Electronic Supplementary Information (ESI)

for

Substrate-Dependent Aromatic Ring Fission of Catechol and 2-Aminophenol with O_2 Catalyzed by a Nonheme Iron Complex of a Tripodal N_4 Ligand

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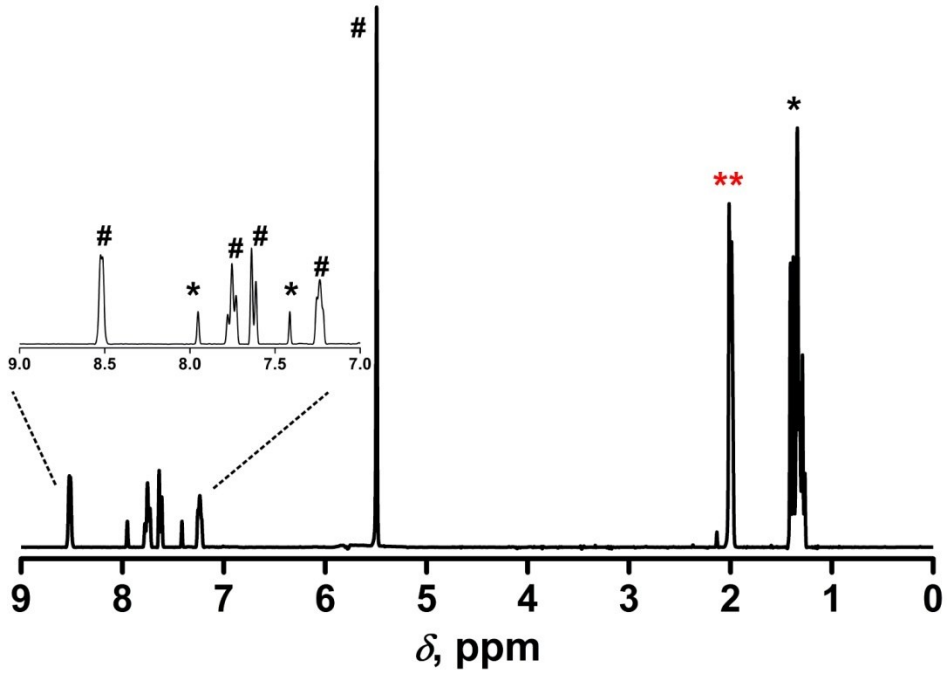

Fig. S1 ^{1}H NMR spectrum (300 MHz, CD_3CN, 298 K) of $[(TPA)Fe^{III}(ISQ)]^{2+}$ (**3**). The peak marked with ** originates from residual solvent, while the peaks marked with # are derived from TPA ligand and the peaks marked with * are from ISQ backbone.

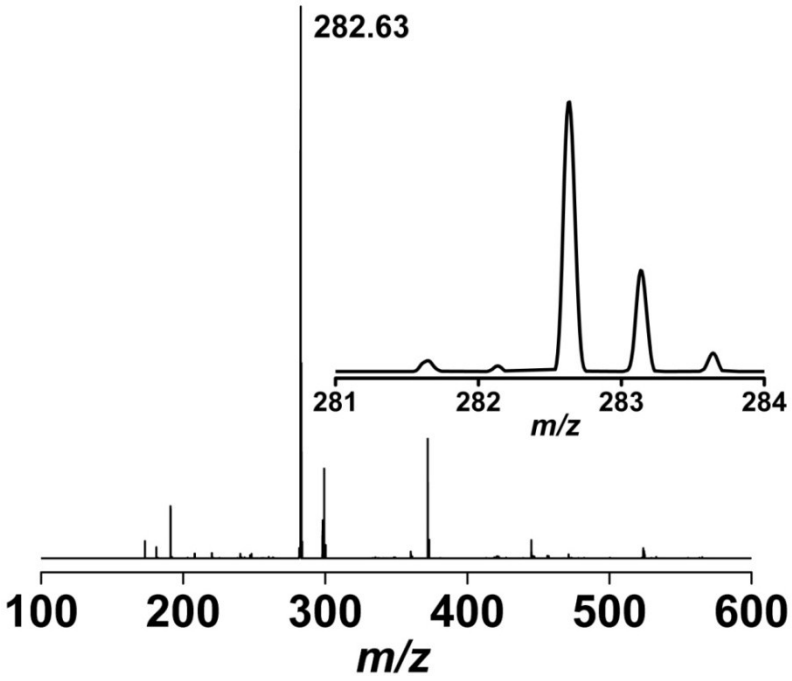

Fig. S2 ESI-mass spectrum (positive ion mode, acetonitrile) of $[(TPA)Fe^{III}(ISQ)]^{2+}$ (**3**).

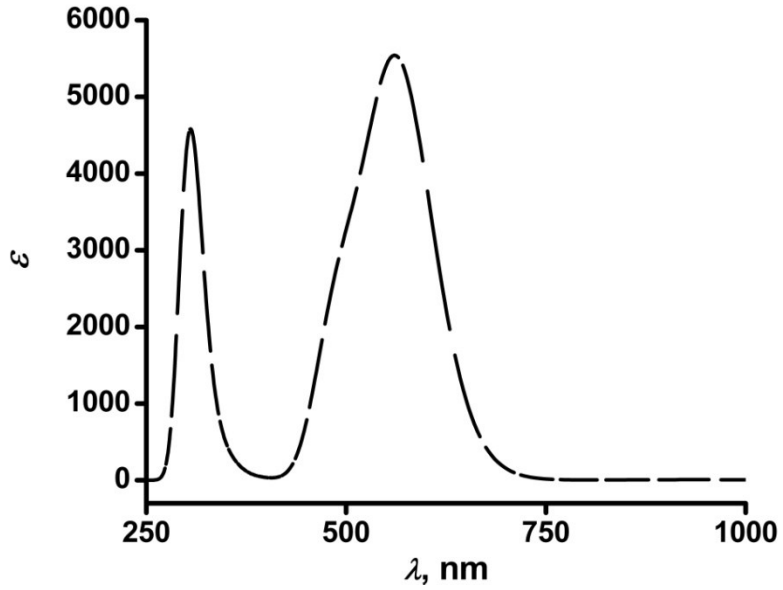

Fig. S3 TD-DFT calculated spectrum of complex **3.**

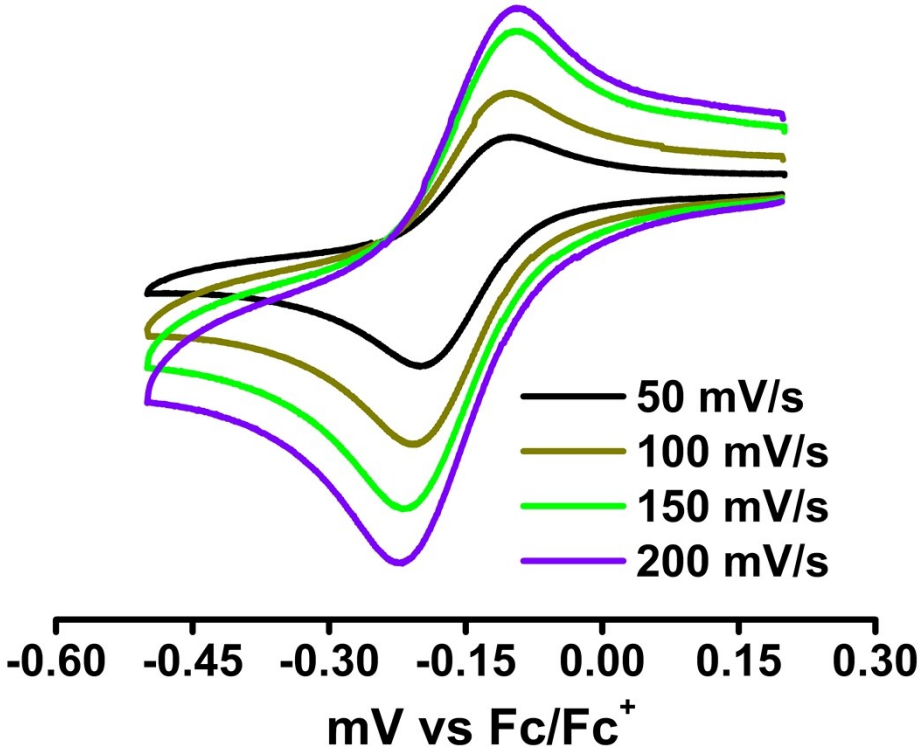

Fig. S4 Cyclic voltammogram of complex **3** in acetonitrile recorded at different scan rates with a platinum working electrode, Ag/AgCl reference electrode, and $(Et_4N)ClO_4$ as the supporting electrolyte.

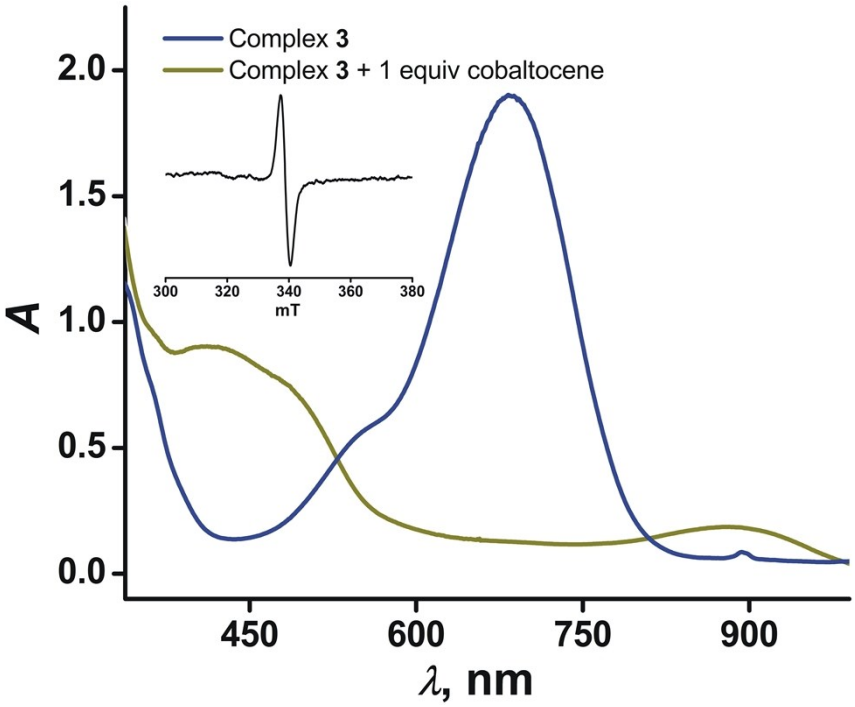

Fig. S5 Optical spectra (a) of complex **3** (0. 3 mM in acetonitrile) and (b) of complex **3** with cobaltocene (1 equiv). Inset: X-band EPR spectrum at 77 K after treatment of an acetonitrile solution of **3** with cobaltocene.

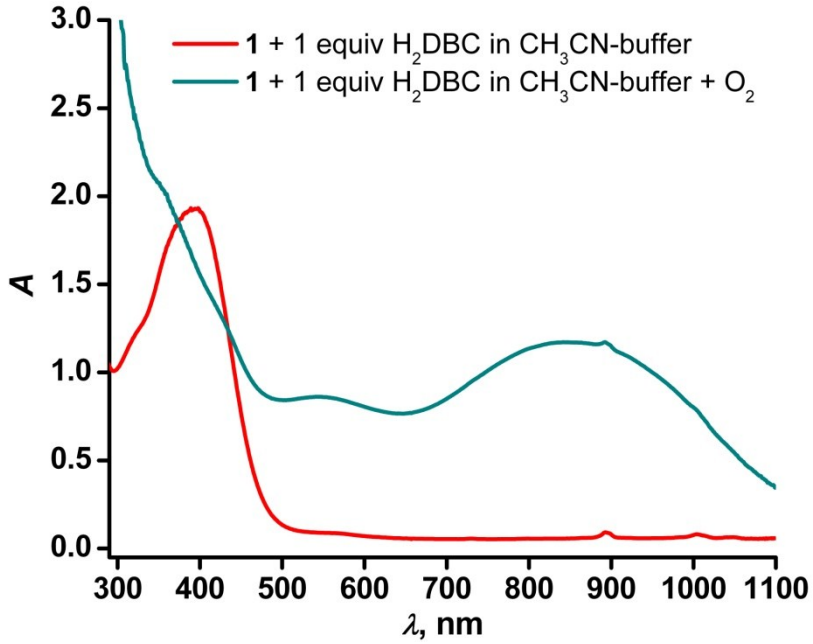

Fig. S6 Formation of $[(TPA)Fe^{III}(DBC)]^{+}$ (**2**) by mixing equimolar amounts of **1** (0.3 mM) and H_2DBC in acetonitrile-phthalate buffer of pH 5.0 under aerobic condition.

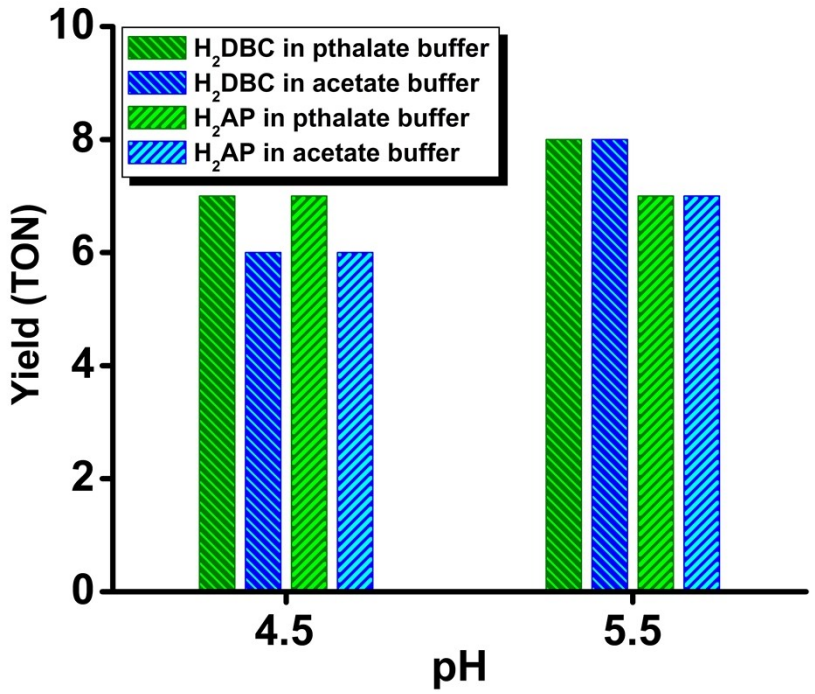

Fig. S7 Plot of catalytic TON vs pH for catechol and 2-aminophenol cleavage reaction in acetonitrile-acetate buffer (0.01 mmol of catalyst **1** and 10 equiv of substrate).

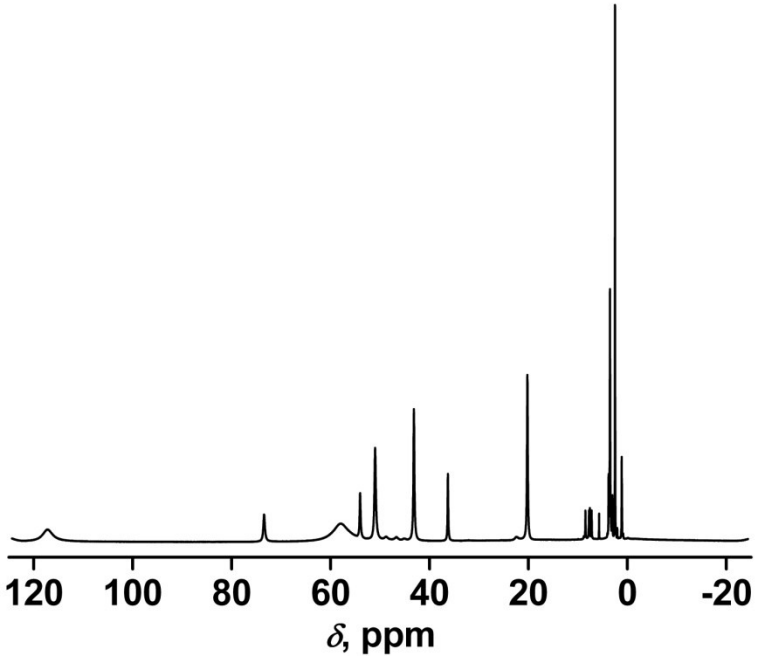

Fig. S8 ^{1}H NMR spectrum (300 MHz, DMSO-d_6, 298 K) of $[(TPA)Fe^{II}(picolinate)]^{+}$ (**4**).

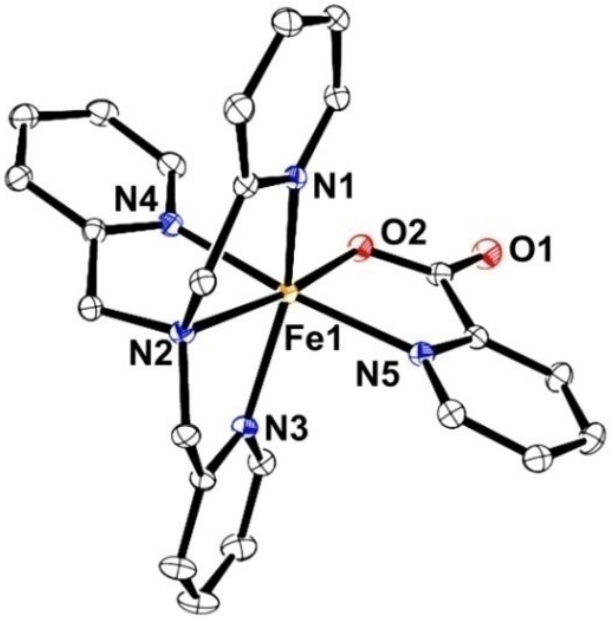

Fig. S9 ORTEP plot of the cationic part of **4** with 30% ellipsoid probability. All hydrogen atoms and counter ions have been omitted for clarity. Selected bond distances and bond lengths for **4**: Fe1-O2 2.024(19), Fe1-N4 2.157(19), Fe1-N3 2.169(2), Fe1-N1 2.174(2), Fe1-N5 2.203(2), Fe1-N2 2.246(2), O2-Fe1-N4 91.21(8), O2-Fe1-N3 106.46(8), N4-Fe1-N3 97.05(7), O2-Fe1-N1 102.45(7), N4-Fe1-N1 84.46(7), N3-Fe1-N1 150.99(8), O2-Fe1-N5 77.87(7), N4-Fe1-N5 169.07(9), N3-Fe1-N5 85.75(8), N1-Fe1-N5 98.24(8), O2-Fe1-N2 170.84(8), N4-Fe1-N2 79.63(9), N3-Fe1-N2 74.93(8), N1-Fe1-N2 76.89(7), N5-Fe1-N2 111.29(8).

Table S1 Calculated bond parameters for $[(TPA)Fe^{III}(ISQ)]^{2+}$ with S=0 spin state.

Distances /Angles (Å)/(°)	**Crystallographic**	**Calculated (ub3lyp/6-311g) S=0**
Fe1-N1	1.962(6)	2.00694
Fe1-N2	1.948(6)	1.98654
Fe1-N3	1.983(6)	2.00613
Fe1-N4	1.978(6)	2.02820
Fe1-N5	1.845(6)	1.92935
Fe1-O1	1.921(5)	1.98878
C19-C20	1.452(10)	1.44600
C20- C21	1.343(9)	1.37649
C21- C22	1.433(10)	1.46580
C22- C23	1.359(10)	1.37116
C23- C24	1.413(9)	1.42951
C24- C19	1.422(9)	1.48742
C24-N5	1.353(9)	1.32582
C19-O1	1.276(7)	1.29070
N5-Fe1-O1	82.5(2)	80.24380
N5-Fe1-N2	100.2(3)	101.50285
O1-Fe1-N2	177.2(2)	178.21275
N5-Fe1-N1	98.4(2)	96.91808
O1-Fe1-N1	91.5(2)	90.40322
N2-Fe1-N1	87.7(2)	89.01071
N5-Fe1-N4	173.2(3)	172.66261
O1-Fe1-N4	90.7(2)	92.41881
N2-Fe1-N4	86.6(2)	85.83437
N1-Fe1-N4	82.1(2)	83.03807
N5-Fe1-N3	97.9(2)	97.11562
O1-Fe1-N3	89.7(2)	90.59079
N2-Fe1-N3	90.3(2)	89.56779
N1-Fe1-N3	163.7(2)	165.89610
N4-Fe1-N3	81.6(2)	82.86379
Energy (kJ/mol)		-4501.575×10^3

Table S2 Selected list of vertical excitations computed at the TD-DFT/ub3lyp/6-311g level of theory for $[(TPA)Fe^{III}(ISQ)]^{2+}$.

Exited state	Wavelength (nm)	f	Energy (eV)	Transition	Experimental (λ, nm)
3	565.7	0.2162	2.1917	HOMO-1→LUMO (61%)	685
6	492.3	0.0971	2.5182	HOMO-3→LUMO (82%)	545
15	327.7	0.0226	3.783	HOMO-8→LUMO (95%)	327
17	311.4	0.0926	3.982	HOMO-10→LUMO (80%)	
22	298.5	0.0981	4.153	HOMO-1→LUMO+1 (86%)	

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