Supporting Information

Theoretical Insights into Ester-Directed Reactions between Propiolates with 1,2-Benzisoxazoles by Au(I)-Catalyst: [4+2]-Annulation vs Michael-Type Products

Kaifeng Wang[1], Qiao Wu[1], Yuxia Liu[1,2*], Lingjun Liu[1], Guang Chen[1,3], Yulin Li[4], Siwei Bi[1,*]

1 School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, 273165, P. R. China. E-mail: liuyuxia2008@163.com, siweibi@126.com, Fax: +86-537-4456305 ; Tel: +86-537-4458308

2 Shaanxi Key Laboratory of Chemical Additives for Industry, College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China

3 Ministry of Education, Key Laboratory of Hainan Trauma and Disaster Rescue, College of Emergency and Trauma, Hainan Medical University, Haikou 571199, China

4 Key Laboratory of Tibetan Medicine Research & Qinghai Key Laboratory of Qinghai-Tibet Plateau Biological Resuorces, Northwest Institute of Plateau Biology, Chinese Academy of Science, Xining 810001, Qinghai P. R. China

Contents

1.TableS1-S3..... S3-S5

2.Figures S1-S8 ..... S6-S13

3. Energies S14-S16

Table S1. Calculated free-energy barriers (kcal/mol) calculated using different functions and basis sets for two alkene dissociation steps involved in Figures 2 and 5.

		IM5→TS5-9	IM20 → TS20-21
^{Optimization}B3LYP// $^{\text{Single-point}}$M06		13.8	35.3
Optimization	B3LYP[a]//lanl2dz	22.0	43.4
	PBE0[a]//lanl2dz	26.0	46.1
Single-point	BMK-D3//def2tvp	21.9	40.4
	WB97XD[b]//SDD	16.2	33.4
	M06-2X-D3[b]//SDD	19.7	40.9
	M06[b/]/SDD	15.6	38.1

[a] 6-31G (d, p) for C, H, O, and N atoms in the gas phase.

[b] 6-311+G(d, p) for C, H, O, and N atoms.

Table S2. Relative free energies (given in kcal/mol) for the crucial transition states in different alkyl-substituted propiolate systems.

	leading to P_1		**leading to P_2**
	nucleophilic cyclization TS	alkene release TS	nitrilium dissociation TS
^{t}Bu-substitution	-25.7	-33.2	-20.8
^{i}Pr-substitution	-24.7	-23.8	-17.5
Et-substitution	-29.0	-11.5	-20.5
Me-substitution	-31.4	Unlocated	-20.8

Table S3. Calculated free-energy barriers (kcal/mol) calculated using different functions and basis sets for two H-shift steps involved in Figures S2 and S4.

		IM2→TS2-6-2a	**IM13→TS13-14-2a**
^{Optimization}B3LYP// $^{\text{Single-point}}$M06		25.8	27.8
Optimization	M06[a]//SDD	24.7	29.1
Single-point	BMK-D3//def2tvp	25.5	27.8
	WB97XD[b]//SDD	23.8	25.6
	M06-2X-D3[b]//SDD	26.7	29.0

[a] 6-31G (d, p) for C, H, O, and N atoms in the 1,2-dichloroethane.

[b] 6-311+G(d, p) for C, H, O, and N atoms.

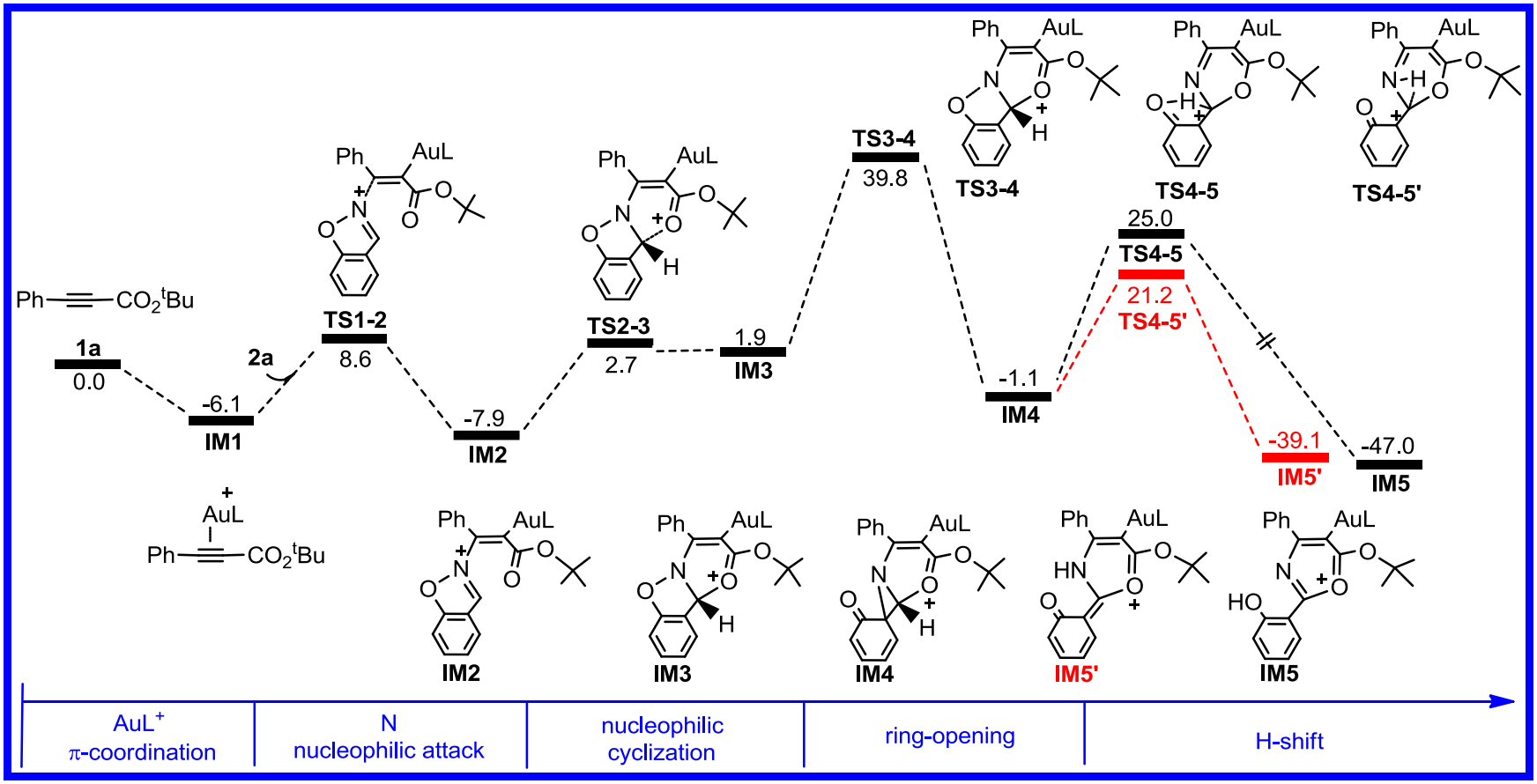

Figure S1. Calculated free energy profiles in DCE solvent for forming the 6-alkoxy-1,3-oxazin-1-ium species **IM5** from **1a**. The relative free energies and bond distances are given in kcal/mol and Å, respectively. L = IPr

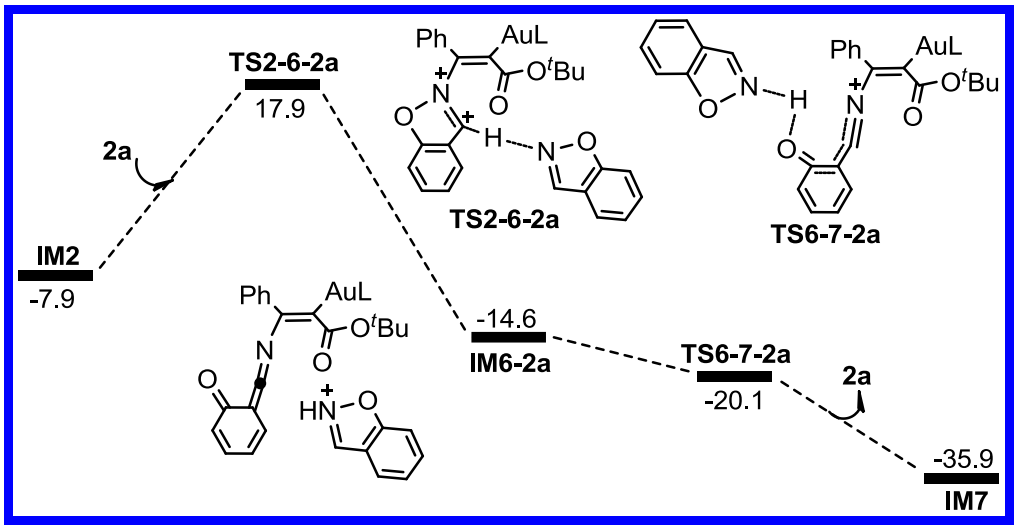

Figure S2. Calculated free energy profiles in DCE solvent for the **2a**-assisted H-shift from **IM2**. The relative free energies are given in kcal/mol. L = IPr

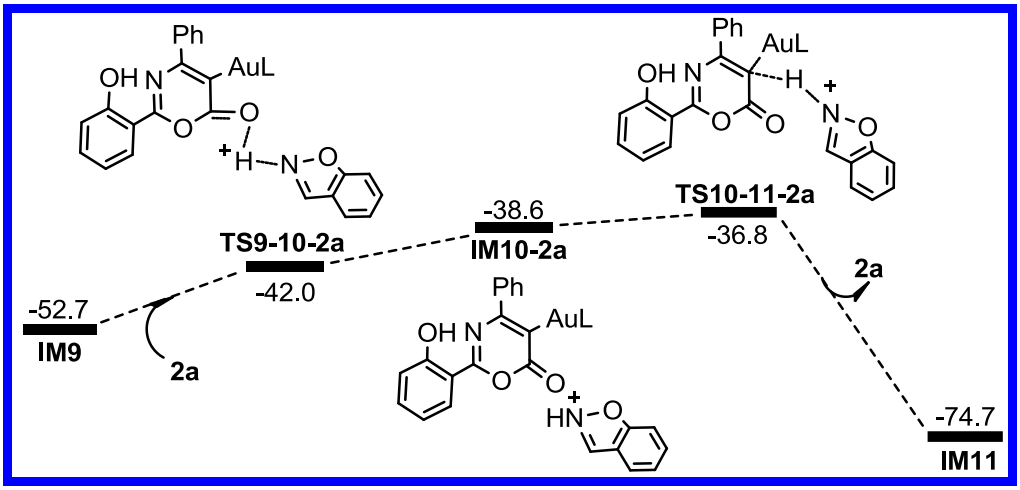

Figure S3. Calculated free energy profiles in DCE solvent for the **2a**-assisted protodeauration from **IM9**. The relative free energies are given in kcal/mol. L = IPr

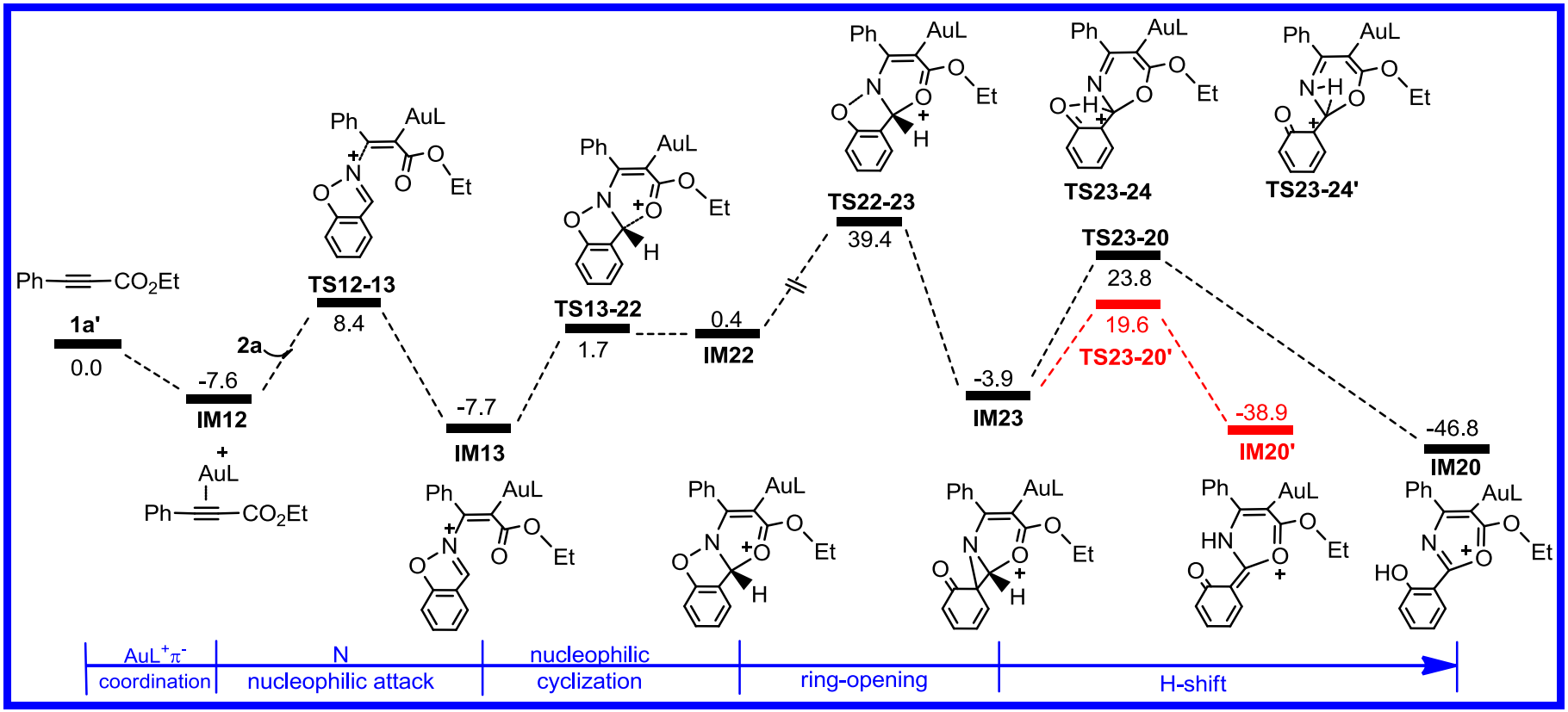

Figure S4. Calculated free energy profiles in DCE solvent for forming the common intermediate proposed by Liu's experiment from substrate **1a'**. The relative free energies are given in kcal/mol. L = IPr

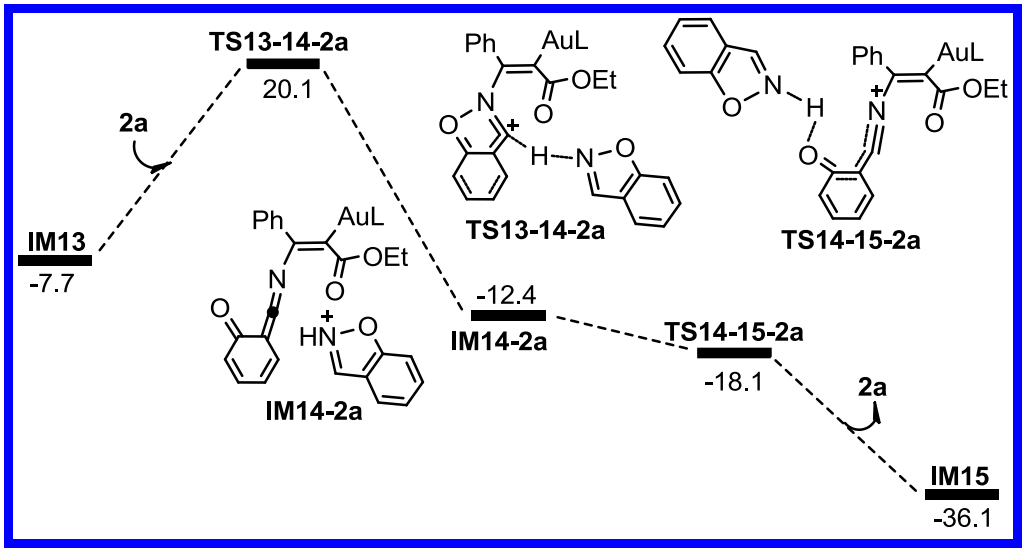

Figure S5. Calculated free energy profiles in DCE solvent for the **2a**-assisted H-shift from **IM13**. The relative free energies are given in kcal/mol. L = IPr

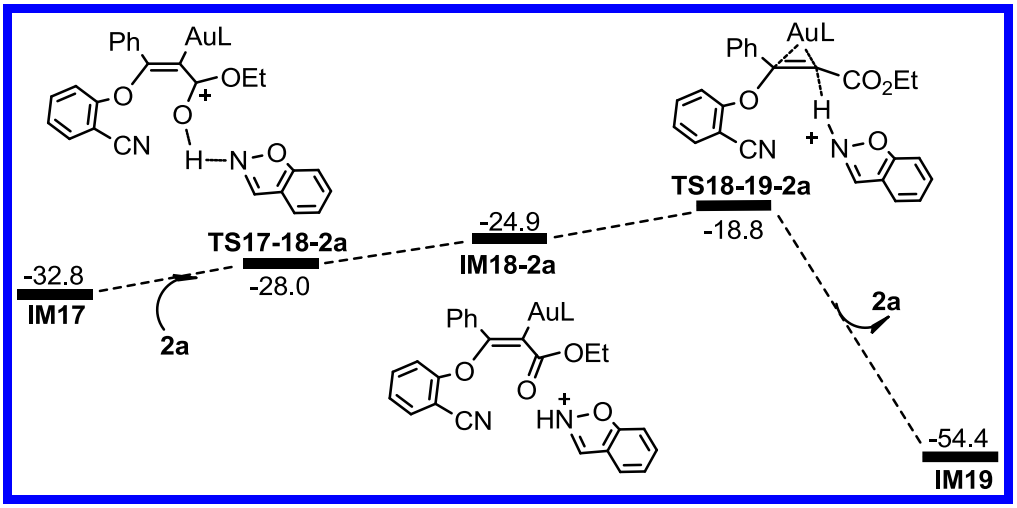

Figure S6. Calculated free energy profiles in DCE solvent for the **2a**-assisted protodeauration from **IM17**. The relative free energies are given in kcal/mol. L = IPr

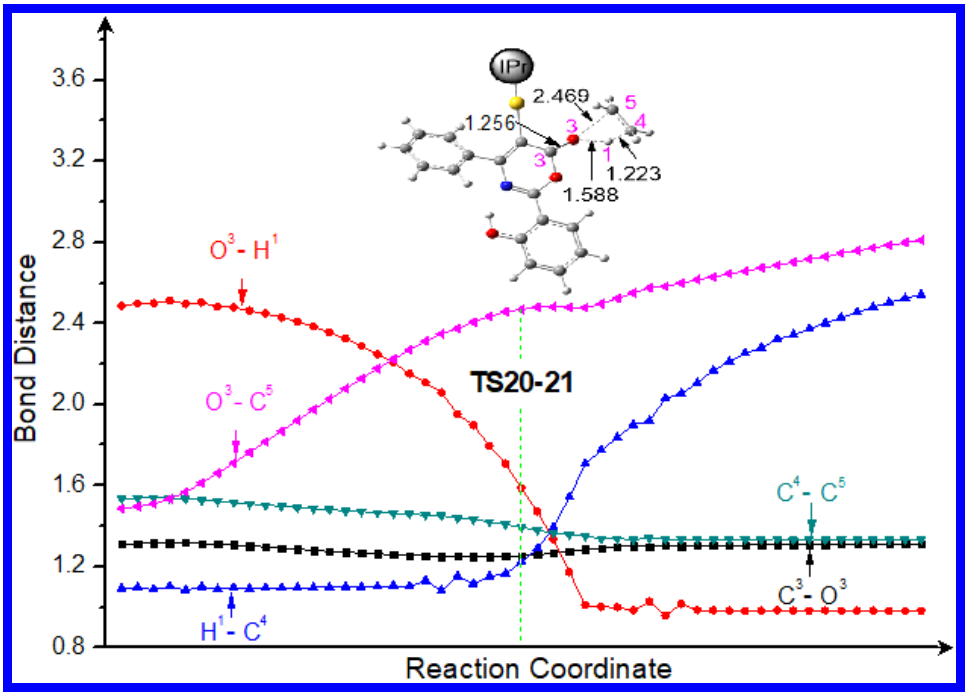

Figure S7. A diagram of the key bond length scans for **TS20-21** along the IRC pathway. The bond distances are given in Å.

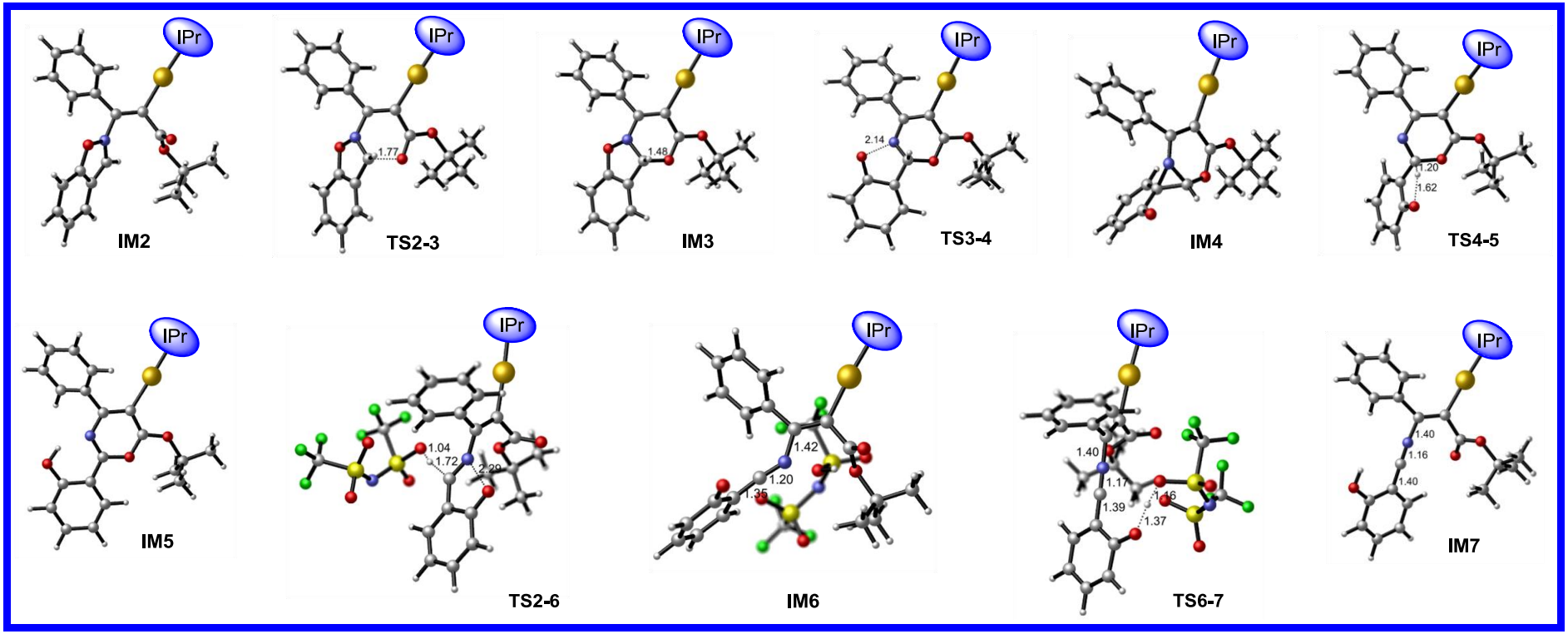

Figure S8. Optimized structures with selected structural parameters for key stationary points shown in Figure 1. The bond distances are given in Å.

Table S4. Calculated Gibbs free energies in the gas-phase using B3LYP functional, single-point HF energies in DCE solvent using M06 functional, and imaginary frequencies for all structures in the present work. The relative energies and the imaginary frequencies are given in Hartree and cm^{-1}, respectively.

Structure	Gibbs Free Energy (B3LYP gas-phase optimized calculation)	Solvation HF Energy(M06 single-point calculation)	Imaginary Frequency
1a	-654.015305	-653.9419058	
IM1	-1948.906499	-1949.07318	
2a	-399.599431	-399.512115	
TS1-2	-2348.497946	-2348.585064	-231.31
IM2	-2348.5175	-2348.618482	
TS2-3	-2348.501297	-2348.607209	-245.91
IM3	-2348.502554	-2348.61109	
TS3-4	-2348.442696	-2348.547014	-202.42
IM4	-2348.484541	-2348.610411	
TS4-5	-2348.46228	-2348.563515	-782.37
TS4-5'	-2348.427748	-2348.569169	-1510.17
IM5'	-2348.565108	-2348.6705	
TS2-6-2a	-2748.06042	-2748.10531	-97.6
TS2-6	-4175.725059	-4175.39488	-109.09
IM6-2a	-2748.126878	-2748.1587946	
IM6	-4175.760504	-4175.44287	
TS6-7-2a	-2748.128395	-2748.1655699	-251.28
TS6-7	-4175.787899	-4175.45684	-610.65
IM7	-2348.540129	-2348.659285	
TS7-5	-2348.534634	-2348.64382	-127.55
TS7-8	-2348.523211	-2348.62971	-334.83

IM5	-2348.577669	-2348.68661	
IM8	-2348.544286	-2348.64986	
TS5-9	-2348.542194	-2348.65191	-136.98
IM9	-2191.429371	-2191.53176	
TS9-10-2a	-2591.033457	-2591.04537	-12.28
TS9-10	-4018.701408	-4018.34177	-349.02
IM10-2a	-2591.016676	-2591.04257	
IM10	-4018.68094	-4018.34293	
TS10-11-2a	-2591.01748	-2591.03579	-1105.69
TS10-11	-4018.681648	-4018.3376	-1079.70
IM11	-2191.457765	-2191.5644	
P_1	-896.561173	-896.417305	
IM12	-1870.332725	-1870.483324	
TS12-13	-2269.921691	-2269.994258	-191.00
IM13	-2269.941481	-2270.026912	
TS13-14-2a	-2669.483412	-2669.511144	-113.74
TS13-14	-4097.147786	-4096.801962	-118.38
IM14-2a	-2669.54761	-2669.56618	
IM14	-4097.181673	-4096.846537	
TS14-15-2a	-2669.551509	-2669.571332	-257.97
TS14-15	-4097.216031	-4096.860322	-607.54
IM15	-2269.964589	-2270.067099	
TS15-16	-2269.945206	-2270.038056	-325.32
IM16	-2269.963686	-2270.056947	
TS16-17	-2269.947784	-2270.036072	-286.95
IM17	-2269.966596	-2270.066667	
TS17-18-2a	-2669.567146	-2669.582947	-337.22
TS17-18	-4097.224851	-4096.88169	-978.26
IM18-2a	-2669.551282	-2669.58593	

IM18	-4097.212158	-4096.879015	
TS18-19-2a	-2669.547905	-2668.709172	-1203.41
TS18-19	-4097.206742	-4096.8736107	-802.97
IM19	-2269.983284	-2270.10104	
P_2	-975.088064	-974.9494387	
TS15-20	-2269.959405	-2270.059148	-106.31
IM20	-2270.003804	-2270.09729	
TS20-21	-2269.927712	-2270.029959	-564.37
IM21	-2191.431082	-2191.533392	
TS13-22	-2269.925279	-2270.017237	-253.33
IM22	-2269.927058	-2270.020846	
TS22-23	-2269.866703	-2269.955758	-197.08
IM23	-2269.908283	-2270.025058	
TS23-20	-2269.883221	-2269.972159	-711.68
TS23-20'	-2269.85317	-2269.979114	-1503.94
IM20’	-2270.002269	-2270.096101	