Supporting Information

Substituent effect on the spin-crossover behaviour in series mononuclear Fe(II) complexes from thio-pybox ligands

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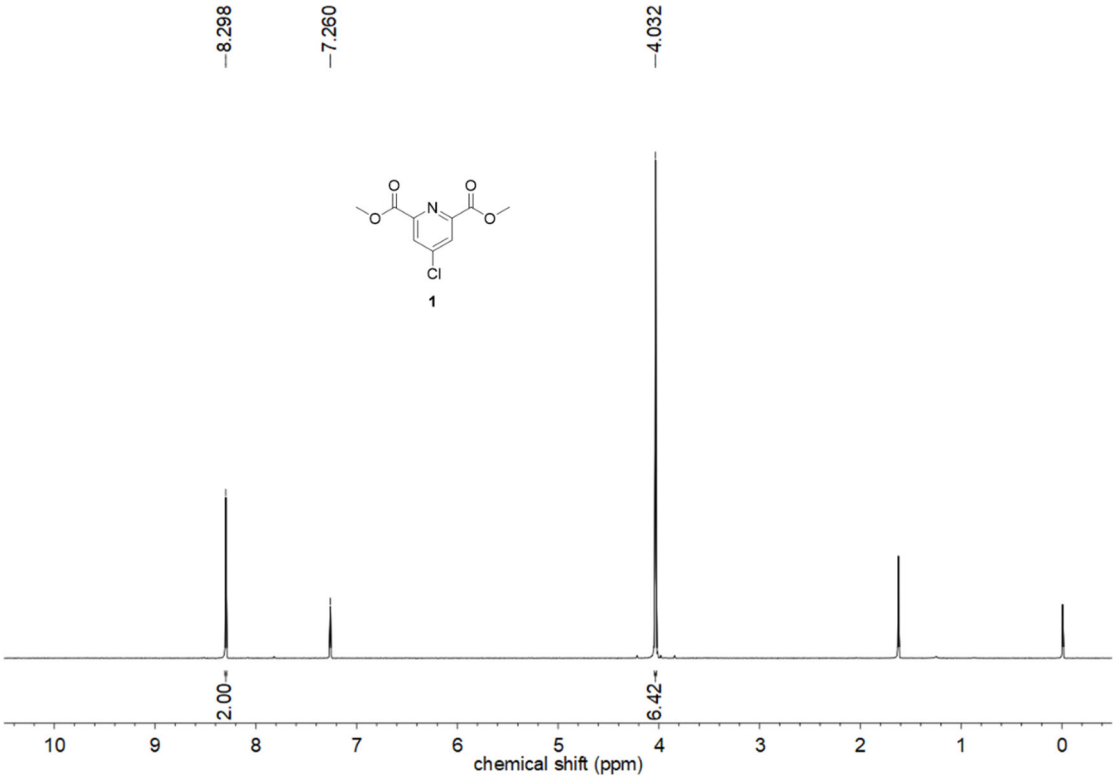


Fig. S1 ^{1}H NMR spectrum of compound **1** (400 MHz) in $CDCl_3$.

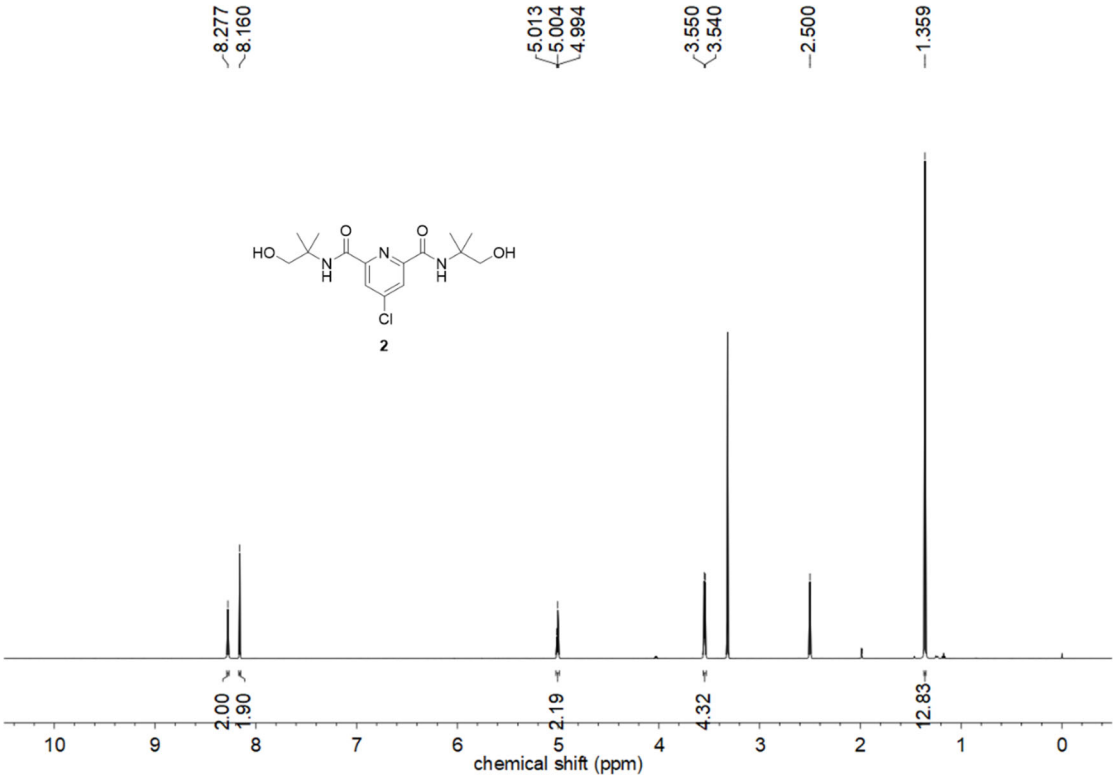


Fig. S2 ^{1}H NMR spectrum of compound **2** (600 MHz) in DMSO-d_6.

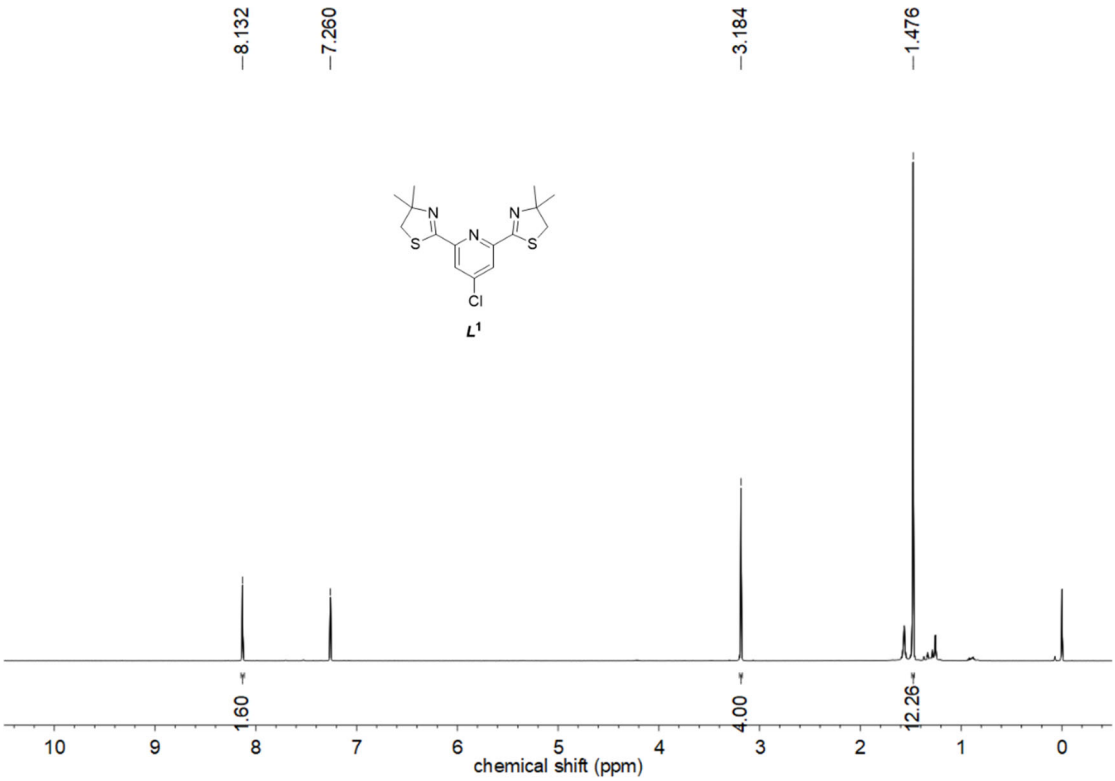


Fig. S3 ^{1}H NMR spectrum of compound ***L*^{1}** (600 MHz) in $CDCl_3$.

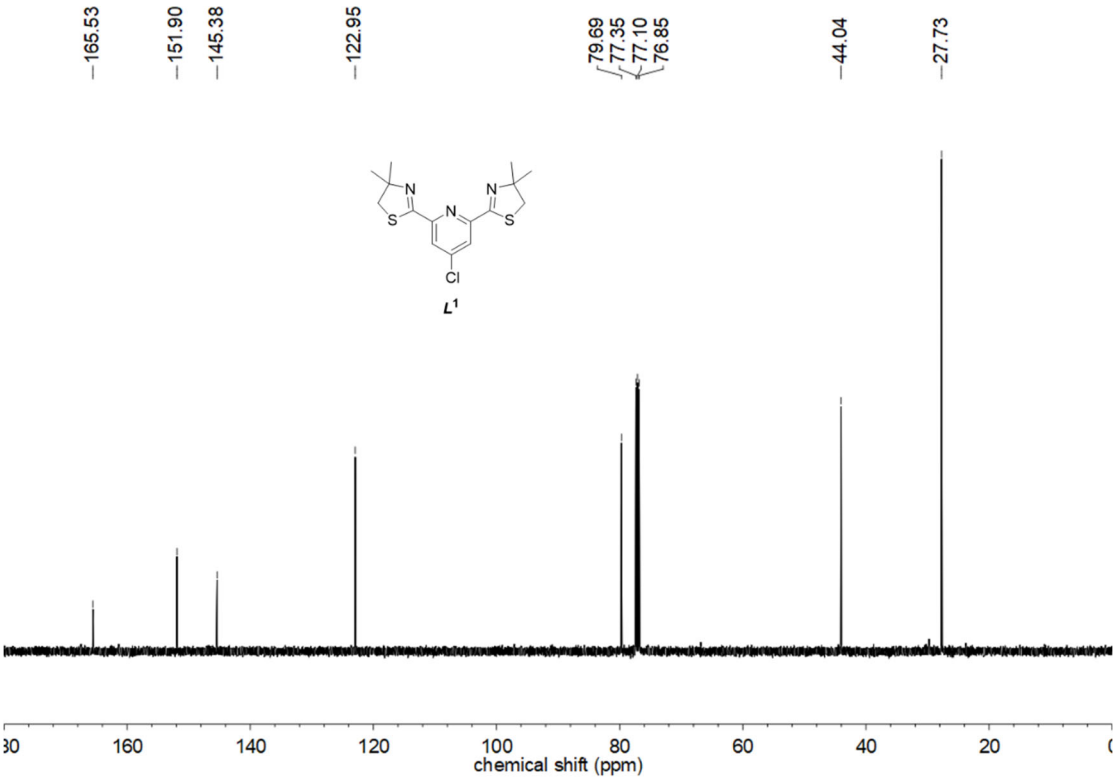


Fig. S4 ^{13}C NMR spectrum of compound ***L*^{1}** (125 MHz) in $CDCl_3$.

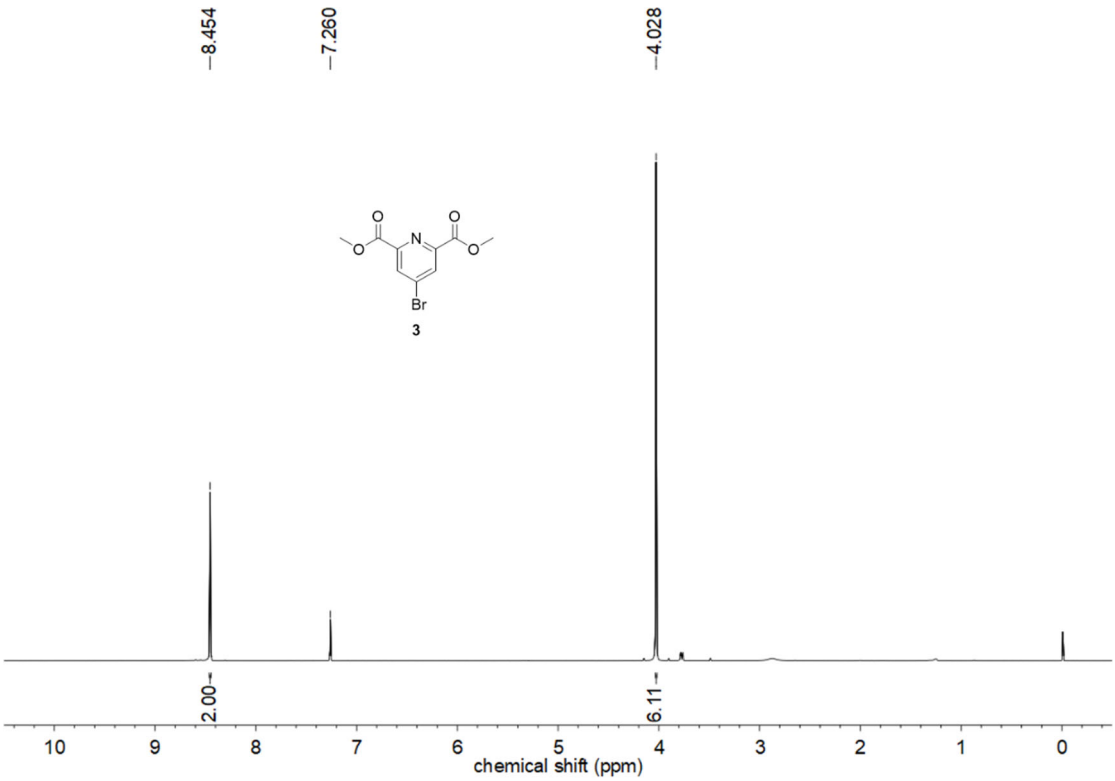


Fig. S5 ^{1}H NMR spectrum of compound **3** (600 MHz) in $CDCl_3$.

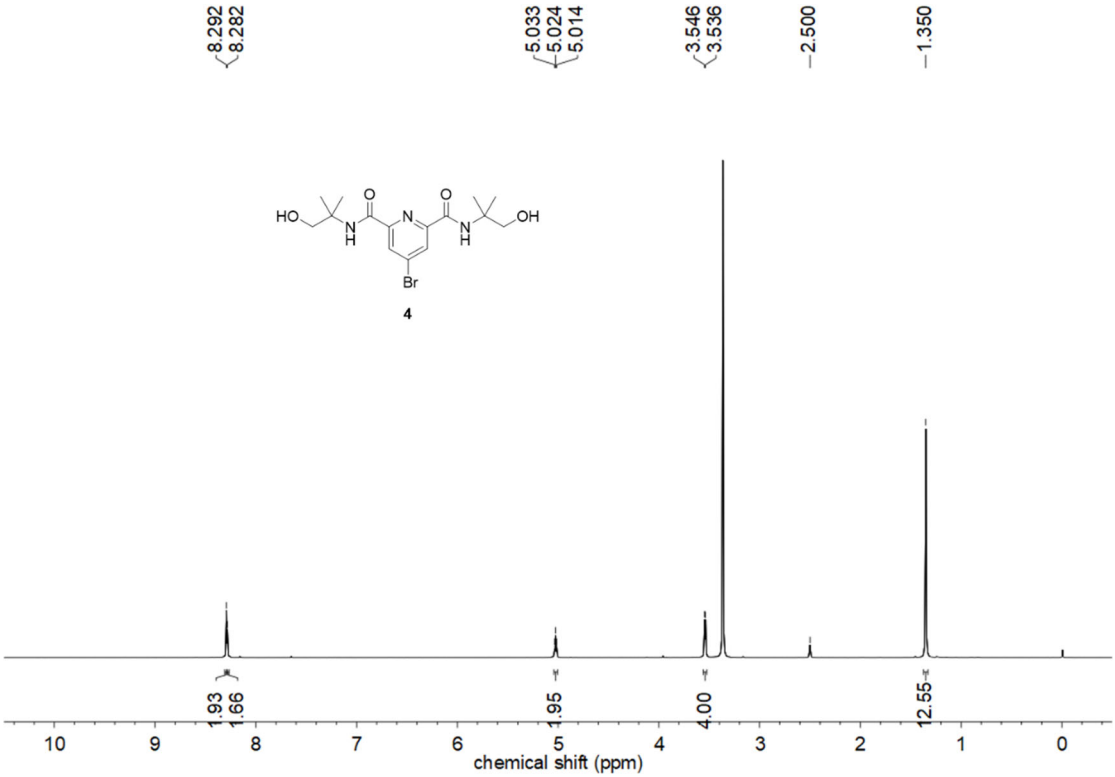


Fig. S6 ^{1}H NMR spectrum of compound **4** (600 MHz) in DMSO-d_6.

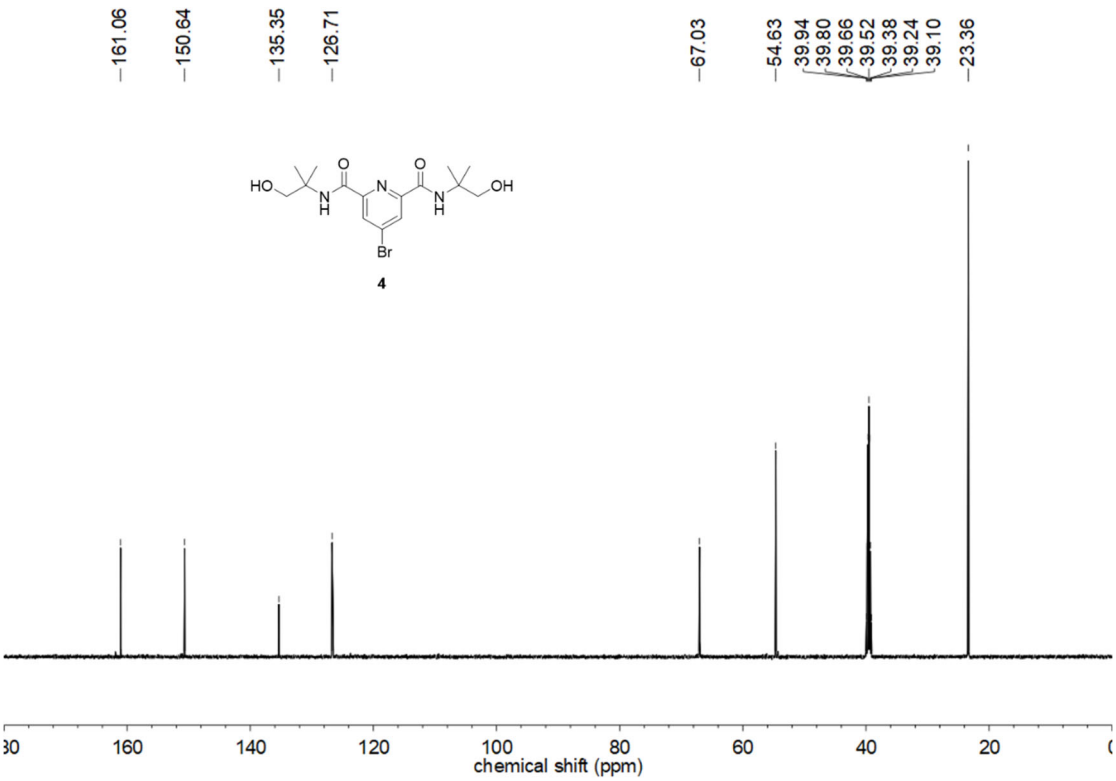


Fig. S7 ^{13}C NMR spectrum of compound **4** (125 MHz) in DMSO-d_6.

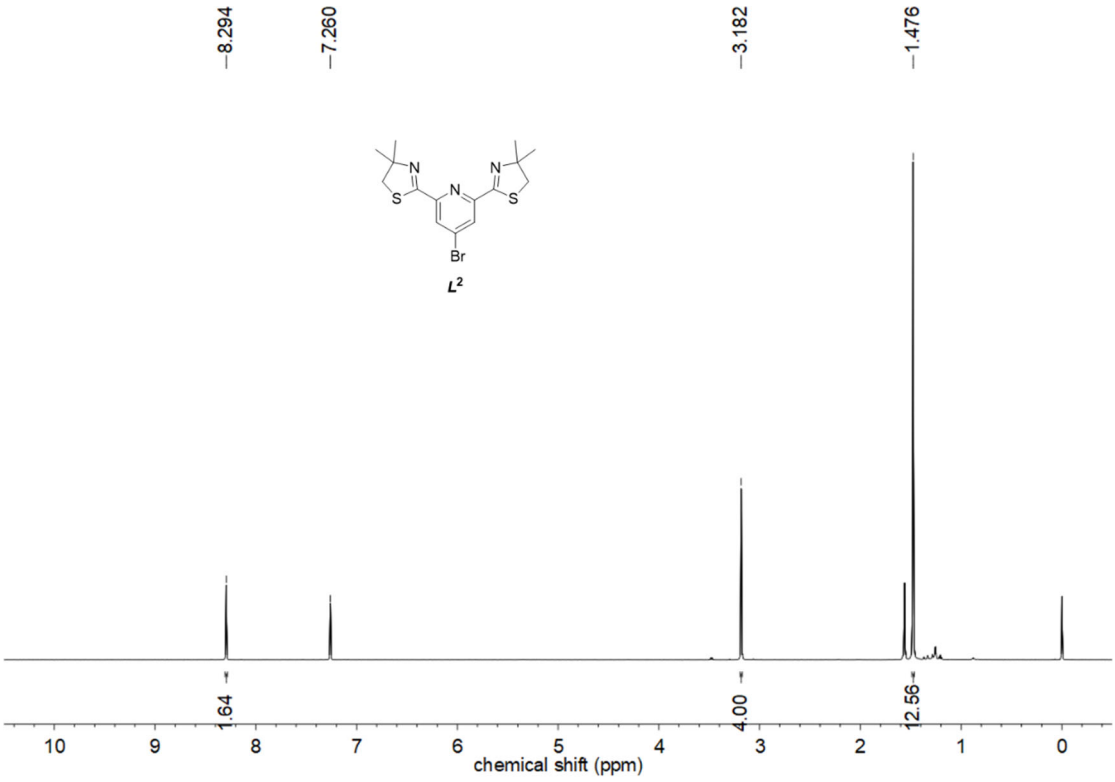


Fig. S8 ^{1}H NMR spectrum of compound ***L*²** (600 MHz) in $CDCl_3$.

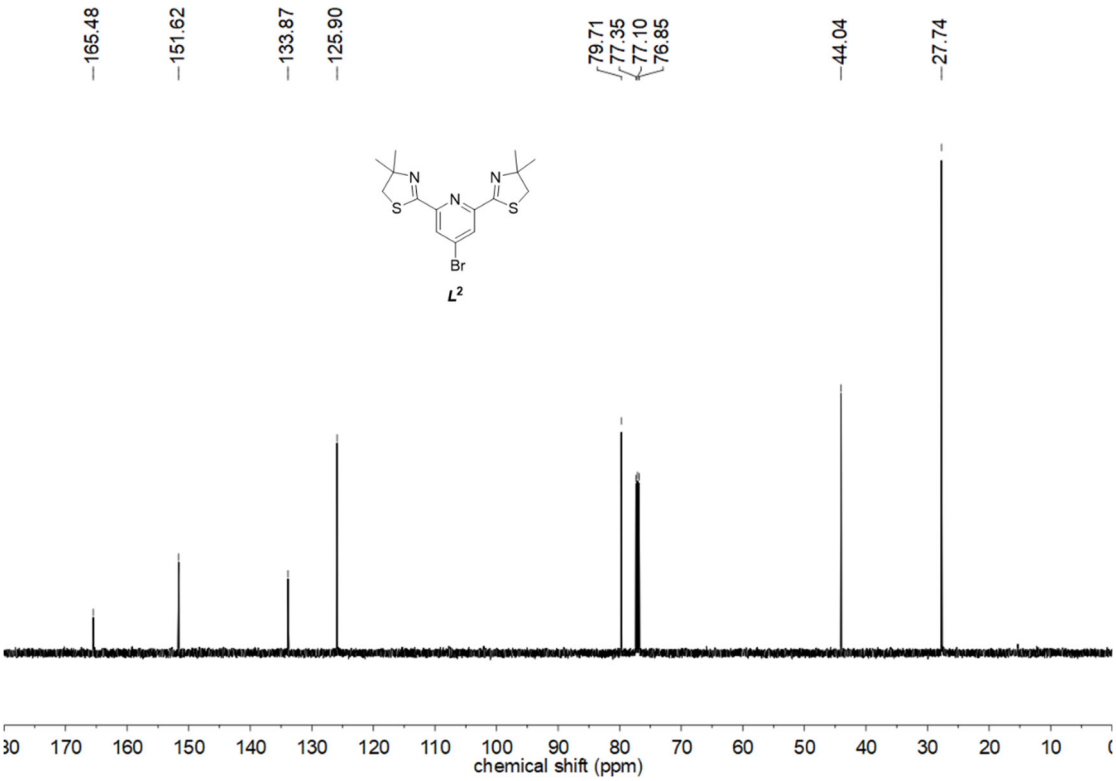


Fig. S9 ^{13}C NMR spectrum of compound ***L*²** (125 MHz) in $CDCl_3$.

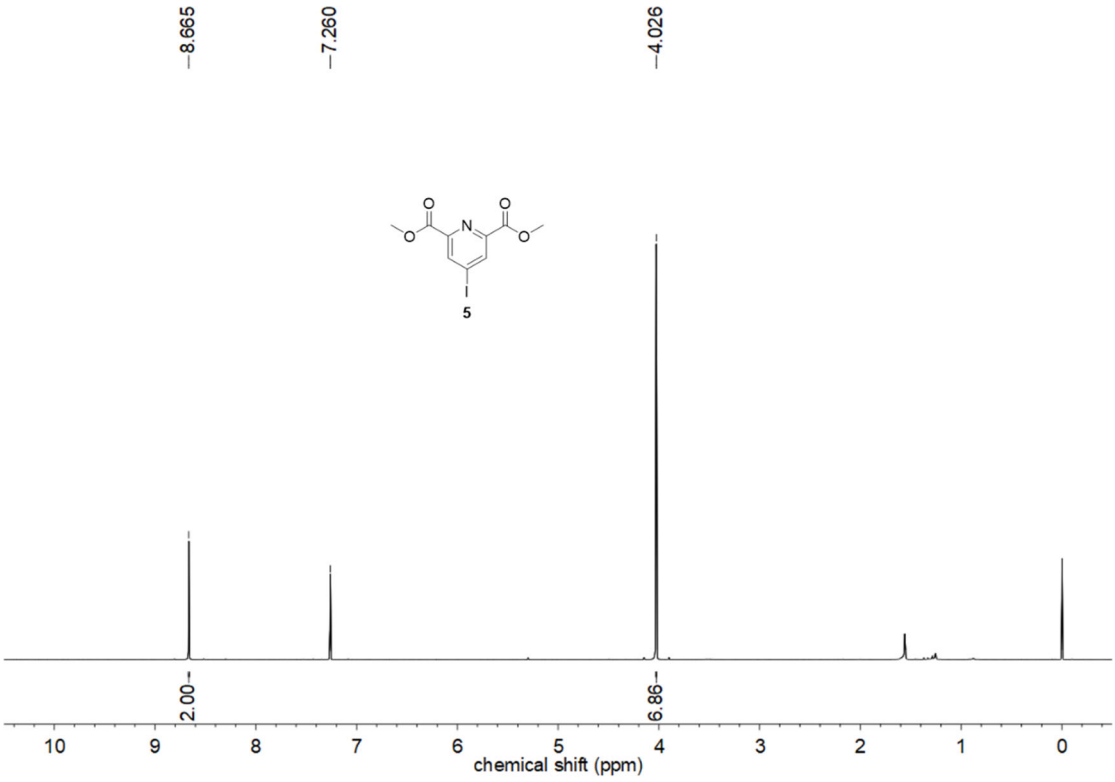


Fig. S10 ^{1}H NMR spectrum of compound **5** (600 MHz) in $CDCl_3$.

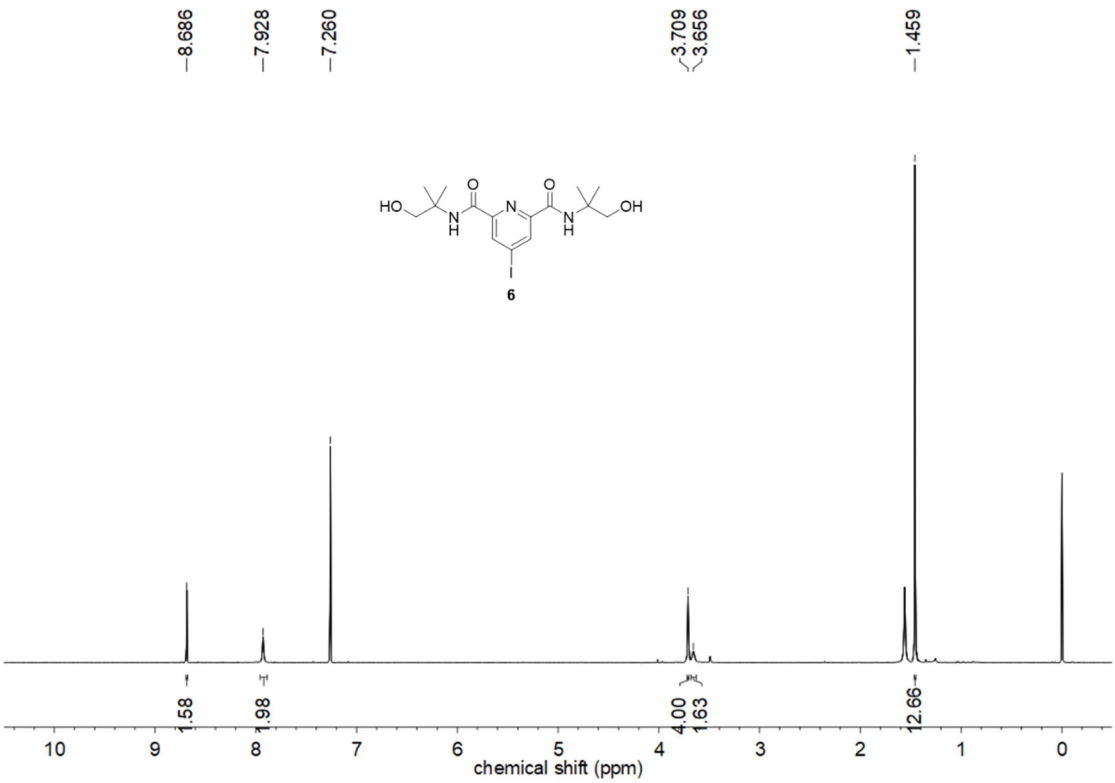


Fig. S11 ^{1}H NMR spectrum of compound **6** (600 MHz) in $CDCl_3$.

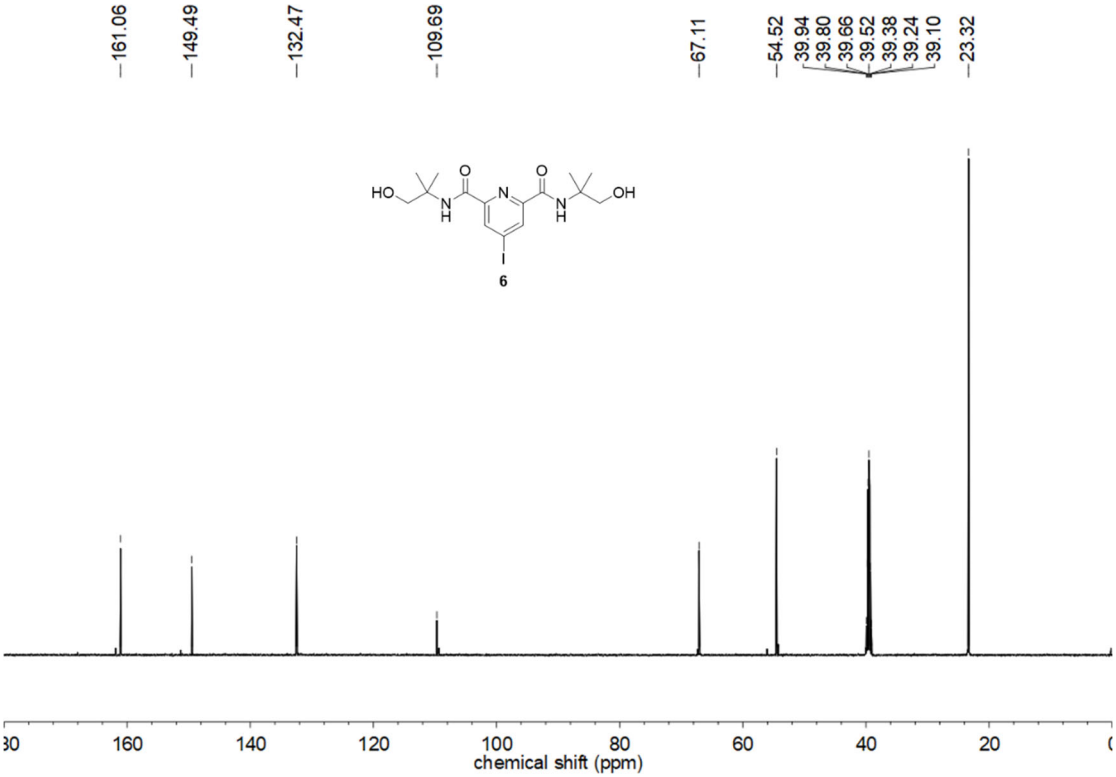


Fig. S12 ^{13}C NMR spectrum of compound **6** (125 MHz) in DMSO-d_6.

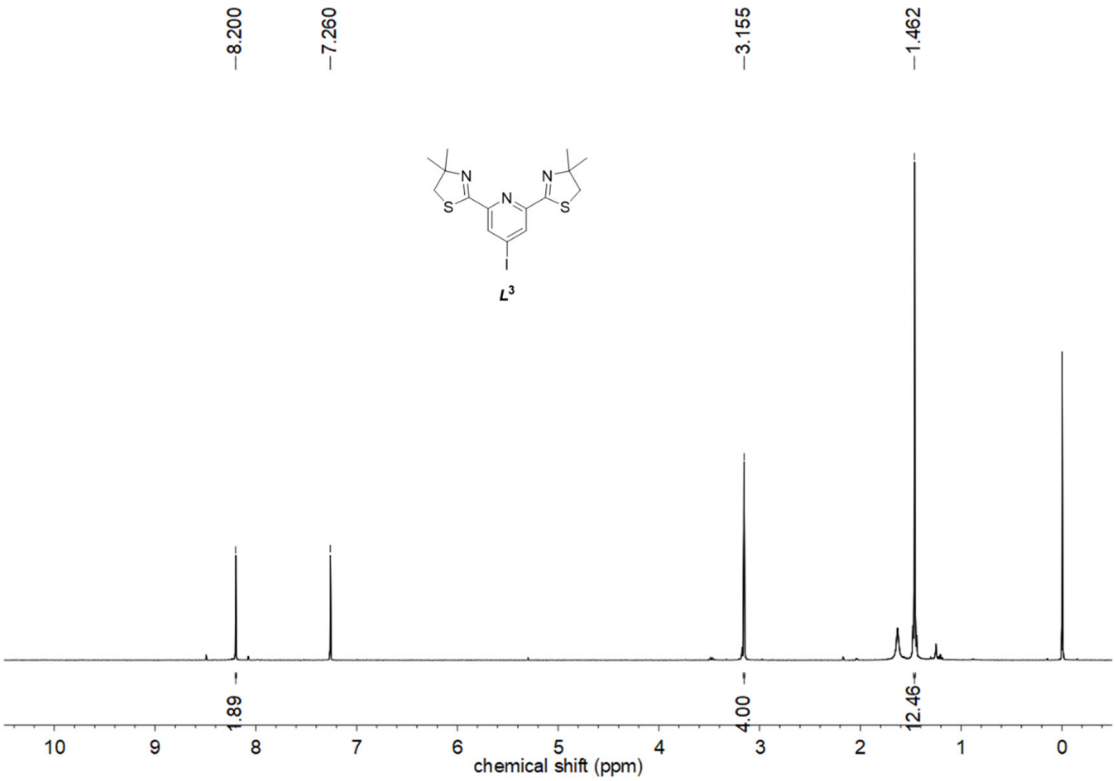


Fig. S13 ^{1}H NMR spectrum of compound $\boldsymbol{L^3}$ (600 MHz) in $CDCl_3$.

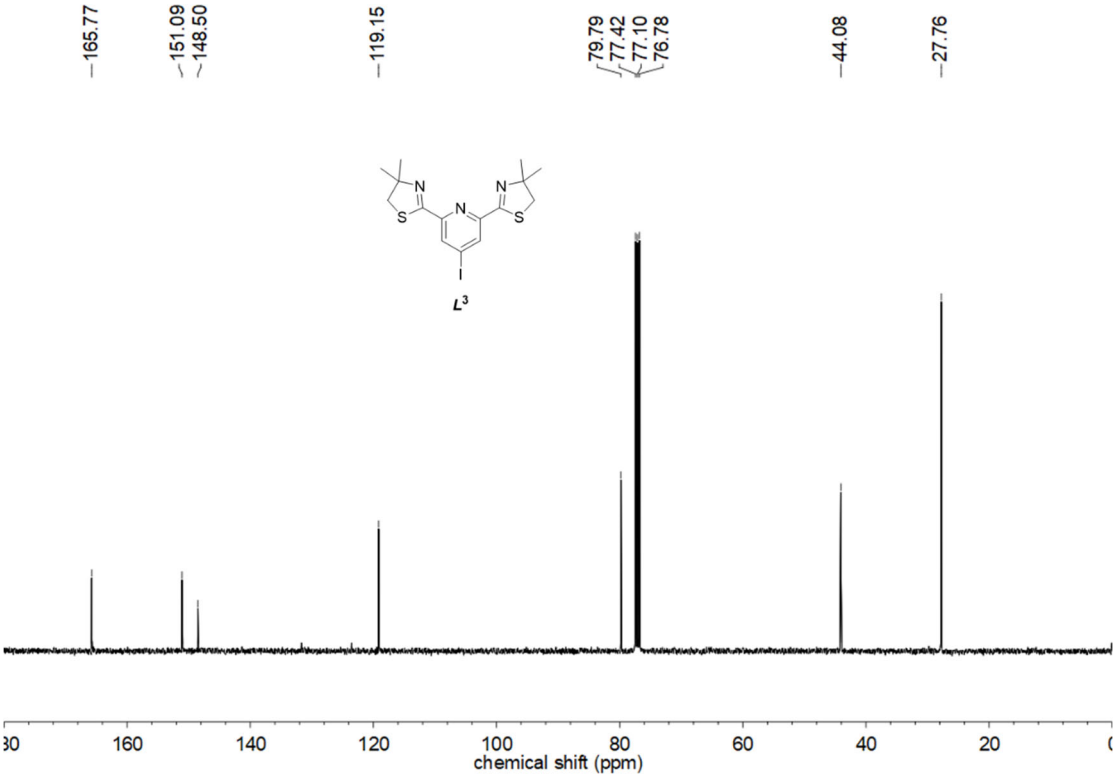


Fig. S14 ^{13}C NMR spectrum of compound $\boldsymbol{L^3}$ (125 MHz) in $CDCl_3$.

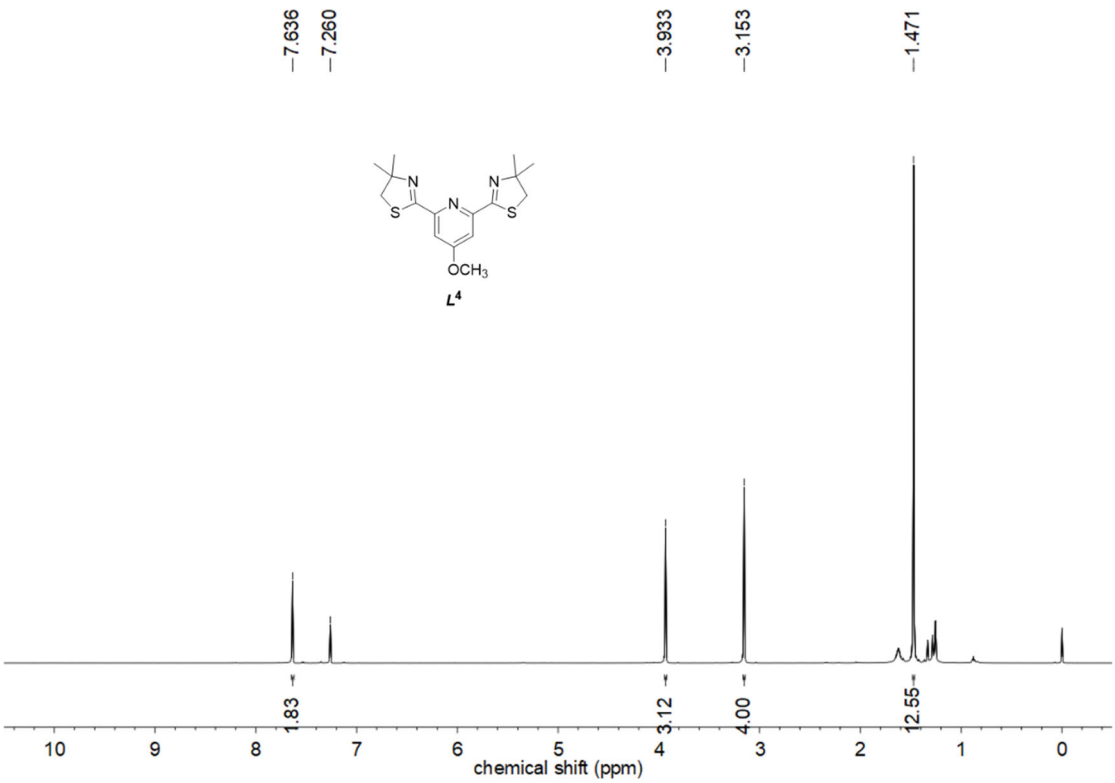


Fig. S15 ^{1}H NMR spectrum of compound ***L*^{4}** (600 MHz) in $CDCl_3$.

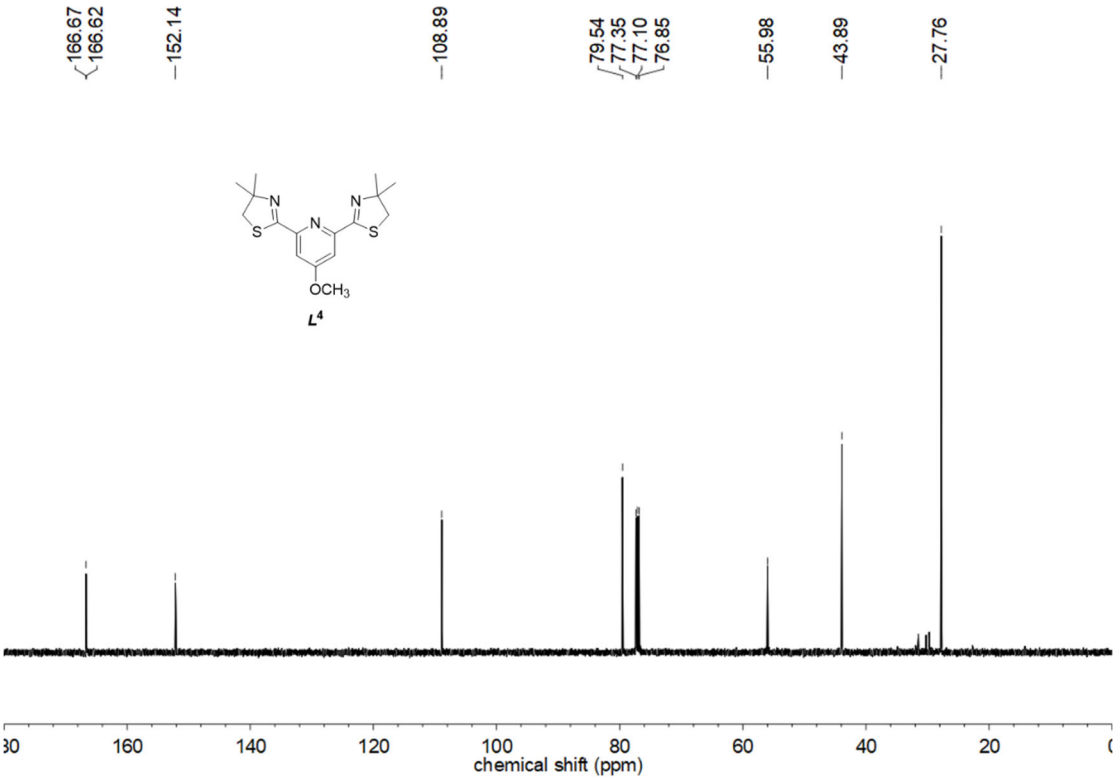


Fig. S16 ^{13}C NMR spectrum of compound ***L*^{4}** (125 MHz) in $CDCl_3$.

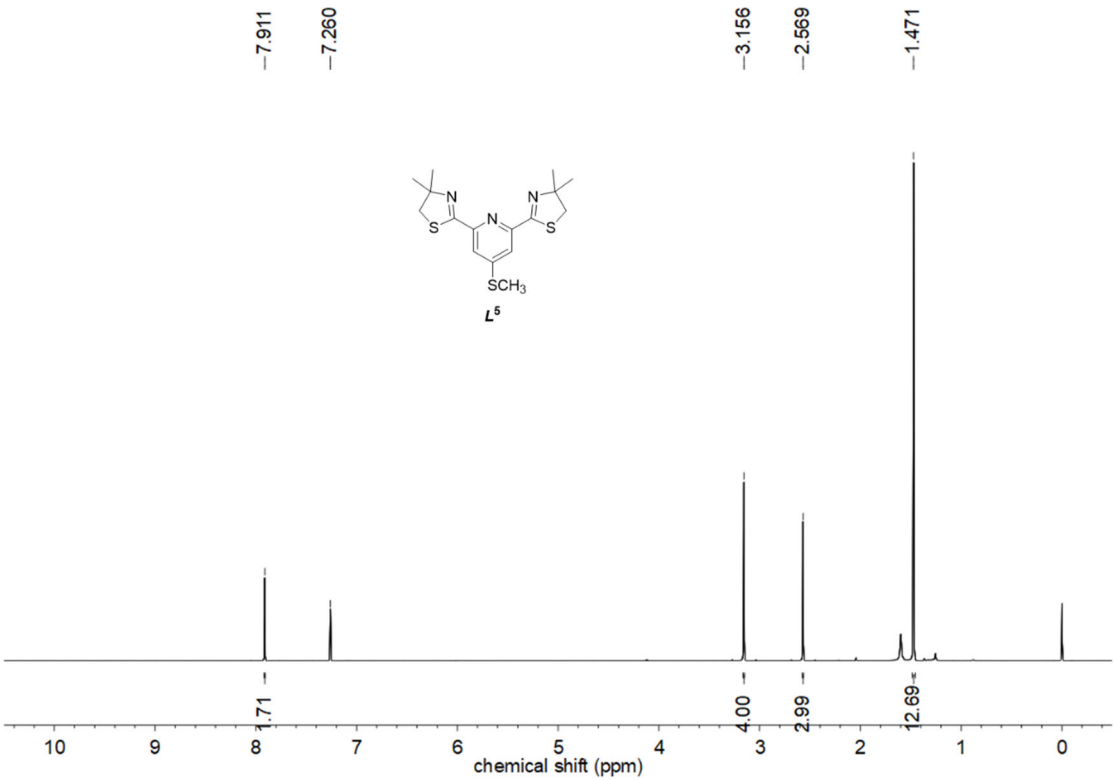


Fig. S17 ^{1}H NMR spectrum of compound ***L*^{5}** (600 MHz) in $CDCl_3$.

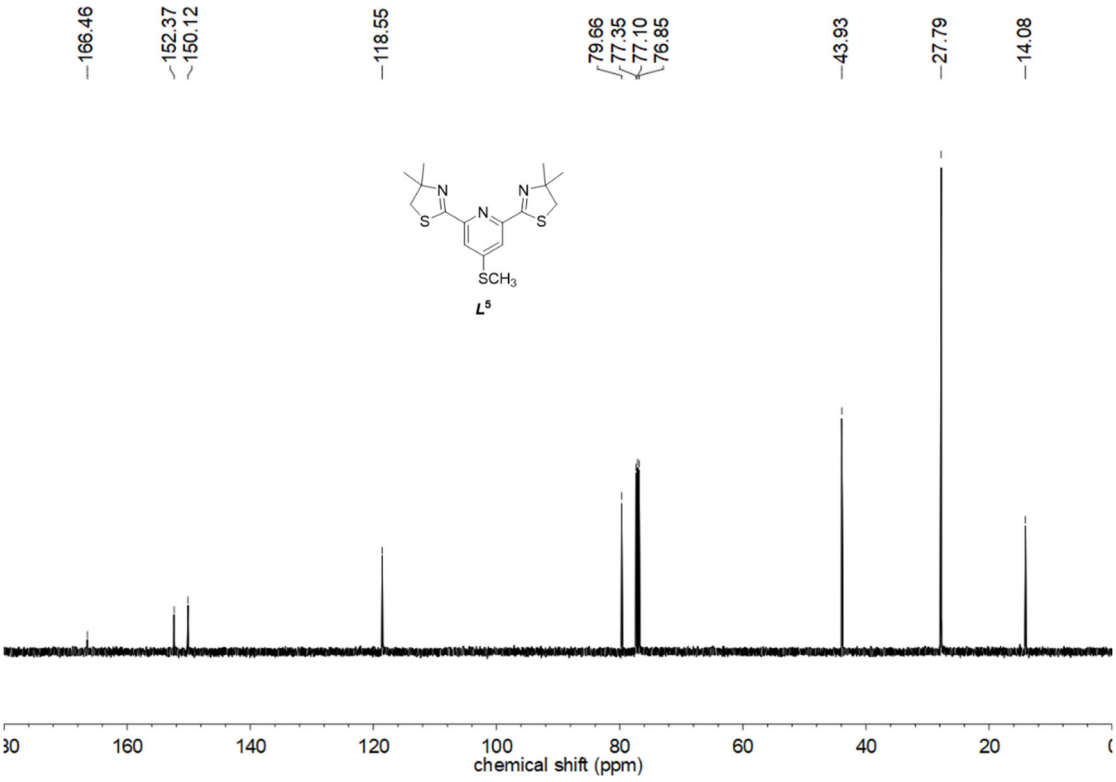


Fig. S18 ^{13}C NMR spectrum of compound ***L*^{5}** (125 MHz) in $CDCl_3$.

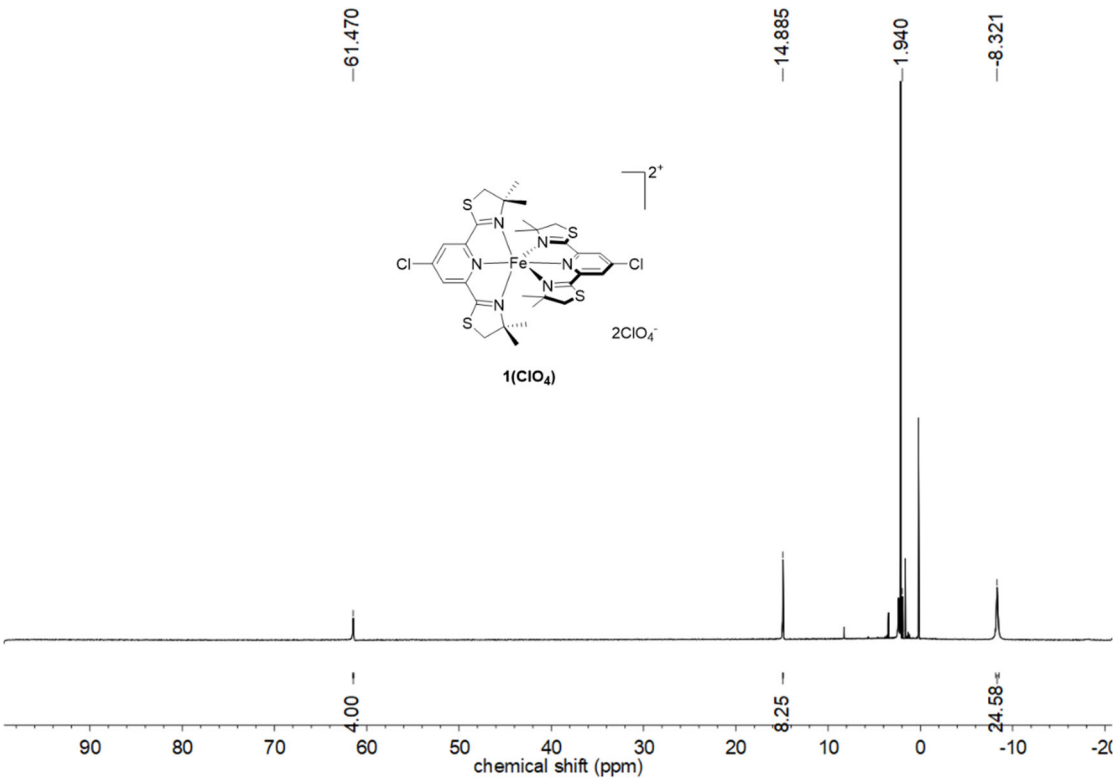


Fig. S19 ^{1}H NMR spectrum of **1(ClO$_4$)** (400 MHz) in CD_3CN at 293 K.

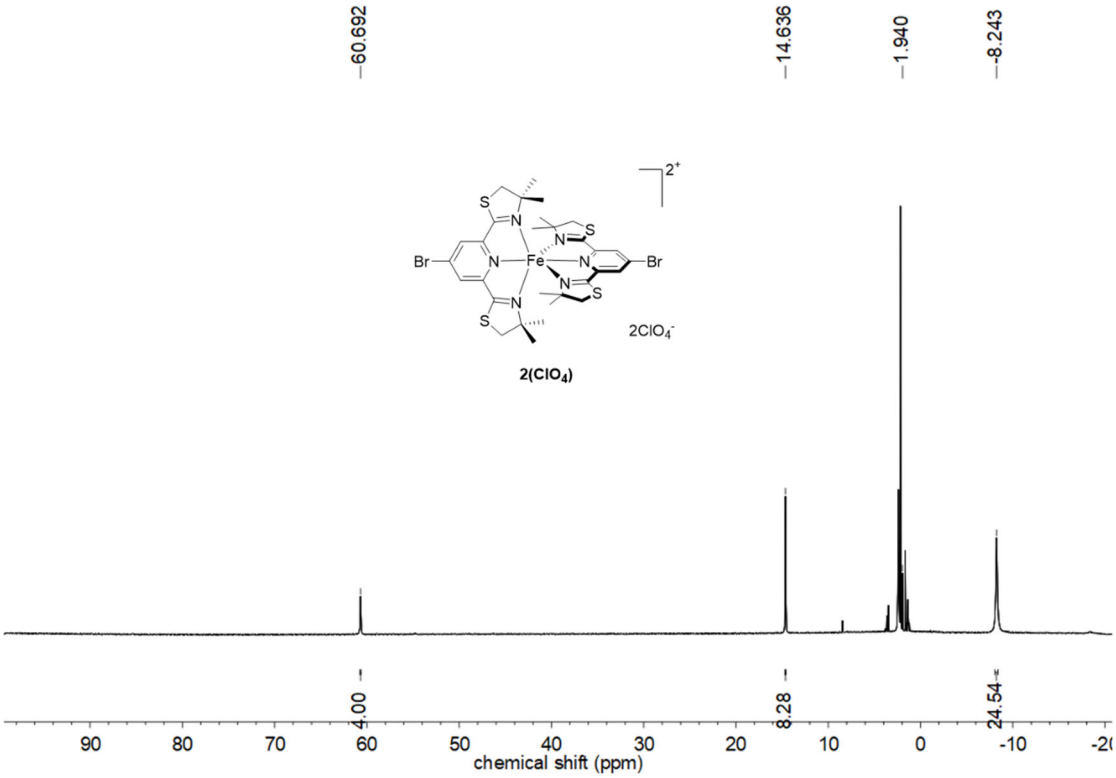


Fig. S20 ^{1}H NMR spectrum of **2(ClO$_4$)** (400 MHz) in CD_3CN at 293 K.

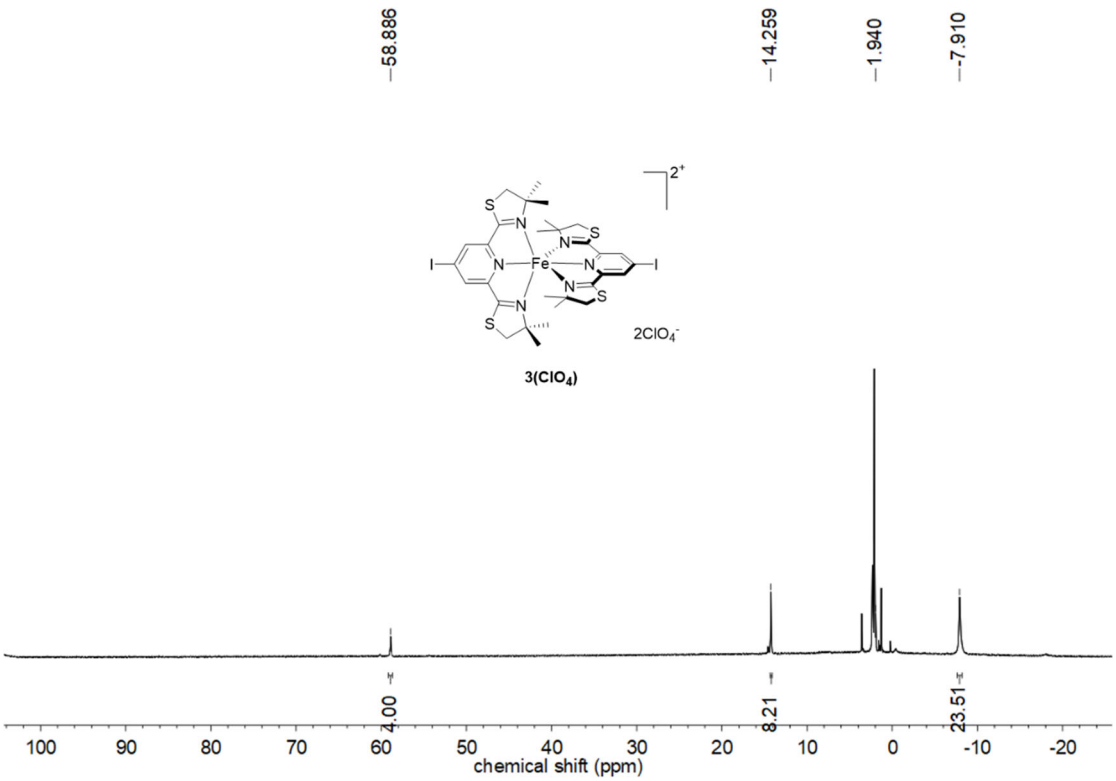


Fig. S21 ^{1}H NMR spectrum of **3(ClO$_4$)** (400 MHz) in CD$_3$CN at 293 K.

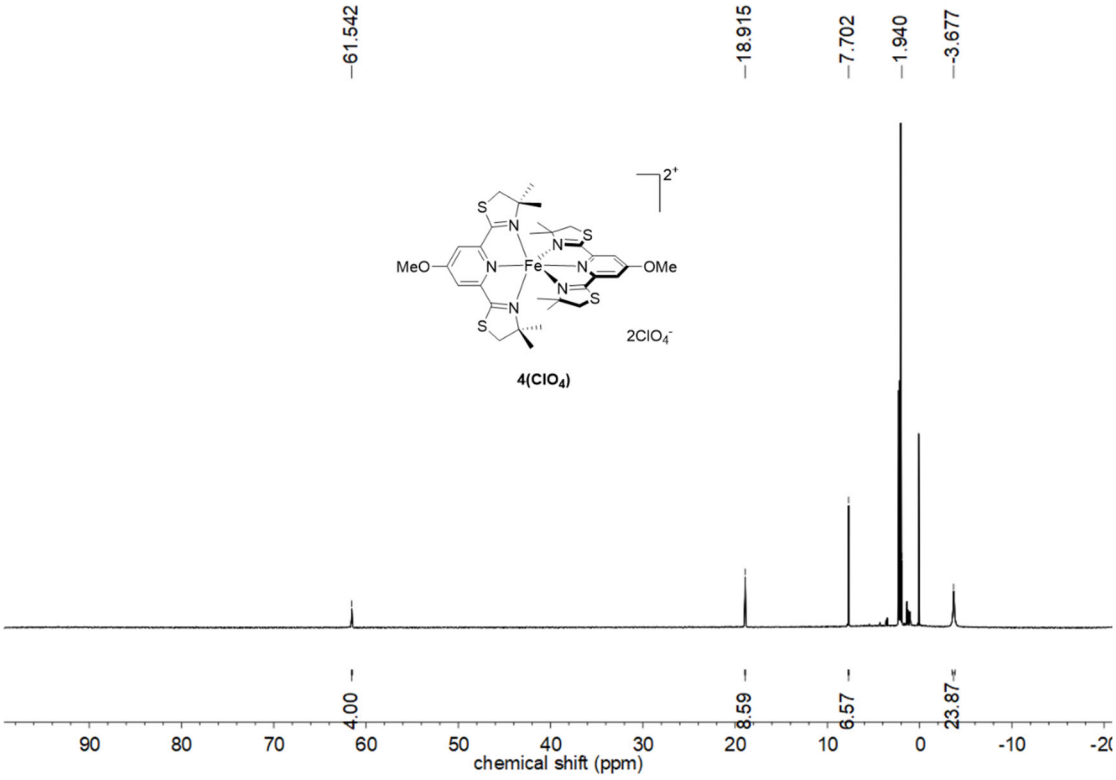


Fig. S22 ^{1}H NMR spectrum of **4(ClO$_4$)** (400 MHz) in CD$_3$CN at 293 K.

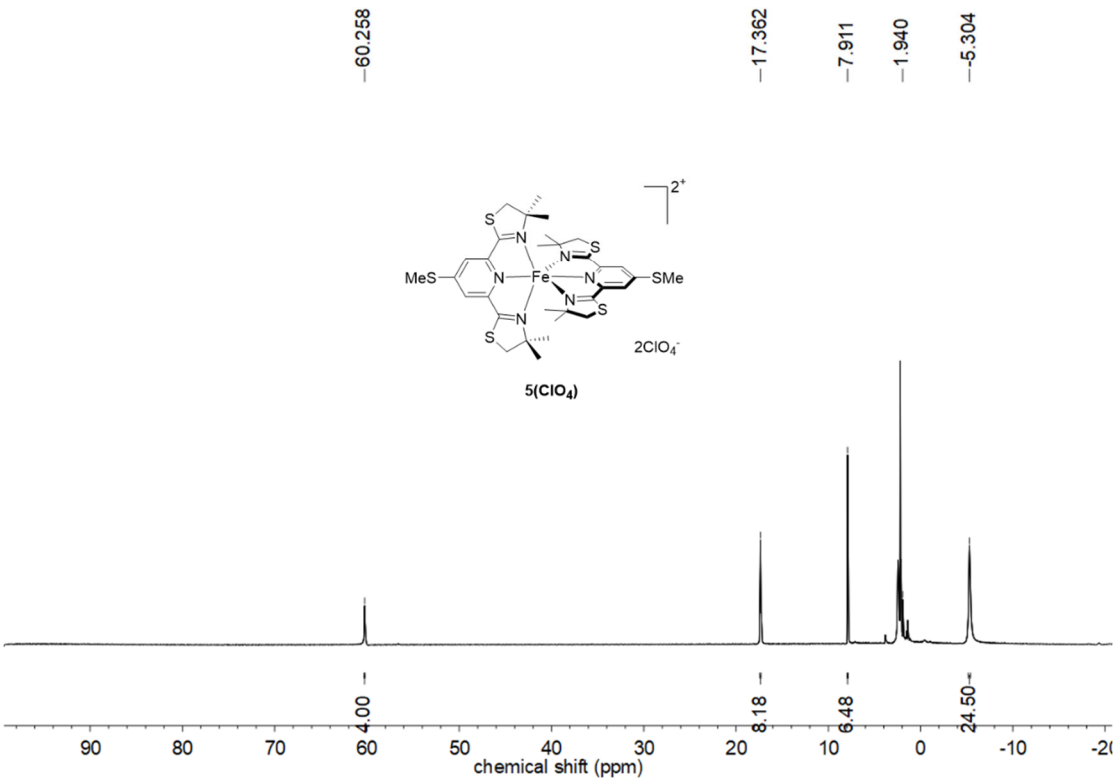


Fig. S23 ^{1}H NMR spectrum of **5(ClO$_4$)** (400 MHz) in CD_3CN at 293 K.

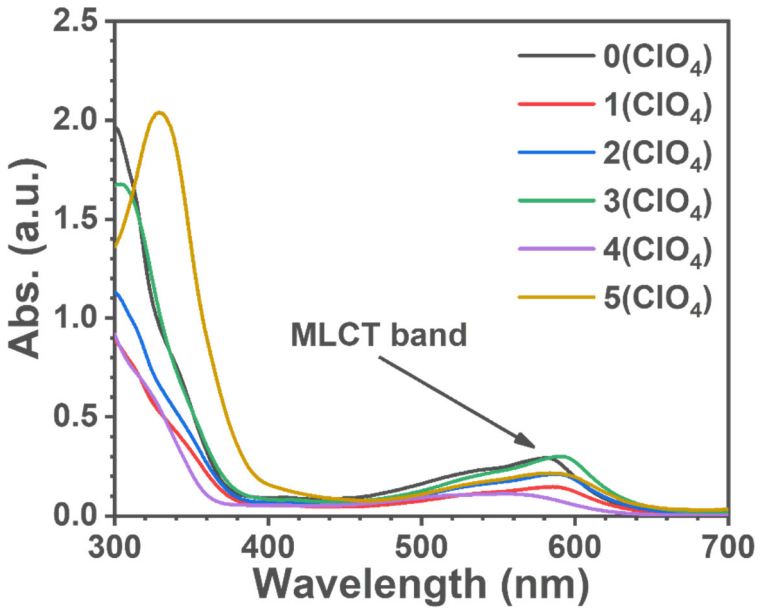


Fig. S24 The UV-vis spectra of six $[Fe(thio\text{-}pybox)_2]^{2+}(ClO_4^-)_2$ type complexes in the 1.0×10^{-5} M acetonitrile solution at ambient temperature. The MLCT absorption peaks are 581 nm for **0(ClO$_4$)**, 585 nm for **1(ClO$_4$)**, 588nm for **2(ClO$_4$)**, 591 nm for **3(ClO$_4$)**, 547 nm for **4(ClO$_4$)**, and 578 nm for **5(ClO$_4$)**, respectively.

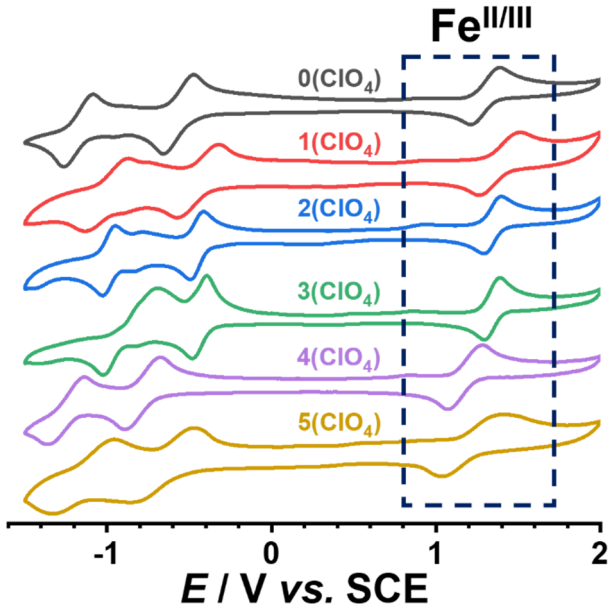


Fig. S25 Cyclic voltammograms of six complexes in 1 mM acetonitrile solution, which give the $E_{1/2}$ values of reversible $Fe^{II/III}$ redox process as 1.29 V for **0(ClO₄)**, 1.38 V for **1(ClO₄)**, 1.34 V for **2(ClO₄)**, 1.33 V for **3(ClO₄)**, 1.17 V for **4(ClO₄)**, and 1.19 V for **5(ClO₄)**, respectively. Reference is saturated calomel electrode (SCE) and the scan rate is 400 mV s^{-1}.

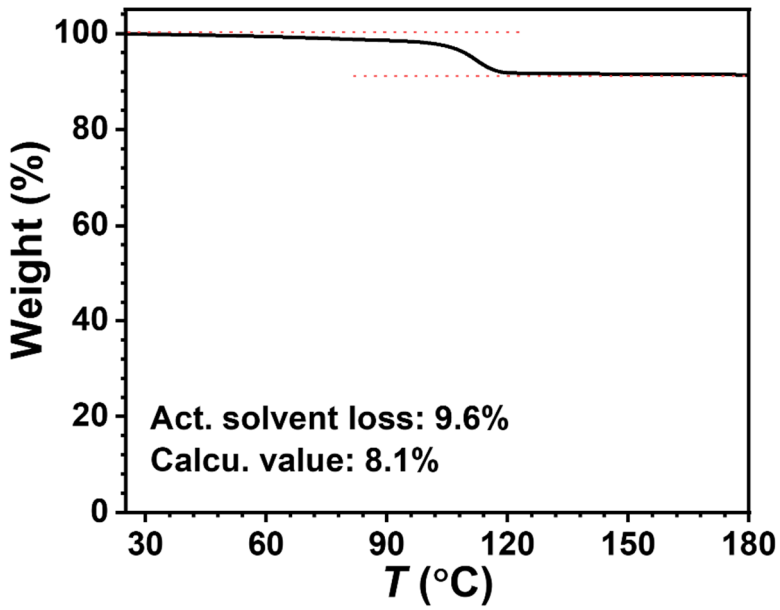


Fig. S26 The TGA trace of **1(ClO₄)** upon heating to 180 °C, and the weight loss indicates the removal of lattice solvents (about 2 acetonitrile per complex).

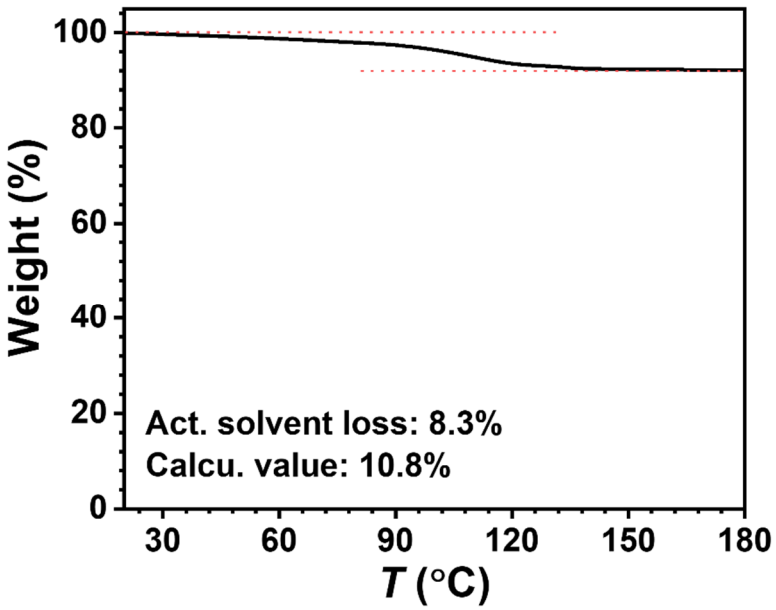


Fig. S27 The TGA trace of **2(ClO$_4$)** upon heating to 180 °C, and the weight loss indicates the removal of lattice solvents (about 1 acetonitrile and 1 ether per complex).

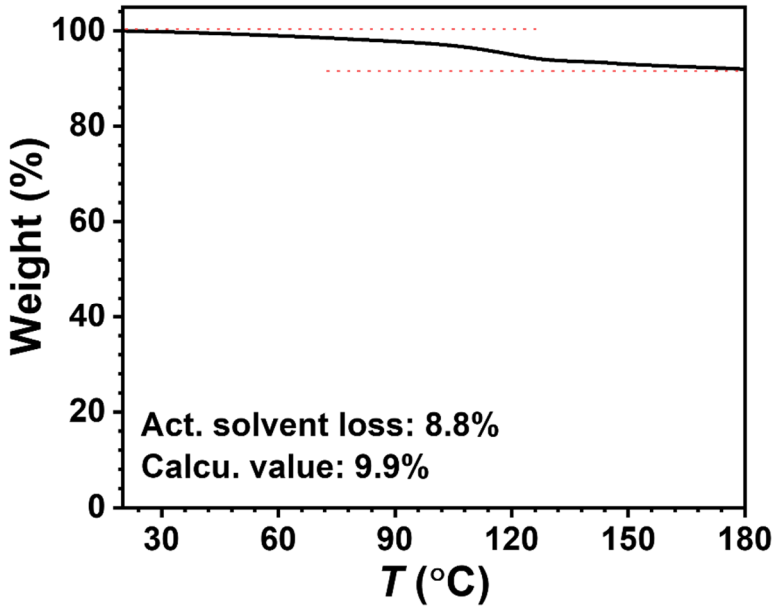


Fig. S28 The TGA trace of **3(ClO$_4$)** upon heating to 180 °C, and the weight loss indicates the removal of lattice solvent (about 3 acetonitrile per complex).

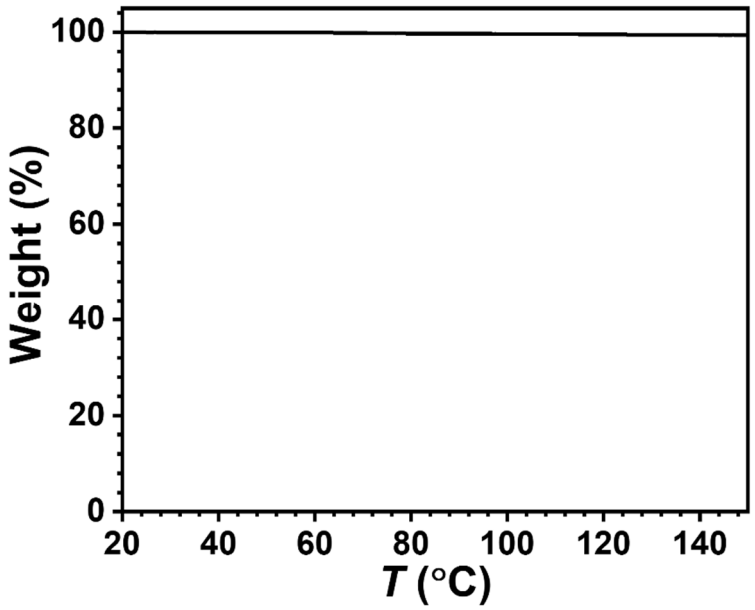


Fig. S29 The TGA trace of **4(ClO$_4$)** upon heating to 150 °C, and the no weight loss is consistent with that observed from single crystal X-ray structure.

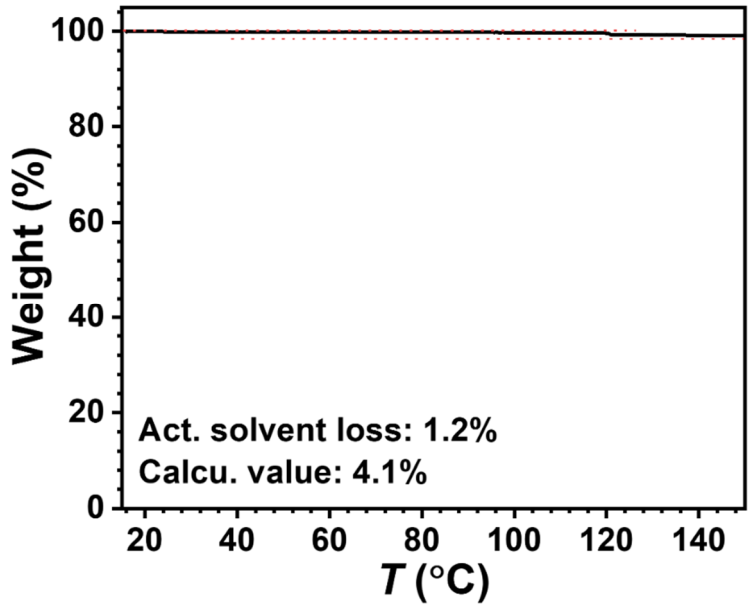


Fig. S30 The TGA trace of **5(ClO$_4$)** upon heating to 150 °C. According to the structure from single crystal X-ray structure, there is one acetonitrile lattice solvent per complex. The observed weight loss is considerably lower than the theoretical value which is due to the rapid solvent loss when the crystals are taken out from the mother liquid.

SI2 Structural details of the complexes

Table S1 Crystal data, data collection, solution, and refinement information of complexes in this work

	1(ClO_4)	**2(ClO_4)**	**3(ClO_4)**	**4(ClO_4)**	**5(ClO_4)**
Formula	$C_{31.50}H_{39}Cl_4FeN_{6.75}O_8S_4$	$C_{30}H_{36}Br_2Cl_2FeN_6O_8S_4$	$C_{30}H_{36}Cl_2FeI_2N_6O_8S_4$	$C_{32}H_{42}Cl_2FeN_6O_{10}S_4$	$C_{34}H_{45}Cl_2FeN_7O_8S_6$
formula weight	966.08	1023.46	1117.44	925.71	998.88
crystal system	*P*cca	*P*cca	*P*cca	$P2_1/c$	$P2_1/c$
space group	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
a, Å	19.0094(9)	19.0337(7)	19.1548(12)	9.9867(6)	20.1136(10)
b, Å	11.1022(6)	11.1991(3)	11.3494(7)	18.5365(14)	14.9411(6)
c, Å	20.9788(11)	21.0585(6)	21.0565(14)	21.3125(13)	14.0387(6)
α, deg	90	90	90	90	90
β, deg	90	90	90	92.538(2)	95.382(2)
γ, deg	90	90	90	90	90
V, $Å^3$	4427.5(4)	4488.8(2)	4577.6(5)	3941.5(4)	4200.3(3)
Z	4	4	4	4	4
T, K	120.0 (2)	120.0 (2)	153.0 (2)	120.0 (2)	120.0 (2)
F(000)	1989	2064	2208	1920	2072
D_C, g cm^{-3}	1.449	1.514	1.621	1.560	1.580
μ, mm^{-1}	0.823	2.470	2.025	0.793	0.843
λ, Å	0.71073	0.71073	1.34139	0.71073	0.71073
crystal size, mm^3	0.22 × 0.21 × 0.19	0.26× 0.24 × 0.22	0.13× 0.12 × 0.09	0.30 × 0.25 × 0.2	0.28 × 0.25 × 0.22
T_{min} and T_{max}	0.6483, 0.7456	0.5940, 0.7456	0.4055, 0.7512	0.6198, 0.7456	0.6532, 0.7456
θ_{min}, θ_{max}, deg	2.336, 27.296	2.321, 26.841	3.652, 56.151	2.397, 27.448	2.727, 26.271
no. total reflns.	28427	28828	28128	48511	30026
no. uniq. reflns, R_{int}	5075, 0.0451	5152, 0.0518	4697, 0.1043	8962, 0.0562	9645, 0.0641
no. obs. [$I \geq 2\sigma(I)$]	3771	3633	2792	7397	6046
no. params	268	247	248	510	536
*R*1 [$I \geq 2\sigma(I)$]	0.0724	0.0504	0.1145	0.0348	0.0667
*wR*2 (all data)	0.2256	0.1193	0.3706	0.0910	0.1795
S	1.035	1.086	1.297	1.023	1.033
$\Delta\rho^a$, e/ $Å^3$	1.923, -1.096	0.769, -1.260	2.592, -1.465	0.653, -0.519	1.123, -0.735
max. and mean Δ/σ^b	0.000, 0.000	0.001, 0.000	0.000, 0.000	0.001, 0.000	0.000, 0.000
CCDC	2141555	2141556	2141557	2141558	2141559

[a] Max and min residual density. [b] Max and mean shift/σ.

Table S2 Selected bond lengths (Å) for the single crystal structures of **1-5**

Fe1		Fe2		Fe3		Fe4		Fe5	
T (K)	120 K	*T* (K)	120 K	*T* / K	153 K	*T* / K	120 K	*T* / K	120 K
Fe-N1	2.233	Fe-N1	2.262	Fe-N1	2.266	Fe-N1	2.250	Fe-N1	2.289
Fe-N2	2.077	Fe-N2	2.077	Fe-N2	2.084	Fe-N2	2.083	Fe-N2	2.090
Fe-N3	2.262	Fe-N3	2.236	Fe-N3	2.227	Fe-N3	2.230	Fe-N3	2.234
Fe-N1’	2.233	Fe-N1’	2.262	Fe-N1’	2.266	Fe-N4	2.233	Fe-N4	2.228
Fe-N2’	2.077	Fe-N2’	2.077	Fe-N2’	2.084	Fe-N5	2.086	Fe-N5	2.087
Fe-N3’	2.262	Fe-N3’	2.236	Fe-N3’	2.227	Fe-N6	2.240	Fe-N6	2.265

Table S3 Summary of the structural parameters and spin state in the family of compounds reported in this work.

Entry	*T* (K)	Σ (°)	θ (°)	ϕ (°)	Fe–N_{av} (Å)	*S* (O_h)	*S* (T_h)	Spin state	μ_{rms}
Fe1	120	137.855	85.627	174.599	2.191	4.942	6.923	HS	0.402
Fe2	120	127.461	85.581	174.049	2.192	4.990	6.925	HS	0.415
Fe3	153	139.921	85.477	173.627	2.192	5.055	6.900	HS	0.472
Fe4	120	139.991	88.956	174.552	2.187	5.087	6.586	HS	0.294
Fe5	120	141.881	89.432	171.709	2.199	5.263	6.494	HS	0.214

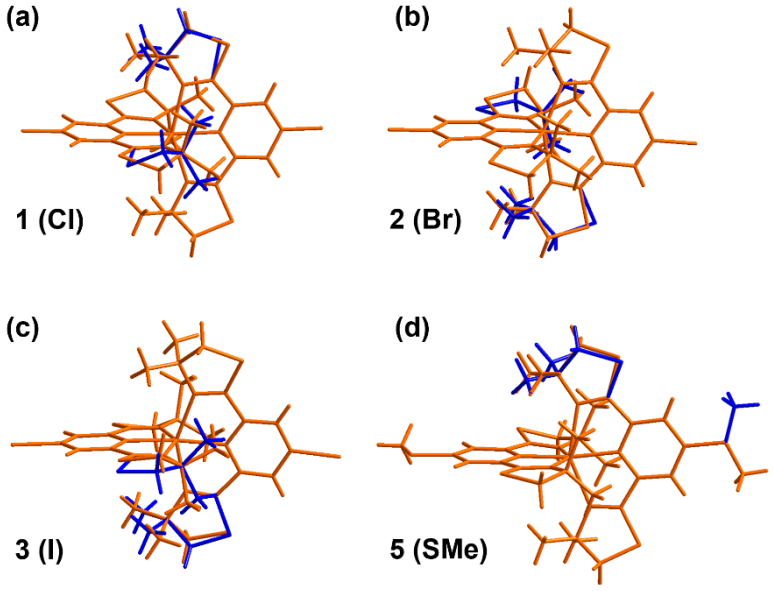


Fig. S31 The position disorder in complex cation of (a) **1(ClO$_4$)**, (b) **2(ClO$_4$)**, (c) **3(ClO$_4$)**, and **5(ClO$_4$)**.

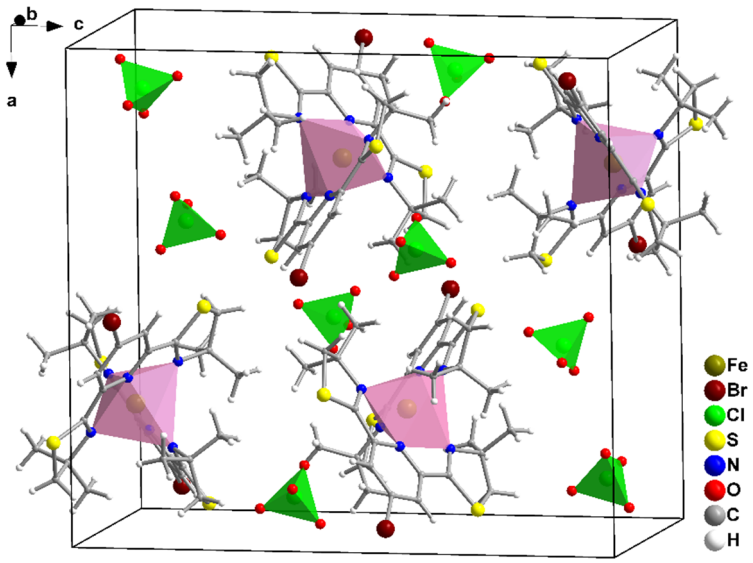


Fig. S32 View of the packing diagram of **2(ClO$_4$)** in a unit cell, the lattice solvents are omitted for clarity.

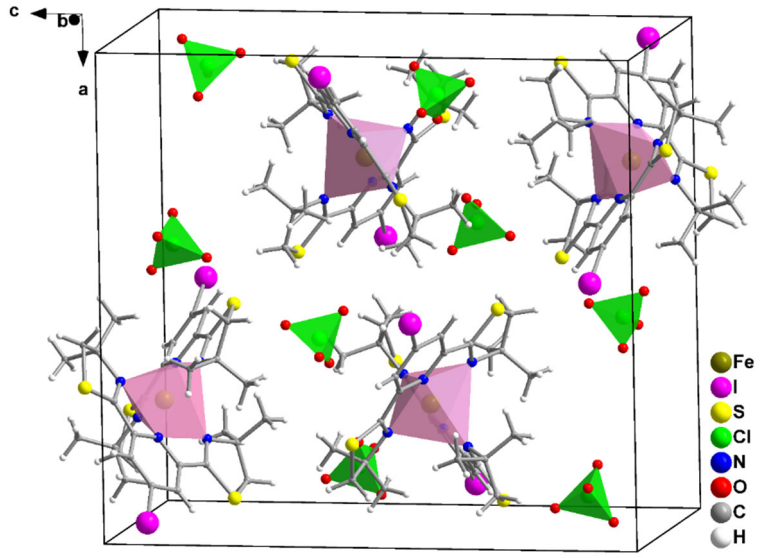


Fig. S33 View of the packing diagram of **3(ClO$_4$)** in a unit cell, the lattice solvents are omitted for clarity.

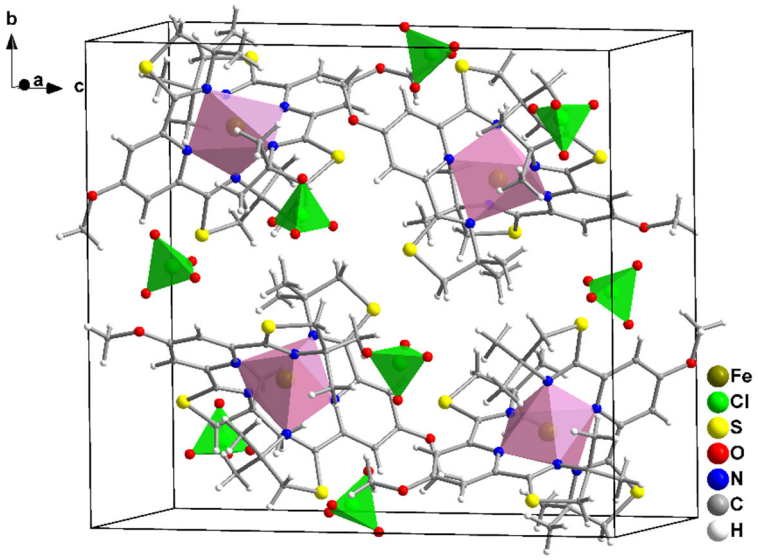


Fig. S34 View of the packing diagram of **4(ClO$_4$)** in a unit cell, the lattice solvents are omitted for clarity.

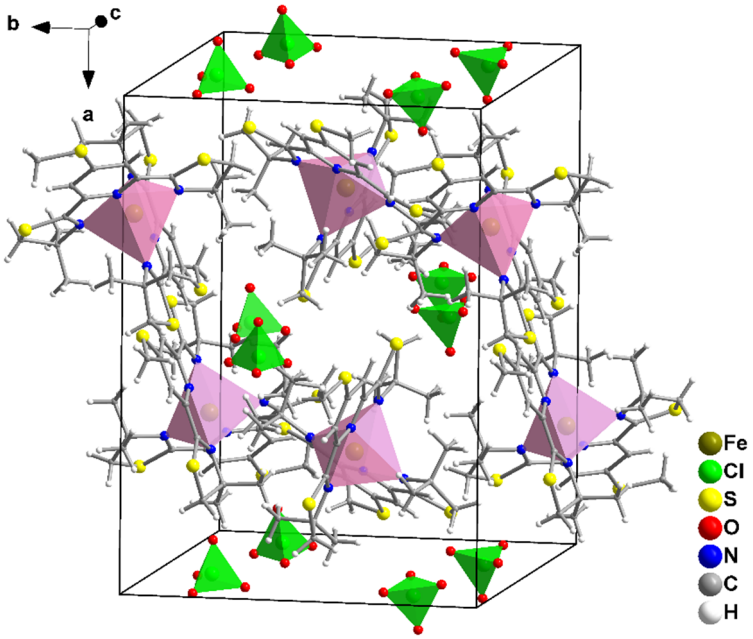


Fig. S35 View of the packing diagram of **5(ClO$_4$)** in a unit cell, the lattice solvents are omitted for clarity.

SI3 Supplementary magnetic properties

SI3.1 Solid-state magnetic properties

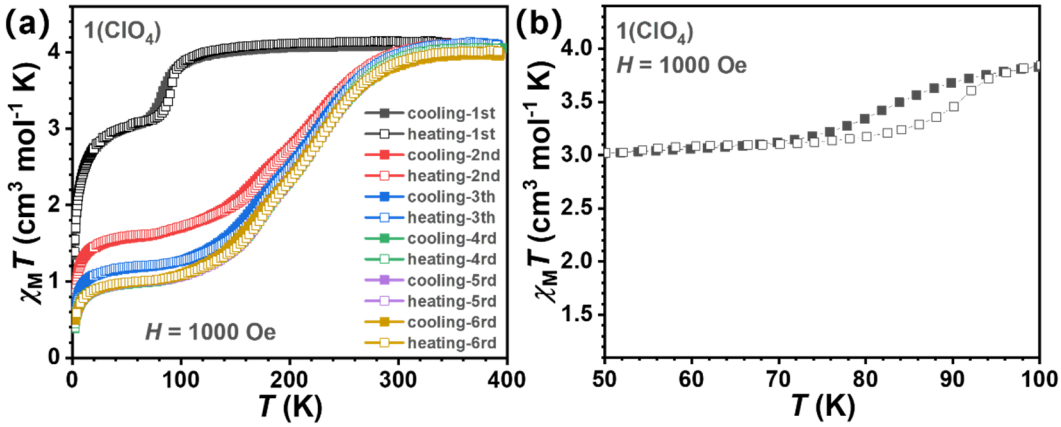


Fig. S36 The complete measurement scanning of variable-temperature susceptibilities for **1(ClO$_4$)**, which shows the lattice solvent-dependent spin transition behavior.

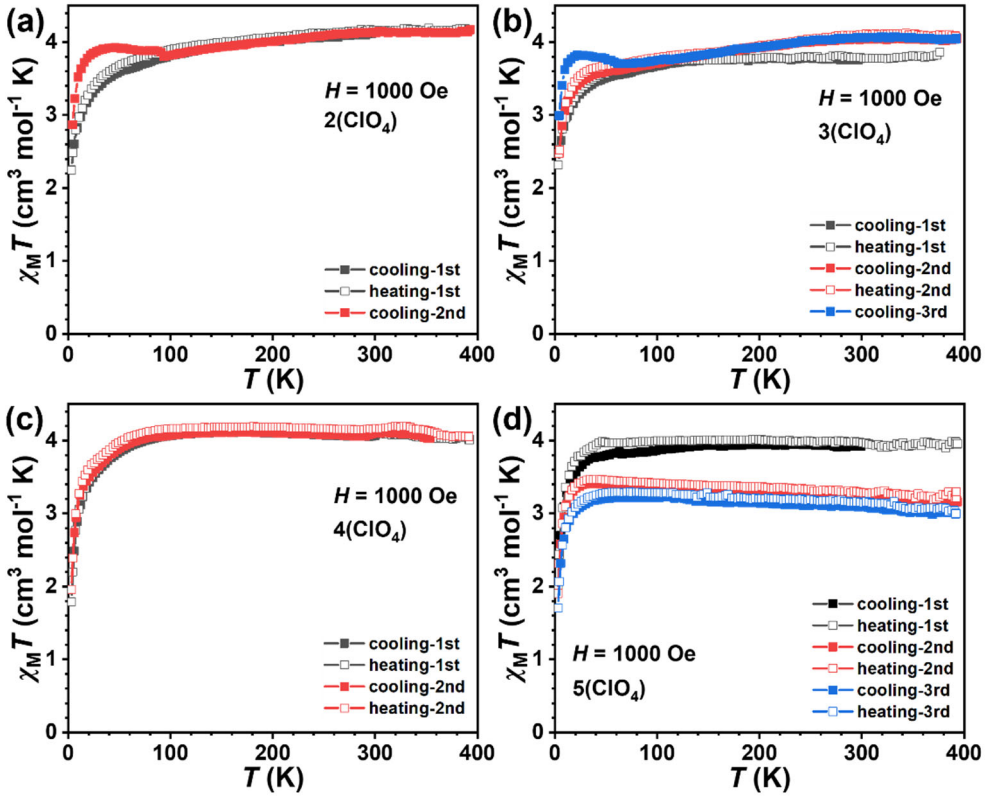


Fig. S37 Temperature dependence of $\chi_M T$ for (a) **2(ClO$_4$)**, (b) **3(ClO$_4$)**, (c) **4(ClO$_4$)**, and (d) **5(ClO$_4$)** upon successive scanning.

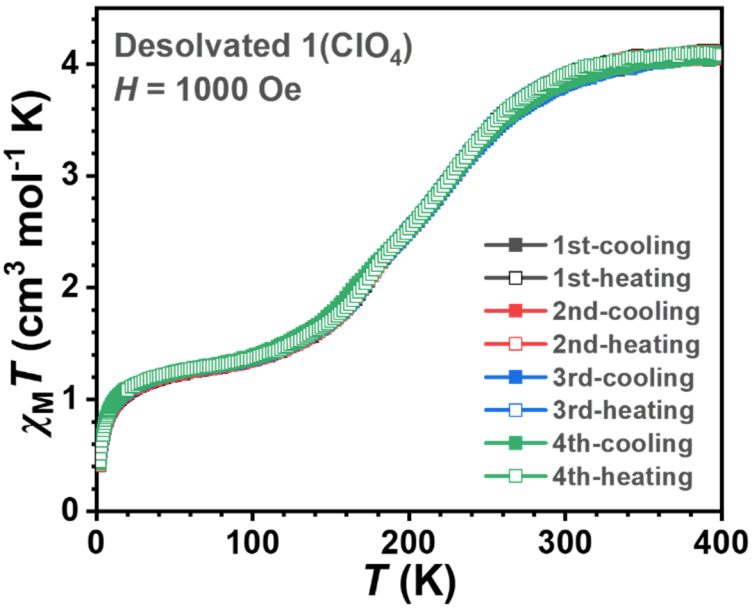


Fig. S38 Temperature dependence of $\chi_M T$ for desolvated **1(ClO$_4$)** upon successive four scanning cycles.

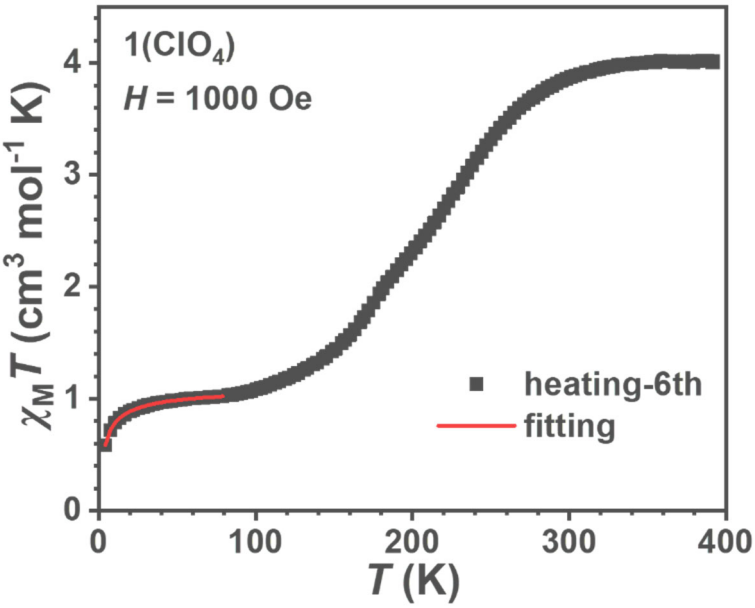


Fig. S39 Experimental dc magnetic data (plot, the 6th heating semi-cycle) together with fitting curves using program PHI (solid red line) for complex **1(ClO$_4$)**. Fitting parameters: $S = 2$, $g = 2.32$, $D = -13.14$ cm^{-1}, $E = 4.83$ cm^{-1}.

SI3.2 Solution-state magnetic properties

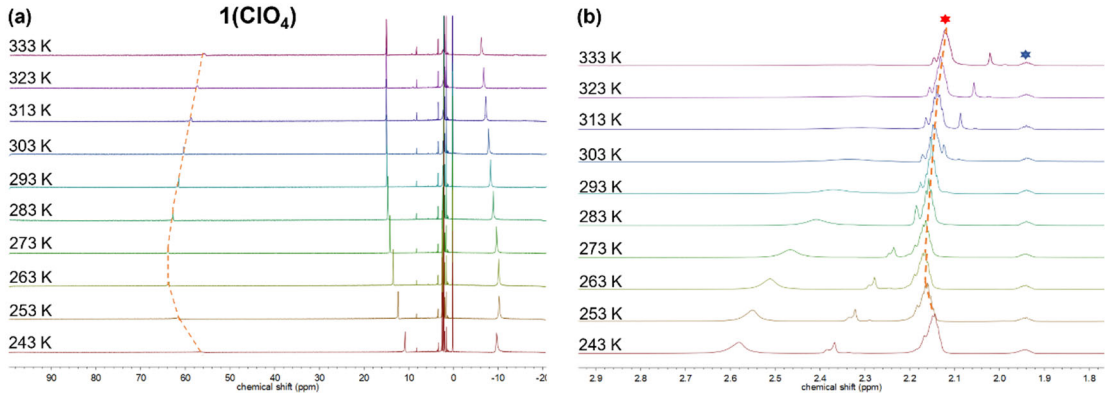


Fig. S40 (a) Stacked spectra, obtained by the Evans' ^{1}H NMR method, from 243 to 333 K for **1(ClO$_4$)** (5.0×10^{-3} mol L^{-1}) in CD_3CN (400 MHz); (b) The enlarged region of solvent residual peaks (* represent the solvent residual signals).

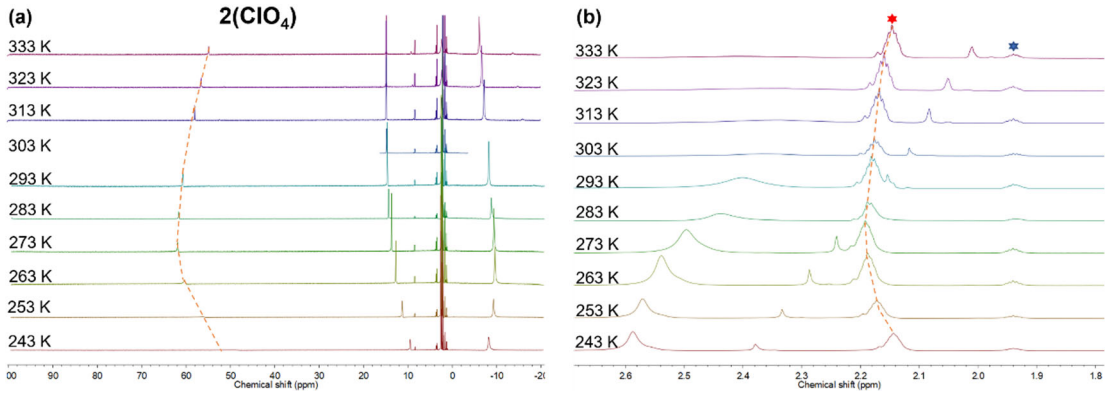


Fig. S41 (a) Stacked spectra, obtained by the Evans' ^{1}H NMR method, from 243 to 333 K for **2(ClO$_4$)** (5.0×10^{-3} mol L^{-1}) in CD_3CN (400 MHz); (b) The enlarged region of solvent residual peaks (* represent the solvent residual signals).

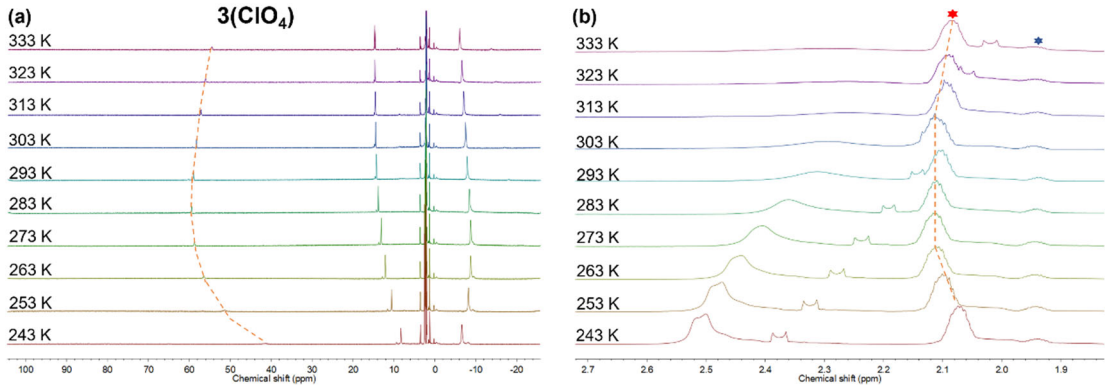


Fig. S42 (a) Stacked spectra, obtained by the Evans' ^{1}H NMR method, from 243 to 333 K for **3(ClO$_4$)** (5.0×10^{-3} mol L^{-1}) in CD_3CN (400 MHz); (b) The enlarged region of solvent residual peaks (* represent the solvent residual signals).

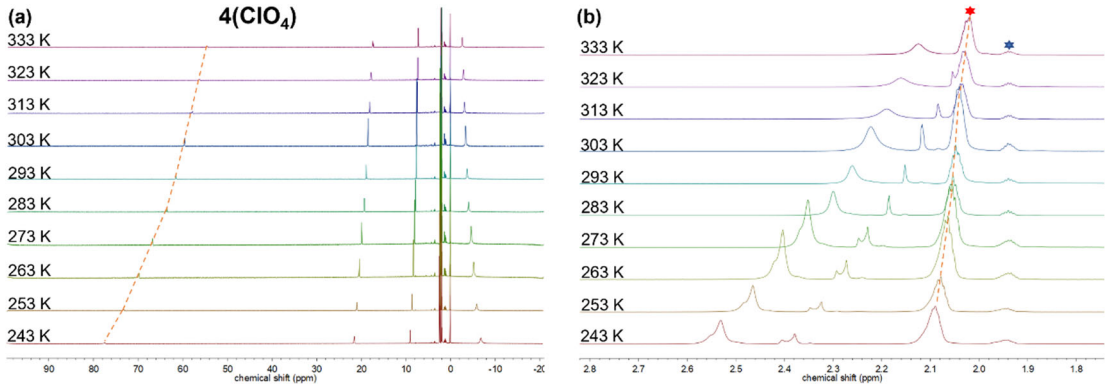


Fig. S43 (a) Stacked spectra, obtained by the Evans' ^{1}H NMR method, from 243 to 333 K for **4(ClO$_4$)** (5.0×10^{-3} mol L^{-1}) in CD_3CN (400 MHz); (b) The enlarged region of solvent residual peaks (* represent the solvent residual signals).

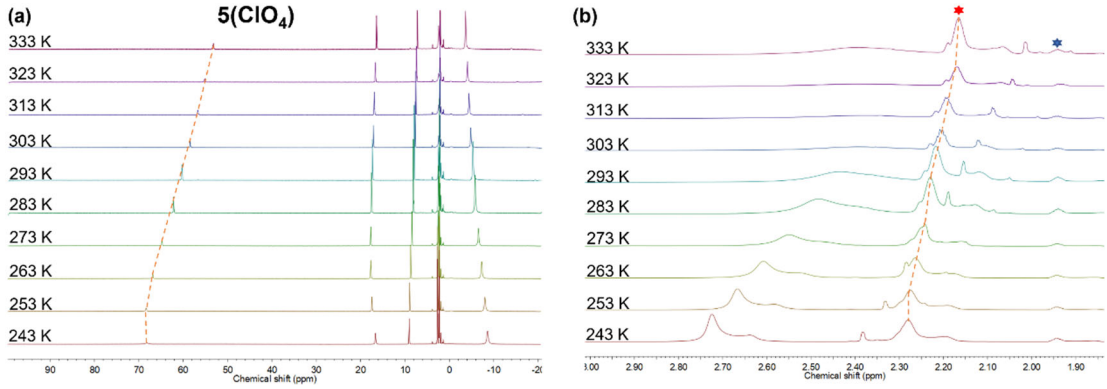


Fig. S44 (a) Stacked spectra, obtained by the Evans' ^{1}H NMR method, from 243 to 333 K for **5(ClO$_4$)** (5.0×10^{-3} mol L^{-1}) in CD_3CN (400 MHz); (b) The enlarged region of solvent residual peaks (* represent the solvent residual signals).

Table S4 The calculated $\chi_M T$ values of six complexes at multiple temperatures according to the Evans' method (equation 1).

T (K)	243	253	263	273	283	293	303	313	323	333
0(ClO$_4$)	2.435	2.903	3.345	3.756	3.814	3.815	3.848	3.851	/	/
1(ClO$_4$)	3.040	3.378	3.584	3.705	3.749	3.781	3.853	3.843	3.840	3.847
2(ClO$_4$)	2.883	3.253	3.514	3.701	3.799	3.833	3.883	3.892	3.885	3.855
3(ClO$_4$)	2.553	3.072	3.417	3.606	3.702	3.757	3.849	3.845	3.846	3.837
4(ClO$_4$)	3.867	3.872	3.838	3.850	3.865	3.840	3.827	3.859	3.844	3.864
5(ClO$_4$)	3.871	3.880	3.883	3.886	3.880	3.873	3.884	3.891	3.874	3.886

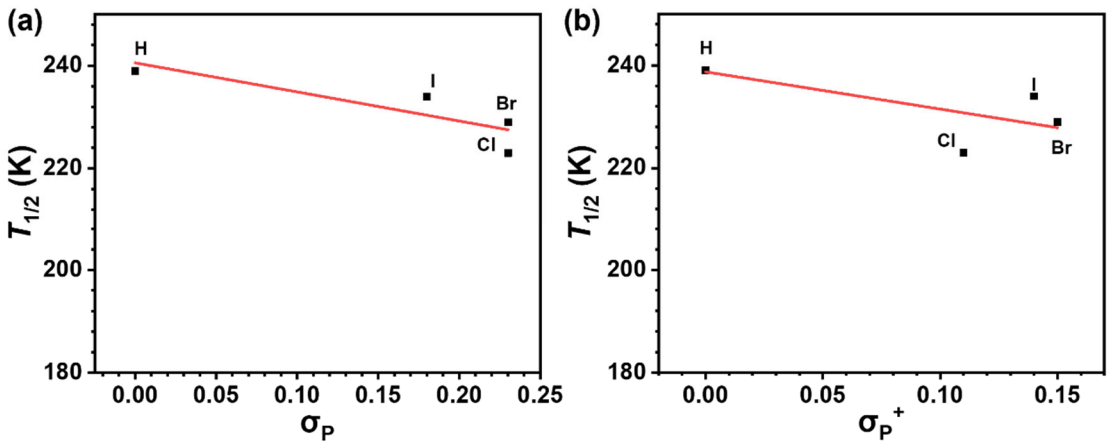


Fig. S45 Plots of $T_{1/2}$ *vs*. substituent Hammett parameters (a) σ_P and (b) σ_P^+. σ_P^+ is a modified Hammett parameter that accounts for conjugation of the ligand substituents with a positively charged reaction center.[1]

SI4 The details of DFT calculations

SI4.1 Cartesian coordinates for the 12 optimized geometries

Table S5 Cartesian coordinates for the optimized geometries of **0(ClO_4)** in singlet state.

Atom	x	y	z	Atom	x	y	z
Fe	-0.011343	0.004092	0.001225	H	3.607129	2.522174	-1.952734
N	1.403768	1.44339	0.465335	H	2.099154	1.713908	-2.334554
N	-0.03566	-0.100256	1.898921	H	0.528515	3.379559	-1.200702
N	-1.417459	-1.486356	0.270912	H	1.9929	4.362635	-1.208545
N	1.466208	-1.379358	-0.425143	H	1.073007	4.17162	0.287782
N	0.031095	0.12911	-1.894167	H	3.738981	3.847235	0.502574
N	-1.521117	1.392622	-0.312516	H	4.26928	2.155285	0.572201
C	2.256144	2.42924	-0.283924	H	1.430054	1.300102	4.582772
C	1.571217	1.554443	1.745733	C	-0.062909	-0.257679	4.649696
C	0.759396	0.704753	2.619888	H	-1.548339	-1.800728	4.375316
C	-0.840991	-0.983751	2.508576	H	-3.666134	-3.950744	-0.029851
C	-1.616332	-1.741514	1.525251	H	-4.258352	-2.295175	0.201759
C	-2.210879	-2.407023	-0.608357	H	-0.43417	-3.196498	-1.586114
C	2.430791	-2.228198	0.352176	H	-1.852612	-4.23623	-1.704451
C	1.656383	-1.501052	-1.701184	H	-0.960073	-4.144981	-0.183092
C	0.869033	-0.650275	-2.594781	H	-3.32595	-0.784078	-1.537001
C	-0.775963	0.996749	-2.523401	H	-3.489631	-2.347298	-2.338233
C	-1.653945	1.677407	-1.569252	H	-2.009422	-1.427187	-2.542554
C	-2.46245	2.1969	0.537145	H	4.162234	-0.980377	-0.112977
C	2.851904	1.838538	-1.556213	H	4.322271	-1.941522	1.359339
C	1.405861	3.656888	-0.615387	H	3.297265	-0.506932	1.361462
C	3.409154	2.821242	0.665233	H	1.602437	-2.129189	2.36335
S	2.761639	2.660065	2.363412	H	2.470654	-3.609163	2.000191
C	0.776144	0.651172	4.010803	H	0.856628	-3.370469	1.330781
C	-0.886304	-1.089195	3.894444	H	2.234134	-4.219699	-0.570948
S	-2.788352	-2.941189	1.979999	H	3.91231	-3.670471	-0.39292
C	-3.377464	-2.938531	0.252848	H	1.60319	-1.230536	-4.538727
C	-1.304503	-3.562399	-1.04117	H	0.108612	0.324258	-4.641771
C	-2.785656	-1.688563	-1.82326	H	-1.419398	1.830879	-4.406288
C	3.621415	-1.355871	0.75911	H	-0.831946	3.046581	1.697944
C	1.79046	-2.863703	1.580137	H	-2.34928	3.940464	1.806314
C	2.892283	-3.349177	-0.603144	H	-1.357968	4.06829	0.34975
S	2.815917	-2.654472	-2.288954	H	-3.526596	0.438794	1.260236

C	0.930053	-0.587007	-3.983179	H	-3.895867	1.935156	2.117708
C	-0.760549	1.127999	-3.908606	H	-2.373847	1.121356	2.429074
S	-2.875098	2.807419	-2.07114	H	-3.958533	3.678225	-0.098135
C	-1.698761	3.382983	1.1277	H	-4.430509	2.003536	-0.439755
C	-3.092559	1.362888	1.646383	H	-0.073772	-0.319194	5.732282
C	-3.588578	2.697382	-0.396446	H	0.138904	0.401299	-5.722988
H	3.338696	0.880358	-1.36886				

Table S6 Cartesian coordinates for the optimized geometries of **0(ClO_4)** in quintet state.

Atom	x	y	z	Atom	x	y	z
Fe	-0.009506	0.001693	-0.000608	H	4.002327	2.10548	1.852378
N	1.470495	-0.20431	1.722933	H	2.524396	2.273038	0.912613
N	-0.289702	-1.940117	0.749246	H	0.952839	2.140443	2.902038
N	-1.61729	-0.906189	-1.299423	H	2.430214	2.260609	3.862828
N	1.572539	-0.196563	-1.613733	H	1.272057	0.964542	4.18817
N	0.306628	1.952496	-0.70331	H	3.864724	0.202246	4.025468
N	-1.480697	1.298283	1.149888	H	4.326592	-0.513924	2.469433
C	2.472592	0.680639	2.386353	H	0.907495	-4.005644	3.116838
C	1.433531	-1.377486	2.253446	C	-0.654014	-4.49448	1.713449
C	0.451304	-2.374672	1.774001	H	-2.165744	-4.673642	0.186481
C	-1.202661	-2.73935	0.185477	H	-3.992952	-1.526218	-3.569598
C	-1.933851	-2.097668	-0.928087	H	-4.506281	-0.897742	-1.992789
C	-2.400241	-0.45639	-2.484612	H	-0.5869	-0.145139	-3.637402
C	2.428323	-1.299904	-2.138088	H	-2.050718	-0.293025	-4.616034
C	1.858779	0.936712	-2.154971	H	-1.331329	-1.735658	-3.892011
C	1.200394	2.170743	-1.674279	H	-3.317828	1.200555	-1.414
C	-0.382974	2.968884	-0.174195	H	-3.44543	1.303666	-3.173645
C	-1.384071	2.541206	0.827742	H	-1.908548	1.656107	-2.390613
C	-2.519846	1.06135	2.192624	H	4.236981	-0.60936	-1.12897
C	3.201071	1.545229	1.364009	H	4.20738	-2.341829	-1.474719
C	1.732984	1.559806	3.396807	H	3.223661	-1.694733	-0.157288
C	3.482535	-0.241671	3.106261	H	1.328447	-2.972802	-1.302011
S	2.575019	-1.772501	3.511705	H	2.247954	-3.361509	-2.751423
C	0.298067	-3.659672	2.289432	H	0.742065	-2.448213	-2.89266
C	-1.418875	-4.035459	0.645459	H	2.271564	-1.121648	-4.33178
S	-3.238965	-2.9162	-1.744953	H	3.940043	-1.23637	-3.738553
C	-3.671882	-1.333714	-2.545878	H	2.171023	3.619341	-2.950682
C	-1.536915	-0.674525	-3.730136	H	0.761304	4.519527	-1.590096
C	-2.788754	1.011648	-2.350408	H	-0.737952	5.100847	-0.154461
C	3.5941	-1.492412	-1.163835	H	-1.07094	0.125581	3.510202
C	1.632573	-2.591904	-2.278957	H	-2.545299	0.667473	4.319798

C	2.946687	-0.844491	-3.519642	H	-1.321381	1.848219	3.836897
S	3.022301	0.979172	-3.453894	H	-3.752211	-0.151701	0.871346
C	1.453452	3.452802	-2.154992	H	-4.145702	-0.302128	2.587471
C	-0.176112	4.282044	-0.589887	H	-2.704105	-1.089346	1.954409
S	-2.475341	3.69112	1.554806	H	-3.820458	2.535109	3.191505
C	-1.817906	0.920549	3.544418	H	-4.316741	2.161702	1.531012
C	-3.324088	-0.194603	1.874918	H	-0.797964	-5.499905	2.093843
C	-3.458095	2.292203	2.192638	H	0.942813	5.531027	-1.936864
H	3.646549	0.940237	0.57291				

Table S7 Cartesian coordinates for the optimized geometries of **1(ClO_4)** in singlet state.

Atom	x	y	z	Atom	x	y	z
Fe	0	0	-0.000033	H	1.572387	-2.152635	4.138045
N	-0.372396	-1.467395	1.415876	H	0.084652	-1.199884	4.120439
N	0.372393	1.467389	1.415882	H	1.326798	-3.446605	0.640294
N	-1.898784	0.000023	-0.000045	H	2.087818	-3.739602	2.204152
N	1.898784	-0.000024	-0.000041	H	2.404178	-2.232473	1.365181
N	-0.372346	1.467427	-1.415928	H	-0.248902	-3.829622	3.785195
N	0.372349	-1.467423	-1.415932	H	-0.460488	-4.358088	2.105687
C	0.445158	-2.356607	2.307642	H	-1.494216	0.668087	3.188533
C	-1.641675	-1.627884	1.620755	H	-1.572397	2.15262	4.138049
C	-0.445163	2.356598	2.307649	H	-0.08466	1.19987	4.120444
C	1.641671	1.627878	1.620764	H	-1.3268	3.446601	0.640303
C	-2.568014	-0.798463	0.845034	H	-2.087825	3.739592	2.204159
C	-2.567984	0.798522	-0.845136	H	-2.404181	2.232466	1.365182
C	2.568012	0.798461	0.845041	H	0.248894	3.829609	3.785208
C	2.567986	-0.798519	-0.845134	H	0.460482	4.358081	2.105703
C	-1.641618	1.627953	-1.620815	H	-4.488913	-1.480922	1.561513
C	0.445245	2.35676	-2.307548	C	-4.654552	0.000041	-0.000076
C	1.641621	-1.627948	-1.620817	H	-4.48886	1.481014	-1.561649
C	-0.44524	-2.356754	-2.307557	H	4.48891	1.480919	1.561526
C	0.922284	-1.539605	3.508802	C	4.654552	-0.00004	-0.000067
C	1.631099	-2.971555	1.574654	H	4.488864	-1.481007	-1.561646
C	-0.488134	-3.496268	2.775529	H	1.494349	0.668383	-3.18862
S	-2.186247	-2.829338	2.750418	H	1.572672	2.153086	-4.137857
C	-0.922292	1.539592	3.508806	H	0.084909	1.200379	-4.120589
C	-1.631103	2.971547	1.574661	H	1.326741	3.446563	-0.639998
C	0.488127	3.496258	2.775541	H	2.08786	3.739791	-2.203765
S	2.18624	2.829329	2.750432	H	2.404206	2.232559	-1.364973
C	-3.955436	-0.828092	0.880605	H	-0.248762	3.829947	-3.784953
C	-3.955405	0.828171	-0.880738	H	-0.460451	4.358198	-2.105391

C	3.955433	0.828091	0.880615	H	-1.494344	-0.668374	-3.188625
C	3.955407	-0.828166	-0.880733	H	-1.572663	-2.153073	-4.137868
S	-2.186143	2.829492	-2.750407	H	-0.084901	-1.200364	-4.120593
C	0.922483	1.539959	-3.508797	H	-1.326738	-3.446563	-0.640013
C	1.63112	2.971646	-1.574401	H	-2.087853	-3.739786	-2.203782
C	-0.488043	3.496461	-2.775342	H	-2.404203	-2.232558	-1.364986
S	2.18615	-2.829481	-2.750414	H	0.248771	-3.829934	-3.784966
C	-0.922476	-1.539948	-3.508804	H	0.460457	-4.358192	-2.105406
C	-1.631116	-2.971644	-1.574415	Cl	-6.365443	0.000057	-0.000092
C	0.48805	-3.496452	-2.775354	Cl	6.365443	-0.000053	-0.00008
H	1.49421	-0.6681	3.188534				

Table S8 Cartesian coordinates for the optimized geometries of **1(ClO_4)** in quintet state.

Atom	x	y	z	Atom	x	y	z
Fe	-0.000018	-0.000013	-0.000244	H	1.146397	-2.351378	4.339806
N	-0.602399	-1.577922	1.52685	H	-0.308664	-1.351526	4.24032
N	0.602304	1.579741	1.525278	H	1.059296	-3.595415	0.805744
N	-2.09377	-0.000556	-0.000304	H	1.801562	-3.861307	2.387055
N	2.093765	0.00055	-0.000296	H	2.089292	-2.347923	1.535566
N	-0.602864	1.577833	-1.526789	H	-0.719635	-3.971914	3.855465
N	0.602792	-1.57967	-1.525208	H	-0.80472	-4.491265	2.162091
C	0.122683	-2.506422	2.440676	H	-1.167014	0.864245	3.391203
C	-1.880731	-1.700304	1.619018	H	-1.146483	2.35653	4.337293
C	-0.122654	2.509354	2.438046	H	0.308468	1.356402	4.238995
C	1.880634	1.70213	1.617226	H	-1.059055	3.596653	0.801868
C	-2.762322	-0.826119	0.81333	H	-1.801456	3.864284	2.382825
C	-2.762579	0.825263	-0.813478	H	-2.08917	2.34999	1.532922
C	2.762237	0.827014	0.812464	H	0.719881	3.976229	3.851297
C	2.762507	-0.826162	-0.812594	H	0.804898	4.49385	2.157394
C	-1.881245	1.699551	-1.619323	H	-4.685904	-1.534109	1.505857
C	0.122003	2.506416	-2.440661	C	-4.850564	-0.000231	0.00045
C	1.881173	-1.701383	-1.617525	H	-4.68636	1.533785	-1.504877
C	-0.121943	-2.509349	-2.438045	H	4.68584	1.53572	1.504246
C	0.553165	-1.716222	3.677258	C	4.850461	0.000235	0.00047
C	1.336476	-3.110272	1.743714	H	4.686318	-1.535385	-1.503231
C	-0.866366	-3.630528	2.830837	H	1.167224	0.860362	-3.39128
S	-2.541296	-2.923365	2.670587	H	1.146477	2.351363	-4.339385
C	-0.553288	1.720572	3.675481	H	-0.30817	1.350871	-4.240172
C	-1.336349	3.112535	1.740335	H	1.057576	3.596258	-0.805685
C	0.866513	3.633787	2.827007	H	1.799935	3.862448	-2.386898
S	2.541381	2.926331	2.667377	H	2.088584	2.349395	-1.535138

C	-4.150465	-0.859548	0.848163	H	-0.720643	3.971132	-3.856074
C	-4.150728	0.858998	-0.847574	H	-0.806581	4.490814	-2.162834
C	4.150378	0.860469	0.847279	H	-1.167395	-0.864453	-3.390396
C	4.150655	-0.859914	-0.846659	H	-1.146524	-2.356478	-4.336889
S	-2.542124	2.921854	-2.671567	H	0.308014	-1.355714	-4.238838
C	0.553292	1.7161	-3.6769	H	-1.057315	-3.59754	-0.801858
C	1.335259	3.111175	-1.743541	H	-1.799796	-3.865432	-2.38273
C	-0.867521	3.629899	-2.831419	H	-2.088438	-2.351491	-1.532519
S	2.542243	-2.924805	-2.668366	H	0.720935	-3.975417	-3.851946
C	-0.553379	-1.720428	-3.675125	H	0.806796	-4.493403	-2.158187
C	-1.335106	-3.113459	-1.7402	Cl	-6.559857	-0.000036	0.000913
C	0.867705	-3.633146	-2.827622	Cl	6.559741	0.000047	0.00094
H	1.166806	-0.860135	3.392074				

Table S9 Cartesian coordinates for the optimized geometries of **2(ClO$_4$)** in singlet state.

Atom	x	y	z	Atom	x	y	z
Br	6.555803	0.000053	-0.000509	C	1.605156	3.027281	1.590309
C	4.677371	0.000164	-0.000199	C	0.940566	1.557917	3.528899
C	3.975808	-0.831251	0.881531	C	-0.519065	3.509749	2.828047
C	3.975611	0.831623	-0.881724	S	-2.225002	-2.828151	-2.777911
C	2.582979	-0.802619	0.847259	C	0.940715	-1.558068	-3.528842
H	4.508299	-1.48558	1.562551	C	-0.518554	-3.510105	-2.827808
C	2.582786	0.803129	-0.847013	C	1.60567	-3.027198	-1.590242
H	4.507951	1.48586	-1.56295	H	-2.383104	-2.298803	1.35379
N	1.909804	0.000364	0.000286	H	-2.060744	-3.790535	2.229803
C	1.659199	-1.633155	1.633579	H	-1.276918	-3.514497	0.667932
C	1.658858	1.633568	-1.63328	H	-0.113191	-1.18319	4.137585
Fe	0	-0.000014	0.000339	H	-1.572316	-2.187455	4.163904
S	2.225403	-2.82752	2.778321	H	-1.541046	-0.70873	3.194603
N	0.383064	-1.48366	1.432782	H	-0.113237	1.18325	-4.137258
S	2.224993	2.828166	-2.777868	H	-1.572272	2.187641	-4.163997
N	0.382748	1.483872	-1.432652	H	-1.541365	0.708973	-3.19457
N	-1.909803	-0.000379	0.000273	H	-2.383152	2.298288	-1.353149
N	-0.383064	1.483631	1.432775	H	-2.061825	3.789856	-2.229826
N	-0.382749	-1.483897	-1.432664	H	-1.277532	3.514863	-0.667985
C	0.519078	-3.50975	2.828096	H	-4.508299	1.485593	1.56251
C	-0.431539	-2.381605	2.334481	H	-4.677371	-0.000151	-0.000239
C	0.51854	3.510112	-2.827749	H	-4.50795	-1.485843	-1.562994
C	-0.431885	2.381774	-2.334278	H	2.3831	2.298747	1.353743
C	-2.58298	0.802612	0.847238	H	2.060765	3.790502	2.229727
C	-2.582785	-0.803134	-0.847036	H	1.276919	3.514436	0.66787

C	-1.659197	1.633143	1.633561	H	0.113201	1.183213	4.137583
C	0.431545	2.381589	2.334453	H	1.572332	2.18747	4.163873
C	-1.658859	-1.633575	-1.633303	H	1.541048	0.708725	3.194603
C	0.431878	-2.381784	-2.334314	H	-0.491092	4.387989	2.177092
H	0.491109	-4.388003	2.177158	H	-0.284064	3.819986	3.847817
H	0.284079	-3.819968	3.847873	H	0.113227	-1.183217	-4.137264
C	-1.60515	-3.027324	1.590362	H	1.572255	-2.187617	-4.164035
C	-0.940557	-1.557912	3.528912	H	1.541363	-0.708971	-3.194575
H	0.490375	4.388328	-2.176761	H	-0.490392	-4.388336	-2.17684
H	0.283592	3.820352	-3.847527	H	-0.283609	-3.820325	-3.847593
C	-0.940724	1.558082	-3.528822	H	2.383156	-2.298343	-1.353204
C	-1.605676	3.027158	-1.590179	H	2.061804	-3.789885	-2.229914
C	-3.975809	0.831257	0.881497	H	1.277531	-3.514923	-0.668058
C	-3.97561	-0.831615	-0.88176	Br	-6.555803	-0.000019	-0.000571
S	-2.225395	2.827527	2.778286				

Table S10 Cartesian coordinates for the optimized geometries of **2(ClO_4)** in quintet state.

Atom	x	y	z	Atom	x	y	z
Br	6.750866	0.000175	-0.001247	C	1.300943	3.214883	1.745215
C	4.874247	0.000478	-0.000542	C	0.565232	1.740833	3.655079
C	4.171463	-0.887939	0.820129	C	-0.910178	3.662362	2.876728
C	4.171119	0.888979	-0.820831	S	-2.587264	-2.9357	-2.687367
C	2.777703	-0.849461	0.794482	C	0.566362	-1.740638	-3.6543
H	4.705171	-1.587074	1.453762	C	-0.908307	-3.662911	-2.876389
C	2.777384	0.850882	-0.794152	C	1.302314	-3.214469	-1.744285
H	4.704538	1.587843	-1.45501	H	-2.064879	-2.472013	1.498588
N	2.102907	0.000892	0.000476	H	-1.75995	-3.950915	2.413172
C	1.90385	-1.736248	1.601501	H	-0.999399	-3.729311	0.828127
C	1.90312	1.73742	-1.601027	H	0.284949	-1.332572	4.209768
Fe	0.000001	0.000009	0.000616	H	-1.143429	-2.376374	4.33364
S	2.588658	-2.93394	2.688028	H	-1.204327	-0.911718	3.338663
N	0.619399	-1.64133	1.501545	H	0.283903	1.332684	-4.209086
S	2.587266	2.935699	-2.687366	H	-1.144869	2.375992	-4.332767
N	0.618767	1.641754	-1.501052	H	-1.205071	0.911279	-3.337778
N	-2.102906	-0.000892	0.000476	H	-2.066241	2.471496	-1.497993
N	-0.619401	1.641337	1.501548	H	-1.761351	3.950783	-2.411908
N	-0.618761	-1.641753	-1.501061	H	-1.00071	3.728482	-0.826968
C	0.910166	-3.662358	2.876723	H	-4.705173	1.587065	1.453765
C	-0.10109	-2.562061	2.44032	H	-4.874244	-0.000486	-0.000541
C	0.908309	3.662912	-2.87638	H	-4.704532	-1.587848	-1.455012

C	-0.102347	2.562057	-2.439632	H	2.06487	2.472032	1.498585
C	-2.777703	0.849459	0.794483	H	1.759939	3.950931	2.413174
C	-2.77738	-0.850883	-0.794154	H	0.999384	3.729328	0.82813
C	-1.903853	1.736248	1.601504	H	-0.284947	1.332579	4.20977
C	0.101084	2.562071	2.440323	H	1.143426	2.376387	4.333641
C	-1.903114	-1.737419	-1.601031	H	1.20433	0.911733	3.338663
C	0.10235	-2.562055	-2.439643	H	-0.856855	4.550742	2.24149
H	0.856838	-4.550737	2.241484	H	-0.764633	3.963349	3.915918
H	0.76462	-3.963346	3.915913	H	-0.283905	-1.332681	-4.209095
C	-1.300954	-3.214868	1.745214	H	1.144866	-2.37599	-4.33278
C	-0.565233	-1.740822	3.655078	H	1.205072	-0.911278	-3.337791
H	0.854336	4.551471	-2.241453	H	-0.854331	-4.551471	-2.241464
H	0.762563	3.963416	-3.915679	H	-0.762565	-3.963412	-3.91569
C	-0.566362	1.740641	-3.654289	H	2.066245	-2.471493	-1.498008
C	-1.302309	3.214471	-1.744271	H	1.761355	-3.95078	-2.411923
C	-4.171463	0.887933	0.820131	H	1.000716	-3.728481	-0.826982
C	-4.171115	-0.888984	-0.820832	Br	-6.750863	-0.000188	-0.001247
S	-2.588666	2.933936	2.688032				

Table S11 Cartesian coordinates for the optimized geometries of **3(ClO_4)** in singlet state.

Atom	x	y	z	Atom	x	y	z
I	0.000227	6.805902	-0.000179	C	-3.525851	-0.567819	2.864004
C	0.000134	4.697241	-0.000075	C	-0.837657	-3.99072	0.873786
C	0.837657	3.99072	0.873786	C	0.837441	-3.990702	-0.87387
C	-0.837441	3.990702	-0.87387	S	2.833483	-2.268889	-2.779325
C	0.808815	2.595671	0.840825	C	1.583191	0.915586	-3.551824
H	1.501535	4.512304	1.554091	C	3.069753	1.565187	-1.619726
C	-0.808724	2.595653	-0.840766	C	3.525836	-0.567737	-2.863775
H	-1.501247	4.512272	-1.554257	H	2.341778	-2.336864	1.361646
N	0	1.928705	0.000081	H	3.822149	-2.028858	2.26649
C	1.645915	1.678174	1.636756	H	3.571166	-1.227108	0.708118
C	-1.645843	1.678144	-1.636661	H	1.192942	-0.091575	4.155478
Fe	0	0	0.000127	H	2.213806	-1.539659	4.193926
S	2.833504	2.268951	2.779434	H	0.744089	-1.525294	3.208357
N	1.511609	0.400372	1.457299	H	-1.192938	-0.091384	-4.155359
S	-2.833483	2.268889	-2.779325	H	-2.213534	-1.539668	-4.193793
N	-1.511576	0.400357	-1.457128	H	-0.743825	-1.525005	-3.208214
N	-1.511609	-0.400372	1.457299	H	-2.341529	-2.337004	-1.361716
N	0	-1.928705	0.000081	H	-3.821999	-2.028968	-2.266388
N	1.511576	-0.400357	-1.457128	H	-3.570911	-1.227359	-0.707966

C	3.525851	0.567819	2.864004	H	-2.341778	2.336864	1.361646
C	2.411505	-0.398001	2.363926	H	-3.822149	2.028858	2.26649
C	-3.525836	0.567737	-2.863775	H	-3.571166	1.227108	0.708118
C	-2.411445	-0.398035	-2.363796	H	-1.192942	0.091575	4.155478
C	-1.645915	-1.678174	1.636756	H	-2.213806	1.539659	4.193926
C	-2.411505	0.398001	2.363926	H	-0.744089	1.525294	3.208357
C	-0.808815	-2.595671	0.840825	H	-4.41492	-0.537012	2.227999
C	0.808724	-2.595653	-0.840766	H	-3.82061	-0.349939	3.8922
C	1.645843	-1.678144	-1.636661	C	-0.000134	-4.697241	-0.000075
C	2.411445	0.398035	-2.363796	H	-1.501535	-4.512304	1.554091
H	4.41492	0.537012	2.227999	H	1.501247	-4.512272	-1.554257
H	3.82061	0.349939	3.8922	H	1.192938	0.091384	-4.155359
C	3.069945	-1.565048	1.619802	H	2.213534	1.539668	-4.193793
C	1.583344	-0.915706	3.551947	H	0.743825	1.525005	-3.208214
H	-4.414839	0.536958	-2.227667	H	2.341529	2.337004	-1.361716
H	-3.820724	0.349833	-3.891931	H	3.821999	2.028968	-2.266388
C	-1.583191	-0.915586	-3.551824	H	3.570911	1.227359	-0.707966
C	-3.069753	-1.565187	-1.619726	H	4.414839	-0.536958	-2.227667
S	-2.833504	-2.268951	2.779434	H	3.820724	-0.349833	-3.891931
C	-3.069945	1.565048	1.619802	I	-0.000227	-6.805902	-0.000179
C	-1.583344	0.915706	3.551947				

Table S12 Cartesian coordinates for the optimized geometries of **3(ClO_4)** in quintet state.

Atom	x	y	z	Atom	x	y	z
I	0.000181	7.009986	-0.000476	C	-3.665295	-0.948191	2.89426
C	0	4.902714	-0.000158	C	-0.885878	-4.194933	0.821174
C	0.885878	4.194933	0.821174	C	0.885978	-4.194834	-0.821295
C	-0.885978	4.194834	-0.821295	S	2.924733	-2.619621	-2.699137
C	0.848463	2.799092	0.795779	C	1.75102	0.544482	-3.659431
H	1.588798	4.717639	1.459843	C	3.239761	1.267209	-1.755757
C	-0.848757	2.798992	-0.795529	C	3.665667	-0.947719	-2.893631
H	-1.588808	4.717478	-1.460117	H	2.499058	-2.025707	1.490084
N	-0.000203	2.128573	0.000222	H	3.965276	-1.731795	2.431634
C	1.737178	1.926335	1.606103	H	3.769569	-0.9575	0.849497
C	-1.737477	1.92613	-1.605738	H	1.33034	0.301515	4.210985
Fe	0	0	0.000133	H	2.387661	-1.11655	4.342344
S	2.923929	2.619947	2.700007	H	0.930483	-1.191616	3.336238
N	1.65522	0.641112	1.508345	H	-1.330661	0.302047	-4.210874
S	-2.924733	2.619621	-2.699137	H	-2.387735	-1.116186	-4.342526
N	-1.655199	0.640901	-1.508201	H	-0.930388	-1.191276	-3.336638

N	-1.65522	-0.641112	1.508345	H	-2.49819	-2.026066	-1.490203
N	0.000203	-2.128573	0.000222	H	-3.964547	-1.732641	-2.431689
N	1.655199	-0.640901	-1.508201	H	-3.769164	-0.958542	-0.84942
C	3.665295	0.948191	2.89426	H	-2.499058	2.025707	1.490084
C	2.576152	-0.07228	2.45012	H	-3.965276	1.731795	2.431634
C	-3.665667	0.947719	-2.893631	H	-3.769569	0.9575	0.849497
C	-2.576136	-0.072532	-2.449923	H	-1.33034	-0.301515	4.210985
C	-1.737178	-1.926335	1.606103	H	-2.387661	1.11655	4.342344
C	-2.576152	0.07228	2.45012	H	-0.930483	1.191616	3.336238
C	-0.848463	-2.799092	0.795779	H	-4.558444	-0.90217	2.265039
C	0.848757	-2.798992	-0.795529	H	-3.959969	-0.805687	3.935737
C	1.737477	-1.92613	-1.605738	C	0	-4.902714	-0.000158
C	2.576136	0.072532	-2.449923	H	-1.588798	-4.717639	1.459843
H	4.558444	0.90217	2.265039	H	1.588808	-4.717478	-1.460117
H	3.959969	0.805687	3.935737	H	1.330661	-0.302047	-4.210874
C	3.240298	-1.266567	1.755764	H	2.387735	1.116186	-4.342526
C	1.750937	-0.544754	3.65933	H	0.930388	1.191276	-3.336638
H	-4.558682	0.901273	-2.264252	H	2.49819	2.026066	-1.490203
H	-3.960498	0.805342	-3.935079	H	3.964547	1.732641	-2.431689
C	-1.75102	-0.544482	-3.659431	H	3.769164	0.958542	-0.84942
C	-3.239761	-1.267209	-1.755757	H	4.558682	-0.901273	-2.264252
S	-2.923929	-2.619947	2.700007	H	3.960498	-0.805342	-3.935079
C	-3.240298	1.266567	1.755764	I	-0.000181	-7.009986	-0.000476
C	-1.750937	0.544754	3.65933				

Table S13 Cartesian coordinates for the optimized geometries of **4(ClO_4)** in singlet state.

Atom	x	y	z	Atom	x	y	z
Fe	0.001526	0.048966	-0.000625	H	2.386224	-1.564291	-2.126906
N	-0.449683	-1.353841	-1.38573	H	-0.414952	-3.768096	-3.759764
N	-1.874704	0.041432	0.143061	H	-0.581668	-2.049838	-4.254679
N	-0.247374	1.509542	1.389653	H	-4.592693	-1.440803	-1.269046
N	0.269711	1.449488	-1.436572	H	-4.678708	0.029223	0.361143
N	1.880365	0.035793	-0.120105	H	-4.384808	1.520836	1.917159
N	0.42653	-1.369973	1.378588	H	-0.27627	4.423089	2.048465
C	0.33214	-2.332226	-2.249899	H	0.122417	3.928047	3.726084
C	-1.75271	-1.540348	-1.525416	H	0.477423	1.268387	4.068555
C	-2.62886	-0.760439	-0.659595	H	1.968918	2.241677	3.933828
C	-2.502279	0.850163	1.050519	H	1.813331	0.72701	3.005188
C	-1.513502	1.679489	1.732335	H	2.561868	2.313246	1.094775
C	0.666313	2.41552	2.202792	H	2.274548	3.839248	1.949753

C	-0.636528	2.269063	-2.34069	H	1.389659	3.505329	0.4384
C	1.542439	1.649688	-1.735024	H	-0.21894	1.02996	-4.110545
C	2.524818	0.852359	-1.009023	H	-1.73658	1.967741	-4.194418
C	2.618206	-0.792912	0.670276	H	-1.656115	0.511389	-3.171379
C	1.726166	-1.588629	1.506962	H	-2.587046	2.063457	-1.351387
C	-0.366736	-2.221504	2.362463	H	-2.360191	3.576497	-2.249274
C	0.699454	-3.559916	-1.389711	H	-1.551474	3.364294	-0.673687
C	1.591635	-1.713701	-2.873479	H	0.204953	4.318672	-2.168902
C	-0.626557	-2.748586	-3.402101	H	-0.08866	3.786616	-3.857385
S	-2.33787	-2.689504	-2.711721	H	4.421416	1.53713	-1.831651
C	-4.029513	-0.791536	-0.594582	C	4.686511	0.008588	-0.305573
C	-3.888755	0.866546	1.194555	H	4.568565	-1.534216	1.253202
S	-1.936069	2.893145	2.921666	H	0.435506	-4.265542	2.018319
C	-0.228929	3.569528	2.746154	H	0.354887	-3.788751	3.747586
C	1.26175	1.60683	3.372176	H	-2.441057	-1.994815	1.675547
C	1.784522	3.045482	1.359008	H	-2.072697	-3.546694	2.447933
C	-1.083898	1.383451	-3.522763	H	-1.504653	-3.244398	0.785258
C	-1.851635	2.844141	-1.59823	H	0.262992	-1.086354	4.138061
C	0.228421	3.455639	-2.856386	H	-1.271783	-1.981359	4.323556
S	1.969276	2.846362	-2.93969	H	-1.236092	-0.476476	3.369395
C	3.912734	0.872804	-1.127212	O	-6.003306	0.102089	0.55276
C	4.019374	-0.844111	0.608461	O	6.014082	0.080061	-0.475999
S	2.289666	-2.824562	2.6143	C	-6.880055	-0.710908	-0.265217
C	0.548377	-3.426711	2.725984	C	6.874715	-0.765282	0.326211
C	-1.670574	-2.77501	1.768195	H	-6.672053	-1.784143	-0.110798
C	-0.664716	-1.383222	3.621886	H	-6.777639	-0.442325	-1.331174
H	1.324468	-3.268455	-0.531605	H	-7.893727	-0.474012	0.082816
H	1.274968	-4.277751	-1.999706	H	7.894885	-0.517252	0.006033
H	-0.201958	-4.076485	-1.016982	H	6.668357	-1.831413	0.127017
H	1.370707	-0.7536	-3.367694	H	6.752895	-0.537482	1.399604
H	1.990489	-2.403375	-3.637873				

Table S14 Cartesian coordinates for the optimized geometries of **4(ClO_4)** in quintet state.

Atom	x	y	z	Atom	x	y	z
Fe	-0.002631	0.062111	-0.005349	H	1.995447	-0.653157	-2.814238
N	-0.695336	-0.795366	-1.968409	H	-0.949456	-2.254926	-5.002899
N	-2.05073	-0.010653	0.156522	H	-1.052151	-0.465248	-4.906854
N	-0.450498	1.013389	1.992929	H	-4.783133	-0.8565	-1.686587
N	0.527187	2.022184	-0.930303	H	-4.857592	-0.089704	0.367825
N	2.055882	0.040669	-0.094526	H	-4.552827	0.75196	2.347021

N	0.611289	-1.958577	0.86392	H	-0.669131	3.46269	3.736274
C	-0.026584	-1.407017	-3.169064	H	-0.315895	2.341266	5.090494
C	-2.000083	-0.883439	-2.03455	H	0.248534	-0.196423	4.380619
C	-2.812674	-0.458884	-0.875183	H	1.681611	0.831469	4.67641
C	-2.674702	0.428651	1.287592	H	1.613625	-0.204648	3.22192
C	-1.727748	0.983607	2.277947	H	2.201081	1.981842	1.973359
C	0.370535	1.59374	3.111167	H	1.977396	3.031118	3.394453
C	-0.251438	3.185226	-1.47839	H	1.010064	3.321293	1.920402
C	1.819219	2.185227	-1.060576	H	0.131755	2.670649	-3.581098
C	2.72727	1.1014	-0.630426	H	-1.356625	3.62205	-3.308532
C	2.771757	-1.022499	0.353405	H	-1.320755	1.887091	-2.879443
C	1.910899	-2.110773	0.867569	H	-2.189038	2.696524	-0.584617
C	-0.097523	-3.133343	1.482023	H	-1.954327	4.42653	-0.937113
C	0.370038	-2.854166	-2.804794	H	-1.129749	3.688674	0.466748
C	1.210122	-0.596919	-3.586193	H	0.705253	4.990649	-0.593011
C	-1.076439	-1.399717	-4.320865	H	0.510596	5.072162	-2.374576
S	-2.732085	-1.515183	-3.507405	H	4.647075	1.995665	-1.148774
C	-4.212342	-0.507405	-0.822562	C	4.8678	0.028441	-0.253325
C	-4.059538	0.396405	1.437597	H	4.702805	-1.958523	0.661114
S	-2.276345	1.652938	3.810911	H	0.782555	-4.923686	0.491838
C	-0.602569	2.401033	4.028981	H	0.763215	-5.019378	2.28409
C	1.013943	0.430886	3.893993	H	-2.12654	-2.671816	0.806368
C	1.45091	2.537696	2.559163	H	-1.827186	-4.39816	1.121531
C	-0.725148	2.814159	-2.89999	H	-1.172372	-3.644351	-0.360243
C	-1.449698	3.514534	-0.574152	H	0.487917	-2.609031	3.536464
C	0.723108	4.402671	-1.526524	H	-0.998255	-3.596788	3.411874
S	2.42221	3.702182	-1.718189	H	-1.04531	-1.861548	2.990213
C	4.116477	1.137673	-0.725485	O	-6.17845	-0.092622	0.580249
C	4.171278	-1.076446	0.295851	O	6.195918	0.129407	-0.375501
S	2.588999	-3.627799	1.455149	C	-7.064372	-0.562097	-0.467466
C	0.886584	-4.342864	1.424077	C	7.035979	-0.960249	0.08347
C	-1.380263	-3.477054	0.709009	H	-6.852404	-1.617702	-0.710471
C	-0.428843	-2.774097	2.945609	H	-6.973634	0.073212	-1.365506
H	1.020255	-2.863442	-1.914842	H	-8.073825	-0.471009	-0.046404
Fe	0.923587	-3.313776	-3.641909	H	8.06284	-0.631186	-0.121057
N	-0.520284	-3.474061	-2.600649	H	6.817499	-1.882599	-0.481964
N	0.956666	0.461537	-3.758927				

Table S15 Cartesian coordinates for the optimized geometries of **5(ClO_4)** in singlet state.

Atom	x	y	z	Atom	x	y	z

Fe	-0.001489	-0.017604	-0.041721	H	-1.087214	4.54777	1.608378
N	1.916464	-0.140104	-0.032802	H	-1.965827	2.852329	3.334122
N	0.495169	1.525452	1.310488	H	-1.38896	1.187347	3.259171
N	-1.918636	0.120083	-0.070569	H	-2.294968	1.889182	1.903761
N	-0.524433	-1.328611	1.523598	H	0.555777	2.490837	4.118836
N	0.303225	-1.657339	-1.346612	H	0.57216	4.126662	3.434331
N	-0.278251	1.369877	-1.612911	H	-4.608927	-1.1025	1.526522
C	2.538808	-1.050664	-0.806953	C	-4.701753	0.326072	-0.109913
C	2.643737	0.68053	0.740929	H	-4.362454	1.725797	-1.733317
C	1.775306	1.599876	1.493685	H	1.31997	-0.426082	3.298298
C	-0.242005	2.604984	2.062915	H	1.233575	-1.778006	4.426466
C	-2.661455	-0.579331	0.801419	H	-0.17925	-0.74732	4.18486
C	-2.523865	0.927078	-0.963931	H	1.117411	-3.455904	1.058843
C	0.211891	-2.148311	2.551154	H	1.821259	-3.580766	2.671353
C	-1.808128	-1.395558	1.679723	H	2.204434	-2.192827	1.665785
C	1.564807	-1.894295	-1.518578	H	-0.623753	-3.423223	4.144948
C	-0.563364	-2.581977	-2.164751	H	-0.779733	-4.121762	2.523558
C	0.597394	2.106072	-2.598701	H	-2.267517	-3.88021	-1.925136
C	-1.534731	1.621931	-1.804308	H	-2.489899	-2.306928	-1.179051
C	3.917429	-1.158872	-0.842956	H	-1.449899	-3.518978	-0.404822
C	4.032188	0.630396	0.774298	H	0.074693	-4.167018	-3.559718
S	2.413784	2.779037	2.619472	H	0.240792	-4.616986	-1.854266
C	-0.52056	3.766913	1.096263	H	-1.723793	-2.466756	-3.988094
C	-1.548309	2.091517	2.670498	H	-0.207222	-1.566426	-4.066796
C	0.696877	3.06959	3.2056	H	-1.576394	-0.922786	-3.148678
C	-4.049	-0.511863	0.81401	H	0.07467	0.835074	-4.299495
C	-3.900328	1.061019	-1.012248	H	1.465081	0.260876	-3.367009
C	0.67042	-1.212625	3.680618	H	1.635623	1.64812	-4.441667
C	1.407166	-2.882212	1.940589	H	-0.003488	3.524292	-4.174903
C	-0.797076	-3.193173	3.09506	H	-0.114115	4.196493	-2.538016
S	-2.468408	-2.45333	2.908446	H	2.562633	1.854501	-1.688442
S	2.061089	-3.214857	-2.55365	H	1.642494	3.230595	-1.047491
C	-1.760047	-3.09436	-1.360735	H	2.381264	3.313586	-2.646133
C	0.319455	-3.794928	-2.566277	S	6.437608	-0.495963	-0.142197
C	-1.041169	-1.833562	-3.416888	S	-6.432456	0.539778	-0.238772
C	0.959153	1.149316	-3.743982	C	7.100102	0.745214	1.015063
C	-0.240488	3.294483	-3.137445	C	-7.118629	-0.538043	1.059753
C	1.867326	2.652716	-1.944174	H	8.181904	0.629947	0.955944
S	-2.002726	2.78984	-3.020753	H	6.786283	0.546636	2.039265
H	4.393717	-1.903836	-1.470313	H	6.842649	1.758208	0.707616
C	4.702976	-0.300048	-0.041459	H	-6.799855	-0.223021	2.052778
H	4.578648	1.303688	1.420965	H	-6.882065	-1.585843	0.877946

H	-1.109842	3.433441	0.242845	H	-8.197937	-0.408983	0.985469
H	0.404972	4.21361	0.727294				

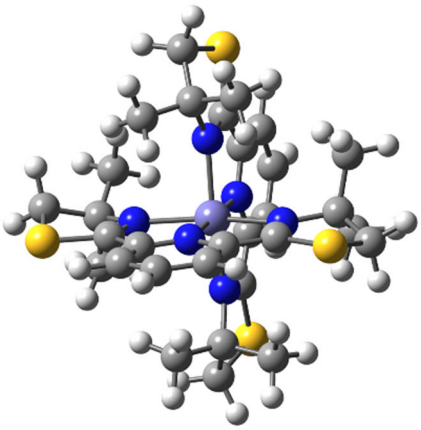
Table S16 Cartesian coordinates for the optimized geometries of **5(ClO_4)** in quintet state.

Atom	x	y	z	Atom	x	y	z
Fe	0.000939	0.01951	-0.04262	H	0.761492	-4.62996	1.94173
N	-2.094691	0.146342	-0.03339	H	1.666603	-2.8729	3.565147
N	-0.717784	-1.59625	1.445963	H	1.062537	-1.21543	3.474968
N	2.095466	-0.14247	-0.0742	H	1.975434	-1.90886	2.123518
N	0.76012	1.487503	1.548807	H	-0.933124	-2.42916	4.301262
N	-0.519378	1.774235	-1.45207	H	-1.004052	-4.08583	3.672896
N	0.482546	-1.57248	-1.64384	H	4.79898	1.185167	1.417127
C	-2.721402	1.050263	-0.81012	C	4.884643	-0.35072	-0.11507
C	-2.822914	-0.66937	0.742876	H	4.535868	-1.85714	-1.63339
C	-1.99898	-1.59113	1.567401	H	-1.010007	0.688239	3.389304
C	-0.061384	-2.65129	2.282095	H	-0.875416	2.067891	4.484444
C	2.845972	0.608594	0.745212	H	0.513823	1.004786	4.236797
C	2.700709	-1.00305	-0.91416	H	-0.796251	3.675805	1.08636
C	0.111415	2.364817	2.573516	H	-1.499734	3.804123	2.70146
C	2.045148	1.499302	1.621635	H	-1.877301	2.410164	1.693292
C	-1.792493	1.925795	-1.56943	H	1.080579	3.632816	4.100894
C	0.261665	2.705066	-2.32785	H	1.164528	4.305914	2.463381
C	-0.314618	-2.36239	-2.63898	H	1.974029	4.018702	-2.18237
C	1.750481	-1.7748	-1.75262	H	2.182516	2.493151	-1.32763
C	-4.100405	1.153455	-0.85049	H	1.151945	3.76146	-0.64038
C	-4.211833	-0.63509	0.762175	H	-0.513984	4.194267	-3.76418
S	-2.739894	-2.68024	2.732471	H	-0.62255	4.717318	-2.07483
C	0.225355	-3.86209	1.379628	H	1.368294	2.553184	-4.18654
C	1.236401	-2.12367	2.896771	H	-0.108962	1.583711	-4.16703
C	-1.064616	-3.03277	3.402759	H	1.315183	1.048284	-3.26309
C	4.23424	0.546559	0.75156	H	0.245204	-1.09646	-4.33258
C	4.076742	-1.1438	-0.95848	H	-1.205095	-0.56163	-3.47046
C	-0.339361	1.473274	3.74141	H	-1.280301	-1.96503	-4.53939
C	-1.084301	3.10596	1.971348	H	0.41465	-3.79311	-4.15391
C	1.182649	3.38425	3.045717	H	0.446571	-4.43357	-2.50107
S	2.813751	2.581576	2.77353	H	-2.274035	-2.0962	-1.7338
S	-2.400595	3.194675	-2.6216	H	-1.382542	-3.49839	-1.11483
C	1.461247	3.275655	-1.56741	H	-2.120759	-3.54731	-2.71815
C	-0.692258	3.859046	-2.74368	S	-6.618392	0.466365	-0.17342
C	0.733424	1.921546	-3.56117	S	6.612268	-0.57133	-0.23842

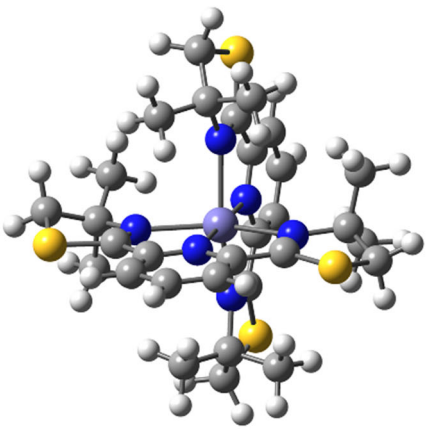
C	-0.654316	-1.43689	-3.81666	C	-7.281456	-0.7793	0.979191
C	0.582047	-3.53828	-3.10862	C	7.30615	0.591557	0.980436
C	-1.596352	-2.90687	-2.00536	H	-8.363526	-0.67305	0.909385
S	2.319429	-2.97741	-2.8996	H	-6.97866	-0.57638	2.005761
H	-4.579435	1.897618	-1.47642	H	-7.012134	-1.79011	0.67509
C	-4.886228	0.287295	-0.05885	H	6.992804	0.344051	1.994024
H	-4.759065	-1.30954	1.406623	H	7.068213	1.624588	0.729425
H	0.844905	-3.5717	0.530401	H	8.384966	0.457238	0.908595
H	-0.697859	-4.30603	1.00123				

SI4.2 The optimized geometric structures and the summary of their structural parameters

(a)



(b)

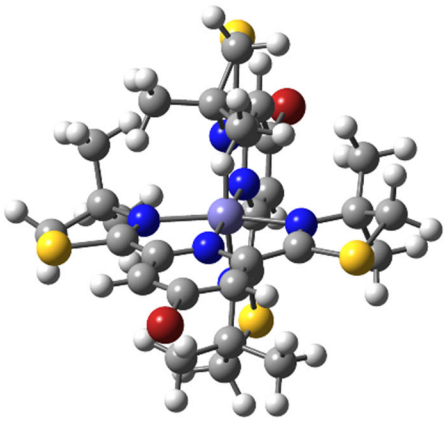


(c)

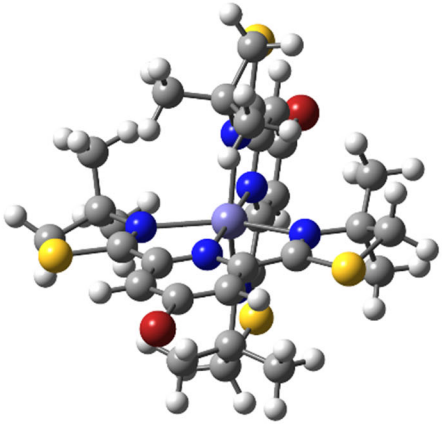
Spin state	Singlet	Quintet
Fe-N_1	2.071	2.281
Fe-N_2	1.901	2.100
Fe-N_3	2.067	2.257
Fe-N_4	2.069	2.268
Fe-N_5	1.900	2.097
Fe-N_6	2.075	2.274
Fe-N_{av}	2.014	2.213

Fig. S46 The geometrically optimized (a) singlet and (b) quintet state structures, and (c) the summary of Fe–N bond lengths in the calculated structures of complex **0**.[2]

(a)



(b)

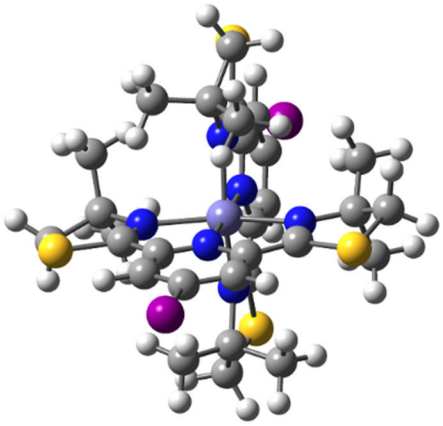


(c)

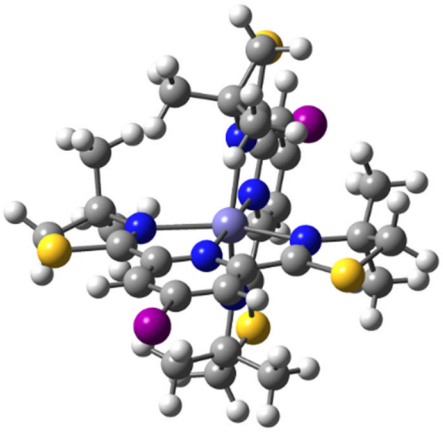
Spin state	Singlet	Quintet
Fe-N_1	1.910	2.103
Fe-N_2	2.098	2.309
Fe-N_3	2.098	2.309
Fe-N_4	1.910	2.103
Fe-N_5	2.098	2.309
Fe-N_6	2.098	2.309
Fe-N_{av}	2.035	2.240

Fig. S47 The geometrically optimized (a) singlet and (b) quintet state structures, and (c) the summary of Fe–N bond lengths in the calculated structures of complex **2**.

(a)



(b)

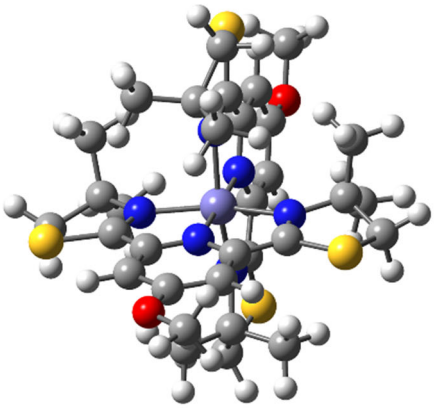


(c)

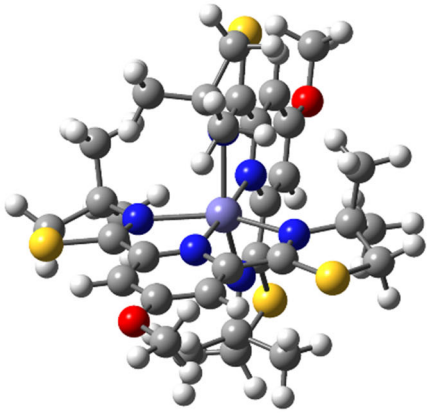
Spin state	Singlet	Quintet
Fe-N_1	1.929	2.129
Fe-N_2	2.137	2.329
Fe-N_3	2.137	2.329
Fe-N_4	2.137	2.329
Fe-N_5	1.929	2.129
Fe-N_6	2.137	2.329
Fe-N_{av}	2.068	2.262

Fig. S48 The geometrically optimized (a) singlet and (b) quintet state structures, and (c) the summary of Fe–N bond lengths in the calculated structures of complex **3**.

(a)



(b)

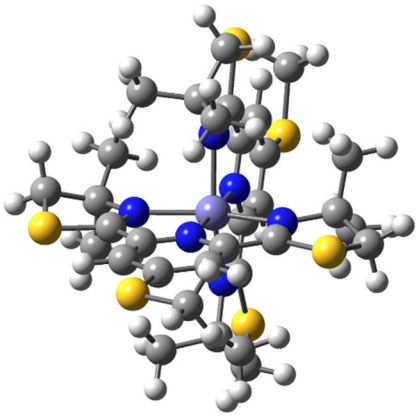


(c)

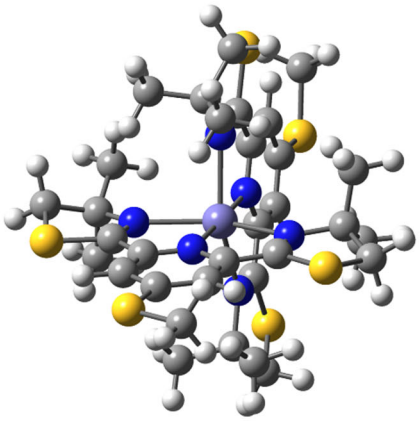
Spin state	Singlet	Quintet
Fe-N_1	2.022	2.251
Fe-N_2	1.882	2.056
Fe-N_3	2.032	2.258
Fe-N_4	2.024	2.231
Fe-N_5	1.883	2.061
Fe-N_6	2.024	2.284
Fe-N_{av}	1.978	2.190

Fig. S49 The geometrically optimized (a) singlet and (b) quintet state structures, and (c) the summary of Fe–N bond lengths in the calculated structures of complex **4**.

(a)



(b)



(c)

Spin state	Singlet	Quintet
Fe-N_1	1.922	2.099
Fe-N_2	2.111	2.311
Fe-N_3	1.922	2.101
Fe-N_4	2.108	2.294
Fe-N_5	2.118	2.310
Fe-N_6	2.114	2.309
Fe-N_{av}	2.049	2.237

Fig. S50 The geometrically optimized (a) singlet and (b) quintet state structures, and (c) the summary of Fe–N bond lengths in the calculated structures of complex **5**.

Table S17 Summary of some key structural parameters of the optimized structures **0**–**5** at different spin states.

complex	spin state	Σ (°)	θ (°)	ϕ (°)	Fe–N_{av} (Å)	S (O_h)	S (T_h)
0	singlet	89.262	89.020	179.173	2.014	2.346	9.428
	quintet	138.171	89.931	178.367	2.213	4.922	6.647
1	singlet	69.713	87.953	180.000	2.015	2.402	9.389
	quintet	138.846	88.053	179.995	2.216	4.988	6.653
2	singlet	81.371	87.995	180.000	2.035	2.501	9.274
	quintet	143.436	84.890	179.995	2.240	5.275	6.710
3	singlet	94.484	87.900	180.000	2.068	2.668	9.090
	quintet	147.508	84.681	179.995	2.262	5.534	6.561
4	singlet	86.079	89.185	179.026	1.978	2.159	9.661
	quintet	132.035	89.831	176.679	2.190	4.653	6.924
5	singlet	88.181	88.998	179.251	2.049	2.702	8.938
	quintet	138.178	86.753	178.862	2.237	5.295	6.511

Table S18 The optimized single point energies of six $[Fe(S\text{-}pybox)_2]^{2+}$complexes in the high-spin (HS) and low-spin (LS) states and their energy gaps.

Complex	R	*E*(HS) (Ha)	*E*(LS)/Ha	*ΔE*(LS–HS) (Ha)	*ΔE*(LS–HS) (kcal mol^{-1})
Fe0	H	-4350.3447129	-4350.3278349	0.0168780	10.58
Fe1	Cl	-5269.442739	-5269.4279737	0.0147653	9.27
Fe2	Br	-9497.3602109	-9497.3441776	0.0160333	10.06
Fe3	I	-3231.7297876	-3231.7133885	0.0163991	10.29
Fe4	OMe	-4579.3393205	-4579.3205513	0.0187692	11.78
Fe5	SMe	-5225.2729526	-5225.2539154	0.0190372	11.94

SI5 References

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2. Pan, Y.; Meng, Y. S.; Liu, Q.; Gao, W. Q.; Liu, C. H.; Liu, T.; Zhu, Y. Y. Construction of SCO-Active Fe(II) Mononuclear Complexes from the Thio-pybox Ligand. *Inorg. Chem.* **2020,** 59 (11), 7398-7407 DOI: 10.1021/acs.inorgchem.9b03506.