

Supplementary Information

Pyridine Coordination Enabled Stepwise PT/ET N–H transfer and Metal-independent C–C cleavage Mechanism for Cu-Mediated Dehydroacylation of Unstrained Ketones

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1. Evaluation of density functionals

In order to evaluate the dependency of density functionals for the calculation results of this copper mediated system, we also calculated the Gibbs free energies of ³IM3 and ³TS2, which are key structures for C–C homolysis, using other seven widely-used and/or recently developed density functionals, including ωB97X¹, B3LYP-D3^{2, 3}, B3PW91-D3^{4, 5}, HSE06^{6, 7}, PBEh1PBE⁸, M06⁹ and M06-2X⁹. The structures of ³IM3 and ³TS2 were re-optimized individually using each functional. As shown in Table S1, M06 gives the lowest relative free energy of 17.5 kcal/mol, while ωB97X-D gives the highest relative free energy of 23.8 kcal/mol. The difference of relative free energies obtained using those density functionals are less than 6.3 kcal/mol, which indicates that this copper mediated system has a moderate dependence of density functionals. The ωB97X-D functional includes dispersion corrections and has a gradually varied exact exchange energy from short-range to long-range for better accuracy, thus we use the ωB97X-D functional in our computational study for this system.

Table S1. Absolute and relative free energies of ³IM3 and ³TS2 obtained by using different density functionals.

Functionals	Absolute free energies (Hartree)		Relative free energies (kcal/mol)
	³ IM3	³ TS2	³ IM3 → ³ TS2
M06-2X	-4843.362653	-4843.325885	23.1
B3LYP-D3	-4844.260707	-4844.231196	18.5
B3PW91-D3	-4843.591812	-4843.561941	18.7
M06	-4843.013879	-4842.986002	17.5
PBEh1PBE	-4842.015377	-4841.981572	21.2

HSE06	-4841.982833	-4841.949500	20.9
ω B97X	-4843.79984	-4843.764437	22.2
ω B97X-D	-4804.416831	-4804.378881	23.8

2. Evaluation of spin states

In order to find out correct spin states in the reaction, we calculated different spin states of some key structures in the proposed mechanism. The structures listed in Table S2 were re-optimized with different spin states. The free energy profile in the reaction coordinate reported in the text contains the spin states with lower energies.

Table S2. Absolute and relative free energies of different spin states.

Complexes	Absolute free energies (Hartree)		Relative free energies (kcal/mol)
	Singlet	Triplet	Singlet \rightarrow Triplet
IM0	-4194.321413	-4194.391480	-43.9
IM1	-5072.600166	-5072.679448	-49.8
IM2	-5072.648674	-5072.667233	-11.6
IM3	-4843.669170	-4843.702042	-20.6
IM8	-4843.700550	-4843.702648	-1.3
TS3	-4843.672846	-4843.661464	7.1
IM9	-4843.738967	-4843.683265	35.0

3. mechanisms of mononuclear mediated ketone dehydroacylation

Copper carboxylates often exist in a dimeric form, so we calculated the dimerization product of copper(II) carboxylate and found a 15.1 kcal/mol more stable triplet dimer complex **³IM0**. The mechanism of mononuclear mediated dehydroacylation of 4-phenyl-2-butanone to the corresponding olefin was calculated and the total free energy barrier was found up to 27.9 kcal/mol (**³IM0** \rightarrow **²TS2s**), thus we propose the dimers of copper(II) carboxylates as valid oxidants in the dehydroacylation reaction.

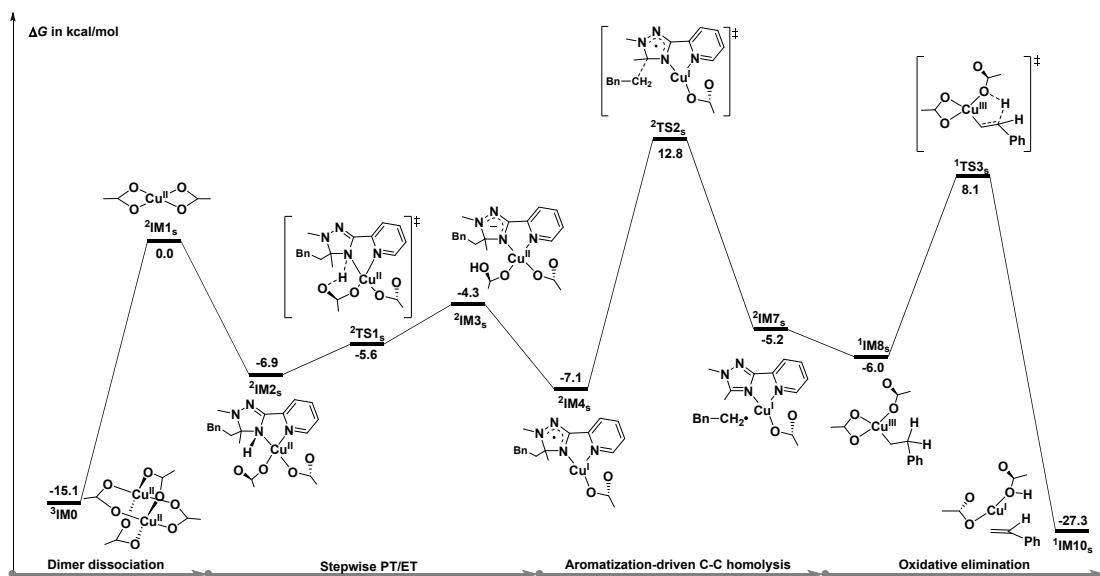


Fig. S1 Free energy profile for mononuclear copper(II) mediated dehydroacylation with MPHA.

4. Relative electronic energies curve with the increasing of O–H distance

Proton transfer from N–H to the terminal oxygen could not be located, so we scanned the distance of O–H bond from 1.05 to 1.35 Å and the results shows an energy descending curve.

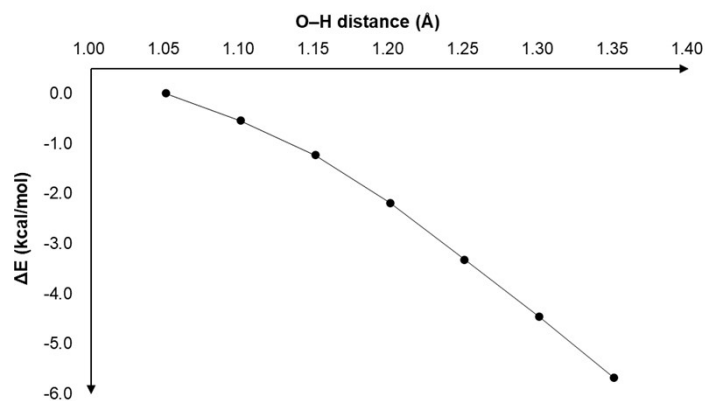


Fig. S2 Calculated relative electronic energies with the increasing of O–H distance in $^3\text{IM2}^{\text{Ph}}$.

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