(5)-H(5B)	108.8	C(15)-C(16)-H(16)	118.8
O(3)-C(6)-N(1)	105.61(18)	F(1)-C(17)-S(1)	110.7(2)
O(3)-C(6)-H(6)	110.4	F(1)-C(17)-F(2)	108.0(2)
O(3)-C(6)-C(12)	110.13(19)	F(1)-C(17)-F(3)	107.7(2)
N(1)-C(6)-H(6)	110.4	F(2)-C(17)-S(1)	111.52(18)

F(3)-C(17)-S(1)	111.3(2)	C(22)-C(23)-H(23B)	109.6
F(3)-C(17)-F(2)	107.5(2)	H(23A)-C(23)-H(23B)	108.2
O(7)-C(18)-H(18)	108.1	O(8)-S(2)-O(9)	114.64(15)
O(7)-C(18)-C(19)	109.7(2)	O(8)-S(2)-C(24)	103.37(15)
O(7)-C(18)-C(23)	110.7(2)	O(9)-S(2)-C(24)	102.13(14)
C(19)-C(18)-H(18)	108.1	O(10)-S(2)-O(8)	115.11(14)
C(19)-C(18)-C(23)	112.0(2)	O(10)-S(2)-O(9)	114.65(15)
C(23)-C(18)-H(18)	108.1	O(10)-S(2)-C(24)	104.69(16)
C(18)-C(19)-H(19A)	109.6	F(4)-C(24)-S(2)	110.4(2)
C(18)-C(19)-H(19B)	109.6	F(5)-C(24)-S(2)	110.4(2)
C(18)-C(19)-C(20)	110.4(2)	F(5)-C(24)-F(4)	107.7(3)
H(19A)-C(19)-H(19B)	108.1	F(6)-C(24)-S(2)	111.2(2)
C(20)-C(19)-H(19A)	109.6	F(6)-C(24)-F(4)	107.4(3)
C(20)-C(19)-H(19B)	109.6	F(6)-C(24)-F(5)	109.7(3)
C(19)-C(20)-H(20A)	109.4	C(25)-O(11)-H(11A)	123(2)
C(19)-C(20)-H(20B)	109.4	O(11)-C(25)-H(25)	108.3
H(20A)-C(20)-H(20B)	108.0	O(11)-C(25)-C(26)	108.2(3)
C(21)-C(20)-C(19)	111.3(3)	O(11)-C(25)-C(30)	111.2(3)
C(21)-C(20)-H(20A)	109.4	C(26)-C(25)-H(25)	108.3
C(21)-C(20)-H(20B)	109.4	C(30)-C(25)-H(25)	108.3
C(20)-C(21)-H(21A)	109.3	C(30)-C(25)-C(26)	112.3(3)
C(20)-C(21)-H(21B)	109.3	C(25)-C(26)-H(26A)	108.8
C(20)-C(21)-C(22)	111.5(3)	C(25)-C(26)-H(26B)	108.8
H(21A)-C(21)-H(21B)	108.0	H(26A)-C(26)-H(26B)	107.7
C(22)-C(21)-H(21A)	109.3	C(27)-C(26)-C(25)	113.8(4)
C(22)-C(21)-H(21B)	109.3	C(27)-C(26)-H(26A)	108.8
C(21)-C(22)-H(22A)	109.4	C(27)-C(26)-H(26B)	108.8
C(21)-C(22)-H(22B)	109.4	C(26)-C(27)-H(27A)	109.2
C(21)-C(22)-C(23)	111.3(2)	C(26)-C(27)-H(27B)	109.2
H(22A)-C(22)-H(22B)	108.0	C(26)-C(27)-C(28)	112.0(4)
C(23)-C(22)-H(22A)	109.4	H(27A)-C(27)-H(27B)	107.9
C(23)-C(22)-H(22B)	109.4	C(28)-C(27)-H(27A)	109.2
C(18)-C(23)-C(22)	110.1(2)	C(28)-C(27)-H(27B)	109.2
C(18)-C(23)-H(23A)	109.6	C(27)-C(28)-H(28A)	109.6
C(18)-C(23)-H(23B)	109.6	C(27)-C(28)-H(28B)	109.6
C(22)-C(23)-H(23A)	109.6	C(27)-C(28)-C(29)	110.3(4)

H(28A)-C(28)-H(28B)	108.1	C(30)-C(29)-H(29B)	109.4
C(29)-C(28)-H(28A)	109.6	C(25)-C(30)-C(29)	110.6(4)
C(29)-C(28)-H(28B)	109.6	C(25)-C(30)-H(30A)	109.5
C(28)-C(29)-H(29A)	109.4	C(25)-C(30)-H(30B)	109.5
C(28)-C(29)-H(29B)	109.4	C(29)-C(30)-H(30A)	109.5
H(29A)-C(29)-H(29B)	108.0	C(29)-C(30)-H(30B)	109.5
C(30)-C(29)-C(28)	111.2(4)	H(30A)-C(30)-H(30B)	108.1
C(30)-C(29)-H(29A)	109.4		

Table S17. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **B**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	19(1)	19(1)	22(1)	-10(1)	-2(1)	-2(1)
S1	24(1)	22(1)	23(1)	-7(1)	2(1)	-2(1)
F1	58(1)	62(1)	24(1)	-13(1)	2(1)	3(1)
F2	45(1)	43(1)	41(1)	-14(1)	-18(1)	5(1)
F3	78(2)	46(1)	57(1)	-20(1)	-25(1)	-21(1)
O1	34(1)	21(1)	21(1)	-9(1)	3(1)	-5(1)
O2	26(1)	22(1)	24(1)	-7(1)	-3(1)	-6(1)
O3	28(1)	19(1)	26(1)	-11(1)	-1(1)	-2(1)
O4	31(1)	45(1)	28(1)	0(1)	6(1)	-6(1)
O5	45(1)	34(1)	35(1)	-8(1)	-1(1)	12(1)
O6	40(1)	30(1)	41(1)	-1(1)	-14(1)	-12(1)
O7	35(1)	20(1)	32(1)	-9(1)	-4(1)	-7(1)
N1	22(1)	17(1)	21(1)	-9(1)	0(1)	-3(1)
N2	21(1)	18(1)	24(1)	-7(1)	-2(1)	-2(1)
N3	22(1)	24(1)	28(1)	-11(1)	-4(1)	-2(1)
C1	32(1)	20(1)	24(1)	-6(1)	-2(1)	-6(1)
C2	27(1)	17(1)	20(1)	-5(1)	1(1)	-6(1)
C3	26(1)	22(1)	22(1)	-6(1)	0(1)	-7(1)
C4	22(1)	18(1)	22(1)	-7(1)	-3(1)	-5(1)
C5	30(1)	20(1)	24(1)	-7(1)	-2(1)	-2(1)
C6	24(1)	17(1)	23(1)	-10(1)	0(1)	-2(1)
C7	22(1)	21(1)	19(1)	-6(1)	-1(1)	-3(1)
C8	28(1)	26(1)	26(1)	-8(1)	-6(1)	-2(1)
C9	28(1)	26(1)	26(1)	-5(1)	-6(1)	1(1)
C10	29(1)	23(1)	34(1)	-9(1)	-3(1)	1(1)
C11	27(1)	21(1)	34(1)	-11(1)	-4(1)	-1(1)
C12	22(1)	22(1)	22(1)	-9(1)	0(1)	-1(1)
C13	26(1)	30(1)	36(1)	-16(1)	-3(1)	1(1)
C14	24(1)	34(1)	44(2)	-16(1)	-8(1)	4(1)
C15	25(1)	37(2)	40(2)	-16(1)	-9(1)	-1(1)
C16	24(1)	29(1)	35(1)	-15(1)	-6(1)	-2(1)

C17	40(1)	30(1)	30(1)	-12(1)	-3(1)	-7(1)
C18	29(1)	18(1)	27(1)	-7(1)	-1(1)	-6(1)
C19	33(1)	24(1)	34(1)	-11(1)	3(1)	-3(1)
C20	55(2)	20(1)	53(2)	-13(1)	7(2)	-7(1)
C21	58(2)	36(2)	56(2)	-20(2)	9(2)	-24(2)
C22	38(2)	38(2)	42(2)	-10(1)	5(1)	-15(1)
C23	31(1)	30(1)	28(1)	-10(1)	0(1)	-7(1)
S2	37(1)	29(1)	24(1)	-6(1)	-1(1)	-6(1)
F4	69(1)	76(2)	49(1)	-41(1)	-20(1)	10(1)
F5	50(1)	71(2)	140(3)	-48(2)	13(2)	-29(1)
F6	79(2)	35(1)	53(1)	-13(1)	-13(1)	5(1)
O8	62(1)	39(1)	27(1)	-12(1)	-2(1)	-1(1)
O9	42(1)	50(1)	41(1)	-8(1)	-2(1)	-17(1)
O10	52(1)	45(1)	37(1)	-1(1)	-7(1)	7(1)
C24	38(2)	41(2)	43(2)	-18(1)	-1(1)	-6(1)
O11	35(1)	49(1)	30(1)	-16(1)	-4(1)	4(1)
C25	40(2)	57(2)	34(2)	-10(1)	4(1)	-3(1)
C26	36(2)	83(3)	74(3)	-40(2)	-4(2)	-12(2)
C27	47(2)	125(4)	44(2)	-29(2)	-13(2)	21(2)
C28	59(3)	99(4)	74(3)	24(3)	-12(2)	16(3)
C29	89(4)	44(2)	183(7)	-22(3)	-45(4)	1(2)
C30	64(2)	82(3)	70(3)	-49(2)	-29(2)	25(2)

Table S18. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **B**.

	x	y	z	U(eq)
H1	5710(40)	3580(30)	1300(30)	52(11)
H7	3520(60)	2080(40)	1690(40)	90(17)
H1A	4055	5125	1515	30
H1B	5629	5141	1235	30
H3A	7023	4459	2656	27
H3B	6834	5636	2661	27
H4	4942	4030	4890	24
H5A	4776	6619	2860	29
H5B	3602	6389	2366	29
H6	2823	4601	4594	25
H8	7783	3151	4790	31
H9	8910	1520	4727	33
H10	7890	408	4109	35
H11	5915	994	3462	32
H13	823	6146	3569	36
H14	-732	6123	2533	40
H15	-449	4795	1688	39
H16	1343	3515	1926	33
H18	3271	757	3465	29
H19A	4911	16	2382	37
H19B	3912	239	1605	37
H20A	3892	-1458	2399	52
H20B	3565	-1137	3418	52
H21A	1571	-1485	3031	58
H21B	1763	-741	2022	58
H22A	1161	-131	3848	47
H22B	167	83	3070	47
H23A	1535	1214	2021	35
H23B	1185	1556	3031	35
H11A	5660(40)	3190(30)	-90(30)	48(11)

H25	8001	3680	-775	54
H26A	9538	3243	289	73
H26B	8301	3917	753	73
H27A	7545	2546	1782	87
H27B	9075	2533	1872	87
H28A	8577	904	1787	103
H28B	9728	1280	957	103
H29A	8175	656	240	124
H29B	6961	1352	705	124
H30A	9019	2066	-788	82
H30B	7497	2101	-918	82

Table S19. Torsion angles [°] for **B**.

Fe1-O1-C1-C2	47.4(2)	O7-C18-C19-C20	179.7(2)
Fe1-O7-C18-C19	-141.61(19)	O7-C18-C23-C22	-179.9(2)
Fe1-O7-C18-C23	94.4(2)	N1-C2-C3-O2	-33.6(2)
Fe1-N1-C2-C1	9.9(2)	N1-C2-C5-O3	9.3(2)
Fe1-N1-C2-C3	-111.29(16)	N1-C4-C7-N2	-18.9(3)
Fe1-N1-C2-C5	132.35(15)	N1-C4-C7-C8	162.3(2)
Fe1-N1-C4-O2	138.66(14)	N1-C6-C12-N3	24.4(3)
Fe1-N1-C4-C7	18.9(2)	N1-C6-C12-C13	-153.3(2)
Fe1-N1-C6-O3	-154.99(14)	N2-C7-C8-C9	-1.8(4)
Fe1-N1-C6-C12	-36.3(2)	N3-C12-C13-C14	-1.9(4)
Fe1-N2-C7-C4	9.1(3)	C1-C2-C3-O2	-153.89(19)
Fe1-N2-C7-C8	-172.06(18)	C1-C2-C5-O3	130.5(2)
Fe1-N2-C11-C10	173.6(2)	C2-N1-C4-O2	16.5(2)
Fe1-N3-C12-C6	1.4(3)	C2-N1-C4-C7	-103.3(2)
Fe1-N3-C12-C13	179.0(2)	C2-N1-C6-O3	-35.0(2)
Fe1-N3-C16-C15	-176.9(2)	C2-N1-C6-C12	83.7(2)
O1-C1-C2-N1	-35.8(3)	C3-O2-C4-N1	-38.5(2)
O1-C1-C2-C3	79.0(2)	C3-O2-C4-C7	82.5(2)
O1-C1-C2-C5	-152.3(2)	C3-C2-C5-O3	-100.2(2)
O2-C4-C7-N2	-137.0(2)	C4-O2-C3-C2	44.8(2)
O2-C4-C7-C8	44.2(3)	C4-N1-C2-C1	131.6(2)
O3-C6-C12-N3	140.2(2)	C4-N1-C2-C3	10.4(2)
O3-C6-C12-C13	-37.5(3)	C4-N1-C2-C5	-105.9(2)
O4-S1-C17-F1	179.6(2)	C4-N1-C6-O3	79.0(2)
O4-S1-C17-F2	-60.1(2)	C4-N1-C6-C12	-162.35(19)
O4-S1-C17-F3	59.9(2)	C4-C7-C8-C9	176.9(2)
O5-S1-O4-Fe1	-23.1(4)	C5-O3-C6-N1	41.9(2)
O5-S1-C17-F1	59.5(2)	C5-O3-C6-C12	-76.4(2)
O5-S1-C17-F2	179.8(2)	C5-C2-C3-O2	76.6(2)
O5-S1-C17-F3	-60.2(2)	C6-O3-C5-C2	-31.2(2)
O6-S1-O4-Fe1	113.7(3)	C6-N1-C2-C1	-107.5(2)
O6-S1-C17-F1	-63.1(2)	C6-N1-C2-C3	131.25(18)
O6-S1-C17-F2	57.1(2)	C6-N1-C2-C5	14.9(2)
O6-S1-C17-F3	177.2(2)	C6-N1-C4-O2	-97.0(2)

C6-N1-C4-C7	143.26(19)	C21-C22-C23-C18	-55.8(3)
C6-C12-C13-C14	175.7(2)	C23-C18-C19-C20	-57.0(3)
C7-N2-C11-C10	-1.1(4)	O8-S2-C24-F4	-177.5(2)
C7-C8-C9-C10	-1.2(4)	O8-S2-C24-F5	63.5(3)
C8-C9-C10-C11	3.0(4)	O8-S2-C24-F6	-58.5(3)
C9-C10-C11-N2	-1.9(4)	O9-S2-C24-F4	-58.2(2)
C11-N2-C7-C4	-175.8(2)	O9-S2-C24-F5	-177.2(3)
C11-N2-C7-C8	3.0(4)	O9-S2-C24-F6	60.8(3)
C12-N3-C16-C15	0.9(4)	O10-S2-C24-F4	61.6(2)
C12-C13-C14-C15	1.0(4)	O10-S2-C24-F5	-57.3(3)
C13-C14-C15-C16	0.7(5)	O10-S2-C24-F6	-179.4(2)
C14-C15-C16-N3	-1.7(4)	O11-C25-C26-C27	68.7(4)
C16-N3-C12-C6	-176.7(2)	O11-C25-C30-C29	-66.9(4)
C16-N3-C12-C13	1.0(4)	C25-C26-C27-C28	53.3(5)
C17-S1-O4-Fe1	-136.0(3)	C26-C25-C30-C29	54.5(5)
C18-C19-C20-C21	54.9(3)	C26-C27-C28-C29	-52.8(6)
C19-C18-C23-C22	57.4(3)	C27-C28-C29-C30	54.2(6)
C19-C20-C21-C22	-54.3(4)	C28-C29-C30-C25	-55.3(6)
C20-C21-C22-C23	54.9(4)	C30-C25-C26-C27	-54.4(5)

Table S20. Hydrogen bonds and close contacts for **B** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1...O11	0.92(4)	1.69(4)	2.575(3)	161(4)
O7-H7...O8	0.95(6)	1.80(6)	2.735(3)	168(5)
O11-H11A...O9	0.93(4)	1.83(4)	2.744(3)	167(4)

REFERENCE NUMBER: jonon101

CRYSTAL STRUCTURE REPORT

$C_{18}\ H_{21}\ F_6\ Fe\ N_3\ O_{11}\ S_2$

or

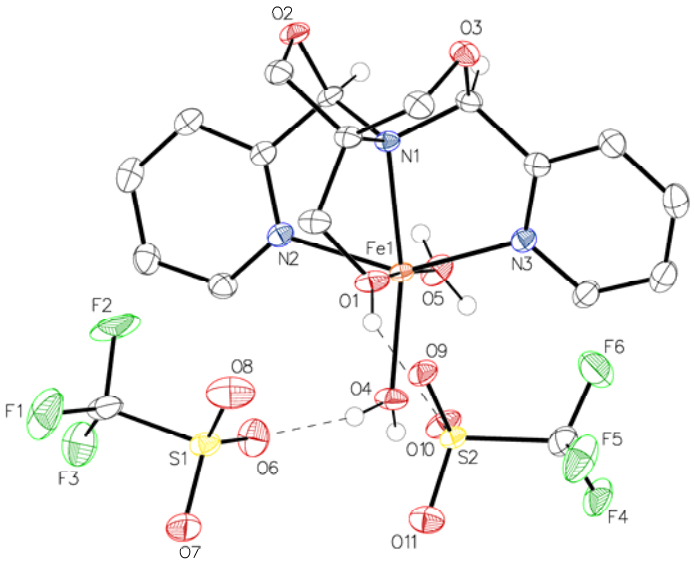
$[(\kappa^4\text{-L})Fe(OH_2)_2][OTf]_2$

C

Report prepared for:

Dr. O. Nachtigall, Prof. W. Jones

November 11, 2020



William W. Brennessel

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120 Trustee Road

Rochester, NY 14627

Data collection

A crystal (0.204 x 0.107 x 0.073 mm^3) was placed onto a thin glass optical fiber or a nylon loop and mounted on a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.00(10) K. A preliminary set of cell constants and an orientation matrix were calculated from a small sampling of reflections.[1] A short pre-experiment was run, from which an optimal data collection strategy was determined. The full data collection was carried out using a PhotonJet (Cu) X-ray source with frame times of 0.20 and 0.80 seconds and a detector distance of 31.2 mm. Series of frames were collected in 0.50º steps in ω at different 2θ, κ, and ϕ settings. After the intensity data were corrected for absorption, the final cell constants were calculated from the xyz centroids of 20479 strong reflections from the actual data collection after integration.[1] See Table S21 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT 2018/2[2] and refined using SHELXL.[3] The space group $P2_1/c$ was determined based on systematic absences. Most or all non-hydrogen atoms were assigned from the solution. Full-matrix least squares / difference Fourier cycles were performed which located any remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The O-H hydrogen atoms were found from the difference Fourier map and refined freely. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0306$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.0825$ (F^2, all data).

Structure description

The structure is the one suggested. The asymmetric unit contains one dicationic iron complex and two triflate anions in general position. Hydrogen bonding links all species along [010] (see figures and Table S27).

Structure manipulation and figure generation were performed using Olex2 1.3-ac4.[4] Unless noted otherwise all structural diagrams containing anisotropic displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B04 Hutchison Hall, Department of Chemistry, University of Rochester. The instrument was purchased with funding from NSF MRI program grant CHE-1725028. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

[1] *CrysAlisPro*, version 171.40.84a; Rigaku Corporation: Oxford, UK, 2020.

[2] Sheldrick, G. M. *SHELXT*, version 2018/2; *Acta. Crystallogr.* **2015**, *A71*, 3-8.

[3] Sheldrick, G. M. *SHELXL*, version 2018/3; *Acta. Crystallogr.* **2015**, *C71*, 3-8.

[4] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Olex2*, version 1.3-ac4; *J. Appl. Cryst.* **2009**, *42*, 339-341.

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

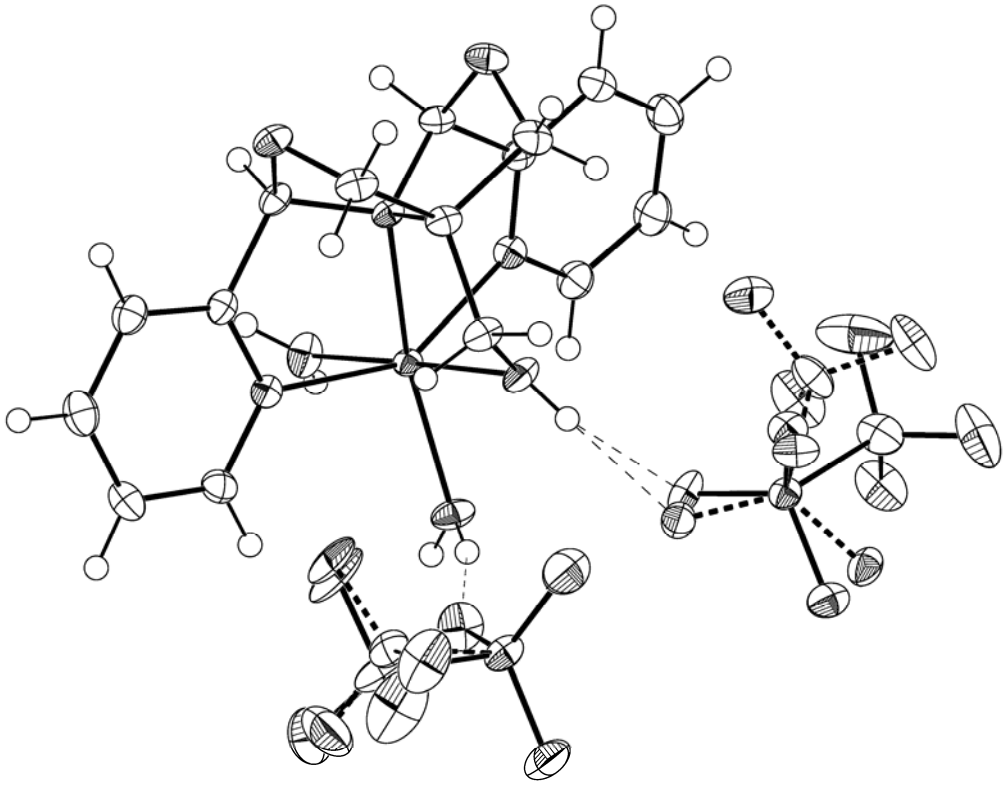
$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

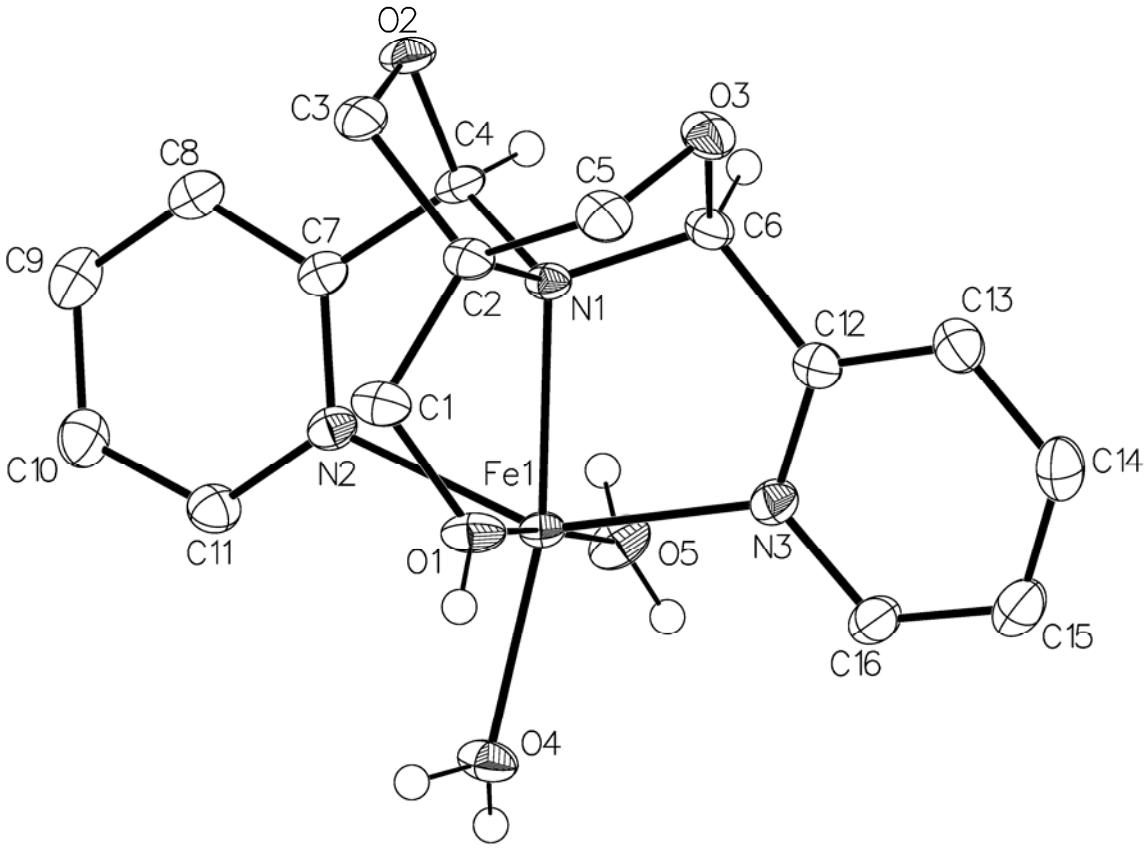
where $w = 1 \,/\, [\sigma^2 (F_o^2) + (aP)^2 + bP]$ and

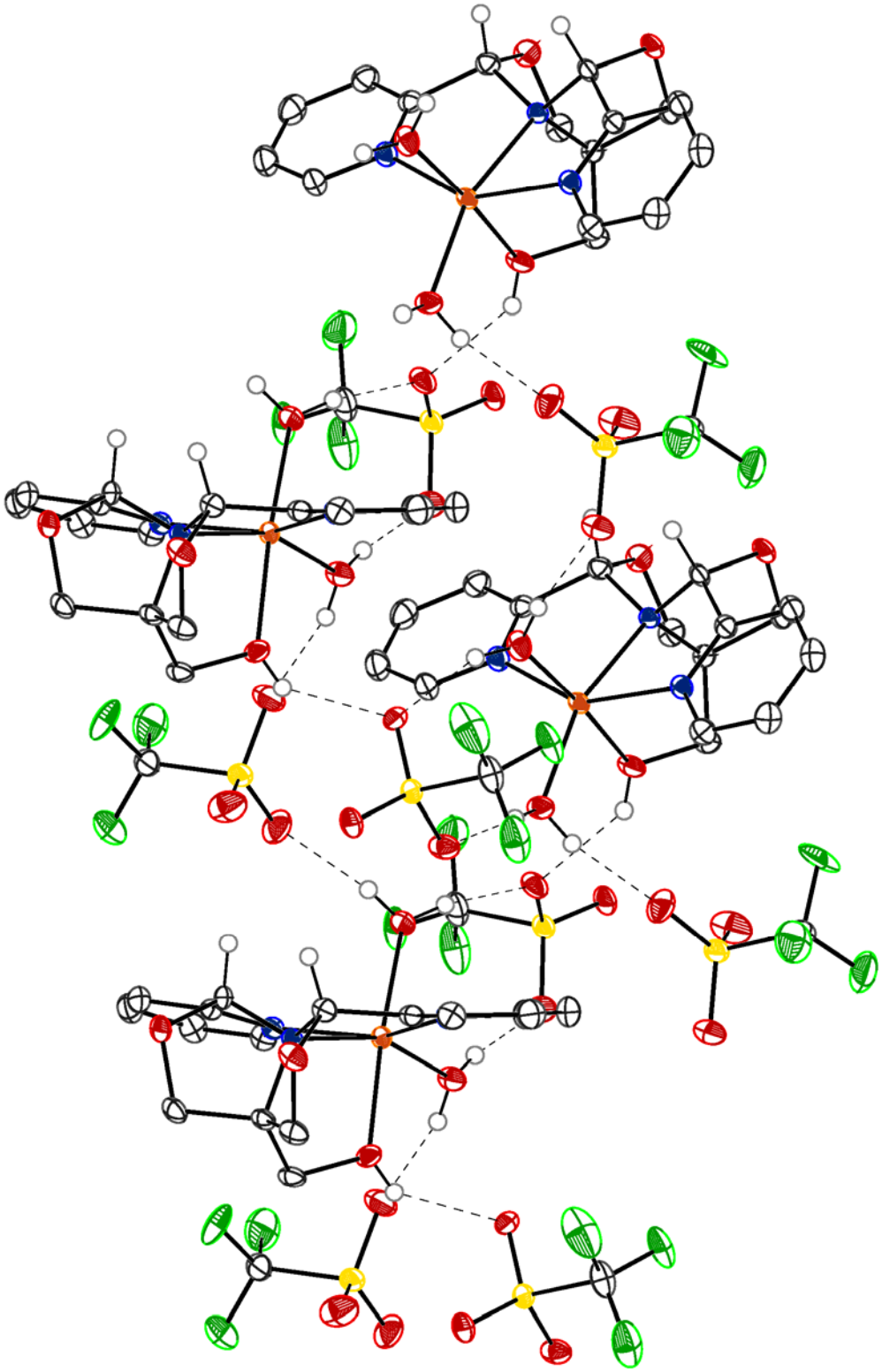
$$P = 1/3 \max (0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters




O2
C3
C4
O3
C8
C5
C7
C6
C9
C2
N1
C12
C13
C1
C10
N2
Fe1
C14
C11
O1
O5
N3
C16
C15
O4



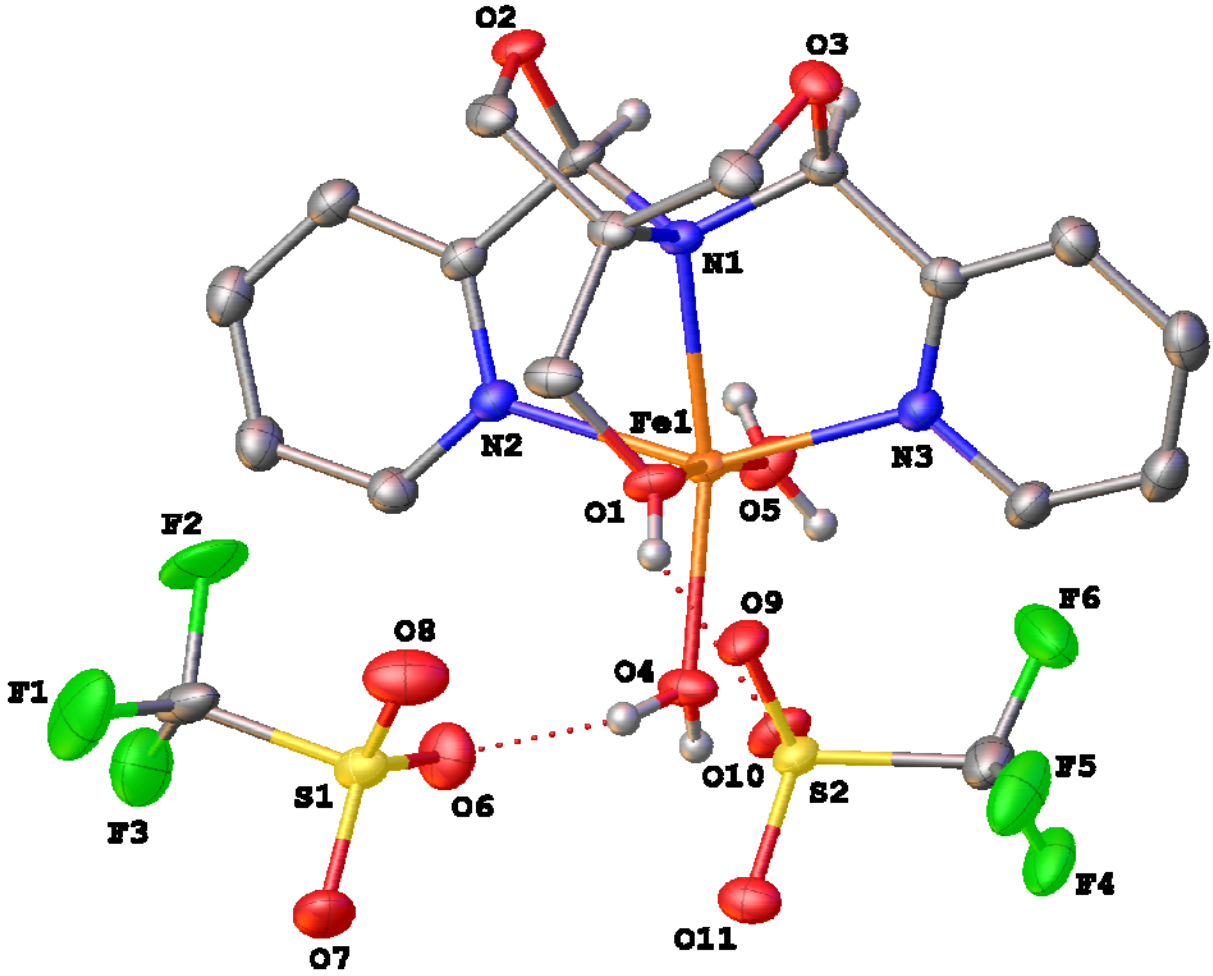

O2
O3
N1
N2
Fe1
N3
O1
O5
F2
O9
F6
O8
O4
F1
S1
O6
O10
S2
F5
F3
F4
O7
O11

Table S21. Crystal data and structure refinement for **C**.

Identification code	jonon101	
Empirical formula	C18 H21 F6 Fe N3 O11 S2	
Formula weight	689.35	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.3968(2) Å	α = 90°
	b = 9.43800(10) Å	β = 100.509(2)°
	c = 20.5184(3) Å	γ = 90°
Volume	2550.81(6) Å^3	
Z	4	
Density (calculated)	1.795 Mg/m^3	
Absorption coefficient	7.280 mm^{-1}	
F(000)	1400	
Crystal color, morphology	colourless, block	
Crystal size	0.204 x 0.107 x 0.073 mm^3	
Theta range for data collection	3.355 to 77.699°	
Index ranges	$-16 \le h \le 16$, $-11 \le k \le 11$, $-26 \le l \le 24$	
Reflections collected	33019	
Independent reflections	5380 [R(int) = 0.0449]	
Observed reflections	5089	
Completeness to theta = 74.504°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00000 and 0.56339	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5380 / 306 / 491	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2sigma(I)]	R1 = 0.0306, wR2 = 0.0814	
R indices (all data)	R1 = 0.0325, wR2 = 0.0825	
Largest diff. peak and hole	0.327 and -0.514 e.Å^{-3}	

Table S22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **C**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Fe1	3160(1)	5390(1)	7187(1)	13(1)
O1	2360(1)	3595(1)	7485(1)	21(1)
O2	98(1)	6982(1)	6816(1)	20(1)
O3	952(1)	6639(1)	8325(1)	22(1)
O4	4225(1)	3949(1)	6997(1)	22(1)
O5	4053(1)	7101(2)	6934(1)	23(1)
N1	1659(1)	6225(1)	7384(1)	14(1)
N2	2231(1)	5642(2)	6214(1)	16(1)
N3	3524(1)	6035(2)	8190(1)	17(1)
C1	1291(1)	3625(2)	7247(1)	20(1)
C2	908(1)	5053(2)	7449(1)	16(1)
C3	-77(1)	5542(2)	6983(1)	21(1)
C4	1157(1)	7054(2)	6814(1)	16(1)
C5	811(1)	5159(2)	8183(1)	21(1)
C6	1794(1)	6997(2)	8026(1)	17(1)
C7	1387(1)	6427(2)	6174(1)	16(1)
C8	745(1)	6701(2)	5576(1)	21(1)
C9	989(1)	6157(2)	4999(1)	25(1)
C10	1857(2)	5335(2)	5036(1)	23(1)
C11	2456(1)	5107(2)	5652(1)	20(1)
C12	2781(1)	6568(2)	8475(1)	17(1)
C13	2909(1)	6790(2)	9153(1)	22(1)
C14	3844(2)	6504(2)	9544(1)	26(1)
C15	4628(2)	6021(2)	9247(1)	26(1)
C16	4434(1)	5783(2)	8572(1)	22(1)
S1	2530(1)	533(1)	6296(1)	21(1)
O6	3189(1)	1746(2)	6346(1)	31(1)
O7	3004(1)	-782(2)	6165(1)	33(1)
O8	1887(1)	457(2)	6782(1)	39(1)
F1	1094(10)	-195(6)	5278(9)	60(3)
F2	1187(12)	2006(12)	5551(9)	53(2)

F3	2250(10)	1121(10)	5003(4)	47(2)
C17	1734(9)	852(8)	5483(4)	31(2)
F1'	845(8)	-96(7)	5534(8)	44(2)
F2'	1095(13)	2158(11)	5573(9)	39(2)
F3'	1965(12)	810(20)	5037(5)	49(2)
C17'	1543(8)	904(10)	5569(4)	24(2)
S2	3539(1)	618(1)	8471(1)	16(1)
F4	5203(2)	1083(3)	9306(1)	36(1)
F5	4072(2)	-68(4)	9716(1)	47(1)
F6	3887(3)	2147(4)	9524(2)	56(1)
O9	2483(5)	566(11)	8521(7)	22(2)
O10	3819(6)	1749(5)	8070(3)	25(1)
O11	3956(2)	-751(3)	8319(2)	24(1)
C18	4212(3)	959(4)	9301(2)	29(1)
F4'	4726(2)	2529(3)	9176(1)	39(1)
F5'	3758(2)	1411(4)	9732(1)	37(1)
F6'	3137(2)	3028(3)	9031(1)	37(1)
O9'	2505(5)	251(11)	8475(8)	22(2)
O10'	3733(6)	1429(6)	7909(2)	22(1)
O11'	4284(2)	-439(3)	8700(2)	26(1)
C18'	3807(3)	1964(4)	9137(2)	26(1)

Table S23. Bond lengths [Å] and angles [°] for **C**.

Fe(1)-O(1)	2.1521(13)	C(6)-H(6)	0.9800
Fe(1)-O(4)	2.0594(13)	C(6)-C(12)	1.522(2)
Fe(1)-O(5)	2.1295(13)	C(7)-C(8)	1.389(2)
Fe(1)-N(1)	2.2636(13)	C(8)-H(8)	0.9300
Fe(1)-N(2)	2.1627(15)	C(8)-C(9)	1.384(3)
Fe(1)-N(3)	2.1167(15)	C(9)-H(9)	0.9300
O(1)-H(1)	0.81(3)	C(9)-C(10)	1.388(3)
O(1)-C(1)	1.426(2)	C(10)-H(10)	0.9300
O(2)-C(3)	1.432(2)	C(10)-C(11)	1.386(3)
O(2)-C(4)	1.4205(19)	C(11)-H(11)	0.9300
O(3)-C(5)	1.433(2)	C(12)-C(13)	1.388(2)
O(3)-C(6)	1.419(2)	C(13)-H(13)	0.9300
O(4)-H(4A)	0.84(4)	C(13)-C(14)	1.384(3)
O(4)-H(4B)	0.84(3)	C(14)-H(14)	0.9300
O(5)-H(5A)	0.85(3)	C(14)-C(15)	1.384(3)
O(5)-H(5B)	0.84(3)	C(15)-H(15)	0.9300
N(1)-C(2)	1.517(2)	C(15)-C(16)	1.381(3)
N(1)-C(4)	1.466(2)	C(16)-H(16)	0.9300
N(1)-C(6)	1.487(2)	S(1)-O(6)	1.4377(14)
N(2)-C(7)	1.341(2)	S(1)-O(7)	1.4420(15)
N(2)-C(11)	1.342(2)	S(1)-O(8)	1.4349(16)
N(3)-C(12)	1.341(2)	S(1)-C(17)	1.833(5)
N(3)-C(16)	1.344(2)	S(1)-C(17')	1.837(6)
C(1)-H(1A)	0.9700	F(1)-C(17)	1.326(5)
C(1)-H(1B)	0.9700	F(2)-C(17)	1.333(5)
C(1)-C(2)	1.527(2)	F(3)-C(17)	1.327(6)
C(2)-C(3)	1.552(2)	F(1')-C(17')	1.321(6)
C(2)-C(5)	1.537(2)	F(2')-C(17')	1.328(6)
C(3)-H(3A)	0.9700	F(3')-C(17')	1.320(6)
C(3)-H(3B)	0.9700	S(2)-O(9)	1.438(5)
C(4)-H(4)	0.9800	S(2)-O(10)	1.439(4)
C(4)-C(7)	1.524(2)	S(2)-O(11)	1.463(3)
C(5)-H(5C)	0.9700	S(2)-C(18)	1.805(4)
C(5)-H(5D)	0.9700	S(2)-O(9')	1.429(5)

S(2)-O(10')	1.446(5)	C(4)-N(1)-Fe(1)	109.65(9)
S(2)-O(11')	1.429(3)	C(4)-N(1)-C(2)	104.13(12)
S(2)-C(18')	1.852(5)	C(4)-N(1)-C(6)	114.14(13)
F(4)-C(18)	1.331(4)	C(6)-N(1)-Fe(1)	111.17(10)
F(5)-C(18)	1.325(4)	C(6)-N(1)-C(2)	104.76(12)
F(6)-C(18)	1.315(4)	C(7)-N(2)-Fe(1)	117.03(11)
F(4')-C(18')	1.332(4)	C(7)-N(2)-C(11)	118.24(15)
F(5')-C(18')	1.341(4)	C(11)-N(2)-Fe(1)	124.70(12)
F(6')-C(18')	1.338(4)	C(12)-N(3)-Fe(1)	118.26(12)
O(1)-Fe(1)-N(1)	73.65(5)	C(12)-N(3)-C(16)	118.61(15)
O(1)-Fe(1)-N(2)	96.69(5)	C(16)-N(3)-Fe(1)	122.68(12)
O(4)-Fe(1)-O(1)	86.11(5)	O(1)-C(1)-H(1A)	110.3
O(4)-Fe(1)-O(5)	90.84(6)	O(1)-C(1)-H(1B)	110.3
O(4)-Fe(1)-N(1)	158.84(5)	O(1)-C(1)-C(2)	106.91(14)
O(4)-Fe(1)-N(2)	101.57(6)	H(1A)-C(1)-H(1B)	108.6
O(4)-Fe(1)-N(3)	109.16(6)	C(2)-C(1)-H(1A)	110.3
O(5)-Fe(1)-O(1)	175.67(5)	C(2)-C(1)-H(1B)	110.3
O(5)-Fe(1)-N(1)	109.70(5)	N(1)-C(2)-C(1)	111.01(13)
O(5)-Fe(1)-N(2)	86.93(5)	N(1)-C(2)-C(3)	103.43(13)
N(2)-Fe(1)-N(1)	75.35(5)	N(1)-C(2)-C(5)	102.40(13)
N(3)-Fe(1)-O(1)	89.34(5)	C(1)-C(2)-C(3)	112.63(14)
N(3)-Fe(1)-O(5)	88.76(6)	C(1)-C(2)-C(5)	114.57(15)
N(3)-Fe(1)-N(1)	77.33(5)	C(5)-C(2)-C(3)	111.74(14)
N(3)-Fe(1)-N(2)	149.02(6)	O(2)-C(3)-C(2)	105.76(14)
Fe(1)-O(1)-H(1)	128(2)	O(2)-C(3)-H(3A)	110.6
C(1)-O(1)-Fe(1)	114.10(10)	O(2)-C(3)-H(3B)	110.6
C(1)-O(1)-H(1)	112(2)	C(2)-C(3)-H(3A)	110.6
C(4)-O(2)-C(3)	104.66(13)	C(2)-C(3)-H(3B)	110.6
C(6)-O(3)-C(5)	103.27(12)	H(3A)-C(3)-H(3B)	108.7
Fe(1)-O(4)-H(4A)	131(3)	O(2)-C(4)-N(1)	106.61(13)
Fe(1)-O(4)-H(4B)	113(2)	O(2)-C(4)-H(4)	110.0
H(4A)-O(4)-H(4B)	108(3)	O(2)-C(4)-C(7)	110.06(13)
Fe(1)-O(5)-H(5A)	127(2)	N(1)-C(4)-H(4)	110.0
Fe(1)-O(5)-H(5B)	122(2)	N(1)-C(4)-C(7)	110.18(13)
H(5A)-O(5)-H(5B)	111(3)	C(7)-C(4)-H(4)	110.0
C(2)-N(1)-Fe(1)	112.77(10)	O(3)-C(5)-C(2)	103.37(14)

O(3)-C(5)-H(5C)	111.1	C(16)-C(15)-C(14)	118.45(18)
O(3)-C(5)-H(5D)	111.1	C(16)-C(15)-H(15)	120.8
C(2)-C(5)-H(5C)	111.1	N(3)-C(16)-C(15)	122.69(17)
C(2)-C(5)-H(5D)	111.1	N(3)-C(16)-H(16)	118.7
H(5C)-C(5)-H(5D)	109.1	C(15)-C(16)-H(16)	118.7
O(3)-C(6)-N(1)	106.75(13)	O(6)-S(1)-O(7)	114.39(10)
O(3)-C(6)-H(6)	109.6	O(6)-S(1)-C(17)	100.5(2)
O(3)-C(6)-C(12)	110.31(14)	O(6)-S(1)-C(17')	104.4(3)
N(1)-C(6)-H(6)	109.6	O(7)-S(1)-C(17)	100.1(4)
N(1)-C(6)-C(12)	110.89(13)	O(7)-S(1)-C(17')	106.8(4)
C(12)-C(6)-H(6)	109.6	O(8)-S(1)-O(6)	115.37(10)
N(2)-C(7)-C(4)	117.54(14)	O(8)-S(1)-O(7)	115.29(10)
N(2)-C(7)-C(8)	122.52(16)	O(8)-S(1)-C(17)	108.5(5)
C(8)-C(7)-C(4)	119.92(15)	O(8)-S(1)-C(17')	98.0(4)
C(7)-C(8)-H(8)	120.6	F(1)-C(17)-S(1)	113.7(5)
C(9)-C(8)-C(7)	118.77(17)	F(1)-C(17)-F(2)	107.8(7)
C(9)-C(8)-H(8)	120.6	F(1)-C(17)-F(3)	107.5(5)
C(8)-C(9)-H(9)	120.4	F(2)-C(17)-S(1)	106.1(10)
C(8)-C(9)-C(10)	119.19(17)	F(3)-C(17)-S(1)	114.3(6)
C(10)-C(9)-H(9)	120.4	F(3)-C(17)-F(2)	107.0(7)
C(9)-C(10)-H(10)	120.8	F(1')-C(17')-S(1)	107.8(5)
C(11)-C(10)-C(9)	118.43(17)	F(1')-C(17')-F(2')	108.7(8)
C(11)-C(10)-H(10)	120.8	F(2')-C(17')-S(1)	115.1(11)
N(2)-C(11)-C(10)	122.84(17)	F(3')-C(17')-S(1)	107.7(7)
N(2)-C(11)-H(11)	118.6	F(3')-C(17')-F(1')	108.2(7)
C(10)-C(11)-H(11)	118.6	F(3')-C(17')-F(2')	109.1(8)
N(3)-C(12)-C(6)	117.97(15)	O(9)-S(2)-O(10)	115.4(5)
N(3)-C(12)-C(13)	121.91(16)	O(9)-S(2)-O(11)	113.8(4)
C(13)-C(12)-C(6)	120.06(15)	O(9)-S(2)-C(18)	105.5(6)
C(12)-C(13)-H(13)	120.5	O(10)-S(2)-O(11)	112.6(3)
C(14)-C(13)-C(12)	118.95(17)	O(10)-S(2)-C(18)	105.7(3)
C(14)-C(13)-H(13)	120.5	O(11)-S(2)-C(18)	102.36(19)
C(13)-C(14)-H(14)	120.4	O(9')-S(2)-O(10')	116.6(6)
C(13)-C(14)-C(15)	119.27(17)	O(9')-S(2)-O(11')	116.7(5)
C(15)-C(14)-H(14)	120.4	O(9')-S(2)-C(18')	102.7(6)
C(14)-C(15)-H(15)	120.8	O(10')-S(2)-C(18')	100.7(2)

O(11')-S(2)-O(10')	114.6(4)	F(6)-C(18)-F(5)	107.8(4)
O(11')-S(2)-C(18')	101.9(2)	F(4')-C(18')-S(2)	111.8(3)
F(4)-C(18)-S(2)	110.4(2)	F(4')-C(18')-F(5')	107.4(3)
F(5)-C(18)-S(2)	111.8(3)	F(4')-C(18')-F(6')	107.2(3)
F(5)-C(18)-F(4)	108.5(3)	F(5')-C(18')-S(2)	111.7(3)
F(6)-C(18)-S(2)	109.9(3)	F(6')-C(18')-S(2)	111.2(3)
F(6)-C(18)-F(4)	108.4(3)	F(6')-C(18')-F(5')	107.3(4)

Table S24. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **C**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	10(1)	14(1)	16(1)	1(1)	4(1)	1(1)
O1	16(1)	14(1)	33(1)	6(1)	8(1)	3(1)
O2	10(1)	21(1)	28(1)	0(1)	4(1)	3(1)
O3	17(1)	25(1)	26(1)	-6(1)	10(1)	-2(1)
O4	16(1)	16(1)	36(1)	-3(1)	10(1)	0(1)
O5	15(1)	24(1)	30(1)	8(1)	3(1)	-4(1)
N1	10(1)	12(1)	19(1)	0(1)	4(1)	0(1)
N2	13(1)	16(1)	19(1)	2(1)	4(1)	-1(1)
N3	14(1)	18(1)	19(1)	1(1)	2(1)	-1(1)
C1	15(1)	14(1)	33(1)	0(1)	10(1)	-2(1)
C2	11(1)	15(1)	24(1)	-1(1)	7(1)	-2(1)
C3	12(1)	21(1)	29(1)	-4(1)	5(1)	-2(1)
C4	10(1)	16(1)	21(1)	2(1)	1(1)	2(1)
C5	18(1)	23(1)	26(1)	-1(1)	10(1)	-4(1)
C6	15(1)	16(1)	21(1)	-3(1)	6(1)	1(1)
C7	14(1)	15(1)	20(1)	3(1)	3(1)	-1(1)
C8	16(1)	22(1)	24(1)	3(1)	1(1)	1(1)
C9	21(1)	32(1)	21(1)	3(1)	0(1)	-4(1)
C10	23(1)	31(1)	17(1)	0(1)	5(1)	-2(1)
C11	18(1)	23(1)	21(1)	0(1)	7(1)	1(1)
C12	16(1)	14(1)	21(1)	0(1)	5(1)	-2(1)
C13	23(1)	22(1)	21(1)	-2(1)	5(1)	-1(1)
C14	32(1)	27(1)	18(1)	-1(1)	1(1)	-2(1)
C15	23(1)	28(1)	25(1)	2(1)	-4(1)	0(1)
C16	17(1)	24(1)	23(1)	1(1)	0(1)	2(1)
S1	15(1)	16(1)	31(1)	0(1)	4(1)	0(1)
O6	28(1)	28(1)	36(1)	-1(1)	3(1)	-12(1)
O7	33(1)	24(1)	39(1)	-2(1)	-1(1)	11(1)
O8	35(1)	32(1)	56(1)	11(1)	24(1)	4(1)
F1	48(3)	38(2)	80(6)	-1(2)	-28(4)	-16(2)
F2	42(4)	35(3)	77(4)	13(2)	-2(3)	27(2)

F3	52(4)	56(3)	30(2)	4(2)	-1(2)	3(2)
C17	17(3)	18(2)	56(4)	-5(2)	-1(3)	4(2)
F1'	27(3)	39(2)	55(5)	1(2)	-18(2)	-9(2)
F2'	31(3)	28(3)	54(4)	7(3)	-3(3)	19(3)
F3'	50(5)	74(6)	23(2)	-4(3)	8(3)	8(4)
C17'	15(3)	27(4)	29(3)	2(2)	0(2)	6(2)
S2	12(1)	18(1)	20(1)	1(1)	3(1)	1(1)
F4	16(1)	60(2)	30(1)	-5(1)	1(1)	-8(1)
F5	27(1)	87(2)	24(1)	13(1)	3(1)	-7(1)
F6	36(2)	71(3)	60(3)	-41(2)	7(2)	2(2)
O9	12(2)	28(5)	26(3)	0(3)	4(1)	1(2)
O10	17(2)	18(2)	38(3)	11(2)	1(2)	1(2)
O11	20(1)	20(1)	35(2)	0(1)	12(1)	-2(1)
C18	16(2)	42(2)	28(2)	-5(2)	2(1)	1(2)
F4'	33(1)	53(2)	32(1)	-8(1)	5(1)	-26(1)
F5'	38(2)	57(2)	17(1)	-1(1)	8(1)	-17(2)
F6'	47(2)	28(1)	37(1)	-8(1)	10(1)	7(1)
O9'	15(2)	21(4)	30(2)	-9(3)	4(2)	-5(2)
O10'	22(2)	21(2)	22(2)	2(2)	4(2)	1(2)
O11'	21(2)	25(2)	34(2)	11(1)	13(1)	7(1)
C18'	26(2)	35(2)	19(2)	-3(2)	8(2)	-12(2)

Table S25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **C**.

	x	y	z	U(eq)
H1	2570(20)	2800(30)	7564(14)	41(8)
H4A	4760(30)	4070(40)	6845(17)	66(10)
H4B	3970(20)	3170(40)	6852(15)	49(8)
H5A	4700(30)	7170(30)	7012(15)	53(9)
H5B	3790(20)	7810(30)	6724(14)	40(7)
H1A	963	2857	7441	24
H1B	1146	3522	6769	24
H3A	-208	4958	6587	25
H3B	-654	5478	7206	25
H4	1386	8041	6860	19
H5C	147	4845	8248	26
H5D	1328	4597	8460	26
H6	1796	8020	7945	21
H8	161	7241	5564	25
H9	577	6339	4592	30
H10	2032	4946	4656	28
H11	3039	4560	5678	24
H13	2375	7126	9343	26
H14	3943	6635	10000	31
H15	5270	5860	9497	31
H16	4955	5435	8373	26

Table S26. Torsion angles [°] for **C**.

Fe1-O1-C1-C2	-52.86(16)	C2-N1-C6-C12	101.44(15)
Fe1-N1-C2-C1	-9.73(17)	C3-O2-C4-N1	-41.04(16)
Fe1-N1-C2-C3	-130.76(11)	C3-O2-C4-C7	78.44(16)
Fe1-N1-C2-C5	112.98(12)	C3-C2-C5-O3	-78.27(16)
Fe1-N1-C4-O2	153.45(10)	C4-O2-C3-C2	31.98(16)
Fe1-N1-C4-C7	34.04(15)	C4-N1-C2-C1	109.06(15)
Fe1-N1-C6-O3	-140.84(11)	C4-N1-C2-C3	-11.96(16)
Fe1-N1-C6-C12	-20.65(16)	C4-N1-C2-C5	-128.22(14)
Fe1-N2-C7-C4	-0.52(19)	C4-N1-C6-O3	94.51(16)
Fe1-N2-C7-C8	178.09(13)	C4-N1-C6-C12	-145.31(14)
Fe1-N2-C11-C10	-177.72(14)	C4-C7-C8-C9	177.91(16)
Fe1-N3-C12-C6	-14.1(2)	C5-O3-C6-N1	39.91(17)
Fe1-N3-C12-C13	168.84(13)	C5-O3-C6-C12	-80.66(16)
Fe1-N3-C16-C15	-170.62(15)	C5-C2-C3-O2	97.63(16)
O1-C1-C2-N1	38.33(18)	C6-O3-C5-C2	-44.41(16)
O1-C1-C2-C3	153.77(14)	C6-N1-C2-C1	-130.77(15)
O1-C1-C2-C5	-77.04(17)	C6-N1-C2-C3	108.21(14)
O2-C4-C7-N2	-140.80(15)	C6-N1-C2-C5	-8.05(16)
O2-C4-C7-C8	40.6(2)	C6-N1-C4-O2	-81.09(16)
O3-C6-C12-N3	141.49(15)	C6-N1-C4-C7	159.50(13)
O3-C6-C12-C13	-41.4(2)	C6-C12-C13-C14	-174.51(17)
N1-C2-C3-O2	-11.82(17)	C7-N2-C11-C10	0.2(3)
N1-C2-C5-O3	31.83(16)	C7-C8-C9-C10	1.1(3)
N1-C4-C7-N2	-23.5(2)	C8-C9-C10-C11	-0.9(3)
N1-C4-C7-C8	157.84(15)	C9-C10-C11-N2	0.2(3)
N1-C6-C12-N3	23.4(2)	C11-N2-C7-C4	-178.61(15)
N1-C6-C12-C13	-159.42(16)	C11-N2-C7-C8	0.0(2)
N2-C7-C8-C9	-0.7(3)	C12-N3-C16-C15	1.5(3)
N3-C12-C13-C14	2.5(3)	C12-C13-C14-C15	0.8(3)
C1-C2-C3-O2	-131.74(14)	C13-C14-C15-C16	-2.8(3)
C1-C2-C5-O3	152.10(14)	C14-C15-C16-N3	1.7(3)
C2-N1-C4-O2	32.54(16)	C16-N3-C12-C6	173.46(15)
C2-N1-C4-C7	-86.87(15)	C16-N3-C12-C13	-3.6(3)
C2-N1-C6-O3	-18.74(17)	O6-S1-C17-F1	174.5(6)

O6-S1-C17-F2	-67.2(8)	O9-S2-C18-F5	61.5(5)
O6-S1-C17-F3	50.5(8)	O9-S2-C18-F6	-58.1(5)
O6-S1-C17'-F1'	-173.2(7)	O10-S2-C18-F4	-54.9(4)
O6-S1-C17'-F2'	-51.7(10)	O10-S2-C18-F5	-175.8(4)
O6-S1-C17'-F3'	70.2(10)	O10-S2-C18-F6	64.6(5)
O7-S1-C17-F1	57.1(6)	O11-S2-C18-F4	63.1(3)
O7-S1-C17-F2	175.4(7)	O11-S2-C18-F5	-57.8(3)
O7-S1-C17-F3	-66.9(7)	O11-S2-C18-F6	-177.4(3)
O7-S1-C17'-F1'	65.3(7)	O9'-S2-C18'-F4'	-175.0(6)
O7-S1-C17'-F2'	-173.3(9)	O9'-S2-C18'-F5'	64.6(7)
O7-S1-C17'-F3'	-51.3(9)	O9'-S2-C18'-F6'	-55.2(6)
O8-S1-C17-F1	-64.1(7)	O10'-S2-C18'-F4'	-54.3(5)
O8-S1-C17-F2	54.3(7)	O10'-S2-C18'-F5'	-174.7(4)
O8-S1-C17-F3	172.0(6)	O10'-S2-C18'-F6'	65.4(4)
O8-S1-C17'-F1'	-54.3(8)	O11'-S2-C18'-F4'	63.8(3)
O8-S1-C17'-F2'	67.1(9)	O11'-S2-C18'-F5'	-56.5(3)
O8-S1-C17'-F3'	-170.9(9)	O11'-S2-C18'-F6'	-176.4(2)
O9-S2-C18-F4	-177.6(5)		

Table S27. Hydrogen bonds and close contacts for **C** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1...O10	0.81(3)	2.05(3)	2.728(7)	140(3)
O1-H1...O10'	0.81(3)	2.05(3)	2.782(8)	150(3)
O4-H4A...O11#1	0.84(4)	1.82(4)	2.649(3)	169(3)
O4-H4A...O11'#1	0.84(4)	1.90(4)	2.722(3)	164(3)
O4-H4B...O6	0.84(3)	1.89(3)	2.713(2)	165(3)
O5-H5A...O10#1	0.85(3)	2.06(3)	2.871(8)	158(3)
O5-H5A...O10'#1	0.85(3)	2.19(3)	2.992(8)	156(3)
O5-H5B...O7#2	0.84(3)	1.94(3)	2.766(2)	170(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z+3/2 #2 x,y+1,z

REFERENCE NUMBER: jonon96

CRYSTAL STRUCTURE REPORT

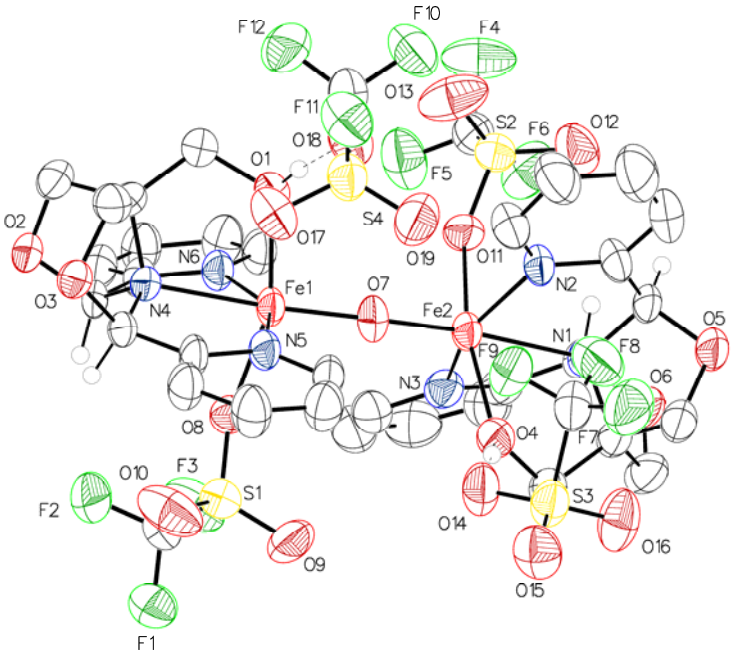
C36 H30 F12 Fe2 N6 O19 S4

D

Report prepared for:

Olaf Nachtigall

January 14, 2021



William W. Brennessel

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120 Trustee Road

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Data collection

A crystal (0.105 x 0.059 x 0.044 mm^3) was placed onto a thin glass optical fiber or a nylon loop and mounted on a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.00(10) K. A preliminary set of cell constants and an orientation matrix were calculated from a small sampling of reflections.[1] A short pre-experiment was run, from which an optimal data collection strategy was determined. The full data collection was carried out using a PhotonJet (Cu) X-ray source with frame times of 6.14 and 24.57 seconds and a detector distance of 31.2 mm. Series of frames were collected in 0.50º steps in ω at different 2θ, κ, and ϕ settings. After the intensity data were corrected for absorption, the final cell constants were calculated from the xyz centroids of 9515 strong reflections from the actual data collection after integration.[1] See Table S28 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT[2] and refined using SHELXL.[3] The space group *P*-1 was determined based on intensity statistics. Most or all non-hydrogen atoms were assigned from the solution. Full-matrix least squares / difference Fourier cycles were performed which located any remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

The intensity data were scaled and reduced[1] according to non-merohedral twin law [-1 0 0 / 0.194 0.108 -0.894 / -0193 -1.108 -0.108], a 180 degree rotation around reciprocal lattice [0 -0.71 0.71]. There were 7843 unique isolated reflections in the first component, 7746 unique isolated reflections in the second component, and 3299 unique overlapping reflections. The mass ratio of components refined to 0.607(2):0.393(2).

The final full matrix least squares refinement converged to $R1 = 0.1074$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.3316$ (F^2, all data).

Structure description

The structure is the one suggested. The asymmetric unit contains two metal centers, each coordinated by one tetradentate ligand and one triflato ligand, bridged by an oxo ligand and two triflate anions. Both triflato ligands were modeled as disordered over two positions each: S1, 0.89:0.11 and S2, 0.70:0.30. The CF_3 portion of triflate anion S3 is modeled as disordered over two positions (0.65:0.35). Triflate anion S4 is modeled as disordered over two positions (0.73:0.27).

Structure manipulation and figure generation were performed using Olex2.[4] Unless noted otherwise all structural diagrams containing anisotropic displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B04 Hutchison Hall, Department of Chemistry, University of Rochester. The instrument was purchased with funding from NSF MRI program grant CHE-1725028. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

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[1] *CrysAlisPro*, version 171.41.84a; Rigaku Corporation: Oxford, UK, 2020.

[2] Sheldrick, G. M. *SHELXT*, version 2018/2; *Acta. Crystallogr.* **2015**, *A71*, 3-8.

[3] Sheldrick, G. M. *SHELXL*, version 2018/3; *Acta. Crystallogr.* **2015**, *C71*, 3-8.

[4] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Olex2*, version 1.3-ac4; *J. Appl. Cryst.* **2009**, *42*, 339-341.

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o{}^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

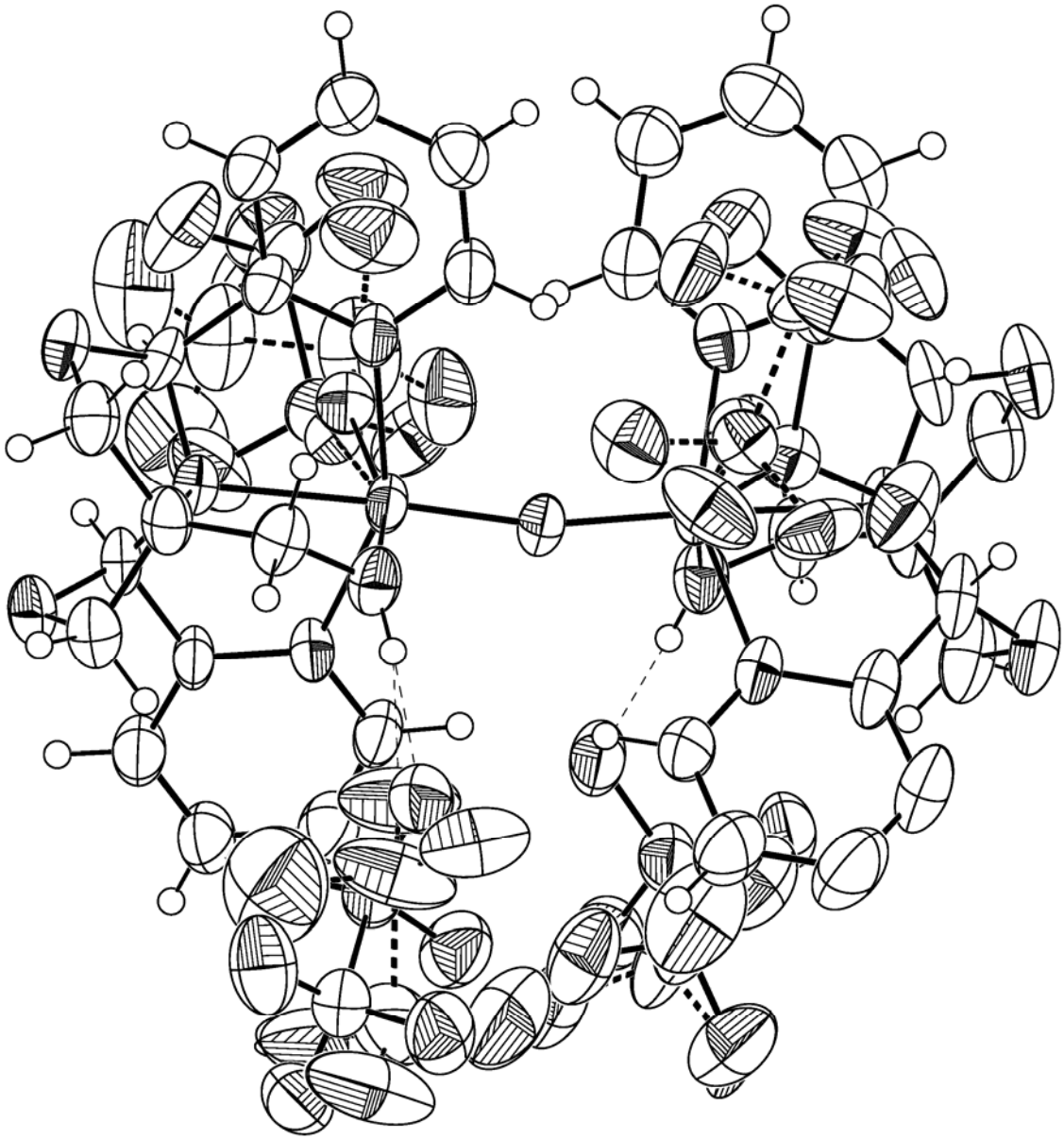
$$wR2 = [\Sigma[w(F_o^2 - F_c{}^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

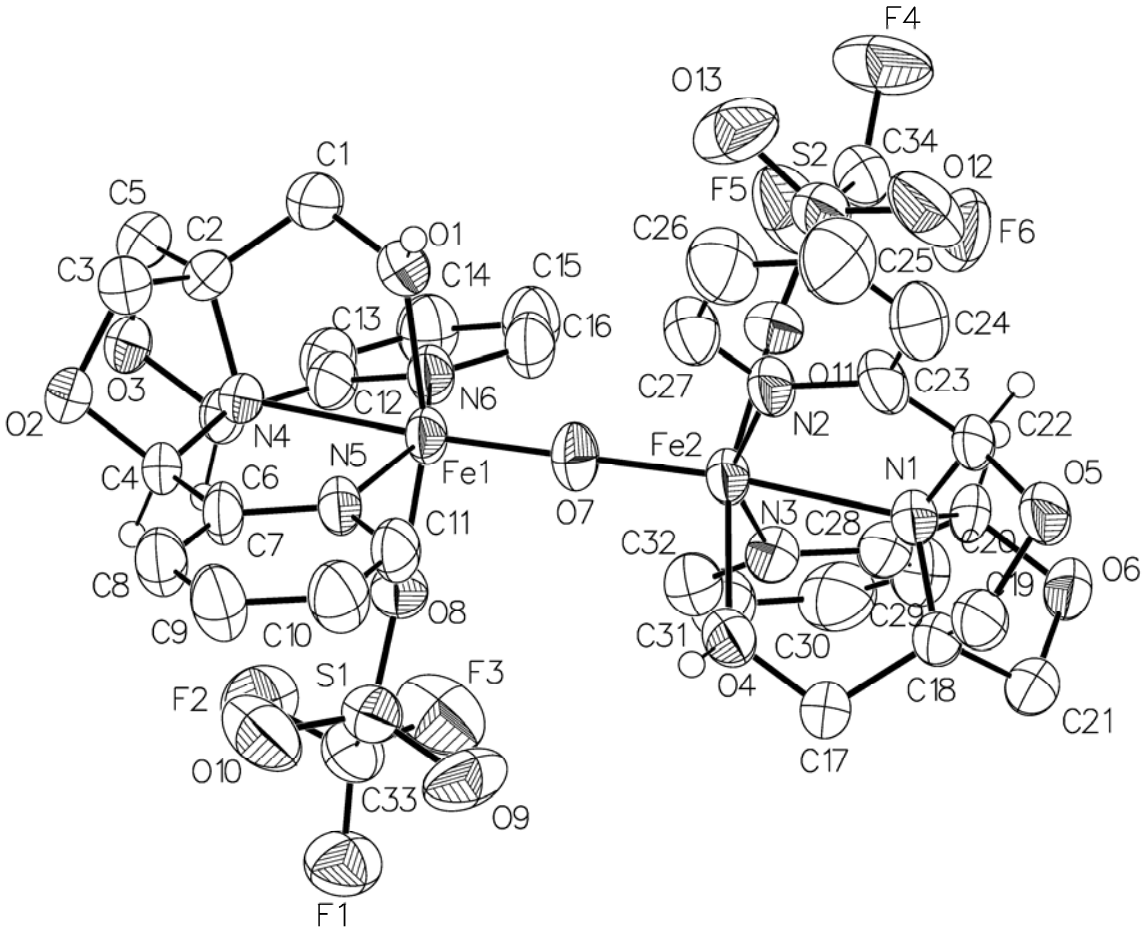
where $w = 1 \,/\, [\sigma^2 (F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \text{ max } (0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma[w(F_o^2 - F_c{}^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters

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S2
C34
O12
F5
F6
C1
C5
C2
O1
C26
C25
C3
C14
C15
C24
C13
C16
C27
O11
C23
O3
C12
N6
C22
O2
N4
N5
Fe1
O7
Fe2
N2
N1
O5
C4
C6
C11
N3
C28
C7
C32
C29
O6
C8
O8
C19
C9
C10
C31
C30
S1
F3
O4
C18
C21
F2
C17
O10
C33
O9
F1

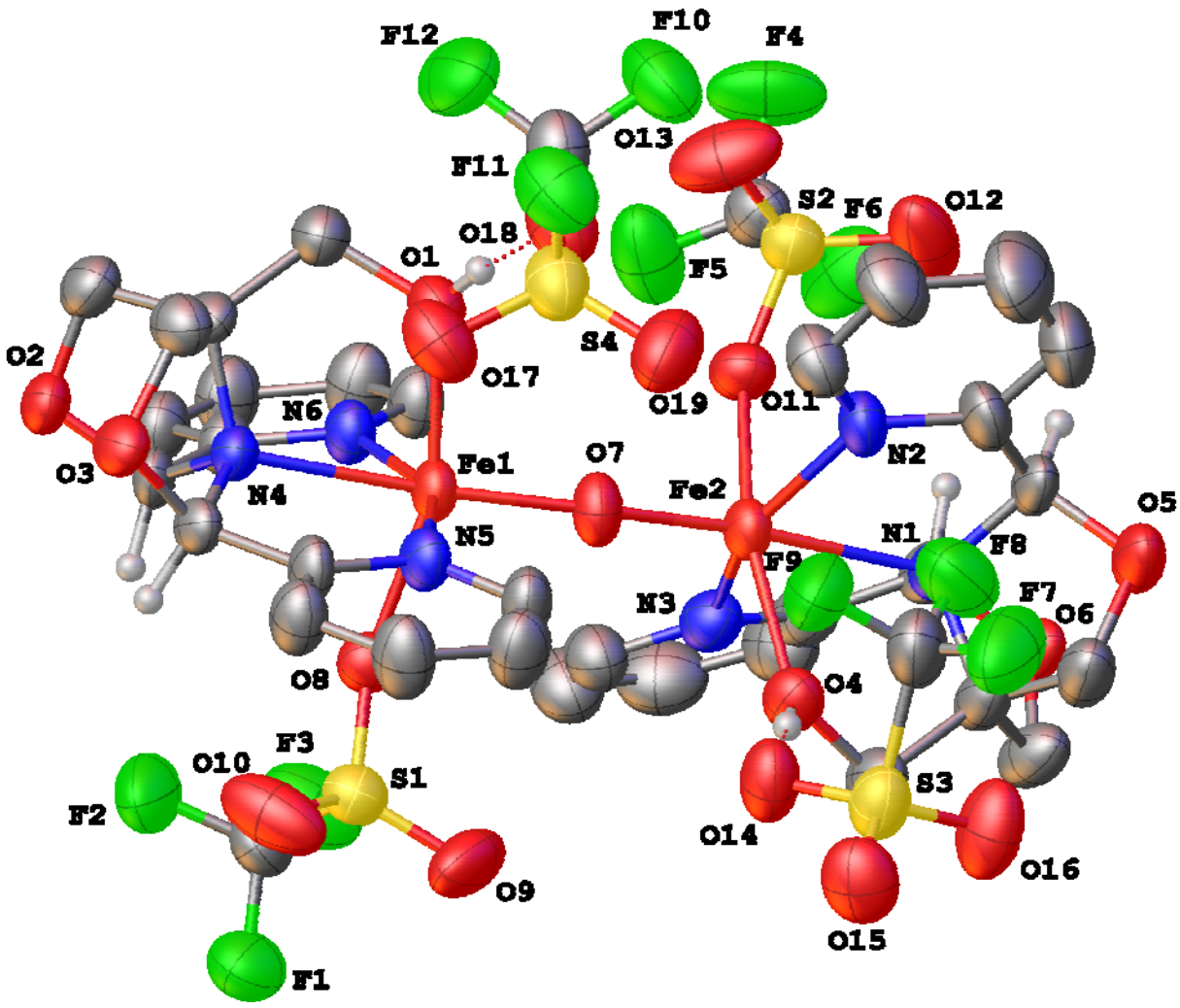
F12
F10
F4
O13
F11
S2
F6
O12
O18
O1
F5
S4
O2
O17
O19
O11
N6
N2
O3
Fe1
O7
Fe2
O5
N4
N5
N1
F8
F9
F7
O6
N3
O8
O4
F3
O10
S1
S3
F2
O14
O16
O9
O15
F1

Table S28. Crystal data and structure refinement for **D**.

Identification code	jonon96	
Empirical formula	C36 H30 F12 Fe2 N6 O19 S4	
Formula weight	1318.60	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 13.3866(5) Å	α = 97.802(4)°
	b = 13.6776(9) Å	β = 97.381(3)°
	c = 14.4554(5) Å	γ = 106.208(5)°
Volume	2479.2(2) Å^3	
Z	2	
Density (calculated)	1.766 Mg/m^3	
Absorption coefficient	7.416 mm^{-1}	
F(000)	1328	
Crystal color, morphology	red, block	
Crystal size	0.105 x 0.059 x 0.044 mm^3	
Theta range for data collection	3.134 to 78.878°	
Index ranges	$-16 \le h \le 16$, $-15 \le k \le 17$, $-18 \le l \le 16$	
Reflections collected	18888	
Independent reflections	18888 [R(int) = ?]	
Observed reflections	12885	
Completeness to theta = 74.504°	99.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00000 and 0.70803	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18888 / 764 / 969	
Goodness-of-fit on F^2	1.287	
Final R indices [I>2sigma(I)]	R1 = 0.1074, wR2 = 0.2853	
R indices (all data)	R1 = 0.1483, wR2 = 0.3316	
Largest diff. peak and hole	1.181 and -1.133 e.Å^{-3}	

Table S29. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **D**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Fe1	3005(1)	6734(1)	1544(1)	39(1)
Fe2	2166(1)	8493(1)	3066(1)	42(1)
S1	5613(2)	7998(2)	2213(2)	51(1)
F1	7275(7)	9322(6)	1821(7)	74(2)
F2	6312(6)	8238(7)	628(5)	91(3)
F3	5804(6)	9470(6)	1210(7)	90(2)
O8	4543(5)	7694(6)	1647(6)	46(2)
O9	5730(9)	8645(8)	3080(5)	80(3)
O10	6069(7)	7189(7)	2190(9)	95(3)
C33	6292(6)	8799(7)	1437(6)	59(2)
S1A	5465(18)	8510(20)	2030(20)	102(9)
F1A	7400(60)	9070(40)	2040(40)	71(15)
F2A	6670(50)	7810(50)	910(40)	120(18)
F3A	6910(60)	7540(50)	2320(60)	135(17)
O8A	4627(14)	7500(30)	1830(40)	33(10)
O9A	5660(80)	9000(50)	2970(30)	84(17)
O10A	5400(60)	9080(50)	1310(40)	99(16)
C33A	6650(30)	8180(40)	1800(40)	93(14)
O1	1596(4)	5559(4)	1028(4)	48(1)
O2	3828(4)	4103(4)	453(4)	48(1)
O3	3723(4)	5515(4)	-1079(4)	48(1)
O4	3318(4)	8829(5)	4266(4)	52(1)
O5	991(5)	9716(6)	5349(5)	70(2)
O6	2054(6)	11487(5)	4245(5)	69(2)
O7	2563(5)	7521(4)	2396(4)	49(1)
N1	1799(5)	9709(5)	4010(5)	50(2)
N2	973(5)	7605(5)	3685(5)	48(1)
N3	2964(5)	9900(5)	2643(5)	49(1)
N4	3446(4)	5664(4)	474(4)	38(1)
N5	3602(5)	5825(5)	2381(4)	43(1)
N6	2832(5)	7333(5)	280(4)	44(1)

C1	1479(6)	5008(7)	79(6)	52(2)
C2	2516(6)	4811(6)	-99(5)	45(2)
C3	2689(6)	3858(6)	250(7)	52(2)
C4	4155(5)	5140(5)	940(5)	40(2)
C5	2683(7)	4827(7)	-1130(6)	54(2)
C6	3905(6)	6244(6)	-239(5)	42(2)
C7	4089(6)	5184(6)	1977(5)	44(2)
C8	4526(7)	4589(7)	2497(6)	56(2)
C9	4465(9)	4642(9)	3450(7)	67(2)
C10	3981(9)	5322(9)	3859(7)	66(2)
C11	3575(7)	5901(7)	3318(5)	50(2)
C12	3358(6)	7068(6)	-392(5)	44(2)
C13	3435(7)	7526(7)	-1177(6)	52(2)
C14	2948(8)	8269(8)	-1288(6)	60(2)
C15	2395(8)	8549(8)	-596(6)	61(2)
C16	2346(7)	8068(7)	174(6)	52(2)
C17	3608(7)	9838(7)	4811(6)	55(2)
C18	2626(7)	10184(7)	4893(6)	58(2)
C19	2063(8)	9736(10)	5677(7)	70(3)
C20	798(6)	9293(7)	4392(6)	54(2)
C21	2838(8)	11365(8)	4973(7)	67(3)
C22	1797(7)	10597(6)	3518(6)	57(2)
C23	473(7)	8103(8)	4235(6)	59(2)
C24	-348(9)	7573(10)	4640(8)	80(3)
C25	-681(11)	6494(11)	4448(10)	94(4)
C26	-161(9)	5986(10)	3877(9)	80(3)
C27	672(7)	6565(7)	3516(7)	56(2)
C28	2581(7)	10693(6)	2853(6)	55(2)
C29	2860(9)	11567(8)	2410(8)	70(3)
C30	3526(10)	11584(8)	1767(9)	78(3)
C31	3938(8)	10787(7)	1569(8)	69(2)
C32	3650(7)	9955(7)	2037(7)	58(2)
S2	-197(4)	8210(4)	1765(4)	50(1)
F4	-1288(10)	8726(15)	379(14)	96(6)
F5	361(11)	9150(13)	318(10)	90(4)
F6	-210(12)	9945(8)	1398(8)	89(4)

O11	960(7)	8536(10)	2032(9)	52(2)
O12	-709(9)	8535(14)	2479(7)	89(4)
O13	-613(12)	7182(7)	1288(10)	92(5)
C34	-333(10)	9025(9)	901(8)	57(3)
S2A	-43(10)	8039(9)	1477(10)	52(3)
F4A	-1258(16)	8940(30)	490(30)	64(7)
F5A	300(20)	9950(18)	1090(20)	89(8)
F6A	100(30)	8560(30)	110(20)	98(10)
O11A	959(15)	8640(20)	2100(20)	52(2)
O12A	-883(16)	7730(20)	1970(20)	78(8)
O13A	60(30)	7259(17)	794(17)	81(8)
C34A	-279(19)	8982(16)	796(17)	58(6)
S3	3852(2)	7562(2)	6169(2)	57(1)
O14	4061(6)	7630(6)	5224(4)	66(2)
O15	4534(6)	7154(6)	6725(5)	74(2)
O16	3648(8)	8452(6)	6641(5)	80(2)
F7	2270(20)	6350(20)	6745(13)	101(7)
F8	1851(12)	7050(20)	5584(13)	97(6)
F9	2492(16)	5797(17)	5359(14)	91(5)
C35	2553(13)	6637(13)	5959(11)	77(4)
F7A	2330(30)	6360(30)	6840(18)	73(8)
F8A	1860(30)	6470(50)	5420(20)	123(11)
F9A	2860(40)	5570(20)	5710(40)	101(12)
C35A	2690(20)	6450(20)	6030(20)	82(8)
S4	1057(3)	3813(2)	2644(2)	59(1)
F10	-844(7)	2682(8)	2718(7)	85(3)
F11	395(7)	1985(6)	3025(6)	78(2)
F12	-153(8)	2074(8)	1591(7)	90(3)
O17	1924(7)	3556(8)	2318(7)	73(3)
O18	565(8)	4359(8)	2030(7)	69(3)
O19	1183(9)	4229(8)	3623(6)	78(3)
C36	54(9)	2570(10)	2475(6)	62(3)
S4A	196(11)	3629(10)	2098(11)	111(6)
F10A	1140(20)	2810(30)	3340(30)	210(20)
F11A	-560(30)	2070(30)	2800(30)	154(12)
F12A	10(40)	3670(30)	3620(30)	200(20)

O17A	-755(16)	3860(20)	1790(20)	102(10)
O18A	1140(19)	4490(20)	2280(30)	109(12)
O19A	300(30)	2770(30)	1460(40)	168(16)
C36A	220(20)	2930(20)	3060(20)	106(8)

Table S30. Bond lengths [Å] and angles [°] for **D**.

Fe(1)-O(8)	2.084(6)	O(4)-H(4)	0.8550
Fe(1)-O(8A)	2.089(14)	O(4)-C(17)	1.415(10)
Fe(1)-O(1)	2.079(5)	O(5)-C(19)	1.443(11)
Fe(1)-O(7)	1.791(5)	O(5)-C(20)	1.386(9)
Fe(1)-N(4)	2.233(5)	O(6)-C(21)	1.449(11)
Fe(1)-N(5)	2.089(6)	O(6)-C(22)	1.425(9)
Fe(1)-N(6)	2.114(6)	N(1)-C(18)	1.512(10)
Fe(2)-O(4)	2.074(6)	N(1)-C(20)	1.508(11)
Fe(2)-O(7)	1.779(5)	N(1)-C(22)	1.489(12)
Fe(2)-N(1)	2.210(6)	N(2)-C(23)	1.337(9)
Fe(2)-N(2)	2.100(7)	N(2)-C(27)	1.344(11)
Fe(2)-N(3)	2.135(7)	N(3)-C(28)	1.339(10)
Fe(2)-O(11)	2.074(7)	N(3)-C(32)	1.342(11)
Fe(2)-O(11A)	2.072(12)	N(4)-C(2)	1.502(9)
S(1)-O(8)	1.473(7)	N(4)-C(4)	1.489(9)
S(1)-O(9)	1.396(7)	N(4)-C(6)	1.477(9)
S(1)-O(10)	1.403(8)	N(5)-C(7)	1.347(8)
S(1)-C(33)	1.824(10)	N(5)-C(11)	1.351(10)
F(1)-C(33)	1.315(9)	N(6)-C(12)	1.339(9)
F(2)-C(33)	1.317(8)	N(6)-C(16)	1.355(10)
F(3)-C(33)	1.319(9)	C(1)-H(1A)	0.9700
S(1A)-O(8A)	1.479(15)	C(1)-H(1B)	0.9700
S(1A)-O(9A)	1.396(13)	C(1)-C(2)	1.533(10)
S(1A)-O(10A)	1.397(13)	C(2)-C(3)	1.525(12)
S(1A)-C(33A)	1.819(17)	C(2)-C(5)	1.537(12)
F(1A)-C(33A)	1.316(13)	C(3)-H(3A)	0.9700
F(2A)-C(33A)	1.314(12)	C(3)-H(3B)	0.9700
F(3A)-C(33A)	1.316(13)	C(4)-H(4A)	0.9800
O(1)-H(1)	0.8593	C(4)-C(7)	1.507(10)
O(1)-C(1)	1.439(9)	C(5)-H(5A)	0.9700
O(2)-C(3)	1.448(9)	C(5)-H(5B)	0.9700
O(2)-C(4)	1.416(8)	C(6)-H(6)	0.9800
O(3)-C(5)	1.433(10)	C(6)-C(12)	1.531(10)
O(3)-C(6)	1.410(8)	C(7)-C(8)	1.374(11)

C(8)-H(8)	0.9300	C(30)-C(31)	1.366(15)
C(8)-C(9)	1.382(13)	C(31)-H(31)	0.9300
C(9)-H(9)	0.9300	C(31)-C(32)	1.391(14)
C(9)-C(10)	1.386(12)	C(32)-H(32)	0.9300
C(10)-H(10)	0.9300	S(2)-O(11)	1.470(9)
C(10)-C(11)	1.355(13)	S(2)-O(12)	1.400(9)
C(11)-H(11)	0.9300	S(2)-O(13)	1.401(9)
C(12)-C(13)	1.371(11)	S(2)-C(34)	1.808(11)
C(13)-H(13)	0.9300	F(4)-C(34)	1.321(9)
C(13)-C(14)	1.367(12)	F(5)-C(34)	1.325(10)
C(14)-H(14)	0.9300	F(6)-C(34)	1.317(9)
C(14)-C(15)	1.392(12)	S(2A)-O(11A)	1.467(12)
C(15)-H(15)	0.9300	S(2A)-O(12A)	1.401(11)
C(15)-C(16)	1.367(12)	S(2A)-O(13A)	1.402(12)
C(16)-H(16)	0.9300	S(2A)-C(34A)	1.796(14)
C(17)-H(17A)	0.9700	F(4A)-C(34A)	1.310(11)
C(17)-H(17B)	0.9700	F(5A)-C(34A)	1.311(11)
C(17)-C(18)	1.529(10)	F(6A)-C(34A)	1.314(11)
C(18)-C(19)	1.543(15)	S(3)-O(14)	1.439(7)
C(18)-C(21)	1.547(14)	S(3)-O(15)	1.418(7)
C(19)-H(19A)	0.9700	S(3)-O(16)	1.425(7)
C(19)-H(19B)	0.9700	S(3)-C(35)	1.802(16)
C(20)-H(20)	0.9800	S(3)-C(35A)	1.813(18)
C(20)-C(23)	1.539(14)	F(7)-C(35)	1.320(11)
C(22)-H(22)	0.9800	F(8)-C(35)	1.322(11)
C(22)-C(28)	1.503(13)	F(9)-C(35)	1.318(11)
C(23)-C(24)	1.384(14)	F(7A)-C(35A)	1.329(12)
C(24)-C(25)	1.394(18)	F(8A)-C(35A)	1.330(12)
C(25)-C(26)	1.382(16)	F(9A)-C(35A)	1.327(12)
C(26)-H(26)	0.9300	S(4)-O(17)	1.420(8)
C(26)-C(27)	1.382(13)	S(4)-O(18)	1.445(8)
C(27)-H(27)	0.9300	S(4)-O(19)	1.422(8)
C(28)-C(29)	1.414(15)	S(4)-C(36)	1.811(14)
C(29)-H(29)	0.9300	F(10)-C(36)	1.338(10)
C(29)-C(30)	1.366(17)	F(11)-C(36)	1.329(10)
C(30)-H(30)	0.9300	F(12)-C(36)	1.319(10)

S(4A)-O(17A)	1.429(11)	O(7)-Fe(2)-O(11A)	101.5(10)
S(4A)-O(18A)	1.435(11)	N(2)-Fe(2)-N(1)	78.6(3)
S(4A)-O(19A)	1.446(12)	N(2)-Fe(2)-N(3)	151.9(3)
S(4A)-C(36A)	1.792(19)	N(3)-Fe(2)-N(1)	75.7(3)
F(10A)-C(36A)	1.306(12)	O(11)-Fe(2)-N(1)	88.5(5)
F(11A)-C(36A)	1.310(12)	O(11)-Fe(2)-N(2)	86.4(4)
F(12A)-C(36A)	1.314(12)	O(11)-Fe(2)-N(3)	81.9(4)
O(8)-Fe(1)-N(4)	85.2(3)	O(11A)-Fe(2)-O(4)	159.9(9)
O(8)-Fe(1)-N(5)	88.8(3)	O(11A)-Fe(2)-N(1)	84.2(10)
O(8)-Fe(1)-N(6)	80.4(3)	O(11A)-Fe(2)-N(2)	86.5(8)
O(8A)-Fe(1)-N(4)	83.6(15)	O(11A)-Fe(2)-N(3)	79.9(7)
O(8A)-Fe(1)-N(6)	91.4(15)	O(8)-S(1)-C(33)	97.5(4)
O(1)-Fe(1)-O(8)	160.9(3)	O(9)-S(1)-O(8)	113.7(5)
O(1)-Fe(1)-O(8A)	159.2(14)	O(9)-S(1)-O(10)	118.5(7)
O(1)-Fe(1)-N(4)	76.5(2)	O(9)-S(1)-C(33)	106.9(5)
O(1)-Fe(1)-N(5)	92.6(2)	O(10)-S(1)-O(8)	113.5(5)
O(1)-Fe(1)-N(6)	89.6(2)	O(10)-S(1)-C(33)	103.5(5)
O(7)-Fe(1)-O(8)	98.9(3)	S(1)-O(8)-Fe(1)	143.1(5)
O(7)-Fe(1)-O(8A)	100.3(16)	F(1)-C(33)-S(1)	112.7(7)
O(7)-Fe(1)-O(1)	99.5(2)	F(1)-C(33)-F(2)	107.4(8)
O(7)-Fe(1)-N(4)	175.9(2)	F(1)-C(33)-F(3)	107.7(8)
O(7)-Fe(1)-N(5)	101.8(2)	F(2)-C(33)-S(1)	111.5(7)
O(7)-Fe(1)-N(6)	105.3(2)	F(2)-C(33)-F(3)	105.7(8)
N(5)-Fe(1)-O(8A)	77.0(13)	F(3)-C(33)-S(1)	111.5(6)
N(5)-Fe(1)-N(4)	77.7(2)	O(8A)-S(1A)-C(33A)	104(2)
N(5)-Fe(1)-N(6)	152.0(2)	O(9A)-S(1A)-O(8A)	113.1(18)
N(6)-Fe(1)-N(4)	75.7(2)	O(9A)-S(1A)-O(10A)	119(2)
O(4)-Fe(2)-N(1)	76.3(2)	O(9A)-S(1A)-C(33A)	107(5)
O(4)-Fe(2)-N(2)	94.4(3)	O(10A)-S(1A)-O(8A)	113.0(18)
O(4)-Fe(2)-N(3)	90.4(3)	O(10A)-S(1A)-C(33A)	97(5)
O(4)-Fe(2)-O(11)	164.3(4)	S(1A)-O(8A)-Fe(1)	146(3)
O(7)-Fe(2)-O(4)	98.1(2)	F(1A)-C(33A)-S(1A)	103(4)
O(7)-Fe(2)-N(1)	174.4(3)	F(1A)-C(33A)-F(3A)	107.5(19)
O(7)-Fe(2)-N(2)	101.9(3)	F(2A)-C(33A)-S(1A)	117(5)
O(7)-Fe(2)-N(3)	104.8(3)	F(2A)-C(33A)-F(1A)	106.9(19)
O(7)-Fe(2)-O(11)	97.2(5)	F(2A)-C(33A)-F(3A)	107.0(19)

F(3A)-C(33A)-S(1A)	114(5)	O(1)-C(1)-H(1A)	109.5
Fe(1)-O(1)-H(1)	130.0	O(1)-C(1)-H(1B)	109.5
C(1)-O(1)-Fe(1)	116.6(4)	O(1)-C(1)-C(2)	110.8(6)
C(1)-O(1)-H(1)	107.5	H(1A)-C(1)-H(1B)	108.1
C(4)-O(2)-C(3)	103.0(5)	C(2)-C(1)-H(1A)	109.5
C(6)-O(3)-C(5)	105.3(5)	C(2)-C(1)-H(1B)	109.5
Fe(2)-O(4)-H(4)	131.8	N(4)-C(2)-C(1)	110.5(6)
C(17)-O(4)-Fe(2)	117.1(5)	N(4)-C(2)-C(3)	102.0(6)
C(17)-O(4)-H(4)	109.0	N(4)-C(2)-C(5)	104.1(6)
C(20)-O(5)-C(19)	104.3(6)	C(1)-C(2)-C(5)	112.8(7)
C(22)-O(6)-C(21)	106.5(6)	C(3)-C(2)-C(1)	114.2(7)
Fe(2)-O(7)-Fe(1)	167.5(3)	C(3)-C(2)-C(5)	112.2(6)
C(18)-N(1)-Fe(2)	113.5(4)	O(2)-C(3)-C(2)	103.6(6)
C(20)-N(1)-Fe(2)	112.2(5)	O(2)-C(3)-H(3A)	111.0
C(20)-N(1)-C(18)	103.7(6)	O(2)-C(3)-H(3B)	111.0
C(22)-N(1)-Fe(2)	109.7(5)	C(2)-C(3)-H(3A)	111.0
C(22)-N(1)-C(18)	104.0(7)	C(2)-C(3)-H(3B)	111.0
C(22)-N(1)-C(20)	113.5(6)	H(3A)-C(3)-H(3B)	109.0
C(23)-N(2)-Fe(2)	118.0(6)	O(2)-C(4)-N(4)	106.6(5)
C(23)-N(2)-C(27)	119.6(7)	O(2)-C(4)-H(4A)	109.4
C(27)-N(2)-Fe(2)	122.4(5)	O(2)-C(4)-C(7)	110.8(6)
C(28)-N(3)-Fe(2)	115.6(6)	N(4)-C(4)-H(4A)	109.4
C(28)-N(3)-C(32)	119.7(8)	N(4)-C(4)-C(7)	111.3(5)
C(32)-N(3)-Fe(2)	123.3(6)	C(7)-C(4)-H(4A)	109.4
C(2)-N(4)-Fe(1)	113.7(4)	O(3)-C(5)-C(2)	106.0(6)
C(4)-N(4)-Fe(1)	111.0(4)	O(3)-C(5)-H(5A)	110.5
C(4)-N(4)-C(2)	105.8(5)	O(3)-C(5)-H(5B)	110.5
C(6)-N(4)-Fe(1)	109.1(4)	C(2)-C(5)-H(5A)	110.5
C(6)-N(4)-C(2)	104.0(5)	C(2)-C(5)-H(5B)	110.5
C(6)-N(4)-C(4)	113.2(5)	H(5A)-C(5)-H(5B)	108.7
C(7)-N(5)-Fe(1)	118.3(5)	O(3)-C(6)-N(4)	106.5(6)
C(7)-N(5)-C(11)	118.9(6)	O(3)-C(6)-H(6)	110.1
C(11)-N(5)-Fe(1)	122.7(5)	O(3)-C(6)-C(12)	110.9(6)
C(12)-N(6)-Fe(1)	117.0(5)	N(4)-C(6)-H(6)	110.1
C(12)-N(6)-C(16)	119.0(7)	N(4)-C(6)-C(12)	109.1(5)
C(16)-N(6)-Fe(1)	123.4(5)	C(12)-C(6)-H(6)	110.1

N(5)-C(7)-C(4)	118.4(6)	N(1)-C(18)-C(17)	110.2(6)
N(5)-C(7)-C(8)	121.0(7)	N(1)-C(18)-C(19)	102.6(7)
C(8)-C(7)-C(4)	120.6(6)	N(1)-C(18)-C(21)	105.0(7)
C(7)-C(8)-H(8)	120.1	C(17)-C(18)-C(19)	111.2(8)
C(7)-C(8)-C(9)	119.9(7)	C(17)-C(18)-C(21)	113.5(8)
C(9)-C(8)-H(8)	120.1	C(19)-C(18)-C(21)	113.5(7)
C(8)-C(9)-H(9)	120.8	O(5)-C(19)-C(18)	101.3(8)
C(8)-C(9)-C(10)	118.4(8)	O(5)-C(19)-H(19A)	111.5
C(10)-C(9)-H(9)	120.8	O(5)-C(19)-H(19B)	111.5
C(9)-C(10)-H(10)	120.3	C(18)-C(19)-H(19A)	111.5
C(11)-C(10)-C(9)	119.4(8)	C(18)-C(19)-H(19B)	111.5
C(11)-C(10)-H(10)	120.3	H(19A)-C(19)-H(19B)	109.3
N(5)-C(11)-C(10)	122.3(7)	O(5)-C(20)-N(1)	107.5(7)
N(5)-C(11)-H(11)	118.8	O(5)-C(20)-H(20)	109.3
C(10)-C(11)-H(11)	118.8	O(5)-C(20)-C(23)	111.2(8)
N(6)-C(12)-C(6)	117.3(6)	N(1)-C(20)-H(20)	109.3
N(6)-C(12)-C(13)	122.2(7)	N(1)-C(20)-C(23)	110.2(6)
C(13)-C(12)-C(6)	120.5(6)	C(23)-C(20)-H(20)	109.3
C(12)-C(13)-H(13)	120.4	O(6)-C(21)-C(18)	105.3(7)
C(14)-C(13)-C(12)	119.2(7)	O(6)-C(22)-N(1)	106.1(7)
C(14)-C(13)-H(13)	120.4	O(6)-C(22)-H(22)	109.5
C(13)-C(14)-H(14)	120.4	O(6)-C(22)-C(28)	112.5(8)
C(13)-C(14)-C(15)	119.2(8)	N(1)-C(22)-H(22)	109.5
C(15)-C(14)-H(14)	120.4	N(1)-C(22)-C(28)	109.6(6)
C(14)-C(15)-H(15)	120.4	C(28)-C(22)-H(22)	109.5
C(16)-C(15)-C(14)	119.2(8)	N(2)-C(23)-C(20)	119.0(8)
C(16)-C(15)-H(15)	120.4	N(2)-C(23)-C(24)	121.5(9)
N(6)-C(16)-C(15)	121.3(7)	C(24)-C(23)-C(20)	119.4(7)
N(6)-C(16)-H(16)	119.3	C(23)-C(24)-C(25)	119.1(9)
C(15)-C(16)-H(16)	119.3	C(26)-C(25)-C(24)	118.9(10)
O(4)-C(17)-H(17A)	109.6	C(25)-C(26)-H(26)	120.5
O(4)-C(17)-H(17B)	109.6	C(27)-C(26)-C(25)	118.9(11)
O(4)-C(17)-C(18)	110.1(7)	C(27)-C(26)-H(26)	120.5
H(17A)-C(17)-H(17B)	108.1	N(2)-C(27)-C(26)	121.9(8)
C(18)-C(17)-H(17A)	109.6	N(2)-C(27)-H(27)	119.0
C(18)-C(17)-H(17B)	109.6	C(26)-C(27)-H(27)	119.0

N(3)-C(28)-C(22)	118.3(8)	F(4A)-C(34A)-F(5A)	109.9(15)
N(3)-C(28)-C(29)	120.4(9)	F(4A)-C(34A)-F(6A)	109.4(15)
C(29)-C(28)-C(22)	121.2(8)	F(5A)-C(34A)-S(2A)	117.9(18)
C(28)-C(29)-H(29)	120.7	F(5A)-C(34A)-F(6A)	109.5(16)
C(30)-C(29)-C(28)	118.7(9)	F(6A)-C(34A)-S(2A)	89(2)
C(30)-C(29)-H(29)	120.7	O(14)-S(3)-C(35)	102.7(6)
C(29)-C(30)-H(30)	119.5	O(14)-S(3)-C(35A)	105.3(9)
C(31)-C(30)-C(29)	121.1(10)	O(15)-S(3)-O(14)	114.8(4)
C(31)-C(30)-H(30)	119.5	O(15)-S(3)-O(16)	115.4(5)
C(30)-C(31)-H(31)	121.1	O(15)-S(3)-C(35)	106.9(7)
C(30)-C(31)-C(32)	117.8(10)	O(15)-S(3)-C(35A)	95.9(14)
C(32)-C(31)-H(31)	121.1	O(16)-S(3)-O(14)	114.2(4)
N(3)-C(32)-C(31)	122.3(8)	O(16)-S(3)-C(35)	100.5(7)
N(3)-C(32)-H(32)	118.8	O(16)-S(3)-C(35A)	108.9(11)
C(31)-C(32)-H(32)	118.8	F(7)-C(35)-S(3)	112.5(16)
O(11)-S(2)-C(34)	99.8(6)	F(7)-C(35)-F(8)	107.5(13)
O(12)-S(2)-O(11)	113.7(8)	F(8)-C(35)-S(3)	109.6(12)
O(12)-S(2)-O(13)	117.4(10)	F(9)-C(35)-S(3)	111.8(12)
O(12)-S(2)-C(34)	103.7(7)	F(9)-C(35)-F(7)	107.9(12)
O(13)-S(2)-O(11)	112.8(8)	F(9)-C(35)-F(8)	107.4(12)
O(13)-S(2)-C(34)	107.0(7)	F(7A)-C(35A)-S(3)	112(2)
S(2)-O(11)-Fe(2)	142.2(9)	F(7A)-C(35A)-F(8A)	105.1(15)
F(4)-C(34)-S(2)	112.6(13)	F(8A)-C(35A)-S(3)	115(2)
F(4)-C(34)-F(5)	107.7(11)	F(9A)-C(35A)-S(3)	112.4(18)
F(5)-C(34)-S(2)	116.7(10)	F(9A)-C(35A)-F(7A)	106.9(15)
F(6)-C(34)-S(2)	105.5(9)	F(9A)-C(35A)-F(8A)	104.6(16)
F(6)-C(34)-F(4)	106.6(10)	O(17)-S(4)-O(18)	113.5(6)
F(6)-C(34)-F(5)	107.1(11)	O(17)-S(4)-O(19)	117.7(7)
O(11A)-S(2A)-C(34A)	100.8(12)	O(17)-S(4)-C(36)	103.3(5)
O(12A)-S(2A)-O(11A)	113.7(14)	O(18)-S(4)-C(36)	102.2(6)
O(12A)-S(2A)-O(13A)	115.0(16)	O(19)-S(4)-O(18)	113.2(6)
O(12A)-S(2A)-C(34A)	108.9(15)	O(19)-S(4)-C(36)	104.7(5)
O(13A)-S(2A)-O(11A)	113.3(14)	F(10)-C(36)-S(4)	110.9(8)
O(13A)-S(2A)-C(34A)	103.4(15)	F(11)-C(36)-S(4)	108.8(8)
S(2A)-O(11A)-Fe(2)	142.2(16)	F(11)-C(36)-F(10)	108.2(9)
F(4A)-C(34A)-S(2A)	119(3)	F(12)-C(36)-S(4)	112.3(8)

F(12)-C(36)-F(10)	108.6(10)	O(19A)-S(4A)-C(36A)	91(3)
F(12)-C(36)-F(11)	107.9(9)	F(10A)-C(36A)-S(4A)	114(2)
O(17A)-S(4A)-O(18A)	114.9(14)	F(10A)-C(36A)-F(11A)	114.4(16)
O(17A)-S(4A)-O(19A)	111.4(15)	F(10A)-C(36A)-F(12A)	113.8(18)
O(17A)-S(4A)-C(36A)	117.8(17)	F(11A)-C(36A)-S(4A)	107(2)
O(18A)-S(4A)-O(19A)	111.2(15)	F(11A)-C(36A)-F(12A)	115.0(17)
O(18A)-S(4A)-C(36A)	108.5(19)	F(12A)-C(36A)-S(4A)	91(3)

Table S31. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **D**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	43(1)	44(1)	36(1)	1(1)	13(1)	22(1)
Fe2	42(1)	47(1)	40(1)	-1(1)	10(1)	23(1)
S1	44(1)	54(1)	52(1)	7(1)	7(1)	14(1)
F1	56(4)	81(5)	76(6)	10(4)	16(4)	5(3)
F2	73(5)	111(6)	71(4)	-10(4)	34(4)	4(4)
F3	68(5)	83(5)	128(6)	54(5)	27(4)	16(4)
O8	46(3)	50(4)	43(4)	6(3)	4(3)	17(3)
O9	75(6)	96(7)	44(4)	-9(4)	6(4)	-4(6)
O10	54(5)	73(5)	165(10)	38(6)	16(5)	24(4)
C33	44(4)	70(6)	60(5)	5(4)	18(4)	14(4)
S1A	53(11)	91(17)	127(18)	-33(14)	-16(12)	6(12)
F1A	59(19)	100(30)	30(20)	-20(20)	2(19)	0(20)
F2A	70(30)	100(30)	130(30)	-80(20)	-20(20)	0(30)
F3A	70(30)	120(30)	200(40)	30(30)	10(30)	10(20)
O8A	20(12)	42(13)	28(14)	1(10)	-8(10)	3(10)
O9A	70(20)	60(20)	90(20)	-31(16)	2(18)	8(19)
O10A	70(30)	80(30)	140(30)	40(30)	20(30)	0(30)
C33A	40(19)	90(30)	120(30)	-30(20)	10(20)	9(16)
O1	38(3)	53(3)	53(3)	1(2)	11(2)	15(2)
O2	46(3)	41(3)	53(3)	-8(2)	8(2)	16(2)
O3	47(3)	56(3)	39(3)	-8(2)	9(2)	20(2)
O4	48(3)	63(3)	49(3)	2(2)	4(2)	28(3)
O5	55(3)	102(5)	53(3)	-21(3)	3(3)	43(4)
O6	68(4)	63(4)	73(4)	-23(3)	-11(3)	41(3)
O7	59(3)	54(3)	45(3)	7(2)	22(2)	29(3)
N1	44(3)	57(4)	49(4)	-10(3)	1(3)	27(3)
N2	45(3)	59(4)	44(3)	0(3)	15(3)	25(3)
N3	49(4)	48(3)	50(4)	-2(3)	2(3)	19(3)
N4	36(3)	41(3)	36(3)	-3(2)	7(2)	14(2)
N5	45(3)	45(3)	44(3)	0(2)	9(3)	24(3)
N6	47(3)	50(3)	39(3)	2(3)	10(3)	25(3)

C1	44(4)	58(5)	48(4)	-4(3)	9(3)	13(3)
C2	39(4)	39(4)	49(4)	-10(3)	4(3)	8(3)
C3	45(4)	49(4)	61(5)	-1(4)	9(4)	17(3)
C4	37(3)	40(3)	43(4)	-7(3)	7(3)	19(3)
C5	53(4)	55(5)	47(4)	-9(3)	3(3)	20(4)
C6	41(3)	56(4)	29(3)	-2(3)	13(3)	20(3)
C7	51(4)	48(4)	41(4)	0(3)	14(3)	29(3)
C8	65(5)	68(5)	47(4)	6(4)	12(4)	38(4)
C9	78(6)	83(6)	58(5)	16(5)	17(5)	51(6)
C10	76(6)	86(7)	46(5)	10(4)	13(4)	42(5)
C11	56(4)	63(5)	38(4)	2(3)	14(3)	30(4)
C12	49(4)	50(4)	36(3)	2(3)	12(3)	18(3)
C13	57(5)	61(5)	41(4)	4(3)	15(3)	21(4)
C14	76(6)	67(5)	47(5)	14(4)	17(4)	32(5)
C15	81(6)	66(5)	49(5)	14(4)	13(4)	42(5)
C16	60(5)	58(5)	46(4)	4(3)	13(4)	32(4)
C17	47(4)	55(5)	60(5)	-12(4)	2(4)	22(4)
C18	48(4)	74(6)	48(4)	-18(4)	-5(3)	32(4)
C19	58(5)	101(8)	48(5)	-16(5)	0(4)	40(5)
C20	45(4)	74(5)	44(4)	-19(4)	3(3)	32(4)
C21	61(5)	66(6)	67(6)	-20(4)	-12(4)	33(5)
C22	56(5)	45(4)	66(5)	-19(4)	-6(4)	31(4)
C23	46(4)	82(6)	57(5)	-1(4)	17(4)	33(4)
C24	73(7)	99(8)	74(7)	-3(6)	37(6)	33(6)
C25	88(8)	102(10)	94(9)	10(7)	51(7)	16(7)
C26	67(6)	78(7)	97(8)	16(6)	38(6)	15(5)
C27	54(5)	54(5)	67(5)	14(4)	25(4)	22(4)
C28	53(4)	46(4)	60(5)	-5(3)	-4(4)	21(4)
C29	70(6)	54(5)	86(7)	2(5)	9(5)	27(5)
C30	75(7)	56(6)	92(8)	15(5)	4(6)	10(5)
C31	66(6)	55(5)	83(7)	7(5)	22(5)	14(4)
C32	52(5)	57(5)	64(5)	2(4)	13(4)	18(4)
S2	44(2)	57(2)	48(3)	7(2)	4(2)	18(2)
F4	69(7)	91(9)	113(12)	38(8)	-35(7)	13(6)
F5	93(8)	144(12)	68(7)	42(8)	29(6)	74(9)
F6	121(10)	70(5)	85(7)	-6(5)	-8(6)	61(6)

O11	43(3)	58(4)	50(4)	1(3)	-1(3)	18(3)
O12	65(6)	168(13)	56(6)	23(7)	10(5)	67(8)
O13	103(10)	48(6)	102(10)	5(5)	-34(8)	13(6)
C34	55(7)	61(7)	57(7)	3(5)	4(5)	29(6)
S2A	44(5)	46(5)	57(6)	5(4)	2(4)	7(3)
F4A	51(10)	88(18)	62(13)	8(11)	11(9)	38(10)
F5A	71(14)	70(11)	120(20)	43(11)	-6(13)	7(10)
F6A	100(20)	170(30)	61(14)	41(15)	31(13)	100(20)
O11A	43(3)	57(4)	51(4)	0(4)	-1(3)	18(3)
O12A	57(11)	98(19)	83(17)	45(14)	27(12)	12(11)
O13A	100(20)	62(12)	62(13)	-12(10)	-7(12)	17(13)
C34A	43(11)	78(11)	57(13)	25(10)	16(9)	19(9)
S3	65(1)	66(1)	47(1)	4(1)	9(1)	34(1)
O14	77(4)	83(4)	52(3)	8(3)	18(3)	46(4)
O15	79(5)	89(5)	73(4)	26(4)	14(4)	48(4)
O16	120(7)	79(5)	64(4)	12(3)	24(4)	64(5)
F7	108(15)	99(13)	75(9)	-1(8)	36(9)	-4(10)
F8	60(6)	148(17)	84(9)	17(9)	14(6)	35(9)
F9	83(9)	101(9)	71(8)	-22(7)	21(7)	11(7)
C35	71(9)	105(10)	56(8)	-5(7)	18(7)	35(8)
F7A	50(12)	110(20)	57(11)	-15(11)	20(10)	29(12)
F8A	77(13)	180(30)	83(14)	-11(18)	-11(11)	20(17)
F9A	100(20)	82(12)	100(20)	-24(13)	56(18)	-4(11)
C35A	71(14)	114(15)	52(12)	-20(12)	16(9)	27(13)
S4	62(2)	54(2)	65(2)	8(1)	22(2)	20(1)
F10	60(5)	78(6)	122(7)	15(5)	33(5)	23(4)
F11	76(5)	65(5)	106(6)	28(4)	28(5)	29(4)
F12	86(6)	76(6)	95(6)	-24(5)	1(5)	28(5)
O17	61(5)	82(6)	90(7)	25(5)	30(5)	31(5)
O18	69(6)	63(6)	87(7)	20(5)	30(6)	27(5)
O19	92(7)	74(6)	62(5)	0(4)	21(5)	17(5)
C36	69(7)	64(7)	64(6)	11(5)	23(6)	31(6)
S4A	94(9)	73(7)	135(11)	50(8)	-32(8)	-17(6)
F10A	109(18)	290(50)	350(60)	260(50)	110(20)	120(20)
F11A	160(20)	112(17)	200(30)	99(17)	20(20)	26(17)
F12A	250(50)	170(30)	230(30)	60(30)	180(40)	90(30)

O17A	82(17)	120(30)	90(20)	48(19)	5(15)	1(16)
O18A	84(17)	104(19)	110(20)	58(16)	-12(19)	-20(19)
O19A	170(40)	120(30)	170(20)	-20(30)	30(30)	10(20)
C36A	89(16)	110(17)	140(20)	51(15)	35(16)	51(13)

Table S32. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **D**.

	x	y	z	U(eq)
H1	1189	5157	1323	72
H4	3554	8438	4591	78
H1A	1271	5409	-373	62
H1B	926	4353	-13	62
H3A	2386	3749	815	63
H3B	2380	3243	-236	63
H4A	4885	5476	873	48
H5A	2627	4138	-1451	64
H5B	2158	5074	-1473	64
H6	4666	6571	-24	50
H8	4861	4150	2209	68
H9	4743	4232	3807	80
H10	3935	5380	4500	79
H11	3267	6368	3602	60
H13	3813	7334	-1629	63
H14	2986	8584	-1819	72
H15	2063	9056	-658	73
H16	1972	8249	634	62
H17A	4089	10316	4512	66
H17B	3970	9844	5438	66
H19A	2109	9046	5714	84
H19B	2350	10180	6291	84
H20	232	9510	4063	65
H22	1089	10482	3158	68
H26	-368	5267	3737	96
H27	1036	6225	3147	67
H29	2596	12120	2554	84
H30	3701	12146	1459	93
H31	4396	10801	1135	82
H32	3944	9418	1927	70

Table S33. Torsion angles [°] for **D**.

Fe1-O1-C1-C2	40.3(8)	O9-S1-C33-F2	174.0(8)
Fe1-N4-C2-C1	10.2(8)	O9-S1-C33-F3	-68.1(9)
Fe1-N4-C2-C3	-111.6(5)	O10-S1-O8-Fe1	64.2(10)
Fe1-N4-C2-C5	131.6(5)	O10-S1-C33-F1	-72.7(8)
Fe1-N4-C4-O2	140.1(4)	O10-S1-C33-F2	48.2(8)
Fe1-N4-C4-C7	19.1(7)	O10-S1-C33-F3	166.0(8)
Fe1-N4-C6-O3	-153.8(4)	C33-S1-O8-Fe1	172.6(8)
Fe1-N4-C6-C12	-34.1(6)	O8A-Fe1-O7-Fe2	76(2)
Fe1-N5-C7-C4	-1.3(9)	O8A-S1A-C33A-F1A	-175(4)
Fe1-N5-C7-C8	178.1(7)	O8A-S1A-C33A-F2A	67(4)
Fe1-N5-C11-C10	-178.8(8)	O8A-S1A-C33A-F3A	-59(4)
Fe1-N6-C12-C6	8.3(9)	O9A-S1A-O8A-Fe1	82(8)
Fe1-N6-C12-C13	-170.1(6)	O9A-S1A-C33A-F1A	-55(4)
Fe1-N6-C16-C15	169.6(7)	O9A-S1A-C33A-F2A	-173(4)
Fe2-O4-C17-C18	41.4(9)	O9A-S1A-C33A-F3A	61(4)
Fe2-N1-C18-C17	10.7(10)	O10A-S1A-O8A-Fe1	-57(8)
Fe2-N1-C18-C19	-107.7(6)	O10A-S1A-C33A-F1A	69(4)
Fe2-N1-C18-C21	133.3(6)	O10A-S1A-C33A-F2A	-49(4)
Fe2-N1-C20-O5	136.4(6)	O10A-S1A-C33A-F3A	-175(4)
Fe2-N1-C20-C23	15.0(8)	C33A-S1A-O8A-Fe1	-162(6)
Fe2-N1-C22-O6	-153.4(5)	O1-Fe1-O7-Fe2	-110.0(17)
Fe2-N1-C22-C28	-31.7(8)	O1-C1-C2-N4	-30.8(9)
Fe2-N2-C23-C20	-0.4(10)	O1-C1-C2-C3	83.5(8)
Fe2-N2-C23-C24	177.6(8)	O1-C1-C2-C5	-146.9(7)
Fe2-N2-C27-C26	-175.6(9)	O2-C4-C7-N5	-131.1(7)
Fe2-N3-C28-C22	12.0(10)	O2-C4-C7-C8	49.5(10)
Fe2-N3-C28-C29	-164.1(7)	O3-C6-C12-N6	135.6(7)
Fe2-N3-C32-C31	161.8(8)	O3-C6-C12-C13	-46.0(10)
O8-Fe1-O7-Fe2	64.5(18)	O4-Fe2-O7-Fe1	-118.5(17)
O8-S1-C33-F1	170.8(7)	O4-C17-C18-N1	-31.7(11)
O8-S1-C33-F2	-68.3(7)	O4-C17-C18-C19	81.3(9)
O8-S1-C33-F3	49.6(7)	O4-C17-C18-C21	-149.2(8)
O9-S1-O8-Fe1	-75.2(10)	O5-C20-C23-N2	-129.3(8)
O9-S1-C33-F1	53.2(9)	O5-C20-C23-C24	52.7(11)

O6-C22-C28-N3	132.0(8)	C4-N4-C6-C12	-158.2(6)
O6-C22-C28-C29	-51.9(11)	C4-C7-C8-C9	179.6(9)
N1-C18-C19-O5	-36.1(8)	C5-O3-C6-N4	39.2(7)
N1-C18-C21-O6	7.4(10)	C5-O3-C6-C12	-79.4(7)
N1-C20-C23-N2	-10.1(11)	C5-C2-C3-O2	77.7(8)
N1-C20-C23-C24	171.9(9)	C6-O3-C5-C2	-29.8(8)
N1-C22-C28-N3	14.2(10)	C6-N4-C2-C1	-108.3(7)
N1-C22-C28-C29	-169.8(8)	C6-N4-C2-C3	129.9(6)
N2-Fe2-O7-Fe1	145.2(17)	C6-N4-C2-C5	13.1(7)
N2-C23-C24-C25	-1.8(18)	C6-N4-C4-O2	-96.8(6)
N3-Fe2-O7-Fe1	-26.0(18)	C6-N4-C4-C7	142.2(6)
N3-C28-C29-C30	0.1(15)	C6-C12-C13-C14	-179.2(8)
N4-C2-C3-O2	-33.2(7)	C7-N5-C11-C10	-2.9(13)
N4-C2-C5-O3	9.5(8)	C7-C8-C9-C10	-1.5(16)
N4-C4-C7-N5	-12.6(10)	C8-C9-C10-C11	0.7(17)
N4-C4-C7-C8	167.9(8)	C9-C10-C11-N5	1.5(16)
N4-C6-C12-N6	18.6(9)	C11-N5-C7-C4	-177.4(7)
N4-C6-C12-C13	-163.0(7)	C11-N5-C7-C8	2.0(12)
N5-Fe1-O7-Fe2	155.2(17)	C12-N6-C16-C15	-0.8(13)
N5-C7-C8-C9	0.2(14)	C12-C13-C14-C15	0.6(15)
N6-Fe1-O7-Fe2	-17.9(18)	C13-C14-C15-C16	-0.4(16)
N6-C12-C13-C14	-0.9(14)	C14-C15-C16-N6	0.5(15)
C1-C2-C3-O2	-152.3(6)	C16-N6-C12-C6	179.3(7)
C1-C2-C5-O3	129.3(7)	C16-N6-C12-C13	1.0(12)
C2-N4-C4-O2	16.4(7)	C17-C18-C19-O5	-153.9(7)
C2-N4-C4-C7	-104.6(7)	C17-C18-C21-O6	127.9(8)
C2-N4-C6-O3	-32.3(7)	C18-N1-C20-O5	13.6(8)
C2-N4-C6-C12	87.5(6)	C18-N1-C20-C23	-107.8(7)
C3-O2-C4-N4	-37.8(7)	C18-N1-C22-O6	-31.7(8)
C3-O2-C4-C7	83.4(7)	C18-N1-C22-C28	90.0(7)
C3-C2-C5-O3	-100.0(7)	C19-O5-C20-N1	-38.0(10)
C4-O2-C3-C2	44.3(7)	C19-O5-C20-C23	82.8(9)
C4-N4-C2-C1	132.2(7)	C19-C18-C21-O6	-103.9(9)
C4-N4-C2-C3	10.4(7)	C20-O5-C19-C18	46.0(10)
C4-N4-C2-C5	-106.4(6)	C20-N1-C18-C17	132.7(8)
C4-N4-C6-O3	82.0(7)	C20-N1-C18-C19	14.2(8)

C20-N1-C18-C21	-104.7(8)	O13-S2-C34-F5	-77.7(14)
C20-N1-C22-O6	80.2(8)	O13-S2-C34-F6	163.5(12)
C20-N1-C22-C28	-158.1(6)	C34-S2-O11-Fe2	163.7(14)
C20-C23-C24-C25	176.1(11)	O11A-Fe2-O7-Fe1	56.4(19)
C21-O6-C22-N1	37.6(10)	O11A-S2A-C34A-F4A	-149(2)
C21-O6-C22-C28	-82.3(10)	O11A-S2A-C34A-F5A	-13(3)
C21-C18-C19-O5	76.7(9)	O11A-S2A-C34A-F6A	99(2)
C22-O6-C21-C18	-27.5(10)	O12A-S2A-O11A-Fe2	73(4)
C22-N1-C18-C17	-108.4(8)	O12A-S2A-C34A-F4A	-29(2)
C22-N1-C18-C19	133.1(7)	O12A-S2A-C34A-F5A	107(2)
C22-N1-C18-C21	14.2(8)	O12A-S2A-C34A-F6A	-141(2)
C22-N1-C20-O5	-98.6(8)	O13A-S2A-O11A-Fe2	-60(4)
C22-N1-C20-C23	140.0(7)	O13A-S2A-C34A-F4A	93(2)
C22-C28-C29-C30	-176.0(9)	O13A-S2A-C34A-F5A	-130(2)
C23-N2-C27-C26	1.7(15)	O13A-S2A-C34A-F6A	-18(2)
C23-C24-C25-C26	2(2)	C34A-S2A-O11A-Fe2	-170(3)
C24-C25-C26-C27	0(2)	O14-S3-C35-F7	171.1(12)
C25-C26-C27-N2	-1.8(19)	O14-S3-C35-F8	-69.4(11)
C27-N2-C23-C20	-177.8(8)	O14-S3-C35-F9	49.5(13)
C27-N2-C23-C24	0.2(14)	O14-S3-C35A-F7A	-174(2)
C28-N3-C32-C31	-3.9(14)	O14-S3-C35A-F8A	-54(2)
C28-C29-C30-C31	-1.7(17)	O14-S3-C35A-F9A	66(2)
C29-C30-C31-C32	0.6(17)	O15-S3-C35-F7	49.9(14)
C30-C31-C32-N3	2.2(16)	O15-S3-C35-F8	169.4(11)
C32-N3-C28-C22	178.8(8)	O15-S3-C35-F9	-71.7(14)
C32-N3-C28-C29	2.7(13)	O15-S3-C35A-F7A	69(2)
O11-Fe2-O7-Fe1	57.4(18)	O15-S3-C35A-F8A	-171(2)
O11-S2-C34-F4	165.3(13)	O15-S3-C35A-F9A	-52(2)
O11-S2-C34-F5	39.9(15)	O16-S3-C35-F7	-70.9(13)
O11-S2-C34-F6	-78.8(13)	O16-S3-C35-F8	48.6(12)
O12-S2-O11-Fe2	53.9(17)	O16-S3-C35-F9	167.5(13)
O12-S2-C34-F4	-77.2(12)	O16-S3-C35A-F7A	-51(2)
O12-S2-C34-F5	157.5(13)	O16-S3-C35A-F8A	69(2)
O12-S2-C34-F6	38.7(12)	O16-S3-C35A-F9A	-171(2)
O13-S2-O11-Fe2	-83.1(18)	O17-S4-C36-F10	-177.6(8)
O13-S2-C34-F4	47.6(13)	O17-S4-C36-F11	63.5(8)

O17-S4-C36-F12	-55.9(8)	O17A-S4A-C36A-F11A	57(3)
O18-S4-C36-F10	-59.5(8)	O17A-S4A-C36A-F12A	-59(3)
O18-S4-C36-F11	-178.5(7)	O18A-S4A-C36A-F10A	-43(3)
O18-S4-C36-F12	62.1(8)	O18A-S4A-C36A-F11A	-170(3)
O19-S4-C36-F10	58.7(9)	O18A-S4A-C36A-F12A	74(3)
O19-S4-C36-F11	-60.3(8)	O19A-S4A-C36A-F10A	70(3)
O19-S4-C36-F12	-179.6(8)	O19A-S4A-C36A-F11A	-57(2)
O17A-S4A-C36A-F10A	-176(3)	O19A-S4A-C36A-F12A	-174(3)

Table S34. Hydrogen bonds and close contacts for **D** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1...O18	0.86	1.72	2.568(12)	170.6
O1-H1...O18A	0.86	1.75	2.50(3)	145.1
O4-H4...O14	0.85	1.75	2.602(8)	177.9