SUPPORTING INFORMATION

The Enzyme-like Catalytic Hydrogen Abstraction Reaction Mechanisms of Cyclic Hydrocarbons with Magnesium-Diluted Fe-MOF-74

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Table S1. Comparison of Fe-O bond lengths (Å) of Fe/(Mg)-MOF-74 using B3LYP-D3 and M06-L-D3 methods.

Project / Bond	EXP[a]	B3LYP-D3	Relative Error	M06-L-D3	Relative Error
Fe-O_1	2.067	2.064	-0.15%	2.065	-0.10%
Fe-O_2	2.166	2.168	0.10%	2.169	0.14%
Fe-O_3	2.077	2.070	-0.34%	2.075	-0.10%
Fe-O_4	2.022	2.016	-0.30%	2.017	-0.25%
Fe-O_5	2.054	2.052	-0.10%	2.053	-0.05%

[a] Parameters obtained from crystal structure of Fe/(Mg)-MOF-74.

Table S2. The Calculated $^5\Delta H$, $^3\Delta H$, $^5\Delta G$, $^3\Delta G$ for various species of the oxidation reaction of CHD catalyzed by Fe(Mg)-MOF-74.

species / project	**A+N_2O +CHD**	**B**	**TS1**	**C**	**D**	**TS2**	**E**	**F**	**TS3**	**G**	**A+N_2+ H_2O+benzene**
$^5\Delta H$ (kcal/mol)	0.0	-8.5	10.9	-24.1	-33.7	-30.2	-53.8	-56.1	-50.9	-88.4	-62.8
$^3\Delta H$ (kcal/mol)	31.2	29.0	32.4	-5.2	-14.5	-9.8	-34.1	-35.6	-27.7	-61.7	-31.6
$^5\Delta G$ (kcal/mol)	0.0	0.6	20.4	-17.0	-21.9	-17.5	-42.6	-45.1	-39.1	-78.5	-73.1
$^3\Delta G$ (kcal/mol)	31.6	38.3	43.1	1.6	-2.2	4.7	-22.4	-23.8	-14.3	-50.3	-41.5

Table S3. The Calculated $^{5}\Delta H$ and $^{5}\Delta G$ for various species of the oxidation reaction of CHA catalyzed by Fe(Mg)-MOF-74.

species / project	**H**	**TS4**	**I**	**TS5**	**J**
$^{5}\Delta H$ (kcal/mol)	0.0	8.1	-5.2	-4.3	-34.0
$^{5}\Delta G$ (kcal/mol)	0.0	9.2	-5.0	-4.0	-32.2

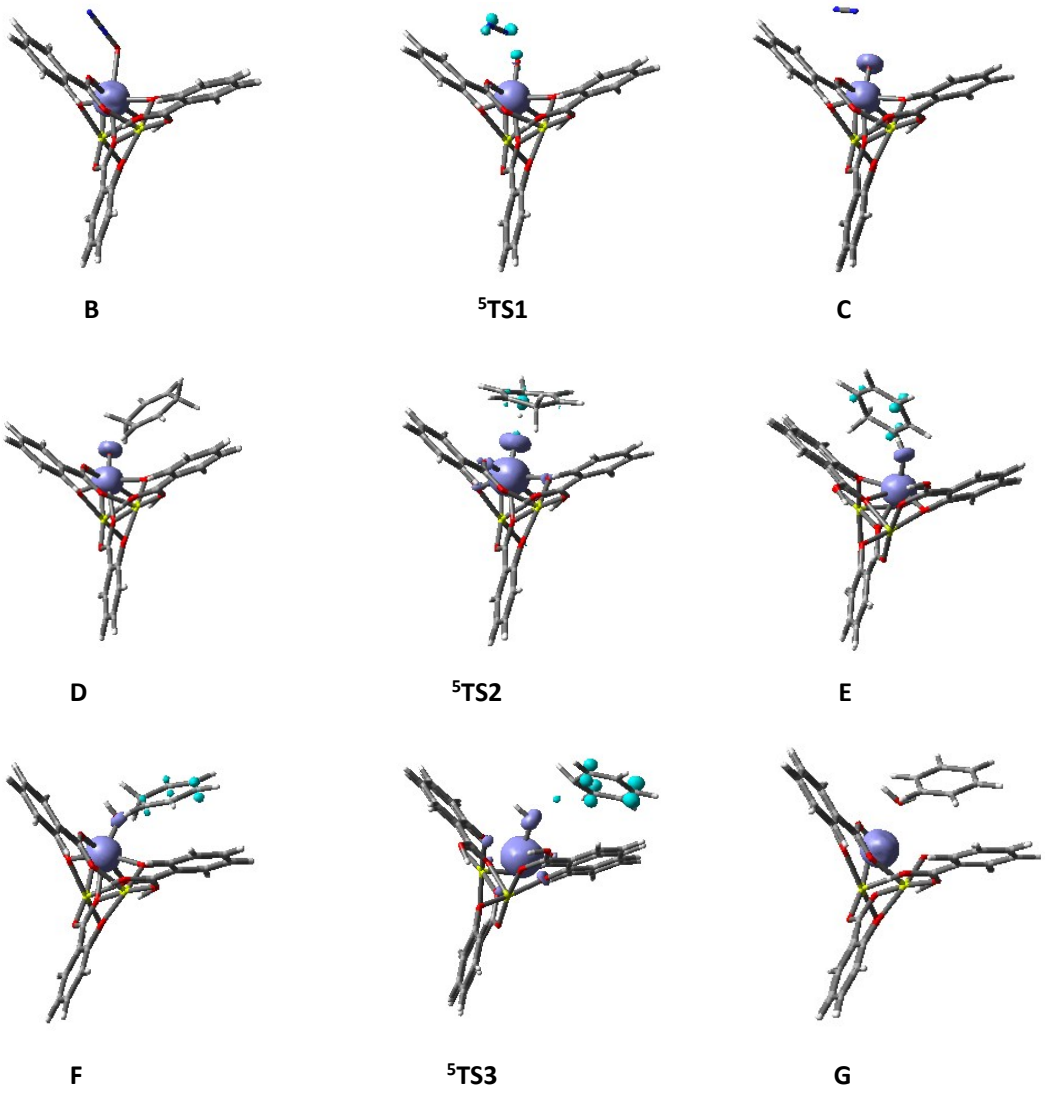
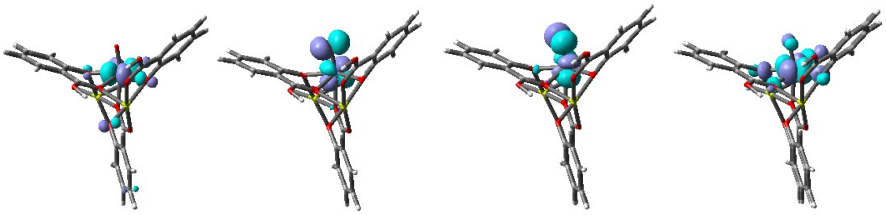


Fig. S1. The calculated spin density distribution of **^{5}TS1**, **^{5}TS2**, **^{5}TS3** and **B~G** species.

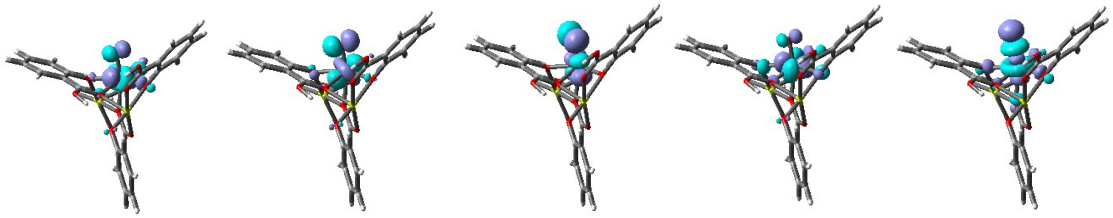
Spin Natural Orbitals of **^{5}A-O**



δ π^* π^* σ^*_{xy}

(1.00 *e*) (1.00 *e*) (1.00 *e*) (1.00 *e*)

Natural Orbitals of **^{5}A-O**

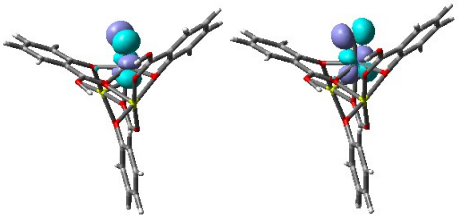


δ π^* π^* σ^*_{xy} $\sigma^{*}_{z^2}$

(1.00 *e*) (1.00 *e*) (1.00 *e*) (1.00 *e*) (0.00 *e*)

(a)

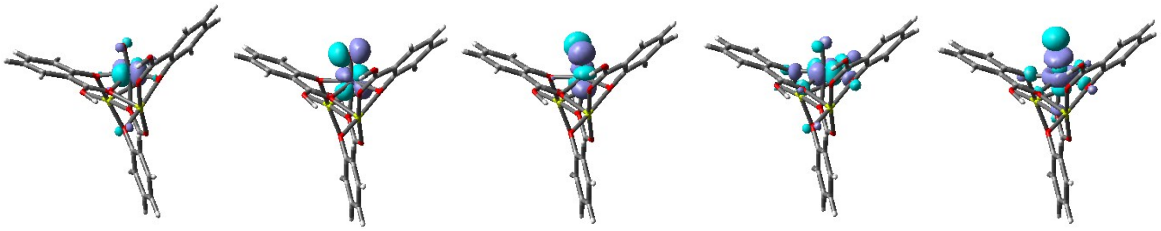
Spin Natural Orbitals of **^{3}A-O**



π^* π^*

(1.00 *e*) (1.00 *e*)

Natural Orbitals of **^{3}A-O**

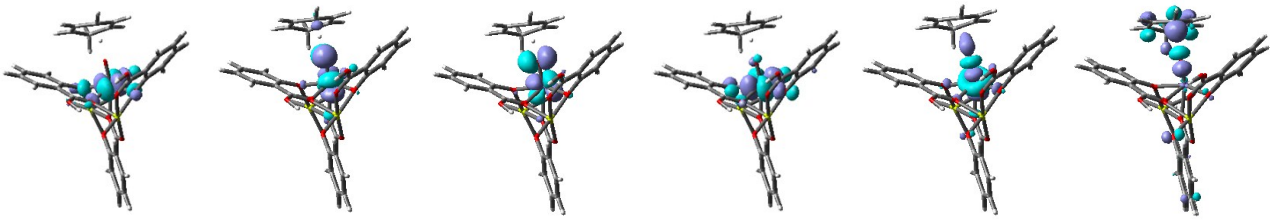


δ π^* π^* σ^*_{xy} $\sigma^{*}_{z^2}$

(2.00 *e*) (1.00 *e*) (1.00 *e*) (0.00 *e*) (0.00 *e*)

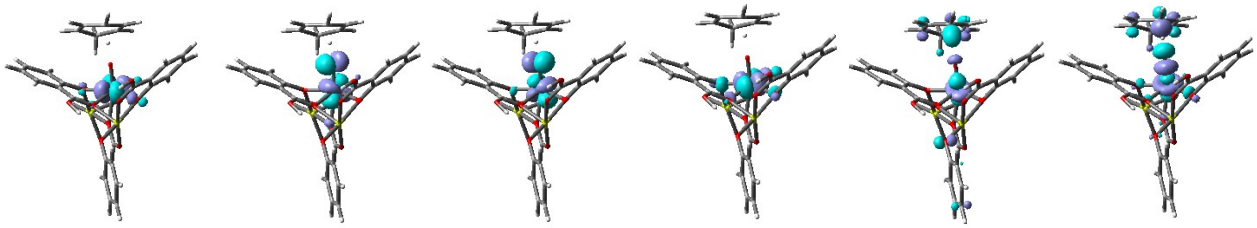
(b)

Spin Natural Orbitals of **^{5}TS2**



δ	π^*	π^*	σ^*_{xy}	$\sigma^*_{z^2}$	ϕ_C+2P(O)
(1.00 *e*)	(1.00 *e*)	(1.00 *e*)	(1.00 *e*)	(0.70 *e*)	(-0.70 *e*)

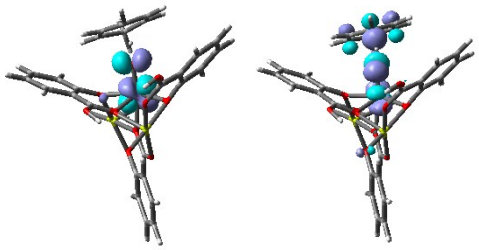
Natural Orbitals of **^{5}TS2**



δ	π^*	π^*	σ^*_{xy}	$\phi_C+\sigma^*_{z^2}$	$\phi_C+\sigma^*_{z^2}$
(1.00 *e*)	(1.00 *e*)	(1.00 *e*)	(1.00 *e*)	(1.77 *e*)	(0.23 *e*)

(c)

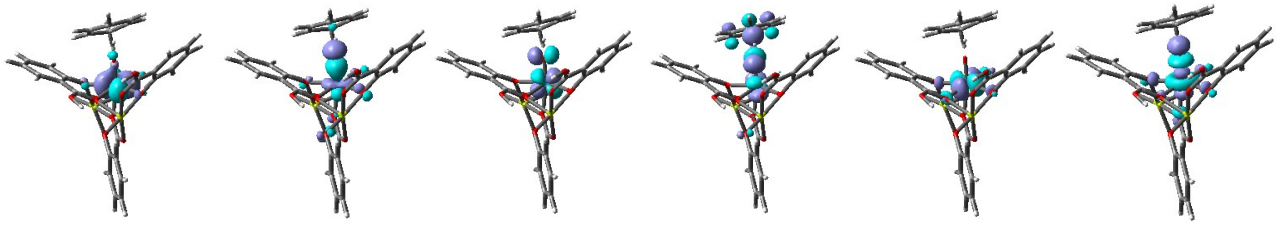
Spin Natural Orbitals of **^{3}TS2**



π^* $\pi^*+\phi_C$

(1.00 *e*) (1.00 *e*)

Natural Orbitals of **^{3}TS2**



δ d_{yz} π^* $\pi^*+\phi_C$ σ^*_{xy} $\sigma^{*}{}^{2}_{z}$

(2.00 *e*) (2.00 *e*) (1.00 *e*) (1.00 *e*) (0.00 *e*) (0.00 *e*)

(d)

Fig. S2. The calculated spin natural orbitals, natural orbitals and their occupations of (a) **^{5}A-O**; (b) **^{3}A-O**; (c) **^{5}TS2**; and (d) **^{3}TS2** for the first hydrogen abstraction reaction. The negative occupation in φ_C denotes β spin electron.