

# **Linear Correlation between C-H Activation Barrier and C-Cu/C-H Bond Dissociation Energy Gap in Cu-Promoted C-H Activation of Heteroarenes**

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## Computational methods

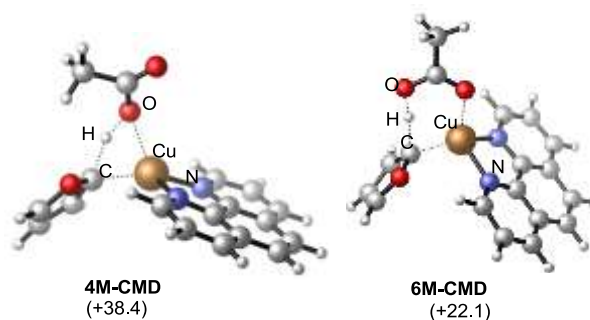
All calculations are performed with G09 program.<sup>1</sup> Gas phase geometry optimization, gas phase single point calculations and solution phase single point calculations were conducted in this study. In the gas phase geometry optimization, different DFT functionals (including B3LYP, M05, M06 and M06L) with 6-31G(d) basis set were performed on concerned intermediates and transition states. Considering M05 functional gives the best performance, different effective core potentials (ECPs) on Cu (including ECP of LanL2MB, SDD, LanL2DZ with an additional polarization function  $\text{Cu}(\zeta(f) = 3.525)$ ) and 6-31G(d) basis set on the other atoms were conducted to examine basis set effects. Frequency analysis was performed to provide the thermal correction of the Gibbs free energy and verify that each stationary point is a local minimum or transition state.

Based on the gas phase optimized geometries (M05/6-31G(d)), gas phase single point calculations were calculated by using different functionals (including B3LYP, M05, M06 and M06L), in which 6-31G(d) with an additional polarization function  $\text{Cu}(\zeta(f) = 3.525)$  was performed on Cu, 6-311++G(d,p) or 6-311++G(2df,2p) basis set was performed on the other atoms. The self-consistent reaction field (SCRF) with CPCM solvation model and UAHF radii were used in the solution phase single point calculations. The 6-31G(d) with an additional polarization function  $\text{Cu}(\zeta(f) = 3.525)$  was used for Cu, and 6-311++G(d,p) basis set was used for the other atoms. Toluene and 1,4-dioxane were used as solvent. Corresponding to the computational method reported by Guo et al,<sup>2</sup> B3LYP/6-311++G(2df,2p)/PCM(DMSO)/ Bondi//B3LYP/6-31G(d) was used to calculate energy properties concerned with the pKa.

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Jr. Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski,

- J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox D. J. Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.
2. Shen, K.; Fu, Y.; Li, J. N.; Liu, L.; Guo, Q. X. *Tetrahedron* **2007**, *63*, 1568.

## CMD transition states



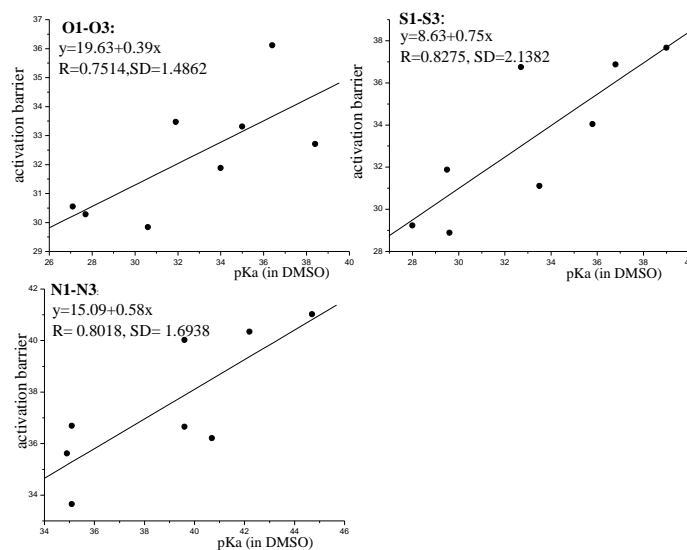
**Figure S1.** Optimized structures of **4M-CMD** and **6M-CMD** of C(2)-H of furan. The Gibbs free energy are given in kcal/mol.

In this study, the C-H activation of furan was taken as an example to examine the relative facility of four-membered-cyclic CMD transition state (**4M-TS**) and six-membered-cyclic CMD transition state (**6M-TS**) (Figure S1). It's found that **6M-TS** is energetically much more feasible than **4M-TS**, similar to the observations found in previous study on Pd-,<sup>1</sup> Rh-<sup>2</sup> and Ir-catalyzed<sup>3</sup> C-H bond activation processes.

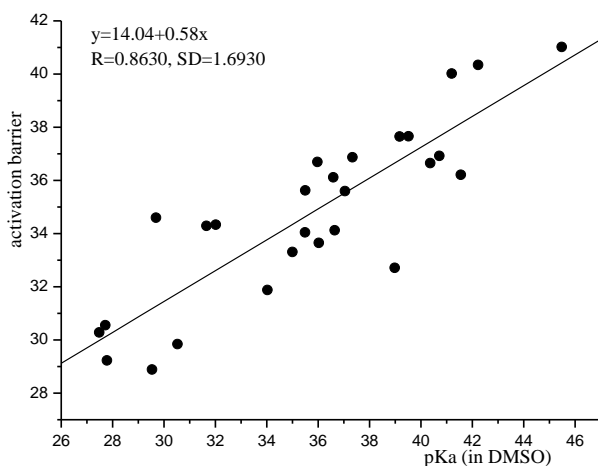
## References

1. (a) Sun, H. Y.; Gorelsky, S. I.; Stuart, D. R.; Campeau, L. C.; Fagnou, K. *J. Org. Chem.* **2010**, *75*, 8180. (b) Rousseaux, S.; Gorelsky, S. I.; Chung, B. K. W.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 10692. (c) Davies, D. L.; Donald, S. M.; Macgregor, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 13754.
2. Zhang, Q.; Yu, H. Z.; Li, Y. T.; Liu, L.; Huang, Y.; Fu, Y. *Dalton Trans*, **2013**, *42*, 4175.
3. (a) Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Macgregor, S. A.; Polleth, M. *J. Am. Chem. Soc.* **2006**, *128*, 4210. (b) Ess, D. H.; Bischof, S. M.; Oxgaard, J.; Periana, R. A.; Goddard, W. A. *Organometallics*. **2008**, *27*, 6440.

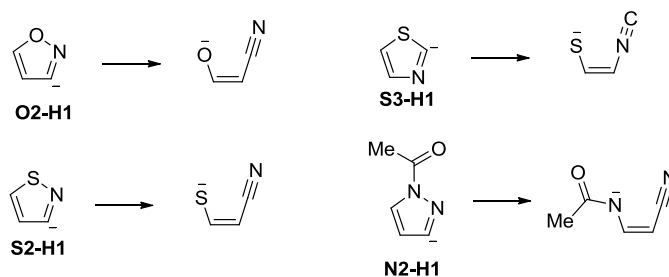
## Detailed linear correlation



**Figure S2.** The linear correlation plots between pKa and C-H activation barrier ( $\Delta G^\ddagger$ ) for heteroarenes **O1-O3**, **S1-S3** and **N1-N3**, respectively.

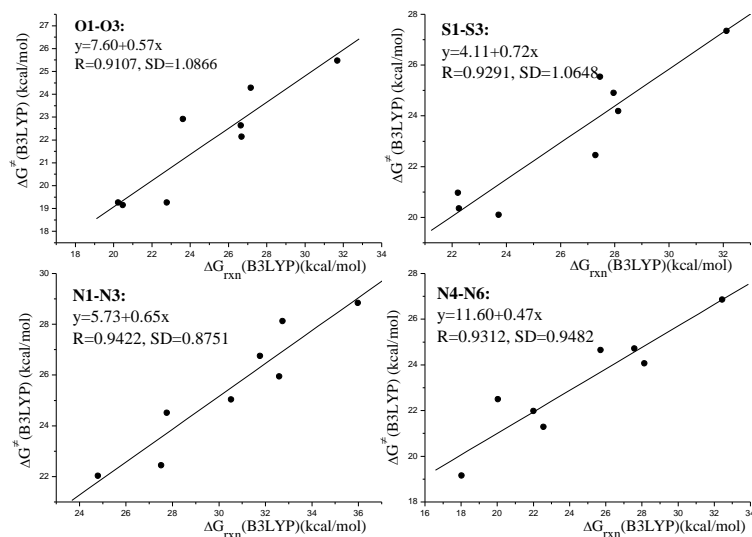


**Figure S3.** The linear correlation plots between re-calculation pKa and C-H activation barrier ( $\Delta G^\ddagger$ ) for all the substrates.



Note that the above structures undergo ring-opening reactions after optimization. Similar observations have also been reported in Guo's study (Tetrahedron, 2007, 63, 1568). For simplicity,

the calculation results of these data were not taken into account in the correlation fits. The treatment does not affect our conclusion that the correlations between pKa and C-H activation barrier depend on different types of heteroarenes.



**Figure S4.** The linear correlation plots between reaction energy ( $\Delta G_{\text{rxn}}$ ) and C-H activation barrier ( $\Delta G^\ddagger$ ) for heteroarenes **O1-O3**, **S1-S3**, **N1-N3** and **N4-N6**, respectively.

Figure S2 indicates that the correlations between pKa and C-H activation barrier depend on different types of heteroarenes. While Figure S4 shows that the correlations between reaction energy and C-H activation barrier are independent of heteroarenes.

**Table S1.** Comparison of the linear correlations between TS bond energy ( $\Delta E_{\text{tbe}}$ ) and C-H activation barrier ( $\Delta G^\ddagger$ ) for all concerted substrates calculated at Method/6-31G(d) level.

Method	$\Delta G^\ddagger = A + B * \Delta E_{\text{tbe}}$		R	SD (kcal/mol)
	A	B		
<b>B3LYP</b>	73.29	-0.49	-0.8492	1.4528
<b>M05</b>	75.69	-0.50	-0.8105	1.6419
<b>M06</b>	55.72	-0.37	-0.7857	1.9499
<b>M06L</b>	77.23	-0.54	-0.8487	1.6871

**Table S2.** Comparison of the linear correlations between C-H activation barrier ( $\Delta G^\ddagger$ ) and reaction energy ( $\Delta G_{\text{rxn}}$ ) or TS bond energy ( $\Delta E_{\text{tbe}}$ ) calculated at M05/Basis sets level.

Basis Sets <sup>a</sup>	$\Delta G_x$	$\Delta G^\ddagger = A + B * \Delta G_x$		R	SD (kcal/mol)
		A	B		
<b>Lanl2DZ</b>	$\Delta G_{\text{rxn}}$	9.29	0.68	0.9272	1.1027
	$\Delta E_{\text{tbe}}$	64.95	-0.45	-0.6775	2.1652

<b>LanL2MB</b>	$\Delta G_{\text{rxn}}$	9.01	0.73	0.9025	1.4144
	$\Delta E_{\text{tbe}}$	73.05	-0.54	-0.6988	2.3488
<b>SDD</b>	$\Delta G_{\text{rxn}}$	12.92	0.61	0.8635	1.3581
	$\Delta E_{\text{tbe}}$	66.57	-0.45	-0.7172	1.8763

<sup>a</sup> Effective core potentials (including LanL2MB, SDD, LanL2DZ with an additional polarization function  $\text{Cu}(\zeta(f) = 3.525)$ ) was used on Cu, 6-31G(d) was used on the other atoms.

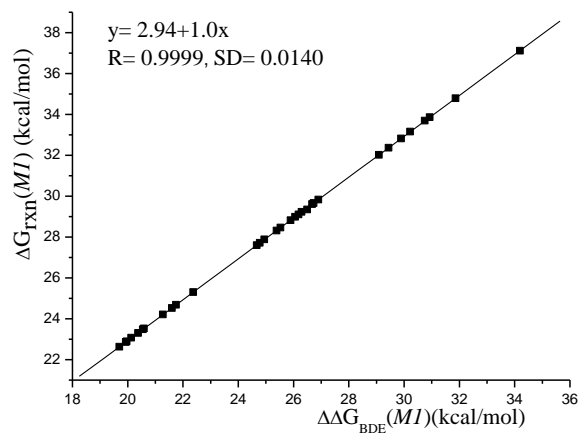
*Table S1 and Table S2 indicate that the correlations between C-H activation barrier and TS bond energy strongly depend on the calculation methods, while the linear correlations between the C-H activation energy barrier and reaction energy are always excellent.*

**Table S3.** Comparison of the linear correlations between the C-H activation energy barrier and reaction energy calculated at different single point calculation levels.

Method		$\Delta G^\ddagger = A + B * \Delta G_{\text{rxn}}$		R	SD (kcal/mol)
		A	B		
<b>B3LYP</b>	BS1 <sup>a</sup>	8.03	0.71	0.9474	0.9637
	BS2 <sup>b</sup>	8.78	0.68	0.9367	1.0247
<b>M05</b>	BS1	8.05	0.66	0.9359	0.9897
	BS2	8.99	0.63	0.9315	0.9819
<b>M06</b>	BS1	2.23	0.76	0.9271	1.1881
	BS2	3.25	0.71	0.9303	1.1098
<b>M06L</b>	BS1	0.29	0.77	0.9477	1.0281
	BS2	1.56	0.73	0.9461	1.0002
<b>MI<sup>c</sup></b>	toluene <sup>d</sup>	6.91	0.70	0.9343	1.1674
	1,4-dioxane <sup>d</sup>	6.48	0.71	0.9364	1.1489

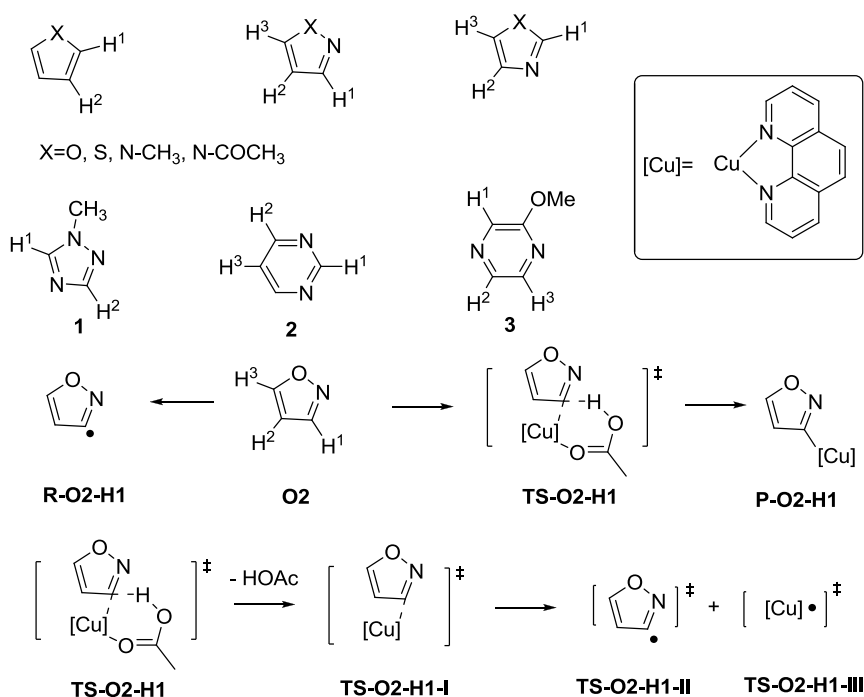
<sup>a</sup> BS1:6-31G(d) with an an additional polarization function  $\text{Cu}(\zeta(f) = 3.525)$  on Cu, 6-311++G(d,p) on the other atoms. <sup>b</sup> BS2: 6-31G(d) with an an additional polarization function  $\text{Cu}(\zeta(f) = 3.525)$  on Cu, 6-311++G(2df,2p) on the other atoms. <sup>c</sup> MI: M06L/(6-31G(d)+f:6-311++G(d,p))/M05/6-31G(d). <sup>d</sup> different solvents including toluene and 1,4-dioxane were selected for solution phase single point calculation (self-consistent reaction field(SCRF) method with CPCM model and RADII=UAHF).

*From Table S3, we could see an excellent linear correlations between the C-H activation energy barrier and the reaction energy still exists even considering solvent effect ( $R > 0.93$ ,  $SD < 1.2$  kcal/mol).*





## Energies of species involved in this study



**Table S4.** Thermal correction of Gibbs free energy (TCG, hartree), Gibbs free energy (G, hartree) and total electronic energies (E, hartree) of concerned intermediates and transition states calculated using B3LYP and several different DFT functionals (with 6-31G(d) basis set).

	B3LYP			M05		
	TCG	G	E	TCG	G	E
Cu(phen)(OAc)	0.176233	-2440.290721	-2440.4669537	0.178507	-2439.759074	-2439.9375806
HOAc	0.034787	-229.046999	-229.0817867	0.036032	-228.929567	-228.9655991
O1	0.043923	-229.976658	-230.0205816	0.044277	-229.825182	-229.8694593
O2	0.031933	-246.002784	-246.0347167	0.032498	-245.854102	-245.8866004
O3	0.032577	-246.037296	-246.0698726	0.032996	-245.892440	-245.9254364
S1	0.039647	-552.962982	-553.0026285	0.039858	-552.838873	-552.8787309
S2	0.028134	-569.012590	-569.0407242	0.028551	-568.893683	-568.9222334
S3	0.028211	-569.018842	-569.0470537	0.028507	-568.900899	-568.9294061
N1	0.081690	-249.396156	-249.4778465	0.081698	-249.203355	-249.2850525
N2	0.069662	-265.443714	-265.5133764	0.071170	-265.255198	-265.3263677
N3	0.070407	-265.456944	-265.5273509	0.069363	-265.271697	-265.3410596
N4	0.089076	-362.733440	-362.8225155	0.090121	-362.490349	-362.5804704
N5	0.077233	-378.769829	-378.8470619	0.078229	-378.532605	-378.6108339
N6	0.077433	-378.790227	-378.8676604	0.078183	-378.553864	-378.6320472
TS-O1-H1	0.237606	-2670.232089	-2670.4696951	0.239464	-2669.549658	-2669.7891228
TS-O1-H2	0.234928	-2670.226789	-2670.4617171	0.239339	-2669.544271	-2669.7836101
TS-O2-H1	0.225293	-2686.256989	-2686.4822824	0.227080	-2685.577769	-2685.8048491
TS-O2-H2	0.224239	-2686.257442	-2686.4816812	0.227048	-2685.579156	-2685.8062041

TS-O2-H3	0.225645	-2686.262810	-2686.4884552	0.227658	-2685.583192	-2685.8108496
TS-O3-H1	0.226184	-2686.297501	-2686.5236851	0.227887	-2685.620666	-2685.8485522
TS-O3-H2	0.226534	-2686.289331	-2686.5158646	0.227988	-2685.614633	-2685.842621
TS-O3-H3	0.226065	-2686.297331	-2686.5233959	0.228249	-2685.621190	-2685.8494384
TS-S1-H1	0.231864	-2993.217927	-2993.4497917	0.232983	-2992.565875	-2992.798858
TS-S1-H2	0.232160	-2993.210137	-2993.4422974	0.235209	-2992.556467	-2992.7916763
TS-S2-H1	0.221718	-3009.262603	-3009.484321	0.223783	-3008.613621	-3008.8374046
TS-S2-H2	0.220197	-3009.264758	-3009.4849545	0.223932	-3008.615724	-3008.8396563
TS-S2-H3	0.220537	-3009.270883	-3009.4914193	0.223580	-3008.622020	-3008.8456001
TS-S3-H1	0.221972	-3009.276141	-3009.4981123	0.223009	-3008.628766	-3008.8517749
TS-S3-H2	0.221630	-3009.269883	-3009.4915129	0.223179	-3008.622532	-3008.8457106
TS-S3-H3	0.220410	-3009.277526	-3009.4979359	0.221789	-3008.631339	-3008.8531276
TS-N1-H1	0.275811	-2689.646967	-2689.9227787	0.279085	-2688.923758	-2689.2028428
TS-N1-H2	0.274510	-2689.640914	-2689.9154247	0.277406	-2688.918132	-2689.1955381
TS-N2-H1	0.263515	-2705.689630	-2705.9531442	0.265601	-2704.972065	-2705.2376661
TS-N2-H2	0.261782	-2705.693098	-2705.9548804	0.265008	-2704.975756	-2705.2407641
TS-N2-H3	0.264243	-2705.695372	-2705.959615	0.267437	-2704.978708	-2705.2461451
TS-N3-H1	0.264753	-2705.712553	-2705.9773054	0.267225	-2704.994838	-2705.2620628
TS-N3-H2	0.263779	-2705.705035	-2705.9688138	0.266558	-2704.987450	-2705.2540082
TS-N3-H3	0.264308	-2705.711905	-2705.9762126	0.267205	-2704.995625	-2705.2628304
TS-N4-H1	0.283821	-2802.988325	-2803.2721455	0.284757	-2802.217965	-2802.502722
TS-N4-H2	0.281216	-2802.981352	-2803.262568	0.283951	-2802.209359	-2802.4933095
TS-N5-H1	0.270881	-2819.021260	-2819.292141	0.273799	-2818.253711	-2818.5275103
TS-N5-H2	0.269664	-2819.022205	-2819.2918694	0.272740	-2818.255737	-2818.5284772
TS-N5-H3	0.272653	-2819.025530	-2819.2981835	0.274974	-2818.261015	-2818.5359886
TS-N6-H1	0.271445	-2819.050425	-2819.3218701	0.273061	-2818.284685	-2818.5577456
TS-N6-H2	0.271115	-2819.041569	-2819.3126843	0.271045	-2818.277204	-2818.5482495
TS-N6-H3	0.272750	-2819.047042	-2819.319792	0.276073	-2818.281603	-2818.5576761
P-O1-H1	0.185296	-2441.177843	-2441.3631387	0.186153	-2440.613157	-2440.7993108
P-O1-H2	0.185740	-2441.169889	-2441.3556288	0.185614	-2440.608338	-2440.7939524
P-O2-H1	0.173444	-2457.208861	-2457.3823048	0.174231	-2456.647959	-2456.8221905
P-O2-H2	0.173783	-2457.204036	-2457.3778191	0.175292	-2456.644297	-2456.819589
P-O2-H3	0.172487	-2457.214248	-2457.3867349	0.174451	-2456.652215	-2456.8266663
P-O3-H1	0.174616	-2457.248377	-2457.4229931	0.174289	-2456.688046	-2456.8623355
P-O3-H2	0.174917	-2457.237743	-2457.4126605	0.175374	-2456.680689	-2456.8560626
P-O3-H3	0.174030	-2457.244712	-2457.4187421	0.174516	-2456.687522	-2456.8620377
P-S1-H1	0.182061	-2764.163219	-2764.3452793	0.183361	-2763.627701	-2763.8110622
P-S1-H2	0.181437	-2764.155517	-2764.3369539	0.182703	-2763.620217	-2763.80292
P-S2-H1	0.170518	-2780.212554	-2780.3830714	0.169359	-2779.680979	-2779.8503379
P-S2-H2	0.170034	-2780.211492	-2780.3815263	0.171653	-2779.681476	-2779.8531293
P-S2-H3	0.170210	-2780.220839	-2780.3910489	0.172083	-2779.690718	-2779.862801
P-S3-H1	0.170089	-2780.227157	-2780.3972458	0.170484	-2779.697666	-2779.8681497
P-S3-H2	0.170475	-2780.218005	-2780.3884803	0.171003	-2779.688510	-2779.8595136
P-S3-H3	0.170087	-2780.224762	-2780.3948485	0.171621	-2779.695753	-2779.8673738

P-N1-H1	0.224422	-2460.591249	-2460.815671	0.225069	-2459.985950	-2460.2110188
P-N1-H2	0.223962	-2460.582541	-2460.8065024	0.224252	-2459.978382	-2460.2026337
P-N2-H1	0.212952	-2476.635260	-2476.8482118	0.213353	-2476.035697	-2476.24905
P-N2-H2	0.212406	-2476.635508	-2476.8479134	0.214876	-2476.035413	-2476.2502884
P-N2-H3	0.212758	-2476.643190	-2476.8559484	0.212869	-2476.044247	-2476.2571161
P-N3-H1	0.214034	-2476.661159	-2476.8751929	0.214857	-2476.061452	-2476.2763098
P-N3-H2	0.212914	-2476.650041	-2476.8629543	0.213761	-2476.050433	-2476.2641942
P-N3-H3	0.213119	-2476.656818	-2476.8699367	0.214167	-2476.058331	-2476.2724981
P-N4-H1	0.232063	-2573.945225	-2574.1772889	0.233747	-2573.287773	-2573.5215201
P-N4-H2	0.231514	-2573.925467	-2574.1569809	0.231861	-2573.272219	-2573.5040801
P-N5-H1	0.219185	-2589.972564	-2590.1917491	0.221397	-2589.322615	-2589.5440121
P-N5-H2	0.219521	-2589.968702	-2590.188223	0.222083	-2589.319614	-2589.5416967
P-N5-H3	0.221024	-2589.978473	-2590.1994967	0.221700	-2589.330355	-2589.5520545
P-N6-H1	0.220683	-2590.005239	-2590.2259225	0.221287	-2589.351559	-2589.5728464
P-N6-H2	0.219265	-2589.989984	-2590.2092493	0.220560	-2589.340776	-2589.5613362
P-N6-H3	0.220921	-2589.998005	-2590.2189255	0.221703	-2589.350558	-2589.5722614

	M06			M06L		
	TCG	G	E	TCG	G	E
Cu(phen)(OAc)	0.177549	-2439.666721	-2439.8442705	0.178495	-2440.109734	-2440.2882293
HOAc	0.035524	-228.923882	-228.9594059	0.035425	-229.020651	-229.056076
O1	0.043727	-229.821413	-229.8651402	0.043559	-229.943356	-229.9869145
O2	0.031943	-245.846087	-245.8780302	0.031762	-245.973627	-246.0053887
O3	0.032533	-245.884740	-245.9172731	0.032343	-246.007319	-246.0396613
S1	0.039416	-552.805935	-552.8453504	0.039584	-552.920942	-552.9605259
S2	0.028040	-568.858388	-568.8864281	0.028081	-568.974806	-569.0028867
S3	0.027993	-568.864274	-568.8922666	0.028066	-568.980188	-569.0082542
N1	0.080865	-249.202568	-249.2834321	0.081079	-249.353698	-249.4347773
N2	0.069977	-265.250136	-265.3201124	0.070085	-265.404117	-265.4742021
N3	0.070226	-265.265268	-265.3354936	0.070608	-265.417070	-265.487678
N4	0.088591	-362.487004	-362.5755945	0.089227	-362.686190	-362.7754167
N5	0.076984	-378.524168	-378.6011518	0.077449	-378.726707	-378.8041568
N6	0.077708	-378.545537	-378.6232454	0.077046	-378.746474	-378.8235194
TS-O1-H1	0.238586	-2669.462660	-2669.701246	0.238741	-2670.023777	-2670.2625175
TS-O1-H2	0.238511	-2669.456811	-2669.695322	0.239135	-2670.016068	-2670.2552028
TS-O2-H1	0.226418	-2685.486218	-2685.7126365	0.226101	-2686.052265	-2686.2783653
TS-O2-H2	0.227363	-2685.486554	-2685.7139172	0.226969	-2686.051472	-2686.2784407
TS-O2-H3	0.227057	-2685.492442	-2685.7194989	0.226899	-2686.057979	-2686.2848773
TS-O3-H1	0.226769	-2685.529623	-2685.7563919	0.227646	-2686.091414	-2686.3190602
TS-O3-H2	0.226837	-2685.523991	-2685.7508276	0.227287	-2686.084190	-2686.311477
TS-O3-H3	0.226815	-2685.530686	-2685.7575013	0.226669	-2686.092418	-2686.3190868
TS-S1-H1	0.233294	-2992.447986	-2992.6812799	0.234427	-2993.000988	-2993.235415
TS-S1-H2	0.234878	-2992.440694	-2992.6755715	0.235198	-2992.992911	-2993.2281094
TS-S2-H1	0.221918	-3008.495546	-3008.717464	0.222448	-3009.050313	-3009.272761

TS-S2-H2	0.223485	-3008.497550	-3008.7210343	0.223969	-3009.050584	-3009.2745531
TS-S2-H3	0.222399	-3008.504591	-3008.7269903	0.223770	-3009.057927	-3009.2816968
TS-S3-H1	0.222162	-3008.508681	-3008.7308431	0.223230	-3009.062987	-3009.2862166
TS-S3-H2	0.222020	-3008.502489	-3008.7245097	0.222761	-3009.056324	-3009.2790853
TS-S3-H3	0.221657	-3008.511473	-3008.7331306	0.223770	-3009.063609	-3009.2873794
TS-N1-H1	0.275638	-2688.844453	-2689.1200915	0.276608	-2689.433431	-2689.7100388
TS-N1-H2	0.277300	-2688.833120	-2689.1104204	0.276965	-2689.423297	-2689.7002612
TS-N2-H1	0.264512	-2704.883124	-2705.1476356	0.265369	-2705.475316	-2705.7406854
TS-N2-H2	0.265452	-2704.885361	-2705.1508134	0.265915	-2705.476898	-2705.7428122
TS-N2-H3	0.264318	-2704.893912	-2705.1582302	0.267728	-2705.483184	-2705.7509119
TS-N3-H1	0.266243	-2704.909438	-2705.1756806	0.266456	-2705.499970	-2705.7664263
TS-N3-H2	0.264461	-2704.900565	-2705.1650258	0.265201	-2705.490627	-2705.7558282
TS-N3-H3	0.265142	-2704.910337	-2705.1754789	0.265969	-2705.499931	-2705.7659005
TS-N4-H1	0.284001	-2802.131990	-2802.41599074	0.284918	-2802.771232	-2803.0561501
TS-N4-H2	0.282531	-2802.121844	-2802.4043749	0.282902	-2802.759502	-2803.0424043
TS-N5-H1	0.271588	-2818.162974	-2818.4345624	0.272861	-2818.802946	-2819.0758078
TS-N5-H2	0.272533	-2818.162916	-2818.4354496	0.272771	-2818.802905	-2819.0756758
TS-N5-H3	0.275439	-2818.171811	-2818.4472494	0.274990	-2818.812550	-2819.0875403
TS-N6-H1	0.273118	-2818.194036	-2818.4671537	0.273680	-2818.834259	-2819.1079393
TS-N6-H2	0.270608	-2818.185268	-2818.4558759	0.271466	-2818.823409	-2819.094875
TS-N6-H3	0.273974	-2818.194915	-2818.4688894	0.274921	-2818.832006	-2819.1069265
P-O1-H1	0.184490	-2440.529134	-2440.7136235	0.187231	-2440.986111	-2441.1733419
P-O1-H2	0.187010	-2440.520446	-2440.7136235	0.187076	-2440.979794	-2441.1668707
P-O2-H1	0.173057	-2456.554494	-2456.7275511	0.174013	-2457.018535	-2457.1925477
P-O2-H2	0.175165	-2456.553202	-2456.7283678	0.174997	-2457.017241	-2457.1922387
P-O2-H3	0.173218	-2456.563301	-2456.7365192	0.175039	-2457.024925	-2457.1999639
P-O3-H1	0.173264	-2456.597992	-2456.7712557	0.172917	-2457.058140	-2457.2310566
P-O3-H2	0.174805	-2456.592278	-2456.7670838	0.175665	-2457.049590	-2457.2252546
P-O3-H3	0.174443	-2456.597731	-2456.7721746	0.175172	-2457.056416	-2457.2315876
P-S1-H1	0.182151	-2763.513175	-2763.6953258	0.183069	-2763.964950	-2764.1480194
P-S1-H2	0.181911	-2763.505304	-2763.6872151	0.181926	-2763.956626	-2764.1385524
P-S2-H1	0.170795	-2779.564958	-2779.7357523	0.170558	-2780.014715	-2780.1852732
P-S2-H2	0.170721	-2779.563832	-2779.7345525	0.170703	-2780.015693	-2780.1863956
P-S2-H3	0.171916	-2779.572309	-2779.7442245	0.171759	-2780.025234	-2780.1969921
P-S3-H1	0.170475	-2779.578964	-2779.7494392	0.170776	-2780.028320	-2780.1990964
P-S3-H2	0.170171	-2779.570677	-2779.7408486	0.171044	-2780.022009	-2780.1930528
P-S3-H3	0.170640	-2779.576707	-2779.7473467	0.170388	-2780.028339	-2780.1987268
P-N1-H1	0.224404	-2459.905751	-2460.130155	0.224595	-2460.394545	-2460.6191396
P-N1-H2	0.223206	-2459.896007	-2460.1192132	0.224305	-2460.383816	-2460.6081212
P-N2-H1	0.212751	-2475.944109	-2476.15686	0.211844	-2476.437991	-2476.6498348
P-N2-H2	0.213412	-2475.948564	-2476.1619761	0.211880	-2476.440427	-2476.6523075
P-N2-H3	0.213178	-2475.958541	-2476.1717186	0.215005	-2476.447018	-2476.6620231
P-N3-H1	0.210369	-2475.981565	-2476.1919346	0.213955	-2476.465990	-2476.6799446
P-N3-H2	0.212798	-2475.965418	-2476.1782161	0.213443	-2476.453684	-2476.6671264

P-N3-H3	0.213420	-2475.973833	-2476.1872536	0.214285	-2476.461606	-2476.675891
P-N4-H1	0.232524	-2573.205052	-2573.4375756	0.234168	-2573.748402	-2573.98257
P-N4-H2	0.232102	-2573.185441	-2573.4175435	0.232320	-2573.720728	-2573.9530483
P-N5-H1	0.220296	-2589.233732	-2589.4540287	0.220096	-2589.765573	-2589.9856697
P-N5-H2	0.220375	-2589.229388	-2589.4497629	0.218874	-2589.768964	-2589.987838
P-N5-H3	0.220871	-2589.243207	-2589.4640778	0.221049	-2589.784143	-2590.0051923
P-N6-H1	0.220507	-2589.267805	-2589.4883126	0.222050	-2589.811769	-2590.0338189
P-N6-H2	0.219376	-2589.252730	-2589.4721065	0.220308	-2589.787672	-2590.0079803
P-N6-H3	0.220603	-2589.264200	-2589.4848029	0.221625	-2589.799918	-2590.0215434

**Table S5.** Total electronic energies (E, hartree) of concerned fragments involved in transition states calculated using B3LYP and several different DFT functionals (with 6-31G(d) basis set).

	<b>B3LYP</b>	<b>M05</b>	<b>M06</b>	<b>M06L</b>
TS-O1-H1-I	-2441.3443358	-2440.7814377	-2440.693955	-2441.1567599
TS-O1-H1-II	-229.3122081	-229.1668753	-229.1622597	-229.2853101
TS-O1-H1-III	-2211.8640072	-2211.4415169	-2211.3508076	-2211.6968101
TS-O1-H2-I	-2441.3347071	-2440.7759253	-2440.689174	-2441.1497744
TS-O1-H2-II	-229.3199907	-229.1694705	-229.1659695	-229.2894182
TS-O1-H2-III	-2211.8643456	-2211.4410947	-2211.3607199	-2211.6958765
TS-O2-H1-I	-2457.357104	-2456.7978568	-2456.7034901	-2457.1710065
TS-O2-H1-II	-245.3329842	-245.1899061	-245.1812149	-245.309692
TS-O2-H1-III	-2211.8636571	-2211.44097	-2211.3504863	-2211.6932427
TS-O2-H2-I	-2457.3555115	-2456.7974565	-2456.7067032	-2457.1726212
TS-O2-H2-II	-245.3269755	-245.1844037	-245.1762574	-245.3056134
TS-O2-H2-III	-2211.8639819	-2211.4413819	-2211.3607048	-2211.6954779
TS-O2-H3-I	-2457.3637687	-2456.8027974	-2456.7107649	-2457.1791017
TS-O2-H3-II	-245.3287726	-245.1858002	-245.1768025	-245.3057278
TS-O2-H3-III	-2211.8634463	-2211.4418568	-2211.3618763	-2211.6957973
TS-O3-H1-I	-2457.3991782	-2456.8427273	-2456.7525589	-2457.2139679
TS-O3-H1-II	-245.361859	-245.2235326	-245.2145118	-245.3366794
TS-O3-H1-III	-2211.8634269	-2211.4408569	-2211.349853	-2211.692836
TS-O3-H2-I	-2457.3910753	-2456.8354666	-2456.7447247	-2457.2058834
TS-O3-H2-II	-245.3649824	-245.2272679	-245.2181732	-245.34166
TS-O3-H2-III	-2211.8629812	-2211.4410766	-2211.3502456	-2211.6826622
TS-O3-H3-I	-2457.3982611	-2456.8417143	-2456.7494852	-2457.2132942
TS-O3-H3-II	-245.3603554	-245.2219434	-245.2132226	-245.3371759
TS-O3-H3-III	-2211.8638113	-2211.4418109	-2211.3621478	-2211.6964925
TS-S1-H1-I	-2764.3242831	-2763.7901853	-2763.6738105	-2764.1292452
TS-S1-H1-II	-552.2983434	-552.1801452	-552.1474482	-552.2631904
TS-S1-H1-III	-2211.8637359	-2211.4408371	-2211.3616763	-2211.696045
TS-S1-H2-I	-2764.3176056	-2763.7844732	-2763.6700046	-2764.1232521
TS-S1-H2-II	-552.3031999	-552.1850759	-552.1518672	-552.2680693
TS-S1-H2-III	-2211.8634974	-2211.4410863	-2211.3607009	-2211.6959601
TS-S2-H1-I	-2780.3594851	-2779.8306325	-2779.7095095	-2780.1674067

TS-S2-H1-II	-568.3485332	-568.2355146	-568.1981887	-568.3144738
TS-S2-H1-III	-2211.8631406	-2211.4405828	-2211.3501535	-2211.6947797
TS-S2-H2-I	-2780.3598383	-2779.8318018	-2779.7144428	-2780.1691799
TS-S2-H2-II	-568.3398214	-568.2272018	-568.1911759	-568.3090353
TS-S2-H2-III	-2211.8634733	-2211.4413346	-2211.3501796	-2211.6955798
TS-S2-H3-I	-2780.367529	-2779.8396785	-2779.7215683	-2780.1764546
TS-S2-H3-II	-568.3383331	-568.2253264	-568.1897587	-568.3070249
TS-S2-H3-III	-2211.8630145	-2211.4411506	-2211.3502092	-2211.6954322
TS-S3-H1-I	-2780.373566	-2779.844578	-2779.7228897	-2780.1797377
TS-S3-H1-II	-568.3528145	-568.2407334	-568.2015243	-568.3165373
TS-S3-H1-III	-2211.8634267	-2211.4410967	-2211.3610469	-2211.6829267
TS-S3-H2-I	-2780.3667442	-2779.8386921	-2779.7187221	-2780.1737792
TS-S3-H2-II	-568.3481235	-568.2372109	-568.1989024	-568.3153339
TS-S3-H2-III	-2211.8629932	-2211.4409114	-2211.36074	-2211.6930508
TS-S3-H3-I	-2780.3722066	-2779.8445529	-2779.7246613	-2780.1809728
TS-S3-H3-II	-568.3416947	-568.2298192	-568.1928233	-568.3098172
TS-S3-H3-III	-2211.8631005	-2211.4411367	-2211.3502124	-2211.6953799
TS-N1-H1-I	-2460.7974661	-2460.1954678	-2460.11269	-2460.6043975
TS-N1-H1-II	-248.7714952	-248.5843303	-248.5826077	-248.7353749
TS-N1-H1-III	-2211.8650371	-2211.4402112	-2211.3613084	-2211.6972553
TS-N1-H2-I	-2460.7898232	-2460.1889767	-2460.1039575	-2460.5940219
TS-N1-H2-II	-248.7737353	-248.5864316	-248.5854409	-248.7381985
TS-N1-H2-III	-2211.8637708	-2211.4404435	-2211.3603817	-2211.6962172
TS-N2-H1-I	-2476.8274362	-2476.2296644	-2476.1397641	-2476.6339611
TS-N2-H1-II	-264.81169434	-264.630778	-264.6240184	-264.7787872
TS-N2-H1-III	-2211.8625895	-2211.4404476	-2211.3602091	-2211.682017
TS-N2-H2-I	-2476.828351	-2476.2324606	-2476.1435217	-2476.6363401
TS-N2-H2-II	-264.8077936	-264.6264317	-264.6204495	-264.7763159
TS-N2-H2-III	-2211.8641717	-2211.4407993	-2211.3602133	-2211.6956475
TS-N2-H3-I	-2476.8358102	-2476.2374656	-2476.1519379	-2476.646017
TS-N2-H3-II	-264.808731	-264.6274788	-264.620796	-264.776322
TS-N2-H3-III	-2211.8625217	-2211.4406594	-2211.3607862	-2211.6964777
TS-N3-H1-I	-2476.8539796	-2476.2563491	-2476.1707667	-2476.6608463
TS-N3-H1-II	-264.8242775	-264.644359	-264.6369997	-264.7892275
TS-N3-H1-III	-2211.8624913	-2211.4403495	-2211.3495235	-2211.6951403
TS-N3-H2-I	-2476.8437299	-2476.2464958	-2476.1584154	-2476.6497384
TS-N3-H2-II	-264.8254502	-264.645909	-264.6389628	-264.7920236
TS-N3-H2-III	-2211.8627201	-2211.4405827	-2211.3494801	-2211.6954487
TS-N3-H3-I	-2476.8511813	-2476.2547811	-2476.1684014	-2476.660075
TS-N3-H3-II	-264.8215687	-264.6411236	-264.6345965	-264.78855920
TS-N3-H3-III	-2211.8647426	-2211.4406197	-2211.3496349	-2211.69651723
TS-N4-H1-I	-2574.1459959	-2573.4946764	-2573.4082231	-2573.9491804
TS-N4-H1-II	-362.1129344	-361.8768443	-361.8721428	-362.0735608
TS-N4-H1-III	-2211.8625144	-2211.4394089	-2211.359342	-2211.695241

TS-N4-H2-I	-2574.1359684	-2573.4843235	-2573.3960045	-2573.9355758
TS-N4-H2-II	-362.1180972	-361.8817452	-361.8769835	-362.0787588
TS-N4-H2-III	-2211.8635227	-2211.44053	-2211.3604253	-2211.6960047
TS-N5-H1-I	-2590.1681823	-2589.5210905	-2589.4283066	-2589.9696393
TS-N5-H1-II	-378.1460393	-377.9155106	-377.904974	-378.1084281
TS-N5-H1-III	-2211.8633679	-2211.4404356	-2211.3497071	-2211.6942578
TS-N5-H2-I	-2590.1667683	-2589.5214852	-2589.4288346	-2589.9705151
TS-N5-H2-II	-378.1416814	-377.9113927	-377.9013865	-378.1064738
TS-N5-H2-III	-2211.8635137	-2211.4411629	-2211.3499776	-2211.6954817
TS-N5-H3-I	-2590.1746801	-2589.5316763	-2589.4411268	-2589.9816889
TS-N5-H3-II	-378.1411564	-377.91028276	-377.9002751	-378.1056982
TS-N5-H3-III	-2211.863694	-2211.4414226	-2211.3506796	-2211.6962941
TS-N6-H1-I	-2590.1973167	-2589.5525666	-2589.4632767	-2590.0025997
TS-N6-H1-II	-378.1631515	-377.9337591	-377.9233316	-378.1236397
TS-N6-H1-III	-2211.8630058	-2211.4390671	-2211.3481879	-2211.6944261
TS-N6-H2-I	-2590.1884529	-2589.5417769	-2589.4509625	-2589.9896162
TS-N6-H2-II	-378.1644541	-377.9356929	-377.9257346	-378.1269423
TS-N6-H2-III	-2211.8627846	-2211.4406741	-2211.3497574	-2211.695358
TS-N6-H3-I	-2590.1964019	-2589.551155	-2589.4620954	-2590.0020145
TS-N6-H3-II	-378.16105	-377.9315526	-377.9224821	-378.1237372
TS-N6-H3-III	-2211.8619919	-2211.4401283	-2211.3491762	-2211.6933901

**Table S6.** Thermal correction of Gibbs free energy (TCG, hartree), Gibbs free energy (G, hartree) and total electronic energies (E, hartree) of concerned intermediates and transition states calculated using 6-31G(d) basis set and three different effective core potentials (with M05 functional).

	6-31G(d)			LANL2DZ <sup>a</sup>		
	TCG	G	E	TCG	G	E
Cu(phen)(OAc)	0.178507	-2439.759074	-2439.9375806	0.175482	-995.711805	-995.8872874
HOAc	0.036032	-228.929567	-228.9655991	0.035994	-228.925779	-228.9617729
O1	0.044277	-229.825182	-229.8694593	0.044293	-229.821378	-229.8656712
O2	0.032498	-245.854102	-245.8866004	0.032552	-245.849639	-245.8821914
O3	0.032996	-245.892440	-245.9254364	0.033036	-245.888457	-245.9214931
S1	0.039858	-552.838873	-552.8787309	0.039853	-552.833785	-552.8736387
S2	0.028551	-568.893683	-568.9222334	0.028562	-568.888435	-568.916997
S3	0.028507	-568.900899	-568.9294061	0.028524	-568.895627	-568.9241508
N1	0.081698	-249.203355	-249.2850525	0.081642	-249.198723	-249.2803646
N2	0.071170	-265.255198	-265.3263677	0.071153	-265.250071	-265.3212248
N3	0.069363	-265.271697	-265.3410596	0.068615	-265.267590	-265.3362057
N4	0.090121	-362.490349	-362.5804704	0.090129	-362.484069	-362.574198
N5	0.078229	-378.532605	-378.6108339	0.078271	-378.525847	-378.6041183
N6	0.078183	-378.553864	-378.6320472	0.078219	-378.547396	-378.6256154
TS-O1-H1	0.239464	-2669.549658	-2669.7891228	0.237274	-1225.489904	-1225.7271778
TS-O1-H2	0.239339	-2669.544271	-2669.7836101	0.236860	-1225.486472	-1225.7233316
TS-O2-H1	0.227080	-2685.577769	-2685.8048491	0.224345	-1241.519504	-1241.7438487

TS-O2-H2	0.227048	-2685.579156	-2685.8062041	0.226625	-1241.519589	-1241.7462145
TS-O2-H3	0.227658	-2685.583192	-2685.8108496	0.226256	-1241.523108	-1241.7493641
TS-O3-H1	0.227887	-2685.620666	-2685.8485522	0.225390	-1241.560736	-1241.7861259
TS-O3-H2	0.227988	-2685.614633	-2685.842621	0.226324	-1241.554762	-1241.7810856
TS-O3-H3	0.228249	-2685.621190	-2685.8494384	0.224118	-1241.563579	-1241.7876966
TS-S1-H1	0.232983	-2992.565875	-2992.798858	0.234020	-1548.505057	-1548.739077
TS-S1-H2	0.235209	-2992.556467	-2992.7916763	0.233541	-1548.496903	-1548.7304443
TS-S2-H1	0.223783	-3008.613621	-3008.8374046	0.221359	-1564.553077	-1564.7744359
TS-S2-H2	0.223932	-3008.615724	-3008.8396563	0.224167	-1564.554934	-1564.7791006
TS-S2-H3	0.223580	-3008.622020	-3008.8456001	0.220469	-1564.564836	-1564.7853051
TS-S3-H1	0.223009	-3008.628766	-3008.8517749	0.221710	-1564.568528	-1564.7902381
TS-S3-H2	0.223179	-3008.622532	-3008.8457106	0.220917	-1564.562137	-1564.7830546
TS-S3-H3	0.221789	-3008.631339	-3008.8531276	0.221773	-1564.571761	-1564.7935338
TS-N1-H1	0.279085	-2688.923758	-2689.2028428	0.275930	-1244.864754	-1245.1406842
TS-N1-H2	0.277406	-2688.918132	-2689.1955381	0.275489	-1244.858699	-1245.1341878
TS-N2-H1	0.265601	-2704.972065	-2705.2376661	0.263047	-1260.911555	-1261.1746014
TS-N2-H2	0.265008	-2704.975756	-2705.2407641	0.264306	-1260.914797	-1261.1791036
TS-N2-H3	0.267437	-2704.978708	-2705.2461451	0.263754	-1260.919754	-1261.1835079
TS-N3-H1	0.267225	-2704.994838	-2705.2620628	0.264879	-1260.934117	-1261.198996
TS-N3-H2	0.266558	-2704.987450	-2705.2540082	0.264865	-1260.926328	-1261.1911928
TS-N3-H3	0.267205	-2704.995625	-2705.2628304	0.264249	-1260.936286	-1261.2005343
TS-N4-H1	0.284757	-2802.217965	-2802.502722	0.283034	-1358.155786	-1358.4388199
TS-N4-H2	0.283951	-2802.209359	-2802.4933095	0.280722	-1358.149163	-1358.4298857
TS-N5-H1	0.273799	-2818.253711	-2818.5275103	0.271323	-1374.192828	-1374.4641502
TS-N5-H2	0.272740	-2818.255737	-2818.5284772	0.272188	-1374.193636	-1374.4658247
TS-N5-H3	0.274974	-2818.261015	-2818.5359886	0.274864	-1374.200088	-1374.4749524
TS-N6-H1	0.273061	-2818.284685	-2818.5577456	0.271188	-1374.220330	-1374.4915181
TS-N6-H2	0.271045	-2818.277204	-2818.5482495	0.270795	-1374.212998	-1374.4837926
TS-N6-H3	0.276073	-2818.281603	-2818.5576761	0.274562	-1374.221268	-1374.4958296
P-O1-H1	0.186153	-2440.613157	-2440.7993108	0.187151	-996.563853	-996.7510042
P-O1-H2	0.185614	-2440.608338	-2440.7939524	0.185172	-996.560964	-996.7461364
P-O2-H1	0.174231	-2456.647959	-2456.8221905	0.175936	-1012.598607	-1012.774543
P-O2-H2	0.175292	-2456.644297	-2456.819589	0.174105	-1012.597144	-1012.7712487
P-O2-H3	0.174451	-2456.652215	-2456.8266663	0.175464	-1012.603189	-1012.7786529
P-O3-H1	0.174289	-2456.688046	-2456.8623355	0.176297	-1012.640272	-1012.8165698
P-O3-H2	0.175374	-2456.680689	-2456.8560626	0.176247	-1012.631567	-1012.807814
P-O3-H3	0.174516	-2456.687522	-2456.8620377	0.175605	-1012.638322	-1012.8139269
P-S1-H1	0.183361	-2763.627701	-2763.8110622	0.183388	-1319.579478	-1319.7628655
P-S1-H2	0.182703	-2763.620217	-2763.80292	0.182003	-1319.571939	-1319.7539422
P-S2-H1	0.169359	-2779.680979	-2779.8503379	0.172216	-1335.632016	-1335.8042315
P-S2-H2	0.171653	-2779.681476	-2779.8531293	0.171085	-1335.633149	-1335.8042343
P-S2-H3	0.172083	-2779.690718	-2779.862801	0.171713	-1335.642761	-1335.8144747
P-S3-H1	0.170484	-2779.697666	-2779.8681497	0.171788	-1335.648090	-1335.8198783
P-S3-H2	0.171003	-2779.688510	-2779.8595136	0.171280	-1335.638968	-1335.810248



P-S3-H3	0.171621	-2779.695753	-2779.8673738	0.171642	-1335.647608	-1335.8192501
P-N1-H1	0.225069	-2459.985950	-2460.2110188	0.225197	-1015.935232	-1016.160429
P-N1-H2	0.224252	-2459.978382	-2460.2026337	0.223342	-1015.929842	-1016.1531843
P-N2-H1	0.213353	-2476.035697	-2476.24905	0.214361	-1031.985255	-1032.1996158
P-N2-H2	0.214876	-2476.035413	-2476.2502884	0.212740	-1031.988160	-1032.2009003
P-N2-H3	0.212869	-2476.044247	-2476.2571161	0.213524	-1031.993945	-1032.2074694
P-N3-H1	0.214857	-2476.061452	-2476.2763098	0.215137	-1032.010414	-1032.2255506
P-N3-H2	0.213761	-2476.050433	-2476.2641942	0.215125	-1031.999472	-1032.2145961
P-N3-H3	0.214167	-2476.058331	-2476.2724981	0.214471	-1032.008417	-1032.2228876
P-N4-H1	0.233747	-2573.287773	-2573.5215201	0.232835	-1129.232056	-1129.464891
P-N4-H2	0.231861	-2573.272219	-2573.5040801	0.231577	-1129.221519	-1129.4530967
P-N5-H1	0.221397	-2589.322615	-2589.5440121	0.221384	-1145.271814	-1145.4931982
P-N5-H2	0.222083	-2589.319614	-2589.5416967	0.220362	-1145.270370	-1145.4907316
P-N5-H3	0.221700	-2589.330355	-2589.5520545	0.221118	-1145.275371	-1145.4964889
P-N6-H1	0.221287	-2589.351559	-2589.5728464	0.221580	-1145.299932	-1145.521512
P-N6-H2	0.220560	-2589.340776	-2589.5613362	0.221069	-1145.289307	-1145.5103762
P-N6-H3	0.221703	-2589.350558	-2589.5722614	0.221015	-1145.296557	-1145.5175716

	LANL2MB <sup>a</sup>			SDD <sup>a</sup>		
	TCG	G	E	TCG	G	E
Cu(phen)(OAc)	0.178426	-995.698111	-995.8765378	0.174678	-996.906351	-997.081029
HOAc	0.035994	-228.925779	-228.9617729	0.035994	-228.925779	-228.9617729
O1	0.044293	-229.821378	-229.8656712	0.044293	-229.821378	-229.8656712
O2	0.032552	-245.849639	-245.8821914	0.032552	-245.849639	-245.8821914
O3	0.033036	-245.888457	-245.9214931	0.033036	-245.888457	-245.9214931
S1	0.039853	-552.833785	-552.8736387	0.039853	-552.833785	-552.8736387
S2	0.028562	-568.888435	-568.916997	0.028562	-568.888435	-568.916997
S3	0.028524	-568.895627	-568.924150	0.028524	-568.895627	-568.9241508
N1	0.081642	-249.198723	-249.2803646	0.081642	-249.198723	-249.2803646
N2	0.071153	-265.250071	-265.3212248	0.071153	-265.250071	-265.3212248
N3	0.068615	-265.267590	-265.3362057	0.068615	-265.267590	-265.3362057
N4	0.090129	-362.484069	-362.574198	0.090129	-362.484069	-362.574198
N5	0.078271	-378.525847	-378.6041183	0.078271	-378.525847	-378.6041183
N6	0.078219	-378.547396	-378.6256154	0.078219	-378.547396	-378.6256154
TS-O1-H1	0.237357	-1225.474198	-1225.7115549	0.236824	-1226.684203	-1226.9210267
TS-O1-H2	0.238082	-1225.470960	-1225.7090421	0.236016	-1226.680612	-1226.9166271
TS-O2-H1	0.225741	-1241.503584	-1241.7293251	0.224476	-1242.712059	-1242.936535
TS-O2-H2	0.227281	-1241.505546	-1241.7328265	0.225116	-1242.713844	-1242.9389603
TS-O2-H3	0.226975	-1241.507880	-1241.7348547	0.225386	-1242.716860	-1242.942246
TS-O3-H1	0.225776	-1241.545030	-1241.7708066	0.225704	-1242.753834	-1242.9795382
TS-O3-H2	0.225755	-1241.539635	-1241.76539	0.225423	-1242.749073	-1242.9744954
TS-O3-H3	0.225383	-1241.546648	-1241.7720309	0.225185	-1242.756023	-1242.9812071
TS-S1-H1	0.233418	-1548.491840	-1548.725258	0.232679	-1549.699317	-1549.9319959
TS-S1-H2	0.234402	-1548.482268	-1548.71667	0.232126	-1549.691284	-1549.9234094
TS-S2-H1	0.221474	-1564.537836	-1564.75931	0.221088	-1565.746434	-1565.9675227

TS-S2-H2	0.223862	-1564.541609	-1564.7654705	0.220292	-1565.751049	-1565.9713407
TS-S2-H3	0.223114	-1564.549826	-1564.7729404	0.220376	-1565.757596	-1565.9779721
TS-S3-H1	0.221999	-1564.553789	-1564.7757879	0.220878	-1565.762435	-1565.9833137
TS-S3-H2	0.221492	-1564.546095	-1564.7675869	0.221373	-1565.754863	-1565.976236
TS-S3-H3	0.223174	-1564.557160	-1564.7803343	0.220497	-1565.765674	-1565.9861714
TS-N1-H1	0.277991	-1244.846035	-1245.1240257	0.271887	-1246.062470	-1246.3343572
TS-N1-H2	0.276419	-1244.843675	-1245.120093	0.274649	-1246.053051	-1246.3276996
TS-N2-H1	0.262593	-1260.896399	-1261.1589924	0.263146	-1262.105207	-1262.3683529
TS-N2-H2	0.265858	-1260.899702	-1261.1655601	0.262680	-1262.109868	-1262.3725489
TS-N2-H3	0.267472	-1260.903830	-1261.1713027	0.262121	-1262.114564	-1262.3766848
TS-N3-H1	0.264165	-1260.919870	-1261.1840351	0.263788	-1262.128550	-1262.3923381
TS-N3-H2	0.264098	-1260.911420	-1261.1755184	0.264242	-1262.120823	-1262.3850645
TS-N3-H3	0.266371	-1260.921338	-1261.1877096	0.263555	-1262.130515	-1262.3940701
TS-N4-H1	0.283091	-1358.139964	-1358.423055	0.283473	-1359.348194	-1359.6316676
TS-N4-H2	0.284756	-1358.130781	-1358.4155369	0.279549	-1359.343988	-1359.6235371
TS-N5-H1	0.271711	-1374.177975	-1374.4496862	0.271427	-1375.385574	-1375.6570005
TS-N5-H2	0.273291	-1374.179272	-1374.4525624	0.271992	-1375.386422	-1375.6584139
TS-N5-H3	0.272926	-1374.188558	-1374.4614842	0.274879	-1375.392519	-1375.6673976
TS-N6-H1	0.272017	-1374.203553	-1374.4755707	0.271747	-1375.412651	-1375.6843982
TS-N6-H2	0.271130	-1374.197177	-1374.4683071	0.270184	-1375.407148	-1375.677332
TS-N6-H3	0.272403	-1374.210258	-1374.482661	0.274095	-1375.414276	-1375.6883706
P-O1-H1	0.187209	-996.549788	-996.7369969	0.186450	-997.762763	-997.9492128
P-O1-H2	0.185567	-996.547361	-996.732928	0.185400	-997.758547	-997.9439478
P-O2-H1	0.176080	-1012.584691	-1012.7607715	0.176090	-1013.795947	-1013.9720369
P-O2-H2	0.173842	-1012.584061	-1012.7579029	0.173389	-1013.795430	-1013.9688187
P-O2-H3	0.175531	-1012.588844	-1012.7643743	0.175643	-1013.800874	-1013.9765173
P-O3-H1	0.176345	-1012.625848	-1012.8021927	0.176413	-1013.838247	-1014.0146603
P-O3-H2	0.176256	-1012.617799	-1012.7940546	0.176330	-1013.829370	-1014.0057006
P-O3-H3	0.175784	-1012.623971	-1012.7997544	0.175718	-1013.836098	-1014.0118166
P-S1-H1	0.183414	-1319.566186	-1319.7495994	0.183331	-1320.776839	-1320.9601703
P-S1-H2	0.181003	-1319.560056	-1319.7410591	0.181763	-1320.769870	-1320.9516332
P-S2-H1	0.172276	-1335.618623	-1335.7908994	0.172406	-1336.829398	-1337.0018036
P-S2-H2	0.170163	-1335.620940	-1335.7911029	0.170707	-1336.830854	-1337.0015613
P-S2-H3	0.171286	-1335.629775	-1335.8010605	0.171914	-1336.839797	-1337.011711
P-S3-H1	0.172117	-1335.634557	-1335.8066744	0.171724	-1336.845553	-1337.0172775
P-S3-H2	0.171534	-1335.625271	-1335.7968054	0.171296	-1336.836633	-1337.0079294
P-S3-H3	0.170871	-1335.635054	-1335.8059243	0.171652	-1336.844612	-1337.0162639
P-N1-H1	0.225413	-1015.921658	-1016.1470708	0.224601	-1017.133664	-1017.3582648
P-N1-H2	0.224429	-1015.915880	-1016.1403092	0.223927	-1017.127503	-1017.3514302
P-N2-H1	0.214861	-1031.971510	-1032.1863718	0.214347	-1033.183445	-1033.3977919
P-N2-H2	0.214346	-1031.973419	-1032.1877647	0.213125	-1033.185626	-1033.3987507
P-N2-H3	0.211104	-1031.982655	-1032.1937586	0.213578	-1033.191500	-1033.4050786
P-N3-H1	0.215321	-1031.996572	-1032.2118937	0.215198	-1033.208055	-1033.4232535
P-N3-H2	0.215218	-1031.985982	-1032.2011994	0.215140	-1033.197633	-1033.412773

P-N3-H3	0.214699	-1031.994720	-1032.2094185	0.213908	-1033.206644	-1033.4205517
P-N4-H1	0.233219	-1129.217962	-1129.4511807	0.233405	-1130.428676	-1130.6620817
P-N4-H2	0.232342	-1129.208023	-1129.4403653	0.230628	-1130.420714	-1130.6513424
P-N5-H1	0.220135	-1145.259637	-1145.4797716	0.221035	-1146.469932	-1146.6909675
P-N5-H2	0.220308	-1145.257105	-1145.4774126	0.220281	-1146.467933	-1146.6882138
P-N5-H3	0.219743	-1145.263287	-1145.4830293	0.220919	-1146.472294	-1146.6932121
P-N6-H1	0.220982	-1145.286087	-1145.5070696	0.221571	-1146.497261	-1146.7188318
P-N6-H2	0.221267	-1145.275647	-1145.4969146	0.221048	-1146.487182	-1146.7082298
P-N6-H3	0.220899	-1145.282937	-1145.5038366	0.220631	-1146.493767	-1146.7143978

<sup>a</sup> Effective core potentials (including LanL2MB, SDD, LanL2DZ with an additional polarization function  $\text{Cu}(\zeta(f) = 3.525)$ ) was used on Cu, 6-31G(d) was used on the other atoms.

**Table S7.** Total electronic energies (E, hartree) of concerned fragments involved in transition states calculated using 6-31G(d) basis set and three different Effective core potentials (with M05 functional).

	6-31G(d)	LANL2DZ <sup>a</sup>	LANL2MB <sup>a</sup>	SDD <sup>a</sup>
TS-O1-H1-I	-2440.7814377	-996.7316498	-996.7190488	-997.9284509
TS-O1-H1-II	-229.1668753	-229.1629416	-229.162934	-229.1632295
TS-O1-H1-III	-2211.4415169	-767.4313883	-767.4218908	-768.6227493
TS-O1-H2-I	-2440.7759253	-996.7290955	-996.7159884	-997.9234436
TS-O1-H2-II	-229.1694705	-229.1658434	-229.1654117	-229.166111
TS-O1-H2-III	-2211.4410947	-767.4302579	-767.4216795	-768.6227386
TS-O2-H1-I	-2456.7978568	-1012.7453752	-1012.734321	-1013.9412185
TS-O2-H1-II	-245.1899061	-245.1852841	-245.1847476	-245.1854676
TS-O2-H1-III	-2211.44097	-767.4321322	-767.4212967	-768.6225539
TS-O2-H2-I	-2456.7974565	-1012.7507187	-1012.7383487	-1013.9448845
TS-O2-H2-II	-245.1844037	-245.1797619	-245.1794712	-245.1801847
TS-O2-H2-III	-2211.4413819	-767.4301845	-767.421351	-768.6227557
TS-O2-H3-I	-2456.8027974	-1012.7517546	-1012.7402411	-1013.946463
TS-O2-H3-II	-245.1858002	-245.1812069	-245.1811732	-245.1814716
TS-O2-H3-III	-2211.4418568	-767.4312616	-767.4219738	-768.6228421
TS-O3-H1-I	-2456.8427273	-1012.788675	-1012.7759976	-1013.9857753
TS-O3-H1-II	-245.2235326	-245.2191198	-245.2186531	-245.2193224
TS-O3-H1-III	-2211.4408569	-767.4322419	-767.4172955	-768.6224609
TS-O3-H2-I	-2456.8354666	-1012.7850085	-1012.7729632	-1013.9816399
TS-O3-H2-II	-245.2272679	-245.2229489	-245.2225377	-245.2232387
TS-O3-H2-III	-2211.4410766	-767.43191452	-767.4215064	-768.6225014
TS-O3-H3-I	-2456.8417143	-1012.7910961	-1012.7780481	-1013.9877456
TS-O3-H3-II	-245.2219434	-245.2178397	-245.2176146	-245.2181012
TS-O3-H3-III	-2211.4418109	-767.4316718	-767.4221051	-768.6227832
TS-S1-H1-I	-2763.7901853	-1319.7420721	-1319.7308172	-1320.9379428
TS-S1-H1-II	-552.1801452	-552.1751425	-552.1751915	-552.1753842
TS-S1-H1-III	-2211.4408371	-767.4312977	-767.4216521	-768.6227053
TS-S1-H2-I	-2763.7844732	-1319.7372974	-1319.7247679	-1320.931322
TS-S1-H2-II	-552.1850759	-552.1803418	-552.1799264	-552.1806123

TS-S1-H2-III	-2211.4410863	-767.4305533	-767.421646	-768.6227017
TS-S2-H1-I	-2779.8306325	-1335.7779792	-1335.7667641	-1336.9743019
TS-S2-H1-II	-568.2355146	-568.2302403	-568.2299199	-568.2304586
TS-S2-H1-III	-2211.4405828	-767.4318168	-767.4214229	-768.6225451
TS-S2-H2-I	-2779.8318018	-1335.7849674	-1335.7725007	-1336.9780395
TS-S2-H2-II	-568.2272018	-568.2220174	-568.2217135	-568.2224434
TS-S2-H2-III	-2211.4413346	-767.4305076	-767.421515	-768.6227594
TS-S2-H3-I	-2779.8396785	-1335.7872024	-1335.7772453	-1336.9825682
TS-S2-H3-II	-568.2253264	-568.2203406	-568.2198609	-568.2207446
TS-S2-H3-III	-2211.4411506	-767.4311944	-767.4217053	-768.6227678
TS-S3-H1-I	-2779.844578	-1335.7920966	-1335.7807028	-1336.9885901
TS-S3-H1-II	-568.2407334	-568.2353916	-568.2351969	-568.2354998
TS-S3-H1-III	-2211.4410967	-767.431998	-767.4199284	-768.6225933
TS-S3-H2-I	-2779.8386921	-1335.7872975	-1335.7747168	-1336.9836915
TS-S3-H2-II	-568.2372109	-568.2318014	-568.2314444	-568.2321219
TS-S3-H2-III	-2211.4409114	-767.4316752	-767.4216551	-768.6225284
TS-S3-H3-I	-2779.8445529	-1335.7948643	-1335.7845005	-1336.9906355
TS-S3-H3-II	-568.2298192	-568.2245197	-568.2243962	-568.2247643
TS-S3-H3-III	-2211.4411367	-767.4314679	-767.4218122	-768.6227311
TS-N1-H1-I	-2460.1954678	-1016.1460993	-1016.1351222	-1017.3421435
TS-N1-H1-II	-248.5843303	-248.5796608	-248.579854	-248.5798673
TS-N1-H1-III	-2211.4402112	-767.43116872	-767.4211267	-768.6226061
TS-N1-H2-I	-2460.1889767	-1016.1405502	-1016.1275648	-1017.3362165
TS-N1-H2-II	-248.5864316	-248.5819906	-248.5816618	-248.5821764
TS-N1-H2-III	-2211.4404435	-767.4301474	-767.4214776	-768.6224009
TS-N2-H1-I	-2476.2296644	-1032.1797704	-1032.1679439	-1033.3764484
TS-N2-H1-II	-264.630778	-264.625427	-264.6250573	-264.6256069
TS-N2-H1-III	-2211.4404476	-767.43154981	-767.421207	-768.6222409
TS-N2-H2-I	-2476.2324606	-1032.1837358	-1032.1728515	-1033.3798334
TS-N2-H2-II	-264.6264317	-264.6214044	-264.6209566	-264.6216722
TS-N2-H2-III	-2211.4407993	-767.4307934	-767.4213425	-768.622639
TS-N2-H3-I	-2476.2374656	-1032.1874318	-1032.1793786	-1033.3833483
TS-N2-H3-II	-264.6274788	-264.6224159	-264.6219843	-264.6225272
TS-N2-H3-III	-2211.4406594	-767.43168310	-767.4214593	-768.6226104
TS-N3-H1-I	-2476.2563491	-1032.2051771	-1032.1930412	-1033.4019603
TS-N3-H1-II	-264.644359	-264.6390885	-264.6387782	-264.6392496
TS-N3-H1-III	-2211.4403495	-767.431523	-767.4171565	-768.6222908
TS-N3-H2-I	-2476.2464958	-1032.1968548	-1032.1849694	-1033.3937316
TS-N3-H2-II	-264.645909	-264.6407642	-264.6404076	-264.6410693
TS-N3-H2-III	-2211.4405827	-767.431295	-767.419724	-768.6223164
TS-N3-H3-I	-2476.2547811	-1032.2055869	-1032.1953261	-1033.4011703
TS-N3-H3-II	-264.6411236	-264.6362384	-264.6360081	-264.6365144
TS-N3-H3-III	-2211.4406197	-767.4313822	-767.4210499	-768.622655
TS-N4-H1-I	-2573.4946764	-1129.442326	-1129.4281874	-1130.6383376

TS-N4-H1-II	-361.8768443	-361.8705485	-361.8704732	-361.8706143
TS-N4-H1-III	-2211.4394089	-767.4319416	-767.4224638	-768.6226199
TS-N4-H2-I	-2573.4843235	-1129.4338796	-1129.4237481	-1130.6305819
TS-N4-H2-II	-361.8817452	-361.8755103	-361.8744245	-361.8758361
TS-N4-H2-III	-2211.44053	-767.4310115	-767.4214781	-768.6226621
TS-N5-H1-I	-2589.5210905	-1145.4688939	-1145.4583708	-1146.6645354
TS-N5-H1-II	-377.9155106	-377.9084603	-377.9080499	-377.908692
TS-N5-H1-III	-2211.4404356	-767.4319045	-767.4175032	-768.622197
TS-N5-H2-I	-2589.5214852	-1145.4717483	-1145.4597515	-1146.666865
TS-N5-H2-II	-377.9113927	-377.9043874	-377.9039881	-377.9047325
TS-N5-H2-III	-2211.4411629	-767.4301749	-767.4213932	-768.6219839
TS-N5-H3-I	-2589.5316763	-1145.4813284	-1145.4687792	-1146.6764134
TS-N5-H3-II	-377.91028276	-377.9035899	-377.9040194	-377.9038714
TS-N5-H3-III	-2211.4414226	-767.4309193	-767.4215235	-768.6216309
TS-N6-H1-I	-2589.5525666	-1145.4939204	-1145.477357	-1146.6909874
TS-N6-H1-II	-377.9337591	-377.9267712	-377.9264998	-377.9270046
TS-N6-H1-III	-2211.4390671	-767.4326964	-767.4226115	-768.6221715
TS-N6-H2-I	-2589.5417769	-1145.4890314	-1145.4773371	-1146.6857827
TS-N6-H2-II	-377.9356929	-377.9290154	-377.9286077	-377.9293586
TS-N6-H2-III	-2211.4406741	-767.4316849	-767.417133	-768.6224417
TS-N6-H3-I	-2589.551155	-1145.500812	-1145.4892935	-1146.6955594
TS-N6-H3-II	-377.9315526	-377.925492	-377.9249487	-377.9258451
TS-N6-H3-III	-2211.4401283	-767.4304842	-767.4216125	-768.621812

<sup>a</sup> Effective core potentials (including LanL2MB, SDD, LanL2DZ with an additional polarization function  $\text{Cu}(\zeta(f) = 3.525)$ ) was used on Cu, 6-31G(d) was used on the other atoms.

**Table S8.** Total electronic energies (E, hartree) of concerned intermediates and transition states calculated at different single point levels

	B3LYP		M05		M06	
	BS1 <sup>a</sup>	BS2 <sup>b</sup>	BS1	BS2	BS1	BS2
Cat.	-2440.6833735	-2440.7444068	-2440.1019557	-2440.1520169	-2440.0392676	-2440.0969709
HOAc	-229.164685	-229.1776364	-229.0313718	-229.0433972	-229.03086154	-229.0443185
O1	-230.0876695	-230.1032455	-229.9215205	-229.9350252	-229.92533461	-229.9402586
O2	-246.1035912	-246.1203477	-245.9405045	-245.9550432	-245.93893251	-245.9552524
O3	-246.1406754	-246.1567128	-245.9810591	-245.9950718	-245.98001221	-245.9959452
S1	-553.0731299	-553.0918589	-552.9329747	-552.9506722	-552.9095268	-552.9273647
S2	-569.1144685	-569.1369562	-568.9792918	-569.0005925	-568.9528083	-568.9748448
S3	-569.1211825	-569.1400305	-568.9873483	-569.0051851	-568.9590062	-568.9774569
N1	-249.5486687	-249.5656499	-249.3387427	-249.35321	-249.34883256	-249.36482775
N2	-265.5874201	-265.6046729	-265.3830064	-265.39782191	-265.38725177	-265.4039816
N3	-265.6017392	-265.6191041	-265.398186	-265.41312253	-265.40307526	-265.42003383
N4	-362.926575	-362.9498466	-362.6604971	-362.68039636	-362.6694675	-362.6918785
N5	-378.9543212	-378.9780636	-378.6938928	-378.71431809	-378.697055	-378.7203159
N6	-378.9753713	-378.9990567	-378.7156126	-378.7359787	-378.719503	-378.7428555

TS-O1-H1	-2670.7552757	-2670.8308834	-2670.0081533	-2670.0705051	-2669.9592467	-2670.0305554
TS-O1-H2	-2670.7484095	-2670.8241938	-2670.0039771	-2670.0666671	-2669.9547627	-2670.026334
TS-O2-H1	-2686.7707365	-2686.847545	-2686.0267418	-2686.0904366	-2685.9720993	-2686.0450417
TS-O2-H2	-2686.7708044	-2686.8475001	-2686.0289547	-2686.0923572	-2685.9739568	-2686.0466468
TS-O2-H3	-2686.7761636	-2686.8526791	-2686.0319896	-2686.0951787	-2685.9781118	-2686.0505989
TS-O3-H1	-2686.8124765	-2686.8887288	-2686.0704679	-2686.1336641	-2686.0162195	-2686.0888525
TS-O3-H2	-2686.8056904	-2686.8818584	-2686.065732	-2686.1289748	-2686.01178	-2686.0844128
TS-O3-H3	-2686.8127524	-2686.8887721	-2686.0719238	-2686.1347772	-2686.0179839	-2686.0902713
TS-S1-H1	-2993.7406967	-2993.8196093	-2993.0220399	-2993.0886827	-2992.9452742	-2993.0197184
TS-S1-H2	-2993.7326509	-2993.8113751	-2993.0146102	-2993.0811826	-2992.9381412	-2993.0123905
TS-S2-H1	-3009.7779456	-3009.859902	-3009.0627571	-3009.1324602	-3008.9827323	-3009.0607664
TS-S2-H2	-3009.7788704	-3009.8609668	-3009.0654834	-3009.135243	-3008.9855206	-3009.0635727
TS-S2-H3	-3009.7854843	-3009.8672271	-3009.0717278	-3009.1411993	-3008.992758	-3009.0705176
TS-S3-H1	-3009.791913	-3009.8704984	-3009.0777325	-3009.1442018	-3008.9959215	-3009.070599
TS-S3-H2	-3009.7848557	-3009.863568	-3009.0712823	-3009.1379944	-3008.9897503	-3009.0645454
TS-S3-H3	-3009.7925666	-3009.8715736	-3009.0799228	-3009.1467466	-3008.9980133	-3009.0730504
TS-N1-H1	-2690.2123333	-2690.2895299	-2689.4242616	-2689.4877937	-2689.3850639	-2689.4574803
TS-N1-H2	-2690.2050142	-2690.2822978	-2689.417166	-2689.4809672	-2689.3749383	-2689.4477216
TS-N2-H1	-2706.2456532	-2706.3231135	-2705.461507	-2705.5255908	-2705.4129546	-2705.4864464
TS-N2-H2	-2706.2481511	-2706.3255046	-2705.4655868	-2705.5294759	-2705.4167719	-2705.4900703
TS-N2-H3	-2706.2537414	-2706.3309684	-2705.4706112	-2705.5342495	-2705.4246949	-2705.4976293
TS-N3-H1	-2706.2698925	-2706.3470908	-2705.4860889	-2705.549792	-2705.4414096	-2705.5145336
TS-N3-H2	-2706.2614302	-2706.3388662	-2705.478105	-2705.5421901	-2705.4307187	-2705.5042719
TS-N3-H3	-2706.2693941	-2706.3467832	-2705.4874613	-2705.5512326	-2705.442238	-2705.5154028
TS-N4-H1	-2803.5948976	-2803.6778958	-2802.7498009	-2802.8183204	-2802.7087135	-2802.7872415
TS-N4-H2	-2803.5869395	-2803.6705789	-2802.7423759	-2802.8116152	-2802.6980575	-2802.7773002
TS-N5-H1	-2819.6184514	-2819.7022361	-2818.7779192	-2818.8474509	-2818.7290108	-2818.8088779
TS-N5-H2	-2819.6194048	-2819.7030304	-2818.7804378	-2818.849697	-2818.7303917	-2818.8099744
TS-N5-H3	-2819.6257792	-2819.7086977	-2818.7880322	-2818.8565807	-2818.743577	-2818.8221574
TS-N6-H1	-2819.6476489	-2819.7306773	-2818.8076763	-2818.8764395	-2818.7609069	-2818.8401178
TS-N6-H2	-2819.6394098	-2819.7231519	-2818.7992919	-2818.8688087	-2818.7505481	-2818.8304974
TS-N6-H3	-2819.6468481	-2819.7301737	-2818.8093485	-2818.8781908	-2818.764689	-2818.8439109
P-O1-H1	-2441.5754276	-2441.6381858	-2440.9607098	-2441.0114722	-2440.9073079	-2440.9657917
P-O1-H2	-2441.5696966	-2441.6325964	-2440.9574179	-2441.0083706	-2440.9032768	-2440.9619212
P-O2-H1	-2457.5966034	-2457.6602903	-2456.9857821	-2457.0375247	-2456.9275887	-2456.9873328
P-O2-H2	-2457.5937427	-2457.6574961	-2456.9849099	-2457.0365623	-2456.9247648	-2456.9845272
P-O2-H3	-2457.6018064	-2457.6653203	-2456.990609	-2457.0420631	-2456.9314733	-2456.9909889
P-O3-H1	-2457.6362689	2457.6994284	-2457.028267	-2457.0794466	-2456.9675017	-2457.0268892
P-O3-H2	-2457.6284213	-2457.6916361	-2457.0209775	-2457.0724341	-2456.963189	-2457.0228302
P-O3-H3	-2457.6347678	-2457.6980254	-2457.0269079	-2457.0782374	-2456.9680282	-2457.0276002
P-S1-H1	-2764.5628025	-2764.6287177	-2763.9768827	-2764.0317535	-2763.8947423	-2763.9562875
P-S1-H2	-2764.5542472	-2764.6199287	-2763.9684079	-2764.0231068	-2763.8866856	-2763.9478289
P-S2-H1	-2780.601395	-2780.6700167	-2780.0190433	-2780.0764536	-2779.9324912	-2779.9970143
P-S2-H2	-2780.6019504	-2780.6710215	-2780.0212596	-2780.079181	-2779.9358768	-2780.0009074

P-S2-H3	-2780.6119722	-2780.6812797	-2780.0316211	-2780.0897954	-2779.9456811	-2780.0110981
P-S3-H1	-2780.6165464	-2780.6826953	-2780.0356263	-2780.090762	-2779.9493355	-2780.0116432
P-S3-H2	-2780.6073921	-2780.6731389	-2780.0265458	-2780.0814353	-2779.9406169	-2780.002416
P-S3-H3	-2780.6159324	-2780.6820735	-2780.03663	-2780.0917751	-2779.9488405	-2780.0111535
P-N1-H1	-2461.0313016	-2461.0956556	-2460.374307	-2460.4262164	-2460.3293967	-2460.3889801
P-N1-H2	-2461.0236825	-2461.0880959	-2460.3673601	-2460.4193848	-2460.3204142	-2460.3801813
P-N2-H1	-2477.067284	-2477.1317654	-2476.4151325	-2476.4674459	-2476.3632252	-2476.4236738
P-N2-H2	-2477.0682025	-2477.1327244	-2476.417828	-2476.4700433	-2476.3644283	-2476.42484
P-N2-H3	-2477.0758387	-2477.1401372	-2476.4249623	-2476.4769128	-2476.3732757	-2476.4332932
P-N3-H1	-2477.0933609	-2477.1576805	-2476.4417719	-2476.4937948	-2476.3921721	-2476.4523771
P-N3-H2	-2477.0814904	-2477.1460814	-2476.4299513	-2476.482375	-2476.3787954	-2476.4394604
P-N3-H3	-2477.0901047	-2477.1545247	-2476.4399285	-2476.4920235	-2476.3893928	-2476.4496683
P-N4-H1	-2574.4219923	-2574.4923992	-2573.7070273	-2573.7641535	-2573.6612215	-2573.7270797
P-N4-H2	-2574.4084724	-2574.4790906	-2573.6958894	-2573.7532372	-2573.6476224	-2573.7137111
P-N5-H1	-2590.4435269	-2590.5144137	-2589.7355451	-2589.7934063	-2589.6829336	-2589.7498554
P-N5-H2	-2590.4427036	-2590.5135377	-2589.7362108	-2589.7938315	-2589.6814916	-2589.7482162
P-N5-H3	-2590.4515266	-2590.5229561	-2589.7444573	-2589.8026227	-2589.6931451	-2589.7602642
P-N6-H1	-2590.4731494	-2590.5433738	-2589.7664638	-2589.823567	-2589.7139104	-2589.7801836
P-N6-H2	-2590.4616945	-2590.5326017	-2589.7538334	-2589.8116867	-2589.7014897	-2589.7685234
P-N6-H3	-2590.4712433	-2590.5432145	-2589.7650558	-2589.8237752	-2589.7139887	-2589.7818417

	<b>M06L</b>		<b>M06L(toluene)<sup>c</sup></b>	<b>M06L(1,4-dioxane)<sup>c</sup></b>	<b>B3LYP(DMSO)<sup>d</sup></b>
	<b>BS1</b>	<b>BS2</b>	<b>BS1</b>	<b>BS1</b>	
Cat.	-2440.4907253	-2440.5440706	-2440.5057063	-2440.5048097	-2440.9539629
HOAc	-229.129088	-229.141636	-229.14023961	-229.13958761	_____
O1	-230.0508083	-230.0647509	-230.05596755	-230.05566854	-230.10720249
O2	-246.069606	-246.0839257	-246.0769528	-246.07650422	-246.1286413
O3	-246.1052484	-246.1196451	-246.11180337	-246.11141625	-246.16376765
S1	-553.02737029	-553.04385805	-553.0321303	-553.0318548	-553.0951836
S2	-569.0714655	-569.0910304	-569.0775596	-569.0771894	-569.14282766
S3	-569.0769905	-569.0936217	-569.0828945	-569.082543	569.14636599
N1	-249.504954	-249.5199442	-249.5106467	-249.5103143	-249.57172932
N2	-265.5456358	-265.56060853	-265.553805	-265.5533164	-265.61293653
N3	-265.55925183	-265.57464504	-265.56900365	-265.5684103	-265.63072601
N4	-362.8735335	-362.8946791	-362.8808096	-362.88038096	-362.95872194
N5	-378.9038738	-378.9251022	-378.9153559	-378.91464806	-378.99353883
N6	-378.9232509	-378.9447933	-378.9337831	-378.93314917	-379.01212456
TS-O1-H1	-2670.5321652	-2670.5984628	-2670.5477836	-2670.5468533	-2671.025526
TS-O1-H2	-2670.52577	-2670.5922284	-2670.5411996	-2670.5402808	-2671.0238079
TS-O2-H1	-2686.5489473	-2686.6157875	-2686.5668541	-2686.5657749	-2687.0463921
TS-O2-H2	-2686.5496141	-2686.6161652	-2686.5674596	-2686.5663902	-2687.0478717
TS-O2-H3	-2686.5548413	-2686.6212771	-2686.5725584	-2686.5714955	-2687.0518295
TS-O3-H1	-2686.5896266	-2686.6565715	-2686.6075572	-2686.6064855	-2687.0864164
TS-O3-H2	-2686.5829521	-2686.6499829	-2686.599685	-2686.5986851	-2687.0779101

TS-O3-H3	-2686.5901577	-2686.6568213	-2686.6075585	-2686.6065239	-2687.0874306
TS-S1-H1	-2993.509061	-2993.5781193	-2993.5248319	-2993.5238922	-2994.015549
TS-S1-H2	-2993.5011423	-2993.5700612	-2993.5163406	-2993.5154349	-2994.0054167
TS-S2-H1	-3009.5478409	-3009.6195471	-3009.5645746	-3009.5635653	-3010.0555816
TS-S2-H2	-3009.5492224	-3009.6208336	-3009.5659981	-3009.5649935	-3010.0583664
TS-S2-H3	-3009.5571396	-3009.6283807	-3009.574461	-3009.5734182	-3010.06638
TS-S3-H1	-3009.5609827	-3009.6298581	-3009.5780897	-3009.5770635	-3010.0670529
TS-S3-H2	-3009.5539979	-3009.6230462	-3009.5701322	-3009.5691646	-3010.0587504
TS-S3-H3	-3009.5617724	-3009.6309093	-3009.5788874	-3009.5778667	-3010.0702515
TS-N1-H1	-2689.9867356	-2690.0541162	-2690.0036519	-2690.0026403	-2690.4851819
TS-N1-H2	-2689.976665	-2690.0443418	-2689.9930277	-2689.9920458	-2690.4769138
TS-N2-H1	-2706.0179167	-2706.085554	-2706.0367522	-2706.0356107	-2706.5207477
TS-N2-H2	-2706.0206711	-2706.0880686	-2706.0393802	-2706.0382562	-2706.5250867
TS-N2-H3	-2706.0284969	-2706.0956069	-2706.0479866	-2706.0468173	-2706.5284895
TS-N3-H1	-2706.0436121	-2706.1111558	-2706.0625137	-2706.0613692	-2706.5443319
TS-N3-H2	-2706.033075	-2706.1010378	-2706.0521317	-2706.0509677	-2706.5375468
TS-N3-H3	-2706.0437151	-2706.1112903	-2706.0639701	-2706.0627488	-2706.5487252
TS-N4-H1	-2803.360118	-2803.4332735	-2803.3783037	-2803.3772096	-2803.874471
TS-N4-H2	-2803.3478256	-2803.4216372	-2803.3669681	-2803.3658269	-2803.8697559
TS-N5-H1	-2819.3815089	-2819.4552053	-2819.4021741	-2819.4009169	-2819.9043719
TS-N5-H2	-2819.3827053	-2819.456095	-2819.4048589	-2819.4035189	-2819.9093198
TS-N5-H3	-2819.3940899	-2819.4666119	-2819.41563	-2819.4143323	-2819.9115515
TS-N6-H1	-2819.412539	-2819.4859082	-2819.4327391	-2819.4315171	-2819.9291612
TS-N6-H2	-2819.4005525	-2819.4746147	-2819.4207311	-2819.4195201	-2819.9235384
TS-N6-H3	-2819.4133518	-2819.4866978	-2819.4330399	-2819.431873	-2819.9305325
P-O1-H1	-2441.3768926	-2441.4313293	-2441.3911023	-2441.390225	
P-O1-H2	-2441.371943	-2441.4265067	-2441.3869305	-2441.3860162	
P-O2-H1	-2457.3993524	-2457.4539853	-2457.4147708	-2457.4138214	
P-O2-H2	-2457.3977039	-2457.4524261	-2457.4151628	-2457.4140978	
P-O2-H3	-2457.4041617	-2457.4586942	-2457.4208528	-2457.4198298	
P-O3-H1	-2457.4356496	-2457.4904875	-2457.4555853	-2457.4543771	
P-O3-H2	-2457.4304703	-2457.48551	-2457.4443547	-2457.4435048	
P-O3-H3	-2457.4366867	-2457.4916307	-2457.4530029	-2457.4520042	
P-S1-H1	-2764.3555719	-2764.4127222	-2764.370317	-2764.3694178	
P-S1-H2	-2764.3470969	-2764.4039503	-2764.3617712	-2764.3608776	
P-S2-H1	-2780.3939103	-2780.4531581	-2780.4117149	-2780.4106174	
P-S2-H2	-2780.3966997	-2780.4563759	-2780.4130981	-2780.4120991	
P-S2-H3	-2780.406248	-2780.4661874	-2780.4238962	-2780.4228184	
P-S3-H1	-2780.4089202	-2780.4663179	-2780.4228872	-2780.4220307	
P-S3-H2	-2780.4010843	-2780.4581518	-2780.4143117	-2780.4134997	
P-S3-H3	-2780.4094412	-2780.4668681	-2780.4260134	-2780.4250018	
P-N1-H1	-2460.8288249	-2460.8843684	-2460.8432678	-2460.8423718	
P-N1-H2	-2460.8206056	-2460.8762369	-2460.835561	-2460.8346408	
P-N2-H1	-2476.8645296	-2476.9200965	-2476.8804508	-2476.8794587	



P-N2-H2	-2476.8659335	-2476.9214718	-2476.8838175	-2476.8827215
P-N2-H3	-2476.8735958	-2476.9288811	-2476.893421	-2476.8922067
P-N3-H1	-2476.890503	-2476.9461196	-2476.9060482	-2476.9050814
P-N3-H2	-2476.8779088	-2476.9339062	-2476.8941291	-2476.8931127
P-N3-H3	-2476.8877486	-2476.9434079	-2476.9065563	-2476.9053913
P-N4-H1	-2574.2149951	-2574.2764493	-2574.2298581	-2574.228953
P-N4-H2	-2574.1944698	-2574.2561818	-2574.2113144	-2574.2102965
P-N5-H1	-2590.2303488	-2590.2920216	-2590.2474777	-2590.2464173
P-N5-H2	-2590.2303295	-2590.2919728	-2590.2517416	-2590.2504316
P-N5-H3	-2590.2423655	-2590.3045691	-2590.2665974	-2590.26511
P-N6-H1	-2590.2607183	-2590.3221194	-2590.2772591	-2590.2762448
P-N6-H2	-2590.2472189	-2590.3093403	-2590.2642328	-2590.2631947
P-N6-H3	-2590.259537	-2590.3225058	-2590.2802814	-2590.279023

<sup>a</sup> BS1:6-31G(d) with an additional polarization function Cu( $\zeta(f) = 3.525$ ) on Cu, 6-311++G(d,p) on the other atoms. <sup>b</sup> BS2: 6-31G(d) with an additional polarization function Cu( $\zeta(f) = 3.525$ ) on Cu, 6-311++G(2df,2p) on the other atoms. <sup>c</sup> different solvents including toluene and 1,4-dioxane were selected for solution phase single point calculation (self-consistent reaction field (SCRf) method with CPCM model and RADII=UAHF). <sup>d</sup> B3LYP/6-311++G(2df,2p)/PCM(DMSO)/Bondi/B3LYP/6-31G(d).

**Table S9.** Thermal correction of Gibbs free energy (TCG, hartree), Gibbs free energy (G, hartree) and total electronic energies (E, hartree) of concerned radicals calculated using B3LYP or M05 functional (with 6-31G(d)) and total electronic energies (E, hartree) calculated at *MI* level.

	B3LYP			M05			<i>MI</i> <sup>a</sup>
	TCG	G	E	TCG	G	E	
[Cu•]	—	—	—	0.132832	-2211.340045	-2211.4728767	-2211.8612215
H•	-0.010654	-0.510927	-0.5002728	-0.010654	-0.505862	-0.495208	-0.5034306
R-O1-H1	0.030273	-229.290997	-229.32127	0.030588	-229.145198	-229.1757859	-229.354438
R-O1-H2	0.030681	-229.291003	-229.3216843	0.031017	-229.145147	-229.1761645	-229.3562088
R-O2-H1	0.017994	-245.321632	-245.339626	0.018596	-245.177682	-245.1962783	-245.3773979
R-O2-H2	0.018730	-245.314329	-245.3330592	0.019258	-245.171346	-245.1906038	-245.3726097
R-O2-H3	0.018117	-245.319317	-245.3374341	0.018675	-245.175551	-245.1942259	-245.3748197
R-O3-H1	0.018835	-245.352464	-245.3712986	0.019290	-245.213173	-245.2324634	-245.4083986
R-O3-H2	0.019313	-245.353422	-245.3727352	0.019711	-245.214843	-245.2345538	-245.4113516
R-O3-H3	0.019041	-245.349211	-245.3682518	0.019469	-245.210051	-245.2295198	-245.4069842
R-S1-H1	0.026182	-552.280131	-552.3063128	0.026469	-552.161556	-552.1880245	-552.3350504
R-S1-H2	0.026253	-552.284604	-552.3108572	0.026536	-552.166437	-552.1929726	-552.3388841
R-S2-H1	0.014484	-568.342308	-568.3567926	0.015039	-568.228344	-568.2433832	-568.3884854
R-S2-H2	0.014905	-568.332069	-568.3469734	0.015349	-568.219123	-568.234472	-568.381477
R-S2-H3	0.014973	-568.330649	-568.3456213	0.015356	-568.217342	-568.2326972	-568.3803302
R-S3-H1	0.014855	-568.345948	-568.3608028	0.015292	-568.232841	-568.2481328	-568.3917426
R-S3-H2	0.014828	-568.341893	-568.3567217	0.015193	-568.230217	-568.2454098	-568.3894534
R-S3-H3	0.014972	-568.334234	-568.3492058	0.015202	-568.221953	-568.2371551	-568.383439
R-N1-H1	0.067562	-248.711675	-248.7792367	0.068048	-248.524144	-248.5921912	-248.809664
R-N1-H2	0.068369	-248.711923	-248.7802924	0.068703	-248.524728	-248.593431	-248.8117132
R-N2-H1	0.056128	-264.762357	-264.8184855	0.057766	-264.579545	-264.6373117	-264.853854

R-N2-H2	0.058196	-264.755715	-264.8139116	0.057603	-264.575277	-264.6328797	-264.850681
R-N2-H3	0.055883	-264.759936	-264.8158185	0.057694	-264.576919	-264.6346127	-264.8511821
R-N3-H1	0.056601	-264.776732	-264.8333321	0.055827	-264.596877	-264.652704	-264.8665165
R-N3-H2	0.057164	-264.776349	-264.8335122	0.057338	-264.596229	-264.6535674	-264.8682588
R-N3-H3	0.056622	-264.772166	-264.8287879	0.058040	-264.590257	-264.6482974	-264.8638908
R-N4-H1	0.074021	-362.050512	-362.1245326	0.075555	-361.812964	-361.8885195	-362.179169
R-N4-H2	0.075600	-362.049508	-362.1251084	0.076180	-361.812865	-361.8890448	-362.1804159
R-N5-H1	0.063605	-378.099668	-378.1632729	0.064819	-377.868121	-377.9329394	-378.2223897
R-N5-H2	0.063968	-378.093632	-378.1576001	0.065063	-377.862288	-377.9273504	-378.2182237
R-N5-H3	0.063506	-378.092935	-378.1564408	0.064903	-377.861292	-377.9261944	-378.2161199
R-N6-H1	0.063627	-378.108109	-378.171736	0.064606	-377.877279	-377.9418847	-378.2288341
R-N6-H2	0.064029	-378.108777	-378.1728062	0.064594	-377.878960	-377.9435541	-378.2314708
R-N6-H3	0.063158	-378.106331	-378.1694894	0.064308	-377.875592	-377.9398997	-378.2286521

<sup>a</sup> M06L/(6-31G(d)+f:6-311++G(d,p))/M05/6-31G(d)

**Table S10.** Thermal correction of Gibbs free energy (TCG, hartree), Gibbs free energy (G, hartree) and total electronic energies (E, hartree) of selected experimental substrates calculated at M05/6-31G(d) and total electronic energies (E, hartree) calculated at *MI* level.

	M05			<i>MI</i> <sup>a</sup>
	TCG	G	E	
1	0.059130	-281.326272	-281.3854016	-281.6025678
2	0.050001	-264.089544	-264.1395447	-264.3529075
3	0.079188	-378.530294	-378.6094822	-378.9009825
TS-1-H1	0.255772	-2721.053428	-2721.3091998	-2722.0891566
TS-1-H2	0.251866	-2721.047262	-2721.2991276	-2722.0774057
TS-2-H1	0.244794	-2703.803100	-2704.0478945	-2704.8229475
TS-2-H2	0.245174	-2703.805693	-2704.0508671	-2704.825991
TS-2-H3	0.244110	-2703.809688	-2704.0537979	-2704.8285935
TS-3-H1	0.273907	-2818.245920	-2818.5198269	-2819.3738489
TS-3-H2	0.273401	-2818.247190	-2818.5205905	-2819.3736586
TS-3-H3	0.274545	-2818.249845	-2818.5243901	-2819.3736585
P-1-H1	0.203514	-2492.123257	-2492.3267713	-2492.938147
P-1-H2	0.201620	-2492.110972	-2492.3125913	-2492.9238273
P-2-H1	0.191658	-2474.869578	-2475.0612361	-2475.6717864
P-2-H2	0.192505	-2474.873548	-2475.0660534	-2475.6753213
P-2-H3	0.192409	-2474.875241	-2475.0676506	-2475.6778001
P-3-H1	0.222151	-2589.314838	-2589.5369885	-2590.2256432
P-3-H2	0.222546	-2589.311084	-2589.5336299	-2590.2211475
P-3-H3	0.222017	-2589.310996	-2589.5330128	-2590.2221368
R-1-H1	0.045163	-280.649792	-280.6949543	-280.9083468
R-1-H2	0.046264	-280.648268	-280.6945322	-280.9087421
R-2-H1	0.036166	-263.427876	-263.4640421	-263.6730497
R-2-H2	0.036432	-263.431506	-263.4679378	-263.6772408
R-2-H3	0.036295	-263.419340	-263.4556352	-263.6669192

R-3-H1	0.065654	-377.870144	-377.9357973	-378.2237952
R-3-H2	0.065857	-377.866899	-377.9327567	-378.2204459
R-3-H3	0.066025	-377.870039	-377.9360638	-378.2239161

<sup>a</sup> M06L/6-31G(d)+f:6-311++G(d,p)/M05/6-31G(d)

**Table S11.** Total electronic energies (E, hartree) of concerned fragments of selected experimental substrates transition states calculated at M05/6-31G(d).

	M05		M05
TS-1-H1-I	-2492.9174639	TS-2-H3-I	-2475.6573269
TS-1-H1-II	-280.9015423	TS-2-H3-II	-263.6586516
TS-1-H1-III	-2211.8477454	TS-2-H3-III	-2211.8482448
TS-1-H2-I	-2492.9048618	TS-3-H1-I	-2590.2080025
TS-1-H2-II	-280.9023318	TS-3-H1-II	-378.2154936
TS-1-H2-III	-2211.8474181	TS-3-H1-III	-2211.8470671
TS-2-H1-I	-2475.6526918	TS-3-H2-I	-2590.2025456
TS-2-H1-II	-263.6630893	TS-3-H2-II	-378.2117434
TS-2-H1-III	-2211.8466074	TS-3-H2-III	-2211.8426402
TS-2-H2-I	-2475.6566147	TS-3-H3-I	-2590.2033479
TS-2-H2-II	-263.6683912	TS-3-H3-II	-378.2151451
TS-2-H2-III	-2211.8468576	TS-3-H3-III	-2211.8477308