A Biologically Inspired Iron Complex for the Homogeneous Reduction of Cr(VI) to Cr(III)

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Supporting Information Table of Contents:

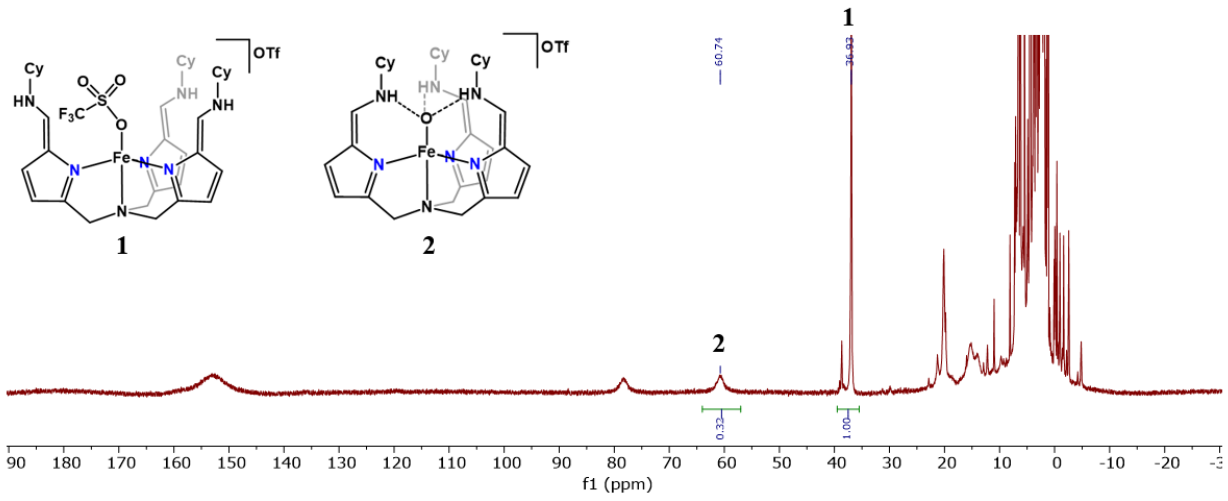

Figure S1. A representative ^{1}H NMR spectrum from the generation of the calibration curve (test 2, entry 10) (500 MHz, CD_3CN).

Entry	Test 1				**[N(afa^{Cy})$_3$FeOTf]OTf (1)**		**[N(afa^{Cy})$_3$FeO]OTf (2)**	
	mL **1**	mL **2**	mmol **2**/ mmol **1**	Integration	$\Delta\nu_{1/2}$ (Hz)	δ(^{1}H) (ppm)	$\Delta\nu_{1/2}$ (Hz)	δ(^{1}H) (ppm)
1	1.9	0.1	0.052632	0.03	40.29	36.85	53.41	60.49
2	1.8	0.2	0.111111	0.06	34.42	36.85	352.86	60.70
3	1.7	0.3	0.176471	0.09	28.78	36.87	451.09	60.65
4	1.6	0.4	0.25	0.11	34.49	36.87	521.66	60.73
5	1.5	0.5	0.333333	0.13	34.42	36.87	354.0	60.73
6	1.4	0.6	0.428571	0.17	38.28	36.88	567.44	60.73
7	1.3	0.7	0.538462	0.19	36.37	36.88	565.53	60.85
8	1.2	0.8	0.666667	0.22	38.19	36.89	600.81	60.83
9	1.1	0.9	0.818182	0.27	34.45	36.90	647.54	60.72
10	1.0	1.0	1	0.29	28.73	36.93	719.07	60.91
11	0.9	1.1	1.222222	0.38	38.44	36.95	680.92	60.56
12	0.8	1.2	1.5	0.46	36.56	36.94	657.08	60.68
13	0.7	1.3	1.857143	0.5	36.51	36.94	650.41	60.76
14	0.6	1.4	2.333333	0.59	42.23	36.95	678.06	60.66

Table S1. ^{1}H NMR chemical shifts (δ(^{1}H)) and the line halfwidths ($\Delta\nu_{1/2}$) of one selected resonance from **1** and **2**, and the integration value of the selected **2** resonance for mixtures of **1**

and **2** in the indicated ratios from Test 1. (The selected resonances from **1** and **2** are indicated in in the representative spectra depicted in **Figure S1.**)

Entry	Test 2				**[N(afa^{Cy})$_3$FeOTf]OTf (1)**		**[N(afa^{Cy})$_3$FeO]OTf (2)**	
	mL **1**	mL **2**	mmol **2**/ mmol **1**	Integration	$\Delta\nu_{1/2}$ (Hz)	δ(^{1}H) (ppm)	$\Delta\nu_{1/2}$ (Hz)	δ(^{1}H) (ppm)
1	1.9	0.1	0.052632	0.06	34.68	36.85	81.06	60.65
2	1.8	0.2	0.111111	0.06	29.07	36.89	435.85	61.09
3	1.7	0.3	0.176471	0.09	30.84	36.88	562.67	60.48
4	1.6	0.4	0.25	0.11	30.81	36.90	553.13	60.71
5	1.5	0.5	0.333333	0.16	36.14	36.89	432.43	60.60
6	1.4	0.6	0.428571	0.19	34.24	36.90	592.23	60.58
7	1.3	0.7	0.538462	0.21	30.65	36.91	629.43	60.72
8	1.2	0.8	0.666667	0.27	36.27	36.90	695.23	60.48
9	1.1	0.9	0.818182	0.28	32.26	36.92	608.44	60.51
10	1.0	1.0	1	0.32	38.26	36.93	689.51	60.74
11	0.9	1.1	1.222222	0.39	38.49	36.93	700.00	60.64
12	0.8	1.2	1.5	0.45	36.54	36.85	716.21	60.62
13	0.7	1.3	1.857143	0.53	27.06	36.95	655.17	60.59
14	0.6	1.4	2.333333	0.57	38.44	36.95	680.92	60.56

Table S2. ^{1}H NMR chemical shifts (δ(^{1}H)) and the line halfwidths ($\Delta\nu_{1/2}$) of one selected resonance from **1** and **2**, and the integration value of the selected **2** resonance for mixtures of **1** and **2** in the indicated ratios from Test 2.

Entry	Test 2				**[N(afa^{Cy})$_3$FeOTf]OTf (1)**		**[N(afa^{Cy})$_3$FeO]OTf (2)**	
	mL **1**	mL **2**	mmol **2**/ mmol **1**	Integration	$\Delta\nu_{1/2}$ (Hz)	$\delta(^1H)$ (ppm)	$\Delta\nu_{1/2}$ (Hz)	$\delta(^1H)$ (ppm)
1	1.9	0.1	0.052632	0.03	34.97	36.84	50.54	58.99
2	1.8	0.2	0.111111	0.06	37.95	36.84	404.36	60.92
3	1.7	0.3	0.176471	0.09	38.08	36.84	389.1	60.64
4	1.6	0.4	0.25	0.11	36.15	36.84	570.3	60.74
5	1.5	0.5	0.333333	0.13	32.37	36.71	553.13	60.61
6	1.4	0.6	0.428571	0.17	36.28	36.71	637.05	60.61
7	1.3	0.7	0.538462	0.19	28.53	36.73	638.01	60.64
8	1.2	0.8	0.666667	0.22	38.13	36.74	566.48	60.43
9	1.1	0.9	0.818182	0.27	34.32	36.73	618.93	60.43
10	1.0	1.0	1	0.29	36.21	36.75	641.82	60.55

Table S3. ^{1}H NMR chemical shifts ($\delta(^1H)$) and the line halfwidths ($\Delta\nu_{1/2}$) of one selected resonance from **1** and **2**, and the integration value of the selected **2** resonance for mixtures of **1** and **2** in the indicated ratios from Test 3.

Summary

Entry	mL **1**	mL **2**	mmol **2**/ mmol **1**	Average Integration	Standard Deviation	Standard Error
1	1.9	0.1	0.052632	0.06	0.025166	0.01453
2	1.8	0.2	0.111111	0.06	0.005774	0.003333
3	1.7	0.3	0.176471	0.09	0.011547	0.006667
4	1.6	0.4	0.25	0.11	0.005774	0.003333
5	1.5	0.5	0.333333	0.16	0.025166	0.01453
6	1.4	0.6	0.428571	0.19	0.025166	0.01453
7	1.3	0.7	0.538462	0.21	0.030551	0.017638
8	1.2	0.8	0.666667	0.27	0.032146	0.018559
9	1.1	0.9	0.818182	0.28	0.015275	0.008819
10	1.0	1.0	1	0.32	0.025166	0.01453
11	0.9	1.1	1.222222	0.39	0	0
12	0.8	1.2	1.5	0.45	0.021213	0.015
13	0.7	1.3	1.857143	0.53	0.021213	0.015
14	0.6	1.4	2.333333	0.57	0.007071	0.005
				Average	0.017945	0.010819

Table S4. The average integration value of the selected **2** resonance for mixtures of **1** and **2** in the indicated ratios from Tests 1-3 with the standard deviation and standard error

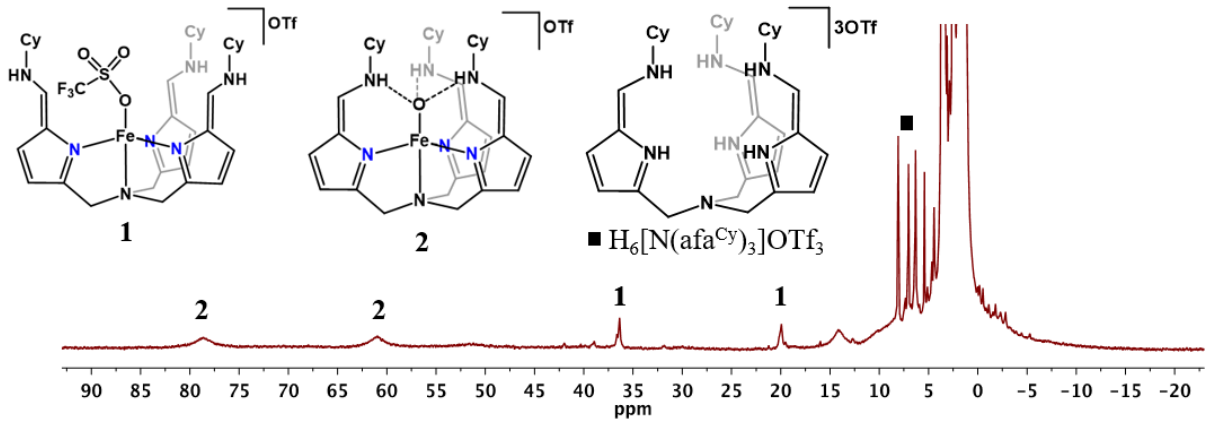

Figure S2. ^{1}H NMR spectrum of the reaction of 4 equiv of **1** and 1 equiv of K_2CrO_4, which furnished **2** and $H_3N(pi^{Cy})_3$ • 3 HOTf (500 MHz, CD_3CN).

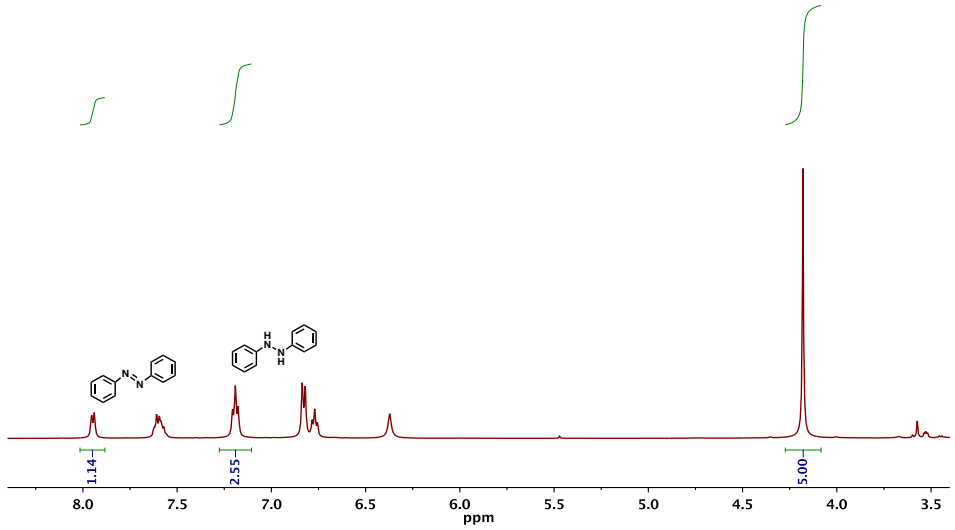

Figure S3. ^{1}H NMR spectrum of the quantification of chromate reduction using 1,2-diphenylhydrazine, demonstrating the formation of 2.47 equiv of **2** (500 MHz, CD_3CN).

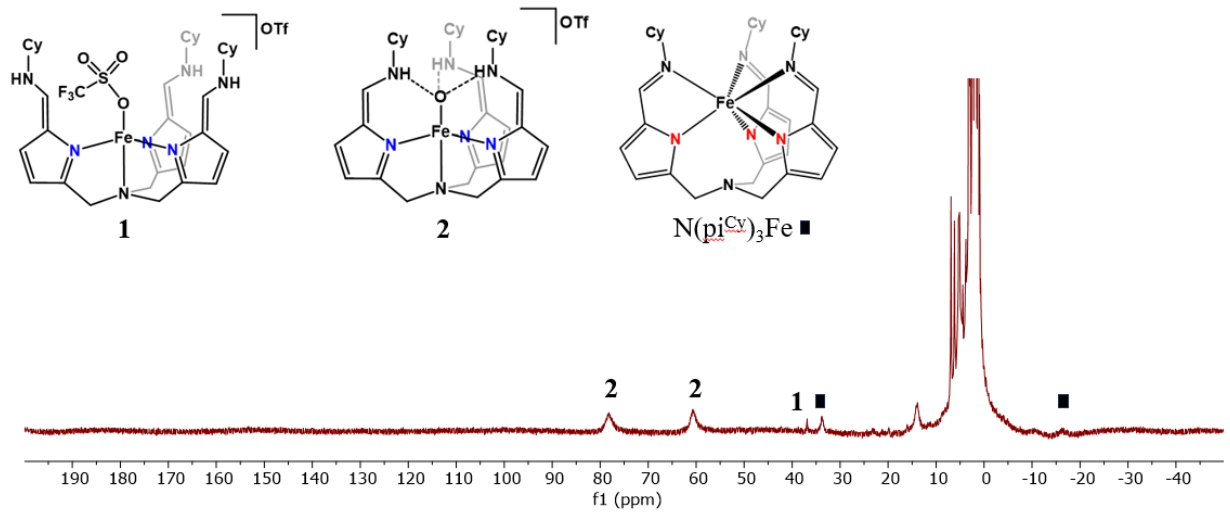

Figure S4. ^{1}H NMR spectrum of the stoichiometric reduction of $[TBA]_2Cr_2O_7$ by **1** in the presence of triethyl amine.

		[N(afa^{Cy})$_3$FeOTf]OTf (1)		**[N(afa^{Cy})$_3$FeO]OTf (2)**	
Aliquot	Integration	δ(^{1}H) (ppm)	$\Delta\nu_{1/2}$ (Hz)	δ(^{1}H) (ppm)	$\Delta\nu_{1/2}$ (Hz)
A – 20	0.12	36.69	30.43	60.82	631.33
B – 20	0.15	36.7	32.42	60.95	549.32
C – 20	0.15	36.69	37.94	60.55	483.51
A – 60	0.16	36.69	32.55	60.78	536.92
B – 60	0.14	36.7	28.66	69.62	745.77
Average	0.144				
% yield	97.7				

Table S5. ^{1}H NMR chemical shifts (δ(^{1}H)) and the line halfwidths ($\Delta\nu_{1/2}$) of one selected resonance from **1** and **2**, and the integration value of the selected **2** resonance for the reduction of $[TBA]_2Cr_2O_7$ by **1.**

		[N(afa^{Cy})$_3$FeOTf]OTf (1)		**[N(afa^{Cy})$_3$FeO]OTf**	
Aliquot	Integration	δ(^{1}H) (ppm)	$\Delta\nu_{1/2}$ (Hz)	δ(^{1}H) (ppm)	$\Delta\nu_{1/2}$ (Hz)
A	0.11	36.66	30.97	60.74	635.15
B	0.11	36.67	30.97	60.81	373.84
C	0.12	36.66	30.74	60.5	668.53
Average	0.113				
% yield	99.5				

Table S6. ^{1}H NMR chemical shifts (δ(^{1}H)) and the line halfwidths ($\Delta\nu_{1/2}$) of one selected resonance from **1** and **2**, and the integration value of the selected **2** resonance for the reduction of $[TBA]_2Cr_2O_7$ by **1**.

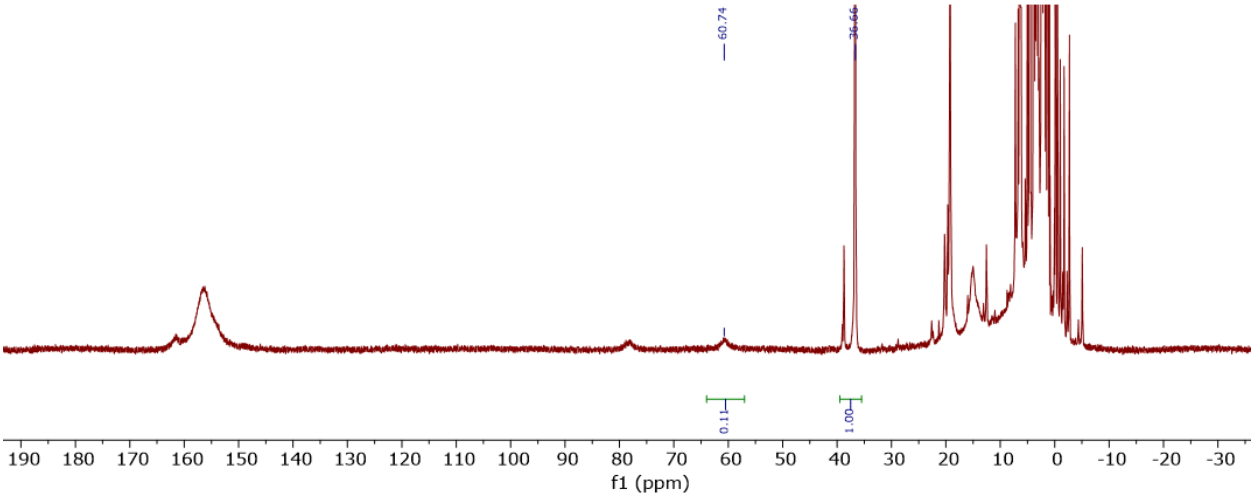

Figure S5. A representative ^{1}H NMR spectrum of the reduction of $[TBA]_2Cr_2O_7$ by **1** (trial 2, aliquot A) (500 MHz, CD_3CN).

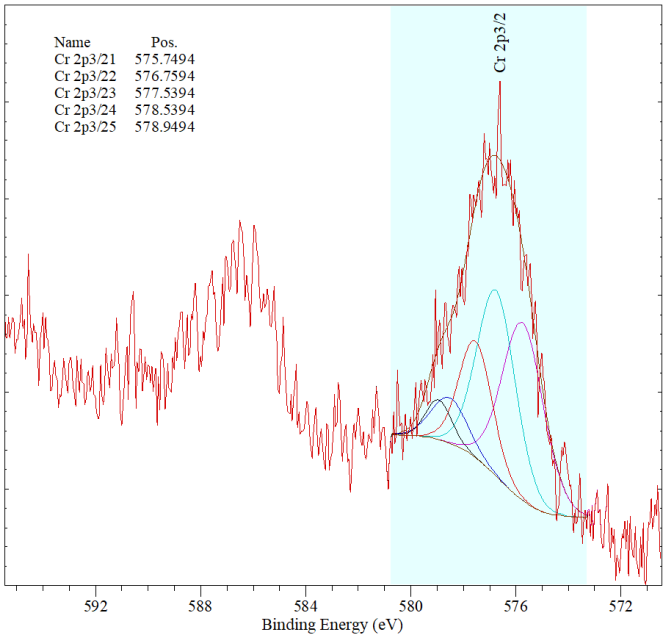

Figure S6. XPS analysis of the precipitated material from the large scale reduction of $[TBA]_2Cr_2O_7$.