The axial ligand effects on the distinct reaction tunnelings for methane hydroxylation by nonheme iron(IV)–oxo complexes

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Supporting Information

1. Table

Table S1. Relative B3LYP energies (kcal mol^{-1}) for methane C-H bond hydroxylation by $[Fe^{IV}(O)(NH_3)_4(L)]^+$ complexes.

	Point	ΔE(el) (B1)	ΔZPE (B1)	ΔH (B1)	-TΔS (B1)	ΔG (B1)	ΔG (B2)	ΔG (B2+vdw)
1-O_2CCF_3	^{3}**R+CH$_4$**	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	^{3}**TS$_{H\sigma}$**	37.06	-6.81	29.56	9.89	39.45	34.60	30.19
	^{3}**I$_\sigma$**	29.98	-5.16	24.70	9.35	34.05	30.40	26.10
	^{3}**TS$_{Re\sigma}$**	36.30	-4.56	32.51	6.44	38.95	34.86	29.16
	^{3}**P$_\sigma$**	-15.63	-0.27	-15.23	6.38	-8.85	-15.81	-20.31
	^{3}**TS$_{H\pi}$**	29.85	-4.72	24.74	9.60	34.33	24.57	20.94
	^{3}**I$_\pi$**	21.37	-3.26	18.36	8.29	26.65	15.54	12.71
	^{3}**TS$_{Re\pi}$**	31.50	-3.27	28.62	7.33	35.95	26.09	22.96
	^{3}**P$_\pi$**	-15.04	-0.03	-14.43	6.43	-8.00	-15.09	-19.71
	^{5}**R+CH$_4$**	7.71	-4.19	4.51	-2.82	1.68	3.20	0.72
	^{5}**TS$_{H\sigma}$**	29.06	-8.45	21.64	5.57	27.21	20.62	16.33
	^{5}**I$_\sigma$**	20.62	-7.37	15.02	3.87	18.89	13.89	9.46
	^{5}**TS$_{Re\sigma}$**	24.72	-6.57	19.60	4.73	24.32	18.10	12.52
	^{5}**P$_\sigma$**	-27.74	-2.70	-29.37	5.21	-24.16	-32.20	-36.87
	^{5}**TS$_{H\pi}$**	37.68	-7.50	30.82	6.72	37.53	29.17	23.52
	^{5}**I$_\pi$**	29.44	-5.54	25.02	5.55	30.57	20.62	16.04
	^{5}**TS$_{Re\pi}$**	32.41	-6.31	27.02	6.26	33.27	23.11	18.57
	^{5}**P$_\pi$**	-27.66	-2.29	-29.07	5.74	-23.33	-32.22	-36.76
1-NCS	^{3}**R+CH$_4$**	0.00	0.00	0.00	0.00	0.00	0.00	1.44
	^{3}**TS$_{H\sigma}$**	39.31	-5.66	32.52	11.35	43.87	37.68	35.47
	^{3}**I$_\sigma$**	29.09	-4.89	25.61	5.23	30.85	15.49	12.83
	^{3}**TS$_{Re\sigma}$**	36.56	-3.78	33.75	6.43	40.18	25.21	21.08
	^{3}**P$_\sigma$**	-14.54	1.19	-13.74	9.36	-4.37	-10.59	-13.47
	^{3}**TS$_{H\pi}$**	29.05	-3.04	25.50	9.89	35.39	24.53	22.30
	^{3}**I$_\pi$**	20.28	-1.99	18.09	9.32	27.41	15.33	14.03
	^{3}**TS$_{Re\pi}$**	30.86	-1.28	29.08	10.36	39.45	27.60	25.91
	^{3}**P$_\pi$**	-14.47	0.89	-13.26	7.24	-6.02	-10.76	-13.60
	^{5}**R+CH$_4$**	6.68	-2.74	4.35	-1.11	3.25	0.95	0.00
	^{5}**TS$_{H\sigma}$**	29.49	-7.47	22.12	7.94	30.06	19.89	17.01
	^{5}**I$_\sigma$**	20.78	-6.14	15.99	4.82	20.81	11.38	8.49
	^{5}**TS$_{Re\sigma}$**	25.08	-5.13	20.81	6.60	27.42	16.99	12.88
	^{5}**P$_\sigma$**	-28.53	-1.16	-28.70	5.92	-22.77	-30.48	-33.84
	^{5}**TS$_{H\pi}$**	36.37	-6.15	30.88	6.79	37.68	27.44	23.16
	^{5}**I$_\pi$**	27.99	-4.43	25.36	3.60	28.96	18.91	15.74
	^{5}**TS$_{Re\pi}$**	31.37	-4.94	27.93	4.49	32.42	22.90	19.48

	$^5P_\pi$	-28.48	-1.11	-28.59	5.82	-22.76	-30.30	-33.72
1-NC	$^3R+CH_4$	0.00	0.00	0.00	0.00	0.00	0.00	0.42
	$^3TS_{H\sigma}$	40.21	-6.18	33.74	8.68	42.42	37.73	34.29
	$^3I_\sigma$	29.69	-5.23	26.00	4.66	30.67	17.49	13.73
	$^3TS_{Re\sigma}$	36.94	-3.55	34.27	6.51	40.78	26.22	21.12
	$^3P_\sigma$	-12.94	0.41	-11.83	5.36	-6.46	-11.49	-15.35
	$^3TS_{H\pi}$	28.93	-3.42	24.67	10.39	35.05	24.09	20.87
	$^3I_\pi$	20.17	-1.77	18.66	7.99	26.64	14.95	12.70
	$^3TS_{Re\pi}$	31.64	-1.73	30.80	6.05	36.85	26.91	24.14
	$^3P_\pi$	-12.83	0.04	-11.94	4.95	-6.98	-12.36	-16.51
	$^5R+CH_4$	6.80	-2.69	5.02	-2.46	2.56	1.93	0.00
	$^5TS_{H\sigma}$	30.56	-7.72	23.14	7.15	30.28	21.68	17.82
	$^5I_\sigma$	22.22	-5.93	17.44	5.80	23.24	14.79	10.74
	$^5TS_{Re\sigma}$	26.41	-5.33	22.64	4.25	26.88	19.74	14.52
	$^5P_\sigma$	-27.18	-1.06	-26.16	2.57	-23.59	-30.46	-34.84
	$^5TS_{H\pi}$	36.00	-6.49	29.79	7.26	37.06	27.17	21.91
	$^5I_\pi$	27.69	-4.86	23.74	5.75	29.49	18.74	14.57
	$^5TS_{Re\pi}$	31.27	-5.07	27.16	5.84	33.00	22.39	18.05
	$^5P_\pi$	-27.32	-1.31	-26.98	3.69	-23.28	-30.43	-34.85
1-F	$^3R+CH_4$	0.00	0.00	0.00	0.00	0.00	0.00	0.48
	$^3TS_{H\sigma}$	40.64	-5.55	35.04	8.30	43.35	37.23	35.68
	$^3I_\sigma$	26.99	-5.05	22.93	5.79	28.73	15.21	11.82
	$^3TS_{Re\sigma}$	37.55	-3.45	35.55	5.12	40.67	26.09	21.18
	$^3P_\sigma$	-5.76	0.61	-4.28	5.98	1.71	-9.12	-13.39
	$^3TS_{H\pi}$	30.87	-3.58	27.61	7.32	34.94	26.25	23.23
	$^3I_\pi$	22.71	-1.99	21.12	7.37	28.49	17.85	15.81
	$^3TS_{Re\pi}$	35.61	-1.63	34.79	6.47	41.27	29.70	27.10
	$^3P_\pi$	-5.89	0.66	-4.88	7.27	2.39	-9.40	-13.67
	$^5R+CH_4$	6.17	-2.49	5.10	-3.93	1.17	1.73	0.00
	$^5TS_{H\sigma}$	30.01	-7.16	23.45	6.41	29.86	20.87	17.19
	$^5I_\sigma$	20.20	-5.40	15.81	5.90	21.72	12.71	9.18
	$^5TS_{Re\sigma}$	26.72	-5.37	22.49	4.92	27.42	18.71	13.81
	$^5P_\sigma$	-24.73	-1.01	-23.76	3.17	-20.58	-32.88	-37.01
	$^5TS_{H\pi}$	37.77	-6.30	32.23	6.02	38.26	29.32	24.42
	$^5I_\pi$	26.93	-4.83	23.53	4.65	28.19	15.31	12.22
	$^5TS_{Re\pi}$	32.43	-5.55	28.14	4.89	33.04	19.00	15.15
	$^5P_\pi$	-24.65	-1.53	-25.00	5.09	-19.91	-32.85	-36.91
1-Cl	$^3R+CH_4$	0.00	0.00	0.00	0.00	0.00	0.00	1.19
	$^3TS_{H\sigma}$	36.67	-5.45	30.66	9.24	39.90	35.90	32.79
	$^3I_\sigma$	29.41	-3.89	25.62	8.07	33.68	31.82	28.88

	$^3TS_{R\sigma}$	35.34	-2.63	32.81	7.94	40.75	37.88	33.81
	$^3P_\sigma$	-16.86	0.81	-15.10	4.98	-10.11	-13.39	-16.73
	$^3TS_{H\pi}$	29.93	-3.83	25.97	8.53	34.50	24.85	22.23
	$^3I_\pi$	21.61	-1.89	19.52	9.15	28.67	16.00	14.20
	$^3TS_{R\pi}$	30.48	-2.18	28.86	6.38	35.25	26.09	24.11
	$^3P_\pi$	-16.82	1.24	-14.26	3.99	-10.26	-13.83	-14.23
	$^5R+CH_4$	6.54	-2.70	5.38	-4.32	1.06	1.22	0.00
	$^5TS_{H\sigma}$	28.43	-7.21	21.84	6.33	28.17	20.51	17.33
	$^5I_\sigma$	19.67	-6.16	14.90	4.36	19.26	12.86	9.64
	$^5TS_{R\sigma}$	24.04	-5.16	19.87	5.58	25.45	18.13	13.79
	$^5P_\sigma$	-29.17	-1.15	-28.11	1.74	-26.37	-31.07	-34.63
	$^5TS_{H\pi}$	36.47	-6.03	31.03	6.78	37.82	27.57	23.06
	$^5I_\pi$	28.42	-4.82	24.53	5.46	29.99	19.42	16.07
	$^5TS_{R\pi}$	31.62	-5.15	28.59	2.60	31.19	22.03	18.50
	$^5P_\pi$	-29.10	-1.43	-29.28	4.32	-24.95	-31.38	-34.94
1-N_3	$^3R+CH_4$	0.00	0.00	0.00	0.00	0.00	0.00	2.35
	$^3TS_{H\pi}$	28.87	-4.50	23.94	9.31	33.23	22.97	21.59
	$^3I_\pi$	19.85	-2.73	17.19	8.55	25.74	13.34	12.90
	$^3TS_{R\pi}$	30.64	-2.24	28.36	8.65	37.00	25.39	24.43
	$^3P_\pi$	-13.56	0.66	-12.41	6.41	-6.00	-10.59	-13.17
	$^5R+CH_4$	5.44	-3.58	2.07	-0.64	1.42	0.07	0.00
	$^5TS_{H\sigma}$	28.94	-7.70	20.93	8.86	29.79	20.01	17.98
	$^5I_\sigma$	19.85	-6.17	13.98	7.71	21.69	11.33	9.40
	$^5TS_{R\sigma}$	24.69	-6.09	19.47	5.83	25.30	17.06	13.88
	$^5P_\sigma$	-27.40	-1.73	-28.99	7.91	-21.08	-32.97	-35.46
	$^5TS_{H\pi}$	35.00	-6.71	28.02	9.26	37.28	24.84	21.33
	$^5I_\pi$	26.36	-5.67	21.92	4.90	26.82	15.82	13.57
	$^5TS_{R\pi}$	30.53	-5.69	25.54	6.44	31.98	17.51	14.89
	$^5P_\pi$	-27.37	-1.87	-27.85	4.43	-23.42	-32.50	-35.03
1-OH	$^3R+CH_4$	0.00	0.00	0.00	0.00	0.97	0.00	2.10
	$^3TS_{H\pi}$	28.48	-4.33	24.25	7.77	32.99	23.21	21.84
	$^3I_\pi$	19.24	-3.03	17.21	4.84	23.02	13.83	14.00
	$^3TS_{R\pi}$	35.22	-2.77	32.73	7.41	41.11	27.65	26.58
	$^3P_\pi$	-4.17	-1.16	-4.75	6.23	2.45	-11.66	-14.62
	$^5R+CH_4$	4.18	-3.41	1.56	-2.53	0.00	0.18	0.00
	$^5TS_{H\sigma}$	30.23	-8.97	22.18	4.74	27.89	21.00	18.63
	$^5I_\sigma$	19.63	-7.28	14.30	2.94	18.21	11.32	9.38
	$^5TS_{R\sigma}$	27.10	-6.51	22.29	3.00	26.26	17.70	14.34
	$^5P_\sigma$	-23.19	-2.91	-24.24	2.74	-20.53	-32.46	-34.77
	$^5TS_{H\pi}$	33.68	-7.41	26.53	6.83	34.34	25.00	21.64

$^5\mathbf{I}_{\pi}$	23.49	-6.58	18.19	4.43	23.59	11.38	9.84
$^5\mathbf{TS}_{\mathbf{Re}\pi}$	30.25	-6.31	25.55	3.76	30.28	16.57	14.01
$^5\mathbf{P}_{\pi}$	-23.16	-3.08	-24.84	4.06	-19.81	-32.40	-34.71

ΔG (B1) relative energies at B3LYP/B1 level;

ΔG (B2) relative energies at B3LYP/B2//B3LYP/B1 level;

ΔG (B2+vdw) relative energies at B3LYP-D/B2//B3LYP/B1 level.

Table S2. Relative PBE0 energies (kcal mol^{-1}) for methane C-H bond hydroxylation by $[Fe^{IV}(O)(NH_3)_4(L)]^+$ complexes.

	Point	ΔE(el) (B1)	ΔZPE (B1)	ΔH (B1)	-TΔS (B1)	ΔG (B1)	ΔG (B2)
1-O_2CCF_3	^{3}**R+CH$_4$**	0.00	4.33	0.00	0.00	1.94	0.00
	^{3}**TS$_{H\sigma}$**	33.50	-2.68	26.96	6.54	35.44	31.22
	^{3}**I$_\sigma$**	25.12	-0.69	21.07	6.08	29.08	25.82
	^{3}**TS$_{H\pi}$**	26.99	0.01	23.16	7.13	32.23	21.89
	^{3}**I$_\pi$**	18.24	1.08	16.38	4.72	23.04	12.40
	^{5}**R+CH$_4$**	5.26	0.00	2.47	-4.41	0.00	0.93
	^{5}**TS$_{H\sigma}$**	22.30	-4.33	14.79	4.78	21.51	14.05
	^{5}**I$_\sigma$**	12.01	-2.91	6.44	4.05	12.43	5.70
	^{5}**TS$_{H\pi}$**	32.98	-3.48	25.89	6.37	34.20	24.82
	^{5}**I$_\pi$**	24.38	-1.66	20.76	2.14	24.84	15.59
1-NCS	^{3}**R+CH$_4$**	0.00	2.86	0.00	0.00	0.00	1.04
	^{3}**TS$_{H\sigma}$**	35.78	-2.40	30.23	9.44	39.67	35.32
	^{3}**I$_\sigma$**	24.29	-1.71	20.97	6.12	27.10	12.24
	^{3}**TS$_{H\pi}$**	26.20	-0.05	22.70	10.36	33.06	22.74
	^{3}**I$_\pi$**	17.21	0.88	15.56	7.95	23.51	13.18
	^{5}**R+CH$_4$**	4.52	0.00	2.09	-1.13	0.96	0.00
	^{5}**TS$_{H\sigma}$**	22.90	-4.49	15.67	7.78	23.45	14.78
	^{5}**I$_\sigma$**	12.43	-2.99	7.81	5.47	13.29	5.24
	^{5}**TS$_{H\pi}$**	31.85	-2.88	26.54	7.50	34.04	24.07
	^{5}**I$_\pi$**	23.07	-1.61	19.83	5.45	25.28	15.24
1-NC	^{3}**R+CH$_4$**	0.00	2.73	0.00	3.47	0.00	0.26
	^{3}**TS$_{H\sigma}$**	36.82	-2.85	31.17	11.70	39.40	34.81
	^{3}**I$_\sigma$**	24.62	-2.11	21.66	7.47	25.67	12.86
	^{3}**TS$_{H\pi}$**	26.08	-0.20	23.19	11.44	31.17	21.49
	^{3}**I$_\pi$**	17.06	0.81	15.48	11.12	23.13	12.07
	^{5}**R+CH$_4$**	4.52	0.00	2.75	0.82	0.09	0.00
	^{5}**TS$_{H\sigma}$**	23.85	-4.75	16.53	11.05	24.11	15.36
	^{5}**I$_\sigma$**	13.60	-3.04	9.48	7.79	13.81	7.14
	^{5}**TS$_{H\pi}$**	31.41	-3.40	25.89	10.31	32.73	22.95
	^{5}**I$_\pi$**	22.65	-1.19	20.26	7.89	24.69	14.10
1-F	^{3}**R+CH$_4$**	0.00	2.70	0.00	2.74	0.69	0.65
	^{3}**TS$_{H\pi}$**	28.19	-0.62	25.00	11.04	34.00	24.24
	^{3}**I$_\pi$**	19.83	0.59	18.20	9.78	25.94	15.38
	^{5}**R+CH$_4$**	3.77	0.00	2.05	0.00	0.00	0.00
	^{5}**TS$_{H\sigma}$**	22.84	-4.58	16.24	8.91	23.10	15.28
	^{5}**I$_\sigma$**	11.46	-3.18	6.85	7.85	12.66	5.13
	^{5}**TS$_{H\pi}$**	33.15	-3.49	27.58	9.64	35.18	25.41

	$^5\mathbf{I}_\pi$	21.81	-2.00	18.46	7.70	24.13	10.92
1-Cl	$^3\mathbf{R+CH_4}$	0.00	3.51	0.00	0.00	1.73	1.06
	$^3\mathbf{TS}_{\mathbf{H}\sigma}$	33.23	-2.35	27.50	7.46	36.71	33.60
	$^3\mathbf{I}_\sigma$	24.83	-1.14	20.60	7.29	29.62	28.22
	$^3\mathbf{TS}_{\mathbf{H}\pi}$	27.10	-0.93	22.75	7.89	32.38	23.14
	$^3\mathbf{I}_\pi$	18.58	0.80	16.52	6.73	24.99	13.88
	$^5\mathbf{R+CH_4}$	4.09	0.00	1.86	-3.59	0.00	0.00
	$^5\mathbf{TS}_{\mathbf{H}\sigma}$	21.62	-4.30	14.18	6.86	22.77	15.02
	$^5\mathbf{I}_\sigma$	11.03	-3.37	5.27	5.04	12.04	5.92
	$^5\mathbf{TS}_{\mathbf{H}\pi}$	31.86	-3.35	25.43	7.05	34.21	24.20
	$^5\mathbf{I}_\pi$	23.47	-1.92	19.21	5.04	25.98	15.72
1-OH	$^3\mathbf{R+CH_4}$	0.00	2.89	0.40	0.00	1.71	2.06
	$^3\mathbf{TS}_{\mathbf{H}\pi}$	25.73	-0.41	22.41	9.68	33.40	22.49
	$^3\mathbf{I}_\pi$	16.49	0.83	14.22	10.25	25.78	12.45
	$^5\mathbf{R+CH_4}$	1.98	0.00	0.00	-1.30	0.00	0.00
	$^5\mathbf{TS}_{\mathbf{H}\sigma}$	22.98	-4.83	16.02	7.01	24.33	16.90
	$^5\mathbf{I}_\sigma$	11.23	-3.02	7.01	5.39	13.71	6.12
	$^5\mathbf{TS}_{\mathbf{H}\pi}$	29.12	-3.41	22.88	9.25	33.44	22.44
	$^5\mathbf{I}_\pi$	18.45	-2.63	14.60	5.07	20.98	13.18
1-N_3	$^3\mathbf{R+CH_4}$	0.00	3.06	0.00	0.00	1.63	2.05
	$^3\mathbf{TS}_{\mathbf{H}\pi}$	25.98	-1.20	22.26	6.80	30.69	22.24
	$^3\mathbf{I}_\pi$	16.76	0.82	14.85	8.01	24.49	12.45
	$^5\mathbf{R+CH_4}$	3.17	0.00	1.13	-2.76	0.00	0.00
	$^5\mathbf{TS}_{\mathbf{H}\sigma}$	22.16	-4.40	14.87	7.47	23.98	16.13
	$^5\mathbf{I}_\sigma$	11.43	-2.95	6.73	4.84	13.19	6.12
	$^5\mathbf{TS}_{\mathbf{H}\pi}$	30.56	-3.87	24.50	6.07	32.20	22.46
	$^5\mathbf{I}_\pi$	21.42	-2.63	16.92	5.16	23.71	13.18

ΔG (B1) relative energies at PBE0/B1 level;

ΔG (B2) relative energies at PBE0/B2// PBE0/B1 level.

Table S3. Spin populations of the reactant, transition state, intermediate, and product for $[Fe^{IV}(O)(NH_3)_4(L)]^+$, (1-L) with L = F^-, N_3^-, NC^-, NCS^-, Cl^-, and OH^-.[a]

		RC		TS_H		IM		TS_{Re}		P	
		S=1	S=2	S=1	S=2	S=1	S=2	S=1	S=2	S=1	S=2
		σ/π	σ/π	σ/π	σ/π	σ/π	σ/π	σ/π	σ/π	σ/π	σ/π
1-F	Fe	1.32/1.32	3.18/3.18	2.42/1.04	3.98/2.87	2.81/0.99	4.26/2.82	2.45/1.26	4.15/3.13	1.99/1.95	3.78/3.78
	O	0.77/0.77	0.58/0.58	0.04/0.51	0.08/0.38	0.06/0.09	0.26/0.09	0.24/-0.10	0.22/0.01	0.00/0.01	0.01/0.01
	CH_3	0.00/0.00	0.00/0.00	-0.41/0.55	-0.45/0.57	-0.97/0.98	-0.97/0.98	-0.76/0.83	-0.59/0.83	0.00/0.00	0.01/0.01
	H[b]	0.00/0.00	0.00/0.00	0.03/-0.05	0.03/-0.04	0.00/0.02	0.00/0.01	0.01/0.01	0.01/0.02	0.00/0.00	0.00/0.00
1-N_3	Fe	—/1.29	3.17/3.17	—/1.01	4.02/2.93	—/0.98	4.19/2.87	—/1.41	4.11/3.19	—/1.94	3.75/3.78
	O	—/0.76	0.62/0.62	—/0.53	0.06/0.43	—/0.08	0.27/0.04	—/-0.10	0.28/-0.14	—/0.01	0.01/0.01
	CH_3	—/0.00	0.00/0.00	—/0.54	-0.51/0.55	—/0.97	-0.97/0.97	—/0.72	-0.83/0.82	—/0.00	0.01/0.01
	H[b]	—/0.00	0.00/0.00	—/-0.05	0.03/-0.04	—/0.00	0.00/0.00	—/0.01	0.01/0.01	—/0.00	0.00/0.00
1-NC	Fe	1.26/1.26	3.13/3.13	2.52/1.02	3.98/2.90	2.82/0.99	4.24/2.85	2.52/1.33	4.15/3.17	2.01/2.01	3.81/3.81
	O	0.80/0.80	0.65/0.65	0.11/0.52	0.12/0.44	0.09/0.10	0.30/0.05	0.17/-0.06	0.31/-0.13	0.00/0.00	0.01/0.01
	CH_3	0.00/0.00	0.00/0.00	-0.61/0.58	-0.47/0.56	-0.97/0.97	-0.97/0.97	-0.73/0.79	-0.82/0.83	0.01/0.01	0.01/0.01
	H[b]	0.00/0.00	0.00/0.00	0.05/-0.05	0.02/-0.04	0.01/0.00	0.00/0.00	0.00/0.01	0.01/0.01	0.00/0.00	0.00/0.00
1-NCS	Fe	1.26/1.26	3.13/3.13	2.41/1.01	3.99/2.89	2.77/0.98	4.23/2.84	2.47/1.42	4.05/3.15	2.03/2.02	3.82/3.82
	O	0.78/0.78	0.61/0.61	0.09/0.51	0.09/0.42	0.25/0.10	0.30/0.05	0.18/-0.10	0.27/-0.13	0.00/0.01	0.01/0.01
	CH_3	0.00/0.00	0.00/0.00	-0.42/0.58	-0.47/0.57	-0.97/0.97	-0.97/0.97	-0.71/0.73	-0.60/0.84	0.01/0.01	0.01/0.01
	H[b]	0.00/0.00	0.00/0.00	0.03/-0.05	0.02/-0.04	0.01/0.00	-0.00/0.00	0.00/0.01	0.01/0.01	0.00/0.00	0.00/0.00
1-Cl	Fe	1.31/1.31	3.17/3.17	2.50/1.04	3.95/2.93	2.74/1.00	4.20/2.88	2.54/1.46	4.08/3.06	2.02/2.02	3.80/3.80
	O	0.76/0.76	0.60/0.60	0.12/0.52	0.11/0.41	0.28/0.09	0.31/0.04	0.28/-0.11	0.30/-0.08	0.01/0.01	0.01/0.01
	CH_3	0.00/0.00	0.00/0.00	-0.62/0.56	-0.47/0.57	-0.97/0.95	-0.96/0.97	-0.78/0.72	-0.72/0.91	0.01/0.01	0.01/0.01
	H[b]	0.00/0.00	0.00/0.00	0.04/-0.05	0.03/-0.04	0.01/0.00	0.00/0.00	0.01/0.01	0.01/0.00	0.00/0.00	0.00/0.00
1-OH	Fe	—/1.32	3.19/3.19	—/1.03	3.98/2.93	—/0.96	4.23/2.82	—/1.44	4.16/3.12	—/1.91	3.76/3.76
	O	—/0.74	0.58/0.58	—/0.51	0.02/0.43	—/0.07	0.21/0.07	—/-0.08	0.23/-0.09	—/0.00	0.00/0.00
	CH_3	—/0.00	0.00/0.00	—/0.53	-0.46/0.53	—/0.98	-0.98/0.98	—/0.65	-0.85/0.82	—/0.01	0.01/0.01
	H[b]	—/0.00	0.00/0.00	—/-0.06	0.04/-0.05	—/0.00	0.01/0.01	—/0.01	0.01/0.01	—/0.00	0.00/0.00

[a] Values from Mulliken population analysis. [b] The transferred hydrogen.

Table S4. Mulliken charge analysis of the reactant, transition state, intermediate, and product for $[Fe^{IV}(O)(NH_3)_4(L)]^+$, (1-L) with L = $CF_3CO_2^-$, F^-, N_3^-, NC^-, NCS^-, Cl^-, and OH^-.[a]

		RC		TS_H		IM		TS_{Re}		P	
		S=1	S=2	S=1	S=2	S=1	S=2	S=1	S=2	S=1	S=2
		σ/π	σ/π	σ/π	σ/π	σ/π	σ/π	σ/π	σ/π	σ/π	σ/π
1-O_2CCF_3	Fe	0.42/0.42	0.75/0.75	0.56/0.59	0.91/0.72	0.56/0.39	0.96/0.66	0.56/0.44	0.90/0.76	0.58/0.56	0.88/0.90
	O	-0.52/-0.52	-0.49/-0.49	-0.71/-0.61	-0.59/-0.60	-0.77/-0.68	-0.69/-0.66	-0.68/-0.61	-0.66/-0.59	-0.51/-0.51	-0.49/-0.51
	CH_3	-0.13/-0.13	-0.13/-0.13	-0.04/-0.07	-0.02/0.07	0.01/0.01	0.02/0.01	0.01/0.02	0.13/0.13	0.23/0.23	0.24/0.25
	H[b]	0.13/0.13	0.13/0.13	0.31/0.32	0.23/0.32	0.31/0.30	0.30/0.31	0.34/0.32	0.35/0.33	0.36/0.35	0.36/0.37
1-F	Fe	0.46/0.46	0.81/0.81	0.71/0.44	0.90/0.54	0.70/0.46	0.90/0.71	0.71/0.48	0.92/0.79	0.62/0.71	0.91/0.91
	O	-0.59/-0.59	-0.56/-0.56	-0.67/-0.64	-0.60/-0.62	-0.70/-0.73	-0.77/-0.71	-0.62/-0.60	-0.68/-0.62	-0.50/-0.47	-0.51/-0.50
	CH_3	-0.13/-0.13	-0.13/-0.13	-0.16/-0.14	-0.08/0.12	0.01/0.01	0.01/0.01	0.09/-0.03	0.06/0.08	0.22/0.25	0.25/0.24
	H[b]	0.13/0.13	0.13/0.13	0.32/0.32	0.27/0.32	0.30/0.30	0.32/0.32	0.35/0.32	0.34/0.34	0.35/0.37	0.36/0.36
1-N_3	Fe	—/0.35	0.68/0.68	—/0.32	0.77/0.63	—/0.30	0.79/0.61	—/0.39	0.86/0.68	—/0.64	0.87/0.87
	O	—/-0.54	-0.52/-0.52	—/-0.64	-0.64/-0.63	—/-0.71	-0.74/-0.69	—/-0.59	-0.67/-0.61	—/-0.48	-0.52/-0.51
	CH_3	—/-0.13	-0.13/-0.13	—/-0.12	-0.04/-0.10	—/0.01	0.01/0.01	—/0.06	0.03/0.09	—/0.24	0.24/0.24
	H[b]	—/0.13	0.13/0.13	—/0.31	0.28/0.33	—/0.29	0.32/0.30	—/0.32	0.34/0.33	—/0.36	0.36/0.36
1-NC	Fe	0.31/0.31	0.63/0.63	0.47/0.24	0.78/0.55	0.51/0.25	0.81/0.51	0.53/0.33	0.82/0.58	0.53/0.52	0.81/0.80
	O	-0.53/-0.53	-0.53/-0.50	-0.68/-0.62	-0.59/-0.60	-0.68/-0.69	-0.72/-0.66	-0.64/-0.61	-0.67/-0.59	-0.51/-0.51	-0.50/-0.50
	CH_3	-0.13/-0.13	-0.13/-0.13	-0.08/-0.08	-0.05/0.08	0.01/0.01	0.02/0.01	0.09/0.02	0.06/0.08	0.22/0.22	0.25/0.24
	H[b]	0.13/0.13	0.13/0.13	0.31/0.30	0.26/0.33	0.33/0.30	0.32/0.31	0.35/0.32	0.35/0.33	0.35/0.35	0.36/0.36
1-NCS	Fe	0.30/0.30	0.63/0.63	0.64/0.29	0.72/0.61	0.51/0.28	0.82/0.54	0.57/0.38	0.85/0.62	0.56/0.54	0.84/0.84
	O	-0.53/-0.53	-0.50/-0.50	-0.62/-0.61	-0.58/-0.60	-0.77/-0.68	-0.71/-0.65	-0.63/-0.60	-0.66/-0.59	-0.51/-0.52	-0.50/-0.50
	CH_3	-0.13/-0.13	-0.13/-0.13	-0.10/-0.09	-0.05/-0.07	0.01/0.01	0.02/0.01	0.11/0.06	0.19/0.08	0.22/0.22	0.25/0.24
	H[b]	0.13/0.13	0.13/0.13	0.27/0.31	0.26/0.32	0.31/0.30	0.32/0.31	0.35/0.32	0.35/0.33	0.35/0.35	0.36/0.37
1-Cl	Fe	0.28/0.28	0.63/0.63	0.44/0.28	0.74/0.60	0.49/0.30	0.79/0.59	0.48/0.38	0.82/0.63	0.50/0.50	0.82/0.81
	O	-0.54/-0.54	-0.51/-0.51	-0.68/-0.63	-0.58/-0.62	-0.77/-0.70	-0.74/-0.69	-0.67/-0.62	-0.67/-0.60	-0.50/-0.51	-0.50/-0.50
	CH_3	-0.13/-0.13	-0.13/-0.13	-0.07/-0.10	-0.05/0.07	0.01/0.01	0.02/0.01	0.04/0.08	0.12/0.03	0.23/0.24	0.24/0.25
	H[b]	0.13/0.13	0.13/0.13	0.32/0.31	0.26/0.32	0.31/0.30	0.32/0.31	0.34/0.33	0.35/0.33	0.36/0.36	0.36/0.36
1-OH	Fe	—/0.64	0.79/0.79	—/0.46	0.88/0.78	—/0.48	0.90/0.76	—/0.48	0.97/0.77	—/0.86	0.93/0.92
	O	—/-0.60	-0.58/-0.58	—/-0.67	-0.62/-0.65	—/-0.77	-0.78/-0.74	—/-0.59	-0.68/-0.63	—/-0.50	-0.51/-0.51
	CH_3	—/-0.13	-0.13/-0.13	—/-0.16	-0.11/-0.14	—/0.00	0.01/0.01	—/0.02	-0.01/0.06	—/0.23	0.23/0.23
	H[b]	—/0.13	0.13/0.13	—/0.32	0.28/0.33	—/0.30	0.31/0.32	—/0.32	0.33/0.33	—/0.35	0.36/0.36

[a] Values from Mulliken population analysis. [b] The transferred hydrogen.

2. Schematic MO diagram of $^{3}TS_{H\sigma}$, $^{3}TS_{H\pi}$, $^{5}TS_{H\sigma}$, and $^{5}TS_{H\pi}$ for $[Fe^{IV}(O)(NH_3)_4(L)]^{+}$. (a) 1-F; (b) 1-Cl; (c) 1-NCS; (d) 1-NC; (e) 1-N_3; (g) 1-OH. Quasi-restricted orbitals were employed.

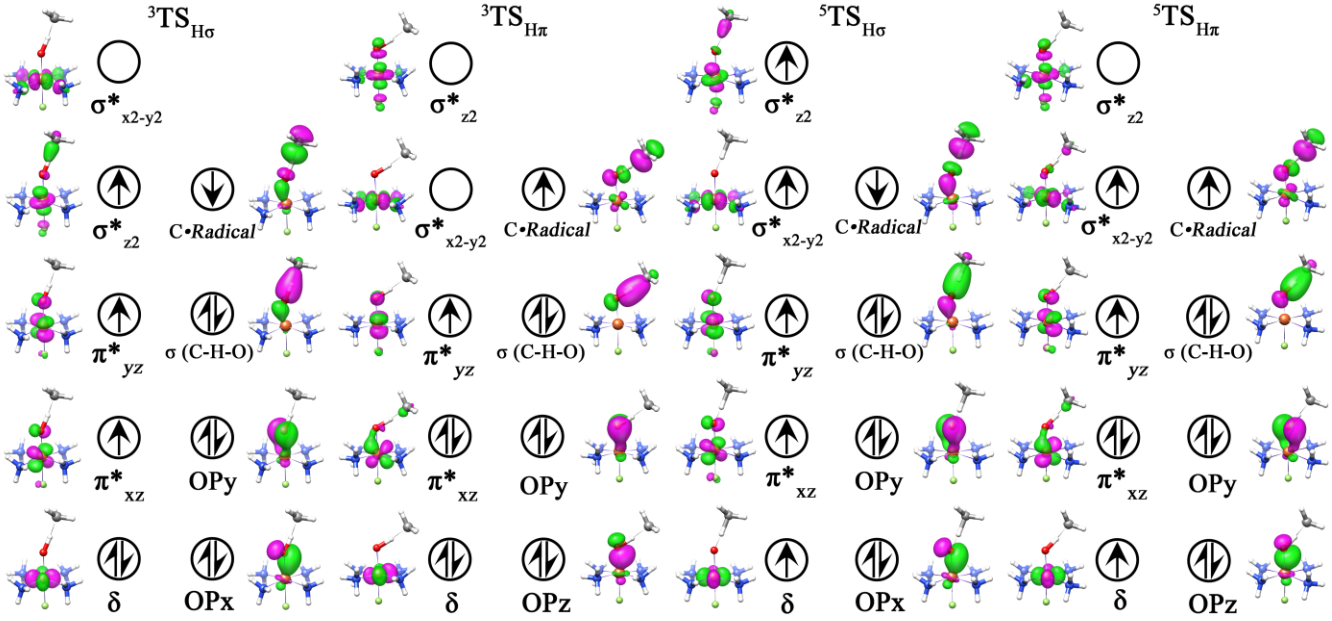

Fig. S1a Schematic MO diagram of $^{3}TS_{H\sigma}$, $^{3}TS_{H\pi}$, $^{5}TS_{H\sigma}$, and $^{5}TS_{H\pi}$ for 1-F.

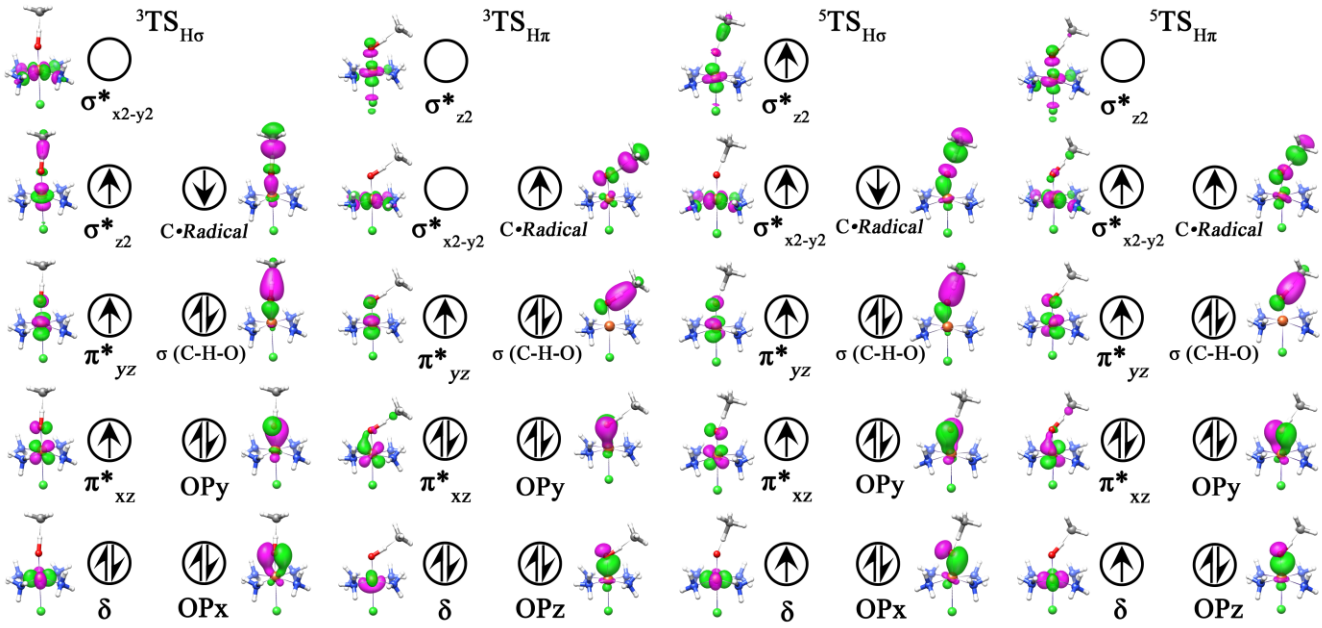

Fig. S1b Schematic MO diagram of $^3TS_{H\sigma}$, $^3TS_{H\pi}$, $^5TS_{H\sigma}$, and $^5TS_{H\pi}$ for 1-Cl.

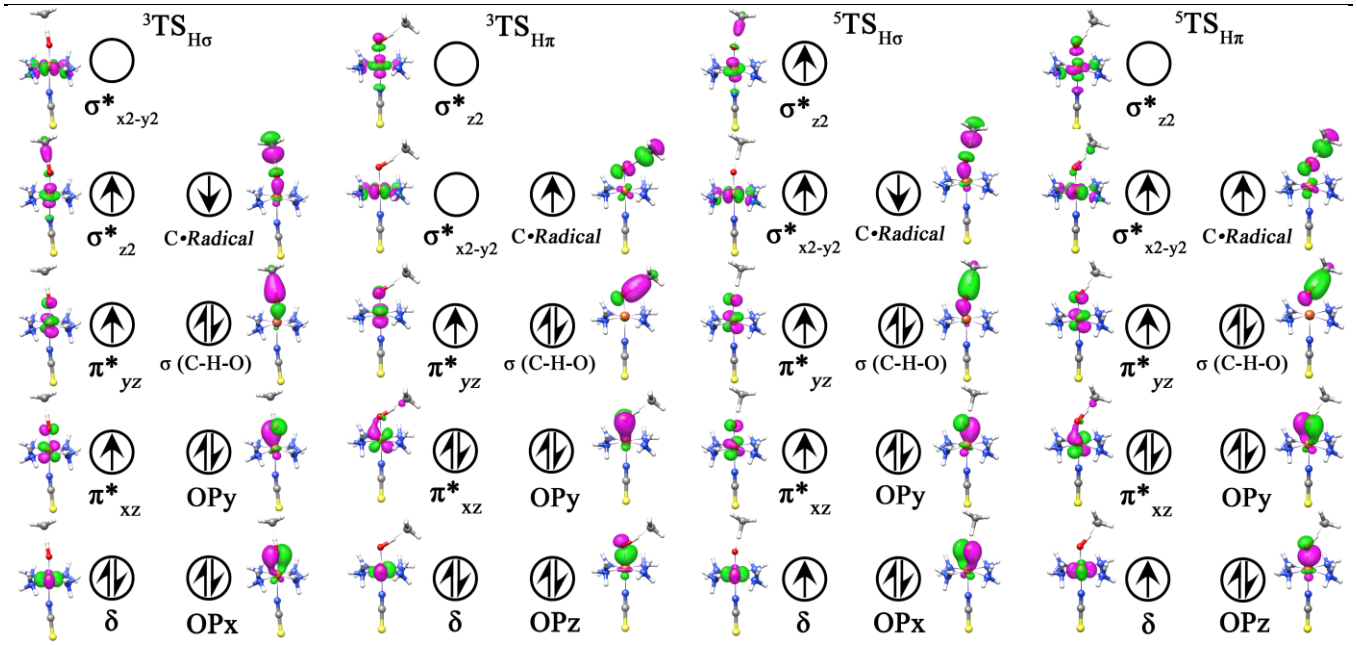

Fig. S1c Schematic MO diagram of $^3TS_{H\sigma}$, $^3TS_{H\pi}$, $^5TS_{H\sigma}$, and $^5TS_{H\pi}$ for 1-NCS.

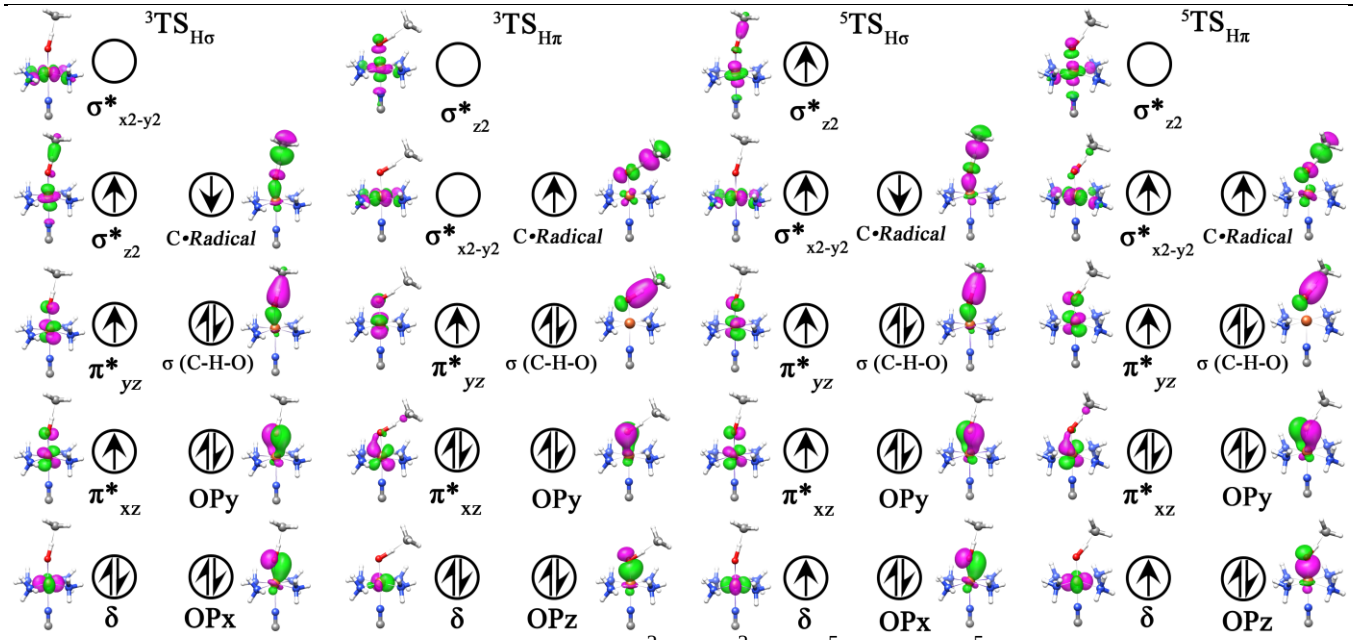

Fig. S1d Schematic MO diagram of $^3TS_{H\sigma}$, $^3TS_{H\pi}$, $^5TS_{H\sigma}$, and $^5TS_{H\pi}$ for 1-NC.

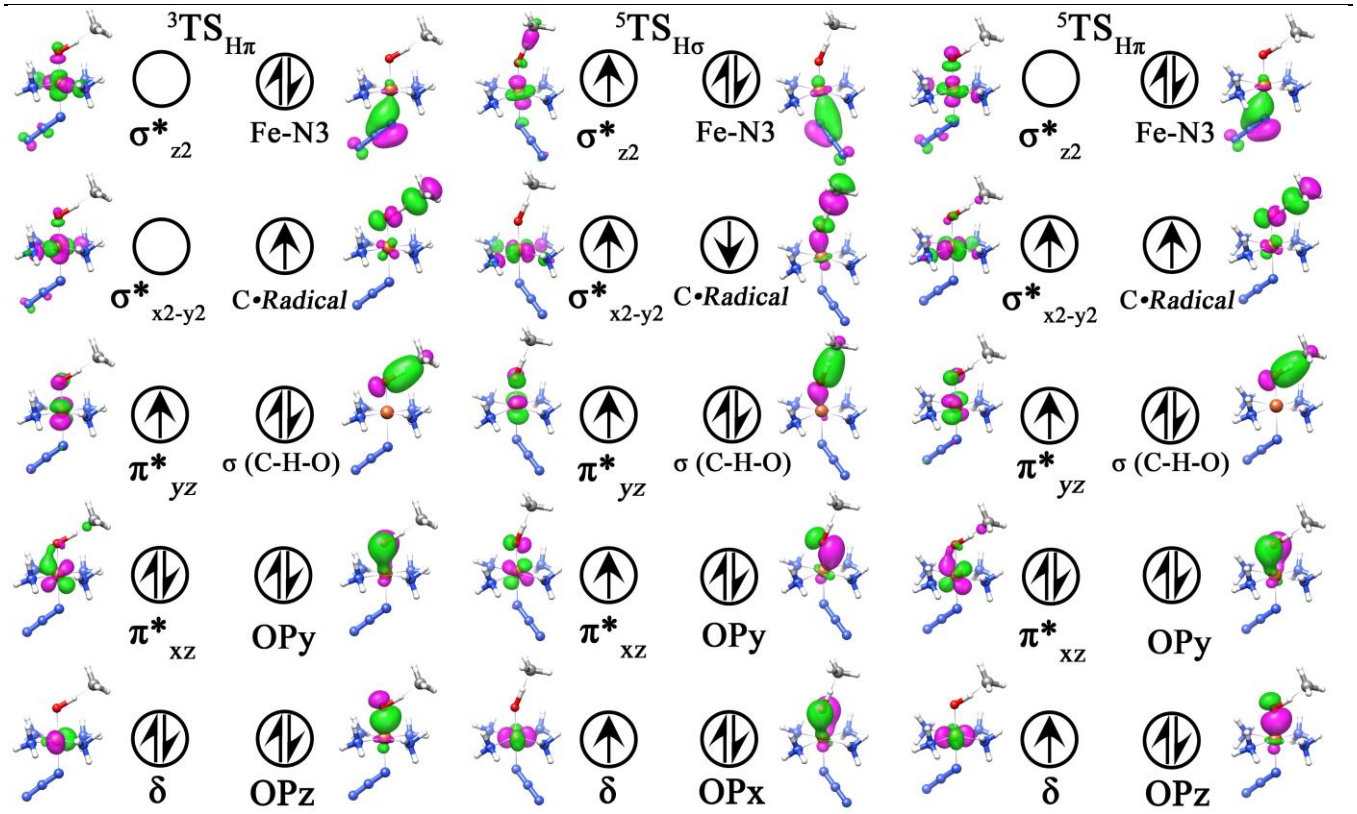

Fig. S1e Schematic MO diagram of $^3TS_{H\pi}$, $^5TS_{H\sigma}$, and $^5TS_{H\pi}$ for 1-N_3.

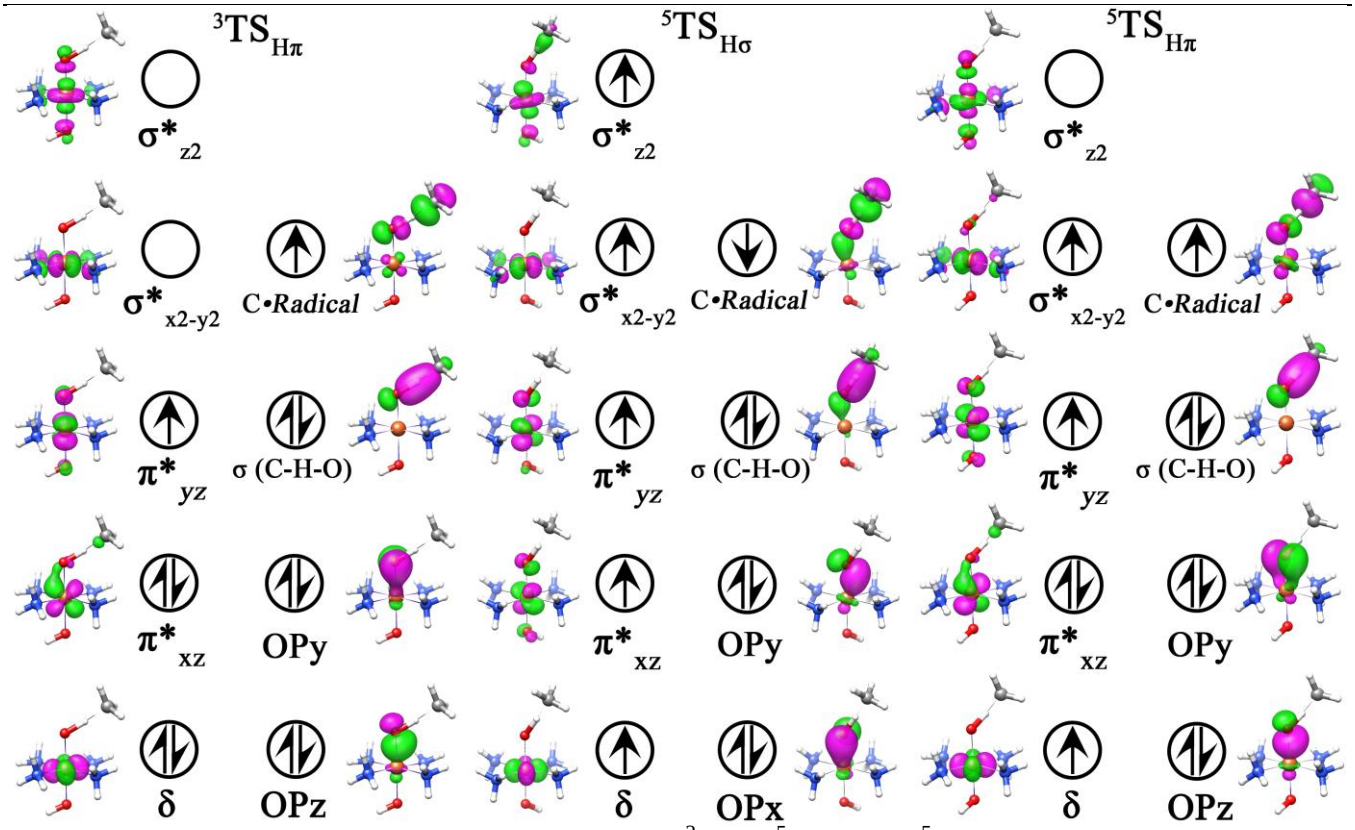

Fig. S1f Schematic MO diagram of $^3TS_{H\pi}$, $^5TS_{H\sigma}$, and $^5TS_{H\pi}$ for 1-OH.

3. The energy profile of methane hydroxylation by the $[Fe^{IV}(O)(NH_3)_4(L)]^+$ complexes in the triplet and quintet states at the B3LYP/B2//B3LYP/B1 level. (a) 1-F; (b) 1-Cl; (c) 1-NCS; (d) 1-NC; (e) 1-N_3; (f) 1-OH.

In system (a) **1-F**

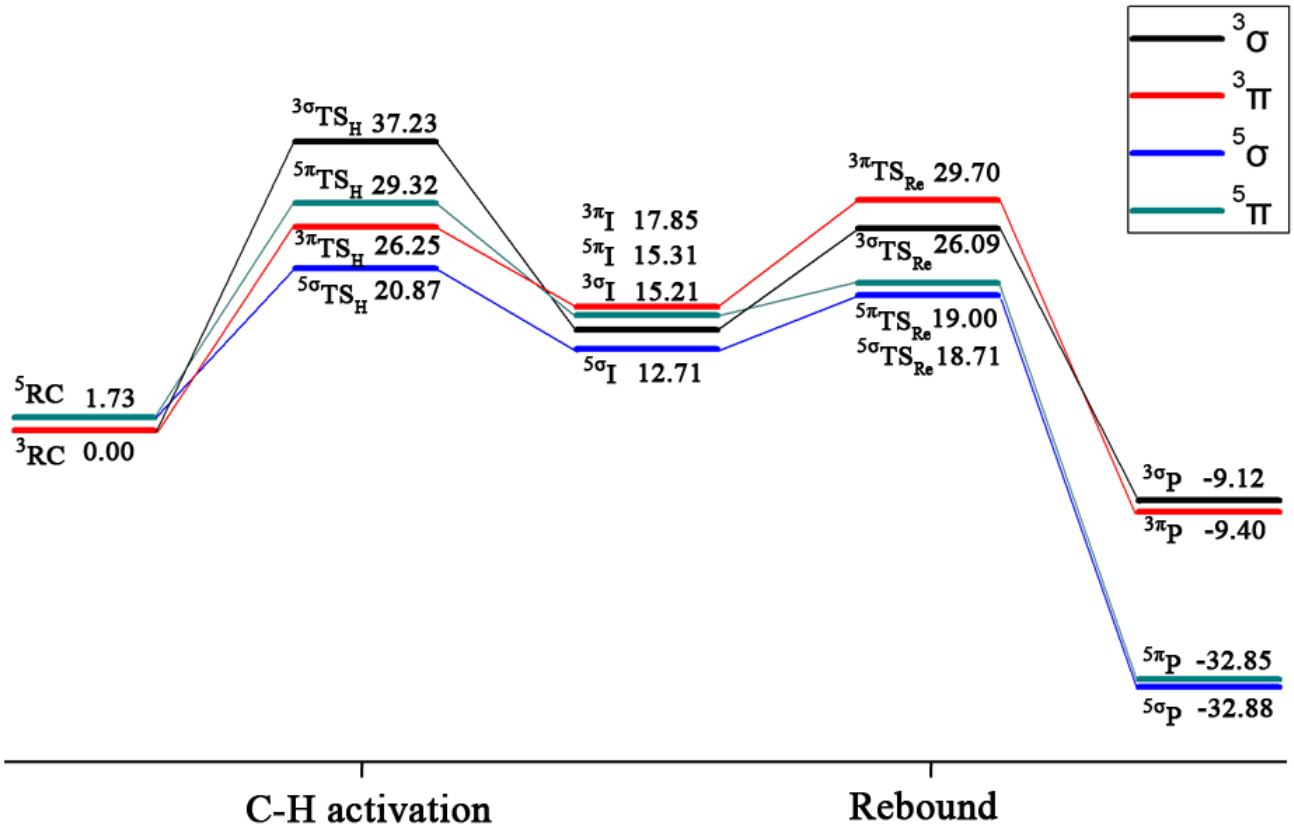

Fig. S2a Schematic Gibbs free energy (ΔG) surfaces for methane hydroxylation by 1-F in acetonitrile solution.

In system (b) **1-Cl**

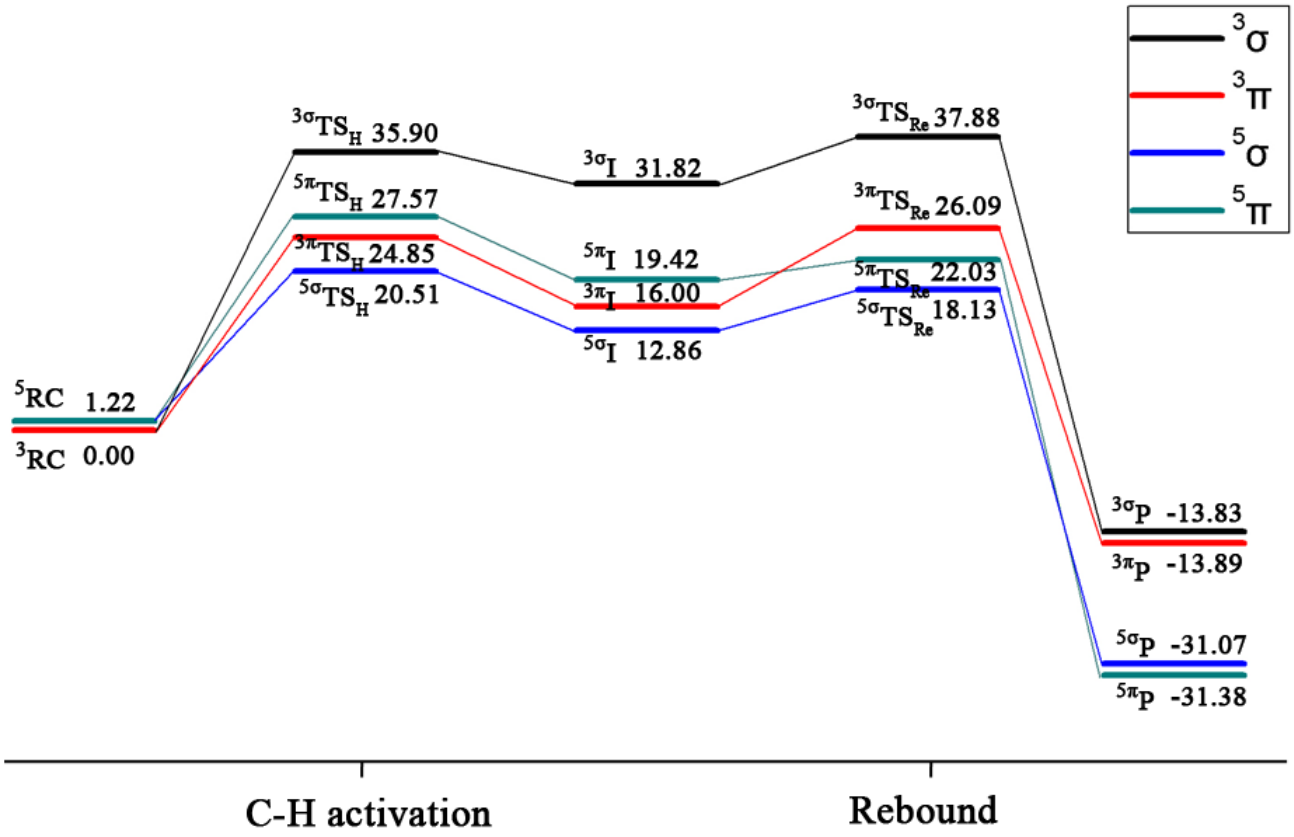

Fig. S2b Schematic Gibbs free energy (ΔG) surfaces for methane hydroxylation by 1-Cl in acetonitrile solution.

In system (c) **1-NCS**

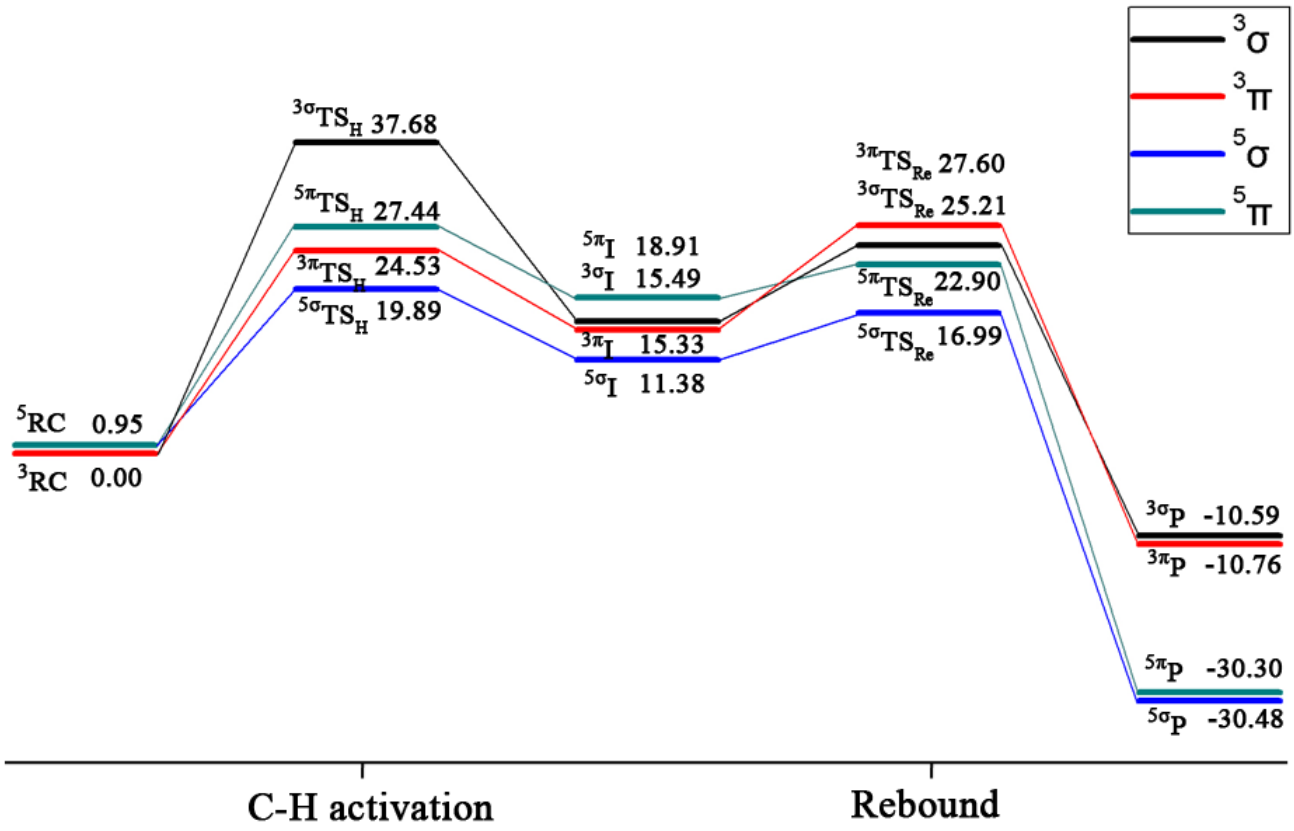

Fig. S2c Schematic Gibbs free energy (ΔG) surfaces for methane hydroxylation by 1-NCS in acetonitrile solution.

In system (d) **1-NC**

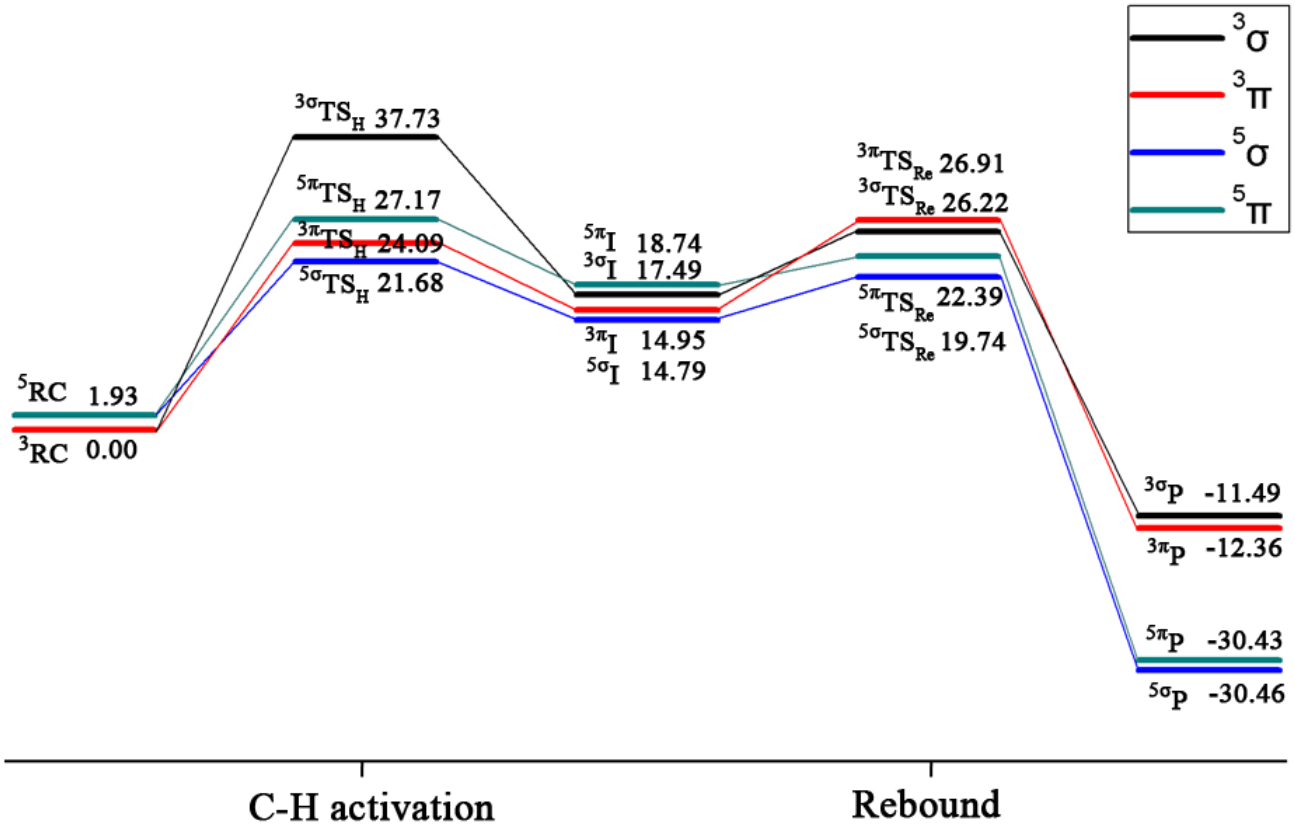

Fig. S2d Schematic Gibbs free energy (ΔG) surfaces for methane hydroxylation by 1-NC in acetonitrile solution.

In system (e) **1-N_3**

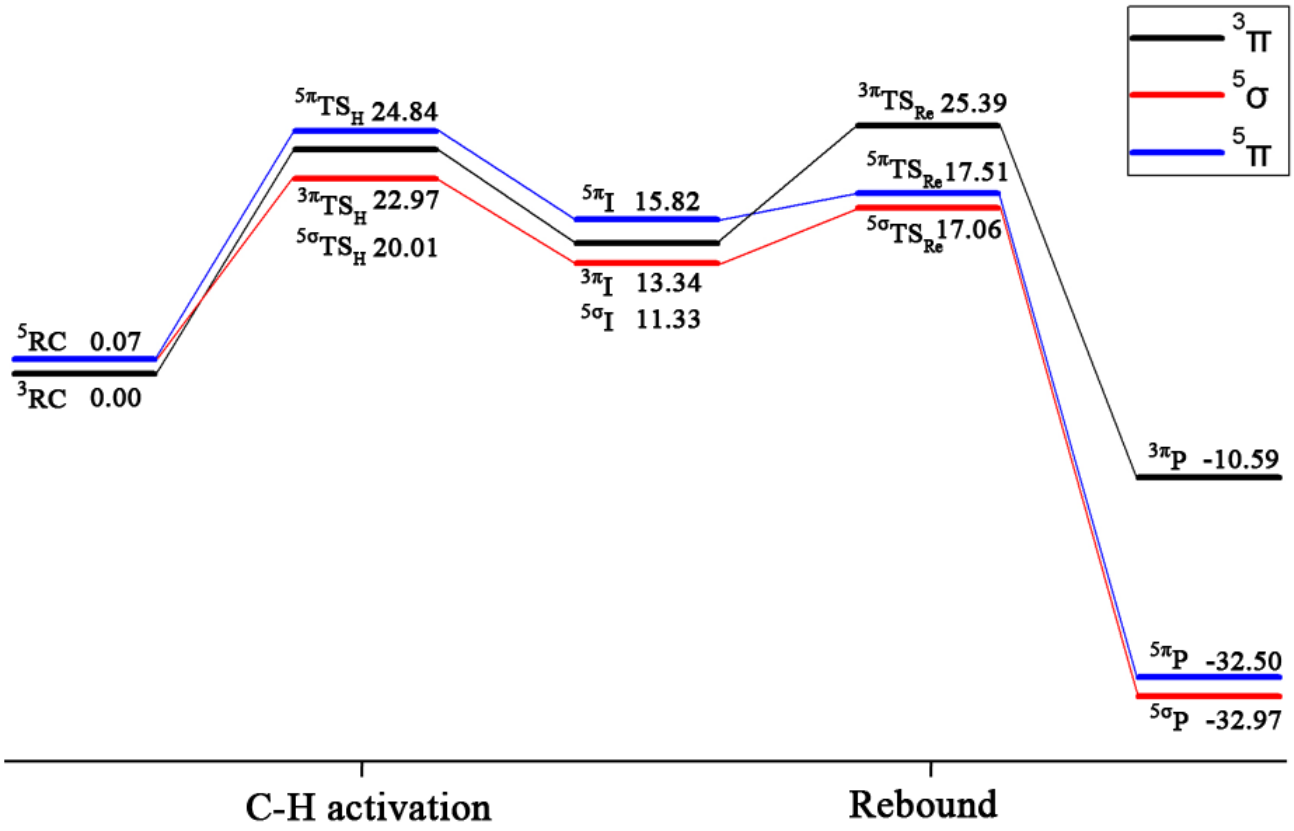

Fig. S2e Schematic Gibbs free energy (ΔG) surfaces for methane hydroxylation by 1-N_3 in acetonitrile solution.

In system (f) **1**-OH

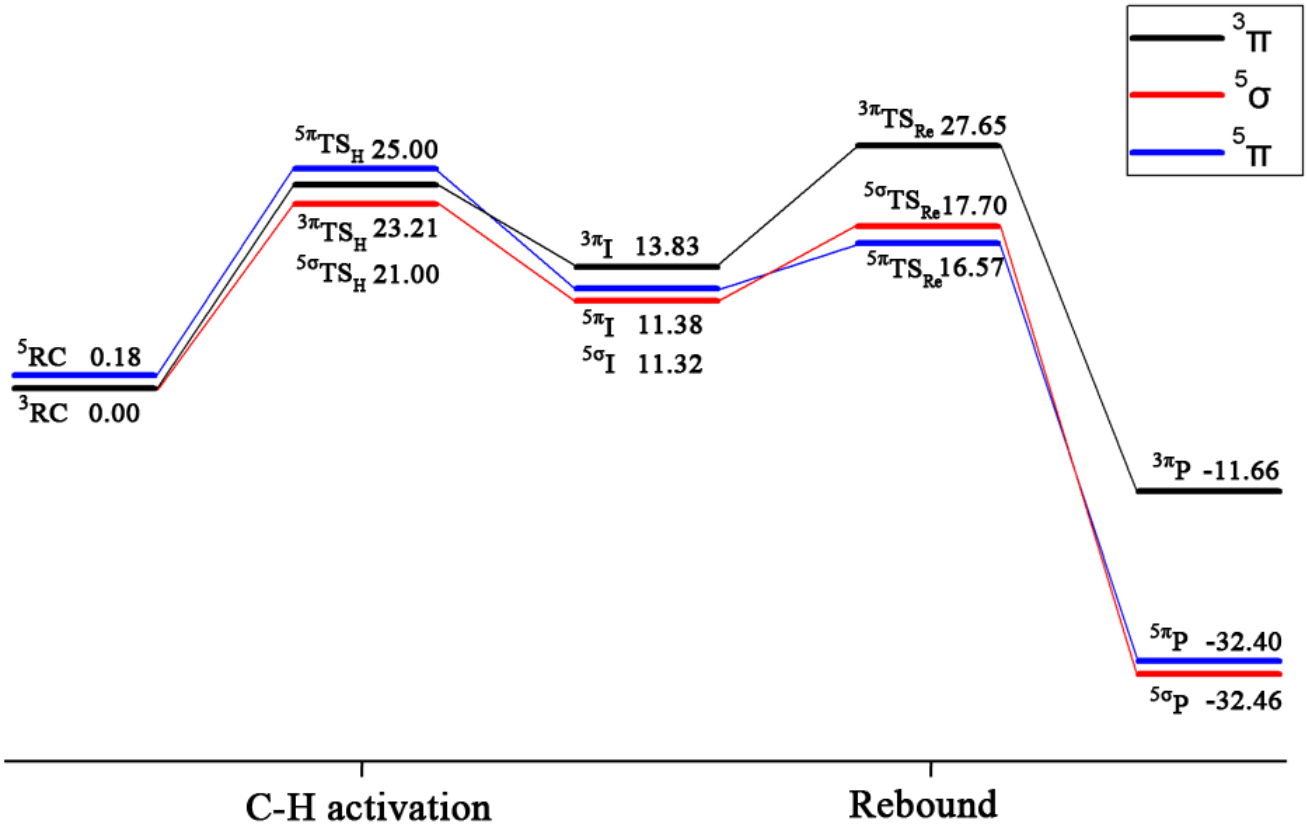

Fig. S2f Schematic Gibbs free energy (ΔG) surfaces for methane hydroxylation by 1-OH in acetonitrile solution.

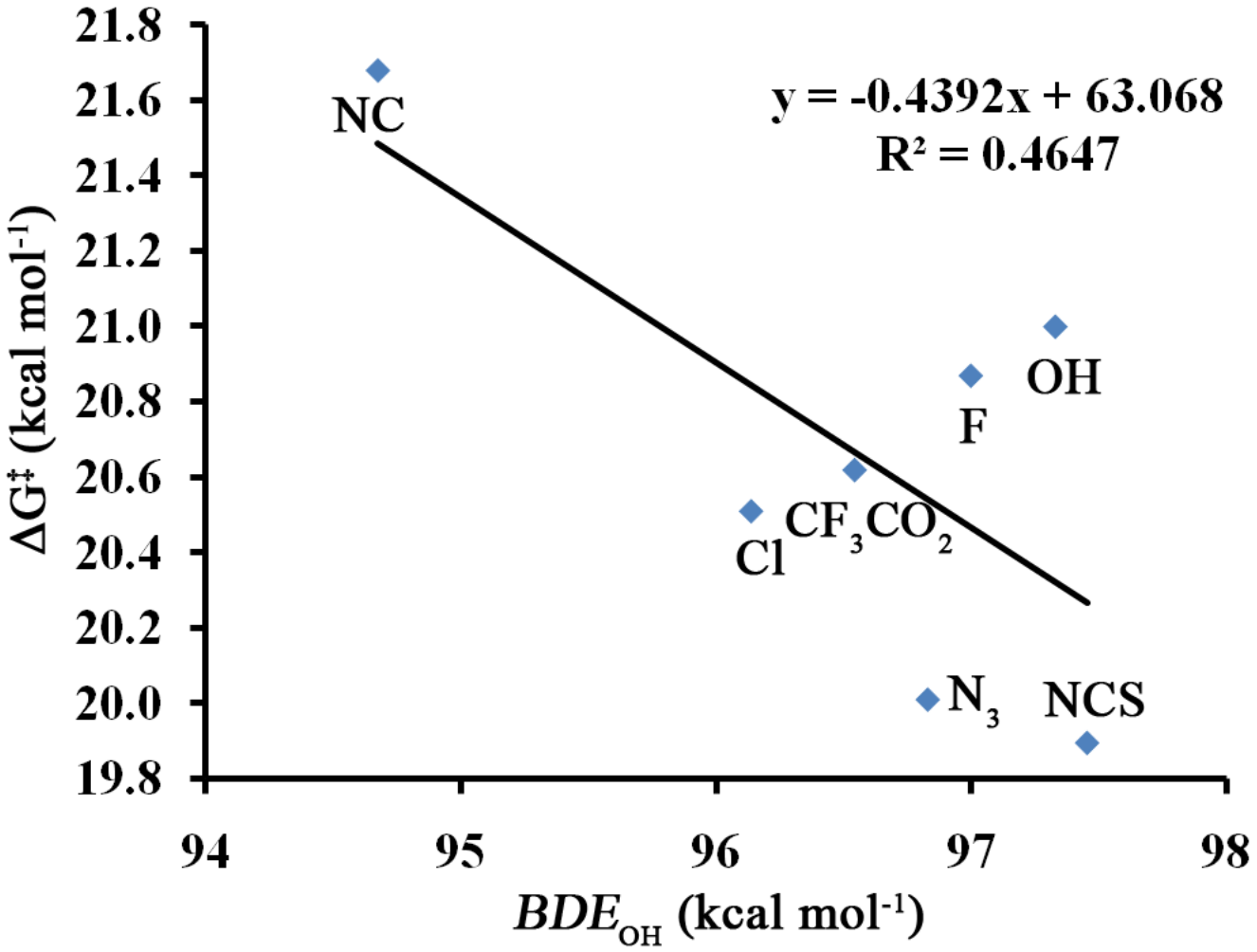

Fig. S3 Correlation of methane hydroxylation ^{5}σ-pathway barrier height with BDE_{OH} without inclusion of the RE_{FeOH}. Models tested were $[Fe^{IV}(O)(NH_3)_4(L)]^+$ (1-L) with L = N_3^-, OH^-, NC^-, NCS^-, F^-, Cl^-, and $CF_3CO_2^-$.

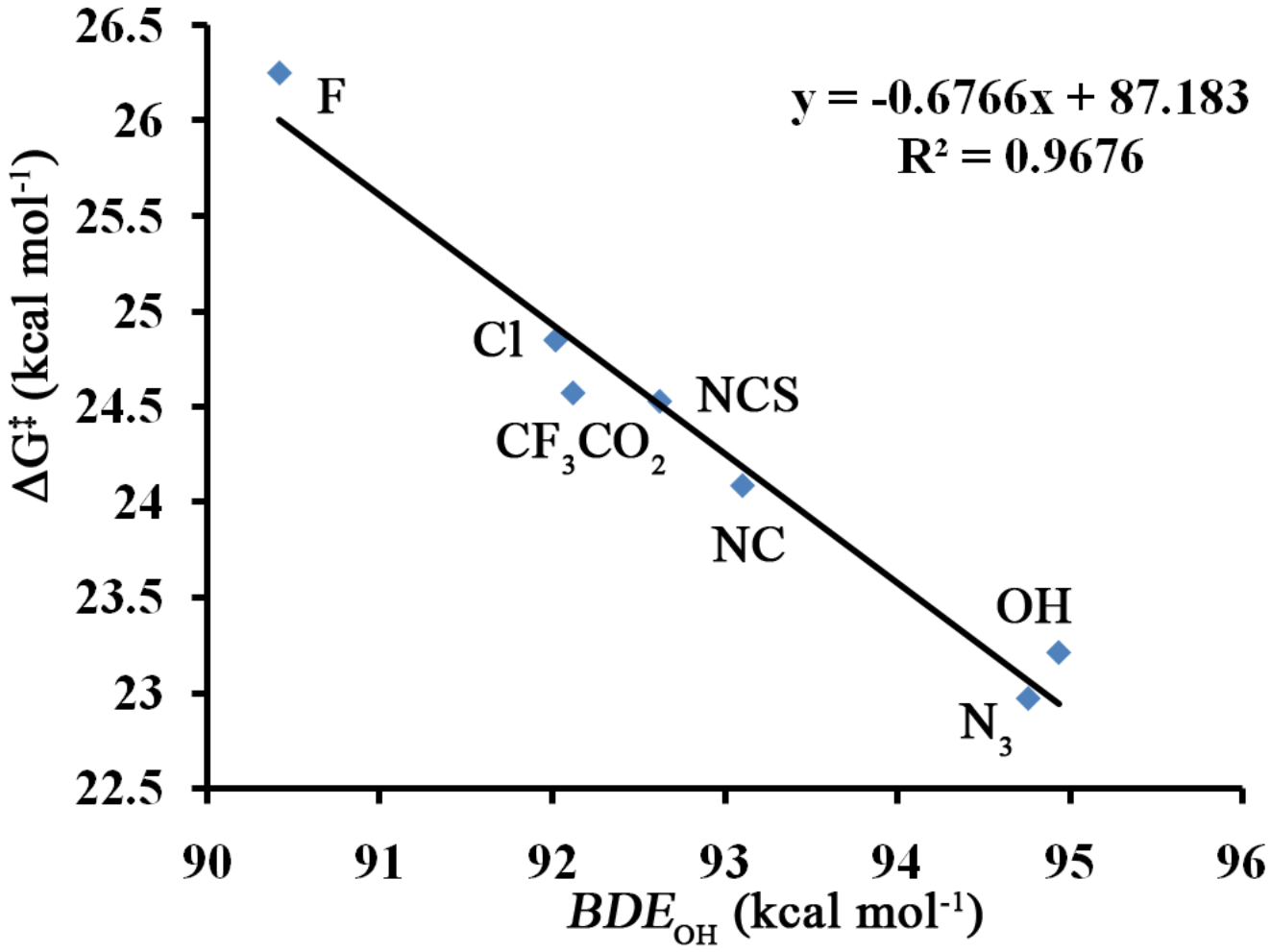

Fig. S4 Correlation of methane hydroxylation $^3\pi$-pathway barrier height with BDE_{OH} without inclusion of the RE_{FeOH}. Models tested were $[Fe^{IV}(O)(NH_3)_4(L)]^+$ (1-L) with L = N_3^-, OH^-, NC^-, NCS^-, F^-, Cl^-, and $CF_3CO_2^-$.